Lutetium complexes with the 1,3-diphenylcyclopentadienyl ligand. Syntheses and molecular structures of the complexes {(Ph₂C₅H₃)Lu(C₂Ph₄)(THF)} and {(Ph₂C₅H₃)LuCl₂(THF)₃}

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The reaction of LuCl₃(THF)₃ with Na(1,3-Ph₂C₅H₃) followed by the *in situ* reaction with Na₂[Ph₄C₂] produced (1,3-Ph₂C₅H₃)Lu(Ph₄C₂)(THF) (1). The structure of **1** was established by X-ray diffraction. In the crystal structure of **1**, the bis-allyl η^6 -coordination of the tetraphenylethylene dianion to the lutetium cation was observed. The structures of (1,3-Ph₂C₅H₃)LuCl₂(THF)₃ and (C₅H₅)LuCl₂(THF)₃ were determined by X-ray diffraction.

Key words: organolanthanide compounds, lutetium, dianion, tetraphenylethylene, diphenylcyclopentadiene.

In the last 10–15 years, extensive study has been given to lanthanide complexes with substituted cyclopentadienyl ligands, in which both the nature of the ligands and the degree of substitution in the cyclopentadienyl ring were varied. However, lanthanide complexes with phenyl-substituted cyclopentadienyl ligands have received little attention. A few complexes with the following polyphenyl-substituted cyclopentadienyl ligands are known: $C_5Me_3Ph_2$, $1 C_5HPh_4$, $2 and C_5Ph_5$. $3 Only (C_5HPh_4)_2La{N(SiHMe_2)_2}$ (see Ref. 2) and {(C_5Ph_5)Yb(THF)(C_2Ph)}_2 (see Ref. 3c) were structurally characterized.

Earlier,^{4,5} we have reported the synthesis of homoleptic lutetium and yttrium *ate*-complexes with the tetraphenylethylene dianion containing the complex anion $[Ln(Ph_4C_2)_2]^-(Ln = Lu \text{ or } Y)$ and the heteroleptic complex $(C_5H_5)Lu(Ph_4C_2)(THF)_2$, in which the bis- η^3 -allyl coordination of the tetraphenylethylene dianion was observed. In the latter complex, the lutetium atom is additionally coordinated by two THF molecules. Consequently, the cyclopentadienyl and tetraphenylethenide ligands are insufficient to saturate the coordination sphere of the metal atom. The widely used alkyl and trimethylsilyl substituents in the cyclopentadienyl anion exhibit the pronounced electron-donating properties and influence the Ln—ligand bond parameters.

To minimize the electronic effect of the substituents on the electron density distribution in the complexes, we chose Ph groups as substituents in the cyclopentadienyl ligand. These groups have weak electron-withdrawing rather than electron-donating properties and are also bulky.

In the present study, we synthesized and investigated the heteroleptic complex $(1,3-Ph_2C_5H_3)Lu(Ph_4C_2)$ and its synthetic precursor $(1,3-Ph_2C_5H_3)LuCl_2$.

Results and Discussion

The reaction of lutetium chloride with sodium diphenylcyclopentadienide and disodium tetraphenylethylene in anhydrous THF produced the $(Ph_2C_5H_3)Lu(Ph_4C_2)(THF)$ complex (1), which was isolated as a purple microcrystalline powder highly sensitive to atmospheric moisture and oxygen (Scheme 1).

The structure of complex 1 was established by X-ray diffraction (Fig. 1, Tables 1 and 2). A strong shift of the absorption band of the coordinated tetraphenylethylene dianion ($\lambda_{max} = 390$ nm) to shorter wavelengths com-

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Reagents and conditions: *i*. 1)NaOEt, Et₂O-EtOH, 2) PhCOCH₂Br; *ii*. NaOH (dilut.), 80 °C, 5 h; *iii*. 1)PhLi, 2) HCl (dilut.); *iv*. NaH (excess), THF.

pared to the sodium and potassium adducts of tetraphenylethylene ($\lambda_{max} = 485 \text{ nm}$)⁶ is evidence for the strong coordination of the tetraphenylethylene dianion to the Lu³⁺ cation.⁴ The shift of the absorption band in the spectrum of complex 1 ($\Delta\lambda_{max} = 95 \text{ nm}$) is the maximum of all the shifts observed in the spectra of lanthanide complexes with the tetraphenylethylene dianion, whereas the smallest shift (75 nm) is observed for the complex with the unsubstituted Cp ligand, (C₅H₅)Lu(Ph₄C₂)(THF)₂. Apparently, the introduction of Ph substituents decreases

Table 1. Selected bond lengths (d) in complex 1



Fig. 1. Overall view of the complex $(Ph_2C_5H_3)Lu(Ph_4C_2) \cdot THF$ (6). The hydrogen atoms are omitted.

the electron density on the atoms of the Cp ring, which, in turn, reduces the electron density on the lutetium cation and results in a strengthening of the $Lu-(C_2Ph_4)$ bond and, consequently, in a larger shift of the absorption band of the tetraphenylethylene dianion.

The reaction under consideration affords two organolutetium by-products, *viz.*, a red precipitate of the $[Na(THF)_5][Lu(Ph_4C_2)_2]$ complex (6% yield based on lutetium) described in our earlier study⁴ and a colorless substance, which was not isolated.

The previously unknown 1,3-diphenylcyclopentadienyllutetium dichloride $(Ph_2C_5H_3)LuCl_2(THF)_3$ (2) is, most likely, an intermediate in the synthesis of 1 starting from lutetium chloride. We synthesized complex 2 by the

Bond	d/Å	Bond	d/Å	Bond	d∕Å	Bond	$d/{ m \AA}$
C(18)–C(19)	1.503(4)	$\overline{Lu(1)-C(4)}$	2.578(3)	Lu(1) - O(1)	2.269(2)	C(1) - C(5)	1.434(5)
Lu(1) - C(18)	2.422(3)	Lu(1) - C(5)	2.568(3)	Lu(1) - C(19)	2.462(3)	C(3) - C(12)	1.478(4)
Lu(1) - C(26)	2.637(3)	C(1) - C(6)	1.481(5)	Lu(1) - C(32)	2.641(3)	C(19)-C(38)	1.491(5)
Lu(1) - C(27)	2.585(3)	C(18)-C(20)	1.487(4)	Lu(1) - C(37)	2.538(3)	C(38)-C(43)	1.395(5)
C(18)-C(26)	1.445(4)	C(20)-C(21)	1.393(4)	C(19)-C(32)	1.426(4)	C(42)-C(43)	1.372(5)
C(26)-C(27)	1.446(4)	C(21)-C(22)	1.387(5)	C(32)-C(37)	1.431(5)	C(41) - C(42)	1.388(5)
C(27)-C(28)	1.402(4)	C(22)-C(23)	1.373(5)	C(36)-C(37)	1.410(4)	C(40) - C(41)	1.383(5)
C(28)-C(29)	1.359(5)	C(23)-C(24)	1.394(5)	C(35)-C(36)	1.365(5)	C(39)-C(40)	1.385(5)
C(29)-C(30)	1.416(5)	C(24)-C(25)	1.384(4)	C(34)-C(35)	1.406(5)	C(38)-C(39)	1.405(5)
C(30)-C(31)	1.369(5)	C(20)-C(25)	1.413(5)	C(33)-C(34)	1.361(5)	C(12)–C(13)	1.406(5)
C(26)-C(31)	1.429(5)	C(6) - C(7)	1.396(5)	C(32)-C(33)	1.440(4)	C(13) - C(14)	1.386(5)
C(1) - C(5) - Lu	2.316	C(7) - C(8)	1.387(5)	C(1) - C(2)	1.413(4)	C(14) - C(15)	1.362(5)
centroid		C(8) - C(9)	1.364(6)	C(2) - C(3)	1.428(4)	C(15)-C(16)	1.392(5)
Lu(1) - C(1)	2.625(3)	C(9) - C(10)	1.395(5)	C(3) - C(4)	1.409(4)	C(16) - C(17)	1.393(5)
Lu(1) - C(2)	2.639(3)	C(10) - C(11)	1.390(5)	C(4) - C(5)	1.401(4)	C(12) - C(17)	1.383(5)
Lu(1) - C(3)	2.645(3)	C(6)-C(11)	1.386(5)				

Scheme 1

Table 2. Selected bond angles in complex 1

Angle	Value
Bond angle	ω/deg
C(18) - C(19) - C(32)	118.7(3)
C(19) - C(18) - C(26)	115.8(3)
C(18)-C(26)-C(27)	120.2(3)
C(19) - C(32) - C(37)	121.6(3)
C(19) - C(32) - C(33)	123.7(3)
C(18) - C(26) - C(31)	125.7(3)
C(33) - C(32) - C(37)	114.6(3)
C(27)-C(26)-C(31)	114.0(3)
C(32) - C(19) - C(38)	120.4(3)
C(18) - C(19) - C(38)	119.0(3)
C(19) - C(18) - C(20)	120.1(3)
C(19) - C(18) - C(20)	120.1(3)
C(18)-C(19)-C(38)	119.0(3)
C(19) - C(38) - C(43)	120.8(3)
C(18)-C(20)-C(21)	120.5(3)
C(39) - C(38) - C(43)	116.6(3)
C(21)-C(20)-C(25)	116.4(3)
C(20)-C(18)-C(26)	122.5(3)
Dihedral angle	φ/deg
C(11) - C(6) - C(1) - C(2)	11.5(5)
C(13) - C(12) - C(3) - C(2)	3.0(5)
C(21) - C(20) - C(18) - C(19)	20.5(5)
C(27) - C(26) - C(18) - C(19)	18.6(4)
C(33)-C(32)-C(19)-C(18)	166.9(3)
C(39) - C(38) - C(19) - C(18)	141.8(3)

reaction of sodium 1,3-diphenylcyclopentadienide with lutetium chloride tris-tetrahydrofuranate $LuCl_3(THF)_3$ in THF (Scheme 2). Complex **2** was isolated as a colorless crystalline compound, which is readily soluble in THF and toluene and decomposes in air.

In complex **1**, lutetium is coordinated by five carbon atoms of the cyclopentadienyl ring, six atoms of the tetraphenylethylene dianion (*ipso-* and *ortho-*carbon atoms of the aromatic rings and the carbon atoms of the ethylScheme 2

Na(Ph₂C₅H₃) + LuCl₃(THF)₃
$$\longrightarrow$$

(Ph₂C₅H₃)LuCl₂(THF)₃ + NaCl.
2

idene fragment), and one tetrahydrofuran molecule. The interaction between the tetraphenylethylene dianion and the lutetium cation can be best described as the bis-allyl η^6 -coordination of the tetraphenylethylene dianion analogous to that found in the [Na(diglyme)_2][Lu(Ph_4C_2)_2] and (C_5H_5)Lu(Ph_4C_2)(THF)_2 complexes.⁴

In complex 1, the Lu–C¹, Lu–C², and Lu–C³ distances (Table 3) are similar to those found⁴ in the [Na(diglyme)₂][Lu(Ph₄C₂)₂](THF)_{0.5} (3) and {CpLu(Ph₄C₂)(DME)}(DME) (4) complexes. The general atomic numbering of the carbon atoms in the complexes with the tetraphenylethylene ligand is given below.



In complex 1, only one THF molecule is coordinated to lutetium. The coordination number of lutetium is 8, which is lower than that in complex 4 (coordination number is 9). The structures of 1 and 3 are most suitable for a comparison because the coordination number of Lu in both complexes is 8. In complex 1, the Lu–C² distances are slightly longer, whereas the Lu–C¹ distances are shorter than those in 3 (average Lu–C² distances are 2.639 and 2.619 Å and the average Lu–C¹ distances are 2.442 and 2.466 Å in 1 and 3, respectively). The pairwise comparison of the Lu–C¹, Lu–C², and Lu–C³ distances

Table 3. Selected bond lengths in the lutetium complexes with the tetraphenylethylene dianion*

Bond	1				4				
$C^1 - C^1$	1.503(4)		1.5	07(3)	1.5	07(3)	1.507(5)		
Ln-C ¹	2.422(3)	2.462(3)	2.481(2)	2.478(2)	2.441(2)	2.463(2)	2.493(3)	2.470(3)	
$Ln-C^2$	2.637(3)	2.641(3)	2.643(2)	2.615(2)	2.610(2)	2.607(2)	2.703(3)	2.763(3)	
Ln-C ³	2.585(3)	2.538(3)	2.581(2)	2.524(1)	2.567(2)	2.588(2)	2.665(4)	2.723(4)	
$C^{1}-C^{2}$	1.445(4)	1.426(4)	1.438(3)	1.446(3)	1.434(2)	1.438(3)	1.435(5)	1.443(5)	
$C^{2}-C^{3}$	1.446(4)	1.431(5)	1.440(3)	1.446(3)	1.443(3)	1.436(3)	1.437(5)	1.418(5)	
$C^{3}-C^{4}$	1.402(4)	1.410(4)	1.405(3)	1.404(3)	1.404(3)	1.406(3)	1.402(5)	1.397(5)	
$C^{4}-C^{5}$	1.359(5)	1.365(5)	1.372(3)	1.379(3)	1.378(3)	1.374(3)	1.383(5)	1.378(5)	
$C^{5}-C^{6}$	1.416(5)	1.406(5)	1.411(3)	1.410(3)	1.404(3)	1.405(4)	1.378(5)	1.405(5)	
$C^{6}-C^{7}$	1.369(5)	1.361(5)	1.370(3)	1.379(3)	1.372(3)	1.372(3)	1.372(5)	1.372(5)	
$C^{2}-C^{7}$	1.429(5)	1.440(4)	1.438(3)	1.424(3)	1.435(3)	1.440(3)	1.428(5)	1.435(5)	
$C^{1}-C^{8}$	1.487(4)	1.491(5)	1.485(3)	1.480(3)	1.482(3)	1.481(3)	1.484(4)	1.483(4)	

* The atomic numbering scheme corresponds to the structural formula presented above.

in compounds 1 and 4 shows that these distances in complex 4 are longer than those in 1 due to the higher coordination number. In heteroleptic complexes 1 and 4 (taking into account the 0.055 Å difference between the ionic radii of Lu^{3+} for the coordination numbers 9 and 8), the $Lu-C^1$ distances are shorter than those in homoleptic complex 3 due, apparently, to the higher steric crowding of 1 compared to that of 4 and even of 3. The tetraphenylethylene dianion in complex 1, like that in 4, is coordinated asymmetrically. One of the $Lu-C^3$ distances (Lu-C(37)) is 0.047 Å shorter than the opposite distance (Lu-C(27)). Interestingly, the opposite situation is observed for the corresponding $Lu-C^1$ distances (Lu-C(18)bond is 0.040 Å shorter than the Lu-C(19) bond).

It is of interest to follow changes in the structure of **1** in going from the crystalline state to solution. However, the complex character of the ¹H and ¹³C NMR spectra did not allow us to make an unambiguous assignment for all signals. Nevertheless, the ¹H and ¹³C NMR and COSY ¹H–¹H spectroscopic data confirm the presence of five nonequivalent protons in the Ph group of the tetraphenylethylene dianion coordinated to lutetium. The spectroscopic data suggest that several exchange processes proceed in a solution of this compound. To reveal the exchange processes and estimate their activation parameters, we recorded the 2D ¹H EXSY NMR spectrum. The spectrum showed that two dynamic processes with similar activation energies (69.7 \pm 0.8 and 71.3 \pm 0.8 kJ mol⁻¹) proceed in a THF solution of 1 due to the hindered rotation of the Ph rings. Earlier,⁴ we have observed the hindered rotation of one of the Ph rings of the tetraphenylethylene ligand in complex 4. Presumably, the dynamic processes in complex 1 are associated with the hindered rotation of both the Ph groups of the tetraphenylethenide ligand and the substituted cyclopentadienyl anion.

In spite of the fact that several lutetium monocyclopentadienyl complexes have been described,^{1,3a,7,8} $Lu(C_5H_5)(O_3SCF_3)_2(THF)_3$ is the only structurally characterized LuCp'X₂-type lutetium complex.⁹ The $(C_5H_5)LuCl_2(THF)_3$ complex (5) is most useful for a comparison of the structural parameters of complexes 1, 2, and 4. However, the structure of this complex was unknown¹⁰ at the beginning of the present study. Hence, we determined the structure of 5 by X-ray diffraction.

The structures of the $(Ph_2C_5H_3)LuCl_2(THF)_3$ (2) and $Lu(C_5H_5)Cl_2(THF)_3$ (5) complexes (Figs 2 and 3, Tables 4 and 5) are similar to those of other lanthanide monocyclopentadienyl complexes $LnCp'X_2(THF)_3$. The lutetium cation is in a pseudooctahedral environment with the coordination number 8. The cyclopentadienyl ring is η^5 -coordinated to the lutetium cation. The chloride anions are in the *trans* positions with respect to each other. The coordinated THF molecules are in the *mer* positions.

The Lu-O(2) distances between the lutetium atom and the oxygen atom of tetrahydrofuran coordinated in



Fig. 2. Overall view of the complex $(Ph_2C_5H_3)LuCl_2 \cdot 3THF$ (5). The hydrogen atoms are omitted.



Fig. 3. Overall view of the complex $(C_5H_5)LuCl_2 \cdot 3THF$ (7). The hydrogen atoms are omitted.

the *trans* position to the cyclopentadienyl ring are 0.096 Å (for 2) and 0.083 Å (for 5) longer than the Lu-O(1) and Lu-O(3) distances due, presumably, to the deviation of the lutetium cation by 0.547 Å (for 2) and 0.542 Å (for 5) from the Cl(1), Cl(2), O(1), O(3) plane toward the cyclopentadienyl ring. An analogous deviation of the lanthanide atom toward the cyclopentadienyl ligand by 0.53 Å (yttrium) and 0.68 Å (cerium) and an elongation of the $Ln-O_{THF}$ bonds were observed for the CpEuCl₂(THF)₃ (see Ref. 10) and $(C_5H_5)LnX_2(THF)_3$ (X = Cl, Ln = Nd, Sm, Gd, Ho, Er, Yb, Y; X = Br, Ln = Yb; X = I, $Ln = Tm)^{11a-i}$ compounds and for the substituted cyclopentadienyl derivatives Cp'LnX₂(THF)₃.^{11k-m} In complexes 2 and 5, the Lu-O(1) and Lu-O(3) distances are in the range characteristic of the Lu-O_{THF} distances in the lutetium bis-cyclopentadienyl complexes Cp'₂LuX · L

Bond	d	∕/Å	Bond	$d/\text{\AA}$	Bond	d /1	Å	Bond	d∕Å
	2	5	2			2	5	2	
Lu–Cl(1)	2.584(1)	2.6024(7)	C(1)–C(6)	1.475(5)	Lu-O(1)	2.330(3)	2.318(2)	C(3)-C(12)	1.474(5)
Lu-Cl(2)	2.579(1)	2.6004(7)	C(6) - C(7)	1.392(6)	Lu - O(2)	2.421(3)	2.396(2)	C(12)-C(13)	1.399(6)
C(1) - C(5) - Lu			C(7) - C(8)	1.382(6)	Lu - O(3)	2.321(3)	2.309(2)	C(13)-C(14)	1.403(6)
centroid	2.389	2.354	C(8) - C(9)	1.383(7)	C(1) - C(2)	1.428(6)	1.414(4)	C(14) - C(15)	1.372(6)
Lu-C(1)	2.672(4)	2.661(3)	C(9) - C(10)	1.373(7)	C(2) - C(3)	1.416(5)	1.408(4)	C(15)-C(16)	1.381(7)
Lu-C(2)	2.672(4)	2.636(3)	C(10)-C(11)	1.376(6)	C(3) - C(4)	1.418(6)	1.407(4)	C(16)-C(17)	1.384(6)
Lu-C(3)	2.709(4)	2.624(3)	C(6)-C(11)	1.420(6)	C(4) - C(5)	1.385(6)	1.410(4)	C(12)-C(17)	1.399(5)
Lu-C(4)	2.673(4)	2.627(3)			C(1) - C(5)	1.420(5)	1.406(4)		
Lu-C(5)	2.648(4)	2.661(3)							

Table 4. Selected bond lengths (d) in complexes 2 and 5

Table 5. Selected angles in complexes 2 and 5

Angle	φ/deg				
	2	5			
Cl(1)-Lu(1)-Cl(2)	155.82(3)	154.96(2)			
Cl(1)-Lu(1)-O(1)	84.37(8)	89.51(5)			
Cl(1)-Lu(1)-O(2)	78.39(8)	77.47(5)			
Cl(1)-Lu(1)-O(3)	87.95(7)	86.79(5)			
Cl(2) - Lu(1) - O(1)	87.60(7)	85.33(5)			
Cl(2)-Lu(1)-O(2)	77.60(8)	77.52(5)			
Cl(2)-Lu(1)-O(3)	88.71(8)	87.18(5)			
O(1) - Lu(1) - O(2)	77.2(1)	75.14(7)			
O(2) - Lu(1) - O(3)	75.3(1)	78.85(7)			
O(1) - Lu(1) - O(3)	152.4(1)	153.92(7)			
C(1)-C(5)-Lu-O(1) centroid	105.2	103.0			
C(1)-C(5)-Lu-O(2) centroid	177.4	178.1			
C(1)-C(5)-Lu-O(3) centroid	102.3	102.9			
C(1)-C(5)-Lu-Cl(1) centroid	102.7	103.1			
C(1)-C(5)-Lu-Cl(2) centroid	101.5	102.0			
$C(1)-C(5)/C(6)-C(11)^*$	23.5				
$C(1)-C(5)/C(12)-C(17)^*$	11.7				

* The dihedral angles between the planes of the cyclopentadienyl ring and the phenyl groups in complex **2**.

Table	6.	Bond	lengths	(d) in	some	lutet	ium	cycl	lopen	tad	ienyl	comp	lexes
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distances in complex 5 are similar to those in the $(C_5H_5)Lu(O_3SCF_3)_2(THF)_3$ complex. In compound 2, these distances are somewhat longer. The Lu-Cl distances in complexes 2 and 5 are 0.06–0.10 Å longer than the corresponding distances in the alkyl- and trimethylsilyl-substituted lutetium bis-cyclopentadienyl complexes $LuCp'_{2}Cl(THF)$. In complex 2, the Lu–C distance is the longest of all lutetium complexes with the coordination number 8, which is apparently associated with the steric influence of the diphenylcyclopentadienyl ligand. A comparison of the average Lu-C(Cp) distances in complexes 2 (2.675 Å) and 1 (2.611 Å) and in complexes 5 (2.641 Å) and 4 (2.593 Å) revealed the expected elongation of the Lu-Cp bonds in the presence of bulky substituents in the Cp ring, as well as the unexpected, at first glance, shortening of the Lu-Cp bonds upon the replacement of two chloride ligands by the bulkier tetraphenylethenide ligand. The latter fact remains unclear. Probably, the formalism, which we used to compare the structural data and which assumes that the tetraphenylethylene dianion is four-coordinated, does not provide an adequate de-

scription of systems containing organic dianions as ligands.

with the coordination number 8 (Table 6). The $Lu-O_{THF}$

Complex	Coordi-		Reference			
	nation number	Lu–C _{Cp} (aver.)	Lu-Centroid	Lu-Cl	Lu-O _{THF} (aver.)	
$Lu(C_5H_5)_2Cl(THF)$	8	2.56	2.29 (aver.)	2.50	2.27	12
$Lu(C_5Me_5)_2Cl(THF)$	8	2.62	2.34 (aver.)	2.52	2.34	13
Lu(TMS ₂ C ₅ H ₃) ₂ I(THF)Lu(TMS ₂ C ₅ I	H ₃) 8	2.61	2.32	_	2.31	14
(TMSC ₅ H ₄)I(THF)	8	2.61	2.32	_	2.31	14
$Lu(C_5Me_5)(\eta^6-C_5H_4C_2H_4SPh)Cl$	8	2.60	2.30	2.53	_	15
$Lu(C_5H_5)(O_3SCF_3)_2(THF)_3$	8	2.62	2.34	_	2.30, 2.37 (trans-Cp)	9
$Lu(C_5H_5)Cl_2(THF)_3$	8	2.64	2.35	2.60	2.31, 2.40 (trans-Cp)	*
Lu(Ph ₂ C ₅ H ₃)Cl ₂ (THF) ₃	8	2.68	2.39	2.58	2.33, 2.42 (trans-Cp)	*
$Lu(Ph_2C_5H_3)(Ph_4C_2)(THF)$	8	2.61	2.32	_	2.27	*
$Lu(C_5H_5)(Ph_4C_2)(DME)$	9	2.59	2.30	_	2.42 (O _{DME})	4
$Lu(\eta^5 - C_5H_5)_3(THF)$	10	2.69	2.42 (aver.)	_	2.39	16

* The present study.

It is also cannot be ruled out that the shortening of the Lu-Cp bonds in this case is associated with the electron density transfer from the dianionic ligand through the metal atom to the antibonding orbital of the Cp ligand.

To conclude, we synthesized the previously unavailable lutetium complexes with the diphenylcyclopentadienyl ligand. A comparison of the structural parameters of the complexes with the general formulas $Cp'LnCl_2$ and $Cp'Ln(Ph_4C_2)$ ($Cp' = C_5H_5$ or $Ph_2C_5H_3$) showed that the introduction of the electron-rich tetraphenylethylene dianion into organolanthanide compound leads to changes in the Ln-Cp' bond parameters.

Experimental

All the complexes under study are extremely sensitive to atmospheric oxygen and moisture. Hence, the synthesis and preparation of samples were carried out in sealed evacuated Schlenk-type apparatus. The solvents were purified and stored according to procedures described earlier.⁴ The LuCl₃(THF)₃ complex was isolated by extraction of anhydrous lutetium trichloride, which was prepared from the hexahydrate,¹⁷ with hot THF. Tetraphenylethylene (Acros, 98%) was purified by recrystallization from toluene and dried *in vacuo*. Diphenylcyclopentadiene was synthesized according to a known procedure¹⁸ in 27% yield (as a mixture of isomers of 1,3- and 1,4-diphenylcyclopentadiene) and purified by recrystalliza-

Table 7. Crystallographic data for complexes 1, 2, and 5

tion from ethanol and vacuum sublimation. Sodium 1,3-diphenylcyclopentadienide was prepared by the metallation of a mixture of isomers of diphenylcyclopentadiene with excess sodium hydride in THF. The ¹H and ¹³C NMR spectra were recorded on Bruker WM-250, Bruker AM-300, and Bruker DRX-500 instruments. The electronic absorption spectra were measured on a Specord 50PC spectrophotometer in THF in sealed evacuated apparatus. The lutetium content in the samples was determined by the direct complexometric titration using the Xylenol Orange indicator.

(1,3-Diphenylcyclopentadienide)(1,1',2,2'-tetraphenylethenediide)lutetium tetrahydrofuranate, $(\eta^{5}-1,3 Ph_2C_5H_3$)Lu(η^6 -Ph₄C₂)(THF) (1). A solution of sodium 1,3-diphenylcyclopentadienide in THF (40 mL), which was prepared from diphenylcyclopentadiene (0.871 g, 3.99 mmol) and sodium hydride (0.356 g, 15 mmol), was added with stirring to a suspension of LuCl₃ • 3THF (1.980 g, 3.99 mmol) in THF (20 mL) for 30 min. The reaction mixture was stirred for 2 days. Then a solution of disodium tetraphenylethylene, which was prepared from tetraphenylethylene (1.330 g, 3.99 mmol), was added with vigorous stirring for 3 h. The mixture was stirred for 2 days and refluxed for 4 h, THF was removed in vacuo, the solid residue was extracted with THF at room temperature (5×50 mL), and the extract was concentrated. The purple finely crystalline precipitate was washed with a small amount of THF (3×3 mL), dried in vacuo, and extracted with toluene at room temperature. The toluene extract was concentrated, and the dry residue was washed with toluene (3×15 mL) and dried in vacuo. The product was recrystallized from a small amount of THF and dried in vacuo. Compound 1 was obtained in a yield of 1.609 g (46%). Found (%): Lu, 21.89. C₄₇H₄₁OLu. Calculated (%): Lu, 21.95.

Parameter	1	2	5
Molecular formula	Lu(C ₅ H ₃ Ph ₂)Cl ₂ (THF)	$Lu(C_5H_3Ph_2)(C_2Ph_4)(THF)$	Lu(C ₅ H ₅)Cl ₂ (THF) ₃
Empirical formula	C ₂₉ H ₃₇ Cl ₂ LuO ₃	C ₄₇ H ₄₁ LuO	$C_{17}H_{29}Cl_2LuO_3$
Molecular weight	679.46	796.77	527.27
Temperature/K	120	110	100
Crystal dimensions	$0.40 \times 0.20 \times 0.20$	$0.32 \times 0.24 \times 0.20$	$0.28 \times 0.22 \times 0.20$
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.6763(7)	11.4228(6)	7.7535(4)
b/Å	12.8638(9)	23.078(1)	16.8153(9)
c/Å	22.053(2)	13.2685(6)	14.6973(8)
α/deg	90.0	97.425(1)	95.419(1)
$V/Å^3$	2745.0(3)	3468.5(3)	1907.6(2)
Ζ	4	4	4
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.644	1.526	1.836
Linear absorption, μ/cm^{-1}	38.19	28.83	54.66
θ -Scan range, deg	1.83-29.50	2.52-29.00	1.84-29.50
Number of measured reflections	24536	23913	11870
Number of independent reflections	7617	9041	5258
R _{int}	0.0348	0.0378	0.0270
Number of reflections with $I > 2\sigma(I)$	6580	6510	4509
Number of variables	317	442	208
R_1 based on reflections with $I > 2\sigma(I)$	2.89	3.38	2.27
wR_2 based on all reflections	6.38	6.26	4.94
GOOF based on F^2	1.009	1.040	0.992

Electronic absorption spectrum (THF) $\lambda_{max}/nm: 320, 390, 560.$ ¹H NMR (500 MHz, THF-d₈), δ : 4.59–4.63 (m, 1 H); 5.82–5.86 (m, 2 H); 5.88–5.90 (m, 1 H); 5.95–5.99 (m, 1 H); 6.53–6.58 (m, 1 H); 6.61–6.64 (m, 1 H); 6.69–6.74 (m, 1 H); 6.77–6.82 (m, 1 H); 6.87–6.93 (m, 2 H); 6.96–7.02 (m, 1 H); 7.03–7.08 (m, 2 H); 7.14–7.22 (m, 6 H); 7.22–7.27 (m, 1 H); 7.27–7.33 (m, 2 H); 7.34–7.42 (m, 4 H); 7.50–7.54 (m, 1 H); 7.58–7.62 (m, 2 H); 7.68–7.72 (m, 2 H); 7.93–7.98 (m, 1 H). ¹³C{¹H} NMR (75 MHz, THF-d₈), δ : 88.4, 88.6, 95.0, 95.5, 102.3, 111.5, 112.2, 112.5, 114.5, 119.5, 122.3, 122.4, 122.5, 125.3, 125.8, 126.7, 126.8, 127.9, 128.1, 128.3, 128.4, 128.7, 129.35, 129.36, 129.6, 133.3, 133.9, 135.7, 136.5, 138.9, 140.6, 141.0, 143.1, 144.1, 144.9.

Dark-red crystals of the by-product insoluble in toluene were washed three times with toluene and recrystallized from THF. The lutetium content, the electronic absorption spectrum, and the ¹H and ¹³C NMR spectra of the product were identical to those for the $[Na(THF)_5][Lu(Ph_4C_2)_2]$ complex described earlier.⁴ The product was obtained as red crystals in a yield of 0.302 g (0.247 mmol, 6% based on lutetium).

[1,3-Diphenylcyclopentadienidelutetium dichloride] tristetrahydrofuranate, (η⁵-1,3-Ph₂C₅H₃)LuCl₂(THF)₃ (2). The LuCl₃(THF)₃ complex (1.755 g, 3.53 mmol) was added with stirring to a solution of sodium diphenylcyclopentadienide in THF (50 mL), which was prepared from diphenylcyclopentadiene (0.786 g, 3.60 mmol) and sodium hydride (0.297 g, 12.4 mmol). The reaction mixture was stirred for 24 h. The product was extracted with THF (3×50 mL), the extract was concentrated, and the dry residue was extracted with toluene (3×50 mL) and recrystallized from THF. Colorless crystals of (1,3-Ph₂C₅H₃)LuCl₂(THF)₃ were obtained in a yield of 1.270 g (1.87 mmol, 53%). Found (%): Lu, 25.99. C₂₉H₃₇O₃LuCl₂. Calculated (%): Lu, 25.75. ¹H NMR (250 MHz, THF-d₈), δ: 6.62 (d, 2 H); 7.00–7.12 (m, 3 H); 7.23–7.35 (t, 4 H); 7.77 (d, 4 H). ¹³C{¹H} NMR (75 MHz, THF-d₈), δ: 110.4, 110.8, 126.1, 126.6, 127.0, 129.5, 138.9.

[Cyclopentadienidelutetium dichloride] tris-tetrahydrofuranate, (η^5 -C₅H₅)LuCl₂(THF)₃ (5). Complex 5 was synthesized according to a known procedure¹⁵ from lutetium chloride tris-tetrahydrofuranate and sodium cyclopentadienide in 51% yield. ¹H NMR (250 MHz, THF-d₈, 297 K), δ : 6.15 (s). ¹³C{¹H} NMR (63 MHz, THF-d₈), δ : 111.1.

X-ray diffraction study of complexes 1, 2, and 5. Single crystals of 1, 2, and 5 were grown by crystallization from THF. Samples were prepared for the X-ray diffraction study according to a procedure described earlier.¹⁹ X-ray diffraction data for compounds 1 and 2 were collected on a Smart 1000 CCD diffractometer (λ (Mo-K α) = 0.71072 Å); for compound 5, on a Smart APEX II CCD diffractometer (λ (Mo-K α) = 0.71072 Å). The crystallographic data and the principal refinement statistics for complexes 1, 2, and 5 are given in Table 7. Semiempirical absorption corrections were applied based on equivalent reflections with the use of the SADABS program.²⁰ The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms with the use of the SHELXTL-97 program package. All hydrogen atoms in the structures of 1, 2, and 5 were positioned geometrically and refined using a riding model. In all structures, uncoordinated solvent molecules are absent.

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References

- 1. H. Heijden, P. van der Pasman, E. J. M. de Boer, and C. J. Schaverien, *Organometallics*, 1989, **8**, 1459.
- M. G. Klimpel, H. W. Gorlitzer, M. Tafipolsky, M. Spiegler, W. Scherer, and R. Anwander, *J. Organomet. Chem.*, 2002, 647, 236.
- (a) R. Zhang and M. Tsutsui, *Chem. Abstr.*, 1982, **98**, 198374;
 (b) H. Schumann, J. Winterfeld, M. Glanz, R. D. Kohn, and H. Hemling, *J. Organomet. Chem.*, 1994, **481**, 275;
 (c) C. M. Forsyth, G. B. Deacon, L. D. Field, C. Jones, P. C. Junk, D. L. Kay, A. F. Masters, and A. F. Richards, *Chem. Commun.*, 2006, 1003.
- 4. D. M. Roitershtein, M. E. Minyaev, K. A. Lyssenko, P. A. Belyakov, and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2060 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, 10, 2152].
- 5. D. M. Roitershtein, J. W. Ziller, and W. J. Evans, J. Am. Chem. Soc., 1998, **120**, 11342.
- M. Szwarc, Carbanions. Living Polymer and Electron Transfer Processes, Interscience, New York, 1968.
- 7. A. L. Wayda, J. Organomet. Chem., 1989, 361, 73.
- S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, 1963, 2, 904.
- 9. H. Schumann, J. A. Meese-Marktscheffel, A. Dietrich, and F. Gorlitz, *J. Organomet. Chem.*, 1989, **377**, C5.
- 10. Cambridge Structural Database System, Version 5.27, 2005.
- 11. (a) Y. Guangdi, F. Yuguo, J. Zhongsheng, X. Yan, and Ch. Wenqi, J. Organomet. Chem., 1987, 322, 57; (b) G. Depaoli, U. Russo, G. Valle, F. Grandjean, A. F. Williams, and G. J. Long, J. Am. Chem. Soc., 1994, 116, 5999; (c) Zh. Wu, Zh. Xu, X. You, X. Zhou, and L. Shi, J. Coord. Chem., 1992, 26, 329; (d) Zh. Wu, Zh. Xu, X. You, X. Zhou, H. Wang, and Y. Yang, Polyhedron, 1993, 12, 795; (e) C. S. Day, V. W. Day, R. D. Ernst, and S. H. Vollmer, Organometallics, 1982, 1, 998; (f) M. Adam, X.-F. Li, W. Oroschin, and R. D. Fischer, J. Organomet. Chem., 1985, **296**, C19; (g) X. Zhou, Zh. Wu, H. Ma, Zh. Xu, and X. You, Polyhedron, 1994, 13, 375; (h) G. B. Deacon, G. D. Fallon, and D. L. Wilkinson, J. Organomet. Chem., 1985, 293, 45: (i) G. V. Khoroshen'kov, A. A. Fagin, M. N. Bochkarev, S. Dechert, and H. Schumann, Izv. Akad. Nauk, Ser. Khim., 2003, 1627 [Russ. Chem. Bull., Int. Ed., 2003, 9, 1715]; (j) P. N. Hazin, J. C. Huffman, and J. W. Bruno, Organometallics, 1987, 6, 23; (k) W.-P. Leung, F.-Qu. Song, F. Xue, Z.-Y. Zhang, and T. C. W. Mak, J. Organomet. Chem., 1999, 582, 292; (1) Zuowei Xie, Shaowu Wang, Zhong-Yuan Zhou, and T. C. W. Mak, Organometallics, 1999, 18, 1641.
- 12. Ch. Ni, Zh. Zhang, D. Deng, and Ch. Qian, J. Organomet. Chem., 1986, 306, 209.
- L. Gong, A. Streitwieser, Jr., and A. Zalkin, *Chem. Commun.*, 1987, 460.
- 14. Z. Xie, Zh. Liu, F. Xue, Z. Zhang, and T. C. W. Mak, J. Organomet. Chem., 1997, 542, 285.
- H. Schumann, K. Hermann, S. H. Muhle, and S. Dechert, Z. Anorg. Allg. Chem., 2003, 629, 1184.

- 16. Ch. Ni, D. Deng, and Ch. Qian, *Inorg. Chim. Acta*, 1985, **110**, L7.
- W. A. Herrmann, in Synthetic Methods of Organometallic and Inorganic Chemistry, Vol. 6, Lanthanides and Actinides; Ed. F. T. Edelmann, Verlag, Stuttgart, 1997, 2.
- (a) L. F. Tietze und Th. Eicher, Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium, Georg Thieme Verlag, Stuttgart, New York, 1991;
 (b) R. Riemschneider and R. Nerin, Monastsh. Chem., 1960, 829;
 (c) G. C. Poretta, M. Scalzo, F. Chimenti, A. Bolasco, and M. Biava, Il Farmaco, 1987, 42, 629;
 (d) C. Paal and Ber. Deutsch, Chem. Ges., 1883, 16, 2865;
 (e) D. G. Farnum, A. Mostashari, and A. A. Hagedorn, J. Org. Chem., 1971, 36, 698;
 (f) L. G. Greifenstein, J. B. Lambert, R. J. Nienhuis,

G. E. Drucker, and G. A. Pagani, *J. Am. Chem. Soc.*, 1981, **103**, 7753; (g) W. Borsche and W. Menz, *Ber. Deutsch. Chem. Ges.*, 1908, **41**, 190; (h) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, 1965, **87**, 4533.

- D. M. Roitershtein, A. M. Ellern, M. Yu. Antipin, L. F. Rybakova, Yu. T. Struchkov, and E. S. Petrov, *Mendeleev Commun.*, 1992, 118.
- G. M. Sheldrick, *SADABS*, 1997, Bruker AXS Inc., Madison, WI-53719, USA.

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