

Structural Insights into Phenoxide- Containing Alkali Metal Magnesiates with Extensions to the d-block

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A thesis submitted to the Department of Pure and Applied Chemistry, University of Strathclyde, in part fulfilment of the requirements for a degree of *Doctor of Philosophy*

2021

Dedicated to my gran:

Elizabeth

Acknowledgments

Although I was the one who carried out the work reported in this thesis, it was by no means a one-man effort and I could not have done it without the support and encouragement of others. I would therefore like to take this opportunity to thank anyone who has helped in any way to get me to this point.

First of all, I would like to thank my supervisor Dr. Charles O'Hara for giving me the opportunity to complete my PhD as part of his research group. His ideas, support and guidance have been invaluable throughout the course of my PhD. I would also like to thank the other inorganic academics Prof. Robert Mulvey, Dr. Stuart Robertson and Prof. Eva Hevia, before her recent move to Switzerland, for their helpful suggestions at group meetings and other helpful discussions. Thanks to Dr. Chris Dodds for giving me the opportunity to demonstrate in the undergraduate inorganic teaching lab and for the many insightful conversations and words of encouragement. Thank you to Dr. Alan Kennedy for all his help with X-ray crystallography and for having the patience to fix my X-ray structures. Thanks to Jannie -Anne for all her help with glassware, particularly for replacing the many items I have broken over the years, and for ensuring that the lab ran smoothly. I must also say thanks to Craig Irving for all his help with NMR, without which, some of the work in thesis might not have happened. His stories and conversations/rants were always a highlight of any stressful day. I would also like to thank Prof. Philippe Gros for hosting me in his lab upon my brief visit to the University of Lorraine, Nancy, and Dr. Sabrina Touchet for her supervision and for showing me around the department.

No acknowledgments would be complete without mention of the other students and post-docs who I have worked alongside during my PhD. Their support and encouragement were second to none and without it, particularly at the beginning of my studies when chemistry was not going my way, I may not have made it to the end. I would therefore like to thank the current and past members of the O'Hara, Mulvey, Robertson and Hevia groups; Sonia, Ross, Etienne, Vicky, Michael F, Richard, Pasquale, Stephen (Towie), Scott, Michael W, Annie, Jen, Pete, Gillian, Thomas, Gerd and Sumanta. I would like to thank Dr. Michael Fairley for his friendship and for mentoring me in the lab, first of all as a masters student then again when I returned to start my PhD. He always available to answer my questions no matter how basic they were and to give me advice whenever I needed it. Furthermore, his stories were always a source of encouragement by making me realise that no matter how bad I thought things

were going, they were probably going worse for him. Thanks to everyone else, who at the end of many a stressful week could always be relied upon to go for a pint (or five) at the Ark. Your friendship has made my PhD all the more enjoyable.

I also have to say a huge thank you to my family; in particular, my mum and dad, Marjory and Andrew. Your support and encouragement have been a constant from an early age, beginning with the unenviable task of making sure that I completed homework and studied for exams at school, to supporting me financially when I decided to move away from home and go to university. I will be forever grateful for all the things you have done for me and they are major reasons why I am in the position I am today. Having said this, I'm sure that my mum will also be grateful that I have completed my PhD as I will no longer be a "perpetual student". I would also like to thank my sister, Alison, and my gran, Betty, who have provided many words of support and encouragement over the years.

Finally, I want to say the biggest thank you of all to my fiancée Cara for putting up with me for the last four years. Cara has been a constant source of encouragement and has always been there to lend her moral support when I've been struggling, particularly through the dark days of COVID-19 lockdowns and the writing of this thesis. She has listened to many rants about chemistry which I am perfectly aware she has no interest in whatsoever. Thank you for the countless number of dinners you have cooked, coffees and teas you have made and all the glasses of wine/beer/rum/whisky you have poured. I simply could not have done it without you.

Abstract

The application of alkoxide and phenoxide ligands in the synthesis of alkali metal magnesiates is becoming more widespread with the resulting magnesiates finding applications in metal-halogen exchange. This project develops the structural chemistry of heterobimetallic sodium magnesiates containing the phenoxide ligand 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol [(*rac*)-BIPHEN]. Nine sodium magnesiates, **2-10**, have been prepared and characterised by X-ray crystallography and/or multinuclear NMR spectroscopy. Introduction of sodium as the alkali metal was found to have a detrimental impact on the stability of the resulting magnesiates in comparison to their lithium analogues, making them more prone to undergo disproportionation in the presence of ethereal solvents. This instability could be circumvented through judicious choice of Lewis donor ligand.

The reactivities of sodium magnesiates, **3** and **5** which contain *N, N, N', N'*-tetramethylethylenediamine (TMEDA) and *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA) respectively, were examined in metal-halogen exchange with iodoarenes in an attempt to ascertain if sodium magnesiates containing the (*rac*)-BIPHEN phenoxide ligand were sufficiently reactive to carry out two-fold metal-halogen exchange. A difference was observed in the reactivity of the two magnesiates upon moving from bidentate TMEDA to tridentate PMDETA, with **3** generally possessing a higher reactivity than **5**, indicating that sodium likely has a role to play in metal-halogen exchange. It is postulated that coordination of the iodoarene to a vacant coordination site on sodium could prime the substrate to undergo metal-halogen exchange. Utilising the chiral variant (**5**)-**3** in metal-halogen exchange followed by electrophilic quenching of the metallated intermediate produced chiral alcohols **11**, **12** and **13**, thus demonstrating the synthetic utility of sodium magnesiates of this type by giving access to asymmetric synthesis.

Finally, utilisation of the (*rac*)-BIPHEN phenoxide ligand for the synthesis of heterobimetallic complexes was extended to alkali metal zincates. Two novel inverse lithium zincates, **15** and **16**, were prepared and characterised by X-ray crystallography and multinuclear NMR spectroscopy. Attempts to generate a conventional lithium zincate through the reaction of (*rac*)-BIPHEN with the *tetra*- and *tris*(alkyl) lithium zincates $\text{Li}_2\text{ZnR}_4(\text{TMEDA})_2$, $\text{Li}_2\text{ZnR}_4((R,R)\text{-TMEDA})_2$ and $\text{LiZnR}_3(\text{PMDETA})$ revealed these complexes to react as monometallic lithium bases, leading to the isolation of the tetranuclear lithium phenoxides **17**, **18** and **19**. A surprising alkali metal effect was observed upon switching to the *tris*(alkyl) sodium zincates

NaZnR₃(PMDETA) and NaZnR₃(15-crown-5) which were found to react as bimetallic dialkyl bases to generate the sodium zincates **22** and **23**. KZnR₃(PMDETA) was also found to react with (*rac*)-BIPHEN as a dialkyl base; however, only the homoleptic potassium zincate **24** could be isolated as a result of disproportionation.

Peer-Reviewed Publications

“Structural and metal-halogen exchange studies of sodium magnesiate biphenolate complexes” – C. Yeardley, A. R. Kennedy, P. C. Gros, S. Touchet, M. Fairley, R. McLellan, A. J. Martínez-Martínez and C. T. O’Hara, *Dalton Trans.*, 2020, **49**, 5257-5263.

Conference Presentations

Poster Presentations

“An Introduction to Nickel Amide Chemistry with Potential for Application in C-H Activation Chemistry” C. Yeardley, S. Bruna and C. T. O’Hara – Dalton, University of Warwick, March 2018.

“ β -Diketiminato Ligands and Their Application in Synthesis of Novel Nickel Complexes” C. Yeardley and C. T. O’Hara – Universities of Scotland Inorganic Conference (USIC), University of Edinburgh, September 2018.

“Structural studies of (*rac*)-BIPHEN Sodium Magnesiates and Their Reactivity in Metal-Halogen Exchange” C. Yeardley, A. R. Kennedy, C. T. O’Hara – Dalton Young Members Event (DYME), May 2019.

Oral Presentation

“Structural studies of (*rac*)-BIPHEN Sodium Magnesiates and Their Reactivity in Metal-Halogen Exchange” – Universities of Scotland Inorganic Conference (USIC), University of Glasgow, August 2019.

Abbreviations

(*rac*)-BIPHEN – 5, 5', 6, 6'-tetramethyl-3, 3'-di-*tert*-butyl-1, 1'-biphenyl-2, 2'-diol

12-crown-4 – 1, 4, 7, 10-tetraoxacyclododecane

15-crown-5 – 1, 4, 7, 10, 13-pentaoxacyclopentadecane

18-crown-6 – 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane

Am – Alkali metal

AMMMg – Alkali Metal Mediated Magnesiation

AMMZn – Alkali Metal Mediated Zincation

Ar – Generic aryl group

C₆D₆ – Deuterated benzene

CDCl₃ – Deuterated chloroform

CIPE – Close Induced Proximity Effect

d₈-THF – Deuterated THF

d₈-Tol – Deuterated toluene

DA/DA(H) – Diisopropylamide/Diisopropylamine

DABCO – 1,4-diazabicyclo[2.2.2]octane

DME – 1, 2-dimethoxyethane

DMG – Directing Metallating Group

DmmM – Directed *meta meta* Metalation

DMP/DMP(H) – Dimethylpiperidide/Dimethylpiperidine

DoM – Directed *ortho* metalation

DomM – Directed *ortho meta* Metallation

DOSY – Diffusion ordered NMR spectroscopy

DSE – Dissipated Spheres and Ellipsoids

ECC – External Calibration Curve

Et – Ethyl group

Et₂O – Diethyl ether

FG- Functional group

GooF – Goodness of fit

HMBC – Heteronuclear Multiple Bond Correlation

HMDS/HMDS(H) – 1, 1, 1, 3, 3, 3-hexamethyldisilazide/1, 1, 1, 3, 3, 3-hexamethyldisilazane

HSQC – Heteronuclear Single Quantum Coherence

ⁱPr – *iso*-propyl group

K – Kelvin

LD – Lewis donor

Me – Methyl group

Me₂Zn – Dimethyl zinc

Me₆-TREN – Tris[2-(dimethylamino)ethyl]amine

MgⁿBu₂ – di-*n*-butylmagnesium

ⁿBu – *n*-butyl group

ⁿBu₂Zn – di-*n*-butyl zinc

ⁿBuLi – *n*-butyllithium

ⁿBuNa – *n*-butylsodium

NHC – *N*-heterocyclic carbene

NMR – Nuclear Magnetic Resonance

OAr – Generic aryloxy group

OR – Generic alkoxide group

PMDTA - *N, N, N', N', N'* - Pentamethyldiethylenetriamine

ppm – parts per million

R – Generic alkyl group

Rac – Racemic

RT – Room temperature

^tBu – *tert*-butyl group

^tBu₂Zn – di-*tert*-butyl zinc

^tBuLi – *tert*-butyllithium

TEEDA - *N, N, N', N'*-Tetraethylethylenediamine

THF – Tetrahydrofuran

THP – Tetrahydropyran

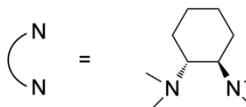
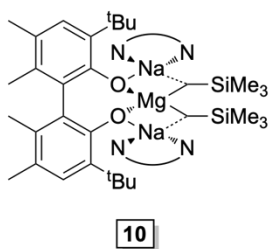
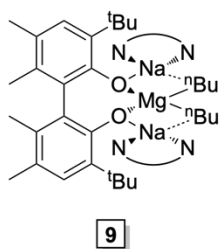
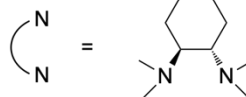
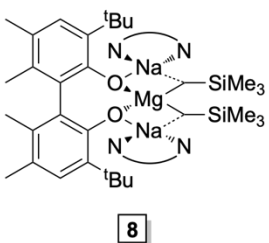
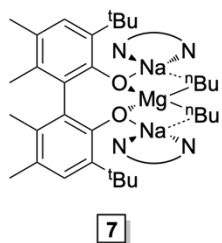
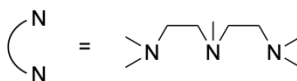
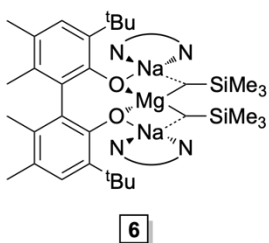
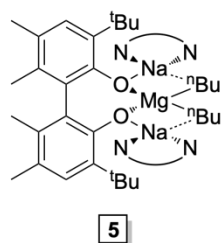
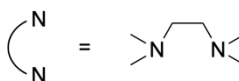
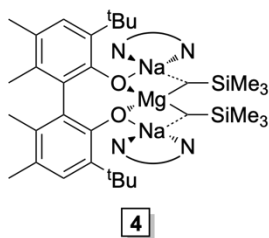
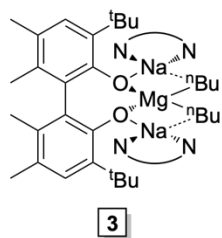
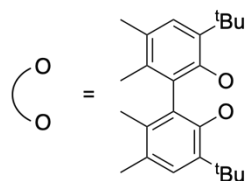
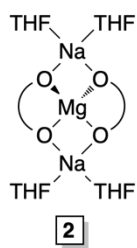
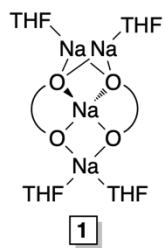
TMCD - *N, N, N', N'* - Tetramethyl-1,2-diaminocyclohexane

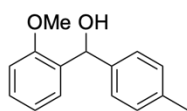
TMEDA – *N, N, N', N'* - Tetramethylethylenediamine

TMP/TMP(H) - 2,2,6,6-tetramethylpiperidide/2,2,6,6-tetramethylpiperidine

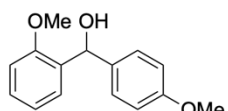
X - Halogen

Table of Numbered Compounds

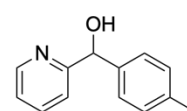




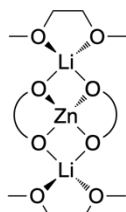
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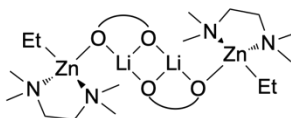
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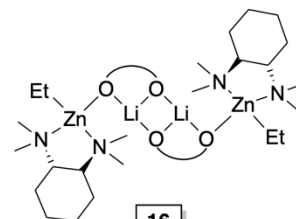
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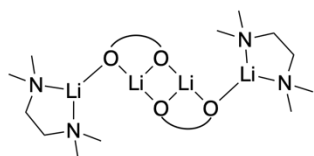
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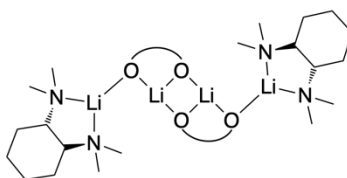
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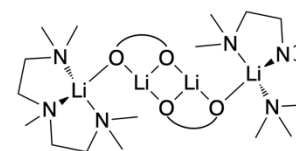
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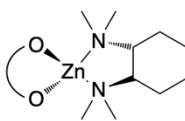
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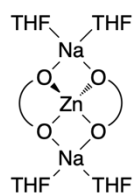
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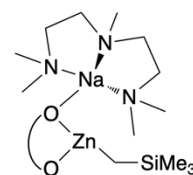
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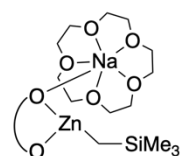
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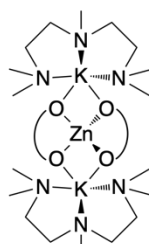
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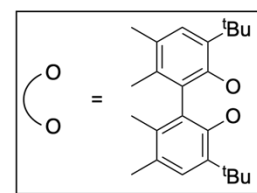


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Chapter 1 – Introduction to Polar Organometallic Chemistry

Polar organometallic reagents such as organolithiums and organomagnesiums have been at the forefront of synthetic chemistry for decades and are considered prized reagents for use in a number of applications. The transformation of a relatively inert hydrogen-carbon bonds into much more labile and reactive metal-carbon bonds through abstraction of a proton from an organic substrate has proved an indispensable tool in synthetic chemistry. First pioneered almost 100 years ago by Schlenk and Bergmann¹, organolithium reagents are perhaps the most widely utilised class of organometallic reagents to date and as such, they are commercially available in numerous different forms including the most commonly used butyllithium's and lithium amides. Similarly, first developed in the early 20th century by the man whose name these reagents bear, Grignard reagents have long since been established as an indispensable tool.² While not as kinetically basic as their organolithium counterparts, they too have found extremely widespread use in synthetic chemistry. This chapter is intended to give an insight into the fundamental structural chemistry of these monometallic reagents.

1.1 Organolithium Reagents

At first glance these compounds may appear simple, however the depiction as simple organometallic species with the formula RLi , where R is either Me, Ph, ^nBu , ^sBu , ^tBu or some variant thereof, is merely a simplification. The actual structure of organolithium reagents is far more complex, with reagents adopting complex aggregated structures.³ As organolithium compounds show a strong structure reactivity relationship, it is important to understand the aggregation states of these reagents in order to use them effectively. Examining some of the more common organolithium reagents, methyllithium and $^n\text{butyllithium}$, shows that in absence of a Lewis base they adopt a tetrameric and hexameric parent structure respectively. An important feature in the formation of these oligomers is the construction of Li_3 'triangles' or faces which are capped by the α -carbon atoms of the alkyl chains in a μ_3 fashion.⁴ A combination of these Li_3 faces leads to the formation tetrahedral (methyllithium) and octahedral ($^n\text{butyllithium}$) aggregates.^{5,6} A closer examination of these two aggregate structures reveals that in the case of the hexameric structure of $^n\text{butyllithium}$, two faces of the octahedron remain uncapped by α -carbon atoms. These uncapped faces have been shown to be located on opposite sides of the octahedron. In both aggregates, the lithium

atoms remain coordinatively saturated with a minimum of four contacts to the other lithium atoms. The nature of the bonding present within these oligomeric structures can be thought of as four centre – two electron bonding.

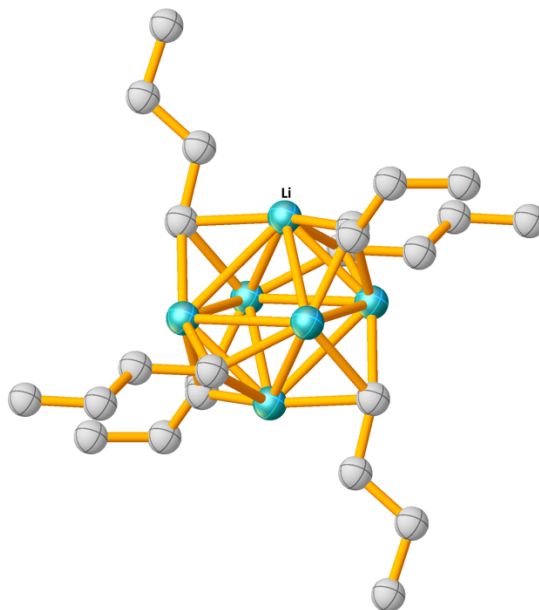


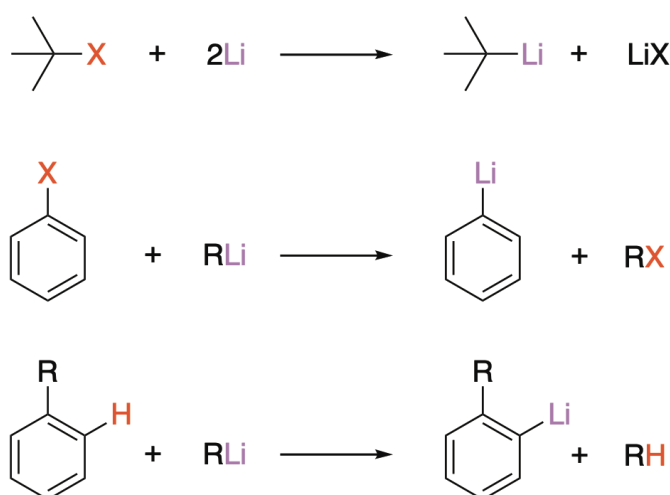
Figure 1: Hexameric aggregation state of (n BuLi) $_6$.

It is possible however to deaggregate these oligomeric structures and is typically achieved by the addition of a Lewis basic donor. Commonly used Lewis donors include, but are not limited to, *N, N, N', N'*-tetramethylethylenediamine (TMEDA), dimethoxyethane (DME), tetrahydrofuran (THF) or diethyl ether. Deaggregation of the parent structure can lead to a marked increase in reactivity as well as an increase in solubility.³ Turning once again to methyllithium, the addition of Lewis donors such as TMEDA, DME or THF does not result in deaggregation of the tetrameric parent structure but rather. This is thought to be due to the stability of the tetrameric unit present in the parent structure and as result, donors such as TMEDA merely coordinate to the lithium atoms form bridging interactions to adjacent tetramers.⁷ Addition of donors such as (+)-sparteine will however produce dimeric aggregates of methyllithium.⁸ In the case of n butyllithium however, several deaggregated structures are known. Addition of TMEDA leads to deaggregation of the hexameric parent structure forming either the dimeric species [n BuLi(TMEDA)] $_2$ or the polymeric species [$(n$ BuLi) $_4$ (TMEDA)] $_{\infty}$ while addition of THF leads to the formation of a tetrameric species.^{9,10} No monomeric species has been isolated for either of these two alkylolithiums. It is thought that a greater steric bulk is required in order to support formation of stable monomers in such highly reactive species. This theory was consolidated by the work of several groups

including of Strohmann who isolated the solid-state structure of monomeric ^tbutyllithium using the ligands (-)-sparteine and TEEDA [where TEEDA is (N,N,N',N'-tetraethylethylenediamine)].^{11,12}

1.1.1 Preparation of Organolithium Reagents

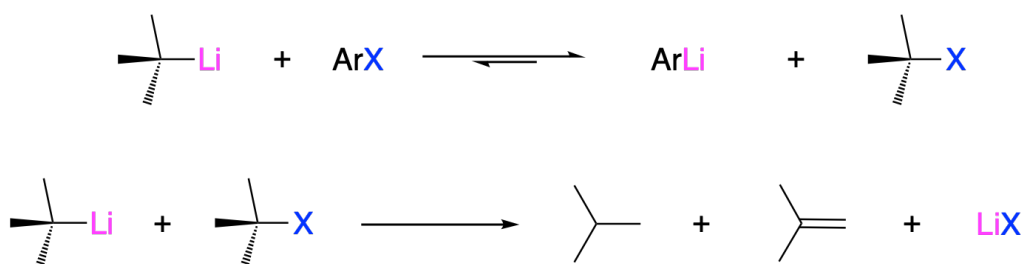
There are several different methods including deprotonation, transmetalation and metal-halogen exchange that can be employed for the preparation of organolithium reagents, however, these methods ultimately rely on the formation of an organolithium reagent from reaction lithium metal with an organic substrate (Scheme 1).¹³ Common alkylolithiums such as ⁿbutyl, ^sbutyl, ^tbutyl or methyllithium can be prepared from lithium metal through reductive insertion into a C-X (where X can be a halogen or hydrogen) bond of the desired alkyl group. This reductive insertion occurs through displacement of the X component with transfer of the organic group to the metal centre. Although a range of functional groups can be tolerated as the X component of C-X, halides are generally the functional group of choice for such reactions.¹⁴



Scheme 1: Synthesis of organolithiums by reductive insertion (top), lithium-halogen exchange (middle) and deprotonation (bottom).

Alternative approaches such as deprotonation and metal-halogen exchange are attractive concepts for the preparation of organolithium complexes as the conditions required for the syntheses are generally more user friendly and therefore can accommodate a wider range of functional groups. Focussing first of all on metal-halogen exchange, this facile reaction which was first reported by Wittig¹⁵ and Gilman¹⁶ has been used extensively in synthetic

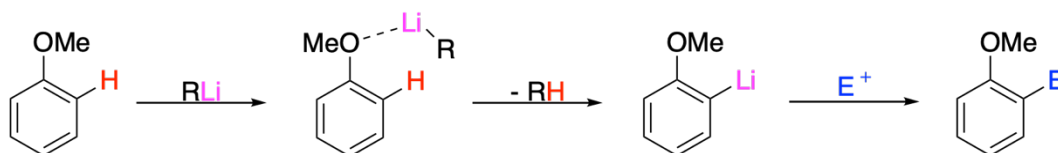
chemistry for the preparation of organometallic complexes and intermediates. Further work by Gilman has shown that the lithium-halogen exchange exists as an equilibrium with it favouring formation of the parent organolithium species.¹⁴ The lithium-halogen exchange reaction is extremely rapid, with reactions known to proceed within minutes at temperatures as low as $-100\text{ }^{\circ}\text{C}$. Cryogenic temperatures are typically employed in order to control the high kinetic reactivity of the organolithium bases and to avoid potential side reactions.¹⁷ Despite this rapid reactivity, chlorinated substrates tend not to react, and lithium-halogen exchange is almost exclusively carried out using substrates functionalised with bromine or iodine. The reactivity of common alkyl lithium reagents is as follows; $t\text{-butyl} > s\text{-butyl} > i\text{-butyl} > n\text{-butyl}$. Not only is $t\text{-butyl}$ lithium the most reactive of the common alkyl lithium reagents, but it also has one further advantage in that its superior reactivity allows it to react with the initial halogen containing by-product of the exchange ($t\text{-butyl}$ bromide or $t\text{-butyl}$ iodide) to form the corresponding lithium salt (Scheme 2). Formation of these lithium salts, which have poor solubilities provides a driving force for reaction, shuttling the equilibrium towards formation of the desired exchange product.¹⁸



Scheme 2: Reactivity of $t\text{-BuLi}$ in metal-halogen exchange.

Turning now to deprotonation, it has been extensively used as a method of generating lithiated intermediates. Despite their high reactivity in the deprotonation of relatively less basic hydrogen atoms, organolithium reagents such as $n\text{-butyl}$ lithium often struggle to deprotonate more complex molecules such as benzene or toluene without the addition of additives such as TMEDA or by taking advantage of directing group effects. One prominent example of this later method has been termed Directed ortho Metalation (DoM).^{19,20} DoM has been studied extensively and not only allows for deprotonation of aromatic substrates with relatively simple organolithium bases such as $n\text{-butyl}$ lithium but also provides a convenient method for controlling the regioselectivity of the deprotonation.²¹ There are a number of directing groups that are compatible with the process including the commonly used methoxy (OMe) functionality. DoM can be considered a three-step process (Scheme 3),

the first of which involves coordination of the alkyllithium base by the directing group. This is followed by deprotonation *ortho* to the site of the direct group to give the lithiated intermediate. The third and final step in the process involves quenching of the lithiated intermediate with an electrophile.



Scheme 3: Directed ortho metalation (DoM) of Anisole.

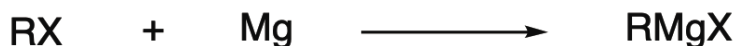
1.2 Organomagnesium Reagents

Dating back over 100 years, Grignard reagents can be considered as the foundation of modern organomagnesium chemistry.² These reagents which, at the simplest level, can be considered as organomagnesium halides RMgX (where R is an organic group and X is a halogen) have found wide-spread use throughout synthetic chemistry. Compared to their organolithium counterparts, the Mg-C bond is far less polarised than that of the Li-C bond and as a result Grignard reagents possess a higher degree of covalent bond character and subsequently a lower reactivity.²² This lower reactivity means however, that while Grignard reagents may be less reactive bases, they possess a far superior functional group tolerance and generally show greater chemoselectivity. The lower reactivity of organomagnesium species such as Grignard reagents allows them to be used in nucleophilic addition reactions, a key carbon-carbon bond forming reaction that would not be possible using the more reaction organolithium reagents.

1.2.1 Preparation of Organomagnesium

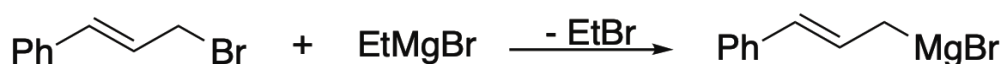
Organomagnesium reagents can be prepared in a variety of ways. For Grignard reagents, the most common route to their preparation is through the oxidative addition of magnesium metal with an organohalide (Scheme 4).² Although the most common synthetic methodology for the preparation of Grignard reagents, the method does have significant drawbacks. Perhaps the most significant of these drawbacks is the low reactivity of the magnesium metal towards toward certain organic halides. As a result, it is often necessary to activate the magnesium metal prior to addition of the organohalide. Activation of the magnesium metal can be achieved in a number of ways including; mechanical activation²³, chemical activation

by addition of iodine or dibromomethane²⁴ or by reduction of magnesium halide salts by Li, Na or K metals to form highly reactive magnesium powders known as Rieke magnesium.^{25,26} One further drawback of this oxidative addition process is that it typically requires the use of ethereal solvents such as THF or diethyl ether which can limit the potential of the reactions for scale up.



Scheme 4: Synthesis of Grignard reagents by oxidative addition.

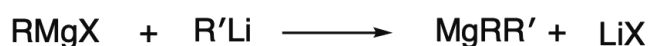
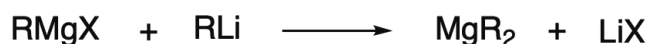
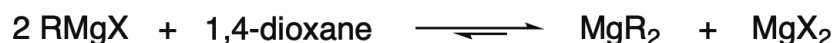
Another method commonly employed for the generation of organomagnesium reagents is metal-halogen exchange. Starting from a simple organomagnesium species such as a Grignard reagent, it is possible to generate new and highly functionalised organomagnesium reagents bearing a number of sensitive functional groups which would not have been compatible with the oxidative addition process outlined previously.²⁷ This reaction was first reported as long ago as 1931 when Prévost reacted the simple Grignard reagent EtMgBr with cinnamyl bromide to generate the functionalised Grignard reagent cinnamylmagnesium bromide (Scheme 5).²⁸ This concept has been developed immensely over the years and has been applied in the synthesis of a vast array of Grignard reagents bearing sensitive and synthetically useful functional groups.²⁹



Scheme 5: Synthesis of cinnamylmagnesium bromide by magnesium-halogen exchange.

So far only the preparation of monoalkyl Grignard reagents has been discussed. It is also possible to prepare a number of dialkyl magnesiums (MgR_2 where R is an organic group).³⁰ These species are typically prepared through either salt metathesis or by the addition of dioxane to a solution of a Grignard reagent to alter the Schlenk equilibrium to favour the formation of the dialkyl species (Scheme 6).^{31–33} Addition of dioxane to a solution of Grignard leads to polymerisation of the magnesium halide salt component. This polymerisation acts as a driving force and shuttles the Schlenk equilibrium to the right in favour of formation of the dialkylmagnesium species.^{34,35} Salt metathesis is typically carried out using another organometallic reagent such as an alkyllithium. Reaction of an alkyllithium with a Grignard reagent leads to transmetalation of the alkyl group from the alkyllithium to the magnesium centre with subsequent loss of the lithium salt. Similar to the dioxane polymerisation

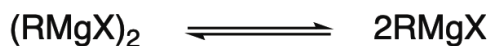
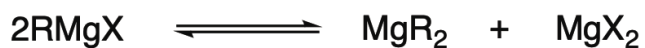
method, loss of the halide salt acts as a strong driving force for the reaction to produce the dialkylmagnesium species. One major advantage of using the salt metathesis method for the preparation of dialkylmagnesiums is the potential to synthesise heteroleptic dialkylmagnesiums. This method of synthesis can also avoid the formation of dioxane adducts of the dialkylmagnesium species.³¹



Scheme 6: Synthesis of dialkylmagnesiums by dioxane polymerisation (top), salt metathesis for the synthesis of homoleptic complexes (middle) and salt metathesis for the synthesis of heteroleptic complexes (bottom).

1.2.2 Schlenk Equilibrium

Similar to organolithium complexes, the solid and solution state-structure Grignard reagents are much more complicated than expected given their representation with the formula RMgX . This formula is in fact an empirical one with Grignard reagents being known to form complex aggregated species which are ultimately governed by the Schlenk equilibrium. First investigated in 1929 by Schlenk and Schlenk Jr., the Schlenk equilibrium dictates that Grignard reagents are in equilibrium with the corresponding magnesium dihalides and diorganomagnesium species.^{36,37} Several studies have been conducted to investigate the structures of Grignard reagents in solution-state using a number of different methods including NMR and IR spectroscopies and more recently by computational methods.^{38–40} These works have shown that Grignard reagents adopt a range of conformations in solution including dimers and other highly aggregated oligomers. Grignard reagents have also been extensively studied in the solid state and have been found to adopt a range of aggregated structures.⁴¹ In order to accommodate these additional findings, the Schlenk equilibrium has been modified to account for the formation of dimeric species as well as higher aggregates and ate species (Scheme 7).⁴²



Scheme 7: General Schlenk equilibrium (top), dimerisation equilibrium (middle) and modified Schlenk equilibrium (bottom).

Furthermore, the solution state behaviour of Grignard reagents is known to have a strong dependence on not only the solvent but also on the identity of the halide atom.^{43,44} It is shown that in Et₂O, Grignard reagents containing Br or I halogen atoms are monomeric at low concentrations. As this concentration is increased, these monomeric species begin to aggregate. In the case of Grignard reagents that contain Cl as the halogen atoms, these complexes are primarily dimeric over a range of concentrations. Investigation of the same Grignard reagents in THF showed that they remain monomeric even as the concentration is increased. In the case of fluorine containing Grignard reagents, they were found to be dimeric across a range of concentrations in both Et₂O and THF. This is thought to be caused by the propensity of fluorine atoms to form bridging interactions compared to the other halogens.

Chapter 2 – Structural Studies of Alkali Metal Magnesiates

2.1 An Introduction to Alkali Metal ‘ate’ Chemistry

The term ‘ate’ is a generic term used to describe homo- and heterobimetallic complexes and was first introduced by Wittig in 1966 after the synthesis and characterisation of Ph_3MgLi .⁴⁵ The first ‘ate’ complex however, was in fact prepared by Wanklyn as far back as 1858 when he prepared the homoleptic sodium zincate NaZnEt_3 .⁴⁶ These types of complexes are typically prepared through the combination of two organometallic fragments that come together to form a new bimetallic species. Within the main group elements, the most common classes of these bimetallic complexes are the alkali metal magnesiates, zincates and aluminates. These heterobimetallic complexes are traditionally synthesised through a combination of an alkali metal (Li, Na or K) organometallic fragment with that of a magnesium, zinc, or aluminium organometallic species. Furthermore, these complexes exhibit a diverse structural chemistry and as a result, the generic term of ‘ate’ can be further subdivided into two categories; contacted ion pairs (e.g., LiMgR_3 , $\text{Li}_2\text{Mg}_2\text{R}_6$ or Li_2MgR_4) or solvent separated ion pairs (e.g. $\text{Li}^+\text{MgR}_3^-$). A further distinction can be made between these ate complexes and that is the assignment of the ate complexes as either high or lower order.⁴⁷ Stemming from the pioneering structural work of Weiss, who noted that contacted ion pair structures prefer a linear structure with the metal atoms being connected by bridging anionic ligands, higher and lower order ate complexes are defined by the ratio of alkali metal to non-alkali metal (Figure 2).⁷ A bimetallic complex containing an alkali metal to non-alkali metal ratio of 1:1 is defined as being lower order while a bimetallic complex containing an alkali metal to non-alkali metal ratio of 2:1 it is classed as being higher order.

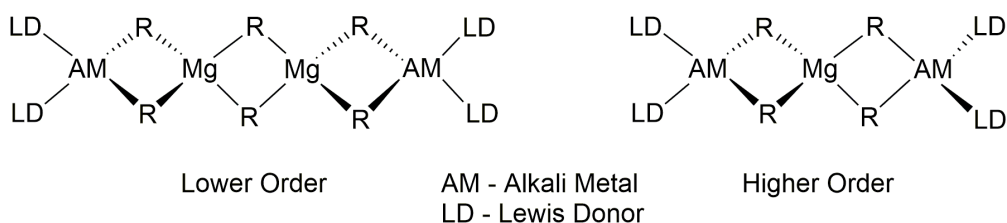


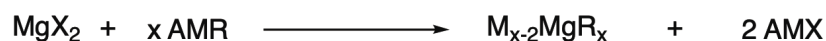
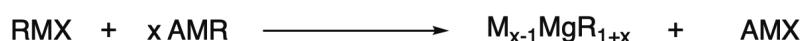
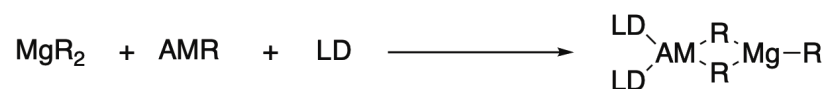
Figure 2: Weiss motifs representing lower order magnesiates (left) and higher order magnesiates (right).

In the case of alkali metal magnesiates, the more Lewis acidic magnesium occupies the central position with the alkali metal atoms being located on the periphery of the structure,

solvated by Lewis donor molecules. This situation is represented visually by the Weiss motifs shown in Figure 2. For lower order ates, the most common geometry adopted by the central magnesium atom is trigonal planar while in their higher order counterparts, a tetrahedral coordination mode is favoured. It is usually the case that the formation of the higher or lower order magnesiate can be favoured simply by adjusting the stoichiometries of the two parent organometallic species in the reaction mixture.

2.1.2 Synthesis of Magnesiate Complexes

As mentioned above, alkali metal ate complexes can be prepared through a combination of an organoalkali metal fragment with another organometallic species. Focussing now on alkali metal magnesiate chemistry, the most common routes to their preparation is through co-complexation, salt metathesis, inclusion of an alkali metal halide salt or by deprotonation (Scheme 8).⁴⁸ The most widely used of these three methods is co-complexation which can be regarded simply as the combination of the desired alkali metal and magnesium organometallic components with a suitable Lewis donor. This method has been used extensively in the preparation of a range of magnesiate complexes including both homo and heteroleptic magnesiates.⁴⁹ This method is particularly suited for the synthesis of mixed ligand heteroleptic systems such as mixed alkyl/amido magnesiates and mixed alkyl/alkoxide magnesiates. Preparation of magnesiates by complexes by salt metathesis, although not as common, is typically achieved by the reaction of a Grignard reagent or a magnesium halide salt with an excess of the desired alkali metal organometallic component.^{50,51} This method again allows for the synthesis of a wide range of magnesiate complexes although it is best suited to the synthesis of homoleptic magnesiates. The final method which can be used to prepare bimetallic magnesiate complexes is the addition of alkali metal halide salts. This method has rose to prominence in recent years following the pioneering work of Knochel and co-worker who prepared 'turbo' Grignard and 'turbo' Hauser reagents by the addition of LiCl to solutions of Grignard and Hauser reagents respectively.^{52,53} A range of additives including other salts such as NaCl have been investigated; however, a lesser degree of improvement in the reactivity of the new bimetallic reagents was observed which therefore lead to the conclusion that LiCl was the optimum additive.



LD = Lewis Donor

AM = Alkali Metal

Scheme 8: Co-Complexation (top) and salt metathesis (middle and bottom) methods for preparation of alkali metal magnesiate complexes.

2.2 Structure and Coordination Chemistry of Alkali Metal Magnesiates

2.2.1 Homoleptic Alkali Metal Magnesiates

Magnesiates comprising completely of carbanionic ligands have been the most widely prepared. The most common of these are the lower order *tris*(alkyl) magnesiates AmMgR_3 and the higher order *tetra*(alkyl) magnesiates Am_2MgR_4 (where Am = Li, Na or K).⁵⁴ Magnesiates such as these are known to adopt both contacted⁵⁵ and solvent separated ion pair structures.⁵⁶ Of these two types of magnesiate, the lower order *tris*(alkyl) form has been the more heavily utilised of the two. It is often the case that chelating donors are required in their synthesis to prevent the formation of highly aggregated or polymeric species. Thus, diamine and triamine donors such as TMEDA, (*R,R*)-TMEDA, (-)-sparteine or PMDETA are routinely used to prepare monomeric forms of the aforementioned structures. Owing to the commercial availability of the starting materials, more structural studies have been carried out involving lithium magnesiates than any other alkali metal magnesiate.⁵⁷

Although less common than their lithium analogues, there are several examples of homoleptic sodium magnesiates containing all carbanionic and all amido ligands.⁵⁸ One of the first crystallographically characterised, solvent free sodium magnesiates was $\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3$ (Figure 3).⁵⁹ This lower order ate complex was prepared via co-complexation of $\text{Na}(\text{CH}_2\text{SiMe}_3)$ with $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$. In the solid state, the magnesium atom adopts a trigonal planar coordination geometry and is bound to three CH_2SiMe_3 ligands. However, unlike in the traditional Weiss motif which depicts two bridging ligands and a single terminal ligand, the solid state structure of $\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3$ contains a single bridging

ligand connecting the sodium and magnesium centres. Moreover, $\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3$ was isolated as a polymeric solvent free complex which forms a 12 atom fused ring system that propagates to form a honeycomb like polymeric network. Without the presence of a Lewis donor, the sodium atom's coordination sphere is satisfied by the formation of a bridging interaction to an alkyl group on a neighbouring molecule.

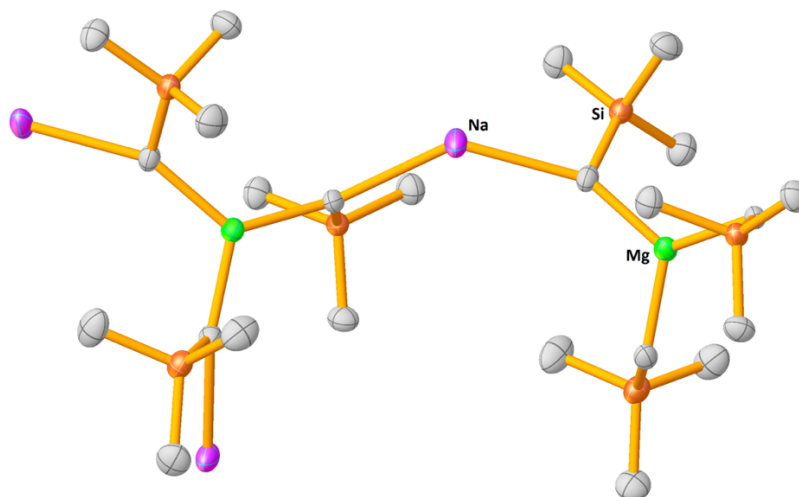


Figure 3: Solid-state structure of $[\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3]_\infty$.

Turning now to the n -butyl related homoleptic sodium magnesiate NaMg^nBu_3 , the effects of donor solvents can be clearly seen. Unlike $[\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3]_\infty$, donor-free NaMg^nBu_3 has yet to be structurally characterised in the solid-state. Upon addition of the diamine donor DABCO [where DABCO is 1,4-diazabicyclo[2.2.2]octane] the higher order solvent separated ion pair magnesiate $\{[\text{Na}_2(\text{DABCO})_3(\text{toluene})]^{2+}(\text{Mg}^n\text{Bu}_4)^{2-}\}_\infty$ was isolated (Figure 4).⁶⁰ The dicationic moiety consists of two sodium atoms which are tetrahedrally coordinated to the π face of a single molecule of toluene and to three separate DABCO ligands, one of which functions as a bridging ligand between the two sodium atoms within in the same molecule. The other two DABCO ligands allow the species to propagate by bonding to sodium atoms in adjacent molecules. The di-anionic moiety contains a tetrahedrally coordinated magnesium atom bound to four n -butyl ligands and is contained interstitially within the cationic framework created by the polymerisation of the sodium units.

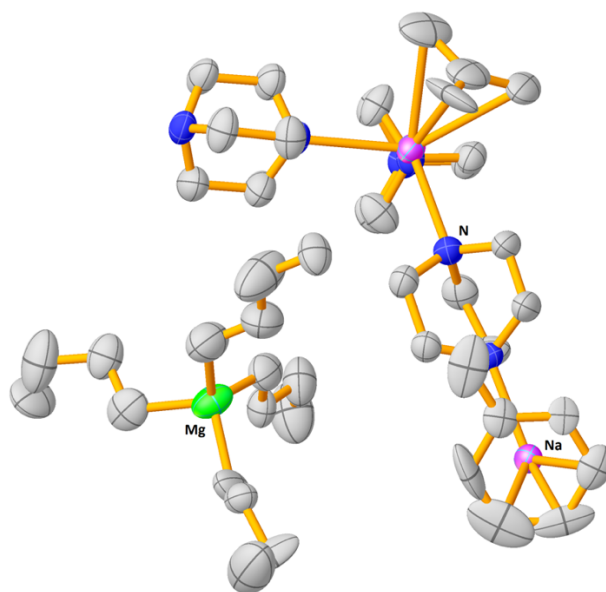


Figure 4: Solid-state structure of $\{[\text{Na}_2(\text{DABCO})_3(\text{toluene})]^{2+}(\text{MgBu}_4)^{2-}\}_\infty$.

There are also several examples in the literature of *tris*(amido) alkali metal magnesiates.⁶¹ Once again focussing on the structural characteristics of sodium magnesiates, these homoleptic complexes are known to exist as of both contacted and solvent separated ion pairs and have a diverse structural chemistry. One of the first structurally characterised examples of a *tris*(amido) sodium magnesiate was the TMEDA solvated $[(\text{TMEDA})\text{NaMg}(\text{NiPr}_2)_3]$.⁶² This magnesiate was synthesised through a modified deprotonation technique in which the parent amine, diisopropylamine $[\text{DA}(\text{H})]$ was added to a mixture of n -butylsodium and di- n -butylmagnesium in a hydrocarbon solvent. Using the same synthetic approach, our group has also successfully prepared and characterised the *tris*(amido) magnesiate $[(\text{TMEDA})\text{NaMg}(\text{cis-DMP})_3]$ containing the slightly bulkier *cis*-DMP ligand in place of (where *cis*-DMP is *cis*-2,6-dimethylpiperidide).⁶³ Both magnesiates were found to adopt the common Weiss motif expected for a *tris*(amido) magnesiate in the solid-state. For $[(\text{TMEDA})\text{NaMg}(\text{NiPr}_2)_3]$, the solid-state structure contains three DA molecules, two of which act as bridging ligands between the magnesium and sodium centres with the third molecule of DA binding terminally to the magnesium centre. Examining the solid-state structure of $[(\text{TMEDA})\text{NaMg}(\text{cis-DMP})_3]$ the same situation is observed with two bridging and one terminal *cis*-DMP ligand. Thus, the magnesium atoms of $[(\text{TMEDA})\text{NaMg}(\text{NiPr}_2)_3]$ and $[(\text{TMEDA})\text{NaMg}(\text{cis-DMP})_3]$ have trigonal planar coordination geometries while the sodium atoms, on account of the chelating binding mode of TMEDA in each complex, adopt a distorted tetrahedral geometry. In each case, the Mg-N bond lengths for the bridging amido ligands are longer than those of the Mg-N bond lengths for the terminal amido ligand. An

increase in bond lengths of the bridging ligands are common in mixed metal complexes as a result of sharing of electron density between multiple atoms. This lengthening is accompanied by a weakening of the bond which results in the bridging ligand being the most reactive. The donor solvent free forms of [(TMEDA)NaMg(NiPr₂)₃] or [(TMEDA)NaMg(*cis*-DMP)₃] have yet to be characterised in the solid-state but both have been shown to be potent bases, with [(TMEDA)NaMg(NiPr₂)₃] in particular being capable of carrying out a number of unique deprotonations.⁶⁴ Several *tris*(amido) magnesiates containing the utility amine HMDS(H) (where HMDS(H) is 1,1,1,3,3,3,-hexamethyldisilazane) have also been characterised including [((-)-sparteine)₂Na]⁺{Mg(HMDS)₃}⁻, [(((*R,R*)-TMCDAs)₂Na]⁺{Mg(HMDS)₃}⁻ (Figure 5) and [(TMEDA)₂Na]⁺[Mg(HMDS)₃]⁻ (where HMDS is 1,1,1,3,3,3,-hexamethyldisilazide).^{65,66} Unlike the previous example using DA and *cis*-DMP these magnesiates exist as solvent separated species. All three of these homoleptic magnesiates contain a common *tris*(HMDS) anionic moiety in which the magnesium atom adopts a trigonal planar geometry in binding to all three HMDS ligands. This *tris*(HMDS) anion is a common structural feature and can be found in a number of other alkali metal magnesiates.^{67–69} The cationic moiety of each of these complexes contains a sodium atom which is bound to the respective Lewis donor in an η² chelating fashion. In the case of the chiral Lewis donors, (-)-sparteine and (*R,R*)-TMCDAs, the sodium atoms adopt a tetrahedral geometry while in the case of TMEDA, the sodium atom displays an unusual distorted square planar geometry. Hill and co-workers have also characterised a series of homoleptic alkali metal magnesiates containing the *tris*(HMDS) anion, this time using an *N*-heterocyclic carbene (NHC) in place of a Lewis donor molecule.⁷⁰ The magnesium anion adopts the same trigonal planar geometry; however, in the case of the sodium magnesiate, the sodium atom adopts a linear coordination geometry bound to two NHC ligands. This unusual linear, two coordinate geometry is not altogether surprising given the well documented ability of NHC ligands to support metal atoms in unconventional geometries and oxidation states.

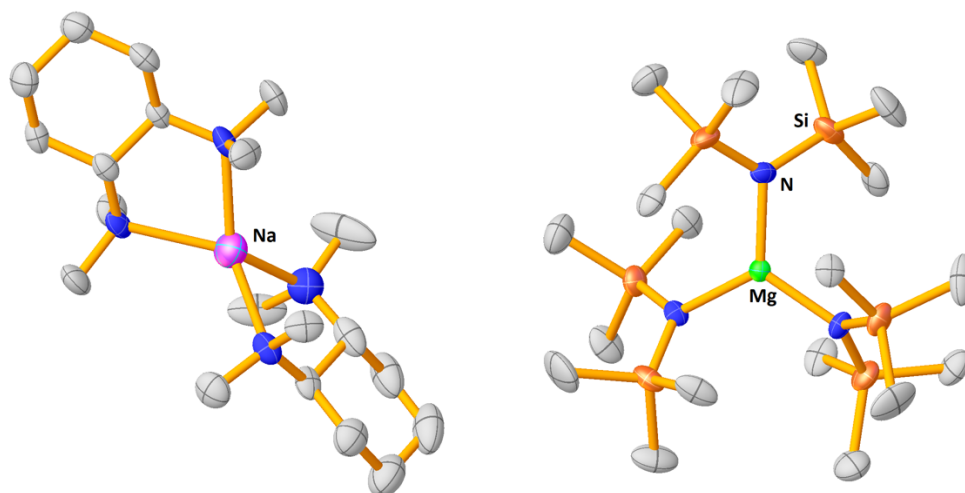


Figure 5: Solid-state structure of $\{[(R,R)\text{-TMCD A}]_2\text{Na}^+[\text{Mg}(\text{HMDS})_3]^- \}$.

2.2.2 Heteroleptic Alkali Metal Magnesiates

One important class of heteroleptic magnesiates is the mixed alkyl/amido magnesiates which again possess a diverse structural chemistry. Examples of this type of complex include the sodium magnesiates $[(\text{TMEDA})\text{Na}(\mu\text{-}^n\text{Bu})\text{-(}\mu\text{-TMP)}\text{Mg}(\text{TMP})]$,⁷¹ $[((-)\text{-sparteine})\text{Na}(\mu\text{-}^n\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$,⁷² $[(\text{Et}_2\text{O})\text{Na}(\mu\text{-HMDS})_2\text{Mg}(^t\text{Bu})]$ ⁷³ and $[(\text{TMEDA})\text{Na}(\mu\text{-CH}_2\text{SiMe}_3)\text{-(}\mu\text{-TMP)}\text{Mg}(\text{TMP})]$ (Figure 6).⁷⁴ All four complexes exist as discrete monomeric units in the solid-state. An interesting structural feature of TMP-containing complexes is that they contain a bridging alkyl and bridging amido ligand. The sodium atoms adopt a distorted tetrahedral geometry due to the narrow bite angle of the chelating TMEDA and (-)-sparteine ligands while the magnesium centres adopt a distorted trigonal planar geometry binding to two TMP ligands, one bridging and one terminal, as well as the bridging n butyl alkyl ligand. For $[(\text{Et}_2\text{O})\text{Na}(\mu\text{-HMDS})_2\text{Mg}(^t\text{Bu})]$ however, both HMDS ligands act as the bridge ligands while the t butyl ligand is bound in a terminal fashion. Inclusion of a monodentate ether molecule as the Lewis base and not a bidentate donor such as TMEDA or (-)-sparteine means that both sodium and magnesium atoms adopt distorted tetrahedral geometries. Turning now to the solvent free-complex $[\text{Na}(\mu\text{-HMDS})_2\text{Mg}(^n\text{Bu})]_\infty$ a more complex coordination chemistry is observed.⁶⁶ As may be expected for a solvent-free species, the structure was determined to be polymeric. Both magnesium and sodium centres adopt distorted trigonal planar geometries, with the HMDS ligands acting as bridging ligands between the two metal centres. The coordination sphere of the magnesium atom is complete by formation of a bond to the n butyl ligand. As the species is polymeric, the polymer propagates through an interaction between the sodium of one molecular unit and the alkyl ligand of a neighbouring

one. Studying the structural chemistry of these complexes with various Lewis donors highlights the rich and complex structural chemistry of bimetallic magnesiates. As mentioned previously, the addition of Lewis donors such as TMEDA can lead to the deaggregation of polymeric structures. Thus, addition of two equivalents of TMEDA leads to the formation of the monomeric species $[(\text{TMEDA})_2\text{Na}(\mu\text{-}^n\text{Bu})\text{Mg}(\text{HMDS})_2]$.⁶⁶ It is worth noting here that the bridging group linking the two metal centres is now the n -butyl alkyl ligand and the HMDS amide ligands are now terminally bound to the magnesium. In contrast to the mixed alkyl/amido magnesiates mentioned above however, addition of a single equivalent of TMEDA does not lead to formation of a monomeric species but rather to the formation of the polymeric complex $\{[\text{Na}(\mu\text{-HMDS})]_2\text{Mg}(\mu\text{-}^n\text{Bu})_2(\text{TMEDA})\}_\infty$ with inclusion of TMEDA within the new polymeric structure.⁶⁶ $\{[\text{Na}(\mu\text{-HMDS})]_2\text{Mg}(\mu\text{-}^n\text{Bu})_2(\text{TMEDA})\}_\infty$ is more accurately described as an 'inverse magnesiate'. The first example of an 'inverse' ate complex was given by Hevia and co-workers and describes the situation whereby the most Lewis acid metal, which would normally accept the additional anionic ligand to form the ate species no longer does so.⁴⁹ In the case of $\{[\text{Na}(\mu\text{-HMDS})]_2\text{Mg}(\mu\text{-}^n\text{Bu})_2(\text{TMEDA})\}_\infty$ the more Lewis acidic di- n -butylmagnesium fragment is now acting as a Lewis basic entity, solvating the now more Lewis acidic dimeric NaHMDS.

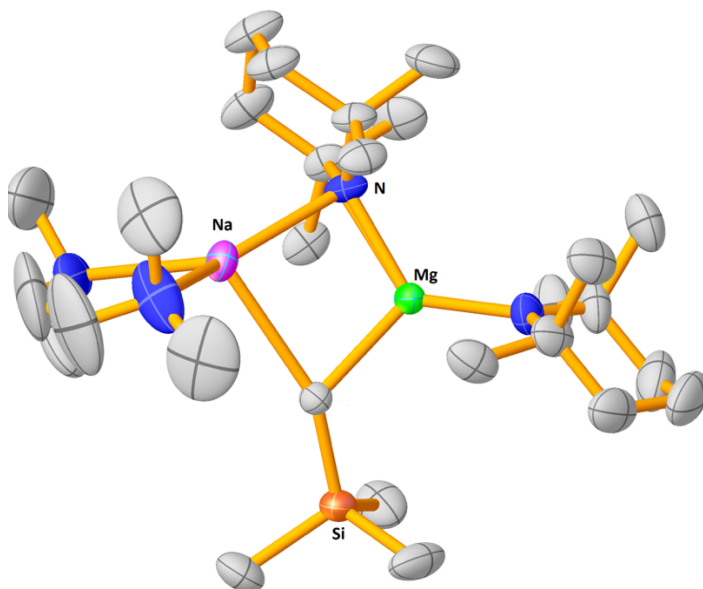


Figure 6: Solid-state structure of $[(\text{TMEDA})\text{Na}(\mu\text{-CH}_2\text{SiMe}_3)\text{-(}\mu\text{-TMP)}\text{Mg}(\text{TMP})]$.

A further class of heteroleptic alkali metal magnesiates that merit discussion are those which contain a mix of alkyl and alkoxide ligands. Magnesiates of this type can be prepared by inclusion of alcohol or phenol-based ligands in place of the more traditional alkyl or amide

based ligands or by controlled exposure of an existing magnesiate to atmospheric oxygen. This latter method has been used successfully for the synthesis of the alkoxide containing magnesiate $[\text{Na}_2\text{Mg}_2(\text{OCH}_2\text{SiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4]_\infty$.⁷⁵ The formation of this alkoxide containing species can be rationalised as the product of co-complexation between $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ and the sodium alkoxide $\text{NaOCH}_2\text{SiMe}_3$ consisting of a dimeric arrangement of two $\text{NaMgR}_2(\text{OR})$ units. Complexes of this type have also been described as inverse crown ethers.⁷⁶ This name arises from the reversal of the usual nomenclature for crown ether molecules in which the Lewis basic host ring system traps the Lewis acid guest. For an inverse crown ether the opposite is true and the polycationic Lewis acidic ring system, in this case the $(\text{NaCMg})_2$, traps the Lewis basic species. These inverse crown ether complexes have been shown to incorporate a number of species including ranging from alkoxides^{77–79} to hydrides^{80,81} as well as oxo and peroxy ligands (Figure 7).^{82–84}

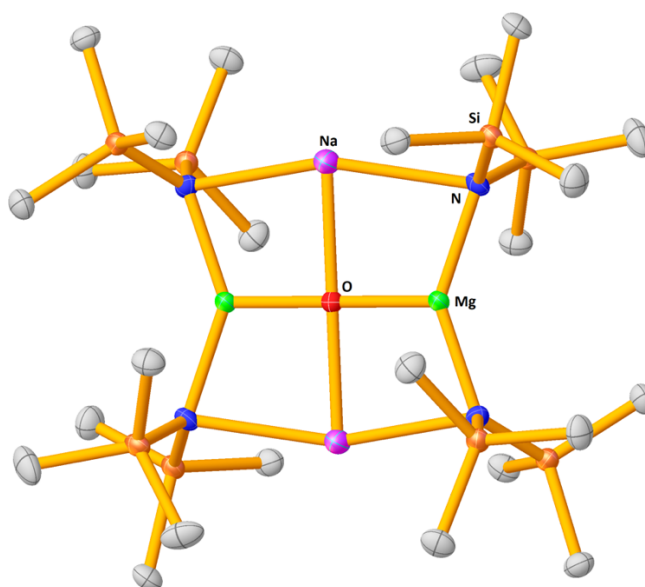


Figure 7: Solid-state structure of inverse crown ether $\{\text{Na}_2\text{Mg}_2[\text{N}(\text{SiMe}_3)_2]_4(\text{O})\}$.

Although until this point the discussion of the structural chemistry of bimetallic magnesiates has focussed on sodium magnesiates, a brief discussion of the structure of the turbo Grignard and turbo Hauser bases will be undertaken due to the prevalence of their use in synthetic chemistry. Despite a wealth of literature relating to the reactivity of turbo Grignard reagents, comparatively little is known about their solid-state structures.⁸⁵ Knochel initially proposed that LiCl binds to the Grignard reagent through bridging chlorine atoms to form a four membered Mg-Cl-Li-Cl ring or as a solvent separated ion pair containing an anionic magnesiate fragment.^{52,86} To date there has been no crystallographic evidence of either proposed structure. Studying solutions of the turbo Grignard reagent $\text{iPrMgCl} \cdot \text{LiCl}$, Lerner

and co-workers were able to isolate and characterise the solid-state structure of the parent Grignard reagent $i\text{PrMgCl}$ which was shown to adopt a neutral open-cube geometry but crucially there was no incorporation of LiCl .⁸⁷ In the same study, they utilised the bulkier turbo Grignard reagent $\text{DisylMgCl} \cdot \text{LiCl}$ [where Disyl is $(\text{Me}_3\text{Si})_2\text{CH}$] and managed to isolate the oxidation product $\{[\text{DisylOMgCl}][\text{LiCl}(\text{THF})_2]\}_2$ (Figure 8). Although not an ideal structure owing to the presence of bridging oxygen groups and issues with the rational synthesis of the complex, the structure was found to contain two Mg-Cl-Li-Cl rings therefore serving as the first crystallographic evidence to support the formation of such architectures for turbo Grignard reagents.

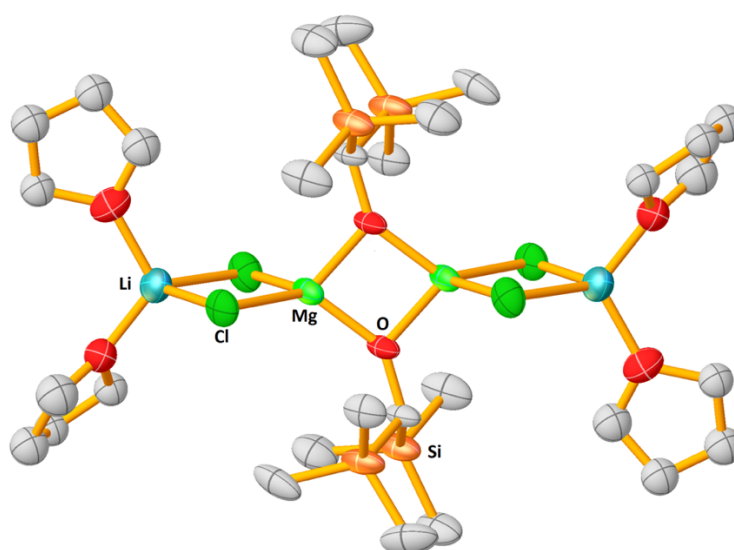


Figure 8: Solid-state structure of $\{[\text{DisylOMgCl}][\text{LiCl}(\text{THF})_2]\}_2$.

Studies have also carried been out in order to assess the composition of these bimetallic complexes in solution using NMR spectroscopy as well as using other techniques such as electron spray ionisation (ESI) and quantum chemical calculations.^{86,88} Using ^1H DOSY NMR spectroscopy, the group of Stalke have shown that addition of LiCl to a solution of $n\text{BuMgCl}$ leads to the association of the two components and depending on solvent effects and the number of coordinated THF molecules within the species, this association could be quantitative. This association is further supported by quantum chemical calculations which suggest that a combination of $n\text{BuMgCl}$ and LiCl could lead to the formation of ate species within solution.

Turning now to the magnesium amide complexes known as turbo Hauser bases, the structural picture is a little clearer, owing to the successful characterisation of the solid-state

structure of $\text{TMPMgCl} \cdot \text{LiCl}$ (Figure 9).⁸⁹ Examining this structure, the four membered Mg-Cl-Li-Cl ring proposed for the turbo Grignard reagents by Knochel is clearly present. The central magnesium atom adopts a distorted tetrahedral geometry and is bound to two bridging chlorine atoms and to the nitrogen atom of the terminal transoid-disposed TMP ligand. The coordination sphere of the Li atom is similarly completed through coordination to two molecules of THF. A dimeric variant of this structure has also been isolated, this time containing diisopropylamide in the place of TMP (Figure 9).⁹⁰ A key difference between the two structures are the positions adopted by the reactive amido ligands. In the case of the turbo Hauser base $\text{TMPMgCl} \cdot \text{LiCl}$, the reactive TMP ligand is located in a terminal position bound solely to the magnesium atom whereas for the dimeric complex $\{[(\text{THF})_2\text{Li}(\mu\text{-Cl})_2\text{Mg}(\mu\text{-DA})]_2\}$, the reactive DA ligands are located in the centre of the complex as bridging ligands.

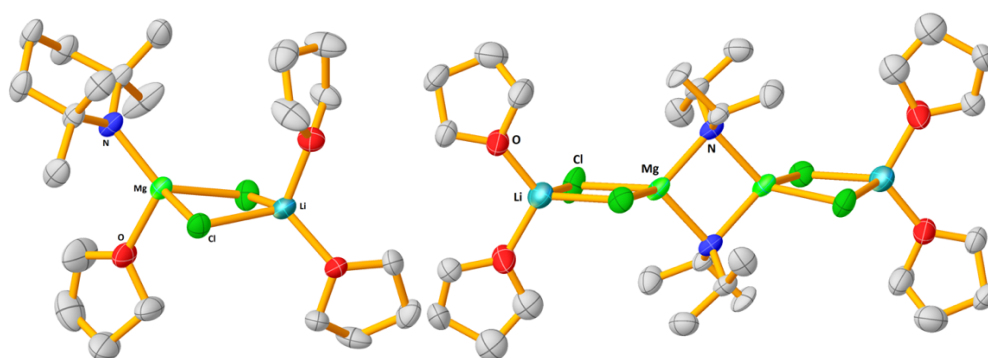


Figure 9: Solid-state structures of the turbo Hauser bases $\text{TMPMgCl} \cdot \text{LiCl}$ (left) and $\{[(\text{THF})_2\text{Li}(\mu\text{-Cl})_2\text{Mg}(\mu\text{-DA})]_2\}$ (right).

2.3 Aims

The aim of this chapter is to give an insight into the complex structural chemistry of a series of heteroleptic alkyl/phenoxide sodium magnesiates using the ditopic (*rac*)-BIPHEN ligand (Figure 10). Phenoxide ligands of this type can possess a form of chirality known as axial chirality which arises from the hindered rotation around the central bond linking the two aryl rings and as result often find application in asymmetric synthesis.⁹¹ The large steric bulk of these ligands makes them ideal for stabilising metal centres whilst, particularly in the case of BIPHEN, they provide highly diagnostic chemical shift values which makes these ligands ideal probes for monitoring of reactions by NMR spectroscopy. Furthermore, these axially chiral ligands can be prepared using a variety of methods and can include of a vast array of functionalities enabling the steric and electronic parameters of these ligands to fine-tuned.^{92,93}

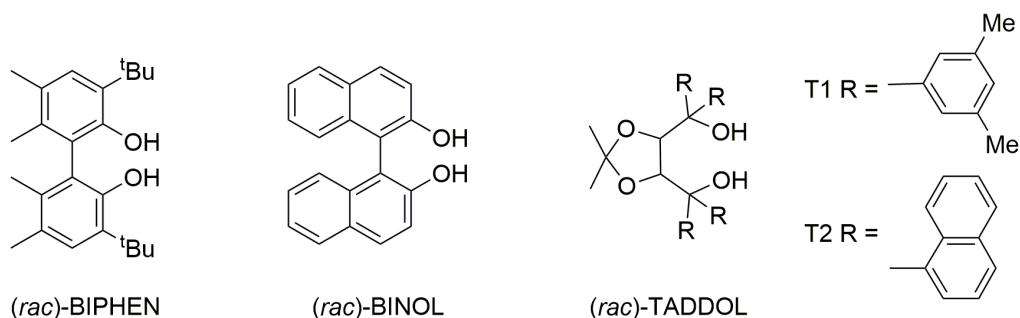


Figure 10: Common phenoxides used for the generation of chiral main group complexes shown in their racemic forms.

Despite their frequent use, a relatively small number of complexes containing the (*rac*)-BIPHEN have been characterised in the solid state. Of those structures characterised, only a few are bimetallic complexes and of these bimetallic structures, the only alkali metal contained within them is lithium. Thus, this work is focussed on the synthesis and characterisation of sodium magnesiates containing the (*rac*)-BIPHEN ligand in order to further the understanding of main group bimetallic complexes bearing these prized ligands. Building on a previous study from within our group which focussed on the synthesis and structure of a series of lithium magnesiates containing the (*rac*)-BIPHEN, a comparison will be made, where appropriate, to their heavier sodium analogues in order to assess any alkali metal effects that may play a part in the coordination chemistry of these ligands. As structure is often linked to reactivity it is important that a good understanding of the underlying structure and coordination chemistry of the new bimetallic sodium magnesiate reagents is known in order to fully rationalise their reactivity.

2.4 Results and Discussion

2.4.1 Synthetic Approach for Synthesis of Sodium Magnesiates

Previously, the lithium magnesiates $[(rac)\text{-BIPHEN}]\text{Li}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$, $[(rac)\text{-BIPHEN}]\text{Li}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_3$ and $[(rac)\text{-BIPHEN}]\text{Li}_2\text{Mg}(\text{}^n\text{e}^o\text{Pen})_2(\text{THF})_2$ have been synthesised by our group (Figure 11).⁹⁴ As a precursor to these studies, the homometallic lithium precursor $[(rac)\text{-BIPHEN}]\text{Li}_4(\text{THF})_4$ was also studied. In order to synthesise these complexes, a simple co-complexation approach was used. The parent diol, $(rac)\text{-BIPHEN-H}_2$ (Figure 10), was first deprotonated using two molar equivalents of $^n\text{BuLi}$ to generate the tetranuclear precursor $[(rac)\text{-BIPHEN}]\text{Li}_4(\text{THF})_4$. Complexation of this tetranuclear precursor with the desired dialkyl magnesium followed by addition of stoichiometric amounts of THF as a donor solvent yielded the desired magnesiate in good yields.

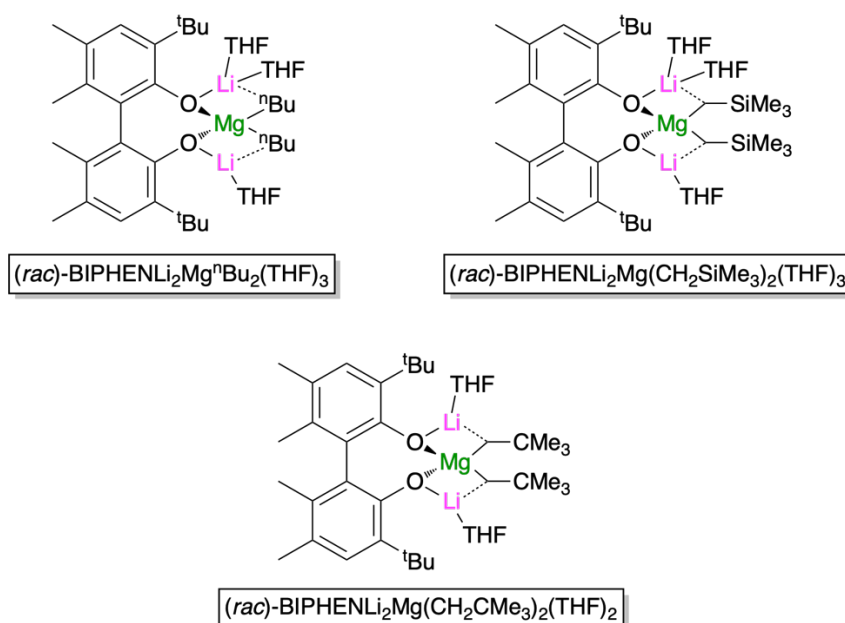
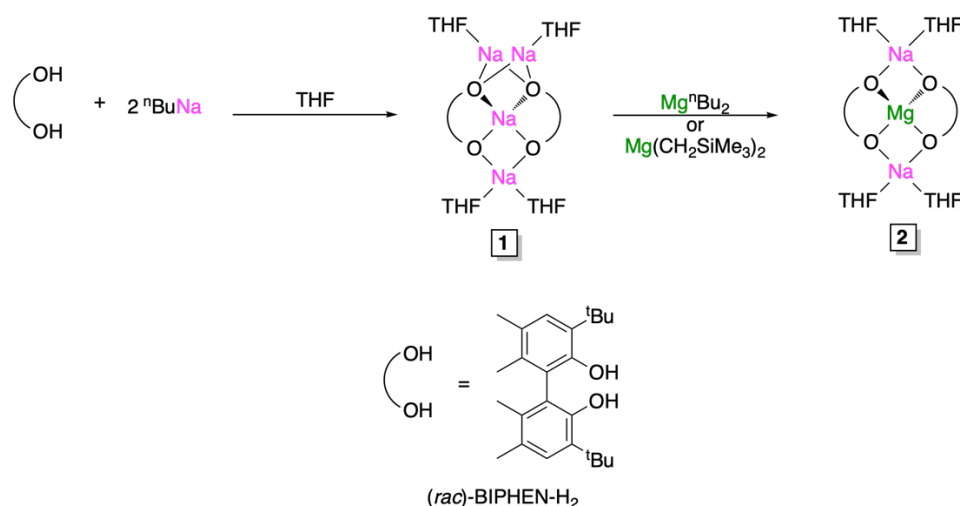


Figure 11: Lithium magnesiates previously characterised in the solid-state containing the $(rac)\text{-BIPHEN}$ ligand.

A similar approach was therefore initially utilised in an attempt to synthesise and characterise the corresponding sodium magnesiates. Our investigation began by probing the formation of homometallic sodium precursor which was proposed to have a similar if not identical structure to that of the homometallic lithium precursor previously reported by our group. To this end, a solution of $(rac)\text{-BIPHEN-H}_2$ was added to a suspension of $^n\text{butylsodium}$ in hexane at $-10\text{ }^\circ\text{C}$ in a 1:2 molar ratio to give a colourless solution. The solution was

concentrated *in vacuo* to the point of incipient crystallisation then a stoichiometric amount of THF was added to once again give a colourless solution. This solution was subsequently stored at $-18\text{ }^{\circ}\text{C}$ for 24 hours after which time colourless block shaped crystals were deposited. Analysis of these crystals by X-ray crystallography revealed the structure to be that of the desired sodium phenoxide $(\text{BIPHEN})_2\text{Na}_4(\text{THF})_4$ (**1**).

After this initial success, it appeared that the reactivity of sodium was mimicking that of lithium and that it would allow for the synthesis of a range of isostructural magnesiates. Our next step therefore was to investigate the synthesis of the mixed alkyl/phenoxide sodium magnesiate $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$. To this end, di-*n*-butylmagnesium was combined with a hexane solution **1** to produce a white precipitate. THF was then added in an attempt to dissolve the precipitate, however, no dissolution was achieved at ambient temperature. The suspension was therefore gently heated until dissolution of the precipitate was achieved after which the solution was allowed to cool slowly to ambient temperature before being stored $-33\text{ }^{\circ}\text{C}$. Upon storage of the solution at sub-ambient temperature for 24 hours a crop of large colourless crystals was formed. X-ray crystallographic analysis of the crystals revealed the product of the reaction to be the BIPHEN-rich dimeric species $(\text{BIPHEN})_2\text{Na}_2\text{Mg}(\text{THF})_4$ (**2**) and not the desired sodium magnesiate $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$. Isolation of a similar BIPHEN-rich species has previously been reported by our group during the course of investigations into the corresponding (*rac*)-BIPHEN containing lithium magnesiates.⁹⁴ The formation of the homoleptic species was attributed to thermal decomposition of the desired dialkyl species in accordance with the Schlenk equilibrium (See Chapter 1). Assuming a similar decomposition pathway was active for the heavier sodium magnesiates, the reaction was repeated, this time ensuring tight control of the reaction temperature by not allowing the reaction mixture to rise above $-5\text{ }^{\circ}\text{C}$ during co-complexation. In order to avoid the need for heating of the solution a small excess of THF was added in order to aid dissolution of the aforementioned precipitate after which the solution was immediately stored at $-33\text{ }^{\circ}\text{C}$. A colourless crystalline material was again isolated and analysed by X-ray crystallography and NMR spectroscopy, however, the product was again determined to be the BIPHEN rich dimeric species **2** (Scheme 9).

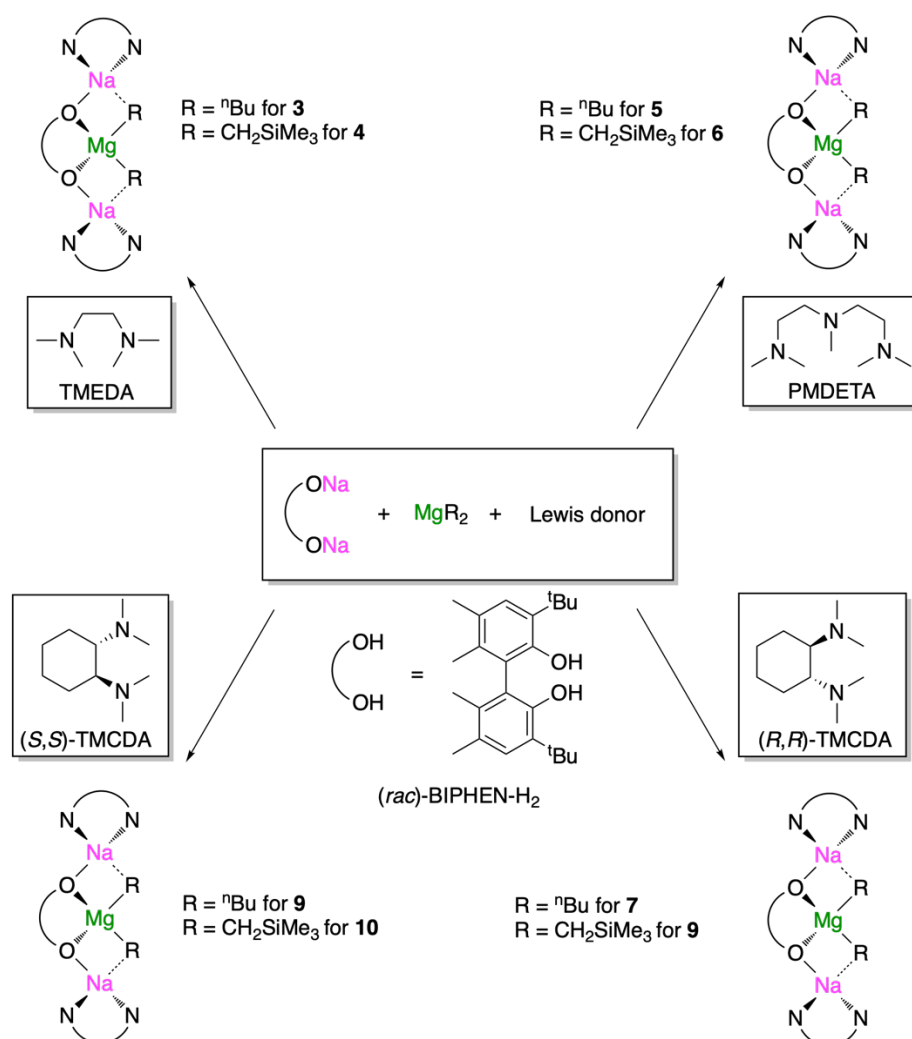


Scheme 9: Synthetic method for the preparation of **1** and **2**.

The reaction was repeated, replacing di-*n*-butylmagnesium with the bulkier dialkylmagnesium $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$. Co-complexation of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ with **1** again produced a white suspension which was found to be soluble upon addition of a stoichiometric amount of THF with slow warming to ambient temperature. This colourless solution was stored at $-33\text{ }^\circ\text{C}$ and produced a colourless block-like crystals. Subsequent analysis of the crystals by X-ray crystallography revealed the complex to have an identical unit cell to that of the crystals of the previous reaction using di-*n*-butylmagnesium. A ^1H NMR spectrum of the material confirmed that the product of the reaction was indeed that of **2** not the desired magnesiate $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_3$. After multiple failed attempts to isolate the dialkyl sodium magnesiates $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_3$ and $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$ it was clear that the synthetic approach to their synthesis must be altered.

Therefore, it was decided that alternative Lewis donors must be used, preferably those which bind in a chelating fashion. The simple diamine TMEDA was chosen as the Lewis donor and the synthetic procedure was modified accordingly. Deprotonation of the parent (rac)-BIPHEN-H₂ was achieved by addition of the diol to a suspension of *n*-butylsodium in hexane which had been sonicated and cooled to $-10\text{ }^\circ\text{C}$. The white suspension was stirred until a clear solution was formed after which di-*n*-butylmagnesium was added, forming a white suspension. TMEDA was then added and unlike the reactions involving THF, gave a colourless solution even at sub-ambient temperatures. This colourless solution was then stored at $-18\text{ }^\circ\text{C}$ for 24 hours after which time a colourless crystalline material was deposited. Although not suitable for analysis by X-ray crystallography, the material was analysed by NMR

spectroscopy and the structure assigned as $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$ (**3**) *vide infra* (Figure 10).



Scheme 10: Synthetic approach used for the synthesis of complexes **4-10**.

Following the successful isolation of **3** the reaction was repeated using the $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ as the dialkylmagnesium component and the corresponding magnesiate $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{TMEDA})_2$ (**4**) was isolated and fully characterised by X-ray crystallography and multinuclear NMR spectroscopy. The isolation of these two magnesiates using the bidentate donor TMEDA lead us to investigate what other donors would be tolerated by the system. To this end, the reaction was repeated using PMDETA, (R,R) -TMCDA and (S,S) -TMCDA as Lewis donors and led to the successful isolation of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{PMDETA})_2$ (**5**), $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{PMDETA})_2$ (**6**), $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCDA})_2$ (**7**), $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((R,R)\text{-TMCDA})_2$ (**8**), $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((S,S)\text{-TMCDA})_2$ (**9**) and $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((S,S)\text{-TMCDA})_2$ (**10**).

TMCDA)₂ (**10**) which have been fully characterised in the solid-state by X-ray crystallography and/or in solution by multinuclear NMR spectroscopy (Scheme 10).

2.4.3 Structural Characterisation of Sodium Magnesiates

2.4.3.1 (BIPHEN)₂Na₄(THF)₄ (**1**)

Our investigations began by concentrating on the disodium phenoxide complex (BIPHEN)₂Na₄(THF)₄ **1** as the precursor to magnesiate formation (0.145 g, 26 % yield). The solid-state structure of the disodium phenoxide **1** was determined to be a dimeric THF solvate (Figure 12). For each molecule of this tetranuclear sodium species there is an imposed 2-fold symmetry with two of the sodium atoms contained within the structure being located on this axis. As a result, the complex contains three distinct sodium environments. Interestingly, despite using the racemic form of the BIPHEN ligand in the preparation of **1**, the crystals which were isolated and analysed by X-ray diffraction were found to have the chiral space group P4₂2₁2. This situation is made possible by having a single crystallographically unique (*i.e.* a single enantiomer) of the BIPHEN ligand per unit cell of the complex. This spontaneous resolution of the racemic ligand into its enantiomerically pure form is thought to occur for only approximately 5 – 10 % of racemic compounds. In order for this spontaneous resolution to take place, conglomerates or physical mixtures of a single enantiomer must form in solution.^{95–98} In the absence of any driving force to the resolution of the racemic mixture, it is thought that this must be the case here. Evidence of this enantiopure form is further reinforced by the Flack parameter which was calculated to be 0.018(14) for **1**.⁹⁹

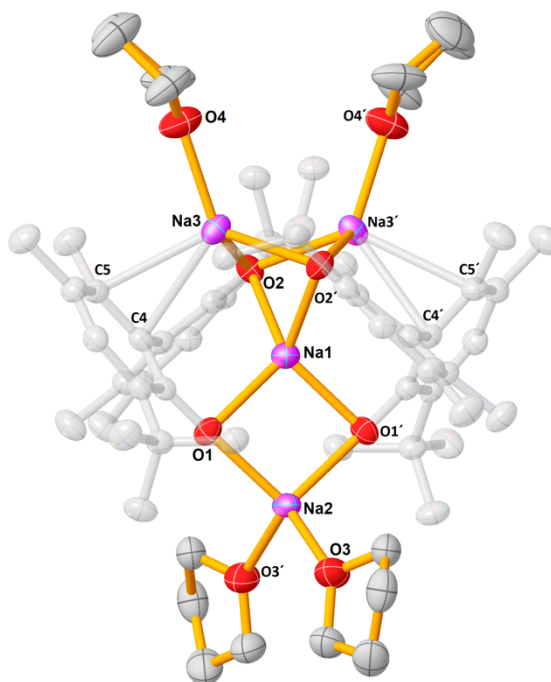


Figure 12: Solid-state structure of $(\text{BIPHEN})_2\text{Na}_4(\text{THF})_4$, **1**. Hydrogen atoms and disorder in THF molecules are omitted for clarity. Thermal ellipsoids are set to 50% probability level. Phenoxide ligands are *R R* orientated. Key bond distances (Å) and bond angles (°): Na(1)–O(1), 2.217(2); Na(1)–O(2), 2.313(2); Na(2)–O(1), 2.199(2); Na(2)–O(3), 2.308(3); Na(2)–O(3'), 2.308(3); Na(3)–O(2), 2.265 (2); Na(3)–O(2'), 2.298(2); Na(3)–O(4), 2.298(3); Na(3)–C(4), 2.878(3); Na(3)–C(5), 2.808(3); O(1)–Na(1)–O(1'), 92.49(11); O(1)–Na(1)–O(2), 110.87(7); O(2)–Na(1)–O(2'), 78.01(10); O(1)–Na(2)–O(1'), 93.45(12), O(3)–Na(2)–O(3'), 103.62(14); O(2)–Na(3)–O(2'), 79.27(8); O(2)–Na(3')–O(2'), 79.27(8).

Turning now to the organometallic framework of **1**, the central sodium atom Na1, and Na2 on the periphery of the molecule were both found to be four coordinate, adopting distorted tetrahedral geometries (sum of bond angles for Na1 and Na2 are 664.1° and 661.1° respectively). Na1 bonds exclusively to the O atoms of the BIPHEN ligands in a non-uniform manner with a mean Na–O bond length of 2.265 Å. Na2 is also bound to both BIPHEN molecules through a single Na–O bond to each ligand [Na2–O1 2.199(2) Å]. The coordination sphere of Na2 is complete by coordination to two molecules of THF [Na2–O3 2.310(4) Å]. The remaining sodium atoms Na3/Na3' each make short contacts with five atoms. Each sodium atom coordinates to a single oxygen atom on both BIPHEN ligands and a single molecule of THF. The remaining contacts are $\eta^2 \pi$ interactions with the adjacent phenyl rings located on the BIPHEN backbone. These interactions were found to be 2.878(3) Å and 2.808(3) Å for Na3–C4 and Na3–C5 respectively.

Focussing now on the solution-state behaviour of **1**, the ^1H and ^{13}C NMR spectra are easily interpreted. The (*rac*)-BIPHEN ligand is an extremely useful probe for monitoring the solution state behaviours as it produces relatively simple spectra with multiple diagnostic groups which allow for easy assignment of the structure. The ^1H NMR spectrum of **1** contains singlet resonances at δ 1.30, 1.56 and 2.07 ppm in the aliphatic region of the and a single resonance at δ 6.69 ppm in the aromatic region of the spectra which correspond to the t butyl, methyl and aromatic hydrogen atoms of the BIPHEN ligand. These resonances have integration values of 36, 12, 12 and four hydrogen atoms respectively which is in good agreement with the solid-state structure of **1**. The resonances associated with the THF ligands are also present as two multiplets located at δ 1.73 and 3.58 ppm; however, as the spectrum was collected in d_8 -THF the integration values of these resonances may no longer be representative of the structure due to the fluxional nature of the THF ligands. The ^{13}C NMR spectrum of **1** was again in good agreement with the solid-state structure with the methyl and t butyl groups of the BIPHEN backbone being located at δ 16.7, 20.3 and δ 30.3, 34.8 ppm respectively. Furthermore, the aromatic region contained six resonances at δ 116.2, 125.9, 132.4, 133.1, 133.7, 165.1 ppm all of which correspond to the aromatic carbons of the BIPHEN phenyl rings and also two resonances at δ 26.2 and 68.0 ppm which correspond to the carbon atoms of the THF ligands.

2.4.3.2 (BIPHEN) $_2$ Na $_2$ Mg(THF) $_4$ (**2**)

Initial attempts to produce dialkyl sodium magnesiates [(*rac*)-BIPHEN]Na $_2$ Mg n Bu $_2$ (THF) $_4$ and [(*rac*)-BIPHEN]Na $_2$ Mg(CH $_2$ SiMe $_3$) $_2$ (THF) $_4$ via co-complexation of either $^n\text{Bu}_2\text{Mg}$ or Mg(CH $_2$ SiMe $_3$) $_2$ with **1** leads to the formation of BIPHEN rich product (BIPHEN) $_2$ Na $_2$ Mg(THF) $_4$ **2** (0.197 g, 37 % yield) when THF was used as the Lewis donor (Figure 13). The solid-state structure of BIPHEN rich **2** was found to have crystallographically imposed symmetry. The central magnesium atom was found to sit on a threefold axis while sodium atoms Na1/Na1' sit on a twofold axis. Once again, the crystal which was analysed by X-ray crystallography was found to be enantiopure crystallising in the chiral space group I222. Presumably the same driving force leading to the deracemization of the (*rac*)-BIPHEN ligand of **1** is again acting upon the phenoxide ligand in **2**.¹⁰⁰ The Flack parameter for **2** was calculated to be – 0.16(17) which is in good agreement with the crystal being enantiopure. The central magnesium atom Mg1 is four coordinate with a distorted tetrahedral geometry (sum of bond angles 665.6°. For a perfectly tetrahedrally coordinated atom the sum of bond angles would be 657°) bonding exclusively to the oxygen atoms of both BIPHEN ligands [Mg1-O1 1.960(16)

Å]. These magnesium to oxygen bond lengths are consistent with those reported by Ko and co-workers for the homometallic magnesium BIPHEN dimer.¹⁰¹ The sodium atoms Na1/Na1' were also found to be four coordinate adopting a distorted tetrahedral geometry (sum of bond angles 662.1°). Each sodium atom is bound to a single oxygen atom of both BIPHEN ligands [Na1-O1 2.2372(19) Å] and their coordination spheres are completed by complexation to two molecules of THF [Na1-O2 2.270(7) Å].

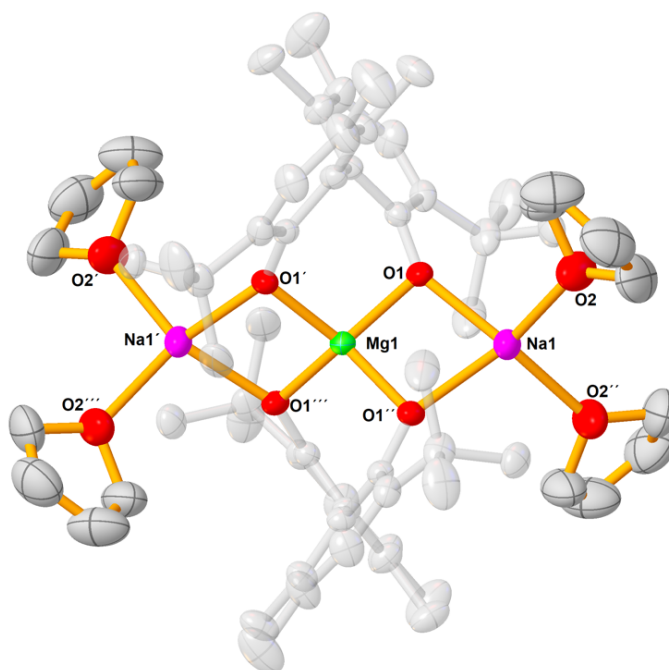


Figure 13: Solid-state structure of (BIPHEN)₂MgNa₂(THF)₄, **2**. Hydrogen atoms and disorder in THF molecules are omitted for clarity. Thermal ellipsoids are set to 50% probability level. Phenoxide ligands are *R R* orientated. Key bond distances (Å) and bond angles (°): Mg(1)–O(1), 1.960(16); Mg(1)–Na(1), 3.0914(14); Mg(1)–Na(1'), 3.0913(14); Na(1)–O(1), 2.2372(19); Na(1)–O(2), 2.270(7); O(1)–Mg(1)–O(1'), 102.72(9); O(1)–Mg(1)–O(1''), 92.32(9); O(1)–Mg(1)–O(1'''), 137.67(10); Na(1)–Mg(1)–Na(1'), 180; O(1)–Na(1)–O(1''), 78.38(38); O(2)–Na(1)–O(2''), 101.5(2).

Turning now to the solution-state behaviour of **2**, the spectra are similar to that of **1**. For the ¹H spectrum the hydrogen atoms of the ^tbutyl and two sets of methyl groups are located at δ 1.15, 1.45 and 2.04 ppm respectively, with integrations of 36, 12 and 12 hydrogen atoms. The aromatic hydrogen atoms are once again located as a single resonance at δ 6.72 ppm with an integration value corresponding to four hydrogen atoms. The ¹³C NMR spectrum is also similar with that of **1** with the methyl groups located at δ 16.9 and 20.3 ppm, the ^tbutyl groups at δ 31.1 and 34.6 ppm and the aromatic carbons at δ 120.7, 125.8, 132.7, 132.9,

134.2, 161.3 ppm. The resonances associated with the THF ligands are located in the ^1H spectrum as multiplets at δ 1.77 and 3.61 ppm and in the ^{13}C spectrum at δ 26.2 and 68.0 ppm. Once again, the integration values for the THF hydrogen atoms are not reliable as the spectrum was collected using d_8 -THF.

2.4.3.3 $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$ (**3**)

Exclusion of THF or any other coordinating solvents combined with the introduction of TMEDA as the Lewis donor prevented formation of the BIPHEN-rich dimeric disproportionation product and allowed for isolation of the dialkyl sodium magnesiate $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$ **3** as a microcrystalline solid (0.216 g, 56 % yield). Multiple attempts have been made to characterise **3** in the solid-state; however, it has not been possible to isolate crystals of sufficient quality. As **3** was found to be extremely soluble in hydrocarbon solvents, the structure of **3** has been characterised using NMR spectroscopic data obtained from ^1H , ^{13}C and HSQC NMR spectroscopy. Beginning with the ^1H NMR spectrum, two multiplets are visible in the negative region of the spectrum at δ -0.79 and -0.31 ppm which indicates a high degree of shielding (Figure 14). These resonances have therefore been assigned to the Mg-CH_2 methylene hydrogen atoms which appear as two distinct multiplets and not as a single resonance due to diastereotopic splitting.¹⁰² This splitting arises from inclusion of the (rac) -BIPHEN ligand which renders the two hydrogen atoms of each methylene group inequivalent to each other.

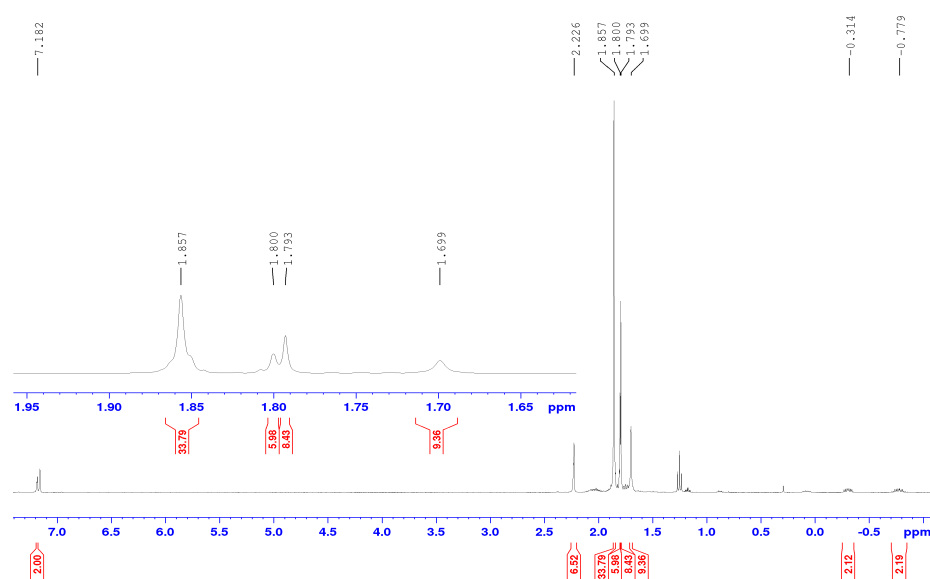


Figure 14: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$, **3**
(400 MHz, C_6D_6 , 300 K).

The two methyl groups and aromatic hydrogen atoms of the (*rac*)-BIPHEN ligand are located at δ 1.80, 2.22 and 7.18 ppm respectively. Unlike **1** and **2** where resonance associated with the ^tbutyl groups of the (*rac*)-BIPHEN ligand appear as a single resonance, in the ¹H NMR spectrum of **3** these groups appear as two separate resonances with an integration value indicating nine hydrogen atoms per environment. One of these resonances is located as a broad singlet at δ 1.69 ppm while the other is obscured by the resonance associated with the methyl groups of TMEDA. The integration value of this resonance was found to be 33 which correlates with the above situation where one resonance with an integration of 24 (CH₃ TMEDA) is superimposed upon the resonance of the ^tbutyl group which has an integration of nine hydrogen atoms. A subsequent HSQC NMR spectrum showed that the broad singlet correlated with the carbon atom associated with the methyl groups of the TMEDA ligand but also the carbon atom of the ^tbutyl groups of the (*rac*)-BIPHEN ligand (Figure 15). The remaining hydrogen atoms of the TMEDA ligand, the bridging CH₂ groups were assigned to the resonance at δ 1.79 ppm with an integration value of eight hydrogen atoms. The ¹³C NMR spectrum is also in good agreement with the proposed structure and the with the ¹H spectrum. The resonances associated with methyl groups of the (*rac*)-BIPHEN ligand were located at δ 17.5 and 20.8 ppm, the ^tbutyl groups at δ 31.2 and 35.3 ppm and the aromatic carbon atoms at δ 119.6, 127.3, 132.1, 132.7, 135.9 and 162.7 ppm. Moreover, the terminal methyl and bridging methylene groups of the TMEDA ligand were assigned to the resonances located at δ 45.5 and 57.0 ppm respectively. The α -carbon of the alkyl ligands were located at δ 8.84 ppm while the other carbon atoms of the alkyl chains were located at δ 14.9 and 32.8-33.7 ppm in the ¹³C NMR spectrum.

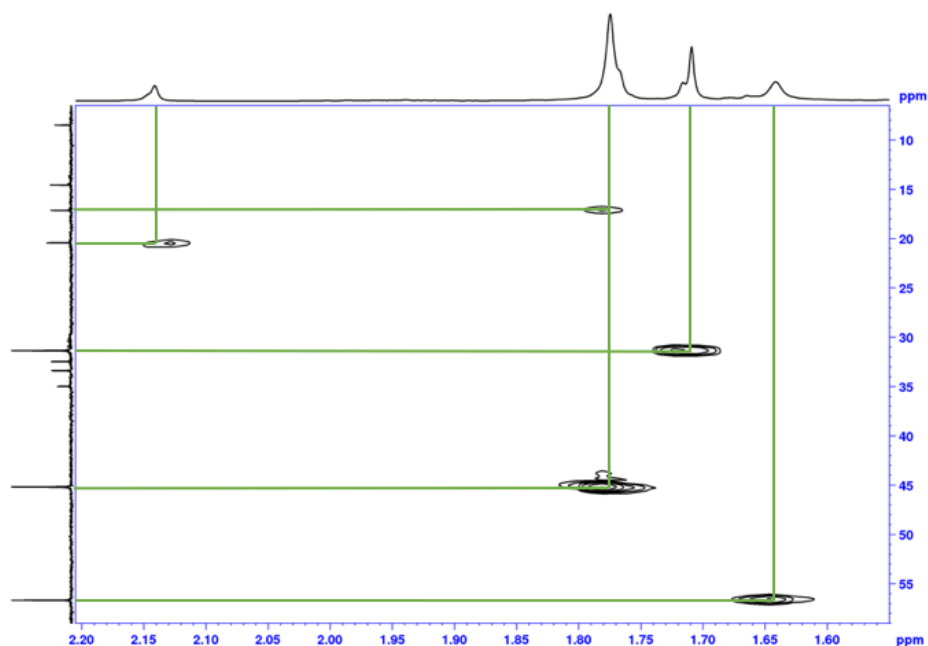


Figure 15: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$, **3** (C_6D_6 , 300 K).

2.4.3.4 $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{TMEDA})_2$ (**4**)

Following on from the isolation of **3** the reaction was repeated this time using the monosilyl CH_2SiMe_3 ligand as the alkyl component of the parent magnesium species. Inclusion of this new alkyl ligand lead to isolation $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{TMEDA})_2$ (**4**) as large colourless crystals which allowed for their characterisation by X-ray crystallography (yield 0.087 g, 45 %). Analysis of the X-ray crystallographic data revealed **4** to be monomeric, crystallising in the $P2_1/n$ space group. Unlike the structures of **1** and **2**, no crystallographic symmetry is imposed on **4**. The solid-state structure of **4** (Figure 16) was found to contain a central magnesium atom (Mg1) which is four coordinate and adopts a tetrahedral coordination geometry (sum of bond angles 655.9°). The magnesium atom Mg1 is bound to both oxygen atoms of the *(rac)*-BIPHEN backbone in an η^2 chelating binding mode through two magnesium to oxygen bonds. The Mg-O bond lengths were found to be identical within experimental error at $2.0105(14)$ Å and $2.0034(14)$ Å for Mg1-O1 and Mg1-O2 respectively. The coordination sphere of the central magnesium atom is completed by two Mg-C single bonds to the alkyl ligands. The bond lengths for these Mg-C bonds were found to identical within experimental error at $2.201(2)$ Å and $2.195(2)$ Å for Mg1-C25 and Mg1-C26 respectively. Both sodium atoms Na1 and Na2 were found to be four-coordinate, adopting a distorted tetrahedral geometry (sum of bond angles 677.98° and 676.75° respectively). Sodium atoms Na1 and Na2 each form a bond to a single oxygen atom of the *(rac)*-BIPHEN

[Na1-O2 2.2508(17) Å and Na2-O1 2.2129(15) Å] and a contact to the α -carbon of the adjacent alkyl ligand. Each sodium atom is capped by a single molecule of TMEDA which is bound in a non-uniform fashion (average Na-N bond length 2.54 Å) which completes their coordination sphere.

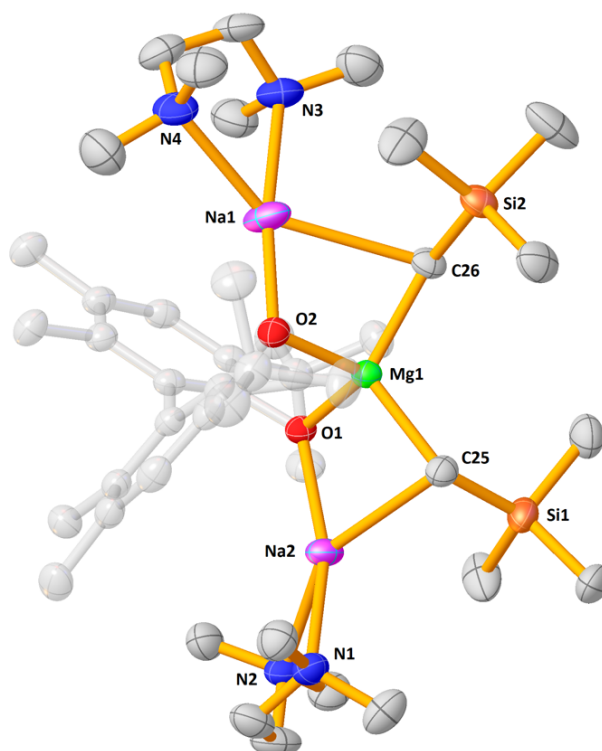


Figure 16: Solid-structure of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(TMEDA)₂, **4**. Hydrogen atoms and disorder in PMDETA molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *S* orientated. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 2.0105(14); Mg(1)-O(2), 2.0034(14); Mg(1)-C(25), 2.201(2); Mg(1)-C(26), 2.195(2); Mg(1)-Na(1), 3.1031(13); Mg(1)-Na(2), 3.1288(10); Na(1)-O(2), 2.2508(17); Na(1)-N(3), 2.647(18); Na(1)-N(4), 2.506(16); Na(1)-C(26), 2.841(2); Na(2)-O(1), 2.2129(15); Na(2)-N(1), 2.469(2); Na(2)-N(2), 2.5527(19), Na(2)-C(25), 2.796(2); O(1)-Mg(1)-O(2), 96.38(6); O(1)-Mg(1)-C(25), 103.05(7); O(1)-Mg(1)-C(26), 117.76(7); O(2)-Mg(1)-C(25), 120.15(7); O(2)-Mg(1)-C(26), 102.05(7); C(25)-Mg(1)-C(26), 116.51(8); Na(1)-C(26)-Mg(1), 74.86(6); O(2)-Na(1)-C(26), 78.86(6); N(3)-Na(1)-N(4), 72.30(3); O(1)-Na(2)-C(25), 81.50(6); Na(2)-C(25)-Mg(1), 76.50(16); N(1)-Na(2)-N(2), 73.49(7).

Examining the solution-state behaviour of **4**, the ¹H NMR spectrum showed two doublets in the shielded region of the spectrum at δ –2.08 and –1.16 ppm each with an integration value of two which correspond to Mg-CH₂ hydrogen atoms (Figure 17). The presence of two sets

of doublets rather than a single resonance tells us that the hydrogen atoms are once again diastereotopic ($J = 12$ Hz). It is worth noting that the chemical shift of these two methylene groups has been shifted to a much lower chemical shift than what was observed for the analogous hydrogen atoms of **3** (Figure 14). The remaining hydrogen atoms of the SiMe_3 group were located at δ 0.40 ppm and the resonances associated with the TMEDA ligands appear at δ 1.67 and 1.77 ppm for the bridging methylene and terminal methyl groups respectively. Turning now to the (*rac*)-BIPHEN ligand, the methyl groups attached to the phenyl ring systems are located at δ 1.83 and 2.23 ppm while the aromatic hydrogen atoms appear at δ 7.12 ppm. Interestingly, the resonance associated with the t butyl group of the (*rac*)-BIPHEN backbone appears a singlet at δ 1.74 ppm with an integration value of 18. This is in contrast to **3** in which these two groups were rendered inequivalent which suggests this change in the two spectra arises from a difference in the alkyl ligand. The ^{13}C NMR spectrum of **4** can also be fully assigned. Starting with the resonances associated with the (*rac*)-BIPHEN ligand the methyl groups appear at δ 18.3 and 20.7 ppm, the t butyl groups at δ 31.8 and 35.3 ppm and the aromatic carbons at δ 120.1, 127.2, 132.4, 132.6, 135.7, 162.5 ppm. The TMEDA ligands are located at δ 45.7 and 57.0 ppm for the methyl and methylene carbons respectively while the methyl groups of the alkyl ligand appear at δ 5.08 ppm along with the $\text{Mg}-\text{CH}_2$ methylene carbons at δ -6.68 ppm.

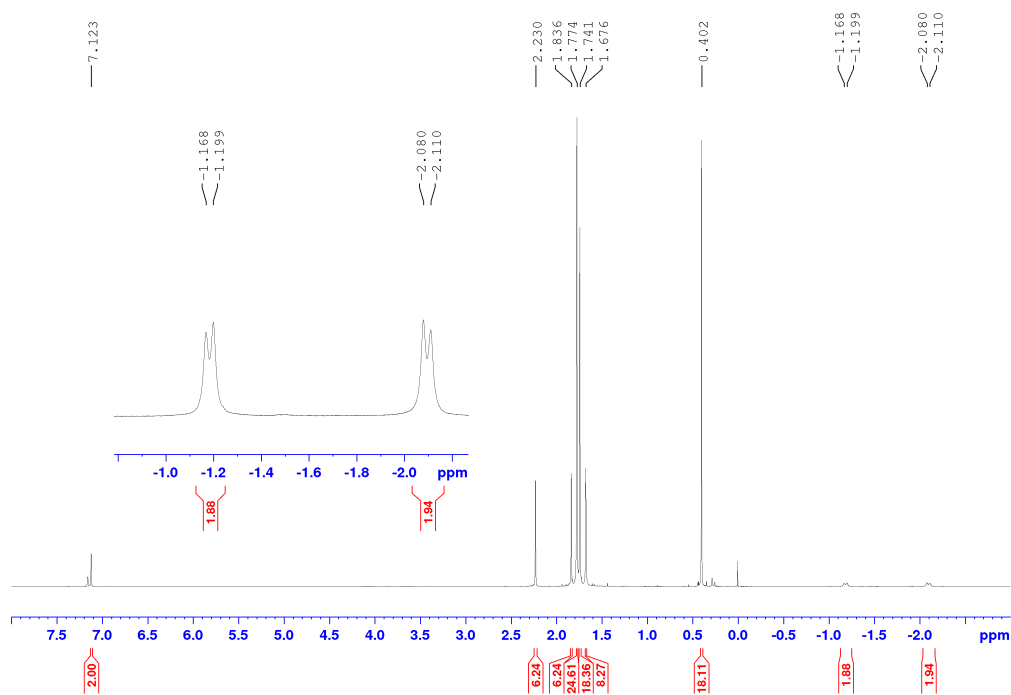


Figure 17: ^1H NMR Spectrum of $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{TMEDA})_2$, **4** (400 MHz, C_6D_6 , 300 K).

2.4.3.5 [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (**5**)

In an attempt to further the investigation into the coordination chemistry of sodium magnesiates containing the (*rac*)-BIPHEN ligand, the tridentate donor PMDETA was introduced as the Lewis donor and led to the isolation of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (**5**) (0.245 g, 56 % yield). Upon analysis by X-ray crystallography, **5** was found to crystallise in the P_n space group as a monomer with no crystallographically imposed symmetry (Figure 18). The core structure is typical of a higher order alkali metal magnesiate, adopting a classic Weiss motif containing a central four coordinate magnesium atom with a distorted tetrahedral geometry (sum of bond angles 674.18 °). The (*rac*)-BIPHEN acts as a chelating ligand, binding to the magnesium centre through two Mg-O single bonds which were found to be identical in length within experimental error at 2.011(3) and 2.009(3) Å for Mg1-O1 and Mg1-O2 respectively. The magnesium to carbon bonds are also identical within experimental error at 2.203(6) and 2.204(3) Å for Mg1-C42 and Mg1-C44 respectively. Coordination of the larger tridentate PMDETA leads to an increase in the coordination number of the sodium atoms from four to five. One molecule of PMDETA is coordinated to each sodium atom with an average Na-N bond length of 2.564 Å for Na1 and 2.541 Å for Na2. Each sodium atom also forms a bond to a single oxygen atom of the (*rac*)-BIPHEN ligand (Na1-O1 2.279(3) Å and Na2-O2 2.267(3) Å) along with a medium range contact with the methylene carbon atoms of the alkyl ligands (Na1-C44 2.690(5) Å and Na2-C43 2.688(6) Å). This increase in coordination number for the sodium atoms may suggest that there are vacant coordination sites accessible for the sodium atoms of the previous structures containing the bidentate TMEDA ligand.

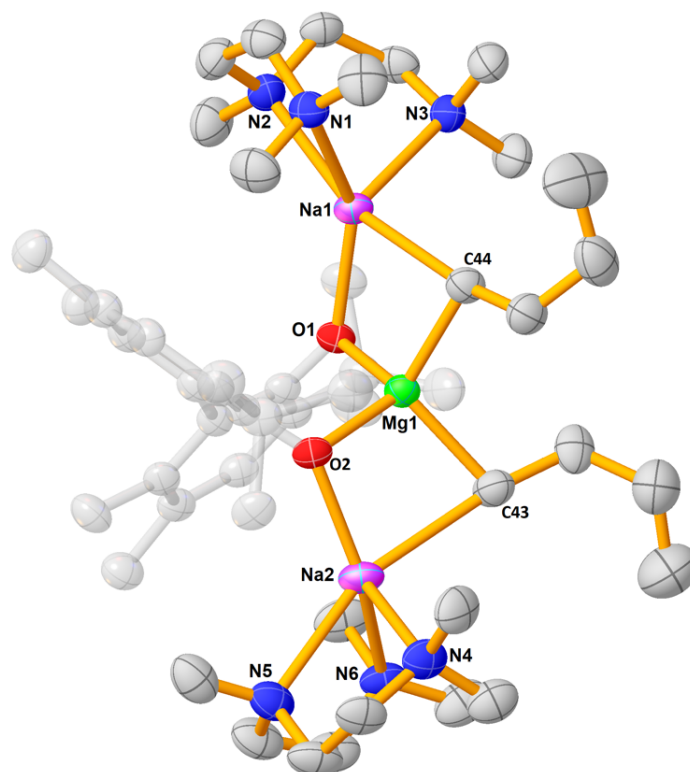


Figure 18: Solid-state structure of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{PMDETA})_2$, **5**. Hydrogen atoms and disorder in PMDETA molecules are omitted for clarity. Thermal ellipsoids are set to 50% probability level. Phenoxide ligand is *R* orientated. Key bond distances (Å) and bond angles (°): Mg(1)–O(1), 2.011(3); Mg(1)–O(2), 2.009 (3); Mg(1)–C(43), 2.203(6); Mg(1)–C(44), 2.204(5); Mg(1)–Na(1), 3.146(2); Mg(1)–Na(2), 3.137(2); Na(1)–O(1), 2.279(3); Na(1)–N(1), 2.614(4); Na(1)–N(2), 2.558(4); Na(1)–N(3), 2.520(4); Na(2)–O (2), 2.267(3); Na(2)–N(4), 2.492(5); Na(2)–N(6), 2.618(4); Na(1)–C(44), 2.690(5); Na(2)–C(43), 2.688(6); O(1)–Mg(1)–O(2), 99.35(13), C(43)–Mg (1)–C(44), 107.7(2); Na(1)–C(44)–Mg(1), 79.3(2); Na(2)–C(43)–Mg(1), 79.1 (2); O(1)–Na(1)–C(44), 82.0(1); O(2)–Na(2)–C(43), 91.9(3).

Complex **5** was found to be highly soluble in non-coordinating hydrocarbon solvents allowing for facile characterisation in solution. Beginning with the ^1H NMR spectrum of **5** (Figure 19), four singlet resonances were observed at δ 1.77, 1.90 and 2.31 and 7.14 ppm which were assigned to the 'butyl, two sets of methyl groups and aromatic hydrogen atoms respectively. The PMDETA ligands were located at δ 1.82, 1.86 and 1.93 ppm for the bridging methylene, internal methyl (NMe) and terminal methyl (NMe₂) groups respectively. The characteristic methylene groups of the alkyl ligands bound to the magnesium centre, which normally appear as two sets of distinct multiplets due to their diastereotopic nature, appear as a single broad multiplet at δ –0.75 ppm with an integration value corresponding to four hydrogen atoms. This suggests that the hydrogen atoms of the methylene groups attached directly to

the magnesium centre are no longer diastereotopic. In order for this to be the case, a solvent separated species in which the alkyl ligands are no longer incorporated into the same molecule as the (*rac*)-BIPHEN ligand would have to be formed within solution. This situation was thought to be unlikely given that the solution was prepared using a non-coordinating solvent and isolated crystalline material with no excess Lewis donor present.

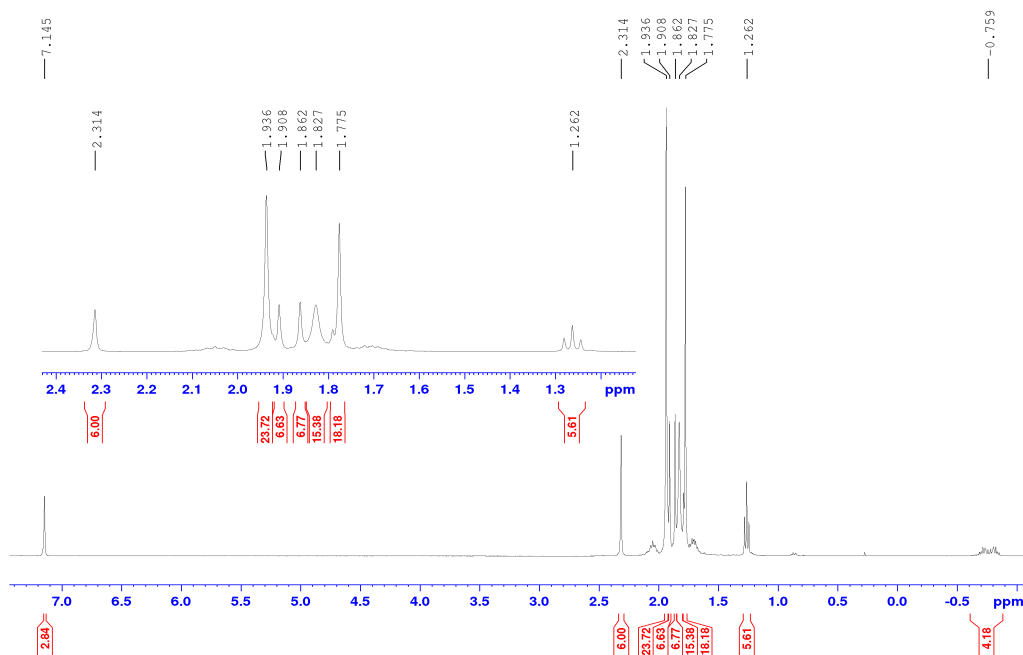


Figure 19: ^1H NMR spectrum of $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{PMDETA})_2$, **5**
(400 MHz, C_6D_6 , 300 K).

It was therefore proposed that what appears as one broad multiplet could in fact be produced by the superimposition of two signals upon each other and that a low temperature study may lead to resolution of the resonance(s) in question. If the broad multiple observed at $\delta -0.75$ ppm at ambient temperature was to resolve into two distinct signals when the sample was cooled, then it would provide a clear indication that the hydrogen atoms remain diastereotopic and that the inclusion of PMDETA as the Lewis donor has altered the properties of the magnesiate in a way that prevents this phenomenon from being observed at ambient temperature. If when cooled the broad resonance does not resolve, then it could mean that the original resonance observed at ambient temperature arises from the superimposition of one resonance upon another. With this information in hand, a low temperature ^1H NMR spectroscopic study of **5** was carried out (Figure 20). Stepwise cooling of the solution initially showed little difference in the resonances associated with methylene hydrogen atoms. Upon reaching -30°C , the broad multiplet that was observed at ambient

temperature resolved into a broad triplet-like resonance. Although it was not possible to resolve the broad multiplet observed at ambient temperature into two distinct resonances, the imperfect nature of the triplet obtained at $-30\text{ }^{\circ}\text{C}$ once again suggests that multiple resonances could be superimposed. Further cooling of the solution led to a loss in intensity of the resonances of interest and was attributed to the poor solubility of **5** at low temperatures. The ^{13}C NMR spectrum is in good agreement with the ^1H NMR spectrum and the structure obtained in the solid-state.

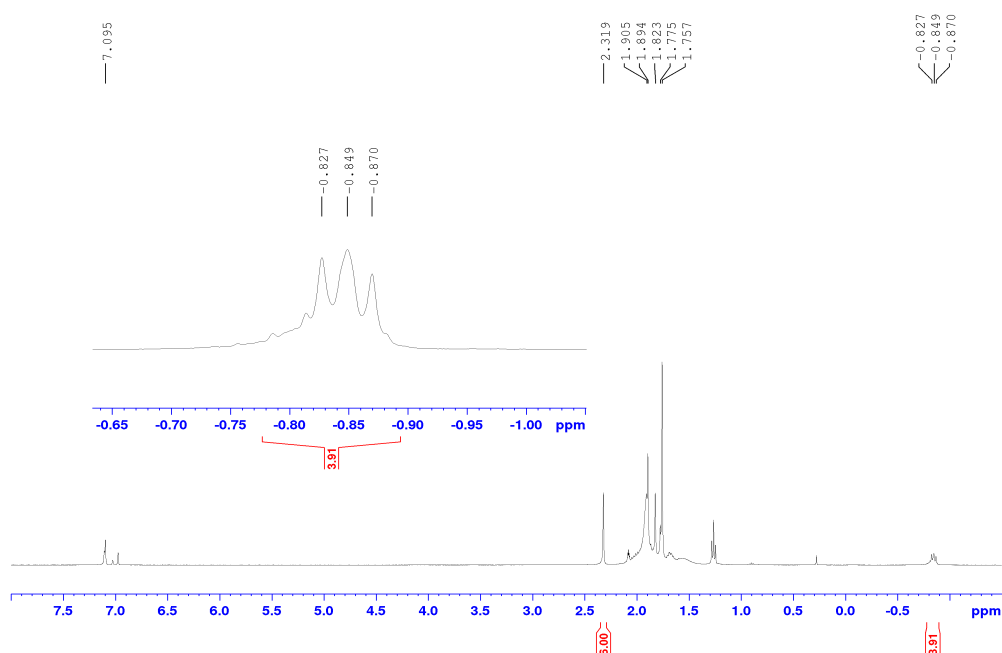


Figure 20: Low temperature ^1H NMR spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{PMDETA})_2$, **5** (400 MHz, $\text{d}_8\text{-Tol}$, 263 K).

2.4.3.6 [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(PMDETA)₂ (**6**)

Having observed the interesting solid- and solution-state behaviour of **5**, our investigations continued using the dialkylmagnesium reagent Mg(CH₂SiMe₃)₂ with PMDETA as the Lewis donor to produce [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(PMDETA)₂ (**6**) (0.253 g, 58 % yield). X-ray crystallographic analysis revealed **6** to be a monomeric toluene solvate, crystallising in the P2₁/c space group (Figure 21). The solid-state structure of this higher order magnesiate once again took the form of the classic Weiss motif with the organometallic core of the complex comprising of two Mg-O-Na-C rings. The central magnesium atom Mg1 was found to be four coordinate forming bonds to both oxygen atoms of (*rac*)-BIPHEN and to the two alkyl ligands in a distorted tetrahedral geometry (sum of bond angles 655.44 °). The bond lengths for the magnesium to oxygen bonds Mg1-O1 and Mg1-O2 were found to deviate only marginally [Mg1-O1 2.0270(17) Å and Mg1-O2 2.0204(17) Å] while the magnesium to carbon bonds Mg1-C25 and Mg1-C29 to the two alkyl ligands were identical within experimental error [Mg1-C25 2.197(3) Å and Mg1-C29 2.211(3) Å]. Turning now to the two sodium atoms, each atom forms a bond to a single oxygen of the (*rac*)-BIPHEN ligand [Na1-O1 2.2918(18) Å and Na2-O2 2.3030(17) Å] along with a contact to the methylene carbon of the alkyl ligands [Na1-C29 2.744(3) Å and Na2-C25 2.746(3) Å]. The coordination sphere of both sodium atoms is completed by coordination of a single molecule of PMDETA which bonds non-uniformly with an average Na-N bond length of 2.550 Å. The coordination numbers for the sodium atoms Na1 and Na2 are consistent with that of **5** which also contains the tridentate donor PMDETA [range: Na(1)-N(2), 2.523(3) to Na(1)-N(3), 2.593(3) Å].

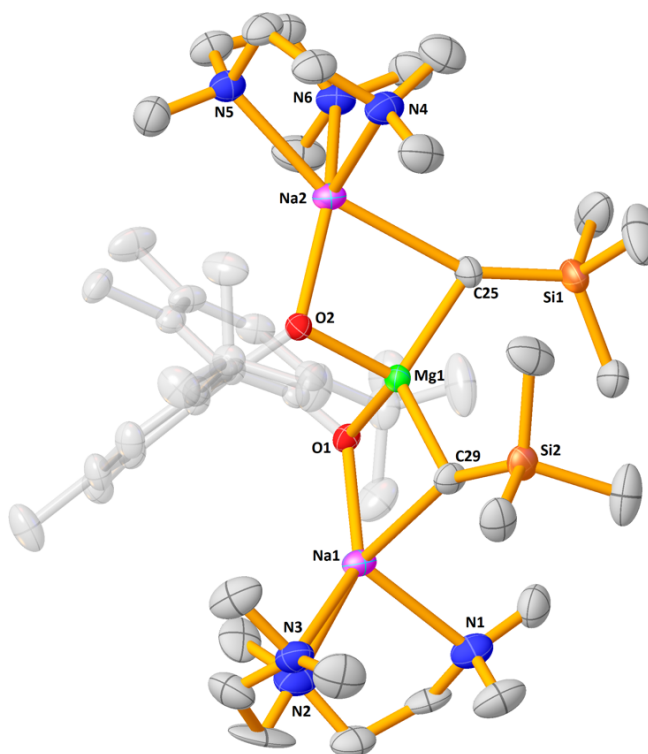


Figure 21: Solid-structure of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{PMDETA})_2$, **6**. Hydrogen atoms and disorder in PMDETA molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *S* orientated. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 2.0270(17); Mg(1)-O(2), 2.0204(17); Mg(1)-C(25), 2.197(3); Mg(1)-C(29), 2.211(3); Mg(1)-Na(1), 3.2336(11); Mg(1)-Na(2), 3.2700(11); Na(1)-O(1), 2.2918(18); Na(1)-N(1), 2.536(3); Na(1)-N(2), 2.523(3); Na(1)-N(3), 2.593(3); Na(1)-C(29), 2.744(3); Na(2)-O(2), 2.3030(17); Na(2)-N(4), 2.533(2); Na(2)-N(5), 2.553(2); Na(2)-N(6), 2.582(2); Na(2)-C(25), 2.746(3); O(1)-Mg(1)-O(2), 98.50(7); O(1)-Mg(1)-C(25), 117.96(9); O(1)-Mg(1)-C(29), 100.55(8); O(2)-Mg(1)-C(29), 117.61(9); O(2)-Mg(1)-C(25), 100.01(8); C(25)-Mg(1)-C(29), 120.83(10); Na(1)-C(29)-Mg(1), 80.70(8); O(1)-Na(1)-C(29), 80.21(7); O(2)-Na(2)-C(25), 79.08(7); Na(2)-C(25)-Mg(1), 82.02(8).

Turning now to the solution-state behaviour of **6**, the ^1H NMR spectrum showed three singlet resonances in the aliphatic region at δ 1.76, 1.83 and 2.28 ppm which were assigned to the *t*butyl and two sets of methyl groups of the (*rac*)-BIPHEN respectively (Figure 22). Turning now to the PMDETA ligands, three resonances were observed at δ 1.81, 1.83 and 1.94 ppm which were assigned to the bridging methylene, internal methyl (NMe) and terminal (NMe₂) methyl groups respectively. The aromatic region of the spectrum contained a single resonance at δ 7.13 ppm which corresponds to the two aromatic hydrogen atoms of the (*rac*)-BIPHEN ligand. Returning to the aliphatic region, a singlet was observed at δ 0.52 ppm

and was assigned as to the SiMe_3 groups of the alkyl ligands while in the shielded region of the spectrum a broad singlet was observed at $\delta -2.03$ ppm which was assigned to the Mg-CH_2 methylene protons. Interestingly the methylene groups of the alkyl ligands bound directly to the magnesium centre once again appear as a single resonance and do not display any diastereotopic splitting.

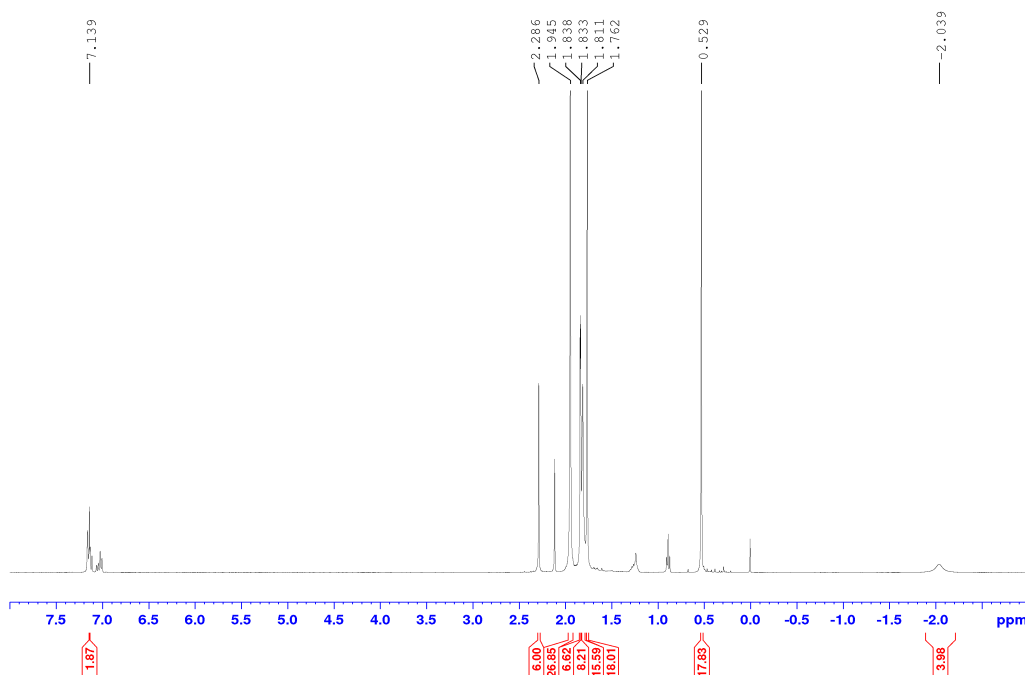


Figure 22: ^1H NMR spectrum of $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{PMDETA})_2$, **6** (400 MHz, C_6D_6 , 300 K).

A low temperature ^1H NMR spectroscopic study was carried out to further investigate the solution-state behaviour of **6**, specifically to give a greater insight into the lack of splitting observed for the methylene hydrogen atoms of the alkyl ligands. Cooling a solution of **6** in d_8 -toluene to 0°C led to the resolution of the broad singlet at $\delta -2.03$ ppm into two distinct singlets at $\delta -2.26$ and -2.03 ppm. Further cooling of the solution to -20°C led to the resolution of these new resonances into two distinct doublets at $\delta -2.28$ and -2.01 ppm each with an integration of two hydrogen atoms (Figure 23). In the absence of β -hydrogen atoms the only way in which this splitting could have occurred, even at low temperature, is if the hydrogen atoms have been rendered magnetically inequivalent. In turn, this demonstrates retention of the solid-state structure of **6** in solution with inclusion of the (*rac*)-BIPHEN as part of a contacted ion pair structure. The ^{13}C NMR spectrum of **6** was in good agreement with both the ^1H NMR spectrum and the solid-state structure.

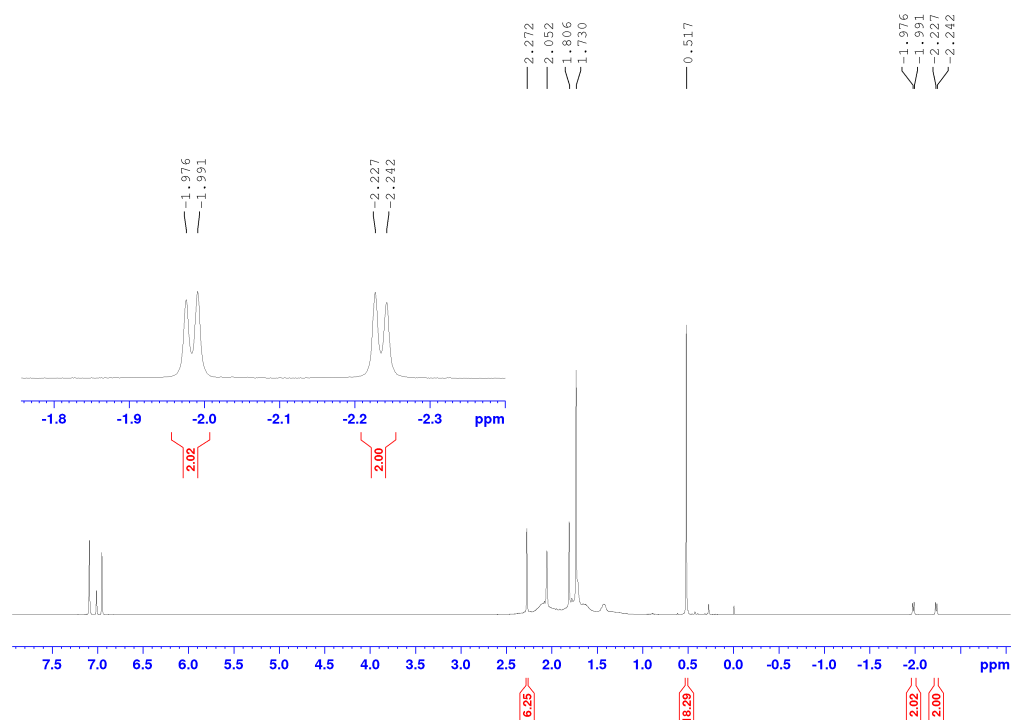


Figure 23: ^1H NMR of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{PMDETA})_2$, **6**
(400 MHz, d_8 -Tol, 253 K).

2.4.3.7 $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCD})_2$ (**7**)

The final Lewis donors used in this study were the two enantiomers of TMCD. These donor ligands were chosen as a low-cost alternative to the enantiopure form of the BIPHEN ligand as a method of introducing chirality into the magnesiates. Despite multiple attempts, it was not possible to characterise the solid-state structure of **7** as no crystalline material could be isolated from the reaction that was of suitable quality for analysis by single crystal X-ray diffraction. The reaction did reproducibly produce a microcrystalline white solid which allowed for characterisation of **7** to be performed in solution.

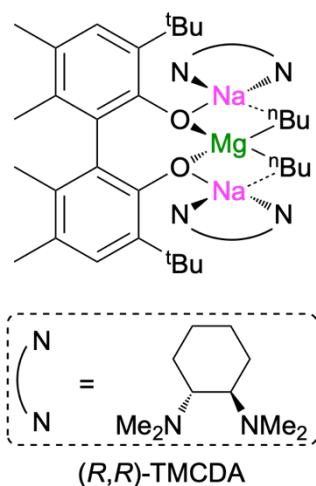


Figure 24: Proposed Structure of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCDA})_2$, **7**.

Beginning with the ^1H NMR spectrum of **7**, two broad multiplets were observed at δ -0.71 and -0.33 ppm and were assigned to the hydrogen atoms of the methylene groups of the two n butyl ligands (Figure 25). The appearance of these two resonances in the shielded region of the spectrum indicates that they are bound directly to the magnesium centre while the unusual splitting pattern observed for the two resonances arises as a result of diastereotopic splitting induced by the *(rac)*-BIPHEN ligand. Moreover, this splitting is indicative that the magnesium atom is bound to the *(rac)*-BIPHEN ligand and that the structure of **7** in solution is in good agreement with the proposed structure (Figure 24) and would essentially be isostructural with the metallo-ligand structure of **5** with replacement of PMDETA for *(R,R)*-TMCDA. The terminal methyl group of the n butyl ligands appear as a triplet at δ 1.26 ppm while the internal CH_2 groups of the n butyl ligands appear as a broad multiplet at δ 2.07 ppm. Focussing now on the chiral *(R,R)*-TMCDA ligand, two broad resonances appear at δ 0.66 and 1.41 ppm, both with integration values of eight hydrogen atoms and were assigned to CH_2 groups of the cyclohexyl ring systems. Using HSQC NMR spectroscopy (Figure 27), the remaining hydrogen atoms of the cyclohexyl rings of *(R,R)*-TMCDA were assigned to the broad doublet at δ 1.82 ppm while the terminal methyl groups were assigned to the broad singlet resonance located at δ 1.91 ppm. As well as the *(R,R)*-TMCDA ligands, the resonances at δ 1.82 and 1.91 ppm were also assigned to the t butyl and methyl groups of the *(rac)*-BIPHEN ligand respectively. The remaining methyl groups of the *(rac)*-BIPHEN ligand appear as two singlets at δ 2.26 and 2.28 ppm while the aromatic hydrogen atoms of the same ligand appear as two overlapping singlets at δ 7.22 and 7.23 ppm. The appearance of more than one resonance for the methyl groups and aromatic hydrogen atoms is indicative of a loss of equivalence between the two phenyl rings of the *(rac)*-BIPHEN ligand.

This loss of equivalence in the (*rac*)-BIPHEN was not observed in solution for the previously characterised dialkyl phenoxide sodium magnesiates **3-6**.

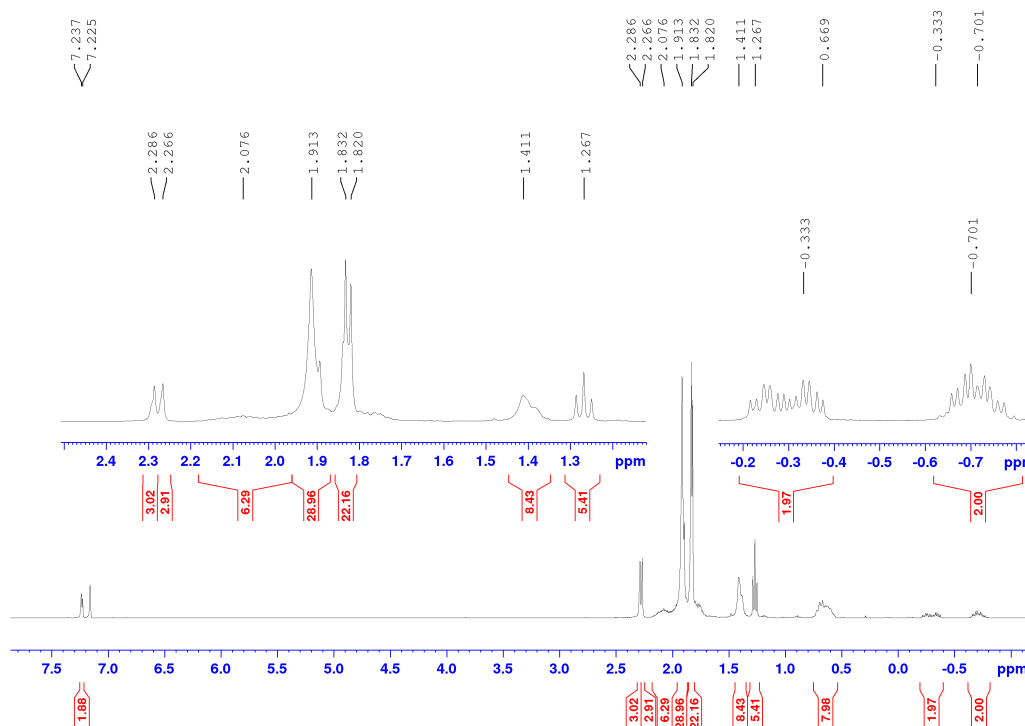


Figure 25: ^1H NMR spectrum of $[(\text{rac})\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCD})_2$, **7** (400 MHz, C_6D_6 , 300K).

Examination of the ^{13}C NMR spectrum of **7** gives further evidence for the loss of equivalency between the two ring systems of the (*rac*)-BIPHEN ligand (Figure 26). To expand, four distinct resonances are observed for the methyl groups at δ 17.8, 17.9, 20.8 and 20.9 ppm as well as two resonances for both the primary and quaternary carbon atoms of the t butyl groups at δ 31.9 and 32.1 ppm, and δ 35.4 and 35.4 ppm respectively. Finally, the aromatic region of the spectrum contains 12 distinct resonances which indicates that each carbon atoms of the two phenyl rings have been rendered magnetically inequivalent. Similar to the (*rac*)-BIPHEN ligand, inequivalence is also observed for the carbon atoms of the two n butyl ligands. The two methylene groups bound directly to magnesium appear as two distinct resonances at δ 9.0 and 9.1 ppm along with the terminal methyl groups at δ 14.8 and 14.9 ppm while the remaining methylene groups of the butyl chain appear as four distinct resonances at δ 32.8, 33.1, 33.6 and 33.7 ppm. This contrasts directly with the situation observed in the solution-state for **5** in which the two n butyl ligands remained equivalent and a single resonance was observed for each set of carbon atoms. Moreover, only three resonances were observed for

the (*R,R*)-TMCDAs at δ 21.2, 25.4, 63.8 ppm which were assigned to the carbon atoms of the cyclohexane ring system. The terminal methyl groups of the (*R,R*)-TMCDAs were tentatively assigned to the extremely broad resonance located at approximately δ 40.1 ppm. The presence of only a single set of resonances for the (*R,R*)-TMCDAs donor ligand helps to rule out the formation of a secondary product in solution.

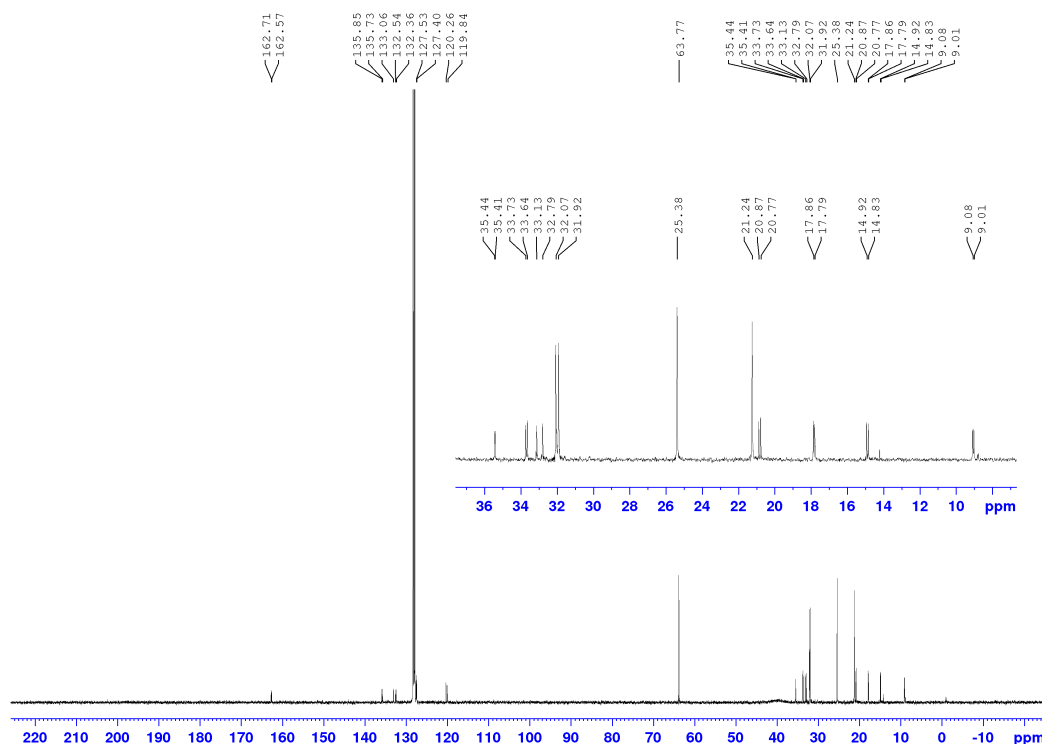


Figure 26: ^{13}C NMR spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCDAs})_2$, **7** (100 MHz, C_6D_6 , 300K).

Given its surprisingly complex solution-state behaviour, **7** was analysed further using HSQC NMR spectroscopy in order to reinforce the assignments of the aforementioned resonances associated with the (*rac*)-BIPHEN, (*R,R*)-TMCDAs and n butyl ligands in both the ^1H and ^{13}C NMR spectra (Figure 27). To expand, beginning with the n butyl ligands, clear correlations were observed between the two broad multiplets located at δ -0.70 and -0.33 ppm in the ^1H NMR spectrum which were assigned to the methylene groups of the alkyl ligand bound directly to the magnesium centre and the two resonances located in the ^{13}C NMR spectrum at δ 9.0 and 9.1 ppm. Similarly, the triplet located at δ 1.26 ppm in the ^1H NMR spectrum shows a clear correlation to the two resonances located in the ^{13}C NMR spectrum at δ 14.8 and 14.9 ppm which were assigned to the terminal CH_3 groups of the two alkyl ligands. The chemical shifts for the methylene and terminal methyl groups of the n butyl ligands are consistent with values

reported in the literature for related magnesiate complexes.⁹⁴ The broad resonances located at δ 0.66 and 1.41 ppm in the ^1H NMR spectrum were assigned to two sets of magnetically inequivalent CH_2 groups which are part of the cyclohexane rings of the (*R,R*)-TMCDA ligand. Both these resonances show a common correlation to two resonances located in the ^{13}C NMR spectrum at δ 21.2 and 25.4 ppm which were also assigned to the (*R,R*)-TMCDA ligand. The presence of these common correlations indicates that these two sets of resonances belong to the same ligand. The broad doublet like resonances located in the ^1H NMR spectrum of **7** at δ 1.83 ppm was proposed to represent both the $^t\text{butyl}$ groups of the (*rac*)-BIPHEN ligand and the NCH groups of the cyclohexane rings of (*R,R*)-TMCDA. Pleasingly, the HSQC NMR spectrum was found to be in good agreement with this assignment and showed two sets of correlations for this resonance, one to the two resonances located in the ^{13}C NMR spectrum at δ 31.9 and 32.1 ppm which was assigned to the primary carbon atoms of the $^t\text{butyl}$ groups of the (*rac*)-BIPHEN ligand and a second to the resonance located at δ 63.8 ppm which was assigned to the NCH groups of the (*R,R*)-TMCDA ligands. Furthermore, the integration value of this resonances in the ^1H NMR spectrum was calculated to be 22 hydrogen atoms which is consistent with the assignment of these two functionalities. The remaining broad resonance in the ^1H NMR spectrum at δ 1.91 ppm was assigned to the methyl groups of the (*rac*)-BIPHEN ligand along with the methyl groups of the (*R,R*)-TMCDA ligands. Analysis of the HSQC spectrum of **7** showed a clear correlation between this resonance and those located at δ 17.8 and 17.9 ppm in the ^{13}C NMR spectrum which are in good agreement with the expected chemical shifts for the methyl groups of the (*rac*)-BIPHEN ligand. Finally, the two resonances located in the ^1H NMR spectrum at δ 2.26 and 2.28 ppm which were also assigned to the methyl groups of the (*rac*)-BIPHEN ligand showed correlations to the two resonances located in the ^{13}C NMR spectrum at δ 20.8 and 20.9 ppm. Once again, these chemical shifts are in good agreement with the expected chemical shifts of the methyl groups of the (*rac*)-BIPHEN ligand. Unfortunately no other correlations were observed in the HSQC NMR spectrum for this resonance to indicate the presence of the methyl groups of the (*R,R*)-TMCDA ligands.

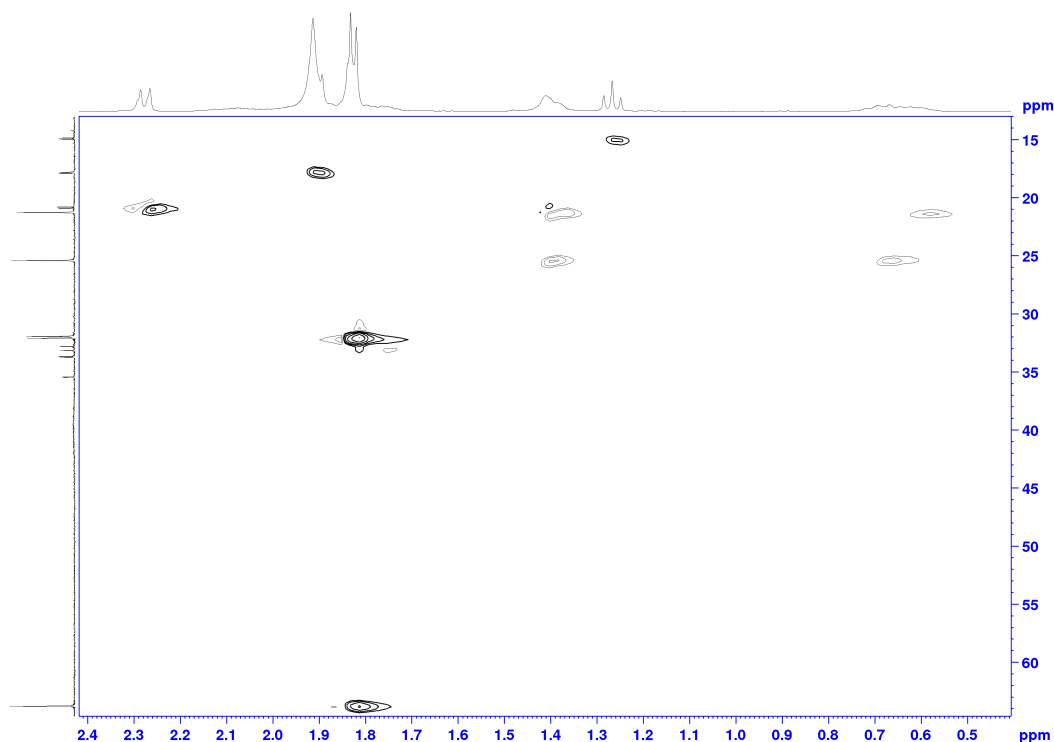


Figure 27: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((R,R)\text{-TMCDA})_2$, **7** (C_6D_6 , 300 K).

2.4.3.8 $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((R,R)\text{-TMCDA})_2$ (**8**)

In this section, focus turned to replacing the n butyl ligands in **7** with CH_2SiMe_3 in an attempt to grow X-ray quality crystals of a higher order magnesiate containing (R,R) -TMCDA. This would help to provide supporting evidence for the structure proposed in section 2.4.3.7 and led to the isolation of the higher order magnesiate $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((R,R)\text{-TMCDA})_2$ **8** (0.193 g, 41 % yield) (Figure 28). Unlike **4-6**, **8** contains an imposed 2-fold axis of symmetry with half a molecule of (rac) -BIPHEN and one sodium atom per asymmetric unit. Overall, the structure can be considered monomeric and was found to crystallise in the space group $P4_12_12$, which confirms the that **8** is indeed a chiral magnesiate. The magnesium atom (Mg1) was found to be four coordinate adopting a distorted tetrahedral geometry (sum of bond angles 657.25°) as are the two sodium atoms Na1/Na1' (sum of bond angles 677.64°). These geometries are consistent with the classic Weiss motif for higher order magnesiates which form contacted ion pair structures. On account of the imposed symmetry, both magnesium to oxygen bonds are of equal length, as are both magnesium to carbon bonds. The central magnesium atom Mg1 is bound to the (rac) -BIPHEN ligand through two magnesium-oxygen bonds [Mg1-O1 1.995(2) Å] and to the alkyl ligands via two magnesium

to carbon single bonds [Mg1-C23 2.205(3) Å]. Sodium atoms Na1/Na1' both form a single bond to the (*rac*)-BIPHEN ligand [Na1-O1 2.226(2) Å] along with a stabilising interaction with the methylene group of the alkyl ligand [Na1-C23 2.728(4) Å]. Each sodium atom is coordinated to a single molecule of (*R,R*)-TMCDA which is bound in a non-uniform manner [Na1-N1 2.458(3) Å and Na1-N2 2.520(3) Å] to complete their coordination sphere.

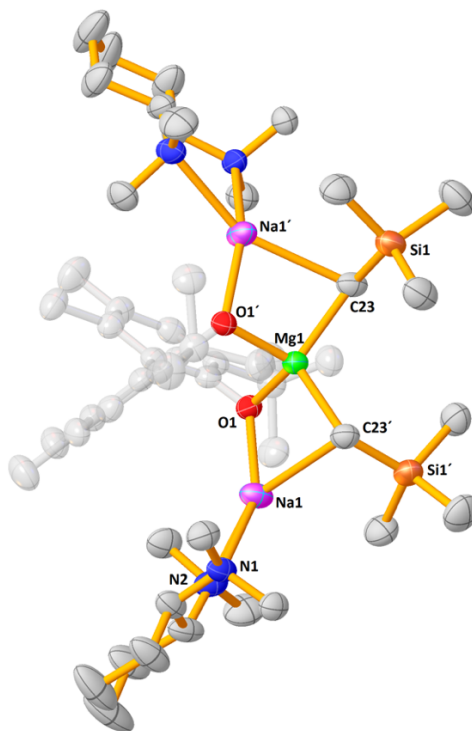


Figure 28: Solid-structure of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((R,R)\text{-TMCDA})_2$, **8**. Hydrogen atoms and disorder in (*R,R*)-TMCDA molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *S* orientated. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 1.995(2); Mg(1)-C(23), 2.205(3); Mg(1)-Na(1), 3.1147(12); Na(1)-O(1), 2.226(2); Na(1)-N(1), 2.458(3); Na(1)-N(2), 2.520(3); Na(1)-C(23), 2.728(4); O(1)-Mg(1)-O(1'), 95.36(12); O(1)-Mg(1)-C(23'), 101.03(10); C(23)-Mg(1)-C(23'), 113.08(18); Na(1)-C(23')-Mg(1), 77.50(10); O(1)-Na(1)-C(23'), 81.15(9); N(1)-Na(1)-N(2), 70.18(9).

The ^1H NMR spectrum of **8** (Figure 29) showed two doublets in the shielded region of the spectrum at δ -2.07 and -1.08 ppm which were assigned to the Mg-CH₂ methylene groups of the alkyl ligands. It is worth noting that once again these hydrogen atoms appear as two distinct doublets (J = 12 Hz) at ambient temperature, akin to what was observed in the ^1H NMR spectrum of **4** (Figure 17), and not as a single resonance like that observed for **6** (Figure 22) which once again indicating their diastereotopic nature. Continuing with the aliphatic region of the spectrum, the SiMe₃ groups of the alkyl ligands were located at δ 0.45 ppm

while the methyl and ^tbutyl groups of the (*rac*)-BIPHEN ligand were located at δ 1.86, 2.27 ppm and δ 1.78 ppm respectively. The three broad resonances at δ 0.45, 0.75, 1.44 ppm were assigned to the hydrogen atoms located on the cyclohexane rings of the (*R,R*)-TMCDAs ligands while the resonance at δ 1.91 ppm was assigned to the hydrogen atoms of the terminal methyl groups of the same ligand. The broadness of the resonances associated with the TMCDAs donor ligands was attributed to rapid ring flipping in the cyclohexane ring systems. A low temperature study was carried out; however, even at temperatures as low as –50 °C no resolution of these signals was observed. Finally, the aromatic region of the spectrum was found to contain a single resonance at δ 7.16 ppm which was assigned to the hydrogen atoms located on the phenyl rings of the (*rac*)-BIPHEN ligand. The presence of a single resonance gives further evidence that only one (*rac*)-BIPHEN containing species is present in solution. The ¹³C NMR spectrum was in good agreement with both the solid-state structure and the ¹H NMR spectrum. It is worth noting that in the ¹H and ¹³C NMR spectra of **8** a small quantity of TMS is observed which was attributed to partial decomposition.

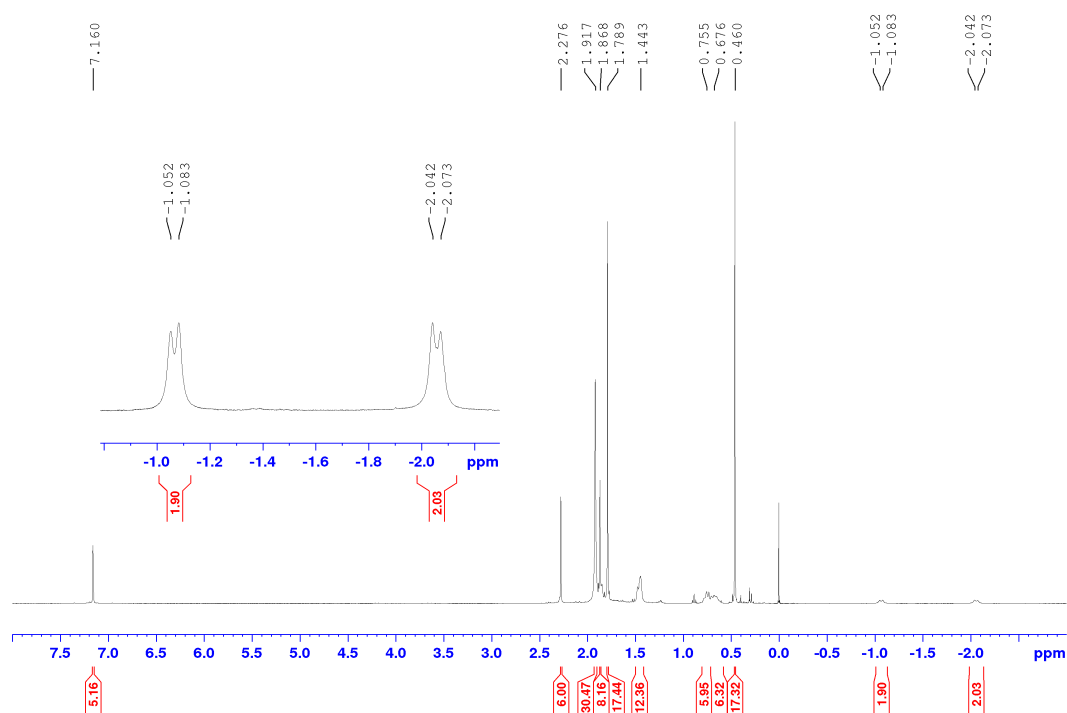


Figure 29: ¹H NMR Spectrum of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*R,R*)-TMCDAs)₂, **8** (400 MHz, C₆D₆, 300 K).

2.4.3.9 [(*rac*)-BIPHEN]Na₂MgⁿBu₂((*S,S*)-TMCDA)₂ (**9**)

In keeping with the situation observed with **7**, it was not possible to isolate crystalline material of suitable quality to allow for the characterisation of the solid-state structure of **9** by single crystal X-ray diffraction. Despite multiple attempts only microcrystalline powders could be isolated from the reaction. As a result, the characterisation of **9** was carried out in solution using multinuclear NMR spectroscopy.

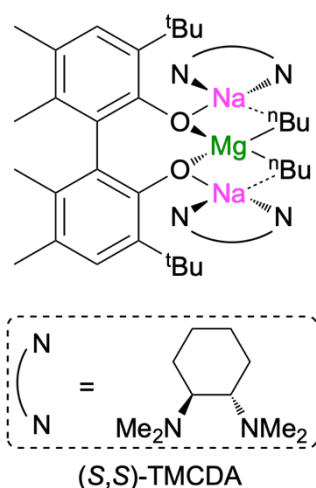


Figure 30: Proposed Structure of [(*rac*)-BIPHEN]Na₂MgⁿBu₂((*S,S*)-TMCDA)₂, **9**.

Beginning with the ¹H NMR spectrum of **9** (Figure 31), it showed a high degree of similarity with that of **7** (Figure 25). The methylene groups of the alkyl ligands bound directly to the magnesium centre appear as two broad multiplets at δ −0.67 and −0.27 ppm. Once again, the appearance of two distinct resonances in the shielded region of the spectrum comes as a result of diastereotopic splitting of the Mg-CH₂ hydrogen atoms which is induced by the (*rac*)-BIPHEN ligand. In the absence of a solid-state structure, this splitting provided further support that the predicted structure of **9** (Figure 30) is retained in solution. The remaining hydrogen atoms of the two ⁿbutyl ligands, the terminal CH₃ and internal CH₂ groups, appear as a triplet at δ 1.26 ppm and broad multiplet at δ 2.08 ppm respectively. The methylene groups of the cyclohexyl rings of the (*S,S*)-TMCDA ligands appear as two broad resonances at δ 0.67 and 1.42 ppm, while the remaining hydrogen atoms of the cyclohexyl rings, namely those attached to the α-carbon which are in turn directly attached to the nitrogen atoms, are located as part of the broad doublet located at δ 1.82 ppm. Finally, the terminal methyl groups (NMe₂) of the (*S,S*)-TMCDA ligands appear as broad singlet at δ 1.91 ppm. As well as the hydrogen atoms of the (*S,S*)-TMCDA ligands, the broad resonances at δ 1.82 and 1.91

ppm were also assigned to the ^tbutyl and methyl groups respectively of the (*rac*)-BIPHEN ligand. The remaining methyl groups of the (*rac*)-BIPHEN ligand appear as two singlets at δ 2.26 and 2.28 ppm along with the aromatic hydrogen atoms at δ 7.22 and 7.23 ppm. The appearance of two distinct resonances for each of these hydrogen atom environments is indicative of a loss in equivalence between the two phenyl rings of the (*rac*)-BIPHEN ligand. A similar situation was observed in solution for **7**.

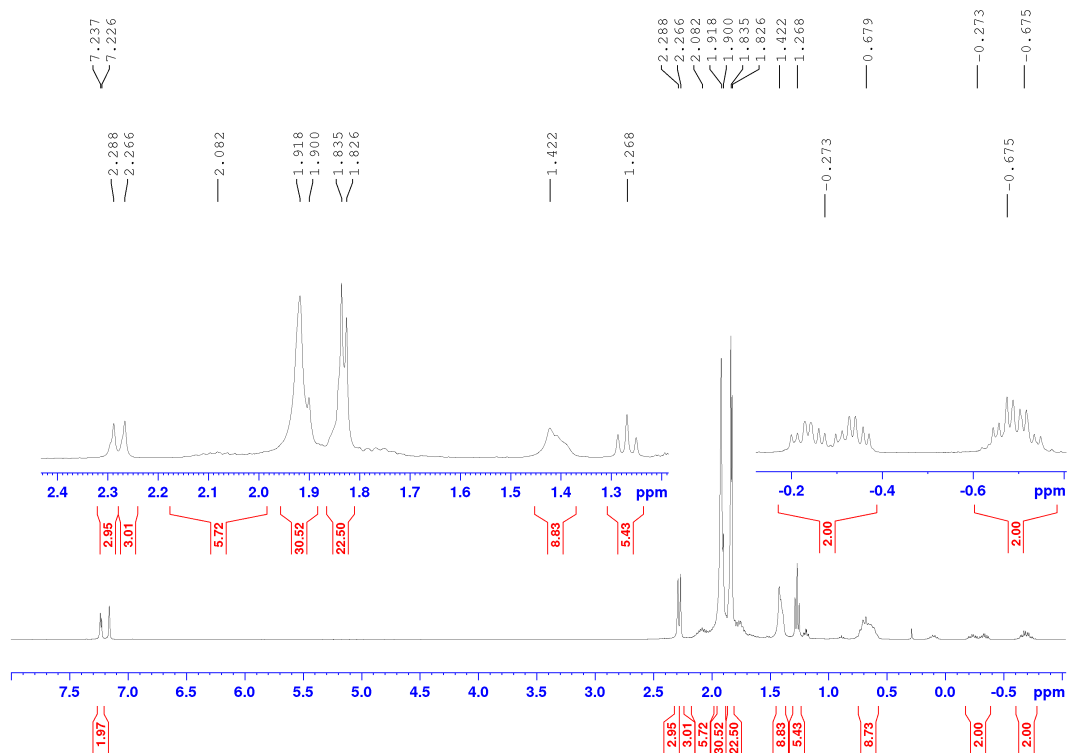


Figure 31: ¹H NMR spectrum of [(*rac*)-BIPHEN]Na₂MgⁿBu₂((*S,S*)-TMEDA)₂, **9** (400 MHz, C₆D₆, 300K).

The ¹³C NMR spectrum of **9** provides further evidence to support the loss of equivalence with the (*rac*)-BIPHEN ligand (Figure 32). Beginning with the (*rac*)-BIPHEN ligand, four distinct resonances were observed for the methyl groups at δ 17.8, 17.9, 20.8 and 20.9 ppm as well as two resonances for both the primary and quaternary carbon atoms of the ^tbutyl groups at δ 32.0 and 32.1 ppm, and δ 35.4 and 35.5 ppm respectively. Finally, the aromatic region of the spectrum was found to contain 12 distinct resonances which indicates that each carbon atom of the two phenyl rings have been rendered magnetically inequivalent. Furthermore, inequivalence in the carbon atoms of the two ⁿbutyl ligands was also observed. The two methylene groups bound directly to magnesium appear as two distinct resonances as δ 9.0 and 9.1 ppm along with the terminal methyl groups at δ 14.8 and 14.9 ppm while the

which appeared in the ^1H NMR spectrum at δ 1.26 ppm was found to correlate with the two resonances located in the ^{13}C NMR spectrum at δ 14.8 and 14.9 ppm. Both sets of resonances assigned to the methylene and methyl groups of the alkyl ligands were found to be in good agreement with reported chemical shift values found in literature and were also consistent with the other n -butyl containing magnesiates described above.⁹⁴ Focussing now on the broad multiplets which appear at δ 0.67 and 1.42 ppm in the ^1H NMR spectrum which were assigned to the cyclohexane rings (*S,S*)-TMCDL ligands, these resonances show a single correlation to both resonances located in the ^{13}C NMR spectrum at δ 21.4 and 25.4 ppm. These values are consistent with those reported for **7** which contains the opposite enantiomer of the TMCDL ligand and further support their assignment. The broad doublet-like resonance found in the ^1H NMR spectrum at δ 1.82 – 1.83 ppm was tentatively assigned to both the t -butyl groups of the (*rac*)-BIPHEN ligands as well as the hydrogen atoms of the tertiary NCH groups located on the cyclohexane rings of (*S,S*)-TMCDL. From the HSQC NMR spectrum it is clear that two species are indeed represented by this broad resonance. The first of these correlations was observed with the two resonances located in the ^{13}C NMR spectrum at δ 32.0 and 32.1 ppm. These values are consistent with the assignment of these resonances as the primary $\text{C}(\text{CH}_3)_3$ carbon atoms of the t -butyl groups. The second correlation observed for the broad doublet was with the resonance located in the ^{13}C NMR spectrum at δ 63.8 ppm which was assigned to the NCH groups of the (*S,S*)-TMCDL ligands. Furthermore, the integration value of the broad doublet was calculated to be 22 hydrogen atoms which is in good agreement with the resonance being representative of the t -butyl and NCH groups. The broad singlet located at δ 1.91 ppm was also tentatively assigned as being representative of multiple hydrogen atom environments. Based on the integration value which was calculated to be 30 hydrogen atoms, it was proposed that this resonance represents two of the four (*rac*)-BIPHEN methyl groups as well as the methyl groups of the (*S,S*)-TMCDL ligands. Analysis of the HSQC NMR spectrum did indeed show a correlation between the shoulder peak located at δ 1.82 ppm with the two resonances located in the ^{13}C NMR spectrum at δ 17.8 and 17.9 ppm which is in good agreement with their assignment as the methyl groups of (*rac*)-BIPHEN ligand. Once again, no additional correlations were observed for this resonance in the HSQC NMR spectrum to suggest the presence of the terminal methyl groups of the (*S,S*)-TMCDL ligands. A similar situation was observed for the terminal methyl groups of the (*R,R*)-TMCDL ligands of **7**. Finally, the two resonances located at δ 2.26 and 2.28 ppm in the ^1H NMR spectrum which were assigned to the remaining methyl groups of the (*rac*)-BIPHEN ligand showed clear correlations to the two resonances located at δ 20.8 and 20.9

ppm in the ^{13}C NMR. The chemical shifts of these resonances in both the ^1H and ^{13}C NMR spectra are consistent with their assignment as the methyl groups of the (*rac*)-BIPHEN ligand.

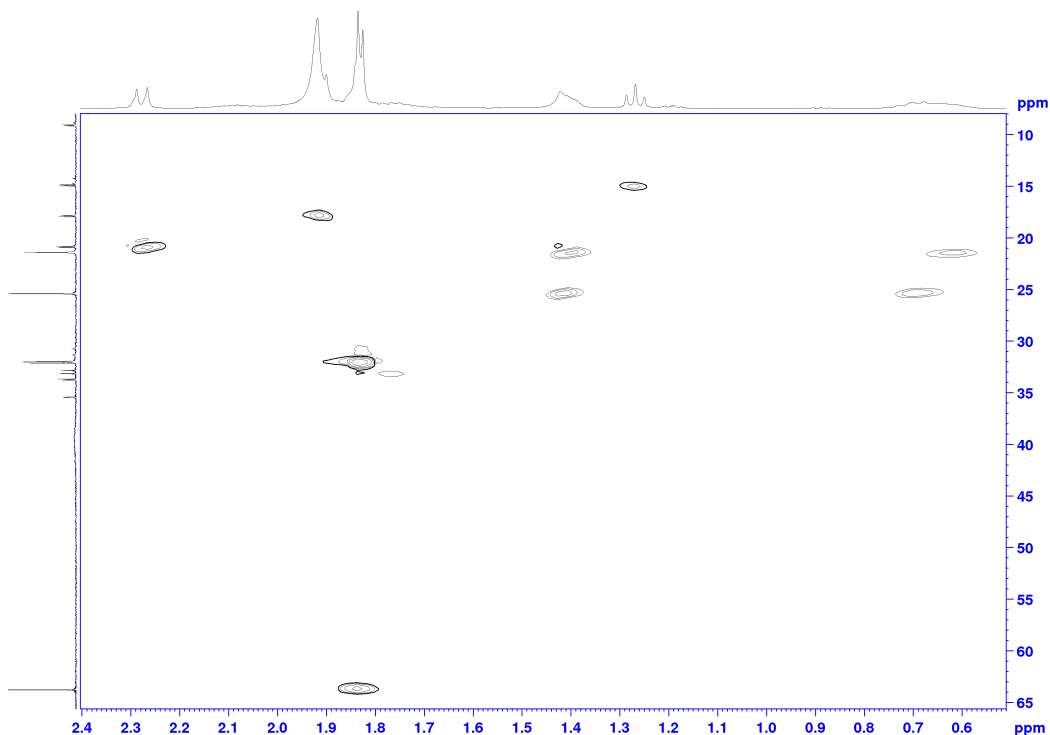


Figure 33: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}^n\text{Bu}_2((S,S)\text{-TMCDA})_2$, **9** (C_6D_6 , 300K).

2.4.3.10 $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((S,S)\text{-TMCDA})_2$ (**10**)

The structural investigation into sodium magnesiates containing the (*rac*)-BIPHEN ligand were concluded with the synthesis and isolation $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((S,S)\text{-TMCDA})_2$ **10** (0.197 g, 42 % yield) (Figure 34). As the only difference between the synthetic procedure used for the synthesis of **8** and **10** was the enantiomer of the Lewis donor, the two structures were expected to be essentially identical. This was confirmed by X-ray crystallographic analysis of **10** which revealed it to be the corresponding mirror image of **8**. Complex **10** crystallised in the space group $P4_32_12$ which is again a chiral space group and confirms the chiral nature of the complex. The coordination geometries of the magnesium and sodium atoms are once again found to be distorted tetrahedral (sum of bond angles 657.55° and 677.59° respectively) with the central magnesium atom binding to the (*rac*)-BIPHEN and alkyl ligands through two magnesium-oxygen and two magnesium-carbon single bonds [Mg1-O1 1.9965(19) Å and Mg1-C23 2.205(3) Å]. Sodium atoms Na1/Na1' are bound to the (*rac*)-BIPHEN ligand through a single sodium-oxygen bond [Na1-O1 2.231(2) Å] whilst forming stabilising interactions with the methylene carbons of the alkyl ligands [Na1-C23'

2.739(3) Å]. Na1/Na1' are coordinated to a single molecule of (*S,S*)-TMCDAs each, which are bound in a non-uniform manner [Na1-N1 2.512(3) Å and Na1-N2 2.462(3) Å] to complete their coordination spheres.

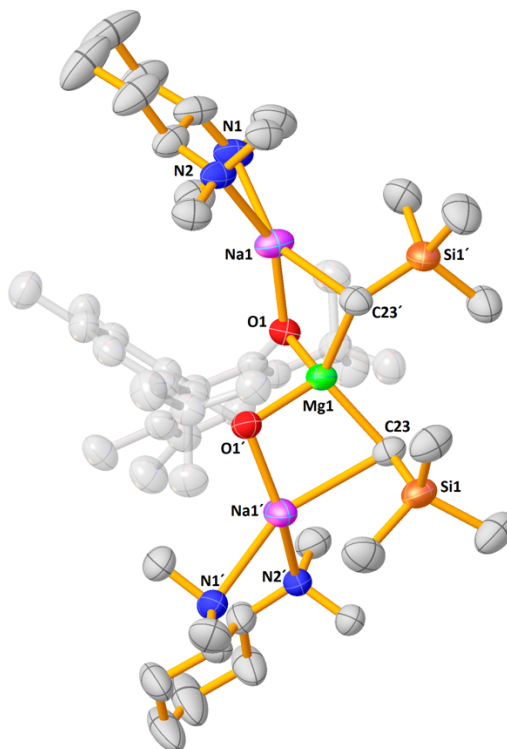


Figure 34: Solid state structure of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((S,S)\text{-TMCDAs})_2$, **10**. Hydrogen atoms and disorder in (*S,S*)-TMCDAs molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *R* orientated. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 1.9965(19); Mg(1)-C(23), 2.202(3); Mg(1)-Na(1), 3.1249(11); Na(1)-O(1), 2.231(2); Na(1)-N(1), 2.512(3); Na(1)-N(2), 2.462(3); Na(1)-C(23'), 2.739(3); O(1)-Mg(1)-O(1'), 95.76(11); O(1)-Mg(1)-C(23'), 100.94(9); C(23)-Mg(1)-C(23'), 112.69(16); Na(1)-C(23')-Mg(1), 77.61(9); O(1)-Na(1)-C(23'), 80.70(8); N(1)-Na(1)-N(2), 70.56(8).

Just as in the solid-state, the solution-state behaviour of **10** is almost identical to that of **8**. The methylene protons of the alkyl ligands appear as two distinct doublets at δ -2.12 and -1.12 ($J = 12$ Hz) along with the SiMe_3 groups at δ 0.41 ppm (Figure 35). Focussing on the (*rac*)-BIPHEN ligand, the two sets of methyl groups appear at δ 1.81 and 2.22 ppm, the *t*butyl groups at δ 1.73 ppm and the aromatic hydrogen atoms at δ 7.11 ppm. Similar to **8**, the resonances associated with the (*S,S*)-TMCDAs ligands are broad and undefined. The hydrogen atoms of the cyclohexane rings appear as two broad resonances at δ 0.74 and 1.47 ppm

while the terminal methyl groups attached to the nitrogen atoms appear at δ 1.96 ppm. A low temperature study of **10** was carried out in order to better resolve the resonances associated with the hydrogen atoms of the cyclohexane rings however no resolution could be achieved even when temperatures as low as $-50\text{ }^{\circ}\text{C}$ were employed. Moreover, the ^{13}C NMR spectrum is in good agreement with the ^1H NMR spectrum and the solid-state structure. Once again, as was observed for **8**, a small amount of TMS was visible in both the ^1H and ^{13}C NMR spectra for **10** after crystallisation which was attributed to partial decomposition.

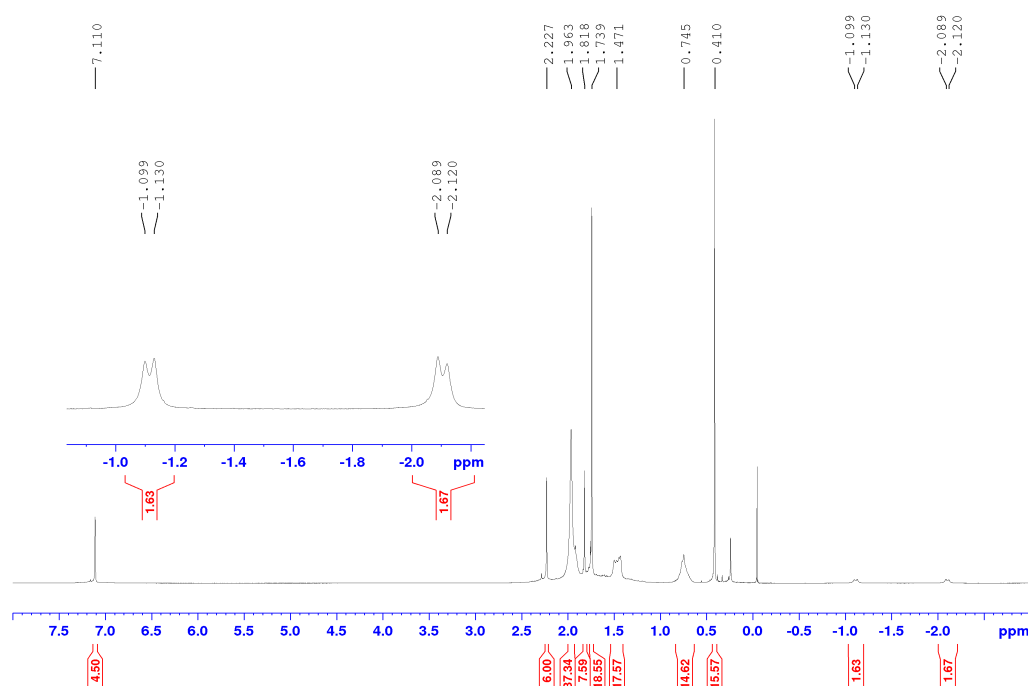


Figure 35: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_2((S,S)\text{-TMCD})_2$, **10** (400 MHz, C_6D_6 , 300 K).

2.4.4 Investigation of Ligand Effects

As alluded to earlier, it is of vital importance that the solid- and solution-state structure of magnesiate reagents is fully understood in order to rationalise their reactivity. Focussing on the solid-state structures of magnesiates **4**, **5**, **6**, **8**, and **10**, a comparison was made in order to assess the potential effects of variation of the Lewis donor and alkyl ligand on the organometallic framework of the magnesiate.

Table 1: List of mean bond lengths for key bonds in **4-6**, **8** and **10**.

Complex	Mean bond lengths (Å)					
	Mg-O	Mg-C	Na-O	Na-C	Na-N	Mg-Na
4	2.006	2.198	2.231	2.818	2.543	3.115
5	2.010	2.203	2.273	2.689	2.552	3.141
6	2.023	2.204	2.297	2.745	2.553	3.251
8	1.995	2.205	2.226	2.728	2.489	3.114
10	1.996	2.202	2.231	2.739	2.487	3.124

In order to make as fair a comparison as possible, the magnesiates **4**, **6**, **8** and **10** containing the alkyl ligands (CH_2SiMe_3) will be discussed first in order to assess the effects of changing the Lewis donor. From Table 1 it is immediately clear there is a high level of similarity between the four structures. Starting with the organometallic core, the Mg-O bond lengths are virtually identical with less than 0.03 Å of difference between the four structures. The Mg-C bond lengths, which intuitively should ultimately impact the reactivity of the magnesiates also remains consistent across the series, independent of the donor identity, with a deviation in the bond lengths of less than 0.01 Å. Focussing now on the periphery of the structures slightly more variation in the bond length is observed. This however would be expected given that the Lewis donor in each case is being altered. Nevertheless, the Na-O bond lengths remain consistent with the largest difference observed between **6** and **8** at 0.071 Å. Turning now to the contact made between the sodium atoms and the methylene carbons of the alkyl ligands, the solid-state structures of **6**, **8** and **10** are in good agreement with each other and show very little deviation in the length of the contact while **4** shows a lengthening of the bond, albeit marginally, compared to the other complexes. The largest difference in the Na-C bond length was observed between **4** and **8**, for which the difference in Na-C bond length was found to be 0.09 Å. The Na-N bond lengths show very little degree of alteration despite a change in the Lewis donors. Complexes **8** and **10** have the shortest average Na-N bond lengths of the four magnesiates by approximately 0.066 Å. Surprisingly however, despite the increase in the coordination number of the sodium atoms in **6**, it does not appear to correlate with a marked change in the Na-N bond lengths with a difference of only 0.01 Å when compared to **4**. The one marked difference observed between the four structures is in the distance between the sodium and magnesium atoms. This interatomic distance remains virtually unchanged with the exception of **6** where on average the sodium and magnesium atoms are greater than 0.12 Å further apart. Given that **6** contains the

tridentate Lewis donor PMDETA, this increase in the distance between sodium and magnesium atoms could point towards a sequestering of the sodium atom by the PMDETA ligand. If this were true, then a bulkier Lewis donor or one with a greater denticity could perhaps lead to the formation of a solvent separated ion pair structure.

Focussing now on the effect of changing the alkyl ligand, a comparison can be made between the structures of magnesiates **5** and **6**. Very little alteration is observed in the key bond lengths of these two complexes with the Mg-O, Mg-C and Na-N bond lengths remaining virtually unchanged. Only a small variation is observed in the Na-O and Na-C bond lengths, both of which were found to be marginally shorter in **5**. Once again, the interatomic Mg-Na distance is noticeably longer in **6**. Given that both complexes contain the same Lewis donor, it appears that the identity of the alkyl group may be having an effect here. It could be possible that the bulkier alkyl ligands present in **6** lead to a degree of steric hinderance with the PMDETA ligands, thus forcing the sodium atoms to move further away from the magnesium centre.

Table 2: List of key bond angles for complexes **4-6**, **8** and **10**.

Complex	Mean bond angle (°)					
	O-Mg-O	C-Mg-C	O-Mg-C (cis)	O-Mg-C (trans)	O-Na-C	Na-C-Mg
4	103.05	116.51	90.45	118.95	80.18	75.68
5	95.35	107.70	101.60	121.65	86.65	79.2
6	98.50	120.83	100.28	117.78	79.64	81.36
8	95.36	113.08	101.03	123.44	81.15	77.50
10	95.79	112.69	100.95	123.61	80.70	77.61

Concentrating now on variations in key bond angles around the magnesium centre caused by variation of the donor ligands, Table 2 shows that for **4** the bite angle of the (*rac*)-BIPHEN ligand is wider than that of the other four complexes. Turning now to the angle made between the two alkyl ligands and the magnesium centre, it was found that the angle was widest for **6**. This correlates well with the bond lengths examined in Table 1 as it was shown that for **6** the interatomic distance between the sodium and magnesium atoms were longest for this complex. It therefore follows that if the sodium atoms have moved further away from the central magnesium atom then this will alleviate any steric repulsion between the alkyl

ligands by allowing them to move further apart which would result in an increase in the C-Mg-C bond angle. The other bond angles around the magnesium centres remain consistent across the four complexes with the exception of the O-Mg-C (*cis*) bond angles of **4** for which the mean angles are much shorter. It correlates however that the O-Mg-O bond angle are large and this would lead to a contraction of the bond angles to the other ligands across the magnesium centre. Focussing now on the angles around the sodium atoms, only the bond angles to the organometallic core have been considered and not the angles made with the donor ligands. Examining the O-Na-C and Na-C-Mg bonds it can be seen in each case that the values are consistent across the four structures with the exception of **6** which shows an increase in the Na-C-Mg bond angle. This increase can again be rationalised based on the change in the interatomic magnesium-sodium distance observed for this complex. If the sodium atom is being partially sequestered by the PMDETA ligand and moved further from the core of the molecule then it follows that this would be accompanied by an increase in the bond angles.

Examining now the effect that the alkyl ligand has on the solid-state structure of the magnesiate, a comparison was made between **5** and **6**. Overall the two structures show good levels of consistency with the exception of the C-Mg-C and O-Na-C bond angles. For **5** which contains ⁿbutyl ligands the average C-Mg-C bond angle was measured to be 107.70 ° compared to 120.83 ° for **6** which contains the monosilyl ligand CH₂SiMe₃. The more acute bond angle for the ⁿbutyl containing **5**, suggests the conformational flexibility and lesser steric bulk of the butyl chains reduces the degree of steric hinderance between the two alkyl chains. If so, this may have important consequences regarding the reactivity of the two complexes. In the case of the O-Na-C bond angle the opposite case is true, and the angle is larger in **5** than it is in **6**. This increase in bond angle for **5** may be due to the difference in the interatomic magnesium-sodium distance as the magnesium and sodium atoms are closer together in **5** which would account for the increase in the bond angle.

2.4.5 Investigation of Alkali Metal Effects

A key goal of this study was to investigate the effect of varying the alkali metal on the overall structure of the final magnesiate and was achieved by comparing the key bond lengths and bond angles of the sodium magnesiates **3-10** with their lithium analogues reported by our group.⁹⁴ This was somewhat precluded however by the increased propensity of the sodium magnesiate complexes to undergo disproportionation which subsequently required the use

of chelating ligands in order to stabilise them and allow for their isolation. As a result, a comparison can only be made to the core of the organometallic framework *i.e.* the key bond lengths and bond angles surrounding the central magnesium atoms without introducing a degree of uncertainty regarding potential ligand effects.

Beginning with the homometallic precursors to magnesiate formation, **1** and its lithium counterpart $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$, a full comparison can be made as both complexes were prepared using the same Lewis donor (Figure 36).⁹⁴ An immediate difference noted between the two complexes is that $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$ is a racemic complex as denoted by its space group $C2/c$ whereas **1** crystallised in an enantiopure form. As the same synthetic method was used, this may suggest an inherent difference in the physical properties of the two crystal systems in solution.¹⁰⁰ Examination of the organometallic framework of both complexes reveals them to be essentially isostructural with only subtle differences in the key bond lengths and bond angles which were expected given the relative increase in size moving from lithium to sodium. The mean bond length of the Na-O bonds for the central sodium atom Na1 in **1** were found to be 2.265 Å while for $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$ the mean central Li-O bond length for the central lithium atom was found to be 1.974 Å, a difference of 0.291 Å. For the four coordinate sodium atom Na2, the mean Na-O_(BIPHEN) bond length was calculated to be 2.199 Å compared to the 1.875 Å for the corresponding Li-O_(rac-BIPHEN) bonds in $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$, a difference of 0.324 Å. Both complexes form a four membered M-O-M-O ring (where M = Na for **1** and Li for $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$) which is highly distorted from planarity. The bond lengths of the Na-O_(BIPHEN) bonds were found to be 2.265 and 2.298 Å for **1** while the corresponding Li-O_(rac-BIPHEN) bond lengths were reported as 1.901 and 1.907 Å. This leads to a difference of 0.364 and 0.391 Å respectively for the two sets of bonds. The interatomic distance between the two sodium atoms was found to be 3.170 Å while the corresponding distance between the two lithium atoms was reported as 2.587 Å. The increase in the Na-O bond lengths are uniform across the structural framework of **1** and were therefore attributed simply to the increase in the relative size of the sodium atoms compared to that of lithium. Despite the increased bond lengths of complex **1** in comparison to $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$ the bond angles remain virtually unchanged with the exception of the bond angles within the four membered Na-O-Na-O and Li-O-Li-O rings. In the case of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$ the Li-O-Li angle was reported as 84.53° whereas for **1** the corresponding O-Na-O bond angle was found to be 79.27°, a contraction of approximately 5° as a result of the inclusion of the larger sodium atom. It would be envisioned that this led to an increase

in the ring strain and could possibly result in an increase in the reactivity of the homometallic sodium complex compared to its lithium congener.

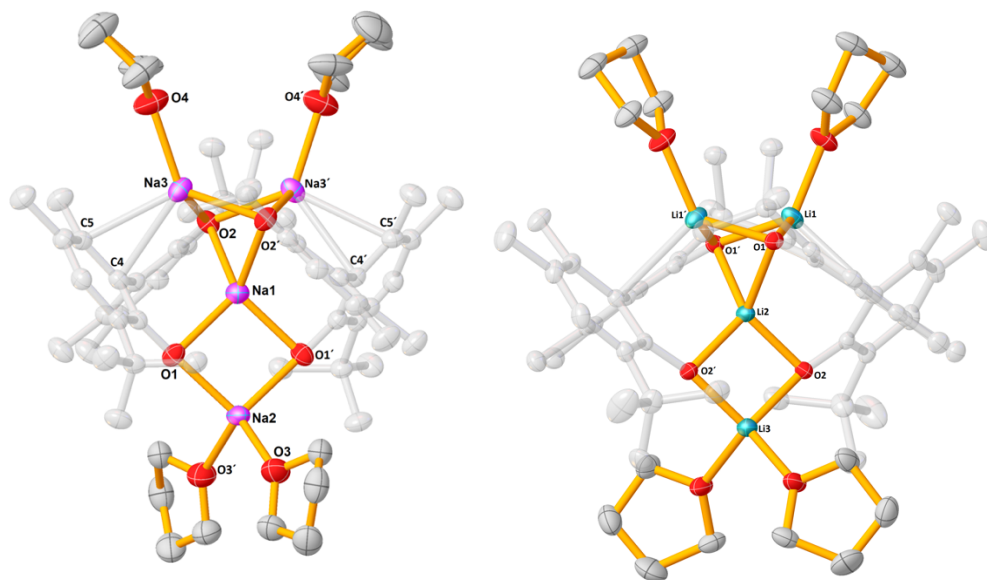


Figure 36: Solid state structure of **1** (left) and its lithium analogue $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$ (right).

Although the lithium analogue of **2** has been reported in the literature, the authors comment that the data was only of sufficient quality to allow for a brief description of molecular connectivity but not an in-depth discussion of structural parameters.⁹⁴ As a result, it has not been possible to make a direct comparison of the key structural features of the two species, however, molecular connectivity clearly shows the two structures to adopt the same structural framework. One conclusion that can be drawn from the structure of **2** is that the lengths of the $\text{Mg-O}_{(\text{BIPHEN})}$ bonds are in good agreement with its homometallic counterpart $[(rac)\text{-BIPHEN}]_2\text{Mg}_2(\text{THF})_2$.¹⁰¹ A comparison between **1** and **2** revealed an elongation of the mean $\text{Na-O}_{(\text{BIPHEN})}$ bond lengths in **2** from 2.1190 Å to 2.2373 Å respectively upon inclusion of magnesium within the structure.

Table 3: Comparison of mean bond lengths and bond angles of [(*rac*)-BIPHEN]Li₂Mg(CH₂SiMe₃)₂(THF)₃⁹⁴ with **4**, **6**, **8**, and **10**

Magnesiate	Mean bond lengths (Å)		Bond angles (°)	
	Mg-C	Mg-O	C-Mg-C	O-Mg-O
[(<i>rac</i>)-BIPHEN]Li ₂ Mg(CH ₂ SiMe ₃) ₂ (THF) ₃	2.206	2.014	128.51	98.23
4	2.198	2.006	116.51	103.05
6	2.204	2.023	120.83	98.50
8	2.205	1.995	113.08	95.36
10	2.202	1.996	112.69	95.79

For sodium magnesiates **4**, **6**, **8** and **10**, a tentative comparison of the key bond lengths and bond angles around the magnesium centre has been made to their most appropriate lithium magnesiate analogue [(*rac*)-BIPHEN]Li₂Mg(CH₂SiMe₃)₂(THF)₃ (Table 3).⁹⁴ Beginning with the key bond lengths, only minor deviation was observed in both the Mg-O_[(*rac*)-BIPHEN] and Mg-C_{alkyl} distances. This indicates that these bond lengths are independent of the identity of both the alkali metal and the donor solvent. Examination of the key bond angles around the magnesium centre revealed small variations in the bite angles (O-Mg-O) of the (*rac*)-BIPHEN ligand with bite angles of the phenoxide ligand being most acute when (*R,R*) and (*S,S*)-TMCDAs are incorporated in the structure. A larger difference was observed for the C-Mg-C angle between the alkyl ligands and the magnesium centre. For the lithium complex [(*rac*)-BIPHEN]Li₂Mg(CH₂SiMe₃)₂(THF)₃ this angle was reported to be 128.51°, a difference of between 8° and 16° to the sodium magnesiates **4**, **6**, **8** and **10** and would appear to show some degree of dependence on the identity of the alkali metal cation.

Table 4: Comparison of mean bond lengths and bond angles of [(*rac*)-BIPHEN]Li₂ⁿBu₂(THF)₃⁹⁴ with **5**.

Magnesiate	Average Bond Lengths (Å)		Bond Angles (°)	
	Mg-C	Mg-O	C-Mg-C	O-Mg-O
[(<i>rac</i>)-BIPHEN]Li ₂ ⁿ Bu ₂ (THF) ₃	2.201	2.012	123.29	97.36
5	2.203	2.010	107.70	95.35

Turning now to the ⁿbutyl-containing **5** and its closest related lithium analogue [(*rac*)-BIPHEN]Li₂MgⁿBu₂(THF)₃ a similar trend to that of the previously discussed complexes is

observed whereby there is very little deviation in the core structure of the two magnesiates.⁹⁴ Both $\text{Mg-C}_{(\text{alkyl})}$ and $\text{Mg-O}_{((\text{rac})\text{-BIPHEN})}$ bond lengths for **5** and $[(\text{rac})\text{-BIPHEN}]\text{Li}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$ are virtually identical which tells us that inclusion of the heavier alkali metal has at most a minimal impact on the bond lengths surrounding the magnesium centre. Examining the bond angles around the central magnesium atom, the O-Mg-O bond angles are virtually identical with a variation of less than 3° while a larger variation is once again observed for C-Mg-C bond angles. To elaborate, the C-Mg-C bond angle in **5** was found to be 107.70° while for the lithium complex $[(\text{rac})\text{-BIPHEN}]\text{Li}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$ the same bond angle was measured at 123.29° , a difference of over 15° . Obviously due to the difference in Lewis basic donor, a note of caution should be exercised when comparing these two molecules.

2.4.6 Solution-State Stability of Complexes **3** and **4**

Assuming that the aforementioned disproportionation process that prevented isolation of the desired sodium magnesiates in the presence of THF is a thermodynamic decomposition pathway, the magnesiates containing chelating donors were subjected to increased temperatures for prolonged periods of time. If when monitoring the magnesiates by ^1H NMR spectroscopy no change was observed in their spectra it would prove that utilisation of a chelating donor could prevent this decomposition pathway. Beginning with C_6D_6 solutions of **3** and **4** (Figure 37), they were initially studied at ambient temperature and showed no degradation after several hours. The solutions were next heated at 55°C for a further 12 hours. Monitoring of the ^1H NMR spectra revealed no change after this time. A combination of these results demonstrates that inclusion of TMEDA imparts a high degree of thermodynamic stability upon **3** and **4**, subsequently preventing disproportionation.

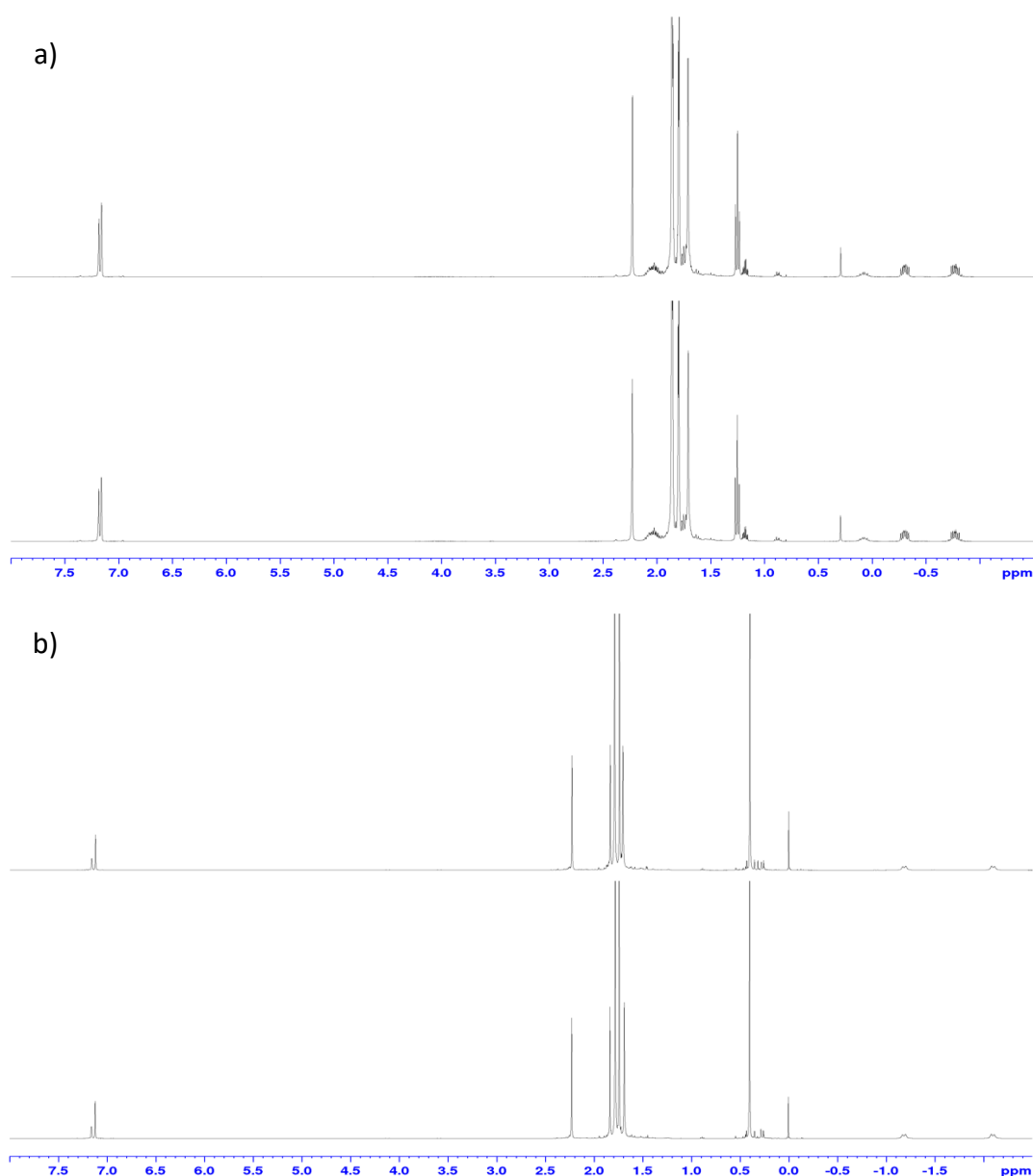


Figure 37: a) Overlay of ^1H NMR spectra of **3** after heating at 55 °C in C_6D_6 0 h (bottom) and after 12 h (top). b) Overlay of ^1H NMR spectra of **4** after heating at 55 °C in C_6D_6 for 0 h (bottom) and after 12 h (top).

With this result in hand, it was decided to repeat the study in the presence of THF. Solutions of **3** and **4** were prepared this time using d_8 -THF as the solvent (Figure 38). From the initial ^1H NMR spectrum of both complex it is immediately clear that in bulk THF the TMEDA donor ligands are fully uncoordinated from the magnesiate. Despite the rapid displacement of the chelating ligand, the magnesiate remained stable at ambient temperature for several hours, indicating that once formed the magnesiate is indeed stable in the presence of THF. The d_8 -THF solutions of **3** and **4** were subjected to heating at 55 °C for 12 hours upon which a

noticeable change in the ^1H NMR spectra of both complexes was observed (Figure 38). In the parent spectra, a single resonance was observed in the aromatic regions and is diagnostic of there being a single species within the solution which contains the (*rac*)-BIPHEN ligand. After heating, the solutions were found to contain multiple resonances in the aromatic region which is indicative of the formation of new (*rac*)-BIPHEN containing species. A similar situation was also observed in the aliphatic region of the spectra where multiple new resonances were formed. Furthermore, these changes were accompanied by the loss of the two distinct resonances observed in the negative region of the spectra corresponding to the Mg-CH_2 hydrogen atoms along with a colour change in the solutions from colourless to yellow. A combination of these results led us to conclude that the changes observed in the two spectra are as a direct result of decomposition of **3** and **4**, potentially because of disproportionation.

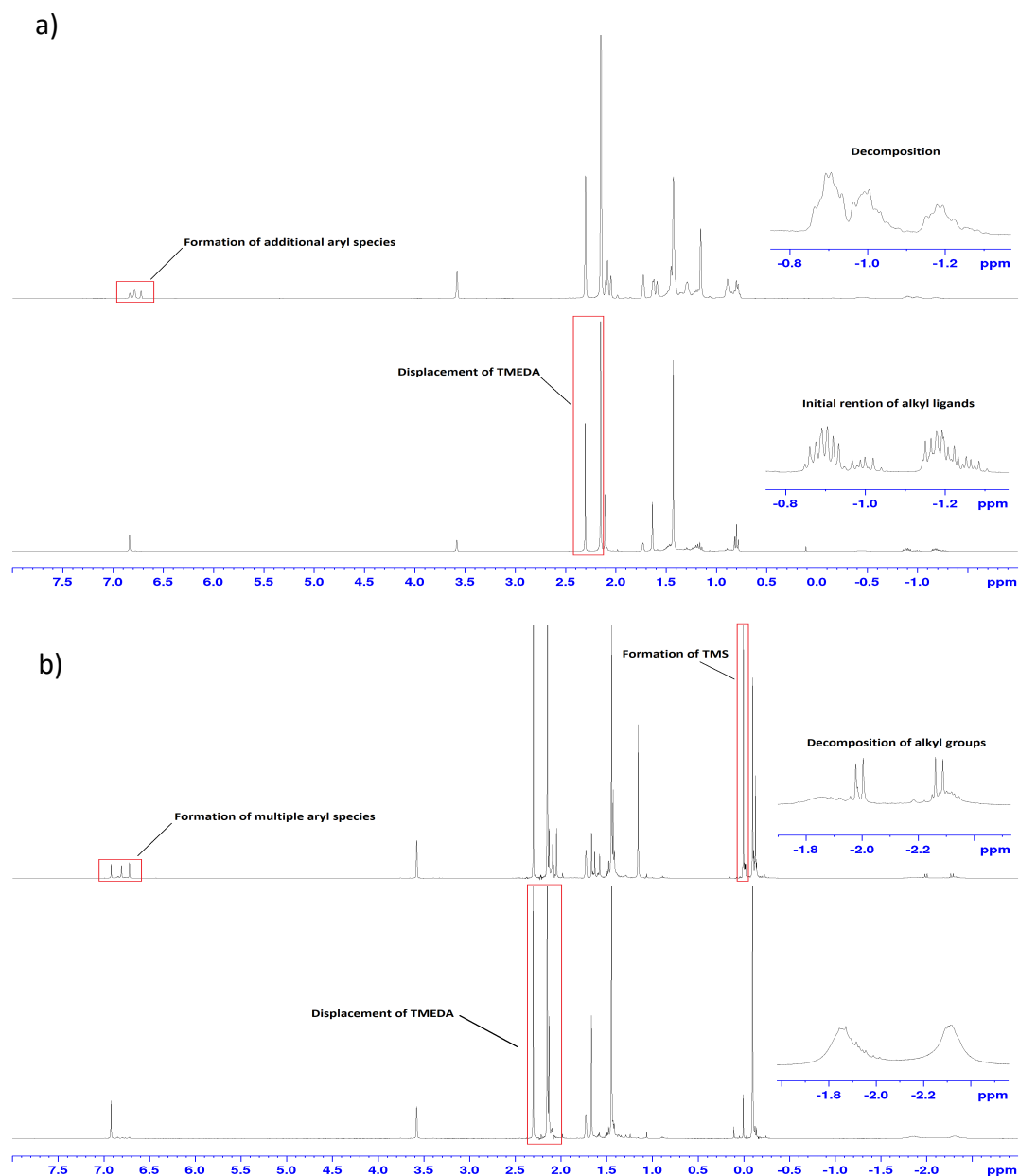


Figure 38: a) Overlay of ^1H NMR spectra of **3** after heating at 55 $^\circ\text{C}$ in $\text{d}_8\text{-THF}$ 0 h (bottom) and after 12 h (top). b) Overlay of ^1H NMR spectra of **4** after heating at 55 $^\circ\text{C}$ in $\text{d}_8\text{-THF}$ for (bottom) and after 12 h (top).

2.5 Conclusions and Outlook

This work has provided a much-needed insight into the structural chemistry of mixed alkyl/phenoxide sodium magnesiate complexes through the synthesis of nine new heterobimetallic sodium magnesiates. During the course of this investigation the monometallic precursor to these magnesiates was also investigated and fully characterised, adding to the overall understanding of these new complexes. It has been shown that in

comparison to their lithium counterparts these new sodium magnesiates are more susceptible to decomposition via disproportionation and require the use of chelating donors in order to prevent this undesired process from occurring.

By using a different bi- and tri-dentate donors to stabilise these new sodium magnesiates, it has provided the opportunity to investigate the effects that the identity of such donor ligands had on the structures of the magnesiate complexes in question. Although initially considered to be a drawback to their synthetic utility, inclusion of these donor ligands and exclusion of coordinating solvent such as THF was found to produce a more stable magnesiate that was found to be thermally robust over a greater range of temperatures. This increased thermal stability of **3** and **4** could potentially allow for their application in reactions requiring previously incompatible conditions. Furthermore, by utilising the chiral donors (*R,R*)- and (*S,S*)-TMCDa it provided a simple and cost effective way of generating chiral disodium dialkylmagnesium phenoxides without requiring the use of the extremely expensive enantiopure form of the BIPHEN ligand. If these chiral magnesiates are found to have sufficient reactivity, this would provide an exciting new entry point into asymmetric synthesis.

2.6 Further Work

As it stands, there are a number of aspects relating to this section of work which merit further investigation. Firstly, the scope of structural investigation could be expanded by introducing a variety of alternative organic ligands as part of the organomagnesium precursor. Beginning with alkyl ligands, the inclusion of ^sbutyl and ^tbutyl ligands would allow for a direct structural comparison to be made with the existing ⁿbutyl containing complex, **5**, while the inclusion of methyl, ethyl or ^{neo}pentyl ligands could produce a series of structures which would allow for an investigation into what role, if any, the identity of the alkyl ligand has on the structural chemistry of such the magnesiate complexes. Additionally, amide ligands such as HMDS or TMP could be introduced by utilising the diamido magnesium complexes Mg(HMDS)₂ and Mg(TMP)₂. Moreover, the scope of the donor ligands could also be expanded to include the bulky tetradentate nitrogen-based donor Me₆-TREN. Inclusion of this ligand could potentially provide a valuable insight into the structural chemistry of these magnesiate complexes through a direct comparison with the magnesiate complexes already characterised containing the bi- and tridentate nitrogen based donors TMEDA, (*R,R*) and (*S,S*)-TMCDa, and PMDETA. The scope of Lewis donors could be further extended to include the crown ether

ligands 12-crown-4, 15-crown-5 and 18-crown-6 along with other oxygen-based donors such as diethyl ether, dimethoxyethane (DME) or 1,4-dioxane. These could provide valuable insight into the apparent instability of these magnesiate complexes in the presence of oxygen-based donors and if the disproportionation of the desired magnesiate complexes can be effectively suppressed simply by increasing the steric bulk or denticity of the donor ligand. Furthermore, by altering the stoichiometry of the alkali metal to non-alkali metal from 2:1 to 1:1 combined with the inclusion of bulkier ligands such as Me₆-TREN or the crown ether ligands may allow for successful isolation and structural characterisation of a lower order sodium alkylmagnesium phenoxide complex. Characterisation of such a complex would be of major significance as the related lithium alkylmagnesium phenoxides have been heavily utilised for a number of transformations without any solid-state structural characterisation of the complexes.^{103–105} Several attempts have been made to isolate the structure of these lower order complexes; however, none have been successful to date.

Secondly, in light of the recent study by Hevia detailing the complex solution-state behaviour and Schlenk equilibrium of mixed alkyl/alkoxide lithium magnesiates in THF solutions, it would be prudent to expand the solution-state studies of **3-10** to further assess their behaviour in THF solution.¹⁰⁶ Through preliminary investigations into the solution-state behaviour of **3** and **4** it has already been shown that in the presence of THF these complexes become thermally unstable and are prone to decomposition especially at elevated temperatures. It has also been shown through the isolation of **2** that in the presence of THF, these magnesiate complexes are prone to undergo disproportionation, giving rise to the homoleptic BIPHEN rich magnesium phenoxide **2**. It would therefore be interesting to investigate by NMR spectroscopy if formation of both the homoleptic disodium magnesium phenoxide and *tetra*(alkyl) sodium magnesiate can be observed in THF solutions of **3-10**.

It may also be of interest to expand the scope of alkali metals to include the heavier elements potassium, rubidium and caesium. The structural chemistry of potassium magnesiates have been heavily studied in recent years, however; due to the reactivity of their parent organometallic complexes, the structural chemistry of caesium or rubidium magnesiates have not been explored to the same extent. Given the larger size of the heavier alkali metals and their propensity to form soft π -type interactions with aromatic ring systems, inclusion of these heavier metal could give rise to exciting new structural motifs with alternative coordination modes. Finally, the scope of this chemistry could be extended by replacing

magnesium with calcium. This would provide an exciting opportunity to study the structural chemistry of calcium complexes, something which is currently gaining a lot of attention.

2.7 Experimental

2.7.1 Synthesis of $[\text{BIPHEN}]_2\text{Na}_4(\text{THF})_4$ (1)

$[\text{BIPHEN}]_2\text{Na}_4(\text{THF})_4$ was prepared by the addition of a solution of (*rac*)-BIPHEN- H_2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared $^n\text{BuNa}$ (0.08 g, 1 mmol) in hexane (5 ml) at -10°C . The suspension was stirred for 1 hour with slow warming to ambient temperature. The solvent was removed *in vacuo* and THF (3 ml) was added to give a colourless solution. The solution was subsequently stored at -33°C to yield colourless crystals of $[\text{BIPHEN}]_2\text{Na}_4(\text{THF})_4$ (yield 0.145 g, 26 %). ^1H NMR (400.13 MHz, 300 K, $\text{d}_8\text{-THF}$): δ 1.30 [36H, bs, 4 x $\text{C}(\text{CH}_3)_3$], 1.56 (12H, bs, 4 x CH_3), 1.73 (10H, m, OCH_2CH_2 , THF), 2.07 (12H, bs, 4 x CH_3), 3.58 (10H, m, OCH_2CH_2 , THF), 6.69 (4H, s, 4 x Ph-H). ^{13}C NMR (100.62 MHz, 300 K, $\text{d}_8\text{-THF}$): δ 16.7 (4 x CH_3 , BIPHEN), 20.3 (4 x CH_3 , BIPHEN), 26.2 (THF), 30.3 [4 x $\text{C}(\text{CH}_3)_3$], 34.8 [4 x $\text{C}(\text{CH}_3)_3$], 68.0 (THF), 116.2, 125.9, 132.4, 133.1, 133.7, 165.1 (Ph, BIPHEN).

2.7.2 Synthesis of $[\text{BIPHEN}]_2\text{Na}_2\text{Mg}(\text{THF})_4$ (2)

$[\text{BIPHEN}]_2\text{Na}_2\text{Mg}(\text{THF})_4$ was prepared by the addition of a solution of (*rac*)-BIPHEN- H_2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared $^n\text{BuNa}$ (0.08 g, 1 mmol) in hexane (5 ml) at -10°C . The suspension was stirred for 30 minutes after which commercial Mg^nBu_2 (0.5 ml, 0.5 mmol, 1 M solution in heptane) was added to create a white suspension. The suspension was allowed to warm to ambient temperature and THF was added dropwise to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at -33°C to give $[\text{BIPHEN}]_2\text{Na}_2\text{Mg}(\text{THF})_4$ as colourless crystals (yield 0.197 g, 37%). $[\text{BIPHEN}]_2\text{Na}_2\text{Mg}(\text{THF})_4$ can also be prepared by using $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ as a replacement for Mg^nBu_2 . ^1H NMR (400.13 MHz, 300 K, $\text{d}_8\text{-THF}$): δ 1.15 [36H, bs, 4 x $\text{C}(\text{CH}_3)_3$], 1.45 (12H, s, 4 x CH_3), 1.77 (14H, m, OCH_2CH_2 , THF), 2.04 (12H, s, 4 x CH_3), 3.61 (10H, m, OCH_2CH_2 , THF), 6.72 (4H, s, 4 x Ph-H). ^{13}C NMR (100.62 MHz, 300 K, $\text{d}_8\text{-THF}$): δ 16.9 (4 x CH_3 , BIPHEN), 20.4 (4 x CH_3 , BIPHEN), 26.18 (THF), 31.1 [4 x $\text{C}(\text{CH}_3)_3$, BIPHEN], 34.6 [4 x $\text{C}(\text{CH}_3)_3$, BIPHEN], 68.0 (THF), 120.7, 125.8, 132.7, 132.9, 134.2, 161.3 (Ph, BIPHEN).

2.7.3 Synthesis of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ (3)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution in heptane) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time TMEDA (0.15 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at –33 °C. After storage at sub-ambient temperature the solution was filtered to yield [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ as a microcrystalline powder (yield 0.216 g, 56 %). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –0.79 (2H, m, MgCH₂), –0.31 (2H, m, MgCH₂), 1.25 (6H, t, CH₃), 1.69 [9H, bs, C(CH₃)₃], 1.79 (8H, bs, CH₂, TMEDA), 1.80 (6H, s, CH₃), 1.85 [33H, bs, CH₃ TMEDA and C(CH₃)₃], 2.22 (6H, s, CH₃), 7.18 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ 8.8 (2 x MgCH₂), 14.9 (2 x CH₃, butyl), 17.5 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 31.7 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 32.8–33.7 (CH₂, Butyl), 35.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 45.5 (TMEDA), 57.0 (TMEDA), 119.6, 127.3, 132.1, 132.7, 135.9, 162.7 [Ph, (*rac*)-BIPHEN].

2.7.4 Synthesis of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(TMEDA)₂ (4)

[(*rac*)-BIPHEN]Na₂MgR₂(TMEDA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which Mg(CH₂SiMe₃)₂ (0.10 g, 0.5 mmol) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time TMEDA (0.15 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at –33 °C to give a large crop of colourless crystals of [(*rac*)-BIPHEN]Na₂MgR₂(TMEDA)₂ (yield 0.174 g, 42 %). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –2.08 (2H, d, MgCH₂), –1.16 (2H, d, MgCH₂), 0.40 (18H, s, SiMe₃), 1.67 (8H, bs, CH₂, TMEDA), 1.74 [18H, s, C(CH₃)₃], 1.77 (24H, s, CH₃ TMEDA), 1.83 (6H, s, CH₃), 2.23 (6H, s, CH₃), 7.12 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ –6.7 (2 x MgCH₂), 5.1 (SiMe₃), 18.3 [2 x CH₃, (*rac*)-BIPHEN], 20.7 [2 x CH₃, (*rac*)-BIPHEN], 31.8 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 35.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 45.7 (TMEDA), 57.0 (TMEDA), 120.1, 127.2, 132.4, 132.6, 135.7, 162.5 [Ph, (*rac*)-BIPHEN].

2.7.5 Synthesis of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (5)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution in heptane) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time PMDETA (0.21 ml, 1 mmol) was added to give a white suspension. The suspension was concentrated *in vacuo* then heated gently to give a colourless solution. The solution was then allowed to cool slowly to ambient temperature to give colourless crystals of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (yield 0.245 g, 56 %). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –0.75 (4H, m, MgCH₂), 1.26 (6H, t, CH₃), 1.77 [18H, bs, C(CH₃)₃], 1.82 (16H, bs, CH₂, PMDETA), 1.86 (6H, s, CH₃, PMDETA), 1.90 (6H, s, CH₃), 1.93 (24H, bs, CH₃, PMDETA), 2.31 (6H, s, CH₃), 7.14 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ 8.8 (2 x MgCH₂), 14.9 (2 x CH₃, Butyl), 18.0 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 32.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 33.5 (2 x CH₂, Butyl), 34.0 (2 x CH₂, Butyl), 35.5 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 44.2 (PMDETA), 45.6 (PMDETA), 54.1 (PMDETA), 57.1 (PMDETA), 119.9, 126.6, 132.6, 134.1, 134.8, 163.1 [Ph, (*rac*)-BIPHEN].

2.7.6 Synthesis of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(PMDETA)₂ (6)

[(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(PMDETA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which Mg(CH₂SiMe₃)₂ (0.10 g, 0.5 mmol) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time PMDETA (0.21 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at –18 °C to give a large crop of colourless crystals of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂(PMDETA)₂ (yield 0.253 g, 58 %). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –2.03 (4H, bs, 2 x MgCH₂), 0.52 (18H, s, SiMe₃), 1.76 [18H, s, C(CH₃)₃], 1.81 (16H, bs, CH₂, PMDETA), 1.83 (6H, s, CH₃, PMDETA), 1.83 (6H, s, CH₃), 1.94 (24H, s, CH₃, PMDETA), 2.28 (6H, s, CH₃), 7.13 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ –9.0 (2 x MgCH₂), 6.2 (SiMe₃), 17.9 [2 x CH₃, (*rac*)-BIPHEN], 20.7 [2 x CH₃, (*rac*)-BIPHEN], 33.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 35.4 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 44.6 (CH₃, PMDETA) 45.8 (Me,

PMDETA), 54.1 (CH₂, PMDETA), 57.2 (PMDETA), 120.4, 126.8, 132.7, 134.2, 135.0, 163.0 [Ph, (*rac*)-BIPHEN].

2.7.7 Synthesis of [(*rac*)-BIPHEN]Na₂MgⁿBu₂((*R,R*)-TMCDA)₂ (7)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂((*R,R*)-TMCDA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution in heptane) was added slowly to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time (*R,R*)-TMCDA (0.19 ml, 1 mmol) was added to give a colourless solution. The solution was concentrated *in vacuo* and the solution stored at –33 °C to give a microcrystalline solid (0.197 g, 45 % crystalline yield). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –0.70 (2H, m, 2 x MgCH₂), –0.33 (2H, m, 2 x MgCH₂), 0.66 (8H, bm, 4 x CH₂), 1.26 (6H, t, 2 x CH₃, butyl), 1.41 (8H, bm, 4 x CH₂), 1.82-1.83 [23H, d, 2 x C(CH₃)₃ (*rac*)-BIPHEN and 4 x NCH TMCD], 1.90-1.91 [28H, bs, 4 x CH₃ TMCD and 2 x CH₃ (*rac*)-BIPHEN], 2.26 (3H, s, CH₃), 2.28 (3H, s, CH₃), 7.22-7.23 (2H, m, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): 9.0 (MgCH₂, butyl), 9.1 (MgCH₂, butyl), 14.8 (CH₃, butyl), 14.9 (CH₃, butyl), 17.8 [CH₃, (*rac*)-BIPHEN], 17.9 [CH₃, (*rac*)-BIPHEN], 20.8 [CH₃, (*rac*)-BIPHEN], 20.9 [CH₃, (*rac*)-BIPHEN], 21.2 (4 x CH₂, TMCD), 25.4 (4 x CH₂, TMCD), 32.0 [C(CH₃)₃, (*rac*)-BIPHEN], 32.1 [C(CH₃)₃, (*rac*)-BIPHEN], 32.8 (CH₂, butyl), 33.1 (CH₂, butyl), 33.6 (CH₂, butyl), 33.7 (CH₂, butyl), 35.4 [C(CH₃)₃, (*rac*)-BIPHEN], 35.4 [C(CH₃)₃, (*rac*)-BIPHEN], 40.0 (4 x NCH₃, TMCD), 63.8 (4 x NCH, TMCD), 119.8, 120.3, 127.4, 127.5, 132.4, 132.5, 133.1, 135.7, 135.9, 162.6, 162.7 [Ph, (*rac*)-BIPHEN].

2.7.8 Synthesis of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*R,R*)-TMCDA)₂ (8)

[(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*R,R*)-TMCDA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which Mg(CH₂SiMe₃)₂ (0.10 g, 0.5 mmol) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time (*R,R*)-TMCD (0.19 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at –18 °C to give colourless crystals of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂ ((*R,R*)-TMCD)₂ (0.193 g, 41% crystalline yield). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –2.07 (2H, d, 2 x MgCH₂), –1.08 (2H, d, 2 x MgCH₂), 0.45 (18H,

s, SiMe₃), 0.45 (5H, m, TMCD), 0.75 (5H, m, TMCD), 1.44 (10H, m, TMCD), 1.78 [18H, s, C(CH₃)₃], 1.86 (6H, s, CH₃), 1.91 (24H, bs, TMCD), 2.27 (6H, s, CH₃), 7.16 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ –6.0 (2 x MgCH₂), 5.0 (CH₃, SiMe₃), 18.6 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 21.9 (TMCD), 25.5 (TMCD), 32.0 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 35.4 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 63.8 (TMCD), 120.09, 127.6, 132.7, 133.0, 135.6, 162.5 [Ph, (*rac*)-BIPHEN].

2.7.9 Synthesis of [(*rac*)-BIPHEN]Na₂MgⁿBu₂((*S,S*)-TMCD)₂ (9)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂((*S,S*)-TMCD)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution in heptane) was added slowly to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time (*S,S*)-TMCD (0.19 ml, 1 mmol) was added to give a colourless solution. The solution was concentrated *in vacuo* and the solution stored at –33 °C to a white microcrystalline powder (0.216 g, 49 % yield). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ –0.67 (2H, m, 2 x MgCH₂), –0.27 (2H, m, 2 x MgCH₂), 0.67 [8H, bm, 4 x CH₂ (*S,S*)-TMCD], 1.26 (6H, t, 2 x CH₃, butyl), 1.42 [8H, bs, 4 x CH₂ (*S,S*)-TMCD], 1.82-1.83 [22H, d, 2 x C(CH₃)₃ (*rac*)-BIPHEN and 4 x NCH TMCD], 1.90-1.91 [30H, bs, 4 x CH₃ TMCD and 2 x CH₃ (*rac*)-BIPHEN], 2.26 (3H, s, CH₃), 2.28 (3H, s, CH₃), 7.22-7.23 (2H, m, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): 9.0 (MgCH₂, butyl), 9.1 (MgCH₂, butyl), 14.5 (CH₃, butyl), 15.0 (CH₃, butyl), 17.8 [CH₃, (*rac*)-BIPHEN], 17.9 [CH₃, (*rac*)-BIPHEN], 20.8 [CH₃, (*rac*)-BIPHEN], 20.9 [CH₃, (*rac*)-BIPHEN], 21.4 [4 x CH₂, (*S,S*)-TMCD], 25.4 [4 x CH₂, (*S,S*)-TMCD], 32.0 [C(CH₃)₃, (*rac*)-BIPHEN], 32.1 [C(CH₃)₃, (*rac*)-BIPHEN], 32.8 (CH₂, butyl), 33.1 (CH₂, butyl), 33.7 (CH₂, butyl), 33.8 (CH₂, butyl), 35.4 [C(CH₃)₃, (*rac*)-BIPHEN], 35.5 [C(CH₃)₃, (*rac*)-BIPHEN], 39.3 [4 x NCH₃, (*S,S*)-TMCD], 63.8 [4 x NCH, (*S,S*)-TMCD], 119.8, 120.3, 127.4, 127.5, 132.4, 132.6, 133.1, 133.1, 135.7, 135.8, 162.6, 162.7 [Ph, (*rac*)-BIPHEN].

2.7.10 Synthesis of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*S,S*)-TMCD)₂ (10)

[(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*S,S*)-TMCD)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which Mg(CH₂SiMe₃)₂ (0.10 g, 0.5 mmol) was added to

create a white suspension. The suspension was stirred at $-10\text{ }^{\circ}\text{C}$ for 5 minutes after which time (*S,S*)-TMCDa (0.19 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at $-18\text{ }^{\circ}\text{C}$ to give colourless crystals of [(*rac*)-BIPHEN]Na₂Mg(CH₂SiMe₃)₂((*S,S*)-TMCDa)₂ (0.197 g, 42% crystalline yield). ¹H NMR (400.13 MHz, 300 K, C₆D₆): δ -2.12 (2H, d, 2 x MgCH₂), -1.12 (2H, d, 2 x MgCH₂), 0.41 (18H, s, SiMe₃), 0.74 [9H, m, (*S,S*)-TMCDa], 1.47 [11H, m, (*S,S*)-TMCDa], 1.73 [18H, s, C(CH₃)₃], 1.81 (6H, s, CH₃), 1.96 [24H, bs, (*S,S*)-TMCDa], 2.22 (6H, s, CH₃), 7.11 (2H, s, Ph-H). ¹³C NMR (100.62 MHz, 300 K, C₆D₆): δ -6.1 (2 x MgCH₂), 5.0 (SiMe₃), 18.6 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 22.8 [CH₂, (*S,S*)-TMCDa], 25.7 [CH₂, (*S,S*)-TMCDa], 32.0 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 35.4 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 40.3 [CH₃, (*S,S*)-TMCDa], 63.9 [NCH, (*S,S*)-TMCDa], 120.1, 127.6, 132.8, 133.0, 135.6, 162.5 [Ph, (*rac*)-BIPHEN].

Chapter 3: Reactivity of Magnesiate Complexes

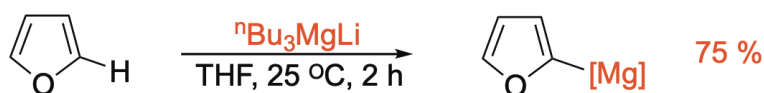
Traditionally, reactions such as deprotonation or metal-halogen exchange have been carried out utilising highly polar organometallic reagents such as organolithium or organomagnesium reagents. While these reagents are generally highly reactive and efficient, they produce intermediates with highly polarised metal-carbon bonds, particularly for those intermediates generated from alkylolithiums. These intermediates are often susceptible to decomposition. Furthermore, the high reactivity of these complexes which makes them ideal candidates for use in metalation and metal-halogen exchange can often be regarded as their downfall as it can limit their functional group tolerance. Although organomagnesium reagents are orders of magnitude less reactive than their organolithium counterparts and subsequently show a much greater functional group tolerance, both reagents typically require the use of sub ambient temperatures and are incompatible with a variety of functional groups.

An alternative to these monometallic bases are bimetallic complexes such as alkali metal magnesiates. As outlined in the previous chapter, alkali metal magnesiates are formed through a combination of an alkali metal organometallic compound with a magnesium one. These new bimetallic complexes often display unique reactivities, carrying out transformations that would not be achievable using their monometallic precursors.¹⁰⁷ Moreover, these bimetallic complexes can be used under much more user friendly conditions such as temperatures closer to ambient temperature and offer an improved functional group tolerance.¹⁰⁸ These bimetallic species also tend to show an enhanced solubility, something that was first demonstrated by Coates when combining $^n\text{BuLi}$ with Me_2Mg .¹⁰⁹ Upon coining the term 'ate', Wittig also provided a rationale for the increased reactivity observed for these complexes, attributing it to anionic activation of the ligands surrounding the central metal atom.¹¹⁰ Not only does this rationale explain the increase in reactivity, it also accounts for the role reversal of the metal centres of these complexes in their reactivity. Interestingly, despite alkali metal organometallic complexes being considerably more reactive than their group 2 counterparts, reactions typically occur involving the less reactive (less electropositive) group 2 metal centre. In the case of alkali metal magnesiates, metalation or metal-halogen exchange reactions are referred to as Alkali Metal Mediated Magnesiations (AMMMg).¹¹¹

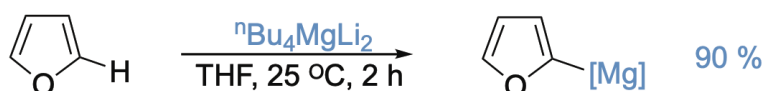
3.1 Metalation Chemistry

Owing to the commercial availability of the starting materials, *tris*(alkyl) and *tetra*(alkyl) lithium magnesiate are one class of bimetallic complex that have been intensely studied for the purpose of deprotonation chemistry. Early examples of the unique reactivity of these complexes was highlighted by the work of Mongin. Utilising the *tris*(alkyl) and *tetra*(alkyl) lithium magnesiate LiMgBu_3 and Li_2MgBu_4 the group of Mongin were able to carry out regioselective deprotonations on a range of substrates including furans (Scheme 11),¹¹² thiophenes,¹¹³ benzoxazoles,¹¹⁴ halogenated aromatics^{115,116} and pyridines.¹¹⁷ While metallation of these substrates is achievable using monometallic bases such as alkyllithiums, the reactions typically require cryogenic temperatures to circumvent undesired side reactions whereas by using bimetallic magnesiate bases these reactions can be carried out at or closer to ambient temperatures. Furthermore the aryl intermediates produced in these reactions have been shown to have a greater stability compared to their lithium analogues allowing for onward reactivity in a range of transformations.¹¹⁸ These early studies combined with more recent works, allow us to establish a difference in the reactivity of lower and higher order magnesiate. As demonstrated by the work of Mongin for the deprotonation of furans, a higher yield of metallated product was achieved using the higher order *tetra*(alkyl) magnesiate Li_2MgBu_4 .¹¹² Hevia et al. have also documented a similar trend in reactivity when studying the metallation of anisole with *tris*- and *tetra*(alkyl) potassium magnesiate KMgR_3 and $\text{K}_2\text{MgR}_4(\text{PMDETA})_2$ (where $\text{R} = \text{CH}_2\text{SiMe}_3$).¹¹⁹ While the higher order PMDETA solvate gave an almost quantitatively yield of metallated product, the lower order magnesiate gave a comparatively low yield of only 10 %. This trend has since been considered general and it is widely accepted that higher order magnesiate are more reactive than their lower order analogues.

Lower Order



Higher Order



Scheme 11: Metallation of furan using the lower order (top) and higher order (bottom) n butyl-containing lithium magnesiates.

Another widely used class of alkali metal magnesiates used in metallation chemistry are mixed alkyl/amido magnesiates. The reactivity of this type of magnesiate is typified by $[(\text{TMEDA})\text{Na}(\mu\text{-}n\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$ (where TMP = 2,2,6,6-tetramethylpiperidide) which was shown by Mulvey and co-workers to react smoothly with benzene to produce the resultant aryl/amido magnesiate $[(\text{TMEDA})\text{Na}(\mu\text{-Ph})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$.⁷¹ Once again the deprotonation is carried out by the less electropositive magnesium centre through loss of the bridging n butyl ligand that is replaced with the newly generated phenyl anion, trapping the newly formed anion within the structure. Proof of this reactivity is clearly shown in the crystal structure of the complex which shows the magnesium centre interacting with the carbon atom at which deprotonation has occurred, with the phenyl anion orientated in such a way as to form a π -interaction with the sodium atom (Figure 39). As neither of the monometallic parent components $n\text{BuNa}$ or $\text{Mg}(\text{TMP})_2$ are capable of carrying out the deprotonation of benzene, this reaction clearly demonstrates the synergistic effect of the two metal centres on the reactivity of the complex. In a follow up study, Mulvey and co-workers have demonstrated that $[(\text{TMEDA})\text{Na}(\mu\text{-}n\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$ will also deprotonate toluene to give $[(\text{TMEDA})\text{Na}(\mu\text{-C}_6\text{H}_4\text{CH}_3)(\mu\text{-TMP})\text{Mg}(\text{TMP})]$.¹²⁰ Remarkably, this magnesiation occurs regioselectively at the *meta* position of the aromatic ring, leaving the most acidic hydrogen atoms of the methyl groups untouched. Once again monometallic magnesium bases are not capable of deprotonating toluene. While other monometallic bases such as alkylolithiums or alkylsodiums are capable of carrying out this transformation, deprotonation will occur exclusively with loss of a hydrogen from the methyl group to generate the benzyl (PhCH_2^-) anion. This is the thermodynamically favoured product as not only do the hydrogen atoms of the methyl group have a lower pK_a than the ring hydrogen

atoms, but the negative charge can also be delocalised throughout the π -system. Since this reactivity is not always observed when using bimetallic bases, it shows that alkali metal mediated magnesiation (AMMMg) can be used not only as a method for increasing the reactivity of monometallic magnesium bases but also a way of achieving unique regioselectivity. Furthermore, it has been shown that replacement of the n -butyl ligand with the more reactive t -butyl variant leads to the formation of $[(\text{TMEDA})\text{Na}(\mu\text{-}^t\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$ which is capable of carrying out the double deprotonation of benzene.¹²¹ Addition of half a molar equivalent of benzene to a solution of $[(\text{TMEDA})\text{Na}(\mu\text{-}^t\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$ leads to the formation of $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})\text{Mg}(\text{TMP})]_2\text{C}_6\text{H}_4$ in which benzene has been regioselectively deprotonated at the one and four positions. The solid-state structure of the product once again shows that the reaction is an example of AMMMg whereby the magnesium centre interacts directly with the carbon atom at which deprotonation has occurred.

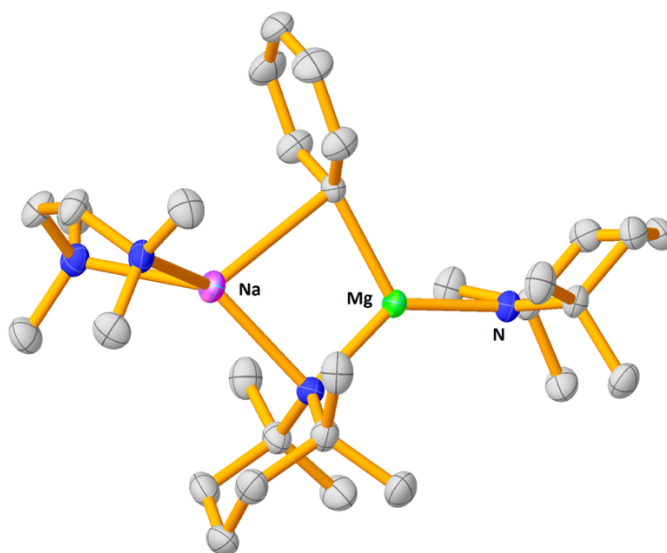


Figure 39: Solid-state structure of $[(\text{TMEDA})\text{Na}(\mu\text{-Ph})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$.

The double deprotonation of an aromatic substrate using a sodium magnesiate was first reported in 1999 by Mulvey and co-workers.¹²² It was discovered that upon addition of benzene or toluene to a mixture of n -BuNa, di- n -butylmagnesium and TMP(H) in a 1:1:3 molar ratio the complexes $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_4)]$ and $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_4\text{CH}_3)]$ were obtained. These complexes are best described as inverse crowns in which the newly formed dianionic molecule is located within the centre of a 12 membered dicationic ring. Furthermore, this metallation was shown to be regioselective with deprotonation occurring at the one and four positions of benzene which is consistent with the regioselectivity reported for

$[(\text{TMEDA})\text{Na}(\mu\text{-}^t\text{Bu})(\mu\text{-TMP})\text{Mg}(\text{TMP})]$.¹²¹ In the case of toluene, the reaction was also regioselective with metalation occurring at the two and five positions of the aromatic ring to give the *ortho-meta'* metallated product. This type of reaction has been termed templated deprotonation and has been extensively studied since its inception. More recently, O'Hara and co-workers have shown that this technique can be used to carry out the regioselective deprotonation of a wide range of aromatic substrates using the sodium magnesiate ' $\text{Na}_4\text{Mg}_2(\text{TMP})_6\text{}^n\text{Bu}_2$ '.¹²³ Using aromatic substrates such as anisole it was established that deprotonation will occur at *ortho* and *meta'* positions of the aromatic ring while for substituted anilines such as *N,N*-dimethylaniline deprotonation will occur at the *meta* and *meta'* positions (Figure 40). These reactions can be viewed as an extension of the concept of directed *ortho* metallation (DoM) and have therefore been termed directed *ortho-meta'* metallation (DomM) and directed *meta-meta'* metalation (DmmM). The difference in selectivity is thought to be caused by the hindered rotation of the N-C(*ipso*) bond which provides steric protection to the *ortho* position of the aromatic ring in the case of the aniline derivatives. This regioselectivity can also be influenced by the alkyl ligand of the parent magnesiate whereby replacing the *n*butyl ligands for the bulkier CH_2SiMe_3 leads to DmmM being achieved for toluene and not DomM.¹²⁴ This gives further evidence that the largest driving force for this templated metallation is in fact the preorganisation of the magnesiate into a macrocyclic structure which places the alkyl ligands in the ideal position to carry out the deprotonation.

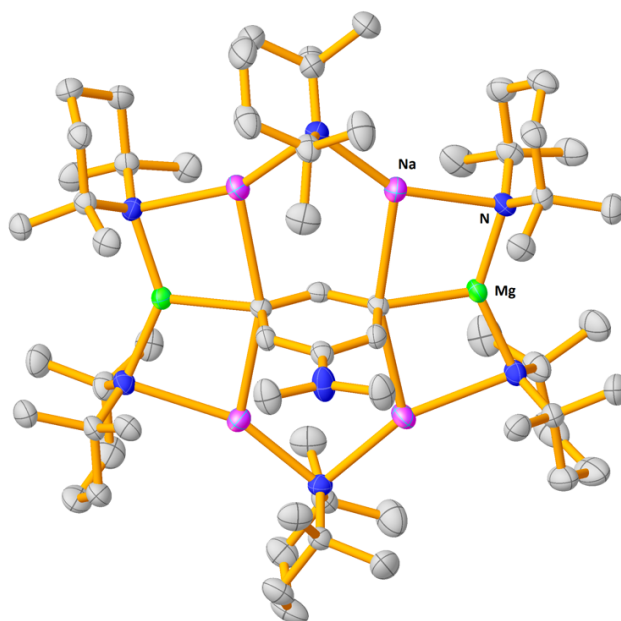
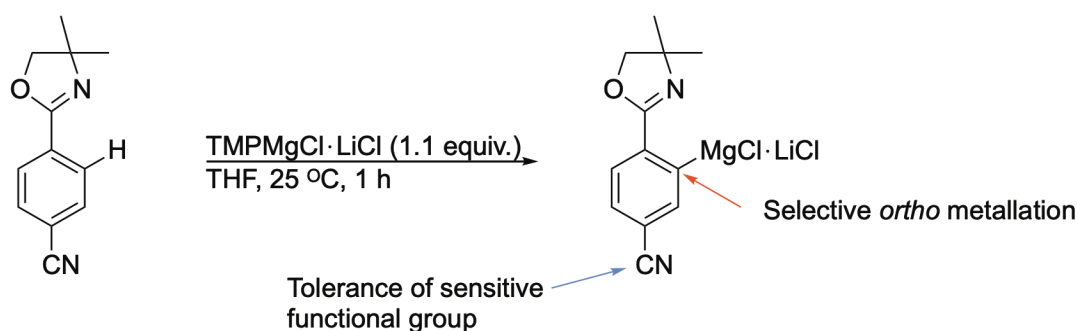


Figure 40: Solid-state structure of $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_3\text{NMe}_2\text{-}3,5)]$ depicting DmmM of *N,N*-dimethylaniline.

Although the structure of the ⁿbutyl-containing magnesiate has yet to be crystallographically characterised its existence in solution has been confirmed by NMR spectroscopic studies which clearly show the existence of a species containing two ⁿbutyl ligands and correlates with deprotonation of the substrate via loss of the ⁿbutyl ligands.¹²⁵ This situation is further supported by the isolation of the solid-state structure of the macrocyclic potassium magnesiates [KMg(TMP)₂ⁿBu]₄ and [KMg(TMP)₂ⁿBu]₆ in which the ⁿbutyl ligands are clearly visible.¹²⁵ Moreover, KMg(TMP)₂ⁿBu₆ has been reported to be capable of carry out a six-fold monodeprotonation of benzene with subsequent trapping of all six phenyl anions within its macrocyclic core.¹²⁶ Applications of Na₄Mg₂(TMP)₆ⁿBu₂ have been further extended to include polyaromatic systems.¹²⁷ In this recent publication O'Hara and co-workers have shown that through variation of the molar equivalents of magnesiate relevant to the substrate it is possible to achieve di and tetradeprotonations. For the substrates *para*-terphenyl and 1,3,5-triphenylbenzene, treatment with one equivalent Na₄Mg₂(TMP)₆ⁿBu₂ gave doubly deprotonated products while addition of a second equivalent of base led to formation of the tetradeprotonated species [Na₄Mg₂(TMP)₆]₂(3,3'',5,5''-*para*-terphenyl-tetra-ide) and [Na₄Mg₂(TMP)₆]₂(3,3'',5,5''-(1',3',5'-triphenylbenzene)-tetra-ide). Examination of the solid-state structures of these complexes revealed a surprising conformational flexibility of the 12 membered Na₄Mg₂(TMP)₆ rings which adopts a concave geometry encapsulating the *para*-terphenyl molecule and a convex geometry in the case of triphenylbenzene. 'Na₄Mg₂(TMP)₆ⁿBu₂' has also recently been utilised as part of a two-step demetallation and metal-halogen exchange strategy to give access to polyfunctionalised arenes.¹²⁸ Moreover, when this procedure is carried out in combination with the Grignard reagent ⁱPrMgCl, it can provide facile access to *meta*-functionalised arenes through selective metal-halogen exchange.

First prepared by Knochel in 2006, the turbo Hauser base TMPMgCl·LiCl has been shown to be a potent bimetallic base for metallation chemistry.⁵³ Prepared via the deprotonation of TMP(H) by the turbo Grignard reagent ⁱPrMgCl·LiCl, this bimetallic base has a high kinetic basicity combined with an increased functional group tolerance and solubility. Initial examination of this new base's reactivity with isoquinoline gave a >90 % yield of magnesiated product after two hours at ambient temperature. Furthermore, TMPMgCl·LiCl is capable of carrying out deprotonations with an alternative regioselectivity compared to monometallic bases. An example of this enhanced reactivity, functional group tolerance and difference in regioselectivity is demonstrated by the work of Clososki and co-workers who have shown

that $\text{TMPMgCl}\cdot\text{LiCl}$ will regioselectively deprotonate cyanophenyl-2-oxazolines at the *ortho* position while the monometallic amide LiTMP gives a mixture of mono and disubstituted products with *meta* selectivity (Scheme 12).¹²⁹ Furthermore, alkyllithium bases were found to be incompatible with the cyano functionality. The groups of Knochel and others have since developed and extended the applications of these monoamido bases for the metallation of a number of substrates containing sensitive functional groups as well as sought after structural scaffolds such as pyridines and pyrimidines.^{130–139} The increased basicity of $\text{TMPMgCl}\cdot\text{LiCl}$ has been attributed to the deaggregation of the highly aggregated structures which are known to form in solution for magnesium amides. This theory is supported by the solid-state structure of $\text{TMPMgCl}\cdot\text{LiCl}$ which was discussed in chapter 1 (Figure 9).



Scheme 10: Selective metallation of Functionalization of 4-cyanophenyl-2-oxazoline using $\text{TMPMgCl}\cdot\text{LiCl}$.

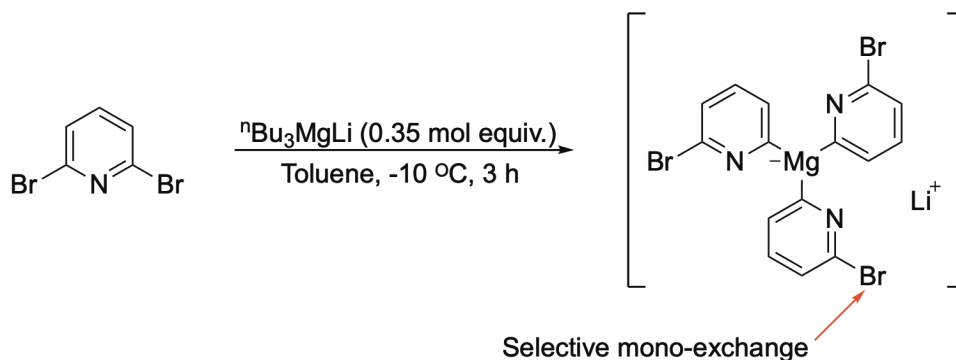
Despite $\text{TMPMgCl}\cdot\text{LiCl}$ clearly being a potent base, it failed to deprotonate the moderately activated aromatic substrate *tert*-butylbenzoate leading to the development of a second class of turbo Hauser bases of the general form $(\text{R}_2\text{N})_2\text{Mg}\cdot 2\text{LiCl}$.¹⁴⁰ These *bis*(amido) complexes can be prepared either via transmetalation of R_2NLi with MgCl_2 or in the case of the $(\text{TMP})_2\text{Mg}\cdot 2\text{LiCl}$ by addition of one equivalent of LiTMP to a solution of $\text{TMPMgCl}\cdot\text{LiCl}$. This latter method allows for preparation of the *bis*(amido) complexes *in situ* which is advantageous due to their relatively low solution stability in comparison to the *mono*(amido) bases which can be stored as solutions with no loss of reactivity over prolonged periods of time. The *bis*(amido) complexes were found to have a much higher kinetic basicity compared to *mono*(amido) counterparts, with $(\text{TMP})_2\text{Mg}\cdot 2\text{LiCl}$ generally being the most reactive, and gave high yields of the aforementioned *tert*-butylbenzoate which the *mono*(amido) bases could not deprotonate within one hour at 0 °C.¹⁴⁰ Despite this increase in reactivity these reagents retain a high degree of functional group tolerance and can be utilised for the

metallation of substrates in the presence of sensitive functional groups such as esters, nitriles and ketones.^{141,142} Furthermore, the *bis*(amido) complexes retain a good degree of regioselectivity which has been exploited in their development as synthetically useful bases.¹⁴³ The reactivity of both *mono*- and *bis*(amido) bimetallic amides produced via inclusion of LiCl with traditional magnesium amides highlights the synergistic nature of their reactivity.

3.2 Metal-Halogen Exchange

Bimetallic complexes have been heavily utilised in metal-halogen exchange due to their unique reactivities.¹⁴⁴ First reported in 2000 by Oshima, the *tris*(alkyl) lithium magnesiates ${}^n\text{Bu}_3\text{LiMg}$ and $i\text{Pr}^n\text{Bu}_2\text{LiMg}$ were utilised for the metal-halogen exchange of a range of aryl and alkynyl bromides and iodides in the presence of sensitive functional groups such as esters and nitriles.¹⁴⁵ The study showed that both ${}^n\text{Bu}_3\text{MgLi}$ and $i\text{Pr}^n\text{Bu}_2\text{MgLi}$ allowed metal-halogen exchange to be carried out under mild conditions. $i\text{Pr}^n\text{Bu}_2\text{MgLi}$ was found to be the more reactive of the two bases allowing for the magnesiation of aryl iodides at temperatures as low as $-78\text{ }^\circ\text{C}$ whereas ${}^n\text{Bu}_3\text{MgLi}$ was not able to carry out this transformation when cryogenic temperatures were employed. A follow up study by the same group developed the reactivity of these magnesiates further, fine tuning their reactivities and expanding the scope their chemistry to include heteroaryl and cyclopropyl iodides and bromides.¹⁴⁶ $i\text{Pr}^n\text{Bu}_2\text{MgLi}$ was once again found to be a more reactive base than its *tris*(n butyl) counterpart and could smoothly magnesiate a range of brominated and iodinated substrates at $-78\text{ }^\circ\text{C}$. Furthermore, this follow up study highlighted the good levels of selectivity that can be achieved using *tris*(alkyl) magnesiates. Whereas dimagnesiation of 1,3- and 1,4-diiodobenzene was observed using ${}^n\text{Bu}_3\text{MgLi}$, these substrates could be selectively monomagnesiated using the $\text{Me}_2{}^n\text{BuMgLi}$.¹⁴⁶ $\text{Me}_2{}^n\text{BuMgLi}$ was also used in metal-halogen exchange with iodo- and bromopyridine giving the corresponding pyridylmagnesiates in good yields while the analogous reaction with ${}^n\text{Bu}_3\text{MgLi}$ gave low yields of the desired pyridyl magnesiates and various side products. This selectivity and functional group tolerance are brought about by inclusion of less reactive methyl groups which decrease the rate at which the second exchange occurs, allowing for isolation of the mono exchange product. Further to this, Ida and Mase have shown that by controlling the stoichiometry of the reaction along with careful solvent choice ${}^n\text{Bu}_3\text{MgLi}$ can be used to selectively monomagnesiate dibromo and di-iodopyridines.¹⁴⁷ They also found that using a sub-stoichiometric amount of magnesiate (0.35 mol equiv.) a 3-fold monomagnesiation of 2,6-dibromopyridine could be

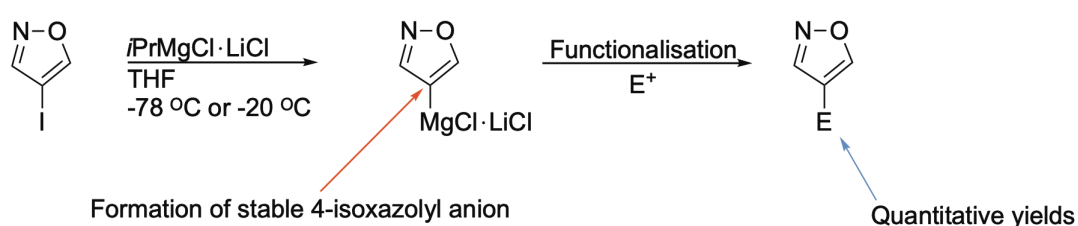
achieved (Scheme 12). Carrying out the reaction in toluene gave yields of 90 % for the monomagnesiated product and showed a tolerance of excess base whereas when the reaction was repeated using THF as the bulk solvent, it led to the isolation of a significant amount of the dimagnesiated product (45 % of difunctionalised product after work up).



Scheme 12: Selective mono magnesium-bromine exchange of 2,6-dibromopyridine using $n\text{Bu}_3\text{MgLi}$.

The final class of ‘turbo’ reagent to be discussed are the turbo Grignards. Unlike the turbo Hauser bases which are almost exclusively used in deprotonation chemistry, turbo Grignard’s are predominantly used in metal-halogen exchange. Once again, these ‘turbo’ reagents show an increased reactivity and functional group tolerance when compared to the monometallic Grignard reagents when utilised for metal-halogen exchange. First introduced in 2004 by Knochel, these bimetallic bases can be synthesised by the addition of one equivalent of lithium chloride to a conventional Grignard reagent.⁵² Using the magnesium-bromine exchange reaction with 4-bromanisole as a test reaction, Knochel and co-workers demonstrated that the conventional Grignard reagent $i\text{PrMgCl}$ gave an 18 % conversion to the metallated product after 68 hours whereas the turbo Grignard $i\text{PrMgCl}\cdot\text{LiCl}$ gave an 84 % yield of the metallated product within one hour. The functional group tolerance of the new reagent was subsequently investigated and it was found to allow the exchange to be carried out in the presence of sensitive functionalities including esters, nitriles, halogens, aldehydes and ketones and even highly sensitive azines.^{148–150} Moreover, turbo Grignards maintain good level of selectivity and are capable of carrying out selective metal-halogen exchange of polyhalogenated substrates¹⁵¹ as well as allowing for reactions to be carried out using non-cryogenic temperatures.^{152,153} These reagents can also be used for the preparation of alkyl and alkenylmagnesium species.¹⁵⁴ More recently, Fuse and Nakamura have utilised the turbo Grignard $i\text{PrMgCl}\cdot\text{LiCl}$ in metal-halogen exchange with 4-iodoisoxazole.¹⁵⁵ Direct

functionalisation of these sensitive molecules by polar organometallic reagents are normally precluded due to undesirable ring-opening chemistry; however, utilising $i\text{PrMgCl}\cdot\text{LiCl}$ 4-iodoisoxazole was smoothly metalated to give the 4-isoxazolyl anion without ring-opening taking place (Scheme 13). This metalated intermediate could then be directly functionalised by addition of a suitable electrophile. Moreover, turbo Grignard reagents have found application in the synthesis of natural products.^{156,157} Analogous to the turbo Hauser bases, the increased reactivity of turbo Grignard reagents is thought to be caused by coordination of LiCl to the magnesium centre which leads to deaggregation of the highly aggregated Grignard species in solution.



Scheme 13: Direct functionalisation of 4-isoxazoles using $i\text{PrMg}\cdot\text{LiCl}$.

In an effort to further increase the reactivity of the turbo Grignard complexes, Knochel and co-workers next developed the dialkylmagnesium reagents $i\text{Pr}_2\text{Mg}\cdot 2\text{LiCl}$ and $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiCl}$.⁸⁶ $i\text{Pr}_2\text{Mg}\cdot 2\text{LiCl}$ can be prepared using the dioxane polymerisation method outlined in Chapter 1 by taking two equivalents of $i\text{PrMgCl}$ and treating it with a 10 vol % solution of dioxane while $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiCl}$ can be prepared by simple salt metathesis of $^s\text{BuLi}$ with $^s\text{BuMgCl}$. The increase in reactivity of these new dialkylmagnesium reagents compared to the conventional turbo Grignard is highlighted by the reaction of the electron rich 4-bromoanisole. Beginning with $i\text{PrMgCl}\cdot\text{LiCl}$, conversion to the metallated product of only 31 % was achieved whereas with the more reactive dialkylmagnesium $i\text{Pr}_2\text{Mg}\cdot 2\text{LiCl}$, quantitative conversion was achieved in under 10 hours at 25 °C. Similarly, double metal-halogen exchange can be achieved using $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiCl}$ and the extremely electron rich 1-bromo-3,4,5-trimethoxybenzene which, after electrophilic quenching, gave the final functionalised product in a 90 % yield. Despite their increased reactivity compared to their monoalkyl counterparts, the dialkylmagnesium complexes $i\text{Pr}_2\text{Mg}\cdot 2\text{LiCl}$ and $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiCl}$ have not been utilised to the same extent.

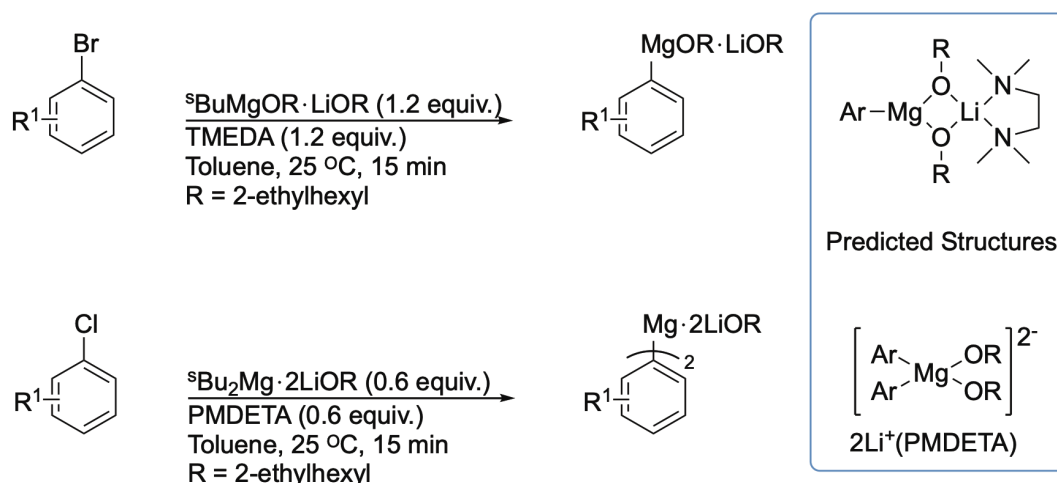
The work of Oshima has shown it is often necessary to modify *tris*(alkyl) magnesiates such as $^n\text{Bu}_3\text{MgLi}$ in order to control their reactivity and selectivity.¹⁴⁶ One way of altering the

reactivity of these magnesiates is to include less reactive methyl ligands, however, these modified magnesiate still contain excess reactive alkyl ligands which have the potential to participate in undesired side reactions. An alternative class of ligand which allow for the preparation of alkali metal magnesiate complexes are alkoxides and phenoxides. Early examples of this include studies by Richey who has shown that the addition of alkoxide salts can increase the reactivity of organomagnesium complexes by the formation of ate complexes.^{158–160} Alkoxide complexes generated *in situ* have also been shown to affect the reaction outcome by directing effects.^{161,162}

Recently, the group of Knochel has developed a new class of mixed alkyl/alkoxide lithium magnesiate using 2-ethylhexanol as the alkoxide ligand.¹⁶³ With the general formulas $^s\text{BuMgOR}\cdot\text{LiOR}$ and $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiOR}$, both lower and higher order magnesiates can be prepared in toluene via reaction of di-*n*-butylmagnesium with 2-ethylhexanol followed by co-complexation with one and two equivalent(s) of $^s\text{BuLi}$ respectively. These new alkoxide containing magnesiates possess an exceptionally high reactivity with the lower order species $^s\text{BuMgOR}\cdot\text{LiOR}$ capable of carrying out the magnesiation of the electron rich, and normally unreactive, 4-bromoanisole in less than 15 minutes at 25 °C giving a final yield of 85 % of functionalised product (Scheme 14). The yield of functionalised product could be further increased to 99 % when stoichiometric TMEDA was added to the reaction mixture. Interestingly, when the reaction solvent was changed from toluene to the more polar THF, the yield decreased to only 14 %, indicating a strong preference for non-polar solvents. As an indication of the reactivity of these new alkoxide containing magnesiates, the turbo Grignard reagents $i\text{PrMgCl}\cdot\text{LiCl}$ and $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}_2$ gave yields of only 1 and 13 % under the same reaction conditions. Even more remarkably, the higher order species $^s\text{Bu}_2\text{Mg}\cdot 2\text{LiOR}$ was shown to be sufficiently reactive to affect double magnesium-chlorine exchange under mild conditions in non-polar solvents. Addition of stoichiometric amounts of PMDETA to the reaction mixture allowed for the magnesiation of 2-chloro-1,4-dimethoxybenzene, giving a 73 % yield of functionalised product in under one hour at ambient temperature. Despite the high levels of reactivity displayed by these mixed alkyl alkoxide complexes, they also retain high levels of regioselectivity.¹⁶⁴

Although the reactivity of these heteroleptic lithium magnesiates has been well studied, comparatively little is known about their structural compositions. NMR spectroscopic studies have been utilised to confirm their composition in solution. The group of Hevia have recently

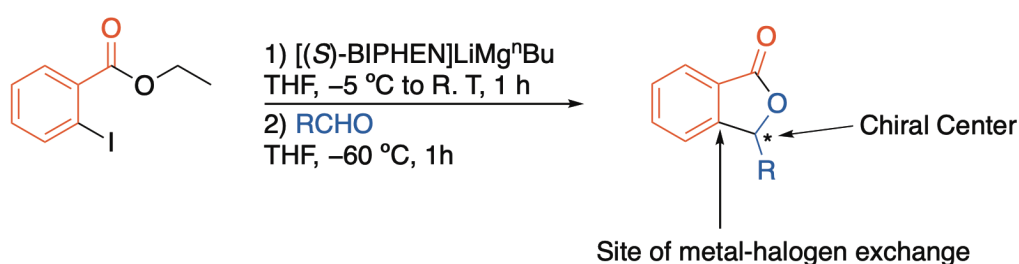
discovered that in solution complexes such as $\text{LiMg}^s\text{Bu}_2(\text{OR})$ (where $\text{OR} = 2\text{-ethylhexyl}$) exist in equilibrium with the alkyl rich (alkoxide free) $\text{Li}_2\text{Mg}^s\text{Bu}_4$ and the alkoxide rich (alkyl free) $\text{Mg}(\text{OR})_2$.¹⁰⁶ $\text{Li}_2\text{Mg}^s\text{Bu}_4$ was found to be highly reactive in metal-halogen exchange which subsequently led Hevia and co-workers to conclude that although the alkoxide ligand is vital for the formation of the active species it is not part of the active species which carries out the metal-halogen exchange.



Scheme 14: Metal-halogen exchange using magnesium alkoxides and predicted solution state structures for the reaction intermediates.

A further benefit of alkoxide and phenoxide ligands is their ability to provide an entry point into asymmetric synthesis. One of the first to recognise the potential of chiral phenoxide ligands in magnesiate chemistry was Noyori who utilised (*S*)-BINOL phenoxide ligand to synthesise lithium magnesiates which were employed in the alkylation of aldehydes and ketones.¹⁶⁵ The groups of Gros and Mongin have exploited these chiral phenoxide ligands in metal-halogen exchange chemistry to functionalise heteroaromatic scaffolds such as pyridines and pyrazines.^{103,104,166} Using the TADDOL, BINOL and BIPHEN ligands, Gros and Mongin were able to create chiral lithium magnesiates that functioned as efficient exchange reagents, capable of carrying out metal-halogen exchange with 2-bromopyridine at ambient temperature using a sub-stoichiometric amounts of magnesiate. By trapping the metallated intermediate produced in each case with aldehydes they were able to synthesise a range of pyridyl-carbinols in good yields. Ultimately, the enantiomeric excess (*ee*) was found to be highly dependent on the reaction temperature and required the use of cryogenic temperatures as low as $-100\text{ }^\circ\text{C}$ to ensure good *ee* values. While the use of cryogenic temperatures ensured good enantiomeric excesses were obtained, it led to a decrease in the

overall yield of the product. Higher order magnesiate were once again found to be more reactive than their lower order counterparts, giving consistently higher yields under comparable conditions. Interestingly, the reactivity of these magnesiate was found to vary markedly when pyrazines were employed as the substrate.¹⁶⁶ While efficient metal-halogen exchange could be achieved using a sub-stoichiometric amount of magnesiate when iodopyridines were utilised as substrates, reaction with iodopyrazine required the use of an equimolar amount of magnesiate in order to give sufficient levels of conversion. Although the overall yield of final functionalised product was lower when pyrazine was employed compared to pyridine, high level of enantioselectivity were achieved.



Scheme 15: Synthesis of chiral 3-substituted isobenzofuranones using the chiral magnesiate [(S)-BIPHEN]LiMgⁿBu.

More recently, the group of Gros has used the lower order magnesiate [(S)-BIPHEN]LiMgⁿBu to perform metal-halogen of ethyl-2-iodobenzoate leading to the formation of various tri-substituted chiral isobenzofuranones with good yields and enantioselectivities (Scheme 15).¹⁰⁵ In an attempt to increase the yield, the reaction was repeated using the higher order magnesiate [(S)-BIPHEN]Li₂MgⁿBu₂, however, no increase in yield was observed. Furthermore, the use of bulky aryl or naphthyl substituents on the TADDOL ligand resulted in incomplete metal-halogen exchange.¹⁰⁵ The intolerance for bulky substituents of the TADDOL ligand and the lack of reactivity of the higher order magnesiate complex, suggest that this particular reaction is highly dependent on the steric properties of the phenoxide ligand. During the investigation of the solid-state structures of lithium magnesiate containing the (*rac*)-BIPHEN ligand, our group has previously demonstrated the reactivity of [(*rac*)-BIPHEN]Li₂MgⁿBu₂(THF)₃ with 2-bromopyridine.⁹⁴ The exchange proceeded smoothly at -60 °C giving the double metal-halogen exchange product [(*rac*)-BIPHEN]Li₂Mg(2-pyridyl)₂(THF)₂ (Figure 41). Furthermore, the solid-state structure of this metallated intermediate highlights the potential influence the alkali metal may have on the outcome of the reaction. Interactions formed between the pyridine nitrogen atoms and the

lithium cations may play a significant role in stabilising the metalated intermediate during metal-halogen exchange.

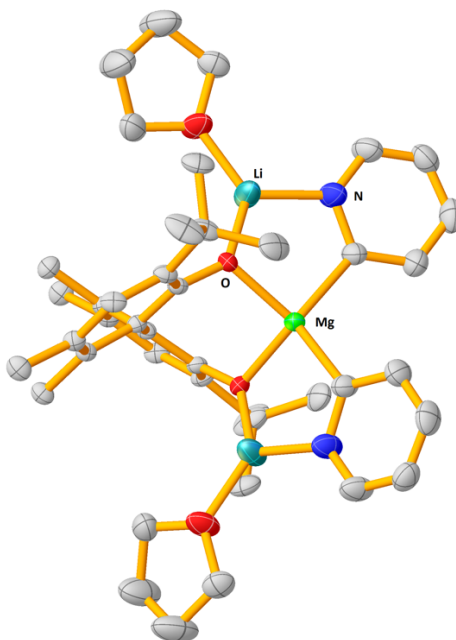


Figure 41: Solid-state structure of $[(rac)\text{-BIPHEN}]\text{Li}_2\text{Mg}(\text{2-pyridyl})_2(\text{THF})_2$ depicting the double metal-halogen exchange of $[(rac)\text{-BIPHEN}]\text{Li}_2\text{Mg}^n\text{Bu}_2(\text{THF})_3$ with 2-bromopyridine.

3.3 Aims

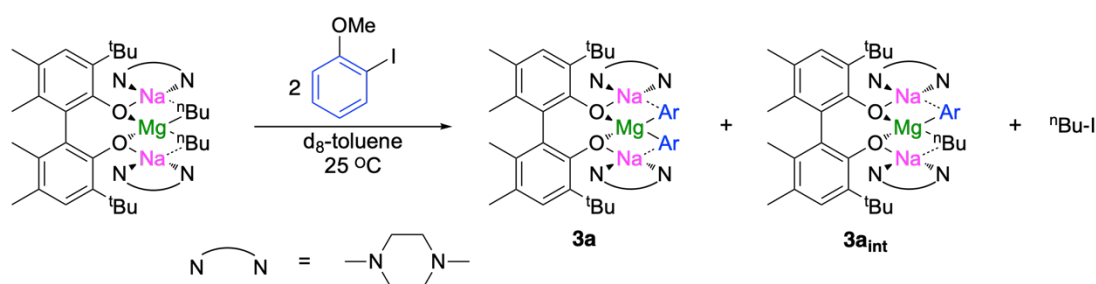
Despite the wealth of knowledge relating to magnesiate species in metal-halogen exchange, to the best of our knowledge there are no examples in the literature of sodium magnesiates being used for this application. As has been shown earlier in this chapter, sodium magnesiates are heavily utilised for metallation chemistry and are highly reactive bases. The aim of this chapter is to explore the reactivity of mixed alkyl/alkoxide sodium magnesiates for metal-halogen exchange and where possible draw comparison to their lithium counterparts in order to understand why lithium magnesiates are used preferentially over sodium magnesiates in metal-halogen exchange.

3.4 Results and Discussion

3.4.1 Reactivity of **3** in Magnesium-Halogen Exchange

3.4.1.1 Electron Rich Substrates

Owing to the precedence in the literature for alkyl/phenoxide magnesiates containing reactive ⁿbutyl ligands, our investigation into the reactivity of the sodium magnesiates complexes characterised in Chapter 2 began with **3**. Given that no precedence could be found in the literature for the reactivity of sodium magnesiates in metal-halogen exchange, aryl-iodides were selected as the halogenated substrates as these are known to be the most reactive aryl-halogens. Using freshly prepared crystalline **3** in a J Young's NMR tube, an initial reaction was carried out using two equivalents of 2-iodoanisole in d₈-toluene at ambient temperature (Scheme 16). Toluene was chosen as the reaction solvent in an attempt to prevent displacement of the TMEDA donor ligands. Furthermore, Knochel has recently shown that high yields of metal-halogen exchange reactions can be achieved using alkali metal magnesiates and zincates bearing alkoxide ligands in this non-polar medium.^{163,167} Electron rich anisole derivatives were chosen as the substrate as the methoxy (OMe) group provides a diagnostic resonance that allows for the reaction to be easily tracked by ¹H NMR spectroscopy.



Scheme 16: Reaction of **3** with 2-iodoanisole.

After fifteen minutes reaction time the ¹H NMR spectrum of the crude reaction mixture showed **3** to have successfully carried out metal-halogen exchange with 2-iodoanisole (Figure 42). To expand on this, the aliphatic region showed a singlet at δ 3.33 ppm which can be assigned to the methoxy groups of the anisole ligand of the newly formed diaryl magnesiate. A second singlet δ 3.29 ppm was assigned as a methoxy group of the monoalkyl-monoaryl intermediate **3a_{int}** formed from exchange of a single butyl group of the parent magnesiate. Both these resonances are shifted slightly downfield compared to the

resonance for free 2-iodoanisole at δ 3.19 ppm giving a good indication that they are incorporated into the new metal-aryl complex. Furthermore, the aliphatic region clearly shows a triplet, two sets of multiplets and a further triplet resonance at δ 0.65, 1.11, 1.38 and 2.68 ppm respectively which were assigned as iodobutane. Moreover, the appearance of these resonances was accompanied by almost complete loss of the two multiplets in the shielded region of the spectrum at δ -0.82 and -0.25 ppm which is indicative of the loss of the two sets of n butyl ligands of the parent magnesiate. Complete assignment of the aromatic region of the spectrum is precluded by the use of 1,2,3,4-tetraphenylnaphthalene as an internal standard; however, a doublet is visible at δ 7.94 ppm and has been assigned as the hydrogen atoms of the newly metallated anisole ligands of **3a**. This doublet is shifted downfield from that of unreacted 2-iodoanisole at δ 7.59 ppm. Based on the internal standard, a yield of 60 % for **3a** was obtained after 15 minutes. Returning to the aliphatic region of the spectrum, multiple resonances are observed which could be attributed to the methyl and t butyl groups of the (*rac*)-BIPHEN ligand. As the reaction progresses these additional resonances can be seen to disappear leaving only a single set of resonances once the reaction has reached completion (Figure 43). The presence of multiple resonances associated with these groups gives further evidence of multiple (*rac*)-BIPHEN containing species being present within the reaction mixture and serves as an indication that the reaction has not reached completion.

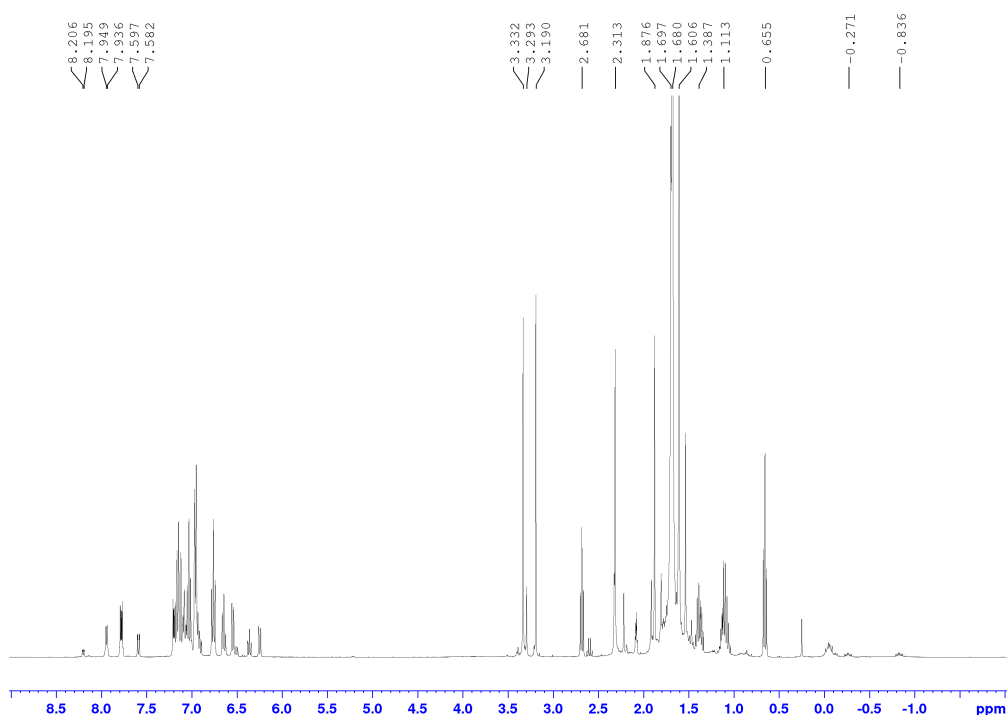


Figure 42: ^1H NMR Spectrum of the reaction of **3** with 2-iodoanisole after 15 minutes (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

The reaction was allowed to proceed and a further ^1H NMR spectrum was collected after one hour. The singlet at δ 3.29 which had been assigned as the monoalkyl-monoaryl intermediate was no longer visible and the intensity of the singlet at δ 3.33 along with resonances assigned as iodobutane had increased. Subsequently, this corresponded with an increase in the yield from 60 % to 80 %. Furthermore, the multiplets assigned to the methylene groups of the alkyl ligands of the parent magnesiate in the shielded region were now only present in trace amounts. The reaction mixture was allowed to stand overnight at ambient temperature and a final ^1H NMR spectrum was collected the next morning (Figure 43). The spectrum showed a further increase in yield of **3a** from 80 % to 90 % indicating that the parent magnesiate was not fully consumed after one hour. Moreover, the spectrum showed that there was no further reactivity between **3a** and the iodobutane that was formed *in situ*. This stands in contrast to that which was reported for the lower order lithium magnesiate [(*S*)-BIPHEN]LiMgⁿBu by Gros.¹⁰⁵ The final spectrum also shows a significant amount of unreacted 2-iodoanisole present in the reaction mixture, however based on the aliphatic region of the spectrum, the major product of the reaction appears to be **3a** as evidenced by the intensity of the singlet at δ 3.33 ppm.

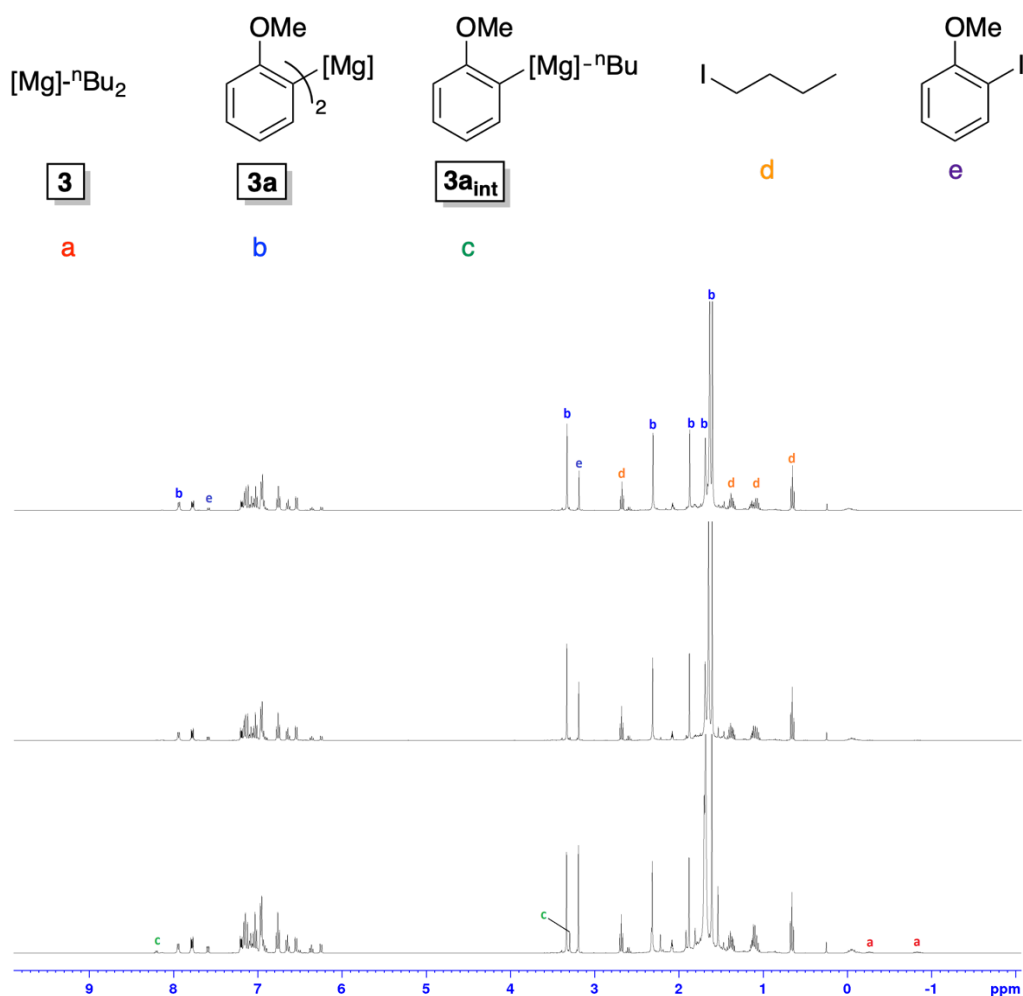
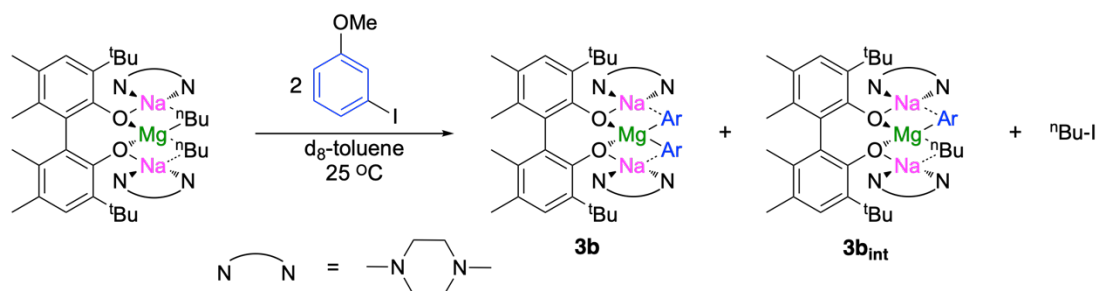


Figure 43: Overlay of ^1H NMR spectra for reaction of **3** with 2-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d_8 -tol, 300 K).

Investigation of the reactivity of **3** with electron rich substrates moved to 3- and 4-iodoanisole to assess the effect of *meta*- and *para*-substitution patterns on the metal-halogen exchange. Beginning with 3-iodoanisole, two equivalents of the substrate were combined with one equivalent of **3** in d_8 -toluene at ambient temperature (Scheme 17).



Scheme 17: Reaction of **3** with 3-iodoanisole.

Monitoring the reaction by ^1H NMR spectroscopy (Figure 44) showed a large drop off in reactivity of **3**. The ^1H NMR spectrum of the reaction mixture after 15 minutes showed that metal-halogen exchange had occurred; however, the diaryl magnesiate **3b** was only obtained in a 14 % yield. The ^1H NMR spectrum of the reaction mixture contained two singlets at δ 3.54 and 3.59 ppm which were again assigned to be the methoxy groups of **3b** and **3b_{int}** respectively and are shifted downfield from 3-iodoanisole which was assigned to the singlet at δ 3.10 ppm. Iodobutane is present albeit in trace amounts as evidenced by the resonances present at δ 0.65, 1.11, 1.38 and 2.68 ppm. Interestingly, the spectrum suggested a greater amount of the monoalkyl-monoaryl magnesium species to be present than the desired diaryl magnesium complex **3b**. After one hour however, the ^1H NMR spectrum of the reaction mixture showed a clear increase in the amount of **3b** present (Figure 44). The increase in the amount of **3b** within the reaction mixture is accompanied by an increase in the intensities of the resonances associated with iodobutane and a decrease in the intensity of the Mg-CH_2 resonances in the shielded region of the spectrum. Continued monitoring of the reaction overnight showed a further increase in the yield of complex **3b** to 91 % with full consumption of **3** and no subsequent reactivity with iodobutane (Figure 44).

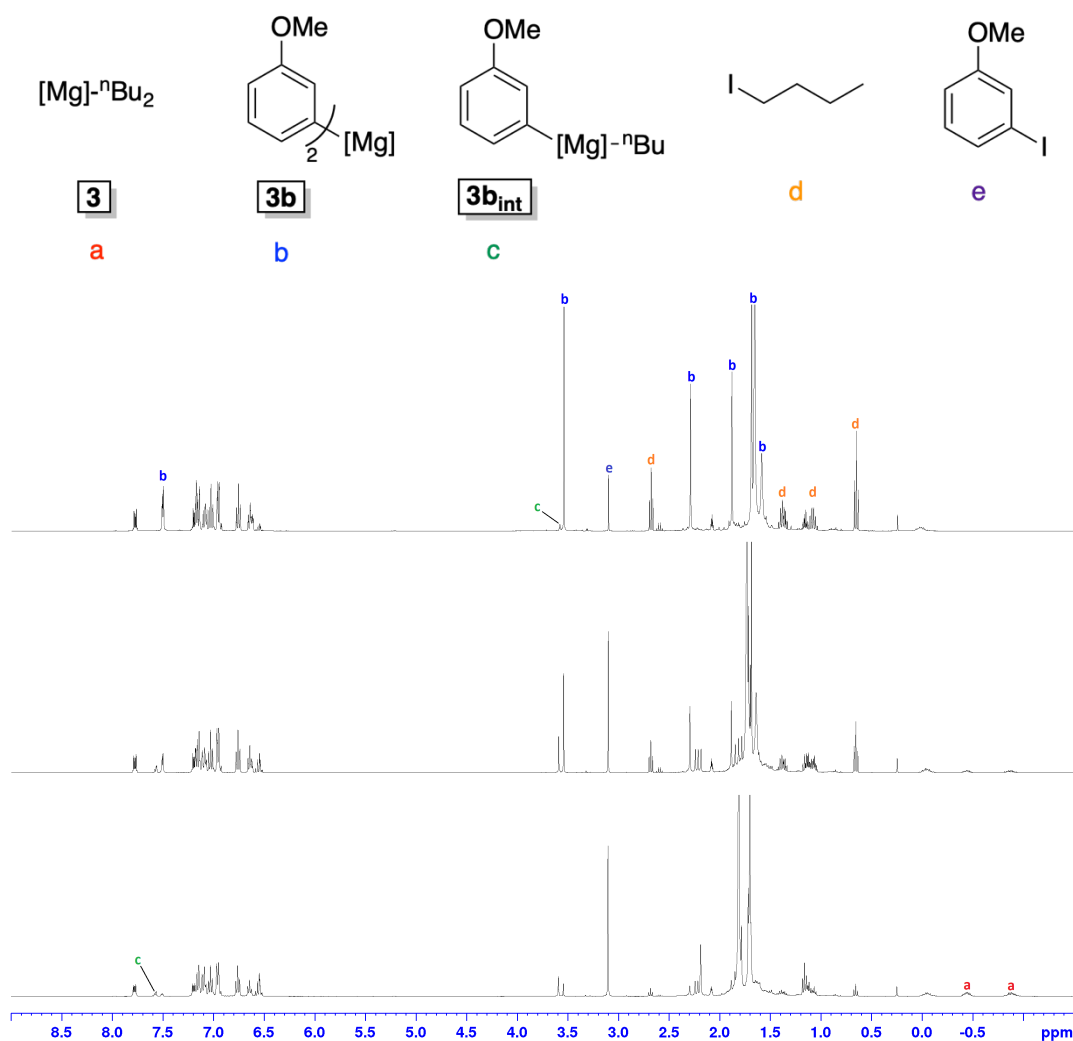
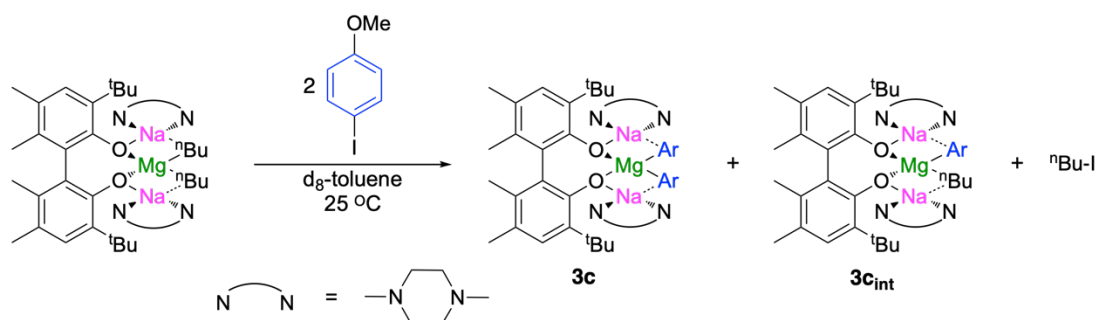


Figure 44: Overlay of ¹H NMR spectra for reaction of **3** with 3-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d₈-tol, 300 K).

Finally, the reactivity of **3** was probed using 4-iodoanisole. *Para*-substituted anisole derivatives are known to be challenging substrates for metal-halogen exchange due to the unfavourable position of the halogen relative to the electron donating methoxy group.¹⁶³ With this trend in reactivity in mind, the reactivity of **3** was probed with two equivalents of 4-iodoanisole in d₈-toluene at ambient temperature (Scheme 18).



Scheme 18: Reaction of **3** with 4-iodoanisole.

After fifteen minutes the ^1H NMR spectrum of the reaction mixture revealed that metal-halogen exchange had occurred; however, only trace amounts of the desired diarylmagnesiates **3c** had formed (6 % yield) (Figure 45). The reaction was allowed to proceed at ambient temperature and was analysed again by ^1H NMR spectroscopy after one hour to reveal a modest increase in the yield of **3c** to 20 % (Figure 45). The reaction was left to proceed for a further 12 hours and a final ^1H NMR spectrum was collected. The spectrum revealed that even after prolonged reaction times **3** was not fully converted to **3c** as evidenced by the presence of two multiplets in the shielded region of the spectrum at δ –0.85 and –0.42 ppm giving a final yield of 79 %. The aliphatic region of the spectrum shows only a single resonance at δ 3.44 ppm which suggests that only the diaryl magnesium complex **3c** is now present. This resonance is shifted downfield from that of the methoxy group of 4-iodoanisole which is present at δ 3.14 ppm and serves as a good indication that the new resonances are incorporated into the diaryl magnesium complex. Concomitant formation of iodobutane was also observed as evidenced by the resonances at δ 0.65, 1.07, 1.38 and 2.67 ppm.

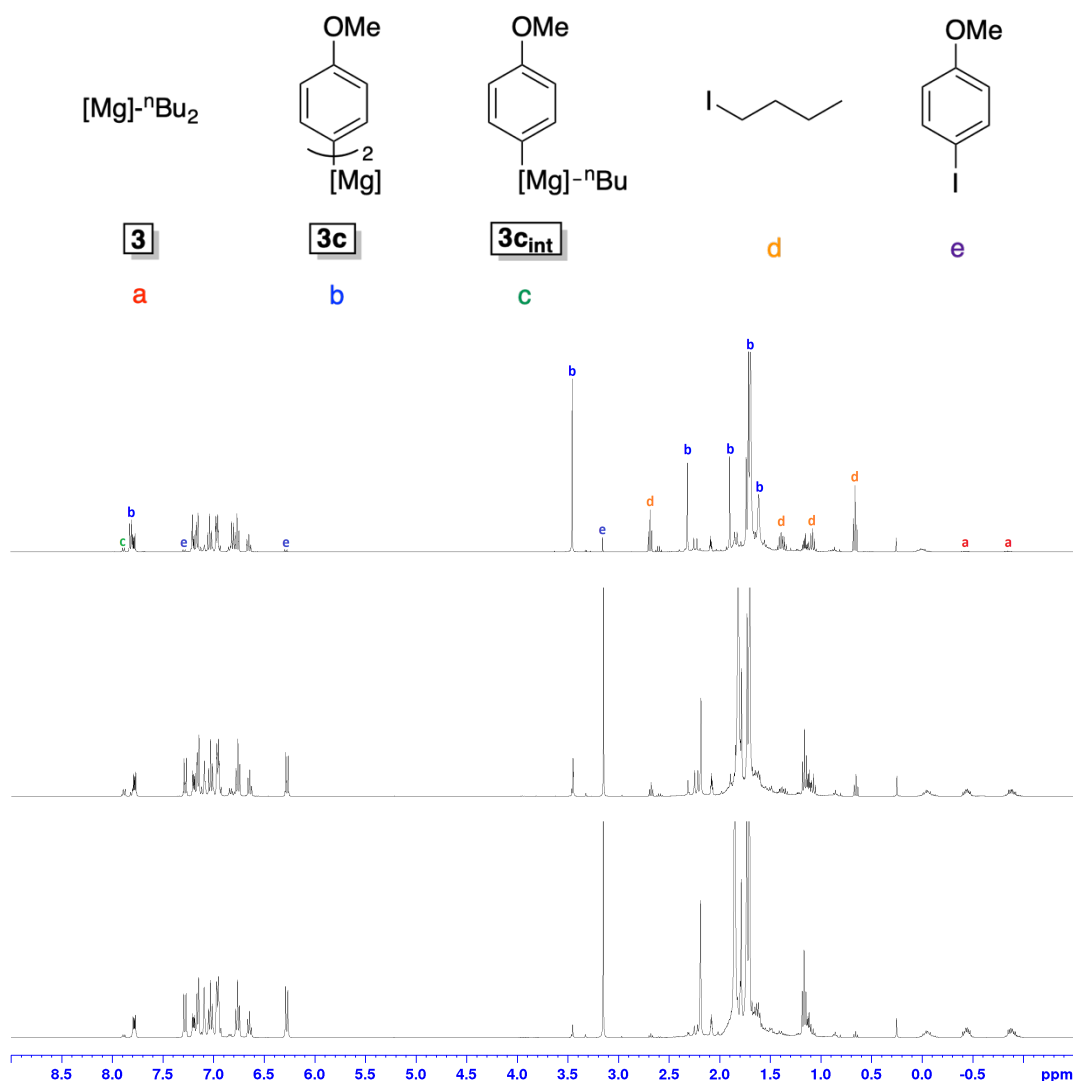


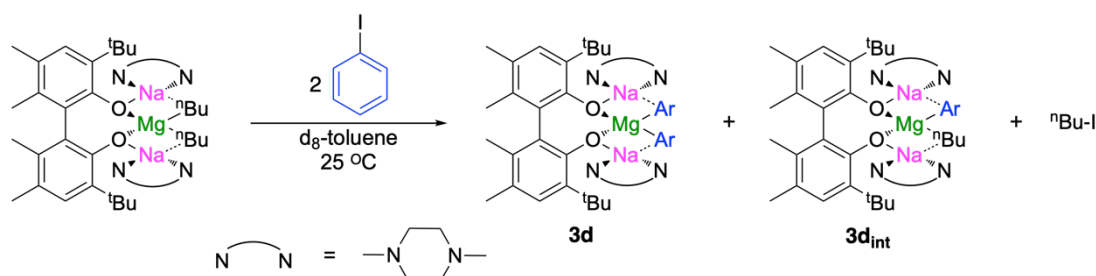
Figure 45: Overlay of ^1H NMR spectra for reaction of **3** with 4-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, $\text{d}_8\text{-tol}$, 300 K).

Overall, these data show that **3** is sufficiently reactive to carry out metal-halogen exchange with electron rich iodoanisoles. The reactivity of **3** decreased as the site of exchange was moved further from the methoxy substituent with 2- and 4-iodoanisole being most and least reactive substrates respectively. Given that metal-halogen exchange is accelerated by electron withdrawing substituents it is somewhat surprising that 2-iodoanisole would be the most reactive of the substrates examined when considering the electron rich nature of the substrate. A possible explanation for this increased reactivity is that while the methoxy group is electron donating and should therefore act to reduce the rate at which metal-halogen exchange occurs, it may also be acting as a directing group to increase the reaction rate. Functional groups such as the methoxy substituent of anisole has been utilised extensively

as a directing group for direct *ortho* metallation (DoM) so it is possible a similar effect is occurring during metal-halogen exchange.²¹

3.4.1.2 Non-Functionalised Substrates

The reactivity of **3** was next examined in metal-halogen exchange using iodobenzene as it contained no functional groups which could influence the reactivity. Following the same protocol used to investigate the reactivity of **3** with the iodoanisole derivatives, **3** was combined with two equivalents of iodobenzene in d_8 -toluene in a J Young's capped NMR tube (Scheme 20). The reaction was carried out at ambient temperature and was monitored using ^1H NMR spectroscopy.



Scheme 20: Reaction of **3** with iodobenzene.

After an initial 15-minute period, the ^1H NMR spectrum of the reaction mixture revealed the metal-halogen exchange between **3** and iodobenzene to be sluggish giving **3d** in a 10 % yield (Figure 46). Examining the ^1H NMR spectrum in more detail, the aliphatic region showed only a trace amounts of iodobutane to have formed as evidenced by the presence of the resonances located at δ 0.65, 1.11, 1.38 and 2.67 ppm. The lack of reactivity was further highlighted by the presence of the two multiplets in the shielded region of the spectrum δ – 0.88 and –0.43 ppm corresponding to the methylene groups of the n butyl ligands of **3**. The aromatic region of the spectrum showed the formation of two new doublets at δ 7.92 and 8.00 ppm which is indicative of formation of a secondary exchange product. A similar situation was observed for the previous reaction of **3** with 2-, 3-, and 4-iodoanisole.

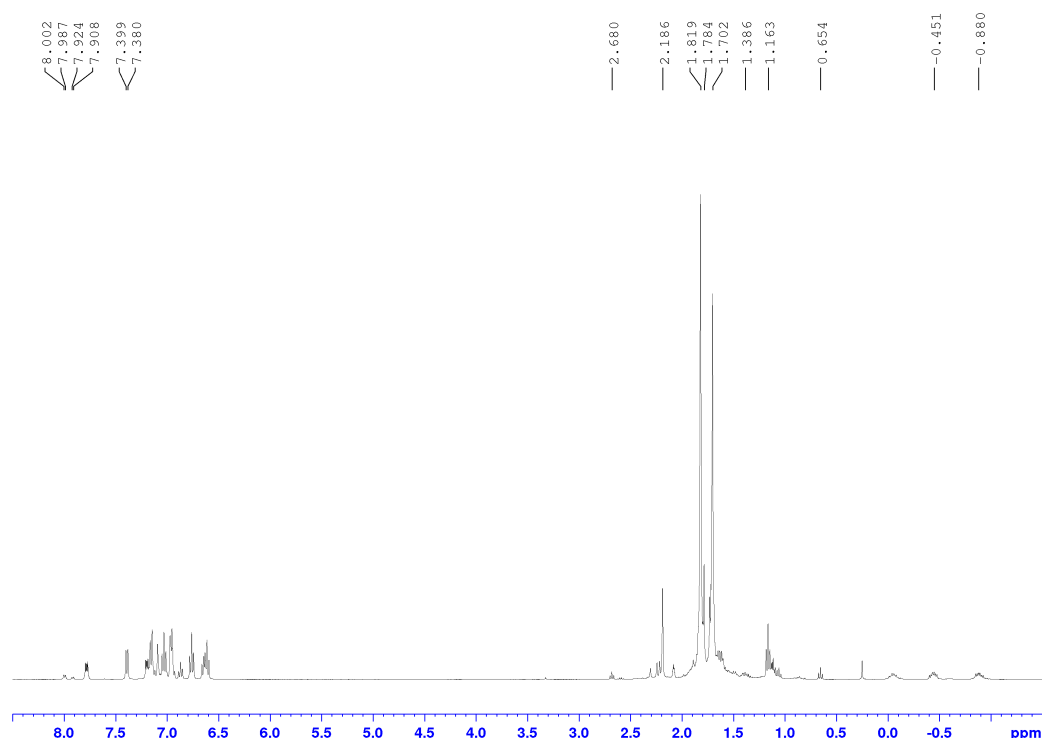


Figure 46: ^1H NMR Spectrum of the reaction of **3** with iodobenzene after 15 minutes (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

After one hour, the ^1H NMR spectrum of the reaction mixture showed an increase in the intensity of the doublet located at δ 7.92 ppm which was assigned to **3d** along with a concomitant increase in the amount of iodobutane contained within the reaction mixture (Figure 47). A second aromatic resonance remained at δ 8.00 ppm which is indicative of the presence of a second exchange product. Despite the increase in yield of **3d**, a significant amount of the parent magnesiate remained as evidenced by the multiplets in the shielded region of the spectrum at δ -0.89 and -0.45 ppm. The reaction was left to proceed for an additional 12 hours after which a final ^1H NMR spectrum of the reaction mixture was collected (Figure 47). This final spectrum showed **3** to have been fully consumed giving a final yield of 90 % for **3d**. Examining the ^1H NMR spectrum in more detail, the aliphatic region of the spectrum no longer contained any resonances in the shielded region of the spectrum characteristic of the alkyl ligands of **3** which is indicative of their conversion into iodobutane. Furthermore, three singlets were observed at δ 1.68, 1.88 and 2.30 ppm which were assigned to the methyl and t butyl groups of the (*rac*)-BIPHEN ligand. Multiple resonances were observed in this region of the previous spectra which is indicative of multiple (*rac*)-BIPHEN containing species within the reaction mixture. The aromatic region of the spectrum was

found to contain a doublet at δ 7.92 ppm; however, the other resonances associated the benzene ring were obscured by the tetraphenylnaphthalene standard.

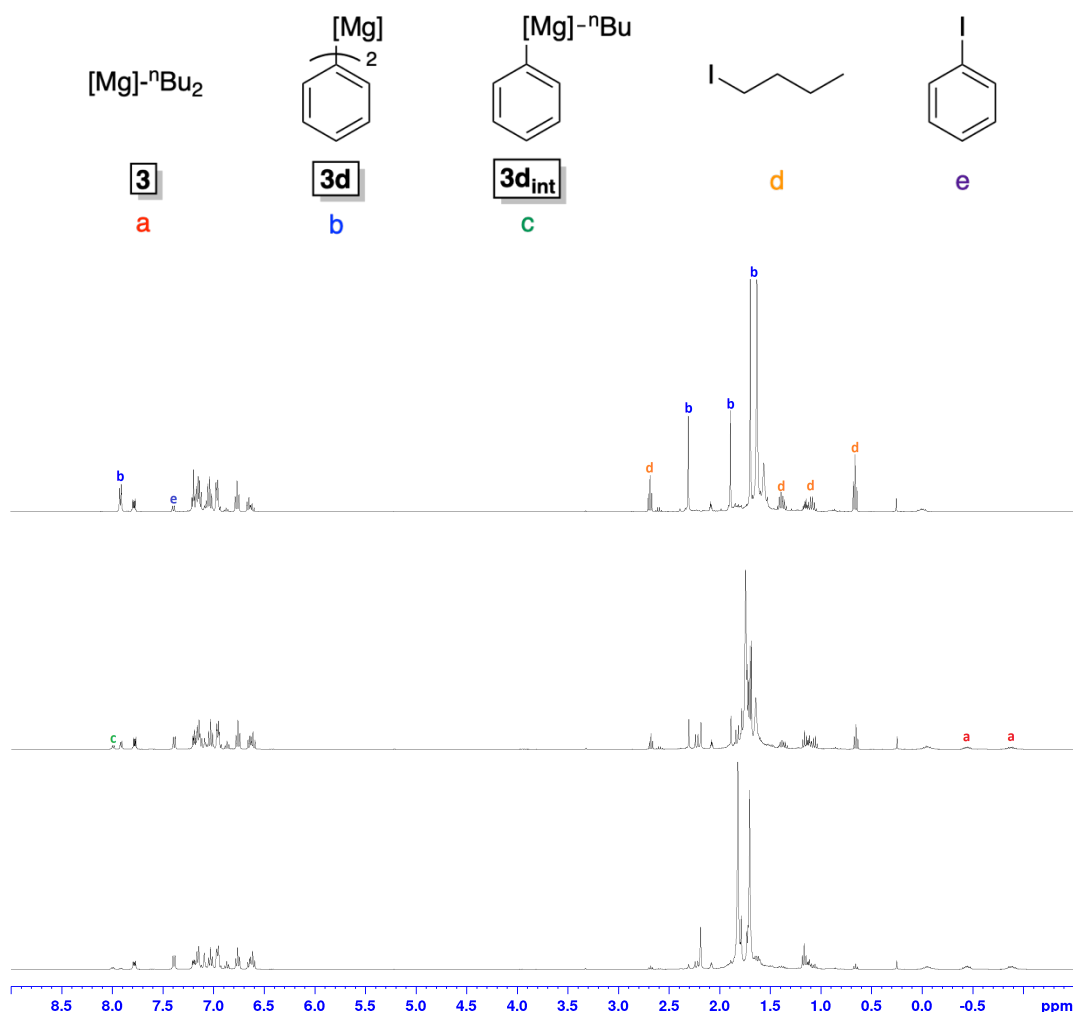
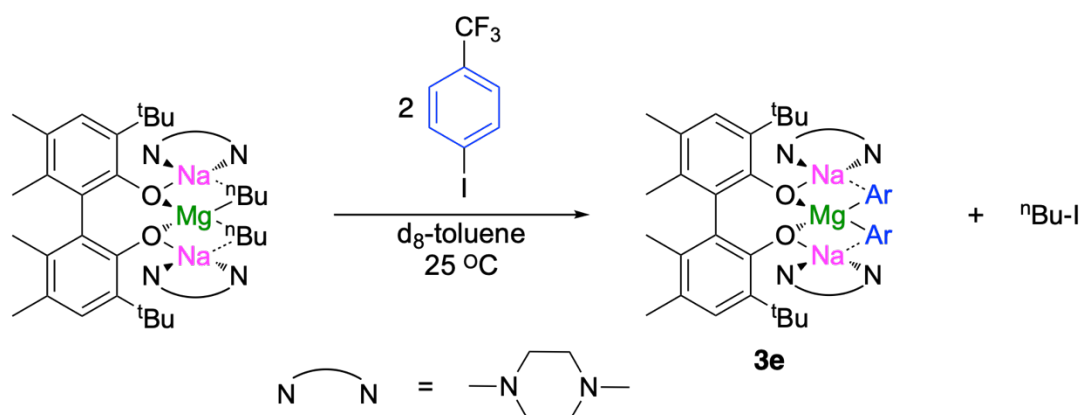


Figure 47: Overlay of ^1H NMR spectra for reaction of **3** with iodobenzene after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, $\text{d}_8\text{-tol}$, 300 K).

3.4.1.3 Electron Poor and Heterocyclic Substrates

Investigation into the reactivity of **3** was completed by examining its reactivity with the electron deficient substrates 1-iodo-4-(trifluoromethyl)benzene and 2-iodopyridine. The heterocyclic pyridine was included here due to the precedence of its use in metal-halogen exchange with magnesiate complexes and its importance of pyridine scaffolds in medicinal chemistry.¹⁶⁸ The investigation into the reactivity of **3** with electron deficient substrates began with 1-iodo-4-(trifluoromethyl)benzene which was chosen due to the highly electron withdrawing nature of the CF_3 group. The reaction was probed using isolated **3** in $\text{d}_8\text{-toluene}$

to which two equivalents of 1-iodo-4-(trifluoromethyl)benzene were added at ambient temperature and reaction was monitored using ^1H NMR spectroscopy (Scheme 21).



Scheme 21: Reaction of **3** with 1-iodo-4-(trifluoromethyl)benzene.

After 15 minutes of reaction time the reaction mixture showed complete consumption of **3** giving the new diaryl magnesiate **3e** in an 87 % yield (Figure 48). Examination of the ^1H NMR spectrum of the reaction mixture in more detail showed no resonances to be present in the shielded region of the spectrum which is indicative of the consumption of the n-butyl ligands of the **3**. Furthermore, the loss of the resonances associated with alkyl ligands of **3** was accompanied by concomitant formation of iodobutane as evidenced by the presence of the four resonances at δ 0.65, 1.10, 1.38 and 2.68 ppm. In the aromatic region of the spectrum two doublets were found to be present at δ 7.36 and 7.93 ppm which were assigned to the aromatic hydrogen atoms of the new aryl ligands. This splitting pattern is consistent with what would be expected from a di-substituted benzene ring system whilst the chemical shift values are indicative of formation of a new metal-aryl complex and are shifted downfield from free 1-iodo-4-(trifluoromethyl)benzene.

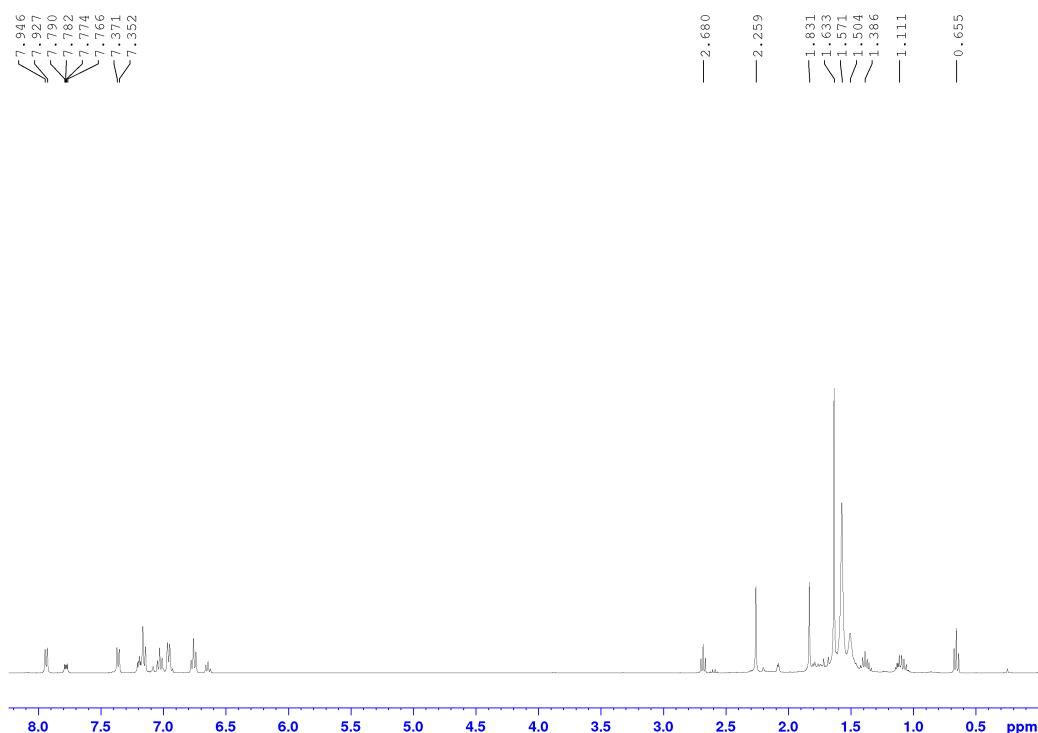


Figure 48: ^1H NMR Spectrum of the reaction of **3** with 1-iodo-4-(trifluoromethyl)benzene after 15 minutes (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

The reaction mixture was monitored for a further hour after which a final ^1H NMR spectrum was collected (Figure 49). Analysis of the ^1H NMR spectrum after this time revealed change in the spectrum which once again demonstrates that the newly formed diaryl magnesiate **3e** does not participate in any further reaction with iodobutane. This also demonstrated that the **3e** formed from the exchange of 4-iodobenzotrifluoride with **3** is stable at ambient temperature for prolonged periods of time.

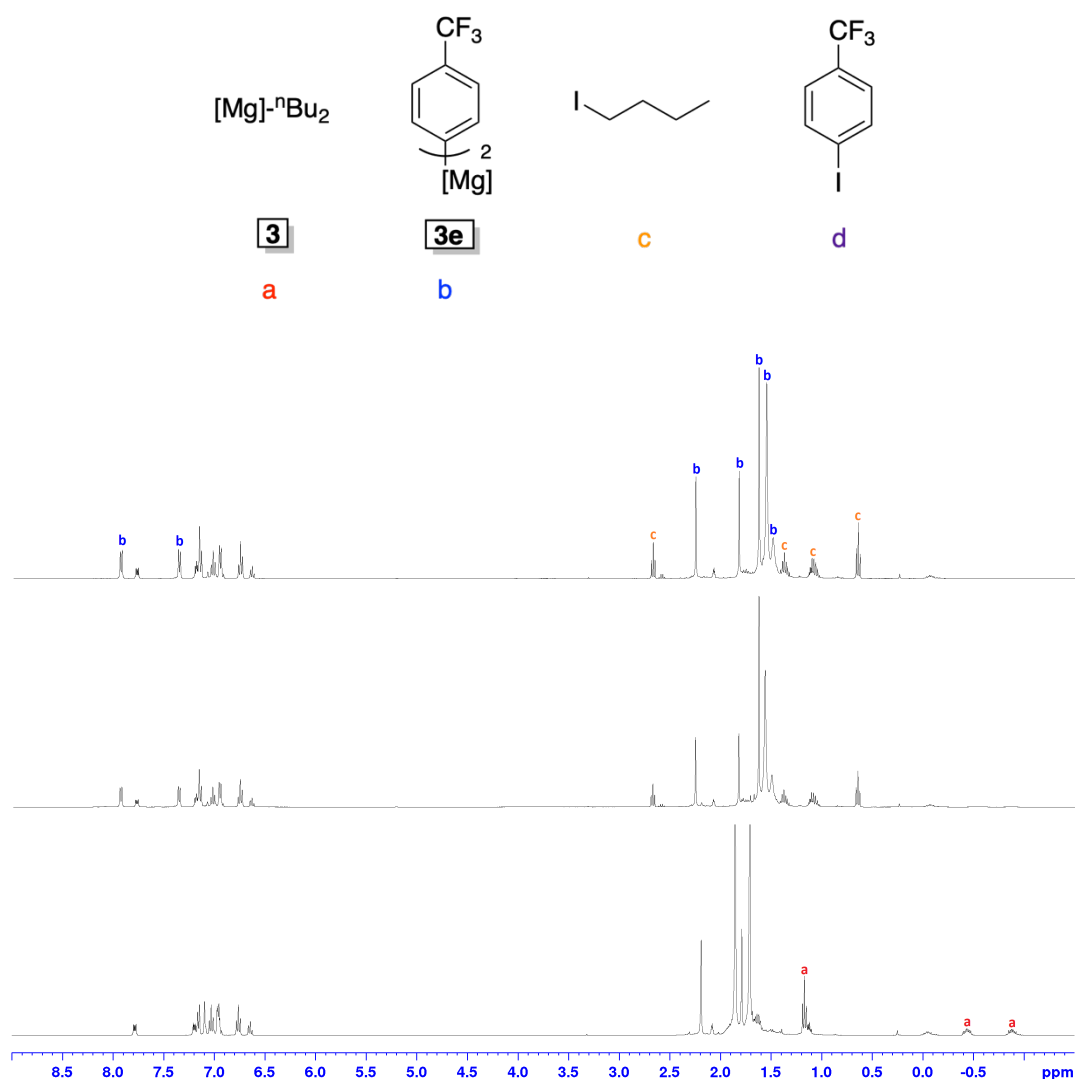
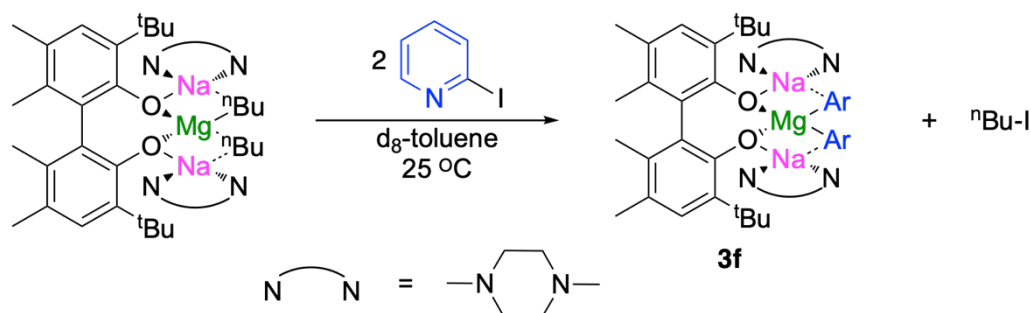


Figure 49: Overlay of ^1H NMR spectra for reaction of **3** (bottom) with 1-iodo-4-(trifluoromethyl)benzene after 15 minutes (middle) and 1 hour (top) (400 MHz, d_8 -Tol, 300 K).

The final substrate investigated in reaction with **3** was the electron deficient heterocycle 2-iodopyridine. The reaction was once again probed using the same synthetic procedure as used for the other substrates mentioned above. Performing the reaction in a J Young's NMR tube, isolated **3** was combined with two equivalents of 2-iodopyridine in d_8 -toluene at ambient temperature and the reaction tracked using ^1H NMR spectroscopy (Scheme 22).



Scheme 22: Reaction of **3** with 2-iodopyridine.

A colour change in the reaction mixture from colourless to dark green was observed upon addition of 2-iodopyridine to the solution of **3**. Examining the ¹H NMR spectrum of the reaction mixture after an initial 15-minute time period (Figure 50) showed complete consumption of **3** as evidenced by the lack of the diagnostic multiplets in the shielded region of the spectrum corresponding to the methylene hydrogen atoms of the *n*-butyl alkyl ligands giving **3f** in a 78 % yield. This was accompanied by the concomitant formation of iodobutane as evidenced by the appearance of four resonances at δ 0.65, 1.09, 1.38 and 1.68 ppm. The ¹H NMR spectrum of the reaction mixture was also found to contain a singlet at δ 1.52 ppm along with two singlets at δ 1.91 and 2.26 ppm which were assigned to the *t*-butyl group and methyl groups of the (*rac*)-BIPHEN ligand for **3f** respectively. The methyl and bridging methylene groups of the TMEDA ligands were assigned to the two singlets which appear at δ 1.82 and 1.89 ppm. Turning now to the aromatic region of the spectrum, two doublets were observed at δ 7.90 and 8.35 ppm which were assigned to the aromatic hydrogen atoms of the monosubstituted pyridine ring systems. Moreover, these resonances were found to be shifted downfield from that of 2-iodopyridine giving a good indication that they are part of a metalated species. Once again, the remaining aromatic resonances associated with the pyridyl ligands are not visible as they have been obscured by the tetraphenylnaphthalene standard.

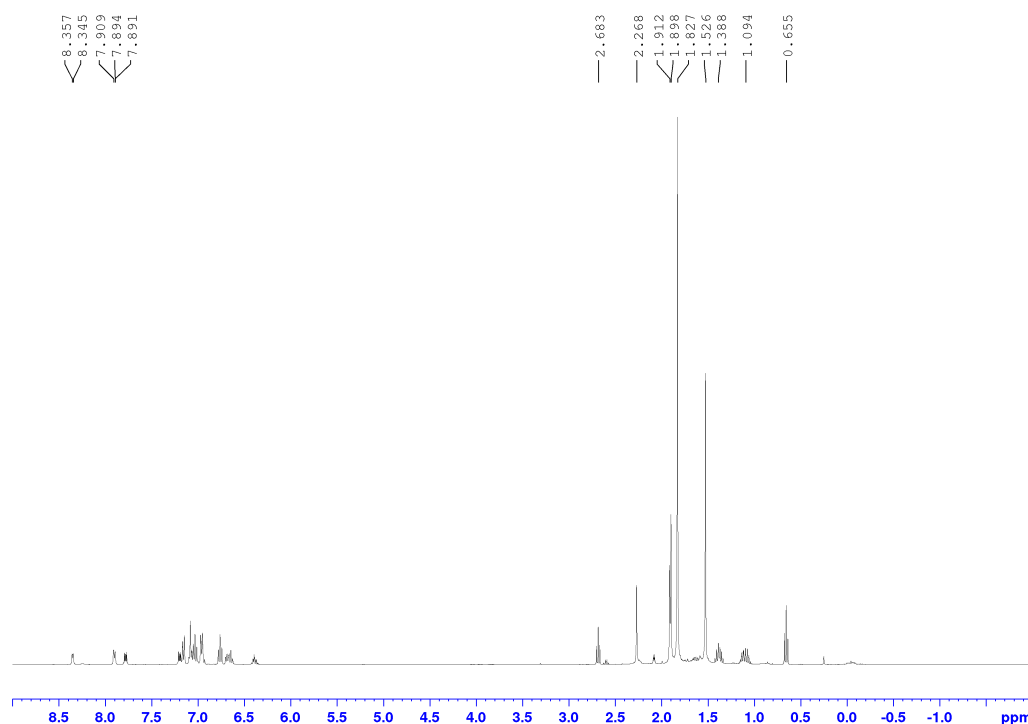


Figure 50: ^1H NMR Spectrum of the reaction of **3** with 2-iodopyridine after 15 minutes (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

The reaction was allowed to proceed for a further hour after which time a final ^1H NMR spectrum of the reaction mixture was collected (Figure 51). Analysis of the spectrum showed no further reaction had taken place and also that no further exchange was observed between **3f** and iodobutane. Furthermore, the yield of **3f** remained unaltered demonstrating the stability of the newly generated heteroaryl magnesiate **3f** in solution at ambient temperature.

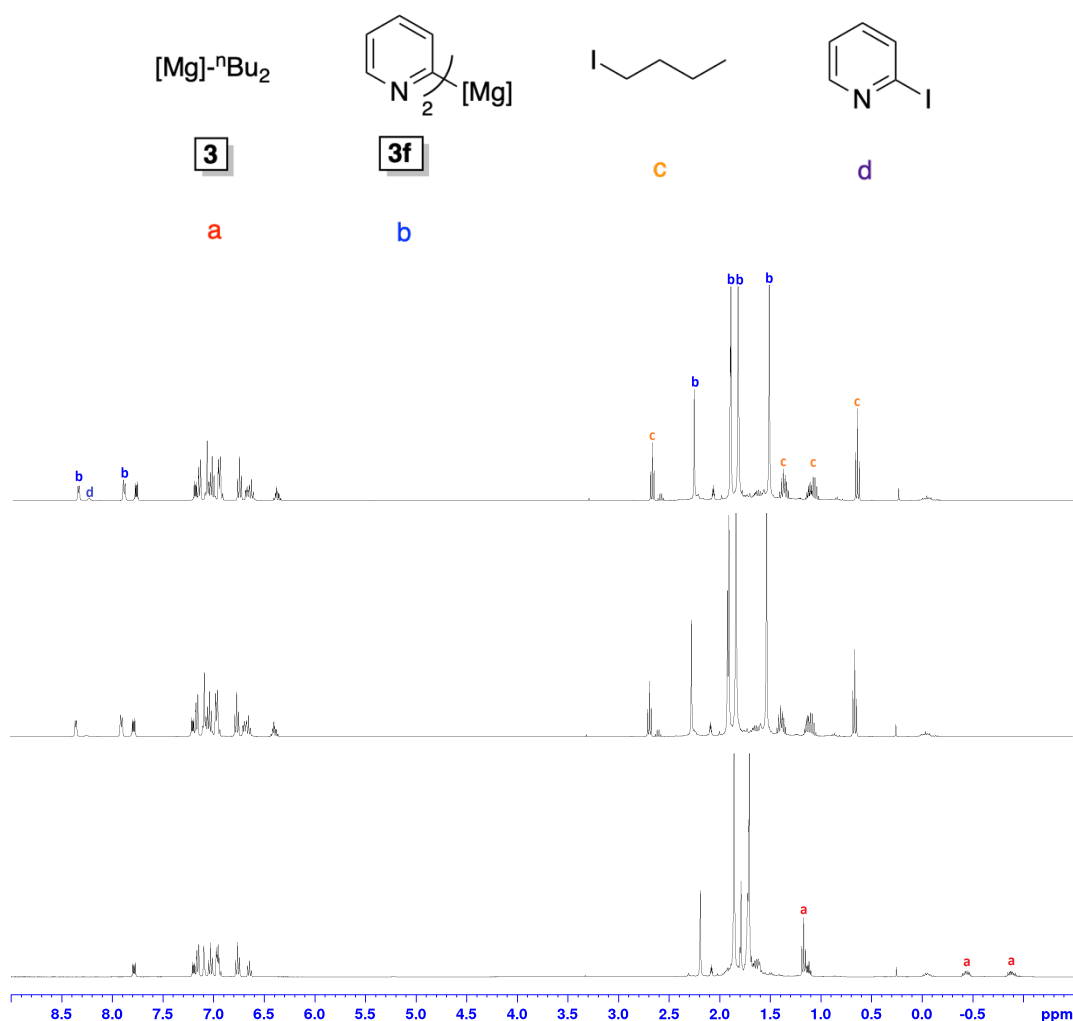
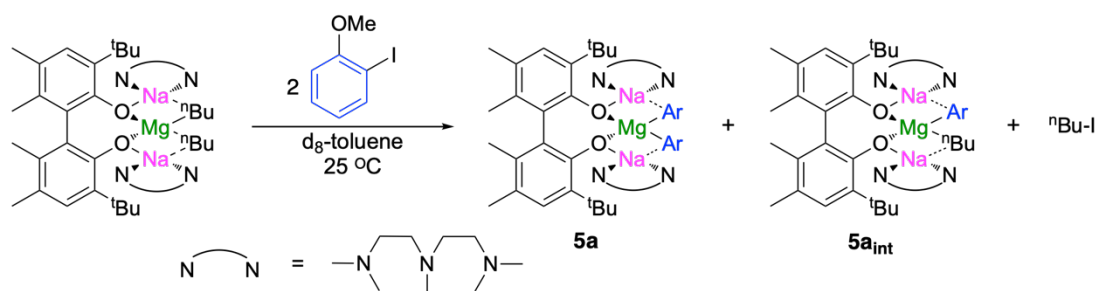


Figure 51: Overlay of ^1H NMR spectra for reaction of **3** (bottom) with 2-iodopyridine after 15 minutes (middle) and 1 hour (top) (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

3.4.3 Reactivity of **5** in Magnesium-Halogen Exchange

3.4.3.1 Electron Rich Substrates

The reactivity of **5** in metal-halogen exchange was first probed two using equivalents of 2-iodoanisole with the goal of achieving double metal-halogen exchange. To this end, isolated **5** was combined with two equivalents of 2-iodoanisole in $\text{d}_8\text{-toluene}$ (Scheme 23). 1,2,3,4-tetraphenyl naphthalene was added as an internal standard and the reaction was monitored by ^1H NMR spectroscopy at ambient temperature.



Scheme 23: Reaction of **5** with 2-iodoanisole.

After 15 minutes reaction time, the ^1H NMR spectrum of the reaction mixture showed metal-halogen exchange to have occurred giving the desired diaryl magnesiate **5a** in a 30 % yield (Figure 52). Examining the ^1H NMR spectrum of the reaction mixture after this initial time point, the aliphatic region of the spectrum was found to contain resonances at δ 0.65, 1.13, 1.38 and 2.68 ppm indicative of the formation of iodobutane. Two new resonances were observed at δ 3.34 and 3.35 ppm which were assigned to the methoxy groups of metallated anisole intermediates present within the reaction mixture. The first of these resonances at δ 3.34 ppm was tentatively assigned as the monoalkyl-monoaryl intermediate **5a_{int}** arising from the exchange of a single n butyl ligand of **5** while the second resonance located at δ 3.35 ppm was assigned to the methoxy groups of **5a**. Both of these resonances were found to be shifted downfield from that of a standard of 2-iodoanisole for which the methoxy group was located at δ 3.19 ppm. This change in the chemical shift is indicative of metallation having occurred to form a metal-aryl complex. Examining the aromatic region of the spectrum, two sets of resonances were located at δ 7.92 and 8.18 ppm and were assigned as aromatic hydrogen atoms of **5a** and **5a_{int}** respectively. These two resonances were shifted to a higher chemical shift than that of 2-iodoanisole which is located in the ^1H NMR spectrum of the reaction mixture at δ 7.59 ppm.

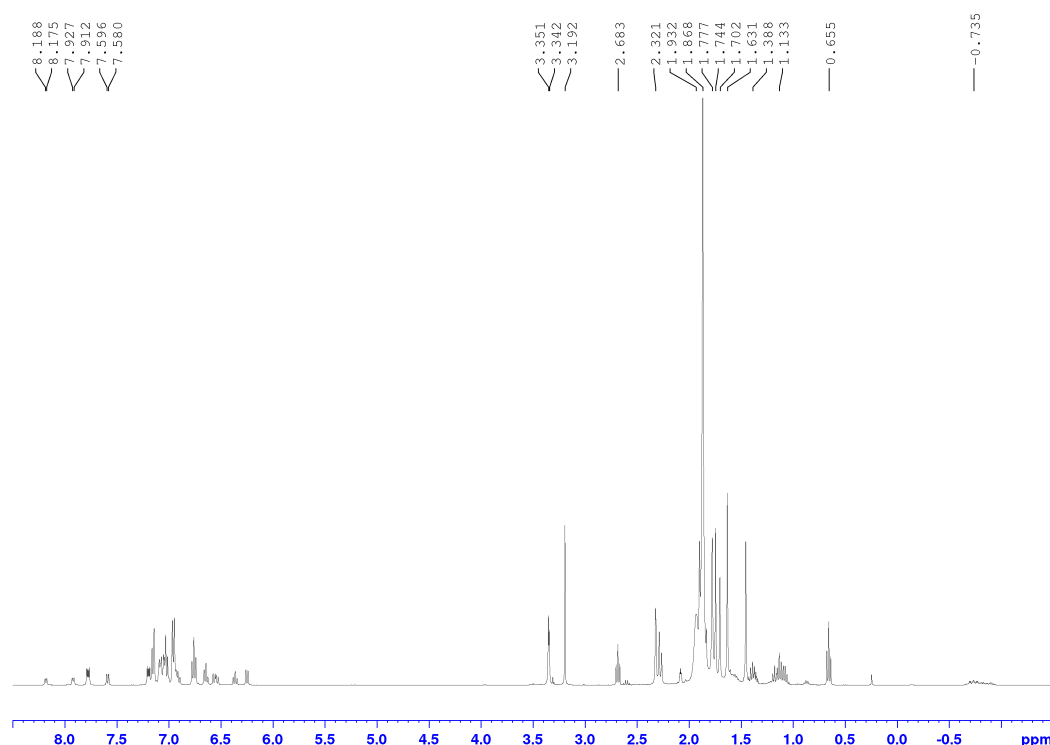


Figure 52: ^1H NMR Spectrum of the reaction of **5** with 2-iodoanisole after 15 minutes (400 MHz, d_8 -Tol, 300 K).

The reaction was allowed to proceed for one hour, after which time the ^1H NMR spectrum of the reaction mixture showed an increase in the intensity of the resonances located at δ 3.35 and 7.92 ppm which were assigned to the methoxy groups and aromatic hydrogen atoms respectively of **5a** (Figure 53) giving **5a** in a 65% yield. A concomitant increase was also observed in the amount of iodobutane present within the reaction mixture. These observations were accompanied by a decrease in the intensity of the resonances assigned to the monoalkyl-monoaryl intermediate **5a_{int}** located at δ 3.34 and 8.18 ppm. The decrease in the intensity of these resonances is indicative of the consumption of this species over time and provides further evidence for their assignment as a reaction intermediate. Despite the increase in yield of **5a**, the parent magnesiate **5** was not fully consumed and a broad multiplet remained at δ -0.73 ppm in the shielded region of the spectrum. Due to this sluggish reactivity, the reaction was monitored for a further two hours to assess if the total consumption of **5** could be achieved; however, a maximum yield of 75 % was achieved with trace amounts of **5** remaining. The reaction was therefore left to proceed for an additional 12 hours after which time the formation of a pale-yellow precipitate was observed. Analysis of the reaction mixture by ^1H NMR spectroscopy after this time show that full consumption of **5** had been achieved as evidenced by the disappearance of the resonance in the shielded

region of the spectrum (Figure 53). A small amount of 2-iodoanisole was observed as evidenced by the resonance located at δ 3.19 ppm. An additional resonance was observed at δ 3.34 ppm which has been tentatively assigned to the methoxy group of the monoalkyl-monoaryl intermediate **5a_{int}**; however, no resonances characteristic of the alkyl ligand of this species was observed in the ^1H NMR spectrum. Despite the ^1H NMR spectrum suggesting **5** to be fully consumed, the final yield of **5a** was found to have decreased to 67 %. This decrease in yield combined with the formation of a solid precipitate in the reaction mixture led to the conclusion that **5a** is poorly soluble at ambient temperature leading to the formation of the aforementioned pale-yellow precipitate.

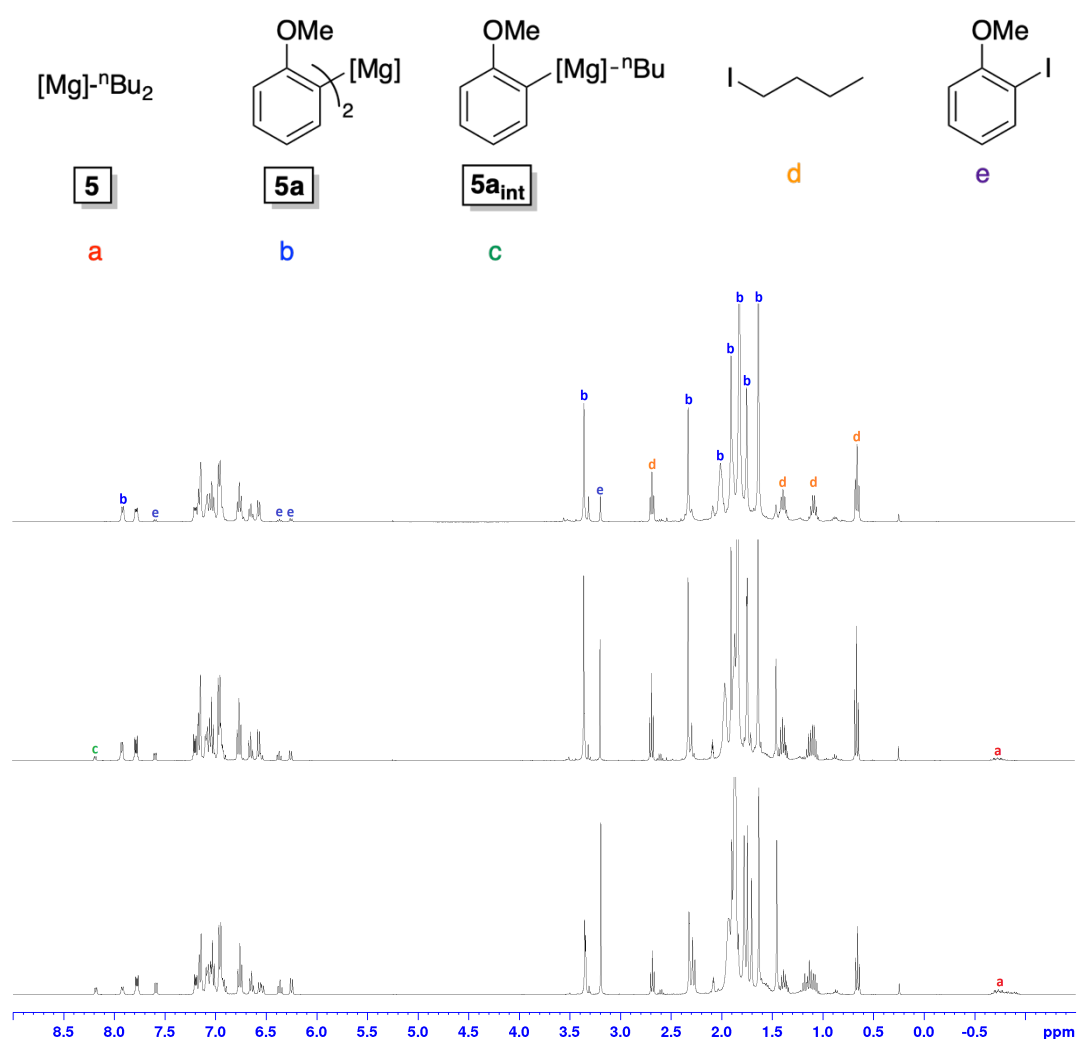
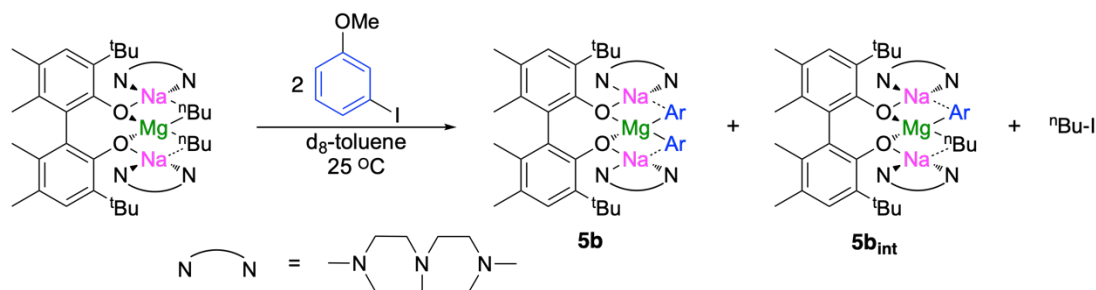


Figure 53: Overlay of ^1H NMR spectra for reaction of **5** with 2-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d_8 -Tol, 300 K).

The reactivity of **5** was next probed using the *meta* substituted 3-iodoanisole. Two equivalents of 3-iodoanisole were combined with isolated **5** in d_8 -toluene and the reaction was once again monitored using ^1H NMR spectroscopy at ambient temperature (Scheme 24).



Scheme 24: Reaction of **5** with 3-iodoanisole.

Analysis of the reaction mixture after an initial 15 minute time period revealed metal-halogen exchange to have occurred, albeit sluggishly, with only trace amount of iodobutane having formed as evidenced by the four resonances located at δ 0.65, 1.12, 1.38 and 2.67 ppm (Figure 54). Furthermore, two singlets were found to be present at δ 3.61 and 3.63 ppm which were assigned to the methoxy groups of the newly metallated anisole substrate **5b** and **5b_{int}** respectively. Although the second of these resonances is only present in trace amounts, its presence is indicative of the formation of multiple anisole containing species within the reaction mixture which is consistent with observations for previous reactions of both **3** and **5** with anisole derivatives. Due to the presence of tetraphenylinaphthalene as an internal standard, the aromatic region of the spectrum was of limited diagnostic value; however, a new resonance was observed at δ 7.42, shifted downfield compared to 3-iodoanisole, which was assigned to the aromatic hydrogen atoms of the newly metallated anisole ligands of **5b**. Despite the appearance of these new resonances, it was apparent that **5** remained largely unreacted as evidenced by presences of the resonances located at δ – 0.85 and 1.18 ppm which were assigned to the methylene and terminal methyl groups respectively of the n butyl ligands of **5**.

The reaction was allowed to proceed at ambient temperature for one hour and the reaction mixture was again analysed by ^1H NMR spectroscopy (Figure 54). The ^1H NMR spectrum showed an increase in the intensity of the signals assigned to iodobutane as well as the methoxy groups of **5b** and **5b_{int}**. This was accompanied by an increase in the intensity of the resonance assigned to the aromatic hydrogen atoms of the anisole ligands of **5b** at δ 7.42 giving a further indication of the increase in yield of **5b**. Interestingly, a second multiplet was

observed at δ -0.60 ppm in the shielded region of the spectrum indicating the formation of a second alkyl containing organometallic species. Moreover, this was accompanied by a substantial increase in the intensity of the resonance located in the aliphatic region at δ 3.63 ppm which was assigned to the methoxy group of **5b_{int}**. These observations would therefore suggest that the newly formed multiplet in the shielded region of the spectrum belongs to the Mg-CH₂ methylene hydrogen atoms of the alkyl ligand of **5b_{int}**. The observation of these hydrogen atoms as a separate resonance in the ¹H NMR spectrum was not observed for the reaction of other substrates.

The reaction was allowed to continue for an additional 12 hours, after which time, the ¹H NMR spectrum of the reaction mixture revealed that **5** had not been fully consumed, giving **5b** in a 65 % yield (Figure 54). To expand, an increase in the intensity of the resonance located at δ 3.61 ppm which was assigned to the methoxy groups of the anisole ligands of **5b** was observed. This was accompanied by an increase in the intensity of the resonance located at δ 7.42 ppm which was also assigned to the anisole ligands of **5b**. These observations were accompanied by a concomitant increase in the amount of iodobutane present within the reaction mixture. Interestingly, despite an increase in **5b**, two multiplets remained in the shielded region of the ¹H NMR spectrum at δ -0.83 and -0.61 ppm which were initially taken to be representative of the alkyl ligands of the parent magnesiate **5**. However, based on the presence of the singlet located at δ 3.63 ppm assigned to the methoxy group of **5b_{int}**, these resonances were subsequently assigned as being the two diastereotopic Mg-CH₂ hydrogen atoms of this monoalkyl-monoaryl intermediate. The appearance of these hydrogen atoms as two distinct resonances gives a good indication that they do not correspond to unreacted **5** for which the Mg-CH₂ hydrogen atoms appear as a single broad resonance. Additionally, as the reaction did not reach completion, multiple resonances are observed in the aliphatic region of the spectrum which could potentially be assigned to the ^tbutyl and methyl groups of (*rac*)-BIPHEN ligand. Given that **5b_{int}** persist within the reaction mixture even after prolonged reaction times, these additional resonances could potentially be the ^tbutyl and methyl groups of the (*rac*)-BIPHEN ligand for this intermediate species.

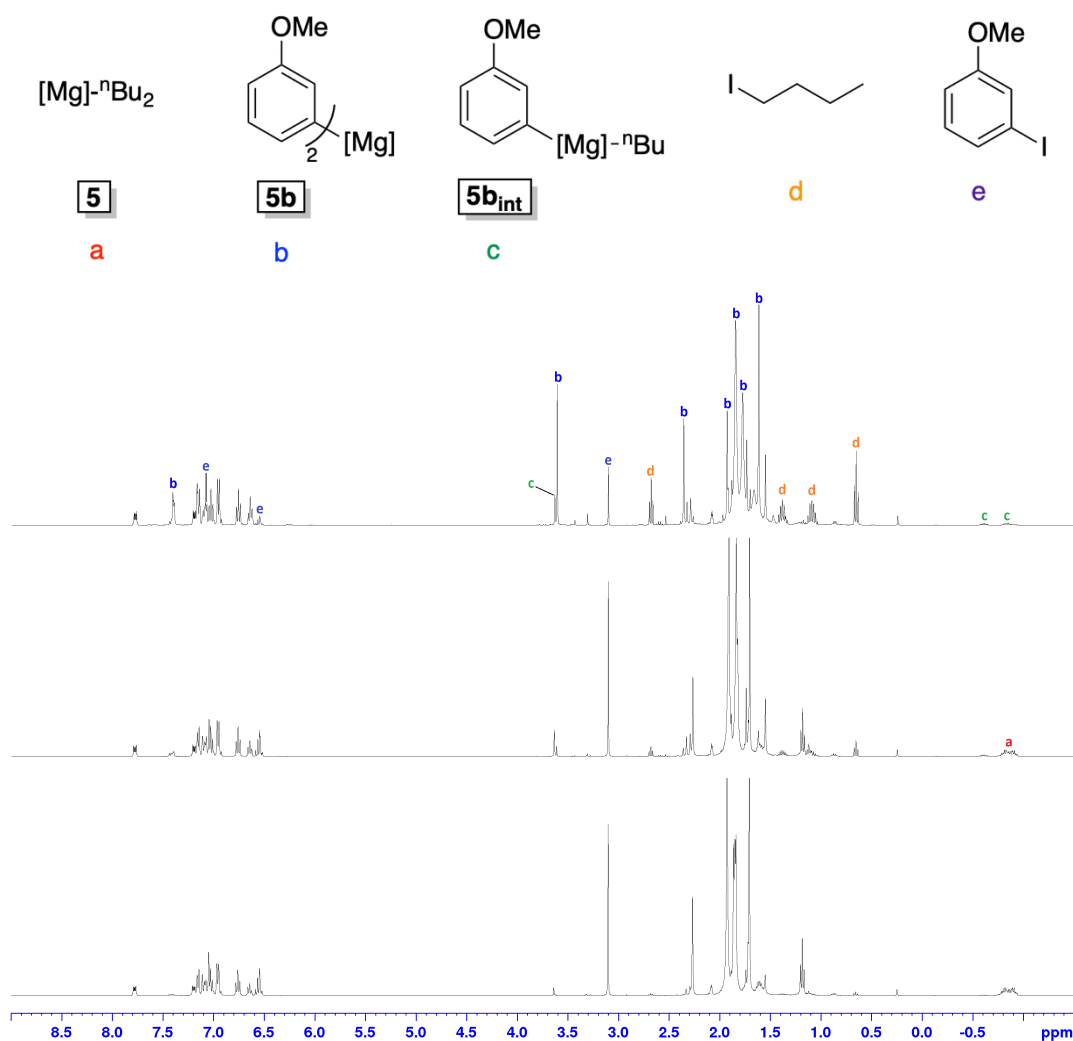
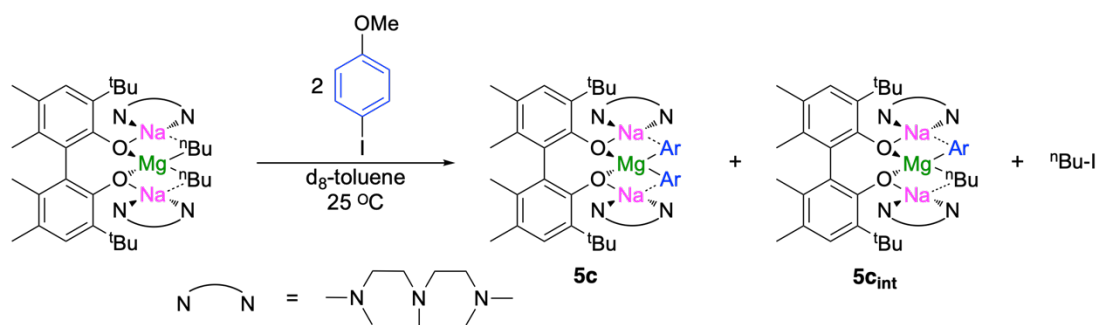


Figure S4: Overlay of ¹H NMR spectra for reaction of **5** with 3-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d₈-Tol, 300 K).

Finally, the reactivity of **5** with electron rich substrates was probed using 4-iodoanisole (Scheme 25). Based on the precedence in the literature for this particular substrate and from data obtained from previous reactions, the reactivity of **5** with 4-iodoanisole was anticipated to be extremely slow.



Scheme 25: Reaction of **5** with 4-iodoanisole.

Analysis of the reaction mixture following the addition of two equivalents of 4-iodoanisole to a solution of **5** in d_8 -toluene at ambient temperature appeared to show that no reaction had occurred after an initial 15 minute time period (Figure 55). Examining the ^1H NMR spectrum of the reaction mixture in more depth did show the formation of trace amounts of a metallated anisole-containing species as evidenced by the appearance of a singlet at δ 3.56 ppm accompanied by the concomitant formation of trace amounts of iodobutane. A doublet resonance was also formed in trace amounts in the aromatic region of the at δ 7.66 ppm providing further evidence for the formation of a metallated aryl species. The reaction was left to proceed at ambient temperature for one hour before the reaction mixture was analysed by ^1H NMR spectroscopy. Very little difference was observed in the ^1H NMR spectrum indicating that **5** remained virtually unreacted with the major components of the reaction mixture being the parent magnesiate **5** and 4-iodoanisole (Figure 55). The reaction was left to proceed overnight and a final ^1H NMR spectrum was collected the following day. The ^1H NMR spectrum of the reaction mixture showed a large amount of **5** to remain within the reaction mixture along with unreacted 4-iodoanisole as evidenced by the resonances δ -0.84 pm and δ 3.14 ppm respectively (Figure 55). Even after this prolonged reaction time, the final yield of **5c** was found to be only 20 %. Expanding on the appearance of the ^1H NMR spectrum, two resonances were now found to be present at δ 3.46 and 3.48 ppm which are indicative of the presence of two metallated anisole species within the reaction mixture. Interestingly, the resonances located at δ 3.46 and 3.48 ppm were found to be present in a 1:1 ratio indicating an equal amount of the two species. The singlet at δ 3.46 ppm has been tentatively assigned to the monoalkyl-monoaryl intermediate **5c_{int}** while the resonance located at δ 3.48 ppm has been tentatively assigned to the methoxy groups of the anisole ligands **5c**. The appearance of these two resonances is accompanied by an increase in the intensity of the resonances located in the aromatic region of the spectrum at δ 7.42 ppm. Moreover, concomitant formation of iodobutane was observed as evidenced by the four

resonances located at δ 0.65, 1.12, 1.38 and 2.67 ppm which provides further evidence for metal-halogen exchange to have taken place. Interestingly, a second resonance was also observed in the shielded region of the spectrum at δ -0.60 ppm. This is consistent with the formation of a second alkyl containing organometallic species within the reaction mixture and in combination with the presence of the singlet at δ 3.46 ppm provides further evidence for the formation of the proposed monoalkyl-monoaryl species **5c_{int}** (Figure 55). Due to the reaction not going to completion even after 19 hours the final ^1H NMR spectrum is more complex than would have been anticipated. The aliphatic region (2.5 – 1.5 ppm) of the spectrum was found to contain several resonances which could not be definitively assigned. Due to the fact that **5** is persistent within the reaction mixture alongside **5c** and **5c_{int}** there are a multitude of resonances present which could potentially be assigned to the methyl and t butyl groups of the (*rac*)-BIPHEN ligand (Figure 55). Furthermore, the tetraphenylnaphthalene standard leads to the complication of the aromatic region of the spectrum, with multiple resonances believed to be related to both **5c** and **5c_{int}** being obscured. The inclusion of tetraphenylnaphthalene within the reaction mixture from commencement of the reaction was necessary however, in order to allow for the calculation of yields as the reaction progressed.

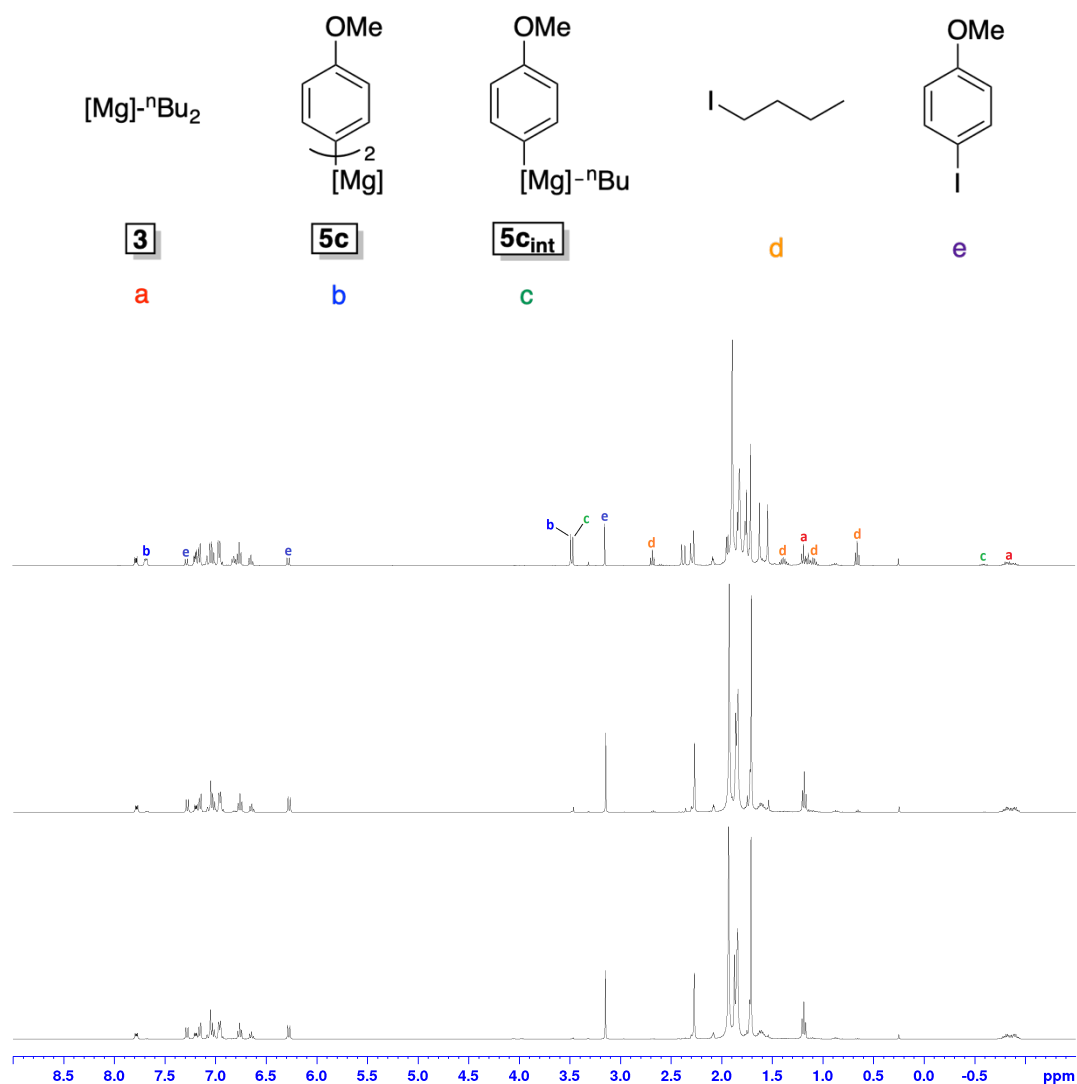
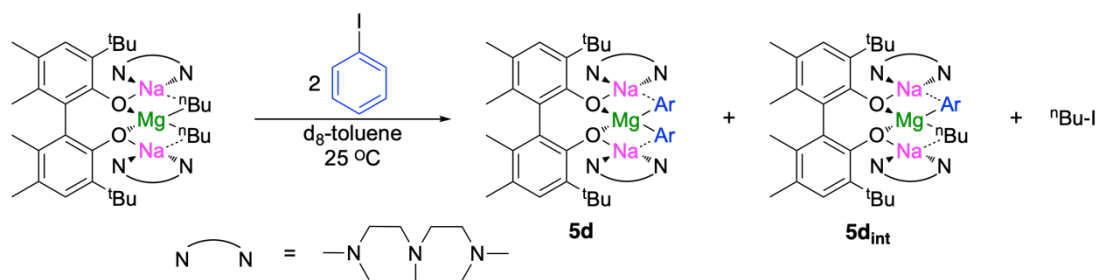


Figure 55: Overlay of ^1H NMR spectra for reaction of **5** with 4-iodoanisole after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d_8 -Tol, 300 K).

3.4.3.2 Non-Functionalised Substrates

The reactivity of **5** was next probed using iodobenzene, the simplest iodoarene which contains no functional groups that could influence the reactivity. Complex **5** was therefore anticipated to react slower with iodobenzene than with 2-iodoanisole but faster than 4-iodoanisole due to the unfavourable positioning of the electron donating methoxy substituent relative to the halogen atom. With this in hand, the reactivity of **5** was probed using two equivalents of iodobenzene in d_8 -toluene at ambient temperature while the reaction was monitored by ^1H NMR spectroscopy (Scheme 26).



Scheme 26: Reaction of **5** with iodobenzene.

The initial ^1H NMR spectrum of the reaction mixture after 15 minutes revealed no reaction to have occurred (Figure S6). The reaction was left to proceed for one hour after which time a ^1H NMR spectrum of the reaction mixture was collected and again showed no significant reaction to have occurred (Figure S6). To expand, the aliphatic region of the ^1H NMR spectrum showed only trace amounts of iodobutane to have formed. Furthermore, the n butyl ligands of **5** remained intact as evidenced by the presence of broad multiplet in the shielded region of the spectrum at δ -0.86 ppm along with a triplet at δ 1.17 ppm corresponding to the methylene and terminal methyl groups respectively. The reaction was left to continue for a further 12 hours at ambient temperature and a final ^1H NMR spectrum was collected. The spectrum showed that **5** was only partially converted to the corresponding diaryl magnesiate **5d** with concomitant formation of iodobutane, giving **5d** in a 57 % yield. Furthermore, two multiplets were observed in the shielded region of the spectrum at δ -0.86 and -0.61 ppm. The first of these resonances is indicative of the retention of the alkyl ligands of **5** while the appearance of the second resonance at δ -0.61 ppm is indicative of the formation of a monoalkyl-monoaryl intermediate **5d_{int}**. Turning to the aromatic region of the spectrum, a doublet was observed at δ 7.78 ppm which was assigned to the hydrogen atoms anisole ligands of **5d** and was found to be shifted downfield from free iodobenzene. Moreover, a second doublet was found to be present in trace amounts at δ 7.57 ppm and provides further evidence for the formation of the monoalkyl-monoaryl intermediate **5d_{int}**. The appearance of the resonances at δ -0.61 ppm and δ 7.57 ppm which have been tentatively assigned to this intermediate are consistent with the observations made during the reaction of **5** with the anisole derivatives outlined previously. Once again, due to the reaction not reaching completion, the aliphatic region of the spectrum ($1.5 - 2.5$ ppm) was found to contain multiple resonances which could not be definitively assigned (Figure S6). Based on observations made from previous reactions, these resonances are most likely representative of the t butyl and methyl ligands of the (*rac*)-BIPHEN ligand as well as the PMDETA donor ligand. Given that three magnesiate species, **5**,

5d and **5d_{int}**, are present simultaneously within the reaction mixture, multiple resonances in this region of the spectrum are to be expected. The presence of both **5d** and **5d_{int}** has also led to the complication of the aromatic region of the spectrum with the appearance of multiple overlapping resonances.

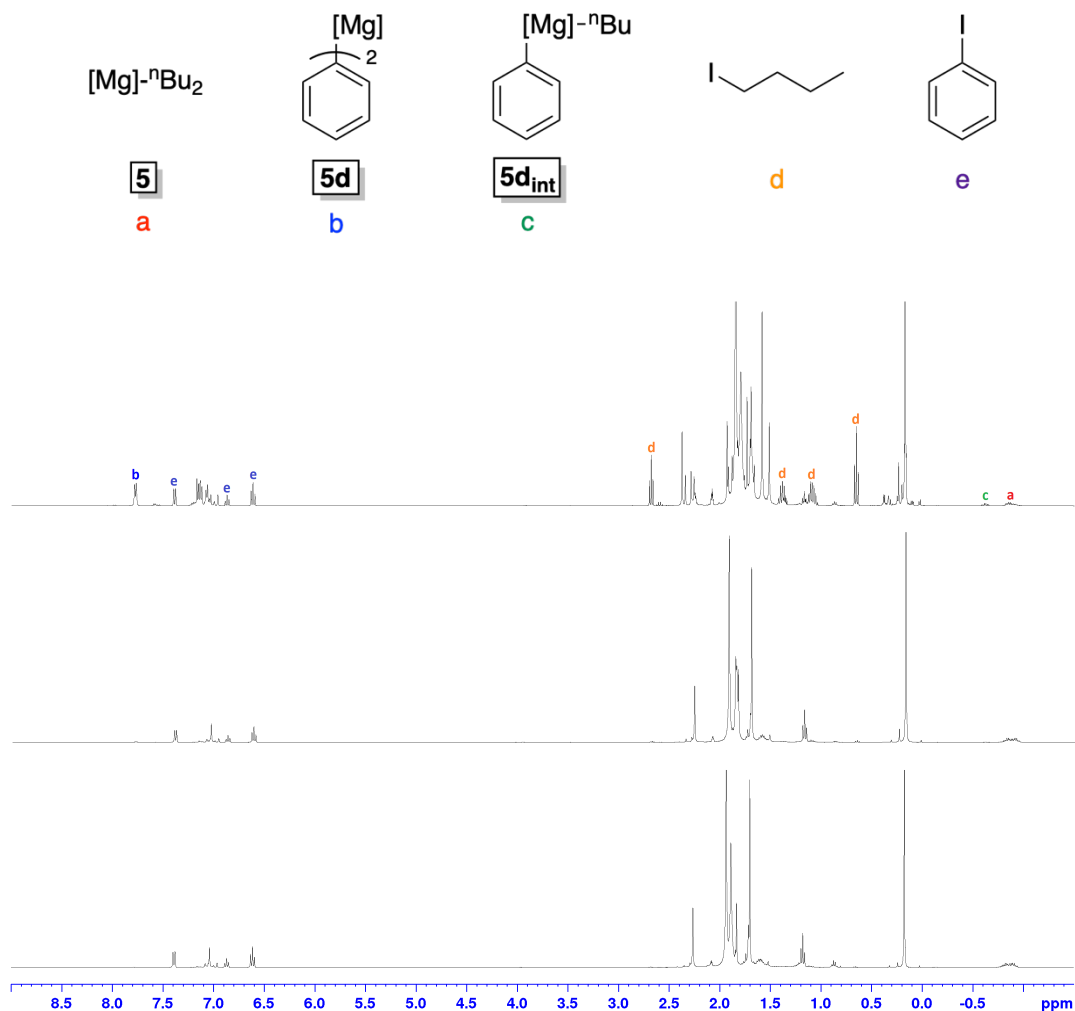
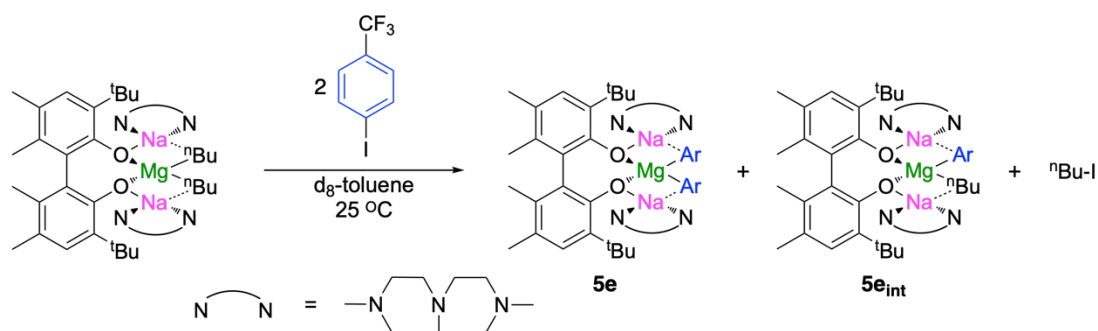


Figure 56: Overlay of the ^1H NMR spectra for reaction of **5** with iodobenzene after 15 minutes (bottom), 1 hour (middle), and 12 hours (top) (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

3.4.3.3 Electron Deficient Substrates

The reactivity of **5** was next investigated using the electron deficient substrates 1-iodo-4-(trifluoromethyl)benzene and 2-iodopyridine. Due to the electron deficient nature of these substrates, it was envisioned that **5** would display a high level of reactivity, as was the case for **3**. With this in mind, the reactivity of **5** was first probed using 1-iodo-4-(trifluoromethyl)benzene.



Scheme 27: Reaction of **5** with 1-iodo-4-(trifluoromethyl)benzene.

Isolated **5** was combined with two equivalents of 4-iodobenzotrifluoride in d_8 -toluene at ambient temperature and was monitored using ^1H NMR spectroscopy (Scheme 27). Analysis of the reaction mixture after 15 minutes showed the formation of two new multiplets in the aromatic region of the spectrum at δ 7.37 and 7.82 ppm which were assigned to the two sets of aromatic hydrogen atoms of the aryl ligands of **5e** along with concomitant formation of iodobutane as evidenced by the resonances located at δ 0.65, 1.11, 1.38 and 2.68 ppm (Figure 57). The appearance of these resonances is indicative that metal-halogen exchange has occurred; however, **5e** was obtained in an unexpectedly low yield of 24 %. Examining the ^1H NMR spectrum of the reaction mixture after this initial time period in more depth, the aliphatic region of the spectrum was found to contain two multiplets in the shielded region of the spectrum at δ -0.85 and -0.62 ppm. These resonances are characteristic of diastereotopic methylene hydrogen atoms and were therefore assigned as the MgCH_2 hydrogen atoms of the alkyl ligand of the monoalkyl-monoaryl intermediate **5e_{int}** (Scheme 27). The presence of these resonances is indicative that full conversion of **5** to **5e** had not been achieved after 15 minutes.

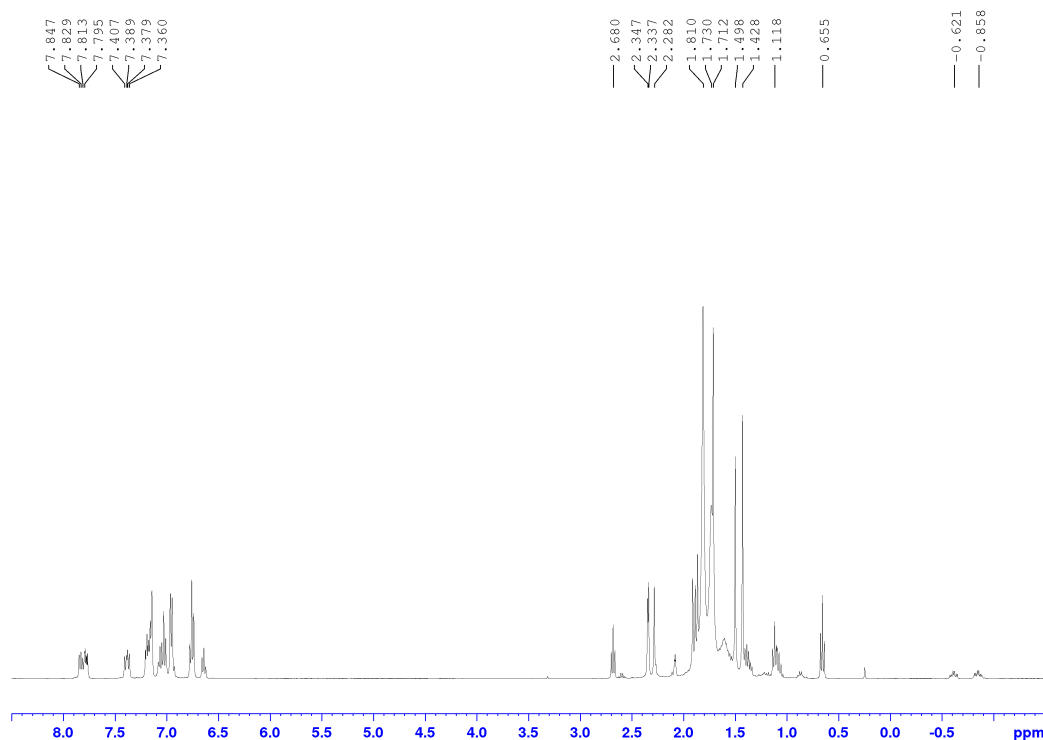


Figure 57: ^1H NMR Spectrum of the reaction of **5** with 1-iodo-4-(trifluoromethyl)benzene after 15 minutes (400 MHz, d_8 -Tol, 300 K).

The reaction was left to proceed for a further hour after which time the reaction mixture was again analysed by ^1H NMR spectroscopy (Figure 58). An increase in the intensity of the two doublets in the aromatic region at δ 7.40 and 7.81 ppm assigned to aryl ligands of **5e** was observed along with a similar increase in the amount of iodobutane contained within the reaction mixture. Surprisingly, given the strong electron withdrawing effect of the CF_3 group and the optimum positioning of the iodine atom at the most electron deficient *para* position, the reaction was found to be incomplete. To expand, trace amounts of the two resonances located in the shielded region of the spectrum at δ -0.85 and -0.62 ppm remained. Subsequent ^1H spectra were collected which continued to show traces of the intermediate species even after an additional two hours of reaction time. This would indicate that conversion of **5e_{int}** to the diaryl magnesiate **5e** is slow at ambient temperature. In order to assess whether or not full conversion of **5** to the corresponding diaryl magnesiate **5e** was possible, the reaction was allowed to continue for an addition 12 hours. Pleasingly, analysis of the ^1H NMR spectrum of the reaction mixture after this time showed that the resonances assigned to the intermediate species **5e_{int}** had been completely consumed as evidence by the disappearance of the resonances in the shielded region of the spectrum (Figure 58). Furthermore, the aliphatic region was now found to contain three distinct singlets at δ 1.49,

1.88 and 2.34 ppm in a ratio of 3:1:1 which were assigned to the ^tbutyl and methyl groups of the (*rac*)-BIPHEN ligand respectively. Throughout the reaction multiple resonances were observed in this region which could be attributed to these groups indicating the presence of multiple species within the solution. The presence of a single resonance for each functional group after 12 hours suggests that the reaction has reached completion. Turning to the aromatic region of the spectrum, two doublets were observed at δ 7.40 and 7.81 ppm in a 1:1 ratio. This is consistent with the formation of a disubstituted aromatic system as would be expected given the predicted structure of **5e** (Scheme 27). Returning to the aliphatic region of the spectrum, iodobutane remains present within the reaction mixture as evidenced by the resonances at δ 0.65, 1.09, 1.38 and 2.68 ppm which indicates that no further reactivity occurs between the newly generated **5e** and the reaction by-product. Despite the slow reactivity of **5** with 1-iodo-4-(trifluoromethyl)benzene, **5e** was obtained in a high yield of 84 %.

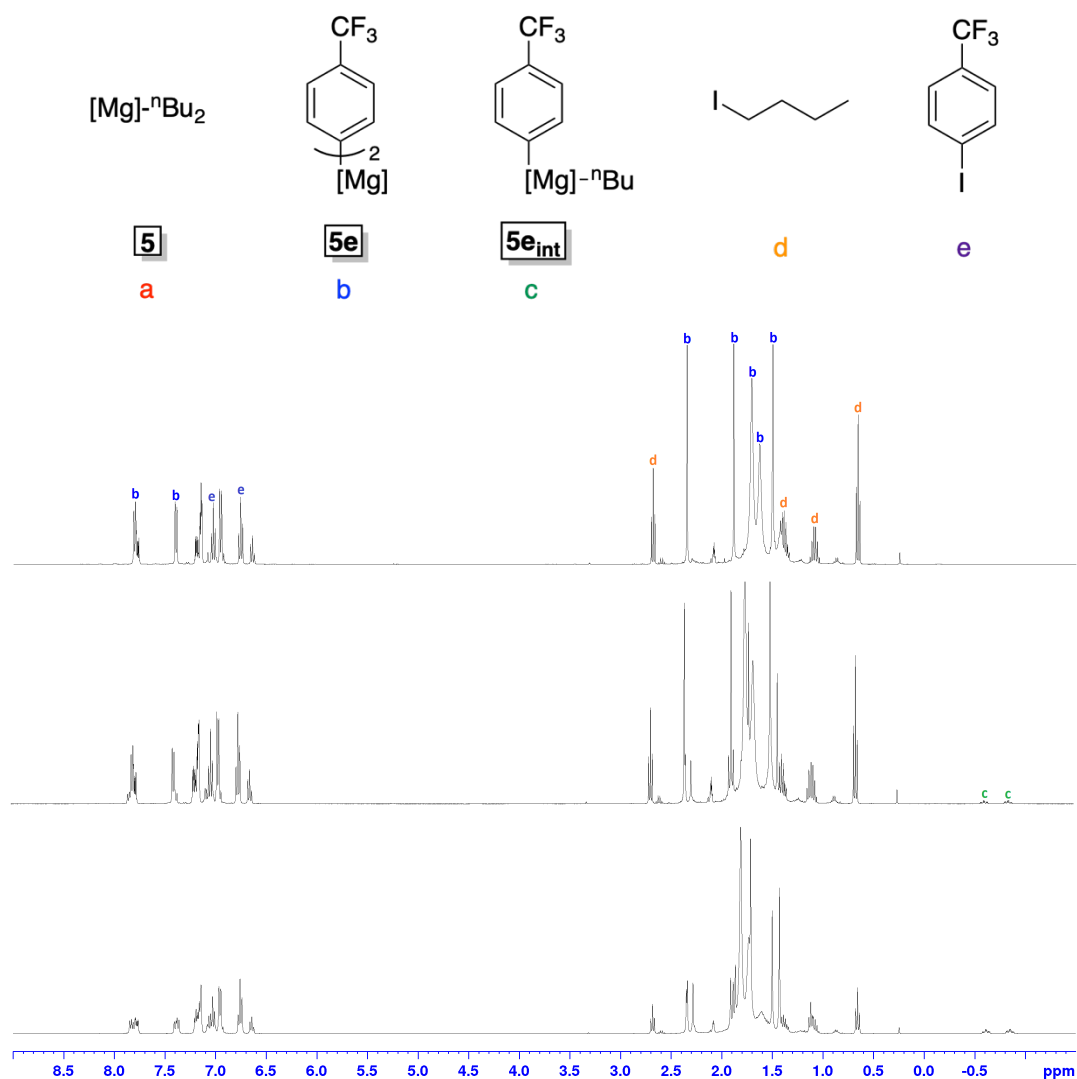
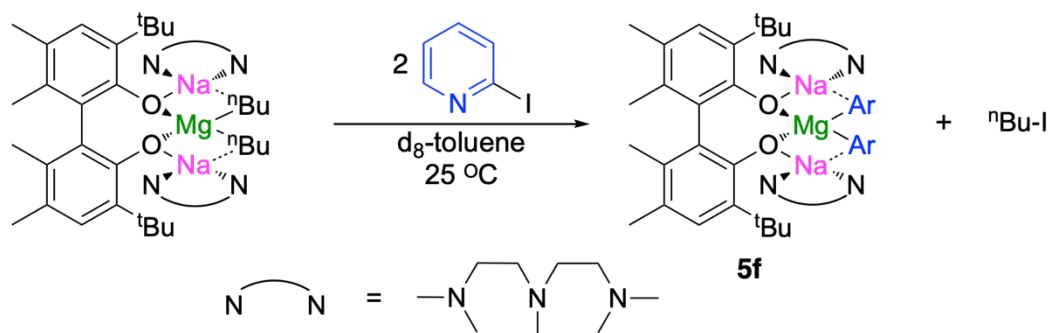


Figure 58: Overlay of 1H NMR spectra for reaction of **5** with 1-iodo-4-(trifluoromethyl)benzene after 15 minutes (bottom), 1 hour (middle) and 19 hours (top) (400 MHz, d_8 -Tol, 300 K).

The final substrate used to investigate the reactivity of **5** was 2-iodopyridine. Isolated **5** was therefore combined with two equivalents of 2-iodopyridine in d_8 -toluene in a J Youngs cap NMR tube and the reaction monitored using 1H NMR spectroscopy at ambient temperature (Scheme 28).



Scheme 28: Reaction of **5** with 2-iodopyridine.

A colour change from colourless to dark yellow was observed immediately upon addition of 2-iodopyridine to a solution of **5**. The reaction mixture was analysed after an initial 15-minute time period and pleasingly showed that **5** had been fully consumed to give **5f** in an 80% yield (Figure 59).

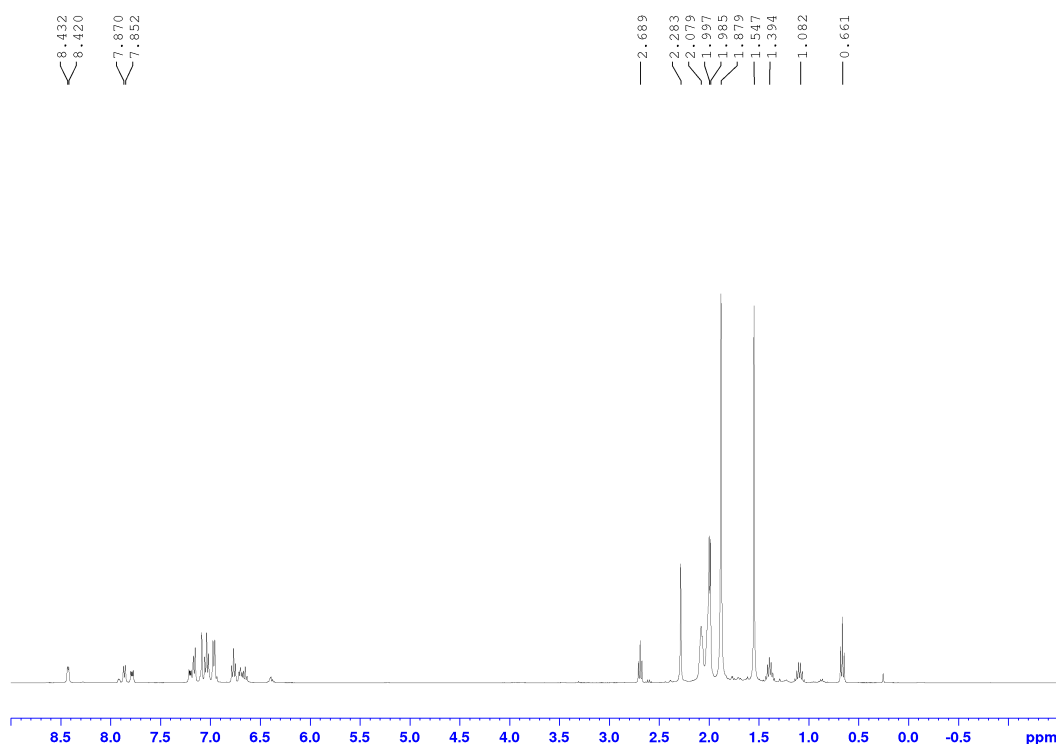


Figure 59: ^1H NMR Spectrum of the reaction of **5** with 2-iodopyridine after 15 minutes (400 MHz, $\text{d}_8\text{-Tol}$, 300 K).

Examining the ^1H NMR spectrum of the reaction mixture in more detail, the aromatic region of the spectrum was found to contain two doublets at δ 7.86 and 8.43 ppm which are indicative of the formation of new metal-pyridine complex. Formation of the metallated

pyridyl ligands was confirmed by the concomitant formation of iodobutane as evidenced by the resonances located at δ 0.66, 1.10, 1.39 and 2.68 ppm. The aliphatic region of the spectrum was found to contain two singlets at δ 1.54 and 2.28 ppm in a 3:1 ratio which were assigned to both ^tbutyl groups and a single set of methyl groups of the (*rac*)-BIPHEN ligand. A broad singlet was found to be present at δ 1.88 ppm and was assigned to the methyl groups attached to the terminal nitrogen atoms (NMe₂) of the PMDETA ligands. What appears as a doublet at δ 1.98 and 1.99 ppm is believed to be two singlets superimposed upon one another with one resonance representing the methylene groups of the PMDETA ligand while the other is thought to be the second set of methyl groups of the (*rac*)-BIPHEN ligand. No resonances were observed in the aliphatic or aromatic regions of the spectrum to suggest the formation of any intermediate species. Despite full consumption of **5** being observed, the reaction mixture was allowed to stand at ambient temperature for a further hour after which time it was analysed to assess the stability of the newly formed pyridyl magnesiate **5f** (Figure 60). Pleasingly the ¹H NMR spectrum of the reaction mixture showed no change, indicating no further reactivity between **5f** and iodobutane or any thermodynamic decomposition. A visual inspection of the reaction mixture revealed a further colour change from dark yellow to dark green accompanied by the deposition of a small amount of crystalline material. Attempts were made to isolate this crystalline material in order to characterise the solid-state structure of **5f**, however, the material proved to be of insufficient quality for analysis by single crystal X-ray diffraction.

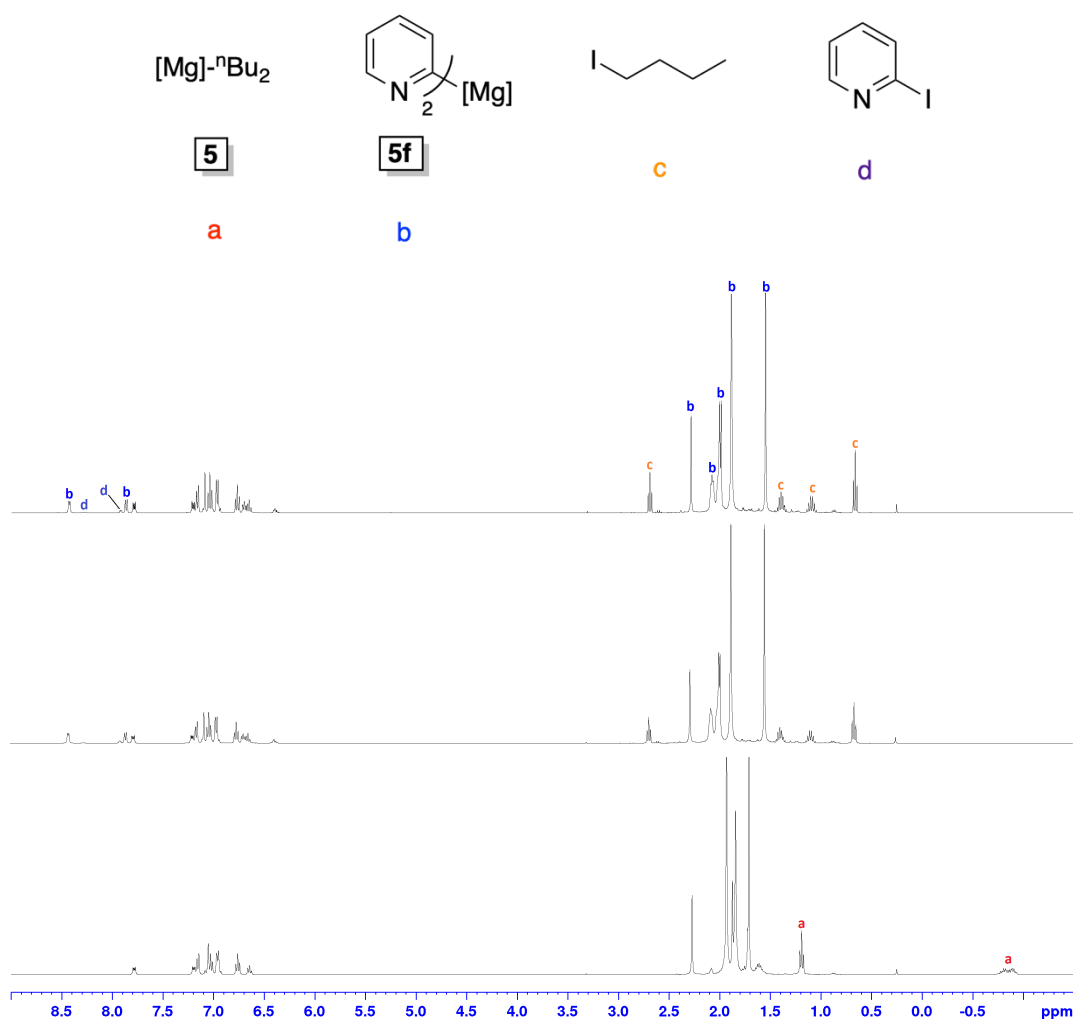


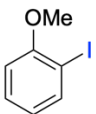
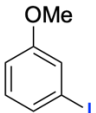
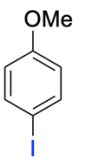
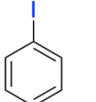
Figure 60: Overlay of ^1H NMR spectra for reaction of **5** (bottom) with 2-iodopyridine after 15 minutes (middle) and 1 hour (top) (400 MHz, d_8 -Tol, 300 K).

3.5 Donor Ligand Effects in Metal-Halogen Exchange

During our investigation into the reactivity of **3** and **5** a difference was noted in their reactivities. Complex **3** appeared to be the more reactive of the two substrates, reacting faster with both electron rich and electron poor substrates. Examining their reactivity with electron rich iodoanisoles in more detail (Table 5), **3** could be fully converted into the corresponding diaryl magnesiates **3a** and **3b** in high yields of 90 % with 2- and 3-iodoanisole while a drop-off in reactivity was observed for 4-iodoanisole giving **3c** in a lower yield of 79 %. In contrast to this however, full consumption of **5** was observed only when 2-iodoanisole was employed as the substrate, giving **5a** in a 77 % yield. Reaction with 3-iodoanisole achieved only partial conversion to **5b** in a moderate yield of 65 % while reaction of **5** with 4-iodoanisole gave only partial conversion and a low final yield of **5c** of only 20 %. Turning

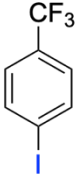
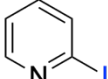
now to the reactivities of **3** and **5** with the simple aryl halide iodobenzene, **3** was once again found to be more reactive of the two magnesiates achieving double magnesium-iodine exchange with two equivalents of iodobenzene to give **3d** in a high yield of 90 %. Unlike **3**, **5** was only able to achieve partial conversion with iodobenzene, giving the desired diaryl magnesiate **5d** in a comparatively low yield of only 57 %.

Table 5: Maximum yield of diaryl magnesiate from reaction of **3a-d** and **5a-d** with 2-, 3-, 4-iodoanisole and iodobenzene. [a] – yield after 19 hours.

Substrate	Yield using 3 ^[a]	Yield using 5 ^[a]
	90 %	77 %
	91 %	65 %
	79 %	20 %
	90 %	57 %

Focussing now on the reactivity of **3** and **5** with the electron deficient substrates (Table 6), **3** was found to react rapidly with 1-iodo-4-(trifluoromethyl)benzene, giving **3e** in a high yield of 78 % within 15 minutes. Reaction of **5** with 1-iodo-4-(trifluoromethyl)benzene also gave the diaryl magnesiate **5e** in a high yield of 84 %; however, the reaction was much slower with full consumption of **5** only be achieved after prolonged reaction times greater than three hours. The reactivity of **3** and **5** were finally probed using the electron deficient heterocyclic substrate 2-iodopyridine. Unlike with previous substrates where **3** has been shown to be the more reactive of the two magnesiates, both **3** and **5** were able to achieve highly efficient double metal-halogen exchange within 15 minutes at ambient temperature in non-polar solvent giving the corresponding dipyriddy magnesiates **3f** and **5f** in 78 and 80 % yields respectively.

Table 6: Maximum yield of diaryl magnesiates **3e-f** and **5e-f** from reaction of **3** and **5** with 1-iodo-4-(trifluoromethyl)benzene and 2-iodopyridine.[a] – yield after 15 minutes [b] – yield after 19 hours.

Substrate	Yield using 3 ^[a]	Yield using 5
	87 %	84 % ^[b]
	78 %	80 % ^[a]

Given that both **3** and **5** contain the same alkyl and phenoxide ligands, the difference in their observed reactivities has been attributed to the variation of the Lewis donor ligands. Interestingly, the data obtained from *in situ* monitoring of the reactivities of **3** and **5** have shown the more reactive magnesiate to be produced using the smaller TMEDA ligand. This stands in contrast to the work of Knochel who found that for their work on dialkyl lithium magnesiates the larger tridentate donor PMDETA produced the more reactive magnesiate.¹⁶³ One potential explanation for the reduced reactivity of **5** lies in the increased coordination number of the sodium atoms. For **5**, inclusion of the tridentate donor PMDETA led to the two sodium atoms having a coordination number of five. Although the structure of **3** has not yet been characterised in the solid-state, its structure can be inferred from NMR spectroscopic data collected in hydrocarbon solution and from the solid-state structural characterisation of the related magnesiate **4** (Figure 16), from which it has been proposed that the sodium atoms of **3** will have a coordination number of four. Assuming this is correct, the sodium atoms of **3** possess a vacant coordination site available for the halogenated substrate to coordinate to through its functional group. Our group has already shown coordination of this type to occur through isolation of the reaction intermediate for the reaction between the lithium magnesiates [(*rac*)-BIPHEN]Li₂MgⁿBu₂(THF)₃ and [(*rac*)-BIPHEN]Li₂Mg(CH₂SiMe₃)₂(THF)₃ with 2-bromopyridine (Figure 41).⁹⁴ A similar type of interaction is therefore proposed to occur between the methoxy groups of the anisole derivatives and the nitrogen atom of 2-iodopyridine with the sodium atoms of **3** and **5**. Coordination of the substrate to the sodium atoms of **3** and **5** is likely to have an accelerating effect on the reaction by positioning the halogen atom in close proximity to the alkyl ligands thereby priming the substrate to undergo metal-halogen exchange. Therefore, it stands to

reason that due to its lower coordination number and vacant coordination site, the sodium atoms of **3** will be more readily accessible to allow for coordination of substrate molecules (Figure 61). This is consistent with the higher reactivity observed for **3** compared to **5** as no such vacant coordination site is accessible due to the increased denticity of the PMDETA ligand. Any coordination of the substrate to the sodium atoms of **5** will potentially have to occur with displacement of one of the coordinating arms of the PMDETA ligand which would lead to the observed decrease in reactivity (Figure 61). Lengthening of the Na-N bond length for a PMDETA solvated sodium atom upon formation of an secondary bridging interaction has previously been reported by our group.¹⁶⁹ Pre-coordination of the substrate in this way would explain why both **3** and **5** were found to react more efficiently with 2-iodoanisole than with 3- and 4-iodoanisole for which a marked decrease in reactivity was observed. This decrease could be due to the sub-optimal positioning of the halogen atoms relative to the coordinating methoxy groups of these latter two substrates. Furthermore, this would also explain why the reactivities of **3** and **5** with iodobenzene, which contains no functional groups capable of coordinating to the magnesiate, were found to be sluggish and give low yields of diaryl magnesiate, particularly for **5**.

Moreover, pre-coordination of the substrate in this way provides an explanation for the efficiency of both **3** and **5** in metal-halogen exchange with 2-iodopyridine. As the pyridine nitrogen atoms are stronger donors than the oxygen atoms of the methoxy groups of the anisole derivatives, displacement of a single arm of the PMDETA ligands becomes facile therefore allowing coordination of the substrate to the sodium atoms to occur (Figure 61). The ease at which this coordination takes place is reflected in the reactivities of the **3** and **5** with 2-iodopyridine which were found to be similar. Moreover, it has been shown from an examination of the solid-state structures of **4** and **6** (Chapter 2) that the donor ligand does not influence the bond lengths surrounding the magnesium centre and that the bond lengths of the reactive Mg-C alkyl bonds remain virtually identical between the two complexes. This further suggests that the observed difference in the reactivity of **3** and **5** arises from the ease at which pre-coordination of the substrate to the sodium atoms of the two complexes can occur.

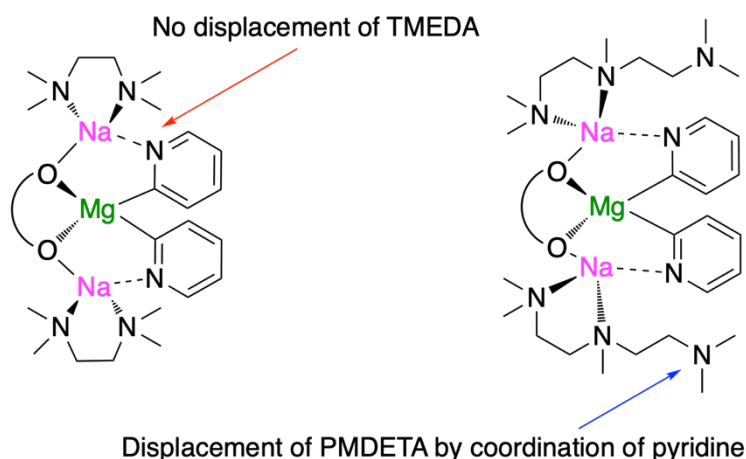


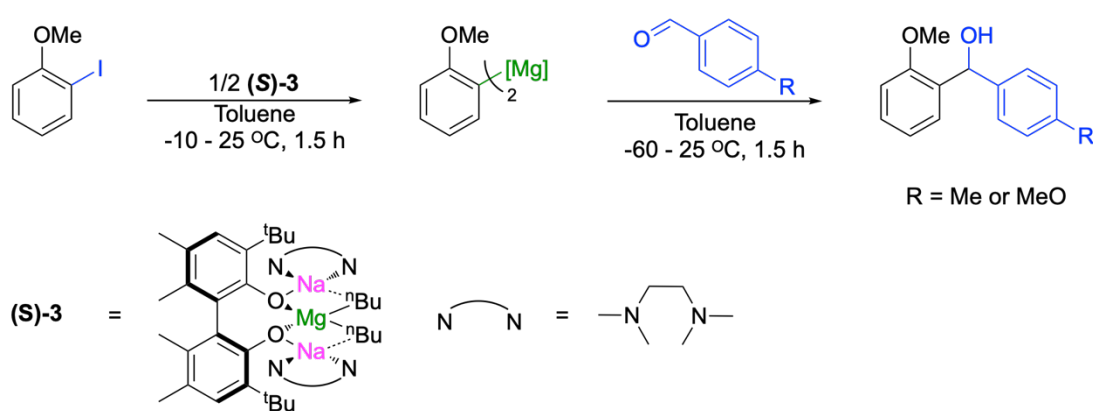
Figure 61: Possible structures of magnesiated intermediates for the reaction of **3** (left) and **5** (right) with 2-iodopyridine.

The reduction in reactivity upon moving from the bidentate donor TMEDA to the tridentate PMDETA may also be caused by the increase in steric bulk. Gros et al. have shown in a recent study that metal halogen exchange could only be achieved using a lower order lithium magnesiate containing the BIPHEN ligand.¹⁰⁵ Use of the bulkier TADDOL ligand furnished the product in lower yields while the usually more reactive higher order magnesiate was found to be less reactive than its lower order counterpart. It could therefore be possible that inclusion of the bulkier PMDETA restricts access to the magnesium centre which in turn hinders the formation of the desired diaryl species. This could also provide an explanation as to why larger amounts of the monoalkyl-monoaryl intermediates were observed in the ¹H NMR spectra of the reaction mixtures of **5** with 3- and 4-iodoanisole when compared to the analogous reaction of these substrates with **3**.

3.6 Scale up of Reaction and Extension to Asymmetric Synthesis

With the data gathered from the NMR spectroscopic experiments in hand, it was deemed prudent to carry out the reactions on a larger scale to assess the synthetic applicability of the sodium magnesiates. Furthermore, the reactions were carried out using enantiopure (*S*)-BIPHEN, in order to produce the corresponding chiral alcohol via electrophilic quenching of the metallated intermediate with a suitable aldehyde. Having demonstrated its superior reactivity, the enantiopure form of (*S*)-**3** was utilised for these reactions. To this end, the reaction was scaled up to a 0.5 mmol scale and performed using standard Schlenk techniques. The active magnesiate (*S*)-**3** was generated *in situ* from a combination of (*S*)-BIPHEN, PhCH₂Na, MgⁿBu₂ and TMEDA in a 1:2:1:2 ratio using toluene as the reaction

solvent. Beginning the investigation with 2-iodoanisole, two equivalents of the iodinated substrate were added to a solution of **(S)**-**3** at ambient temperature and the reaction was left to proceed for 1.5 hours after which time the reaction was cooled to $-60\text{ }^{\circ}\text{C}$ before the metallated intermediate was trapped by addition of two equivalents of *p*-tolualdehyde to give the corresponding alcohol **11** (Scheme 29). Although metal-halogen exchange can be carried out at room temperature, cryogenic conditions are required for the electrophilic quench in order to enhance the enantioselectivity and prevent racemisation. A temperature of $-60\text{ }^{\circ}\text{C}$ was chosen as the temperature at which this should be carried out based on precedence in the literature for similar reactions involving lithium magnesiates.^{94,103–105}

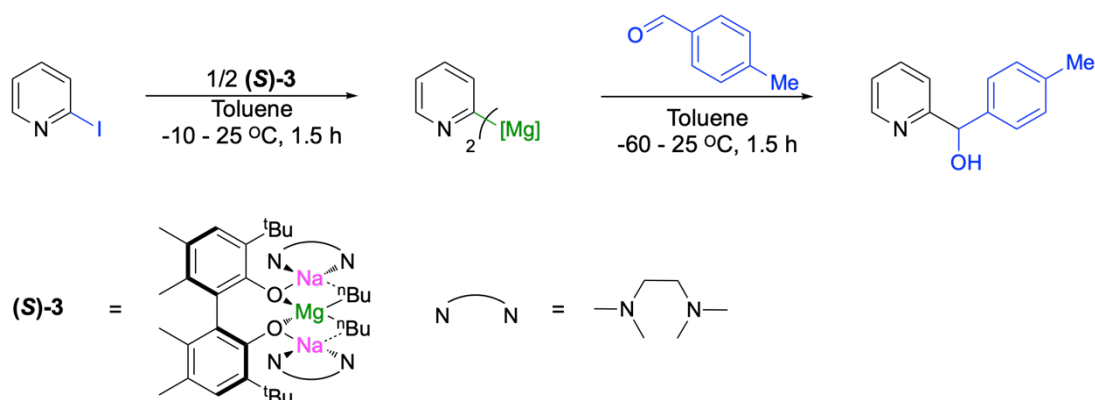


Scheme 29: Reaction of **(S)**-**3** with 2-iodoanisole followed by electrophilic quenching to give **11** (where R = Me) and **12** (where R = OMe).

Pleasingly, after purification, the desired chiral alcohol **11** was obtained in a 55 % yield with enantiomeric excess (*ee*) of 38 %. This result demonstrates that sodium magnesiates can be used in metal-halogen on a synthetically relevant scale and allow for the synthesis of chiral alcohols through electrophilic quenching of the metallated intermediates with aldehydes. Comparing the final yield of the chiral alcohol **11** obtained using standard Schlenk techniques with that of metallated intermediate **3a** obtained in the NMR spectroscopic experiments suggest the reaction to be less efficient on a larger scale. The reaction was repeated under the same conditions using *p*-anisaldehyde to furnish the corresponding chiral alcohol **12** in a 56 % yield and a 42 % *ee* indicating a consistency in the reactivity of **(S)**-**3** (Scheme 29). The modest yield of **12** obtained after electrophilic quenching of the reaction was initially attributed to the sluggish reactivity of the metallated intermediate with the electron rich *p*-anisaldehyde at cryogenic temperatures. Subsequent analysis of the crude reaction mixture by GCMS however showed the crude product mixture to contain a substantial amount of

unreacted 2-iodoanisole which indicates the metal-halogen exchange 2-iodoanisole with **(S)-3** to be inefficient under these conditions.

With the results from the reaction of **(S)-3** with electron rich 2-iodoanisole in hand, the reaction was repeated using the electron deficient substrate 2-iodopyridine. To this end, two equivalents of 2-iodopyridine were added to a solution of **(S)-3** in toluene and the reaction was allowed to proceed for 1.5 hours after which the reaction mixture was cooled to $-60\text{ }^{\circ}\text{C}$ and two equivalents of tolualdehyde were added to furnish the chiral alcohol **13** (Scheme 30). Upon work up and purification of the reaction mixture the corresponding chiral 2-pyridylcarbinol **13** was isolated in a 42 % yield with an *ee* of 22 %. Once again, this isolated yield is considerably less than the yield of magnesiated intermediate **3f** that was produced when the reaction was carried out at a lower scale. Analysis of the crude product mixture by GCMS once again showed significant amounts of unreacted 2-iodopyridine. This is consistent with the finding of the reaction of 2-iodoanisole with **(S)-3** and suggests that optimisation of the reaction conditions may be required in order to maximise the efficiency of metal-halogen exchange.



Scheme 30: Reaction of **(S)-3** with 2-iodopyridine followed by electrophilic quench to give **13**.

3.7 Conclusions and Outlook

This work has furthered the knowledge and understanding of sodium magnesiates by expanding their synthetic applications to include metal-halogen exchange. To the best of our knowledge this work is the first report concerning the use of such magnesiates in metal-halogen exchange. Utilising the mixed alkyl/phenoxide sodium magnesiates [(*rac*)-BIPHEN] $\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{TMEDA})_2$ (**3**) and [(*rac*)-BIPHEN] $\text{Na}_2\text{Mg}^n\text{Bu}_2(\text{PMDETA})_2$ (**5**) highly efficient

double magnesium-iodine exchange was achieved using electron rich and electron poor substrates. Furthermore, the high solubility of these magnesiates in hydrocarbon solvents allowed for these reactions to be carried out in a non-polar medium. This latter feature is of importance when considering the potential for use of bimetallic species in metal-halogen exchange on an industrial scale as it allows for reactions to transition away from highly volatile solvents such as diethyl ether or THF. Complex **3** generally possesses a higher level of reactivity when compared to **5** and which could infer greater participation of the alkali metal in the exchange process than previously proposed. The fact that **3** which contains four coordinate sodium atoms was found to be more reactive than **5** which contains five coordinate sodium atoms has led us to conclude that the reactivity of these two magnesiates is dependant to some degree on substrate coordination. By incorporating the larger tridentate donor PMDETA in **5** a previously vacant coordination site on the sodium atom has been occupied, therefore preventing the substrate from coordinating to the magnesiate. For **3** where this coordination site remains available the substrate can coordinate freely to the magnesiate without interference by the ligand thereby increasing the rate of the reaction.

The enantiopure (*S*)- form of the BIPHEN ligand was used to create a chiral variant of **3**, (*S*)-**3**. This new chiral sodium magnesiate was used in reaction with 2-iodoanisole and 2-iodopyridine to produce the corresponding chiral alcohols **11-13** upon electrophilic quenching of the metalated intermediates with aldehydes. To the best of our knowledge this is the first reported case of such complexes being used for these applications. Only modest yields of alcohols **11-13** were obtained with analysis of the crude reaction mixtures by GCMS showing there to be unreacted 2-iodoanisole and 2-iodopyridine. Compared to the high levels of conversion achieved during NMR scale reactions, the low yields of chiral alcohols **11-13** suggest that the conditions employed for the metal-halogen exchange reactions involving (*S*)-**3** require extensive optimisation. Despite the poor yield of chiral alcohol, no product could be identified in the GCMS trace of the crude reaction mixture to suggest that the (*S*)-**3** had participated in any competing side reactions such as alkylation of the aldehyde upon electrophilic quenching. This does not account for the low yield of alcohol obtained but does show that the (*S*)-**3** has good levels of selectivity which could have important implications for its use in the presence of sensitive functional groups.

3.8 Further work

It was during this work that our investigations were disrupted by the COVID-19 pandemic and as a result, it was not possible to fully investigate the reactivity of **3-10**. This disruption has therefore left several areas in which this work could be expanded. One such area of this work which merits further investigation is the scope of reaction for magnesiates **3** and **5**. As the primary aim of the investigation into the reactivity of **3** and **5** was to establish proof of concept and to assess if double metal-halogen exchange was possible using these magnesiates, all reactions were carried out with inclusion of the internal standard from the outset of the reaction. This in turn led to the complication of the ^1H NMR spectra, particularly the aromatic region, which resulted in some resonances not being clearly observed. It could therefore be beneficial to repeat these reactions without the standard present in order to give a more detailed insight into aromatic region of each spectrum. Magnesiates **3** and **5** have nonetheless been shown to be efficient reagents in metal-halogen exchange, however, their reactivity only covers a small number of substrates and an even more limited number of functional groups. It would therefore also be prudent to extend the substrate scope to include more complex substrates especially those which contain sensitive functional groups such as esters or nitro groups. This work could initially be carried out on the NMR scale to establish proof of concept before being carried out on a larger scale. By carrying out the exchange on a larger scale this would also provide an opportunity for optimisation of the reaction, something which this work has also flagged as a potential issue requiring further work, as well as further functionalisation of the metallated arylmagnesium intermediates through electrophilic quenching or transition metal cross coupling. Further functionalisation of the metallated intermediates also provides the opportunity to employ these magnesiates in the synthesis of 'real world' molecules to prove their synthetic utility.

Moreover, the reactivity of n -butyl containing magnesiates **7** and **9** should be investigated as a matter of priority as no data on their reactivity was obtained prior to the closure of the University due to COVID-19. To this end, the reactivity of **7** and **9** as metal-halogen exchange reagents should be undertaken using the same substrate scope as used for **3** and **5** as this would provide an ideal opportunity for a comparison between the reactivity of the four complexes. This comparison could potentially give a further insight into the reactivity of the magnesiate complexes containing bi- and tridentate amine donors. Based on the trend in reactivity observed for **3** and **5**, the reactivity of **7** and **9** should resemble that of **3** as (*R,R*)-TMCD and (*S,S*)-TMCD are bidentate donors. If this were the case, the reactivity of **7** and

9 could have important implications regarding the availability of a vacant coordination site on the sodium atoms and the effect this has on the overall reactivity of the sodium magnesiates. If **7** and **9** were to prove to be efficient metal-halogen exchange reagents using a limited substrate scope it would be sensible to expand the scope in line with that was proposed above for **3** and **5** and to undertake an optimisation of the reaction as a whole. Furthermore, as **7** and **9** are chiral magnesiates, electrophilic quenching of the metallated intermediate should generate a chiral product. Assuming the reaction has been properly optimised and good yields of the final product can be achieved after electrophilic quenching, the reaction product should be analysed to determine if any enantiomeric excess (*ee*) has been achieved and if **7** or **9** can provide a cheap and cost-effective entry point into asymmetric metal-halogen exchange.

This work revealed a surprising difference in the reactivity of the two sets of magnesiates containing the ⁿbutyl and CH₂SiMe₃ alkyl ligands. It has so far only been possible to carry out preliminary reactions using **4** with the electron deficient substrates 1-iodo-4-(trifluoromethyl)benzene and 2-iodopyridine; however, these reactions clearly showed lower levels of conversion to the corresponding diaryl magnesiate after one hour than what was achieved using **3**. The low reactivity observed for **4** is all the more surprising given the recent work of Hevia and co-workers who have utilised the CH₂SiMe₃ ligand for the synthesis and characterisation of alkali metal manganates which were subsequently shown to be efficient metal-halogen exchange reagents.¹⁷⁰ As a result, a piece of further work associated with this project that could give interesting results would be to fully investigate the reactivity of **4**, **6**, **8** and **10**. Although preliminary reactions involving **4** appear to show that inclusion of the CH₂SiMe₃ produces a less reactive magnesiate for metal-halogen exchange compared to those containing the ⁿbutyl ligand, the reactivity of **6**, **8** and **10** should also be investigated in metal-halogen exchange to assess if the poor reactivity is unique to **4** or is a general trend in all the magnesiates containing the CH₂SiMe₃ alkyl ligand. If the results of these studies show that magnesiates **4**, **6**, **8** and **10** have low levels of reactivity in metal-halogen exchange then their reactivity as metallating agents should be investigated as there is a strong precedence in the literature for bimetallic complexes containing the CH₂SiMe₃ ligand functioning as powerful bases. As with the metal-halogen exchange studies, the investigation into the reactivity of these magnesiates as metallating reagents could begin on the NMR scale using simple substrates which contain acidic hydrogen atoms in order to establish proof of concept. From here the substrate scope could be expanded to include more complex

substrates with less acidic hydrogen atoms to assess the relative strength of the bases before introducing sensitive functional groups and increasing the scale of the reaction to allow for further functionalisation of the metallated intermediates in order to establish their synthetic utility.

3.9 Experimental

3.9.1 Preparation of Magnesiates **3** and **5**

3.9.1.1 [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ (**3**)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time TMEDA (0.15 ml, 1 mmol) was added to give a pale-yellow solution. The solution was concentrated *in vacuo* and the solution stored at –33 °C. After storage at sub-ambient temperature the solution was filtered to yield [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ as a microcrystalline powder (0.216 g, 56 % yield). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ –0.79 (2H, m, MgCH₂), –0.314 (2H, m, 2 x MgCH₂), 1.25 (6H, t, CH₃ butyl), 1.69 [9H, bs, C(CH₃)₃ (*rac*)-BIPHEN], 1.79 (8H, bs, CH₂, TMEDA), 1.80 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 1.85 [33H, bs, CH₃ TMEDA and C(CH₃)₃ (*rac*)-BIPHEN], 2.22 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 7.18 [2H, s, Ph (*rac*)-BIPHEN]. ¹³C NMR (100.62 MHz, 298 K, C₆D₆): δ 8.8 (2 x MgCH₂), 14.9 (2 x CH₃, butyl), 17.5 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 31.7 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 32.8–33.7 (CH₂, butyl), 35.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 45.5 (TMEDA), 57.0 (TMEDA), 119.6, 127.3, 132.1, 132.7, 135.9, 162.7 [Ph, (*rac*)-BIPHEN].

3.9.1.2 [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (**5**)

[(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ was prepared by the addition of a solution of (*rac*)-BIPHEN-H₂ (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at –10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to create a white suspension. The suspension was stirred at –10 °C for 5 minutes after which time PMDETA (0.21 ml, 1 mmol) was added to give a white suspension. The suspension was concentrated *in vacuo* then heated gently to give a colourless solution. The solution was then allowed to cool slowly to ambient temperature to give colourless crystals of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (0.245 g, 56 % yield). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ –0.75 (4H, m, 2 x MgCH₂), 1.26 (6H, t, CH₃ butyl), 1.77 [18H, bs, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.82

(16H, bs, CH₂ PMDETA), 1.86 (6H, s, CH₃ PMDETA), 1.90 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 1.93 (24H, bs, CH₃ PMDETA), 2.31 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 7.14 (2H, s, Ph-H (*rac*)-BIPHEN). ¹³C NMR (100.62 MHz, 298 K, C₆D₆): δ 8.8 (2 x MgCH₂), 14.9 (2 x CH₃, butyl), 18.0 [2 x CH₃, (*rac*)-BIPHEN], 20.8 [2 x CH₃, (*rac*)-BIPHEN], 32.3 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 33.5 (CH₂, butyl), 34.0 (CH₂, butyl), 35.5 [2 x C(CH₃)₃, (*rac*)-BIPHEN], 44.2 (PMDETA), 45.6 (PMDETA), 54.1 (PMDETA), 57.1 (PMDETA), 119.9, 126.6, 132.6, 134.1, 134.8, 163.1 [Ph, (*rac*)-BIPHEN].

3.9.2 General Procedure for NMR Scale Metal-Halogen Exchange Reactions for **3a-f**

All reactions were carried out on an NMR scale using a 2:1 ratio of substrate to magnesiate. [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ (**3**) (0.029 g, 0.0377 mmol) was combined with tetraphenylnaphthalene (0.010 g, 0.025 mmol) as the internal standard. D₈-toluene (0.5 ml) was then added, and the resulting suspension was sonicated to give a homogeneous solution. The desired substrate (0.0754 mmol) was added, and the reaction was monitored at regular intervals by ¹H NMR spectroscopy. Yields were obtained from NMR spectroscopic integrals relative to the internal standard.

3.9.3 General Procedure for NMR Scale Metal-Halogen Exchange Reactions for **5a-f**

All reactions NMR reactions were carried out using a 2:1 ratio of substrate to magnesiate. [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (**5**) (0.033 g, 0.0377 mmol) was combined with tetraphenylnaphthalene (0.010 g, 0.025 mmol) or hexamethylcyclotrisiloxane as the internal standard in a J Young's capped NMR tube. D₈-toluene (0.5 ml) was then added, and the resulting suspension was sonicated to give a homogeneous solution. The desired substrate (0.0754 mmol) was then added, and the reaction was monitored at regular intervals by ¹H NMR spectroscopy. Yields were obtained from NMR spectroscopic integrals relative to the internal standard.

3.9.4 Calculation of NMR yields

All NMR yields were based on the No. moles of **3** or **5** which were calculated using a known amount of internal standard. Based on the integration value of a selected resonance of the internal standard and of the product, the No. moles of the product can be calculated using equation 1:

$$\text{equation 1. } \frac{\text{Integration of Sample} \times \text{No. H atoms of Standard}}{\text{Integration of Standard} \times \text{No. H atoms of Sample}} \times \text{No. moles of standard}$$

The final yield was then be calculated from the No.moles of the product and the No.moles of magnesiate according to equation 2:

$$\text{equation 2. } \frac{\text{No. moles of product}}{\text{No. Moles of magnesiate}} \times 100$$

3.9.5 NMR Scale Metal-Halogen Exchange Reactions

Tetraphenylnaphthalene was chosen as the internal standard due to its high solubility and abundance of stand-alone resonances which could be used for yield calculations. All reactions, with the exception of the reaction of **5** with iodobenzene, were carried out in the presence of tetraphenylnaphthalene in order to allow for the reaction to be monitored *in situ* and yields to be calculated at various time points, not just when the reaction had reached completion.

3.9.5.1 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄OMe)₂(TMEDA)₂ **3a**

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.60 [18H, s, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.63 [24H, bs, N(CH₃)₂ TMEDA], 1.69 (8H, bs, CH₂, TMEDA), 1.87 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.31 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 3.33 (6H, s, 2 x CH₃ C₆H₄OMe), 6.55 (2H, d, Ar C₆H₄OMe), 7.11 [2H, s, Ar (*rac*)-BIPHEN], 7.94 (2H, d, Ar C₆H₄OMe) (90 % yield by NMR).

Tetraphenylnaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.2 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄OMe)₂(TMEDA)₂ **3b**

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.58 (8H, vbs, CH₂, TMEDA), 1.65 [24H, bs, N(CH₃)₂ TMEDA], 1.68 [18H, s, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.88 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.29 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 3.54 (6H, s, 2 x CH₃ C₆H₄OMe), 7.17 [2H, s, Ar (*rac*)-BIPHEN], 7.50 (4H, m, Ar C₆H₄OMe) (91 % yield by NMR).

Tetraphenylnaphthalene Standard - ^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.3 [(*rac*)-BIPHEN] $\text{Na}_2\text{Mg}(\text{C}_6\text{H}_4\text{OMe})_2(\text{TMEDA})_2$ **3c**

^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 1.60 (8H, vbs, CH_2 , TMEDA), 1.68 [24H, bs, $\text{N}(\text{CH}_3)_2$ TMEDA], 1.70 [18H, bs, 2 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 1.89 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 2.31 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 3.44 (6H, s, 2 x CH_3 $\text{C}_6\text{H}_4\text{OMe}$), 7.20 [s, Ar-H (*rac*)-BIPHEN], 7.82 (4H, d, Ar-H $\text{C}_6\text{H}_4\text{OMe}$) (79 % yield by NMR).

Tetraphenylnaphthalene Standard - ^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.4 [(*rac*)-BIPHEN] $\text{Na}_2\text{Mg}(\text{C}_6\text{H}_5)_2(\text{TMEDA})_2$ **3d**

^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 1.55 (8H, vbs, CH_2 , TMEDA), 1.62 [24H, bs, $\text{N}(\text{CH}_3)_2$ TMEDA], 1.68 [18H, bs, 2 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 1.88 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 2.30 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 7.19 [2H, s, Ar-H (*rac*)-BIPHEN], 7.92 (4H, d, Ar-H C_6H_5) (90 % yield by NMR).

Tetraphenylnaphthalene Standard - ^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.5 [(*rac*)-BIPHEN] $\text{Na}_2\text{Mg}(\text{C}_6\text{H}_4\text{CF}_3)_2(\text{TMEDA})_2$ **3e**

^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 1.51 (8H, vbs, CH_2 , TMEDA), 1.56 [24H, bs, $\text{N}(\text{CH}_3)_2$ TMEDA], 1.62 [18H, bs, 2 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 1.82 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 2.25 [6H, s, 2 x CH_3 , (*rac*)-BIPHEN], 7.15 [2H, s, Ar (*rac*)-BIPHEN], 7.36 (4H, d, Ar-H $\text{C}_6\text{H}_4\text{CF}_3$), 7.93 (4H, d, Ar-H $\text{C}_6\text{H}_4\text{CF}_3$). $^{19}\text{F}\{^1\text{H}\}$ (376.4 MHz, 300 K, d_8 -tol): $-\text{61.89}$ (s, 2 x CF_3 , $\text{C}_6\text{H}_4\text{CF}_3$) (87 % yield by NMR).

Tetraphenylnaphthalene Standard - ^1H NMR (400.13 MHz, 300 K, d_8 -tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.6 [(*rac*)-BIPHEN]Na₂Mg(Py)₂(TMEDA)₂ 3f

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.51 [18H, bs, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.83 [24H, bs, N(CH₃)₂ TMEDA], 1.90 (8H, vbs, CH₂, TMEDA), 1.91 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.26 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 7.08 [s, Ar (*rac*)-BIPHEN], 7.90 (3H, m, Py), 8.30 (2H, d, Py) (78 % yield by NMR).

Tetraphenylnaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.7 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄OMe)₂(PMDETA)₂ 5a

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.63 [18H, s, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.72 [6H, bs, 2 x NCH₃, PMDETA] 1.81 (24H, bs, 4 x (NCH₃)₂ PMDETA), 1.85 (8H, m, CH₂ PMDETA), 1.89 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 1.96 (8H, m, PMDETA), 2.32 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 3.35 (6H, s, 2 x CH₃ C₆H₄OMe), 6.57 (2H, d, Ar-H C₆H₄OMe), 7.13 [2H, s, Ar-H (*rac*)-BIPHEN], 7.91 (2H, d, Ar-H C₆H₄OMe) (77 % yield by NMR).

Tetraphenylnaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.8 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄OMe)₂(PMDETA)₂ 5b

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.61 [18H, s, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.66 (PMDETA), 1.77 [vbs, PMDETA], 1.84 (vbs, PMDETA), 1.93 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.35 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 3.60 (6H, s, 2 x CH₃ C₆H₄OMe), 7.16 [s, Ar-H (*rac*)-BIPHEN], 7.40 (5H, m, Ar-H C₆H₄OMe) (65 % yield by NMR).

Tetraphenylnaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.9 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄OMe)₂(PMDETA)₂ 5c

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.53 [s, C(CH₃)₃ (*rac*)-BIPHEN], 1.61 [s, C(CH₃)₃ (*rac*)-BIPHEN], 1.70 [s, C(CH₃)₃ (*rac*)-BIPHEN], 1.74 (bs, PMDETA), 1.81 (vbs, PMDETA), 1.88 (bs, PMDETA), 1.92 [s, CH₃, (*rac*)-BIPHEN], 1.94 [s, CH₃, (*rac*)-BIPHEN], 2.26 [s, CH₃, (*rac*)-BIPHEN],

2.29 [s, CH₃, (*rac*)-BIPHEN], 2.35 [s, CH₃, (*rac*)-BIPHEN], 2.38 [s, CH₃, (*rac*)-BIPHEN], 3.48 (CH₃ C₆H₄OMe), 7.68 (m, Ar-H C₆H₄OMe) (20 % yield by NMR).

Tetraphenylinaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.10 [(*rac*)-BIPHEN]Na₂Mg(C₆H₅)₂(PMDETA)₂ **5d**

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.51 [s, C(CH₃)₃ (*rac*)-BIPHEN], 1.58 [bs, C(CH₃)₃ (*rac*)-BIPHEN], 1.69 (bs, PMDETA), 1.73 (s, PMDETA), 1.79 (vbs, PMDETA), 1.84 (vbs, PMDETA), 1.93 [s, CH₃, (*rac*)-BIPHEN], 2.25 [s, CH₃, (*rac*)-BIPHEN], 2.28 [s, CH₃, (*rac*)-BIPHEN], 2.34 [s, CH₃, (*rac*)-BIPHEN], 2.37 [s, CH₃, (*rac*)-BIPHEN], 7.78 (d, Ar C₆H₅) (57 % yield by NMR).

3.9.5.11 [(*rac*)-BIPHEN]Na₂Mg(C₆H₄CF₃)₂(PMDETA)₂ **5e**

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.49 [18H, bs, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.62 (20H, vbs, PMDETA), 1.70 [26H, vbs, PMDETA], 1.88 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.34 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 7.14 [s, Ar (*rac*)-BIPHEN], 7.40 (4H, d, Ar C₆H₄CF₃), 7.81 (4H, d, Ar C₆H₄CF₃).
¹⁹F{¹H} (376.4 MHz, 300 K, d₈-tol): -61.77 (s, 2 x CF₃, C₆H₄CF₃) (87 % yield by NMR).

Tetraphenylinaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.5.12 [(*rac*)-BIPHEN]Na₂Mg(Py)₂(PMDETA)₂ **5f**

¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 1.55 [18H, bs, 2 x C(CH₃)₃ (*rac*)-BIPHEN], 1.88 [24H, bs, 4 x N(CH₃)₂ PMDETA], 1.98 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 2.00 (16H, vbs, PMDETA), 2.07 (8H, CH₂ PMDETA), 2.28 [6H, s, 2 x CH₃, (*rac*)-BIPHEN], 6.70 (2H, m, Py), 7.09 [2H, s, Ar-H (*rac*)-BIPHEN], 7.87 (2H, m, Py), 8.43 (2H, d, Py) (80 % yield by NMR).

Tetraphenylinaphthalene Standard - ¹H NMR (400.13 MHz, 300 K, d₈-tol): δ 6.64 (2H, t, Ar), 6.7 (4H, t, Ar), 6.97 (7H, m, Ar), 7.02 (5H, t, Ar), 7.16 (4H, d, Ar), 7.20 (2H, m, Ar), 7.78 (2H, m, Ar).

3.9.6 Scale up and Asymmetric Synthesis

3.9.6.1 Preparation of [(S)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ (S)-3

[(S)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ was prepared *in situ* via co-complexation of sodiated (S)-BIPHEN with MgⁿBu₂ followed by addition of TMEDA. PhCH₂Na (0.114 g, 1 mmol) was added to a clean dry Schlenk and toluene (5 ml) was added. The orange suspension was then cooled to –10 °C for 15 minutes after which a solution of (S)-BIPHEN (0.177 g, 0.5 mmol) in toluene (3 ml) was added. The orange suspension was stirred until a colourless solution was formed and MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to produce a white suspension. TMEDA (0.15 ml, 1 mmol) was then added immediately to give a pale-yellow solution which was allowed to slowly warm to ambient temperature. (S)-3 was used without any further purification or analysis.

3.9.6.2 Reaction of (S)-3 with 2-iodoanisole to produce 11

To a solution of (S)-3 prepared as outlined above was added two equivalents of 2-iodoanisole (0.13 ml, 1 mmol) at ambient temperature. The solution was stirred for 1.5 hours at ambient temperature then was subsequently cooled to –60 °C. The solution was left to equilibrate at this temperature for 15 minutes prior to addition of two equivalents of tolualdehyde (0.17 ml, 1 mmol). Upon addition of the aldehyde a darkening of the colour of the solution was noted, transitioning from pale yellow to a darker yellow. The solution was allowed to warm slowly back to ambient temperature over the course of 1.5 hours, after which time the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl. The organic layer was extracted with ethyl acetate (3 x 10 ml) and dried over MgSO₄ and purified using flash column chromatography using an 80:20 mixture of cyclohexane/ethyl acetate as eluant (0.125 g, 55 % yield). ¹H NMR (400.13 MHz, 298 K, CDCl₃): δ 2.30 (3H, s, CH₃), 3.84 (3H, s, OCH₃), 6.06 (1H, d, CCH(O)HC), 6.92 (1H, d, Ar-CH), 6.97 (1H, td, Ar-CH), 7.16 (2H, d, 2 Ar-CH), 7.27 (1H, bs, Ar-CH), 7.28 (2H, m, 2 x Ar-CH), 7.30 (1H, m, Ar-CH). ¹³C NMR (100.62 MHz, 298 K, CDCl₃): δ 21.1 (CH₃), 55.4 (OCH₃), 72.1 (CCH(OH)C), 110.7, 120.8, 126.5, 127.8, 128.6, 128.9, 132.1, 136.8, 140.3, 156.6 (Ar). [HPLC conditions: Lux® Amylose-2 column 4.6 x 100 mm 5µm, H₂O/ACN isocratic 58/42 t_R = 4.60 min (minor) and t_R = 5.51 min (major)].

3.9.6.2 Reaction of (S)-3 with 2-iodoanisole to produce 12

To a solution of (S)-3 prepared as outlined above was added two equivalents of 2-iodoanisole (0.13 ml, 1 mmol) at ambient temperature. The solution was stirred for 1.5 hours at ambient temperature then was subsequently cooled to -60°C . The solution was left to equilibrate at this temperature for 15 minutes prior to addition of two equivalents of anisaldehyde (0.18 ml, 1 mmol). Upon addition of the aldehyde a darkening of the colour of the solution was noted, transitioning from pale yellow to a darker yellow. The solution was allowed to warm slowly back to ambient temperature over the course of 1.5 hours, after which time the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl . The organic layer was extracted with ethyl acetate (3 x 10 ml) and dried over MgSO_4 and purified using flash column chromatography using an 80:20 mixture of cyclohexane/ethyl acetate as eluant (0.136 g, 56 % yield). ^1H NMR (400.13 MHz, 298 K, CDCl_3): δ 3.81 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 6.04 (1H, d, $\text{CCH}(\text{OH})\text{C}$), 6.87 (1H, bs, Ar-CH), 6.89 (2H, m, 2 x Ar-CH), 6.92 (1H, bs, OH), 6.97 (1H, td, Ar-CH), 7.28 (2H, d, 2 x Ar-CH), 7.30 (2H, d, 2 x Ar-CH). ^{13}C NMR (100.62 MHz, 298 K, CDCl_3): δ 55.3 (OCH_3), 55.4 (OCH_3), 71.6 ($\text{CCH}(\text{OH})\text{C}$), 110.7, 113.6, 120.8, 127.7, 127.8, 128.6, 132.2, 135.5, 156.7, 158.8 (Ar). [HPLC conditions: Lux[®] Amylose-2 column 4.6 x 100 mm 5 μm , $\text{H}_2\text{O}/\text{ACN}$ isocratic 58/42 t_R = 3.89 min (minor) and t_R = 4.86 min (major)].

3.9.6.3 Reaction of (S)-3 with 2-Iodopyridine and to produce 13

To a solution of (S)-3 prepared as outlined above was added two equivalents of 2-iodopyridine (0.10 ml, 1 mmol) at ambient temperature. The solution was stirred for 1.5 hours at ambient temperature, inducing a colour change in the solution from pale yellow to orange, followed by cooling to -60°C . The solution was left to equilibrate at this temperature for 15 minutes prior to addition of two equivalents of tolualdehyde (0.17 ml, 1 mmol). The solution was allowed to warm slowly back to ambient temperature over the course of 1.5 hours, after which time the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl . The organic layer was extracted with ethyl acetate (3 x 10 ml) and dried over MgSO_4 and purified using flash column chromatography using an 80:20 mixture of cyclohexane/ethyl acetate as eluant (0.085 g, 42 % yield). ^1H NMR (400.13 MHz, 298 K, CDCl_3): δ 2.35 (3H, s, CH_3), 5.20 (1H, vbs, OH), 5.75 (1H, s, $\text{CCH}(\text{OH})\text{C}$), 7.15 (1H, bs, Ar-CH), 7.17 (2H, bs, 2 x Ar-CH), 7.21 (1H, td, Ar-CH), 7.28 (2H, m, 2 x Ar-CH), 7.63 (1H, td, Ar-CH), 8.59 (1H, d, Ar-CH). ^{13}C NMR (100.62 MHz, 298 K, CDCl_3): δ 21.1 (CH_3), 74.8 ($\text{CCH}(\text{OH})\text{C}$), 121.3, 122.3, 127.0, 129.3, 136.8, 140.4, 147.8, 161.1. [HPLC conditions: Lux[®] Cellulose-3

column 4.6 x 100 mm 5 μ m, H₂O/MeOH isocratic 58/42 t_R = 21.43 min (minor) and t_R = 25.49 min (major)].

Chapter 4 – Structural Studies of Alkali Metal Zincates

Zinc is located in the first row of the d block of the periodic table but is often considered to be a pseudo main group metal as it reacts to produce complexes where the zinc predominantly adopts the +2 oxidation state. The adoption of a single, stable oxidation state comes as a direct consequence of the special stabilisation gained through having a d^{10} electronic configuration.¹⁷¹ Although this may lead to similarities in their structural chemistry, one crucial way in organozinc and organomagnesium complexes differ is in their reactivity. As zinc has a higher electronegativity than magnesium, 1.61 vs 1.35 respectively, this results in organozinc reagents possessing a much greater covalent character to their bonding when bonding to non-metals. As a result of the greater covalent character in their bonding, alkyl and dialkyl zinc reagents are generally less reactive than their organomagnesium counterparts.¹⁷¹ Although they may be less reactive kinetically, organozinc reagents have been shown to both regio- and chemoselective bases with a good functional group tolerance while their metallated intermediates are often more stable, making them more amenable towards further functionalisation. One way in which the reactivity of these complexes can be enhanced is through the synthesis of alkali metal zincates. Alkali metal zincates represent some of the first ever reported alkali metal ate complexes. More than 160 years ago, the pioneering work of Wanklyn led to the discovery of the NaZnEt_3 which was prepared through the reaction of sodium metal with ZnEt_2 .^{46,172} Like many of the early mixed metal complexes, alkali metal zincates received comparatively little attention compared to their monometallic counterparts such as Grignard and alkyllithium reagents, with common transformations such as metalation and metal-halogen exchange being viewed almost entirely as the domain of these highly polar, monometallic reagents. As with alkali metal magnesiates, interest in these bimetallic zinc complexes have increased dramatically over the past decades as their potential as highly versatile reagents for carrying out a number of prized transformations has finally been realised.^{47,107,111}

Since their initial discovery by Wanklyn, the use of alkali metal zincates has become increasingly widespread as a method of enhancing the low levels of reactivity of monometallic organozinc reagents. This field has expanded rapidly in recent years with numerous reports of alkyl, amido and mixed alkyl amido zincates exhibiting a tremendous enhancement in reactivity compared to their monometallic components, similar to the increase observed in the reactivity for alkali metal magnesiates.¹⁷³ Moreover, these highly reactive alkali metal zincates have been shown to retain their aforementioned functional

group tolerance, all of which combine to make alkali metal zincates potent synthetic tools for a number of key transformations. In addition to the similarity in reactivity of the two types of bimetallic complexes, alkali metal zincates also frequently adopt similar structural motifs to that of their true main group bimetallic counterparts, alkali metal magnesiates.⁵⁷ Alkali metal zincates generally fall into two categories, namely the lower order triorganozincates and the higher order tetraorganozincates.

4.1 Triorganozincates

Triorganozincate can be grouped into two categories, namely homoleptic or heteroleptic zincates. Both types of triorganozincate have been extensively studied and have been shown to be synthetically useful tools for a range of transformation.^{107,144,173,174}

4.1.1 *Tris(alkyl) and Mixed Alkyl/Aryl Zincates*

Triorganozincates themselves are, to date, the more common of the two main forms of alkali metal zincates. These bimetallic complexes generally take the form AmZnR_3 ($\text{Am}^+\text{ZnR}_3^-$) (where Am = alkali metal) with the zinc centre adopting a trigonal planar geometry surrounded by three anionic ligands to form a 16 electron complex.¹⁷⁵ Early examples of this type of complex include the sodium and potassium zincates $\text{NaZn}(\text{CH}_2\text{CMe}_3)_3$ (Figure 62), $\text{KZn}(\text{CH}_2\text{CMe}_3)_3$ and $\text{KZn}(\text{CH}_2\text{SiMe}_3)_3$ published by the group of Purdy.¹⁷⁶ Through crystallographic studies they were able to determine the solid state structure of the three zincates and revealed them to adopt the aforementioned AmZnR_3 (where Am = Na or K) structure in which the zinc atoms are surrounded by three anionic ligands with a trigonal planar coordination geometry. As the reactions were carried out in benzene with no additional donor solvents present, all three complexes were found to exist as discrete dimeric aggregates. In the case of $\text{KZn}(\text{CH}_2\text{SiMe}_3)_3$ however, the potassium cations were found to be solvated with benzene molecules while in the alkali metal cations of $\text{NaZn}(\text{CH}_2\text{CMe}_3)_3$ and $\text{KZn}(\text{CH}_2\text{CMe}_3)_3$ were found to form interactions outside of their discrete dimeric units (Figure 62). Furthermore, the group were able to isolate of the mixed alkyl/aryl zincate $\text{KZn}(\text{CH}_2\text{SiMe}_3)_2\text{Ph}$, the formation of which was attributed to deprotonation of a benzene solvent molecule by the $\text{KZn}(\text{CH}_2\text{SiMe}_3)_3$. As alkyl and dialkylzinc reagents are known to be extremely poor bases, this early study highlights the significant increase in reactivity obtained for organozinc complex upon formation of an alkali metal zincate.

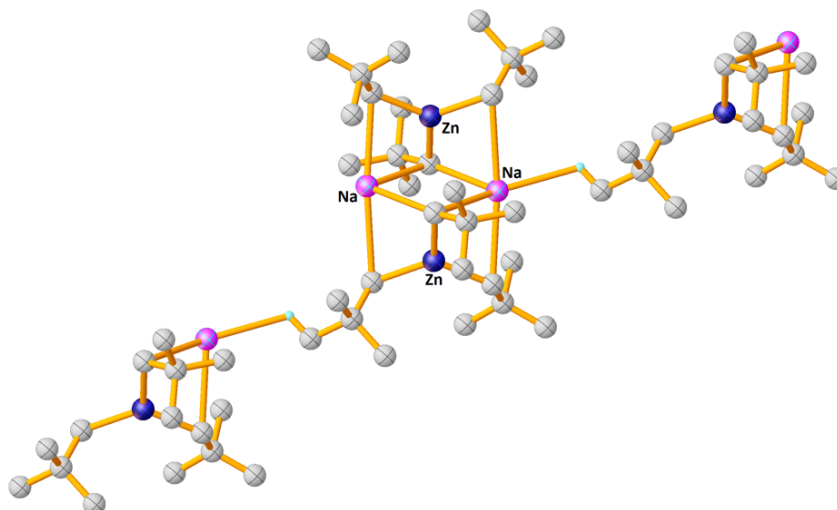


Figure 62: Solid-state structure of polymeric $\text{NaZn}(\text{CH}_2\text{CMe}_3)_3$.

Following on from this early work, the group of Hevia have carried out detailed studies into the structural chemistry of a series of *tris*(alkyl) alkali metal zincates containing the carbanionic CH_2SiMe_3 ligand.¹⁷⁷ This ligand is particularly useful in polar main group organometallic chemistry as it provides good levels of stability, partly due to the lack of β -hydrogen atoms (eliminating issues surrounding β -hydrogen elimination which is a common decomposition route for organometallic chemistry) and a reasonable degree of steric bulk. Utilising a co-complexation approach in which equimolar amounts of AmR and ZnR_2 (where $\text{Am} = \text{Li}, \text{Na}$ or K and $\text{R} = \text{CH}_2\text{SiMe}_3$) were combined in hydrocarbon solvent, Hevia and co-workers were able to isolate and characterise, in the solid-state, a series of homoleptic *tris*(alkyl) alkali metal zincates taking the form AmZnR_3 (where $\text{Am} = \text{Li}, \text{Na}$ and K). All three zincates, LiZnR_3 , NaZnR_3 and KZnR_3 , were found form to novel infinitely aggregated structures in the absence of any donor solvent which despite their identical empirical formula were subsequently shown to adopt different supramolecular motifs. The monomeric unit of each of these three zincates was again shown to consist of the classical AmZnR_3 motif (where $\text{Am} = \text{Li}, \text{Na}$ or K) in which the zinc atom was shown to be three coordinate adopting a trigonal planar coordination environment. For LiZnR_3 and NaZnR_3 , the alkali metals are connected to the zinc centre via the formation of two bridging interactions with the methylene groups of two CH_2SiMe_3 ligands with the polymer propagating through an interaction formed between the third methylene group of the zincate anion to the alkali metal of an adjacent molecule. For the KZnR_3 however, which can be regarded as a polymorph of the dimeric structure reported Purdy,¹⁷⁶ the alkali metal is linked to the zinc centre through a single CH_2SiMe_3 ligand which coordinates to the potassium through both the methylene CH_2 and a single

methyl CH_3 of the SiMe_3 group. In each case, the alkali metals form three Am-CH_2 interactions while their coordination sphere is satisfied by an electrostatic type interaction with an adjacent CH_3 of a SiMe_3 group.

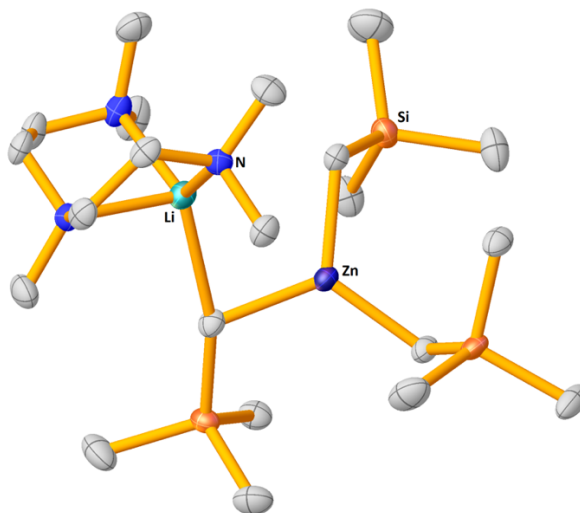
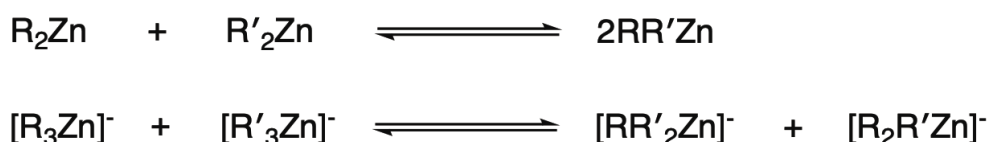


Figure 63: Solid-state Structure of $(\text{PMDETA})\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$.

By incorporating the chelating diamine and triamine donors TMEDA and PMDETA, Hevia and co-workers were able to isolate and characterise the monomeric *tris*(alkyl) lithium and sodium zincates $(\text{PMDETA})\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$ (Figure 63) and $(\text{TMEDA})_2\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$.¹⁷⁷ The donor solvents PMDETA and TMEDA coordinate to the alkali metal cations and complete their coordination sphere. This capping of the alkali metal cation prevents formation of any interactions between the alkali metal and the alkyl ligands of the neighbouring zincate anion which in turns leads to deaggregation of the polymeric structure. The *tris*(aryl) zincate LiZnPh_3 has also been reported by the same group and has, along with its higher order counterpart Li_2ZnPh_4 , been shown to be a potent base which once again displays a reactivity that is considerably higher than its monometallic parent complex.¹⁷⁸

Building on the work outlined above, the groups of Hevia and Robertson have further contributed to the understanding of triorganozincates through their investigations into the behaviour of heteroleptic alkyl/aryl lithium zincates in both the solid-state and in solution.¹⁷⁹ Utilising a simple co-complexation approach, they combined equimolar quantities PhLi and $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ in hexane followed by addition of PMDETA or TMEDA to isolate the heteroleptic zincate $(\text{PMDETA})\text{LiZn}(\text{CH}_2\text{SiMe}_3)_2\text{Ph}$ and homoleptic zincate $(\text{TMEDA})\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$ respectively. Through their isolation of the homoleptic zincate $(\text{TMEDA})\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$ a common issue encountered in the formation of heteroleptic

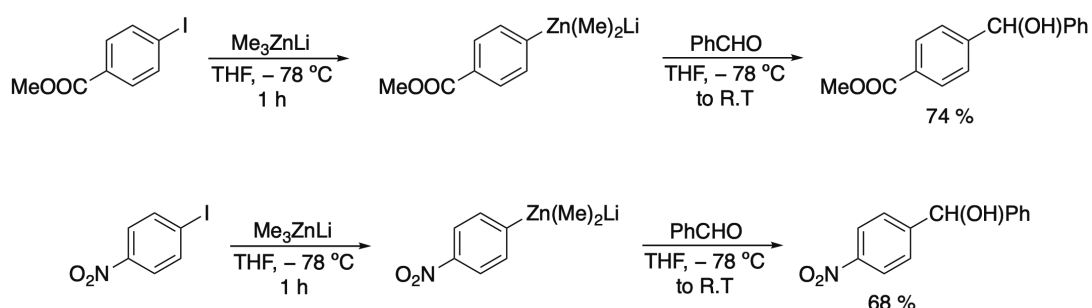
zincates is highlighted which is disproportionation due to a Schlenk-like equilibrium (Scheme 31). This ligand rearrangement/redistribution is common for bimetallic zincates and can ultimately lead to the formation of multiple species within solution despite the initial mixture being of reliable composition. Furthermore, by conducting the co-complexation of PhLi and $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ in benzene, it was possible to isolate the novel, highly aggregated complex $\text{Zn}_3\text{Li}_4(\text{CH}_2\text{SiMe}_3)_5\text{Ph}_5$ which was found to exist as a polymeric species in the absence of any Lewis donor. The asymmetric unit of this species was described as a co-complex of three distinct parts, $\text{LiZn}(\text{CH}_2\text{SiMe}_3)_2\text{Ph}$, $\text{LiZn}(\text{CH}_2\text{SiMe}_3)_3$ and Li_2ZnPh_2 , and again serves to highlight the high levels of reactivity and structural complexity encountered through formation of alkali metal zincates.



Scheme 31: Schlenk-like equilibria for dialkyl zinc and heteroleptic organozincate species.

Not only has the structural chemistry of *tris*(alkyl) zincates been studied in more depth in recent years, there have also been several reports outlining their reactivity in transformations such as metal-halogen exchange.¹⁴⁴ Despite these reports however, *tris*(alkyl) zincates have not been utilised to the same extent as their magnesium counterparts. Among the first examples of such a reagent to be used in metal-halogen exchange was the *tris*(alkyl) zincate LiZn^nBu_3 which was utilised for monofunctionalisation of dibromoalkenes.¹⁸⁰ Utilising cryogenic temperatures of -85°C not only were the desired alkenylzinc complexes obtained in high yields of 83 - 95 %, they were also found to be conformationally stable in the presence of excess dibromoalkene whereas the analogous alkenyllithium species were not. Moreover, *tris*(alkyl) zincates of this type are sufficiently reactive to allow for the functionalisation of aromatic and heterocyclic substrates. Utilising the lithium zincate LiZnMe_3 , Sakamoto and co-workers were able to achieve good yields of up to 74 % of functionalised substrate after electrophilic quenching of the metallated intermediate.¹⁸¹ The less reactive methyl group was chosen as the reactive alkyl ligand in this case due to its low transferability and as a result, LiZnMe_3 was found to react smoothly, giving selective metal-halogen exchange even in the presence of highly sensitive ester and nitro functionalities which are incompatible with highly polar organolithium reagents (Scheme 32). The same zincate has been utilised for the functionalisation of 3-iodo-1-phenylsulfonylindole, giving access to the 3-substituted isomer without any evidence of

isomerisation to the thermodynamically-favoured 2-substituted isomer which is often observed for the corresponding lithiated species.¹⁸² The more reactive zincate, LiZn^tBu_3 , was found to react readily with electron rich substrates such as 2-iodoanisole giving yields of up to 83 % after electrophilic quenching with benzaldehyde.¹⁸³ Although this zincate is more reactive, the steric bulk of the t butyl ligand once again gives it a low transferability which results in the zincate retaining a good level of functional group tolerance and enables functionalisation of substrates bearing sensitive functional groups such as esters.



Scheme 32: Iodine zinc exchange of aryl iodides bearing sensitive functional groups.

4.1.2 Mixed Alkyl/Amido Zincates

First structurally characterised in 1994 by Westerhausen, dialkylamido zincates represent a synthetically important class of triorganozincates.¹⁸⁴ Unlike their *tris*(alkyl) counterparts, dialkylamido zincates have been utilised mainly in metallation chemistry for which they have been shown to be highly potent yet selective bases. A landmark discovery in the area of lithium dialkylamido zincates was made by the group of Kondo in 1999 when they prepared the mixed alkyl/amido lithium zincate $\text{TMPZn}(^t\text{Bu})_2\text{Li}$ and highlighted its reactivity as a chemoselective base in directed *ortho* metallation reactions with a range of aromatic substrates.¹⁸⁵ Preparing $\text{TMPZn}(^t\text{Bu})_2\text{Li}$ *in situ* by co-complexing Zn^tBu_2 and LiTMP in bulk THF, Kondo and co-workers proposed the active species to contain a $\text{ZnTMP}(^t\text{Bu})_2$ zincate anion and lithium cation and were able to show that co-complexation of the two parent organometallic complexes prior to carrying out the deprotonation was essential in order to obtain good results. Reactions of this type have subsequently been referred to as alkali metal mediated zincation (AMMZn).¹¹¹

Despite this early studied into the reactivity of dialkylamido zincate $\text{TMPZn}(^t\text{Bu})_2\text{Li}$ carried out by Kondo and Uchiyama, the structure of this reagent remained elusive until certain examples were reported 2006 by the group of Mulvey.¹⁸⁶ Analysis of the solid-state structure

of Kondo's formulation revealed it to form a contacted ion pair type structure in which the two metal centres were linked by a bridging TMP ligand and a long-range Li-CH₃ interaction to one of the ^tbutyl groups bound to the zinc centre. By replacing the THF donor with the tertiary aromatic amide *N,N*-diisopropylbenzamide, Mulvey and co-workers were also able to isolate the lithium zincate $\{[(i\text{Pr})_2\text{NC(Ph)(=O)]Li}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}\}$. This occurs when THF is excluded from the reaction mixture and instead diisopropylbenzamide acts as a donor, solvating the lithium and importantly it is not deprotonated. $[(\text{THF})\text{Li}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ was subsequently shown to be dibasic, deprotonating two equivalents of anisole with concomitant loss of both ^tbutyl ligands.¹⁸⁷ Elaborating on the reactivity of $[(\text{THF})\text{Li}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$, through crystallographic studies of the parent zincate $[(\text{THF})\text{Li}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ and intermediates isolated from deprotonation of a range of substrates, Mulvey and co-workers were able to show that deprotonation was achieved with overall retention of the TMP ligand which contrasted with computation studies carried out at the time which suggested the reaction could occur via deprotonation of the substrate by the kinetically more basic amide group.^{188,189} This difference in theoretical and experimentally observed results led Mulvey and co-worker to examine the nature of this reaction further and in so doing they were able to establish that the deprotonation of aromatic substrates by $[(\text{THF})\text{Li}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ was achieved by a two-step mechanism.¹⁹⁰ This two-step mechanism was found to proceed with initial deprotonation of the substrate by the TMP ligand with concomitant formation of free amine $[\text{TMP(H)}]$ within the reaction mixture. The free amine was then subsequently deprotonated by one of the remaining alkyl ligands, regenerating the amide with concomitant loss of butane gas thus giving rise to the crystallographically observed overall alkyl basicity.^{191,192}

The effects that the identity of the alkyl and amido ligands have on the structure of dialkyl amidozincates has also been investigated. By studying the co-complexation of Me₂Zn with LiTMP using TMEDA as the Lewis donor, Mulvey and Hevia were able to isolate and structurally characterise the dialkylamido zincate $[(\text{TMEDA})\text{Li}(\mu\text{-TMP})(\mu\text{-Me})\text{ZnMe}]$.⁴⁹ Analysis of the crystal structure showed it to be isostructural with that of its butyl-containing analogues. The TMP ligand once again functions as the bridging ligand between the two metal centres while one of the methyl groups bound to zinc forms a secondary bridging interaction and the remaining methyl group is bound terminally to zinc. While the identity of the alkyl ligand appeared to have little effect on the final structure of the alkali metal zincate, it was shown to have important implications for the formation of the complex. Using

combination of ^1H , ^{13}C and ^7Li NMR spectroscopy the authors found that unlike the previous example when bulky $^t\text{Bu}_2\text{Zn}$ was employed, co-complexation of Me_2Zn with LiTMP occurred without addition of a Lewis donor. In contrast to this, the identity of the amide ligand has been shown to have a major influence on the outcome of the reaction as co-complexation of Me_2Zn with the less sterically bulky lithium amide, LiHMDS , produced the inverse lithium zincate $[\text{Li}_2(\text{HMDS})_2(\text{Me})_2\text{Zn}(\text{TMEDA})]_\infty$ (Figure 64).⁴⁹ This inverse zincate was described as an adduct of neutral $(\text{LiHMDS})_2$ and $\text{Me}_2\text{Zn}(\text{TMEDA})$ in which the zinc fragment can be considered to be acting like a donor solvent molecule towards the dimeric LiHMDS . A single bridging interaction was observed between one of the methyl groups of the $\text{Me}_2\text{Zn}(\text{TMEDA})$ fragment and one of the lithium atoms of the dimeric LiHMDS core in the asymmetric unit of the polymeric structure. The polymer then propagates through an interaction formed between the second methyl group of $\text{Me}_2\text{Zn}(\text{TMEDA})$ and a lithium atom of an adjacent LiHMDS dimer.

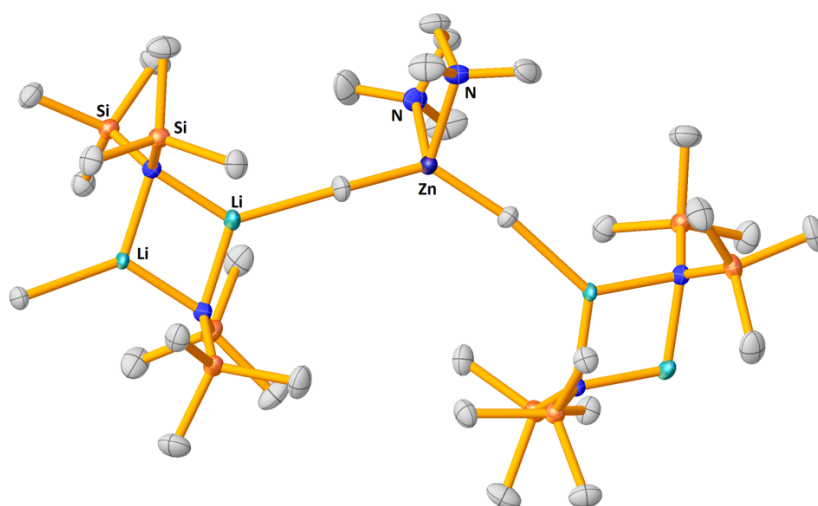


Figure 64: Solid-state structure of the inverse lithium zincate $[\text{Li}_2(\text{HMDS})_2(\text{Me})_2\text{Zn}(\text{TMEDA})]_\infty$.

Turning now to heavier alkali metal zincates e.g. sodium zincates, an even earlier study carried out in 2005, again by the group of Mulvey, led to the preparation and characterisation of the TMEDA solvated sodium zincate $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$.¹⁹³ Much like that of the lithium zincate discussed above, the core of the sodium zincate was found to contain a five membered (NaNZnCC) ring with the TMP ligand acting as a bridging ligand connecting the two metal centre. A secondary bridging interaction was also observed in the form of a long-range Na-CH_3 interaction between the sodium atom and one of the terminally bound $^t\text{butyl}$ groups. Mulvey and co-workers were able to isolate the

hetero(*tri*)leptic sodium zincate $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\text{Ph})\text{Zn}^t\text{Bu}]$ from the reaction of the parent zincate $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ with benzene.¹⁹³ Analysis of the solid-state structure of the new hetero(*tri*)leptic species showed direct replacement of the bridging *t*-butyl ligand with the newly generated phenyl anion. The ability of the sodium zincate $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ to deprotonate non-activated aromatic substrates such as benzene once again highlights the extremely high levels of reactivity that alkali metal zincates possess. Since this initial study, the reactivity of $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ as a highly efficient base has been studied with a range of substrates including cyclic and polycyclic aromatic molecules,^{192,194,195} N-heterocyclic carbenes (NHC's)¹⁹⁶ and metallocenes such as ferrocene.^{197,198} The synthetic utility of this sodium zincate has most recently been highlighted by Mulvey and Robertson by utilising $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-}^t\text{Bu})\text{Zn}^t\text{Bu}]$ to achieve the regioselective 1, 1', 3, 3'-tetrazincation of ferrocene.¹⁹⁹ Analysis of the reaction product $\{\text{Na}_4(\text{TMP})_4(^t\text{Bu})_4[(\text{C}_5\text{H}_3)_2\text{-Fe}]\}$, shows that of the four zinc atoms present in the structure, two retain a terminally bound *t*-butyl ligand. Interestingly, this tetra-zincated ferrocene scaffold has been shown to undergo further reaction with excess toluene, functioning as an alkyl base to produce a new complex in which the two terminal *t*-butyl ligands have been replaced with benzyl groups and the overall structure of the organometallic framework is retained. Reaction of the tetra-zincated scaffold with excess pyridine; however, sees the zincate react as an amido base deprotonating the pyridine heterocycle at the 4 position to generate the pyridine solvated sodium zincate $\{[\text{Na}\cdot 4\text{py}][\text{Zn}(\text{Py})_2(^t\text{Bu})\cdot\text{py}]\}_\infty$. Upon reaction with pyridine, the tetrasodium tetrazinc scaffold is destroyed and the new pyridine solvated sodium zincate forms an infinitely aggregated polymeric chain.

Moreover, by replacing the highly reactive *t*Bu ligand for the slightly less reactive CH_2SiMe_3 , Mulvey was able to synthesis the mixed alkyl/amido zincate $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-CH}_2\text{SiMe}_3)\text{Zn}(\text{CH}_2\text{SiMe}_3)]$ and $[(\text{PMDETA})\text{K}(\mu\text{-TMP})(\mu\text{-CH}_2\text{SiMe}_3)\text{Zn}(\text{CH}_2\text{SiMe}_3)]$ which allowed for the successful metalation of highly sensitive cyclic ethers and ethene respectively.²⁰⁰ Not only did the use of AMM₂Zn allow for smooth metalation of THF, tetrahydropyran (THP) and ethene, the highly sensitive and reactive anions were captured and retained within the structure of the resultant zincates. Through analysis of the crystalline product of the reaction of both THF and THP with $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-CH}_2\text{SiMe}_3)\text{Zn}(\text{CH}_2\text{SiMe}_3)]$ Mulvey and co-workers were able to show unequivocally that deprotonation had occurred at the α -position relative to the oxygen atom in each case with concomitant loss of a single CH_2SiMe_3 ligand

to form tetramethylsilane (TMS). A similar situation was observed for the reaction of ethene with the potassium zincate $[(\text{PMDETA})\text{K}(\mu\text{-TMP})(\mu\text{-CH}_2\text{SiMe}_3)\text{Zn}(\text{CH}_2\text{SiMe}_3)]$ where analysis of the crystalline reaction product clearly showed retention of the vinyl $\text{CH}_2=\text{CH}^-$ anion which was found to be formally bound to the zinc atom through a σ -bond, indicative of deprotonation having occurred with loss of a CH_2SiMe_3 ligand, while the unsaturated π -system engages with the K cation.

4.2 Tetraorganozincates

A further class of alkali metal zincates are the tetraorganozincates. These higher order zincates are also sometimes referred to, misleadingly, as highly coordinated zincates. These higher order zincates take the general form $[\text{Am}^{2+}\text{ZnR}_4^{2-}]$ with the central zinc atom adopting a tetrahedral or distorted tetrahedral coordination environment. Inclusion of a fourth anionic ligand results in tetraorganozincates forming 18 electron complexes; however, it is important to note that this electron count does not imply any similarity or connection to the 18 electron rule that normally governs the reactivity of first row transition metal complexes.²⁰¹ Considering the wealth of information available on the structure, composition and reactivity of lower order triorganozincates, comparatively little information is available for their higher order tetraorganozincate counterparts, particularly in terms of structural characterisation.⁵⁷

Focussing first of all on their solid-state structural chemistry, tetraorganozincates can be subdivided into two further categories, namely homoleptic and heteroleptic. Relatively few solid-state structures of tetraorganozincates have been published compared to their magnesiate counterparts. For the structures which have been reported, the vast majority are homoleptic with very few examples of heteroleptic complexes having been published to date. The first tetraorganozincate to be structurally characterised was the unsolvated homoleptic lithium zincate Li_2ZnMe_4 reported by Weiss.²⁰² Other early work in this area includes the work of the groups of Fröhlich and van Koten, who successfully characterised the solid-state structures of a number of *tetra*(alkyl) and *tetra*(aryl) zincates respectively, such as $[\text{Li}(\text{TMEDA})_2\text{Zn}(\text{CH}_2\text{SiMe}_2\text{SiMe}_2\text{CH}_2)_2]$ and $[\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4]$.^{203–205} Further work relating to the structural characterisation of homoleptic tetraorganozincates was carried out by the group of Hevia who successfully characterised the *tetra*(amido) $(\text{TMEDA})_2\text{Li}_2\text{Zn}_2(\text{NMe}_2)_6$, which was found to exist as a dimer in the solid state, and *tetra*(alkyl) $(\text{TMEDA})_2\text{Li}_2\text{Zn}(\text{Me})_4$.²⁰¹ Due to it adopting a dimeric form in the solid-state, $(\text{TMEDA})_2\text{Li}_2\text{Zn}_2(\text{NMe}_2)_6$ contains two zinc atoms that are bound to four anionic ligands in a

distorted tetrahedral environment and could therefore be considered a tetraorgano- or 'highly coordinated' zincate. Crucially however, this is not an example of a higher order zincate as the alkali metal to non-alkali metal ratio remains 1:1. Although $(\text{TMEDA})_2\text{Li}_2\text{Zn}_2(\text{NMe}_2)_6$ fits the description of a 'highly aggregated' zincate it is best described as a lower order zincate akin to the triorganozincates discussed above. This example serves to highlight the misleading nature of the term 'highly aggregated' when applied to tetraorganozincates.

Turning now to the *tetra*(alkyl) zincate $(\text{TMEDA})_2\text{Li}_2\text{Zn}_2(\text{Me})_4$, this is a genuine example of a higher order zincate as the ratio of alkali metal to non-alkali metal is found to be 2:1.²⁰¹ Interestingly, $(\text{TMEDA})_2\text{Li}_2\text{Zn}(\text{Me})_4$ was isolated as the sole product of the reaction regardless of whether a ratio of 1:1 or 2:1 for MeLi to Me_2Zn was employed (Figure 65). This result was attributed to the presence of an equilibrium between the lower order $(\text{TMEDA})\text{LiZn}(\text{Me})_3$ and higher order $(\text{TMEDA})_2\text{Li}_2\text{Zn}(\text{Me})_4$ in solution. This result highlights the complex nature of bimetallic complexes in the solution state. In the same report, Hevia and co-workers were also able to successfully isolate the first mixed alkyl/amido higher order zincate. Reasoning that two of the most commonly used ligands in organozincate chemistry, TMP and *t*-butyl would be too bulky to allow for formation of a higher order tetraorganozincate, they opted to use the less sterically demanding organometallic components lithium dimethylamine and dimethyl zinc. This led to successful isolation of monoalkyltris(amido) zincate $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}(\text{NMe}_2)_3]$ which was described as a contacted ion pair structure containing a dianionic $[\text{ZnMe}(\text{NMe}_2)_3]^{2-}$ core which is coordinated to two $[\text{Li}(\text{TMEDA})]^+$ cations.²⁰¹ The most recent structural characterisation of a higher order zincate was made by the groups of Hevia and Capriati who, during their investigation into the reactivity of tetraorganozincates with nitroolefins, characterised the higher order lithium zincates $(\text{TMEDA})_2\text{Li}_2\text{ZnEt}_4$ and $((R,R)\text{-TMCD})_2\text{Li}_2\text{ZnEt}_4$.²⁰⁶

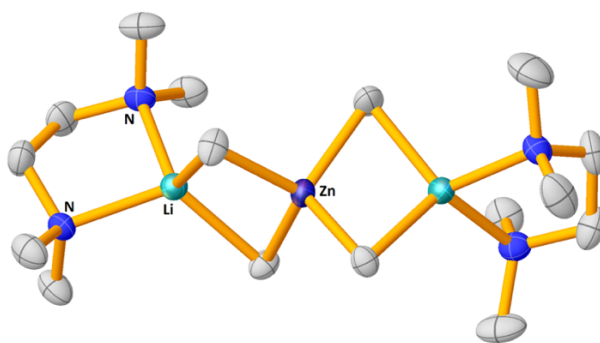


Figure 65: Solid-state structure of $(\text{TMEDA})_2\text{Li}_2\text{Zn}(\text{Me})_4$.

The group of Mulvey has also successfully characterised two homoleptic sodium tetraorganozincate zincates, $\{[(\text{TMEDA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$ and $\{[(\text{PMDETA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$, utilising the aromatic heterocycle pyrrole.²⁰⁷ The two structures were found to have the same basic dianionic $[\text{Zn}(\text{NC}_4\text{H}_4)_4]^{2-}$ core in which the tetrahedrally coordinated zinc atom is bound to four anionic pyrrole ligands. Despite a high degree of structural similarity surrounding the core of these two complexes, a significant difference was observed in the coordination environment of their sodium cations. For $\{[(\text{TMEDA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$ the bidentate nature of the TMEDA ligand exposed two vacant coordination sites on each of the sodium atoms which allowed them to form two $\eta^5 \pi$ -type interactions with the pyrrole ring systems. For $\{[(\text{PMDETA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$ which contains the larger, tridentate PMDETA ligand, only one of these vacant coordination sites was available which caused the sodium atoms to form only one $\eta^5 \pi$ -type interaction with a single pyrrole ring. Initially isolated from the reaction of pyrrole with a combination of $^n\text{BuNa}$ and $^n\text{Bu}_2\text{Zn}$ in a 1:1:1 ratio, $\{[(\text{TMEDA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$ once again highlights the complex solution state behaviour of bimetallic zincates. This complexity is further reinforced by the fact that when the reaction was repeated in order to increase the yield of $\{[(\text{TMEDA})\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4\}$ by using the correct stoichiometric ratio of reactants based on the isolated solid-state structure e.g. a 2:1:4 ratio of $^n\text{BuNa}$, $^n\text{Bu}_2\text{Zn}$ and pyrrole, analysis of the reaction product by ^1H NMR spectroscopy showed significantly contamination with a second product which was attributed the $[\text{NaZn}(\text{NC}_4\text{H}_4)_3]_\infty$.

Despite only a small number of tetraorganozincates having been characterised in the solid-state, they have already been shown to be extremely efficient reagents for use in a range of reactions. One such example of their unique reactivity is given by the work of Kondo and Sakamoto have utilised the higher order zincate Li_2ZnMe_4 , amongst others, for a range of reactions including inter- and intramolecular epoxide ring opening and zinc-bromine exchange reactions.²⁰⁸ In each case the higher order zincates outperformed their lower order counterparts and in the case of metal-halogen exchange the lower order zincate LiZnMe_3 failed to give any conversion to the desired product after electrophilic trapping of the metalated intermediate. This once again highlights that an increase in reactivity is often observed due to the formation of a higher order ate complex. The group of Uchiyama have reported the tetraorganozincate $\text{Li}_2\text{Zn}^t\text{Bu}_4$ to be a highly reactive yet highly selective reagent for metal-halogen exchange.²⁰⁹ Remarkably, they were able to achieve chemoselective metal-halogen exchange of functionalised benzene scaffolds containing sensitive functional

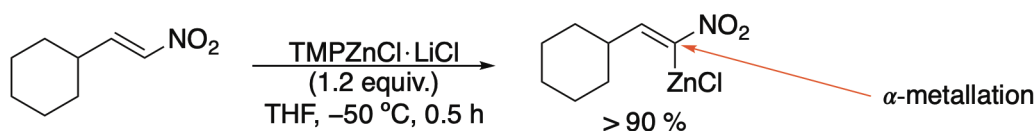
groups such as esters and amides. Furthermore, $\text{Li}_2\text{Zn}^t\text{Bu}_4$ was found to smoothly carry out zinc-iodine exchange for a number of aromatic molecules such as 4-iodophenol which contains an extremely sensitive, acidic hydrogen atom. Meanwhile, the higher order zincate $\text{Li}_2\text{Zn}^n\text{Bu}_4\cdot\text{TMEDA}$ has been shown to be sufficiently reactive yet selective enough to carry out chemoselective metal-halogen exchange on a range of bromopyridines.²¹⁰ Gros and co-workers were able to show that this zinc-bromine exchange could be carried out at ambient temperature in non-polar solvent and that efficient metal-halogen exchange could be achieved using sub-stoichiometric amounts of $\text{Li}_2\text{Zn}^n\text{Bu}_4\cdot\text{TMEDA}$. Interestingly, it was reported that the analogous zincate $\text{Li}_2\text{Zn}^t\text{Bu}_4\cdot\text{TMEDA}$ could not be employed as the exchange reagent in sub-stoichiometric quantities due to the tendency of $\text{Li}_2\text{Zn}^t\text{Bu}_4\cdot\text{TMEDA}$ to react with $^t\text{BuBr}$ produced *in situ*. Moreover, Gros and co-workers revealed that in the absence of TMEDA, the zincate $\text{Li}_2\text{Zn}^n\text{Bu}_4$ was only capable of affecting monozincation of dibromopyridines while $\text{Li}_2\text{Zn}^n\text{Bu}_4\cdot\text{TMEDA}$ was capable of promoting double metal-halogen exchange. More recent uses of tetraorganozincates include the aforementioned work of Hevia and Capriati who utilised homoleptic higher order lithium zincates for the functionalisation of nitroolefins through nucleophilic addition under mild conditions with good levels of chemoselectivity.²⁰⁶

4.3 Turbo Zincate Complexes

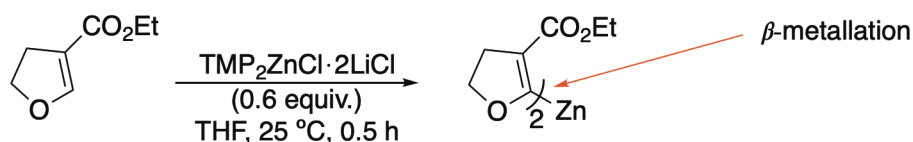
Much like their organomagnesium counterparts, the reactivity of organozinc reagents in reactions such as metal-hydrogen exchange (deprotonation) and metal-halogen exchange can be greatly enhanced through the inclusion of LiCl. One such example of this type of complex is the monoamido lithium zincate $\text{TMPZnCl}\cdot\text{LiCl}$.²¹¹ First reported by Knochel in 2009, this bimetallic complex can be prepared through the simple co-complexation of ZnCl_2 with LiTMP and has been shown to be a potent yet tolerant base capable carrying out chemoselective deprotonations of a range of substrates containing sensitive functional groups under mild conditions.²¹² Furthermore, utilisation of the highly kinetically reactive diamido lithium zincate $\text{TMP}_2\text{Zn}\cdot 2\text{LiCl}$ has been reported to smoothly deprotonate a range of olefinic species giving access to several highly sensitive species such as α -zincated nitroolefins and β -zincated trifluoromethyl ketones (Scheme 33).²¹³ In addition, doubling the stoichiometric ratio of TMP by co-complexing zinc chloride with the turbo Hauser base $\text{TMPMgCl}\cdot\text{LiCl}$ in a 1:2 ratio in THF generates the heterotrimetallic species $\text{TMP}_2\text{Zn}\cdot 2\text{MgCl}_2\cdot 2\text{LiCl}$.²¹⁴ This trimetallic species was found to be capable of bringing about the zincation of sensitive aromatic heterocycles such as 2-phenyl-1,3,4-oxadiazole and *N*-

tosyl-1,2,4-triazole under more user friendly conditions with reaction temperatures of 25 °C and –45 °C respectively. By way of contrast, the lithiated and magnesiated derivatives of these two substrates are prone to fragmentation, something which did not occur when $\text{TMP}_2\text{Zn}\cdot 2\text{MgCl}_2\cdot 2\text{LiCl}$ was employed as the base, while the bimetallic magnesiate complex $\text{TMPMgCl}\cdot \text{LiCl}$ was only capable of carrying out metalation of the substrates when cryogenic temperatures of –70 °C were employed. More recently this trimetallic species has been utilised for the selective functionalisation of 2-pyridones and 2,7-naphthyridones which are highly prized structural scaffolds for application in medicinal chemistry.²¹⁵ Inorganic salt activation of this type has also been implied in the reactivity of the *tris*(amido) lithium zincate LiZnTMP_3 which is typically prepared through co-complexation of ZnCl_2 and LiTMP in the presence of the Lewis donor TMEDA.²¹⁶

α -Metallation of Unsaturated Nitroolefins



β -Metallation of Unsaturated Esters



Scheme 33: α -metallation of nitroolefins and β -metallation of esters using turbo zincates $\text{TMPZnCl}\cdot \text{LiCl}$ and $\text{TMP}_2\text{ZnCl}\cdot 2\text{LiCl}$.

Hevia and co-workers have reported a similar class of Mg-Zn hybrid complexes that have been found to be potent reagents for metal-halogen exchange and addition reactions as well having important implications for ZnCl_2 catalysed reactions.^{217–219} Unlike the turbo reagents reported by Knochel, these Mg-Zn hybrid complexes have been structurally characterised and are known to adopt both contacted and solvent separated ion pairs. This structural diversity is exemplified by the two complexes $[(\text{THF})_4\text{MgCl}_2\text{Zn}(\text{tBu})\text{Cl}]$ and $[\{\text{Mg}_2\text{Cl}_3(\text{THF})_6\}^+\{\text{Zn}(\text{tBu})_3\}^-]$ (Figure 66) which exist as a contacted ion pair or a solvent separated ion pair depending on the stoichiometry of Grignard reagent employed.²¹⁷ Typically produced through a metathesis reaction between the desired Grignard species and

zinc chloride in THF solution, the solvent separated species has been reported to be a highly reactive reagent for metal-halogen exchange with iodoaryls such as 4-iodotoluene, reacting through all three *t*-butyl ligands to produce the *tris*(aryl) complex $[\{\text{Mg}_2\text{Cl}_3(\text{THF})_6\}^+\{\text{Zn}(p\text{-tol})_3\}^-]$ in high yields. This *tris*(aryl) zincate has been structurally characterised and clearly shows that the reaction occurs with zincation of the substrate. The high reactivity of this type of Mg-Zn hybrid is nicely demonstrated by way of comparison with the reactivity of the dialkyl zinc complex $t\text{-Bu}_2\text{Zn}$ and the Grignard reagent $t\text{-BuMgCl}$ with the Mg-Zn hybrid produced from the metathesis reaction of $t\text{-BuMgCl}$ and ZnCl_2 in a 3:1 ratio. Utilising 4-iodoanisole as the substrate of choice, Hevia and co-workers showed that after 10 minutes neither the Grignard or dialkyl zinc reagents showed any reactivity whereas the Mg-Zn hybrid complex gave greater than 95 % conversion to the metallated anisole.²¹⁹ Furthermore, due to the zincated nature of the intermediates, these complexes allow for further functionalisation of the metallated intermediate through transition metal catalysed processes such as Negishi cross couplings. This work by the group of Hevia not only highlights the enhanced reactivity of bimetallic complexes over their monometallic counterparts but also the importance of understanding the fundamental structural chemistry of such bimetallic complexes.

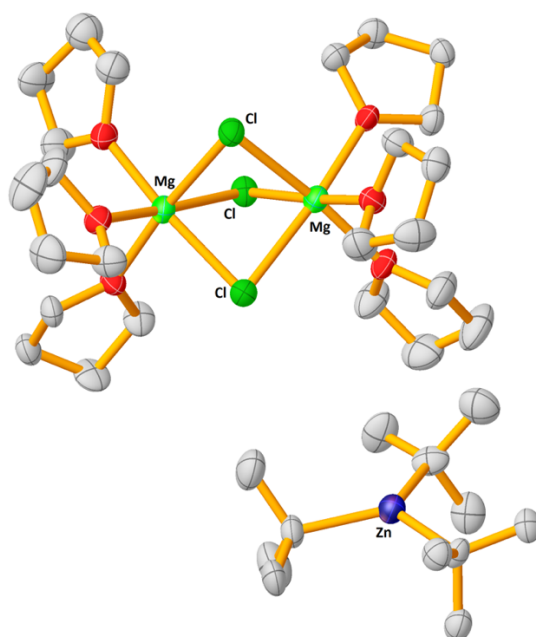


Figure 66: Solid-state structure of $[\{\text{Mg}_2\text{Cl}_3(\text{THF})_6\}^+\{\text{Zn}(t\text{-Bu})_3\}^-]$.

4.4 Organozinc Alkoxides

4.4.1 Homometallic Organozinc Alkoxides

Zinc alkoxides and aryloxides represent an important class of complexes in relation to their role as catalytically active complexes which are used in a number of synthetically useful transformations such as the polymerisation of lactic acid derivatives.²²⁰ The solution-state behaviour of organozinc alkoxides, aryloxides and other related complexes are governed by complex Schlenk-like equilibria which often give rise to the formation of multiple species within solution and allow for facile conversion between aggregation states.²²¹ As with many organometallic complexes, structure is often linked to reactivity and as such, a knowledge of the structural chemistry of organozinc alkoxides and aryloxides is essential in order to fully understand their reactivity. Organozinc alkoxides (RZnOR') or aryloxides (RZnOAr) can be prepared either through alcoholysis or controlled oxidation of the desired diorganozinc reagent with the resulting organozinc alkoxides or aryloxides forming complex aggregated structures.^{222,223} Aggregation of this type arises as a consequence of the tendency of zinc to attain either trigonal planar or tetrahedral coordination geometries with the alkoxide (RO^-) or aryloxide (ArO^-) ligands bridging between the zinc centres.

Organozinc alkoxides or aryloxides commonly form dimers,²²⁴ cubanes²²⁵ or trinuclear spiro type aggregates.²²⁶ Formation of a particular aggregation state can be dependent on factors such as the steric bulk of the alkyl and alkoxide/phenoxide ligands as well as the solvent. The effect of steric bulk on the final aggregation state of organozinc alkoxides/aryloxides has been neatly demonstrated by Driess through the study of the reaction of dimethyl zinc with a range of 2,6-disubstituted phenols.²²⁷ Driess was able to show that as the steric bulk of the substituents increased, in the order of $\text{H} > \text{Me} > i\text{Pr} > t\text{Bu}$, a different aggregate was formed each time. Although multiple aggregation states were reported, a dimeric complex was only isolated when the bulkiest t butyl substituent was used. Bulky ligands are essential for the formation of dimeric complexes of this type, either as the organic ligand bound directly to the zinc centre or as part of the alkoxide/aryloxide group in order to prevent further aggregation. The sterically bulky t butyl ligand has also been used by the group of Lewinski to produce the solvated dimeric aggregate $\{[t\text{BuZn}(\mu\text{-O}^t\text{Bu})(\text{THF})]_2\}$ through the controlled oxidation of $t\text{Bu}_2\text{Zn}$ in bulk THF.²²⁸ Further study of this complex also highlighted the rich structural chemistry of organozinc alkoxide complexes and the propensity of such species to undergo changes in aggregation state. Through the conversion of the solvated dimer

$\{[{}^t\text{BuZn}(\mu\text{-O}^t\text{Bu})(\text{THF})]_2\}$ Lewinski and co-workers were able to synthesise and characterise both the trimeric cluster like complex $[({}^t\text{BuZnO}^t\text{Bu})_3]$ and tetrameric cubane $[({}^t\text{BuZnO}^t\text{Bu})_4]$.²²⁵ The trimeric species $[({}^t\text{BuZnO}^t\text{Bu})_3]$ represents one of the first structurally characterised trimeric organozinc alkoxides (Figure 67); however, it does not adopt a classical cyclic structure but rather it adopts a unique cluster like motif. This cluster like motif was found to consist of an oxygen bridged dimer coordinated to an additional alkyl zinc alkoxide unit. The zinc atom of this additional alkylzinc alkoxide unit coordinates to the oxygen bridged dimer through both bridging oxygen atoms while the remain alkoxide oxygen atom coordinates to a single zinc atom of the dimeric unit. The tetrameric cubane on the other hand adopts a conventional cubane structure in which each zinc atom is four coordinate and is bound to three bridging alkoxide ligands and one terminal alkyl ligand.

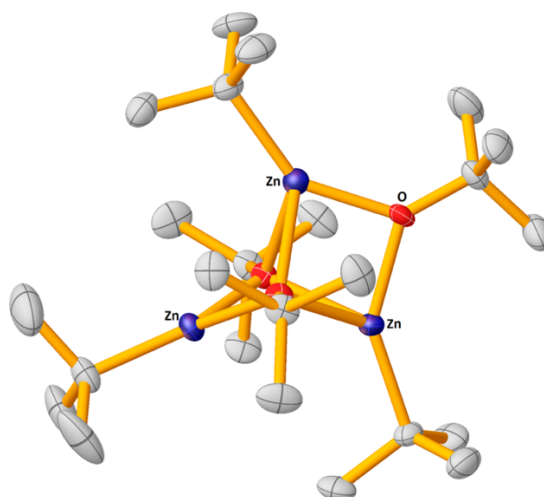


Figure 67: Solid-state structure of $[({}^t\text{BuZnO}^t\text{Bu})_3]$.

Spirocyclic motifs are also a common aggregation state for organozinc alkoxide and aryloxide complexes and are prone to form as a result of ligand reorganisation. One example of a complex which adopts a spirocyclic motif is the alkylzinc aryloxide $[(\text{EtZn})_2\text{Zn}(\text{OAr})_4]$ (where OAr = *ortho*-hydroxybiphenol).²²⁹ This spirocyclic complex is constructed from two (ZnOZnO) rings and has a linear chain arrangement in which the central zinc atom, which links the two rings, is tetrahedrally coordinated to four OAr aryloxide ligands while the outer two zinc atoms are coordinated to two OAr ligands and a terminal ethyl group in a trigonal planar geometry. Lewinski and co-workers were also able to isolate the dimeric THF solvate $[\text{EtZnOAr}(\text{THF})]_2$ from a bulk THF solution. The authors remark that the two different crystallisation outcomes are indicative of ligand redistribution occurring as a result Schlenk-

like equilibrium. The presence of a monomer-dimeric equilibrium was subsequently proven using NMR spectroscopic techniques.

The THF solvated alkylzinc aryloxide $[(rac)\text{-BIPHEN}]_2\text{Zn}_3\text{Et}_2(\text{THF})_2$ [where $(rac)\text{-BIPHEN}$ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-biphenyl-2,2'-diol] has also been reported to adopt a similar spirocyclic motif (Figure 68).¹⁰¹ The group of Ko were initially trying to produce the monomeric zinc phenoxide $[(rac)\text{-BIPHEN}]\text{Zn}(\text{THF})_2$; however, only the spirocyclic $[(rac)\text{-BIPHEN}]_2\text{Zn}_3\text{Et}_2(\text{THF})_2$ was isolated from the reaction even when the reaction was performed with equimolar amounts of Et_2Zn and $(rac)\text{-BIPHEN}$. An identical product, this time obtained in a higher yield, was produced when the reaction was repeated using a ratio of $\text{Et}_2\text{Zn}:(rac)\text{-BIPHEN}$ of 1.5:1 which strongly suggests that $[(rac)\text{-BIPHEN}]_2\text{Zn}_3\text{Et}_2(\text{THF})_2$ is formed as a result of a Schlenk-like equilibrium. The $(rac)\text{-BIPHEN}$ aryloxide ligand has also been used to prepared the hetero(*tri*)leptic complex $[(rac)\text{-BIPHEN}]\text{Zn}[\mu\text{-OCH}(i\text{Pr})_2]_2\text{Zn}_2\text{Et}_2$ which contains both alkoxide and aryloxide ligands.²³⁰ The central zinc atom at the centre of the spirocyclic motif is tetrahedrally coordinated to four oxygen atoms, two from the ditopic aryloxide ligand and one from each of the monotopic alkoxide ligands. The two external zinc atoms were found to have trigonal planar geometries and are bound to a single oxygen atom from both the alkyl- and aryloxide ligands as well as the terminal ethyl group. Interestingly, Chisholm and co-workers did not observe any ligand rearrangement or Schlenk-like equilibrium products to form during the reaction.

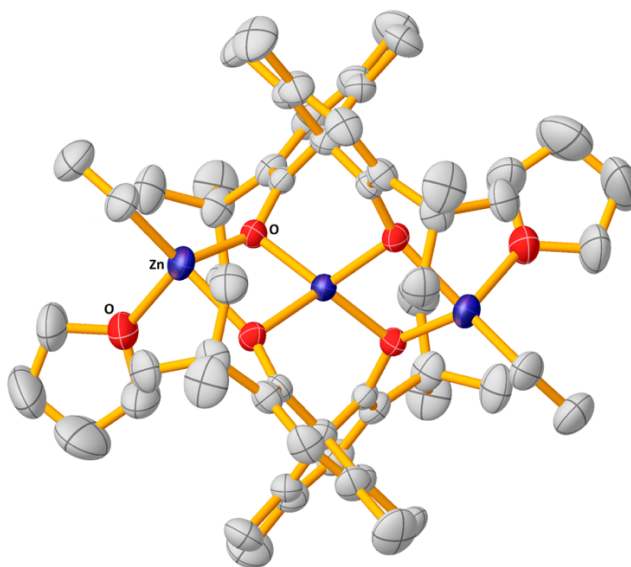


Figure 68: Solid-state structure of $[(rac)\text{-BIPHEN}]_2\text{Zn}_3\text{Et}_2(\text{THF})_2$.

A more recent study by the group of Lewinski has highlighted the extremely complex nature of these Schlenk-like equilibria for organozinc alkoxides/aryloxides, through isolation and characterisation of two new aggregates, namely the roof-like trimer $[(^t\text{BuZn})_3(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)]$ (Figure 69) and ladder-like tetramer $[(\text{PhZn})_4(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)_2]$.²³¹ The roof-like trimer $[(^t\text{BuZn})_3(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)]$ was found to be composed of two Zn_2O_3 rings which are connected through the central Zn-O bond while the ladder-like tetramer, $[(\text{PhZn})_4(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)_2]$, was described as being constructed from two connected Zn_2O_2 rings or four Zn-O rungs. Isolation of these two vastly different aggregation states also highlights the influence that steric bulk can have on the final structural outcome. Both complexes were produced by the alcoholysis of $^t\text{Bu}_2\text{Zn}$ and Ph_2Zn with equimolar amount of diphenylmethanol. Lewinski and co-workers were also able to isolate two spirocyclic complexes, $[(^t\text{BuZn})_2\text{Zn}(\mu\text{-OC(H)Ph}_2)_4]$ and $[(\text{Ph})_2\text{Zn}(\mu\text{-OC(H)Ph}_2)_4]$, upon dissolution and prolonged storage of the roof- and ladder-like complexes in toluene. Both complexes are essentially isostructural with the only difference being the two terminally bound *t*-butyl and phenyl ligands. An additional tetrameric cubane aggregate $[\text{PhZn}(\mu_3\text{-OPh}_2)]_4$ was also isolated in low yields from the reaction of Ph_2Zn with diphenylmethanol upon addition of hexane to the reaction mixture by slow diffusion. In light of these observations the group also carried out detailed solution state studies of both reaction mixtures to further investigate their aggregation in solution. Taking isolated crystals of the roof-like trimer $[(^t\text{BuZn})_3(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)]$ in toluene, Lewinski and co-workers were able to observe slow conversion to the spirocyclic complex $[(^t\text{BuZn})_2\text{Zn}(\mu\text{-OC(H)Ph}_2)_4]$ upon warming to ambient temperature. After a period of 24 hours, it was reported that the solution had equilibrated to a mixture of not just the roof-like trimer and the spirocyclic species but to a mixture containing a third species which was attributed to the dimeric form of the alkyl zinc alkoxide $[^t\text{BuZnOPh}]_2$. A similar equilibrium was observed for the ladder-like aggregate $[(\text{PhZn})_4(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)_2]$ which, when dissolved in toluene, was found to rapidly convert to the spirocyclic complex even at temperatures as low as $-78\text{ }^\circ\text{C}$ with trace amount of the cubane type complex also being present. Interestingly, it was reported that by adding an excess of the Ph_2Zn starting material, conversion to the spirocyclic aggregation state could be completely suppressed.

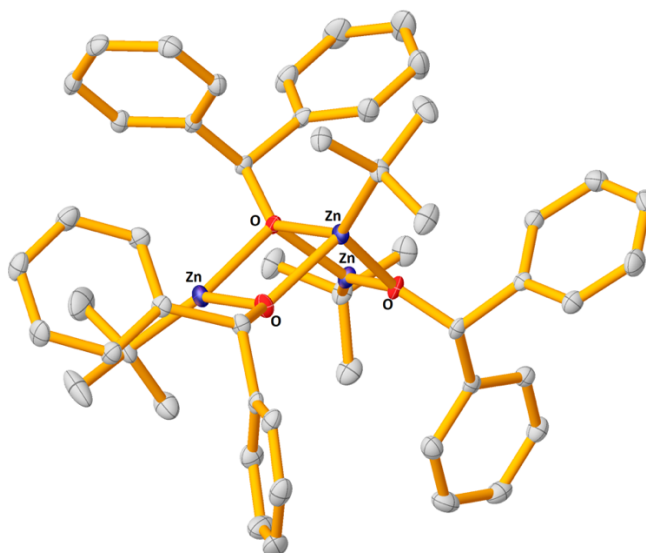


Figure 69: Solid-state structure of $[(^t\text{BuZn})_3(\mu\text{-OC(H)Ph}_2)_2(\mu_3\text{-OC(H)Ph}_2)]$.

4.4.2 Heterobimetallic Organozinc Alkoxides

In recent years, the formation of alkali metal ate complexes has been heavily utilised as a method of enhancing the reactivity of traditionally less reactive organometallic species.¹⁰⁷ Compared to the wealth of structural data available for tri- and tetraorganozincates, comparatively few organozincate species bearing alkoxide or aryloxy ligands have been characterised in the solid-state. Despite the paucity of structural characterisation, these bimetallic complexes have been implicated in a number of transformations.²³² This lack of structural characterisation of mixed metal zinc alkoxides and aryloxides is all the more surprising given that bimetallic combinations of these types, particularly Li/Zn combinations, have been indicated as being reactive species in a number of reactions.^{232,233} Early examples of bimetallic organozinc alkoxide complexes which have been structurally characterised include the lithium alkylzinc alkoxide $[(\text{THF})[\text{Li}(^t\text{Bu})\text{OZn}(\text{O}^t\text{Bu})\text{Me}]]_2$.²³⁴ This lithium triorganozincate was found to form a dimeric heterocubane structure in the solid-state similar to the common cubane structure reported for a number of monometallic organozinc alkoxides. Both zinc atoms are tetrahedrally coordinated and are connected to each other by two μ_3 -bridging alkoxide groups, which, in turn, also link the two zinc atoms to the alkali metal atoms. The two lithium atoms are similarly linked to each other through the remaining two alkoxide groups which are also μ_3 -bridging while their coordination sphere is complete by coordination to a single molecule of THF solvent.

A similar structure has been reported for the analogous THF solvated potassium siloxide $[(\text{THF})_2\text{K}(\text{MeZn})(\text{OSiMe}_3)_2]_2$.²³⁵ This potassium siloxide analogue was isolated from the reaction Me_2Zn with the corresponding potassium siloxide KOSiMe_3 and is depicted as once again adopting a heterocubane type motif in which the zinc and potassium centres are connected through two μ_3 -bridging alkoxide groups. Investigating the role in which effective solvation of the alkali metal atoms by donor solvents plays in the formation of these aggregated species, Driess and co-workers repeated the reaction first of all with incorporation of the diamine donor TMEDA then again with the exclusion of all donor solvents and replacement of the potassium siloxide KOSiMe_3 for potassium *tert*-butoxide KO^tBu . These changes led to the isolation of the mixed potassium zinc siloxide $[(\text{TMEDA})\text{KZn}(\text{OSiMe}_3)_3]_2$ and potassium alkylzinc alkoxide $[\text{K}(\text{MeZn})_3(\text{O}^t\text{Bu})_4]_\infty$ respectively.²³⁵ The structure of $[(\text{TMEDA})\text{KZn}(\text{OSiMe}_3)_3]_2$ was described as adopting a face-fused double heterocubane-like structure in which two of the corner are missing (Figure 70). As a result, this double cubane-like complex was found to contain four μ_2 -bridging siloxide unit linking the potassium and zinc centres along the edges of the structure and two μ_3 -bridging siloxide units linking both the zinc and potassium atoms in the core of the complex. Not only did inclusion of TMEDA lead to a change in aggregation state, but it also caused the loss of the two alkyl groups which were retained in the THF solvated cubane. The monopotassium alkylzinc alkoxide adopts a similar heterocubane structure to that of the previously mentioned THF solvated siloxide complex, only this time a single potassium atom is incorporated in the structure. Moreover, the complex was found to be polymeric, propagating through an interaction between the potassium atom and a methyl group bound to a zinc atom of an adjacent cubane unit. A monolithium alkylzinc alkoxide has also been reported by Wheatley and was again found to be polymeric in the absence of any donor solvent, propagating through Li-CH_3 intermolecular interactions.²³⁶ Driess and co-workers have also reported a series of solvated lithium alkylzinc alkoxides of the form $\{[\text{Li}(\text{THF})(\text{RZn})_3(\text{OR}')_4]\}$ (where $\text{R} = \text{Me}$ or Et and $\text{R}' = ^i\text{Pr}$ or ^tBu) which once again adopt a heterocubane type motif.²³⁷ These bimetallic complexes were isolated by hydrolysis or alcoholysis of a mixture of the dialkylzinc and lithium alkoxide components and were found to exist as discrete cubane aggregates. Each metal centre was tetrahedrally coordinated and were linked by μ_3 -bridging alkoxide ligands. By carrying out the reactions in bulk THF, Driess was able to ensure that the lithium atom would be coordinatively saturated, therefore preventing the formation of any polymeric species. Thomas and Gros have also reported the

use of zincate systems for the ring opening polymerisation of lactide, however, no structural characterisation of the zincate complexes were carried.²³³

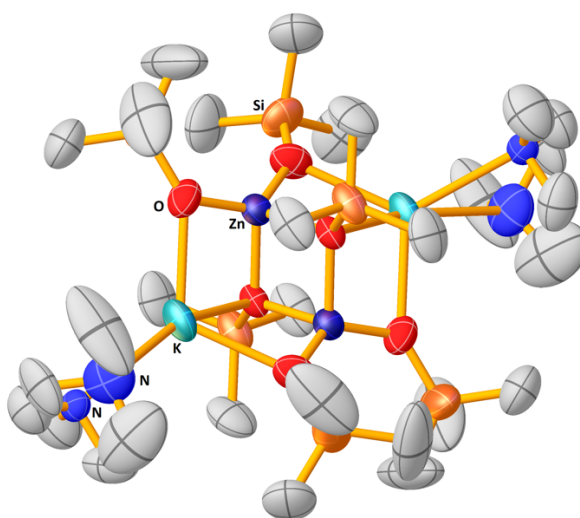


Figure 70: Solid-state structure of $[(\text{TMEDA})\text{KZn}(\text{OSiMe}_3)_3]_2$.

A number of heterobimetallic zinc phenoxide complexes have also been structurally characterised. Unlike their bimetallic alkoxide counterparts, these phenoxide complexes tend to form spirocyclic motifs in the solid-state. Examples of these types complexes include the heterobimetallic lithium and sodium zinc phenoxides $(\text{TBBP})_2\text{ZnLi}_2(\text{THF})_4$ and $(\text{TBBP})_2\text{ZnNa}_2(\text{THF})_4$ (where TBBP = 3,3',5,5'-tetra-tert-butyl-2,2'-biphenol).²³⁸ In each of these complexes, the zinc atoms were found to adopt distorted tetrahedral coordination geometries and are bound to four oxygen atoms from the phenoxide ligands. The alkali metals, lithium and sodium, were also found to adopt distorted tetrahedral coordination geometries and are bound to two oxygen atoms of the phenoxy ligands and two THF molecules. Similar structural motifs have been reported by the group of Doerr for a series of potassium zinc phenoxides utilising monotopic, fluorinated phenol ligands.²³⁹ One such example of this type of complex is the potassium zinc phenoxide $[\text{K}(18\text{-crown-6})]_2[\text{Zn}(\text{OAr}^{\text{F}})_4]$ (Figure 71) (where OAr^{F} = 3,5-bis(trifluoromethyl)phenol) in which the central zinc atom is bound to four phenoxide oxygen atoms from four individual phenoxy ligands in a distorted tetrahedral coordination geometry. Each potassium cation is bound to two phenoxide ligands, maintaining the contacted ion pair structure, while their coordination sphere is completed by coordination to a single 18-crown-6 crown ether ligand. Finally, a double spirocyclic motif has been reported for heterometallic lithium and sodium zinc phenoxides $(\text{L})_2\text{Zn}_2\text{Li}_2(\text{THF})_4$ and $(\text{L})_2\text{Zn}_2\text{Na}_2(\text{THF})_4$ (where L = 2,6-bis(3,5-bis-*t*-butyl-2-hydroxybenzyl)-4-

^tbutylphenol).²⁴⁰ This eye-catching structural motif consists of two central zinc atoms which are each bound to four oxygen atoms of the two tritopic phenoxide ligands in a distorted tetrahedral coordination environment. The alkali metal atoms also adopt a tetrahedral coordination geometry and are bound to two oxygen atoms of the phenoxide ligands and two molecules of THF.

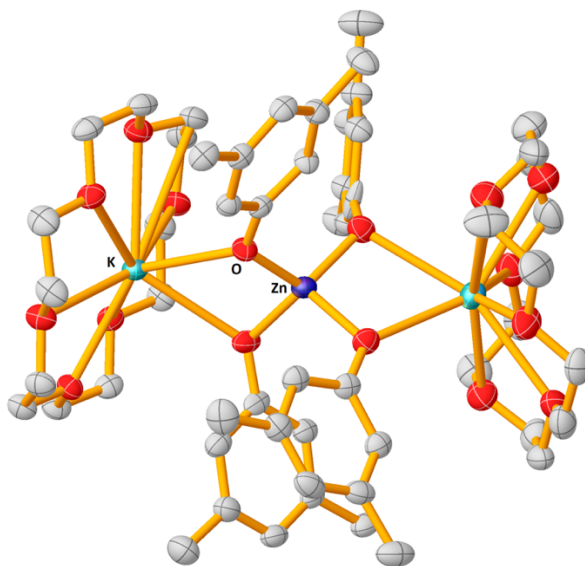


Figure 71: Solid-state structure of $[K(18\text{-crown-}6)]_2[Zn(OAr^F)_4]$.

4.5 Aims

The aim of this work was to synthesise and characterise a series of lithium, sodium and potassium zincates containing the ditopic phenoxide ligand (*rac*)-BIPHEN in order to give an insight into the complex structural chemistry of such species. Investigations would begin by looking at the co-complexation of a range of commercially available dialkyl zinc reagent such as Me_2Zn , Et_2Zn and $^n\text{Bu}_2\text{Zn}$ before moving on to non-commercially available ZnR_2 (where $\text{R} = \text{CH}_2\text{SiMe}_3$) and $^t\text{Bu}_2\text{Zn}$ with the lithium phenoxide $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$.⁹⁴ This co-complexation approach was chosen to allow for a direct comparison to be made between any novel lithium alkylzinc phenoxides created and their previously characterised magnesium counterparts. Following these initial investigations, the scope would then be extended to investigate the structural chemistry of related sodium and potassium alkylzinc phenoxide species. Comparisons could then be made between the different alkali metal alkylzinc phenoxides in order to provide an insight into what effect the identity of the alkali metal has on the structural chemistry of such complexes. Following on from the structural characterisation studies, a secondary aim of this work was to provide an insight into the reactivity of alkali metal alkylzinc phenoxides in metal-halogen exchange. Ultimately, the reactivity of the potential alkali metal alkylzinc phenoxides in metal-halogen exchange would then be compared to that of their magnesium analogues in order to provide a valuable insight into the relative reactivities of heterobimetallic alkylzinc and alkylmagnesium phenoxides.

4.6 Results and Discussion

4.6.1 Synthesis and Characterisation of Lithium Zincates

4.6.1.1 $[\text{BIPHEN}]_2\text{ZnLi}_2(\text{DME})_2$ (**14**)

Building on our previous work focussed on the structure and formation principles of lithium and sodium magnesiates, we decided to extend the scope of the work to include an investigation into the synthesis and characterisation of alkali metal zincates. Zinc is often considered as a pseudo main group metal and as such, alkali metal zincates have frequently been shown to display a similar structural chemistry to that of the corresponding alkali metal magnesiates. To a lesser extent, there is also a degree of similarity in reactivity of the two species. With this in mind, our investigation began with studying the simple co-complexation

of commercially available dialkyl zinc reagent Et_2Zn with the with lithium phenoxide (*rac*)-BIPHENLi. From our previous work on lithium magnesiates, THF was chosen as the donor solvent. Co-complexation of Et_2Zn with a solution of the (*rac*)-BIPHENLi in non-polar solvent gave a white precipitate from which, a colourless solution was obtained by addition of a minimal amount of THF while heating the suspension to reflux. Slow cooling of the resulting solution gave large colourless crystals; however, assignment of the solid-state structure by single crystal X-ray diffraction was not possible as the crystals degraded rapidly when exposed to atmospheric air and moisture. The crystalline material was therefore analysed by ^1H NMR spectroscopy. Interestingly, upon analysis of the ^1H NMR spectrum, no resonances were observed which could represent a metal to carbon bond of the ethyl group which is indicative of decomposition via disproportionation. Decomposition of this type has been well documented for bimetallic ate complexes and similar decomposition pathways have previously been reported by our groups for both lithium and sodium magnesiates of this type, both in the presence of THF. We have subsequently shown that by careful selection of chelating donor ligands, disproportionation of this type can be suppressed.

To this end, the reaction was repeated using the bidentate oxygen-based donor dimethoxyethane (DME). To our surprise however, single crystal X-ray diffraction revealed the reaction product to be the dimeric lithium zincate $(\text{BIPHEN})_2\text{ZnLi}_2(\text{DME})_2$ (**14**) (Figure 72) which crystallised in the orthorhombic crystal system in the chiral space group $P2_12_12$ (0.180 g, 37 % yield). Crystallisation of **14** in this particular space groups indicates that spontaneous deracemisation of the (*rac*)-BIPHEN ligand has occurred.^{100,241} A similar phenomenon was observed for the sodium phenoxide **1** and the heterobimetallic sodium magnesiate **2**. Isolation of homoleptic **14** confirms that lithium zincates of this type are equally sensitive to disproportionation as their magnesium counterparts discussed in Chapter 2. Furthermore, isolation of **14** implies that oxygen-based donors may produce zincate species that are more susceptible to disproportionation and that this process cannot be suppressed simply by inclusion of a chelating donor. Examining the organometallic framework of **14** in more depth, it was found to adopt a classic spirocyclic motif in which the central zinc atom adopts a distorted tetrahedral geometry (sum of bond angles 666.33°) and is bound to the four oxygen atoms of the two phenoxide ligands [Zn1-O1 1.960(3) Å and Zn1-O2 1.971(3) Å]. The two lithium atoms also adopt a distorted tetrahedral geometry (sum of bond angles 662.5°) forming a bond to a single oxygen of each phenoxide ligand [Li1-O1' 1.899(9) Å and Li1-O2 1.882(9) Å] while their coordination sphere is complete by coordination to a single molecule

of DME [Li1-O3 2.001(11) Å and Li1-O4 1.985(10) Å]. The central zinc atom is separated from these peripheral lithium atoms by an interatomic distance of 2.708(9) Å.

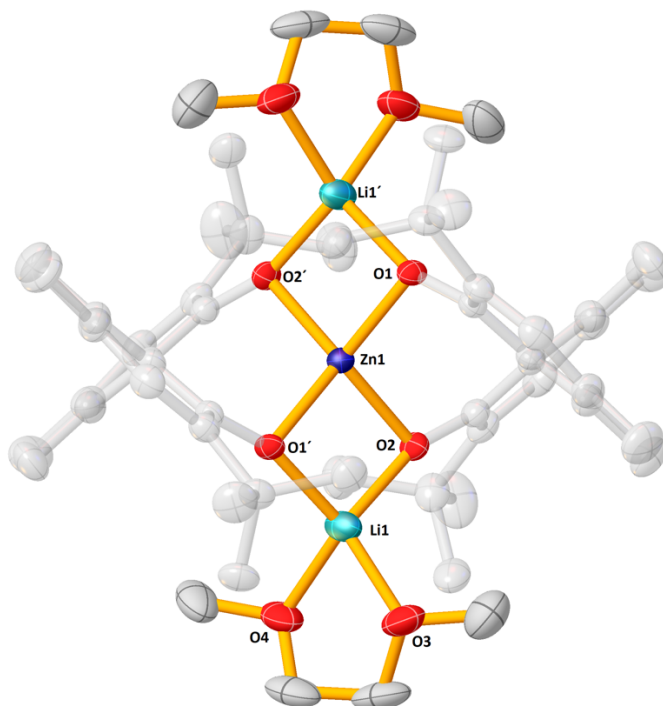


Figure 72: Solid-state Structure of (BIPHEN)₂ZnLi₂(DME)₂ (**14**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *R R* orientated. Key bond distances (Å) and bond angles (°): Zn(1)–O(1), 1.960(3); Zn(1)–O(2), 1.971(3); Zn(1)–Li(1), 2.708(9); Li(1)–O(1'), 1.899(9); Li(1)–O(2), 1.882(9); Li(1)–O(3), 2.001(11); Li(1)–O(4), 1.985(10); O(1)–Zn(1)–O(2), 105.88(13); O(1)–Zn(1)–O(1'), 139.03(19); O(1)–Zn(1)–O(2'), 88.54(13); O(2)–Zn(1)–O(2'), 138.46(19); O(1')–Li(1)–O(4), 110.3(5); O(2)–Li(1)–O(3), 112.5(5); O(3)–Li(1)–O(4), 81.6(4).

The solution-state data for **14** is indicative of the solid-state structure being retained in solution. Beginning with the ¹H NMR spectrum, the ^tbutyl groups of the BIPHEN ligand appear as a singlet at δ 1.42 ppm while the methyl groups of the same ligand appear as two distinct singlets at δ 1.80 and 2.31 ppm. The remaining hydrogen atoms of the BIPHEN ligand, the aromatic hydrogen atoms, appear a sharp singlet in the aromatic region of the spectrum at δ 7.20 ppm. The hydrogen atoms of the DME ligands appear as two singlets at δ 2.67 and 2.90 ppm. Interestingly, the integration values of these two resonances were found to be two and eight hydrogen atoms respectively which would suggest that the bridging CH₂ methylene hydrogen atoms of the DME backbone are no longer equivalent. Turning now to the ¹³C NMR spectrum of **14**, two resonances are observed at δ 17.0 and 20.7 ppm which

were assigned to the methyl groups of the BIPHEN ligand. Likewise, two resonances were also observed for the ^tbutyl groups at δ 31.1 and 34.8 ppm which were assigned to the primary and quaternary carbon atoms respectively. Six resonances were observed in the aromatic region of the ¹³C NMR spectrum at δ 122.6, 126.3, 132.8, 132.9, 134.5 and 160.0 ppm which correspond to the aromatic carbon atoms of the BIPHEN ligand. The presence of only six aromatic resonances is indicative that equivalence in the phenyl rings of the BIPHEN ligands has been retained. Returning to the aliphatic region of the spectrum, the carbon atoms of the DME ligands appear as four resonances at δ 23.05, 32.0, 58.3 and 69.6 ppm which gives a further indication that the bridging methylene groups have been rendered inequivalent. No other resonances were observed in either the ¹H or ¹³C spectra to suggest the formation of any secondary products through ligand rearrangement or Schlenk-like equilibrium and that the solid-state structure of **14** appears to be retained in solution using non-coordinating solvent.

4.6.1.2 [(*rac*)-BIPHEN]₂Li₂Zn₂Et₂(TMEDA)₂ (**15**)

Moving away from oxygen-based donors, the reaction was repeated once again, this time using the nitrogen-based donor TMEDA. The order of addition was also altered so that deprotonation of (*rac*)-BIPHEN would be achieved using Et₂Zn rather than an organolithium base. Deprotonation of the (*rac*)-BIPHEN ligand using Et₂Zn is known to produce the trinuclear ((*rac*)-BIPHEN)₂Zn₃Et₂ which was deemed to be a potentially ideal starting material for co-complexation with a range of alkyl lithium species.¹⁰¹ To this end, Et₂Zn was added to a solution of (*rac*)-BIPHEN in hexane at –10 °C. This colourless solution was allowed to warm slowly to ambient temperature over a period of two hours, after which time it was cooled back to –10 °C and ^tBuLi was added followed by TMEDA to give a white suspension. This suspension was subsequently warmed to ambient temperature with no dissolution of the white precipitate taking place. The solvent was therefore removed under reduced pressure and toluene was added, after which the suspension was heated to reflux to give a colourless solution. The solution was left to cool slowly to ambient temperature and after a 24-hour period produced large, colourless, block-shaped crystals. Analysis of these crystals by single crystal X-ray diffraction unexpectedly revealed the product to be the inverse lithium zincate [(*rac*)-BIPHEN]₂Li₂Zn₂Et₂(TMEDA)₂ (**15**) (Figure 73) which crystallised as a toluene solvate in the trigonal crystal system in the space group R-3c (0.165 g, 29 % yield).

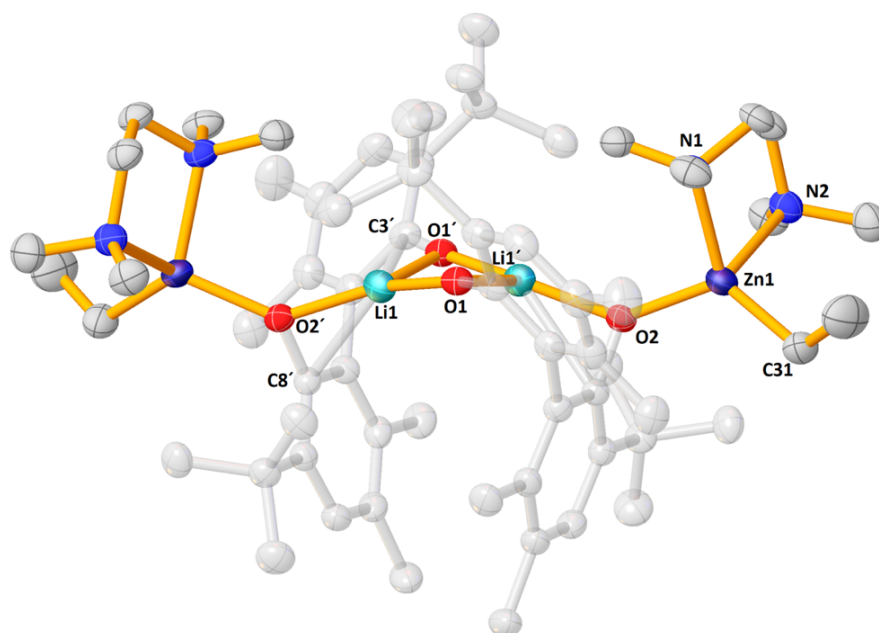


Figure 73: Solid-state structure of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2(\text{TMEDA})_2$ (**15**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *S S* orientated. Key bond distances (Å) and bond angles (°): Zn(1)–O(2), 1.9652(16); Zn(1)–N(1), 2.098(2); Zn(1)–N(2), 2.350(2); Zn(1)–C(31), 1.986(3); Li(1)–O(1), 1.824(5); Li(1)–O(1'), 1.903(4); Li(1)–O(2'), 1.908(5); Li(1)–C(3'), 2.771(5); Li(1)–C(8'), 2.415(5); Li(1)–Li(1'), 2.430(8); N(1)–Zn(1)–N(2), 81.24(8); O(2)–Zn(1)–C(31), 124.10(10); Zn(1)–O(2)–Li(1'), 139.80(15); O(1)–Li(1)–O(1'), 95.9(2); O(1)–Li(1)–O(2'), 153.0(2); Li(1)–O(1)–Li(1'), 81.4(2).

The solid-state structure can be viewed as an open dimer consisting of two $\{[(rac)\text{-BIPHEN}]\text{LiZnEt(TMEDA)}\}$ subunits. Interestingly, *(rac)*-BIPHEN no longer functions as a chelating ligand but has instead formed a single bond to both the lithium and zinc metal centres. This type of non-chelating binding for the *(rac)*-BIPHEN ligand has previously been reported for alkyl lithium phenoxides, however, to the best of our knowledge this is the first example in which it binds to two different metal centres.²³⁰ This binding mode was also found to be in direct contrast to that adopted for the *(rac)*-BIPHEN ligand in the lithium magnesiates previously reported by our group and also that of **3-10** reported in Chapter 2.⁹⁴ Examining the structure in greater detail, the central lithium atom Li1 was found to be five coordinate, bonding to a single oxygen atom of one *(rac)*-BIPHEN ligand [Li1–O1 1.824(5) Å] whilst forming two bridging interactions to both oxygen atoms of the adjacent *(rac)*-BIPHEN ligand [Li1–O1' 1.903(4) Å and Li1–O2' 1.908(5) Å]. Assignment of Li1–O1' and Li1–O2' as bridging interactions is supported by the marginal elongation in bond length relative to Li1–O1. Furthermore, Li1 also forms an η^2 π -type interaction with both oxygen bearing carbon atoms

of the phenyl rings of the (*rac*)-BIPHEN backbone. Turning now to the zinc atom Zn1, it was found to be four coordinate, adopting a distorted tetrahedral geometry (sum of bond angles 648.75 °) as is bound to a single oxygen atom of the (*rac*)-BIPHEN ligand [Zn1-O2 1.9652(16) Å] and the α -carbon of the ethyl ligand [Zn1-C31 1.986(3) Å]. Its coordination sphere is completed by the unorthodox coordination to the Lewis donor TMEDA [Zn1-N1 2.098(2) Å and Zn1-N2 2.350(2) Å], despite there being an alkali metal being present.

Thus **15** is best described as an inverse lithium zincate or a 'lithiate' in which the traditional Lewis acid/Lewis base relationship has been reversed. To expand, ate complexes are bimetallic species in which two metals are combined with one possessing a greater Lewis acidity thereby allowing it to accept more electron density. Typically, for alkali metal ate complexes, the non-alkali metal such as magnesium, zinc or aluminium has a greater Lewis acidity leading to the formation of magnesiates, zincates or aluminates. For **15** this Lewis acidity relationship between the lithium and zinc has been reversed with Li1 now acting as the stronger Lewis acid, accepting more electron density as it is coordinated to three anionic ligand fragments. In contrast, Zn1 is only coordinated to two anionic ligand fragments and the neutral TMEDA donor. Structures of this type are extremely rare with only one other inverse zincate, (LiHMDS)₂ZnMe₂(TMEDA), having been reported to date.⁴⁹ Hevia and co-workers attributed the formation of this inverse zincate to the coordination of Me₂Zn(TMEDA) to dimeric (LiHMDS)₂, which is a known aggregation state of LiHMDS. Although Li-BIPHEN is known to adopt a dimeric motif in THF, the formation of **15** is unlikely to occur via coordination of an organozinc fragment to this dimeric species as both the lithium and zinc atoms are bound to the same ligand. Furthermore, the initial deprotonation of the (*rac*)-BIPHEN ligand was carried out using Et₂Zn to generate the corresponding zinc phenoxide.¹⁰¹ In addition, formation of a grey precipitate was observed upon exposure of a solution of **15** to light which could indicate the formation of ^tBu₂Zn as a coproduct of the reaction. As ^tBu₂Zn is light sensitive the formation of a grey precipitate could arise as a result of decomposition. One possible explanation for the formation of **15** would therefore be that upon addition of ^tBuLi to a solution of [(*rac*)-BIPHEN]₂Zn₃Et₂, the central zinc atom is substituted for lithium in a transmetalation type rearrangement, which in turn leads to the formation of ^tBu₂Zn and **15**.

Given the propensity of zinc alkoxides and phenoxides to form complex aggregates in solution, it is often the case that the isolated structure is in fact not representative of the

complex in solution. With this in mind, the solution-state behaviour of **15** was studied using a combination of ^1H , ^7Li , ^{13}C and ^1H DOSY NMR spectroscopy. Our investigation was carried exclusively using non-coordinating solvents in order to prevent displacement of TMEDA and to try to circumvent decomposition of **15** by disproportionation. Examining the ^1H NMR spectrum **15** (Figure 74), a broad multiplet was observed at δ 0.05 ppm along with a triplet at δ 1.22 ppm which were found to have integration values of four and six hydrogen atoms respectively. These two resonances were therefore assigned as the CH_2 and CH_3 hydrogen atoms of the two ethyl ligands. Two singlet resonances were observed at δ 1.52 and 1.67 ppm and were assigned to the t butyl groups of the (*rac*)-BIPHEN ligand while the broad resonance located at δ 1.87 ppm with a small shoulder peak at δ 1.86 ppm was assigned to the TMEDA ligands. Due to the broadness of the resonance at δ 1.87 ppm, it was not possible to make a distinction between the terminal CH_3 and bridging CH_2 hydrogen atom environments; however, the assignment of this resonance as TMEDA was confirmed using a combination of ^{13}C and HSQC NMR spectra. Completing the assignment of the aliphatic region of the spectrum, the four singlet resonances located at δ 1.99, 2.16, 2.37 and 2.45 ppm, each with an integration values of six hydrogen atoms, were assigned to the methyl groups of the (*rac*)-BIPHEN ligand. Finally, the aromatic hydrogen atoms of the two sets of phenyl rings of the (*rac*)-BIPHEN ligands appear as two singlets at δ 7.09 and 7.20 ppm, further reinforcing the inequivalence of the two ring systems. Turning now to the ^7Li spectrum, a single major resonance was observed at δ 0.60 ppm indicating the presence of a single lithium environment for $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2(\text{TMEDA})_2$ which is in good agreement with the solid-state structure. Two additional resonances were also observed in the spectrum; however, they are only present in trace amounts and have been attributed to small amounts of decomposition.

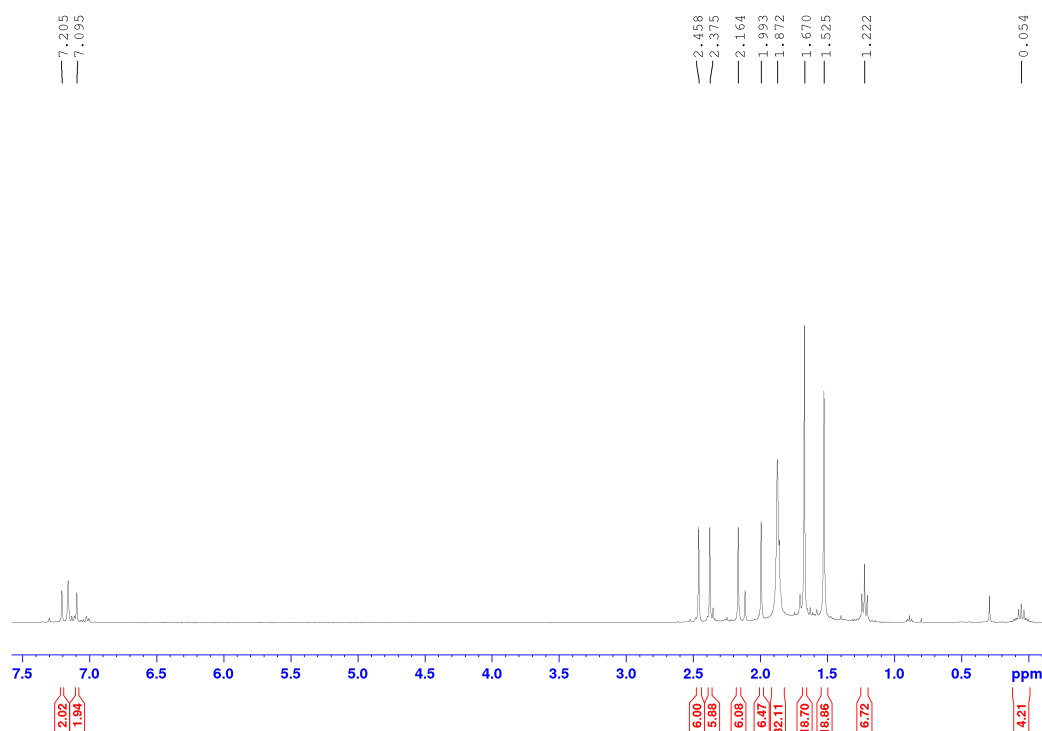


Figure 74: ^1H NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2(\text{TMEDA})_2$, **15**
(400 MHz, C_6D_6 , 300 K).

The loss of equivalency between the two phenyl ring systems of the two (*rac*)-BIPHEN ligands is further highlighted by its ^{13}C NMR spectrum (Figure 75). To expand, four resonances appeared at δ 18.1, 18.3, 20.7 and 21.4 ppm which were assigned to the methyl groups where each resonance represents two carbon atoms. A similar situation was observed for the *t*butyl groups which also appeared as four resonances at δ 31.1 and 31.4 ppm for the primary carbon atoms $[\text{C}(\underline{\text{C}}\text{H}_3)_3]$ and δ 35.1 and 35.2 ppm for the quaternary $[\underline{\text{C}}(\text{CH}_3)_3]$ carbon atoms. In the aromatic region of the spectrum, 12 resonances are visible ranging from δ 125.8 - 163.0 ppm, which is once again consistent with the two rings systems no longer being equivalent. This inequivalence could potentially arise from a difference between the two phenyl rings of a single (*rac*)-BIPHEN ligand and not because of a difference between the two individual (*rac*)-BIPHEN ligands present within the structure of **15**. If so, this would be in good agreement with the solid-state structure of **15** which unambiguously shows that the two oxygen atoms of the (*rac*)-BIPHEN ligand are bound to two different metals in the solid-state. If the solid-state structure were to be retained in solution, then this would lead to the creation of two chemically inequivalent ring systems.

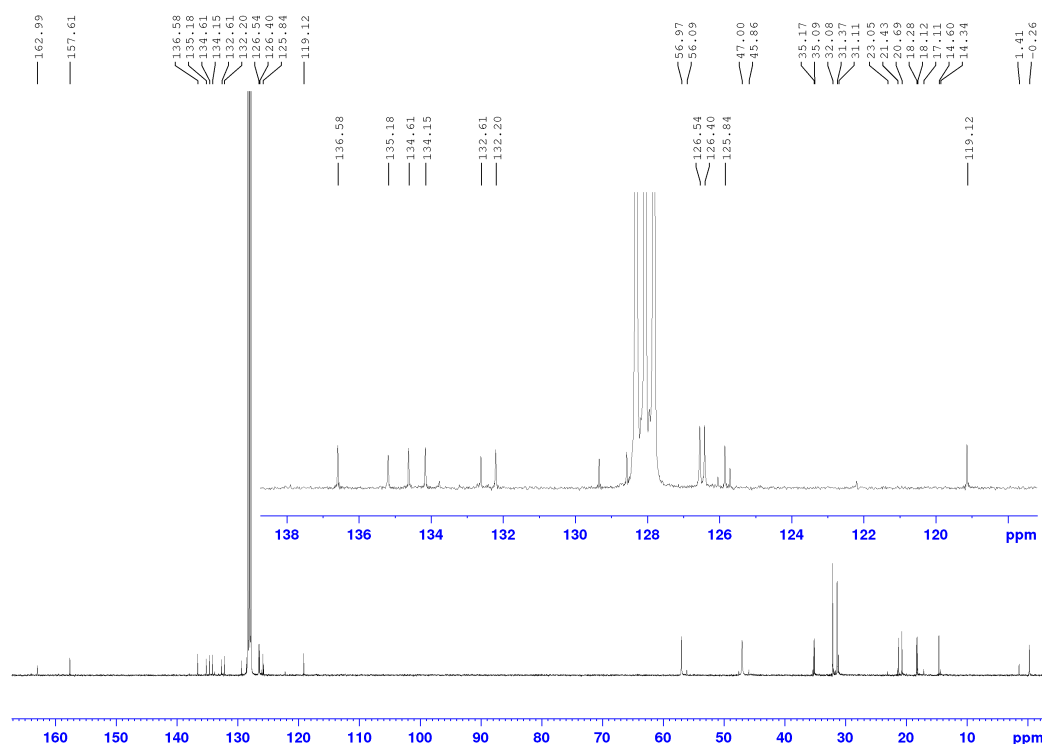


Figure 75: ^{13}C NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2(\text{TMEDA})_2$, **15**
(100 MHz, C_6D_6 , 300 K).

In order to gain a more detailed insight into the solution state structure of **15**, its solution-state behaviour was further probed using ^1H DOSY NMR spectroscopy (Figure 76). Pleasingly, the ^1H DOSY NMR spectrum revealed the resonances assigned to the *(rac)*-BIPHEN and ethyl ligands to have similar diffusion coefficients, 6.109×10^{-10} and $5.751 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ respectively, which is indicative of their inclusion within the same structural fragment. This in turn is provided evidence that the solid-state structure of **15** was retained in solution. A small difference was observed in the diffusion coefficient of TMEDA ($7.142 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) which is marginally lower than those of the *(rac)*-BIPHEN and ethyl ligands. This may suggest some degree of fluxionality in the coordination of the TMEDA ligands and is consistent with the broad nature of these resonances in the ^1H NMR spectrum of **15**.

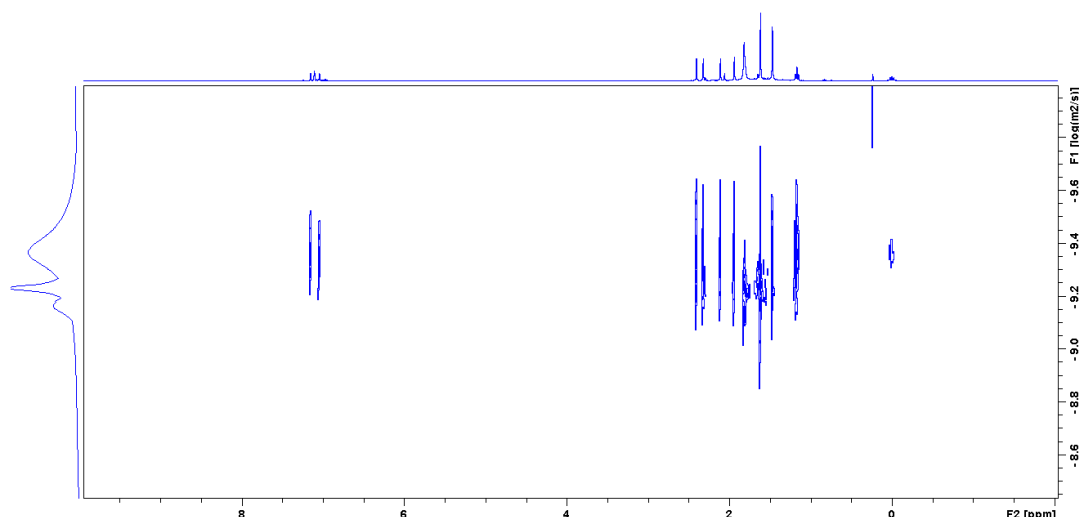


Figure 76: ^1H DOSY NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2(\text{TMEDA})_2$, **15** (C_6D_6 , 300 K).

4.6.1.3 $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(R,R)\text{-TMCD}A]_2$ (**16**)

With the initial result of **15** in hand, the reaction was repeated using (R,R) -TMCD A as the donor in an attempt to synthesise a chiral inverse lithium zincate. Deprotonation of (rac) -BIPHEN with Et_2Zn followed by co-complexation with $^t\text{BuLi}$ and addition of (R,R) -TMCD A gave a colourless solution upon refluxing in toluene. Slow cooling of the resulting solution led to the formation of large colourless crystal suitable for X-ray diffraction. Analysis of the crystals by X-ray crystallography revealed the structure to be the desired chiral inverse lithium zincate $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(R,R)\text{-TMCD}A]_2$ (**16**) (Figure 77) which crystallised in the orthorhombic crystal system in the space group $\text{P}2_12_12$ (0.125 g, 20 % yield).

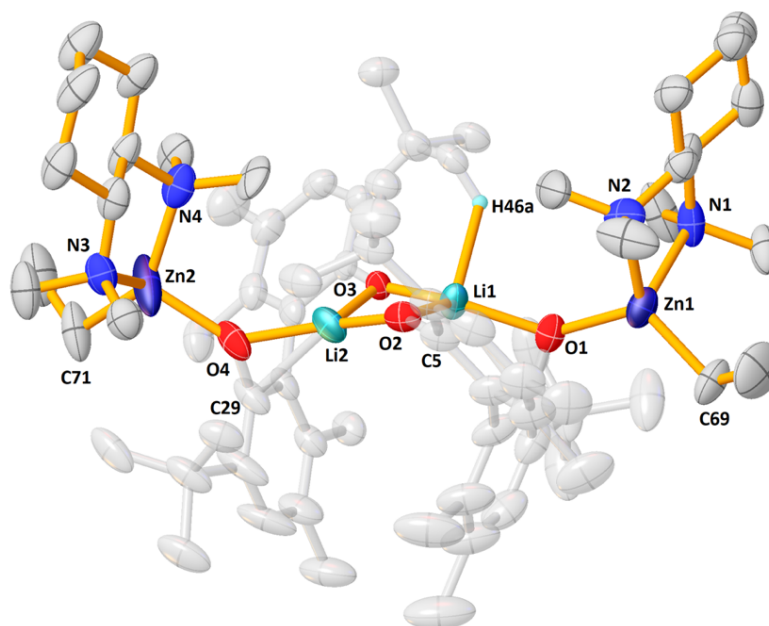


Figure 77: Solid-state structure of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(R,R)\text{-TMCD}]_2$ **16**. Hydrogen atoms and disorder in the *(rac)*-BIPHEN, *(R,R)*-TMCD and ethyl ligands are omitted for clarity. Phenoxide ligands are *S S* orientated. Thermal ellipsoids are set to 50 % probability level. Key bond distances (Å) and bond angles (°): Zn(1)–O(1), 1.967(3); Zn(1)–N(1), 2.285(5); Zn(1)–N(1), 2.131(5); Zn(1)–C(69), 1.995(5); Zn(2)–O(4), 1.960(4); Zn(2)–N(3), 2.343(11); Zn(2)–N(4), 2.01(2); Zn(2)–C(71), 1.976(11); Li(1)–O(1), 1.927(8); Li(1)–O(2), 1.889(8); Li(1)–O(3), 1.801(8); Li(1)–C(5), 2.740(9); Li(1)–C(8), 2.361(9); Li(1)–Li(2), 2.429(11); Li(2)–O(2), 1.842(9); Li(2)–O(3), 1.882(8); Li(2)–O(4), 1.903(9); Li(2)–C(29), 2.371(10); N(1)–Zn(1)–N(2) 80.37(11), O(1)–Zn(1)–C(69), 120.7(2); O(1)–Li(1)–O(2), 113.0(4); O(1)–Li(1)–O(3), 146.5(5); O(2)–Li(1)–O(3), 96.9(4); Li(1)–O(2)–Li(2); 81.2(4); Li(1)–O(3)–Li(2), 82.4(4); O(2)–Li(2)–O(3), 95.7(4); O(4)–Li(2)–O(2), 154.4(5); O(4)–Li(2)–O(3), 109.2(4); N(3)–Zn(2)–N(4), 82.2(5); O(4)–Zn(2)–C(71), 113.6(4).

Complex **16** was found to be essentially isostructural with **15**, from which only minor deviations were observed in key bond lengths and bond angles. The core Li–O–Li–O four membered ring is retained with coordination to ethyl zinc fragment through a single μ_2 bridging oxygen atom and remains almost planar. One key difference in the two structures is however the difference in coordination number for the two central lithium atoms. In the solid-state structure of **15**, the central lithium atoms were both found to be five coordinate, whereas in **16**, Li1 was found to be of six coordinate while Li2 remained five coordinate. The increase in coordination number for Li1 is caused by the formation of a long-range agostic type interaction with an adjacent *t*butyl group of the *(rac)*-BIPHEN ligand (Li1–H46 2.190 Å). The coordination sphere of Li1 is completed by binding to three oxygen atoms from the

phenoxide ligands [Li1-O1 1.927(8) Å Li1-O2 1.889(8) Å and Li1-O3 1.801 Å] and an $\eta^2 \pi$ -type interaction with a single carbon on each of the phenyl rings [Li1-C5 2.740(9) Å and Li1-C8 2.361(9) Å] of the (*rac*)-BIPHEN backbone. Turning now to the zinc atoms, Zn1 was again found to be four coordinate, adopting a distorted tetrahedral geometry (sum of bond angles 649.1 °) and is bound to a single oxygen atom of the (*rac*)-BIPHEN ligand [Zn1-O1 1.967(3) Å] and the α -carbon of the ethyl group [Zn1-C69 1.995(5) Å]. The coordination sphere of Zn1 is complete by coordination to a single molecule of (*R,R*)-TMCDAs in a non-uniform fashion [Zn1-N1 2.285(5) Å and Zn1-N2 2.131(5) Å].

An attempt was made to characterise the solution-state behaviour of **16** using a combination of ^1H , ^7Li , ^{13}C and HSQC NMR spectroscopy. Beginning with the ^1H NMR spectrum of **16** (Figure 78), multiple resonances were observed for the methyl, t butyl and aromatic hydrogen atoms of the (*rac*)-BIPHEN ligand which once again indicates loss of equivalence between the two phenyl ring systems of the (*rac*)-BIPHEN ligands, as observed for **15**. To expand, the methyl groups appear as four broad singlets at δ 2.03, 2.20, 2.38 and 2.48 ppm while the t butyl groups appear as two distinct resonances at δ 1.58 and 1.71 ppm along with the aromatic hydrogen atoms at δ 7.13 and 7.20 ppm. Focussing now on the ethyl ligands, the hydrogen atoms of the methylene groups bound directly to zinc appear as a broad multiplet at δ 0.11 ppm while the terminal CH_3 groups appear as a broad triplet at δ 1.26 ppm. The lack of diastereotopic splitting of the resonance assigned to the methylene groups is indicative that the (*rac*)-BIPHEN ligand remains bound to both lithium and zinc and no longer functions as a bidentate ligand which is consistent with the solid-state structure. Analysis of the integration value of the resonance assigned to the CH_3 groups of the ethyl ligands revealed it to be considerably higher than anticipated. This combined with the broadness of the resonance suggested that it was representative of multiple species. This was subsequently confirmed using HSQC NMR spectroscopy (Figure 80) which showed a clear correlation between the broad resonance located at δ 1.26 ppm in the ^1H NMR spectrum with two resonances in the ^{13}C NMR spectrum at δ 14.9 ppm and 24.9 ppm. The first of these two resonances was assigned to the carbon atoms of the terminal methyl groups of the ethyl ligands while the second resonance was assigned to the carbon atoms of the cyclohexyl rings of the (*R,R*)-TMCDAs ligands. These assignments are consistent with the integration value of 15 hydrogen atoms obtained for this resonance in the ^1H NMR spectrum. Furthermore, a second correlation was observed between the resonance at δ 24.9 ppm in the ^{13}C NMR spectrum with the broad singlet at δ 0.56 ppm in the ^1H NMR spectrum which was

subsequently assigned to the remaining the remaining CH_2 groups of the (*R,R*)-TMCDA ligands (Figure 80).

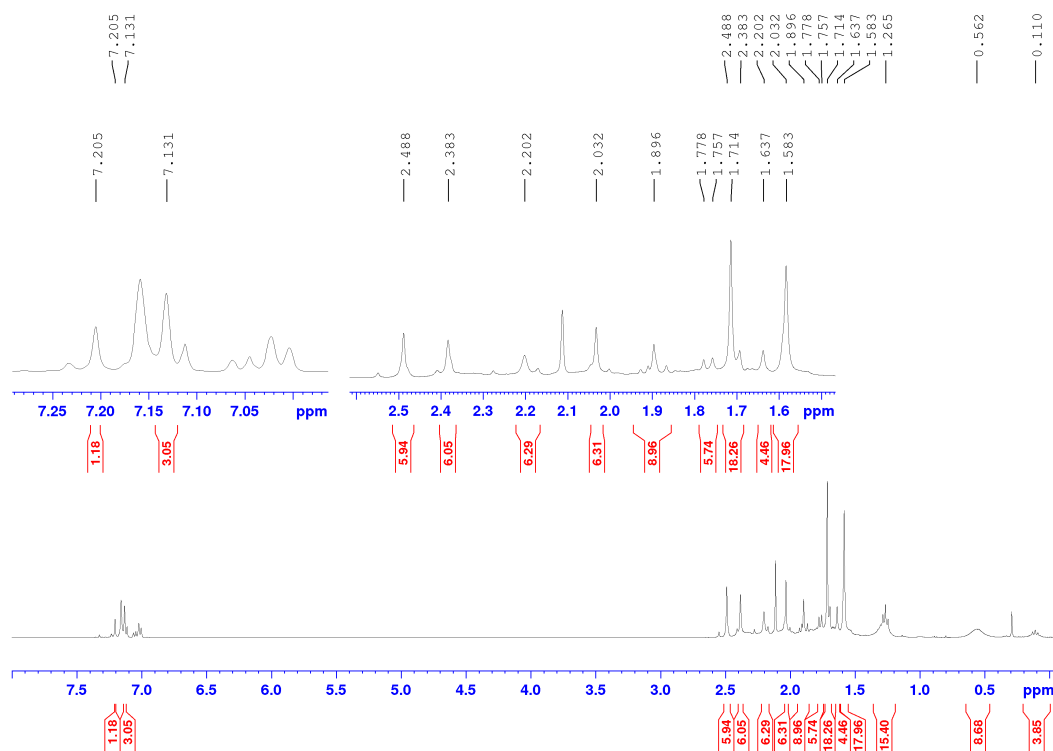


Figure 78: ^1H NMR spectrum of $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(\text{R,R})\text{-TMCDA}]_2$, **16** (400 MHz, C_6D_6 , 300 K).

The complexity of the ^1H NMR spectrum of **16** is reflected in its ^{13}C NMR spectrum (Figure 79) and remains consistent with the loss of equivalence in the (*rac*)-BIPHEN ligands. The methyl groups of the (*rac*)-BIPHEN ligand appear as four resonances at δ 18.3, 18.4, 20.7 and 21.3 ppm with each resonance representing two carbon atoms. Likewise, the t butyl ligands also appear as four resonances with the methyl groups appearing at δ 31.5 and 32.4 ppm and the two quaternary carbons appearing at δ 35.2 and 35.6 ppm. The aromatic region of the spectrum was found to contain 14 major resonances ranging from δ 119.3 ppm to 164.1 ppm. The presence of two additional resonances in this region of the spectrum could point towards a further loss of equivalence in the aromatic ring systems. Assignment of the ethyl ligands remained possible with the methylene groups bound directly to the zinc centres appearing at δ 0.0 ppm while the terminal CH_3 groups of the ligands are located at δ 14.9 ppm. The CH_2 groups of the cyclohexane rings of the (*R,R*)-TMCDA ligands were assigned to the resonances located at δ 21.4 and 24.9 ppm while the NCH groups were assigned to the resonance at δ 63.7 ppm. Unfortunately, it has not been possible to make a definitive assignment of the terminal methyl groups of the (*R,R*)-TMCDA ligands.

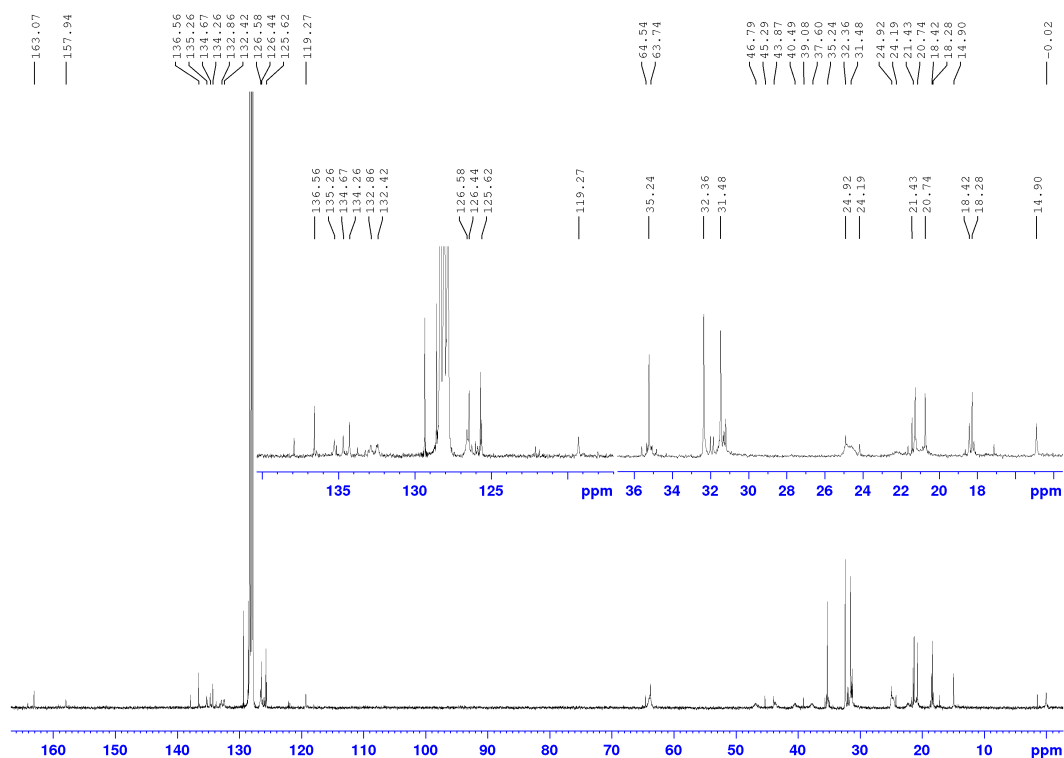


Figure 79: ^{13}C NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(R,R)\text{-TMCD}]_2$, **16**
(100 MHz, C_6D_6 , 300 K).

The reaction was repeated using other dialkyl and diamido zinc complexes such as $^n\text{Bu}_2\text{Zn}$, ZnR_2 (where $\text{R} = \text{CH}_2\text{SiMe}_3$), $^t\text{Bu}_2\text{Zn}$ and $\text{Zn}(\text{HMDS})_2$ however no structural characterisation has so far been possible. Fast decomposition of the reaction mixture upon exposure to light was observed for the reaction mixture obtained using $^t\text{Bu}_2\text{Zn}$. As such, it was not possible to obtain any informative NMR spectroscopic information.

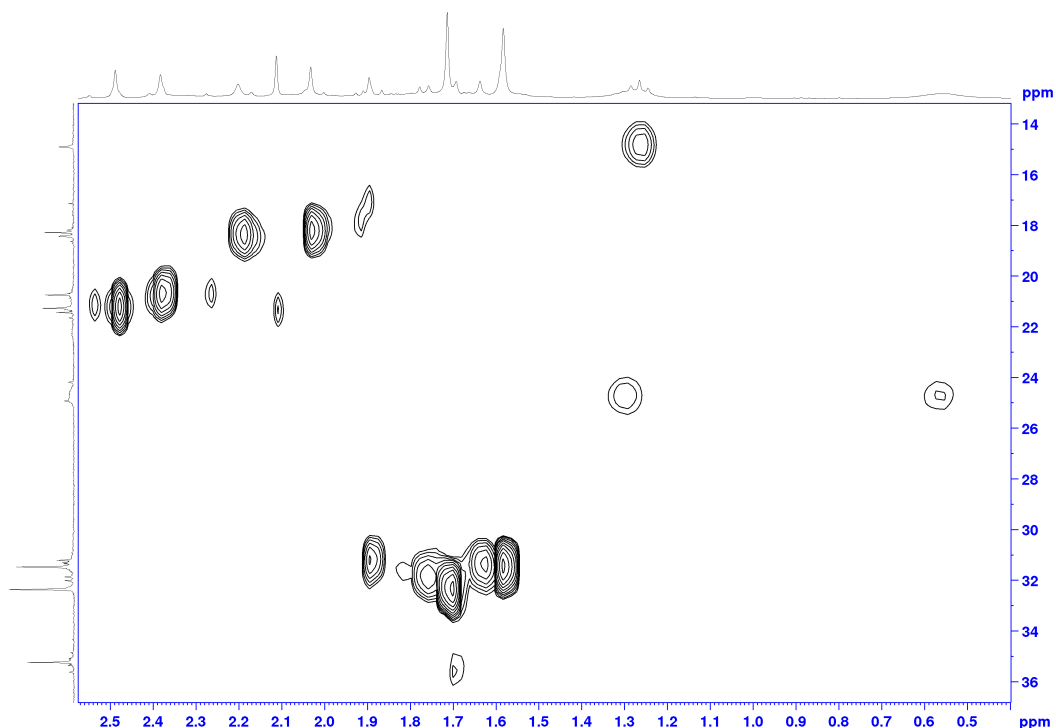


Figure 80: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_2\text{Zn}_2\text{Et}_2[(R,R)\text{-TMCDAs}]_2$, **16** (C_6D_6 , 300 K).

4.6.2 Synthesis and Characterisation of Lithium Phenoxides

4.6.2.1 $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$ (**17**)

In an attempt to synthesise a mixed alkyl phenoxide lithium zincate, the synthetic approach was adapted. Rather than carrying out the deprotonation of *(rac)*-BIPHEN with the dialkyl zinc reagent followed by co-complexation with the desired alkyllithium, it was decided to use a lithium zincate to carry out the deprotonation of the parent phenoxide ligand to ensure the correct stoichiometric ratio of both metals. It was hoped by utilising the ‘pre-formed’ zincate that the formation of the inverse zincates could be suppressed despite them being interesting results in their own right. Formation of the aforementioned inverse lithium zincates was indeed eliminated; however, the resulting product from the reaction of the higher order lithium zincate $\text{LiZnR}_4(\text{TMEDA})_2$ was not the desired lithium zincate but the tetranuclear lithium phenoxide $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$ (**17**) (Figure 81) which crystallised in the orthorhombic crystal system in the $\text{Pna}2_1$ space group (0.114 g, 24 % yield).

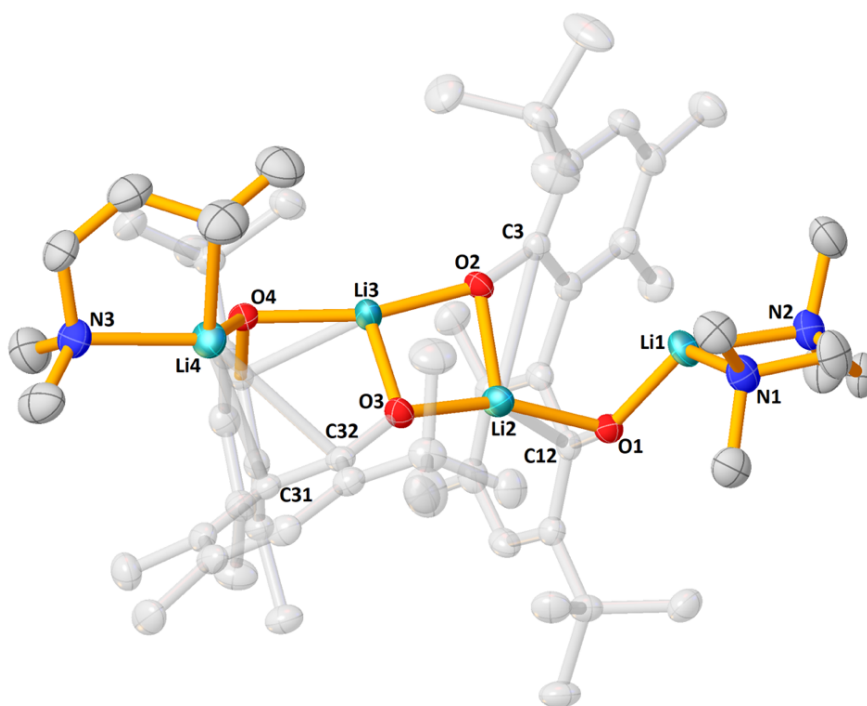


Figure 81: Solid State Structure of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$ **17**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *R S* orientated. Key bond distances (Å) and bond angles (°): Li(1)-O(1), 1.789(5); Li(1)-N(1), 2.190(5); Li(1)-N(2), 2.079(5); Li(1)-Li(2), 3.034(6); Li(2)-O(1), 1.936(5); Li(2)-O(2), 1.885(5); Li(2)-O(3), 1.826(5); Li(2)-C(3), 2.773(5); Li(2)-C(12), 2.322(5); Li(2)-Li(3), 2.431(6); Li(3)-O(2), 1.845(5); Li(3)-O(3), 1.886(5); Li(3)-O(4), 1.942(5); Li(3)-C(27), 2.372(5); Li(3)-Li(4), 3.102(7); Li(4)-O(4), 1.848(5); Li(4)-N(3), 2.185(6); Li(4)-N(4), 2.136(6); Li(4)-C(31), 2.624(6); Li(4)-C(32), 2.777(6); N(1)-Li(1)-N(2), 85.88(19); Li(1)-O(1)-Li(2), 109.0(2); O(1)-Li(2)-O(2), 104.5(2); O(1)-Li(2)-O(3), 159.9(3); O(2)-Li(2)-O(3), 95.5(2); Li(2)-O(2)-Li(3), 81.4(2); Li(2)-O(3)-Li(3), 81.8(2); O(2)-Li(3)-O(3), 94.9(2); O(2)-Li(3)-O(4), 162.3(3); N(3)-Li(4)-N(4), 84.4(2); Li(4)-O(4)-Li(3), 109.8(2).

Examining the organometallic framework of **17** showed it to adopt a similar overall structure to the inverse zincates reported previously (Figures 73 and 77). Beginning with the core of the structure, the Li-O-Li-O four membered ring which was present in both inverse zincates is retained within the structure. Both lithium atoms Li2 and Li3 are coordinated to three oxygen atoms from two (*rac*)-BIPHEN ligands, however their overall coordination number was found to be different. Li2 has a coordination number of five and is coordinated to the three oxygen atoms [Li2-O1 1.936(5) Å Li2-O2 1.885(5) Å and Li2-O3 1.826 Å] and forms an η^2 π -type interaction with the oxygen bearing carbon atoms [Li2-C3 2.773 Å and Li2-C12 2.322 Å] of the (*rac*)-BIPHEN phenyl rings. In contrast to this, Li3 was found to only be four

coordinate as a result of forming a single η^1 π -type interaction with the phenyl ring system of the (*rac*)-BIPHEN backbone [Li3-C27 2.372(5) Å] along with coordination to three phenoxide oxygen atoms [Li3-O2 1.845(5) Å, Li3-O3 1.886(5) Å and Li3-O4 1.942(5) Å]. Turning now to the periphery of the molecule, a difference is also observed in the coordination number of lithium atoms Li1 and Li4 (Figure 81). Interestingly, Li1 was found to have a coordination number of three, forming a single bond to the oxygen atom of the (*rac*)-BIPHEN ligand [Li1-O1 1.789(5) Å] while its coordination sphere is completed by coordination to a single molecule of TMEDA [Li1-N1 2.190 Å and Li1-N2 2.079 Å]. Despite the positioning of adjacent to the π system of the (*rac*)-BIPHEN phenyl ring in the crystal structure, no π -type interactions are formed. The shortest interatomic distance between Li1 and the carbon atoms of the ring system was found to be greater than 3 Å, rendering the formation of any stabilising interactions unlikely. Li4 on the other hand forms an η^2 π -type interaction with the ipso carbon [Li4-C31 2.624(6) Å] and the *ortho* carbon bound to the phenoxide oxygen atom [Li4-C32 2.77(6) Å]. Li4 is also bound to a single oxygen of the (*rac*)-BIPHEN ligand [Li4-O4 1.848(5) Å] and its coordination sphere is completed by coordination to a single molecule of TMEDA [Li4-N3 2.185(6) Å and Li4-N4 2.136(6) Å]. Examination of the interatomic distances between the lithium atoms revealed that the distance between Li1-Li2 [3.034(6) Å] to be slightly shorter than that of Li4-Li3 [3.102(7) Å]. However, both these distances are considerably longer than the interatomic distances separating the two lithium atoms Li2 and Li3 that are part of the core Li-O-Li-O ring [Li2-Li3 2.431(6) Å].

Examining the solution-state behaviour of **17**, it was immediately obvious that the equivalency of the two (*rac*)-BIPHEN phenoxide ligands had been lost, as evidenced by the appearance of multiple sets of resonances for the methyl groups, ^tbutyl groups and aromatic hydrogen atoms in both the ¹H (Figure 82) and ¹³C NMR (Figure 83) spectra. This was found to be in direct contrast with (*rac*)-BIPHENLi₄(THF)₄ previously characterised by our group in which the sets of two phenyl rings of the phenoxide ligands remained magnetically equivalent.⁹⁴ This further highlights the unique bonding situation in these ‘open’ dimeric systems in which the phenoxide ligands are bound to two different metal centres. As with the previous inverse zincates **15** and **16**, **17** was once again found to be poorly soluble in non-coordinating solvent.

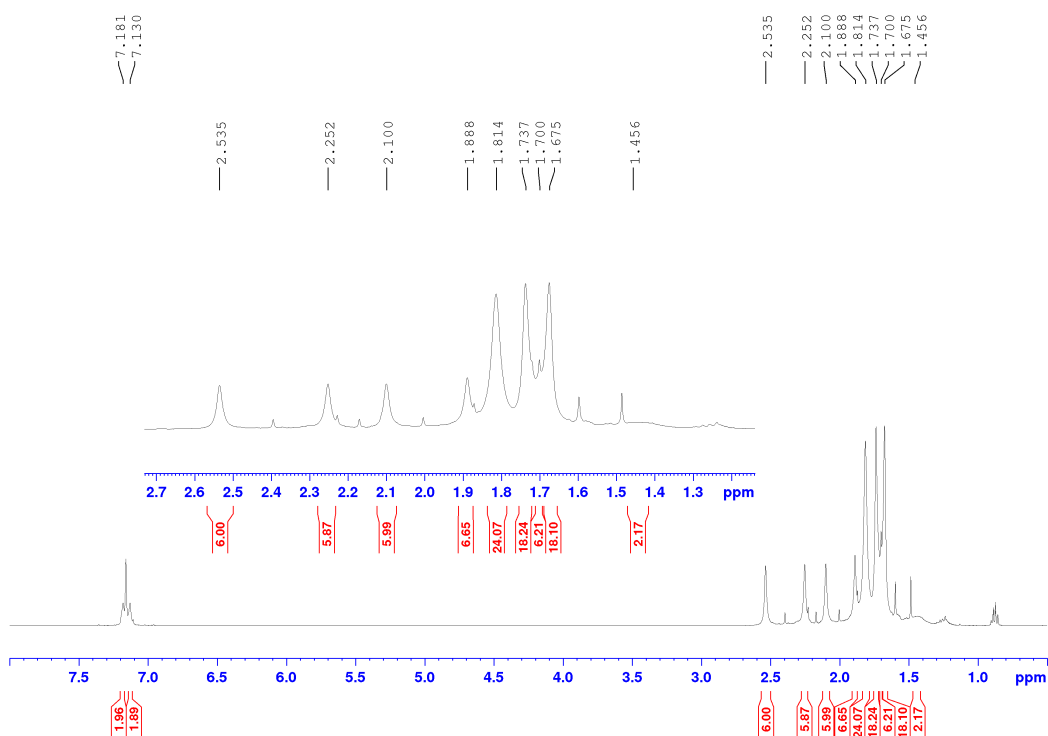


Figure 82: ^1H NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$, **17** (400 MHz, C_6D_6 , 300 K).

Beginning with the ^1H NMR spectrum (Figure 82), the t butyl groups of the (*rac*)-BIPHEN ligands were assigned to the two broad singlet resonances which appeared at δ 1.67 and 1.73 ppm while the methyl groups were assigned to the four resonances at δ 1.88, 2.10, 2.25 and 2.53 ppm. The aromatic hydrogen atoms of the phenyl rings were located as two broad singlets in the aromatic region of the spectrum at δ 7.13 and 7.18 ppm with integration values consistent with there being two hydrogen atoms in each environment. Focussing now on the TMEDA ligands, a broad singlet was observed at δ 1.81 ppm in the aliphatic region of the spectrum with an integration corresponding to 24 hydrogen atoms and was assigned to the terminal methyl groups of the donor ligand. The remaining methylene CH_2 groups of TMEDA could only be identified using a combination of ^1H , ^{13}C and HSQC NMR spectroscopy. The HSQC NMR spectrum of **17** (Figure 84) revealed a correlation between the resonance located at δ 56.5 ppm the ^{13}C NMR spectrum of complex with two resonances in the ^1H NMR spectrum at δ 1.45 and a 1.70 ppm. These two resonances were found to have integration values of two and six hydrogen atoms respectively and were therefore assigned as bridging CH_2 groups of the TMEDA ligands. The splitting of these resonances suggests a loss of equivalence for one of the bridging CH_2 groups, while the broadness of the resonance assigned to the terminal methyl groups of TMEDA could suggest fluxional coordination of the donor ligand.

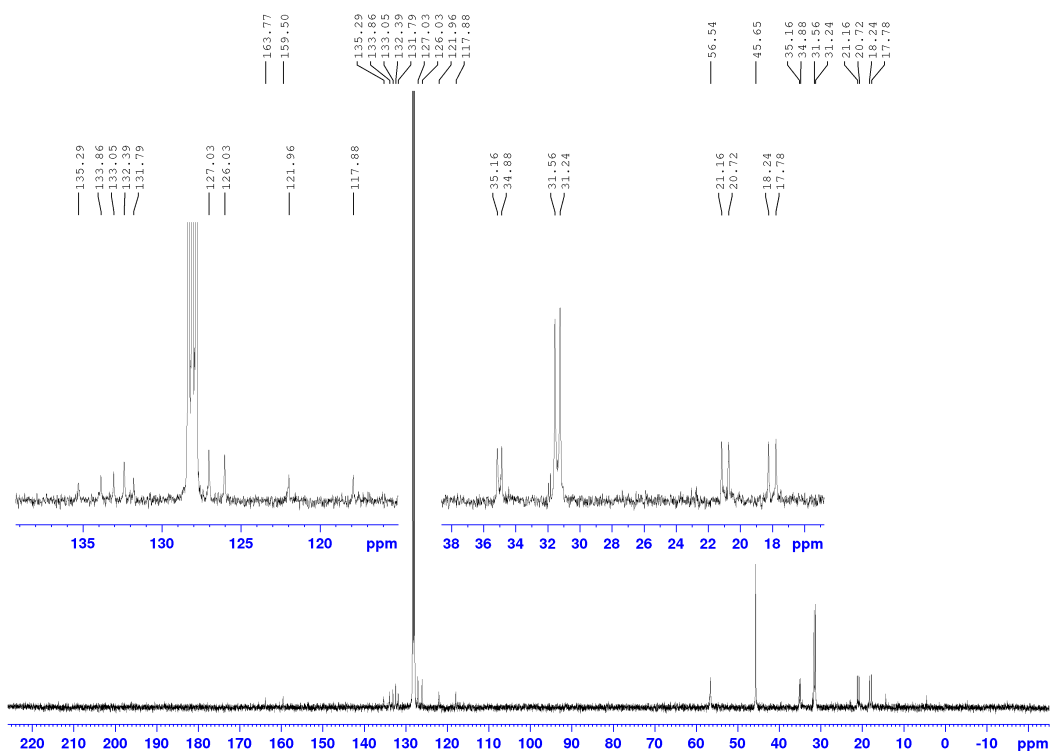


Figure 83: ^{13}C NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$, **17** (100 MHz, C_6D_6 , 300 K).

Turning now to the ^{13}C NMR spectrum, the methyl groups bound of the (*rac*)-BIPHEN ligand appeared as four individual resonances in the aliphatic region of the spectrum at δ 17.8, 18.2, 20.7 and 21.2 ppm while the primary and quaternary carbon atoms of the *t*butyl groups were located as two distinct sets of resonances at δ 31.2 and 31.6 ppm and δ 34.9 and 35.2 ppm respectively. Completing the aliphatic region of the spectrum, the terminal methyl and bridging methylene groups of the TMEDA ligands appeared at δ 45.7 and 56.5 ppm respectively. The aromatic region of the spectrum was found to contain 12 resonances with chemical shift values ranging from δ 117.9 ppm to 163.8 ppm and is consistent with the loss of equivalence in phenyl rings of the (*rac*)-BIPHEN ligands. Using 2D HSQC NMR spectroscopy (Figure 84) it was possible to identify the two sets of non-quaternary aromatic carbons as being those located at δ 126.0 and 127.0 ppm. The ^7Li spectrum of the complex was found to contain two distinct resonances which would suggest that there are two separate lithium environments in solution. These data appear to indicate that in non-coordinating solvent, the dimeric structure of **17** characterised in the solid-state (Figure 81) is retained in solution.

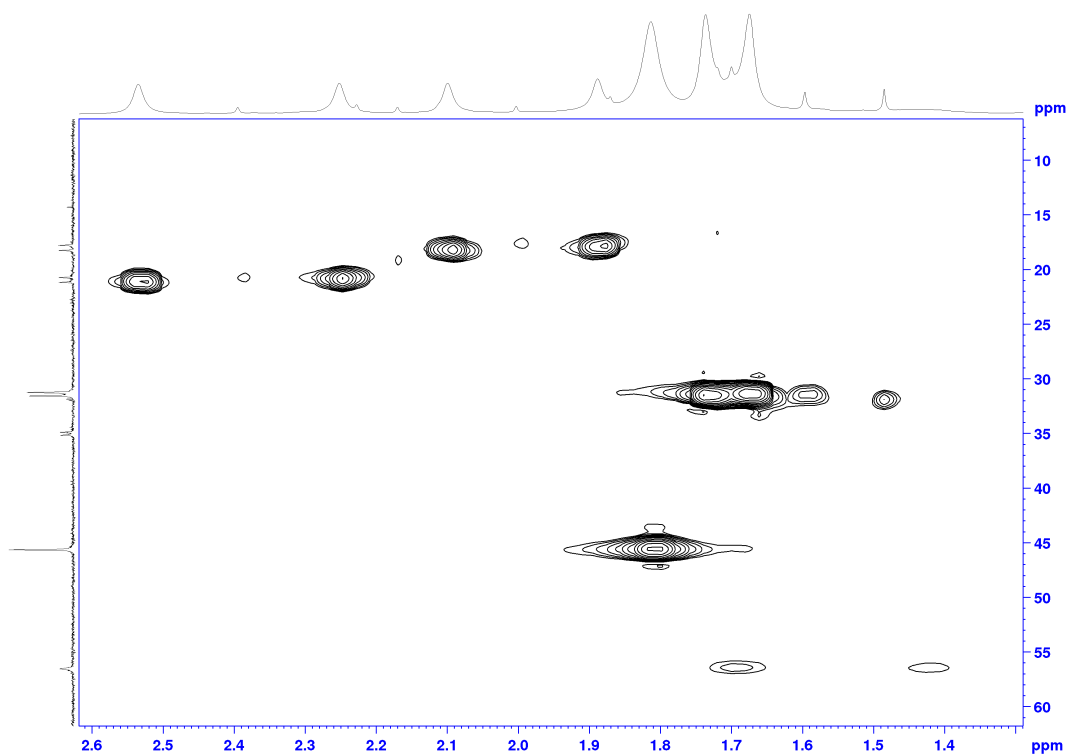


Figure 84: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$, **17** (C_6D_6 , 300 K).

4.6.2.2 $[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD}]_2$ (**18**)

The reaction was repeated using the chiral donor ligand (*R,R*)-TMCD to form the higher order zincate $\text{Li}_2\text{ZnR}_4[(R,R)\text{-TMCD}]_2$ with the end goal of creating a chiral mixed alkyl/phenoxide zincate. Reaction of this zincate mixture with (*rac*)-BIPHEN produced a colourless solution upon refluxing the reaction mixture in toluene from which colourless crystals were isolated. Analysis of these crystals by single crystal X-ray diffraction revealed the product to be the chiral lithium phenoxide $[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD}]_2$ (**18**) (Figure 85) which crystallised as a hexane solvate in the monoclinic crystal system in the space group *I*2 (0.085 g, 16 % yield).

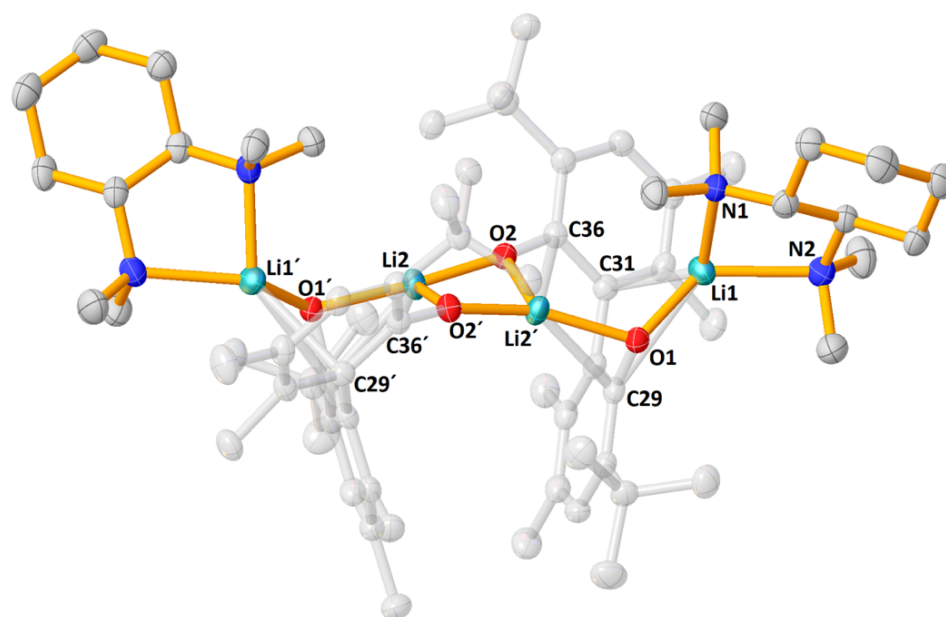


Figure 85: Solid-state Structure of $[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCDA}]_2$, **18**. Hydrogen atoms and disorder in (R,R) -TMCDA are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *S S* orientated. Key bond distances (Å) and bond angles (°): Li(1)-O(1), 1.875(6); Li(1)-N(1), 2.100(6); Li(1)-N(2), 2.104(6); Li(1)-C(29), 2.730(6); Li(1)-C(31), 2.582(7); Li(2)-O(1'), 1.938(5); Li(2)-O(2), 1.835(5); Li(2)-O(2'), 1.911(6); Li(2)-C(29'), 2.342(6); Li(2)-C(36'), 2.754(6); N(1)-Li(1)-N(2), 84.7(2); Li(1)-O(1')-Li(2'), 118.7(3); O(2)-Li(2)-O(2'), 94.8(2); Li(2)-O(2)-Li(2'), 82.3(3); O(2)-Li(2)-O(1'), 156.3(3); O(1')-Li(2)-O(2'), 108.7(3).

Analysis of the solid-state structure of **18** showed its organometallic framework to exhibit a similar open dimeric motif as the previously discussed **17**. To expand, the central lithium atom Li2 was found to be five coordinate and is coordinated to three oxygen atoms from two (rac) -BIPHEN ligands [Li2-O1' 1.938(5) Å, Li2-O2 1.835(5) Å and Li2-O2' 1.911(6) Å] which forms the core Li-O-Li-O four membered ring. The coordination sphere of Li2 is completed by the formation of an η^2 π -type interaction [Li2-C29' 2.342(6) Å and Li2-C36' 2.754(6) Å]. Turning now to the lithium atom on the periphery of the complex, Li1, it was also found to be five coordinate. Li1 is bound to a single oxygen atom of a (rac) -BIPHEN ligand and also forms η^2 π -type interaction with the phenyl rings of the (rac) -BIPHEN ligand. The coordination sphere of Li1 is completed by coordination to a single molecule of (R,R) -TMCDA. It is worth noting here the difference in coordination numbers of the peripheral lithium atoms when compared to **17**. In the solid-state structure of **17**, only one of the peripheral lithium atoms forms a π -type interaction with the phenyl ring of the (rac) -BIPHEN backbone while the other remained three coordinate, bound exclusively to the oxygen atoms of the

phenoxide ligand and the nitrogen atoms of TMEDA. Inclusion of (*R,R*)-TMEDA appears to have altered the conformation of the structure in such a way that both lithium atoms are now within close enough proximity to the phenyl rings of the (*rac*)-BIPHEN ligand in order to form these stabilising π -type interactions. Furthermore, an increase in coordination number for one of the lithium atoms of the Li_2O_2 core was observed upon inclusion of (*R,R*)-TMEDA for the inverse zincate **16** compared to its TMEDA containing analogue **15**. This would suggest that when (*R,R*)-TMEDA is utilised as the Lewis donor, the lithium atoms sit in closer proximity to the π system of the phenoxide ligand. The reaction was repeated using a two-step synthetic approach in which deprotonation of the (*rac*)-BIPHEN- H_2 was carried out using $^n\text{BuLi}$ prior to co-complexation with ZnR_2 and addition of (*R,R*)-TMEDA. The reaction once again yielded a white suspension which was recrystallised from hot toluene to produce colourless crystals upon slow cooling to ambient temperature. Analysis of these crystals by single crystal X-ray diffraction revealed the reaction product to be **18**. This result shows that not only is outcome of the reaction independent of the identity of the alkyllithium reagent but also that inclusion of the dialkylzinc reagent ZnR_2 appears to play no role in the formation of **18**. Furthermore, this would suggest that the higher order lithium zincate $\text{Li}_2\text{ZnR}_4((\text{R,R})\text{-TMEDA})_2$ reacts with (*rac*)-BIPHEN as a monometallic lithium base and not as a bimetallic lithium zincate.

Focussing now on the solution-state behaviour of **18**, inclusion of (*R,R*)-TMEDA severely complicated the ^1H (Figure 86) and ^{13}C (Figure 87) NMR spectra. As a result, it has not been possible to fully assign the two spectra. By using a combination of ^1H , ^{13}C and HSQC spectroscopy, however, it has been possible to make tentative assignments of some of the functional groups of the (*rac*)-BIPHEN ligand. The complexity of the ^1H and ^{13}C NMR spectra for **18** could be indicative of the formation of diastereomers. As diastereomers are magnetically inequivalent, this would account for the presence of multiple resonances associated with the (*rac*)-BIPHEN ligands.

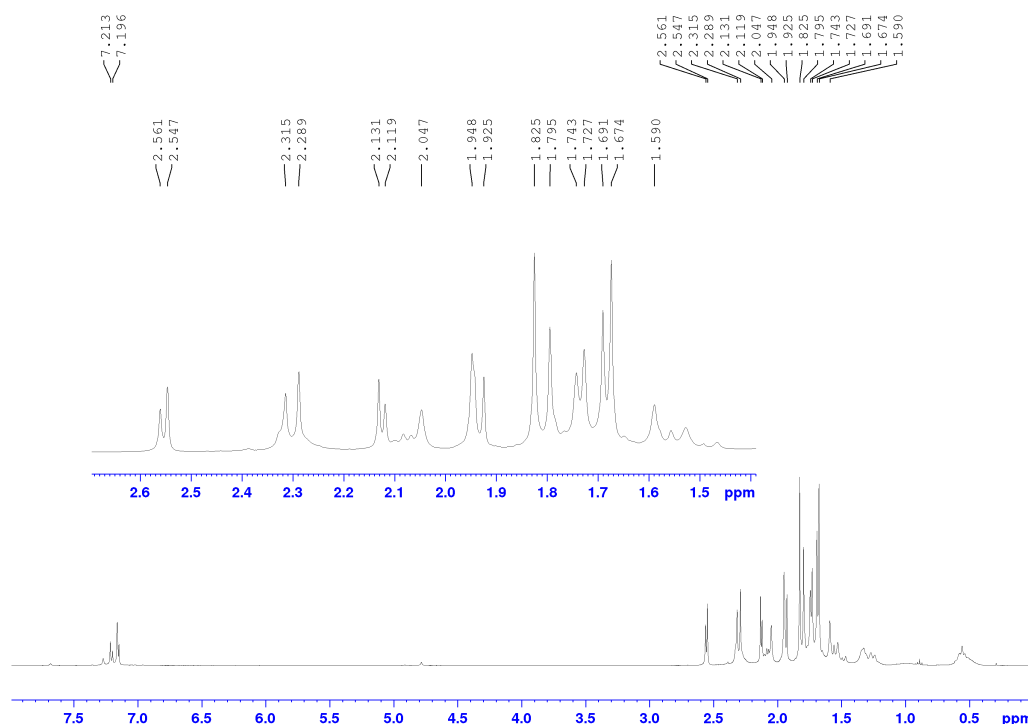


Figure 86: ^1H NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD}]_2$, **18**
(400 MHz, C_6D_6 , 300 K).

To expand, the HSQC NMR spectrum of **18** (Figure 88) showed clear correlations between the resonances located at δ 1.92, 2.11, 2.28 and 2.56 ppm in the ^1H NMR spectrum with those found in the ^{13}C NMR spectrum at δ 17.9, 18.3, 20.9 and 21.3 ppm respectively. Based on these correlations these resonances were assigned to the methyl groups attached the (*rac*)-BIPHEN ligand. Despite the correlations in the HSQC NMR spectrum being between these four sets of values, a second set of resonances were also observed in the ^{13}C NMR spectrum at δ 18.1, 18.4, 20.9 and 21.4 ppm. This could potentially suggest the formation of a second species or that inclusion of the (*R,R*)-TMCD has eliminated the remaining equivalence in the phenyl ring systems. Furthermore, the chemical shift values of all eight resonances were found to be in good agreement with those of the corresponding methyl groups of **17**. A clear correlation was also observed between the two sets of resonances located at δ 1.67 and 1.82 ppm in the ^1H NMR spectrum and the two resonances found in the ^{13}C NMR spectrum at δ 31.1 and 31.8 ppm respectively. Based on these correlations and their chemical shifts, these resonances were assigned to the primary carbon atoms of t butyl groups of the (*rac*)-BIPHEN ligands. The quaternary carbon atoms of the t butyl groups were assigned to the resonances which appear at δ 34.9 and 35.3 ppm. Once again, a second set of resonances were observed which could potentially be assigned to carbon atoms of the

^tbutyl ligands at δ 31.4, 31.6, 35.2 and 35.4 ppm. This is similar to the situation observed for the methyl groups of the (*rac*)-BIPHEN and again is suggestive of a loss of equivalence between all four ring systems.

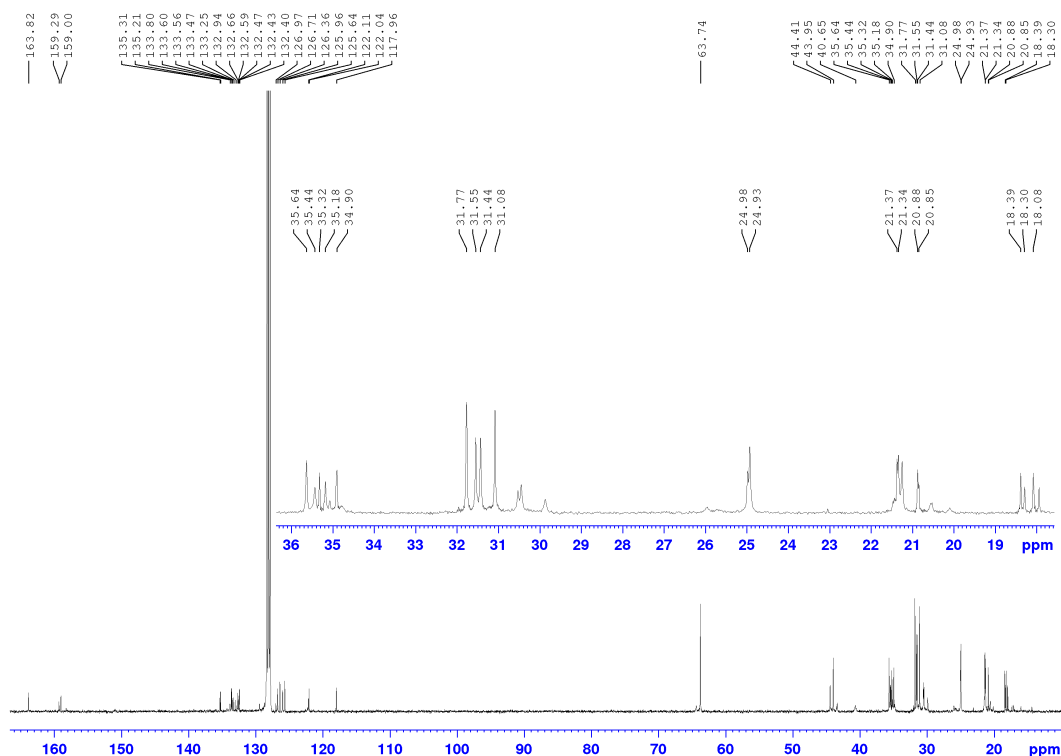


Figure 87: ^{13}C NMR spectrum $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD}]_2$, **18** (100 MHz, C_6D_6 , 300 K).

Moreover, the aromatic region of the ^{13}C NMR spectrum was found to contain 24 resonances which is consistent with solid-state structure of **18**. Returning to the aliphatic region of the spectrum and the (*R,R*)-TMCD ligands, correlations were observed between the broad multiplets in the ^1H NMR spectrum at δ 0.55 and 1.32 ppm with two resonances in the ^{13}C NMR spectrum at δ 21.4 and 25.0 ppm and were assigned to the cyclohexyl rings of the two (*R,R*)-TMCD ligands. Finally, the tertiary carbon atoms of the (*R,R*)-TMCD ring systems appear at δ 63.7 ppm in the ^{13}C NMR spectrum and show a clear correlation with the resonance located at δ 1.69 ppm in the ^1H NMR spectrum. Although clear correlations are observed in the HSQC NMR spectrum for both the (*rac*)-BIPHEN ligand and the cyclohexane rings of (*R,R*)-TMCD of **18**, it has not been possible to obtain accurate integration values for any of the resonances associated with the two ligands in the ^1H NMR spectrum (Figure 86). Furthermore, no assignment of the terminal methyl groups of the (*R,R*)-TMCD ligand were possible. As with previous complexes containing the both the (*R,R*) and (*S,S*)- ligands, no clear resonances were observed in the ^{13}C NMR spectrum which prevented any attempt at

assignment using HSQC NMR spectroscopy. Despite this however, the assignments which could be made were consistent with data obtained in the solution-state for **17** and the solid-state structure of **18**.

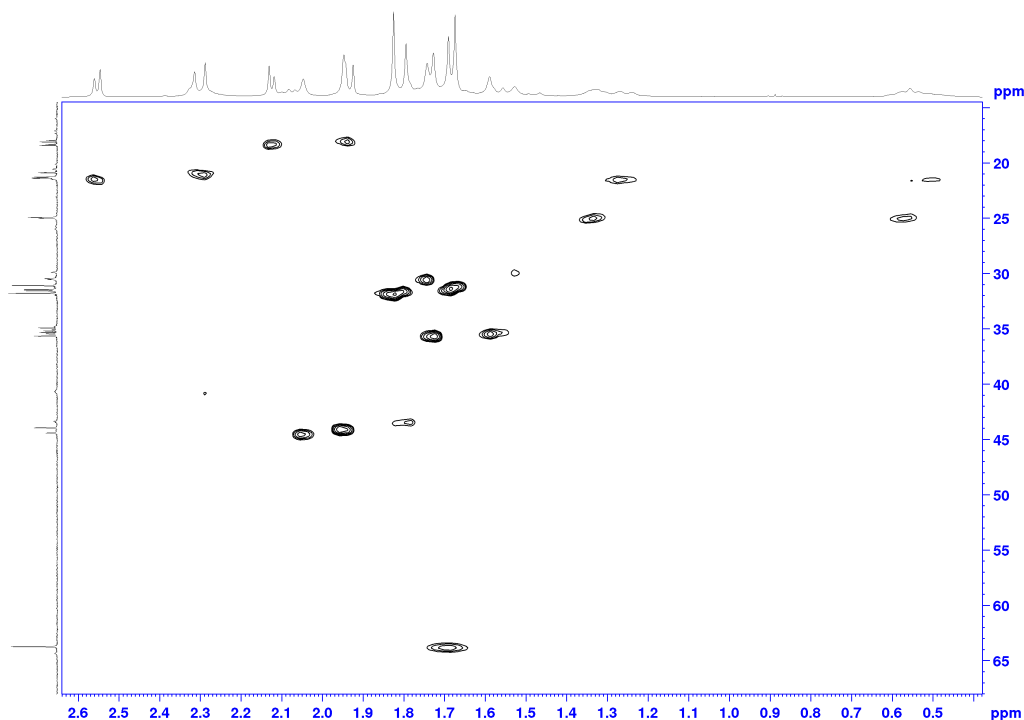


Figure 88: HSQC NMR Spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCDA}]_2$, **18** (C_6D_6 , 300 K).

4.6.2.3 $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$ (**19**)

In an attempt to gain further insight into the reactivity of lithium zincates with the phenoxide ligand (*rac*)-BIPHEN the reaction was repeated utilising the lower order lithium zincate $\text{LiZnR}_3(\text{PMDETA})$. It was proposed at this stage of the investigation that due to the smaller atomic radius of zinc in comparison with magnesium, that the zinc centre may not be able to accommodate two alkyl ligands as well as the (*rac*)-BIPHEN ligand. With the majority of structurally characterised zincates being triorganozincates, it was thought therefore that a bimetallic mixed alkyl/phenoxide lithium zincate could be produced utilising the lower order zincate $\text{LiZnR}_3(\text{PMDETA})$. In addition, $\text{LiZnR}_3(\text{PMDETA})$ has previously been characterised in both the solid-state and in solution therefore providing a greater insight into the starting material.¹⁷⁷ The reaction of $\text{LiZnR}_3(\text{PMDETA})$ with an equimolar amount of (*rac*)-BIPHEN was therefore carried out using the same synthetic procedure as used for the two previously characterised complexes followed by re-crystallisation of the reaction mixture from hot toluene to give a crop of large, colourless crystals. Analysis of these crystals by single crystal

X-ray diffraction revealed the product to be the PMDETA solvated tetranuclear lithium phenoxide $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$ (**19**) (Figure 89). Complex **19** crystallised as a toluene solvate in the orthorhombic crystal system in the space group $Fdd2$ (0.137 g, 25 % yield).

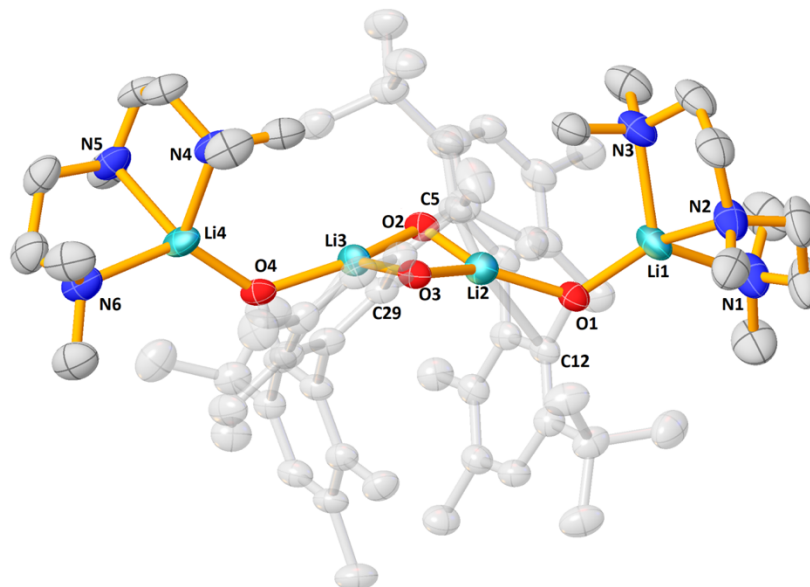


Figure 89: Solid State Structure of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$, **19**. Hydrogen atoms and disorder in PMDETA ligands are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *R R* orientated. Key bond distances (Å) and bond angles (°): Li(1)-O(1), 1.839(10); Li(1)-N(1), 2.233(12); Li(1)-N(2), 2.233(13); Li(1)-N(3), 2.176(13); Li(1)-Li(2), 3.402(14); Li(2)-O(1), 1.934(10); Li(2)-O(2), 1.920(11); Li(2)-O(3), 1.827(10); Li(2)-C(5), 2.746(11); Li(2)-C(12), 2.363(10); Li(2)-Li(3), 2.414(14); Li(3)-O(2), 1.830(9); Li(3)-O(3), 1.922(11); Li(3)-O(4), 1.929(10); Li(3)-C(29), 2.761(10); Li(3)-C(36), 2.362(10); Li(3)-Li(4), 3.423(14); Li(4)-O(4), 1.866(10); Li(4)-N(4), 2.161(12); Li(4)-N(5), 2.247(11); Li(4)-N(6), 2.163(12); Li(1)-O(1)-Li(2), 128.8(5); O(1)-Li(2)-O(2), 113.6(5); O(1)-Li(2)-O(3), 148.0(6); O(2)-Li(2)-O(3), 97.4(5); Li(2)-O(2)-Li(3), 80.1(4); Li(2)-O(3)-Li(3), 80.1(4); O(2)-Li(3)-O(3), 97.3(5); O(2)-Li(3)-O(4), 149.7(6); O(3)-Li(3)-O(4), 112.8(4); Li(4)-O(4)-Li(3), 128.9(5).

Analysis of the solid-state structure of **19** showed the complex to contain the same core structure as the two previously characterised lithium phenoxides **17** and **18**. The core of the complex once again contains a four membered Li-O-Li-O ring with bond lengths and bond angles similar to those of **17** and **18**. Focussing on the core of the molecule, both Li2 and Li3 are five coordinate, bound to three oxygen atoms from two (*rac*)-BIPHEN ligands [Li2-O1 1.934(10) Å, Li2-O2 1.920(11) Å, Li2-O3 1.827(10) Å and Li3-O2 1.830(9) Å, Li3-O3 1.922(11)

Å, Li3-O4 1.929(10) Å]. Their coordination sphere is completed by the formation of two π -type interactions with the oxygen bearing carbons of the (*rac*)-BIPHEN phenyl rings [Li2-C5 2.746(11) Å, Li2-C12 2.363(10) Å and Li3-C29 2.716(10) Å, Li3-C36 2.362(10) Å]. Turning now to the outer two lithium atoms, Li1 and Li4, were both found to be four coordinate. Each lithium atom is bound to one (*rac*)-BIPHEN ligand through a single Li-O bond [Li1-O1 1.839(10) Å and Li4-O4 1.866(10) Å] and their coordination sphere is completed by coordination to a single molecule of PMDETA [Li1-N1 2.233(12) Å, Li1-N2 2.233(13) Å, Li1-N3 2.176(13) Å and Li4-N4 2.161(12) Å, Li4-N5 2.247(11) Å, Li4-N6 2.163(12) Å]. In contrast to the previous structures of **17** and **18**, neither Li1 nor Li4 were found to form any π -type interactions with the phenyl rings of the (*rac*)-BIPHEN ligand. The lack of any long-range stabilising interactions between the peripheral lithium atoms and the phenyl rings of the phenoxide ligands was attributed to the increase in denticity of the PMDETA ligand. This increase in denticity allows PMDETA to effectively cap the lithium atoms therefore preventing any further coordination which could potentially influence the stability and reactivity of the complex.

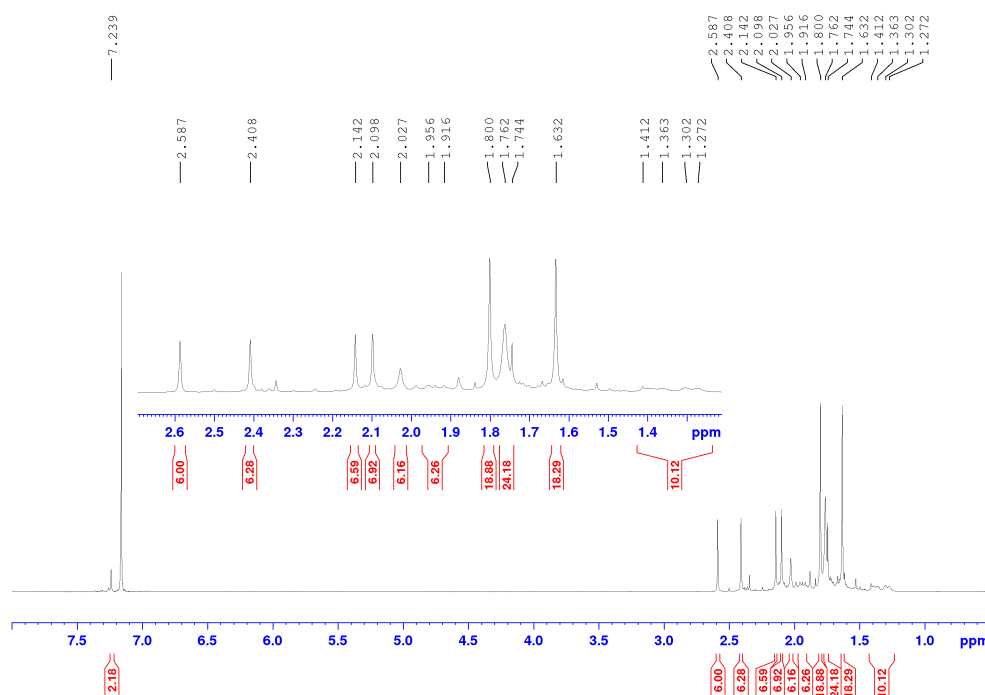


Figure 90: ^1H NMR spectrum of $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$, **19** (400 MHz, C_6D_6 , 300 K).

The solution-state behaviour of **19** was probed using a combination of ^1H , ^{13}C , HSQC and ^1H DOSY NMR spectroscopy. Beginning with the ^1H NMR spectrum (Figure 90), inequivalence was once again observed in the two phenyl ring systems of the (*rac*)-BIPHEN ligands. As a

result, the *t*butyl groups (*rac*)-BIPHEN ligands appear as two broad singlets at δ 1.63 and 1.80 ppm while the methyl groups of the same ligand appear as four broad singlets at δ 2.09, 2.14, 2.40 and 2.58 ppm. Only one set of aromatic hydrogen atoms of the (*rac*)-BIPHEN ligands were visible, with the other being obscured by the residual solvent signal and appear as a singlet at δ 7.23 ppm. Returning to the aliphatic region of the spectrum, the bridging methylene groups of the PMDETA ligand appear as two broad multiplets, the first of which ranges from δ 1.27 - 1.41 ppm and was found to have an integration value of ten hydrogen atoms while the second multiplet ranges from δ 1.91 - 1.95 ppm with an integration value of six hydrogen atoms. The methyl groups attached to the external nitrogen atoms (NMe₂) of the PMDETA ligands appear as a broad singlet with a significant shoulder peak at δ 1.76 ppm while the methyl groups attached to the internal nitrogen atoms appear as a singlet at δ 2.02 ppm.

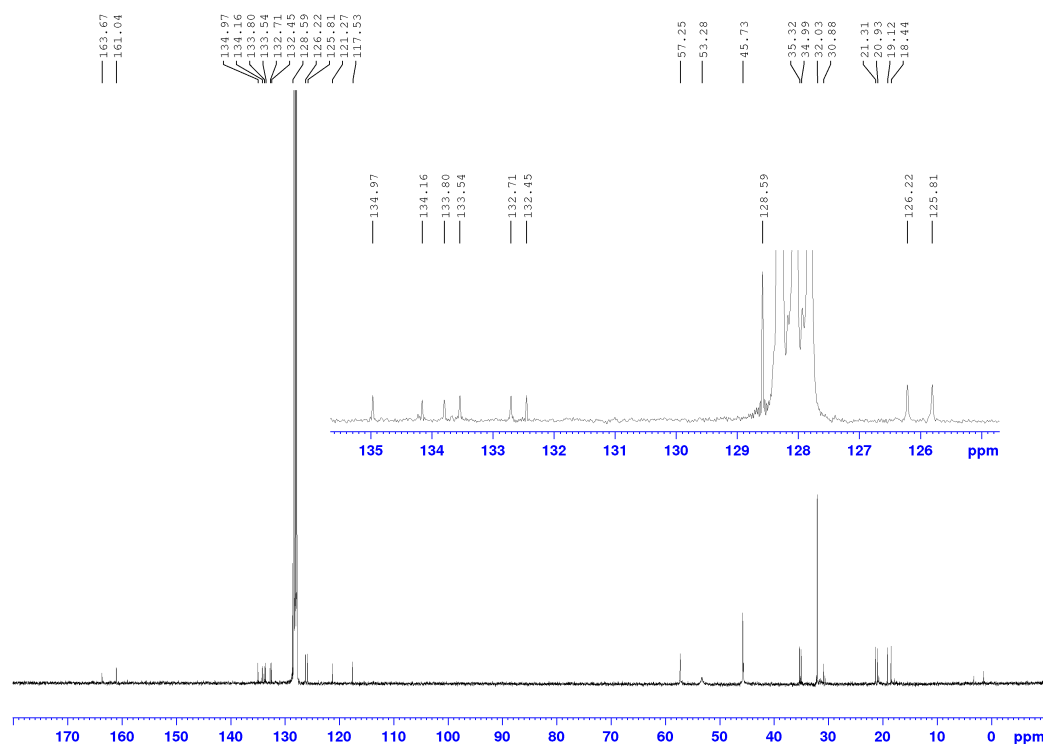


Figure 91: ¹³C NMR spectrum of [(*rac*)-BIPHEN]₂Li₄(PMDETA)₂, **19** (100 MHz, C₆D₆, 300 K).

Turning now to the ¹³C NMR spectrum of **19**, it was found to be in good agreement with the ¹H NMR spectrum and further highlights the inequivalence observed between the two phenyl ring systems of the (*rac*)-BIPHEN ligand (Figure 91). To expand, the methyl groups of the (*rac*)-BIPHEN ligand appear as four resonances at δ 18.4, 19.1, 20.9 and 21.3 ppm with each resonance representing two carbon atoms. For the *t*butyl ligands however, only three

resonances were observed. All four primary carbon atoms [$\text{C}(\underline{\text{C}}\text{H}_3)$] appear as a single resonance at δ 32.0 ppm while the quaternary carbon atoms [$\underline{\text{C}}(\text{CH}_3)$] appear as two distinct resonances at δ 35.0 and 35.3 ppm. The aromatic region of the spectrum was found to contain 12 resonances ranging from δ 117.5 ppm to 163.7 ppm which is consistent with the loss of equivalence between the two phenyl rings of the (*rac*)-BIPHEN ligand. Once again, each resonance observed in the aromatic region of the spectrum is representative of two carbon atoms. Focussing now on the PMDETA ligands, the methyl groups bound to the external (NMe_2) and internal (NMe) nitrogen atoms appear at δ 30.9 and 45.7 ppm respectively. The first of these two resonances was shown by HSQC NMR spectroscopy (Figure 92) to correlate with the shoulder peak observed in the ^1H NMR spectrum at δ 1.74 ppm while the second of the two resonances was shown to correlate to both the resonances at δ 1.76 and δ 2.02 ppm. This would suggest that one of the methyl groups bound to the external nitrogen atoms has been rendered magnetically inequivalent. Further analysis of **19** using ^1H DOSY NMR spectroscopy showed that only a single species was present in solution. Interestingly, the ^1H DOSY NMR spectrum showed a small difference in the diffusion coefficient of the PMDETA ($6.089 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) and (*rac*)-BIPHEN ligands ($5.636 \times 10^{-10} \text{ m}^2\text{s}^{-1}$). This difference in diffusion coefficient is indicative of fluxional coordination of the PMDETA donor ligands and mirrors the situation observed in solution for **15**. This fluxional coordination could provide a potential explanation for the inequivalence induced in the methyl groups of the PMDETA ligands. Based on the magnetic inequivalence observed for both the (*rac*)-BIPHEN and PMDETA ligands of **19** it is unlikely that a solvent separated species is formed.

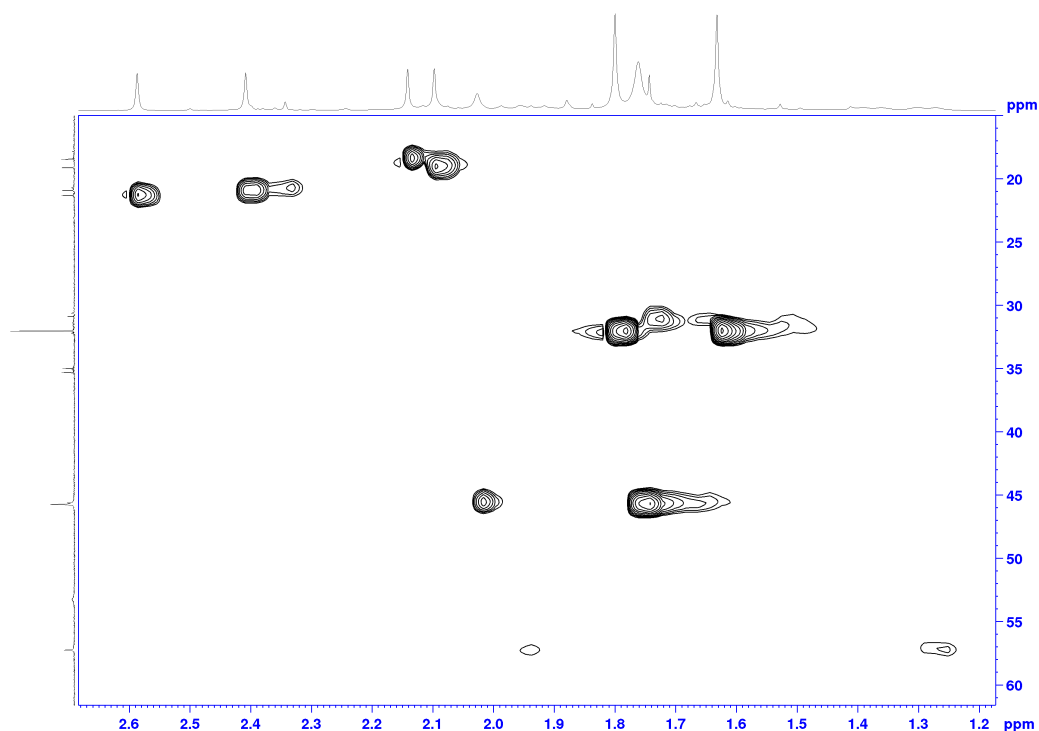


Figure 92: HSQC NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$, **19** (C_6D_6 , 300 K).

Although no bimetallic alkylzinc phenoxides were produced, the isolation of **17**, **18** and **19** provides an invaluable insight into the reactivity of the parent lithium zincates. These results suggest that despite previous reports of similar zincate mixtures being efficient bases for the alkali metal mediated zincation (AMMZn) of various substrates, it appears that in reaction with (*rac*)-BIPHEN these bimetallic complexes function as simple monometallic bases giving rise to the lithiated product. Deprotonation appears to be carried out by the more kinetically reactive alkyllithium species to give the isolated lithium phenoxides and the corresponding dialkyl zinc reagents as the co-products of the reaction. Moreover, this suggest that co-complexation of ZnR_2 with the lithium phenoxide produced *in situ* does not take place. This stands in direct contrast to the reactivity of the less bulky Et_2Zn reagent which was utilised in the synthesis of the inverse zincates **15** and **16**. Although surprising, monometallic reactivity of this type has recently been reported for the corresponding sodium zincate NaZnR_3 which was found to react as a monometallic sodium base for the deprotonation of ketones to produce the corresponding sodium enolate and ZnR_2 .²⁴² Lithium phenoxides **17**, **18** and **19** can therefore be viewed as the TMEDA, (*R,R*)-TMEDA and PMDETA adducts of the previously reported $[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{THF})_4$.⁹⁴ These new complexes adopt a 'open' dimeric structure in which the (*rac*)-BIPHEN phenoxide ligands no longer functions as chelating ligand. This change in bonding mode for the phenoxide ligands presumably arises due to the

increase in steric bulk of the di- and tridentate donors which prevents the 'closed' dimeric structure from forming.

4.6.2.4 $\{(rac)\text{-BIPHEN}\}\text{Zn}(R,R)\text{-TMCD A}$ (**20**)

In an attempt to gain further insight into the reactivity of the bulky CH_2SiMe_3 ligand, the reaction between $(rac)\text{-BIPHEN}$ and ZnR_2 (where $\text{R} = \text{CH}_2\text{SiMe}_3$) was carried out using a modified co-complexation approach similar to that used in the synthesis of the inverse zincates **15** and **16**. Deprotonation of the parent $(rac)\text{-BIPHEN}$ ligand was first carried out using the dialkyl zinc base ZnR_2 to produce the corresponding zinc phenoxide. This was followed by addition of $t\text{BuLi}$ and $(R,R)\text{-TMCD A}$ as the donor ligand. Surprisingly, this did not lead to isolation of the corresponding inverse lithium zincate but to the isolation of the chiral, monomeric zinc phenoxide $\{(rac)\text{-BIPHEN}\}\text{Zn}(R,R)\text{-TMCD A}$ (**20**) (Figure 93) (0.068 g, 23 % yield). Complex **20** crystallised as a toluene solvate in the monoclinic crystal system in the C2 space group. Examining the organometallic framework of **20** revealed the central zinc atom to be tetrahedrally coordinated (sum of bond angles 655.33°) to two oxygen atoms of the phenoxide ligand [Zn1-O1 1.922(3) Å and Zn1-O2 1.901(2) Å] and two nitrogen atoms of $(R,R)\text{-TMCD A}$ [Zn1-N1 2.108(3) Å and Zn1-N2 2.080(3) Å]. Vidal-Ferran and co-workers have recently published a series of related complexes using a 3,3',5,5' functionalised 2,2'-biphenol ligands with a variety of 1,2-cyclohexyldiamine donors which exhibit a strong structural resemblance to **20**.²⁴³ The structural resemblance between **20** and those complexes published by Vidal-Ferran is further reinforced upon analysis of the Zn-O and Zn-N bond lengths which were found to be in good agreement in all cases. Unfortunately, due to the complex solution-state behaviour of **20**, it was not possible to assign the ^1H or ^{13}C NMR spectra of the complex. One potential explanation for this complexity is the formation of diastereomers arising from complexation of the chiral diamine donor $(R,R)\text{-TMCD A}$ with both the R and S enantiomers of the BIPHEN ligand present within the racemic mixture used for the synthesis of **20**. Dynamic ligand rearrangements could also occur leading to the formation of multiple aggregated forms in solution. Rearrangements of this type have been documented for zinc phenoxides and other related complexes.^{221,231}

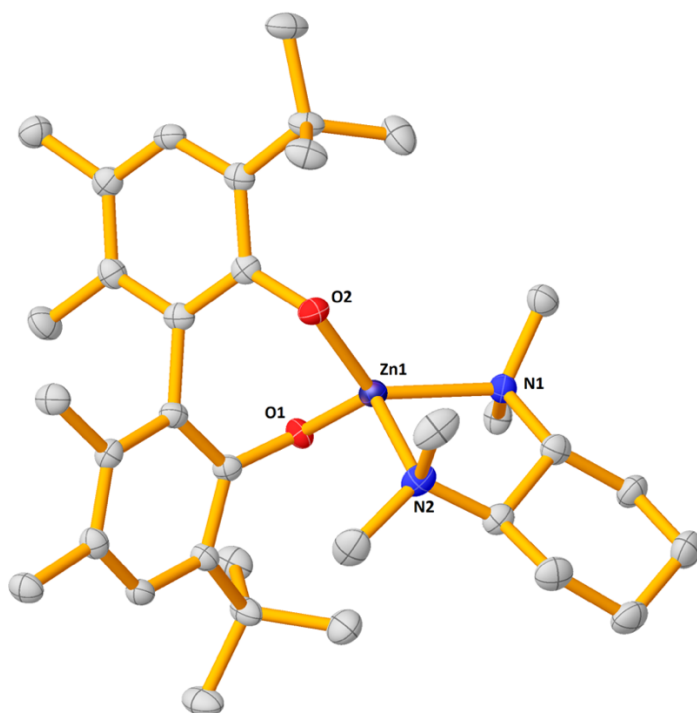
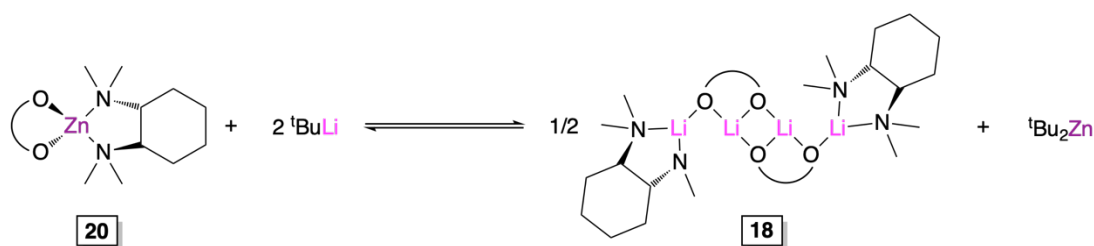


Figure 93: Solid State Structure of $\{(rac)\text{-BIPHEN}\}\text{Zn}(R,R)\text{-TMCD A}$, **20**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *R* orientated. Key bond distances (Å) and bond angles (°): Zn(1)-O(1), 1.922(3); Zn(1)-O(2), 1.901 (2); Zn(1)-N(1), 2.108(3); Zn(1)-N(2), 2.080(3); O(1)-Zn(1)-O(2), 111.06(11); N(1)-Zn(1)-N(2), 86.16(12); O(1)-Zn(1)-N(1), 108.62(11); O(1)-Zn(1)-N(2), 120.42(13); O(2)-Zn(1)-N(1), 128.12; O(2)-Zn(1)-N(2), 100.92(11).

Despite utilising the same co-complexation approach that led to the isolation of **15** and **16**, employment of the bulkier CH_2SiMe_3 ligand does not lead to the formation of a heteroleptic inverse zincate. One plausible explanation for the formation of **20** is as a result of a ligand reorganisation caused by Schlenk-like equilibria. One potential equilibrium that would account for the formation of **20** is depicted in scheme 34 which shows that in the presence of two equivalents of $^t\text{BuLi}$, **20** could potentially exist in equilibrium with $[(rac)\text{-BIPHEN}]_2\text{Li}_4((R,R)\text{-TMCD A})_2$ (**18**) and $^t\text{Bu}_2\text{Zn}$. The isolation of **20** from the reaction mixture would suggest that this equilibrium lies strongly to the left favouring the formation of the monomeric zinc phenoxide. Moreover, the formation of $^t\text{Bu}_2\text{Zn}$ as a reaction co-product has also been proposed for inverse zincates **15** and **16**. Although the modified co-complexation approach used for the synthesis of **20** once again failed to produce a bimetallic alkyl zincate incorporating the CH_2SiMe_3 ligand, it does potentially provide a valuable insight into the formation of the lithium phenoxides **17**, **18** and **19**.



Scheme 34: Potential equilibrium for the formation of $\{(rac)\text{-BIPHEN}\}\text{Zn}(R,R)\text{-TMCDAs}$, **20**.

4.6.3 Synthesis and Characterisation of Sodium Zincates

4.6.3.1 $[(rac)\text{-BIPHEN}]_2\text{ZnNa}_2(\text{THF})_4$ (**21**)

With the results of our studies into lithium zincates in hand, it was decided to continue our investigation into the synthesis and characterisation of mixed alkyl/phenoxide alkali metal zincates by incorporating the heavier alkali metal sodium. To this end, Et_2Zn was added to a solution of $[(rac)\text{-BIPHEN}]_2\text{Na}_4$ in order to form a co-complex. As with previous reactions, the resulting suspension formed upon co-complexation of the dialkylzinc reagent with the alkali metal phenoxide was found to be insoluble in non-coordinating solvents, even when heated to reflux, without the addition of a donor solvent. PMDETA was therefore added as a donor ligand in an attempt to produce a solution; however, even with heating to reflux, dissolution of the white precipitate was not achieved. Despite results from previous experiments which appeared to show that bimetallic mixed alkyl/phenoxides were susceptible to disproportionation when THF was employed as the bulk reaction solvent, THF was added dropwise to the refluxing reaction mixture. Addition of THF led to the formation of a colourless homogeneous solution. Subsequent slow cooling of the solution produced large colourless crystals (0.043 g, 8 % yield). Analysis of these crystals by single crystal X-ray diffraction revealed the structure to be that of the $(rac)\text{-BIPHEN}$ rich dimer $[(rac)\text{-BIPHEN}]_2\text{ZnNa}_2(\text{THF})_4$ (**21**) (Figure 94) which crystallised in the monoclinic crystal system in the $C2/c$ space group. The structure of **21** was found to be analogous to that of the magnesium complex $[(rac)\text{-BIPHEN}]_2\text{MgNa}_2(\text{THF})_4$ (**2**) (Figure 13) which was discussed in Chapter 2. The formation of **21** was once again attributed to ligand rearrangement which arises as a result of Schlenk-like equilibrium. Isolation of the homoleptic $(rac)\text{-BIPHEN}$ rich product demonstrates that not only do bimetallic magnesium and zinc phenoxides form similar structural motifs, but they are also susceptible to disproportionation in the presence of ethereal solvents such as THF.

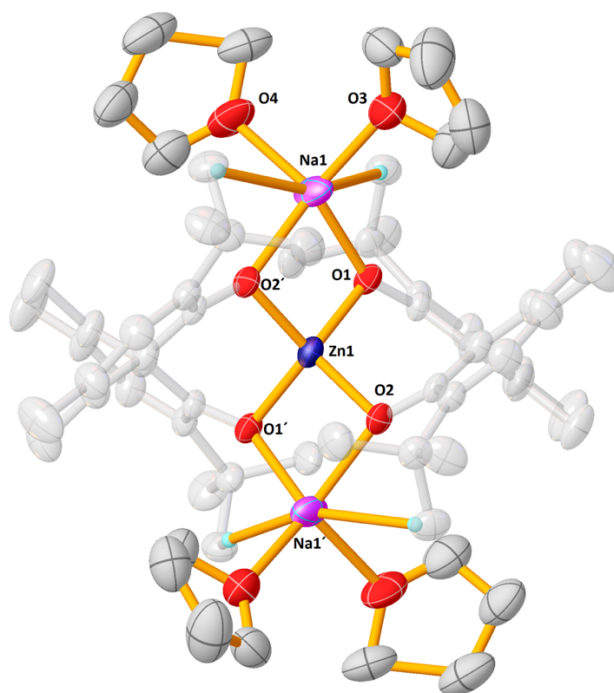


Figure 94: Solid-state structure of $[(rac)\text{-BIPHEN}]_2\text{ZnNa}_2(\text{THF})_4$, **21**. Hydrogen atoms and disorder in the THF molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligands are *S S* orientated. Key bond distances (Å) and bond angles (°): Zn(1)-O(1), 1.9627(17); Zn(1)-O(2), 1.9730(15); Na(1)-O(1), 2.190(2); Na(1)-O(2'), 2.255(2); Na(1)-O(3), 2.27(2); Na(1)-O(4), 2.391(15); Zn(1)-Na(1), 3.0717(12); O(1)-Zn(1)-O(2), 104.19(7); O(1)-Zn(1)-O(1'), 137.36(10); O(1)-Zn(1)-O(2'), 91.94(7); O(2)-Zn(1)-O(2'), 134.87(10); Zn(1)-O(1)-Na(1), 95.27(7); O(1)-Na(1)-O(2'), 79.08(7); Na(1)-Zn(1)-Na(1'), 170.85(6).

Examining the solid-state structure in more depth, it was found to contain a spirocyclic motif consisting of two Na-O-Zn-O ring systems. The central zinc atom Zn1 was found to be four coordinate, forming a single bond to the four oxygen atoms of the two (*rac*)-BIPHEN ligands [Zn1-O1 1.9627(17) Å and Zn1-O2 1.9730(15) Å], with a distorted tetrahedral geometry (sum of bond angles 663.95 °). These Zn-O bond lengths were found to be in good agreement with those reported in the literature for zinc alkoxides and aryloxides containing similar spirocyclic motifs.²²⁹ The sodium atom Na1 was also found to adopt a distorted tetrahedral geometry (sum of bond angles 659.34 °) and is bound to a single oxygen atom from the two (*rac*)-BIPHEN ligands [Na1-O1 2.190(2) Å and Na1-O2' 2.255(2) Å]. The coordination sphere of Na1 is completed by coordination to two molecules of THF [Na1-O3 2.27(2) Å Na1-O4 2.391(15) Å]. In addition to these, each sodium atom also forms two agostic type interactions with CH₃ groups of the neighbouring ^tbutyls of the (*rac*)-BIPHEN phenoxide ligands. Despite the

aforementioned structural similarity between **21** and **2**, no such agostic interactions were observed in the solid-state structure of the homoleptic magnesium species. Furthermore, **21** exhibits a structural resemblance to that of the heterobimetallic sodium zinc phenoxide containing the 3,3',5,5'-tetra-^tbutyl-2,2'-biphenolate ligand previously reported by Wu.²³⁸ Both complexes contain central zinc atoms that are bound to four oxygen atoms of the phenoxide ligands and adopt a tetrahedral coordination geometry. The average Zn-O bond lengths of the two complexes were found to be in good agreement and in most cases were within experimental error. The sodium atoms of both complexes are also bound to four oxygen atoms, two from each of the phenoxide ligands and two molecules of THF. The Na-O bond lengths in the two complexes were found to be in good agreement and like **21** the sodium atoms in structure reported by Wu form similar agostic type interactions with the adjacent ^tbutyl groups.

A comparison of [(*rac*)-BIPHEN]₂ZnNa₂(THF)₄ (**21**) with its magnesium counterpart [BIPHEN]₂MgNa₂(THF)₄ (**2**) revealed a high degree of structural similarity with only minor discrepancies in the key bond lengths and bond angles (Figure 95). The average Zn-O bond length found in **21** was found to be marginally longer at a mean of 1.9628 Å compared to the mean Mg-O bond length of 1.9589 Å found in **2** while the bite angles of the BIPHEN ligand for the two complexes were found to be 104.19(7) ° and 102.72(9) ° respectively. Turning now to the sodium atoms, the interatomic Zn-Na and Mg-Na were also found to differ only marginally, with the Zn-Na distance in **21** measured at 3.0717(12) Å while the corresponding Mg-Na distance in **2** was measured at 3.0914(14) Å. The marginal differences observed in the key bond lengths of the two complexes is consistent with the ionic radii for Zn²⁺ and Mg²⁺ being very similar.²⁴⁴ Examining the Na-Zn-Na and Na-Mg-Na bond angles running through the centre of the complex does however reveal a surprising difference. For sodium magnesiate **2** the Na-Mg-Na axis was found to be completely linear with a bond angle of 180 °. In contrast to this is the Na-Zn-Na bond angle in **21** was found to be 170.85(6) ° which represents a significant deviation from linearity. This deviation from linearity in the Na-Zn-Na axis could arise as a result of the sodium atoms forming two agostic type interactions with the ^tbutyl groups of the (*rac*)-BIPHEN ligands. Interestingly, **21** crystallised in the C2/c space group meaning that it is not a chiral complex which implies that the (*rac*)-BIPHEN ligand has retained its racemic character. This is in contrast to its magnesium counterpart **2** which, as discussed previously, crystallised as an enantiopure complex in the orthorhombic space group I222. Moreover, this difference implies that the driving force responsible for the

spontaneous deracemisation of the (*rac*)-BIPHEN ligand during formation of **2** is absent in the synthesis of **21**.^{100,241}

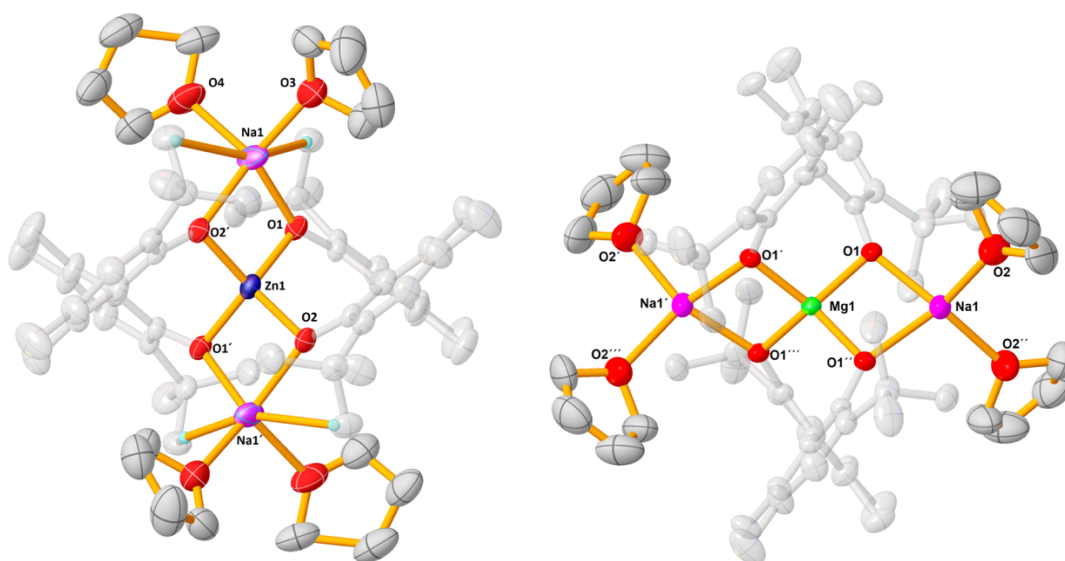


Figure 95: Solid-state structures of $[(rac)\text{-BIPHEN}]_2\text{ZnNa}_2(\text{THF})_4$, **21** (left) and $[(\text{BIPHEN})_2\text{Na}_2\text{Mg}(\text{THF})_4]$, **2** (right).

Focussing now on the characterisation of **21** in the solution-state, analysis by ^1H and ^{13}C NMR spectroscopy clearly indicated that $[(rac)\text{-BIPHEN}]_2\text{ZnNa}_2(\text{THF})_4$ is the sole crystalline product of the reaction. Beginning with the ^1H NMR spectrum, three singlets are observed in the aliphatic region of the spectrum corresponding to the substituent groups of the (*rac*)-BIPHEN ligands with the t butyl groups appearing as singlet at δ 1.16 ppm and the methyl groups as two distinct singlets at δ 1.45 and 2.05 ppm. Completing the aliphatic region of the spectrum are two multiplets at δ 1.77 and 3.61 ppm which correspond to the THF ligands. The aromatic region of the spectrum was found to contain only a single resonance at δ 6.71 ppm which was assigned to the aromatic hydrogen atoms of the (*rac*)-BIPHEN ligands. No other resonances were observed in the ^1H NMR spectrum which gives a good indication that the solid-state structure is retained in solution. Turning now to the ^{13}C NMR spectrum, it was also found to be in good agreement with the solid-state structure of **21** being retained in solution. The methyl groups of the (*rac*)-BIPHEN ligands were located at δ 17.0 and 20.5 ppm while the primary $[\text{C}(\text{CH}_3)_3]$ and quaternary $[\text{C}(\text{CH}_3)_3]$ carbon atoms of the t butyl groups appear at δ 31.2 and 34.8 ppm respectively. The aromatic carbon atoms of the (*rac*)-BIPHEN ligand are located at δ 121.3, 125.9, 133.1, 133.5, 134.2 and 162.2 ppm in the aromatic region of the spectrum. Completing the assignment of the ^{13}C spectrum of **21**, the THF ligands

were located at δ 26.4 and 68.2 ppm. The presence of only six resonances in the ^{13}C NMR spectrum indicates that the two (*rac*)-BIPHEN ligands remain equivalent. This is consistent with the ^1H and ^{13}C NMR spectra of the previously reported homoleptic magnesium analogue **2**.

4.6.3.2 $\{(\textit{rac})\text{-BIPHEN}\}\text{Na}(\text{PMDETA})\text{ZnR}$ (**22**)

The reactivity of sodium zincates with (*rac*)-BIPHEN was initially probed using the lower order sodium zincate $\text{NaZnR}_3(\text{PMDETA})$ (where $\text{R} = \text{CH}_2\text{SiMe}_3$). Based on the results of the previous reactions for which disproportion was observed in the presence of ethereal solvents such as THF and DME, PMDETA was utilised as the Lewis donor in an attempt to prevent disproportionation. Investigations began using an equimolar amount of $\text{NaZnR}_3(\text{PMDETA})$, prepared *in situ* by combining NaR , ZnR_2 and PMDETA in a 1:1:1 molar ratio, and one molar equivalent of (*rac*)-BIPHEN which were combined in hexane to give a white suspension. Removal of the solvent and all volatiles *in vacuo* followed by addition of benzene and heating to reflux gave a pale-yellow homogenous solution. Slow cooling of this solution over the course of 48 hours yielded large colourless crystals (0.143 g, 41 % yield). Analysis of these crystals by single crystal X-ray diffraction revealed the product to be a monomeric lower order mixed alkyl/phenoxide sodium zincate $\{(\textit{rac})\text{-BIPHEN}\}\text{Na}(\text{PMDETA})\text{ZnR}$, **22**, which crystallised as a benzene solvate in the monoclinic crystal system in the space group $\text{P}2_1/\text{n}$ (Figure 96).

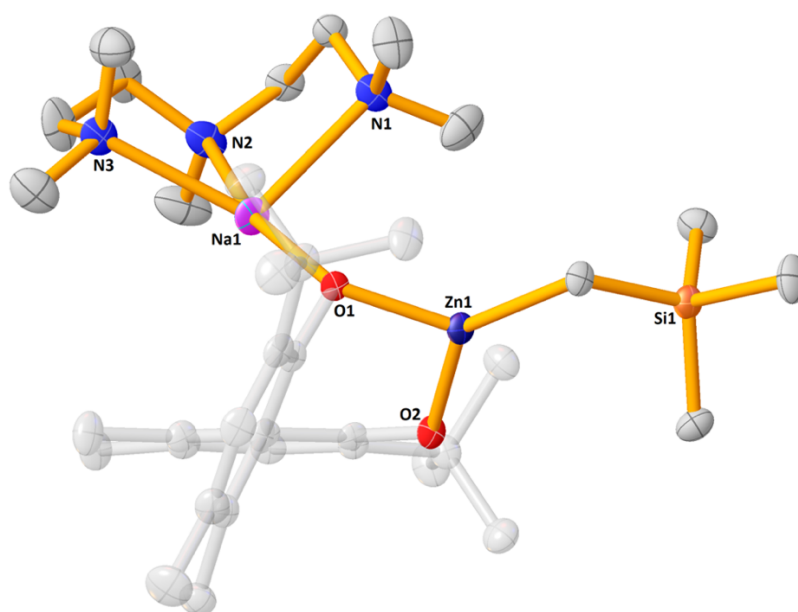


Figure 96: Solid-State structure of $\{(rac)\text{-BIPHEN}\}\text{Na(PMDETA)ZnR}$, **22**. Hydrogen atoms and disorder in the PMDETA ligand are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *S* orientated. Key bond distances (Å) and bond angles (°): Zn(1)-O(1), 1.9675(16); Zn(1)-O(2), 1.8969(16); Zn(1)-C(34) 1.964(2); Zn(1)-Na(1), 3.615; Na(1)-O(1), 2.251(2); Na(1)-N(1), 2.543(2); Na(1)-N(2), 2.468(11); Na(1)-N(3), 2.543(3); O(1)-Zn(1)-O(2), 99.77(7); O(1)-Zn(1)-C(34) 128.51(8); O(2)-Zn(1)-C(34), 131.64(8); Zn(1)-C(34)-Si(1), 120.43(12); Na(1)-O(1)-Zn(1), 117.81(8); N(1)-Na(1)-N(3), 108.48(8); N(1)-Na(1)-N(2), 75.04(19); N(2)-Na(1)-N(3), 72.5(2).

Examining the solid-state structure in more detail, the central zinc atom is located within a central 7-membered (CCOZnOCC) heteroatomic ring. Zn1 was found to be three coordinate, adopting a distorted trigonal planar geometry (sum of bond angles 359.92 °), and is bound to both oxygen atoms of the (*rac*)-BIPHEN ligand [Zn1-O1 1.9675(16) Å and Zn1-O2 1.8969(16) Å] and to the α -carbon atom of the alkyl ligand [Zn1-C34 1.964(2) Å]. The lengthening of the Zn1-O1 bond relative to that of Zn1-O2 is caused by a reduction in the electron density as a consequence of coordination of O1 to the sodium atom Na1. The sodium atom Na1 was found to be four coordinate, adopting a heavily distorted tetrahedral geometry (sum of bond angles 636.43 °) and is bound to a single oxygen of the (*rac*)-BIPHEN ligand [Na1-O 2.251(2) Å] while coordination to a single molecule of PMDETA completes its coordination sphere [Na1-N1 2.543(2) Å, Na1-N2 2.468(11) Å and Na1-N3 2.543(3) Å]. Interestingly, the PMDETA ligand appears to be orientated in such a way that the outer nitrogen atoms (N1 and N3) are located on the same side of the sodium atom i.e., pointing

away from the phenoxide ligand which has the effect of seemingly exposing the sodium atom to the phenyl ring. Despite the orientation of the PMDETA ligand and its positioning adjacent to the phenyl ring of the (*rac*)-BIPHEN ligand, Na1 was not found to form any π -type interactions. From the crystal structure, the shortest interatomic distance between Na1 and the carbon atoms of the phenyl ring was found to be 3.153 Å which is too long to allow for the formation of any additional interactions. Interestingly, **22** does not conform to the typical Weiss motif that is adopted by the majority of mixed metal ate complexes as there is only a single bridging atom linking the two metal centres. Although less common, a similar bonding situation was observed in the solid-state structure of the lower order lithium zincate (PMDETA)LiZnR₃ which was also found to contain only a single bridging interaction between the two metal centres.¹⁷⁷

Turning now to the solution-state behaviour of **22**, the complex was analysed using a combination of ¹H, ¹³C and HSQC NMR spectroscopy. Beginning with the ¹H NMR spectrum (Figure 97), a multiplet was observed in the shielded region of the spectrum at δ –0.46 ppm with an integration value of two hydrogen atoms and was assigned as the methylene group of the CH₂SiMe₃ ligand bound directly to zinc centre while the methyl groups of the alkyl ligand were assigned to the broad singlet present at δ 0.31 ppm. The appearance of the hydrogen atoms of the methylene group of the alkyl ligand as a multiplet occurs as a result of diastereotopic splitting and is caused by incorporation of the (*rac*)-BIPHEN ligand within the structure which renders the two hydrogen atoms inequivalent ($J = 12$ Hz). This type of splitting would normally give rise to two distinct doublets; however, due to second order splitting, a quartet like splitting pattern is observed.²⁴⁵ Diastereotopic splitting of the methylene group of the alkyl ligand provides a good indication that the solid-state structure is retained in solution. Non-equivalence within the (*rac*)-BIPHEN ligand was once again observed as evidenced by the appearance of two sets resonances for both the ^tbutyl groups and aromatic hydrogen atoms. To expand, the ^tbutyl groups appear as two broad singlets at δ 1.71 and 1.85 ppm while a further two broad singlets were also found to be present in the aromatic region of the spectrum at δ 7.21 and 7.28 ppm. Interestingly, the methyl groups of the (*rac*)-BIPHEN ligand also appear as two singlets at δ 1.88 and 2.25 ppm which would appear to indicate that equivalence has been retained between the two sets of methyl groups. This is in contrast to the previous structures for which the equivalence between the two sets of methyl groups was lost. Completing the assignment of the ¹H NMR spectrum of **22**, the PMDETA ligand was assigned to the resonances located at δ 1.48, 1.72 and 1.83 ppm.

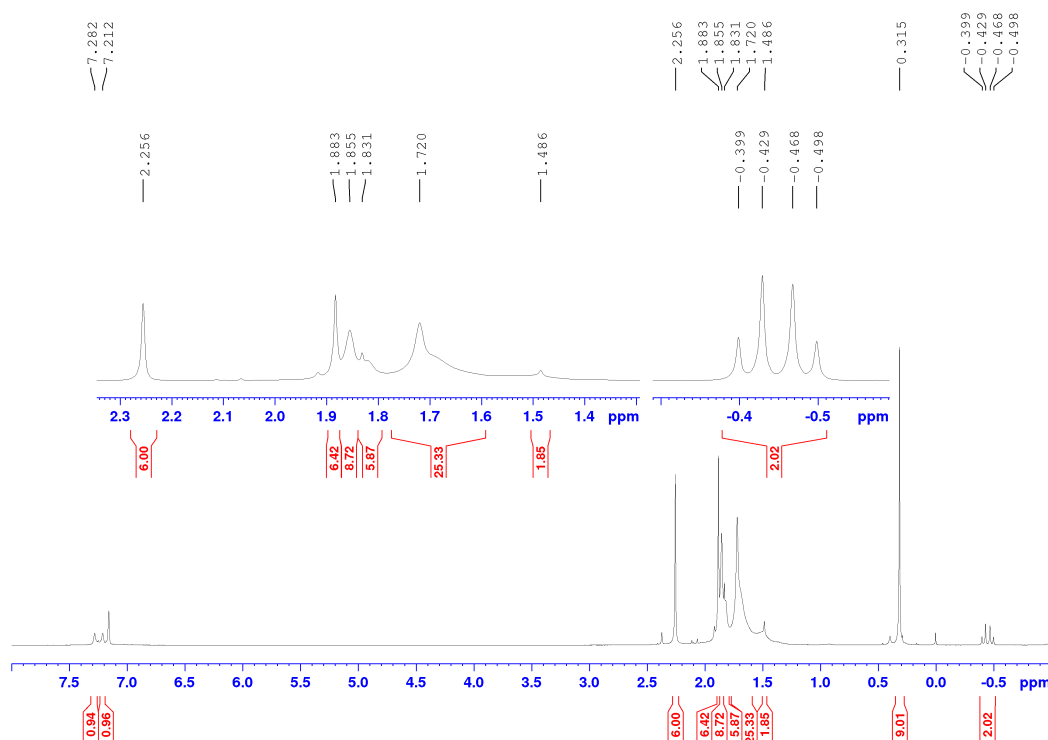


Figure 97: ^1H NMR spectrum of $\{(\text{rac})\text{-BIPHEN}\}\text{Na(PMDETA)ZnR}$, **22** (400 MHz, C_6D_6 , 300 K).

Focussing now on the ^{13}C NMR spectrum of **22** (Figure 98), two resonances were observed at δ -5.9 and 3.3 ppm which were assigned to the methylene and methyl groups of the alkyl ligand respectively. The methyl groups of the (*rac*)-BIPHEN ligand were assigned to the three resonances which were found to be present at δ 17.2 , 17.6 and 20.6 ppm. The appearance of three resonances in the ^{13}C NMR for the methyl groups of the (*rac*)-BIPHEN ligand suggests the two sets of methyl groups do not remain equivalent despite no such inequivalence being observed in the ^1H NMR spectrum (Figure 97). For the *t*butyl groups of the (*rac*)-BIPHEN ligand, the terminal methyl groups [$\text{C}(\underline{\text{C}}\text{H}_3)_3$] appear as two resonances at δ 30.7 and 31.9 ppm while the two sets of quaternary carbons [$\underline{\text{C}}(\text{CH}_3)_3$] were found to be present at δ 35.2 and 35.4 ppm. Completing the assignment of the (*rac*)-BIPHEN ligand, the aromatic region of the spectrum was found to contain 12 resonances ranging from δ 119.6 ppm to 162.6 ppm which once again is consistent with a loss of equivalence between the two ring systems. Returning to the aliphatic region of the spectrum, the remaining resonances at δ 32.2 , 44.1 , 45.3 , 53.6 and 57.0 ppm were assigned to the PMDETA ligand. Assignment of PMDETA ligand was confirmed using HSQC NMR spectroscopy (Figure 99). Examination of the HSQC NMR spectrum of **22** showed a clear correlation between the three resonances assigned to the PMDETA ligand in the ^1H NMR spectrum and the resonances in the ^{13}C NMR spectrum at δ

32.2, 44.1, 45.3, 53.6 and 57.0 ppm. Based on these correlations, the resonance at δ 1.48 ppm was assigned to a single CH_2 group while the broad resonance at δ 1.72 ppm was assigned to three of the methyl groups along with the remaining bridging CH_2 groups. Finally, the resonance located at δ 1.83 ppm was assigned to the remaining methyl group.

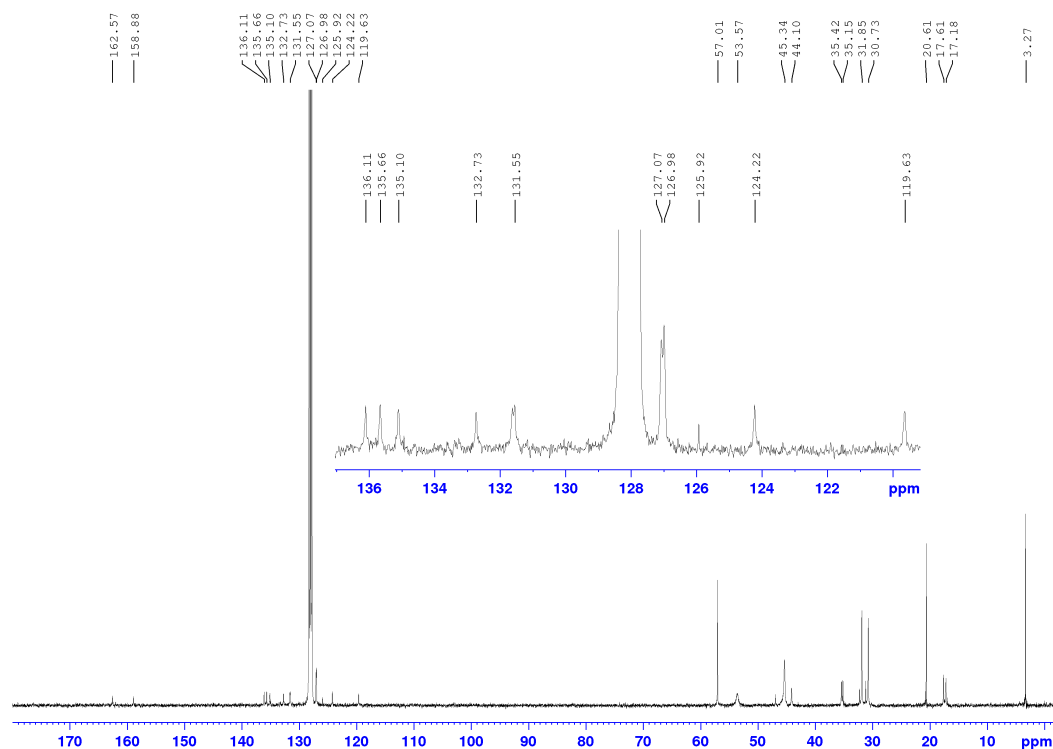


Figure 98: ^{13}C NMR spectrum of $\{(\text{rac})\text{-BIPHEN}\}\text{Na}(\text{PMDETA})\text{ZnR}$, **22** (100 MHz, C_6D_6 , 300 K).

The inequivalence observed between the two ring systems of the (*rac*)-BIPHEN ligand is consistent with the solid-state structure of **22** (Figure 96) which clearly shows the sodium atom Na1 to be bound through a single oxygen atom to the phenoxide ligand. This bonding situation will result in one of the phenyl rings having a greater interaction with the alkali metal atom which will lead to an alteration in the electronic properties of the ring system which will in turn give rise to the observed inequivalence.

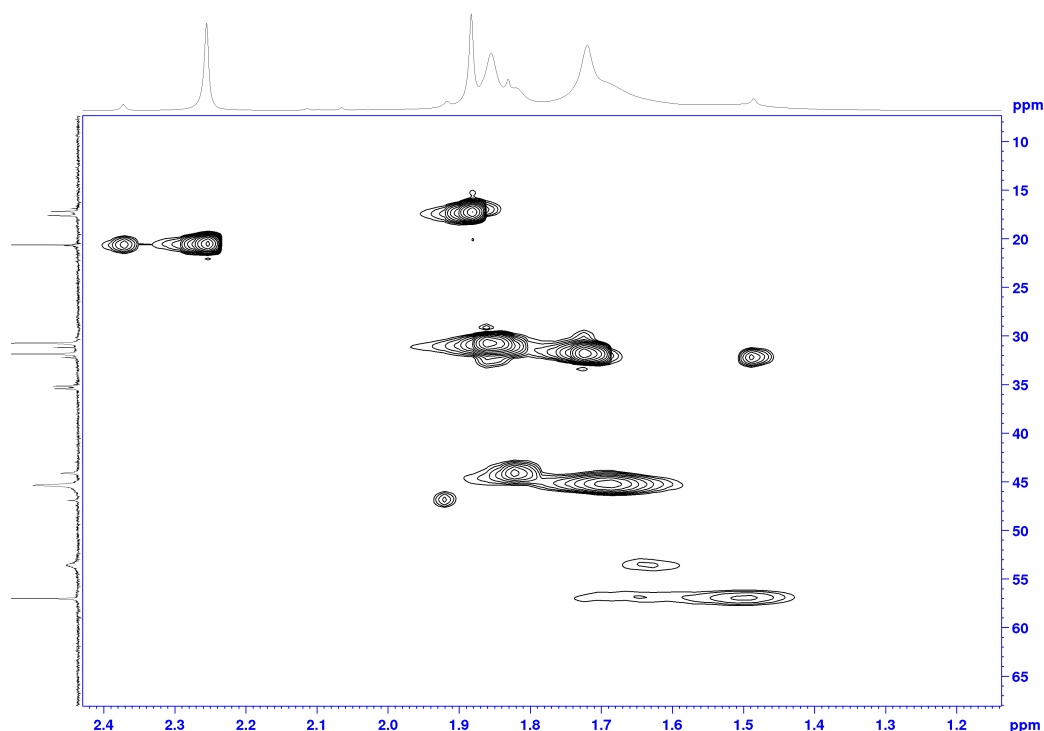


Figure 99: HSQC NMR spectrum of $\{(rac)\text{-BIPHEN}\}\text{Na(PMDETA)ZnR}$, **22** (C_6D_6 , 300 K).

4.6.3.3 $\{(rac)\text{-BIPHEN}\}\text{Na(15-crown-5)ZnR}$ (**23**)

Following the synthesis of **22**, the reaction was repeated except the crown ether 15-crown-5 was used in place of PMDETA in an attempt to sequester the sodium atom and produce a solvent separated ion pair zincate. To this end, the sodium zincate NaZnR_3 was reacted with $(rac)\text{-BIPHEN}$ in a 1:1 molar ratio in hexane followed by addition of 15-crown-5 to give a white solid. All volatiles were subsequently removed *in vacuo* before addition of benzene and heating to reflux to give a pale-yellow solution. Slow cooling of this solution to ambient temperature followed by allowing the solution to stand at ambient temperature for 48 hours produced large, colourless, block shaped crystals (0.095 g, 25 % yield). Analysis of these crystals by single crystal X-ray diffraction revealed the product to be a monomeric mixed alkylzinc phenoxide sodium zincate $\{(rac)\text{-BIPHEN}\}\text{Na(15-crown-5)ZnR}$, **23**, which crystallised in the $P2_1/c$ space group as a benzene solvate (Figure 100). Isolation of **23** once again demonstrated the ability of bimetallic NaZnR_3 to function as a dialkyl base.

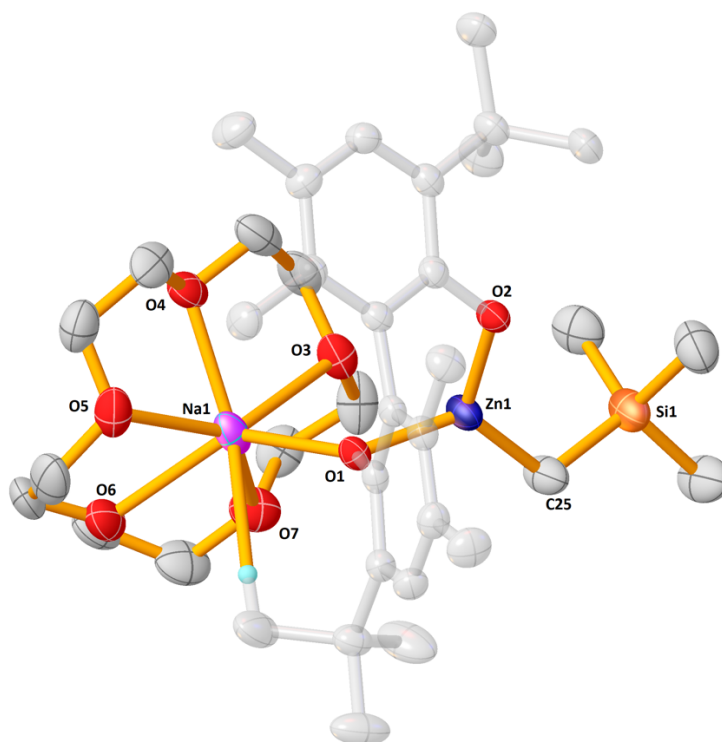


Figure 100: Solid-state structure of $\{(rac)\text{-BIPHEN}\}\text{Na(15-crown-5)ZnR}$, **23**. Hydrogen atoms and disorder in the 15-crown-5 ligand are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand is *R* orientated. Key bond distances (Å) and bond angles (°): Zn(1)-O(1), 1.9630(13); Zn(1)-O(2), 1.8975(13); Zn(1)-C(25) 1.970(2); Zn(1)-Na(1), 3.5970(9); Na(1)-O(1), 2.2399(15); Na(1)-O(3), 2.497(9); Na(1)-O(4), 2.303(11); Na(1)-O(5), 2.402(8); Na(1)-O(6), 2.462(6); Na(1)-O(7), 2.527(3); O(1)-Zn(1)-O(2), 102.30(6); O(1)-Zn(1)-C(25) 129.25(8); O(2)-Zn(1)-C(25), 125.44(9); Zn(1)-C(25)-Si(1), 117.53(13); Na(1)-O(1)-Zn(1), 117.55(6).

An in-depth examination of the organometallic framework of **23** unambiguously showed the structure to be a contacted ion pair, with a single Na-O bond holding the co-complex together. The sodium atom Na1 was found to be seven coordinate, forming a single bond to the five oxygen atoms of the 12-crown-5 ligand [mean Na1-O_(crown) 2.438 Å], with the sodium atom sitting considerably out of the plane of the ligand, as well as the aforementioned bond to a single oxygen of the *(rac)*-BIPHEN ligand [Na1-O1 2.2399(15) Å]. The coordination sphere of Na1 is completed by the formation of an agostic type interaction with a single CH₃ of one of the ^tbutyl groups located on *(rac)*-BIPHEN backbone (Na1-H23c 2.420 Å). Interestingly, no agostic type interaction of this kind was observed for the sodium atom of **22**. The central zinc atom Zn1 was found to be three coordinate adopting a distorted trigonal planer coordination geometry (sum of bond angles 356.99 °) and is bound to the two oxygen atoms of the

phenoxide ligand [Zn1-O1 1.9630(13) and Zn1-O2 1.8975(13) Å] forming a seven membered (CCOZnOCC) heteroatomic ring. The coordination sphere of Zn1 is complete by the formation of a single bond to the α -carbon of the CH₂SiMe₃ alkyl ligand [Zn1-C25 1.979(2) Å].

Turning to the solution-state behaviour of **23**, the complex was found to be poorly soluble in non-coordinating solvent and as a result, only the ¹H NMR spectrum of the complex could be assigned at ambient temperature. Examining the ¹H NMR spectrum of **23** in deuterated benzene (Figure 101), the methylene group of the alkyl ligand bound directly to the zinc centre appeared as two distinct resonances at δ -0.61 and -0.53 ppm in the shielded region of the spectrum. The appearance of multiple resonances for these hydrogen atoms was once again attributed to diastereotopic splitting which has rendered the two hydrogen atoms of the methylene group inequivalent ($J = 12$ Hz). The unexpected appearance of this resonance is caused by roofing of the expected set of doublets and arises because of second order splitting. A similar splitting was observed for the hydrogen atoms of the methylene group **22**; however, it was less pronounced and led to the resonance taking the form of a quartet.²⁴⁵ As with previous magnesiate and zincate complexes containing the (*rac*)-BIPHEN ligand, observation of diastereotopic splitting is indicative of retention of the solid-state structure in solution. The remaining hydrogen atoms of the alkyl ligand, the terminal CH₃ groups, appear as a singlet at δ 0.36 ppm. Focussing now on the phenoxide ligand, the ^tbutyl groups appear as two singlets at δ 1.79 and 1.83 ppm which, when integrated together, combine to give a value of 18 hydrogen atoms. The appearance of two resonances for the hydrogen atoms of the ^tbutyl groups is consistent with solid-state structure of **23** in which one of the phenyl rings will have a greater interaction with the sodium atom, thereby rendering the two rings inequivalent. The methyl groups of the (*rac*)-BIPHEN ligand appear as two distinct singlets at δ 1.90 and 2.30 ppm while the aromatic hydrogen atoms appear a singlet at δ 7.25 ppm. Interestingly, the appearance of the aromatic hydrogen atoms as a single resonance would suggest that equivalence has been retained between the two phenyl ring systems of the phenoxide ligand which is in contrast to **22**. Finally, the 15-crown-5 ligand appears as a broad singlet at δ 2.89 ppm.

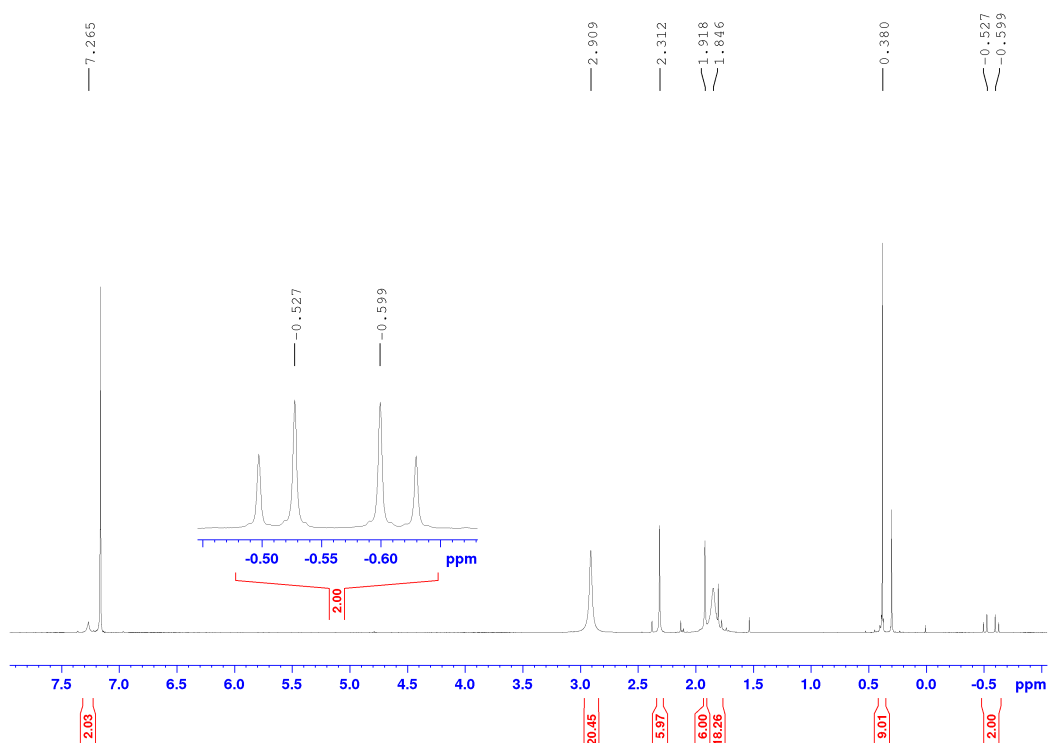


Figure 101: ^1H NMR spectrum of $\{(\text{rac})\text{-BIPHEN}\}\text{Na}(15\text{-crown-5})\text{ZnR}$, **23**
(400 MHz, C_6D_6 , 300 K).

Due to the poor solubility of **23** in non-coordinating solvent, the ^{13}C NMR spectrum of the complex was recorded at 363 K in deuterated toluene (Figure 102). At this elevated temperature, the methylene group of the alkyl ligand was found to appear at δ –6.15 ppm along with the terminal methyl groups at δ 3.19 ppm. The methyl groups of the (*rac*)-BIPHEN ligand were found to appear as a singlet at δ 16.9 ppm while the t butyl groups appeared as two resonances at δ 31.7 and δ 35.2 ppm which were assigned to the primary $[\text{C}(\underline{\text{C}}\text{H}_3)_3]$ and quaternary $[\underline{\text{C}}(\text{CH}_3)_3]$ carbon atoms respectively. Completing the aliphatic region of the spectrum, the resonance which was located at δ 68.9 ppm was assigned to the 15-crown-5 ligand. Turning now to the aromatic region of the spectrum, only five resonances were visible at δ 126.0, 128.4, 133.6, 133.9 and 135.2 ppm all of which were assigned to the aromatic carbons of the (*rac*)-BIPHEN ligand. Despite the use of elevated temperatures, observation of the remaining quaternary carbon atom which, in the spectra of previous complexes, appeared at approximately δ 160.0 ppm remained elusive.

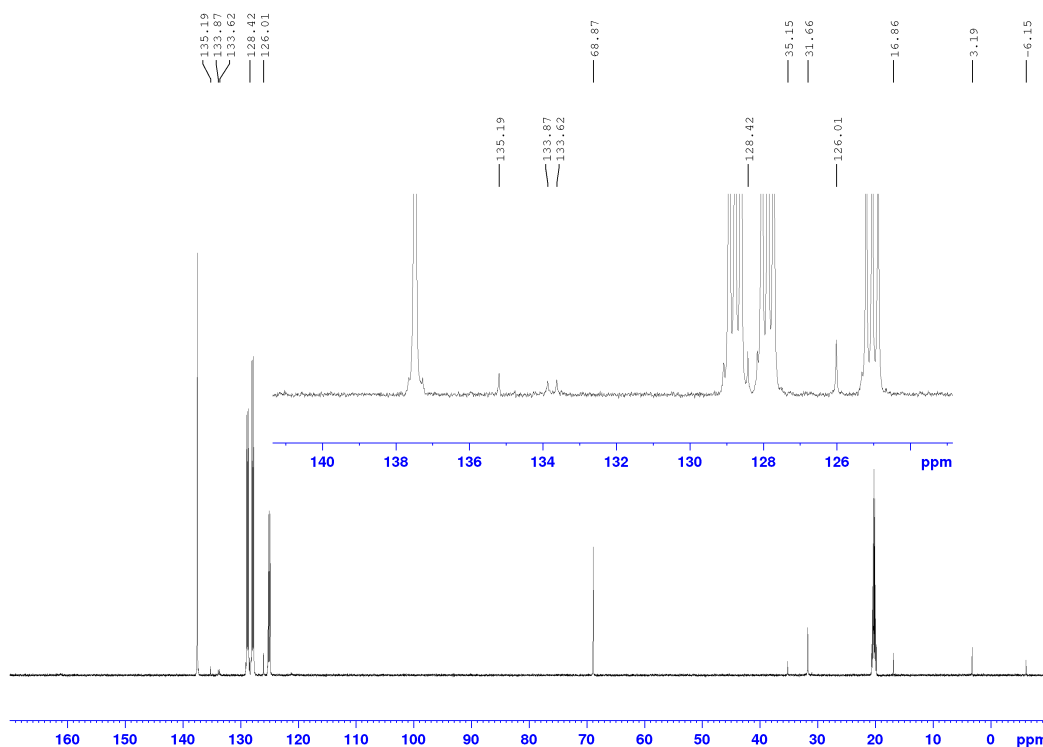


Figure 102: ^{13}C NMR spectrum of $\{(\text{rac})\text{-BIPHEN}\}\text{Na}(15\text{-Crown-5})\text{ZnR}$, **23**
(100 MHz, $d_8\text{-Tol}$, 363 K).

In a final attempt to observe the presence of the remaining carbon atom, an HMBC NMR spectrum was obtained (Figure 103). Pleasingly, the spectrum showed a clear and obviously correlation between an aromatic hydrogen atom and an area of the ^{13}C NMR spectrum baseline at δ 161.2 ppm. This correlation serves to indicate the presence of the previously unobservable carbon atom. Finally, **23** was analysed using ^1H DOSY NMR spectroscopy. The resulting spectrum showed that no monomer-dimer or Schlenk-like equilibrium exists in solution and that the solid-state structure is retained. The diffusion coefficients for the (*rac*)-BIPHEN, CH_2SiMe_3 and 15-crown-5 ligands were calculated to be 6.366×10^{-10} , 6.308×10^{-10} and $6.408 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ respectively, indicating that the contacted ion pair structure is retained in solution.

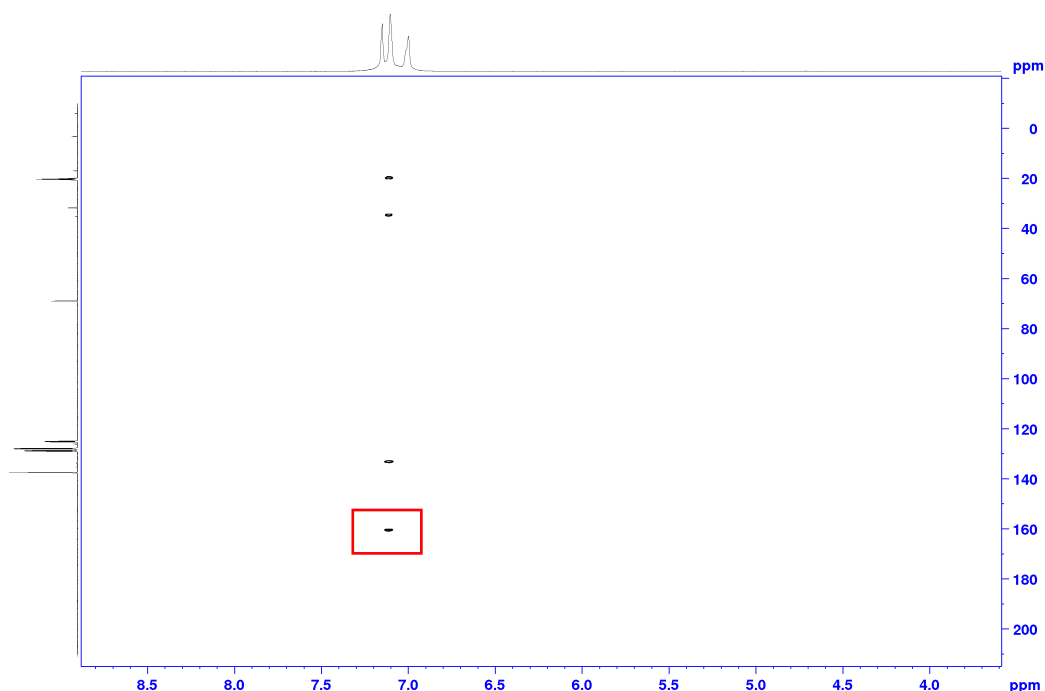


Figure 103: HMBC NMR spectrum of $\{(rac)\text{-BIPHEN}\}\text{Na}(15\text{-crown-5})\text{ZnR}$, **23** ($d_8\text{-Tol}$, 363 K).

4.6.3.4 Structural Comparison of **22** and **23**

A marked difference was observed in the orientation of the phenyl ring systems of the (*rac*)-BIPHEN ligands relative to the sodium atoms of the two sodium zincates **22** and **23**. As alluded to above, the sodium atom of **23** was found to form a long-range interaction with a ^tbutyl group of the (*rac*)-BIPHEN backbone whereas no such interaction was observed for the corresponding sodium atom of **22**. For **22** the sodium atom is positioned adjacent to one of the phenyl rings of the (*rac*)-BIPHEN phenoxide ligand with PMDETA adopting a conformation which appears to expose the sodium atom to the π -system of the phenyl ring. The ^tbutyl group is therefore positioned facing away from the sodium cation, precluding the formation of any interaction (Figure 104). In comparison, the sodium atom of **23** is no longer located in close proximity to the phenyl ring, but rather it is located facing the ^tbutyl group thereby allowing it to form the observed interaction (Figure 104). The difference in orientation of the phenyl ring towards the sodium cation has been attributed to the inclusion of the bulkier, higher denticity crown ether ligand which is not capable of adopting a geometry in which the sodium atom can be presented towards the face of the phenyl ring. Moreover, although no π -type interactions were observed in the crystal structure of **22**, the

observed difference in orientation of the phenyl ring toward the sodium cations in the two structures may suggest that some degree of interaction does in fact occur.

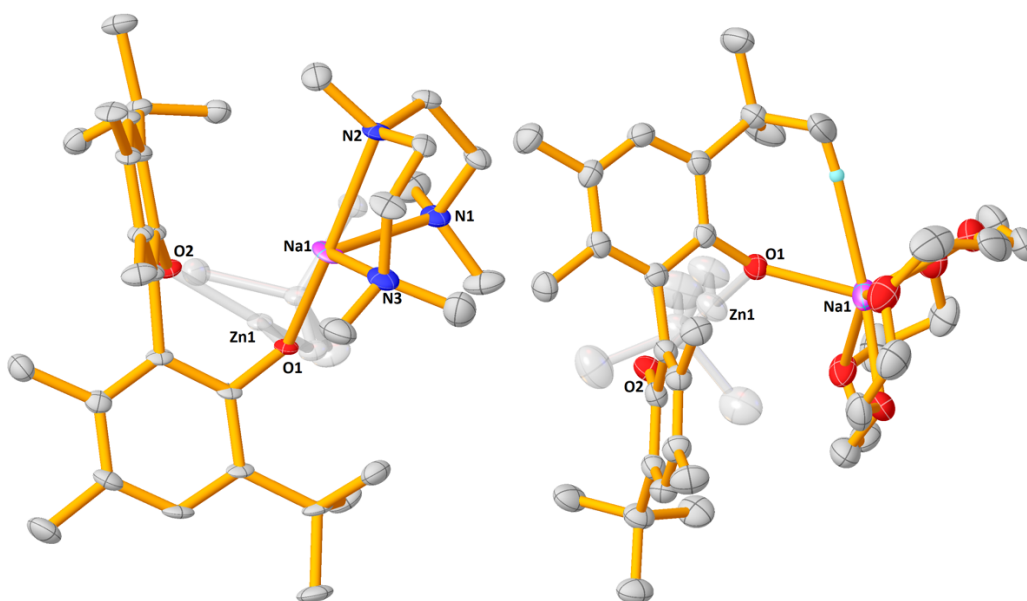


Figure 104: Structural comparison of $\{(rac)\text{-BIPHEN}\}\text{Na(PMDETA)ZnR}$ **22** (left) and $\{(rac)\text{-BIPHEN}\}\text{Na(15-crown-5)ZnR}$ **23** (right).

Despite the difference in the orientation of the *(rac)*-BIPHEN ligand, the key bond lengths and bond angles for the two structures of **22** and **23** show very little deviation. Focussing on the key bond lengths (Table 7) and bond angles (Table 8), only minor deviations were observed between solid-state structures of the two complexes. This high degree of similarity between the two structures is highlighted by the bond lengths of the $\text{Na-O}_{((rac)\text{-BIPHEN})}$ bonds which differ by less and 0.1 Å in length despite the sodium atom of **23** having a higher coordination number than that of the sodium atom found in **22**. This suggests that the identity of the Lewis donor ligand appears to have little impact on the key bond lengths of the final sodium zincate.

Table 7: Mean bond lengths for key bonds in complexes **22** and **23**.

Complex	Mean bond length (Å)			
	Zn-O	Zn-C	Na-O	Zn-Na
22	1.9322	1.9640	2.2510	3.6150
23	1.9302	1.9790	2.2399	3.5970

A marginal difference was observed in the bite angles of the (*rac*)-BIPHEN ligand which contracted by approximately 3° giving the ligand a more acute bite angle in **22**. The reaction of NaZnR₃ with the (*rac*)-BIPHEN phenoxide ligand was repeated multiple times using various donors including TMEDA, (*R,R*)-TMEDA, Me₆-TREN, 12-crown-4 and 18-crown-6 in an attempt to generate a series of novel mixed alkylzinc phenoxide sodium zincates; however, no crystals of suitable quality for analysis by single crystal X-ray diffraction were obtained.

Table 8: Key bond angles in complexes **22** and **23**.

Complex	Bond angle (°)			
	O-Zn-O	O-Zn-C	Zn-C-Si	Zn-O-Na
22	99.77(7)	128.51(8) 131.64(8)	120.42(12)	117.81(8)
23	102.30(6)	129.25(8) 125.44(9)	117.53(13)	117.55(6)

4.6.4 Synthesis and Characterisation of Potassium Zincates

4.6.4.1 [(*rac*)-BIPHEN]₂ZnK₂(PMDTA)₂ (**24**)

Our investigation into mixed alkyl/phenoxide alkali metal zincates was further extended to include potassium as the alkali metal. Building on the results of previous work outlined in this chapter, our investigations began by examining the reactivity of the lower order *tris*(alkyl) potassium zincate KZnR₃(PMDTA) (where R = CH₂SiMe₃). This combination of alkyl ligand and donor was chosen due to the promising results obtained using the lighter alkali metal derivative NaZnR₃(PMDTA) which led to the isolation of **22** and **23**. Our investigation began with the addition of an equimolar amount of (*rac*)-BIPHEN to a suspension of KZnR₃(PMDTA), which had been prepared *in situ* by combining KR, ZnR₂ and PMDTA in a 1:1:1 ratio, at -10 °C before allowing the suspension to gradually warm to ambient temperature over one hour. All volatiles were removed *in vacuo* to give a pale orange solid

which, after addition of benzene and heating to reflux, produced a homogenous orange solution. The resulting solution was cooled slowly to ambient temperature and was allowed to stand at this temperature for five days, after which time a small crop of colourless crystals were deposited (0.081g, 14 % yield). Analysis of these crystals by single crystal X-ray diffraction revealed the product to be the dimeric potassium zincate $[(rac)\text{-BIPHEN}]_2\text{Zn}_2\text{K}_2(\text{PMDETA})_2$, **24**, which crystallised in the monoclinic crystal systems in the $C2/c$ space group (Figure 105). The low yield in which **24** was isolated was attributed to the high solubility of the complex in hydrocarbon solvent.

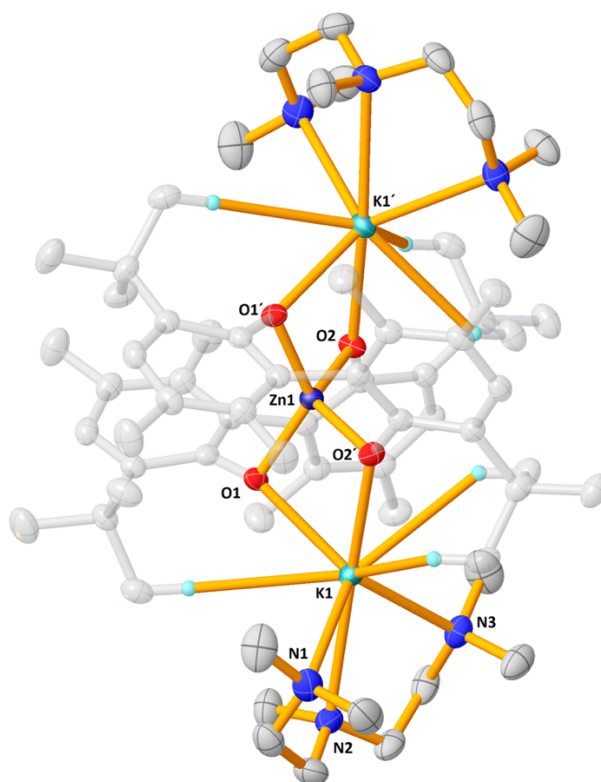


Figure 105: Solid-state structure of $[(rac)\text{-BIPHEN}]_2\text{Zn}_2\text{K}_2(\text{PMDETA})_2$, **24**. Hydrogen atoms and disorder in the PMDETA ligands are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Phenoxide ligand orientation is *RR*. Key bond distances (Å) and bond angles (°): Zn(1)-O(1), 1.9677(10); Zn(1)-O(2), 1.9760(10); Zn(1)-K(1), 3.3939(3); K(1)-O(1), 2.5752(11); K(1)-O(2'), 2.7224(11); K(1)-N(1), 2.9115(16); K(1)-N(2), 2.9818(15); K(1)-N(3), 2.8897(15); O(1)-Zn(1)-O(1'), 126.58(6); O(1)-Zn(1)-O(2), 108.46(4); O(1)-Zn(1)-O(2'), 96.90(4); O(2)-Zn(1)-O(2'), 121.85(7); O(1)-K(1)-O(2'), 67.65(3); N(1)-K(1)-N(2), 62.13(5); N(1)-K(1)-N(3), 108.68(5); N(2)-K(1)-N(3), 62.07(4); K(1)-Zn(1)-K(1'), 150.378(15).

Examining the organometallic framework of **24**, the central zinc atom is bound to the four oxygen atoms of two (*rac*)-BIPHEN ligand [Zn1-O1 1.9677(10) and Zn1-O2 1.9760(10) Å] in a

distorted tetrahedral coordination geometry (sum of bond angles 658.89 °). The potassium atoms were found to be six coordinate, bound to two oxygen atoms of the (*rac*)-BIPHEN ligand [K1-O1 2.5752(11) and K1-O2' 2.7224(11) Å] and a single molecule of PMDETA [K1-N1 2.9115(16), K1-N2 2.9818(15) and K1-N3 2.8897(15) Å]. The coordination sphere of the potassium atoms is completed by the formation of an agostic type interaction with a ^tbutyl group of the (*rac*)-BIPHEN ligand (K1-H22 2.751 Å). Two additional interactions between the potassium cations and ^tbutyl groups were observed; however, these agostic-type interactions were found to be much longer at 3.080 and 3.077 Å which suggests they are much weaker interactions.

Examining the solution-state behaviour of **24** beginning with its ¹H NMR spectrum (Figure 106), both (*rac*)-BIPHEN ligands of the homoleptic dimer were found to remain equivalent. To expand, the ^tbutyl groups appear a singlet at δ 1.48 ppm while the methyl groups appear as two singlets at δ 1.82 and 2.36 ppm. The integration values of these three resonances were calculated to be 36, 12 and 12 respectively. The PMDETA ligands were found to appear as three distinct singlets at δ 1.85, 1.96 and 2.03 ppm which were assigned to the internal (NMe) methyl groups, external (NMe₂) methyl groups and bridging methylene groups respectively. The integration values for these resonances were calculated to be 6, 24 and 16 respectively and are indicative of inclusion of two molecules of PMDETA within the solution-state structure of **24**. The aromatic region of the spectrum was found to contain a single resonance at δ 7.17 ppm with an integration value of four hydrogen atoms which was assigned to the aromatic hydrogen atoms of the (*rac*)-BIPHEN ligand. For the ¹H NMR spectrum, the integration values of all the resonances assigned to both the (*rac*)-BIPHEN and PMDETA ligands are consistent with the solid-state structure of **24** (Figure 105).

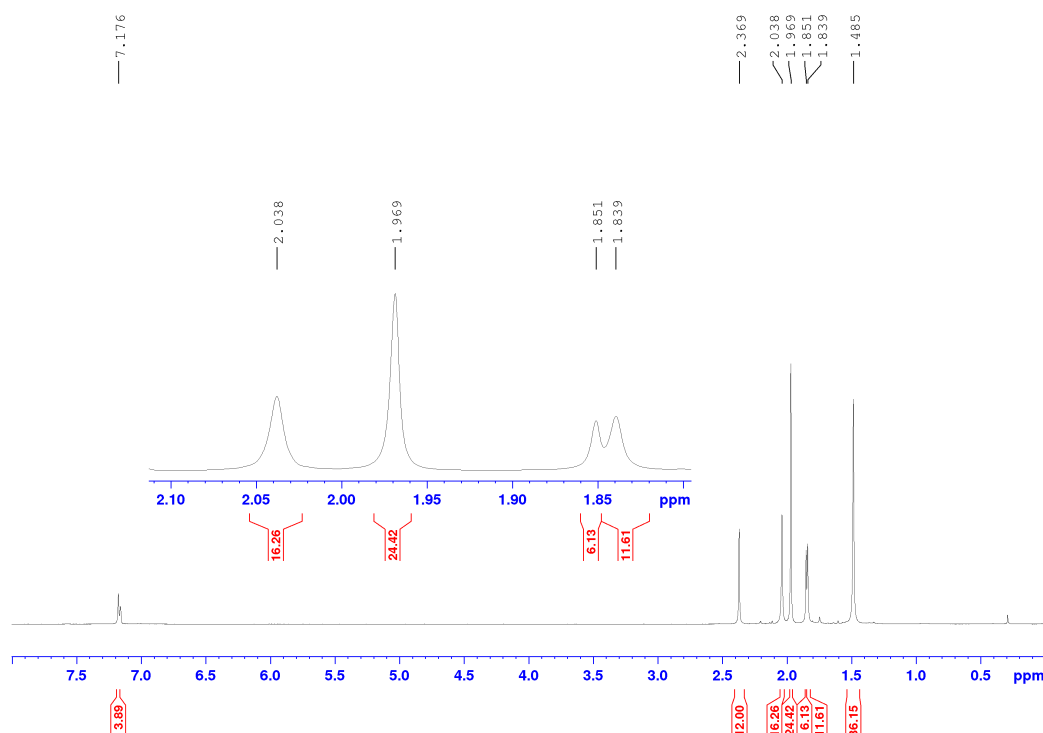


Figure 106: ^1H NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{ZnK}_2(\text{PMDETA})_2$, **24** (400 MHz, C_6D_6 , 300 K).

Turning now to the ^{13}C NMR spectrum of **24** (Figure 107), the methyl groups of the (*rac*)-BIPHEN ligand were assigned to the two resonances present in the aliphatic region of the spectrum at δ 17.3 and 20.7 ppm while the primary $[\text{C}(\underline{\text{C}}\text{H}_3)_3]$ and quaternary $[\underline{\text{C}}(\text{CH}_3)_3]$ carbon atoms of the *t*butyl ligands were assigned to the two resonances present at δ 31.7 and 34.8 ppm respectively. The internal (NMe) and external (NMe₂) methyl groups of the PMDETA ligands were assigned to the resonances which appeared at δ 41.6 and 45.8 ppm while the remaining methylene groups of the PMDETA ligands were assigned to the two resonances located at δ 56.9 and 57.7 ppm. The aromatic region of the spectrum was found to contain six distinct resonances ranging from δ 120.8 ppm to 163.2 ppm, all of which were assigned to the aromatic carbon atoms of the (*rac*)-BIPHEN phenoxide ligands. The number of resonances present in the ^{13}C NMR spectrum are consistent with the solid-state structure of **24**. Additionally, this highlights that the equivalence between the phenyl ring systems of the two (*rac*)-BIPHEN ligands has been maintained. Assignment of the (*rac*)-BIPHEN and PMDETA ligands in both the ^1H and ^{13}C NMR spectrum were further reinforced using HSQC NMR spectroscopy which showed clear and obvious correlations between the two sets of resonances assigned to each ligand.

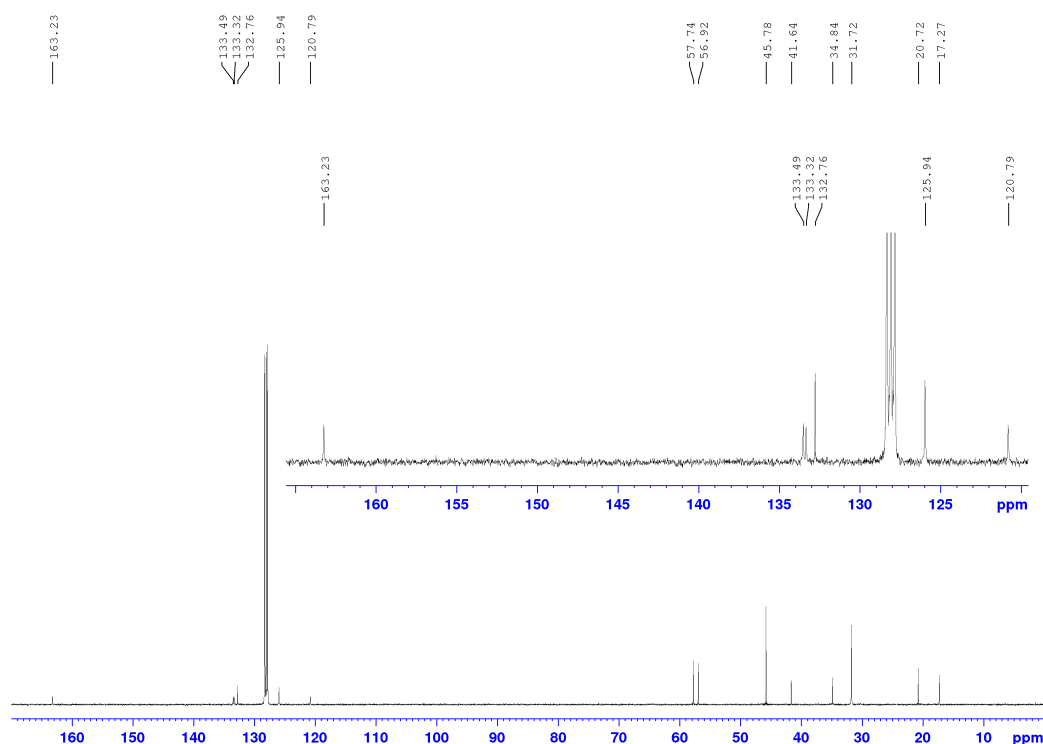


Figure 107: ^{13}C NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{ZnK}_2(\text{PMDETA})_2$ (100 MHz, C_6D_6 , 300 K).

The data obtained from the ^1H , ^{13}C and HSQC NMR spectra all strongly suggested that the solid-state structure appeared to remain intact in solution. Analysis of the solution-state structure of **24** by ^1H DOSY NMR spectroscopy (Figure 108); however, revealed this not to be the case. To expand, in the ^1H DOSY NMR spectrum the resonances assigned to the (*rac*)-BIPHEN and PMDETA ligands were found to have different diffusion coefficients which is indicative of their existence as two separate species in solution. The formation of a second zincate species can be ruled out as each of the resonances assigned to both the (*rac*)-BIPHEN and PMDETA ligands showed a single correlation in the diffusion spectrum. If a second species were to be formed as part of a monomer-dimer or Schlenk-like equilibrium, then a second set of correlations for each resonance would be expected. It was therefore concluded that the solid-state structure of **24** is not retained in solution but rather that it exists as a solvent separated ion pair. Based on the solid-state structure, the anionic fragment of this solvent separated structure was proposed to be $\{[(rac)\text{-BIPHEN}]_2\text{Zn}\}^{2-}$ with the cationic species consisting of some combination of the potassium cations and PMDETA ligands (Figure 109).

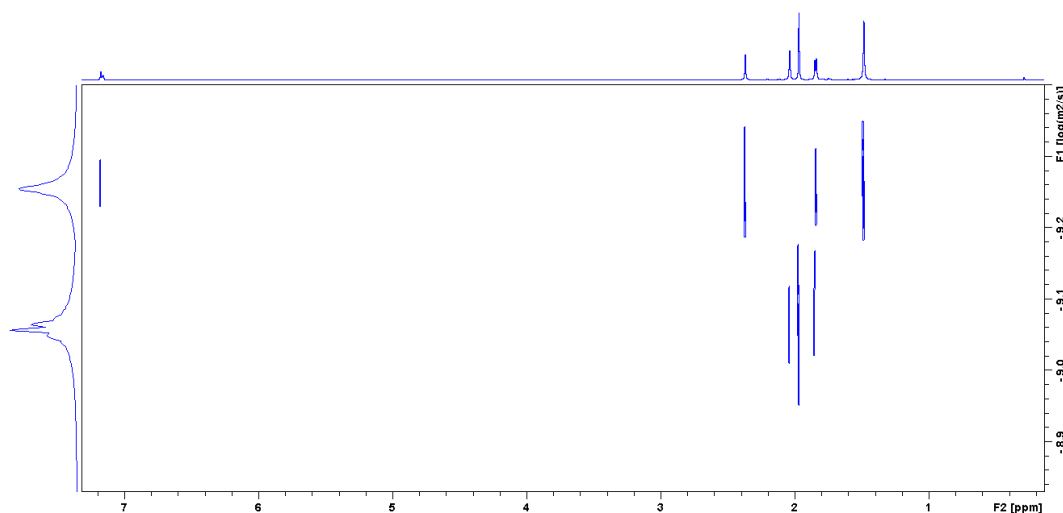


Figure 108: ^1H DOSY NMR spectrum of $[(rac)\text{-BIPHEN}]_2\text{ZnK}_2(\text{PMDETA})_2$, **24** (C_6D_6 , 300 K).

Addition of tetraphenylanthracene as an internal standard allowed for an estimation of the molecular weight for each species to be made.^{246–248} For the *(rac)*-BIPHEN containing fragment, the estimated molecular weight was calculated to be 757 g/mol which was found to be in good agreement with the proposed anionic fragment $\{[(rac)\text{-BIPHEN}]_2\text{Zn}\}^{2-}$ (Figure 109) which has a molecular weight of 770.42 g/mol giving an error of only 2 % in the dissipated spheres and ellipsoids (DSE) external calibration curve. Turning now to the cationic fragment of the structure the estimated molecular weight was calculated to be 361 g/mol. Three possible identities for cationic fragment were therefore proposed based on the solid-state structure of **24**. The first of these structures was proposed to consist of a PMDETA solvated potassium cation $[\text{K}(\text{PMDETA})_2]^+$ which has a molecular weight of 385.71 g/mol giving a 7 % error in the DSE external calibration curve. Despite this relatively low error value, the formation of $[\text{K}(\text{PMDETA})_2]^+$ does not account for the second potassium cation and therefore does not allow for correct charge balance between the two species. $\{[\text{KPMDETA}]_2\}^{2+}$ was therefore proposed as a second possible cationic fragment as it accounts for both potassium cations; however, with a molecular weight of 424.80 g/mol this species was not found to be in good agreement with the experimentally obtained molecular weight and gave an error of 18 % in the DSE external calibration. The final cationic species which was proposed was $[(\text{PMDETA})\text{K}(\text{C}_6\text{D}_6)_2]^+$ in which the potassium cation is coordinated to a single molecule of PMDETA and two molecules deuterated benzene. With a molecular weight of 380.63 g/mol, $[(\text{PMDETA})\text{K}(\text{C}_6\text{D}_6)_2]^+$ is in good agreement with the experimentally calculated estimated molecular weight of 361 g/mol giving an error of 5 % in the DSE external calibration curve. The propensity of potassium cations to form π -type interaction with aromatic ring systems has been well documented, including structural evidence to support

the solvation of a potassium cation by deuterated benzene which therefore suggests that the formation of species as $[(\text{PMDETA})\text{K}(\text{C}_6\text{D}_6)_2]^+$ is plausible.^{249,250,251} Based on these data the solution-state structure of **24** is proposed to be the solvent separated ion pair $\{[(\text{rac})\text{-BIPHEN}]_2\text{Zn}\}\{[(\text{PMDETA})\text{K}(\text{C}_6\text{D}_6)_2]^+\}$ (Figure 109).

Table 9: Calculated diffusion coefficients and the predicted molecular weight of solvent separated ions in solution for **24**.

Ligand	Diffusion coefficient (m^2s^{-1})	Estimated molecular weight	Structural fragment (molecular weight, experimental error)
<i>(rac)</i> -BIPHEN	5.386×10^{-10}	757 g/mol	$\{[(\text{rac})\text{-BIPHEN}]_2\text{Zn}\}^{2-}$ (770
	5.628×10^{-10}		g/mol, 2 %)
	5.396×10^{-10}		
PMDETA	8.588×10^{-10}	361 g/mol	$[(\text{PMDETA})\text{K}(\text{C}_6\text{D}_6)_2]^+$
	8.672×10^{-10}		(380 g/mol, 5 %)
	8.456×10^{-10}		

The formation of **24** was attributed to disproportion, a common decomposition pathway that was observed for both lithium and sodium zincates in the presence of DME and THF respectively as well as the sodium magnesiate outline in Chapter 2. It is somewhat surprising that this decomposition pathway remains active despite the inclusion of the chelating donor PMDETA, as it had been shown to be proficient at blocking this decomposition pathway for the sodium zincate and magnesiate complexes discussed previously. This would suggest that PMDETA is no longer capable of providing sufficient steric protection to the much larger, softer, potassium centre in order to prevent disproportionation from occurring. The reaction was subsequently repeated using the tetradentate $\text{Me}_6\text{-TREN}$ ligand in an attempt to isolate a monomeric potassium zincate; however, despite multiple attempts, no crystalline material of suitable quality for analysis by single crystal X-ray diffraction was isolated. In each case an orange solution was produced which yielded an amorphous white powder in very low yields. Attempts were made to characterise the solid by multinuclear NMR spectroscopy, but the crystalline material was found to be insoluble in non-coordinating solvent thereby precluding any characterisation by NMR spectroscopy. Repeating the reaction using the crown ether 18-crown-6 yielded a similar white microcrystalline solid. Once again, the crystalline material

was not suitable for analysis by X-ray crystallography and was completely insoluble in non-coordinating solvent.

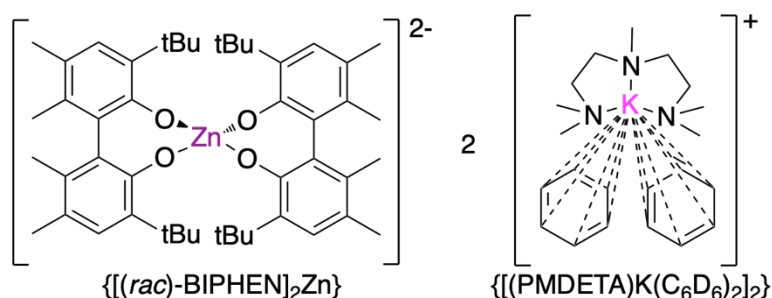
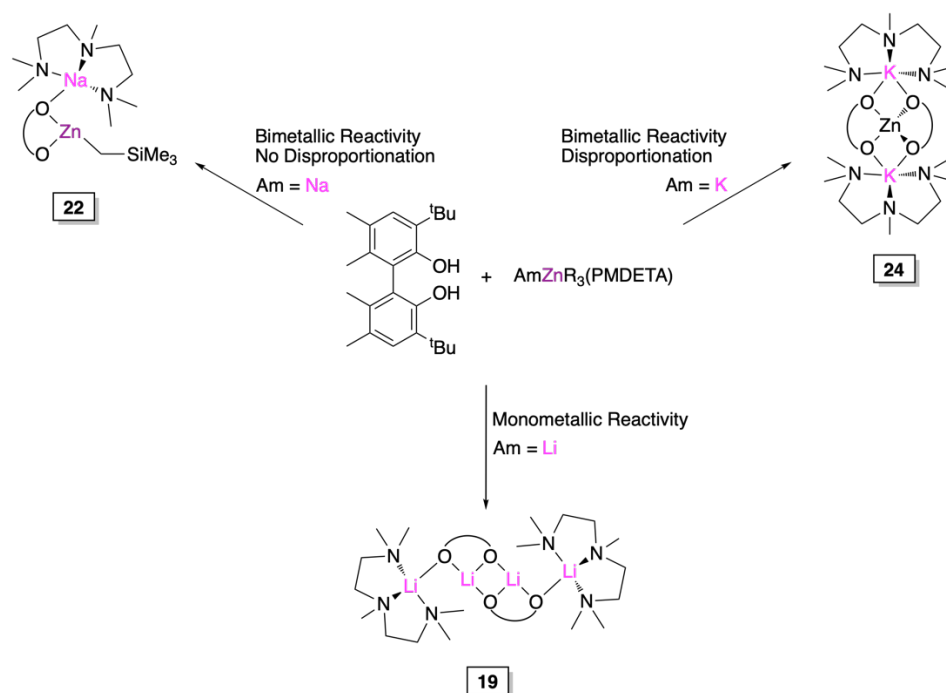


Figure 109: Proposed solution-state structure of **24**.

4.6.4.2 Alkali Metal Effect

Although the reaction of $\text{KZnR}_3(\text{PMDETA})$ with *(rac)*-BIPHEN did not yield the desired mixed alkyl/phenoxide potassium zincate, it does serve as an indication of a surprising alkali metal effect for the reaction of *(rac)*-BIPHEN with alkali metal zincates of the type $\text{AmZnR}_3(\text{PMDETA})$ (where Am = Li, Na or K) (Scheme 35). Harking back to results outlined previously in this chapter, the lithium zincate $\text{LiZnR}_3(\text{PMDETA})$ was found to function as a monoalkyl base giving the tetranuclear lithium phenoxide $\left[(rac)\text{-BIPHEN} \right]_2 \text{Li}_4(\text{PMDETA})_2$, **19** as the sole crystalline product of the reaction. Furthermore, this was found to be in contrast to the reactivity of heavier alkali metal analogue $\text{NaZnR}_3(\text{PMDETA})$ which reacted as a dialkyl base, yielding the bimetallic complex $\left\{ (rac)\text{-BIPHEN} \right\} \text{Na}(\text{PMDETA}) \text{ZnR}$, **22**. The potassium zincate $\text{KZnR}_3(\text{PMDETA})$ was also found to react as a dialkyl base in reaction with *(rac)*-BIPHEN giving the *(rac)*-BIPHEN rich (alkyl free) $\left[(rac)\text{-BIPHEN} \right]_2 \text{ZnK}_2(\text{PMDETA})_2$, **24**, as a result of disproportionation.



Scheme 35: Reaction of $\text{AmZnR}_3(\text{PMDETA})$ (where Am = Li, Na or K) with (*rac*)-BIPHEN.

These results clearly show the alkali metal to have a major influence on the final outcome of the reaction and highlights the importance of understanding the fundamental reactivity of such species. Moreover, the distinct differences in the compositions of the three phenoxides highlights the versatile reactivity of bimetallic zinc bases in simple deprotonation reactions. This could be particularly relevant for the preparation of zinc alkoxides/aryloxides for further organic transformations such as metal-halogen exchange, metallation or catalysis.

4.7 Conclusion and Outlook

This work has provided a much-needed insight into the complex structural chemistry of bimetallic alkylzinc phenoxide complexes through the synthesis and characterisation of a number of lithium, sodium and potassium zincates. The isolation of the inverse lithium zincates **15** and **16** demonstrates a surprising difference between the structural chemistries of lithium alkylmagnesium and lithium alkylzinc phenoxides containing the (*rac*)-BIPHEN ligand. Furthermore, the isolation of these inverse zincates was only possible using the commercially available Et_2Zn as the dialkylzinc component of the reaction. Despite multiple attempts to isolate analogous structures using various dialkylzinc complexes such as Me_2Zn , ${}^n\text{Bu}_2\text{Zn}$, R_2Zn (where $\text{R} = \text{CH}_2\text{SiMe}_3$) and ${}^t\text{Bu}_2\text{Zn}$ no such complexes were obtained which therefore suggests that the identity of the alkyl ligand may play a key role in the formation

of such inverse zincate complexes. Moreover, this work provided an unexpected insight into the reactivity of the alkali metal zincates $\text{Li}_2\text{ZnR}_4(\text{TMEDA})_2$, $\text{Li}_2\text{ZnR}_4((R,R)\text{-TMEDA})_2$ and $\text{LiZnR}_3(\text{PMDETA})$ which were found to react as monometallic lithium bases and not dibasic lithium zincates when employed in reaction with (*rac*)-BIPHEN leading to the formation of the tetranuclear lithium phenoxides **17**, **18** and **19**.

Furthermore, this work has also provided a structural insight into sodium alkylzinc phenoxides through the isolation of **22** and **23**. These complexes were found to exist as monomeric species in the solid-state with an eye-catching structural motif in which the sodium and zinc metal centres are connected through a single bridging interaction. More importantly, the isolation of **22** revealed the existence of a surprising alkali metal effect in the reactivity of the parent zincates $\text{LiZnR}_3(\text{PMDETA})$ and $\text{NaZnR}_3(\text{PMDETA})$. The formation of **22** clearly shows that $\text{NaZnR}_3(\text{PMDETA})$ is capable of functioning as a dibasic complex, bringing about the two-fold deprotonation of the (*rac*)-BIPHEN ligand with retention of both metals within the same complex. This was found to stand in direct contrast with the reactivity observed for $\text{LiZnR}_3(\text{PMDETA})$ which reacted solely as a monometallic base giving rise to the corresponding lithium phenoxide. The isolation of **23** in which the crown ether 15-crown-5 was utilised as a donor ligand clearly demonstrates that this dibasic reactivity is not limited to $\text{NaZnR}_3(\text{PMDETA})$ and further highlights the existence of an alkali metal effect.

Finally, despite the unexpected isolation of the inverse lithium zincates **15** and **16**, which clearly show a strong deviation in structural chemistry from that of their magnesium counterparts, this work has shown that similarities do exist between alkali metal organozinc and organomagnesium phenoxides. Through the isolation of the homoleptic bimetallic lithium, sodium and potassium zinc phenoxides **14**, **21** and **24**, these three complexes demonstrate that zinc phenoxides of this type are equally susceptible to disproportionation as their magnesium counterparts (Chapter 2), particularly in the presence of oxygen-based donors. Complex **21** in particular highlights the similarity between alkali metal zinc and magnesium phenoxides through their propensity to disproportionate in the presence of THF as it was found to be isostructural in the solid-state with its magnesium counterpart **2**. Meanwhile, **14** and **24** give an invaluable insight into the formation of these homoleptic species by showing that disproportionation cannot be prevented simply by increasing the denticity of the donor ligand, something that was initially proposed after studying the related alkali metal organomagnesium phenoxides. Moreover, the isolation of

24 further reinforces the existence of the previously mentioned alkali metal effect as it implies that the potassium zincate $\text{KZnR}_3(\text{PMDETA})$ must have reacted as a bimetallic base giving rise to the desired potassium alkylzinc phenoxide which in turn leads to the formation of **24** as a result of disproportionation.

4.8 Further Work

Due to time restrictions imposed by COVID-19 pandemic there are several areas of this work which remain unfinished and merit further investigation. The first of area of the project which could be investigated further is the structural and reactivity studies of lithium zincates. Beginning with the inverse lithium zincates **15** and **16**, a more rigorous investigation into their formation could be carried out to fully establish what role, if any, the identity of the dialkylzinc complex has on their formation. Given that the corresponding inverse magnesiate complexes have not yet been isolated, it may also be worth investigating computationally why inverse zincates appear to form preferentially rather than the traditional zincates and to make a comparison with the related magnesiate complexes. Moving away from structural characterisation of lithium alkylzinc phenoxides, an additional avenue of investigation which could be of interest would be to carry out further research into the seemingly monometallic reactivity of the lithium zincates $\text{Li}_2\text{ZnR}_4(\text{TMEDA})_2$, $\text{Li}_2\text{ZnR}_4((R,R)\text{-TMEDA})_2$ and $\text{LiZnR}_3(\text{PMDETA})$. A potential starting point for this investigation would be to examine the structural characteristics of the alkali metal zincates $\text{Li}_2\text{ZnR}_4(\text{TMEDA})_2$, $\text{Li}_2\text{ZnR}_4((R,R)\text{-TMEDA})_2$ in detail, both in the solid-state and in solution in order to firmly establish that a co-complex is indeed formed in each case and that the two organometallic components do not remain as separate entities. A study of this type has already been carried out into the behaviour of $\text{LiZnR}_3(\text{PMDETA})$ by the group of Hevia.¹⁷⁷ Following the structural characterisation of the aforementioned alkali metal zincates, their reactivities could be probed with a range of diol substrates to establish if this somewhat surprising monometallic reactivity is unique to the (*rac*)-BIPHEN ligand or is more widely observed with diol substrates in general. In each case the dialkyl zinc component has been relegated to the role of an innocent spectator species, however, it may also be worthwhile investigating if this is truly the case or if the presence of the zinc reagent is required for observed outcome of the reaction.

Turning now to the section of this work relating to sodium zincates, this section perhaps has the most potential for expansion. One way in which this area could be developed further would be to first investigate the inclusion of different alkyl ligands. This investigation could

be carried out first of all using easily accessible commercially available starting materials such as Me_2Zn , Et_2Zn or $^n\text{Bu}_2\text{Zn}$ as well as non-commercially available species such as $^t\text{Bu}_2\text{Zn}$. If the synthesis of the corresponding sodium alkylzinc phenoxide complexes was to prove possible, a structural comparison could then be made between the series of structures to assess whether or not the identity of the alkyl ligand has an effect on the final structure of the complex. Furthermore, the reactivity of these potential complexes could then be investigated in reactions such as metal-halogen exchange and a comparison made to the corresponding alkali metal organomagnesium phenoxides which, in turn could provide valuable information on the relative reactivities of organozinc and organomagnesium complexes of this type. The scope of this study could then be expanded to investigate what effect the inclusion of common nitrogen based Lewis donors such as TMEDA, (*R,R*)-TMEDA and $\text{Me}_6\text{-TREN}$ as well as the crown ethers 12-crown-4 and 18-crown-6 have on the overall structure of the corresponding sodium alkylzinc phenoxides through comparisons with **22** and **23**. Some preliminary reactions into these complexes was carried out; however, no structural characterisation was possible and in the case of the crown ether complexes, solids were isolated which were found to be insoluble in common organic solvents. If the synthesis of any sodium alkylzinc phenoxides were to prove possible using any of the donors mentioned above it would be prudent to investigate their reactivity once again starting with metal-halogen exchange as comparisons could then be drawn to their organomagnesium counterparts.

Additionally, higher order sodium zincates such as $\text{Na}_2\text{ZnR}_4(\text{PMDETA})_2$ should be investigated in reaction with (*rac*)-BIPHEN to establish if it is possible to produce the corresponding higher order disodium diorganozinc phenoxide. This would also provide a useful comparison with corresponding higher order lithium zincates which reacted as monometallic lithium bases and not as dibasic zincates. This may also shed further light on the surprising alkali metal effect observed between lithium and sodium zincates in reaction with (*rac*)-BIPHEN. Finally, moving away from sodium alkylzinc phenoxides, a potentially interesting avenue of investigation would be to replace the alkyl ligand with an amide to produce a sodium amidozinc phenoxide. Given the precedence in the literature for the synthetic utility of mixed metal amidozincates as potent bases for the functionalisation of a range of substrates, inclusion of an amide such as TMP could produce a highly basic zincate. Moreover, if the formation any sodium amidozinc phenoxide was to prove possible and the resulting complex

was found to exhibit a good level of reactivity, it could potentially provide an exciting new entry point into asymmetric synthesis using the chiral form of the BIPHEN ligand.

Focussing now on the section of this work relating potassium alkylzinc phenoxides, this work should be expanded in line with those investigations into the structure and formation of the sodium alkylzinc phenoxides outlined above. The identity of both the alkyl and Lewis donor ligands could be altered in order to assess what effect this has on the structure of the resulting potassium alkylzinc phenoxides. Not only would this provide an interesting structural comparison to any potential lithium or sodium zincates which could be prepared, it may also give a valuable insight into the nature of the proposed Schlenk-like equilibrium which led to the formation of the homoleptic potassium zincate $[(rac)\text{-BIPHEN}]_2\text{ZnK}_2(\text{PMDETA})_2$, **24**, as well as the nature of alkali metal effect observed for the reaction of the alkali metal zincates of the type $\text{AmZnR}_3(\text{PMDETA})$ (where Am = Li, Na or K) with *(rac)*-BIPHEN. A particularly interesting avenue of investigation would be to fully assess what effect the use sterically encumbered donor ligands has on isolation of potassium alkylzinc phenoxides in which the reactive alkyl ligands are retained. The reactivity of higher order zincate species such as $\text{K}_2\text{ZnR}_3(\text{PMDETA})_2$ could also be investigated to establish whether or not the formation of any dipotassium dialkylzinc phenoxides are possible. If the isolation of any potassium alkylzinc or dialkylzinc phenoxides were to prove successful, then their reactivity in metal-halogen exchange or metallation type reactions should be explored and their reactivity compared to the analogous lithium or sodium complexes.

4.9 Experimental

4.9.1 Synthesis of [BIPHEN]₂ZnLi₂(DME)₂ (**14**)

Method 1

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to – 10 °C, was added Et₂Zn (0.91 ml, 0.75 mmol, 0.82 M solution in hexane). The colourless solution was stirred for two hours with gradual warming to ambient temperature, after which time the solution was cooled back to –10 °C. ^tBuLi (0.29 ml, 0.5 mmol, 1.7 M solution in heptane) was then added followed by DME (0.052 ml, 0.5 mmol) to give a white suspension. The suspension was allowed to warm to ambient temperature before being heated to reflux to give a colourless solution. Slow cooling of the resulting solution in a hot water Dewar produced a crop of colourless crystals after 18 hours (0.180 g, 37 % yield).

Method 2

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to –10 °C, was added Me₂Zn (0.91 ml, 0.75 mmol, 0.82 M solution in heptane). The colourless solution was stirred for two hours with gradual warming to ambient temperature, after which time the solution was cooled back to –10 °C. ^tBuLi (0.29 ml, 0.5 mmol, 1.7 M solution in heptane) was then added followed by DME (0.052 ml, 0.5 mmol) to give a white suspension. The suspension was allowed to warm to ambient temperature before being heated to reflux to give a colourless solution. Slow cooling of the resulting solution in a hot water Dewar produced a crop of colourless crystals after 18 hours (0.184 g, 38 % yield).

¹H NMR (400 MHz, 300 K, C₆D₆); δ 1.44 [36H, s, 4 x C(CH₃)₃], 1.80 [12H, s, 4 x CH₃ (*rac*)-BIPHEN], 2.31 [12H, s, 4 x CH₃ (*rac*)-BIPHEN], 2.67 (4H, bs, DME), 2.90 (16H, s, DME), 7.20 [4H, s, 4 x Ph-H (*rac*)-BIPHEN]. ¹³C{¹H} NMR (100 MHz, 300 K, C₆D₆); δ 17.0 [4 x CH₃, (*rac*)-BIPHEN], 20.6 [4 x CH₃, (*rac*)-BIPHEN], 31.1 [4 x C(CH₃)₃, (*rac*)-BIPHEN], 34.8 [4 x C(CH₃)₃, (*rac*)-BIPHEN], 58.2 (4 x CH₃ and 2 x CH₂, DME), 69.6 (2 x CH₂, DME), 122.6, 126.2, 132.8, 132.9, 134.5, 160.1 [Ph, (*rac*)-BIPHEN]. ⁷Li NMR (155 MHz, 300 K, C₆D₆); δ –0.38.

4.9.2 Synthesis of [(*rac*)-BIPHEN]₂Li₂Zn₂Et₂(TMEDA)₂ (15)

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to –10 °C, was added Et₂Zn (0.91 ml, 0.75 mmol, 0.82 M solution in hexane). The colourless solution was stirred for two hours with gradual warming to ambient temperature, after which time the solution was cooled back to –10 °C. ^tBuLi (0.29 ml, 0.5 mmol, 1.7 M solution in heptane) was then added followed by TMEDA (0.075 ml, 0.5 mmol) to give a white suspension. The suspension was allowed to warm to ambient temperature and all volatiles were removed *in vacuo* to yield a white solid. Toluene (4 ml) was added and the suspension was heated to reflux to give a pale-yellow solution. Slow cooling of the resulting solution in a hot water Dewar produced a crop of colourless crystals after 18 hours (0.165 g, 29 % yield).

¹H NMR (400 MHz, 300 K, C₆D₆); δ 0.05 (4H, m, 2 x Zn-CH₂), 1.22 (6H, t, ZnCH₂CH₃), 1.52 [18H, s, C(CH₃)₃], 1.67 [18H, s, C(CH₃)₃], 1.87 (32H, bs, TMEDA), 1.99 [6H, s, CH₃ (*rac*)-BIPHEN], 2.16 [6H, s, CH₃ (*rac*)-BIPHEN], 2.37 [6H, s, CH₃ (*rac*)-BIPHEN], 2.45 [6H, s, CH₃ (*rac*)-BIPHEN], 7.09 [2H, s, Ph-H (*rac*)-BIPHEN], 7.20 [2H, s, Ph-H (*rac*)-BIPHEN]. ¹³C{¹H} NMR (100 MHz, 300 K, C₆D₆) δ –0.26 (2 x CH₂, ZnCH₂CH₃), 14.3 (2 x CH₃, ZnCH₂CH₃), 14.6 (2 x CH₃, ZnCH₂CH₃), 18.1 [2 x CH₃, (*rac*)-BIPHEN], 18.3 (2 x CH₃, (*rac*)-BIPHEN), 20.7 [2 x CH₃, (*rac*)-BIPHEN], 21.2 [2 x CH₃, (*rac*)-BIPHEN], 31.1 (2 x CH₂, TMEDA), 31.4 [C(CH₃)₃, (*rac*)-BIPHEN], 32.1 [C(CH₃)₃, (*rac*)-BIPHEN], 35.1 [C(CH₃)₃, (*rac*)-BIPHEN], 35.2 [C(CH₃)₃, (*rac*)-BIPHEN], 47.0 (CH₃, TMEDA), 57.0 (TMEDA), 119.1, 125.8, 126.4, 126.5, 132.2, 132.2, 134.2, 134.6, 135.2, 136.6, 157.6, 163.0 [Ph, (*rac*)-BIPHEN]. ⁷Li NMR (155 MHz, 300 K, C₆D₆) δ –0.47, –0.19, 0.60.

4.9.3 Synthesis of [(*rac*)-BIPHEN]₂Li₂Zn₂Et₂[(*R,R*)-TMCD] (16)

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to –10 °C, was added Et₂Zn (0.91 ml, 0.75 mmol, 0.82 M solution in hexane). The colourless solution was stirred for two hours with gradual warming to ambient temperature, after which time the solution was cooled back to –10 °C. ^tBuLi (0.29 ml, 0.5 mmol, 1.7 M solution in heptane) was then added followed by (*R,R*)-TMCD (0.095 ml, 0.5 mmol) to give a white suspension. The suspension was allowed to warm to ambient temperature and all volatiles were removed *in vacuo* to yield a white solid. Toluene (4 ml) was added and the suspension was heated to reflux to give a pale-yellow solution. Slow cooling of the resulting solution in a hot water Dewar produced a crop of colourless crystals after 18 hours (0.125 g, 20 % yield).

^1H NMR (400 MHz, 300 K, C_6D_6) δ 0.11 (4H, m, 2 x ZnCH_2), 0.56 [9H, vbs, (*R,R*)-TMCD], 1.26 [15H, m, 2 x ZnCH_2CH_3 and 4 x C_{H_2} (*R,R*)-TMCD], 1.58 [18H, s, 2 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 1.71 [18H, m, 2 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 2.03 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.20 [6H, m, 2 x CH_3 (*rac*)-BIPHEN], 2.38 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.48 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 7.13 [3H, bs, 3 x Ph-H (*rac*)-BIPHEN], 7.20 [1H, bs, Ph-H (*rac*)-BIPHEN]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 0.00 (2 x CH_2 , ZnCH_2CH_3), 14.9 (2 x CH_3 , ZnCH_2CH_3), 18.3 [2 x CH_3 , (*rac*)-BIPHEN], 18.4 [2 x CH_3 , (*rac*)-BIPHEN], 20.7 [2 x CH_3 , (*rac*)-BIPHEN], 21.3 [2 x CH_3 , (*rac*)-BIPHEN], 21.4 [CH_2 , (*R,R*)-TMCD], 24.9 [CH_2 , (*R,R*)-TMCD], 31.5 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 32.4 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.2 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.6 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 63.7 [NCH , (*R,R*)-TMCD], 119.3, 125.6, 126.4, 126.6, 132.4, 132.9, 133.2, 133.7, 134.3, 134.7, 135.3, 135.6, 157.9, 163.07, 164.0 [Ph, (*rac*)-BIPHEN]. ^7Li NMR (155 MHz, 300 K, C_6D_6) δ – 0.07, 0.65.

4.9.4 Synthesis of $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$ (17)

LiR (1 ml, 1 mmol, 1 M solution in pentane) was combined with ZnR_2 (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour prior to the addition of TMEDA (0.15 ml, 1 mmol) to give a turbid white solution. The solution was cooled to -10°C for 10 minutes and (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was warmed slowly to ambient temperature over one hour to give a white suspension. The solvent and all volatiles were removed *in vacuo* to give a white solid to which toluene (4 ml) was added. The white suspension was then heated to reflux to give a pale-yellow solution which was allowed to cool slowly to ambient temperature for 12 hours after which a crop of large, colourless crystals was deposited (0.114 g, 24 % yield).

^1H NMR (400 MHz, 300 K, C_6D_6) δ 1.45 (2H, vbm, CH_2 TMEDA), 1.67 (20H, bs, 2 x $\text{C}(\text{CH}_3)_3$), 1.70 (6H, s, 3 x CH_2 TMEDA), 1.73 [20H, bs, 2 x $\text{C}(\text{CH}_3)_3$], 1.81 (24H, bs, 4 x CH_3 TMEDA), 1.88 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.09 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.25 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.53 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 7.13 [2H, bs, 2 x Ph-H (*rac*)-BIPHEN], 7.18 [2H, bs, 2 x Ph-H (*rac*)-BIPHEN]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 17.8 [2 x CH_3 , (*rac*)-BIPHEN], 18.2 [2 x CH_3 , (*rac*)-BIPHEN], 20.7 [2 x CH_3 , (*rac*)-BIPHEN], 21.2 [2 x CH_3 , (*rac*)-BIPHEN], 31.2 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 31.6 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 34.9 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.2 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 45.6 [4 x CH_3 , TMEDA], 56.5 [4 x CH_2 , TMEDA], 117.9, 122.0,

126.0, 127.0, 121.8, 132.4, 133.0, 133.9, 135.3, 159.5, 163.8 [Ph, (*rac*)-BIPHEN]. ^7Li NMR (155 MHz, 300 K, C_6D_6) δ -0.43, 0.64.

4.9.5 Synthesis of $[(\text{rac})\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD A}]_2$ (**18**)

Method 1

LiR (1 ml, 1 mmol, 1 M solution in pentane) was combined with ZnR_2 (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour prior to the addition of (*R,R*)-TMCD A (0.19 ml, 1 mmol) to give a colourless solution. The solution was cooled to $-10\text{ }^\circ\text{C}$ for 10 minutes to give a white suspension before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was slowly warmed to ambient temperature over one hour to give a white suspension. The solvent and all volatiles were removed *in vacuo* to give a white solid to which toluene (4 ml) was added. The white suspension was then heated to reflux to give a pale-yellow solution which was allowed to cool slowly to ambient temperature for 18 hours after which a crop of large, colourless crystals was deposited (0.104 g, 19 % yield).

Method 2

$^n\text{BuLi}$ (0.625 ml, 1 mmol, 1.6 M solution in hexane) was combined with ZnR_2 (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour prior to the addition of (*R,R*)-TMCD A (0.19 ml, 1 mmol) to give a turbid solution. The solution was cooled to $-10\text{ }^\circ\text{C}$ for 10 minutes to give a white suspension before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was warmed slowly to ambient temperature over one hour to give a white suspension. The solvent and all volatiles were removed *in vacuo* to give a white solid to which toluene (4 ml) was added. The white suspension was then heated to reflux to give a pale-yellow solution which was allowed to cool slowly to ambient temperature for 18 hours after which a crop of large, colourless crystals was deposited (0.085 g, 16 % yield).

It has not been possible to fully assign the solution-state spectra of **18**. No assignment of the terminal methyl groups of the (*R,R*)-TMCD A ligands was possible and no accurate integration values could be obtained in the ^1H NMR spectrum. All assignments are made tentatively using chemical shift values from related complexes as reference.

^1H NMR (400 MHz, 300 K, C_6D_6) δ 0.55 [m, CH_2 , (*R,R*)-TMCD], 1.32 [m, CH_2 , (*R,R*)-TMCD], 1.67 [s, $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 1.69 [s, NCH, (*R,R*)-TMCD], 1.82 [s, $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 1.92 [s, CH_3 , (*rac*)-BIPHEN], 2.11 [s, CH_3 , (*rac*)-BIPHEN], 2.28 [s, CH_3 , (*rac*)-BIPHEN], 2.56 [s, CH_3 , (*rac*)-BIPHEN], 7.12 [Ph-H, (*rac*)-BIPHEN], 7.21 [Ph-H, (*rac*)-BIPHEN]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 17.9 [2 x CH_3 , (*rac*)-BIPHEN], 18.3 [2 x CH_3 , (*rac*)-BIPHEN], 20.9 [2 x CH_3 , (*rac*)-BIPHEN], 21.3 [2 x CH_3 , (*rac*)-BIPHEN], 21.4 [CH_2 , (*R,R*)-TMCD], 24.9 [CH_2 , (*R,R*)-TMCD], 31.1 [$\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 31.8 [$\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 34.9 [$\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.3 [$\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 118.0, 122.0, 122.1, 125.6, 126.0, 126.4, 126.7, 127.0, 132.4, 132.4, 132.5, 132.6, 132.7, 133.3, 133.5, 133.6, 133.6, 133.8, 135.2, 135.3, 159.0, 159.3, 163.8 [Ph, (*rac*)-BIPHEN]. ^7Li NMR (155 MHz, 300 K, C_6D_6) δ -0.05, 0.77.

4.9.6 Synthesis of $[(\textit{rac})\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$ (19)

LiR (0.5 ml, 0.5 mmol, 1 M solution in pentane) was combined with ZnR_2 (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour prior to the addition of PMDETA (0.105 ml, 0.5 mmol) to initially give a colourless solution followed by a turbid solution. The solution was then cooled to -10°C for 10 minutes to give a white suspension before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was warmed slowly to ambient temperature over one hour to give a white suspension. The solvent and all volatiles were removed *in vacuo* to give a white solid to which benzene (5 ml) was added. The white suspension was then heated to reflux to give a pale-yellow solution which was placed in a hot water Dewar to cool slowly to ambient temperature followed by standing at ambient temperature for a further 24 hours to give a crop of large, colourless crystals (0.137 g, 25 % yield).

^1H NMR (400 MHz, 300 K, C_6D_6) δ 1.27-1.41 (10H, vbm, CH_2 PMDETA), 1.63 [18H, s, 2 x $\text{C}(\text{CH}_3)_3$], 1.76 (24H, s, 4 x CH_3 PMDETA), 1.80 [18H, s, 2 x $\text{C}(\text{CH}_3)_3$], 1.91-1.95 (6H, vbm, CH_2 PMDETA), 2.02 (6H, bs, 2 x CH_3 PMDETA), 2.09 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.14 [6H, bs, 2 x CH_3 (*rac*)-BIPHEN], 2.40 [6H, s, 2 x CH_3 (*rac*)-BIPHEN], 2.58 [6H, s, 2 x CH_3 (*rac*)-BIPHEN], 7.23 [2H, s, 2 x Ph-H (*rac*)-BIPHEN]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 18.4 [2 x CH_3 , (*rac*)-BIPHEN], 19.1 [2 x CH_3 , (*rac*)-BIPHEN], 20.9 [2 x CH_3 , (*rac*)-BIPHEN], 21.3 [2 x CH_3 , (*rac*)-BIPHEN], 30.9 (CH_3 , PMDETA), 32.0 [4 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.0 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.3 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 45.6 (CH_3 , PMDETA), 45.7 (CH_3 , PMDETA), 57.3 (8

x CH₂, PMDETA), 117.5, 121.3, 125.8, 126.2, 132.5, 132.7, 133.5, 133.8, 134.2, 135.0, 161.0, 163.7 [Ph, (*rac*)-BIPHEN]. ⁷Li NMR (155 MHz, 300 K, C₆D₆) δ -0.26, -0.04, 0.16, 0.72.

4.9.7 Synthesis of {(*rac*)-BIPHEN}Zn(*R,R*)-TMCD (20)

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to -10 °C, was added ZnR₂ (0.91 ml, 0.75 mmol). The colourless solution was stirred with gradual warming to ambient temperature over two hours, after which time the solution was cooled again to -10 °C. ^tBuLi (0.29 ml, 0.5 mmol, 1.7 M solution in heptane) was then added followed by (*R,R*)-TMCD (0.095 ml, 0.5 mmol) to give a pale-yellow suspension. The suspension was allowed to warm to ambient temperature and all volatiles were removed *in vacuo* to yield a pale-yellow solid. Toluene (4 ml) was added and the suspension was heated to reflux to give a pale-yellow solution. Slow cooling of the resulting solution to ambient temperature produced a crop of colourless crystals after 18 hours (0.068 g, 23 % yield).

Due to the complex solution-state behaviour of **20**, it was not possible to assign the ¹H or ¹³C NMR spectra of the complex. This complexity has been attributed to the potential for dynamic ligand rearrangement leading to the formation of multiple aggregation states in solution for zinc phenoxide complexes.

4.9.8 Synthesis of [(*rac*)-BIPHEN]₂ZnNa₂(THF)₄ (21)

To a solution of (*rac*)-BIPHEN (0.177 g, 0.5 mmol) in hexane (5 ml), cooled to -10 °C, was added Et₂Zn (0.8 ml, 0.5 mmol, 0.62 M solution in hexane). The colourless solution was stirred for 2 hours with gradual warming to ambient temperature for 1 hour, after which time the solution was cooled again to -10 °C. NaR (0.11 g, 1 mmol) was added followed by PMDETA (0.21 ml, 1 mmol) to give a white suspension. The suspension was allowed to warm to ambient temperature before being heated to reflux; however, no dissolution of the white precipitate was achieved. THF was therefore added dropwise to produce a colourless solution. Slow cooling of the resulting solution to ambient temperature produced a crop of colourless crystals (0.43 g, 8 % yield).

¹H NMR (400 MHz, 300 K, d₈-THF) δ 1.16 [36H, s, 4 x C(CH₃)₃, (*rac*)-BIPHEN], 1.45 [12H, s, 4 x CH₃, (*rac*)-BIPHEN], 1.77 (8H, m, THF), 2.05 [12H, s, 4 x CH₃ (*rac*)-BIPHEN], 3.61 (8H, m, THF), 6.71 (4H, s, 4 x Ph-H (*rac*)-BIPHEN]. ¹³C{¹H} NMR (100 MHz, 300 K, d₈-THF) δ 17.0 [4 x CH₃,

(*rac*)-BIPHEN], 20.5 [4 x CH₃, (*rac*)-BIPHEN], 26.4 (OCH₂CH₂, THF), 31.2 [4 x C(CH₃)₃, (*rac*)-BIPHEN], 34.8 [4 x C(CH₃)₃, (*rac*)-BIPHEN], 68.2 (OCH₂CH₂, THF), 121.3, 125.9, 133.1, 133.5, 134.2, 162.2 [Ph, (*rac*)-BIPHEN].

4.9.9 Synthesis of {(*rac*)-BIPHEN}Na(PMDETA)ZnR (22)

NaR (0.055 g, 0.5 mmol) was combined with ZnR₂ (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour. PMDETA (0.105 ml, 0.5 mmol) was subsequently added to initially give a colourless solution then a white suspension. The suspension was then cooled to –10 °C for 10 minutes to give a white suspension before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was warmed slowly to ambient temperature over one hour to give a white suspension. All solvent and volatiles were removed *in vacuo* to give a white solid to which toluene (5 ml) was added. Heating the solution to reflux followed by slow cooling to ambient temperature gave a crop of colourless crystals after 48 hours (0.143 g, 41 % yield).

¹H NMR (400 MHz, 300 K, C₆D₆) δ –0.49 - –0.39 [2H, m, ZnCH₂Si(CH₃)₃], 0.31 [9H, s, ZnCH₂Si(CH₃)₃], 1.48 (2H, bs, PMDETA), 1.72 [25H, vbs, C(CH₃)₃ and PMDETA], 1.83 (6H, bs, PMDETA), 1.85 [9H, bs, C(CH₃)₃], 1.88 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 2.25 [6H, s, 2 x CH₃ (*rac*)-BIPHEN], 7.21 [1H, s, Ph-H (*rac*)-BIPHEN], 7.28 [1H, s, Ph-H (*rac*)-BIPHEN]. ¹³C{¹H} NMR (100 MHz, 300 K, C₆D₆) δ –5.9 (CH₂, ZnCH₂Si(CH₃)₃), 3.3 [Si(CH₃)₃, ZnCH₂Si(CH₃)₃], 17.1 [2 x CH₃, (*rac*)-BIPHEN], 17.6 [2 x CH₃, (*rac*)-BIPHEN], 20.6 [2 x CH₃, (*rac*)-BIPHEN], 30.7 [C(CH₃)₃, (*rac*)-BIPHEN], 31.9 [C(CH₃)₃, (*rac*)-BIPHEN], 32.2 (PMDETA), 35.2 [C(CH₃)₃, (*rac*)-BIPHEN], 35.4 [C(CH₃)₃, (*rac*)-BIPHEN], 44.1 (PMDETA), 45.3 (PMDETA), 53.6 (PMDETA), 57.0 (PMDETA), 119.6, 124.2, 125.9, 127.0, 127.1, 131.6, 132.7, 135.1, 135.7, 136.1, 158.8, 162.6 [Ph, (*rac*)-BIPHEN].

4.9.10 Synthesis of {(*rac*)-BIPHEN}Na(15-crown-5)ZnR (23)

NaR (0.055 g, 0.5 mmol) was combined with ZnR₂ (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour. The suspension was then cooled to –10 °C for 10 minutes before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added followed by 15-crown-5 (0.098 ml, 0.5 mmol) to give a pale-yellow suspension. The suspension was warmed slowly to ambient temperature over one hour after which time, the solvent and all volatiles were removed *in vacuo* to give a pale-yellow solid. Addition of

benzene (3 ml) followed by heating to reflux gave a pale-yellow solution which was allowed to cool to ambient temperature, giving a crop of colourless crystals after 48 hours (0.095 g, 25 % yield).

^1H NMR (400 MHz, 300 K, C_6D_6) δ -0.61 - -0.53 [2H, m, $\text{ZnCH}_2\text{Si}(\text{CH}_3)_3$], 0.36 [9H, s, $\text{ZnCH}_2\text{Si}(\text{CH}_3)_3$], 1.79 - 1.83 [18H, m, $\text{C}(\text{CH}_3)_3$], 1.90 [6H, s, 2 x CH_3 (*rac*)-BIPHEN], 2.30 [6H, s, 2 x CH_3 (*rac*)-BIPHEN], 2.89 (20H, bs, 15-crown-5), 7.25 (2H, bs, 2 x Ph-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 363 K, d_8 -Tol) δ -6.2 [CH_2 , $\text{ZnCH}_2\text{Si}(\text{CH}_3)_3$], 3.2 [$\text{Si}(\text{CH}_3)_3$, $\text{ZnCH}_2\text{Si}(\text{CH}_3)_3$], 16.9 [2 x CH_3 , (*rac*)-BIPHEN], 20.3 [2 x CH_3 , (*rac*)-BIPHEN], 31.7 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 35.1 [2 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 68.9 (15-crown-5), 126.0, 128.4, 133.6, 133.9, 135.2 [Ph, (*rac*)-BIPHEN].

4.9.11 Synthesis of [(*rac*)-BIPHEN] $_2\text{ZnK}_2(\text{PMDETA})_2$ (**24**)

KR (0.066 g, 0.5 mmol) was combined with ZnR_2 (0.11 ml, 0.5 mmol) in hexane (5 ml) to give a white suspension which was stirred at ambient temperature for one hour. PMDETA (0.105 ml, 0.5 mmol) was added to initially give a colourless solution then a white suspension. The suspension was then cooled to -10°C for 10 minutes before (*rac*)-BIPHEN (0.177 g, 0.5 mmol) was added to give a colourless solution. The solution was warmed slowly to ambient temperature for one hour to give a pale-yellow suspension. All solvent and volatiles were removed *in vacuo* to give an off-white solid to which benzene (5 ml) was added. Heating the solution to reflux followed by slow cooling to ambient temperature gave a crop of colourless crystals after five days (0.081 g, 14 % yield).

^1H NMR (400 MHz, 300 K, C_6D_6) δ 1.48 [36H, s, 4 x $\text{C}(\text{CH}_3)_3$ (*rac*)-BIPHEN], 1.83 [12H, s, 4 x CH_3 (*rac*)-BIPHEN], 1.85 (6H, s, NCH_3 PMDETA), 1.96 [24H, s, $\text{N}(\text{CH}_3)_2$ PMDETA], 2.03 (16H, s, 8 x CH_2 PMDETA), 2.36 [12H, s, 4 x CH_3 (*rac*)-BIPHEN], 7.17 [4H, s, 4 x Ph-H (*rac*)-BIPHEN]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 17.3 [4 x CH_3 , (*rac*)-BIPHEN], 20.7 [4 x CH_3 , (*rac*)-BIPHEN], 31.7 [4 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 34.8 [4 x $\text{C}(\text{CH}_3)_3$, (*rac*)-BIPHEN], 41.6 [2 x CH_3 , (*rac*)-BIPHEN], 45.8 (8 x CH_3 , PMDETA), 56.9 (4 x CH_2 , PMDETA), 57.7 (4 x CH_2 , PMDETA), 120.8, 125.9, 132.8, 133.3, 133.5, 163.2 [Ph, (*rac*)-BIPHEN].

Chapter 5 – General Experimental

5.1 Reagent Handling and Solvent Purification

All reactions and manipulations were carried out under a protective argon or nitrogen atmosphere using standard Schlenk and glovebox techniques. Hexane, THF, toluene and diethyl ether were dried by refluxing over sodium using benzophenone as an indicator and distilled under a nitrogen atmosphere prior to use.²⁵² Benzene, TMEDA, PMDETA, DME and 1,4-dioxane were dried by refluxing over calcium hydride and were distilled under nitrogen before being collected and sorted over 4 Å molecular sieves. (*R,R*)-TMEDA was prepared according to literature before being distilled under dynamic vacuum and being stored over 4 Å molecular sieves prior to use.²⁵³ C₆D₆, d₈-THF and d₈-tol were degassed using freeze-pump-thaw methods and were stored over 4 Å molecular sieves. All other reagents were purchased from commercial sources and were stored over 4 Å molecular sieves where appropriate and used without any further purification unless otherwise stated.

5.1.1 Synthesis of ⁿBuNa

NaO^tBu (3.84 g, 40 mmol) was suspended in hexane (60 ml) and cooled to 0 °C for 15 minutes. ⁿBuLi (25 ml, 40 mmol, 1.6 M solution in hexane) and the resulting white suspension was allowed to warm to ambient temperature and was stirred for 12 hours. The white suspension was then filtered to give a white solid which was washed with hexane (3 x 15 ml) before being dried *in vacuo* to give a white solid which stored in an inert atmosphere glovebox. (typical yield 2.1 g, 65 %).

5.1.2 Synthesis of PhCH₂Na

NaO^tBu (0.96 g, 10 mmol) was suspended in toluene (40 ml) and cooled to 0 °C for 15 minutes. ⁿBuLi (6.53 ml, 10 mmol, 1.53 M solution in hexane) to give an orange suspension which was allowed to warm to ambient temperature and was stirred for 12 hours. The following morning the solid was isolated via by canula filtration. The orange solid was then washed with hexane (15 ml) with the solvent being removed by canula filtration. This process was repeated until the filtrate was no longer coloured (colour change from pale-yellow to colourless). The solid was then dried *in vacuo* and stored in an inert atmosphere glovebox (0.66 g, 57 % yield).

5.1.3 Synthesis of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$

Magnesium turnings were stirred under vacuum at ambient temperature for 30 minutes before ether (100 ml) was added. $\text{Me}_3\text{SiCH}_2\text{Cl}$ (19 ml) was then added dropwise as a solution in ether (50 ml) over 15 minutes. The solution was then refluxed for one hour prior to the addition of dioxane (10 ml) as a solution in ether (80 ml) to give a grey suspension. The suspension was stirred at ambient temperature for 12 hours before being filtered through a pad of glass wool and celite and washed with ether (3 x 20 ml) to yield the product as a colourless solution. The solvent was removed *in vacuo* to yield an off-white residue. This solid was sublimed under dynamic vacuum at 165 °C to yield the final product as a white solid (typical yield 3 g, 56 %). ^1H NMR (400 MHz, 300 K, C_6D_6) δ -1.21 (4H, s, 2 x MgCH_2), 0.33 (18H, s, 2 x SiMe_3).

5.1.4 Synthesis of $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$

Dried ZnCl_2 (4.08g, 30 mmol) was suspended in ether (60 ml) and was stirred at ambient temperature for 15 minutes. The suspension was then cooled to 0 °C for 15 minutes and $\text{Li}(\text{CH}_2\text{SiMe}_3)$ (60 ml, 60 mmol, 1 M solution in pentane) was added to give a white suspension. The suspension was allowed to warm to ambient temperature and was stirred for an additional 12 hours. The suspension was then filtered through a pad of glass wool and celite to give a colourless solution. The solvent was removed *in vacuo* to give a crude reaction mixture. This crude product was distilled under dynamic vacuum at 45 °C to yield the product as a highly pyrophoric, colourless liquid which was stored under a protective nitrogen atmosphere at -20 °C (typical yield 3.78g, 53 %). ^1H NMR (400 MHz, 300 K, C_6D_6) δ -0.74 (4H, s, 2 x ZnCH_2), 0.00 (18H, s, 2 x SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 300 K, C_6D_6) δ 3.1.

5.1.5 Synthesis of $^t\text{Bu}_2\text{Zn}$

Dried ZnCl_2 (5.45 g, 40 mmol) was suspended in ether (80 ml) and sonicated for 5 minutes to aid dissolution. The solution was cooled to 0 °C and $^t\text{BuLi}$ (48 ml, 80 mmol, 1.7 M in pentane) was added to give a white suspension. The reaction was covered in order to prevent decomposition of $^t\text{Bu}_2\text{Zn}$ through exposure to light and was stirred for 3 hours at ambient temperature. During this time a separate sublimation apparatus was dried under vacuum and flushed with nitrogen. The suspension was then filtered through a pad of celite and glass wool to give the product as a colourless solution. The solution was then concentrated to

approximately 10 ml before being transferred to the sublimation apparatus. The remaining solvent was removed under reduced pressure and the crude mixture sublimed at ambient temperature under dynamic vacuum, collecting the pure product as a white solid on a cold finger cooled to $-30\text{ }^{\circ}\text{C}$. The solid was then weighted before being stored a solution in hexane under a protective nitrogen atmosphere at $-30\text{ }^{\circ}\text{C}$. The solution was titrated before use.

5.2 Analytical techniques

NMR spectra were recorded on Bruker AVIII or AVIIHD Nanobay 400 MHz or AVII+ 600 MHz spectrometers operating at 400.13 MHz for ^1H , 100.26 MHz for ^{13}C , 155.47 MHz for ^7Li and 376.4 MHz for $^{19}\text{F}\{^1\text{H}\}$. All ^{13}C and ^{19}F NMR spectra were proton decoupled. ^1H , ^{13}C , ^7Li and ^{19}F chemical shifts are expressed in parts per million (δ , ppm) with spectra calibrated to residual solvent peaks where appropriate. HSQC NMR spectra were recorded on AVIII or AV400 400 MHz spectrometers using the pulse program hsqcedetgsp.3. HMBC spectra were recorded on a AV600 MHz spectrometer using the pulse program hmbcgpdpndqf. ^1H DOSY NMR spectra were recorded using an AV 400 MHz spectrometer using the pulse program dstegp3s. Solutions of compounds to be analysed by DOSY were made to 30 mM concentrations (0.015 mmol) in either C_6D_6 or $\text{d}_8\text{-THF}$ (0.5 ml) and 1,2,3,4-tetraphenylnaphthalene (0.015 mmol) was used as an internal standard. Experiments were carried out in accordance with the external calibration methods introduced by Stalke.^{246–248}

X-ray crystallography data for complexes **1-10** and **14-24** were collected at 123 K on Oxford Diffraction Excalibur or Gemini instruments using monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) Cu $\text{K}\alpha$ ($\lambda = 1.54184\text{ \AA}$) radiation. All structures were solved using direct methods and refined to convergence on F^2 for all independent reflections by either Gauss Newton methods using OLEX2²⁵⁴ or by a full-matrix least squares method using SHELXL.²⁵⁵ Complex **2** contained a region of disordered solvent that could not be adequately modelled. The contribution of this feature to the structure was removed using the SQUEEZE routine within the PLATON program suite.²⁵⁶ A total of 79 electron equivalents were removed from approximately $248\text{ \AA}^3$ of space which corresponds to approximately two THF molecules per unit cell.

GCMS was carried out using a Shimadzu QP2010. Analytical High Performance Liquid Chromatography (HPLC) was performed on a Merck Hitachi Lachrom system with diode array UV detectors, using Lux® Cellulose-3 and Amylose-2 columns with dimensions $4.6 \times 100\text{ mm}$ $5\mu\text{m}$.

5.2.3 Crystal Structure Data and refinement Details for Compounds Reported in this Thesis

Table 10: Chapter 2 – **1, 2, 4** and **5**.

Compound	[BIPHEN] ₂ Na ₄ (THF) ₄ 1	[BIPHEN] ₂ Na ₂ Mg(THF) ₄ 2	(<i>rac</i>)-BIPHENNa ₂ MgR ₂ (TMEDA) ₂ 4	(<i>rac</i>)-BIPHENNa ₂ Mg ⁿ Bu ₂ (PMDTA) ₂ 5
Formula	C _{65.6} H ₉₉ Na ₄ O _{8.4}	C ₆₄ H ₉₆ MgNa ₂ O ₈	C ₄₄ H ₈₆ MgNa ₂ Si ₂ O ₂ N ₄	C ₅₀ H ₉₆ MgN ₆ Na ₂ O ₂
Molecular Mass	1114.20	1063.69	829.63	883.61
Crystals System (space group)	Tetragonal (P4 ₁ 2 ₁ 2)	Orthorhombic (I222)	Monoclinic (P2 ₁ /n)	Monoclinic (P _n)
a/Å	13.33310(10)	11.3684(11)	12.0832(2)	12.9924(3)
b/Å	13.33310(10)	15.6863(16)	23.2548(5)	14.0108(3)
c/Å	37.0015(5)	18.5667(12)	12.8204(3)	15.4464(5)
α/°	90	90	90	90
β/°	90	90	94.9340(10)	100.040(3)
γ/°	90	90	90	90
V/Å³	6577.81(13)	3311.0(5)	5268.79(17)	2768.71(13)
Z	4	2	4	2
λ/ Å	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Measured Reflections	25584	7323	24701	27167
Unique Reflections	6448	3269	10305	8631
Observed Reflections	6182	2829	8801	7768
R_{int}	0.0202	0.0234	0.0552	0.0506
Goof	1.074	1.043	1.075	1.038
R(on F, obs refs only)	0.453	0.0426	0.0671	0.0713
wR (on F², all data)	0.1365	0.1128	0.1995	0.1896
Largest diff. peak/hole e/ Å³	0.52/−0.27	0.21/−0.19	0.81/−0.43	1.09/−0.28
Flack	0.018(14)	−0.16(17)	n/a	0.07(4)

Table 11: Chapter 2 continued – **6, 8 and 10.**

Compound	$[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgR}_2(\text{PMDTA})_2$ 6	$[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgR}_2[(R,R)\text{-TMCD A}]_2$ 8	$[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgR}_2[(S,S)\text{-TMCD A}]_2$ 10
Formula	$\text{C}_{61.6}\text{H}_{111.62}\text{MgNa}_2\text{Si}_2\text{O}_2\text{N}_6$	$\text{C}_{52}\text{H}_{98}\text{MgNa}_2\text{Si}_2\text{O}_2\text{N}_4$	$\text{C}_{52}\text{H}_{98}\text{MgNa}_2\text{Si}_2\text{O}_2\text{N}_4$
Molecular Mass	1094.91	937.81	937.81
Crystals System (space group)	Monoclinic (P2 ₁ /c)	Tetragonal (P4 ₁ 2 ₁ 2)	Tetragonal (P4 ₃ 2 ₁ 2)
a/Å	12.9978(3)	15.8436(4)	15.8864(2)
b/Å	13.6893(3)	15.8436(4)	15.8864(2)
c/Å	40.1978(8)	32.1247(12)	30.0775(5)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	93.545(2)	90	90
$\gamma/^\circ$	90	90	90
V/Å ³	7138.7(3)	8063.9(5)	8095.6(2)
Z	4	4	4
$\lambda/\text{\AA}$	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)
Measured Reflections	41990	23738	23927
Unique Reflections	14036	7900	7743
Observed Reflections	11081	6500	6115
R _{int}	0.0323	0.0344	0.0258
Goof	1.022	1.017	1.036
R(on F, obs refs only)	0.0697	0.0527	0.0464
wR (on F ² , all data)	0.2195	0.1554	0.1365
Largest diff. peak/hole e/ Å ³	0.90/−0.36	0.44/−0.19	0.36/−0.24
Flack	n/a	0.059(14)	0.031(13)

Table 12: Chapter 4 – 14, 15 and 16.

Compound	[BIPHEN]Li ₂ Zn(DME) ₂ 14	[(<i>rac</i>)-BIPHEN] ₂ Li ₂ Zn ₂ Et ₂ (TMEDA) ₂ 15	[(<i>rac</i>)-BIPHEN] ₂ Li ₂ Zn ₂ Et ₂ [(<i>R,R</i>)-TMEDA] ₂ 16
Formula	C _{29.98} H _{46.62} Zn _{0.5} LiO ₄	C ₆₄ H ₁₀₆ Zn ₂ Li ₂ O ₄ N ₄	C ₈₆ H ₁₃₄ Zn ₂ Li ₂ O ₄ N ₄
Molecular Mass	510.67	1140.14	1432.58
Crystals System (space group)	Orthorhombic (P2 ₁ 2 ₁ 2)	Trigonal (R-3c)	Orthorhombic (P2 ₁ 2 ₁ 2 ₁)
a/Å	17.6485(3)	39.9955(9)	16.25169(16)
b/Å	14.7938(2)	39.9955(9)	21.5400(3)
c/Å	11.7409(2)	22.9844(5)	23.3297(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	120	90
V/Å ³	3065.41(8)	31840.9(16)	8166.82(17)
Z	4	18	4
λ/ Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Measured Reflections	15758	52846	55385
Unique Reflections	5834	7049	16119
Observed Reflections	5345	5828	14405
R _{int}	0.0956	0.0986	0.0396
Goof	1.074	1.038	1.038
R(on F, obs refs only)	0.0706	0.0547	0.0593
wR (on F ² , all data)	0.1972	0.1716	0.1419
Largest diff. peak/hole e/ Å ³	1.10/−0.88	0.95/−0.43	0.71/−1.06
Flack	−0.09(5)	n/a	−0.017(9)

Table 13: Chapter 4 continued – **17, 18, 19** and **20**.

Compound	$[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{TMEDA})_2$ 17	$[(rac)\text{-BIPHEN}]_2\text{Li}_4[(R,R)\text{-TMCD A}]_2$ 18	$[(rac)\text{-BIPHEN}]_2\text{Li}_4(\text{PMDETA})_2$ 19	$\{(rac)\text{-BIPHEN}\}\text{Zn}(R,R)\text{-TMCD A}$ 20
Formula	$\text{C}_{60}\text{H}_{96}\text{Li}_4\text{O}_4\text{N}_4$	$\text{C}_{74}\text{H}_{122}\text{Li}_4\text{O}_4\text{N}_4$	$\text{C}_{78}\text{H}_{122}\text{Li}_4\text{O}_4\text{N}_6$	$\text{C}_{41}\text{H}_{62}\text{ZnO}_2\text{N}_4$
Molecular Mass	965.16	1159.51	1235.57	680.29
Crystals System (space group)	Orthorhombic (Pna2 ₁)	Monoclinic (I2)	Orthorhombic (Fdd2)	Monoclinic (C2)
a/Å	27.1961(30)	24.4209(6)	35.8686(12)	27.7018(3)
b/Å	10.49740(10)	16.0124(3)	30.7843(8)	11.47390(10)
c/Å	20.8580(2)	21.9326(6)	27.6967	24.9746(4)
α/°	90	90	90	90
β/°	90	121.348(4)	90	108.1270(10)
γ/°	90	90	90	90
V/Å³	5954.71(10)	7324.5(4)	30582.4(15)	7544.14(17)
Z	4	4	16	8
λ/ Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Measured Reflections	44172	29550	54146	30766
Unique Reflections	11585	13297	14570	14161
Observed Reflections	10961	11669	11009	13170
R_{int}	0.0289	0.0291	0.1675	0.0289
Goof	1.029	1.047	1.010	1.026
R(on F, obs refs only)	0.0435	0.0463	0.0892	0.0376
wR (on F², all data)	0.1229	0.1277	0.2576	0.1013
Largest diff. peak/hole e/ Å³	0.69/−0.23	0.23/−0.23	0.47/−0.33	0.50/−0.26
Flack	0.0(2)	0.0(3)	−0.1(4)	0.010(11)

Table 14: Chapter 4 continued – **21, 22, 22** and **23**.

Compound	$[(rac)\text{-BIPHEN}]_2\text{Na}_2\text{Zn}(\text{THF})_4$ 21	$\{(rac)\text{-BIPHEN}\}\text{NaZnR}(\text{PMDTA})$ 22	$\{(rac)\text{-BIPHEN}\}\text{NaZnR}(15\text{-crown-5})$ 23	$[(rac)\text{-BIPHEN}]_2\text{ZnK}_2(\text{PMDTA})_2$ 24
Formula	$\text{C}_{64}\text{H}_{96}\text{ZnNa}_2\text{O}_8$	$\text{C}_{37}\text{H}_{66}\text{NaZnSiO}_2\text{N}_3$	$\text{C}_{44}\text{H}_{69}\text{NaZnSiO}_7$	$\text{C}_{66}\text{H}_{110}\text{K}_2\text{ZnO}_4\text{N}_6$
Molecular Mass	1104.85	701.37	826.44	1195.16
Crystals System (space group)	Monoclinic (C2/c)	Monoclinic (P2 ₁ /n)	Monoclinic (P2 ₁ /c)	Monoclinic (C2/c)
a/Å	25.3220(5)	12.6767(2)	20.2327(3)	24.4891(4)
b/Å	11.6709(2)	17.7515(2)	12.55820(10)	12.61360(10)
c/Å	23.8870(5)	18.3788(2)	19.8780(3)	25.3342(2)
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	118.504(3)	105.2160(10)	112.786(2)	119.459(2)
$\gamma/^\circ$	90	90	90	90
V/Å ³	6203.6(3)	3990.80(9)	4656.56(12)	6813.8(2)
Z	4	4	4	4
$\lambda/\text{\AA}$	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)
Measured Reflections	21211	33817	41451	28759
Unique Reflections	6115	7915	9211	6634
Observed Reflections	5458	6619	7836	5970
R _{int}	0.0194	0.1233	0.0320	0.0360
GooF	1.048	1.033	1.033	1.034
R(on F, obs refs only)	0.0639	0.0605	0.0477	0.0356
wR (on F ² , all data)	0.2020	0.1774	0.1404	0.0973
Largest diff. peak/hole e/ Å ³	1.05/−0.51	1.05/−1.11	0.54/−0.42	0.39/−0.22

Chapter 6 – References

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