Synthesis, DFT Studies, and Reactions of Scandium and Yttrium Dialkyl Cations Containing Neutral *fac*-N₃ and *fac*-S₃ Donor Ligands

Cara S. Tredget,[†] Eric Clot,^{*,‡} and Philip Mountford^{*,†}

Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K., and Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-UM1-ENSCM, cc 1501, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

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Reaction of Sc(CH₂SiMe₃)₃(THF)₂ with 1,4,7-trithiacyclononane gave Sc([9]aneS₃)(CH₂SiMe₃)₃, the first organometallic group 3 complex of $[9]aneS_3$ ($[9]aneS_3 = 1,4,7$ -trithiacyclononane). The corresponding reaction for yttrium gave equilibrium mixtures of $Y([9]aneS_3)(CH_2SiMe_3)_3$ and starting materials. Density functional theory (DFT) was used to compare the energies of formation and metal-ligand interaction energies for M([9]aneS₃)R₃ with those for the previously reported fac-N₃ donor complexes M(fac-N₃)R₃ $(R = Me \text{ or } CH_2SiMe_3; fac-N_3 = 1,4,7-trimethyltriazacyclononane (Me_3[9]aneN_3) \text{ or } HC(Me_2pz)_3).$ Reaction of M(CH₂SiMe₃)₃(THF)₂ with [NHMe₂Ph][BAr^F₄] (Ar^F = C₆F₅) in the presence of a facecapping ligand L (L = HC(Me₂pz)₃, Me₃[9]aneN₃, or [9]aneS₃) gave the cationic complexes $[M(L)(CH_2SiMe_3)_2(THF)]^+$, which has been structurally characterized for M = Sc and L = [9]aneS_3. The corresponding base-free cations $[M(L)(CH_2SiMe_3)_2]^+$ were studied by ²⁹Si NMR spectroscopy and/ or DFT and found to possess β -Si-C agostic alkyl groups in most instances. The isolated cations [Sc(*fac*- N_3 (CH₂SiMe₃)₂(THF)]⁺ underwent THF substitution reactions with OPPh₃ or pyridine, Sc-alkyl migratory insertion with carbodiimides, and C-H bond metathesis with PhCCH. The olefin polymerization capabilities of a series of complexes M(L)R₃ have been determined. The scandium complexes were found to be very productive for ethylene polymerization for $L = HC(Me_2pz)_3$, $Me_3[9]aneN_3$, or [9]aneS₃ and $R = CH_2SiMe_3$ when activated with 1 equiv of $[CPh_3][BAr^F_4]$. When activated with 2 equiv of $[CPh_3][BAr^F_4]$, the compounds were also very active for the polymerization of 1-hexene.

Introduction

In the last 10 years in particular, noncyclopentadienyl group 3 and lanthanide compounds have attracted an increasing amount of attention.^{1–4} Some of this work has been focused toward catalytic transformations, and in particular olefin polymerization.^{5–8} In the latter regard, several research groups have recently targeted mono- or dicationic alkyl derivatives as analogues of the well-known cationic group 4 Ziegler-type polymerization catalysts.^{9–11} In our laboratory^{12–23} we have been developing the stoichiometric and catalytic reactions of early transition metal organometallic complexes containing *fac*-coordinating N₃-donor ligands (Figure 1) such as 1,3,5-trimethyltriazacyclohexane (Me₃[6]aneN₃), 1,4,7-trimethyltriazacyclonane (Me₃[9]aneN₃), and tris(3,5-dimethyl)pyrazolylmethane (HC(Me₂pz)₃, a neutral analogue of the anionic tris(pyrazolyl)hydroborate family [HB(R₂pz)₃]⁻). These readily prepared chelating ligands provide

* Institut Charles Gerhardt Montpellier.



Figure 1. fac-N₃ donor ligands used in this contribution.

well-defined coordination environments and have been widely exploited in coordination chemistry in general. The "hard" nitrogen donors are highly compatible with the "hard" early transition metals and group 3/lanthanide elements.

Bercaw was the first to report organometallic $Me_3[9]aneN_3$ complexes of group 3, namely, $M(Me_3[9]aneN_3)Me_3$ (M = Sc

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^{*} Corresponding authors. E-mail: philip.mountford@chem.ox.ac.uk; clot@ univ-montp2.fr.

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or Y).²⁴ Their reactions with [NHMe₂Ph][BAr^F₄] or BAr^F₃ were also described (Ar^F = C₆F₅). For M = Y the reaction with [NHMe₂Ph][BArF₄] led to decomposition and loss of $Me_3[9]aneN_3$. For M = Sc, the corresponding reaction in THF gave a product tentatively formulated as [Sc(Me₃[9]aneN₃)- $Me_2(THF)$ [BAr^F₄]. Activation of Sc(Me₃[9]aneN₃)Me₃ with BAr_{3}^{F} on the NMR tube scale in THF- d_{8} provided a system competent for ethylene polymerization at 80 °C, but no welldefined compound was isolated. Hessen subsequently found that tetradentate triazacyclononane-based ligands containing chelating amide groups formed very active, well-defined ethylene polymerization catalysts for group 3 and lanthanide metals.^{25–29} Other group 3 catalyst systems based on fac-N₃-type neutral and monoanionic ligands have also been reported recently by the same group.^{30,31} Related open-chain systems have also recently been described.32

In other work with fac-N₃-type monoanionic ligands, Piers³³ and Bianconi³⁴ reported scandium and yttrium tris(pyrazolyl)hydroborate complexes of the type M{HB(R₂pz)₃}(CH₂SiMe₃)₂- $(THF)_n$ (R = Me or ^tBu, n = 1 or 0), but these showed either no (Sc) or negligible activity toward ethylene polymerization. Okuda et al. were the first to report structurally authenticated (but catalytically inactive) rare earth alkyl cations based on O-donor crown ethers.^{35,36} Very recently Gade and co-workers reported a series of C_3 -symmetric rare earth complexes M(ⁱPrtrisox)(CH₂SiMe₂R)₃ (R = Me or Ph) capable of the isospecific polymerization of 1-hexene and other α -olefins.^{37,38} Interestingly, based on in situ NMR experiments, alkyl dications of the type " $[M(^{i}Pr-trisox)(CH_{2}SiMe_{2}R)]^{2+}$ " were proposed to be the active species in these systems. Indeed, Okuda et al. have

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Organometallics, Vol. 27, No. 14, 2008 3459

polymerization.^{36,39–42} Recently it has been reported that the presence of neutral S-donor groups may be beneficial to the performance of certain group 4 alkyl polymerization catalysts.⁴³ Unsurprisingly, the non-cyclopentadienyl organometallic chemistry of the group 3 metals is dominated by "hard" N- and O-donor ligands.¹⁻⁴ Although some noteworthy examples are known of anionic bis(phenolate) ligands incorporating additional neutral thioether donors,^{44,45} neutral or cationic organometallic complexes based entirely on "soft" sulfur-donor ligands have yet to be described.

The commercially available macrocycle 1,4,7-trithiacyclononane ($[9]aneS_3$) is the all-sulfur donor analogue of Me₃[9]aneN₃. [9]aneS₃ has an extensive coordination chemistry of the later transition and p-block metals (ca. 250 organometallic complexes alone have been reported).^{46–48} However, apart from our recent communication,49 no organometallic rare earth compounds (or indeed organotransition metal compounds before group 6) containing $[9]aneS_3$ have so far been reported. The only rare earth complexes reported so far for [9]aneS3 are $La([9]aneS_3)I_3(MeCN)_2$ and $U([9]aneS_3)I_3(MeCN)_2$.⁵⁰

We recently described the synthesis and structures of a range of group 3 fac-N₃-coordinated complexes $M(fac-N_3)X_3$ (M = Sc, Y; X = Cl or CH₂SiMe₃; fac-N₃ = Me₃[6]aneN₃, Me₃[9]aneN₃, or HC(Me₂pz)₃).¹⁷ In this contribution we report the first rare earth organometallic complexes of [9]aneS₃ along with a number of well-defined, THF-stabilized cationic dialkyl complexes containing neutral fac-N3 or -S3 donor ligands. DFT studies comparing the ligand complexation energetics of $Me_3[9]aneN_3$, $HC(Me_2pz)_3$, and $[9]aneS_3$ are reported, together with related studies of the structures of the base-free dialkyl cations $[M(L)(CH_2SiMe_3)_2]^+$ (which could also be observed by NMR spectroscopy in some instances). Selected C-H activation and migratory insertion reactions of well-defined scandium dialkyl cations are reported. The abilities of the complexes $M(L)(CH_2SiMe_3)_3$ to act as precatalysts for the polymerization of ethylene and 1-hexene are also disclosed. Part of this work has been communicated.49,51

Results and Discussion

Trithiacyclononane Complexes: Synthesis and Structures. Reaction of Sc(CH₂SiMe₃)₃(THF)₂ with 1 equiv of [9]aneS₃ in cold toluene followed by removal of the volatiles under reduced pressure gave $Sc([9]aneS_3)(CH_2SiMe_3)_3$ (1) as an air-sensitive, white solid in 75% isolated yield (eq 1). Prolonged exposure to

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vacuum led to decomposition, possibly due to loss of $[9]aneS_3$. Compound **1** is the first organometallic derivative of $[9]aneS_3$ for any group 3 or rare earth metal.



The solution NMR data and crystallographic data (see below) are consistent with the six-coordinate structure illustrated in eq 1. The CH₂SiMe₃ groups appear as singlets in the ¹H and ¹³C{¹H} spectra with values in the expected ranges. The inequivalent methylene hydrogens of [9]aneS₃ (i.e., "up" and "down" with respect to Sc) appear as two sets of multiplets (relative integrals 6 H each) at ca. 2.25 and 1.45 ppm in the ¹H spectrum, consistent with coordination of the ligand to the Sc(CH₂SiMe₃)₃ moiety in solution. No exchange was observed between free and coordinated [9]aneS₃ on the NMR time scale. When the reaction between Sc(CH₂SiMe₃)₃(THF)₂ and [9]aneS₃ was monitored by ¹H NMR spectroscopy at 293 K in toluene d_8 , it was found to lead to only ca. 85% conversion to 1 and THF, in a temperature-dependent equilibrium. Cooling the sample to 241 K shifted the equilibrium slightly back toward the starting materials (ca. 75% conversion at this temperature). This is to be anticipated since formation of 1 requires one [9]aneS₃ ligand to displace two THF molecules from Sc(CH₂SiMe₃)₃(THF)₂, which is an entropically favored process. The reversibility of eq 1 was confirmed by the addition of 5 equiv of THF to a pure sample of 1, which led to complete displacement of [9]aneS₃. Furthermore, addition of 1 equiv of the fac-N₃ donor ligands HC(Me₂pz)₃ or Me₃[9]aneN₃ to 1 in C₆D₆ also gave quantitative displacement of [9]aneS₃ to form the previously reported Sc(fac-N₃)(CH₂SiMe₃)₃ (2 or 3, respectively).¹⁷ Addition of 1 equiv. of [9]aneS₃ to pure samples of either Sc(fac-N₃)(CH₂SiMe₃)₃ compound failed to give any reaction, confirming that the positions of these equilibria are governed by thermodynamic factors (eq 2). The ready displacement of [9]aneS₃ by THF and the fac-N₃ species is consistent with expectations based on the hardness of these O- and N-donor ligands.



The reaction between $Y(CH_2SiMe_3)_3(THF)_2$ and $[9]aneS_3$ has also been followed by NMR spectroscopy in toluene- d_8 (eq 1). At 293 K only ca. 60% conversion to the *fac*-coordinated product $Y([9]aneS_3)(CH_2SiMe_3)_3$ (4) was observed, reducing to ca. 50% at 241 K. Unfortunately, 4 could not be isolated on the preparative scale, but was characterized *in situ* by ¹H and ¹³C NMR spectroscopy. The NMR spectra of 4 were analogous to those of 1, in particular showing two sets of ¹H multiplets for the coordinated [9]aneS₃. ⁸⁹Y coupling to the Y-bound CH₂ groups was observed in the ¹³C spectrum.

Diffraction-quality crystals of $Sc([9]aneS_3)(CH_2SiMe_3)_3$ (1) were grown from a toluene-pentane solvent mixture at -80



Figure 2. Displacement ellipsoid plot (20% probability) of Sc([9]aneS₃)(CH₂SiMe₃)₃ (1). H atoms and toluene of crystallization omitted for clarity. Selected distances (Å): Sc(1)–S(1) 2.7947(7), Sc(1)–S(2) 2.7799(6), Sc(1)–S(3) 2.8039(6), Sc(1)–C(7) 2.250(2), Sc(1)–C(11) 2.265(2), Sc(1)–C(15) 2.231(2). Selected angles (deg): S(1)–Sc(1)–S(2) 74.439(18), S(1)–Sc(1)–S(3) 74.240(17), S(2)–Sc(1)–S(3) 74.380(18), C(7)–Sc(1)–C(11) 109.66(9), C(7)–Sc(1)–C(15) 106.75(8), C(7)–Sc(1)–C(15) 103.74(9).

°C. The molecular structure is shown in Figure 2 together with selected bond distances and angles. Molecules of 1 contain sixcoordinate scandium centers bound to three CH₂SiMe₃ ligands and a *fac*-coordinated [9]aneS₃. The Sc-S bonds lie in the range 2.7799(6)-2.8039(6) Å. Although there are very few previously determined distances to compare these to, they are within the range of those reported by Okuda for two six-coordinate thioether-bridged scandium bis(phenolate) complexes (av 2.867, range 2.744(2) - 2.873(1) Å).⁴⁴ The Sc-CH₂ distances in 1 (av 2.249 Å) lie within the general range for compounds containing a Sc-CH₂SiMe₂R (R = Me or Ph) group (range 2.166-2.295, av 2.232 Å).^{52,53} However, they are noticeably shorter than those in the closely related fac-N₃ complexes Sc{HC(Me₂pz)₃}(CH₂-SiMe₃)₃ (2, av 2.280 Å) and Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₃ (3, av 2.281 Å).¹⁷ The shorter Sc-CH₂ distances in 1 indicate that the bonding to the alkyl ligands in this complex is less perturbed by the *fac*-coordinated ligand compared to that in the N₃-donor complexes, again suggesting that [9]aneS₃ bonds less well to the $Sc(CH_2SiMe_3)_3$ fragment than the analogous nitrogen macrocycle Me₃[9]aneN₃ or related podand ligand HC(Me₂pz)₃. Further examination of the geometry of the Sc(CH₂SiMe₃)₃ fragments in the three complexes 1, 2, and 3 appears to confirm this. Thus the C-Sc-C angles in 1 (av 106.7°) are significantly less compressed than those in 2 (av 100.5°) and 3 (av 100.8°). Accordingly, the displacement of Sc from the plane defined by the three CH_2SiMe_3 methylene carbons in 1 (0.85 Å) is significantly less than in 2 (1.05 Å) or 3 (1.04 Å).

DFT Studies of Ligand Binding Abilities. Compound **1** is unique in group 3 organometallic chemistry, whereas complexes of the type $Sc(fac-N_3)R_3$ based on $Me_3[9]aneN_3^{17}$ or other N_3 donor ligands^{17,30,33,34} are fairly well-established (as are O-donor crown ether complexes^{35,36}). The NMR tube experiments described above (eqs 1 and 2) found that [9]aneS₃ is displaced by both THF and *fac*-N₃ donor ligands. To gain further insight into these processes, DFT calculations probing the underlying

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Figure 3. Thermodynamic cycle considered to analyze the formation energy ΔE_{form} of the M(L)R₃ complexes as a sequence of three steps: (i) deformation of the MR₃ fragment, $\Delta E_{\text{def}}(M)$; (ii) deformation of the ligand, $\Delta E_{\text{def}}(L)$; (iii) interaction between the two fragments in the geometry of the complex, $\Delta E_{\text{int}}(M \cdots L)$. L = Me₃[9]aneN₃, HC(Me₂pz)₃, or [9]aneS₃; R = Me or CH₂SiMe₃; M = Sc or Y. $\Delta E_{\text{form}} = \Delta E_{\text{def}}(M) + \Delta E_{\text{def}}(L) + \Delta E_{\text{int}}(M \cdots L)$. See Table 1 for further details.

electronic energies of the reactions in eqs 1 and 2 were carried out for a series of model systems $M(L)R_3$ (M = Sc or Y, R = Me or CH₂SiMe₃; L = Me₃[9]aneN₃, HC(Me₂pz)₃, or [9]aneS₃; see Computational Details for further information).

$$MR_{3}(THF)_{2} + L \xrightarrow{\Delta E_{exch}} M(L)R_{3} + 2 THF$$

$$L = Me_{3}[9]aneN_{3}, HC(Me_{2}pz)_{3} \text{ or } [9]aneS_{3};$$

$$M = Sc \text{ or } Y; R = CH_{2}SiMe_{3} \text{ or } Me$$
(3)

Figure 3 assesses the formation energies, ΔE_{form} , of various model complexes $M(L)R_3$ from the separated hypothetical fragments MR₃ and free ligands L. The overall formation energies (see Table 1) have been decomposed into three main parts: (i) the energy, $\Delta E_{def}(M)$, required to deform the free MR₃ fragment to its geometry in the $M(L)R_3$ complex; (ii) the corresponding preorganization energy for the ligand, $\Delta E_{def}(L)$; (iii) the interaction energy, $\Delta E_{int}(M \cdots L)$, between the preorganized MR₃ and L moieties. Table 1 also gives the distance dof M in $M(L)R_3$ above the plane defined by the $M-CH_2$ or M–CH₃ carbons of the alkyl ligands. This is a measure of the extent of deformation (pyramidalization) of the MR₃ fragments from their equilibrium geometries ($d \approx 0.4$ Å, see Table 1). Table 1 also provides the calculated electronic energy ΔE_{exch} for the substitution of two THFs in $MR_3(THF)_2$ by L (R = Me or CH_2SiMe_3 ; eq 3). We have not attempted to estimate entropies for the processes, which, to a first approximation are assumed to be effectively constant within the two different systems (i.e., Figure 3 and eq 3). Where the experimental data are available, the agreement between the calculated and observed geometries of the various complexes M(L)(CH₂SiMe₃)₃ is very good.

Entries 1-3 of Table 1 list the energetic parameters for ligand bonding to Sc(CH₂SiMe₃)₃. The ΔE_{form} values predict that both Me₃[9]aneN₃ and HC(Me₂pz)₃ form stronger complexes with $Sc(CH_2SiMe_3)_3$ than [9]aneS₃ does, in accord with eq 2 and our previous report that Me₃[9]aneN₃ displaces HC(Me₂pz)₃ from M{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (M = Sc or Y).¹⁷ However, although the difference in ΔE_{form} between 2 and 1 is only 14.3 kJ mol⁻¹, this is *not* a direct reflection of the differences in the metal-ligand interaction energy ($\Delta E_{int}(M \cdots L)$) for the HC(Me₂pz)₃ and [9]aneS₃ ligands themselves. As shown in Table 1, the $\Delta E_{int}(M \cdots L)$ values for the two fac-N₃ donors $(-260.4 \text{ and } -236.6 \text{ kJ mol}^{-1})$ are considerably more favorable than for $[9]aneS_3$ (-156.7 kJ mol⁻¹). The origin of the unexpectedly small difference in the overall ΔE_{form} between 2 and 1 is instead attributed to the higher preorganization energy of both the Sc(CH₂SiMe₃)₃ (95.0 vs 62.0 kJ mol^{-1}) and ligand $(35.8 \text{ vs } 3.3 \text{ kJ mol}^{-1})$ fragments for the N₃-donor case. The higher $\Delta E_{def}(M)$ value for 2 (and 3) compared to 1 relates to the more extensive pyramidalization of Sc(CH₂SiMe₃)₃ in the former systems (cf. the larger *d* values computed in Table 1 and found experimentally, *vide supra*). This presumably maximizes metal–ligand bonding interactions in the *fac*-N₃ systems. The consistently smaller $\Delta E_{def}(L)$ values for both Me₃[9]aneN₃ and [9]aneS₃ compared to HC(Me₂pz)₃ are attributed to the well-known "macrocyclic effect" for these highly preorganized ligands.⁵⁴

The general trends for the bulky $Sc(L)(CH_2SiMe_3)_3$ systems are found for the smaller trimethyl homologues $Sc(L)Me_3$ (entries 4–6). The ΔE_{form} values are more favorable for all ligands, which relates primarily to the smaller deformation energies $\Delta E_{def}(M)$. In fact a pronounced β -Si–C agostic interaction is present in the fragments M(CH₂SiMe₃)₃ (M = Sc or Y), and this contributes to add extra stabilization. Thus deformation of the fragment to accommodate the incoming L ligand is energetically more costly compared to the same process for ScMe₃, where such an agostic interaction is absent.

For the yttrium congeners (entries 7–9) there is a somewhat larger difference between the ΔE_{form} value for the [9]aneS₃ complex **4** and both *fac*-N₃ complexes. Again, this does not relate primarily to the intrinsic $\Delta E_{\text{int}}(M \cdots L)$ values (which vary by no more than ca. 10 kJ mol⁻¹ from Sc to Y), but to the different extents of stabilization of the M(CH₂SiMe₃)₃ deformation energies for the larger metal center. Thus for Me₃[9]aneN₃ and HC(Me₂pz)₃ the deformation energies decrease by ca. 31 and 26 kJ mol⁻¹, respectively, whereas for M([9]aneS₃)(CH₂SiMe₃)₃ the decrease from M = Sc to Y is only ca. 17 kJ mol⁻¹. This is because the deformation of the MR₃ fragment in all three compounds M([9]aneS₃)R₃ (**1**, **7**, and **4**) is systematically lower (as indicated by the smaller *d* values) than for the corresponding *fac*-N₃ systems.

The calculated ΔE_{exch} values for THF displacement from M(CH₂SiMe₃)₃(THF)₂ according to eq 3 follow the same trends as the ΔE_{form} values for M = Sc and Y. For Me₃[9]aneN₃ the formation of 3 or 8 from the bis(THF) species is exothermic. In contrast, for both HC(Me₂pz)₃ and [9]aneS₃ it is endothermic, but for different reasons as discussed above. In both of the latter cases it appears that entropic contributions are essential for the formation of the M(L)(CH₂SiMe₃)₃ complexes. The more positive ΔE_{exch} for the formation of **4** compared to that for **1** is consistent with the lower extent of conversion of Y(CH₂SiMe₃)₃(THF)₂ to Y([9]aneS₃)(CH₂SiMe₃)₃ as found in the NMR experiments. It is also interesting to note that although HC(Me₂pz)₃ reacts with Sc(CH₂SiMe₃)₃(THF)₂ in C₆D₆ or CD_2Cl_2 to quantitatively form $M{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2) (despite the positive calculated ΔE_{exch} value),¹⁷ when pure 2 is dissolved in THF- d_8 , an equilibrium mixture of **2**, HC(Me₂pz)₃, and Sc(CH₂SiMe₃)₃(THF-d₈)₂ is formed. However, Me₃[9]aneN₃ is not displaced from 3 under the same conditions, again in agreement with Table 1. The ΔE_{exch} values for the hypothetical trimethyl complexes MMe₃(THF)₂ follow the same trend as for M(CH₂SiMe₃)₃(THF)₂.

Synthesis and Reactivity of THF-Stabilized Dialkyl Cations. The remainder of this contribution is concerned with the synthesis, bonding, and reactivity of cationic complexes.

Scheme 1 shows the preparative-scale syntheses of the new THF-stabilized cations $[M{HC(Me_2pz)_3}(CH_2SiMe_3)_2(THF)]^+$ (M = Sc (10⁺) or Y (11⁺)). They were isolated in 71–73% yield in analytically pure form as their $[BArF_4]^-$ salts (Ar^F = C₆F₅) by precipitation from THF solution on addition of pentane, the SiMe₄ and NMe₂Ph side-products remaining in the supernatants. NMR tube experiments in CD₂Cl₂ showed that 10⁺ or

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Table 1. Formation Energies, ΔE_{form} , of the M(L)R₃ Complexes and Energetic Contributions Defined According to the Thermodynamic Cycle Shown in Figure 3 (parameter "*d*" is the distance between the metal atom and the plane of the three C atoms bonded to the metal; $\Delta E_{\text{exch}} =$ ligand exchange energy defined according to eq 3; all energies given in kJ mol⁻¹)

	8 8	0.	0 1 /	0 0	- /		
entry	compound	$\Delta E_{\rm form}$	$\Delta E_{\rm int}(\mathbf{M}\cdots\mathbf{L})$	$\Delta E_{def}(M)$	$\Delta E_{\text{def}}(L)$	d (Å) ^a	ΔE_{exch}
1	Sc(Me ₃ [9]aneN ₃)(CH ₂ SiMe ₃) ₃ (3)	-138.6	-260.4	102.2	19.5	1.002	-10.5
2	$Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2)	-105.8	-236.6	95.0	35.8	1.031	22.3
3	$Sc([9]aneS_3)(CH_2SiMe_3)_3(1)$	-91.5	-156.7	62.0	3.3	0.807	36.6
4	$Sc(Me_{3}[9]aneN_{3})Me_{3}$ (5)	-211.6	-263.5	33.9	18.0	0.997	-4.8
5	$Sc{HC(Me_2pz)_3}Me_3$ (6)	-177.0	-243.2	27.2	39.1	0.949	-0.2
6	$Sc([9]aneS_3)Me_3$ (7)	-135.0	-149.9	11.9	3.0	0.757	40.0
7	$Y(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (8)	-172.5	-260.2	71.2	16.5	0.991	-18.3
8	$Y{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (9)	-146.2	-249.2	68.7	34.2	1.083	7.9
9	$Y([9]aneS_3)(CH_2SiMe_3)_3$ (4)	-109.0	-156.0	45.0	2.0	0.762	45.1

^a Values for the MR₃ fragment: Sc(CH₂SiMe₃)₃, 0.459 Å; ScMe₃, 0.379 Å; Y(CH₂SiMe₃)₃, 0.354 Å.







^{*a*} $[BAr^{F_4}]^-$ anions omitted for clarity.

11⁺ can also be formed quantitatively by reaction of $M{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (M = Sc (2) or Y (9)¹⁷) with [Ph₃C][BAr^F₄] in the presence of THF, forming the expected Ph₃CCH₂SiMe₃ side-product.²⁰ However, it is more convenient and efficient to use the "one-pot" route in Scheme 1, as this avoids the need to isolate and purify the intermediate tris(alkyl) species. Attempts to grow diffraction-quality crystals of 10-**BAr^F**₄ or 11-**BAr^F**₄ were unsuccessful. An alternative anion [BPh₄]⁻ was used in the reaction of 2 with [NHEt₃][BPh₄], which formed [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂(THF)][BPh₄] (10-**BPh**₄) in 43% isolated yield, but again diffraction-quality crystals could not be obtained. However, the X-ray structure of a [9]aneS₃ analogue of [M{HC(Me₂pz)₃}(CH₂SiMe₃)₂(THF)]⁺ has been obtained and is discussed below.

The ¹H and ¹³C NMR spectra of **10-BAr^F**₄ showed the expected resonances for the THF-stabilized C_s -symmetric cation illustrated in Scheme 1. In particular, two sets of Me₂pz group resonances were seen (2:1 intensity ratio for the groups *trans* to CH₂SiMe₃ and THF, respectively), and the diastereotopic methylene protons of the alkyl ligands appeared as a pair of mutually coupled doublets. The ¹⁹F NMR spectrum showed no evidence for anion coordination in CD₂Cl₂ for **10**⁺ or any of the species reported herein. In contrast to **10**⁺, the ¹H and ¹³C NMR spectra of **11**⁺ in CD₂Cl₂ showed only one Me₂pz group environment, even at low temperatures, and the alkyl methylene protons appeared as a broad doublet (²J_{YH} = 2.9 Hz) indicative of a dynamic process (the THF gave rise to ¹H multiplet

resonances at 3.99 and 2.03 ppm, consistent with it remaining coordinated in solution). The nature of the fluxional process has not been established but appears to be effectively an inplace rotation of the *fac*-N₃ ligand as reported previously for related systems.¹³ Addition of OPPh₃ (1 equiv) to **11-BAr^F**₄ gave the adduct [Y{HC(Me₂pz)₃}(CH₂SiMe₃)₂(OPPh₃)][BAr^F₄] (**12-BAr^F**₄) in reasonable isolated yield. In this case the *C_s*-symmetric cation **12**⁺ showed the expected resonances (e.g., two Me₂pz ring environments and doublets of doublets for the methylene linkages of the neosilyl ligands).

As mentioned in the Introduction, Bercaw has reported the reactions of the trimethyl complexes M(Me₃[9]aneN₃)Me₃ (M = Sc or Y) with [NHMe₂Ph][BAr^F₄].²⁴ In the case of yttrium only decomposition products were obtained; for scandium no well-defined compound could be isolated. Encouraged by the results for the tris(3,5-dimethylpyrazolyl)methane systems 10^+ and 11^+ , we turned to the triazacyclononane-supported neosilyl analogues. As for M{HC(Me₂pz)₃}(CH₂SiMe₃)₃, reaction of $M(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (M = Sc (3) or Y (8)¹⁷) with $[Ph_3C][BAr^F_4]$ in CD_2Cl_2 in the presence of THF gave quantitative conversion to well-defined cations [M(Me₃[9]aneN₃)- $(CH_2SiMe_3)_2(THF)]^+$ (M = Sc (13⁺) or Y (14⁺). However, as for the tris(3,5-dimethyl)pyrazolylmethane systems, the compounds 13-BAr^F₄ and 14-BAr^F₄ are most cost-effectively and conveniently prepared using one-pot reactions (Scheme 1) starting from M(CH₂SiMe₃)₃(THF)₂, [NHMe₂Ph][BAr^F₄], and Me₃[9]aneN₃ which affords them in ca. 50% isolated yield. In contrast to the tris(3,5-dimethylpyrazolyl)methane reactions, which work best in THF solution, the Me₃[9]aneN₃ complexes are most cleanly prepared in chlorobenzene. The analytically pure compounds $13-BAr_{4}^{F}$ and $14-BAr_{4}^{F}$ have been fully characterized and their NMR spectra are comparable to those of 10-BAr^F₄ and 11-BAr^F₄.



In a similar manner, the one-pot reaction of $Sc(CH_2SiMe_3)_3(THF)_2$, $[NHMe_2Ph][BAr^F_4]$, and $[9]aneS_3$ in chlorobenzene afforded the cationic fac-S₃ complex $[Sc([9]aneN_3)(CH_2SiMe_3)_2(THF)][BAr^F_4]$ (**15-BAr**^F₄) in ca. 50% yield (eq 4). When followed on the NMR scale in CD₂Cl₂ the conversion is quantitative with no unreacted [9]aneS₃. Analogous experiments found that **15-BAr**^F₄ can also be formed from previously isolated $Sc([9]aneN_3)(CH_2SiMe_3)_3$ and $[NHMe_2Ph][BAr^F_4]$ in the presence of THF (1 equiv). The NMR data are consistent with the structure shown in eq 4, although



Figure 4. Displacement ellipsoid plot (25% probability) of $[Sc([9]aneS_3)(CH_2SiMe_3)_2(THF)]^+$ (15^+) . H atoms and $[BArF_4]^-$ anion omitted for clarity. Selected distances (Å): Sc(1)–S(1) 2.7696(10), Sc(1)–S(2) 2.7623(10), Sc(1)–S(3) 2.6920(9), Sc(1)–C(7) 2.154(2), Sc(1)–C(11) 2.175(2), Sc(1)–O(1) 2.150(2). Selected angles (deg): S(1)–Sc(1)–S(2) 73.77(3), S(1)–Sc(1)–S(3) 76.41(3), S(2)–Sc(1)–S(3)76.83(3),C(7)–Sc(1)–C(11)111.19(15),C(7)–Sc(1)–O(1) 97.92(13), C(11)–Sc(1)–O(1) 103.26(12).

the coordinated [9]aneS₃ appears to be undergoing fast in-place rotation on the NMR time scale even at -80 °C in CD₂Cl₂. As for neutral **1**, the [9]aneS₃ ligand can be displaced from the scandium on the addition of an excess of THF.

Single crystals of 15-BAr^F₄ were grown from a pentane-chlorobenzene solution. The molecular structure of 15^+ is shown in Figure 4 along with selected bond distances and angles. Compound 15-BAr^F₄ contains the first structurally characterized group 3 or rare earth cation containing a thioether donor ligand. The cation 15^+ contains an approximately octahedral scandium center with a *fac*- κ^3 -coordinated [9]aneS₃ ligand, two neosilyl groups, and a THF. The Sc-S distances *trans* to the alkyl groups (2.7704(10) and 2.7617(10) Å) are longer than that *trans* to THF (2.6921(9) Å) but shorter than those in 1 (av 2.793 Å), consistent with the formal cationic charge for scandium and the reduced steric crowding in 15^+ . The Sc-C distances (2.154(2) and 2.175(2) Å) are also shorter than in 1 (av 2.249 Å), for the same reason. One other cation containing a Sc-CH₂SiMe₃ group has been structurally characterized, namely, the five-coordinate $[Sc{PhC(NAr)_2}(CH_2SiMe_3)(THF)_2]^+$ (Ar = 2,6-C₆H₃ⁱPr₂, $Sc-CH_2 = 2.165(2) \text{ Å}).^{55}$



The NMR tube-scale reaction of Y(CH₂SiMe₃)₃(THF)₂ with [NHMe₂Ph][BAr^F₄] and [9]aneS₃ in CD₂Cl₂ appears to form the seven-coordinate cation [Y([9]aneS₃)(CH₂SiMe₃)₂(THF)₂]⁺ (**16**⁺, eq 5). Cation **16**⁺ contains two coordinated THF ligands and two CH₂SiMe₃ groups, the methylene protons of which appear as doublets (²J_{HY} = 3.2 Hz), suggesting C_s symmetry

as illustrated in eq 5. The spectra are unchanged at -80 °C. As for 15^+ the [9]aneS₃ ligand gives rise to two sets of methylene ¹H signals for the hydrogens positioned "up" and "down" with regard to the metal center. However, due to the rapid in-place rotational fluxional process, only one type of ¹³CH₂ resonance is observed for the methylene carbons even at -80 °C. In principle the NMR data for 16^+ could also be consistent with a six-coordinate cation $[Y([9]aneS_3)(CH_2SiMe_3)_2(THF)]^+$ (analogous to 15^+) undergoing fast exchange with the remaining THF molecule. It is not possible to exclude this possibility on the available evidence. We note, however, that Okuda has reported structural evidence for both the eight-coordinate [Y(12-crown-4)(CH₂SiMe₃)(THF)₃]²⁺ and $[Y(12\text{-crown-4})Me_2(THF)_2]^+$ and seven-coordinate $[YMe_2(THF)_5]^+$ cations.^{36,40} As in the case of 15^+ and the neutral M([9]aneS₃)(CH₂SiMe₃)₃ systems, addition of an excess of THF to 16^+ causes complete displacement of the [9]aneS₃ ligand. It was not possible to isolate 16-**BAr** $^{F}_{4}$ on the preparative scale.

Synthesis and NMR and DFT Studies of Base-Free **Cations.** Addition of $[Ph_3C][BAr^F_4]$ (1 equiv) to a solution of Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₃ (3) in CD₂Cl₂ formed the basefree cation $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2]^+$ (17⁺), which is stable for several hours at -80 °C (although is less stable at room temperature). Addition of THF quantitatively forms the adduct $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2(THF)]^+$ (13⁺). The ¹⁹F NMR spectrum of 17^+ is consistent with a noncoordinated $[BAr^{F_4}]^{-}$ anion. The cation 17⁺ is highly fluxional even at -80 °C, showing one N-Me group signal for the macrocyclic ligand and one set of alkyl group resonances. Analogous results were found for Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (2), which formed the fluxional cation $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2]^+$ (19⁺) on reaction with $[Ph_3C]^+$. Neither **19-BAr**^F₄ nor **17-BAr**^F₄ could be isolated in the solid state. Attempts to form [Sc([9]aneS₃)(CH₂- $SiMe_{3}_{2}^{\dagger}$ or the corresponding yttrium cations from [Y(fac- N_3)(CH₂SiMe₃)₂]⁺ (*fac*-N₃ = Me₃[9]aneN₃, HC(Me₂pz)₃) at low temperature in either CD₂Cl₂ or C₆D₅Br gave mixtures of products or oily precipitates.

The low valence electron counts and coordination numbers for 17⁺ and 19⁺ suggest the possibility of agostic bonding, most likely via β -Si-C···Sc interactions, which are widespread throughout the rare earth and electron-deficient early transition metals.⁵⁶⁻⁶⁵ Of particular relevance to 17⁺ and 19⁺ is our recent report of the macrocycle-supported titanium imido cation [Ti(Me₃[9]aneN₃)(N^tBu)(CH₂SiMe₃)]⁺ (18⁺), which possesses a β -Si-C agostic alkyl group.²⁰ The agostic interaction was detected by ²⁹Si NMR spectroscopy through an upfield-shifted resonance of -15.9 ppm (cf. the nonagostic neutral precursor Ti(Me₃[9]aneN₃)(N^tBu)(CH₂SiMe₃)₂ with δ = -1.8 ppm, CD₂Cl₂). DFT calculations found a β -Si-C agostic structure and reproduced the ²⁹Si shifts very well indeed,²⁰ thus showing

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how ²⁹Si NMR can be a diagnostic tool bridging experiment and theory in these types of systems.

The cation [Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₂]⁺ (17⁺) could in principle exist as one of three main isomers: nonagostic (17a⁺); β -Si-C agostic (17b⁺); doubly agostic (17c⁺). An analogous situation could arise for 19⁺ (and, by analogy, all other [(L)M(CH₂SiMe₃)₂]⁺ species). To explore these possibilities further, a series of ²⁹Si NMR measurements and DFT calculations were carried out.

The tris(alkyl) compounds Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (**2**) and Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₃ (**3**) have nonagostic ground states according to X-ray crystallography¹⁷ and serve as benchmarks for the ²⁹Si NMR and DFT studies. The observed ²⁹Si NMR resonances are -3.9 and -3.5 ppm, respectively (CD₂Cl₂). The computed structures show good agreement with those determined by X-ray crystallography. The computed average ²⁹Si shifts are -2.5 and -2.4 ppm, respectively, showing excellent agreement with experiment and validating the methodology (the individual values for the independent alkyl groups range from -0.6 to -3.7 ppm).

The dialkyl cations 17^+ and 19^+ each show only a single ²⁹Si NMR resonance at -80 °C, which appear at -2.2 and -3.4 ppm, respectively. In the case of 17^+ , for example, these data might be equally consistent with a nonagostic ground state $(17a^+)$ or a fluxional monoagostic system $17b^+$ with a time-averaged ²⁹Si chemical shift. A doubly agostic species (e.g., $17c^+$) appears to be inconsistent with the -2.2 ppm ²⁹Si shift observed.

The DFT-computed structure of $[Sc(Me_3[9]aneN_3)(CH_2-SiMe_3)_2]^+$ (17⁺) is shown in Figure 5 along with selected parameters. Cation 17⁺ has a pseudo-octahedral Sc center and

features one β -Si-C agostic alkyl group with a compressed $Sc{-}CH_2{-}Si$ bond angle of 100.6° and a closest $Sc{\cdots}Me$ contact of 2.877 Å. Within this SiMe₃ group the Si-C distance for the methyl closest to Sc is 1.944 Å, which is lengthened in comparison with the other two Si-Me distances (1.900, 1.897 Å) as noted previously for β -Si-C agostic systems.^{20,60,64} The nonagostic alkyl group serves as a reference point with a Sc-CH₂-Si bond angle of 138.2° and Si-Me distances of 1.898, 1.899, and 1.905 Å. The computed ²⁹Si values for 17⁺ are 3.6 (nonagostic ligand) and -13.0 (agostic group), giving an averaged calculated shift of -4.7 ppm, which is in good agreement with the experimental value of -2.2 ppm. Taken together, the experimental NMR data and DFT calculations suggest that the real cation 17^+ possesses a β -Si-C agostic ground state, but that the two alkyl groups are in fast exchange on the NMR time scale.

At first sight, the similarity of the observed ²⁹Si NMR shifts for **17**⁺ and **19**⁺ suggests that the cationic tris(3,5-dimethylpyrazolyl)methane system might also possess one agostic and one nonagostic alkyl ligand. However, the full DFT-computed structure of [Sc{HC(3,5-Me₂pz)₃}(CH₂SiMe₃)₂]⁺ (**19**⁺, Figure 5) adopts an approximately trigonal-bipyramidal, nonagostic ground state with Sc-CH₂-Si angles of 121.8° and 133.4°, Si-Me distances in the range 1.895-1.911 Å, and a closest Sc····Me separation of 3.805 Å. The calculated ²⁹Si NMR shifts for the two independent alkyl ligands of **19**⁺ are -0.4 and -0.6 ppm. The calculated average shift of -0.5 ppm is again comparable within error to that observed experimentally (-3.4 ppm). To test whether the HC(3,5-Me₂pz)₃ ligand 3-position methyl groups were sterically impeding the development of an agostic interaction in **19**⁺, the hypothetical 4,5-ring substituted



Figure 5. DFT-computed structure of $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2]^+$ (**17**⁺) and $[Sc\{HC(3,5-Me_2pz)_3\}(CH_2SiMe_3)_2]^+$ (**19**⁺). Selected parameters for **17**⁺: (i) for the β -Si-C agostic alkyl group Si-Me = 1.944 (closest to Sc), 1.893, 1.890 Å, closest Sc ··· Me = 2.877 Å, Sc-CH₂-Si = 100.6°; (ii) for the nonagostic alkyl group Si-Me = 1.898, 1.899, 1.905 Å, Sc-CH₂-Si = 138.2°. Selected parameters for **19**⁺: Si-Me distances 1.895-1.911 Å, Sc-CH₂-Si = 121.8° and 133.4°, Sc ··· Me = 3.805 and 4.209 Å. Key: Sc, red; Si, yellow; N, blue; C and H, white.

isomer [Sc{HC(4,5-Me₂pz)₃}(CH₂SiMe₃)₂]⁺ (**20**⁺) was evaluated by DFT. Although a slightly more strongly agostic structure was found, as judged for example by ²⁹Si shifts of 0.0 and -4.3 ppm and Sc-CH₂-Si angles of 121.5° and 113.5°, it appears that such tris(pyrazolyl)methane-type *fac*-N₃ ligands may be better donors to the metal centers than Me₃[9]aneN₃ and inhibit the formation of additional interactions.

Although we were not able to observe the base-free $[9]aneS_3$ or yttrium cations $[M(L)(CH_2SiMe_3)_2]^+$ (M = Sc, L = [9]aneS₃; $M = Y, L = Me_3[9]aneN_3$ or $HC(Me_2pz)_3)$ experimentally, we computed their ground-state structures at the DFT level for the purposes of comparing the effect of varying the donor ligand L and metal. All three cations $[Sc([9]aneS_3)(CH_2SiMe_3)_2]^+$ (21⁺) and $[Y(fac-N_3)(CH_2SiMe_3)_2]^+$ (fac-N₃ = Me₃[9]aneN₃ (22⁺) or HC(Me₂pz)₃ **23**⁺)) feature β -Si-C agostic interactions. For 21^+ computed ²⁹Si shifts of -21.9 (agostic) and 3.3 ppm were found. The geometry of 21^+ is similar to that of the Me₃[9]aneN₃ analogue, 17^+ , but (as suggested by the more negative ²⁹Si shift) the β -Si-C agostic interaction is even more pronounced. The Sc-CH₂-Si (agostic) bond angle is 92.9° (cf. 100.6° in 17⁺) and the longest Si-C distance is 1.978 Å (methyl closest to Sc, cf. 1.944 Å in 17^+). For the yttrium cations 22^+ and 23^+ the computed ²⁹Si shifts for the agostic alkyls are -15.3 and -13.5 ppm, respectively, and 1.3 and -0.5 ppm for the nonagostic alkyls. In both yttrium cations the agostic interactions appear to be more strongly developed than for their scandium congeners, as judged by M-CH₂-Si bond angles of 96.4° and 100.8° and Si-C distances of 1.971 and 1.949 Å (methyls closest to Y) for the agostic CH₂SiMe₃ groups. Again it appears that it is the tris(pyrazolyl)methane complex (23^+) that forms the less strong β -Si-C interaction.

These calculations show that both the *fac*-N₃ or *fac*-S₃ ligand and the metal in the base-free cations $[(L)M(CH_2SiMe_3)_2]^+$ have significant effects on their ability to develop ground-state β -Si-C agostic interactions. In particular, [9]aneS₃ appears to result in the most developed β -Si-C agostic interaction among the $[Sc(L)(CH_2SiMe_3)_2]^+$ cations, presumably to compensate for the *fac*-S₃ ligand's weaker donor ability. However, in these fluxional dialkyl systems, the ²⁹Si data alone are insufficient to distinguish between agostic and nonagostic ground states.

Selected Stoichiometric Reactions: Lewis Base Adducts, Carbodiimide Insertion, and C–H Bond Activation. The reaction chemistry of group 3 alkyl cations is in its infancy, and so we report here a brief account of selected stoichiometric reactions of $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2(THF)]^+$ (10⁺) and $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2(THF)]^+$ (13⁺). We focused particularly on these two *fac*-N₃ systems because of the higher stability of the scandium cations compared to the yttrium ones and the higher stability of the N₃ donor complexes compared to their [9]aneS₃ analogues. Schemes 2 and 3 summarize the results of reactions with Lewis bases, phenyl acetylene, and carbodiimides. The reactions of neutral group 3 alkyls with alkynes^{66–69} and carbodiimides^{69,70} are well-established. In contrast, the first reactions of alkynes with rare earth alkyl

Scheme 2. Selected Reactions of [Sc{HC(Me₂pz)₃}(CH₂Si-Me₃)₂(THF)][BAr^F₄] (10-BAr^F₄)^a



^{*a*} $[BAr^{F_4}]^{-}$ anions are omitted for clarity.





 a [BAr^F₄]⁻ anions are omitted for clarity.

cations have only very recently been described,⁷¹ and reactions with carbodiimides remain unexplored. Several substrates of this type were therefore selected for investigation.

Addition of OPPh₃ (1 equiv) to **10-BAr**^F₄ gave the adduct [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂(OPPh₃)][BAr^F₄] (**24-BAr**^F₄), the analogue of **12-BAr**^F₄ mentioned above. The formation of **10**⁺ and all the new compounds in Schemes 2 and 3 were quantitative by ¹H NMR spectroscopy in CD₂Cl₂, but variable yields were obtained on the preparative scale owing to the

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Table 2. Ethylene Polymerization Data for the Tris(alkyl) Complexes $Sc(L)R_3$ Activated by [CPh₃][BAr^F₄]^a

precatalyst	PE yield (g)	productivity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)	$M_{ m w}$	$M_{ m n}$	$M_{ m w}/M_{ m n}$
$Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2)	7.9	830	297 000	7920	37
$Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3)	7.1	730	532 000	6820	78
$Sc(Me_3[6]aneN_3)(CH_2SiMe_3)_3$ (30)	0.1	10	243 000	3780	64
$Sc([9]aneS_3)(CH_2SiMe_3)_3$ (1)	8.4	860	187 000	2245	83
$Sc(Me_{3}[9]aneN_{3})Me_{3}$ (5)	0.4	40	433 000	4590	95
$Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3) ^b	9.1	910	421 000	9090	46
Sc(CH ₂ SiMe ₃) ₃ (THF) ₂	0	0			

^{*a*} Conditions unless otherwise stated: 6 bar of C₂H₄; 250 mL of toluene; run time = 10 min; activation temperature 33–36 °C; Sc:B = 1:1; catalyst loading = 5 or 10 μ mol; Sc:Al = 1:500; productivity data are for duplicate runs. ^{*b*} Sc:B = 1:2.

sometimes oily nature of the products. Similarly, **10-BAr**^F₄ reacts with pyridine to form [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂-(py)][BAr^F₄] (**25-BAr**^F₄). Pyridine adducts of group 3 and 4 alkyl species are often unstable to alkane elimination via metalation of the *ortho*-C–H bond.^{20,41,72,73} However, even after prolonged gentle heating (ca. 50 °C), cation **25**⁺ does not show any signs of SiMe₄ elimination or degradation.

Cation 10^+ reacts with di-*p*-tolyl carbodiimide in CD₂Cl₂ to give the amidinate product [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)-{TolNC(CH₂SiMe₃)NTol}]⁺ (26⁺) as judged by ¹H NMR and ¹³C NMR spectroscopy. Attempts to isolate 26-BAr^F₄ or its homologues on a preparative scale were unsuccessful. However, reaction of 13-BAr^F₄ with di-isopropyl carbodiimide gave quantitative formation of [Sc(Me₃[9]aneN₃)(CH₂SiMe₃)-{¹PrNC(CH₂SiMe₃)N¹Pr}][BAr^F₄] (27-BAr^F₄) which was isolated and fully characterized. An imido titanium analogue of 27⁺, [Ti(Me₃[9]aneN₃)(N^tBu){¹PrNC(CH₂SiMe₃)N¹Pr}]⁺, was recently prepared by an analogous route. Hou et al. reported the first carbodiimide insertion into a (neutral) rare earth metal-alkyl bond in 2002,⁷⁰ but ours is the first example of the corresponding reaction for an alkyl cation.

Addition of PhCCH (1 equiv) to $10-BAr^{F_{4}}$ gave SiMe₄ (as judged by an NMR tube-scale reaction in CD₂Cl₂) and the acetylide complex [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)(CCPh)- $(THF)][BAr_{4}^{F}]$ (**28-BAr**₄) via a C-H bond activation reaction. Products of alkyne insertion into a Sc-CH₂SiMe₃ bond were not observed. The NMR spectra of 28^+ feature six distinct pyrazolyl ring methyl carbons, confirming the unsymmetric nature of 28^+ . Reaction of 13-BAr^F₄ with PhCCH (Scheme 3) gave an analogous product, [Sc(Me₃[9]aneN₃)(CH₂SiMe₃)- $(CCPh)(THF)][BAr_{4}^{F}]$ (29-BAr₄), showing three inequivalent macrocycle N-Me groups. No reaction was observed between 10-BAr^F₄ or 13-BAr^F₄ and PhCCMe. No further Sc-CH₂SiMe₃ bond substitution or other reaction was observed between 28- $BAr^{F_{4}}$ or 29-BAr^{F_{4}} and an additional equivalent of PhCCH, in contrast to very recent results from Hessen et al. for a cationic organo-yttrium system supported by a triamine-amide ligand.⁷¹

Ethylene Polymerization Studies. As mentioned in the Introduction, olefin polymerization by cationic group 3 and lanthanide compounds is an area of ongoing interest.^{5–10} Table 2 summarizes the ethylene polymerization results obtained for a series of scandium tris(alkyl) complexes activated with $[Ph_3C][BAr^F_4]$ (TB) in the presence of AlⁱBu₃ as scavenger. Negligible activity was found for either of the yttrium compounds Y(*fac*-N₃)(CH₂SiMe₃)₃ (8 or 9) or the bis(THF) complex Sc(CH₂SiMe₃)₃(THF)₂, which was assessed as a control experiment. Preliminary results for some of the compounds using

 $BAr_{F_3}^{F_3}$ as a cocatalyst were disclosed in a recent communication and are consistent with the wider study reported here.⁵¹

High productivities were found for $Sc{HC(Me_2pz)_3}(CH_2-SiMe_3)_3$ (2) and $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3) (ca. 830 and 730 kg mol⁻¹ h⁻¹ bar⁻¹, respectively). These are competitive with the best values previously described in the literature for this metal, but fall some way short of the highest described for cationic lanthanide systems in general (up to ca. 3000 kg mol⁻¹ h⁻¹ bar).⁵⁻⁸ Changing from $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3) to the previously reported $Sc(Me_3[6]aneN_3)(CH_2SiMe_3)_3$ (30)¹⁷ with a smaller triazacyclic ligand showed negligible productivity under these conditions.



In this context we note that titanium catalyst systems of the type Ti(*fac*-N₃)(NR)Cl₂/MAO also showed productivity dependencies in the order *fac*-N₃ = Me₃[6]aneN₃ \ll Me₃[9]aneN₃ \approx HC(Me₂pz)₃.^{18,22,74} On the other hand, while the vanadium tris(pyrazolyl)methane systems V{HC(Me₂pz)₃}(NR)Cl₂/MAO were able to polymerize ethylene, the corresponding macrocyclic systems V(Me₃[9]aneN₃)(NR)Cl₂/MAO were totally inactive.²³ It is also interesting to compare the performances of the very productive scandium precatalysts **2** and **3** with those of the yttrium systems **8** and **9**, which were inactive. Hessen has reported very active, related yttrium catalysts supported by triazacyclonane ligands that contain additional pendant anionic donors.^{25,27–29} It would appear that these "anchor points" are important in imparting stability on the catalytic systems for the larger metal.

Interestingly, the thioether complex $Sc([9]aneS_3)(CH_2SiMe_3)_3$ (1) was also highly productive, with a figure of merit comparable to both 2 and 3. Although sulfur donors are generally viewed as being detrimental for later transition metal catalysts, in the case of these group 3 cationic systems the change from $Me_3[9]aneN_3$ to $[9]aneS_3$ does not damage productivity. This is apparently in accord with recent reports for certain cationic group 4 Ziegler-type catalyst systems.⁴³

Bercaw has previously reported that mixtures of scandium trimethyl complex Sc(Me₃[9]aneN₃)Me₃ (**5**) and BAr^F₃ in THF- d_8 were competent for the polymerization of ethylene at 80 °C on the NMR scale. To make a quantitative comparison between **5** and the other tris(trimethylsilyl) systems in Table 2, we assessed **5** under the same conditions. Compound **5** reproducibly

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Table 3. 1-Hexene Polymerization Data for the Tris(alkyl) Complexes $Sc(fac-N_3)R_3$ Activated by [CPh₃][BAr^F4]^a

precatalyst	Sc:TB ^b	temp (°C)	time	conversion (%, NMR)	isolated yield (g)	$M_{n(calcd)}^{c}$	$M_{n(GPC)}$	$M_{\rm w}/M_{\rm n}$
$Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2)	1:1	22	24 h	0	0			
Sc(Me ₃ [9]aneN ₃)(CH ₂ SiMe ₃) ₃ (3)	1:1	22	30 min	88	0.5	22 220	5 980	12.2
$Sc(Me_{3}[6]aneN_{3})(CH_{2}SiMe_{3})_{3}$ (30)	1:1	22	18 h	34	d	8590	d	d
$Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2)	1:2	22	10 min	100	0.6	50 500	11 140	2.6
$Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3)	1:2	22	10 min	100	0.8	50 500	29 610	2.3
$Sc(Me_3[9]aneN_3)Me_3 5)$	1:2	22	10 min	95	0.7	47 970	16 000	2.3
$Sc(Me_{3}[6]aneN_{3})(CH_{2}SiMe_{3})_{3}$ (30)	1:2	22	10 min	76	0.7	38,380	36 290	2.2
$Sc([9]aneS_3)(CH_2SiMe_3)_3$ (1)	1:2	22	10 min	46	0.3	23,290	13 280	5.8
$Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2)	1:2	0	20 min	85	0.6	42,920	46 120	1.7
$Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (3)	1:2	0	2.5 h	20	0.1	10,100	35 440	7.3
Sc(Me ₃ [6]aneN ₃)(CH ₂ SiMe ₃) ₃ (30)	1:2	0	7 h	58	0.3	29,290	102 220	3.6
Sc(CH ₂ SiMe ₃) ₃ (THF) ₂	1:2	22	24 h	0	0			

^{*a*} Conditions: 600 equiv of 1-hexene, 20 μ mol of precatalyst, 5 mL of C₆H₅Cl. ^{*b*} TB = [Ph₃C][BAr^F₄]. ^{*c*} Assuming 2 PH (for Sc:TB = 1:1) or 1 PH (Sc:TB = 1:2) chains per metal center at the given NMR % conversions and that all of the precatalyst is activated. ^{*d*} Polymer could not be isolated.

showed a much lower productivity (ca. 40 kg mol⁻¹ h⁻¹ bar⁻¹) than **3** on activation with TB/AlⁱBu₃. Analogous results were found using BAr^F₃ as an activator. The reasons for the difference between **3** and **5** are unclear. It is conceivable that the more sterically accessible first-formed cation [Sc(Me₃[9]aneN₃)Me₂]⁺ might more readily undergo homo- or heterobimetallic deactivation reactions of the type well-established for group 4 metallocenium and related cations.^{75,76}

Finally we evaluated the productivity of Sc(Me₃[9]aneN₃)-(CH₂SiMe₃)₃ (**3**) using 2 equiv of TB. As discussed below, **3** and a number of other rare earth compounds of the type Ln(*fac*-N₃)(CH₂SiMe₃)₃ polymerize 1-hexene to a significant extent only when 2 equiv of activator are employed.^{37,38} In group 4 Ziegler catalyst systems an increase in productivity has also been reported when an excess of activator has been employed.^{77,78} However, although the productivity of the **3**/2 TB/AlⁱBu₃ system (ca. 910 mol⁻¹ h⁻¹ bar⁻¹) was reproducibly somewhat higher than for **3**/1 TB/AlⁱBu₃, we did not observe the same kind of dramatic increase in performance noted for 1-hexene polymerization below.

Table 2 also summarizes the PE molecular weight characteristics as determined by GPC. The M_n values in all instances are very low (indicative of facile chain transfer processes), and the polydispersity indices (PDI, M_w/M_n) are very broad indeed. Such large PDI values may imply that multiple active species are present or several chain transfer modes are operative. Analysis of the PE formed with **2** or **3** by NMR spectroscopy (100 °C, 1,2-C₆D₄Cl₂) showed linear PE with only saturated (methyl group) end groups. Isopropyl end groups (such as might arise from chain transfer to AlⁱBu₃^{79,80}) were not detected, indicating that chain transfer is probably taking place through an uncontrolled homolytic process. Unfortunately, attempts to run the polymerization experiments at lower temperatures gave negligible productivity.

1-Hexene Polymerization Studies. Relatively few examples of the polymerization of α -olefins by cationic group 3 complexes have been reported to date.^{5–8,37,38,40,81,82} Table 3 summarizes our results for the polymerization of 1-hexene as a representative

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 α -olefin using Sc(L)(CH₂SiMe₃)₃ (L = HC(Me₂pz)₃ (2), Me₃[9]aneN₃ (3), Me₃[6]aneN₃ (30), or [9]aneS₃ (1)) and Bercaw's Sc(Me₃[9]aneN₃)Me₃ (5) for comparison. No activity was found for either of the yttrium complexes Y(*fac*-N₃)(CH₂SiMe₃)₃ (8 or 9) under any of the conditions assessed. By way of a control experiment, no activity was found for the THF complex Sc(CH₂SiMe₃)₃(THF)₂ under our conditions.

Initial polymerization studies were carried out in C₆H₅Cl using 1 equiv of [Ph₃C][BAr^F₄] (TB) or [NHMe₂Ph][BAr^F₄] activator. No activity was found with the anilinium activator, presumably due to coordination of the NMe₂Ph side-product to the so-formed alkyl cations. NMR tube-scale reactions (C_6D_5Br) between 2 and $[NHMe_2Ph][BAr^{F_4}]$ supported this hypothesis, the spectra being consistent with the formation of $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2(NMe_2Ph)]^+$, the analogue of $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2(L)]^+$ (L = THF (10⁺), OPPh₃ (24^+) , or py (25^+)). No polymerization was found with 2 and TB (1 equiv), whereas the triazacyclononane-supported 3 achieved 88% conversion of 1-hexene to polyhexene (PH) within 30 min. However, analysis of the PH by GPC found a broad PDI of 12.2 and a very low M_n value of ca. 6000 compared to that expected for one (44 440) or two (22 220) chains per precatalyst metal center, suggesting that some form of chain transfer process is taking place under these conditions. ¹H NMR analysis of the PH from these experiments found only saturated (methyl) end groups, indicating the chain transfer probably involves noncontrolled radical cleavage. ¹³C NMR analysis found that the PHs formed in all of these systems are predominantly atactic. The sterically more "open" triazacyclohexane complex 30 does not lead to higher productivity, as might have been hoped for, achieving only 34% conversion by NMR after 18 h. This could be consistent with more effective binding of the solvent and/or anion to the dialkyl cation. It was not possible to isolate the PHs in this case due to their apparent low molecular weights.



Following on from Okuda's reports of well-defined dicationic lanthanide polymerization catalysts, 39,40 Gade showed that activation of the complex Sc(ⁱPr-trisox)(CH₂SiMe₃)₃ (**31**) with 2 equiv of TB gave a very productive 1-hexene polymerization

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catalyst system.³⁷ We therefore assessed the polymerization capabilities of the $Sc(L)R_3$ complexes using a Sc:TB ratio of 1:2. Again neither of the $Y(fac-N_3)(CH_2SiMe_3)_3$ were active under these conditions.

Activation of $Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3$ (2) and Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₃ (3) with 2 equiv of TB under conditions otherwise identical to those used for the 1 equiv experiments gave much higher productivities (100% conversion within 10 min). GPC analysis of the resultant PHs revealed improved molecular weight distributions of 2.6 and 2.3, respectively (cf. 12.2 for the 3/1 TB catalyst system), but the $M_{\rm n}$ values of 11 140 and 29 610 were still lower than that expected (50 500) assuming all of the metal centers were activated to a species of the type " $[Sc(L)R]^{2+}$ " (R = CH₂SiMe₃ or polyhexyl). The trimethyl complex $Sc(Me_3[9]aneN_3)Me_3$ (5) exhibited similar behavior to that of 3, in contrast to the situation found for the ethylene polymerization studies (Table 2). The triazacyclohexane complex 30 also catalyzes the production of PHs on activation with 2 equiv of TB. The productivity (76%) conversion after 10 min) is lower than that of the larger macrocycle analogue 3 or 5. The agreement between the found (36 290) and calculated (38 380) $M_{\rm n}$ values was much better, but the PDI of 2.2 is far from that expected (1.0) for a welldefined system forming 1 PH chain per metal center. The [9]aneS₃ complex 1 was also productive upon activation with 2 equiv of TB. However, the conversion of 1-hexene (46%) was significantly lower than found using the fac-N₃-supported catalysts, and the PDI of the PHs produced (5.8) was also much poorer. No further experiments were performed using 1.

As expected, reducing the polymerization temperature to 0 °C gave a reduction in productivity (85% conversion within 20 min for 2/2 TB and only 20% for 3/2 TB after 2.5 h). For 2 the experimental M_n value of 46 120 was in good agreement with that expected (42 920) and the PDI was 1.7, indicating that 2/2TB gives the best "control" of the molecular weights and their distribution at this temperature. In contrast, 3/2 TB afforded PHs with a high PDI of 7.3 and a M_n of 35 440, which is higher than that expected (10 100). Similarly, 30/2 TB gave PHs with a PDI of 3.6 (cf. 2.2 at 22 °C) and a very high M_n of 102 220 compared with that expected (29 290). Therefore it is certainly clear that not all of the metal centers are activated (or active) in these last two instances. Indeed, the apparently good agreement between found and calculated M_n values in the cases of 2/2 TB (0 °C) and 30/TB (22 °C) may be fortuitous given the PDIs of 1.7 and 2.2, respectively, and possibly result from a combination of chain transfer processes and less than 100% precatalyst activation.

It is interesting to compare our data in Table 3 with those described by Gade for the Sc(ⁱPr-trisox)(CH₂SiMe₃)₃ (**31**)/2 TB catalyst system. At 21, 0, and -30 °C, conversions of 88% (PDI = 2.22), 64% (PDI = 2.36), and 30% (PDI = 1.18) were found. However, as for our systems, chain transfer and/or incomplete activation is clearly evident in these systems with ca. 3 PH chains formed per precatalyst center at 21 °C and only 0.16 chain per metal at -30 °C (based on the reported M_n values). Similarly, all of the PHs produced by **31** possessed saturated end groups according to NMR spectroscopy.

Encouraged by Gade's report of the observation of a red dialkyl cation " $[Sc(^{i}Pr-trisox)(CH_2SiMe_3)(solvent)_n]^{2+}$ " in CD₂Cl₂ at room temperature on treating **31** with 2 equiv of TB, we set out to investigate analogous behavior for our systems. However, since our dialkyl monocations $[Sc(fac-N_3)(CH_2SiMe_3)_2]^+$ (*fac*-N₃ = HC(Me₂pz)₃ or Me₃[9]aneN₃) slowly decomposed in CD₂Cl₂ at room temperature, we also

conducted parallel NMR studies in C₆D₅Cl, which is also a better mimic of the chlorobenzene polymerization solvent. Analogous results were found for **2** and **3**, and so we focused on the former since the **2**/2 TB catalyst system gave the best agreement between found and expected molecular weight at 0 °C. Furthermore, the podand ligand HC(Me₂pz)₃ is a closer match to ⁱPr-trisox and offers the best chance of comparing the data for Gade's **31**/2 TB system with ours.

Reaction of Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (2) with 1 equiv of TB in C₆D₅Cl formed the previously mentioned dialkyl monocation $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2]^+$ (19⁺). This reaction was slower than the corresponding one in CD₂Cl₂. Addition of 1-hexene to an NMR tube containing 19^+ (in either CD_2Cl_2 or C₆D₅Cl) gave no reaction even after 24 h, consistent with the results shown in Table 3. Addition of 2 or 3 equiv of TB to a solution of **2** in C_6D_5Cl showed only formation of the dialkyl monocation 19^+ and unreacted $[CPh_3]^+$. The same reaction in CD_2Cl_2 again showed only formation of 19^+ , but in this case the decomposition of 19^+ to an unknown mixture was somewhat faster than in the 1 equiv of TB case ($t_{1/2} \approx 30$ min). Finally we found that addition of TB (1 equiv) to an NMR sample containing the preformed dialkyl monocation 19^+ and unreacted 1-hexene (prepared as above, in either C_6D_5Cl or CD_2Cl_2) gave rapid conversion of the 1-hexene to PHs. After all the 1-hexene had been polymerized, ca. 80% of the original 19^+ still remained (as judged against an internal standard). No evidence for a new HC(Me₂pz)₃-containing species was found.

It appears from the NMR tube experiments that formation of a simple monoalkyl dication $[Sc(L)(CH_2SiMe_3)(solvent)_n]^{2+}$ under these conditions does not readily occur. Nonetheless, it is evident that a second equivalent of TB is essential for the efficient polymerization of 1-hexene. Although the relative rates would vary depending on reaction conditions, it appears that propagation of chain growth may be fast compared to initiation. This would account for the relatively high M_n values found in some of our own systems (Table 3) and also in the lower temperature polymerization experiments on the Sc(ⁱPrtrisox)(CH₂SiMe₃)₃ (**31**) system. Further work is clearly needed before a satisfactory understanding emerges of the various M(L)R₃/2 TB/ α -olefin polymerization systems reported to date.

Conclusions

The neutral face-capping (fac-N₃) ligands Me₃[9]aneN₃ and $HC(Me_2pz)_3$ are effective supporting groups for developing the stoichiometric and catalytic chemistry of cationic scandium, but are somewhat less suitable for yttrium with regard to polymerization catalysis. This larger metal appears to require either a larger ring size (cf. the crown ether complexes of Okuda^{35,36}) or an anionic "anchoring" pendant arm as reported by Hessen.²⁷⁻²⁹ Interestingly, the "soft" ligand [9]aneS₃ can also be used to stabilize both neutral and cationic organoscandium complexes, despite the low intrinsic metal-ligand binding energy. This is attributed to the well-known "macrocycle effect" (a combination of enthalpic and entropic contributions) associated with such cyclic ligands and the smaller reorganization energy of the Sc(CH₂SiMe₃)₃ fragment in the case of Sc([9]aneS₃)-(CH₂SiMe₃)₃. Lewis base-stabilized dialkyl cations using fac-N₃ donor ligands are readily accessible for both scandium and vttrium and in the former case undergo stoichiometric ligand substitution or Sc-alkyl bond reactions. According to DFT, the electron-deficient base-free dialkyl cations [M(L)(CH₂SiMe₃)₂]⁺ are usually stabilized by a β -Si-C agostic interaction, but the extent of this depends on both the metal center and the ligand L. Experimentally, it was not possible to obtain direct ²⁹Si NMR

evidence of a "frozen out" β -Si-C agostic species. The scandium complexes $Sc(L)(CH_2SiMe_3)_3$ (L = [9]aneS₃, Me₃[9]aneN₃, HC(Me₂pz)₃) were all very productive precatalysts for the polymerization of ethylene, but the polymer properties as assessed by GPC indicate the presence of very poorly defined active species. Changing from Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₃ to Y(Me₃[9]aneN₃)(CH₂SiMe₃)₃, Sc(Me₃[9]aneN₃)Me₃, or Sc(Me₃-[6]aneN₃)(CH₂SiMe₃)₃ gave inactive catalyst systems, showing how delicately balanced this polymerization system is in terms of metal, macrocycle ring size, and initiating alkyl group. A range of complexes Sc(L)R₃ were also active for the polymerization of 1-hexene in the presence of 2 equiv of $[CPh_3][BAr^{F_4}]$ activator. No direct evidence for the formation of a dication of the type $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)]^{2+}$ could be gained using NMR spectroscopy, although it is clear that both equivalents of [CPh₃][BAr^F₄] activator are required for high (or in some instances, any) productivity.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Protio- and deutero-solvents were predried over activated 4 Å molecular sieves and were refluxed over the appropriate drying agent, distilled, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H}, ¹⁹F, and ²⁹Si NMR spectra were recorded on Varian Mercury-VX 300, Varian Unity Plus 500, and Bruker AV500 spectrometers. ¹H and ¹³C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional ¹H-¹H and ¹³C-¹H NMR experiments. ¹H and ¹³C spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ¹⁹F and ²⁹Si spectra were referenced externally to CFCl3 and tetramethylsilane, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between NaCl plates and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}) . Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory or by the Elemental Analysis Service at the London Metropolitan University.

Starting Materials. The compounds $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc or Y),⁸³ M{HC(Me_2pz)_3}(CH_2SiMe_3)_3 (M = Sc or Y),¹⁷ Sc(Me_3[9]aneN_3)Me_3,²⁴ M(Me_3[9]aneN_3)(CH_2SiMe_3)_3 (M = Sc or Y),¹⁷ and Sc(Me_3[6]aneN_3)(CH_2SiMe_3)_3^{17} were prepared according to the literature methods. Other reagents were purchased and used without further purification.

Sc([9]aneS₃)(CH₂SiMe₃)₃ (1). To a solution of Sc(CH₂SiMe₃)₃-(THF)₂ (400 mg, 0.88 mmol) in cold (0 °C) toluene (20 mL) was added a solution of [9]aneS₃ (160 mg, 0.88 mmol) in toluene (20 mL). The solution was stirred at 0 °C for 5 h, after which time the volatiles were removed under reduced pressure to afford **1** as a white solid. Yield: 321 mg (75%). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): 2.25 (6 H, m, SCH₂), 1.45 (6 H, m, SCH₂), 0.47 (27 H, s, SiMe₃), 0.15 (6 H, s, ScCH₂) ppm. ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): 43.0 (ScCH₂), 31.2 (SCH₂), 4.3 (SiMe₃) ppm. IR (NaCl plates, Nujol mull): 1413 (w), 1234 (w), 1246 (s), 875 (s), 823 (m), 745 (m) cm⁻¹. EI-MS: m/z = 225.3 (12%) [M - 3CH₂SiMe₃]⁺, 179.8 (100%) [[9]aneS₃]⁺. Anal. Found (calcd for C_{1 8}H₄₅S₃ScSi₃): C, 44.1 (44.0); H, 9.2 (9.3).

In Situ Synthesis of Y([9]aneS₃)(CH₂SiMe₃)₃ (4). A solution of Y(CH₂SiMe₃)₃(THF)₂ (5.0 mg, 0.01 mmol) in toluene- d_8 was added to solid [9]aneS₃ (1.8 mg, 0.01 mmol) to give a clear colorless solution. The ¹H NMR spectrum showed a mixture of 4, THF, and the starting materials, with ca. 50% conversion to 4 at 241 K. ¹H NMR (toluene- d_8 , 299.9 MHz, 241 K): 1.97 (6 H, m, SCH₂), 1.23 (6 H, m, SCH₂), 0.35 (27 H, s, SiMe₃), -0.53 (6 H, br s, YCH₂). ¹³C{¹H} NMR (toluene- d_8 , 75.5 MHz, 241 K): 36.6 (YCH₂, d, ¹ J_{CY} = 35 Hz), 30.5 (SCH₂), 4.6 (SiMe₃) ppm.

[Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂(THF)][BAr^F₄] (10-BAr^F₄). To a cold (-78 °C) Schlenk tube containing Sc(CH₂SiMe₃)₃(THF)₂ (0.20 g, 0.44 mmol) and $[\text{NHMe}_2\text{Ph}][\text{BAr}^{\text{F}_4}]$ (0.36 g, 0.44 mmol) was added THF (5 mL). To this solution was added a solution of HC(Me₂pz)₃ (0.13 g, 0.44 mmol) in THF (5 mL). The solution was stirred at -78 °C for 2 h, after which time it was allowed to warm to RT and concentrated in vacuo to ca. 2 mL; then pentane (10 mL) was added. The supernatant was carefully decanted away to leave a pale oil, which upon drying *in vacuo* gave 10-BAr^{F}_{4} as a spongy cream solid. Yield: 0.40 g (71%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.90 (1 H, s, HC(Me2pz)3), 6.19 (1 H, s, 4-HC(Me2pz)3 trans THF), 6.08 (2 H, s, 4-HC(Me2pz)3 trans CH₂SiMe₃), 4.24 (4 H, m, OCH₂CH₂), 2.76 (3 H, s, 3-HC(Me₂pz)₃ trans THF), 2.60 (3 H, s, 5-HC(Me₂pz₃)₃ trans THF), 2.54 (6 H, s, 3-HC(Me₂pz)₃ trans CH₂SiMe₃), 2.37 (6 H, s, 5-HC(Me₂pz)₃ trans CH_2SiMe_3), 2.16 (4 H, m, OCH_2CH_2), 0.35 (2 H, d, $^2J = 11.7$ Hz, CH_2SiMe_3 , 0.11 (2 H, d, ${}^2J = 11.7$ Hz, CH_2SiMe_3), -0.23 (18 H, s, Si<u>Me</u>₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.4 MHz, 293 K): 155.5 (3-HC(Me₂pz)₃, trans THF), 154.5 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 147.6 (br d, 2-C₆F₅), 141.6 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 141.4 (5-HC(Me₂pz)₃ trans THF), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 109.1 (4-Me₂pz trans CH₂SiMe₃), 108.9 (4-HC(Me2pz)3 trans THF), 73.3 (OCH2CH2), 68.1 (HC(Me2pz)3, 25.4 (OCH₂CH₂), 16.4 (5-HC(Me₂pz)₃ trans THF), 15.0 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 11.5 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 11.2 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 3.5 (SiMe₃), 1.1 (ScCH₂) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.5 (d, 2-C₆F₅), -164.1 (t, 4-C₆F₅), -67.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1643 (w), 1514 (m), 1306 (w), 1240 (w), 1085 (s), 1035 (m), 979 (s), 861 (m), 768 (w), 774 (w), 156 (w) cm⁻¹. Anal. Found (calcd for C52H52BF20N6OScSi2): C 49.2, (49.2); H 4.1, (4.1); N 6.6, (6.6).

[Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂(THF)][BPh₄] (10-BPh₄). To a cold (-78 °C) Schlenk tube containing Sc(CH₂SiMe₃)₃(THF)₂ (0.10 g, 0.22 mmol), HC(Me2pz)3 (0.07 g, 0.22 mmol), and [NHEt₃][BPh₄] (0.09 g, 0.22 mmol) was added THF (20 mL). The orange suspension was stirred at -78 °C for 30 min and then allowed to warm to RT, giving a clear orange solution. This was allowed to stir for a further 30 min, after which time the mixture was concentrated in vacuo to 2 mL and pentane (20 mL) added. A pale oil formed and was isolated by carefully decanting away the supernatant. Upon drying in vacuo 10-BPh₄ was obtained as a spongy cream solid. Yield: 87 mg (43%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.78 (1 H, s, HC(Me₂pz)₃), 7.30 (8 H, m, m-B(C₆<u>H</u>₅)₄), 6.98 (8 H, t, ³J = 7.3 Hz, o-B(C₆<u>H</u>₅)₄), 6.83 (4 H, t, ${}^{3}J = 7.0 \text{ Hz}, p-B(C_{6}H_{5})_{4}), 6.15 (1 \text{ H}, \text{ s}, 4-HC(Me_{2}pz)_{3}, trans \text{ THF}),$ 6.01 (2 H, s, 4-HC(Me2pz)3, trans CH2SiMe3), 4.21 (4 H, m, OCH2CH2), 2.75 (3 H, s, 3-HC(Me2pz)3 trans THF), 2.47 (3 H, s, 5-HC(Me2pz)3 trans THF), 2.39 (6 H, s, 3-HC(Me2pz)3 trans CH₂SiMe₃), 2.34 (6 H, s, 5-HC(Me₂pz)₃ trans CH₂SiMe₃), 2.13 (4 H, m, OCH₂CH₂), 0.34 (2 H, d, ${}^{1}J = 11$ Hz, ScCH₂), 0.09 (2 H, d, ${}^{1}J = 11 \text{ Hz}, \text{ ScC}\underline{\text{H}}_{2}), -0.23 (18 \text{ H}, \text{ s}, \text{Si}\underline{\text{Me}}_{3}) \text{ ppm. } {}^{13}\text{C} \{{}^{1}\text{H}\} \text{ NMR}$ NMR (CD₂Cl₂, 75.5 MHz, 293 K): 155.3 (3-HC(Me₂pz)₃ trans THF), 154.4 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 141.7 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 141.3 (5-HC(Me₂pz)₃ trans THF), 136.2 (m-B(C₆H₅)₄), 125.8 (*o*-B(C₆H₅)₄), 122.0 (*p*-B(C₆H₅)₄), 109.1 (4-HC(Me2pz)3 trans CH2SiMe3), 108.9 (4-HC(Me2pz)3 trans THF), 73.2 (OCH₂CH₂), 68.0 (HC(Me₂pz)₃), 25.8 (OCH₂CH₂), 15.1 (3-

⁽⁸³⁾ Lappert, M. F.; Pearce, R. J. Chem. Soc., Chem. Commun. 1973, 126.

HC($\underline{Me_2pz}$)₃ trans CH₂SiMe₃), 14.9 (3-HC($\underline{Me_2pz}$)₃ trans THF), 11.8 (5-HC($\underline{Me_2pz}$)₃ trans THF), 11.3 (5-HC($\underline{Me_2pz}$)₃ trans CH₂SiMe₃), 3.5 (Si<u>Me₃</u>) ppm. IR (NaCl plates, Nujol mull): 1567 (m), 1416 (m), 1305 (m), 1239 (m), 1094 (m), 1035 (s), 1018 (s), 981 (w), 861 (s), 733 (m), 705 (s), 732 (m), 666 (w) cm⁻¹. Anal. Found (calcd for C₅₂H₇₂BN₆OScSi₂): C 68.8, (68.7); H 7.9, (7.9); N 9.2, (9.2).

 $[Y{HC(Me_2pz)_3}(CH_2SiMe_3)_2(THF)][BAr^F_4]$ (11-BAr^F₄). To a cold (-78 °C) Schlenk tube containing Y(CH₂SiMe₃)₃(THF)₂ (0.20 g, 0.40 mmol) and [NHMe₂Ph][BAr^F₄] (0.32 g, 0.40 mmol) was added THF (5 mL). To this was added a solution of HC(Me₂pz)₃ (0.12 g, 0.40 mmol) in THF (5 mL). The solution was stirred at -78 °C for 1.5 h, after which time it was allowed to warm to RT and concentrated in vacuo to ca. 2 mL. Pentane (10 mL) was added to give a pale oil, from which the supernatant was decanted. Upon drying in vacuo 11-BAr^F₄ formed as a spongy offwhite solid. Yield: 0.39 g (73%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.92 (1 H, s, HC(Me₂pz)₃), 6.12 (3 H, s, 4-HC(Me₂pz)₃), 3.99 (4 H, m, br, OCH₂CH₂), 2.56-2.49 (18 H, s, br, HC(Me₂pz)₃), 2.03 (4 H, m, br, OCH₂CH₂), -0.17 (18 H, s, SiMe₃), -0.42 (4 H, d, ${}^{2}J_{HY} = 2.9$ Hz, YCH₂) ppm. ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 75.5 MHz, 293 K): 154.7 (3-HC(Me₂pz)₃), 147.6 (br d, 2-C₆F₅), 142.3 $(5-HC(Me_2pz_3)_3)$, 137.8 (br d, $4-C_6F_5$), 135.9 (br d, $3-C_6F_5$), 108.9 (4-HC(Me₂pz₃)₃), 71.0 (OCH₂CH₂), 68.7 (HC(Me₂pz)₃), 38.6 (d, ${}^{1}J_{CY} = 40 \text{ Hz}, \text{ YCH}_{2}$, 25.8 (OCH₂CH₂), 15.0 (HC(Me₂pz)₃), 11.5 (HC(Me2pz)3), 3.9 (SiMe3) ppm. ¹⁹F NMR (CD2Cl2, 282.2 MHz, 293 K): -133.5 (d, 2-C₆F₅), -164.0 (t, 4-C₆F₅), -167.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1642 (m), 1601 (w), 1568 (m), 1513 (s), 1391 (m), 1376 (s), 1306 (m), 1238 (w), 1086 (s), 1035 (m), 979 (s), 859 (m), 774 (m), 768 (w) cm⁻¹. Anal. Found (calcd for C₅₂H₅₂BF₂₀N₆OSi₂Y): C 47.6, (47.6); H 3.9, (3.9); N 6.4, (6.4).

[Y{HC(Me₂pz)₃}(CH₂SiMe₃)₂(OPPh₃)][BAr^F₄] (12-BAr^F₄). To Schlenk tube containing $[Y{HC(Me_2pz)_3}(CH_2SiMe_3)_2-$ (THF)][BAr^F₄] (0.10 mg, 0.08 mmol) and PPh₃O (0.02 g, 0.08 mmol) was added CH_2Cl_2 (15 mL). The off-white solution was stirred at RT for 1 h. The volatiles were removed under reduced pressure to leave 12-BAr $^{F}_{4}$ as a spongy white solid. Yield: 64 mg (56%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.89 (1 H, s, HC(Me₂pz)₃), 7.69-7.47 (15 H, m, PPh₃O), 6.13 (1 H, s, 4-Me₂pz₃ trans PPh₃O, 5.85 (2 H, s, 4-HC(Me₂pz)₃ trans CH₂SiMe₃), 2.90 (3 H, s, 3-HC(Me₂pz)₃ trans PPh₃O), 2.58 (3 H, s, 5-HC(Me₂pz)₃ trans PPh₃O), 2.53 (6 H, s, 3-HC(Me₂pz)₃ trans CH₂SiMe₃), 1.75 (6 H, s, 5-HC(Me₂pz)₃ trans CH₂SiMe₃), -0.34 (18 H, s, SiMe₃), -0.47 (2 H, dd, ²J = 11.0 Hz, ² $J_{HY} = 2.1$ Hz, YC<u>H</u>₂), -0.64 (2 H, dd, ${}^{2}J = 10.6$ Hz, ${}^{2}J_{HY} = 3.2$ Hz) ppm. ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 75.5 MHz, 293 K): 154.6 (3-HC(Me2pz)3 trans PPh3O), 153.8 (3-HC(Me2pz)3 trans CH2SiMe3), 147.6 (br d, 2-C6F5), 141.2 (5-HC(Me₂pz)₃ trans PPh₃O), 141.1 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 134.3 (PPh₃O), 132.6 (PPh₃O), 132.4 (PPh₃O), 129.4 (PPh₃O), 129.3 (PPh₃O), 108.1 (4-HC(Me₂pz)₃ trans PPh₃O), 107.9 (4-HC(Me₂pz)₃ trans CH₂SiMe₃), 67.9 (HC(Me₂pz)₃), 32.9 (d, ${}^{1}J_{CY} = 38$ Hz, YCH₂), 15.5 (3-HC(Me2pz)3 trans PPh3O), 14.2 (3-HC(Me2pz)3 trans CH2SiMe3), 11.4 (5-HC(Me2pz)3 trans PPh3O), 11.2 (5-HC(Me2pz)3 trans CH₂SiMe₃), 3.5 (SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1643 (w), 1569 (w), 1513 (m), 1308 (w), 1236 (w), 1140 (m), 1122 (m), 1085 (s), 1035 (m), 979 (s), 903 (w), 861 (m), 802 (m), 774 (w) cm⁻¹. Anal. Found (calcd for C₆₆H₅₉BF₂₀N₆OPYSi₂): C 52.2, (52.2); H 3.9, (3.9); N 5.5, (5.5).

[Sc(Me₃[9]aneN₃)(CH₂SiMe₃)₂(THF)][BAr^F₄] (13-BAr^F₄). To a Schlenk tube containing Sc(CH₂SiMe₃)₃(THF)₂ (0.20 g, 0.44 mmol) and [NHMe₂Ph][BAr^F₄] (0.36 g, 0.44 mmol) was added C₆H₅Cl (15 mL). To this stirring solution was added Me₃[9]aneN₃ (86 μ L, 0.44 mmol) via microlitre syringe. The solution was stirred at RT for 2 h, after which time it was concentrated to 2 mL and pentane (20 mL) added. An off-white oil precipitated and was isolated by carefully decanting away the supernatant. Upon drying in vacuo the 13-BAr^F₄ formed as a spongy off-white solid. Yield: 0.22 g (43%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 4.45 (4 H, m, br, OCH2CH2), 3.25 (2 H, m, NCH2), 3.15 (3 H, s, NCH3, trans THF), 3.0-2.7 (10 H, m, NCH2), 2.6 (6 H, s, NCH3, trans CH₂SiMe₃), 0.01 (18 H, s, Si<u>Me₃</u>), -0.12 (2 H, d, ${}^{2}J = 11.9$ Hz, $ScCH_2$, -0.18 (2 H, d, ${}^2J = 11.9$ Hz, $ScCH_2$) ppm. ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 75.5 MHz, 293 K): 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 74.8 (OCH₂CH₂), 55.9 (NCH₂), 55.8 (NCH2), 55.2 (NCH3, trans THF), 50.9 (NCH2), 49.7 (NCH3, trans CH₂SiMe₃), 25.5 (OCH₂CH₂), 3.3 (SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.5 (d, 2-C₆F₅), -164.1 (t, 4-C₆F₅), -167.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1643 (w), 1601 (w), 1514 (m), 1299 (w), 1273 (m), 1259 (m), 1241 (m), 1153 (w), 1084 (s), 1003 (m), 978 (s), 899 (w), 846 (m), 817 (m) cm⁻¹. Anal. Found (calcd for C₄₅H₅₁BF₂₀N₃OScSi₂): C 47.3, (47.3); H 4.6, (4.5); N 3.6. (3.7).

 $[Y(Me_3[9]aneN_3)(CH_2SiMe_3)_2(THF)][BAr^{F_4}]$ (14-BAr^{F_4}). To a Schlenk tube containing Y(CH₂SiMe₃)₃(THF)₂ (0.20 g, 0.40 mmol) and [NHMe2Ph][BArF4] (0.32 g, 0.40 mmol) was added C_6H_5Cl (15 mL). To this stirring solution was added $Me_3[9]aneN_3$ (78 μ L, 0.40 mmol) via a microlitre syringe. The solution was allowed to stir at RT for 2 h, after which time it was concentrated to 2 mL and pentane (20 mL) added. An off-white oil formed, which was isolated by carefully decanting away the supernatant. Upon drying *in vacuo* 14-BAr^F₄ formed as a spongy solid. Yield: 0.26 g (54%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 263 K): 4.32 (4 H, m, OCH2CH2), 3.20-2.20 (12 H, m, NCH2), 2.87 (3 H, s, NCH3, trans THF), 2.56 (6 H, s, NCH₃, trans CH₂SiMe₃), -0.10 (18 H, s, Si<u>Me</u>₃), -0.77 (4 H, s, br s, YC<u>H</u>₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 263 K): 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 72.6 (OCH₂CH₂), 47.5 (NCH₃, trans THF), 47.0 $((N\underline{C}H_3, trans CH_2SiMe_3), 39.5 (d, {}^{1}J_{CY} = 43 Hz, Y\underline{C}H_2), 25.1$ (OCH₂CH₂), 2.9 (SiMe₃) ppm. NCH₂ resonances obscured by CD₂Cl₂. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 263 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1643 (m), 1601 (w), 1514 (s), 1376 (s), 1300 (w), 1274 (m) 1240 (m), 1152 (w), 1085 (s), 1003 (s), 978 (s), 850 (m), 768 (m) cm⁻¹. Anal. Found (calcd for C₄₅H₅₁BF₂₀N₃OSi₂Y): C 45.5, (45.6); H 4.2, (4.3); N 3.4, (3.5).

 $[Sc([9]aneS_3)(CH_2SiMe_3)_2(THF)][BAr^F_4]$ (15-BAr^F₄). To a Schlenk tube containing Sc(CH₂SiMe₃)₂(THF)₂ (0.1 g, 0.22 mmol), $[NHMe_2Ph][BAr_4^F]$ (0.18 g, 0.22 mmol), and $[9]aneS_3$ (0.04 g, 0.22 mmol) was added C_6H_5Cl (10 mL). The solution was stirred at RT for 2 h, after which time it was concentrated under reduced pressure to 1 mL. Pentane (15 mL) was added to the reaction mixture, which caused an oil to precipitate. The oil was isolated by carefully decanting away the pentane layer. Drying the oil gave $15-BAr^{F_4}$ as an off-white solid. Care must be taken not to expose the product to prolonged periods under dynamic vacuum. Yield: 123 mg (48%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 4.38 (4 H, m, OCH₂CH₂), 3.26 (6 H, m, SCH2, down), 3.02 (6 H, m, SCH2, up), 2.20 (4 H, m, OCH₂CH₂), 0.31 (2 H, d, ${}^{2}J$ = 12 Hz, ScCH₂), 0.49 (2 H, d, ${}^{2}J$ = 12 Hz, ScCH₂), -0.04 (18 H, s, ScCH₂SiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 198 K): 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 74.6 (OCH₂CH₂), 32.9 (SCH₂), 32.5 (ScCH₂), 25.8 (OCH₂CH₂), 3.1 (ScCH₂SiMe₃) ppm. ¹⁹F NMR $(CD_2Cl_2, 282.2 \text{ MHz}, 293 \text{ K}): -133.8 \text{ (d, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 133.8 \text{ (t, } 2\text{-}C_6F_5), -162.9 \text{ (t, } 2\text{-}C_6F_$ 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): XXXXX cm⁻¹. Anal. Found (calcd For C₄₂H₄₂BF₂₀OS₃ScSi₂): C, 42.9 (42.8); H, 3.7 (3.7).

In Situ Synthesis of $[Y([9]aneS_3)(CH_2SiMe_3)_2(THF)_2]$ -[BAr^F₄] (16-BAr^F₄). A solution of $Y(CH_2SiMe_3)_3(THF)_2$ (5.0 mg, 0.01 mmol) in CD₂Cl₂ (0.7 mL) was added to solid [NHMe₂Ph][BAr^F₄] (8.1 mg, 0.01 mmol). This solution was added to solid [9]aneS₃ (1.8 mg, 0.01 mmol). The ¹H NMR spectrum of the reaction mixture was recorded immediately, showing 100% conversion to **16-BAr**^F₄. ¹H NMR (CD₂Cl₂, 299.9 MHz, 213 K): 4.04 (8 H, m, OC<u>H</u>₂CH₂), 3.21 (6 H, m, SC<u>H</u>₂, down), 3.01 (6 H, m, SC<u>H</u>₂, up), 2.06 (8 H, m, OCH₂C<u>H</u>₂), -0.04 (18 H, s, YCH₂Si<u>Me</u>₃), -0.7 (4 H, d, ²*J*_{HY} = 3.2 Hz, YC<u>H</u>₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 213 K): 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 71.3 (O<u>C</u>H₂CH₂), 39.7 (Y<u>C</u>H₂, ¹*J*_{YC} = 35 Hz), 32.6 (S<u>C</u>H₂), 25.6 (OCH₂<u>C</u>H₂), 3.9 (YCH₂Si<u>Me</u>₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm.

In Situ Synthesis of $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2][BAr^F_4]$ (17-BAr^F₄). A solution of Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3 (0.01 g, 0.02 mmol) in CD₂Cl₂ was added to solid $[Ph_3C][BAr^F_4]$ (0.02 g, 0.02 mmol) to give a yellow solution. NMR analysis showed immediate quantitative conversion to 17-BAr^F₄. ¹H NMR (CD₂Cl₂, 299.9 MHz, 193 K): 2.98–2.89 (12 H, m, br, NCH₂), 2.74 (9 H, br s, NCH₃), 0.02 (4 H, s, ScCH₂), -0.08 (18 H, s, SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 193 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. ²⁹Si NMR (HMQC ¹H-observed, CD₂Cl₂, 299.9 MHz, 193 K): -3.4 ppm.

In Situ Synthesis of $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2][BAr^F_4]$ (19-BAr^F_4). A solution of Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_3 (0.01 g, 0.017 mmol) in CD_2Cl₂ was added to solid [CPh₃][BAr^F_4] (0.015 g, 0.017 mmol) to give a yellow solution. NMR analysis showed immediate quantitative conversion to 19-BAr^F_4. ¹H NMR (CD_2Cl₂, 299.9 MHz, 193 K): 7.89 (1 H, s, <u>HC(Me_2pz)_3</u>), 6.16 (3 H, s, 4-HC(Me_2pz)_3), 2.61 (9 H, s, HC(Me_2pz)_3), 2.56 (9 H, s, HC(Me_2pz)_3), 0.70 (4 H, s, br, ScCH₂), -0.02 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR (CD_2Cl₂, 75.5 MHz, 193 K): 153.6 (3-HC(Me_2pz)_3), 147.6 (br d, 2-C₆F₅), 142.6 (5-HC(Me_2pz)_3), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 109.4 (4-HC(Me_2pz)_3), 68.5 (HC(Me_2pz)_3), 15.4 (HC(Me_2pz)_3), 11.4 (HC(HC(Me_2pz)_3), 3.0 (SiMe_3) ppm. ¹⁹F NMR (CD_2Cl₂, 282.2 MHz, 193 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. ²⁹Si NMR (HMQC ¹H-observed, CD_2Cl₂, 299.9 MHz, 193 K): -2.2 ppm.

[Sc{HC(Me2pz)_3}(CH2SiMe3)_2(OPPh3)][BArF4] (24-BArF4). To a Schlenk tube containing [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂-(THF)][BAr^F₄] (0.10 mg, 0.08 mmol) and PPh₃O (0.02 g, 0.08 mmol) was added CH₂Cl₂ (15 mL). The off-white solution was stirred at RT for 1 h, and then the volatiles were removed in vacuo to give 24-BAr^F₄ as a spongy white solid. Yield: 70 mg (60%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.90 (1 H, s, <u>H</u>C(Me₂pz)₃), 7.68-7.47 (15 H, m, PPh₃O), 6.15 (1 H, s, 4-HC(Me₂pz)₃ trans PPh₃O), 5.80 (2 H, s, 4-HC(Me₂pz)₃ trans CH₂SiMe₃), 2.73 (3 H, s, 3-HC(Me₂pz)₃ trans PPh₃O), 2.59 (3 H, s, 5-HC(Me₂pz)₃ trans PPh₃O), 2.54 (6 H, s, 3-HC(Me₂pz)₃ trans CH₂SiMe₃), 1.74 (6 H, s, 5-HC(Me₁pz)₃ trans CH₂SiMe₃), 0.22 (2 H, d, ${}^{2}J = 11.8$ Hz, $ScCH_2$, 0.15 (2 H, d, ²J = 11.8 Hz, $ScCH_2$), -0.32 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 153.5 (3-HC(Me2pz)3 trans PPh3O), 154.4 (3-HC(Me2pz)3 trans CH2SiMe3), 147.6 (br d, 2-C₆F₅), 140.6 (5-Me₂pz₃ trans PPh₃O), 140.5 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 133.2 (OPPh₃), 133.0 (OPPh₃), 129.6 (OPPh₃), 129.5 (OPPh₃), 108.7 (4-HC(Me₂pz)₃ trans PPh₃O, 108.5 (4-HC(Me₂pz)₃ trans CH₂SiMe₃), 68.1 (HC(Me₂pz)₃), 16.5 (3-HC(Me₂pz)₃ trans PPh₃O), 14.9 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 11.4 (5-HC(Me₂pz)₃ trans PPh₃O), 11.2 (5-HC(Me₂pz)₃ trans CH₂SiMe₃), 3.5 (SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, $4-C_6F_5$), -166.9 (app. t, $3-C_6F_5$) ppm. IR (NaCl plates, Nujol mull): 1643 (w), 1592 (w), 1571 (w), 1513 (s), 1308 (m), 1237 (w), 1142 (m), 1121 (s), 1085 (s), 1035 (m), 979 (s), 863 (m), 774 (w), 660 (m)cm⁻¹. Anal. Found (calcd for C₆₆H₅₉BF₂₀N₆OPScSi₂ • 0.5(CH₂Cl₂)): C 52.7, (52.6); H 4.1, (4.0); N 5.5, (5.5).

[Sc{HC(Me₂pz)₃)(CH₂SiMe₃)₂(py)][BAr^F₄] (25-BAr^F₄). To a solution of [Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₂(THF)][BAr^F₄] (0.10 g, 0.08 mmol), in CH₂Cl₂ (10 mL), was added pyridine (13 μ L, 0.16

mmol) via microlitre syringe. After 30 min the solution was concentrated to 2 mL and pentane (15 mL) was added. An offwhite oil precipitated and was isolated by carefully decanting the supernatant. Drying the oil *in vacuo* gave 25-BAr^F₄ as a spongy off-white solid. Yield: 37 mg (37%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 8.69 (2 H, app. s, br, o-C₅<u>H</u>₅N), 8.12 (1 H, tt, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.5$ Hz, *p*-C₅<u>H</u>₅N), 7.99 (1 H, s, <u>H</u>C(Me₂pz)₃), 7.63 (2 H, app.t, ${}^{3}J = 6.4$ Hz), 6.24 (1 H, s, 4-HC(Me₂pz)₃ trans py), 6.03 (2 H, s, 4-HC(Me₂pz)₃, trans CH₂SiMe₃), 2.83 (3 H, s, 3-HC(Me₂pz)₃ trans py), 2.64 (3 H, s, 5-HC(Me₂pz)₃, trans py), 2.57 (6 H, s, 3-HC(Me2pz)3 trans CH2SiMe3), 1.76 (6 H, s, 5-HC(Me2pz)3, trans CH₂SiMe₃), 0.53 (2 H, d, ${}^{2}J = 11$ Hz, ScCH₂), 0.28 (2 H, s, ${}^{2}J =$ 11.7 Hz, ScCH₂), -0.26 (18 H, SiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 155.5 (3-HC(Me₂pz)₃ trans py), 154.9 (3-HC(Me2pz)3 trans CH2SiMe3), 147.6 (br d, 2-C6F5), 149.7 (p-C5H5N), 141.6 (5-HC(Me2pz)3 trans CH2SiMe3), 141.5 (5-HC(Me₂pz)₃ trans py), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 126.1 (m-C₅H₅N), 109.2 (4-HC(Me₂pz)₃ trans CH₂SiMe₃), 109.1 (4-HC(Me₂pz)₃ trans py), 68.3 (HC(Me₂pz)₃), 34.5 (ScCH₂), 14.6 (3-HC(Me₂pz)₃ trans CH₂SiMe₃), 14.2 (3-HC(Me₂pz)₃ trans py), 11.5 (5-HC(Me₂pz)₃ trans py), 11.3 (4-HC(Me₂pz)₃ trans CH₂SiMe₃), 3.4 (SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1643 (w), 1606 (w), 1569 (w), 1514 (s), 1306 (m), 1240 (w), 1086 (m), 1040 (m), 979 (s), 861 (m), 774 (w) cm⁻¹. Anal. Found (calcd for $C_{53}H_{49}BF_{20}N_7$ -ScSi₂ • 1.5(CH₂Cl₂)): C 47.0, (46.6); H 3.7, (3.8); N 7.4, (7.0).

In Situ Synthesis of [Sc{HC(Me₂pz)₃}(CH₂SiMe₃){TolNC- $(CH_2SiMe_3)NTol\}][BAr^F_4]$ (26-BAr^F₄). To a solution of $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2(THF)][BAr^F_4] (15 mg, 0.012 mmol)$ in CD₂Cl₂ (0.7 mL) was added TolNCNTol (2.6 mg, 0.012 mmol). The ¹H NMR spectrum showed quantitative conversion to 26-BAr^F₄. ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.9 (1 H, s, $HC(Me_2pz)_3)$, 7.13 (4 H, d, ${}^{3}J = 7.8$ Hz, 2,6- $NC_6H_4CH_3$), 6.85 (4 H, d, ${}^{3}J = 8.3$ Hz, 3,5-NC₆<u>H</u>₄CH₃), 6.06 (2 H, s, 4-HC(Me₂<u>pz</u>)₃, trans TolNC(CH₂SiMe₃)NTol), 6.04 (1 H, s, 4-HC(Me₂pz)₃ trans CH₂SiMe₃), 2.58 (6 H, s, $5-HC(Me_2pz)_3$, trans TolNC(CH₂SiMe₃)NTol), 2.49 (3 H, s, 5-HC(Me₂pz)₃, trans CH₂SiMe₃), 2.43 (3 H, s, 3-HC(Me₂pz)₃, trans CH₂SiMe₃), 2.32 (6 H, s, NCC₆H₄CH₃), 1.96 (6 H, s, 3-HC(Me₂pz)₃, trans TolNC(CH₂SiMe₃)NTol), 0.33 (2 H, s, CH₂SiMe₃), -0.13 (9 H, s, ScCH₂SiMe₃), -0.65 (9 H, s, TolNC(CH₂SiMe₃)NTol) ppm. $^{13}C{^{1}H}$ NMR (CD₂Cl₂, 75.5 MHz, 293 K): 179.3 (TolNC(CH₂SiMe₃)NTol), 155.5 $(3-HC(Me_2pz)_3)$ trans TolN(CH₂SiMe₃)NTol), 154.4 (3-HC(Me₂pz)₃, trans CH₂SiMe₃), 147.6 (br d, 2-C₆F₅), 144.3 (1-NC(CH₂SiMe₃)NC₆H₄CH₃), 142.2 (5-HC(Me2pz)3, trans TolNC(CH2SiMe3)NTol), 141.4 (5-HC(Me2pz)₃, trans CH₂SiMe₃), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 134.5 $(4-NC(CH_2SiMe_3)\underline{C}_6H_4CH_3),$ 130.1 ((6 -NC(CH₂SiMe₃)C₆H₄CH₃), 125.3 (5-NC(CH₂SiMe₃)C₆H₄CH₃), 108.9 (4-HC(Me₂pz)₃ trans TolNC(CH₂SiMe₃)NTol), 108.7 (4-HC(Me₂pz)₃ trans CH₂SiMe₃), 68.5 (HC(Me₂pz)₃), 20.9 (NC₆H₄CH₃), 14.0 (3-HC(Me₂pz)₃, trans CH₂SiMe₃), 13.9 (3-HC(Me2pz)3, trans TolNC(CH2SiMe3)NTol), 11.3 (5-HC(Me2pz)3, trans TolNC(CH₂SiMe₃)NTol), 11.2 (5-HC(Me₂pz)₃, trans CH₂SiMe₃), 2.7 (NC(CH₂SiMe₃), 0.0 (ScCH₂SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm.

[Sc(Me₃[9]aneN₃)(CH₂SiMe₃){ⁱPrNC(CH₂SiMe₃)NⁱPr}][BAr^F₄] (27-BAr^F₄). To a Schlenk tube containing Sc(CH₂SiMe₃)₃(THF)₂ (0.10 g, 0.22 mmol) and [NHMe₂Ph][BAr^F₄] (0.18 g, 0.22 mmol) was added C₆H₅Cl (15 mL). To this stirring solution was added 1,4,7-Me₃[9]aneN₃ (43 μ L, 0.22 mmol) via microlitre syringe. The solution was stirred at RT for 30 min (generating 13-BAr^F₄ *in situ*), after which time ⁱPrNCNⁱPr (34 μ L, 0.22 mmol) was added. The solution was stirred for a further 30 min, and then pentane (25 mL) was added. An oil formed, which was isolated by carefully decanting away the supernatant. The oil was carefully dried in vacuo to give 27-BAr^F₄ as an off-white oil. Care must be taken not to leave the product under dynamic vacuum for long periods. Yield: 125 mg (47%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 3.65 (2 H, sept, ${}^{3}J = 6.5$ Hz, NC(<u>H</u>)(CH₃)₂), 3.34–2.73 (12H, m, NC<u>H₂</u>), 3.05 (6 H, s, NCH₃ trans CH₂SiMe₃), 2.49 (3 H, s, NCH₃ trans ⁱPrNC(R)NⁱPr), 2.17 (2 H, s, ⁱPrNC(CH₂SiMe₃)NⁱPr), 1.34 (6 H, d, ${}^{3}J = 6.5$ Hz, NCH(CH₃)₂), 1.30 (6 H, d, ${}^{3}J = 6.5$ Hz, NCH(CH₃)₂), 0.18 (9 H, s, ⁱPrNC(CH₂SiMe₃)NⁱPr), -0.09 (9 H, s, ScCH₂Si<u>Me₃</u>), -0.30 (2 H, s, ScCH₂SiMe₃) ppm. ¹³C{¹H} NMR $(CD_2Cl_2,\ 75.5\ MHz,\ 293\ K):\ 147.6$ (br d, $2\text{-}C_6F_5),\ 137.8$ (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 135.0 (B(C₆F₅)₄), 55.8 (NCH₂), 55.3 (NCH₂), 55.0 (NCH₂), 49.6 (NCH₃), 49.45 (NCH₃), 48.6 (NCH₃), 26.6 (NCH(CH₃)₂), 25.8 (NCH(CH₃)₂), 18.5 (NC(CH₂SiMe₃)), 3.5 (ScCH₂Si<u>Me₃</u>), -0.0 (NC(CH₂Si<u>Me₃</u>)) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 1642 (m), 1513 (s), 1463 (s), 1379 (s), 1257 (m), 1211 (w), 1179 (w), 1083 (s), 1003 (m), 978 (s), 910 (w), 854 (m), 774 (m), 756 (m) cm⁻¹. Anal. Found (calcd for C₄₉H₆₁BF₂₀N₅ScSi: C 48.7, (48.6); H 4.9, (5.1); N 5.9, (5.8).

[Sc{HC(Me₂pz)₃}(CH₂SiMe₃)(CCPh)(THF)][BAr^F₄] (28-BAr^F₄). То solution of а $[Sc{HC(Me_2pz)_3}(CH_2SiMe_3)_2(THF)][BAr^F_4] (0.20 \text{ g}, 0.16 \text{ mmol})$ in CH₂Cl₂ (10 mL) was added PhCCH (17.4 μ L, 0.16 mmol) via microlitre syringe. The light green solution was stirred at RT for 30 min, and the volatiles were removed *in vacuo* to give $28-BAr_{4}^{F}$ as a spongy off-white solid. Yield: 131 mg (64%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.90 (1 H, s, HC(Me₂pz)₃), 7.33 (2 H, m, o-C₆H₅), 7.23 (3 H, m, o,p-C₆H₅), 6.17 (1 H, s, 4-HC(Me2pz)3), 6.18 (1 H, s, 4-HC(Me2pz)3), 6.04 (1 H, s, 4-HC(Me₂pz)₃), 4.51 (2 H, m, OCH₂CH₂), 4.25 (2 H, m, OCH₂CH₂), 2.92 (3 H, s, 3-HC(Me₂pz)₃), 2.59 (3 H, s, $5-HC(\underline{Me_2pz})_3)$, 2.58 (3 H, s, $5-HC(\underline{Me_2pz})_3)$, 2.54 (3 H, s, 3-HC(Me₂pz)₃), 2.51 (3 H, s, 5-HC(Me₂pz)₃), 2.49 (3 H, s, 3-HC(Me₂pz)₃), 2.18 (4 H, m, OCH₂CH₂), 0.42 (1 H, d, ${}^{2}J = 11.7$ Hz, ScCH₂), 0.31 (1 H, d, ${}^{2}J = 11.7$ Hz, ScCH₂), -0.14 (9 H, s, ScCH₂Si<u>Me₃</u>) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 156.2 $3-HC(Me_2pz)_3)$, 155.3 $(3-HC(Me_2pz)_3)$, 154.8 (3-HC(Me₂pz)₃), 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 131.8 (ScCCC₆H₅), 128.5 (ScCCC₆H₅), 127.2 (ScCCC₆H₅), 109.1 (4-HC(Me₂pz)₃), 109.0 (4-HC(Me₂pz)₃), 73.6 (OCH₂CH₂), 68.2 (HC(Me₂pz)₃), 25.8 (OCH₂CH₂), 15.6 (3-HC(Me2pz)3), 14.9 (3-HC(Me2pz)3), 14.6 (3-HC(Me2pz)3), 11.4 (5-HC(Me₂pz)₃), 11.3 (5-HC(Me₂pz)₃), 11.1 (5-HC(Me₂pz)₃), 3.42 (ScCH₂SiMe₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 2071 (w, C≡C), 1643 (m), 1596 (w), 1568 (m), 1513 (s), 1305 (m), 1262 (s), 1201 (w), 1086 (s), 1039 (m), 979 (s), 859 (s), 775 (m), 756 (m) cm⁻¹. Anal. Found (calcd for C56H46BF20N6OScSi2.CH2Cl2): C 50.6, (50.1); H 3.8, (3.5); N 6.4, (6.1).

[Sc(Me₃[9]aneN₃)(CH₂SiMe₃)(CCPh)(THF)][BAr^F₄] (29-**BAr**^{\mathbf{F}_4). To a Schlenk tube containing Sc(CH₂SiMe₃)₃(THF)₂ (0.10} g, 0.22 mmol) and [NHMe₂Ph][BAr^F₄] (0.18 g, 0.22 mmol) was added C₆H₅Cl (15 mL). To this stirring solution was added 1,4,7-Me₃[9]aneN₃ (43 μ L, 0.22 mmol) via microlitre syringe. The solution was stirred at RT for 1 h (generating $13-BAr^{F_4}$ in situ), after which time PhCCH (24 μ L, 0.22 mmol) was added. After a further 30 min the volume was reduced to 1 mL and pentane (15 mL) was added. A dark oil formed, which was isolated by carefully decanting away the supernatant. Upon drying *in vacuo* the **29-BAr**^{F_4} formed as a spongy off-white solid. Care must be taken not to leave the product under dynamic vacuum for extended periods of time. Yield: 125 mg (52%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.35-7.25 (5 H, m, ScCCC₆H₅), 4.78 (2 H, m, OCH₂CH₂), 4.60 (2 H, m, OCH₂CH₂), 3.23 (3 H, s, NCH₃), 2.9 – 2.6 (12 H, m, br,

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parameter	$1 \cdot 0.5(C_7H_8)$	15-BAr ^F 4		
empirical formula	C21.5H49S3ScSi3	C42H42BF20OS3ScSi2		
fw	533.04	1150.89		
temp/K	150	150		
wavelength/Å	0.71073	0.71073		
space group	C2/c	$P\overline{1}$		
a/Å	20.0776(4)	10.7691(2)		
b/Å	15.6656(3)	12.7989(3)		
c/Å	20.0619(4)	17.9114(4)		
α/deg	90	81.1573(8)		
β/deg	100.0286(9)	86.3644(9)		
γ/deg	90	86.7330(10)		
V/Å ³	6213.6(2)	2431.73(9)		
Ζ	8	2		
$d(\text{calcd})/\text{Mg} \cdot \text{m}^{-1}$	1.140	1.572		
abs coeff/mm ⁻¹	0.562	0.440		
R indices ^a	$R_1 = 0.0350$	$R_1 = 0.0514$		
$[I > 3\sigma(I)]$	$R_{\rm w} = 0.0436$	$R_{\rm w} = 0.0637$		

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|; R_{w} = \sqrt{\{\sum w(|F_{o}| - |F_{c}|)^{2} / \sum w|F_{o}|^{2}\}}.$

NC<u>H</u>₂), 2.78 (3 H, s, NC<u>H</u>₃), 2.71 (3 H, s, NC<u>H</u>₃), 2.43 (4 H, m, OCH₂C<u>H</u>₂), -0.08 (9 H, s, ScCH₂Si<u>M</u>e₃), 0.00 (1 H, d, ²*J* = 11.7 Hz, ScC<u>H</u>₂), -0.15 (1 H, d, ²*J* = 11.9 Hz, ScC<u>H</u>₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 147.6 (br d, 2-C₆F₅), 137.8 (br d, 4-C₆F₅), 135.9 (br d, 3-C₆F₅), 131.7 (ScCC<u>C</u>₆H₅), 130.1 (ScCC<u>C</u>₆H₅), 128.8 (ScCC<u>C</u>₆H₅), 128.6 (ScCC<u>C</u>₆H₅), 75.4 (O<u>C</u>H₂CH₂, 56.4 (N<u>C</u>H₂), 56.1 (N<u>C</u>H₂), 55.4 (N<u>C</u>H₂), 51.4 (N<u>C</u>H₃), 50.4 (N<u>C</u>H₃), 49.0 (N<u>C</u>H₃), 25.6 (OCH₂<u>C</u>H₂), 3.2 (ScCH₂Si<u>M</u>e₃) ppm. ¹⁹F NMR (CD₂Cl₂, 282.2 MHz, 293 K): -133.8 (d, 2-C₆F₅), -162.9 (t, 4-C₆F₅), -166.9 (app. t, 3-C₆F₅) ppm. IR (NaCl plates, Nujol mull): 2071 (w, C≡C), 1643 (m), 1514 (s), 1201 (w), 1085 (s), 1001 (m), 978 (s), 888 (m), 852 (w), 775 (m), 756 (m), 723 (m) cm⁻¹. Anal. Found (calcd for C₄₃H₄₀BF₂₀N₃OScSi): C 48.0, (47.9); H 3.7, (3.7); N 3.9, (3.9).

Crystal Structure Determinations of Sc([9]aneS₃)(CH₂Si-Me₃)₃ · 0.5(C₇H₈) (1 · 0.5(C₇H₈)) and [Sc([9]aneS₃)(CH₂SiMe₃)₂-(THF)][BAr^F₄] (15-BAr^F₄). 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.⁸⁴ The structures were solved by direct methods (SIR9285), and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.86 Other details of the structure solution and refinements are given in the Supporting Information (CIF data). 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. See Notice to Authors, Issue No. 1.

Procedure for the Polymerization of Ethylene. A typical ethylene polymerization run was carried out as follows with all manipulations under ethylene (~1 atm) working gas until the mixture was quenched. Stock solutions of Sc{HC(Me₂pz)₃}(CH₂Si-Me₃)₃ (6 mg, 10 μ mol in 25 mL of toluene) and [Ph₃C][BAr^F₄] (9.2 mg, 10 μ mol in 20 mL of toluene) were made up. Toluene (225 mL) was added to AlⁱBu₃ (1 M toluene solution, 5 mL, 5 mmol) and transferred to the reactor, which was fitted with an external heat bath set to 40 °C. The mixture was stirred for 10 min

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Scandium and Yttrium Dialkyl Cations

(1000 rpm) to scrub the apparatus and allow the toluene solution to equilibrate to approximately 35 °C. Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (6 mg, 10 μ mol in 25 mL of toluene) was added to the reactor, followed by [Ph₃C][BAr^F₄] (10 μ mol in 20 mL of toluene). A dynamic ethylene pressure of 6 bar was applied. The temperature and ethylene uptake were monitored and the reaction was run for 10 min, after which the ethylene flow was stopped and the pressure carefully released. The reactor lid was removed and the reaction mixture quenched by the careful dropwise addition of MeOH (approximately 10 mL). Distilled water (50 mL) was then added and the mixture acidified to pH 1 (10% HCl in MeOH) (approximately 25 mL). The reaction mixture was stirred for 16 h and then filtered. The solid PE was washed with distilled water (1000 mL) and dried at approximately 60 °C to constant weight.

Procedure for the Polymerization of 1-Hexene. A typical 1-hexene polymerization run was carried out as follows. To a stirring solution of Sc{HC(Me₂pz)₃}(CH₂SiMe₃)₃ (12 mg, 20 μ mol) in C₆H₅Cl (2.5 mL) was added 1-hexene (1.48 mL, 12 mmol). To this mixture was added a solution of [CPh₃][BAr^F₄] (40 mg, 40 μ mol) in C₆H₅Cl (2.5 mL). The reaction mixture became extremely viscous almost immediately. After 10 min the reaction mixture was quenched with wet THF. The polyhexene was isolated by precipitation in EtOH and was dried *in vacuo*.

Computational Details. All the calculations have been performed with the Gaussian03 package⁸⁷ at the B3PW91 level.^{88,89} The scandium and yttrium atoms were represented by the relativistic

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effective core potential (RECP) from the Stuttgart group and the associated basis sets.⁹⁰ The Si and S atoms were represented by RECP from the Stuttgart group and the associated basis sets,⁹¹ augmented by a d polarization function.⁹² The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set.⁹³ Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima on the potential energy surface. NMR chemical shifts were computed using the GIAO method^{94,95} at the B3PW91 level. For the NMR parameters, all electron calculations were considered where the basis set for Sc was the TZP basis set of Ahlrichs,⁹⁶ and all the other atoms were described with the IGLOO-II basis set.⁹⁷ For the NMR calculations on Y complexes, the Y atom was described with the RECP from Dolg et al. and the associated basis set.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of $1 \cdot 0.5(C_7H_8)$ and 15-BAr^F₄. Cartesian coordinates for the molecules optimized and electronic energies (au) at the B3PW91 level for the neutral molecules. This information is available free of charge via the Internet at http://pubs.acs.org.

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