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Unusual crystalline heterobimetallic trinuclear β-diketiminates $[Yb\{L(\mu\text{-}Li(thf)\}_2]$ and $[Yb\{L'(\mu\text{-}Li(thf)\}_2]\cdot thf$ $[L, L' = \{N(SiMe_3)C(R)\}_2CH, R = Ph, C_6H_4Ph\text{-}4]$†

Anthony G. Avent, Alexei V. Khvostov, Peter B. Hitchcock and Michael F. Lappert*
The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ. E-mail: m.f.lappert@sussex.ac.uk

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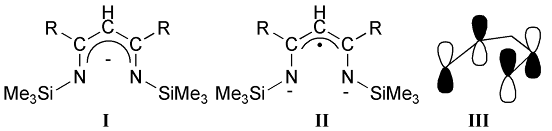
$YbCl_3$ with successively 2KL or 2KL′ and then > 2Li in thf yields crystalline $[Yb\{L(\mu\text{-}Li(thf)\}_2]$ 1 or $[Yb\{L'(\mu\text{-}Li(thf)\}_2]\cdot thf$ 2, characterised by X-ray, multinuclear NMR spectral and VT magnetic susceptibility data; 1 and 2 are best formulated as Yb(II) complexes having *dianionic* L^{2-} or L'^{2-} ligands, L or L′ = $\{N(SiMe_3)C(R)\}_2CH$ (R = Ph or C_6H_4Ph-4).

From small beginnings in the 1960s, the area of metal β-diketiminates is burgeoning. In a forthcoming review, we noted that about 450 such complexes for 43 metals have been described in *ca.* 140 publications, 38 of them in 2001.[1] The β-diketiminates, *e.g.* **I**, have a useful role as *monoanionic* spectator ligands, by virtue of their strong binding to metals, their tuneable and extensive steric demands and their diversity of bonding modes. They often stabilise complexes in unusually low metal oxidation states[2] and/or coordination numbers,[3] as cations,[4] or others containing a coligand which is multiply bonded to the metal.[5] Many complexes are thus coordinatively and electronically unsaturated and this is a key to their function as catalysts for processes as varied as olefin oligo-, poly- and copolymerisation,[6] ring-opening polymerisation of lactide or related monomers,[7] and copolymerisation of an epoxide and carbon dioxide,[8] and as structural models for a Type 1 Cu protein active site.[9]

Now we draw attention to the novel ytterbium complexes $[Yb\{L(\mu\text{-}Li(thf)\}_2]$ and $[Yb\{L'(\mu\text{-}Li(thf)\}_2]\cdot thf$ [L, L′ = $\{N(SiMe_3)C(R)\}_2CH$, R = Ph **1** or C_6H_4Ph-4 **2**]. These are best formulated in terms of *dianionic* β-diketiminato ligands L^{2-} or L'^{2-}, *i.e.* **II**, each bridging a thf-bound lithium ion and the central Yb(II) spiro centre. The implication is that the π* (LUMO) **III** of the NCCCN array is sufficiently energetically accessible to accept an electron, the resulting L^{2-} or L'^{2-} having radical character. As evidence we draw attention to the unusually long average C–N but 'normal' C–C bond lengths in **1** of 1.413 and 1.427 Å, respectively. These may be compared with corresponding values in $[MgL_2]$ (1.305 and 1.413 Å)[10] and $[NdL_2Cl]$ (1.307 and 1.443 Å);[3] data for $[YbL_2]$ are not yet available.[3]



I **II** **III**

L R = Ph, **L′** R = C_6H_4Ph-4

$YbCl_3$ with 2KL or 2LiL′ [from $LiCH(SiMe_3)_2$ and $2(4\text{-}PhC_6H_4CN)$,[11]] in thf and reduction with Li yielded the crystalline complex **1** or **2**, respectively, Scheme 1.‡

$$\underset{\textbf{2},\ 52\%,\ \text{dark blue}}{[Yb\{L'(\mu\text{-}Li(thf))\}_2]\cdot thf} \longleftarrow YbCl_3 \longrightarrow \underset{\textbf{1},\ 64\%,\ \text{dark violet}}{[Yb\{L(\mu\text{-}Li(thf))\}_2]}$$

Scheme 1 Synthesis of the crystalline complexes **1** and **2**.

Crystalline **1** (Fig. 1) is a heterotrinuclear complex, almost of C_2 symmetry.§ Each ligand, by virtue of its four-coordinate nitrogen atoms, bridges the ytterbium spiro-centre with the thf-bound lithium atoms. The NCCCN skeletal atoms of each almost planar ligand are parallel to within 6°. The angle between the N1–Yb–N2 and N3–Yb–N4 planes is 86° and the angle between each of the planes and the corresponding NCCCN moiety is 85°. Each of the three-coordinated lithium atoms [also Li1···C17 2.801(4) Å and Li2···C42 2.861(4) Å] is in a pyramidal environment [Σ 342.2° (Li1) or 343.8 °(Li2)]. The endocyclic YbNCCCN bond lengths are substantially delocalised. The geometric parameters for crystalline **2**§ are closely similar to those of **1**, as shown in the legend to Fig. 1.

A plot for solid **1** of reversed magnetic susceptibility χ_M^{-1} at 5 kG as a function of temperature (Fig. 2) may be deconvoluted into three regions: (a) high (220–300 K) and low (5–170 K) temperature, each linear and satisfying the Curie–Weiss Law, $\chi_M^{-1} = (T - \theta)C^{-1}$, corresponding to magnetic moments 1.08 μ_B (θ, 57 K) and 1.30 μ_B (θ, −2 K) for (a) and (b), respectively; and (c) the intermediate range (170–220 K) which is non-linear, probably reflecting the changing population of at least two species. The possibility that **1** be formulated as containing Yb^0 is unlikely, because its $4f^{14}6s^2$ configuration would require that $[Yb^0\{L^{-1}(\mu\text{-}Li(thf)\}_2]$ be diamagnetic.

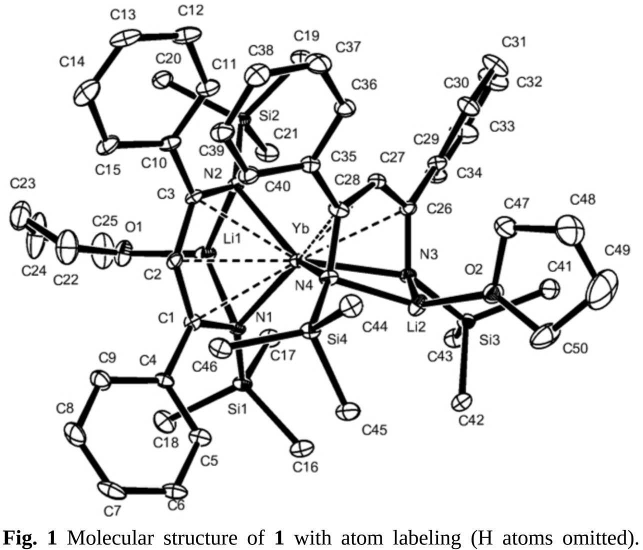


Fig. 1 Molecular structure of **1** with atom labeling (H atoms omitted). Selected bond lengths (Å) and angles (°); corresponding data for **2** in parentheses: Yb–N1 2.319(4) [2.308(5)], Yb–N2 2.344(5) [2.314(4)], Yb–N3 2.313(5) [2.304(4)], Yb–N4 2.328(5) [2.323(5)], Yb–C1 2.542(6) [2.523(5)], Yb–C2 2.561(6) [2.561(6)], Yb–C3 2.524(6) [2.517(6)], Yb–C26 2.523(6) [Yb–C34 2.537(6)], Yb–C27 2.570(5) [Yb–C35 2.570(5)], Yb–C28 2.552(5) [Yb–C36 2.536(6)], Li1–N1 1.991(12) [1.970(11)], Li1–N2 1.997(11) [2.039(12)], Li1–O1 1.924(13) [1.949(10)], Li2–N3 2.015(11) [2.007(12)], Li2–N4 1.978(11) [1.997(12)], Li2–O2 1.919(11) [1.914(11)], N1–C1 1.419(7) [1.416(7)], N2–C3 1.409(7) [1.412(7)], N3–C26 1.415(7) [N3–C34 1.408(7)], N4–C28 1.410(7) [N4–C36 1.402(7)], C1–C2 1.428(7) [1.418(8)], C2–C3 1.425(8) [1.426(8)], C26–C27 1.427(8) [C34–C35 1.443(8)], C27–C28 1.426(8) [C35–C36 1.410(8)]; N1–Yb–N2 79.37(16) [79.33(16)], N3–Yb–N4 79.07(17) [80.09(17)], N1–Li–N2 96.6(5) [94.7(4)], N3–Li–N4 95.4(5) [96.1(5)].

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† Electonic supplementary information (ESI) available: NOE data for **1** and NMR data for **2**. See http://www.rsc.org/suppdata/cc/b2/b203321f/

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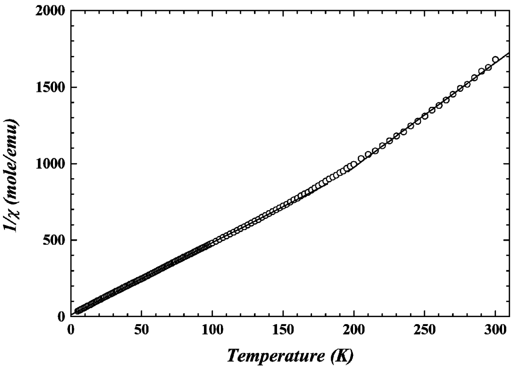

Fig. 2 Reversed magnetic susceptibility of solid **1** as a function of *T*.

The NMR spectra of **1** in C_6D_6 showed that the ambient temperature ^{1}H, ^{13}C, ^{29}Si and ^{7}Li chemical shifts, although relatively sharp (except the thf signals), were significantly paramagnetically shifted.¶ The ^{1}H NMR of phenyl protons showed the alternating high and low frequency paramagnetic shifts and lack of attenuation with increasing distance from the metal that are characteristic of π spin delocalisation. The spectrum stands in contrast to the broad, highly shifted resonances expected for the protons of ligands in complexes with an ytterbium-centred unpaired electron.[12]

For each L ligand of **1**, one N($SiMe_3$)C(Ph) moiety **A** was chemically distinct from the other **B**. This is consistent with the solution structure being similar to that in the crystal, a notion supported by ^{1}H NOE studies which demonstrated one principal interaction (1 in Fig. 3); additionally, protons of $(SiMe_3)^{\mathbf{A}}$ interacted substantially with the *o*- and *m*-protons of $Ph^{\mathbf{B}}$, but those of $(SiMe_3)^{\mathbf{B}}$ only weakly with the *o*-protons of $Ph^{\mathbf{A}}$. A saturation transfer experiment involving irradiation of the *p*-protons of $Ph^{\mathbf{B}}$ showed that the **A** and **B** moieties were exchanging at a rate of *ca.* 1 s^{-1} at 323 K; this is attributed to a rotation of the L ligands relative to one another. From a heteronuclear ^{6}Li{^{1}H} NOE study it is evident that at 323 K thf was not bound to Li and was either dissociated or bound to Yb. Even at this higher temperature, Li interacts with both $(SiMe_3)^{\mathbf{A}}$ and $(SiMe_3)^{\mathbf{B}}$ [(3) and (2), respectively in Fig. 3] being located at almost equal distances from each of the $SiMe_3$ groups at room temperature. For NOE numerical data and NMR data of **2**, see ESI.†

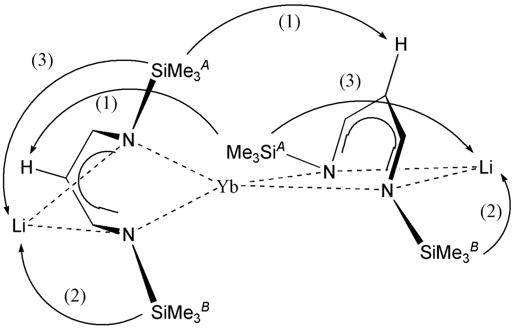

Fig. 3 ^{1}H/^{1}H NOE [(1)] and ^{6}Li/^{1}H NOE [(2) and (3)] interactions in **1**.

The dianionic character of the coordinated β-diketiminato ligands L and L′ in **1** and **2** is probably stabilised by electron-delocalisation extending into the $SiMe_3$ and aryl subtituents. We consider that the isolation and characterisation of the crystalline complexes **1** and **2** opens a new chapter in the increasingly important field of β-diketiminatometal chemistry, which we are continuing vigorously to pursue.

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Notes and references

‡ *Synthesis*: $YbCl_3$ (0.23 g, 0.82 mmol) was added to a stirred solution of KL (0.67 g, 1.65 mmol) in thf (100 ml). The yellow suspension was stirred for 24 h; Li (0.014 g, 1.98 mmol) at *ca.* 20 °C was added. The dark blue reaction mixture was stirred until the metal had dissolved, then solvent was evaporated and the residue was extracted by pentane (100 ml). The extract was concentrated to yield upon cooling dark violet crystals of **1** (0.56 g, 64%). Similarly, from $YbCl_3$ (2.28 g, 8.16 mmol), LiL′ (8.57 g, 16.32 mmol) and Li (0.17 g, 24.48 mmol) in thf (200 ml), followed by extraction of the thf-free solid with ether, were obtained dark blue crystals of **2** (6.11 g, 52%).

§ *Crystal data*: **1** $C_{50}H_{74}Li_2N_4O_2Si_4Yb$, M = 1062.41, triclinic, space group $P1$, a = 12.2107(6), b = 14.2913(9), c = 18.5158(10) Å, α = 70.479(3), β = 75.806(3), γ = 65.376(3)°, U = 2747.2(3) Å^3, Z = 2, D_c = 1.28 g cm^{-3}, μ(Mo-Kα, λ = 0.71073 Å) = 1.83 mm^{-1}, T = 173(2) K, 18996 reflections measured, 9627 unique (R_{int} = 0.066). Refinement on all F^2, final R_1 = 0.050 (for 7645 reflections with $I > 2\sigma(I)$), wR_2 = 0.110 (for all data).

2 $C_{74}H_{90}Li_2N_4O_2Si_4Yb\cdot C_4H_{10}O$, M = 1440.90, triclinic, space group $P\bar{1}$, a = 15.4776(6), b = 16.1498(9), c = 17.3031(10) Å, α = 63.695(2), β = 82.531(3), γ = 84.167(3)°, U = 3839.6(3) Å^3, Z = 2, D_c = 1.25 g cm^{-3}, μ(Mo-Kα, λ = 0.71073 Å) = 1.33 mm^{-1}, T = 173(2) K, 21885 reflections measured, 13492 unique (R_{int} = 0.062). Refinement on all F^2, final R_1 = 0.060 (for 10056 reflections with $I > 2\sigma(I)$), wR_2 = 0.125 (for all data). Program: SHELXL-97.[13]

CCDC reference numbers 183393 and 183394. See http://www.rsc.org/suppdata/cc/b2/b203321f/ for crystallographic data in CIF or other electronic format.

¶ *NMR Spectral data* for **1** (293 K, C_6D_6, 300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 49.7 MHz for ^{29}Si, 116.6 MHz for ^{7}Li) ^{1}H: δ 10.98 (t, *J* 7.26 Hz, 4 H, p-H^B of Ph), 9.96 (d, *J* 7.62 Hz, 8 H, o-H^A of Ph), 9.73 (d, *J* 7.69 Hz, 8 H, o-H^B of Ph), 9.53 (t, *J* 7.28 Hz, 4 H, p-H^A of Ph), 5.38 (t, *J* 7.55 Hz, 8 H, m-H^A of Ph), 5.07 (t, *J* 7.66 Hz, 8 H, m-H^B of Ph), 3.57 (br s, 8 H, OCH_2CH_2, thf), 1.22 (br.s., 8 H, OCH_2CH_2, thf), 0.40 (s, 18 H, $Si(CH_3)_3{}^A$), 0.23 (s, 18 H, $Si(CH_3)_3{}^B$), −1.92 (s, 2 H, CH). ^{13}C{^{1}H}: δ 213.28 (*ipso*-C^B of Ph), 206.96 (*ipso*-C^A of Ph), 206.22 (CH), 143.08 (m-CH^B of Ph), 141.14 (m-CH^A of Ph), 102.60 (p-CH^B of Ph), 100.47 (p-CH^A of Ph), 85.33 (o-CH^A of Ph), 82.60 (o-CH^B of Ph), 68.48 (br s, OCH_2CH_2, thf), 24.93 (br s, OCH_2CH_2, thf), −1.94 ($Si(CH_3)_3{}^A$), −4.78 ($Si(CH_3)_3{}^B$), −24.67 (NC(Ph^A)CH), −84.87 (NC(Ph^B)CH). ^{29}Si{^{1}H}: δ −1.15 (s, $SiMe_3{}^A$), −20.40 (s, $SiMe_3{}^B$). ^{7}Li{^{1}H}: δ 10.05 (br s, $\Delta\omega_{½}$ 21.68 Hz).

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