

Diphenylbutadiene-bridged gadolinium complex [GdCl₂(THF)₃]₂(μ-Ph₂C₄H₄) · 3THF: the synthesis and crystal structure

Nina S. Emelyanova^a, Alexander A. Trifonov^a, Lev N. Zakharov^a,
Alexander F. Shestakov^b, Yuri T. Struchkov^c, Mikhail N. Bochkarev^{a,*}

^a Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinin St., 49, Nizhny Novgorod, 603600, Russia

^b Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

^c A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov st., 28, 117813 Moscow, Russia

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Abstract

The diphenylbutadiene-bridged gadolinium complex [GdCl₂(THF)₃]₂(μ-Ph₂C₄H₄) · 3THF (**1**) has been obtained by the reaction of Gd(III) chloride with diphenylbutadienepotassium. The molecular structure of **1** was determined by X-ray diffraction. The complex **1** has a binuclear structure in which a bridging diphenylbutadiene ligand is η⁴-bonded to the Gd atoms connecting two GdCl₂(THF)₃ units. Both Gd atoms have a distorted octahedral environment. At the Gd atom the two Cl atoms are in trans positions and the four other coordination sites are occupied by the three O atoms of THF molecules and the η⁴-bonded C₄H₄ fragment of a diphenylbutadiene ligand. In the two η⁴-bonded GdC₄H₄ fragments one of the Gd–C η⁴-distances is significantly elongated (2.86(3) and 2.97(3) Å) compared with other three (2.65(3)–2.69(3) and 2.67(3)–2.77(3) Å). The magnetic moment of Gd, equal to 8.1 BM, is typical for Gd³⁺ compounds that is evidence for a formal charge of DPBD ligand of –2 in complex **1**. However, the expected distribution of the C–C bond of the diene fragment as long–short–long is not realized. © 1997 Elsevier Science S.A.

Keywords: Gadolinium; Diphenylbutadiene; X-ray diffraction

1. Introduction

Rare earth complexes with acyclic dienes are of considerable interest as possible intermediate species in the processes of stereospecific polymerization of conjugated dienes on lanthanide catalysts [1]. However, only a few such types of complex with bridged ligands are isolated in the individual state. Three complexes [K(THF)₂(μ-Ph₂C₄H₄)₂Lu(THF)₂], **2**, [2], [I₂La(THF)₃(μ-η⁴:η⁴-Ph₂C₄H₄)LaI₂(THF)₃], **3**, [3] and [(C₅Me₅)₂La(THF)](μ-η¹:η³-C₄H₆)(C₅Me₅)₂La], **4**, [4] were structurally characterized. The butadiene group has approximately η⁴-symmetric bonding in **2** and **3** and η¹:η³-unsymmetric bonding in **4**, its formal charge being –2 in all cases.

In addition, the complexes Cp₂Lu(C₁₀H₈)(dme) [5], Cp₂Lu(C₁₄H₁₀) [6] and [(C₅Me₅)₂Sm(μ-η²:η⁴-PhCHCH₂)Sm(C₅Me₅)₂] [7] are known in which the

coordinated diene moiety is a part of a conjugated cyclic system. In the first two complexes its coordination (intermediate between η² and η⁴ types) is accompanied by distortion of the flat structure of naphthalene and anthracene ligands. In the latter the double bond of the ethylene fragment of styrene in combination with the neighbouring C–C link of the phenyl ring comes out as an η⁴-coordinated diene ligand.

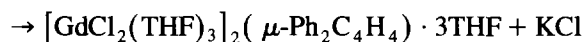
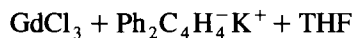
In the present work we describe the synthesis, molecular structure and quantum chemical analysis of the electronic structure of complex [GdCl₂(THF)₃]₂(μ-Ph₂C₄H₄) · 3THF, **1**, (μ-η⁴:η⁴-*cis*-1,4-diphenylbuta-1,3-diene)-hexakis-(tetrahydrofurane)-tetrachlorine-digadolinium(III) · tris(tetrahydrofurane).

2. Results and discussion

Addition of GdCl₃ to THF solution of 3 equiv. of *trans*-1,4-diphenylbuta-1,3-diene potassium (DPBD[–]K⁺) leads to a colour change from red-brown

* Corresponding author.

to dark brown. The red paramagnetic crystals of product **1** are precipitated from the obtained mixture at -10°C .



Complex **1** is very sensitive to air and moisture but stable under inert atmosphere. The effective magnetic moment per Gd atom is equal to 8.1 BM. It is interesting to point out that, in spite of the excess of DPBD^-K^+ used in this reaction, the complete reduction of Gd does not occur. Previously we have found that the reaction of LuCl_3 with DPBD^-K^+ in the ratio 1:3 under the same conditions affords heterobimetallic complex $[\text{K}(\text{THF})_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4)_2 \text{Lu}(\text{THF})_2]$ [2]. Taking into account these data one may suppose that both kinds of product are formed in these reactions. But in the case of

Gd we failed to isolate the bimetallic complex whereas in the case of Lu the mixed Cl/DPBD product has not been isolated. The low yield of compound **1** (15%) is indirect confirmation of such an assumption.

An X-ray study has shown that the molecule of **1** has a binuclear structure in which a bridging DPBD ligand is η^4 -bonded to the Gd atoms connecting two $\text{GdCl}_2(\text{THF})_3$ units (Fig. 1, Tables 1 and 2). (The crystal of **1** also includes three solvating THF molecules.) The two Gd atoms have a distorted octahedral environment. At the Gd atom the two Cl atoms are in trans positions and the four other coordination sites are occupied by the three O atoms of THF molecules and the η^4 -bonded C_4H_4 fragment of a DPBD ligand. Thus the disposition of the Cl atoms, THF molecules and η^4 -bonded C_4H_4 fragment at the Gd atoms in **1** is similar to that in the known complexes of $\text{CpLnX}_2(\text{THF})$

Table 1

Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U	Atom	x	y	z	U
Gd(1)	9991(1)	-3085(1)	4627(1)	25(1) ^a	Gd(2)	7970(1)	-1933(1)	4655(1)	26(1) ^a
Cl(1)	9917(4)	-3637(3)	6530(7)	41(3) ^a	Cl(2)	10417(4)	-2816(3)	2632(6)	38(3) ^a
Cl(3)	8052(4)	-1422(3)	6570(6)	38(3) ^a	Cl(4)	7578(4)	-2183(3)	2615(6)	38(3) ^a
O(1)	9738(11)	-3942(8)	3735(16)	42(8) ^a	O(2)	10784(10)	-2533(8)	5563(15)	38(7) ^a
O(3)	11132(10)	-3571(8)	4543(16)	38(8) ^a	O(4)	7171(10)	-2531(8)	5522(17)	44(8) ^a
O(5)	8201(10)	-1069(10)	3795(17)	42(9) ^a	O(6)	6864(10)	-1458(9)	4596(14)	45(8) ^a
C(1)	8168(13)	-3489(12)	4357(23)	18(10) ^a	C(2)	8140(14)	-3877(12)	5279(28)	47(13) ^a
C(3)	7715(17)	-4323(16)	5242(25)	48(14) ^a	C(4)	7323(22)	-4421(14)	4407(42)	61(19) ^a
C(5)	9379(21)	-4087(18)	3470(49)	108(26) ^a	C(6)	7764(21)	-3594(12)	3422(31)	58(15) ^a
C(7)	8598(14)	-3015(10)	4435(22)	22(9) ^a	C(8)	8772(13)	-2739(10)	5353(25)	29(10) ^a
C(9)	9214(15)	-2277(12)	5383(26)	30(12) ^a	C(10)	9384(16)	-2052(13)	4295(31)	48(14) ^a
C(11)	9797(14)	-1504(12)	4299(26)	35(11) ^a	C(12)	10152(17)	-1376(11)	3418(25)	45(11) ^a
C(13)	10554(16)	-960(13)	3284(25)	46(12) ^a	C(14)	10605(14)	-574(13)	4152(30)	35(13) ^a
C(15)	10261(17)	-709(13)	5159(29)	45(14) ^a	C(16)	9852(16)	-1127(11)	5218(23)	30(11) ^a
C(17)	9784(17)	-4487(15)	4181(32)	57(15) ^a	C(18)	9385(24)	-4824(13)	3431(34)	90(17) ^a
C(19)	9379(27)	-4577(19)	2443(42)	136(25) ^a	C(20)	9437(18)	-4003(15)	2513(27)	53(14) ^a
C(21)	10817(17)	-2377(11)	6723(28)	46(13) ^a	C(22)	11145(21)	-1886(20)	6778(36)	87(22) ^a
C(23)	11609(17)	-1837(16)	5839(38)	78(19) ^a	C(24)	11372(16)	-2295(13)	5024(33)	65(15) ^a
C(25)	11463(18)	-3785(15)	3572(25)	67(14) ^a	C(26)	11891(21)	-4235(16)	3947(24)	70(16) ^a
C(27)	12141(19)	-4021(20)	4946(39)	101(22) ^a	C(28)	11521(22)	-3722(21)	5562(35)	113(23) ^a
C(29)	6579(15)	-2759(14)	4929(33)	73(15) ^a	C(30)	6336(19)	-3165(13)	5791(33)	65(16) ^a
C(31)	6759(18)	-3132(15)	6820(26)	66(15) ^a	C(32)	7140(13)	-2654(13)	6729(22)	33(11) ^a
C(33)	8153(15)	-525(14)	4280(31)	60(15) ^a	C(34)	8240(20)	-151(12)	3522(26)	64(15) ^a
C(35)	8766(17)	-408(11)	2744(26)	39(12) ^a	C(36)	8451(16)	-976(13)	2626(21)	36(12) ^a
C(37)	6475(17)	-1228(14)	3625(26)	49(14) ^a	C(38)	6013(18)	-814(17)	3977(31)	73(18) ^a
C(39)	5746(19)	-1063(20)	5077(29)	81(20) ^a	C(40)	6479(14)	-1298(16)	5594(29)	59(15) ^a
O(7)	8990(22)	-427(17)	9900(33)	156(15)	C(41)	9533(27)	-617(21)	8170(43)	126(18)
C(42)	9989(36)	-701(28)	9016(54)	191(29)	C(43)	9581(34)	-729(26)	9914(51)	176(26)
C(44)	8932(29)	-303(24)	8715(45)	144(22)	O(8)	6059(18)	610(14)	5832(30)	177(12)
C(45)	6694(27)	258(22)	5331(46)	235(20)	C(46)	7193(26)	655(20)	5864(38)	155(17)
C(39)	5746(19)	-1063(20)	5077(29)	81(20) ^a	C(40)	6479(14)	-1298(16)	5594(29)	59(15) ^a
O(7)	8990(22)	-427(17)	9900(33)	156(15)	C(41)	9533(27)	-617(21)	8170(43)	126(18)
C(42)	9989(36)	-701(28)	9016(54)	191(29)	C(43)	9581(34)	-729(26)	9914(51)	176(26)
C(44)	8932(29)	-303(24)	8715(45)	144(22)	O(8)	6059(18)	610(14)	5832(30)	177(12)
C(45)	6694(27)	258(22)	5331(46)	235(20)	C(46)	7193(26)	655(20)	5864(38)	155(17)
C(47)	6898(28)	573(24)	7206(43)	247(21)	C(48)	6351(28)	365(23)	6791(45)	195(19)
O(9)	9564(17)	-2408(14)	9338(27)	162(11)	C(49)	9130(20)	-1953(16)	9612(34)	94(12)
C(50)	8719(29)	-2358(23)	10339(47)	228(21)	C(51)	8361(27)	-2461(23)	9281(41)	181(19)
C(52)	8944(23)	-2603(21)	8555(39)	138(16)					

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized $U(i,j)$ tensor.

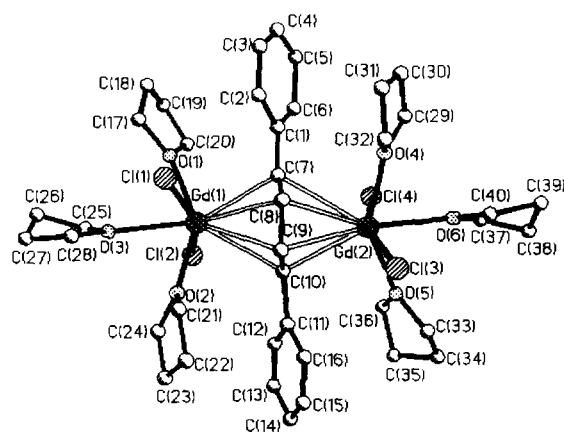


Fig. 1. The general view of $[\text{GdCl}_2(\text{THF})_2]_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4)$.

type ($X = \text{Cl}, \text{Br}$) [8] with the difference that Cp ligand is substituted for a diene fragment. The $\text{GdCl}_2(\text{THF})_2$ units in **1** are twisted relative to each other: the torsion angle $\text{Cl}(1)\text{Gd}(1)\dots\text{Gd}(2)\text{Cl}(3)$ is 53.3° . In contrast the two LaI_2 groups in the analogous complex **3** are actually in the same plane [3].

The Cl and O atoms lying in the equatorial positions are noticeably bent away from the central part of the molecule. The $\text{O}(3)\text{Gd}(1)\text{O}(1,2)$, $\text{O}(6)\text{Gd}(2)\text{O}(4,5)$ and

$\text{O}(3)\text{Gd}(1)\text{Cl}(1,2)$, $\text{O}(6)\text{Gd}(2)\text{Cl}(3,4)$ angles ($74.4(7)$, $74.7(7)$; $75.8(7)$, $73.5(7)^\circ$ and $80.4(5)$, $79.2(5)$; $80.9(5)$, $80.8(5)^\circ$ respectively) are considerably less than the ideal octahedral angle of 90° . The $\text{Cl}(1)\text{Gd}(1)\text{Cl}(2)$, $\text{Cl}(3)\text{Gd}(2)\text{Cl}(4)$ and $\text{O}(1)\text{Gd}(1)\text{O}(2)$, $\text{O}(4)\text{Gd}(2)\text{O}(5)$ angles between the Cl and O atoms in trans positions are $158.6(3)$, $160.5(3)^\circ$ and $148.9(7)$, $149.3(7)^\circ$ respectively. In **3**, similar distortions of the octahedral coordination at the La atom were found: the $\text{O}(3)\text{LaO}(1,2)$, $\text{O}(3)\text{LaI}(1,2)$ and $\text{I}(1)\text{LaI}(2)$, $\text{O}(1)\text{LaO}(2)$ angles are 74.1 , 75.9 , 80.6 , 79.0° and 159.50 , 150.0° respectively [3].

The $\text{Gd}(1)\text{-Cl}(1,2)$ and $\text{Gd}(2)\text{-Cl}(3,4)$ distances ($2.681(8)$, $2.631(8)$ Å and $2.643(8)$, $2.647(8)$ Å respectively) in **1** are close to each other. The average Gd–O distance (2.47 Å) between the Gd atoms and the $\text{O}(3,6)$ atoms in the apical positions is noticeably longer by 0.07 Å than that for the $\text{O}(1,2)$ and $\text{O}(4,5)$ atoms in the equatorial positions (2.40 Å). In **3**, the value of the similar difference of the La–O distances is 0.08 Å.

The diene group of the DPBD ligand is not planar: the torsion angle $\text{C}(7)\text{C}(8)\text{-C}(9)\text{C}(10)$ is 10.2° . The observed DPBD structure distortions in **1** are close to those found in complex **4**, where the similar torsion angle is 15.3° [4]. As in **2**, the plane of the butadiene

Table 2

Selected interatomic distances (Å) and bond angles (deg)

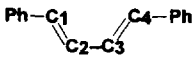
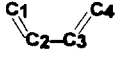
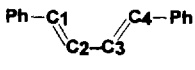
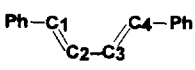
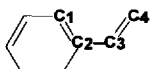
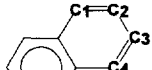
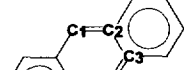
$\text{Gd}(1)\text{-Cl}(1)$	2.681(8)	$\text{Gd}(2)\text{-Cl}(3)$	2.643(8)	$\text{C}(1)\text{-C}(2)$	1.48(4)
$\text{Gd}(1)\text{-Cl}(2)$	2.631(8)	$\text{Gd}(2)\text{-Cl}(4)$	2.647(8)	$\text{C}(2)\text{-C}(3)$	1.38(5)
$\text{Gd}(1)\text{-O}(1)$	2.44(2)	$\text{Gd}(2)\text{-O}(4)$	2.39(2)	$\text{C}(3)\text{-C}(4)$	1.28(6)
$\text{Gd}(1)\text{-O}(2)$	2.34(2)	$\text{Gd}(2)\text{-O}(5)$	2.44(2)	$\text{C}(4)\text{-C}(5)$	1.41(7)
$\text{Gd}(1)\text{-O}(3)$	2.51(2)	$\text{Gd}(2)\text{-O}(6)$	2.44(2)	$\text{C}(5)\text{-C}(6)$	1.55(5)
$\text{Gd}(1)\text{-C}(7)$	2.69(3)	$\text{Gd}(2)\text{-C}(7)$	2.97(3)	$\text{C}(1)\text{-C}(6)$	1.39(5)
$\text{Gd}(1)\text{-C}(8)$	2.65(3)	$\text{Gd}(2)\text{-C}(8)$	2.67(3)	$\text{C}(11)\text{-C}(12)$	1.30(4)
$\text{Gd}(1)\text{-C}(9)$	2.67(3)	$\text{Gd}(2)\text{-C}(9)$	2.69(3)	$\text{C}(12)\text{-C}(13)$	1.31(4)
$\text{Gd}(1)\text{-C}(10)$	2.86(3)	$\text{Gd}(2)\text{-C}(10)$	2.77(3)	$\text{C}(13)\text{-C}(14)$	1.43(5)
$\text{C}(7)\text{-C}(8)$	1.34(4)	$\text{C}(1)\text{-C}(7)$	1.45(4)	$\text{C}(14)\text{-C}(15)$	1.42(5)
$\text{C}(8)\text{-C}(9)$	1.43(4)	$\text{C}(10)\text{-C}(11)$	1.59(4)	$\text{C}(15)\text{-C}(16)$	1.31(4)
$\text{C}(9)\text{-C}(10)$	1.47(5)			$\text{C}(11)\text{-C}(16)$	1.46(4)
$\text{Cl}(1)\text{-Gd}(1)\text{-Cl}(2)$	158.6(3)	$\text{Cl}(3)\text{-Gd}(2)\text{-Cl}(4)$	160.5(3)		
$\text{O}(1)\text{-Gd}(1)\text{-O}(2)$	148.9(7)	$\text{O}(4)\text{-Gd}(2)\text{-O}(5)$	149.3(7)		
$\text{O}(3)\text{-Gd}(1)\text{-C}(7)$	153.8(7)	$\text{O}(6)\text{-Gd}(2)\text{-C}(7)$	142.6(7)		
$\text{O}(3)\text{-Gd}(1)\text{-C}(8)$	161.0(8)	$\text{O}(6)\text{-Gd}(2)\text{-C}(8)$	151.6(8)		
$\text{O}(3)\text{-Gd}(1)\text{-C}(9)$	150.3(8)	$\text{O}(6)\text{-Gd}(2)\text{-C}(9)$	160.4(8)		
$\text{O}(3)\text{-Gd}(1)\text{-C}(10)$	141.9(8)	$\text{O}(6)\text{-Gd}(2)\text{-C}(10)$	154.9(8)		
$\text{Gd}(1)\text{-C}(7)\text{-C}(1)$	121.3(17)	$\text{Gd}(2)\text{-C}(7)\text{-C}(1)$	121.2(18)		
$\text{Gd}(1)\text{-C}(7)\text{-C}(8)$	73.6(16)	$\text{Gd}(2)\text{-C}(7)\text{-C}(8)$	64.0(15)		
$\text{Gd}(1)\text{-C}(8)\text{-C}(7)$	77.3(17)	$\text{Gd}(2)\text{-C}(8)\text{-C}(7)$	89.1(17)		
$\text{Gd}(1)\text{-C}(8)\text{-C}(9)$	75.3(16)	$\text{Gd}(2)\text{-C}(8)\text{-C}(9)$	75.1(16)		
$\text{Gd}(1)\text{-C}(9)\text{-C}(8)$	73.4(16)	$\text{Gd}(2)\text{-C}(9)\text{-C}(8)$	73.9(15)		
$\text{Gd}(1)\text{-C}(9)\text{-C}(10)$	81.8(18)	$\text{Gd}(2)\text{-C}(9)\text{-C}(10)$	77.6(17)		
$\text{Gd}(1)\text{-C}(10)\text{-C}(9)$	67.7(16)	$\text{Gd}(2)\text{-C}(10)\text{-C}(9)$	71.3(16)		
$\text{Gd}(1)\text{-C}(10)\text{-C}(11)$	125.2(18)	$\text{Gd}(2)\text{-C}(10)\text{-C}(11)$	113.4(18)		
$\text{Gd}(1)\text{-C}(7)\text{-Gd}(2)$	117.1(9)	$\text{C}(1)\text{-C}(7)\text{-C}(8)$	127.8(25)		
$\text{Gd}(1)\text{-C}(8)\text{-Gd}(2)$	130.8(11)	$\text{C}(7)\text{-C}(8)\text{-C}(9)$	125.4(27)		
$\text{Gd}(1)\text{-C}(9)\text{-Gd}(2)$	128.9(12)	$\text{C}(8)\text{-C}(9)\text{-C}(10)$	114.8(27)		
$\text{Gd}(1)\text{-C}(10)\text{-Gd}(2)$	118.4(11)	$\text{C}(9)\text{-C}(10)\text{-C}(11)$	116.3(28)		

fragment in **1** is not coincident with the phenyl ring planes: the dihedral angles between the average planes of the C(7)–C(10), C(1)–C(6) and C(11)–C(16) fragments are 26.3° and 18.9° respectively. The close values of similar angles (23.5 and 21.3°) were found for η^4 -coordinated DPBD ligand in **2** [2]. The C(7)–C(8), C(8)–C(9) and C(9)–C(10) distances in the coordinated butadiene fragment are 1.34(4), 1.43(4) and 1.47(5) Å. The distribution of the C–C bond lengths for the diene in **1** is in contrast to the long–short–long and short–long–

short bond distances found in **2** and **3** respectively. Unfortunately, the low accuracy of the C–C distances in **1** (see Section 3) and the existence of the disorder of the C(2) and C(3) carbon atoms of the diene in **3** make it impossible for a more precise discussion of the C–C distances found for the diene in these structures.

The butadiene fragment of the DPBD ligand in **1** is a bridge η^4 -bonded to the Gd(1) and Gd(2) atoms connecting the GdCl₂(THF)₃ units. In the two η^4 -bonded GdC₄H₄ fragments one of the Gd–C η^4 -distances is

Table 3
Coordination mode of diene moiety in organolanthanide compounds ^a

Ligand M	Distances (Å)				Angles (deg)			
	M–C ₁ M–C ₂ M–C ₃ M–C ₄	C ₁ –C ₂	C ₂ –C ₃	C ₃ –C ₄	C ₁ –C ₂ –C ₃	C ₂ –C ₃ –C ₄	C ₁ –C ₂ –C ₃ –C ₄	
 Lu	2.527(8) 2.50(1) 2.540(9) 2.529(8)	1.42(2) (1.333)	1.38(1) (1.437)	1.44(1) (1.333)	125.6(8)	123.4(9)	~ 0	[2] [13]
 La	2.688(4) 2.759(4) 2.734(4) 2.894(4)	1.406(6) (1.341)	1.396(6) (1.463)	1.469(5) (1.341)	126.2(4) (123.3)	15.3(7) (123.3)	~ 0	[3] [14]
 La	2.89(1) 2.76(2) 2.82(1) 2.94(1)	1.25(2) (1.333)	1.49(3) (1.437)	1.25(2) (1.333)			~ 0	[4] [13]
 Gd	2.69(3), 2.77(3) 2.65(3), 2.69(3) 2.67(3), 2.67(3) 2.86(3), 2.97(3)	1.34(4) (1.333)	1.43(4) (1.437)	1.47(5) (1.333)	125.4(27)	114.8(27)	10.2 ~ 0	this work [13]
 Sm	2.772(17) 2.850(16) 2.732(15) 2.674(15)	1.401(24) (1.387)	1.449(21) (1.464)	1.468(22) (1.319)	124.7(15) (123.5)	122.9(14) (127.6)	~ 0 ~ 0 ^b	[7] [15]
 Lu	2.406(6) 2.579(8) 2.562(8) 2.397(8)	1.46(1) (1.378)	1.36(1) (1.411)	1.46(1) (1.376)	118.5(8) (120.9)	120.9(8) (120.1)	~ 0 ~ 0	[5] [16]
 Lu	2.44(2) 2.71(2) 2.73(2) 2.45(2)	1.48(2) (1.399)	1.45(2) (1.428)	1.47(2) (1.399)	116.1(9) (119.3)	116.4(9) (119.3)	~ 0 ~ 0	[6] [17]

^a Values in brackets correspond to free ligand.

^b Data for substituted styrene.

significantly elongated compared with the other three: 2.86(3) Å for the Gd(1)–C(10) bond vs. 2.65(3)–2.69(3) Å for the Gd(1)–C(7), Gd(1)–C(8), Gd(1)–C(9) bonds, and 2.97(3) Å for the Gd(2)–C(7) bond vs. 2.67(3)–2.77(3) Å for the Gd(2)–C(8), Gd(2)–C(9), Gd(2)–C(10) bonds. The three shortest Gd–C distances for η^4 -bonding in **1** are comparable with the average Gd–C η^6 -distance in $[\text{Gd}(\eta^6\text{-Bu}_3\text{C}_6\text{H}_3)_2]$ 2.63 Å [9] and η^5 -distance in $[\text{GdCp}_2\text{Cl}]_4$ 2.67 Å [10], but longer than the Gd–C σ -bond length, 2.412 Å, in $[\text{PhGdCl}_2(\text{THF})_4]$ [11]. Thus the bonding of each Gd atom with the diene fragment in **1** can be described as an η^3 -type and the bridging function of DPBD as a $\mu:2\eta^3$. Similar differences between the La–C distances for allyl η^3 -bonding (2.688, 2.759, 2.734 Å and 2.894 Å) were found in **4** [4]. An unsymmetric $\mu\text{-}\eta^1\text{:}\eta^3$ -bonding of butadiene in **4** seems to be caused by additional coordination of the THF molecule at the second La atom. However, in the molecule of **3** containing two equivalent La atoms the distribution of La–C distances (2.89(1), 2.76(2), 2.82(2) and 2.94(1) Å) corresponds better to η^2 -coordination of the middle C–C bond of the diene fragment. The possibility of various types of allyl group coordination with the same Sm–C distances (2.63–2.67 Å) in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCH}_2)$ and with rather different Sm–C distances (2.55–2.73 Å) in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCHMe})$ and $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu, \eta^3\text{-CH}_2\text{CHCHCH}_2\text{-})]_2$ is well demonstrated in Ref. [12]. An analogous situation has been observed for coordination of the diene moiety too. Table 3 contains a comparison of the structures of diene fragments in known organolanthanide compounds, and shows this variety of coordination modes for the diene group.

The magnetic moment of Gd, typical for Gd^{3+} compounds, is evidence that the formal charge of the DPBD ligand is equal to -2 in complex **1**, $[\text{GdCl}_2(\text{THF})_3]_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4)^{2-}$. Additional electrons are placed on the lowest DPBD π^* -orbital, which has bonding character with respect to the middle C–C bond and antibonding character with respect to the side C–C bonds of the diene fragment [2]. Therefore, from the formal point of view, its geometrical structure should correspond to the formula $\text{Ph}-\text{CH}^{(-)}-\text{CH}=\text{CH}-\text{CH}^{(-)}-\text{Ph}$. A significant shortening of the middle C–C bond of the DPBD ligand is actually observed, if it is a terminal one in an ionic complex, see complex **2** in Table 3.¹ At that, the diene fragment keeps its planar structure.

¹ For comparison we cite the characteristics of typically ionic complexes: $[(\text{Ph}-\text{CH}=\text{CMe}-\text{CMe}=\text{CH}-\text{Ph})\text{M}(\text{THF})_3]$ M = Ca, Sr, C₁–C₂, C₃–C₄ = 1.45–1.51 Å, C₂–C₃ = 1.38 Å [18] and $\text{Ga}(\text{C}_4\text{H}_6)$ C₁–C₂, C₃–C₄ = 1.475 Å, C₂–C₃ = 1.396 Å, [19].

However, at a bridge arrangement of a diene ligand in ionic complexes **1** and **3** (see Table 3) the expected distribution of the C–C bond as long–short–long is not realized. (In the special case of an unsymmetric complex **4**, butadiene separately performs functions of allyl and alkyl ligands.)

It is possible to believe that a reason for this discrepancy consists in intermolecular Coulombic interactions, as retaining of the elongated $\tilde{\text{N}}(8)\text{--}\tilde{\text{N}}(9)$ bond, despite the charge transfer, facilitates torsion rotation of the diene fragment, at which a decrease of the distances Gd(1)–C(7) and Gd(2)–C(10) between centres of opposite charges is achieved.

3. Experimental section

All reactions were carried out under vacuum using standard Schlenk techniques. THF was distilled at sodium benzophenone immediately before use. *trans*-1,4-Diphenylbuta-1,3-diene was purified by recrystallization from hexane. Magnetic susceptibility measurements were carried out by the method in Ref. [20].

3.1. Preparation of $[\text{GdCl}_2(\text{THF})_3]_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4) \cdot 3\text{THF}$

To a mixture of 0.786 g (20.1 mmol) of potassium and of 4.146 g (20.1 mmol) of *trans*-1,4-diphenylbuta-1,3-diene 60 ml of THF was added. The reaction mixture was stirred for 2 days at room temperature until the potassium gradually dissolved. The resulting red-brown solution was added to a suspension of 1.772 g (6.722 mmol) of GdCl_3 in 30 ml of THF. The precipitate of GdCl_3 dissolved and the solution turned dark brown. Cooling of the reaction mixture at -10°C for 24 h yields red crystals of **1**. They were washed with cold THF and dried for 24 h under vacuum. Yield 0.5 g (15%). The compound decomposes under heating above 120°C . Gd analysis: calculated 24.0%, found 24.2%.

The X-ray study of **1** was carried out using a Sintex P2₁ diffractometer at 153 K (Mo K α radiation, graphite monochromator, θ – 2θ scan in the range $3 < 2\theta < 46^\circ$, 10314 measured reflections from which 4094 observed reflections with $F < 4\sigma(F)$). The crystals of **1** are monoclinic at 153 K, $a = 19.288(4)$, $b = 24.986(5)$, $c = 12.061(2)$ Å, $\beta = 90.12(3)^\circ$, $V = 5794.5(3.2)$ Å³, $d_{\text{calc}} = 1.096$ g cm⁻³, $Z = 4$, space group $P2_1/n$.

The structure was solved by a combination of direct and difference map methods. The Gd and Cl atoms were located by direct methods, the other non-hydrogen atoms were located by subsequent electron densities synthesis. Besides the main molecule $[\text{GdCl}_2(\text{THF})_3]_2(\mu\text{-Ph}_2\text{C}_4\text{H}_4)$, the crystals of **1** also contain three solvent THF molecules. The positions of H atoms were calculated using the usual geometric

conditions. The absorption of X-rays in the crystal ($\mu(\text{Mo K}\alpha) = 2.52 \text{ mm}^{-1}$) was taken into account by the DIFABS program [21] ($T_{\text{min}} = 0.82$, $T_{\text{max}} = 1.16$). The structure was refined by the least squares procedure with anisotropic temperature factors for all non-hydrogen atoms of the main molecule and isotropic ones for the C and O atoms of the solvated THF molecules. All calculations were performed using the SHELXTL-PLUS package [22]. The next weight scheme $w^{-1} = \sigma^2(F) + 0.0019F^2$ was used. The final discrepancy factors are $R = 0.092$, $R_w = 0.105$, $S = 2.62$. There are nine THF molecules in the crystal structure of **1** which are characterized by significant thermal parameters. For three solvated THF molecules the large values of thermal parameters seem to be related to the existence of disorder in their positions. All our attempts to solve this disorder failed. This fact is a reason for the high values of final R factors for **1**.

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