

Synthesis and X-Ray Crystal Structure of Cyclooctatetraenyllanthanide Alkyl Complexes $[\text{Li}(\text{thf})_2\{\mu\text{-}(\eta^2\text{:}\eta^8\text{-C}_8\text{H}_8)\}\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ (Ln = Y, Sm, Lu; thf = tetrahydrofuran)

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The metathetic reaction $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})(\text{thf})_2]$ (Ln = Y, Sm, Lu) with $\text{LiCH}(\text{SiMe}_3)_2$ results in the formation of the cyclooctatetraenyllanthanide alkyl complexes $[\text{Li}(\text{thf})_2\{\mu\text{-}(\eta^2\text{:}\eta^8\text{-C}_8\text{H}_8)\}\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ (Ln = Y **1a**, Sm **1b**, Lu **1c**); **1b** has been structurally characterized by X-ray crystallography.

Since the preparation of uranocene $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$, the first cyclooctatetraenyl complex of an f block element, by Streitwieser and Müller-Westerhoff¹ in 1968 only a few other cyclooctatetraenyllanthanide compounds have been described, for example complexes with sandwich anions $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)_2]^{-2}$ and mixed sandwich compounds $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_4\text{R})]$ with unsubstituted³ and substituted⁴ cyclopenta-

dienyl ligands. Only three cyclooctatetraenyllanthanide alkyl and aryl complexes, $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\text{CH}_2\text{SiMe}_3)(\text{thf})]_5$ and $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2(\text{thf})]$ (Ln = Er, Lu)^{5,6} are known and only one of them has been characterised by an X-ray crystal structure. In this communication, we report the synthesis of a new type of anionic cyclooctatetraenyllanthanide bisalkyl complex $[\text{Li}(\text{thf})_2\{\mu\text{-}(\eta^2\text{:}\eta^8\text{-C}_8\text{H}_8)\}\text{Ln}\{\text{CH}(\text{Si}$

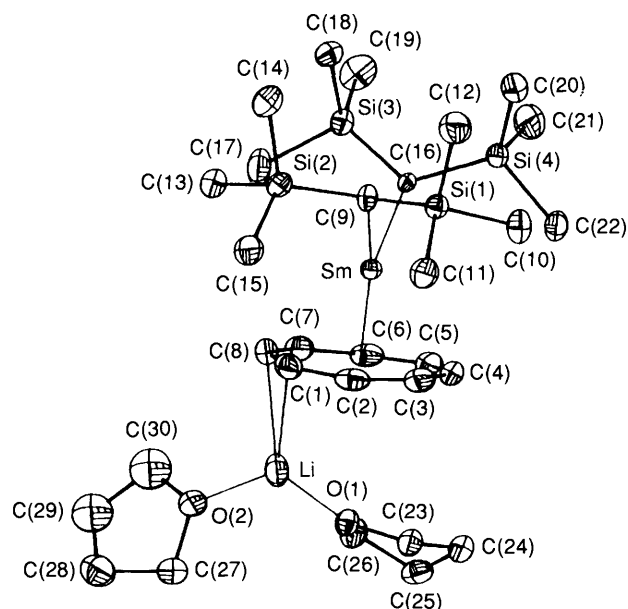
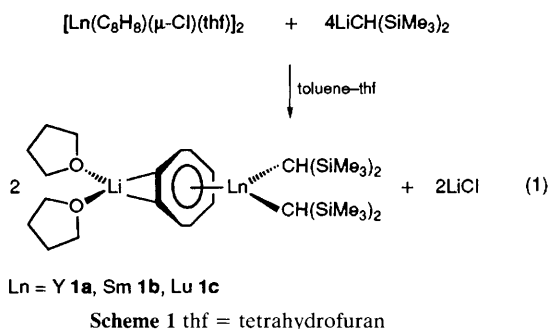


Fig. 1 Perspective ORTEP⁷ view with the adopted numbering scheme of $[\text{Li}(\text{thf})_2\{\mu\text{-}(\eta^2\text{-}\eta^8\text{-C}_8\text{H}_8)\}\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ **1b** (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): O(1)–Li 1.859(7), O(2)–Li 1.929(8); C₈H₈(centroid)–Sm–C(9) 133.1(1), C₈H₈(centroid)–Sm–C(16) 127.2(1), Sm–C(9)–Si(1) 116.9(2), Sm–C(9)–Si(2) 113.0(2), Sm–C(16)–Si(1) 115.1(1), Sm–C(16)–Si(4) 117.0(2), C(9)–Sm–C(16) 99.5(1), O(1)–Li–O(2) 106.9(4), O(1)–Li–C(1) 126.8(3), O(1)–Li–C(8) 127.9(3), O(2)–Li–C(1) 125.0(3), O(2)–Li–C(8) 104.4(3).

Me₃)₂]₂ (Ln = Y **1a**, Sm **1b**, Lu **1c**) and the characterisation of the Sm compound by an X-ray structural analysis.

Complexes **1a–c** were prepared by treatment of $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})(\text{thf})_2]$ (Ln = Y, Sm, Lu)^{2b,5} with LiCH(SiMe₃)₂ (1 : 4) in toluene–thf at –78 °C in reasonable yields (51% **1a**, 55% **1b**, 62% **1c**) and purity. The SiMe₃ groups in **1a–c** enhance their solubility in aromatic solvents such as toluene or benzene as well as in apolar solvents such as hexane. Colourless crystals of **1a** and **1c** as well as red crystals of the Sm derivative **1b** were obtained after cooling a concentrated hexane solution.[†] All three compounds decompose rapidly in

[†] NMR data for **1a**: ¹H NMR (C₆D₆, 25 °C): δ –1.55 [s, 2 H, CH(SiMe₃)₂], 0.48 (s, 36 H, SiMe₃), 1.22 (m, 8 H, thf), 2.85 (m, 8 H, thf), 6.57 (s, 8 H, C₈H₈); ¹³C NMR (C₆D₆, 25 °C): δ 4.9 [CH(SiMe₃)₂], 6.4 (SiMe₃), 25.2 and 68.1 (thf), 93.4 (C₈H₈). **1b**: ¹H NMR (C₆D₆, 25 °C): δ –0.71 (s, ν_{1/2} 6 Hz, 36 H, SiMe₃), 1.10 (m, 8 H, thf), 2.76 (m, 8 H, thf), 9.15 (s, ν_{1/2} 12 Hz, 8 H, C₈H₈), CH(SiMe₃)₂ not found; ¹³C NMR (C₆D₆, 25 °C): δ 1.5 [d, ¹J(¹H, ¹³C) 68 Hz, CH(SiMe₃)₂], 2.7 [q, ¹J(¹H, ¹³C) 23 Hz, SiMe₃], 24.9 and 67.4 [t, ¹J(¹H, ¹³C) 27 Hz, thf], 79.4 [d, ¹J(¹H, ¹³C) 29 Hz, C₈H₈]. **1c**: ¹H NMR (C₆D₆, 25 °C): δ –1.78 [s, 2 H, CH(SiMe₃)₂], 0.47 (s, 36 H, SiMe₃), 1.07 (m, 8 H, thf), 2.65 (m, 8 H, thf), 6.55 (s, 8 H, C₈H₈); ¹³C NMR (C₆D₆, 25 °C): δ 6.4 [CH(SiMe₃)₂], 6.6 (SiMe₃), 25.0 and 68.0 (thf), 92.5 (C₈H₈). Satisfactory elemental analyses were obtained for compounds **1a** (C, H, Y), **1b** (C, H, Sm) and **1c** (C, H, Lu).

the presence of air and moisture, but they are stable in an inert atmosphere with decomposition points >100 °C.

Neutral complexes $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)\{\text{CH}(\text{SiMe}_3)_2(\text{thf})\}]$ could not be isolated after using a 1 : 2 molar ratio of $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})(\text{thf})_2]$ and LiCH(SiMe₃)₂. Instead **1a** was formed as a consequence of the better steric and electronic saturation of the central lanthanide ion in **1a** compared to $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)\{\text{CH}(\text{SiMe}_3)_2\}(\text{thf})]$. If reaction (1) is carried out in thf, $[\text{Li}(\text{thf})_x][\text{Ln}(\eta^8\text{-C}_8\text{H}_8)_2]$ (Ln = Y **2a**, Sm **2b**, Lu **2c**) can be identified as a side product together with **1a–1c** by ¹H NMR spectroscopy,[‡] which is in accordance with a similar observation made by Wayda in the course of the reaction of $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})(\text{thf})_2]$ (Ln = La, Lu) with LiCH₂SiMe₃ in thf.⁵

The X-ray structural analysis of **1b**§ (Fig. 1) shows the samarium atom coordinated by two CH(SiMe₃)₂ groups and one η⁸-bonded cyclooctatetraenyl ring, and lithium which has two short contacts only to two carbon atoms of the cyclooctatetraenyl ligand. The Sm–C distances Sm–C(9) and Sm–C(16) [2.529(4) and 2.562(3) Å] are in good agreement with such in other organolanthanide compounds containing the CH(SiMe₃)₂ ligand, e.g. $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2]$ [*d*(La–C): 2.651(8) and 2.627(10) Å]¹¹ or $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2]$ [*d*(Ce–C): 2.508(6) and 2.556(5) Å]¹² taking into account the different size of the metal ions. The Sm–C₈H₈(centroid) distance is 1.969(1) Å [individual samarium carbon distances range from 2.643(4) up to 2.728(5) Å], which is significantly longer compared with other cyclooctatetraenyl-lanthanide complexes such as $[\text{Lu}(\eta^8\text{-C}_8\text{H}_8)(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2(\text{thf})]$ [*d*{(C₈H₈)–Lu}: 1.775 Å]⁶ or $[\text{Lu}(\eta^8\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\{\text{CH}_2(\text{C}_6\text{H}_5)\}_5)]$ [*d*{(C₈H₈)–Lu}: 1.645 Å],^{4c} even taking into account the difference in ionic radii from Sm to Lu of 0.043 Å¹³ and the increased coordination number of Sm. This can be explained by the fact that the cyclooctatetraenyl system is electrostatically attracted by both the samarium and the lithium ion. Similar elongations of lanthanide to cyclooctatetraenyl bonds have been observed in $[\text{K}(\text{diglyme})][\text{Ce}(\eta^8\text{-C}_8\text{H}_8)_2]$ ¹⁴ and $[\text{K}(\text{diglyme})][\text{Yb}(\eta^8\text{-C}_8\text{H}_8)_2]$.¹⁵ To our knowledge the X-ray structure of **1b** shows the first example of a cyclooctatetraenyl–lithium coordination. There are only two short contacts from the alkali metal to carbon atoms, Li–C(1) [2.384(8) Å] and Li–C(8) [2.395(8) Å]. The long distances Sm–C(9) and Sm–C(16) together with the almost equal angles Sm–C–Si [between 113.0(2) and 117.0(2)°] indicate a strong ionic character of the bonds between samarium and the CH(SiMe₃)₂ ligands.

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[‡] ¹H NMR data (²H₈thf, 25 °C) for **2a**: δ 5.71 (s); **2b**: δ 13.32 (s, ν_{1/2} 50 Hz), **2c**: δ 5.65 (s).

§ Crystal data for **1b**: C₃₀H₆₂LiO₂Si₄Sm, *M*_r = 724.45 g mol^{–1}, crystal size 0.28 × 0.18 × 0.15 mm³, monoclinic, space group *P*2₁/*c* with *a* = 10.274(1), *b* = 20.594(2), *c* = 18.210(2) Å, β = 103.67(1)°, *V* 3743.7(7) Å³, *Z* = 4, *D*_c = 1.29 g cm^{–3}; 8221 reflections (1 ≤ 2θ ≤ 53°, ω–2θ-scan, *T* 110 K) collected on an Enraf-Nonius CAD 4 diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data corrected for Lorentz polarisation and absorption (DIFABS,⁸ μ = 16.16 cm^{–1}, min./max. correction factors 0.916/1.052). Structure solved by Patterson methods (SHELXS-86)⁹ and refined by blocked least-squares (SHELX-76)¹⁰ to *R* = 0.030, *R*_w = 0.023, w^{–1} = σ²(*F*); 5193 reflections with *F*_o > 4σ(*F*_o); 559 parameters. H-atoms located from a difference Fourier map and refined isotropically.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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