

The first metal complexes containing the 1,4-cyclohexa-2,5-dienyl ligand (benzene 1,4-dianion); synthesis and structures of $[K(18\text{-crown-6})][Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\text{C}_6\text{H}_6)]$ ($Ln = \text{La}, \text{Ce}\dagger$)

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The reaction of $[Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_3]$ or $[(Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\mu\text{-Cl}))_2]$ ($Ln = \text{La}, \text{Ce}$) with K or C_8K and 18-crown-6 in benzene at ambient temperature yields the crystalline, deep red salts $[K(18\text{-crown-6})][Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\text{C}_6\text{H}_6)]$ ($Ln = \text{La}$ 1, Ce 2), formulated as containing the $Ln^{III}(1,4\text{-cyclohexa-2,5-dienyl})$ moiety, on the basis of their X-ray structures, spectra and hydrolysis to give cyclohexa-1,4-diene.

Recently we showed that the reaction of a tris(cyclopentadienyl)lanthanide(III) complex $[LnCp'_3]$ with Li or K in dimethoxyethane (dme) at ambient temperature gave in high yield the lanthanocene(III) methoxide $[(LnCp'_2(\mu\text{-OMe}))_2]$ [$Ln = \text{Ce}$, $Cp' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$ or $\eta^5\text{-C}_5\text{H}_3\text{Bu}^t\text{-1,3}$; $Ln = \text{Nd}$, $Cp' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$ or $[Nd\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\mu\text{-OMe})]_2Li(dme)]$.¹ It was postulated that the Ln^{II} complex $LnCp'_2$ was a transient intermediate.

We now report that treatment of $[Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_3]$ or $[(Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\mu\text{-Cl}))_2]$ ($Ln = \text{La}, \text{Ce}$) with a potassium mirror or C_8K and 18-crown-6 in benzene under similarly mild conditions afforded (Scheme 1) the tight ion pairs **1** ($Ln = \text{La}$) and **2** ($Ln = \text{Ce}$) containing the remarkable anions $[Ln\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\text{C}_6\text{H}_6)]^-$, which in principle can be regarded as either (benzene)lanthanocene(II) or (1,4-cyclohexa-2,5-dienyl)lanthanocene(III) anions. The latter representation is the more appropriate, in the light of X-ray crystallographic[‡] and UV–VIS and NMR spectral data,[§] as well as their hydrolysis products which included (GCMS) cyclohexa-1,4-diene and a smaller proportion of benzene.

X-Ray quality crystals (the cited yields refer to these) of **1** and **2** were obtained by concentrating the filtered solutions of the products. The crystalline, deep red salts **1** and **2** gave satisfactory microanalysis, were exceedingly air- and moisture-sensitive, and both decomposed above ca. 80 °C. The crystals were sparingly soluble in cold aromatic hydrocarbons or Et_2O but dissolved readily in tetrahydrofuran.

The X-ray structure of **1** is illustrated in Fig. 1, while Figs. 2 and 3 show simplified bonding patterns within the C_6H_6 ligand and the $Ln(\text{C}_6\text{H}_6)$ moiety, respectively. The C_6H_6 ligand adopts a boat conformation, the fold angle [*i.e.* the dihedral angle between the $\text{C}(28)\text{C}(23)\text{C}(24)\text{C}(25)$ and

$\text{C}(28)\text{C}(27)\text{C}(26)\text{C}(25)$ planes] being ca. 24° for both **1** and **2**. The average $Ln\text{--}C$ distances of ca. 2.63 Å (Fig. 3) to the 1,4-positions of the $[\text{C}_6\text{H}_6]^{2-}$ may be compared with the 2.548(1) Å for the $Ln\text{--}C_{\text{aryl}}$ distance in $[La(\eta^5\text{-C}_5\text{H}_5)_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}]$, the only aryllanthanocene complex for which X-ray data are available;² the latter has $La\text{--}C(\text{Cp})$ distances ranging from 2.785(4) to 2.926(5) Å similar to those found in **1**, Fig. 1. Likewise, the $K\text{--}C(\text{C}_6\text{H}_6)$ distances in **1** are comparable to those reported for $K[\text{Sn}(\text{CH}_2\text{Bu}^t)_3](\eta^6\text{-C}_6\text{H}_5\text{Me})$, 3.18–3.59 Å.³

The diene-diyll nature of some coordinated arene ligands has been discussed.⁴ For example in $[\text{TaCl}_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})(\eta^6\text{-C}_6\text{H}_5\text{Me})]$

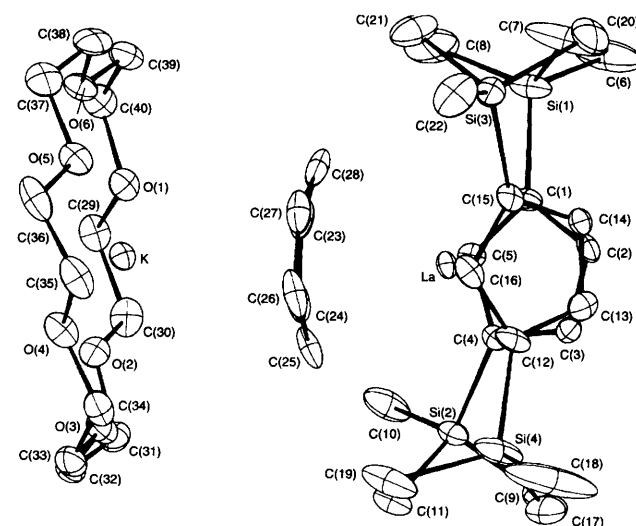


Fig. 1 CAMERON representation of the X-ray structure of **1**. Selected bond lengths (Å) and angles (°) for **1** (in parentheses for the isomorphous salt **2**) (see also Figs. 2 and 3): $Ln\text{--}C(1)$ to $Ln\text{--}C(5)$ [$C(1)$ shortest, $C(4)$ longest] 2.862(5)–2.943(5) [2.833(5)–2.909(5)]; $K\text{--}C(23)$ to $K\text{--}C(28)$ [$C(23)\text{--}C(24)$ shortest, $C(25)\text{--}C(28)$ longest] 3.097(6)–3.458(7) [3.087(5)–3.462(6)]; dihedral angle between $\text{C}(28)\text{C}(23)\text{C}(24)\text{C}(25)$ and $\text{C}(28)\text{C}(27)\text{C}(26)\text{C}(25)$ planes 23.6(4) [23.5(3)].

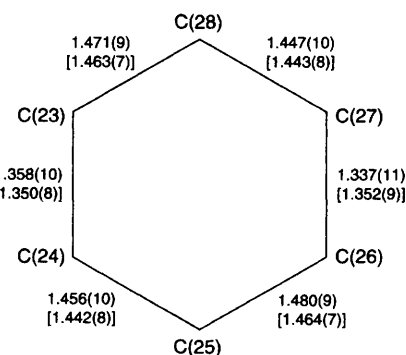
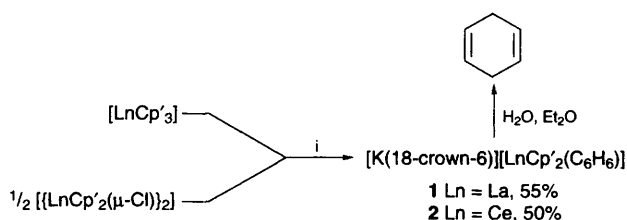


Fig. 2 C–C bond lengths (Å) in the C_6H_6 ligand for crystalline **1** [2]



Scheme 1 Reagents and conditions: i, K or 18-crown-6, C_6H_6 , ca 20 °C, $-\text{KX}$, $X = \text{Cp}'$ or Cl ; $\text{Cp}' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$

C₆Me₆), the tantalum distances to the 1,4-carbon atoms of the arene are *ca.* 0.265 Å shorter than those to the other four carbon atoms, the arene ring having a fold angle of 26.8°, and the mean C(2)–C(3) and C(5)–C(6) distances in the arene of 1.375 Å are shorter than the mean of 1.462 Å for the remaining C–C bonds. For the most recent paper on this topic, see [Nb(η⁶-C₆H₃Me₃-1,3,5)(μ-I)₂]₂.⁵ Bonding between an arene and a lanthanide metal has been reviewed.⁶ Particularly relevant to the present work are observations relating to the binding of naphthalene⁷ or anthracene⁸ to lutetium, which show similar modes of arene–Lu binding. For example, from Lu(η⁵-C₅H₅)Cl₂ and 2Na(C₁₀H₈) in dme there was obtained the crystallographically characterised, diamagnetic [Lu(η⁵-C₅H₅)(C₁₀H₈)(dme)], which upon hydrolysis yielded 1,4- and 1,2-dihydronaphthalene.⁷

The reaction pathway leading to compounds **1** or **2** probably involves an initially formed (from C₆H₆, K and 18-crown-6) benzene radical anion or [C₆H₆]²⁻. If the former, then the 4f metal intermediate would be Ln^{II}{η⁵-C₅H₃(SiMe₃)₂-1,3}₂ [obtained by X[•] loss following an SET transfer from K or [C₆H₆]⁻ to Ln^{III}{η⁵-C₅H₃(SiMe₃)₂-1,3}₂X [X = Cl, {η⁵-C₅H₃(SiMe₃)₂-1,3} A]; while for the latter, the [C₆H₆]²⁻ would simply behave as a nucleophile, displacing X⁻ from A.

Complexes **1** and **2** showed UV–VIS absorption bands rather similar to those observed for solutions of K in benzene of (i) perhydridibenzo-18-crown-6 (λ_{max} 300, 435 nm)^{9a} or dme (λ_{max} 285, 435 nm),^{9b} attributed to benzene anion. X-Ray crystallographic evidence is available for the existence both of an arene dianion and a radical anion; thus, from C₆H₂(SiMe₃)₄-1,2,4,5 and 2Li or Na in dme, there was obtained the crystalline, dark brown [Li(dme)]₂[η⁶-C₆H₂(SiMe₃)₄-1,2,4,5]⁴ or the dark red, solvent-separated ion pair [Na(dme)]₃[C₆H₂(SiMe₃)₄-1,2,4,5]⁵. Compound **4** had a nearly planar C₆ ring with twelve nearly equivalent Li–C distances of 2.366 Å, while **5** was shown to have a slightly distorted C₆ unit. In **4**, the C(1)–C(2) and C(4)–C(5) bonds were longer (mean 1.555 Å) than the remaining C–C bonds, mean 1.406 Å.¹⁰ In **5**, the C–C bond distances ranged from 1.401(4) to 1.466(4) Å.¹¹ Hydrolysis of **4** yielded mainly 1,3,4,6-tetrakis(trimethylsilyl)cyclohexa-1,4-diene.¹⁰ It is interesting that the C–C distances in **1** and **2** show a quite different pattern of electron localisation (Fig. 2) for the C₆ skeleton than that found in **4**.

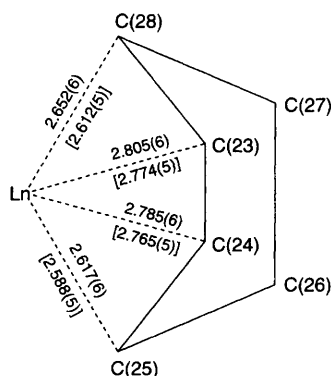


Fig. 3 Ln–C bond lengths (Å) in the Ln–C₆H₆ moiety for crystalline **1** [**2**]; Ln–C(27) 2.811(6) [2.787(5)], Ln–C(26) 2.794(6) [2.784(5)] Å

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Footnotes

† No reprints available.

‡ *Crystal data* for **1** [2·0.5C₆H₆]: C₄₃H₇₅KLaO₆Si₄ [C₄₃H₇₅CeKO₆Si₄], *M* = 978.4 [979.6], *T* = 173(2) K, monoclinic, space group *P*2₁/*n* (non-standard no. 14); *a* = 14.236(4) [14.185(10)], *b* = 16.580(5) [16.544(3)], *c* = 22.567(9) [22.592(7)] Å, β = 106.26(3) [106.09(4)]°, *U* = 5114(3) [5094(4)] Å³, *Z* = 4, *D*_c = 1.27 [1.28] g cm⁻³, μ = 1.05 [1.11] mm⁻¹, *F*(000) = 2052 [2056], crystal size 0.35 × 0.30 × 0.20 [0.40 × 0.40 × 0.30] mm. For **1**, a total of 12311 unique reflections with θ = 2–28°, were collected. Reflections with *I* > 2σ(*I*) 8090, *R* [for *I* > 2σ(*I*)] 0.058. For **2**, a total of 8936 unique reflections with θ = 2–25° was collected. Reflections with *I* > 2σ(*I*) 6718, *R* [for *I* > 2σ(*I*)] 0.044. An Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα radiation was used (λ = 0.71073 Å). Data were corrected for Lorentz and polarisation effects and for absorption using psi-scan data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/181.

§ *Spectroscopic data*: the ¹H NMR spectra in C₆D₆ showed, for both **1** and **2**, no peaks attributed to the 1,4-cyclohexa-2,5-dienyl moiety probably because of an exchange with the deuteriated benzene. Moreover the anionic nature of the lanthanocenate(III) moiety have affected the positions of the cyclopentadienyl protons; their chemical shifts were considerably different from those of the starting material. Due to the low solubility in cold C₆D₆, the NMR spectra were run at 333 K. ¹H (300 MHz) of **1**, δ 7.24 (d, 4 H, ⁴*J* 1.9 Hz), 5.14 (t, 2 H, ⁴*J* 2.0 Hz), 3.04 (s, 24 H), 0.46 (s, 36 H) [*cf.* the ¹H NMR spectral chemical shifts for [La{η⁵-C₅H₃(SiMe₃)₂-1,3}₃]: δ 6.81 (d, 6 H, ⁴*J* 1.9 Hz), 6.87 (t, 3 H, ⁴*J* 1.9 Hz), 0.32 (s, 54 H); ¹H NMR (300 MHz) of **2**, δ 27.14 (br, 4 H), 17.28 (br, 2 H), 2.84 (s, 24 H), –4.56 (s, 36 H). UV–VIS (benzene, λ_{max}/nm, 293 K) for **1** [**2**] 486, 338 (sh) 279 [461, 340 (sh) 278]. The IR spectra in Nujol for **1** and **2** were identical and showed the following ν_{max} bands: 1554w, 1351m, 1242m, 1113vs, 1077s, 963m, 831s cm⁻¹.

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