The First Example of a Crystalline Subvalent Organolanthanum Complex: [K([18]crown-6)-(η^2-C_6H_6)$_2$][(LaCp$^{tt}_2$)$_2$(μ-η^6:η^6-C_6H_6)]•2C_6H_6 (Cp^{tt} = η^5-$C_5H_3Bu^t_2$-1,3)

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A major focus of our recent researches on 4f (Ln) chemistry relates to the redox behavior of various tricyclopentadienylmetal(III) complexes [LnCp$^x_3$] [Cp^x = η^5-$C_5H_3(SiMe_3)_2$-1,3 (≡ Cp″) or η^5-$C_5H_3(CMe_3)_2$-1,3 (≡ Cp^{tt})]. For the system [LaCp″$_3$] **1** with an excess of potassium, we have shown that the nature of the product is dependent on the reaction medium, Scheme 1.[2,3] Features of particular interest were (i) the ready cleavage of the C−O bond of 1,2-dimethoxyethane (DME) yielding the colorless [{LaCp″$_2$(μ-OMe)}$_2$],[2] (ii) the intermediacy in this reaction of the blue temperature-dependent equilibrium mixture containing the first unequivocally (EPR)-characterized organolanthanide(II) compounds {other than those of Sm, Eu or Yb, or [TmI$_2$(DME)$_3$];[4] cf. also Ce[5a] and Nd[5b]} **2** and **3**,[2] (iii) the dark red, X-ray-authenticated salt [K([18]crown-6)][LaCp″$_2$(C_6H_6)] **4**, containing the (1,4-cyclohexa-2,5-dienyl)bis{η^5-1,3-bis(trimethylsilyl)cyclopentadienyl}-lanthanate(III) ion (the first example of a ligated benzenide-1,4-dianion),[3] and (iv) the measurement of the $La^{3+} \rightarrow La^{2+}$ reduction potential ($E_{1/2}$ = −2.8 V) by cyclic voltammetry of **1** in tetrahydrofuran (THF) at 25 °C.[2] We now report on the related [LaCp$^{tt}_3$] **5**−K system, which inter alia has provided the first example of a crystalline (X-ray) subvalent lanthanum complex **6**, additionally notable for containing a planar bridging C_6H_6 ligand, and on further aspects of the [LaCp″$_3$] **1**−K system.

Treatment of [LaCp″$_3$] **1** (2 mol) with K (ca. 3 mol) and [18]-crown-6 (3 mol) in benzene at ambient temperature gave a dark green precipitate **7**, as well as the benzene-soluble [K([18]crown-6][Cp″]. Compound **7** was also slowly (over 7 d) obtained (Scheme 1) from **4** in benzene at 70 °C. UV−vis, EPR, and NMR spectra of **7** in DME, as well as its mass spectrum, have been recorded,[6] from which we conclude that **7** contains La(II). Suitable crystals for X-ray diffraction were not obtained; attention was therefore switched to the [LaCp$^{tt}_3$]−K system, with salient data summarized in Scheme 2.

Cyclic voltammetry on [LaCp$^{tt}_3$] **5** in THF at 25 °C showed that **5** is significantly more resistant to reduction than [LaCp″$_3$] **1** by ca. 0.3 V,[7] consistent with the notion that the pendant $SiMe_3$ groups of Cp″ are able to stabilize a metal-centered La(II) anion, whereas Bu^t groups have the reverse effect.

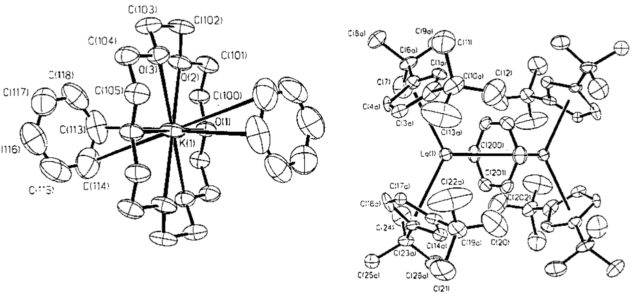

Figure 1. Molecular structure of [K([18]crown-6)(η^2-C_6H_6)$_2$][(LaCp$^{tt}_2$)$_2$-(μ-η^6:η^6-C_6H_6)] **6** showing 50% probability ellipsoids and atom labeling. Selected bond lengths (Å) in the cation: K(1)−O(2) 2.748(5), K(1)−O(1) 2.824(4), K(1)−O(3) 2.847(4); K−C(113) 3.270(10), K−C(114) 3.495(11).

When **5** was treated with an excess of K in DME at −40 °C, the dark violet-blue solution **8**, indicative of a lanthanum(II) species,[2] was much more transient than that of **2**/**3** in the [LaCp″$_3$] system; at ambient temperature **8** instantly reverted to the colorless [{LaCp$^{tt}_2$(μ-OMe)}$_2$] **9**.[8]

The reaction of **5** with an excess of K and [18]crown-6 in benzene at 20 °C was monitored spectroscopically;[9] initially a dark red solution **10** was obtained, with characteristics similar to those of **4**; **10** gradually became dark green and slowly (1 week) deposited dark green, extremely air- and light-sensitive single crystals of the X-ray-characterized salt **6**.[10]

The molecular structure of crystalline **6** shows the centrosymmetric anion (Figure 1) to be dinuclear, with two η^5-Cp$_2^{tt}$La moieties bridged by a planar η^6-C_6H_6 ligand. There is disorder of the substituted cyclopentadienyl ligands,[11] a common feature in this type of compound; hence, dimensions involving the disordered [Cp^{tt}]$^-$ ligands must be treated with caution. From Figure 1 it is evident that the planarity of the η^6-C_6H_6 ligand is not a consequence of disorder. The bridging η^6-C_6H_6 is regarded as a benzenide anion **6a**, having C−C distances which do not differ significantly; this contrasts with the situation for the benzenide dianion **4a** of **4**, (the atom labeling for **4a** corresponds to that in the literature[3]) showing its 1,4-diene π-localization.[3]

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[2] Cassani, M. C.; Lappert, M. F.; Laschi, F. *Chem. Commun.* **1997**, 1563.

[3] Cassani, M. C.; Gun'ko, Yu. K.; Hitchcock, P. B.; Lappert, M. F.; *Chem. Commun.* **1996**, 1987.

[4] Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 133.

[5] (a) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* **1976**, *113*, 321. (b) Wedler, M.; Recknagel, A.; Edelmann, F. T. *J. Organomet Chem.* **1990**, *395*, C26.

[6] Data on **7** (see also Supporting Information). ^{1}H NMR spectrum (THF-d_8, 298 K): δ 14.0 (br, $\Delta\nu_{1/2}$ 200 Hz, 2H), 1.62 (br, $\Delta\nu_{1/2}$ 30 Hz, 36H); (THF-d_8, 323 K): δ 13.0 (br, $\Delta\nu_{1/2}$ 140 Hz, 2H), 4.00 (br, $\Delta\nu_{1/2}$ 60 Hz, 4H), 1.43 (br, $\Delta\nu_{1/2}$ 25 Hz, 36H). UV−vis (DME, 298 K): λ_{max} 571, 678 (sh) nm [cf. La^{2+} in CaF$_2$ (showing a very broad band centered at ca. 550 nm, with onset of absorption at ca. 700 nm: McClure, D. S.; Kiss, Z. J.; *J. Chem. Phys.* **1963**, *39*, 3251)]. EI-MS: m/z 557 ([LaCp″$_2$]$^+$, 43%), 485 ([LaCp″$_2$ − 72]$^+$, 45%) and 73 ([SiMe$_3$]$^+$, 100%).

[7] The cyclic voltammograms of [LaCp$^{tt}_3$] **5** in THF at 25 °C with 0.2 mol dm^{-1} [NBu$_4$][PF$_6$] as supporting electrolyte at a vitreous carbon working electrode (scan rate 50 mV s^{-1}) showed a reversible 1-electron reduction, $E_{1/2}$ ($La^{3+} \rightarrow La^{2+}$) = −3.1 V [relative to the Fc$^+$/Fc couple; ferrocene (Fc) as internal standard]. Experiments were replicated at scan rates of 10, 25, 75, 100, 125, 175, 300, and 500 mV s^{-1}.

[8] Yield of crystalline **9**, 54%. Anal. calcd (%) for **9**: C, 61.8; H, 8.65. Found: C, 60.6; H, 8.33. Selected spectroscopic data for **9**: ^{1}H NMR (PhMe-d_8, 298 K): δ 6.21 (t, J = 2.5 Hz, 2H), 6.17 (d, J = 2.5 Hz, 4H), 3.42 (s, 3H), 1.33 (s, 36H). DEPT135 ^{13}C NMR (tol-d_8, 298 K): δ 140.8 (C_q), 110.0 (CH), 108.0 (CH), 54.5 (OCH$_3$), 33.2 (CCH$_3$) 33.0 (CCH$_3$).

[9] Treatment of **5** (0.28 mmol) with K (0.8 mmol) and [18]-crown-6 (0.64 mmol) in C_6H_6 (2.5 mL) at 20 °C gave the dark red **10** [^{1}H NMR (C_6D_6, 298K) δ 6.88 (d, J = 2.5 Hz, 4H), 4.86 (t, J = 2.5 Hz, 2H), 3.1 (s, 24H), 1.52 (s, 36H) [cf. ^{1}H NMR for [LaCp$^{tt}_3$] **5**: δ 6.27 (d, J = 2.6 Hz, 6H), 6.19 (t, J = 2.6 Hz, 3H), 1.33 (s, 54H)]. After ca. 1 h at 20 °C the ^{1}H NMR spectral signals began to decrease, and they were replaced by a broad resonance at δ 9.0 ($\Delta\nu_{1/2}$ 200 Hz). Dark green crystals of **6** (0.025 mmol) were precipitated after a week at 4 °C. The EPR spectrum of the green mixture prior to precipitation was recorded (see Supporting Information).

[10] Crystal data for **6**·2C_6H_6: $C_{94}H_{138}KLa_2O_6$, dark green, M = 1680.96, T = 180 K, triclinic, space group $P\bar{1}$; a = 11.955(5) Å, b = 13.775(5) Å, c = 14.311(5) Å, α = 89.99(2)°, β = 85.479(13)°, γ = 83.67(2)°, V = 2335(2) Å^3, Z = 1, D_c = 1.195 g cm^{-3}, μ (Mo Kα) = 0.994 mm^{-1}, F(000) = 883, crystal size 0.4 × 0.3 × 0.2 mm. A total of 12116 unique reflections with θ = 1.43°−25.00°, was collected. Reflections with $I > 2\sigma(I)$ 7370, R [for $I > 2\sigma(I)$] 0.0504. A Siemens 3-circle diffractometer equipped with a SMART CCD area detector with graphite-monochromated Mo Kα radiation was used (λ = 0.71073 Å), GOF(F^2) = 1.020.

[11] The disorder in the cyclopentadienyl rings, C(1)−C(5) and C(14)−C(18) is such that each ring has an alternative component (A and B), each having 50% occupancy; see Supporting Information.

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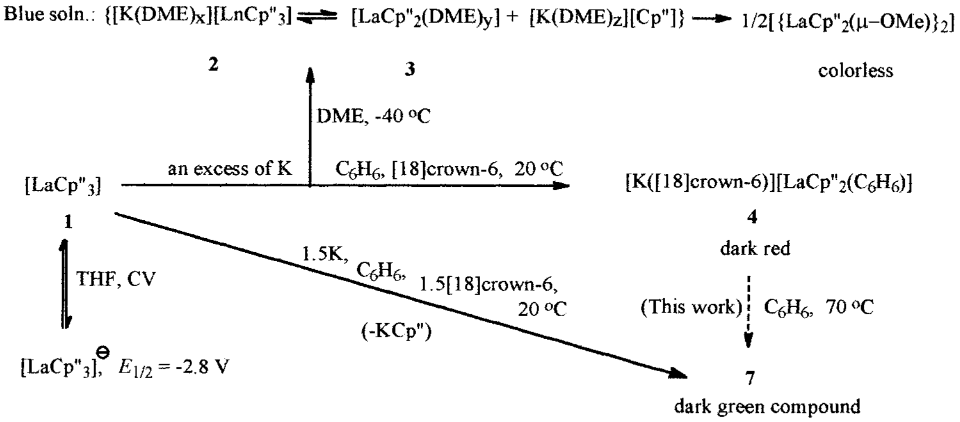
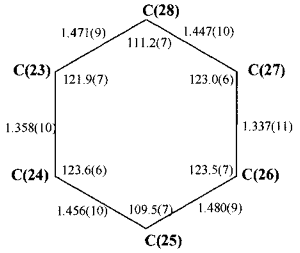
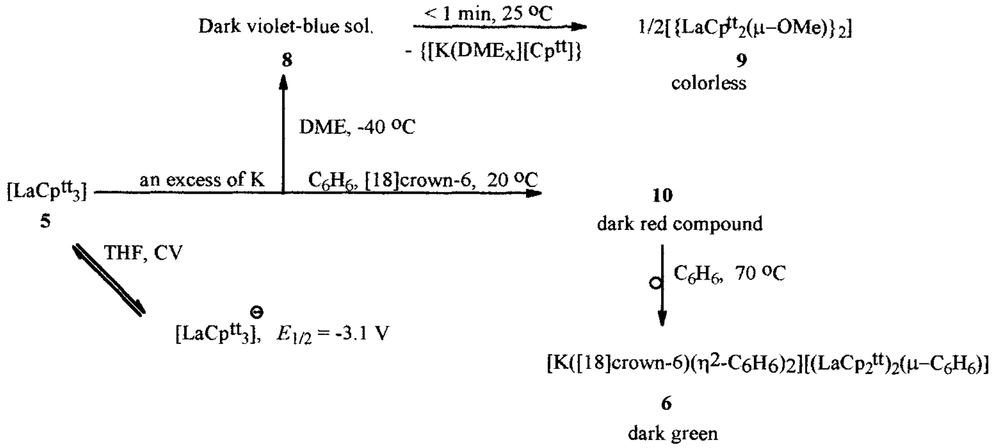
Scheme 1

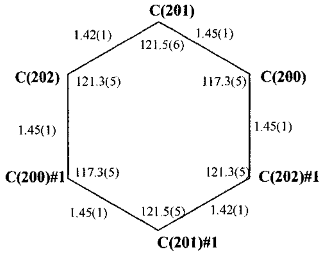




4a

Scheme 2





6a

The geometric parameters for **6a** and **4a** demonstrate a pattern for the C_6 skeleton different from that found for $[Li(DME)]_2[\eta^6\text{-}C_6H_2(SiMe_3)_4\text{-}1,2,4,5]$ **11**[12] and the solvent-separated ion pair of $[Na(DME)_3][C_6H_2(SiMe_3)_4\text{-}1,2,4,5]$ **12**,[13] the only other X-ray-characterized examples of ligated benzenide-type anions. The dianion of **11** had a nearly planar C_6 ring with twelve almost equal Li−C distances, av. 2.366 Å, long C(1)−C(2) and C(4)−C(5) bonds (av. 1.553 Å), the remainder being shorter (av. 1.408 Å).[12] The monoanion of **12** had a more distorted C_6 unit with the C−C bonds ranging from 1.401(4) to 1.466(4) Å.[12]

The La−C(C_6H_6) distances in **6** range from 2.75(1) to 2.79(1) Å, compared with an average of 2.635(6) Å for the La−C(28) and La−C(25) and an average of 2.799(6) Å for the remaining four La−C(C_6H_6) distances in **4**.[3] The La−C(Cp) distances in **6** lack precision (vide supra) but *formally* range from 2.82(1) to 3.12(1) Å (av. 2.97(1) Å), compared with 2.86(1) and 2.94(1) Å (av. 2.90(1) Å) in **4**;[3] in principle, on the basis of precedents for related Ln(II)/Ln(III) pairs, e.g., Sm or Yb, the Ln−C(Cp) distance is expected to be ca. 0.1 Å longer for Ln(II) than Ln(III).[14] The crown ether-coordinated potassium in the cation of **6** shows K−O bond lengths similar to those found in related complexes,[17] with K showing weak η^2-interaction with two molecules of benzene located above and below the crown ether.[18]

In summary, we have achieved the first synthesis of a crystallographically authenticated subvalent organolanthanum compound **6**, which we formulate as a salt containing as anion two $Cp^{tt}{}_2La(II)$ moieties bridged by an η^6-benzenide monoanionic ligand, and have shown that a range of unusual organolanthanum compounds can arise from redox chemistry of tricyclopentadienyllanthanum(III) compounds. An alternative formulation of the anion as comprising two $Cp^{tt}{}_2La(III)$ moieties bridged by an $[\eta^6\text{-}C_6H_6]^{3-}$ seems to us less plausible.

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Supporting Information Available: Tables of crystal data, final atom coordinates, anisotropic thermal parameters, complete positional parameters, and bond distances and angles for **6** and some EPR spectroscopic data (19 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H.; *J. Am. Chem. Soc.* **1991**, *113*, 7081.

(13) Bock, H.; Ansari, M.; Nagel, N.; Havlas, Z.; *J. Organomet. Chem.* **1995**, *499*, 63.

(14) For example, the average Yb−C(Cp) distance in $[Yb(\eta^5\text{-}C_5H_4SiMe_3)_2(THF)_2]$ is 2.75 Å,[15] compared with 2.64 Å in $[Yb(\eta^5\text{-}C_5H_5)_3]$.[16]

(15) Lappert, M. F.; Yarrow, P. I. W.; Atwood, J. L.; Shakir, B.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1980**, 987.

(16) Eggers, S. H.; Kopf, J.; Fisher, R. D. *Acta Crystallogr. Sect. C.* **1987**, *43*, 24.

(17) Gerisch, M.; Heinemann, F. W.; Bögel, H.; Steinborn, D.; *J. Organomet. Chem.* **1996**, *548*, 247.

(18) Viebrock, H.; Panther, T.; Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1995**, *491*, 19.