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Synthesis, structure and catalytic activity of new iminophenolato complexes of scandium and yttrium

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

The reaction of equimolar amounts of 2-(2,4,6-$Me_3C_6H_2N{=}CH$)(6-Bu^t)C_6H_3OH (HL^1) with $M(CH_2SiMe_3)_3(THF)_3$ (M = Sc or Y) under mild conditions gives $M(CH_2SiMe_3)_2(THF)(L^1)$. The trigonal-bipyramidal structure of these dialkyls was confirmed crystallographically for M = Sc. Whereas the scandium complex is stable in solution at room temperature, the yttrium derivative slowly disproportionates to give $Y(L^1)_3$ which is also accessible from $Y(CH_2SiMe_3)_3(THF)_3$ and three HL^1. The X-ray structure of $Y(L^1)_3$ indicates a chiral tris-chelate complex. While the reaction of the related ligand (2-CyN=CH)(6-Bu^t)C_6H_3OH (HL^2, Cy = cyclohexyl) with $Sc(CH_2SiMe_3)_3(THF)_3$ gives the expected dialkyl $Sc(CH_2SiMe_3)_2(THF)(L^2)$, the reaction with the yttrium analogue affords the six-coordinate monoalkyl product $Y(CH_2SiMe_3)(THF)(L^2)_2$. This product is stable in solution towards disproportionation. The reaction of $Y[N(SiMe_3)_2]_3$ with (2-$C_6F_5N{=}CH$)(6-Bu^t)C_6H_3OH (HL^3) affords $Y\{N(SiMe_3)_2\}(L^3)_2$ and $Y(L^3)_3$. Both complexes are seven-coordinate in the solid state due to Y···F co-ordination to the C_6F_5 substituents. The scandium alkyl complexes are efficient catalysts for the ring-opening polymerisation of ε-caprolactone.

Keywords: Scandium; Yttrium; Chelate complexes; Ring-opening polymerisation

1. Introduction

Following the success of lanthanide metallocene complexes as high-activity ethene polymerisation catalysts [1–3], Group 3 metal complexes with new ligand structures continue to attract considerable attention, because of their catalytic potential. Recent examples include benzamidinato [4–6], guanidinato [7], diketiminato [8–10], aminotroponiminato [11], diamido [12], bis(phenolato) [13] and iminopyrrolato complexes [14]. The combination of sterically demanding ligands and Lewis acidic lanthanide metal centres has given rise to a series of often highly active catalysts for the polymerisation of cyclic esters [15]. We report here the synthesis of scandium and yttrium complexes bearing moderately bulky 2-iminophenolato ligands. The new complexes provide excellent catalysts for the ring-opening polymerisation of ε-caprolactone.

2. Results and discussion

The 2-iminophenol ligands HL^1 and HL^2 were prepared by condensation of *t*-butylsalicylaldehyde with 2,4,6-trimethylaniline and cyclohexylamine, respectively. The reactions of the lithium or sodium salts of these ligands with $MCl_3(THF)_3$ (M = Sc, Y) did not lead to clean products. However, protolysis of the trialkyls $M(CH_2SiMe_3)_3(THF)_3$ (M = Sc or Y) with equimolar amounts of HL^1 in light petroleum at −20 °C resulted in tetramethylsilane elimination and the formation of scandium and yttrium N–O chelate complexes $M(CH_2SiMe_3)_2(THF)(L^1)$ as pale yellow (**1**, M = Sc) or light orange (**2**, M = Y) crystalline solids in high purity and essentially quantitative yields (Scheme 1).

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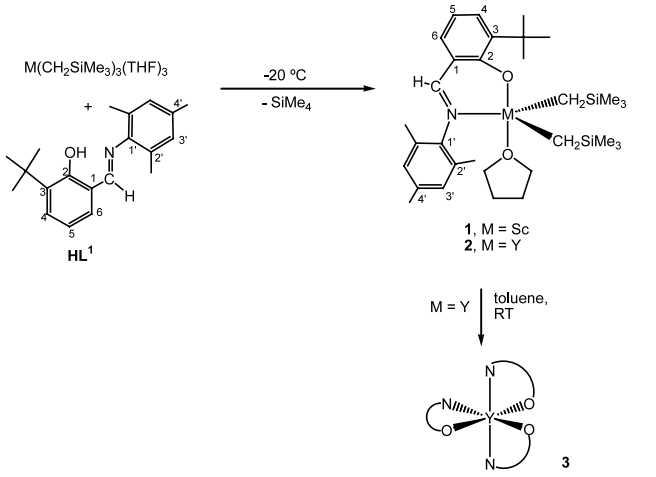


Scheme 1.

The NMR spectra in C_6D_6 at room temperature indicate C_s symmetry of the complexes. While this work was in progress, Piers et al. reported the synthesis of sterically more hindered complexes $M(CH_2SiMe_2Ph)(N{-}O)_2$ (M = Sc, Y) bearing $N{-}C_6H_3Pr^i_2$ substituents which undergo cyclometallation reactions [16].

The crystal structure of **1** (Fig. 1) confirms a trigonal-bipyramidal structure. Selected bond lengths and angles are collected in Table 1. N(1), C(30) and C(40) form the equatorial ligands, in a rather distorted arrangement, with one wide (134.92(7)°) and one more acute (115.80(7)°) N–Sc–C angle. The N(1)ScC(30)C(40) core is planar, with an angle sum around Sc of 359.89°. The axial positions are occupied by the phenolate-oxygen and THF ligands (angle O(1)–Sc–O(5) 161.55(6)°). The Sc–O(1) distance to the phenolate oxygen of 1.993(2) Å is much shorter than the Sc–C distances, while the Sc–N donor bond formed by the imino-nitrogen is significantly longer than the Sc–O(5) interaction with the THF ligand.

The yttrium complex **2** proved not to be stable in solution at room temperature. After about 1 day,

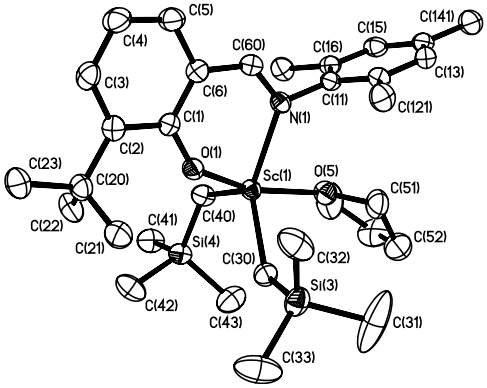


Fig. 1. Molecular structure of $Sc(CH_2SiMe_3)_2(THF)(L^1)$ (**1**), showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability.

Table 1
Selected bond lengths (Å) and angles (°)

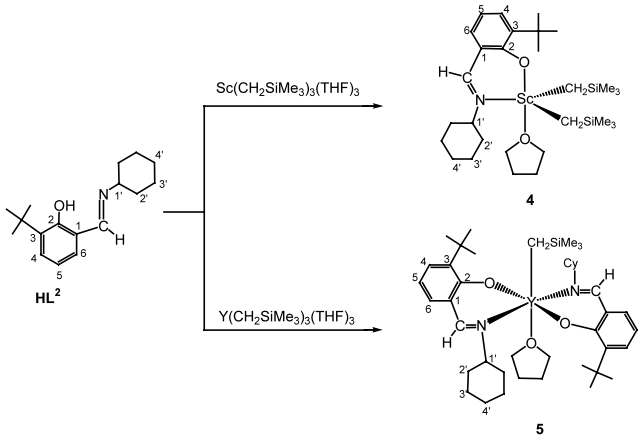
Sc(CH$_2$SiMe$_3$)$_2$(THF)(L^1) (**1**)			
Sc–O(1)	1.993(2)	Sc–O(5)	2.217(2)
Sc–C(30)	2.236(2)	Sc–C(40)	2.246(2)
Sc–N(1)	2.323(2)	Si(3)–C(30)	1.844(2)
N(1)–C(60)	1.305(3)	N(1)–C(11)	1.455(2)
C(1)–O(1)	1.318(3)	C(51)–O(5)	1.460(3)
O(1)–Sc–O(5)	161.55(6)	O(1)–Sc–C(30)	95.31(8)
O(5)–Sc–C(30)	90.90(8)	O(1)–Sc–C(40)	100.93(8)
O(5)–Sc–C(40)	93.36(8)	C(40)–Sc–C(30)	109.17(8)
O(1)–Sc–N(1)	79.61(6)	O(5)–Sc–N(1)	83.70(6)
C(30)–Sc–N(1)	134.92(7)	C(40)–Sc–N(1)	115.80(7)
Y(L^1)$_3$ (**3**)			
Y–O(1)	2.177(3)	Y–O(2)	2.177(2)
Y–O(3)	2.157(3)	Y–N(1)	2.541(3)
Y–N(2)	2.489(3)	Y–N(3)	2.525(3)
O(1)–C(1)	1.331(4)	C(11)–N(1)	1.309(5)
N(1)–C(12)	1.462(5)		
O(1)–Y–O(3)	163.49(9)	O(2)–Y–O(3)	96.33(9)
O(1)–Y–O(2)	90.31(9)	O(1)–Y–N(2)	97.43(10)
O(2)–Y–N(2)	75.93(10)	O(3)–Y–N(3)	75.02(9)
O(1)–Y–N(3)	101.11(9)	O(2)–Y–N(3)	165.69(10)
N(2)–Y–N(3)	93.90(10)	O(3)–Y–N(1)	89.69(10)
O(1)–Y–N(1)	74.23(10)	O(2)–Y–N(1)	100.27(10)
N(2)–Y–N(1)	170.95(10)	N(1)–Y–N(3)	91.19(10)
C(1)–O(1)–Y	142.8(2)	C(21)–O(2)–Y	136.9(2)
C(31)–N(2)–Y	122.2(2)	C(51)–N(3)–Y	122.1(2)
Y{N(SiMe$_3$)$_2$}(L^3)$_2$ (**7**)			
Y–O(1)	2.141(3)	Y–O(2)	2.156(3)
Y–N(3)	2.252(3)	Y–N(1)	2.487(3)
Y–N(2)	2.495(3)	Y–F(17)	2.831(2)
Y–F(37)	2.858(2)	O(1)–C(1)	1.324(5)
C(11)–N(1)	1.316(5)	N(1)–C(12)	1.423(4)
O(1)–Y–O(2)	99.95(10)	O(1)–Y–N(3)	127.41(11)
O(2)–Y–N(3)	132.52(11)	O(1)–Y–N(1)	74.78(10)
O(2)–Y–N(1)	93.50(11)	N(3)–Y–N(1)	95.69(11)
O(1)–Y–N(2)	90.82(10)	O(2)–Y–N(2)	74.25(10)
N(2)–Y–N(3)	104.80(11)	N(1)–Y–N(2)	159.40(10)
O(1)–Y–F(17)	131.37(8)	O(2)–Y–F(17)	66.93(8)
N(1)–Y–F(17)	60.47(9)	N(3)–Y–F(17)	77.74(9)
Y–O(1)–C(1)	141.8(2)	Y–F(17)–C(17)	109.5(2)
F(17)–Y–F(37)	151.83(7)	Y–N(3)–Si(2)	116.4(2)
Y(L^3)$_3$ (**8**)			
Y–O(1)	2.161(2)	Y–O(2)	2.153(3)
Y–O(3)	2.165(2)	Y–N(1)	2.495(3)
Y–N(2)	2.541(3)	Y–N(3)	2.504(3)
Y–F(17)	2.806(2)	O(1)–C(1)	1.323(4)
C(11)–N(1)	1.309(4)	N(1)–C(12)	1.418(4)
O(2)–C(21)	1.317(4)	O(3)–C(41)	1.319(4)
O(1)–Y–O(2)	94.69(9)	O(1)–Y–O(3)	108.96(9)
O(2)–Y–O(3)	155.44(9)	O(3)–Y–N(1)	86.32(10)
O(2)–Y–N(3)	113.86(10)	O(1)–Y–N(1)	75.00(10)
O(2)–Y–N(1)	93.76(10)	N(3)–Y–N(1)	148.20(10)
O(1)–Y–N(2)	156.04(10)	O(2)–Y–N(2)	73.02(9)
N(2)–Y–N(3)	79.94(10)	N(1)–Y–N(2)	125.22(10)
O(1)–Y–F(17)	130.84(8)	O(2)–Y–F(17)	69.50(8)
O(3)–Y–F(17)	89.45(8)	N(2)–Y–F(17)	64.89(8)
N(1)–Y–F(17)	60.76(9)	N(3)–Y–F(17)	142.36(8)
Y–O(1)–C(1)	144.6(2)	Y–F(17)–C(17)	111.4(2)
Y–N(1)–C(11)	124.8(3)	Y–N(1)–C(12)	119.2(2)
Y–N(2)–C(31)	126.9(2)	Y–N(2)–C(32)	118.9(2)

toluene solutions of **2** gave rise to a new product, the tris(chelate) complex $Y(L^1)_3$ (**3**), isolated as orange crystals. The same compound **3** was prepared by reacting $Y(CH_2SiMe_3)_3(THF)_3$ with three molar equivalents of HL^1 in toluene at room temperature. By contrast, the scandium analogue **1** is thermally stable and persists in solution at room temperature for several days.

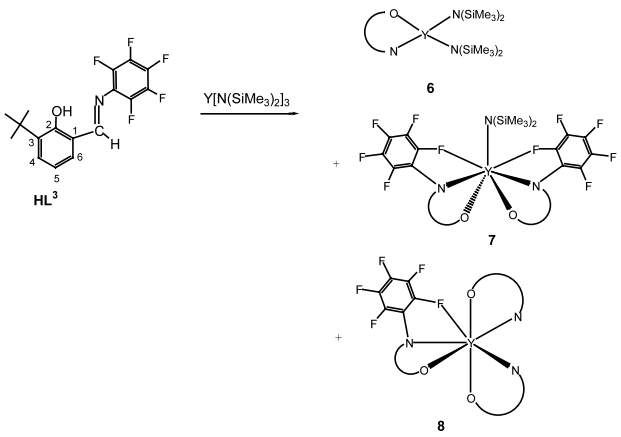
Crystals of **3** suitable for X-ray crystallography were grown from toluene (Fig. 2 and Table 1). The structure shows a racemic tris-chelate complex with two nitrogen and two oxygen atoms mutually in *trans* positions. The nitrogen atoms are trigonal-planar, and the mesityl substituents adopt a conformation approximately perpendicular to the $YONC_3$ rings.

The reaction of Group 3 metal alkyls with the cyclohexyl substituted ligand HL^2 proceeds slightly differently. The reaction of HL^2 with the scandium trialkyl at −20 °C gives $Sc(CH_2SiMe_3)_2(THF)(L^2)$ (**4**) as a pale-yellow solid. By contrast, protolysis of the yttrium trialkyl with either 1 or 2 molar equivalents of HL^2 gives the monoalkyl product, $Y(CH_2SiMe_3)(THF)(L^2)_2$ (**5**). In contrast to the related but bulkier $(N–O)_2MR$ complexes reported by Piers [16], product **5** retains one THF ligand. The NMR spectrum shows two identical N–O chelates (Scheme 2). Unlike **2**, complex **5** is thermally stable and exists in solution unchanged for several days even on heating to 60 °C.

The reaction of the pentafluorophenyl substituted ligand HL^3 with $Y[N(SiMe_3)_2]_3$ in benzene or toluene at 25–60 °C gave a variety of products (Scheme 3). Monitoring an equimolar mixture by ^{1}H-NMR indicated the formation of $Y\{N(SiMe_3)_2(L^3)$ (**6**) alongside $Y\{N(SiMe_3)(L^3)_2$ (**7**), in a ratio of 1:2.3. By contrast, a repeat of this reaction on a preparative scale gave a mixture of **7** (yellow needles) and $Y(L^3)_3$ **8** (yellow cubes). Compound **8** is also prepared in 60% yield as the only isolable product by reacting HL^3 with $Y[N(SiMe_3)_2]_3$ in a molar ratio of 2:1. The bis-amido complex **6** could not be isolated.



Scheme 2.



Scheme 3.

Compounds **7** and **8** were characterised by X-ray crystallography. Both complexes differ from the previously discussed examples by showing an increased coordination number of seven. In **7**, the two phenolate-oxygen atoms are ca. *trans* to the amido ligand (Fig. 3). As expected, the Y–N(3) bond to the amido ligand (2.252(3) Å)is shorter than the donor interactions to the imino-nitrogen atoms (average 2.491(3) Å). The Y–O distances and Y–O–C angles correspond closely to the values of complex **3**. Two bonds to two of the *ortho*-

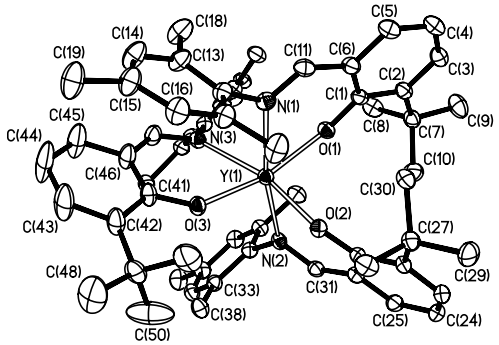


Fig. 2. Molecular structure of $Y(L^1)_3$ (**3**), showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability.

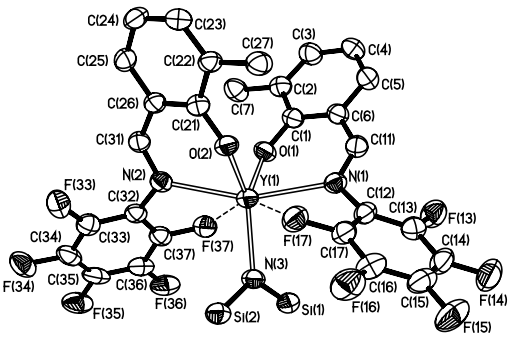
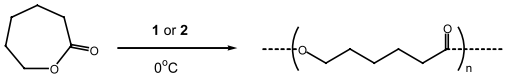


Fig. 3. Molecular structure of $Y\{N(SiMe_3)_2\}(L^3)_2$ (**7**), showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability.

fluorine atoms complete the coordination geometry, average 2.845(2) Å, with a rather wide F–Y–F angle of 151.83(7)°. These Y···F interactions are significantly longer than the Y–F distance in $(C_5H_4SiMe_3)_2Y(\mu\text{-}Me)B(C_6F_5)_3$ (2.366(3) Å) [17]. Complex **8** (Fig. 4) shows only one Y···F bond to one of the three C_6F_5 substituents in the solid state, with a bond distance of 2.806(2) Å. In agreement with the long Y···F distances, these yttrium–fluorine interactions are weak: the ^{19}F-NMR chemical shifts of **7** and **8** in $CDCl_3$ or C_6D_6 are essentially identical to the spectrum of the free ligand and give no indication for persistent Y···F coordination in solution.



(1)

The scandium complex **1** is a highly effective catalyst for the ring-opening polymerisation of ε-caprolactone (Eq. (1)). Mixtures of catalyst and monomer at 0 °C in a ratio of 1:110 led to rapid polymerisation, with quantitative conversion after 1 min. The polymer had a weight-average molecular weight of 71 000 and a polydispersity of 2.9. Longer reaction times gave mainly oils, most probably because of back-biting and formation of cyclic oligomers once the monomer was consumed. The yttrium complex **2** was also active but gave products of moderate molecular weights. NMR analysis of the polymers gave no indication of the nature of end groups; for example $-CH_2SiMe_3$ groups resulting from a possible alkyl transfer in the initiation stage could not be detected.

3. Experimental

3.1. General considerations

All operations were performed under a nitrogen atmosphere using standard Schlenk-line or glove box techniques. After drying over KOH, THF was distilled from sodium benzophenone. Light petroleum (boiling point (b.p.) 40–60 °C) and toluene were purified by distillation from sodium. Anhydrous yttrium trichloride (ALFA) was used as received. $ScCl_3(THF)_3$ was prepared from Sc_2O_3 (Aldrich) [18,19], the compounds $M(CH_2SiMe_3)_3(THF)_3$ from $MCl_3(THF)_3$ according to published procedures [20,21]. All other chemicals were commercially available and used as received unless otherwise stated. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX300 spectrometer (^{1}H, 300 MHz, ^{13}C, 75.47 MHz) in C_6D_6 at room temperature (r.t.). The assignment of all proton and carbon resonance in the spectra was carried out by means of the appropriate ^{13}C–^{1}H heteronuclear correlation (HETCOR). The microanalytical laboratory of this department performed elemental analyses.

3.2. N-(3-tert-Butyl-2-hydroxy)benzylidene(2,4,6-trimethyl)aniline (HL^1)

To a solution of 3-*t*-butylsalicylaldehyde (1.92 ml, 11.6 mmol) in toluene (40 ml) was added 2,4,6-trimethylaniline (2.86 ml, 11.6 mmol) at r.t. After stirring 10 min 0.22 g (1.16 mmol) of *p*-toluenesulphonic acid monohydrate was added as catalyst. The mixture was refluxed for 8 h, the solution concentrated under vacuum and extracted with 50 ml of diethyl ether. The ether solution was dried with anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude product was recrystallised from light petroleum at −30 °C to give yellow crystals, yield 3.22 g (94%). ^{1}H-NMR (300 MHz, C_6D_6): δ 14.24 (s, 1H, OH), 7.79 (s, 1H, CH=N), 7.37 (dd, $^4J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^6), 6.86 (dd, $^4J_{HH} = 1.6$ Hz, $^3J_{HH} = 7.7$ Hz, 1H, CH^4), 6.78 (t, $^3J_{HH} = 7.5$ Hz, 1H, CH^5), 6.75 (s, 2H, $CH^{3'}$), 2.15 (s, 3H, *p*-Me), 1.99 (s, 6H, *o*-Me), 1.61 (s, 9H, Bu^t). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 168.0 (CH=N), 161.5 (COH), 146.3 ($C^{1'}$), 138.2 (C^1), 134.4 ($C^{4'}$), 131.0

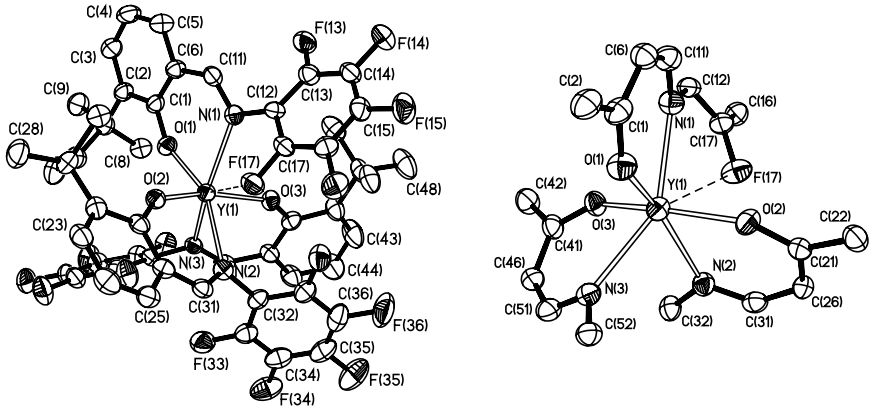


Fig. 4. Molecular structure of Y $(L^3)_3$ (**8**). Left: structure showing the atomic numbering scheme. Right: coordination geometry of **8**, with most ligand atoms omitted for clarity.

(C^4), 130.7 (C^6), 129.4 ($C^{3'}$), 128.6 ($C^{2'}$), 119.4 (C^3), 118.7 (C^5), 35.4 (CMe_3), 29.8 (CMe_3), 21.0 (*p*-Me), 18.6 (*o*-Me). Anal. Calc. for $C_{20}H_{25}NO$: C, 81.3; H, 8.5; N, 4.7. Found: C, 81.4; H, 8.5; N, 4.5%.

3.3. *N*-(3-*tert*-butyl-2-hydroxy)benzylidenecyclohexylamine (HL^2)

The synthetic procedure was the same as for compound HL^1, using 3-*t*-butylsalicylaldehyde (1.92 ml, 11.6 mmol) and cyclohexylamine (1.32 ml, 11.6 mmol) to give HL^2 as yellow crystals, yield 2.86 g (95%). ^{1}H-NMR (300 MHz, C_6D_6): δ 14.64 (s, 1H, OH), 7.89 (s, 1H, CH=N), 7.35 (dd, $^4J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, CH^6), 6.93 (dd, $^4J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, CH^4), 6.81 (t, $^3J_{HH} = 7.4$ Hz, 1H, CH^5), 2.74 (m, 1H, $CH^{1'}$), 1.62 (s, 9H, Bu^t), 1.59–1.09 (m, 10H, $CH^{2'}$ or $CH^{3'}$ or $CH^{4'}$). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 163.5 (CH=N), 161.4 (COH), 137.8 (C^1), 130.0 (C^4), 129.6 (C^6), 119.5 (C^3), 118.2 (C^5), 67.7 ($C^{1'}$), 35.4 (CMe_3), 34.5, 24.5 ($C^{2'}$ or $C^{3'}$), 29.8 (CMe_3), 25.91 ($C^{4'}$). Anal. Calc. for $C_{17}H_{25}NO$: C, 78.7; H, 9.7; N, 5.4. Found: C, 78.9; H, 9.8; N, 5.3%.

3.4. $Sc(CH_2SiMe_3)_2(THF)(L^1)$ (**1**)

To a solution of $Sc(CH_2SiMe_3)_3(THF)_3$ (0.35 g, 0.71 mmol) in light petroleum (30 ml) was added a solution of HL^1 (0.21 g, 0.71 mmol) in petroleum (10 ml) at −20 °C. After stirring at this temperature for 2 h the solution was decanted and concentrated in vacuum. The reaction mixture was filtered and the solid was dried in vacuum. The crude product was recrystallised from toluene (15 ml) to give **1** as pale yellow crystals, yield 0.33 g (80%). ^{1}H-NMR (300 MHz, C_6D_6): δ 7.58 (s, 1H, CH=N), 7.52 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^6), 6.83 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^4), 6.66 (t, $^3J_{HH} = 7.2$ Hz, 1H, CH^5), 6.61 (s, 2H, $CH^{3'}$), 3.68 (br, 4H, THF), 2.08 (s, 3H, *p*-Me), 1.92 (s, 6H, *o*-Me), 1.80 (s, 9H, Bu^t), 1.18 (br, 4H, THF), 0.30 (s, 4H, $ScCH_2$), 0.28 (s, 18H, $SiMe_3$). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 174.6 (CH=N), 166.8 (COSc), 149.1 ($C^{1'}$), 140.0 (C^1), 135.3 ($C^{4'}$), 134.4 (C^4), 134.3 (C^6), 130.1 ($C^{2'}$), 129.4 ($C^{3'}$), 123.1 (C^3), 116.7 (C^5), 70.9 (THF), 40.1 ($ScCH_2$), 35.7 (CMe_3), 31.2 (CMe_3), 25.0 (THF), 20.8 (*p*-Me), 19.5 (*o*-Me), 4.6 ($SiMe_3$). Anal. Calc. for $C_{32}H_{54}NO_2Si_2Sc$: C, 65.5; H, 9.3; N, 2.4. Found: C, 65.8; H, 9.4; N, 2.2%.

3.5. $Y(CH_2SiMe_3)_2(THF)(L^1)$ (**2**)

The synthetic procedure was the same as for complex **1**, using HL^1 (0.21 g, 0.71 mmol) and $Y(CH_2SiMe_3)_3(THF)_3$ (0.43 g, 0.71 mmol) in light petroleum (40 ml) at −20 °C to give **2** as a pale orange solid, yield 0.38 g, 85%. ^{1}H-NMR (300 MHz, C_6D_6): δ 7.60 (d, $^3J_{YH} = 1.3$ Hz, 1H, CH=N), 7.52 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^6), 6.85 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^4), 6.65 (t, $^3J_{HH} = 7.6$ Hz, 1H, CH^5), 6.60 (s, 2H, $CH^{3'}$), 3.52 (br, 4H, THF), 2.07 (s, 3H, *p*-Me), 1.92 (s, 6H, *o*-Me), 1.77 (s, 9H, Bu^t), 1.12 (br, 4H, THF), 0.33 (s, 18H, $SiMe_3$), −0.25 (d, $^2J_{YH} = 2.1$ Hz, 4H, YCH_2). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 174.5 (CH=N), 166.9 (d, $^2J_{YC} = 2.9$ Hz, COY), 148.3 ($C^{1'}$), 140.5 (C^1), 135.2 ($C^{4'}$), 135.0 (C^6), 134.1 (C^4), 129.9 ($C^{2'}$), 129.6 ($C^{3'}$), 123.3 (C^3), 116.3 (C^5), 70.5 (THF), 35.7 (CMe_3), 34.6 (d, $^1J_{YC} = 40.9$ Hz, YCH_2), 30.3 (CMe_3), 24.9 (THF), 20.8 (*p*-Me), 19.2 (*o*-Me), 4.7 ($SiMe_3$). Anal. Calc. for $C_{32}H_{54}NO_2Si_2Y$: C, 61.0; H, 8.6; N, 2.2. Found: C, 61.3; H, 8.7; N, 2.0%.

3.6. $Y(L^1)_3$ (**3**)

A solution of complex **2** (0.30 g, 0.47 mmol) in toluene (40 ml) was stirring at r.t. for 24 h. The solvent was removed in vacuum, leaving an orange solid. The crude product was washed three times with cold petroleum (10 ml) and dried in vacuum to give **3** (0.09 g, 60% based on HL^1). ^{1}H-NMR (300 MHz, C_6D_6): δ 7.81 (d, $^3J_{YH} = 1.7$ Hz, 3H, CH=N), 7.30 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 3H, CH^6), 6.97 (s, 3H, $CH^{3'}$ or $CH^{5'}$), 6.80 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 3H, CH^4), 6.53 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH^5), 6.50 (s, 3H, $CH^{3'}$ or $CH^{5'}$), 2.40 (s, 9H, *p*-Me), 2.15 (s, 9H, *o*-Me), 1.95 (s, 9H, *o*-Me), 0.98 (s, 27H, CMe_3). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 176.5 (CH=N), 165.8 (d, $^2J_{YC} = 3.0$ Hz, COY), 148.4 ($C^{1'}$), 140.6 (C^1), 136.2 ($C^{4'}$), 135.2 (C^6), 134.8 (C^4), 130.1, 129.8 ($C^{2'}$ or $C^{6'}$), 131.2, 128.1 ($C^{3'}$ or $C^{5'}$), 123.1 (C^3), 115.3 (C^5), 36.1 (CMe_3), 26.1 (CMe_3), 22.7 (*p*-Me), 20.2 (*o*-Me), 18.9 (*o*-Me). Anal. Calc. for $C_{60}H_{72}N_3O_3Y$: C, 62.6; H, 6.3; N, 3.6. Found: C, 62.7; H, 6.4; N, 3.4%.

3.7. $Sc(CH_2SiMe_3)_2(THF)(L^2)$ (**4**)

Following the synthetic procedure described for **1** and **2**, HL^2 (0.27 g, 1.03 mmol) and $Sc(CH_2SiMe_3)_3(THF)_3$ (0.46 g, 1.03 mmol) gave **4** as a pale-yellow solid, yield 0.45 g (80%). ^{1}H-NMR (300 MHz, C_6D_6): δ 8.19 (s, 1H, CH=N), 7.43 (dd, $^4J_{HH} = 1.4$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, CH^6), 7.09 (dd, $^4J_{HH} = 1.4$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, CH^4), 6.76 (t, $^3J_{HH} = 7.6$ Hz, 1H, CH^5), 4.47 (tt, $^4J_{HH} = 3.3$ Hz, $^3J_{HH} = 11.6$ Hz, 1H, $CH^{1'}$), 4.06 (br, 4H, THF), 2.24–0.98 (m, 10H, $CH^{2'}$ or $CH^{3'}$or $CH^{4'}$), 1.50 (s, 9H, Bu^t), 1.43 (br, 4H, THF), 0.21 (s, 9H, $SiMe_3$), −0.01 (br, 4H, $ScCH_2$). ^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6): δ 167.5 (CH=N), 164.2 (COSc), 138.3 (C^1), 133.9 (C^4), 132.1 (C^6), 124.4 (C^3), 116.9 (C^5), 71.4 (THF), 60.68 ($C^{1'}$), 35.4 (CMe_3), 35.3 ($ScCH_2$), 33.7, 24.4 ($C^{2'}$ or $C^{3'}$), 29.91 (CMe_3), 26.2 ($C^{4'}$), 25.3 (THF), 4.3 ($SiMe_3$). Anal. Calc. for $C_{29}H_{54}NO_2Si_2Sc$: C, 63.3; H, 9.9; N, 2.5. Found: C, 63.7; H, 9.8; N, 2.3%.

3.8. $Y(CH_2SiMe_3)(THF)(L^2)_2$ (5)

The synthetic procedure was similar to that described for **4**, except for the use of two equivalents of HL^2. The same compound is formed from one equivalent of HL^2, in reduced yield. The reaction of HL^2 (0.30 g, 1.15 mmol) with $Y(CH_2SiMe_3)_3(THF)_3$ (0.35 g, 0.57 mmol) gives **5** as an orange solid, yield 0.33 g (75%). ^{1}H-NMR (300 MHz, C_6D_6): δ 8.01 (s, 2H, CH=N), 7.52 (dd, $^4J_{HH} = 1.3$ Hz, $^3J_{HH} = 7.9$ Hz, 2H, CH^6), 7.06 (dd, $^4J_{HH} = 1.3$ Hz, $^3J_{HH} = 7.9$ Hz, 2H, CH^4), 6.72 (t, $^3J_{HH} = 7.5$ Hz, 2H, CH^5), 3.8 (br, 4H, THF), 3.51 (br, 2H, $CH^{1'}$), 1.75 (s, 18H, Bu^t), 1.76–1.20 (m, 20H, $CH^{2'}$ or $CH^{3'}$ or $CH^{4'}$), 1.43 (br, 4H, THF), 0.36 (s, 9H, $SiMe_3$), −0.52 (d, $^2J_{YH} = 6$ Hz, 2H, YCH_2). $^{13}C\{^1H\}$-NMR (75.47 MHz, C_6D_6): δ 168.7 (CH=N), 166.1 (COY), 139.3 (C^1), 134.6 (C^4), 131.9 (C^6), 123.7 (C^3), 115.3 (C^5), 70.6 (THF), 67.1 ($C^{1'}$), 35.6 (CMe_3), 33.8, 26.1 ($C^{2'}$ or $C^{3'}$), 30.3 (CMe_3), 27.3 (d, $^1J_{YC} = 39.1$ Hz, YCH_2), 25.7 ($C^{4'}$), 25.2 (THF), 5.0 ($SiMe_3$). Anal. Calc. for $C_{42}H_{67}N_2O_3SiY$: C, 65.9; H, 8.8; N, 3.6. Found: C, 65.8; H, 8.3; N, 3.8%.

3.9. Reaction of 2-C_6F_5N=CH(6-Bu^t)C_6H_3OH (HL^3) with $Y[N(SiMe_3)_2]_3$ (ratio 2:1)

$Y[N(SiMe_3)_2]_3$ (30 mg, 0.058 mmol) and 2-C_6F_5N=CH(6-Bu^t)C_6H_3OH (HL^3) (19.9 mg, 0.058 mmol) were dissolved in 0.50 ml of benzene-d_6 at 20 °C in an NMR tube equipped with a Young teflon cap. Spectra of the clear yellow solution recorded at intervals from 15 h to 1 week and after heating to 60 °C show the liberation of $HN(SiMe_3)_2]_3$, as well as two new sets of signals attributed to the complexes $Y\{N(SiMe_3)_2\}_2(L^3)$ (**6**) and $Y\{N(SiMe_3)_2\}(L^3)_2$ (**7**), at a ratio of 1:2.3.

3.9.1. Compound 6

^{1}H-NMR (C_6D_6): δ: 8.03 (s, 1H, CH=N), 7.33 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^6) 6.90 ($^3J_{HH} = 9$ Hz, 1H, CH^4), 6.54 (t, $^3J_{HH} = 9.0$ Hz, 2H, CH^5), 1.34 (s, 9H, Bu^t) 0.30 (s, 36H ($SiMe_3$). $^{19}F\{^1H\}$-NMR: δ: −150.6 (*o*-F), −159.6 (b, *p*-2F), −162.7 (t, br, *m*-2F). $^{13}C\{^1H\}$-NMR (75.47 MHz, C_6D_6): δ: 177.6 (CH=N), 143.2 ($C^{1'}$), 140.7 (C^1), 138.6 ($C^{4'}$), 135.9 (C^4), 135.5 (C^6), 127.8 ($C^{2'}$), 122.4 ($C^{3'}$), 117.8 (C^3), 116.5 (C^5), 35.16 (CMe_3), 29.59 (CMe_3), 4.49 ($SiMe_3$).

3.9.2. Compound 7

^{1}H-NMR (C_6D_6): δ: 7.87 (s, 1H, CH=N) 7.33 (dd, $^4J_{HH} = 1.7$ and 7.5 Hz, 1H, CH^6), 6.90 (t, $^3J_{HH} = 9$ Hz, 1H, CH^4), 6.54 (t, $^3J_{HH} = 9$ Hz, 1H, CH^5), 1.19 (s, 9H, Bu^t), 0.28 (s, 18H, $SiMe_3$). $^{19}F\{^1H\}$-NMR: δ: −151.8 (*o*-F), −158.6 (br, *p*-F), −161.2 (br,*m*-F). $^{13}C\{^1H\}$-NMR (75.47 MHz, C_6D_6): δ: 176.9 (CH=N), 143.2 ($C^{1'}$), 140.8 (C^1), 137.0 ($C^{4'}$), 136.4 (C^4), 135.9 (C^6), 127.5 ($C^{2'}$), 122.5 ($C^{3'}$), 119.2 (C^3), 117.1 (C^5), 35.05 (CMe_3), 29.26 (CMe_3) 4.79 ($SiMe_3$).

3.10. $Y\{N(SiMe_3)_2\}(L^3)_2$ (7) and $Y(L^3)_3$ (8)

To a solution of $Y[N(SiMe_3)_2]_3$ (384 mg, 0.674 mmol) in toluene (2.5 ml) at r.t. was added a solution of HL^3 (463 mg, 0.675 mmol) in toluene (2.5 ml). The reaction mixture was stirred for 12 h at 60 °C. The resulting yellow–brown solution was evaporated, cold petrol was added to the crude product, and the mixture was kept at −26 °C. A bright yellow solid was obtained which consisted of a mixture of crystalline $Y(NR_2)(L^3)_2$ (**7**) and $Y(L^3)_3$ (**8**). Concentrating and cooling the supernatant to −60 °C provided another crop of **8** as yellow cubes. Compound **8**: ^{1}H-NMR ($CDCl_3$): δ: 8.22 (s, 1H, CH=N), 7.40 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^6), 7.00 (dd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 7.5$ Hz, 1H, CH^4), 6.63 (t, $^3J_{HH} = 7.2$ Hz, 1H, CH^5), 1.04 (s, 9H, Bu^t). $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ: −150.8 (*o*-F), -159.3 (br, *p*-F), −162.3 (br, *m*-F). $^{13}C\{^1H\}$-NMR (75.47 MHz, $CDCl_3$): δ 178.2 (CH=N), 143.2 ($C^{1'}$), 140.6 (C^1), 138.6 ($C^{4'}$), 136.9 (C^4), 135.9 (C^6), 127.5 ($C^{2'}$), 122.2 ($C^{3'}$), 119.2 (C^3), 116.1 (C^5), 34.97 (CMe_3), 29.68 (CMe_3) Anal. Calc. for $C_{51}H_{39}F_{15}N_3O_3Y$: C, 54.85; H, 3.52; N, 3.76. Found: C, 54.95; H, 4.17; N, 3.58%.

3.11. Synthesis of $Y(L^3)_3$ (8)

A mixture of $Y[N(SiMe_3)_2]_3$ (384 mg, 0.674 mmol) and HL^3 (463 mg, 1.35 mmol) in toluene (5 ml) was stirred for 12 h at 60 °C. The resulting solution was evaporated and residue recrystallised from light petroleum to give **8** as yellow crystals (60%).

3.12. X-ray crystallography

Crystals coated with dry nujol were mounted on a glass fibre under a cold nitrogen stream. Data were collected at 140(1) K on a Rigaku *R*-Axis IIc image plate diffractometer equipped with a rotating anode X-ray source (Mo–K_α radiation, $\lambda = 0.71069$ Å) and graphite monochromator. Data were processed using the DENZO/SCALEPACK [22] programs. The structure was determined by direct methods in the SHELXS program [23] and refined by full-matrix least-squares methods, on $F^{2'}$s, in SHELXL [24]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms were taken from [25]. Computer programs used were as noted above or on Table 2 [26].

Table 2
Crystallographic data of complexes **1**, **3**, **7** and **8**

	1	**3**	**7**	**8**
Formula	$C_{32}H_{54}NO_2ScSi_2$	$C_{60}H_{72}N_3O_3Y$	$C_{40}H_{44}F_{10}N_3O_2Si_2Y$	$C_{56}H_{51}F_{15}N_3O_3Y$
Crystal size, mm	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.2	0.5 × 0.2 × 0.2	0.2 × 0.1 × 0.1
M_r	585.9	1015.20	933.87	1187.91
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$(no. 2)	$P\bar{1}$	$P2_1/n$
a (Å)	12.404(3)	10.266(2)	11.308(2)	13.115(3)
b (Å)	17.034(3)	12.111(2)	13.363(3)	26.048(5)
c (Å)	16.432(3)	23.973(5)	16.698(3)	16.320(3)
α (°)	90	87.84(3)	92.95(3)	90
β (°)	90.57(3)	77.96(3)	106.28(3)	104.46(3)
γ (°)	90	76.14(3)	113.44(3)	90
Z	4	4	2	4
V (Å^3)	3471.7(12)	2829.9(10)	2183.8(8)	5399(2)
D_{calc} (g cm^{-3})	1.121	1.191	1.420	1.462
μ(Mo–K$_\alpha$) (mm^{-1})	3.1	1.076	1.470	1.178
θ Range (°)	$2.03 \leq \theta \leq 25.39$	$2.09 \leq \theta \leq 25.35$	$2.08 \leq \theta \leq 25.35$	$1.78 \leq \theta \leq 23.50$
Reflections measured	11765	14412	12458	15210
Independent reflections	6359	9052	7435	7807
R_{int}	0.025	0.0816	0.0762	0.0687
wR_2 (all data), R_1 [a]	0.1154, 0.0507	0.1539, 0.0810	0.1159, 0.0847	0.0875, 0.0855

[a] $w = [s^2(F_o^2) + (0.0266P)^2 + 0.606P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

4. Supplementary Material

Tables with crystal and structure refinement data for complexes **1**, **3**, **7** and **8**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 185598 and 185599, 188005 and 188006 for compounds **1**, **3** and **7** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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