

Heteroleptic t-Butyl Lanthanoid Complexes: Synthesis and X-Ray Crystal Structure of Monomeric Bis(cyclopentadienyl)(t-butyl)lutetium Tetrahydrofuranate

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Summary $(C_5H_5)_2Lu(Bu^t)$, synthesized from $[(C_5H_5)_2LuCl]_2$ and Bu^tLi in pentane-tetrahydrofuran at $-78^\circ C$, crystallizes from toluene as a monomeric tetrahydrofuran solvate which contains a 2.37 \AA Lu-C σ bond and a short (2.31 \AA) Lu-O distance; the analogous erbium complex is prepared similarly but, in the ytterbium case, the reaction generates $(C_5H_5)_2Yb$.

ALTHOUGH interest in the organometallic chemistry of the lanthanoid elements is rapidly increasing, the lanthanoid metal-carbon σ bond has been structurally characterized for only four molecules: two anionic complexes, $[Li(THF)_4][Lu(C_5H_5)_2]^-$ and $[Li(THF)_4][Yb\{CH(SiMe_3)_2\}_3Cl]^-$,² (THF = tetrahydrofuran) and two neutral, alkyl-bridged complexes, $(C_5H_5)_2Yb(\mu-Me)_2AlMe_2$ ³ and $[(C_5H_5)_2Yb(\mu-Me)]_2$.⁴ As part of our general investigation of lanthanoid-carbon σ bonds,⁵⁻⁷ and our specific study of t-butyl complexes,⁵ we report here the synthesis, characterization, and X-ray crystal structure determination of a neutral, monomeric lanthanoid alkyl complex, $(C_5H_5)_2Lu(Bu^t)(THF)$. This new member of the important general class of bis(cyclopentadienyl)lanthanoid alkyl complexes⁸ is the first reported example in which the alkyl group contains β -hydrogens. As a neutral monomer, this complex allows the first direct structural comparison with neutral bridged bis(cyclopentadienyl)lanthanoid alkyls, and demonstrates the importance of the ligand *vis-à-vis* the solvent in the dimerization of lanthanoid alkyls.

The complexes, $(C_5H_5)_2Ln(Bu^t)(THF)$ ($Ln = Er, Lu$), were synthesized by treatment of a pentane solution of Bu^tLi with a THF solution of $[(C_5H_5)_2LnCl]_2$ at $-78^\circ C$, followed by stirring at room temperature for 12 h. The solvent was removed and the residue was extracted with toluene. Removal of solvent from this extract and re-extraction with toluene provides a solution from which the complexes crystallize at $0^\circ C$ in analytically pure form as the monomeric THF solvates. In contrast, when the alkyl group is methyl, the analogous procedure generates dimeric, alkyl-bridged species, $[(C_5H_5)_2Ln(\mu-Me)]_2$.^{4,8}

The analogous t-butyl ytterbium complex, $(C_5H_5)_2Yb(Bu^t)(THF)$, could not be prepared in a similar manner. Under the reaction conditions, $[(C_5H_5)_2YbCl]_2$ is immediately reduced to $(C_5H_5)_2Yb$ (identified by i.r., near i.r.-visible, and 1H n.m.r. spectroscopy). This reduction constitutes another facile synthesis of a divalent ytterbium complex.^{6,9}

The pink erbium and off-white lutetium complexes are extremely air- and moisture-sensitive. They are thermally stable at room temperature. The complexes are slightly soluble in alkane solvents and are soluble in toluene and THF. Characterization was effected by complete elemental analysis (Lu), complexometric metal analysis (Er),

1H n.m.r. [$Lu, C_6D_6: \delta 6.02$ (10H, s, C_5H_5), 3.14 (4H, m, THF), 1.30 (9H, s, Bu^t), and 0.96 (4H, m, THF)], ^{13}C n.m.r. [$Lu, C_6D_6: \delta 110.31$ (d, $J 166$ Hz, C_5H_5), 72.85 (t, $J 151$ Hz, THF), 37.61 (s, CM_{e3}), 35.41 (q, $J 120$ Hz, CM_{e3}), and 25.08 (t, $J = 132$ Hz, THF) p.p.m.], and i.r. spectroscopy. The i.r. spectra (Nujol mulls) of both complexes exhibit absorptions characteristic of Bu^t (1455 cm^{-1}) and of C_5H_5 ($1010, 770 \text{ cm}^{-1}$) groups. Absorptions assignable to coordinated THF appear as shoulders on the cyclopentadienyl bands ($1040, 890 \text{ cm}^{-1}$). A series of absorptions at $2770, 2740$, and 2680 cm^{-1} are also found in these spectra. Such absorptions have previously been observed in anionic transition and f element organometallic alkyl complexes and have been assigned as C-H stretching frequencies lowered by interaction of an alkyl hydrogen with the counteraction, e.g. $Li-H_3C$.^{5,10,11} If this assignment is correct, the perturbation of $\nu(CH)$ in the neutral $(C_5H_5)_2Ln(Bu^t)(THF)$ complexes may be due to a Ln^{3+} interaction with the methyl groups of the t-butyl ligand, since no lithium is present in these compounds. This interaction is subtle, however, since the X-ray structure of the lutetium complex indicates no gross deformation of the carbon skeleton of the t-butyl group toward lutetium.

A single crystal of $(C_5H_5)_2Lu(Bu^t)(OC_4H_8)$ was obtained from a toluene solution thermostatted at $0^\circ C$ and was examined by X-ray diffraction. *Crystal data:* $C_{18}H_{27}LuO$, orthorhombic, space group $Pnma$, $M = 434.4$, $a = 16.066(7)$, $b = 12.790(5)$, $c = 8.699(4) \text{ \AA}$, $U = 1787.5 \text{ \AA}^3$, $D_c = 1.61 \text{ g cm}^{-3}$, $Z = 4$, $F(000) = 856$, $\lambda(Mo-K\alpha) = 0.71069 \text{ \AA}$, $\mu(Mo-K\alpha) = 57.9 \text{ cm}^{-1}$. The crystal structure was solved from 976 independent observed reflections and refined to

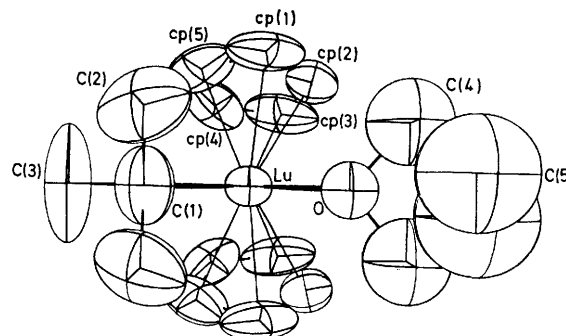


FIGURE. Molecular structure of $(C_5H_5)_2Lu(Bu^t)(THF)$ with the atoms represented by their 50% probability ellipsoids for thermal motion. Other important lengths and angles include: Lu-centroid 2.36 \AA ; \angle centroid-Lu-centroid' 125.6° ; centroid-Lu-C(1) 110° ; centroid-Lu-O 106° ; C(1)-Lu-O 94.1° .

$R = 0.046$. A view of the molecule (which resides on a crystallographic mirror plane) is shown in the Figure.† The disorder of the carbon atoms of the THF molecule is apparent and is illustrated by the large isotropic spheres.

The Lu–C σ bond length of 2.47(2) Å compares favourably with the 2.45 Å value found in the structure of [Li(THF)₄]-[Lu(C₆H₃Me₂)₄].¹ Although no other lutetium structures have been reported, the title compound may be compared with [Li(THF)₄][Yb{CH(SiMe₃)₂}₃Cl]², since Yb³⁺ and Lu³⁺ only differ by 0.01 Å in radius.¹² The ytterbium complex contains Yb–C σ bond lengths which average 2.38(1) Å. Hence, both known Lu–C σ bond lengths are significantly longer, possibly owing to steric crowding in both complexes. The average Lu–C η distance, 2.63(1) Å, is also slightly larger than expected in comparison with Yb–C η distances which range from 2.585(8)¹³ to 2.61 Å^{3,4} in bis(cyclopentadienyl)ytterbium(III) complexes. On the other hand, the distance between the THF oxygen atom and lutetium, 2.31(2) Å, is shorter than would be expected based on the structures of (C₅H₅)₃Ln(THF), (Ln = La,¹⁴ Gd,¹⁵ and Y¹⁴). The Y–O length in the latter complex is 2.454(7) Å, and Y³⁺ is only ca. 0.05 Å larger than Lu³⁺.¹² This structural feature is consistent with the fact that THF remains co-ordinated to the metal centre during recrystallization from toluene. Although the Lu–C σ bond length in the title compound is longer than that in [Li(THF)₄][Yb{CH(SiMe₃)₂}₃Cl], it is still shorter than the Yb–C σ distances in

the neutral bridging methyl complexes (C₅H₅)₂Yb(μ -Me)₂-AlMe₂³ [2.56(2), 2.61(2) Å] and [(C₅H₅)₂Yb(μ -Me)]₂⁴ [2.54(2), 2.49(2) Å].

The synthesis of these compounds proves that bis(cyclopentadienyl)lanthanoid alkyls, in which the alkyl group contains a β -hydrogen atom, are not necessarily unstable. In addition, the structure of the lutetium complex demonstrates that dimeric structures are not always favoured in non-polar solvents by this class of compound. Steric congestion at the metal centre obviously plays a role, not only in dictating the monomeric nature of the complexes but also in their inability to undergo facile decomposition *via* β -hydrogen elimination. However, the lutetium complex will decompose in the solid state at 75 °C to yield 2-methylpropane and 2-methylpropene in the ratio 2:2:1. In contrast, the homoleptic *t*-butyl complex, [Li(THF)₄][SmBu₄], decomposes in solution⁵ and in the solid state to form, almost exclusively, 2-methylpropane.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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