η^6-Arene derivatives of titanium(IV), zirconium(IV) and hafnium(IV) [1]

Fausto Calderazzo [a], Isabella Ferri [a], Guido Pampaloni [a,*], Sergei Troyanov [b,*,2]

[a] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Via Risorgimento 35, I-56126 Pisa, Italy*
[b] *Moscow State University, Chemistry Department, Vorobjevy Gory, 119899 Moscow, Russia*

Abstract

The structure of the ionic product $[Ti(\eta^6\text{-}Me_6C_6)Cl_3]AlCl_4$ **1** has been determined by an X-ray diffraction experiment: orthorhombic; $a = 12.890(4)$, $b = 8.609(2)$, $c = 9.168(3)$ Å; $V = 1017.4(6)$ Å^3, $Z = 2$; $d_{calc} = 1.584$ g cm^{-3}. Tetrachlorogallates of titanium(IV) of general formula $[Ti(\eta^6\text{-arene})Cl_3]GaCl_4$ (arene $= 1,2,4,5\text{-}Me_4C_6H_2$, Me_6C_6), have been obtained by reaction of $TiCl_4$ with the appropriate arene in the presence of $GaCl_3$ in toluene. Formation of complexes with less methyl-substituted arene ligands (MeC_6H_5, $1,4\text{-}Me_2C_6H_4$ and $1,3,5\text{-}Me_3C_6H_3$) has been established by ^{13}C-NMR spectroscopy.

The MCl_4/Me_6C_6/benzene system gives, either in the presence or in the absence of aluminium trichloride, covalent (M = Zr) or ionic (M = Hf) compounds of formula $Zr(\eta^6\text{-}Me_6C_6)Cl_2(\mu\text{-}Cl)_3ZrCl_3$ **4** and $[Hf(\eta^6\text{-}Me_6C_6)Cl_3]Hf_2Cl_9$ **5**. Compounds **4** and **5** have been fully characterized by conventional methods including X-ray crystallography. Compound **5**: orthorhombic; $a = 17.662(6)$, $b = 8.960(3)$, $c = 17.683(6)$ Å; $V = 2798.4(16)$ Å^3, $Z = 4$; $d_{calc} = 2.666$ g cm^{-3}.

Keywords: Titanium; Zirconium; Hafnium; η-Arene derivatives; X-ray structures

1. Introduction

Vacating a coordination position is frequently an essential prerequisite for subsequent metal–ligand bond formation. When a metal halide is involved and a coordination position around the metal is to be vacated without modifying its oxidation state, use can be made of several reagents, the more frequently used being silver or thallium(I) salts of weakly coordinating anions (e.g. $AgBF_4$ or $TlPF_6$) [1] or aluminium halides.

As far as arene derivatives are concerned, treatment of a metal halide with aluminium trihalide in the presence of an aromatic hydrocarbon has allowed the preparation of ionic bis-arene derivatives of transition elements [2–4], uranium [5] and Main Group elements [6,7]. Also, the reaction of metal halides with AlX_3 may result in the formation of covalently bonded halide-

bridged complexes involving both aluminium and the metal coordinating the aromatic hydrocarbon. A recent example of this type is represented by the formation of the tetrachloroaluminato η^6-arene complexes of lanthanide(III) [8]. Moreover, derivatives of Tl(I) [9], Pb(II) [10], and Sn(II) [11] have been obtained and structurally characterized, thus showing the ability of Main Group elements to coordinate an arene ligand even in an η^6 fashion [12]. The chemistry and crystallography of Group 4 metals have recently been reviewed [13].

Thus, aluminium halides may behave in two different ways in their reactions with metal halides in the presence of aromatic hydrocarbons: (i) they may function as dehalogenating agents thus leaving free coordination sites available for the arene; (ii) they may add across the metal–halide bond with formation of arene-bonded $M(\mu\text{-}X)_n AlX_{4-n}$ systems, as in the case of Main Group elements and lanthanides.

Recent work from our Laboratories [14] has extended some earlier work [15] on the reaction between $TiCl_4$ and aromatic hydrocarbons. By use of $AlCl_3$ as halide abstractor, ionic η^6-arene complexes of titanium(IV) were isolated as analytically pure solids. By this method,

---

the synthesis was extended to tetrahalo complexes other than the chloride, admittedly less stable:

$$TiX_4 + AlX_3 + arene \rightarrow \left[Ti(\eta^6\text{-arene})X_3\right]AlX_4 \quad (1)$$
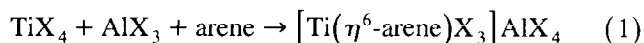
arene = $1,3,5\text{-Me}_3C_6H_3$, X = Cl, Br;

$1,2,4,5\text{-Me}_4C_6H_2$, X = Cl;

arene = Me_6C_6, X = Cl, **1**, Br, I.

Halide abstraction by AlX_3 from TiX_4 is consistent with the higher Al–Cl bond strength (511.3 ± 0.8 kJ mol^{-1}) with respect to the Ti–Cl bond strength (494 kJ mol^{-1}) in the diatomic molecules [16]. As the metal–chloride bond strength is expected to increase on descending a vertical sequence of elements from titanium to zirconium and hafnium, the halide abstracting capacity of $AlCl_3$ is expected to decrease in the same order. This paper reports some new results which confirm this expectation. In fact, both zirconium and hafnium are unaffected by $AlCl_3$, and η^6-arene complex formation occurs giving the covalent $Zr(\eta^6\text{-}Me_6C_6)Cl_2(\mu\text{-Cl})_3ZrCl_3$ **4** or the ionic $[Hf(\eta^6\text{-}Me_6C_6)Cl_3]Hf_2Cl_9$ **5** respectively.

Furthermore, as the Ga–Cl bond strength is 481 ± 13 kJ mol^{-1}, one would expect that $GaCl_3$ could still act as a halide abstractor from $TiCl_4$ if sufficient stability were gained by forming a bond to the aromatic hydrocarbon. This expectation has also been confirmed by the results of this paper.

Part of this work was communicated in a preliminary form [17].

2. Experimental section

All operations were carried out in a conventional vacuum line using standard Schlenk-tube techniques under an atmosphere of prepurified argon. The reaction vessels were oven dried prior to use. Solvents were dried by conventional methods.

Titanium was determined by measuring the absorbance at 410 nm after addition of H_2O_2 to the solution obtained by dissolving the sample in a mixture of dilute HNO_3 and H_2SO_4. Aluminium, gallium, hafnium and zirconium contents were determined by ICP-AES analyses using a Perkin-Elmer Elan 4000 instrument or by gravimetric determination as Al_2O_3, Ga_2O_3, HfO_2, and ZrO_2 respectively. Chloride analyses were performed using the Volhard method, after decomposition of the sample with a mixture of dilute HNO_3 and H_2SO_4.

Infrared spectra were recorded with a Perkin-Elmer model FT 1725X instrument on solutions or Nujol and polychlorotrifluoroethylene (PCTFE) mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. NMR spectra (^{1}H: 200 MHz, ^{13}C: 50 MHz, reference TMS) were recorded with a Varian Gemini 200 BB spectrometer. X-ray powder diffraction measurements were made with a HZG-4 powder diffractometer using Cu K α radiation.

The following reagents are commercially available and were used without further purification: $AlCl_3$ (Carlo Erba RPE), $GaCl_3$ (Fluka), Ph_3CCl (Fluka), $1,2,3,4\text{-}Me_4C_6H_2$ (Fluka), Me_6C_6 (Janssen Chimica). $TiCl_4$ (Carlo Erba) was distilled at atmospheric pressure and stored at 4°C under argon. $ZrCl_4$ (Fluka) and $HfCl_4$ (CESUS Chimie, France) were purified by treatment with boiling $SOCl_2$ followed by heating at 200°C (ca. 10^{-2} mmHg). The tetrahydrofuran adducts MCl_4-$(THF)_2$, M = Ti, Zr, Hf [18] and the hexamethylbenzene derivative $[Ti(\eta^6\text{-}Me_6C_6)Cl_3]AlCl_4$ **1** [14] were prepared according to the literature.

2.1. NMR study of the $TiCl_4 / GaCl_3 / arene$ system in C_6D_6 (arene = MeC_6H_5, $1,4\text{-}Me_2C_6H_4$ and $1,3,5\text{-}Me_3C_6H_3$)

$GaCl_3$ and the arene were added to C_6D_6 (1 ml) in a 1 : 1 molar ratio, affording yellow solutions which were

Table 1
$^{13}C\{^1H\}$-NMR spectra of $[Ti(\eta^6\text{-}Me_6C_6)Cl_3]GaCl_4$ in C_6D_6

Arene	Uncoordinated arene δ (ppm)	(Arene + $GaCl_3$) + $TiCl_4$ δ (ppm)	$\Delta\delta$ (ppm)
MeC_6H_5	137.86	154.02	+16.16
	129.34	135.82 (t, J_{CD} = 25 Hz)	+6.48
	128.54	131.6 (t, J_{CD} = 25 Hz)	+3.06
	125.68	a	—
	21.62	24.27	+2.86
$1,4\text{-}Me_2C_6H_4$	134.64	150.26	+15.62
	129.24	138–136(m)	—
	21.62	23.91	+2.94
$1,3,5\text{-}Me_3C_6H_3$	137.49	154.61	+17.12
	127.33	134.01 (t, J_{CD} = 25 Hz)	+7.33
	21.24	24.82	+3.58

a Signals superimposed with those of C_6D_6.

examined by $^{13}C\{^1H\}$-NMR spectroscopy. The solution was then treated with $TiCl_4$ (molar ratio $TiCl_4/GaCl_3$ 1), causing the formation of a biphasic liquid system consisting of a pale yellow upper layer and a red lower one. The red lower layer was examined by $^{13}C\{^1H\}$-NMR spectroscopy (Table 1).

2.2. Synthesis of $[Ti(\eta^6$-1,2,4,5-$Me_4C_6H_2)Cl_3]GaCl_4$ 2

Addition of $GaCl_3$ (0.37 g, 2.10 mmol) to a solution of $TiCl_4$ (0.38 g, 2.00 mmol) and 1,2,4,5-tetramethylbenzene (0.29 g, 2.16 mmol) in toluene (20 ml) caused the immediate formation of a red biphasic liquid system. After 4 h stirring at room temperature, the upper layer was removed via cannula while the lower one was treated with heptane (20 ml), causing the formation of a yellow solid which was filtered off, dried in vacuo (0.19 g, 16% yield) and identified as $[Ti(\eta^6$-1,2,4,5-$Me_4C_6H_2)Cl_3]GaCl_4 * 0.3$ toluene. Anal. Found: Cl, 47.4; Ti, 8.7. $C_{12.1}H_{16.4}Cl_7GaTi$ Calc. Cl, 47.0; Ti, 9.1%. $^{13}C\{^1H\}$-NMR (CD_2Cl_2) δ: 153.21 (s), 141.69 (s), 25.13 (s) ppm. ^1H-NMR (CD_2Cl_2) δ: 8.12 (s), 2.84 (s) ppm. The solvent from the filtered solution was evaporated in vacuo affording a liquid substance which was not further characterized.

2.3. Synthesis of $[Ti(\eta^6$-$Me_6C_6)Cl_3]GaCl_4$ 3

Addition of $GaCl_3$ (0.32 g, 1.82 mmol) to a solution of $TiCl_4$ (0.35 g, 1.84 mmol) and hexamethylbenzene (0.30 g, 1.85 mmol) in toluene (30 ml) caused the immediate formation of a red biphasic liquid system. After 12 h stirring at room temperature, a bright yellow solid formed. The solid was recovered by filtration, washed with heptane $(2 \times 5$ ml) and dried in vacuo, affording 0.69 g of $[Ti(\eta^6$-$Me_6C_6)Cl_3]GaCl_4 * 0.3$ toluene (67% yield). Anal. Found: Cl, 44.0; Ti, 9.1. $C_{14.1}H_{20.4}Cl_7GaTi$ Calc.: Cl, 44.7; Ti, 8.6%. IR (Nujol mull): 1602m, 1303m, 1290s, 1070s, 1012w, 988w, 797w, 450vs, 390s cm^{-1}. $^{13}C\{^1H\}$-NMR (CD_2Cl_2) δ: 151.10 (s), 22.45 (s) ppm. ^1H-NMR (CD_2Cl_2) δ: 2.81 (s) ppm.

2.4. Synthesis of $Zr(\eta^6$-$Me_6C_6)Cl_2(\mu$-$Cl)_3ZrCl_3$ 4

$ZrCl_4$ (2.78 g, 11.93 mmol) was added to a solution of hexamethylbenzene (0.99 g, 6.10 mmol) in benzene (100 ml). After 48 h stirring at room temperature the solid was recovered by filtration, washed with benzene $(2 \times 5$ ml) and dried in vacuo, affording 3.16 g of $Zr(\eta^6$-$Me_6C_6)Cl_2(\mu$-$Cl)_3ZrCl_3$ (86% yield). Anal. Found: Cl, 44.5; Zr, 29.5. $C_{12}H_{18}Cl_8Zr_2$ Calc.: Cl, 45.1; Zr, 29.0%. IR (PCTFE and Nujol mull): 2927w, 1440m, 1377s, 1262m, 1099m, 1065m-s, 803m, 750s, 599s, 449s cm^{-1}. ^1H-NMR (CD_2Cl_2) δ: 2.51 (s) ppm.

2.5. Synthesis of $[Hf(\eta^6$-$Me_6C_6)Cl_3]Hf_2Cl_9$ 5

To a solution of hexamethylbenzene (0.32 g, 1.97 mmol) in benzene (50 ml) $HfCl_4$ (1.78 g, 5.56 mmol) was added. After 48 h stirring at room temperature the solid was recovered by filtration, washed with benzene $(2 \times 5$ ml) and dried in vacuo, affording 1.73 g of $[Hf(\eta^6$-$Me_6C_6)Cl_3]Hf_2Cl_9$ (83% yield). Anal. Found: Cl, 35.5; Hf, 47.6. $C_{12}H_{18}Cl_{12}Hf_3$ Calc.: Cl, 37.9; Hf, 47.7%. IR (PCTFE and Nujol mull): 2927s, 2857w, 1456m, 1382s, 1263m, 1099m, 1068m-s, 1023m, 804m-s, 598s, 449s cm^{-1}. ^1H-NMR (CD_2Cl_2) δ: 2.82 (s) ppm.

2.6. Synthesis of hexamethylbenzene complexes from $MCl_4(THF)_2$, M = Ti, Zr, Hf

2.6.1. Titanium
$TiCl_4(THF)_2$ (0.96 g, 2.88 mmol) was added to a suspension of hexamethylbenzene (0.47 g, 2.90 mmol) and $AlCl_3$ (0.77 g, 5.77 mmol) in toluene (20 ml). The solids dissolved quickly, affording a red solution. After 2 h stirring an additional amount of $AlCl_3$ (0.41 g, 3.07 mmol) was added, causing the formation of a bright yellow solid. After 12 h stirring at room temperature, the solid was collected by filtration, washed with heptane (10 ml) and dried in vacuo. It was analytically and spectroscopically identified as $[Ti(\eta^6$-$Me_6C_6)Cl_3]AlCl_4$ (0.73 g, 52% yield) by comparison with an authentic sample obtained from $TiCl_4$, hexamethylbenzene and $AlCl_3$ as previously described [13].

2.6.2. Zirconium
$ZrCl_4(THF)_2$ (0.99 g, 2.62 mmol) was added to a solution of hexamethylbenzene (0.43 g, 2.65 mmol) in toluene (25 ml). The addition of $AlCl_3$ (0.69 g, 5.17 mmol) caused the solution to change from colourless to yellow. After 24 h stirring at room temperature the solid was recovered by filtration, washed with toluene (10 ml) and heptane (10 ml) and dried in vacuo, affording 0.65 g of $Zr(\eta^6$-$Me_6C_6)Cl_2(\mu$-$Cl)_3ZrCl_3$ (79% yield) (Cl and Zr analyses) whose IR spectrum was superimposable with that of compound 4, prepared as described above.

2.6.3. Hafnium
$HfCl_4(THF)_2$ (1.12 g, 2.41 mmol) was added to a solution of hexamethylbenzene (0.13 g, 0.80 mmol) in toluene (25 ml). The addition of $AlCl_3$ (0.64 g, 4.80 mmol) caused a change in colour of the solution, from colourless to yellow. After 24 h stirring at room temperature the solid was recovered by filtration, washed with toluene (5 ml) and heptane (5 ml) and dried in vacuo, affording 0.39 g of $[Hf(\eta^6$-$Me_6C_6)Cl_3]Hf_2Cl_9$ (42% yield) (Cl and Hf analyses) whose IR spectrum was

superimposable with that of compound **5**, prepared as described above.

2.7. Reaction of MCl_4 with Ph_3CCl: synthesis of $[Ph_3C][M_2Cl_9]$, $M = Zr$, Hf

Only the reaction with $ZrCl_4$ is described in detail, that with $HfCl_4$ being performed similarly. Ph_3CCl (0.27 g, 0.97 mmol) was added to a suspension of $ZrCl_4$ (0.45 g, 1.93 mmol) in CH_2Cl_2 (20 ml). Rapid dissolution of $ZrCl_4$ was observed, with formation of an orange–yellow solution. The volume of the solution was reduced in vacuo to 5 ml, followed by the addition of heptane (25 ml), causing the formation of a dark yellow crystalline solid (0.56 g, 78% yield) which was identified as $[Ph_3C][Zr_2Cl_9]$. Anal. Found: Cl, 42.4; Zr, 23.5. $C_{19}H_{15}Cl_9Zr_2$ Calc.: Cl, 42.8; Zr, 24.5%. IR (Nujol mull): 1582vs, 1481s, 1450vs, 1356vs, 1294s, 1185m-s, 995m, 840w, 806w, 767m, 701s, 623m, 609m cm^{-1}). $[Ph_3C][Hf_2Cl_9]$: yellow, 85% yield. Anal. Found: Cl, 34.7; Hf, 38.3. $C_{19}H_{15}Cl_9Hf_2$ Calc.: Cl, 34.7; HF, 38.8%. IR (Nujol mull): 1582vs, 1482s, 1450vs, 1356vs, 1294s, 1186m-s, 995m, 840w, 806w, 768m, 702s, 623w, 609w cm^{-1}.

2.8. X-ray structure determinations of 1, 4 and 5

Crystals of compounds **1**, **4**, and **5** were grown in sealed glass ampoules consisting of two compartments, one containing a dilute benzene solution of the compound, slowly concentrated by evaporation of the solvent into the other compartment, cooled at 0°C. The crystals were placed into thin-wall glass capillaries and sealed off.

Intensity data were collected on a single-crystal four-circle diffractometer STADI-4 (Stoe) at low temperature (compound **1**) or room temperature (compounds **4** and **5**). Crystallographic data and details of the structure determinations of compounds **1** and **5** are given in Table 2. In the case of the structure of **5**, an empirical absorption correction was applied based on Ψ-scanning of five reflections. All structures were solved using direct methods (SHELXS-86 [19]) and refined by SHELXS-93 [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in geometrically calculated positions supported by the difference Fourier maps (HFIX) and then treated (with common U_H) as belonging to the rigid CH_3 groups. The final difference maps showed no significant peaks above the general background. Atomic coordinates and equivalent thermal parameters are listed in Table 3, selected bond distances are given in Table 4.

3. Results and discussion

Recently, Bengtsson and coworkers [21], on the basis of spectroscopic investigations (NMR, Raman and UV–

Table 2
Crystal data and details of the structure determination of compounds $[Ti(\eta^6\text{-}Me_6C_6)Cl_3]AlCl_4$ **1** and $[Hf(\eta^6\text{-}Me_6C_6)Cl_3]Hf_2Cl_9$ **5**

Compound	1	5
Chemical formula	$C_{12}H_{18}AlCl_7Ti$	$C_{12}H_{18}Cl_{12}Hf_3$
Formula weight	485.29	1123.13
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pmn2_1$ (No. 31)	$Pca2_1$ (No. 29)
Cell parameters (Å)		
a	12.890(4)	17.662(6)
b	8.609(2)	8.960(3)
c	9.168(3)	17.683(6)
V (Å³)	1017.4(6)	2798.4(16)
Z	2	4
d_{calc} (g cm⁻³)	1.584	2.666
μ (cm⁻¹)	13.7	122.5
Crystal size (mm³)	0.1×0.2×0.2	0.15×0.15×0.35
Temperature (K)	160	293
θ_{max} (deg)	27	23
No. of unique reflections	1223	2026
No. of reflections with $F^2 > 2\sigma(F^2)$	1030	1842
No. of refined parameters	107	252
R_1 [a]	0.032	0.043
wR_2	0.069	0.105

[a] $R = \Sigma|\Delta F|/\Sigma|\Delta F_o|$; $F = F_o(hkl) - F_c(hkl)$.

vis) as well as liquid X-ray scattering, showed that $GaCl_3$ in benzene or $1,3,5\text{-}Me_3C_6H_3$ forms $1:1$ η^6 complexes. As far as $1,3,5\text{-}Me_3C_6H_3$ is concerned, the ^{13}C-NMR spectrum shows resonances due to the ring carbon atoms whose positions depend slightly on the $GaCl_3$ concentration and are in the range 136.3 to 140.2 ppm (the solvent is not specified).

We have observed that when a solution of arene (MeC_6H_5, $1,4\text{-}Me_2C_6H_4$, $1,3,5\text{-}Me_3C_6H_3$) in C_6D_6 is treated with the hydrocarbon soluble $GaCl_3$, the ^{13}C-NMR spectrum of the resulting yellow solution shows a downfield shift of the resonances due to both the ring and methyl carbon atoms (downfield shifts between 3 and 0.5 ppm with respect to the free arene in the same solvent are observed). Moreover, triplets with a separation between the peaks of ca. 25 Hz are present in the spectra, therefore suggesting that a H/D process has taken place, as already noticed in the $TiCl_4/AlCl_3/$ arene/C_6D_6 systems [14]. In the case of the $GaCl_3/1,3,5\text{-}Me_3C_6H_3/C_6D_5CD_3$ system, we observe the resonance due to the quaternary carbon atoms at 139.9 ppm (the resonance due to the same carbon atom in the absence of $GaCl_3$ is at 137.4 ppm in the same solvent).

The downfield shift becomes more pronounced upon addition of $TiCl_4$ to the previous solution of gallium trichloride (downfield shifts between 17 and 3 ppm with respect to the free arene), thus suggesting that η^6-arene complexes of titanium(IV) are formed. Although product isolation was not always possible due to the formation of intractable oils, tetrachlorogallate derivatives of

titanium(IV) of general formula [Ti(η^6-arene)Cl$_3$]GaCl$_4$, arene = 1,2,4,5-Me$_4$C$_6$H$_2$, Me$_6$C$_6$ have been isolated for the more methyl-substituted arenes as moisture-sensitive, crystalline, yellow–orange compounds.

Taking into consideration that no shift of the resonances of toluene was observed when treated with TiCl$_4$/AlCl$_3$ [14], it appears that GaCl$_3$ is a better promoter than AlCl$_3$ of arene complexation, shifting equilibrium (2) to the right:

$$\text{TiCl}_4 + \text{arene} + \text{MCl}_3 \underset{M=Al, Ga}{\rightleftharpoons} \left[\text{Ti}\left(\eta^6\text{-arene}\right)\text{Cl}_3\right]\text{MCl}_4 \qquad (2)$$
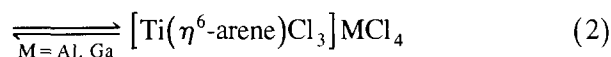
Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for compounds **1** and **5**

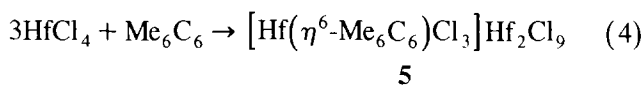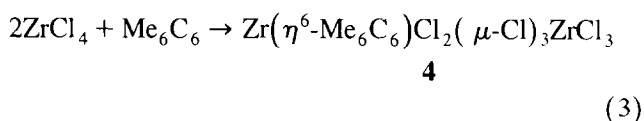| Atom	x	y	z	U_{eq} ($\mathring{A}^2$) [a]
Compound 1				
Ti	0	257(1)	1985(1)	19(1)
Cl(1)	1320(1)	−1336(1)	2100(1)	34(1)
Cl(2)	0	999(2)	−283(2)	66(1)
Cl(3)	5000	2964(2)	3472(2)	26(1)
Cl(4)	3642(1)	6207(1)	2260(1)	37(1)
Cl(5)	5000	3938(2)	−221(2)	58(1)
Al	5000	4832(2)	1952(2)	21(1)
C(1)	546(2)	1056(4)	4507(4)	19(1)
C(2)	1101(2)	2028(4)	3526(4)	21(1)
C(3)	554(3)	3009(4)	2538(4)	22(1)
C(11)	1123(3)	51(4)	5584(4)	26(1)
C(21)	2272(2)	2088(5)	3550(6)	33(1)
C(31)	1137(3)	4086(4)	1532(5)	34(1)
Compound 5				
Hf(1)	9687.4(6)	9437(1)	5380.3(6)	40(1)
Hf(2)	10837.2(5)	12081(1)	4391.9(6)	37(1)
Hf(3)	11922.4(6)	6452(1)	7247.3(6)	39(1)
Cl(1)	9956(4)	9954(8)	3962(3)	46(2)
Cl(2)	11125(3)	10025(7)	5366(4)	48(1)
Cl(3)	9720(4)	12341(7)	5328(4)	49(2)
Cl(4)	9664(6)	9465(10)	6702(4)	77(3)
Cl(5)	9922(5)	6899(7)	5153(4)	59(2)
Cl(6)	8386(4)	9411(9)	5147(5)	67(2)
Cl(7)	10266(4)	13785(9)	3556(5)	62(2)
Cl(8)	11580(5)	13805(8)	5057(5)	65(2)
Cl(9)	11768(4)	11204(8)	3572(5)	64(2)
Cl(10)	12475(5)	7313(10)	6147(5)	77(2)
Cl(11)	10804(4)	5427(10)	6845(5)	63(2)
Cl(12)	11585(5)	8599(8)	7879(5)	69(2)
C(1)	13071(16)	4673(32)	7263(18)	52(7)
C(2)	12476(14)	3732(25)	7408(12)	36(5)
C(3)	12007(15)	4004(28)	8049(16)	46(6)
C(4)	12182(13)	5169(29)	8563(13)	39(6)
C(5)	12812(14)	6096(26)	8394(18)	47(7)
C(6)	13270(15)	5889(26)	7762(13)	38(6)
C(11)	13604(19)	4322(41)	6572(18)	74(10)
C(21)	12299(20)	2442(33)	6876(20)	70(10)
C(31)	11370(14)	2962(34)	8256(18)	59(8)
C(41)	11729(14)	5363(34)	9270(14)	50(7)
C(51)	13038(16)	7261(34)	8988(16)	55(7)
C(61)	13909(19)	6772(45)	7587(24)	87(11)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Selected bond distances and angles for compounds **1** and **5**

Compound 1			
Ti–Cl(1)	2.188(1)	C(1)–C(1a)	1.408(6)
Ti–Cl(2)	2.176(2)	C(1)–C(2)	1.421(5)
Ti–C(1)	2.513(3)	C(1)–C(11)	1.509(5)
Ti–C(2)	2.517(3)	C(2)–C(3)	1.425(5)
Ti–C(3)	2.526(3)	C(2)–C(21)	1.511(4)
Al–Cl(3)	2.128(2)	C(3)–C(3a)	1.429(7)
Al–Cl(4)	2.132(1)	C(3)–C(31)	1.508(5)
Al–Cl(5)	2.136(2)		
Cl(2)–Ti–Cl(1)	103.30(5)	Cl(1a)–Ti–Cl(1)	102.11(6)
Cl(2)–Ti–C(2a)	111.04(10)	Cl(1)–Ti–C(2)	85.07(8)
Cl(1)–Ti–C(3)	110.99(8)		
Compound 5			
Hf(1)–Cl(1)	2.595(6)	C(1)–C(2)	1.37(4)
Hf(1)–Cl(2)	2.593(6)	C(1)–C(6)	1.45(4)
Hf(1)–Cl(3)	2.604(6)	C(1)–C(11)	1.57(4)
Hf(1)–Cl(4)	2.337(8)	C(2)–C(3)	1.42(4)
Hf(1)–Cl(5)	2.346(7)	C(2)–C(21)	1.52(4)
Hf(1)–Cl(6)	2.335(7)	C(3)–C(4)	1.42(4)
Hf(2)–Cl(1)	2.576(7)	C(3)–C(31)	1.51(4)
Hf(2)–Cl(1)	2.576(7)	C(4)–C(5)	1.42(3)
Hf(2)–Cl(2)	2.573(6)	C(4)–C(41a)	1.49(3)
Hf(2)–Cl(3)	2.586(7)	C(5)–C(6)	1.39(4)
Hf(2)–Cl(7)	2.353(7)	C(5)–C(51)	1.53(4)
Hf(2)–Cl(8)	2.343(7)	C(6)–C(61)	1.41(4)
Hf(2)–Cl(9)	2.328(7)		
Hf(3)–Cl(10)	2.310(8)		
Hf(3)–Cl(11)	2.292(7)		
Hf(3)–Cl(12)	2.303(7)		
Hf(3)–C(1)	2.58(3)		
Hf(3)–C(2)	2.64(2)		
Hf(3)–C(3)	2.62(3)		
Hf(3)–C(4)	2.63(2)		
Hf(3)–C(5)	2.59(3)		
Hf(3)–C(6)	2.60(3)		
Cl(1)–Hf(1)–Cl(3) 77.5(2)		Cl(6)–Hf(1)–Cl(1)	90.6(3)
Cl(2)–Hf(1)–Cl(1) 77.0(2)		Cl(6)–Hf(1)–Cl(2)	164.6(3)
Cl(4)–Hf(1)–Cl(1) 65.5(3)		Cl(6)–Hf(1)–Cl(3)	91.5(3)
Cl(4)–Hf(1)–Cl(2) 91.4(3)		Cl(6)–Hf(1)–Cl(4)	99.2(3)
Cl(4)–Hf(1)–Cl(3) 91.5(3)		Cl(6)–Hf(1)–Cl(5)	97.7(3)
Cl(4)–Hf(1)–Cl(5)100.6(3)		Cl(11)–Hf(3)–Cl(12)	105.2(3)
Cl(5)–Hf(1)–Cl(1) 88.6(2)		Cl(11)–Hf(3)–Cl(10)	103.7(3)
Cl(5)–Hf(1)–Cl(2) 91.3(2)		Cl(12)–Hf(3)–Cl(10)	103.8(3)
Cl(5)–Hf(1)–Cl(3)163.4(2)			

It has been found that a suspension of MCl$_4$, M = Zr or Hf, stirred for 48 h at room temperature in Me$_6$C$_6$ containing benzene, led to η^6-Me$_6$C$_6$ derivatives of zirconium(IV) and hafnium(IV) according to:

$$2\text{ZrCl}_4 + \text{Me}_6\text{C}_6 \rightarrow \text{Zr}\left(\eta^6\text{-Me}_6\text{C}_6\right)\text{Cl}_2\left(\mu\text{-Cl}\right)_3\text{ZrCl}_3$$

$$\mathbf{4}$$

$$(3)$$

$$3\text{HfCl}_4 + \text{Me}_6\text{C}_6 \rightarrow \left[\text{Hf}\left(\eta^6\text{-Me}_6\text{C}_6\right)\text{Cl}_3\right]\text{Hf}_2\text{Cl}_9 \qquad (4)$$

$$\mathbf{5}$$

Owing to their moderate solubility and stability in dichloromethane, the derivatives were studied by ^{1}H-NMR spectroscopy. The spectra show a singlet at δ 2.51 ppm in the case of zirconium and at δ 2.82 ppm for the hafnium derivative. By taking into consideration that the ionic titanium(IV) hexamethylbenzene derivatives $[Ti(\eta^6-Me_6C_6)Cl_3]X$, $X = Ti_2Cl_9$, $AlCl_4$ show a single resonance at δ 2.8 ppm (almost independent of the anion) [14,15c], the compound could be formulated as $[Hf(\eta^6-Me_6C_6)Cl_3]Hf_2Cl_9$. The assignment was confirmed by the X-ray diffractometric experiment described later in this paper.

In contrast the singlet at higher field in the case of zirconium could be explained by the formation of a neutral arene derivative of zirconium(IV). While this work was in progress, a compound of molecular structure $Zr(\eta^6-Me_6C_6)Cl_2(\mu-Cl)_3ZrCl_3$ was reported by Floriani and coworkers [22], obtained by reaction of $ZrCl_4$ with Me_6C_6 in boiling 1,2-dichlorobenzene. In spite of the drastically different synthetic procedure compound 4 was found, by X-ray crystallography on a single crystal [23], to be identical with that obtained by Floriani and coworkers.

Owing to the low solubility of zirconium and hafnium tetrachlorides in the reaction medium, the reactions require some hours to go to completion. They become faster using the tetrahydrofuran adducts $MCl_4(THF)_2$, which are monomeric in the solid state at least for titanium and zirconium [24]. With these precursors, $AlCl_3$ must also be used in order to complex the THF molecule released in the reaction [25]. We have observed that, even working in the presence of an excess of $AlCl_3$, no halide abstraction from the tetrachloride by $AlCl_3$ takes place. Moreover, the reaction of MCl_4 with $AlCl_3/Me_6C_6$ in benzene gave compounds 4 and 5 contaminated by variable amounts of aluminum chloride due to the low solubility of $AlCl_3$ in benzene.

Compounds 1 and 5 have been studied by X-ray diffraction methods and their structural data, in combination with those of compound 4, definitely establish that the hexamethylbenzene derivatives of titanium, zirconium and hafnium in the oxidation state IV exist either as cationic or covalent species.

The structure of compound 1 consists of $[Ti(\eta^6-Me_6C_6)Cl_3]^+$ cations and $[AlCl_4]^-$ anions. The cation in 1 (Fig. 1) shows a higher symmetry than that reported previously for the same cation in $[Ti(\eta^6-Me_6C_6)Cl_3]Ti_2Cl_9$ [15c] due to the fact that the Ti and Cl(2) atoms lie on a mirror plane. At the same time, the three-legged piano stool geometry of the cation has a non-crystallographic C_{3v} symmetry. The Ti–Cl (2.176–2.188 Å) and Ti–C (2.513–2.526 Å) bond distances and the Cl–Ti–Cl bond angles (102.1–103.3°) are in narrow ranges of values.

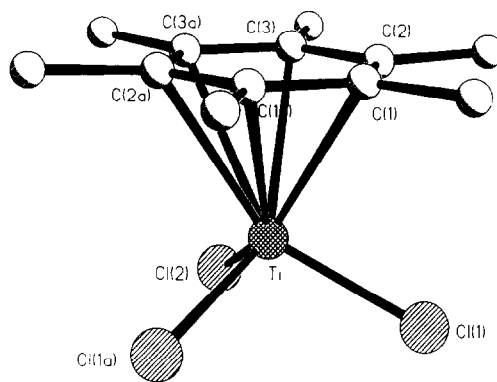As far as the structure of $[Hf(\eta^6-Me_6C_6)Cl_3]Hf_2Cl_9$, 5 is concerned, see Fig. 2, the cation possesses the same

Fig. 1. View of the $[Ti(\eta^6-Me_6C_6)Cl_3]^+$ cation in 1 with the labelling scheme used. The atoms labelled "a" are related by a symmetry plane.

overall geometry as in compounds 1 and $[Ti(\eta^6-Me_6C_6)Cl_3]Ti_2Cl_9$ (5 and $[Ti(\eta^6-Me_6C_6)Cl_3]Ti_2Cl_9$ are isotypic), with longer Hf–Cl (2.292–2.310 Å) and Hf–C (2.58–2.64 Å) bond distances due to the difference in the ionic radii of Ti(IV) (0.605 Å) and Hf(IV) (0.71 Å) [26]. The Cl–Hf–Cl bond angles (103.8–105.2°) are larger than the corresponding angles in 1 and $[Ti(\eta^6-Me_6C_6)Cl_3]Ti_2Cl_9$, probably due to the longer distance between the centroid of the hexamethylbenzene ligand from the metal in 5 (2.195 Å) with respect to the corresponding distance in 1 (2.079 Å).

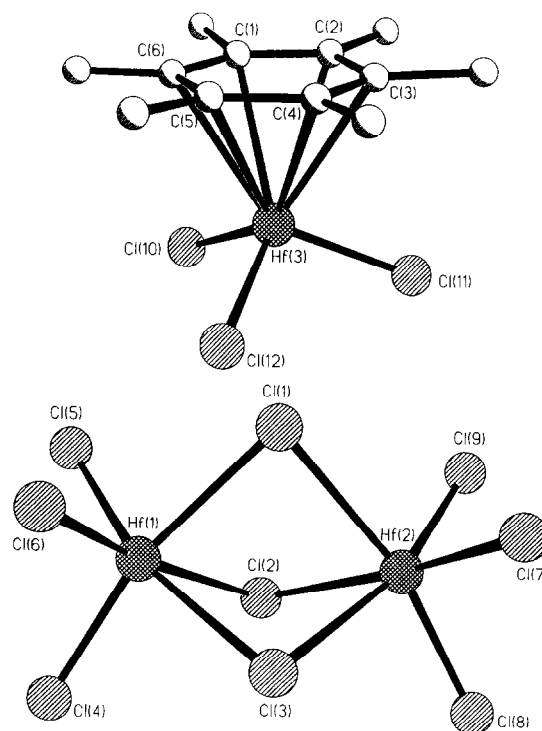In spite of the negligible difference in the ionic radii of Zr(IV) and Hf(IV) (0.72 and 0.71 Å [26] respec-

Fig. 2. View of the $[Hf(\eta^6-Me_6C_6)Cl_3]^+$ cation and the $[Hf_2Cl_9]^-$ anion in 5 with the labelling scheme used.

tively), the average Zr-ring carbon atom distance of 2.744 Å is much longer than in the hafnium compound (2.61 Å). In the Zr_2Cl_8 moiety of **4** and in the $[Hf_2Cl_9]^-$ anion of **5**, the metal atoms are connected via three bridging chlorides with relatively short M $\cdots$ M distances (3.682 and 3.576 Å respectively). These values are close to each other but significantly shorter than the Zr $\cdots$ Zr distance (3.962 Å) in $ZrCl_4$ [27] because of different connections of $ZrCl_6$ octahedra, i.e. edge-sharing in $ZrCl_4$ and face-sharing in **4** and **5**.

The overall geometry of the $[Hf_2Cl_9]^-$ anion can be described as two octahedra sharing a triangular face. As found for $[Ti_2Cl_9]^-$ in compound **6**, the Hf–Cl$_{terminal}$ distances (2.328–2.352 Å) are significantly shorter than the Hf–Cl$_{bridging}$ ones (2.573–2.604 Å).
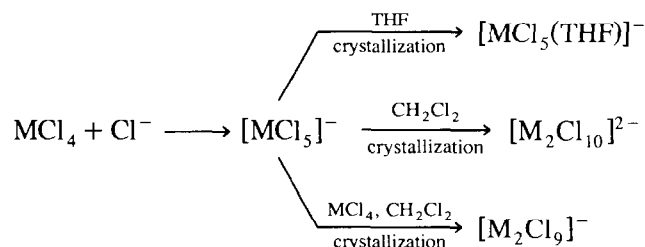
As far as we know, compound **5** belongs to the restricted family of structurally characterized arene derivatives of early transition metals in oxidation state IV. Concerning hafnium, a few compounds have been structurally characterized, namely $\{Hf[(\eta^5\text{-}C_5H_3)(SiMe_3)_2]Me_2(\eta^6\text{-toluene})\}[BMe(C_6F_5)_3]$ [28]. $(\mu\text{-}\eta^{12}\text{-arene})Hf_2I_4(PMe_2Ph)_4$ [29], $Hf(\eta^6\text{-}MeC_6H_5)_2(SnMe_3)_2$ [30].

Owing to the fact that compound **5** contains the still unknown $[Hf_2Cl_9]^-$ anion, and that the $[Zr_2Cl_9]^-$ anion is described in two papers only [31], we decided to look in more detail at the formation of these species. Some years ago we reported that $[CPh_3]_2[M_2Cl_{10}]$, M = Zr, Hf compounds can be obtained by reaction of CPh_3Cl with the appropriate metal tetrachloride in 1:1 molar ratio in CH_2Cl_2 [32], and that the $[MCl_5(THF)]^-$ anion is obtained in THF [33]. We have now found that when operating in dichloromethane but with an MCl_4/CPh_3Cl molar ratio of 2, high yields of $[CPh_3][M_2Cl_9]$ are obtained according to:

$$CPh_3Cl + 2MCl_4 \rightarrow [CPh_3][M_2Cl_9] \qquad (5)$$
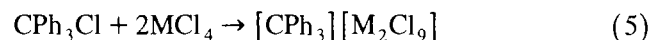
M = Zr, Hf

We can therefore suggest, for the MCl_4/Cl^- system, a sequence of reactions such as in the following scheme:

$$MCl_4 + Cl^- \longrightarrow [MCl_5]^- \quad \begin{array}{l} \xrightarrow[\text{crystallization}]{\text{THF}} [MCl_5(THF)]^- \\[1ex] \xrightarrow[\text{crystallization}]{CH_2Cl_2} [M_2Cl_{10}]^{2-} \\[1ex] \xrightarrow[\text{crystallization}]{MCl_4,\ CH_2Cl_2} [M_2Cl_9]^- \end{array}$$

M = Zr, Hf

4. Conclusions

This paper has shown that the products arising from the reaction between $MCl_4/Me_6C_6/AlCl_3$ in benzene

depend on the metal, and that the following products can be obtained:

M	Compound
Ti	$[Ti(\eta^6\text{-}Me_6C_6)Cl_3]AlCl_4$, **1**
Zr	$Zr(\eta^6\text{-}Me_6C_6)Cl_2(\mu\text{-}Cl)_3ZrCl_3$, **4**
Hf	$[Hf(\eta^6\text{-}Me_6C_6)Cl_3]Hf_2Cl_9$, **5**

The formation of the covalent complex of zirconium(IV), $Zr(\eta^6\text{-}Me_6C_6)Cl_2(\mu\text{-}Cl)_3ZrCl_3$ **4** may at first sight appear unexpected because of the close similarities in the chemistry (including structural chemistry [34]) of zirconium and hafnium derivatives in the oxidation state IV.

It has to be pointed out, however, that while titanium(IV) and hafnium(IV) are tetracoordinate in their cationic $\eta^6 - Me_6C_6$ complexes **1** and **5** (the arene ligand is considered to occupy one coordination site) and have NVE of 12, zirconium(IV) reaches hexacoordination and an NVE of 16 in compound **4**. It is therefore quite evident that a delicate balance between covalent bond formation and lattice energy in ionic structure is the basis for the drastically different results for the tetrachlorides of titanium and hafnium on the one side and zirconium on the other.

Both the larger Al–Cl bond dissociation energy with respect to Ti–Cl and the smaller size of $[AlCl_4]^-$ with respect to $[Ti_2Cl_9]^-$ probably explain the function of $AlCl_3$ in triggering the formation of compound **1**. The stronger Hf–Cl bond energy with respect to Ti–Cl explains why $AlCl_3$ does not play any role in the reaction between $HfCl_4$ and Me_6C_6, and why the formation of $[Hf_2Cl_9]^-$ as counterion is observed instead.

References and notes

[1] M. Bochmann, *Angew. Chem., Int. Ed. Engl., 31* (1992) 1181; K. Seppelt, *Angew. Chem., Int. Ed. Engl., 32* (1993) 1025; S.H. Strauss, *Chem. Rev., 93* (1993) 927.
[2] J.F. Helling and D.M. Braitsch, *J. Am. Chem. Soc., 92* (1970)

7207; D. Mandon and D. Astruc, *J. Organomet. Chem.*, *369* (1989) 383; T.S. Cameron, A. Linden, K.C. Sturge and M.J. Zavorotko, *Helv. Chim. Acta*, *75* (1992) 294.

[3] E.O. Fischer and H.H. Lindner, *J. Organomet. Chem.*, *1* (1964) 307.

[4] H.H. Lindner and E.O. Fischer, *J. Organomet. Chem.*, *12* (1968) P18.

[5] F.A. Cotton and W. Schwotzer, *Organometallics*, *4* (1985) 942; G.C. Campbell, F.A. Cotton, J.F. Haw and W. Schwotzer, *Organometallics*, *5* (1986) 274.

[6] W. Frank, J. Weber and E. Fuchs, *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 74.

[7] W. Frank and B. Dincher, *Z. Naturforsch.*, *42B* (1987) 828.

[8] B. Fan, Q. Shen and Y. Lin, *J. Organomet. Chem.*, *376* (1989) 61, *377* (1989) 51; F.A. Cotton and W. Schwotzer, *Organometallics*, *6* (1987) 1275; P. Biagini, G. Lugli and R. Millini, *Gazz. Chim. Ital.*, *124* (1994) 217; H. Liang, Q. Shen, J. Guan and Y. Lin, *J. Organomet. Chem.*, *474* (1994) 113; H. Liang, Q. Shen, S. Jin and Y. Lin, *J. Chem. Soc., Chem. Commun.*, (1992) 480.

[9] Th. Auel and E.L. Amma, *J. Am. Chem. Soc.*, *90* (1968) 5941.

[10] A.G. Gash, P.F. Rodesiler and E.L. Amma, *Inorg. Chem.*, *13* (1974) 2429.

[11] P.F. Rodesiler, Th. Auel and E.L. Amma, *J. Am. Chem. Soc.*, *97* (1975) 7405; M.S. Weininger, P.F. Rodesiler and E.L. Amma, *Inorg. Chem.*, *18* (1979) 751; H. Schmidbaur, T. Probst, O. Stiegelmann and G. Müller, *Z. Naturforsch.*, *44B* (1989) 1175; H. Schmidbaur, T. Probst, B. Huber, G. Müller and C. Krüger, *J. Organomet. Chem.*, *365* (1989) 53; H. Schmidbaur, T. Probst, B. Huber, O. Steigelmann and G. Müller, *Organometallics*, *8* (1989) 1567.

[12] Some recent papers (G.R. Fuentes, P.S. Coan, W.E. Streib and K.G. Caulton, *Polyhedron*, *10* (1991) 2371; D.L. Clark, J.C. Watkin and J.C. Huffman, *Inorg. Chem.*, *31* (1992) 1556; D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincent-Hollis, J.G. Watkin and B.D. Zwick, *Inorg. Chem.*, *33* (1994) 5903; W.J. Evans, M.A. Ansari and S.I. Khan, *Organometallics*, *14* (1995) 558; W.J. Evans, R. Anwander, M.A. Ansari and J.W. Ziller, *Inorg. Chem.*, *34* (1995) 5) report the synthesis and the crystal and molecular structure of compounds containing a multihapto interaction between a potassium ion and an aromatic hydrocarbon.

[13] S. Troyanov, *J. Organomet. Chem.*, *475* (1994) 139.

[14] F. Calderazzo, G. Pampaloni and A. Vallieri, *Inorg. Chim. Acta*, *229* (1995) 179.

[15] (a) H.L. Krauss and H. Hüttmann, *Z. Naturforsch.*, *18B* (1963) 976; (b) C. Dijkgraaf, *J. Phys. Chem.*, *69* (1965) 660; (c) E. Solari, C. Floriani, K. Schenk, A. Chiesi-Villa, C. Rizzoli, M.

Rosi and A. Sgamellotti, *Inorg. Chem.*, *33* (1994) 2018 and references cited therein.

[16] D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, Boca Raton, FL, 73rd edn. 1992.

[17] F. Calderazzo, I. Ferri, G. Pampaloni and S. Troyanov, *XIth FECHEM Conf. on Organometallic Chemistry*, *10–15 September 1995, Parma Italy.*

[18] L.E. Manzer, *Inorg. Synth.*, *21* (1982) 135.

[19] G.M. Sheldrick, SHELXS-86, *Program for the Solution of Crystal Structures*, University of Göttingen, 1986.

[20] G.M. Sheldrick, SHELXS-93, *Program for the Solution of Crystal Structures*, University of Göttingen, 1993.

[21] S. Ulvenlund, A. Wheatley and L.A. Bengtsson, *J. Chem. Soc., Dalton Trans.*, (1995) 255 and references cited therein.

[22] E. Solari, F. Musso, R. Ferguson, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, *34* (1995) 1510.

[23] Crystal data and details of the structure determination of compound **4**: orthorhombic, space group *Pnma* (No. 62); $a = 19.520(6)$, $b = 13.189(3)$, $c = 8.352(2)$ Å; $V = 2150.2(10)$ Å^3, $Z = 4$; $d_{calc} = 1.941$ g cm^{-3}, $\mu = 19.6$ cm^{-1}; crystal size $0.2 \times 0.3 \times 0.4$ mm^3; $T = 293$ K; $\theta_{max} = 24°$; number of unique reflections, 1772; number of reflections with $F^2 > 2\sigma(F^2)$, 1296; number of refined parameters, 110; $R_1 = 0.038$; $wR_2 = 0.092$.

[24] T. Lis, J. Ejfler, J. Utko and P. Sobota, *Pol. J. Chem.*, *66* (1992) 93; *Chem. Abstr.*, *117* (1992) 161388g; F. Bökman and H. Bertagnolli, *Ber. Bunsenges. Phys. Chem.*, *98* (1994) 947.

[25] A.H. Cowley, M.C. Cushner, R.E. Davies and P.E. Riley, *Inorg. Chem.*, *20* (1981) 1179; N. Carlene Means, C. Mitchell Means, S.G. Bott and J.L. Atwood, *Inorg. Chem.*, *26* (1987) 1466.

[26] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr.*, *25B* (1969) 925.

[27] B. Krebs, *Z. Anorg. Allg. Chem.*, *378* (1970) 263.

[28] S.J. Lancaster, O.B. Robinson, M. Bochmann, S.J. Coles and M.B. Hursthouse, *Organometallics*, *14* (1995) 2456.

[29] F.A. Cotton, P.A. Kibala and W.A. Wojtczak, *J. Am. Chem. Soc.*, *113* (1991) 1462.

[30] F.G.N. Cloke, K.P. Cox, M.L.H. Green, J. Bashkin and K. Prout, *J. Chem. Soc., Chem. Commun.*, (1981) 117.

[31] S. Lata, S.N. Dubey and D.M. Puri, *J. Ind. Chem. Soc.*, *60* (1983) 911, *Chem. Abstr.*, *101* (1984) 121874a; J.I. Bullock, F.W. Parrett and N.J. Taylor, *Can. J. Chem.*, *52* (1974) 2880.

[32] F. Calderazzo, G. Pampaloni, P. Pallavicini and P.F. Zanazzi, *J. Chem. Soc., Dalton Trans.*, (1990) 2743.

[33] P. Biagini, F. Calderazzo, G. Pampaloni and P.F. Zanazzi, *Gazz. Chim. Ital.*, *117* (1987) 27.

[34] ZrCl$_4$ and HfCl$_4$ are isotypic: R. Niewa and H. Jacobs, *Z. Kristall.*, *210* (1995) 687.