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Ytterbium(II) amides and crown ethers: addition versus amide substitution

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Abstract

New Yb(II) amides [Yb(NPh$_2$)$_2$(THF)$_4$] (**1**) and Yb{NPh(SiMe$_3$)}$_2$(THF)$_x$ ($x = 1$ or 3) (**2**) were obtained by the salt elimination method and the structure of the dimer [Yb{NPh(SiMe$_3$)}{μ-NPh(SiMe$_3$)}(THF)]$_2$ (**2a**) was determined. Reactions of the amides **1**, **2** and [Yb{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (**3**) with [18]crown-6 gave the crystalline structurally characterised molecular complex [Yb(NPh$_2$)$_2$([18]crown-6)] (**4**) in the case of the smaller NPh$_2^-$ ligand and the salt [Yb{N(SiMe$_3$)$_2$}([18]crown-6)][Yb{N(SiMe$_3$)$_2$}$_3$] (**5**) with the bulky bis(trimethylsilyl)amido ligand. Crystalline **4** has a "threaded" structure with the NPh$_2$ groups on the opposite sides of the [18]crown-6 ligand and the N – Yb – N′ angle of 176.6°. An X-ray diffraction study of the related potassium amide [K([18]crown-6)(NPh$_2$)] (**6**) reveals that the K ion coordinates to one of the Ph-rings rather than to the amido nitrogen atom. There is significant delocalisation of negative charge in the amido ligand of crystalline **6**, unlike in **4**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ytterbium(II) amides; Crown ether; Structure; NMR spectra

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1. Introduction

The complexation of lanthanoid (Ln) ions by crown ethers has been widely explored [1] and a number of crystalline complexes (most of which have inorganic counteranions, such as halide, nitrate or hydroxide) were characterised by X-ray diffraction. Rare examples of other anionic ligands include triflate [1d] and *p*-sulfonatocalix[4]arene in a peculiar "ferris wheel" type La(III) complex [1e]. By contrast, the chemistry of (crown ether)–Ln organometallic complexes is still undeveloped and no structural information is available on Ln(II) compounds containing coordinated crown ethers.

Recently we have reported on a variety of reactions of some tris(cyclopentadienyl)lanthanoid(III) complexes with potassium metal in the presence of [18]crown-6 and an arene [2]. Among the crystalline compounds isolated were those of formula [K([18]crown-6)][LnCp$''_2$(C$_6$H$_6$-1,4)], [K([18]crown-6)(η^2-C$_6$H$_6$)$_2$][{Ln(η^5-C$_5$H$_3$-Bu$^t_2$-1,3)$_2$}$_2$(μ-η^6:η^6-C$_6$H$_6$)] and [K([18]crown-6)(η^2-PhMe)$_2$][{Ln(η^5-C$_5$H$_4$SiMe$_2$Bu^t-1,3)$_3$}$_2$(μ-H)] (Ln = La or Ce, Cp$''$ = C$_5$H$_3$(SiMe$_3$)$_2$-1,3). However, no reaction was observed when [LnCp$''_3$] (Ln = La, Ce, Pr or Nd) was treated with [18]crown-6 in benzene [2e]. By contrast, Ln(II) cyclopentadienides [LnCp$''_2$] (Ln = Sm or Yb) were found to react with [18]crown-6 in aromatic solvents with the displacement of a cyclopentadienyl ligand by the crown ether and the formation of the crystalline salt [SmCp$''$([18]crown-6)][SmCp$''_3$]·0.5C$_6$H$_6$ or [YbCp$''$([18]crown-6)][Cp$''$]·3C$_6$H$_6$ [3]. In this paper we describe extensions of this study to some Yb(II) organoamides.

2. Results and discussion

2.1. Synthesis of Yb amides **1–3** and X-ray crystal structure of **2a**

The starting Yb amides bearing different substituents on the nitrogen atom [Yb{NRR′}$_2$(THF)$_n$]$_x$ (**1–3**) (Scheme 1) were obtained by a salt elimination reaction using YbI$_2$ and the corresponding potassium amide

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$$YbI_2 + 2KNRR' \xrightarrow{THF} [Yb\{NRR'\}_2(THF)_n]_x + 2KI$$

1: R = R' = Ph, n = 4, x = 1
2a: R = Ph, R' = SiMe$_3$, n = 1, x = 2
2b: R = Ph, R' = SiMe$_3$, n = 3, x = 1
3: R = R' = SiMe$_3$, n = 2, x = 1

Scheme 1.

KNRR′ in THF. The extremely low solubility in THF of the resulting KI allowed the straightforward isolation of the Yb amides free from *ate*-complexes to be achieved; the latter are often formed when a Li or Na amide is used as starting material. In some early examples, isolation of either the neutral Yb(II) bis(trimethylsilyl)amide or an ionic *ate*-complex was accomplished by varying only work-up procedures [4]; whereas $NaNPh_2$ with $Ln(\eta^5\text{-}C_5H_4Me)_2Cl$ in THF gave only the *ate*-complex $[Ln(NPh_2)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4Me)_2Na(THF)_2]_\infty$ (Ln = Sm or Er) independent of the Ln/N ratio [5]. Bis(diphenylamido)ytterbium crystallised from a concentrated THF solution as the tetrakis-THF adduct **1**. The amides **2** and **3** were recrystallised from hexane. Fractional crystallisation of the former from hexane gave two different $Yb\{NPh(SiMe_3)\}_2$–THF adducts: (i) the less soluble were deep red blocks and needles of the 1:1 adduct **2a** (as determined by ^{1}H-NMR spectroscopy) and (ii) the more soluble orange–brown plates of the 1:3 adduct **2b**. The formation of the latter as a mononuclear tris-THF adduct was consistent with steric effects, these increasing in the sequence $NPh_2 < NPh(SiMe_3) < N(SiMe_3)_2$. Except for the above-mentioned differences in the integration of the THF absorptions, the ^{1}H- and ^{13}C-NMR spectra of **2a** and **2b** were very similar. Since these data were not structurally definitive, an X-ray diffraction study of **2a** was carried out.

The molecular structure of crystalline **2a** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. In the crystal, compound **2a** consists of dimeric molecules, each Yb atom bearing one terminal (*d*[Yb–N] 2.326(4) and 2.353(4) Å) and one bridging (average *d*[Yb–N] 2.497 Å) amido ligand. The coordination sphere of the Yb atom is completed by a THF molecule with Yb–O distances of 2.438(3) and 2.402(3) Å and a close interaction with the *ipso*-carbon atoms of the Ph rings of the bridging ligands (2.872 and 2.763 Å), which is in the same range as the Yb–C(Cp″) distances in the sterically hindered Yb(II) cationic cyclopentadienide [YbCp″([18]crown-6)][Cp″] [3]. Such a short Ln···C$_{ipso}$ contact in arylamido complexes was previously observed only in the neodymium heterometallic cluster $[\{Me_2Al(\mu\text{-}Me)_2\}_2Nd(\mu_3\text{-}NPh)(\mu\text{-}Me)AlMe]_2$ [6].

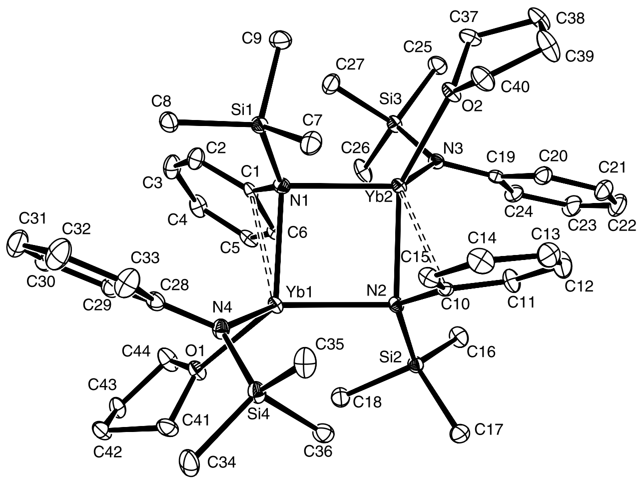
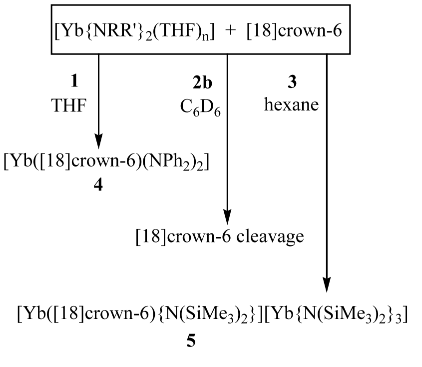


Fig. 1. Molecular structure and atom numbering scheme for $[Yb\{NPh(SiMe_3)\}_2(THF)]_2$ (**2a**).

Table 1
Selected bond lengths (Å) and angles (°) in **2a**

Bond lengths			
Yb1–N4	2.326(4)	Yb2–N3	2.353(4)
Yb1–N1	2.465(4)	Yb2–N1	2.506(4)
Yb1–N2	2.499(4)	Yb2–N2	2.518(4)
Yb1–O1	2.438(3)	Yb2–O2	2.402(3)
Yb1···C1	2.872	Yb2···C10	2.763
Yb1···C6	2.953		
N1–C1	1.396(6)	N2–C10	1.412(5)
N3–C19	1.392(6)	N4–C28	1.391(6)
Bond angles			
N1–Yb1–N2	86.31(12)	N1–Yb2–N2	85.03(12)
Yb1–N1–Yb2	94.63(13)	Yb1–N2–Yb2	93.48(12)



Scheme 2.

2.2. Reactions of Yb(II) amides with [18]crown-6

[18]Crown-6 reacted easily with each of the ytterbium(II) amides **1**–**3**, but the reaction outcome varied with the nature of the amide substituents (Scheme 2). It is noteworthy that trivalent Ln (Ln = La or Lu) amides with bulky $\bar{N}(SiMe_3)_2$ ligands did not react with [18]crown-6 in benzene-d_6 solution.

The diphenylamido complex **1** gave the thermally stable 1:1 crown ether adduct **4**, which was sparingly soluble in cold THF. The product composition was confirmed by ^{1}H-NMR spectroscopy, microanalysis and finally by an X-ray diffraction study. Variable temperature ^{1}H-NMR spectra showed that at low temperature (−60 °C) two sets of Ph proton signals were observed, which coalesced into a broad line at −5 °C and then gave one set of three broad absorptions for the *o*-, *m*- and *p*-H, respectively, at higher temperatures. This behaviour suggests that there are two different modes of amido ligand coordination in **4** which exchange rapidly at r.t., probably through dissociation–association processes.

The C_1 symmetric amido ligand $\bar{N}$Ph(SiMe$_3$) of complex **2b** is probably too bulky to form a similar 1:1 adduct. No crystalline material was isolated when the reaction was carried out in THF, Et$_2$O or hexane. When one equivalent of [18]crown-6 was added to a C$_6$D$_6$ solution of **2b** in an NMR spectral tube, a dark brown oily precipitate formed and the major component in the solution was free crown ether. After 30 min of vigorous shaking the oil had dissolved yielding a bright orange solution. The ^{1}H-NMR spectrum showed a number of broad absorptions assigned to a cleaved crown ether with the characteristic signals for the vinyl protons of the OCH=CH$_2$ group. In a better resolved ^{13}C-NMR spectrum, recorded after ca. 5 h, sets of signals corresponded to the coordinated $\bar{N}$RR′ ligand, free HNRR′ (as a result of the crown ether deprotonation by the $\bar{N}$RR′ anion), cleaved [18]crown-6 and free THF (from the starting **2b**). Similar crown ether deprotonation and ring-opening by an amido anion was observed previously in the reactions of alkali earth metal (M) amides [M{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] with crown ethers [7]. Recently a Ba amido complex containing cleaved [18]crown-6 was structurally characterised [8] and our NMR spectral assignments are based on comparisons with data for the barium complex. Longer reaction periods (more than 2 days) led to the appearance of very broad paramagnetic signals with a decrease of signal intensity in the diamagnetic range, Yb(II) being oxidised to paramagnetic Yb(III) species.

In the case of the more basic $\bar{N}$(SiMe$_3$)$_2$ anion, the deprotonation and splitting of the crown ether in the [Yb{NRR′}$_2$(THF)$_n$]/[18]crown-6 (1:1) system was found to be faster than with complex **2b**. The ^{1}H-NMR spectrum showed signals of the free amine and a vinyl group after a few minutes. The crystalline product **5** was isolated in a good yield only when a 2:1 (Yb/crown) stoichiometry was applied and the reaction was carried out in cold hexane (Scheme 2). Excess Yb(II) amide **3** was required to bind $\bar{N}$(SiMe$_3$)$_2$ anions. The Lu(III) amide [Lu{N(SiMe$_3$)$_2$}$_3$] was tested as an alternative trapping agent for $\bar{N}$(SiMe$_3$)$_2$, because it was known that [M{N(SiMe$_3$)$_2$}$_3$] (M = Sc, Yb, or Lu) can be deprotonated by NaN(SiMe$_3$)$_2$ with the formation of $[\overline{\text{MCH}_2\text{SiMe}_2\text{N}}\text{SiMe}_3\{\text{N(SiMe}_3)_2\}_2]^-$ anions [9]. However, only complex **5** was obtained in hexane at −10 °C and crown ether splitting occurred when the solvent was replaced by benzene and the mixture was warmed up to r.t., unreacted [Lu{N(SiMe$_3$)$_2$}$_3$] being recovered in a high yield.

The blue crystalline complex **5** was extremely air-sensitive and thermally unstable; direct light caused decolouration of the exposed surface. An X-ray diffraction study showed the presence of separate anions [Yb{N(SiMe$_3$)$_2$}$_3$]$^-$ and highly disordered cations. Although this disorder was not resolved, the ionic structure of **5** was confirmed by multinuclear NMR spectroscopy (Table 2). A mixture of ^{t}BuOMe/C$_6$D$_6$ (4:1) was found to be the best solvent for these NMR studies, because the solubility of **5** in hydrocarbon solvents was too low (especially for deriving ^{171}Yb-NMR spectral data). In THF-d_8 (where the solubility of **5** is high) the SiMe$_3$ protons of the cation and the anion gave only one broad signal; the presence of solvent residual protons at δ 3.58 obscured the signal of the

Table 2
NMR spectral chemical shifts (δ) for **5** (293 K)

Nucleus, solvent	[18]Crown-6			Anion	Cation	HN(SiMe$_3$)$_2$
	A	B	Minor component			
^{1}H, ^{t}BuOMe/C$_6$D$_6$	3.96	3.88	3.42	0.081	−0.002	−0.068
^{13}C, ^{t}BuOMe/C$_6$D$_6$	68.65		70.45	5.63	5.32	2.47
^{29}Si, ^{t}BuOMe/C$_6$D$_6$ [a]				−17.03	−13.68	N.F. [b]
^{171}Yb, ^{t}BuOMe/C$_6$D$_6$ [a]				851	252	
^{1}H, Et$_2$O/C$_6$D$_6$	3.66	3.46	N.F.	0.159	−0.060	N.F.
^{13}C, Et$_2$O/C$_6$D$_6$	68.34		70.28	5.67	5.16	N.F.
^{1}H, C$_6$D$_5$CD$_3$	3.21	3.13	3.31	0.574	0.167	0.087
^{13}C, C$_6$D$_5$CD$_3$	67.54		70.27	5.31	4.75	1.73
^{1}H, C$_4$D$_8$O	4.08	3.92	3.58	0.036 (broad)		−0.018

[a] At 298 K.

[b] N.F., not found.

coordinated crown ether (minor component), whereas the upfield shifted OCH_3 signal of ^{t}BuOMe at δ 2.99 left the crown ether proton area at δ 3–4 clear. Two $SiMe_3$ absorptions in the appropriate 1:3 ratio were observed in the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra. Also two signals but in a 1:1 ratio ($\delta = 855.2$ for the anion and $\delta = 265.8$ for the cation) were found in the ^{171}Yb-NMR spectrum at 253 K, the former being close to the shift of the sodium ytterbate(II) complex Na[Yb{$N(SiMe_3)_2$}$_3$] and the latter outside the normal range (at δ 614–1228) for a simple Yb(II) amido complex [10]. This, and the strongly upfield shifted ^{171}Yb signal for **4** ($\delta = 24.4$ at 273 K), is attributed to the unusually high (compared to other Yb diamides) Yb coordination number (C.N. = 7 or 8) in these compounds.

The most prominent feature of the ^{1}H-NMR spectrum of **5** was an *AA′BB′* pattern for the crown ether protons; the chemical shifts and *A* to *B* peak-to-peak separation were strongly concentration and solvent dependent. This observation confirms the presence in solution of the [Yb([18]crown-6){$N(SiMe_3)_2$}]$^+$ cation, in which the crown ether has two different faces. Weak cation–solvent or cation–anion interaction may be responsible for the observed variations in the position of the [18]crown-6 ^{1}H-NMR spectral signals. A similar *AA′BB′* pattern for the coordinated crown ether protons was found in R_2AlX- or R_2Mg-crown ether systems attributed to [RAlX(crown)]$^+$ or [RMg(crown)]$^+$ cations [11]. However, in the Mg system such a cation was detected only in the non-polar solvent C_6D_6 but not in Et_2O-d_{10} [11b]. In the majority of the NMR spectra of complex **5**, a minor component (5–10%) was detected in the crown ether area along with a small amount of free amine (Table 2). These impurities were formed during the sample preparation and their quantity was reduced by using large crystals and by protecting the samples from direct light.

*2.3. X-ray crystal structures of [Yb(NPh_2)$_2$([18]crown-6)] (**4**) and [K([18]crown-6)(NPh_2)] (**6**)*

In order to compare structural features attributable to a diphenylamido-coordinated lanthanoid or an alkali metal–crown ether complex cation, the potassium compound [K([18]crown-6)(NPh_2)] (**6**) was prepared, by addition of [18]crown-6 to a THF solution of $KNPh_2$. X-ray quality crystals were obtained by slow cooling the hot solution of **6** in a mixture of THF and toluene. The ORTEP drawings of **4** and **6** are shown in Figs. 2 and 3, respectively, and selected intramolecular distances and angles are presented in Table 3.

The eight-coordinate Yb atom in crystalline **4** is at the centre of a distorted hexagonal bipyramid, formed by the six equatorial oxygen atoms of the crown ether and the two apical nitrogen atoms of the diphenylamido groups. The average Yb–O distance of 2.594 Å is ca. 0.04 Å longer than in the cation of the only other structurally characterised Yb(II)–crown ether complex, [YbCp″([18]crown-6)][Cp″] [3], or in the amidoytterbium(II) complex containing the dianionic deprotonated 4,13-diaza-18-crown-6 (DAC) ligand Yb[Yb{$N(SiMe_3)_2$}(μ-DAC)]$_2$ [12]. The Yb–N distances of 2.538(3) and 2.568(3) Å are the longest known terminal amido–ytterbium(II) bonds (the second longest were found in the above-mentioned Yb–DAC complex, 2.43(3) and 2.44(3) Å [12], and in [Yb(9-carbazolyl)$_2$(THF)$_2$(dme)], 2.43(3) and 2.45(2) Å [13]). Such elongation of Yb–N and Yb–O bond distances may be due to the significant steric strain in complex **4**.

The structure of **6** is that of a contact ion pair comprising the [K([18]crown-6)]$^+$ cation and NPh_2^- anion (Fig. 3). In contrast to the Yb complex **4**, there is

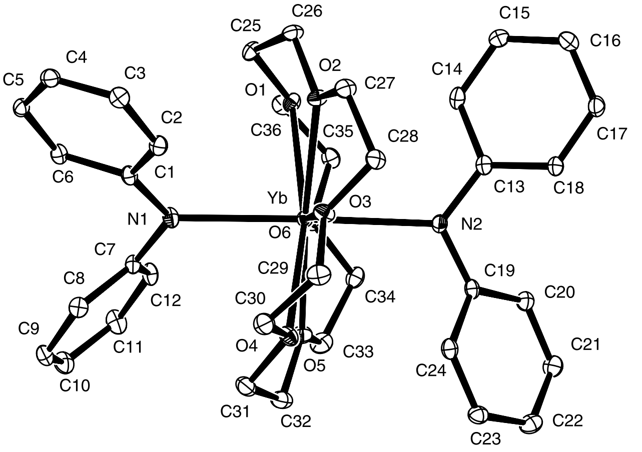


Fig. 2. Molecular structure and atom numbering scheme for [Yb([18]crown-6)(NPh_2)$_2$] (**4**).

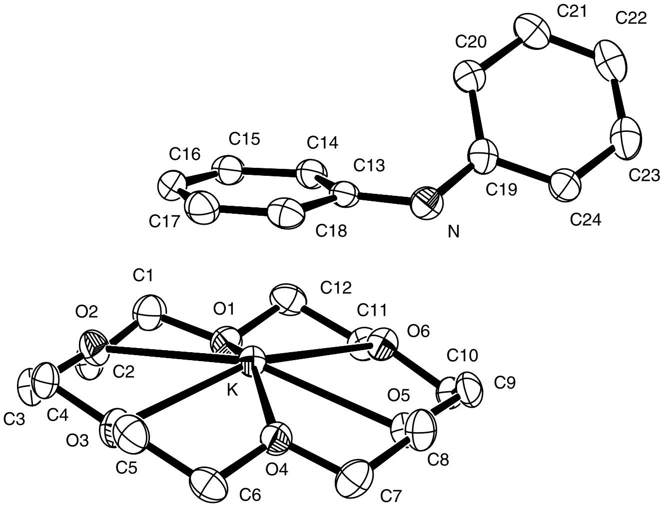


Fig. 3. Molecular structure and atom numbering scheme for [K([18]crown-6)(NPh_2)] (**6**).

Table 3
Selected bond lengths (Å) and angles (°) in **4** and **6**

Bond lengths ***(4)***			
Yb–N1	2.538(3)	Yb–N2	2.568(3)
Yb–O1	2.605(3)	Yb–O2	2.574(2)
Yb–O3	2.574(3)	Yb–O4	2.643(3)
Yb–O5	2.507(3)	Yb–O6	2.658(3)
N1–C1	1.387(5)	N2–C13	1.400(5)
N1–C7	1.403(5)	N2–C19	1.398(5)
Bond angles ***(4)***			
N1–Yb–N2	176.57(10)		
C1–N1–C7	114.8(3)	C19–N2–C13	116.1(3)
C1–N1–Yb	124.5(2)	C19–N2–Yb	118.9(2)
C7–N1–Yb	120.6(2)	C13–N2–Yb	124.9(3)
Bond lengths ***(6)***			
K–O1	2.864(3)	K–C13	3.390(4)
K–O2	2.813(3)	K–C14	3.234(4)
K–O3	2.882(3)	K–C15	3.180(4)
K–O4	2.818(3)	K–C16	3.274(4)
K–O5	2.820(3)	K–C17	3.358(4)
K–O6	2.862(3)	K–C18	3.391(4)
N–C13	1.368(5)	N–C19	1.364(5)
Bond angles ***(6)***			
C13–N–C19	120.3(3)		

no close K–N contact in **6**, but rather a close K–η^6-Ph interaction which suggests significant delocalisation of negative charge onto the Ph-rings. As a consequence, the C–N bonds are considerably shorter (1.364(5) and 1.368(5) Å) than in **4** (average 1.397 Å) or in [Li([12]crown-4)(NPh_2)] (1.388 Å) [14], but somewhat similar to those in [$PEtPh_3$][NPh_2] (1.373 Å) [15]. Further confirmation of more substantial negative charge delocalisation in the potassium amide **6** was obtained by comparing the ^{1}H-NMR spectra of **6** and **4**; the signals of the Ph protons in **6** were strongly shifted upfield (for the *p*-H, the difference was 0.53 ppm).

3. Experimental

3.1. Materials and procedures

All manipulations were carried out under vacuum or Ar by Schlenk techniques. Solvents were dried and distilled over sodium–potassium alloy (pentane, hexane) or sodium–benzophenone (Et_2O, THF) and stored over a K or Na mirror under Ar. The compounds KNRR′ were prepared from KH and the corresponding amine in THF and used without isolation. [18]Crown-6 (Aldrich) was exposed to a dynamic vacuum for 1 day and stored under an Ar atmosphere. The triamides [Ln{$N(SiMe_3)_2$}$_3$] (Ln = La or Lu) were prepared by a literature procedure [16].

Microanalyses were carried out by Medac Ltd. (Brunel University). Due to desolvation or instability, satisfactory elemental analysis data for compounds **1**, **2a** and **5** were not obtained. The NMR spectra were recorded using the following Bruker instruments: DPX 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz) and AMX 500 (^{29}Si, 49.7; ^{171}Yb, 87.5 MHz) and calibrated internally to residual solvent resonances in the case of ^{1}H and ^{13}C spectra; external $SiMe_4$ and [$Yb(C_5Me_5)_2$(THF)] were used for ^{29}Si and ^{171}Yb spectra, respectively. All NMR spectra other than ^{1}H were proton-decoupled and recorded at ambient temperature unless otherwise stated.

3.2. Synthesis of $Yb(NPh_2)_2(THF)_4$ (*1*)

YbI_2 (1.60 g, 3.75 mmol) was added to a stirred solution of $KNPh_2$ (1.55 g, 7.48 mmol) in tetrahydrofuran (70 ml). The light orange suspension was stirred for 24 h, and then filtered. The filtrate was concentrated to yield orange crystals of **1** (3.82 g, 64%). ^{1}H-NMR (δ, C_6D_6/pyridine-d_5): 7.30 (d, $J = 7.32$ Hz, 8H), 7.07 (d, $J = 7.32$ Hz, 8H), 6.56 (t, $J = 7.32$ Hz, 4H), 3.51 (s, 16H, THF), 1.41 (s, 16H, THF). ^{13}C-NMR (δ, C_6D_6/pyridine-d_5): 157.21, 129.89, 119.88, 115.33, 67.70 (THF), 25.67 (THF). ^{171}Yb-NMR (δ, C_4D_8O/C_4H_8O): 487.1.

3.3. Synthesis of [Yb{$NPh(SiMe_3)$}{μ-$NPh(SiMe_3)$}-(THF)]$_2$ (*2a*) and [Yb{$NPh(SiMe_3)$}$_2$(THF)$_3$] (*2b*)

A solution of $KNPh(SiMe_3)$ (1.211 g, 5.52 mmol) (prepared from 0.911 g of $HNPh(SiMe_3)$ and an excess of KH in 20 ml of THF) was added to $YbI_2(THF)_2$ (1.557 g, 2.76 mmol) in THF (40 ml) at room temperature (r.t.) and the mixture was stirred overnight. The bright orange mixture was filtered, the solvent was removed under vacuum and the residue was extracted with warm (ca. 40 °C) hexane. Crystallisation at 20 °C gave **2a** (0.11 g, 7%) as dark red blocks and needles. ^{1}H-NMR (δ, C_6D_6): 7.11 (t, 4H), 6.89 (d, 4H), 6.65 (t, 2H), 3.19 (s, 4H), 1.10 (s, 4H), 0.32 (s, 18H). ^{13}C-NMR (δ, C_6D_6): 156.8, 130.2, 121.5, 115.8, 68.7, 24.3, 1.95.

The mother liquor was concentrated to ca. 1/4 of its volume and stored at 0 °C for 2 days yielding **2b** (1.486 g, 75%), as brown–orange plates. ^{1}H-NMR (δ, C_6D_6): 7.15 (t, 4H, $+C_6D_5H$), 6.90 (d, 4H), 6.67 (t, 2H), 3.42 (s, 12H), 1.27 (s, 12H), 0.40 (s, 18H). ^{13}C-NMR (δ, C_6D_6): 129.7, 121.5, 115.8, 67.8, 24.7, 2.11 (*ipso*-*C*(Ph) was not observed). Anal. Found: C, 49.5; H, 7.14; N, 4.08. Calc. for $C_{30}H_{52}N_2O_3Si_2Yb$: C, 50.2; H, 7.30; N, 3.90%.

3.4. Synthesis of [Yb{$N(SiMe_3)_2$}$_2$(THF)$_2$] (*3*)

A filtered solution of $KN(SiMe_3)_2$ (1.350 g, 6.79 mmol) (prepared from 1.09 g of $HNPh(SiMe_3)$ and an excess of KH in 20 ml of THF) was added to $YbI_2(THF)_2$ (1.937 g, 3.39 mmol) in THF (40 ml) at r.t.

and the mixture was stirred overnight. The brown–orange mixture was filtered, the solvent was removed from the filtrate in vacuo and the residue was extracted with hexane. Concentration of the solution to a small volume followed by crystallisation at −27 °C gave **3** (1.73 g, 80%), as bright orange crystals. The ^{1}H- and ^{13}C-NMR spectra of the product were identical to those reported in the literature [10].

*3.5. Synthesis of [Yb([18]crown-6)(NPh$_2$)$_2$] (**4**)*

[18]Crown-6 (0.08 g, 0.3 mmol) was added to a stirred solution of **1** (0.24 g, 0.3 mmol) in tetrahydrofuran (70 ml). The yellow solution was stirred for 1 h. The solvent was removed in vacuo to give a yellow solid, which was washed with pentane (30 ml) and dried in vacuo, yielding **4** (0.21 g, 91%). ^{1}H-NMR (δ, C_4D_8O): 7.00 (br s, 8H), 6.93 (br s, 8H), 6.49 (br s, 4H), 3.60 (br s, 24H, [18]crown-6). ^{171}Yb-NMR (δ, C_4D_8O/C_4H_8O): 24.4 (273 K), 30.8 (213 K). Anal. Found: C, 54.9; H, 5.85; N, 3.66. Calc. for $C_{36}H_{44}N_2O_6Yb$: C, 55.9; H, 5.73; N, 3.62%.

*3.6. Synthesis of [Yb([18]crown-6){N(SiMe$_3$)$_2$}]-[Yb{N(SiMe$_3$)$_2$}$_3$] (**5**)*

A hexane solution of [18]crown-6 (0.095 g, 0.36 mmol) was added to a solution of **3** (0.4742 g, 0.74 mmol) in hexane (20 ml) at −10 °C in a Schlenk tube protected from direct light by aluminium foil. During ca. 5 min the colour of the mixture changed to blue with simultaneous precipitation of blue oily drops and microcrystals. The crystallisation was complete in ca. 3 h at 0 °C. The colourless supernatant liquid was removed by a cannula, the residue was washed with cold hexane and dried in vacuo, yielding complex **5** (0.4214 g, 91%), as a light blue crystalline powder. Large crystals (which were easier to handle and less light-sensitive) were obtained when the concentrated Et_2O solution of **5** was layered with pentane and stored at −27 °C for 1 week. NMR-spectral data are presented in Table 2.

*3.7. Synthesis of [K([18]crown-6)(NPh$_2$)] (**6**)*

[18]Crown-6 (2.43 g, 9.2 mmol) was added to a stirred solution of $KNPh_2$ (1.90 g, 9.2 mmol) (synthesised from $HNPh_2$ and KH) in tetrahydrofuran (70 ml). The mixture was stirred for 1 h. Solvent was removed in vacuo to yield a pale yellow solid, which was washed with hexane (60 ml) and dried in vacuo, yielding **6** (3.99 g, 92%). ^{1}H-NMR (δ, C_4D_8O): 6.80 (d, $J = 7.32$ Hz, 4H), 6.71 (t, $J = 7.32$ Hz, 4H), 5.96 (t, $J = 7.32$ Hz, 2H), 3.51 (br s, 24H, [18]crown-6). ^{13}C-NMR (δ, C_4D_8O): 159.07, 128.78, 118.83, 110.27, 70.89. Anal. Found: C, 60.6; H, 6.99; N, 2.99. Calc. for $C_{24}H_{34}KNO_6$: C, 61.1; H, 7.27; N, 2.97%.

Table 4
Crystal data and details of data collection and structure refinement for **2a**, **4** and **6**

Compound	**2a**	**4**	**6**
Empirical formula	$C_{44}H_{72}N_4O_2Si_4Yb_2$	$C_{36}H_{44}N_2O_6Yb$	$C_{24}H_{34}KNO_6$
Formula weight	1147.50	773.77	471.62
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)	Pc (No.13)
a (Å)	20.8915(4)	8.5368(2)	9.6670(5)
b (Å)	13.8636(3)	29.3406(8)	10.1606(6)
c (Å)	18.6723(3)	13.7061(4)	12.3875(8)
β (°)	111.641(1)	106.804(2)	102.186(4)
V (Å^3)	5026.9(2)	3286.4(2)	1189.3(1)
Z	4	4	2
D_{calc} (Mg m^{-3})	1.52	1.56	1.32
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	3.83	2.89	0.26
F(000)	2304	1568	504
Crystal size (mm)	0.10 × 0.10 × 0.05	0.20 × 0.10 × 0.05	0.20 × 0.15 × 0.10
Theta range for data collection (°)	4.56–25.05	3.73–25.02	3.92–27.87
Reflections collected	36 055	22 536	7119
Independent reflections	8823 ($R_{int} = 0.064$)	5731 ($R_{int} = 0.058$)	4211 ($R_{int} = 0.057$)
Data/restraints/parameters	8823/0/505	5731/0/406	4211/2/289
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.033$, $wR_2 = 0.061$	$R_1 = 0.031$, $wR_2 = 0.063$	$R_1 = 0.048$, $wR_2 = 0.134$
Goodness-of-fit on F^2	1.037	1.008	0.773
Largest difference peak and hole (e Å^{-3})	0.84 and −0.78	1.13 and −0.82 (near Yb)	0.24 and −0.31

3.8. X-ray structure determinations for *2a*, *4* and *6*

Data for the crystal structure determination were collected on a KappaCCD area detector at 173(2) K. Crystal data and refinement details are listed in Table 4. Empirical absorption corrections [17] were applied for **2a** and **4**. The structures were solved by direct methods and refined using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in riding mode.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171222 for compound **2a**, CCDC no. 171223 for compound **4** and CCDC no. 171224 for compound **6**. 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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