Organoamido- and Aryloxolanthanoids, 15[◇]
Organometallic Compounds of the Lanthanoids, 116[◇◇]

Syntheses of Low Coordination Number Divalent Lanthanoid Organoamide Complexes, and the X-ray Crystal Structures of Bis[(*N*-2,6-diisopropylphenyl)(*N*-trimethylsilyl)amido]bis(tetrahydrofuran)samarium(II) and -ytterbium(II)

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Received October 15, 1996

Keywords: Mercury / Lanthanides / Lanthanoid(II) complexes / (*N*-2,6-Diisopropylphenyl)(*N*-trimethylsilyl)amide complexes / Bis(trimethylsilyl)amide complexes

The mercury(II) amide complex $Hg[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$ (**1**) was prepared by reaction of $HgBr_2$ with $Li[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]$ in diethyl ether solvent. Redox transmetallation reactions of **1** with elemental samarium, europium or ytterbium in THF solvent (THF = tetrahydrofuran), generated the novel divalent complexes $Ln[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$ with Ln = Sm (**2**), Eu (**3**) and Yb (**4**). **4** was also synthesized by reaction of elemental ytterbium, $HgPh_2$ and $HN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)$ in THF solvent. This generally more convenient approach has also been applied to the preparation of $Ln[N(SiMe_3)_2]_2(THF)_2$ [Ln = Sm (**5**), Yb (**6**)] by reaction of the metals with $HgPh_2$ and $HN(SiMe_3)_2$. Thermal desolvation of **4** under high vacuum gave $Yb[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)$ (**7**), whereas under identical conditions **6** yielded the solvent-free complex $\{Yb[N(SiMe_3)_2]_2\}_2$ (**8**). The new compounds **1**–**4** and **7** are hydrocarbon soluble and ^{171}Yb-NMR spectra were recorded for **4**, **6**, **7** and **8**. X-ray crystal structure determinations of **2** and **4** revealed four-coordinate, distorted tetrahedral metal environments augmented by weak Ln···*ipso*-C(aryl) interactions.

Introduction

The chemistry of the lanthanoid elements is dominated by complexes which have the metal in the trivalent state[2]. However, there is significant interest in complexes of the divalent lanthanoids, accesible primarily for Sm ($4f^6$), Eu ($4f^7$), and Yb ($4f^{14}$), due to their extensive redox chemistry. For example, SmI_2 has proven to be an excellent one-electron reductant for selective transformations of organic substrates[3], and reductive defluorination of fluorocarbons by organolanthanoid(II) compounds has been achieved[4]. Oxidations of divalent species such as $Sm(C_5Me_5)_2$ and $Yb(C_5R_5)_2$ (R = H or Me) have been utilized as a simple synthetic route to a number of unique $LnCp_2X$ species[2a,2c,4a,5] and also expedited entry into lanthanoid(III) catalytic manifolds[6]. Lanthanoid(II) complexes containing the σ-bonded organoamide ligand $N(SiMe_3)_2$ have yielded hydrocarbon-soluble and crystalline compounds (e.g. monomeric $Ln[N(SiMe_3)_2]_2L$, L = neutral donor(s), bimetallic $Na\{Ln[N(SiMe_3)_2]_3\}$ and dimeric $\{Ln[N(SiMe_3)_2]_2\}_2$)[7]. Recent research in lanthanoid(III) amide chemistry has focused on complexes with modified silyl-amide ligands including bulky $N(SiMe_3)Ar$ (Ar = $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}iPr_2C_6H_3$), which has allowed the isolation of some rare examples of stable heteroleptic $Ln(NRR')_2X$ complexes[8]. We now report the redox transmetallation syntheses and chemistry of *divalent* lanthanoid amides incorporating $[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]$ ligands, including the single crystal X-ray structure analyses of $Ln[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$ (Ln = Sm, Yb; THF = tetrahydrofuran), as well as new halide-free syntheses of $Ln[N(SiMe_3)_2]_2(THF)_2$ (Ln = Sm or Yb) from the lanthanoid metal, $HgPh_2$ and $HN(SiMe_3)_2$.

Results and Discussion

Syntheses and Characterization

Redox transmetallation syntheses of lanthanoid complexes (Scheme 1, *n* = 2 or 3) are well established and provide convenient, halide-free preparative methods[2a,c].

[◇] Part 14: Ref.[1a]. – [◇◇] Part 115: Ref.[1b].

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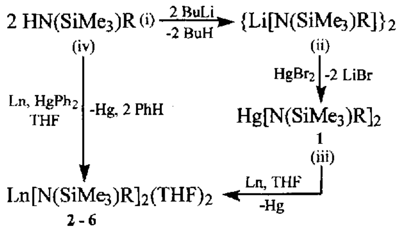
Scheme 1

$$\mathrm{Ln} + n\,\mathrm{ML} \longrightarrow \mathrm{Ln(L)}_n + n\,\mathrm{M}$$

Thus, for organoamidolanthanoids the syntheses of divalent $\mathrm{Ln[N(SiMe_3)_2]_2(DME)}$ (DME = 1,2-dimethoxyethane) from $\mathrm{Hg[N(SiMe_3)_2]_2}$[9] or $\mathrm{Sn[N(SiMe_3)_2]_2}$[10] and elemental lanthanoids have been described. The new redox transmetallation reagent $\mathrm{Hg[N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2}$ (**1**) was synthesized by a standard metathesis reaction from $\mathrm{Li[N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)]}$[11] and $\mathrm{HgBr_2}$ in diethyl ether solvent [Scheme 2 (ii), R = 2,6-$i\mathrm{Pr_2C_6H_3}$] followed by workup in petrol ether and sublimation. The white crystalline, mildly air-sensitive product melts at 177–179 °C, considerably higher than the analogous $\mathrm{Hg[N(SiMe_3)_2]_2}$, which is a liquid at room temperature (m.p. 11 °C)[12]. Notable features in the NMR spectra of **1** were: (i) two *i*Pr methyl ^{1}H and ^{13}C{^{1}H} signals but only a single methine resonance, similar to that observed for $\mathrm{Li[N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)]}$[11] and similarly indicating restricted rotation of the aryl group, and (ii) a single, room temperature ^{199}Hg{^{1}H}-NMR line at $\delta = -1283$ (relative to $\mathrm{HgMe_2}$) in [D$_6$]benzene solution compared to $\delta = -1061$ for neat $\mathrm{Hg[N(SiMe_3)_2]_2}$[13]. A molecular ion was absent in the mass spectrum and the only mercury-containing ion corresponded to loss of a methyl fragment from **1**. The remaining ions appeared to be organic fragments, the most significant being $\mathrm{N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)^+}$. Interestingly, an ion corresponding to $\mathrm{[N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2^+}$ was also observed and presumably arose due to elimination of Hg(0) from **1** within the spectrometer.

Scheme 2



The transmetallation reaction of **1** with an excess of either Sm, Eu or Yb metals in THF solvent generated, in good yield, the new lanthanoid(II) organoamide complexes $\mathrm{Ln[N(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2(THF)_2}$ [Ln = Sm (**2**), Eu (**3**), Yb (**4**)] (Scheme 2 (iii), R = 2,6-$i\mathrm{Pr_2C_6H_3}$). The mercurial was found to be more reactive with Eu and Yb, transmetallation occurring at room temperature, whereas heating to 60 °C was required for Sm. An excess of lanthanoid metal was used in these reactions to ensure complete consumption of the mercurial. No reaction was observed between **1** and Yb in diethyl ether at room temperature or in toluene at 60 °C.

The ytterbium complex **4** was also prepared by reaction of Yb metal, diphenylmercury and $\mathrm{HN(SiMe_3)(2,6\text{-}\mathit{i}Pr_2C_6H_3)}$ [Scheme 2 (iv), R = 2,6-$i\mathrm{Pr_2C_6H_3}$]. Synthesis of **2** by this method was less satisfactory and only a very low yield (<5%) was obtained. This synthetic method was also advantgeously applied to the preparation of $\mathrm{Ln[N(SiMe_3)_2]_2(THF)_2}$ [Ln = Sm (**5**), Yb (**6**)] from the appropriate lanthanoid element, diphenylmercury and $\mathrm{HN(SiMe_3)_2}$ [Scheme 2 (iv), R = $\mathrm{SiMe_3}$]. In these examples the reaction proved more general, with both Sm and Yb complexes readily accesible.

The reactions described above parallel previous versatile syntheses of divalent organometallic[14a,e], aryloxo[14b,c,f], and organoamido[14b,d] lanthanoid complexes which have utilized $\mathrm{Hg(C_6F_5)_2}$ as the organomercury reagent. These redox transmetallation reactions have been shown for Yb[14] to occur by initial formation of $\mathrm{Yb(C_6F_5)_2}$[15] followed by protolysis of the organoytterbium species by a weak organic acid (Scheme 3, R = $\mathrm{C_6F_5}$).

Scheme 3

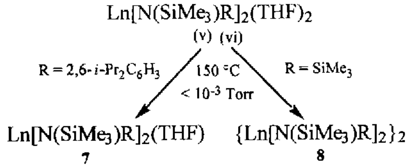
$$\mathrm{Yb} \xrightarrow[\text{-Hg}]{\mathrm{HgR_2}} \mathrm{YbR_2} \xrightarrow[\text{-2 RH}]{\text{2 HL}} \mathrm{Yb(L)_2}$$

An analogous reaction sequence can be envisaged for the current examples (e.g. Scheme 3, R = $\mathrm{C_6H_5}$). The formation of $\mathrm{YbPh_2}$ from activated Yb and $\mathrm{HgPh_2}$ in THF solution has been claimed on the basis of hydrolysis of reaction mixtures and further reaction chemistry (e.g. with $\mathrm{Ph_3SnCl}$ giving $\mathrm{Ph_4Sn}$)[16], but contrasts observations of mixed oxidation state products (by Vis/near-IR spectroscopy of filtered reaction solutions)[17] and the X-ray structure determination of the Yb(II)/Yb(III) complex $\mathrm{Yb_2Ph_5(THF)_4}$ from $\mathrm{Yb(C_{10}H_8)(THF)_2}$ and $\mathrm{HgPh_2}$[18]. Recently the synthesis, from elemental lanthanoids activated by $\mathrm{LnI_3}$ and $\mathrm{HgPh_2}$, and the X-ray structure determination of trivalent $\mathrm{LnPh_3(THF)_3}$ (Ln = Er, Tm) have been described in addition to further claims of reactions of $\mathrm{HgPh_2}$ with Eu and Yb leading to $\mathrm{LnPh_2(THF)_2}$ (Ln = Eu, Yb)[19].

These last observations provide an encouraging basis for the use of $\mathrm{HgPh_2}$ in one-pot redox transmetallation/protolytic ligand exchange reactions, of which (iv) in Scheme 2 represents the first successful applications. It has a distinct advantage over $\mathrm{Hg(C_6F_5)_2}$ due to the higher reactivity of the resulting "in situ" Ln–Ar species, consistent with the relative acidities of $\mathrm{C_6F_5H}$ (pK_a in THF = 25)[14a] and $\mathrm{C_6H_6}$ (p$K_\mathrm{a} \approx 43$)[20]. Indeed reaction of $\mathrm{Yb(C_6F_5)_2}$ with $\mathrm{HN(SiMe_3)_2}$ (pK_a in THF = 30)[21] does not occur, and indicates that the synthesis of $\mathrm{Yb[N(SiMe_3)_2]_2}$ from $\mathrm{Yb/Hg(C_6F_5)_2/HN(SiMe_3)_2}$, analogous to (iv) in Scheme 2, is unlikely. A wider application of $\mathrm{Ln/HgPh_2/HL}$ reactions for the synthesis of lanthanoid complexes should be possible and this is currently being pursued. These preparations of $\mathrm{Ln[N(SiMe_3)_2]_2(THF)_2}$ (Ln = Sm, Yb) represent a convenient source of these synthetically valuable compounds from commercially available materials. Whilst the reactions were carried out using an excess of the lanthanoid metal to ensure complete consumption of the mercurial, the metal residues from these preparations, consisting of the excess lanthanoid metals and precipitated Hg, could be used as a source of activated lanthanoid metals in further reactions in which the presence of mercury could be tolerated.

The amide complexes can be readily recrystallized from aliphatic solvents without loss of THF. However, when heated to 150 °C under reduced pressure, **4** loses one molecule of THF and converts to orange-brown Yb[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$(THF) (**7**) [Scheme 4 (v), R = 2,6-*i*Pr$_2$C$_6$H$_3$]. Under the same conditions **6** loses both molecules of THF, giving the known solvent-free dimer {Yb[N(SiMe$_3$)]$_2$}$_2$ (**8**)[7d,h] [Scheme 4 (vi) R = SiMe$_3$].

Scheme 4



These results provide a direct comparison of N(SiMe$_3$)$_2$ vs. N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$) ligation at the same metal centre. The former is clearly less bulky given the structural characterization of dimeric and five-coordinate {M[N(SiMe$_3$)$_2$]$_2$Cl(THF)}$_2$, (M = Gd, Yb)[22] in contrast to monomeric and four coordiante Nd[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$]Cl(THF)[8]. The formation of THF-free and dimeric three-coordinate **8** suggests that **7** may be monomeric and three coordinate. It can be argued that the initial product from the desolvation of **6** is also a mono-THF complex viz. Yb[N(SiMe$_3$)$_2$]$_2$(THF) which may be unstable due to inadequate steric shielding of the metal centre and hence may dimerize and eliminate further THF to yield **8**.

The new lanthanoid organoamide complexes described above have been characterized by elemental analyses, IR and NMR spectra and by X-ray structure determination for **2** and **4** (see below). Whilst the syntheses of a number of ether complexes of the type Ln[N(SiMe$_3$)$_2$]$_2$(L)$_2$ have been reported[7] and **5** has been structurally characterized[7e], **6** has not been fully described until now. Spectral data for **5**[7e,f] and **8**[7d,h] were in agreement with those reported. The ^{1}H-NMR data for **5**[7e] has recently been updated[7f] and are consistent with the current results. For **8**, the ^{171}Yb-NMR resonance (δ = 784) recorded at 293 K appropriately lies between reported values at 263 K (δ = 796)[23] and 304 K (δ = 779)[24]. IR spectra were consistent with the presence of the amide ligand[8] and coordinated THF[25]. For diamagnetic Yb (4f^{14}), normal-range NMR spectra were observed whilst for Sm (4f^6) there was a significant paramagnetic influence, although assignments were readily determined by peak integration and multiplicities. However strongly paramagnetic Eu (4f^7) gave only a very broad peak (ca. 15 ppm) in an otherwise featureless spectrum. In all cases only a single set of ligand ^{1}H and ^{13}C resonances was observed and, for **4**, **6**, and **7**, a single, broad ^{171}Yb-NMR line at room temperature (Table 1). Presumably these complexes undergo fast (on the NMR timescale) exchange processes possibly involving partial dissociation of the ether ligands and resulting in a time-averaged spectrum. The *i*Pr ^{1}H resonances for **4** and **7** revealed one doublet and one septet for the methyl and methine groups respectively. However, the ^{1}H-NMR spectrum of **2**, although paramagnetically shifted and broadened, clearly showed two broad peaks, each integrating for 12 protons and assigned to the *i*Pr CH$_3$ groups, but only a single peak for the CH group. This parallels features of the spectra of Hg[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$ (above) and Li[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)][11] and indicates restricted rotation of the 2,6-*i*Pr$_2$C$_6$H$_3$ group around the N−C bond, giving different *i*Pr methyl environments above and below the C$_6$ plane. Given the virtually identical structures of **2** and **4** (see below), the single *i*Pr methyl resonance for the Yb complexes presumably results from accidental magnetic equivalence of the methyl environments. The ^{171}Yb-NMR resonances of complexes **4**, **6** and **7** (Table 1) were near the chemical shift region reported for Yb[N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$[23]. Observed chemical shifts for **4** and **6** in THF solution were at lower frequencies than in toluene and suggest differing structures. This may be due to partial dissociation of THF from **4** in noncoordinating media since higher frequency ^{171}Yb-NMR peaks are generally, but not always, associated with lower coordination numbers for closely related complexes [e.g. **4** and **7** (Table 1): Yb(OAr)$_2$(THF)$_3$ δ(^{171}Yb) = 286 at 233 K[14c] and Yb(OAr)$_2$(THF)$_2$ δ(^{171}Yb) = 345 at 298 K (Ar = 2,6-*t*Bu$_2$-4-MeC$_6$H$_2$)[7h]].

Table 1. ^{171}Yb-NMR chemical shift data (δ) for Yb(II) diorganoamides

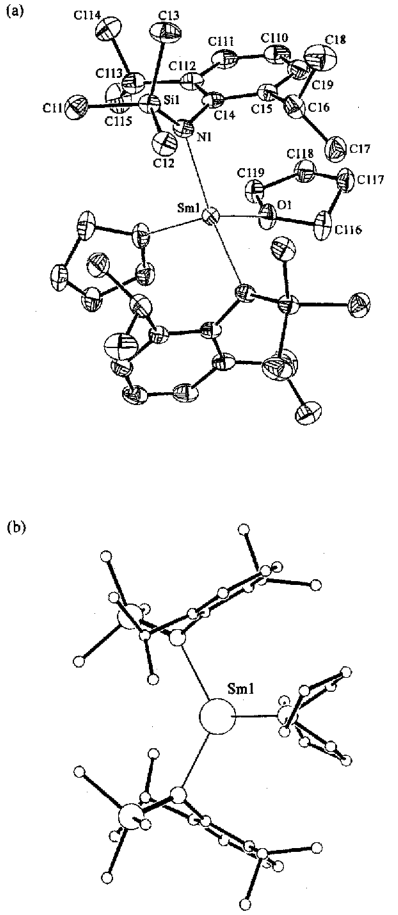
Compound	Solvent	*T* (K)	δ (^{171}Yb)	$\Delta\nu_{1/2}$ (Hz)	ref.
Yb[N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$	OEt$_2$	193	614[a]	70	[23]
4	THF	296	623	40	[b]
	toluene	296	629	40	[b]
7	toluene	297	638	70	[b]
6	THF	296	670	200	[b]
	toluene	296	683	300	[b]
8	toluene	293	784[c]	200	[b]
Yb[N(SiMe$_3$)$_2$]$_2$(py)$_2$	py	213	919	200	[23]
Na{Yb[N(SiMe$_3$)$_2$]$_3$}	toluene	193	947	190	[23]
Yb[N(SiMe$_3$)$_2$]$_2$(dmpe)	toluene	193	1228	60	[23]

[a] ^1J(^{171}Yb−^{14}N) 117 Hz. – [b] This work. – [c] Chemical shift data previously reported for (**8**): δ = 796 at 263 K[23], 779 at 304 K[24].

Crystal Structure Analyses

The molecular structure, atom numbering scheme for one molecule of **2** and selected bond length and angle data for **2** and **4** are shown in Figure 1. The structures of **2** and **4** are similar in their overall geometric appearance and both showed two crystallographically independent molecules in the unit cell. However, whilst one molecule for **4** was well behaved, the second molecule was disordered over two positions, except for Yb(2) and two of the aryl carbon atoms which were common to both disordered parts, and this presumably contributed to the relatively large *R* indices for **4** and the large estimated standard deviations of the bond length and angle data for the second molecule. The origin of the disorder is not known, but appears unlikely to be due to a phase transition induced by cooling. In the following discussion only data for the well behaved molecule in **4** are considered. The relative orientations of the amide ligand pair on a single metal were different in the two independent molecules in **2**, such that, discounting minor bond length and angle variations, the molecules are nonsuperimposable

Figure 1. (a) ORTEP plot of one independent molecule of Sm[N(SiMe$_3$)(2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(THF)$_2$ (**2**)[a], drawn at 30% probability level: hydrogen atoms are omitted for clarity; (b) side view of **2**



[a] Selected bond distance (Å) and angle (°) data with estimated standard deviations in parentheses: **2** Sm(1)–N(1) 2.481(3), Sm(2)–N(2) 2.458(3), Sm(1)–O(1) 2.537(3), Sm(2)–O(2) 2.539(3), Sm(1)···C(14) 2.920(9), Sm(2)···C(24) 2.934(9), N(1)–Sm(1)–N(1)′ 127.0(2), N(2)–Sm(2)–N(2)′ 121.6(2), O(1)–Sm(1)–O(1)′ 81.14(14), O(2)–Sm(2)–O(2)′ 84.28(13), Si(1)–N(1)–Sm(1) 138.4(2), Si(2)–N(2)–Sm(2) 137.3(2), C(14)–N(1)–Sm(1) 93.5(2), C(24)–N(2)–Sm(2) 95.1(2). **4** (not shown) Yb(1)–N(1) 2.354(7), Yb(1)–O(1) 2.390(6), Yb(1)···C(1) 2.872(9), N(1)–Yb–N(1)′ 128.2(3), O(1)–Yb–O(1)′ 90.5(3), Si(1)–N(1)–Yb 137.8(4), C(1)–N(1)–Yb(1) 96.8(5). Data for the second (disordered) molecule of **4** are listed in the supplementary material.

mirror images in the *solid state.* **4** is similar although it is complicated by the disorder in the second molecule.

The Sm and Yb atoms in **2** and **4** are surrounded principally by the two oxygen atoms from the THF ligands and the two amide nitrogen atoms. These ligating atoms form a distorted tetrahedron (Figure 1a), a classical lanthanoid structural motif reminiscent of the numerous pseudo tetrahedral Cp$_2$LnL$_2$ structures[2]. A twofold rotation axis bisects the O–Ln–O angle. The distortions from a regular tetrahedral metal environments are evident from the large N–Ln–N and small O–Ln–O angles and presumably result from steric repulsion between the two bulky amide ligands. The geometry of the metal coordination sphere for **2** is similar to the structure of the analogous **5**[7e] but with larger N–Sm–N angles [e.g. for **5**, N–Sm–N 118.0(3)°][7e] consistent with the increased steric bulk of N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$) compared with N(SiMe$_3$)$_2$. The metal-nitrogen distances in **2** are marginally longer than those in **5** [Sm–N 2.442(9) and 2.424(9) Å][7e], whilst the metal–oxygen distances are smaller [Sm–O **5** 2.586(9), 2.607(9) Å][7e]. For **4**, bond length data are similar to the appropriate bond lengths in four-coordinate Yb[N(SiMe$_3$)$_2$]$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$) [Yb–N, 2.331(13) Å][7b] and Yb(O-2,6-*t*Bu$_2$-4-MeC$_6$H$_3$)$_2$(THF)$_2$ [Yb–O(THF), 2.369(10) and 2.382(10) Å][14c]. The differences in the bond lengths between **2** and **4** are as expected given that the ionic radius for Sm(II) is approximately 0.14 Å larger than that of Yb(II) for the same coordination number[26]. The amide ligands are bound to the metal centre through a near-planar nitrogen [Σ(°) = 359.6–360.0] and there is a marked difference between the Ln–N–Si and Ln–N–C angles. Associated with the acute Ln–N–C angles are close Ln···*ipso*-C(aryl) distances of 2.920(9) and 2.934(9) Å for **2** and 2.872(9) Å for **4** which, although long compared with Ln–C(Ph) of phenyllanthanoid complexes [e.g. 2.511(8) Å in Sm(C$_5$Me$_5$)$_2$Ph(THF)[27]; av. 2.42 Å (terminal) and 2.60 Å (bridging) in YbPh$_2$(THF)(μ-Ph)$_3$Yb(THF)$_3$[18]], are considered weak but significant bonding interactions. Similar structural features have previously been observed for trivalent Nd[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$Cl(THF) [Si–N–Nd 139.4(1)°, *ipso*-C–N–Nd 96.7(1)°, Nd–*ipso*-C 2.814(2) Å][8] and group-4 metal derivatives such as Zr[N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$Cl$_2$[28]. The latter is particularly instructive as one N(SiMe)(2,6-*i*Pr$_2$C$_6$H$_3$) ligand is similar to the above [i.e. Si–N–Zr 138.29(12)°, *ipso*-C–N–Zr 101.8(2)°, Zr–*ipso*-C 2.732(3) Å] whilst the other shows near identical angles [Si–N–Zr 120.93(11)°, *ipso*-C–N–Zr 119.1(2)°] and has no close Zr–*ipso*-C distance. In a recent review of lanthanoid complexes with neutral π-donor ligands[29], metal–carbon distances were compared by subtraction of the appropriate ionic radii. In the current structures, this yields values of 1.85, 1.86 (**2**) and 1.97 (**4**) Å, which compare well with the range (1.89–2.22 Å) for established examples of intramolecular interactions involving lanthanoid elements and pendant ligand phenyl groups and also intermolecular π-arene–Ln bonding observed in dimeric [Ln(OAr)$_3$]$_2$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) complexes[29]. In addition, agostic Ln···CH$_3$ interactions typically observed in Ln(II)–N(SiMe$_3$)$_2$ complexes[7] have Ln···C distances (Sm···H$_3$C–Si, 3.32(1)–3.46(1) and Yb···H$_3$C–Si, 2.86–3.50 Å) often significantly longer than Ln···*ipso*-C in the present structures.

We are grateful to the *Australian Research Council* for financial support and for an Australian Postdoctoral Fellowship (C. M. F.).

Experimental Section

The compounds described here are extremely air- and moisture-sensitive and consequently all operations were carried out in an inert atmosphere (argon, nitrogen). Handling methods and solvent purification were as described previously[1a]. Light petroleum refers to the fraction boiling between 40–60 °C. IR data (4000–650 cm^{-1}) were obtained for Nujol mulls sandwiched between NaCl plates with a Perkin Elmer 1600 FTIR spectrometer. Room temperature (20 °C) NMR spectra were recorded on a Bruker AC 200 MHz (^{1}H, ^{13}C) or AM 300 MHz (^{199}Hg, ^{171}Yb) spectrometer. The chemical shift references were the residual solvent signals ([D$_6$]benzene δ_H = 7.15, δ_C = 128.0; [D$_8$]THF δ_H = 1.73, 3.58, δ_C = 25.3, 67.4) or external $HgMe_2$ (neat) (^{199}Hg, δ = 0.0) or $Yb(C_5Me_5)_2(THF)_2$ (0.15 M solution in THF) (^{171}Yb, δ = 0.0). Degrees of substitution for ^{13}C nuclei were determined using $^{1}H-^{13}C$ *J*-modulation pulse sequences. [D$_6$]benzene (Cambridge Isotopes) was dried over sodium/potassium alloy and [D$_8$]THF (Cambridge Isotopes) was dried over CaH_2. The deuterated solvents were then vacuum-transferred to greaseless Schlenk tubes and stored under purified argon. Metal analyses were by EDTA titration with xylenol orange indicator and hexamine buffer of solutions prepared by digestion of accurately weighed samples in conc. HNO_3/2% conc. H_2SO_4 followed by dilution with water. Microanalytical data (C, H, N) were determined either by the Campbell microanalytical service, University of Otago, New Zealand or by Chemical and Microanalytical Servies Pty. Ltd. Belmont, Australia. Lanthanoid elements as powders or distilled metal ingots were obtained from Research Chemicals or Rhône-Poulenc. Diphenyl mercury was purchased from Aldrich or prepared from PhHgOAc and PhMgBr and twice recrystallized from light petroleum before use. 1,1,1,3,3,3-Hexamethyldislazane was obtained from Aldrich and dried over activated molecular sieves; *N*-trimethylsilyl-2,6-diisopropylaniline was prepared by a literature procedure[30]. All amines were distilled into greaseless Schlenk tubes and stored under argon. *N*-Lithio-*N*-trimethylsilyl-2,6-diisopropylaniline was prepared by the literature method[11].

Bis[N-(2,6-diisopropylphenyl)-N-(trimethylsilyl)amido]mercury(II) (**1**): A mixture of $HgBr_2$ (6.5 g, 18 mmol) and $Li[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]$ (9.2 g, 36 mmol) in diethyl ether (80 ml) was stirred at room temperature for 4 h. The solvent was removed under vacuum and the white residue was treated with light petroleum (60 ml). The resulting grey-white suspension was filtered and the clear and colourless filtrate was evaporated to dryness and gave 11.6 g (92%) of white crystalline $Hg[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$, which was further purified by vacuum sublimation (120−130 °C, 10^{-3} Torr). − M.p.: 177−179 °C. − IR: $\tilde{\nu}$ = 1572 cm^{-1} w, 1314 s, 1247 vs, 1194 s, 1107 m, 1041 m, 951 s, 934 vs, 882 w, 851 s, 833 vs, 793 s, 740 m, 723 m, 674 w. − ^{1}H NMR ([D$_6$]benzene): δ = 0.20 [s, 18 H, Si(C*H*$_3$)$_3$], 0.99 [d, *J* = 7 Hz, 12 H, CH(C*H*$_3$)], 1.22 [d, *J* = 7 Hz, 12 H, CH(C*H*$_3$)], 3.87 (sept, *J* = 7 Hz, 4 H, C*H*), 6.98 (s, 6 H, *m*-H, *p*-H). − $^{13}C\{^{1}H\}$ NMR ([D$_6$]benzene): δ = 2.5 [Si(*C*H$_3$)$_3$], 23.4 [CH(*C*H$_3$)], 24.5 [CH(*C*H$_3$)], 27.4 (*C*H), 123.5 (*m*-C), 125.0 (*p*-C), 143.3 (*o*-C), 146.4 (*ipso*-C). − $^{199}Hg\{^{1}H\}$ NMR (toluene, 293 K): δ = 1283 ($\Delta\nu_{1/2}$ 126 Hz). − MS (70 eV, EI): *m/z* (%): 683 {679−685} (0.5) [$M^+ - CH_3$], 496 (0.15) [$\{N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)\}_2^+$], 249 (35) [$HN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)^+$], 248 (95) [$N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)^+$], 73 (100) [$SiMe_3^+$]. − $C_{30}H_{52}HgN_2Si_2$ (697.5): calcd. C 51.66, H 7.51, N 4.02; found C 51.60, H 7.59, N 4.48.

Bis[N-(2,6-diisopropylphenyl)-N-(trimethylsilyl)amido]bis(tetrahydrofuran)samarium(II) (**2**): (a) A mixture of samarium powder (0.75 g, 5.0 mmol) and $Hg[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$ (1.40 g, 2.0 mmol) in THF (40 ml) was stirred at 60 °C for 20 h. The resulting dark brown mixture was filtered to remove the precipitated Hg and excess of samarium metal, and the filtrate was evaporated to dryness. The solid residue was recrystallized from light petroleum (30 ml) and gave 1.03 g (65%) of purple-brown crystals of $Sm[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$. − IR: $\tilde{\nu}$ = 1582 cm^{-1} w, 1412 s, 1316 s, 1254 vs, 1235 s, 1198 m, 1155 w, 1140 w, 1104 w, 1028 m, 946 vs, 875 m, 830 vs, 771 s, 735 br. m, 652 br. m. − ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = −14.8 (br s, 4 H, C*H*), −2.3 [br. s, 12 H, CH(C*H*$_3$)], −1.8 [br. s, 18 H, Si(C*H*$_3$)$_3$], 5.3 (br. s, 8 H, THF), 5.49 (d, *J* = 7 Hz, 4 H, *m*-H), 8.13 (t, *J* = 7 Hz, 2 H, *p*-H), 10.6 [br. s, 12 H, CH(C*H*$_3$)], 15.4 (br. s, 8 H, THF). ([D$_6$]benzene/[D$_8$]-THF, 2:1): δ = −17.0 (br. s, 4 H, C*H*), −2.9 [br. s, 12 H, CH(C*H*$_3$)], −1.4 [br. s, 18 H, Si(C*H*$_3$)$_3$], 5.41 (d, *J* = 7 Hz, 4 H, *m*-H), 7.4 [br. s, 12 H, CH(C*H*$_3$)], 8.32 (t, *J* = 7 Hz, 2 H, *p*-H). − $^{13}C\{^{1}H\}$ NMR: ([D$_6$]benzene): δ = 13.7 [Si(*C*H$_3$)$_3$], 24.4 [br., CH(*C*H$_3$)], 32.6, (THF), 63.2 (br., *C*H), 69.2 [br., CH(*C*H$_3$)], 109.4 (*p*-C), 120.7 (THF), 129.8 (*m*-C), 162.0 (br., *ipso*-C), 173.4 (br., *o*-C). − $C_{38}H_{68}N_2O_2Si_2Sm$ (791.5): calcd. C 57.66, H 8.66, N 3.54, Sm 19.00; found C 57.90, H 7.97, N 3.45, Sm 18.59. (b) A mixture of samarium powder (1.50 g, 10.0 mmol), $HgPh_2$ (1.77 g, 5.0 mmol), $HN(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)$ (2.49 g, 10 mmol) and mercury (ca. 0.1 g) in THF (60 ml) was stirred and heated at 65 °C for 20 h. The resulting dark brown mixture was filtered through a celite pad and the solvent was removed under vacuum. The brown oily residue was washed with light petroleum (30 ml) and the remaining dark purple-brown solid was recrystallized from hot light petroleum (20 ml) and gave 0.11 g. (3.0%) of $Sm[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$ (IR, ^{1}H-NMR identification).

Bis[N-(2,6-diisopropylphenyl)-N-(trimethylsilyl)amido]bis(tetrahydrofuran)europium(II) (**3**) A mixture of europium pieces (0.60 g, 4.0 mmol), $Hg[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$ (0.35 g, 0.50 mmol) and mercury (ca. 0.1 g) in thf (30 ml) was stirred at room temperature for 40 h. The resulting bright yellow solution with grey suspended solids was filtered through a celite pad and the filtrate was evaporated to dryness. Recrystallization of the yellow residue from light petroleum (20 ml) at −20 °C gave 0.27 g. (68%) of bright yellow crystalline $Eu[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$. − IR: $\tilde{\nu}$ = 1582 cm^{-1} m, 1412 s, 1316 s, 1254 vs, 1235 vs, 1198 m, 1154 w, 1141 w, 1106 w, 1027 s, 946 br. vs, 875 m, 832 br. vs, 770 s, 733 m, 652 m. − $C_{38}H_{68}N_2O_2Si_2Eu$ (739.1): calcd. C 57.55, H 8.64, N 3.53; found C 58.82, H 9.21, N 4.00.

Bis[N-(2,6-diisopropylphenyl)-N-(trimethylsilyl)amido]bis(tetrahydrofuran)ytterbium(II) (**4**) (a) A mixture of ytterbium powder (0.70 g, 4.0 mmol) and $Hg[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$ (1.40 g, 2.0 mmol) in THF (30 ml) was stirred at room temperature for 40 h. The resulting orange solution with grey suspended solids was filtered through a celite pad and the filtrate was evaporated to dryness. Recrystallization of the orange residue from hot light petroleum (60 ml) gave 1.10 g. (67%) of $Yb[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)_2$ as large orange crystals. − IR: $\tilde{\nu}$ = 1582 cm^{-1} w, 1415 s, 1312 s, 1250 s, 1237 s, 1196 m, 1154 w, 1143 w, 1107 w, 1040 w, 1023 m, 934 br. s, 874 m, 831 br. s, 769 s, 732 br. m, 656 m. − ^{1}H NMR ([D$_6$]benzene): δ = 0.46 [s, 18 H, Si(C*H*$_3$)$_3$], 1.09 (br. s, 8 H, β-THF), 1.28 [d, *J* = 7 Hz, 24 H, CH(C*H*$_3$)$_2$], 3.06 (br. s, 8 H, α-THF), 4.03 (sept, *J* = 7 Hz, 4 H, C*H*), 6.87 (t, *J* = 8 Hz, 2 H, *p*-H), 7.09 (d, *J* = 8 Hz, 4 H, *m*-H). − $^{13}C\{^{1}H\}$ NMR ([D$_6$]benzene): δ = 4.5 [Si(*C*H$_3$)$_3$], 25.0 (β-THF), 25.7 [CH(*C*H$_3$)$_2$], 27.1 (*C*H), 69.5 (α-THF), 118.4 (*p*-C), 123.5 (*m*-C), 144.0 (*o*-C), 152.9 (*ipso*-C). − ^{171}Yb NMR (THF, 293 K): δ = 623 ($\Delta\nu_{1/2}$ 40 Hz), (toluene, 293 K): δ = 629 ($\Delta\nu_{1/2}$ 40 Hz). − $C_{38}H_{68}N_2O_2Si_2Yb$ (814.2): calcd. C 56.06, H 8.42, N 3.44; found C 56.38, H 8.06, N 3.48. (b) A mixture of ytterbium powder (1.73 g, 10.0 mmol), $HgPh_2$ (1.77 g, 5.0 mmol), $HN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)$ (2.49 g, 10.0 mmol) in THF (60 ml) was stirred and heated at 65 °C for 20 h. The resulting orange solution with grey suspended solids was treated as above giving 1.98 g (48%) of $Yb[N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2(THF)_2$ (IR and ^{1}H- and $^{13}C\{^{1}H\}$-NMR identification). − $C_{38}H_{68}N_2O_2Si_2Yb$ (814.2): calcd. Yb 21.25; found Yb 21.11.

Bis[N,N-bis(trimethylsilylamido)]bis(tetrahydrofuran)samarium(II) (**5**) A mixture of samarium powder (1.50 g, 10.0

mmol), $HgPh_2$ (1.77 g, 5.0 mmol) and $HN(SiMe_3)_2$ (1.61 g, 10.0 mmol) in THF (60 ml) was stirred and heated at 60 °C for 36 h. The resulting mixture was filtered through a celite pad and the dark purple-brown filtrate was evaporated to dryness. Recrystallization of the residue from light petroleum (15 ml) at −20 °C gave 2.31 g (75%) of dark purple crystalline $Sm[N(SiMe_3)_2]_2(THF)_2$. – IR: $\tilde{\nu}$ = 1306 cm^{-1} w, 1241 s, 1172 w, 1154 w, 1066 vs, 1034 s, 919 w, 873 s, 822 vs, 748 s, 723 m, 659 m. – ^1H NMR ([D_6]benzene): δ = −1.30 (br. s, 8H, THF), −0.74 (br. s, 8H, THF), 4.73 [br. s, 36H, $Si(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR ([D_6]benzene): δ = 25.3 (THF), 25.5 [$Si(CH_3)_3$], 146.6 (THF). – $C_{20}H_{52}N_2O_2Si_4Sm$ (615.4): calcd. Sm 24.44; found Sm 24.31.

Bis[N,N-bis(trimethylsilylamido)]bis(tetrahydrofuran)ytterbium(II) (**6**) A mixture of ytterbium powder (1.73 g, 10.0 mmol), $HgPh_2$ (1.77 g, 5.0 mmol) and $HN(SiMe_3)_2$ (2.5 ml, 12 mmol) in THF (40 ml) was stirred and heated at 60 °C for 20 h. The resulting orange solution with grey suspended solids was filtered through a celite pad and the filtrate was evaporated to dryness. Recrystallization of the orange residue from light petroleum (20 ml) at −40 °C gave 1.82 g (57%) of $Yb[N(SiMe_3)_2]_2(THF)_2$ as bright orange crystals. – IR: $\tilde{\nu}$ = 1237 cm^{-1} vs, 1054 vs, 1028 s, 970 w, 920 w, 872 vs, 824 vs, 747 s, 659 s. – ^1H NMR ([D_6]benzene): δ = 0.40 [s, 36H, $Si(CH_3)_3$], 1.22 (br. s, 8H, β-THF), 3.53 (br. s, 8H, α-THF). – $^{13}C\{^1H\}$ NMR ([D_6]benzene): δ = 5.6 [$Si(CH_3)_3$], 25.0 (β-THF), 69.8 (α-THF). – ^{171}Yb-NMR spectrum (toluene, 294 K). δ = 683 ($\Delta\nu_{1/2}$ 300 Hz). – $C_{20}H_{52}N_2O_2Si_4Yb$ (638.0): calcd. C 37.65, H 8.22, N 4.39, Yb 27.12; found C 37.71, H 8.24, N 4.38, Yb 26.88.

Bis[N-(2,6-diisopropylphenyl)-N-(trimethylsilyl)amido]-(tetrahydrofuran)ytterbium(II) (**7**) Solid (**4**) (0.81 g, 1.0 mmol) was heated at 150 °C under vacuum ($<10^{-3}$ Torr) for 3 h. The resulting dark coloured material was recrystallized twice from light petroleum (30 ml) at −30 °C and yielded 0.35 g (47%) of $Yb[N(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2(THF)$ as red-brown crystals. – IR: $\tilde{\nu}$ = 1586 cm^{-1} w, 1417 vs, 1333 w, 1310 s, 1256 s, 1236 vs, 1198 m, 1142 w, 1104 w, 1050 w, 1039 m, 1015 m, 952 br. s, 867 w, 829 br. vs, 775 s, 739 br. m, 656 m. – ^1H NMR ([D_6]benzene): δ = 0.46 (s, 18H, $Si[CH_3)_3]$, 0.86 (br. m, 4H, β-THF), 1.21 [d, J = 7 Hz, 24H, $CH(CH_3)_2$], 2.28 (br. m, 4H, α-THF), 4.03 (sept, J = 7 Hz, 4H, CH), 6.78 (t, J = 8 Hz, 2H, *p*-H), 7.01 (d, J = 8 Hz, 4H, *m*-H). – $^{13}C\{^1H\}$ NMR ([D_6]benzene): δ = 3.9 [$Si(CH_3)_3$], 24.8 [$CH(CH_3)_2$], 25.0 (β-THF), 26.8 (CH), 68.8 (α-THF), 119.2 (*p*-C), 124.5 (*m*-C), 143.3 (*o*-C), 150.8 (*ipso*-C). – ^{171}Yb NMR (toluene, 297 K): δ = 638 ($\Delta\nu_{1/2}$ 70 Hz). – $C_{34}H_{60}N_2OSi_2Yb$ (742.1): calcd. C 55.03, H 8.15, N 3.77; found C 55.43, H 8.23, N 4.36.

Tetrakis[N,N-bis(trimethylsilylamido]diytterbium(II) (**8**) Solid (**6**) (0.64 g, 1.0 mmol) was heated at 150 °C under vacuum ($>10^{-3}$ Torr) for 3 h. The resulting dark-coloured material was extracted with light petroleum (30 ml), filtered and the filtrate evaporated to dryness and gave 0.35 g (80%) of $\{Yb[N(SiMe_3)_2]_2\}_2$ as a red-orange powder. – IR: $\tilde{\nu}$ = 1250 cm^{-1} vs, 1018 br. s, 970 br. s, 863 s, 830 br. vs, 755 m, 665 m. – ^1H NMR ([D_6]benzene): δ = 0.35 [s, $Si(CH_3)_3$]. – ^{171}Yb NMR (toluene, 293 K): δ = 784 ($\Delta\nu_{1/2}$ 160 Hz). – $C_{24}H_{72}N_4Si_8Yb_2$ (987.6): calcd. Yb 35.04; found Yb 37.10.

X-ray Crystallography

2. Crystal Data: $C_{38}N_{68}N_2O_2Si_2Sm$, M = 791.5 g mol^{-1}, crystal size 0.10 × 0.20 × 0.25 mm, a = 20.628(7), b = 9.9532(2), c = 20.986(3) Å, β = 102.23(2)°, V = 4211(2) Å^3, Z = 4, ρ_{calcd} = 1.249 g cm^{-3}, μ = 1.421 mm^{-1}, $F(000)$ = 1664, monoclinic, space group *P*2/*n* (No. 13), two independent heavy-atom molecules in the asymmetric unit.

Single crystals were grown by slow cooling to room temperature of a hot saturated light petroleum solution. A representative crystal was selected at low temperature[31] and glued to a glass fibre and placed in the cold nitrogen stream of the diffractometer. Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.7107 Å) at 240 K. A total number of 8239 measured reflections in the range 1° < 2Θ < 50° (h, k, $\pm l$) were obtained with a variable scan time and a $\omega - 2\Theta$ scan technique; 6748 [R(int) = 0.0241] independent reflections of which 6698 were considered observed [$F_o > 4\sigma(F_o)$] and were used for refinement. Lorentz and polarization corrections were applied to intensity data. Atomaic scattering factors used for neutral atoms were corrected for anomalous dispersion. The positions of the two independent Sm atoms were determined from a three-dimensional Patterson synthesis. The calculated difference Fourier map revealed all other missing non-hydrogen atoms of both half Sm molecules. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (C−H 0.96 Å, U_{iso} = 0.08 Å^2). Refinement of 407 parameters was by full-matrix least squares. After all atoms had been added to the model an empirical absorption correction was applied (DIFABS[32] min. 0983, max. 1.165). The final residual values were $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0312$; $\omega R2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.0942$, $w = 1/\sigma^2(F_o)$; goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2} = 0.797$; $\Delta\rho$(max./min.) = max. 0.590 eÅ^{-3} and min. −0.694 eÅ^{-3}. All calculations were performed on an IBM Risk 6000 computer using the SHELX 93[33] software package. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation and the depository number CSD-100029.

4. Crystal data: $C_{38}N_{68}N_2O_2Si_2Yb$, M = 814.2 g mol^{-1}, crystal size 0.20 × 0.20 × 0.15 mm, a = 21.454(7), b = 9.873(3), c = 21.667(10) Å, β = 115.53(3)°, V = 4144(2) Å^3, Z = 4, ρ_{calcd} = 1.305 g cm^{-3}, μ = 2.35 mm^{-1}, $F(000)$ = 1696, monoclinic, space group *P*2/*n* (No. 13), two independent heavy-atom molecules in the asymmetric unit. Single crystals were grown by slow cooling to room temperature of a hot saturated light petroleum solution. A representative crystal was covered in hydrocarbon oil and placed in the cold nitrogen stream of the diffractometer. Intensity data were collected with an Nicolet (Siemens) R3m/V four-circle diffractometer with graphite monochromatized Mo-K_α radiation (λ = 0.7107 Å) at 173 K. A total number of 7506 measured reflections in the range 3° < 2Θ < 50° ($-23 \leq h \leq 25$, $-11 \leq k \leq 0$, $-25 \leq l \leq 0$) were obtained with a variable scan time and an $\omega - 2\Theta$ scan technique; 7301 [R(int) = 0.0946] independent reflections of which 4177 were considered observed [$F_o \geq 4\sigma(F_o)$] and were used for refinement. Structure solution was by Patterson methods and refinement of 582 parameters was by full-matrix least squares on F^2. One of the independent half molecules in the asymmetric unit was disordered over two positions, except for atoms Yb(2), C(21) and C(26); occupancies were allowed to freely refine. All non-hydrogen atoms were refined anisotropically, thermal parameters for disordered atoms were restrained to reasonable values. The hydrogen atoms were placed in idealized positions using a riding model. The final residual values [$I > 2\sigma(I)$] were $R1 = 0.0591$; $\omega R2 = 0.0868$ (all data, $R1 = 0.1380$; $\omega R2 = 0.1164$), $w = [\sigma^2(F_o^2) + (0.0272P)^2 + 4.31P]^{-1}$ $\{P = [\max.(F_o^2) + 2F_o^2]/3\}$; goodness of fit = 1.016. Residual electron density max. 0.685 eÅ^{-3} and min. −0.828 eÅ^{-3}. All calculations were performed on an IBM PC using the SHELX 93[33] software package. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation and the depository number CSD-100029.

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