Organoamido- and Aryloxo-Lanthanoids, 23[‡]

Aryl Ether C−O Bond Activation by Organoamidolanthanoid(II) Complexes

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Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 65th birthday

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The reaction of ytterbium metal, $HgPh_2$ and *N*-(2-methoxyphenyl)-*N*-(trimethylsilyl)amine (L^1H) or *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine (L^2H) in tetrahydrofuran (thf) unexpectedly yielded the ytterbium(III) complexes $[Yb(L^1)_2(\mu\text{-}OMe)]_2$ **(1)** and $[Yb(L^2)_2(OPh)(thf)]$ **(2)**, the structures of which were established by X-ray crystallography. These are considered to be derived from C–O bond cleavage of the ligand aryl ether moiety by an initially formed Yb^{II} species, e.g. the thermally unstable, but crystallographically authenticated $[Yb(L^1)_2(thf)_2]$ **(3)**, which was independently prepared from $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ and L^1H.

Introduction

Divalent lanthanoid complexes react with a number of oxygen-containing substrates due to the oxophilicity of these metals and the large $Ln^{3+} \rightarrow Ln^{2+}$ reduction potentials (Ln = Yb,Sm).[2] For example, tetrahydrofuran (thf) solutions of SmI_2 have found extensive applications in organic synthesis as a selective reducing agent for ketones.[2−4] Other LnL_2 species are capable of stoichiometric reactions with ketones, forming metal-bound ketyl radical anions,[5,6] and the reductive coupling of carbon dioxide by $Sm(C_5Me_5)_2$ complexes has been reported.[7] Whilst $Sm(C_5Me_5)_2$-induced deoxygenation of epoxides is facile, yielding $[Ln(C_5Me_5)_2(\mu\text{-}O)]_2$,[8] transformations of unstrained carbon−oxygen single bonds occur only under unusual circumstances. For example, thermolytic cleavage of diethyl ether by very low coordinate ytterbium(II) complexes has been reported[9,10] and photolysis of 1,2-dimethoxyethane (dme) solutions of YbI_2 gives the methoxide complex $[YbI_2(\mu\text{-}OMe)(dme)]_2$.[11] Furthermore, cleavage of dme by highly novel La^{II} or Ce^{II} organometallic complexes was recently reported.[12−14] These few examples of C−O cleavage of alkyl ethers contrast the numerous stable coordination complexes of divalent lanthanoids with these ligands.[15,16]

In this contribution, we report the unexpected cleavage of the aryl ether C−O single bond of the anionic bidentate N,O-ligands L^1, L^2 [L^1 = $N(SiMe_3)C_6H_4\text{-}2\text{-}OMe$, L^2 = $N(SiMe_3)C_6H_4\text{-}2\text{-}OPh$] by a ytterbium(II) centre and the characterisation of the lanthanoid(III) products $[Yb(L^1)_2(\mu\text{-}OMe)]_2$ **(1)** and $[Yb(L^2)_2(OPh)(thf)]$ **(2)**. The latter is the first structurally authenticated lanthanoid complex with an unsubstituted phenoxide ligand; surprisingly, for a sterically undemanding ligand, it is nonbridging. The synthesis and characterisation of the thermally unstable, proposed ytterbium(II) precursor $[Yb(L^1)_2(thf)_2]$ **(3)** are also described.

Results and Discussion

We initially attempted to prepare novel ytterbium(II) complexes of the bidentate N,O-ligands L^1 and L^2 (for preparations and the X-ray crystal structure of L^1H see Experimental Section) by a redox transmetallation/ligand exchange reaction (Equation 1).

$$\mathrm{Ln^0 + HgPh_2 + 2LH \longrightarrow \underset{L\,=\,L^1\ or\ L^2}{Ln(L)_2 + 2PhH + Hg^0}} \qquad (1)$$

This route has previously been utilised for the preparation of $Ln(NRR')_2$ species including $[Ln\{N(SiMe_3)Ar\}_2(thf)_2]$ (Ar = $C_6H_3\text{-}2,6\text{-}iPr_2$, Ln = Sm, Yb).[17] The current reactions afford moderate to low yields of red-orange crystals after workup. The presence of L^1 or L^2 was evident from the infrared spectra, but the products were shown to contain Yb^{III} by the observation of $f \leftarrow f$ transitions near 1000 nm[18] in the electronic spectra. Furthermore, the analytical data did not fit the compositions $Yb(L^1)_3$ or $Yb(L^2)_3$ and thus the formation of heteroleptic Yb^{III} species was indicated. X-ray crystallography subsequently revealed that the products were the alkoxide and aryloxide complexes $[Yb(L^1)_2(\mu\text{-}OMe)]_2$ **(1)** and $[Yb(L^2)_2(OPh)(thf)]$ **(2)** (Figure 1 and 2).

Complex **1** crystallises as two virtually identical, but independent, dimers each having two bridging methoxide ligands, chelating L^1 coordination and hexacoordinate ytterbium atoms of an irregular geometry. Both molecules are sited on crystallographic twofold axes through the methox-

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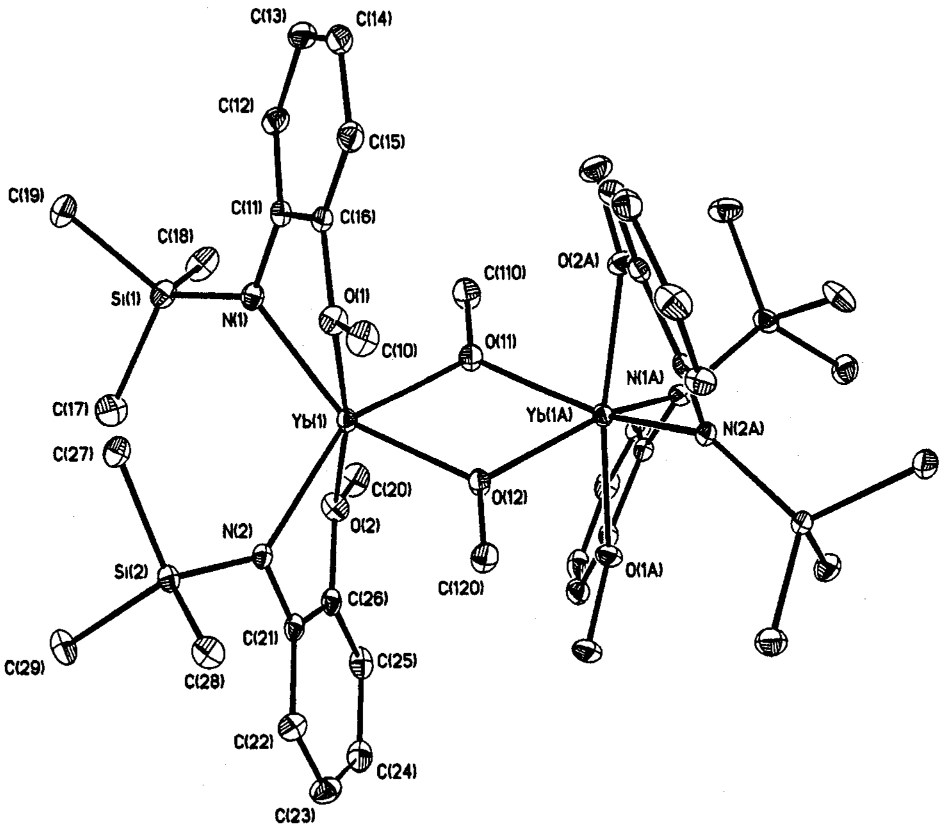


Figure 1. ORTEP view of one molecule of $[Yb(L^1)_2(\mu\text{-}OMe)]_2$ **(1)** drawn with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Yb(1)−O(1) 2.346(2), Yb(1)−O(2) 2.355(2), Yb(1)−N(1) 2.250(3), Yb(1)−N(2) 2.245(3), Yb(1)−O(11) 2.221(2), Yb(1)−O(12) 2.217(2); O(1)−Yb(1)−O(2) 171.09(8), N(1)−Yb(1)−N(2) 112.7(1), N(2)−Yb(1)−O(1) 106.24(9), N(1)−Yb(1)−(O2) 102.03(9), N(2)−Yb(1)−O(2) 71.16(9), N(1)−Yb(1)−O(1) 70.80(9), O(12)−Yb(1)−O(11) 72.5(1), O(12)−Yb(1)−N(2) 91.12(9), O(11)−Yb(1)−N(2) 147.90(7), O(12)−Yb(1)−N(1) 149.79(8), O(11)−Yb(1)−N(1) 93.2(1), O(12)−Yb(1)−O(1) 85.27(6), O(11)−Yb(1)−O(1) 99.85(6), O(12)−Yb(1)−O(2) 103.17(6), O(11)−Yb(1)−O(2) 85.60(6), Yb(1)−O(11)−Yb(1A) 107.4(1), Yb(1)−O(12)−Yb(1A) 107.6(1); symmetry transformation: −x, y, −z + 3/2

ide ligands, hence the four-membered Yb_2O_2 rings are planar. The geometry of the methoxide bridges, with larger O−Yb−O than Yb−O−Yb angles is virtually identical to that of $[CeCp''_2(\mu\text{-}OMe)]_2$ [Cp" = $\eta\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2$].[12] The near equal Yb−OMe distances are comparable with the *longer* of the two Yb−OMe distances 2.210(6), 2.152(4) Å,[11] in $[YbI_2(\mu\text{-}OMe)(dme)]_2$, where the Yb−OMe bond lengthening was attributed to the *trans* influence of the iodide ligand.[11] In **1**, the two methoxide ligands have the same relative dispositions to the amide nitrogens. One nitrogen is *transoid* to each methoxide and hence exerts a *trans* influence. However, the present lengthening may also be attributed to steric crowding, since the Yb−O(ether) distances approach values expected for crowded systems.[19] The ether oxygen atoms of the L^1 ligands are approximately *trans*, with Yb−O bond lengths somewhat larger than those of the dme ligands in $[\{YbI_2(\mu\text{-}OMe)(dme)\}_2]$, 2.317(6) and 2.308(5) Å.[11] Surprisingly, the angle between the nitrogens of the bulky aryl(trimethylsilyl)amide groups is *cisoid* [c.f. *transoid* O(ether)−Yb−O(ether)], although this is consistent with the *fac*-coordination of the alkyl(trimethylsilyl)amide groups in tris(*N*,*N*-dimethyl-*N′*-trimethylsilylethane-1,2-diaminato)lanthanoid(III) complexes.[20] In a similar manner, the bulky carbazolate (cbz) ligands are *cisoid* in six coordinate $[Ln(cbz)_2(thf)_4]$ (Ln = Yb and Sm).[21,22] The Yb−N distances are nearly identical with those of six coordinate $[YbL_2(\mu\text{-}Cl)_2Li(thf)_2]$ [L = $Me_2Si(O\textit{t}Bu)(N\textit{t}Bu)$], 2.247(5) and 2.225(5) Å,[23] implying a similar steric congestion.

In contrast to **1**, complex **2** crystallises as discrete monomers with two independent, but similar, molecules comprising the asymmetric unit, one being displayed in Figure 2. The ytterbium atoms are hexacoordinate, each with an irregular coordination sphere provided by two chelating L^2 ligands, a terminal phenoxide and a coordinated thf. The relative orientation of the L^2 ligands, with the ether-OPh groups coordinated in an approximately *cis* arrangement, is different from that of L^1 in **1**. One of the Yb−O(ether) bond lengths is significantly longer than the other, attributable to its *trans* disposition relative to the phenoxide oxygen. A meaningful *trans*-influence for aryloxide ligands in lanthanoid complexes has been reported.[19] Both the shorter Yb−O(ether) and the Yb−O(thf) bond lengths are of a similar magnitude to the mutually *trans* Yb−O(ether) distances in **1**. As with **1**, the bulky silylamide groups are *cisoid*, and whilst the N−Yb−N angle is marginally smaller than in **1**, there is no significant change in the Yb−N distances. The Yb−OPh distance is comparable to, albeit marginally smaller than, those of terminal 2,6-disubstituted aryloxide ligands bound to six coordinate ytterbium(III) {e.g.

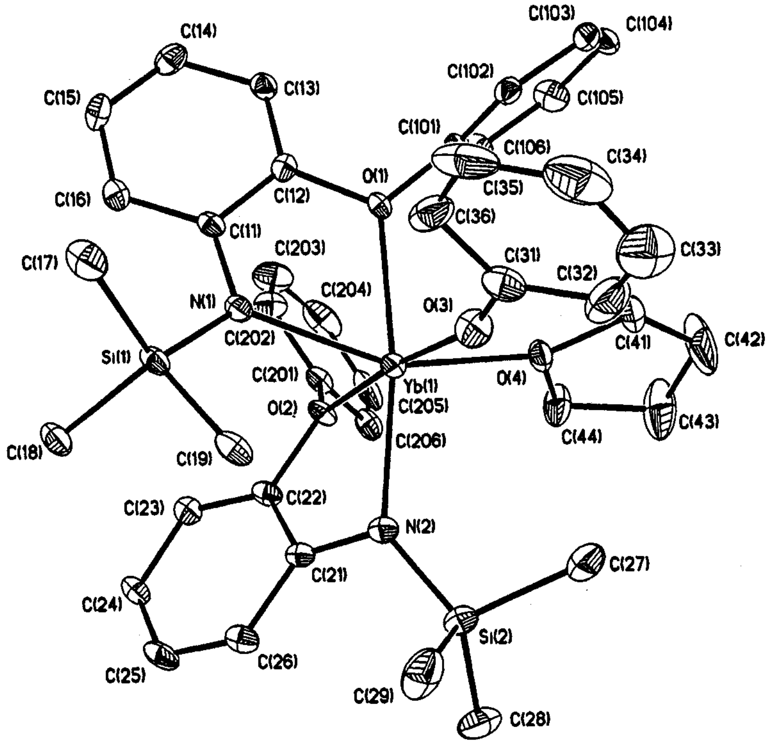


Figure 2. ORTEP view of one molecule of [Yb(L^2)$_2$(OPh)(thf)] **(2)** drawn with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Yb(1)−O(1) 2.380(4), Yb(1)−O(2) 2.459(5); Yb(1)−O(3) 2.023(6), Yb(1)−O(4) 2.357(4), Yb(1)−N(1) 2.250(5), Yb(1)−N(2) 2.247(5), O(3)−Yb(1)−N(2) 108.4(2), O(3)−Yb(1)−N(1) 104.3(2), N(2)−Yb(1)−N(1) 107.0(2), O(3)−Yb(1)−O(4) 86.1(2), N(2)−Yb(1)−O(4) 95.6(2), N(1)−Yb(1)−O(4) 150.3(2), O(3)−Yb(1)−O(1) 95.9(2), N(2)−Yb(1)−O(1) 155.2(2), N(1)−Yb(1)−O(1) 70.7(2), O(4)−Yb(1)−O(1) 80.7(2), O(3)−Yb(1)−O(2) 173.2(2), N(2)−Yb(1)−O(2) 69.9(2), N(1)−Yb(1)−O(2) 82.5(2), O(4)−Yb(1)−O(2) 87.5(2), O(1)−Yb(1)−O(2) 85.4(2)

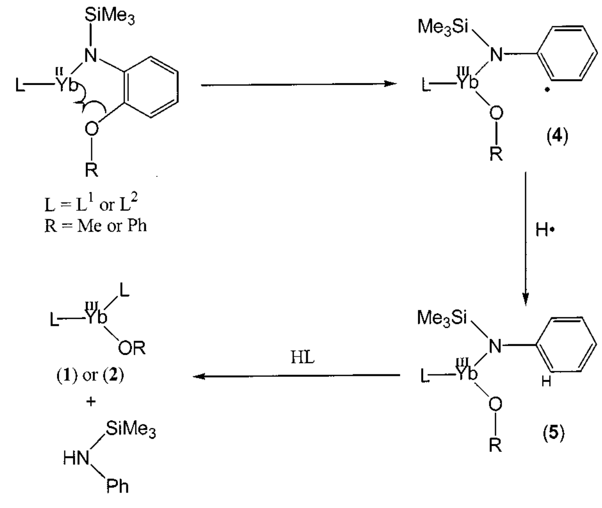
in [Yb(MeC_5H_4)(OAr)$_2$(thf)], 2.040(4) and 2.078(4) Å[24] and [Yb(OAr)Cl_2(thf)$_3$], 2.083(5) Å;[25] Ar = C_6H_2−2,6-*t*Bu$_2$-4-Me}, consistent with reduced crowding in **2**. The structure of **2** is novel as the first authenticated example of an unsubstituted phenoxide bound to a lanthanoid centre.[16,26] There must be a fine balance between formation of a six coordinate μ-OPh (thf-free) species and the observed thf-coordinated structure **2**, since OPh is only marginally bulkier than thf.[27]

The methoxide and phenoxide groups in **1** and **2** are derived from the ligands L^1 and L^2, respectively. There was some ambiguity arising from the use of dme as a recrystallisation solvent in our initial isolation of **1**, since dme could be a OMe source.[11−14] However, the same product is formed in similar yield in the absence of dme (Experimental Section), i.e. where the crude product of the redox transmetallation/ligand exchange was treated with diethyl ether and recrystallised from hexane. We propose that the formation of **1** and **2** occurs by a one-electron transfer from Yb^{II} to an L^1 or L^2 ligand, Ar−O bond cleavage, formation of a Yb^{III}−OR (R = Me or Ph) bond, and then protolysis of the intermediate **5** by L^1H or L^2H (Scheme 1) present as reactants (Equation 1). In confirmation, we have shown that [Yb(L^1)$_2$(thf)$_2$] **(3)** (see below) is converted into **1** in the presence of an excess of L^1H in hexane (see Experimental Section). A GC-MS analysis of the hydrolysed filtrate after the isolation of **2** showed the presence of phenol, *o*-phenoxyaniline and aniline, the last consistent with hydrolysis of the proposed product HNPh($SiMe_3$) and hence with prior proton abstraction (probably from the solvent[28]) by the aryl radical **4** (Scheme 1). The first two are the expected products of hydrolysis of the isolated [Yb(L^2)$_2$(OPh)(thf)] **(2)**. Instability of *N*-trimethylsilylamines to hydrolysis in the present systems was established by partial conversion of L^1H into *o*-methoxyaniline on exposure to air. Whilst a mechanism involving reduction of the aryl ether by ytterbium metal (analogous to alkali metal cleavage of ethers)[29] may also be plausible, it would seem less likely since, under similar conditions, we have previously utilised methoxy-substituted aryloxide ligands in the presence of Yb metal without detection of ether cleavage.[30]

We have also prepared the thermally unstable divalent ytterbium complex [Yb(L^1)$_2$(thf)$_2$] (**3**), by a ligand exchange reaction of [Yb{N($SiMe_3$)$_2$}$_2$(thf)$_2$][17] with L^1H in toluene at −78 °C (Equation 2).

$$\mathrm{Yb\{N(SiMe_3)_2\}_2 + 2L^1H \longrightarrow Yb(L^1)_2 + HN(SiMe_3)_2} \qquad (2)$$

The divalent complex **3** was characterised by spectroscopic methods and a single crystal structure determination. Satisfactory elemental analyses were not obtained, even for single crystals, presumably due to the instability of the complex, but the ^1H NMR spectrum is consistent with the proposed composition. The structure of **3** (Figure 3), determined at 123 K, shows a monomeric complex with the ytterbium atom situated on a twofold axis and surrounded



Scheme 1

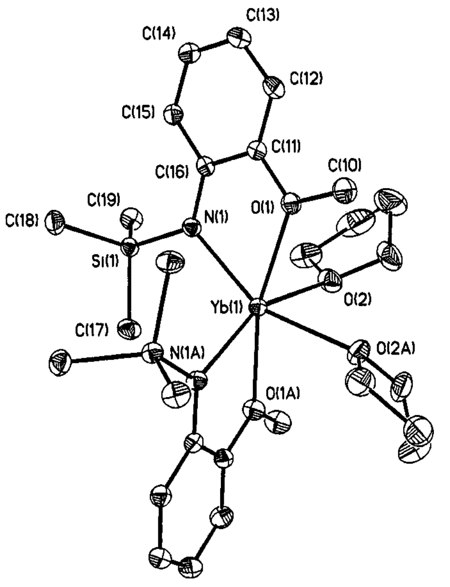


Figure 3. ORTEP view of [Yb(L^1)$_2$(thf)$_2$] (3) drawn with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Yb(1)−O(1) 2.458(2), Yb(1)−O(2) 2.494(2); Yb(1)−N(1) 2.386(2), N(1A)−Yb(1)−N(1) 108.81(12), N(1A)−Yb(1)−O(1) 121.79(8), N(1)−Yb(1)−O(1) 67.71(8), N(1)−Yb(1)−O(1A) 121.79(8), O(1)−Yb(1)−O(1A) 165.43(11), N(1A)−Yb(1)−O(2) 154.33(9), N(1)−Yb(1)−O(2) 89.45(9), O(1)−Yb(1)−O(2) 81.36(9), O(1A)−Yb(1)−O(2) 87.48(8), N(1A)−Yb(1)−O(2A) 89.48(8), O(1A)−Yb(1)−O(2A) 81.35(9), O(2)−Yb(1)−O(2A) 80.01(14); symmetry transformation: −x + 1, y, −z + 3/2

by two chelating L^1 ligands and two *cis* thf molecules with an irregular six-coordinate geometry. The orientation of the L^1 ligands is similar to that found in **1** above, with comparable *transoid* O(ether)−Yb−O(ether) and *cisoid* N−Yb−N angles (Figure 3). The Yb−N distance of **3** is comparable with or shorter than those of [Yb(cbz)$_2$(thf)$_2$(dme)] [2.43(3), 2.45(2) Å][30] and **3** has a similar N−Yb−N angle to that of the unidentate carbazolyl ligands (107.3(7) °).[31] The Yb−O(thf) distance is longer than <Yb−O(thf)> of the six coordinate complex [Yb{PhC(NSiMe$_3$)$_2$}$_2$(thf)$_2$] (2.415 Å)[32] which has *trans* thf ligands since each thf oxygen of **3** is *transoid* to an amide nitrogen. Further, the *cis* thf coordination geometry in **3** is similar to that of [Yb(cbz)$_2$(thf)$_2$(dme)] [Yb−O(thf) 2.41(2), 2.48(2) Å; O(thf)−Yb−O(thf) 87.6(6) °].[31] It is noteworthy that there are only a few examples of bidentate, ether supported, amide ligands attached to a divalent lanthanoid, e.g. deprotonated 4,13-diaza-18-crown-6[33] and Me$_2$Si(O*t*-Bu)(N*t*Bu).[23]

Compounds **1** and **2** are unique examples of the products of O−C(Ar) bond activation by a lanthanoid(II) centre. The ligands L^1 and L^2 also show the ability to stabilise heteroleptic lanthanoid(III) complexes with sterically undemanding co-ligands e.g. OMe, OPh.

Experimental Section

All reactions were carried out under dry nitrogen using dry box and standard Schlenk techniques. Solvents were dried by distillation from sodium wire/benzophenone. IR data (4000−650 cm^{-1}) were recorded for Nujol mulls sandwiched between NaCl plates with a Perkin−Elmer 1600 FTIR spectrometer. NMR spectra were obtained with a Bruker AC 300 MHz (^{1}H) spectrometer. The ytterbium(III) complexes gave unresolvable, uninterpretable, broadened spectra. Mass spectra were recorded with a VG Trio-1 GC mass spectrometer. Each listed *m/z* value for Yb-containing ions is the most intense peak of a cluster pattern in good agreement with the calculated pattern. GC-MS measurements were carried out using helium as a carrier gas and run on a Hewlett-Packard 5890A instrument interfaced to a VG Trio-1 GC mass spectrometer using a XTI-5 column (30m, 0.32 mm id) (bonded 5% phenyl − 95% dimethylpolysiloxane). The temperature program started at 50 °C (2 min) and then was increased by 10 °C/min to 280 °C. Retention times are measured in minutes from injection. Elemental analyses (C,H,N) were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Ytterbium analyses of digested samples were by complexiometric titration with [Na$_2$EDTA].[1,34] [Yb{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] was prepared according to a reported procedure.[17] Commercial HgPh$_2$ (Aldrich) and lanthanoid powders (Rhône-Poulenc) were used as received.

[L^1H]: To a stirred solution of *o*-methoxyaniline (18 mL, 0.16 mol) in ether (100mL) at 0 °C was slowly added *n*BuLi (100 mL, 0.16 mol). After complete addition a white solid was obtained which was stirred and warmed to room temperature (ca. 1 h). Following cooling to 0 °C, Me$_3$SiCl (18.5 mL, 0.16 mol) was slowly added and the reaction mixture was allowed to warm to room temperature (ca. 1 h). The solvent volume was then reduced in vacuo until a residual oil remained which was vacuum distilled and upon cooling formed a colourless moisture-sensitive (see below) crystalline solid (26.7 g, 85%). − m.p. 25−27 °C − IR: $\tilde{\nu}$ = 3401 vs, 3043 s, 2956 vs, 2901 s, 2884 s, 1599 vs, 1504 vs, 1460 s, 1446 s, 1386 vs, 1322 vs, 1289 vs, 1238 vs, 1215 vs, 1174 s, 1113 vs, 1050 s, 1031 vs, 902 vs, 842 vs, 776 s, 735 vs, 689 s, 620 w, 590 w cm^{-1}. − MS: *m/z* (%) = 195 (80) [M$^+$], 180 (50) [(L^1)$^+$ − Me], 165 (100) [(L^1)$^+$ − 2Me], 150 (60) [(L^1)$^+$ − 3Me], 135 (45) [C$_6$H$_5$ONSi$^+$], 108 (19) [C$_6$H$_4$OMe$^+$], 73 (75) [SiMe$_3{}^+$], 58 [SiMe$_2{}^+$]. − ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 0.16 [s, 9 H, Si(C*H*$_3$)$_3$], 3.31 [s, 3 H, OC*H*$_3$], 4.26 [br s, 1 H, N*H*], 6.57 [dd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1 H, H-6], 6.74 [ddd, 1 H, H-5], 6.88 [m, 2 H, H-3, H-4]. − $C_{10}H_{17}NOSi$, (195.34): calcd. C 61.49, H 8.77, N 7.17; found C 61.66, H 8.89, N 7.29.

A sample of L^1H was exposed to air for 5 h, diluted with CHCl$_3$, and analysed by GC-MS: R_t (rel. int.) = 9.73 (100), *m/z* (%) = 123

(90) [$CH_3OC_6H_4NH_2^+$]; R_t = 12.51 (25), *m/z* (%) = 195 (20) [L^1H^+]; no $SiMe_3$-containing decomposition products, e.g. Me_3SiOH, were observed.

[L^2H]: As for L^1H above, 16.9 mL of a solution of *n*BuLi (1.6 M in hexanes) was added dropwise to a stirred solution of *o*-phenoxyaniline (5 g, 27 mmol) in ether (50 mL) at 0 °C. After complete addition a white solid was obtained which was stirred and warmed to room temperature (ca. 1 h) and Me_3SiCl (3.5 mL, 27 mmol) was slowly added. The reaction mixture was stirred for another 5 h. The reaction solution was decanted from the LiCl formed and the solvent volume was then reduced in vacuo until a residual oil remained. This was vacuum distilled and upon cooling formed a colourless moisture-sensitive crystalline solid (5.3 g, 76%). − m.p. 33−35 °C − IR: $\tilde{\nu}$ = 3401 vs, 1606 vs, 1589 s, 1583 s, 1499 s, 1307 vs, 1253 vs, 1240 vs, 1217 s, 1161 s, 1099 vs, 1072 s, 1038 s, 912 vs, 841 s, 750 vs, 689 vs. cm^{-1}. − MS: *m/z* (%) = 257 (60) [M^+], 242 (61) [$(L^2)^+$ − Me], 226 (15) [$(L^2)^+$ − Me_2H], 211 (5) [$(L^2)^+$ − Me_3H], 165 (100) [$OC_6H_4NHSiMe_2^+$], 150 (40) [$C_6H_4ONHSiMe^+$], 135 (30) [$C_6H_4OSiNH^+$], 73 (35) [$SiMe_3^+$], 58 (10) [$SiMe_2^+$]. − ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.07 [s, 9 H, $Si(CH_3)_3$], 4.14 [br s, 1 H, NH], 6.57−6.63 [ddd, 1 H, H-4], 6.76−6.80 [tt, 1 H, H-5], 6.82−6.88 [dd, 1 H, H-3], 6.90−7.02 [m, 6 H, H-6, H-2′,H-3′,H-4′,H-5′,H-6′] − $C_{15}H_{19}NOSi$ (257.41): calcd. C 69.99, H 7.44, N 5.44; found C 69.98, H 7.57, N 5.60.

[$Yb(L^1)_2(\mu\text{-}OMe)]_2$ (1): Method 1. A mixture of ytterbium powder (0.69 g, 4.0 mmol), $HgPh_2$ (0.71 g, 2.0 mmol) and L^1H (0.82 g, 4.0 mmol) in thf (60 mL) was stirred and heated at 60 °C for 24 h. Evaporation to dryness of the filtered reaction mixture gave a red oil. Treatment of the residue with dme (20 mL), evaporation to dryness, and then treatment with hexane (15 mL) afforded red/orange crystals of **1** on standing (0.45 g, 19%). − IR (Nujol): $\tilde{\nu}$ = 1590 vs, 1560 vs, 1314 w, 1287 s, 1242 s, 1204 vs, 1160 vs, 1115 vs, 1050 vs, 1033 vs, 1005 vs, 916 br s, 843 s, 832 s, 782 vs, 768 vs, 723 s, 670 s, 642 vs, 596 vs cm^{-1}. − Vis/near IR (dme): λ_{max} (ε) = 431 (304), 911 (22), 978 (63) nm (dm^3mol^{-1}). − MS: *m/z* (%) = 990 (<1) [M^+ − L^1], 368 (<1) [$(YbL^1)^+$]. − $C_{42}H_{70}N_4O_6Si_4Yb_2$ (1185.47): calcd. C 42.55, H 5.95, N 4.73; found C 42.55, H 5.68, N 4.91.

Method 2: From a similar reaction [with Yb (0.30 g, 1.7 mmol), $HgPh_2$ (0.35 g, 1.0 mmol) and L^1H (0.41 g, 2.0 mmol)], the resulting red oil was treated with diethyl ether instead of dme. Evaporation and recrystallisation of the residue from hexane (20 mL) gave **1** (0.22 g, 23%). The spectroscopic and X-ray properties were identical with those of the product from Method 1.

[$Yb(L^2)_2(OPh)(thf)$] (2): A mixture of ytterbium powder (0.17 g, 1.0 mmol), $HgPh_2$ (0.35 g, 1.0 mmol) and L^2H (0.51 g, 2.0 mmol) in thf (40 mL) was stirred and heated at 60 °C for 24 h. The resulting mixture was filtered and the dark red filtrate evaporated to dryness. Recrystallisation from toluene (20 mL) and standing overnight gave orange crystals (0.18 g, 21%). − IR (Nujol): $\tilde{\nu}$ = 1718 w, 1621 s, 1588 vs, 1554 s, 1307 vs, 1288 s, 1241 s, 1190 vs, 1158 vs, 1101 vs, 1070 vs, 1045 vs, 863 m, 830 br m, 807 m, 786 m, 756 s, 736 s, 706 s, 695 vs, 630 vs, 602 s, 594 s cm^{-1}. − Vis/near IR (dme): λ_{max} (ε) = 416 (401), 919 (31), 982 (73) nm (dm^3mol^{-1}). − MS: *m/z* (%) = 779 (<1) [M^+ − thf], 686 (<1) [$(YbL^2_2)^+$], 613 (<1) [$(YbL^2_2)^+$ − $SiMe_3$], 430 (<1) [$(YbL^2)^+$]. − $C_{40}H_{49}N_2O_4Si_2Yb$ (851.03): calcd. C 56.45, H 5.80, N 3.29; found C 56.41, H 5.77, N 3.59. The reaction filtrate of **2** was hydrolysed with H_2O (15 mL) and this mixture extracted with $CHCl_3$ (30 mL) which was then reduced under vacuum to 5 mL and analysed by GC-MS. − GC-MS: R_t (rel. int.) = 2.62 (80), *m/z* (%) = 93 (10) [$C_6H_5NH_2^+$]; R_t = 7.12 (5), *m/z* (%) = 94 (100) [$C_6H_5OH^+$]; R_t = 17.35 (95), *m/z* (%) = 185 (100) [$C_6H_5OC_6H_4NH_2^+$].

[$Yb(L^1)_2(thf)_2$] (3): A toluene solution (5 mL) of L^1H (0.31 g, 2.0 mmol) was added to a toluene solution (40 mL) of [$Yb(N(SiMe_3)_3)_2(thf)_2$] (0.65 g, 1.0 mmol) at −78 °C. The reaction mixture was warmed to −20 °C and dark red crystals formed overnight (0.54 g, 76%). − IR (Nujol): $\tilde{\nu}$ = 1584 vs, 1552 vs, 1320 sh s, 1296 br s, 1251 s, 1203 vs, 1162 vs, 1116 vs, 1054 vs, 1010 vs, 934 br s, 831 br s, 765 s, 723 s, 668 s, 617 vs, 593 vs cm^{-1}. − Vis/near IR (dme): λ_{max} (ε) = 487 sh (201) nm (dm^3mol^{-1}). − ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.44 [s, 18 H, $Si(CH_3)_3$], 1.19 [br s, 8 H, β-*H* (thf)], 3.35 [s, 8 H, α-*H* (thf)], 3.47 [s, 6 H, OCH_3], 6.54−6.59 [m (br), 4 H, Ar], 7.03 [s (br), 4 H, Ar]. − $C_{28}H_{48}N_2O_4Si_2Yb$ (705.90): calcd. C 47.64, H 6.85, N 3.97, Yb, 24.51; found C 41.75, H 5.90, N 4.63, Yb, 25.59. A sample of diamagnetic **3** in

Table 1. Crystal data and refinement parameters

Compound	**L^1H**[a]	**1**	**2**	**3**
Formula	$C_{10}H_{17}NOSi$	$C_{42}H_{70}N_4O_6Si_4Yb_2$	$C_{40}H_{49}N_2O_4Si_2Yb$	$C_{28}H_{48}N_2O_4Si_2Yb$
M	195.34	1185.47	851.03	705.90
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
Space group	*P*4/*n*	*C*2/*c*	*P*2(1)/n	C2/*c*
a (Å)	25.5964(5)	24.1340(4)	24.3109(3)	15.5139(2)
b (Å)		19.1294(3)	15.0605(2)	11.3411(2)
c (Å)	7.0684(2)	23.6252(4)	24.5560(2)	19.2898(3)
β (°)		112.150(1)	118.833(1)	112.368(1)
V ($Å^3$)	4631.0(13)	10102.1(3)	7876(3)	3138.6(11)
Z	16	4	8	4
ρ_{calcd} ($g.cm^{-3}$)	1.121	1.559	1.435	1.494
μ (cm^{-1})	1.69	38.20	24.76	30.89
F(000)	1696	4752	3464	1440
$2\theta_{max}$ (°)	55.8	60.06	55.8	60.04
N_{total}	18145	35621	97744	22197
N, N_o	5497, 4209	14634, 12012	17146, 12246	4212, 3947
$A^*_{min, max}$		0.524, 0.714	0.754, 0.784	0.906, 1.11
R, R_w [$I>2\sigma(I)$]	0.039, 0.090	0.028, 0.067	0.054, 0.122	0.029, 0.083
R, R_w (all data)	0.060, 0.098	0.044, 0.089	0.100, 0.165	0.033, 0.084
Goodness of Fit	1.037	1.151	1.118	1.039

[a] The asymmetric unit comprises two independent, similar, well separated (no H-bonding), molecules. Bond lengths and angles were as expected,[36] and the details are available in the supplementary data.

C_6D_6 was shown to convert into a paramagnetic species upon heating at 60 °C for 24h by ^1H NMR spectroscopy.

To **3** (0.47 g, 0.66 mmol) in hexane (30 mL) was added L^1H (0.13 g, 0.66 mmol). The resulting mixture was heated to 60 °C for 12h. The reaction mixture was then allowed to stand for 3 weeks at room temperature and the solvent volume was reduced to 3 mL under vacuum giving crystals of **1** which was identified by a unit cell determination and an IR spectrum.

X-ray Crystal Structure Analysis: Crystals were mounted under viscous oil onto a glass fibre. Low temperature ($\approx$123 K) data were collected on an Enraf−Nonius CCD area-detector diffractometer (Mo-K_α radiation, λ = 0.71073 Å, frames comprised 1.0° increments in φ and ω yielding a sphere of data) using proprietary software (Nonius B.V., 1998). Each data set was merged (R_{int} as quoted) to N unique reflections and the structures were solved by conventional methods and refined, with anisotropic thermal parameter forms for the non-hydrogen atoms, by full-matrix least-squares on all F^2 data using the SHELX 97 software package.[35] Hydrogen atoms were included in calculated positions and allowed to ride on the parent carbon atom with isotropic thermal parameters. For **1**, the methoxide carbon atoms lie on crystallographic twofold axes and therefore two sets of hydrogens atoms, each with occupancies of 0.5, were placed on each carbon, disordered about the axes. Crystal and refinement data are listed in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146332 (L^1H), -143939 **(1)**, -143940 **(2)**, -143941 **(3)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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