Synthesis of Bis(2-methoxyethylcyclopentadienyl) Complexes of Early Lanthanide Chlorides and the *X*-Ray Structure of the Lanthanum Complex

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$[(MeOCH_2CH_2C_5H_4)_2Ln(\mu\text{-}Cl)]_2$ (Ln = La, Pr, and Nd) complexes have been synthesized by the reaction between $LnCl_3$ and $MeOCH_2CH_2C_5H_4Na$ in tetrahydrofuran; a single-crystal *X*-ray study has shown that the lanthanum complex is a chlorine-bridged dimer with lanthanum(III) in a pseudo-octahedral co-ordination geometry if the cyclopentadienyl ring is regarded as occupying a single polyhedral vertex.

Biscyclopentadienyl lanthanide chlorides, $(C_5H_5)_2LnCl$, are of importance in the synthetic chemistry of organolanthanides. Probably owing to the lanthanide contraction effect and co-ordination unsaturation, such complexes of the early lanthanides have not yet been synthesized, however.[1] Only recently has a $(C_5H_5)_2NdCl$ derivative been characterized in higher co-ordination solvated form: $[(C_5H_5)_2Nd(\mu\text{-}Cl)(thf)]_2$ (thf = tetrahydrofuran).[2] In order to develop the organometallic chemistry of the early lanthanides (La—Nd), attempts have been made to stabilize biscyclopentadienyl lanthanide chlorides by using the more bulky pentamethylcyclopentadienyl,[3,4] bis(trimethylsilyl)cyclopentadienyl,[4,5] and hexamethylindenyl[6] groups as ligands. In another approach, we have used ring-bridged biscyclopentadienyl ligands, *e.g.* 1,1′-trimethylene-,[7] 1,1′-(3-oxopentamethylene)-,[8] 1,1′-(*m*-xylene-α,α′-diyl)-, and 1,1′-(*p*-xylene-α,α′-diyl)-biscyclopentadienyl,[9] and pyridine-2,6-diylbis(methylenecyclopentadienyl),[10] to stabilize early lanthanocene chlorides. We think that the good co-ordination environment and the oxophilicity of the metal greatly enhance the stability[11] of the complexes formed. In order to synthesize high co-ordination number biscyclopentadienyl lanthanide chlorides, the ether-substituted cyclopentadienyl ligand, $MeOCH_2CH_2C_5H_4$, has been used and shown to be an efficient ligand for stabilizing biscyclopentadienyl complexes of early lanthanide chlorides.

We now describe the synthesis of such ether-substituted cyclopentadienyl lanthanide chlorides, with the high co-ordination number of ten: $[(MeOCH_2CH_2C_5H_4)_2Ln(\mu\text{-}Cl)]_2$ (Ln = La, Pr, and Nd), and the *X*-ray crystallographic investigation of the lanthanocene complex. Reactions of anhydrous lanthanum, praseodymium, or neodymium trichloride with 2-methoxyethylcyclopentadienylsodium (2 equiv.) in thf solution, followed by removal of solvent and sublimation at 140—240 °C and 10^{-4} mmHg afford complexes (**1**)—(**3**) in 60—70% yields.†

$[(MeOCH_2CH_2C_5H_4)_2Ln(\mu\text{-}Cl)]_2$
(**1**) Ln = La
(**2**) Ln = Pr
(**3**) Ln = Nd

^1H NMR data for (**1**) indicated intramolecular oxygen co-ordination because all proton resonances were shifted to lower field compared with $MeOCH_2CH_2C_5H_4Na$. XPS studies also revealed co-ordination between the metal and the ligand oxygen atoms.[11,12] Compound (**1**) was not easy to characterise on the basis of spectroscopic data and so a single-crystal *X*-ray analysis was completed.‡ Structural information was not hitherto available for biscyclopentadienyllanthanum chloride complexes. The skeletal geometry of complex (**1**) is illustrated in Figure 1.

Complex (**1**) is a chlorine-bridged dimer. The lanthanum atom is co-ordinated by two cyclopentadienyl ligands, and two oxygen and two chlorine atoms. The bond parameters indicate that the structure has a pseudo-octahedral co-ordination geometry if the $C(\eta^5)$-bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex. However, the formal co-ordination number of La^{III} is ten. The $La–C(\eta^5)$ bond

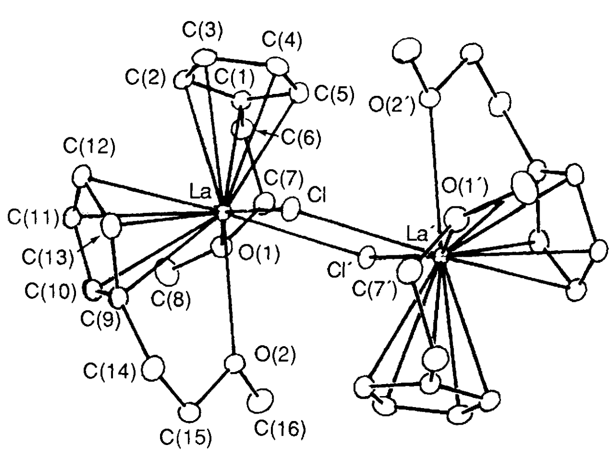

Figure 1. Molecular structure and atom numbering scheme for complex (**1**). Selected bond distances (Å) and angles (°) are as follows: La–Cl 2.914(7), La–Cl′ 2.958(7), La–O(1) 2.666(2), La–O(2) 2.775(2), La–Cp(1′) 2.843, La–Cp(2′) 2.835, La–La′ 4.708, Cl–La–Cl′ 73.41(2), La–Cl–La′ 106.59(2), O(1)–La–O(2) 76.40(8), Cl–La–O(1) 152.55(6), Cl–La–O(2) 88.53(6), Cl′–La–O(1) 79.76(6), Cl′–La–O(2) 69.01(5) (Cp = centroid of cyclopentadienyl ring).

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† *Spectroscopic data:* IR (KBr) for (**1**): ν(C–O–C) 1080m and 1045s cm^{-1}, ν(cyclopentadienyl) 3080m, 1445s, 975m, and 745vs cm^{-1}, ν(La–Cl) 220s cm^{-1}; for (**2**): ν(C–O–C) 1060s and 1045s cm^{-1}, ν(cyclopentadienyl) 3080m, 1440s, 992m, and 775vs cm^{-1}, ν(Pr–Cl) 225s cm^{-1}; for (**3**): ν(C–O–C) 1060s and 1045s cm^{-1}, ν(cyclopentadienyl) 3080m, 1440s, 991w, and 780vs cm^{-1}, ν(Nd–Cl) 225s cm^{-1}; ^1H NMR ($[^2H_8]$tetrahydrofuran) for (**1**): δ 2.60 (t, 2H, $MeOCH_2CH_2$), 3.40 (s, 3H, MeO), 3.60 (t, 2H, $MeOCH_2CH_2$), and 5.63 (s, 4H, $2C_5H_4$). Possibly a 'twinkling' effect of the cyclopentadienyl protons led to their equality, and a single ^1H NMR peak.

‡ *Crystal data* for (**1**): $C_{32}H_{44}Cl_2La_2O_4$, M = 841.4, monoclinic, space group $P2_1/n$, a = 8.726(7), b = 12.367(5), c = 14.562(4) Å, β = 93.91(4)°, V = 1567.8 Å^3, Z = 2, μ(Mo-K_α) = 29.061 cm^{-1}, D_c = 1.782 g cm^{-3}, $F(000)$ = 832, 6771 unique reflections were measured to $2\theta_{max.}$ 70°, 5079 reflections with $F^2 > 3\sigma(F^2)$ were used in the refinement, R = 0.038. All crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K_α radiation (λ = 0.7107 Å). The data sets were corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

lengths range from 2.78 to 2.89 Å, similar to the value reported for (η-C_5H_5)$_3$La(thf),[13] but shorter than the corresponding values for other chlorine-bridged biscyclopentadienyl lanthanide chloride dimers after correction for their effective ionic radii. This shows that the La–C(η^5) bonding is somewhat stronger.

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