

Scandium and yttrium complexes of the diamide–diamine donor ligand (2-C₅H₄N)CH₂N(CH₂CH₂NSiMe₃)₂: chloride, primary and secondary amide, benzamidinate and alkyl functionalised derivatives

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Five- and six-coordinate scandium and yttrium complexes of the recently described diamide–diamine donor ligand N₂NN' (where H₂N₂NN' = (2-C₅H₄N)CH₂N{CH₂CH₂N(H)SiMe₃}₂) are described. Reaction of ScCl₃ with Li₂N₂NN' gave five-coordinate [ScCl(N₂NN')] **1** in excellent yield. The corresponding reaction with YCl₃ in tetrahydrofuran (thf) or pyridine (py) solution afforded “ate” complexes best described as [YCl(N₂NN')(L)]·1.5(LiCl) (L = thf **2** or py **3**). The two chloride complexes **1** and **2** are useful starting materials for primary and secondary amide, benzamidinate and alkyl complexes of Sc and Y supported by the N₂NN' ligand. Thus reaction of **1** or **2** with LiN(SiMe₃)₂·Et₂O, LiNMe₂ or LiNHR (R = ^tBu or Ar, where Ar = 2,6-C₆H₃Pr₂) gave the corresponding five-coordinate amide derivatives [M(NRR'')(N₂NN')] (M = Sc, R = R'' = SiMe₃ **4** or Me **6**, or R = H, R'' = ^tBu **8** or Ar **9**; M = Y, R = R'' = SiMe₃ **5**, or R = H, R'' = Ar **10**). The crystal structure of **5** is described. The σ-bond metathesis reaction of [Sc(NMe₂)(N₂NN')] **6** with Ar_FNH₂ (Ar_F = C₆F₅) gave the corresponding primary fluorenylamide derivative **7**. The reaction of **1** or **2** with Li[PhC(NSiMe₃)₂] gave the fluxional, six-coordinate benzamidinate derivatives [M{PhC(NSiMe₃)₂}(N₂NN')] (M = Sc **11** or Y **12**), the crystal structures of which are reported. Finally, reaction of **1** with LiCH₂SiMe₃ formed the alkyl derivative [Sc(CH₂SiMe₃)(N₂NN')] **13** in reasonable yield; the crystal structure of **13** is described.

Introduction

While there is an extensive “classic” coordination chemistry of scandium and yttrium in a wide range of ligand environments, the organometallic and organometallic-related chemistry of these Group 3 metals has generally been dominated by compounds with cyclopentadienyl and related ligands.¹ For example, Group 3 metal complexes incorporating the cyclopentadienyl ligand and its homologues can act as catalysts for polymerisation,² hydrogenation,³ hydroboration,⁴ hydrosilylation⁵ and hydroamination/cyclisation⁶ processes. Over the last five to ten years the organometallic and organometallic-related chemistry of scandium and yttrium in non-cyclopentadienyl environments has grown enormously. New (or renewed) ligand environments include the tetratolylporphyrins,⁷ tris(pyrazolyl)borates,⁸ variously functionalised benzamidinates,⁹ N₂P₂- and NP₂-donors,¹⁰ mixed amide–alkoxides,¹¹ oxazolinates,¹² and functionalised triazacyclononanes¹³ or related macrocycles.¹⁴

Of particular relevance to this contribution are Group 3 complexes supported by a range of di- and tri-dentate bis(amide) ligands.¹⁵ In addition, Scott and co-workers very recently described Group 3 complexes of certain tetradentate triamide–amine (“tren”) ligands, both as “ate” complexes **I** (Chart 1) and as halide-free, trigonal monopyramidal complexes **II** obtained upon high vacuum sublimation.¹⁶ Tren ligands have in general been extremely successful in developing p-block, early- to mid-transition metal, lanthanide and actinide chemistry.^{16,17} Despite these successes, however, as a trianionic moiety the versatility of this ligand is hampered in certain regards for developing new lanthanide, and Group 3 since there are no metal electrons remaining for binding additional anionic ligands in such M(tren) fragments.

As a kind of “dianionic tren” variant we have developed the diamide–diamine donor ligands (2-C₅H₄N)CH₂N(CH₂CH₂-

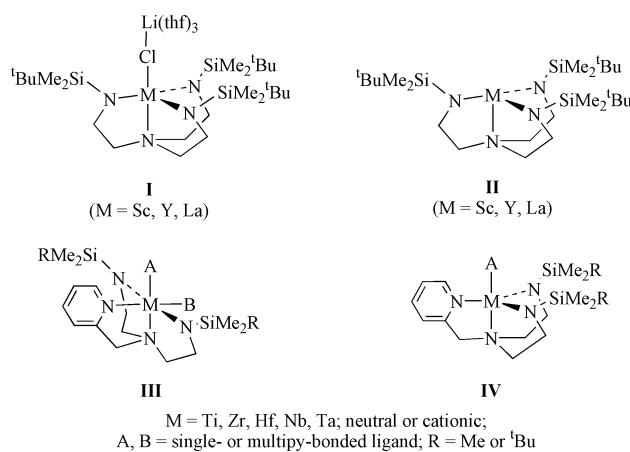
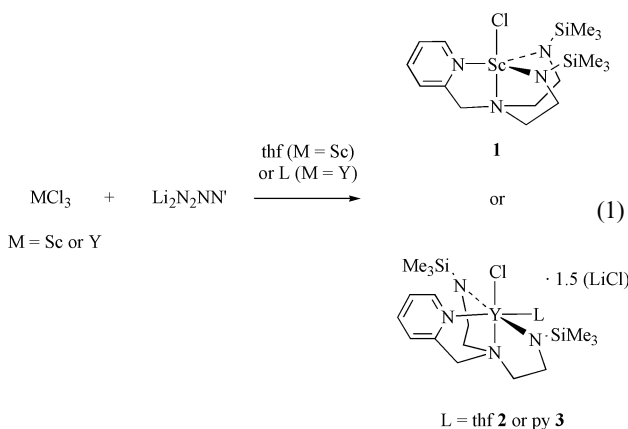


Chart 1

NSiMe₂R)₂ [R = Me (abbreviated as N₂NN') or ^tBu]¹⁸ which support new five- and six-coordinate, coordination and organometallic, Groups 4 and 5, singly- and multiply-bonded complexes, examples of which are given as **III** and **IV** in Chart 1. Unlike established dianionic N₄-donor ligands such as the porphyrins¹⁹ and dibenzotetraaza[14]annulenes²⁰ which promote square base pyramidal geometries for five-coordinate complexes, the tetradentate N₂NN' ligand gives “tren-like” trigonal bipyramidal coordination geometries, as well as offering considerable scope for variation of the ligand’s steric and electronic characteristics close to the metal centre by changing the amide nitrogen substituents. In this paper we describe new scandium and yttrium complexes of the N₂NN' ligand. A preliminary account of part of this work has been published.^{18a}

Results and discussion

The dilithiated ligand precursor $\text{Li}_2\text{N}_2\text{NN}'$ (where $\text{Li}_2\text{N}_2\text{NN}' = (2\text{-C}_5\text{H}_4\text{N})\text{CH}_2\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{Li})\text{SiMe}_3\}_2$) was prepared in multi-gram quantities from $\text{H}_2\text{N}_2\text{NN}'$ according to previously described procedures.^{18b} Eqn. 1 summarises the synthesis of the scandium and yttrium monochloride derivatives $[\text{ScCl}(\text{N}_2\text{NN}')] \mathbf{1}$ and $[\text{YCl}(\text{N}_2\text{NN}')(\text{L})]\cdot 1.5(\text{LiCl})$ ($\text{L} = \text{thf}$ **2** or py **3**).



Thus addition of $\text{Li}_2\text{N}_2\text{NN}'$ to a white suspension of ScCl_3 in thf cooled to -78°C and subsequent work-up gave **1** as a well-defined, pentane-soluble cream-coloured powder in 91% isolated yield. The corresponding reaction of $\text{Li}_2\text{N}_2\text{NN}'$ with YCl_3 (or $[\text{YCl}_3(\text{thf})_3]$) gave a benzene-soluble material tentatively described as the “ate” complex $[\text{YCl}(\text{N}_2\text{NN}')(\text{thf})]\cdot 1.5(\text{LiCl})$ **2** on the basis of its NMR spectra and by comparison with the better characterised pyridine analogue **3** (*vide infra*). Although samples of **2** as first obtained are soluble in benzene, further handling or attempts to purify this highly sensitive material led to apparent decomposition and the formation of insoluble products; a satisfactory elemental analysis could not be obtained. Speculating that loss of the comparatively weak donor thf ligand might be a contributing factor to the behaviour of **2** we prepared the pyridine analogue from $\text{Li}_2\text{N}_2\text{NN}'$ and YCl_3 in pyridine as a solvent. Subsequent work-up gave better-behaved and -defined samples of the pentane-soluble “ate” complex formulated as $[\text{YCl}(\text{N}_2\text{NN}')(\text{py})]\cdot 1.5(\text{LiCl})$ **3** in 71% yield.

The exact structural formulation of **2** and **3** are unknown as it was not possible to obtain diffraction-quality crystals of either compound. The ^1H and ^{13}C NMR spectra of **1–3** all show resonances attributable to a tetra-coordinated $\text{N}_2\text{NN}'$ ligand and the comparative simplicity of the spectra are consistent with the compounds possessing C_s symmetry. Coordination of the pyridyl moiety of $\text{N}_2\text{NN}'$ to the metal centres in **1–3** is indicated by the substantial downfield chemical shifts (range δ 9.33–9.85) of the pyridyl group *ortho*-hydrogens in comparison with that for the “free” protio ligand $\text{H}_2\text{N}_2\text{NN}'$ (δ 8.47) in the same solvent.^{18b} By ^1H NMR integration against the $\text{N}_2\text{NN}'$ resonances there is one equivalent of thf or pyridine for **2** and **3**, respectively. The presence of LiCl in **3** was established by ^7Li NMR spectroscopy; the elemental analysis for **3** is also consistent with the proposed formula. The difference in behaviour between the five-coordinate, base-free scandium compound **1** and the yttrium systems **2** and **3** is attributed to the larger size and higher Lewis acidity of the heavier congener.

The close relationship between **2** and **3** was established by the addition of an excess of pyridine to the thf adduct **2** which led immediately to the formation of the pyridine adduct **3**: the sample of **3** prepared in this manner was indistinguishable from those prepared directly from $\text{Li}_2\text{N}_2\text{NN}'$ and YCl_3 in pyridine. Conversely, heating a sample of **3** to 80°C under high vacuum (1×10^{-6} mbar) led to the loss of pyridine and yielded a very air- and moisture-sensitive pink compound. This could not be unambiguously identified but is thought to be a Lewis base-

free species such as “ $[\text{YCl}(\text{N}_2\text{NN}')]\cdot 1.5(\text{LiCl})$ ”. Subsequent addition of thf to this material resulted in the formation of **2**. Attempts to obtain a salt-free compound of the type $[\text{YCl}(\text{N}_2\text{NN}')]\cdot x$ from **2** or **3** by high vacuum sublimation at temperatures above 80°C or by solvent extraction or by refluxing in non-coordinating solvents led to decomposition products. Alternative routes to compounds of the type $[\text{Y}(\text{X})(\text{N}_2\text{NN}')]$ ($\text{X} = \text{I}$ or OSO_2CF_3) from YI_3 or $\text{Y}(\text{OSO}_2\text{CF}_3)_3$ and $\text{Li}_2\text{N}_2\text{NN}'$ were unsuccessful.

The compounds $[\text{ScCl}(\text{N}_2\text{NN}')]$ **1** and $[\text{YCl}(\text{N}_2\text{NN}')(\text{thf})]\cdot 1.5(\text{LiCl})$ **2** are precursors to new primary or secondary amide, benzamidinate or (for **1**) alkyl complexes by substitution reactions with the appropriate lithiated reagent. The new reactions are summarised in Scheme 1. For the scandium derivatives it is possible to start either from previously isolated **1** or from samples of **1** prepared *in situ* (the latter method provides the highest overall yield based on ScCl_3). For the yttrium derivatives it is much more convenient to use *in situ* prepared **2** owing to the difficulties associated with isolating and handling this compound.

Reaction of $\text{LiN}(\text{SiMe}_3)_2\cdot\text{Et}_2\text{O}$ with thf solutions of **1** or **2** (prepared *in situ*) at -78°C gave the pentane-soluble bis(trimethylsilylamide) derivatives $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}(\text{N}_2\text{NN}')]$ ($\text{M} = \text{Sc}$ **4** or Y **5**) in *ca.* 65% yields. The dimethylamide derivative $[\text{Sc}(\text{NMe}_2)(\text{N}_2\text{NN}')]$ **6** was made in a similar way by reaction of LiNMe_2 with $[\text{ScCl}(\text{N}_2\text{NN}')]$ **1** in benzene. Attempts to prepare an yttrium analogue of **6** were unsuccessful, possibly because the smaller NMe_2 group does not allow sufficient steric protection of the metal centre. Diffraction-quality crystals of **5** were grown from pentane and its molecular structure is illustrated in Fig. 1, and selected bond lengths and angles are listed in Table 1.

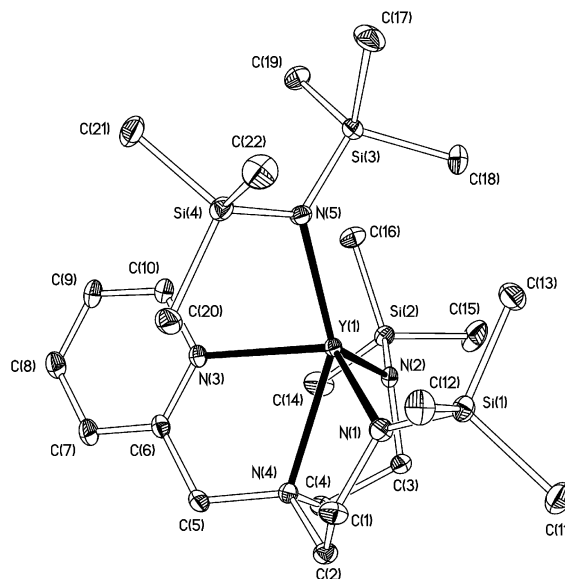
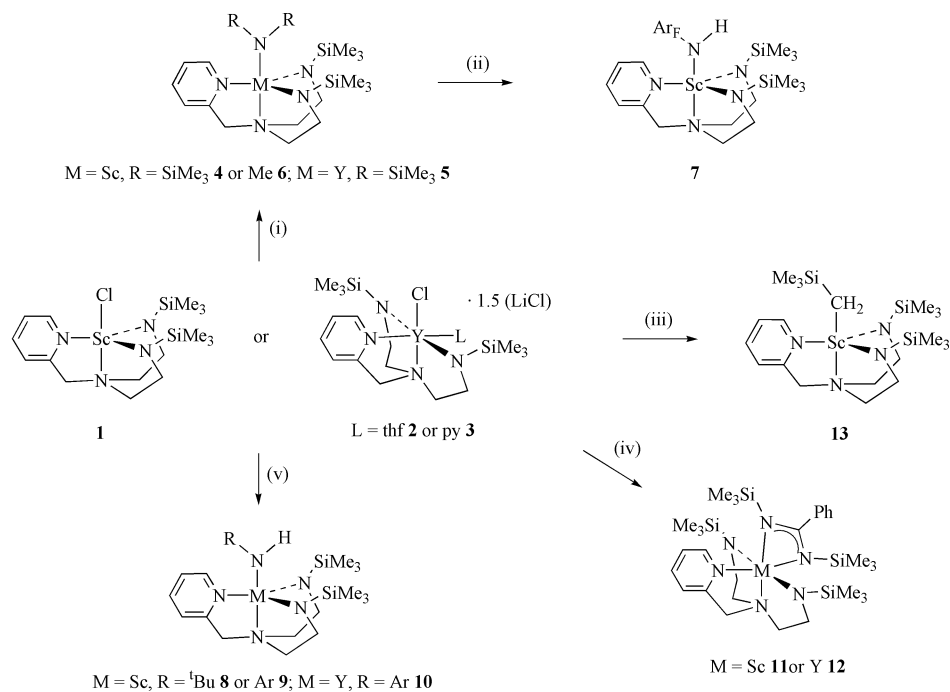


Fig. 1 Molecular structure of $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\text{N}_2\text{NN}')]$ **5**. Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity.

The geometry around the metal centre in **5** may best be described as distorted trigonal bipyramidal in which the yttrium metal centre is situated above the equatorial plane defined by $\text{N}(1)$, $\text{N}(2)$ and $\text{N}(3)$ of the $\text{N}_2\text{NN}'$ ligand which, in turn, is bound in a tetradentate manner. The angle subtended at $\text{Y}(1)$ between the (formally) axial nitrogen atoms is considerably distorted from the ideal value of 180° [$\text{N}(4)\text{--Y}(1)\text{--N}(5) = 148.72(8)^\circ$] possibly due to steric interactions between the trimethylsilyl groups of the $\text{N}(\text{SiMe}_3)_2$ moiety and those of the $\text{N}_2\text{NN}'$ ligand.

The three $\text{Y}\text{--N}_{\text{amide}}$ bond lengths $\text{Y}(1)\text{--N}(1) = 2.235(2) \text{ \AA}$, $\text{Y}(1)\text{--N}(2) = 2.245(2) \text{ \AA}$ and $\text{Y}(1)\text{--N}(5) = 2.289(2) \text{ \AA}$ differ only slightly, although that to $\text{N}(5)$ is the longest, possibly due to the



Scheme 1 For the following preparations the compounds **1** or **2** were prepared *in situ* according to eqn. 1: synthesis of **4**, **5**, **9**, **10**, **12**. Reagents and conditions. (i) for R = SiMe₃: LiN(SiMe₃)₂·Et₂O, thf, -78 °C then rt, 30–60 min, 62 or 67%; for R = Me: LiNMe₂, benzene, rt, 61%; (ii) (from **6**) Ar_FNH₂, benzene, rt, 20 min, 74%; (iii) LiCH₂SiMe₃, benzene, rt, 20 min, 58%; (iv) Li[PhC(NSiMe₃)₂], benzene (for M = Sc) or thf, rt or -78 °C then rt, 15 min or 1 h, 83 or 70%; (v) LiNH^tBu or LiNHAr, benzene or thf, rt or -78 °C then rt, 10–60 min, 57–76%.

Table 1 Selected bond distances (Å) and angles (°) for [Y{N(SiMe₃)₂}(N₂NN')]**5**

Y(1)–N(1)	2.235(2)	N(1)–Si(1)	1.711(2)
Y(1)–N(2)	2.245(2)	N(2)–Si(2)	1.716(2)
Y(1)–N(3)	2.473(2)	N(5)–Si(3)	1.717(2)
Y(1)–N(4)	2.537(2)	N(5)–Si(4)	1.703(2)
Y(1)–N(5)	2.289(2)		
N(1)–Y(1)–N(2)	112.87(9)	Y(1)–N(1)–Si(1)	129.26(13)
N(1)–Y(1)–N(3)	124.76(8)	Y(1)–N(1)–C(1)	115.28(17)
N(2)–Y(1)–N(3)	91.71(8)	Si(1)–N(1)–C(1)	115.26(18)
N(1)–Y(1)–N(4)	72.37(8)	Y(1)–N(2)–Si(2)	133.04(12)
N(2)–Y(1)–N(4)	75.91(8)	Y(1)–N(2)–C(3)	107.99(17)
N(3)–Y(1)–N(4)	66.83(7)	Si(2)–N(2)–C(3)	112.86(18)
N(1)–Y(1)–N(5)	109.14(9)	Y(1)–N(5)–Si(3)	123.89(12)
N(2)–Y(1)–N(5)	127.20(8)	Y(1)–N(5)–Si(3)	114.42(12)
N(3)–Y(1)–N(5)	89.55(8)	Si(3)–N(5)–Si(4)	121.55(13)
N(4)–Y(1)–N(5)	148.72(8)		

presence of two SiMe₃ substituents on this atoms. The Y–N_{amide} distances are similar to those previously observed for five-coordinated yttrium compounds containing amide donor atoms [range 2.250(6)–2.353(4) Å].^{15c,21} The amide nitrogen atoms N(1), N(2) and N(5) are effectively sp² hybridised with the sums of the angles subtended at each of them being in the range *ca.* 354–360°. The bond length to the pyridyl nitrogen atom is shorter than that to the sp³ hybridised amine nitrogen atom as expected. The Y(1)–N(4) bond length is unexceptional and falls mid-range with regard to published values for Y–N(sp³) dative bonds.²² With the amide nitrogen atoms all potentially able to act as three electron donors, the complex has a maximum formal valence electron count of 16 electrons (subject to orbital availability).

The protons in closest proximity to the metal centre are positioned more than *ca.* 3 Å away from the metal centre. These distances are significantly longer than would be expected if C–H...Y agostic interactions were present.²³ The notion that no agostic interactions are present in the molecule is further evidenced by the uniformity of all of the Si–C bond lengths and the normality of the N–Si–C bond angles.

The ¹H and ¹³C NMR data for [Y{N(SiMe₃)₂}(N₂NN')]**5** are consistent with the solid state structure; those of [Sc{N(SiMe₃)₂}(N₂NN')]**4** and [Sc(NMe₂)(N₂NN')]**6** are analogous to those of **5** and suggest that these compounds possess similar structures. The SiMe₃ groups of the N(SiMe₃)₂ ligand in **5** are inequivalent in the solid, in both **4** and **5** they appear as a singlet (integrating as 18 H) in the ¹H NMR spectra at all temperatures down to -80 °C implying that there is a low barrier to rotation about the M–N(SiMe₃)₂ bonds. While the pyridyl group *ortho*-hydrogens of **4** and **5** appear downfield of that in H₂N₂NN' as is usually observed for bound pyridyl groups, in **6** the resonance appears at 8.23 ppm, which is 0.24 ppm upfield of that in the “free ligand”. While this direction of change in chemical shift is relatively unusual, it has been seen in the zirconium dialkyl complexes [ZrR₂(N₂NN')] (R = CH₂SiMe₃, CH₂CMe₃ or CH₂-Ph)²⁴ and is likely to be a result of anisotropic shielding effects.

Although Sc and Y compounds with secondary amide ligands NR₂, where R typically has a C or Si atom bound to nitrogen, are ubiquitous in Group 3 amide chemistry, those with *primary* amide ligands N(H)R are considerably less common (complexes with N–H functionalised *amine* ligands are better known, however²⁵). Examples in scandium chemistry are [Sc(η⁵-C₅H₅){N(SiMe₂CH₂PⁱPr₂)₂}(NHR)] (R = ^tBu or Ph)^{10c} and [Sc{PhC(NSiMe₃)₂}(NHR)] (hereafter Ar = 2,6-C₆H₃-ⁱPr₂).^{9e} We had speculated that primary amide complexes [M(NHR)(N₂NN')] (M = Sc, Y) might be viable entry points to anionic imido complexes [M(NR)(N₂NN')] (imides are as yet unknown in Group 3 chemistry) which would be isoelectronic with the neutral Group 4 imido complexes [M(NR)(N₂NN')] (M = Ti, R = ^tBu or Ar; M = Zr, R = Ar) that we have reported elsewhere.^{18a,24} Ultimately our attempts to convert the Group 3 primary complexes [M(NHR)(N₂NN')] (*vide infra*) to the corresponding amides were unsuccessful, but we nevertheless report their syntheses and properties here since they are unusual derivatives in Group 3 amide chemistry.

The perfluorinated primary aryamide complex [Sc(NHC₆F₅)(N₂NN')]**7** was made *via* a transamination (σ-bond metathesis) reaction between [Sc(NMe₂)(N₂NN')]**6** and Ar_FNH₂ (Ar_F = C₆F₅) in benzene and was isolated in 74% yield as a pale brown solid (Scheme 1). When the reaction was followed by ¹H

NMR spectroscopy in benzene- d_6 the conversion was quantitative and the only by-product was NHMe_2 ; there was no evidence for protonolysis of the chelating (and presumably less basic) $\text{N}_2\text{NN}'$ ligand to form $\text{H}_2\text{N}_2\text{NN}'$. The primary amide complexes $[\text{M}(\text{NHR})(\text{N}_2\text{NN}')] \text{ where } \text{R} = \text{'Bu} \text{ or Ar were made by transmetalation reactions between LiNHR and the metal chloride } \mathbf{1} \text{ or } \mathbf{2} \text{. In the case of scandium these reactions yielded } [\text{Sc}(\text{NH}'\text{Bu})(\text{N}_2\text{NN}')] \mathbf{8} \text{ and } [\text{Sc}(\text{NHAr})(\text{N}_2\text{NN}')] \mathbf{9} \text{ in reasonable yields. The yttrium analogue of } \mathbf{8} \text{ was not sufficiently stable to be isolated, possibly due to inadequate steric protection, but reaction of LiNHR with } \textit{in situ} \text{ generated } \mathbf{2} \text{ at } -78^\circ\text{C} \text{ gave pentane-soluble } [\text{Y}(\text{NHAr})(\text{N}_2\text{NN}')] \mathbf{10} \text{ as an orange microcrystalline powder in 76\% yield after crystallisation at } -30^\circ\text{C} \text{. The new compounds } \mathbf{7}\text{--}\mathbf{10} \text{ give rise to the expected } ^1\text{H}, ^{13}\text{C} \text{ and (for } \mathbf{7}) ^{19}\text{F} \text{ NMR spectra. The } \text{N}_2\text{NN}' \text{ sub-spectra feature molecular } C_s \text{ symmetry and support the structures proposed in Scheme 1. The } ^1\text{H} \text{ NMR spectra of the more sterically crowded arylamide complexes } \mathbf{9} \text{ and } \mathbf{10} \text{ remain unchanged down to } -80^\circ\text{C} \text{ and feature a single pair of (mutually coupled) doublet (12 H) and septet (2 H) resonances for the ring } \textit{iso}\text{-propyl groups at all temperatures examined. The primary amide N-H resonance was clearly observed in all cases (range } \delta \text{ ca. } 5.4\text{--}2.9) \text{. For } \mathbf{7} \text{ and } \mathbf{8} \text{ a } \nu(\text{N-H}) \text{ band was observed in their IR spectra in the range } 3360\text{--}3380 \text{ cm}^{-1} \text{. The values are in the region associated with amide groups which do not form an } \alpha\text{-agostic interaction with the metal centre (namely ca. } 3250\text{--}3450 \text{ cm}^{-1} \text{).}^{11a,26} \text{ For the arylamide complexes } [\text{M}(\text{NHAr})(\text{N}_2\text{NN}')] \mathbf{9} \text{ and } \mathbf{10} \text{ } \nu(\text{N-H}) \text{ bands could not be confidently assigned.}$

Another class of ligand that has enjoyed recent attention in Group 3 chemistry are the benzamidinates $\text{PhC}(\text{NSiMe}_3)_2$ and their homologues.⁹ Indeed, benzamidinates have been widely exploited as monoanionic, bidentate supporting ligands for both main group and transition metal complexes.²⁷ The syntheses of the benzamidinate complexes $[\text{M}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')] \text{ (M = Sc } \mathbf{11} \text{ or } \mathbf{12}) \text{ are summarised in Scheme 1. Thus reaction of Li}\{\text{PhC}(\text{NSiMe}_3)_2\} \text{ with } [\text{ScCl}(\text{N}_2\text{NN}')] \mathbf{1} \text{ in benzene, or with } \textit{in situ} \text{ generated } [\text{YCl}(\text{N}_2\text{NN}')] \text{ (thf)} \cdot 1.5(\text{LiCl}) \mathbf{2} \text{ in thf at } -78^\circ\text{C} \text{, gave the corresponding benzamidinate complexes in good to excellent yields. For both compounds diffraction-quality crystals were grown from pentane solution and the solid state X-ray structures were determined. The molecular structures are shown in Figs. 2 and 3, and selected bond lengths and angles are listed in Tables 2 and 3.}$

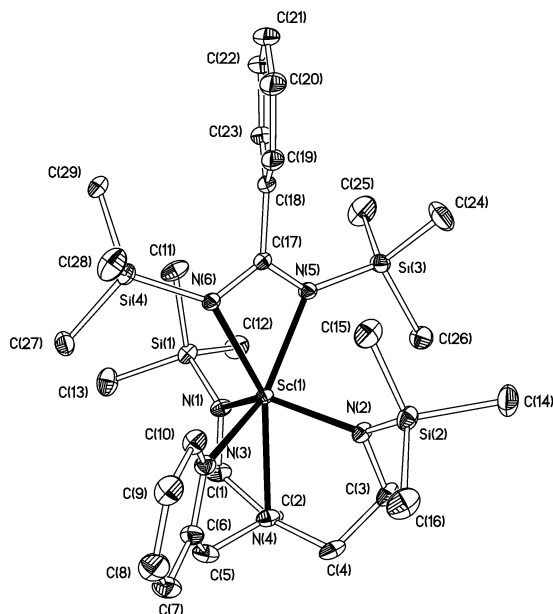


Fig. 2 Molecular structure of $[\text{Sc}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')] \mathbf{11}$. Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity.

Table 2 Selected bond distances (\AA) and angles ($^\circ$) for $[\text{Sc}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')] \mathbf{11}$

Sc(1)–N(1)	2.118(1)	Sc(1)–N(5)	2.251(1)
Sc(1)–N(2)	2.118(1)	Sc(1)–N(6)	2.269(1)
Sc(1)–N(3)	2.393(1)	N(5)–C(17)	1.323(2)
Sc(1)–N(4)	2.431(1)	N(6)–C(17)	1.334(2)
N(1)–Sc(1)–N(2)	131.02(5)	N(5)–Sc(1)–N(6)	60.26(4)
N(1)–Sc(1)–N(3)	113.18(5)	Sc(1)–N(1)–Si(1)	131.92(7)
N(2)–Sc(1)–N(3)	88.10(5)	Sc(1)–N(1)–C(1)	120.4(1)
N(1)–Sc(1)–N(4)	73.82(5)	C(1)–N(1)–Si(1)	107.6(1)
N(2)–Sc(1)–N(4)	74.41(5)	Sc(1)–N(2)–Si(2)	130.38(7)
N(3)–Sc(1)–N(4)	68.63(5)	Sc(1)–N(2)–C(3)	114.0(1)
N(1)–Sc(1)–N(5)	97.64(5)	C(3)–N(2)–Si(2)	112.7(1)
N(2)–Sc(1)–N(5)	91.26(5)	Sc(1)–N(5)–Si(3)	133.33(7)
N(3)–Sc(1)–N(5)	139.20(5)	Sc(1)–N(5)–C(17)	91.45(9)
N(4)–Sc(1)–N(5)	149.31(5)	Si(3)–N(5)–C(17)	133.5(1)
N(1)–Sc(1)–N(6)	106.81(5)	Sc(1)–N(6)–Si(4)	139.89(7)
N(2)–Sc(1)–N(6)	119.14(5)	Sc(1)–N(6)–C(17)	90.37(8)
N(3)–Sc(1)–N(6)	84.79(4)	Si(4)–N(6)–C(17)	127.1(1)
N(4)–Sc(1)–N(6)	150.31(5)		

Table 3 Selected bond distances (\AA) and angles ($^\circ$) for $[\text{Y}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')] \mathbf{12}$

Y(1)–N(1)	2.262(3)	Y(1)–N(5)	2.380(3)
Y(1)–N(2)	2.259(3)	Y(1)–N(6)	2.410(2)
Y(1)–N(3)	2.525(3)	N(5)–C(17)	1.330(4)
Y(1)–N(4)	2.557(3)	N(6)–C(17)	1.340(4)
N(1)–Y(1)–N(2)	127.5(1)	N(5)–Y(1)–N(6)	57.14(9)
N(1)–Y(1)–N(3)	110.00(11)	Y(1)–N(1)–Si(1)	128.51(15)
N(2)–Y(1)–N(3)	86.95(11)	Y(1)–N(1)–C(1)	120.4(2)
N(1)–Y(1)–N(4)	71.2(1)	Si(1)–N(1)–C(1)	111.0(2)
N(2)–Y(1)–N(4)	71.3(1)	Y(1)–N(2)–Si(2)	127.59(16)
N(3)–Y(1)–N(4)	66.8(1)	Y(1)–N(2)–C(3)	120.4(2)
N(1)–Y(1)–N(5)	102.1(1)	Si(2)–N(2)–C(3)	115.6(2)
N(2)–Y(1)–N(5)	93.35(11)	Y(1)–N(5)–Si(3)	131.95(15)
N(3)–Y(1)–N(5)	139.1(1)	Y(1)–N(5)–C(17)	92.8(2)
N(4)–Y(1)–N(5)	150.7(1)	Si(3)–N(5)–C(17)	133.9(2)
N(1)–Y(1)–N(6)	110.6(1)	Y(1)–N(6)–Si(4)	139.14(14)
N(2)–Y(1)–N(6)	119.8(1)	Y(1)–N(6)–C(17)	91.29(19)
N(3)–Y(1)–N(6)	87.5(1)	Si(4)–N(6)–C(17)	127.5(2)
N(4)–Y(1)–N(6)	152.1(1)		

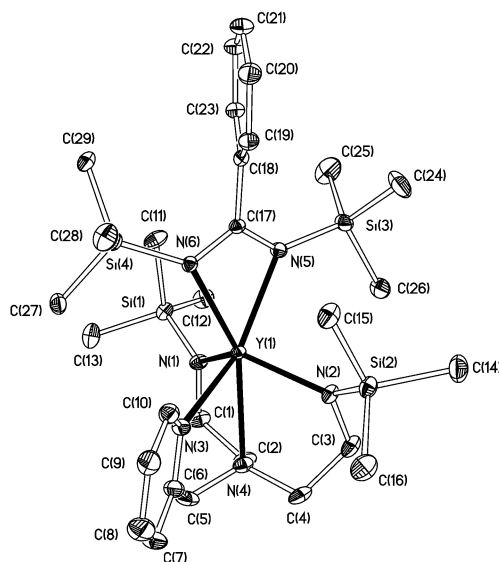


Fig. 3 Molecular structure of $[\text{Y}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')] \mathbf{12}$. Displacement ellipsoids are drawn at the 20% probability level. H atoms omitted for clarity.

The solid state structures of $\mathbf{11}$ and $\mathbf{12}$ are isomorphous and will be discussed together. Neither structure adopts an easily categorised coordination geometry and both are best described as distorted octahedral with the amide nitrogens of the $\text{N}_2\text{NN}'$

ligands occupying the formally axial coordination sites. In each instance the N₂NN' ligand is tetradentate and the sum of the angles subtended at the amide nitrogens N(1) and N(2) is approximately 360° implying sp² hybridisation. As for the five-coordinate compound [Y{N(SiMe₃)₂}(N₂NN')] **5**, the M–N_{pyridyl} bond distances in **11** and **12** are significantly longer than those for the M–N_{amine} bonds. The PhC(NSiMe₃)₂ ligands in **11** and **12** are bound in a characteristic bidentate manner with no significant differences between the internal PhC–N distances implying that both coordination sites at the metal centre are effectively equivalent.

Nonetheless, there is a small but significant difference between the M–N_{amidinate} bond lengths in the two compounds, with the M–N_{amidinate} distance for the nitrogen *cis* to the pyridyl moiety being the longer. In both compounds the M–N_{amidinate} distances are at the long end of the range of values previously reported for Group 3 benzamidinate complexes,^{9,28,29} presumably reflecting the six-coordination of the metal centres and the presence of the good amide donors of N₂NN'.

Molecules of **11** and **12** are fluxional at room temperature on the NMR timescale. Thus the N₂NN' ligand sub-spectra indicate apparent molecular C_s symmetry and the two SiMe₃ groups of the PhC(NSiMe₃)₂ ligands appear as single resonances (integrating as 18 H with respect to N₂NN'). This is not consistent with the solid state structures which clearly place the latter groups in very different environments. Furthermore, the (Ph)CN₂ core of the benzamidinate ligand is twisted with respect to the approximate mirror plane passing through the N_{pyridyl}, N_{amine} and M atoms of the M(N₂NN') fragments in **11** and **12** so that the two N₂NN' ligand SiMe₃ groups are also in chemically slightly different environments. Cooling toluene-d₈ solutions of **11** and **12** to –40 °C causes the fluxional process (apparent rotation about the M ⋯ C(Ph)N₂ vector) that exchanges the benzamidinate SiMe₃ groups to be frozen out while the two N₂NN' SiMe₃ groups remain equivalent on the NMR timescale to –90 °C suggesting that the PhC(NSiMe₃)₂ ligand is still “rocking” either side of the mirror plane mentioned above at this temperature. Such fluxional behaviour (apparent net rotation about a M ⋯ C(Ph)N₂ vector) is characteristic of many benzamidinate complexes and sometimes can never be frozen out on the NMR timescale.³⁰

Finally we describe attempts to prepare organo-scandium and -yttrium complexes with the N₂NN' ligand. Of a wide range of organo-lithium, -magnesium and -zinc reagents examined for the reactions of both *in situ* generated and previously isolated examples of [ScCl(N₂NN')] **1** and [YCl(N₂NN')(thf)]·1.5(LiCl) **2**, only the reaction of **1** with LiCH₂SiMe₃ gave isolable products on the preparative scale (Scheme 1). Thus addition of LiCH₂SiMe₃ to a benzene solution of **1** at room temperature followed by standard work-up gave reasonable yields of orange, pentane-soluble [Sc(CH₂SiMe₃)(N₂NN')] **13**, the crystal structure of which has been determined. The molecular structure is shown in Fig. 4 and selected bond lengths and angles are listed in Table 4.

The solid state structure of **13** features a five coordinate metal centre with a tetradentate N₂NN' ligand. The geometry around the metal is a distorted trigonal bipyramid in which the best equatorial plane is defined by N(1), N(2) and N(3). The Sc–N distances are all somewhat shorter than those in [Sc{PhC(NSiMe₃)₂}(N₂NN')] **11** (consistent with the higher coordination number and apparent valence electron count of the latter) and are within normal ranges.^{28,29} The Sc–N_{pyridyl} distance is again slightly shorter than Sc–N_{amine}. The sum of the angles around N(1) and N(2) are 355.1 and 359.4° respectively indicating that they are effectively sp² hybridised and therefore may act as three electron donors. The Sc–CH₂SiMe₃ distance of 2.2885(17) Å is similar to those in other scandium complexes containing a terminal alkyl ligand.^{28,29} None of the hydrogen atoms (placed geometrically) are within bonding distance of Sc(1). The SiMe₃ group of the alkyl ligand is oriented [Sc(1)–

Table 4 Selected bond distances (Å) and angles (°) for [Sc(CH₂SiMe₃)(N₂NN')] **13**

Sc(1)–N(1)	2.0748(17)	Sc(1)–C(17)	2.2885(17)
Sc(1)–N(2)	2.0613(14)	N(1)–Si(1)	1.7096(17)
Sc(1)–N(3)	2.3388(17)	N(2)–Si(2)	1.7014(16)
Sc(1)–N(4)	2.3606(14)	C(17)–Si(3)	1.8347(17)
N(1)–Sc(1)–N(2)	110.94(7)	N(4)–Sc(1)–C(17)	155.43(6)
N(1)–Sc(1)–N(3)	128.69(6)	Sc(1)–N(1)–C(1)	114.6(1)
N(2)–Sc(1)–N(3)	101.74(6)	Sc(1)–N(1)–Si(1)	124.85(9)
N(1)–Sc(1)–N(4)	77.08(6)	C(1)–N(1)–Si(1)	115.75(14)
N(2)–Sc(1)–N(4)	80.96(6)	Sc(1)–N(2)–C(3)	112.04(12)
N(3)–Sc(1)–N(4)	70.15(6)	Sc(1)–N(2)–Si(2)	132.52(8)
N(1)–Sc(1)–C(17)	105.85(6)	C(3)–N(2)–Si(2)	114.74(12)
N(2)–Sc(1)–C(17)	118.91(6)	Sc(1)–C(17)–Si(3)	115.54(8)
N(3)–Sc(1)–C(17)	90.52(6)		

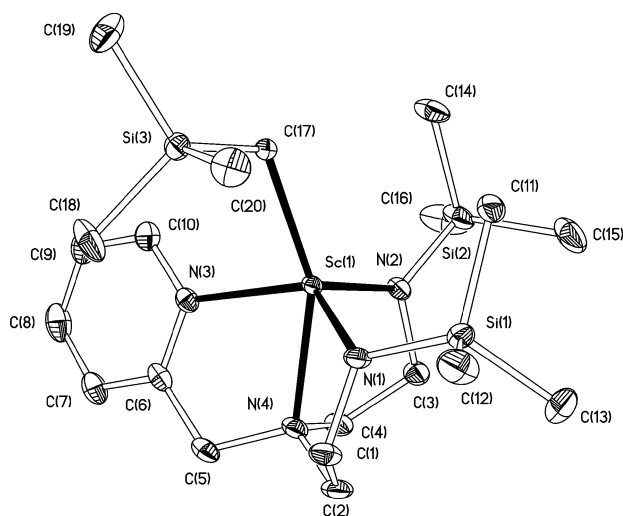


Fig. 4 Molecular structure of [Sc(CH₂SiMe₃)(N₂NN')] **13**. Displacement ellipsoids are drawn at the 20% probability level. H atoms omitted for clarity.

C(17)–Si(3) 115.54(8)°] into one of the “pockets” formed between the pyridyl group and the N₂NN' SiMe₃ substituents. The angles subtended at Si(3) are unexceptional and, combined with the unexceptional Si(3)–C_{Me} bond lengths, suggests that no agostic interaction is present between any hydrogen atoms of the alkyl ligand and the metal centre which has an apparent valence electron count of 14 (assuming each amide nitrogen donor is able to donate three electrons). The solution ¹H and ¹³C NMR spectra are consistent with the solid state structure and suggest that **13** possesses C_s symmetry on the NMR timescale. The mono-alkyl compound **13** is thermally stable at room temperature for several days in benzene-d₆ but decomposes rapidly at temperatures above 60 °C.

Conclusion

The diamide–diamine donor ligand N₂NN' is a useful supporting ligand in scandium and yttrium chemistry. In all cases examined the pyridyl donor remains firmly coordinated to the metal centres of the the new chloride, primary and secondary amide, benzamidinate and alkyl products reported. In its five-coordinate complexes the N₂NN' ligand promotes approximate trigonal bipyramidal coordination geometries somewhat reminiscent of those of the trianionic “tren” ligands used widely for early- to mid-transition metal chemistry.

Experimental

General methods and instrumentation

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon

using standard Schlenk-line or dry-box techniques at room temperature unless stated otherwise. Solvents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over appropriate agents, distilled under reduced pressure and stored under N₂ in J. Young ampoules. NMR samples of air- and moisture-sensitive compounds were prepared in the dry-box in 5 mm Wilmad tubes, equipped with a Young's Teflon valve.

¹H and ¹³C-¹H NMR spectra were recorded on a Varian Mercury 300 or Varian Unity Plus 500 spectrometer. ¹H and ¹³C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two dimensional ¹H-¹H and ¹³C-¹H correlation NMR experiments. All spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$). Chemical shifts are quoted in ppm and coupling constants in Hertz.

Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Infrared data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectroscopy services of the University of Oxford's Dyson Perrins Laboratory. Combustion elemental analyses were carried out by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory and Mikroanalytisches Labor Pascher, Germany.

The compound Li₂N₂NN' was prepared as reported previously.^{18b} Lithiated amides were prepared by reaction of the corresponding amines with ⁿBuLi in either hexanes or diethyl ether.

Syntheses

[ScCl(N₂NN')] (**1**). To a suspension of ScCl₃ (0.62 g, 4.12 mmol) in thf (20 ml) cooled to -78 °C was added dropwise a solution of Li₂N₂NN' (1.44 g, 4.08 mmol) in thf (10 ml). The reaction mixture was allowed to warm to rt and stirred for a further 1 h after which time the volatiles were removed under reduced pressure to yield a brown solid. This was extracted into benzene (4 × 50 ml) and the extracts filtered. The volatiles were removed under reduced pressure to give [ScCl(N₂NN')] **1** as a cream solid. Yield: 1.55 g (91%). ¹H NMR (300.1 MHz, 298 K, benzene-d₆): δ 9.33 (1 H, d, ³J = 4.8 Hz, 6-C₅H₄N), 6.67 (1 H, dd, ³J = 7.5, 8.1 Hz, 4-C₅H₄N), 6.27 (1 H, t, ³J = 4.8, 7.5 Hz, 5-C₅H₄N), 6.14 (1 H, d, ³J = 8.1 Hz, 3-C₅H₄N), 3.44 (2 H, m, NCH₂CH₂NSi), 3.18 (2 H, m, NCH₂CH₂NSi), 3.10 (2 H, s, C₅H₄NCH₂), 2.74 (2 H, m, NCH₂CH₂NSi), 2.21 (2 H, m, NCH₂CH₂NSi), 0.52 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 158.9 (2-C₅H₄N), 152.9 (6-C₅H₄N), 139.5 (4-C₅H₄N), 123.3 (5-C₅H₄N), 122.1 (3-C₅H₄N), 57.3 (NCH₂CH₂NSi), 56.9 (C₅H₄NCH₂), 45.8 (NCH₂CH₂NSi), 1.9 (Si(CH₃)₃). IR (CsBr plates, Nujol): 1606 (m), 1572 (m), 1348 (w), 1309 (w), 1245 (s), 1157 (w), 1145 (w), 1082 (m), 1056 (m), 1039 (w), 1023 (m), 987 (w), 942 (s), 924 (m), 862 (w), 833 (m), 675 (w), 662 (w), 645 (w), 633 (w), 619 (w), 570 (m), 551 (w), 484 (w), 452 (m), 430 (m) cm⁻¹. EI mass spectrum: *m/z* 401 ([M - CH₃]⁺, 6%), 371 ([M - 3 CH₃]⁺, 3%), 343 ([M - Si(CH₃)₃]⁺, 2%). Elemental analysis for C₁₆H₃₂ClN₄ScSi₂: found (calculated): C, 46.5 (46.1); H, 8.0 (7.7); N, 13.4 (13.4)%.

[YCl(N₂NN')(thf)]·1.5(LiCl) (**2**). To a mixture of solid YCl₃ (153 mg, 0.78 mmol) and Li₂N₂NN' (275 mg, 0.78 mmol) cooled to -78 °C was added thf (20 ml). The mixture was allowed to warm to rt and stirred for a further 30 min before the volatiles were removed under reduced pressure. The resulting off-white, sticky solid was extracted into benzene (40 ml), and filtered before the volatiles were removed under reduced pressure to give [YCl(N₂NN')(thf)]·1.5(LiCl) **2** as an off-white solid. Yield: 218 mg (47%). Attempts to further handle or purify this material invariably lead to apparent decomposition and

a satisfactory elemental analysis could not be obtained. ¹H NMR (500.0 MHz, 298 K, benzene-d₆): δ 9.69 (1 H, d, ³J = 4.5 Hz, 6-C₅H₄N), 6.81 (1 H, dd, 4-C₅H₄N), 6.42 (2 H, m, ³J = 4.5 Hz, 3-, 5-C₅H₄N), 3.74 (4 H, br s, 2-, 5-C₄H₈O), 3.48 (2 H, m, NCH₂CH₂NSi), 3.44 (2 H, s, C₅H₄NCH₂), 3.23 (2 H, m, NCH₂CH₂NSi), 2.81 (2 H, m, NCH₂CH₂NSi), 2.29 (2 H, m, NCH₂CH₂NSi), 1.43 (4 H, br s, 3-, 4-C₄H₈O), 0.28 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (125.7 MHz, 298 K, benzene-d₆): δ 159.0 (2-C₅H₄N), 152.7 (6-C₅H₄N), 138.5 (4-C₅H₄N), 122.8 (5-C₅H₄N), 122.5 (3-C₅H₄N), 69.9 (2-, 5-C₄H₈O), 58.5 (NCH₂CH₂NSi), 57.2 (C₅H₄NCH₂), 44.8 (NCH₂CH₂NSi), 25.5 (3-, 4-C₄H₈O), 0.8 (Si(CH₃)₃). IR (CsBr plates, Nujol): 1607 (s), 1572 (m), 1489 (w), 1377 (s), 1346 (w), 1330 (w), 1309 (m), 1157 (w), 1145 (w), 1098 (s), 1066 (s), 1018 (s), 985 (w), 943 (m), 925 (m), 899 (m), 860 (w), 830 (s), 766 (m), 726 (m), 664 (s), 633 (w), 613 (w), 565 (m), 549 (w), 417 (m) cm⁻¹.

[YCl(N₂NN')(py)]·1.5(LiCl) (**3**). To a mixture of solid YCl₃ (271 mg, 1.39 mmol) and Li₂N₂NN' (486 mg, 1.39 mmol) cooled to -78 °C was added pyridine (20 ml). The mixture was allowed to warm to rt and stirred for a further 30 min before the volatiles were removed under reduced pressure yielding a red solid which was extracted into benzene (3 × 20 ml). After filtering, the volatiles were removed under reduced pressure. The remaining orange solid was triturated with pentane and dried to give [YCl(N₂NN')(py)]·1.5(LiCl) **3** as a pale pink solid. Yield: 590 mg (71%). ¹H NMR (500.0 MHz, 298 K, benzene-d₆): δ 9.85 (1 H, d, ³J = 4.5 Hz, 6-C₅H₄N), 8.99 (2 H, br s, *o*-C₅H₅N), 6.93 (1 H, m, *p*-C₅H₅N), 6.77 (1 H, dd, ³J = 7.5, 8.0 Hz, 4-C₅H₄N), 6.68 (2 H, m, *m*-C₅H₅N), 6.42 (1 H, dd, ³J = 4.5, 8.0 Hz, 5-C₅H₄N), 6.36 (1 H, d, ³J = 7.5 Hz, 3-C₅H₄N), 3.58 (2 H, m, NCH₂CH₂NSi), 3.47 (2 H, s, C₅H₄CH₂), 3.30 (2 H, m, NCH₂CH₂NSi), 2.93 (2 H, m, NCH₂CH₂NSi), 2.36 (2 H, m, NCH₂CH₂NSi), 0.84 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (125.7 MHz, 298 K, benzene-d₆): δ 158.9 (2-C₅H₄N), 152.9 (6-C₅H₄N), 150.9 (*o*-C₅H₅), 138.4 (4-C₅H₄N), 137.3 (*p*-C₅H₅), 123.6 (5-C₅H₄N), 122.7 (*m*-C₅H₅), 122.4 (3-C₅H₄N), 58.4 (NCH₂CH₂NSi), 57.1 (C₅H₄NCH₂), 46.1 (NCH₂CH₂NSi), 1.2 (Si(CH₃)₃). ⁷Li NMR (194.3 MHz, 298 K, benzene-d₆): δ -0.49. IR (CsBr plates, Nujol): 1600 (m), 1571 (w), 1307 (w), 1284 (w), 1246 (m), 1152 (w), 1140 (w), 1086 (s), 1058 (w), 1037 (m), 1002 (w), 945 (w), 928 (s), 843 (s), 791 (w), 757 (w), 727 (w), 697 (m), 670 (w), 624 (w), 582 (w), 551 (w) cm⁻¹. EI mass spectrum: *m/z* 460 ([M - C₅H₅N, 1.5 LiCl]⁺, 3%), 425 ([M - C₅H₅N, Cl, 1.5 LiCl]⁺, 6%). Elemental analysis for C₂₁H₃₇ClN₅Si₂·1.5 LiCl: found (calculated): C, 41.4 (41.8); H, 6.7 (6.2); N, 11.8 (11.6)%.

[Sc{N(SiMe₃)₂}(N₂NN')] (**4**). To a suspension of ScCl₃ (60 mg, 0.40 mmol) in thf (5 ml) cooled to -78 °C was added dropwise a solution of Li₂N₂NN' (139 mg, 0.40 mmol) in thf (5 ml). The solution was allowed to warm to rt and stirred for a further 45 min before being recooled to -78 °C. A cooled solution of LiN(SiMe₃)₂·Et₂O (95.6 mg, 0.40 mmol) in thf (5 ml) was added dropwise and the mixture was again allowed to warm to rt. Stirring for a further 30 min resulted in a dark red solution from which the volatiles were removed under reduced pressure. The residues were extracted into pentane (3 × 15 ml), filtered and the volatiles removed under reduced pressure to give [Sc{N(SiMe₃)₂}(N₂NN')] **4**. Yield: 144 mg (67%). ¹H NMR (300.1 MHz, 298 K, benzene-d₆): δ 9.10 (1 H, d, ³J = 5.4 Hz, 6-C₅H₄N), 6.79 (1 H, dd, ³J = 7.5, 7.8 Hz, 4-C₅H₄N), 6.60 (1 H, dd, ³J = 5.4, 7.5 Hz, 5-C₅H₄N), 6.24 (1 H, d, ³J = 7.8 Hz, 3-C₅H₄N), 3.37 (2 H, m, NCH₂CH₂NSi), 3.24 (2 H, s, C₅H₄NCH₂), 2.79 (2 H, m, NCH₂CH₂NSi), 2.65 (2 H, m, NCH₂CH₂NSi), 2.27 (2 H, m, NCH₂CH₂NSi), 0.45 (18 H, s, N(Si(CH₃)₂)₂), 0.37 (18 H, s, NSi(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 158.8 (2-C₅H₄N), 151.6 (6-C₅H₄N), 139.1 (4-C₅H₄N), 122.8 (5-C₅H₄N), 121.6 (3-C₅H₄N), 65.7 (NCH₂CH₂NSi), 64.2 (C₅H₄NCH₂), 46.1 (NCH₂CH₂NSi), 6.2 (N(Si(CH₃)₂)₂), 2.1 (NSi(CH₃)₃). IR (CsBr plates, Nujol): 1606

(m), 1572 (w), 1302 (w), 1245 (s), 1146 (w), 1066 (w), 1031 (w), 1017 (w), 945 (s), 929 (s), 876 (w), 834 (s), 783 (w), 756 (w), 742 (w), 665 (m), 621 (w), 578 (w), 559 (w), 527 (w), 482 (w), 438 (m) cm^{-1} . EI mass spectrum: m/z 541 ($[\text{M}]^+$, 2%), 526 ($[\text{M} - \text{CH}_3]^+$, 6%), 381 ($[\text{M} - \text{N}(\text{Si}\{\text{CH}_3\}_3)_2]^+$, 14%). Elemental analysis for $\text{C}_{22}\text{H}_{50}\text{N}_5\text{ScSi}_4$: found (calculated): C, 48.5 (48.8); H, 9.3 (9.3); N, 12.9 (12.9)%.

[Y{N(SiMe₃)₂}(N₂NN')] (5). To a mixture of solid YCl₃ (110 mg, 0.56 mmol) and Li₂N₂NN' (197 mg, 0.56 mmol) cooled to -78°C was added thf (15 ml). The mixture was allowed to warm to rt and stirred for a further 10 min to give an orange solution. The solution was again cooled to -78°C and a solution of LiN(SiMe₃)₂·Et₂O (122 mg, 0.51 mmol) in thf (10 ml) was added dropwise. After complete addition the solution was allowed to warm to rt and stirred for a further 1 h before the volatiles were removed under reduced pressure. The resulting light orange solid was extracted into pentane (3 × 15 ml), filtered, and the volatiles were removed under reduced pressure to give [Y{N(SiMe₃)₂}(N₂NN')] **5** as an orange solid. Yield: 183 mg (62%). Colourless single crystals suitable for X-ray diffraction were grown from a saturated pentane solution left standing in a vibration-free environment for 2 d. ¹H NMR (300.1 MHz, 298 K, benzene-d₆): δ 9.04 (1 H, d, ³J = 4.8 Hz, 6-C₅H₄N), 6.77 (1 H, dd, ³J = 7.5, 8.1 Hz, 4-C₅H₄N), 6.46 (1 H, dd, ³J = 4.8, 8.1 Hz, 5-C₅H₄N), 6.24 (1 H, d, ³J = 7.5 Hz, 3-C₅H₄N), 3.48 (2 H, m, NCH₂CH₂NSi), 3.15 (2 H, s, C₅H₄NCH₂), 2.96 (2 H, m, NCH₂CH₂NSi), 2.58 (2 H, m, NCH₂CH₂NSi), 2.21 (2 H, m, NCH₂CH₂NSi), 0.44 (18 H, s, N(Si{CH₃})₃), 0.31 (18 H, s, NSi(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 159.3 (2-C₅H₄N), 150.6 (6-C₅H₄N), 139.3 (4-C₅H₄N), 122.9 (5-C₅H₄N), 122.6 (3-C₅H₄N), 65.0 (NCH₂CH₂NSi), 62.3 (C₅H₄NCH₂), 45.0 (NCH₂CH₂NSi), 5.6 (N(Si{CH₃})₃), 1.9 (NSi(CH₃)₃). IR (CsBr plates, Nujol): 1608 (m), 1571 (w), 1343 (w), 1305 (w), 1270 (w), 1245 (s), 1165 (w), 1142 (w), 1078 (w), 1049 (w), 1030 (w), 1018 (w), 981 (s), 931 (s), 875 (w), 828 (s), 776 (m), 738 (m), 664 (m), 645 (w), 632 (w), 608 (m), 572 (w), 552 (w), 487 (w), 455 (w), 422 (m), 407 (m) cm^{-1} . EI mass spectrum: m/z 570 ($[\text{M} - \text{CH}_3]^+$, 13%), 482 ($[\text{M} - \text{N}(\text{Si}\{\text{CH}_3\}_3)_2]^+$, 24%), 425 ($[\text{M} - \text{N}(\text{Si}\{\text{CH}_3\}_3)_2]^+$, 24%). Elemental analysis for $\text{C}_{22}\text{H}_{50}\text{N}_5\text{Si}_4\text{Y}$: found (calculated): C, 45.2 (45.1); H, 8.7 (8.6); N, 11.9 (12.0)%.

[Sc(NMe₂)(N₂NN')] (6). To a solution of [ScCl(N₂NN')] **1** (120 mg, 0.29 mmol) in benzene (5 ml) was added a slurry of LiNMe₂ in benzene (5 ml) producing no immediate colour change. The mixture was stirred for 25 min after which time the volatiles were removed under reduced pressure. The remaining brown solid was extracted into pentane (15 ml), filtered, and the volatiles removed under reduced pressure. The orange oil was dissolved in benzene (5 ml) and the volatiles were removed under reduced pressure from a frozen mixture cooled to 0°C to afford [Sc(NMe₂)(N₂NN')] **6** as a pale orange solid. Yield: 75 mg (61%). ¹H NMR (300.1 MHz, 298 K, benzene-d₆): δ 8.23 (1 H, d, ³J = 4.8 Hz, 6-C₅H₄N), 6.72 (1 H, dt, ³J = 7.5, 7.8 Hz, 4-C₅H₄N), 6.37 (1 H, t, ³J = 4.8, 7.5 Hz, 5-C₅H₄N), 6.17 (1 H, d, ³J = 7.8 Hz, 3-C₅H₄N), 3.41 (2 H, m, NCH₂CH₂NSi), 3.25 (2 H, m, NCH₂CH₂NSi), 3.20 (6 H, s, N(CH₃)₂), 3.13 (2 H, s, C₅H₄NCH₂), 2.66 (2 H, m, NCH₂CH₂NSi), 2.19 (2 H, m, NCH₂CH₂NSi), 0.51 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 159.7 (2-C₅H₄N), 151.9 (6-C₅H₄N), 139.0 (4-C₅H₄N), 123.4 (5-C₅H₄N), 122.2 (3-C₅H₄N), 57.4 (overlapping NCH₂CH₂NSi and C₅H₄NCH₂), 45.5 (NCH₂CH₂NSi), 44.7 (N(CH₃)₂), 1.7 (Si(CH₃)₃). IR (CsBr plates, Nujol): 1606 (m), 1573 (w), 1297 (w), 1239 (s), 1147 (w), 1088 (m), 1016 (w), 932 (s), 867 (w), 830 (s), 758 (w), 741 (w), 677 (m), 549 (w), 524 (w), 446 (w) cm^{-1} . EI mass spectrum: m/z 381 ($[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 45%) Elemental analysis for $\text{C}_{18}\text{H}_{38}\text{N}_5\text{ScSi}_2 \cdot 0.25\text{C}_5\text{H}_{12}$: found (calculated): C, 51.2 (52.1); H, 9.3 (9.3); N, 15.0 (15.8)%.

[Sc(NHAr_F)(N₂NN')] (7). To an orange solution of [Sc(NMe₂)(N₂NN')] **6** (102 mg, 0.24 mmol) in benzene (5 ml) was added a solution of Ar_FNH₂ (44 mg, 0.24 mmol) in benzene (5 ml) resulting in an immediate decrease in colour intensity. The solution was stirred at rt for 20 min before the volatiles were removed under reduced pressure. The resulting light brown material was redissolved in benzene (2 ml) and the benzene then slowly removed under reduced pressure from a frozen mixture giving [Sc(NHAr_F)(N₂NN')] **7** as a light brown solid. Yield: 121 mg (74%). ¹H NMR data (300.1 MHz, 298 K, benzene-d₆): δ 8.33 (1 H, d, ³J = 4.8 Hz, 6-C₅H₄N), 6.78 (1 H, dd, ³J = 8.1, 7.8 Hz, 4-C₅H₄N), 6.23 (1 H, dd, ³J = 4.8, 7.8 Hz, 5-C₅H₄N), 6.19 (1 H, d, ³J = 8.1 Hz, 3-C₅H₄N), 5.02 (1 H, s, NH), 3.39 (2 H, m, NCH₂CH₂NSi), 3.13 (2 H, s, C₅H₄NCH₂), 3.10 (2 H, m, NCH₂CH₂NSi), 2.62 (2 H, m, NCH₂CH₂NSi), 2.18 (2 H, m, NCH₂CH₂NSi), 0.31 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 158.9 (2-C₅H₄N), 150.0 (6-C₅H₄N), 149.2 (*i*-C₆F₅), 139.4 (4-C₅H₄N), 139.0 (*o*-C₆F₅, ¹J = 245 Hz), 137.8 (*p*-C₆F₅, ¹J = 234 Hz), 132.5 (*m*-C₆F₅, ¹J = 197 Hz), 123.5 (5-C₅H₄N), 122.6 (3-C₅H₄N), 59.5 (NCH₂CH₂NSi), 58.3 (C₅H₄NCH₂), 44.8 (NCH₂CH₂NSi), 1.2 (Si(CH₃)₃). ¹⁹F NMR (282.3 MHz, 298 K, benzene-d₆): δ -162.8 (2 F, *m*, *o*- or *m*-C₆F₅), -167.9 (2 F, *m*, *m*- or *o*-C₆F₅), -183.8 (1 F, *m*, *p*-C₆F₅). IR (CsBr plates, Nujol): 3366 (m), 1646 (m), 1608 (m), 1591 (w), 1572 (w), 1515 (s), 1504 (s), 1352 (w), 1299 (w), 1249 (s), 1158 (m), 1110 (w), 1068 (m), 1031 (w), 1006 (s), 967 (m), 938 (w), 927 (w), 870 (w), 835 (s), 792 (w), 770 (w), 735 (w), 676 (m), 629 (w), 572 (m), 487 (m), 453 (m), 437 (w) cm^{-1} . EI mass spectrum: m/z 235 ($[\text{M} - 2\text{Si}(\text{CH}_3)_3, \text{NHC}_6\text{F}_5]^+$, 86%), 182 ($[\text{NHC}_6\text{F}_5]^+$, 34%). Elemental analysis for $\text{C}_{22}\text{H}_{33}\text{F}_5\text{N}_5\text{ScSi}_2$: found (calculated): C, 47.2 (46.9); H, 6.2 (5.9); N, 12.1 (12.4)%.

[Sc(NH^tBu)(N₂NN')] (8). To a solution of [ScCl(N₂NN')] **1** (146 mg, 0.35 mmol) in benzene (10 ml) was added a solution of LiNH^tBu (27.7 mg, 0.35 mmol) in benzene (10 ml). The mixture was stirred for 10 min to give an opaque orange/brown mixture from which the volatiles were removed under reduced pressure. The remaining orange solid was extracted into pentane and the resulting orange solution was filtered. The volatiles were removed under reduced pressure giving [Sc(NH^tBu)(N₂NN')] **8** as a light brown solid. Yield: 102 mg (64%). ¹H NMR (300.1 MHz, 298 K, benzene-d₆): δ 9.44 (1 H, d, ³J = 5.4 Hz, 6-C₅H₄N), 6.75 (1 H, dd, ³J = 8.1, 7.2 Hz, 4-C₅H₄N), 6.42 (1 H, dd, ³J = 5.4, 7.2 Hz, 5-C₅H₄N), 6.22 (1 H, d, ³J = 8.1 Hz, 3-C₅H₄N), 3.46 (2 H, m, NCH₂CH₂NSi), 3.10 (2 H, s, C₅H₄NCH₂), 3.08 (2 H, m, NCH₂CH₂NSi), 2.89 (1 H, s, NH), 2.49 (2 H, m, NCH₂CH₂NSi), 2.10 (2 H, m, NCH₂CH₂NSi), 1.48 (9 H, s, C(CH₃)₃), 0.46 (18 H, s, Si(CH₃)₃). ¹³C-¹H NMR (75.5 MHz, 298 K, benzene-d₆): δ 159.6 (2-C₅H₄N), 153.3 (6-C₅H₄N), 139.0 (4-C₅H₄N), 122.5 (5-C₅H₄N), 122.3 (3-C₅H₄N), 61.3 (NCH₂CH₂NSi), 59.2 (C₅H₄NCH₂), 52.8 (C(CH₃)₃), 44.7 (NCH₂CH₂NSi), 35.6 (C(CH₃)₃), 0.5 (Si(CH₃)₃). IR (CsBr plates, Nujol): 3386 (w), 1606 (m), 1573 (w), 1300 (w), 1259 (w), 1240 (s), 1153 (w), 1083 (s), 1016 (m), 985 (w), 943 (s), 830 (s), 801 (w), 758 (w), 742 (w), 691 (w), 678 (w), 645 (w), 634 (w), 569 (w), 556 (w), 443 (m) cm^{-1} . EI mass spectrum: m/z 453 ($[\text{M}]^+$, 1%), 438 ($[\text{M} - \text{CH}_3]^+$, 2%), 381 ($[\text{M} - \text{NHC}(\text{CH}_3)_3]^+$, 65%). Elemental analysis for $\text{C}_{20}\text{H}_{42}\text{N}_5\text{ScSi}_2$: found (calculated): C, 52.0 (53.0); H, 9.4 (9.3); N, 14.8 (15.4)%.

[Sc(NHAr)(N₂NN')] (9). To a suspension of ScCl₃ (60 mg, 0.40 mmol) in thf (5 ml) cooled to -78°C was added dropwise a solution of Li₂N₂NN' (139 mg, 0.40 mmol) in thf (5 ml). The reaction mixture was allowed to warm to rt and stirred for a further 45 min after which time the orange/brown solution was cooled to -78°C before a solution of LiNHAr (73 mg, 0.40 mmol) in thf (5 ml) was added dropwise. The mixture was allowed to warm to rt and stirred for a further 60 min after which time the volatiles were removed under reduced pressure. The resulting brown solid was extracted into pentane (30 ml),

filtered, concentrated to 5 ml and cooled to $-80\text{ }^{\circ}\text{C}$ affording $[\text{Sc}(\text{NHAr})(\text{N}_2\text{NN}')]$ **9** as an orange crystalline which was isolated and dried *in vacuo*. Yield: 125 mg (57%). ^1H NMR (300.1 MHz, 298 K, benzene- d_6): δ 8.53 (1 H, d, $^3J = 5.1$ Hz, 6- $\text{C}_5\text{H}_4\text{N}$), 7.13 (2 H, d, $^3J = 7.5$ Hz, *m*- C_6H_3), 6.82 (1 H, t, $^3J = 7.5$ Hz, *p*- C_6H_3), 6.63 (1 H, dd, $^3J = 8.1$, 7.2 Hz, 4- $\text{C}_5\text{H}_4\text{N}$), 6.24 (1 H, d, $^3J = 7.2$ Hz, 3- $\text{C}_5\text{H}_4\text{N}$), 6.08 (1 H, dd, $^3J = 5.1$, 8.1 Hz, 5- $\text{C}_5\text{H}_4\text{N}$), 5.39 (1 H, s, NH), 3.44 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 3.24 (2 H, s, $\text{C}_5\text{H}_4\text{NCH}_2$), 3.11 (4 H, m, overlapping $\text{NCH}_2\text{CH}_2\text{NSi}$ and $\text{CH}(\text{CH}_3)_2$), 2.60 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.22 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 1.23 (12 H, d, $^3J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.39 (18 H, s, $\text{Si}(\text{CH}_3)_3$). ^{13}C - $\{^1\text{H}\}$ NMR (75.5 MHz, 298 K, benzene- d_6): δ 158.6 (2- $\text{C}_5\text{H}_4\text{N}$), 152.0 (*i*- C_6H_5), 151.7 (6- $\text{C}_5\text{H}_4\text{N}$), 139.1 (4- $\text{C}_5\text{H}_4\text{N}$), 133.4 (*o*- C_6H_5), 123.5 (5- $\text{C}_5\text{H}_4\text{N}$), 123.4 (*m*- C_6H_3), 121.9 (3- $\text{C}_5\text{H}_4\text{N}$), 115.0 (*p*- C_6H_3), 60.9 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 59.2 ($\text{C}_5\text{H}_4\text{NCH}_2$), 44.8 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 30.1 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 1.5 ($\text{Si}(\text{CH}_3)_3$). IR (CsBr plates, Nujol): 1607 (m), 1589 (w), 1570 (w), 1333 (m), 1301 (w), 1255 (s), 1240 (s), 1157 (w), 1140 (w), 1121 (w), 1106 (w), 1074 (s), 1053 (w), 1031 (w), 1013 (m), 987 (w), 975 (w), 942 (s), 931 (s), 896 (w), 875 (m), 833 (s), 796 (m), 750 (m), 692 (w), 674 (m), 646 (w), 635 (w), 621 (w), 587 (w), 567 (m), 546 (w) 433 (m) cm^{-1} . EI mass spectrum: m/z 557 ($[\text{M}]^+$, 6%), 542 ($[\text{M} - \text{CH}_3]^+$, 4%), 471 ($[\text{M} - 2\text{CH}(\text{CH}_3)_2]^+$, 35%), 381 ($[\text{M} - \text{NHC}_6\text{H}_3(\text{CH}(\text{CH}_3)_2)_2]^+$, 100%). Elemental analysis for $\text{C}_{28}\text{H}_{50}\text{N}_5\text{ScSi}_2$: found (calculated): C, 59.7 (60.3); H, 9.2 (9.0); N, 12.3 (12.6)%.

[Y(NHAr)(N₂NN')] (**10**). To a mixture of YCl_3 (113 mg, 0.58 mmol) and $\text{Li}_2\text{N}_2\text{NN}'$ (203 mg, 0.58 mmol) cooled to $-78\text{ }^{\circ}\text{C}$ was added thf (10 ml). The reaction mixture was stirred for 1 min before being allowed to warm to rt after which it was stirred for a further 10 min. The resulting clear orange solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of LiNHAr (106 mg, 0.58 mmol) in thf (5 ml) was added dropwise. The mixture was again allowed to warm to rt and stirred for a further 45 min after which time the volatiles were removed under reduced pressure. The resulting orange solid was extracted into pentane (30 ml) and filtered. Concentration of the solution to 5 ml followed by cooling to $-30\text{ }^{\circ}\text{C}$ afforded $[\text{Y}(\text{NHAr})(\text{N}_2\text{NN}')]$ **10** as an orange micro-crystalline solid which was isolated and dried *in vacuo*. Yield: 264 mg (76%). ^1H NMR (500.0 MHz, 298 K, benzene- d_6): δ 8.44 (1 H, d, $^3J = 5.5$ Hz, 6- $\text{C}_5\text{H}_4\text{N}$), 7.18 (2 H, d, $^3J = 7.5$ Hz, *m*- C_6H_3), 6.82 (1 H, t, $^3J = 7.5$ Hz, *p*- C_6H_3), 6.62 (1 H, dd, $^3J = 8.0$, 7.5 Hz, 4- $\text{C}_5\text{H}_4\text{N}$), 6.22 (1 H, d, $^3J = 8.0$ Hz, 3- $\text{C}_5\text{H}_4\text{N}$), 6.06 (1 H, dd, $^3J = 7.5$, 5.5 Hz, 5- $\text{C}_5\text{H}_4\text{N}$), 4.60 (1 H, s, NH), 3.42 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 3.21 (4 H, m, overlapping $\text{NCH}_2\text{CH}_2\text{NSi}$ and $\text{CH}(\text{CH}_3)_2$), 3.17 (2 H, s, $\text{C}_5\text{H}_4\text{NCH}_2$), 2.61 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.19 (2 H, m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 1.27 (12 H, d, $^3J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.35 (18 H, s, $\text{Si}(\text{CH}_3)_3$). ^{13}C - $\{^1\text{H}\}$ NMR (125.7 MHz, 298 K, benzene- d_6): δ 159.2 (2- $\text{C}_5\text{H}_4\text{N}$), 153.4 (*i*- C_6H_5), 151.2 (6- $\text{C}_5\text{H}_4\text{N}$), 139.3 (4- $\text{C}_5\text{H}_4\text{N}$), 133.0 (*o*- C_6H_5), 123.6 (5- $\text{C}_5\text{H}_4\text{N}$), 123.2 (*m*- C_6H_3), 122.5 (3- $\text{C}_5\text{H}_4\text{N}$), 114.1 (*p*- C_6H_3), 60.1 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 58.6 ($\text{C}_5\text{H}_4\text{NCH}_2$), 44.5 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 29.9 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$), 1.1 ($\text{Si}(\text{CH}_3)_3$). IR (CsBr plates, Nujol): 1605 (m), 1589 (w), 1569 (w), 1426 (s), 1350 (w), 1341 (w), 1304 (w), 1260 (m), 1239 (m), 1158 (w), 1139 (w), 1085 (m), 1055 (w), 1034 (w), 1013 (m), 935 (s), 869 (m), 829 (s), 789 (w), 747 (m), 671 (m), 644 (w), 616 (w), 540 (w), 418 (m) cm^{-1} . EI mass spectrum: m/z 601 ($[\text{M}]^+$, 5%), 586 ($[\text{M} - \text{CH}_3]^+$, 2%), 514 ($[\text{M} - 2\text{CH}(\text{CH}_3)_2]^+$, 15%), 425 ($[\text{M} - \text{NHC}_6\text{H}_3(\text{CH}(\text{CH}_3)_2)_2]^+$, 13%). Elemental analysis for $\text{C}_{28}\text{H}_{50}\text{N}_5\text{Si}_2\text{Y}$: found (calculated): C, 55.9 (55.9); H, 8.4 (8.4); N, 11.5 (11.6)%.

[Sc{PhC(NSiMe₃)₂}(N₂NN')] (**11**). To a light brown solution of $[\text{ScCl}(\text{N}_2\text{NN}')]$ **1** (103 mg, 0.25 mmol) in benzene (5 ml) was added a colourless solution of $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ (65 mg, 0.25 mmol) in benzene (5 ml) to give immediately an orange colouration to the opaque reaction mixture. The mixture was stirred at rt for 15 min before the volatiles were removed under

reduced pressure giving a brown solid which was extracted with pentane (3×10 ml). The volatiles were removed under reduced pressure affording $[\text{Sc}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')]$ **11** as an off-white solid. Yield: 132 mg (83%). Colourless single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution over a period of 30 min. ^1H NMR (300.1 MHz, 233 K, toluene- d_8): δ 9.00 (1 H, br d, 6- $\text{C}_5\text{H}_4\text{N}$), 7.79 (2 H, br d, *o*- C_6H_5), 7.10 (3 H, br m, *m*-, *p*- C_6H_3), 6.80 (1 H, br t, 4- $\text{C}_5\text{H}_4\text{N}$), 6.50 (1 H, br t, 5- $\text{C}_5\text{H}_4\text{N}$), 6.22 (1 H, br d, 3- $\text{C}_5\text{H}_4\text{N}$), 3.60 (2 H, br s, $\text{NCH}_2\text{CH}_2\text{NSi}$), 3.28 (2 H, s, $\text{C}_5\text{H}_4\text{NCH}_2$), 3.20 (2 H, br s, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.73 (2 H, br s, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.09 (2 H, br s, $\text{NCH}_2\text{CH}_2\text{NSi}$), 0.42 (9 H, s, $\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 0.37 (18 H, s, $\text{NSi}(\text{CH}_3)_3$), -0.08 (9 H, s, $\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$). ^{13}C - $\{^1\text{H}\}$ NMR (75.5 MHz, 233 K, toluene- d_8): δ 183.0 ($\text{C}_6\text{H}_5\text{C}$), 158.2 (2- $\text{C}_5\text{H}_4\text{N}$), 150.2 (6- $\text{C}_5\text{H}_4\text{N}$), 143.7 (*i*- C_6H_5), 138.3 (4- $\text{C}_5\text{H}_4\text{N}$), 126.9 (*o*- C_6H_5), 123.2 (3- $\text{C}_5\text{H}_4\text{N}$), 121.8 (5- $\text{C}_5\text{H}_4\text{N}$), 59.1 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 56.7 ($\text{C}_5\text{H}_4\text{NCH}_2$), 46.5 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 3.5 ($\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 2.47 ($\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 1.8 ($\text{NSi}(\text{CH}_3)_3$). IR (CsBr plates, Nujol): 2725 (w), 2678 (w), 1662 (m), 1607 (s), 1573 (m), 1306 (w), 1250 (s), 1167 (w), 1154 (m), 1145 (w), 1078 (m), 1064 (w), 1056 (w), 1036 (w), 1005 (w), 989 (m), 932 (m), 844 (s), 795 (w), 757 (m), 703 (m), 677 (m), 644 (w), 631 (w), 603 (w), 584 (w), 663 (m), 489 (s), 447 (w), 423 (s), 406 (w) cm^{-1} . EI mass spectrum: m/z 644 ($[\text{M}]^+$, 1%), 571 ($[\text{M} - \text{Si}(\text{CH}_3)_3]^+$, 10%), 352 ($[\text{M} - 4\text{Si}(\text{CH}_3)_3]^+$, 2%). Elemental analysis for $\text{C}_{29}\text{H}_{55}\text{N}_6\text{ScSi}_4$: found (calculated): C, 53.1 (54.0); H, 9.1 (8.6); N, 13.0 (13.0)%.

[Y{PhC(NSiMe₃)₂}(N₂NN')] (**12**). To a mixture of YCl_3 (95 mg, 0.49 mmol) and $\text{Li}_2\text{N}_2\text{NN}'$ (170 mg, 0.49 mmol) cooled to $-78\text{ }^{\circ}\text{C}$ was added thf (10 ml). The mixture was warmed to rt and stirred for a further 15 min before being cooled back to $-78\text{ }^{\circ}\text{C}$. To the orange reaction mixture a colourless solution of $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ (131 mg, 0.48 mmol) in thf (5 ml) was added. The mixture was again allowed to warm to rt and after further stirring for 1 h an orange/brown mixture persisted. After the volatiles were removed under reduced pressure the remaining solid was extracted into pentane (40 ml) and filtered. Concentrating the pentane solution to *ca.* 5 ml gave diffraction-quality, colourless crystals of $[\text{Y}\{\text{PhC}(\text{NSiMe}_3)_2\}(\text{N}_2\text{NN}')]$ **12**. Yield: 235 mg (70%). ^1H NMR (300.1 MHz, 233 K, toluene- d_8): δ 8.87 (1 H, d, $^3J = 4.8$ Hz, 6- $\text{C}_5\text{H}_4\text{N}$), 7.61 (2 H, d, $^3J = 6.9$ Hz, *o*- C_6H_5), 7.12 (3 H, m, *m*-, *p*- C_6H_3), 6.90 (1 H, dd, $^3J = 7.8$, 7.8 Hz, 4- $\text{C}_5\text{H}_4\text{N}$), 6.60 (1 H, dd, $^3J = 4.8$, 7.8 Hz, 5- $\text{C}_5\text{H}_4\text{N}$), 6.22 (1 H, d, $^3J = 7.8$ Hz, 3- $\text{C}_5\text{H}_4\text{N}$), 3.58 (2 H, br m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 3.22 (4 H, br s, $\text{C}_5\text{H}_4\text{NCH}_2$, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.73 (2 H, br m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 2.08 (2 H, br m, $\text{NCH}_2\text{CH}_2\text{NSi}$), 0.38 (27 H, s, $\text{NSi}(\text{CH}_3)_3$, $\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 0.0 (9 H, s, $\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$). ^{13}C - $\{^1\text{H}\}$ NMR (75.5 MHz, 233 K, toluene- d_8): δ 183.3 ($\text{C}_6\text{H}_5\text{C}$), 159.4 (2- $\text{C}_5\text{H}_4\text{N}$), 149.4 (6- $\text{C}_5\text{H}_4\text{N}$), 144.4 (*i*- C_6H_5), 138.6 (4- $\text{C}_5\text{H}_4\text{N}$), 126.5 (*o*- C_6H_5), 124.0 (3- $\text{C}_5\text{H}_4\text{N}$), 122.1 (5- $\text{C}_5\text{H}_4\text{N}$), 59.7 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 56.3 ($\text{C}_5\text{H}_4\text{NCH}_2$), 45.5 ($\text{NCH}_2\text{CH}_2\text{NSi}$), 3.3 ($\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 2.4 ($\text{C}_6\text{H}_5\text{C}(\text{NSi}\{\text{CH}_3\}_3)_2$), 1.2 ($\text{NSi}(\text{CH}_3)_3$). IR (CsBr plates, Nujol): 2720 (m), 2672 (w), 1646 (w), 1607 (s), 1572 (m), 1333 (w), 1308 (w), 1170 (w), 1154 (m), 1144 (m), 1130 (w), 1086 (s), 1057 (w), 1038 (m), 1003 (w), 987 (w), 931 (m), 839 (m), 791 (w), 756 (m), 704 (m), 678 (m), 644 (w), 629 (m), 619 (w), 603 (m), 577 (m), 554 (s), 481 (s), 439 (s), 418 (w) cm^{-1} . EI mass spectrum: m/z 586 ($[\text{M} - \text{NSi}(\text{CH}_3)_3$, $\text{CH}_3]^+$, 3%), 538 ($[\text{M} - \text{C}_6\text{H}_5$, $\text{Si}(\text{CH}_3)_3]^+$, 1%). Elemental analysis for $\text{C}_{29}\text{H}_{55}\text{N}_6\text{Si}_4\text{Y}$: found (calculated): C, 49.5 (50.5); H, 8.7 (8.1); N, 11.4 (12.2)%.

[Sc(CH₂SiMe₃)(N₂NN')] (**13**). To a solution of $[\text{ScCl}(\text{N}_2\text{NN}')]$ **1** (119 mg, 0.29 mmol) in benzene (5 ml) was added a solution of $\text{LiCH}_2\text{SiMe}_3$ in benzene (5 ml) to produce immediately an orange/brown clear solution. After 1 min the mixture became slightly opaque and was allowed to stir for a further 20 min before the volatiles were removed under reduced pressure. The brown solid was extracted into pentane (10 ml)

Table 5 X-Ray data collection and processing parameters for [Y{N(SiMe₃)₂}(N₂NN')} **5**, [Sc{PhC(NSiMe₃)₂}(N₂NN')} **11**, [Y{PhC(NSiMe₃)₂}(N₂NN')} **12** and [Sc(CH₂SiMe₃)(N₂NN')} **13**

	5	11	12	13
Formula	C ₂₂ H ₅₀ N ₅ Si ₄ Y	C ₂₉ H ₅₅ N ₆ ScSi ₄	C ₂₉ H ₅₅ N ₆ Si ₄ Y	C ₂₀ H ₄₃ N ₄ ScSi ₃
Formula weight	585.93	645.10	689.05	468.81
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	9.281(1)	11.064(1)	11.4020(3)	12.131(1)
<i>b</i> /Å	17.696(2)	20.177(2)	20.0640(7)	13.069(1)
<i>c</i> /Å	19.399(2)	16.808(2)	16.8640(5)	17.548(1)
<i>a</i> °	90.0	90.0	90.0	90.0
<i>β</i> °	90.0	92.17(1)	93.423(2)	90.0
<i>γ</i> °	90.0	90.0	90.0	90.0
<i>V</i> /Å ³	3186.0(6)	3749.5(6)	3851.1(5)	2782.1(3)
<i>Z</i>	4	4	4	4
<i>μ</i> (Mo- <i>K</i> _α)/mm ⁻¹	2.01	0.35	1.67	0.40
Total reflections	17528	19051	17138	15718
Observed reflections	5692 [<i>I</i> > 3σ(<i>I</i>)]	6145 [<i>I</i> > 3σ(<i>I</i>)]	4702 [<i>I</i> > 3σ(<i>I</i>)]	5037 [<i>I</i> > 3σ(<i>I</i>)]
<i>R</i> ₁ ^a , <i>R</i> _w ^b	0.0289, 0.0332 [<i>I</i> > 3σ(<i>I</i>)]	0.0347, 0.0403 [<i>I</i> > 3σ(<i>I</i>)]	0.0276, 0.0360 [<i>I</i> > 3σ(<i>I</i>)]	0.0299, 0.0372 [<i>I</i> > 3σ(<i>I</i>)]

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; ^b $R_w = \sqrt{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2}$.

and the resulting orange solution was filtered before the volatiles were removed under reduced pressure to give [Sc(CH₂SiMe₃)(N₂NN')} **13** as an orange solid. Yield: 77 mg (58%). Colourless diffraction-quality crystals of **13** were grown from a saturated pentane solution allowed to stand in a vibrational-free environment for 3 d. ¹H NMR (300.1 MHz, 298 K, benzene-*d*₆): δ 8.80 (1 H, d, ³*J* = 5.4 Hz, 6-C₅H₄N), 6.77 (1 H, dd, ³*J* = 7.5, 7.8 Hz, 4-C₅H₄N), 6.42 (1 H, dd, ³*J* = 5.4, 7.5 Hz, 5-C₅H₄N), 6.27 (1 H, d, ³*J* = 7.8 Hz, 3-C₅H₄N), 3.35 (2 H, m, NCH₂CH₂NSi), 3.11 (2 H, s, C₅H₄NCH₂), 3.07 (2 H, m, NCH₂CH₂NSi), 2.41 (2 H, m, NCH₂CH₂NSi), 2.07 (2 H, m, NCH₂CH₂NSi), 0.42 (18 H, s, NSi(CH₃)₃), 0.21 (9 H, s, CH₂Si(CH₃)₃), 0.05 (2 H, s, CH₂Si(CH₃)₃). ¹³C-{¹H} NMR (75.5 MHz, 298 K, benzene-*d*₆): δ 159.3 (2-C₅H₄N), 150.6 (6-C₅H₄N), 139.2 (4-C₅H₄N), 123.0 (5-C₅H₄N), 122.6 (3-C₅H₄N), 60.9 (NCH₂CH₂NSi), 58.8 (C₅H₄NCH₂), 44.4 (NCH₂CH₂NSi), 30.7 (CH₂Si(CH₃)₃), 4.5 (CH₂Si(CH₃)₃), 1.8 (NSi(CH₃)₃). IR (KBr plates, Nujol): 1608 (s), 1572 (m), 1377 (w), 1344 (w), 1302 (w), 1242 (s), 1155 (w), 1143 (w), 1068 (m), 1017 (m), 985 (w), 945 (m), 924 (m), 834 (s), 784 (w), 759 (w), 740 (w), 678 (w), 669 (w), 646 (w), 633 (w), 570 (m), 557 (m), 455 (s) cm⁻¹. EI mass spectrum: *m/z* 381 ([M - CH₂Si(CH₃)₃]⁺, 4%), 249 ([M - 3 Si(CH₃)₃]⁺, 6%), 322 ([M - 2 Si(CH₃)₃ - CH₂Si(CH₃)₃, H]⁺, 87%). Elemental analysis for C₂₀H₄₃N₄ScSi₃: found (calculated): C, 50.3 (51.2); H, 9.6 (9.3); N, 11.9 (12.0)%.

Crystal structure determinations for [Y{N(SiMe₃)₂}(N₂NN')} (5**), [Sc{PhC(NSiMe₃)₂}(N₂NN')} (**11**), [Y{PhC(NSiMe₃)₂}(N₂NN')} (**12**) and [Sc(CH₂SiMe₃)(N₂NN')} (**13**). Crystal data collection and processing parameters are given in Table 5. Crystals were immersed in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius DIP2000 image plate diffractometer equipped with an Oxford Cryosystems low-temperature device.³¹ Data were collected at low temperature using Mo-*K*_α radiation; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs.³² Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using SIR92.³³ Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically. Refinement of an absolute structure (Flack) parameter³⁴ for **5** and **13** yielded values of 0.01(10) and 0.03(2), respectively. Extinction corrections were applied as required.³⁵ Crystallographic calculations were performed using SIR92³³ and CRYSTALS.³⁶**

CCDC reference numbers 170227 and 176539–176541.

See <http://www.rsc.org/suppdata/dt/b1/b111469g/> for crystallographic data in CIF or other electronic format.

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