

Novel N-heterocyclic activations mediated by magnesium reagents having sterically hindered ligands

By
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To my mum and dad, just a small thank you.

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Abstract

Building on recent advances on the synthesis of homometallic Mg compounds bearing highly sterically demanding ligands, but going significantly beyond the state-of-the-art, this thesis report focuses on the synthesis of new sodium magnesiate and magnesium reagents supported by bulky *N*-chelating ligands $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$ and $\{\text{Ar}^*\text{N}=\text{C}(\text{Me})\text{CH}(\text{Me})\text{NAr}^*\}^-$ (nacnac) as well as their exploitation within the areas of deprotonative metallation, heterocyclic activation and catalytic application in hydroamination reactions of organic heterocumulenes.

Firstly, a series of novel sodium magnesiate bearing the sterically demanding bis(amido)silyl ligand $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$ ($\text{Ar}^* = 2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3$) has been prepared. Thus alkyl derivatives $[\{\text{Na}(\text{THF})_6\}^+\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{R})(\text{THF})]^-$ ($\text{R} = \text{Bu}$, **2**; CH_2SiMe_3 , **5**) have been synthesised and isolated as crystalline solids by reacting bis(amine)silyl $[\text{Ph}_2\text{Si}(\text{NHAr}^*)_2]$ **1** with the relevant sodium magnesiate $\text{NaMg}(\text{Bu})\text{R}_2$ (prepared *in situ* by co-complexation of BuNa with the relevant magnesium alkyl MgR_2). In addition, compound **5** has been used as a precursor for the synthesis of a new series of amido sodium magnesiate $[\{\text{Na}(\text{THF})_6\}^+\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{NR}_2)(\text{THF})_x]^-$ ($\text{NR}_2 = \text{HMDS}$, $x=1$, **6**; $\text{NR}_2 = \text{NPh}_2$, $x=1$, **7**; $\text{NR}_2 = \text{N}^i\text{Pr}_2$, $x=1$, **8**; $\text{NR}_2 = \text{DMP}$, $x=1$, **9**; $\text{NR}_2 = \text{TMP}$, $x=0$, **10**). The reactions of NH_2Ar^* and pyrrole with complex **5** led to the formation of mixed-metal complexes $[\{\text{Na}(\text{THF})_6\}^+\{\text{Ph}_2\text{Si}(\text{NAr}^*)(\text{NHAr}^*)\}\text{Mg}(\text{NHAr}^*)_2(\text{THF})]^-$ **11** and $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)(\text{NHAr}^*)\}\text{Mg}(\text{NC}_4\text{H}_4)_2(\text{THF})\text{Na}(\text{THF})_2]^-$ **12** respectively.

Reactivity studies disclosed that TMP derivative **10** was able to carry out the α -magnesiumation of thiophene to yield $[\{\text{Na}(\text{THF})_6\}^+\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{C}_4\text{H}_3\text{S})(\text{THF})]^-$ **13**. In moving to reactivity studies with 1,3 benzoazoles complex **2** promotes the chemoselective magnesiumation of methylbenzimidazole (MeBIm) to yield $[\{\text{Na}(\text{THF})_5\}_2^+\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{MeBIm}^*)]_2^-$ **14** ($\text{MeBIm}^* = \text{methylbenzimidazolyl}$), analysis of bond parameters, NMR data and DFT studies suggest that *N*-methylbenzimidazolyl ligand displays a metal carbene character. The

reaction of **2** with benzothiazole (Btz) promotes a unique activation process of this heterocycle initiating an unprecedented cascade of reactions, where the initial magnesiation of Btz is followed by an intricate sequence of C-C coupling, ring opening, benzothiazolyl insertion into a C=N bond and intramolecular deprotonation leading to the ring opening and functionalisation of three Btz molecules resulting in novel sodium magnesiate $[L_2Mg_2Na_2(THF)_5]$ **15**. Extending these studies to the diazine molecule quinoxaline allows the synergic entrapment of radical anion (Qox^{\bullet}) in the form of dimer $[\{Na(THF)_6\}_2^+ \{(Ph_2Si(NAr^*)_2)Mg(Qox^{\bullet})\}_2^-]$ **20** resulting from the homoleptic cleavage of Mg-C bond in the alkyl precursor **2**. EPR studies show that **20** is diamagnetic in the solid-state dimeric structure.

Homometallic magnesium species $[(^{Dipp}nacnac)Mg(Bu)(THF)]$ **22** and $[(^{Dipp}nacnac)Mg(TMP)]$ **23** were prepared and structurally defined and their reactivity towards 1,3-benzoxazoles has been assessed. Reactions of **22** and **23** with benzoxazole allowed the isolation in both cases of $[(^{Dipp}nacnac)Mg\{O(o-C_6H_4)NC\}(THF)]$ **24** resulting from ring cleavage of benzoxazolyl anion. Benzothiazole (Btz) was magnesiated at the C2 position by the amido derivative to form $[\{(^{Dipp}nacnac)Mg(Btz^*)\}_2]$ **25** (Btz* = 2-benzothiazolyl), however when **22** was reacted with Btz a novel activation of Btz occurred in a cascade reaction involving magnesiation, C-C coupling and ring opening resulting in $[(^{Dipp}nacnac)Mg\{(Btz^*)C(H)=N(2-C_6H_4-1-S)\}]$ **26**. Complex **23** when reacted with nitrogen derivative methylbenzimidazole (MeBIm) promotes the magnesiation at the C2 position to yield $[\{(^{Dipp}nacnac)Mg(MeBIm^*)\}_2]$ **27**. In contrast alkyl derivative **22** only coordinated to MeBIm through the lone pair on the N to yield $[(^{Dipp}nacnac)Mg(Bu)(MeBIm)]$ **28**.

Studies assessing the catalytic ability of sodium magnesiates to promote the hydroamination of isocyanates and carbodiimides, show that homoleptic $[NaMg(CH_2SiMe_3)_2]$ **32** can effectively catalyse at room temperature the reactions of $HNPh_2$ with several aliphatic isocyanates to yield the relevant ureas $[(NHR)C(=O)(NPh_2)]$ (R = ^tBu, **29**, R = Cy, **39**, R = Et, **43**) in yields ranging from 99 to 100%. Similarly tris(amido) complex $[NaMg(NPh_2)_3]$ **30** catalyses the trimerisation of aryl isocyanates under mild reaction conditions. The isolation of key intermediates

of the stoichiometric reactions provided important information to propose a possible catalytic cycle. Guanidines [(NHR)C(=NR)NPh₂] (R = Cy, **48**, R = ⁱPr, **49**) could be prepared in good-moderate yields (64-65%) by reacting NHPPh₂ with RN=C=NR using **30** as a catalyst.

Publications

1. "Magnesium-Mediated Benzothiazole Activation: A Room Temperature Cascade of C-H Deprotonation, C-C Coupling, Ring-Opening, and Nucleophilic Addition Reactions"; V. L. Blair, W. Clegg, A. R. Kennedy, **Z. Livingstone**, L. Russo and E. Hevia, *Angew.Chem.Int.Ed.*, **2011**, 50, 9857.
2. "Isomeric and chemical consequences of the direct magnesiation of 1,3 benzoazoles using β -diketiminato stabilised magnesium bases"; S. E. Baillie, V. L. Blair T. D. Bradley, W. Clegg, J. Cowan, R. W. Harrington, A. Hernan-Gomez, A. R. Kennedy, **Z. Livingstone**, S. D. Robertson and E. Hevia, (manuscript submitted).

Publications out with this work

1. "New Insights into Addition Reactions of Dialkylzinc Reagents to Trifluoromethyl Ketones: Structural Authentication of a β -hydride Elimination Product Containing a Tetranuclear Zinc Chain"; E. Hevia, A. R. Kennedy, J. Klett, **Z. Livingstone** and M. D. McCall, *Dalton Trans.*, **2010**, 39, 520.

Oral Presentations

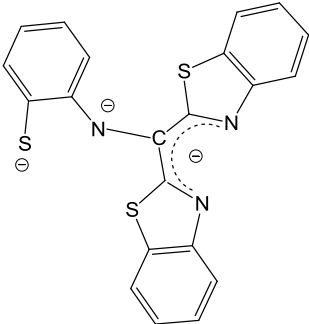
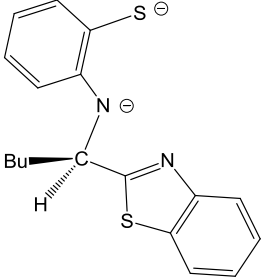
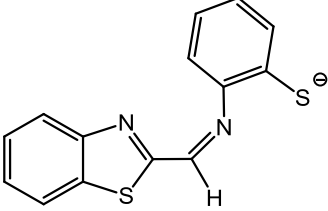
1. "Novel N-heterocyclic activations via a sodium magnesiation with a steric support"; University of Strathclyde, Inorganic Research Day, June 2011
2. "New Sodium Magnesiates with Bulky Bis(amido) Ligands: Structural Tailoring for Deprotonation and Addition Reactions"; Universities of Scotland Inorganic Conference, Durham University, Durham, July 2010.

Poster Presentations

1. "Magnesium Mediated Benzothiazole Activation: a Room Temperature Cascade of C-H Deprotonation, C-C Coupling and Ring-Opening Reactions"; North West Organic Conference, Liverpool University, Liverpool, July 2012.
2. "Magnesium Mediated Benzothiazole Activation: a Room Temperature Cascade of C-H Deprotonation, C-C Coupling and Ring-Opening Reactions"; Universities of Scotland Inorganic Conference, Glasgow University, Glasgow, July 2011. Awarded judge's choice in poster competition.
3. "Magnesium Mediated Benzothiazole Activation: a Room Temperature Cascade of C-H Deprotonation, C-C Coupling and Ring-Opening Reactions"; RSC Dalton Division Meeting on Main Group Chemistry, London Imperial College, London, July 2011. Awarded 1st prize in poster competition.
4. "Magnesium Mediated Benzothiazole Activation: a Room Temperature Cascade of C-H Deprotonation, C-C Coupling and Ring-Opening Reactions"; International American Chemical Society Meeting, Anaheim, March 2011.

Abbreviations

Å	Ångström
Ad	adamantyl
AMMM	alkali-metal mediated metallation
AMMMg	alkali-metal mediated magnesiation
Ar	aryl
Ar*	2,6- ⁱ Pr ₂ -C ₆ H ₃
b	broad
bipy	bipyridine
Boz	benzoxazole
Btz	benzothiazole
Btz*	benzothiazolyl
Bu	butyl
^t Bu	<i>tert</i> -butyl
Bz	benzyl
C ₆ D ₆	deuterated benzene
CIPE	complex-induced proximity effect
COSY	¹ H- ¹ H correlated NMR spectroscopy
Cp	cyclopentadienyl
CSD	crystallographic structure database
Cy	cyclohexyl
DA(H)	diisopropylamine
DFT	density functional theory
Dipp	diisopropylphenyl
DoM	directed <i>ortho</i> metallation
DMAP	4-dimethylaminopyridine
DMP(H)	dimethylpiperidide
dpq	2,3-bis(2-pyridyl)quinoxaline
en	ethylenediamine
EPR	electron paramagnetic resonance
Et	ethyl

fc	ferrocenyl
g	grams
HMDS(H)	hexamethyldisilazane
HSQC	heteronuclear single quantum coherence
ⁱ Pr	isopropyl
IPr	1,3-bis-(2,2-diisopropylphenyl)imidazol-2-ylidene
L	
L*	
L'	
m	multiplet
Me	methyl
MeBIm	methylbenzimidazole
MeBIm*	methylbenzimidazolyl
Mes	mesityl
ml	millilitre
nacnac	[{2,6- ⁱ Pr ₂ C ₆ H ₃)N(Me)C ₂ CH]
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
PEPPSI	pyridine-enhanced precatalyst preparation, stabilization, and initiation

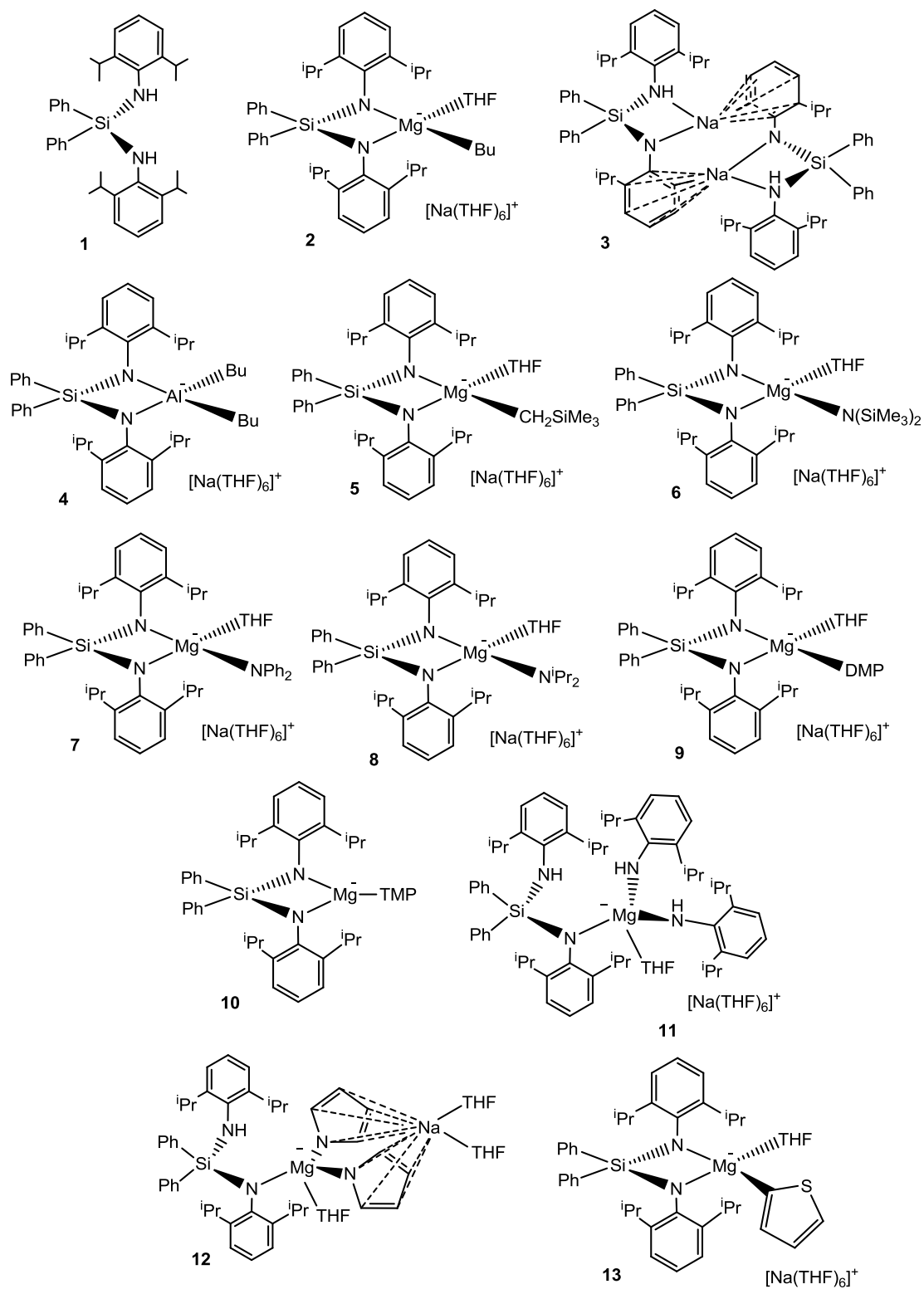
Ph	phenyl
ppm	parts per million
q	quartet
Qox	quinoxaline
s	singlet
TEMPO	(2,2,2,6,6-tetramethyl-1-piperidinyloxy)
d ₈ -THF	deuterated tetrahydrofuran
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMP(H)	tetramethylpiperidine

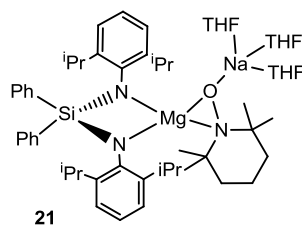
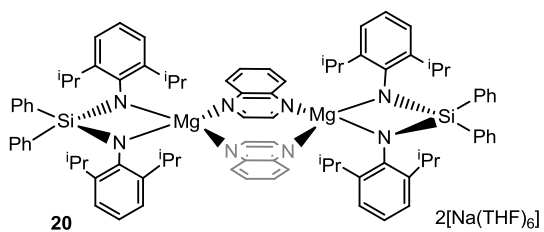
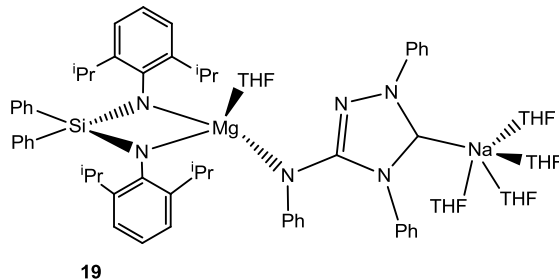
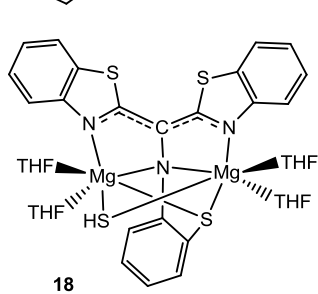
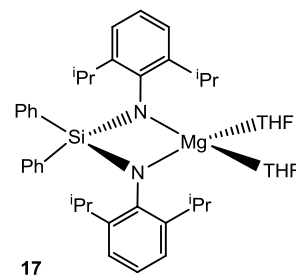
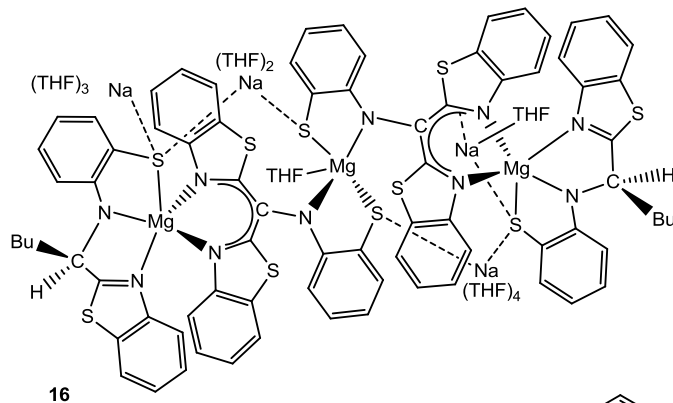
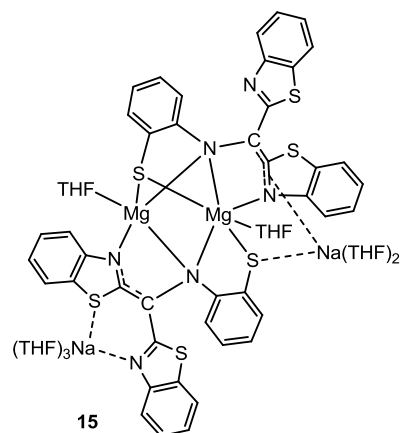
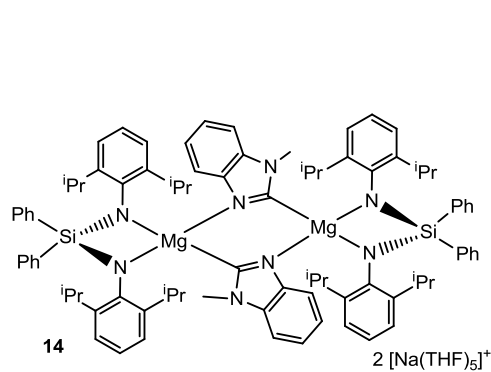
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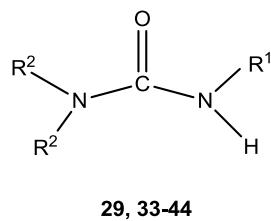
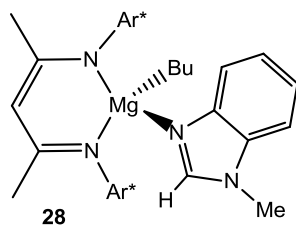
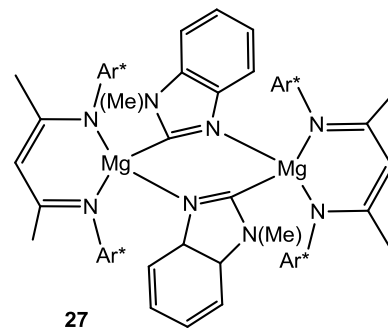
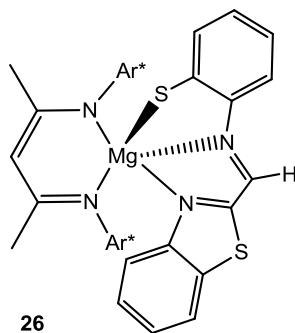
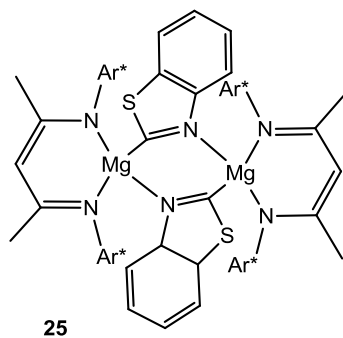
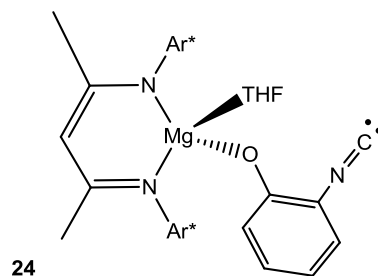
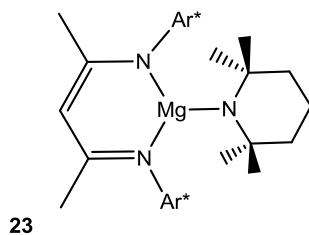
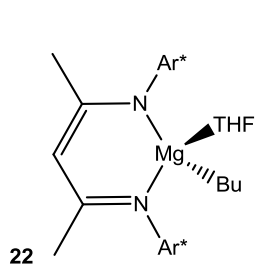
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$[\{\text{Na}(\text{THF})_5\}^+ \{\text{Mg}(\text{NPh}_2)[(\text{NCy})\text{C}(=\text{NCy})(\text{NPh}_2)]_2\}^-]$	50







R ¹	R ²	compound
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^t Bu	Bu	33
^t Bu	Bz	34
^t Bu	Py	35
^t Bu	Ar*	36
Cy	Bu	37
Cy	Bz	38
Cy	Ph	39
Cy	Py	40
Cy	Ar*	41
Et	Ar*	42
Et	Ph	43
Et	Py	44

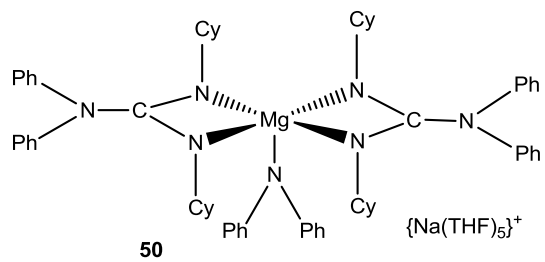
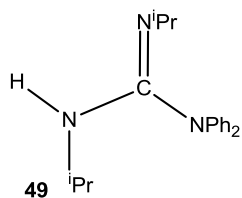
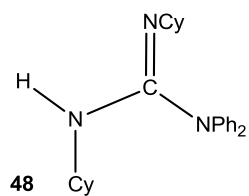
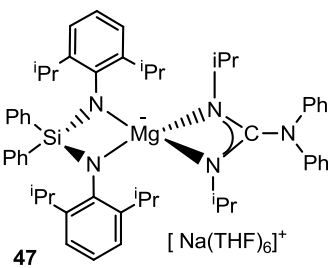
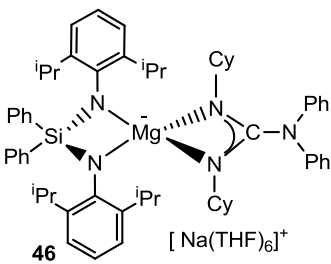
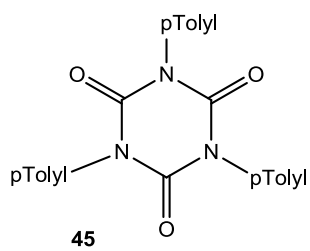
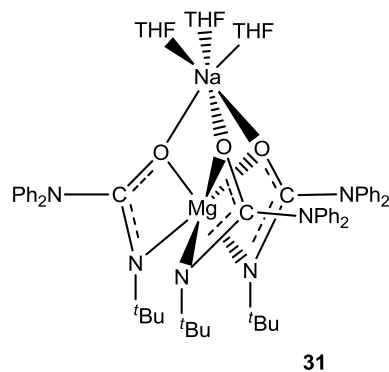
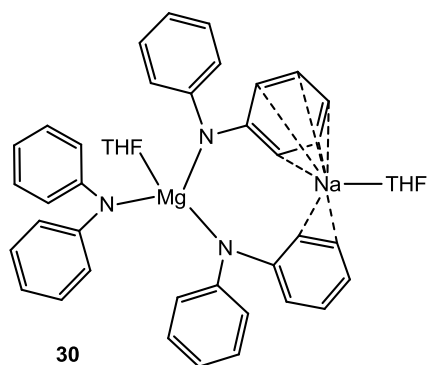


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