A Family of Scandium and Yttrium Tris((trimethylsilyl)methyl) Complexes with Neutral N_3 Donor Ligands

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The first group 3 organometallic compounds containing the tris(3,5-dimethylpyrazolyl)methane ($HC(Me_2pz)_3$) and 1,3,5-trimethyltriazacyclohexane ($Me_3[6]aneN_3$) ligands are reported, together with the homologous 1,4,7-triazacyclononane-supported compounds and trichloride derivatives for many of the ligands. Reaction of $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc, Y) with $Me_3[9]aneN_3$ (1,4,7-trimethyltriazacyclononane), $HC(Me_2pz)_3$, or $Me_3[6]aneN_3$ gave the corresponding tris((trimethylsilyl)methyl) derivatives $M(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (M = Sc (**1**), Y (**2**)), $M\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (M = Sc (**3**), Y (**4**)), and $M(Me_3[6]aneN_3)(CH_2SiMe_3)_3$ (M = Sc (**12**), Y (**13**)). Reaction of **3** with 2,6-dimethylphenol (ArOH) gave the tris(aryloxide) derivative $Sc\{HC(Me_2pz)_3\}(OAr)_3$ (**9**), and reaction of $HC(Me_2pz)_3$ with MCl_3 gave $M\{HC(Me_2pz)_3\}Cl_3$ (M = Sc (**5**), Y(**6**)). Attempts to prepare tris((trimethylsilyl)methyl) complexes with the more sterically demanding tris(3-R-pyrazolyl)methanes (R = ^iPr, Ph, ^tBu) or the related tris(pyrazolyl)methylsilane ligand were unsuccessful. However, the trichlorides $M\{HC(^iPrpz)_3\}Cl_3$ (M = Sc (**7**), Y (**8**)) and $M\{MeSi(Me_2pz)_3\}Cl_3$ (M = Sc (**10**), Y (**11**)) could be made. In related studies the reaction of $ScCl_3(THF)_3$ with $Me_3[6]aneN_3$ afforded $Sc(Me_3[6]aneN_3)Cl_3$ (**14**), but the yttrium congener could not be prepared. The compounds **1**, **3**, **4**, **9**, **11**, and **14** have been crystallographically characterized. Competitive ligand exchange reactions for the tris(alkyl) compounds $M(L)(CH_2SiMe_3)_3$ established the binding preference $L = Me_3[9]aneN_3 > Me_3[6]aneN_3 > HC(Me_2pz)_3$ for M = Sc and $L = Me_3[9]aneN_3 > HC(Me_2pz)_3 > Me_3[6]aneN_3$ for M = Y. Reaction of $ScR_3(THF)_2$ (R = CH_2SiMe_3, Ph) with 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyltriazacyclononane (HL^1) or 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyltriazacyclononane (HL^2) gave organoscandium derivatives of mono(phenoxy)-substituted triazacyclononane ligands, namely $Sc(L^1)R_2$ (R = CH_2SiMe_3 (**15**), Ph (**17**)) and $Sc(L^2)(CH_2SiMe_3)_2$ (**16**). Reaction of **15** with 2 equiv of TolOH (Tol = *p*-tolyl) afforded $Sc(L^1)(OTol)_2$ (**18**), which was crystallographically characterized.

Introduction

Non-cyclopentadienyl organometallic compounds of group 3 (and the lanthanide 4f elements) are currently attracting considerable attention. A range of neutral and (especially) anionic supporting ligands have recently been employed in these efforts, and this work has recently been comprehensively reviewed.[1−3] One particular emphasis has been on the synthesis and reactivity (including olefin polymerization catalysis[4−6]) of cationic alkyl derivatives; Okuda has very recently reviewed the latter rapidly evolving area.[7] Our present contribution reports the development of scandium and yttrium tris((trimethylsilyl)methyl) complexes supported by a family of neutral *fac*-coordinated N_3 donor ligands, together with some related systems. Bercaw[8] reported the first group 3 complexes of 1,4,7-trimethyltriazacyclononane ($Me_3[9]aneN_3$; see Chart 1 for the ligands used herein and the nomenclature adopted), namely $M(Me_3[9]aneN_3)X_3$ (**I** in Chart 2; M = Sc, Y; X = Cl, Me). Reaction of $Sc(Me_3[9]aneN_3)Me_3$ with BAr^F_3 ($Ar^F = C_6F_5$) in THF-d_8 afforded a species (not isolated) which was formulated as $Sc(Me_3[9]aneN_3)Me_2(\mu\text{-}Me)BAr^F_3$. The NMR spectra of this compound were broad, but the compound nonetheless “proved competent” for ethylene polymerization at 80 °C (no activity data were given). Hessen subsequently disclosed the triazacyclononane−amide group 3 complexes **II** (Chart 2, M = Y,[9] La[10]). Activation of the yttrium congener with $[PhNMe_2H][BAr^F_4]$ forms a cationic alkyl complex which is active for the polymerization of ethylene.[9] Okuda has

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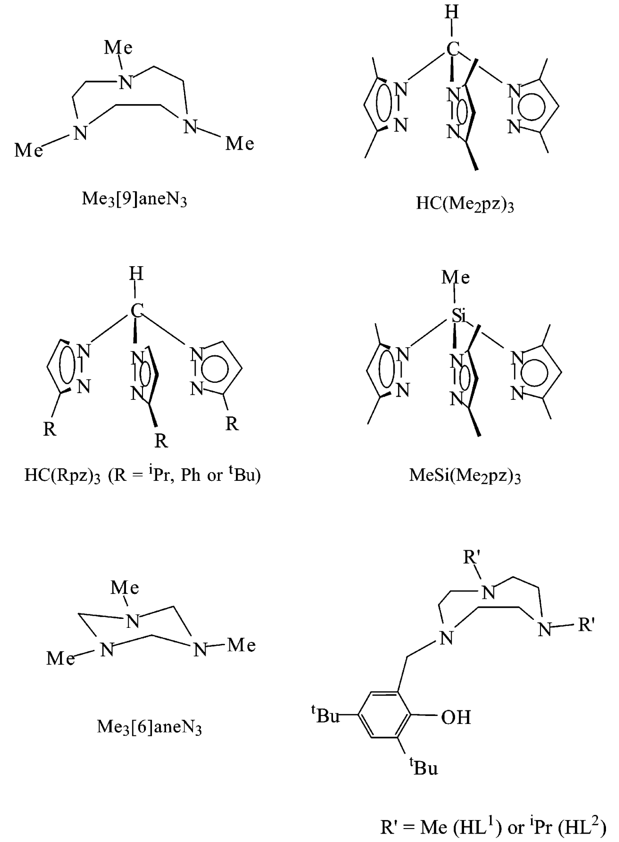
Chart 1



recently employed crown ethers (O donors) to stabilize both neutral and cationic lanthanide (trimethylsilyl)methyl complexes such as **III** (Chart 2), which was the first structurally characterized cationic lanthanide−alkyl complex.[11] However, the cationic crown ether complexes were not catalytically active. In a recent communication[12] we reported that the tris((trimethylsilyl)methyl) complexes $Sc(L)(CH_2SiMe_3)_3$ (L = $Me_3[9]aneN_3$, $HC(Me_2pz)_3$) formed highly active ethylene polymerization catalysts on activation with $BAr^F{}_3$. These are the most active ethylene polymerization catalysts reported to date for cationic scandium systems. Furthermore, $Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ was the first group 3 organometallic compound of $HC(Me_2pz)_3$,[13] which is the neutral analogue of the very widely exploited tris(pyrazolyl)hydroborate ligand, $[HB(Me_2pz)_3]^-$.[14−16] The CH_2SiMe_3 ligands appear to be critical to good catalyst activity, since Bercaw's $Sc(Me_3[9]aneN_3)Me_3$ gave about 15% of the activity under otherwise identical conditions.[17] The cationic alkyl complex $[Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)]^+$ was isolated as its $[BAr^F{}_4]^-$ salt.[12] Full details of our work on the synthesis and stoichiometric and catalytic chemistry of *cationic* alkyl systems will be reported in a future contribution.

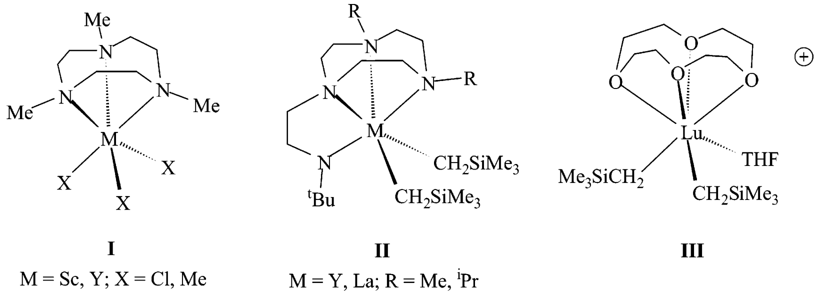
In this paper we report the synthesis and structural characterization of new organo−scandium and −yttrium complexes of $Me_3[9]aneN_3$, as well as the first group 3 organometallic and coordination complexes of $HC(Me_2pz)_3$ and 1,3,5-trimethyltriazacyclohexane ($Me_3[6]aneN_3$). We also report the first group 3 complexes of $MeSi(Me_2pz)_3$ as well as organoscandium derivatives of mono(phenoxy)-substituted triazacyclononane ligands (L^1 and L^2; Chart 1). This family of compounds forms the basis for exploring further the stoichiometric and catalytic chemistry of group 3 neutral and cationic alkyl complexes.[18]

Results and Discussion

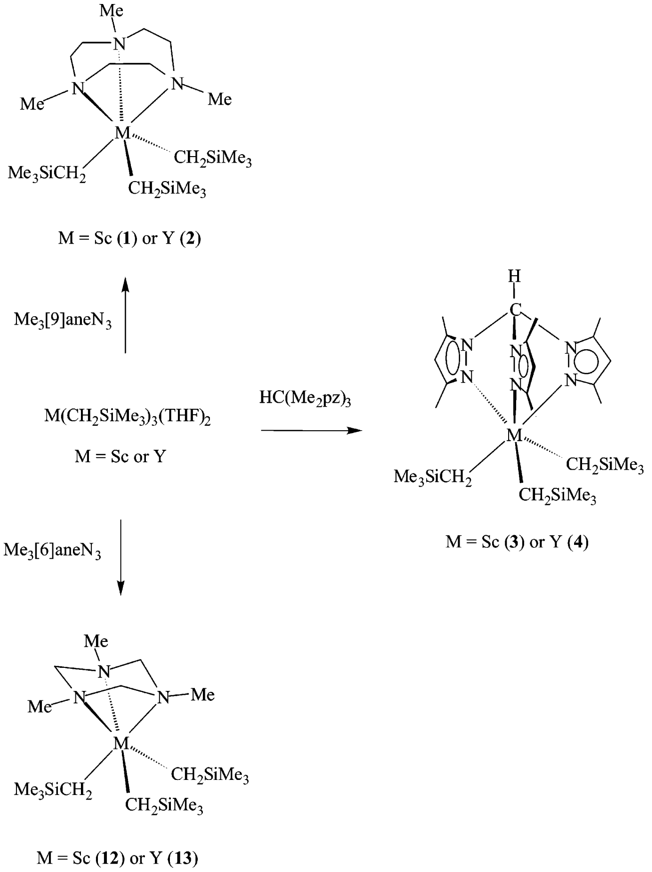
The syntheses of the new tris((trimethylsilyl)methyl) complexes of scandium and/or yttrium are summarized in Scheme 1. All start from the readily available $M(CH_2SiMe_3)_3(THF)_2$ starting materials[19] and previously reported face-capping ligands.[20−23]

Compounds with $Me_3[9]aneN_3$ Ligands. Triazacyclononanes and their N-functionalized derivatives have been used as effective face-capping ligands across the full range of transition, main-group, and lanthanide metals. However, their organometallic chemistry in group 3 is comparatively underdeveloped, as discussed above. The compounds $M(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (M = Sc (**1**), Y (**2**)) were readily obtained as pale air- and moisture-sensitive solids in ca. 60−70% isolated yield. The NMR spectra of the new compounds suggest C_{3v} symmetry. The "up" and "down" (with respect to the metal) ring methylene protons appear as mutually coupled second-order multiplets consistent with the macrocycle being κ^3 bound to the $M(CH_2SiMe_3)_3$ fragment, the methylene and $SiMe_3$ protons of which appear as singlets. As shown by ^1H NMR spectroscopy in C_6D_6, the reactions to form **1** and **2** are quantitative. The X-ray structure of **1** has been determined and is discussed below. However, for this compound (and **2** and some other alkyl complexs reported herein) we have been unable to gain satisfactory elemental analysis, especially for carbon. For example, diffraction-quality crystals of **1** consistently gave lower than expected carbon analysis (in three different analytical laboratories), even when combustion aids were used. We believe that on the basis of the NMR spectra and several X-ray crystal structures that the compounds are authentic and analytically pure but that either their lability on heating or incomplete combustion is responsible for the disappointing elemental analyses.

Chart 2



Scheme 1. Synthesis of New Tris((trimethylsilyl)methyl) Complexes of $Me_3[9]aneN_3$, $HC(Me_2Pz)_3$, and $Me_3[6]aneN_3$



Crystals of **1** contain two independent molecules in the asymmetric unit, and there are no significant differences between them. One of the two molecules is represented in Figure 1, and selected bond lengths and angles for both of them are listed in Table 1. The geometry at Sc is approximately octahedral, and while the $Sc-CH_2$ distances (average 2.279 Å) and $Sc-CH_2-Si$ angles (average 135.7°) are within previously reported[24,25] ranges (distances, range 2.166−2.295, average 2.232 Å; angles, range 115.5−149.8, average 131.7°) for compounds containing a $Sc-CH_2SiR_3$ ligand (R_3 = Me_3 or Me_2Ph), they are certainly among the largest reported to date. However, precise comparisons cannot be made, since there is no six-coordinate tris((triorganosilyl)methyl) derivative among the 15 compounds containing a $Sc-CH_2SiR_3$ linkage listed on the current Cambridge Crystallographic Database.[24,25] The structurally characterized compounds closest to **1** (and also to **3** described below) are Piers' $Sc(CH_2SiMe_2Ph)_3(THF)_2$ (average $Sc-CH_2$ = 2.251 Å, average $Sc-CH_2-Si$ = 123.4°)[26] and $Sc\{HB(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)$ (average $Sc-CH_2$ = 2.251 Å, average $Sc-CH_2-Si$ = 134.9°), the latter being formally zwitterionic with a positive charge at Sc and a negative charge at boron.[27] The

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (1)[a]

Sc(1)−N(1)	2.4688(15)	[2.4537(14)]
Sc(1)−N(2)	2.4604(14)	[2.4664(14)]
Sc(1)−N(3)	2.4726(14)	[2.4583(14)]
Sc(1)−C(10)	2.2887(17)	[2.2799(17)]
Sc(1)−C(14)	2.2970(17)	[2.2952(16)]
Sc(1)−C(18)	2.2574(18)	[2.2572(18)]
N(1)−Sc(1)−N(2)	71.81(5)	[71.30(5)]
N(1)−Sc(1)−N(3)	71.21(5)	[72.20(5)]
N(2)−Sc(1)−N(3)	70.87(5)	[71.52(5)]
N(1)−Sc(1)−C(10)	158.16(6)	[160.02(6)]
N(2)−Sc(1)−C(10)	90.90(6)	[92.94(6)]
N(3)−Sc(1)−C(10)	90.85(6)	[91.49(6)]
N(1)−Sc(1)−C(14)	91.34(6)	[90.53(5)]
N(2)−Sc(1)−C(14)	159.42(5)	[158.01(6)]
N(3)−Sc(1)−C(14)	92.89(6)	[91.52(5)]
C(10)−Sc(1)−C(14)	102.20(6)	[101.62(6)]
N(1)−Sc(1)−C(18)	94.13(7)	[97.34(6)]
N(2)−Sc(1)−C(18)	93.17(6)	[94.79(6)]
N(3)−Sc(1)−C(18)	160.83(6)	[164.70(6)]
C(10)−Sc(1)−C(18)	100.20(7)	[96.12(7)]
C(14)−Sc(1)−C(18)	99.93(7)	[99.88(6)]
Sc(1)−C(10)−Si(1)	131.02(9)	[125.38(9)]
Sc(1)−C(14)−Si(2)	135.87(9)	[138.36(9)]
Sc(1)−C(18)−Si(3)	141.35(10)	[142.31(10)]

[a] Values in brackets correspond to the other crystallographically independent molecule in the asymmetric unit.

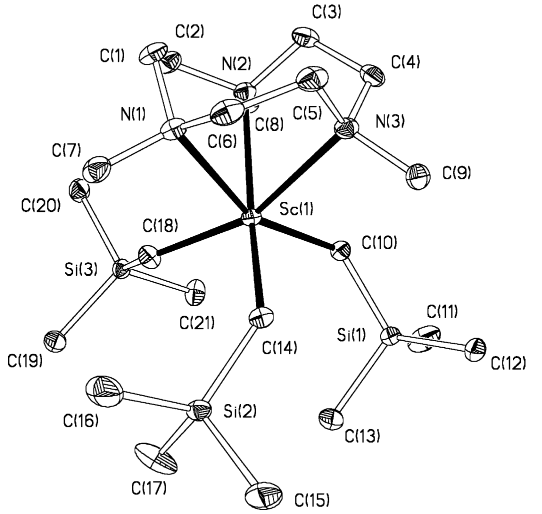


Figure 1. Displacement ellipsoid plot (25% probability) of one of the two crystallographically independent molecules of $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (**1**). H atoms are omitted for clarity.

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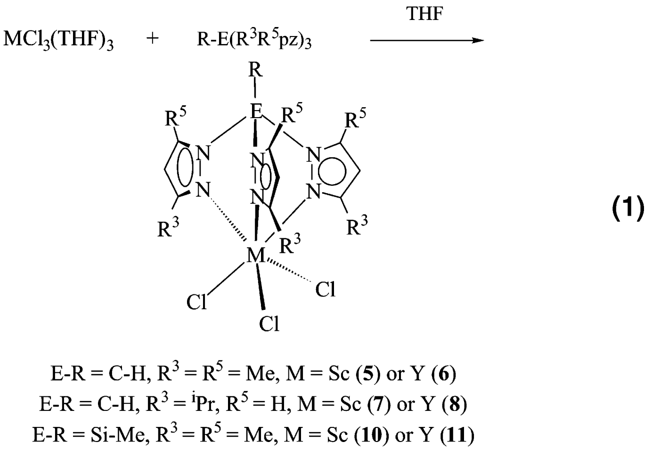
relatively long Sc−CH_2 distances and obtuse Sc−CH_2−Si angles in **1** are attributed to the six-coordinate, comparatively crowded environment in this compound. While there is some variation between the individual Sc−CH_2 distances and Sc−CH_2−Si angles, it is not clear why this should be, on the basis of the intermolecular disposition of the CH_2SiMe_3 groups. The Sc−N distances (average 2.463 Å) are considerably longer than in Bercaw's $Sc(Me_3[9]aneN_3)Cl_3$ (average 2.337 Å),[8] due to the additional steric crowding in **1** and the better donor ability of CH_2SiMe_3 in comparison to Cl.

Compounds with Tris(pyrazolyl)methane and Tris(pyrazolyl)methylsilane Ligands. Tris(pyrazolyl)methane ligands[13] are the neutral analogues of the tris(pyrazolyl)hydroborates,[14−16] among which $[HB(Me_2pz)_3]^-$ ("Tp*") is the most widely used. Tris(pyrazolyl)hydroborate derivatives of the group 3 (and lanthanide) elements in general are extremely well-known,[28] and within group 3 the organometallic compounds $Y\{HB(Me_2pz)_3\}R_2(THF)$ (R = CH_2SiMe_3, Ph),[29] $Sc\{HB(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)$, and $Sc\{HB(^tBu,Mepz)_3\}(CH_2SiMe_3)_2$[27] have recently been described by Bianconi (yttrium) and Piers. In contrast, only one tris(pyrazolyl)methane compound of the rare-earth metals has so far been described, namely $Ce\{HC(pz)_3\}(NO_3)_4$, which was disclosed in a crystallographic report in 2002,[30] and no rare-earth tris(pyrazolyl)silane compound has been reported at all.

As summarized in Scheme 1, the compounds $M\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (M = Sc (**3**), Y (**4**)) are readily prepared from $M(CH_2SiMe_3)_3(THF)_2$ in ca. 60−70% isolated yields as pale-colored solids. Their NMR spectra feature resonances attributed to coordinated $HC(Me_2pz)_3$ groups as well as CH_2SiMe_3 ligands and are consistent with C_{3v}-symmetrical products. NMR tube-scale syntheses are quantitative.

Attempts to prepare homologues of **3** and **4** using the different ring 3-substituted ligands $HC(Rpz)_3$ (R = ^iPr, Ph, ^tBu; see Chart 1) gave either ill-defined mixtures (R = ^iPr or Ph) or no reaction at all. The complexation reactions therefore appear to be rather sensitive to the nature of the pyrazolyl ring 3-substituent. For comparison and completeness we also attempted to prepare trichloride derivatives of the $HC(Me_2pz)_3$ and $HC(Rpz)_3$ ligands (eq 1). The compounds $M\{HC(Me_2pz)_3\}Cl_3$ (M = Sc (**5**), Y(**6**)) were readily isolated (ca. 75% yield), as were the ring 3-isopropyl-substituted homologues $M\{HC(^iPrpz)_3\}Cl_3$ (M = Sc (**7**), Y(**8**)). However, ill-defined products were again formed with $HC(Phpz)_3$, while no reaction at all occurred with the most sterically demanding ligand, $HC(^tBupz)_3$. The compounds **5**−**8** are the first group 3 trichloride compounds of tris(pyrazolyl)methane, and their NMR spectra show the expected C_{3v} symmetry. A structurally characterized tris(pyrazolyl)methylsilane analogue is discussed later; the tris(pyrazolyl)methane complexes are assumed to have comparable molecular structures.



(1)

E-R = C-H, $R^3 = R^5$ = Me, M = Sc (**5**) or Y (**6**)
E-R = C-H, $R^3 = {}^iPr$, R^5 = H, M = Sc (**7**) or Y (**8**)
E-R = Si-Me, $R^3 = R^5$ = Me, M = Sc (**10**) or Y (**11**)

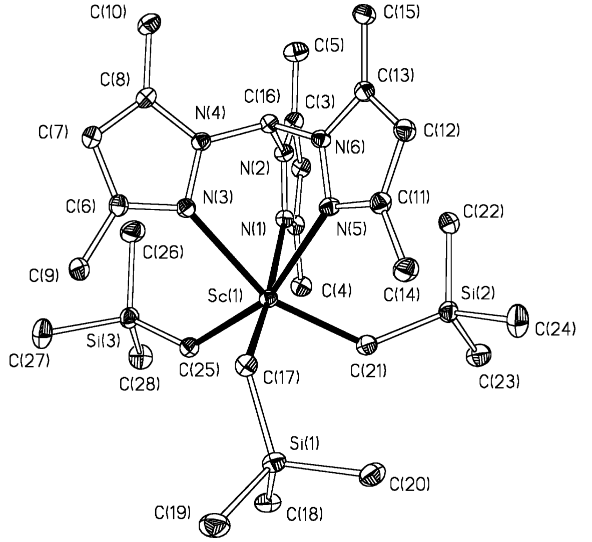


Figure 2. Displacement ellipsoid plot (25% probability) of $Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (**3**). H atoms and toluene molecules of crystallization are omitted for clarity.

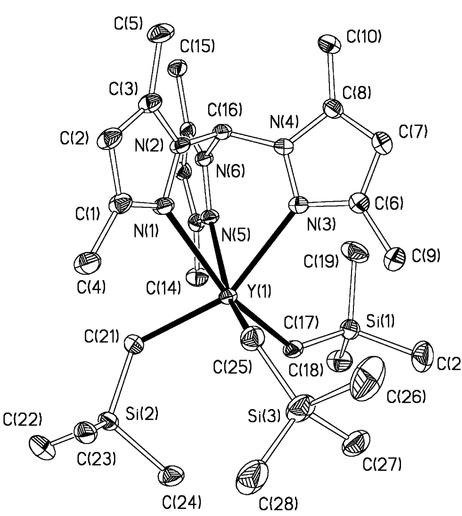


Figure 3. Displacement ellipsoid plot (25% probability) of $Y\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (**4**). H atoms are omitted for clarity.

The X-ray structures of the tris((trimethylsilyl)methyl) compounds **3** and **4** have been determined. Displacement ellipsoid plots are shown in Figures 2 and 3, and selected distances and angles are listed in Tables 2 and 3. The structures are broadly similar but will be discussed in turn.

Molecules of **3**, like those of **1**, feature an approximately octahedral scandium center. The average Sc−N distance (2.420 Å) is somewhat shorter than that in **1** (2.463 Å), but this could to some extent be a consequence of the change in N atom hybridization from sp^3 in $Me_3[9]aneN_3$ to sp^2 in Me_2pz and the associated reduction in covalent radius. Further discussion of the differences

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Sc{HC(Me$_2$Pz)$_3$}(CH$_2$SiMe$_3$)$_3$ (3)

Sc(1)−N(1)	2.3996(17)	Sc(1)−C(17)	2.291(2)
Sc(1)−N(3)	2.4422(17)	Sc(1)−C(21)	2.269(2)
Sc(1)−N(5)	2.4173(17)	Sc(1)−C(25)	2.281(2)
N(1)−Sc(1)−N(3)	76.63(6)	C(17)−Sc(1)−C(21)	99.87(8)
N(1)−Sc(1)−N(5)	77.76(6)	N(1)−Sc(1)−C(25)	90.20(7)
N(3)−Sc(1)−N(5)	70.83(6)	N(3)−Sc(1)−C(25)	89.34(7)
N(1)−Sc(1)−C(17)	168.87(7)	N(5)−Sc(1)−C(25)	158.61(7)
N(3)−Sc(1)−C(17)	93.98(7)	C(17)−Sc(1)−C(25)	95.72(9)
N(5)−Sc(1)−C(17)	93.63(8)	C(21)−Sc(1)−C(25)	105.89(9)
N(1)−Sc(1)−C(21)	87.50(7)	Sc(1)−C(17)−Si(1)	122.37(11)
N(3)−Sc(1)−C(21)	158.13(7)	Sc(1)−C(21)−Si(2)	134.55(12)
N(5)−Sc(1)−C(21)	91.35(7)	Sc(1)−C(25)−Si(3)	135.52(12)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Y{HC(Me$_2$Pz)$_3$}(CH$_2$SiMe$_3$)$_3$ (4)

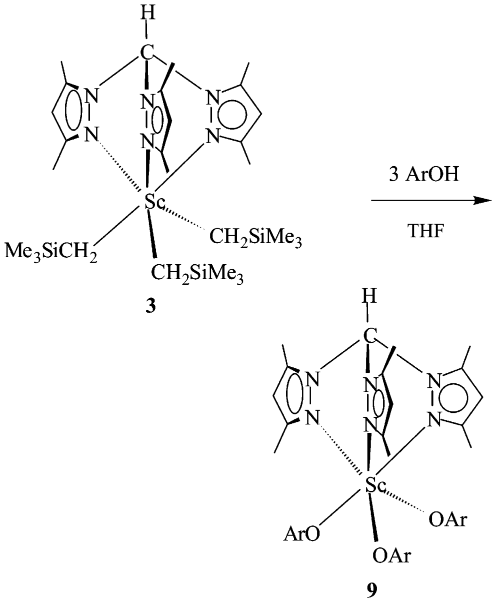
Y(1)−N(1)	2.601(2)	Y(1)−C(17)	2.434(3)
Y(1)−N(3)	2.563(2)	Y(1)−C(21)	2.448(3)
Y(1)−N(5)	2.596(2)	Y(1)−C(25)	2.420(4)
N(1)−Y(1)−N(3)	70.80(8)	C(17)−Y(1)−C(21)	99.42(11)
N(1)−Y(1)−N(5)	70.11(8)	N(1)−Y(1)−C(25)	90.75(11)
N(3)−Y(1)−N(5)	70.59(8)	N(3)−Y(1)−C(25)	89.60(11)
N(1)−Y(1)−C(17)	160.68(10)	N(5)−Y(1)−C(25)	155.84(11)
N(3)−Y(1)−C(17)	97.10(10)	C(17)−Y(1)−C(25)	104.51(13)
N(5)−Y(1)−C(17)	91.91(10)	C(21)−Y(1)−C(25)	104.31(12)
N(1)−Y(1)−C(21)	87.94(10)	Y(1)−C(17)−Si(1)	136.35(16)
N(3)−Y(1)−C(21)	154.89(10)	Y(1)−C(21)−Si(2)	125.32(16)
N(5)−Y(1)−C(21)	90.02(9)	Y(1)−C(25)−Si(3)	137.0(2)

in Sc−N distances between **1** and **3** is limited by the paucity of crystallographic data for pairs of homologous complexes M(Me$_3$[9]aneN$_3$)(L)$_n$ and M{HC(Me$_2$pz)$_3$}(L)$_n$. Data for just one pair of such compounds are available, namely Ti(Me$_3$[9]aneN$_3$)(N^{t}Bu)Cl$_2$ (average Ti−N$_{\text{macrocycle}}$ = 2.377 Å)[31] and Ti{HC(Me$_2$pz)$_3$}(N^{t}Bu)Cl$_2$[32] (average Ti−N$_{\text{Me}_2\text{pz}}$ = 2.291 Å). In these two compounds there is also a decrease in metal−N distance on going from the Me$_3$[9]aneN$_3$ to the HC(Me$_2$pz)$_3$ ligand.

The average Sc−CH$_2$ distance in **3** (2.280 Å) is indistinguishable from that in **1** (2.279 Å), but the average Sc−CH$_2$−Si angle (130.8°) and range of values (122.37(11)−135.52(12)°) is somewhat less than those in **1** (average 135.7°, range 125.38(9)−142.31(10)°). A closer inspection of **3** shows that two of the SiMe$_3$ groups (containing Si(2) and Si(3)) are oriented "up" toward the HC(Me$_2$pz)$_3$ ligand and are partially accommodated in the clefts between pairs of Me$_2$pz rings. The other SiMe$_3$ (Si(1)) is oriented "down", and this has the smaller Sc−CH$_2$−Si angle (122.37(11)° subtended at C(17)), possibly indicative of reduced steric repulsion for this individual moiety (but see below).

The structure of **4** is very similar to that of **3** but features one SiMe$_3$ (Si(1)) oriented "up" and two "down". However, in this case the angle subtended at C(17) (136.35(16)°, associated with the "up" SiMe$_3$) is indistinguishable from that at C(25) for one of the "down" SiMe$_3$ groups, and so it is probably unsafe to advance a simple explanation of the trends in M−CH$_2$−SiMe$_3$ angles in the compounds reported herein. The average Y−CH$_2$−SiMe$_3$ angle in **4** (132.9°) is rather similar to that in **3** (130.8°) and also in Evans' 6-coordinate Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$[33] (average 134.6°) and Okuda's 7-coordinate Y(CH$_2$SiMe$_3$)$_3$(12-crown-4)[11] (average 129.2°). These last two compounds (being the only two previously reported structurally authenticated tris((trimethylsilyl)methyl)yttrium complexes) have average Y−CH$_2$ distances of 2.427 and 2.417 Å, respectively, which are comparable to that of **4** (average 2.420 Å).

As for the Me$_3$[9]ane systems **1** and **2**, the combustion analyses for crystallographically authenticated **3** and **4** were reproducibly poor (note, however, that the trichlorides **5**−**8** did not exhibit this problem). To gain further support for the authenticity of these compounds, the alcoholysis reaction of **3** with ArOH (3 equiv; Ar = 2,6-C$_6$H$_3$Me$_2$) was carried out to form analytically pure Sc{HC(Me$_2$pz)$_3$}(OAr)$_3$ (**9**) in 81% isolated yield (eq 2).



(2)

When it was followed on an NMR tube scale (CD$_2$Cl$_2$), the reaction was quantitative and the sole side product was SiMe$_4$. The room-temperature ^{1}H and ^{13}C NMR spectra of **9** showed broad resonances for the ortho and meta groups of the Ar substituent, consistent with restricted rotation about the Sc−OAr bonds. At −20 °C the fluxional process was frozen out and the spectra were consistent with the solid-state structure, as determined by X-ray crystallography (Figure 4, with selected bond distances and angles given in Table 4) showing, for example, two *o*-methyl group environments for the OAr ligands at δ 2.48 ppm ("down", away from the HC(Me$_2$pz)$_3$ ligand) and 1.19 ppm ("up"). The relatively high field shift of the "up" *o*-Me resonance is attributed to the shielding ring-current effects of nearby Me$_2$pz ligands.

In the solid state, molecules of **9** lie on crystallographic 3-fold rotation axes which render all three OAr (and also Me$_2$pz rings) strictly equivalent. The Sc−N distance of 2.3543(19) Å is significantly shorter than the average value of 2.420 Å for Sc{HC(Me$_2$pz)$_3$}(CH$_2$SiMe$_3$)$_3$ (**3**), reflecting the reduced trans influence of OAr in comparison with CH$_2$SiMe$_3$. The Sc−O distance of

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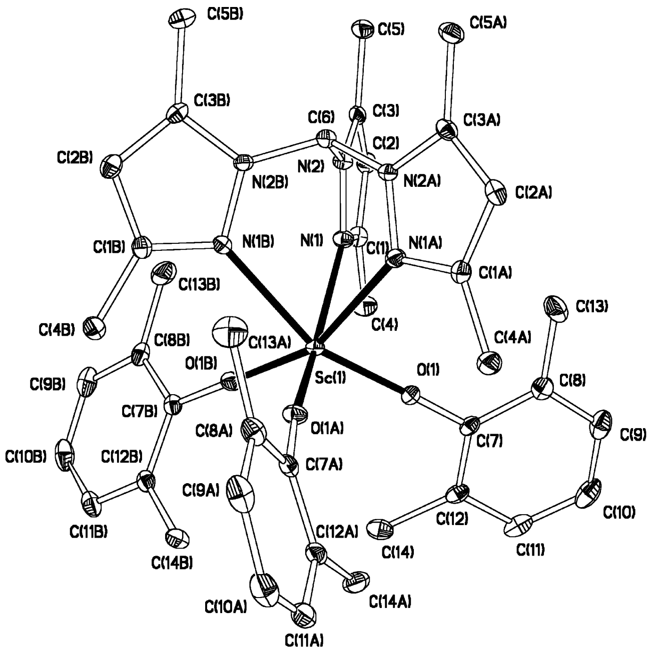

Figure 4. Displacement ellipsoid plot (25% probability) of $Sc\{MeSi(Me_2pz)_3\}(OAr)_3$ (**9**). H atoms and benzene molecules of crystallization are omitted for clarity. Atoms carrying the suffixes A and B are related to their counterparts by the symmetry operators $-y, x - y + 1, z$ and $-x + y - 1, -x, z$, respectively.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Sc\{MeSi(Me_2Pz)_3\}(OAr)_3$ (9)[a]

Sc(1)−O(1)	1.9615(16)	Sc(1)−N(1)	2.3543(19)
N(1)−Sc(1)−N(1A)	75.20(7)	Sc(1)−N(1)−N(2)	123.41(13)
O(1)−Sc(1)−N(1)	85.92(7)	Sc(1)−N(1)−C(1)	131.84(16)
O(1)−Sc(1)−O(1A)	103.74(6)	Sc(1)−O(1)−C(7)	174.41(17)

[a] Atoms carrying the suffix A are related to their counterparts by the symmetry operator $-y, x - y + 1, z$.

1.9615(16) Å is within known ranges for such linkages (range, 1.853−2.149; average 1.975 Å for eight examples).[24,25]

We also attempted to prepare analogous tris((trimethylsilyl)methyl) compounds using the homologous silicon-capped ligand $MeSi(Me_2pz)_3$ in reaction with $M(CH_2SiMe_3)_3(THF)_2$. There have been only three reports of complexes of this ligand to date, and none from group 3.[23,34,35] Surprisingly, these reactions gave rather complicated mixtures on both the preparative and NMR tube scales. However, the trichloride derivatives $M\{MeSi(Me_2pz)_3\}Cl_3$ (M = Sc (**10**), Y (**11**)) could readily be prepared in 79 and 54% isolated yields, respectively (eq 1), and, being the first group 3 complexes of this ligand, are included here for completeness. Attempted alkylations of these compounds with $LiCH_2SiMe_3$ have so far been inconclusive.

Diffraction-quality crystals containing two independent molecules of **11** per asymmetric unit (together with two CH_2Cl_2 molecules of crystallization) were grown from a dichloromethane solution. There are no substantial differences between the two molecules, and the structure of one of them is shown in Figure 5. Selected bond lengths and angles for both molecules are listed in Table 5. Compound **11** possesses an approximately octahedral yttrium center with average Y−N and Y−Cl distances of 2.464 and 2.568 Å, respectively, which are within the known ranges. However, a more detailed comparison with literature data is limited by the paucity of relevant systems. Just one structure containing a six-coordinate "YN_3Cl_3" core has been reported, this being a very poor quality determination (e.g. $R = 0.139$) of the tris(pyrazolyl)hydroborate-supported anion $[Y\{HB(Me_2pz)_3\}Cl_3]^-$, which has average Y−N and Y−Cl distances of 2.434 and 2.572 Å, respectively.[36] Only one paper describing structures of tris(pyrazolyl)silane complexes has appeared, this being for the M(0), d^6 compounds $M\{MeSi(Me_2pz)_3\}(CO)_3$ (M = Cr, Mo, W).[35]

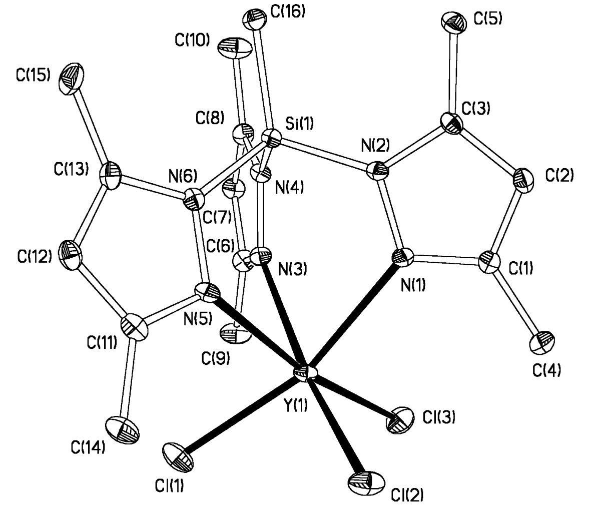

Figure 5. Displacement ellipsoid plot (25% probability) of one of the two crystallographically independent molecules of $Y\{MeSi(Me_2pz)_3\}Cl_3$ (**11**). H atoms and dichloromethane molecule of crystallization are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $Y\{MeSi(Me_2Pz)_3\}Cl_3$ (11)

Y(1)−Cl(1)	2.5527(10)	[2.5768(9)]
Y(1)−Cl(2)	2.5782(10)	[2.5775(10)]
Y(1)−Cl(3)	2.5678(10)	[2.5528(10)]
Y(1)−N(1)	2.454(3)	[2.448(3)]
Y(1)−N(3)	2.466(3)	[2.481(3)]
Y(1)−N(5)	2.488(3)	[2.447(3)]
Cl(1)−Y(1)−Cl(2)	97.68(4)	[96.64(3)]
Cl(1)−Y(1)−Cl(3)	98.13(4)	[100.67(3)]
Cl(2)−Y(1)−Cl(3)	95.93(4)	[103.16(4)]
Cl(1)−Y(1)−N(1)	163.75(7)	[168.27(7)]
Cl(2)−Y(1)−N(1)	90.32(7)	[90.74(7)]
Cl(3)−Y(1)−N(1)	95.06(7)	[86.42(7)]
Cl(1)−Y(1)−N(3)	91.67(7)	[90.71(7)]
Cl(2)−Y(1)−N(3)	166.34(7)	[167.65(7)]
Cl(3)−Y(1)−N(3)	92.56(7)	[85.11(7)]
N(1)−Y(1)−N(3)	78.26(10)	[80.52(9)]
Cl(1)−Y(1)−N(5)	87.53(7)	[92.02(7)]
Cl(2)−Y(1)−N(5)	92.10(7)	[92.36(7)]
Cl(3)−Y(1)−N(5)	169.45(7)	[158.53(7)]
N(1)−Y(1)−N(5)	78.02(9)	[78.53(9)]
N(3)−Y(1)−N(5)	78.32(10)	[77.42(9)]

Compounds with $Me_3[6]aneN_3$ Ligands. 1,3,5-Triazacyclohexane ligands have smaller ring sizes than their $R_3[9]aneN_3$ homologues, and their coordination

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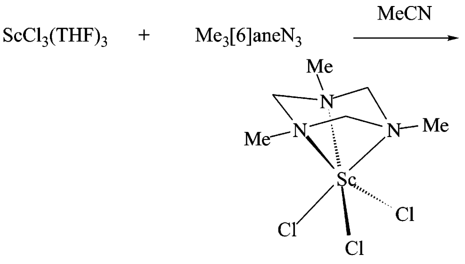
chemistry in general is less extensively developed in comparison (although in general their syntheses are much more straightforward and the scope for easy variation of the N substituents potentially limitless[37]). Recently, Köhn and co-workers have shown how R_3[6]ane-supported chromium complexes can be highly effective mimics of the Phillips-type catalysts,[38] and so we have chosen to target group 3 tris(alkyl) complexes of $Me_3[6]aneN_3$. Only one report of rare-earth complexes supported by triazacyclohexane ligands has so far appeared,[39] these being the recently described praseodynium species $Pr(Me_3[6]aneN_3)_2(OTf)_3$ and $[Pr_2(Et_3[6]aneN_3)_2(OTf)_4(\mu\text{-}OTf)_3]^-$.

As in the previous syntheses (Scheme 1), reaction of $Me_3[6]aneN_3$ with $M(CH_2SiMe_3)_3(THF)_2$ afforded the corresponding products $M(Me_3[6]aneN_3)(CH_2SiMe_3)_3$ (M = Sc (**12**), Y (**13**)) as pale yellow solids in ca. 70−80% isolated yield. The reactions were again quantitative on the NMR tube scale in C_6D_6. The NMR spectra suggest C_{3v}-symmetric products, and the *fac*-κ^3 coordination of the $Me_3[6]aneN_3$ is indicated by the presence of a pair of mutually coupled doublets for the ring methylene protons in the ^{1}H NMR spectra. We have not been able to obtain diffraction crystals of **12** and **13**, but their structures are supported by that of the trichloride $Sc(Me_3[6]aneN_3)Cl_3$ (**14**), which was prepared in 66% isolated yield according to eq 3. Reaction of **14** with $LiCH_2SiMe_3$ (3 equiv) in C_6D_6 on an NMR tube scale afforded complete conversion to **12**. Attempts to prepare an yttrium analogue of **14** have so far been unsuccessful.



14

(3)

The molecular structure of **14** is shown in Figure 6, and selected bond distances and angles are listed in Table 6. The molecules lie across crystallographic mirror planes and contain an octahedral Sc center and *fac*-coordinated $Me_3[6]aneN_3$ ligand. Compound **14** is analogous to Bercaw's $Sc(Me_3[9]aneN_3)Cl_3$, and key parameters between the two can be compared: average Sc−Cl = 2.378 (**14**) and 2.406 Å; average Sc−N = 2.332 (**14**) and 2.337 Å; average N−Sc−N = 59.5 (**14**) and 74.9°. The longer Sc−Cl distance in $Sc(Me_3[9]aneN_3)Cl_3$ is attributed to the fact that the N donors of the macrocycle lie more strictly trans to the Sc−Cl bonds (average $N{-}Sc{-}Cl_{trans}$ = 163.7°) than in **14** (average $N{-}Sc{-}Cl_{trans}$ = 145.5°) and so exert a larger trans influence. The smaller average N−Sc−N angle in **14** is because of the smaller ring size of $Me_3[6]aneN_3$. Analogous trends are seen in the homologous pair[40,41] $Fe(Me_3[n]aneN_3)Cl_3$ ($n = 6, 9$): average Fe−Cl = 2.249 ($n = 6$) and 2.303 Å; average Fe−N = 2.254 ($n = 6$) and 2.246 Å; average N−Fe−N = 61.0 ($n = 6$) and 78.0°.

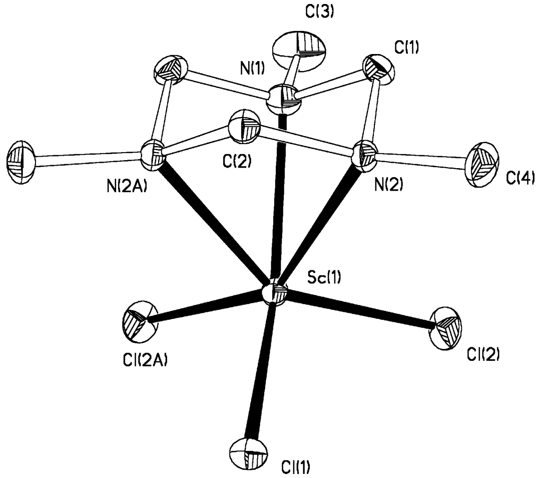


Figure 6. Displacement ellipsoid plot (30% probability) of $Sc(Me_3[6]aneN_3)Cl_3$ (**14**). H atoms are omitted for clarity. Atoms carrying the suffix A are related to their couterparts by the symmetry operator x, $^3/_2 - y$, z.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $Sc(Me_3[6]aneN_3)Cl_3$ (14)[a]

Sc(1)−Cl(1)	2.3829(5)	Sc(1)−N(1)	2.3306(15)
Sc(1)−Cl(2)	2.3727(3)	Sc(1)−N(2)	2.3331(9)
Cl(1)−Sc(1)−Cl(2)	105.721(14)	Cl(2)−Sc(1)−N(2)	92.97(2)
Cl(2)−Sc(1)−Cl(2A)	106.67(2)	Cl(2)−Sc(1)−N(2A)	147.95(3)
Cl(1)−Sc(1)−N(1)	147.05(4)	N(1)−Sc(1)−N(2)	59.46(4)
Cl(2)−Sc(1)−N(1)	93.56(3)	N(2)−Sc(1)−N(2A)	59.47(5)
Cl(1)−Sc(1)−N(2)	92.48(3)		

[a] Atoms carrying the suffix A are related to their counterparts by the symmetry operator x, $^3/_2 - y$, z.

Competitive Binding Studies. Having prepared the new families of organo-group 3 complexes (i.e. the $HC(Me_2pz)_3$- and $Me_3[6]aneN_3$-supported systems), as well as the homologous compounds with $Me_3[9]aneN_3$, it was of interest to compare the experimental relative binding preferences of the $M(CH_2SiMe_3)_3$ fragments for the various ligands. Such factors may be relevant in the design of catalytic systems based on *fac*-N_3 ligands. We probed the binding preferences through a series of competitive NMR tube scale reactions in C_6D_6 in which each $M(fac\text{-}L_3)(CH_2SiMe_3)_3$ complex in Scheme 1 was treated with 1 equiv of another of the *fac*-L_3 donor ligands. The results for the yttrium and scandium systems are described in turn.

For the yttrium compounds **2**, **4**, and **13** the ligand binding preference is $Me_3[9]aneN_3 > HC(Me_2pz)_3 > Me_3[6]aneN_3$, with a ligand higher in the binding order being able to quantitatively displace a ligand from lower down the order (reaction times at room temperature were in the range 1−24 h). The binding preference of $Me_3[9]aneN_3$ over $Me_3[6]aneN_3$ may be rationalized in terms of coordination bite angle, with the larger ligand matching the metal better (Köhn has described the metal−ligand orbital directional mismatch typically associated with R_3[6]ane systems[38]). It is also consistent with our previous work on the titanium imido systems

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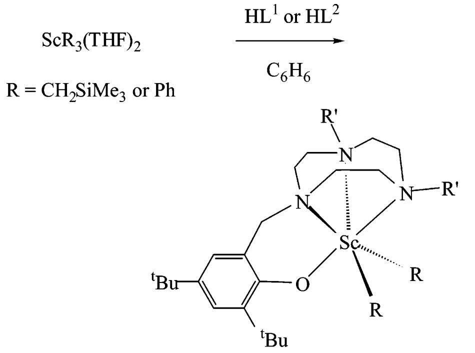
$Ti(Me_3[n]aneN_3)(N^tBu)Cl_2$ ($n = 6, 9$),[31,42] in which $Me_3[9]aneN_3$ quantitatively displaced coordinated $Me_3[6]aneN_3$. The binding preference of $Me_3[9]aneN_3$ over $HC(Me_2pz)_3$ (which both appear to have a similar match at the metal in terms of bite angle) may be attributed in general terms to the "macrocylic effect".[43] This expression embraces a number of contributing factors, enthalpic and entropic, and further studies would be needed to unravel the various contributions.

The scandium systems **1**, **3**, and **12** show a different binding order among the N_3 donor ligands. In this case the preference is $Me_3[9]aneN_3 > Me_3[6]aneN_3 > HC(Me_2pz)_3$, and again a ligand higher in the binding order is able to displace quantitatively a ligand from lower down the order. The relative positions of $Me_3[9]aneN_3$ and $Me_3[6]aneN_3$ can be rationalized as above, on the basis of ligand ring size. However, it was surprising that $Me_3[6]aneN_3$ would, over the course of several hours at room temperature, quantitatively displace $HC(Me_2pz)_3$ from **3** to form **12**. It appears that there may be a delicate balance between bite angle and steric and (for $Me_3[6]aneN_3$) macrocyclic/preorganization effects for the two ligands $Me_3[6]aneN_3$ and $HC(Me_2pz)_3$ in the scandium and yttrium systems. We note in this context that Piers has reported[27] that the related tris(pyrazolyl)hydroborate scandium complexes are prone to *fac*-N_3 ligand displacement (albeit with anionic alkyl reagents). Bianconi has reported that this is not apparently the case for congeneric yttrium systems.[29] However, Carpentier has recently reported (in contrast to Bianconi's findings) that reaction of $Y\{HB(Me_2pz)_3\}Cl_2(THF)$ with a range of lithium or potassium salts (including $LiCH_2SiMe_3$) led essentially to the formation of $M[HB(Me_2pz)_3]$ (M = Li, K).[44] It appears that the stability of *fac*-N_3 donor ligands toward displacement from group 3 metals may be sensitive to a number of subtle experimental factors.

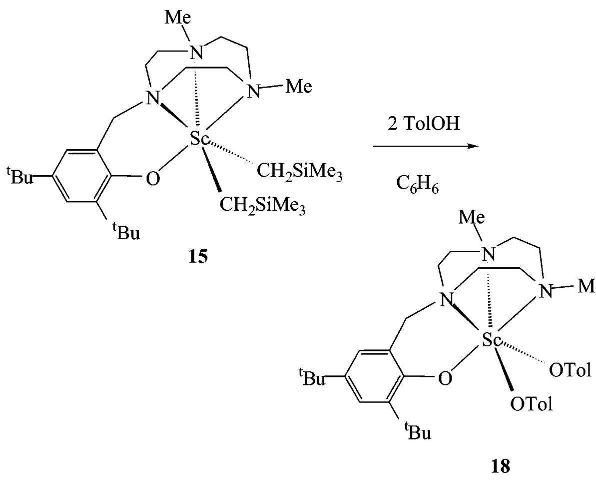
Organoscandium Complexes of Pendant Arm Functionalized Triazacyclononanes. Although pendant arm functionalized macrocycles have a rich and extensive coordination chemistry (e.g., in the areas of selective ion binding, sensors, and bioinorganic chemistry),[43,45–47] they have only recently started to be employed in organometallic and related chemistry. As mentioned above, Hessen has described catalytic and stoichiometric chemistry arising from triazacyclononane−amide group 3 complexes **II** (Chart 2). Recently Arnold[48] and Peters[49] have reported cyclopentadienyl-functionalized triazacyclonane ligands, and Meyer has used a series of uranium complexes of tris(hydroxybenzyl)-substituted triazacyclononanes to considerable effect in the small-molecule binding chemistry of uranium.[50,51] We have recently reported[52,53] work on neutral and cationic organoaluminum and -indium complexes of phenoxy- and alkoxy-functionalized triazacyclononane ligands, including compounds derived from the previously reported[52,54] protio ligands HL^1 and HL^2 (Chart 1). Following Hessen's work on the triazacyclononane−amide systems **II**, we were interested to prepare group 3 compounds based on triazacyclononane−phenoxide ligands.

Reaction of the protio ligands HL^1 and HL^2 with $Sc(CH_2SiMe_3)_3(THF)_2$ in cold benzene afforded the compounds $Sc(L^1)(CH_2SiMe_3)_2$ (**15**) and $Sc(L^2)(CH_2SiMe_3)_2$ (**16**) in ca. 50−70% isolated yields (eq 4). The corresponding reaction of HL^1 with $ScPh_3(THF)_2$ gave $Sc(L^1)Ph_2$ (**17**) in 38% isolated yield, but reaction of HL^1 with $Y(CH_2SiMe_3)_3(THF)_2$ did not give a clean product on either the preparative or NMR tube scale (C_6D_6). Use of the more sterically demanding protio ligand HL^2 (N-isopropyl-substituted homologue) appeared to give an yttrium congener of **16**, but the data for this compound were somewhat ambiguous. Unlike the rather simple NMR spectra of C_{3v}-symmetric $M(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (**1** and **2**), those of **15**−**18** show (as expected) no molecular symmetry and are consistent with the structures proposed in eq 4, in which a deprotonated hydroxybenzyl arm is coordinated to the metal center. Furthermore, compounds **15** and **16** showed the appropriate molecular ions (correct *m*/*z* and isotope distribution pattern) in their EI mass spectra. We were unable to grow diffraction-quality crystals of the organometallic compounds. However, the protonolysis reaction of **15** with TolOH (2 equiv, Tol = *p*-tolyl) cleanly afforded $SiMe_4$ (identified in an NMR tube scale reaction) and $Sc(L^1)(OTol)_2$ (**18**, eq 5), which has been



(4)

R' = Me, R = CH_2SiMe_3 (**15**) or Ph (**17**)
R' = ^iPr, R = CH_2SiMe_3, (**16**)



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(5)

18

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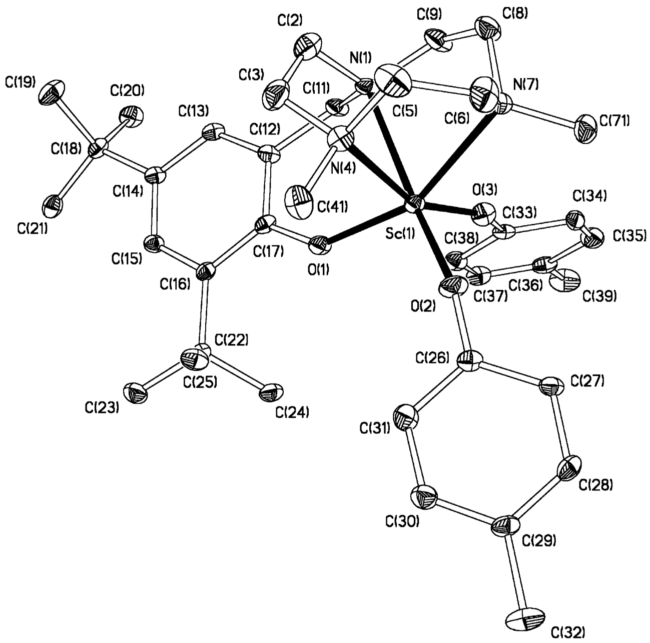

Figure 7. Displacement ellipsoid plot (20% probability) of Sc(L^2)(OTol)$_2$ (**18**). H atoms and benzene molecule of crystallization are omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Sc(L^2)(OTol)$_2$ (18)

Sc(1)−N(1)	2.367(5)	Sc(1)−O(1)	1.981(4)
Sc(1)−N(4)	2.411(6)	Sc(1)−O(2)	1.949(4)
Sc(1)−N(7)	2.360(5)	Sc(1)−O(3)	1.963(5)
N(1)−Sc(1)−N(4)	73.3(2)	O(1)−Sc(1)−O(2)	106.2(2)
N(1)−Sc(1)−N(7)	74.6(2)	N(1)−Sc(1)−O(3)	91.3(2)
N(4)−Sc(1)−N(7)	73.2(2)	N(4)−Sc(1)−O(3)	158.7(2)
N(1)−Sc(1)−O(1)	82.9(2)	N(7)−Sc(1)−O(3)	88.7(2)
N(4)−Sc(1)−O(1)	92.8(2)	O(1)−Sc(1)−O(3)	100.0(2)
N(7)−Sc(1)−O(1)	156.1(2)	O(2)−Sc(1)−O(3)	102.8(2)
N(1)−Sc(1)−O(2)	161.3(2)	Sc(1)−O(1)−C(17)	141.1(4)
N(4)−Sc(1)−O(2)	89.8(2)	Sc(1)−O(2)−C(26)	162.5(4)
N(7)−Sc(1)−O(2)	93.4(2)	Sc(1)−O(3)−C(33)	158.5(4)

crystallographically characterized (see below). The NMR spectra of **18** are analogous to those of **15**, except that the resonances for the two inequivalent CH_2SiMe_3 groups are replaced by resonances for two OTol ligands.

The molecular structure of **18** is illustrated in Figure 7, and selected distances and angles are listed in Table 7. Molecules of **18** possess the expected C_1 symmetry in the solid state and contain approximately octahedral scandium centers. The triazacyclononane ligand moiety is coordinated facially, and the OTol ligands are in different environments, one being trans to the macrocycle nitrogen N(1) bearing the phenoxide pendant arm of the macrocycle ligand and the other being trans to an NMe. The Sc−O bond lengths (average 1.964 Å) are within the known ranges[24,25] and are identical within error to that in **9** (1.9615(16) Å). The Sc−N bond lengths (average 2.379 Å) are within previous ranges for triazacyclononane−scandium systems[8,46] with aryloxy or halide coligands (range 2.328−2.412, average 2.356 Å for three examples) but are clearly shorter than those in **1** (average 2.463). The angles subtended at the nonchelating aryloxide oxygen atoms are similar at 158.5(4) and 162.5(4)°, whereas the angle subtended at O(1) (part of the pendant arm) is more acute at 141.1(4)°, due to the constraining nature of the pendant arm.

Conclusions

In this paper we have described effective synthetic routes to the first group 3 organometallic and coordination compounds containing the tris(pyrazolyl)methane and triazacyclohexane ligands. Together with the new triazacyclononane analogues M(Me_3[9]aneN_3)(CH_2SiMe_3)$_3$ (**1** and **2**) these tris((trimethylsilyl)methyl) compounds form the basis for a comprehensive study of the stoichiometric and catalytic chemistry of cationic alkyl and related complexes derived from the new classes of compound as a function of macrocycle ring size (R_3[6]aneN_3 vs R_3[9]aneN_3 systems), topology (the podand-like HC(Me_2pz)$_3$ vs macrocyclic R_3[9]aneN_3), and face-capping ligand substitution in general. Such studies are underway and will be reported in due course, together with investigations of related M(*fac*-L_3)R_3 (R = alkyl) complexes of the lanthanides. The syntheses and structures of **15**−**18** are analogous to those of Hessen's triazacyclononane−amide systems **II**. Reports on the chemistry of these new complexes will also be described at a later date.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Protio solvents were predried over activated 4 Å molecular sieves, purged with N_2, and dried either by refluxing over an appropriate alkali metal or alloy or (HPLC grade, nonstabilized as appropriate) by passage through a column of activated alumina.[55] Deuterio 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, $^{13}C\{^1H\}$ and ^{13}C NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional $^1H-{}^1H$ and $^{13}C-{}^1H$ NMR experiments. ^1H and ^{13}C spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as KBr pellets or 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 the Chemistry Laboratory Oxford and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory, by Mikroanalytisches Labor Pascher, Germany, or by the Elemental Analysis Service, London Metropolitan Univeristy.

Literature Preparations and Other Starting Materials. The compounds M(CH_2SiMe_3)$_3$(THF)$_2$ (M = Sc, Y),[19] ScPh_3(THF)$_2$,[56] Me_3[9]aneN_3,[20] Me_3[6]aneN_3,[21] HC(Me_2pz)$_3$ and HC(Rpz)$_3$ (R = ^{i}Pr, Ph, ^{t}Bu),[22] MeSi(Me_2pz)$_3$,[23] 1-(3,5-di-*tert*-butyl-

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2-hydroxybenzyl)-4,7-dimethyl-triazacyclononane (HL^1),[52] and 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyltriazacyclononane (HL^2)[54] were prepared according to published methods. All other compounds and reagents were purchased and used without further purification.

$Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (1). $Sc(CH_2SiMe_3)_3(THF)_2$ (152 mg, 0.34 mmol) was dissolved in cold (7 °C) benzene (15 mL) and stirred for the dropwise addition of a solution of $Me_3[9]aneN_3$ (58 mg, 0.34 mmol) in benzene (15 mL). The mixture was warmed to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure to afford **1** as a pale yellow solid. Yield: 94 mg (59%). Diffraction-quality crystals were grown from slow diffusion of pentane into a saturated toluene solution. ^1H NMR (C_6D_6, 500.0 MHz, 293 K): 2.32 (9 H, s, NMe), 2.26 (6 H, m, NCH_2), 1.56 (6 H, m, NCH_2), 0.42 (27 H, s, $SiMe_3$), −0.23 (6 H, s, $ScCH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 53.6 (NCH_2CH_2N), 48.1 (NMe), 2.5 ($SiMe_3$); CH_2SiMe_3 not observed. IR (KBr pellet): 2940 (s), 2894 (s), 2860 (s), 2822 (m), 1494 (m), 1464 (s), 1424 (w), 1384 (w), 1366 (m), 1300 (m), 1246 (s), 1234 (s), 1206 (w), 1154 (w), 1126 (w), 1080 (m), 1068 (m), 1008 (s), 876 (s), 852 (s), 818 (s), 774 (w), 748 (m), 720 (m), 666 (m), 604 (w), 578 (w), 450 (m), 420 (w), 402 (w) cm^{-1}. FI-HRMS for $[Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_2]^+$: found (calcd for $C_{17}H_{43}N_3ScSi_2$) *m/z* 390.2561 (390.2555). Anal. Found (calcd for $C_{21}H_{54}N_3ScSi_3$): C, 50.3 (52.8); H, 11.2 (11.4); N, 8.5 (8.8).

$Y(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (2). $Y(CH_2SiMe_3)_3(THF)_2$ (290 mg, 0.587 mmol) was dissolved in cold (7 °C) benzene (15 mL) and stirred for the dropwise addition of a solution of $Me_3[9]aneN_3$ (101 mg, 0.587 mmol) in benzene (15 mL). The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure to afford **2** as a white solid. Yield: 207 mg (68%). ^1H NMR (C_6D_6, 500.0 MHz, 293 K): 2.30 (9 H, s, NMe), 2.20 (6 H, m, NCH_2), 1.56 (6 H, m, NCH_2), 0.41 (27 H, s, $SiMe_3$), −0.67 (6 H, d, YCH_2, $J_{HY} = 2.6$ Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 54.4 (NCH_2), 47.8 (NMe), 35.3 (YCH_2, $J_{CY} = 36$ Hz), 4.9 ($SiMe_3$) ppm. IR (KBr pellet): 2822 (s), 1492 (m), 1464 (s), 1366 (m), 1302 (w), 1246 (m), 1234 (m), 1208 (w), 1154 (w), 1128 (w), 1068 (m), 1008 (s), 858 (s), 818 (m), 744 (m), 716 (m), 668 (m), 572 (w), 572 (w), 424 (w), 408 (w) cm^{-1}. Anal. Found (calcd for $C_{21}H_{54}N_3Si_3Y$): C, 40.4 (48.3); H, 8.4 (10.4); N, 8.5 (8.1).

$Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (3). To a yellow solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.100 g, 0.24 mmol) in benzene (10 mL) was added a solution of $HC(Me_2pz)_3$ (0.070 g, 0.24 mmol) in benzene (5 mL) to give an orange solution. After the mixture was stirred at room temperature for 4 h, the volatiles were removed under reduced pressure to give an orange solid, which was washed with benzene (2 × 10 mL) to afford **3** as a pale orange solid. Yield: 0.09 g (65%). Diffraction-quality crystals were grown from a toluene−pentane mixture. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): 7.03 (1H, s, $HC(Me_2pz)_3$), 5.21 (3H, s, 4-$N_2C_3Me_2H$), 2.66 (9H, s, 5-$N_2C_3Me_2H$), 1.35 (9H, s, 3-$N_2C_3Me_2H$), 0.60 (6H, s, $ScCH_2$), 0.27 (27H, s, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 500.0 MHz, 298 K): 154.2 (5-$N_2C_3Me_2H$), 137.7 (3-$N_2C_3Me_2H$), 107.8 (4-$N_2C_3Me_2H$), 67.5 ($HC(Me_2pz)_3$), 38.2 ($ScCH_2$), 16.3 (5-$N_2C_3Me_2H$), 10.2 (3-$N_2C_3Me_2H$), 4.8 ($SiMe_3$) ppm. IR (NaCl plates, Nujol): 1562 (w), 1412 (w), 1321 (w), 1261 (s), 1093 (s), 1021 (s), 863 (w), 863 (w), 801 (s), 701 (w) cm^{-1}. Anal. Found (calcd for $C_{28}H_{55}N_6ScSi_3$): C, 50.3 (55.6); H, 7.7 (9.2); N, 13.7 (13.9).

$Y\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (4). To a colorless solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.370 g, 0.74 mmol) in benzene (10 mL) was added a solution of $HC(Me_2pz)_3$ (0.220 g, 0.74 mmol) in benzene (10 mL). The resulting dark brown solution was allowed to stir at room temperature for 1 h. The volume of the solution was reduced to 10 mL and hexane (30 mL) was added resulting in the formation of a brown precipitate which was filtered. The resulting solid was re-extracted into benzene (10 mL) and addition of hexane (20 mL) afforded **4** as a light brown solid. Yield: 0.28 g (58%). Diffraction-quality crystals were grown from a saturated toluene solution. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): 6.99 (1H, s, $HC(Me_2pz)_3$), 5.18 (3H, s, 4-$N_2C_3Me_2H$), 2.61 (9H, s, 3-$N_2C_3Me_2H$), 1.32 (9H, s, 5-$N_2C_3Me_2H$), 0.33 (27H, s, $SiMe_3$), −0.02 (6H, d, $J_{HY} = 2.8$ Hz, CH_2SiMe_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, 298 K): 154.3 (3-$N_2C_3Me_2H$), 138.5 (5-$N_2C_3Me_2H$), 107.6 (3-$N_2C_3Me_2H$), 67.9 ($HC(Me_2pz)_3$), 32.4 (YCH_2, $J_{CY} = 33$ Hz), 15.7 (3-$N_2C_3Me_2H$), 10.2 (5-$N_2C_3Me_2H$), 5.0 ($SiMe_3$). IR (NaCl plates, Nujol): 2360 (m), 2342 (w), 1959 (w), 1618 (w), 1562 (w), 1459 (m), 1413 (w), 1261 (s), 1093 (s), 1020 (s), 863 (w), 800 (s), 705 (w), 669 (w) cm^{-1}. Anal. Found (calcd for $C_{28}H_{55}N_6Si_3Y$): C, 49.9 (51.8); H, 7.9 (8.5); N, 12.3 (13.0).

$Sc\{HC(Me_2pz)_3\}Cl_3$ (5). A suspension of $ScCl_3$ (0.057 g, 0.38 mmol) in THF (10 mL) was refluxed for 10 min to give a colorless solution, which was cooled. To this was added a yellow solution of $HC(Me_2pz)_3$ (0.110 g, 0.38 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 4 h. The resultant white solid was filtered away from the colorless solution and dried to afford **5**. Yield: 0.14 g (77%). ^1H NMR (CD_2Cl_2, 500.0 MHz, 298 K): 7.91 (1H, s, $HC(Me_2pz)_3$), 6.09 (3H, s, 4-$N_2C_3Me_2H$), 2.72 (9H, s, 5-$N_2C_3Me_2H$), 2.54 (9H, s, 3-$N_2C_3Me_2H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.5 MHz, 298 K): 158.6 (5-$N_2C_3Me_2H$), 142.2 (3-$N_2C_3Me_2H$), 111.0 (4-$N_2C_3Me_2H$), 70.2 ($HC(Me_2pz)_3$) 17.5 (5-$N_2C_3Me_2H$), 13.3 (3-$N_2C_3Me_2H$). IR (NaCl plates, Nujol): 1619 (w), 1563 (m), 1413 (w), 1305 (w), 1261 (m), 1065 (m), 1044 (m), 910 (w), 862 (w), 706 (w), 407 (w) cm^{-1}. Anal. Found (calcd for $C_{16}H_{22}N_6ScCl_3{\cdot}1.1THF$): C, 46.2 (46.3); N, 15.7 (15.9); H, 6.4 (5.9). EI^+ MS: *m/z* 413 $[M - Cl]^+$, 60%.

$Y\{HC(Me_2pz)_3\}Cl_3$ (6). To a suspension of YCl_3 (0.048 g, 0.25 mmol) in THF (10 mL) was added a solution of $HC(Me_2pz)_3$ (0.080 g, 0.25 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 16 h, resulting in a white precipitate and yellow supernatant. Filtration afforded $[YCl_3\{HC(Me_2pz)_3\}]$ as a white solid. Yield: 0.09 g (74%). ^1H NMR (CD_2Cl_2, 500.0 MHz, 298 K): 7.91 (1H, s, $HC(Me_2pz)_3$), 6.08 (3H, s, 4-$N_2C_3Me_2H$), 2.65 (9H, s, 3-$N_2C_3Me_2H$), 2.52 (9H, s, 5-$N_2C_3Me_2H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, 298 K): 156.1 (3-$N_2C_3Me_2H$), 140.9 (5-$N_2C_3Me_2H$), 108.7 (4-$N_2C_3Me_2H$), 67.9 ($HC(Me_2pz)_3$), 14.0 (3-$N_2C_3Me_2H$), 10.5 (5-$N_2C_3Me_2H$). IR (NaCl plates, Nujol): 1562 (m), 1413 (m), 1304 (m), 1261 (m), 1064 (m), 1042 (m), 905 (m), 861 (m), 801 (m), 706 (m) cm^{-1}. Anal. Found (calcd for $C_{16}H_{22}Cl_3N_6Y{\cdot}1.1THF$): C, 42.7 (42.8); N, 14.8 (14.7); H, 5.7 (5.4). EI^+ MS: *m/z* 456 $[M - Cl - H]^+$, 70%; 457 $[M - Cl]^+$, 50%.

$Sc\{HC(^iPrpz)_3\}Cl_3$ (7). A suspension of $ScCl_3(THF)_3$ (0.100 g, 0.272 mmol) in THF (20 mL) was refluxed for 30 min to give a colorless solution, which was then cooled. To this was added a 0.15 M solution of $HC(^iPrpz)_3$ (0.272 mmol) in benzene. The reaction mixture was stirred at room temperature for ca. 12 h, during which time a white precipitate formed. The reaction volume was then reduced to ca. 10 mL, and pentane (10 mL) was added. The precipitate was isolated and dried to afford **7** as a white solid. Yield: 0.085 g (64%). ^1H NMR (C_5D_5N, 300.0 MHz, 298 K): 9.122 (1H, s, $HC(3\text{-}^iPrpz)_3$), 7.915 (3H, d, $^3J = 2.6$ Hz, $HC(NCHCHC(^iPr)N)_3$), 6.275 (3H, d, $^3J = 2.4$ Hz, $HC(NCHCHC(^iPr)N)_3$), 2.95 (3H, sept., $^3J = 3.1$ Hz, Me_2CH), 1.18 (18H, d, $^3J = 7.0$ Hz, $HCMe_2$). ^{13}C NMR (C_5D_5N, 75 MHz, 298 K): 161.2 ($HC(NCHCHC(^iPr)N)_3$), 130.9 ($HC(NCHCHC(^iPr)N)_3$), 104.79 ($HC(NCHCHC(^iPr)N)_3$), 84.04 ($HC(3\text{-}^iPrpz)_3$), 28.53 (Me_2CH), 22.91 (Me_2CH). IR (NaCl plates, Nujol): 1529 (w), 1461 (m), 1377 (m), 1243 (m), 1018.8 (m), 856 (w), 801 (m) cm^{-1}. Anal. Found (calcd for $C_{19}H_{28}N_6Cl_3Sc$): C, 46.6 (46.4); N, 17.1 (17.1); H, 5.8 (5.7).

$Y\{HC(^iPrpz)_3\}Cl_3$ (8). A suspension of $YCl_3(THF)_3$ (0.500 g, 1.22 mmol) in THF (50 mL) was refluxed for 30 min to give a colorless solution, which was then cooled. To this was added

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a 0.15 M solution of HC(^{i}Prpz)$_3$ in benzene (1.22 mmol), and the resulting mixture was stirred at 40 °C for 4 days to give a white precipitate. The reaction mixture was reduced in volume to ca. 20 mL, and pentane (25 mL) was added. The white precipitate was isolated by filtration and dried to afford **8** as a white solid. Yield: 0.490 g (75%). ^{1}H NMR (C$_5$D$_5$N, 500.0 MHz, 298 K): 9.10 (1H, s, *H*C(3-^{i}Prpz)$_3$), 7.91 (3H, d, ^3J = 2.3 Hz, HC(NC*H*CHC(^{i}Pr)N)$_3$), 6.27 (3H, d, ^3J = 2.7 Hz, HC(NCHC*H*C(^{i}Pr)N)$_3$), 2.93 (1H, sept, ^3J = 3.1 Hz, Me$_2$C*H*), 1.40 (18H, d, ^3J = 6.7 Hz, HC*Me*$_2$). ^{13}C NMR (C$_5$D$_5$N, 75 MHz, 298 K): 160.3 (HC(NCHCH*C*(^{i}Pr)N)$_3$), 130.0 (HC(N*C*HCHC(^{i}Pr)N)$_3$), 103.9 (HC(NCH*C*HC(^{i}Pr)N)$_3$), 83.2 (H*C*(3-^{i}Prpz)$_3$), 27.7 (Me$_2$*C*H), 22.0 (*Me*$_2$CH). IR (NaCl plates, Nujol): 1530 (m), 1460 (m), 1331 (w), 1240 (m), 1198 (w), 1083 (m), 1018 (m), 853 (w) cm^{-1}. Anal. Found (calcd for C$_{19}$H$_{28}$N$_6$Cl$_3$Y): C, 42.7 (42.6); N, 15.7 (15.7); H, 5.7 (5.3).

Sc{HC(Me$_2$pz)$_3$}(OAr)$_3$ (9). To a pale orange solution of **3** (0.110 g, 0.18 mmol) in THF (10 mL) was added a solution of 2,6-dimethylphenol (0.060 g, 0.53 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 2 h, and the volume was reduced to 5 mL. Pentane (15 mL) was added and a white solid formed. Filtration afforded **9** as a white solid. Yield: 0.10 g (81%). ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 253 K): 7.88 (1H, s, *H*C(Me$_2$pz)$_3$), 6.83 (2H, d, ^3J = 7.1 Hz, *m*-OC$_6$*H*$_3$Me$_2$ "down"), 6.63 (2H, d, ^3J = 7.1 Hz, *m*-OC$_6$*H*$_3$Me$_2$ "up"), 6.34 (1H, apparent t, apparent ^3J = 7.1 Hz, *p*-OC$_6$*H*$_3$Me$_2$), 5.87 (3H, s, 4-N$_2$C$_3$Me$_2$*H*), 2.54 (9H, s, 5-N$_2$C$_3$*Me*$_2$H), 2.48 (9H, s, OC$_6$H$_3$*Me*$_2$ "down"), 1.88 (9H, s, 3-N$_2$C$_3$*Me*$_2$H), 1.19 (9H, s, OC$_6$H$_3$*Me*$_2$ "up"). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, 253 K): 162.5 (*ipso*-OC$_6$H$_3$Me$_2$), 155.1 (3-N$_2$*C*$_3$Me$_2$H), 138.4 (5-N$_2$*C*$_3$Me$_2$H), 127.6 (*o*-O*C*$_6$H$_3$Me$_2$ "down"), 127.4 (*o*-O*C*$_6$H$_3$Me$_2$ "up"), 114.9 (*p*-O*C*$_6$H$_3$Me$_2$), 108.1 (4-N$_2$*C*$_3$Me$_2$H), 67.2 (H*C*(Me$_2$pz)$_3$), 18.4 (OC$_6$H$_3$*Me*$_2$ "down"), 16.3 (OC$_6$H$_3$*Me*$_2$ "up"), 12.9 (3-N$_2$C$_3$*Me*$_2$H), 11.0 (5-N$_2$C$_3$*Me*$_2$H). IR (NaCl plates, Nujol): 2852 (s), 2316 (w), 1590 (m), 1563 (m), 1378 (m), 1304 (m), 1260 (s), 1238 (w), 1092 (m), 1042 (w), 867 (w), 800 (m) cm^{-1}. Anal. Found (calcd for C$_{40}$H$_{49}$N$_6$O$_3$Sc): C, 68.0 (68.0); N, 11.8 (11.9); H, 6.9 (7.0). FI$^+$ MS: *m/z* 706 [M]$^+$, 10%.

Sc{MeSi(Me$_2$pz)$_3$}Cl$_3$ (10). To a slurry of ScCl$_3$(THF)$_3$ (0.100 g, 0.277 mmol, 1.0 equiv) in toluene (10 mL), a solution of MeSi(Me$_2$pz)$_3$ (0.089 g, 0.277 mmol, 1.0 equiv) in toluene (10 mL) was added. The reaction mixture was stirred at room temperature for ca. 15 h, during which time a white precipitate was formed. The white solid was isolated by filtration, washed with toluene, and dried to give **10** as a white solid. Yield: 106 mg (79%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 298 K): 6.11 (3H, s, 4-N$_2$C$_3$Me$_2$*H*), 2.85 (9H, s, 3- N$_2$C$_3$*Me*$_2$H), 2.44 (9H, s, 5-N$_2$C$_3$*Me*$_2$H), 1.65 (3H, s, *Me*Si(Me$_2$pz)$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz, 298 K): 161.98 (3-N$_2$*C*$_3$Me$_2$H), 149.36 (5-N$_2$*C*$_3$Me$_2$H), 113.00 (4-N$_2$*C*$_3$Me$_2$H), 16.89 (3-N$_2$C$_3$*Me*$_2$H), 14.70 (5-N$_2$C$_3$*Me*$_2$H), 1.30 (*Me*Si(Me$_2$pz)$_3$). IR (NaCl plates, Nujol): 3135 (w), 3098 (w), 1602 (w), 1567 (s), 1451 (s), 1276 (m), 1295 (s), 1035 (s), 985 (m), 803 (s), 739 (m) cm^{-1}. Anal. Found for C$_{16}$H$_{24}$Cl$_3$N$_6$ScSi·0.9C$_7$H$_8$: C, 47.5 (47.6); N, 14.7 (14.9); H, 5.6 (5.6).

Y{MeSi(Me$_2$pz)$_3$}Cl$_3$ (11). To a slurry of YCl$_3$(THF)$_3$ (0.100 g, 0.243 mmol, 1.0 equiv) in toluene (10 mL) was added a solution of MeSi(Me$_2$pz)$_3$ (0.080 g, 0.243 mmol, 1.0 equiv) in toluene (10 mL). The reaction mixture was stirred at room temperature for ca. 15 h, during which time a white precipitate was formed. The white solid was isolated by filtration, washed with toluene, and dried. A residual impurity was removed by sublimation to leave **11** as a white solid. Yield: 68 mg (54%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 298 K): 6.03 (3H, s, 4-N$_2$C$_3$Me$_2$*H*), 2.68 (9H, s, 3- N$_2$C$_3$*Me*$_2$H), 2.34 (9H, s, 5-N$_2$C$_3$*Me*$_2$H), 1.53 (3H, s, *Me*Si(Me$_2$pz)$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz, 298 K): 161.46 (3-N$_2$*C*$_3$Me$_2$H), 150.39 (5-N$_2$*C*$_3$Me$_2$H), 112.68 (4-N$_2$*C*$_3$Me$_2$H), 15.93 (3-N$_2$C$_3$*Me*$_2$H), 14.76 (5-N$_2$C$_3$*Me*$_2$H), 1.59 (*Me*Si(Me$_2$pz)$_3$). IR (NaCl plates, Nujol): 3277 (w), 1564 (m), 1457 (s), 1377 (m), 1323 (w), 1263 (s), 1147 (s), 983 (w), 799 (s), 729 (w) cm^{-1}. Anal. Found (calcd for C$_{16}$H$_{24}$N$_6$SiCl$_3$Y·CH$_2$Cl$_2$): C, 33.3 (33.5); N, 13.6 (13.8); H, 4.3 (4.3). EI$^+$ MS: *m/z* 523 [M]$^+$, 1%.

Sc(Me$_3$[6]aneN$_3$)(CH$_2$SiMe$_3$)$_3$ (12). To a solution of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (400 mg, 0.887 mmol) in cold (0 °C) toluene (20 mL) was added dropwise a solution of Me$_3$(6)aneN$_3$ (125 μL, 0.887 mmol) in toluene (10 mL). The reaction mixture was stirred at for 3 h at 0 °C, after which time the volatiles were removed under reduced pressure to afford **12** as a pale yellow solid. Yield: 313 mg (80%). ^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 293 K): 3.32 (3 H, d, *J* = 9.0 Hz, NCH$_2$), 1.82 (3 H, d, *J* = 8.8 Hz, NCH$_2$), 1.61 (9 H, s, NCH$_3$), 0.45 (27 H, s, SiMe$_3$), −0.21 (6 H, s, C*H*$_2$SiMe$_3$). ^{13}C{^{1}H} NMR: (C$_6$D$_6$, 75.0 MHz, 293 K): 76.6 (NCH$_2$), 38.5 (NCH$_3$), 4.5 (SiMe$_3$) (*C*H$_2$SiMe$_3$ not observed). IR (NaCl plates, Nujol): 1468 (m), 1268 (s), 1235 (s), 1169 (m), 1117 (s), 1015 (m), 940 (m), 864 (s), 745 (m), 670 (m) cm^{-1}. EI-MS: *m/z* 348 (100%) [M − CH$_2$SiMe$_3$]$^+$, 261 (40%) [M − 2 CH$_2$SiMe$_3$]$^+$. Anal. Found (calcd for C$_{18}$H$_{48}$N$_3$ScSi$_3$): C, 49.5 (49.6); H, 11.1 (11.1); N, 9.6 (9.6).

Y(Me$_3$[6]aneN$_3$)(CH$_2$SiMe$_3$)$_3$ (13). To a solution of YCH$_2$SiMe$_3$)$_3$(THF)$_2$ (150 mg, 0.303 mmol) in cold (0 °C) toluene (20 mL) was added dropwise a solution of Me$_3$(6)aneN$_3$ (42 μL, 0.303 mmol) in toluene (10 mL). The reaction mixture was stirred at for 3 h at 0 °C, after which time the volatiles were removed under reduced pressure to afford **13** as a pale yellow solid. Yield: 100 mg (68%). ^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 293 K): 3.28 (3 H, d, ^2J = 9.5 Hz, NCH$_2$), 1.77 (3 H, d, ^2J = 8.2 Hz, NCH$_2$), 1.59 (9 H, s, NCH$_3$), 0.46 (27 H, s, SiMe$_3$), −0.62 (6 H, d, J_{HY} = 2.6 Hz, C*H*$_2$SiMe$_3$). ^{13}C{^{1}H} NMR: (C$_6$D$_6$, 75.0 MHz, 293 K): 76.5 (NCH$_2$), 38.6 (NCH$_3$), 36.2 (*C*H$_2$SiMe$_3$, J_{CY} = 34.7 Hz), 4.8 (SiMe$_3$) ppm. IR (NaCl plates, Nujol): 1456 (m), 1113 (m), 939 (w), 859 (s), 667 (m) cm^{-1}. EI-MS: *m/z* 392.1 (27%) [M − CH$_2$SiMe$_3$]$^+$, 304 (25%) [M − 2CH$_2$SiMe$_3$]$^+$. Anal. Found (calcd for C$_{18}$H$_{48}$N$_3$Si$_3$Y): C, 45.0 (45.0); H, 10.0 (10.1); N, 8.6 (8.8).

Sc(Me$_3$[6]aneN$_3$)Cl$_3$ (14). To a solution of ScCl$_3$(THF)$_3$ (125 mg, 0.395 mmol) in MeCN (5 mL) was added Me$_3$[6]aneN$_3$ (47.7 μL, 0.395 mmol). The reaction mixture was stirred at room temperature for 3 h. Pentane (10 mL) was added and the resulting solid isolated by filtration to afford **14** as a white solid. Yield: 64 mg (66%). Diffraction-quality crystals were grown from a saturated dichloromethane solution. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 293 K): 4.23 (3 H, d, ^2J = 8.8 Hz, NCH$_2$), 3.52 (3 H, s, ^2J = 7.6 Hz, NCH$_2$), 2.57 (9 H, s, NCH$_3$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz, 293 K): 76.98 (NCH$_2$), 39.58 (NCH$_3$) ppm. IR (NaCl plates, Nujol): 1113 (s), 1181 (m), 936 (m) cm^{-1}. EI-MS: *m/z* 244 (35%) [M − Cl]$^+$, 209 (3%) [M − 2 Cl]$^+$, 129 (30%). Anal. Found (calcd for C$_6$H$_{15}$Cl$_3$N$_3$Sc): C, 25.7 (25.7); H, 5.4 (5.4); N, 14.6 (14.9).

Sc(L^1)(CH$_2$SiMe$_3$)$_2$ (15). To a solution of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (280 mg, 0.62 mmol) in cold (7 °C) benzene (20 mL) was added dropwise a solution of HL^1 (232 mg, 0.62 mmol) in cold benzene. The solution was warmed to room temperature and stirred for a further 1 h. The volatiles were removed under reduced pressure to afford **15** as a pale yellow solid. Yield: 252 mg (68%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 293 K): 7.60 (1H, d, ^4J = 1.9 Hz, 4-C$_6$*H*$_2$^{t}Bu$_2$), 7.00 (1H, d, ^4J = 1.9 Hz, 6-C$_6$*H*$_2$^{t}Bu$_2$), 4.49 (1H, d, ^2J = 12.2 HzC*H*$_2$Ar), 3.15 (1H, td, ^2J = 10.8 Hz, ^3J = 5.6 Hz, NCH$_2$CH$_2$N), 3.05 (1H, td, ^2J = 10.8 Hz, ^3J = 5.6 Hz, NCH$_2$CH$_2$N), 2.87 (1H, d, *J* = 12.2 Hz, C*H*$_2$Ar), 2.50 (3H, s, NMe), 2.14−1.22 (9H, overlapping m, NCH$_2$CH$_2$N), 2.10 (3H, s, NMe), 1.80 (9H, s, CMe$_3$), 1.35 (9H, s, CMe$_3$), 0.89 (1H, d, *J* = 12.4 Hz, NCH$_2$CH$_2$N), 0.46 (9H, s, SiMe$_3$), 0.34 (9H, s, SiMe$_3$), −0.20 (1H, d, *J* = 11.5 Hz, ScCH$_2$), −0.29 (1H, d, *J* = 11.5 Hz, ScCH$_2$), −0.36 (1H, d, *J* = 11.5 Hz, ScCH$_2$), −0.50 (1H, d, *J* = 11.5 Hz, ScCH$_2$). ^{13}C{^{1}H} NMR: (C$_6$D$_6$, 125.7 MHz, 293 K): 161.5 (2-C$_6$H$_2$^{t}Bu$_2$), 137.4 (3- or 5-C$_6$H$_2$^{t}Bu$_2$), 136.2 (5- or 3-C$_6$H$_2$^{t}Bu$_2$), 125.4 (6-C$_6$H$_2$^{t}Bu$_2$), 124.5 (4-C$_6$H$_2$^{t}Bu$_2$), 124.1 (1-C$_6$H$_2$^{t}Bu$_2$), 64.3 (N*C*H$_2$Ar), 58.8 (NCH$_2$CH$_2$N), 57.6 (NCH$_2$CH$_2$N), 55.8 (NCH$_2$CH$_2$N), 52.5 (NCH$_2$CH$_2$N), 52.3 (NCH$_2$CH$_2$N), 50.3 (NMe), 49.7 (NMe), 49.1 (NCH$_2$CH$_2$N), 35.6

Table 8. X-ray Data Collection and Processing Parameters for $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (1), $Sc\{HC(Me_2Pz)_3\}(CH_2SiMe_3)_3\cdot 2C_7H_8$ ($3\cdot 2C_7H_8$), $Y\{HC(Me_2Pz)_3\}(CH_2SiMe_3)_3$ (4), $Sc\{HC(Me_2Pz)_3\}(OAr)_3\cdot 4C_6H_6$ ($9\cdot 4C_6H_6$), $Y\{MeSi(Me_2Pz)_3\}Cl_3\cdot CH_2Cl_2$ ($11\cdot CH_2Cl_2$), and $Sc(Me_3[6]aneN_3)Cl_3$ (14)and $Sc(L^2)(OTol)_2\cdot C_6H_6$ ($18\cdot C_6H_6$)

	1	**3**·$2C_7H_8$	**4**	**9**·$4C_6H_6$	**11**·CH_2Cl_2	**14**	**18**·C_6H_6
empirical formula	$C_{21}H_{54}N_3ScSi_3\cdot 2C_{17}H_8$	$C_{28}H_{55}N_6ScSi_3$	$C_{28}H_{55}N_6Si_3Y$	$C_{40}H_{49}N_6O_3Sc\cdot 4C_6H_6$	$C_{16}H_{24}Cl_3N_6SiY\cdot CH_2Cl_2$	$C_6H_{15}Cl_3N_3Sc$	$C_{37}H_{54}N_3O_3Sc\cdot C_6H_6$
fw	477.89	789.28	648.95	1019.29	608.69	280.52	711.93
temp/K	150	150	150	150	150	150	150
wavelength/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.71073
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P31c$	$P2_1/n$	$P2_1/m$	$P2_1/c$
a/Å	19.2407(2)	12.4871(2)	11.0526(2)	14.7505(6)	10.0211(1)	7.5676(2)	13.3324(5)
b/Å	18.5432(2)	16.0885(2)	11.6252(2)	14.7505(6)	30.7707(3)	12.1539(4)	14.1401(7)
c/Å	18.6490(2)	24.0879(3)	17.1350(3)	15.4170(4)	16.9809(2)	7.8780(2)	21.400(1)
α/deg	90	90	81.8126(9)	90	90	90	90
β/deg	115.6548(5)	101.2652(4)	85.5181(8)	90	95.1016(3)	118.5146(14)	90.670(3)
γ/deg	90	90	71.3772(7)	120	90	90	90
V/Å^3	5997.74(11)	4745.99(11)	2063.86(6)	2905.0(2)	5215.42(10)	636.69(3)	4034.0(9)
Z	8	4	2	2	8	2	4
d(calcd)/Mg m^{-3}	1.058	1.105	1.044	1.165	1.550	1.463	1.17
abs coeff/mm^{-1}	0.377	0.264	1.522	0.18	2.812	1.172	0.22
R indices[a]							
R1	0.0349	0.0452	0.0489	0.0507	0.0373	0.0271	0.0658
wR2	0.0418	0.0536	0.0529	0.0557	0.0428	0.0379	0.0636

[a] R indices with $I > n\sigma(I)$; $n = 3$ except for **18**·C_6H_6, where $n = 2$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)\}^{1/2}$.

(CMe_3), 34.2 (CMe_3), 32.1 (CMe_3), 30.8 (CMe_3), 4.7 ($SiMe_3$), 4.4 ($SiMe_3$), 1.4 ($ScCH_2$). IR (KBr plates, Nujol): 1605 (s), 1317 (m), 1286 (s), 1261 (m), 1235 (s), 1104 (s), 1017 (m), 879 (s), 813 (m), 773 (m), 749 (m), 723 (m), 667 (w), 548 (w), 475 (w) cm^{-1}. EI-HRMS for $[Sc(L^1)(CH_2SiMe_3)]^+$: found (calcd for $C_{27}H_{51}N_3OScSi$) m/z 506.3348 (506.3361). Anal. Found (calcd for $C_{31}H_{62}N_3OScSi_2$): C, 60.0 (62.7); H, 9.3 (10.5); N, 6.2 (7.1).

$Sc(L^2)(CH_2SiMe_3)_2$ (16). To a stirred solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (119 mg, 0.29 mmol) in cold (7 °C) benzene (15 mL) was added a solution of HL^2 (123 mg, 0.29 mmol) in cold benzene (15 mL). The solution was warmed to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure to afford **16** as a pale yellow solid. Yield: 96 mg (51%). ^1H NMR (C_6D_6, 500.0 MHz, 293 K): 7.6 (1H, d, J = 2.4 Hz, 4-$C_6H_2{}^tBu_2$), 7.0 (1H, d, J = 2.2 Hz, 6-$C_6H_2{}^tBu_2$), 4.7 (1H, d, J = 12.7 HzNCH_2Ar), 3.78 (1H, app sept, J = 5.6 Hz, $CHMe_2$), 3.33 (1H, app sept, J = 6.5 Hz, $CHMe_2$), 3.14 (1H, m, NCH_2CH_2N), 2.90 (1H, d, J = 12.7 Hz, NCH_2Ar), 2.48 (2H, m, NCH_2CH_2N), 2.14−1.34 (9H, overlapping m, NCH_2CH_2N), 1.86 (9H, s, CMe_3), 1.40 (3H, d, J = 6.4 Hz, $CHMe_2$), 1.37 (9H, s, CMe_3), 0.72 (3H, d, J = 6.6 Hz, $CHMe_2$), 0.57 (3H, d, J = 6.3 Hz, $CHMe_2$), 0.48 (9H, s, $SiMe_3$), 0.40 (3H, d, J = 6.4 Hz, $CHMe_2$), 0.24 (9H, s, $SiMe_3$), −0.01 (1H, d, ^2J = 11.2 Hz, $ScCH_2$), −0.09 (1H, d, ^2J = 11.2 Hz, $ScCH_2$), −0.19 (1H, d, ^2J = 11.2 Hz, $ScCH_2$), −0.30 (1H, d, ^2J = 11.2 Hz, $ScCH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 160.1 (2-$C_6H_2{}^tBu_2$), 137.4 (3-$C_6H_2{}^tBu_2$), 136.4 (5-$C_6H_2{}^tBu_2$), 124.6 (6-$C_6H_2{}^tBu_2$), 124.5 (4-$C_6H_2{}^tBu_2$), 123.9 (1-$C_6H_2{}^tBu_2$), 65.8 (NCH_2Ar), 56.0 ($CHMe_2$), 55.1 ($CHMe_2$), 54.6 (NCH_2CH_2N), 54.2 (NCH_2CH_2N), 51.7 (NCH_2CH_2N), 43.1 (NCH_2CH_2N), 42.8 (NCH_2CH_2N), 35.8 (CMe_3), 34.2 (CMe_3), 32.1 (CMe_3), 31.4 (CMe_3), 23.4 ($CHMe_2$), 21.2 ($CHMe_2$), 14.1 ($CHMe_2$), 13.9 ($CHMe_2$), 4.8 ($SiMe_3$), 4.3 ($SiMe_3$) ppm (not observed: 2 × $ScCH_2$). IR (KBr pellet): 2948 (s), 2900 (s), 2866 (m), 2818 (w), 1604 (w), 1478 (s), 1440 (m), 1414 (m), 1384 (m), 1362 (m), 1312 (s), 1286 (m), 1264 (w), 1236 (m), 1204 (w), 1160 (w), 1148 (w), 1134 (w), 1118 (w), 1080 (w), 1062 (w), 1016 (w), 968 (w), 948 (w), 900 (m), 876 (s), 844 (s), 812 (m), 748 (m), 730 (m), 666 (m), 646 (w), 598 (w), 586 (w), 546 (m), 466 (w), 452 (w), 404 (w) cm^{-1}, EI-MS: m/z 649 (50%) $[M]^+$. Anal. Found (calcd for $C_{35}H_{70}N_3OScSi_2$): C, 63.3 (64.7); H, 10.9 (10.9); N, 6.5 (6.5).

$Sc(L^1)Ph_2$ (17). To a stirred solution of $ScPh_3(THF)_2$ (115 mg, 0.27 mmol) in cold (7 °C) benzene (15 mL) was added a solution of HL^{2e} (102 mg, 0.27 mmol) in cold benzene (15 mL). The solution was warmed to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure to afford **17** as a white solid. Yield: 62 mg (38%). ^1H NMR (C_6D_6, 500.0 MHz, 293 K): 8.44 (2 H, d, J = 7.3 Hz, 2-C_6H_5), 8.15 (2 H, d, J = 7.3 Hz, 2-C_6H_5), 7.63 (1 H, s, 4-$C_6H_2{}^tBu_2$), 7.49 (2 H, t, J = 7.3 Hz, 3-C_6H_5), 7.35 (1 H, t, J = 7.3 Hz, 4-C_6H_5), 7.29 (2 H, t, J = 7.3 Hz, 3-C_6H_5), 7.16 (1 H, t, J = 7.3 Hz, 4-C_6H_5), 6.92 (1 H, s, 6-$C_6H_2{}^tBu_2$), 4.53 (1 H, d, J = 12.2 Hz, NCH_2Ar), 3.36 (1 H, m, NCH_2CH_2N), 3.27 (1 H, m, NCH_2CH_2N), 2.68 (3 H, s, NMe), 2.55 (1 H, d, J = 12.2 Hz, NCH_2Ar), 2.20−1.20 (9 H, overlapping m, NCH_2CH_2N), 2.00 (3 H, s, NMe), 1.87 (9 H, s, CMe_3), 1.39 (9 H, s, CMe_3), 0.93 (1 H, m, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): 161.3 (2-$C_6H_2{}^tBu_2$), 138.6 (2-C_6H_5), 138.0 (2-C_6H_5), 137.9 (3- or 5-$C_6H_2{}^tBu_2$), 136.5 (5- or 3-$C_6H_2{}^tBu_2$), 126.6 (3-C_6H_5), 126.5 (3-C_6H_5), 125.5 (4-C_6H_5), 125.4 (4-C_6H_5), 125.0 (6-$C_6H_2{}^tBu_2$), 124.5 (4-$C_6H_2{}^tBu_2$), 124.3 (1-$C_6H_2{}^tBu_2$), 64.6 (NCH_2Ar), 58.9 (NCH_2CH_2N), 57.5 (NCH_2CH_2N), 56.0 (NCH_2CH_2N), 53.0 (NMe), 52.4 (NMe), 49.9 (NCH_2CH_2N), 49.5 (NCH_2CH_2N), 35.7 (CMe_3), 34.2 (CMe_3), 32.2 (CMe_3), 30.6 (CMe_3) ppm (not observed: 2 × 1-C_6H_5). IR (KBr pellet, cm^{-1}): 3038 (w), 2952 (s), 2902 (s), 2864 (s), 2826 (w), 1724 (w), 1700 (w), 1602 (w), 1476 (s), 1438 (m), 1412 (m), 1384 (m), 1362 (m), 1314 (s), 1284 (s), 1262 (m), 1240 (m), 1202 (w), 1168 (w), 1136 (w), 1104 (w), 1105 (m), 1006 (m), 992 (m), 878 (w), 840 (m), 810 (w), 800 (w), 772 (w), 722 (w), 706 (m), 680 (m), 634 (w), 610 (w), 546 (m), 504 (w), 490 (w), 472 (w), 440 (w), 422 (w), 408 (w) cm^{-1}. Anal. Found (calcd for $C_{35}H_{50}N_3OSc\cdot 0.4C_6H_6$): C, 74.4 (74.3); H, 8.9 (8.7); N, 7.2 (7.0).

$Sc(L^1)(OTol)_2$ (18). To a stirred solution of $Sc(L^1)(CH_2SiMe_3)_2$ (**15**; 90 mg, 0.14 mmol) in cold (7 °C) benzene (20 mL) was added dropwise TolOH (20 mg, 0.28 mmol) in cold benzene (20 mL). The solution was warmed to room temperature and stirred for 1 h before removing the volatiles under reduced pressure to afford **18** as a white powder. Yield: 40 mg (49%). Diffraction-quality crystals were grown from a saturated benzene solution at room temperature. ^1H NMR (C_6D_6, 500.0 MHz, 293 K): 7.59 (1 H, d, J = 2.4 Hz, 4-$C_6H_2{}^tBu_2$), 7.14 (2 H, m, C_6H_4Me), 7.08 (2 H, d, J = 6.3 Hz, C_6H_4Me), 6.98−6.92 (5 H, overlapping m, 6-$C_6H_2{}^tBu_2$, C_6H_4Me), 4.55 (1 H, d, J = 12.7 Hz, CH_2Ar), 3.34 (1 H, td, ^2J = 12.7 Hz, ^3J = 5.4 Hz, NCH_2CH_2N), 2.95 (1 H, td, ^2J = 12.7 Hz, ^3J = 5.4 Hz, NCH_2CH_2N), 2.87 (1 H, d, J = 12.7, CH_2Ar), 2.50 (3 H, s, NMe), 2.26 (3 H, s, C_6H_4Me), 2.25 (3 H, s, C_6H_4Me), 2.24−1.24 (9 H, m, NCH_2CH_2N), 2.15 (3 H, s, NMe), 1.77 (9 H, s, CMe_3), 1.40 (9 H, s, CMe_3), 1.05 (1 H, d, J = 10.3 Hz, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 163.3 (1-C_6H_4Me), 163.0 (1-C_6H_4Me), 161.4 (2-$C_6H_2{}^tBu_2$), 137.1 (3- or 5-$C_6H_2{}^tBu_2$), 136.5 (5- or

$3\text{-}C_6H_2{}^tBu_2$), 130.2 ($4\text{-}C_6H_4Me$), 128.2 ($4\text{-}C_6H_4Me$), 125.4 ($4\text{-}C_6H_2{}^tBu_2$), 125.0 (C_6H_4Me), 124.7 ($6\text{-}C_6H_2{}^tBu_2$), 124.4 (C_6H_4Me), 123.7 ($1\text{-}C_6H_2{}^tBu_2$), 119.5 (C_6H_4Me), 119.3 (C_6H_4Me), 64.3 (NCH_2Ar), 57.8 (NCH_2CH_2N), 56.1 (NCH_2CH_2N), 56.0 (NCH_2CH_2N), 52.6 (NCH_2CH_2N), 51.5 (NCH_2CH_2N), 48.7 (NCH_2CH_2N), 48.5 (NMe), 48.1 (NMe), 35.6 (CMe_3), 34.2 (CMe_3), 32.2 (CMe_3), 30.6 (CMe_3), 20.9 (C_6H_4Me), 20.8 (C_6H_4Me). IR (KBr plates, Nujol): 1606 (s), 1504 (s), 1414 (m), 1350 (w), 1286 (s), 1260 (m), 1204 (w), 1164 (m), 1102 (m), 1074 (m), 1008 (m), 992 (w), 876 (s), 840 (m), 808 (m), 770 (m), 746 (m), 722 (m), 544 (s), 516 (w), 470 (w), 422 (w), 404 (w) cm^{-1}. EI-HRMS for $[Sc(L^2)(OTol)]^+$: found (calcd for $C_{30}H_{47}N_3O_2Sc$) *m/z* 526.3204 (526.3227). A satisfactory combustion analysis was not obtained, even from the single crystals.

Crystal Structure Determinations of $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$ (1), $Sc\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3\cdot 2C_7H_8$ ($3\cdot 2C_7H_8$), $Y\{HC(Me_2pz)_3\}(CH_2SiMe_3)_3$ (4), $Sc\{HC(Me_2pz)_3\}(OAr)_3\cdot 4C_6H_6$ ($9\cdot 4C_6H_6$), $Y\{HC(Me_2pz)_3\}Cl_3\cdot CH_2Cl_2$ ($11\cdot CH_2Cl_2$), $Sc(Me_3[6]aneN_3)Cl_3$ (14), and $Sc(L^2)(OTol)_2\cdot C_6H_6$ ($18\cdot C_6H_6$). Crystal data collection and processing parameters are given in Table 8. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. Intensity data were processed using the DENZO-SMN package.[57] The structures were solved using the direct-methods program SIR92,[58] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[59] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically, except for the CH_2SiMe_3 atoms of **1** and **3**, which were located from Fourier difference syntheses and positionally and isotropically refined.

Additional Comments on the Crystal Structures. Crystals of **1** have two crystallographically independent molecules in the asymmetric unit which adopt very similar geometries. One of the trimethylsilyl groups (that of Si(3)) of **4** was disordered, and this was modeled as being due to the presence of two conformers related by rotation about the Si(3)−C(25) bond; coordinates, anisotropic displacement parameters, and site occupancies of the disordered carbon atoms were refined, subject to restraint of the Si−C bond lengths to 1.90(2) Å and of the C−Si−C angles to 109.5(2)°; similarly, restraints were applied to the displacement parameters of the C atoms and those of Si(3). Moleclues of **14** are located on crystallographic mirror planes. Crystals of $\mathbf{18}\cdot C_6H_6$ were weak diffractors, and despite an extended data collection time (36 h), a data to parameter ratio of only ca. 7:1 (threshold $I > 2\sigma(I)$) was achieved; the C_6H_6 molecule of crystallization was disordered and was refined in a rigid-body approximation.

Full listings of atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for the seven structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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