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Journal of Organometallic Chemistry 582 (1999) 292–300
Journal of Organo metallic Chemistry

Synthesis and X-ray structures of trivalent lanthanide (+)-neomenthylcyclopentadienyl complexes

Wing-Por Leung *, Fu-Quan Song, Feng Xue, Ze-Ying Zhang, Thomas C.W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received 14 December 1998

Abstract

Trivalent lanthanide (+)-neomenthylcyclopentadienyl complexes $[Cp^R_2Ln(\mu\text{-}Cl)]_2$ (Ln = Sm (**1**), Yb (**2**), Y (**3**), Lu (**4**); Cp^R = (+)-neomenthylcyclopentadienyl)] and $Cp^RLnX_2(THF)_3$ [X = Cl, Ln = Sm (**6**), Gd (**7**), Yb (**8**), Y (**9**), Lu (**10**); X = I, Ln = Sm (**11**), Yb (**12**)) have been prepared by metathetical reactions of lanthanide halide with appropriate alkali-metal (+)-neomenthylcyclopentadienyl complexes. X-ray structural analysis has revealed that compounds **1** and **3** are chloro-bridged dimers with the asymmetric plane described by Ln_2Cl_2 almost perpendicular to the plane described by the four cyclopentadienyl ring centroids. The monomeric compound $Cp^RLnI_2(THF)_3$ (**11**) adopts a pseudo-octahedral geometry with the two iodine atoms taking the *trans*-positions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lanthanide; Neomenthylcyclopentadienyl; Metathetical reactions

1. Introduction

Organolanthanide compounds have been found to exhibit catalytic activities in various chemical transformations, such as in C–H bond activation [1–3], olefin cyclohydroamination [4–6], and olefin polymerization [7]. Organolanthanide complexes containing chiral cyclopentadienyl ligands have recently attracted interest as chiral organolanthanide complexes $Me_2Si(Cp')(C_5H_3R^*)Ln$ ($Cp' = C_5Me_4$, $C_5H_3(SiMe_3)$, $C_5H_3(Bu^t)$; R^* = chiral auxiliary) had been found to be highly active in stereospecific catalytic hydrogenation [8,9] and hydrosilylation [10]. Among the organolanthanide complexes organolanthanide halide complexes are indispensable precursors for new types of lanthanide metal complexes containing Ln–C, Ln–H, Ln–N, or Ln–O bonds.

We have recently reported the synthesis of a series of alkali-metal (+)-neomenthylcyclopentadienyl complexes [11]. In this paper, the synthesis and structures of a series of lanthanide(III) (+)-neomenthylcyclopentadienyl compounds are described.

2. Results and discussion

2.1. Synthesis of bis((+)-neomenthyl-cyclopentadienyl)lanthanide chlorides

Treatment of two equivalents of $NaCp^R$ (Cp^R = (+)-neomenthylcyclopentadienyl) with anhydrous lanthanide trichloride in THF at room temperature (r.t.) afforded the organolanthanide chlorides $[Cp^R_2Ln(\mu\text{-}Cl)]_2$ (Ln = Sm, Yb, Y) in yields ranging from 60 to 70% (Eq. (1)).

$$LnCl_3 + 2NaCp^R \rightarrow [Cp^R_2Ln(\mu\text{-}Cl)]_2 + 2NaCl \qquad (1)$$

Ln = Sm (**1**), Yb (**2**), Y (**3**), Lu (**4**)
Cp^R = (+)-neomenthylcyclopentadienyl

Attempts to prepare the early lanthanide analogues such as La(III), Ce(III), Pr(III), and Nd(III) were unsuccessful as pure compounds had not been obtained. It was discovered that during the course of the reaction in Eq. (1), treatment of lanthanide trichlorides with sodium or potassium salt of (+)-neomenthylcyclopentadienyl in THF afforded a homogeneous solution and no precipitation of NaCl or KCl was observed. This was presumably due to the formation of soluble organolanthanide NaCl or KCl adducts in the THF

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* Corresponding author. Fax: +852-260-35057.
E-mail address: kevinleung@cuhk.edu.hk (W.-P. Leung)

PII: S0022-328X(99)00072-8

solution. The NaCl or KCl can be precipitated out by adding a non-polar solvent such as hexane. ^{1}H-NMR spectroscopy and elemental analysis had indicated that compounds **1**–**4** isolated from recrystallization in THF/hexane were solvent-free compounds with a composition similar to $(C_5Me_5)_2LnCl$ [12,13] and $[((Me_3Si)_2C_5H_3)_2LnCl]$ [14]. Further reaction of bis-((+)-neomenthylcyclopentadienyl)yttrium chloride (**3**) with sodium bis(trimethylsilyl) amide in THF afforded the amido-derivative $[Cp^R_2Y{-}N(SiMe_3)_2]$ (**5**) in a good yield (70%) (Eq. (2)).

$$[Cp^R_2YCl]_2 + 2NaN(SiMe_3)_2 \rightarrow 2Cp^R_2Y{-}N(SiMe_3)_2 + 2NaCl \qquad (2)$$

Compounds **1**–**5** have shown good solubility in polar solvents such as ether, THF, DME, CH_2Cl_2, and hydrocarbon solvents such as benzene and toluene. However, attempts to prepare the yttrium alkyl compound $Cp^R_2Y{-}Me$ with yttrium to carbon σ-bond by the metathesis reaction of yttrium chloride **3** with LiMe in THF have been unsuccessful, only the colourless crystalline compound $LiCp^R$ was isolated as confirmed by its ^{1}H-NMR spectrum and X-ray structure analysis. In contrast, the reaction of $(C_5Me_5)_2ScCl$ with LiMe afforded $(C_5Me_5)_2ScMe$ in the solvent mixture of ether and hexane and $(C_5Me_5)_2ScCl(THF)$ was obtained when THF was used as the solvent. This suggests that the THF adduct complex is not very reactive towards metathesis reaction in THF solution [15,16].

The ^{1}H- and ^{13}C-NMR spectra of compounds **3**, **4** and **5** recorded were normal, while compounds **1** and **2** were found to be paramagnetic as the signals observed in the ^{1}H-NMR spectra were shifted towards low fields for the cyclopentadienyl protons, and shifted towards high field for the neomenthyl group protons. The specific optical rotations values ($[\alpha]^{20}_D$) of dimeric compounds **1**, **3** and **4** have been obtained.

2.2. Synthesis of (+)-neomenthylcyclopentadienyl lanthanide dihalides

The synthesis of mono-(+)-neomenthylcyclopentadienyl lanthanide dichloride complexes was accomplished by the reaction of anhydrous lanthanide trichlorides with one equivalent of sodium (+)-neomenthylcyclopentadienyl in THF as shown in Eq. (3).

$$LnCl_3 + NaCp^R + 3THF \rightarrow Cp^RLnCl_2(THF)_3 + NaCl \qquad (3)$$

Ln = Sm (**6**), Gd (**7**), Yb (**8**), Y (**9**), Lu (**10**)

^{1}H-NMR spectroscopic studies had shown that compounds **6**–**10** are coordinated with three THF molecules, which is also consistent with the elemental analysis results. Optical rotation values ($[\alpha]^{20}_D$) in the range of 9–10° for these compounds further suggests that a similar coordination sphere exists around the metal centre among these monocyclopentadienyl lanthanide chlorides.

Attempts to prepare the trivalent lanthanide complexes containing one (+)-neomenthylcyclopentadienyl ligand for early lanthanide elements such as La(III), Ce(III), Pr(III) and Nd(III) have been unsuccessful. Good quality crystals of mono-(+)-neomenthylcyclopentadienyl lanthanide dichlorides for X-ray diffraction have not been obtained.

Alternatively, trivalent lanthanide triiodides had been used as starting materials for preparing mono-cyclopentadienyl lanthanide complexes. Treatment of lanthanide triiodides [17] with one equivalent of potassium (+)-neomenthylcyclopentadienyl in THF at r.t. afforded mono-neomenthylcyclopentadienyl lanthanide diiodides (Eq. (4)).

$$LnI_3 + KCp^R + 3THF \rightarrow Cp^RLnI_2(THF)_3 + KI \qquad (4)$$

Ln = Sm (**11**), Yb (**12**)

^{1}H-NMR spectrum of **11** showed that three THF molecules were coordinated to the samarium centre. An optical rotation of 9.42° for compound **11** is similar to those results of compounds **6**–**10**. Single crystals of **11** suitable for X-ray diffraction were obtained by recrystallization in THF. The X-ray structural analysis of **11** was consistent with the results of NMR and elemental analysis.

2.3. X-ray structures of $[Cp^R_2Ln(\mu\text{-}Cl)]_2$ (Ln = Sm (1), Y (3))

Single crystals of **1** and **3** suitable for X-ray analysis were obtained by recrystallization in THF/hexane mixture (2:1). X-ray structural analyses revealed that compounds **1** and **3** are dimeric. Molecular structures of **1** and **3** with the atom numbering scheme are shown in Figs. 1 and 2. Selected bond distances and bond angles for **1** and **3** are given in Tables 1 and 2. A summary of structural parameters is listed in Table 7.

The coordination sphere of samarium in **1** differs from the solvated $[(C_5H_4Me)_2Sm(\mu\text{-}Cl)(THF)]_2$, as the neomenthyl substituted cyclopentadienyl ligand is comparatively larger than the methyl substituted cyclopentadienyl ligand, hence, there is less room for additional THF molecules in the coordination sphere of the chloro-bridged dimer of **1**. It has been reported that attempts to prepare chloro-bridged samarium compounds with the more bulky $C_5Me_5^-$ ligands resulted in the formation of a trimeric compound $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ [12], which allows the samarium centers to expand further to reduce the congested coordination sphere. For the same reason, a smaller ligand such as the $C_5H_5^-$ ligand forms the solvent-free double chloro-bridged dimeric compound $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ [18], while pentamethyl cyclopentadienyl ligands form the single chloro-bridged compound $[(C_5Me_5)_2YCl(\mu\text{-}Cl)Y(C_5Me_5)]$ so as to reduce the intramolecular congestion of a dimeric structure.

The Sm_2Cl_2 plane in **1** is nearly perpendicular (89.7°) to the plane described by the four centroids of the cyclopentadienyl ring. The (+)-neomenthyl groups attached to the cyclopentadienyl rings in each Cp^R_2Sm unit are positioned in a *trans* orientation with respect to each other in order to minimize the steric interaction, and the (+)-neomenthyl groups in a different Cp^R_2Sm unit on same side of Sm_2Cl_2 plane adopt a *cis* orientation arrangement. Similarly *trans* orientation arrangements of substitutes in similar $(C_5H_4R)_2Ln$ units are also found in compounds such as $[(C_5H_4Me)_2Yb(\mu\text{-}Cl)]_2$ [19], $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$ [20], $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$ [20], and $[(C_5H_4Bu^t)_2Ce(\mu\text{-}OCHMe_2)]_2$ [21].

The structural data of **1** and **3** have shown that the Ln–Cl distances of the Ln_2Cl_2 irregular four-membered ring are comparatively different from the symmetric square plane in analogous lanthanide dimeric complexes such as $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ [18] and $[(Me_3SiC_5H_4)_2Y(\mu\text{-}Cl)]_2$ [20]. The four different bond distances of Cp_{cent}–Ln are lie in the range of 2.4–2.5 Å for samarium cyclopentadienyl compounds and 2.3–2.4 Å for yttrium compounds (Tables 3 and 4). The Cp_{cent}–Ln–Cp_{cent} angles of 134.7 and 128.7° for **1**, 132.0 and 128.9° for **3** are comparable to the range of angles around 130° in typical bis(cyclopentadienyl) lanthanide complexes. The bond distances and bond angles of some bis(cyclopentadienyl) lanthanide halides found in the literature are listed for comparison in Table 3 for samarium compounds and in Table 4 for yttrium compounds.

2.4. X-ray structure of $SmCp^RI_2(THF)_3$ (**11**)

X-ray structural analysis has revealed that (+)-neomenthyl cyclopentadienyl samarium diiodides (**11**) is solvated with three THF molecules. The molecular structure of **11** is shown in Fig. 3. Selected bond distances and bond angles are given in Table 5. The structural parameters are listed in Table 7.

The structure of **11** adopts a pseudo-octahedral geometry with the iodine atoms bonded to samarium in a *trans* fashion. The samarium atom is deviated from the four-membered plane described by I(1), I(2), O(1) and O(3) at 0.622 Å.

The cyclopentadienyl ligand is bonded to samarium in a pentahapto fashion at a distance of 2.729 Å ($Sm–C_{ring(av)}$). The dihedral angle between the cyclopentadienyl ring and plane described by I(1)I(2), O(1)O(3) is 5.5°. The I(1)–Sm(1)–I(2) angle of 157.1° is comparable to that of the analogous dihalides (see Table 6) except for the $(MeOCH_2CH_2C_5H_4)SmI_2(THF)_3$ (90.0°), in which an intramolecular coordination was found.

A comparison of the $[Cp^R_2Sm(\mu\text{-}Cl)]_2$ (**1**) and $Cp^RSmI_2(THF)_3$ (**11**) has shown that they have same coordination number of eight and different coordination environments. The Cp_{cent}–Sm distance in **11** (2.453 Å) is significantly larger than that in **1** (2.407 Å), which indicates the coordination sphere around samarium in **11** is more crowded than that in $[Cp^R_2Sm(\mu\text{-}Cl)]_2$ (**1**).

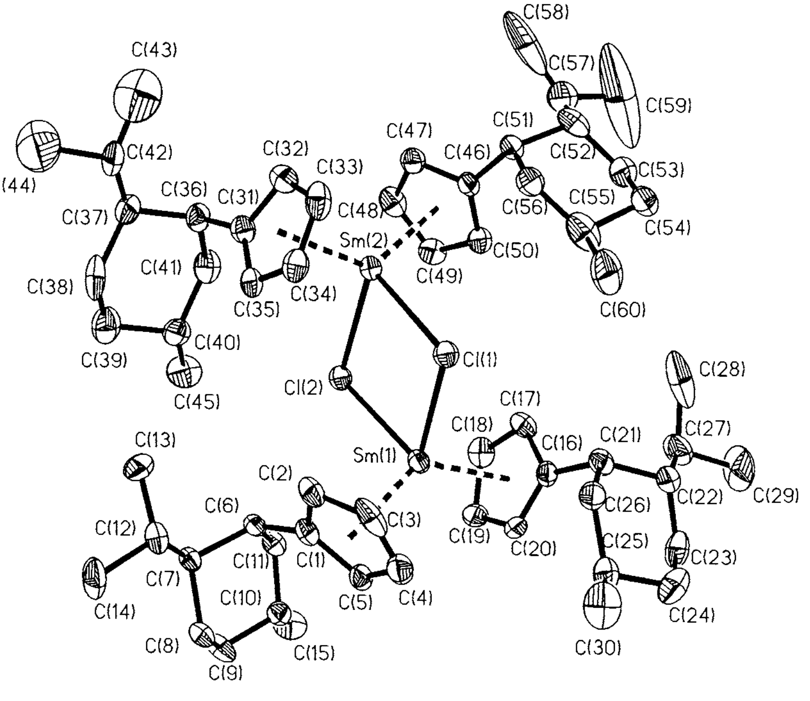

Fig. 1. Molecular structure of $[Cp^R_2Sm(\mu\text{-}Cl)]_2$ (**1**).

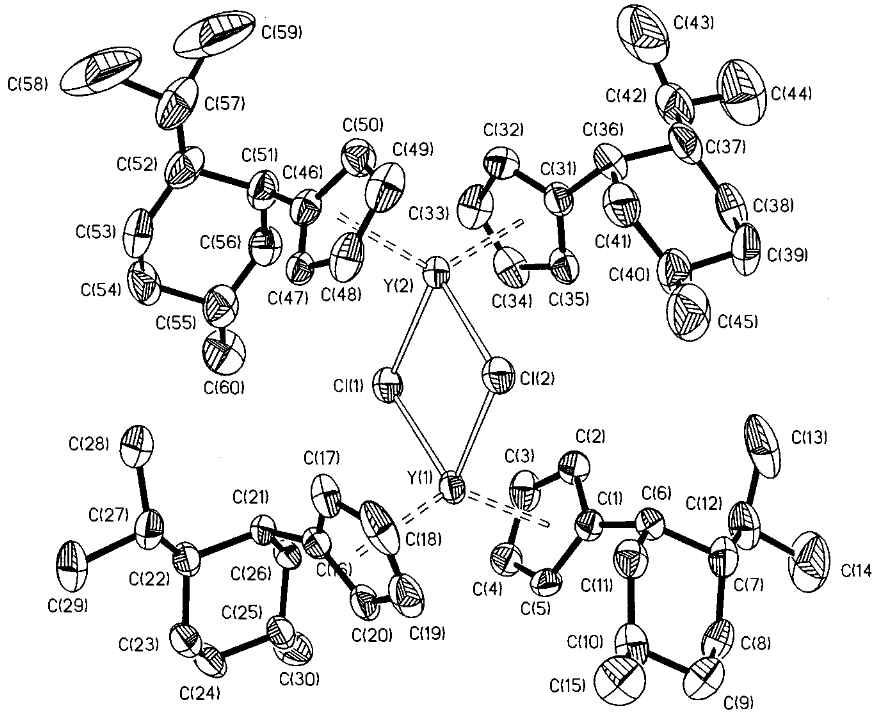

Fig. 2. Molecular structure of $[Cp^R_2Y(\mu\text{-}Cl)]_2$ (**3**).

3. Experimental

All manipulations were carried out under an inert atmosphere of high-purity argon or dinitrogen using standard Schlenk techniques or in a dinitrogen glovebox due to the fact that most compounds involved are extremely air and moisture sensitive. Solvents were dried over and distilled from CaH_2 (hexane, CH_2Cl_2) and/or sodium benzophenone (ether, THF, toluene) and degassed twice prior to use. Deuterated solvents C_6D_6 and C_5D_5N were dried over molecular sieves (4 Å). ^1H- and ^{13}C-NMR spectra were recorded on 250 and 300 MHz using Bruker WM-250 and DPX-300 spectrometers, mass spectra were recorded on a 5989-In spectrometer. Specific optical rotations were recorded on a Perkin–Elmer Polarimeter 341 under dinitrogen atmosphere. $(MCp^R)_\infty$ (M = Na and K) were prepared according to previous methods [11].

3.1. Preparation of *[Cp$^R_2$Sm(μ-Cl)]$_2$* (*1*)

To a stirring suspension of anhydrous $SmCl_3$ (0.9 g, 3.50 mmol) in THF (30 ml) was added a solution of $NaCp^R$ (7.02 mmol, 13.5 ml, 0.52 M in THF) at r.t. After stirring the resulting reaction mixture for 5 h it was concentrated and hexane (5 ml) was added to cause precipitation of solids. The solids formed were separated by centrifugation and the yellow supernatant was collected by filtration. The solids were washed with THF (2 × 10 ml) and filtered. The filtrates and the supernatant were combined and concentrated and hexane was added to form a saturated solution. The resulting yellow solution was stored at −30°C, yellow crystals which formed were collected and dried under vacuum to give compound **1** (1.38 g, 66.6%). M.p. 162°C. $[\alpha]^{20}_D = +54.85°$ (THF). ^1H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ −15.6 (1H), −3.54 to −3.58 (neomenthyl), 8.85 (1H), 13.47 (1H), 15.55 (1H), 19.96 (1H). MS (EI, 70 eV): 1150 (0.25%, $[M-Cl]^+$), 950 (0.9%, $[M-Cp^R-Cl]^+$), 558 (100%, $[Cp^R_2Sm]^+$), 392 (35.7%, $[Cp^RSmCl]^+$), 355 (24.82%, $[Cp^RSm]^+$). Anal. Found: C, 61.19; H, 8.18; Sm, 24.58; Calc. for $C_{30}H_{46}ClSm$: C, 60.83; H, 7.77; Sm, 25.40%.

3.2. Preparation of *[Cp$^R_2$Yb(μ-Cl)]$_2$* (*2*)

The procedure was similar to that of compound **1**. To a stirring suspension of anhydrous $YbCl_3$ (0.35 g, 1.25 mmol) in THF (15 ml) was added a solution of $NaCp^R$ (2.6 mmol, 5 ml, 0.52 M in THF) at r.t. The resulting red solution was stirred for 10 h at r.t., and was then concentrated to ca. 10 ml. Hexane (4 ml) was added to precipitate solids. The solids were separated by centrifugation and the supernatant was collected by filtration. The filtrate was concentrated under vacuum and stored at −30°C. A red–brown needle-like crystalline solid was collected and dried to give compound **2** (0.47 g, 61.2%). M.p. 168°C. ^1H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ −11.3 (s, 2H), −5.9 (2H), 0.5–2.3 (neomenthyl), 3.1 (2H), 5.0–6.76 (8H, CpH), MS (EI, 70 eV): 615 (12.43%, $[Cp^R_2YbCl]^+$), 579 (84.43%, $[Cp^R_2Yb]^+$), 412 (62.75%, $[Cp^RYbCl]^+$), 377 (55.96%, $[Cp^RYb]^+$), 91 (100%). Anal. Found: C, 58.70; H, 7.65; Calc. for $C_{30}H_{46}ClYb$: C, 58.58; H, 7.48%.

3.3. Preparation of $[Cp^R_2Y(\mu\text{-}Cl)]_2$ (**3**)

The procedure was similar to that of **2**. Treatment of a suspension of anhydrous YCl_3 (0.70 g, 3.54 mmol) in THF (30 ml) with $NaCp^R$ (7.13 mmol, 31 ml, 0.23 M in THF) afforded a colourless crystalline compound **3** (1.34 g, 71.2%). M.p. 175°C. $[\alpha]^{20}_D = +49.80°$ (THF). ^{1}H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ 0.59 (d, 6H, $J = 6.6$ Hz), 0.78 (d, 6H, $J = 6.6$ Hz), 0.92 (d, 6H, $J = 6.4$ Hz), 1.02–2.24 (neomenthyl), 3.39 (s, 2H), 6.02 (d, 2H, $J = 2.7$ Hz), 6.11 (d, 2H, $J = 2.6$ Hz), 6.16 (d, 2H, $J = 2.5$ Hz), 6.28 (d, 2H, $J = 2.7$ Hz). ^{13}C-NMR (C_6D_6/C_5D_5N (2:1), 62.5 MHz): δ 20.58, 22.39, 23.34, 24.37, 28.36, 36.17, 37.71, 49.86, 41.66, 108.59, 110.03, 114.63, 114.85, 29.63, 130.84. MS (EI, 70 eV): 532 (0.5%, $[1/2M]^+$), 496 (16.8%, $[Cp^R_2Y]^+$), 329 (29.0%, $[Cp^RYCl]^+$), 204 (57.7%, $[HCp^R]^+$), 91 (100%). Anal. Found: C, 67.00; H, 8.68; Y, 15.38. Calc. for $C_{30}H_{46}ClY$: C, 67.60; H, 8.64, Y, 17.09%.

Table 1
Bond distances (Å) and angles (°) for **1** [a]

Bond lengths			
Sm(1)–Cl(1)	2.735(9)	Sm(2)–C(31)	2.745(4)
Sm(1)–Cl(2)	2.738(1)	Sm(2)–C(32)	2.658(4)
Sm(2)–Cl(1)	2.756(1)	Sm(2)–C(33)	2.617(5)
Sm(2)–Cl(2)	2.753(9)	Sm(2)–C(34)	2.653(5)
Sm(1)–C(1)	2.729(3)	Sm(2)–C(35)	2.687(4)
Sm(1)–C(2)	2.672(4)	Sm(2)–C(46)	2.773(3)
Sm(1)–C(3)	2.646(4)	Sm(2)–C(47)	2.705(3)
Sm(1)–C(4)	2.660(4)	Sm(2)–C(48)	2.624(4)
Sm(1)–C(5)	2.706(2)	Sm(2)–C(49)	2.664(5)
Sm(1)–C(16)	2.746(4)	Sm(2)–C(50)	2.724(4)
Sm(1)–C(17)	2.733(4)	Cp_{cent1}–Sm(1)	2.394
Sm(1)–C(18)	2.702(5)	Cp_{cent2}–Sm(1)	2.459
Sm(1)–C(19)	2.666(4)	Cp_{cent3}–Sm(2)	2.386
Sm(1)–C(20)	2.659(4)	Cp_{cent4}–Sm(2)	2.429
Bond angles			
Sm(1)–Cl(1)–Sm(2)	97.29(4)	Cp_{cent2}–Sm(1)–Cl(2)	108.3
Sm(1)–Cl(2)–Sm(2)	97.27(4)	Cp_{cent3}–Sm(1)–Cp_{cent4}	128.7
Cl(1)–Sm(1)–Cl(2)	82.95(3)	Cp_{cent3}–Sm(1)–Cl(1)	107.8
Cl(2)–Sm(2)–Cl(1)	82.27(3)	Cp_{cent3}–Sm(1)–Cl(2)	110.3
Cp_{cent1}–Sm(1)–Cp_{cent2}	134.7	Cp_{cent4}–Sm(1)–Cl(1)	111.1
Cp_{cent1}–Sm(1)–Cl(1)	109.5	Cp_{cent4}–Sm(1)–Cl(2)	106.8
Cp_{cent1}–Sm(1)–Cl(2)	107.3	plane(1)/plane(2)	89.7
Cp_{cent2}–Sm(1)–Cl(1)	101.7		

[a] Cp_{cent} is the centroid of cyclopentadienyl ring; plane(1) is plane defined by Cp_{cent1}, Cp_{cent2}, Cp_{cent3}, Cp_{cent4}, Sm(1) and Sm(2); plane(2) is plane defined by Sm(1), Sm(2), Cl(1) and Cl(2).

Table 2
Bond distances (Å) and angles (°) for **3** [a]

Bond distances			
Y(2)–Cl(1)	2.693(4)	Y(2)–C(31)	2.691(9)
Y(2)–Cl(2)	2.696(4)	Y(2)–C(32)	2.631(9)
Y(1)–Cl(1)	2.671(5)	Y(2)–C(33)	2.604(11)
Y(1)–Cl(2)	2.676(4)	Y(2)–C(34)	2.597(11)
Y(1)–C(1)	2.660(13)	Y(2)–C(35)	2.658(12)
Y(1)–C(2)	2.647(11)	Y(2)–C(46)	2.687(14)
Y(1)–C(3)	2.599(12)	Y(2)–C(47)	2.661(12)
Y(1)–C(4)	2.572(12)	Y(2)–C(48)	2.635(13)
Y(1)–C(5)	2.616(12)	Y(2)–C(49)	2.590(13)
Y(1)–C(16)	2.681(9)	Y(2)–C(50)	2.623(14)
Y(1)–C(17)	2.624(12)	Cp_{cent1}–Y(1)	2.331
Y(1)–C(18)	2.601(12)	Cp_{cent2}–Y(1)	2.340
Y(1)–C(19)	2.593(11)	Cp_{cent3}–Y(2)	2.347
Y(1)–C(20)	2.651(7)	Cp_{cent4}–Y(2)	2.351
Bond angles			
Cl(1)–Y(1)–Cl(2)	83.5(1)	Cp_{cent2}–Y(1)–Cl(2)	108.3
Cl(1)–Y(2)–Cl(2)	82.7(1)	Cp_{cent3}–Y(2)–Cp_{cent4}	128.9
Y(1)–Cl(1)–Y(2)	97.0(2)	Cp_{cent3}–Y(2)–Cl(1)	107.5
Y(1)–Cl(2)–Y(2)	96.8(2)	Cp_{cent3}–Y(2)–Cl(2)	110.7
Cp_{cent1}–Sm(1)–Cp_{cent2}	132.0	Cp_{cent4}–Y(2)–Cl(1)	109.8
Cp_{cent1}–Y(1)–Cl(1)	108.0	Cp_{cent4}–Y(2)–Cl(2)	107.6
Cp_{cent1}–Y(1)–Cl(2)	107.7	plane(1)/plane(2)	89.3
Cp_{cent2}–Y(1)–Cl(1)	106.6		

[a] Cp_{cent} denotes the centroid of cyclopentadienyl ring; plane(1) is plane defined by Cp_{cent1}, Cp_{cent2}, Cp_{cent3}, Cp_{cent4}, Y(1) and Y(2); plane(2) is plane defined by Y(1), Y(2), Cl(1) and Cl(2).

3.4. Preparation of $[Cp^R_2Lu(\mu\text{-}Cl)]_2$ (**4**)

The procedure was similar to that of **2**. Treatment of a suspension of anhydrous $LuCl_3$ (0.40 g, 1.42 mmol) in THF (20 ml) with a solution of $NaCp^R$ (2.88 mmol, 12.5 ml, 0.23 M in THF) afforded a colorless crystalline compound **4** (0.53 g, 60.6%). M.p. 170°C. $[\alpha]^{20}_D = +42.50°$ (THF). ^{1}H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): (0.58 (d, 6H, $J = 6.6$ Hz), 0.81 (d, 6H, $J = 6.6$ Hz), 0.90 (d, 6H, $J = 6.4$ Hz), 1.00–2.30 (neomenthyl), 3.42 (s, 2H), 5.92 (d, 2H, $J = 2.5$ Hz), 6.08 (d, 2H, $J = 2.6$ Hz), 6.21 (d, 2H, $J = 2.5$ Hz), 6.35 (d, 2H, $J = 2.6$ Hz). MS (EI, 70 eV): 618 (1.5%, $1/2M^+$), 582 (14.3%, $[Cp^R_2Lu]^+$), 204 (46.6%, $[HCp^R]^+$). Anal. Found: C, 57.75; H, 86.98. Calc. for $C_{30}H_{46}ClLu$: C, 58.39; H, 7.46%.

3.5. Preparation of $Cp^R_2Y–N(SiMe_3)_2$ (**5**)

To a stirring solution of Cp^R_2YCl (0.36 g, 0.68 mmol) in THF (10 ml) was added $NaN(SiMe_3)_2$ (0.7 mmol, 0.7 ml 1.0 M in THF) at r.t. After stirring the reaction mixture for 4 h, the solvent was removed under vacuum and hexane (10 ml) was added to extract the product. The solution mixture was filtered and the extract was concentrated under vacuum. After being stored at − 30°C, a colorless crystalline solid was formed and collected to afford compound **5** (0.31 g, 69.6%). ^{1}H-NMR (C_6D_6, 300 MHz): δ 0.08 (br.s, 6H), 0.26 (br.s, 6H), 1.5–2.0 (neomenthyl), 3.19 (br.s, 2H), 5.90 (m, 2H), 6.23 (m, 4H), 6.51 (m, 2H). ^{13}C-NMR (C_6D_6, 75 MHz): δ 1.37, 2.66, 20.26, 21.60, 22.55, 24.09, 28.75, 30.01, 36.08, 38.57, 42.40, 49.39, 108.49, 113.31, 115.23, 119.88, 129.17. Anal. Found: C, 71.52; H, 10.94; N, 3.26; Calc. for $C_{36}H_{64}Si_2NY$: C, 70.59; H, 10.45; N, 2.14%.

3.6. Preparation of *Cp^{R}SmCl$_2$(THF)$_3$* (**6**)

A suspension of anhydrous $SmCl_3$ (1.3 g, 5.06 mmol, 58% excess) in THF (20 ml) was stirred for 1 h at 60°C and was then cooled to r.t. To the resulting suspension was added a solution of NaCp^R (3.20 mmol, 20 ml, 0.16 M in THF) and stirred for 10 h at r.t. Hexane (5 ml) was added to cause precipitation of solids. The solids were separated by centrifugation and washed with THF (2 × 10 ml), the filtrates were combined with the supernatant and concentrated to 20 ml. Hexane (5 ml) was added to form a saturated solution and set aside at − 30°C overnight, yellow powder solids formed and were collected to give compound **6** (1.55 g, 75.9%). M.p. 155°C. ^{1}H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ − 0.35–2.80 (neomenthyl), 1.42 (m, 12H, THF), 3.52 (m, 12H, THF), 8.50 (s, 1H), 9.56 (s, 1H), 9.63 (s, 1H), 10.62 (s, 1H). MS (EI, 70 eV): 425 (0.2%, $[M-3\text{THF}]^+$), 204 (5.5%, $[\text{HCp}^R]^+$), 71 (49.7%). $[\alpha]^{20}_D = +10.32°$ (THF). Anal. Found: C, 48.95; H, 7.69; Sm, 22.52, Calc. for $C_{27}H_{47}O_3Cl_2Sm$: C, 50.60; H, 7.34; Sm, 23.47%.

3.7. Preparation of *Cp^{R}GdCl$_2$(THF)$_3$* (**7**)

The procedure was similar to that of **6**. A suspension of anhydrous $GdCl_3$ (0.6 g, 2.27 mmol) in THF (15 ml) was refluxed at 65°C for 1 h and then cooled to 0°C. To the resulting suspension was added a solution of NaCp^R (2.29 mmol, 4.4 ml, 0.52 M in THF). The reaction mixture was warmed to r.t. and stirred for 10 h and the solid residues were removed by centrifugation. The supernatant was concentrated and hexane was added. The solution was stored at − 30°C overnight to give a colorless powder solid compound **7** (0.45 g, 30.6%). M.p. 150°C. $[\alpha]^{20}_D = +11.42°$ (THF). Anal. Found: C, 48.84; H, 7.56; Calc. for $C_{27}H_{47}O_3Cl_2Gd$: C, 50.06; H, 7.26. MS (EI, 70 eV): 81 (100%), 204 (42.6%, $[\text{HCp}^R]^+$), 361 (13.2%, $[\text{Cp}^R\text{Gd}]^+$), 408 (42.8%, $[(\text{HCp}^R)_2]^+$), 431 (3.0%, $[M-3\text{THF}]^+$).

3.8. Preparation of *Cp^{R}YbCl$_2$(THF)$_3$* (**8**)

The procedure was similar to that of **6**. Treatment of anhydrous $YbCl_3$ (0.50 g, 1.79 mmol) with a solution of NaCp^R (1.82 mmol, 3.5 ml, 0.52 M in THF) afforded a red–brown crystalline solid compound **8** (0.40 g, 34%). M.p. 154°C. Anal. Found: C, 46.42; H, 6.86; Calc. for $C_{27}H_{47}O_3Cl_2Yb$: C, 48.87; H, 7.09. MS (EI, 70 eV): 377 (10.1%, $[\text{HCp}^R\text{Yb}]^+$), 204 (32.0%, $[\text{HCp}^R]^+$).

3.9. Preparation of *Cp^{R}YCl$_2$(THF)$_3$* (**9**)

The procedure was similar to that of **6**. Treatment of anhydrous YCl_3 (0.8 g, 4.05 mmol) with a solution of NaCp^R (4.16 mmol, 8 ml, 0.52 M in THF) afforded a colorless crystalline solid compound **9** (1.22 g, 51.8%). M.p. 147°C. ^{1}H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ 0.66 (s, 3H), 0.68 (s, 3H), 0.76–2.36 (neomenthyl), 1.40 (m, 12H, THF), 3.53 (m, 12H, THF), 6.37 (br.d, 2H), 6.48 (br.d, 1H), 6.75 (br.d, 1H). MS (EI, 70 eV, *m*/*e*): 362 (11.9%, $[M-3\text{THF}]^+$), 204 (20.4%, $[\text{HCp}^R]^+$). $[\alpha]^{20}_D = +10.06°$ (THF). Anal. Found: C, 54.23; H, 8.22; Calc. for $C_{27}H_{47}O_3Cl_2Y$: C, 55.76; H, 8.09%.

3.10. Preparation of *Cp^{R}LuCl$_2$(THF)$_3$* (**10**)

The procedure was similar to that of **6**. Treatment of anhydrous $LuCl_3$ (0.35 g, 1.24 mmol) with a solution of NaCp^R (1.25 mmol, 2.4 ml, 0.52 M in THF) afforded a colorless crystalline solid compound **10** (0.35 g, 42.4%). M.p. 152°C. ^{1}H-NMR (C_6D_6/C_5D_5N (2:1), 250 MHz): δ 0.69–2.4 (neomenthyl), 1.42 (m, 12H, THF), 3.58 (m,

Table 3
Bond distances (Å) and angles (°) for some bis(cyclopentadienyl) samarium halides

Compounds	Cp_{cent}–Sm	Sm–X	Cp–Sm–Cp	Ref.
$[(C_5Me_5)_2SmCl]_3$	2.44, 2.45, 2.47	2.847, 2.887, 2.892	128.2, 127.8	[12]
$(MeOCH_2CH_2C_5H_4)_2SmI$	2.44, 2.43	3.119	123.8	[30]
$(C_5Me_5)_2SmI(THF)$	2.47, 2.46, 2.44, 2.45	3.043, 3.052	136.0, 137.0	[31]
$(C_5Me_5)_2SmCl(THF)$	2.47, 2.43, 2.45, 2.45	2.709, 2.765	133, 136	[31]
$(C_5Me_5)_2SmI(C_6H_{10}N_4)$	2.73 (Sm–$C_{(av.\ ring)}$)	3.100	137	[32]
$(PhCH_2OCH(Me)CH_2C_5H_4)_2SmI$	2.43, 2.45	3.088	123.7	[33]
$[(R^*C_5H_4)_2SmCl]_2$ (**1**)	2.394, 2.459, 2.386, 2.429	2.735, 2.738, 2.756, 2.753	134.0, 128.0	This work

Table 4
Bond distances (Å) and angles (°) for some bis(cyclopentadienyl) yttrium halides

Compounds	Cp_{cent}–Ln	Ln–X	Cp–Y–Cp	Ref.
$[(C_5H_5)_2YCl]_2$	2.38, 2.37	2.710, 2.769	–	[18]
$[(C_5Me_5)_2YCl]_2$	–	2.579_{term}, 2.640_{brid}, 2.776_{brid}	–	[13]
$[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2]$	Y–C(av. ring), 2.66, 2.67	2.575, 2.650, 2.620	–	[20]
$[(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$				
$[(Me_3SiC_5H_4)_2YCl]_2$	2.339, 2.339	2.704, 2.684	130.1	[20]
$(MeOCH_2CH_2C_5H_4)_2YI$	2.39, 2.39	3.057	125.6	[34]
$(C_5Me_5)_2YCl(YHF)$	2.382, 2.379, 2.373, 2.388	136.2, 136.6	2.579, 2.577	[31]
$[(R^*C_5H_4)_2YCl]_2$ (**3**)	2.331, 2.340, 2.347, 2.351	2.671, 2.676, 2.693, 2.696	132.0, 128.9	This work

12H, THF), 6.35 (d, 2H), 6.52 (d, 1H), 6.66 (d, 1H). MS (EI, 70 eV, *m*/*e*): 379 (6.9%, $[Cp^RLu]^+$), 204 (31.5%, $[HCp^R]^+$). $[\alpha]_D^{20} = +9.56°$ (THF). Anal. Found: C, 46.23; H, 6.82; Calc. for $C_{27}H_{47}O_3Cl_2Lu$: C, 48.72; H, 7.07%.

*3.11. Preparation of $Cp^RSmI_2(THF)_3$ (**11**)*

To a stirring brown suspension of SmI_3 (0.30 g, 0.57 mmol) in THF, freshly prepared from the reaction of Sm metal (0.085 g, 0.57 mmol) with I_2 (0.215 g, 0.85 mmol) in THF (30 ml), was added KCp^R (0.137 g, 0.57 mmol) at 0°C. The reaction mixture was warmed to r.t. and stirred for 10 h to form a yellow suspension. The solid residues were removed by filtration and washed with THF (2 × 15 ml). The filtrates were combined and concentrated. Hexane (4 ml) was added to the solution and stored at $-30°C$ to yield yellow crystals which were collected and dried under vacuum to give compound **11** (0.39 g, 82.8%). M.p. 165°C. $[\alpha]_D^{20} = +9.42°$ (THF). ^1H-NMR (C_6D_6/C_5D_5N (2:1), 300 MHz): δ -1.18 (s, 1H), -0.01 (s, 3H), 0.00–3.35 (neomenthyl), 1.41 (s, 12H, THF), 3.51 (s, 12H, THF), 8.53 (s, 1H), 10.86 (d, 2H), 11.36 (s, 1H). Anal. Found: C, 39.36; H, 5.58; Sm, 17.76. Calc. for $C_{27}H_{47}O_3I_2Sm$: C, 39.37; H, 5.71; Sm, 18.27%.

*3.12. Preparation of $Cp^RYbI_2(THF)_3$ (**12**)*

The procedure was similar to that of **11**. The treatment of YbI_3 (0.25 g, 0.45 mmol) with KCp^R (0.110 g, 0.45 mmol) in THF at r.t. afforded a brown crystalline compound **12** (0.28 g, 73.3%). M.p. 174°C. Anal. Found: C, 37.65; H, 5.68. Calc. for $C_{27}H_{47}O_3I_2Yb$: C, 38.21; H, 5.54%.

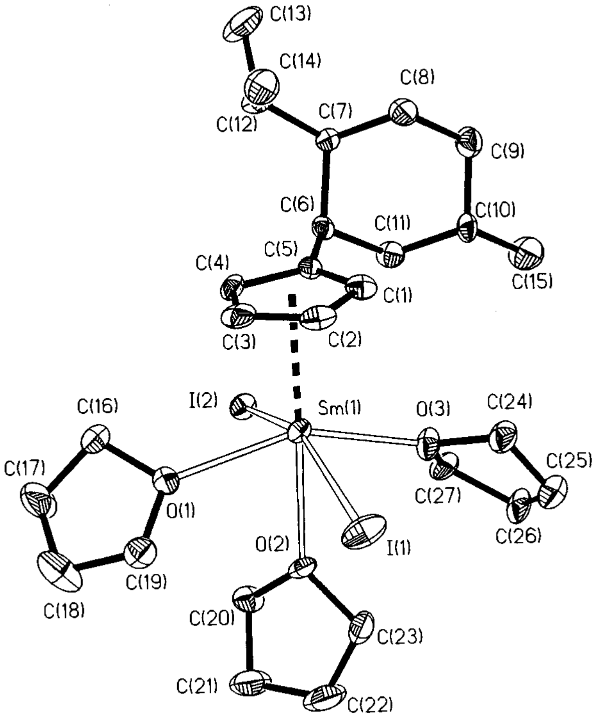

Fig. 3. Molecular structure of $Cp^RSmI_2(THF)_3$ (**11**).

Table 5
Selected bond distances (Å) and angles (°) for **11** [a]

Bond distances			
Sm(1)–I(1)	3.139(1)	Sm(1)–C(4)	2.698(12)
Sm(1)–I(2)	3.140(1)	Sm(1)–C(5)	2.800(12)
Sm(1)–O(1)	2.458(10)	C(1)–C(2)	1.395(19)
Sm(1)–O(2)	2.572(9)	C(1)–C(5)	1.403(16)
Sm(1)–O(3)	2.437(8)	C(2)–C(3)	1.349(21)
Sm(1)–C(1)	2.767(13)	C(3)–C(4)	1.437(20)
Sm(1)–C(2)	2.703(15)	C(4)–C(5)	1.445(17)
Sm(1)–C(3)	2.675(14)	Cp_{cent1}–Sm(1)	2.453(15)*
Bond angles			
I(1)–Sm(1)–I(2)	157.1(1)	O(1)–Sm(1)–O(3)	152.9(3)
I(1)–Sm(1)–O(1)	88.6(2)	O(2)–Sm(1)–O(3)	76.5(3)
I(2)–Sm(1)–O(1)	5.5(2)	Cp_{cent1}–Sm(1)–I(1)	100.5(16)
I(1)–Sm(1)–O(2)	78.4(2)	Cp_{cent1}–Sm(1)–I(2)	102.3(16)
I(2)–Sm(1)–O(2)	78.7(2)	Cp_{cent1}–Sm(1)–O(1)	101.5(16)
O(1)–Sm(1)–O(2)	76.4(3)	Cp_{cent1}–Sm(1)–O(2)	177.6(16)
I(1)–Sm(1)–O(3)	85.7(2)	Cp_{cent1}–Sm(1)–O(3)	105.6(16)
I(2)–Sm(1)–O(3)	89.5(2)	plane(1)/plane(2)	5.5

[a] Cp_{cent1} is the centroid of cyclopentadienyl ring. Plane(1) is plane of cyclopentadienyl ring, plane(2) is described by I(1), I(2), O(1) and O(3).

Table 6
Structural parameters for some monocyclopentadienyl lanthanide dihalides

Compounds	Cp–Ln	X–Ln–X	Ln–X	Ln–O(THF)	Ref.
$(C_5H_5)Ycl_2(THF)_3$	2.373	155.1	2.630, 2.625	2.35, 2.50, 2.34	[35]
$(C_5H_5)NdCl_2(THF)_3$	2.503	155.9	2.719, 2.712	2.445, 2.529, 2.448	[36]
$(C_5H_5)ErCl_2(THF)_3$	2.383	154.85	2.620, 2.613	2.350, 2.452, 2.365	[37]
$(C_5H_5)YbCl_2(THF)_3$	2.389	154.85	2.598, 2.591	2.355, 2.417, 2.365	[38]
$(C_5H_5)YbBr_2(THF)_3$	2.358	155.31	2.771, 2.779	2.335, 2.438, 2.348	[38]
$(C_5Me_5)CeI_2(THF)_3$	2.523	152.18	3.227, 3.173	2.540, 2.540, 2.511	[39]
$(MeOCH_2CH_2C_5H_4)SmI_2(THF)_3$	2.41	95.00	3.092, 3.086	2.514, 2.456, 2.519	[30]
$Cp^RSmI_2(THF)_3$ (**11**)	2.453	157.1	3.139, 3.140	2.458, 2.572, 2.437	This work

Table 7
Selected crystallographic and data collection parameters for compounds **1**, **3** and **11**

	1	**3**	**11**
Molecular formula	$C_{60}H_{92}Cl_2Sm_2$	$C_{60}H_{92}Cl_2Y_2$	$C_{27}H_{47}I_2O_3Sm$
Molecular weight	1188.97	1062.1	823.8
Color and habit	Yellow prism	Colorless prism	Yellow prism
Crystal size (mm)	0.20 × 0.30 × 0.50	0.10 × 0.20 × 0.40	0.10 × 0.32 × 0.70
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2$	$C2$	$P2_12_12_1$
a (Å)	36.099(5)	35.899(7)	10.532(2)
b (Å)	7.507(2)	7.505(2)	12.650(3)
c (Å)	28.818(5)	28.728(6)	23.941(5)
α (°)	–	–	–
β (°)	121.52(1)	121.59(3)	–
γ (°)	–	–	–
V (Å^3)	6657(2)	6593(6)	3162.1(16)
Z	4	4	4
$D_{calc.}$ (g cm^{-3})	1.186	1.070	1.730
Absorption coefficient (mm^{-1})	1.857	1.863	3.833
Scan type and rate (deg min^{-1})	ω, 8.0–32.0	60 oscillation photos; $\phi = 0$–180°, $\Delta\phi = 3°$; 8 min per frame	ω, 8.0–32.0
$2\theta_{max}$ (°)	4–55	3.0–55.0	4.0–55.0
Unique data (R_{int})	7108 (0.0277)	10965 (0.0726)	4073 (0.0000)
Observed data	2914 [$F > 4\sigma(F)$]	6778 [$F > 6\sigma(F)$]	2814 [$F > 6\sigma(F)$]
No. variables (ρ)	578	580	299
R	0.0445	0.0572	0.0396
wR	0.1223	0.0645	0.0512
Weighting scheme	0.0785, 0.3195	0.0000	0.0004
Goodness-of-fit	1.041	2.07	1.27
Large and mean Δ/σ	−0.603, 0.038	0.093, 0.004	0.001, 0.000
$\Delta\rho_{max}$ (e Å^{-1})	0.663, −0.534	0.98, −0.82	0.97, −0.80

4. X-ray crystallography

Suitable single crystals were mounted and sealed in Lindemann glass capillaries under dinitrogen. X-ray intensities were measured at 294 K on MSC/Rigaku AFC7R four-circle diffractometer **1** and **11**, and on MSC/Rigaku Raxis IIc imaging-plate diffractometer for **3** with rotating-anode generator powered at 50 kV and 90 mA by using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) [22–24]. Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ω-scan data of selected strong reflections over a range of 2θ angles for **1** and **11** [25].

All crystal structures were determined by the direct method, which yielded the positions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The computations **3** and **11** were performed on an IBM compatible PC with the SHELXL-PLUS program package, where, $w^{-1} = \sigma^2(F) + |g|F^2$, $R = R_F = \Sigma\|F_o| - |F_c\| = \Sigma|F_o|$, $R_w = [\Sigma w(F_o - F_c)]/[\Sigma w(F_o)]$, $GOF = S = \{[\Sigma w(F_o - F_c)^2]/(n-p)\}^{1/2}$. The computation of **1** was performed using the SHELXL-93 program package [26–28], where $w^{-1} = \sigma^2(F_o^2) = (a \times P)^2 = b \times P$, $P = (F_o^2 + 2F_c^2)$, $R = R_1 =$

$\Sigma\|F_o| - |F_c\| = \Sigma|F_o|$, $R_w = wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$, $\mathrm{GOF} = S = \{[\Sigma w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [29].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC-113689 for compound **1**, CCDC-113690 for compound **3** and CCDC-113688 for compound **11**. 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; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

Acknowledgements

This research was supported by the Hong Kong Research Grants Council Earmarked Grants CUHK 317/96P.

References

[1] I.P. Rothwell, in: C.L. Hill (Ed.), Activation of Functionalised Alkanes, Wiley, New York, 1989, p. 151.

[2] P.L. Watson, in: J.A. Davies, P.L. Watson, J.F. Liebman, A. Greenberg (Eds.), Selective Hydrocarbon Activation, VCH, New York, 1990, p. 79.

[3] H. Raba, J.Y. Saillard, R. Hoffmann, J. Am. Chem. Soc. 108 (1986) 4327.

[4] F.T. Edelmann (Ed.), in: Topics in Current Chemistry 179, Organolanthanide Chemistry, Synthesis Structure Catalysis, Springer, Berlin, 1996, p. 1.

[5] M.A. Gagne, L. Brard, V.P. Conticello, M.A. Giardello, C.L. Stern, T.J. Marks, Organometallics 11 (1992) 2003.

[6] M. Gagne, S.P. Nolan, T.J. Marks, Organometallics 9 (1990) 1716.

[7] H. Yasuda, M. Furo, H. Yamamoto, Macromolecules 25 (1992) 5115.

[8] M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagne, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10241.

[9] P.W. Roesky, U. Denninger, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 4486.

[10] P.-F. Fu, L. Brard, Y. Li, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 7157.

[11] W.-P. Leung, F.-Q. Song, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1997) 4307.

[12] W.J. Evans, D.K. Drummond, J.W. Grate, H. Zhang, J.L. Atwood, J. Am. Chem. Soc. 109 (1987) 3928.

[13] W.J. Evans, T.T. Peterson, M.D. Rausch, W.E. Hunter, H. Zhang, J.L. Atwood, Organometallics 3 (1985) 554.

[14] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Chem. Commun. (1981) 1190.

[15] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[16] M.E. Thompson, J.E. Bercaw, Pure Appl. Chem. 56 (1984) 1.

[17] D.L. Deng, C.T. Qian, F.Q. Song, Z.Y. Wang, G. Wu, P.J. Zheng, S. Jin, Y. Lin, J. Organomet. Chem. 458 (1993) 83.

[18] E.B. Lobkovskii, G.L. Sdoveichik, B.M. Bulichev, A.B. Zh. Erofeev, Strukt. Khim. (1984) 25.

[19] W.C. Baker, L.D. Brown, K.N. Raymond, Inorg. Chem. 14 (1975) 1376.

[20] W.J. Evans, M.S. Sollberger, J.L. Shreeve, J.M. Olofson, J.H. Hain, J.W. Ziller, Inorg. Chem. 31 (1992) 2492.

[21] S.D. Stults, R.A. Andersen, A. Zalkin, Organometallics 9 (1990) 1623.

[22] J. Tanner, K. Krause, Rigaku J. 11 (1994) 4; J. Tanner, K. Krause, Rigaku J. 7 (1990) 28.

[23] K.L. Krause, G.N. Phillips, Jr., J. Appl. Crystallogr. 25 (1992) 146.

[24] M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka, T.J. Higashi, Appl. Crystallogr. 25 (1992) 348.

[25] T. Higashi, ABSCOR—An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo, (c) 1995.

[26] G.M. Sheldrick, SHELXL PC Manual, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

[27] G.M. Sheldrick, in: D. Sayre (Ed.), Computational Crystallography, Oxford University Press, New York, 1982, p. 506.

[28] G.M. Sheldrick, Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases, Oxford University Press, New York, 1985, p. 175.

[29] (a) J.A. Ibers, W.C. Hamilton, International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, vol. 4, 1974, pp. 55, 99, 149. (b) J.A. Ibers, W.C. Hamilton, International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, vol. 3, 1974, p. 278.

[30] D.L. Deng, C.T. Qian, F.Q. Song, Z.Y. Wang, Sci. China Ser. B 24 (1994) 120.

[31] W.J. Evans, W. Grate, K.R. Levan, I. Bloom, T.T. Peterson, R.J. Doedens, H. Zhang, J.L. Atwood, Inorg. Chem. 25 (1986) 3614.

[32] W.J. Evans, D.K. Drummond, L.A. Hughes, H. Zhang, J.L. Atwood, Polyhedron 7 (1988) 1693.

[33] A.A. Trifonov, P. van de Weghe, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 527 (1997) 225.

[34] C. Qian, X. Zheng, B. Wang, D. Deng, J. Sun, J. Organomet. Chem. 466 (1994) 101.

[35] X. Zhou, Z. Wu, H. Ma, Z. Xu, X. You, Polyhedron 13 (1994) 375.

[36] G. Yang, Y. Fan, Z. Jin, Y. Xing, W. Chen, J. Organomet. Chem. 322 (1987) 57.

[37] C.S. Day, V.W. Day, R.D. Ernst, S.H. Vollmer, Organometallics 1 (1982) 998.

[38] G.B. Deacon, G.D. Fallon, D.L. Wilkinson, J. Organomet. Chem. 293 (1985) 45.

[39] P.N. Hazin, J.C. Huffman, J.W. Bruno, Organometallics 6 (1987) 23.