1726 *Russian Chemical Bulletin, International Edition, Vol. 61, No. 9, pp. 1726—1732, September, 2012*

Polyphenylcyclopentadienyl complexes of rare earth elements

D. M. Roitershtein,[a,b]★ M. E. Minyaev,[a,c] A. A. Mikhaylyuk,[a,d] K. A. Lyssenko,[c] I. V. Glukhov,[c] P. A. Belyakov[b]

[a]*L. Ya. Karpov Institute of Physical Chemistry,*
6 buld., 3-1/12, per. Obukha, 105064 Moscow, Russian Federation.
Fax: +7 (495) 917 2490
[b]*N. D. Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax:+7 (499) 135 5328. E-mail: roiter@server.ioc.ac.ru
[c]*A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085
[d]*A. V. Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences,*
21 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 633 8520

Reaction of $LnCl_3(thf)_x$ (Ln = Y, La, Yb, Lu) with $NaCp^{Ph\mathit{n}}$ ($Cp^{Ph\mathit{n}}$ = 1,3-$Ph_2C_5H_3$, 1,2,4-$Ph_3C_5H_2$, Ph_4C_5H) leads to formation of monocyclopentadienyl dichloride complexes $Yb(Ph_2C_5H_3)Cl_2(thf)_3$ (**1**), $Ln(Ph_3C_5H_2)Cl_2(thf)_3$ (Ln = Y (**2**), Lu (**3**)), $La(Ph_4C_5H)Cl_2(thf)_3$ (**4**). Molecular structures of **1**, **2** and the polynuclear complex $[(Ph_3C_5H_2)_3Lu_4(Cl)_7(O)(thf)_3]$ (**5**), which is a partial hydrolysis product of **3**, have been established by the X-ray method.

Keywords: organolanthanides, yttrium, lanthanum, ytterbium, lutetium, diphenylcyclopentadiene, triphenylcyclopentadiene, tetraphenylcyclopentadiene, phenylcyclopentadienyl complexes.

Intensive progress of organolanthanide chemistry is resulted from the fundamental interest to the nature of the lanthanide—carbon bond in different types of organolanthanides, possible applications of 4f-element organic derivatives. Monocyclopentadienyl dichloride complexes $LnCpCl_2(thf)_3$ were among the first explored organolanthanides, which were synthesized in 1960-s.[1,2] Analogous dichloride complexes with substituted cyclopentadienyl ligands attract one´s interest as convenient precursors in synthesis of heteroleptic complexes $LnCp'(L)_x(solv)_m$ (solv is σ-donor ligand).

Presently, cyclopentadienyl rare earth complexes with trimethylsilyl and alkyl substituents in the cyclopentadienyl ligand and also indenyl and fluorenyl complexes of rare earth metals have been studied. However, organolanthanides with phenyl substituted cyclopentadienyl ligands have been poorly studied so far. Crystal structures only of a few polyphenylcyclopentadienyl rare earth complexes have been established earlier: Lu(1,3-$Ph_2C_5H_3$)$Cl_2(thf)_3$,[3] Lu(1,3-$Ph_2C_5H_3$)(Ph_4C_2)(thf),[3] [(1,2,4-$Ph_3C_5H_2$)$Nd(BH_4)_3]_2[Mg(thf)_6]$,[4] $(C_5HPh_4)_2La\{N(SiHMe_2)_2\}$,[5] $\{(C_5Ph_5)Yb(thf)(C_2Ph)\}_2$ (see. Ref. 6) and $\{C_5(4\text{-}Bu^n\text{-}C_6H_4)_5\}_2Ln$ (Ln = Sm, Yb).[7] Dihalide complexes of rare earth metals with tri- and tetraphenyl subtituted cyclopentadienyl ligands are unknown.

The goal of the present work is synthesis, structural studies of rare earth metals complexes with polyphenyl substituted cyclopentadienyl ligands $Ln(C_5H_{5-n}Ph_n)Cl_2(thf)_3$ (n = 2—4) and study of the influence of steric and electronic effects of the phenyl substituents in the cyclopentadienide anion on Ln—Cp bond peculiarities in comparison with other monocyclopentadienyl complexes, e. g., with dihalide complexes $Ln(C_5H_{5-n}R_n)Hal_2(thf)_3$.

Results and discussion

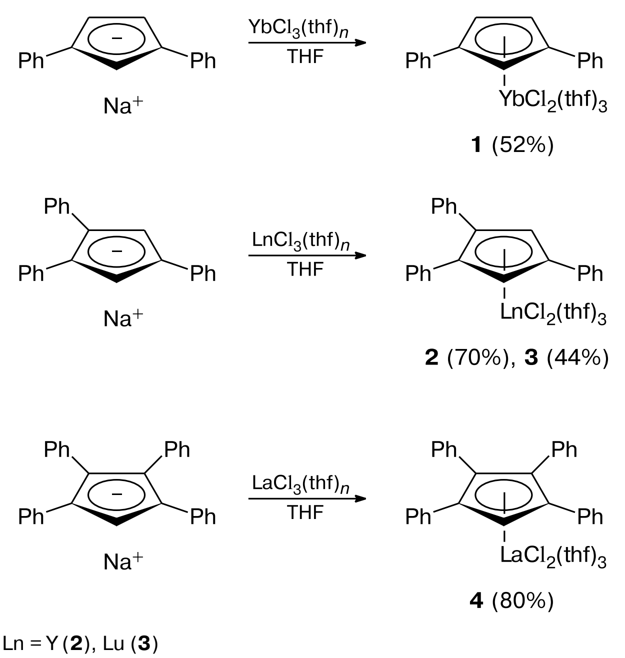
Reaction of soduim 1,3-diphenyl-, 1,2,4-triphenyl- and 1,2,3,4-tetraphenylcyclopentadienides with lanthanide and yttrium trichloride tetrahydrofuranates in 1:1 ratio in THF results in formation of corresponding monocyclopentadienyl dichloride rare earth complexes: Yb(1,3-$Ph_2C_5H_3$)$Cl_2(thf)_3$ (**1**), Ln(1,2,4-$Ph_3C_5H_2$)$Cl_2(thf)_3$ (Ln = Y (**2**), Lu (**3**)), $La(Ph_4C_5H)Cl_2(thf)_3$ (**4**) (Scheme 1). the complexes are obtained as light-violet (**1**) and colorless (**2**—**4**) microcrystalline powders decomposing in air and being readily soluble in THF and toluene.

^1H NMR spectra of complexes **2**—**4** appear to be nearly uninformative due to a large number of overlapping signals from magnetically nonequivalent phenyl ring protons. Thus, proton signals from cyclopentadienyl ring and

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1710—1716, September, 2012.

1066-5285/12/6109-1726

Scheme 1



phenyl groups are observed as complex multiplets at 6.9—7.4 (**2**), 6.8—7.4 (**3**) and 7.0—7.8 ppm (**4**) in ^{1}H NMR spectra.

Therefore, X-ray diffraction method was applied to determine structures of **1** and **2** (Tables 1—3). Molecular structures of compouns **1** and **2** (Figs 1 and 2) are similar to other lanthanide cyclopentadienyl dihalide complexes LnCp´Hal$_2$(thf)$_3$ with coordination number (CN) of 8 (see Refs 2, 3). Compound **1** is isostructural with Lu(1,3-Ph$_2$-C$_5$H$_3$)Cl$_2$(thf)$_3$ (see Ref. 3). Phenyl ring rotation angles with respect to the plane of the cyclopentadienyl ring are in the range of 9.3—39.2° for complexes **1** and **2**. The largest rotation angles in compound **2** (31.2—39.2°) are observed for the phenyl rings at positions 1 and 2 of the 1,2,4-triphenylcyclopentadienyl ligand. $C_{ipso(Ph)}$—$C_{ipso(Cp)}$ bond lengths in compounds **1** and **2** (1.445—1.484 Å) are slightly shorter than a single C-C bond length. $C_{ipso(Ph)}$ carbon atoms are slightly out of the plane of the cyclopentadienyl ring by 0.05—0.13 Å from the metal in complex **1** and by 0.07—0.28 Å in **2**, locating away from the metal atom. $C_{ipso(Ph)}$—$C_{ipso(Cp)}$—$Cp_{centroid}$ angles are in the range of 175.6—168.3° in complexes **1** and **2**.

Crystallization of **3** from THF—pentane mixture allowed us to isolate poorly soluble in THF complex [{(η^5-1,2,4-Ph$_3$C$_5$H$_2$)Lu}$_3${Lu(thf)$_3$}(μ_3-Cl)(μ_2-Cl)$_6$(μ_4-O)](thf)$_2$ (**5**), apparently formed as a result of partial hydrolysis of **3**. Its crystal structure was established by X-ray diffraction method (Fig. 3, Tables 1 and 4). Four lutetium cations in [(Ph$_3$C$_5$H$_2$)$_3$Lu$_4$Cl$_7$O(thf)$_3$] are connected via μ_4-oxygen atom and thus form a distorted tetrahedron Lu$_4$(μ_4-O). Atom Cl(1) is μ_3-coordinated with three lutetium cations Lu(1), Lu(2), Lu(3) having CN of 8 and being are η^5-coordinated with 1,2,4-triphenylcyclopentadienyl ligands. The other chlorine atoms are μ_2-bound to

Table 1. Crystallographic data for complexes Yb(Ph$_2$C$_5$H$_3$)Cl$_2$(thf)$_3$ (**1**), [Y(Ph$_3$C$_5$H$_2$)Cl$_2$(thf)$_3$](thf)$_{0.5}$ (**2**) and [(Ph$_3$C$_5$H$_2$)$_3$Lu$_4$Cl$_7$O(thf)$_3$](thf)$_2$ (**5**)

Parameter	**1**	**2**	**5**
Empirical formula	$C_{29}H_{37}Cl_2YbO_3$	$C_{37}H_{45}Cl_2O_{3.50}Y$	$C_{89}H_{91}C_{l7}Lu_4O_6$
Molecular mass	677.53	705.54	2204.65
T/K	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a/Å	9.6450(9)	23.500(5)	14.1202(12)
b/Å	12.881(1)	13.580(3)	25.705(2)
c/Å	21.987(2)	21.030(4)	23.345(3)
β/deg	90	96.07(3)	104.596(4)
V/Å^3	2731.6(4)	6674(2)	8199.8(14)
Z	4	4	4
d_{calc}/g·cm^{-3}	1.647	1.404	1.786
μ/mm^{-1}	3.648	1.945	5.055
Range, θ/deg	1.83—29.00	1.94—27.00	1.20—28.50
Number of measured reflections	21090	45672	85672
Number of unique reflections	7240	17044	20777
R_{int} (%)	4.81	—	3.78
Number of reflections with $I > 2\sigma(I)$	6349	4810	16714
Number of refined parameters	317	742	950
R_1 ($I > 2\sigma(I)$)	3.16	6.33	2.70
wR_2 (all parameters)	6.61	24.98	6.29
GOOF on F^2	1.000	0.659	0.964

Table 2. Selected bond lengths (d) in complexes **1** and **2**[a]

Bond	d/Å		
	1	**2***	
		A	**B**
Ln—Cl(1)	2.591(1)	2.601(2)	2.577(2)
Ln—Cl(2)	2.583(1)	2.560(2)	2.598(2)
Ln—O(1)	2.334(3)	2.302(5)	2.341(5)
Ln—O(2)	2.416(3)	2.490(5)	2.484(5)
Ln—O(3)	2.354(3)	2.337(5)	2.332(5)
Ln—C(1)	2.683(4)	2.727(7)	2.739(8)
Ln—C(2)	2.671(5)	2.762(7)	2.772(8)
Ln—C(3)	2.700(4)	2.720(7)	2.692(8)
Ln—C(4)	2.681(5)	2.679(7)	2.691(7)
Ln—C(5)	2.653(5)	2.621(7)	2.662(7)
Centroid Cp—Ln	2.391	2.423	2.431

[a] Two crystallographically unique molecules.

Table 3. Selected valent angles (ω) in complexes **1** and **2**[a]

Angle	ω/deg		
	1	**2***	
		A	**B**
Cl(1)—Ln—Cl(2)	156.12(4)	154.50(7)	152.48(8)
Cl(1)—Ln—O(1)	88.05(8)	83.7(1)	82.6(1)
Cl(1)—Ln—O(2)	78.78(9)	78.1(1)	77.6(1)
Cl(1)—Ln—O(3)	84.13(8)	90.2(1)	89.2(2)
Cl(2)—Ln—O(1)	88.90(9)	85.2(1)	83.7(1)
Cl(2)—Ln—O(2)	77.55(9)	77.2(1)	76.5(1)
Cl(2)—Ln—O(3)	87.66(8)	89.6(1)	92.9(1)
O(1)—Ln—O(2)	75.1(1)	78.6(2)	79.8(2)
O(2)—Ln—O(3)	77.3(1)	74.9(2)	74.6(2)
O(1)—Ln—O(3)	152.3(1)	153.6(2)	154.3(2)
Centroid Cp—Ln—Cl(1)	102.6	102.5	103.6
Centroid Cp—Ln—Cl(2)	101.2	102.6	103.2
Centroid Cp—Ln—O(1)	102.1	105.0	106.5
Centroid Cp—Ln—O(2)	176.9	176.3	173.6
Centroid Cp—Ln—O(3)	105.5	101.4	99.1

[a] Two crystallographically unique molecules.

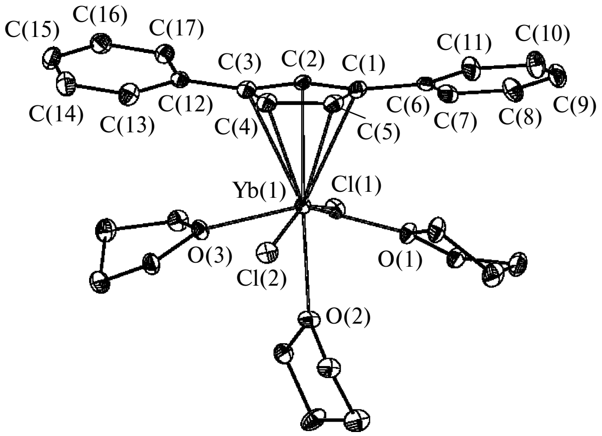


Fig. 1. Molecular structure of the complex **1**. Hydrogen atoms are omitted for clarity.

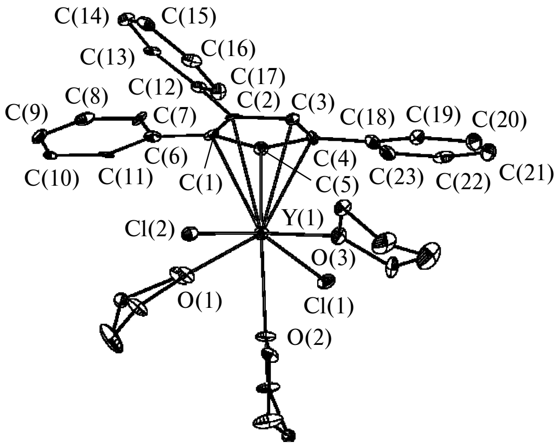


Fig. 2. Structure of one of the two crystallographically unique molecules of the complex **2**. Hydrogen atoms are omitted for clarity.

metal atoms. Cation Lu(4) (C.N. is 7) is coordinated with three THF molecules. The structural fragment $Lu_4(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)$ possesses C_{3v} symmetry. Complexes $[(\eta^5\text{-}C_5H_9\text{-}C_5H_4)_3Er_4(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)(thf)_3]$ (see Ref. 8) and $[(\eta^5\text{-}CH_3\text{-}C_5H_4)_3Yb_4(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)\text{-}(thf)_3]$ (see Ref. 9) have molecular structures analogous to **5**.

In order to explore the influence of steric and/or electronic effects of ligands on the interaction Ln^{3+}—Cp´ (Cp´ is cyclopentadienyl anion or its substituted analogues), a number of structural parameters of such fragments were analysed for all monocyclopentadienyl complexes of yttrium and lanthanides(III) available from the Cambridge Structural Database (CSD)[8]. Mono- and polynuclear complexes which had each lanthanide atom being coordinated to only one cyclopentadienyl ligand were taken into consideration. Compounds with electron deficient Ln—L—Ln bonds were excluded from the sample as well as complexes with uncertain lanthanide coordination numbers. Generally accepted formalism designates a metal cation coordination number to be equal to the number of electron pairs donated to the metal[10]. Structures with $R_1 > 10\%$ have also been excluded. The final set of compounds consists of 426 crystal structures of complexes with the composition mentioned above (603 crystallographically independent fragments Ln^{3+}—Cp´).

To our opinion, a more convenient comparison parameter is the difference between the values of Ln—$Cp_{centroid}$ distance and Ln^{3+}ionic radii (see Ref. 11) of the corresponding lanthanide coordination number[10]: $R_{Cp} = d(Ln^{3+}—Cp_{centroid}) - r(Ln^{3+})$. For example, the com-

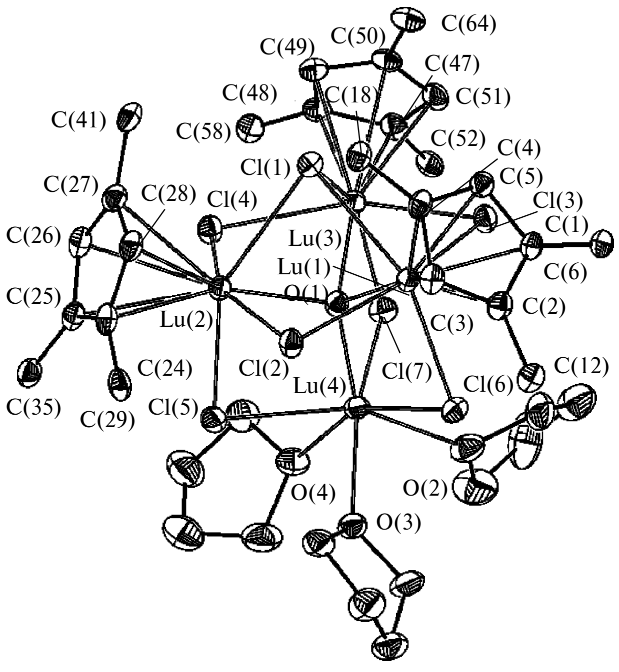


Fig. 3. Structure of the complex **5**. Only *ipso*-atoms of phenyl groups are shown. Hydrogen atoms and uncoordinated THF molecules are omitted for clarity.

plex Lu(η^5-1,3-$Ph_2C_5H_3$)(η^6-Ph_4C_2)(thf) (see Ref. 3) has CN (Lu) = 8, d(Lu—$Cp_{centroid}$) = 2.316 Å, $r(Lu^{3+})$ = 1.117 Å (see Ref. 11), R_{Cp} = d(Lu—$Cp_{centroid}$) – $r(Lu^{3+})$ = 1.199 Å values. If ionic radii values for some coordination numbers were missing in the literature[11], earlier described[10] correction was applied in our calculations for extrapolation of the ionic radii to the necessary coordination number.

Coordination numbers of Ln^{3+} in the sample from CSD are within the range of 5—10. The R_{Cp} values for the complexes varied in the range from 1.08 to 1.42 Å. Although the reliable correlation between R_{Cp} and the ligand nature of was not well-established within the sample, it can be noted that the largest R_{Cp} values of were found for complexes with relatively low coordination numbers (C.N. of 5 or 6) (Table 5). This might be due to the presence of bulky ligands, which impose steric hindrance, and hence increase the distance Ln—Cp´. The minimum R_{Cp} values were found for complexes with C.N. of 8 or 9 having electron-excessive ligands, e.g., with cyclooctatetraene dianion, and also in complexes with nitrate anion and in polynuclear complexes {(η^5-C_5H_5)$_{12}$(μ_3-Cl)$_{24}$$Sm_{12}$}, [($\eta^5$-$C_5Me_5$)Tm($NCCH_3$)$_6$]$I_2$ (see Table 5).

In case of cyclooctatetraene dianion, partial electron density transfer from an electron-excessive ligand through the metal to the π^*-anti-bonding orbital of the cyclopentadienyl ligand is one possible reason for lowering R_{Cp} values. In case of significant decrease of the R_{Cp} values, one may assume that the lanthanide—cyclopentadienyl ligand bond has essentially covalent nature.

If within the chosen sample only compounds LnCp´X_2(solv)$_m$ (X is halogen or analogues; m = 2, 3; solv is σ-donor ligands, CN 7, 8; 38 crystal structures, 42 crystallographically independent molecules) were considered, it was found that R_{Cp} values for this type of complexes vary in a narrow interval: from 1.21 to 1.31 Å. This supports a similarity of the LnCp´bond nature in all compounds of the LnCp´X_2(solv)$_m$ type. The R_{Cp} values for the complexes LnCp´X_2(solv)$_m$ lie in the range of the average R_{Cp} values for all monocyclopentadienyl complexes of lanthanides (III) and yttrium of the sample.

For more correct analysis of the latter sample, the structures with systematic errors (the absence of hydrogen atoms in the crystallographic model) were excluded from the sample. This resulted in reduction of sample to 26 compounds (29 crystallographically independent molecules), which revealed a correlation between increase of R_{Cp} values and growth of both the number of bulky substituents in the cyclopentadienyl ligand and their steric

Table 4. Selected valent bond lengths (d) in the complex **5**

Bond	d/Å	Bond	d/Å	Bond	d/Å
Lu(1)—Cl(1)	2.7646(9)	Lu(4)—Cl(7)	2.6632(9)	Lu(2)—C(24)	2.634(3)
Lu(1)—Cl(2)	2.6109(9)	Lu(1)—O(1)	2.266(2)	Lu(2)—C(25)	2.691(3)
Lu(1)—Cl(3)	2.6498(9)	Lu(2)—O(1)	2.263(2)	Lu(2)—C(26)	2.653(3)
Lu(1)—Cl(6)	2.5855(9)	Lu(3)—O(1)	2.253(2)	Lu(2)—C(27)	2.608(3)
Lu(2)—Cl(1)	2.7899(9)	Lu(4)—O(1)	2.133(2)	Lu(2)—C(28)	2.570(3)
Lu(2)—Cl(2)	2.6355(9)	Lu(4)—O(2)	2.328(3)	Lu(3)—C(47)	2.681(4)
Lu(2)—Cl(4)	2.6009(9)	Lu(4)—O(3)	2.297(3)	Lu(3)—C(48)	2.660(4)
Lu(2)—Cl(5)	2.5884(9)	Lu(4)—O(4)	2.385(3)	Lu(3)—C(49)	2.597(4)
Lu(3)—Cl(1)	2.7524(9)	Lu(1)—C(1)	2.653(3)	Lu(3)—C(50)	2.619(4)
Lu(3)—Cl(3)	2.6274(9)	Lu(1)—C(2)	2.701(3)	Lu(3)—C(51)	2.638(4)
Lu(3)—Cl(4)	2.6456(9)	Lu(1)—C(3)	2.657(3)	Centroid C(1—5)—Lu(1)	2.350
Lu(3)—Cl(7)	2.5986(9)	Lu(1)—C(4)	2.624(3)	Centroid C(24—28)—Lu(2)	2.341
Lu(4)—Cl(5)	2.6735(9)	Lu(1)—C(5)	2.588(3)	Centroid C(47—51)—Lu(3)	2.348
Lu(4)—Cl(6)	2.7242(9)				

Table 5. R_{Cp} values for some monocyclopentadienyl complexes of lantanides(III) and yttrium

Complex	CSD code[8]	C.N.	R_{Cp}/Å	Reference
Compounds with maximum R_{Cp}				
$\{[\eta^5\text{-}C_5Me_4(TMS)]_4(\eta^2\text{-}NCH—Ph)_4(\eta^3\text{-}NEt)_2Y_4\}$	FEVQIH	*	1.395, 1.424	12
$\{(\eta^5\text{-}C_5Me_5)Ce[\eta^1\text{-}CH(TMS)_2]_2\}$	JAYMIF	5	1.422	13
$\{(\eta^5\text{-}C_5Me_5)Ce[\eta^1\text{-}N(TMS)_2]_2\}$	JAYMOL	5	1.418	13
$\{[\eta^5\text{-}C_5Me_4(TMS)]_4(\eta^3\text{-}NEt)_4Y_4\}$	FEVQON	6	1.395—1.414	12
$[Li(tmeda)_2][(\eta^5\text{-}C_5Me_5)La(\eta^1\text{-}Me)_3]$	CUTGUT	6	1.413	14
$\{[\eta^5\text{-}C_5Me_4(TMS)]_4(\eta^3\text{-}NCH_2Ph)_4Lu_4\}$	AVEXII	6	1.412, 1.413	15
$\{(\mu_2\text{-}\eta^1{:}\eta^1\text{-}OBu^t)_2[(\eta^5\text{-}C_5Me_5)Ce(\eta^1\text{-}OBu^t)]_2\}$	KASYIM	6	1.394, 1.404	16
$\{(\eta^5\text{-}C_5Me_5)La[\eta^1\text{-}CH(TMS)_2]_2\}$	KADCUN	5	1.402	17
$[Li(dme)_3][(\eta^5\text{-}C_5H_4Me)La(\eta^1\text{-}NPh_2)_3]$	VULKOC	6	1.397	18
Compounds LnCp´X_2(solv)$_m$				
$[La(\eta^5\text{-}Flu)I_2(py)_3](PhMe)_{0.5}$	FIXFIC	8	1.309, 1.294	19
$[Nd(\eta^5\text{-}Flu)I_2(py)_3](thf)$	FIXFEY	8	1.293	19
$[Tm(\eta^5\text{-}C_5HPr^i{}_4)Cl_2(dme)]$	SEWWAT	7	1.278	20
$[Tm\{\eta^5\text{-}1,3\text{-}Bu^t{}_2\text{-}2\text{-}[OTmI_2(thf)_3]C_5H_2\}I_2(thf)_2]$	IMOFAR	7	1.277	21
$[Yb(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)Cl_2(thf)_2]$	SEWVIA	7	1.275, 1.274	20
$[Lu(\eta^5\text{-}1,3\text{-}Ph_2C_5H_3)Cl_2(thf)_3]$	IFUHEX	8	1.273	3
$[Yb(\eta^5\text{-}B_{10}C_2H_{11}—SiMe_2—C_5H_4)Cl_2(thf)_3]$	HOJWIM	8	1.269	22
$[Nd(\eta^5\text{-}B_{10}C_2H_{11}—SiMe_2—C_5H_4)Cl_2(thf)_3]$	VAGGEP	8	1.269	23
$[Yb(\eta^5\text{-}C_5HPr^i{}_4)Cl_2(dme)]$	UHIDIY	7	1.267	24
$[La\{\eta^5\text{-}1,2,4\text{-}(TMS)_3C_5H_2\}I_2(py)_3]$	OLOYET	8	1.257	25
$[La(\eta^5\text{-}Bu^t—C_5H_4)I_2(py)_3]$	MALYII	8	1.252	26
$[Er(\eta^5\text{-}C_5H_5)Cl_2(thf)_3]$	BOBWAQ	8	1.247	27
$[Ce(\eta^5\text{-}Bu^tC_5H_4)I_2(py)_3]$	MALYAA	8	1.243	26
$[Ce(\eta^5\text{-}C_5Me_5)I_2(thf)_3]$	FEYWOV	8	1.240, 1.233	28
$[Nd(\eta^5\text{-}Bu^tC_5H_4)I_2(py)_3]$	MALXON	8	1.238	26
$[Lu(\eta^5\text{-}C_5H_5)Cl_2(thf)_3]$	IFUHOH	8	1.238	3
$[Sm\{\eta^5\text{-}(2\text{-}Pr^i\text{-}5\text{-}Me—C_6H_9)—C_5H_4\}I_2(thf)_3]$	BIQVOM	8	1.236	29
$[Ho(\eta^5\text{-}C_5H_5)Cl_2(thf)_3]$	YEFVUA	8	1.235	30
$[Nd(\eta^5\text{-}C_5Me_5)I_2(py)_3](PhMe)$	WIPLOW	8	1.232	31
$[Lu(\eta^5\text{-}C_5H_5)(OTf)_2(thf)_3]$	VEBKAO	8	1.227	32
$[Yb(\eta^5\text{-}Me—C_5H_4)(NCS)_2(thf)_3]$	QUCZAP	8	1.221	33
$[La\{\eta^5{:}\eta^1{:}\eta^1\text{-}1,3\text{-}(NMe_2)_2—C_5H_3\}I_2(thf)]$	QUHQOZ	8	1.220	34
$[Gd(\eta^5\text{-}C_5H_5)Cl_2(thf)_3]$	YAGHUJ01	8	1.216	35
$[Tm(\eta^5\text{-}C_5H_5)I_2(thf)_3]$	IWUJOZ	8	1.213	36
$[Y(\eta^5\text{-}C_5H_5)Cl_2(thf)_3]$	WEWZED	8	1.213	37
$[La\{\eta^5{:}\eta^1{:}\eta^1\text{-}1,2\text{-}(NMe_2)_2—C_5H_3\}I_2(thf)](thf)_{0.5}$	QUHQIT	8	1.211	34
Compounds with minimum R_{Cp}				
$\{(\eta^5\text{-}C_5Me_4H)Yb(\eta^8\text{-}C_8H_8)\}$	ABIFIA	8	1.120	38
$\{(\eta^5\text{-}C_5Me_5)Lu(\eta^8\text{-}C_8H_8)\}$	VAPZIV	8	1.117	39
$[Na(thf)_6]\{[Na(thf)_4](\mu_2\text{-}\eta^2{:}\eta^1\text{-}NO_3)_2[(\eta^5\text{-}C_5Me_5)Nd(\eta^2\text{-}NO_3)_2]_2\}$	PAGNAN	9	1.116	40
$[(\eta^5\text{-}C_5Me_5)Tm(NCCH_3)_6]I_2$	SELMEC	9	1.113—1.114	41
$[K(18\text{-}crown\text{-}6)](\mu_2\text{-}\eta^2{:}\eta^1\text{-}NO_3)_2[(\eta^5\text{-}C_5Me_5)Nd(\eta^2\text{-}NO_3)]$	PAGNER	9	1.106	40
$\{[Na(thf)_2](\mu_2\text{-}\eta^2{:}\eta^1\text{-}NO_3)_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}NO_3)[(\eta^5\text{-}C_5Me_5)Nd]\}$	PAGNIV	9	1.106	40
$\{(\eta^5\text{-}C_5Me_4H)Lu(\eta^8\text{-}C_8H_8)\}$	LAWREG	8	1.095	42
$\{(\eta^5\text{-}C_5Me_4Et)Lu(\eta^8\text{-}C_8H_8)\}$	YEZNAS	8	1.088	43
$\{(\eta^5\text{-}C_5H_5)_{12}(\mu_3\text{-}Cl)_{24}Sm_{12}\}$	NICHOW	9	1.079—1.094	44

* Fragments with C.N. 6.

hindrance (see Table 5). However, the R_{Cp} value poorly correlated with the type of halide ligands X, σ-donor ligands «solv», and electronic effects of the substituents in the cyclopentadienyl ring.

R_{Cp} values for complexes **1** (1.266 Å) and **2** (1.264, 1.272 Å) lie in the range, which is inherent for LnCp´X_2(solv)$_m$, closer to the maximum values due to steric hindrance of di- and triphenylcyclopentadienyl ligands. Because of the presence of the bulky triphenyl cyclopentadienyl ligand, R_{Cp} values are higher for the complex **5** (1.233, 1.224 and 1.231 Å), than for analogous tetranuclear complexes $[(C_5H_9—C_5H_4)_3Er_4Cl_7O(thf)_3]$ (1.181, 1.182 and 1.189 Å), $[(CH_3—C_5H_4)_3Yb_4Cl_7O(thf)_3]$ (1.194, 1.179 and 1.195 Å)[8].

In the present work polyphenylsubstituted monocyclopentadienyl dichloride complexes $Yb(1,3\text{-}Ph_2C_5H_3)Cl_2(thf)_3$, $Y(1,2,4\text{-}Ph_3C_5H_2)Cl_2(thf)_3$, $Lu(1,2,4\text{-}Ph_3C_5H_2)Cl_2(thf)_3$ and $La(Ph_4C_5H)Cl_2(thf)_3$ have been synthesized. The presence of phenyl substituents in the cyclopentadienyl ligand decreases the tendency of $LnCp'X_2$ complexes to metathesis and facilitates their isolation, preventing formation of bis- and tris-cyclopentadienyl derivatives.

We have compared main structural parameters of monocyclopentadienyl complexes of yttrium and lanthanides using the CSD data. Intermediate values of R_{Cp} (the difference between the length of $Ln—Cp_{centroid}$ and ionic radii of Ln^{3+}) among all considered monocyclopentadienyl yttrium and lanthanide(III) complexes have been observed for complexes $Ln(Ph_nC_5H_{5-n})Cl_2(thf)_3$ (n = 2—3). This phenomenon is observed despite of their apparent high steric hindrance due to the presence of several phenyl substituents in the cyclopentadienyl ring.

Experimental

All synthetic operations and sample preparations for analysis were carried out in sealed glass Schlenk-type evacuated vessels. Solvents were purified before earlier[45]. $LnCl_3(thf)_3$ were obtained by hot THF extraction of anhydrous trichlorides of yttrium and lanthanides, prepared by dehydration of corresponding hydrates[46]. Diphenylcyclopentadiene[3], 1,2,4-triphenylcyclopenta-1,3-diene[47—49] and 1,2,3,4-tetraphenylcyclopenta-1,3-diene[50,51] were synthesized as described in literature. Polyphenylcyclopentadiens were purified by recrystallization from EtOH, followed by sublimation under vacuum. Sodium polyphenylcyclopentadienides were obtained by reaction of corresponding polyphenylcyclopentadiens with excess of sodium hydride in THF under reflux.

^{1}H NMR spectra were recorded on Bruker DRX-500 and Bruker WM-250 NMR spectrometers. Lanthanide content was determined by direct complexometric titration in the presence of Xylenol Orange indicator. Chlorine content was determined by potentiometric titration with silver nitrate.

Dichloro 1,3-diphenylcyclopentadienide tris(tetrahydrofuranate) ytterbium, $Yb(C_5H_3Ph_2)Cl_2(thf)_3$ (1). To a stirred solution of sodium diphenylcyclopentadienide obtained from 0.676 g (3.1 mmol) of diphenylcyclopentadiene and 0.282 g (11.7 mmol) of sodium hydride in 50 mL of THF, 1.662 g (3.0 mmol) of $YbCl_3(thf)_3$ was added. The mixture was stirred for 24 h. The product was extracted with THF (3×50 mL), the mixture was concentrated and the residue was extracted with toluene (3×50 mL), the extract was evaporated, and the residue was recrystallyzed from THF and dried under vacuum. Obtained 1.090 g (1.62 mmol, 54%) of light-violet microcrystals. Found (%): Yb, 25.70; Cl, 10.60. $C_{29}H_{37}Cl_2YbO_3$. Calculated (%): Yb, 25.54; Cl, 10.46.

Dichloro 1,2,4-triphenylcyclopentadienide tris(tetrahydrofuranate) yttrium, $Y(Ph_3C_5H_2)Cl_2(thf)_3$ (2). Complex **2** was obtained as described for **1** starting from 0.884 g (3 mmol) 1,2,4-triphenylcyclopenta-1,3-diene, 0.25 g (10 mmol) of sodium hydride and 1.247 g (2.94 mmol) of $YCl_3(thf)_3$. Obtained 1.327 g (2.05 mmol, 70%) as colorless microcrystalline product. Found (%): Y, 13.72; Cl, 10.90. $C_{35}H_{41}Cl_2O_3Y$. Calculated (%): Y, 13.28; Cl, 10.59. ^{1}H NMR (500 MHz, THF-d_8, δ): 6.85—6.93 (m, 1 H); 6.94—7.26 (m, 12 H); 7.28—7.42 (m, 4 H).

The difference between the composition of the complex **2** found by X-ray structure analysis ($Y(C_5H_2Ph_3)Cl_2(thf)_{3.5}$) and from chemical analysis ($Y(C_5H_2Ph_3)Cl_2(thf)_3$) can be explained by the easy loss of the non-coordinated THF molecule upon prolonged drying of the complex under vacuum.

Dichloro 1,2,4-triphenylcyclopentadienide tris(tetrahydrofuranate) lutetium, $Lu(Ph_3C_5H_2)Cl_2(thf)_3$ (3). Complex **3** was obtained as described for the complex **1** starting from 1.107 g (3.76 mmol) 1,2,4-triphenylcyclopenta-1,3-diene, 0.265 g (11 mmol) sodium hydride and 1.833 g (3.69 mmol) $LuCl_3(thf)_3$. Obtained 1.205 g (1.61 mmol, 44%) as colorless microcrystals $Lu(1,2,4\text{-}Ph_3C_5H_2)Cl_2(thf)_3$. Found (%): Lu, 23.40; Cl, 9.56. Calculated (%): Lu, 23.16; Cl, 9.38. ^{1}H NMR (500 MHz, THF-d_8, δ): 6.84—6.86 (m, 1 H); 6.90—7.22 (m, 12 H); 7.28—7.35 (m, 4 H).

Dichloro 1,2,3,4-tetraphenylcyclopentadienide tris(tetrahydrofuranate) lanthanum, $La(Ph_4C_5H)Cl_2(thf)_3$ (4). Complex **4** was synthesized as described for the complex **1** starting from 1.537 g (4.15 mmol) 1,2,3,4-tetraphenylcyclopentadiene, 0.293 g (12 mmol) of sodium hydride and 1.469 g (4.07 mmol) of $LaCl_3(thf)_2$. Obtained 2.529 g (3.27 mmol, 80%) of colorless $La(Ph_4C_5H)Cl_2(thf)_3$. Found (%): La, 17.94; Cl, 9.16. Calculated (%): La, 17.46; Cl, 8.91. ^{1}H NMR (250 MHz, THF-d_8, δ): 7.0—7.8 (m).

X-ray structure analysis of complexes 1, 2 and 5. Crystalline samples of the complexes for X-ray analysis were obtained from THF (**1** and **2**) or THF—toluene mixture (**2**). Single crystals of **5** were obtained by slow diffusion of pentane into the THF solution of **3** (pentane solution of **3**, 3 : 1 *V*/*V*). Samples of **1**, **2** and **5** were prepared as described earlier. The diffraction data were collected using Smart 1000 CCD and Smart APEX II CCD diffractometers (λ(Mo-Kα) 0.71072 Å). Crystallographic data and main refinement parameters for complexes **1**, **2** and **5** are presented in the Table 1. Multiple attempts to obtain good X-ray quality single crystals of **2** under different conditions failed. Analysis of the reciprocal space showed that all selected crystals had multiple components. Therefore, further refinement of **2** was carried out using the intensity statistics for two main domains (HKLF 5, BASF = 0.25). For complexes **1**, **2** and **5** the data were processed applying semi-empirical absorption corrections based on intensities of equivalent reflections using the program SADABS. The structures were solved by direct methods and refined by full-matrix least squares anisotropically (for hydrogen atoms — isotropically) against F^2 using the SHELXTL-97 program package. All hydrogen atoms were placed in ideal geometrical positions and refined as riding atoms.

The work was accomplished with financial support from the Russian Foundation for Fundamental Research (grants 11-03-00043 and 10-03-00953).

References

1. S. Manastyrskyj, R. E. Maginn, M. Dubeck, *Inorg. Chem.*, 1963, **2**, 904.
2. R. Poli, *Chem. Rev.*, 1991, **91**, 509.
3. D. M. Roitershtein, M. E. Minyaev, A. A. Mikhaylyuk, K. A. Lyssenko, P. A. Belyakov, M. Yu. Antipin, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 1978.
4. M. Visseaux, P. Zinck, M. Terrier, A. Mortreux, P. Roussel, *J. Alloys Comp.*, 2008, **451**, 352.
5. M. G. Klimpel, H. W. Gorlitzer, M. Tafipolsky, M. Spiegler, W. Scherer, R. Anwander, *J. Organomet. Chem.*, 2002, **647**, 236.
6. C. M. Forsyth, G. B. Deacon, L. D. Field, C. Jones, P. C. Junk, D. L. Kay, A. F. Masters, A. F. Richards, *Chem. Commun.*, 2006, 1003.
7. C. Ruspic, J. R. Moss, M. Schurmann, S. Harder, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 2121.
8. *Cambridge Structural Database System*, Version 5.32, 2010 (updates Feb. 2011).
9. X. Zhou, H. Ma, Z. Wu, X. You, Z. Xu, X. Huang, *J. Organomet. Chem.*, 1995, **503**, 11.
10. K. N. Raymond, Ch. W. Eigenbrot, Jr., *Acc. Chem. Res.*, 1980, **13**, 276.
11. R. D. Shannon, *Acta Cryst.*, *Sect. A*, 1976, **32**, 751.
12. D. Cui, M. Nishiura, Z. Hou, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 959.
13. H. J. Heeres, A. Meetsma, J. H. Teuben, R. D. Rogers, *Organometallics*, 1989, **8**, 2637.
14. H. Schumann, I. Albrecht, J. Pickardt, E. Hahn, *J. Organomet. Chem.*, 1984, **276**, 5.
15. D. Cui, O. Tardif, Z. Hou, *J. Am. Chem. Soc.*, 2004, **126**, 1312.
16. H. J. Heeres, J. H. Teuben, R. D. Rogers, *J. Organomet. Chem.*, 1989, **364**, 87.
17. H. van der Heijden, C. J. Schaverien, A. G. Orpen, *Organometallics*, 1989, **8**, 255.
18. J. Guan, S. Jin, Y. Lin, Q. Shen, *Organometallics*, 1992, **11**, 2483.
19. G. R. Giesbrecht, J. C. Gordon, D. L. Clark, B. L. Scott, *Appl. Organomet. Chem.*, 2005, **19**, 98.
20. M. D. Walter, D. Bentz, F. Weber, O. Schmitt, G. Wolmershäuser, H. Sitzmann, *New J. Chem.*, 2007, **31**, 305.
21. I. L. Fedushkin, V. I. Nevodchikov, M. N. Bochkarev, S. Dechert, H. Shumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2003, **52**, 154.
22. Z. Xie, S. Wang, Z.-Y. Zhou, T. C. W. Mak, *Organometallics*, 1999, **18**, 1641.
23. Z. Xie, S. Wang, Z.-Y. Zhou, F. Xue, T. C. W. Mak, *Organometallics*, 1998, **17**, 489.
24. H. Sitzmann, O. Schmitt, F. Weber, G. Wolmershäuser, *Z. Anorg. Allg. Chem.*, 2001, **627**, 12.
25. G. R. Giesbrecht, D. L. Clark, J. C. Gordon, B. L. Scott, *Appl. Organomet. Chem.*, 2003, **17**, 473.
26. T. Mehdoui, J.-C.Berthet, P. Thuéry, M. Ephritikhine, *Dalton Trans.*, 2005, 1263.
27. C. S. Day, V. W. Day, R. D. Ernst, S. H. Vollmer, *Organometallics*, 1982, **1**, 998.
28. P. N. Hazin, J. C. Huffman, J. W. Bruno, *Organometallics*, 1987, **6**, 23.
29. W.-P. Leung, F.-Q. Song, F. Xue, Z.-Y. Zhang, T. C. W. Mak, *J. Organomet. Chem.*, 1999, **582**, 292.
30. Z. Wu, Z. Xu, X. You, X. Zhou, H. Wang, Y. Yang, *Polyhedron*, 1993, **12**, 795.
31. D. L. Clark, J. C. Gordon, B. L. Scott, J. G. Watkin, *Polyhedron*, 1999, **18**, 1389.
32. H. Schumann, J. A. Meese-Marktscheffel, A. Dietrich, *J. Organomet. Chem.*, 1989, **377**, C5.
33. G. B. Deacon, C. M. Forsyth, D. L. Wilkinson, *Chem.-Eur. J.*, 2001, **7**, 1784.
34. I. L. Fedushkin, S. Dechert, H. Schumann, *Organometallics*, 2000, **19**, 4066.
35. Z. Wu, Z. Xu, X. You, X. Zhou, L. Shi, *J. Coord. Chem.*, 1992, **26**, 329.
36. G. V. Khoroshenkov, A. A. Fagin, M. N. Bochkarev, S. Dechert, H. Shumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2003, **52**, 1715.
37. X. Zhou, Z. Wu, H. Ma, Z. Xu, X. You, *Polyhedron*, 1994, **13**, 375.
38. W. J. Evans, M. A. Johnston, R. D. Clark, J. W. Ziller, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1609.
39. H. Schumann, R. D. Köhn, F.-W. Reier, A. Dietrich, J. Pickardt, *Organometallics*, 1989, **8**, 1388.
40. W. J. Evans, D. G. Giarikos, P. S. Workman, J. W. Ziller, *Inorg. Chem.*, 2004, **43**, 5754.
41. W. J. Evans, T. M. Champagne, B. L. Davis, N. T. Allen, G. W. Nyce, M. A. Johnston, Y.-C. Lin, A. Khvostov, J. W. Ziller, *J. Coord. Chem.*, 2006, **59**, 1069.
42. H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, *J. Organomet. Chem.*, 1993, **456**, 77.
43. H. Schumann, J. Winterfeld, M. Glanz, R. D. Köhn, H. Hemling, *J. Organomet. Chem.*, 1994, **481**, 275.
44. W. P. Kretschmer, J. H. Teuben, S. I. Troyanov, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 88.
45. D. M. Roitershtein, M. E. Minyaev, K. A. Lyssenko, P.A. Belyakov, M. Yu. Antipin, *Russ. Chem. Bull.* (*Int. Ed.*), 2004, **53**, 2152.
46. W. A. Herrmann, *Lanthanides and Actinides in Synthetic Methods of Organometallic and Inorganic Chemistry* (*Herrman/Brauer*), Ed. F. T. Edelmann, Verlag, Stuttgart, 1997, **6**, 34.
47. S. Kostanecki, G. Rossbach, *Ber. Deutsch. Chem. Ges.*, 1896, **413**, 1488.
48. F. H. Newmann, *Justus Liebig´s Ann. Chem.*, 1898, **302**, 236.
49. W. Dilthey, W. Schommer, *J. Prakt. Chem.*, 1933, **136**, 293.
50. J. R. Jonson, O. Crimmitt, *Organic Syntheses*, 1943, **23**, 92.
51. M. P. Castellani, J. M. Wright, S. J. Geib, A. L. Rheingold, W. C. Trogler, *Organometallics*, 1986, **5**, 1116.
52. D. M. Roitershtein, A. M. Ellern, M. Yu. Antipin, L. F. Rybakova, Yu. T. Struchkov, E. S. Petrov, *Mendeleev Commun.*, 1992, **2**, 118.

Received March 27, 2012;
in revised form July 3, 2012