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Synthesis, X-ray Crystal Structure, and Phosphine-Exchange Reactions of the Hafnium(III)–Hafnium(III) Dimer $Hf_2Cl_6(PEt_3)_4$

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Reduction of $HfCl_4$ with sodium–potassium alloy in the presence of PEt_3 yields the dark green hafnium(III)–hafnium(III) dimer $Hf_2Cl_6(PEt_3)_4$. The X-ray crystal structure shows that molecules of $Hf_2Cl_6(PEt_3)_4$ consist of two octahedral hafnium centers that are connected by a hafnium–hafnium bond and two bridging chloride ligands. The two independent molecules in the unit cell have slightly different structures due to differences in the relative orientations of the ethyl groups of the PEt_3 ligands. In both molecules, the PEt_3 groups are trans to the bridging chloride ligands. Average distances and angles for the two independent molecules: Hf–Hf = 3.097 (1) and 3.118 (1) Å, Hf–P = 2.748 (2) and 2.761 (2) Å, $Hf–Cl_t$ = 2.417 (2) and 2.415 (2) Å, $Hf–Cl_b$ = 2.533 (2) and 2.538 (2) Å, $Hf–Cl_b–Hf$ = 75.38 (5) and 75.78 (4)°, $Cl_b–Hf–Cl_b$ = 104.62 (5) and 104.22 (5)°, $Cl_t–Hf–Cl_t$ = 165.75 (6) and 165.33 (6)°, and P–Hf–P = 92.67 (5) and 98.95 (6)°. The triethylphosphine complex undergoes exchange with trimethylphosphine to afford successively the complexes $Hf_2Cl_6(PEt_3)_3(PMe_3)$, $Hf_2Cl_6(PEt_3)_2(PMe_3)_2$, $Hf_2Cl_6(PEt_3)(PMe_3)_3$, and $Hf_2Cl_6(PMe_3)_4$; two of the three possible isomers of $Hf_2Cl_6(PEt_3)_2(PMe_3)_2$ are formed. The sequential replacement of PEt_3 groups by PMe_3 was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Interestingly, the J_{PP} coupling constants for phosphorus nuclei attached to different hafnium centers are <2 Hz, while the J_{PP} coupling constants for adjacent phosphines are small at 3–4 Hz. Crystal data for $Hf_2Cl_6(PEt_3)_4$ at −75 °C: monoclinic, space group $P2_1/c$, with a = 10.256 (4) Å, b = 18.787 (8) Å, c = 20.275 (6) Å, β = 94.52 (3)°, V = 3894 (4) Å^3, Z = 4, R_F = 0.028, and R_{wF} = 0.035 for 326 variables and 5081 data with $I > 2.58\sigma(I)$.

Introduction

One of the characteristic features of the d-block elements is that they are able to form polynuclear compounds in which there is strong metal–metal bonding.[1,2] Between the 1960s and 1980s, representative complexes that contain metal–metal bonds had been prepared for every transition element save one: hafnium. Only very recently (1990) were the first crystallographically-characterized examples of compounds that contain Hf–Hf bonds described.[3,4] Reduction of $HfCl_4$ in the presence of tertiary phosphines yielded the dinuclear hafnium(III) complexes $Hf_2Cl_6(dippe)_2$ and $Hf_2Cl_6(PMe_2Ph)_4$, where dippe = 1,2-bis(diisopropylphosphino)ethane.

It is interesting to note that analogous zirconium(III) dimers had been prepared by a similar synthetic route as early as 1981.[5] The lapse of nearly 10 years between the discovery of $Zr_2Cl_6(PEt_3)_4$ and the preparation of a hafnium(III) analogue may be related to the relative difficulty in reducing hafnium(IV) starting materials: hafnium has the most negative reduction potentials of all the transition elements.[6] Whereas sodium amalgam is sufficiently reducing to convert Zr^{IV} to Zr^{III} quickly and efficiently, this reductant was not particularly effective in our hands for the reduction of Hf^{IV} to Hf^{III}, especially when trialkylphosphines were chosen as the ancillary ligands.[3] Instead, the synthesis of $Hf_2Cl_6(dippe)_2$ was best carried out using the stronger reductant sodium–potassium alloy.[3]

We now describe the preparation of the triethylphosphine complex $Hf_2Cl_6(PEt_3)_4$ by this method and report the details of its X-ray crystal structure. In addition, we describe the reaction of this complex with PMe_3 to give $Hf_2Cl_6(PMe_3)_4$. This phosphine-exchange reaction has been studied by $^{31}P\{^1H\}$ NMR spectroscopy, and the intermediate $Hf_2Cl_6(PEt_3)_x(PMe_3)_{4-x}$ species have been identified. Interestingly, the $^{31}P–^{31}P$ coupling constants are unusually small in these dinuclear molecules.

Results and Discussion

Treatment of a toluene suspension of $HfCl_4$ with sodium–potassium alloy in the presence of triethylphosphine yields a brown-green solution from which deep green crystals of the hafnium(III) dimer $Hf_2Cl_6(PEt_3)_4$ may be isolated.

$$2HfCl_4 + 2Na/K + 4PEt_3 \rightarrow Hf_2Cl_6(PEt_3)_4 + 2(Na/K)Cl$$

As we have noted earlier,[3] sodium–potassium alloy is the preferred reducing agent, since $HfCl_4$ is reduced only slowly or not at all by other reductants such as sodium or sodium amalgam. The product is diamagnetic, and all four phosphine ligands are equivalent in the ^1H and ^{31}P NMR spectra. The ^{31}P NMR coordination chemical shift ($\delta_{coord} - \delta_{free}$) is +17 ppm.

A brief mention of $Hf_2Cl_6(PEt_3)_4$ was made in 1990 by Cotton and Kibala, who prepared solutions thought to contain this dimer.[7] The product isolated upon treatment of these solutions with ethylene or 1,2-dichloroethane, $Hf_2(C_2H_4)Cl_6(PEt_3)_4$, lends support to the contention that $Hf_2Cl_6(PEt_3)_4$ was in fact present, even though the latter compound was not isolated or characterized.

X-ray Crystal Structure of $Hf_2Cl_6(PEt_3)_4$. Single crystals of $Hf_2Cl_6(PEt_3)_4$ crystallize from toluene in space group $P2_1/c$ with two independent half-molecules in the asymmetric unit, each residing on a crystallographic inversion center (Figure 1). Crystal data are given in Table I, while final atomic coordinates and important bond distances and angles are presented with estimated standard deviations in Tables II and III.

The structure of $Hf_2Cl_6(PEt_3)_4$ is very similar to those of the other three crystallographically-characterized hafnium(III) dimers

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Table I. Crystal Data for $Hf_2Cl_6(PEt_3)_4$

$C_{24}H_{60}Cl_6P_4Hf_2$	space gp: $P2_1/c$
a = 10.256 (4) Å	T = –75 °C
b = 18.787 (8) Å	λ = 0.710 73 Å
c = 20.275 (6) Å	ρ_{calcd} = 1.778 g cm^{-3}
β = 94.52 (3)°	μ_{calcd} = 58.76 cm^{-1}
V = 3894 (4) Å^3	transm coeff = 0.162–0.447
Z = 4	R_F = 0.028
mol wt = 1042.34	R_{wF} = 0.035

Table II. Atomic Coordinates for $Hf_2Cl_6(PEt_3)_4$

	x/a	y/b	z/c
Hf(1)	0.05319 (3)	0.07658 (1)	0.01093 (1)
Cl(1)	0.0957 (2)	–0.00772 (8)	–0.08214 (8)
Cl(2)	0.2424 (2)	0.04257 (8)	0.08229 (8)
Cl(3)	–0.1172 (2)	0.14021 (9)	–0.05412 (9)
P(1)	0.0113 (2)	0.18177 (8)	0.10104 (9)
P(2)	0.2365 (2)	0.15612 (9)	–0.04809 (9)
C(1)	–0.1392 (8)	0.1754 (4)	0.1441 (4)
C(2)	–0.2642 (8)	0.1779 (4)	0.0981 (5)
C(3)	0.0017 (7)	0.2722 (3)	0.0648 (3)
C(4)	–0.0386 (8)	0.3318 (3)	0.1110 (4)
C(5)	0.1401 (8)	0.1921 (4)	0.1694 (4)
C(6)	0.1353 (9)	0.1379 (5)	0.2230 (4)
C(7)	0.3478 (7)	0.1076 (4)	–0.0980 (3)
C(8)	0.4329 (8)	0.0551 (4)	–0.0594 (4)
C(9)	0.1704 (8)	0.2255 (4)	–0.1052 (4)
C(10)	0.1069 (9)	0.1944 (5)	–0.1700 (4)
C(11)	0.3485 (7)	0.2070 (4)	0.0106 (4)
C(12)	0.4682 (7)	0.2394 (4)	–0.0163 (4)
Hf(2)	0.54677 (3)	0.00355 (1)	0.42876 (1)
Cl(4)	0.3609 (2)	–0.06978 (8)	0.46881 (8)
Cl(5)	0.6967 (2)	–0.09621 (8)	0.43769 (9)
Cl(6)	0.4054 (2)	0.09973 (8)	0.39024 (8)
P(3)	0.7588 (2)	0.07484 (9)	0.38418 (9)
P(4)	0.4482 (2)	–0.0557 (1)	0.3107 (1)
C(13)	0.9090 (7)	0.0512 (4)	0.4359 (3)
C(14)	1.0384 (7)	0.0815 (4)	0.4172 (4)
C(15)	0.8085 (7)	0.0619 (4)	0.3005 (3)
C(16)	0.8561 (8)	–0.0146 (4)	0.2869 (4)
C(17)	0.7547 (8)	0.1719 (3)	0.3917 (4)
C(18)	0.6754 (9)	0.2114 (4)	0.3370 (4)
C(19)	0.2724 (7)	–0.0482 (4)	0.2982 (3)
C(20)	0.2042 (8)	–0.0796 (4)	0.2362 (4)
C(21)	0.5001 (9)	–0.0223 (6)	0.2338 (4)
C(22)	0.4755 (9)	0.0559 (7)	0.2209 (4)
C(23A)	0.506 (1)	–0.1454 (5)	0.2870 (7)
C(24A)	0.455 (2)	–0.1995 (5)	0.3329 (7)
C(23B)	0.440 (1)	–0.1546 (5)	0.3158 (8)
C(24B)	0.567 (1)	–0.1849 (6)	0.2917 (8)

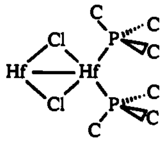
Table III. Selected Bond Distances and Angles for $Hf_2Cl_6(PEt_3)_4$

molecule 1		molecule 2	
	Bond Distances (Å)		
Hf(1)–Hf(1)′	3.097 (1)	Hf(2)–Hf(2)′	3.118 (1)
Hf(1)–Cl(1)	2.528 (2)	Hf(2)–Cl(4)	2.537 (2)
Hf(1)–Cl(1)′	2.537 (2)	Hf(2)–Cl(4)′	2.539 (2)
Hf(1)–Cl(2)	2.414 (2)	Hf(2)–Cl(5)	2.422 (2)
Hf(1)–Cl(3)	2.420 (2)	Hf(2)–Cl(6)	2.408 (2)
Hf(1)–P(1)	2.748 (2)	Hf(2)–P(3)	2.765 (2)
Hf(1)–P(2)	2.748 (2)	Hf(2)–P(4)	2.758 (2)
	Bond Angles (deg)		
Cl(2)–Hf(1)–Cl(3)	165.75 (6)	Cl(5)–Hf(2)–Cl(6)	165.33 (6)
Cl(1)–Hf(1)–P(1)	172.81 (5)	Cl(4)–Hf(2)–P(3)	176.06 (5)
Cl(1)′–Hf(1)–P(2)	171.11 (5)	Cl(4)′–Hf(2)–P(4)	174.24 (5)
P(1)–Hf(1)–P(2)	92.67 (5)	P(3)–Hf(2)–P(4)	98.95 (6)
Hf(1)–Cl(1)–Hf(1)′	75.38 (5)	Hf(2)–Cl(4)–Hf(2)′	75.78 (4)
Cl(1)–Hf(1)–Cl(1)′	104.62 (5)	Cl(4)–Hf(2)–Cl(4)′	104.22 (5)
Cl(1)′–Hf(1)–P(1)	81.70 (5)	Cl(4)′–Hf(2)–P(3)	77.16 (5)
Cl(1)–Hf(1)–P(2)	81.46 (5)	Cl(4)–Hf(2)–P(4)	79.95 (6)
Cl(1)–Hf(1)–Cl(2)	95.95 (5)	Cl(4)–Hf(2)–Cl(5)	92.55 (5)
Cl(1)–Hf(1)–Cl(3)	93.57 (6)	Cl(4)–Hf(2)–Cl(6)	93.61 (5)
Cl(2)–Hf(1)–Cl(1)′	90.89 (5)	Cl(5)–Hf(2)–Cl(4)′	97.14 (6)
Cl(2)–Hf(1)–P(1)	87.27 (5)	Cl(5)–Hf(2)–P(3)	83.60 (5)
Cl(2)–Hf(1)–P(2)	81.93 (5)	Cl(5)–Hf(2)–P(4)	86.55 (6)
Cl(3)–Hf(1)–Cl(1)′	96.95 (6)	Cl(6)–Hf(2)–Cl(4)′	94.23 (5)
Cl(3)–Hf(1)–P(1)	82.13 (6)	Cl(6)–Hf(2)–P(3)	89.95 (5)
Cl(3)–Hf(1)–P(2)	89.04 (6)	Cl(6)–Hf(2)–P(4)	81.44 (6)

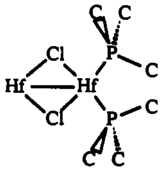
$Hf_2Cl_6(dippe)_2$,[3] $Hf_2Cl_6(PMe_2Ph)_4$,[4] and $Hf_2I_6(PMe_2Ph)_4$:[8] an edge-shared bioctahedron with the phosphine ligands located trans to the two bridging chloride atoms. The structure of $Hf_2Cl_6(PEt_3)_4$ is also closely related to that of the zirconium analogue $Zr_2Cl_6(PEt_3)_4$[5] although, curiously, crystals of these two compounds are not isomorphous.

A comparison of bond distances and angles of $Hf_2Cl_6(PEt_3)_4$ with those of analogous group 4 $M_2Cl_6(PR_3)_4$ dimers shows the following trends: (1) The M–M distances increase in the order Hf–Hf < Zr–Zr < Ti–Ti, and typical M–M bond lengths are ca. 3.10 Å (Hf), 3.14 Å (Zr), and 3.44 Å (Ti). The Hf–Hf and Zr–Zr bond lengths are comparable to those of 3.127 and 3.179 Å, respectively, for the bulk metals, whereas the Ti–Ti distance in $Ti_2Cl_6(dippe)_2$[9] is much longer than that of 2.896 Å in bulk Ti. (2) The M–Cl and M–P distances increase in the order Ti–X < Hf–X < Zr–X and closely follow the sum of the covalent radii of the metal and the ligand atom. (3) The $M–Cl_b–M$ angles of ca. 76° for the hafnium complexes and ca. 78° for the zirconium complexes are acute and reflect the presence of strong metal–metal bonding. (4) The $Cl_t–M–Cl_t$ angles are ca. 162–169° and are smaller than 180° due to nonbonded repulsions between the terminal chloride ligands on the adjacent metal centers.

Interestingly, the two independent $Hf_2Cl_6(PEt_3)_4$ molecules in the asymmetric unit have somewhat different bond distances and angles. For example, the Hf–Hf and Hf–P distances are 0.021 (1) and 0.013 (2) Å shorter in molecule 1. More significantly, the P–Hf–P angle is 6.23 (6)° smaller in molecule 1. These differences are associated with differences in the disposition of the ethyl substituents of the phosphine ligands. In both molecules, the phosphines are disposed in such a fashion that one α-carbon atom of each phosphine is approximately in the plane of the $Hf(\mu-Cl)_2Hf$ core. However, the structural difference between molecule 1 and molecule 2 is illustrated by the following:



molecule 1



molecule 2

The corresponding torsion angles are given in Table IV.

It is evident that there must be significant steric repulsion between the two ethyl substituents that point toward each other in molecule 2. There is one significant contact between the two relevant ethyl groups; the H(15B)–H(22B) contact of 2.20 (1) Å and the H(16B)–H(21B) contact of 2.27 (1) Å are within the 2.40 Å sum of the van der Waals radii for two hydrogen atoms.[10] This steric congestion has been relieved to a considerable extent by opening up the P–Hf–P angle (and somewhat by lengthening the Hf–P bonds) in molecule 2 relative to molecule 1.

There is one other case of a group 4 $M_2Cl_6(PR_3)_4$ compound that crystallizes with two independent molecules in the asymmetric unit: $Zr_2Cl_6(dppe)_2$, where dppe is 1,2-bis(diphenylphosphino)ethane.[11] However, in this molecule, the conformational freedom of the dppe ligand is constrained by the bidentate structure; as a result, the bond distances and angles in the two independent molecules are rather similar.

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Table IV. Torsion Angles (deg) for the Ethyl Substituents of the Phosphine Ligands in $Hf_2Cl_6(PEt_3)_4$

molecule 1		molecule 2	
Hf(1)′-Hf(1)-P(1)-C(1)	-20.5 (3)	Hf(2)′-Hf(2)-P(3)-C(13)	52.3 (2)
Hf(1)′-Hf(1)-P(1)-C(3)	-140.6 (2)	Hf(2)′-Hf(2)-P(3)-C(15)	171.5 (3)
Hf(1)′-Hf(1)-P(1)-C(5)	101.3 (3)	Hf(2)′-Hf(2)-P(3)-C(17)	-63.0 (3)
Hf(1)′-Hf(1)-P(2)-C(7)	-16.1 (3)	Hf(2)′-Hf(2)-P(4)-C(19)	43.3 (3)
Hf(1)′-Hf(1)-P(2)-C(9)	104.9 (6)	Hf(2)′-Hf(2)-P(4)-C(21)	163.5 (4)
Hf(1)′-Hf(1)-P(2)-C(11)	-136.7 (3)	Hf(2)′-Hf(2)-P(4)-C(23A)	-90.7 (5)
		Hf(2)′-Hf(2)-P(4)-C(23B)	-58.8 (4)

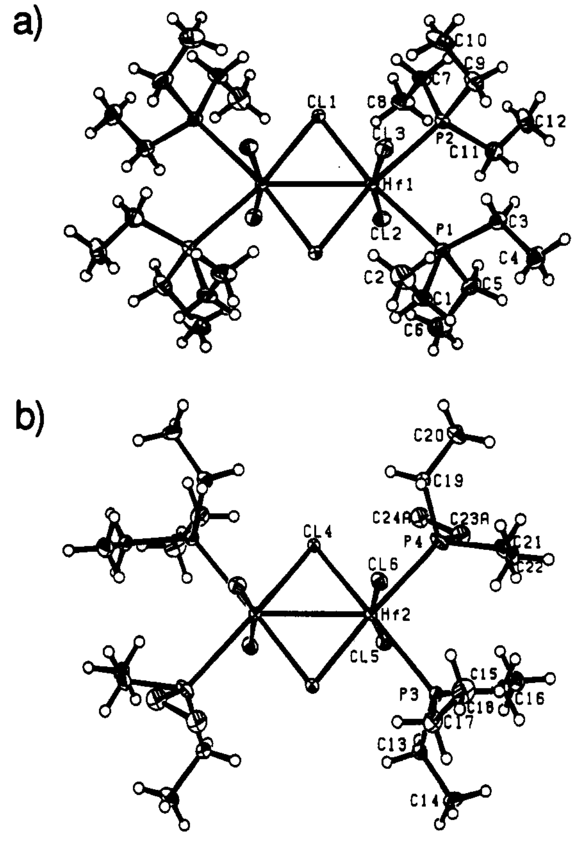


Figure 1. ORTEP diagram of $Hf_2Cl_6(PEt_3)_4$: (a) molecule 1; (b) molecule 2. The ellipsoids represent the 35% probability density surfaces.

Phosphine-Exchange Studies. Treatment of $Hf_2Cl_6(PEt_3)_4$ with excess trimethylphosphine in toluene yields a green precipitate, which has been identified as the phosphine-exchange product $Hf_2Cl_6(PMe_3)_4$.

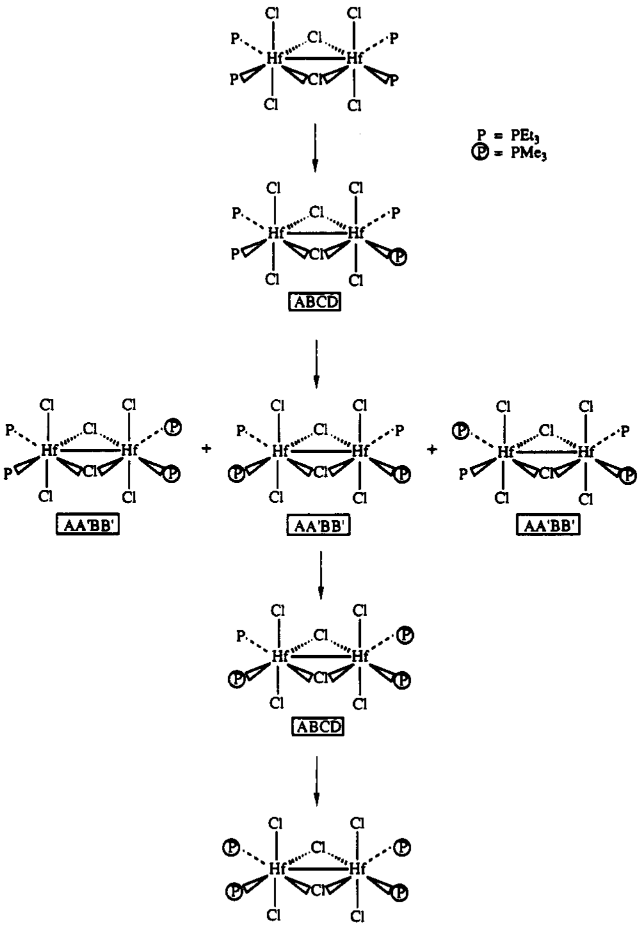
$$Hf_2Cl_6(PEt_3)_4 + 4PMe_3 \rightarrow Hf_2Cl_6(PMe_3)_4 + 4PEt_3$$

This species is only slightly soluble in aromatic solvents. The $^{31}P\{^1H\}$ NMR spectrum of this product consists of a singlet at δ -24.4, which corresponds to a coordination chemical shift of +38 ppm. The ^1H NMR spectrum of $Hf_2Cl_6(PMe_3)_4$ is a doublet at δ 1.44 (J_{PH} = 6.5 Hz); the absence of any virtual coupling in the ^1H NMR line shape suggests that the phosphorus–phosphorus coupling constants are small. This suggestion has been confirmed by the following experiments.

An NMR tube charged with a toluene-d_8 solution of $Hf_2Cl_6(PEt_3)_4$ was cooled to -80 °C and treated with PMe_3. The tube was then placed in the probe of an NMR instrument which had been precooled to -80 °C, and the sample was monitored as the temperature was gradually raised.

Initially, only $Hf_2Cl_6(PEt_3)_4$, PMe_3, and trace amounts of free PEt_3 are seen in the $^{31}P\{^1H\}$ spectrum; however, as the temperature is raised, $Hf_2Cl_6(PEt_3)_4$ reacts to give a succession of exchange products (see Scheme I). At -80 °C, no exchange is apparent, but at -60 °C, new peaks that correspond to a species of stoichiometry $Hf_2Cl_6(PEt_3)_3(PMe_3)$ are clearly seen. At -50 °C, two new species of stoichiometry $Hf_2Cl_6(PEt_3)_2(PMe_3)_2$ become apparent,[12] and at -40 °C, $Hf_2Cl_6(PEt_3)(PMe_3)_3$ can be identified in the $^{31}P\{^1H\}$ NMR spectrum. Finally, at -30 °C, $Hf_2Cl_6(PMe_3)_4$ is the predominant product, and at higher temperatures it is the only species in the $^{31}P\{^1H\}$ NMR spectrum besides PEt_3 and excess PMe_3.[13] Chemical shifts and coupling constants for these species are collected in Table V.

Scheme I



The first substitution product, $Hf_2Cl_6(PEt_3)_3(PMe_3)$, exhibits an ABCD spin system, with $J_{AB} \sim J_{CD} \sim 4$ Hz. All of the other coupling constants are less than the 1.9-Hz line widths of the ^{31}P NMR resonances. The unique PMe_3 ligand has a chemical shift ($\delta_D \sim -26$) that is distinct from those of the three PEt_3 ligands ($\delta_A \sim \delta_B \sim \delta_C \sim -3$). The PMe_3 ligand is coupled to only one of the three PEt_3 groups, and we assume that this 4.2-Hz coupling is to the PEt_3 ligand that is bound to the same hafnium center. Presumably, the other resolvable coupling of 3.5 Hz is between the two chemically inequivalent PEt_3 groups that are bound to

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[12] *Three* isomers of $Hf_2Cl_6(PEt_3)_2(PMe_3)_2$ are possible, but curiously only two are apparent in the ^{31}P NMR spectra. It is possible that the two isomers that have PMe_3 groups on opposite hafnium centers have identical ^{31}P NMR chemical shifts and are therefore not distinguishable.

[13] This succession of products seen in this phosphine-exchange study is similar to that resulting from addition of PMe_3 or PMe_2Ph to the quadruply-bonded dimolybdenum complex $Mo_2Me_4(PEt_3)_4$: Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953–3955.

Table V. $^{31}P\{^1H\}$ NMR Chemical Shifts and Coupling Constants for the $Hf_2Cl_6(PEt_3)_x(PMe_3)_{4-x}$ Species

cmpd	spin system	chem shift	coupl const[a]
$Hf_2Cl_6(PEt_3)_4$	A_4	$\delta_A = -3.35$ (s)	
$Hf_2Cl_6(PEt_3)_3(PMe_3)$	ABCD	$\delta_A = -2.46$ (d)	$J_{AB} = 3.5$
		$\delta_B = -3.01$ (d)	$J_{CD} = 4.2$
		$\delta_C = -2.94$ (d)	
		$\delta_D = -25.84$ (d)	
$Hf_2Cl_6(PEt_3)_2(PMe_3)_2$	AA'BB'	$\delta_A = -1.47^b$ (d)	$J_{AB} = 4.2$
		$\delta_B = -25.71$ (d)	
	AA'BB'	$\delta_A = -1.47^b$ (s)	
		$\delta_B = -25.63$ (s)	
$Hf_2Cl_6(PEt_3)(PMe_3)_3$	ABCD	$\delta_A = -0.89$ (d)	$J_{AB} = 2.2$
		$\delta_B = -24.89^b$ (d)	$J_{CD} = 3.6$
		$\delta_C = -24.89^b$ (d)	
		$\delta_D = -25.28$ (d)	
$Hf_2Cl_6(PMe_3)_4$	A_4	$\delta_A = -24.41$ (s)	

[a] Couplings constants in hertz. Coupling constants that do not appear in the table are equal to zero or are undefined. [b] Overlapping peaks.

the other hafnium center. Thus, the $^3J_{PP}$ couplings between phosphine ligands bound to *different* hafnium atoms are all essentially zero.[14]

The $^{31}P\{^1H\}$ NMR spectra of the subsequent substitution products can be interpreted similarly. Two isomers of the disubstituted product $Hf_2Cl_6(PEt_3)_2(PMe_3)_2$ are formed; one has the PMe_3 groups bound to different hafnium centers, while the other has both PMe_3 groups bound to the same hafnium atom. The trisubstituted product, $Hf_2Cl_6(PEt_3)(PMe_3)_3$, is again an ABCD spin system. In all cases, the couplings between phosphines bound to the same Hf center are ca. 4 Hz and all other coupling constants are <2 Hz.

Phosphorus–phosphorus couplings between phosphine ligands attached to low-valent group 4 metals are sometimes unexpectedly small; for example, we have seen $^2J_{PP}$ values of less than 5 Hz for coupling between mutually trans PR_3 groups in some mononuclear Ti^{II} complexes.[15] Whether or not there are electronic reasons[16] for small $^2J_{PP}$ coupling constants in low-valent group 4 complexes, in the present $Hf_2Cl_6(PR_3)_4$ molecules, the $^2J_{PP}$ coupling constants may be small merely because the phosphine ligands attached to each hafnium center are mutually cis. However, this explanation cannot account for the small $^3J_{PP}$ coupling constants for phosphine ligands on different hafnium centers, especially since such couplings can be relatively large in other dinuclear systems.[14]

Concluding Remarks. The crystallographic study of $Hf_2Cl_6(PEt_3)_4$ adds to the small but growing number of compounds known to possess a Hf–Hf bond. The Hf–Hf bond distance in this molecule of 3.104 (1) Å falls within the 3.089–3.395-Å range found for the three other crystallographically-characterized Hf^{III} dimers. The presence of two independent $Hf_2Cl_6(PEt_3)_4$ molecules in the asymmetric unit affords an opportunity to evaluate how "deformable" this dimer is. In fact, due to differences in the rotational conformations of the triethylphosphine ligands, the P–Hf–P angles in the two independent molecules are significantly different, and thus the potential energy surface must be rather flat along this reaction coordinate.

Phosphine-exchange studies have been carried out, and $Hf_2Cl_6(PEt_3)_4$ reacts with PMe_3 to give $Hf_2Cl_6(PMe_3)_4$ via a series of mixed-phosphine complexes of stoichiometry $Hf_2Cl_6(PEt_3)_x(PMe_3)_{4-x}$. These intermediates have been detected by $^{31}P\{^1H\}$ NMR spectroscopy, and interestingly, the P–P coupling constants for these molecules are small and never larger than 5 Hz. No P–P coupling between phosphine ligands on opposite hafnium centers was evident.

We are continuing to explore the reactivity of these hafnium(III) dimers.

Experimental Section

All operations were carried out under vacuum or argon. Toluene was distilled under nitrogen from sodium. Hafnium tetrachloride (Strem) was sublimed before use. The sodium–potassium alloy had a stoichiometry $NaK_{2.8}$ and was prepared according to a literature recipe.[17] Triethylphosphine[18] and trimethylphosphine[19] were prepared as described elsewhere.

Elemental analyses were performed by Mr. Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded as Nujol mulls on a Perkin-Elmer 599B instrument using KBr plates. The NMR data were recorded on a General Electric QE-300 spectrometer (^1H NMR, 300 MHz) or on a General Electric GN-500 spectrometer (^{31}P NMR, 202.44 MHz). Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^1H) or 85% H_3PO_4 (^{31}P).

Hexachlorotetrakis(triethylphosphine)dihafnium(III). To a slurry of hafnium tetrachloride (2.56 g, 7.99 mmol) in toluene (50 mL) were added triethylphosphine (2.36 mL, 15.99 mmol) and excess sodium–potassium alloy (0.5 mL). The mixture was allowed to stir at room temperature, during which time the solution turned deep brown-green and a black precipitate formed. After being stirred for 4 h, the mixture was filtered and the filtrate was concentrated to 30 mL and cooled to −20 °C. The deep green crystals that formed were collected, and a further crop of crystals was obtained by concentrating and cooling the supernatant. Yield: 0.85 g (20%). Anal. Calcd: C, 27.7; H, 5.90; Cl, 20.4; P, 11.8; Hf, 34.2. Found: C, 27.6; H, 5.91; Cl, 20.0; P, 11.6; Hf, 34.2. IR (cm^{-1}): 2730 w, 1415 s, 1280 w, 1255 s, 1030 s, 1000 sh, 978 m, 760 s, 750 s, 725 m, 710 s, 685 sh, 660 w, 610 m. ^1H NMR (C_6D_6, 20 °C): δ 2.04 (br s, PCH_2CH_3), 1.15 (br s, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ −3.4 (s).

Hexachlorotetrakis(trimethylphosphine)dihafnium(III). To a solution of $Hf_2Cl_6(PEt_3)_4$ (0.54 g, 0.52 mmol) in toluene (45 mL) was added excess trimethylphosphine (0.70 mL, 6.7 mmol). The mixture was allowed to stir at room temperature for 6 h, during which time the solution color faded to pale green and a green powder formed. After the solution had settled at −20 °C for 18 h, the powder was isolated by filtration, washed with pentane (30 mL), and dried under vacuum. Yield: 0.12 g (24%). Anal. Calcd: C, 16.5; H, 4.15; Cl, 24.3; P, 14.2; Hf, 40.8. Found: C, 18.0; H, 4.40; Cl, 23.6; P, 13.3; Hf, 40.3. IR (cm^{-1}): 1430 sh, 1415 m, 1300 m, 1285 m, 950 s, 840 w, 775 m, 725 m, 664 w. ^1H NMR (C_6D_6, 20 °C): δ 1.44 (d, PMe_3, $J_{PH} = 6.5$ Hz). ^{31}P NMR (C_6D_6, 20 °C): δ −24.4 (s).

Crystallographic Studies.[20] Single crystals of $Hf_2Cl_6(PEt_3)_4$, grown from toluene, were mounted on glass fibers using Paratone-N oil (Exxon) and were immediately cooled to −75 °C in a nitrogen stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions. The diffraction symmetry was supported by examinations of the axial photographs. Least-squares refinement using 25 reflections yielded the cell dimensions given in Table I.

Data were collected in one quadrant of reciprocal space ($+h,-k,\pm l$) using measurement parameters listed in Table I. Systematic absences for $0k0$ ($k \neq 2n$) and $h0l$ ($k \neq 2n$) were consistent only with space group $P2_1/c$. The measured intensities were reduced to standard factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied. Systematically absent reflections were deleted, and symmetry-equivalent reflections were

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(14) Interestingly, $^3J_{PP}$ couplings as large as 39 Hz have been seen between phosphine ligands bound to different molybdenum centers in quadruply-bonded dimolybdenum species: Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 2041–2042.

(15) Spencer, M. D.; Morse, P. M.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.*, in press.

(16) The d-orbitals are unusually high in energy in low-valent group 4 complexes; as a consequence, π-back-bonding to the phosphine ligands may be enhanced and σ-donation from the phosphine to the metal may be weakened. If this is the case, near-zero J_{PP} coupling constants could arise in certain compounds if, for example, coupling through the π-bonding framework were similar in magnitude but opposite in sign to the coupling through the σ-bonds.

(17) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

(18) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156.

(19) Luetkens, M. L.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P. *Inorg. Synth.* **1989**, *26*, 7–12.

(20) For details of the crystallographic procedures and programs used, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977–4982.

averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by Patterson (SHELXS-86) and weighted difference Fourier methods. The positions of the hafnium atoms were deduced from a Patterson map, and subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms, including two disordered positions for ethyl carbons C(23) and C(24). The disordered ethyl carbon geometries were constrained to be equivalent, and a site occupancy factor was refined for these atoms. The site occupancy factor refined to 0.509 (7) for group "A". Hydrogen atoms attached to ordered carbon atoms were included in the refinement as fixed contributors in "idealized" positions with C–H = 0.95 Å. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.477/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was varied for the hydrogen atoms. An empirical isotropic extinction parameter was also refined, which converged to 1.7×10^{-8}. Successful convergence was indicated by the maximum shift/error of 0.042 in the last cycle. Final refinement parameters are given in Table I. The largest peaks in the final difference Fourier map were located in the vicinity of the hafnium atoms (+2.14 e/Å^3). A final analysis of variance between observed and calculated structure factors showed a slight dependence on sin θ.

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Supplementary Material Available: Tables of full crystal data, calculated hydrogen atom positions, anisotropic thermal parameters, and complete bond distances and angles for $Hf_2Cl_6(PEt_3)_4$ (5 pages). Ordering information is given on any current masthead page.