# Displacement of a cyclopentadienyl ligand by a crown ether from a lanthanocene(II) [LnCp''$_2$]; crystal structures of the first cationic lanthanoid(II) complexes, [SmCp''([18]-crown-6)][SmCp''$_3$]·0.5C$_6$H$_6$ and [YbCp''([18]-crown-6)][Cp'']·3C$_6$H$_6$ [Cp'' = η$^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3]

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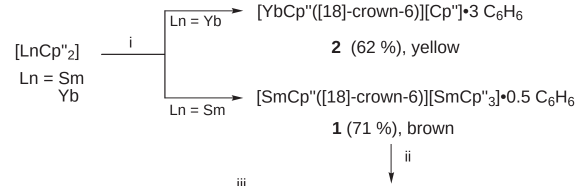
**Treatment of [SmCp''$_2$] or [YbCp''$_2$] with [18]-crown-6 in benzene at ambient temperature yields the X-ray characterised, crystalline salts [SmCp''([18]-crown-6)][SmCp''$_3$]·0.5C$_6$H$_6$ 1 and [YbCp''([18]-crown-6)][Cp'']·3C$_6$H$_6$ 2; 1 with K in toluene affords [K([18]-crown-6)(η$^2$-PhMe)$_2$][SmCp''$_3$], also accessible from [SmCp''$_2$], K[Cp''] and [18]-crown-6 in toluene [Cp'' = η$^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3].**

The use of crown ethers to solubilise lanthanoid (Ln) halides or nitrates is well documented.[1] By contrast, the chemistry of (crown ether)Ln organometallic complexes is still undeveloped, although we have recently studied the reactions of some tri(cyclopentadienyl)lanthanoid(III) complexes with potassium in the presence of [18]-crown-6 and an arene, which have yielded the crystalline salts [K([18]-crown-6)(C$_6$H$_6$)$_2$][{LaCp'$_2$}$_2$(μ,η-C$_6$H$_6$)][2a] and [K([18]-crown-6)(η$^2$-PhMe)$_2$][(LnCp''$_2$)$_2$(μ,η-PhMe)] [Cp' = η$^5$-C$_5$H$_3$Bu$^t{}_2$-1,3; Cp'' = η$^5$-C$_5$H$_3$(SiMe$_3$)$_2$-1,3; Ln = Ce or Pr].[2b]

We now report (*a*) two facile, but diverse, cyclopentadienyl displacement reactions from a lanthanocene(II) [LnCp''$_2$] (Ln = Sm or Yb) by a crown ether, affording (Scheme 1) the crystalline [SmCp''([18]-crown-6)][SmCp''$_3$]·0.5C$_6$H$_6$ **1** or [YbCp''([18]-crown-6)][Cp'']·3C$_6$H$_6$ **2**; (*b*) the partial redistribution of **2** in toluene into **2** and [YbCp''$_2$([18]-crown-6)]; (*c*) the synthesis from a toluene solution of another crystalline tri(cyclopentadienyl)samarate(II) [K([18]-crown-6)(η$^2$-PhMe)$_2$][SmCp''$_3$]·0.5PhMe **3** from either **1** and K, or [SmCp''$_2$], K[Cp''] and [18]-crown-6 (Scheme 1); and (*d*) the X-ray structures of **1–3**.‡ Further features of interest are that **1** and **2** are the first examples of cationic lanthanoid(II) complexes, **2** the first lanthanoid salt containing a cyclopentadienide counter-ion, and **1** and **3** are new members of the rare family of salts containing a lanthanate(II) anion.[3]

Each of the crystalline salts **1–3** gave satisfactory microanalytical results, as well as IR and NMR§ spectra. The latter in [$^2$H$_8$]toluene or [$^2$H$_6$]benzene for **1** and **3** were complicated by the paramagnetism of the f$^6$ Sm$^{II}$ causing strongly shifted signals, but were substantially temperature-invariant in the range 0 to +50 °C. The $^{29}$Si{$^1$H} NMR spectra of **1** at 25 °C showed two signals at $\delta$ 98.50 ([SmCp''([18]-crown-6)]$^+$) and $\delta$ −58.59 ([SmCp''$_3$]$^-$) in the appropriate 1 : 3 ratio. By contrast, for the case of the diamagnetic f$^{14}$ Yb$^{II}$ salt **2**, there was partial redistribution in toluene solution, readily monitored, especially by $^{171}$Yb{$^1$H} and $^{29}$Si{$^1$H} (three signals at $\delta$ 44.47, −2.49 and −19.68 in a 1 : 1 : 3 ratio at 25 °C), but also $^1$H NMR spectra in the same temperature regime; cooling below −10 °C led to crystallisation of **2**. The $^{171}$Yb{$^1$H} NMR spectra in [$^2$H$_8$]toluene revealed two signals at 25 °C: $\delta$ −82.46, assigned to **2**, and $\delta$ 14.44, assigned to [YbCp''$_2$([18]-crown-6)] {*cf.*[4] $\delta$ 0 for [Yb(η$^5$-C$_5$Me$_5$)$_2$(thf)$_2$] in thf at 296 K}; whereas at 50 °C a single broad signal at $\delta$ −1.77 was observed, indicative of a fast exchange process between the two species but a decrease in the relative contribution of **2**. Lowering the temperature to −10 °C led to a decrease in relative intensity and shift of the higher frequency signal to $\delta$ 30.35, and simultaneously an enhancement in relative intensity and shift of the lower frequency signal to $\delta$ −32.43. These data show that in toluene or benzene there is an equilibrium between **2** and the neutral complex [YbCp''$_2$([18]-crown-6)], with the latter favoured at higher temperatures.



**Scheme 1** Synthesis of the crystalline cyclopentadienyllanthanoid(II) salts **1**–**3**. *Reagents and conditions*: i, [18]-crown-6, benzene, 12 h, *ca.* 20 °C; ii, K (mirror), toluene, 3 h, *ca.* −30 °C, iii, toluene, 5 h, *ca.* 20 °C.

Crystalline **1** consists of well separated ions, Fig. 1. The cation [SmCp''([18]-crown-6)]$^+$ has a sandwich-like structure; the Sm is located within the cavity of the quasi-parallel Cp'' and the crown ligand, the latter being distorted due to strong O(6) atom deviation. The centroid of the Cp'' ring and the six oxygen atoms of the crown ether form a strongly distorted pentagonal bipyramidal arrangement around Sm. The crown ether is disordered 0.57 : 0.43 over two orientations, approximately related by mirror symmetry, with two carbon positions in common. The Sm(1)–C$_{sp^2}$ distances are in the range 2.828(6) to 2.913(6) Å [to C(5) shortest, to C(3) longest] with Sm(1)–Cp''(centroid) 2.606(6) Å; this compares with 2.553 Å in [Sm(Cp'')Cp'''(thf)] [Cp''' = η$^5$-C$_5$H$_2$(SiMe$_3$)$_3$-1,2,4)].[5] The average Sm(1)–O distance of 2.714 Å [ranging from 2.571(9) to 2.829(9) Å, to O(5) shortest, to O(3) longest] is *ca.* 0.15–0.2 Å longer than in Sm$^{III}$ crown ether complexes.[1e] The [SmCp''$_3$]$^-$ anion in **1** has the Sm in an almost trigonal planar arrangement with respect to the centroids of the three Cp'' ligands, as in [SmCp''$_3$].[6] The Sm(2)–C$_{sp^2}$ distances are in the range 2.816(6) to 3.092(6) Å [to C(39) shortest, to C(26) longest], with two Sm–Cp''(centroid) distances of 2.701(6) and one of 2.670(6) Å, compared with 2.698(5) to 2.807(5) Å in [SmCp''$_3$].[6]

Crystalline **2**, likewise, has well separated ions, the nearest Yb contact to the anion being 6.58 Å. The sandwich-like nature of the cation [YbCp''([18]-crown-6)]$^+$ resembles that of **1**. The Yb(1)–C$_{sp^2}$ distances, ranging from 2.739 to 2.814 Å [to C(5) shortest, to C(3) longest], as well as *d*[Yb–Cp''(centroid)] 2.508(7) Å, are significantly longer than in [{YbCp''$_2$}$_\infty$], having Yb–C$_{sp^2}$ from 2.654(5) to 2.684(6) with Yb–Cp''(centroid) 2.382 and 2.366 Å.[7] The Yb–O distances range from 2.519(5) to 2.583(6) Å [to O(4) shortest, to O(1) longest]. The anion is such that two Cp' groups lie across inversion centres with the disorder only partially resolved and hence the dimensions are unreliable.

Crystalline **1** and **3** have identical anions. The asymmetric unit contains two cations and two anions and one toluene solvate molecule. The six K–O bond lengths range from 2.72(2) to 2.83(2) Å and the K···C(from $\eta^2$-PhMe) contacts are 3.53(3) Å.

A reaction which has some analogy with the formation of salt **1** from [SmCp"$_2$] is that between $MgR_2$ or Mg(Br)R and a cryptand or an azacrown ether to yield [MgR(macrocycle)][$MgR_3$] or [MgR(macrocycle)][Mg(Br)$R_2$], which show fluxionality in [$^2H_6$]benzene involving exchange of R as between cation and anion (*e.g.* R = Bu$^i$).[8]

The formation of the [SmCp"$_3$]$^-$ counter anion in **1** contrasts with the [Cp"]$^-$ of **2** in the related ytterbium reaction. We suggest that [SmCp"([18]-crown-6)][Cp"] is first formed, but captures a further molecule of [SmCp"$_2$] to give **1**; the lack of reaction between **2** and [YbCp"$_2$] is attributed to steric hindrance, $Yb^{2+}$ being significantly smaller than $Sm^{2+}$.

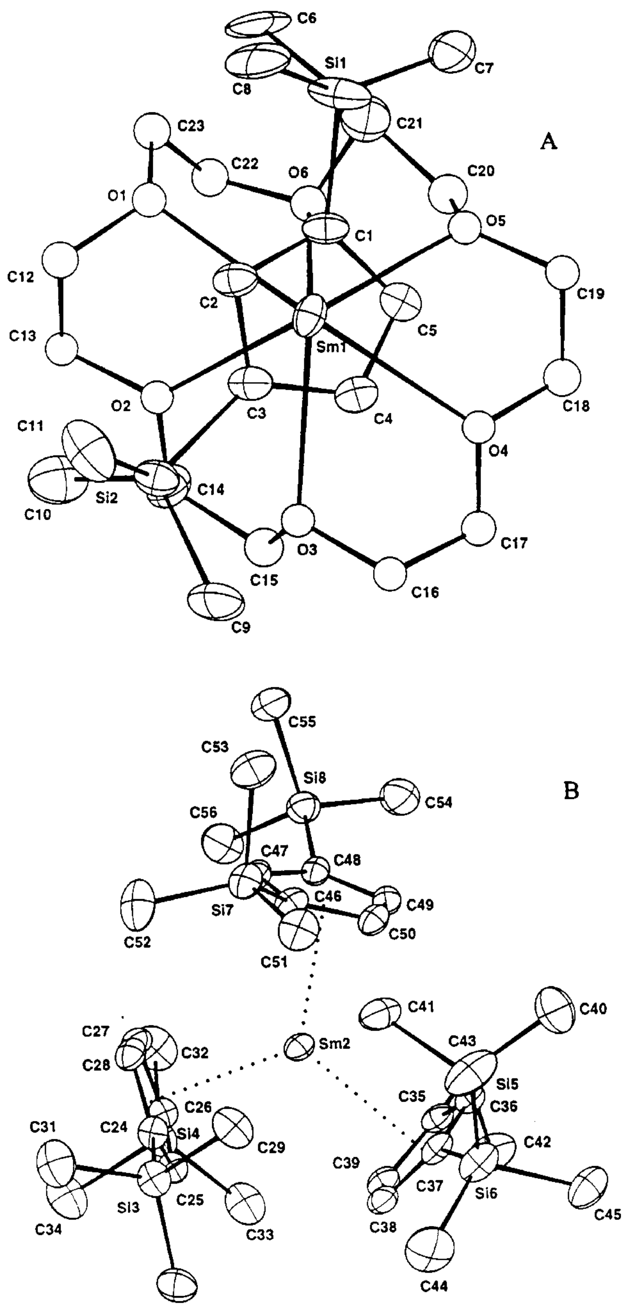


**Fig. 1** The structure of cation (**A**) and anion (**B**) in **1**; selected bond lengths and angles are in the text

The results here presented open up a new chapter in organolanthanoid chemistry; the cationic lanthanoid(II) complexes, in particular **1**, are expected to have a rich chemistry. For **2**, we shall replace [Cp]$^-$ by a weakly coordinating anion.

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## Notes and References

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No reprints available.

‡ *Crystal data*: **1**, $C_{59}H_{111}O_6Si_8Sm_2$, $M$ = 1441.9, $T$ = 173(2) K, monoclinic, space group $P2_1/n$ (no. 14), $a$ = 19.902(7), $b$ = 14.610(4), $c$ = 26.89(2) Å, $\beta$ = 107.10(4)°, $U$ = 7474(6) Å$^3$, $F$(000) = 2996, $Z$ = 4, $D_c$ = 1.28 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 1.73 mm$^{-1}$, specimen 0.40 × 0.35 × 0.20 mm$^3$, 9128 unique reflections for $2 < \theta < 22°$, $R_1$ = 0.041 for 7379 reflections with $I > 2\sigma(I)$, $wR_2$ = 0.109 (all data), $S$ = 1.048; **2**, $C_{52}H_{84}O_6Si_4Yb$, $M$ = 1090.59, $T$ = 173(2) K, monoclinic, space group $P2_1/n$ (no. 14), $a$ = 12.168(5), $b$ = 39.88(2), $c$ = 12.858(6) Å, $\beta$ = 115.46(4)°, $U$ = 5634(4) Å$^3$, $F$(000) = 2280, $Z$ = 4, $D_c$ = 1.29 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 1.79 mm$^{-1}$, specimen 0.30 × 0.30 × 0.10 mm$^3$, 9935 unique reflections for $2 < \theta < 25°$, $R_1$ = 0.058 for 8259 reflections with $I > 2\sigma(I)$, $wR_2$ = 0.227 (all data), $S$ = 1.134; **3**, $C_{59}H_{103}\underline{K}O_6Si_6Sm\cdot 0.5(C_7H_8)$, $M$ = 1312.5, $T$ = 173(2) K, triclinic, space group $P1$ (no. 2), $a$ = 11.895(3), $b$ = 17.148(10), $c$ = 37.923(11) Å, $\alpha$ = 87.03(3), $\beta$ = 84.19(2), $\gamma$ = 69.87(3)°, $U$ = 7224(5) Å$^3$, $F$(000) = 2780, $Z$ = 4, $D_c$ = 1.21 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 1.01 mm$^{-1}$, specimen 0.20 × 0.10 × 0.10 mm$^3$, 13461 unique reflections for $2 < \theta < 20°$, $R_1$ = 0.095 for 7363 reflections with $I > 2\sigma(I)$, $wR_2$ = 0.289 (all data), $S$ = 1.19. An Enraf-Nonius CAD-4 diffractometer, $\lambda$(Mo-K$\alpha$) 0.71073 Å, absorption corrections, solution by direct methods, full-matrix least-squares refinement on all $F^2$. CCDC 182/943.

§ *Selected spectroscopic data*: for **1**: $^{29}$Si{$^1$H} NMR (49.7 MHz, 298 K, [$^2H_8$]toluene): $\delta$ 98.50, −58.59 (1 : 3); for **2**: $^1$H NMR (300 MHz, 298 K, $C_6D_6$): $\delta$ 6.71 (br, 3H, Cp-ring, free Cp"$^-$), 6.42 (br, 3H, Cp-ring), 3.16 (br, s, 24H, 18-crown-6), 0.66 (br, 18H, $SiMe_3$), 0.41 (s, 18H, $SiMe_3$ , free Cp"$^-$); the $^1$H NMR spectrum also contains signals assigned to [YbCp"$_2$([18]-crown-6)]: $\delta$ 6.58 (br, m, 3H, Cp-ring), 3.44 (br, s, 24H, 18-crown-6), 0.47 (s, 36H, $SiMe_3$); $^1$H NMR (300 MHz, 323 K, $C_6D_6$): $\delta$ 6.60 (vbr sh, 3H, Cp-ring), 3.47 (br sh, 24H, 18-crown-6), 0.50 (vbr, 36H, $SiMe_3$); $^{29}$Si{$^1$H} NMR (49.7 MHz, 298 K, [$^2H_8$]toluene): $\delta$ 44.47 ([YbCp"([18]-crown-6)]$^+$), −2.49 (free Cp"$^-$), −19.68 ([YbCp"$_2$([18]-crown-6)]) (rel. ratios: 1 : 1 : 3); $^{171}$Yb{$^1$H} NMR (43.77 MHz, 298 K, [$^2H_8$]toluene): $\delta$ 14.44 ($\Delta w_{1/2}$ = 45 Hz), −82.46 ($\Delta w_{1/2}$ = 130 Hz); (43.77 MHz, 323 K, [$^2H_8$]toluene): $\delta$ −1.77 ($\Delta w_{1/2}$ = 90 Hz); (43.77 MHz, 263 K, [$^2H_8$]toluene): $\delta$ 30.35 ($\Delta w_{1/2}$ = 30 Hz), −32.43 ($\Delta w_{1/2}$ = 145 Hz).

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