Synthesis of cationic cerium compounds $[Cp_2^*Ce(L)_2][BPh_4]$ (L = tetrahydrofuran or tetrahydrothiophene) and the crystal structure of the tetrahydrothiophene derivative

H.J. Heeres, A. Meetsma and J.H. Teuben *

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (Netherlands)

(Received March 5th, 1991)

Abstract

Protolysis of the cerium alkyl $Cp_2^*CeCH(SiMe_3)_2$ (1) by triethylammoniumtetraphenylborate provides a useful route to cationic cerium compounds $[Cp_2^*Ce(L)_2][BPh_4]$ (2, L = tetrahydrofuran; 3, L = tetrahydrothiophene). The crystal structure of the tetrahydrothiophene derivative was determined by X-ray diffraction, which showed it to consist of discrete $[Cp_2^*Ce(THT)_2]^+$ and BPh_4^- ions. The Cp^* ring-centroids (Cent) and the sulphur atoms in the cation form a distorted tetrahedron with a Cent–Ce–Cent angle of 134.57(6)° and Ce–S distances of 3.058(1) and 3.072(1) Å.

Introduction [1*]

The chemistry of cationic compounds of the early transition metals and actinide elements has developed rapidly in the past 5 years [2]. This interest arises from the suggestions that such cationic species play a major role in the polymerization of olefins by Ziegler–Natta and Kaminsky type catalyst systems. Indeed, well-defined cationic Group 4 alkyls and hydrides, $[Cp_2MR]^+$ (Cp = cyclopentadienyl or substituted cyclopentadienyl ligand; R = alkyl or H), display a rich olefin chemistry [2a–d,2j–l], and some are very active oligo- and polymerization catalysts. Detailed investigations have shown them to be useful model systems for a better understanding of the fundamental aspects of olefin oligomerization and polymerization by early transition metal catalysts.

Cationic organolanthanide chemistry is much less developed than early transition metal chemistry and to our knowledge only two such species have been reported [3]. Oxidation of the divalent $Cp_2^*Sm(THF)_2$ with $AgBPh_4$ afforded a novel samarium(III) cation, $[Cp_2^*Sm(THF)_2][BPh_4]$ [3a]. The crystal structure was established by X-ray diffraction and the complex shown to be monomeric in the solid
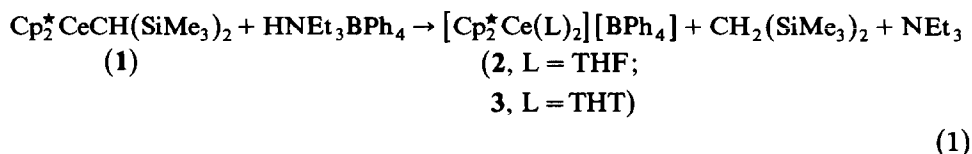
---

* Reference number with asterisk indicates a note in the list of references.

state. Recently, Bruno and coworkers reported [3b] the preparation of lanthanum and cerium cations $[Cp_2''Ln(NCMe)(DME)][BPh_4] \cdot 1/2DME$ from trivalent lanthanide iodide precursors and $AgBPh_4$; however, the coordinated ligands are rather loosely bound to the cations and satisfactory elemental analyses could not be obtained.

As a part of our investigation on the reactivity of early lanthanide (La and Ce) carbyls and hydrides, we herein report the reactions of $Cp_2^*CeCH(SiMe_3)_2$ (**1**) with triethylammoniumtetraphenylborate, $HNEt_3BPh_4$. We have shown previously [4] that the Ce–C bond in **1** is, despite the bulk of the alkyl group, susceptible to attack by substrates with active NH and OH groups, and so it was also expected to react with trialkylammoniumtetraalkylborates. The BPh_4 anion was chosen as a counter-ion because it is generally less reactive than halogenated borates [5].

Results and discussion

Treatment of THF or THT solutions of $Cp_2^*CeCH(SiMe_3)_2$ with $HNEt_3BPh_4$ resulted in abstraction of the alkyl ligand and the formation of novel cationic cerium compounds $[Cp_2^*Ce(L)_2][BPh_4]$, (**2**, L = THF; **3**, L = THT, eq. 1)

$$Cp_2^*CeCH(SiMe_3)_2 + HNEt_3BPh_4 \rightarrow \left[Cp_2^*Ce(L)_2\right][BPh_4] + CH_2(SiMe_3)_2 + NEt_3$$
$$\text{(1)} \qquad\qquad\qquad \text{(2, L = THF;}$$
$$\text{3, L = THT)}$$

$$(1)$$

Compound **2** was isolated as orange needles and **3** as blue-green crystals. No coordination of NEt_3 to the cerium center was observed under these conditions. As expected for ionic molecules, both **2** and **3** are essentially insoluble in aromatic and aliphatic hydrocarbon solvents. The THF derivative is even poorly soluble in THF. However, it dissolves in a polar, chlorinated solvent such as CD_2Cl_2 and shows ^1H-NMR resonances at δ 6.50, 6.41, 6.29 (all BPh_4), 5.70 (Cp^*) and two broad THF resonances shifted upfield at δ −6.3 (β-THF) and −22.6 (α-THF) ppm. The integrated intensities of the resonances are in accord with the proposed structure. Unfortunately, the stability of **2** in this solvent is rather limited, and complete decomposition to unidentified organocerium compounds takes place within 4 h at room temperature. By analogy to cationic zirconium systems [2k], it is probable that the electrophilic cation abstracts a Cl atom from the solvent. The IR spectra of **2** display clear absorptions associated with the THF (C–O–C) unit at 1010 (ν_{as}) and 860 (ν_s) cm^{-1}. These values are typical for THF molecules coordinated to trivalent lanthanide metal centers [4a,6]. When the THT derivative **3** is redissolved in THF-d_8, the ^1H-NMR resonances of free THT are observed, together with characteristic resonances from $[Cp_2^*Ce(THF-d_8)_2][BPh_4]$. This implies that exchange of coordinated Lewis bases takes place readily in these systems.

An X-ray diffraction study was carried out for the THF compound and the molecular structure found is depicted in Fig. 1. A list of key distances and angles is given in Table 1, and final positional parameters in Table 2. The crystal consists of discrete $[Cp_2^*Ce(THF)_2]$ cations and BPh_4 anions. The cation has an ordinary bent-metallocene structure, with the THT ligands arranged in the girdle between the Cp^* ligands. The Cent1–Ce–Cent2 angle of 134.57(6)° is similar to that in
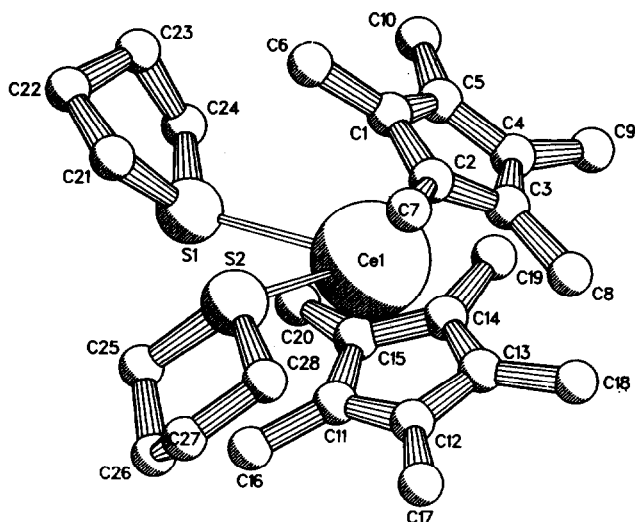
Fig. 1. PLUTO drawing of the cation of **3** with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

$[Cp_2^*Sm(THF)_2]^+$ [3a] and also well within the range observed for various neutral Cp_2^*LnX compounds (131–138°) [7]. The average Ce-internal ring carbons distances are 2.74(3) Å for ring 1 (C1–C5) and 2.75(2) Å for ring 2 (C11–C15). These values are somewhat smaller than those for neutral $Cp_2^*CeCH_2Ph$ (2.76(3) and 2.80(3) Å) [8]. The Cp* ligands exhibit no special features; the Ce–Cent distances (Ce–Cent1 = 2.465(2) Å; Ce–Cent2 = 2.474(2) Å), the dished shaped conformation of the rings, and the regular *endo* and *exo* C–C distances are quite normal. The Cp* rings in **3** are, as in most bis(pentamethylcyclopentadienyl)lanthanide compounds, oriented in a staggered conformation [3a]. Interestingly, an eclipsed conformation was found for the related Sm cation $[Cp_2^*Sm(THF)_2][BPh_4]$ [3a]. In an eclipsed conformation there can be severe strain between the methyl groups of the opposed Cp* ligands but this orientation of the Cp* ligands in the samarium cation probably relieves unfavorable interactions between the Cp* ligands and the coordinated THF molecules. This type of strain is less likely in **3** because the coordination sphere around Ce^{3+} is significantly larger than that around Sm^{3+} [9]. Furthermore, the THT molecules in **3** are further away from the metal center than the THF molecules in the samarium case owing to differences in the radii of sulphur and oxygen [9].

Table 1

Selected bond distances and angles for $[Cp_2^*Ce(THT)_2][BPh_4]$ (3)

Bond distances (Å)			
Ce(1)–Cent1	2.465(2)	S(1)–C(21)	1.832(5)
Ce(1)–Cent2	2.474(2)	S(1)–C(24)	1.842(5)
Ce(1)–S(1)	3.058(1)	S(2)–C(25)	1.846(6)
Ce(1)–S(2)	3.072(1)	S(2)–C(28)	1.832(6)
Bond angles (°)			
Cent1–Ce(1)–Cent2	134.57(6)	S(1)–Ce(1)–S(2)	70.90(3)

Complex **3** is a rare example of a structurally characterized organometallic cerium compound containing Ce–S dative bonds. The Ce–S distances differ marginally, and are 3.058(1) Å (Ce–S1) and 3.072(1) Å (Ce–S2). The dihedral angles between the S1–Ce–S2 and the THT ($C\alpha$–S–$C\alpha'$) planes are 46.2(2)° (C21–S1–C24) and 52.0(2)° (C25–S2–C28), and imply that the THT ligands lie significantly out of the equatorial plane. Inspection of the molecular structures of cationic bent-metallocenes of early transition metals and actinides shows a large variation in these dihedral angles [2]. An angle close to 90° was found for $[Cp_2ZrMe(THF)]^+$ [2k] whereas one close to 0° was found for $[Cp_2^*TiMe(THF)][BPh_4]$ [2j]. A perpendicular arrangement of the coordinated Lewis bases is thought to increase the amount of π-donation from oxygen to the metal and thus seems to be electronically favored. However, the angle is generally significantly reduced to relieve steric strain between the Cp/Cp* rings and the coordinated Lewis bases.

The reactivity of these electrophilic early lanthanide cations towards small unsaturated substrates is currently under investigation. Evans et al. [3a] found that the related Sm cation, $[Cp_2^*Sm(THF)_2]^+$, does not react with neutral substrates such as CO, azobenzene, ethylene, phenylacetylene and pyridine, in accordance with the very tight bonding of the THF molecules. However, preliminary investigations show that **3** rapidly reacts with terminal alkynes such as t-butylacetylene to give insoluble pink crystals. Although the identiity of this material has not yet been established, the result clearly demonstrates that the use of a larger metal (Ce instead of Sm) in combination with a poorer Lewis base (THT instead of THF) enhances the reactivity of these cationic lanthanide compounds.

Experimental

General considerations

All the compounds described are extremely air-sensitive and manipulations were carried out by Schlenk or glovebox techniques under nitrogen. THF and NMR solvents (benzene-d_6, THF-d_8) were distilled from Na/K alloy. THT was distilled from K and stored over molecular sieves. $Cp_2^*CeCH(SiMe_3)_2$ (1) was prepared from $[Cp_2^*CeCl]_n$ and $LiCH(SiMe_3)_2$ according to a published procedure [4]. t-Butylacetylene was distilled before use and stored over molecular sieves. $HNEt_3BPh_4$ was synthesized by the procedure developed by Barker and coworkers [10].

IR spectra were recorded on a Pye–Unicam SP3-300 spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million relative to TMS ($\delta = 0.00$ ppm). Proton spectra were determined by reference to residual protons in deuterated solvents (benzene-d_6, δ 7.15; THF-d_8, δ 1.72 ppm). Elemental analyses were performed in the Microanalytical Department of this Institute; the percentages shown are the average of at least two independent determinations.

Preparation of $[Cp_2^*Ce(THF)_2][BPh_4]$ (2)

5.6 mL of a 0.08 *M* solution of $HNEt_3BPh_4$ in THF was added from a syringe to a solution of 274 mg (0.48 mmol) of **1** in THF (15 mL); the color of the solution changed immediately from deep-red to orange. The solution was stirred for another 15 min at room temperature and then concentrated to ca 5 mL. Slow diffusion of pentane into the solution produced large orange needles of **2** in 58% yield (247 mg,

Table 2

Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms with esd's in parentheses

	x	y	z	U_{eq} (Å^2) ^{a}
Residue 1				
Ce(1)	0.24240(2)	0.16409(1)	0.24986(1)	0.01880(1)
S(1)	0.2293(1)	0.33305(6)	0.14072(6)	0.0271(2)
S(2)	0.1753(1)	0.32926(8)	0.35052(7)	0.0402(3)
C(1)	0.4979(4)	0.2050(3)	0.3557(3)	0.033(1)
C(2)	0.4307(4)	01643(3)	0.4121(2)	0.030(1)
C(3)	0.4034(3)	0.0714(2)	0.3866(2)	0.025(1)
C(4)	0.4556(3)	0.0538(3)	0.3143(2)	0.027(1)
C(5)	0.5113(4)	0.1366(3)	0.2949(3)	0.032(1)
C(6)	0.5535(5)	0.3013(3)	0.3646(4)	0.052(2)
C(7)	0.4088(5)	0.2066(3)	0.4940(3)	0.048(2)
C(8)	0.3371(4)	0.0049(3)	0.4327(3)	0.034(1)
C(9)	0.4740(4)	−0.0388(3)	0.2774(3)	0.040(1)
C(10)	0.5717(5)	0.1497(4)	0.2197(4)	0.053(2)
C(11)	−0.0167(3)	0.1396(3)	0.1410(2)	0.027(1)
C(12)	−0.0011(3)	0.0739(3)	0.2064(2)	0.026(1)
C(13)	0.0886(3)	0.0078(2)	0.1917(2)	0.025(1)
C(14)	0.1328(4)	0.0342(2)	0.1189(2)	0.025(1)
C(15)	0.0678(4)	0.1153(3)	0.0881(2)	0.026(1)
C(16)	−0.1147(4)	0.2155(3)	0.1240(3)	0.040(1)
C(17)	−0.0689(4)	0.0735(3)	0.2791(3)	0.038(1)
C(18)	0.1127(4)	−0.0820(3)	0.2361(3)	0.032(1)
C(19)	0.2213(4)	−0.0179(3)	0.0757(3)	0.032(1)
C(20)	0.075(4)	0.1596(3)	0.0055(2)	0.033(1)
C(21)	0.3052(4)	0.4410(3)	0.1942(3)	0.036(1)
C(22)	0.3738(5)	0.4830(3)	0.1319(3)	0.042(1)
C(23)	0.4367(5)	0.4057(3)	0.0928(3)	0.042(1)
C(24)	0.3260(4)	0.331793)	0.0597(3)	0.031(1)
C(25)	0.0333(6)	0.3963(4)	0.2880(3)	0.053(2)
C(26)	−0.0824(6)	0.3771(4)	0.3283(4)	0.061(2)
C(27)	−0.0172(6)	0.3765(4)	0.4235(4)	0.058(2)
C(28)	0.0966(6)	0.3074(3)	0.4378(3)	0.049(2)
Residue 2				
C(29)	0.1198(4)	0.2440(2)	0.6708(2)	0.026(1)
C(30)	0.1495(4)	0.1659(3)	0.6275(2)	0.031(1)
C(31)	0.0551(5)	0.1186(3)	0.5605(3)	0.040(1)
C(32)	−0.0775(5)	0.1489(3)	0.5326(3)	0.046(2)
C(33)	−0.1116(4)	0.2255(3)	0.5721(3)	0.042(1)
C(34)	−0.0135(4)	0.2723(3)	0.6395(3)	0.033(1)
C(35)	0.3217(4)	0.2289(2)	0.8223(2)	0.022(1)
C(36)	0.2768(4)	0.1407(2)	0.8337(2)	0.027(1)
C(37)	0.3472(5)	0.0865(3)	0.9009(3)	0.035(1)
C(38)	0.4648(5)	0.1185(3)	0.9596(3)	0.039(1)
C(39)	0.5120(4)	0.2060(3)	0.9513(3)	0.039(1)
C(40)	0.4404(4)	0.2597(3)	0.8843(3)	0.031(1)
C(41)	0.1791(4)	0.3734(2)	0.8031(2)	0.025(1)
C(42)	0.0680(4)	0.3515(3)	0.8349(2)	0.030(1)
C(43)	0.0194(4)	0.4115(3)	0.8863(3)	0.035(1)
C(44)	0.0820(5)	0.4963(3)	0.9111(3)	0.039(1)
C(45)	0.1939(5)	0.5196(3)	0.8833(3)	0.038(1)
C(46)	0.2401(4)	0.4590(3)	0.8301(3)	0.031(1)

Table 2 (continued)

	x	y	z	U_{eq} (Å^2) ^{a}
Residue 2				
C(47)	0.3418(4)	0.3459(2)	0.6976(2)	0.028(1)
C(48)	0.4735(4)	0.3207(3)	0.7045(3)	0.034(1)
C(49)	0.5549(5)	0.3657(4)	0.6604(3)	0.051(2)
C(50)	0.5035(7)	0.4364(4)	0.6068(3)	0.060(2)
C(51)	0.3728(7)	0.4609(3)	0.5955(3)	0.054(2)
C(52)	0.2927(5)	0.4165(3)	0.6403(3)	0.041(1)
B(1)	0.2396(4)	0.2974(3)	0.7474(2)	0.022(1)

^{a} $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i a_j \mathbf{a}_i \cdot \mathbf{a}_j$.

0.28 mmol). IR (cm^{-1}): 3050 (m), 3030 (m), 2710 (w), 2130 (w), 1580 (m), 1480 (m), 1430 (m), 1380 (m), 1270 (w), 1180 (w), 1140(w), 1030(m), 1010(m), 860 (sh), 840 (m), 740 (s), 730 (s), 700 (s), 610 (m). ^{1}H-NMR (THF-d_8, 40°C): δ 6.44 (t, 4H, $J = 7.5$ Hz, 1w < 5 Hz, p-C$_6$H$_5$); 6.16 (t, 8H, $J = 7.5$ Hz, 1w < 5Hz, m-C$_6$H$_5$); 5.8 (s, 8H, 1w = 16 Hz, o-C$_6$H$_5$); 5.6 (s, 30H, 1w = 35 Hz, Cp*). Anal. Found: C, 71.48; H, 7.59; Ce, 16.35. C$_{52}$H$_{66}$BCeO$_2$ calcd.: C, 71.46; H, 7.61; Ce, 16.03%.

Preparation of [Cp$_2^*$Ce(THT)$_2$][BPh$_4$] (3)

A suspension of 530 mg (0.93 mmol) of **1** and 388 mg (0.92 mmol) of HNEt$_3$BPh$_4$ in 25 mL of THT was stirred at room temperature. After 10 min, all the ammonium salt had dissolved to give a clear green solution. When the solution was kept at room temperature, blue-green crystals separated. Yield of **3** 429 mg (0.47 mmol, 51%). IR (cm^{-1}): 3040 (m), 3000 (m), 2720 (w), 2110 (w), 1580 (m), 1480 (m), 1420 (m), 1370 (m), 1300 (w), 1250 (m), 1180 (w), 1140 (m), 1025 (m), 1010 (m), 840 (m), 740 (s), 730 (s), 700 (s), 670 (m), 600 (m). **3** is essentially insoluble in benzene-d_6 and satisfactory NMR spectra could not be obtained in this solvent. Attempts to dissolve **3** in THF-d_8 resulted in the formation of free THT and **2**-THF-d_8. Anal Found: C, 68.99; H, 7.28; Ce, 15.30; S, 7.05. C$_{52}$H$_{66}$BCeS$_2$ calcd.: C, 68.92; H, 7.34; Ce, 15.46; S, 7.08%.

NMR tube reaction of 3 with an excess of t-butylacetylene

58 μL (0.47 mmol) of t-butylacetylene was added from a syringe to a benzene-d_6 suspension of **3** (21.5 mg; 0.024 mmol); the color of the solution turned from slightly purple to pink. After 1 day at room temperature, all the **3** had dissappeared and pink crystals had separated. No catalytic dimerization of the excess of t-butylacetylene to 2,4-di-t-butyl-1-buten-3-yne (as found for Cp$_2^*$CeCH(SiMe$_3$)$_2$ [11]) was observed.

X-Ray data collection, structure determination and refinement for 3

A blue-green parailelepiped crystal, obtained directly from the reaction mixture, was glued on the tip of a glass-fiber which was placed in the cold nitrogen stream of the low temperature unit mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Unit cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range $11.3 < \theta < 21.71°$ A triclinic unit cell was diagnosed from the presence of higher

Table 3

---

a. Crystal data and details of the structure determination

Chemical formula	$(C_{10}H_{15})Ce(SC_4H_8)_2 \cdot B(C_6H_5)_4$
Formula weight, g mol^{-1}	906.14
Crystal system	triclinic
Space group, no. 10	$P\bar{1}$, 2
a, Å	10.299(1)
b, Å	14.689(1)
c, Å	16.003(1)
α, deg	91.583(8)
β, deg	106.226(9)
γ, deg	91.226(9)
V, Å^3	2322.6(3)
Z	2
D_{calc}, g cm^{-3}	1.296
$F(000)$, electrons	946
$\mu(\text{Mo-}K_\alpha)$, cm^{-1}	11.1
Approx. crystal dimension, mm	$0.25 \times 0.30 \times 0.55$

b. Data collection

Diffractometer	Enraf–Nonius CAD-4F
Radiation, Å	Mo-K_α, 0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.33, 27.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.985 + 0.35 \text{ tg } \theta$
Data set	h: $-13 \rightarrow 12$; k: $-18 \rightarrow 18$; l: $-1 \rightarrow 20$
Crystal-to-receiving-aperture distance, mm	173
Horizontal, vertical aperture, mm	$3.2 + \text{tg } \theta$; 4.0
Reference reflections, rms dev. in %	$2\bar{2}2$, 2.5; $\bar{0}2\bar{2}$, 4.7
Drift correction	1.000–1.064
X-ray exposure time, h	182.1
Total data	11201
Unique data	10090
Observed data $(I \geqslant 2.5\sigma(I))$	9398
$R1\ (= \Sigma(I - \bar{I})/\Sigma I)$	0.018
$R2 = (\Sigma\sigma/\Sigma I)$	0.009
Number of equivalent reflections	2222

c. Refinement

Number of reflections	9398
Number of refined parameters	747
Final agreement factors:	
$\quad R_F = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.038
$\quad wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.046
Weighting scheme	1
$\quad S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m-n)]^{1/2}$	1.845
$\quad m = $ number of observations	
$\quad n = $ number of variables	
Residual electron density in final	
$\quad$ difference Fourier map, e/Å^3	-1.3, 4.1
Max. (shift/σ) final cycle	0.527
Average (shift/σ) final cycle	0.011

lattice symmetry [12]. This choice was confirmed by the solution and the successful refinement. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements [13]. The two reference reflections, measured every 3 h, showed a variation of 6% during the 182.1 h exposure to the X-rays. The net intensities of the data were corrected for scale variation and for Lorentz and polarization effects, but not for absorption. (Correction for absorption was judged to be unnecessary in view of the observed intensity variation, up to 8%, for a $360°$ ψ scan of the close to axial reflection (004).) Intensities of equivalent reflections were averaged, resulting in 9398 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86) [14]. The positions and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL). A subsequent difference-Fourier map indicated slight disorder of one of the THT ligands [S(2) $\cdots$ C(28)]. No other disorder features were recognized. Attempts to find a satisfactory disorder model failed. The hydrogen atoms of the disordered ring were introduced at calculated positions (C–H = 1.0 Å) and refined with fixed geometry with respect to their carrier atoms. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of all of the remaining hydrogen atoms, which were included in the refinement with isotropic thermal parameters. Refinement based on F_o by blocked full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged satisfactorily at $R_F = 0.038$ ($R_w = 0.046$). A final difference Fourier calculation revealed residual electron density only in the vicinity of the disordered ring S(2) $\cdots$ C(28) (minimum and maximum residual densities -1.3 and 4.1 e/Å^3 near S(2); next peak 1.3 e/Å^3). Crystal data and details of the structure determination are listed in Table 3. Scattering factors were taken from Cromer and Mann [15]. Anomalous dispersion factors are those given by Cromer and Liberman [16]. All calculations were carried out on the CDC-Cyber 962-31 170/760 computer of the University of Groningen with the program packages XTAL [17], EUCLID (calculation of geometric data) [18] and a locally modified version of the program PLUTO (preparation of illustrations) [19].

Supplementary material available. Tables of hydrogen atom positions, thermal parameters, a complete list of bond distances and angles, tables of F_Q, F_C and $\sigma(F)$, and a perspective ORTEP drawing (50% level) are available from the authors.

References and notes

1 The following abbreviations are used: Cp* = η^5-C$_5$Me$_5$; Cp″ = η^5-1,3-C$_5$H$_3$(SiMe$_3$)$_2$; THF = tetrahydrofuran; THT = tetrahydrothiophene; Cent = centroid of a Cp* ligand; lw = linewidths of the NMR resonances at half maximum.

2 (a) R.F. Jordan, W.E. Dasher and S.F. Echols, J. Am. Chem. Soc., 108 (1986) 1718; (b) R.F. Jordan, C.S. Bajgor, W.E. Dasher and A.L. Rheingold, Organometallics, 6 (1987) 1041; (c) J.J. Eisch, A.M.

Piotrowski, S.K. Brownstein, E.J. Gabe and F.L. Lee, J. Am. Chem. Soc., 107 (1985) 7219; (d) M. Bochmann and L.J. Wilson, J. Chem. Soc., Chem. Commun., (1986) 1610; (e) Z. Lin, J.-F. Le Marechal, M. Sabat and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 4127; (f) K. Berhalter and U. Thewalt, J. Organomet. Chem., 332 (1987) 123; (g) H. Aslan, J. Forster, K. Yunlu and R.D. Fischer, ibid., 355 (1988) 79; (h) Th. Klapotke, Polyhedron, 7 (1988) 1221; (i) U. Thewalt and W. Lasser, J. Organomet. Chem., 363 (1989) C12; (j) M. Bochmann, A.J. Jagger, L.M. Wilson, M.B. Hursthouse and M. Motevalli, Polyhedron, 8 (1989) 1838; (k) R.F. Jordan, P.K. Bradley, R.E. Lapointe and D.F. Taylor, New J. Chem., 14 (1990) 505; (l) J.J.W. Eshuis, Y.Y. Tan, J.H. Teuben and J. Renkema, J. Mol. Catal., 62 (1990) 277.

3 (a) W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller and D. Alvarez, Jr., Organometallics, 9 (1990) 2124; (b) P.N. Hazin, J.W. Bruno and G.K. Schulte, ibid., 9 (1990) 416.

4 (a) H.J. Heeres, J. Renkema, M. Booij, A. Meetsma and J.H. Teuben, Organometallics, 7 (1988) 2495; (b) H.J. Heeres, J.H. Teuben and R.D. Rogers, J. Organomet. Chem., 364 (1989) 87.

5 Recent investigations have shown that the B–C or phenyl–CH bonds of BPh_4 anions may be activated under certain conditions. See: (a) G.G. Hlatky, H.W. Turner and R.R. Eckman, J. Am. Chem. Soc., 111 (1989) 2728; (b) C. Bianchini, A. Meli, F. Laski, F. Vizza and P. Zanolli, Inorg. Chem., 28 (1989) 227.

6 (a) A.B. Sigalov, L.F. Rybakova, O.P. Syutkina, R.R. Shifrina, Yu.S. Bogachev, I.L. Zhuravleva and I.P. Beletskaya, Bull. Acad. Sci. USSR., Ser. Chem. Soc., (1983) 833; (b) D.L. Clark, A.P. Sattelberger, S.G. Bott and R.N. Vrtis, Inorg. Chem., 28 (1989) 1771.

7 W.J. Evans, J.M. Olofson, H. Zhang and J.L. Atwood, Organometallics, 7 (1988) 629.

8 M. Booij, A. Meetsma and J.H. Teuben, Organometallics (accepted).

9 Ionic radii (6-coordinate compounds) are: Ce^{3+}, 1.01 Å; Sm^{3+}, 0.958 Å. See: R.D. Shannon, Acta Crystallogr., A32 (1976) 751.

10 B.J. Barker and P.J. Sears, J. Phys. Chem., 78 (1974) 2687.

11 H.J. Heeres and J.H. Teuben, Organometallics, 10 (6) (1991) (in press).

12 A.L. Spek, J. Appl. Crystallogr., 21 (1977) 578.

13 Y. Le Page, J. Appl. Crystallogr., 20 (1987) 264.

14 G.M. Sheldrick, SHELXS86, Program for crystal structure solution, Univ. of Göttingen, 1986.

15 D.T. Cromer and J.B. Mann, Acta Crystallogr., A24 (1968) 321.

16 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.

17 S.R. Hall and J.M. Stewart (Eds.) XTAL2.6 User's Manual, Universities of Western Australia, Australia and Maryland, USA, 1987.

18 A.L. Spek, The EUCLID package, in D. Sayre (Ed), Computational Crystallography, Oxford Univ. Press, London, 1982, p. 528.

19 A. Meetsma, Extended version of the program PLUTO, Univ. of Groningen, 1986, unpublished; W.D.S. Motherwell and W. Clegg, PLUTO, program for plotting molecular and crystal structures, Univ. of Cambridge, 1978, unpublished.