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

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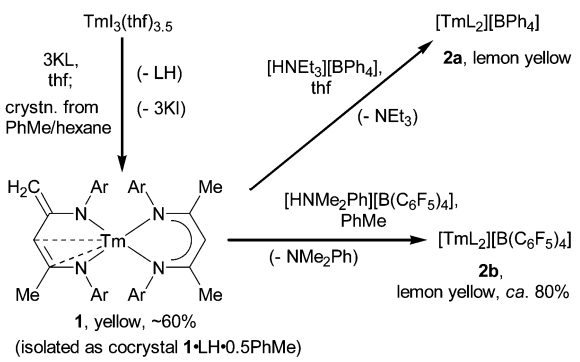
Attempted synthesis of sterically demanding bis- or tris-β-diketiminato complexes of lanthanoids resulted in ligand deprotonation and the formation of complexes containing both a "normal" and a deprotonated ligand; one of these on protonation gave the first cationic β-diketiminato–Ln complex.

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($C_6H_3Pr^i_2$-2,6)C(Me)}$_2$CH]$^-$ (= 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)}$_2$CH]$^-$) where L'^{dep} is the *C*,*N*,*N*′-tridentate bicyclic ligand.



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 ^{1}H 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′)$_2$I 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 ^{1}H-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**.‡

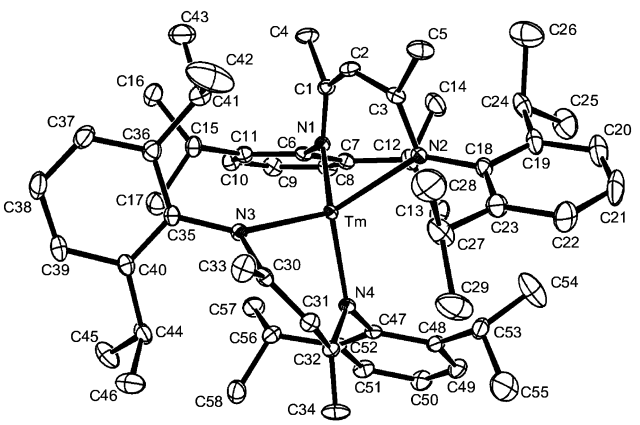


Fig. 1 ORTEP drawing and atom numbering scheme for complex **1** (20% ellipsoids; non-coordinated LH and toluene solvate molecules are not shown). Selected bond lengths (Å) and angles (°): Tm–N1 2.273(2), Tm–N2 2.301(2), Tm–N3 2.207(2), Tm–N4 2.161(2), N1–C1 1.317(3), N2–C3 1.345(3), C1–C2 1.430(4), 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).

† 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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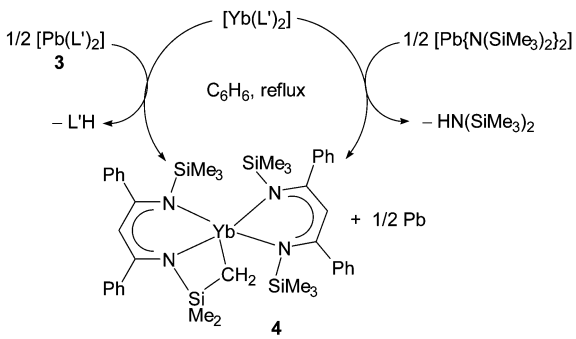
The thulium atom in molecule **1** is at the spiro-junction of two *N*,*N*′-chelating ligands: N1 and N2 of L^- and N3 and N4 of the deprotonated $[L^{dep}]^{2-}$. The TmL ring has the boat conformation (κ^2-ligand-to-metal bonding mode) and is significantly, but far from completely, π-delocalised (*e.g.*, 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 $[Tm\{N(SiMe_2CH_2)_2\}_3(\mu\text{-}Cl)Li(OEt_2)_3]$ (2.179(2)–2.189(2) Å).[8] The ligand $[L^{dep}]^{2-}$ has previously featured in $[Ge(L^{dep})(H)B(H)(\mu\text{-}H)_2Li(OEt_2)_3]$[3a] and $[Ti(L^{dep})(NC_6H_3Pr^i_2\text{-}2,6)(OEt_2)]$,[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 $Ce(L')_2Cl$ 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 $[Yb\{N(SiMe_3)_2\}_2\{N(SiMe_3)\text{-}Si(Me)_2CH_2\}Na(thf)_3]$ (**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 $[Yb\{N(SiMe_3)C(C_6H_4Me\text{-}4)CHC(adamantyl\text{-}1)N(SiMe_3)\}_2]$).

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 $2[A]^- \rightarrow [A^{dep}]^{2-} + [AH]$ (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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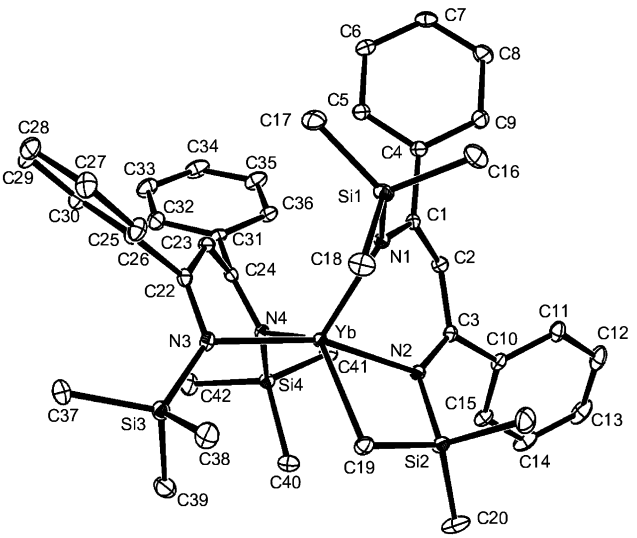

Fig. 2 ORTEP drawing and atom numbering scheme for complex **4** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Yb–N1 2.265(2), Yb–N2 2.289(2), Yb–N3 2.328(2), Yb–N4 2.272(2), Yb–C19 2.406(3), N1–C1 1.348(3), N2–C3 1.316(3), N3–C22 1.338(3), N4–C24 1.328(3), C1–C2 1.398(4), C2–C3 1.417(4), 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, α = 70.187(1), β = 83.689(1), γ = 75.243(1)°, V = 4140.99(10) $Å^3$, Z = 2, T = 173(2) K, μ = 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, β = 98.971(1), V = 15421.5(4) $Å^3$, Z = 8, T = 173(2) K, μ = 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, α = 89.975(1), β = 97.414(1), γ = 93.140(1)°, V = 2262.16(7) $Å^3$, Z = 2, T = 173(2) K, μ = 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, α = 89.620(1), β = 86.087(1), γ = 79.121(1)°, V = 2280.13(6) $Å^3$, Z = 2, T = 173(2) K, μ = 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, α = 89.319(1), β = 86.149(1), γ = 79.253(1)°, V = 2311.81(6) $Å^3$, Z = 2, T = 173(2) K, μ = 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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