Heteroleptic ytterbium(II) complexes supported by a bulky β-diketiminato ligand†

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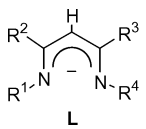
Heteroleptic β-diketiminatoytterbium(II) complexes [{Yb(**L**)(μ-I)(thf)}$_2$] [**1**: **L** = {N(Ar*)C(Me)}$_2$CH = L^1, **2**: **L** = {N(SiMe$_3$)C(Ph)}$_2$CH = L^2; Ar* = C$_6$H$_3$^{i}Pr$_2$-2,6] were prepared by a salt elimination [from YbI$_2$(thf)$_2$ and K**L**] or by a ligand redistribution [from YbI$_2$(thf)$_2$ and Yb**L**$_2$] reaction. Complexes **1** and **2** were convenient precursors to some new Yb(II) heteroleptic compounds. Thus, reaction of **1** and **2** with KN(SiMe$_3$)$_2$ yielded the mononuclear amido compounds [Yb(**L**){N(SiMe$_3$)$_2$}(thf)] (**3**: **L** = L^1 and **4**: **L** = L^2). Similarly, **1** with K{N(H)Ar*} gave [Yb(L^1){N(H)Ar*}(thf)] (**5**). Complex **3** was also obtained *via* a protolytic reaction of [Yb{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] with HL^1 at an elevated temperature. Treatment of **1** with slightly less than a stoichiometric amount of K{CH(SiMe$_3$)$_2$} afforded [Yb(L^1){CH(SiMe$_3$)$_2$}(thf)] (**6**), while using even a small excess of the alkyl reagent resulted in the deprotonation of the β-diketiminato ligand and the formation of the known dimer [{Yb(L^3)(thf)}$_2$] [**7**, L^3 = N̄(Ar*)C(Me)C(H)C(C̄H$_2$)N(Ar*)]. Compounds **1** or **2** reacted with KCPh$_3$ in thf yielding [Yb(L^1){η^5-C$_6$H$_5$CPh$_2$}(thf)] (**8**) or [Yb(CPh$_3$)$_2$(thf)$_2$] (**9**), respectively; the latter has two differently coordinated CPh$_3$ ligands. The molecular structures of **1**, **2**, **4**, **5**, **6**, **8** and **9** were determined by X-ray diffraction.

Introduction

β-Diketiminato ligands (shown in delocalised monoanionic form **L**) have recently received significant attention in Group 3 metal and lanthanide chemistry as an attractive alternative to the ubiquitous cyclopentadienyl ligands.[1] Two distinct types of β-diketiminato ligands, different by their methods of preparation and electronic and steric properties, were first introduced into lanthanide chemistry in 1994 by us (type **A**)[2] and Drees and Magull (type **B**).[3] Type **A** ligands are redox-active, undergoing facile one- or two-electron reduction chemically or electrochemically.[4] With the more resistant to reduction type **B** ligand (R^1 = R^4 = CH$_2$CH$_2$NEt$_2$; R^2 = R^3 = Me), isolation of a crystalline Sc^I compound was achieved.[5] Most of the recent studies on the rare earth metal β-diketiminates deal with metal(III) complexes of Sc,[6] Y and the lanthanides;[7] less explored are lanthanide(II) β-diketiminato complexes, which have only been described for Sm (a single example)[8a] and Yb.[2,4,8]



L

A: R^1 = SiMe$_3$ = R^4; R^2 - aryl, R^3 - aryl or alkyl

B: R^1, R^4 - aryl or alkyl; R^2, R^3 - alkyl

Homoleptic bis(β-diketiminate)s Yb**L**$_2$ were described for type **A** (various R^2 and R^3 substituents)[8a,8b] and **B** (a single example)[8d] ligands. More promising as potential reagents or catalysts are heteroleptic complexes. A few such compounds with a type **B** ligand (**L** = L^1: R^1 = R^4 = C$_6$H$_3$^{i}Pr$_2$-2,6; R^2 = R^3 = Me) have recently been reported.[8c,8e] Mononuclear cyclopentadienyl, indenyl and aryloxo derivatives [Yb(L^1)R(thf)] (R = η^5-C$_5$H$_4$Me, η^5-C$_9$H$_7$, OC$_6$H$_2$^{t}Bu$_2$-2,6-Me-4) were obtained by Na/K alloy reduction of the corresponding Yb^{III} chlorides,[8c] while the amide [Yb(L^1){N(SiMe$_3$)$_2$}(thf)] was prepared by a one-pot reaction from YbI$_2$, HL^1 and 2KN(SiMe$_3$)$_2$,[8e] the method originally employed for the synthesis of the Ca analogue.[9] This ytterbium(II) amide was then used as a starting material for dinuclear hydrido and hydroxo compounds in reactions with PhSiH$_3$ and H$_2$O, respectively.[8e] Attempted synthesis of a heteroleptic Yb(II) alkyl from Yb(L^1)$_2$ and YbR′$_2$(thf)$_2$ (R′ = CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2) resulted in deprotonation of one of the Me substituents of the β-diketiminato ligand backbone.[8d] Mono-β-diketiminatoytterbium(II) halides remained unknown. It is interesting, that with a related guanidinato ligand, homoleptic lanthanide(II) compounds Ln(Giso)$_2$ [Ln = Sm, Eu, Yb; Giso = {N(C$_6$H$_3$^{i}Pr$_2$-2,6)}$_2$CN(C$_6$H$_{11}$)$_2$] have been isolated from both 1 : 2 and 1 : 1 reactions of LnI$_2$ and K(Giso).[10] Only with Ln = Yb was a small amount (6%) of a monoguanidinatoytterbium(II) iodide available; the latter redistributed readily in thf solution to give the homoleptic complex and YbI$_2$(thf)$_x$.[10]

The aim of the present study was to develop synthetic methods for the preparation of β-diketiminatoytterbium(II) iodides using both type **A** [L^1 = {N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH] and **B** [L^2 = {N(SiMe$_3$)C(Ph)}$_2$CH] ligands and explore their potential as starting materials for various mixed-ligand Yb^{II} compounds.

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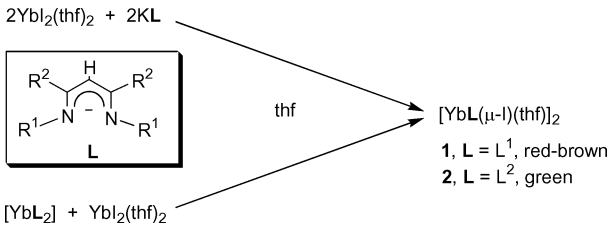
† Electronic supplementary information (ESI) available: PGSE NMR data for complexes **5** and **8**. CCDC reference numbers 706860–706866. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b818969b

Results and discussion

Synthesis and structures of β-diketiminatoytterbium(II) iodides 1 and 2

Reaction of $YbI_2(thf)_2$ with one equivalent of KL^1 or KL^2 in thf afforded the β-diketiminatoytterbium(II) iodides $[\{YbL(\mu\text{-}I)(thf)\}_2]$ [**L** = L^1 (**1**) or L^2 (**2**)] in good yields. Complexes **1** and **2** were also obtained *via* the ligand redistribution route from $Yb(L^1)_2$ or $Yb(L^1)_2$, respectively, Scheme 1. It is noteworthy that LiL^1 failed to react with $YbI_2(thf)_2$ in refluxing thf.



Scheme 1 Compounds **1** and **2** (L^1: $R^1 = C_6H_3{}^iPr_2$-2,6, R^2 = Me; L^2: $R^1 = SiMe_3$, R^2 = Ph).

Complex **1** was fairly soluble in aromatic hydrocarbons or hot thf. Its EI mass-spectrum revealed a dinuclear molecular ion peak (with the loss of thf ligands), which suggests that the dimeric structure of **1**, determined by X-ray crystallography (*vide infra*), is quite stable. Coordinated thf was removed from **1** by heating at 150 °C (10^{-2} Torr) for 1 h; the resulting compound showed a very similar ^{1}H NMR spectrum to that of **1** (the thf signals were absent), but its solubility in aromatic solvents was significantly lower. Complex **2** was insoluble in hydrocarbons or Et_2O but dissolved well in thf at room temperature, which may be attributed to dissociation of the dimer in this donor solvent. While freshly prepared samples of **2** in thf-d_8 showed one set of signals for the β-diketiminato ligand (in ^{1}H, ^{13}C and ^{29}Si NMR spectra), the second set (at *ca.* 2 : 5 ratio) appeared either after storing for several days at room temperature or by heating for 2 h at 60 °C. The presence of only one signal in the ^{171}Yb NMR spectrum (δ 1018 ppm) excludes a ligand redistribution, as $[Yb(L^2)_2]$ has a very characteristic downfield shift of δ 2434 ppm.[8b]

The crystalline compounds **1** and **2** have dimeric structures through bridging iodide atoms, as shown in Fig. 1 (skeletal view); their selected geometrical parameters are given in Table 1. The most significant difference between the two complexes is that the β-diketiminato ligand is κ^2-bonded and nearly planar (maximum deviation 0.055 Å) in **1**, but η^5-bonded in **2** (the C2 atom is out of the N1C1C3N2 plane by 0.221 Å). The Yb atom in **1** is in a distorted square pyramid (thf in the apical position; Yb off the basal plane by 0.413 Å towards the thf ligand). The Yb–N bond lengths are similar to those in the homoleptic β-diketiminate $[Yb(L^1)_2]$ (2.382(2) and 2.398(2) Å)[8d] or in the heteroleptic guanidinate $[\{Yb(Giso)(\mu\text{-}I)(thf)\}_2]$ (2.373(3) and 2.426(3) Å),[10] while the Yb–O bond in **1** is much shorter than in the latter (2.441(3) Å). In complex **2** the Yb–N bonds are slightly shorter but the Yb–O are longer than the corresponding distances in **1**. The bridging Yb–I distances in **1** and **2** are very close to each other and to such distances in Yb^{II} guanidinato[10,11] or bulky cyclopentadienyl[12] complexes.

Table 1 Selected bond distances (Å) and angles (°) for **1** and **2**

1[a]		**2**[b]	
Bond distances/Å			
Yb–N1	2.414(4)	Yb–N1	2.342(4)
Yb–N2	2.398(4)	Yb–N2	2.385(4)
Yb–O	2.364(4)	Yb–O	2.414(4)
Yb–I	3.1418(5)	Yb–I	3.2063(4)
Yb–I′	3.1031(5)	Yb–I′	3.0993(5)
		Yb–C1	2.847(6)
		Yb–C3	2.885(5)
		Yb–C2	2.899(6)
Bond angles/°			
N1-Yb–N2	78.77(14)	N1-Yb–N2	79.63(15)
I–Yb–I′	83.595(12)	I–Yb–I′	89.89(1)
O–Yb–N1	99.08(15)	O–Yb–N1	134.78(15)
O–Yb–N2	97.33(16)	O–Yb–N2	84.75(15)

[a] Symmetry transformation to generate equivalent atoms: ′ $-x + 1/2, -y + 3/2, -z + 1$. [b] Symmetry transformation to generate equivalent atoms: ′ $-x, -y, -z$.

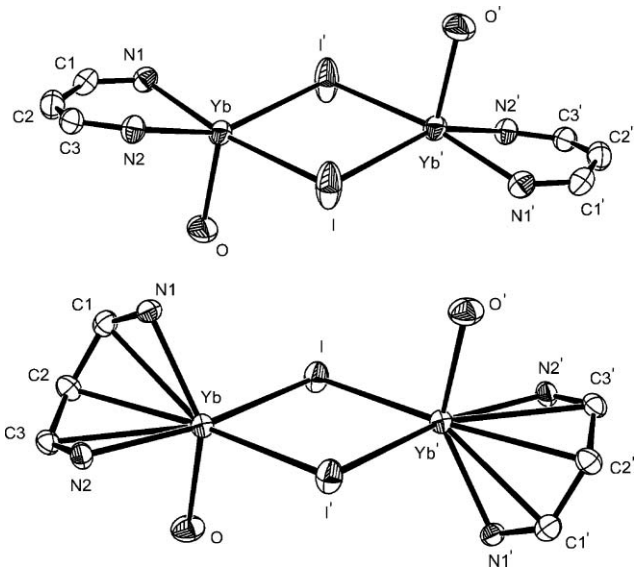
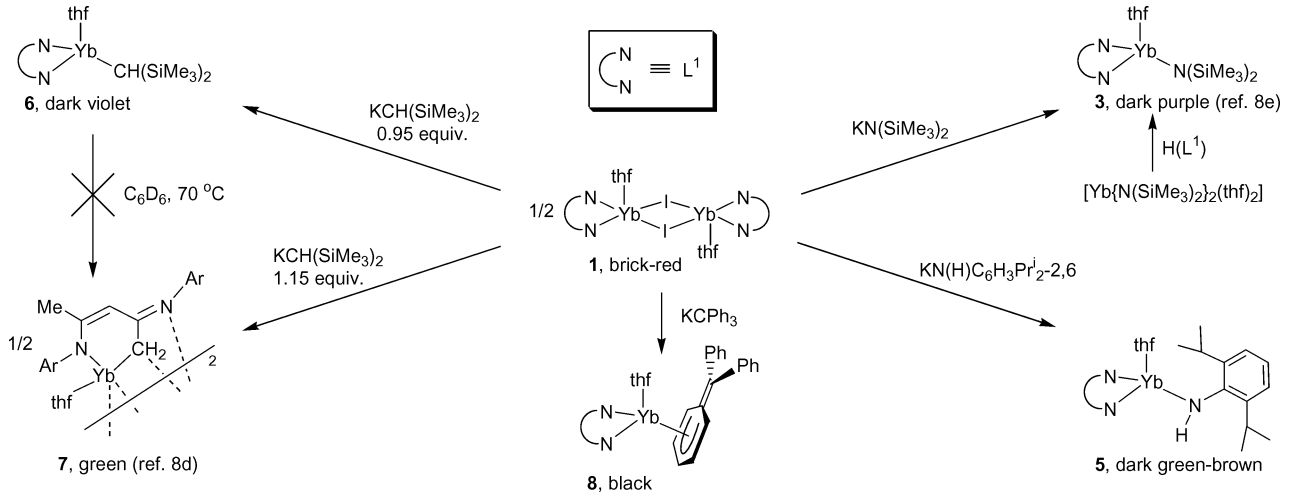


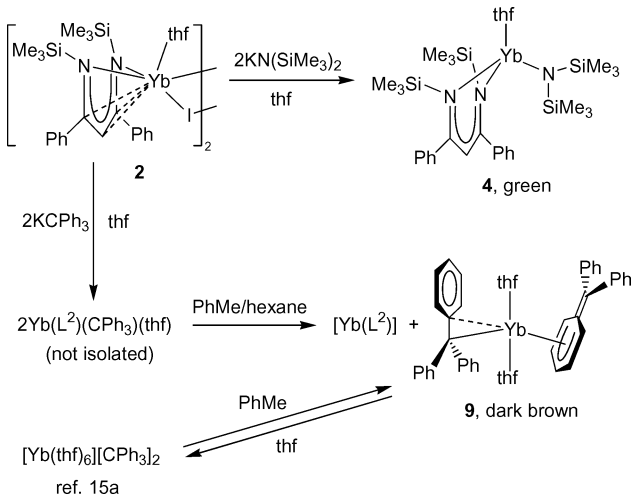
Fig. 1 Molecular structure of compounds **1** (top) and **2** (bottom) (50% thermal ellipsoids; all substituents of the β-diketiminato ligands and the CH_2 groups of thf ligands are omitted for clarity).

Reactions of β-diketiminatoytterbium(II) iodides 1 and 2

To evaluate the suitability of compounds **1** and **2** as heteroleptic Yb^{II} precursors, their reactions with selected potassium reagents were studied (Schemes 2 and 3). Thus, treatment of **1** with $KN(SiMe_3)_2$ in thf at room temperature readily produced the known[8e] ytterbium(II) amide $[Yb(L^1)\{N(SiMe_3)_2\}(thf)]$ (**3**). The latter was also obtained by the protolytic reaction of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ with HL^1. However, the activity of HL^1 as a protic reagent was very low; no reaction was observed in either hexane or thf at room temperature and the complete transformation of HL^1 to **3** required refluxing the mixture in thf for 2 d.



Scheme 2 Reactions of compound **1** with selected potassium amides and hydrocarbyls [$L^1 = \{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH$].



Scheme 3 Synthesis of complexes **4** and **9** [$L^2 = \{N(SiMe_3)C(Ph)\}_2CH$].

The metathetical reaction of **1** and K{N(H)Ar*} gave [Yb(L^1){N(H)Ar*}(thf)] (**5**) (Scheme 2). This compound was originally isolated in low yield as a by-product from the synthesis of [Yb(L^1)$_2$] when K(L^1) was prepared *in situ* by metallation of HL^1 with K metal. Apparently, the reductive cleavage of a C–N bond in HL^1 was the source of K{N(H)Ar*}; similar bond cleavage was observed upon reduction of, for example, [Ti(L^1)Cl$_2$] or [Ti(C_5Me_4H)(L^1)Cl] with K/Na alloy,[13a] and a Mn^{II} analogue of complex **5** (with an NHC carbene ligand in place of thf) was isolated from a reaction of [Mn(L^1)I(NHC)] and Na/K alloy.[13b] According to ^1H and ^{13}C NMR spectroscopic studies in C_6D_6 solution, compound **5** is stable towards ligand redistribution (in contrast to the Ca analogue[14]); a broad peak at δ 3.51 ppm had distinct Yb satellites and thus it was assigned to the primary anilido NH group.

The molecular structure of the crystalline **5** is shown in Fig. 2; the essential geometrical parameters are given in Table 2. The Yb coordination environment can be described as distorted tetrahedral, but there is an additional contact between the Yb atom and a Me group of one of the isopropyl substituent of the anilido ligand (Yb···C38, 2.998 Å; *cf.*,[14] in the Ca analogue Ca···C38

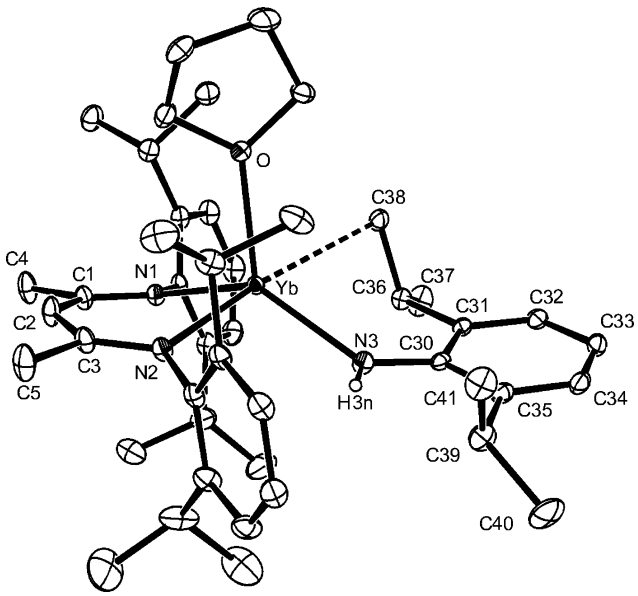


Fig. 2 Molecular structure of **5** (20% thermal ellipsoids; only the anilido H atom is shown; benzene solvate molecule is omitted for clarity).

or Ca···C36 are longer than 3.2 Å). The Yb–N3 (anilido) bond is only slightly shorter than the Yb–N1 or Yb–N2 (β-diketiminato) bond and may be compared to that in the 4-coordinate Yb^{II} Me_3Si-substituted anilides [Yb{N($SiMe_3$)Ar*}$_2$(thf)$_2$] (2.354(7) Å)[15a] and [Yb{N($SiMe_3$)Ph}{μ-N($SiMe_3$)Ph}(thf)]$_2$ (terminal bonds, 2.326(4) and 2.353(4) Å).[15b] The β-diketiminato ligand in **5** is delocalised and nearly planar, as in **1**.

The reaction of **1** with KCH($SiMe_3$)$_2$ in a 1 : 1.9 molar ratio (Scheme 2) yielded the expected heteroleptic ytterbium(II) alkyl [Yb(L^1){CH($SiMe_3$)$_2$}(thf)] (**6**). However, the outcome of the reaction depended dramatically on the chosen reagent stoichiometry: when a small excess of the potassium alkyl was taken (1 : 2.3), a product was the known[8d] compound [{Yb(L^3)(thf)}$_2$] (**7**) containing the deprotonated ligand L^3 [$L^3 = \bar{N}(Ar^*)C(Me)C(H)C(\bar{C}H_2)N(Ar^*)$] as dark green crystals (a dark red colour was reported in ref. 8d). The isolated complex **7** had the ^1H and ^{13}C NMR solution spectra and crystal unit cell parameters

Table 2 Selected bond distances (Å) and angles (°) for the β-diketiminatoytterbium compounds **5**, **6**, **8** and **4**

	5 (X = N3)	**6** (X = C30 [C30B])[a]	**8** (X = M1)[b]	**4** (X = N3)
Bond distances/Å				
Yb–N1	2.382(2)	2.404(5) [2.405(5)]	2.342(9)	2.403(3)
Yb–N2	2.340(2)	2.401(5) [2.401(5)]	2.345(9)	2.392(3)
Yb–O	2.399(2)	2.383(4) [2.371(5)]	2.366(8)	2.422(3)
Yb–X	2.327(2)	2.562(8) [2.549(7)]	2.451(1)	2.341(3)
Bond angles/°				
N1–Yb–N2	80.67(6)	80.57(18) [80.85(17)]	80.7(3)	83.46(10)
N1–Yb–X	133.29(7)	128.3(2) [125.2(2)]	121.3(3)	117.27(11)
N2–Yb–X	98.83(7)	125.5(2) [128.0(2)]	122.5(3)	113.03(11)
O–Yb–X	125.28(6)	118.7(2) [116.6(2)]	121.0(3)	138.58(10)
O–Yb–N1	99.91(6)	95.66(18) [99.56(18)]	99.5(3)	95.64(10)
O–Yb–N2	101.99(6)	98.65(18) [98.37(18)]	103.2(3)	94.05(10)

[a] Data for the second independent molecule of **6** are given in square brackets. [b] M1 is the centroid of the C2 to C7 ring.

almost identical to the reported[8d] values. The ^{1}H and ^{13}C NMR spectra of complex **6** revealed the alkyl ligand CH group signals at δ −1.65 (with ^{171}Yb satellites, $J(^{1}H–^{171}Yb)$ = 28.9 Hz) and 22.9 ppm, respectively, which are similar to the corresponding data for the dialkyl complex [Yb{CH(SiMe$_3$)$_2$}$_2$(OEt$_2$)$_2$] (δ −1.55 and 27.34 ppm, $J(^{1}H–^{171}Yb)$ = 30 Hz).[2] In contrast to the latter, the ^{171}Yb NMR spectrum of **6** showed only a singlet at δ 1021 ppm (the ^{171}Yb–^{1}H coupling was not resolved due to line broadening).

In C_6D_6 solution, the heteroleptic complex **6** demonstrated a remarkable stability towards (i) the deprotonation of a Me group of the β-diketiminato ligand by the alkyl group (*cf.*, the lability of Yb(L^1){CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2}[8d]) and (ii) ligand redistribution. Thus, no changes in the ^{1}H and ^{13}C NMR spectra of **6** were observed after storing for several months at ambient temperature in a sealed tube, while heating such a sample for 3 h at 70 °C resulted in only 20% conversion (decomposition pathway ii) to the homoleptic compound [Yb(L^1)$_2$] (the second expected product, Yb{CH(SiMe$_3$)$_2$}$_2$(thf)$_2$, decomposed under the reaction conditions giving CH$_2$(SiMe$_3$)$_2$ as the only detectable species). No complex **7** or any other complex containing the deprotonated ligand L^3 (decomposition pathway i) was found in this experiment. It is noteworthy that in the group 3 and the lanthanide series L^1 was easily deprotonated to L^3. Thus, complexes containing L^3 were isolated from the reactions of [Y(L^1)I$_2$(dme)] and KCH$_2$SiMe$_3$,[7r] TmI$_3$(thf)$_{3.5}$ and K(L^1)[7p] or [La(L^1)Br$_2$(thf)$_2$] and KCH$_2$Ph,[7s] the latter two bases being apparently weaker than [CH(SiMe$_3$)$_2$]$^-$. Similar transformation was also observed in β-diketiminatotitanium(IV) (*e.g.*, in the reaction of [Ti(L^1)(=CH^{t}Bu)(OTf)] with KCH$_2$Ph)[16a] and calcium chemistry (decomposition of the thermally unstable [Ca(L^1){CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2}], *cf.* ref. 8d for the Yb analogue).[16b] The decomposition pathway *via* deprotonation of an aryl isopropyl group (found in [Sc(L^1)(CH$_2$R)$_2$] R = Ph, Bu^t or SiMe$_3$[6c]) has been ruled out for **6**.

The structure of compound **6** was further confirmed by a single-crystal X-ray diffraction study (Fig. 3) showing the distorted tetrahedral geometry around the Yb atom and the nearly planar

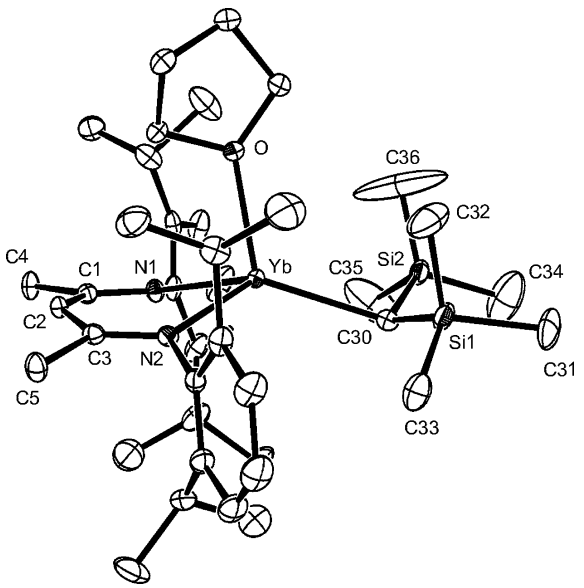


Fig. 3 Molecular structure of **6** (20% thermal ellipsoids; all H atoms and the second independent molecule of **6** are omitted for clarity).

β-diketiminato ligand core (C2 is out of the N1C1C3N2 plane by *ca.* 0.13 Å). The low quality of the structural data does not warrant a detailed discussion of the geometric parameters of **6** (selected data are given in Table 2).

The reaction of **1** with KCPh$_3$ in thf or toluene (Scheme 2) cleanly produced the heteroleptic trityl compound [Yb(L^1){η^5-C$_6$H$_5$CPh$_2$}(thf)] (**8**), which is the first structurally characterised (Fig. 4) lanthanide complex featuring a metal–trityl bond (previously reported Yb^{II} complexes [Yb(thf)$_6$][CPh$_3$]$_2$ and [{Yb(μ-Cl)(thf)$_4$}$_2$][CPh$_3$]$_2$,[17a] as well as [Ca(thf)$_6$][CPh$_3$]$_2$[17b] had ion-separated structures). The Yb coordination environment in **8** can be described as distorted tetrahedral considering that the Ph ring bound to the Yb atom (five Yb–C distances ranging from 2.734(10) to 2.878(11) Å) occupies a single coordination site. A similar geometry around the Yb atom was observed

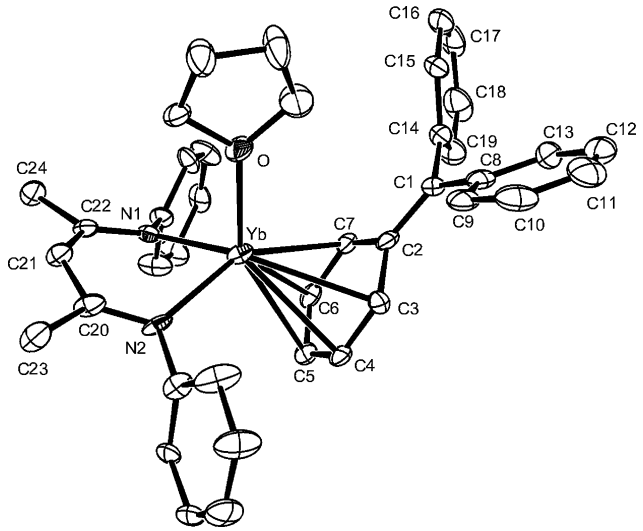


Fig. 4 Molecular structure of **8** (20% thermal ellipsoids; all H atoms and the isopropyl substituents of the β-diketiminato ligand are omitted for clarity).

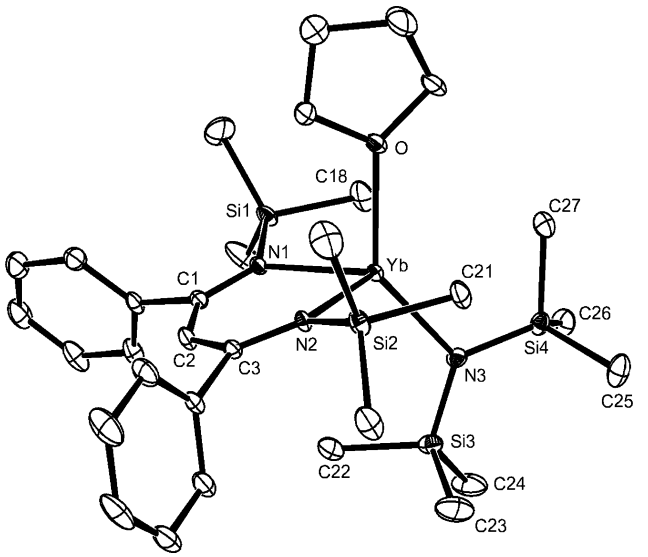


Fig. 5 Molecular structure of **4** (20% thermal ellipsoids; all H atoms and the isopropyl substituents of the β-diketiminato ligand are omitted for clarity).

in β-diketiminatoytterbium(II) complexes with cyclopentadienyl and indenyl ligands.[8c] The trityl ligand bonding mode and the arrangement of the Ph rings relative to the central C atom are close to those in the anionic Ti complex $[K(15\text{-crown-}5)_2][Ti(CO)_4(\eta^5\text{-}C_6H_5CPh_2)]$ (and the C_6H_4OMe-4 analogue).[18a] Based on this analogy, the ligand in **8** is depicted schematically as η^5-dienyl (Scheme 2), although the negative charge is more delocalised than in the Ti complex.[18b]

The ^1H and ^{13}C NMR spectra of complex **8** showed only one set of Ph resonances at 233–293 K, in contrast to the solid-state structure (the Ti-trityl complex[18a] showed two sets of signals at 0 °C). Such a result would be consistent with the presence of either a solvent-separated ligand (as in the ionic compounds $[M(thf)_6][CPh_3]_2$, M = Yb[17a] or Ca[17b]) or a contact ion pair (CIP) with a fast (on the NMR time-scale) exchange between the three Ph groups of the $[CPh_3]^-$ ligand. The ^1H pulsed gradient spin-echo (PGSE) NMR diffusion measurements on both toluene and thf solutions of **8** showed the strongly pronounced CIP behaviour (see ESI†) similar to that of complex **5**.

Similarly to compound **1**, the bis(trimethylsilyl)-β-diketiminatoytterbium(II) iodide **2** reacted cleanly with $KN(SiMe_3)_2$ in thf producing the expected amido complex $[Yb(L^2)\{N(SiMe_3)_2\}(thf)]$ (**4**) as dark green crystals, Scheme 3. The latter was highly soluble in hydrocarbons, demonstrating the appropriate signals in its ^1H and ^{13}C NMR spectra with broadened peaks for the thf ligand.

The molecular structure of **4** was determined by single-crystal X-ray diffraction. The coordination environment of the Yb atom in **4** can be described as distorted tetrahedral (Fig. 5), with a nearly planar L^2 ligand core and the Yb atom 0.480(5) Å out of the N1C1C2C3N2 plane (*cf.*, Yb is 1.712(5) Å out of the N1C1C3N2 plane in the η^5-bonded compound **2**). The Yb–N and Yb–O distances in **4** are slightly longer than those in **5** apparently due to the presence of two long range Yb···C(Me) contacts (av. 3.06 Å) to the $SiMe_3$ substituents of the β-diketiminato ligand. Such Yb···C(Me) intramolecular contacts are common in complexes containing a $YbNSiMe_3$ moiety, *e.g.*, 3.06 Å in $[Yb\{N(SiMe_3)_2\}_2(dmpe)]$; the latter has a closely similar Yb–N amido bond length of 2.331(13) Å.[19]

The reaction of **2** with $KCPh_3$ was not so straightforward as in the case of **1**. While the precipitation of the KI by-product was observed, the desired heteroleptic trityl complex did not crystallise upon removal of the solvent. Prolonged storing led to ligand redistribution and crystallisation of the sparingly soluble bis-trityl compound $[Yb(CPh_3)_2(thf)_2]$ (**9**), Scheme 3.

An X-ray diffraction study shows that **9** contains two independent molecules in the unit cell, which have similar geometric parameters (Table 3). The two CPh_3 ligands are differently bonded to the Yb atom: one interacts mainly *via* its central carbon atom (C1 in Fig. 6), while the other is η^5-bonded *via* one of the Ph rings (C22 to C26 atoms in Fig. 6) similar to that found in complex **8**. The Yb–$C_{central}$ bond lengths in the two independent molecules of **9** (2.619(7) and 2.596(7) Å) can be compared to Yb–C distances in the alkyl complexes **6** (2.562(8) and 2.549(7) Å) and

Table 3 Selected bond distances (Å) and angles (°) for **9** [a]

Bond distances/Å			
Yb–O1	2.369(5)	Yb1B–O1B	2.382(5)
Yb–O2	2.374(7)	Yb1B–O2B	2.381(5)
Yb–M1	2.501(7)	Yb1B–M1B	2.507(7)
Yb–C1	2.619(7)	Yb1B–C1B	2.596(7)
Bond angles/°			
O1–Yb–O2	90.3(2)	O1B–Yb1B–O2B	94.5(2)
O1–Yb–C1	115.7(2)	O1B–Yb1B–C1B	113.0(2)
O2–Yb–C1	98.7(2)	O2B–Yb1B–C1B	101.0(2)
O1–Yb–M1	108.3(2)	O1B–Yb1B–M1B	106.1(2)
O2–Yb–M1	106.0(2)	O2B–Yb1B–M1B	101.8(2)
M1–Yb–C1	128.9(2)	M1B–Yb1B–C1B	132.5(2)

[a] M1 and M1B are the centroids of the C21 to C26 and C21B to C26B rings, respectively.

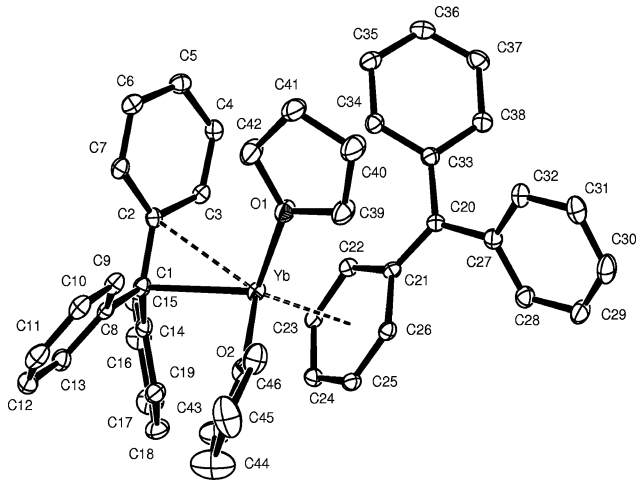


Fig. 6 Molecular structure of **9** (20% thermal ellipsoids; all H atoms and the second independent molecule of **9** are omitted for clarity).

[Yb(Tp){CH(SiMe$_3$)$_2$}] (2.55(6) Å; Tp = HB{N$_2$C$_3$H^{t}Bu-3-Me-5}$_3$)[20] or in the Yb-benzyl compound [Yb{CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2}$_2$(thf)$_2$] (2.640(3) and 2.661(3) Å).[8e] The overall coordination environment of the Yb atom in **9** can be described as distorted tetrahedral with each CPh$_3$ ligand occupying a single site.

Various metal–trityl coordination modes were previously observed in alkali metal complexes; this fact was explained by the flat potential energy surfaces of ion pairs involving highly delocalised carbanions.[21] Such considerations can also now be applied to the ytterbium(II)-trityl complexes with CIP structures.

Room temperature ^{1}H and ^{13}C NMR spectroscopy in C$_7$D$_8$ showed that both ligands and all the Ph substituents in **9** are equivalent, whereas the low solubility in aromatic hydrocarbons did not permit a low-temperature study. In thf, the dark brown complex **9** immediately converted into the red ionic compound [Yb(thf)$_6$][CPh$_3$]$_2$ and the reverse transformation was achieved by heating the latter in toluene (**9** crystallised upon cooling). The Ca analogue of **9** and its conversion to the structurally characterised ionic compound [Ca(thf)$_6$][CPh$_3$]$_2$ were reported, but no details on the former was given.[17b]

Conclusions

We have shown that two bulky β-diketiminatoytterbium(II) iodides **1** and **2** are readily prepared in a good yield by the salt elimination or ligand redistribution method. These compounds were convenient precursors to heteroleptic amides (including the primary anilide **5** and the bis(trimethylsilyl)amide **4**) and hydrocarbyls (including the bis(trimethylsilyl)methyl compound **6** and the trityl derivative **8**). In reactions with such strong bases as KCH(SiMe$_3$)$_2$, an excess of the potassium reagent should be avoided to prevent deprotonation of the β-diketiminato ligand substituents (with the formation of **7**). Considering the striking resemblance of the behaviour of Ca and Yb β-diketiminates,[8d,8e] a chemistry similar to that reported here can be expected in the β-diketiminatocalcium series.

Experimental

General methods

All manipulations were carried out in an atmosphere of dry argon using standard Schlenk tube techniques or under vacuum in a sealed all-glass apparatus. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over a potassium mirror. The NMR spectra were recorded on a DPX 300 or AM-500 Bruker spectrometer with residual solvent signals as internal reference (^{1}H and ^{13}C{^{1}H}) or with an external reference (SiMe$_4$ for ^{29}Si and [Yb(C$_5$Me$_5$)$_2$(thf)] for ^{171}Yb). Elemental analyses were carried out at the London Metropolitan University (satisfactory elemental analyses for **5**, **8** and **9** were not obtained due to their high air- and moisture-sensitive nature). The compounds HL^1,[22] K(L^2),[4c] and KN(H)(C$_6$H$_3$^{i}Pr$_2$-2,6)[23] were prepared by published procedures. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were measured in sealed capillaries.

Synthesis of K(L^1)

HL^1 (4.40 g, 10.5 mmol) was dissolved in hexane (60 mL) and ^{n}BuLi (6.6 mL of 1.6 *M* solution in hexanes) was added at room temperature. Sublimed KO^{t}Bu (1.18 g, 10.52 mmol) was added quickly to this warm solution with vigorous stirring producing a yellow solution. After stirring for 5 h at ambient temperature, a light-yellow microcrystalline solid precipitated, which was washed with hexane (2 × 20 cm^3) and dried in a vacuum yielding KL (4.08 g, 84%). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.16–7.13 (m, 4 H, *m*-H), 7.03 (m, 2 H, *p*-H), 4.79 (s, 1 H, middle CH), 3.33 (septet, 4 H, J = 6.9 Hz, C*H*Me$_2$), 1.87 (s, 6 H, NC*Me*), 1.25 (d, 12 H, J = 6.9 Hz, CH*Me*$_2$), 1.07 ppm (d, 12 H, J = 6.9 Hz, CH*Me*$_2$).

Synthesis of [{Yb(μ-I)(L^1)(thf)}$_2$] (1). YbI$_2$(thf)$_2$ (2.23 g, 3.90 mmol) and K(L^1) (1.74 g, 3.81 mmol) were stirred in thf (50 mL) at 60 °C for 2 h. The solvent was removed in a vacuum and the residue was extracted with toluene (2 × 20 mL). Slow evaporation of toluene using the vacuum-transfer technique (fast crystallisation resulted in the formation of a wool-like polycrystalline material) produced brick-red crystals of **1**, which were washed with hexane and dried in a vacuum (2.08 g, 69%) (found: C 49.9, H 6.49, N 3.53. C$_{66}$H$_{98}$I$_2$N$_4$O$_2$Yb$_2$ (MW 1579.36) requires C 50.2, H 6.25, N 3.55%). Melting was not observed up to 310 °C. EI MS *m*/*z* (%, assignment): 1433 (0.1, [M – 2thf]$^+$), 1008 (0.8, [Yb(L^1)$_2$]$^+$), 718 (10, [M/2 – thf]$^+$), 403 (70, [HL^1 – Me]$^+$), 202 (100, [N(C$_6$H$_3$^{i}Pr$_2$-2,6)CCH$_3$]$^+$). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.19–7.15 (br s, 6 H, CH$_{arom}$ overlapping with solvent), 4.80 (s, 2 H, CH$_{middle}$), 3.63 (br s, 8 H, thf), 3.30 (septet, 8 H, C*H*Me$_2$), 1.62 (s, 12 H, NC*Me*), 1.34 (d, 24 H, CH*Me*$_2$), 1.22 ppm (d, 24 H, CH*Me*$_2$ + br s, 8 H, thf). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 165.3 (N*C*Me), 146.3 (*ipso*-C), 141.9 (*o*-C), 124.7 (*p*-C), 123.9 (*m*-C), 95.1 (C$_{middle}$), 70.1 (thf), 28.5 (*C*HMe$_2$), 26.0 (CH*Me*$_2$), 25.1 (thf), 25.0 (NC*Me*), 24.7 ppm (CH*Me*$_2$). ^{171}Yb{^{1}H} NMR (C$_6$D$_6$/C$_6$H$_6$, 298 K): δ 729.2 ppm.

Synthesis of [{Yb(μ-I)(L^2)(thf)}$_2$] (2). YbI$_2$ (0.95 g, 2.23 mmol) was added to a stirred solution of K(L^2) (0.90 g, 2.22 mmol) in thf (100 mL). The green-brown suspension was stirred for 24 h and filtered. The filtrate was concentrated to yield upon cooling green crystals of **2** (1.42 g, 87%) (found: C 39.9, H 5.19, N 3.65.

$C_{50}H_{74}I_2N_4O_2Si_4Yb_2$ (MW 1475.37) requires C 40.7, H 5.06, N 3.80%). The following NMR spectra were recorded on a freshly prepared sample of **2**. ^{1}H NMR (thf-d_8, 293 K; integration is given for a monomer): δ 7.42 (m, 4 H, *o*-H of Ph), 7.29 (m, 6 H, *m*- and *p*-H of Ph), 5.10 (s, 1 H, CH_{middle}), 3.62 (m, 4 H, thf), 1.77 (m, 4 H, thf), 0.01 ppm (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (thf-d_8, 293 K): δ 173.17 (N*C*Ph), 148.17 (*ipso*-C of Ph), 128.82 (*p*-CH of Ph), 128.43 and 128.34 (*m*- and *o*-CH of Ph), 101.07 (CH_{middle}), 68.10 (thf), 26.25 (thf), 3.16 ppm ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (thf-d_8, 298 K): δ –4.43 ppm ($SiMe_3$). $^{171}Yb\{^1H\}$ NMR (C_7D_8/thf, 298 K): δ 1018.1 ppm. UV-vis. (thf): λ/nm 407 s, 663 w.

Synthesis of [Yb(L^1){N(SiMe$_3$)$_2$}(thf)] (3). Solid $KN(SiMe_3)_2$ (0.062 g, 0.31 mmol) was added to a suspension of compound **1** (0.254 g, 0.16 mmol) in thf (10 mL) at –40 °C. Upon stirring the mixture for a few minutes at room temperature, **1** dissolved and KI precipitated to give a purple-red solution. The reaction mixture was evaporated to dryness in a vacuum and the residue was extracted with pentane. Slow evaporation of the extract produced purple microcrystalline **6** (0.169 g, 60%). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra (C_6D_6, 293 K) were similar to those in the literature.[8e]

Synthesis of [Yb(L^2){N(SiMe$_3$)$_2$}(thf)] (4). Solid $KN(SiMe_3)_2$ (0.070 g, 0.35 mmol) was added to a solution of compound **2** (0.245 g, 0.17 mmol) in thf (10 mL) at –40 °C. The mixture was allowed to warm up to room temperature and was stirred for 2 h. The solvent was removed in a vacuum and the dark green residue was extracted with pentane (2 × 5 mL). The extract was concentrated and stored at –27 °C for 1 week yielding green crystals of **4** (0.189 g, 73%), mp 140–141 °C (with dec.) (found: C 48.1, H 7.07, N 5.51. $C_{31}H_{55}N_3OSi_4Yb$ (MW 771.17) requires C 48.3, H 7.19, N 5.45%). ^{1}H NMR (C_7D_8, 293 K): δ 7.26 (m, 4 H, *o*-H of Ph), 6.98 (m, 6 H, *m*- and *p*-H of Ph), 5.01 (s, 1 H, CH_{middle}), 3.66 (br s, 4 H, thf), 1.39 (br s, 4 H, thf), 0.47 (s, 18 H, $SiMe_3$ of amide), 0.16 ppm (s, 18 H, $SiMe_3$ of L^2). ^{13}C NMR (C_7D_8, 293 K): δ 174.6 (N*C*Ph), 148.7 (*ipso*-C of Ph), 127.8, 127.4 and 126.6 (CH of Ph), 107.5 (CH_{middle}), 69.4 (thf), 25.4 (thf), 5.64 ($SiMe_3$ of amide), 2.68 ppm ($SiMe_3$ of L^2).

Synthesis of [Yb(L^1){N(H)Ar*}(thf)] (5). Solid KN(H)-$C_6H_3{}^i$Pr$_2$-2,6 (0.231 g, 1.07 mmol) was added to a suspension of compound **1** (0.835 g, 0.53 mmol) in thf (20 mL) at –40 °C. Upon stirring the mixture for a few minutes at room temperature, **1** dissolved and KI precipitated to give a brown solution. The reaction mixture was stirred for 2 h, evaporated to dryness in a vacuum and the residue was extracted with toluene (2 × 5 mL). The toluene solution was concentrated, covered with hexane and stored at –10 °C overnight yielding black crystals of **5**·PhMe (0.450 g, 46%). Recrystallisation of this material from benzene–pentane produced X-ray quality crystals of **5**·C_6H_6. ^{1}H NMR (C_6D_6, 293 K): δ 7.16–7.15 (two s, CH_{arom} of L^1 + solvent and C_6H_6), 7.08 (d, 2 H, *m*-CH of amido-Ar*), 6.64 (t, 1 H, *p*-CH of amido-Ar*), 4.77 (s, 1 H, CH_{middle}), 3.52 (br s, 1 H, NH), 3.38 (br m, 8 H, thf), 3.27 (septet, 4 H, C*H*Me$_2$ of L^1), 2.57 (br septet, 2 H, C*H*Me$_2$ of amido-Ar*), 1.62 (s, 6 H, NC*Me*), 1.23–1.14 ppm (two d, 36 H, CH*Me*$_2$ + br s, 4 H, thf). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 165.1 (N*C*Me), 156.9 (*ipso*-C of amido-Ar*), 146.1 (*ipso*-C of L^1), 141.6 (*o*-C of L^1), 130.1 (*o*-C of amido-Ar*), 128.5 (C_6H_6), 124.8 (*p*-C of L^1), 124.1 (*m*-C of L^1), 122.4 (*m*-C of amido-Ar*), 110.1 (*p*-C of amido-Ar*), 95.1 (C_{middle}), 69.4 (thf), 29.4 (*C*HMe$_2$ of amido-Ar*), 28.3 (*C*HMe$_2$ of L^1), 25.2 (thf), 25.0, 24.8, 24.6 (CH*Me*$_2$ and NC*Me* of L^1), 22.7 ppm (CH*Me*$_2$ of amido-Ar*).

Synthesis of [Yb(L^1){CH(SiMe$_3$)$_2$}(thf)] (6). Solid $KCH(SiMe_3)_2$ (0.142 g, 0.72 mmol) was added to a suspension of compound **1** (0.604 g, 0.38 mmol) in thf (10 mL) at –40 °C. Upon stirring the mixture for a few minutes at room temperature, **1** dissolved and KI precipitated to give a red-brown solution. The reaction mixture was evaporated to dryness in a vacuum and the residue was extracted with pentane. Slow evaporation of the extract produced violet crystals of **6**, which were washed with cold pentane and dried in a vacuum (0.369 g, 59% based on Yb), mp 135–138 °C (with dec.) (found: C 58.6, H 8.25, N 3.54. $C_{40}H_{68}N_2OSi_2Yb$ (MW 822.19) requires C 58.4, H 8.34, N 3.41%). ^{1}H NMR (C_6D_6, 293 K): δ 7.16-7.14 (br s, 3 H, CH_{arom} overlapping with solvent), 4.76 (s, 1 H, CH_{middle}), 3.50 (br s, 4 H, thf), 3.23 (br m, 4 H, C*H*Me$_2$), 1.62 (s, 12 H, NC*Me*), 1.34 (br s, 12 H, CH*Me*$_2$), 1.22 (d, 12 H, CH*Me*$_2$ + br s, 4 H, thf), 0.15 (s, 18 H, $SiMe_3$), –1.65 ppm [s, with ^{171}Yb satellites, $J(^1H–^{171}Yb)$ = 28.9 Hz, 1 H, C*H*(SiMe$_3$)$_2$]. $^{13}C\{^1H\}$ NMR (C_7D_8, 293 K): δ 165.4 (N*C*Me), 146.4 (*ipso*-C), 141.2 (*o*-C), 124.9 (*p*-C), 124.1 (*m*-C), 93.0 (C_{middle}), 69.3 (thf), 28.4 (*C*HMe$_2$), 25.4 (CH*Me*$_2$), 25.3 (NC*Me*), 25.0 (thf), 24.5 (CH*Me*$_2$), 22.9 [*C*H(SiMe$_3$)$_2$], 5.96 ppm ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6/C_6H_6, 298 K): δ –7.26 ppm ($SiMe_3$). ^{171}Yb NMR (C_6D_6/C_6H_6, 298 K): δ 1021.3 ppm (br s, $\Delta w_{1/2}$ ~ 60 Hz; no detectable ^{171}Yb–^{1}H coupling).

Isolation of [{Yb(L^3)(thf)}$_2$] (7). Solid $KCH(SiMe_3)_2$ (0.075 g, 0.37 mmol) was added to a cold suspension of compound **1** (0.245 g, 0.16 mmol) in thf (10 mL). After stirring at room temperature overnight, the initially formed dark red solution (as above) became pale with precipitation of a dark green microcrystalline solid. The supernatant liquid was removed by decantation and the solid was extracted with hot thf (2 × 20 mL; extraction was incomplete). Storing of the concentrated extracts at room temperature yielded **7** as small dark green rhombic plates and blocks (0.098 g, 46%), mp 145–150 °C (with dec.). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra (thf-d_8, 293 K) were similar to those in the literature.[8d]

Synthesis of [Yb(L^1){η^5-C$_6$H$_5$CPh$_2$}(thf)] (8). Solid $KCPh_3$ (0.075 g, 0.26 mmol) was added to a suspension of compound **1** (0.166 g, 0.12 mmol) in thf (5 mL) at –40 °C. Upon stirring the mixture for a few minutes at room temperature, **1** dissolved and KI precipitated to give a very dark brown solution. The reaction mixture was stirred for 2 h and filtered, the filtrate was evaporated to dryness in a vacuum and the residue was extracted with toluene (2 × 3 mL). The toluene solution was concentrated, covered with hexane and stored at –10 °C overnight yielding black crystals of **8** (0.182 g, 83%). ^{1}H NMR (C_7D_8, 293 K): δ 7.13–7.00 (br m, 6 H, CH_{arom} overlapping with the solvent), 6.97 (d, 6 H, J = 7.7 Hz, *o*-H), 6.59 (t, 6 H, J = 7.5 Hz, *m*-H), 6.19 (t, 3 H, J = 7.0 Hz, *p*-H), 4.65 (s, 1 H, CH_{middle}), 3.89 (br s, 4 H, thf), 3.31 (br m, 2 H, C*H*Me$_2$), 2.81 (br m, 2 H, C*H*Me$_2$), 1.52 (s, 6 H, NC*Me*), 1.34 (br s, 4 H, thf) 1.20–1.08 ppm (br m, 12 H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_7D_8, 293 K): δ 165.9 (N*C*Me), 146.5 (*ipso*-C of Ar*), 144.0 (*ipso*-C of Ph), 141.5 (*o*-C of Ar*), 129.2 (*m*-CH of Ph), 125.2 (*p*-CH of Ar*), 123.9 (*m*-CH of Ar*), 123.2 (*o*-CH of Ph), 114.1 (*p*-CH of Ph), 100.3 (*C*Ph$_3$), 94.2 (C_{middle}), 70.5 (thf), 28.6 (*C*HMe$_2$), 25.6

Table 4 Crystal data and structure refinement for **1**, **2**, **4**, **5**, **6**, **8** and **9**

Compound	**1**	**2**	**4**	**5**	**6**	**8**	**9**
Empirical formula	$C_{66}H_{98}I_2N_4O_2Yb_2$	$C_{50}H_{74}I_2N_4O_2Si_4Yb_2$	$C_{31}H_{55}N_3OSi_4Yb$	$C_{45}H_{67}N_3OYb{\cdot}C_6H_6$	$C_{40}H_{68}N_2OSi_2Yb$	$C_{52}H_{64}N_2OYb$	$C_{46}H_{46}O_2Yb{\cdot}C_7H_8$
Formula weight	1579.36	1475.37	771.18	917.16	822.18	906.09	896.00
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	28.3326(4)	15.0479(4)	9.8514(2)	10.1873(1)	13.6465(2)	23.6608(5)	10.1293(2)
b/Å	12.4318(2)	15.8523(7)	21.2659(4)	12.2671(1)	16.2031(2)	9.0274(2)	20.7321(4)
c/Å	21.8144(4)	12.3722(6)	19.0709(4)	20.0249(2)	19.7654(3)	21.7827(4)	21.6554(5)
α/°	90	90	90	79.262(1)	98.537(1)	90	111.214(1)
β/°	116.695(1)	96.760(3)	101.922(1)	80.762(1)	97.971(1)	100.391(1)	96.485(1)
γ/°	90	90	90	76.620(1)	98.946(1)	90	91.056(1)
U/Å^3	6864.6(2)	2930.8(2)	3909.15(14)	2373.81(4)	4279.39(10)	4576.4(2)	4203.73(15)
Z	4	2	4	2	4	4	4
D_{calcd}/Mg m^{-3}	1.53	1.67	1.31	1.28	1.28	1.32	1.42
μ/mm^{-1}	3.65	4.35	2.54	2.01	2.27	2.08	2.27
F(000)	3136	1440	1584	956	1712	1872	1832
Reflections collected	31 737	14 868	33 366	46 538	44 846	32 206	63 001
Independent reflections	6020 [R_{int} = 0.064]	5121 [R_{int} = 0.056]	6902 [R_{int} = 0.068]	10 787 [R_{int} = 0.056]	14 833 [R_{int} = 0.053]	6287 [R_{int} = 0.089]	15 191 [R_{int} = 0.071]
Reflections with $I > 2\sigma(I)$	5009	4096	5605	9950	12 434	4811	12 460
Data/restraints/parameters	6020/0/345	5121/0/289	6902/0/361	10 787/0/538	14 833/0/833	6287/0/505	15 191/28/952
Goodness-of-fit on F^2	1.019	1.097	1.034	1.018	1016	1.231	1.154
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.038$, w$R_2 = 0.077$	$R_1 = 0.037$, w$R_2 = 0.083$	$R_1 = 0.029$, w$R_2 = 0.060$	$R_1 = 0.024$, w$R_2 = 0.056$	$R_1 = 0.054$, w$R_2 = 0.138$	$R_1 = 0.075$, w$R_2 = 0.134$	$R_1 = 0.059$, w$R_2 = 0.133$
R indices (all data)	$R_1 = 0.052$, w$R_2 = 0.083$	$R_1 = 0.053$, w$R_2 = 0.089$	$R_1 = 0.042$, w$R_2 = 0.065$	$R_1 = 0.028$, w$R_2 = 0.058$	$R_1 = 0.065$, w$R_2 = 0.148$	$R_1 = 0.102$, w$R_2 = 0.1458$	$R_1 = 0.075$, w$R_2 = 0.141$
Largest diffraction peak and hole/e A^{-3}	1.25 and –1.49	0.90 and –1.07	0.41 and –0.80	0.84 and –0.87 (near Yb)	5.66 and –1.81	1.06 and –1.44	2.11 and –1.74 (near Yb)

(thf), 25.1, 24.9, 24.7, 24.4, 24.0 ppm (NC*Me* and CH*Me*$_2$, not fully resolved).

Synthesis of [Yb(CPh$_3$)$_2$(thf)$_2$] (9). Solid KCPh$_3$ (0.150 g, 0.52 mmol) was added to a solution of compound **2** (0.372 g, 0.25 mmol) in thf (20 mL) at –40 °C. The mixture was allowed to warm up to room temperature and was stirred for 2 h. The solvent was removed in a vacuum and the residue (a dark brown tar) was extracted with toluene (2 × 5 mL). The extract was concentrated, covered with hexane and stored at –10 °C for 1 week yielding black crystals of **9**·PhMe (0.175 g, 39% based on Yb). ^{1}H NMR (C_7D_8, 300 K): δ 7.18 (d, 12 H, $J = 7.7$ Hz, *o*-H), 6.79 (t, 12 H, $J = 7.5$ Hz, *m*-H), 6.32 (t, 6 H, $J = 7.0$ Hz, *p*-H), 3.32 (br s, 8 H, thf), 1.25 ppm (br s, 8 H, thf) (peaks of solvate PhMe were overlapping with the solvent signals). ^{13}C{^{1}H} NMR (C_7D_8, 300 K): δ 145.1 (*ipso*-C of Ph), 129.6 (*m*-CH of Ph), 123.5 (*o*-CH of Ph), 115.4 (*p*-CH of Ph), 94.4 (*C*Ph$_3$), 70.3 (thf), 25.4 ppm (thf).

Crystal data and refinement details for 1, 2, 4, 5, 6, 8 and 9

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated MoKα radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas.

In **4** the C30 atom of the thf ligand is disordered and the two alternative positions were left isotropic. In **5** the H atom bound to N3 (H3n) was refined, all the other H atoms were placed on calculated positions and were refined in a riding mode. For **6** a somewhat low quality of crystals resulted in several problems with the structure solution, including the presence of four residual peaks which have no chemical sense (the separation between these peaks mirrors that of the two independent Yb atoms like "ghost" images at very low occupancy). Complex **8** crystallised as very thin needles having weak and rather fuzzy diffraction. In **9** there are two independent molecules of the Yb complex. There are also two independent molecules of toluene solvate, one ordered and one disordered; both solvate molecules were refined with isotropic C atoms, and the disordered solvate molecule had SADI constraints and H atoms omitted; attempts to refine the non-disordered solvate anisotropically resulted in unacceptable ellipsoids and were abandoned. In all the figures only the larger occupancy orientation is shown for disordered ligands. Absorption corrections using MULTISCAN were applied. The structures were refined by a full-matrix least-squares procedure based on F^2, using SHELXL-97.[24] Further details are in Table 4.

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