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Lutetium complexes with tetraphenylethylene dianion. Synthesis and structure

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The reactions of dipotassium and disodium salts of the tetraphenylethylene dianion with $LuCl_3(THF)_3$ or $CpLuCl_2(THF)_3$ yielded the homoleptic *ate*-complexes $[Na(THF)_5][Lu(Ph_2CCPh_2)_2]$ (**1**) and $[K(THF)_5][Lu(Ph_2CCPh_2)_2]$ (**2**) or the heteroleptic complex $CpLu(Ph_2CCPh_2)(THF)_2$ (**4**), respectively. Recrystallization of complex **1** from a diglyme—THF mixture afforded $[Na(diglyme)_2][Lu(Ph_2CCPh_2)_2](THF)_{0.5}$ (**3**). Recrystallization of complex **4** from 1,2-dimethoxyethane gave $[CpLu(Ph_2CCPh_2)(DME)](DME)$ (**5**). The structures of complexes **3** and **5** were established by X-ray diffraction analysis. In both complexes, the unusual η^6-coordination of the $(Ph_2CCPh_2)^{2-}$ dianion to lutetium is observed. The Lu—C distances vary from 2.441(2) to 2.643(2) Å (**3**) and from 2.470(3) to 2.763(3) Å (**5**). In complexes **3** and **5**, a redistribution of the C—C bond lengths was observed in the Ph groups coordinated to lutetium. Studies by ^1H, ^{13}C, and 2D NMR spectroscopy demonstrated that the η^6-coordination of the tetraphenylethylene dianion in homoleptic *ate*-complexes **1** and **2** is retained in a THF solution, whereas the coordination of this dianion in heteroleptic complex **4** changes from η^6 to η^4.

Key words: organolanthanides, lutetium, dianion, tetraphenylethylene.

In the last two decades, organolanthanide chemistry has attracted growing attention.[1] However, the spectrum of ligands used in this field of chemistry is rather narrow. Singly charged anions are primarily used as ligands in organometallic chemistry of 4f elements. The cyclopentadienyl ligands, their substituted derivatives, heteroatomic cyclopentadienyl ligands, and, particularly, the pentamethylcyclopentadienyl ligands are still most commonly used in this field.[2] Hence, a search for new types of ligands for the synthesis of 4f-element complexes seems to be of importance.

In this connection, di- and polyanionic organic ligands are of particular interest. Earlier, it has been noted[3] that bulky negatively charged ligands play an important role in stabilization of such compounds. The use of polyanionic ligands in organolanthanide chemistry has started from the discovery of cyclooctatetraene derivatives.[1b,4] Another example of the use of dianionic ligands is the synthesis of complexes with carborane dianions.[5] Compounds with the dianions of naphthalene,[6] anthracene,[7] other aromatic hydrocarbons, and their heteroatomic analogs,[7c,8] the pyrene trianion, and the benzene dianion[9] are known. The essentially covalent nature of the Lu—C bond was revealed[7b] in lutetium complexes with the anthracene dianion. Earlier,[10] we have synthesized an yttrium compound with the tetraphenylethylene dianion and established its structure. In this compound, the dianionic ligand is η^6-coordinated to the yttrium atom. In the present study, we synthesized new homo- and heteroleptic lutetium complexes with the tetraphenylethylene dianion.

Results and Discussion

Synthesis of lutetium complexes. Potassium and sodium salts of the tetraphenylethylene dianion react with lutetium trichloride in THF to form homoleptic *ate*-complexes **1** and **2**.

$$LuCl_3(THF)_3 + 2\,M_2[Ph_2CCPh_2] \longrightarrow$$

$$\longrightarrow \underset{\mathbf{1,\,2}}{[M(THF)_5][Lu(Ph_2CCPh_2)_2]} + 3\,MCl$$

M = Na (**1**), K (**2**)

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Compounds **1** and **2** were prepared as extremely air-sensitive dark-red crystals. Complex **2** is readily soluble in THF, whereas complex **1** is only poorly soluble in this solvent. Recrystallization of **1** from a diglyme—THF mixture afforded the $[\mathrm{Na(diglyme)_2}][\mathrm{Lu(Ph_2CCPh_2)_2}](\mathrm{THF})_{0.5}$ complex (**3**), whose structure was established by X-ray diffraction analysis (Fig. 1, Tables 1—3). The reaction of $(\mathrm{C_5H_5})\mathrm{LuCl_2} \cdot 3\mathrm{THF}$ with the disodium salt of tetraphenylethylene gave heteroleptic lutetium complex **4**.

$$\mathrm{CpLuCl_2(THF)_3 + Na_2[Ph_2CCPh]_2} \longrightarrow$$

$$\longrightarrow \mathrm{CpLu(Ph_2CCPh_2)(THF)_2 + 3\ NaCl}$$

4

Dark-red pyrophoric complex **4** is soluble in THF and 1,2-dimethoxyethane (DME) and poorly soluble in toluene and diethyl ether. The crystals of $[\mathrm{CpLu(Ph_2CCPh_2)(DME)}](\mathrm{DME})$ (**5**) suitable for X-ray diffraction study were grown from a dioxane—DME mixture (Fig. 2, see Tables 1—3).

Strong coordination of the tetraphenylethylene dianion to the lutetium cation in all the above-mentioned complexes is confirmed by the fact that the absorption band in the UV-Vis spectra of compounds **1**, **2** ($\lambda_{\max}$= 395 and 397 nm, respectively, THF), and **4** ($\lambda_{\max}$= 410 nm, THF) is strongly shifted to a short-wavelength region compared to the absorption maximum in the spectra of alkali

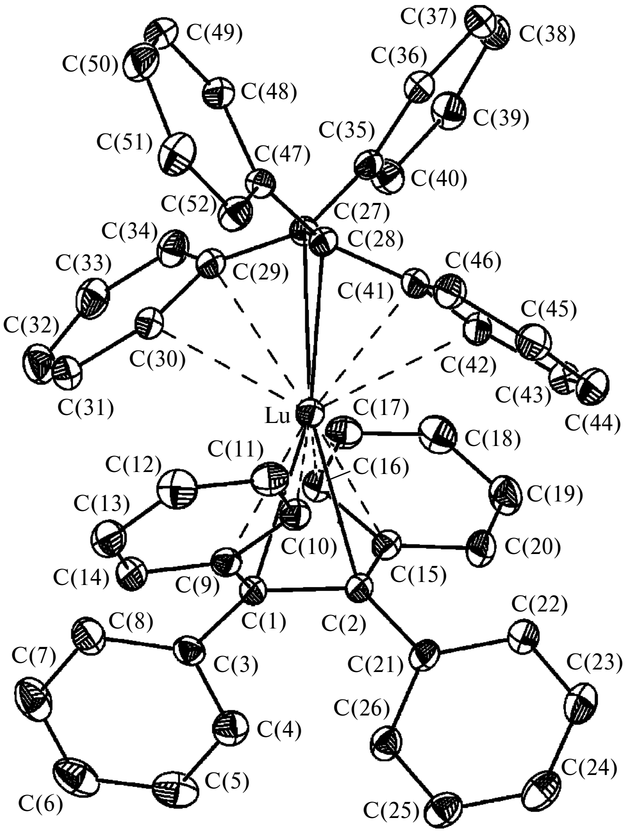


Fig. 1. Overall view of the anion in complex **3**. Hydrogen atoms are omitted.

Table 1. Crystallographic data for complexes **3** and **5**

Parameter	**3**	**5**
Formula	$\mathrm{C_{52}H_{40}Lu \cdot (NaC_{12}H_{28}O_6) \cdot 0.5\ (C_4H_8O)}$	$\mathrm{C_{35}H_{40}O_2Lu \cdot (C_4H_{10}O_2)}$
Molecular weight	1167.20	752.72
Dimensions (mm)	0.3×0.2×0.2	0.4×0.3×0.2
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	13.3297(9)	12.710(1)
b/Å	14.4281(9)	13.943(1)
c/Å	16.352(1)	18.977(2)
α/deg	71.179(1)	90.0
β/deg	70.427(1)	104.857(2)
γ/deg	83.399(1)	90.0
V/Å^3	2804.6(3)	3250.7(5)
Z	2	4
d_{calc}/g cm^{-3}	1.382	1.538
Linear absorption, μ/cm^{-1}	18.21	30.77
θ-Scan range/deg	2.5—32.5	2.0—30.0
Number of measured reflections	34906 (R_{int} = 0.0226)	30287 (R_{int} = 0.0432)
Number of independent reflections	19379	9383
Number of reflections with $I > 2\sigma(I)$	16413	7174
Number of parameters in refinement	973	575
R_1 based on reflections with $I > 2\sigma(I)$	0.0318	0.0347
wR_2 based on all reflections	0.0825	0.0851
GOOF on F^2	0.983	1.108

Table 2. Selected bond lengths (d) in complexes **3** and **5**

Bond	d/Å	
	3	**5**
Lu—C(1)/	2.481(2)/	2.493(3)
Lu—C(27)	2.478(2)[a]	
Lu—C(2)/	2.441(2)/	2.470(3)
Lu—C(28)	2.463(2)	
Lu—C(9)/	2.643(2)/	2.703(3)
Lu—C(29)	2.615(2)	
Lu—C(10)/	2.581(2)/	2.665(4)
Lu—C(30)	2.524(1)	
Lu—C(15)/	2.610(2)/	2.763(3)
Lu—C(41)	2.607(2)	
Lu—C(16)/	2.567(2)/	2.723(4)
Lu—C(42)	2.588(2)	
C(1)—C(2)/	1.507(3)/	1.507(5)
C(27)—C(28)	1.507(3)	
C—C_{ipso}		
C(1)—C(9)/	1.438(3)/	1.435(5)
C(27)—C(29)	1.434(2)	
C(2)—C(15)/	1.446(3)/	1.443(5)
C(28)—C(41)	1.438(3)	
C(1)—C(3)/	1.485(3)/	1.484(4)
C(27)—C(35)	1.482(3)	
C(2)—C(21)/	1.480(3)/	1.483(4)
C(28)—C(47)	1.481(3)	
C_{ipso}—C_o (coord.)[b]		
C(9)—C(10)/	1.440(3)/	1.437(5)
C(29)—C(30)	1.443(3)	
C(15)—C(16)/	1.446(3)/	1.418(5)
C(41)—C(42)	1.436(3)	
C(9)—C(14)/	1.438(3)/	1.428(5)
C(29)—C(34)	1.435(3)	
C(15)—C(20)/	1.424(3)/	1.435(5)
C(41)—C(46)	1.440(3)	
C_{ipso}—C_o (uncoord.)[c]	1.407(3)—	1.405(5)—
	1.411(3)	1.413(5)
C_o—C_m (coord.)		
C(10)—C(11)/	1.405(3)/	1.402(5)
C(30)—C(31)	1.404(3)	
C(16)—C(17)/	1.404(3)/	1.397(5)
C(42)—C(43)	1.406(3)	
C(13)—C(14)/	1.370(3)/	1.372(5)
C(33)—C(34)	1.372(3)	
C(19)—C(20)/	1.379(3)/	1.372(5)
C(45)—C(46)	1.372(3)	
C_o—C_m (uncoord.)	1.387(3)—	1.387(5)—
	1.392(3)	1.397(5)
C_m—C_o (coord.)		
C(11)—C(12)/	1.372(3)/	1.383(5)
C(31)—C(32)	1.378(3)	
C(17)—C(18)/	1.379(3)/	1.378(5)
C(43)—C(44)	1.374(3)	
C(12)—C(13)/	1.411(3)/	1.378(5)
C(32)—C(33)	1.404(3)	
C(18)—C(19)/	1.410(3)/	1.405(5)
C(44)—C(45)	1.405(4)	
C_m—C_o (uncoord.)	1.383(4)—	1.374(5)—
	1.390(3)	1.396(5)

[a] The values for two Ph_2CCPh_2 groups in complex **3** are separated by a slash.

[b] The C—C bond lengths in the phenyl rings coordinated to lutetium are marked "coord.".

[c] The ranges of the bond lengths in the phenyl rings uncoordinated to lutetium.

metal salts with the tetraphenylethylene dianion (λ_{max}= 485 nm).[11] This shift is generally indicative of an efficient interaction between an organic anion and a counterion.[12] It can be concluded that the tetraphenylethylene dianion is strongly coordinated to the lanthanide ion both in homo- and heteroleptic complexes.

Solid-state structure. In the two complexes under study, the tetraphenylethylene dianion is coordinated to the lutetium cation in a similar fashion, which resembles the coordination mode observed in the yttrium complex $[Na(THF)_6][Y(Ph_2CCPh_2)_2]$.[10] In compound **3**, the complex anion $[Lu(Ph_2CCPh_2)_2]^-$ (see Fig. 1) consists of two tetraphenylethylene dianions coordinated to the Lu^{3+} cation. The sodium cation is coordinated by two diglyme molecules. In complex **5** (see Fig. 2), the lutetium ion is coordinated by the tetraphenylethylene dianion, the Cp ligand, and one DME molecule.

An interesting structural feature of complexes **3** and **5** is the presence of six short intramolecular Lu—C contacts for each coordinated tetraphenylethylene dianion. The Lu—C(1) and Lu—C(2) contacts (Lu—C(27) and Lu—C(28)) have the shortest lengths (average distances are 2.466(2) Å in **3** and 2.482(3) Å in **5**, see Table 2), the Lu—$C_{o\text{-phen}}$ distance is somewhat longer (2.565(2) Å in **3** and 2.684(4) Å in **5**), and, finally, the longest Lu—$C_{ipso\text{-phen}}$ distances are 2.619(2) Å in **3** and 2.743(4) Å in **5**. Hence, the tetraphenylethylene dianion in complexes **3** and **5** can be considered as the η^6-coordinated ligand. In both complexes, the C(1)—C(2) and C(27)—C(28) bonds in the coordinated tetraphenylethylene ligand are substantially elongated (to 1.507(3) Å) and can be assigned to C—C single bonds, as opposed to the double bond (1.356(3) Å) in tetraphenylethylene.[13] An analogous elongation of the C=C bond (1.51(1) Å) has been found earlier[14] in $[Cs(diglyme)]_2[Ph_2CCPh_2]$.

The presence of this C—C single bond indicates that there is no conjugation between the "left" and "right" parts of the dianion, and the tetraphenylethylene ligand in complexes **3** and **5** can be described as coordinated in a bis-η^3 fashion. The character of the metal—ligand inter-

Table 3. Selected bond angles (ω) and dihedral angles (φ) in complexes **3** and **5**

Angle	**3**	**5**
Bond angle	ω/deg	
C—C—C_{ipso} (coord.)		
C(1)—C(2)—C(15)/ C(27)—C(28)—C(41)	117.2(2)/ 116.8(2)	115.6(3)
C(2)—C(1)—C(9)/ C(28)—C(27)—C(29)	116.9(2)/ 116.3(2)	116.9(3)
C—C—C_{ipso} (uncoord.)		
C(1)—C(2)—C(21)/ C(27)—C(28)—C(47)	117.5(2)/ 117.3(2)	119.0(3)
C(2)—C(1)—C(3)/ C(28)—C(27)—C(35)	117.3(2)/ 118.2(2)	117.7(3)
C—C_{ipso}—C_o (coord.)		
C(1)—C(9)—C(10)/ C(27)—C(29)—C(30)	120.6(2)/ 120.2(2)	120.9(3)
C(2)—C(15)—C(16)/ C(28)—C(41)—C(42)	120.0(2)/ 120.5(2)	121.1(3)
C(1)—C(9)—C(14)/ C(27)—C(29)—C(34)	125.4(2)/ 125.5(2)	124.6(3)
C(2)—C(15)—C(20)/ C(28)—C(47)—C(48)	125.4(2)/ 118.7(2)	124.4(3)
C—C_{ipso}—C_o (uncoord.)	119.1(2)— 125.5(2)	119.7(3)— 124.9(3)
C_o—C_{ipso}—C_o (coord.)	114.0(2)— 114.4(2)	114.5(3)— 114.6(3)
C_o—C_{ipso}—C_o (uncoord.)	115.9(2)— 116.3(2)	115.4(3)— 115.7(3)
Dihedral angle	φ/deg	
C(9)—C(1)—C(2)—C(15)/ C(29)—C(27)—C(28)—C(41)	135.0/ −136.6	147.1
C(3)—C(1)—C(2)—C(15)/ C(29)—C(27)—C(28)—C(47)	62.0/ −61.8	−54.4
C(21)—C(2)—C(1)—C(9)/ C(35)—C(27)—C(28)—C(41)	61.9/ −61.4	−52.9
C(1)—C(2)—C(15)—C(17)/ C(27)—C(28)—C(41)—C(43)*	21.6/ 16.2	−28.5
C(2)—C(1)—C(9)—C(11)/ C(28)—C(27)—C(29)—C(31)	16.4/ 25.2	18.9
C(2)—C(1)—C(3)—C(5)/ C(28)—C(27)—C(35)—C(37)	24.2/ 24.2	−25.2
C(1)—C(2)—C(21)—C(25)/ C(27)—C(28)—C(47)—C(49)	24.5/ 29.4	−11.3

* The C—C—C_{ipso}—C_{meta} pseudodihedral angles. In all cases, the C_{meta} atom is in the *trans* position with respect to the C—C bond.

action in compounds **3** and **5** is best represented as the induced formation of two allyl-type fragments in the tetraphenylethylene dianion under the action of the triply charged Lu^{3+} cation.

The tetraphenylethylene ligand in complex **5** is asymmetrically coordinated. The dihedral angle between the plane of the Cp ligand and the plane through the C(1),C(9),C(10) atoms differs from that between this ligand and the plane through the C(2),C(15),C(16) atoms (72.1° and 28.6°, respectively). In complex **5**, the distance between the Lu atom and one of the coordinated *ortho*-carbon atoms, *viz.*, Lu—C(10), is 0.058 Å shorter than another analogous distance (Lu—C(16)). This difference is attributable to repulsion between the Cp and tetraphenylethylene ligands, resulting in elongation of the Lu—C_o (Lu—C(16)) and Lu—C_{ipso} (Lu—C(15)) bonds. The latter is 0.06 Å longer than the Lu—C(9) bond.

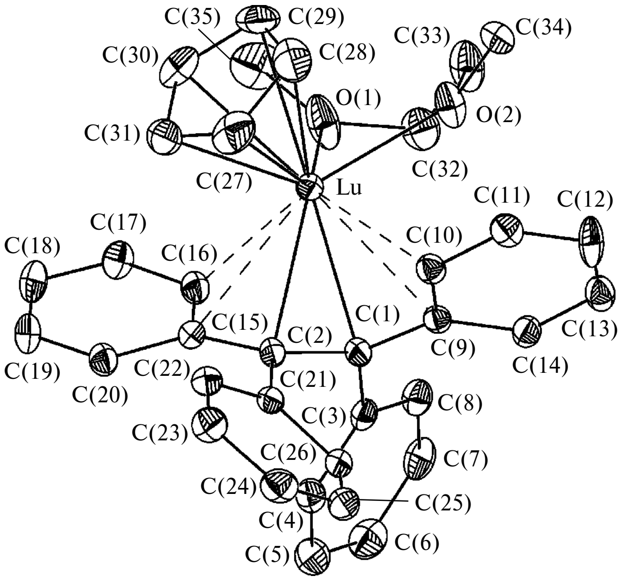


Fig. 2. Overall view of complex **5**. Hydrogen atoms are omitted.

The presence of the Lu—C_o contacts in compounds **3** and **5** leads to a decrease in the Lu...H distances for the hydrogen atoms bound to the coordinated C_o atoms (2.53—2.57 Å and 2.53—2.63 Å in complexes **3** and **5**, respectively). Nevertheless, the Ph rings involved in coordination remain planar (deviations of the carbon atoms from the planes are smaller than 0.015 Å).

The above-described coordination mode of the tetraphenylethylene dianion is similar to that of the allyl anions in f-element complexes. The Lu—C distances in complexes **3** and **5** are comparable to the corresponding distances in two structurally characterized organometallic compounds of lutetium. In $Lu(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2(\eta^3\text{-}2,4\text{-}Me_2C_5H_5)$,[15] one dimethylpentadienyl ligand is η^3-coordinated to the Lu atoms and can be considered as the substituted allyl anion. The Lu—C distances in this fragment are 2.53(1), 2.64(1), and 2.60(1) Å. The second lutetium compound, $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)Lu(\eta^5{:}\eta^3\text{-}MeC_5H_5CH_2CH_2CHMeC_3H_3Me)$,[16] is also a pentadienyl derivative of lutetium, in which the Lu—C distances in the allyl fragment are 2.440(6), 2.629(5), and 2.656(5) Å. In both complexes, lutetium has a coordination number of eight on the assumption that the pentadienyl anion is a six-electron-donor ligand and the allyl anion is a four-electron-donor ligand. Hence, the observed Lu—C distances in complexes **3** and **5** are in good agreement with the hypothesis about the "double allyl coordination" of the tetraphenylethylene dianion. Presumably, the dianionic ligand in compounds **3** and **5** occupies four coordination sites, with the result that lutetium has a coordination number of 8 in **3** and 9 in **5**.

Another analogy can be found in benzyl derivatives (and their heteroatomic analogs) of lanthanides and transition metals. This type of complexes contains the same Ar—C(R)$_2$—M structural motif (Table 4). In all known complexes, there are short M—C$_{o\text{-Ar}}$ and M—C$_{ipso\text{-Ar}}$ contacts. To exclude the differences in the coordination number, ionic radii, and the nature of binding, let us compare the differences between the M—C$_o$ and M—C$_{\text{benz}}$ distances and between the M—C$_{ipso}$ and M—C$_{\text{benz}}$ distances. Their values can characterize the efficiency of the M—C$_o$ interaction in each complex. The smaller this value, the stronger the interaction. The smallest M—C$_o$ – M—C$_{\text{benz}}$ differences are observed for organolanthanide derivatives with dianionic ligands. Palladium and platinum derivatives, which have a well-known tendency to form allyl complexes, are characterized by the most similar values. An analogous tendency has been described for several lanthanide compounds with dianions of nitrogen-containing heterocyclic compounds.[8,9,28]

Behavior of the complexes in solution. To make sure that the short contacts between the *ortho* positions of the Ph groups and the Lu cation, which were revealed by X-ray diffraction, are retained in solution, we studied complexes **1**, **2**, and **4** by NMR spectroscopy. The ^{1}H NMR spectra of compounds **1** and **2** (Fig. 3) have two different sets of signals for protons. One set corresponds to the protons of the Ph groups interacting with the lutetium cation, whereas another set corresponds to the protons of the remote Ph groups. Potassium derivative **2** was used in most NMR experiments because of its better solubility. The assignment of the signals was made based on the ^{1}H—^{1}H COSY NMR spectrum (Fig. 4). At room temperature, the signals in the spectrum of complex **2** are slightly broadened due to dynamic processes, whose occurrence was confirmed by the ^{1}H NMR spectroscopic data in a temperature range of 250—330 K (Fig. 5). We failed to reach the coalescence temperature for complexes **2** and **4** because of limitations associated with the boiling point of the solvent (THF-d$_8$).

At 250 K, all protons of one set of the Ph groups coordinated to lutetium are nonequivalent on the NMR time scale. A broadening of the signals with increasing temperature can be associated with rotation of the Ph groups about the =C—C$_{ipso}$ bond. To elucidate the causes of broadening of the signals, we performed a saturation transfer experiment. Irradiation of the signal for the H(5) proton (δ 4.72) at 320 K results in the saturation transfer to the signal for the H(1) proton (δ 7.67), whereas the width of the signal for the H(3) proton (δ 6.16) remains unchanged with increasing temperature. This can occur

Table 4. The M—C bond lengths (Å) in complexes with the benzyl-type ligands Ar—C(R)$_2$—M

Compound	M—C$_{\text{benz}}$	M—C$_o$	M—C$_{ipso}$	Δ(M—C$_o$) – (M—C$_{\text{benz}}$)	Δ(M—C$_{ipso}$) – (M—C$_{\text{benz}}$)	Reference
$Zr(CH_2Ph)_3(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)$	2.28	2.94	2.59	0.66	0.31	17
$Zr(CH_2\text{-}p\text{-}C_6H_4F)_3(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)$	2.26	3.16	2.64	0.90	0.38	17
$Mo(CH_2\text{-}p\text{-}C_6H_4Me)Cp(CO)_2$	2.269	2.480	2.364	0.21	0.095	18
$Fe_2(C_5H_4\text{—}CPh_2)(CO)_5$	2.113	2.240	2.166	0.12	0.053	19
$Ru_2(C_5H_4\text{—}CPh_2)(CO)_5$	2.236	2.322	2.342	0.11	0.086	20
$CoCH_2Ph[P(Ome)_3]_3$	2.036	2.408	2.118	0.37	0.081	21
$RhCH_2C_6Me_5[P(O\text{—}Pr^i)_3]_2$	2.128	2.453	2.246	0.33	0.12	22
$PdCPh_3(acac)$	2.103	2.202	2.159	0.099	0.056	23
$PtCPh_3(acac)$	2.081	2.153	2.127	0.072	0.046	23
$Th(CH_2Ph)_3(Cp^*)$	2.58	3.35	2.87	0.77	0.29	24
$Th(CH_2Ph)_4(dmpe)$	2.53	3.31	2.86	0.78	0.33	25
$U(CH_2Ph)_3Me(dmpe)$	2.54	3.089	2.758	0.55	0.22	25
$Ce(CH_2Ph)(C_5Me_5)_2$	2.596	2.882	2.885	0.286	0.289	26
$(LaCp^*{}_2)_2(C_{14}H_{10})$	2.689	2.849	2.886	0.160	0.197	7d
$(SmCp^*{}_2)_2(C_{14}H_{10})$	2.595	2.840	2.791	0.245	0.196	7c
$(SmCp^*{}_2)_2(C_{16}H_{10})$	2.662	2.730	2.799	0.068	0.137	7c
$(SmCp^*{}_2)_2(C_{18}H_{12})$	2.688	2.708	2.828	0.020	0.120	7c
$Sm_2Cp^*{}_4(CH_2CHPh)$	2.732	2.772	2.850	0.040	0.118	27
$[Y(CPh_2\text{—}CPh_2)_2]^-$	2.524	2.610	2.683	0.086	0.159	10
$[Lu(CPh_2\text{—}CPh_2)_2]^-$	2.466	2.565	2.619	0.099	0.153	*
$[CpLu(CPh_2\text{—}CPh_2)(DME)]$	2.470	2.723	2.763	0.253	0.293	*
	2.493	2.665	2.703	0.172	0.210	

* The present study.

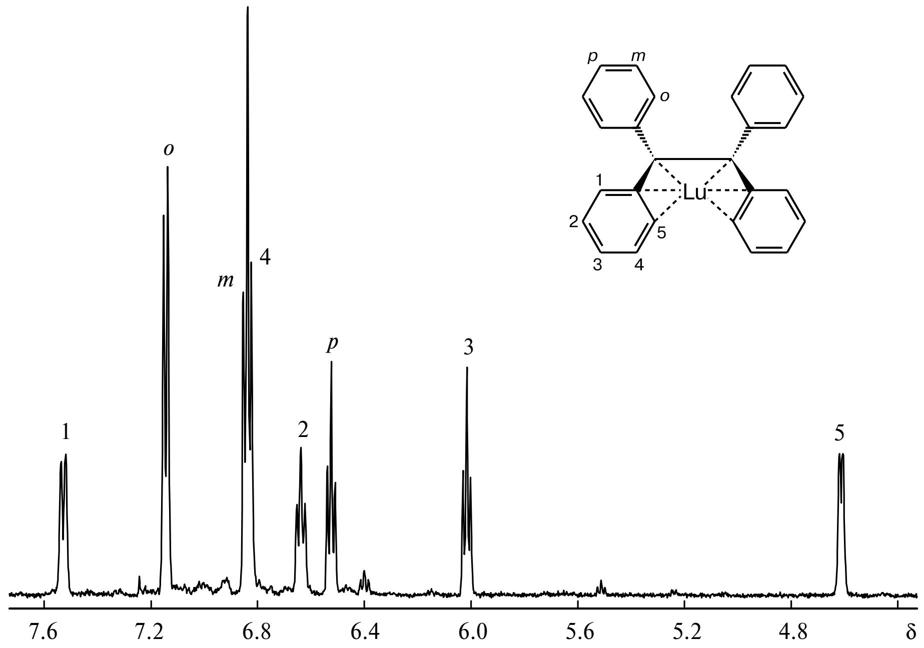


Fig. 3. ^{1}H NMR spectrum of complex **2** (500 MHz, 255 K, THF-d$_8$).

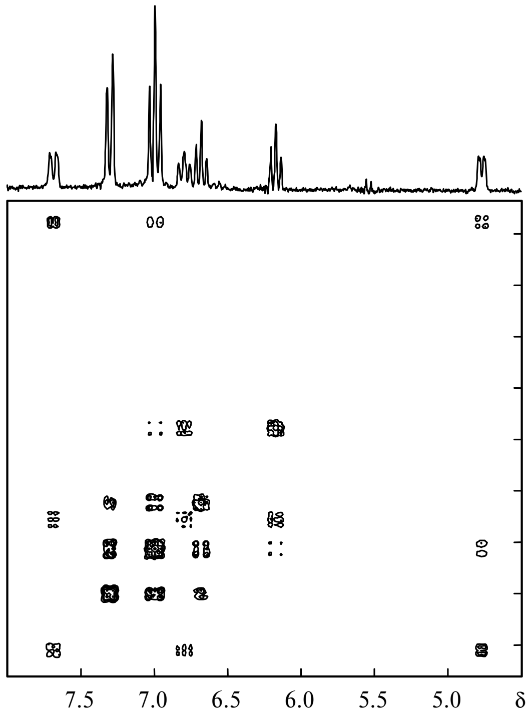


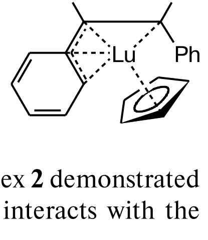
Fig. 4. ^{1}H—^{1}H COSY NMR spectrum of complex **2** (500 MHz, 297 K, THF-d$_8$).

only in the case of hindered rotation of the benzene ring about the =C—C$_{ipso}$ bond.[29]

In addition, the intensity of the signal for H_o (δ 7.27) (distant Ph groups) changes due to the Overhauser effect.[30] The results of ^{1}H NMR experiments are indicative of the nonequivalence of all protons of the Ph groups interacting with the Lu atoms. A complete analysis of the spectrum of complex **2** at 250 K using the CALM program* allowed us to calculate all constants $^3J_{\mathrm{H,H}}$ (see the Experimental section). The ^{13}C NMR spectrum shows six different signals for the Ph groups interacting with the lutetium atoms, which is consistent with the assumption of the nonequivalence of all six carbon atoms of the Ph ring.

The signals for the *ortho*-C(5) atoms coordinated to lutetium are substantially shifted upfield (δ 98.1) and have the smallest constant $^1J_{\mathrm{C,H}}$ (145 Hz). The chemical shifts in the ^{1}H and ^{13}C NMR spectra and the spin-spin coupling constants $^1J_{\mathrm{C,H}}$ for the C(5) and H(5) atoms are closer to the corresponding paremeters for the H$_{anti}$ protons of the allyl anions that are coordinated to transition metals or Groups III and IV 4f-metals than to the corresponding values for the Ph anions.[16,31]

Due to the presence of the Cp ligand in complex **4** resulting in the nonequivalence of the Ph groups interacting with lutetium, the ^{1}H and ^{13}C NMR spectra of complex **4** are more complicated, which did not allow us to perform the complete assignment of the signals in these spectra. A comparison of the ^{1}H NMR spectrum of complex **4** with the data for homoleptic *ate*-complex **2** demonstrated that only one of four Ph groups in **4** interacts with the



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* V. N. Khlopkov, E. V. Kirev, A. G. Shakhatuni, and A. O. Krasavin, http://nmr.ioc.ac.ru/software.htm#calm.

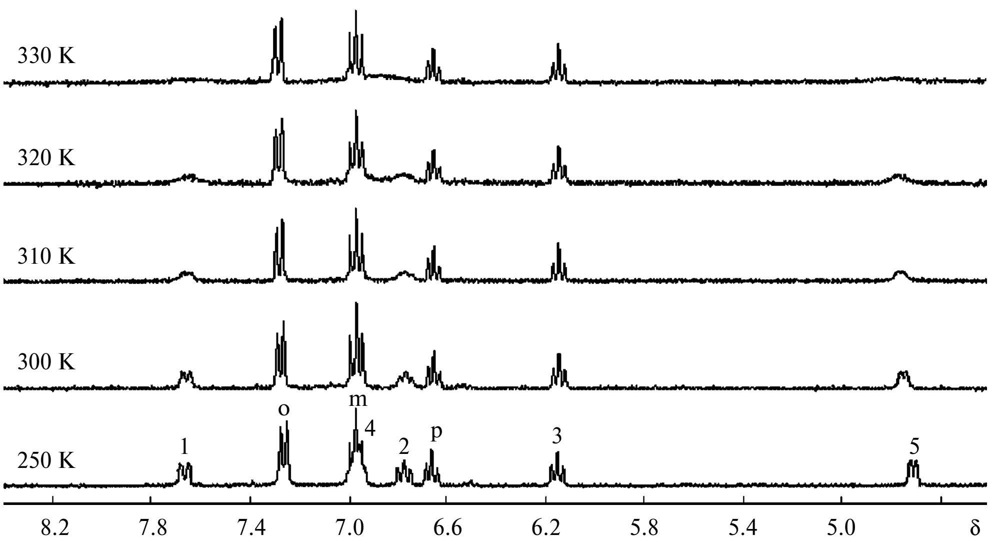


Fig. 5. ^{1}H NMR spectra of complex **2** at different temperatures.

lutetium atom. The signals for the *ortho* protons of this Ph group (δ 4.85 and 7.50) are observed in the same region as the signal of complex **2**, and their integral intensities correspond to one proton. The ^{13}C NMR spectrum shows 17 different signals, 16 of which belong to the tetraphenylethylene ligand. The observed complex spectral pattern (compared to the NMR spectrum of complex **2**) suggests that the asymmetric coordination of the tetraphenylethylene ligand observed in the solid state is enhanced in solution giving rise to the η^4-coordination mode of the tetraphenylethylene dianion. The proposed model of coordination agrees well with the observed upfield shift of only one proton of the Ph group.

Nature of the lutetium—tetraphenylethylene dianion bond. The X-ray diffraction and NMR spectroscopic data provide evidence that the short contacts between the lutetium atom and the *ortho*-carbon atoms found both in the solid phase and a THF solution can be interpreted as a result of a specific interaction between the dianionic ligand and the strongly polarizing lutetium cation. There are two plausible explanations for this effect. First, an agostic interaction between the C_o—H bond of the phenyl group and the Lu atom can occur. Second, the electron density redistribution within the Ph group coordinated to the lutetium cation can take place, resulting in an allyl-type interaction between the metal atom and the Ph group of the dianionic tetraphenylethylene ligand. Both types of interactions would lead to an upfield shift of the signals for the H(5) and C(5) atoms in the NMR spectra and the nonequivalence of all protons and carbon atoms.

However, an agostic interaction should substantially decrease the spin-spin coupling constants $^1J_{\mathrm{C(5),H(5)}}$ and should have no noticeable effect on the C—C bond lengths in the Ph ring, whereas an "allyl-type" interaction can substantially change the C—C bond lengths in the Ph group.

The C—C distances in the Ph rings, which are not coordinated to lutetium, vary in a range of 1.386—1.410 Å (Fig. 6, *b*). A noticeable redistribution of the C—C bond lengths is observed in the Ph rings interacting with the Lu atom (Fig. 6, *a*): the C_{ipso}—C(1) and C_{ipso}—C(5) bonds are elongated, and the C_{ipso}—C_{vinyl} bonds are shortened. At the same time, the C(2)—C(3) and C(4)—C(5) bonds are slightly shortened, whereas the C(3)—C(4) bond is somewhat elongated compared to the analogous bonds in other phenyl rings.

The spin-spin coupling constants $^3J_{\mathrm{H,H}}$ for the phenyl protons can serve as a source of information on the redistribution of the bond lengths in the Ph groups in solution. The constants $^3J_{\mathrm{H,H}}$ for the protons at the C atoms involved in the shortest C—C bonds are higher than the spin-spin coupling constants with other protons of the same Ph group. There are no substantial differences in the constants $^3J_{\mathrm{H,H}}$ for the protons of the Ph rings, which are not coordinated to the Lu cation. Hence, a change in the bond lengths in the Ph groups coordinated to lutetium is a

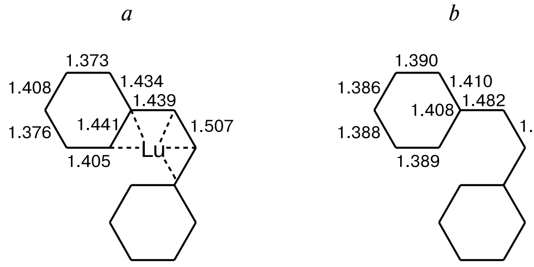
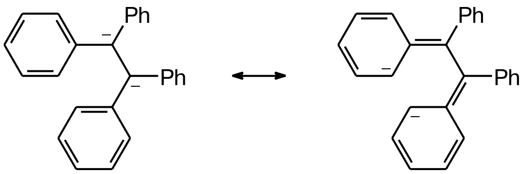


Fig. 6. The C—C bond lengths (Å) in the phenyl rings coordinated to lutetium (*a*) and remote from lutetium (*b*) in complex **3** (average values for four phenyl rings are given).

consequence of the influence of the coordinated lutetium atom on the redistribution of an excessive negative charge within the tetraphenylethylene ligand (Scheme 1).

Scheme 1



Changes in the bond lengths in the monosubstituted benzene ring have been observed earlier[32] for Ph—X compounds, where X is an electron-donating group. Nevertheless, the distorted benzene ring retains the C_{2v} symmetry in most structures, in contrast to compounds **3** and **5**.

Therefore, the tetraphenylethylene dianion can act as a bulky ligand in 4f-metal complexes. Coordination of the tetraphenylethylene dianion to the Ln^{3+} cation leads to an essential electron density redistribution in the dianion, resulting in a substantial change in the C—C bond lengths in the Ph rings.

Experimental

The complexes under study are extremely sensitive to atmospheric oxygen and moisture. Hence, the synthesis and preparation of samples were carried out in an all-sealed evacuated Schlenk-type apparatus. Diethyl ether, tetrahydrofuran, dimethoxyethane, and dioxane were distilled over a potassium—sodium eutectic under argon and stored over disodium anthracene in evacuated vessels with Teflon stopcocks. Toluene was distilled over sodium and stored over a potassium-sodium eutectic. Diglyme was refluxed over sodium and distilled *in vacuo*. The $LuCl_3(THF)_3$ and $CpLuCl_2(THF)_3$ complexes were prepared according to procedures published earlier.[33,34] Tetraphenylethylene (Aldrich) was purified by recrystallization from a toluene—ethanol mixture and dried *in vacuo*. Studies by ^1H and ^{13}C NMR spectroscopy were carried out on Bruker AM-300 and Bruker DRX-500 NMR spectrometers. The electronic absorption spectra were recorded on a Specord spectrophotometer in a THF solution. The lutetium content was determined by direct complexometric titration using xylenol orange indicator.

Sodium[pentakis(tetrahydrofuranate)]bis(1,1´,2,2´-tetraphenylethenediide)lutetium (1). A solution of $Na_2(Ph_4C_2)$ in THF (60 mL), which was prepared from tetraphenylethylene (1.499 g, 4.51 mmol) and a sodium mirror, was added to a stirred suspension of $LuCl_3 \cdot 3THF$ (1.118 g, 2.25 mmol) in THF (30 mL) in a sealed evacuated Schlenk tube. The reaction mixture was stirred for 5 h, $LuCl_3 \cdot (THF)_3$ being dissolved within a few minutes. After 5 h, precipitation started. Then the colored precipitate was extracted with refluxing THF for 5 days. The solvent was distilled off and the dark-red solid residue was washed with THF (3×10 mL) and dried *in vacuo* for 3 h. Complex **1** was obtained as dark-red microcrystals in a yield of 1.687 g (62%). Found (%): Lu, 14.42. $C_{72}H_{80}LuNaO_5$. Calculated (%): Lu, 14.77. UV (THF), λ_{max}/nm: 395, 530 (sh). ^1H NMR (300 MHz, THF-d_8), δ: 4.80 (dd, 4 H); 6.20 and 6.70 (both t, 4 H each); 6.80 (br.t, 4 H); 7.00 (t, 12 H); 7.30 (d, 8 H); 7.70 (dd, 4 H).

Sodium[bis(bismethoxyethyl ether)][bis(1,1´,2,2´-tetraphenylethenediide)lutetium semi(tetrahydrofuranate), $[Na(diglyme)_2][Lu(Ph_2CCPh_2)_2](THF)_{0.5}$ (3). A mixture of diglyme (10 mL) and THF (25 mL) was added to compound **1** (0.401 g). The resulting solution was stirred for one day. Subsequent slow evaporation of the solvents afforded red crystals of **3**. The crystals were washed with a small amount of THF, and a crystal suitable for X-ray diffraction analysis was selected using a technique described earlier.[7a]

Potassium[pentakis(tetrahydrofuranate)]bis(1,1´,2,2´-tetraphenylethenediide)lutetium (2). Complex **2** (1.324 g, 85%) was prepared analogously to complex **1** starting from a potassium mirror instead of a sodium mirror, tetraphenylethylene (0.860 g, 2.587 mmol), and $LuCl_3(THF)_3$ (0.644 g, 1.294 mmol). Found (%): Lu, 14.47. $C_{72}H_{80}KLuO_5$. Calculated (%): Lu, 14.58. UV (THF), λ_{max}/nm: 397, 535 (sh). T.decomp. 257—259 °C. ^1H NMR (500 MHz, THF-d_8, 250 K), δ: 4.72 (dd, 4 H, H(5)); 6.16 (t, 4 H, H(3)); 6.67 (t, 4 H, H_p); 6.78 (t, 4 H, H(2)); 6.98 (m, 12 H, H_m, H(4)); 7.27 (d, 8 H, H_o); 7.67 (dd, 4 H, H(1)); $^3J_{(H(1),H(2))}$ = 8.5 Hz, $^3J_{(H(2),H(3))}$ = 6.9 Hz, $^3J_{(H(3),H(4))}$ = 7.0 Hz, $^3J_{(H(4),H(5))}$ = 6.8 Hz, $^3J_{(o,m)}$ = 7.6 Hz, $^3J_{(m\ p)}$ = 7.2 Hz ($^3J_{H,H}$ were calculated using the CALM program[23]). $^{13}C\{^1H\}$ NMR (75 MHz, THF-d_8), δ: 86.9 (=C); 98.1 (C(5), $^1J_{C,H}$ = 145 Hz); 112.6 (C(3), $^1J_{C,H}$ = 160 Hz); 122.1 (C_p, $^1J_{C,H}$ = 156 Hz); 120.6 (C(1), $^1J_{C,H}$ = 157 Hz); 128.5 (C_o, $^1J_{C,H}$ = 153 Hz); 130.4 (C_m, $^1J_{C,H}$ = 156 Hz); 133.2 (C(4), $^1J_{C,H}$ = 153 Hz); 141.1 (C_{ipso}); 141.5 (C(2), $^1J_{C,H}$ = 155 Hz); 146.6 (C_i).

(1,1´,2,2´-Tetraphenylethenediide)cyclopentadienylbis(tetrahydrofuran)lutetium (4). A solution of $Na_2(Ph_4C_2)$ in THF (50 mL), which was prepared from tetraphenylethylene (0.400 g, 1.20 mmol) and a sodium mirror, was added to a stirred solution of $CpLuCl_2 \cdot 3THF$ (0.635 g, 1.20 mmol) in THF (20 mL) in a sealed evacuated apparatus. The reaction mixture was stirred for 5 h and then the solvent was distilled off *in vacuo*. The residue was extracted with THF and the extract was concentrated. The residue was washed with a small amount of the solvent (~10 mL) and dried *in vacuo*. Compound **4** was obtained in a yield of 0.464 g (54%) as dark-red microcrystals. Found (%): Lu, 24.39. $C_{39}H_{41}LuO_2$. Calculated (%): Lu, 24.41. UV (THF), λ_{max}/nm: 410, 520 (sh). ^1H NMR (500 MHz, THF-d_8), δ: 4.85 (dd, 1 H); 5.94 (s, 5 H); 5.98 and 6.25 (both t, 1 H each); 6.77—6.86 (m, 4 H); 6.87—6.97 (m, 3 H); 7.01—7.19 (m, 5 H); 7.31 and 7.40 (both m, 2 H each); 7.50 (m, 1 H). $^{13}C\{^1H\}$ NMR (62.9 MHz, THF-d_8), δ: 88.8, 95.3, 113.1 (C_5H_5), 114.7, 120.8, 123.0, 123.1, 129.1, 129.2, 129.5, 129.8, 133.7, 139.3, 141.3, 143.5, 146.6, 146.8.

(1,1´,2,2´-Tetraphenylethenediide)cyclopentadienylbis(dimethoxyethane)lutetium, $[CpLu(Ph_2CCPh_2)(DME)](DME)$ (5). A weighed sample of **4** was dissolved in anhydrous dioxane and the solvent was removed by evaporation. This operation was repeated two times. Subsequent recrystallization of the residue from dimethoxyethane afforded crystals of **5** suitable for X-ray diffraction analysis.

X-ray diffraction study of complexes 3 and 5. X-ray diffraction data sets were collected on a Smart 1000 CCD diffractometer

(λ(Mo-Kα) = 0.71072 Å) at 110 K. The crystallographic data and main characteristics of the refinement of complexes **3** and **5** are given in Table 1. The semiempirical absorption correction was applied using the SADABS program. Both structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic (isotropic for hydrogen atoms) displacement parameters against F^2 using the SHELXTL-97 program package. Analysis of difference electron density maps revealed disorder of the THF molecules in complex **3** and of the coordinated DME molecules in complex **5**. All hydrogen atoms in the ordered fragments of complexes **3** and **5** were revealed from difference electron density maps and refined isotropically. The positions of the hydrogen atoms in the disordered THF solvate molecules in complex **3** and the DME solvate molecules in complex **5** were calculated geometrically and refined using a riding model.

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