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Synthesis and studies on reactivities of tetrahydrofurfurylcyclopentadienyl lanthanide chlorides $Cp^sLnCl_2\cdot 2THF$ (Ln = Dy, Ho, Gd) and $Cp^s_2LnCl\cdot$(Ln = Sm, Dy). The crystal structures of Cp^s_2SmCl and $Cp^s_2Sm\cdot(C_3N_2HMe_2)$

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Abstract

Reactions of lanthanide trichloride with two or one equivalent of tetrahydrofurfurylcyclopentadienyl (Cp^s) sodium salt in THF afford bis(tetrahydrofurfurylcyclopentadienyl)lanthanide chloride complexes Cp^s_2LnCl [Ln = Sm (**1**), Dy (**2**)] and mono(tetrahydrofurfurylcyclopentadienyl)lanthanide dichloride complexes $Cp^sLnCl_2\cdot 2THF$ [Ln = Dy (**3**), Ho (**4**), Gd (**5**)], respectively. Treatment of **1** with one equivalent of $NaPzMe_2$ ($PzMe_2$ = 3,5-dimethylpyrazolate) forms $Cp^s_2SmPzMe_2$ (**6**). Complex **3** reacts with one equivalent of CpNa to yield the mixed-ring complex $[Cp^sCpDyCl]_2$ (**7**). Complexes **1**–**7** have been characterized by elemental analyses, infrared and mass spectroscopies. The X-ray structural analyses show that **1** and **6** are unsolvated monomers. In complex **1**, the Sm atom is surrounded by two Cp^s rings, one chlorine atom and two oxygen atoms of the side-chain to form a distorted trigonal bipyramid. The coordination number of central metal is nine. In complex **6**, the Sm atom is coordinated by two Cp^s rings, two nitrogen atoms of 3,5-dimethylpyrazolate, and two oxygen atoms of the side-chain with a distorted tetragonal bipyramid geometry. The coordination number of the Sm atom is ten. The investigation result shows that the strong intramolecular chelating coordination and the high steric crowding result in the lower activity of **6** toward methyl methacrylate polymerization. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Tetrahydrofurfurylcyclopentadienyl; Pyrazolate; Organolanthanide; Crystal structures; Synthesis

1. Introduction

In recent years, the substituted cyclopentadienyl ligands with donor-functionalized side chains have attracted increasing interests in organolanthanide chemistry because these donor-functionalized side chains can increase the stability of highly reactive organolanthanide complexes by forming the intramolecular chelating coordination with the central metal, and for biscyclopentadienyl complexes of early lanthanides, the enhanced stability offers the opportunity to explore the reactivity of the remaining ligands. In addition, the intramolecular coordination may play an important role in the catalytic process [1–6]. Consequently, varieties of ether- or amino-substituted cyclopentadienyl groups including some asymmetric chelating cyclopentadienyl and tridentate chelating cyclopentadienyl systems have been used to prepare lanthanide complexes [7–10]. Recently, Edward investigated the influence of the tetrahydrofurfuryl substituent on the property of biscyclopentadienyl zirconium dichlorides and found that $Cp^s_2ZrCl_2$ is more stable than the biscyclopentadienyl zirconium dichlorides without the intramolecular coordination [11]. However, few lanthanocenes including the tetrahydrofurfurylcyclopentadienyl ligand have been prepared [12]. To further understand the influence of the chelating action on the structures and the properties of cyclopentadienyl organolanthanide complexes and to reveal possible applications of organolanthanide complexes in homogeneous catalysis and stoichiometric re-

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actions, we herein report the synthesis of five new tetrahydrofurfurylcyclopentadienyl lanthanide chloride complexes Cp^s_2LnCl [Ln = Sm (**1**), Dy (**2**)], $Cp^sLnCl_2{\cdot}2THF$ [Ln = Dy (**3**), Ho (**4**), Gd (**5**)], and some results on the reactivities of these complexes.

2. Results and discussion

2.1. Synthesis and characterization of Cp^s_2LnCl [Ln = Sm (1), Dy (2)]

Treatment of tetrahydrofurfurylcyclopentadiene with excessive sodium yielded the substituted cyclopentadienyl sodium salt (Cp^sNa). The THF adducts of $LnCl_3$ reacted with two equivalents of tetrahydrofurfurylcyclopentadienyl sodium salt in THF at room temperature (r.t.) to form the unsolvated complexes Cp^s_2LnCl [Ln = Sm (**1**), Dy (**2**)].

$$LnCl_3(THF)_4 + 2NaCp^s \rightarrow \underset{Ln = Sm\ (\mathbf{1}),\ Dy\ (\mathbf{2})}{Cp^s_2LnCl} + 2NaCl$$

Complexes **1** and **2** are highly soluble in polar solvents such as THF. As expected, **1** and **2** are more stable against air and moisture than the corresponding unsubstituted cyclopentadienyl lanthanide complexes. It requires several hours exposure to air until decomposition can be recognized by discoloration of the complexes. Complexes **1** and **2** have been characterized by elemental analysis, infrared and mass spectroscopies. The mass spectra show clearly their molecular ion peaks and relative fragments, such as $[M^+]$, $[Cp^s_2Ln]^+$, $[Cp^s_2Ln\text{–}C_4H_7O]^+$, $[Cp^sLnCl]^+$, $[Cp^sLn]^+$, etc., indicating **1** and **2** to be unsolvated monomeric structures. The IR spectra of **1** and **2** are very similar and display four characteristic absorption peaks of the η^5-Cp^s group at approximately 3062, 1440, 1012 and 780 cm^{-1}. The absorption peak of the C–O–C asymmetric stretching vibration for the tetrahydrofurfuryl substituent on the cyclopentadienyl ring appears at approximately 1045 cm^{-1}, which shifts to lower frequency ($\Delta\nu = 30$–40 cm^{-1}) compared with that of free Cp^sNa molecule (1079 cm^{-1}). This implies that the oxygen atom of the tetrahydrofurfuryl group is coordinated to the central metal [13–15].

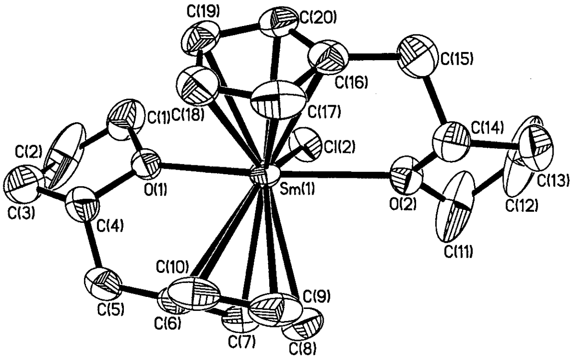

Fig. 1. ORTEP drawing of complex **1**.

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Sm(1)–O(1)	2.484(4)	Sm (1)–C(16)	2.722(6)
Sm(1)–O(2)	2.490(5)	Sm(1)–C(17)	2.709(6)
Sm(1)–Cl(1)	2.676(1)	Sm(1)–C(18)	2.713(6)
Sm(1)–C(6)	2.733(7)	Sm(1)–C(19)	2.717(6)
Sm(1)–C(8)	2.715(7)	Sm(1)–C(20)	2.720(7)
Sm(1)–C(9)	2.713(7)	Sm(1)–Cent1 [a]	2.451
Sm(1)–C(7)	2.757(7)	Sm(1)–Cent2 [a]	2.445
Sm(1)–C(10)	2.711(7)		
Bond angles			
O(1)–Sm(1)–O(2)	158.37(2)	O(2)–Sm(1)–Cl(1)	79.27(1)
O(1)–Sm(1)–Cl(1)	79.14(1)		

[a] Cent1 and Cent2 define the centroid of the ring atoms C6–C10 and C16–C20, respectively.

2.2. Structure of complex 1

The single crystal of complex **1** suitable for X-ray structural analysis was obtained from THF. Fig. 1 shows the molecular structure of **1**. Selected bond parameters are listed in Table 1. The molecule crystallizes as well-separated unsolvated monomeric units. The Sm^{3+} ion is coordinated by two Cp^s rings, one chloride and two oxygen atoms of the tetrahydrofurfuryl substituents to form a distorted trigonal bipyramid. The coordination number of the central metal Sm^{3+} is nine. The O(1)–Sm–O(2) angle of 158.4° in **1** is similar to the corresponding value observed in $[(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)OCH_2Ph]_2SmI$, 159.4° [16]. The Sm–O distances (2.48(1) and 2.49(1) Å) are similar to the Sm ← :O(THF) donor distance of 2.51(1) Å in complex $Cp_3Sm(THF)$ [17], but are slightly shorter than the values observed in $[(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)O\text{–}CH_2Ph]_2SmI$ (2.56(2) and 2.57(2) Å) [16] due to the decrease of the steric congestion around the donor atom in **1**. The Sm–C distances in **1** range from 2.709(7) to 2.757(7) Å and average 2.721(7) Å. The average value is equal to that found in complex $[(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)OCH_2Ph]_2SmI$ (2.72(3) Å) [16]. The length of Sm–Cl bond (2.676(2) Å) in **1** is similar to that observed in $[(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)\text{-}OMe]_2SmCl$ (2.668(3) Å) [18].

2.3. Synthesis and characterization of monotetrahydrofurfurylcyclopentadienyl lanthanide dichloride complexes $Cp^sLnCl_2{\cdot}2THF$ [Ln = Dy (3), Ho (4), Gd (5)]

The THF adducts of the lanthanide trichloride reacted with one equivalent of Cp^sNa at r.t. to afford monotetrahydrofurfurylcyclopentadienyl lanthanide

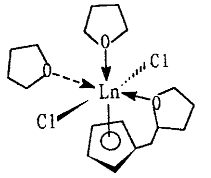

Fig. 2. The proposed structure for complexes **3**–**5**.

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **6**

Bond lengths			
Sm(1)–N(1A)	2.409(3)	Sm(1)–C(3)	2.748(4)
Sm(1)–N(1)	2.409(3)	Sm(1)–C(3A)	2.748(4)
Sm(1)–O(1A)	2.524(2)	Sm(1)–C(2)	2.759(4)
Sm(1)–O(1)	2.524(2)	Sm(1)–C(2A)	2.759(4)
Sm(1)–C(4)	2.744(4)	Sm(1)–C(5)	2.761(3)
Sm(1)–C(4A)	2.744(4)	Sm(1)–C(5A)	2.761(3)
Sm(1)–C(1)	2.770(4)	Sm(1)–C(1A)	2.770(4)
Bond angles			
N(1A)–Sm(1)–N(1)	33.34(1)	N(1A)–Sm(1)–O(1)	85.29(9)
N(1A)–Sm(1)–O(1A)	78.11(9)	N(1)–Sm(1)–O(1)	78.11(9)
N(1)–Sm(1)–O(1A)	85.29(9)	O(1A)–Sm(1)–O(1)	162.70(1)

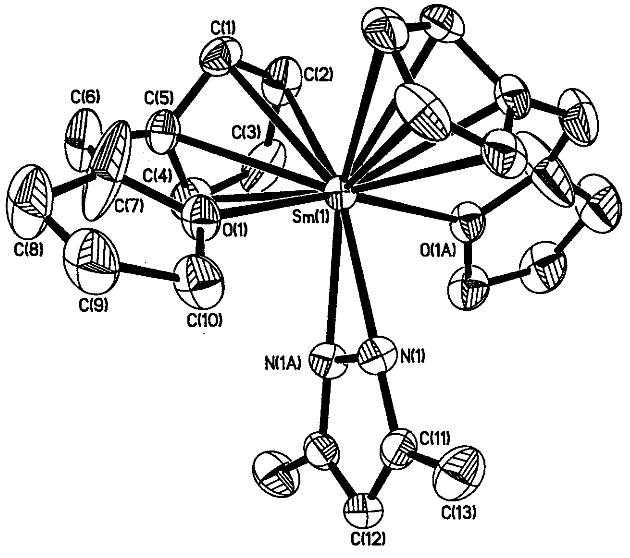

Fig. 3. ORTEP drawing of complex **6**.

dichloride complexes $Cp^sLnCl_2 \cdot 2THF$ [Ln = Dy (**3**), Ho (**4**), Gd (**5**)].

$$LnCl_3(THF)_x + NaCp^s \xrightarrow[\text{Ln = Dy (3), Ho (4), Gd (5)}]{} Cp^sLnCl_2 \cdot 2THF + NaCl$$

These complexes are sensitive to air and moisture. Complexes **3**–**5** have been characterized by elemental analysis, infrared and mass spectroscopies. Satisfactory elemental analyses were obtained. In the mass spectra, complex **5** display a molecular ion peak. Although **3** and **4** do not display molecular ion peaks, their main fragments are observed, such as $[M^+ - THF]$, $[M^+ - 2THF]$, $[Cp^sLnCl]^+$, $[Cp^sLn]^+$, $[LnCl_2]^+$, etc. In IR spectra, complexes **3**–**5** display the characteristic absorption of C–O–C asymmetric stretching vibration at approximately 1050 cm^{-1}, which is similar to that of complexes **1** and **2**. This suggests that an intramolecular chelating coordination is also present in complexes **3**–**5** as structurally confirmed in **1** [13–15].

Based on the above results of elemental and spectral analyses, the structure of complexes **3**–**5** may be proposed as shown in Fig. 2. It is interesting to note that complexes **3**–**5** are only coordinated to two THF molecules, one less than the number of coordinated THF molecules in the unsubstituted monocyclopentadienyl lanthanide dichloride complexes. This may be attributed to the chelating coordination action, which satisfies the requirement of the coordination saturation of the central metal ion and prevents the additional THF molecule from bonding to the central metal.

2.4. Reaction of **1** with $NaPzMe_2$

Recently, we studied the reaction of cyclopentadienyl lanthanide pyrazolate complexes with dimethylsilicone [19,20] and found that Me_2SiO can only be inserted into the Ln–N (bridging) bond. To understand the cyclopentadienyl effect further, in specially, to know whether the side-arm action of cyclopentadienyl group can change the bonding mode of the pyrazolate ligand in $Cp_2Ln(PzMe_2)$-type complexes and make it transform from chelating to bridging coordination, which favors the Me_2SiO insertion occurring. We synthesized a new lanthanide pyrazolate complex $Cp^s_2SmPzMe_2$ (**6**) by the reaction of **1** and $NaPzMe_2$. The structure of complex **6** was confirmed by the X-ray single crystal diffraction. The IR spectra of **6** display four characteristic absorptions of η^5-Cp^s at 3059, 1440, 1014 and 780 cm^{-1}. In addition, **6** exhibit ν(Ln–N) stretching bands at 480 and 462 cm^{-1}, typical of lanthanide pyrazolate complexes [19] (see Table 2).

2.5. Structure of complex **6**

As shown in Fig. 3, complex **6** is a solvent-free monomer, in which the Sm atom is surrounded by two tetrahydrofurfurylcyclopentadienyl groups, two donor oxygen atoms from the ring substituents and two nitrogen atoms from 3,5-dimethylpyrozolate anion to form a distorted tetragonal bipyramid. The coordination number of the Sm ion is ten. The Sm–C (Cp^s) distances range from 2.770(4) to 2.761(3) Å, and average 2.756(3) Å. The average distance of Sm–O bonds (2.524(2) Å) in complex **6** is slightly longer than that observed in complex **1** (2.487(4) Å) due to the increase in the steric crowding. The distances of Sm–N bonds (2.409(3), 2.409(3) Å) are slightly longer than those observed in $Cp_2Er(PzMe_2)(THF)$ (2.25(2), 2.28(2) Å) [20], after the differences in the metallic radii are subtracted [21]. This may result from the higher steric congestion compared with complex $Cp_2Er(PzMe_2)(THF)$ [20].

Recent research has shown that lanthanocene complexes are highly active catalysts for methacrylate and acrylate polymerization [22–24]. However, we found that the catalytic activity of **6** toward methacrylate polymerization is very low. This may be attributed to the strong chelating coordination between the donor atom of the side-chain substituent and the central metal, which results in that the space around the metal center is overcongested and unfavorable for the methacrylate molecule to approach the metal center. Moreover, attempts to insert Me_2SiO into Ln–N bond of **6** are unsuccessful.

2.6. Reaction of $Cp^{s}DyCl_2\cdot 2THF$ with one equivalent of CpNa

Treatment of **3** with one equivalent of CpNa·(Cp = C_5H_5) in THF at r.t. afforded the mixed-ring organolanthanide complex $[Cp^{s}CpDyCl]_2$ (**7**).

$$\underset{\mathbf{(3)}}{2Cp^{s}DyCl_2\cdot 2THF} + 2NaCp \rightarrow \underset{\mathbf{(7)}}{[Cp^{s}CpDyCl]_2} + 2NaCl$$

Complex **7** is soluble in ethers such as THF but less soluble in hydrocarbon solvents such as hexane at r.t., and sensitive toward air and moisture. Complex **7** has been characterized by elemental analysis, infrared and mass spectroscopies. The mass spectra data such as $[M_2^+ - Cl]$, $[M_2^+ - CpH]$, $[M_2^+ - 2Cp^{s} - CpH]$, $[M^+]$, $[Cp^{s}CpDy]^+$, $[Cp^{s}DyCl]^+$, $[CpDyCl]^+$ indicate that complex **7** is a solvent-free dimer structure. Significantly, when **7** was heated in sealed capillary, it decomposed at 198–200°C and then melted at 250°C. The mass spectra data indicate the decomposition products are Cp^{s}_2DyCl and Cp_2DyCl. So we deduce that the complex **7** may be unstable to heat, and easily disproportionate to form homogeneous bis(cyclopentadienyl)lanthanide complexes Cp^{s}_2DyCl and Cp_2DyCl.

3. Conclusions

Using the tetrahydrofurfurylcyclopentadienyl ligand, a series of stable chloride and pyrazolate complexes of lanthanocenes have been prepared and structurally characterized. The investigation results indicate that the stronger chelating action of the side chain oxygen atom to the lanthanide metal for biscyclopentadienyl-type complexes prevent THF from coordinating to the central metal. Moreover, although the chelating coordination is very useful in increasing the stability of organolanthanide complexes, the effect could result in the lower activity of complex **6** toward methyl methacrylate polymerization.

4. Experimental

4.1. General procedures

The complexes described below are sensitive to air and moisture. Therefore all the manipulations were performed under purified nitrogen using Schlenk techniques with rigorous exclusion of air and moisture. All solvents were refluxed and distilled over sodium benzophenone ketyl immediately before use. 3,5-Dimethylpyrazole [25], tetrahydrofurfurylcyclopentadiene [26] and $LnCl_3$ (Ln = Sm, Gd, Dy, Ho) [27] were prepared by the literature procedures. Tetrahydrofurfuryl chloride was purchased from Fluka and was used as received. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Rapid CHN–O analyzer. Metal analyses for lanthanides were accomplished using the literature method [28]. Infrared spectra were obtained on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a HP5989A instrument operating in EI mode at a resolving power of 1000. The crystal samples of the respective complexes were rapidly introduced by the direct inlet techniques without any heating. The ion source temperature was 200°C. The values of m/z are referred to the isotopes ^{12}C, ^{1}H, ^{16}O, ^{14}N, ^{35}Cl, ^{152}Sm, ^{158}Gd, ^{164}Dy, ^{165}Ho.

4.2. Preparation of $Cp^{s}Na$

Excessive sodium (2.0 g, 0.087 mol) was added to a solution of tetrahydrofurfurylcyclopentadiene (7.0 ml) in 30 ml THF. This resulting mixture was stirred overnight at r.t. After stopping agitation, a colorless solution was obtained. The solution was titrated by HCl (0.0549 M) before use.

*4.3. Synthesis of **1** and **2***

To a suspension of anhydrous $SmCl_3$ (1.02 g, 3.97 mmol) in THF (30 ml) was added dropwise $Cp^{s}Na$ (0.216 M THF solution, 37.0 ml, 7.99 mmol) with rigorous stirring at 0°C, then stirred for 48 h at ambient temperature. The precipitate was separated and the clear solution was concentrated to approximately 7 ml. Yellow crystals were obtained by cooling at −15°C. Yield 59%. Anal. Calc. for $C_{20}H_{26}O_2SmCl$: C, 49.61; H, 5.41; Sm, 31.05. Found: C, 49.51; H, 5.34; Sm, 31.02%. MS (EI): m/z (fragment, relative intensity %) = 485 [M^+, 3.1], 450 [$Cp^{s}_2Sm^+$, 2.0], 406 [$M^+ - C_5H_5CH_2$, 0.9], 379 [$Cp^{s}(Cp^{s}{-}C_4H_7O)Sm^+$, 0.8], 378 [$Cp^{s}(Cp^{s}{-}C_4H_8O)Sm^+$, 1.1], 336 [$Cp^{s}SmCl^+$, 8.1], 301 [$Cp^{s}Sm^+$, 4.6], 150 [$Cp^{s}H$, 8.0], 71 [$C_4H_7O$, 100]. IR ($cm^{-1}$): 3200 m, 3126 m, 3101 m, 3059 m, 2919 s, 2855 s, 2726 m, 1462 s, 1440 m, 1377 s, 1164 m, 1049 m, 1012 m, 891 w, 778 m, 245 w.

Using the same procedure described for **1**, complex **2** could be really obtained. Yield 52%. Anal. Calc. for $C_{20}H_{26}O_2DyCl$: C, 48.39; H, 5.28; Dy, 32.74. Found: C, 48.25; H, 5.21; Dy, 32.16%. MS (EI): *m*/*z* (fragment, relative intensity %) = 497 [M^+, 5.0], 462 [$M^+ - Cl$, 2.5], 391 [$Cp^s(Cp^s–C_4H_7O)Dy^+$, 1.5], 390 [$Cp^s(Cp^s–C_4H_8O)Dy^+$, 1.6], 348 [Cp^sDyCl^+, 8.8], 313 [Cp^sDy^+, 0.7], 199 [$DyCl^+$, 0.8], 150 [Cp^sH, 3.1], 71 [$C_4H_7O^+$, 100]. IR (cm^{-1}): 3200 m, 3126 m, 3101 m, 3059 m, 2919 s, 2855 s, 2726 m, 1462 s, 1440 m, 1377 s, 1164 m, 1070 m, 1053 m, 1014 m, 891 w, 778 m, 245 w.

*4.4. Synthesis of **3–5***

To a suspension of $DyCl_3$ (1.50 g, 5.58 mmol) in THF (40 ml) was added dropwise Cp^sNa (0.216 M THF solution, 26.0 ml, 5.61 mmol) with rigorous stirring at 0°C. After being stirred for 48 h at ambient temperature. The precipitate was separated and the solution was concentrated at approximately 10 ml. Colorless crystals were obtained by cooling the solution at − 15°C. Yield 41%, m.p. (dec.) 131°C. Anal. Calc. for $C_{18}H_{29}O_3DyCl_2$: C, 41.04; H, 5.55; Dy, 30.84. Found: C, 40.40; H, 5.47; Dy, 30.67%. MS (EI), *m*/*z* (fragment, relative intensity %) = 455 [$M^+ - THF$, 1.0], 383 [$Cp^sDyCl_2^+$, 0.7], 348 [Cp^sDyCl^+, 11.3], 313 [Cp^sDy^+, 1.0], 234 [$DyCl_2^+$, 1.0], 150 [Cp^sH, 5.9], 85 [$C_4H_7OCH_2^+$, 1.1], 71 [THF, 100]. IR (cm^{-1}): 3170 m, 3045 m, 2919 s, 2855 s, 2728 m, 2666 m, 1463 s, 1440 m, 1377 s, 1303 m, 1154 m, 1072 m, 1052 m, 1010 m, 871 w, 780 m, 245 w.

Using the same procedure described for **3**, complexes **4** and **5** could be readily obtained.

$Cp^sHoCl_2 \cdot 2THF$ (**4**): pale yellow crystals, yield 30%, m.p. (dec.) 130°C. Anal. Calc. for $C_{18}H_{29}O_3HoCl_2$: C, 40.85; H, 5.52; Ho, 31.16. Found: C, 40.01; H, 5.35; Ho, 30.87%. MS (EI): *m*/*z* (fragment, relative intensity %) = 456 [$M^+ - THF$, 0.3], 384 [$M^+ - 2THF$, 1.2], 314 [Cp^sHo^+, 42.4], 235 [$HoCl_2^+$, 2.0], 150 [Cp^sH, 1.0], 85 [$C_5H_9O^+$, 1.1], 72 [THF, 57.4], 71 [$C_4H_7O^+$, 85.1]. IR (cm^{-1}): 3163 m, 3044 m, 2919 s, 2855 s, 2728 m, 2661 m, 1463 s, 1440 m, 1374 s, 1309 m, 1171 m, 1071 m, 1056 m, 1013 m, 863 w, 767 m, 244 w.

$Cp^sGdCl_2 \cdot 2THF$ (**5**): colorless crystals, yield 35%, m.p. (dec.) 129°C. Anal. Calc. for $C_{18}H_{29}O_3GdCl_2$: C, 41.45; H, 5.60; Gd, 30.15. Found: C, 41.01; H, 5.50; Gd, 30.27%. MS (EI): *m*/*z* (fragment, relative intensity %) = 521 [M^+, 0.3], 449 [$M^+ - THF$, 0.4], 377 [Cp^sGdCl_2, 0.9], 342 [Cp^sGdCl^+, 1.0], 307 [Cp^sGd^+, 0.8], 150 [Cp^sH, 3.2], 72 [THF, 52.4], 71 [$C_4H_7O^+$, 79.3]. IR (cm^{-1}): 3170 m, 3050 m, 2919 s, 2855 s, 2728 m, 2666 m, 1463 s, 1440 m, 1377 s, 1343 m, 1299 m, 1303 m, 1154 m, 1072 m, 1051 m, 1010 m, 892 w, 780 m, 245 w.

*4.5. Synthesis of **6***

To a solution of **1** (0.42 g, 0.87 mmol) in 30 ml THF was added an equal equivalent THF solution of $NaPzMe_2$ (0.103 g, 0.87 mmol) which was obtained by the reaction of $HPzMe_2$ and excessive NaH in THF at r.t. After stirring for 24 h, the precipitate was separated and the clear solution was concentrated to approximately 4 ml. Then, hexane was added until a cloudy precipitate was observed. Yellow crystals were obtained by cooling at − 15°C. Yield 64% (0.29 g). Anal. Calc. for $C_{25}H_{33}N_2O_2Sm$: C, 55.21; H, 6.12; N, 5.15; Sm, 27.65. Found: C, 54.82; H, 6.03; N, 4.91; Sm, 27.54%. IR (cm^{-1}): 3200 m, 3126 m, 3101 m, 3059 m, 3030 m, 2919 s, 2855 s, 726 m, 1575 m, 1462 s, 1440 m, 1377 s, 1305 m, 1164 m, 1044 m, 1032 m, 1014 m, 885 m, 778 m, 672 m, 480 w, 462 w.

*4.6. Synthesis of **7***

To a solution of $Cp^sDyCl_2 \cdot 2THF$ (0.72 g, 1.37 mmol) in 30 ml THF was added dropwise CpNa (0.12 g, 1.37 mmol) at 0°C with rigorous stirring. After being stirred for 24 h at ambient temperature. The precipitate was separated and the clear solution was concentrated to approximately 5 ml, and cooled at − 15°C to afford colorless crystals of complex **6**. Yield 41%, m.p. (dec.) 198–200°C. Anal. Calc. for $C_{30}H_{36}O_2Dy_2Cl_2$: C, 43.70; H, 4.40; Dy, 39.42. Found: C, 43.27; H, 4.56; Dy, 39.36%. MS (EI): *m*/*z* (fragment, relative intensity %) = 791 [$M_2^+ - Cl$, 3.2], 760 [$M_2 - CpH$, 2.6], 497 [Cp_2^sDyCl, 3.2], 462 [$M_2^+ - 2Cp^s–CpH$, 22.8], 413 [M^+ 17.7], 378 [$M^+ - Cl$, 98.8], 348 [Cp^sDyCl, 82.5], 329 [Cp_2DyCl, 2.0], 312 [$Cp^sDy - 1$, 32.6], 294 [Cp_2Dy, 4.0], 264 [CpDyCl, 21.0], 229 [CpDy, 5.6], 199 [DyCl, 23.6], 164 [Dy, 3.5], 150 [Cp^sH, 3.2], 65 [Cp, 32.4]. IR (cm^{-1}): 3170 m, 3070 m, 3040 m, 2728 s, 2666 m, 1463 s, 1440 m, 1377 s, 1367 m, 1303 m, 1154 m, 1049 m, 1010 m, 881 w, 780 m, 245 m.

*4.7. X-ray structure determinations of **1** and **6***

Crystals of **1** and **6** suitable for X-ray analysis were sealed in thin-walled glass capillaries under argon. Data were collected on a Bruker Smart 1000 diffractometer using the $\omega - 2\theta$ technique at 293 K. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS [29].

The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods, expanded using Fourier techniques [30]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in refinement. All calculations were performed using the

Table 3
Crystal data and structure refinements for complexes **1** and **6**

Compound	**1**	**6**
Empirical formula	$C_{20}H_{26}ClO_2Sm$	$C_{25}H_{31}N_2O_2Sm$
Formula weight	484.21	541.87
Crystal color	Yellow	Yellow
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	*Pbcn*
Crystal dimensions (mm)	0.4 × 0.30 × 0.10	0.40 × 0.30 × 0.30
a (Å)	11.8301(8)	14.5895(11)
b (Å)	12.2459(8)	10.1682(7)
c (Å)	13.4283(9)	15.8796(11)
β (°)	90	90
Z	4	4
V (Å^3)	1945.4(2)	2355.7(3)
D_{calc} (g cm^{-3})	1.653	1.528
F(000)	964	1092
μ (cm^{-1})	31.64	25.15
Wavelength (Å)	Mo–K_α (0.71073)	Mo–K_α (0.71073)
Reflections collected	8110	10 392
Independent reflections	3445 ($R_{int} = 0.0654$)	2418 ($R_{int} = 0.0234$)
Observed reflection [$I > 2\sigma(I)$]	3193	1591
Parameters	217	137
Goodness-of-fit	1.074	1.007
R	0.0307	0.0215
R_W	0.0752	0.0553

SHELXS-97 crystallographic software package [31]. The crystallographic data for the complexes **1** and **6** are listed in Table 3.

5. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data centre, CCDC nos. 143937–143938 for compounds **1** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] C.T. Qian, X. Zheng, B. Wang, D.L. Deng, J. Sun, J. Organomet. Chem. 466 (1994) 101.
[2] W.A. Herrmann, R.A. Florian, C. Munk, W. Scherer, Chem. Ber. 126 (1993) 331.
[3] K.C. Hultzsch, T.P. Spanoik, T. Okuda, Organometallics 16 (1997) 4845.
[4] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
[5] C.T. Qian, H.F. Li, J. Sun, W.L. Nie, J. Organomet. Chem. 585 (1999) 59.
[6] H. Schumann, F. Erbstein, R. Weimann, J. Demschuk, J. Organomet. Chem. 536–537 (1997) 541.
[7] C.T. Qian, D. Zhou, J. Organomet. Chem. 445 (1993) 79.
[8] G.A. Molander, H. Schumann, E.C.E. Rothenthal, J. Demtschuk, Organometallics 15 (1996) 3817.
[9] K.C. Hultzsch, T.P. Spanoik, T. Okuda, Organometallics 17 (1998) 485.
[10] B. Wang, D.L. Deng, C.T. Qian, New J. Chem. 19 (1995) 515.
[11] E.A.H. Griffiths, I.R. Gould, S. Ramdas, Chem. Commun. (1998) 2177.
[12] Q.C. Liu, J.L. Huang, Y.L. Qian, A.S.C. Chan, Polyhedron 18 (1999) 2345.
[13] W.J. Evans, T.A. Ulibarri, J. Am. Chem. Soc. 109 (1987) 4292.
[14] C.T. Qian, Z.W. Xie, Y. Huang, J. Organomet. Chem. 323 (1987) 285.
[15] C.T. Qian, Z.W. Xie, Y. Huang, J. Organomet. Chem. 398 (1990) 251.
[16] A.A. Trifonov, P.V. Weghe, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 527 (1997) 225.
[17] Z.Z. Wu, Z. Xu, X.Z. You, X.G. Zhou, X.Y. Huang, Polyhedron 13 (1994) 379.
[18] H. Schumann, E.C.E. Rosenthal, J. Demtschuk, Organometallics 17 (1998) 5324.
[19] X.G. Zhou, W.W. Ma, Z.E. Huang, R.F. Cai, X.Z. You, X.Y. Huang, J. Organomet. Chem. 545–546 (1997) 309.
[20] X.G. Zhou, Z.E. Huang, R.F. Cai, L.B. Zhang, L.X. Zhang, X.Y. Huang, Organometallics 18 (1999) 4128.
[21] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 435.
[22] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908.
[23] H. Yasuda, M. Furo, H. Yamamoto, K. Yokota, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115.
[24] H. Yamamoto, M.A. Giardello, L. Brard, T.J. Marks, in: 206th ACS National Meeting, Chicago, August 22–27, Part 1, INOR 461, 1993.
[25] R.H. Wiely, P.E. Hexner, Org. Synth. Colloid 4 (1992) 351.
[26] Q.S. Huang, Y.L. Qian, Synthesis 10 (1987) 910.
[27] J.B. Reed, B.S. Hopkins, L.F. Audrieth, Inorg. Synth. 1 (1939) 28.
[28] C.T. Qian, C.Q. Ye, H.Z. Lu, T.L. Zhou, Y.W. Ge, J. Organomet. Chem. 247 (1983) 161.
[29] G.M. Sheldrick, SADABS, A Program for Empirical Absorption Correction, Göttingen, Germany, 1998.
[30] SHLXTL PLUS, Siemens Analytical X-ray Institute Inc., XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactive Molecular Graphics, 1990.
[31] G.M. Sheldrick, SHELXL-97, Program for the refinement of the crystal structure, University of Göttingen, Germany, 1997.