The first metal complexes containing the 1,4-cyclohexa-2,5-dienyl ligand (benzene 1,4-dianion); synthesis and structures of $[K(18\text{-crown-}6)][Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(C_6H_6)]$ (Ln = La, Ce)†

M. Cristina Cassani, Yurii K. Gun'ko, Peter B. Hitchcock and Michael F. Lappert
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

The reaction of $[Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ or $[(Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}Cl))_2]$ (Ln = La, Ce) with K or C_8K and 18-crown-6 in benzene at ambient temperature yields the crystalline, deep red salts $[K(18\text{-crown-}6)][Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(C_6H_6)]$ (Ln = La 1, Ce 2), formulated as containing the Ln^{III}(1,4-cyclohexa-2,5-dienyl) moiety, on the basis of their X-ray structures, spectra and hydrolysis to give cyclohexa-1,4-diene.

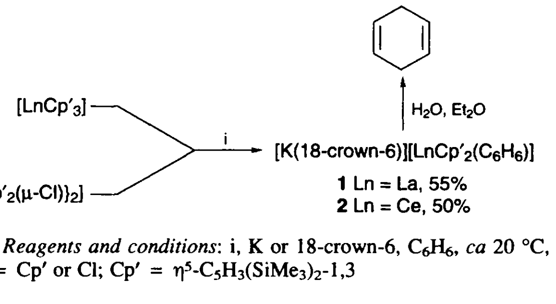
Recently we showed that the reaction of a tris(cyclopentadienyl)lanthanide(III) complex $[LnCp'_3]$ with Li or K in dimethoxyethane (dme) at ambient temperature gave in high yield the lanthanocene(III) methoxide $[\{LnCp'_2(\mu\text{-}OMe)\}_2]$ [Ln = Ce, Cp′ = $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ or $\eta^5\text{-}C_5H_3Bu^t{}_2\text{-}1,3$; Ln = Nd, Cp′ = $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$] or $[Nd\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}OMe)\}_2Li(dme)]$.[1] It was postulated that the Ln^{II} complex $LnCp'_2$ was a transient intermediate.

We now report that treatment of $[Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ or $[(Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}Cl))_2]$ (Ln = La, 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 = La) and **2** (Ln = Ce) containing the remarkable anions $[Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(C_6H_6)]^-$, which in principle can be regarded as either (benzene)lanthanocenate(II) or (1,4-cyclohexa-2,5-dienyl)lanthanocenate(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 $Ln(C_6H_6)$ moiety, respectively. The C_6H_6 ligand adopts a boat conformation, the fold angle [*i.e.* the dihedral angle between the C(28)C(23)C(24)C(25) and C(28)C(27)C(26)C(25) planes] being *ca.* 24° for both **1** and **2**. The average La–C distances of *ca.* 2.63 Å (Fig. 3) to the 1,4-positions of the $[C_6H_6]^{2-}$ may be compared with the 2.548(1) Å for the La–C_{aryl} distance in $[La(\eta^5\text{-}C_5H_5)_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, the only aryllanthanocene complex for which X-ray data are available;[2] the latter has La–C(Cp) distances ranging from 2.785(4) to 2.926(5) Å similar to those found in **1**, Fig. 1. Likewise, the K–C(C_6H_6) distances in **1** are comparable to those reported for $K\{Sn(CH_2Bu^t)_3\}(\eta^6\text{-}C_6H_5Me)$, 3.18–3.59 Å.[3]

The diene-diyl nature of some coordinated arene ligands has been discussed.[4] For example in $[TaCl_2(OC_6H_3Pr^i{}_2\text{-}2,6)(\eta^6\text{-}$



Scheme 1 *Reagents and conditions*: i, K or 18-crown-6, C_6H_6, *ca* 20 °C, $-KX$, X = Cp′ or Cl; Cp′ = $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$

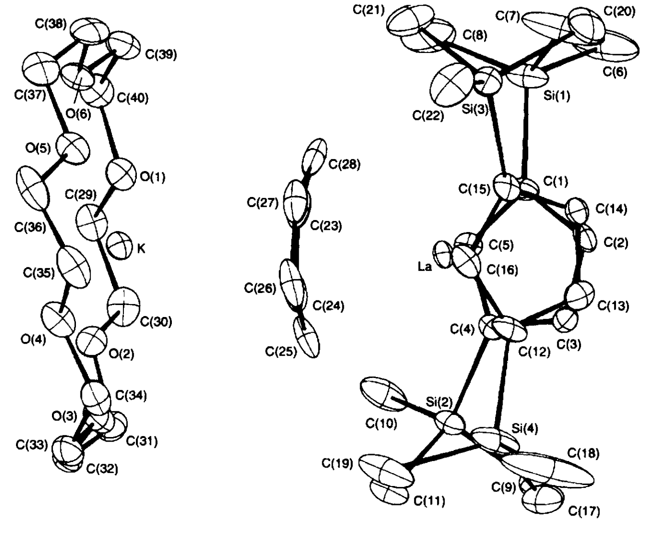


Fig. 1 CAMERON representation of the X-ray structure of **1**. Selected bond lengths (Å) and angles (°) for **1** (in parentheses for the isomorphous salt **2**) (see also Figs. 2 and 3): Ln–C(1) to Ln–C(5) [C(1) shortest, C(4) longest] 2.862(5)–2.943(5) [2.833(5)–2.909(5)]; K–C(23) to K–C(28) [C(23)–C(24)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

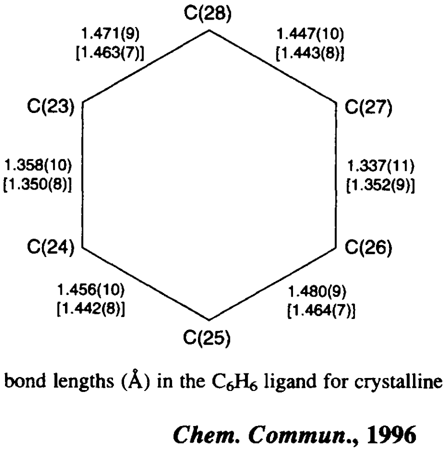


Fig. 2 C–C bond lengths (Å) in the C_6H_6 ligand for crystalline **1** [**2**]

$C_6Me_6)]$, 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 $[\{Nb(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\mu\text{-}I)_2\}_2]$.[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 naphthalene[7] or anthracene[8] to lutetium, which show similar modes of arene–Lu binding. For example, from $Lu(\eta^5\text{-}C_5H_5)Cl_2$ and $2Na(C_{10}H_8)$ in dme there was obtained the crystallographically characterised, diamagnetic $[Lu(\eta^5\text{-}C_5H_5)(C_{10}H_8)(dme)]$, 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 C_6H_6, K and 18-crown-6) benzene radical anion or $[C_6H_6]^{2-}$. If the former, then the 4f metal intermediate would be $Ln^{II}\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2$ [obtained by X$^\bullet$ loss following an SET transfer from K or $[C_6H_6]^-$ to $Ln^{III}\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X$ [X = Cl, $\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}$ **A**]; while for the latter, the $[C_6H_6]^{2-}$ 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*) perhydrodibenzo-18-crown-6 (λ_{max} 300, 435 nm)[9*a*] or dme (λ_{max} 285, 435 nm),[9*b*] attributed to benzene anion. X-Ray crystallographic evidence is available for the existence both of an arene dianion and a radical anion; thus, from $C_6H_2(SiMe_3)_4$-1,2,4,5 and 2Li or Na in dme, there was obtained the crystalline, dark brown $[Li(dme)]_2[\eta^6\text{-}C_6H_2(SiMe_3)_4\text{-}1,2,4,5]$ **4**[10] or the dark red, solvent-separated ion pair $[Na(dme)_3][C_6H_2(SiMe_3)_4\text{-}1,2,4,5]$ **5**.[11] Compound **4** had a nearly planar C_6 ring with twelve nearly equivalent Li–C distances of 2.366 Å, while **5** was shown to have a slightly distorted C_6 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 C_6 skeleton than that found in **4**.

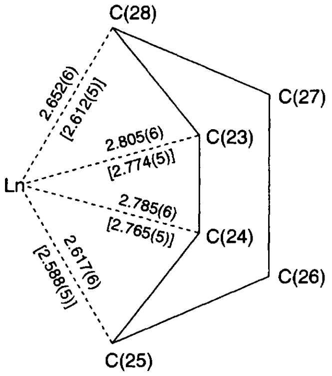


Fig. 3 Ln–C bond lengths (Å) in the Ln–C_6H_6 moiety for crystalline **1** [**2**]; Ln–C(27) 2.811(6) [2.787(5)], Ln–C(26) 2.794(6) [2.784(5)] Å

We thank the Royal Society (Yu. K. G) and the European Community (M. C. C.) for the provision of fellowships and EPSRC for other support.

Footnotes

† No reprints available.

‡ *Crystal data* for **1** [**2**·$0.5C_6H_6$]: $C_{43}H_{75}KLaO_6Si_4$ [$C_{43}H_{75}CeKO_6Si_4$], M = 978.4 [979.6], T = 173(2) K, monoclinic, space group $P2_1/n$ (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)] Å^3, 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 $I > 2\sigma(I)$ 8090, R [for $I > 2\sigma(I)$] 0.058. For **2**, a total of 8936 unique reflections with θ = 2–25° was collected. Reflections with $I > 2\sigma(I)$ 6718, R [for $I > 2\sigma(I)$] 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 C_6D_6 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 C_6D_6, the NMR spectra were run at 333 K. ^1H (300 MHz) of **1**, δ 7.24 (d, 4 H, ^4J 1.9 Hz), 5.14 (t, 2 H, ^4J 2.0 Hz), 3.04 (s, 24 H), 0.46 (s, 36 H) [*cf.* the ^1H NMR spectral chemical shifts for $[La\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$: δ 6.81 (d, 6 H, ^4J 1.9 Hz), 6.87 (t, 3 H, ^4J 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}.

References

1 Yu. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Organomet. Chem*, 1995, **499**, 213.
2 M. P. Hogerheide, J. Boersma, A. L. Spek and G. van Koten, *Organometallics*, 1996, **15**, 1505.
3 P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1993, 554.
4 D. J. Arney, P. A. Wexler and D. E. Wigley, *Organometallics*, 1990, **9**, 1282 and references therein.
5 M. Yoon, J. Lin, V. G. Young and G. J. Miller, *J. Organomet. Chem.*, 1996, **507**, 31.
6 G. B. Deacon and Q. Shen, *J. Organomet. Chem.*, 1996, **511**, 1.
7 A. V. Protchenko, L. N. Zakharov, M. N. Bochkarev and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **447**, 209.
8 D. M. Roitershtein, L. F. Rybakova, E. S. Petrov, A. M. Ellern, M. Yu. Antipin and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **460**, 39.
9 (*a*) B. Kaempf, S. Raynal, A. Collet, F. Schué, S. Boileau and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 611; (*b*) C. L. Gardner, *J. Chem. Phys.*, 1966, **45**, 572.
10 A. Sekiguchi, K. Ebata, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1991, **113**, 7081.
11 H. Bock, M. Ansari, N. Nagel, and Z. Havlas, *J. Organomet. Chem.*, 1995, **499**, 63.

Received, 13th May 1996; Com. 6/03823G