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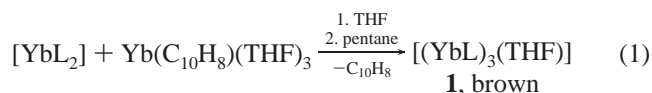
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Mono-, Di-, and Trianionic β -Diketiminato Ligands: A Computational Study and the Synthesis and Structure of $[(YbL)_3(THF)]$, $L = [N(SiMe_3)C(Ph)_2CH]$ Odile Eisenstein,^{*,†} Peter B. Hitchcock,[‡] Alexei V. Khvostov,[‡] Michael F. Lappert,^{*,‡} Laurent Maron,^{*,§} Lionel Perrin,[†] and Andrey V. Protchenko[‡]*LSDSMS (UMR 5636), Université Montpellier 2, 34095, Montpellier Cedex 5, France, The Chemistry Laboratory, University of Sussex, Brighton, BN1 9QJ, UK, and Laboratoire de Physique Quantique - IRSAMC (UMR 5626), Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France*

Received June 25, 2003; E-mail: m.f.lappert@sussex.ac.uk; eisenst@univ-montp2.fr; laurent.maron@irsamc.ups-tlse.fr

Although the +3 metal oxidation state is ubiquitous for complexes of the lanthanides (Ln), an increasing minority (classically Sm, Eu, Yb; and more recently La, Ce, Pr, Nd, Tm) are also found as Ln(II).¹ We now show that Yb clusters unusually also have a β -diketiminato ligand (generally L^-) of variable valency: L^- , L^{2-} , L^{3-} .

Reduction of the homoleptic Yb(II) β -diketiminato $[YbL_2]$ ($L = [N(SiMe_3)C(Ph)_2CH]^-$) with ytterbium-naphthalene gave the trinuclear complex $[(YbL)_3(THF)]$ (**1**), having three differently coordinated ligands, one of which is a "normal" terminal monoanionic β -diketiminato, while the other two are doubly reduced bridging trianionic ligands. In the vast majority of metal β -diketiminates, the ligand is monoanionic;² however, we have recently shown that $[YbL_2]$ with Li metal gave $[Yb\{\mu-L\}Li(THF)_2]_2$ (**2**) containing singly reduced dianionic ligands.³ To prepare a related homometallic Yb β -diketiminato, the highly reactive Yb-naphthalene complex⁴ was used as an alkali metal-free reducing agent. In THF solution, a deep blue compound, apparently a solvated Yb(II) mono- β -diketiminato $YbL(THF)_n$, was formed, but removing the solvent led to the mixed valence Yb(II)/Yb(III) trinuclear cluster **1** (eq 1).



The structure of **1** was determined by X-ray crystallography.⁵ The molecule consists of an $YbL(THF)$ moiety ($Yb3$ in Figure 1) η^5 -coordinated by one of the C_6H_5 rings of a tightly packed Yb_2L_2 cluster ($Yb1$ and $Yb2$). The geometric parameters in $YbL(THF)$ are very similar to those in the Yb(II) β -diketiminates $[YbL_2]$ ⁶ and $[YbL(\mu-I)(THF)_2]_2$,⁷ which suggests that the $Yb3$ atom is in the +2 oxidation state and the ligand is a "normal" monoanionic β -diketiminato L^- . Both ligands in Yb_2L_2 are bridging, and the changes in the C–N and C–C bond lengths, as compared to those in $YbL(THF)$, indicate that two-electron reduction of L^- had occurred with one negative charge delocalized on a C_6H_5 ring (Scheme 1). Apparently, coordination of Yb by one of the C_6H_5 substituents of a singly reduced ligand L^{2-} promotes further reduction of the ligand to L^{3-} . In the two C_6H_5 rings coordinated to $Yb3$ and $Yb1$, the C_{ipso} – C_{ortho} bonds are slightly longer and the exocyclic C_{ipso} –C bonds are shorter than those in the L^- of $YbL(THF)$. A similar C–C bond lengths pattern was found in a Ti-bound C_6H_5 ring of the trityl complex $[K(15\text{-crown-5})_2][Ti(CO)_4(\eta^5-C_6H_5CPh_2)]$.⁸

The $Yb2$ atom of Yb_2L_2 is connected to four N atoms with rather short Yb–N distances (2.215(5), 2.224(5), 2.265(5), and 2.431(5)

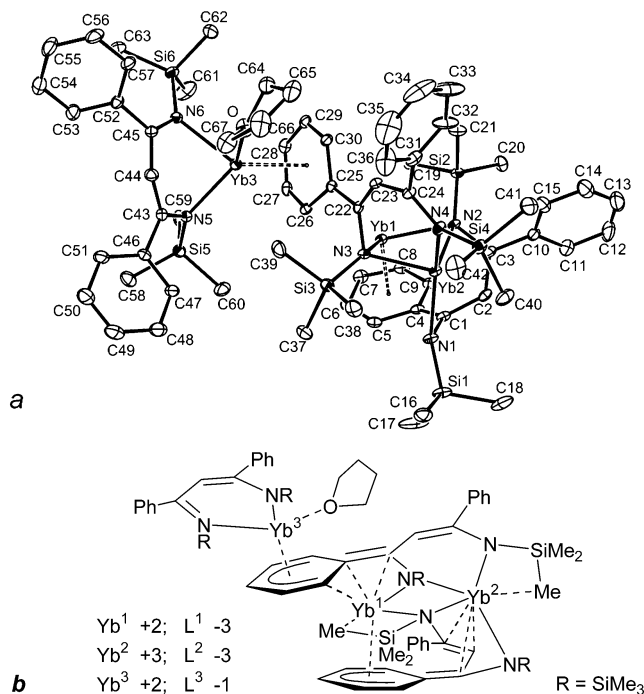
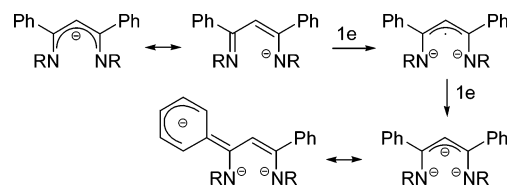
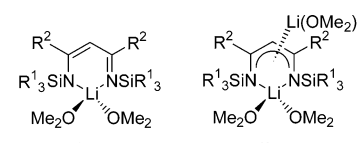


Figure 1. (a) ORTEP drawing of **1** showing 20% thermal ellipsoids; (b) schematic representation of **1** with metal and ligand charges.

Scheme 1. Consecutive Two-Electron Reduction of β -Diketiminato Ligand

Å); three of these are considerably shorter than the Yb(II)–N bonds in $[YbL_2]$ (2.396–2.423 Å)⁶ or Yb(II) bis(trimethylsilyl)amides (2.33–2.44 Å),⁹ but compare well with the Yb(III)–N bond lengths in Me_3Si -substituted amides (2.16–2.24 Å).¹⁰ The $Yb1$ atom of Yb_2L_2 is connected to two nitrogens of different β -diketiminato ligands with longer Yb–N bonds (2.427(5) and 2.480(5) Å) as well as in an η^6 -fashion to a negatively charged C_6H_5 ring with the Yb–C distances ranging from 2.566(6) to 2.801(7) Å (av. 2.709 Å), which is similar to Yb(II)–C(Cp - η^5) bond lengths (2.66–2.78 Å).¹¹ These observations lead us to conclude that the $Yb2$ atom in **1** is in the +3 state, while $Yb1$ and $Yb3$ retain the original +2 oxidation state. The presence of the highly paramagnetic Yb(III) in complex **1** is consistent with its very complicated ¹H NMR

[†] Université Montpellier 2.[‡] University of Sussex.[§] Université Paul Sabatier.

Table 1. HOMO and LUMO Energy (au) and Ph-to-L Torsion Angle (deg) for Model Compounds **3** and **4**


| compound | $E(\text{HOMO})$ | $E(\text{LUMO})$ | ω |
|---|------------------|------------------|----------|
| $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}, \mathbf{3a}$ | -0.16544 | -0.01325 | 72 |
| $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}, \mathbf{3b}$ | -0.17901 | -0.03406 | 59 |
| $\text{R}^1 = \text{H}, \text{R}^2 = \text{H}, \mathbf{3c}$ | -0.17874 | -0.01473 | |
| $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}, \mathbf{4b}$ | -0.09983 | -0.03813 | 37 |
| $\text{R}^1 = \text{H}, \text{R}^2 = \text{H}, \mathbf{4c}$ | -0.08877 | -0.00185 | |

spectrum, with signals in the 110 to -60 ppm range. An interesting feature of complex **1** is a very close Yb1...Yb2 contact (3.275 Å), which is the shortest Yb...Yb distance in an organometallic Yb compound.¹²

The assessment of the electron distribution in **1** is not feasible because of its size, but information can be gathered via computational studies of related systems. ONIOM (DFT-B3PW91/UHF) calculations¹³ with all atoms in the QM domain but Me of SiMe₃ and Ph on L were first carried out on [Yb{(μ-L)Li(THF)}₂] (**2**). THF is represented at the QM level by Me₂O. Geometry optimization of **2** gives geometry close to the solid-state structure.³ An NBO charge analysis (Yb, 1.73; L, -1.8) supports a Yb^{II}/L⁻² charge distribution. Additional proof of the capability for L⁻ to carry further negative charges is provided by calculations of L⁻ⁿ with the appropriate number of Li⁺ to preserve electroneutrality. Systems (**3a-c**) and (**4b,c**) in which L is expected to be L⁻¹ and L⁻², respectively, have been optimized using the DFT (B3PW91) method. **3a-c** are models of decreasing complexity for [Li{(N(SiMe₃)C(Ph))₂CH}(THF)₂] (**5**).¹⁷ **3a** agrees well with **5**. The short C-N bond distance (1.324 Å) in **3b** is close to the 1.321(10) Å for **5**; the longer C-N distance (1.392 Å) in **4b** is close to the average C-N distance of 1.413 Å in **2**. Another significant difference between **3a-b** and **4b** comes from the orientation of the phenyl rings. Proceeding from L⁻¹ to L⁻² decreases the torsion angle ω of the phenyl ring with the diketiminato skeleton (Table 1). These facts confirm that **2** contains L⁻².

To prove that L⁻³ is present in **1**, we calculated Li(OMe)₂-2-{YbL''}₂ (L'' = N(SiH₃)C(Ph)CHCHN(SiH₃)) **6**, a close model of **1**, in which Yb1 and Yb2 are represented with 10-e and 11-e ECPs, respectively.^{14a} The coordination around each Yb is well reproduced (Supporting Information), and the Yb1-Yb2 distance is too long by only 4%. The NBO charges are +1.7 and +2.5 for Yb1 and Yb2, respectively, and the total electron density on each L is around -2.5. These results are compatible with the assignments: Yb1(II), Yb2(III), and L⁻³.

The ability of L to be reduced is qualitatively rationalized by the HOMO and LUMO energies in **3** and **4** (Table 1). The LUMO of **3** is negative, especially for **3b**, and still remains negative for **4** even if the HOMO energy is raised because of the increase in local negative charge. The phenyl rings thus play a key role by extending the conjugation and also in providing the ability of L to accept additional charge.

Mixed valence Yb^{II}/Yb^{III} clusters, [Yb₄Cp*₆(μ-F)₄](PhMe)₂, [Yb^{II}-Cp*₂(μ-F)Yb^{III}Cp*₂] (Cp* = η⁵-C₅Me₅), and [Yb₂Ph₅(THF)₄], are already known,¹⁸ but novel features of the Yb^{II}/Yb^{III} cluster **1** are (i) the presence in **1** of a ligand of variable valency (L⁻/L⁻³), while **2** has two L⁻² ligands; (ii) a short Yb...Yb contact in **1**; and (iii) the synthesis of **1** from two Yb(II) reagents.

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Supporting Information Available: Experimental details, ¹H NMR spectroscopic data, X-ray crystallographic data for **1** (CIF), Cartesian coordinates of the optimized complexes (CC1), and NBO charge distribution in **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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