

A novel transformation of a zirconium imido compound and the development of a new class of N₃ donor heteroscorpionate ligand†

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Reaction of the dimeric zirconium imido compound $[\text{Zr}_2(\mu\text{-NAr})_2\text{Cl}_4(\text{THF})_4]$ with tris(3,5-dimethylpyrazolyl)methyl silane very selectively gave $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{Si}(\text{Me})\text{NAr}\}\text{Cl}_3]$ (**1**), a highly active pre-catalyst for ethylene polymerisation; a more general and versatile route to N₃ donor heteroscorpionate compounds was achieved *via* the protio ligand $(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})\text{N}(\text{H})^i\text{Pr}$ for which neutral and cationic organometallic Group 3 and 4 derivatives are reported (Ar = 2,6-C₆H₃ⁱPr₂).

Poly(pyrazolyl) based (“scorpionate”) ligands (see Chart 1) are widely exploited over a broad range of transition metal applications including organometallic, catalytic, bioinorganic and supramolecular contexts.^{1–6} The axially symmetric anionic tris(pyrazolyl)borates (*e.g.*, **I**)^{3,4} and their neutral analogues the tris(pyrazolyl)alkanes (*e.g.*, **II**)^{1,5} are complemented by the anionic “heteroscorpionates” of type **III** in which a neutral pyrazolyl ring has been formally substituted by an “arm” bearing an anionic donor “X” which is almost exclusively a CS₂, CO₂, aryloxide or alkoxide functional group.^{2,6,7} Despite the extensive later transition metal literature for heteroscorpionates **III**, there are only a few reports of the use of such ligands in Group 4,^{8–11} and only one of these features any applications in either organometallic chemistry or catalysis.⁸ Only one (very recent) report of the use of N₂O or N₂S heteroscorpionates in Group 3 coordination chemistry has appeared.¹²

Although monoanionic N₂O and N₂S donor ligands **III** themselves are extremely well known, no amide-based analogue (X = anionic N donor) has yet been reported. Chelating di- and tri-anionic polyamide ligands have been immensely important in advancing the fundamental and catalytic chemistry of the early

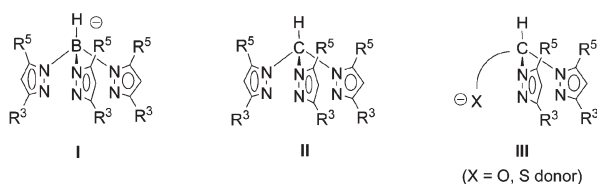


Chart 1 Important poly(pyrazolyl) ligands (illustrated for the more common ring 3,5-disubstituted systems).

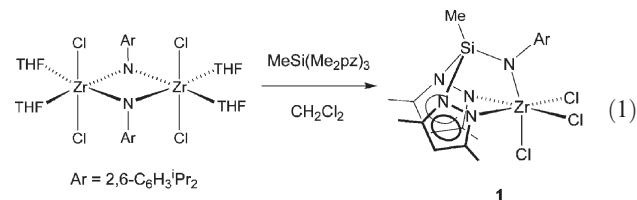
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† Electronic supplementary information (ESI) available: characterising data for the new compounds, polymer data and crystallographic data for **1** and **5**. See DOI: 10.1039/b513927a

transition metals in particular.^{13–15} Therefore a monoanionic, *fac* coordinating N₃ amide-based ligand would be a valuable addition to the rather limited range of monoanionic N₃ donors so far employed in early transition metal chemistry.^{15,16} The presently available systems are:¹⁶ the pendant arm functionalised amidinates (which have a non-constrained coordination geometry (*fac* or *mer*) and can be prone to donor arm decoordination and ligand redistribution for the early transition metals); bis(imino)pyrrolyl ligands which enforce a *mer* coordination geometry; and the ubiquitous tris(pyrazolyl)borates which can be prone to facile displacement in Group 3, while in Group 4 (despite giving rise to highly active ethylene polymerisation catalysts upon activation with methyl aluminoxane (MAO)¹⁷) they are susceptible to very facile B–N bond cleavage reactions.¹⁸

In this contribution we report the unique transformation of a bridging imido group into a new class of heteroscorpionate ligand (the complex of which is a highly active ethylene polymerisation catalyst). We also describe the rational, modular synthesis of another type of N₃ donor heteroscorpionate ligand and its neutral and cationic early transition metal derivatives.

The pyrazolyl silane ligand $\text{MeSi}(\text{Me}_2\text{pz})_3$ is a silicon analogue of the tris(pyrazolyl)alkanes, but its coordination chemistry has been very little studied (three reports to date, none from Group 4).⁵ The reaction of $\text{MeSi}(\text{Me}_2\text{pz})_3$ with the dimeric zirconium imido complex $[\text{Zr}_2(\mu\text{-NAr})_2\text{Cl}_4(\text{THF})_4]$ (Ar = 2,6-C₆H₃ⁱPr₂)^{19,20} is summarised in eqn (1). After 3 h at room temperature in CH_2Cl_2 the heteroscorpionate compound $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{Si}(\text{Me})\text{NAr}\}\text{Cl}_3]$ (**1**) was obtained in 62% isolated yield (assuming 1 equiv. of imido dimer is required to form 1 equiv. of **1**). The X-ray structure of **1** (Fig. 1)† is consistent with the solution NMR data and confirms the presence of a *fac*-ZrCl₃ fragment supported by a monoanionic N₃ donor heteroscorpionate ligand. The former imido group of $[\text{Zr}_2(\mu\text{-NAr})_2\text{Cl}_4(\text{THF})_4]$ forms the amide donor of the new ligand which is the first in its class.



The reaction to form **1** was entirely reproducible and the same heteroscorpionate product was also obtained in THF or benzene as solvent or when 1 equiv. $\text{MeSi}(\text{Me}_2\text{pz})_3$ was used per equiv. of zirconium dimer. Compound **1** was the only identifiable product when the reaction was followed by ¹H NMR spectroscopy. The

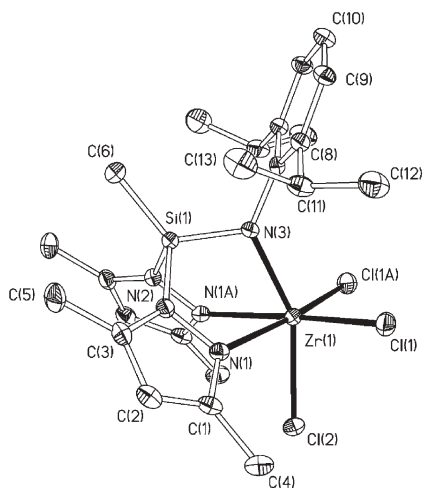
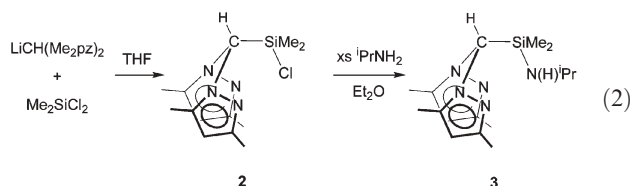


Fig. 1 Molecular structure of $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{Si}(\text{Me})\text{NAr}\}\text{Cl}_3]$ (**1**).

fate of the “Zr(NAr)Cl(Me₂pz)” fragment required by mass balance is unknown at this time, as is the mechanism of this remarkable transformation. Terminal Group 4 imido compounds (*i.e.* having a non-bridging, multiply-bonded linkage M=NR) are known to couple with a range of unsaturated linkages and also to activate C–H and other element–hydrogen bonds.^{21,22} While the net Si–N bond activation by a *bridging* imido ligand in $[\text{Zr}_2(\mu\text{-NAr})_2\text{Cl}_4(\text{THF})_4]$ is unique in this context, it is reminiscent of the recently reported Me₂pz ligand displacement from boron by CH₂Ph in $[\text{Zr}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{CH}_2\text{Ph})]^+$.¹⁸

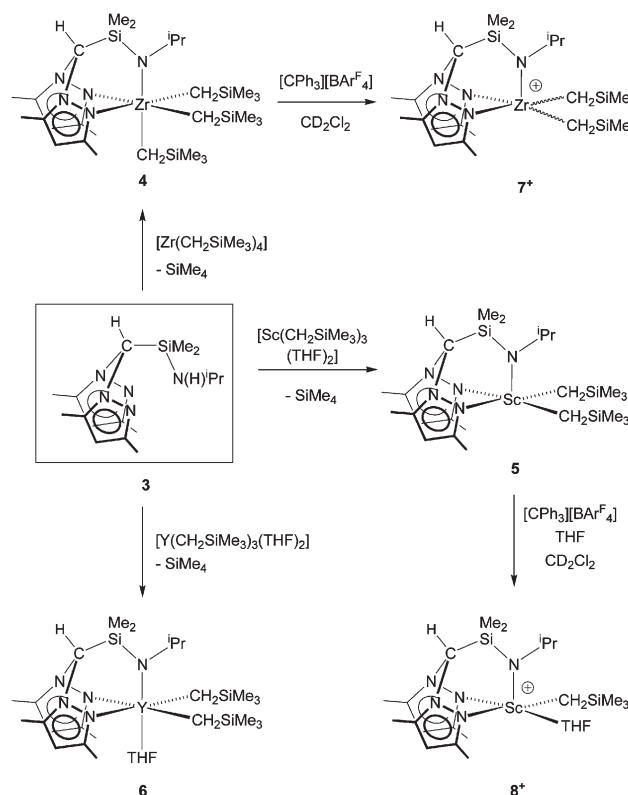
The novel heteroscorpionate compound **1** is formally related to Jordan’s tris(pyrazolyl)borate-supported trichlorides $[\text{Zr}\{\text{HB}(\text{R}^3\text{R}^5\text{pz})_3\}\text{Cl}_3]$ ¹⁷ and Grassi’s N₂O donor heteroscorpionate $[\text{Zr}\{\text{HC}(\text{Me}_2\text{pz})_2(\text{C}_6\text{H}_2(\text{tBu})_2\text{O})\}(\text{CH}_2\text{Ph})_3]$ ⁸ which are both olefin polymerisation precatalysts. We found that when activated at room temperature with MAO, **1** is a very highly active polymerisation catalyst and forms polyethylene with a productivity in excess of 3120 kg(PE) mol⁻¹ h⁻¹ bar⁻¹ ($M_w = 432,500$; $M_w/M_n = 2.5$) accompanied by a very rapid exotherm. This productivity is more than an order of magnitude superior to that of the Grassi system at this temperature, and is comparable to the MAO-activated tris(pyrazolyl)borate systems for similar run times.¹⁷

The results obtained for **1** conclusively establish the new class of N₃ donor heteroscorpionate ligand as a viable contender with other monoanionic scorpionate systems presently available. However, although a number of different dimeric imido compounds $[\text{Zr}_2(\mu\text{-NR})_2\text{Cl}_4(\text{L})_n]$ are available in the literature,²⁰ the scope of the chemistry starting from these systems would inevitably be limited. Therefore, encouraged by the results for **1**, we developed a new and potentially highly flexible synthesis of N₃ donor heteroscorpionate ligands as outlined in eqn (2). This route allows for modification of the pyrazolyl ring- and amide N-substituents, both key variables based on what is already known about poly(pyrazolyl) ligand^{1–6} and amide donor chemistry.^{13,15}



As shown in eqn (2), Me₂SiCl₂ reacts readily with LiCH(Me₂pz)₂ to form (Me₂pz)₂CHSi(Me)₂Cl (**2**) as a white solid in 76% yield. Preliminary results show that **2** reacts smoothly with an excess of a range of primary alkyl amines, but here we focus on the reaction with ⁱPrNH₂ which afforded (Me₂pz)₂CHSi(Me)₂N(H)ⁱPr (**3**) as a pale oil in 74% yield on a gram scale (the yield for neither **2** nor **3** has so far been optimised). Scheme 1 summarises preliminary studies of the reactions of **3** with various Group 3 and 4 metal alkyls. Alkane or amine elimination reactions are frequently the routes of choice to early transition metal organometallic and similar complexes as the precursors are readily available and “ate” complex formation is avoided, and so we have focused on these protocols.

Reaction of protio ligand **3** with $[\text{Zr}(\text{CH}_2\text{SiMe}_3)_4]$ formed the six-coordinate tris(alkyl) compound $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)_3]$ (**4**) which shows two inequivalent CH₂SiMe₃ ligand environments in its ¹H NMR spectrum at low temperature. Reaction with $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ gave the five-coordinate product $[\text{Sc}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)_2]$ (**5**), whereas with $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ another six-coordinate complex, namely $[\text{Y}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**6**) was obtained. The air- and moisture-sensitive compounds are stable for many days in solution under an inert atmosphere. The X-ray structure of **5** has been determined as shown in Fig. 2.† The new N₃ donor heteroscorpionate ligand adopts the expected *fac* coordination mode and the overall geometry at scandium is square base pyramidal. The structure of **5** and NMR data for **6** suggest that the THF donor in the latter lies *trans* to the amide donor.



Scheme 1 Synthesis of Group 3 and 4 complexes of the N₃ donor heteroscorpionate ligand **3**. Anion omitted for **7**⁺ and **8**⁺.

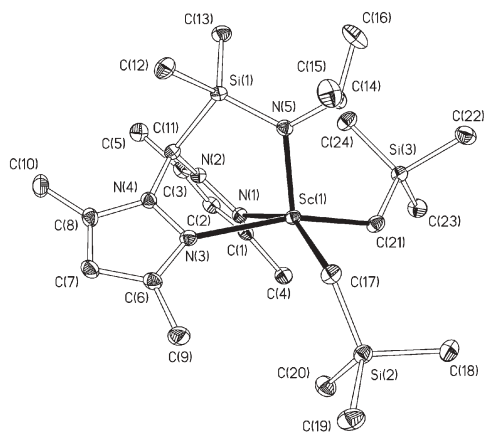


Fig. 2 Molecular structure of $[\text{Sc}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)_2]$ (**5**).

Bearing in mind that tris(pyrazolyl)borate-supported zirconium dialkyl cations rapidly undergo N_3 donor ligand degradation above $0\text{ }^\circ\text{C}$ ¹⁸ we carried out the reaction between **4** and $[\text{CPh}_3][\text{BAR}^{\text{F}}_4]$ in CD_2Cl_2 ($\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$). The ^1H and ^{19}F NMR spectra of the product mixture showed the formation of a stable (for at least several hours at room temperature) dialkyl cation $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)_2]^+$ (**7⁺**) and separated $[\text{BAR}^{\text{F}}_4]^-$ anion. This suggested that such alkyl cations may be viable olefin polymerisation catalysts. Subsequent evaluation of **4** with $[\text{CPh}_3][\text{BAR}^{\text{F}}_4]$ cocatalyst in toluene in the presence of Al^iBu_3 gave an ethylene polymerisation productivity of $315\text{ kg(PE) mol}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$ ($M_w = 458,000$; $M_w/M_n = 4.9$).[§]

Recently, rare earth alkyl cations have gained much attention.²³ Preliminary NMR tube scale studies showed that reaction of **5** with $[\text{CPh}_3][\text{BAR}^{\text{F}}_4]$ in the presence of THF formed the stable (in solution) monoalkyl cation $[\text{Sc}\{(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}^i\text{Pr}\}(\text{CH}_2\text{SiMe}_3)(\text{THF})]^+$ (**8⁺**). Addition of ethylene to the NMR sample afforded a white precipitate of polyethylene. Further studies are presently under way.

In conclusion, we have discovered a unique transformation of a zirconium imido compound giving the first member of a new class of monoanionic *fac* N_3 donor heteroscorpionate ligand. We have established a second type of such ligand for early transition metal and rare earth chemistry, and have also demonstrated its viability in key areas of current interest including olefin polymerisation and the generation of well-defined alkyl cations. The high-yielding and modular synthesis of the protio ligand $(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}(\text{H})^i\text{Pr}$ (**3**) allows for straightforward and systematic modification of both the pyrazolyl ring- and amide N-substituents, which are key variables for the future development of these systems. We are presently exploring monoanionic N_3 donor heteroscorpionate chemistry for a range of early transition and rare earth metals and their applications.

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Notes and references

‡ *Crystal data*: for $\text{C}_{27}\text{H}_{42}\text{Cl}_3\text{N}_5\text{OSiZr}$ (**1·THF**), $M = 678.33$, orthorhombic, space group $Pnma$, $a = 20.1923(7)$, $b = 17.1332(6)$, $c = 9.1763(3)$ Å, $V = 3174.62(19)$ Å³, $T = 150\text{ K}$, $Z = 4$, $\mu = 0.665\text{ mm}^{-1}$, 18858 reflections measured, 4056 unique, $R_{\text{int}} = 0.068$. Final R values $R_1 = 0.0400$ and $R_w = 0.0471$ (for $I > 3\sigma(I)$); for $\text{C}_{24}\text{H}_{50}\text{N}_5\text{ScSi}$ (**5**), $M = 537.91$, triclinic, space group $P\bar{1}$, $a = 10.4827(2)$, $b = 10.9399(3)$, $c = 14.6107(4)$ Å, $\alpha = 82.0937(10)$, $\beta = 89.6905(11)$, $\gamma = 72.2736(12)^\circ$, $T = 150\text{ K}$, $Z = 2$, $\mu = 0.367\text{ mm}^{-1}$, 27522 reflections measured, 7134 unique, $R_{\text{int}} = 0.047$. Final R values $R_1 = 0.0383$ and $R_w = 0.0444$ (for $I > 3\sigma(I)$). CCDC 285656 and 285657. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513927a

§ Polymerisation conditions: For **1**, 6 bar C_2H_4 , 2.5 μmol , 1500 equiv. MAO, 250 mL toluene, 10 min. For **4**, 6 bar C_2H_4 , 10 μmol **4**, 1 equiv. $[\text{CPh}_3][\text{BAR}^{\text{F}}_4]$, 5 mmol Al^iBu_3 , 250 mL toluene, 10 min.

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