New reactions of β-diketiminatolanthanoid complexes: sterically induced self-deprotonation of β-diketiminato ligands†

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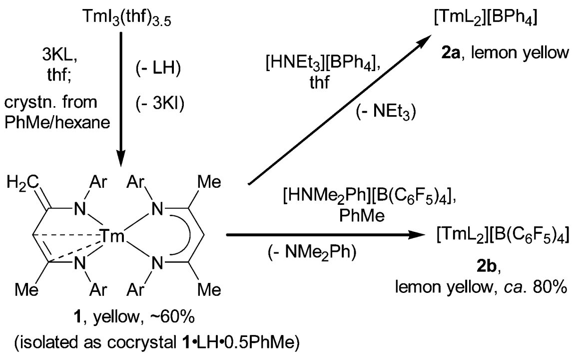
Attempted synthesis of sterically demanding bis- or tris-β-diketiminato complexes of lanthanoids resulted in ligand deprotonation and the formation of complexes containing both a "normal" and a deprotonated ligand; one of these on protonation gave the first cationic β-diketiminato–Ln complex.

The use of β-diketiminates as important monoanionic spectator ligands is well documented.[1] However, recent observations have shown that in selected instances such coordinated ligands may themselves undergo transformations. Examples include reduction of certain Li or Yb β-diketiminates to produce di- or trianionic analogues,[2] and deprotonation, resulting in the formation of dianionic ligand–metal complexes.[3] The latter process occurred either (a) thermally, by alkane elimination from a Ca[3c] or Sc[3d] β-diketiminate containing an adjacent alkyl ligand (examples of a complex-induced proximity effect, CIPE[4]); or (b) for a Ge,[3a] Sc,[3b] or Ti[3e] complex, by use of an external strong base—a carbanion[3a,e] or $^{-}N(SiMe_3)_2$.[3b]

We now report the new self-deprotonation reaction of the β-diketiminato ligand in sterically hindered lanthanoid (Ln) complexes, which resulted in formation of new compounds: (i) the thulium(III) complex $[TmL(L^{dep})]$ (**1**), containing both the monoanionic β-diketiminato ligand $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]^-$ (= L^-) as well as its deprotonated derivative $[L^{dep}]^{2-}$; (ii) the salts $[TmL_2]X$ (**2a**, **2b**) *via* protonation of **1**; (iii) the unprecedented cyclometallated ytterbium(III) complex $[YbL'(L'^{dep})]$ (**4**) (L' = $[\{N(SiMe_3)C(Ph)\}_2CH]^-$) where L'^{dep} is the *C*,*N*,*N'*-tridentate bicyclic ligand.



1, yellow, ~60%
(isolated as cocrystal **1**•LH•0.5PhMe)

Scheme 1 Synthesis of **1** and **2** (Ar = $C_6H_3Pr^i_2$-2,6).

The preparation of the complexes **1**, **2a** and **2b** is outlined in Scheme 1; the yields of the crystalline compounds were not optimised. A Tm(III) iodide–KL reaction was initially carried out in a 1 : 2 molar stoichiometry, in an attempt to make TmL_2I, but **1** was the only crystalline product. It may be that successive transient intermediates along the pathway to **1** were $[TmL_2]I$ and $[TmL_2][L]$. It is noted that a bis(β-diketiminato)ytterbium(III) complex was not accessible from $YbCl_3$ + 2LiL in thf, $[YbCl_2(L)(thf)_2]$ being isolated;[5] the radii of the Tm^{3+} (0.880 Å) and the Yb^{3+} (0.868 Å) are almost identical. Complex **1** was also isolated in a modest yield upon the work up of a reaction mixture of $[TmI_2(dme)_3]$ and 2KL in thf. The CH_2 group of **1** was readily protonated, using an appropriate $[HNR_2R'][BAr'_4]$; the salt **2a** was thermally unstable and its formation was confirmed by ^1H NMR spectroscopy, while the salt **2b** was isolated in a good yield. Complexes **2a** and **2b** are rare examples of salts containing a homoleptic bis-β-diketiminatometal cation. A bis(β-diketiminato)thulium iodide $Tm(L')_2I$ has been reported.[6]

The molecular formulae of complexes **1**, **2a** and **2b**, as shown in Scheme 1, were consistent with their elemental analyses and ^1H-NMR spectra (19 CH_3 signals, in the wide range δ 241 to δ −245 ppm, for **1**; but only 10 such signals for **2a** or **2b**). Single crystal X-ray data were obtained for **1**‡ (Fig. 1) and **2b**.‡

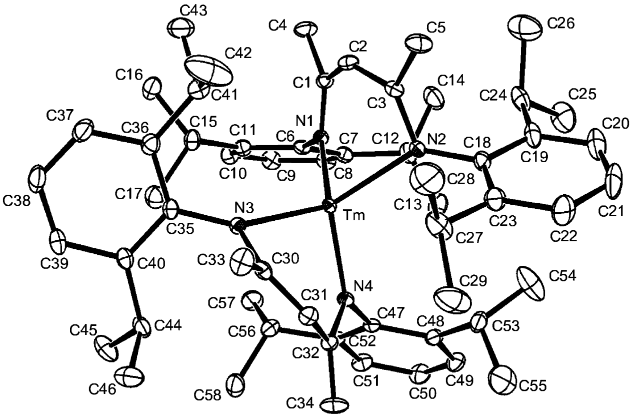


Fig. 1 ORTEP drawing and atom numbering scheme for complex **1** (20% ellipsoids; non-coordinated LH and toluene solvate molecules are not shown). Selected bond lengths (Å) and angles (°): Tm–N1 2.273(2), Tm–N2 2.301(2), Tm–N3 2.207(2), Tm–N4 2.161(2), N1–C1 1.317(3), N2–C3 1.345(3), C1–C2 1.430(4), C2–C3 1.384(4), N3–C30 1.401(3), N4–C32 1.400(3), C30–C31 1.350(4), C31–C32 1.493(3), C30–C33 1.524(3), C32–C34 1.330(4), Tm–C30 2.717(3), Tm–C31 2.826(3), N1–Tm–N2 87.25(7), N3–Tm–N4 96.35(7).

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† Electronic supplementary information (ESI) available: synthesis and characterisation of **1**, **2b**, **3**, **4** and **4a**. See http://www.rsc.org/suppdata/cc/b4/b416549g/

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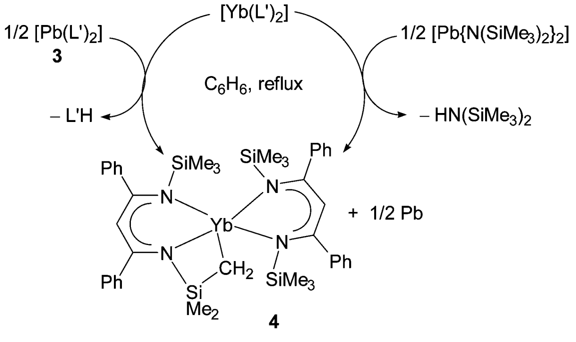
The thulium atom in molecule **1** is at the spiro-junction of two *N*,*N*′-chelating ligands: N1 and N2 of L$^-$ and N3 and N4 of the deprotonated [L^{dep}]$^{2-}$. The TmL ring has the boat conformation (κ^2-ligand-to-metal bonding mode) and is significantly, but far from completely, π-delocalised (*e.g.*, the endocyclic N–C bond lengths are unequal, with N1–C1 almost 0.03 Å shorter than N2–C3). The Tm(L^{dep}) moiety is best described as implicating η^3-1-azaallyl (N3–C30–C31) and amido(N4)-centred bonds to the Tm atom; thus, the Tm···C30 and Tm···C31 contacts are near the upper range of the Tm–C(η^5-Cp) distances (2.598–2.829, av. 2.670 Å) of [TmCp$_3$],[7] whereas the Tm···C32 contact in **1** is longer at 2.908(3) Å. The Tm–N4 bond length is *ca.* 0.026 Å shorter than the average Tm–N distance of 2.187 Å in the tetracoordinated Tm(III) amide [Tm{N(SiMe$_2$CH$_2$)$_2$}$_3$(μ-Cl)Li(OEt$_2$)$_3$] (2.179(2)–2.189(2) Å).[8] The ligand [L^{dep}]$^{2-}$ has previously featured in [Ge(L^{dep})(H)B(H)(μ-H)$_2$Li(OEt$_2$)$_3$][3a] and [Ti(L^{dep})(NC$_6$H$_3$Pr$^i_2$-2,6)(OEt$_2$)],[3e] but only the latter has closely similar M(L^{dep}) geometric parameters (apart from the shorter M–N bond lengths) to those in **1**. The ligand bite angle for L^{dep} is 9.1° wider than for L, thus facilitating the Tm···C(30 or 31) close contacts in Tm(L^{dep}).

The crystalline salt **2b** comprises a well-separated ion pair; there are two independent pairs. The geometric parameters of the cation are closely similar to those in the Tm(L) moiety of **1**, with Tm–N bond lengths of 2.232 Å (range 2.214(7)–2.250(7) Å) and ligand bite angles of 89.2(3)° and 85.2(2)° (molecule A) or 88.8(2)° and 89.1(2)° (molecule B).

Homoleptic Ln(III) β-diketiminates are rare, doubtless for steric reasons.[9] Attempts to make a bis(β-diketiminato)cerium alkyl from Ce(L′)$_2$Cl and LiCH(SiMe$_3$)$_2$ yielded [Ce(L′){CH(SiMe$_3$)$_2$}$_2$].[6] Thus we sought an alternative oxidative approach to an Ln(L′)$_3$ complex, based on an analogy with a strategy which had successfully been employed to make sterically encumbered tricyclopentadienides of Sm(III) and U(IV).[10] The first step was to prepare [Pb(L′)$_2$] (**3**) (see supplementary data†), which is the first structurally characterised Pb β-diketiminate and an unprecedented group 14 metal(II) bis(κ^2-β-diketiminate).[1]

The preparation of the cyclometallated ytterbium(III) β-diketiminate [Yb(L′)(L′^{dep})] (**4**) is illustrated in Scheme 2. In one experiment, a product **4a**, a co-crystal of **4** (76%) and Yb(L′)$_2$ (24%), was isolated in place of **4**, as revealed by crystallography.‡ It is possible that a transient intermediate in the [YbL$_2$]–**3** system was [Yb(L′)$_2$][L′], in which the third loosely attached ligand deprotonates one of the Me groups activated by the Yb···Me agostic interaction. Examples of base-induced cyclometallation of bis(trimethylsilyl)amidometal complexes are known, including the conversion of [Yb{N(SiMe$_3$)$_2$}$_3$] into [Yb{N(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)Si(Me)$_2$CH$_2$}Na(thf)$_3$] (**5**).[11]



Scheme 2 Syntheses of **4**.

The structure of the crystalline compound **4**, determined by single crystal X-ray diffraction,‡ is illustrated in Fig. 2. The central Yb atom is joined through N3 and N4 to form a boat-shaped β-diketiminatoytterbium moiety; and *via* N1, N2 and C19 to the bicyclic ligand [L′^{dep}]$^{2-}$. The endocyclic bond distances and angles of the 4-membered ring of **4** are similar to those in the corresponding ring of **5**.[11] The Yb–N3(N4) distances are shorter than in [Yb(L′)$_2$] (av. 2.410 Å),[12] in agreement with the difference in Yb^{3+} and Yb^{2+} ionic radii. The bonding mode in the Yb(L′) moiety of **4** is close to η^5, the dihedral angle between the N3–C22–C24–N4 and N3–Yb–N4 planes being 63.7° (*cf.*,[12] 10.8° in the κ^2-bonded [Yb(L′)$_2$] and 67.5° in the η^5-bonded [Yb{N(SiMe$_3$)C(C$_6$H$_4$Me-4)CHC(adamantyl-1)N(SiMe$_3$)}$_2$]).

The structure of crystalline **4a** showed that the ligand L′ in the molecule of Yb(L′)$_2$ adopts the same η^5-bonding mode as in **4**, in contrast to the κ^2-bonding found in the crystal of isolated [Yb(L′)$_2$].[12]

In conclusion, the following observations are noteworthy. (1) A β-diketiminato ligand in a highly encumbered Ln complex may undergo a facile deprotonation of the type 2[A]$^-$ → [A^{dep}]$^{2-}$ + [AH] (A = L′ or L). (2) Protonation of the thulium complex [TmL(L^{dep})] (**1**), using an appropriate ammonium tetraarylborate, is a convenient route to the first homoleptic cationic lanthanoid salt **2a** or **2b**, notable for containing a potentially highly electrophilic cation. (3) The compound [Yb(L′)(L′^{dep})] (**4**) is significant for possessing the new bicyclic ligand [L′^{dep}]$^{2-}$, which may well be found more widely. (4) The oxidative route, based on a Pb(II) reagent, is likely to find more general application, particularly for complexes of metals having available adjacent oxidation states.

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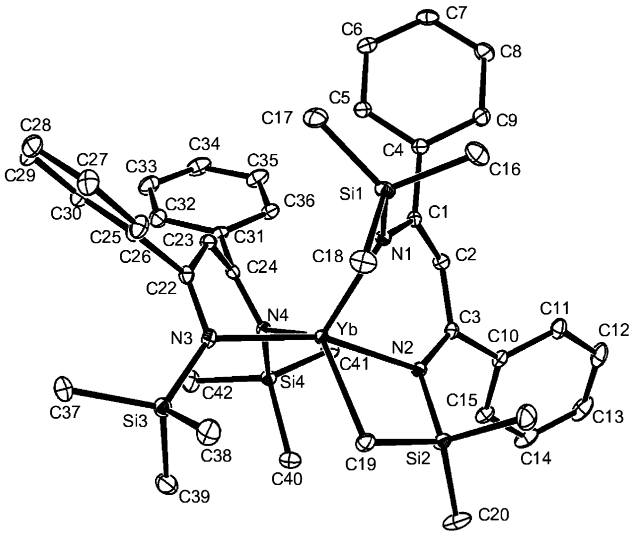

Fig. 2 ORTEP drawing and atom numbering scheme for complex **4** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Yb–N1 2.265(2), Yb–N2 2.289(2), Yb–N3 2.328(2), Yb–N4 2.272(2), Yb–C19 2.406(3), N1–C1 1.348(3), N2–C3 1.316(3), N3–C22 1.338(3), N4–C24 1.328(3), C1–C2 1.398(4), C2–C3 1.417(4), C22–C23 1.414(4), C23–C24 1.420(3), N1–Yb–N2 79.93(7), N3–Yb–N4 82.37(7), N2–Yb–C19 70.48(9).

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Notes and references

‡ *Crystal data:* for **1**·LH·0.5PhMe (yellow prism 0.25 × 0.20 × 0.10 mm^3): $[C_{58}H_{81}N_4Tm]\cdot(C_{29}H_{42}N_2)\cdot 0.5(C_7H_8)$, $M = 1467.91$, triclinic, space group $P\bar{1}$, $a = 10.9404(2)$, $b = 16.9293(2)$, $c = 24.5836(3)$ Å, $\alpha = 70.187(1)$, $\beta = 83.689(1)$, $\gamma = 75.243(1)°$, $V = 4140.99(10)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 1.12$ mm^{-1}, 14519 independent reflections [$R_{int} = 0.058$], final $R1 = 0.034$ [for 12932 reflections with $I > 2\sigma(I)$], $wR2 = 0.082$ (all data). For **2b** (yellow prism 0.20 × 0.15 × 0.10 mm^3): $[C_{82}H_{82}BF_{20}N_4Tm]$, $M = 1683.26$, monoclinic, space group $P2_1/c$, $a = 27.9702(3)$, $b = 19.9944(3)$, $c = 27.9170(4)$ Å, $\beta = 98.971(1)$, $V = 15421.5(4)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\mu = 1.25$ mm^{-1}, 26992 independent reflections [$R_{int} = 0.075$], final $R1 = 0.070$ [for 20129 reflections with $I > 2\sigma(I)$], $wR2 = 0.155$ (all data). For **3** (yellow plate 0.20 × 0.20 × 0.05 mm^3): $[C_{42}H_{58}N_4Si_4Pb]$, $M = 938.47$, triclinic, space group $P\bar{1}$, $a = 11.3492(2)$, $b = 12.1384\ (2)$, $c = 16.5846(3)$ Å, $\alpha = 89.975(1)$, $\beta = 97.414(1)$, $\gamma = 93.140(1)°$, $V = 2262.16(7)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 3.87$ mm^{-1}, 8131 independent reflections [$R_{int} = 0.055$], final $R1 = 0.031$ [for 7692 reflections with $I > 2\sigma(I)$], $wR2 = 0.079$ (all data). For **4** (orange hexagonal prism 0.40 × 0.35 × 0.30 mm^3): $[C_{42}H_{57}N_4Si_4Yb]$, $M = 903.32$, triclinic, space group $P\bar{1}$, $a = 11.2608(1)$, $b = 12.8457(2)$, $c = 16.0891(3)$ Å, $\alpha = 89.620(1)$, $\beta = 86.087(1)$, $\gamma = 79.121(1)°$, $V = 2280.13(6)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 2.19$ mm^{-1}, 7714 independent reflections [$R_{int} = 0.036$], final $R1 = 0.022$ [for 7714 reflections with $I > 2\sigma(I)$], $wR2 = 0.053$ (all data). For **4a** (brown prism 0.30 × 0.30 × 0.30 mm^3): $[C_{42}H_{57}N_4Si_4Yb]$, $M = 903.32$, triclinic, space group $P\bar{1}$, $a = 11.2433(2)$, $b = 12.9389(2)$, $c = 16.2117(3)$ Å, $\alpha = 89.319(1)$, $\beta = 86.149(1)$, $\gamma = 79.253(1)°$, $V = 2311.81(6)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 2.16$ mm^{-1}, 10926 independent reflections [$R_{int} = 0.037$], final $R1 = 0.041$ [for 10399 reflections with $I > 2\sigma(I)$], $wR2 = 0.094$ (all data). The structure is disordered, with 74% as shown and 26% as $[YbL'_2]$. The lower occupancy atom sites for the alternative $N3Si3Me_3$ moiety were included as isotropic atoms with H atoms omitted. Data collection Kappa CCD. Refinement using SHELXL-97. CCDC numbers 254749–254753 for complexes **1**, **2b**, **3**, **4** and **4a**, respectively. See http://www.rsc.org/suppdata/cc/b4/b416549g/ for crystallographic data in .cif or other electronic format.

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