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Journal of Organometallic Chemistry 647 (2002) 145–150

Journal of Organometallic Chemistry

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New N- and O-donor ligand environments in organoscandium chemistry

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Received 14 September 2001; accepted 2 October 2001

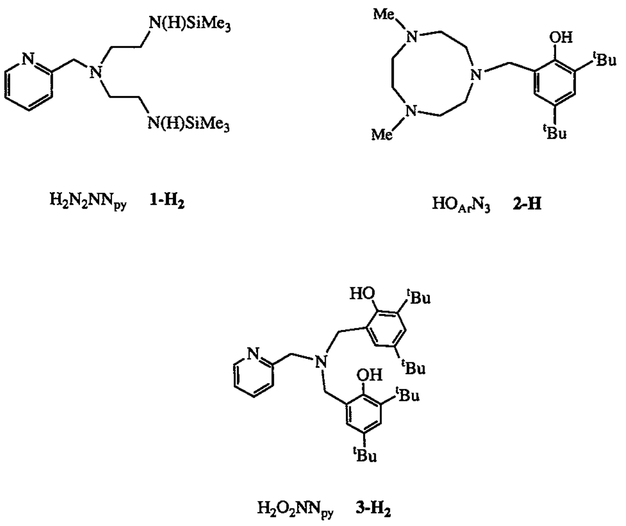
Abstract

The synthesis and characterisation of three new classes of organoscandium compound with non-cyclopentadienyl, mono- or di-anionic supporting ligands possessing N_4-, N_3O- or N_2O_2-donor atom sets are described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Scandium; Macrocycle; Polyamide; Aryloxide; X-ray

1. Introduction

Although there is a rich and diverse coordination chemistry of scandium in a range of different ligand environments, the organometallic chemistry of this element is generally dominated by mono- and bis-cyclopentadienyl complexes [1]. Recent exceptions to this general position are 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 described by Fryzuk [4]; and the fascinating low (i.e. less than $+3$) oxidation state arene sandwich and related complexes made by Cloke and coworkers [1e,5]. We have been developing the coordination and organometallic chemistry of early transition metal and main group metal complexes in alternative (to cyclopentadienyl) ligand environments, and have recently reported the use of the diamido–diamine N_2NN_{py} (**1**) [6] and triazacyclononane-derived $O_{Ar}N_3$ (**2**) ligands [7] (see Fig. 1). Very recently, Kol and coworkers reported an example of the use of the tetradentate bis(phenoxide) ligand O_2NN_{py} (**3**) [8] in organozirconium chemistry [9], and we are also developing these and related bis(aryloxide)- and bis(alkoxide)-diamine ligands in the organometallic chemistry of the Group 4 elements [6,10]. To date there have been no reports of the use of the N_2NN_{py} (**1**), $O_{Ar}N_3$ (**2**) or O_2NN_{py} (**3**) ligands in Group 3 organometallic chemistry, although very recently Hessen and coworkers reported yttrium alkyl complexes with linked triazacyclononane-amide monoanionic ancilliary ligands related to the $O_{Ar}N_3$ system [11]. Bercaw has reported scandium and yttrium trichloride and trimethyl derivatives supported by the neutral 1,4,7-trimethyl-1,4,7-triazacyclononane ligand [12]. Here we describe three new examples of scandium organometallic (and corresponding halide) derivatives that offer new



$H_2N_2NN_{py}$ **1-H$_2$**

$HO_{Ar}N_3$ **2-H**

$H_2O_2NN_{py}$ **3-H$_2$**

Fig. 1. Ligand precursors and the abbreviations used.

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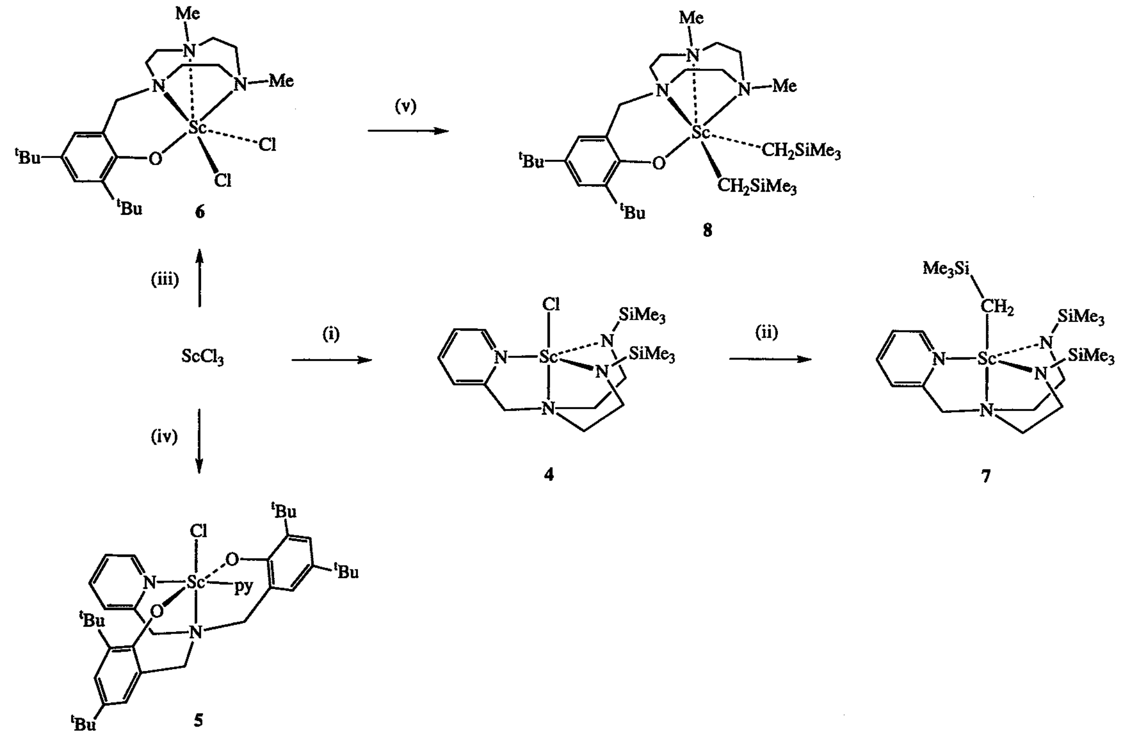
PII: S0022-328X(01)01359-6



Scheme 1. Reagents and yields: (i) $Li_2N_2NN_{py}$, thf, −78 °C to r.t., 2 h, 91%; (ii) $LiCH_2SiMe_3$, benzene, r.t., 20 min, 58%; (iii) $KO_{Ar}N_3$, thf, r.t., 24 h, 77% [7d]; (iv) $Na_2O_2NN_{py}$ and pyridine (excess), thf, −78 °C to r.t., 6 h, 75%; (v) $LiCH_2SiMe_3$ (two equivalents), C_6D_6, r.t., 18 h, >95% (NMR).

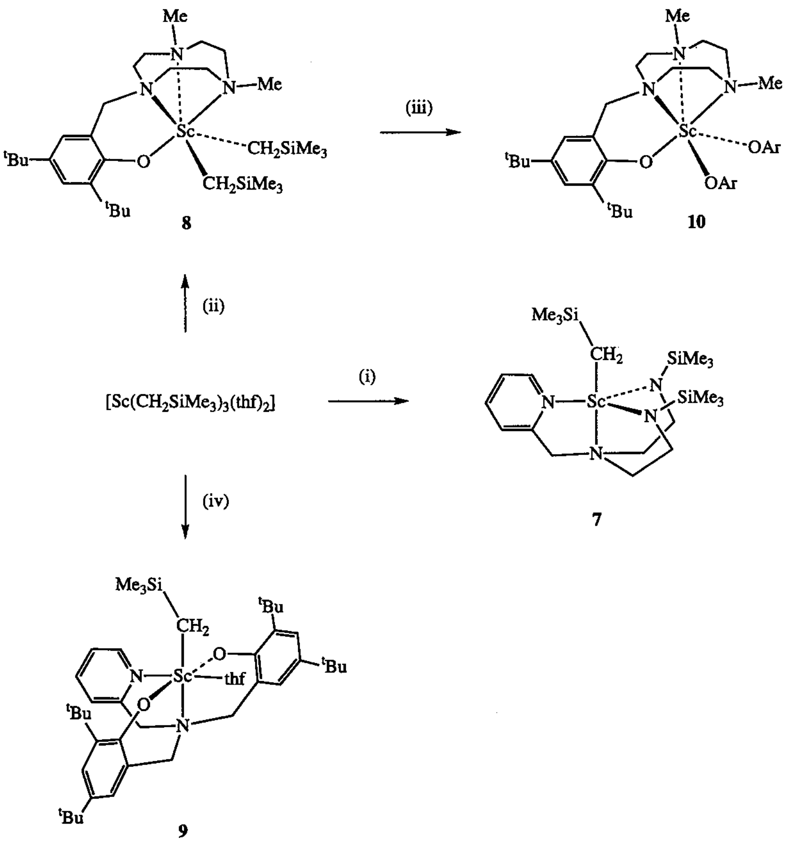
entry points to the organometallic chemistry of this and other Group 3 elements with mono- or di-anionic supporting ligands possessing N_4-, N_3O- or N_2O_2-donor atom sets.

2. Results and discussion

The ligand presursors $H_2N_2NN_{py}$ (**1–H₂**) [6], $HO_{Ar}N_3$ (**2–H**) [7d] and $H_2O_2NN_{py}$ (**3–H₂**) [8], and their alkali metal salts $Li_2N_2NN_{py}$ (**1–Li₂**) [6], $KO_{Ar}N_3$ (**2–K**) [7d] and $Na_2O_2NN_{py}$ (**3–Na₂**) [10] are straighforwardly prepared. Two entry points to organoscandium complexes have been explored, namely starting either from $ScCl_3$ and a metallated ligand precursor (Scheme 1), or from the readily prepared $[Sc(CH_2SiMe_3)_3(thf)_2]$ [13] and the appropriate protio ligand precursor (Scheme 2). The strategies shown in Scheme 1 are, in principle, more general than those in Scheme 2 owing to the greater diversity of organic substituents that could be subsequently introduced by chloride ligand metathesis with, for example, organo-Group 1 or -2 reagents. The chemistry summarised in Schemes 1 and 2 establishes without doubt that all three ligands are compatible with supporting new organometallic chemistry of scandium [14].

Reaction of $ScCl_3$ with $Li_2N_2NN_{py}$ (**1–Li₂**) in thf at −78 °C followed by benzene extraction afforded five-coordinate $[Sc(N_2NN_{py})Cl]$ (**4**) in 91% yield. A similar reaction between $ScCl_3$ and $Na_2O_2NN_{py}$ (**3–Na₂**) in the presence of an excess of pyridine gave six-coordinate $[Sc(O_2NN_{py})Cl(py)]$ (**5**) in 75% yield. Attempts to carry out this reaction in pure thf (i.e. in the absence of added pyridine) gave mixtures consistent with the formation of mono- and bi-nuclear scandium complexes of O_2NN_{py} [15], although no single component could be isolated. We have very recently reported that reaction of $KO_{Ar}N_3$ (**2–K**) with $ScCl_3$ gives $[Sc(O_{Ar}N_3)Cl_2]$ (**6**) in 77% yield [7d], but no Group 3 organometallic complexes of the $O_{Ar}N_3$ ligand were prepared at that time. The crystal structure of $[Sc(O_2NN_{py})Cl(py)]\cdot C_6H_6$ (**5·C₆H₆**) has been determined and the molecular structure of **5** is shown in Fig. 2 along with selected bond distances [16]. The Sc atom possesses approximately octahedral coordination geometry with the Cl ligand positioned *trans* to the tertiary amine donor of O_2NN_{py}. Notably, the aryl rings of the phenoxide moieties in **5** adopt a rather 'flat' arrangement and are somewhat bent away from the pyridine ligand. This makes for a very open sixth coordination site (i.e. the one occupied by pyridine) accounting for the six-coordinate nature of **5** as opposed to the five coordinate complex found for **4**.

Preliminary metathesis experiments with $LiCH_2SiMe_3$ have shown that the monochloride complexes **4**–**6** are entry points to new scandium alkyl



Scheme 2. Reagents and yields: (i) $H_2N_2NN_{py}$, C_6D_6, r.t., 18 h, > 95% (NMR); (ii) $HO_{Ar}N_3$, benzene, 7 °C to r.t., 2 h, 68%; (iii) HOAr (two equivalents), benzene, 7 °C to r.t., 2 h, 49%; (iv) $H_2O_2NN_{py}$, thf, − 78 °C to r.t., 3 h, 47%.

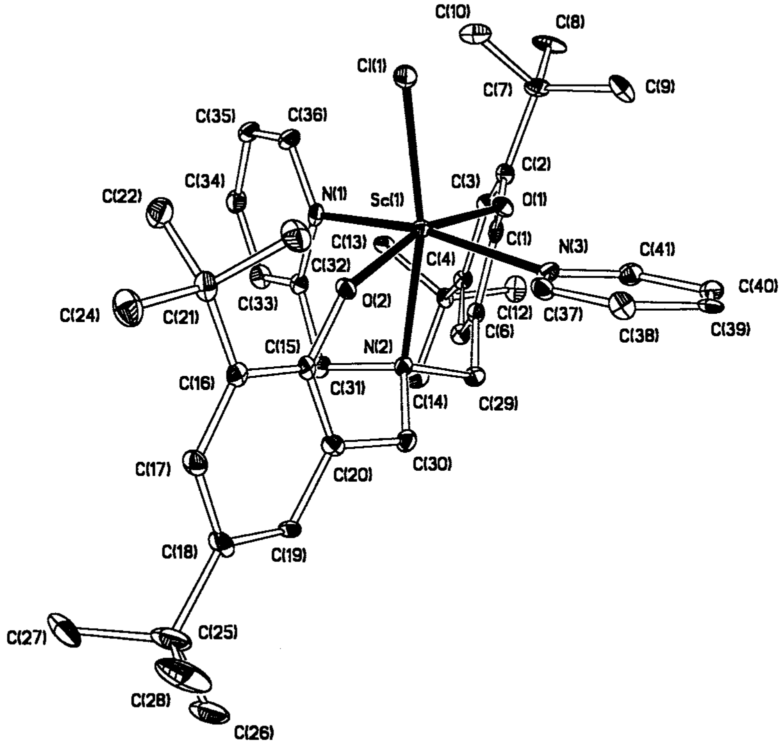


Fig. 2. Displacement ellipsoid plot (20%) of $[Sc(O_2NN_{py})Cl(py)]$ (5). H atoms and benzene molecule of crystallisation omitted for clarity. Selected bond data: Sc(1)–Cl(1), 2.431(2); Sc(1)–N(1), 2.303(6); Sc(1)–N(2), 2.381(5); Sc(1)–N(3), 2.310(5); Sc(1)–O(1), 2.002(4); and Sc(1)–O(2), 1.968(4) Å.

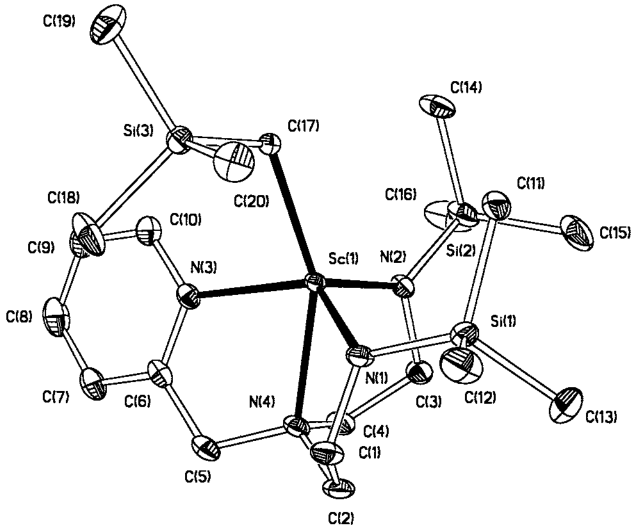


Fig. 3. Displacement ellipsoid plot (20%) of [Sc(N_2NN_{py})(CH_2SiMe_3)] (**7**). H atoms omitted for clarity. Selected bond distances: Sc(1)–N(1), 2.075(2); Sc(1)–N(2), 2.062(1); Sc(1)–N(3), 2.340(2); Sc(1)–N(4), 2.361(1); and Sc(1)–C(17), 2.287(2) Å; Sc(1)–C(17)–Si(3), 115.54(8)°.

complexes. Thus reaction of [Sc(N_2NN_{py})Cl] (**4**) with $LiCH_2SiMe_3$ in benzene gave the five-coordinate alkyl complex [Sc(N_2NN_{py})(CH_2SiMe_3)] (**7**) in 58% isolated yield. Diffraction-quality crystals were obtained from a saturated pentane solution and the molecular structure is shown in Fig. 3 along with selected bond lengths and angles. The Sc centre in **7** has an approximately trigonal bipyramidal coordination geometry and a formal 14 valence electron count, assuming that each amido nitrogen of the N_2NN_{py} ligand can act as a three electron donor. The orientation of the alkyl group in **7** appears to minimise adverse interactions between it and the $SiMe_3$ substituents of the N_2NN_{py} ligand. There is no evidence for agostic interactions in the solid state.

NMR tube scale reactions of [Sc($O_{Ar}N_3$)Cl_2] (**6**) with two equivalents of $LiCH_2SiMe_3$ affords quantitative yields of the *cis*-dialkyl compound [Sc($O_{Ar}N_3$)(CH_2SiMe_3)$_2$] (**8**). The NMR spectra of **8** are identical to those of samples prepared from [Sc(CH_2SiMe_3)$_3$(thf)$_2$] and $HO_{Ar}N_3$ (**2–H**) as summarised in Scheme 2 (see above) [17]. Preliminary reactions between [Sc(O_2NN_{py})Cl(py)] (**5**) and $LiCH_2SiMe_3$ gave a compound tentatively assigned as [Sc(O_2NN_{py})(CH_2SiMe_3)(py)]. We have not isolated this material in pure form as yet, although we have fully characterised the thf-coordinated analogue, [Sc(O_2NN_{py})(CH_2SiMe_3)(thf)] (**9**) (Scheme 2).

Thus (Scheme 2) reaction of [Sc(CH_2SiMe_3)$_3$(thf)$_2$] with the protio ligand precursors $H_2N_2NN_{py}$ (**1–H₂**), $HO_{Ar}N_3$ (**2–H₂**) or $H_2O_2NN_{py}$ (**3–H₂**) give reasonable to good yields of the corresponding mono- or di-alkyl complexes [Sc(N_2NN_{py})(CH_2SiMe_3)] (**7**), [Sc($O_{Ar}N_3$)(CH_2SiMe_3)$_2$] (**8**) or [Sc(O_2NN_{py})(CH_2SiMe_3)(thf)] (**9**), respectively, with elimination of $SiMe_4$ (one or two equivalents). The orientation of the CH_2SiMe_3 group as being *cis* to the O_2NN_{py} pyridyl donor in **9** was estab-

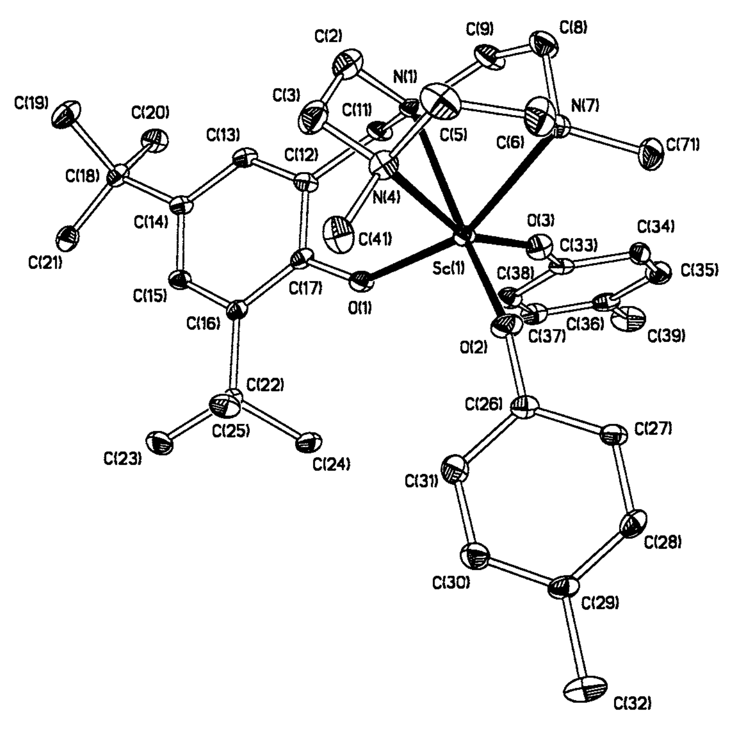


Fig. 4. Displacement ellipsoid plot (20%) of [Sc($O_{Ar}N_3$)(OAr)$_2$] (**10**). H atoms and benzene molecule of crystallisation omitted for clarity. Selected bond distances: Sc(1)–N(1), 2.367(5); Sc(1)–N(4), 2.411(6); Sc(1)–N(7), 2.360(5); Sc(1)–O(1), 1.981(4); Sc(1)–O(2), 1.949(4); and Sc(1)–O(3), 1.963(5) Å.

lished by an nOe experiment; the presence of thf in this complex (but its absence in the related [Sc(N_2NN_{py})(CH_2SiMe_3)]) testifies to the apparently less sterically crowding nature of the O_2NN_{py} ligand in comparison to the related N_2NN_{py}. We were unable to obtain diffraction-quality crystals of the dialkyl complex [Sc($O_{Ar}N_3$)(CH_2SiMe_3)$_2$] (**8**), and so to establish further its identity we treated it with two equivalents of *p*-cresol (HO–4-C_6H_4Me). This protonolysis reaction yielded two equivalents of $SiMe_4$ (observed by ^{1}H-NMR spectroscopy) and the bis(aryloxide) complex [Sc($O_{Ar}N_3$)(OAr)$_2$] (**10**, OAr = O–4-C_6H_4Me). The $O_{Ar}N_3$ ligand sub-spectra of **10** are comparable to those of the precursor **8**. The molecular structure of **10** as determined by X-ray crystallography is illustrated in Fig. 4 together with selected bond lengths. Fig. 4 confirms the proposed molecular structure and lends support to that also proposed for [Sc($O_{Ar}N_3$)(CH_2SiMe_3)$_2$] (**8**).

In conclusion, we have described new organoscandium and related complexes of three new ligand environments for the organometallic chemistry of this element. Work is in progress to probe and define the reaction chemistry of the new complexes and their heavier Group 3 congeners and homologues.

3. Supplementary material

Crystallographic data have been depoisited with the Cambride Crystallographic Data Centre, deposition numbers for compounds **5·C_6H_6**, **7** and **10·C_6H_6**: CCDC 170226, CCDC 170227 and CCDC 170228, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EK, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the University of Oxford, EPSRC and Leverhulme Trust for support of this work. We also thank Dr G.A. Vaughan (Exxon Chemical Co.) for a generous gifts of $ScCl_3$, and Dr T. Toupance for helpful discussions.

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[14] NMR, IR and mass spectroscopic data are fully consistent with the proposed structures. Satisfactory C, H and N combustion analyses have been obtained for all of the new compounds except for the spectroscopically pure $O_{Ar}N_3$-supported compounds **8** and **10**, despite repeated recrystallisations. The EI-mass spectrum of **8** showed an isotope envelope corresponding to $[M-CH_2SiMe_3]^+$; that of **10** showed the expected molecular ion. In addition, the X-ray structure of **10** is fully consistent with the proposed structure. The ^{1}H- and ^{13}C-NMR data for **8** are analogous to those of a fully characterised yttrium analogue [17].

[15] The corresponding reaction with YCl_3 gives the binuclear, seven-coordinate yttrium complex [Y(O_2NN_{py})$_2$(μ-Cl)$_2$(py)$_2$] as established by X-ray crystallography. B.R. Tyrrell, P. Mountford, unpublished results.

[16] X-ray data: For [Sc(O_2NN_{py})Cl(py)]·C_6H_6 (**5·C_6H_6**): $C_{47}H_{61}ClN_3O_2Sc$, $M = 780.43$, monolinic, spacegroup $C2/c$, $a = 27.0551(8)$, $b = 17.8450(5)$, $c = 19.0419(8)$ Å, $\beta = 95.537(1)°$, $U = 9150.5(5)$ Å^3, $Z = 8$, $T = 150$ K, $\mu = 0.26$ mm^{-1}, 10384 independent reflections ($R_{merge} = 0.11$) with 2577 having $I > 3\sigma(I)$ and 4820 having $I > \sigma(I)$ and used in refinement of 457 parameters, final R indices: $R = 0.0667$ [$I > 3\sigma(I)$] and $R_w = 0.0882$ [$I > \sigma(I)$]. For [Sc(N_2NN_{py})(CH_2SiMe_3)] (**7**): $C_{20}H_{43}N_4ScSi_3$, $M = 468.81$, $T = 175$ K, orthorhombic, space-

group $P2_12_12_1$, $a = 12.131(1)$, $b = 13.069(1)$, $c = 17.548(1)$ Å, $U = 2782.1(5)$ Å^3, $Z = 4$, $\mu = 0.40$ mm^{-1}, 5422 independent reflections ($R_{\mathrm{merge}} = 0.02$) with 5037 having $I > 3\sigma(I)$ used in the refinement of 268 parameters, final R indices: $R = 0.030$ and $R_w = 0.0368$. For $[\mathrm{Sc(O_{Ar}N_3)(OAr)_2}]\cdot \mathrm{C_6H_6}$ (**$10\cdot C_6H_6$**): $C_{43}H_{60}N_3O_3Sc$, $M = 711.93$, $T = 150$ K, monoclinic, spacegroup $P2_1/c$, $a = 13.3324(5)$, $b = 14.1401(7)$, $c = 21.400(7)$ Å, $\beta = 90.670(3)°$, $U = 4034.0(4)$ Å^3, $Z = 4$, $\mu = 0.22$ mm^{-1}, 4202 independent reflections ($R_{\mathrm{merge}} = 0.03$) with 2799 having $I > 2\sigma(I)$ used in the refinement of 406 parameters, final R indices: $R = 0.0658$ and $R_w = 0.0636$.

[17] We have recently made and fully characterised an yttrium analogue of **8**, namely $[\mathrm{Y\{(2\text{-}O\text{–}3,5\text{-}C_6H_2{}^tBu_2)CH_2({}^iPr_2)[9]aneN_3\}\text{-}(CH_2SiMe_3)_2}]$. N.A.H. Male, P. Mountford, unpublished results.