Bimetallic Lanthanide Complexes with Lanthanide–Transition Metal Bonds. Molecular Structure of $(C_4H_8O)(C_5H_5)_2Lu–Ru(CO)_2(C_5H_5)$. The Use of ^{139}La NMR Spectroscopy

Irina P. Beletskaya,*[1a] **Alexander Z. Voskoboynikov**,*[1b] **Elena B. Chuklanova**,[1b] **Natalia I. Kirillova**,[1b] **Alla K. Shestakova**,[1b] **Inna N. Parshina**,[1b] **Alexei I. Gusev**,[1b] **and Gusein K.-I. Magomedov**[1b]

Contribution from the State Scientific Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow 111123, Russia, and Department of Chemistry, Moscow State University, V-234, Moscow, GSP, 119899, Russia

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Abstract: The reactions of $Cp_2LuCl(THF)$ (**1**), $\{Cp''_2Lu(\mu\text{-}Cl)\}_2$ (**2**), $Cp^*_2Lu(\mu\text{-}Cl)_2Na(THF)_2$ (**3**), and $LaI_3(THF)_3$ with the salt $Na[CpRu(CO)_2]$ yielded heterobimetallic complexes $(THF)_nX_2LnRu(CO)_2Cp$ (Ln = Lu, $n = 1$, X = C_5H_5 (Cp) (**4**) or 1,3-$(Me_3Si)_2C_5H_3$ (Cp'') (**5**); $n = 0$, X = C_5Me_5 (Cp*) (**6**); Ln = La, $n = 3$, X = I (**9**)). The structure of **4** has been established by X-ray crystal analysis ($P2_1/n$, $a = 14.083$ (2) Å, $b = 8.347$ (2) Å, $c = 17.331$ (2) Å, $\beta = 106.98°$, $Z = 4$, $d_{calc} = 2.04$ g/cm^3, $R = 0.0373$, $R_w = 0.0369$). Complex **4** is the first example of a compound characterized by X-ray crystal structure in which there is a direct lanthanide–metal bond (Lu–Ru 2.955 (2) Å) without the additional coordination through bridging ligands. According to IR and NMR evidence the Ln–Ru bond in **4–6** and **9** is stable in solutions. Reactivity of cluster complexes toward HCl, H_2O, $HgCl_2$, $i\text{-}Pr_2CO$, MeI, H_2, CO, $PhMeSiH_2$, and $Me_3SiC{\equiv}CSiMe_3$ has been investigated. Reaction of **5** with HCl and H_2O yielded **2** and $\{Cp''_2Lu(\mu\text{-}OH)\}_2$ (**10**), structures of which have been determined by X-ray crystal analysis (**2**: $P\bar{1}$, $a = 10.744$ (3) Å, $b = 11.821$ (2) Å, $c = 12.966$ (3) Å, $\alpha = 71.54$ (1)°, $\beta = 85.32$ (2)°, $\gamma = 74.83$ (1)°, $Z = 1$, $d_{calc} = 1.38$ g/cm^3, $R = 0.0202$, $R_w = 0.0206$; **10**: $P2_1/n$, $a = 15.638$ (6) Å, $b = 15.787$ (2) Å, $c = 12.188$ (1) Å, $\beta = 99.06°$, $Z = 2$, $d_{calc} = 1.37$ g/cm^3, $R = 0.0280$, $R_w = 0.0298$). Both **2** and **10** possess similar dimeric structures with a pair of bridging ligands Cl or OH, respectively. Average distances are 2.62 Å for Lu–Cl and 2.26 Å for Lu–O. ^{139}La spectroscopy has been used for studying Schlenk type equilibria for both cyclopentadienyl complexes Cp_3La, $CpLaI_2$, and $\{Cp''_2La(\mu\text{-}Cl)\}_2$ and bimetallic complexes $X_2La–Ru(CO)_2Cp$.

Introduction

Synthetic approaches to various types of bimetallic complexes of lanthanides in the oxidation states +3[2] and +2[2a,3] have been recently developed. Mono-, di-, and trisubstituted complexes of trivalent lanthanides $X_2Ln[M(CO)_nL_m]$, $XLn[M(CO)_nL_m]_2$, and $Ln[M(CO)_nL_m]_3$ and also the $Ln[M(CO)_nL_m]_2$ and $XLn[M(CO)_nL_m]$ complexes for divalent samarium, europium, and ytterbium have been synthesized.

These compounds revealed a lot of interesting structural features in solution and in the solid state.[2b] According to X-ray crystal analysis, the isocarbonyl bonding Ln–OC–M, where the bridging carbonyl is incorporated between lanthanide and transition metal atoms, is the predominant type of bonding for this class of compounds. This type of bonding has been observed for both monosubstituted and trisubstituted complexes $(THF)Cp^*_2YbOCCo(CO)_3$[4a] and $(THF)_5La[OCMo(CO)_2Cp]_3$,[4b] as well as for some other types of complexes of lanthanides[4c] and other oxophilic metals (U, Ti, Zr, V, Al, Mg, etc.).[5] For the erbium complex $(EtOH)(H_2O)_4Er[Mo(CO)_3Cp]_3$ a weak interaction between erbium and molybdenum atoms was proven, and the carbonyl there is of the semibridging kind (Figure 1).[6,7] This is the first and only known example of π-coordination of the CO ligand with an f-element. The stability of this unusual compound might be explained by the decrease of oxophilicity of the erbium atom owing to the coordination with five small donor ligands. Some ionic carbonyl metalates of lanthanides have been

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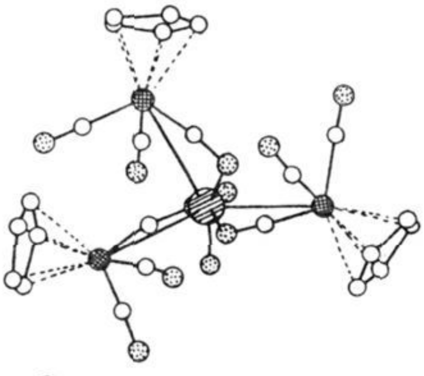


Figure 1. View of $(EtOH)(H_2O)_4Er[(C_5H_5)Mo(CO)_3]_3$.[6,7]

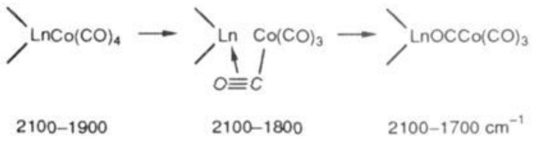
Table I. The Types of Lanthanide–Transition Metal Bonding

Bonding type [a]	An example	Chatacteristic bond length, Å	
		Ln–O(CO)	Ln–M
 Ionic	$[Cl_2Lu(THF)_5][Co(CO)_4]$[b]	5.577 min.	
 μ(σ)–CO or μ–OC	$(THF)_5La[OCMo(CO)_2Cp]_3$[c]	2.444 ave.	
 μ(π)–CO + Ln–M	$(EtOH)(H_2O)_4Er[Mo(CO)_3Cp]_3$[d]	1.983 ave.	3.143 ave.[f]
 Ln–M	$(THF)Cp_2LuRu(CO)_2Cp$[e]		2.955[g]

[a] ○ C ● Ln ● O ○ M. [b] Ref. 8b. [c] Ref. 4b. [d] Ref. 6. [e] Authors' results. [f] Sum of metallic radii $R_{Er} + R_{Mo} = 3.14$. [g] Sum of metallic radii $R_{Er} + R_{Mo} = 3.08$.

discovered in the series $[X_2(THF)_5Ln][Co(CO)_4]$ (X = I, Ln = Sm;[8a] X = Cl, Ln = Lu[8b]). Thus, as much as three different types of bonding have been discovered to date in the solid state (Table I).

Before our preliminary report on the structure of $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$ (compound **4** below), which included an Lu–Ru distance,[10a] no structure with a bond between a lanthanide and a transition metal unsupported by bridging ligands had been confirmed by X-ray analysis.[10b,c] However, investigations of solution IR spectra have revealed numerous examples of equilibria, in which both free ions X_2Ln^+ and $^-M(CO)_nL_m$ and ion pairs (contact ion pair (CIP) and solvent separated ion pair (SSIP)) as well as covalent forms with isocarbonyl bonds X_2Ln–$OCM(CO)_{n-1}L_m$ and direct lanthanide–metal bonds X_2Ln–$M(CO)_nL_m$ were involved. For example, the trisubstituted complexes $Ln[Co(CO)_4]_3$, obtained by oxidative addition of $Co_2(CO)_8$ to lanthanide metals, displayed in IR spectra of freshly prepared samples the bands characteristic for the terminal CO groups.[7,11] But, on keeping these solutions for some time a band of half-bridging carbonyl first developed and then vanished to give way to the band with characteristic frequency for the bridging carbonyl (isocarbonyl group) (eq 1).



(1)

Using $X_2Ln[Co(CO)_4]$, where X = Hal, Cp, we have shown that such equilibria between ionic and bridged forms can be shifted toward the bridged isocarbonyl form by removal of THF, by either thermal or photochemical activation (eq 2), X = Hal:

$$[(THF)_{n+l}X_2Ln][Co(CO)]_4 \xrightarrow[-THF]{} (THF)_nX_2LnOCCo(CO)_3 \quad (2)$$

The formation of different forms of complexes in solution or in the solid state complies with Pearson's HSAB principle.[12] For example, in the case of the most thoroughly studied ytterbium–cobalt $X_2Yb[Co(CO)_4]$ complexes, where X = Hal, Cp, Cp*, $Co(CO)_4$, the decrease of the oxophilicity of the ytterbium cation along the series $[(THF)_4Cl_2Yb]^+ > [(THF)Cp_2Yb]^+ > [(THF)Cp^*_2Yb]^+ > [(THF)_4[(OC)_4Co]_2Yb]^+$ leads to a decrease of relative content of those species (CIP, SSIP) in which the cation is solvated by THF molecules. For softer Lewis acids, $[(THF)Cp^*_2Yb]^+$ and, particularly, $(THF)_4[(OC)_4Co]_2Yb^+$, the cation can potentially coordinate either the cobalt or the carbonyl oxygen of $Co(CO)_4^-$, forming either $X_2YbCo(CO)_4$ or $X_2YbOCCo(CO)_3$ in solution. Yet so soft an anion as $Co(CO)_4^-$ is unlikely to be able to form lanthanide–metal bonds. The formation of a direct lanthanide–metal bond is more likely for hard anions, in which the charge is localized at the metal atom.

Fenske–Hall molecular orbital calculations of the anions $CpCr(CO)_3^-$ and $CpFe(CO)_2^-$ have demonstrated that in the former species charge is well-delocalized over the whole system, while for the latter charge is mostly localized at the metal atom.[13] As a consequence, isocarbonyl bonding can be expected to occur in the metal carbonyl complexes of lanthanides (and of other early transition metals) with the $CpMo(CO)_3$ group[2b,5] (an analogue of $CpCr(CO)_3$), while for similar compounds with the $CpRu(CO)_2$ group (an analogue of $CpFe(CO)_2$) a structure with metal–metal bonding is the most probable.[14] This has been demonstrated for derivatives of some early transition metals.[15]

The majority of the studied carbonyl metalates of divalent lanthanides $XLn[M(CO)_nL_m]$ and $Ln[M(CO)_nL_m]_2$ are known from their IR spectra to possess lanthanide-to-metal bonding,[2a,3,7] which is obviously due to the decrease of oxophilicity in the lower oxidation state. However, there is only one X-ray confirmed example of carbonyl metalates of divalent lanthanides, $\{[(CH_3CN)_3YbFe(CO)_2(\mu\text{-}OC)_2]_2\cdot CH_3CN\}_\infty$.[10b] This polymeric

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(15) Cluster structures have been proven also for thorium and uranium derivatives $Cp'_2(X)AnRu(CO)_2Cp$, where Cp′ = Cp*, X = Cl, I;[16] Cp′ = X = Cp,[17] as well as for $Cp_3UFe(CO)_2Cp$.[17]

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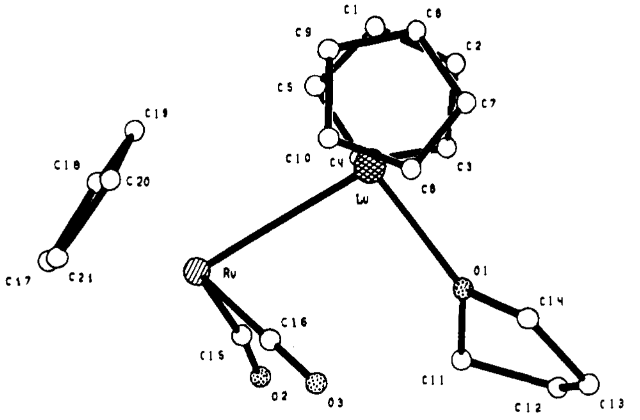

Figure 2. PLUTO view of $(THF)(C_5H_5)_2LuRu(CO)_2(C_5H_5)$ (**4**).

compound has direct Yb–Fe bonding and two independent distances of 3.012 (1) and 3.009 (1) Å. These distances are shorter than the sum of the Yb and Fe metallic radii (3.19 Å[9]). Besides, each ytterbium atom is coordinated in addition by two oxygen atoms of the carbonyl ligands on iron atoms of neighboring Yb–Fe moieties of the "polymeric ladder".

The present work is aimed at the syntheses of complexes with direct lanthanide–metal bonds unsupported by bridging carbonyl ligands, as well as the investigation of their behavior in solution. In studying the state of lanthanum complexes in THF solution by means of ^{139}La spectroscopy, these compounds have been found to be prone to disproportionation. These equilibria have been investigated for the relatively simple complexes Cp'_2LaX and $Cp'LaX_2$, and for some cluster complexes containing the fragment $>LaRu(CO)_2Cp$.

Results and Discussion

Since Ln–M bonds are most likely to be formed if M = $Fe(CO)_2Cp$ and $Ru(CO)_2Cp$, we have started by studying the reaction of $Na[Fe(CO)_2Cp]$ and $Na[Ru(CO)_2Cp]$ with Cp_2LuCl in THF. On mixing THF solutions of $Na[Fe(CO)_2Cp]$ and $Cp_2LuCl(THF)$ at −20 °C a dark-yellow solution is formed, which contains the bimetallic complex $Cp_2LuFe(CO)_2Cp$ having IR bands at 1946 adn 1859 cm^{-1} (THF). A similar complex of thorium, $Cp_3ThFe(CO)_2Cp$, shown by X-ray crystal analysis to contain a Th–Fe bond, has two IR bands at 1927 and 1859 cm^{-1} (toluene).[17] We were not able to isolate a crystalline Fe–Lu bimetallic complex.[18] IR spectra have shown that the complex undergoes quantitative decomposition on keeping a THF solution at room temperature for 1 h, giving $[CpFe(CO)_2]_2$ and a small quantity of $HFe(CO)_2Cp$ as the only iron-containing products, and no identified lutetium compounds.

However, a similar reaction with $Na[CpRu(CO)_2]$ resulted in the formation of more thermally stable bimetallic complexes, which have been isolated and unambiguously characterized.

Synthesis and Structure of $X_2Lu–Ru(CO)_2Cp$ Complexes. The reaction of bis(cyclopentadienyl)lutetium chlorides **1–3** with an equimolar amount of $Na[CpRu(CO)_2]$ in THF at 20 °C produced the corresponding heterobimetallic complexes **4–6**. ^1H NMR spectra showed that the reactions of cyclopentadienyl and bis(trimethylsilyl)cyclopentadienyl complexes of lutetium were quantitative. Bimetallic derivatives **4** and **5** were isolated with 62% and 58% yields of purified compounds, respectively. These compounds are colorless microcrystalline solids that are extremely sensitive to both moisture and air. In the reaction of the lutetium complex with bulky donor pentamethylcyclopentadienyl ligands a coordinatively unsaturated complex **6** has been isolated in 52% yield upon treatment of the reaction mixture with hot toluene.

Table II. Atom Coordinates and Temperature Factors ($Å^2$)[a] for $(C_4H_8O)(C_5H_5)_2Lu\text{-}Ru(C_5H_5)(CO)_2$ (**4**)

atom	X	Y	Z	U^b
Lu	0.0098	0.1326	0.1866	0.027 (1)
Ru	0.5164 (1)	0.4020 (2)	0.8578 (1)	0.033 (1)
O1	0.3707 (8)	0.5242 (12)	0.6298 (7)	0.035 (7)
O2	0.5098 (13)	0.7575 (17)	0.8385 (9)	0.083 (14)
O3	0.2978 (8)	0.3828 (22)	0.7738 (8)	0.076 (12)
C1	0.6801 (12)	0.3879 (25)	0.6578 (11)	0.053 (12)
C2	0.6141 (13)	0.4647 (24)	0.5929 (11)	0.050 (12)
C3	0.5853 (12)	0.6076 (22)	0.6230 (12)	0.051 (13)
C4	0.6315 (12)	0.6158 (21)	0.7039 (11)	0.046 (11)
C5	0.6917 (11)	0.4791 (25)	0.7261 (10)	0.047 (13)
C6	0.3758 (11)	0.1408 (21)	0.6376 (10)	0.046 (12)
C7	0.4231 (14)	0.1583 (22)	0.5759 (10)	0.056 (13)
C8	0.5185 (14)	0.1039 (22)	0.6064 (13)	0.055 (13)
C9	0.5362 (13)	0.0575 (21)	0.6875 (15)	0.065 (18)
C10	0.4426 (14)	0.0815 (20)	0.7042 (10)	0.048 (12)
C11	0.3621 (12)	0.6888 (21)	0.6523 (10)	0.044 (11)
C12	0.2985 (14)	0.7632 (21)	0.5767 (11)	0.049 (12)
C13	0.2240 (12)	0.6352 (25)	0.5426 (11)	0.063 (13)
C14	0.2725 (12)	0.4806 (22)	0.5767 (12)	0.056 (15)
C15	0.5086 (14)	0.6179 (21)	0.8405 (10)	0.049 (14)
C16	0.3808 (12)	0.3875 (25)	0.8055 (10)	0.049 (11)
C17	0.1689 (13)	0.3805 (22)	0.9865 (10)	0.047 (11)
C18	0.6755 (12)	0.3705 (24)	0.9306 (11)	0.055 (12)
C19	0.6502 (13)	0.2337 (250	0.8820 (10)	0.051 (13)
C20	0.5738 (13)	0.1550 (23)	0.9085 (11)	0.057 (13)
C21	0.5575 (13)	0.2473 (26)	0.9722 (10)	0.054 (13)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$$\underset{\mathbf{1}}{Cp_2LuCl(THF)} + Na[CpRu(CO)_2] \xrightarrow[-NaCl]{THF,\ 20\ ^\circ C} \underset{\mathbf{4}}{(THF)Cp_2LuRu(CO)_2Cp} \tag{3}$$

$$0.5\underset{\mathbf{2}}{\{Cp''_2Lu(\mu\text{-}Cl)\}_2} + Na[CpRu(CO)_2] \xrightarrow[-NaCl]{THF,\ 20\ ^\circ C} \underset{\mathbf{5}}{(THF)Cp''_2LuRu(CO)_2Cp} \tag{4}$$

$$\underset{\mathbf{3}}{Cp^*_2Lu(\mu\text{-}Cl)_2Na(THF)_2} + Na[CpRu(CO)_2] \xrightarrow[(2)\ toluene,\ 70\ ^\circ C\ -NaCl]{(1)\ THF,\ 20\ ^\circ C} \underset{\mathbf{6}}{Cp^*_2LuRu(CO)_2Cp} \tag{5}$$

The structure of bimetallic complex **4** has been determined by X-ray crystal analysis (Figure 2). The final atom coordinates and temperature factors, bond lengths, and selected angles are given in Tables II and III. The complex turned out to possess a direct metal–metal bonding. The Lu-Ru distance is 2.995 (2) Å, which is somewhat smaller than the sum of the metallic radii of Lu and Ru being equal to 3.08 Å.[9] The ruthenium atom has a "piano stool" configuration. The (OC)RuLu angles are 87.1 (6) and 77.2 (6)°, the (OC)Ru(CO) angle is 88.9 (8)°, and the CpRu(CO) and CpRuLu angles are 129.9, 136.8, and 117.1°, correspondingly, where Cp refers to the center of the cyclopentadienyl ring. Similar coordination of the ruthenium atom with almost the same angles has been found for $Cp^*_2Th(I)Ru(CO)_2Cp$ (**7**)[16] and $Cp_2Zr[Ru(CO)_2Cp]_2$ (**8**)[20] complexes. The coordination

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(18) Recently, heterobimetallic compound $\{Cp^*_2Sm(\mu\text{-}OC)_2FeCp^*\}_2$ has been prepared by the reaction of $Cp^*_2Sm(THF)_2$ with $[Cp^*Fe(CO)_2]_2$.[19a] This compound turned out to have two bridging carbonyl ligands and no metal–metal bonding, that is obviously due to both steric bulk of C_5Me_5 ligands and specific electronic properties of $Cp^*Fe(CO)_2$ fragment. The analogous compound with $Cp^*Ru(CO)_2$ could not be prepared this way.[19b]

(19) (a) Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. *Chem. Ber.* **1991**, *124*, 1373. (b) Edelmann, F. T., private communication.

(20) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

Table III. Bond Distances (Å) and Selected Angles (deg) for $(THF)Cp_2LuRu(CO)_2Cp$ (**4**)

Bond Distances			
Lu–Ru	2.955 (2)	Lu–O(1)	2.32 (1)
Lu–C(1)	2.59 (2)	Lu–C(2)	2.62 (2)
Lu–C(3)	2.66 (2)	Lu–C(4)	2.65 (2)
Lu–C(5)	2.62 (2)	Lu–C(6)	2.63 (2)
Lu–C(7)	2.62 (2)	Lu–C(8)	2.62 (2)
Lu–C(9)	2.61 (2)	Lu–C(10)	2.62 (2)
Ru–C(15)	1.82 (2)	Ru–C(16)	1.86 (2)
Ru–C(17)	2.28 (2)	Ru–C(18)	2.24 (2)
Ru–C(19)	2.29 (2)	Ru–C(20)	2.29 (2)
Ru–C(21)	2.29 (2)	O(1)–C(11)	1.44 (2)
O(1)–C(14)	1.47 (2)	O(2)–C(15)	1.17 (2)
O(3)–C(16)	1.14 (2)	C(1)–C(2)	1.39 (3)
C(1)–C(5)	1.38 (3)	C(2)–C(3)	1.41 (3)
C(3)–C(4)	1.36 (3)	C(4)–C(5)	1.41 (3)
C(6)–C(7)	1.42 (3)	C(6)–C(10)	1.35 (2)
C(7)–C(8)	1.37 (3)	C(8)–C(9)	1.41 (3)
C(9)–C(10)	1.44 (3)	C(11)–C(12)	1.49 (3)
C(12)–C(13)	1.49 (3)	C(13)–C(14)	1.50 (3)
C(17)–C(18)	1.43 (3)	C(17)–C(21)	1.39 (3)
C(18)–C(19)	1.40 (3)	C(19)–C(20)	1.45 (3)
C(20)–C(21)	1.42 (3)		
Angles[a]			
Ru–Lu–O(1)	98.4 (3)	Lu–Ru–C(15)	87.1 (6)
Lu–Ru–C(16)	77.2 (6)	C(15)–Ru–C(16)	88.9 (8)
Ru–C(16)–O(3)	178 (2)	Ru–C(15)–O(2)	172 (2)
A1–Ru–A2	123.9	A1–Lu–Ru	110.0
A2–Lu–Ru	109.8	A1–Lu–O(1)	107.4
A2–Lu–O(1)	104.2	A3–Ru–Lu	117.1
A3–Ru–C(15)	129.9	A3–Ru–C(16)	136.8

[a] A1, A2, and A3 refer to the centers of Cp rings.

sphere of the lutetium atom also contains two cyclopentadienyl ligands and an oxygen atom of THF. Atoms of Ru and O and the centers of cyclopentadienyl ligands make a distorted tetrahedron, with the CpLuCp and RuLuO(1) angles most heavily deviating from tetrahedron to 123.9 and 98.4 (3)°, respectively. Other angles in the lutetium coordination polyhedron are almost perfectly tetrahedral; they fall in the 104.2–111.0° range. The molecule has a staggered conformation, close to that found in complex **7** (conformation **A**, X = THF).

The planes of the cyclopentadienyl rings coordinated to the lutetium atom make an angle of 124.4° with each other and angles of 28.6 and 26.9° with the RuLuO(1) plane. The plane of the Cp ligand coordinated to the Ru atom is practically perpendicular to the RuLuO(1) plane with the interplane angle of 93.4°.

The Ru–CO and Ru–C(Cp) distances are 1.83 (2), 1.86 (2), and 2.243–2.294 (2) Å, respectively, being close to the analogous distances in **7** and **8**. The Lu–O(1) distance 2.32 (1) Å is between the Lu–O(THF) distances in the cationic complex $[Cl_2Lu(THF)_5]^+$ [8b] of 2.36 and 2.37 Å and that in the neutral complex $Cp_2LuCl(THF)$ of 2.27 Å,[21] and close to the corresponding distance in the alkyl complex $Cp_2Lu(C_4H_9\text{-}t)(THF)$ of 2.31 Å.[22] The Lu–C(Cp) distances are in the typical range of 2.59–2.66 (2) Å.[23]

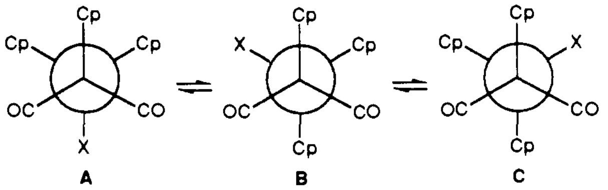
The IR spectrum of the THF solution of **4** displayed two bands in the carbonyl region at 2027 and 1965 cm^{-1}. Such a spectral pattern is common for the fragments $CpRu(CO)_2$ in bimetallic clusters with a ruthenium carbonyl group. For instance, the IR spectrum of **7** has bands at 2023 and 1959 cm^{-1} (THF),[16] and that of $Me_3GeRu(CO)_2Cp$ has bands at 2009 and 1954 cm^{-1} (hexane).[24]

Table IV. Temperature Dependence of Resonance Line Half-Widths ($\Delta\nu_{1/2}$) for ^1H NMR Spectra of a THF Solution of $(THF)Cp_2LuRu(CO)_2Cp$ (**4**)

T, °C	$\Delta\nu_{1/2}$(CpLu), Hz	$\Delta\nu_{1/2}$(CpRu), Hz
30	5.16	4.36
5	2.96	2.57
–20	1.93	1.89
–35	1.18	1.56
–40	1.32	2.03

The persistence of the Lu–Ru bond in solutions was also confirmed by ^{13}C NMR spectroscopy. The spectrum of **4** in THF displayed resonances at 86.6 and 112.5 ppm of carbons of cyclopentadienyl rings at ruthenium and lutetium atoms correspondingly, and also a single resonance of ruthenium carbonyls at 211.9 ppm. Actinide derivatives show a similar resonance line: for **7** at 204.5 ppm (toluene)[16] and for $Cp_3ThRu(CO)_2Cp$ at 209.5 ppm (THF).[17] Spectral features of solutions of complexes **5** and **6** are similar to those of **4**. Neither IR nor NMR spectroscopy reveal any other species except binuclear complexes with metal–metal bonding in THF solutions.

Considerable broadening of lines in ^1H NMR spectra of THF solutions of **4** and **5** suggested the possibility of fluxional behavior on the part of these compounds. The temperature dependence of line half-widths ($\Delta\nu_{1/2}$) of ^1H NMR spectra of **4** is given in Table IV. Below room temperature the resonance lines of protons of cyclopentadienyl rings at lutetium and ruthenium atoms underwent successive narrowing. For the thorium and uranium complexes $Cp_2(X)AnRu(CO)_2Cp$ (X = Hal, Cp)[16,17] quite the opposite was observed. The dynamic behavior of the latter compounds in solution was due to the equilibrium between the conformers (eq 6) with hindered rotation around the An–Ru bond.



(6)

Broadening of resonance lines in ^1H NMR spectra of THF solutions of **4** and **5** might be accounted for by the reversible dissociation of the THF ligand from the coordination sphere of the lanthanide atom of bimetallic complexes (eq 7).

$$(THF)Cp_2LuRu(CO)_2Cp \rightleftarrows THF + Cp_2LuRu(CO)_2Cp \quad (7)$$

Another possible explanation of dynamic behavior would be the degenerate exchange of cyclopentadienyl ligands at the lutetium atom (homoexchange, eq 8). The ionic character of

$$(THF)Cp^1Cp^2LuRu(CO)_2Cp + (THF)Cp^3Cp^4LuRu(CO)_2Cp \overset{THF}{\rightleftharpoons} (THF)Cp^1Cp^3LuRu(CO)_2Cp + (THF)Cp^2Cp^4LuRu(CO)_2Cp \quad (8)$$

Lu–Cp bonds makes possible such an exchange. Obviously this homoexchange is accompanied by simultaneous dissociation of THF ligands (eq 7). Dynamic behavior of cyclopentadienyl ligands in organometallic derivatives of lanthanides has been

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[21] Ni, C.; Zhang, Z.; Deng, D.; Qian, C. J. *J. Organomet. Chem.* **1986**, *306*, 209.

[22] Schumann, H.; Genthe, W.; Bruncks, N. *Angew. Chem.* **1981**, *93*, 126.

[23] Bochkarev, M. E.; Kalinina, G. S.; Zacharov, L. N.; Horoshev, S. Ja. *Organitscheskiye proyizvodniye redkozemel'nikh elementov* (*Organic Derivaties of Rare-earth-elements*); Moscow, Nauka, 1989.

[24] Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1633.

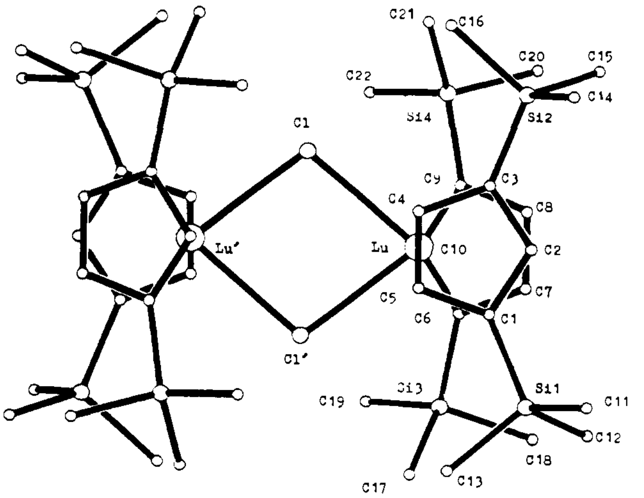

Figure 3. PLUTO view of $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2Lu(\mu\text{-}Cl)\}_2$ (**2**).

reported earlier.[25] For similar complexes of actinides such behavior has never been observed: this behavior is obviously associated with the smaller ionic character of the An(IV)–Cp bond in comparison with Ln(III)–Cp bonds.[26]

Similar temperature dependence of line half-widths has been established for complex **5** ($\Delta\nu_{1/2}$(CpRu) = 10.55 Hz at 20 °C).

Thus, the apparent fluxional behavior of complexes **4** and **5** in THF solution at temperatures not far from room temperature is accounted for by equilibrium 7 or 8, and not eq 6 (X = THF). Hindered rotation about the metal–metal bond should begin to be manifested in the appearance of NMR spectra only at lower temperatures because of the lack of conformational rigidity due to dynamic behavior of ligands at the lutetium atom (Cp and THF). This conclusion can be confirmed by the experimental data. The results presented in Table IV show that on lowering the temperature below −35 °C resonance lines again start to broaden, which means the system is coming to the state when equilibrium 6 between conformers becomes predominantly among all possible processes.

Contrary to complexes **4** and **5**, for **6** there is no considerable broadening of resonance lines in the ^{1}H NMR spectrum of a THF solution at 20 °C. This compound turned out to have no THF ligand, which makes the dissociation process in eq 7 impossible. Besides, the difference in thermodynamics of ligand exchange processes roots in the differences in covalent character of the involved Cp–Lu bonds. Pentamethylcyclopentadienyl ligands, being the strongest electron donating ligands in the series, form the tightest covalent bonds in comparison with cyclopentadienyl or bis(trimethylsilyl)cyclopentadienyl ligands. The half-widths of resonance lines in ^{1}H NMR spectra increase along the same series ($\Delta\nu_{1/2}$(CpRu) is equal to 1.55 Hz for **6**, 3.53 Hz for **4**, and 10.55 Hz for **5** at 20 °C in THF solution).

The Synthesis of $(THF)_3I_2LaRu(CO)_2Cp$. The reaction of equimolar amounts of lanthanum triiodide and $Na[CpRu(CO)_2]$ in THF at −30 °C has produced complex **9** isolated in 68% yield (eq 9).

$$LaI_3(THF)_3 + Na[CpRu(CO)_2] \xrightarrow[-NaI]{THF} \underset{\mathbf{9}}{(THF)_3I_2LaRu(CO)_2Cp} \quad (9)$$

From the IR and ^{13}C NMR spectral evidence complex **9** contains La–Ru bond. For instance, in the ^{13}C NMR spectrum the resonance of carbonyl carbons is at 204.3 ppm, which corresponds to higher covalent character of the La–Ru bond, in comparison with that for complexes **4**–**6**, for which these resonances were found to be at 211.9, 210.7, and 215.5 ppm, respectively. It is also worth noting that for **9**, as for **4** and **5**, the resonance lines of protons of CpRu in the ^{1}H NMR spectrum ($\Delta\nu_{1/2}$ = 5.50 Hz at 20 °C) are broadened, which is likely due to the reversible dissociation of THF ligands or the homoexchange process involving iodide ligands.

The Reactivity of Bimetallic Complexes of Lanthanides with the $CpRu(CO)_2$ Group. The metal–metal bonds in **4**–**6** and **9** are labile toward various electrophilic agents. For instance, the treatment of **5** with water (eq 10), hydrogen chloride (eq 11), and mercury dichloride (eq 12) resulted in the destruction of the compound. The products of these reactions were either isolated or identified by IR and NMR spectroscopy.

$$5 + H_2O \xrightarrow[-30\,°C]{THF} 0.5\underset{\mathbf{10}}{\{Cp''_2Lu(\mu\text{-}OH)\}_2} + HRu(CO)_2Cp \quad (10)$$

$$5 + HCl \xrightarrow[-30\,°C]{THF} 0.5\underset{\mathbf{2}}{\{Cp''_2Lu(\mu\text{-}Cl)\}_2} + HRu(CO)_2Cp \quad (11)$$

$$5 + HgCl_2 \xrightarrow[-30\,°C]{THF} 2 + Hg[Ru(CO)_2Cp]_2 \quad (12)$$

The corresponding thorium bimetallic complexes possess similar reactivity toward electrophilic reagents, as has been shown by their reactions with alcohols.[16]

The structures of complexes **2**[27] and **10** are given in Figures 3 and 4. Atom coordinates and temperature factors as well as selected bond lengths and angles are compiled in Tables V–VIII. These compounds turned out to have similar dimeric structure.[28] Lutetium atoms of **2** and **10** have a distorted tetrahedral coordination with ALuX angles being in the 107.0–110.2° range in **2** and the 107.7–112.6° range in **10**. Cyclopentadienyl rings are in a staggered conformation and make slightly different angles with the plane of the Lu_2X_2 cycle: 23.5 and 28.7° in **2**, 22.6 and 30.2° in **10**.

The substitution of the bridging chloride for the hydroxy group leads to a marked decrease of the Lu–X distance (from 2.624 (1) Å in **2** to 2.261 (4), 2.268 (4) Å in **10**), the Lu···Lu distance (from 4.018 (1) Å in **2** to 3.579 (1) Å in **10**), and the XLuX angle (from 80.3° in **2** to 75.6° in **10**). Both molecules are situated in the symmetry center of the cell. The molecules under study possess local symmetry close to the C_{2h} point group. Local axis 2 goes through the bridging ligand X, and the horizontal symmetry plane goes through the lutetium atoms. The largest distortion is due to trimethylsilyl substituents.

The reaction of bimetallic complex **9** with methyl iodide gave $MeRu(CO)_2Cp$, which was isolated with 58% yield (eq 13), and

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(25) Maginn, R. E.; Manasiyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672. Day, C. S.; Day, V. W.; Ernst, R. D.; Volmer, S. H. *Organometallics* **1982**, *1*, 998.

(26) Marks, T. J.; Fragala, J. L., Eds. *Fundamental and Technological Aspects of Organo-f-element Chemistry*; D. Reidel Publ. Co.: Dordrecht, 1985.

(27) For structural details on analogous complexes of Sc, Pr, and Yb see: Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1190.

(28) Compound **2** has been found by NMR spectroscopy to maintain the dimeric structure in THF solution. On the other hand, compound **10** turned out to dissociate half into monomer **11** according to the equation (for details of the NMR experiment see the Experimental Section)

$$\underset{\mathbf{10}}{\{Cp''_2Lu(\mu\text{-}OH)\}_2} \overset{THF}{\rightleftharpoons} \underset{\mathbf{11}}{2Cp''_2LuOH(THF)}$$

Recently the synthesis and the structures in both solid state and solution of dimeric complexes $\{Cp_2Y(\mu\text{-}OH)\}_2\cdot(PhC{\equiv}CPh)$[29a] and $\{Cp''_2Sm(\mu\text{-}OH)\}_2$[29b] have been investigated.

(29) (a) Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Robinson, G. H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990. (b) Hitchcock, P. B.; Lappert, M. F.; Prashar, S. *J. Organomet. Chem.* **1991**, *413*, 79.

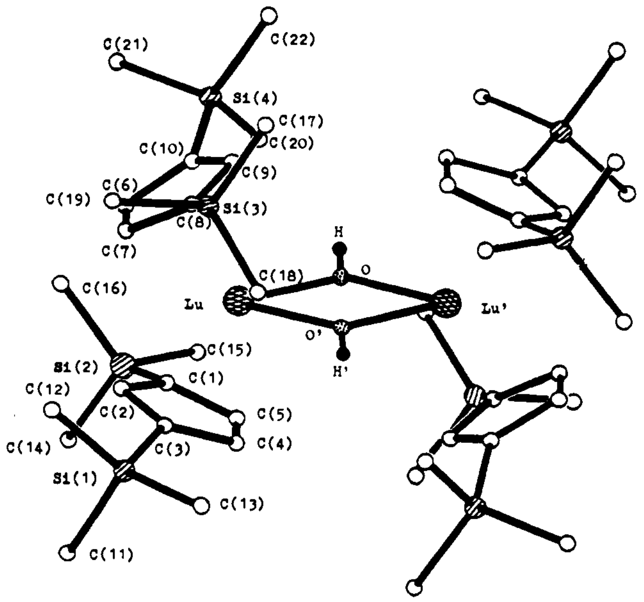
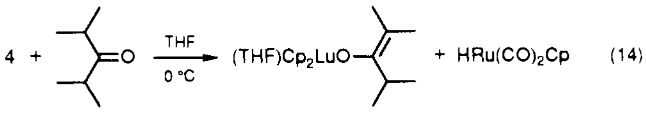


Figure 4. PLUTO view of $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2Lu(\mu\text{-}OH)\}_2$ (**10**).

also $IRu(CO)_2Cp$ and $[CpRu(CO)_2]_2$ as side products.

$$\mathbf{9} + MeI \xrightarrow[0\,°C]{THF} MeRu(CO)_2Cp + (THF)_3LaI_3 \qquad (13)$$

Reaction of complex **4** with an equimolar amount of diisopropyl ketone has led to enolization, and the corresponding lutetium enolate **12** was isolated with 45% yield.



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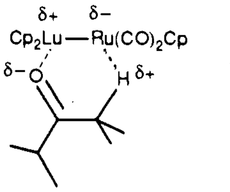
Reaction 14 is likely to proceed via a six-membered transition state similar to that proposed earlier by Marks and co-workers for the reaction of a thorium–ruthenium complex with acetone[17,30]



Bimetallic complexes **4**–**6** and **9** have been found to undergo significant deterioration when kept in THF solution at room temperature. For instance, almost 50% of the lutetium complex **4** decomposed after a month of storage, and lanthanum complex **9** was half decomposed after only 2 weeks.[31]

Table V. Atom Coordinates and Temperature Factors (Å^2)[a] for $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2Lu(\mu\text{-}Cl)\}_2$ (**2**)

atom	*X*	*Y*	*Z*	*U*[b]
Lu	0.0103	0.0164	0.3407	0.037 (1)
Cl	0.0050 (1)	0.1490 (1)	0.4702 (1)	0.053 (1)
Si1	0.2195 (2)	−0.2758 (2)	0.2428 (1)	0.057 (1)
Si2	0.2474 (2)	0.2267 (2)	0.1565 (2)	0.063 (1)
Si3	0.7312 (2)	−0.1627 (2)	0.3403 (2)	0.061 (1)
Si4	0.7387 (2)	0.3493 (1)	0.2434 (1)	0.058 (1)
C1	0.2020 (5)	−0.1269 (5)	0.2693 (4)	0.045 (4)
C2	0.1823 (5)	−0.0082 (5)	0.1908 (4)	0.046 (3)
C3	0.2128 (5)	0.0768 (5)	0.2351 (4)	0.047 (4)
C4	0.2544 (5)	0.0077 (5)	0.3439 (5)	0.048 (4)
C5	0.2475 (5)	−0.1140 (5)	0.3642 (4)	0.048 (4)
C6	0.7965 (5)	−0.0234 (5)	0.2916 (5)	0.047 (4)
C7	0.8659 (5)	0.0135 (5)	0.1937 (4)	0.048 (4)
C8	0.8678 (5)	0.1367 (5)	0.1713 (4)	0.050 (4)
C9	0.8006 (5)	0.1830 (5)	0.2549 (4)	0.047 (4)
C10	0.7580 (5)	0.0827 (5)	0.3284 (4)	0.044 (4)
C11	0.3700 (7)	−0.3051 (7)	0.1655 (8)	0.105 (6)
C12	0.0861 (7)	−0.2727 (6)	0.1574 (6)	0.077 (5)
C13	0.7687 (8)	0.3995 (6)	0.6280 (6)	0.089 (6)
C14	0.4133 (8)	0.1895 (8)	0.0993 (7)	0.106 (6)
C15	0.1302 (8)	0.3120 (7)	0.0419 (6)	0.093 (6)
C16	0.2443 (8)	0.3224 (7)	0.2462 (7)	0.097 (6)
C17	0.8475 (7)	−0.3094 (6)	0.4062 (6)	0.087 (6)
C18	0.6692 (8)	−0.1764 (8)	0.2151 (8)	0.115 (7)
C19	0.5993 (7)	−0.1352 (7)	0.4360 (7)	0.097 (6)
C20	0.6690 (7)	0.4257 (6)	0.1060 (6)	0.082 (5)
C21	0.8633 (7)	0.4260 (6)	0.2575 (7)	0.094 (6)
C22	0.6136 (8)	0.3676 (7)	0.3489 (6)	0.101 (7)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $\{Cp''_2Lu(\mu\text{-}Cl)\}_2$ (**2**)

	Bond Distances		
Lu···Lu	4.018 (1)		
Lu–Cl	2.624 (1)	Lu–Cl	2.632 (1)
Lu–C(1)	2.612 (6)	Lu–C(2)	2.601 (5)
Lu–C(3)	2.612 (5)	Lu–C(4)	2.601 (6)
Lu–C(5)	2.595 (6)	Lu–C(6)	2.626 (6)
Lu–C(7)	2.568 (5)	Lu–C(8)	2.573 (5)
Lu–C(9)	2.625 (6)	Lu–C(10)	2.620 (6)
Si(1)–C(1)	1.858 (6)	Si(2)–C(3)	1.859 (6)
Si(3)–C(6)	1.864 (6)	Si(4)–C(9)	1.864 (6)
C(1)–C(2)	1.423 (8)	C(1)–C(5)	1.426 (7)
C(2)–C(3)	1.420 (8)	C(3)–C(4)	1.428 (8)
C(4)–C(5)	1.399 (8)	C(6)–C(7)	1.422 (8)
C(6)–C(10)	1.431 (8)	C(7)–C(8)	1.397 (8)
C(8)–C(9)	1.427 (8)	C(9)–C(10)	1.421 (8)
	Angles		
Cl–Lu–Cl	80.27 (4)	Lu–Cl–Lu	99.73 (4)
Si(1)–C(1)–C(2)	126.9 (4)	Si(1)–C(1)–C(5)	124.9 (4)
C(2)–C(1)–C(5)	105.3 (5)	C(1)–C(2)–C(3)	110.7 (5)
Si(2)–C(3)–C(2)	126.1 (4)	Si(2)–C(3)–C(4)	125.2 (4)
C(2)–C(3)–C(4)	105.5 (5)	C(3)–C(4)–C(5)	109.0 (5)
C(1)–C(5)–C(4)	109.4 (5)	Si(3)–C(6)–C(7)	126.7 (4)
Si(3)–C(6)–C(10)	126.1 (4)	C(7)–C(6)–C(10)	105.3 (5)
C(6)–C(7)–C(8)	109.4 (5)	C(7)–C(8)–C(9)	109.4 (5)
Si(4)–C(9)–C(8)	125.0 (4)	Si(4)–C(9)–C(10)	127.0 (4)

Bimetallic complexes of lanthanum **9** and lutetium **4** were inert toward molecular hydrogen (0.1 MPa H_2, THF, 25 °C, 72 h),[35] $PhMeSiH_2$ (THF, 90 °C, 10 h),[36] and $Me_3SiC{\equiv}CSiMe_3$ (THF, 90 °C, 8 h). Under CO atmosphere (0.1 MPa) complex **9** was found to decompose almost completely after 2 days, with

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(30) Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920.

(31) Decomposition might be due to either the cleavage of the THF ring[32] or metalation of solvent or Cp ligands of the bimetallic Ln–Ru fragment.[33] Decomposition products have not been investigated. NMR spectra showed that lutetium complex **4** formed $HRu(CO)_2Cp$, $[CpRu(CO)_2]_2$, and an unidentified cyclopentadienyl complex of lutetium on decomposition. As has been mentioned above, complexes with Ln–Fe bonds are still less stable. As to actinide complexes, in a recent article[34] the bond energy of the U–M bond in $Cp_3UFe(CO)_2Cp$ was shown to be smaller than that for $Cp_3URu(CO)_2Cp$ by approximately 10 kcal/mol. In the same article the destruction of bimetallic complexes was demonstrated to be caused by $HM(CO)_2Cp$ present in reaction mixtures.

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(35) Under H_2 pressure (5.0 MPa) **4** was irreversibly converted into $HRu(CO)_2Cp$ and unidentified lutetium complexes in high yield.

Table VII. Atom Coordinates and Temperature Factors (Å^2)^a for $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2Lu(\mu\text{-}OH)\}_2$ (**10**)

atom	*X*	*Y*	*Z*	*U*^{b}
Lu	0.4373	0.5763	0.4134	0.041 (2)
Si1	0.3230 (2)	0.5033 (2)	0.0965 (2)	0.063 (2)
Si2	0.5668 (2)	0.7617 (2)	0.2606 (2)	0.083 (2)
Si3	0.1988 (1)	0.5021 (2)	0.4783 (2)	0.063 (2)
Si4	0.4460 (2)	0.7644 (1)	0.6484 (2)	0.060 (1)
C1	0.5104 (6)	0.6585 (5)	0.2643 (6)	0.058 (5)
C2	0.4246 (5)	0.6416 (5)	0.2120 (6)	0.058 (5)
C3	0.4103 (5)	0.5533 (5)	0.1958 (6)	0.055 (5)
C4	0.4931 (5)	0.5154 (5)	0.2380 (6)	0.052 (5)
C5	0.5507 (5)	0.5772 (5)	0.2780 (6)	0.057 (5)
C6	0.3442 (5)	0.7110 (4)	0.4348 (6)	0.053 (5)
C7	0.2857 (5)	0.6479 (5)	0.3949 (6)	0.054 (5)
C8	0.2835 (4)	0.5856 (5)	0.4793 (6)	0.050 (5)
C9	0.3436 (5)	0.6138 (5)	0.5706 (6)	0.047 (4)
C10	0.3820 (5)	0.6904 (5)	0.5477 (6)	0.050 (5)
C11	0.3437 (8)	0.5271 (9)	−0.0450 (8)	0.116 (10)
C12	0.2152 (7)	0.5457 (7)	0.1100 (10)	0.104 (9)
C13	0.3239 (7)	0.3869 (8)	0.1134 (10)	0.111 (9)
C14	0.5812 (17)	0.7811 (12)	0.1244 (12)	0.312 (26)
C15	0.6712 (8)	0.7598 (8)	0.3466 (14)	0.154 (13)
C16	0.5073 (8)	0.8513 (7)	0.3081 (13)	0.138 (12)
C17	0.1831 (6)	0.4808 (7)	0.6239 (8)	0.083 (7)
C18	0.2251 (6)	0.4005 (6)	0.4142 (10)	0.104 (9)
C19	0.0965 (6)	0.5441 (6)	0.3978 (8)	0.084 (7)
C20	0.5636 (6)	0.7623 (7)	0.6473 (9)	0.094 (7)
C21	0.4087 (8)	0.8724 (6)	0.6145 (8)	0.105 (9)
C22	0.4269 (6)	0.7369 (6)	0.7912 (7)	0.087 (7)
O	0.4413 (3)	0.4371 (3)	0.4599 (4)	0.042 (3)

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} Equivalent isotopic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $\{Cp''_2Lu(\mu\text{-}OH)\}_2$ (**10**)

Bond Distances			
Lu···Lu′	3.579 (1)	C(2)–C(3)	1.42 (1)
Lu–O	2.261 (4)	C(3)–C(4)	1.44 (1)
Lu–O′	2.268 (4)	C(4)–C(5)	1.37 (1)
Lu–C(1)	2.635 (8)	C(1)–C(5)	1.43 (1)
Lu–C(2)	2.640 (7)	C(6)–C(7)	1.39 (1)
Lu–C(3)	2.644 (8)	C(7)–C(8)	1.43 (1)
Lu–C(4)	2.616 (7)	C(8)–C(9)	1.41 (1)
Lu–C(5)	2.605 (7)	C(9)–C(10)	1.40 (1)
Lu–C(6)	2.612 (7)	C(6)–C(10)	1.45 (1)
Lu–C(7)	2.604 (7)	Si(1)–C(3)	1.852 (8)
Lu–C(8)	2.658 (7)	Si(2)–C(1)	1.856 (8)
Lu–C(9)	2.656 (7)	Si(3)–C(8)	1.867 (8)
Lu–C(10)	2.668 (7)	Si(4)–C(10)	1.867 (7)
C(1)–C(2)	1.42 (1)		
Angles			
O–Lu–O′	75.6 (1)	C(2)–C(3)–C(4)	104.1 (7)
Si(1)–C(3)–C(2)	126.3 (6)	C(3)–C(4)–C(5)	109.6 (7)
Si(1)–C(3)–C(4)	125.7 (6)	C(4)–C(5)–C(1)	110.3 (7)
Si(2)–C(1)–C(2)	125.0 (6)	C(5)–C(1)–C(2)	104.6 (7)
Si(2)–C(1)–C(5)	126.1 (6)	C(6)–C(7)–C(8)	109.3 (7)
Si(3)–C(8)–C(7)	125.4 (6)	C(7)–C(8)–C(9)	105.2 (7)
Si(3)–C(8)–C(9)	127.7 (6)	C(8)–C(9)–C(10)	111.7 (7)
Si(4)–C(10)–C(6)	125.5 (6)	C(9)–C(10)–C(6)	105.1 (6)
Si(4)–C(10)–C(9)	127.8 (6)	C(10)–C(6)–C(7)	108.7 (7)
C(1)–C(2)–C(3)	111.4 (7)		

$IRu(CO)_2Cp$ as the main product (65% from NMR data) and unidentified lanthanum-containing compounds, some of them bearing cyclopentadienyl ligands, being formed.

The Use of ^{139}La NMR Spectroscopy for Studying the Structures of Bimetallic Complexes in Solutions. Additional data on the structure of LnX_3 complexes (X = Hal, Cp′, $Ru(CO)_2Cp$, etc.) in solutions can be obtained from NMR spectra of metal nuclei which are highly sensitive to processes occurring in the vicinity of metal atoms. For the metals of group IIIB the easiest and most often used are the NMR spectra of ^{35}Sc, ^{89}Y, and ^{139}La nulei.[26,38]

Before the present work, ^{139}La NMR spectra have been used for studying a vast scope of inorganic derivatives of lanthanum, LaY_3.[26,38,39] This method was also employed for studying complex formation between Cp_3La and THF, nitriles, and isonitriles, etc.[26,39,40] These investigations also revealed an important correlation between the number of atoms nearest to the metal atom (*n*) and the chemical shift of the metal nuclei. With more atoms being bonded the resonance of ^{139}La shifts upfield.[38] The range of chemical shifts for the hitherto known ^{139}La spectra is extremely wide—it extends from + 1090 ppm for $[LaBr_6]^{3-}$ to −578 ppm for $Cp_3La(NCMe)$ (chemical shifts are measured relative to the resonance of $La(ClO_4)_3$ in D_2O–H_2O), which makes this method a sensitive tool for studying processes in the closet coordination shell, even in spite of the considerable broadness of the signals.

Table IX lists the results of our studies on lanthanum derivatives by ^{139}La NMR spectroscopy, in comparison with some earlier data.

The monosubstituted complex of lanthanum, $CpLaI_2$, being one of the rare examples of monocyclopentadienyl complexes of light lanthanides,[41] has been obtained with quantitative yield by the exchange reaction of LaI_3 with CpTl (eq 15).

$$LaI_3(THF)_3 + CpTl \xrightarrow[25\,°C]{THF} \underset{\mathbf{13}}{CpLaI_2(THF)_3} + TlI \qquad (15)$$

This complex is stable in THF solution and has a single narrow ^{139}La resonance at +406 ppm, which conforms nicely with the chemical shift value interpolated for *n* = 10. Though complex **13** is stable toward disproportionation or polymerization in solutions, it is quite prone to Schlenk ligand exchange processes with other lanthanum compounds. We have observed the equilibrium between $CpLaI_2$ and Cp_3La (eq 16) which produces, from NMR spectral evidence, up to 20% of the dicyclopentadienyl complex Cp_2LaI (with initial concentrations of Cp_3La and **13** of 35 mmol/L in THF solution).

$$\underset{\mathbf{13}\ (n\,=\,10)}{CpLaI_2(THF)_3} + \underset{(n\,=\,16)}{Cp_3La(THF)} \rightleftharpoons \underset{\mathbf{14}\ (n\,=\,12)}{2Cp_2LaI(THF)} \qquad (16)$$

The ^{139}La spectrum of this mixture is displayed in Figure 5. Besides two resonances of equal intensity (downfield line of $CpLaI_2$ at +409 ppm and upfield line of Cp_3La at −569 ppm, there is a

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(36) Organolanthanide compounds are known to react with silanes to yield the corresponding hydride complexes of lanthanides and alkylsilanes,[37a] e.g.

$$\{(t\text{-}BuC_5H_4)_2Ln(\mu\text{-}Me)\}_2 \xrightarrow[C_6H_6]{PhMeSiH_2} \{(t\text{-}BuC_5H_4)_2Ln(\mu\text{-}H)\}_2$$

$$2(C_5H_5)_2LuC_6H_4Me\text{-}4(THF) \xrightarrow[C_6H_6]{PhMeSiH_2} \{(C_5H_5)_2Lu(\mu\text{-}H)(THF)\}_2$$

though complexes with C_5Me_5 ligands $Cp^*_2LnCH(SiMe_3)_2$ give silyl derivatives, which were isolated and characterized.[37a,d] Such transformations explain catalytic properties of organolanthanide compounds in the hydrosilylation of olefins.[34,37]

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Table IX. ^{139}La NMR Data

compd	$\delta(^{139}La)$, ppm	$\Delta\nu_{1/2}$, Hz	solvent	*n*
$[n\text{-}Bu_4N]_3[LaBr_6]$[a]	1090	500	CD_3CN	6
$(THF)_3I_2LaRu(CO)_2Cp$ (**9**)	452	2035	THF/THF-d_8	6
$[Et_2H_2N][La(Et_2NCS_2)_4]$[a]	710	2100	CD_3CN	8
$[(THF)_6LaCl_2][Co(CO)_4]$[b]	not found		THF/THF-d_8	8
$\{(THF)CpLa[Ru(CO)_2Cp](\mu\text{-}I)_2Na(THF)_2\}$ (**15**)	−19	1360	THF/THF-d_8	9
$CpLaI_2(THF)_3$ (**13**)	406	815	THF/THF-d_8	10
La(15-crown-5)$(ClO_4)_3$	186	3759	D_2O	11
$La(ClO_4)_3(H_2O)_6$[c]	0	140	D_2O	12
$\{Cp''_2La(\mu\text{-}Cl)\}_2$	−55	18800	THF/THF-d_8	12
$Cp_2LaI(THF)$ (**14**)	−90	165	THF/THF-d_8	12
$[n\text{-}Bu_4N][Cp_3LaBr]$	−419	1270	THF/THF-d_8	16
$[n\text{-}Bu_4N][Cp_3LaI]$	−430	290	THF/THF-d_8	16
$(THF)Cp_2LaRu(CO)_2Cp$ (**17**)	−452	915	THF/THF-d_8	12
$Cp_3La(THF)$	−560	550	THF/THF-d_8	16

[a] Reference 38. [b] Preparation, see ref 8b. [c] Reference compound for ^{139}La chemical shift scale.

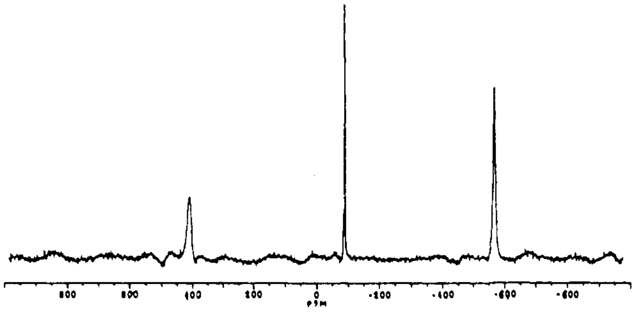

Figure 5. ^{139}La NMR spectrum of an equimolar mixture of $CpLaI_2(THF)_3$ and $Cp_3La(THF)$ in THF/THF-d_8 solution.

new resonance at −90 ppm, which supposedly corresponds to $Cp_2LaI(THF)$ with $n = 12$. This value is close to the resonance of $\{Cp''_2La(\mu\text{-}Cl)\}_2$ at −55 ppm.

A similar study of ^{139}La spectra has been done with the complex $(THF)_3I_2LaRu(CO)_2Cp$ (**9**), which displayed a single resonance line at +452 ppm, being shifted upfield by more than 600 ppm in comparison with the estimated chemical shift for lanthanum nuclei with $n = 6$.

Complex **15** was obtained by the reaction of equimolar amounts of $CpLaI_2$ and $Na[CpRu(CO)_2]$ in THF.

$$CpLaI_2(THF)_3 + Na[CpRu(CO)_2] \xrightarrow{THF} \underset{\mathbf{15}}{\{(THF)CpLa[Ru(CO)_2Cp](\mu\text{-}I)_2Na(THF)_2\}} \quad (17)$$

Complex **15** has a La–Ru bond which was determined from IR and ^{13}C spectral data. In the region of stretching modes of CO groups in the IR spectrum, complex **15** in THF solution has two absorption bands at 2031 and 1965 cm^{-1}. In the ^{13}C NMR spectrum there is a single carbonyl resonance at 212.8 ppm. Elemental analysis showed that **15** is an *ate* complex.

The ^{139}La spectrum of the THF solution of **15** displays a single resonance line at −19 ppm. This resonance is upfield shifted by ca. 500 ppm relative to the estimate for $n = 9$. Prolonged storage of **15** in THF solution has been found to result in disproportionation, which is reflected in both ^{139}La NMR spectra (see Figure 6) and IR, ^{1}H, ^{13}C NMR spectra.[42]

A new resonance line at +452 ppm in the ^{139}La spectrum indicates the formation of complex **9** on decomposition of **15**. It is likely the reversible dissociation of the *ate* complex that is the first stage of this reaction. Bimetallic complex **16** thus formed is unstable and undergoes Schlenk disproportionation in accordance with equilibrium 19. Here, of the three feasible pathways of disproportionation of **16**, the one that really develops is the pathway leaving the La–Ru bond intact. This finding is a solid argument in favor of considerable stability of the La–Ru bond in solution.

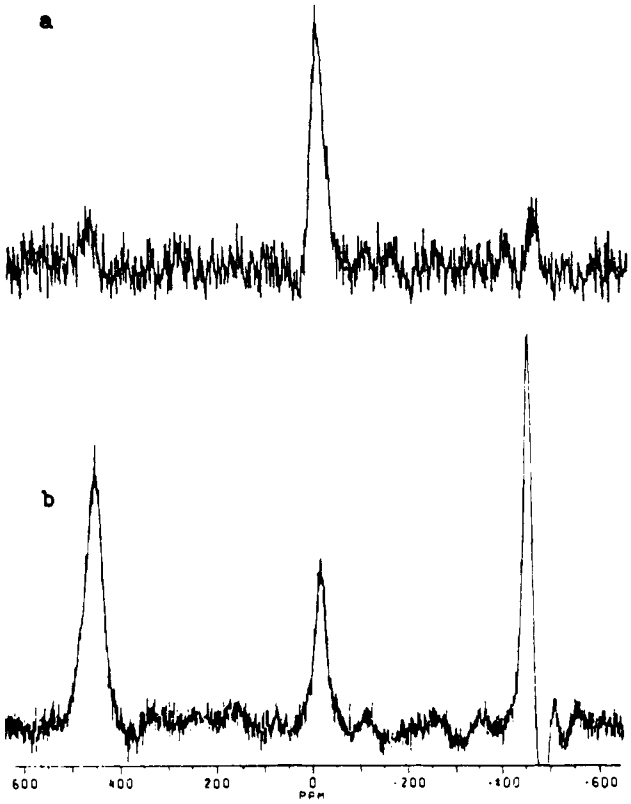

Figure 6. ^{139}La NMR spectra of **15** in THF/THF-d_8 solution: keeping the solution for 20 h at 20 °C (a) and after 5 days (b).

$$\mathbf{15} \overset{THF}{\rightleftarrows} \underset{\mathbf{16}\ (n = 9)}{(THF)_2Cp(I)LaRu(CO)_2Cp} + NaI \quad (18)$$

$$\mathbf{16} \overset{THF}{\rightleftarrows} \underset{\mathbf{17}\ (n = 12)}{(THF)Cp_2LaRu(CO)_2Cp} + \underset{\mathbf{9}\ (n = 6)}{(THF)_3I_2LaRu(CO)_2Cp} \quad (19)$$

Thus, the resonance at −452 ppm in the ^{139}La spectrum must have corresponded to biscyclopentadienyl complex **17**. The resonance is upfield by ca. 400 ppm relative to the estimate for

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(42) Schlenk equilibrium similar to that shown in eq 19 has been investigated by Evans and co-workers[8a] for cobalt carbonyl derivatives of samarium. The most important factor determining the position of such equilibria is roughly the trend for lanthanide atoms to reach maximum coordination number in solution with the lowest possible steric strain. Actinides are more reluctant to undergo such transformations. In particular, Marks and co-workers pointed out that thorium complexes $(C_5H_5)_2(X)ThRu(CO)_2Cp$ (X = Cl, I) do not disproportionate in solution.[15,17] This is most likely accounted for by the higher covalent character of the corresponding bonds.

n = 12. So, the combined data (cf. Table IX) enabled us to conclude that the formation of direct La–Ru bonding can be distinguished by a large upfield shift of ^{139}La compared to the resonances in simple cyclopentadienyl, halide, and THF complexes of lanthanum with other parameters being the same (equal values of *n*). This shift for complexes **9**, **15**, and **17** is in the 400–600-ppm range.[43]

Conclusion

Here we have shown that ruthenium carbonyl derivatives of lanthanides $X_2LnRu(CO)_2Cp$ both in the solid state and in THF solution contain direct lanthanide–ruthenium bonds unsupported by bridging carbonyl ligands. Thus, there is no doubt that the bonds between lanthanides and transition metals unsupported by any bridging ligands can be formed and be quite stable. The formation of such bonds has been inferred earlier only from IR spectra.[2] It was shown that the Ln–Ru bond is reactive toward various electrophilic and nucleophilic agents. Schlenk-type equilibria are ubiquitous in the organometallic compounds of lanthanides due to a high ionicity of the lanthanide–element bonds. In the present article we have given some examples of such behavior. ^{139}La spectroscopy has been found to be a highly informative tool bearing a lot of important information on these processes.

Experimental Section

All manipulations have been done either on a high-vacuum line in an all-glass apparatus equipped with PTFE stopcocks or in an atmosphere of thoroughly purified argon using standard Schlenk technique or in a Vacuum Atmospheres drybox. Tetrahydrofuran for syntheses (and THF-d_8 for NMR measurements) was purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents were distilled and stored over CaH_2. Diisopropyl ketone was dried by K_2CO_3 and distilled immediately before use. Anhydrous $LaCl_3$ and $LuCl_3$ were obtained from commercially available hydrates of "Pure for Chemical Uses" (USSR) grade,[44] $LaI_3(THF)_3$ was prepared by the treatment of lanthanum turnings (99.95% pure) by HgI_2 in THF. 1,3-$(Me_3Si)_2C_5H_4$,[45] C_5Me_5H,[46] CpTl,[44] $Cp_2LuCl(THF)$,[47] $[CpRu(CO)_2]_2$,[44] $PhMeSiH_2$,[48] and $Me_3SiC{\equiv}CSiMe_3$[49] were prepared by the published methods. ^{1}H, ^{13}C, and ^{139}La spectra were recorded with a Bruker AM 360 for 3–10% solutions in THF. Chemical shifts for ^{1}H and ^{13}C were measured relative to TMS, and ^{139}La chemical shifts were measured relative to the resonance of $La(ClO_4)_3$ solution in D_2O. The data of ^{1}H and ^{13}C NMR spectra are given in Table X. IR spectra were taken with a Perkin-Elmer 457 spectrometer using a vacuum-tight cell. C, H microanalyses were done using a set of commercial equipment for CHN microanalyses (Khimlaborpribor, Klin, Russia). Lanthanide content was assayed by titration (EDTA, Xylenol Orange). Electron probe X-ray analyses were done with a scanning electron microscope SEM-505 (Phillips) equipped with a unit for X-ray energy dispersive analysis Edax.

(THF)$Cp_2LuRu(CO)_2Cp$ (4). A cold solution of $Na[CpRu(CO)_2]$, prepared from 1.92 g (4.3 mmol) of $[CpRu(CO)_2]_2$ by reduction with an excess of 1% sodium amalgam in 50 mL of THF was added to a solution of 3.55 g (8.6 mmol) of $Cp_2LuCl(THF)$ in 100 mL of THF cooled to −20 °C. After slow warming to room temperature, the reaction mixture was stirred for 4 h. The solution was decanted from the NaCl precipitate and evaporated to 10 mL. The crystals precipitated at −78 °C were separated, washed with a small amount of cold toluene, and dried in vacuum. Yield 3.2 g (62%) of colorless crystals of **4**, which decompose at 235–250 °C. The solid could be further purified by crystallization from a large amount of toluene. Anal. Calcd for $C_{21}H_{23}LuRuO_3$: C, 42.07; H, 3.84. Found: C, 42.30; H, 3.98. Electron probe microanalysis: Lu:Ru = 1:1. IR (THF) ν(CO) 2027 s, 1965 s cm^{-1}.

$\{Cp''_2Lu(\mu\text{-}Cl)\}_2$ (2). Cp″Na (3.35 g, 14.44 mmol) and 2.03 g (7.21 mmol) of $LuCl_3$ in 100 mL of THF were heated in a sealed evacuated tube in a boiling water bath for 2 h. The solution was decanted from the precipitate and evaporated to dryness. Yield 3.81 g (84%) of colorless needles of **2**, mp 205–206 °C. The complex can be purified by sublimation in vacuum at 10^{-3} Torr and 260–280 °C. Anal. Calcd for $C_{44}H_{84}Lu_2Si_8Cl_2$: C, 41.97; H, 6.68; Lu, 27.82; Na, 0.00. Found: C, 42.11; H, 6.72; Lu, 27.96; Na, 0.04.

$\{Cp''_2La(\mu\text{-}Cl)\}_2$. Cp″Na (0.49 g, 2.11 mmol) and 0.26 g (1.06 mmol) of $LaCl_3$ in 50 mL of THF were heated in a sealed evacuated tube in a boiling water bath for 8 h. The isolation of product was accomplished as for complex **2**. Yield 0.59 g (91%) of white crystals of **16**, mp 223–225 °C. Anal. Calcd for $C_{44}H_{84}La_2Si_8Cl_2$: C, 44.56; H, 7.09; La, 23.46; Na, 0.00. Found: C, 44.70; H, 7.21; La, 23.58; Na, 0.03.

(THF)$Cp''_2LuRu(CO)_2Cp$ (5). To a solution of 3.52 g (2.8 mmol) of $\{Cp''_2Lu(\mu\text{-}Cl)\}_2$ in 50 mL of THF cooled to −20 °C was added a cold solution of $Na[CpRu(CO)_2]$, prepared from 1.26 g (2.8 mmol) of $[CpRu(CO)_2]_2$ by reduction with an excess of 1% sodium amalgam in 50 mL of THF. The reaction mixture was stirred for 5 h at room temperature. The solution was decanted from NaCl precipitate and evaporated to dryness. The residue was recrystallized from 10 mL of toluene. The crystals precipitated at −78 °C were separated, washed with a minimal amount of cold toluene, and quickly dried in vacuum (prolonged drying leads to the loss of a THF molecule). Yield 2.9 g (58%) of colorless crystals of **5**, which decompose at 71 °C. Anal. Calcd for $C_{33}H_{55}LuRuO_3Si_4$: C, 44.64; H, 6.20. Found: C, 44.39; H, 6.02. Electron probe microanalysis: Lu:Ru:Si = 1:1:4. IR (THF) ν(CO) 2029 s, 1967 s cm^{-1}.

$Cp^*_2LuRu(CO)_2Cp$ (6). A mixture of 1.32 g (4.7 mmol) of $LuCl_3$ with 1.47 g (9.3 mmol) of Cp*Na in 100 mL of THF was stirred for 20 h. The solution of *ate* complex formed was cooled to −20 °C and treated with a cold solution of $Na[CpRu(CO)_2]$, prepared from 1.02 g (2.3 mmol) of $[CpRu(CO)_2]_2$ by reduction with an excess of 1% sodium amalgam in 50 mL of THF. After slow warming to room temperature, the reaction mixture was stirred for 7 h. After evaporation to dryness the product was extracted from the residue by hot toluene. Removal of toluene gives crude product, which can be recrystallized from a minimal amount of toluene to yield 1.6 g (52%) of colorless crystals of **6** which decompose at 162 °C. Anal. Calcd for $C_{27}H_{35}LuRuO_2$: C, 48.58; H, 5.25. Found: C, 48.71; H, 6.38. Electron probe microanalysis: Lu:Ru = 1:1. IR (THF) ν(CO) 2019 s, 1960 s cm^{-1}.

Reaction of 5 with H_2O. To 0.289 g (0.33 mmol) of **5** in 10 mL of THF at −30 °C was added 5.5 mL of a 0.06 M solution of H_2O in a THF:toluene (1:1) mixture. The reaction mixture was stirred at this temperature for 1 h and then evaporated to minimal volume. On cooling to −30 °C for 2 h crystalline **10** was formed, separated by filtration, washed by a small amount of cold ether, and dried. Yield 0.174 g (87%) of **10**, mp 122–123 °C. Anal. Calcd for $C_{44}H_{86}Lu_2O_2Si_8$: C, 43.28; H, 7.05; Lu, 28.69. Found: C, 43.11; H, 6.98; Lu, 28.81.

Reaction of 5 with HCl. To 0.34 g (0.38 mmol) of **5** in 10 mL of THF at −30 °C was added 2.3 mL of a 0.17 M solution of HCl in THF. The solution was stirred at this temperature for 1 h and then evaporated to minimal volume. On cooling to −30 °C for 2 h the crystals of chloride **2** were precipitated, separated by filtration, washed by a small amount of cold THF, and dried. Yield 0.152 g (62%) of **2**, mp 205–206 °C. Anal. Calcd for $C_{44}H_{84}Cl_2Lu_2Si_8$: C, 41.97; H, 6.68; Lu, 27.82. Found: C, 42.06; H, 6.72; Lu, 27.70.

Reaction of 5 with $HgCl_2$. To 0.282 g (0.32 mmol) of **5** in 10 mL of THF at −30 °C was added a solution of 0.045 mg (0.16 mmol) of $HgCl_2$ in 10 mL of THF. The reaction mixture was stirred at room temperature for 4 h. The formation of **2** was monitored by ^{1}H and ^{13}C NMR spectra. The reaction mixture was worked up by 5 mL of cold water, and $Hg[Ru(CO)_2Cp]_2$ formed was extracted by toluene (2 × 20 mL). The extract was evaporated to dryness. The product was purified by TLC (Al_2O_3 II grade, hexane:toluene = 1:1) to yield 0.085 g (79%) of $Hg[Ru(CO)_2Cp]_2$ with mp 174–175 °C (lit.[50] mp 173–175 °C). Anal.

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[43] The other possible explanation of the shift by the coordination with NaI present in the reaction mixtures must be rejected, since the formation of *ate* complexes which does not alter the value of *n* should be accompanied by significantly smaller shifts of resonances. The formation of complex anions, as can be demonstrated by the data for Cp_3La (cf. Table IX for $[n\text{-}Bu_4N][Cp_3LaX]$, X = Br, I), is accompanied by the downfield shifts of the corresponding resonances by only slightly more than 100 ppm.

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Table X. ^{1}H and ^{13}C NMR Data

compd	^{1}H NMR[d]	assignment	^{13}C NMR	assignment
4	6.12 (s, 10H)	Cp_2Lu	211.9	CO
	4.92 (s, 5H)	CpRu	112.5	Cp_2Lu
			86.6	CpRu
5	6.37 (t, 2H)	H2 in C_5H_3	210.7	CO
	6.33 (d, 4H)	H4,5 in C_5H_3	129.6	C2 in C_5H_3
	4.94 (s, 5H)	CpRu	123.1	C1,3 in C_5H_3
	0.18 (s, 36H)	Me_3Si	119.4	C4,5 in C_5H_3
			81.6	CpRu
			1.3	Me_3Si
6	4.85 (s, 5H)	CpRu	215.5	CO
	1.87 (s, 30H)	Me	116.4	$\mathit{C_5}Me_5$
			80.5	CpRu
			12.4	Me
15	6.33 (s, 5H)	CpLa	212.8	CO
	5.89 (s, 5H)	CpRu	112.4	CpLa
			86.5	CpRu
17	6.20 (s, 10H)	Cp_2La	213.4	CO
	5.28 (s, 5H)	CpRu	112.6	Cp_2La
			84.1	CpRu
9	5.07 (s, 5H)	CpRu	204.3	CO
			83.5	CpRu
2	6.51 (t, 4H)	H2 in C_5H_3	131.6	C2 in C_5H_3
	6.45 (d, *J* = 1.66, 8H)	H4,5 in C_5H_3	124.5	C1,3 in C_5H_3
	0.21 (s, 72H)	Me_3Si	120.7	C4,5 in C_5H_3
			0.8	Me_3Si
$\{Cp''_2La(\mu\text{-}Cl)\}_2$	6.53 (t, 4H)	H2 in C_5H_3	132.2	C2 in C_5H_3
	6.50 (d, 8H)	H4,5 in C_5H_3	128.1	C1,3 in C_5H_3
	0.22 (s, 72H)	Me_3Si	126.6	C4,5 in C_5H_3
			0.9	Me_3Si
12	6.00 (s, 10H)	Cp	161.3	CO
	1.82 (s, 3H)	MeC=C	111.7	Cp
	1.80 (s, 3H)	MeC=C	110.7	$Me_2\mathit{C}$=
	1.44 (sept, 1H)	CH	23.1	*Me*C=
	0.89 (d, 6H)	*Me*$_2$CH	21.0	*Me*C=
			17.7	CH
			15.7	*Me*$_2$CH
10[b]	6.61 (t, *J* = 1.76, 4H)	H2 in C_5H_3	131.6	C2 in C_5H_3
	6.55 (d, *J* = 1.58, 8H)	H4,5 in C_5H_3	126.9	C1,3 in C_5H_3
	0.31 (s, 72H)	Me_3Si	120.7	C4,5 in C_5H_3
			0.8	Me_3Si
11[c]	6.88 (t, 1H)	H2 in C_5H_3	132.7	C2 in C_5H_3
	6.85 (d, *J* = 1.66, 2H)	H4,5 in C_5H_3	131.2	C1,3 in C_5H_3
	6.75 (t, 1H)	H2 in C_5H_3	129.9	C2 in C_5H_3
	6.72 (d, *J* = 1.65, 2H)	H4,5 in C_5H_3	128.8	C1,3 in C_5H_3
	0.37 (s, 18H)	Me_3Si	124.9	C4,5 in C_5H_3
	0.34 (s, 18H)	Me_3Si	122.2	C4,5 in C_5H_3
			1.8	Me_3Si
			1.4	Me_3Si
13	6.45 (s, 5H)	Cp	115.9	Cp
$[n\text{-}Bu_4N][Cp_3LaBr]$	5.81 (s, 15H)	Cp	110.7	Cp
	3.30 (t, 8H)	NCH_2	59.7	NCH_2
	1.59 (quint, 8H)	$NCH_2C\mathit{H}_2$	25.2	$NCH_2\mathit{C}H_2$
	1.43 (sext, 8H)	$C\mathit{H}_2CH_3$	20.8	$\mathit{C}H_2CH_3$
	1.03 (t, 12H)	CH_3	14.5	CH_3
$[n\text{-}Bu_4N][Cp_3LaI]$	5.86 (s, 15H)	Cp	112.2	Cp
	3.29 (t, 8H)	NCH_2	59.9	NCH_2
	1.57 (quint, 8H)	$NCH_2C\mathit{H}_2$	25.3	$NCH_2\mathit{C}H_2$
	1.42 (sext, 8H)	$C\mathit{H}_2CH_3$	21.0	$\mathit{C}H_2CH_3$
	1.01 (t, 12H)	CH_3	14.4	CH_3

[a] In THF-d_8. [b] The protons of μ-OH were not assigned. [c] The protons of OH were not assigned. [d] *J* values in hertz.

Calcd for $C_{14}H_{10}O_4HgRu_2$: C, 26.05; H, 1.55. Found: C, 26.17; H, 1.60. Electron probe microanalysis: Hg:Ru = 1:2. IR (THF) ν(CO) 2000 s, 1971, 1942 cm^{-1}.

Reaction of 4 with *i*-Pr$_2$CO. To 0.241 g (0.40 mmol) of **4** in 10 mL of THF at −30 °C was added a solution of 0.048 g (0.42 mmol) of *i*-Pr$_2$CO in 10 mL of THF. The solution was stirred at this temperature for 2 h and then at room temperature for an additional 4 h. After evaporation to 5 mL and cooling to −78 °C colorless crystals were precipitated, separated by filtration, washed with cold ether, and dried in vacuum. Yield 0.088 g (45%) of lutetium enolate **12**. Anal. Calcd for $C_{21}H_{31}LuO_2$: C, 51.43; H, 6.49; Lu, 35.71. Found: C, 51.40; H, 6.49; Lu, 35.60.

$Cp_3La(THF)$. CpTl (2.4 g, 8.9 mmol) and 0.45 g (3.2 mmol) of lanthanum turnings were stirred for 80 h in 100 mL of THF at room temperature. A colorless solution was decanted from residual thallium and an excess of lanthanum and evaporated to dryness. Drying in vacuum gives 1.15 g (95%) of colorless crystals of $Cp_3La(THF)$. The product had reasonable purity and was not further purified. Anal. Calcd for $C_{19}H_{23}LaO$: C, 56.16; H, 5.67; La, 34.24. Found: C, 56.23; H, 5.78; La, 34.21. ^{1}H NMR (THF-d_8, 25 °C) δ 6.05 (s, Cp).

$CpLaI_2(THF)_3$ (13). To a suspension of 8.39 g (11.4 mmol) of $LaI_3(THF)_3$ in 300 mL of THF was added 3.07 g (11.4 mmol) of CpTl and the reaction mixture was stirred for 13 h at room temperature. A colorless solution was decanted from the precipitate of TlI and evaporated to dryness. Drying in vacuum gave 7.20 g (94%) of colorless needles of **13** which decompose at 147–149 °C. Anal. Calcd for $C_{17}H_{29}LaI_2O_3$: C, 30.27; H, 4.30; La, 20.62. Found: C, 30.21; H, 4.26; La, 20.69.

$\{(THF)CpLa[Ru(CO)_2Cp](\mu\text{-}I)_2Na(THF)_2\}$ (15). To a solution of 1.29 g (1.91 mmol) of $CpLaI_2(THF)_3$ in 50 mL of THF at −20 °C was added a cold solution of $Na[CpRu(CO)_2]$, prepared from 0.43 g (0.97 mmol)

Table XI. Crystallographic Data for Complexes **2**, **4**, and **10**

	2	**4**	**10**
formula	$Lu_2C_{44}H_{84}Cl_2Si_8$	$LuRuC_{21}H_{23}O_3$	$Lu_2C_{44}H_{86}O_2Si_8$
fw	1258.68	599.45	1221.79
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	10.744 (3)	14.083 (2)	15.638 (6)
b, Å	11.821 (2)	8.347 (2)	15.787 (2)
c, Å	12.966 (3)	17.331 (4)	12.188 (1)
α, deg	71.54 (1)	90.0	90.0
β, deg	85.32 (2)	106.98 (2)	99.06 (2)
γ, deg	74.83 (1)	90.0	90.0
Z	1	4	2
V, Å^3	1508 (1)	1948 (1)	2971 (1)
d (calcd), g·cm^{-3}	1.38	2.04	1.37
diffractometer	Enraf-Nonius CAD-4		
radiation	Mo Kα (λ = 0.71073 Å)		
μ, cm^{-1}	35.3	58.3	34.9
T, °C	23	23	23
scan method	ω–2θ	θ–2θ	θ–2θ
2θ limits (deg)	4–42	4–46	4–46
no. of unique reflctns; total with $I_0 > 2\sigma(I)$	3497, 2933	2321, 1828	4385, 2750
no. of params refined	253	235	253
R^a	0.0202	0.0373	0.0280
$R_\omega{}^b$	0.0203	0.0369	0.0298

[a] $R = \sum|F_c| - |F_c|/\sum F_o$. [b] $R_w = \sum\omega^{1/2}|F_c - F_o|/\sum_{i=0}^{n}\omega^{1/2}F_o$; $\omega = K/(\sigma^2(F_o) = |g|F^2)$.

of $[CpRu(CO)_2]_2$ by reduction with an excess of 1% sodium amalgam in 50 mL of THF. After slow warming to room temperature, the reaction mixture was stirred for 3 h. After evaporation to ca. 10 mL, the crystals precipitated on cooling to −30 °C were filtered off. The crude product was recrystallized from a minimal amount of THF to yield 0.85 g (42%) of colorless crystals of **15**. Anal. Calcd for $C_{24}H_{34}LaRuO_5$: C, 31.34; H, 3.70. Found: C, 31.47; H, 3.79. Electron probe microanalysis: La:Ru:I = 1:1:2. IR (THF) ν(CO) 2031 s, 1965 s cm^{-1}.

$(THF)_3I_2LaRu(CO)_2Cp$ (9). To a suspension of 1.06 g (1.44 mmol) of $LaI_3(THF)_3$ in 50 mL of THF at −30 °C was added a cold solution of $Na[CpRu(CO)_2]$, prepared from 0.33 g (0.74 mmol) of $[CpRu(CO)_2]_2$ by reduction with an excess of 1% sodium amalgam in 30 mL of THF. The solution was stirred at this temperature for 1 h and then at room temperature for an additional 3 h. After evaporation to ca. 5 mL, NaI precipitated on cooling to −30 °C and was filtered off. White crystals which precipitated from the solution after 2 days at −30 °C were separated and dried. Yield 0.81 g (68%) of **9**. Anal. Calcd for $C_{19}H_{29}O_5I_2LaRu$: C, 27.44; H, 3.49. Found: C, 26.95; H, 3.28. Electron probe microanalysis: La:Ru:I = 1:1:2. IR (THF) ν(CO) 2023 s, 1964 s cm^{-1}.

[n-Bu_4N][Cp_3LaBr]. $Cp_3La(THF)$ (0.42 g, 1.03 mmol) and 0.33 g (1.03 mmol) of n-Bu_4NBr in 50 mL of THF were stirred at room temperature for 4 h. The solution was evaporated to 5 mL and cooled to −30 °C. Colorless crystals precipitated and were separated and dried. Yield 0.55 g (81%). Anal. Calcd for $C_{31}H_{51}NBrLa$: C, 56.71; H, 7.77; La, 21.19. Found: C, 56.55; H, 7.70; La, 21.29.

[n-Bu_4N][Cp_3LaI]. The reaction was carried out similarly to preparation of the above compound, starting from 0.35 g (0.86 mmol) of $Cp_3La(THF)$ and 0.32 g (0.86 mmol) of n-Bu_4NI in 50 mL of THF. Yield 0.45 g (74%) of colorless crystals. Anal. Calcd for $C_{31}H_{51}NILa$: C, 52.92; H, 7.25; La, 19.77. Found: C, 52.77; H, 7.12; La, 20.01.

X-ray Crystal Analysis of Complexes 2, 4, and 10. X-ray data acquisition was accomplished with single crystals packed in thin-walled glass capillaries under argon. Crystallographic data are given in Table XI. Absorption correction was not applied. The structures were solved using the heavy-atom technique and refined by the anisotropic least-squares procedure. Hydrogen atoms were located either from the difference Fourier synthesis or geometrically. All computations were run with the SHELX-76 software package on an IBM PC AT.

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Supplementary Material Available: Tables of positional and thermal parameters, bond lengths, bond angles, and molecule plots for **2**, **4**, and **10** (26 pages). Ordering information is given on any current masthead page.