

Highly efficient ethylene polymerisation by scandium alkyls supported by neutral *fac*- κ^3 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*- κ^3 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 elements¹ 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’ $[Sc\{ArNC(tBu)CHC(tBu)NAr\}Me_2]$ ($Ar = 2,6-C_6H_3iPr_2$; 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 $[Y\{(tBu)NCH_2CH_2\}R_2[9]aneN_3](CH_2SiMe_3)_2]$ 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*- κ^3 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 κ^3 -coordinating N_3 donor ligands^{6a} are neutral analogues of the ubiquitous tris(pyrazolyl)hydroborates **III**,^{6b} which are immensely “tunable” to effect desirable properties at the metal centre. In previous studies^{5b,c} we reported the syntheses of a series of linked macrocyclic-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 Hsien and Teuben’s related yttrium system (*vide supra*).^{4b,c} We were also aware that Bercaw and Hajela⁷ 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 $[Sc(ArO-$

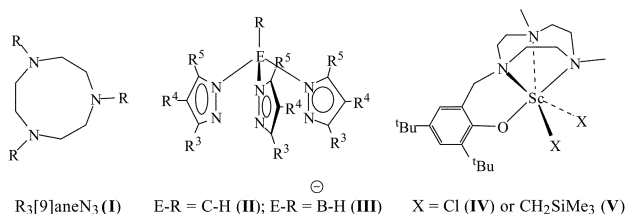


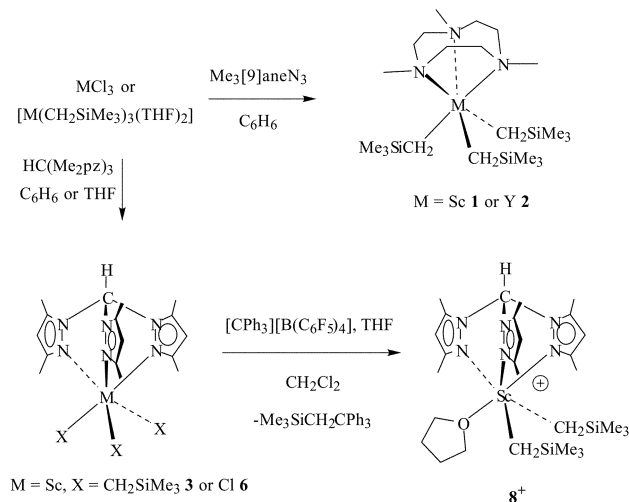
Chart 1

† 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>

$Me_2[9]aneN_3)X_2]$ (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 $[M(L)(CH_2SiMe_3)_3]$ ($M = Sc, Y; L = fac-\kappa^3 N_3$ donor ligand) as shown in Scheme 1 (we reasoned that tridentate 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*- κ^3 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 determined⁹ 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



Scheme 1

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(Me₃[9]aneN₃)(CH₂SiMe₃)₃] (M = Sc **1** or Y **2**) and [M{HC(Me₂pz)₃}(CH₂SiMe₃)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(C₆F₅)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 (tBuNCH₂CH₂)R₂[9]aneN₃ 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 × 10³ 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 N₃ 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(CH₂SiMe₃)₃ scandium complexes **1** and **3** are so much more active than Bercaw’s

Table 1 Ethylene polymerisation with compounds [Sc(ArOMe₂[9]aneN₃)(CH₂SiMe₃)₂] **V**, [M(Me₃[9]aneN₃)(CH₂SiMe₃)₃] (M = Sc **1** or Y **2**) and [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃] (M = Sc **3** or Y **4**)^a

Pre-catalyst	Yield (g)	Activity ^b	<i>M_w</i>	<i>M_p</i> ⁽¹⁾	<i>M_p</i> ⁽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(C₆F₅)₃ co-catalyst; 250 cm³ total volume toluene; 5 bar ethylene pressure delivered on request; run time 60 min; 250 equivs AlⁱBu₃. ^b In kg(PE) mol(Sc)⁻¹ h⁻¹ bar⁻¹. ^c Activation temperature 21 °C; ^d Activation temperature 33 °C.

[Sc(Me₃[9]aneN₃)Me₃], but one reason could be the greater ease with which methyl groups bridge metal centres compared to the bulkier CH₂SiMe₃ (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 interactions¹² from the CH₂SiMe₃ ligands in either the initiating or/and propagating catalytic species derived from **1** and **3**. The failure of the apparently more promising [Sc(ArOMe₂[9]aneN₃)(CH₂SiMe₃)₂] systems to act as ethylene polymerisation catalysts might be accounted for by dimerisation side-reactions of the desired cations *via* μ-OB_r bridges, or by metallation of one of the aryl ring *ortho*-tBu groups as postulated for a C₅Me₅-supported scandium aryloxide system.¹³

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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Notes and references

- For recent reviews and leading references see: W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233**, 131; P. Mountford and B. D. Ward, *Chem. Commun.*, 2003, 1797.
- For recent reviews and leading references see: (a) Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1; (b) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- Compare reference 4c with F. G. N. Cloke, B. R. Elvidge, P. B. Hitchcock and V. M. E. Lamarche, *J. Chem. Soc., Dalton Trans.*, 2002, 2413.
- (a) P. G. Hayes, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 2132; (b) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2001, 637; (c) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2003, 522.
- (a) N. A. H. Male, M. E. G. Skinner, S. Y. Bylikin, P. J. Wilson, P. Mountford and M. Schröder, *Inorg. Chem.*, 2000, **39**, 5483; (b) S. Y. Bylikin, D. A. Robson, N. A. H. Male, L. H. Rees, P. Mountford and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2001, 170; (c) M. E. G. Skinner, B. R. Tyrell, B. D. Ward and P. Mountford, *J. Organomet. Chem.*, 2002, **647**, 145; (d) S. A. Lawrence, M. E. G. Skinner, J. C. Green and P. Mountford, *Chem. Commun.*, 2001, 705.
- (a) D. L. Reger, *Comments Inorg. Chem.*, 1999, **21**, 1; D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold and R. D. Sommer, *J. Organomet. Chem.*, 2000, **607**, 120; (b) S. Trofimenko, *Scorpionates: the coordination chemistry of polypyrazolylborate ligands*, Imperial College Press, London, 1998.
- S. Hajela, W. P. Schaefer and J. E. Bercaw, *J. Organomet. Chem.*, 1997, **532**, 45.
- (a) L. Lee, D. J. Berg, F. W. Einstein and R. J. Batchelor, *Organometallics*, 1997, **16**, 1819; (b) S. Arndt, T. P. Spaniol and J. Okuda, *Chem. Commun.*, 2002, 896; (c) Both [Sc{[12]-crown-4}(CH₂SiMe₃)₂]⁺ and [Sc(CH₂SiMe₃)₃(THF)₂] show negligible activity towards ethylene polymerisation: S. Arndt, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 5075.
- S. E. Brown, S. C. Lawrence, S. R. Dubberley, J. W. Steed, D. A. Tocher, P. Mountford and A. Sella, manuscript in preparation.
- (a) J. Blackwell, C. Lehr, Y. Sun, W. E. Piers, S. D. Pearce-Batchilder, M. J. Zaworotko and V. G. Young Jr., *Can. J. Chem.*, 1997, **75**, 702; (b) D. P. Long and P. A. Bianconi, *J. Am. Chem. Soc.*, 1996, **118**, 12453.
- Y. Tohi, H. Makio, S. Matsui, M. Onda and T. Fujita, *Macromolecules*, 2003, **36**, 523; B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; S. Murtuza, O. L. Casagrande and R. F. Jordan, *Organometallics*, 2002, **21**, 1882; D. Reardon, F. Conan, S. Gambarotta, G. Yap and Q. Wang, *J. Am. Chem. Soc.*, 1999, **120**, 9318.
- For a review see: G. I. Nikonov, *J. Organomet. Chem.*, 2001, **635**, 24.
- W. E. Piers, E. E. Bunel and J. E. Bercaw, *J. Organomet. Chem.*, 1991, **407**, 51.