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LETTER

A simple compound containing the first hafnium(III) to hafnium(III) bond

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The capacity of transition metal atoms in their higher oxidation states and without organic (e.g. $C_5H_5^-$) or π-acid (e.g. CO) ligands to form metal–metal bonds has been explored in several thousand research publications over the last quarter of a century [1]. Positive results have been especially abundant, including bonds of orders up to 4, for the elements in Group 6 (especially Mo), 7 (especially Re), and 8 (Ru, Os, Rh, and Pt). Developments in early transition elements have been relatively scarce in Group 5 and very scarce in Group 4. For the latter, only some edge-sharing bioctahedral species [2] containing zirconium have been described [3]. We have now obtained the hafnium analog to one of the earlier zirconium(III) compounds, both being of the formula $M_2Cl_6(PMe_2Ph)_4$, and shown it to contain a Hf–Hf single bond. This is the first Hf–Hf bond of any kind (excepting, of course, those in the metal and its alloys) and with its discovery there are now one or more compounds with M–M bonds for every transition metal in the series Hf, Ta, W, Re, Os, Ir**, Pt.

Experimental

Preparation of $Hf_2Cl_6(PMe_2Ph)_4$

All manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from appropriate drying agents. $HfCl_4$ (0.32 g, 1.0 mmol, Aldrich), PMe_2Ph (0.30 ml, 2.1 mmol, Strem Chemicals), and 1.0 M Na/Hg (1.0 ml, 1.0 mmol) were stirred vigorously in 20 ml of toluene for 24 h. The brown–olive-green solution of $Hf_2Cl_6(PMe_2Ph)_4$ was filtered through Celite (2 cm) into a Schlenk tube and layered with hexanes (20 ml). Upon standing for a few weeks the solution afforded air sensitive olive-green crystals of $Hf_2Cl_6(PMe_2Ph)_4$. Interestingly, the highest isolated yield (0.22 g, ~20%) was obtained when the mole ratio of hafnium tetrachloride to reducing agent was 2:1.

X-ray crystallography

The structure determination was carried out in a routine fashion by employing methods standard in our laboratory. The calculations were done on a Microvax II computer with a SDP package software

TABLE 1. Crystal data for $Hf_2Cl_6(PMe_2Ph)_4$

Formula	$C_{32}H_{44}Cl_6Hf_2P_4$
Formula weight	1122.3
Space group	$P\bar{1}$
Systematic absences	none
a (Å)	10.335(3)
b (Å)	11.695(3)
c (Å)	8.803(2)
α (°)	90.58(2)
β (°)	92.79(2)
γ (°)	100.48(2)
V (Å^3)	1044.8(9)
Z	1
D_{calc} (g/cm^3)	1.784
Crystal size (mm)	$0.45 \times 0.35 \times 0.20$
μ(Mo Kα) (cm^{-1})	54.823
Data collection instrument	Rigaku AFC5R
Radiation (monochromated in incident beam)	Mo Kα ($\lambda = 0.71073$ Å)
Orientation reflections: no., range (2θ) (°)	25, $20 < 2\theta < 30$
Temperature (°C)	21
Scan method	ω–2θ
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 50$
No. unique data, total	3452
with $F_o^2 > 3\sigma(F_o^2)$	3130
No. parameters refined	199
Transmission factors, max., min.	0.999, 0.567
R^a	0.03123
R_w^b	0.04149
Quality-of-fit indicator^c	0.994
Largest shift/e.s.d., final cycle	0.01
Largest peak (e/Å^3)	1.38

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

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**Iridium gave the first Ir–Ir bond within a simple X_4Ir–IrX_4 context only in 1987 [4].

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employing the structure solution given in ref. 5. All relevant crystallographic information is given in Table 1. A suitable olive-green crystalline plate was mounted and sealed with epoxy glue in a thin-walled capillary filled with degassed mineral oil, to prevent decomposition in the air. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections. Lorentz, polarization and empirical absorption corrections were applied to the data. The positions of the heavy atoms were deduced from the Patterson map. Least-squares cycles and difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. All atoms were refined anisotropically. The atomic positional parameters are reported in Table 2 and selected mean bond distances and angles are reported in the legend to Fig. 1.

Results and discussion

By reduction of $HfCl_4$ with Na/Hg in the presence of phosphines, products that appear to be complexes of Hf(III) containing Cl^- and phosphines as ligands are obtained. One of them, $Hf_2Cl_6(PMe_2Ph)_4$, has been fully characterized by X-ray crystallography and ^{31}P{^{1}H} NMR spectroscopy*, which show that it is a diamagnetic dimer with the structure shown in Fig. 1.

A comparison between $Zr_2Cl_6(PMe_2Ph)_4$ and $Hf_2Cl_6(PMe_2Ph)_4$ shows expected structural similarities. Both are of the somewhat unusual type where all the phosphine ligands are in the central plane. The mean M–Cl_t, M–Cl_b and M–P distances are essentially identical in the two cases, as expected. However, the Hf–Hf distance (3.0886(3) Å) is significantly shorter, by 0.039 Å, than the Zr–Zr distance (3.127(1) Å). This is not surprising since it has been observed previously that in homologous pairs of Nb/Ta and Mo/W compounds the heavier metal gave M–M distances that are shorter by 0.02–0.10 Å.

The existence of a Hf–Hf single bond is shown by the diamagnetism of the molecule coupled with the compression of the central ring along the Hf–Hf line to give Cl_b–Hf–Cl_b angles 14° in excess of 90° and Hf–Cl_b–Hf angles 14° less than 90°, which is a clear indication that the metal atoms are being drawn together by a force in excess of the strong repulsive force that would prevail at such a distance between non-bonded Hf atoms.

Further preparative and structural studies on hafnium compounds as well as zirconium analogs are in progress, as well as attempts to prepare thorium(III) compounds with Th–Th bonds.

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*^{31}P{^{1}H} NMR (81 MHz, benzene/toluene, 20 °C, 85% H_3PO_4 (aq)): $\delta = -16.67$ (s).

TABLE 2. Positional and equivalent isotropic displacement parameters and their e.s.d.s for $Hf_2Cl_6(PMe_2Ph)_4$

Atom	x	y	z	B_{eq} (Å^2)
Hf(1)	0.07127(2)	0.11899(2)	0.06590(2)	2.583(4)
Cl(1)	0.1636(1)	−0.0222(1)	−0.0989(2)	3.42(3)
Cl(2)	0.1610(2)	0.0554(1)	0.3015(2)	4.07(3)
Cl(3)	0.0128(2)	0.2385(2)	−0.1392(2)	4.36(4)
P(1)	−0.0129(2)	0.2720(1)	0.2590(2)	3.38(3)
P(2)	0.3194(2)	0.2499(2)	0.0348(2)	3.79(3)
C(11)	0.1118(7)	0.3924(5)	0.3373(7)	3.6(1)
C(12)	0.1283(8)	0.5011(6)	0.2714(9)	5.0(2)
C(13)	0.231(1)	0.5890(7)	0.323(1)	6.1(2)
C(14)	0.3176(9)	0.5666(7)	0.443(1)	6.4(2)
C(15)	0.2987(9)	0.4585(7)	0.511(1)	5.8(2)
C(16)	0.1965(8)	0.3702(6)	0.4560(8)	4.8(2)
C(17)	−0.0860(9)	0.2021(7)	0.4276(9)	5.7(2)
C(18)	−0.1417(7)	0.3441(7)	0.177(10	5.8(2)
C(21)	0.4150(6)	0.1963(5)	−0.1109(7)	3.0(1)
C(22)	0.3630(7)	0.1900(6)	−0.2589(7)	4.0(1)
C(23)	0.4303(8)	0.1465(7)	−0.3750(8)	4.9(2)
C(24)	0.5479(8)	0.1095(7)	−0.3407(9)	5.0(2)
C(25)	0.6000(7)	0.1163(7)	−0.192(1)	5.4(2)
C(26)	0.5328(7)	0.1580(7)	−0.0764(8)	4.3(1)
C(27)	0.4335(8)	0.266(1)	0.2065(8)	7.6(2)
C(28)	0.3212(9)	0.4019(7)	−0.034(1)	6.9(2)

The equivalent isotropic displacement parameter, B_{eq}, is calculated as: $\frac{1}{3}[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\gamma)abB_{12}+2ac(\cos\beta)acB_{13}+2bc(\cos\alpha)bcB_{23}]$.

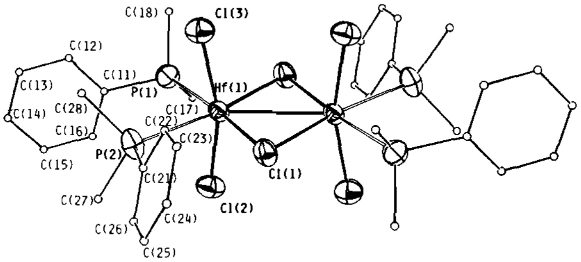

Fig. 1. The structure of the $Hf_2Cl_6(PMe_2Ph)_4$ molecule (ORTEP, the thermal ellipsoids are at 50%, carbon atoms given arbitrary radii for clarity). Mean values of some principal dimensions in this centrosymmetric molecule are: $Hf{-}Cl_b$ 2.524(6), $Hf{-}Cl_t$ 2.412(2), Hf-P 2.752(14) Å; $\angle$P-Hf-P 96.02(5), $\angle Hf{-}Cl_b{-}Hf$ 75.45(4), $\angle Cl_b{-}Hf{-}Cl_b$ 104.55(5), $\angle Hf{-}Hf{-}Cl_t$ 98.6(6)°.

Supplementary material

Full listing of bond distances, bond angles, isotropic equivalent displacement parameters, tables of observed and calculated structure factors for $Hf_2Cl_6(PMe_2Ph)_4$ are available on request from author F.A.C.

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