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Scandium chloride, alkyl and phenyl complexes of diamido-donor ligands

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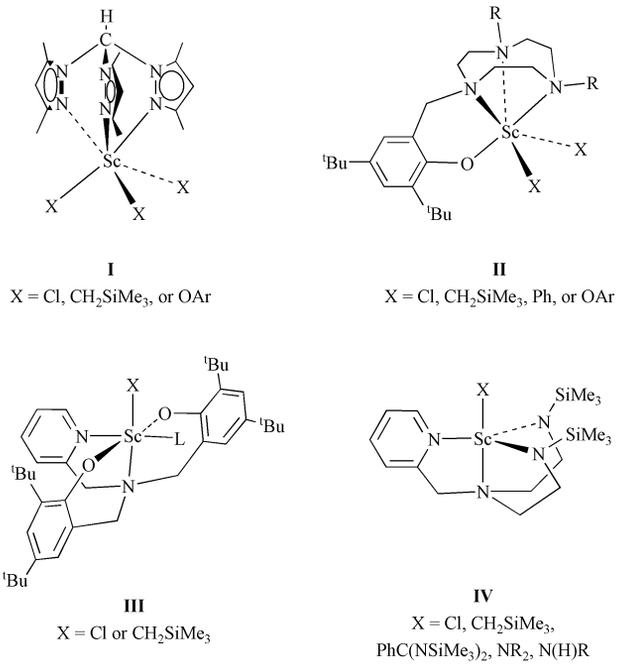
Reactions of the lithiated diamido-pyridine and -amine ligands $Li_2N_2^{TMS}N_{py}$ or $Li_2N_2N^{C2,TMS}$ with $ScCl_3$ in tetrahydrofuran (THF) afforded the five-coordinate scandium chloride derivatives $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1** and $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2** where $N_2^{TMS}N_{py}$ = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ and $N_2N^{C2,TMS}$ = $Me_3SiN(CH_2CH_2NSiMe_3)_2$. The corresponding reactions of $ScCl_3$ with the dilithium salts of the amino N-methylated two-carbon analogue $N_2N^{C2,Me}$ ($N_2N^{C2,Me}$ = $MeN(CH_2CH_2NSiMe_3)_2$) or of the amino N-silylated three-carbon chain analogue $N_2N^{C3,TMS}$ ($N_2N^{C3,TMS}$ = $Me_3SiN(CH_2CH_2CH_2NSiMe_3)_2$) afforded no tractable products. In contrast, reaction of $ScCl_3$with the homologous N-methylated three-carbon chain species $Li_2N_2N^{C3,Me}$ ($N_2N^{C3,Me}$ = $MeN(CH_2CH_2CH_2NSiMe_3)_2$) cleanly gave the THF-free dinuclear, chloride-bridged compound $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3**. The compounds **1**–**3** have been crystallographically characterised. Organometallic analogues of **1** and **2** have been prepared by protonolysis reactions of $H_2N_2^{R'}N_{py}$ ($N_2^{R'}N_{py}$ = $MeC(2\text{-}C_5H_4N)(CH_2NR')_2$ where R′ = $SiMe_3$, Tol (4-C_6H_4Me) or Mes (2,4,6-$C_6H_2Me_3$)) and $H_2N_2N^{C2,R'}$ (R′ = Me or $SiMe_3$) with $[ScR_3(THF)_2]$ (R = CH_2SiMe_3 or Ph) in benzene which gave the five-coordinate alkyl or phenyl compounds $[Sc(N_2^{R'}N_{py})R(THF)]$ (R = CH_2SiMe_3, R′ = $SiMe_3$ **4**, Tol **5** or Mes **6**; R = Ph, R′ = $SiMe_3$ **7**) and $[Sc(N_2N^{C2,R'})(CH_2SiMe_3)(THF)]$ (R′ = Me **8** or $SiMe_3$ **9**). The compound **4** can also be prepared by the reaction of **1** with $LiCH_2SiMe_3$. Reaction of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with $H_2N_2N^{C3,Me}$ afforded no tractable product, and with $H_2N_2N^{C3,TMS}$ in deuterobenzene the labile compound $[Sc(N_2N^{C3,TMS})(CH_2SiMe_3)(THF)]$ **10** was observed by ^1H NMR spectroscopy but could not be isolated. On one occasion the THF-free dimeric alkyl species $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]$ **11** was obtained. This compound possesses one bridging and one terminal amido nitrogen per $N_2^{Tol}N_{py}$ ligand. The X-ray crystal structures of **6** and **11** have been determined. The monomeric compounds **1**, **2** and **6** all have trigonal bipyramidal Sc centres in the solid state; the neutral donors take up the axial sites, and the amido nitrogens and either Cl or CH_2SiMe_3 occupy the equatorial ones.

Introduction

The organometallic and related coordination chemistry of scandium was for a number of years generally dominated by mono- and bis-cyclopentadienyl complexes.[1] Over the past decade, however, a number of new, 'alternative', supporting ligand systems have started to emerge, including: the tetratolylporphyrin systems developed by Arnold *et al.*;[2] the bis(benzamidinato) compounds of Edelmann and Arnold;[3] the recent NP_2-donor ligand-supported systems of Fryzuk *et al.*;[4] the low-valent sandwich and related complexes of Cloke and coworkers;[1e,5] the tris(pyrazolyl)hydroborate, 'nacnac' and other systems studied by Piers *et al.*;[6] Scott's tris(amido)amine complexes,[7] Bazan's boratobenzene complexes[8] and Bercaw's triazacyclononane systems.[9]

We ourselves have recently been interested to develop the organometallic and related chemistry of scandium in previously unexplored or underdeveloped (so far as this element is concerned) ligand environments. Chart 1 shows some of the systems which are currenly being studied in one of our groups.[10] Apart from the neutral tris(3,5-dimethylpyrazolyl)methane-supported complexes **I**, all of the systems shown have mono- or di-anionic, tetradentate ligand sets (**II**–**IV**). So far, the diamido-diamine ligand $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_3)_2$ in **IV** has been the most successful in supporting a range of different ancilliary ligands 'X'. However, this *tetra*dentate ligand is rather rigid and in none of its chemistry to date[10d,11] have we found evidence for lability of the pyridyl donor to generate a potentially vacant ligand site that might, in turn, allow for enhanced reactivity. We were therefore interested to develop scandium systems supported by *tri*dentate diamido-donor ligands. A number of potential ligands of this type are available[12] and the ones chosen for this study are listed in Chart 2 along with the abbreviations used herein.

The diamido-pyridine systems $MeC(2\text{-}C_5H_4N)(CH_2NR)_2$ (abbreviated as $N_2^RN_{py}$) were first developed by us[13] for R = $SiMe_3$ and $SiMe_2{}^tBu$ and have recently been adopted by Schrock and coworkers for R = Mes and 3,5-dichlorophenyl.[14] The diamido-amine systems $RN(CH_2CH_2NSiMe_3)_2$ (abbreviated as $N_2N^{C2,R}$) where R = Me or $SiMe_3$ have been developed by Bertrand and coworkers,[15] Cloke *et al.*[16] and Horton *et al.*[17] We have recently been using some of these ligands in developing early transition metal imido chemistry.[18] Whereas the $N_2N^{C2,R}$ ligands possess two-carbon CH_2CH_2 linkers between the terminal amido and central amino nitrogen donors, the bottom ligands in Chart 2, namely $RN(CH_2CH_2CH_2NSiMe_3)_2$ (abbreviated as $N_2N^{C3,R}$) where R = Me or $SiMe_3$, feature three-carbon linkers and provide overall a more flexible environment



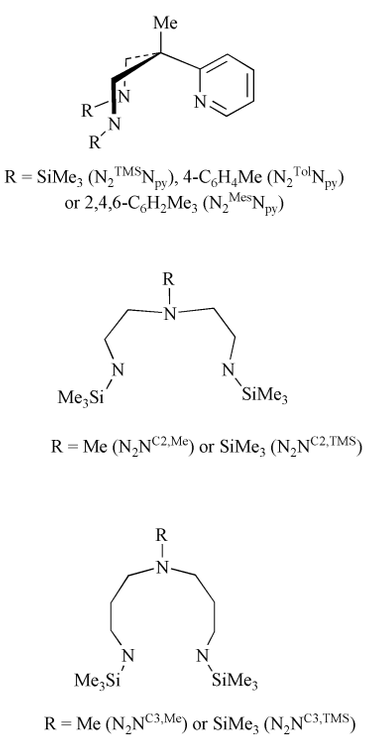
I
X = Cl, CH_2SiMe_3, or OAr

II
X = Cl, CH_2SiMe_3, Ph, or OAr

III
X = Cl or CH_2SiMe_3

IV
X = Cl, CH_2SiMe_3, $PhC(NSiMe_3)_2$, NR_2, N(H)R

Chart 1



R = $SiMe_3$ ($N_2^{TMS}N_{py}$), 4-C_6H_4Me ($N_2^{Tol}N_{py}$) or 2,4,6-$C_6H_2Me_3$ ($N_2^{Mes}N_{py}$)

R = Me ($N_2N^{C2,Me}$) or $SiMe_3$ ($N_2N^{C2,TMS}$)

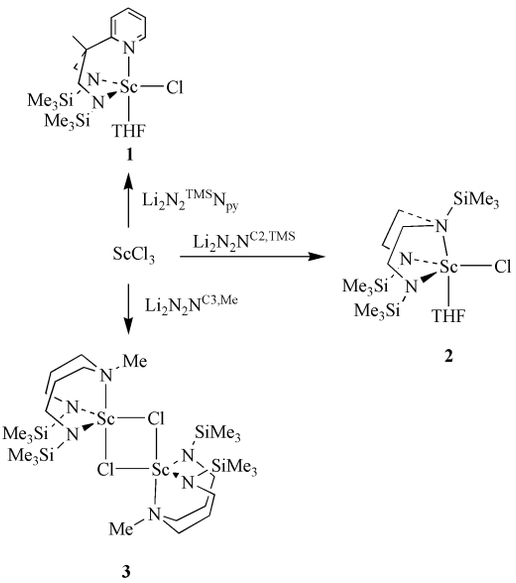
R = Me ($N_2N^{C3,Me}$) or $SiMe_3$ ($N_2N^{C3,TMS}$)

Chart 2

than their two-carbon chain homologues.[19] In this contribution we describe the potential usefulness of the seven ligands in Chart 2 in the organometallic and coordination chemistry of scandium.

Results and discussion

The successful reactions between $ScCl_3$ and certain of the lithiated diamido-donor ligands are summarised in Scheme 1. The additions were carried out in THF at −78 °C, and during the reaction $ScCl_3$ dissolved after addition of the lithiated amide: it was not necessary to prepare and isolate the THF complex $[ScCl_3(THF)_3]$ beforehand. We have not yet been able to obtain well-defined lithiated derivatives of the *N*-aryl-substituted diamido-pyridine ligands $N_2^{Ar}N_{py}$ (Ar = Tol or Mes) and so the



1

2

3

Scheme 1 Reactions of $ScCl_3$ with lithiated diamido-pyridine or -amine ligands. Additions were carried out in THF at −78 °C. See the text and the Experimental section for further details.

only scandium chloride derivative of this ligand system prepared to date is $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1** obtained in 59% isolated yield as a pale yellow air- and moisture-sensitive solid. The NMR data for **1** show resonances attributable to a κ^3-coordinated $N_2^{TMS}N_{py}$ ligand and a coordinated THF ligand. The geometry shown in Scheme 1 has been confirmed by X-ray diffraction as discussed below.

Reaction of $ScCl_3$ with $Li_2N_2N^{C2,Me}$ in THF under identical conditions to those used for the synthesis of **1** afforded only complex mixtures. However, reaction with the amino N-$SiMe_3$ functionalised lithiated ligand $Li_2N_2N^{C2,TMS}$ did give modest isolated yields of the highly soluble, five-coordinate THF adduct $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2** which again has been structurally characterised as discussed below. The ^{1}H NMR spectrum of **2** in C_6D_6 features, in addition to resonances for THF, intense resonances for two types of $SiMe_3$ group (ratio 18H:9H) at 0.28 and 0.14 ppm, and the CH_2CH_2 backbone methylene hydrogens give rise to four sets of mutually coupled, sharp multiplets.

Reaction of $ScCl_3$ with the three-carbon chain, amino N-$SiMe_3$ functionalised $Li_2N_2N^{C3,TMS}$ gave only complex mixtures, but with the less sterically demanding amino *N*-methylated ligand homologue the dinuclear compound $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3** was obtained as a white solid in 80% yield after work-up. The NMR data for **3** feature no resonances for THF and suggest that the molecules possess C_{2v} symmetry in solution on the NMR timescale at room temperature. Thus the $SiMe_3$ groups appear as single resonances in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, and the chemically inequivalent protons of each $CH_2CH_2CH_2$ linkage give rise to six individual, broad multiplets in the ^{1}H spectrum in toluene-d_8 at room temperature. On cooling the NMR sample to 213 K the $SiMe_3$ resonances decoalesced to form two singlets, and the ^{13}C NMR spectrum showed six independent methylene carbons for the two, now inequivalent, $CH_2CH_2CH_2$ linkages. The central amino *N*-methyl group appears as only a unique singlet in both the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. Overall therefore the low temperature data suggest a C_i or C_s symmetric structure for **3** (with two equivalent $N_2N^{C3,Me}$ ligands) rather than the C_{2v} structure implied by the room temperature data. These results are consistent with the solid state structure as discussed below.

The X-ray crystal structures of $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1**, $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2** and $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3** have been determined and are shown in Figs. 1–3. Selected bond lengths and angles are listed in Tables 1–3. The ranges for the

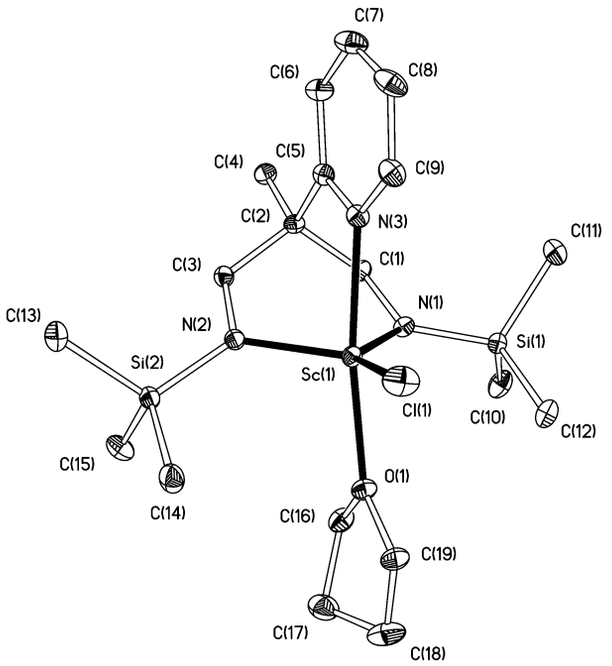


Fig. 1 Molecular structure of $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1**. Displacement ellipsoids are drawn at the 20% probability level. H atoms omitted for clarity.

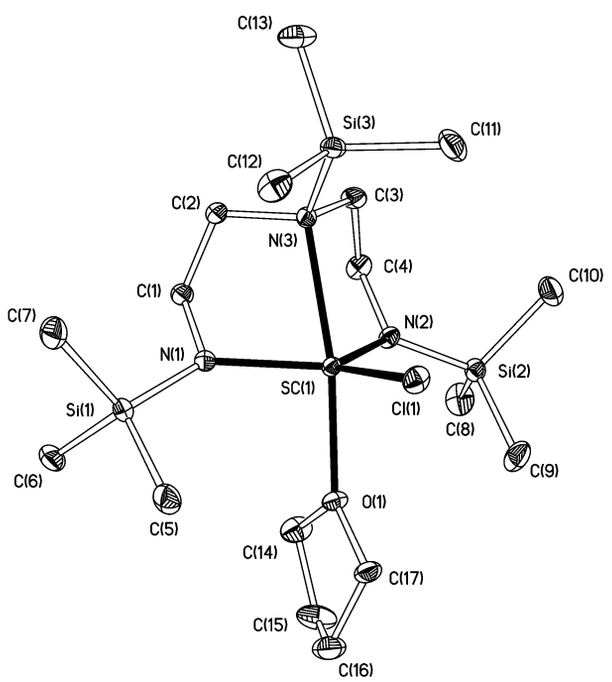


Fig. 2 Molecular structure of $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2**. Displacement ellipsoids are drawn at the 30% probability level. H atoms omitted for clarity.

Sc–O, Sc–N_{amide}, Sc–N_{amine}, Sc–$N_{pyridyl}$ and Sc–Cl distances, as well as those within the ligands themselves, are unremarkable and within ranges previously reported.[20]

The structures of $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1** (Fig. 1) and $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2** (Fig. 2) confirm the five-coordinate monomeric motifs suggested in Scheme 1 on the basis of the NMR data. In each compound the diamido-donor ligand adopts a *fac*, κ^3 coordination mode. The THF ligands lie *trans* to the neutral N-donor atoms. The Sc atoms possess approximately trigonal bipyramidal coordination geometries with the amido N and the Cl atoms lying in the equatorial plane. The geometry at the amido nitrogens themselves is approximately

Table 1 Selected bond distances (Å) and angles (°) for $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1**

Sc(1)–Cl(1)	2.4426(7)	Sc(1)–N(3)	2.288(2)
Sc(1)–N(1)	2.025(2)	Sc(1)–O(1)	2.205(2)
Sc(1)–N(2)	2.024(2)		
Cl(1)–Sc(1)–N(1)	135.79(6)	N(2)–Sc(1)–N(3)	86.54(7)
Cl(1)–Sc(1)–N(2)	122.35(6)	Cl(1)–Sc(1)–O(1)	86.09(4)
N(1)–Sc(1)–N(2)	100.57(7)	N(1)–Sc(1)–O(1)	96.25(7)
Cl(1)–Sc(1)–N(3)	89.45(5)	N(2)–Sc(1)–O(1)	101.22(7)
N(1)–Sc(1)–N(3)	82.53(7)	N(3)–Sc(1)–O(1)	172.22(6)
Sc(1)–N(1)–Si(1)	126.8(1)	Sc(1)–N(2)–Si(2)	129.6(1)
Sc(1)–N(1)–C(1)	114.67(13)	Sc(1)–N(2)–C(3)	114.62(13)
Si(1)–N(1)–C(1)	116.43(14)	Si(2)–N(2)–C(3)	115.30(13)

Table 2 Selected bond distances (Å) and angles (°) for $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2**

Sc(1)–Cl(1)	2.3982(6)	Sc(1)–N(2)	2.044(2)
Sc(1)–O(1)	2.192(2)	Sc(1)–N(3)	2.456(2)
Sc(1)–N(1)	2.044(2)		
Cl(1)–Sc(1)–O(1)	90.07(4)	N(1)–Sc(1)–N(2)	117.71(7)
Cl(1)–Sc(1)–N(1)	122.74(5)	Cl(1)–Sc(1)–N(3)	102.45(4)
O(1)–Sc(1)–N(1)	94.00(6)	O(1)–Sc(1)–N(3)	167.35(6)
Cl(1)–Sc(1)–N(2)	118.24(5)	N(1)–Sc(1)–N(3)	77.85(6)
O(1)–Sc(1)–N(2)	97.52(7)	N(2)–Sc(1)–N(3)	78.20(6)
Sc(1)–N(1)–Si(1)	134.0(1)	Sc(1)–N(2)–Si(2)	130.4(1)
Sc(1)–N(1)–C(1)	109.40(13)	Sc(1)–N(2)–C(4)	113.98(13)
Si(1)–N(1)–C(1)	116.07(14)	Si(2)–N(2)–C(4)	114.02(14)

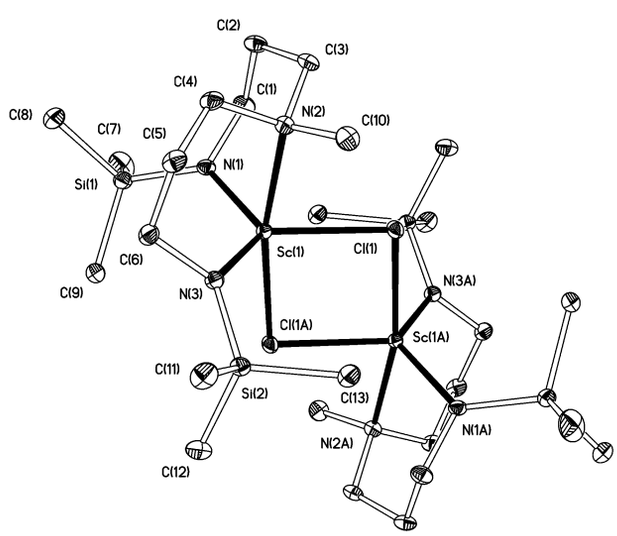
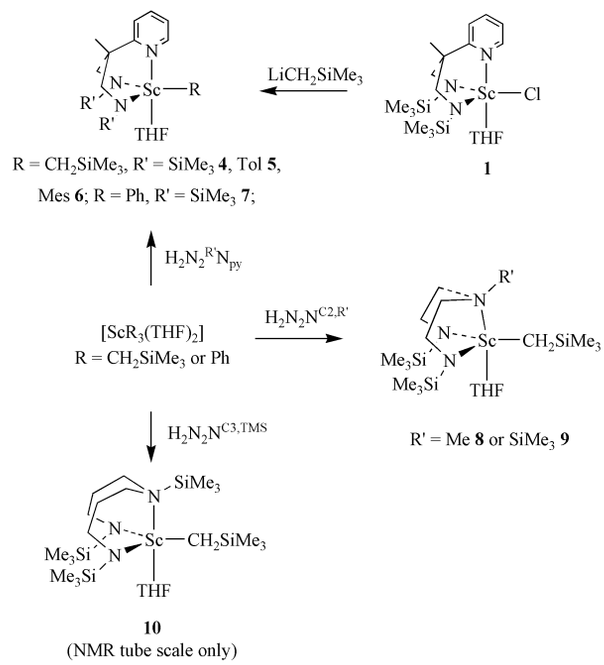


Fig. 3 Molecular structure of one of the two crystallographically independent molecules of $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3** in the asymmetric unit. Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $[1 - x, 1 - y, -z]$.

trigonal planar. There are some small but significant differences between the two structures. As a consequence of the more constraining CH_2CH_2 linkages in **2** the amino nitrogen N(3) is not quite able to occupy properly the axial position so that the N(3)–Sc(1)–O(1) angle of 167.35(6)° is somewhat less than the ideal value of 180°, and the N(3)–Sc(1)–Cl(1) angle of 102.45(4)° is somewhat larger than the ideal 90° required for a trigonal bipyramidal geometry. In **1** the corresponding angles are 172.22(6) and 89.45(5)° which are somewhat closer to the ideal values. The very different Sc(1)–N(3) distances of 2.288(2) and 2.456(2) Å in **1** and **2** underscore the differences deduced by examination of the angles, and also reflect the better donor ability of pyridyl nitrogen atoms compared with that of $SiMe_3$-substituted amines. Interestingly, although the Sc–Cl distance of 2.4426(7) Å in **1** is considerably longer than that of 2.3982(6) Å in **2** the Sc–O distances of 2.205(2) and 2.192(2) are only

Table 3 Selected bond distances (Å) and angles (°) for $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3**. The values in brackets correspond to the other crystallographically independent molecule in the asymmetric unit

Sc(1)–Cl(1)	2.5208(6)	[2.5217(6)]
Sc(1)–Cl(1A)	2.6162(6)	[2.6162(6)]
Sc(1)–N(1)	2.020(2)	[2.026(2)]
Sc(1)–N(2)	2.318(2)	[2.325(2)]
Sc(1)–N(3)	2.029(2)	[2.021(2)]
Cl(1)–Sc(1)–Cl(1A)	80.66(2)	[80.78(2)]
Cl(1)–Sc(1)–N(1)	112.36(5)	[128.72(5)]
Cl(1A)–Sc(1)–N(1)	100.73(5)	[95.83(5)]
Cl(1)–Sc(1)–N(2)	88.52(4)	[88.71(5)]
Cl(1A)–Sc(1)–N(2)	168.61(4)	[168.59(5)]
N(1)–Sc(1)–N(2)	86.62(6)	[87.25(6)]
Cl(1)–Sc(1)–N(3)	127.74(5)	[111.09(5)]
Cl(1A)–Sc(1)–N(3)	96.73(5)	[100.74(5)]
N(1)–Sc(1)–N(3)	119.29(7)	[119.71(7)]
N(2)–Sc(1)–N(3)	87.06(6)	[87.13(6)]
Sc(1)–N(1)–Si(1)	127.96(9)	[127.70(9)]
Sc(1)–N(1)–C(1)	114.23(13)	[114.18(12)]
Si(1)–N(1)–C(1)	117.80(13)	[117.71(13)]
Sc(1)–N(3)–Si(2)	127.64(9)	[128.8(1)]
Sc(1)–N(3)–C(6)	113.71(12)	[115.06(13)]
Si(2)–N(3)–C(6)	118.56(13)	[116.05(13)]



Scheme 2 Reactions of $[Sc(CH_2SiMe_3)_3(THF)_2]$ or $[ScPh_3(THF)_2]$ with diamino-pyridine or -amine ligand precursors. Additions were carried out in C_6H_6 at 7 °C (or in C_6D_6 at rt). See the text and the Experimental section for further details.

marginally different despite the quite different donor abilities of the atoms *trans* to the THF ligands in each case. Possibly the shorter $Sc–N_{amide}$ distances (avg. 2.024 Å) in **1** compared to those in **2** (avg. 2.044 Å) are the origin of the longer Sc–Cl distance in **1**.

Molecules of $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3** (Fig. 3) possess crystallographically-imposed C_i symmetry. There are two crystallographically-independent half-molecules of **3** in the asymmetric unit but there are no very significant differences between them. The $N_2N^{C3,Me}$ ligands adopt κ^3 coordination modes as found for the diamido-donor ligands in **1** and **2**. The geometry at the scandium centres is also approximately trigonal bipyramidal with the two amido nitrogens and one of the Cl ligands occupying the equatorial plane. The geometry at the amido nitrogens is again approximately trigonal planar. The Sc–Cl distances are somewhat longer than those in **1** or **2** as expected for such bridging groups.

At first sight the scandium centres in **3** appear to be a good deal more crowded than those in the other two compounds, but closer inspection shows that the conformations of the two $CH_2CH_2CH_2NSiMe_3$ 'arms' in each ligand is different. Thus the $SiMe_3$ group bonded to N(3) [or N(3A) at Sc(1A)] is oriented towards the other scandium, whereas that attached to N(1) [or N(1A)] bends away into available space. This greater flexibility appears to allow the two monomeric $Sc(N_2N^{C3,Me})Cl$ fragments to approach each other more comfortably than they would in the cases of the hypothetical THF-free moieties $Sc(N_2^{TMS}N_{py})Cl$ and $Sc(N_2N^{C2,TMS})Cl$, since in **1** and **2** the two $SiMe_3$ groups are oriented 'forwards' [*i.e.* towards Cl(1)] in each case. The 'twisted' conformation of the $N_2N^{C3,Me}$ ligands found in the solid state for **3** explains fully the low temperature solution NMR data described above. In related crystallographic studies[19] we have found that in both $[Zr(N_2N^{C3,Me})Cl_2]$ and $[Zr(N_2N^{C3,Me})(CH_2Ph)_2]$ the $CH_2CH_2CH_2NSiMe_3$ 'arms' of $N_2N^{C3,Me}$ also adopt similar conformations to those in **3** and so this feature is not therefore just attributable to the comparatively small covalent radius of scandium.

Scheme 2 summarises the syntheses of organo-scandium compounds supported by the various diamido-donor ligands. Protonolysis routes from $[Sc(CH_2SiMe_3)_3(THF)_2]$[21] and, in one instance, $[ScPh_3(THF)_2]$[22] were chosen so as to avoid needing to access the lithiated $N_2^{Ar}N_{py}$ (Ar = Tol or Mes) ligands for the reasons mentioned above.

Reactions of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with $H_2N_2^{R}N_{py}$ (R = $SiMe_3$, Tol or Mes) in benzene at 7 °C proceed smoothly to form the corresponding alkyl derivatives $[Sc(N_2^{R}N_{py})(CH_2SiMe_3)(THF)]$ (**4**–**6**) in 57–82% yields. For comparison, the reaction of $LiCH_2SiMe_3$ with $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1** was carried out on the NMR tube scale in C_6D_6 at room temperature. After 30 min, **4** was formed in quantitative yield as the only organometallic product. The formation of other diamido-donor-supported scandium alkyl complexes by chloride ligand metathesis was not attempted, although this might well provide a useful alternative route to the organoscandium complexes. The reaction of $H_2N_2^{TMS}N_{py}$ with the triphenyl complex $[ScPh_3(THF)_2]$ afforded the expected product, namely $[Sc(N_2^{TMS}N_{py})Ph(THF)]$ (**7**), in the slightly lower yield of 49%. But this compound, like the starting material $[ScPh_3(THF)_2]$, is thermally unstable at room temperature, quite rapidly decomposing to unknown products and benzene. For this reason it was decided not to prepare other phenyl scandium derivatives in this study.

Scheme 2 also summarises the reactions of the protonated forms of the other diamido-amine donor ligands with $[Sc(CH_2SiMe_3)_3(THF)_2]$. The reactions with the protonated two-carbon linker ligands $H_2N_2N^{C2,R}$ yielded $[Sc(N_2N^{C2,R})(CH_2SiMe_3)(THF)]$ (R = Me **8** or $SiMe_3$**9**) in *ca.* 50% yields as very soluble pale yellow or white solids. Reaction of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with the three-carbon protonated ligands $H_2N_2N^{C3,R}$ (Scheme 2) gave no tractable product for R = Me. With the N-$SiMe_3$-functionalised $H_2N_2N^{C3,TMS}$ a product $[Sc(N_2N^{C3,TMS})(CH_2SiMe_3)(THF)]$ **10** could be observed (with concomitant evolution of $SiMe_4$) on the NMR tube scale in C_6D_6 but could not be made on a preparative scale.

The NMR spectra of **4**–**9** are fully consistent with the structures proposed in Scheme 2. Resonances attributed to diamido-donor ligands, coordinated THF, and either CH_2SiMe_3 or Ph (for **7**) groups are readily visible in the ^1H and ^{13}C NMR spectra. The THF ligand OCH_2 protons (*i.e.* adjacent to oxygen) in the alkyl complexes of the amide N-arylated ligands $N_2^{Ar}N_{py}$ (*i.e.* **5** and **6**) appear somewhat more upfield of those of the amide N-$SiMe_3$-functionalised ligands (*i.e.* **4**, **8** and **9**). This is attributed to anisotropic shielding effects from the tolyl or mesityl aromatic rings for these ligands. This feature is supported by the X-ray structure of $[Sc(N_2^{Mes}N_{py})(CH_2SiMe_3)(THF)]$ **6** (Fig. 4; selected bond lengths and angles are listed in Table 4).

Table 4 Selected bond distances (Å) and angles (°) for $[Sc(N_2^{Mes}N_{py})(CH_2SiMe_3)(THF)]$ **6**

Sc(1)–N(1)	2.090(3)	Sc(1)–C(28)	2.295(3)
Sc(1)–N(2)	2.281(3)	Sc(1)–O(1)	2.222(2)
Sc(1)–N(3)	2.018(3)		
N(1)–Sc(1)–N(2)	82.5(1)	N(2)–Sc(1)–C(28)	93.8(1)
N(1)–Sc(1)–N(3)	98.1(1)	N(2)–Sc(1)–O(1)	171.29(9)
N(1)–Sc(1)–C(28)	148.9(1)	N(3)–Sc(1)–C(28)	112.4(1)
N(1)–Sc(1)–O(1)	92.2(1)	N(3)–Sc(1)–O(1)	102.2(1)
N(2)–Sc(1)–N(3)	85.4(1)	C(28)–Sc(1)–O(1)	87.2(1)

Table 5 Selected bond distances (Å) and angles (°) for $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]$ **11**

Sc(1)–N(1)	2.201(2)	Sc(1)–N(3)	2.280(2)
Sc(1)–N(1A)	2.285(2)	Sc(1)–C(24)	2.248(2)
Sc(1)–N(2)	2.064(2)		
N(1)–Sc(1)–N(1A)	81.74(8)	N(1A)–Sc(1)–N(3)	160.41(7)
N(1)–Sc(1)–N(2)	99.66(8)	N(2)–Sc(1)–N(3)	81.76(7)
N(1A)–Sc(1)–N(2)	103.45(7)	N(1)–Sc(1)–C(24)	141.23(8)
N(1)–Sc(1)–N(3)	78.75(7)	N(1A)–Sc(1)–C(24)	99.60(8)
N(3)–Sc(1)–C(24)	94.48(9)	N(2)–Sc(1)–C(24)	117.27(9)
Sc(1)–N(1)–Sc(1A)	98.26(8)	C(1)–N(1)–C(10)	116.0(2)
Sc(1)–N(1)–C(1)	108.34(14)	Sc(1)–N(2)–C(3)	118.5(2)
Sc(1A)–N(1)–C(1)	110.99(14)	Sc(1)–N(2)–C(17)	126.6(2)
Sc(1)–N(1)–C(10)	107.45(14)	C(3)–N(2)–C(17)	114.7(2)
Sc(1A)–N(1)–C(10)	114.06(14)		

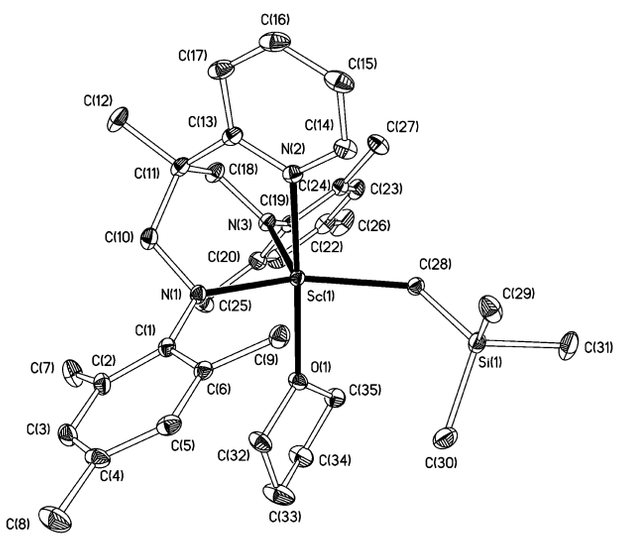


Fig. 4 Molecular structure of $[Sc(N_2^{Mes}N_{py})(CH_2SiMe_3)(THF)]$ **6**. Displacement ellipsoids are drawn at the 20% probability level. H atoms and residual Et_2O molecule of crystallisation omitted for clarity.

The scandium centre in **6** again adopts a trigonal bipyramidal geometry with the pyridyl and THF donors occupying axial coordination sites. The distances and angles in **6** are fairly comparable to those in the related compound $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1** discussed above. The Sc–C distance of 2.295(3) is well within the expected ranges.[20] The $Sc–N_{amide}$ distances of 2.018(3) and 2.09(3) Å are significantly different from each other (in **1** they are *ca.* 2.024 Å and equivalent within error). This is possibly associated with the orientation of the alkyl $SiMe_3$ substituent which orients itself more towards the mesityl group bonded to N(1) [which in turn has the longer bond length to Sc(1)].

On one occasion a few diffraction-quality crystals of the highly insoluble dimer $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]$ **11** were obtained. The molecular structure is shown in Fig. 5 and selected bond lengths and angles are listed in Table 5. The compound **11** is the THF-free version of $[Sc(N_2^{Tol}N_{py})(CH_2SiMe_3)(THF)]$ **5** which, by analogy with **6**, is assumed to

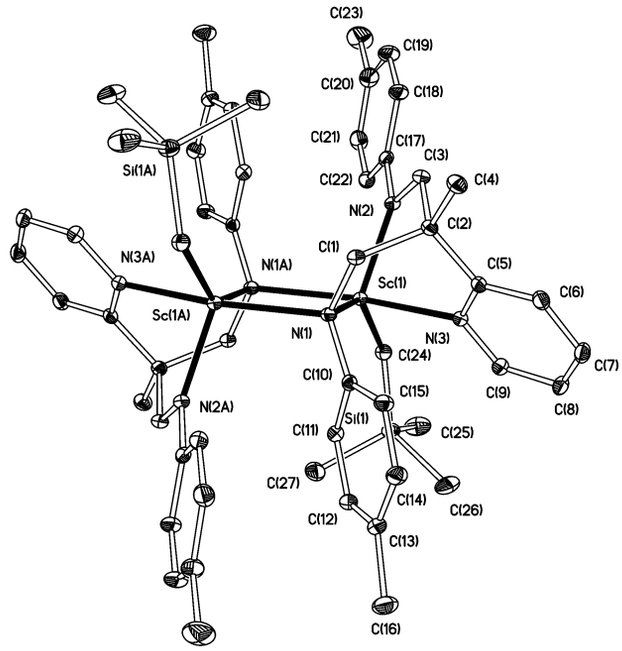


Fig. 5 Molecular structure of $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]$ **11**. Displacement ellipsoids are drawn at the 20% probability level. H atoms and residual toluene molecules of crystallisation omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $[2 - x, -y, 1 - z]$.

be monomeric. Unlike THF-free, dimeric $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3** in which the otherwise four-coordinate scandium atoms are bridged by Cl ligands, in **11** they are bridged by one of the amido nitrogen atoms of each $N_2^{Tol}N_{py}$ ligand. The scandium centres again possess trigonal bipyramidal geometries with [at Sc(1)] the axial sites being occupied by N(1A) and N(3), the $N_{pyridyl}$ donor. The equatorial sites are taken up by one terminal and one bridging amido nitrogen [namely N(2) and N(1), respectively] and the CH_2SiMe_3 ligand itself. The Sc(1)–N(1A) (axial) bond length of 2.285(2) is nearly 0.1 Å longer than Sc(1)–N(1) (equatorial) implying that the former is more dative in nature. A similar trend in the Sc–Cl distances was seen in dinuclear **3** above and is consistent with the general observation that anionic donors in these d^0 MX_3L_2-type systems prefer equatorial coordination sites.[23]

Conclusions

We have employed a range of diamido-donor ligands in the context of developing new organometallic and coordination chemistry of scandium. Such compounds are fairly straightforward to prepare, but there are clear dependencies on the backbone chain length and amino N-substituent of the diamido-amine ligands $N_2N^{Cn,R}$ (n = 2 or 3, R = Me or $SiMe_3$). We are continuing to explore the reactivity of the new compounds and ligands reported herein and also those in Charts 1 and 2, and will report on these studies, along with related work for the heavier Group 3 and lanthanide elements, in due course.

Experimental

General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon

valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H}, and ^{13}C NMR spectra were recorded on Varian Unity Plus 500, Bruker AC 200 and Varian Mercury-VX spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of NOE, DEPT-135, DEPT-90, DEPT-45, and two dimensional ^{1}H–^{1}H and ^{13}C–^{1}H NMR experiments. All spectra were referenced internally to residual protio-solvent (^{1}H) 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 Hz. Infrared spectra were prepared as Nujol mulls between NaCl or KBr plates or as KBr pellets and were recorded on Perkin-Elmer 1600 and 1710 series spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory, the Service Commun de Microanalyse at Strasbourg or Mikroanalytisches Labor Pascher, Germany. Despite all of the compounds being spectroscopically pure, several of them gave carbon elemental analyses that were consistently and persistently low. We attribute this to incomplete sample combustion and carbide formation.

Literature preparations

The compounds $[Sc(CH_2SiMe_3)_3(THF)_2]$,[21] $[ScPh_3(THF)_2]$,[22] $H_2N_2^{TMS}N_{py}$,[13] $Li_2N_2^{TMS}N_{py}$,[13] $H_2N_2^{Mes}N_{py}$,[14] $H_2N_2N^{C2,TMS}$,[16] $Li_2N_2N^{C2,TMS}$,[16] $H_2N_2N^{C2,Me}$,[15] $Li_2N_2N^{C2,Me}$,[19] $H_2N_2N^{C3,TMS}$,[19] $Li_2N_2N^{C3,TMS}$,[19] $H_2N_2N^{C3,Me}$,[19] and $Li_2N_2N^{C3,Me}$,[19] were prepared as reported previously.

$H_2N_2^{Tol}N_{py}$

A Schlenk flask was charged with MeC(2-C_5H_4N)(CH_2NH_2)$_2$ (2.07 g, 12.5 mmol),[13] 4-bromotoluene (4.27 g, 25 mmol), [Pd_2(dba)$_3$] (0.17 g, 0.19 mmol, dba = dibenzylideneacetone), racemic BINAP (0.29g, 0.47 mmol) and NaO^{t}Bu (5.40 g, 56.2 mmol) which were suspended in toluene (150 ml). After stirring the reaction mixture at 110 °C for 24 h, the volatiles were removed *in vacuo* and the brown residue redissolved in Et_2O (75 ml). The resulting solution was washed with H_2O (3 × 30 ml) and then with a saturated aqueous solution of NaCl (3 × 30 ml). After drying over $MgSO_4$ and removal of the volatiles the resulting pale brown material was extracted into pentane (3 × 5 ml). After storing at −30 °C for 24 h, $H_2N_2^{Tol}N_{py}$ crystallized as a pale yellow solid. Yield 66%.

^{1}H NMR data ($CDCl_3$, 200.0 MHz, 298 K): 8.65 (1 H, ddd, H^6, ^3J = 4.8, ^4J = 1.9, ^5J = 1.0 Hz), 7.68 (1 H, dt, H^4, ^3J = 7.4, ^4J = 1.9 Hz), 7.41 (1 H, m, H^3), 7.21 (1 H, m, H^5), 6.99 (4 H, d, *o*-C_6H_4Me, ^3J = 8.1 Hz), 6.56 (4 H, d, *m*-C_6H_4Me, ^3J = 8.1 Hz), 4.17 (2 H, s, NH), 3.59 (2 H, d, CH*H*, ^2J = 12.2 Hz), 3.53 (2 H, d, C*H*H, ^2J = 12.2 Hz), 2.25 (6 H, s, C_6H_4*Me*), 1.53 (3 H, s, Me of $N_2^{Tol}N_{py}$). ^{13}C{^{1}H} NMR data ($CDCl_3$, 52.3 MHz, 298 K): 164.4 (C^2), 148.9 (C^6), 146.7 (*ipso*-C_6H_4Me), 136.7 (C^4), 129.7 (*o*-C_6H_4Me), 126.5 (*p*-C_6H_4Me), 121.3, 121.6 (C^{3,5}), 113.3 (*m*-C_6H_4Me), 52.8 [(CH_2NTol)], 45.6 [*C*(CH_2NTol)$_2$], 23.2 (Me of $N_2^{Tol}N_{py}$), 23.2 (C_6H_4*Me*). Anal. Found (calc. for $C_{23}H_{27}N_3$): C 79.8 (80.0), H 8.0 (7.9), N 11.9 (12.2)%.

$[Sc(N_2^{TMS}N_{py})Cl(THF)]$ (1)

$ScCl_3$ (200 mg, 1.32 mmol) was slurried in THF (20 ml) and cooled to −78 °C. To this vigorously stirred solution was added a solution of $Li_2N_2^{TMS}N_{py}$ (425 mg, 1.32 mmol) in THF (20 ml) dropwise over 10 min. The reaction was allowed to warm to rt and stirred for a further 2 h, after which time all of the $ScCl_3$ had dissolved. The solvent was removed under reduced pressure and the solid residue extracted with benzene (20 ml), filtered, and the solvent removed under reduced pressure to afford **1** as a pale yellow solid. Yield 358 mg (59%). Crystals suitable for X-ray diffraction were grown from a saturated solution in hexanes at −30 °C over 18 h.

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 9.60 [1 H, ddd, H^6, ^3J (H^{5}H^6) = 5.4 Hz, ^4J (H^{4}H^6) = 1.9 Hz, ^5J (H^{3}H^6) = 0.7 Hz], 7.03 [1 H, td, H^4, ^3J (H^{3}H^{4}H^5) = 6.8 Hz, ^4J (H^{4}H^6) = 1.7 Hz], 6.95 [1 H, d, H^3, ^3J (H^{3}H^4) = 8.1 Hz], 6.49 [1 H, ddd, H^5, ^3J = 7.6 Hz, ^3J = 5.5 Hz, ^4J (H^{3}H^5) = 1.1 Hz], 4.14 (4 H, t, OCH_2, ^3J = 6.6 Hz), 3.76 (2 H, d, C*H*H, ^2J = 12.2 Hz), 3.17 (2 H, d, CH*H*, ^2J = 12.2 Hz), 1.30 (4 H, m, OCH_2CH_2), 1.16 (3 H, s, Me of $N_2^{TMS}N_{py}$), 0.04 (18 H, s, $SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 162.4 (C^2), 147.8 (C^6), 138.5 (C^4), 121.1 (C^5), 120.5 (C^3), 72.3 (OCH_2), 62.4 (CH_2NSiMe_3), 48.8 [$C(CH_2NSiMe_3)_2$], 25.3 (OCH_2CH_2), 24.7 (Me of $N_2^{TMS}N_{py}$), 0.2 ($SiMe_3$). IR data (KBr plates, Nujol, cm^{-1}): 2672 (w), 1600 (m), 1568 (w), 1296 (w), 1258 (s), 1242 (s), 1134 (w), 1088 (m), 1066 (s), 1018 (m), 922 (s), 894 (s), 880 (m), 826 (s), 776 (m), 722 (w). Anal. Found (calc. for $C_{19}H_{37}ClN_3OScSi_2$): C 49.1 (49.6), H 8.3 (8.1), N 9.7 (9.1)%.

$[Sc(N_2N^{C2,TMS})Cl(THF)]$ (2)

$ScCl_3$ (200 mg, 1.32 mmol) was slurried in THF (15 ml) and cooled to −78 °C. To this vigorously stirred solution was added a solution of $Li_2N_2N^{C2,TMS}$ (438 mg, 1.32 mmol) in THF (15 ml) dropwise over 10 min. The reaction was allowed to warm to rt and stirred for a further 2 h, after which time all of the $ScCl_3$ had dissolved. The solvent was removed under reduced pressure and the solid residue extracted with benzene (20 ml), filtered, and the solvent removed under reduced pressure. Recrystallisation from a saturated pentane solution afforded **2** as a white solid. Yield 173 mg (28%). Crystals suitable for X-ray diffraction were grown from a saturated pentane solution at −30 °C over 4 days.

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 3.93 (2 H, m, NCH_2), 3.69 (4 H, br. s, OCH_2), 2.98 (2 × 2 H, overalapping 2 × m, NCH_2), 2.35 (2 H, d, NCH_2, ^2J = 11.8 Hz), 1.22 (4 H, m, OCH_2CH_2), 0.28 (9 H, s, amine-$SiMe_3$), 0.14 (18 H, s, amide-$SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 72.1 (OCH_2), 61.5 (NCH_2), 47.5 (NCH_2), 25.3 (OCH_2CH_2), 1.4 (amide-$SiMe_3$), −1.2 (amine-$SiMe_3$). IR data (KBr pellet, cm^{-1}): 2952 (s), 2896 (m), 2838 (m), 1586 (w), 1448 (m), 1400 (m), 1342 (m), 1250 (s), 1072 (s), 1030 (m), 938 (s), 912 (s), 786 (m), 754 (m), 680 (m), 618 (w), 508 (w), 450 (w), 436 (w), 402 (w). Anal. Found (calc. for $C_{17}H_{43}ClN_3OScSi_3$): C 42.4 (43.4), H 9.2 (9.2), N 9.1 (8.9)%. Accurate mass FI-MS for fragment $[Sc(N_2N^{C2,TMS})Cl]^+$: Found (calc. for $C_{13}H_{35}ClN_3ScSi_3$): 397.1392 (397.1386).

$[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ (3)

$ScCl_3$ (200 mg, 1.32 mmol) was slurried in THF (20 ml) and cooled to −78 °C for the dropwise addition of $Li_2N_2N^{C3,Me}$ (412 mg, 1.32 mmol) in THF (20 ml). The reaction was allowed to warm to rt and stirred for a further 3 h. The solvent was removed under reduced pressure, the residue extracted with benzene (2 × 20 ml) and filtered to remove LiCl. The solvent was removed under reduced pressure to afford **3** as a white solid. Yield 389 mg (80%). Crystals suitable for X-ray diffraction were grown by the slow cooling of a saturated solution in hot hexanes to −30 °C over 18 h.

^{1}H NMR data (toluene-d$_8$, 500.0 MHz, 298 K): 3.53 (4 H, br. s, CH_2), 3.35 (4 H, br. s, CH_2), 2.73 (2 × 4 H, 2 × overlapping br. s, CH_2), 2.14 (6 H, s, NMe), 1.52 (4 H, br. s, CH_2), 1.42 (4 H, br. s, CH_2), 0.29 (36 H, s, $SiMe_3$). ^{1}H NMR data (toluene-d$_8$, 500.0 MHz, 213 K): 3.89 (2 H, t, CH_2, ^2J = 13.2 Hz), 3.57 (2 H, t, CH_2, ^2J = 14.7 Hz), 3.41 (2 H, t, CH_2, ^2J = 12.4 Hz), 3.14–3.01 (6 H, overlapping m, CH_2), 2.01 (6 H, s, NMe), 1.70–1.65 (4 H, overlapping m, CH_2), 1.39–1.21 (8 H, overlapping m, CH_2), 0.41 (18 H, s, $SiMe_3$), 0.39 (18 H, s, $SiMe_3$). ^{13}C{^{1}H} NMR data (toluene-d^8, 125.7 MHz, 213 K): 62.2 (CH_2), 58.9 (CH_2), 47.1

(CH_2), 45.4 (CH_2), 44.1 (NMe), 30.6 (CH_2), 29.7 (CH_2), 1.8 ($SiMe_3$), 1.6 ($SiMe_3$). IR data (KBr pellet, cm^{-1}): 2854 (s), 2812 (s), 2740 (w), 2664 (w), 1922 (w), 1870 (w), 1592 (s), 1488 (s), 1438 (m), 1396 (w), 1242 (s), 1208 (s), 1174 (s), 1004 (s), 950 (s), 918 (m), 794 (m), 744 (m), 694 (m), 680 (m), 626 (w), 610 (w), 530 (m), 510 (w), 464 (w), 446 (w), 424 (w), 408 (m). Anal. Found (calc. for $C_{26}H_{66}Cl_2N_6Sc_2Si_4$): C 42.4 (42.4), H 9.3 (9.1), N 11.4 (11.4)%. EI-MS (*m*/*z*): 367 (30%) [½ M]$^+$, 352 (30%) [½ M − Me]$^+$, 332 (20%) [½ M − Cl]$^+$, 221 (15%) [½ M − 2 $SiMe_3$]$^+$.

[Sc($N_2^{TMS}N_{py}$)(CH_2SiMe_3)(THF)] (4) from $H_2N_2^{TMS}N_{py}$ and [Sc(CH_2SiMe_3)$_3$(THF)$_2$]

[Sc(CH_2SiMe_3)$_3$(THF)$_2$] (200 mg, 0.473 mmol) was dissolved in benzene (20 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2^{TMS}N_{py}$ (147 mg, 0.473 mmol) in benzene (20 ml). The resulting pale yellow solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **4** as a pale yellow solid. Yield 138 mg (57%).

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 9.02 [1 H, d, H^6, ^3J (H^5H^6) = 4.6 Hz], 7.06 [1 H, td, H^4, ^3J ($H^3H^4H^5$) = 7.5 Hz, ^4J (H^4H^6) = 1.2 Hz], 6.98 [1 H, dd, H^3, ^3J (H^3H^4) = 8.3 Hz, ^4J (H^3H^5) = 1.0 Hz], 6.60 [1 H, td, H^5, ^3J ($H^4H^5H^6$) = 5.4 Hz, ^4J (H^3H^5) = 1.3 Hz], 4.00 (4 H, br. s, OCH_2), 3.61 (2 H, d, NC*H*H, ^2J = 12.2 Hz), 3.17 (2 H, d, NCH*H*, ^2J = 12.2 Hz), 1.34 (4 H, br. s, OCH_2CH_2), 1.15 (3 H, s, Me of $N_2^{TMS}N_{py}$), 0.42 (9 H, s, CH_2Si*Me*$_3$), 0.04 (18 H, s, $NSiMe_3$), −0.39 (2 H, s, C*H*$_2$$SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 163.3 (C^2), 146.2 (C^6), 138.8 (C^4), 120.8 (C^3), 120.6 (C^5), 71.4 (OCH_2), 62.5 (CH_2NSiMe_3), 48.5 [$C(CH_2NSiMe_3)_2$], 25.3 (OCH_2CH_2), 25.0 (Me of $N_2^{TMS}N_{py}$), 5.0 (CH_2Si*Me*$_3$), 0.6 ($NSiMe_3$), 0.2 (CH_2SiMe_2). IR data (KBr pellet, cm^{-1}): 2946 (s), 2892 (m), 2794 (m), 2732 (w), 2674 (w), 1602 (m), 1570 (w), 1474 (m), 1386 (m), 1366 (w), 1366 (w), 1346 (w), 1240 (s), 1160 (w), 1134 (m), 1070 (s), 1026 (m), 994 (w), 856 (s), 826 (s), 778 (m), 748 (m), 672 (m), 644 (w), 586 (m), 624 (w), 586 (w), 490 (w), 426 (w). Anal. Found (calc. for $C_{23}H_{48}N_3OScSi_3$): C 52.1 (54.0), H 9.6 (9.5), N 8.4 (8.2)%. Accurate mass EI-MS for fragment [Sc($N_2^{TMS}N_{py}$)]$^+$: Found (calc. for $C_{15}H_{29}N_3ScSi_2$) 352.1450 (352.1459).

[Sc($N_2^{TMS}N_{py}$)(CH_2SiMe_3)(THF)] (4) from 1 and $LiCH_2SiMe_3$ (NMR tube scale)

A solution of [Sc($N_2^{TMS}N_{py}$)Cl(THF)] **1** (21.6 mg, 0.047 mmol) and $LiCH_2SiMe_3$ (4.4 mg, 0.047 mmol) in C_6D_6 were transferred to a 5 mm J. Young NMR tube. The ^{1}H NMR spectrum after 30 min showed quantitative formation of [Sc($N_2^{TMS}N_{py}$)(CH_2SiMe_3)(THF)] **4**.

[Sc($N_2^{Tol}N_{py}$)(CH_2SiMe_3)(THF)] (5)

[Sc(CH_2SiMe_3)$_3$(THF)$_2$] (200 mg, 0.444 mmol) was dissolved in benzene (20 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2^{Tol}N_{py}$ (153 mg, 0.444 mmol) in benzene (20 ml). The resulting pale yellow solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **5** as a yellow solid. Yield 165 mg (68%).

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 8.86 [1 H, dd, H^6, ^3J (H^5H^6) = 5.4 Hz, ^4J (H^4H^6) = 1.5 Hz], 7.10 (4 H, d, *o*-C_6H_4Me, ^3J = 8.3 Hz), 7.00 [1 H, td, H^4, ^3J ($H^3H^4H^5$) = 7.8 Hz, ^4J (H^4H^6) = 2.0 Hz], 6.91 [1 H, d, H^3, ^3J (H^3H^4) = 8.3 Hz], 6.78 (4 H, d, *m*-C_6H_4Me, ^3J = 8.3 Hz), 6.52 [1 H, ddd, H^5, ^3J (H^4H^5) = 7.8 Hz, ^3J (H^5H^6) = 5.4 Hz, ^4J (H^3H^5) = 1.5 Hz], 3.76 (4 H, t, OCH_2, ^3J = 6.3 Hz), 3.35 (2 H, d, C*H*H, ^2J = 12.2 Hz), 3.07 (2 H, d, CH*H*, ^2J = 12.2 Hz), 2.23 (6 H, s, C_6H_4*Me*), 1.26 (3 H, s, Me of $N_2^{Tol}N_{py}$), 0.92 (4 H, m, OCH_2CH_2), 0.47 (9 H, s, $SiMe_3$), 0.18 (2 H, s, C*H*$_2$$SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 163.0 (C^2), 152.7 (*ipso*-C_6H_4Me), 146.2 (C^6), 139.0 (C^4), 129.8 (*o*-C_6H_4Me), 123.4 (*p*-C_6H_4Me), 121.7 (C^5), 121.4 (C^3), 112.5 (*m*-C_6H_5Me), 71.6 (OCH_2), 62.3 (CH_2NSiMe_3), 44.1 [$C(CH_2NSiMe_3)_2$], 26.1 (Me of $N_2^{Tol}N_{py}$), 25.0 (OCH_2CH_2), 20.7 (C_6H_4*Me*), 4.4 ($SiMe_3$), −0.1 (CH_2SiMe_3). IR data (KBr pellet, cm^{-1}): 2944 (s), 2916 (s), 2858 (s), 2804 (s), 2734 (w), 2558 (w), 1854 (w), 1610 (s), 1570 (m), 1554 (m), 1504 (s), 1476 (m), 1388 (m), 1288 (s), 1262 (s), 1184 (m), 1146 (m), 1114 (m), 1060 (w), 972 (w), 864 (s), 806 (s), 770 (s), 752 (w), 678 (w), 648 (w), 606 (w), 588 (w), 514 (w), 472 (w). Anal. Found (calc. for $C_{31}H_{44}N_3OScSi$): C 67.6 (67.9), H 7.6 (8.1), N 7.7 (7.7)%.

[Sc($N_2^{Mes}N_{py}$)(CH_2SiMe_3)(THF)] (6)

[Sc(CH_2SiMe_3)$_3$(THF)$_2$] (200 mg, 0.444 mmol) was dissolved in benzene (20 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2^{Mes}N_{py}$ (178 mg, 0.444 mmol) in benzene (20 ml). The resulting pale yellow solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **6** as a pale yellow solid. Yield 219 mg (82%). Crystals suitable for X-ray diffraction study were grown from a saturated solution of **6** in diethyl ether on cooling to −20 °C for 18 h.

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 9.24 [1 H, dd, H^6, ^3J (H^5H^6) = 5.4 Hz, ^4J (H^4H^6) = 2.0 Hz], 7.11 [1 H, td, H^4, ^3J ($H^3H^4H^5$) = 7.8 Hz, ^4J (H^4H^6) = 2.0 Hz], 6.97 [1 H, d, H^3, ^3J (H^3H^4) = 8.3 Hz], 6.90 (4 H, s $C_6H_2Me_3$), 6.75 [1 H, ddd, H^5, ^3J (H^5H^6) = 5.4 Hz, ^3J (H^4H^5) = 7.3 Hz, ^4J (H^3H^5) = 1.0 Hz], 4.01 (2 H, d, C*H*H, ^2J = 11.7 Hz), 3.46 (4 H, t, OCH_2, ^3J = 6.3 Hz), 2.88 (2 H, d, CH*H*, ^2J = 11.7 Hz), 2.31 (12 H, s, *o*-$C_6H_2Me_3$), 2.18 (6 H, s, *p*-$C_6H_2Me_3$), 1.15 (3 H, s, Me of $N_2^{Mes}N_{py}$), 1.05 (4 H, m, OCH_2CH_2), 0.27 (9 H, s, $SiMe_3$), −0.51 (2 H, s, C*H*$_2$$SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 163.8 (C^2), 151.4 (*ipso*-$C_6H_2Me_3$), 146.8 (C^6), 138.7 (C^4), 133.5 (*o*-$C_6H_2Me_3$), 130.2 (*p*-$C_6H_2Me_3$), 129.5 (*m*-$C_6H_2Me_3$), 121.1 (C^5), 121.0 (C^3), 70.5 (OCH_2), 66.8 (CH_2NSiMe_3), 46.7 [$C(CH_2NSiMe_3)_2$], 25.4 (OCH_2CH_2), 25.1 (Me of $N_2^{Mes}N_{py}$), 20.9 (*p*-$C_6H_2Me_3$), 20.1 (*o*-$C_6H_2Me_3$), 4.5 ($SiMe_3$), 0.0 (CH_2SiMe_3). IR data (KBr pellet, cm^{-1}): 2946 (s), 2914 (s), 2856 (s), 2730 (w), 2662 (w), 1598 (s), 1570 (m), 1476 (s), 1436 (m), 1382 (w), 1358 (w), 1340 (w), 1296 (m), 1230 (s), 1154 (m), 1140 (m), 1120 (w), 1096 (m), 1056 (m), 1018 (m), 992 (w), 956 (w), 854 (s), 816 (w), 782 (m), 748 (m), 728 (w), 706 (w), 694 (w), 680 (m), 646 (w), 604 (w), 560 (w), 534 (w), 442 (w), 406 (w). Anal. Found (calc. for $C_{35}H_{52}N_3OScSi$): C 69.3 (69.6), H 8.3 (8.6), N 6.3 (6.9)%.

[Sc($N_2^{TMS}N_{py}$)Ph(THF)] (7)

[$ScPh_3$(THF)$_2$] (200 mg, 0.476 mmol) was dissolved in benzene (15 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2^{TMS}N_{py}$ (147 mg, 0.476 mmol) in benzene (15 ml). The resulting yellow solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **7** as a thermally sensitive, waxy yellow solid. Yield 113 mg (49%).

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 8.31 [1 H, ddd, H^6, ^3J (H^5H^6) = 5.4 Hz, ^4J (H^4H^6) = 1.8 Hz, ^5J (H^3H^6) = 1.2 Hz], 8.20 (2 H, dd, *o*-C_6H_5, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 7.50 (2 H, t, *m*-C_6H_5, ^3J = 7.4 Hz), 7.38 (1 H, td, *p*-C_6H_5, ^3J = 7.4 Hz, ^4J = 1.5 Hz), 6.94–6.89 (2 H, overlapping m, H^3, H^4), 6.17 (1 H, m, H^5), 3.89 (4 H, br. s, OCH_2), 3.78 (2 H, d, C*H*H, ^2J = 12.2 Hz), 3.29 (2 H, d, CH*H*, ^2J = 12.2 Hz), 1.22 (4 H, br. s, OCH_2CH_2), 1.20 (3 H, s, Me of $N_2^{TMS}N_{py}$), 0.13 (18 H, s, $SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 125.7 MHz, 298 K): 163.1 (C^2), 147.5 (C^6), 138.2 (C^4), 137.1 (*o*-C_6H_5), 126.9 (*m*-C_6H_5), 126.0 (*p*-C_6H_5), 120.8 (C^5), 120.3 (C^3), 72.0 (OCH_2), 62.6 (CH_2NSiMe_3), 48.7 [$C(CH_2NSiMe_3)_2$], 25.2 (OCH_2CH_2), 25.1 (Me of $N_2^{TMS}N_{py}$), 0.5 ($SiMe_3$), not observed (*ipso*-C_6H_5). IR data (NaCl plates, Nujol, cm^{-1}): 3196 (w), 3038 (w), 1600 (s), 1570 (m), 1350 (w), 1290 (w), 1246 (s), 1162 (w), 1134 (w), 1070 (m), 1052 (m), 1016 (w), 990 (w), 954 (w), 828 (s), 778 (w), 746 (m), 712 (w), 674 (w),

Table 6 X-Ray data collection and processing parameters for $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ **1**, $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **2**, $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **3**, $[Sc(N_2^{Mes}N_{py})(CH_2SiMe_3)(THF)]\cdot 0.5(Et_2O)$ **6**·0.5(Et_2O) and $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]\cdot 4(C_7H_8)$ **11**·4(C_7H_8)

	1	**2**	**3**	**6**·0.5(Et_2O)	**11**·4(C_7H_8)
Formula	$C_{19}H_{37}ClN_3OScSi_2$	$C_{17}H_{43}ClN_3OScSi_3$	$C_{26}H_{66}Cl_2N_6Sc_2Si_4$	$C_{35}H_{52}N_3OScSi\cdot 0.5(C_4H_{10}O)$	$C_{54}H_{62}N_6Sc_2Si_2\cdot 4(C_7H_8)$
Formula weight	460.11	470.22	736.02	640.93	1319.86
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	19.1126(4)	10.5815(2)	10.6049(2)	9.2011(2)	10.7764(1)
b/Å	13.1361(2)	21.2366(4)	12.1528(2)	10.1961(3)	15.7709(2)
c/Å	19.5217(4)	12.6644(3)	16.7295(4)	20.9786(6)	22.4009(4)
α/°	90	90	79.9117(8)	93.499(5)	90
β/°	90	110.642(1)	77.1004(9)	102.357(5)	93.9372(5)
γ/°	90	90	77.1029(1)	103.593(5)	90
V/Å^3	4901.2(2)	2663.2(1)	2030.75(7)	1855.8(1)	3798.1(1)
Z	8	4	2	2	2
μ(Mo-Kα)/mm^{-1}	0.52	0.52	0.61	0.26	0.26
Total reflections	11 144	9223	17 186	10 528	16 705
Observed reflections[a]	3439	4148	6361	4972	4793
R[b], R_w[c]	0.0341, 0.0246	0.0395, 0.0312	0.0326, 0.0231	0.056, 0.087	0.0433, 0.0257

[a] For reflections with $I > 3\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = \sqrt{\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}}$.

712 (w). Anal. Found (calc. for $C_{25}H_{42}N_3OScSi_2$): C 54.6 (59.9), H 7.6 (8.4), N 8.2 (8.4)%.

$[Sc(N_2N^{C2,Me})(CH_2SiMe_3)(THF)]$ (8)

$[Sc(CH_2SiMe_3)_3(THF)_2]$ (200 mg, 0.444 mmol) was dissolved in benzene (20 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2N^{C2,Me}$ (116 mg, 0.444 mmol) in benzene (20 ml). The resulting pale yellow solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **8** as a pale yellow solid. Yield 110 mg (51%).

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 3.84 (4 H, t, OCH_2, ^3J = 6.8 Hz), 3.29 (2 H, ddd, NC*H*H, ^2J = 13.0 Hz, ^3J = 7.4 Hz, ^3J = 4.4 Hz), 3.09 (2 H, dt, NC*H*H, ^2J = 13.2 Hz, ^3J = 5.2 Hz), 2.69 (2 H, ddd, NCH*H*, ^2J = 11.4 Hz, ^3J = 5.8 Hz, ^3J = 4.4 Hz), 2.34 (2 H, ddd, NCH*H*, ^2J = 12.5 Hz, ^3J = 7.3 Hz, ^3J = 5.2 Hz), 2.28 (3 H, s, NMe), 1.28 (4 H, t, $OCH_2C\mathit{H}_2$, ^3J = 6.8 Hz), 0.32 (9 H, s, $CH_2Si\mathit{Me}_3$), 0.17 (18 H, s, $NSiMe_3$), −0.34 (2 H, s, $C\mathit{H}_2SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 75.5 MHz, 298 K): 71.1 (OCH_2), 61.4 (NCH_2), 45.9 (NCH_2), 44.3 (NMe), 25.6 ($OCH_2\mathit{C}H_2$), 5.1 ($CH_2Si\mathit{Me}_3$), 2.6 ($\mathit{C}H_2SiMe_3$), 2.2 ($NSiMe_3$). IR data (KBr pellet, cm^{-1}): 2948 (s), 2894 (m), 2842 (m), 2812 (m), 2680 (w), 1684 (w), 1594 (m), 1560 (m), 1460 (m), 1400 (w), 1384 (w), 1354 (w), 1242 (s), 1138 (w), 1068 (m), 928 (m), 820 (s), 820 (s), 744 (m), 670 (m), 624 (w), 612 (w), 586 (w), 546 (w), 444 (w), 440 (w), 432 (w), 418 (w). Anal. Found (calc. for $C_{19}H_{48}N_3OScSi_3$): C 49.9 (49.2), H 9.2 (9.1), N 10.4 (10.4)%. Accurate mass EI-MS for fragment $[Sc(N_2N^{C2,Me})]^+$: Found (calc. for $C_{11}H_{29}N_3ScSi_2$): 304.1456 (304.1459).

$[Sc(N_2N^{C2,TMS})(CH_2SiMe_3)(THF)]$ (9)

$[Sc(CH_2SiMe_3)_3(THF)_2]$ (147 mg, 0.326 mmol) was dissolved in benzene (20 ml) and cooled to 7 °C for the dropwise addition of $H_2N_2N^{C2,TMS}$ (104 mg, 0.326 mmol) in benzene (20 ml). The resulting colourless solution was allowed to warm to rt and stirred for 1 h. The volatiles were removed under reduced pressure to afford **9** as a white solid. Yield 79 mg (47%).

^{1}H NMR data (C_6D_6, 500.0 MHz, 298 K): 3.87 (4 H, br. s, OCH_2), 3.54 (2 H, t, NC*H*H, ^2J = 12.4 Hz), 2.98 (2 H, d, NCH*H*, ^2J = 14.2 Hz), 2.89 (2 H, t, NC*H*H, ^2J = 11.5 Hz), 2.33 (2 H, d, NCH*H*, ^2J = 11.5 Hz), 1.29 (4 H, t, $OCH_2C\mathit{H}_2$, ^3J = 6.6 Hz), 0.32 (9 H, s, $SiMe_3$), 0.19 (9 H, s, $SiMe_3$), 0.17 (18H, s, amide-$SiMe_3$), −0.36 (2 H, s, $C\mathit{H}_2SiMe_3$). ^{13}C{^{1}H} NMR data (C_6D_6, 75.5 MHz, 298 K): 71.0 (OCH_2), 60.5 (NCH_2), 47.5 (NCH_2), 26.0 ($OCH_2\mathit{C}H_2$), 5.8 ($SiMe_3$), 2.7 (amide-$SiMe_3$), 0.1 ($SiMe_3$), not observed ($\mathit{C}H_2SiMe_3$). IR data (KBr pellet, cm^{-1}): 2954 (s), 2844 (s), 1680 (w), 1448 (m), 1384 (w), 1346 (m), 1332 (w), 1250 (s), 1128 (w), 1072 (s), 1032 (s), 944 (s), 822 (s), 782 (m), 746 (m), 712 (w), 674 (m), 646 (w), 626 (w), 596 (w), 578 (w), 560 (w), 508 (w), 494 (w), 444 (m), 428 (m). Anal. Found (calc. for $C_{21}H_{52}N_3OScSi_4$): C 47.3 (48.5), H 9.8 (10.1), N 8.1 (8.1)%.

$[Sc(N_2N^{C3,TMS})(CH_2SiMe_3)(THF)]$ (10)

To a solution of $[Sc(CH_2SiMe_3)(THF)_2]$ (19.8 mg, 0.044 mmol) in C_6D_6 (0.5 ml) was added $H_2H_2N^{C3,TMS}$ (15.3 mg, 0.044 mmol) and then transferred to a 5 mm J. Young NMR tube. The ^{1}H NMR spectrum after 30 min showed resonances for $[Sc(N_2N^{C3,TMS})(CH_2SiMe_3)(THF)]$ **10** (assigned by analogy with those for **8** and **9**), $SiMe_4$ and a further equivalent of THF (in fast exchange with the coordinated THF of **10** on the NMR timescale). The compound decomposed into a complex mixture of unidentified products on removal of the volatiles under reduced pressure.

^{1}H NMR data (300.2 MHz, C_6D_6, 298 K): 3.60 (8 H, br. s, overlapping free and coordinated OCH_2), 3.42 (2 H, br. s, CH_2), 3.25 (2 H, br. s, CH_2), 3.02 (2 H, br. s, CH_2), 2.22 (2 H, br. s, CH_2), 1.98 (4 H, br. s, CH_2), 1.41 (8 H, br. s, overlapping free and coordinated $OCH_2C\mathit{H}_2$), 1.22 (9 H, s, $SiMe_3$), 1.20 (18 H, s, amide-$SiMe_3$), 0.1 (9 H, s, amine-$SiMe_3$), 0.0 (27 H, s, $SiMe_4$), −0.15 (2 H, s, $C\mathit{H}_2SiMe_3$).

Crystal structure determinations of $[Sc(N_2^{TMS}N_{py})Cl(THF)]$ 1, $[Sc(N_2N^{C2,TMS})Cl(THF)]$ 2, $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ 3, $[Sc(N_2^{Mes}N_{py})(CH_2SiMe_3)(THF)]\cdot 0.5(Et_2O)$ 6·0.5(Et_2O) and $[Sc_2(N_2^{Tol}N_{py})_2(CH_2SiMe_3)_2]\cdot 4(C_7H_8)$ 11·4(C_7H_8)

Crystal data collection and processing parameters are given in Table 6. Crystals were immersed in a film of inert oil on a glass fibre and transferred to a KappaCCD diffractometer. Data were collected at low temperature using Mo-Kα radiation; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs.[24] Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using SIR92.[25] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Carbon bound hydrogen atoms were placed geometrically and refined in a riding model. Non-hydrogen atoms were refined refined anisotropically. For **6**·0.5(Et_2O) and **11**·4(C_7H_8), residual electron density was modelled as solvent of crystallisation. Extinction corrections and weighting schemes were applied as appropriate. Crystallographic calculations were performed using SIR92,[25] the Nonius OpenMoleN package[26] and CRYSTALS.[27]

CCDC reference numbers 194287–194291.

See http://www.rsc.org/suppdata/dt/b2/b209382k/ for crystallographic data in CIF or other electronic format.

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