# Nonclassical Organolanthanoid Metal Chemistry: [K([18]-crown-6)($\eta^2$-PhMe)$_2$]X (X = [(LnCp$^t{}_3$)$_2$($\mu$-H)], [(LnCp″$_2$)$_2$($\mu$-$\eta^6$:$\eta^6$-PhMe)]) from [LnCp$^x{}_3$], K, and [18]-crown-6 in Toluene (Ln = La, Ce; Cp$^t$ = $\eta^5$-C$_5$H$_4$SiMe$_2$Bu$^t$; Cp″ = $\eta^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3)

Yurii K. Gun'ko,[†] Peter B. Hitchcock, and Michael F. Lappert*

*The Chemistry Laboratory, University of Sussex, Brighton, U.K. BN1 9QJ*

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*Summary: Treatment of [LnCp$^t{}_3$] or [LnCp″$_3$] with potassium and [18]-crown-6 in toluene at ambient temperature yielded two quite different crystalline potassium salts: [K([18]-crown-6)($\eta^2$-PhMe)$_2$]X (X = [(LnCp$^t{}_3$)$_2$($\mu$-H)], [(LnCp″$_2$)$_2$($\mu$-$\eta^6$:$\eta^6$-PhMe)]; Ln = La, Ce; Cp$^t$ = $\eta^5$-C$_5$H$_4$SiMe$_2$Bu$^t$; Cp″ = $\eta^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3).*

A continuing aim in our research on the organometallic chemistry of 4f elements (Ln) is to gain access to subvalent compounds of the early (La, Ce, Pr, Nd) Ln elements and to study their chemistry. Our strategy has been to use a tris(substituted cyclopentadienyl)Ln compound [LnCp$^x{}_3$] as substrate for reaction at ambient temperature with potassium in the presence of a neutral donor. It became evident that the nature of the product depended on the stoichiometry, the reaction medium, and the neutral donor.[1−6] We now demonstrate that the choice of a particular [Cp$^x$]$^-$ ligand is also crucial (Cp$^x$ = Cp″, Cp$^{tt}$, Cp$^t$; Cp″ = $\eta^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3; Cp$^{tt}$ = $\eta^5$-C$_5$H$_3$Bu$^t{}_2$-1,3; Cp$^t$ = $\eta^5$-C$_5$H$_4$SiMe$_2$Bu$^t$).

Three earlier results on such reactions for Ln = La, Ce are relevant. (1) From [LnCp″$_3$] + K in 1,2-dimethoxyethane (dme) the lanthanocene(III) methoxide **A** and ethene were obtained (Ln = La,[1] Ce[2]); for Ln = La, two La(II) intermediates, assigned as **B** and **C**, were observed (EPR spectroscopy).[1] (2) The crystalline compound **D** was formed from [LnCp″$_3$] + 2K + [18]-crown-6 in benzene, the anion of **D** being formulated as Ln$^{3+}$ coordinated to a 1,4-cyclohexa-3,5-dienyl ([C$_6$H$_6$]$^{2-}$) and two [Cp″]$^-$ ligands (Ln = La, Ce, Pr, Nd);[3,4] when the Ln = La reaction was monitored by EPR spectroscopy, La(II) intermediates such as **B** and **C** were identified.[4] (3) The crystalline ion pair **E**, considered to contain as the anion two LaCp$^{tt}{}_2$ moieties bridged by a [C$_6$H$_6$]$^-$ ligand, was the product from [LaCp$^{tt}{}_3$] + $^3/_2$ K + [18]-crown-6 in benzene; [5] the Cp″ analogue has also been made from [LaCp″$_3$].[5,6]

$$[\{\mathrm{LnCp''_2(\mu\text{-}OMe)}\}_2]$$

**A**

$$[\mathrm{LaCp''_3(dme)}_x]^- \qquad [\mathrm{LaCp''_2(dme)}_y]$$

**B** **C**

$$[\mathrm{K([18]\text{-}crown\text{-}6)}][\mathrm{LnCp''_2(C_6H_6)}]$$

**D**

$$[\mathrm{K([18]\text{-}crown\text{-}6)(\eta^2\text{-}C_6H_6)_2}][(\mathrm{LaCp^{tt}{}_2})_2(\mu\text{-}\mathrm{C_6H_6})]$$

**E**

We now report that the outcome of treating [LnCp″$_3$] and [LnCp$^t{}_3$] (Ln = La, Ce) with potassium and [18]-crown-6 in toluene at ambient temperature is quite different, yielding[7] the crystalline salts **1** and **2**, respectively (Scheme 1).

Each of the compounds **1a**,**b** and **2a**,**b**, as well as [K([18]-crown-6][Cp″], gave satisfactory microanalyses

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[†] Present address: The Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland.

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(7) **Representative Syntheses and Selected Spectroscopic Data.** A solution of [CeCp″$_3$] (0.83 g, 1.08 mmol) in toluene (60 mL) was added to a mirror of metallic potassium (0.064 g, 1.64 mmol) at ca. 20 °C. Then [18]-crown-6 (0.43 g, 1.63 mmol) was added, and the mixture was stirred for 3 h until almost all the potassium had dissolved. The decantate was concentrated to ca. 30 mL in vacuo. Deep violet crystals of **1a** (0.52 g, 57%) were gradually deposited. Anal. Calcd for C$_{84}$H$_{140}$Ce$_2$KO$_6$Si$_8$: C, 54.5; H, 7.79. Found: C, 53.9; H, 7.71. $^1$H NMR (C$_6$D$_6$, 333 K): $\delta$ 14.52 (br 4H, Cp ring), 6.98, 7.0, 7.1 (m, 15H, toluene), 3.06 (s, 24H, [18]-crown-6), −1.75 (br, 8H, Cp ring), −3.8 (s, 72H, SiMe$_3$). UV/vis (toluene, 298 K): $\lambda_{\max}$ 295, 390 (br), 535 (br), 670 (br) nm. Further concentration of the rest of the mother liquor (ca. 15 mL) in vacuo and cooling to −22 °C afforded colorless crystals of [K([18]-crown-6)][Cp″] (0.38 g, 80%). $^1$H NMR (C$_6$D$_6$, 333 K): $\delta$ 6.73 (d, 2H, Cp ring), 6.57 (t, 4H, Cp ring), 3.14 (s, 24H, [18]-crown-6), 0.53 (s, 36H, SiMe$_3$). Complex **1b** was prepared analogously as deep violet crystals in 74% yield. Anal. Calcd for C$_{84}$H$_{140}$KLa$_2$O$_6$Si$_8$: C, 54.5; H, 7.79. Found: C, 53.5; H, 7.73. $^1$H NMR (C$_6$D$_6$, 333 K): $\delta$ 6.98, 7.00, 7.09 (m, 15H, toluene), 3.33 (s, 24H, [18]-crown-6), 1.4 (br 4H, Cp ring); 0.82 (br, 8H, Cp ring), 0.62 (s, 72H, SiMe$_3$). UV/vis (toluene, 298 K): $\lambda_{\max}$ 300, 435 (br), 570 (br), 680 (br) nm. Complex **2a** was prepared similarly from [CeCp$^t{}_3$] (0.91 g, 1.34 mmol), metallic potassium (0.078 g, 2.0 mmol), and [18]-crown-6 (0.53 g, 2.0 mmol) in toluene (60 mL), as pale yellow crystals (0.92 g, 71%). Anal. Calcd for C$_{99}$H$_{162}$Ce$_2$KO$_6$Si$_6$: C, 61.5; H, 8.38. Found: C, 59.9; H, 8.21. $^1$H NMR (C$_6$D$_6$, 298 K): $\delta$ 17.83 (br, 12H, Cp), 6.98, 7.0, 7.1 (m, 15H, toluene), 4.90 (br, 12H, Cp), 2.93 (s, 24H, [18]-crown-6), 2.1 (s, 9H, Me), 0.48 (br, 54H, Bu$^t$), −6.63 (vbr, 36H, SiMe$_2$). IR (Nujol): $\nu_{\max}$ 1352 (m), 1285 (br, s), 1249 (s), 1180 (s), 1108 (br, m), 1043 (s), 962 (m), 820 (m), 753 (m) cm$^{-1}$; for [K([18]-crown-6)($\eta^2$-PhMe)$_2$][(CeCp$^t{}_3$)$_2$($\mu$-D)] 1353 (m), 1248 (s), 1178 (s), 1109 (br, m), 1042 (s), 962 (m), 918 (br), 824 (m), 752 (m) cm$^{-1}$. Complex **2b** was prepared analogously as white crystals in 82% yield. Anal. Calcd for C$_{99}$H$_{162}$Ce$_2$KO$_6$Si$_6$: C, 61.5; H, 8.38. Found: C, 58.7; H, 8.01. $^1$H NMR (C$_6$D$_6$, 298 K): $\delta$ 6.98, 7.0, 7.09 (ms, toluene), 6.56 (m, 12 H, Cp), 6.36 (m, 12 H, Cp), 4.3 (br, 1H, H$^-$), 3.08 (s, 24 H, [18]-crown-6), 2.09 (s, 6H, CH$_3$), 1.12 (s, 54 H, Bu$^t$), 0.50 (s, 36 H, SiMe$_2$). The IR spectrum was similar to that of **2a**.

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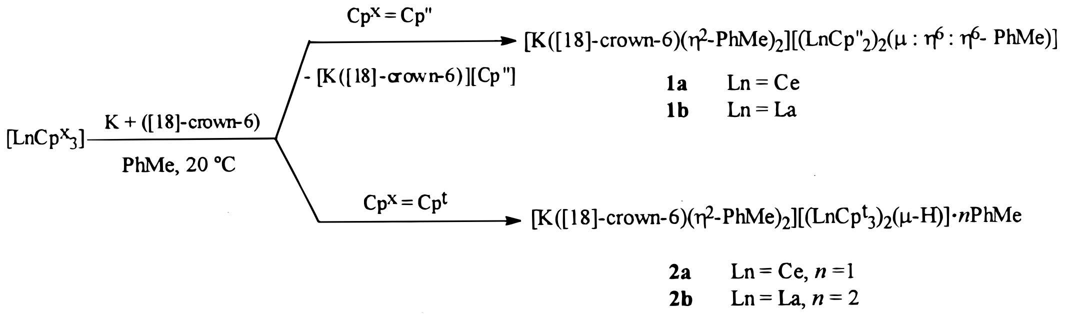
**Scheme 1. Synthesis of Compounds 1 and 2 (Cp″ = $\eta^5$-$C_5H_3(SiMe_3)_2$-1,3; Cp$^t$ = $\eta^5$-$C_5H_4SiMe_2Bu^t$)**



and $^1$H NMR spectra.[7] Those of **1a**,**b** and **2a**, although broad and paramagnetically shifted, showed the expected integrations and were clearly distinct and different from their [LnCp$^x_3$] precursors. The $^1$H NMR spectrum of compound **2b** in $C_6D_6$ displayed in the correct relative intensities appropriate sharp signals for a diamagnetic La(III) compound of [Cp$^t$]$^-$, [18]-crown-6, and toluene ligands and a broad resonance at $\delta$ 4.3, assigned to $\mu_2$-H, which was absent in the spectrum of the deuterated analogue (prepared from toluene-$d_8$ in place of PhMe). Hydrolysis of any of **1a**,**b** and **2a**,**b** afforded toluene (GC-MS) and a small amount of $H_2$ ($^1$H NMR) but no methylcyclohexadiene (cf., cyclohexa-1,4-diene from **D**[3,4] but not **E**[5,6]). Solution EPR spectra of the freshly prepared **1a**,**b** in toluene revealed the characteristic quintet of [PhMe]$^-$.[8] Solid-state EPR spectra showed broad signals for each complex at a $g$ value very close to that of the free electron (2.0023). The intense UV–vis absorptions at 390 and 670 nm for **1a** and 435 and 680 nm for **1b** (of a very dilute solution in toluene; **1a**,**b** were only sparingly soluble)[7] were in the range (ca. 400 and ca. 700 nm) reported for Ce$^{2+}$ and La$^{2+}$ cations incorporated in a $CaF_2$ matrix.[9] The magnetic moments of crystalline samples (Faraday balance) at 293 K were $\mu_{eff}$ = 2.4 $\mu_B$ (**1a**) and $\mu_{eff}$ = 2.2 $\mu_B$ (**1b**).

Single crystals of each of the compounds **1a** and **2a**,**b** were examined by X-ray diffraction. Because of the high disorder associated with the $SiMe_3$ (of Cp″) and Me (of PhMe) groups of **1a** or $SiMe_2Bu^t$ substituents of the Cp$^t$ ligands of **2b**, good-quality structural solutions for these complexes were not achieved.[11] However, they are adequate to provide definitive evidence that their structures are as indicated in Scheme 1; we recognize that it would be inappropriate to discuss fine details of geometric parameters. No such constraint applies to the structure of the crystalline binuclear cerate(III) complex **2a**, illustrated in Figure 1, in which the bridging hydrido ligand was not definitively identified. Its presence is inferred from (i) the Ce···Ce′ separation of 4.513 Å, (ii) the rather similar La···La′ contact of 4.523 Å in **2b** and its diamagnetism (and a $^1$H NMR spectroscopic signal assigned to $\mu$-H), (iii) the Lu···Lu distance of 4.18 Å in [Na(thf)$_6$][(LuCp$_3$)$_2$($\mu$-H)] **F** (prepared from 2 LuCp$_3$ + NaH in thf; although the $\mu$-H$^-$ ligand there was also not located),[12] and (iv) the above $^1$H NMR spectroscopic data.[7]

The [(K[18]-crown-6)($\eta^2$-PhMe)$_2$]$^+$ cation of **2a** lies on an inversion center, the six oxygen atoms occupying the equatorial sites about the central potassium atom

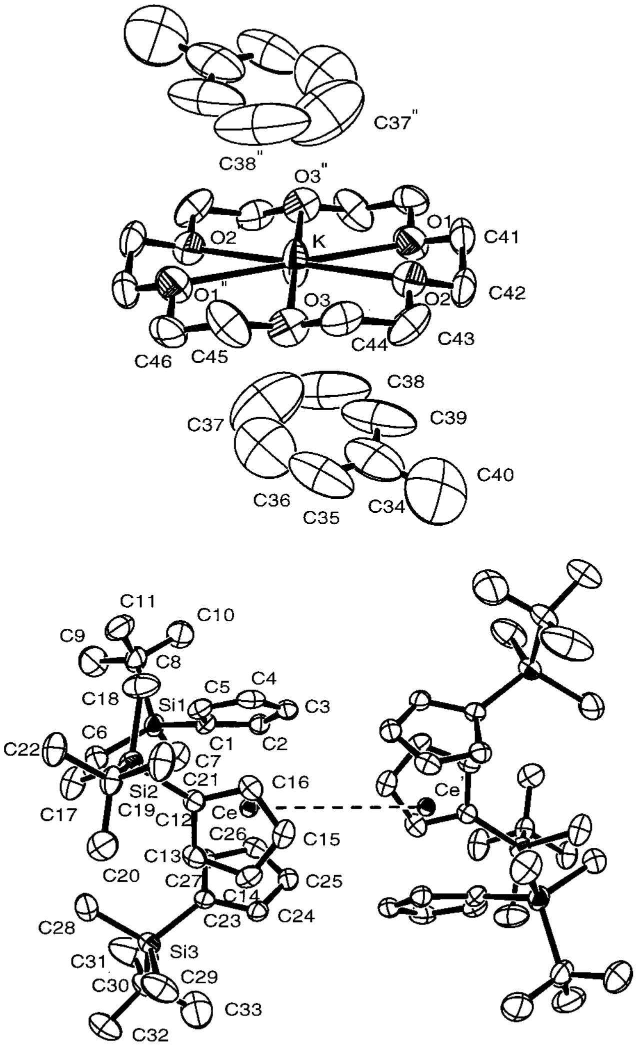


**Figure 1.** Crystal structure of the salt **2a**: (a, top) the cation; (b, bottom) the anion.

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(11) **Crystal Data.** For **1a**: $C_{84}H_{140}Ce_2KO_6Si_8$, monoclinic, space group $C2/c$, $a$ = 11.983(1) Å, $b$ = 33.545(1) Å, $c$ = 26.302(2) Å, $\beta$ = 101.06(1)°, $U$ = 10 376(1) Å$^3$, $Z$ = 4, $D_c$ = 1.04 g cm$^{-3}$, $T$ = 180 K, R1 = 0.097 for 5618 reflections with $I > 2\sigma(I)$, wR2 = 0.344. For **2a**: $C_{99}H_{163}Ce_2KO_6Si_6$, monoclinic, space group $P2_1/c$, $a$ = 14.404(4) Å, $b$ = 12.704(4) Å, $c$ = 29.271(6) Å, $\beta$ = 92.97(2)°, $U$ = 5349(3) Å$^3$, $Z$ = 2, $D_c$ = 1.2 g cm$^{-3}$, $T$ = 173 K, R1 = 0.046 for 9666 reflections with $I > 2\sigma(I)$, wR2 = 0.115. For **2b**: $C_{106}H_{171}KLa_2O_6Si_6$, monoclinic, space group $Cc$ (No. 9), $a$ = 14.029(2) Å, $b$ = 24.648(7) Å, $c$ = 33.00(2) Å, $\beta$ = 98.21(3)°, $U$ = 11293(9) Å$^3$, $Z$ = 4, $D_c$ = 1.19 g cm$^{-3}$, $T$ = 173 K, R1 = 0.101 for 4678 reflections with $I > 2\sigma(I)$, wR2 = 0.290.

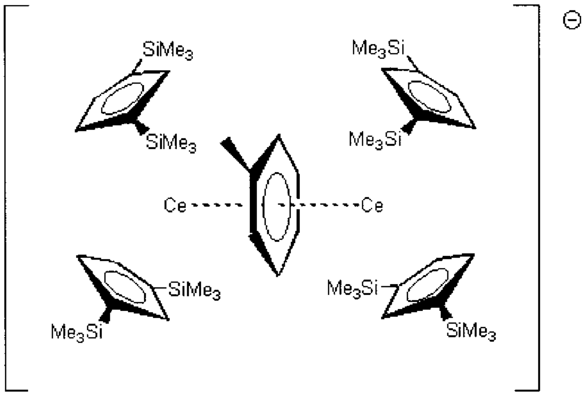
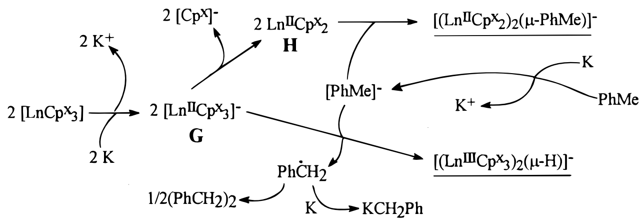


**Figure 2.** Line drawing of the anion of the salt **1a**.

and the two $\eta^2$-toluene ligands in apical positions with its methyl groups arranged in a transoid fashion; the K···C(37) and K···C(38) contacts are 3.40(1) and 3.44(1) Å, while the K−O distances range from 2.78(1) to 2.84(2) Å. The two $CeCp^t_3$ groups of the anion are related by another inversion center. The Ce−C(Cp) bond lengths range from 2.795(4) to 2.931(4) Å, the three Ce−M distances being essentially identical at 2.59(1) Å, compared with an average Lu−M distance of 2.43(2) Å in **F**[12] (where M denotes a centroid of a $Cp^x$ ring). The M−Ce−M′ bond angles of 119.9 ± 1.1° compare with the 116.6 ± 5.0° in the bis[lutecenato(III)] anion of **F**.[12]

Single crystals of **1a** were examined on independent specimens at Reading, Sussex, and Warwick, with identical outcomes (the cited data[11] were collected at Warwick using a CCD detector). The salt **1a** has the same cation as **2a**. The anion of **1a** is centrosymmetric, a planar $\mu$-$\eta^6$:$\eta'^6$-toluene ligand bridging two $CeCp''_2$ moieties (Figure 2). The structure is thus closely similar to that of **E**.[5] We conclude that the anion of the salt **1a** is best represented as a dinuclear cerate(II) complex with a bridging planar toluene anion $[PhMe]^-$; the paramagnetic La analogue **1b**, like **E**,[5] is a La(II) species. A claim for a salt containing a cerate(II) anion $[Ce(cot)_2]^{2-}$ has appeared, on the basis simply of analytical data.[13]

**Scheme 2. Pathways to $[(Ln^{II}Cp^x_2)_2(\mu\text{-}PhMe)]^-$ and $[(Ln^{III}Cp^x_3)_2(\mu\text{-}H)]^-$**



Single crystals of **1b** showed it to be isostructural with **1a**.

We propose that the pathways to the differing anions of the salts **1** and **2** are as shown in Scheme 2. Thus, we suggest that, in the presence of [18]-crown-6, $[LnCp^x_3]$ is reduced to the successive Ln(II) intermediates **G** and **H**, similar to those shown in **B** and **C**. Complex **G**, in the case of $Cp^x = Cp^t$, abstracts a hydrogen atom from toluene, affording the anion of **2a**,**b** with dibenzyl and $[K([18]\text{-crown-6})CH_2Ph]$ (which were identified by $^1H$ NMR spectroscopy) as coproducts. In the Cp″ system, on other hand, this pathway is less favored, because the $Ln^{3+}$ center in $[LnCp''_3]^-$ is sterically more encumbered than in $[LnCp^t_3]$. Hence, $[LnCp''_3]^-$ preferentially eliminates $[Cp'']^-$ to yield **H** ($Cp^x = Cp''$), two molecules of which are then trapped by a bridging $[PhMe]^-$ ligand.

The results here presented offer evidence of the existence of previously unsuspected subvalent organocerium compounds and demonstrate the interesting and novel redox chemistry of Ln(III) compounds (Ln = La, Ce).

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**Supporting Information Available:** Tables of crystal data, final atom coordinates, anisotropic thermal parameters, and all positional parameters and bond distances and angles for **1a** and **2a**,**b**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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