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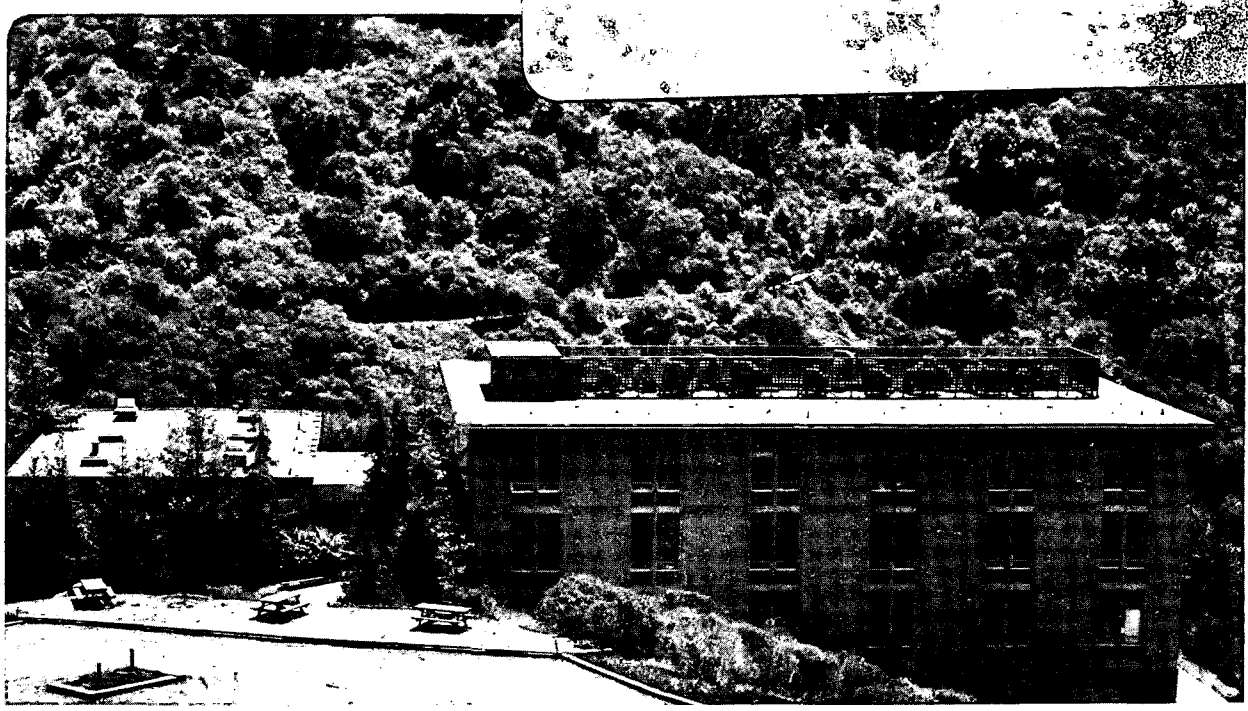
AND EXCHANGE OF COORDINATED SOLVENT

L. Gong, A. Streitwieser, Jr., and A. Zalkin

September 1986



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Structure of $(\eta^5\text{-}C_5(CH_3)_5)_2LuCl(C_4H_8O)$ and Exchange of Coordinated Solvent

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Summary: Reaction of $LuCl_3$ and $2NaC_5Me_5$ in tetrahydrofuran (THF) affords crystals of $(C_5Me_5)_2LuCl(THF)$: x-ray structure determination shows the Lu atom to be in a distorted tetrahedral array in which the Lu-Cl bondlength is 2.53 Å, the average Lu-C(n) bondlength is 2.63 Å and the average Cp-Lu-Cp (ring centers) angle is 137°. Temperature studies of the nmr spectrum show a dynamic equilibrium between coordinated 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) halide compounds have been crystallographically characterized as alkali halide complexes of the general form, $(C_5Me_5)_2LnX_2MS_2$ (X=Cl, I: M=Li, Na: S=coordinated solvent molecules).[1-3] However, no crystal studies of the simple parent solvated bis(pentamethylcyclopentadienyl)lanthanide halides complexes, $(C_5Me_5)_2LnCl(S)$ (S=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 permit ^{1}H NMR studies as well. The compound was prepared from $LuCl_3$ and NaC_5Me_5 in THF[5] and transparent crystals were obtained from toluene. The unit cell contains two crystallographically independent but chemically and geometrically equivalent molecules. The structure for one molecule is shown in Figure 1.

Crystal data: $C_{24}H_{38}LuOCl$, M=552.99, triclinic, space group P1, 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=1.55 g cm^{-3}, Mo-K_α radiation λ=0.71073 Å, μ(MoK_α)=42.94 cm^{-1}, F(000)=1112, 296 K. Refinement converged to give R=0.031, R_w=0.040 for 6746 [$F^2 > 1\ \sigma(F^2)$] data. The atomic coordinates, bond lengths and angles, thermal parameters, experimental details, least-squares planes, additional drawings of the molecules and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. See Notice to Authors, Issue No. 1, 1986.

The molecule with the atom numbering scheme in Figure 1 shows the lutetium atom in the center of a distorted tetrahedral array of two pentamethylcyclopentadienyl (Cp^*) rings, a chloride atom and an oxygen atom of tetrahydrofuran. The structure has the equal mean lutetium-carbon distance of 2.634 Å; the distances of the lutetium atom to the least-squares planes of the cyclopentadienyl (Cp) rings are all close

to 2.34 Å. The angles of C_5Me_5-Lu-C_5Me_5, C_5Me_5-Lu-Cl, C_5Me_5-Lu-THF are 137°, 105°, 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 C_5 ring from Lu. They are displaced by 0.15-0.36 Å (4.5-13°) from the planes of C_5 rings with the largest deviation in each ring being 0.36 Å (13°) for C_{13} and 0.33 Å (12.7 Å) for C_{19}. Such off-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 coordinated Cp^* rings from intramolecular contacts for the methyl groups;[6] in other respects the Cp^* groups have normal geometries. Similar distorted tetrahedral structures and off-plane displacements have also been observed for $Cp^*_2YbCl_2Li(ether)_2$.[1] $(\mu\text{-}N_2)(Cp^*_2ZrN_2)_2$[7] and $Cp^*_2TiCl_2$.[8] in which the distances between metal and C_5 rings are 2.61 Å, 2.54 Å and 2.44 Å, respectively. For larger metal atoms, such as thorium in bis[(2-butene-2,3-diolato]-bis-(pentamethylcyclopentadienyl)thorium] with Th-C_{av}=2.84 Å, however, the methyl groups lie in the plane of C_5 rings.[9] The ring-ring distances play a critical role in these bending phenomena.

In $Cp^*_2LuCl(THF)$, the distance between the metal and C_5 ring planes is 2.63 Å. The closest distances between two methyl groups on each C_5 ring are 3.42 Å (C_{13}-C_{18} and 3.50 Å (C_{13}-C_{19}). In addition, the distances of the chloride and oxygen atoms with the nearest methyl groups on each C_5 ring are 3.23 Å (C_{11}-Cl), 2.95 Å (C_{15}-O), and 2.73 Å (C_{17}-O). These distances are close to or within the sum of the Van de Waals radii. Consequently, the corresponding methyl groups are bent away significantly because of obvious 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 intio SCF MO study of cyclopentadienyllithium has shown that a similar bending of 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 methyl groups, which are not within Van de Waals contacts, 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 Analysis, IR and ^1H NMR spectra are in good agreement with the solid state structure. The ^1H NMR spectrum at room temperature of a toluene-d_8 solution shows chemical shifts of the coordinated THF that are different from those of free THF in toluene-d_8. A variable temperature ^1H 200 MHz NMR study of a solution in toluene-d_8 0.008M in $Cp^*LuCl(THF)$ and 0.023M in free THF showed single nmr peaks for the rapidly exchanging α- and β-protons but separate peaks at -30°C: α-protons, δ_{free} 719.5 Hz, δ_{coord} 680.0 Hz, coalescence temperature = -5.1°C; β-protons, δ_{free} 285.0 Hz, δ_{coord} 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

$$Cp^*LuCl(THF') + THF'' = Cp^*LuCl(THF'') + THF'$$

Note that because of the different chemical shift changes involved, the coalescence temperatures differ for the α- and β-protons of the THF. This result provides the first determination of the bond strength of coordinating solvent in such lanthanide complexes.

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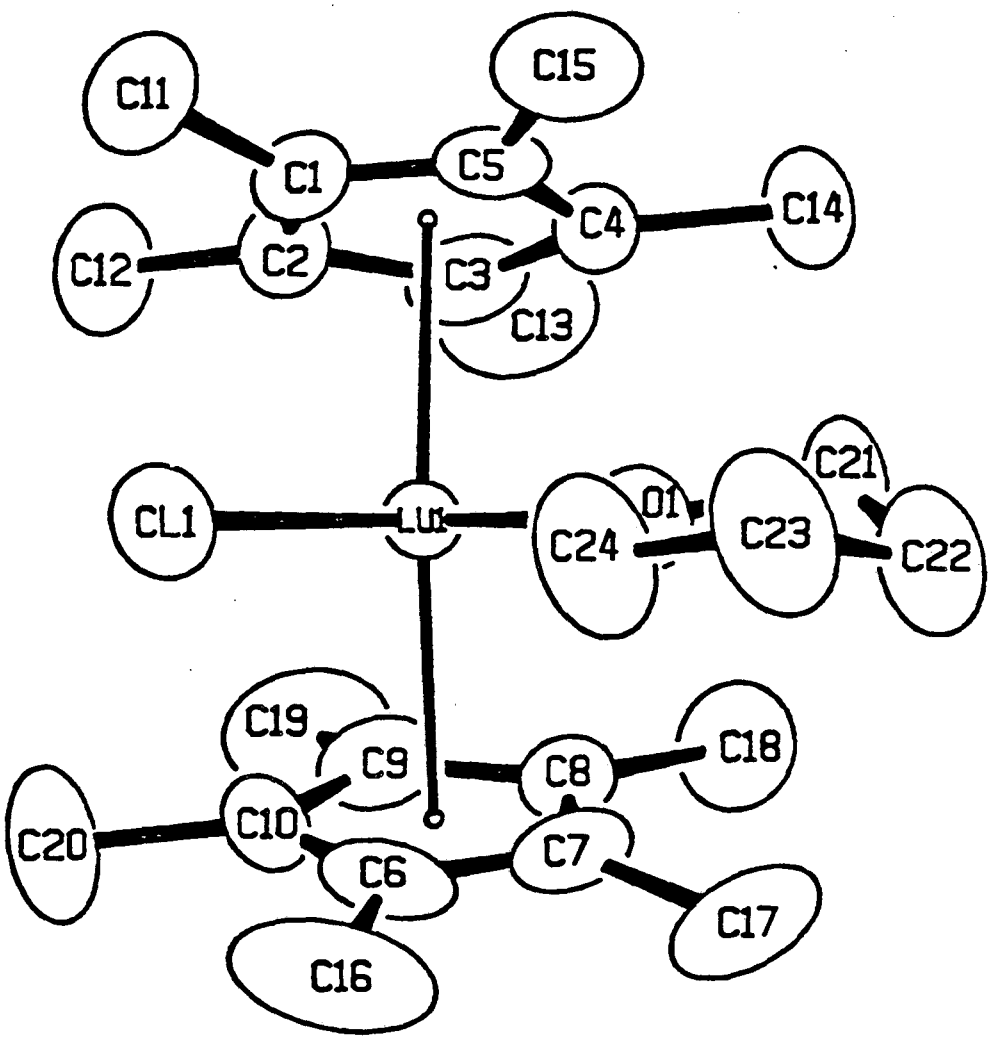
Figure 1. Molecular structure and atom numbering scheme for $(C_5Me_5)_2LuCl(THF)$.


C11
C15
C1
C5
C4
C14
C12
C2
C3
C13
CL1
LU
C24
O1
C23
C21
C22
C19
C9
C8
C18
C20
C10
C7
C6
C17
C16

Supplementary Material

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Structure of $[(CH_3)_5C_5]_2LuCl\cdot OC_4H_8$

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Supplemental Table 1. Positional and Isotropically Equivalent Thermal Parameters with Standard Deviations for $[(CH_3)_5C_5]_2LuCl \cdot OC_4H_8$

Molecule 1

atom	x	y	z	B_{eq} [a]
Lu(1)	0.24457(1)	0.01077(1)	0.12313(3)	2.580(8)
Cl(1)	0.14118(12)	-0.05268(12)	-0.10109(22)	5.07(7)
O(1)	0.13977(28)	-0.08539(25)	0.2926(5)	4.0(1)
C(1)	0.1902(4)	0.1228(4)	0.0804(8)	4.0(2)
C(2)	0.2791(4)	0.1621(4)	0.0635(8)	3.9(2)
C(3)	0.3162(4)	0.1655(4)	0.2120(9)	4.2(2)
C(4)	0.2464(5)	0.1244(4)	0.3195(8)	4.0(2)
C(5)	0.1680(4)	0.0985(4)	0.2372(9)	4.0(2)
C(6)	0.3003(5)	-0.0963(5)	0.0350(11)	5.2(3)
C(7)	0.3218(5)	-0.0801(5)	0.1935(11)	5.3(3)
C(8)	0.3837(4)	-0.0011(5)	0.2106(8)	4.1(3)
C(9)	0.4043(4)	0.0345(4)	0.0606(10)	4.7(2)
C(10)	0.3514(5)	-0.0245(6)	-0.0490(8)	5.3(3)
C(11)	0.1258(6)	0.1194(6)	-0.0425(10)	6.3(4)
C(12)	0.3328(6)	0.2076(5)	-0.0821(10)	6.2(3)
C(13)	0.4131(5)	0.2229(5)	0.2575(13)	7.0(3)
C(14)	0.2552(7)	0.1253(5)	0.4994(9)	6.4(4)
C(15)	0.0739(5)	0.0610(6)	0.3057(12)	6.9(4)
C(16)	0.2386(7)	-0.1815(7)	-0.0350(17)	10.4(6)
C(17)	0.2888(8)	-0.1483(7)	0.3197(15)	9.1(5)
C(18)	0.4327(7)	0.0391(7)	0.3608(11)	7.7(5)
C(19)	0.4861(6)	0.1166(6)	0.0170(14)	8.1(4)
C(20)	0.3588(8)	-0.0135(10)	-0.2266(11)	10.9(8)
C(21)	0.1399(6)	-0.0845(5)	0.4655(8)	5.4(3)
C(22)	0.0778(6)	-0.1713(5)	0.5153(10)	6.5(3)
C(23)	0.0132(6)	-0.1988(6)	0.3844(11)	7.7(4)
C(24)	0.0636(5)	-0.1573(5)	0.2381(10)	6.8(3)

Supplemental Table 1 (continued)

		Molecule2		
atom	$\bar{x}$	y	z	B_{eq}
Lu(2)	0.25076(1)	0.51689(1)	0.37975(3)	2.574(8)
Cl(2)	0.14505(13)	0.46942(13)	0.61155(23)	5.35(7)
O(2)	0.14292(26)	0.42300(26)	0.2175(5)	4.0(1)
C(25)	0.3025(5)	0.6451(4)	0.1971(9)	4.8(3)
C(26)	0.2153(5)	0.6156(4)	0.2022(11)	5.3(3)
C(27)	0.1890(5)	0.6243(5)	0.3559(13)	5.7(3)
C(28)	0.2655(7)	0.6615(4)	0.4447(9)	5.5(3)
C(29)	0.3359(4)	0.6758(4)	0.3437(9)	4.0(2)
C(30)	0.4057(4)	0.5220(5)	0.3634(10)	4.8(3)
C(31)	0.3528(5)	0.4532(5)	0.2738(8)	4.8(3)
C(32)	0.2928(4)	0.3941(4)	0.3777(10)	4.3(2)
C(33)	0.3091(5)	0.4277(4)	0.5282(9)	4.3(3)
C(34)	0.3771(5)	0.5067(5)	0.5217(10)	4.8(3)
C(35)	0.3553(9)	0.6535(7)	0.0401(12)	9.8(6)
C(36)	0.1568(8)	0.5879(7)	0.0577(15)	10.0(5)
C(37)	0.0969(8)	0.6052(8)	0.4107(22)	14.4(8)
C(38)	0.2733(13)	0.6946(8)	0.6140(12)	14.6(10)
C(39)	0.4341(6)	0.7358(5)	0.3827(15)	8.8(4)
C(40)	0.4950(6)	0.5909(6)	0.3102(17)	9.7(5)
C(41)	0.3713(8)	0.4386(8)	0.1010(11)	8.8(6)
C(42)	0.2257(7)	0.3051(5)	0.3416(13)	7.5(4)
C(43)	0.2664(7)	0.3813(7)	0.6798(11)	7.3(4)
C(44)	0.4189(7)	0.5630(6)	0.6629(13)	8.0(5)
C(45)	0.0529(5)	0.3783(6)	0.2710(11)	7.4(3)
C(46)	0.0060(7)	0.3251(8)	0.1293(13)	11.3(5)
C(47)	0.0672(7)	0.3481(8)	-0.0063(13)	10.5(5)
C(48)	0.1548(6)	0.4038(6)	0.0537(9)	6.5(3)

[a] $B_{eq} = 1/3\sum B_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$

Supplemental Table 2. Anisotropic Thermal Parameters (A^2)[b] with Estimated Standard Deviations for $[(CH_3)_5C_5]_2LuCl\cdot OC_4H_8$

Molecule 1

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Lu(1)	2.777(11)	2.504(11)	2.471(11)	1.201(8)	-0.314(8)	-0.312(8)
Cl(1)	5.19(8)	6.06(9)	4.05(8)	2.59(7)	-1.95(7)	-1.79(7)
O(1)	3.91(19)	3.27(18)	3.99(22)	0.87(15)	0.37(16)	0.08(16)
C(1)	4.7(3)	3.85(29)	4.0(3)	2.41(25)	-1.05(26)	-0.36(24)
C(2)	4.9(3)	3.72(28)	3.5(3)	2.12(25)	-0.31(25)	-0.02(23)
C(3)	4.02(29)	2.73(25)	6.0(4)	1.54(22)	-1.88(28)	-1.19(26)
C(4)	6.7(4)	3.04(26)	2.89(28)	2.75(27)	-0.51(27)	-0.42(21)
C(5)	4.28(29)	3.07(26)	5.3(4)	2.36(23)	-0.09(27)	-0.69(25)
C(6)	4.9(3)	4.6(3)	6.9(5)	3.0(3)	0.0(3)	-1.9(3)
C(7)	5.9(4)	4.9(4)	6.6(5)	3.9(3)	1.4(4)	1.9(3)
C(8)	4.4(3)	5.4(4)	3.9(3)	3.44(29)	-0.12(26)	0.16(27)
C(9)	3.36(27)	4.6(3)	6.5(4)	2.19(25)	0.89(28)	1.2(3)
C(10)	6.4(4)	9.4(6)	2.8(3)	6.0(4)	0.07(29)	-0.3(3)
C(11)	6.7(4)	8.2(5)	5.4(4)	4.4(4)	-2.4(4)	-0.6(4)
C(12)	8.0(5)	6.2(4)	4.4(4)	3.1(4)	1.2(4)	1.8(3)
C(13)	4.8(4)	4.4(4)	10.6(7)	0.9(3)	-3.2(4)	-2.1(4)
C(14)	11.3(7)	5.9(4)	3.1(3)	4.7(4)	-1.5(4)	-1.3(3)
C(15)	4.8(4)	7.3(5)	9.4(6)	3.5(4)	2.7(4)	1.7(5)
C(16)	8.6(6)	7.3(6)	15.8(11)	4.2(5)	-3.4(7)	-7.3(7)
C(17)	10.5(7)	8.8(6)	11.1(8)	7.1(6)	4.4(6)	6.2(6)
C(18)	8.4(6)	12.0(8)	5.5(5)	6.8(6)	-3.5(4)	-2.0(5)
C(19)	5.0(4)	6.8(5)	12.3(8)	2.6(4)	3.8(5)	3.4(5)
C(20)	12.3(8)	22.2(14)	3.4(4)	12.4(10)	1.1(5)	1.6(6)
C(21)	7.3(5)	4.4(3)	3.0(3)	1.3(3)	0.3(3)	0.51(25)
C(22)	7.3(5)	4.7(4)	4.7(4)	0.4(3)	0.9(4)	0.5(3)
C(23)	6.7(5)	5.8(5)	6.3(5)	-0.7(4)	1.8(4)	0.5(4)
C(24)	4.9(4)	5.3(4)	5.6(4)	-1.2(3)	-0.0(3)	-0.8(3)

Supplemental Table 2 (continued)

Molecule 2

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Lu(2)	2.643(11)	2.531(11)	2.582(12)	1.204(8)	0.067(8)	0.071(8)
Cl(2)	5.54(9)	6.98(11)	4.18(9)	3.48(8)	1.93(7)	1.48(8)
O(2)	3.13(18)	3.92(20)	4.11(22)	0.81(15)	-0.52(16)	-0.41(17)
C(25)	6.7(4)	3.36(29)	4.5(4)	2.32(29)	0.5(3)	1.00(26)
C(26)	5.8(4)	3.11(29)	7.0(5)	1.81(28)	-2.1(4)	0.8(3)
C(27)	3.9(3)	3.8(3)	9.9(7)	2.29(27)	2.0(4)	2.4(4)
C(28)	10.1(6)	3.3(3)	3.7(3)	3.7(4)	0.6(4)	0.06(25)
C(29)	4.17(29)	3.20(27)	4.6(3)	1.50(23)	-0.20(26)	0.53(24)
C(30)	3.59(28)	4.7(3)	6.8(5)	2.48(26)	0.5(3)	2.0(3)
C(31)	5.8(4)	7.4(5)	3.1(3)	4.8(4)	0.32(28)	0.1(3)
C(32)	4.2(3)	3.40(28)	6.2(4)	2.43(24)	-0.94(29)	-1.13(28)
C(33)	4.7(3)	5.1(3)	4.1(3)	3.14(29)	0.62(27)	1.18(28)
C(34)	4.9(3)	4.9(3)	5.4(4)	2.86(29)	-2.1(3)	-1.1(3)
C(35)	16.0(10)	7.5(6)	5.4(5)	5.0(6)	6.0(6)	2.8(4)
C(36)	10.9(8)	7.2(6)	10.6(8)	2.4(5)	-6.8(7)	0.6(5)
C(37)	9.3(7)	10.6(8)	26.8(17)	8.1(7)	10.7(9)	9.4(10)
C(38)	34.4(21)	8.9(7)	3.9(5)	13.0(11)	2.3(8)	-0.4(5)
C(39)	6.1(5)	4.5(4)	14.3(9)	0.8(3)	-4.4(5)	0.9(5)
C(40)	4.0(4)	7.9(6)	17.4(11)	2.8(4)	3.3(5)	6.0(7)
C(41)	10.8(7)	14.9(10)	3.8(4)	8.7(7)	1.4(4)	-0.1(5)
C(42)	9.0(6)	3.3(3)	10.5(7)	2.9(4)	-3.7(5)	-1.8(4)
C(43)	8.8(6)	9.8(6)	5.3(5)	5.8(5)	2.4(4)	4.3(4)
C(44)	10.0(7)	7.6(5)	7.6(6)	4.7(5)	-5.0(5)	-2.8(5)
C(45)	3.1(3)	8.4(5)	6.7(5)	-0.8(3)	0.7(3)	-0.2(4)
C(46)	6.5(6)	13.0(9)	6.4(6)	-3.0(6)	-2.7(5)	0.7(6)
C(47)	6.8(6)	11.8(8)	6.1(6)	-1.8(5)	-2.2(5)	-2.1(5)
C(48)	5.7(4)	8.3(5)	3.6(4)	1.5(4)	-0.7(3)	-2.2(3)

[b] Temperature factor has the form: $-0.25\exp(h^2a^{*2}B_{11} + 2hka^*b^*B_{12}+\cdots)$.

Supplemental Table 3. Selected Interatomic Distances in $[(CH_3)_5C_5]_2LuCl \cdot OC_4H_8$[a]

Molecule 1		Molecule 2	
Lu(1) - O(1)	2.340(04)	Lu(2) - O(2)	2.336(04)
Lu(1) - Cl(1)	2.529(02)	Lu(2) - Cl(2)	2.517(02)
Lu(1) - C(1)	2.637(07)	Lu(2) - C(25)	2.624(07)
Lu(1) - C(2)	2.608(07)	Lu(2) - C(26)	2.661(07)
Lu(1) - C(3)	2.623(06)	Lu(2) - C(27)	2.629(07)
Lu(1) - C(4)	2.621(06)	Lu(2) - C(28)	2.582(07)
Lu(1) - C(5)	2.638(06)	Lu(2) - C(29)	2.610(06)
Lu(1) - C(6)	2.619(07)	Lu(2) - C(30)	2.612(07)
Lu(1) - C(7)	2.635(07)	Lu(2) - C(31)	2.624(07)
Lu(1) - C(8)	2.622(06)	Lu(2) - C(32)	2.646(06)
Lu(1) - C(9)	2.605(06)	Lu(2) - C(33)	2.628(07)
Lu(1) - C(10)	2.595(07)	Lu(2) - C(34)	2.595(07)
O(1) - C(21)	1.472(08)	O(2) - C(45)	1.443(08)
O(1) - C(24)	1.451(08)	O(2) - C(48)	1.460(09)
C(1) - C(2)	1.362(09)	C(25) - C(26)	1.338(11)
C(1) - C(5)	1.401(10)	C(25) - C(29)	1.388(10)
C(2) - C(3)	1.422(09)	C(26) - C(27)	1.397(12)
C(3) - C(4)	1.405(10)	C(27) - C(28)	1.412(12)
C(4) - C(5)	1.411(09)	C(28) - C(29)	1.383(11)
C(6) - C(7)	1.400(12)	C(30) - C(31)	1.397(11)
C(6) - C(10)	1.400(11)	C(30) - C(34)	1.407(11)
C(7) - C(8)	1.357(10)	C(31) - C(32)	1.408(10)
C(8) - C(9)	1.406(10)	C(32) - C(33)	1.389(10)
C(1) - C(11)	1.527(09)	C(33) - C(34)	1.385(10)
C(2) - C(12)	1.533(10)	C(25) - C(35)	1.558(12)
C(3) - C(13)	1.567(09)	C(26) - C(36)	1.540(12)
C(4) - C(14)	1.543(09)	C(27) - C(37)	1.510(11)
C(5) - C(15)	1.536(10)	C(28) - C(38)	1.537(12)
C(6) - C(16)	1.550(11)	C(29) - C(39)	1.579(10)
C(7) - C(17)	1.551(11)	C(30) - C(40)	1.537(10)
C(8) - C(18)	1.534(10)	C(31) - C(41)	1.536(11)
C(9) - C(10)	1.407(11)	C(32) - C(42)	1.537(10)
C(9) - C(19)	1.560(10)	C(33) - C(43)	1.531(10)
C(10) - C(20)	1.523(11)	C(34) - C(44)	1.533(11)
C(21) - C(22)	1.516(10)	C(45) - C(46)	1.533(13)
C(22) - C(23)	1.510(13)	C(46) - C(47)	1.465(15)
C(23) - C(24)	1.499(12)	C(47) - C(48)	1.482(11)
Cp(1) - Lu(1)	2.340	Cp(4) - Lu(2)	2.336
Cp(2) - Lu(1)	2.331	Cp(3) - Lu(2)	2.342

[a]Cp(1)-Cp(4) are the centroids of atoms C(1)-C(5), C(6)-C(10), C(25)-C(29) & C(30)-C(34) respectively.

Supplemental Table 4. Selected Interatomic Angles (°) in

$[(CH_3)_5C_5]_2LuCl \cdot OC_4H_8$

Molecule 1		Molecule 2	
Cl(1)-Lu(1)-O(1)	89.0(12)	Cl(2)-Lu(2)-O(2)	90.10(13)
Lu(1)-O(1) -C(21)	127.1(4)	Lu(2)-O(2) -C(45)	121.8(5)
Lu(1)-O(1) -C(24)	123.3(4)	Lu(2)-O(2) -C(48)	126.5(4)
C(21)-O(1) -C(24)	109.6(5)	C(45)-O(2) -C(48)	111.7(6)
C(2) -C(1) -C(5)	108.7(6)	C(26)-C(25)-C(29)	110.0(8)
C(2) -C(1) -C(11)	125.4(7)	C(26)-C(25)-C(35)	122.3(9)
C(5) -C(1) -C(11)	125.1(7)	C(29)-C(25)-C(35)	127.1(8)
C(1) -C(2) -C(3)	108.8(6)	C(25)-C(26)-C(27)	108.4(7)
C(1) -C(2) -C(12)	127.0(7)	C(25)-C(26)-C(36)	124.8(10)
C(3) -C(2) -C(12)	123.6(7)	C(27)-C(26)-C(36)	126.3(9)
C(2) -C(3) -C(4)	107.2(6)	C(26)-C(27)-C(28)	106.9(7)
C(2) -C(3) -C(13)	126.1(7)	C(26)-C(27)-C(37)	125.9(11)
C(4) -C(3) -C(13)	125.1(7)	C(28)-C(27)-C(37)	127.0(17)
C(3) -C(4) -C(5)	107.4(6)	C(27)-C(28)-C(29)	107.5(7)
C(3) -C(4) -C(14)	124.8(7)	C(27)-C(28)-C(38)	127.2(11)
C(5) -C(4) -C(14)	126.6(7)	C(29)-C(28)-C(38)	124.6(11)
C(1) -C(5) -C(4)	108.0(6)	C(25)-C(29)-C(28)	107.2(7)
C(1) -C(5) -C(15)	123.8(7)	C(25)-C(29)-C(39)	127.2(8)
C(4) -C(5) -C(15)	127.7(7)	C(28)-C(29)-C(39)	123.8(8)
C(7) -C(6) -C(10)	107.7(7)	C(31)-C(30)-C(34)	108.4(6)
C(7) -C(6) -C(16)	125.4(10)	C(31)-C(30)-C(40)	125.7(9)
C(10)-C(6) -C(16)	126.6(10)	C(34)-C(30)-C(40)	123.8(9)
C(6) -C(7) -C(8)	109.5(7)	C(30)-C(31)-C(32)	107.6(7)
C(6) -C(7) -C(17)	122.7(9)	C(30)-C(31)-C(41)	124.9(8)
C(8) -C(7) -C(17)	127.1(9)	C(32)-C(31)-C(41)	126.2(8)
C(7) -C(8) -C(9)	107.7(7)	C(31)-C(32)-C(33)	107.5(6)
C(7) -C(8) -C(18)	126.5(8)	C(31)-C(32)-C(42)	128.6(8)
C(9) -C(8) -C(18)	125.2(8)	C(33)-C(32)-C(42)	123.8(8)
C(8) -C(9) -C(10)	108.3(7)	C(32)-C(33)-C(34)	109.5(6)
C(8) -C(9) -C(19)	125.5(8)	C(32)-C(33)-C(43)	125.2(8)
C(10)-C(9) -C(19)	124.7(8)	C(34)-C(33)-C(43)	124.9(8)
C(6) -C(10)-C(9)	106.8(7)	C(30)-C(34)-C(33)	107.1(7)
C(6) -C(10)-C(20)	127.6(10)	C(30)-C(34)-C(44)	126.7(8)
C(9) -C(10)-C(20)	125.2(10)	C(33)-C(34)-C(44)	126.0(8)
O(1) -C(21)-C(22)	105.8(6)	O(2) -C(45)-C(46)	104.3(8)
C(21)-C(22)-C(23)	101.4(7)	C(45)-C(46)-C(47)	109.0(7)
C(22)-C(23)-C(24)	106.6(7)	C(46)-C(47)-C(48)	106.7(8)
O(1) -C(24)-C(23)	105.3(7)	O(2) -C(48)-C(47)	107.5(7)
Cp(1)-Lu(1)-Cp(2)	136.66	Cp(4)-Lu(2)-Cp(3)	136.50
Cp(1)-Lu(1)-Cl(1)	105.51	Cp(4)-Lu(2)-Cl(2)	105.71
Cp(2)-Lu(1)-Cl(1)	106.05	Cp(3)-Lu(2)-Cl(2)	106.17
Cp(1)-Lu(1)-O(1)	105.02	Cp(4)-Lu(2)-O(2)	104.75
Cp(2)-Lu(1)-O(1)	104.47	Cp(3)-Lu(2)-O(2)	104.02

Supplemental Table 5. Crystallographic Summary and Data Processing for $[(CH_3)_5C_5]_2LuCl \cdot OC_4H_8$

a, Å[a]	17.125(6)
b, Å	18.246(6)
c, Å	8.512(3)
α, °	91.39(3)
β, °	87.97(3)
γ, °,	116.87(3)
cryst syst	triclinic
space group	$P\bar{1}$
volume, Å^3	2370.9
d(calcd),g/cm^{-3}	1.549
Z	4
temp (°C)	23.0
empirical formula	$C_{24}H_{38}O_1Cl_1Lu_1$
f(000), e	1112
fw	552.99
color	yellow
reflection rules	None.
x-ray	MoKα (graphite monochromated)
wave-length (Ka_1,Ka_2), Å	0.70930,0.71359
crystal size (mm)	0.18 x 0.27 x 0.50
abs coeff, cm^{-1}	42.94
abs corr range	1.94-3.11
cryst decay corr range	0.92-1.03
diffractometer	modified Picker FACS-1
sinθ/λ, min,max	0.054, 0.596
hkl limits	h -20,20; k -21,21; l -10,2
scan type & 2θ limits, °	θ-2θ, 4.4-50.1
scan width, °2θ	1.50 + 0.693 × tanθ
no. of standards, frequency	3, 200
variation of standards (%)	5.41,2.57,3.69
no. scan data	11370
no. unique reflections	8382

Supplemental Table 5. (continued)

Rint[b]	0.022
no. non-zero weighted data	6746 ($F^2 > 1\ \sigma$)
p[c]	0.050
extinction k[d]	9.25×10^{-8}
max % extinction corr	9.1
no. parameters	487
R (non-zero wtd dat)[e]	0.031
Rw[f]	0.040
R (all data)	0.047
Goodness of fit[g]	1.20
max shift/esd in least-square	0.0375
max/min in diff map ($e/Å^3$)	0.87,-0.61

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved MoKa components of 27 reflections ($20°<2\theta<35°$).

[b] R_{int} = agreement factor between equivalent or multiply measured reflections = $\Sigma[I_{hkl} - \langle I_{hkl}\rangle] / \Sigma\langle I_{hkl}\rangle$

[c] In the least-squares, the assigned weights to the data are $1.0/[\sigma(F)]^2$ were derived from $\sigma(F^2) = [S^2 + (pF^2)^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.

[d] Simple extinction correction, (Fobs)corr = (1 + kI)Fobs, where I is the uncorrected intensity and Fobs is the observed scattering amplitude.

[e] $R = \Sigma(|F_{obs}|-|F_{cal}|)/\Sigma|F_{obs}|$

[f] $R_w = \sqrt{[\Sigma w(|F_{obs}|-|F_{cal}|)^2/\Sigma wF_{obs}^2]}$

[g] σ_1 = error in observation of unit weight = $\sqrt{[\Sigma(w(|F_{obs}|-|F_{cal}|)^2)/(n_o-n_v)]}$, where n_o is the number of observations and n_v is the number of variables.

Supplemental Table 6. Least Squares Planes in $[(CH_3)_5C_5]_2LuCl\cdot OC_4H_8$

Plane No. 1

$-7.71626\ x + 17.81169\ y + 1.63871\ z = 0.84603$

Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
C(1)	0.0048(96)	Lu(1)	-2.340(4)
C(2)	-0.0086(96)	C(11)	0.240(16)
C(3)	0.0099(100)	C(12)	0.149(16)
C(4)	-0.0081(106)	C(13)	0.359(16)
C(5)	0.0012(096)	C(14)	0.234(17)
		C(15)	0.171(16(

Plane No. 2

$16.17839\ x - 12.62953\ y - 0.86778\ z = 6.04486$

Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
C(6)	0.0005(119)	Lu(1)	-2.331(41)
C(7)	0.0050(115)	C(16)	0.138(20)
C(8)	-0.0069(106)	C(17)	0.223(19)
C(9)	0.0071(108)	C(18)	0.149(19)
C(10)	-0.0079(133)	C(19)	0.332(18)
		C(20)	0.127(24)

Plane No. 3

$-6.34185\ x + 17.71217\ y - 2.11809\ z = 9.10308$

Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
C(25)	-0.0118(118)	Lu(2)	-2.342(4)
C(26)	0.0064(120)	C(35)	0.133(21)
C(27)	0.0022(138)	C(36)	0.193(20)
C(28)	-0.0125(139)	C(37)	0.131(24)
C(29)	0.0077(98)	C(38)	0.167(28)
		C(39)	0.366(18))

Plane No. 4

$15.74269\ x - 13.64237\ y + 1.39017\ z = -0.24036$

Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
C(30)	0.0118(111)	Lu(2)	-2.336(04)
C(31)	-0.0087(119)	C(40)	0.403(19)
C(32)	-0.0003(105)	C(41)	0.242(20)
C(33)	0.0066(103)	C(42)	0.106(17)
C(34)	-0.0110(106)	C(43)	0.178(18)
		C(44)	0.075(18)

Supplemental Table 6. (continued)

Plane No.5

-8.02733 x + 17.85119 y + 1.53269 z = 0.98749

Distance to the Plane (Å)			
Atoms in the Plane		Atoms not in the Plane	
C(11)	0.069(14)	Lu(1)	-2.570(5)
C(12)	-0.079(13)		
C(13)	0.071(14)		
C(14)	-0.034(15)		
C(15)	-0.024(14)		

Plane No. 6

16.06306 x - 12.91549 y - 0.86085 z = 6.22043

Distance to the Plane (Å)			
Atoms in the Plane		Atoms not in the Plane	
C(16)	-0.013(18)	Lu(1)	-2.537(6)
C(17)	0.058(17)		
C(18)	-0.085(17)		
C(19)	0.067(16)		
C(20)	-0.088(23)		

Plane No. 7

-6.79783 x + 17.68671 y - 2.24216 z = 9.14713

Distance to the Plane (Å)			
Atoms in the Plane		Atoms not in the Plane	
C(35)	-0.094(19)	Lu(2)	-2.561(7)
C(36)	0.056(18)		
C(37)	-0.023(24)		
C(38)	-0.095(27)		
C(39)	0.058(17)		

Plane No. 8

15.45402 x - 13.90270 x + 1.72828 z = -0.10911

C(40)	0.080(19)	Lu(2)	-2.545(7)
C(41)	( )		
C(42)	-0.054(16)		
C(43)	0.100(16)		
C(44)	-0.100(16)		

Supplemental Table 6. (continued)

Plane No. 9

-14.55992 x - 15.26391 y - 0.90825 z = 3.05704

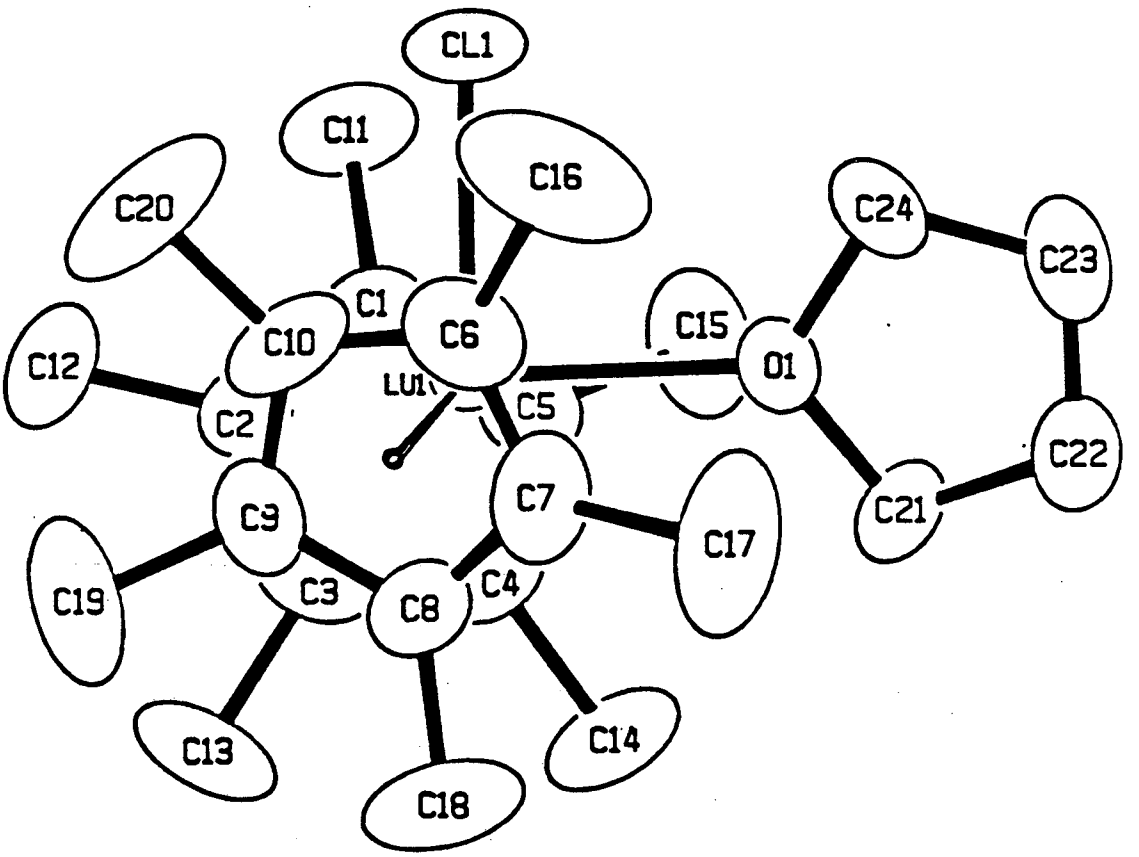
Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
O(1)	0.016(6)	Lu(1)	0.228(12)
C(21)	-0.154(12)		
C(22)	0.223(13)		
C(23)	-0.180(13)		
C(24)	0.054(12)		
Lu(1)	0.228(12)		

Plane NO.10

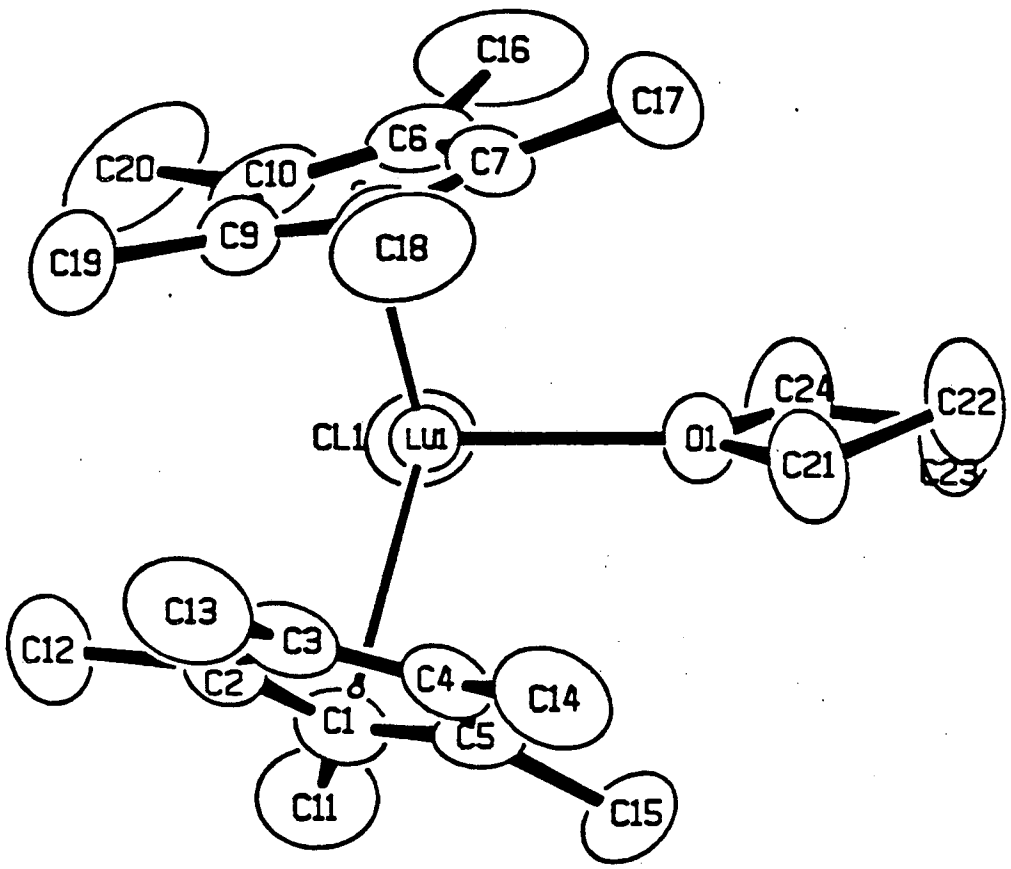
-10.20524 x + 17.19673 y - 2.57496 z = 5.25368

Distance to the Plane (A)			
Atoms in the Plane		Atoms not in the Plane	
O(2)	0.002(7)	Lu(2)	0.098(14)
C(45)	0.014(14)		
C(46)	-0.057(18)		
C(47)	0.063(17)		
C(48)	-0.028(13)		

Supplemental Figure 1. ORTEP view of molecule 1, 50% probability ellipsoids.

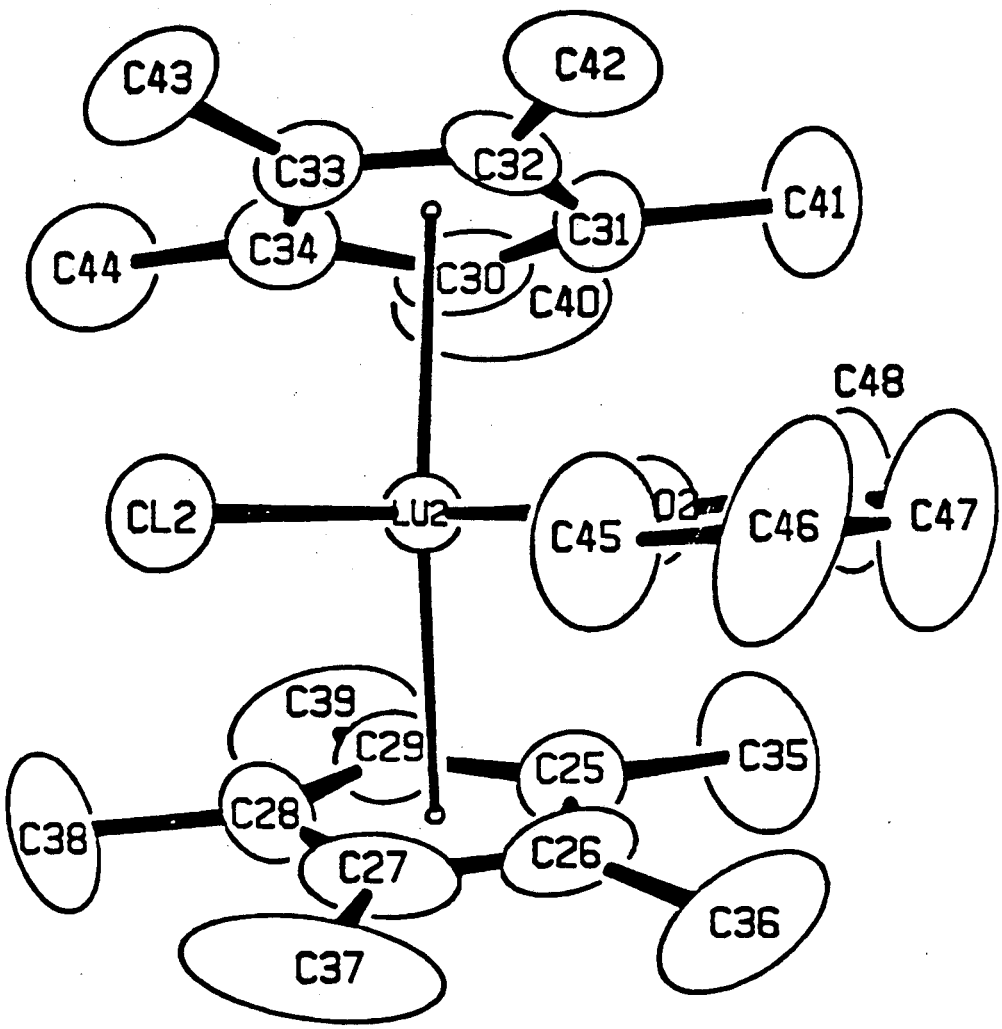


Supplemental Figure 2. ORTEP view of molecule 1 as seen down the Lu(1)-Cl(1) bond; 50% probability ellipsoids.



Supplemental Fig. 3.

ORTEP view of molecule 2, 50% probability ellipsoids. Selected Distances and angles: <Lu(2)-C(Cp)> 2.621(23); <C(Cp)-C(Cp)> 1.396(21); <C(Cp)-C(Me)> 1.540(18); Cp-Lu(2) 2.336,2.342; Lu(2)-Cℓ(2) 2.517(2); Lu(2)-O(2) 2.336(4); Cp(3)-Lu(2)-Cp(4) 136.5; Cp(4)-Lu(2)-Cℓ(2) 105.7; Cp(3)-Lu(2)-Cℓ(2) 106.2; Cp(4)-Lu(2)-O(2) 104.8; Cp(3)-Lu(2)-O(2) 104.0; Cℓ(2)-Lu(2)-O(2) 90.10(13)



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