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Highly efficient ethylene polymerisation by scandium alkyls supported by neutral *fac*-κ³ coordinated N_3 donor ligands†

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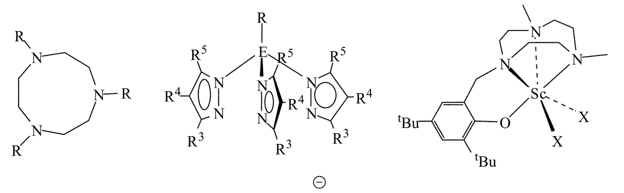
Reaction of $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Sc or Y) with the neutral *fac*-κ³ N_3 donor ligands (L) $Me_3[9]aneN_3$ or $HC(Me_2pz)_3$ gave the corresponding trialkyls $[M(L)(CH_2SiMe_3)_3]$; activation of the scandium congeners with $B(C_6F_5)_3$ in the presence of ethylene afforded highly active polymerisation catalysts ($Me_3[9]aneN_3$ = 1,4,7-trimethyltriazacyclononane).

Much of the recent interest in "post-metallocene" (in general, non-cyclopentadienyl) chemistry of the Group 3 elements[1] is by its very nature linked with the academic and industrial quest for novel types of new olefin polymerisation catalysts.[2] Neutral alkyls of these elements typically have poor olefin polymerisation capability[2,3] and so attention has naturally turned to cationic compounds. Of the few very active Group 3, non-cyclopentadienyl olefin polymerisation precatalysts (giving rise to cationic active species), the only scandium system of merit is Piers' $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}Me_2]$ (Ar = 2,6-$C_6H_3{}^iPr_2$; the activity for polyethylene production has been classified as "moderate"[2b] for borane- or trityl-activated dialkyls)[4a] and the only significantly active systems for yttrium are $[Y\{(^tBuNCH_2CH_2)R_2[9]aneN_3\}(CH_2SiMe_3)_2]$ and $[Y\{PhC(NAr)_2\}(CH_2SiMe_3)_2(THF)_n]$ (n = 1 or 2).[4b,c] All three polymerisation systems feature chelating monoanionic ligands. Here we describe preliminary studies of the synthesis and ethylene polymerisation capability of neutral *fac*-κ³ coordinated $Me_3[9]aneN_3$ and $HC(Me_2pz)_3$ tris(trimethylsilylmethyl) complexes of scandium and comparative studies for yttrium.

We have recently been interested in the potential applications of triazacyclononane[5a–c] **I** (Chart 1) and tris(pyrazolyl)methane[5d] ligands **II** in early transition metal organometallic chemistry. These latter κ³-coordinating N_3 donor ligands[6a] are neutral analogues of the ubiquitous tris(pyrazolyl)hydroborates **III**,[6b] which are immensely "tuneable" to effect desirable properties at the metal centre. In previous studies[5b,c] we reported the syntheses of a series of linked macrocyle-phenoxide compounds, including $[Sc(ArOMe_2[9]aneN_3)X_2]$ (X = Cl **IV** or CH_2SiMe_3 **V**) which we hoped would be effective polymerisation catalysts by analogy with the well-established titanium constrained geometry catalysts[2b] and Hessen and Teuben's related yttrium system (*vide supra*).[4b,c] We were also aware that Bercaw and Hajela[7] had reported that activation of the trimethyl scandium complex $[Sc(Me_3[9]aneN_3)Me_3]$ with $B(C_6F_5)_3$ or $[PhNMe_2H][B(C_6F_5)_4]$ gave only very sluggish olefin polymerisation. However, activation of $[Sc(ArOMe_2[9]aneN_3)X_2]$ (MAO for **IV**, $[CPh_3][B(C_6F_5)_4]$, $B(C_6F_5)_3$ or $[PhNMe_2H][B(C_6F_5)_4]$ for **V**) yielded intractable and inactive (towards PE production) mixtures. Mindful of reports[8a,b] of Y and cationic lanthanide dialkyl complexes stabilised by aza-[18]-crown-6 (deprotonated) and [n]-crown-m (n, m = 12, 4; 15, 5; 18, 6) we decided to target "simple" complexes of the type $[M(L)(CH_2SiMe_3)_3]$ (M = Sc, Y; L = *fac*-κ³ N_3 donor ligand) as shown in Scheme 1 (we reasoned that *tri*dentate ligands – as opposed to the 4- to 6-coordinating ones used in previous studies – ought to allow for a more reactive metal centre in the target cationic complexes, especially for scandium).[8c]

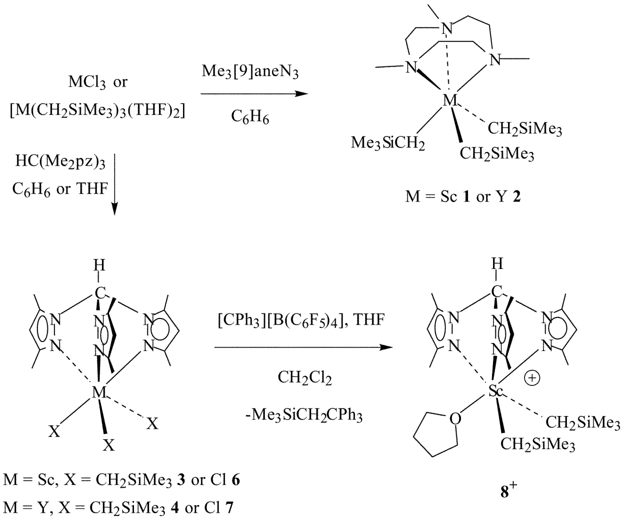
The new compounds† $[M(Me_3[9]aneN_3)(CH_2SiMe_3)_3]$ (M = Sc **1** or Y **2**) and $[M\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3]$ (M = Sc **3** or Y **4**) are easily prepared in reasonable yields from the corresponding readily available $[M(CH_2SiMe_3)_3(THF)_2]$ (Scheme 1). The compounds **1–4** are all obtained as spectroscopically pure compounds but give consistently low %C by combustion analysis. The compounds **1** and **2** are analogues of Bercaw's $[M(Me_3[9]aneN_3)Me_3]$ (M = Sc , Y). To gain further support for **3** and **4** the former was treated with 3 equivs of Ar′OH (Ar′ = 2,6-$C_6H_3Me_2$) forming $[Sc\{HC(Me_2pz)_3\}(OAr')_3]$ **5** in 81% isolated yield. The molecular structure of **5** has been determined and confirms the *fac*-κ³ coordination of $HC(Me_2pz)_3$.† The corresponding trichlorides $[M\{HC(Me_2pz)_3\}Cl_3]$ (M = Sc **6** or Y **7**) are also readily accessible in *ca* 70% isolated yield and the X-ray crystal structure of **7** has been determined[9] confirming those proposed in Scheme 1. The compounds **3–7** are the first Group 3 derivatives of any tris(pyrazolyl)methane ligand.

Reaction of $[Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3]$ **3** with $[CPh_3][B(C_6F_5)_4]$ in CD_2Cl_2 either in the presence of THF (2 equivs) or followed by addition of THF 30 minutes later, quantitatively afforded the cationic species $[Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)]^+$ **8**$^+$ and a non-coordinated $[B(C_6F_5)_4]^-$ anion. Scale up in CH_2Cl_2 afforded **8** as a



$R_3[9]aneN_3$ (**I**) E-R = C-H (**II**); E-R = B-H (**III**) X = Cl (**IV**) or CH_2SiMe_3 (**V**)

Chart 1



Scheme 1

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† Electronic supplementary information (ESI) available: experimental details, characterising data, crystallographic data for **5** and GPC data. See http://www.rsc.org/suppdata/cc/b3/b310867h/

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reasonably stable compound. A scandium tris(dimethylpyrazolyl)hydroborate analogue of **8**$^+$ has been described by Piers[10a] but was completely unreactive towards ethylene polymerisation; an yttrium analogue has, however, been reported by Bianconi to be a moderately active polymerisation catalyst.[10b]

Preliminary ethylene polymerisation studies of the well-defined alkyls [M(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_3$] (M = Sc **1** or Y **2**) and [M{HC(Me$_2$pz)$_3$}(CH$_2$SiMe$_3$)$_3$] (M = Sc **3** or Y **4**) have been carried out (Table 1). Activating 20 μmol of scandium compounds **1** and **3** with one equivalent of B(C$_6$F$_5$)$_3$ in toluene in the presence of ethylene (5 bar) at either *ca* 21 or 33 °C gave a gradual exotherm to over 70 °C during the course of 15–25 minutes. After 60 minutes total run time and standard work-up, *ca*. 22–24 g (for **1**) and 29 g (for **3**) of free-flowing polyethylene was obtained; these quantities equate to “high”[2b] activities in the range *ca*. 200–300 kg(PE) mol^{-1} h^{-1} bar^{-1}, and clearly establish that (unoptimised) **1** and **3** are already competitive with the best post-metallocene scandium based polymerisation catalysts.

The yttrium triazacyclononane compound **2**, in contrast, afforded an activity of only *ca*, 10 kg(PE) mol^{-1} h^{-1} bar^{-1} at 33 °C, and the tris(pyrazolyl)methane homologue **4** afforded no solid ethylene products under the conditions studied to date. This is in contrast to Hessen and Teuben’s results for yttrium with their anionic, chelating (^{t}BuNCH$_2$CH$_2$)R$_2$[9]aneN$_3$ ligand system (*ca*. 700 kg(PE) mol^{-1} h^{-1} bar^{-1} at 30 °C) which might point to an importance of having at least one anionic ligand donor group for the larger metals.[4b]

GPC analysis† of the polymers produced revealed a critical dependence on metal, supporting ligand and activation temperature. For precatalyst **1** activated at 21 °C the polyethylene is approximately bimodal with a very dominant higher molecular weight fraction having $M_p = 575 \times 10^3$ and a minor lower fraction having $M_p = 1070$ (estimated M_w and M_w/M_n for these being 1310 and 1.2, and 936,000 and 15.1 for the minor and major components, respectively). Polymer obtained on activating **1** at 33 °C had a more dominant lower molecular weight fraction and a much broader higher molecular weight fraction, both accompanied by a shift to lower overall M_w. In contrast, polymer from activation of **2** at 33 °C was dominated by a high molecular weight fraction with little low molecular weight material; compound **3** on the other hand (activated at 33 °C) afforded two main fractions with the lower molecular weight one being the dominant. These preliminary experiments indicate that significant control over polymer structure might be gained by simple variation of N$_3$ donor ligand, ligand substituents and polymerisation conditions, especially for the highly active scandium systems. The multiple factors that can influence polymer polydispersities and modalities have been well discussed in the recent literature.[11]

It is not clear at this time why our tris(CH$_2$SiMe$_3$)$_3$ scandium complexes **1** and **3** are so much more active than Bercaw’s [Sc(Me$_3$[9]aneN$_3$)Me$_3$], but one reason could be the greater ease with which methyl groups bridge metal centres compared to the bulkier CH$_2$SiMe$_3$ (thereby leading to catalyst deactivation for the cationic complexes); another contribution could be the favourable stabilisation of electron-deficient cationic metal centres by β-Si–C agostic interactions[12] from the CH$_2$SiMe$_3$ ligands in either the initiating or/and propagating catalytic species derived from **1** and **3**. The failure of the apparently more promising [Sc(ArOMe$_2$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_2$] systems to act as ethylene polymerisation catalysts might be accounted for by dimerisation side-reactions of the desired cations *via* μ-OBr bridges, or by metallation of one of the aryl ring *ortho*-^{t}Bu groups as postulated for a C$_5$Me$_5$-supported scandium aryloxide system.[13]

Table 1 Ethylene polymerisation with compounds [Sc(ArOMe$_2$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_2$] **V**, [M(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_3$] (M = Sc **1** or Y **2**) and [Sc{HC(Me$_2$pz)$_3$}(CH$_2$SiMe$_3$)$_3$] (M = Sc **3** or Y **4**)^a

Pre-catalyst	Yield (g)	Activity^b	M_w	$M_p^{(1)}$	$M_p^{(2)}$
V	0^c	0	—	—	—
1	22.3^c	220	8.47×10^5	1070	575×10^3
1	23.6^d	240	3.53×10^5	560	70.8×10^3
2	0.97^d	10	1.18×10^6	–	851×10^3
3	29.4^d	290	1.92×10^5	2750	537×10^3
4	0^d	0	—	—	—

^{a} Conditions: steel autoclave equipped with removable glass liner, magnetically coupled mechanical stirrer (stirring rate 750 rpm); 20 μmol scandium precatalyst, 20 μmol B(C$_6$F$_5$)$_3$ co-catalyst; 250 cm^3 total volume toluene; 5 bar ethylene pressure delivered on request; run time 60 min; 250 equivs Al^{i}Bu$_3$. ^{b} In kg(PE) mol(Sc)$^{-1}$ h^{-1} bar^{-1}. ^{c} Activation temperature 21 °C; ^{d} Activation temperature 33 °C.

In conclusion, we believe that there is considerable scope for development of the title compounds and the unsaturated substrates which they can activate. Studies of this type on the effects of varying metal (transition and *f* element), solvent, co-catalyst, reaction time and temperature are currently in progress.

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