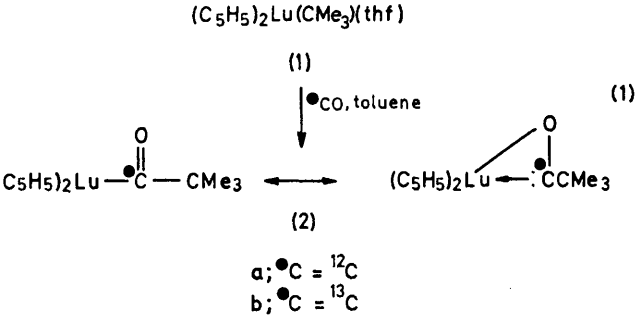
Organolanthanoid Activation of Carbon Monoxide: Single and Multiple Insertion of CO into t-Butyl Lanthanoid Bonds; *X*-Ray Crystallographic Identification of a New Bonding Mode for a Bridging Enedione Diolate Ligand Formed by Formal Coupling of Four CO Molecules

By William J. Evans* and Andrea L. Wayda
(*Department of Chemistry, The University of Chicago, Chicago, Illinois* 60637)

and William E. Hunter and Jerry L. Atwood*
(*Department of Chemistry, The University of Alabama, University, Alabama* 35486)

Summary Carbon monoxide (1 equiv.) reacts with $(C_5H_5)_2Lu(CMe_3)(OC_4H_8)$ at room temperature to form the isolable dihaptoacyl complex $(C_5H_5)_2Lu(\eta^2\text{-}COCMe_3)$, which reacts with additional CO to form the crystallographically characterized bimetallic complex $(C_5H_5)_2LuO_4C_{12}H_{18}Lu(C_5H_5)_2$ in which the two metals are bridged by the enedione diolate ligand 4,5-dihydroxy-2,2,7,7-tetramethyloct-4-ene-3,6-dionato(2 −), which forms 6-membered metallocyclic rings with each metal atom.

Activation of carbon monoxide by early transition-metal organometallic compounds is now well documented.[1,2] Similar reactivity has been demonstrated recently for actinoid organometallic compounds.[3,4] In contrast, no such reactivity has been observed for organolanthanoid complexes.[5] As part of our general investigation of the reactivity of lanthanoid–carbon σ-bonded complexes[6] and our specific study of t-butyl complexes,[7] we now report that $(C_5H_5)_2Lu(CMe_3)(thf)$ (**1**)[7] (thf = tetrahydrofuran) reacts with 1 equiv. of CO to form the dihapto-acyl complex (**2**) Furthermore, reaction of (**1**) with excess of CO ultimately generates a complex in which four molecules of carbon monoxide have been coupled to form an enedione diolate moiety which bridges two lutetium centres.



In toluene solution, freshly crystallized off-white (**1**) (0·56 mmol) reacts with 1 equiv. of CO at room temperature during 2—3 days according to equation (1). Solvent removal yields the pale yellow organolanthanoid acyl (**2**) (0·422 mmol, 75% yield). The air- and moisture-sensitive (**2**) is thermally stable at room temperature. Furthermore, it does not decarbonylate and does not decompose when heated at 100 °C in toluene for 24 h. The complex is slightly soluble in pentane and moderately soluble in toluene and tetrahydrofuran. Complex (**2**) is formulated as $(C_5H_5)_2Lu(\eta^2\text{-}COCMe_3)$ based on characterization by ^1H n.m.r. [C_6D_6: δ 5·94 (s, C_5H_5) and 0·90 (s, CMe_3)], ^{13}C n.m.r. [C_6D_6: δ 108·93 (C_5H_5) and 25·25 p.p.m. (CMe_3)], and i.r. spectroscopy (Nujol mull: 3095w, 3080w, 1765w, br, 1655w, br, 1490s, 1360m, 1350m, 1260w, 1230w, 1010s, 890s, and 780s, br cm^{-1}), complexometric metal analysis (calc. for $LuC_{15}H_{19}O$: Lu, 44·83; found: Lu, 44·29), and isopiestic molecular weight determination (in thf, calc., 390; found, 414). The i.r. absorption at 1490 cm^{-1} is assigned to the C–O stretching frequency of the η^2-$COCMe_3$ unit by analogy with the structurally characterized $(C_5H_5)_2Zr(\eta^2\text{-}COMe)$ (ν_{CO} 1545 cm^{-1})[2] and $(C_5Me_5)_2Th(\eta^2\text{-}COCH_2CMe_3)Cl$ (ν_{CO} 1469 cm^{-1})[4] and from the results of the following ^{13}CO labelling study. The reaction of 90% enriched ^{13}CO (Prochem) with (**1**) gave the yellow acyl complex (**2b**) in which the ν_{CO} absorption had shifted to 1460 cm^{-1} (Fluorolube mull). In addition, the ^{13}C n.m.r. spectrum of (**2b**) contained an additional resonance at δ 380·6 p.p.m. assignable to the acyl carbon (*cf.* δ 360·2 for the thorium acyl[4]).

When a toluene solution of (**1**) (0·53 mmol) is allowed to react with an excess of CO (8·6 mmol), the initially clear, colourless solution undergoes several colour changes (yellow to orange to red) until CO uptake ceases and the solution is deep red-purple [equation (2)]. From this reaction mixture, a deep purple complex (**3**), formally analogous to the thorium enedione diolate complex (**4**),[4] can be isolated by removal of solvent followed by pentane extraction of the deep purple residue. Removal of pentane from this solution yields analytically pure (**3**) (0·084 mmol, 32% yield).

$$2(C_5H_5)_2Lu(CMe_3)(thf) \xrightarrow[\text{toluene, 25 °C}]{\text{excess CO}} \{(C_5H_5)_2Lu[{}^{\bullet}CO(CMe_3){}^{\blacksquare}CO]\}_2 \qquad (2)$$

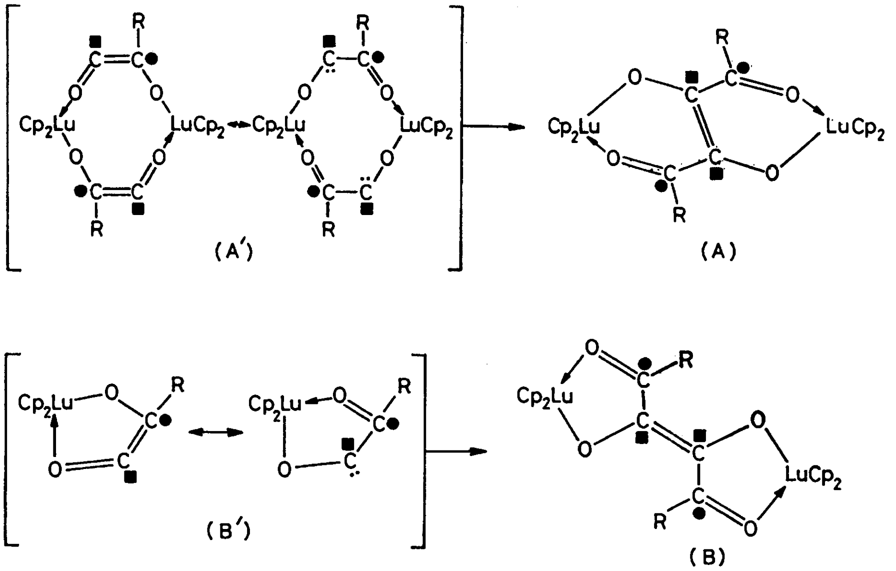
(**3**)

a; ●C = ■C = ^{12}C
b; ●C = ^{12}C; ■C = ^{13}C
c; ●C = ^{13}C; ■C = ^{12}C

$$\{(C_5Me_5)_2ClTh[OC(CH_2CMe_3)CO]\}_2$$

(**4**)

Complex (**3**), which has room-temperature stability and solubility similar to that of (**2**), was characterized by ^1H n.m.r. [C_6D_6: δ 6·14 (s, C_5H_5) and 1·24 (s, CMe_3)], ^{13}C n.m.r. [C_6D_6: δ 111·11 (C_5H_5) and 26·89 p.p.m. ($CMe)_3$], and i.r. spectroscopy (Nujol mull: 1750w, 1650w, 1545m, 1520s,



R = CMe$_3$, Cp = C$_5$H$_5$

SCHEME. Keten–carbene intermediates to enedione diolate structures.

1385m, 1290s, 1260m, 1100s, 1010s, and 780s, br cm^{-1}), elemental analysis, an isopiestic molecular weight determination (in thf, calc., 836; found, 799), and the following labelling studies.

Two ^{13}CO labelled analogues of (**3**) were prepared by reaction of (**2a**) with ^{13}CO, (**3b**), and by reaction of the ^{13}CO enriched (**2b**) with CO, (**3c**). The ^{13}C n.m.r. spectra of these labelled complexes supported the presence of an enedione diolate moiety by comparison with the reported spectra for the analogous derivatives of the thorium enedione diolate complex (**4**).[4] Complex (**3b**) exhibited a resonance at δ 153·1 p.p.m. for the ■C atoms whereas (**3c**) displayed a resonance at δ 215·4 p.p.m. for the ●C atoms [*cf.* δ 158·6 and 217·8 p.p.m. for appropriately labelled (**4**)]. However, although the data indicated that (**3**) was a bimetallic bridged enedione diolate complex, the information at hand was insufficient to determine the geometric disposition of the bridging ligand. Two isomers, structurally related by rotation around the ●C–■C bonds are possible: the six-membered metallocyclic complex (A), formally viewed as arising from the C–C fusion of the intermediate bimetallic keten complex (A′) (Scheme), or the five-membered metallocycle (B), formally viewed as arising from the dimerization of the keten monomer (B′). The latter type of structure is observed for (**4**), with (B′) as the most plausible intermediate[4] [rather than (A′) which, after ■C–■C fusion, would require a change in the oxygen atoms co-ordinated to each thorium atom *via* rotation around the ●C–■C bonds].

In order to resolve the question of the mode of enedione diolate co-ordination in (**3c**), a single crystal of the complex was obtained by slow concentration of a benzene solution at ambient temperature and examined by X-ray dffraction.† The crystal structure was solved from 1580 independent observed reflections and refined to $R = 0{\cdot}038$; *crystal data:* $C_{32}H_{38}Lu_2O_4$, triclinic, space group $P\bar{1}$, $M = 836{\cdot}6$, $a = 8{\cdot}284(4)$, $b = 9{\cdot}522(4)$, $c = 10{\cdot}738(5)$ Å, $\alpha = 68{\cdot}01(4)$, $\beta = 75{\cdot}17(4)$, $\gamma = 80{\cdot}78(4)^\circ$, $U = 737{\cdot}3$ Å^3, $D_c = 1{\cdot}83$ g cm^{-3}, $Z = 1$ (dimer), $F(000) = 404$, $\lambda(\text{Mo-}K_\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 68{\cdot}3$ cm^{-1}. A view of the molecule (which resides on a crystallographic centre of symmetry) is shown in the Figure.

As shown in the Figure, the enedione diolate moiety in (**3c**) exhibits geometry (A), rather than (B), the geometry found for (**4**).[4] Hence, using a 4f element as the activating metal, a new mode of organometallic CO activation and coupling results. The structure observed for (**3c**) could easily arise from intermediate (A′), although this result obviously does not prove the existence of such a precursor. In addition to the different co-ordination modes of the enedione diolate bridge in (**3c**) and (**4**), two other prominent differences between these structures should be noted. The lutetium complex has a much larger O–M–O angle, 76·5 *vs.* 62·7°, and significantly shorter M–O bonds, 2·09 Å *vs.* 2·27 Å and 2·215 Å *vs.* 2·53 Å (even taking into account the fact that eight-co-ordinate Lu^{+3} has a smaller radius, 0·977 Å, than the nine-co-ordinate Th^{+4}, 1·09 Å[9]).

Although the formation of complex (**3**) is the primary reaction occurring in this system, it is not the only reaction pathway as evidenced by the formation of brown, toluene soluble by-products which, as yet, have not yielded to characterization by standard methods (i.r., ^{1}H n.m.r.). The formation of these minor products is apparently enhanced by the sequential synthesis of (**3**) from isolated (**2**).

These studies clearly demonstrate that organolanthanoid

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† Details of the data collection and refinement procedure are given in reference 8. An absorption correction was applied in this case. 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.

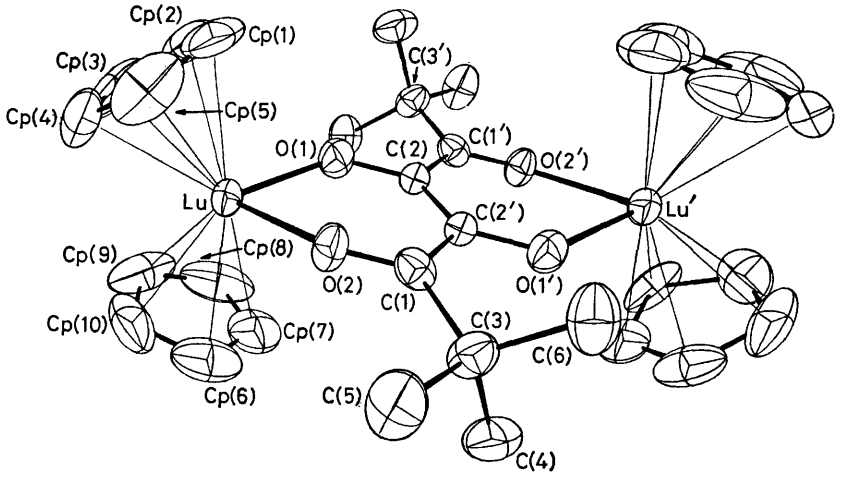

FIGURE. Molecular structure of (**3b**) with the atoms represented by their 50% probability ellipsoids for thermal motion. Important bond lengths (Å) and angles (degrees) include: Lu–O(1), 2·09, Lu–O(2), 2·215, O(1)–C(2), 1·33, C(2)–C(2'), 1·40, C(1)–C(2'), 1·48, C(1)–O(2), 1·24, Lu–cyclopentadienyl (av.), 2·60, ∠Lu–O(2)–C(1), 135, O(2)–C(1)–C(2'), 122, C(1)–C(2')–C(2), 122.

complexes are capable of reacting with CO and forming isolable CO-insertion products. We have observed similar reactivities for related organolanthanoid complexes and the possibility that variation of the ligand environment around the lanthanoid ion may influence reactivity and provide for the isolation of new types of CO-insertion compounds is under investigation. Finally, these results also establish that multiple coupling of CO is achievable without using pentamethyl-substituted cyclopentadienide as co-ligand.

For support of this research we thank the Division of Basic Energy Sciences of the Department of Energy (W. J. E., A. L. W.) and the National Science Foundation (J. L. A., W.E.H.). We also thank Bell Laboratories for a fellowship (to A. L. W.) under the Bell Laboratories Graduate Research Program for Women, and the Camille and Henry Dreyfus Foundation for a Teacher–Scholar Grant (to W. J. E.).

(*Received, 23rd February* 1981;‡ *Com.* 200.)

‡ Received in revised form (including crystallographic details) 24th March 1981.

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