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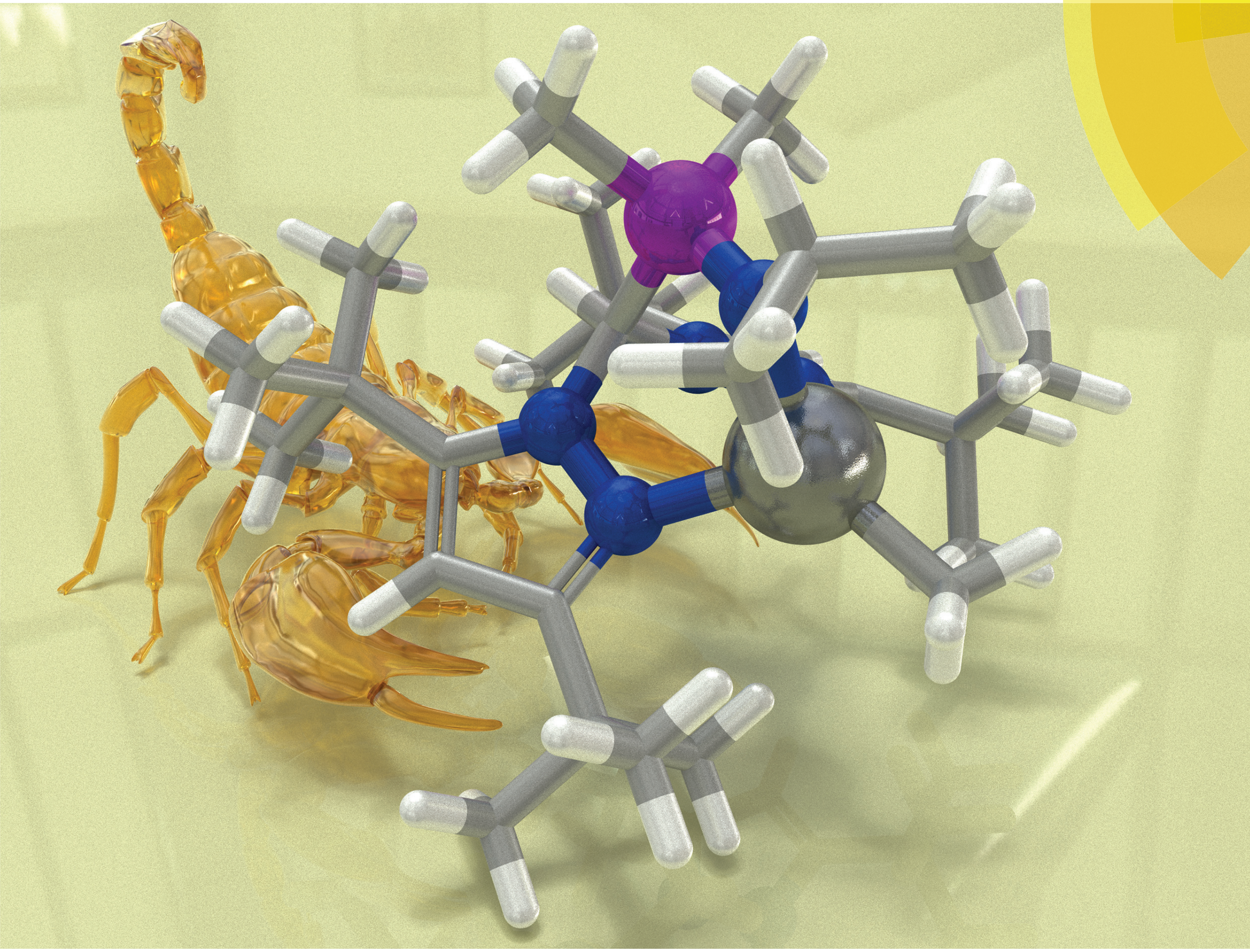

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Magnesium, calcium and zinc [N_2N'] heteroscorpionate complexes†‡

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

A new family of sterically demanding N_2N' heteroscorpionate pro-ligands ($\mathrm{HC(^tBu_2pz)_2SiMe_2N(H)R}$ (R = ^{i}Pr, ^{t}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 3,5-^{t}Bu and 3,5-Me substituted N_2N' ligand families has been conducted. Attempted deprotonation of the pro-ligands with ^{n}BuLi afforded the corresponding lithium salts $\mathrm{Li\{HC(^tBu_2pz)_2SiMe_2NR\}}$ (R = ^{i}Pr (**1**), ^{t}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 $\mathrm{Mg\{HC(^tBu_2pz)_2SiMe_2NR\}Me}$ (R = ^{i}Pr (**5**) and R = Ph (**6**)) were prepared using an excess of the Grignard reagent MeMgCl. Magnesium butyl complexes were synthesised in good yields using the dialkyl precursor $\mathrm{Mg^nBu_2}$ to afford $\mathrm{Mg\{HC(R'_2pz)_2SiMe_2NR\}^nBu}$ (R′ = Me; R = ^{i}Pr (**7**), ^{t}Bu (**8**), Ad (**9**), Ph (**10**). R′ = ^{t}Bu; R = ^{i}Pr (**11**), Ph (**12**)). Protonolylsis reactions were used to synthesise magnesium and calcium amide complexes $\mathrm{Mg\{HC(R'_2pz)_2SiMe_2NR\}\{N(SiHMe_2)_2\}}$ (R′ = Me; R = ^{i}Pr (**13**), ^{t}Bu (**14**), Ph (**15**). R′ = ^{t}Bu; R = Ph (**16**)) or $\mathrm{Mg\{HC(R'_2pz)_2SiMe_2NR\}\{N(SiMe_3)_2\}}$ (R′ = Me; R = ^{i}Pr (**17**), ^{t}Bu (**18**), Ph (**19**). R′ = ^{t}Bu; R = Ph (**20**)), and $\mathrm{Ca\{HC(R'_2pz)_2SiMe_2NR\}\{N(SiMe_2)_2\}}$ (L) (R′ = Me; L = thf; R = ^{i}Pr (**21**), ^{t}Bu (**22**), Ph (**23**). R′ = ^{t}Bu; L = none; R = Ph (**24**). Zinc methyl complexes $\mathrm{Zn\{HC(R'_2pz)_2SiMe_2NR\}Me}$ (R′ = Me; R = ^{i}Pr (**25**), ^{t}Bu (**26**), Ph (**27**). R′ = ^{t}Bu; R = Ph (**28**)) were prepared by reaction of the N_2N' heteroscorpionate pro-ligands with $\mathrm{ZnMe_2}$. 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.

Introduction

Heteroscorpionates, $\mathrm{E(R_npz)_2(X)}$,[1] are a versatile class of tridentate poly(pyrazolyl) ligand where one of the pyrazolyl groups of a classical homoscorpionate, $\mathrm{E(R_npz)_3}$,[2] is replaced by a different C, N, O or S donor. Chiral classes of heteroscorpionate ligands have also been developed.[3] They have demonstrated a wide range of uses in homogeneous catalysis[4] and supramolecular[3c,5] and bioinorganic chemistry,[6] as well as a supporting ligand set for studying fundamental stoichiometric transformations.[7]

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).[8] 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 $\mathrm{L_nMX}$ (L and X = a monoanionic ligand or ligand set) challenging.

Scorpionate ligands have found particular use in the ring-opening polymerisation (ROP) of cyclic esters; Chisholm *et al.* first reported bulky tris(pyrazolyl)hydroborate metal alkoxide complexes $\mathrm{M\{HB(^tBu_2pz)_3\}OR}$ (M = Mg, Zn, Ca) as active polymerisation initiators where stereoselectivity was ascribed to chain-end control.[9] Otero and co-workers have extensively developed heteroscorpionate complexes based on Mg[8a,d,10] and Zn,[10b,11] (κ^3 coordination), demonstrating moderate to good levels of heterotacticity (P_s = 0.78–0.85) or isotacticity (P_i = 0.77), and Al[11c,12] (κ^2 coordination). Cui and co-workers have also reported zwitterionic, achiral N_2N' heteroscorpionate complexes to obtain highly isotactic-biased polylactide (P_i up to 0.85).[13]

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

‡ Electronic supplementary information (ESI) available: Further experimental details, X-ray crystallographic details, CIF files and DFT calculation details. CCDC 1885899–1885910. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04985h

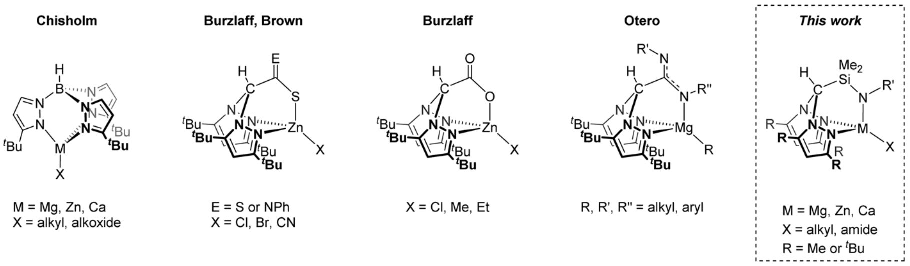


Chart 1 Scorpionate complexes with 3-^{t}Bu substituents.

Use of alkaline earth metals is particularly desirable in homogeneous catalysis as they are earth-abundant and possess low toxicity.[14] 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.[15]

Our group has previously reported on the structures and reactivity of group 2 and group 12 scorpionate complexes.[16] Of particular relevance to our current contribution is our previous communication on the preparation of the N$_2$N′ heteroscorpionate rare earth complex Sc{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_2$ and its ability to polymerise ethylene.[17] Now we have developed a N$_2$N′ heteroscorpionate ligand family with sterically demanding *tert*-butyl substituents in the 3-position to ensure that that only ligation of a single scorpionate ligand occurs, leaving one reactive M–X bond for further controlled reactivity. Herein, we report a study into the synthesis and structure of group 1, 2 and 12 complexes supported by this ligand type.

Results and discussion

Synthesis of a new family of sterically demanding N$_2$N′ heteroscorpionate pro-ligands

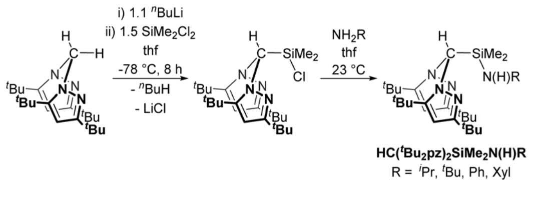
We have previously reported the modular synthesis of the N$_2$N′ heteroscorpionate pro-ligand HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr based on the 3,5-Me pyrazolyl substitution motif.[17] This family has now been extended to include HC(Me$_2$pz)$_2$SiMe$_2$N(H)R (R = ^{t}Bu, Ad, Ph). These new pro-ligands were prepared by the same methodology of nucleophilic attack of the desired amine at electropositive silicon in HC(Me$_2$pz)$_2$SiMe$_2$Cl in 85–96% yield. For R = ^{t}Bu and Ad, an excess of amine was used in order to neutralise the HCl produced by generating the ammonium salt, [RNH$_3$]Cl. For R = Ph, NEt$_3$ is added to act as a superior Brønsted base and quench the HCl produced; the use of an excess of NH$_2$Ph is also unfavourable due to its low volatility (b.p. 184 °C at 1 atm).

The 3,5-^{t}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(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl was prepared by lithiation of the appropriate bis(pyrazolyl)methane followed by *in situ* addition of Li{HC(^{t}Bu$_2$pz)$_2$} to an excess of SiMe$_2$Cl$_2$ (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)$_2$SiMe$_2$Cl using the same methodology resulted in an intractable mixture of products; deprotonation at the apical sp^3 C is stabilised by the inductive effect of the two adjacent α-N atoms whereas the pyrazolyl ring C(5) is sp^2-hybridised and is inductively stabilised by a single α-N atom. Use of a base such as ^{n}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 SiMe$_2$Cl$_2$ electrophile to afford the mixture of substituted products where ring substitution is the major product.[18]

New pro-ligands HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)R (R = ^{i}Pr, ^{t}Bu, Ph, Xyl (Xyl = 2,6-C$_6$H$_3$Me$_2$)) 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-^{t}Bu groups becomes apparent with all but one reaction (that for R = ^{i}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(H)Xyl which is a potent nucleophile and reacts with 1 equivalent of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl in a salt elimination reaction.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)R (R = ^{i}Pr, ^{t}Bu, Ph, Xyl) all displayed the same type of diagnostic resonances. For example, where R = ^{i}Pr, singlets at 6.99 and 6.01 ppm correspond to the apical $\underline{H}$C(^{t}Bu$_2$pz)$_2$ and pyrazolyl N$_2$C$_3$$\underline{H}^{t}Bu_2$ protons, respectively, and are in a 1 : 2 ratio, a consequence of C_s molecular symmetry. Singlets at 1.40 and 1.15 ppm are attributed to the *tert*-butyl groups in the 3- and 5-positions. This assignment is analogous to the 3,5-Me system



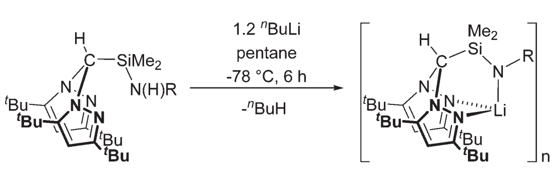
Scheme 1 Synthesis of a new N$_2$N′ heteroscorpionate pro-ligand family. See main text for further details of the second step.

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 $HC(^tBu_2pz)_2SiMe_2N(H)Ph$ 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 that for $HC(^tBu_2pz)_2SiMe_2Cl$ 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 σ* orbital of the Si–Cl bond.

Synthesis and characterisation of N_2N' heteroscorpionate lithium complexes

The preparation of alkali metal complexes of the N_2N' 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,[19] NNS,[8b,19a,20] NNN′[11a,21] and NNCp[22] heteroscorpionate classes have previously been reported; their syntheses all involve deprotonation at the methylene bridge of the appropriate bis(pyrazolyl)methane followed by nucleophilic attack upon a heterocumulene, α,β unsaturated system, aldehyde or imine to afford the desired lithium salt.

Treatment of the N_2N' pro-ligands $HC(^tBu_2pz)_2SiMe_2N(H)R$ with an excess of ^nBuLi at −78 °C afforded complexes formulated as $[Li\{HC(^tBu_2pz)_2SiMe_2NR\}]_n$ (R = ^iPr (**1**), ^tBu (**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, $Li\{HC(^tBu_2pz)_2CH_2NXyl\}(thf)$, which, on standing in the solid state, showed decomposition to the pro-ligand, $HC(^tBu_2pz)_2CH_2N(H)Xyl$.[23] NNE 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 $[Li\{HC(^tBu_2pz)_2CS_2\}]_3$.[20b] Otero and co-workers reported dimeric (thio)acetamidinate NNN′ complexes $[Li\{HC(R'_2pz)_2CNR''E\}]_2$ (R′ = Me, Ph, ^tBu, R″ = achiral or chiral moiety, E = O or S) complexes which provided a versatile route into the synthesis of enantiopure NNN′ ligands.



(1)

R = ^iPr (**1**), ^tBu (**2**), Ph (**3**), Xyl (**4**)

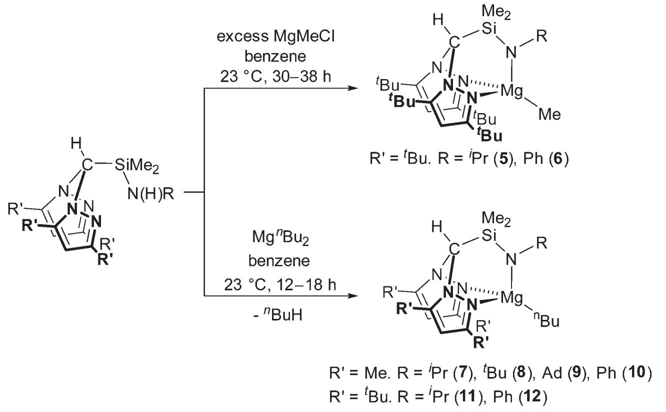
The ^1H NMR spectra of complexes **1–4** all show resonances clearly shifted from those of the pro-ligand values, and the singlet attributed to the N<u>H</u> proton is no longer present. In addition, ^7Li NMR spectra were recorded at 23 °C and −80 °C for the most thermally robust complex, $[Li\{HC(^tBu_2pz)_2SiMe_2NXyl\}]_n$ (**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 ν(N–H) stretch in the pro-ligand being absent. All complexes were also characterised by elemental analysis. The steric demands of the 3,5-^tBu 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_2N' ligands

Treatment of $HC(^tBu_2pz)_2SiMe_2N(H)R$ (R = ^iPr, Ph) with a two-fold excess of MeMgCl afforded $Mg\{HC(^tBu_2pz)_2SiMe_2NR\}Me$ (R = ^iPr (**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 $Mg\{HC(^tBu_2pz)_2SiMe_2NR\}Cl$ (*e.g.* for R = Ph, a molecular ion peak at m/z = 579 was observed). We have previously reported the reaction of $HC(Me_2pz)_2(3,5\text{-}^tBu_2C_6H_3OH)$ with ^nBuMgCl which afforded $Mg\{HC(Me_2pz)_2(3,5\text{-}^tBu_2C_6H_3O)\}_2$ alongside insoluble precipitates of $MgCl_2$ and $[Mg\{HC(Me_2pz)_2(3,5\text{-}^tBu_2C_6H_3O)\}Cl]_n$.[16b] Formation of similar homoleptic sandwich complexes has been reported;[24] in our system, the bulky 3-^tBu substituents act as 'tetrahedral enforcers' preventing sandwich formation.[25] 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 $M\{HB(3\text{-}^tBupz)_3\}$ (M = Tl, K) to afford $Mg\{HB(3\text{-}^tBupz)_3\}R$ or $Mg\{HB(3\text{-}^tBupz)_3\}X$.[26] The preference for alkyl or halide complexes was found to be dependent on the nature of Grignard reagent, steric profile of the tpb ligand, the Schlenk equilibrium and the molar ratio of $M\{HB(3\text{-}^tBupz)_3\}$ to RMgX. Combination of Grignard reagents with alkali metal salts of ligands can be used to prepare metal alkyl complexes successfully.[8d,10a,27]

MgR_2 are therefore more appropriate starting materials for the preparation of the alkyl complexes $Mg\{HC(^tBu_2pz)_2SiMe_2NR'\}R$. The reaction of Mg^nBu_2 with $HC(R'_2pz)_2SiMe_2N(H)R$ (R′ = Me, ^tBu) at 23 °C afforded the corresponding magnesium alkyl complexes $Mg\{HC(R'_2pz)_2SiMe_2NR\}^nBu$ (R′ = Me; R = ^iPr (**7**), ^tBu (**8**), Ad (**9**), Ph (**10**). R′ = ^tBu; R = ^iPr (**11**), Ph (**12**)) in moderate yields (41–66%) (Scheme 2). Consistent with previous observations, the small scale reaction of $HC(^tBu_2pz)_2SiMe_2N(H)^iPr$ with ^nBuMgCl afforded complex **11** alongside $MgCl_2$.

In the ^1H NMR spectra of complexes **7–12**, the same diagnostic resonances were observed and demonstrated clearly



Scheme 2 Synthesis of N$_2$N′ supported magnesium alkyl complexes.

shifted ligand resonances with respect to the pro-ligands. Four multiplets define the ^{n}Bu protons at approximately 2.1, 1.8, 1.3 and 0.4 ppm in all complexes. Two dimensional COSY experiments show that these multiplets represent the 2-^{n}Bu, 3-^{n}Bu, 4-^{n}Bu and 1-^{n}Bu protons respectively.

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$_2$N′ heteroscorpionate ligand coordinated facially in a κ^3 binding mode. The increased steric demands of 3,5-^{t}Bu substituents in complex **5** with respect to 3,5-Me groups in complex **10** are observed through longer M–N$_{pz}$ bond lengths (**5**: 2.1799(16) and 2.1911(16) Å. **10**: 2.1699(19) and 2.138(2) Å) and a more acute N$_{amide}$–Mg–C bond angle (**5**: 122.09(8)° and **10**: 138.18(9)°). The M–N$_{pz}$ and M–C bond lengths are comparable to previously reported four-coordinate tris(pyrazolyl)hydroborate (tpb) magnesium methyl complexes,[28] the NNN′ heteroscorpionate complex Mg{HC(^{t}Bu$_2$pz)$_2$CNEtN^{t}Bu}Me reported by Otero and co-workers,[8d] and the NNO magnesium butyl complex Mg{HC(Me$_2$pz)$_2$(3,5-^{t}Bu$_2$C$_6$H$_3$O)}^{n}Bu reported by our group.[16b]

Straightforward protonolysis reactions with 1 equivalent of the N$_2$N′ heteroscorpionate ligands with 1 equivalent of Mg{N(SiHMe$_2$)$_2$}$_2$ or Mg{N(SiMe$_3$)$_2$}$_2$ yielded Mg{HC(R′$_2$pz)$_2$SiMe$_2$NR}{N(SiHMe$_2$)$_2$} (R′ = Me; R = ^{i}Pr (**13**), ^{t}Bu (**14**), Ph (**15**). R′ = ^{t}Bu; R = ^{t}Bu (**16**)) or Mg{HC(R′$_2$pz)$_2$SiMe$_2$NR}{N(SiMe$_3$)$_2$} (R′ = Me; R = ^{i}Pr (**17**), ^{t}Bu (**18**), Ph (**19**). R′ = ^{t}Bu; R = Ph (**20**)), respectively, in moderate to good isolated yields (49–77%) (Scheme 3). Homoleptic sandwich complexes of the 3,5-Me substituted ligand can be isolated when a 2 : 1 ligand : metal stoichiometry is used, and the molecular structure of Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}$_2$ has been determined by a single crystal X-ray diffraction study (see ESI Fig. S12 and Table S3‡). Using the more sterically demanding 3,5-^{t}Bu substituted ligand, the reactions proceeded cleanly at 60 °C and there was no evidence of sandwich complex formation; indeed, complexes **16** and **20** were the only products of 2 : 1 NMR scale reactions under identical conditions.

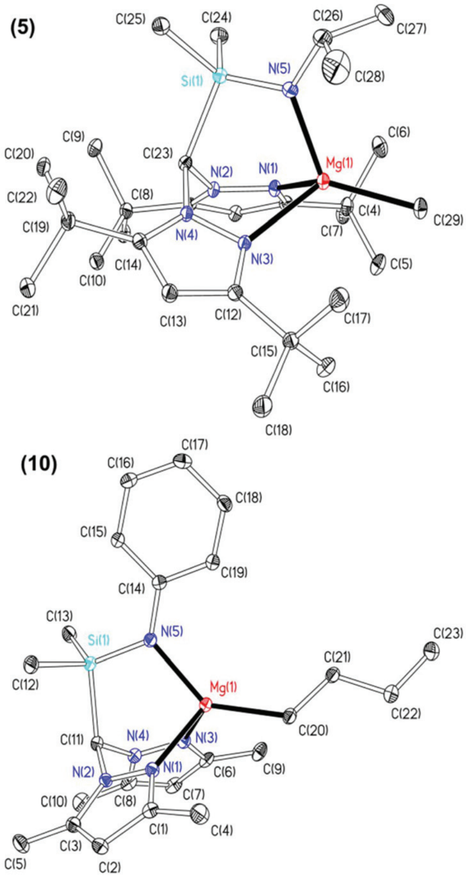
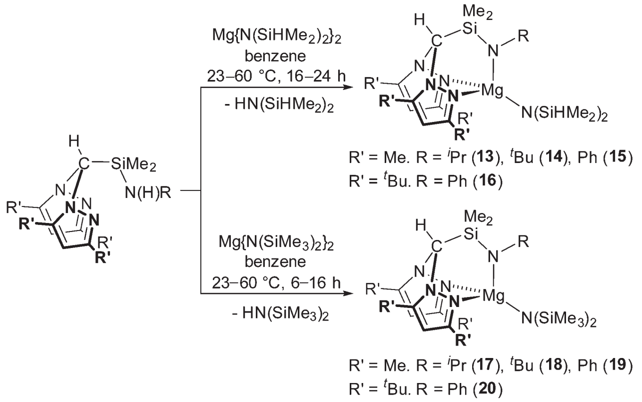


Fig. 1 Thermal displacement ellipsoid drawings (20% probability ellipsoids) of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**, top) and Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}^{n}Bu (**10**, bottom). All hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **5** and **10**

	5	10
Mg(1)–N(1)	2.1799(16)	2.1699(19)
Mg(1)–N(3)	2.1911(16)	2.138(2)
Mg(1)–N(5)	2.0083(17)	2.0436(19)
Mg(1)–C(20)/(29)	2.145(2)	2.144(2)
N(1)–Mg(1)–C(20)/(29)	123.01(7)	112.98(9)
N(3)–Mg(1)–C(20)/(29)	123.88(7)	114.15(9)
N(5)–Mg(1)–C(20)/(29)	122.09(8)	138.18(9)

The NMR spectra of complexes **13–20** are consistent with C_s molecular symmetry on the NMR timescale, assuming fast rotation about the Mg–N(SiHMe$_2$)$_2$ and Mg–N(SiMe$_3$)$_2$ 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$_2$N′ 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-



Scheme 3 Synthesis of N_2N' supported magnesium amide complexes.

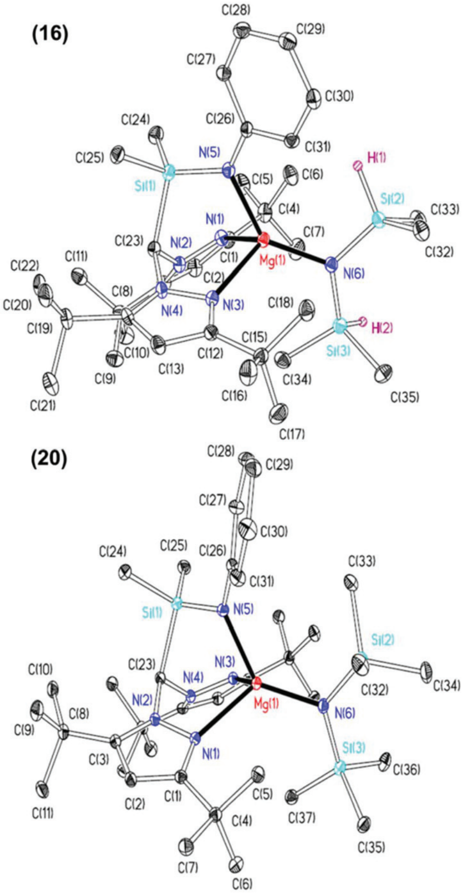
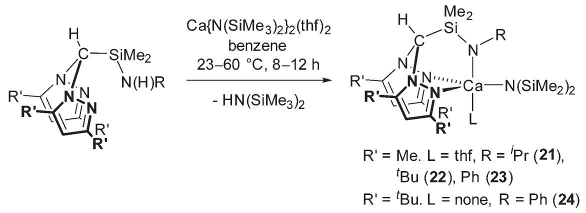


Fig. 2 Thermal displacement ellipsoid drawings (20% probability ellipsoids) of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**16**, top) and Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**, bottom). C-Bound hydrogen atoms have been omitted for clarity.

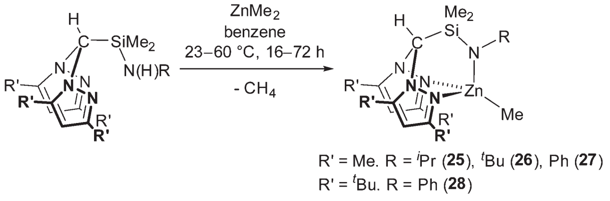
hedral magnesium centres are κ^3 bound to the N_2N' heteroscorpionate ligand. The average Mg–N$_{pz}$ bond lengths (**16:** 2.192 Å. **20:** 2.230 Å) are longer than those in Mg{C(Me$_2$pz)$_3$}{N(SiMe$_3$)$_2$} (2.115 Å) consistent with the changing steric profiles of the three compounds; the Mg–N(SiRMe$_2$)$_2$ distances are within the expected ranges. The largest N–Mg–N(SiRMe$_2$)$_2$ angle and longest Mg–N$_{pz}$ bond in both **16** and **20** are associated 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 lodge into the cleft between the pyrazolyl rings. The smaller average N$_{pz}$–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' = Me, ^{t}Bu) with 1 equivalent of Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$ afforded Ca{HC(Me$_2$pz)$_2$SiMe$_2$NR}{N(SiMe$_2$)$_2$}(thf) (R = ^{i}Pr (**21**), ^{t}Bu (**22**), Ph (**23**)) or, in the case of the more sterically demanding ligand system, thf-free Ca{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_2$)$_2$} (**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-^{t}Bu pro-ligand required elevated temperatures of 60 °C to proceed.



(2)

Due to the similar ionic radii of Mg^{II} and Zn^{II} (Mg$^{II,4\ C.N.}$ = 0.570 Å, Zn$^{II,4\ C.N.}$ = 0.600 Å), zinc alkyl complexes were targeted as a comparison to magnesium alkyl complexes **5–11**. Protonolysis of the N_2N' heteroscorpionate pro-ligands with ZnMe$_2$ afforded Zn{HC(R'$_2$pz)$_2$SiMe$_2$NR}Me (R' = Me; R = ^{i}Pr (**25**), ^{t}Bu (**26**), Ph (**27**). R' = ^{t}Bu; 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.



(3)

Table 2 Selected bond lengths (Å) and angles (°) for complexes **16** and **20**

	16	20
Mg(1)–N(1)	2.167(4)	2.254(2)
Mg(1)–N(3)	2.217(4)	2.206(2)
Mg(1)–N(5)	2.027(4)	2.023(2)
Mg(1)–N(6)	2.002(4)	2.023(2)
N(1)–Mg(1)–N(6)	109.39(15)	123.88(8)
N(3)–Mg(1)–N(6)	119.10(15)	116.93(8)
N(5)–Mg(1)–N(6)	138.33(16)	129.76(8)

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)–C_{CH_3} bond angle (**27**: 135.78(11)° and **28**: 125.94(14)°), longer Zn(1)–N_{pz} (**27**: 2.144(2) and 2.155(2) Å and **28**: 2.171(4) and 2.202(4) Å) and Zn(1)–C_{CH_3} 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-^{t}Bu pyrazolyl substituents. This trend is also observed in other examples of structurally characterised NNN′, NNO,[8e,16b,29] NNCp[4f] heteroscorpionate and tris(pyrazolyl)hydroborate[28b,30] zinc methyl complexes. Otero and co-workers reported the only other example of a structurally characterised NNN′ zinc methyl complex, Zn{HC(^{t}Bu$_2$pz)$_2$CN$_2$^{i}Pr$_2$}Me.[11a] Here some asymmetry in the Zn–N_{pz} bond lengths is observed (2.236(3) and 2.118(3) Å). The M–N_{pz} and M–C_{CH_3} bond lengths in **28** (2.171(4), 2.202(4) and 1.976(3) Å, respectively) are shorter than those in Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**1**) (2.1799(16), 2.1911(16) and 2.145(2) Å, respectively) in accord with zinc being more polarising and covalent.[16b]

Table 3 Selected bond lengths (Å) and angles (°) for complexes **27** and **28**

	27	28
Zn(1)–N(1)	2.144(2)	2.171(4)
Zn(1)–N(3)	2.155(2)	2.202(4)
Zn(1)–N(5)	1.979(2)	1.976(3)
Zn(1)–C(20)	1.981(3)	—
Zn(1)–C(32)		2.041(3)
N(1)–Zn(1)–C(20)	114.48(11)	—
N(1)–Zn(1)–C(32)	—	122.59(14)
N(3)–Zn(1)–C(20)	116.86(11)	—
N(3)–Zn(1)–C(32)	—	120.12(14)
N(5)–Zn(1)–C(20)	135.78(11)	—
N(5)–Zn(1)–C(32)	—	125.94(14)

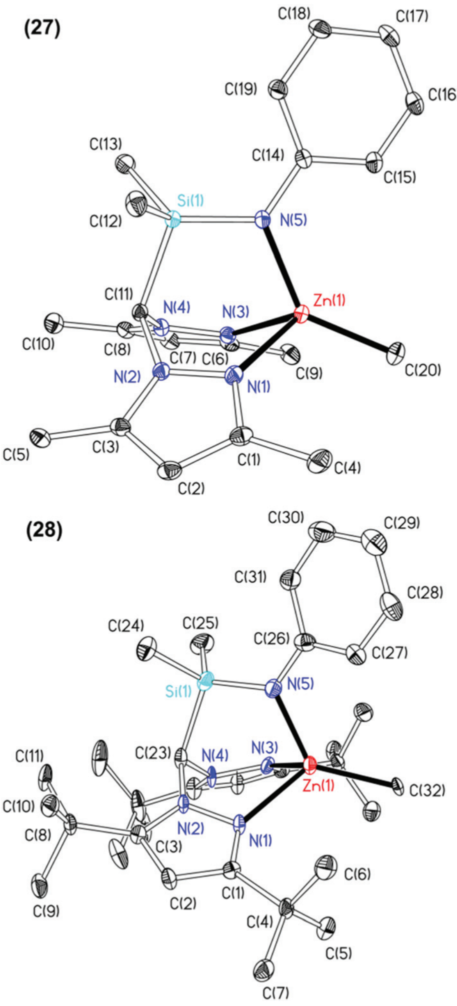


Fig. 3 Thermal displacement ellipsoid drawings (20% probability ellipsoids) of (top) Zn{HC(Me$_2$pz)$_2$SiMe$_2$NPh}Me (**27**, top) and Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (**28**, bottom). All hydrogen atoms have been omitted for clarity.

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

One of the aims of this work was to assess the performance of the NNN′ heteroscorpionate 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.[32] 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(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**16**) and Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**)[a]

	Solvent	Yield[b] (%)	Time[c]	M_n [d,e]	M_w/M_n
16	thf	76	25	71 450	1.86
16	Toluene	79	25	89 740	3.17
20	thf	81	30	66 620	1.67
20	Toluene	73	20	84 840	2.79

[a] [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_w/M_n) 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.[32] 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 heteroscorpionate ligands used as initiators for polymerisation of ε-CL. Examples include zinc amides and alkyls,[11a,b,16b,33] rare earth dialkyls,[34] aluminium alkyls and alkoxides,[35] and magnesium alkyls and amides.[8d,16b,24a] We have previously reported the N_2O heteroscorpionate complex Mg{HC(Me$_2$pz)$_2$(3,5-^{t}Bu$_2$C$_6$H$_3$O)}{N(SiHMe$_2$)$_2$} which afforded complete conversion of 100 equivalents of ε-CL in toluene (but not thf) with high M_n (30 870 g mol^{-1}) and broad PDI (2.76). The related N_2N' magnesium alkyl complexes described by Otero and co-workers, Mg{HC(Me$_2$pz)$_2$CN$_2$R$_2$}R′, afforded rapid polymerisation (*e.g.* R = Et, R′ = CH$_2$SiMe$_3$, 97% conversion of 500 equivalents in 1 minute at 20 °C and R = ^{i}Pr, R′ = CH$_2$SiMe$_3$, 62% at −60 °C) with narrow PDIs (1.41 and 1.12, respectively). The steric demands of the amidinate 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 ε-CL observed using thf as a solvent, it was decided to focus solely on thf-mediated polymerisations. The results are summarised in Table 5.

Table 5 Solution polymerisation of *rac*-LA by Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**16**) and Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**)[a]

	Conv.[b] (%)	Time (h)	M_n [c]	M_n (calcd)[d]	M_w/M_n	k_{obs} (min^{-1})
16	90	1.5	55 080	12 972	1.48	0.03(2)
20	89	0.75	51 480	12 799	1.45	0.04(3)
Ref 8*a*	96	1.0	14 000	13 800	1.09	—
Ref 8*d*	91	0.03	12 800	13 100	1.09	—

[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.[36] [d] Expected M_n (g mol^{-1}) for 1 chain growing per metal centre at the % conversion by ^{1}H NMR spectroscopy.

One of the several interesting contrasts with the ε-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 ε-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 ($P_r \approx 0.5$).

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,[37] yttrium,[38] iron,[39] 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.[40] An example semi-logarithmic plot is shown in Fig. 4 for the catalyst Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**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{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**).

Though there are no other specific examples of scorpionate magnesium amide complexes for lactide polymerisation, complexes **16** and **20** compare well with initiators with respect to the pioneering homoscorpionate tris(pyrazolyl)hydroborate (tpb) magnesium and zinc alkoxides for lactide polymerisation reported by Chisholm.[9c] Kinetic studies under pseudo first order conditions resulted in a value of k_{obs} = 0.039 min^{-1} for Mg{HC(3-^{t}Bupz)$_3$}OEt. When extended to calcium, initiators were found to be two orders of magnitude faster.[9b] Complexes

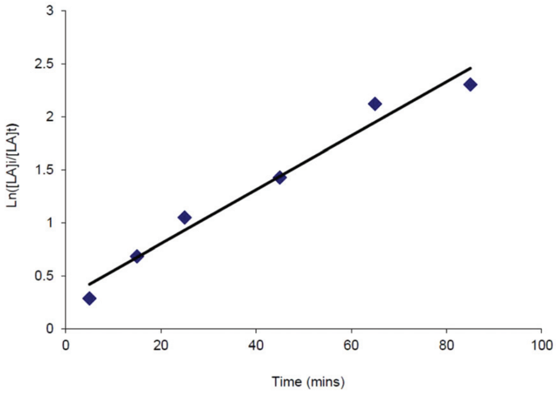


Fig. 4 First order semi-logarithmic plot for *rac*-LA consumption using Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**16**). Conditions [*rac*-LA$_0$] : [**16**] = 100 : 1, 6 mL thf, 70 °C, 0.1 mL aliquots taken at the given intervals.

16 and **20** prove to be slow initiators with respect to some related heteroscorpionate systems.[10a,29a,41] The N_2N' heteroscorpionate magnesium alkyl complex, Mg{HC(^{t}Bu$_2$pz)$_2$CNEtN^{n}Bu}CH$_2$SiMe$_3$, reported by Otero and co-workers was shown to polymerise 200 equivalents of *rac*-LA at 20 °C, reaching with 83% conversion in 2 minutes, to afford heterotactically-enriched PLAs (P_r = 0.70–0.79) with narrow PDIs (1.01–1.05) and no induction period (k_{app} = 2.0 min^{-1}).[8d] These values compare well with the most active magnesium catalysts reported in the literature.[42]

Conclusions

A new family of sterically demanding N_2N' heteroscorpionate pro-ligands (HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)R (R = ^{i}Pr, ^{t}Bu, Ph, Xyl)) has been developed and the synthesis and characterisation of lithium, magnesium, calcium and zinc complexes, M{HC(R'$_2$pz)$_2$SiMe$_2$NR}(X) (M = Mg, Zn, Ca; R' = Me or ^{t}Bu, X = amide or alkyl), supported by both 3,5-^{t}Bu and 3,5-Me substituted N_2N' ligand families has been conducted.

The 3,5-^{t}Bu substituents enabled isolation and characterisation of highly sensitive oligomeric lithium salts, [Li{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NR}]$_n$, which could not be identified with the 3,5-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_2N' 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.

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_6D_6) or P_2O_5 (CD_2Cl_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{^{1}H} NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 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(^{t}Bu$_2$pz)$_2$,[8f] HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr,[17] Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$,[43] Mg{N(SiMe$_3$)$_2$}$_2$ [43] and Mg{N(SiHMe$_2$)$_2$}$_2$ [43] 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. Polymer molecular weights (M_n, M_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(ε-CL) or poly(*rac*-LA) in thf were applied for the experimental samples.[36]

X-ray crystallography

Crystal data collection and processing parameters for HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl, HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph, Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}$_2$, Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}^{n}Bu (**10**), Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}-{N(SiHMe$_2$)$_2$} (**16**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$} (**17**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**19**), Mg{HC(^{t}Bu$_2$pz)$_2$-SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**), Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**25**), Zn{HC(Me$_2$pz)$_2$SiMe$_2$NPh}Me (**27**), Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}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 1885899–1885910.‡ 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 a Enraf-Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[44] The structures were solved with SIR92 [45] or Superflip,[46] and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.[47] Other details of the structure solution and refinements are given in the ESI.‡

Synthetic details and characterising data

$\mathrm{HC(Me_2pz)_2SiMe_2N(H)R}$ (R = ^{t}Bu, Ad) illustrated for R = Ad. To a stirred solution of $\mathrm{HC(Me_2pz)_2SiMe_2Cl}$ (4.00 g, 13.5 mmol) in $\mathrm{Et_2O}$ (60 mL) at 0 °C, was added a solution of $\mathrm{NH_2Ad}$ (5.09 g, 33.7 mmol) in $\mathrm{Et_2O}$ (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 $\mathrm{Et_2O}$ (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 $\mathrm{HC(Me_2pz)_2SiMe_2N(H)Ad}$ as a colourless solid. Yield: 4.71 g (85%). ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz, 293 K): δ 6.14 (1 H, s, $\mathrm{\underline{H}C(Me_2pz)_2}$), 5.67 (2 H, s, $\mathrm{N_2C_3\underline{H}Me_2}$), 2.21 (6 H, s, 3-$\mathrm{N_2C_3H\underline{Me}_2}$), 1.94 (6 H, s, 5-$\mathrm{N_2C_3H\underline{Me}_2}$), 1.90 (3 H, m, Ad), 1.67 (6 H, app. d, app. ${}^3J_{\mathrm{HH}}$ = 3 Hz, Ad), 1.51 (6 H, m, Ad), 0.54 (6 H, s, SiMe). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K): δ 146.5 (3-$\mathrm{N_2\underline{C}_3HMe_2}$), 140.2 (5-$\mathrm{N_2\underline{C}_3HMe_2}$), 106.4 (4-$\mathrm{N_2\underline{C}_3HMe_2}$), 69.9 ($\mathrm{H\underline{C}(Me_2pz)_2}$), 50.0 (1-Ad), 47.6 36.6 (2,4,6,8,9,10-Ad), 30.4 (3,5,7-Ad), 13.8 (3-$\mathrm{N_2C_3H\underline{Me}_2}$), 11.0 (5-$\mathrm{N_2C_3H\underline{Me}_2}$), 2.2 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3342 (m) 2951 (s), 2853 (m), 1560 (s), 1461 (w), 1376 (m), 1258 (m), 1096 (m), 1018 (w), 967 (m), 822 (w), 799 (m), 721 (w). EI-MS: m/z = 411 (100%) $[\mathrm{M}]^+$, 316 (10%) $[\mathrm{M-Me_2pz}]^+$. Anal. found (calcd. for $\mathrm{C_{23}H_{37}N_5Si}$): C, 67.0 (67.1); H, 9.1 (9.1); N, 17.0 (17.0)%.

$\mathrm{HC(Me_2pz)_2SiMe_2N(H)Ph}$. To a stirred solution of $\mathrm{NH_2Ph}$ (1.23 mL, 13.5 mmol) in $\mathrm{Et_2O}$ (20 mL), was added $\mathrm{NEt_3}$ (3.75 mL, 26.9 mmol). This mixture was slowly added to a stirred solution of $\mathrm{HC(Me_2pz)_2SiMe_2Cl}$ (4.00 g, 13.5 mmol) in $\mathrm{Et_2O}$ (50 mL) at 0 °C. The resultant suspension was allowed to warm to 23 °C and stirred for 14 h. The suspension was filtered, the solid washed with $\mathrm{Et_2O}$ (3 × 10 mL) and the volatiles removed under reduced pressure to afford a yellow oily solid which was extracted into pentane (3 × 10 mL) and dried under reduced pressure. The colourless solid was recrystallised from pentane (20 mL) at −30 °C, filtered and dried under reduced pressure to afford $\mathrm{HC(Me_2pz)_2SiMe_2N(H)Ph}$ as a colourless solid. Yield: 4.52 g (95%). ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz, 293 K): δ 7.08 (2 H, t, ${}^3J_{\mathrm{HH}}$ = 7.9 Hz, 3-$\mathrm{C_6H_5}$), 6.74 (1 H, t, ${}^3J_{\mathrm{HH}}$ = 7.5 Hz, 4-$\mathrm{C_6H_5}$), 6.61 (2 H, d, ${}^3J_{\mathrm{HH}}$ = 7.5 Hz, 2-$\mathrm{C_6H_5}$), 6.02 (1 H, s, $\mathrm{\underline{H}C(Me_2pz)_2}$), 5.61 (2 H, s, $\mathrm{N_2C_3\underline{H}Me_2}$), 4.34 (1 H, s, NH), 2.16 (6 H, s, 3-$\mathrm{N_2C_3H\underline{Me}_2}$), 1.73 (6 H, s, 5-$\mathrm{N_2C_3H\underline{Me}_2}$), 0.60 (6 H, s, SiMe). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K): δ 147.7 (3-$\mathrm{N_2\underline{C}_3HMe_2}$), 142.9 (1-$\mathrm{C_6H_5}$), 139.9 (5-$\mathrm{N_2\underline{C}_3HMe_2}$), 129.8 (3-$\mathrm{C_6H_5}$), 118.7 (4-$\mathrm{C_6H_5}$), 117.5 (2-$\mathrm{C_6H_5}$), 106.7 (4-$\mathrm{N_2\underline{C}_3HMe_2}$), 67.0 ($\mathrm{H\underline{C}(Me_2pz)_2}$), 13.9 (3-$\mathrm{N_2C_3H\underline{Me}_2}$), 10.6 (5-$\mathrm{N_2C_3H\underline{Me}_2}$), −0.2 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3345 (m), 2930 (s), 2731 (m), 1602 (w), 1552 (s), 1463 (m), 1376 (w), 1296 (m), 1246 (m), 1145 (w), 1110 (w), 1025 (s), 972 (m), 907 (m), 807 (s), 787 (s), 747 (m), 691 (m). EI-MS: m/z = 353 (100%) $[\mathrm{M}]^+$. Anal. found (calcd for $\mathrm{C_{19}H_{27}N_5Si}$): C, 64.5 (64.5); H, 7.7 (7.7); N, 19.7 (19.7)%.

$\mathrm{HC({}^tBu_2pz)_2SiMe_2Cl}$. To a stirred solution of $\mathrm{H_2C({}^tBu_2pz)_2}$ (15.0 g, 40.3 mmol) in THF (150 mL) at −78 °C, was added ^{n}BuLi (27.7 mL, 44.3 mmol; 1.6 M in hexanes) over a period of 20 minutes. The resultant yellow slurry was stirred for 12 h at −78 °C to afford $\mathrm{LiHC({}^tBu_2pz)_2}$ which was reacted on *in situ*. To a stirred solution of $\mathrm{SiMe_2Cl_2}$ (7.28 mL, 60.4 mmol) in thf (100 mL) at −78 °C was added $\mathrm{LiHC({}^tBu_2pz)_2}$ over a period of 20 minutes. The resultant pale-yellow solution was stirred for 8 h at −78 °C. The volatiles were removed under reduced pressure to give a colourless, oily solid which was extracted into pentane (3 × 40 mL) and dried under reduced pressure. The oily solid was recrystallised from pentane (120 mL) at −80 °C, filtered and dried under reduced pressure to afford $\mathrm{HC({}^tBu_2pz)_2SiMe_2Cl}$ as a colourless powder. Yield: 18.0 g (96%). Diffraction-quality crystals were grown from a pentane solution. ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz, 293 K): δ 6.80 (1 H, s, $\mathrm{\underline{H}C({}^tBu_2pz)_2}$), 6.01 (2 H, s, $\mathrm{N_2C_3\underline{H}{}^tBu_2}$), 1.27 (18 H, s, 3-$\mathrm{N_2C_3H\underline{{}^tBu}_2}$), 1.25 (18 H, s, 5-$\mathrm{N_2C_3H\underline{{}^tBu}_2}$), 0.99 (6 H, s, SiMe). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K): δ 158.8 (3-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 152.3 (5-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 102.7 (4-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 74.0 ($\mathrm{H\underline{C}({}^tBu_2pz)_2}$), 32.9 (3-$\mathrm{N_2C_3H(\underline{C}Me_3)_2}$), 32.1 (5-$\mathrm{N_2C_3H(\underline{C}Me_3)_2}$), 31.4 (3-$\mathrm{N_2C_3H(C\underline{Me}_3)_2}$), 30.7 (5-$\mathrm{N_2C_3H(C\underline{Me}_3)_2}$), 6.7 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 1541 (m), 1531 (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%) $[\mathrm{M}]^+$, 429 (100%) $[\mathrm{M-Cl}]^+$, 372 (82%) $[\mathrm{M-SiMe_2Cl}]^+$. Anal. found (calcd for $\mathrm{C_{25}H_{45}ClN_4Si}$): C, 64.5 (64.6); H, 9.7 (9.8); N, 11.9 (12.0)%.

$\mathrm{HC({}^tBu_2pz)_2SiMe_2N(H)R}$ (R = ^{i}Pr or ^{t}Bu) illustrated for R = ^{i}Pr. To a stirred solution of $\mathrm{HC({}^tBu_2pz)_2SiMe_2Cl}$ (4.00 g, 8.60 mmol) in $\mathrm{Et_2O}$ (60 mL) at 0 °C, was added $\mathrm{NH_2{}^iPr}$ (2.20 mL, 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 $\mathrm{HC({}^tBu_2pz)_2SiMe_2N(H){}^iPr}$ as a thick, colourless oil. Yield: 4.03 g (96%). ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz, 293 K): δ 6.99 (1 H, s, $\mathrm{\underline{H}C({}^tBu_2pz)_2}$), 6.01 (2 H, s, $\mathrm{N_2C_3\underline{H}{}^tBu_2}$), 3.09 (1 H, sept, ${}^3J_{\mathrm{HH}}$ = 6.2 Hz, $\mathrm{\underline{H}CMe_2}$), 1.40 (18 H, s, 3-$\mathrm{N_2C_3H\underline{{}^tBu}_2}$), 1.15 (18 H, s, 5-$\mathrm{N_2C_3H\underline{{}^tBu}_2}$), 0.96 (6 H, d, ${}^3J_{\mathrm{HH}}$ = 6.2 Hz, $\mathrm{HC\underline{Me}_2}$), 0.37 (6 H, s, SiMe). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 75.4 MHz, 293 K): δ 158.1 (3-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 153.9 (5-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 102.5 (4-$\mathrm{N_2\underline{C}_3H{}^tBu_2}$), 76.5 ($\mathrm{H\underline{C}({}^tBu_2pz)_2}$), 43.3 ($\mathrm{H\underline{C}Me_2}$), 32.4 (3-$\mathrm{N_2C_3H(\underline{C}Me_3)_2}$), 32.2 (5-$\mathrm{N_2C_3H(\underline{C}Me_3)_2}$), 30.8 (3-$\mathrm{N_2C_3H(C\underline{Me}_3)_2}$), 30.5 (5-$\mathrm{N_2C_3H(C\underline{Me}_3)_2}$), 28.3 ($\mathrm{HC\underline{Me}_2}$), 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%) $[\mathrm{M}]^+$, 430 (100%) $[\mathrm{M-N(H){}^iPr}]^+$. Anal. found (calcd for $\mathrm{C_{28}H_{53}N_5Si}$): C, 69.0 (68.9); H, 11.1 (11.0); N, 14.2 (14.4)%.

$\mathrm{HC({}^tBu_2pz)_2SiMe_2N(H)Xyl}$. To a stirred solution of $\mathrm{NH_2Xyl}$ (1.06 mL, 8.60 mmol) in $\mathrm{Et_2O}$ (20 mL) at −78 °C, was added ^{n}BuLi (5.37 mL, 8.60 mmol; 1.6 M in hexanes) over a 10 minutes period. The resultant colourless suspension was stirred for 1.5 h at −78 °C to afford LiN(H)Xyl which was reacted on *in situ*. To a stirred solution of $\mathrm{HC({}^tBu_2pz)_2SiMe_2Cl}$ (4.00 g, 8.60 mmol) in $\mathrm{Et_2O}$ (50 mL) at −78 °C, was added LiN

(H)Xyl over a 10 minutes period. The resultant yellow suspension was allowed to warm to 23 °C and stirred for 22 h. The suspension was filtered, the solid washed with Et_2O (3 × 10 mL) and the volatiles removed under reduced pressure to give a yellow oily solid which was extracted into pentane (3 × 10 mL) and dried under reduced pressure. The solid was recrystallised from pentane (20 mL) at −30 °C, filtered and dried under reduced pressure to afford $HC(^tBu_2pz)_2SiMe_2N(H)Xyl$ as an orange solid. Yield: 4.44 g (94%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.18 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 7.00 (2 H, d, $^3J_{HH}$ = 7.0 Hz, 3-$C_6H_3Me_2$), 6.87 (1 H, t, $^3J_{HH}$ = 7.0 Hz, 4-$C_6H_3Me_2$), 6.02 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 3.55 (1 H, s, NH), 2.12 (6 H, s, $C_6H_3\underline{Me}_2$), 1.35 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.12 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.42 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 158.3 (3-$N_2\underline{C}_3H^tBu_2$), 154.2 (5-$N_2\underline{C}_3H^tBu_2$), 143.2 (1-$C_6H_3Me_2$), 133.0 (2-$C_6H_3Me_2$), 128.7 (3-$C_6H_3Me_2$), 122.7 (4-$C_6H_3Me_2$), 102.9 (4-$N_2C_3H^tBu_2$), 75.4 ($H\underline{C}(^tBu_2pz)_2$), 32.4 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.2 (5-$N_2C_3H(\underline{C}Me_3)_2$), 30.8 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.4 (5-$N_2C_3H(C\underline{Me}_3)_2$), 19.7 ($C_6H_3\underline{Me}_2$), 1.3 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3319 (w), 1593 (w), 1537 (m), 1392 (w), 1363 (m), 1341 (m), 1316 (m), 1276 (w), 1237 (m), 1215 (m), 1176 (w), 1159 (w), 1129 (w), 1094 (w), 1070 (w), 1001 (m), 902 (m), 877 (m), 828 (m), 792 (s), 759 (s). EI-MS: *m*/*z* = 429 (100%) $[M - N(H)C_6H_3Me_2]^+$. Anal. found (calcd for $C_{33}H_{55}N_5Si$): C, 72.2 (72.1); H, 10.2 (10.1); N, 12.7 (12.6)%.

[Li{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NR}]$_n$ (R = ^{i}Pr (1), ^{t}Bu (2), Ph (3), Xyl (4)) illustrated for R = Xyl (4). $HC(^tBu_2pz)_2SiMe_2N(H)Xyl$ (0.620 g, 1.13 mmol) was dissolved in pentane (40 mL) and cooled to −78 °C. ^nBuLi (0.840 mL, 1.36 mmol; 1.6 M in hexanes) was diluted with pentane (10 mL), similarly cooled and then added dropwise to the pro-ligand solution to afford a colourless precipitate. The reaction mixture was stirred for 6 h and then allowed to stand overnight, whereby crystallisation took place. The colourless solid was filtered off, washed with cold (−78 °C) pentane (3 × 10 mL) and dried under reduced pressure to afford complex **4** as a colourless powder. Yield: 0.44 g (70%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): 7.39 (2 H, d, $^3J_{HH}$ = 7.4 Hz, 3-$C_6H_3Me_2$), 6.89 (1 H, t, $^3J_{HH}$ = 7.4 Hz, 4-$C_6H_3Me_2$), 6.56 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 5.91 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 2.39 (6 H, s, $C_6H_3\underline{Me}_2$), 1.23 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 1.16 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 0.13 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): 159.7 (3-$N_2\underline{C}_3H^tBu_2$), 157.2 (1-$\underline{C}_6H_3Me_2$), 153.2 (5-$N_2\underline{C}_3H^tBu_2$), 131.8 (2,6-$\underline{C}_6H_3Me_2$), 127.9 (3-$\underline{C}_6H_3Me_2$), 115.4 (4-$C_6H_3Me_2$), 101.3 (4-$N_2C_3H^tBu_2$), 71.5 ($H\underline{C}(^tBu_2pz)_2$), 32.8 (5-$N_2C_3H(\underline{C}Me_3)_2$), 32.0 (3-$N_2C_3H(\underline{C}Me_3)_2$), 31.6 (5-$N_2C_3H(C\underline{Me}_3)_2$), 30.3 (3-$N_2C_3H(C\underline{Me}_3)_2$), 21.01 ($C_6H_3\underline{Me}_2$), 3.24 (SiMe) ppm. ^7Li NMR (toluene-d_8, 194.3 MHz, 218 and 293 K): 2.1 ($N\underline{Li}$) ppm. IR (NaCl plates, Nujol): 1587 (w), 1544 (m), 1418 (s), 1359 (m), 1297 (s), 1235 (m), 1207 (m), 1097 (w), 1064 (w), 1023 (w), 994 (m), 982 (m), 829 (m), 821 (m), 776 (m), 755 (s), 709 (w), 693 (w), 615 (w), 530 (w) cm^{-1}. EI-MS: *m*/*z*: 555 $[M]^+$ (8%), 429 $[M - N(Li)Xyl]^+$ (100%), 371 $[M - SiMe_2N(Li)Xyl]^+$ (8%), Anal. Found (calcd for $C_{33}H_{54}LiN_5Si$): C, 71.4 (71.3); H, 9.7 (9.8); N, 12.7 (12.6)%.

Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NR}Me (R = ^{i}Pr (5), Ph (6)) illustrated for R = ^{i}Pr (5). To a stirred solution of $HC(^tBu_2pz)_2SiMe_2N(H)^iPr$ (0.500 g, 1.02 mmol) in benzene (30 mL), was added MeMgCl (1.02 mL, 3.07 mmol; 3.0 M in thf). The resultant yellow solution was stirred for 38 h. Volatiles were removed under reduced pressure to give a white solid, which was extracted into pentane (3 × 10 mL) 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 **5** as a colourless solid. Yield = 0.35 g (65%). Diffraction-quality crystals were grown from a saturated pentane solution. ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 6.52 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 5.96 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 3.61 (1 H, sept, $^3J_{HH}$ = 6.3 Hz, $\underline{H}CMe_2$), 1.54 (6 H, d, $^3J_{HH}$ = 6.4 Hz, $HC\underline{Me}_2$), 1.52 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.16 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.05 (6 H, s, SiMe), −0.20 (3 H, s, MgMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 163.2 (3-$N_2\underline{C}_3H^tBu_2$), 153.1 (5-$N_2\underline{C}_3H^tBu_2$), 102.9 (4-$N_2\underline{C}_3H^tBu_2$), 69.8 ($H\underline{C}(^tBu_2pz)_2$), 46.8 ($H\underline{C}Me_2$), 33.0 ($HC\underline{Me}_2$), 32.3 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.1 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.6 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.7 (5-$N_2C_3H(C\underline{Me}_3)_2$), 1.2 (SiMe), −3.6 (MgMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2795 (w), 2599 (w), 1615 (w), 1526 (m), 1423 (m), 1348 (m), 1305 (m), 1244 (m), 1220 (m), 1209 (m), 1139 (m), 1111 (m), 1061 (s), 1029 (m), 899 (m), 829 (m), 755 (s), 733 (w), 710 (w). EI-MS: *m*/*z* = 429 (100%) $[HC(^tBu_2pz)_2SiMe_2]^+$. Anal. found (calcd for $C_{29}H_{55}MgN_5Si$): C, 65.9 (66.2); H, 10.4 (10.5); N, 13.1 (13.3)%.

General procedure for the synthesis of Mg{HC(Me$_2$pz)$_2$SiMe$_2$NR}^{n}Bu (R = ^{i}Pr (7), ^{t}Bu (8), Ad (9), Ph (10)) illustrated for R = Ph (10). To a stirred solution of $HC(Me_2pz)_2SiMe_2N(H)Ph$ (0.500 g, 1.41 mmol) in benzene (30 mL), was added Mg^nBu_2 (1.41 mL, 1.41 mmol; 1.0 M in heptanes). The resultant orange solution was stirred for 12 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex **10** as a bright orange solid. Yield = 0.48 g (78%). Diffraction-quality crystals were grown from slow diffusion of hexane into a concentrated toluene solution. ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.35 (2 H, app. t, app. $^3J_{HH}$ = 7.8 Hz, 3-C_6H_5), 7.28 (2 H, app. d, app. $^3J_{HH}$ = 7.2 Hz, 2-C_6H_5), 6.79 (1 H, t, $^3J_{HH}$ = 6.9 Hz, 4-C_6H_5), 5.28 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.04 (1 H, s, $\underline{H}C(Me_2pz)_2$), 2.27 (2 H, m, 2-Mg^nBu), 2.09 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.90 (2 H, m, $^3J_{HH}$ = 7.2 Hz, 3-Mg^nBu), 1.57 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.30 (3 H, t, $^3J_{HH}$ = 7.3 Hz, 4-Mg^nBu), 0.49 (2 H, m, 1-Mg^nBu), 0.05 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 157.7 (1-C_6H_5), 150.4 (3-$N_2\underline{C}_3HMe_2$), 139.5 (5-$N_2\underline{C}_3HMe_2$), 129.5 (3-C_6H_5), 121.7 (2-C_6H_5), 115.0 (4-C_6H_5), 105.9 (4-$N_2\underline{C}_3HMe_2$), 63.3 ($H\underline{C}(Me_2pz)_2$), 33.4 (2-Mg^nBu), 32.7 (3-Mg^nBu), 14.7 (1-Mg^nBu), 12.9 (3-$N_2C_3H\underline{Me}_2$), 10.3 (5-$N_2C_3H\underline{Me}_2$), 8.8 (4-Mg^nBu), −1.4 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2925 (s), 2361 (m), 1587 (s), 1553 (s), 1489 (w), 1457 (w), 1377 (m), 1291 (m), 1183 (m), 1078 (s), 1047 (s), 990 (s), 942 (s), 827 (m), 804 (w), 768 (s), 738 (m), 694 (m). EI-MS: *m*/*z* = 376 (100%) $[M - {}^nBu]^+$. Anal. found (calcd for $C_{23}H_{35}MgN_5Si$): C, 63.7 (63.7); H, 8.1 (8.1); N, 16.2 (16.1)%.

General procedure for the synthesis of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NR}^{n}Bu (R = ^{i}Pr (11), Ph (12)) illustrated for R = Ph (12). To a stirred solution of $HC(^tBu_2pz)_2SiMe_2N(H)Ph$

(0.50 g, 0.96 mmol) in benzene (30 mL), was added Mg^nBu_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%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.29 (2 H, app. t, app. $^3J_{HH}$ = 7.6 Hz, 3-C_6H_5), 7.2 (2 H, d, $^3J_{HH}$ = 8.2 Hz, 2-C_6H_5), 6.82 (1 H, t, $^3J_{HH}$ = 7.3 Hz, 4-C_6H_5), 6.52 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 5.96 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 2.08 (2 H, m, 2-$Mg^nBu$), 1.83 (2 H, app. sext, app. $^3J_{HH}$ = 7.2 Hz, 3-Mg^nBu), 1.47 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.27 (3 H, m, 4-$Mg^nBu$), 1.10 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.49 (2 H, m, 1-$Mg^nBu$), 0.15 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 164.0 (3-$N_2\underline{C}_3H^tBu_2$), 157.1 (1-$C_6H_5$), 153.8 (5-$N_2\underline{C}_3H^tBu_2$), 129.0 (3-$C_6H_5$), 124.4 (2-$C_6H_5$), 116.2 (4-$C_6H_5$), 103.2 (4-$N_2\underline{C}_3H^tBu_2$), 69.2 ($H\underline{C}(^tBu_2pz)_2$), 33.0 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.8 (2-$Mg^nBu$), 32.6 (3-$Mg^nBu$), 32.2 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.5 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.7 (5-$N_2C_3H(C\underline{Me}_3)_2$), 15.8 (1-$Mg^nBu$), 14.6 (4-$Mg^nBu$), 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%) $[HC(^tBu_2pz)_2SiMe_2]^+$. Anal. found (calcd for $C_{35}H_{59}MgN_5Si$): C, 69.7 (69.8); H, 9.9 (9.9); N, 11.7 (11.6)%.

$Mg\{HC(Me_2pz)_2SiMe_2NR\}\{N(SiHMe_2)_2\}$ (R = ^{i}Pr (13), ^{t}Bu (14), Ph (15)) illustrated for R = ^{i}Pr (13). To a stirred solution of $Mg\{N(SiHMe_2)_2\}_2$ (0.450 g, 1.56 mmol) in benzene (20 mL), was added a solution of $HC(Me_2pz)_2SiMe_2N(H)^iPr$ (0.500 g, 1.56 mmol) in benzene (20 mL). The resultant orange solution was stirred for 16 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex **13** as an orange solid. Yield = 0.50 g (68%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 5.41 (2 H, sept, $^3J_{HH}$ = 3.0 Hz, $N(Si\underline{H}Me_2)_2$), 5.34 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.00 (1 H, s, $\underline{H}C(Me_2pz)_2$), 3.85 (1 H, sept, $^3J_{HH}$ = 6.3 Hz, $\underline{H}CMe_2$), 2.36 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.55 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.49 (6 H, d, $^3J_{HH}$ = 6.3 Hz, $HC\underline{Me}_2$), 0.55 (12 H, d, $^3J_{HH}$ = 3.4 Hz, $N(SiH\underline{Me}_2)_2$), −0.90 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 149.9 (3-$N_2\underline{C}_3HMe_2$), 139.4 (5-$N_2\underline{C}_3HMe_2$), 105.8 (4-$N_2\underline{C}_3HMe_2$), 63.8 ($H\underline{C}(Me_2pz)_2$), 47.5 ($H\underline{C}Me_2$), 31.5 ($HC\underline{Me}_2$), 13.8 (3-$N_2C_3H\underline{Me}_2$), 10.4 (5-$N_2C_3H\underline{Me}_2$), 4.6 ($N(SiHMe_2)_2$), 1.3 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2925 (s), 2361 (m), 2067 (w), 1553 (m), 1506 (w), 1459 (s), 1377 (s), 1315 (s), 1280 (m), 1242 (s), 1164 (s), 1132 (m), 1045 (m), 945 (m), 892 (s), 826 (m), 800 (m), 756 (m), 729 (m). EI-MS: m/z = 474 (100%) $[M]^+$, 342 (20%) $[M - N(SiHMe_2)_2]^+$. Anal. found (calcd for $C_{20}H_{42}MgN_6Si_3$): C, 50.2 (50.5); H, 8.7 (8.9); N, 17.6 (17.7)%.

$Mg\{HC(^tBu_2pz)_2SiMe_2NPh\}\{N(SiHMe_2)_2\}$ (16). To a solution of $Mg\{N(SiHMe_2)_2\}_2$ (0.17 g, 0.59 mmol) in benzene (15 mL) was added slowly $HC(^tBu_2pz)_2SiMe_2N(H)Ph$ (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 **16** as an analytically pure, off-white solid. Yield: 0.21 g (53%). Diffraction-quality crystals were grown from a saturated pentane solution at −30 °C. ^1H NMR (C_6D_6, 299.9 MHz, 293 K): 7.26 (2 H, app. t, app. $^3J_{HH}$ = 7.9 Hz, 3-C_6H_5), 7.01 (2 H, d, $^3J_{HH}$ = 7.1 Hz, 2-C_6H_5), 6.84 (1 H, app. t, app. $^3J_{HH}$ = 7.9 Hz, 4-C_6H_5), 6.30 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 6.03 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 5.24 (2 H, sept, $^3J_{HH}$ = 2.7 Hz, $SiMe_2\underline{H}$), 1.59 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.11 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.38 (12 H, $^3J_{HH}$ = 2.7 Hz, $SiH\underline{Me}_2$), −0.05 (6 H, s, $Si\underline{Me}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): 165.5 (3-$N_2\underline{C}_3H^tBu_2$), 156.8 (1-$C_6H_5$), 155.9 (5-$N_2\underline{C}_3H^tBu_2$), 128.8 (3-$C_6H_5$), 126.4 (2-$C_6H_5$), 117.5 (4-$C_6H_5$), 104.7 (4-$N_2\underline{C}_3H^tBu_2$), 69.0 ($H\underline{C}(^tBu_2pz)_2$), 33.1 (5-$N_2C_3H(\underline{C}Me_3)_2$), 33.0 (3-$N_2C_3H(\underline{C}Me_3)_2$), 31.6 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.4 (3-$N_2C_3H(\underline{C}Me_3)_2$), 3.7 ($SiH\underline{Me}_2$), 0.4 ($Si\underline{Me}_2$). IR (NaCl plates, Nujol, cm^{-1}): 2854 (s), 2058 (m), 1586 (w), 1261 (w), 1093 (s), 976 (w), 886 (m), 759 (w). EI-MS: m/z 676 $[M - Mg\{N(SiHMe_2)_2\} - NPh]^+$ (20%). Anal. found (calcd for $C_{35}H_{64}MgN_6Si_3$): C, 62.0 (62.1); H, 9.6 (9.5); N, 12.4 (12.4)%.

$Mg\{HC(Me_2pz)_2SiMe_2NR\}\{N(SiMe_3)_2\}$ (R = ^{i}Pr (17), ^{t}Bu (18), Ph (19)) illustrated for R = ^{i}Pr (17). To a stirred solution of $Mg\{N(SiMe_3)_2\}_2$ (0.480 g, 1.41 mmol) in benzene (20 mL), was added a solution of $HC(Me_2pz)_2SiMe_2N(H)Ph$ (0.500 g, 1.41 mmol) in benzene (20 mL). The resultant yellow solution was stirred for 14 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex **17** as an pale-orange solid. Yield = 0.58 g (77%). Diffraction-quality crystals were grown from slow diffusion of diethyl ether into a concentrated toluene solution. ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.30 (2 H, t, $^3J_{HH}$ = 7.6 Hz, 3-C_6H_5), 6.98 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2-C_6H_5), 6.83 (1 H, t, $^3J_{HH}$ = 7.2 Hz, 4-C_6H_5), 5.37 (2 H, s, $N_2C_3\underline{H}Me_2$), 4.99 (1 H, s, $\underline{H}C(Me_2pz)_2$), 2.42 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.49 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 0.41 (18 H, s, $N(SiMe_3)_2$), −0.13 (SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 157.0 (1-C_6H_5), 150.6 (3-$N_2\underline{C}_3HMe_2$), 140.0 (5-$N_2\underline{C}_3HMe_2$), 129.2 (3-C_6H_5), 125.3 (2-C_6H_5), 117.0 (4-C_6H_5), 106.2 (4-$N_2\underline{C}_3HMe_2$), 62.9 ($H\underline{C}(Me_2pz)_2$), 14.1 (3-$N_2C_3H\underline{Me}_2$), 10.4 (5-$N_2C_3H\underline{Me}_2$), 6.3 ($N(SiMe_3)_2$), −1.1 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2972 (w), 2728 (m), 1581 (s), 1521 (s), 1419 (m), 1377 (s), 1312 (s), 1243 (s), 1172 (m), 1096 (s), 1005 (s), 959 (m), 882 (m), 826 (s), 773 (m). EI-MS: m/z = 536 (40%) $[M]^+$, 376 (85%) $[M - N(SiMe_3)_2]^+$. Anal. found (calcd for $C_{25}H_{44}MgN_6Si_3$): C, 55.8 (55.9); H, 8.3 (8.3); N, 15.6 (15.7)%.

$Mg\{HC(^tBu_2pz)_2SiMe_2NPh\}\{N(SiMe_3)_2\}$ (20). To a solution of $Mg\{N(SiMe_3)_2\}_2$ (0.300 g, 0.87 mmol) in benzene (15 mL) was added slowly $HC(^tBu_2pz)_2SiMe_2N(H)Ph$ (0.45 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 **20** as an analytically pure, off-white solid. Yield: 0.30 g (49%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): 7.24 (2 H, app. t, app. $^3J_{HH}$ = 7.9 Hz, 3-C_6H_5), 6.98 (2 H, d, $^3J_{HH}$ = 7.1 Hz, 2-C_6H_5), 6.83 (1 H, app. t, app. $^3J_{HH}$ = 7.9 Hz, 4-C_6H_5), 6.21 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 6.05 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 1.61 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.07 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.36 (18 H, $Si\underline{Me}_3$), −0.08 (6 H, s, $Si\underline{Me}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): 165.4 (3-$N_2\underline{C}_3H^tBu_2$), 156.8 (1-$C_6H_5$), 156.3 (5-$N_2\underline{C}_3H^tBu_2$), 128.4 (3-$C_6H_5$), 126.9 (2-$C_6H_5$), 118.0 (4-$C_6H_5$), 104.8 (4-$N_2\underline{C}_3H^tBu_2$), 68.5 ($H\underline{C}(^tBu_2pz)_2$), 32.8 (5-$N_2C_3H(\underline{C}Me_3)_2$), 32.6 (3-$N_2C_3H(\underline{C}Me_3)_2$), 31.4 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.2 (3-$N_2C_3H(\underline{C}Me_3)_2$), 6.1 ($Si\underline{Me}_3$), 0.2 ($Si\underline{Me}_2$). IR (NaCl plates, Nujol, cm^{-1}): 2726 (s), 2670 (m), 1589 (w), 1549 (w), 1196 (w), 1167 (w), 1067 (s), 951 (w), 837 (m). Anal. found (calcd for $C_{37}H_{68}MgN_6Si_3$): C, 59.1 (63.0); H, 9.2 (9.7); N, 11.2 (11.9)%. This was the best of several attempts using recrystallised material.

Ca{HC(Me$_2$pz)$_2$SiMe$_2$NR}{N(SiMe$_3$)$_2$}(thf) (R = ^{i}Pr (21), ^{t}Bu (22), Ph (23)) illustrated for R = Ph (23). To a stirred solution of $Ca\{N(SiMe_3)_2\}_2(thf)_2$ (0.710 g, 1.41 mmol) in benzene (20 mL), was added a solution of $HC(Me_2pz)_2SiMe_2N(H)Ph$ (0.500 g, 1.41 mmol) in benzene (20 mL). The resultant dark orange solution was stirred for 12 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex **23** as a brown solid. Yield = 0.65 g (74%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.27 (2 H, t, $^3J_{HH}$ = 7.6 Hz, 3-C_6H_5), 6.87 (2 H, app. d, app. $^3J_{HH}$ = 7.8 Hz, 2-C_6H_5), 6.71 (1 H, app. t, app. $^3J_{HH}$ = 7.6 Hz, 4-C_6H_5), 5.45 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.20 (1 H, s, $\underline{H}C(Me_2pz)_2$), 3.74 (4 H, br s, $OC\underline{H}_2CH_2$), 2.38 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.72 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.34 (4 H, br s, $OCH_2C\underline{H}_2$), 0.45 (18 H, s, $N(SiMe_3)_2$), 0.07 (SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 158.8 (1-C_6H_5), 150.2 (3-$N_2\underline{C}_3HMe_2$), 139.9 (5-$N_2\underline{C}_3HMe_2$), 129.2 (3-C_6H_5), 121.7 (2-C_6H_5), 113.9 (4-C_6H_5), 106.4 (4-$N_2\underline{C}_3HMe_2$), 68.7 ($O\underline{C}H_2CH_2$), 64.7 ($H\underline{C}(Me_2pz)_2$), 25.4 ($OCH_2\underline{C}H_2$), 14.4 (3-$N_2C_3H\underline{Me}_2$), 11.0 (5-$N_2C_3H\underline{Me}_2$), 6.0 ($N(SiMe_3)_2$), 2.9 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2854 (w), 2361 (m), 1576 (s), 1521 (s), 1496 (w), 1458 (s), 1377 (s), 1259 (m), 1019 (m), 975 (m), 881 (m), 837 (w), 722 (s), 667 (m). EI-MS: m/z = 460 (25%) $[M - NPh(thf)]^+$. Anal. found (calcd for $C_{29}H_{51}CaN_6OSi_3$): C, 55.7 (55.8); H, 8.2 (8.2); N, 13.4 (13.5)%.

Ca{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (24). To a stirred solution of $Ca\{N(SiMe_3)_2\}_2(thf)_2$ (0.48 g, 0.96 mmol) in benzene (20 mL), was added a solution of $HC(^tBu_2pz)_2SiMe_2N(H)Ph$ (0.50 g, 0.96 mmol) in benzene (20 mL). The resultant orange solution was stirred at 60 °C for 8 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 × 5 mL, −78 °C) and dried under reduced pressure to afford complex **24** as a pale-yellow solid. Yield = 0.41 g (60%). ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.25 (2 H, t, $^3J_{HH}$ = 7.6 Hz, 3-C_6H_5), 6.79–6.76 (3 H, overlapping t and d, $^3J_{HH}$ = 7.9 Hz and $^3J_{HH}$ = 7.1 Hz, 4-C_6H_5 and 2-C_6H_5), 6.27 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 5.99 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 1.44 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.17 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.28 (18 H, s, $N(SiMe_3)_2$), 0.03 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 164.1 (3-$N_2\underline{C}_3H^tBu_2$), 157.1 (1-$C_6H_5$), 156.6 (5-$N_2\underline{C}_3H^tBu_2$), 129.6 (3-$C_6H_5$), 125.3 (2-$C_6H_5$), 116.7 (4-$C_6H_5$), 103.9 (4-$N_2\underline{C}_3H^tBu_2$), 71.1 ($H\underline{C}(^tBu_2pz)_2$), 33.3 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.8 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.8 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.9 (5-$N_2C_3H(C\underline{Me}_3)_2$), 5.8 ($N(SiMe_3)_2$), 1.4 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 1584 (w), 1549 (w), 1533 (w), 1364 (m), 1197 (w), 1171 (w), 1046 (s), 995 (w), 955 (m), 879 (m), 703 (w), 589 (w). EI-MS: m/z = 429 (40%) $[HC(^tBu_2pz)_2SiMe_2]^+$. Anal. found (calcd for $C_{37}H_{68}CaN_6Si_3$): C, 61.6 (61.6); H, 9.4 (9.5); N, 11.7 (11.7)%.

Zn{HC(Me$_2$pz)$_2$SiMe$_2$NR}Me (R = ^{i}Pr (25), ^{t}Bu (26), Ph (27)) illustrated for R = Ph (27). To a stirred solution of $HC(Me_2pz)_2SiMe_2N(H)Ph$ (0.500 g, 1.41 mmol) in benzene (30 mL), was added $ZnMe_2$ (2.11 mL, 4.23 mmol; 2.0 M in toluene). The resultant light yellow solution was stirred for 15 h. 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 **27** as a white solid. Yield = 0.52 g (85%). Diffraction-quality crystals were grown from slow diffusion of diethyl ether into a concentrated toluene solution. ^1H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.40–7.31 (4 H, overlapping 2 × m, 3-C_6H_5 and 2-C_6H_5), 6.81 (1 H, m, 4-C_6H_5), 5.23 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.00 (1 H, s, $\underline{H}C(Me_2pz)_2$), 1.97 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.51 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 0.13 (3 H, s, ZnMe), 0.01 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 163.6 (1-C_6H_5), 149.4 (3-$N_2\underline{C}_3HMe_2$), 138.5 (5-$N_2\underline{C}_3HMe_2$), 129.4 (3-C_6H_5), 121.1 (2-C_6H_5), 115.1 (4-C_6H_5), 105.7 (4-$N_2\underline{C}_3HMe_2$), 62.8 ($H\underline{C}(Me_2pz)_2$), 12.8 (3-$N_2C_3H\underline{Me}_2$), 10.3 (5-$N_2C_3H\underline{Me}_2$), −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), 1290 (s), 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%) $[M - Me]^+$. Anal. found (calcd for $C_{20}H_{29}N_5SiZn$): C, 55.4 (55.5); H, 6.8 (6.8); N, 16.1 (16.2)%.

Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (28). To a stirred solution of $HC(^tBu_2pz)_2SiMe_2N(H)Ph$ (0.50 g, 0.96 mmol) in benzene (30 mL), was added $ZnMe_2$ (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 (C_6D_6, 299.9 MHz, 293 K): δ 7.32–7.23 (4 H, overlapping 2 × m, 3-C_6H_5 and 2-C_6H_5), 6.79 (1 H, tt, $^3J_{HH}$ = 6.5 Hz and $^4J_{HH}$ = 1.9 Hz, 4-C_6H_5), 6.5 (1 H, s, $\underline{H}C(^tBu_2pz)_2$), 6.01 (2 H, s, $N_2C_3\underline{H}^tBu_2$), 1.45 (18 H, s, 3-$N_2C_3H^t\underline{Bu}_2$), 1.12 (18 H, s, 5-$N_2C_3H^t\underline{Bu}_2$), 0.41 (3 H, s, ZnMe), 0.18 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): δ 162.9 (3-$N_2\underline{C}_3H^tBu_2$), 157.0 (1-$C_6H_5$), 153.1 (5-$N_2\underline{C}_3H^tBu_2$), 129.1 (3-$C_6H_5$), 123.0 (2-$C_6H_5$), 115.8 (4-$C_6H_5$), 103.2 (4-$N_2\underline{C}_3H^tBu_2$), 68.5 ($H\underline{C}(^tBu_2pz)_2$), 32.9 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.3 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.6 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.6 (5-$N_2C_3H(C\underline{Me}_3)_2$), 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%) $[HC(^tBu_2pz)_2SiMe_2]^+$. Anal. found (calcd for $C_{32}H_{53}N_5SiZn$): C, 63.8 (63.9); H, 8.8 (8.9); N, 11.6 (11.7)%.

Conflicts of interest

There are no conflicts to declare.

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