View Online / Journal Homepage / Table of Contents for this issue

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

Sodium, magnesium and zinc complexes of mono(phenolate) heteroscorpionate ligands†

A. Daniel Schofield, Mariana Luna Barros, Michael G. Cushion, Andrew D. Schwarz and Philip Mountford*

Received 29th July 2008, Accepted 11th September 2008
First published as an Advance Article on the web 21st October 2008
DOI: 10.1039/b813116c

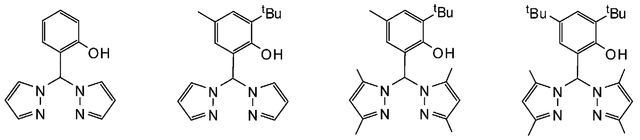
The reaction of bis(3,5-dimethylpyrazolyl)methylphenol $N_2O^{Ar}H$ (**1**) with NaH in THF formed dimeric $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**), which contains a $\kappa^2(N,O)$-bound bidentate N_2O^{Ar} ligand. The reaction of **1** with Mg^nBu_2 gave the four-coordinate monomeric butyl compound $Mg(N_2O^{Ar})^nBu$ (**3**), whereas with ^nBuMgCl, a mixture of products was formed, including the six-coordinate homoleptic species $Mg(N_2O^{Ar})_2$ (**4**). The reaction of $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ with ^nBuMgCl also gave **3**, as did the redistribution reaction of Mg^nBu_2 with **4**. The reaction of **1** with $Mg\{N(SiRMe_2)_2\}_2$ afforded the four-coordinate amide derivatives $Mg(N_2O^{Ar})\{N(SiRMe_2)_2\}$ (R = Me (**6**) or H (**7**)), together with **4**. The reactions of **1** with $ZnMe_2$ or $Zn\{N(SiMe_3)_2\}_2$ gave the monomeric compounds $Zn(N_2O^{Ar})Me$ (**8**) and $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**), respectively. The reaction of **9** with HCl formed $Zn(N_2O^{Ar})Cl$ (**11**), and subsequent addition of $LiN(SiHMe_2)_2$ to **11** led to $Zn(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (**12**). The reaction of **1** with either $Zn\{N(SiMe_3)_2\}_2$ or **9** gave $Zn(N_2O^{Ar})_2$. The compounds **2**, **3**, **4**, **6**, **8**, **9** and **11** were crystallographically characterized. Compound **7** was very active for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) but the process was very poorly controlled as judged by the M_n and polydispersity index of the polymer. Compounds **3**, **8**, **9** and **12** gave poor conversions to poly(ε-CL) over extended periods. $N_2O^{Ar}H$ = 2,4-di-*tert*-butyl-6-(bis(3,5-dimethylpyrazolyl)methyl)phenol.

Introduction

Pyrazole-based ligands, known collectively as poly(pyrazolyl) ligands, are derived from two or more *N*-deprotonated pyrazole rings bound to a main group atom through one of the ring nitrogen atoms. While tris(pyrazolyl) ligands based on aluminium, indium, gallium,[1] silicon[2] and germanium[3] are known, the anionic tris(pyrazolyl)hydroborate ligands[4–7] are the most widespread. First introduced by Trofimenko in 1967,[8] tris(pyrazolyl)hydroborates have become one of the most widely exploited class of ligand in inorganic chemistry,[6] and they have been used to prepare complexes of most metals of the periodic table. Tris(pyrazolyl)methanes are the neutral analogues of the anionic tris(pyrazolyl)hydroborates and are formally derived by replacing the apical $\{BH\}^-$ anionic moiety with the isoelectronic CR group. They (and their anionic methanide analogues[9–12]) have lately received renewed interest, and the synthesis and coordination chemistry of these ligands has been reviewed.[13–15]

The tris(pyrazolyl)hydroborate and tris(pyrazolyl)methane/methanide ligands are examples of *homoscorpionate* ligands in which the three moieties appended to the apical group/atom are the same. A rapidly emerging class of poly(pyrazolyl)alkane-based ligands are the so-called *heteroscorpionates* in which one of the pyrazolyl groups has been replaced by a different (usually) anionic C, O, S or N donor.[16] While much of the early work with heteroscorpionate ligands was primarily concerned with synthetic and structural studies, more recent reports have also focused on catalytic applications in the field of ring-opening or Ziegler–Natta polymerization catalysis, but mostly in the area of N_3 donor ligand sets.[17–23]

We have recently been developing the synthesis and catalytic applications of homo and heteroscorpionate complexes of the main group and early transition metals.[9,10,12,18,24–28] Although our work has so far focused on N_3 donor ligands, we recently became interested in the bis(pyrazolyl)methylphenol (N_2O-type donor) protio-ligands shown in Fig. 1. A number of transition metal phenolate substituted heteroscorpionates have been reported and structurally characterized,[19,29–39] including in one instance for zinc[40] in the context of modelling the binding sites of metalloproteins. Catalytic applications of complexes of these ligands are sparse, with reports for olefin polymerization for group 4[19] and the attempted use of aluminium complexes for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL).[21] No group 1 or group 2 complexes of any bis(pyrazolyl)methylphenolate ligand have been reported. As alluded to above, Milione's very recent report on aluminium complexes derived from $N_2O^{Ar}H$ (**1**, Fig. 1) is the only one for main group metals with this ligand class.[21] This underdevelopment of heteroscorpionate-based phenolate ligands



1 ("$N_2O^{Ar}H$")

Fig. 1 Previously reported bis(pyrazolyl)methylphenol protio-ligands. Compound **1** is the one used in this contribution (abbreviation "$N_2O^{Ar}H$").

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, UK OX1 3TA. E-mail: philip.mountford@chem.ox.ac.uk

† CCDC reference numbers 696837–696843. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b813116c

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

is in contrast to the position for main group, transition metal and f element chelating phenolate ligands in general, which attract widespread interest.[41–49]

In this contribution, we describe the synthesis and structures of a series of new sodium, magnesium and zinc complexes derived from $N_2O^{Ar}H$ (**1**), and an investigation into their ROP capability. Protio-ligand **1** was selected from those shown in Fig. 1 as it offered the highest degree of steric substitution, both proximal and distal to the site of metal complex binding.

Results and discussion

Synthesis of sodium and magnesium complexes of N_2O^{Ar}

Protio-ligand $N_2O^{Ar}H$ (**1**) was prepared in *ca.* 60% yield from bis(3,5-dimethylpyrazolyl)ketone following the general method of Thé and Peterson.[50] Although **1** itself has been mentioned previously,[19,21] its synthesis and characterizing data have not been reported. These are given in the Experimental for completeness. We first describe sodium and magnesium derivatives of **1**. The new compounds and their syntheses are summarized in Scheme 1.

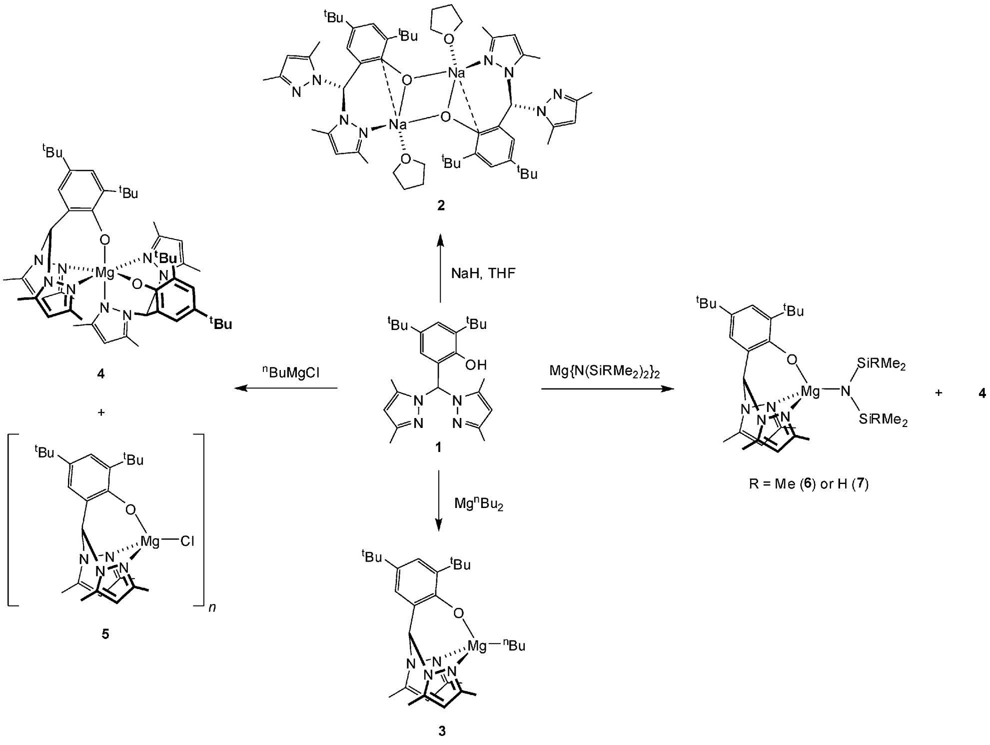
Owing to the favourable Brønsted acidity of the ArOH group, alkali metal phenolates are readily prepared by transmetallation reactions with group 1 alkyls (typically ^{n}BuLi[48]) and/or hydrides (for example, NaH[51]). In addition to being synthetically versatile reagents, alkali metal phenolates show a range of interesting solid-state structures.[48,52–54] While certain sodium bis(pyrazolyl)methylphenolates have been generated *in situ*,[19] they have not been isolated or structurally characterized.

$N_2O^{Ar}H$ (**1**) reacts readily with NaH in THF to form the binuclear complex $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**) in reasonable yield after recrystallization from THF (Scheme 1). The molecular structure is shown in Fig. 2 and selected bond distances and angles are summarized in Table 1. Molecules of **1** lie across crystallographic inversion centres and contain two $Na(\kappa^2\text{-}N_2O^{Ar})(THF)$ units linked through asymmetrically bridging phenoxide moieties (Na(1)–O(1) = 2.3261(13) Å; Na(1)–O(1A) = 2.1785(13) Å). To a first approximation, each Na is four-coordinate, forming close contacts to the aforementioned phenoxide oxygen atoms, the oxygen of a coordinated THF molecule, and a nitrogen atom of one of the pyrazolyl rings (N(1)). The other pyrazolyl ring (containing N(3), N(4)) is not coordinated. There is a further contact to the *ipso* carbon of the phenyl group (Na(1)···C(13) = 2.7946(16) Å), as is typically the case in alkali metal complexes of phenoxide ligands,[48,52–54] bringing the formal coordination number of each Na to five. The central $Na_2(\mu\text{-}O)_2$ moiety in **1** is close to an ideal, planar square arrangement (O(1)–Na(1)–O(1A) = 90.29(5)°; Na(1)–O(1)–Na(1A) = 89.71(5)°).

From the point of view of alkali metal mono(phenoxide) structural chemistry, several $Na_2(OAr)_2(L)_x$ systems have related solid-state features.[55–58] With respect to the coordination chemistry of N_2O^{Ar} complexes (Fig. 1), the aluminium compound

Table 1 Selected distances (Å) and angles (°) for $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**). Atoms carrying the suffix 'A' are related to their counterparts by the operator $-x, 1 - y, 1 - z$

Na(1)–O(1)	2.3261(13)	Na(1)–N(1)	2.4662(15)
Na(1)–O(1A)	2.1785(13)	Na(1)···C(13)	2.7946(16)
Na(1)–O(2)	2.2973(14)		
O(1)–Na(1)–O(2)	126.33(5)	O(1A)–Na(1)–O(1)	90.29(5)
O(1A)–Na(1)–O(2)	125.65(5)	O(1A)–Na(1)–N(1)	124.16(5)
O(1)–Na(1)–N(1)	93.94(5)	O(2)–Na(1)–N(1)	71.15(4)
Na(1)–O(1)–C(13)	96.26(9)	Na(1A)–O(1)–C(13)	173.54(11)
Na(1)–O(1)–Na(1A)	89.71(5)		



Scheme 1 Reactions of $N_2O^{Ar}H$ (**1**) with sodium and magnesium reagents.

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

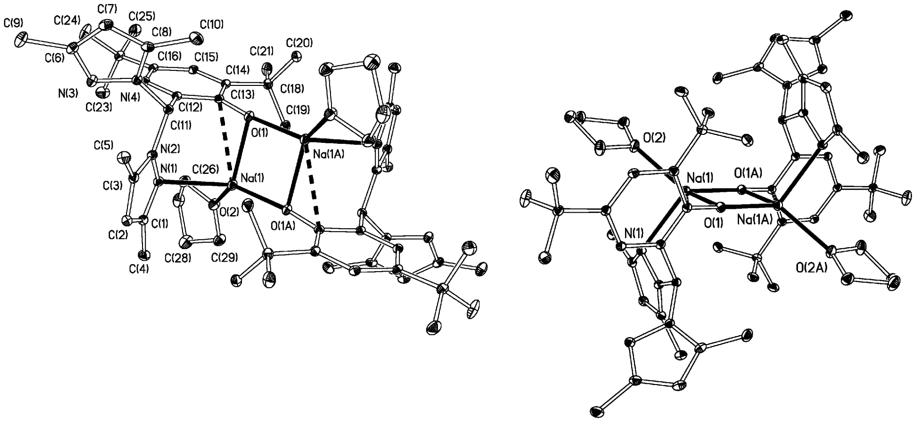


Fig. 2 Displacement ellipsoid plots (25% probability) of [Na(κ^2-N_2O^{Ar})(THF)]$_2$ (**2**). H atoms omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $-x$, $1-y$, $1-z$. Left: approximately perpendicular to the $Na_2(\mu\text{-}O)_2$ plane. Right: approximately parallel to the $Na_2(\mu\text{-}O)_2$ plane.

Al(κ^2-N_2O^{Ar})Me_2 is the only previously reported example of a bidentate coordination mode for this ligand.[21]

At room temperature, the ^{1}H and ^{13}C NMR spectra for **1** show two equivalent Me_2pz ring environments on the NMR timescale, which is inconsistent with the solid-state structure. Cooling a CD_2Cl_2 solution to 183 K led to partial decoalescence of the Me_2pz ring signals (four broad overlapping methyl and two broad pyrazolyl ring methine resonances) consistent with the solid state structure being maintained in solution, at least at low temperatures.

Milione *et al.* reported that treatment of Al(κ^2-N_2O^{Ar})R_2 (R = Me or Et) with B(C_6F_5) generated the cationic complexes [Al(N_2O^{Ar})R]$^+$, which contain a tridentate bis(pyrazolyl)-methylphenolate ligand according to the NMR data (these were not structurally characterized).[21] Scheme 1 summarizes our results regarding the synthesis of neutral magnesium complexes of the type Mg(N_2O^{Ar})X, isoelectronic (for X = alkyl or amide) with the cationic aluminium systems. These are the first magnesium complexes of any N_2O-donor heteroscorpionate ligand.

The reaction of N_2O^{Ar}H (**1**) with Mg^{n}Bu$_2$ gave the "half-sandwich" alkyl derivative Mg(N_2O^{Ar})^{n}Bu (**3**) in good yield. The X-ray structure has also been determined (Fig. 3 and Table 2) and the solution NMR and other data are consistent with this. The solid state structure of **3** and all the new magnesium and zinc complexes of N_2O^{Ar} are compared and discussed below.

Table 2 Selected distances (Å) and angles (°) for Mg(N_2O^{Ar})^{n}Bu (**3**) and Zn(N_2O^{Ar})Me (**8**)

Parameter	**3** (M = Mg)	**8** (M = Zn)
M(1)–O(1)	1.9058(19)	1.9416(14)
M(1)–N(1)	2.122(2)	2.0954(19)
M(1)–N(3)	2.142(2)	2.0935(18)
M(1)–C(26)	2.124(3)	1.974(2)
O(1)–M(1)–N(1)	96.55(8)	98.15(6)
O(1)–M(1)–N(3)	91.88(8)	92.29(6)
O(1)–M(1)–C(26)	126.27(11)	128.78(9)
N(1)–M(1)–N(3)	86.82(8)	85.89(7)
N(1)–M(1)–C(26)	122.08(11)	119.28(10)
N(3)–M(1)–C(26)	123.14(11)	121.95(9)
M(1)–O(1)–C(13)	137.75(16)	132.40(12)

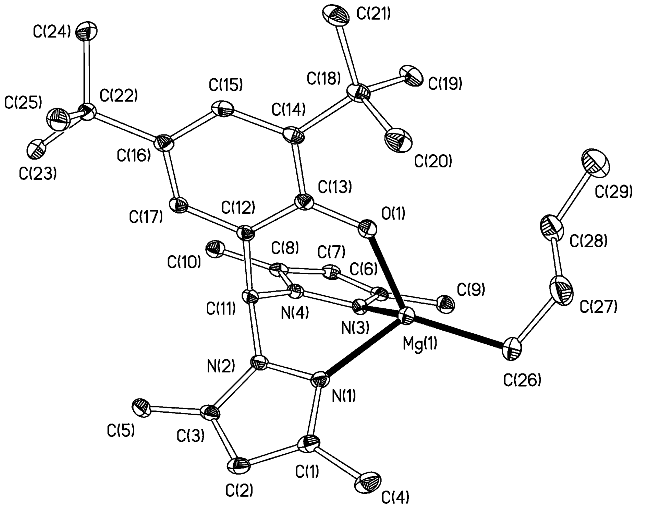


Fig. 3 Displacement ellipsoid plot (20% probability) of Mg(N_2O^{Ar})^{n}Bu (**3**). H atoms omitted for clarity.

This reaction also produces small quantities of the homoleptic ("sandwich") complex Mg(O_2N^{Ar})$_2$ (**4**, discussed below) even when 3 equiv. Mg^{n}Bu$_2$ are used. It is unlikely that **4** arises from a ligand redistribution of **3** (as has been noted with less sterically demanding tris(pyrazolyl)hydroborate magnesium alkyls[59]) since heating a pure sample of **3** in C_6D_6 at 70 °C for 12 h gave no change in the ^{1}H NMR spectrum. In contrast, heating a mixture of Mg^{n}Bu$_2$ and **4** in C_6D_6 formed the half-sandwich species **3**, establishing that this is the thermodynamically favoured product. Therefore, the formation of **4** probably arises from the reaction of first-formed **3** with protio-ligand **1** at a rate that is apparently competitive with that between **1** and Mg^{n}Bu$_2$. This problem was found to be particularly acute using the diamide reagents Mg{N(SiRMe$_2$)$_2$}$_2$ (R = Me or H, see below). Consistent with this observation, the reaction of **3** with **1** on the NMR tube scale quantitatively formed **4**.

A potential alternative synthesis of **3** was found on the NMR tube scale by reaction of [Na(κ^2-N_2O^{Ar})(THF)]$_2$ (**2**) with ^{n}BuMgCl in C_6D_6. Although quantitative formation of **3** appeared to occur as judged by ^{1}H NMR, this reaction could not be scaled up cleanly.

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

Table 3 Selected distances (Å) and angles (°) for $Mg(N_2O^{Ar})_2$ (**4**)

Mg(1)–O(1)	1.979(3)	Mg(1)–O(2)	1.964(3)
Mg(1)–N(1)	2.206(4)	Mg(1)–N(5)	2.187(4)
Mg(1)–N(3)	2.315(4)	Mg(1)–N(7)	2.312(4)
O(1)–Mg(1)–O(2)	98.49(14)	O(1)–Mg(1)–N(1)	85.93(14)
O(2)–Mg(1)–N(1)	101.44(14)	O(1)–Mg(1)–N(3)	91.81(14)
O(2)–Mg(1)–N(3)	168.96(15)	N(1)–Mg(1)–N(3)	83.15(14)
O(1)–Mg(1)–N(5)	100.94(14)	O(2)–Mg(1)–N(5)	87.98(14)
N(1)–Mg(1)–N(5)	167.49(15)	N(3)–Mg(1)–N(5)	86.17(14)
O(1)–Mg(1)–N(7)	172.84(14)	O(2)–Mg(1)–N(7)	87.68(14)
N(1)–Mg(1)–N(7)	89.30(14)	N(3)–Mg(1)–N(7)	82.31(14)
N(5)–Mg(1)–N(7)	82.81(14)	Mg(1)–O(1)–C(13)	139.7(3)
Mg(1)–O(2)–C(38)	144.7(3)		

Difficulties in using this method for the formation of half-sandwich magnesium alkyl complexes of tris(pyrazolyl)hydroborate ligands have been noted previously by Parkin,[60] whereas Otero has reported success using certain N_3 donor heteroscorpionates.[20]

The reaction of the protio-ligand **1** with ^{n}BuMgCl was expected to provide the corresponding chloride species $[Mg(N_2O^{Ar})Cl]_n$ (**5**) by analogy with the synthesis of **3**. However, this reaction gave both the six-coordinate sandwich complex $Mg(O_2N^{Ar})_2$ (**4**) and an insoluble material (Scheme 1). Compound **4** (obtained in 40% yield based on **1**) has been crystallographically characterized (Fig. 4 and Table 3) and the molecular structure is discussed below. The ^{1}H and ^{13}C NMR spectra of **4** show that this structure is maintained in solution since they feature two Me_2pz ring environments for the groups *cis* and *trans* to the phenolate donors.

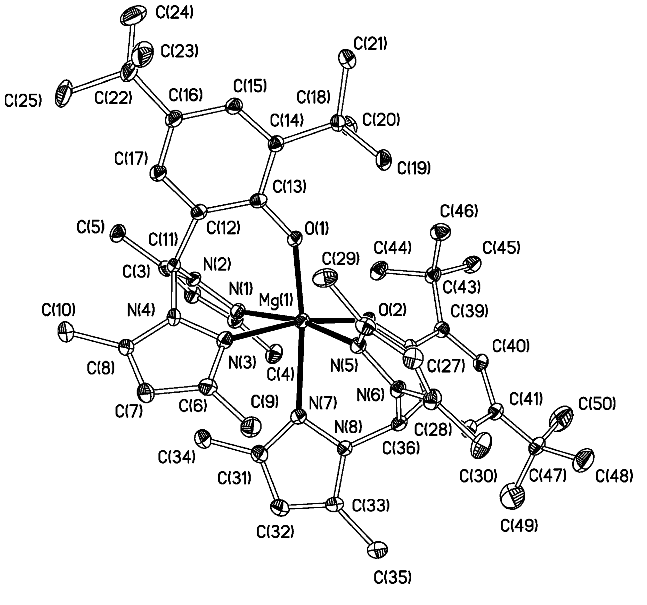


Fig. 4 Displacement ellipsoid plot (20% probability) of $Mg(N_2O^{Ar})_2$ (**4**). H atoms and diethyl ether of crystallization omitted for clarity.

The insoluble precipitate formed alongside **4** is believed to contain a mixture of $MgCl_2$ and $[Mg(N_2O^{Ar})Cl]_n$ (**5**, "*n*" is undetermined), or even polymetallic aggregates of the two components as has been observed previously for transition metal bis(pyrazolyl)methylphenolate complexes.[29–31,33–35,37–39] The EI mass spectrum obtained from this solid gave peak envelopes with the expected isotopic distributions for "$[Mg(N_2O^{Ar})Cl]^+$" (70% of the base peak's intensity (namely $[M - Me]^+$)). The solid state IR spectrum was comparable to that of the crystallographically characterized zinc analogue $Zn(N_2O^{Ar})Cl$ (**11**, see below). Attempts to isolate pure **5** from the $MgCl_2$ led to decomposition.

The ready formation of insoluble (probably oligomeric) scorpionate-type complexes $[Mg(L)X]_n$ (X = halide) has been noted previously in the reactions of the corresponding protio-ligands HL with Grignard reagents.[12] Such reactions have also been shown to give the corresponding homoleptic sandwich derivatives $Mg(L)_2$ *via* Schlenk-type equilibria.[12,61] In principle, the sandwich complex $Mg(O_2N^{Ar})_2$ (**4**) could arise *via* a redistribution reaction of first-formed **5**, and/or by reaction of Mg^nBu_2 (formed from ^{n}BuMgCl *via* the Schlenk equilibrium) with $N_2O^{Ar}H$, which would be present in comparable excess. In a control experiment, the reaction of **1** (2 equiv.) with Mg^nBu_2 afforded **4**, quantitatively.

The reaction of $N_2O^{Ar}H$ (**1**) with the diamide complexes $Mg\{N(SiRMe_2)_2\}_2$ (R = Me or H) gave modest isolated yields of the half-sandwich derivatives $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**6**, 11%) and $Mg(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (**7**, 21%), respectively, as white solids. The NMR spectra of **6** and **7** are comparable to those of the *n*-butyl homologue $Mg(N_2O^{Ar})^nBu$ (**3**). The X-ray structure of **6** has been determined (Fig. 5 and Table 4). This is discussed below and confirms that shown in Scheme 1. The low yields of **6** and **7** can be attributed to the facile formation of the sandwich complex **4** in these reactions. A *ca.* 50% yield of **4** is obtained in the reaction of **1** with $Mg\{N(SiMe_3)_2\}_2$, for example. Attempts

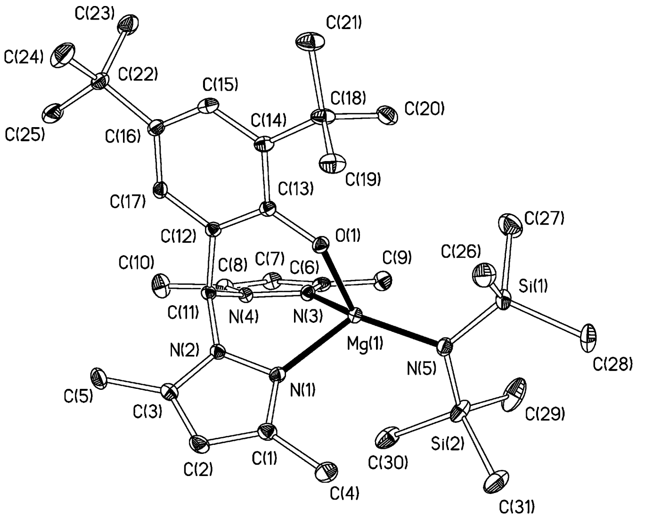


Fig. 5 Displacement ellipsoid plot (20% probability) of $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**6**). H atoms and toluene of crystallization omitted for clarity.

Table 4 Selected distances (Å) and angles (°) for $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**6**) and $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**)

Parameter	**6** (M = Mg)	**9** (M = Zn)
M(1)–O(1)	1.903(2)	1.936(2)
M(1)–N(1)	2.100(3)	2.061(2)
M(1)–N(3)	2.124(3)	2.080(2)
M(1)–N(5)	1.992(3)	1.923(3)
O(1)–M(1)–N(1)	91.13(10)	91.27(9)
O(1)–M(1)–N(3)	95.39(10)	96.78(9)
O(1)–M(1)–N(5)	127.76(11)	126.18(10)
N(1)–M(1)–N(3)	89.26(10)	91.55(9)
N(1)–M(1)–N(5)	122.10(11)	121.61(10)
N(3)–M(1)–N(5)	121.33(11)	120.80(11)
M(1)–O(1)–C(13)	136.54(19)	131.78(17)

This journal is © The Royal Society of Chemistry 2009

to form a calcium analogue of **6** by reaction of **1** (1 equiv.) with $Ca\{N(SiMe_3)_2\}_2(THF)_2$[62] gave a highly insoluble precipitate. When followed by ^1H NMR *ca.* half of the calcium compound remained unreacted, indicating formation of a homoleptic compound "$Ca(N_2O^{Ar})_2$". This reaction was not pursued.

Metal alkoxide and aryloxide complexes are known to be efficient initiators for the ROP of cyclic esters.[49,63–66] We therefore attempted to prepare complexes of the type $Mg(N_2O^{Ar})(OR)$ (R = ^iPr, ^tBu or 2,6-$C_6H_3Me_2$) by protonolysis reactions between the corresponding ROH and $Mg(N_2O^{Ar})X$ (X = ^nBu (**3**), $N(SiMe_3)_2$ (**6**) or $N(SiHMe_2)_2$ (**7**)). Unfortunately, in all cases, unknown mixtures of products were obtained although the ^1H NMR spectra showed successful elimination of the corresponding "HX".

Synthesis of zinc complexes of N_2O^{Ar}

Whereas no N_2O donor heteroscorpionates of Mg had been reported prior to our studies, certain zinc complexes of a homologue of $N_2O^{Ar}H$ (**1**) were described by Carrano in the context of modelling the binding sites of zinc metalloproteins.[40] However, no ROP studies were carried out, nor were amide complexes described. We therefore incorporated a study of zinc analogues of the magnesium complexes $Mg(N_2O^{Ar})X$ (**3–7**) into our study of this chemistry. The new compounds and their syntheses are summarized in Scheme 2 and (where available) their crystal structures are compared with those of the magnesium homologues in a later section.

Heating a solution of $N_2O^{Ar}H$ (**1**) and an excess of $ZnMe_2$ at 60 °C for 14 h gave the monomethyl complex $Zn(N_2O^{Ar})Me$ (**8**) in modest yield. The lower yield and harsher conditions required in this case, compared with those for the reaction with Mg^nBu_2, reflect the higher electronegativity of zinc compared to the group 2 metal. For the same reason, no evidence for formation of the homoleptic sandwich complex $Zn(N_2O^{Ar})_2$ (**10**, see below) was found in this reaction. The NMR spectra for **8** were as expected and consistent with the solid state structure (Fig. 6 and Table 2).

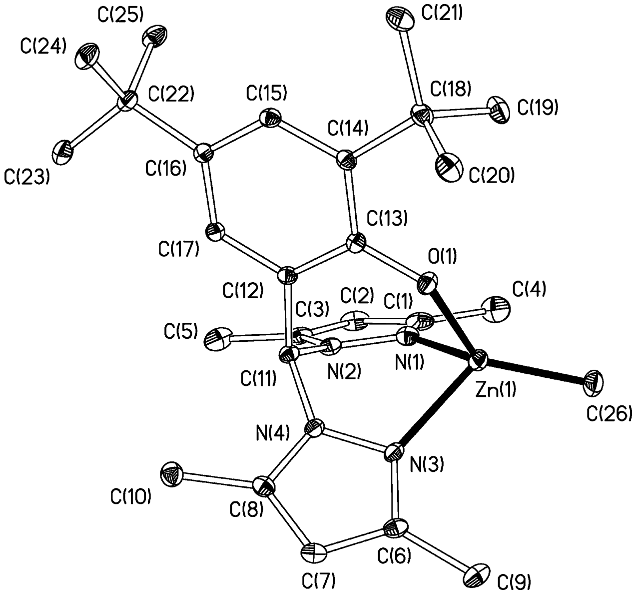
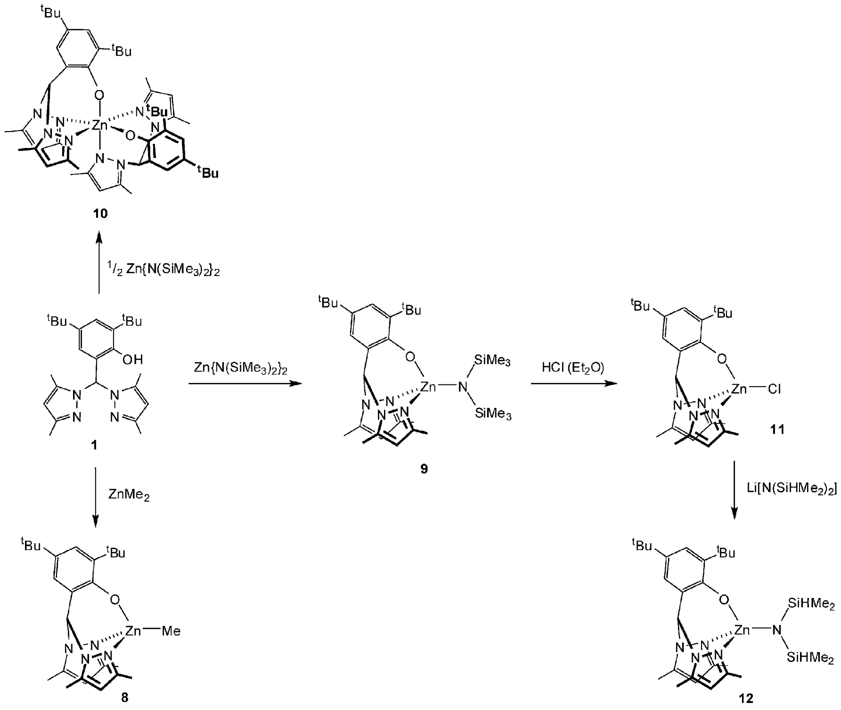


Fig. 6 Displacement ellipsoid plot (25% probability) of $Zn(N_2O^{Ar})Me$ (**8**). H atoms omitted for clarity.

$N_2O^{Ar}H$ (**1**) reacted more readily with $Zn\{N(SiMe_3)_2\}_2$ (3 h, room temperature) to give $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**) as a white solid in 69% yield (Scheme 2). The good yield of **9** contrasts sharply with that for the Mg homologue **6** (11%). The difference is attributed to the negligible extent of formation of $Zn(N_2O^{Ar})_2$ (**10**) and the low solubility of the latter, which allows for easy



Scheme 2 Synthesis of zinc derivatives containing the N_2O^{Ar} ligand.

Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C
Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

separation. The ^{1}H and ^{13}C NMR spectra of **9** are comparable to those of **6** and are consistent with the solid state structure (Fig. 7) discussed below. Although concomitant formation of $Zn(N_2O^{Ar})_2$ (**10**) is not a problem in the synthesis of **9**, the homoleptic compound can be obtained from either $Zn\{N(SiMe_3)_2\}_2$ and 2 equiv. of **1**, or from pre-formed half-sandwich **9** and 1 equiv. of **1** (NMR tube scale only). In contrast to its magnesium homologue, compound **10** is highly insoluble in non-reactive solvents (benzene, THF, pyridine, CH_2Cl_2) and was characterized by elemental analysis and IR spectroscopy.

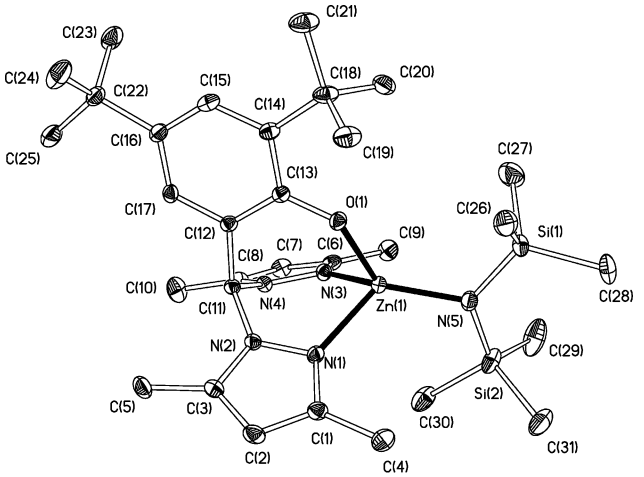


Fig. 7 Displacement ellipsoid plot (20% probability) of $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**). H atoms and toluene of crystallization omitted for clarity.

Surprisingly, the reactions of $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**) with $ZnCl_2$ did not give access to $Zn(N_2O^{Ar})Cl$ (**11**). This compound was therefore prepared from the 1 : 1 reaction of $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**) with HCl (Et_2O solution) in benzene (69% yield). In contrast to $[Mg(N_2O^{Ar})Cl]_n$ (**5**), **11** has acceptable solubility in halogenated solvents and appears to be indefinitely stable in solution (no redistribution reaction to form homoleptic **10**, for example). The molecular structure of **11** has been determined (Fig. 8 and Table 5) and is discussed below. Compound **11** also serves as an entry point to the less bulky amide derivative $Zn(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (**12**) upon reaction with $LiN(SiHMe_2)_2$ in benzene. The NMR spectra of **12** are comparable to those of the magnesium analogue **7**. Compound **12** can also be formed by reaction of $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**) with $HN(SiHMe_2)_2$ at 70 °C for 3 d (NMR tube scale in C_6D_6). No reaction was observed between $Zn(N_2O^{Ar})Me$ (**8**) and $HN(SiHMe_2)_2$ under these conditions.

As for the magnesium systems, we attempted to prepare zinc alkoxide or aryloxide complexes of the type $Zn(N_2O^{Ar})(OR)$ (R = alkyl or aryl, see above). Limited reactivity was found between the various ROH and $Zn(N_2O^{Ar})Me$ (**8**) at room temperature, and the use of more forcing conditions led to decomposition. The reactions of $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**) with ROH were more encouraging on the NMR tube scale (*cf.* its reactions with $N_2O^{Ar}H$ (**1**), HCl and $HN(SiHMe_2)_2$ mentioned above). Regrettably, no well-defined complex could be obtained from these reactions.

Table 5 Selected distances (Å) and angles (°) for $Zn(N_2O^{Ar})Cl$ (**11**)

Zn(1)–Cl(1)	2.1810(5)	Zn(1)–N(1)	2.0494(17)
Zn(1)–O(1)	1.9105(14)	Zn(1)–N(3)	2.0505(16)
O(1)–Zn(1)–N(1)	93.81(6)	N(1)–Zn(1)–Cl(1)	122.04(5)
O(1)–Zn(1)–N(3)	105.55(6)	N(3)–Zn(1)–Cl(1)	116.02(5)
O(1)–Zn(1)–Cl(1)	123.28(4)	Zn(1)–O(1)–C(13)	127.63(12)
N(1)–Zn(1)–N(3)	89.48(6)		

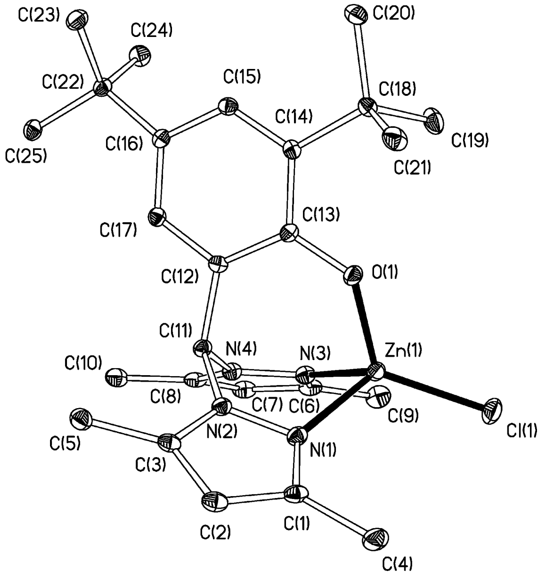


Fig. 8 Displacement ellipsoid plot (25% probability) of $Zn(N_2O^{Ar})Cl$ (**11**). H atoms omitted for clarity.

Structural studies of the magnesium and zinc complexes

As mentioned, we have structurally characterized a number of the magnesium and zinc N_2O^{Ar} complexes. We discuss them systematically in turn here. Table 2 compares key distances and angles for $Mg(N_2O^{Ar})^n$Bu (**3**, Fig. 3) and $Zn(N_2O^{Ar})Me$ (**8**, Fig. 6). Both complexes feature a severely distorted, tetrahedral metal centre with C–M–O and C–M–N angles in the range *ca.* 119–129° and N–M–N and N–M–O angles in the range *ca.* 86–98° owing to the constraining $\kappa^3\text{-}N_2O^{Ar}$ ligand. In general, the M–C, M–N and M–O distances at each metal are within the ranges previously reported for four-coordinate Mg and Zn.[53,54] More specifically the M–C values are also comparable to other "half-sandwich" scorpionate and heteroscorpionate complexes reported previously.[20,22,40,60,67,68]

Significant differences are found on comparing the trends in metal–ligand distances for the different donor types. The four-coordinate effective ionic radii of Mg and Zn (0.71 and 0.74 Å, respectively[69]) are almost the same, with that of Mg being slightly smaller. Although the valence AOs of Zn are the 4s and 4p (with the 3d being semi core-like), the large increase in Z_{eff} arising from crossing the 3d series reduces the radius to nearly that of Mg (3s and 3p valence AOs).[70] The Mg–O distance in **3** is 0.036(2) Å shorter than Zn–O in **8**, whereas the Mg–C distance is 0.150(4) Å longer. The Mg–N distances are also systematically longer for Mg. These differences are attributable to the different bonding characteristics of Mg and Zn. The former is more ionic in nature and so the Mg–O bond will contain a higher ionic character, apparently leading to a shorter bond length compared to Zn. Zinc, with its higher Z_{eff}, is more polarizing and covalent. Therefore, the more polarizable alkyl (and to some extent pyrazolyl N)

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

donors find a more favourable interaction with Zn than with Mg, consistent with recent DFT-computed bond dissociation energies in $\mathrm{N_3}$ donor Zn–Me and Mg–Me scorpionate complexes.[12]

Table 4 compares key distances and angles for the isomorphic pair $\mathrm{M(N_2O^{Ar})\{N(SiMe_3)_2\}}$ (M = Mg (**6**, Fig. 5) or Zn (**9**, Fig. 7)). Again the M–N and M–O distances are within the usual ranges and the overall geometries are comparable to those of **3** and **8**. The Mg–O distance is 0.033(3) shorter than Zn–O, whereas the Mg–N bonds to the pyrazolyl and amide nitrogen atoms are all longer than their Zn analogues. The $\mathrm{M–N_{pz}}$ and M–O distances in **6** and **9** are systematically shorter than those in the alkyl homologues **3** and **8**, despite the larger steric impact of the $\mathrm{N(SiMe_3)_2}$ ligand compared to Me or ^{n}Bu. This is attributed to the better σ-donor ability of the alkyl ligands. The $\mathrm{SiMe_3}$ substituents in **6** and **9** are orientated approximately perpendicular to the plane defined by N(1), N(3) and N(5). This avoids unfavourable interactions between the pyrazolyl methyl groups of C(4) and C(9) and the amide $\mathrm{SiMe_3}$ substituents.

Tables 3 and 5 summarize the bond distances and angles for $\mathrm{Mg(N_2O^{Ar})_2}$ (**4**, Fig. 4) and $\mathrm{Zn(N_2O^{Ar})Cl}$ (**11**, Fig. 6). The Zn complex has an analogous geometry to those of the alkyl and amide homologues. The $\mathrm{Zn–N_{pz}}$ and Zn–O distances in **11** are shorter than those of either $\mathrm{Zn(N_2O^{Ar})Me}$ (**8**) or $\mathrm{Zn(N_2O^{Ar})\{N(SiMe_3)_2\}}$ (**9**), which is consistent with the poorer donor ability and higher electronegativity of Cl.

$\mathrm{Mg(N_2O^{Ar})_2}$ (**4**) contains a six-coordinate Mg atom in an approximately octahedral geometry and overall molecular C_2 symmetry. The phenolate donors occupy mutually *cis* coordination sites with the *ortho*-^{t}Bu substituents orientated above and below the equatorial plane defined by Mg(1), N(3), N(7), O(1) and O(2). A number of homoleptic transition metal complexes of related $\mathrm{N_2O}$ donor heteroscorpionate ligands have been structurally characterized.[29,30,33] In contrast to **4**, these have mutually *trans* phenolate groups with approximately linear O–M–O linkages and molecular C_{2h} symmetry. The Mg–O and Mg–N distances in **4** are significantly longer than in the four-coordinate complexes **3** and **6**, as a consequence of its higher coordination number. The Mg–N distances *trans* to the Mg–O bonds are significantly longer than the *cis* ones (Δ(Mg–N) = 0.109(6), 0.125(6) Å) as a consequence of the greater *trans* influence of the anionic oxygen donors. However, this labilizing effect is not sufficient to force the $\kappa^2(N,O)$ coordination found in $\mathrm{[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2}$ (**2**) or Milione's $\mathrm{Al(\kappa^2\text{-}N_2O^{Ar})R_2}$ (R = Me or Et).[21]

ROP of ε-caprolactone using the magnesium and zinc complexes

While aliphatic polyesters were first made by step polymerization (condensation), ring-opening polymerization (ROP) is the commercial method of choice starting from cyclic esters as monomers. Technologically, two of the most important esters are lactide and ε-caprolactone (ε-CL).[71–73] A number of group 2 and 12 complexes are known to be effective initiators for the ROP of these cyclic esters.[63–66] Among the systems evaluated are $\mathrm{N_3}$ donor homoscorpionate[68,74,75] and (more recently) heteroscorpionate[20,22] Mg, Ca and Zn derivatives. Some of these show good activities and control of the ROP. $\mathrm{N_2O}$-donor heteroscorpionates of groups 2 and 12 have not been studied and this represents a deficiency in this area. We therefore carried out an assessment of the ROP capability of the new alkyl and amide complexes using ε-CL as a test monomer (ε-CL being more readily ring-opened *via* a coordination–insertion mechanism than lactides for example).

In a typical experiment, using either THF or toluene solvent at room temperature, a solution of the chosen initiator was treated with 100 equiv. of ε-CL and the ROP was monitored by taking aliquots, which were evaluated by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

Initial studies using the magnesium amide $\mathrm{Mg(N_2O^{Ar})\{N(SiHMe_2)_2\}}$ (**7**) appeared encouraging. Addition of 100 equiv. of ε-CL to a toluene solution of **7** gave complete conversion to poly(ε-CL) immediately as judged by ^{1}H NMR spectroscopy. However, GPC analysis of the poly(ε-CL) formed indicated rather poor control of the polymerization process: the observed M_n value of 30 870 g mol^{-1} was considerably larger than that expected for 100% conversion (11 410 g mol^{-1}) and the polydispersity index (PDI, M_w/M_n) was 2.76. These data are consistent with slow initiation of the polymerization in comparison with chain growth. Disappointing results were also found in THF. In this case addition of ε-CL to a THF solution of **7** immediately gave a highly viscous solution, which was impossible to stir. However, ^{1}H NMR analysis showed only 22% conversion. GPC analysis yielded experimental M_n and PDI values of 36 390 and 2.64, respectively (the expected M_n is only 2510 in this case).

The zinc amides $\mathrm{Zn(N_2O^{Ar})\{N(SiRMe_2)_2\}}$ (R = Me (**9**) or H (**12**)) were also assessed for the ROP of ε-CL. Both were very poor initiators with sluggish polymerization occurring over 25 h to give conversions of 21 and 10%, respectively. Over this time, the solutions became progressively cloudy, suggesting some sort of catalyst degradation. Although the agreement between found and expected M_n values for the poly(ε-CL) were better than for **7** (found: 2640, 1850; expected: 2400, 1140 g mol^{-1}) the PDIs remained much higher than expected (2.30 and 2.60, respectively). Finally the alkyl complexes $\mathrm{Mg(N_2O^{Ar})}{}^n\mathrm{Bu}$ (**3**) and $\mathrm{Zn(N_2O^{Ar})Me}$ (**8**) were evaluated. At best these showed less than 10% conversion of ε-CL over time and again the solutions became cloudy. The formation of these cloudy mixtures and very poor conversions indicate that, unlike the corresponding $\mathrm{N_3}$ donor scorpionate and heteroscorpionates, the $\mathrm{N_2O^{Ar}}$ species undergo as-yet undetermined degradation processes. Potentially, these involve attack/insertion of the ε-CL at the M–O bond to the $\mathrm{N_2O^{Ar}}$ ligand (despite the bulky *tert*-butyl substituent) as proposed by Milione *et al.* for their cationic aluminium systems. Further detailed experimental work would be required to uncover the exact reasons for the poor activity of the compounds **3**, **8**, **9** and **12**.

Conclusions

We have reported the synthesis and solid state structures of a range of new complexes of the heteroscorpionate ligand $\mathrm{N_2O^{Ar}}$. Well-defined Na and Mg derivatives have been reported for the first time and new zinc complexes of $\mathrm{N_2O}$ donor heteroscorpionate aryloxide ligands have been prepared. The series of crystal structures for the magnesium and zinc alkyl, amide, chloride and sandwich compounds have allowed a systematic structural evaluation of these systems as a function of the "X" ligand in compounds of the type $\mathrm{M(N_2O^{Ar})X}$. Despite the use of the bulky *ortho tert*-butyl group in $\mathrm{N_2O^{Ar}}$, the sandwich compound formation is a significant complication for the more ionic group 2 metals. ROP of ε-caprolactone by half-sandwich complexes $\mathrm{M(N_2O^{Ar})X}$ only

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

proceeded to completion in the case of $\mathrm{Mg(N_2O^{Ar})\{N(SiHMe_3)_2\}}$ (**7**), but poor control of the polymerization process was inferred from the measured poly(ε-CL) molecular weights. The magnesium and zinc alkyls, as well as the zinc amides, provided only very poor ε-CL conversions. Concomitant initiator degradation/side-reactions may be the origin of the poor behaviour. Although metal alkoxide derivatives $\mathrm{M(N_2O^{Ar})OR}$ (R = alkyl or aryl) would likely make for better initiators, these were not accessible experimentally.

Experimental

General methods and instrumentation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent.[76] Deuterated solvents were refluxed over the appropriate drying agent, distilled and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Assignments were confirmed as necessary with the use of DEPT-135, DEPT-90, and two dimensional ^{1}H–^{1}H and ^{13}C–^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls between KBr plates, and the data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

Poly(ε-CL) molecular weights (M_n, M_w were determined using gel permeation chromatography (GCP). GPC analyses were carried out using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min^{-1}. Linear polystyrenes were used as primary calibration standards, and Mark–Houwink corrections for poly(ε-CL) in THF[77] were applied for the experimental samples.

Starting materials

Bis(3,5-dimethylpyrazolyl)ketone, $\mathrm{Mg\{N(SiRMe_2)_2\}_2}$ (R = Me or H), $\mathrm{Zn\{N(SiMe_3)_2\}_2}$ and $\mathrm{LiN(SiHMe_2)}$ were prepared according to the literature methods.[50,78–81] ε-Caprolactone was dried over freshly ground $\mathrm{CaH_2}$ and distilled before use. Other reagents were purchased and used without further purification.

$\mathrm{N_2O^{Ar}H}$ (1). Although $\mathrm{N_2O^{Ar}H}$ has been mentioned in the literature,[19] experimental details and characterization data have not been reported. We therefore give them here for completeness. A mixture of bis(3,5-dimethylpyrazolyl)ketone (5.88 g, 27.0 mmol), 3,5-di-*tert*-butlysalicylaldehyde (6.32 g, 27.0 mmol) and $\mathrm{CoCl_2{\cdot}6H_2O}$ (0.20 g) was heated to 100 °C, stirring rapidly. After 6 h, the blue melt became a blue solid and was cooled to RT. $\mathrm{CH_2Cl_2}$ was added (100 mL) and the resulting blue solution was washed with deionized $\mathrm{H_2O}$ (3 × 30 mL). The organic phase was dried over $\mathrm{MgSO_4}$, filtered and the volatiles removed under reduced pressure yielding $\mathrm{N_2O^{Ar}H}$ (**1**) as a white solid, which was thoroughly dried *in vacuo.* Yield: 6.29 g (57%). ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz, 293 K) δ/ppm: 10.79 (1 H, s, $\mathrm{(Me_2pz)_2CHO^{Ar}}\mathit{H}$), 7.69 (1 H, s, $\mathrm{(Me_2pz)_2C}\mathit{H}\mathrm{O^{Ar}H}$), 7.58 (1 H, d, ^3J = 3 Hz, 4-$\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_2}$), 7.00 (1 H, d, ^3J = 3 Hz, 6-$\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_2}$), 5.59 (2 H, s, $\mathrm{N_2C_3}\mathit{H}\mathrm{Me_2}$), 1.98 (6 H, s, $\mathrm{N_2C_3H}\mathit{Me}_2$), 1.97 (6 H, s, $\mathrm{N_2C_3H}\mathit{Me}_2$), 1.61 (9 H, s, 3-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$), 1.28 (9 H, s, 5-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$) ppm. ^{13}C-{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K) δ/ppm: 153.3 (2-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 148.2 (3 or 5-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 142.2 (5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 141.2 (3 or 5-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 140.0 (3-$\mathit{C}_6\mathrm{H_2}{}^{\mathrm{t}}\mathrm{Bu_2}$), 125.3 (4-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 125.1 (6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 124.7 (1-$\mathit{C}_6\mathrm{H_2(}{}^t\mathrm{Bu)_2}$), 106.9 (4-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 74.7 ($\mathrm{(Me_2pz)_2}\mathit{C}\mathrm{HO^{Ar}H}$), 35.6 (3-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 34.4 (5-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 31.7 (5-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 30.1 (3-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 13.6 ($\mathrm{N_2C_3H}\mathit{Me}_2$), 11.2 ($\mathrm{N_2C_3H}\mathit{Me}_2$). Anal. found (calcd for $\mathrm{C_{25}H_{36}N_4O}$): C 73.4 (73.5), H 8.8 (8.9), N 13.7 (13.6)%. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1556 (s), 1341 (m), 1312 (m), 1251 (w), 1231 (m), 1043 (w), 866 (w), 831 (w), 777 (m), 702 (w), 665 (s). EI-MS: $m/z = 311$ (100%) $\mathrm{[M - Me_2pz]^+}$, 189 (40%) $\mathrm{[M - Me{-}O^{Ar}]^+}$.

$\mathrm{[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2}$ (2). To a slurry of NaH (0.028 g, 1.15 mmol) in THF (10 mL), $\mathrm{N_2O^{Ar}H}$ (**1**, 0.47 g, 1.15 mmol) in THF (30 mL) at 0 °C was added, portion-wise. The mixture was allowed to warm to RT and after 12 h volatiles were removed under reduced pressure. The crude product was recrystallised from THF at –30 °C to give $\mathrm{[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2}$ (**2**) as a white microcrystalline solid. Yield: 0.34 g (52%). ^{1}H NMR ($\mathrm{C_6D_6}$, 500.1 MHz, 293 K) δ/ppm: 8.14 (1 H, br s, $\mathrm{(Me_2pz)_2C}\mathit{H}\mathrm{O^{Ar}}$), 7.00 (2 H, br overlapping s, 4 and 6-$\mathrm{C_6}\mathit{H}_2{}^{\mathrm{t}}\mathrm{Bu_2}$), 5.86 (1 H, br s, 4-$\mathrm{N_2C_3}\mathit{H}\mathrm{Me_2}$), 5.72 (1 H, br s, 4-$\mathrm{N_2C_3}\mathit{H}\mathrm{Me_2}$), 3.16 (4 H, br m, 2-$\mathrm{C_4}\mathit{H}_8\mathrm{O}$), 2.11 (3 H, br s, $\mathrm{N_2C_3H}\mathit{Me}_2$), 1.96 (6 H, br overlapping s, $\mathrm{N_2C_3H}\mathit{Me}_2$), 1.66 (3 H, br s, $\mathrm{N_2C_3H}\mathit{Me}_2$), 1.50 (4 H, br m, 3-$\mathrm{C_4}\mathit{H}_8\mathrm{O}$), 1.33 (9 H, s, 3-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$), 1.08 (9 H, s, 5-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$) ppm. ^{13}C-{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K) δ/ppm: 165.5 (2-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 147.8 (5-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 141.2 (3-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 137.5 (3-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 131.6 (5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 125.6 (4-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 124.5 (6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 122.7 (1-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2}$), 106.7 (4-$\mathrm{N_2}\mathit{C}_3\mathrm{HMe_2}$), 74.5 ($\mathrm{(Me_2pz)_2}\mathit{C}\mathrm{HO^{Ar}}$), 67.8 (2-$\mathit{C}_4\mathrm{H_8O}$), 35.5 (3-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 34.1 (5-$\mathrm{C_6H_2(}\mathit{C}\mathrm{Me_3)_2}$), 32.1 (5-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$), 30.6 (3-$\mathrm{C_6H_2(C}\mathit{Me}_3)_2$), 25.6 (3-$\mathit{C}_4\mathrm{H_8O}$), 13.4 (5-$\mathrm{N_2C_3H}\mathit{Me}_2$), 11.5 (3-$\mathrm{N_2C_3H}\mathit{Me}_2$) ppm. Anal. found (calcd for $\mathrm{C_{58}H_{86}N_8Na_2O_4}$): C 69.4 (69.3), H 8.6 (8.6), N 11.1 (11.2)%. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1603 (m), 1556 (s), 1417 (s), 1359 (m), 1344 (m), 1304 (m), 1230 (m), 1197 (w), 1153 (w), 1123 (m), 1050 (s), 1026 (m), 987 (w), 887 (m), 860 (m), 829 (m), 785 (m), 745 (w), 732 (m), 703 (m), 682 (m), 665 (m), 636 (m), 627 (w).

$\mathrm{Mg(N_2O^{Ar})}{}^n\mathrm{Bu}$ (3). To a solution of $\mathrm{Mg}{}^n\mathrm{Bu_2}$ (1.57 mL, 1.57 mmol; 1 M in heptane,) in toluene at –78 °C (15 mL) was added a solution of N2OArH (**1**, 0.21 g, 0.52 mmol) in toluene (20 mL) dropwise at –78 °C. The pale yellow solution was left at –78 °C for 2 h before being allowed to warm to RT. Volatiles were removed under reduced pressure to yield $\mathrm{Mg(N_2O^{Ar})}{}^n\mathrm{Bu}$ (**3**) as a pale yellow solid, which was washed with pentane (2 × 10 mL) and dried *in vacuo.* The sample contained small amounts of $\mathrm{Mg(N_2O^{Ar})_2}$ (**4**) by ^{1}H NMR. Bulk separation of analytically pure **3** was not possible, but a small number of diffraction-quality

This journal is © The Royal Society of Chemistry 2009

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

crystals were grown by slow evaporation of a solution in diethyl ether. Yield: 0.25 g (90% based on **3**).

Alternative synthesis (NMR tube scale). A solution of ^nBuMgCl (7 μL, 0.014 mmol; 2 M in diethyl ether) was added to $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**, 7.8 mg, 0.07 mmol) in C_6D_6 (0.75 mL), giving a colourless solution and a white precipitate. After 10 min, the ^1H NMR spectrum showed quantitative conversion to **3** and free THF. Attempts to scale up this reaction were unsuccessful.

^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.60 (1H, d,^3J = 3.0 Hz, 4-$C_6H_2{}^tBu_2$), 6.90 (1H, d, ^3J = 3.0 Hz, 6-$C_6H_2{}^tBu_2$), 6.67 (1H, s, $(Me_2pz)_2CHOAr$), 5.14 (2H, s, 4-$N_2C_3HMe_2$), 2.36 (2H, m, 2-Mg^nBu), 2.13 (6H, s, 3-$N_2C_3HMe_2$), 2.06 (2H, m, 3-Mg^nBu), 1.87 (3H, m, 4-Mg^nBu), 1.74 (9H, s, 3-$C_6H_2(CMe_3)2$), 1.68 (6H, s, 5-$N_2C_3HMe_2$), 1.43 (9H, s, 5-$C_6H_2(CMe_3)_2$), 1.41 (2H, m, 1-Mg^nBu) ppm. $^{13}C\text{-}\{^1H\}$ NMR (C6D6, 75.4 MHz, 293 K) δ/ppm: 164.0 (2-$C_6H_2{}^tBu_2$), 149.5 (3-$N_2C_3HMe_2$), 141.6 (3-$C_6H_2{}^tBu_2$), 140.5 (5-$N_2C_3HMe_2$), 133.2 (5-$C_6H_2{}^tBu_2$), 127.0 (4-$C_6H_2{}^tBu_2$), 126.5 (6-$C_6H_2{}^tBu_2$), 121.1 (1-$C_6H_2{}^tBu_2$), 106.3 (4-$N_2C_3HMe_2$), 74.6 ($(Me_2pz)_2CHO^{Ar}$), 36.1 (3-$C_6H_2(CMe_3)_2$), 33.9 (5-$C_6H_2(CMe_3)_2$), 33.0 (2-Mg^nBu), 32.0 (5-$C_6H_2(CMe_3)_2$), 31.5 (3-Mg^nBu), 29.7 (3-$C_6H_2(CMe_3)_2$), 15.0 (1-Mg^nBu), 13.0 (3-$N_2C_3HMe_2$), 11.0 (5-$N_2C_3HMe_2$), 7.3 (4-Mg^nBu). An accurate elemental analysis was not obtained. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1560 (s), 1481 (s), 1363 (m), 1348 (m), 1322 (m), 1242 (m), 1148 (m), 1046 (m), 986 (w), 846 (m), 688 (m), 665 (m), 632 (m). EI-MS: m/z = 429 (5%) $[M - {}^nBu]^+$, 312 (90%) $[(Me_2pz)CHO^{Ar}]^+$, 81 (70%) $[Mg^nBu]^+$.

Reaction of $N_2O^{Ar}H$ (1) with ^nBuMgCl: formation of $Mg(N_2O^{Ar})_2$ (4) and $[Mg(N_2O^{Ar})Cl]_n$ (5). To a solution of ^nBuMgCl (0.69 mmol, 0.35 mL; 2 M in diethyl ether) in benzene (20 mL) at 5 °C, $N_2O^{Ar}H$ (**1**, 0.202 g, 0.50 mmol) in benzene (20 mL) also at 5 °C was added dropwise. After 45 min, the solution was warmed to RT and after 14 h a white precipitate and colourless supernatant had formed. The solution was filtered off, and the precipitate extracted with benzene (3 × 10 mL). The combined filtrates were evaporated to dryness and the residues washed with pentane (3 × 10 mL) and dried *in vacuo* to yield $Mg(N_2O^{Ar})_2$ (**4**) as a white powder. Yield: 0.083 g (40% based on **1**). In an analogous experiment using 0.48 mL ^nBuMgCl solution and 0.28 g **1**, the first-formed white precipitate (believed to contain $[Mg(N_2O^{Ar})Cl]_n$ (**5**) and $MgCl_2$) was isolated, washed thoroughly with benzene and dried *in vacuo*. Yield: 0.20 g.

Data for **4**. ^1H NMR (CD_2Cl_2, 299.9 MHz, 293 K) δ/ppm: 7.26 (2H, d,^3J = 2.7 Hz, 4-$C_6H_2{}^tBu_2$), 7.04 (2H, s, $(Me_2pz)_2CHOAr$), 7.00 (2H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 5.84 (2H, s, 4-$N_2C_3HMe_2$), 5.73 (2H, s, 4-$N_2C_3HMe_2$), 2.49 (6H, s, 3-$N_2C_3HMe_2$), 2.48 (6H, s, 5-$N_2C_3HMe_2$), 2.02 (6H, s, 5-$N_2C_3HMe_2$), 1.34 (18H, s, 3-$C_6H_2(CMe_3)2$), 1.30 (18H, s, 5-$C_6H_2(CMe_3)2$), 0.98 (6H, s, 3-$N_2C_3HMe_2$). $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K) δ/ppm: 164.7 (2-$C_6H_2{}^tBu_2$), 150.0 (5-$N_2C_3HMe_2$), 149.2 (3-$N_2C_3HMe_2$), 140.1 (3-$C_6H_2{}^tBu_2$), 139.2 (5-$N_2C_3HMe_2$), 131.0 (5-$C_6H_2{}^tBu_2$), 127.0 (4-$C_6H_2{}^tBu_2$), 125.5 (6-$C_6H_2{}^tBu_2$), 121.8 (1-$C_6H_2{}^tBu_2$), 106.8 (4-$N_2C_3HMe_2$), 106.5 (4-$N_2C_3HMe_2$), 74.7 ($(Me_2pz)_2CHO^{Ar}$), 36.1 (3-$C_6H_2(CMe_3)_2$), 33.8 (5-$C_6H_2(CMe_3)_2$), 31.9 (5-$C_6H_2(CMe_3)_2$), 31.8 (3-$C_6H_2(CMe_3)_2$), 14.3 (5-$N_2C_3HMe_2$), 12.3 (3- and 5-$N_2C_3HMe_2$), 11.4 (3-$N_2C_3HMe_2$) ppm. Anal. found (calcd for $C_{50}H_{70}N_8O_2Mg$): C 71.2 (71.5), H 8.3 (8.4), N 13.5 (13.4)%. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1562 (m), 1478 (s), 1363 (m), 1351 (m), 1323 (m), 1272 (m), 1249 (m), 1151 (w), 1035 (m), 847 (m), 809 (w), 786 (m), 712 (w), 665 (m). EI-MS: m/z = 839 (90%) $[M]^+$, 744 (5%) $[M - Me_2pz]^+$, 646 (5%) $[M - 2Me_2pz]^+$, 526 (100%) $[Mg(Me_2pz)(N_2O^{Ar})]^+$.

Data for **5**. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1558 (m), 1363 (m), 1351 (m), 1319 (w), 1272 (m), 1248 (m), 1151 (w), 1054 (m), 1043 (m), 967 (w), 848 (m), 818 (m), 783 (w), 750 (w), 714 (m), 687 (w), 666 (m). EI-MS: m/z = 466 (70%) $[M]^+$, 451 (100%) $[M - Me]^+$, 355 (40%) $[M - Me - Me_2pz]^+$.

$Mg(N_2O^{Ar})\{N(SiMe_3)_2\}$ (6). To a solution of $Mg\{N(SiMe_3)_2\}_2$ (0.449 g, 1.30 mmol) in toluene (20 mL) was added a solution of $N_2O^{Ar}H$ (**1**, 0.532 g, 1.30 mmol) in toluene (30 mL) at RT dropwise over 30 min. After 12 h, a significant amount of precipitate was produced (shown to be **4**, *ca.* 50% yield), which was filtered off and washed with toluene (3 × 10 mL). The combined filtrates were evaporated to dryness under reduced pressure, washed with pentane (3 × 10 mL) and dried *in vacuo* yielding $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**6**) as a white solid. Yield: 0.085 g (11%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.54 (1H, d,^3J = 2.7 Hz, 4-$C_6H_2{}^tBu_2$), 6.78 (1H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 6.56 (1H, s, $(Me_2pz)_2CHOAr$), 5.15 (2H, s, 4-$N_2C_3HMe_2$), 2.35 (6H, s, 3-$N_2C_3HMe_2$), 1.70 (9H, s, 3-$C_6H_2(CMe_3)2$), 1.60 (6H, s, 5-$N_2C_3HMe_2$), 1.38 (9H, s, 5-$C_6H_2(CMe_3)2$), 0.55 (18H, s, $Mg\{N(SiMe_3)_2\}$). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K) δ/ppm: 163.4 (2-$C_6H_2{}^tBu_2$), 150.1 (3-$N_2C_3HMe_2$), 141.8 (3-$C_6H_2{}^tBu_2$), 141.0 (5-$N_2C_3HMe_2$), 133.6 (5-$C_6H_2{}^tBu_2$), 126.7 (4-$C_6H_2{}^tBu_2$), 125.1 (6-$C_6H_2{}^tBu_2$), 121.3 (1-$C_6H_2{}^tBu_2$), 106.7 (4-$N_2C_3HMe_2$), 74.4 ($(Me_2pz)_2CHO^{Ar}$), 36.1 (3-$C_6H_2(CMe_3)_2$), 33.8 (5-$C_6H_2(CMe_3)_2$), 32.0 (5-$C_6H_2(CMe_3)_2$), 30.1 (3-$C_6H_2(CMe_3)_2$), 14.0 (3-$N_2C_3HMe_2$), 11.0 (5-$N_2C_3HMe_2$), 6.4 ($Mg\{N(SiMe_3)_2\}$). Anal. found (calcd for $C_{31}H_{53}N_5OSi_2Mg$): C 62.8 (62.9), H 9.1 (9.0), N 11.8 (11.8)%. IR (KBr plates, Nujol mull, ν/cm^{-1}): 1561 (m), 1348 (m), 1007 (m), 888 (w), 845 (m), 665 (m). EI-MS: m/z = 311 (100%) $[(Me_2pz)CHO^{Ar}]^+$, 255 (70%) $[Mg(O^{Ar})(N)_2]^+$, 241 (40%) $[Mg(O^{Ar})N]^+$, 190 (70%) $[Mg(pz)(NSi_2)]^+$, 161 (10%) $[N(SiMe_3)_2]^+$, 94 (90%) $[Mg(NSi_2)]^+$.

$Mg(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (7). A solution of $Mg\{N(SiHMe_2)_2\}_2$ (0.30 g, 1.05 mmol) in benzene (15 mL) was added dropwise to a solution of $N_2O^{Ar}H$ (**1**, 0.33 g, 0.81 mmol) in benzene (15 mL). A light green solution was produced, which was heated to 70 °C for 4 h, during which time a precipitate was formed. This was filtered off and the filtrates evaporated to dryness. The residues were washed with pentane (3 × 20 mL) and dried *in vacuo* yielding $Mg(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (**7**) as a white solid. Yield: 0.09 g (21%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.56 (1H, d,^3J = 2.7 Hz, 4-$C_6H_2{}^tBu_2$), 6.82 (1H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 6.58 (1H, s, $(Me_2pz)_2CHO^{Ar}$), 5.50 (2H, m, $Mg\{N(SiHMe_2)_2\}$), 5.11 (2H, s, 4-$N_2C_3HMe_2$), 2.31 (6H, s, 3-$N_2C_3HMe_2$), 1.73 (9H, s, 3-$C_6H_2(CMe_3)_2$), 1.62 (6H, s, 5-$N_2C_3HMe_2$), 1.40 (9H, s, 5-$C_6H_2(CMe_3)_2$), 0.65 (12H, d, ^3J = 3.3 Hz, $Mg\{N(SiHMe_2)_2\}$). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K) δ/ppm: 163.5 (2-$C_6H_2{}^tBu_2$), 150.0 (3-$N_2C_3HMe_2$), 141.8 (3-$C_6H_2{}^tBu_2$), 140.9 (5-$N_2C_3HMe_2$), 133.6 (5-$C_6H_2{}^tBu_2$), 126.8 (4-$C_6H_2{}^tBu_2$), 125.0 (6-$C_6H_2{}^tBu_2$), 121.2 (1-$C_6H_2{}^tBu_2$), 106.7 (4-$N_2C_3HMe_2$), 74.4 ($(Me_2pz)_2CHO^{Ar}$), 36.2 (3-$C_6H_2(CMe_3)_2$), 33.9 (5-$C_6H_2(CMe_3)_2$), 32.1 (5-$C_6H_2(CMe_3)_2$), 29.9 (3-$C_6H_2(CMe_3)_2$), 13.7 (3-$N_2C_3HMe_2$), 11.0 (5-$N_2C_3HMe_2$), 4.3 ($Mg\{N(SiHMe_2)_2\}$). Anal. found (calcd for $C_{29}H_{49}N_5OSi_2Mg$):

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

C 61.8 (61.7), H 8.7 (8.8), N 12.3 (12.4)%. IR (KBr plates, Nujol mull) ν/cm^{-1}: 2050 (m), 1562 (m), 1349 (m), 1244 (m), 1050 (w), 931 (w), 899 (m), 845 (w), 808 (w), 667 (m). EI-MS: m/z = 311 (100%) $[(Me_2pz)CHO^{Ar}]^+$, 255 (60%) $[Mg(O^{Ar})(N)_2]^+$, 241 (40%) $[Mg(O^{Ar})(N)]^+$, 190 (70%) $[Mg(pz)(NSi_2)]^+$, 133 (10%) $[N(SiHMe_2)_2]^+$, 94 (90%) $[Mg(NSi_2)]^+$.

$Zn(N_2O^{Ar})Me$ (8). A solution of $N_2O^{Ar}H$ (**1**, 0.51 g, 1.26 mmol) in toluene (30 mL) was added to $ZnMe_2$ (1.9 mL, 3.78 mmol; 2 M in toluene). The mixture was heated to 60 °C for 14 h. The volatiles were removed under reduced pressure to give a yellow residue, which was washed with cold pentane (−35 °C, 3 × 20 mL) and dried *in vacuo* to afford $Zn(N_2O^{Ar})Me$ (**8**) as a pale yellow solid. Yield: 0.15 g (25%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.60 (1H, d,^3J = 2.4 Hz, 4-$C_6H_2{}^tBu_2$), 6.88 (1H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 6.65 (1H, s, $(Me_2pz)_2CHO^{Ar}$), 5.18 (2H, s, 4-$N_2C_3HMe_2$), 2.06 (6H, s, 3-$N_2C_3HMe_2$), 1.78 (9H, s, 3-$C_6H_2(C\mathit{Me}_3)2$), 1.69 (6H, s, 5-$N_2C_3HMe_2$), 1.43 (9H, s, 5-$C_6H_2(C\mathit{Me}_3)2$), 0.19 (3H, s, ZnMe). ^{13}C-{^1H} NMR (C_6D_6, 75.4 MHz, 293 K) δ/ppm: 165.1 (2-$C_6H_2{}^tBu_2$), 149.3 (3-$N_2C_3HMe_2$), 142.4 (3-$C_6H_2{}^tBu_2$), 139.6 (5-$N_2C_3HMe_2$), 132.7 (5-$C_6H_2{}^tBu_2$), 126.4 (4-$C_6H_2{}^tBu_2$), 124.8 (6-$C_6H_2{}^tBu_2$), 120.2 (1-$C_6H_2{}^tBu_2$), 106.1 (4-$N_2C_3HMe_2$), 74.5 ($(Me_2pz)_2CHO^{Ar}$), 36.3 (3-$C_6H_2(CMe_3)_2$), 33.9 (5-$C_6H_2(CMe_3)_2$), 32.1 (5-$C_6H_2(CMe_3)_2$), 30.0 (3-$C_6H_2(CMe_3)_2$), 12.9 (3-$N_2C_3HMe_2$), 10.9 (5-$N_2C_3HMe_2$), −15.8 (ZnMe) ppm. Anal. found (calcd for $C_{26}H_{38}N_4OZn$): C 63.9 (64.0), H 7.8 (7.9), N 11.4 (11.5)%. IR (KBr plates, Nujol mull) ν/cm^{-1}: 1558 (m), 1362 (s), 1349 (m), 1324 (m), 1249 (m), 1149 (w), 1046 (m), 845 (m), 834 (m), 783 (w), 710 (m), 689 (w), 665 (m). EI-MS: m/z = 486 (100%) $[M]^+$.

$Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (9). A solution of $Zn\{N(SiMe_3)_2\}_2$ (0.26 g, 0.68 mmol) in toluene (10 mL) was added dropwise to a solution of $N_2O^{Ar}H$ (**1**, 0.21 g, 0.52 mmol) in toluene (30 mL). After 3 h at RT, the mixture was filtered and the filtrates evaporated to dryness under reduced pressure. The residues were washed with pentane (3 × 10 mL) and dried *in vacuo* to give $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**) as a white solid. Yield: 0.23 g (69%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.54 (1H, d,^3J = 3.0 Hz, 4-$C_6H_2{}^tBu_2$), 6.75 (1H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 6.52 (1H, s, $(Me_2pz)_2CHO^{Ar}$), 5.18 (2H, s, 4-$N_2C_3HMe_2$), 2.36 (6H, s, 3-$N_2C_3HMe_2$), 1.72 (9H, s, 3-$C_6H_2(CMe_3)_2$), 1.60 (6H, s, 5-$N_2C_3HMe_2$), 1.38 (9H, s, 5-$C_6H_2(CMe_3)_2$), 0.54 (18H, s, $Zn\{N(SiMe_3)_2\}$). ^{13}C-{^1H} NMR (C_6D_6, 75.4 MHz, 293 K) δ/ppm: 64.0 (2-$C_6H_2{}^tBu_2$), 150.0 (3-$N_2C_3HMe_2$), 142.8 (3-$C_6H_2{}^tBu_2$), 140.3 (5-$N_2C_3HMe_2$), 133.3 (5-$C_6H_2{}^tBu_2$), 126.7 (4-$C_6H_2{}^tBu_2$), 125.2 (6-$C_6H_2{}^tBu_2$), 120.3 (1-$C_6H_2{}^tBu_2$), 106.7 (4-$N_2C_3HMe_2$), 74.4 ($(Me_2pz)_2CHO^{Ar}$), 36.3 (3-$C_6H_2(CMe_3)_2$), 33.8 (5-$C_6H_2(CMe_3)_2$), 32.0 (5-$C_6H_2(CMe_3)_2$), 30.3 (3-$C_6H_2(CMe_3)_2$), 13.8 (3-$N_2C_3HMe_2$), 10.9 (5-$N_2C_3HMe_2$), 6.1 ($Zn\{N(SiMe_3)_2\}$). Anal. found (calcd for $C_{31}H_{53}N_5OSi_2Zn$): C 58.7 (58.8), H 8.5 (8.4), N 10.9 (11.1)%. IR (KBr plates, Nujol mull) ν/cm^{-1}: 1560 (m), 1362 (m), 1344 (m), 1318 (m), 1245 (s), 1049 (m), 991 (s), 885 (s), 847 (s), 833 (s), 782 (w), 711 (w), 691 (w), 666 (m), 612 (m). EI-MS: m/z = 631 (80%) $[M]^+$, 616 (20%) $[M - Me]^+$, 472 (75%) $[M - N(SiMe_3)_2]^+$, 225 (40%) $[Zn\{N(SiMe_3)_2\}]^+$.

$Zn(N_2O^{Ar})_2$ (10). $Zn\{N(SiMe_3)_2\}_2$ (0.088 g, 0.23 mmol) was added to a solution of $N_2O^{Ar}H$ (**1**, 0.20 g 0.48 mmol) in CH_2Cl_2 (10 mL) at RT. After 14 h, the resultant orange suspension was filtered, and the solid residue was washed with hot toluene (70 °C, 3 × 10 mL) and diethyl ether (3 × 10 mL) and then dried *in vacuo* to afford $(N_2O^{Ar})_2$ (**10**) as a white powder. Yield: 0.08 g (39%).

Alternative NMR tube scale synthesis. $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**, 0.0085 g, 0.013 mmol) and $N_2O^{Ar}H$ (**1**, 0.0055 g, 0.013 mmol) were dissolved in C_6D_6 (0.75 mL), giving a pale yellow solution and a precipitate. After 10 min, the ^1H NMR spectrum showed $HN(SiMe_3)_2$ had been quantitatively produced and no **9** remained.

Compound **10** was highly insoluble and therefore NMR analysis could not be carried out. Anal. found (calcd for $C_{50}H_{70}N_8O_2Zn$): C 68.2 (68.2), H 8.1 (8.0), N 12.6 (12.7)%. IR (KBr plates, Nujol mull) ν/cm^{-1}: 1603 (m), 1562 (s), 1360 (s), 1350 (s), 1332 (m), 1316 (m), 1272 (s), 1251 (s), 1150 (m), 1093 (m, br), 1038 (m), 982 (m), 969 (m), 896 (w), 852 (m), 834 (m), 801 (s), 783 (m), 744 (m), 714 (m), 685 (m), 665 (m), 633 (m), 608 (w).

$Zn(N_2O^{Ar})Cl$ (11). To a solution of $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}$ (**9**, 0.68 g, 1.07 mmol) in benzene (25 mL), HCl (1.07 mL, 1.07 mmol; 1 M in diethyl ether) was added at RT. A white precipitate was formed and after 8 h, the mixture was evaporated to dryness under reduced pressure, washed with benzene (3 × 10 mL) and dried *in vacuo* to afford $Zn(N_2O^{Ar})Cl$ (**11**) as a white solid. Yield: 0.38 g (69%). ^1H NMR (CD_2Cl_2, 299.9 MHz, 293 K) δ/ppm: 7.27 (1H, d,^3J = 3 Hz, 4-$C_6H_2{}^tBu_2$), 6.95 (1H, s, $(Me_2pz)_2CHO^{Ar}$), 6.86 (1H, d, ^3J = 3 Hz, 6-$C_6H_2{}^tBu_2$), 6.01 (2H, s, 4-$N_2C_3HMe_2$), 2.48 (6H, s, 5-$N_2C_3HMe_2$), 2.42 (6H, s, 3-$N_2C_3HMe_2$), 1.37 (9H, s, 3-$C_6H_2(C\mathit{Me}_3)2$), 1.26 (9H, s, 5-$C_6H_2(C\mathit{Me}_3)2$). ^{13}C-{^1H} NMR (CD_2Cl_2, 75.4 MHz, 293 K) δ/ppm: 163.2 (2-$C_6H_2{}^tBu_2$), 151.1 (3-$N_2C_3HMe_2$), 142.0 (3-$C_6H_2{}^tBu_2$), 141.6 (5-$N_2C_3HMe_2$), 134.9 (5-$C_6H_2{}^tBu_2$), 127.0 (4-$C_6H_2{}^tBu_2$), 125.7 (6-$C_6H_2{}^tBu_2$), 119.8 (1-$C_6H_2{}^tBu_2$), 107.0 (4-$N_2C_3HMe_2$), 74.3 ($(Me_2pz)_2CHO^{Ar}$), 36.0 (3-$C_6H_2(CMe_3)_2$), 34.0 (5-$C_6H_2(CMe_3)_2$), 31.7 (5-$C_6H_2(CMe_3)_2$), 29.6 (3-$C_6H_2(CMe_3)_2$), 13.2 (3-$N_2C_3HMe_2$), 11.7 (5-$N_2C_3HMe_2$). Anal. found (calcd for $C_{25}H_{35}ClN_4OZn$): C 59.2 (59.1), H 6.9 (6.9), N 10.9 (11.0)%. IR (KBr plates, Nujol mull) ν/cm^{-1}: 1556 (m), 1347 (m), 1315 (m), 1148 (w), 1054 (m), 844 (m), 813 (m), 781 (w), 708 (w), 690 (w), 676 (m), 666 (m). EI-MS: m/z = 506 (10%) $[M]^+$.

$Zn(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (12). To a slurry of $Zn(N_2O^{Ar})Cl$ (**11**, 0.29 g, 0.58 mmol) in benzene (15 mL), $LiN(SiHMe_2)_2$ (0.08 g, 0.58 mmol) in benzene (10 mL) was added at RT. After 24 h, the solution was filtered and the filtrates were evaporated to dryness under reduced pressure to afford $Zn(N_2O^{Ar})\{N(SiHMe_2)_2\}$ (**12**) as a white solid, which was washed with benzene (3 × 5 mL) and dried *in vacuo*. Yield: 0.18 g (35%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K) δ/ppm: 7.56 (1H, d,^3J = 2.7 Hz, 4-$C_6H_2{}^tBu_2$), 6.77 (1H, d, ^3J = 2.7 Hz, 6-$C_6H_2{}^tBu_2$), 6.52 (1H, s, $(Me_2pz)_2CHO^{Ar}$), 5.51 (2H, m, $Zn\{N(Si\mathit{H}Me_2)_2\}$), 5.12 (2H, s, 4-$N_2C_3HMe_2$), 2.34 (6H, s, 3-$N_2C_3HMe_2$), 1.74 (9H, s, 3-$C_6H_2(C\mathit{Me}_3)_2$), 1.60 (6H, s, 5-$N_2C_3HMe_2$), 1.39 (9H, s, 5-$C_6H_2(C\mathit{Me}_3)2$), 0.64 (12H, d, ^3J = 3.3 Hz, $Zn\{N(SiH\mathit{Me}_2)_2\}$). ^{13}C-{^1H} NMR (C_6D_6, 75.4 MHz, 293 K) δ/ppm: 164.1 (2-$C_6H_2{}^tBu_2$), 149.9 (3-$N_2C_3HMe_2$), 142.8 (3-$C_6H_2{}^tBu_2$), 140.2 (5-$N_2C_3HMe_2$), 133.5 (5-$C_6H_2{}^tBu_2$), 126.7 (4-$C_6H_2{}^tBu_2$), 125.2 (6-$C_6H_2{}^tBu_2$), 120.2 (1-$C_6H_2{}^tBu_2$), 106.6 (4-$N_2C_3HMe_2$), 74.4 ($(Me_2pz)_2CHO^{Ar}$), 36.4 (3-$C_6H_2(CMe_3)_2$), 33.8 (5-$C_6H_2(CMe_3)_2$), 32.0 (5-$C_6H_2(CMe_3)_2$), 30.1 (3-$C_6H_2(CMe_3)_2$), 13.5 (3-$N_2C_3HMe_2$), 10.9 (5-$N_2C_3HMe_2$), 3.8 ($Zn\{N(SiHMe_2)_2\}$). Anal. found (calcd for $C_{29}H_{49}N_5OSi_2Zn$): C 57.6 (57.5), H 8.1 (8.2), N 11.5 (11.6)%. IR (KBr plates, Nujol mull, ν/cm^{-1}: 2084 (s), 2054 (s), 1605 (w), 1561 (m), 1347 (m), 1318 (m), 1244 (s), 1148 (m),

View Online

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

Table 6 X-ray data collection and processing parameters for $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (**2**), $Mg(N_2O^{Ar})^nBu$ (**3**), $Mg(N_2O^{Ar})_2{\cdot}C_4H_{10}O$ (**4**$\cdot C_4H_{10}O$), $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}{\cdot}0.5(C_7H_8)$ (**6**$\cdot 0.5(C_7H_8)$), $Zn(N_2O^{Ar})Me$ (**8**), $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}{\cdot}0.35(C_7H_8)$ (**9**$\cdot 0.35(C_7H_8)$) and $Zn(N_2O^{Ar})Cl$ (**11**)

Parameter	**2**	**3**	**4**$\cdot C_4H_{10}O$	**6**$\cdot 0.5(C_7H_8)$	**8**	**9**$\cdot 0.35(C_7H_8)$	**11**
Empirical formula	$C_{58}H_{86}N_8Na_2O_4$	$C_{29}H_{44}MgN_4O$	$C_{50}H_{70}MgN_8O_2\cdot C_4H_{10}O$	$C_{31}H_{53}MgN_5OSi_2\cdot 0.5(C_7H_8)$	$C_{26}H_{38}N_4OZn$	$C_{31}H_{53}ZnN_5OSi_2\cdot 0.35(C_7H_8)$	$C_{25}H_{35}ClN_4OZn$
FW	1005.36	489.00	913.59	638.34	487.99	665.60	508.41
Temp./K	150	150	150	150	150	150	150
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.7107
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	10.9739(2)	11.2537(2)	15.7496(4)	11.5864(2)	10.1798(2)	11.6068(2)	9.81900(10)
b/Å	11.2192(3)	21.1315(5)	17.6620(5)	12.7632(2)	11.0522(3)	12.6722(2)	23.2485(3)
c/Å	11.9206(3)	23.8492(5)	20.2696(5)	14.2935(3)	12.7119(3)	14.2523(3)	11.11250(10)
α/°	77.4985(11)	90	90	105.6153(10)	69.3059(11)	105.2600(8)	90
β/°	79.4223(11)	90	92.8818(17)	104.8024(9)	85.6402(11)	104.7969(8)	94.5044(6)
γ/°	88.4467(12)	90	90	95.2213(10)	79.8464(11)	94.9221(8)	90
V/Å^3	1408.38(6)	5671.5(2)	5631.3(3)	1938.95(6)	1316.83(5)	1928.81(6)	2528.89(5)
Reflections measured	10 896	10 777	17 019	15 046	10 580	15 008	11 508
Unique reflections	6314	5521	9832	8798	5970	8788	5771
R_{int}	0.026	0.053	0.055	0.034	0.031	0.031	0.023
Z	1	8	4	2	2	2	4
D_{calcd}/Mg m^{-3}	1.185	1.145	1.078	1.093	1.231	1.146	1.335
Abs. coeff./mm^{-1}	0.088	0.090	0.77	0.139	0.956	0.729	1.101
R indices^a	$R_1 = 0.0417$	$R_1 = 0.0509$	$R_1 = 0.0826$	$R_1 = 0.0642$	$R_1 = 0.0339$	$R_1 = 0.0513$	$R_1 = 0.0313$
$[I > 3\sigma(I)]$	$R_w = 0.0430$	$R_w = 0.0594$	$R_w = 0.0879$	$R_w = 0.0704$	$R_w = 0.0335$	$R_w = 0.0542$	$R_w = 0.0317$

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}}$.

1050 (m), 1000 (s), 924 (m), 904 (s), 847 (m), 835 (m), 782 (m), 749 (w), 711 (m), 690 (w), 677 (m), 666 (m). EI-MS: $m/z = 471$ (70%) $[M - N(SiHMe_2)_2]^+$.

Crystal structure determinations of $[Na(\kappa^2\text{-}N_2O^{Ar})(THF)]_2$ (2), $Mg(N_2O^{Ar})^nBu$ (3), $Mg(N_2O^{Ar})_2{\cdot}C_4H_{10}O$ (4$\cdot C_4H_{10}O$), $Mg(N_2O^{Ar})\{N(SiMe_3)_2\}{\cdot}0.5(C_7H_8)$ (6$\cdot 0.5(C_7H_8)$), $Zn(N_2O^{Ar})Me$ (8), $Zn(N_2O^{Ar})\{N(SiMe_3)_2\}{\cdot}0.35(C_7H_8)$ (9$\cdot 0.35(C_7H_8)$) and $Zn(N_2O^{Ar})Cl$ (11). Crystal data collection and processing parameters are given in Table 6. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using either an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[82] The structures were solved by direct methods (SIR92[83]) and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.[84] Crystals of **6** and **9** contain fractional occupancy toluene molecules of crystallization disordered over crystallographic inversion centers. These were refined isotropically with a common displacement parameter for the carbon atoms. Geometric restraints were applied to the C–C distances and C–C–C angles. The largest peak in the final Fourier difference map was in the region of the disordered toluene molecule. Crystals of **4** contained diethyl ether molecules of crystallization. These were satisfactorily refined subject to loose restraints applied to the displacement parameters. Further details of the structure solution and refinements are given in the ESI†. A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre.

General procedure for ε-caprolactone polymerization experiments

In a dry-box, a Schlenk tube was charged with *ca.* 35 µmol of the catalyst and a magnetic stirring bar. The tube was transferred to a dual manifold Schlenk line and dissolved in toluene (1.5 mL). A solution of ε-caprolactone (100 equiv.) in toluene (2 mL) was added *via* a steel cannula in one portion. The solutions were stirred for up to 24 h, with aliquots typically being taken at 2, 4 and 6 h. These were quenched with non-dried toluene, evaporated to dryness and analysed by ^1H NMR spectroscopy ($CDCl_3$) and GPC as appropriate. Where appropriate, the remaining solution was pipetted into methanol to precipitate poly(CL), which was washed and dried to a constant weight and analyzed by GPC.

Acknowledgements

This work was supported by the EPSRC, Oxford University's Clarendon Fund and Programme Alβan, the European Union Programme of High Level Scholarships for Latin America, scholarship no. E05D059950MX.

References

1 K. R. Breakell, D. J. Patmore and A. Storr, *J. Chem. Soc., Dalton Trans.*, 1975, 749.
2 E. E. Pullen, A. L. Rheingold and D. Rabinovich, *Inorg. Chem. Commun.*, 1999, 194.
3 A. Steiner and D. Stalke, *Inorg. Chem.*, 1995, **34**, 4846.
4 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.
5 S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115.
6 S. Trofimenko, *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
7 S. Trofimenko, *Polyhedron*, 2004, **23**, 197.
8 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, pp. 3170 and 6288.

Downloaded by Indiana University - Purdue University at Indianapolis on 17 September 2012
Published on 21 October 2008 on http://pubs.rsc.org | doi:10.1039/B813116C

9 S. C. Lawrence, M. E. G. Skinner, J. C. Green and P. Mountford, *Chem. Commun.*, 2001, 705.

10 F. Breher, J. Grunenberg, S. C. Lawrence, P. Mountford and H. Rüegger, *Angew. Chem., Int. Ed.*, 2004, **43**, 2521.

11 I. Krummenacher, H. Rüegger and F. Breher, *Dalton Trans.*, 2006, 1073.

12 H. R. Bigmore, J. Meyer, I. Krummenacher, H. Rüegger, E. Clot, P. Mountford and F. Breher, *Chem.–Eur. J.*, 2008, **14**, 5918.

13 D. L. Reger, *Comments Inorg. Chem.*, 1999, **21**, 1.

14 H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635.

15 C. Pettinari and R. Pettinari, *Coord. Chem. Rev.*, 2005, **249**, 525.

16 C. Pettinari and R. Pettinari, *Coord. Chem. Rev.*, 2005, **249**, 663.

17 S. Milione, S. Montefusco, T. Cuenca and A. Grassi, *Chem. Commun.*, 2003, 1176.

18 R. G. Howe, C. S. Tredget, S. C. Lawrence, S. Subongkoj, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2005, 223.

19 S. Milione, V. Bertolasi, T. Cuenca and A. Grassi, *Organometallics*, 2005, **24**, 4915.

20 L. F. Sánchez-Barba, A. Garcés, M. Fajardo, C. Alonso-Moreno, J. Fernández-Baeza, A. Otero, A. Antinolo, J. Tejeda, A. Lara-Sánchez and M. I. López-Solera, *Organometallics*, 2007, **26**, 6403.

21 S. Milione, F. Grisi, R. Centore and A. Tuzi, *Organometallics*, 2006, **25**, 266.

22 C. Alonso-Moreno, A. Garcés, L. F. Sánchez-Barba, M. Fajardo, J. Fernández-Baeza, A. Otero, A. Lara-Sánchez, A. Antinolo, L. Broomfield, M. I. López-Solera and A. M. Rodríguez, *Organometallics*, 2008, **27**, 1310.

23 A. Otero, J. Fernández-Baeza, A. Antinolo, A. Lara-Sánchez, E. Martinez-Caballero, J. Tejeda, L. F. Sánchez-Barba, C. Alonso-Moreno and M. I. López-Solera, *Organometallics*, 2008, **27**, 976.

24 S. C. Lawrence, B. D. Ward, S. R. Dubberley, C. M. Kozak and P. Mountford, *Chem. Commun.*, 2003, 2880.

25 C. S. Tredget, S. C. Lawrence, B. D. Ward, R. G. Howe, A. R. Cowley and P. Mountford, *Organometallics*, 2005, **24**, 3136.

26 C. S. Tredget, E. Clot and P. Mountford, *Organometallics*, 2008, **27**, 3458.

27 H. R. Bigmore, M. Zuideveld, R. M. Kowalczyk, A. R. Cowley, M. Kranenbrug, E. J. L. McInnes and P. Mountford, *Inorg. Chem.*, 2006, **45**, 6411.

28 H. R. Bigmore, S. R. Dubberley, M. Kranenburg, S. C. Lawrence, A. J. Sealey, J. D. Selby, M. Zuideveld, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2006, 436.

29 T. C. Higgs and C. J. Carrano, *Inorg. Chem.*, 1997, **36**, 298.

30 T. C. Higgs, D. Ji, R. S. Czernuscewicz and C. J. Carrano, *Inorg. Chim. Acta*, 1998, **273**, 14.

31 T. C. Higgs, K. Spartalian, C. J. O'Connor, B. F. Matzanke and C. J. Carrano, *Inorg. Chem.*, 1998, **37**, 2263.

32 B. S. Hammes and C. J. Carrano, *Inorg. Chem.*, 1999, **38**, 3562.

33 T. C. Higgs, D. Ji, R. S. Czernuscewicz and C. J. Carrano, *Inorg. Chim. Acta*, 1999, **286**, 80.

34 S. R. Davie, N. D. Rubie, B. S. Hammes, C. J. Carrano, M. L. Kirk and P. Basu, *Inorg. Chem.*, 2001, **40**, 2632.

35 C. J. Carrano, B. S. Chohan, B. S. Hammes and B. W. Kail, *Inorg. Chem.*, 2003, **42**, 5999.

36 D. Hazra, D. K. Sinha-Mahapatra, V. G. Puranik and A. Sarkar, *J. Organomet. Chem.*, 2003, **671**, 52.

37 J. N. Smith, Z. Shirin and C. J. Carrano, *J. Am. Chem. Soc.*, 2003, **125**, 868.

38 C. R. Warthen and C. J. Carrano, *J. Inorg. Biochem.*, 2003, **94**, 197.

39 J. N. Smith, J. T. Hoffman, Z. Shirin and C. J. Carrano, *Inorg. Chem.*, 2005, **44**, 2012.

40 B. S. Hammes and C. J. Carrano, *Inorg. Chem.*, 1999, **38**, 4593.

41 M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, T. H. and T. Fujita, *Chem. Rec.*, 2004, **4**, 137.

42 M. G. Davidson, C. L. Doherty, A. L. Johnson and M. F. Mahon, *Chem. Commun.*, 2003, 1832.

43 F. Bonnet, A. R. Cowley and P. Mountford, *Inorg. Chem.*, 2005, **44**, 9046.

44 A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chem.–Eur. J.*, 2006, **12**, 169.

45 A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250.

46 M. G. Davidson, C. T. O'Hara, M. D. Jones, C. G. Keir, M. F. Mahon and G. Kociok-Köhn, *Inorg. Chem.*, 2007, **46**, 7686.

47 H. D. Dyer, S. Huijser, A. D. Schwarz, C. Wang, R. Duchateau and P. Mountford, *Dalton Trans.*, 2008, 32.

48 W. Clegg, M. G. Davidson, D. V. Graham, G. Griffen, M. D. Jones, A. R. Kennedy, C. T. O'Hara, L. Russoa and C. M. Thomson, *Dalton Trans.*, 2008, 1295.

49 A. Amgoune, C. M. Thomas and J.-F. Carpentier, *Pure Appl. Chem.*, 2007, **79**, 2013.

50 K. I. Thé and L. K. Peterson, *Can. J. Chem.*, 1973, **51**, 422.

51 T. Toupance, S. R. Dubberley, N. H. Rees, B. R. Tyrrell and P. Mountford, *Organometallics*, 2002, **21**, 1367.

52 K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.

53 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, pp. 1 and 31.

54 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746, The United Kingdom Chemical Database Service.

55 S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1991, 144.

56 C. Stanciu, M. M. Olmstead, A. D. Phillips, M. Stender and P. P. Power, *Eur. J. Inorg. Chem.*, 2003, 3495.

57 D. Zhang and H. Kawaguchi, *Organometallics*, 2006, **25**, 5506.

58 F. Yuan, J. Yang and L. Xiong, *J. Organomet. Chem.*, 2006, **691**, 2534.

59 R. Han and G. Parkin, *J. Organomet. Chem.*, 1990, **393**, C43.

60 R. Han and G. Parkin, *Organometallics*, 1991, **10**, 1010.

61 W. Schlenk and W. Schlenk, *Ber. Dtsch. Chem. Ges.*, 1929, **62B**, 920.

62 Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340.

63 B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215.

64 G. W. Coates, *J. Chem. Soc., Dalton Trans.*, 2002, 467.

65 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.

66 J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602.

67 A. Looney, R. Han, I. B. Gorrel, M. Cornebise, K. Yoon and G. Parkin, *Organometallics*, 1995, **14**, 274.

68 M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold and K. Phomphrai, *J. Am. Chem. Soc.*, 2000, **122**, 11845.

69 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Cryst.*, 1976, **32**, 751.

70 D. M. P. Mingos, *Essential Trends in Inorganic Chemistry*, Oxford University Press, Oxford, 1998.

71 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841.

72 M. Okada, *Prog. Polym. Sci.*, 2002, **27**, 87.

73 C. K. Williams, *Chem. Soc. Rev.*, 2007, **36**, 1573.

74 M. H. Chisholm, J. Gallucci and K. Phomphrai, *Chem. Commun.*, 2003, 48.

75 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717.

76 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

77 M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889.

78 M. Westerhausen, *Inorg. Chem.*, 1991, **30**, 96.

79 H. Bürger, W. Sawodry and U. Wannagat, *J. Organomet. Chem.*, 1965, **3**, 113.

80 C. Zapilko, Y. Liang and R. Anwander, *Chem. Mater.*, 2007, **19**, 3171.

81 J. Eppinger, E. Herdtweck and R. Anwander, *Polyhedron*, 1998, **17**, 1195.

82 Z. Otwinowski, and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, Academic press, New York, 1997.

83 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

84 P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.