Acknowledgements

First and foremost, I would like to thank my *super*visor Dr Eva Hevia for three years packed full of wise words and boundless energy. It has been my absolute pleasure to do chemistry in your lab and I am grateful for all the help you have given me and the endless ideas. Thank you for your care and attention helping to make this thesis the best thesis possible! I couldn't have done any of it without you. If you ever run out of ideas (unlikely, I know) don't forget you could always drown some ants in hexane and run them down the GC (ah, good times!)

Special thanks to fellow Hevias/Hevia Alumni, Matt, Zoe, Vicki, Emma, Thomas, Alberto and the extended family of R5-26; it's been hard work, but you've made it exceedingly good fun. A few choice quotes in memory of my time in the lab: "you're not supposed to just read the slides" (you had to be there, eh Ben?), "if two T-Rexs are fighting in George Square, would they be more interested in each other or eating us?" and "I've been fighting with my hobbit"! Shout out to Ben and Matt for inventing the Sharibu. Bless you both! To all the project students that have worked with me over the years (Andy, Lisa, Nick, Kelvin and Angeles) thank you all for your dedication and contributions to the work!

I must also thank Professor Robert Mulvey for the kind encouragement and suggestions after group meetings, Dr Charlie O'Hara for training in, and use of, the GC, Dr Pablo Garcia-Alvarez for teaching me how to use DOSY (it's super cool!), Craig Irving's unending NMR help and Pat Keating's expertise in the GC/MS. Also, my thanks go to Dr Alan Kennedy, Dr Jan Klett, Dr Luca Russo and Professor Bill Clegg for the numerous X-ray structures, which bring a little bit of sunshine to my life.

Like probably every PhD student before me, I can hardly believe it's now at an end. It's been a wonderful experience and I know that is down to the great people I have had the pleasure to get to know over these past few years. Of all my happy memories, top of the list are: the LA trip – outstanding! Eva and Zoe on the Tower of Terror, just hilarious! The trip to the synchrotron is also high up the list; what geek couldn't love taking a walk around a particle accelerator? Finally, I can't resist it, Brad Pitt filming right outside the university! After our trip to Hollywood, Hollywood came to us.

And now we get to the most important paragraph in the whole thesis: my family. David, my biggest fan, you have never relented in your encouragement or belief in me. I think I've been Mrs Baillie for long enough, what do you say? (Ha ha!) Jonathan and Petra, you kept me sane more than you know and you could always lift my spirit when things weren't going to plan! You have been strong when I needed it and silly when I needed that more. Thank you Baillies! David: DOSY-doh. Jonathan: lunch buddy! Petra: all plastics are polymers, but not all polymers are plastics! Now, how about a cruise?

Abstract

Building on recent successes in mixed-metal chemistry, this research project aims to enhance the understanding of the complicated correlations existing between structural patterns and reactivities of alkali metal magnesiates and zincates together with exploring their applications in a number of fundamental organic transformation reactions such as metallation, alkyl addition and metal-halogen exchange reactions.

Elucidating the effect that donor solvents can exert on the overall constitution of organometallic reagents, a series of novel solvated [(donor)$MMgR_3$] and [$(donor)_2M_2MgR_4$] (donor = THF, dioxane, TMEDA, PMDETA; M = Li, Na, K; R = CH_2SiMe_3) compounds have been prepared and fully characterised both in the solid-state and in solution using multinuclear NMR (including ^{1}H-DOSY NMR) studies. A rich variety of structural motifs has been disclosed which range from simple monomers when polydentate ligands such as PMDETA are employed, such as [(PMDETA)$LiMgR_3$] (**6**) and [$(PMDETA)_2MMgR_4$] (M = Na (**9**), K (**11**)), to much more complex polymeric structures using oxygen donor ligands dioxane or THF, such as [{$(dioxane)_2LiMgR_3$}$_\infty$] (**3**), [{(dioxane)$Li_2Mg_2R_6$}$_\infty$] (**4**) and [{(THF)$LiMgR_3$}$_\infty$] (**2**). The first examples of unsolvated trisalkyl magnesiates [{$NaMgR_3$}$_\infty$] (**12**) and [{$KMgR_3$}$_\infty$] (**16**) have been unveiled which exhibit distinct 2D supramolecular structures in the solid-state constructed exclusively of electron deficient M-C bonds. The ability of novel potassium magnesiates to participate in direct magnesium-hydrogen exchange reactions was assessed with several aromatic and heteroaromatic substrates.

In addition, key reaction intermediates have been structurally defined from metallation, alkyl addition and metal-halogen exchange reactions which provide compelling evidence that the outcome of these reactions are reliant on subtle changes in the coordination sphere of the bimetallic reagent employed. Thus, the reactivity of heteroleptic zincate [(THF)LiZn(TMP)$(t\text{Bu})_2$] (**22**) towards pyrazine has demonstrated that despite the presence of two nucleophilic *t*Bu groups the selective

two-fold deprotonation of the heterocycle pyrazine is preferred to form the unprecedented 2,5-di-zincated pyrazine molecule. These results are in contrast with those observed when pyrazine is confronted by the homoleptic alkyl zincate [(PMDETA)LiZn(*t*Bu)$_3$] (**23**) where the chemoselective addition of a *t*Bu group to the α-C of the heterocycle takes place under mild reaction conditions. Focussing on metal-halogen exchange reactions, the addition of LiO*t*Bu has proved to greatly activate $ZnEt_2$ towards zinc-iodine exchange reactions with 2-iodoanisole under mild conditions.

Novel bimetallic approaches which allow the selective C4 functionalisation of unsaturated N-heterocyclic carbene IPr have been developed. Thus, the first direct zincation of an NHC was achieved by reacting sodium zincate [(TMEDA)Na(TMP)(*t*Bu)Zn(*t*Bu)] with IPr to form [(THF)$_3$Na(IPr*)Zn(*t*Bu)$_2$] (**41**). **41** exhibits a unique chemical profile and can react efficiently with [ClAu(PPh$_3$)] to form an unprecedented bis-gold [ClAu(IPr*)Au(PPh$_3$)] (**47**) species. Extension of these reactivity studies to Na/Mg combinations allows the isolation of the first sodium magnesiate containing a deprotonated carbene molecule [(THF)$_3$Na(IPr*)Mg(CH$_2$SiMe$_3$)$_2$(THF)] (**50**).

Publications

"Synthesis, structural elucidation and diffusion-ordered NMR studies of homoleptic alkyllithium magnesiates: donor-controlled structural variations in mixed-metal chemistry" **Sharon E. Baillie**, William Clegg, Pablo Garcıa-Alvarez, Eva Hevia, Alan R. Kennedy, Jan Klett and Luca Russo, *Organometallics,* **2012**, *31*, 5131.

"New lithium-zincate approaches for the selective functionalisation of pyrazine: direct dideprotozincation vs. nucleophilic alkylation" **Sharon E. Baillie**, Victoria L. Blair, David C. Blakemore, Duncan Hay, Alan R. Kennedy, David C. Pryde and Eva Hevia, *Chem. Commun*., **2012**, *48*, 1985.

"A new polymeric alkyl/alkoxide magnesium–sodium inverse crown complex" **Sharon E. Baillie**, Victoria L. Blair, Eva Hevia and Alan R. Kennedy, *Acta Cryst*., **2011**, *C67*, 249.

"Synthesis and characterization of an infinite sheet of metal–alkyl bonds: unfolding the elusive structure of an unsolvated alkali-metal trisalkylmagnesiate" **Sharon E. Baillie**, William Clegg, Pablo Garcıa-Alvarez, Eva Hevia, Alan R. Kennedy, Jan Klett and Luca Russo, *Chem. Commun.,* **2011**, *47*, 388.

Other publications not related to this work

"Synthesis of mixed alkali-metal-zinc enolate complexes derived from 2,4,6-trimethylacetophenone: new inverse crown structures" **Sharon E. Baillie**, Eva Hevia, Alan R. Kennedy, and Robert E. Mulvey, *Organometallics* **2007,** *26,* 204.

Conference Presentations

1. "*New structural and reactivity insights in magnesiate and zincate chemistry*"; Hamilton-Barrett Postgraduate Prize Award lecture, University of Strathclyde, Oct

2011.

2. "*New structural insights in mixed-metal magnesiate and zincate chemistry*"; 6th WestCHEM Research Day, Glasgow University, June 2011.

3. "*New structural insights in mixed-metal magnesiate and zincate chemistry*"; American Chemical Society, 241st National Meeting, California, March 2011.

Conference Poster Presentations

1. "*New lithium-zincate approaches for the selective functionalization of pyrazine: direct dideprotonation vs. nucleophilic alkylation*"; North West Organic Chemistry Symposium, Liverpool University, July 2012.

2. "*Probing the structures of a series of lithium magnesiates*"; Universities of Scotland Inorganic Conference, Glasgow University, July 2011.

3. "*Unveiling the Structure of Unsolvated Alkali-Metal Magnesiates*"; Royal Society of Chemistry Young Members' Symposium, Manchester University, October 2010.

4. "*Unveiling the Structure of Unsolvated Alkali-Metal Magnesiates*"; Universities of Scotland Inorganic Conference, Durham University, July 2010.

Table of Common Abbreviations

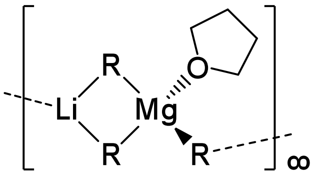
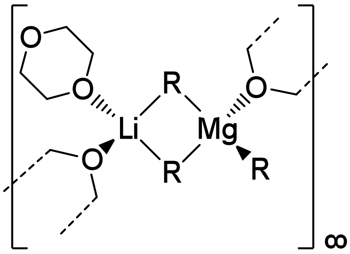
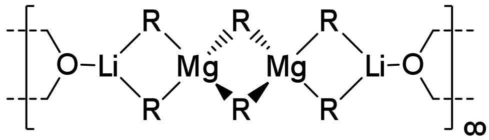
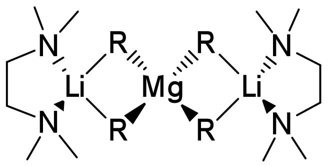
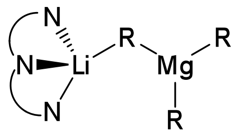
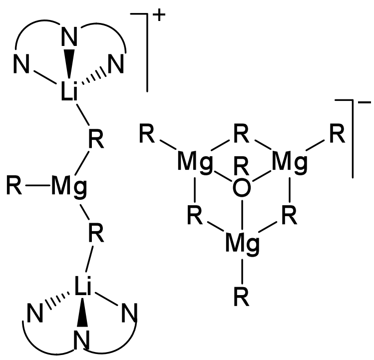
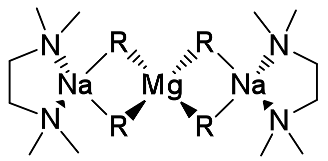
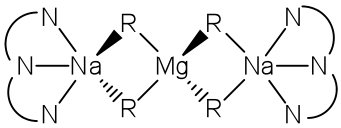
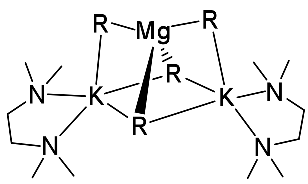
acac	Acetylacetonate
AMM*M*	Alkali-metal-mediated metallation
AMM*Mg*	Alkali-metal-mediated magnesiation
AMM*Mn*	Alkali-metal-mediated manganation
AMM*Zn*	Alkali metal mediated zincation
*a*NHC	*Abnormal* N-Heterocyclic carbene
Ar	Aryl
*n*Bu	$(CH_2)_3CH_3$
*t*Bu	$C(CH_3)_3$
CCDB	Cambridge crystallographic database
CIP	Contacted ion-pair
COSY	^1H-^1H correlated spectroscopy
Cp	Cyclopentadiene anion $(C_5H_5)^-$
DA	Diisopropylamide
DCM	Dichloromethane
DFT	Density functional theory
Dipp	Diisopropylphenyl
DOSY	Diffusion ordered NMR spectroscopy
Dppf	1,1'-bis(diphenylphosphino)ferrocene
Ee	Enantiomeric excess (%)
Et	Ethyl
Et_2O	Diethyl ether
FW	Formula weight
G	Grams
H	Hours
HMDS	Hexamethyldisilazide
HOESY	Heteronuclear Overhauser effect spectroscopy
HSQC	Heteronuclear single quantum correlation spectroscopy
IBu	1,3-di-*tert*-butylmidazol-2-ylidene
ICE	Inverse crown ether

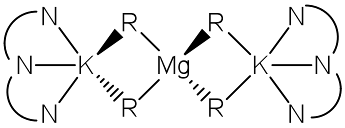
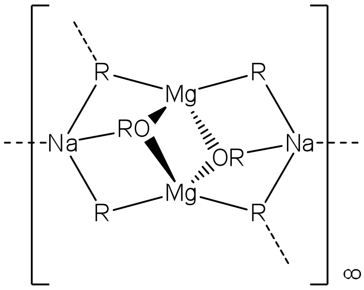
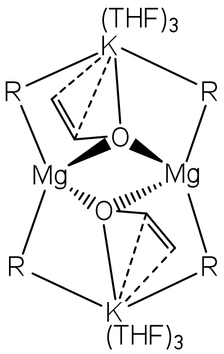
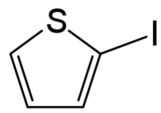
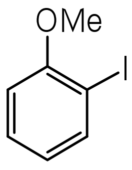
IMes	1,3-dimesityimidazol-2-ylidene
IPr	1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene
IPr*	:C{[N(2,6-iPr$_2$C$_6$H$_3$)]$_2$CHC}
LDA	Lithium diisopropylamide
M	Molar
Me	Methyl
MHz	Megahertz
mL	Millilitres
mmol	Millimoles
NHC	N-Heterocyclic carbene
NHDC	N-Heterocyclic dicarbene
NMP	*N*-methylpyrrolidinone
NMR	Nuclear magnetic resonance s – singlet d – doublet t – triplet q – quartet m – multiplet b – broad
NOESY	Nuclear Overhauser effect spectroscopy
Nu	Nucleophile
PGSE	Pulsed gradient spin echo
Ph	Phenyl
PhN	Phenylnaphthalene
PMDETA	*N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine
Ppm	Parts per million
Pr	Propyl
SSIP	Solvent separated ion-pair
THF	Tetrahydrofuran
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidide
TMP(H)	2,2,6,6-tetramethylpiperidine

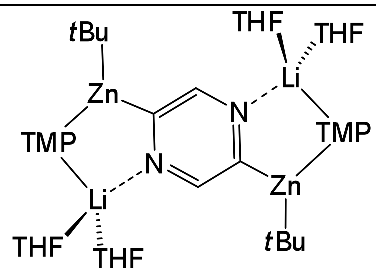
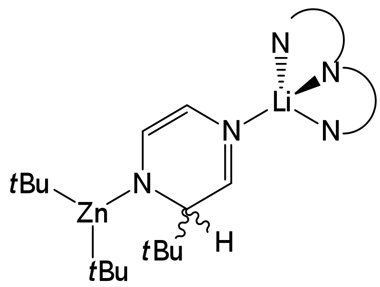
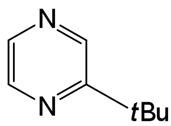
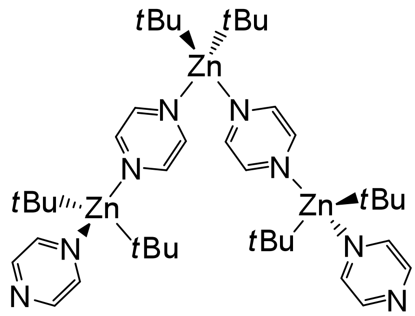
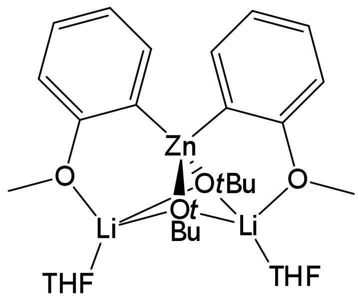
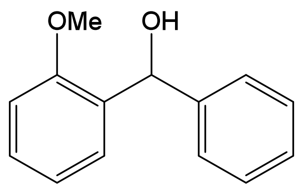
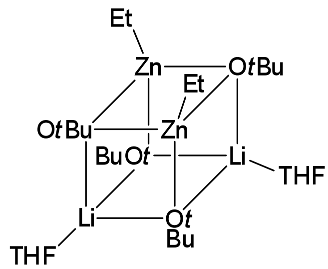
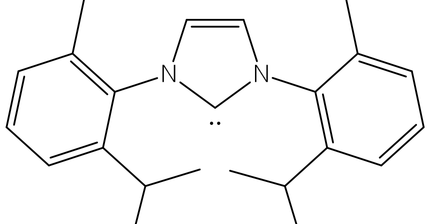
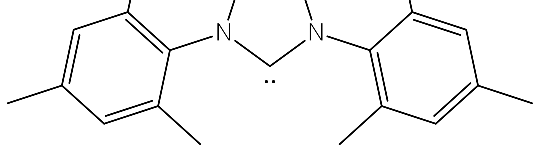
TMS	Trimethylsilyl or tetramethylsilane
TPhN	1,2,3,4-tetraphenylnaphthalene

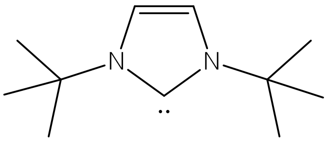
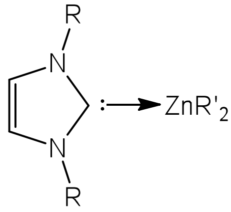
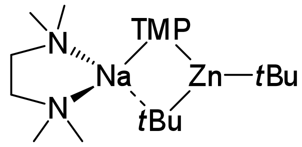
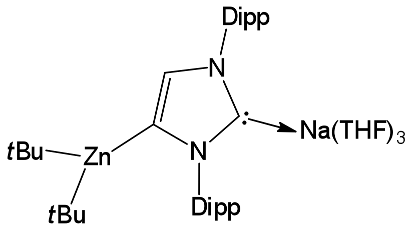
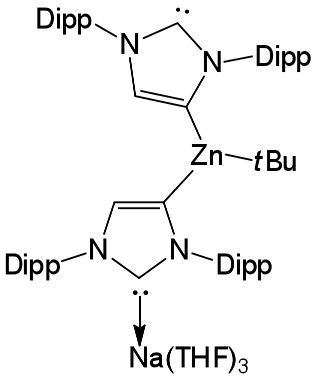
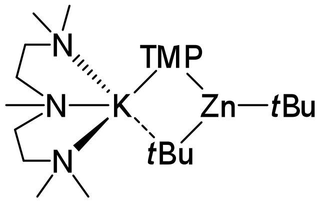
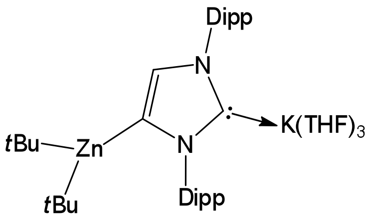
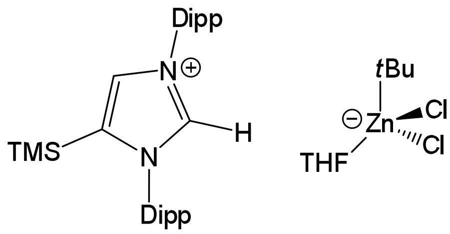
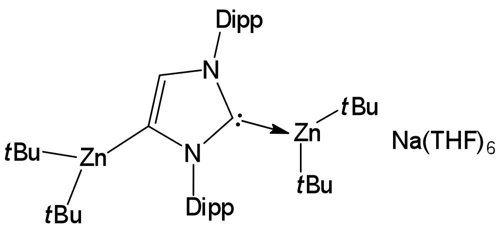
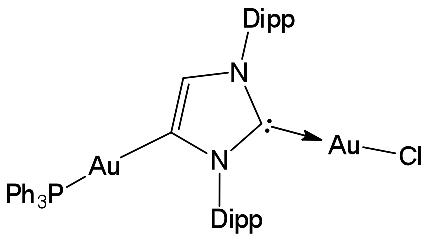
Table of Contents

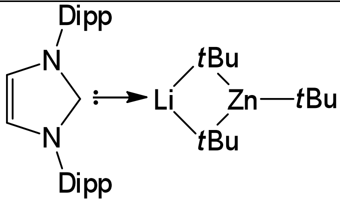
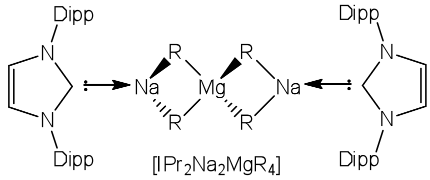
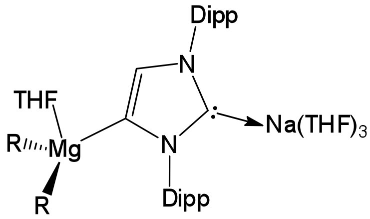
Table of Compounds

Number	Compound	Number	Compound
1	[LiMgR$_3$]	**2**	 [{(THF)LiMgR$_3$}$_\infty$]
3	 [{(dioxane)$_2$LiMgR$_3$}$_\infty$]	**4**	 [{(dioxane)Li$_2$Mg$_2$R$_6$}$_\infty$]
5	 [(TMEDA)$_2$Li$_2$MgR$_4$]	**6**	 [(PMDETA)LiMgR$_3$]
7	 [{(PMDETA)$_2$Li$_2$MgR$_3$}$^+${Mg$_3$R$_6$(OR)}$^-$]	**8**	 [(TMEDA)$_2$Na$_2$MgR$_4$]
9	 [(PMDETA)$_2$Na$_2$MgR$_4$]	**10**	 [(TMEDA)$_2$K$_2$MgR$_4$]

Number	Compound	Number	Compound
11	 [(PMDETA)$_2$K$_2$MgR$_4$]	**12**	[{NaMgR$_3$}$_\infty$]
13	[{(NaR)$_4$}$_\infty$]	**14**	[Na$_2$MgR$_4$]
15	 [{NaMgR$_2$OR}$_\infty$]	**16**	[{KMgR$_3$}$_\infty$]
17	[{(C$_6$H$_6$)KMgR$_3$}$_\infty$]	**18**	[{(Cp$_2$Fe)KMgR$_3$}$_\infty$]
19	 [{(THF)$_3$K(R)(OCH=CH$_2$)MgR}$_2$]	**20**	
21		**22**	[(THF)LiZn(TMP)(*t*Bu)$_2$]

Number	Compound	Number	Compound
23	[(PMDETA)LiZn(*t*Bu)$_3$]	**24**	 [2,5-{(THF)$_2$LiZn(TMP)(*t*Bu)}$_2$(C$_4$N$_2$H$_2$)]
25	 [(PMDETA)Li{C$_4$N$_2$H$_4$(*t*Bu)}Zn(*t*Bu)$_2$]	**26**	
27	 [{Zn(*t*Bu)$_2$}$_3${C$_4$N$_2$H$_4$}$_4$]	**28**	 [(THF)$_2$Li$_2$(O*t*Bu)$_2$Zn(*o*-C$_6$H$_4$-OMe)$_2$]
29		**30**	 [{(THF)Li(O*t*Bu)$_2$ZnEt}$_2$]
31	 IPr	**32**	 IMes

Number	Compound	Number	Compound
33	 IBu	**34-39**	 **34**, R = Dipp, R' = Me **35**, R = Dipp, R' = *t*Bu **36**, R = Mes, R' = Me **37**, R = Mes, R' = *t*Bu **38**, R = *t*Bu, R' = Me **39**, R = *t*Bu, R' = *t*Bu
40	 [(TMEDA)Na(TMP)(*t*Bu)Zn(*t*Bu)]	**41**	 $[(THF)_3Na(IPr^*)Zn(tBu)_2]$
42	 $[(THF)_3Na(IPr^*)Zn(IPr^*)(tBu)]$	**43**	 [(PMDETA)K(TMP)(*t*Bu)Zn(*t*Bu)]
44	 $[(THF)_3K(IPr^*)Zn(tBu)_2]$	**45**	 $[\{TMS\text{-}IPr(H)\}^+\{(THF)Zn(tBu)Cl_2\}^-]$
46	 $[\{Na(THF)_6\}^+\{(tBu)_2Zn(IPr^*)Zn(tBu)_2\}^-]$	**47**	 $[ClAu(IPr^*)Au(PPh_3)]$

Number	Compound	Number	Compound
48	 [IPr·LiZntBu$_3$]	**49**	 [IPr$_2$Na$_2$MgR$_4$]
50	 [(THF)$_3$Na(IPr*)Mg(R)$_2$(THF)]		