First identification by EPR spectra of lanthanum(II) organometallic intermediates (and $E_{\frac{1}{2}}$ for $La^{3+} \rightarrow La^{2+}$) in the C–O bond activation of dimethoxyethane†

M. Cristina Cassani,[a] Michael F. Lappert*[a] and Franco Laschi[b]

[a] *The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Universita' di Siena, Dipartimento di Chimica, Siena, Italy I-53100*

The reaction of $[\mathrm{La(Cp'')_3}]$ with K in dimethoxyethane (dme) at ambient temperature leads to the formation of lanthanocene(III) methoxides *via* persistent paramagnetic lanthanum(II) intermediates that are characterised by EPR spectroscopy and tentatively assigned to $[\mathrm{K(dme)}_x][\mathrm{La(Cp'')_3}]$ and $[\mathrm{La(Cp'')_2(dme)}_y]$ [$\mathrm{Cp''} = \eta^5\text{-}\mathrm{C_5H_3(SiMe_3)_2}$-1,3]; the cyclic voltammogram of $[\mathrm{La(Cp'')_3}]$ in thf is also reported, $E^{\mathrm{red}}_{\frac{1}{2}} = -2.8$ V.

Recently we showed that the reaction of $[\mathrm{Ln(Cp'')_3}]$ [Ln = Ce or Nd, $\mathrm{Cp''} = \eta^5\text{-}\mathrm{C_5H_3(SiMe_3)_2}$-1,3] with K in dimethoxyethane (dme) gave the lanthanocene(III) methoxide $[\{\mathrm{Ln(Cp'')_2(\mu\text{-}OMe)}(\}_2]$.[1] It was postulated that a $\mathrm{Ln^{II}}$ complex was a plausible transient intermediate involved in the C–O bond cleavage.

We now report that treatment of $[\mathrm{La(Cp'')_3}]$ **1** with a K mirror in dme led to the immediate formation of a dark royal blue solution **2** from which a white crystalline mixture was obtained. The latter contained $\mathrm{K(Cp'')}$, $[\{\mathrm{La(Cp'')_2(\mu\text{-}OMe)}\}_2]$ **3**, and an as yet unidentified polynuclear lanthanum methoxide **4**, Scheme 1.‡

The particularly striking feature of this reaction is that the blue solution **2** was paramagnetic and its EPR spectrum revealed it to contain two lanthanum(II) complexes.§ Fig. 1(*a*) shows the ambient-temperature EPR spectrum which consisted of two sets **A** and **B** of well resolved $S = 1/2$ metal-centred octuplets with **A** : **B** *ca.* 1.5 : 1. In each of **A** and **B**, the height of the EPR lines progressively decreased from their centre while concomitantly their peak separation increased from left to right. Each of the **A** and **B** sets arises from the hyperfine coupling of the unpaired electron with the ^{139}La nucleus (99.91% natural abundance, $\mu_1 = +2.776$, $I = 7/2$), with $g_{\mathbf{A}} = 1.972(8)$, $a_{\mathbf{A}}(^{139}\mathrm{La}) = 134.0(5)$ G and $g_{\mathbf{B}} = 1.970(8)$, $a_{\mathbf{B}}(^{139}\mathrm{La}) = 145.0(5)$ G. These hyperfine couplings are of similar magnitude but intermediate between (*i*) the calculated value of 186 G (using spin-polarised unrestricted Hartree–Fock wavefunctions),[2a] and (*ii*) that measured (*ca.* 50 G at 20 K) for a $\mathrm{La^{2+}}$ defect in a $\mathrm{CaF_2}$ lattice; this being, as far as we are aware, the only prior experimental literature value.[3] These data strongly contrasted with those from the EPR spectrum of (*i*) $[\mathrm{La^{3+}@C_{82}{}^{3-}}]$ which consists of eight extremely narrow ($\Delta H = 0.125$ G) equally spaced [$a(^{139}\mathrm{La}) = 1.25$ G] lines of equal height centred at $g = 2.0010$ (1,1,2,2-tetrachloroethane, 293 K);[2a–d] and (*ii*) $[\mathrm{LaI_2(bipy)_2(dme)}]$ [$a(^{139}\mathrm{La}) = 7.4$ G, $g = 2.0031$ (dme, 293 K)], $[\mathrm{LaI_2(bipy)_2(thf)_2}]$ [$a(^{139}\mathrm{La}) = 5.9$ G, $g = 2.0009$ (thf, 293 K)] or $[\mathrm{LaI_2(bipy)(dme)_2}]$ [$a(^{139}\mathrm{La}) = 7.0$ G, $g = 2.0015$ (thf, 293 K)] containing one radical anion ligand (bipy = 2,2-bipyridyl)[4] and underline the significant La orbital character of the actual isotropic spectral pattern.

The EPR spectra recorded at the melting point (200–220 K) of the glassy blue solution **2**, exhibited the isotropic spectral features of **A**, that of **B** being undetected up to 275 K. Fig. 1(*b*) shows the EPR spectrum at 275 K. Upon gradually increasing the temperature, the signals due to **B** started appearing and their intensity steadily increased until at 330 K, **B** became the major species. This behaviour was reversed upon cooling. We conclude that in **2**, **A** and **B** represent distinct species in thermal equilibrium, and a plausible interpretation is that the EPR signals **A** and **B** be assigned to the lanthanum(II) species $[\mathrm{K(dme)}_x][\mathrm{La(Cp'')_3}]$ and $[\mathrm{La(Cp'')_2(dme)}_y]$, respectively.

Similar features to those described above for the $[\mathrm{La(Cp'')_3}]$–K system in dme were observed for those in thf, except that no reaction product involving solvent fragmentation was observed; $\mathrm{K(Cp'')}$ was isolated. The EPR spectral data for the thf system showed two octuplets at 295 K (**A** : **B**, *ca.* 4 : 1): $g_{\mathbf{A}} = 1.969(8)$, $a_{\mathbf{A}}(^{139}\mathrm{La}) = 136.0(8)$ G and $g_{\mathbf{B}} = 1.971(8)$, $a_{\mathbf{B}}(^{139}\mathrm{La}) = 146.0(8)$ G.

In order to investigate the reduction of $[\mathrm{La(Cp'')_3}]$ in an alternative fashion, and to obtain a value for the $\mathrm{La^{3+}}$–$\mathrm{La^{2+}}$ reduction potential, the electrochemical reduction of $[\mathrm{La(Cp'')_3}]$ was examined. The cyclic voltammogram of $[\mathrm{La(Cp'')_3}]$ in thf at a vitreous carbon electrode is shown in Fig. 2. The reduction potential $E_{\frac{1}{2}}$ ($La^{3+} \rightarrow La^{2+}$) was found to be -2.8 V and the process was reversible. The cited $E_{\frac{1}{2}}$ value is relative to the $\mathrm{Fc^+}$–Fc couple, ferrocene (Fc) being used as the internal standard.

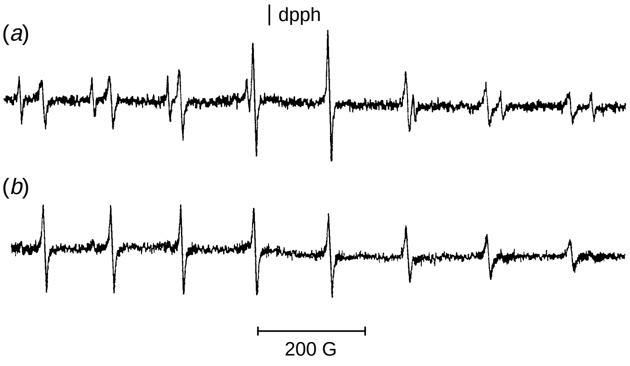
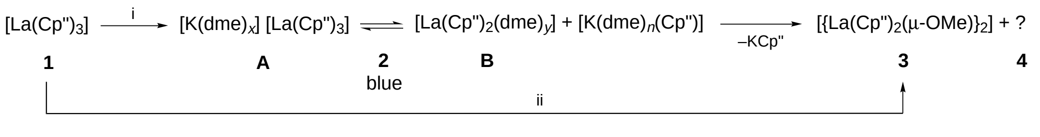


Fig. 1 EPR spectrum of solution **2** in dme at (*a*) 295 and (*b*) 275 K



$$[\mathrm{La(Cp'')_3}] \xrightarrow{\text{i}} [\mathrm{K(dme)}_x]\,[\mathrm{La(Cp'')_3}] \rightleftharpoons [\mathrm{La(Cp'')_2(dme)}_y] + [\mathrm{K(dme)}_n\mathrm{(Cp'')}] \xrightarrow[-\mathrm{KCp''}]{} [\{\mathrm{La(Cp'')_2(\mu\text{-}OMe)}\}_2] + ?$$

Scheme 1 *Reagents and conditions*: i, K mirror, dme, 3 h at −40 °C and then 45 h at 25 °C; ii, MeOH, toluene, 2 h −40 °C. The yield of crystalline **3** (not optimised) was 46% (i) or 50% (ii).

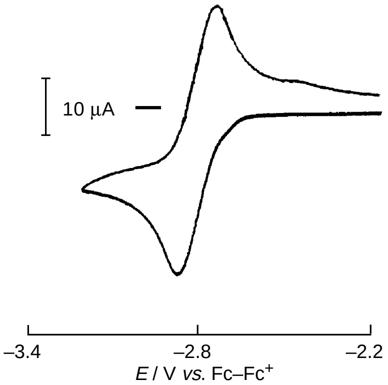


Fig. 2 Cyclic voltammogram of **1** in thf with 0.2 mol dm^{-3} $[\mathrm{NBu_4}][\mathrm{PF_6}]$ as supporting electrolyte at a vitreous carbon working electrode; scan rate 50 mV s^{-1}, 25 °C

By using the NMR-accessible, diamagnetic $\mathrm{La^{III}}$ (f^0), it was further shown that in the reduction of $[\mathrm{La(Cp'')_3}]$ in dme by K, the nature of the final product (like that of the intermediate **A** and **B**) was temperature dependent. When the reduction was initiated at −40 °C, the ^{1}H NMR spectrum in $\mathrm{C_6D_6}$ of the eventually isolated crystalline white solid showed signals attributed not only to K(Cp″) and $[\{\mathrm{La(Cp'')_2(\mu\text{-}OMe)}\}_2]$,‡¶ but also to another species (or mixture) **4** comprising a doublet at δ 6.99 and a singlet at δ 3.47 having *ca.* 10% of the intensity of the corresponding signals in **3**. Repeating the same reaction at ambient temperature, integration showed that the relative abundance of **4** : **3** was *ca.* 1 : 1. A similar trend was observed in the ^{13}C NMR spectra. Homonuclear decoupling and NOE experiments confirmed that the ^{1}H NMR spectral doublet at δ 6.99 and singlet at δ 3.47 be attributed to a second bis(cyclopentadienyl)lanthanum(III) methoxide (the expected triplet for the Cp″ and singlet for the $\mathrm{SiMe_3}$ protons of **4** overlapped with those of **3**); from their relative intensity it is estimated that **4** has three $\mathrm{Cp''^-}$ ligands for each $\mathrm{OMe^-}$. One possible molecular formula, consistent with a $\mathrm{La^{3+}}$ oxidation state, is $[\mathrm{La_6(Cp'')_{12}(OMe)_4O}]$.

From equimolar portions of $[\mathrm{La(Cp'')_3}]$ and methanol, a similar mixture of **3** and **4** was obtained and their relative proportions showed a comparable temperature dependence. Evans *et al.* have previously demonstrated that the reaction of $[\mathrm{Y(\eta\text{-}C_5H_5)_2Cl(thf)}]$ with KOMe gave the polynuclear organoyttrium methoxide oxide $[\{\mathrm{Y(\eta\text{-}C_5H_5)_2(\mu\text{-}OMe)}\}_2\{\mathrm{Y(\eta\text{-}C_5H_5)_2}\}(\mu_3\text{-}\mathrm{O})]^-$.[5]

Among organolanthanide compounds, stable +2 oxidation state complexes were unambiguously established only for those of Yb (f^{14}), Eu(f^7) and Sm(f^6), although claims have been made for $\mathrm{Ce^{II}}$[6] and $\mathrm{Nd^{II}}$.[7] The present results provide definitive evidence for thermally stable organolanthanide(II) complexes, which being oxophilic and powerful reducing agents are able to cleave the C–O bond of dme at ambient temperature (as previously postulated for related Ce and Nd systems).[1]

We thank Drs S. K. Ibrahim and C. J. Pickett for the cyclic voltammetric data, Dr A. G. Avent for the NOE experiment, the European Union for the provision of a Marie Curie Fellowship for M. C. C. and EPSRC for other support.

Footnotes and References

* E-mail: m.f.lappert@sussex.ac.uk

† No reprints available.

‡ *General experimental procedure*: **1** was added to a K mirror in dme at −40 °C. The colour changed immediately to dark blue and after 3 h the mixture was warmed to room temp. and then stirred for 45 h. After filtration, the filtrate was concentrated to a small volume and cooled at −30 °C to give a white crystalline mixture (desolvated by heating for 5 h at 70–80 °C/10^{-2} mmHg). Alternatively, after filtration the solvent was evaporated *in vacuo* and pentane added: a thermolabile, dark green, insoluble product separated from the colourless solution. The nature of the exceedingly air- and moisture-sensitive green product is currently under investigation, while the colourless solution contained K(Cp″), **3** and **4**. After complete removal of coordinated dme the lanthanum(III) methoxides were separated from the K(Cp″) by extraction with toluene.

§ EPR data were taken on an ER 200-D Bruker spectrometer operating at X-band (9.43 GHz); UV–VIS (dme, 298 k): $\lambda_{\max}$ 578.9, 689.8(sh) nm.

¶ *Spectroscopic and analytical data*: K(Cp″) was identified by elemental analysis and by comparing its NMR spectra with those of a separately prepared compound (from HCp″ + KH in thf). The EIMS spectra of the crystalline lanthanum methoxide mixture, obtained either from the reduction in dme or from the protolytic reaction with methanol did not show the dinuclear molecular ion $\mathrm{M^+}$ at m/z = 1178 but the following principal fragments were observed: m/z 1147 $[\mathrm{M} - \mathrm{OCH_3}]^+$, 1133, 1115, 967 $[\mathrm{M} - \mathrm{Cp''}]^+$, 953, 939, 921, 729 and 557 $[\mathrm{La(Cp'')_2}]^+$. ^{1}H NMR ($\mathrm{C_6D_6}$, 293 K) of **3**: δ 7.08 (t, ^4J 1.8 Hz), 6.96 (d, ^4J 1.8 Hz), 3.53 (s), 0.39 (s). DEPT ^{13}C NMR ($\mathrm{C_6D_6}$, 293 K) of **3**: cyclopentadienyl region partially obscured by solvent, δ 130.0 (CH), 125.6 (CH), 54.2 ($\mathrm{OCH_3}$), 1.3 ($\mathrm{SiCH_3}$). IR (Nujol): 3069m, 3042m, 1316m, 1246s, 1208m, 1176w, 1078s, 1051s, 922s, 834vs br, 773s, 751s br, 689s, 640s, 625s cm^{-1}.

1 Yu. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J.Organomet. Chem.*, 1995, **499**, 213.

2 (*a*) R. D. Johnson, M. S. de Vries, J. R. Salem, D. S. Bethune and C. S. Yannoni, *Nature*, 1992, **355**, 239; (*b*) R. D. Johnson, D. S. Bethune and C. S. Yannoni, *Acc. Chem. Res.*, 1992, **25**, 169; (*c*) S. Bandow, H. Shinohara, Y. Saito, M. Ohkohchi and Y. Ando, *J. Phys. Chem.*, 1993, **97**, 6101; (*d*) C. S. Yannoni, H. R. Wendt, M. S. de Vries, R. L. Siemens, J. R. Salem, J. Lyerla, R. D. Johnson, M. Hoinkis, M. S. Crowder, C. A. Brown, D. S. Bethune, L. Taylor, D. Nguyen, P. Jedrzejewsky and H. C. Dorn, *Synthetic Met.*, 1993, **59**, 279.

3 H. Bill and O. Pilla, *J. Phys. C: Solid State Phys.*, 1984, **17**, 3263.

4 M. N. Bochkarev, I. L. Fedushkin, V. I. Nevodchikov, V. K. Cherkasov, H. Schumann, H. Hemling and R. Weimann, *J. Organomet. Chem.*, 1996, **524**, 125.

5 W. J. Evans, M. S. Sollberger, J. L. Shreeve, J. M. Olofson, J. H. Hain and J. W. Ziller, *Inorg. Chem.*, 1992, **31**, 2492.

6 A. Greco, S. Cesca and G. Bertolini, *J. Organomet. Chem.*, 1976, **113**, 321.

7 M. Wedler, A. Recknagel and F. T. Edelmann, *J. Organomet. Chem.*, 1990, **395**, C26.

Received in Basel, Switzerland, 11th April 1997; 7/02493B