Synthesis and ethylene trimerisation capability of new chromium(II) and chromium(III) heteroscorpionate complexes†

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Reaction of $(Me_2pz)_2CHSiMe_2N(H)R$ (R = ^iPr or Ph) or $(Me_2pz)_2CHSiMe_2NMe_2$ with $CrCl_3(THF)_3$ or $CrCl_2(THF)_2$ gave $Cr\{(Me_2pz)_2CHSiMe_2NR^1R^2\}Cl_3$ (R^1 = H, R^2 = ^iPr (**10**) or Ph (**11**); R^1 = R^2 = Me (**15**)) or $Cr\{(Me_2pz)_2CHSiMe_2NR^1R^2\}Cl_2(THF)$ (R^1 = H, R^2 = ^iPr (**12**) or Ph (**13**); R^1 = R^2 = Me (**16**)), respectively. Compounds **10** and **11** were crystallographically characterized and the magnetic behaviour of all the new compounds was evaluated using SQUID magnetometry. Reaction of $CrCl_3(THF)_3$ with $Li\{C(Me_2pz)_3\}(THF)$ gave the zwitterionic complex $Cr\{C(Me_2pz)_3\}Cl_2(THF)$ (**17**) containing an apical carbanion. Reaction of the analogous phenol-based ligand $(Me_2pz)_2CHArOH$ (ArO = $2\text{-}O\text{-}3,5\text{-}C_6H_2{}^tBu_2$) with $CrCl_3(THF)_3$ gave $Cr\{(Me_2pz)_2CHArOH\}Cl_3$ (**19**) whereas the corresponding reaction with $CrCl_2(THF)_2$ unexpectedly gave the Cr(III) phenolate derivative $Cr\{(Me_2pz)_2CHArO\}Cl_2(THF)$ (**20**) which could also be prepared from $CrCl_3(THF)_3$ and the sodiated ligand $[Na\{(Me_2pz)_2CHArO\}(THF)]_2$. Reaction of the corresponding ether $(Me_2pz)_2CHArOMe$ with $CrCl_3(THF)_3$ or $CrCl_2(THF)_2$ gave $Cr\{(Me_2pz)_2CHArOMe\}Cl_3$ (**23**) and $Cr\{(Me_2pz)_2CHArOMe\}Cl_2\text{-}(THF)$ (**24**), respectively. The catalytic performance in ethylene oligomerisation/polymerisation of all of the new Cr(II) and Cr(III) complexes was evaluated. Most of the complexes showed high activity, but produced a Schultz-Flory distribution of α-olefins. Compound **23** had an exceptionally low α-value of 0.37 and showed a preference for 1-hexene and 1-octene formation. While replacing a secondary amine (**10-13**) for a tertiary amine (**15-16**) resulted in loss of catalytic activity, replacing a phenol (**19**) for an anisole (**23**) group afforded a more selective and more active catalyst. Changing from MAO to DIBAL-O as cocatalyst induced a switch in selectivity to ethylene polymerisation.

Introduction

Ethylene oligomerisation and polymerisation belong to the same type of C–C bond formations albeit that the mechanisms are completely different. While the migratory insertion mechanism for the polymerisation of α-olefins is well established,[1] the redox process (oxidative addition, ring expansion, reductive elimination) for selective oligomerisation is still not fully understood.[2] Although significant progress has been made with respect to elucidating mechanistic details and the oxidation state of the active metal species,[3] there are still many questions to be answered. For example, it is not clear how the ancillary ligand system determines the selectivity of the catalyst. Furthermore, finding the right ancillary ligand that results in a selective oligomerisation catalyst (rather than a non-selective oligomerisation or polymerisation catalyst) remains a broadly empirical process relying on exploratory synthesis and screening.

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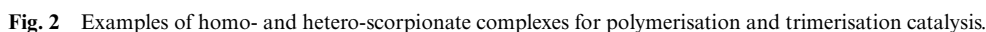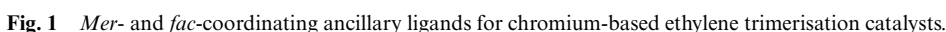
Of all the systems known to trimerise ethylene to 1-hexene, the vast majority are based on chromium. Chromium is an element that provides both potent ethylene polymerisation catalysts[4] and ethylene oligomerisation catalysts (non-selective[5] and selective[2,6,7]). This makes chromium the ideal metal to study the effect of the ancillary ligand system on the catalyst's behaviour. The majority of the reported chromium-based ethylene trimerisation catalysts consist of tridentate heteroatom-containing ancillary ligands. The most well-known ligand systems are the meridionally bonded diphosphinoamines, triphosphines and dithioetheramines, together with the facially bonded triazacycloalkanes and tris(dimethylpyrazolyl)methane (Fig. 1).[6] Bulky cyclopentadienyls and pyrroles can bind to the metal in an η⁵-facial fashion, also occupying 3 metal orbitals.[6a-6b,8] Whilst ligands like diphosphinoamines, triphosphines or dithioetheramines generally exhibit a meridional arrangement in the catalyst precursors, these ligands could also bind facially to the metal. With this in mind, we reasoned that a facial tridentate ancillary ligand might be one of the requisites for a selective chromium ethylene trimerisation catalyst.[9] In this regard we note Braunstein and Hor's recent reports of potent chromium-based trimerisation catalysts stabilised by *fac*-coordinated bis(pyrazolyl)methane based ligands (see below).

As alluded to above, the tris(dimethylpyrazolyl)methane complex $Cr\{H(Me_2pz)_3\}Cl_3$ (**1**, Fig. 2) shows very good selectivity and activity for ethylene trimerisation on activation with

**Fig. 1** *Mer-* and *fac*-coordinating ancillary ligands for chromium-based ethylene trimerisation catalysts.

Fig. 2 Examples of homo- and hetero-scorpionate complexes for polymerisation and trimerisation catalysis.

MAO.[6c] Tris(pyrazolyl)methanes[11-13] are examples of scorpionate ligands, the most well-known examples of which are anionic tris(pyrazolyl)hydroborates $[HB(R_npz)_3]^-$ (R_npz = pyrazolyl or substituted pyrazolyl ring).[14] While *homoscorpionate* ligands have the same three moieties appended to the apical group (*e.g.*, BH, CH), a second important class of poly(pyrazolyl) ligands are the *heteroscorpionates*. Here one of the pyrazolyl groups has been replaced by a different C-, O-, S- or N-donor moiety.[15] While much of the early work with heteroscorpionate complexes was concerned with synthetic and structural studies, several reports have focussed more on their applications in the areas of ring-opening polymerisation of cyclic esters[16-18] (*e.g.* Mg{$(Me_2pz)_2$CHArO}N(SiHMe$_2$)$_2$ (**2**)[18]) and Ziegler–Natta polymerization catalysis[19,20] (*e.g.* Ti{$(Me_2pz)_2$CHArO}Me$_3$ (**3**,

Ar = C$_6$H$_2$^{t}Bu$_2$),[19c] Zr{$(Me_2pz)_2$CHSiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_3$ (**4**) and Sc{$(Me_2pz)_2$CHSiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_2$ (**5**)[20]).

Very recently, preliminary results for Cr(III) ethylene trimerisation precatalysts **7-9** (Fig. 2) featuring heteroscorpionate ligands were disclosed by Braunstein and Hor.[10] The 1-hexene selectivities for all three types of complex **7-9** were competitive with that of the "parent" system **1**, but the N$_2$S donor derivatives (**7**) were significantly less active than their N$_2$O (**8**) and N$_2$N′ (**9**) analogues. These results, alongside the track records of other N$_2$O (*e.g.*, in **2** and **3**) and N$_2$N′ (*e.g.*, in **4-6**) donor ligands, prompted us to report our own results in this area. As described below, we have used several different types of heteroscorpionate complexes of this type with either Cr(II) or Cr(III) centres, secondary or tertiary amine side arms and phenyl ether, phenol or phenolate side arms.
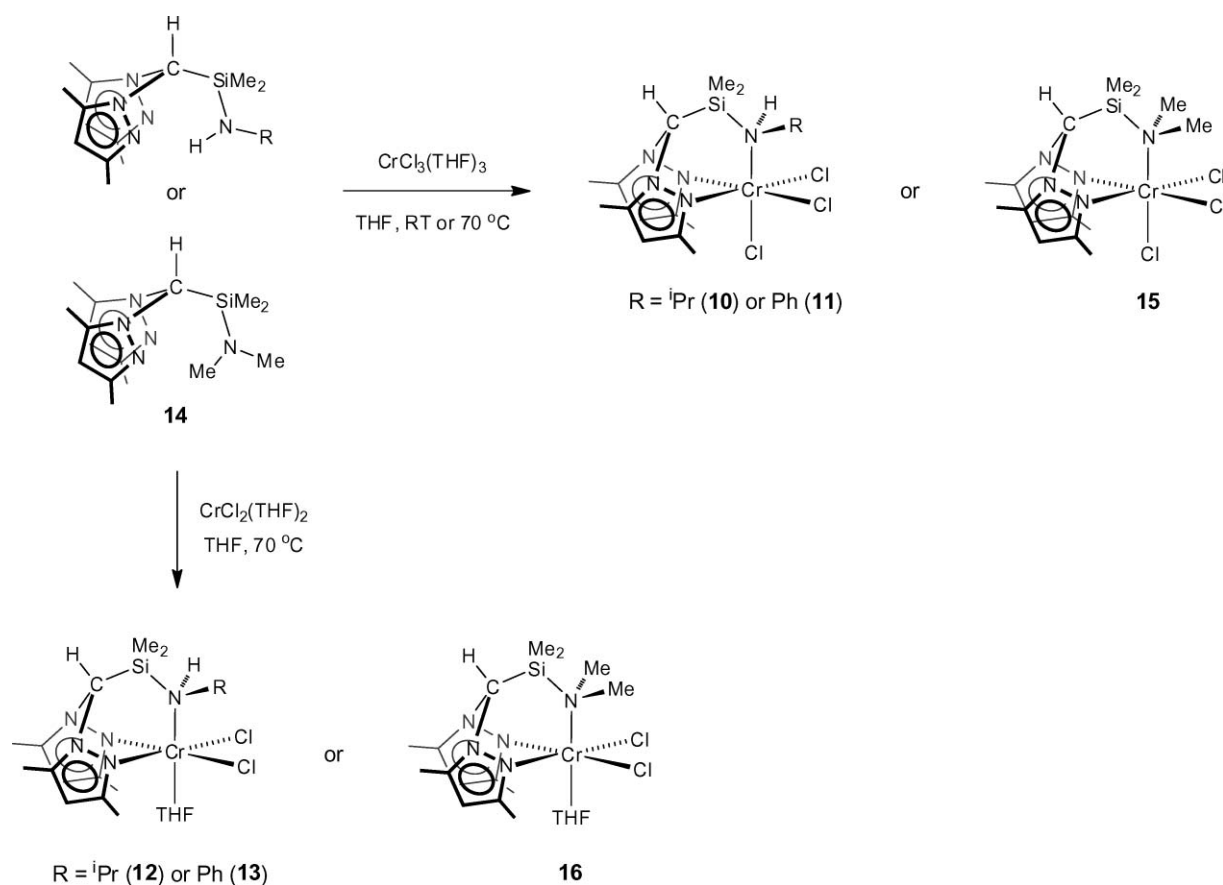
Scheme 1 Synthesis of new Cr(II) and Cr(III) N$_2$N'-donor heteroscorpionate complexes.

Results and discussion

Synthesis of N$_2$N' and N$_3$ donor scorpionate Cr(II) and Cr(III) complexes

Reaction of CrCl$_3$(THF)$_3$ with (Me$_2$pz)$_2$CHSiMe$_2$N(H)R (R = ^{i}Pr or Ph)[20] in THF at room temperature gave a colour change from purple to pale green or pink. After work up and crystallisation from acetonitrile the Cr(III) complexes Cr{(Me$_2$pz)$_2$-CHSiMe$_2$N(H)R}Cl$_3$ (R = ^{i}Pr (**10**) or Ph (**11**)) were obtained in *ca* 85% yield (Scheme 1). Attempted complexation of the sterically more demanding analogue (Me$_2$pz)$_2$CHSiMe$_2$N(H)Ar (Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$) was unsuccessful, even after heating at 70 °C for 24 h. Compounds **10** and **11**, like all the complexes described herein, are paramagnetic and meaningful NMR spectra could not be obtained. The solid state structures (see below) confirm the presence of neutral ligands bound in a *fac*-coordinated manner to CrCl$_3$ moieties. The IR spectra show ν(N–H) absorbances (*ca* 3220 cm^{-1}) red-shifted from those of the free ligands, and the elemental analyses are consistent with the expected composition. Under the conditions of their synthesis and manipulation, neither **10** nor **11** exhibit any tendency to eliminate HCl.

The room temperature, solid state magnetic moments of 3.90 and 3.99 μ_B for **10** and **11** agree well with that expected for an S = $^3/_2$ spin ground state (^{4}A, expected spin-only moment = 3.87 μ_B). The solid state magnetic behaviour of **10** was further investigated by variable temperature SQUID (Superconducting Quantum Interference Device) magnetometry in the range 5-300 K. A plot of 1/χ_m *vs.* temperature is shown in Fig. 3. The observed linear relationship is characteristic of a paramagnetic solid that obeys the Curie–Weiss Law (χ_m = C/(T − θ)). The Weiss temperature (θ) of −4.6 K is typical of a material that orders antiferromagnetically at sufficiently low temperatures.[21]
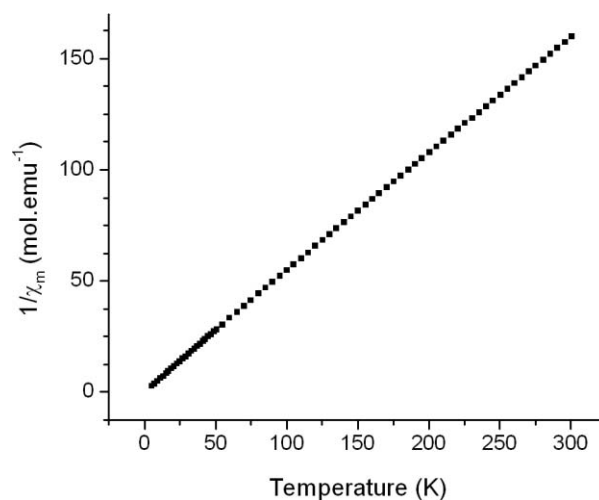

Fig. 3 Magnetic behaviour of Cr{(Me$_2$pz)$_2$CHSiMe$_2$N(H)^{i}Pr}Cl$_3$ (**10**) as determined by variable temperature SQUID magnetometry.
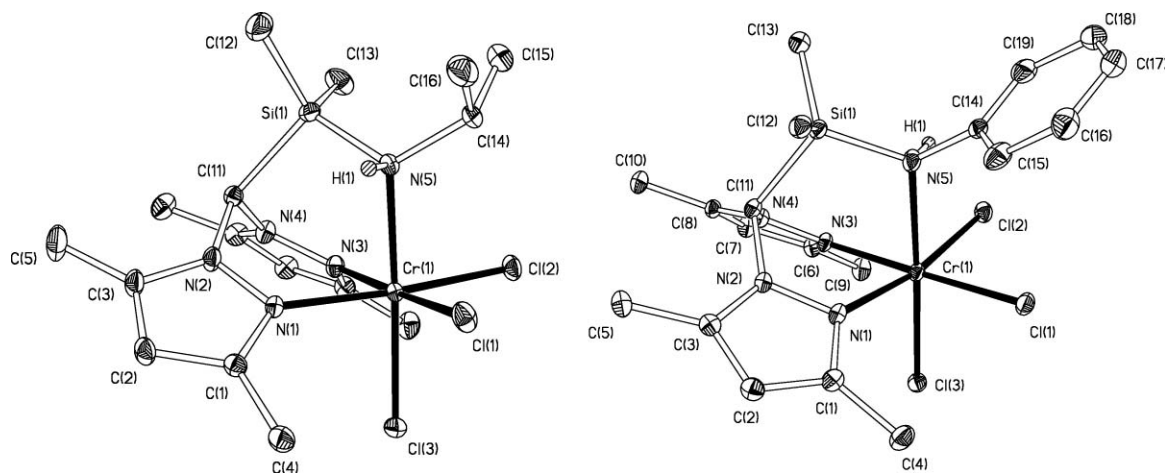
Fig. 4 Displacement ellipsoid plots (20% probability) of Cr{(Me₂pz)₂CHSiMe₂N(H)ⁱPr}Cl₃ (**10**, left) and Cr{(Me₂pz)₂CHSiMe₂N(H)Ph}Cl₃ (**11**, right). C-bound H atoms, dichloromethane of crystallization and minor disorder (for **10**) omitted for clarity.

Table 1 Selected distances (Å) and angles (°) for Cr{(Me₂pz)₂CHSiMe₂N(H)ⁱPr}Cl₃ (**10**) and Cr{(Me₂pz)₂CHSiMe₂N(H)Ph}Cl₃ (**11**). The values in brackets for **10** are for the other orientation of N(5) which is positionally disordered over two sites)

Parameter	10	11
Cr(1)-N(1)	2.129(2)	2.129(3)
Cr(1)-N(3)	2.125(3)	2.141(2)
Cr(1)-N(5)	2.163(10) [2.182(11)]	2.190(3)
Cr(1)-Cl(1)	2.3023(9)	2.2747(9)
Cr(1)-Cl(2)	2.3005(8)	2.3291(9)
Cr(1)-Cl(3)	2.3292(9)	2.3280(8)
N(1)-Cr(1)-N(3)	86.72(9)	86.54(9)
N(1)-Cr(1)-Cl(2)	174.95(7)	169.78(7)
N(3)-Cr(1)-Cl(1)	175.88(8)	178.49(8)
N(5)-Cr(1)-Cl(1)	82.44(18) [93.6(2)]	90.83(8)
N(5)-Cr(1)-Cl(2)	91.6(2) [83.10(19)]	83.33(9)
N(5)-Cr(1)-Cl(3)	173.6(2) [172.47(19)]	178.00(8)
Cl(1)-Cr(1)-Cl(2)	92.97(3)	91.06(3)

The solid state structures of **10** and **11** are shown in Fig. 4, and selected bond distances and angles are compared in Table 1. In general the distances and angles are within the expected ranges.[22,23] Each complex contains a κ^3N–bound (Me₂pz)₂CHSiMe₂N(H)R ligand and an approximately octahedral chromium. There is some positional disorder in the Me₂Si–N(H) linkage of **10** (see Experimental) but this was easily modelled. There are no substantial differences between the principal metric parameters listed in Table 1 for the two compounds. The Cr–N(1,3) distances are slightly shorter than their Cr–N(5) counterparts, possibly reflecting the difference in hybridisation of the two types of nitrogen donor (sp^2 vs sp^3). Somewhat surprisingly, the Cr–Cl(3) (*trans* to N(H)R) distance is slightly longer than the average Cr(1)-Cl(1,2) distances (*trans* to the shorter Cr–N$_{pz}$ bonds).

Cr(II) analogues of **10** and **11** were obtained from the reaction of *in situ* prepared CrCl₂(THF)₂ with the same ligands (Scheme 1) at 70 °C in THF, forming the sky blue THF adducts Cr{(Me₂pz)₂CHSiMe₂N(H)R}Cl₂(THF) (R = ⁱPr (**12**) or Ph (**13**)) in *ca.* 60% yield. As for the Cr(III) analogues, the IR spectra showed the expected ν(N–H) stretches. The solid state magnetic moments of 4.92 and 5.08 μ$_B$, respectively, are in good agreement with that

estimated (4.89 μ$_B$) by the spin-only approximation for a high spin $S = 2$ (⁵E) group state.

For comparison with **10**, the solid state magnetic behaviour of **12** was investigated by variable temperature SQUID magnetometry. A plot of $1/\chi_m$ vs. temperature is shown in Fig. 5. Above *ca.* 60 K the linear plot is again characteristic of a paramagnetic solid that obeys the Curie–Weiss Law, but at lower temperatures there is a deviation from this behaviour which may be due to large zero-field splittings typical of $S = 2$ ground states.
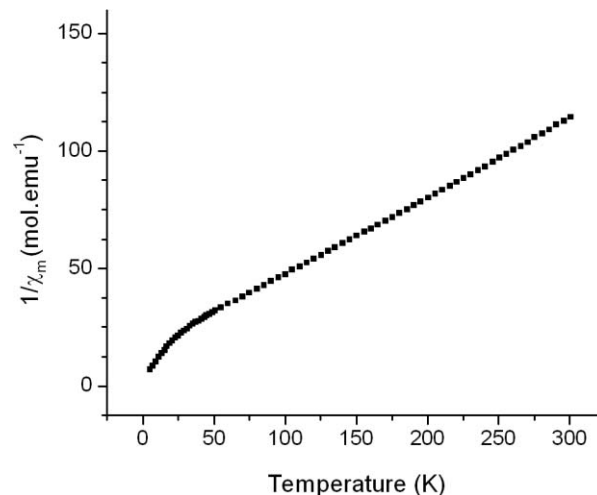

Fig. 5 Magnetic behaviour of Cr{(Me₂pz)₂CHSiMe₂N(H)ⁱPr}Cl₂(THF) (**12**) as determined by variable temperature SQUID magnetometry.

The compounds **10-13** have secondary amine donors (N(H)R). The N-bound H atom could be lost under reaction conditions in the presence of aluminium alkyl species (*cf.* Hor's report for **9**[10b,10c]). To test for this possible effect, we therefore also prepared the new ligand (Me₂pz)₂CHSiMe₂NMe₂ (**14**), containing a pendant NMe₂ donor in place of the N(H)R group in (Me₂pz)₂CHSiMe₂N(H)R. Compound **14** was obtained in 48% yield by reaction of the previously reported[20] chlorosilane (Me₂pz)₂CHSiMe₂Cl with LiNMe₂ in THF. Examination of the crude reaction mixture showed evidence for the formation of

(Me$_2$pz)$_2$CHLi during this process, thus (Me$_2$pz)$_2$CHLi elimination appears to compete with LiCl elimination in this reaction, contributing to the relatively modest yield of **14**.

Reaction of **14** with CrCl$_3$(THF)$_3$ and *in situ* generated CrCl$_2$(THF)$_2$ required slightly more forcing conditions than for the secondary amine analogues (higher temperatures or longer reaction times). The target complexes (Scheme 1) Cr{(Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$}Cl$_3$ (**15**, 87% yield) and Cr-{(Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$}Cl$_2$(THF) (**16**, 67% yield) were nonetheless satisfactorily obtained in analytically pure form. The solid state magnetic moments of 3.79 μ_B and 5.03 μ_B were close to those expected according to the spin-only formula for $S = {}^3/_2$ and $S = 2$ ground states, respectively.

We and others have recently found that free HC(Me$_2$pz)$_3$ is readily deprotonated at the apical C–H bond by lithium, magnesium or zinc alkyl reagents to form zwitterionic tris(pyrazolyl)methan*ide* complexes of the type [M^{n+}{$^-$C(Me$_2$pz)$_3$}X] ($n = 1$, X = alkyl or THF; $n = 2$, X = $^-$C(Me$_2$pz)$_3$) possessing "naked" sp^3 carbanions and formally cationic metals.[24] Deprotonation can also occur once the neutral HC(Me$_2$pz)$_3$ is bound to a transition metal, and this can also form zwitterionic complexes that are highly active Ziegler–Natta polymerisation catalysts.[24b,24d] Under the trimerisation reaction conditions reported for Cr{HC(Me$_2$pz)$_3$}Cl$_3$ (MAO, 80 °C),[6c] there is a possibility that deprotonation of the apical C–H bond occurs. Therefore, in addition to the heteroscorpionate complexes in Scheme 1, we also prepared the zwitterionic, homoscorpionate complex Cr{C(Me$_2$pz)$_3$}Cl$_2$(THF) (**17**) from Li{C(Me$_2$pz)$_3$}(THF)[24a,24b] and CrCl$_3$(THF)$_3$ (eqn (1)). Compound **17** was obtained as a green microcrystalline solid in 40% crystallised yield. The EI mass spectrum shows a fragment peak centred on $m/z = 418$ amu (M^+ - THF) with the correct isotope distribution. The solid state magnetic moment of 3.76 μ_B is consistent with a Cr(III), $S = {}^3/_2$ species as depicted in eqn (1).

(1)
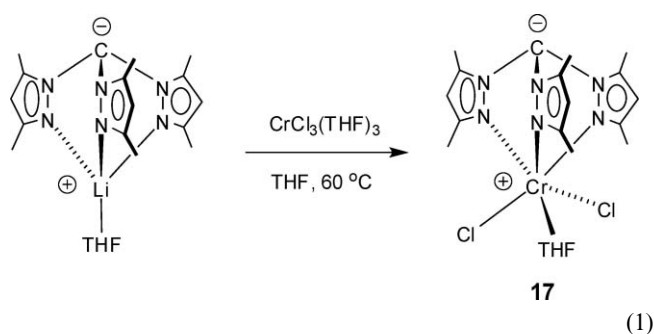
Synthesis of N$_2$O donor heteroscorpionate Cr(II) and Cr(III) complexes

Encouraged by Braunstein and Hor's preliminary reports[10a] concerning the N$_2$O-donor heteroscorpionate Cr(III) complexes **8** (Fig. 2), we also extended our collection of Cr(III) and Cr(II) complexes to include derivatives of the bulky bis(pyrazolyl)methanephenol (Me$_2$pz)$_2$CHArOH (**18**).[18,19c] As mentioned, a number of transition metal and main group metal complexes of **18** and its homologues have been reported,[16,18,19c,25] although none are yet known for chromium. Compared to the situation for chelating phenolate ligands in general (which attract widespread interest in main group, transition metal and *f* element chemistry),[26]

heteroscorpionate-based phenolates in general are somewhat underdeveloped, especially in relation to catalysis.

Reaction of (Me$_2$pz)$_2$CHArOH (**18**) with CrCl$_3$(THF)$_3$ in THF for 12 h at 60 °C gave the phenol complex Cr{(Me$_2$pz)$_2$CHArOH}Cl$_3$ (**19**) as a dark green solid in 73% yield (Scheme 2). The IR spectrum of **19** showed a ν(O–H) band (absent in the otherwise identical methyl ether complexes **23** and **24** discussed below) and the solid state magnetic moment was consistent with Cr(III). Reaction of **18** with CrCl$_2$(THF)$_2$ also gave a dark green product. However, although the elemental analysis was consistent with that anticipated for the target phenol complex Cr{(Me$_2$pz)$_2$CHArOH}Cl$_2$(THF), the expected ν(O–H) band was absent from the IR spectrum. Furthermore, both the solid state (SQUID) and solution (Evans method[27,28]) room temperature magnetic moments (3.72 μ_B and 3.66 μ_B, respectively) were considerably closer to that expected for $S = {}^3/_2$ (Cr(III), 3.87 μ_B) than $S = 2$ (high spin Cr(II), 4.89 μ_B). Thus it appears that reaction of **18** with CrCl$_2$(THF)$_2$ spontaneously forms the Cr(III) *phenolate* complex Cr{(Me$_2$pz)$_2$CHArO}Cl$_2$(THF) (**20**, Scheme 2), perhaps by H atom loss from a first-formed *phenol* intermediate Cr{(Me$_2$pz)$_2$CHArOH}Cl$_2$(THF). By way of verification, we also prepared **20** from CrCl$_3$(THF)$_3$ and the sodiated ligand[18] [Na{(Me$_2$pz)$_2$CHArO}(THF)]$_2$ (**21**). The samples of **20** prepared by the two routes were indistinguishable.

In order to block the spontaneous oxidation process leading to **20**, and to evaluate the influence of the ligand-bound O–H group in **19** on oligomerisation catalysis, we prepared the new ligand (Me$_2$pz)$_2$CHArOMe (**22**) from **21** using MeI in THF (Scheme 2). Reaction of **22** with CrCl$_3$(THF)$_3$ or CrCl$_2$(THF)$_2$ in THF at 70 °C for 12 h gave dark red Cr{(Me$_2$pz)$_2$CHArOMe}Cl$_3$ (**23**) or dark blue Cr{(Me$_2$pz)$_2$CHArOMe}Cl$_2$(THF) (**24**) in very good yields. The solid state magnetic moments of 3.56 μ_B and 4.83 μ_B were close to those expected for Cr(III) and high spin Cr(II) systems, respectively.

Ethylene oligomerisation studies

All of the new N$_2$N' and N$_2$O donor heteroscorpionate complexes, together with the zwitterionic homoscorpionate Cr{C(Me$_2$pz)$_3$}Cl$_2$(THF) (**17**), were evaluated for their ethylene oligomerisation capabilities. We also tested the previously reported[1] complex Cr{HC(Me$_2$pz)$_3$}Cl$_3$ (**1**) under our experimental conditions in order to make valid comparisons. Catalytic runs were carried out in toluene solvent with MAO activation (Al : Cr = 500 : 1) under 35 bar ethylene pressure at 60 °C. The most relevant oligomerisation results are listed in Table 2.

The first observation that can be made is that all new complexes are more active than **1** but invariably produce a Schultz-Flory distribution of oligomers. Whereas most complexes display a typical α-value between 0.59 and 0.67, with an α-value of 0.37 compound **23** shows a significantly higher selectivity for 1-hexene (52.4%) and 1-octene (34.7%). The GC analysis of the oligomers obtained demonstrates that in all cases 98+% of the oligomers are α-olefins. In general, an initial temperature rise of 4-7 °C occurred upon injection of pre-catalyst solution, which remained constant until the catalyst deactivated. Reaction profile assessment of selected active catalysts (**10-13**) showed that catalytic activity had ceased after 30 min, and that either increasing the reactor temperature to 80 °C or reducing it to 30 °C decreased the yield of
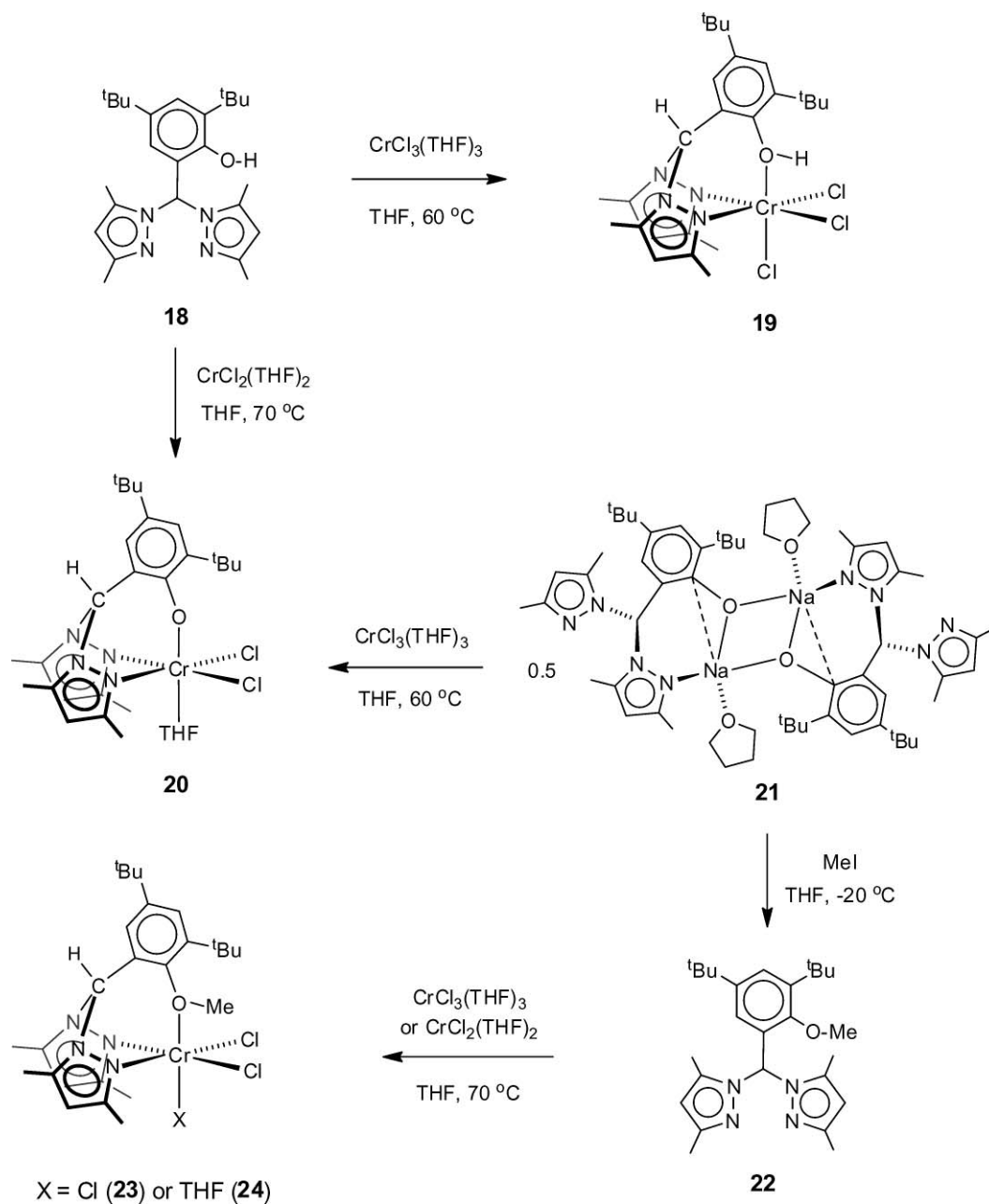
Scheme 2 Synthesis of new Cr(II) and Cr(III) N$_2$O-donor heteroscorpionate complexes.

Table 2 Ethylene oligomerisation results for **10-13**, **19**, **20**, **22**, **23** and **1**[a]

| Pre-catalyst | Yield/mL | Oligomers (mol%) | | | | | | | α | PE/g | Activity (g_{olig} mmol^{-1} h^{-1}) |
		C$_6$	C$_8$	C$_{10}$	C$_{12}$	C$_{14}$	C$_{16}$	C$_{18}$			
10	18.2	30.2	27.2	19.6	9.9	6.9	4.0	2.1	0.61	0.70	1320
11	6.3	37.1	26.8	16.9	9.8	4.6	3.2	1.6	0.59	0.62	770
12	60.7	36.6	25.5	16.8	10.6	6.2	2.4	2.0	0.67	0.20	3250
13	48.5	36.8	26.4	17.8	11.9	4.6	2.5	0.0	0.64	0.28	2650
19	17.4	39.2	25.4	15.5	8.9	5.8	3.1	2.0	0.61	0.35	1280
20	17.0	42.2	25.7	15.1	8.7	5.2	3.0	0.2	0.59	0.10	1300
23	37.0	52.4	34.7	11.8	1.1	0.0	0.0	0.0	0.37	1.80	2310
24	23.9	37.6	25.9	16.2	10.1	4.6	3.6	2.0	0.61	0.38	1580
1	8.9	91.5	0.1	2.4	2.1	1.7	1.3	0.9	0.79	0.16	690

[a] Conditions: 100 mL of toluene, 35 bar C$_2$H$_4$, Al(MAO):Cr = 500; 20 μmol pre-catalyst loading, 30 min, 60 °C.

oligomers while leaving the mass of undesirable polyethylene co-product approximately constant. The polyethylene obtained in all cases shows an extremely broad multimodal product distribution, typical for multiple site chromium catalysts.

When comparing the catalytic behaviour of the various catalysts in more detail, several observations can be made. The divalent complexes **12** and **13** are clearly more active than their trivalent equivalents **10** and **11**, but the selectivity of all four is rather similar. This suggests that both Cr(II) and Cr(III) complexes (**10/12** and **11/13**, respectively) are precursors to the same active species. Based on the lack of selectivity the active species most likely contains chromium in the divalent state.[3]

The effect of changing from a pendant secondary amine to pendant tertiary amine has also been evaluated. Surprisingly, both the trivalent **15** and divalent **16** lack any form of activity. There has been some debate about the role and importance of the NH-functionality in *mer*-SNS and *fac*-NNX ligand systems. Although it was initially assumed that deprotonation of the NH-functionality of the SNS ligand occurs upon activation with MAO, this was found not to be the case. The deprotonated version of the ligand actually afforded an inactive complex and pyridine-based SNS ligands lacking an NH functionality afford active trimerisation catalysts.[3g-3i] Hor and coworkers demonstrated that treating a bis(pyrazolyl)(methyleneamine)methane chromium complex containing a secondary amine with AlMe$_3$ resulted in deprotonation of the amine, which did not affect the catalytic behaviour.[10b] Replacing the secondary amine by a tertiary amine significantly decreased the selectivity for 1-hexene and favoured the production of polyethylene of the corresponding catalysts but did not reduce the catalytic activity.[10c]

The virtually identical yield and product distribution for **19** and **20** suggests that they are both precursors of the same active species, in which the phenol is obviously deprotonated. Furthermore, the THF present in **20** does not inhibit activity, presumably due to the scavenging effects of MAO. The GC analysis of the product mixtures formed from **19** and **20** revealed the unexpected formation of a statistical distribution of odd numbered α-olefins and saturated even numbered oligomers as by-products of the expected distribution of even numbered α-olefins.[5d] The amount of these odd numbered oligomers (approx. 1.3 mL, 6 mmol) is of the order of the amount of MAO in the reaction mixture, which might suggest the mechanism by which they are formed is not catalytic. It is possible that methyl transfer of some kind from MAO (or the AlMe$_3$ in MAO) is responsible for this phenomenon.[5b] Replacing the phenolic hydrogen in **19** for a methyl substituent (**23**), *cf.* changing the pendant NHR donor in **10-13** for NMe$_2$ in **15** and **16**, has an unexpected positive effect on the catalytic activity and selectivity. Although somewhat more polyethylene is formed, the α-value of 0.37 for complex **23** shows an increased selectivity for 1-hexene and 1-octene. Interestingly, the divalent **24** displays a somewhat lower activity than **23** but moreover, the α-value is significantly higher yielding a broader product distribution compared to **23**. This strongly suggests that **23** and **24** do *not* lead to the same active species.

As mentioned above, free tris(dimethylpyrazolyl)methane is readily deprotonated at the apical C–H bond by strong Brønsted bases. It might therefore be possible that deprotonation of the coordinated ligand in Cr{HC(Me$_2$pz)$_3$}Cl$_3$ (**1**) occurs under trimerisation reaction conditions. The catalytic behaviour of the

Table 3 Polymerisation results for selected precatalysts using DIBAL-O as cocatalyst[a]

Pre-catalyst	Polyethylene/g	Activity/kg mol^{-1} h^{-1}
10	0.43	86
13	16.22	3240
15	0.55	110
19	3.40	680
23	5.31	1060

[a] Conditions: 100 mL toluene, 35 bar C$_2$H$_4$, Al:Cr = 500 with 10 μmol pre-catalyst loading, 30 min, 50 °C.

apically-deprotoned Cr{C(Me$_2$pz)$_3$}Cl$_2$(THF) (**17**) was therefore compared with that of **1** under identical conditions. Surprisingly, **17** shows no catalytic activity which strongly suggests that deprotonation of the apical C–H bond of **1** under trimerisation conditions is very unlikely (assuming that the coordinated THF in **17** would be effectively scavenged by the MAO under polymerisation conditions - *cf.* the discussion of **19** and **20** above).

As earlier reports showed that the type of cocatalyst can have a profound effect on the catalytic selectivity,[29] we tested several pre-catalysts (**10**, **13**, **15**, **19**, **23**) with AlMe$_3$ (TMA), Al^{i}Bu$_3$ (TIBAL), DIBAL-O and MMAO-7. TMA and TIBAL did not afford any active catalyst. In agreement with earlier reports, when activated with DIBAL-O all complexes tested produced exclusively polyethylene (Table 3). Interestingly, with MMAO-7 as cocatalyst only precatalyst **10** (20 mol Cr, Al:Cr = 50, 35 bar, 30 min, toluene) gave an active catalyst that produced 6.3 g of PE (activity: 630 kg mol^{-1} h^{-1}). The other pre-catalysts only afforded marginal amounts of polymer, while no oligomers were formed at all.

Conclusions

Reactions of a series of N$_2$N' and N$_2$O donor heteroscorpionate ligands with secondary and tertiary amine donors, as well as phenol and phenyl ether donors, were successfully complexed to Cr(II) and Cr(III). Their solid state structures and magnetic properties have been determined. The tris(pyrazolyl)methanide analogue **17** was also prepared. The ethylene oligomerisation capability of the 11 new complexes was compared with that of the "parent" system Cr{HC(Me$_2$pz)$_3$}Cl$_3$ (**1**) under identical reaction conditions. The results show that very small changes either to the nature of the pendant donor atom (N, O) and/or the presence of an ionisable hydrogen (N–H, O–H) can have a large effect on activity and/or selectivity. Although in almost all cases the new complexes gave an increase in productivity compared to **1**, disappointingly, only one of them (**23**) had any particular selectivity for 1-hexene and 1-octene. Removal of the apical C–H proton from **1** (forming **17**) gave a switch from a highly selective and productive catalyst to an inactive one.

Experimental section

General methods and instrumentation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying

agent.[30] Deuterated solvents were refluxed over the appropriate drying agent, distilled and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Assignments were confirmed as necessary with the use of DEPT-135, DEPT-90, and two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University. SQUID Magnetometry measurements were carried out on a Quantum Design MPMS*XL* at 1000 Oe. Gas chromatography of oligomerisation products was conducted on a Varian 450-GC equipped with an autosampler and a factor four capillary column VF-5 ms 25 M×0.25 MM. A gradient oven temperature program, starting from 50 °C (for 2 min) to 280 °C at a rate of 10 °C min^{-1} and holding at the final temperature for 3 min was employed. The chromatograms were obtained *via* flame ionization detector (FID). As a transport gas ethanol was used.

Starting materials

The following compounds were prepared according to (or by analogy with) literature procedures: CrCl$_3$(THF)$_3$,[31] (R$_2$pz)$_2$CHSiMe$_2$Cl (R = Me or ^{t}Bu),[20] (Me$_2$pz)$_2$CHSiMe$_2$N(H)R (R = ^{i}Pr, Ph or 2,6-C$_6$H$_3$^{i}Pr$_2$),[20] (Me$_2$pz)$_2$CHArOH,[18,19c] [Na-{(Me$_2$pz)$_2$CHArO}(THF)]$_2$,[18] HC(Me$_2$pz)$_3$,[32] Cr{HC(Me$_2$-pz)$_3$}Cl$_2$,[6c] and Li{C(Me$_2$pz)$_3$}(THF).[24a,24b] LiNMe$_2$ was prepared from HNMe$_2$ and ^{n}BuLi in hexanes.[33] Other reagents were obtained commercially and used as received.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$N(H)^{i}Pr}Cl$_3$ (10)

To a purple solution of CrCl$_3$(THF)$_3$ (1.02 g, 2.71 mmol) in THF (30 mL) was added a solution of (Me$_2$pz)$_2$CHSiMe$_2$N(H)^{i}Pr (0.91 g, 2.86 mmol) in THF (30 mL), giving a green solution with a small amount of solid. The resulting mixture was stirred for 4 h at RT. The volume was concentrated by half and hexanes (10 mL) were added to complete crystallisation. The green solid was collected by filtration, washed with hexanes (3 × 5 mL) and dried *in vacuo*. Recrystallisation from a saturated acetonitrile (50 mL) solution at -30 °C afforded **10** as a pale green, microcrystalline solid. Yield: 1.11 g (86%). IR (NaCl plates, Nujol mull, cm^{-1}): 3222 (m, ν_{N-H}), 3134 (w), 1558(m), 1417(s), 1304 (w), 1236(m), 1199(m), 1168 (s), 1125 (w), 1048 (w), 967 (w), 918 (m), 889 (m), 860 (s), 845 (s), 829 (m), 791(s), 765 (w), 687 (w). EI-MS: *m/z* = 440 (5%), [*M* - HCl]$^+$; 405 (20%), [*M*–HCl - Cl]$^+$. Anal. found (calcd. for C$_{16}$H$_{29}$Cl$_3$CrN$_5$Si): C, 40.26 (40.21); H, 6.05 (6.11); N, 14.57 (14.66)%. μ_{eff} = 3.90 μ_B.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$N(H)Ph}Cl$_3$ (11)

To a purple solution of CrCl$_3$(THF)$_3$ (0.30 g, 0.81 mmol) in THF (20 mL) was added a solution of (Me$_2$pz)$_2$CHSiMe$_2$N(H)Ph (0.30 g, 0.85 mmol) in THF (20 mL), giving a light pink solution with a small amount of solid. The resulting mixture was stirred for 4 h at RT. The solution was concentrated to half its volume and hexanes (10 mL) were added to complete crystallisation. The pale pink solid was collected by filtration, washed with hexanes (3 × 5 mL) and dried *in vacuo*. Recrystallisation from a saturated acetonitrile (30 mL) solution at -30 °C afforded **11** as a microcrystalline pink solid. Yield: 0.33 g (84%). IR (NaCl plates, Nujol mull, cm^{-1}): 3221 (m, ν_{N-H}), 3036 (w), 1557 (m), 1493 (w), 1415 (w), 1394 (w), 1045 (m), 851 (s), 797 (m), 698 (m). EI-MS: *m/z* = 439 (50%), [*M* - HCl - Cl]$^+$. Anal. found (calcd. for C$_{19}$H$_{27}$Cl$_3$CrN$_5$Si): C, 44.49 (44.58); H, 5.37 (5.32); N, 13.68 (13.67)%. μ_{eff} = 3.99 μ_B.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$N(H)^{i}Pr}Cl$_2$(THF) (12)

Anhydrous CrCl$_2$ (0.43 g, 3.49 mmol) in THF (40 mL) was heated at 70 °C for 12 h, allowed to cool to RT and a solution of (Me$_2$pz)$_2$CHSiMe$_2$N(H)^{i}Pr (1.09 g, 3.67 mmol) in THF (30 mL) was added. A colour change from pale green to sky blue occurred and a small amount of solid formed. The resulting mixture was stirred for 4 h at 70 °C. The solution was concentrated to one third of its volume and 10 mL of hexanes were added to complete crystallisation. The solid was collected by filtration, washed with cold hexanes (3 × 5 mL) and dried *in vacuo*, yielding **12** as a sky blue solid. Yield: 1.96 g (62%). IR (NaCl plates, Nujol mull, cm^{-1}): 3225 (m, ν_{N-H}), 3084 (w), 3122 (w), 1556 (m), 1416 (m), 1316 (m), 1285 (w), 1239 (w), 953 (w), 876 (m), 855 (m), 788 (m), 752 (w), 724 (w). Anal. found (calcd. for C$_{20}$H$_{37}$Cl$_2$CrN$_5$OSi): C, 46.69 (46.62); H, 7.25 (7.18); N, 13.61 (13.61)%. μ_{eff} = 4.92 μ_B.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$N(H)Ph}Cl$_2$(THF) (13)

Anhydrous CrCl$_2$ (0.28 g, 2.28 mmol) in THF (40 mL) was heated at 70 °C for 12 h, allowed to cool to RT and a solution of HC(Me$_2$pz)$_2$CHSiMe$_2$N(H)Ph (0.85 g, 2.39 mmol) in THF (30 mL) was added. A colour change from pale green to sky blue occurred and a small amount of solid formed. The resulting mixture was stirred for 4 h at 70 °C. The solution was concentrated to one third of its volume and 10 mL of hexanes were added to complete crystallisation. The solid was collected by filtration, washed with cold hexanes (3 × 5 mL) and dried in vacuo, yielding **13** as a sky blue solid. Yield: 1.35 g (61%). IR (NaCl plates, Nujol mull, cm^{-1}): 3202 (m, ν_{N-H}), 3085 (w), 1600 (w), 1591.4 (w), 1554 (m), 1418 (m), 1316 (m), 1234 (m), 1203 (m), 1067 (w), 903 (w), 855 (m), 865 (s), 837 (m), 796 (s), 763 (m), 697 (m), 666 (m). Anal. found (calcd. for C$_{23}$H$_{35}$Cl$_2$CrN$_5$OSi): C, 50.29 (50.36); H, 6.56 (6.43); N, 12.86 (12.77)%. μ_{eff} = 5.08 μ_B.

(Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$ (14)

To a solution of (Me$_2$pz)$_2$CHSiMe$_2$Cl (2.66 g, 8.56 mmol) in THF (40 mL) was added dropwise a solution of lithium dimethylamide (0.46 g, 8.56 mmol) in THF (20 mL). The resulting yellow solution was stirred for 1 h. The volatiles were removed under reduced pressure to give an off white solid which was washed with Et$_2$O

(3 × 50 mL) and dried *in vacuo*. Extraction into hot benzene (3 × 50 mL, 70 °C) followed by removal of the volatiles under reduced pressure gave a yellow oil as the crude product. Recrystallisation from pentane (20 mL) at -30 °C afforded **14** as an analytically pure white solid. Yield: 1.26 g (48%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): 5.91 (1 H, s, (Me$_2$pz)$_2$C*H*SiMe$_2$NMe$_2$), 5.67 (2 H, s, N$_2$C$_3$*H*Me$_2$), 2.46 (6 H, s, CHSiMe$_2$N*Me$_2$), 2.21 (6 H, s, N$_2$C$_3$H*Me$_2$), 1.84 (6 H, s, N$_2$C$_3$H*Me$_2$), 0.48 (6 H, s, (Me$_2$pz)$_2$CHSi*Me$_2$NMe$_2$) ppm. ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): 146.8 (5-N$_2$C$_3$HMe$_2$), 140.1 (3-N$_2$C$_3$HMe$_2$), 106.6 (4-N$_2$C$_3$HMe$_2$), 69.0 ((Me$_2$pz)$_2$*C*HSiMe$_2$NMe$_2$), 38.7 (CHSiMe$_2$N*Me$_2$), 14.1 (N$_2$C$_3$H*Me$_2$), 11.0 (N$_2$C$_3$H*Me$_2$), -1.5 ((Me$_2$pz)$_2$CHSi*Me$_2$NMe$_2$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1553 (m), 1419 (m), 1357 (s), 1319 (w), 1290 (m), 1276 (m), 1175 (m), 1027 (m), 1002 (w), 785 (m), 667 (w), 661 (m). EI-MS: m/z = 261 (15%), [M - NMe$_2$]$^+$; 210 (30%), [M - Me$_2$pz]$^+$; 102 (60%), [M - HC(Me$_2$pz)$_2$]$^+$. Anal. found (calcd. for C$_{15}$H$_{27}$N$_5$Si): C, 58.97 (58.88); H, 8.91 (8.86); N, 22.92 (22.96)%.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$}Cl$_3$ (15)

To a purple solution of CrCl$_3$(THF)$_3$ (1.17 g, 3.14 mmol) in THF (30 mL) was added a solution of (Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$ (**14**) (1.01 g, 3.31 mmol) in THF (20 mL), giving a pink solution with a small amount of solid. The resulting mixture was stirred for 4 h at 70 °C, concentrated to half its volume and hexanes (10 mL) added to complete crystallisation. The solid was collected by filtration, washed with hexanes (3 × 5 mL) and dried *in vacuo*, affording **7** as a pale pink solid. Yield: 1.27 g (87%). IR (NaCl plates, Nujol mull, cm^{-1}): 3087 (w), 1560 (m), 1415 (w), 1304 (w), 1045 (m), 895 (m), 847 (m). Anal. found (calcd. for C$_{15}$H$_{27}$Cl$_3$CrN$_5$Si): C, 38.90 (38.84); H, 5.86 (5.87); N, 15.01 (15.10)%. μ_{eff} = 3.79 μ_B.

Cr{(Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$}Cl$_2$(THF) (16)

Anhydrous CrCl$_2$ (0.22 g, 1.78 mmol) in THF (40 mL) was heated at 70 °C for 12 h, allowed to cool to RT and a solution of (Me$_2$pz)$_2$CHSiMe$_2$NMe$_2$ (**5**) (0.57 g, 1.87 mmol) in THF (15 mL) was added. A colour change from pale green to sky blue occurred and a small amount of solid formed. The resulting mixture was stirred for 4 h at 70 °C, concentrated to one third of its volume and 10 mL of hexanes added to complete crystallisation. The solid was collected by filtration, washed with cold hexanes (3 × 5 mL) and dried *in vacuo*, affording **16** as a turquoise solid. Yield: 0.60 g (67%). IR (NaCl plates, Nujol mull, cm^{-1}): 3085 (w), 1551 (m), 1317 (w), 1238 (w), 901 (m), 848 (m), 760 (w), 700 (w). Anal. found (calcd. for C$_{19}$H$_{35}$Cl$_2$CrN$_5$OSi): C, 45.49 (45.59); H, 6.93 (7.05); N, 13.86 (13.99)%. μ_{eff} = 5.03 μ_B.

Cr{C(Me$_2$pz)$_3$}Cl$_2$(THF) (17)

To a purple solution of CrCl$_3$(THF)$_3$ (0.59 g, 1.57 mmol) in THF (20 mL) was added a solution of [Li{C(Me$_2$pz)$_3$}(THF)] (0.62 g, 1.65 mmol) in THF (30 mL). The mixture was stirred for 12 h at 60 °C, giving an orange solution and a small amount of solid. The volatiles were removed under reduced pressure and the residues were extracted into hot benzene (4 × 20 mL, 60 °C). Volatiles were again removed under reduced pressure giving a green solid. Crystallisation from the minimum volume of toluene at -30 °C yielded **17** as a dark green microcrystalline solid. Yield: 0.27 g

(40%). IR (NaCl plates, Nujol mull, cm^{-1}): 3127 (w), 1556 (m), 1210 (w), 871 (m), 667 (m). EI-MS: m/z = 418 (20%), [M - THF]$^+$. Anal. found (calcd. for C$_{20}$H$_{28}$Cl$_2$CrN$_6$O): C, 48.85 (48.89); H, 5.74 (5.96); N, 16.99 (17.10)%. μ_{eff} = 3.76 μ_B.

Cr{(Me$_2$pz)$_2$CHArOH}Cl$_3$ (19)

To a purple solution of CrCl$_3$(THF)$_3$ (0.82 g, 2.20 mmol) in THF (30 mL) was added a solution of (Me$_2$pz)$_2$CHArOH (0.95 g, 2.32 mmol) in THF (20 mL). The mixture was stirred for 12 h at 60 °C, giving a dark green solution. The volatiles were removed under reduced pressure giving a dark green solid that was washed with hexanes (3 × 10 mL) and dried *in vacuo*. Extraction into toluene (3 × 10 mL) and recrystallisation at -30 °C afforded **19** as a dark green microcrystalline solid. Yield: 0.91 g (73%). IR (NaCl plates, Nujol mull, cm^{-1}): 3367 (br, w), 3191 (w), 3120 (w), 3093 (w), 1596 (w), 1563 (m), 1415 (m), 1343 (s), 1297 (m), 1200 (m), 1161 (m), 1046 (m), 1016 (m), 918 (w), 854 (m), 683 (w). EI-MS: m/z = 530 (20%), [M - HCl]$^+$. Anal. found (calcd. for C$_{25}$H$_{36}$Cl$_3$CrN$_4$O): C, 52.96 (53.03); H, 6.42 (6.40); N, 9.88 (9.89)%. μ_{eff} = 3.39 μ_B.

Cr{(Me$_2$pz)$_2$CHArO}Cl$_2$(THF) (20)

Method 1—from CrCl$_2$. Anhydrous CrCl$_2$ (0.075 g, 0.62 mmol) in THF (30 mL) was heated at 70 °C for 12 h, allowed to cool to RT and a solution of (Me$_2$pz)$_2$CHArOH (0.36 g, 0.63 mmol) in THF (10 mL) was added. A colour change from pale green to dark green occurred and the mixture was stirred for 12 h at 70 °C. The volatiles were removed under reduced pressure to give a green solid that was washed with hexanes (3 × 10 mL) and dried *in vacuo*. Extraction into THF (3 × 10 mL), concentration, and cooling to -30 °C afforded **11** as a dark green microcrystalline solid. Yield: 0.30 g (81%).

Method 2—from CrCl$_3$(THF)$_3$. To a purple solution of CrCl$_3$(THF)$_3$ (0.62 g, 1.7 mmol) in THF (30 mL) was added a solution of [Na{(Me$_2$pz)$_2$CHArO}(THF)]$_2$ (0.88 g, 1.8 mmol) in THF (20 mL). The mixture was stirred for 12 h at 60 °C, giving a dark green solution. The volatiles were removed under reduced pressure giving a dark green solid that was washed with hexanes (3 × 10 mL) and dried *in vacuo*. Extraction into toluene (3 × 10 mL) and cooling to -30 °C afforded **20** as a dark green microcrystalline solid. Yield; 0.47 g (47%). IR (NaCl plates, Nujol mull, cm^{-1}): 3091 (w), 1600 (w), 1562 (m), 1342 (s), 1299 (m), 1201 (w), 1159 (w), 1120 (w), 972 (w), 918 (w), 855 (w), 842 (m), 776 (s), 753 (w), 682 (s). EI-MS: m/z = 566 (20%), [M - Cl]$^+$; 494 (100%), [M - Cl - THF]$^+$. Anal. found (calcd. for C$_{29}$H$_{44}$Cl$_2$CrN$_4$O$_2$): C, 57.79 (57.71); H, 7.30 (7.35); N, 9.33 (9.28)%. μ_{eff} = 3.72 μ_B (solid state); 3.66 μ_B (Evans method,[27,28] toluene-d_8).

(Me$_2$pz)$_2$CHArOMe (22)

To a suspension of [Na{(Me$_2$pz)$_2$CHArO}(THF)]$_2$ (1.68 g, 3.34 mmol) in THF (40 mL) at -20 °C was added MeI (0.23 mL, 3.67 mmol), dropwise. The mixture was allowed to warm to RT and was stirred for a further 6 h, giving a clear yellow solution. The volatiles were removed under reduced pressure and the resultant solid was extracted into pentane (3 × 15 mL). Removal of the volatiles under reduced pressure yielded **22** as a yellow, glassy solid which was recrystallised from pentane at -30 °C to afford **22** as a

Table 4 X-ray data collection and processing parameters for Cr{(Me₂pz)₂CHSiMe₂-N(H)ⁱPr}Cl₃·0.75(CH₂Cl₂) (**10**·0.75(CH₂Cl₂)) and Cr{(Me₂pz)₂CHSiMe₂N(H)Ph}Cl₃·CH₂Cl₂ (**11**·CH₂Cl₂)

Parameter	**10**·0.75(CH₂Cl₂)	**11**·CH₂Cl₂
empirical formula	C₁₆H₂₉Cl₃CrN₅Si·0.75(CH₂Cl₂)	C₁₈H₂₇Cl₃CrN₅Si·CH₂Cl₂
fw	541.58	596.83
T/K	150	150
wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	10.13760(10)	8.5884(2)
b/Å	14.1035(2)	11.9779(4)
c/Å	18.5130(3)	13.6741(5)
α (°)	90	75.1113(14)
β (°)	98.8488(6)	76.7912(14)
γ (°)	90	76.1372(17)
V/Å³	2615.40(6)	1298.79(7)
Reflections measured	11908	10110
Unique reflections	5950	5903
R_{int}	0.024	0.026
Z	4	2
ρ (calcd)/Mg m⁻¹	1.375	1.526
abs coeff/mm⁻¹	0.956	1.020
R indices [$I > 3\sigma(I)$]ᵃ	$R_1 = 0.0517$	$R_1 = 0.0450$
$R_w = 0.0497$	$R_w = 0.0448$	

ᵃ $R1 = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$; $R_w = \sqrt{\{\Sigma w (|F_o| - |F_c|)^2/\Sigma w |F_o|^2\}}$.

yellow microcrystalline solid. Yield: 0.99 g (70%). ¹H-NMR (C₆D₆, 299.9 MHz, 293 K): 7.97 (1 H, s, (Me₂pz)₂C*H*ArOMe), 7.57 (1 H, d, ³J = 3 Hz, 4-C₆*H*₂ⁱBu₂), 7.51 (1 H, d, ³J = 3 Hz, 6-C₆*H*₂ⁱBu₂), 5.70 (2 H, s, N₂C₃*H*Me₂), 3.42 (3 H, s, (Me₂pz)₂CHArO*Me*), 2.16 (6 H, s, 3 or 5 N₂C₃H*Me₂*), 2.01 (6 H, s, 3 or 5 N₂C₃H*Me₂*), 1.44 (9 H, s, 3-C₆H₂(C*Me₃*)₂), 1.25 (9 H, s, 5-C₆H₂(C*Me₃*)₂) ppm. ¹³C-{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): 153.3 (2-C₆H₂ⁱBu₂), 148.2 (3 or 5-N₂C₃HMe₂), 142.2 (5-C₆H₂ⁱBu₂), 141.2 (3 or 5-N₂C₃HMe₂), 140.0 (3-C₆H₂ⁱBu₂), 125.3 (4-C₆H₂ⁱBu₂), 125.1 (6-C₆H₂ⁱBu₂), 124.7 (1-*C*₆H₂(ⁱBu)₂), 106.9 (4-N₂C₃HMe₂), 74.7 ((Me₂pz)₂CHArOH), 35.6 (3-C₆H₂(C*Me₃*)₂), 34.4 (5-C₆H₂(C*Me₃*)₂), 31.7 (5-C₆H₂(C*Me₃*)₂), 30.1 (3-C₆H₂(C*Me₃*)₂), 13.6 (N₂C₃H*Me₂*), 11.2 (N₂C₃H*Me₂*) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3118 (w), 3086 (w), 1557 (m), 1334 (s), 1309 (m), 1293 (m), 1229 (m), 1116 (m), 1158 (m), 1028 (m), 869 (m), 834 (m), 781 (m), 631 (w), 607 (w), 682 (s). EI-MS: m/z = 391 (80%), [M - OMe]⁺; 327 (100%), [M - Me₂pz]⁺. Anal. found (calcd. for C₂₆H₃₈N₄O): C, 73.79 (73.89); H, 9.01 (9.06); N, 13.30 (13.26)%.

Cr{(Me₂pz)₂CHArOMe}Cl₃ (23)

To a purple solution of CrCl₃(THF)₃ (0.65 g, 1.70 mmol) in THF (10 mL) was added a solution of (Me₂pz)₂CHArOMe (0.77 g, 1.80 mmol) in THF (10 mL). The mixture was stirred for 12 h at 70 °C, to form a dark red solution. The volatiles were removed under reduced pressure to give a solid that was washed with hexanes (3 × 10 mL) and dried *in vacuo*. Extraction into toluene (20 mL), concentration and recrystallisation at -30 °C afforded **23** as a red microcrystalline solid. Yield: 0.87 g (86%). IR (NaCl plates, Nujol mull, cm⁻¹): 3300 (w), 1571 (w), 1230 (w), 1202 (w), 869 (w), 667 (m). Anal. found (calcd. for C₂₆H₃₈Cl₃CrN₄O): C, 53.73 (53.75); H, 6.65 (6.59); N, 9.61 (9.64)%. μ_{eff} = 3.56 μ_B.

Cr{(Me₂pz)₂CHArOMe}Cl₂(THF) (24)

Anhydrous CrCl₂ (0.14 g, 1.14 mmol) in THF (15 mL) was heated at 70 °C for 12 h, allowed to cool to RT and a solution of (Me₂pz)₂CHArOMe (0.51 g, 1.21 mmol) in THF (10 mL) was added. A colour change from pale blue to dark blue occurred and the mixture was stirred for a further 12 h at 70 °C. The volatiles were removed under reduced pressure to give a blue solid that was washed with hexanes (3 × 10 mL) and dried *in vacuo*. Extraction into THF (3 × 10 mL), concentration and cooling to -30 °C afforded **24** as a blue, microcrystalline solid. Yield: 0.51 g (72%). IR (NaCl plates, Nujol mull, cm⁻¹): 1700 (w), 1653 (m), 1497 (s), 1458 (s), 1378 (w), 1249 (s), 1120 (w), 964 (w), 922 (w), 842 (m), 737 (w), 664 (s). Anal. found (calcd. for C₃₀H₄₇Cl₂Cr₁N₄O₂): C, 57.96 (58.32); H, 7.38 (7.67); N, 9.31 (9.07)%. μ_{eff} = 4.83 μ_B (solid state).

Crystal structure determinations of Cr{(Me₂pz)₂CHSiMe₂N(H)ⁱPr}Cl₃ (10·0.75(CH₂Cl₂)) and Cr{(Me₂pz)₂CHSiMe₂N(H)Ph}Cl₃ (11·CH₂Cl₂)†

Crystal data collection and processing parameters are given in Table 4. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[34] The structures were solved by direct methods (SIR92[35]) and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.[36] For **10**, the atoms of the CHSiMe₂N(H) moiety were positionally disordered over two sites. The disorder was modelled adequately and refinement proceeded

normally subject to similarity restraints applied to the positional and displacement parameters of the affected fragment. Residual electron density was modelled a 0.75 fractional occupancy CH_2Cl_2 molecule of crystallization. For **11**, Residual electron density was modelled a full occupancy CH_2Cl_2 molecule of crystallization. For both **11** the N-bound H atom was located and positionally refined. Other H atoms (and all H atoms for **10**) were placed in calculated positions (with reference to a Fourier map as far as possible) and refined in a riding model. A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre.

General procedure for ethylene oligomerisation experiments

Catalytic runs were carried out in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighed amount of catalyst was dissolved in 6 mL of toluene in the glove box and pre-activated with 1 mL of co-catalyst solution to increase solubility. The activated catalyst solution was sonicated for 1 min and immediately injected into the preheated reactor already charged with co-catalyst and toluene (total volume 100 mL) and saturated with ethylene. Solutions were heated using a thermostatic bath and charged with 35 bar of ethylene, the stirring rate was increased to 1000 rpm and the ethylene pressure was maintained throughout the run. The oligo/polymerisations were quenched by venting the reactor (after cooling to below 0 °C for oligomerisation runs) and addition of EtOH and HCl. The resulting polymer was isolated by filtration, sonicated with an acidified ethanol solution, rinsed, and thoroughly dried prior to mass determination and GPC analysis. Oligomers were analysed using GC and ^{1}H NMR spectroscopy.

Acknowledgements

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