Monatshefte für Chemie 128, 961–967 (1997)

Monatshefte für Chemie
Chemical Monthly

Synthesis and X-ray Crystal Structure of [1,3-*Bis*(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane]hafnium(IV) Dichloride

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Summary. The tetramethyldisiloxane-bridged hafnocene complex [$HfCl_2\{\mu$-(η^5-$C_5H_4)SiMe_2OSiMe_2(\eta^2$-$C_5H_4)\}$] (**1**) has been prepared by the reaction of $HfCl_4$ with the dilithiated *bis*(cyclopentadienyl)disiloxane $(LiC_5H_4SiMe_2)_2O$ in a molar ratio of 1:2. The new compound was characterized by spectroscopic and X-ray diffraction methods. The crystals are monoclinic of space group $P2_1/c$ and isostructural with the corresponding complexes of titanium and zirconium. The unit cell dimensions are $a = 13.51(1)$ Å, $b = 8.672(7)$ Å, $c = 15.41(1)$ Å, $\beta = 97.15(2)°$, and $Z = 4$.

Keywords. Hafnium; Cyclopentadienyl; *ansa*-Metallocenes; X-ray analysis.

Darstellung und Röntgenkristallstruktur von [1,3-*Bis*(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxan]hafnium(IV)dichlorid

Zusammenfassung. Der tetramethyldisiloxan-überbrückte Hafnocenkomplex [$HfCl_2\{\mu$-(η^5-C_5H_4)-$SiMe_2OSiMe_2(\eta^2$-$C_5H_4)\}$] (**1**) wurde durch Umsetzung von $HfCl_4$ mit dem lithiierten *Bis*(cyclopentadienyl)disiloxan $(LiC_5H_4SiMe_2)_2O$ im Molverhältnis 1:2 dargestellt. Die neue Verbindung wurde spektroskopisch und röntgenographisch charakterisiert. Sie kristallisiert in der monoklinen Raumgruppe $P2_1/c$ und ist isostrukturell mit den entsprechenden Titan- und Zirkoniumkomplexen. Die Dimensionen der Einheitszelle sind $a = 13.51(1)$ Å, $b = 8.672(7)$ Å, $c = 15.41(1)$ Å, $\beta = 97.15(2)°$ und $Z = 4$.

Introduction

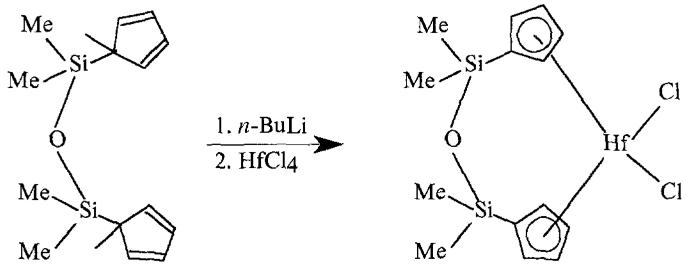
Metallocene derivatives of group 4 transition elements play a significant role in synthetic and catalytic organometallic chemistry. Numerous research efforts have been devoted to the development of modified metallocene-based catalysts that not only exhibit high activity, but also provide stereochemical control over polymer composition and structure. In this way, several group 4 *ansa*-metallocenes with various types of interannular bridges have been prepared [1–6]. In particular, *ansa*-titanocenes and zirconocenes have been intensively studied after *Brintzinger* and *Kaminsky* [1] had demonstrated their applicability as *Ziegler-Natta* catalysts. The bridge in the *ansa* metallocenes has been considered as an instrument to maintain the symmetry of the corresponding active cationic species that are formed during the initial stages of a stereospecific polymerization [7].

Metallocenes containing disiloxane bridges are significant in the research for development of potential supports for homogeneous catalysis [8]. Typical examples of these complexes are the previously described titanocene derivative $[TiCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**2**) [8] and its very recently published zirconocene analogue $[ZrCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**3**) [9]. Here we report the synthesis and structural characterization of the third member of this series, the hafnocene compound $[HfCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2\text{-}OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**1**).

Results and Discussion

Preparation and spectroscopic characterization

The *ansa* ligand, *bis*(cyclopentadienyl)tetramethyldisiloxane, was prepared from cyclopentadienyldimethylchlorosilane by treatment with half an equivalent of water according to the original *Schaaf* method [10]. Metallation of the ligand with *n*-BuLi, followed by the reaction of the dianion with hafnium tetrachloride, gave the *ansa* hafnocene complex **1** as colourless air-stable crystals after recrystallization from toluene-petroleum ether. This process may be summarized in the following scheme:



Scheme 1

Compound **1** was characterized by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. The IR spectrum of **1** contains the characteristic absorptions of the η^5-bonded cyclopentadienyl rings [11] and bands due to dimethylsilyl groups [12]. A strong absorption appearing at $1024\,cm^{-1}$ can be assigned to the Si–O–Si bridge [13]. The ^1H NMR spectrum shows the expected singlet for the equivalent methyl protons and two pseudotriplets corresponding to an AA′BB′ spin system for the cyclopentadienyl protons with an intensity ratio of 12:4:4, respectively. The ^{13}C NMR spectrum exhibits a resonance at $\delta = 0.91$ ppm which was assigned to the methyl carbon atoms and three resonances in the cyclopentadienyl region. One of these signals is due to the carbon atom bearing the silicium atom (C^1), another to the two carbon atoms α to (C^1) and the third to the carbon atoms β to (C^1). The chemical shifts in the ^1H and ^{13}C NMR spectra of **1** were similar to those reported for the zirconocene analogue **3** [9].

Description of the molecular structure of **1**

The configuration of molecule **1** is shown in Fig. 1 which also explains the labeling scheme used throughout the structure analysis. In this structure, the two cyclopentadienyl rings are bonded by the Si–O–Si chain (*ansa* ligand). If the Cp-ring centroids are considered as coordination sites, the coordination geometry about hafnium is a distorted tetrahedron, the other two coordination sites being occupied by the chlorine atoms. The ten Hf–C distances for the Cp rings of **1** fall in the fairly narrow range of 2.473–2.521 Å, establishing a pentahapto type of bonding of the five-membered rings to the hafnium atom. The Hf–Cp (ring centroid) distances are essentially identical and average 2.181 Å. As in the related titanium and zirconium complexes, the metal-Cl distances are slightly different (Hf–Cl(1) = 2.413 Å and Hf–Cl(2) = 2.431 Å) due to the distortion of the *ansa* ligand Si–O–Si with respect to the Cl–Hf–Cl angle [8, 9]. The Cl–Hf–Cl angle (97.61°) falls in the range of 94–105° which corresponds to that expected for d° metallocene chlorides [14]. Also, the Cp–Hf–Cp angle (131.32°) is normal and comparable with other published data (Table 1).

The two Cp rings are essentially planar. The maximum deviation of any carbon atom from planarity in the rings Cp(1) and Cp(2) is 0.006 and 0.007 Å, respectively. The C–C distances within the Cp rings range from 1.378 to 1.423 Å, and the C–C–C bond angles from 104.9° at the bridgehead carbon to 109.7° for the proximal carbons.

The Si atoms show almost tetrahedral coordination with C–Si–C angles ranging from 107.3° to 110.6°. The Si–C distances are fairly regular, varying between 1.848 Å for the Si–C(Me) to 1.876 Å for the Si–C(Cp) bonds (averaged values). The Si–O–Si bond angle of 142.7° and the mean Si–O bond length of 1.639 Å are typical for unstrained siloxanes [16].

The comparison of the data in Table 1 shows that the molecular structure of **1** exhibits practically the same general structural features as the related complexes **2**–**4**.

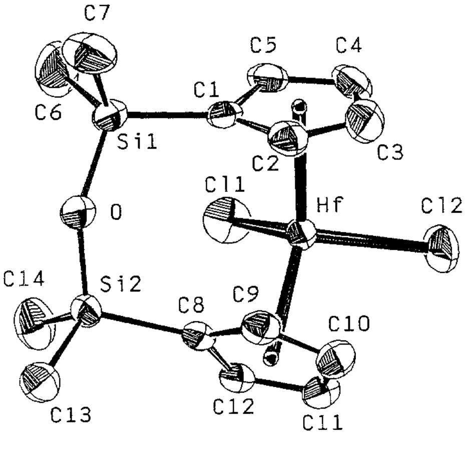


Fig. 1. Molecular structure and atom numbering scheme of [$HfCl_2\{\mu$-(η^5-C_5H_4)$SiMe_2OSiMe_2$-(η^5-C_5H_4)$\}$]

Table 1. Characteristic structural data (averaged values) of $[HfCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**1**) in comparison with corresponding parameters of the related complexes $[TiCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**2**), $[ZrCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}]$ (**3**), and $[HfCl_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)\}]$ (**4**)

	M–Cl (Å)	*M*–Cp (Å)	Cl–*M*–Cp (°)	Cp–*M*–Cp (°)	Si–O (Å)	Si–O–Si (°)	Ref.
1	2.422	2.181	97.61	131.3	1.639	142.7	this work
2	2.435	2.205	98.71	130.9	1.631	143.5	[8]
3	2.360	2.068	96.22	130.8	1.632	141.5	[9]
4	2.423	2.176	95.87	129.5	–	–	[15]

Experimental

General methods and reactants

All manipulations involving reactive organometallics were performed under an inert atmosphere of argon using standard *Schlenk* techniques. Solvents were thoroughly dried and degassed before use. $HfCl_4$ (Aldrich), $SiMe_2Cl_2$, and *n*-BuLi (Merck) were obtained commercially and used as received. $(C_5H_5SiMe_2)_2O$ was prepared as previously described [10]. Elemental analyses (C, H) were performed with a Perkin-Elmer 240C microanalyzer. Solid-state IR spectra were recorded in the 4000–500 cm^{-1} region using a Perkin-Elmer 16 PC FT spectrophotometer. ^1H and ^{13}C NMR spectra were taken on a Bruker AMX-400 spectrometer.

(1,3-Bis(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)hafnium (IV) dichloride

To a stirred solution of $(C_5H_5SiMe_2)_2O$ (2.86 g, 10.9 mmol) in *THF* (100 ml), *n*-butyllithium (13.7 ml, 21.9 mmol) as a solution in hexane was added slowly at room temperature. After stirring for 2 h, a solution of hafnium tetrachloride (3.5 g, 10.9 mmol) in *THF* (30 ml) was added. The reaction mixture was stirred overnight at 20°C. Volatiles were removed under vacuum, and the residue was extracted with boiling toluene. Filtration of the hot solution gave a pale yellow filtrate which, upon concentration, addition of petroleum ether, and cooling to −20°C, gave colourless crystals of the title compound (2.39 g, 43%; m.p.: 172°C).

^1H NMR ($CDCl_3$): $\delta = 0.41$ (s, 12 H, $SiMe_2$), 6.47 (t, 4H, $J = 2.3$ Hz, C_5H_4), 6.79 (t, 4H, $J = 2.3$ Hz, C_5H_4) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 0.91$ ($SiMe_2$), 114.6, 121.3, 125.6 (Cp rings) ppm; IR (KBr): ν(Si–O–Si) = 1024 cm^{-1}.

X-ray crystallographic study

Crystals of **1** suitable for X-ray diffraction were grown by slow cooling of a toluene-petroleum ether solution to −20°C. A crystal with approximate dimensions 0.20 × 0.28 × 0.40 mm was mounted in air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$; they appear in Table 2, along with other crystal collection and refinement data.

Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. *Lorentz*, polarization, and Ψ-scan absorption correction were applied using Crystal Logic software.

The structure was solved by direct methods using the SHELXS-86 [17] program and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 [18]. Hydrogen atoms of C2, C6, C7 and C13 were introduced at calculated positions as riding on bonded atoms; the rest were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

The positional parameters and the equivalent isotropic temperature factors for the non-hydrogen atoms are collected in Table 3. Hydrogen atomic coordinates and a list of structure factors can be obtained from the authors. A selection of bond distances and bond angles is given in Table 4.

Table 2. Summary of x-ray data

Empirical formula	$C_{14}H_{20}Cl_2OSi_2Hf$
Colour (habit)	Colourless prisms
Formula weight	509.87
Temperature (K)	298
Radiation, wavelength	MoKα, 0.71073 Å
Space group	$P2_1/c$
a(Å)	13.51(1)
b(Å)	8.672(7)
c(Å)	15.41(1)
β (°)	97.15(2)
V(Å^3)	1791(3)
Z	4
$D_{\mathrm{calcd}}/D_{\mathrm{measd}}$ (g·cm^{-3})	1.891/1.88
Max. abs. correction mode	1.36
Abs. coeff (μ, mm^{-1})	6.250
Scan mode / speed (°/min)	θ–2θ/3.2
Scan range (°)	2.5 $+\alpha_1\alpha_2$ separation
θ range (°)	1.52 to 24.99
Reflections collected	3259
Independent reflections	3131 [R(int)= 0.0280]
Range of h, k, l	$-15 \rightarrow 16$, $0 \rightarrow 10$, $-18 \rightarrow 0$
F(000)	984
$[\Delta\sigma]_{\max}$	0.002
W^a	$a = 0.0470$, $b = 3.1327$
$[\Delta\rho]_{\max}/[\Delta\rho]\min$ (e/Å^3)	1.692 and -1.267
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3131 /0/228
Goodness-of-fit on F^2	1.130
R indices [2969 refs $I > 2\sigma(I)$]^b	$R_1 = 0.0331$, $wR_2 = 0.0871$
R indices (all data)	$R_1 = 0.0348$, $wR_2 = 0.0890$

[a] $W = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\mathrm{Max}(F_o^2, 0) + 2Fc^2)/3$

[b] R_1 based on Fs, wR_2 based on F^2

Table 3. Positional and equivalent thermal parameters ($\times 10^4$) of the non-H atoms; e.s.d.s in parentheses; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x	y	z	U_{eq}
Hf	1980(1)	970(1)	1796(1)	28(1)
Cl(1)	3322(1)	−718(2)	1508(1)	51(1)
Cl(2)	1293(1)	1444(2)	286(1)	58(1)
Si(1)	2317(1)	−1128(2)	4016(1)	41(1)
Si(2)	3801(1)	1573(2)	3883(1)	30(1)
O	3062(3)	326(4)	4285(2)	41(1)
C(1)	1482(4)	−692(60)	2976(3)	33(1)
C(2)	744(4)	484(7)	2836(4)	39(1)
C(3)	223(5)	332(10)	2013(5)	53(2)
C(4)	586(5)	−979(7)	1612(5)	51(2)
C(5)	1328(4)	−1601(7)	2203(4)	38(1)
C(6)	3041(7)	−2884(9)	3863(6)	83(3)
C(7)	1504(7)	−1363(12)	4903(5)	84(3)
C(8)	3093(3)	2462(5)	2884(3)	29(1)
C(9)	2146(4)	3188(6)	2825(4)	35(1)
C(10)	1906(5)	3817(7)	1987(5)	45(1)
C(11)	2732(4)	3553(7)	1516(4)	41(1)
C(12)	3450(4)	2742(6)	2071(3)	34(1)
C(13)	4122(5)	3098(7)	4704(4)	47(1)
C(14)	4936(5)	651(9)	3583(5)	55(2)

Table 4. Selected bond distances and bond angles for $[\mathrm{HfCl_2}\{\mu\text{-}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{SiMe_2OSiMe_2}(\eta^5\text{-}\mathrm{C_5H_4})\}]$

Bond distances (Å)			
Hf–Cl(1)	2.413(2)	Si(1)–O	1.633(4)
Hf–Cl(2)	2.431(2)	Si(1)–C(1)	1.880(6)
Hf–C(1)	2.478(5)	Si(1)–C(6)	1.841(8)
Hf–C(2)	2.490(5)	Si(1)–C(7)	1.869(8)
Hf–C(3)	2.500(6)	Si(2)–O	1.645(4)
Hf–C(4)	2.521(6)	Si(2)–C(8)	1.873(5)
Hf–C(5)	2.506(5)	Si(2)–C(13)	1.845(6)
Hf–C(8)	2.473(5)	Si(2)–C(14)	1.838(7)
Hf–C(9)	2.485(5)		
Hf–C(10)	2.489(6)		
Hf–C(11)	2.518(6)		
Hf–C(12)	2.504(5)		
Hf–Cp(1)	2.177(1)		
Hf–Cp(2)	2.185(1)		
Angles (°)			
Cl(1)–Hf–Cl(2)	97.61	O–Si(1)–C(1)	110.3(2)
Cl(1)–Hf–Cp(1)	105.87(4)	O–Si(2)–C(8)	108.0(2)
Cl(1)–Hf–Cp(2)	106.74(1)	Si(1)–O–Si(2)	142.7(3)
Cl(2)–Hf–Cp(1)	105.27(4)	Torsional angles (°)	
Cl(2)–Hf–Cp(2)	105.09(5)	C(1)Si(1)OSi(2)	−45.20
Cp(1)–Hf–Cp(2)	131.32(1)	Si(1)OSi(2)C(8)	49.93

Cp(1) and Cp(2) refer to the centroids of the cyclopentadienyl rings C(1)–C(5) and C(8)–C(12), respectively

Acknowledgements

We are grateful to Dr. *A. Troganis*, Dept. Chem., University of Ioannina (Greece), for recording the ^{1}H and ^{13}C NMR spectra. *C. P. Raptopoulou* thanks Mrs. *Athina Athanassiou* for financial support.

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Received March 10, 1997. Accepted May 12, 1997