Mariana Luna Barros, Michael G. Cushion, Andrew D. Schwarz, Zoë R. Turner and Philip Mountford

A new family of sterically demanding N₂N’ heteroscorpionate pro-ligands (HC’Bu₂pz)₂SiMe₂NHR (R = ’Pr, ’Bu, Ph, Xyl) has been prepared via a straightforward modular synthetic route. An extensive study into the synthesis and characterisation of lithium, magnesium, calcium and zinc complexes supported by both 2,5- and 3,5-Me substituted N₂N’ ligands has been conducted. Attempted deprotonation of the pro-ligands with ’BuLi afforded the corresponding lithium salts Li(HC’Bu₂pz)₂SiMe₂NR (R = ’Pr (1), ’Bu (2), Ph (3) and Xyl (4)) but air- and thermal-sensitivity limited the yields of these potentially useful precursors; only the sterically encumbered ligand system allowed clean reactivity. Magnesium methyl complexes Mg(HC’Bu₂pz)₂SiMe₂NRMe (R = ’Pr (5) and R = Ph (6)) were prepared using an excess of the Grignard reagent Mg’Bu₂ to afford Mg(HC’R’₂pz)₂SiMe₂NR’Bu (R = Me; R = ’Pr (7), ’Bu (8), Ad (9), Ph (10), R’ = ’Bu; R = ’Pr (11), Ph (12)). Protonolysis reactions were used to synthesise magnesium and calcium amide complexes Mg(HC’R’₂pz)₂SiMe₂NR(N(SiMe₂)₂) (R = Me; R = ’Pr (13), ’Bu (14), Ph (15), R’ = ’Bu; R = Ph (16)) or Mg(HC’R’₂pz)₂SiMe₂NR(N(SiMe₂)₂) (R = Me; R = ’Pr (17), ’Bu (18), Ph (19), R’ = ’Bu; R = Ph (20)), and Ca(HC’R’₂pz)₂SiMe₂NR(N(SiMe₂)₂) Li (R’ = Me; L = thf; R = ’Pr (21), ’Bu (22), Ph (23), R’ = ’Bu; L = none; R = Ph (24)). Zinc methyl complexes Zn(HC’R’₂pz)₂SiMe₂NRMe (R’ = Me; R = ’Pr (25), ’Bu (26), Ph (27); R’ = ’Bu; R = Ph (28)) were prepared by reaction of the N₂N’ heteroscorpionate pro-ligand with ZnMe₂. In preliminary studies, magnesium amide complexes 16 and 20 were evaluated as initiators for the ring-opening polymerisation (ROP) of ε-caprolactone (ε-CL) and rac-lactide (rac-LA). Although the overall polymerisation control was poor, 16 and 20 were found to be active initiators.

Substitution of the 3-position of the pyrazolyl ring has been demonstrated to clearly influence complex nuclearity; incorporation of sterically demanding tert-butyl substituents is an efficient way to favour mononuclear systems (Chart 1). This is particularly important in the case of group 2 and related metal complexes which are prone to redistribute via the Schlenk equilibrium and makes the synthesis of well-defined heteroleptic compounds LnMX (L and X = a monoanionic ligand or ligand set) challenging.

Heteroscorpionates, E(Rp₂)₂(X), are a versatile class of tridentate poly(pyrazolyl) ligand where one of the pyrazolyl groups of a classical homoscorpionate, E(Rp₂), is replaced by a different C, N, O or S donor. Chiral classes of heteroscorpionate ligands have also been developed. They have demonstrated a wide range of uses in homogeneous catalysis and supramolecular and bioinorganic chemistry, as well as a supporting ligand set for studying fundamental stoichiometric transformations.

Introduction

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This paper is dedicated in admiration and friendship to Professor F. Geoff N. Cloke FRS.

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Dalton Transactions

Mg, Ca and Zn [N₂N’] heteroscorpionate complexes†‡

Dalton Trans.

− 1885910. For ESI and crystallographic data in CIF or other elec-

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Use of alkaline earth metals is particularly desirable in homogeneous catalysis as they are earth-abundant and possess low toxicity. Furthermore, Hill and co-workers have recently demonstrated that the organometallic calcium complexes [(BDI)CaR]₂ are capable of nucleophilic alkylation of benzene, opening new possibilities for catalytic transformations with suitable ligand design.

Our group has previously reported on the structures and reactivity of group 2 and group 12 scorpionate complexes. Of particular relevance to our current contribution is our previous methodology of nucleophilic attack of the desired amine at the electropositive silicon in HC(Me₂pz)₂SiMe₂Cl in 85% yield. This family has now been extended to include HC(Me₂pz)₂SiMe₂N(H)Pr (R = ́Bu, Ad, Ph). These new pro-ligands were prepared by the same methodology of nucleophilic attack of the desired amine at electropositive silicon in HC(Me₂pz)₂SiMe₂Cl in 85–96% yield. For R = ́Bu and Ad, an excess of amine was used in order to neutralise the HCl produced by generating the ammonium salt, [RNH₃]Cl. For R = Ph, NEt₃ is added to act as a superior Bronsted base and quench the HCl produced; the use of an excess of NH₂Ph is also unfavourable due to its low volatility (b.p. 184 °C at 1 atm).

The 3,5-́Bu and parent 3,5-H systems were initially targeted in order to investigate how modifying the stereoelectronic properties of the pyrazolyl rings would affect the subsequent properties of metal–ligand complexes. The ligand precursor HC(́Bu₂pz)₂SiMe₂Cl was prepared by lithiation of the appropriate bis(pyrazolyl)methane followed by in situ addition of Li(HC(́Bu₂pz)₂) to an excess of SiMe₂Cl₂ (Scheme 1).

Attempts to prepare HC(pz)₂SiMe₂Cl using the same methodology resulted in an intractable mixture of products; deprotonation at the apical sp³ C is stabilised by the inductive effect of the two adjacent α-N atoms whereas the pyrazolyl ring C(5) is sp²-hybridised and is inductively stabilised by a single α-N atom. Use of a base such as ́BuLi facilitates both pathways; coordination to N(1) favours C(5) deprotonation and coordination to N(2) favours apical carbon deprotonation. The mixture of lithiated species is trapped out by the hard SiMe₂Cl₂ electrophile to afford the mixture of substituted products where ring substitution is the major product.

New pro-ligands HC(́Bu₂pz)₂SiMe₂N(H)R (R = ́Pr, ́Bu, Ph, Xyl [(Xyl = 2,6-C₆H₃Me₂)]) were then prepared using procedures related to the 3,5-Me system in excellent yields of 94–99%. The influence of the sterically demanding 3,5-́Bu groups becomes apparent with all but one reaction (that for R = ́Pr) taking place at a higher temperature and over a longer time period than for the analogous 3,5-Me substituted homologues. For R = Xyl, lithiation afforded LiN(Xyl) which is a potent nucleophile and reacts with 1 equivalent of HC(́Bu₂pz)₂SiMe₂Cl in a salt elimination reaction.

The ¹H and ¹³C[¹H] NMR spectra of HC(́Bu₂pz)₂SiMe₂N(H)R (R = ́Pr, ́Bu, Ph, Xyl) all displayed the same type of diagnostic resonances. For example, where R = ́Pr, singlets at 6.99 and 6.01 ppm correspond to the apical HC(́Bu₂pz)₂ and pyrazolyl N₂C₂H₂ prosthes, respectively, and are in a 1:2 ratio, a consequence of C₃ molecular symmetry. Singlets at 1.40 and 1.15 ppm are attributed to the tert-buty1 groups in the 3- and 5-positions. This assignment is analogous to the 3,5-Me system.

### Results and discussion

#### Synthesis of a new family of sterically demanding N₂N’ heteroscorpionate pro-ligands

We have previously reported the modular synthesis of the N₂N’ heteroscorpionate pro-ligand HC(Me₂pz)₂SiMe₂N(H)Pr based on the 3,5-Me pyrazolyl substitution motif. This family has now been extended to include HC(Me₂pz)₂SiMe₂N(H)R (R = ́Bu, Ad, Ph). These new pro-ligands were prepared by the same methodology of nucleophilic attack of the desired amine at electropositive silicon in HC(Me₂pz)₂SiMe₂Cl in 85–96% yield. For R = ́Bu and Ad, an excess of amine was used in order to neutralise the HCl produced by generating the ammonium salt, [RNH₃]Cl. For R = Ph, NEt₃ is added to act as a superior Bronsted base and quench the HCl produced; the use of an excess of NH₂Ph is also unfavourable due to its low volatility (b.p. 184 °C at 1 atm).

The 3,5-́Bu and parent 3,5-H systems were initially targeted in order to investigate how modifying the stereoelectronic properties of the pyrazolyl rings would affect the subsequent properties of metal–ligand complexes. The ligand precursor HC(́Bu₂pz)₂SiMe₂Cl was prepared by lithiation of the appropriate bis(pyrazolyl)methane followed by in situ addition of Li(HC(́Bu₂pz)₂) to an excess of SiMe₂Cl₂ (Scheme 1). The specific order of addition and non-stoichiometric conditions are used to prevent the double displacement of Cl⁻. The solid state structure was determined by a single crystal X-ray diffraction study and is depicted in Fig. S10 of the ESI.

Attempts to prepare HC(pz)₂SiMe₂Cl using the same methodology resulted in an intractable mixture of products; deprotonation at the apical sp³ C is stabilised by the inductive effect of the two adjacent α-N atoms whereas the pyrazolyl ring C(5) is sp²-hybridised and is inductively stabilised by a single α-N atom. Use of a base such as ́BuLi facilitates both pathways; coordination to N(1) favours C(5) deprotonation and coordination to N(2) favours apical carbon deprotonation. The mixture of lithiated species is trapped out by the hard SiMe₂Cl₂ electrophile to afford the mixture of substituted products where ring substitution is the major product.

New pro-ligands HC(́Bu₂pz)₂SiMe₂N(H)R (R = ́Pr, ́Bu, Ph, Xyl) all displayed the same type of diagnostic resonances. For example, where R = ́Pr, singlets at 6.99 and 6.01 ppm correspond to the apical HC(́Bu₂pz)₂ and pyrazolyl N₂C₂H₂ proton, respectively, and are in a 1:2 ratio, a consequence of C₃ molecular symmetry. Singlets at 1.40 and 1.15 ppm are attributed to the tert-buty1 groups in the 3- and 5-positions. This assignment is analogous to the 3,5-Me system.
and is supported by two dimensional $^{13}$C-$^1$H correlation experiments. The SiMe singlet resonance at 0.37 ppm appears at a typically low frequency, as expected for methyl protons shielded by an electropositive Si atom. The molecular structure of HC($^7$Bu$_2$pz)$_2$SiMe$_2$N(H)Ph was also determined by a single crystal X-ray crystallographic study (see Fig. S11, Table S1 of the ESI† for further details). This structure shows an intramolecular interaction between the N(Ph)-H and pyrazolyl N atom, and contrasts for HC($^7$Bu$_2$pz)$_2$SiMe$_2$Cl where the Si atom is in a pseudo trigonal bipyramidal environment, apparently as a result of electron donation from the lone pair of the pyrazolyl N(1) into the $\pi^*$ orbital of the Si–Cl bond.

**Synthesis and characterisation of N$_2$N$'$ heteroscorpionate lithium complexes**

The preparation of alkali metal complexes of the N$_2$N$'$ heteroscorpionate ligands was initially targeted in order to offer the potential of reactions via salt metathesis with appropriate metal salts as well as protonolysis routes. Several heteroscorpionate lithium salts from the NNO$'$, NNCp$'$ and NNCp$''$ heteroscorpionate classes have previously been reported; their syntheses all involve deprotonation at the methylène bridge of the appropriate bis(pyrazolyl)methane followed by nucleophilic attack upon a heterocumulene, α,β unsaturated ester or imine to afford the desired lithium salt. Treatment of the N$_2$N$'$ pro-ligands HC($^7$Bu$_2$pz)$_2$SiMe$_2$N(H)R with an excess of $^7$BuLi at about 78 °C afforded complexes formulated as [Li{HC($^7$Bu$_2$pz)$_2$SiMe$_2$NR}]$_n$ (R = $^7$Pr (1), $^7$Bu (2), Ph (3) and Xyl (4)) in poor to good isolated yields (5–70%) as colourless solids (eqn (1)). When thf is used as a reaction solvent, removal of the volatiles under reduced pressure served to leave no coordinated thf. These complexes are all air- and thermally-sensitive, showing degradation in both solution after a few hours and the solid state after 2 weeks when kept at −30 °C. This sensitivity was also noted in the reported thf-stabilised compound, Li[HC($^7$Bu$_2$pz)$_2$CH$_2$NXyl](thf), which, on standing in the solid state, showed decomposition to the pro-ligand, HC($^7$Bu$_2$pz)$_2$CH$_2$N(H)Xyl. NNC heteroscorpionate lithium salts have most commonly been isolated as donor solvent-stabilised adducts. Examples of dimeric and oligomeric complexes have also been reported but are much rarer; Bassanetti et al. described the preparation and characterisation of [Li{HC($^7$Bu$_2$pz)$_2$CS$_2$}]$_{20b}$ Otero and co-workers reported dimeric (thio)acetamidc NN$'$ complex [Li{HC(R$'$Bu$_2$pz)$_2$CNNR$''$}$_2$] (R$'$ = Me, Ph, $^7$Bu, R$''$ = achiral or chiral moiety, E = O or S) complexes which provided a versatile route into the synthesis of enantioenriched NN$'$ ligands.

The $^1$H NMR spectra of complexes 1–4 all show resonances clearly shifted from those of the pro-ligand values, and the singlet attributed to the NH proton is no longer present. In addition, $^7$Li NMR spectra were recorded at 23 °C and −80 °C for the most thermally robust complex, [Li{HC($^7$Bu$_2$pz)$_2$SiMe$_2$NXyl}]$_n$ (4), to investigate the possibility that the lithium salts existed as stabilised aggregates. However, at both high and low temperature a lone singlet was observed at 2.1 ppm. EI-MS data indicated a molecular ion peak at $m/z = 555$. The IR data were also diagnostic with the absorption attributed to $\nu$(N–H) stretch in the pro-ligand being absent. All complexes were also characterised by elemental analysis. The steric demands of the 3,5-$^7$Bu ligand can stabilise complexes 1–4 with respect to sandwich complexes but it is most likely that these complexes exist as oligonuclear species. Analogous reactions with the corresponding 3,5-Me systems did not afford tractable, well-defined products.

**Synthesis and characterisation of magnesium, calcium and zinc alkyl and amide complexes supported by N$_2$N$'$ ligands**

Treatment of HC($^7$Bu$_2$pz)$_2$SiMe$_2$N(H)R with two-fold excess of MgMeCl afforded Mg[HC($^7$Bu$_2$pz)$_2$SiMe$_2$NR]Me (R = $^7$Pr (5) and R = Ph (6)) in low isolated yields (24 and 7%, respectively) which is partially attributed to the high solubility of these complexes in aromatic and aliphatic solvents. EI-MS data of the crude reaction mixtures were also consistent with the presence of Mg[HC($^7$Bu$_2$pz)$_2$SiMe$_2$NR]Cl (e.g. for R = Ph, a molecular ion peak at $m/z = 579$ was observed). We have previously reported the reaction of HC(Me$_2$pz)$_2$(3,5-$^7$Bu$_2$C$_6$H$_5$OH) with $^6$BuMgCl which afforded Mg[HC($^7$Bu$_2$pz)$_2$Cl$(3,5-$^7$Bu$_2$C$_6$H$_5$O)]$_2$ alongside insoluble precipitates of MgCl$_2$. Formation of similar homolectic sandwich complexes has been reported; in our system, the bulky 3-$^7$Bu substituents act as tetrahedral enforcers’ preventing sandwich formation. Parkin and co-workers reported a detailed study of the competitive alkyl and halide bond metathesis of a variety of Grignard reagents (RMgX) with tris(pyrazolyl)hydroborate (tpb) complexes [H(B$_3$Upz)$_3$]$_2$ (M = Ti, K) to afford Mg[HB($^7$Bupz)$_3$] or Mg[HB($^7$Bupz)$_3$]X. The preference for alkyl or halide complexes was found to be dependent on the nature of the Grignard reagent, steric profile of the tpb ligand, the Schlenk equilibrium and the molar ratio of [H(B$_3$Upz)$_3$]$_2$ to RMgX. Combination of Grignard reagents with alkali metal salts of ligands can be used to prepare metal alkyl complexes successfully.

Mg$_2$R are therefore more appropriate starting materials for the preparation of the alkyl complexes Mg[HC($^7$Bu$_2$pz)$_2$SiMe$_2$NR]R. The reaction of Mg$^6$Bu$_2$ with HC($^7$Bu$_2$pz)$_2$SiMe$_2$N(H)R (R = Me, $^7$Bu) at 23 °C afforded the corresponding magnesium alkyl complexes Mg[HC($^7$Bu$_2$pz)$_2$SiMe$_2$NR]Bu (R’ = Me; R = $^7$Pr (7), $^7$Bu (8), Ad (9), Ph (10), R’ = Bu; R = $^7$Pr (11), Ph (12)) in moderate yields (41–66%) (Scheme 2). Consistent with previous observations, the small scale reaction of HC($^7$Bu$_2$pz)$_2$SiMe$_2$N(H)$^7$Pr with $^6$BuMgCl afforded complex 11 alongside MgCl$_2$.

In the $^1$H NMR spectra of complexes 7–12, the same diagnostic resonances were observed and demonstrated clearly...
Mg\{HC(Me2pz)2SiMe2NPh\}2 has been determined by a single crystal X-ray diffraction study (see ESI Fig. S12 and Table S3†). All hydrogens have been omitted for clarity.

The molecular structures of complexes 5 and 10 were elucidated by single-crystal X-ray diffraction studies and are depicted in Fig. 1 with selected metric parameters in Table 1. In both complexes, the magnesium is in a distorted tetrahedral environment with the \(N_2N'\) heteroscorpionate ligand coordinated facially in a \(\kappa^3\) binding mode. The increased steric demands of 3,5-\(t\)-Bu substituents in complex 5 with respect to 3,5-\(t\)-Me groups in complex 10 are observed through longer M-Npz bond lengths: 2.1799(16) and 2.1911(16) Å, respectively. The M-Npz and M-C bond lengths are comparable to previously reported four-coordinate tris(pyrazolyl)hydroborate (tpb) magnesium methyl complexes,28 the \(N_2N'\) heteroscorpionate complex Mg\{HC\{(Bu2pz)2CNEtN\}Pr\}Me reported by Otero and co-workers,8 and the NNO magnesium butyl complex Mg\{HC\{(Me2pz)2SiMe2NR\}{N(SiMe3)2}\}(R = Me) reported by our group.16

Straightforward protonolysis reactions with 1 equivalent of Mg\{N(SiMe3)2\}2 or Mg\{N(SiHMe2)2\}2 yielded Mg\{HC\{(R'pz)2SiMe2NR\}{N(SiMe3)2}\} (R' = Me; R = 4Pr (13), 4Bu (14), Ph (15), R' = 4Bu; R = 4Bu (16)) or Mg\{HC\{(R'pz)2SiMe2NR\}{N(SiMe3)2}\} (R = Me; R = 4Pr (17), 4Bu (18), Ph (19)). R' = 4Bu; R = Ph (20), respectively, in moderate to good isolated yields (49–77%) (Scheme 3).

The NMR spectra of complexes 13–20 are consistent with \(C_4\) molecular symmetry on the NMR timescale, assuming fast rotation about the Mg–N(SiHMe2)2 and Mg–N(SiMe3)2 bonds. Complexes 16, 17, 19 and 20 have been structurally authenticated in the solid state by single crystal X-ray diffraction studies and are the first examples of \(N_2N'\) heteroscorpionate magnesium amide molecular structures. The molecular structures of complex 16 and 20 are depicted in Fig. 2 with selected metric parameters in Table 2 (see ESI Fig. S13 and S14 and Table S2† for complexes 17 and 19). The approximately tetra-
hedral magnesium centres are $κ^3$ bound to the N$_2$N′ hetero-
scorpionate ligand. The average Mg–Npz bond lengths (16: 
2.192 Å, 20: 2.230 Å) are longer than those in Mg(C(Me$_2$pz)$_3$)$_2$N(SiMe$_3$)$_2$ (2.115 Å) consistent with the changing steric profiles 
of the three compounds; the Mg–N(SiRMe$_2$)$_2$ distances are 
within the expected ranges. The largest N–Mg–N(SiRMe$_2$)$_2$ 
angle and longest Mg–Npz bond in both 16 and 20 are associ-
ated with N(5) due to steric repulsion between the methyl 
groups attached to Si(2) and the phenyl group attached to 
N(5). The Si(3)Me$_3$ group has less steric impact as it is able to 
 lodged into the cleft between the pyrazolyl rings. The smaller 
average Npz–Mg–N(SiRMe$_2$)$_2$ angle in 16 (114.2°) compared to 
that in 20 (120.4°) is consistent with the presence of the less 
bulky SiHMe$_2$ group with respect to SiMe$_3$ group.

Treatment of HC(R′$_2$pz)$_2$SiMe$_2$N(H)R (R′$_2$ = Me, tBu) with 
1 equivalent of Ca[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ afforded Ca[HC 
(R′$_2$pz)$_2$SiMe$_2$NR]N(SiMe$_3$)$_2$(thf) (R = tPr (21), tBu (22), Ph 
(23)) or, in the case of the more sterically demanding ligand 
system, thf-free Ca[HC(tBu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$ (24) in 
good yields (60–74%), alongside 1 equivalent of HN(SiMe$_3$)$_2$ 
(eqn (2)). As previously observed, the reaction of the 3,5-Me 
pro-ligand proceeded at 23 °C whilst the bulkier 3,5-tBu pro-
ligand required elevated temperatures of 60 °C to proceed.

Due to the similar ionic radii of Mg$^{II}$ and Zn$^{II}$ (Mg$^{II}$, C.N. = 
0.570 Å, Zn$^{II}$, C.N. = 0.600 Å), zinc alkyl complexes were tar-
gpered as a comparison to magnesium alkyl complexes.

Protonolysis of the N$_2$N′ heteroscorpionate pro-ligands with 
ZnMe$_2$ afforded Zn[HC(R′$_2$pz)$_2$SiMe$_2$NR]Me (R′$_2$ = Me; R = tPr 
(25), tBu (26), Ph (27), R′ = tBu; R = Ph (28)) in good yields 
(70–85%) (eqn (3)). The preparation of complex 28 required an 
elevated temperature of 60 °C, extended reaction time of 72 h 
and an excess of ZnMe$_2$ in order to drive the reaction cleanly 
to completion.

<table>
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<th>Table 2</th>
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<tr>
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<td>N(5)–Mg(1)–N(6)</td>
<td>138.33(16)</td>
</tr>
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Fig. 2  Thermal displacement ellipsoid drawings (20% probability ellip-
soids) of Mg(HC(tBu$_2$pz)$_2$SiMe$_2$NPh)N(SiHMe$_2$)$_2$ (16, top) and Mg(HC 
(tBu$_2$pz)$_2$SiMe$_2$NPh)N(SiMe$_3$)$_2$ (20, bottom). C-Bound hydrogen atoms 
have been omitted for clarity.
The molecular structures of complexes 25, 27 and 28 were elucidated by single crystal X-ray diffraction studies and are depicted in Fig. 3 with selected metric parameters in Table 3 (see ESI Fig. S15, Table S3) for data regarding complex 25. The zinc centre in complexes 27 and 28 is in a distorted tetrahedral coordination environment. The more acute N(5)–Zn(1)–CCH3 bond angle (27: 135.78(11)° and 28: 125.94(14)°), longer Zn(1)–Npz (27: 2.144(2) and 2.155(2) Å and 28: 2.171(4) and 2.202(4) Å) and Zn(1)–CCH3 bond distances (27: 1.981(3) and 28: 2.041(3) Å) of complex 28 with respect to 27 clearly reflect the differing steric demands of the 3,5-Me and 3,5-tBu pyrazolyl substituents. This trend is also observed in other examples of structurally characterised NNN', NNO',≡N NCCp4 heterocorponate and tris(pyrazolyl)hydroborate complexes. Otero and co-workers reported the only other example of a structurally characterised NNN' zinc methyl complex, Zn[HC(Bu2pz)2CN2Pr2]Me. Here some asymmetry in the Zn–Npz bond lengths is observed (2.236(3) and 2.118(3) Å). The M–Npz and M–CCH3 bond lengths in 28 (2.171(4), 2.202(4) and 1.976(3) Å, respectively) are shorter than those in Mg[HC(Bu2pz)2SiMe2NPr2]Me (1) (2.1799(16), 2.1911(16) and 2.145(2) Å, respectively) in accord with zinc being more polarising and covalent.16b

Ring-opening polymerisation of ε-caprolactone and rac-lactide

One of the aims of this work was to assess the performance of the NNN' heterocorponate amide complexes for the catalytic ring-opening polymerisation (ROP) of ε-caprolactone (ε-CL) and rac-lactide (rac-LA) monomers, in light of the success of related complexes and our previous studies into the ROP of cyclic esters.16b,31 An initial study was undertaken using ε-CL owing to the relative ease of its polymerisation with respect to LA due to the favourable release of 7-membered ring strain.

Initial studies at room temperature in thf or toluene showed the amide complexes 16 and 20 to be highly active for the ROP of ε-CL, reaching full conversion of 100 equivalents of ε-CL in 20–30 minutes in either solvent. The results are summarised in Table 4. Both complexes afforded much higher than expected M_n values by gel permeation chromatography (GPC) ([66 620–89 740 g mol⁻¹], consistent with a much faster rate of propagation than rate of initiation in a coordination-insertion mechanism.12 The observed M_n values are in slightly better agreement with calculated M_n for polymerisations performed in thf. This is likely to be due to the effect of thf competing with the monomer for coordination to the metal centre.

Table 4 Solution polymerisation of ε-CL by Mg[HC(Bu2pz)2SiMe2NPh](N(SiHMe2)2) (16) and Mg[HC(Bu2pz)2SiMe2NPh](N(SiMe3)2) (20)α

<table>
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<tr>
<th>Solvent</th>
<th>Yieldb (%)</th>
<th>Timec</th>
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α [ε-CL]:[catalyst] = 100:1, 3.4 mL solvent at 23 °C. b Isolated yield at 100% conversion. c Minutes. d Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark–Houwink corrections. e Expected M_n (g mol⁻¹) for 1 chain growing per metal centre at 100% conversion, ignoring end groups = 11 414.
thus reducing the relative rate of propagation (compared to that in non-coordinating toluene solvent).

The PDIs (polydispersity indices, $M_n/M_w$) for polymerisations performed in thf are also narrower than corresponding polymerisations performed in toluene (although these are collectively all in the moderate to poor range, 1.67–3.17). This is also likely to be a direct consequence of the coordinative nature of thf compared to toluene. Broad PDIs are well-documented to be the result of intra- and inter-molecular transesterification reactions. It is reasonable to assume that the nature of thf compared to toluene. Broad PDIs are well-documented to be the result of intra- and inter-molecular transesterification reactions. It is reasonable to assume that the presence of a thf molecule bound to a metal coordination site would reduce the likelihood of ‘backbiting’ by a growing polymer chain at the metal centre. Due to the viscous nature of the polymer formed and the short times involved, it was not possible to acquire full kinetic data over the course of each polymerisation, nor was it possible to collect MALDI-ToF analysis of polymer samples due to the high observed $M_n$ values. Coordination-insertion has been deduced to be the most likely mechanism of polymerisation with these complexes.

There are a relatively small number of metal complexes supported by horseradish peroxidase ligands used as initiators for polymerisation of e-CL. Examples include zinc and alcohols, rare earth dialkyls, aluminium alkyls and amidoalkoxides, and magnesium alkyls and amides. We have previously reported the $N_2N$ heteroscorpionate complex $\text{Mg}[(\text{HC}((\text{Bu}_2\text{pz})_2\text{SiMe}_2\text{NPh})\text{N}((\text{SiMe}_3)_2)](3.5-\text{Bu}_2\text{C}_6\text{H}_3\text{O})][\text{N}((\text{SiMe}_3)_2)]$ which afforded complete conversion of 100 equivalents in 1 minute at 20 °C and $R = \text{Pr}, R' = \text{CH}_2\text{SiMe}_3$, 97% conversion of 500 equivalents in 1 minute at 20 °C and $R = \text{Pr}, R' = \text{CH}_2\text{SiMe}_3$, 97% conversion of 500 equivalents in 1 minute at 20 °C and $R = \text{Pr}, R' = \text{CH}_2\text{SiMe}_3$, 97% conversion of 500 equivalents in 1 minute at 20 °C and $R = \text{Pr}, R' = \text{CH}_2\text{SiMe}_3$. The steric demands of the amidoamine group were found to be important, with increased bulk resulting in slower initiators.

Polymerisation studies were next extended to the more challenging monomer, rac-LA. Due to the more encouraging results with e-CL observed using thf as a solvent, it was decided to focus solely on thf-mediated polymerisations. The results are summarised in Table 5.

One of the several interesting contrasts with the e-CL polymerisation results is that the rac-LA polymerisations all required elevated temperatures of 70 °C and extended reaction times, largely due to the unfavourable release of the stable 6-membered ring strain in rac-LA when compared to the less thermodynamically stable 7-membered ring strain in e-CL. The observed $M_n$ values (51 080–51 480 g mol$^{-1}$) are again large, and the relatively broad PDIs (1.45–1.48) are also evident in the rac-LA polymerisations, no doubt due in part to the increased tendency of transesterification side reactions at elevated temperatures. Disappointingly, no stereochemical enrichment in the PLA polymer produced was observed ($P = 0.5$).

Despite the relatively poor polymerisation control demonstrated by the complexes tested, kinetic studies were carried out in some cases to investigate further the polymerisation process. All of the catalysts tested showed first order consumption of rac-LA after an initial induction period. Similar induction periods have also been observed in the ROP of cyclic esters using aluminium, yttrium, iron, tin alkoxides and amides. In these instances the induction period was thought to correspond to a period of ligand rearrangement around the metal centre, in order to allow the monomer access to the coordination sphere. An example semi-logarithmic plot is shown in Fig. 4 for the catalyst Mg[(3-′Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$(16). The apparent rate constant for the polymerisation, $k_{obs}$, was 0.03 (2) min$^{-1}$. This compares with a $k_{obs}$ value of 0.04 (3) min$^{-1}$ for the related catalyst Mg[(3-′Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$(20).

Table 5 Solution polymerisation of rac-LA by Mg[(3-′Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$(16) and Mg[(3-′Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$(20).

<table>
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<th>$\text{Time}^a$</th>
<th>$M_n^c$</th>
<th>$M_n^{(\text{calc})}^d$</th>
<th>$M_w/M_n$</th>
<th>$k_{obs}^a$</th>
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<td>12 972</td>
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<td>0.03 (2)</td>
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<tr>
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<td>51 480</td>
<td>12 799</td>
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<td>0.04 (3)</td>
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<td>14 000</td>
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<td>—</td>
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<td>0.03</td>
<td>12 800</td>
<td>13 100</td>
<td>1.09</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Conditions: [rac-LA] : [catalyst] = 100 : 1; 6.0 mL thf at 70 °C, $b$ % conversion by $^1$H NMR spectroscopy. $^c$ Molecular weights (g mol$^{-1}$) determined from GPC using the appropriate Mark–Houwink corrections.$^d$ Expected $M_n$ (g mol$^{-1}$) for 1 chain growing per metal centre at the % conversion by $^1$H NMR spectroscopy.

Fig. 4 First order semi-logarithmic plot for rac-LA consumption using Mg[(HC(Bu$_2$pz)$_2$SiMe$_2$NPh)(N(SiMe$_3$)$_2$)](16) and Mg[(HC(Bu$_2$pz)$_2$SiMe$_2$NPh)(N(SiMe$_3$)$_2$)](20)
16 and 20 prove to be slow initiators with respect to some related heteroscorpionate systems.\textsuperscript{10d,20g,41} The N$_2$N$^+$ heteroscorpionate magnesium alkyl complex, Mg[HC$\{\text{Bu}_2\text{pz}\}_2\text{SiMe}_2\text{N}(\text{H})\text{R}$ ($R = \text{Pr}, \text{Bu}, \text{Ph}, \text{Xyl}$)] has been developed and the synthesis and characterisation of lithium, magnesium, calcium and zinc complexes, M[HC($R'\text{pz}_2\text{SiMe}_2\text{NR}$)]($X$) ($M = \text{Mg, Zn, Ca; } R' = \text{Me or } \text{Bu, } X = \text{amide or alkyl}$), supported by both 3,5-$\text{Bu}$ and 3,5-$\text{Me}$ substituted N$_2$N$^+$ ligand families has been conducted.

The 3,5-$\text{Bu}$ substituents enabled isolation and characterisation of highly sensitive oligomeric lithium salts, [Li[HC($\text{Bu}_2\text{pz}_2\text{SiMe}_2\text{NR}$)]$_n$], which could not be identified with the 3,5-$\text{Me}$ ligand system. Furthermore, they have also successfully ensured that ML$_2$ bis(ligand) complexes do not form even when the M:L reaction stoichiometry is 2:1; retaining structural integrity and avoiding formation of such sandwich complexes is particularly desirable when considering further potential applications in homogeneous catalysis. Preliminary investigations into the polymerisation of ε-caprolactone and rac-lactide indicated poor control of polymerisation but nonetheless active catalysts.

In general, the N$_2$N$^+$ ligand set seems well suited to stabilising a variety of reactive group 2 and 12 complexes with alkyl and amide substituents and provides a platform for further reactivity or catalytic studies.

Conclusions

A new family of sterically demanding N$_2$N$^+$ heteroscorpionate pro-ligands (HC($\text{Bu}_2\text{pz}_2\text{SiMe}_2\text{N}(\text{H})\text{R}$)($R = \text{Pr}, \text{Bu, Ph, Xyl}$)) has been developed and the synthesis and characterisation of lithium, magnesium, calcium and zinc complexes, M[HC($R'\text{pz}_2\text{SiMe}_2\text{NR}$)]($X$) ($M = \text{Mg, Zn, Ca; } R' = \text{Me or } \text{Bu, } X = \text{amide or alkyl}$), supported by both 3,5-$\text{Bu}$ and 3,5-$\text{Me}$ substituted N$_2$N$^+$ ligand families has been conducted.

Experimental details

General considerations

All manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or drybox procedures. Solvents were pre-dried over activated 4 Å molecular sieves and refluxed over sodium (toluene), sodium/potassium (pentane, diethyl ether), or calcium hydride (dichloromethane) under a dinitrogen atmosphere and collected by distillation. Alternatively, solvents were degassed by sparging with dinitrogen and dried by passing through a column of activated alumina. Deuterated solvents were dried over potassium (C$_2$D$_2$O) or P$_2$O$_5$ (CD$_2$Cl$_2$) distilled under reduced pressure, and stored under dinitrogen in J. Young Teflon valve ampoules. Solution NMR samples were prepared under a dinitrogen atmosphere in a drybox, in 5 mm Wilmad NMR tubes possessing Young’s Teflon valves. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 spectrometer or a Bruker AVII 500 spectrometer. $^1$H and $^{13}$C NMR spectra were referenced internally to residual proto-solvent ($^1$H) or solvent ($^1$C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). $^7$Li NMR spectra are referenced relative to LiCl. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Where necessary, $^1$H and $^{13}$C assignments were assisted by the use of two-dimensional $^1$H–$^1$H and $^1$H–$^{13}$C correlation experiments. IR spectra were recorded on a PerkinElmer 1710 or Nicolet magna 560 FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates. IR data are quoted as wavenumbers (cm$^{-1}$) within the range 4000–400 cm$^{-1}$. Mass spectra were recorded by the mass spectrometry service of the University of Oxford Inorganic Chemistry Laboratory. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University. The compounds H$_2$C($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{N}(\text{H})\text{R}$,\text{Pr}$_2$, \text{Bu$_2$pz}$_2$\text{SiMe}_2\text{N}(\text{H})\text{R}$,\text{Pr}$_{25}$, Zn($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{N}$($\text{H})$($\text{Me}$) were prepared according to literature procedures. ε-Caprolactone was dried over freshly ground CaH$_2$, stored over molecular sieves (4 Å) at 4 °C and distilled before use. rac-Lactide was recrystallized twice from toluene and subsequently sublimed twice prior to use. All other reagents were purchased and used without further purification. Polygon molecular weights ($M_\text{nf}$, $M_\text{w}$) were determined by GPC 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. Tetrahydrofuran (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(e-CL) or poly(rac-LA) in thf were applied for the experimental samples.\textsuperscript{36}

X-ray crystallography

Crystal data collection and processing parameters for HC($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{Cl}, HC($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{N}(\text{H})\text{Ph}, Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$, Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$\text{Me} (5), Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$\text{Me} (10), Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$\text{Me} (16), Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$\text{Me} (17), Mg[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP}$]$_2$\text{Me} (19), Mg[HC($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP}$]$_2$\text{Me} (20), Zn[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$Me (25), Zn[HC($\text{Me}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP$(\text{R})$}]$_2$Me (27), Zn[HC($\text{Bu}_2\text{pz}_2$)$_2$\text{SiMe}_2\text{NP}$]$_2$Me (28) are given in Tables S1–3 and Fig. S10–15 of the ESI†. The structures have been deposited in the Cambridge Structural Database as CCDC 1885910–1885910.‡ Crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly under a stream of cold N$_2$ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.\textsuperscript{41} The structures were solved with SIR2\textsuperscript{35} or Superflip\textsuperscript{46} and further refinements and all other crystallographic calculations were performed using the CRYSALS
program suite. Other details of the structure solution and refinements are given in the ESI.

**Synthetic details and characterising data**

**HCl(Me2pz)2SiMe3N(H)R (R = Bu, Ad) illustrated for R = Ad.**

To a stirred solution of HCl(Me2pz)2SiMe3Cl (4.00 g, 13.5 mmol) in Et2O (60 mL) at 0 °C, was added a solution of NH2Ad (5.09 g, 33.7 mmol) in Et2O (20 mL). The resultant white suspension was allowed to warm to 23 °C and stirred for 14 h. The suspension was filtered, the solid washed with Et2O (3 × 10 mL) and the volatiles removed under reduced pressure to give a white oily solid. The oily solid was recrystallised from hexane (20 mL) at −80 °C, filtered and dried under reduced pressure to afford HCl(Me2pz)2SiMe3N(Ad) as a colourless solid. Yield: 4.71 g (85%). 1H NMR (C6D6, 299.9 MHz, 293 K): δ 6.14 (1 H, s, H(Me2pz)), 5.67 (2 H, s, N2C3HMe2), 2.21 (6 H, s, 3-N2C3HMe2), 1.94 (6 H, s, 5-N2C3HMe2), 1.90 (3 H, m, Ad), 1.67 (6 H, app. d, JHH = 3 Hz, Ad), 1.51 (6 H, m, Ad), 0.54 (6 H, s, SiMe). 13C{1H} NMR (C6D6, 75.4 MHz, 293 K): δ 146.5 (3-N2C3HMe2), 140.2 (5-N2C3HMe2), 106.4 (4-N2C3HMe2), 69.9 (HCl(Me2pz)2), 50.0 (1-Ad), 47.6 36.6 (2,4,6,8,9,10-Ad), 30.4 (3.75 mL, 26.9 mmol). This mixture was slowly added to a stirred solution of HC(Me2pz)2SiMe2Cl (4.00 g, 13.5 mmol) in Et2O (50 mL) at 0 °C. The resultant suspension was allowed to warm to 23 °C and stirred for 1.5 h at 30 °C, filtered and dried under reduced pressure and extracted into pentane (3 × 20 mL). The volatiles were removed under reduced pressure to afford HCl(Me2pz)2SiMe3N(Ad) as a colourless powder. Yield: 18.0 g (96%). Diffraction-quality crystals were grown from a pentane solution. 1H NMR (C6D6, 299.9 MHz, 293 K): δ 6.80 (1 H, s, HCl(Me2pz)2), 6.01 (2 H, s, N2C3H(Bu)2), 1.27 (18 H, s, 3-N2C3H(Bu)2), 1.25 (18 H, s, 5-N2C3H(Bu)2), 0.99 (6 H, s, SiMe). 13C{1H} NMR (C6D6, 75.4 MHz, 293 K): δ 158.8 (3-N2C3H(Bu)2), 152.3 (5-N2C3H(Bu)2), 102.7 (4-N2C3H(Bu)2), 74.0 (HCl(Me2pz)2), 32.9 (3-N2C3H(CMe2)), 31.4 (3-N2C3H(CMe2)), 30.7 (5-N2C3H(CMe2)), 6.7 (SiMe). IR (NaCl plates, Nujol mull, cm⁻¹): 1514 (m), 1503 (m), 1361 (s), 1334 (m), 1319 (w), 1249 (s), 1230 (m), 1203 (w), 1125 (w), 1084 (w), 1059 (w), 1012 (w), 999 (m), 867 (w), 844 (w), 652 (w). EI-MS: m/z = 465 (6%), [M]+, 429 (100%) [M – Cl]+, 372 (82%) [M – SiMe2Cl]+.

Anal. found (calcd for C25H41ClN4Si): C, 64.5 (64.6); H, 9.7 (9.8); N, 11.9 (12.0)%.

**HCl(Me2pz)2SiMe3N(H)Ph illustrated for R = Pr.**

To a stirred solution of HCl(Me2pz)2SiMe3Cl (4.00 g, 8.60 mmol) in Et2O (60 mL) at 0 °C, was added NH2Ph (2.20 g, 25.8 mmol). The resultant colourless suspension was allowed to warm to 23 °C and stirred for 20 h. The suspension was filtered, dried under reduced pressure and extracted into pentane (3 × 20 mL). The volatiles were removed under reduced pressure to afford HCl(Me2pz)2SiMe3N(Ph)Pr as a thick, colourless oil. Yield: 4.03 g (96%). 1H NMR (C6D6, 299.9 MHz, 293 K): δ 6.99 (1 H, s, HCl(Me2pz)2), 6.01 (2 H, s, N2C3H(Bu)2), 3.09 (1 H, sept, JHH = 6.2 Hz, HMe2), 1.40 (18 H, s, 3-N2C3H(Bu)2), 1.15 (18 H, s, 5-N2C3H(Bu)2), 0.96 (6 H, d, JHH = 6.2 Hz, HMe2), 0.37 (6 H, s, SiMe). 13C{1H} NMR (C6D6, 75.4 MHz, 293 K): δ 158.1 (3-N2C3H(Bu)2), 153.9 (5-N2C3H(Bu)2), 152.5 (4-N2C3H(Bu)2), 76.5 (HCl(Me2pz)2), 43.3 (HMe2), 32.4 (3-N2C3H(CMe2)), 30.5 (5-N2C3H(CMe2)), 30.7 (3-N2C3H(CMe2)), 28.3 (HMe2), 0.7 (SiMe). IR (NaCl plates, Nujol mull, cm⁻¹): 3363 (w), 2712 (w), 1536 (s), 1394 (s), 1362 (s), 1343 (s), 1316 (s), 1276 (m), 1213 (s), 1168 (s), 1131 (s), 1067 (m), 1021 (s), 1003 (s), 931 (w), 880 (m), 828 (m), 685 (w). EI-MS: m/z = 487 (75%) [M]+, 430 (100%) [M – N(H)Pr]+. Anal. found (calcd for C23H23N2Si): C, 69.0 (68.9); H, 11.1 (11.0); N, 14.2 (14.4)%.
IR (NaCl plates, Nujol mull, cm$^{-1}$): 1587 (s), 1553 (s), 1489 (w), 1457 (w), 1377 (m), 1291 (m), 1183 (m), 1156 (m), 1129 (m), 1101 (m), 1078 (w), 1050 (w), 1002 (m), and 990 (s). EI-MS: $m/z$ = 429 (100%), [M$^+$(4H)]$^+$.

To a stirred solution of HC($\text{Me}_2$pz)$_2$SiMe$_2$Bu$^-$ (1.41 g, 2.77 mmol) in benzene (25 mL), a 1.0 M solution of BuLi (1.41 mL, 1.41 mmol) was added at $-30^\circ$C. The yellow solution was stirred for 38 h. Volatiles were removed under reduced pressure. The solid was recrystallised from pentane (20 mL) at $-30^\circ$C, filtered and dried under reduced pressure to afford complex 4 as a colourless solid. The crude yellow oil was extracted into pentane (20 mL) and dried under reduced pressure.

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**General procedure for the synthesis of Mg[HC($\text{Me}_2$pz)$_2$SiMe$_2$NR]$^+$Bu$^-$**

To a stirred solution of HC($\text{Me}_2$pz)$_2$SiMe$_2$NR$^-$Bu$^-$ (2.41 g, 3.13 mmol) in benzene (40 mL) and cooled to $-78^\circ$C, BuLi (0.80 mL, 1.36 mmol; 1.6 M in hexanes) was added uniformly and then stirred for 1 h. Volatiles were removed under reduced pressure. The solid was recrystallised from pentane (3 × 5 mL, $-78^\circ$C) and dried under reduced pressure to afford complex 5 as a colourless solid. Yield = 0.48 g (78%). Diffraction-quality crystals were grown from slow diffusion of hexane into a concentrated toluene solution.

**General procedure for the synthesis of Mg[HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR]$^+$Bu$^-$**

To a stirred solution of HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR$^-$Bu$^-$ (2.41 g, 1.41 mmol) in benzene (30 mL), was added Mg[HC($\text{Me}_2$pz)$_2$SiMe$_2$NR]Bu$^-$ (2.41 g, 1.41 mmol; 1.0 M in heptanes). The resultant orange solid was stirred for 12 h. Volatiles were removed under reduced pressure. The solid was recrystallised from pentane (3 × 5 mL, $-78^\circ$C) and dried under reduced pressure to afford complex 5 as a colourless solid. Yield = 0.48 g (78%). Diffraction-quality crystals were grown from slow diffusion of hexane into a concentrated toluene solution.

**General procedure for the synthesis of Mg[HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR]$^+$Bu$^-$**

To a stirred solution of HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR$^-$Bu$^-$ (2.41 g, 1.41 mmol) in benzene (30 mL), was added Mg[HC($\text{Me}_2$pz)$_2$SiMe$_2$NR]Bu$^-$ (2.41 g, 1.41 mmol; 1.0 M in heptanes). The resultant orange solid was stirred for 12 h. Volatiles were removed under reduced pressure. The solid was recrystallised from pentane (3 × 5 mL, $-78^\circ$C) and dried under reduced pressure to afford complex 5 as a colourless solid. Yield = 0.48 g (78%). Diffraction-quality crystals were grown from slow diffusion of hexane into a concentrated toluene solution.

**General procedure for the synthesis of Mg[HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR]$^+$Bu$^-$**

To a stirred solution of HC($\text{Bu}_2$pz)$_2$SiMe$_2$NR$^-$Bu$^-$ (2.41 g, 1.41 mmol) in benzene (30 mL), was added Mg[HC($\text{Me}_2$pz)$_2$SiMe$_2$NR]Bu$^-$ (2.41 g, 1.41 mmol; 1.0 M in heptanes). The resultant orange solid was stirred for 12 h. Volatiles were removed under reduced pressure. The solid was recrystallised from pentane (3 × 5 mL, $-78^\circ$C) and dried under reduced pressure to afford complex 5 as a colourless solid. Yield = 0.48 g (78%). Diffraction-quality crystals were grown from slow diffusion of hexane into a concentrated toluene solution.
(0.50 g, 0.96 mmol) in benzene (30 mL), was added Mg/Bu$_2$ (1.92 mL, 1.92 mmol; 1.0 M in heptanes). The resultant yellow solution was stirred for 18 h. Volatiles were removed under reduced pressure to afford a colourless solid, which was washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure. The solid was recrystallised from pentane (15 mL) at −80 °C, filtered and dried under reduced pressure to afford complex 12 as a colourless solid. Yield = 0.38 g (66%).

$^1$H NMR (CD$_3$OD, 299.9 MHz, 293 K): δ 7.29 (2 H, app. sept, $J_{HH} = 7.3$ Hz, 4-C$_6$H$_5$), 6.62 (1 H, t, $J_{HH} = 7.3$ Hz, 4-C$_6$H$_5$), 5.96 (2 H, s, N$_2$C$_3$H$_2$Bu$_2$), 2.08 (2 H, m, Mg/2-Bu$_2$), 1.83 (2 H, app. sext, $J_{HH} = 7.2$ Hz, Mg/2-Bu$_2$), 1.47 (18 H, s, 3-N$_3$C$_2$H$_2$Bu$_2$), 1.27 (3 H, m, 4-Mg/2-Bu$_2$), 1.10 (18 H, s, 5-N$_2$C$_3$H$_2$Bu$_2$), 0.49 (2 H, m, 1-Mg/2-Bu$_2$), 0.15 (6 H, s, SiMe). $^1$C($^1$H) NMR (CD$_3$OD, 75.4 MHz, 293 K): δ 164.0 (3-N$_3$C$_2$H$_2$Bu$_2$), 157.1 (1-C$_6$H$_5$), 153.8 (5-N$_3$H$_2$C$_3$H$_2$Bu$_2$), 129.0 (3-C$_6$H$_5$), 124.4 (2-C$_6$H$_5$), 116.2 (4-C$_6$H$_5$), 103.2 (4-N$_2$C$_3$H$_2$Bu$_2$), 69.2 (HC($^1$Bu$_2$)$_2$), 33.0 (3-N$_3$H$_2$C$_3$H$_2$Bu$_2$), 32.8 (2-Mg/2-Bu$_2$), 32.6 (3-Mg/2-C$_6$H$_5$), 31.5 (3-C$_6$H$_2$C$_3$H$_2$Bu$_2$), 30.7 (5-N$_3$H$_2$C$_3$H$_2$Bu$_2$), 15.8 (1-Mg/2-Bu$_2$), 14.6 (4-Mg/2-Bu$_2$), 0.33 (SiMe). IR (NaCl plates, Nujol mull, cm$^{-1}$): 1587 (s), 1534 (w), 1486 (s), 1425 (w), 1367 (m), 1284 (s), 1222 (w), 1209 (m), 1173 (w), 1148 (w), 1059 (m), 1027 (m), 995 (m), 957 (s), 871 (w), 825 (m), 800 (s), 791 (m), 764 (m). EI-MS: $m/z$ = 429 (60%) [H$_3$C($^1$Bu$_2$)$_2$]$_2$SiMe$_2$].

To a solution of Mg{N(SiMe$_3$)$_2$}$_2$ (0.300 g, 0.87 mmol) in benzene (15 mL) was added slowly HC($^1$Bu$_2$)$_2$SiMe$_2$N(H)Ph (0.50 g, 0.87 mmol) in benzene (15 mL). The mixture was heated to 60 °C and stirred for 6 h. Volatiles were removed under reduced pressure to give a pale-yellow solid. Recrystallisation from a saturated pentane solution at −30 °C yielded complex 16 as an analytically pure, off-white solid. Yield: 0.30 g (49%).

$^1$H NMR (CD$_3$OD, 299.9 MHz, 293 K): δ 7.24 (2 H, app. t, app. $J_{HH} = 7.9$ Hz, 3-C$_6$H$_5$), 7.01 (2 H, d, $J_{HH} = 7.1$ Hz, 2-C$_6$H$_5$), 6.84 (1 H, app. t, app. $J_{HH} = 7.9$ Hz, 4-C$_6$H$_5$), 6.30 (1 H, s, HC($^1$Bu$_2$)$_2$), 6.03 (2 H, s, N$_2$C$_3$H$_2$Bu$_2$), 5.24 (2 H, sept, $J_{HH} = 7.1$ Hz, SiMe$_2$H), 1.59 (18 H, s, 3-N$_3$C$_3$H$_2$Bu$_2$), 1.11 (18 H, s, 5-N$_2$C$_3$H$_2$Bu$_2$), 0.38 (12 H, s, $J_{HH} = 2.7$ Hz, SiMe$_2$). EI-MS: $m/z$ = 544 (100%) $[M - N(SiMe$_3$)$_2$]^{-}$.

Mg(H($^1$Bu$_2$)$_2$)SiMe$_2$NP[H][N(SiMe$_3$)$_2$] (16). To a solution of Mg{N(SiMe$_3$)$_2$}$_2$ (0.17 g, 0.59 mmol) in benzene (15 mL) was added slowly HC($^1$Bu$_2$)$_2$SiMe$_2$N(H)Ph (0.31 g, 0.59 mmol) in benzene (15 mL). The mixture was heated to 60 °C and stirred for 24 h. Volatiles were removed under reduced pressure to give a pale-yellow solid. Recrystallisation from a saturated pentane solution at −30 °C yielded complex 20 as an analytically pure, off-white solid. Yield: 0.30 g (49%).

$^1$H NMR (CD$_3$OD, 299.9 MHz, 293 K): δ 7.24 (2 H, app. t, app. $J_{HH} = 7.9$ Hz, 3-C$_6$H$_5$), 6.98 (2 H, d, $J_{HH} = 7.1$ Hz, 2-C$_6$H$_5$), 6.83 (1 H, app. t, app. $J_{HH} = 7.9$ Hz, 4-C$_6$H$_5$), 6.21 (1 H, s, HC($^1$Bu$_2$)$_2$), 6.05 (2 H, s, N$_2$C$_3$H$_2$Bu$_2$), 5.24 (2 H, sept, $J_{HH} = 7.1$ Hz, SiMe$_2$H), 1.59 (18 H, s, 3-N$_3$C$_3$H$_2$Bu$_2$), 1.11 (18 H, s, 5-N$_2$C$_3$H$_2$Bu$_2$), 0.38 (12 H, s, $J_{HH} = 2.7$ Hz, SiMe$_2$). EI-MS: $m/z$ = 544 (100%) $[M - N(SiMe$_3$)$_2$]^{-}$.
The complex solution was stirred at 60 °C for 8 h. Volatiles were removed (3-N2C6D6, 299.9 MHz, 293 K): 3.87 (2 H, app. d, app. 3.5 Hz), 7.27 (2 H, t, 3-C6H5), 6.79 (1 H, m, 4-C6H5), 5.23 (2 H, s, N5-C6HMe), 5.00 (1 H, s, H(C6D6)2), 1.97 (6 H, s, 3-N5C6HMe), 1.51 (6 H, s, 5-N5C6HMe), 0.13 (3 H, s, ZnMe), 0.01 (6 H, s, SiMe). 13C{1H} NMR (C6D6, 75.4 MHz, 293 K): δ 162.6 (3-C6H5), 149.4 (3-N5C6HMe), 138.5 (5-N5C6HMe), 129.4 (3-C6H5), 121.1 (2-C6H5), 115.1 (4-C6H5), 105.7 (4-N5C6HMe), 62.8 (H(C6D6)2), 12.8 (3-N5C6HMe), 10.3 (5-N5C6HMe), −1.5 (SiMe), −9.8 (ZnMe). IR (NaCl plates, Nujol mull, cm−1): 2923 (w), 2360 (m), 1576 (s), 1521 (w), 1489 (w), 1457 (s), 1376 (s), 1313 (w), 1248 (m), 1141 (w), 991 (w), 949 (s), 853 (w), 835 (m), 771 (m), 722 (w). EI-MS: m/z = 431 (100%) [M]+, 416 (20%) [M – SiMe]. Anal. found (cared for C30H29N5SiZn): C, 55.4 (55.5); H, 6.8 (6.8); N, 16.1 (16.2)%.

Zn[H(C6Pz)2SiMe2NPh]Me (28). To a stirred solution of HC(PrBu2)pSiMe2N(Ph) (0.50 g, 0.96 mmol) in benzene (30 mL), was added ZnMe2 (1.44 mL, 2.88 mmol; 2.0 M in toluene). The resultant clear, colourless solution was stirred at 60 °C for 3 days. Volatiles were removed under reduced pressure, the solid washed with cold hexanes (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex 28 as a colourless solid. Yield = 0.41 g (72%). Diffraction-quality crystals were grown from a pentane solution. 1H NMR (CD6D6, 299.9 MHz, 293 K): δ 7.32–7.23 (4 H, overlapping 2 × m, 3-C6H5 and 2-C6H5), 6.79 (1 H, t, JHH = 6.5 Hz and JHH = 1.9 Hz, 4-C6H5), 6.5 (1 H, s, H(C6D6)2), 6.01 (2 H, s, N5-C6HMe), 1.45 (18 H, s, 3-N5-C6HMe), 1.12 (18 H, s, 5-N5-C6HMe), 0.41 (3 H, s, ZnMe), 0.18 (6 H, s, SiMe). 13C{1H} NMR (CD6D6, 75.4 MHz, 293 K): δ 162.9 (3-N5-C6HMe), 157.0 (1-C6H5), 153.1 (5-N5-C6HMe), 129.1 (3-C6H5), 123.0 (2-C6H5), 115.8 (4-C6H5), 103.2 (4-N5C6HMe), 68.5 (H(C6D6)2), 32.9 (3-N5C6H(CMe)3), 32.3 (3-N5C6H(CMe)3), 31.6 (3-N5C6H(CMe)3), 30.6 (5-N5C6H(CMe)3), 0.0 (SiMe), −3.4 (ZnMe). IR (NaCl plates, Nujol mull, cm−1): 3143 (w), 3060 (w), 1588 (s), 1557 (m), 1542 (m), 1528 (s), 1489 (s), 1396 (w), 1364 (m), 1357 (m), 1291 (s), 1211 (m), 1178 (w), 1169 (m), 1152 (w), 1130 (w), 1075 (w), 1060 (m), 1023 (m), 993 (m), 961 (s), 867 (w), 843 (s), 793 (m), 765 (m), 751 (m), 709 (w), 692 (m). EI-MS: m/z = 429 (100%) [H(C6Pz)2SiMe2]1+. Anal. found (cared for C39H33N5SiZn): C, 63.8 (63.9); H, 8.8 (8.9); N, 11.6 (11.7)%.

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Conflicts of interest

There are no conflicts to declare.

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Notes and references


