Redox chemistry of cerocene: the first heterobimetallic organolanthanide complex†

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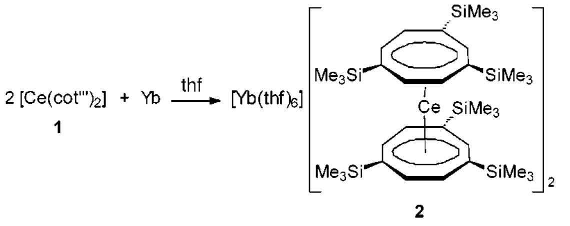
The first heterobimetallic organolanthanide complex containing two different rare earth elements, $[\mathrm{Yb(thf)_6}][\mathrm{Ce(cot''')_2}]_2$ 2 [cot‴ = η^8-1,3,6-$(\mathrm{Me_3Si})_3\mathrm{C_8H_5}$], has been prepared by reacting neutral $[\mathrm{Ce(cot''')_2}]$ with Yb metal in THF; the crystal structure of 2 consists of separated $[\mathrm{Yb(thf)_6}]^{2+}$ and $[\mathrm{Ce(cot''')_2}]^-$ ions.

Extensive electronic structural investigations have been carried out on neutral f-element sandwich complexes of the type $\mathrm{M(cot)_2}$ (M = lanthanide, actinide; cot = η^8-$\mathrm{C_8H_8}$).[1] The electronic structure of cerocene $[\mathrm{Ce(cot)_2}]$ has especially been the subject of much debate for many years.[2] It is now generally accepted that cerocene and its substituted derivatives are not genuine cerium(IV) organometallics. Sophisticated *ab initio* calculations as well as recent experimental data have revealed that the oxidation state of Ce in cerocene is 3+($4f^1$) and that cerocene is best formulated as a sandwich complex containing two coordinated $(\mathrm{cot})^{1.5-}$ ions.[3] Despite this ambiguity in the *formal* oxidation state of cerium in neutral cerocenes, these compounds should exhibit a rich redox chemistry and serve as valuable precursors for novel sandwich complexes of the lanthanide elements. While the parent cerocene is a pyrophoric material and not readily available,[4] the recently discovered polysilylated derivative $[\mathrm{Ce(cot''')_2}]$ **1** [cot‴ = η^8-1,3,6-$(\mathrm{Me_3Si})_3\mathrm{C_8H_5}$][5] appears to be an excellent candidate for such reactivity studies. We report here the use of **1** in the preparation of the first true heterobimetallic organolanthanide complex, *i.e.* the first organolanthanide derivative containing two different lanthanide elements in a single compound.[6]

Stirring a thf solution of **1** in the presence of an excess of $\mathrm{HgCl_2}$-activated Yb powder (< 40 mesh) at room temp. results in a gradual colour change from deep purple to bright green, while the suspended metal powder is partially consumed [eqn. (1)].



(1)

Filtration and crystallisation of the crude product from thf at −25 °C afforded the heterobimetallic ytterbium–cerium complex $[\mathrm{Yb(thf)_6}][\mathrm{Ce(cot''')_2}]_2$ **2** as bright green, highly air-sensitive crystals in 61% yield.‡ Obviously this product is the result of a redox reaction in which the neutral cerocene precursor **1** is reduced to the corresponding sandwich anion $[\mathrm{Ce(cot''')_2}]^-$. The concomitant formation of Yb^{2+} is clearly evidenced by the observation of a relatively sharp ($\nu_{1/2}$ = 15 Hz) ^{171}Yb NMR signal[7] at δ 256.1. As expected, the ^{29}Si NMR spectrum exhibits two signals corresponding to the $\mathrm{SiMe_3}$ substituents.

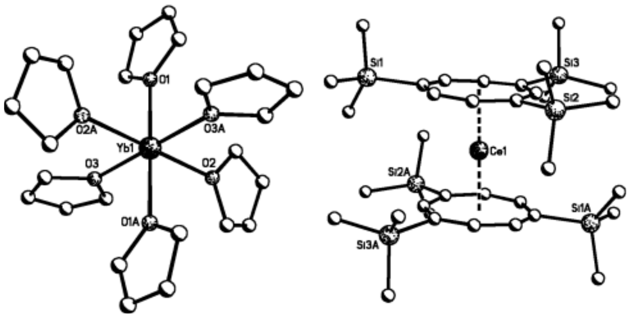


Fig. 1 Solid state structure of **1**; only the $[\mathrm{Yb(thf)_6}]^{2+}$ cation and one of the $[\mathrm{Ce(cot''')_2}]^-$ anions is depicted. Selected av. bond lengths (pm) and angles (°): Yb–O 237.8(5), Ce–$\mathrm{cot_{centre}}$ 205.3(14), Ce–$\mathrm{C_{cot}}$ 272(3), C–$\mathrm{C_{cot}}$ 141.4(11) [139.9(11)–143.6(11)], C–$\mathrm{SiMe_3}$ 188.1(9); O–Yb–O_{cis} 87.7(2)–92.3(2,) O–Yb–O_{trans} 180, $\mathrm{cot_{centre}}$–Ce–$\mathrm{cot_{centre}}$ 180.

X-Ray crystallography confirms the presence of the first organolanthanide complex containing two different rare earth elements in one compound (Fig. 1).§

The crystal structure of **2** consists of separated $[\mathrm{Yb(thf)_6}]^{2+}$ cations and $[\mathrm{Ce(cot''')_2}]^-$ anions. The mean distance between Ce and the ring centroids is 205.3(14) pm, which is in good agreement with the corresponding value in $[\mathrm{Li(thf)_4}][\mathrm{Ce(cot)_2}]$.[8] Quite surprisingly even the presence of six bulky trimethylsilyl substituents at the cyclooctatetraenyl rings does not lead to a significant elongation of these distances. At 237.8(5) the average Yb–O distance is practically identical to that in $[\mathrm{Yb(thf)_6}][\mathrm{CPh_3}]_2$ [239.0(7) pm].[9]

In the present study we have demonstrated that the readily available polysilylated cerocene derivative **1** displays an interesting redox chemistry and may thus serve as a promising precursor for the preparation of novel lanthanide organometallics.

Notes and references

‡ *Spectroscopic data* for **2**: IR (KBr): 1401w, 1307w, 1260vs, 1249vs, 1092s (sh), 1072vs, 1067vs, 1020s, 1000m (sh), 972m, 932m, 909w, 862s, 834vs, 806s (sh), 801vs, 771m, 748s, 719m, 686m, 638m, 549m, 513w, 496w, 462w $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 3.69 (m, 24 H, THF), 2.77 (br, $\nu_{1/2}$ 68 Hz, 16 H, H-4,5,7,8), 2.45 (s br, $\nu_{1/2}$ 43 Hz, 4 H, H-2), 2.19 (s, $\nu_{1/2}$ 10 Hz, 36 H, 6-$\mathrm{SiMe_3}$), 2.00 (s, $\nu_{1/2}$ 10 Hz, 72 H, 1,3-$\mathrm{SiMe_3}$), 1.84 (m, 24 H, thf). ^{29}Si NMR ($\mathrm{CD_3CN}$): δ −11.5 (s), −11.6 (s). ^{171}Yb NMR (thf–$\mathrm{C_6D_6}$): δ 256.1 (s br, $\nu_{1/2}$ 15 Hz).

§ *Crystal data:* $\mathrm{C_{96}H_{184}Ce_2O_7Si_{12}Yb}$. T = 153(2) K, M = 2240.79, triclinic, space group $P\bar{1}$ (no. 2), a = 1473.3(4), b = 1633.8(4), c = 1784.1(5) pm, α = 67.012(12), β = 77.86(2), γ = 75.792(13)°, V = 3.801(2) $\mathrm{nm^3}$, Z = 1, D_c = 0.979 Mg $\mathrm{m^{-3}}$, μ(Mo-Kα) = 1.328 $\mathrm{mm^{-1}}$. A total of 13513 reflections were collected of an oil coated crystal[10] in the θ-range 4.04–22.55°, 9940 of which were independent (R_{int} = 0.0328).

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† Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

Semiempirical absorption correction was applied using 423 ψ-scans.[11] The structure was solved by Patterson methods using SHELXS-93[12] and refined against F_o^2 using the full matrix least squares method with SHELXL-97.[13] An uncoordinated thf molecule was refined isotropically with a site occupation factor of 0.5. All other non-hydrogen atoms were refined anisotropically. The 1,3,6-tris(trimethylsilyl)cyclooctatetraendiide (cot‴) ligands were disordered and refined to a split occupancy of 44:56 in the case of the cot‴ coordinating Ce1 and 51:49 in the case of the cot‴ coordinating Ce2, employing 3975 bond length similarity restraints. $R1$ $[I > 2\sigma(I)] = 0.0622$, $wR2$ (all data) = 0.2049. CCDC 182/1383. See http://www.rsc.org/suppdata/cc/1999/1865/ for crystallographic files in .cif format.

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