# Structure of ($\eta^5$-$C_5Me_5$)$_2$LuCl($C_4H_8O$) and Exchange of Co-ordinated Solvent

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Reaction of $LuCl_3$ and $2NaC_5Me_5$ in tetrahydrofuran (THF) affords crystals of $(C_5Me_5)_2LuCl(THF)$, an *X*-ray structure determination showing the Lu atom to be in a distorted tetrahedral array in which the Lu–Cl bond length is 2.53 Å, the average Lu–C(η) bond length is 2.63 Å, and the ring–Lu–ring angle is 137°; variable temperature n.m.r. spectroscopy shows a dynamic equilibrium between co-ordinated and free THF with a barrier to exchange, $\Delta G^{\ddagger}$, of about 54 kJ mol$^{-1}$ at 0 °C.

The halide derivatives of organolanthanides are important starting materials for further synthetic transformations. Several such bis(pentamethylcyclopentadienyl)lanthanide(III) halides have been crystallographically characterized as alkali halide complexes of the general formula $(C_5Me_5)_2LnX_2M(solv.)_2$ (X = Cl, I; M = Li, Na; solv. = co-ordinated solvent molecules).[1—3] However, no crystal structure studies of the simple parent solvated bis(pentamethylcyclopentadienyl)lanthanide halide complexes, $(C_5Me_5)_2LnCl(solv.)$ [solv. = tetrahydrofuran (THF), *etc.*], have previously been reported.[4] The corresponding ytterbium complex has been reported but crystals suitable for *X*-ray structure determination were not obtained.[1,5] In the present study we chose to work with lutetium because Lu$^{III}$ compounds are diamagnetic and also permit $^1$H n.m.r. studies. The compound was prepared from $LuCl_3$ and $NaC_5Me_5$ following Tilly and Andersen's procedure[5] and transparent crystals of $(C_5Me_5)_2LuCl(THF)$ were obtained from toluene.

The structure is shown in Figure 1† with the lutetium atom at the centre of a distorted tetrahedral array of two pentamethylcyclopentadienyl rings, a chloride atom, and an oxygen atom of tetrahydrofuran. The structure has equal mean lutetium–carbon distances of 2.63 Å; the distance of the lutetium atom to the least-squares plane of the $C_5Me_5$ ring is 2.34 Å. The $C_5Me_5$–Lu–$C_5Me_5$, $C_5Me_5$–Lu–Cl, and $C_5Me_5$–Lu–THF angles are 137, 105, and 105°, respectively. The pendant methyl groups of the $C_5Me_5$ rings are significantly bent from the $C_5$ ring planes, lying on the opposite sides of the $C_5$ rings from Lu. They are displaced by 0.15—0.36 Å (4.5—13°) from the planes of the $C_5$ rings, with the largest deviation in each ring being 0.36 Å (13°) for C(13) and 0.33 Å (12.7°) for C(19). Such out-of-plane displacements have been explained previously for the related system $[(C_5Me_5)_2Yb(THF)]$ in terms of mutual repulsions of the methyl groups in the two co-ordinated $C_5Me_5$ rings from intramolecular contacts for the methyl groups;[6] in other respects the $C_5Me_5$ groups have normal geometries. Similar distorted tetrahedral structures and out-of-plane displacements have also been observed for $(C_5Me_5)_2YbCl_2Li(ether)_2$,[1] $(\mu\text{-}N_2)\{(C_5Me_5)_2ZrN_2\}_2$,[7] and $(C_5Me_5)_2TiCl_2$,[8] in which the distances between the metal, and $C_5$ rings are 2.61, 2.54, and 2.44 Å, respectively. For larger metal atoms, such as thorium in bis[(but-2-ene-2,3-diolato)bis(pentamethylcyclopentadienyl)thorium] with Th–$C_{av.}$ = 2.84 Å, however, the methyl groups lie in the plane of the $C_5$ rings.[9] The ring–ring distances play a critical role in these bending phenomena. The closest distances between two methyl groups on each $C_5$ ring are 3.42 [C(13)–C(18)] and 3.50 Å [C(13)–C(19)]. In addition, the distances of the chloride and oxygen atoms from the nearest methyl groups on each $C_5$ ring are 3.23 [C(11)–Cl], 2.95 [C(15)–O], and 2.73 Å [C(17)–O]. These distances are close to or within the sum of the van der Waals radii. Consequently, the corresponding methyl groups are bent away significantly because of steric repulsions. However, similar comparison shows that some methyl groups are in positions where no obvious steric hindrance effects exist, yet are still bent significantly away from the ring planes. A recent *ab initio* SCF MO study of cyclopentadienyl-lithium showed that a similar bending of the ring hydrogens away from the lithium could be explained simply on the basis of an ionic model consisting of a cyclopentadienyl anion and a point positive charge at the lithium location; such bending puts more negative charge on the face of the ring towards the lithium cation.[10] The same interpretation may apply in the present case to explain why those methyl groups that are not within the van der Waals contact distance are nevertheless bent away from the highly charged Lu$^{3+}$ ion. In the case of thorium, this Coulombic effect is expected to be diminished by the larger distance between ligand and cation.

Mass, i.r., and $^1$H n.m.r. spectra are in good agreement with the solid state structure. The $^1$H n.m.r. spectrum at room temperature of a [$^2H_2$]toluene solution shows chemical shifts of the co-ordinated THF that are different from those of free THF in [$^2H_8$]toluene. A variable temperature 200 MHz $^1$H n.m.r. study of a solution in [$^2H_8$]toluene 0.008 M in $(C_5Me_5)_2LuCl(THF)$ and 0.023 M in free THF showed single n.m.r. peaks for the rapidly exchanging α- and β-protons but

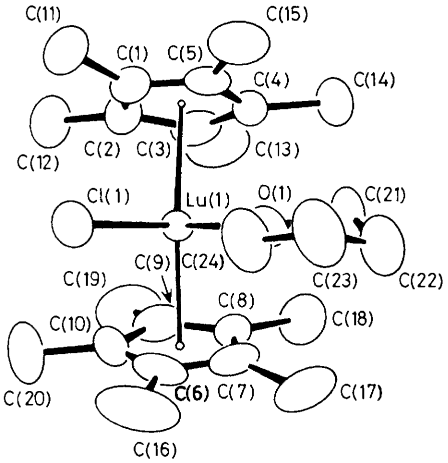

**Figure 1.** Molecular structure and atom numbering scheme for $(C_5Me_5)_2LuCl(THF)$.

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† *Crystal data:* $C_{24}H_{38}LuOCl$, *M* = 553.0; triclinic, space group $P\bar{1}$, *a* = 17.125(6), *b* = 18.246(6), *c* = 8.512(3) Å, α = 91.39(3), β = 87.97(3), γ = 116.87(3)°; *U* = 2370.9 Å$^3$; *Z* = 4, $D_c$ = 1.549 g cm$^{-3}$; *F*(000) = 1112; graphite monochromated Mo-$K_\alpha$ radiation, λ = 0.71073; μ(Mo-$K_\alpha$) = 42.94 cm$^{-1}$; θ–2θ scan, $4.4 < 2\theta < 50.1°$; Picker FACS-1 diffractometer; 11370 reflexions; 8382 unique, and 6746 with $F^2 > 1\sigma(F^2)$ used in the refinement. *R* = 0.031; $R_w$ = 0.047. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

separate peaks at −30 °C: α-protons, $\delta_{free}$ 719.5, $\delta_{co\text{-}ord.}$ 680.0 Hz, coalescence temperature −5.1 °C; β-protons, $\delta_{free}$ 285.0, $\delta_{co\text{-}ord.}$ 220.0 Hz, coalescence temperature 9.8 °C. Rate constants were approximated from the expression $k = 2^{-0.5}\pi\Delta\nu$, and gave an average value for $\Delta G^\ddagger$ of 54 kJ mol$^{-1}$ at 0 °C for the exchange process (1). Owing to the different chemical shift changes involved, the coalescence temperatures differ for the α- and β-protons of the THF. This result provides the first estimation of the bond strength of co-ordinating solvent in such lanthanide complexes.

$$(C_5Me_5)LuCl(THF') + THF'' \rightleftarrows (C_5Me)_5LuCl(THF'') + THF' \quad (1)$$

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the Department of Energy.

*Received, 16th September 1986; Com. 1327*

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