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Isolation and X-ray structure of $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Ln(OH)Cl \cdot 2MgCl_2 \cdot 4THF$ (Ln = Nd, Gd)

Jin Lin, Zhaoyu Wang *

Department of Chemistry, Hebei Normal University, 265 Yuhua Donglu, Shijiazhuang 050016, China

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Abstract

The trichlorides of lanthanum, neodymium, samarium and gadolinium react with an equivalent amount of $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]MgCl$ in THF at room temperature to give $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]LnCl_2 \cdot MgCl_2 \cdot THF$ (Ln = La (**1**), Nd (**2**), Sm (**3**), Gd (**4**)). Complexes **2** and **4** are recrystallized from moist THF–hexane to give the partial hydrolytic crystal $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Ln(OH)Cl \cdot 2MgCl_2 \cdot 4THF$(Ln = Nd (**5**), Gd (**6**)). These compounds have been characterized by ^1H-NMR spectra, as well as by single-crystal X-ray analyses (**5** and **6**). The coordination geometries of Nd (III) and Gd (III) are seriously distorted. The coordination number of Mg is six and the coordination geometry is a distorted octahedron. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkenylcyclopentadienyl; Lanthanide dichloride; Complexes; Synthesis; Crystal structure

1. Introduction

It is known that the cyclopentadienyl light rare-earth chlorides are difficult to prepare because of the disproportionation resulting from the lanthanide contraction. By using substituted cyclopentadienyl groups as ligands, the disproportionation is effectively prevented because steric saturation can be achieved with light rare-earth ions. There have been many reports on the preparation of various alkyl- or trimethylsilyl-substituted cyclopentadienyl rare-earth chlorides since 1980 [1–3]. We have prepared four kinds of novel alkenylcyclopentadienyl rare-earth dichlorides. For these complexes disproportionation is avoided. Their solubilities in non-polar solvents are increased, which is beneficial for use as homogeneous catalysts.

Hydrolysis is a common mode of decomposition for the organolanthanide complexes of yttrium and the f elements, and hydroxide compounds are usually assumed to be the products. But there are only a few reports about the partial hydrolytic crystal structures of organolanthanide complexes [4–6]. Low temperature and a very small impurity of water in inert solvent such as *n*-hexane or toluene are key conditions for partial hydrolysis. The partial hydrolytic crystals $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Ln(OH)Cl \cdot 2MgCl_2 \cdot 4THF$ (Ln = Nd (**5**), Gd (**6**)) were obtained when we recrystallized alkenyl-cyclopentadienyl organolanthanide dichlorides in THF–*n*-hexane at 0°C. In this paper we shall describe the synthesis of alkenylcyclopentadienyl organolanthanide dichlorides and report the X-ray crystallographic analysis of the partial hydrolysis products.

2. Experimental

All operations on these organolanthanide complexes were performed under prepurified argon using Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone under argon immediately before use. Dicyclopentadiene was depolymerized at 170°C and then distilled. 2-Pentanone was dried with anhydrous K_2CO_3, then distilled and the

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* Corresponding author.

E-mail address: lijin123@263.net (Z. Wang)

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118–120°C boiling point fraction collected. Allyl chloride was distilled and dried over anhydrous $CaCl_2$. Anhydrous lanthanide chlorides were prepared by the Taylor method [7].

Analyses of rare-earth metals were by direct complexometric titration with disodium EDTA. Cl analysis was by the Volhardt method and Mg by a WFX-IF atomic absorption spectrophotometer. The ^{1}H-NMR spectrum was obtained in a sealed 5 mm tube on a FX-90Q spectrometer referenced to internal TMS in $CDCl_3$. Carbon and hydrogen analyses were performed by combustion in aluminum cans on an MT-3 Yanaco analyzer. Mass spectra were recorded on a GCMS-QP1000 spectrometer. IR spectra were recorded on a PE-1730 FTIR spectrometer using KBr pellets.

2.1. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]MgCl$

A sample of 6-methyl-6-propyl fulvene (5.36 g, 0.04 mol) (prepared according to the literature method [8]) in ether (30 ml) was added to a mechanically stirred white suspension of allyl magnesium chloride, which was obtained from the reaction of Mg (0.0725 mol) with allyl chloride (5.3 g, 0.066 mol) in 50 ml ether [9]. The mixture was stirred for 1 h. The ether was removed under vacuum and then 80 ml of THF was added. The THF solution was titrated by standard hydrochloric acid using phenolphthalein as indicator [10]. The yield was 58%.

2.2. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$-$LaCl_2{\cdot}MgCl_2{\cdot}THF$(1)

At room temperature, a THF solution of $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]MgCl$ (20 ml, 0.004 mol) was added to a THF (20 ml) solution of $LaCl_3$ (1.0 g, 0.004 mol) which had been magnetically stirred for 4 h in a Schlenk flask. The reaction mixture was stirred for 12 h. The resulting mixture was centrifuged. Concentration of the supernatant followed by addition of *n*-hexane afforded a colorless product, which was washed with 15 ml of *n*-hexane and then dried under reduced pressure to give 0.77 g (35.2%) of **1** as a colorless solid. Anal. Calc. for ($C_{17}H_{27}Cl_4LaMgO$): C 36.96, H 4.89, Cl 25.73, Mg 4.35, La 25.17. Found: C 36.93, H 4.85, C125.64, Mg 4.31, and La 25.08. IR (KBr, cm^{-1}): 3070m, 2950m, 2870m, 2250s, 1657s, 1646s, 1452m, 1375m, 1188w, 1053s, 1025m, 997m, 913s, 780m, 628w, 466s. ^{1}H-NMR ($CDCl_3$)(δ, ppm): 6.30 (s, 4H, C_5H_4), 5.02(m), 4.84(m), 2.63(d) (5H, $CH_2CH{=}CH_2$), 4.01(m), 1.90(m) (8H, THF), 1.30 (s, 3H, CH_3), 1.54–1.42(m), 1.24–1.10 (m), 0.84(t) (7H, C_3H_7).

2.3. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$-$NdCl_2{\cdot}MgCl_2{\cdot}THF$ (2)

The procedure followed was similar to that for **1**. A light blue solid **2** was obtained, Yield 50.7%. Anal. Calc. for ($C_{17}H_{27}Cl_4NdMgO$): C 36.62, H 4.85, C125.49, Mg 4.31, Nd 25.85. Found: C 36.56, H 4.81, C125.41, Mg 4.27, Nd 25.78.

2.4. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$-$SmCl_2{\cdot}MgCl_2{\cdot}THF$ (3)

The procedure followed was similar to that for **1**. A yellow solid **3** was obtained. Yield 68.2%. Anal. Calc. for ($C_{17}H_{27}Cl_4SmMgO$): C 36.23, H 4.79, C125.22, Mg 4.26, Sm 26.64. Found: C 36.16, H 4.72, C125.18, Mg 4.21, Sm 26.59.

2.5. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$-$GdCl_2{\cdot}MgCl_2{\cdot}THF$ (4)

The procedure followed was similar to that for **1**. A light yellow solid **4** was obtained; 60.1%. Anal. Calc. for ($C_{17}H_{27}Cl_4GdMgO$): C 35.79, H 4.74, C124.91, Mg 4.21, Gd 27.54. Found: C 35.68, H 4.76, C124.86, Mg 4.18, Gd 27.48.

2.6. $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Ln(OH)$-$Cl{\cdot}2MgCl_2{\cdot}4THF$ ($Ln = Nd$ (5),Gd (6))

A transparent THF–*n*-hexane solution of **2** and **4** was cooled down to 0°C for several days to afford pale blue (**5**) and pale yellow crystals (**6**), respectively, which were suitable for X-ray crystallographic analyses. Anal. Calc. for ($C_{29}H_{52}Cl_5Mg_2NdO_5$): C 40.95, H 6.12, Cl 20.89, Mg 5.65, Nd 16.97. Found: C 40.92, H 6.10, Cl 20.85, Mg 5.62, Nd 16.93. Anal. Calc. for ($C_{29}H_{52}Cl_5Mg_2GdO_5$): C 40.34, H 6.03, Cl 20.57, Mg 5.56, Gd 18.23. Found: C 40.30, H 6.01, Cl 20.54, Mg 5.54, Gd 18.20.

*2.7. Single-crystal X-ray structure determinations of **5** and **6***

The selected crystal data, data collection and refinement parameters for **5** and **6** are given in Table 1. Crystals suitable for X-ray structure determination were sealed under argon in a thin-walled glass fiber. The determinations of unit cell and the data collections were performed with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal monochrometor.

A total of 6104 and 6011 independent reflections for **5** and **6**, respectively, were collected in the range $2° \leq \theta \leq 25°$ by $\omega/2\theta$ scan technique at 299 K, in which

4751 (**5**) and 4625 (**6**) reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. The corrections of LP and DIFABS absorption were applied to the reflection data.

The structures of **5** and **6** were solved by direct methods (Siemens SHELXTL-PC). $T_{\min} = 0.897$, $T_{\max} = 1.109$ for **5**, and $T_{\min} = 0.881$, $T_{\max} = 1.127$ for **6**. The Nd and Gd atoms were located from an E-map. The other non-hydrogen atoms were determined by successive difference Fourier syntheses. The final refinement by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms was converged with unweighted and weighted agreement factors of 0.073 and 0.086 for **5** or 0.096 and 0.113 for **6** ($I \geq 3\sigma(I)$) with unit weights, $w = 1/(\sigma^2(F) + 0.0001F^2)$, $S = 1.66$ for **5**, $S = 2.34$ for **6**, $(\Delta/\sigma)_{\max} = 0.444$ for **5** and $(\Delta/\sigma)_{\max} = 0.247$ for **6**. The highest peaks on the difference Fourier map had a height of 1.66 e Å^{-3} (apart from Nd (1) 0.95 Å) for *S* and 2.12 e Å^{-3} for **6**. All calculations were performed on a Pentium MMX/166 computer using the SHELXTL-PC program.

Table 1
Crystallographic data for $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Nd(OH)Cl\cdot 2MgCl_2\cdot 4THF$ (**5**) and $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Gd(OH)Cl\cdot 2MgCl_2\cdot 4THF$ (**6**)

	5	6
Formula	$C_{29}H_{52}Cl_5Mg_2NdO_5$	$C_{29}H_{52}Cl_5Mg_2GdO_5$
FW	849.74	862.75
Radiation Mo–K$_\alpha$ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
Unit cell dimensions		
a (Å)	12.698(3)	12.757(3)
b (Å)	13.616(3)	13.571(3)
c (Å)	13.712(3)	13.725(3)
α (°)	68.91(3)	69.22(3)
β (°)	84.34(3)	84.91(3)
γ (°)	63.07(3)	63.48(3)
V (Å^3)	1966(1)	1929(1)
Z	2	2
D (g cm^{-3})	1.412	1.423
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Absorption coefficient (mm^{-1})	1.7297	2.0832
F(000)	840	848
Crystal size (mm^3)	$0.20 \times 0.40 \times 0.40$	$0.35 \times 0.40 \times 0.60$
Range (°)	$2 \leq \theta \leq 25$	$2 \leq \theta \leq 25$
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Measured reflections	6838	6866
Independent reflections	6104	6011
Observed reflections ($I \geq 3\sigma(I)$)	4751	4625
R ($I \geq 3\sigma(I)$)	0.073	0.096
wR ($I \geq 3\sigma(I)$)	0.086	0.113
S	1.66	2.34
Max. residual peak (e Å^{-3})	1.66	2.12

3. Results and discussion

3.1. Synthesis

$LnCl_3$ reacted with $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]MgCl$ in THF at room temperature to give the corresponding $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]LnCl_2\cdot MgCl_2\cdot THF$ with 37–68%.

$$LnCl_3 + [C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2] \xrightarrow{THF} [C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]\text{-}LnCl_2\cdot MgCl_2\cdot THF$$

where Ln = La (**1**), Nd (**2**), Sm (**3**), Gd (**4**).

The complexes are air- and moisture-sensitive and decompose easily when they are heated. They are soluble in polar solvents such as THF but less soluble in non-polar solvents such as *n*-hexane. They are purified by recrystallization.

Partial hydrolytic processes have been observed during the handing of such highly sensitive organometallic compounds. Only a very small impurity of water in an inert solvent such as *n*-hexane causes partial hydrolysis with formation of **5** (yield 32%) and **6** (yield 36%), which are isolated after recrystallization of complexes **2** and **4** in THF–*n*-hexane at 0°C, respectively:

$$[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]\text{-}LnCl_2\cdot MgCl_2\cdot THF \xrightarrow[+\,H_2O]{THF\text{–}n\text{-hexane}} [C_5H_4C(CH_3)(C_3H_7)\text{-}CH_2CH{=}CH_2]Ln(OH)Cl\cdot 2MgCl_2\cdot 4THF$$

where Ln = Nd (**5**) or Gd (**6**).

3.2. Spectra analyses of **1–4**

The IR spectra of the complexes were measured from 4000 to 200 cm^{-1}. The spectral features of these complexes are very similar [3,9,11]. Molecular ion peaks of these complexes were not obtained in the mass spectra, but THF (72, 71), ligand (176) and its fragment peaks (135, 110, 91, 65, 44, 42, 41) appear. In the ^{1}H-NMR spectrum of **1**, 6.30 ppm is assigned to the chemical shift of cyclopentadienyl [12]; 5.02, 4.84, 2.63 ppm to allyl [3]; 4.01, 1.90 ppm to THF [12]; 1.30 ppm to $-CH_3$; and 1.54–1.42, 1.24–1.10, 0.84 ppm to $-CH_2CH_2CH_3$ [9]. The spectra analyses show that these complexes have an alkenylcyclopentadienyl group $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$.

3.3. Structures of **5** and **6**

The single crystals of **5** and **6** are isostructural and isomorphous, so only the structure of **5** is shown in Fig.

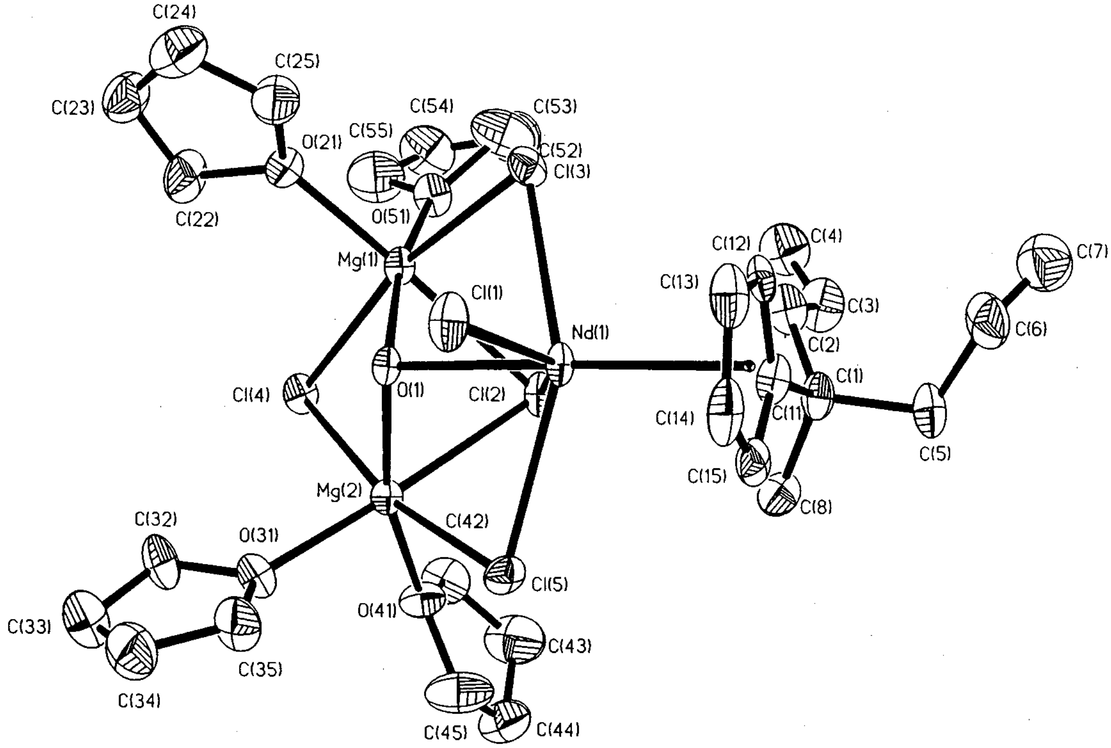

Fig. 1. Crystal structure of $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Nd(OH)Cl{\cdot}2MgCl_2{\cdot}THF$(5)

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Nd(OH)Cl{\cdot}2MgCl_2{\cdot}4THF$ (**5**)

Atom	x	y	z	U_{eq} [a]	Atom	x	y	z	U_{eq} [a]
Nd(1)	1195(1)	3516(1)	3140(1)	42(1)	C(15)	395(7)	3148(8)	1556(7)	70(1)
Mg(1)	3491(3)	3604(3)	4265(3)	45(1)	C(21)	3531(6)	3478(6)	5787(5)	59(1)
Mg(2)	1895(3)	5887(3)	2470(3)	44(1)	C(22)	3708(9)	4242(9)	6173(8)	106(1)
Cl(1)	−458(3)	3963(2)	4507(3)	70(1)	C(23)	3602(9)	3924(9)	7233(8)	107(1)
Cl(2)	3302(2)	3811(3)	2304(2)	54(1)	C(24)	3031(10)	3191(10)	7445(9)	124(1)
Cl(3)	3309(3)	1847(3)	4681(3)	65(1)	C(25)	2916(9)	2973(9)	6558(8)	101(1)
Cl(4)	3362(2)	5511(2)	3449(2)	54(1)	O(31)	761(5)	7469(6)	2662(6)	62(1)
Cl(5)	291(3)	5781(3)	1649(2)	65(1)	C(32)	1119(8)	8030(8)	3160(9)	86(1)
O(1)	1574(4)	4664(5)	3807(4)	38(1)	C(33)	93(9)	8992(9)	3275(10)	117(1)
C(1)	2548(8)	1944(8)	1115(7)	65(1)	C(34)	−875(9)	8843(9)	3057(10)	119(1)
C(2)	3714(8)	1246(9)	1765(9)	79(1)	C(35)	−484(8)	7930(9)	2691(9)	96(1)
C(3)	4856(9)	805(10)	1257(10)	104(1)	O(41)	2394(6)	6688(7)	1023(5)	70(1)
C(4)	5870(10)	407(10)	1741(10)	123(1)	C(42)	3548(8)	6374(9)	688(8)	95(1)
C(5)	2302(9)	1331(9)	486(8)	84(1)	C(43)	3497(10)	6471(11)	−348(9)	159(1)
C(6)	2273(10)	196(9)	1121(9)	106(1)	C(44)	2341(9)	7351(10)	−764(9)	124(1)
C(7)	3113(11)	−824(11)	1117(11)	142(1)	C(45)	1679(9)	7322(10)	87(8)	136(1)
C(8)	2489(9)	3100(9)	298(8)	81(1)	O(51)	5302(5)	2576(6)	4392(6)	66(1)
C(11)	1554(7)	2209(8)	1854(7)	60(1)	C(52)	5943(9)	1396(9)	4510(11)	142(1)
C(12)	1536(7)	1465(7)	2876(7)	61(1)	C(53)	7064(9)	210(10)	4170(10)	154(1)
C(13)	380(7)	1954(8)	3224(8)	82(1)	C(54)	7268(9)	2002(10)	4473(10)	138(1)
C(14)	−297(7)	2967(8)	2410(7)	82(1)	C(55)	6183(9)	2744(10)	4706(10)	153(1)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

1. Their final atomic parameters (for non-hydrogen atoms), selected bond lengths and angles are listed in Tables 2–5, respectively.

The structures of **5** and **6** are very similar. Each of the Nd and Gd atoms is coordinated by one Cl atom, three bridged-chlorine atoms (Cl(2), Cl(3), Cl(5)), one bridged-oxygen atom and one substituted cyclopentadienyl ligand to form a distorted octahedron, respectively. The bond angles Cl(1)–Nd(1)–Cl(2), Cl(3)–Nd(1)–Cl(5), O(1)–Nd(1)Cl(3) and Cl(2)–Nd(1)–

Cl(5) for **5** are 144.3, 143.0, 74.2 and 75.4° and Cl(1)–Gd(1)–Cl(2), Cl(3)–Gd(1)–Cl(5), O(1)–Gd(1)–Cl(3) and Cl(2)–Gd(1)–Cl(5) for **6** are 144.9, 145.0, 75.1 and 76.8°, respectively. The average bond lengths Nd–C (Cn) for **5** and Gd–C (Cn) for **6** are 2.483 and 2.445 Å, respectively, which are longer than those of Pr–C (Cn) (2.536 and 2.533 Å) in the compound (t-BuCp)$_2$PrCl·2THF but shorter than those of Yb–C (Cn) (2.338 and 2.342 Å) in the compound (t-BuCp)$_2$YbCl·THF [13]. The ranges of C–C (cyclopentadienyl ring) bond lengths are from 1.377 to 1.425 Å for **5** and from 1.369 to 1.408 Å for **6**. The bond lengths of Nd–Cl (bridged) are 2.945, 2.789 and 2.780 Å, respectively, which are longer than that of Nd–Cl (non-bridged) (2.679 Å) [14]. The bond lengths of Gd–C1 (bridged) are 2.894, 2.742 and 2.735 Å, respectively, which are longer than that of Gd–C1 (non-bridged) (2.650 Å) [15]. The bond lengths of Nd(1)–O(1) (bridged) and Gd(1)–O(1) (bridged) are 2.442 and 2.405 Å respectively, which are shorter than that of Nd–O (THF) (2.513 Å) and Gd–O (THF) (2.469 Å) [14,15], because the bridged-oxygen atom has a negative charge

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Gd(OH)Cl \cdot 2MgCl_2 \cdot 4THF$ (**6**)

Atom	x	y	z	U_{eq} [a]	Atom	x	y	z	U_{eq} [a]
Gd(1)	1200(1)	3522(1)	3143(1)	56(1)	C(15)	443(10)	3130(11)	1565(10)	87(2)
Mg(1)	3470(3)	3606(4)	4270(4)	57(1)	O(21)	3505(8)	3510(9)	5796(7)	78(2)
Mg(2)	1843(3)	5883(4)	2486(3)	58(1)	C(22)	3659(15)	4253(13)	6194(11)	132(2)
Cl(1)	−434(3)	3983(3)	4469(3)	81(1)	C(23)	3541(15)	3944(13)	7249(11)	118(2)
Cl(2)	3256(3)	3807(3)	2320(3)	68(1)	C(24)	3274(15)	2968(14)	7501(12)	143(2)
Cl(3)	2982(3)	1895(3)	4672(4)	79(1)	C(25)	3082(15)	2834(13)	6589(11)	135(2)
Cl(4)	3653(3)	5512(3)	3453(3)	68(1)	O(31)	766(7)	7464(8)	2677(8)	78(2)
Cl(5)	265(3)	5751(3)	1686(3)	77(1)	C(32)	1097(12)	8040(11)	3174(13)	106(2)
O(1)	1729(6)	4668(7)	3814(7)	57(1)	C(33)	98(12)	9004(14)	3260(15)	138(2)
C(1)	2572(12)	1940(12)	1137(11)	82(2)	C(34)	−905(13)	8925(13)	2982(15)	140(2)
C(2)	3719(13)	1184(13)	1830(13)	100(2)	C(35)	−468(10)	7983(10)	2651(14)	114(2)
C(3)	4854(13)	807(15)	1216(15)	126(2)	O(41)	2366(8)	6601(10)	1017(8)	85(2)
C(4)	5920(15)	416(16)	1742(16)	154(2)	C(42)	3500(12)	6403(12)	689(11)	119(2)
C(5)	2306(14)	1336(13)	477(13)	109(2)	C(43)	3451(15)	6552(17)	−354(13)	218(2)
C(6)	2283(15)	175(13)	1150(15)	125(2)	C(44)	2273(14)	7362(16)	−753(13)	162(2)
C(7)	3208(18)	−809(17)	1208(17)	206(2)	C(45)	1647(14)	7385(16)	99(10)	141(2)
C(8)	2580(14)	2982(15)	327(12)	114(2)	O(51)	5275(7)	2586(8)	4385(8)	75(2)
C(11)	1556(10)	2236(10)	1879(9)	70(2)	C(52)	5900(19)	1437(12)	4479(16)	159(2)
C(12)	1518(12)	1508(10)	2890(10)	86(2)	C(53)	7066(13)	1190(14)	4341(17)	181(2)
C(13)	376(11)	1998(11)	3209(12)	109(2)	C(54)	7195(14)	2219(14)	4182(16)	184(2)
C(14)	−286(11)	3021(11)	2374(11)	100(2)	C(55)	6177(12)	2796(15)	4572(16)	192(2)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 4
Selected bond lengths (Å) for $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Nd(OH)Cl \cdot 2MgCl_2 \cdot 4THF$ (**5**) and $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Gd(OH)Cl \cdot 2MgCl_2 \cdot 4THF$ (**6**) [a]

Bond	Distance	Bond	Distance	Bond	Distance
5					
Nd(1)–Cl(1)	2.679(3)	Mg(2)–Cl(5)	2.506(6)	Mg(2)–Cl(2)	2.653(5)
Nd(1)–Cl(2)	2.945(3)	Mg(2)–O(1)	2.041(6)	Mg(2)–Cl(4)	2.481(5)
Nd(1)–Cl(3)	2.789(3)	Mg(1)–Cl(2)	2.624(5)	C(1)–C(11)	1.533(12)
Nd(1)–Cl(5)	2.780(3)	Mg(1)–Cl(4)	2.532(5)	C(1)–C(2)	1.505(13)
Nd(1)–O(1)	2.442(8)	Mg(1)–Cl(3)	2.529(6)	C(2)–C(3)	1.503(14)
Nd(1)–Cn	2.483	Mg(1)–O(1)	2.017(5)	C(3)–C(4)	1.292(17)
6					
Gd(1)–Cl(1)	2.650(4)	Mg(2)–Cl(5)	2.513(8)	Mg(2)–Cl(2)	2.654(6)
Gd(1)–Cl(2)	2.894(4)	Mg(2)–O(1)	2.038(9)	Mg(2)–Cl(4)	2.490(7)
Gd(1)–Cl(3)	2.742(4)	Mg(1)–Cl(2)	2.619(7)	C(1)–C(11)	1.571(18)
Gd(1)–Cl(5)	2.735(4)	Mg(1)–Cl(4)	2.536(7)	C(1)–C(2)	1.521(19)
Gd(1)–O(1)	2.405(12)	Mg(1)–Cl(3)	2.531(8)	C(2)–C(3)	1.580(23)
Gd(1)–Cn	2.445	Mg(1)–O(1)	2.038(8)	C(3)–C(4)	1.381(27)

[a] Cn is the centroid of the cyclopentadienyl ring defined by C(11)–C(15).

Table 5
Selected bond angles (°) for $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]Nd(OH)Cl\cdot 2MgCl_2\cdot 4THF$ (**5**) and $[C_5H_4C(CH_3)(C_3H_7)CH_2CH{=}CH_2]$-$Gd(OH)Cl\cdot 2MgCl_2\cdot 4THF$ (**6**) [a]

Angle	(°)	Angle	(°)	Angle	(°)
5					
Cl(1)–Nd(1)–Cl(2)	144.3(1)	Cl(5)–Nd(1)–O(1)	73.4(1)	Cl(2)Mg(2)–O(1)	74.4(2)
Cl(1)–Nd(1)–Cl(2)	94.6(1)	Cl(1)–Nd(1)–Cn	102.9	Cl(4)–Mg(2)–O(1)	84.2
Cl(2)–Nd(1)–Cl(3)	74.6(1)	Cl(2)–Nd(1)–Cn	112.7	Cl(5)–Mg(2)–O(1)	86.5(3)
Cl(1)–Nd(1)–Cl(5)	97.3(1)	Cl(3)–Nd(1)–Cn	105.7	Cl(2)–Mg(1)–Cl(4)	83.3(1)
Cl(3)–Nd(1)–Cl(5)	143.0(1)	O(1)–Nd(1)–Cn	176.5	Cl(3)–Mg(1)–Cl(4)	166.6(2)
Cl(1)–Nd(1)–O(1)	80.5(1)	Cl(2)–Mg(2)–Cl(5)	85.5(2)	Cl(2)–Mg(1)–O(1)	75.5(2)
Cl(2)–Nd(1)–O(1)	63.9(1)	Cl(4)–Mg(2)–Cl(5)	167.3(2)	Cl(3)–Mg(1)–O(1)	87.5(3)
Cl(3)–Nd(1)–O(1)	74.2(1)	Cl(2)–Mg(2)–Cl(4)	83.7(1)	Cl(4)–Mg(1)–O(1)	83.4(2)
6					
Cl(1)–Gd(1)–Cl(2)	144.9(2)	Cl(5)–Gd(1)–O(1)	74.0(2)	Cl(2)–Mg(2)–O(1)	74.6(3)
Cl(1)–Gd(1)–Cl(3)	94.6(1)	Cl(1)–Gd(1)–Cn	103.0	Cl(4)–Mg(2)–O(1)	85.0(3)
Cl(2)–Gd(1)–Cl(3)	75.6(1)	Cl(2)–Gd(1)–Cn	112.0	Cl(5)–Mg(2)–O(1)	85.4(4)
Cl(1)–Gd(1)–Cl(5)	95.7(1)	Cl(3)–Gd(1)–Cn	105.4	Cl(2)–Mg(1)–Cl(4)	83.4(2)
Cl(2)–Gd(1)–Cl(5)	76.8(1)	Cl(5)–Gd(1)–Cn	104.6	Cl(2)–Mg(1)–Cl(3)	84.3(2)
Cl(3)–Gd(1)–Cl(5)	145.0(2)	O(1)–Gd(1)–Cn	177.0	Cl(3)–Mg(1)–Cl(4)	165.9(3)
Cl(1)–Gd(1)–O(1)	79.8(2)	Cl(2)–Mg(2)–Cl(5)	85.2(2)	Cl(2)–Mg(1)–O(1)	75.4(3)
Cl(2)–Gd(1)–O(1)	65.2(2)	Cl(4)–Mg(2)–Cl(5)	166.8(2)	Cl(3)–Mg(1)–O(1)	86.4(4)
Cl(3)–Gd(1)–O(1)	75.1(2)	Cl(2)–Mg(2)–Cl(4)	83.6(2)	Cl(4)–Mg(1)–O(1)	83.8(3)

[a] Cn is the centroid of the cyclopentadienyl ring defined by C(11)–C(15).

that enhances the atomic actions between Nd and O atoms or Gd and O atoms.

The bond lengths of C(3)=C(4) are 1.292 Å for **5** and 1.381 Å for **6**, and of C(2)–C(3) are 1.503 Å for **5** and 1.580 Å for **6** in the allyl group. The allyl group does not coordinate to central metal atom, which indicates that the substituent has to stretch outside since the coordination environment around the central metal is considerably crowded.

The coordinations of Mg atoms in **5** and **6** are very similar. Each Mg is coordinated respectively by two THF, three bridged-chlorine atoms and one bridged-oxygen atom to form a distorted octahedrurn, which is caused by the differences of the atoms coordinating to Mg and the steric factors of the atoms. Their corresponding bond lengths and angles are very similar. Their coordination numbers are six.

There are three octahedra in complexes **5** and **6**, respectively. The three octahedra are linked up by three co-planes: (O(1),Cl(2),Cl(3)), (O(1),Cl(2),Cl(5)) and (O(1),C1(2),C1(4)).

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