Heavier Halides of Early Transition Elements by Halide-exchange Reactions. Crystal and Molecular Structure of $[Ph_3C]_2[Hf_2Cl_{10}]$ †

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The decahalogenodimetalates of zirconium(IV) and hafnium(IV) as their triphenylmethyl derivatives $[Ph_3C]_2[M_2Cl_{10}]$ have been obtained by the reaction of $M(BH_4)_4$ with the appropriate Ph_3CX or by addition of Ph_3CX to MX_4. The crystal and molecular structure of $[Ph_3C]_2[Hf_2Cl_{10}]$ has been studied by *X*-ray diffraction methods: triclinic, space group $P\bar{1}$, $a = 15.965(3)$, $b = 12.907(3)$, $c = 10.526(3)$ Å, $\alpha = 99.75(2)$, $\beta = 84.84(2)$, $\gamma = 102.64(2)°$, and $Z = 2$. The structure consists of $[Ph_3C]^+$ cations and $[Hf_2Cl_{10}]^{2-}$ anions, the latter having crystallographic $\bar{1}$ symmetry. The chloride-bridged dimers have a distorted octahedral co-ordination while the $[Ph_3C]^+$ cations have a trigonal-planar geometry around the central carbon. The heavier halides of niobium(V) and tantalum(V) have been prepared from the chlorides by exchange reactions with Pr^iBr (in the case of $NbBr_5$) or with HX in EtBr solution (in the cases of NbI_5 and TaX_5).

Earlier work[1] from these Laboratories has shown that the heavier titanium(IV) halides, $TiBr_4$ and TiI_4, can conveniently be prepared by treating $TiCl_4$ with HX (X = Br or I) in n-heptane as solvent, the driving force presumably originating from the formation of HCl. Moreover, the borohydrides of zirconium(IV) and hafnium(IV) have been used[2] as intermediates for the preparation of the halides MX_4 by reaction with HX (X = Br or I).

This paper reports further exchange reactions with other metal halides of Groups 4 and 5 with RX and HX and the first isolation of the decahalogenodimetalates of zirconium(IV) and hafnium(IV), definitely establishing the crystal and molecular structure of one representative example, namely $[CPh_3]_2[Hf_2Cl_{10}]$.

Results and Discussion

Treatment of $Zr(BH_4)_4$ with triphenylmethyl bromide led to the formation of triphenylmethyl decabromodizirconate(IV). In view of the fact that the reaction was carried out with a stoicheiometric excess of Ph_3CBr [the yields of pure, sublimed $Zr(BH_4)_4$ from $ZrCl_4$ and $LiBH_4$ never exceed 60%] with respect to $Zr(BH_4)_4$, the formation of the $[Zr_2Br_{10}]^{2-}$ anion can be interpreted as being due to reactions (1) and (2). This

$$Zr(BH_4)_4 + 4Ph_3CBr \longrightarrow ZrBr_4 + 4Ph_3CH + 2B_2H_6 \quad (1)$$

$$2ZrBr_4 + 2Ph_3CBr \longrightarrow [Ph_3C]_2[Zr_2Br_{10}] \quad (2)$$

hypothesis has been fully confirmed by the isolation of the same compound prepared by reaction (2). The preparation of these anions has been extended to other bromo and iodo derivatives of both zirconium and hafnium, see equation (3).

$$2MX_4 + 2Ph_3CX \longrightarrow [Ph_3C]_2[M_2X_{10}] \quad (3)$$

The decahalogenodimetalate(IV) dianions as their triphenylmethyl derivatives are well soluble in dichloromethane and are extremely sensitive to moisture. Complexed anions of zirconium(IV) and hafnium(IV) with a halogen/metal molar ratio of 5:1 have been reported in the literature. Electronic spectra in acetonitrile solutions containing both $ZrCl_4$ and Ph_3CCl led Gutmann and co-workers[3] to suggest the existence of the $[Zr_2X_{10}]^{2-}$ anion. The acetonitrile adduct of the pentachlorozirconate(IV) anion $[NEt_4][ZrCl_5(MeCN)]$, has been reported[4] to lose MeCN *in vacuo* giving a product of composition $[NEt_4][ZrCl_5]$. Also, the presence of $[ZrCl_5]^-$ in acetonitrile solution was evidenced spectrophotometrically.[5] The $[ZrCl_5]^-$ anion was suggested to be present in the molten mixture PCl_5–$ZrCl_4$[6] and salt-like products $[ZrCl_3(\text{crown ether})][ZrCl_5(\text{thf})]$ (thf = tetrahydrofuran) have been isolated and structurally characterized.[7] It has recently been found that addition of NEt_4Cl to $ZrOCl_2{\cdot}8H_2O$ or $ZrCl_4$ in thionyl chloride solution gives two products with the same analytical composition $[NEt_4][ZrCl_5]$ but different i.r. spectra and *X*-ray powder data.[8] No similar studies appear to have been carried out for hafnium(IV). Zirconium(IV) and hafnium(IV) are, of course, expected to behave similarly.

In view of the fact that most studies on the $[ZrCl_5]^-$ anion have been conducted in solution and of the uncertainties still existing about the structural features of this anion, it was decided to carry out a diffractometric experiment on the chlorohafnium compound, which definitely established the existence of the $[Hf_2Cl_{10}]^{2-}$ anion. The structure consists of $[Hf_2Cl_{10}]^{2-}$ anions and $[Ph_3C]^+$ cations (Figures 1 and 2).

The $[Hf_2Cl_{10}]^{2-}$ dimeric anions have the crystallographic $\bar{1}$ symmetry and lie on inversion centres at $\frac{1}{2}, 0, \frac{1}{2}$ and $0, \frac{1}{2}, 0$; thus, the asymmetric unit contains two non-equivalent half dimers and two $[Ph_3C]^+$ cations. Non-equivalent groups show similar values for chemically equivalent bond lengths and angles (Table 1). The non-bonding Hf $\cdots$ Hf distances in the dimeric anions are 3.996(1) and 4.035(1) Å. The co-ordination around hafnium is distorted octahedral with an average terminal chloride Cl_t–Hf distance of 2.390 Å (2.393 Å in the other non-equivalent dimer)

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† Bis(triphenylmethylium) di-μ-chloro-bis[tetrachlorohafnate(IV)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

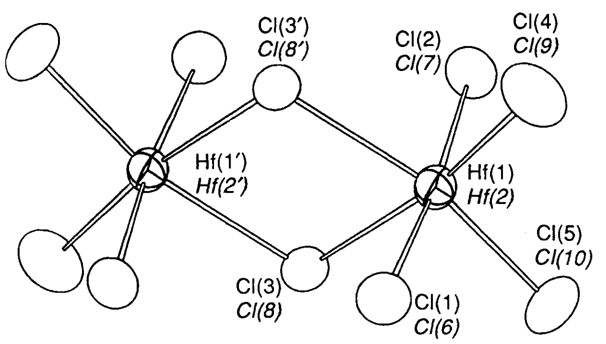

Figure 1. ORTEP view of the anion in $[Ph_3C]_2[Hf_2Cl_{10}]$

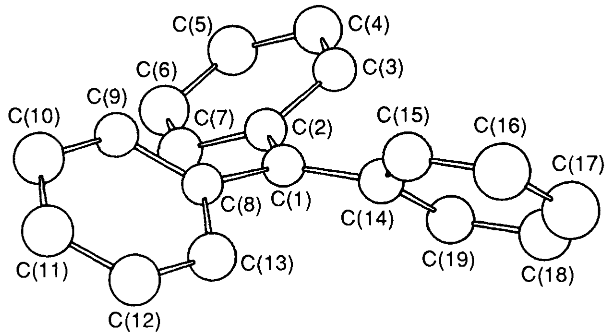

Figure 2. ORTEP view of one of the two cations in $[Ph_3C]_2[Hf_2Cl_{10}]$

Table 1. Relevant bond lengths (Å) and angles (°) in $[Ph_3C]_2[Hf_2Cl_{10}]$ with estimated standard deviations (e.s.d.s) in parentheses referring to the least significant digit

Hf(1)–Cl(1)	2.415(2)	Hf(2)–Cl(6)	2.419(3)
Hf(2)–Cl(2)	2.394(2)	Hf(2)–Cl(7)	2.396(2)
Hf(1)–Cl(3)	2.583(2)	Hf(2)–Cl(8)	2.622(3)
Hf(1)–Cl(4)	2.383(3)	Hf(2)–Cl(9)	2.370(3)
Hf(1)–Cl(5)	2.379(2)	Hf(2)–Cl(10)	2.375(2)
Hf(1)–Cl(3′)	2.574(2)	Hf(2)–Cl(8′)	2.566(2)
C(1)–C(2)	1.460(10)	C(20)–C(21)	1.458(10)
C(1)–C(8)	1.457(8)	C(20)–C(27)	1.463(9)
C(1)–C(14)	1.444(10)	C(20)–C(33)	1.454(8)
Cl(1)–Hf(1)–Cl(2)	174.3(1)	Cl(6)–Hf(2)–Cl(7)	174.9(1)
Cl(1)–Hf(1)–Cl(3)	89.2(0)	Cl(6)–Hf(2)–Cl(8)	88.9(1)
Cl(1)–Hf(1)–Cl(4)	90.5(1)	Cl(6)–Hf(2)–Cl(9)	91.6(1)
Cl(1)–Hf(1)–Cl(5)	92.9(1)	Cl(6)–Hf(2)–Cl(10)	90.3(1)
Cl(1)–Hf(1)–Cl(3′)	86.7(0)	Cl(6)–Hf(2)–Cl(8)	87.0(1)
Cl(2)–Hf(1)–Cl(3)	88.4(1)	Cl(7)–Hf(2)–Cl(8)	87.7(0)
Cl(2)–Hf(1)–Cl(4)	91.1(1)	Cl(7)–Hf(2)–Cl(9)	91.2(1)
Cl(2)–Hf(1)–Cl(5)	92.2(1)	Cl(7)–Hf(2)–Cl(10)	93.3(1)
Cl(2)–Hf(1)–Cl(3′)	87.8(1)	Cl(7)–Hf(2)–Cl(8′)	88.6(0)
Cl(3)–Hf(1)–Cl(4)	172.0(1)	Cl(8)–Hf(2)–Cl(9)	171.4(1)
Cl(3)–Hf(1)–Cl(5)	87.1(1)	Cl(8)–Hf(2)–Cl(10)	87.3(1)
Cl(3)–Hf(1)–Cl(3′)	78.4(0)	Cl(8)–Hf(2)–Cl(3′)	77.9(0)
Cl(4)–Hf(1)–Cl(5)	100.9(1)	Cl(9)–Hf(2)–Cl(10)	101.3(1)
Cl(4)–Hf(1)–Cl(3′)	93.6(1)	Cl(9)–Hf(2)–Cl(8′)	93.6(1)
Cl(5)–Hf(1)–Cl(3′)	165.5(1)	Cl(10)–Hf(2)–Cl(8′)	165.0(1)
Hf(1)–Cl(3)–Hf(1′)	101.6(0)	Hf(2)–Cl(8)–Hf(2′)	102.1(0)
C(2)–C(1)–C(8)	120.3(5)	C(21)–C(20)–C(27)	118.6(5)
C(2)–C(1)–C(14)	119.6(5)	C(21)–C(20)–C(33)	121.8(5)
C(8)–C(1)–C(14)	120.0(5)	C(27)–C(20)–C(33)	119.6(5)

and a bridging chloride Cl_b–Hf distance of 2.594 Å (2.578 in the other non-equivalent dimer). As expected, Hf–Cl_t is significantly shorter than Hf–Cl_b. The structure of the $[Hf_2Cl_{10}]^{2-}$ anion as its triphenylmethyl derivative can be conveniently compared with that of the corresponding titanium(IV) species (PCl_4^+ as cation).[9] The two structures are similar, the co-ordination around titanium also being distorted octahedral. In both the hafnium(IV) and titanium(IV) species the bridging M_2Cl_2 system is asymmetrical, the Ti–Cl_b distances being 2.481 and 2.506 Å while in our case the Hf-Cl_b distances in one of the two non-equivalent dimers are 2.566(2) and 2.622(3) Å. The other non-equivalent dimer has substantially identical Hf-Cl_b distances within experimental error [2.574(2) and 2.583(2) Å]. The average Ti–Cl_t distance in the $[Ti_2Cl_{10}]^{2-}$ dimer is 2.277 Å. Thus, the average Hf–Cl_t distance (2.39 Å) differs by about 0.11 Å from that of the corresponding $[Ti_2Cl_{10}]^{2-}$ anion, as expected on the basis of the difference in ionic radii between Hf^{4+} (0.81 Å) and Ti^{4+} (0.68 Å).[10] The non-bonding Ti $\cdots$ Ti distance in the dimer is 3.885(3) Å[9] in satisfactory agreement with our values for the intermetallic distance, taking into consideration the difference in ionic radii.

The $[Ph_3C]^+$ cation has the expected trigonal planar geometry, with a propeller-like conformation and torsion angles of 38, 29, and 28° around the C(1)–C(2) [1.460(10) Å], C(1)–C(8) [1.457(8) Å] and C(1)–C(14) [1.444(10) Å] bonds for one cation and 27, 38, and 27° around the C(20)–C(21) [1.458(10) Å], C(20)–C(27) [1.463(9) Å], and C(20)–C(33) [1.454(8) Å] bonds for the second cation. The bond distances and angles within the cations (Table 1) are similar to those found for other $[Ph_3C]^+$ derivatives.[11]

The pentabromides and the pentaiodides of niobium and tantalum have been prepared by an exchange reaction from the pentachlorides MCl_5. The exchange reaction was carried out using HX as halogen carrier, according to equation (4). In the case of $NbBr_5$, the product was also obtained through the $NbCl_5$–Pr^iBr system, according to equation (5). As in the case of reaction (4), the driving force for the exchange is the formation of HCl, so the alkyl halide-promoted exchange is believed to be driven by the formation of the lighter alkyl halide. It is interesting that $TaCl_5$ is reported[12] to be well soluble in ethyl bromide and that the colour of the solution becomes yellow-orange. We have verified this also for $NbCl_5$ and attributed it to a slow halide-exchange reaction following a possible MCl_5·EtBr adduct formation.

$$MCl_5 + 5HX \longrightarrow MX_5 + 5HCl \qquad (4)$$

$$NbCl_5 + 5Pr^iBr \longrightarrow NbBr_5 + 5Pr^iCl \qquad (5)$$

The results of the present study offer an alternative route to the preparation of heavier halides of Group 5 elements, usually synthesised through the halogenation of the metal.[13]

Experimental

Unless otherwise stated, all operations were carried out in an atmosphere of prepurified argon. The reaction vessels used were oven dried before use. Solvents were dried by conventional methods.

Infrared spectra were recorded with a Perkin-Elmer model 283 grating instrument on Nujol mulls of the compounds prepared under rigorous exclusion of moisture and oxygen.

Commercially available zirconium tetrachloride (Fluka), hafnium tetrachloride [low (<0.5%) zirconium content (CESUS Chimie, France)], niobium pentachloride (Fluka), and tantalum pentachloride (Fluka) were purified by treatment with boiling $SOCl_2$ followed by heating at 200 °C (10^{-2} mmHg, *ca.* 1.33 Pa).

Triphenylmethyl halides, (Ph_3CX, (X = Cl, Br, or I),[14] and zirconium and hafnium tetrahalides, MX_4, (M = Zr or Hf, X = Br or I),[2] were prepared according to the literature.

Reaction of $Zr(BH_4)_4$ *with* Ph_3CBr. Zirconium tetrachloride (1.98 g, 8.5 mmol) and $LiBH_4$ (0.87 g, 39.9 mmol) were

Table 2. Fractional atomic co-ordinates in $[Ph_3C]_2[Hf_2Cl_{10}]$ with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Hf(1)	0.457 21(2)	0.106 20(3)	0.418 61(4)	C(14)	0.133 6(4)	−0.219 7(4)	0.634 6(6)
Hf(2)	−0.044 50(2)	0.345 19(3)	0.924 65(4)	C(15)	0.077 9(4)	−0.320 1(4)	0.621 1(6)
Cl(1)	0.341 6(1)	0.097 7(2)	0.583 5(2)	C(16)	0.108 5(4)	−0.411 7(4)	0.565 8(6)
Cl(2)	0.572 6(2)	0.097 1(2)	0.258 0(2)	C(17)	0.194 8(4)	−0.403 0(4)	0.523 9(6)
Cl(3)	0.561 1(1)	0.097 9(2)	0.589 3(2)	C(18)	0.250 5(4)	−0.302 6(4)	0.537 4(6)
Cl(4)	0.357 4(2)	0.087 0(3)	0.256 7(3)	C(19)	0.219 9(4)	−0.211 0(4)	0.592 7(6)
Cl(5)	0.498 4(2)	0.296 6(2)	0.467 0(3)	C(20)	0.547 7(5)	0.433 5(8)	0.809 8(9)
Cl(6)	0.087 5(2)	0.355 4(2)	0.790 8(3)	C(21)	0.555 6(4)	0.336 6(4)	0.857 6(6)
Cl(7)	−0.171 6(1)	0.352 1(2)	1.062 8(3)	C(22)	0.632 5(4)	0.300 4(4)	0.833 4(6)
Cl(8)	0.043 7(1)	0.463 9(2)	1.115 2(3)	C(23)	0.640 8(4)	0.207 4(4)	0.877 8(6)
Cl(9)	−0.128 0(2)	0.262 4(3)	0.745 7(3)	C(24)	0.572 1(4)	0.150 5(4)	0.946 3(6)
Cl(10)	−0.018 9(2)	0.193 0(2)	1.002 0(3)	C(25)	0.495 2(4)	0.186 7(4)	0.970 5(6)
C(1)	0.101 5(5)	−0.125 2(8)	0.692 1(9)	C(26)	0.486 9(4)	0.279 7(4)	0.926 1(6)
C(2)	0.154 2(3)	−0.041 6(4)	0.779 9(5)	C(27)	0.625 4(3)	0.515 3(5)	0.792 3(6)
C(3)	0.210 4(3)	−0.071 6(4)	0.854 2(5)	C(28)	0.689 5(3)	0.538 8(5)	0.880 9(6)
C(4)	0.258 2(3)	0.005 2(4)	0.944 3(5)	C(29)	0.763 8(3)	0.616 2(5)	0.863 0(6)
C(5)	0.249 8(3)	0.112 1(4)	0.960 1(5)	C(30)	0.774 1(3)	0.670 0(5)	0.756 5(6)
C(6)	0.193 7(3)	0.142 1(4)	0.885 8(5)	C(31)	0.710 1(3)	0.646 5(5)	0.668 0(6)
C(7)	0.145 8(3)	0.065 2(4)	0.795 7(5)	C(32)	0.635 8(3)	0.569 2(5)	0.685 9(6)
C(8)	0.016 4(3)	−0.114 3(5)	0.663 9(6)	C(33)	0.464 9(3)	0.451 6(5)	0.782 3(7)
C(9)	−0.031 8(3)	−0.054 1(5)	0.752 1(6)	C(34)	0.452 2(3)	0.556 7(5)	0.797 7(7)
C(10)	−0.110 9(3)	−0.040 1(5)	0.719 4(6)	C(35)	0.371 8(3)	0.575 5(5)	0.778 7(7)
C(11)	−0.141 8(3)	−0.086 2(5)	0.598 5(6)	C(36)	0.304 1(3)	0.489 2(5)	0.744 1(7)
C(12)	−0.093 6(3)	−0.146 4(5)	0.510 3(6)	C(37)	0.316 8(3)	0.384 2(5)	0.728 7(7)
C(13)	−0.014 5(3)	−0.160 5(5)	0.543 0(6)	C(38)	0.397 2(3)	0.365 4(5)	0.747 7(7)

vigorously shaken in a Schlenk tube in the presence of Et_2O (1 cm^3). An exothermic reaction took place. The Schlenk tube was connected to a vacuum line and the borohydrido complex was sublimed into a flask maintained at about −78 °C, and dissolved in n-heptane (100 cm^3). The solution was allowed to warm to room temperature and Ph_3CBr (10.39 g, 32.1 mmol) dissolved in toluene (100 cm^3) was added in 30 min. Some bright orange solid precipitated. The mixture was stirred at room temperature for 16 h and cooled at 4 °C. Orange crystals formed which were filtered off, washed with n-heptane, and dried *in vacuo* affording 3.34 g (54% yield with respect to $ZrCl_4$) of $[Ph_3C]_2[Zr_2Br_{10}]$. I.r. spectrum (Nujol mull): 3 060vw, 1 583vs, 1 480s, 1 466s, 1 447vs, 1 377m, 1 361vs, 1 350vs, 1 295s, 1 183m, 1 163w, 1 025vw, 990m, 975vw, 910vw, 834m, 801m, 766m, 751w, 695vs, 652w, 619m, 592vs, 580vs, 475vw, 461vw, and 398m cm^{-1} (Found: Br, 52.9; Zr, 12.5. $C_{38}H_{30}Br_{10}Zr_2$ requires Br, 54.4; Zr, 12.4%).

The same compound (i.r. and elemental analysis) was obtained in 93% yield from Ph_3CBr and $ZrBr_4$ by a procedure similar to that reported in the following section.

Preparation of $[Ph_3C]_2[M_2X_{10}]$ (M = Zr, X = Cl *or* Br; M = Hf, X = Cl *or* I).—$[Ph_3C]_2[Hf_2Cl_{10}]$. A suspension of $HfCl_4$ (2.81 g, 8.8 mmol) in CH_2Cl_2 (50 cm^3) was treated with Ph_3CCl (2.4 g, 8.6 mmol). Immediate dissolution of $HfCl_4$ and formation of a yellow-orange solution was observed. After filtration, n-pentane was added in order to form two layers. After 15 h large orange crystals were present which were filtered off, washed with n-pentane, and dried *in vacuo* affording 5.08 g (96% yield) of $[Ph_3C]_2[Hf_2Cl_{10}]$. I.r. spectrum (Nujol mull): 3 060vw, 1 585vs, 1 560s, 1 480s, 1 450s, 1 380mw, 1 355s, 1 295s, 1 185m, 1 100vw, 1 025vw, 990m, 975w, 945w, 910w, 850w, 835w, 805m, 770m, 755w, 695vs, 650w, 615s, 600m, 460mw, and 400mw cm^{-1} (Found: Cl, 29.2; Hf, 29.9. $C_{38}H_{30}Cl_{10}Hf_2$ requires Cl, 29.6; Hf, 29.8%).

The following compounds were prepared similarly: $[Ph_3C]_2[Zr_2Cl_{10}]$, orange, 88% yield, i.r. (Nujol mull) 3 050vw, 1 585vs, 1 560s, 1 485s, 1 455s, 1 380mw, 1 360s, 1 295s, 1 265w, 1 185m, 1 165vw, 1 025vw, 995s, 975w, 945vw, 915vw, 850vw, 835w, 805m, 770m, 760m, 698s, 655vw, 620m, 605m, 465w, and 398w cm^{-1} (Found: Cl, 33.8; Zr, 17.9. $C_{38}H_{30}Cl_{10}Zr_2$ requires Cl, 34.6; Zr, 17.8%); $[Ph_3C]_2[Hf_2I_{10}]$, deep red, 35% yield, i.r. (Nujol mull) 3 060vw, 1 585vs, 1 484s, 1 466s, 1 453vs, 1 381m, 1 359vs, 1 298s, 1 265w, 1 185m, 996s, 840vw, 805vw, 766vw, 730vw, 696vs, 620m, 604m, 435vw, and 398 m cm^{-1} (Found: Hf, 16.8; I, 59.5. $C_{38}H_{30}Hf_2I_{10}$ requires Hf, 16.9; I, 60.1%).

Preparation of NbX_5 (X = Br *or* I).—(*a*) X = Br. Solid $NbCl_5$ (9.17 g, 34 mmol) was treated at room temperature with Pr^iBr (60 cm^3). The solid partially dissolved, followed by the precipitation of a red crystalline solid. The mixture was stirred at room temperature for 15 h and filtered affording $NbBr_5$ as a dark red crystalline solid (12.56 g, 75% yield) (Found: Br, 81.3; Nb, 18.0. Calc. for Br_5Nb: Br 81.1; Nb, 18.9%).

(*b*) X = I. By operating as described above, a brown-black solid of approximate analytical composition $NbI_{4.9}Cl_{0.1}$ was isolated. The pure pentaiodide was obtained by reaction of $NbCl_5$ with hydrogen iodide. A sample of $NbCl_5$ (1.24 g, 4.6 mmol) was dissolved in EtBr (25 cm^3). The flask was connected to a vacuum line and to a cylinder of hydrogen iodide. From the yellow solution a black solid precipitated instantaneously. The vacuum/HI operation was repeated four times within 2 h and then the suspension was stirred for 15 h at room temperature. The reaction mixture was filtered and the solid was dried *in vacuo* affording NbI_5 (2.75 g, 82% yield) in the form of a brown-black microcrystalline solid (Found: I, 87.1; Nb, 12.9. Calc. for I_5Nb: I, 87.2; Nb, 12.8%).

Preparation of TaX_5 (X = Br *or* I).—The compounds $TaBr_5$ and TaI_5 were prepared in 77 and 83% yields, respectively, by the exchange reaction with HX starting from $TaCl_5$ as described in (*b*) above (Found: Br, 69.0; Ta, 31.6. Calc. for Br_5Ta; Br, 68.8; Ta, 31.2. Found: I, 77.9; Ta, 22.6. Calc. for I_5Ta: I, 77.8; Ta, 22.2%).

X-*Ray Crystal Structure of* $[Ph_3C]_2[Hf_2Cl_{10}]$.—A crystal

(0.2 × 0.12 × 0.08 mm) sealed in a glass capillary was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.7107$ Å). The cell dimensions were determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ ranging between 10 and 20°.

Crystal data. $C_{38}H_{30}Cl_{10}Hf_2$, $M = 1\,198.1$, triclinic, space group $P\bar{1}$, $a = 15.965(3)$, $b = 12.907(3)$, $c = 10.526(3)$ Å, $\alpha = 99.75(2)$, $\beta = 84.84(2)$, $\gamma = 102.64(2)°$, $U = 2082.7$ Å^3, $Z = 2$, $D_c = 1.909$ g cm^{-3}, μ(Mo-K_α) = 58.5 cm^{-1}, $F(000) = 1\,144$.

The intensities of the reflections were measured up to $2\theta = 50°$ and the ω—2θ scan technique was employed. A total of 7 485 reflections were measured; 3 049 having $I < 3\sigma(I)$ were considered as 'unobserved' and excluded from the refinement. Three standard reflections measured periodically showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarisation factors. During the refinement, an empirical absorption correction was applied according to the method of Walker and Stuart;[15] the correction factors were in the range 0.8—1.44.

The structure was solved by Patterson methods and refined by the full-matrix least-squares method using the SHELX 76[16] package of programs. Anisotropic thermal parameters were refined for hafnium and chlorine atoms. The phenyl groups were refined as rigid groups assuming a perfect hexagonal geometry (C–C 1.359 Å). The hydrogen atoms were included at calculated positions (C–H 1.08 Å) and refined with the overall temperature factor $U = 0.07$ Å^2. The refinement converged at $R = 0.031$ and $R' = 0.031$ for 190 parameters and 4 436 observed reflections $\{R' = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}/(\Sigma w F_o^2)^{\frac{1}{2}};\ w = \sigma^2(F_o)^{-1}\}$. The atomic scattering factors were taken from ref. 16 for Cl, C, and H atoms and from ref. 17 for Hf: a correction for anomalous dispersion was included.

The fractional atomic co-ordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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