tration in an attempt to answer this question.

Acknowledgment. This work was supported in part by a grant from the NIH to Brandeis University (BRSG-S07-RR07044). We are grateful to A. Redfield for his generosity in allowing us to use the LDB-500 NMR instrument, which was built with funds from the NIH (GM-20168).

Arenes with Hafnium(II) Moieties Bonded to Both Faces

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No molecular compound of Hf(II) not containing a η^5-C_5H_5 group is yet to be found fully described in the literature. Moreover, compounds in which six-membered arene rings are simultaneously and equivalently bonded to two metal atoms lying opposite to each other above and below the center of the ring are rare.[1,2] We report here the preparation of two compounds that embody both of these features. Crystal structures and a molecular orbital formulation of the bonding are also given.

The compounds are $Hf_2I_4(PMe_2Ph)_4(\mu$-η^{12}-arene), where the arene is benzene (**1**) or toluene (**2**). The compounds were synthesized by reduction of HfI_4 with 2 equiv of Na/Hg in the appropriate arene, followed by addition of 2 equiv of dimethylphenylphosphine. The solutions turned immediately red upon addition of the phosphine. The reaction was allowed to proceed for 24 h, at which time the solution was filtered through Celite and layered with approximately 20 mL of hexane. The appearance of red crystalline plates occurred within 3-5 days. The products were obtained in ca. 30% yields and gave satisfactory elemental analysis.

Both compounds have been characterized by X-ray crystallography.[3] Figure 1 shows a molecule of **1** viewed down the Hf-Hf axis and Figure 2 shows a side view of the molecule of **2**. The two molecules are essentially identical in their dimensions. The Hf-I and Hf-P bond lengths have the following ranges and average values: Hf-I, 2.885-2.916, 2.898 (4) Å; Hf-P, 2.780-2.800, 2.787 (4) Å. The C-C bond lengths within the central rings have a range and mean value of 1.41-1.55 and 1.47 Å, respectively. The Hf-C distances are spread over a considerable range, 2.28-2.55 Å, with a mean of 2.42 Å. This is in accord with the small but real ring puckering that can be seen in Figure 2.

The ^1H NMR spectrum of **2** shows two signals for the central ring at 3.34 (broad mult) and 3.12 ppm (narrow mult) in an intensity ratio of 3:2. The ^{31}P spectrum of **2** is markedly temperature dependent, suggesting that one or more forms of internal rotation occur. The interpretation of the NMR data is not entirely clear at present, but they seem to imply that while the central ring may be rigidly fixed in the cage of $Hf_2I_4P_4$ atoms at -80 °C, it is rotating rapidly on the ^1H NMR time scale at room temperature.

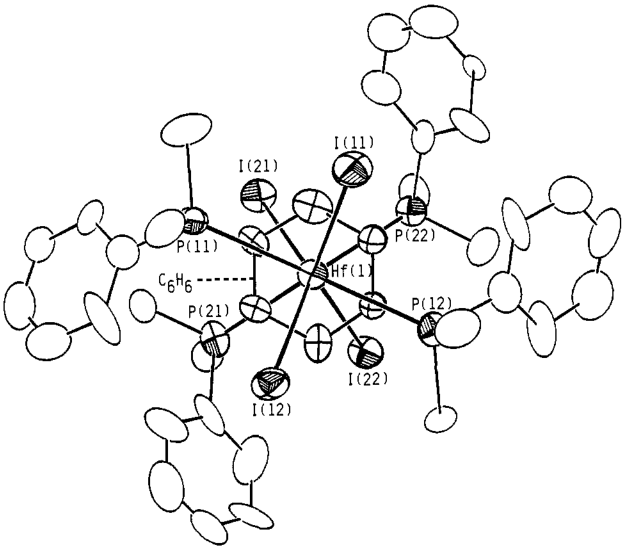

Figure 1. A view of **1** looking down the Hf-Hf axis.

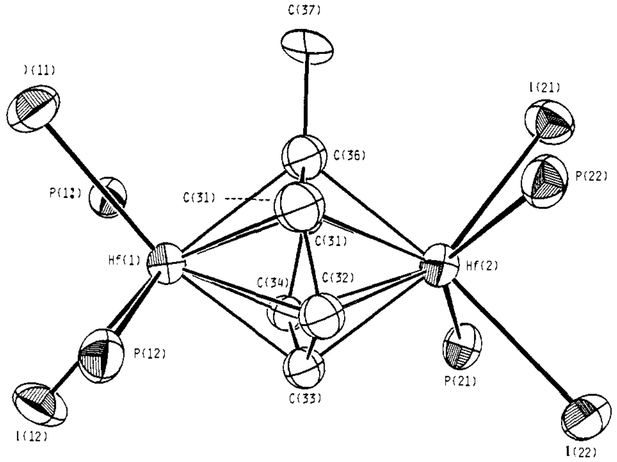

Figure 2. A side view of **2**.

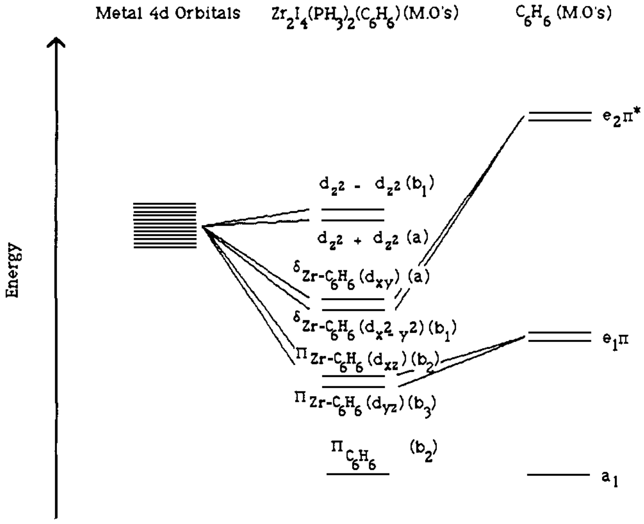

Figure 3. A partial molecular orbital energy level diagram for $Zr_2I_4(PH_3)_2(C_6H_6)$ (D_2 staggered) showing only metal d orbitals and arene π and π^* orbitals.

Finally, we have employed the Fenske-Hall[4] approximation to the Hartree-Fock method to investigate the bonding of the $HfI_2(PMe_2Ph)_2$ moieties to the central benzene ring in **1**. The

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(1) The first one was reported only in 1983: Duff, A. W.; Jones, K.; Goddard, R.; Kraus, H. J.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

(2) Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096.

(3) Compound **1** crystallized in $P2_1/c$ with a = 12.482 (5) Å, b = 13.542 (6) Å, c = 33.857 (15) Å, V = 5722 (7) Å^3, and Z = 4 for an asymmetric unit $Hf_2I_4(PMe_2Ph)_4(C_6H_6)\cdot 2C_6H_6$. With a data/parameter ratio of 7, refinement converged with R = 0.049 and R_w = 0.060. Compound **2** crystallized in $P2_1/c$ with a = 13.612 (6) Å, b = 15.727 (7) Å, c = 22.900 (9) Å, V = 4869 (4) Å^3, and Z = 4 for an asymmetric unit $Hf_2I_4(PMe_2Ph)_4(C_7H_8)$. With a data/parameter ratio of 9, refinement converged with R = 0.049 and R_w = 0.062.

(4) Fenske, R. F.; Hall, M. B. *Inorg. Chem.* **1972**, *11*, 768.

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rotational relationships observed in the crystals of **1** and **2** correspond to an idealized symmetry of D_2. With this structure[5] our calculations (taking the Z axis as the Hf–Hf axis) show that the HOMO and SHOMO are nearly degenerate and are formed by donation of metal d_{xy} and $d_{x^2-y^2}$ electron density into the slightly split components of the empty arene $e_2\pi^*$ orbitals (see Figure 3). The next 16 molecular orbitals below the SHOMO are 8 I lone-pair, 4 M–I σ-bonding, and 4 M–P σ-bonding orbitals, after which we have the filled arene $e_1\pi$ orbitals that donate moderately to and split (by 0.4 eV) the metal d_{xz} and d_{yz} orbitals. The nondegenerate arene π orbital is essentially unperturbed by its surroundings and the metal d_{z^2} orbitals interact with each other only weakly to form a nearly degenerate pair of LUMOs. The bonding is thus understandable in terms of arene frontier orbitals donating to and accepting from metal d orbitals.

With this picture of the bonding it seems likely that rotation of the central arene about the M–M axis will have little electronic hindrance. There is also a clear indication that the dinuclear character is not essential and that $MI_2(PR_3)_2$(arene) species may be capable of existence. These and other ideas are under active study.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant A494.

Supplementary Material Available: Tables of crystallographic parameters, atomic positions, thermal displacements, and bond lengths and angles (16 pages); table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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[5] To make the calculation tractable we have also replaced Hf by Zr and PMe_2Ph by PH_3.

Ab Initio Study of the Structure and Infrared Spectrum of the 1:1 Adduct of SiF_4 and NH_3

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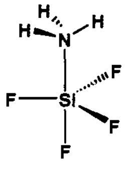
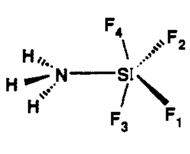
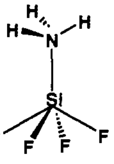
Ault has reported the matrix isolation of a 1:1 adduct of SiF_4 and NH_3.[1-3] On the basis of its infrared spectrum, he proposed that this adduct has a trigonal-bipyramidal arrangement about the central silicon with the NH_3 group in an axial position (I). Subsequent ab initio calculations by Marsden[4] located three stationary points (I–III) on the potential surface and gave theoretical support to Ault's original proposal that I is the structure of the 1:1 adduct. However, no theoretical vibrational analyses were done on these structures, and therefore there is no certainty that any of these are truly minima on the potential surface since some symmetry constraints were imposed in the geometry optimizations. We therefore undertook the vibrational analysis of I–III both to determine which if any are minima and also to obtain the calculated infrared spectra of those that might prove to be minima for comparison with the reported spectrum of the adduct.



I



II



III

Table I. Computed IR Frequencies and Intensities (Given in Parentheses) of I[a]

symmetry	$SiF_4{\cdot}NH_3$	$SiF_4{\cdot}{}^{15}NH_3$	$SiF_4{\cdot}ND_3$
A_1	164 (0.00)	164 (0.00)	117 (0.00)
E	177 (16.39)	176 (15.68)	170 (13.44)
A_1	221 (61.93)	217 (58.87)	209 (51.27)
E	309 (0.82)	308 (0.64)	284 (0.02)
E	421 (63.13)	421 (62.60)	420 (60.61)
A_1	473 (120.35)	471 (122.94)	466 (135.71)
E	764 (54.43)	759 (56.74)	608 (38.93)
A_1	788 (0.22)	788 (0.24)	787 (0.03)
A_1	957 (343.15)	957 (343.08)	957 (348.94)
E	1064 (588.83)	1064 (588.62)	1060 (544.87)
A_1	1439 (249.70)	1431 (246.32)	1097 (140.64)
E	1831 (71.94)	1828 (71.56)	1327 (39.56)
A_1	3696 (19.56)	3692 (18.77)	2643 (16.20)
E	3826 (77.13)	3815 (75.80)	2820 (48.72)

[a] Frequencies in cm^{-1} and intensities in km/mol.

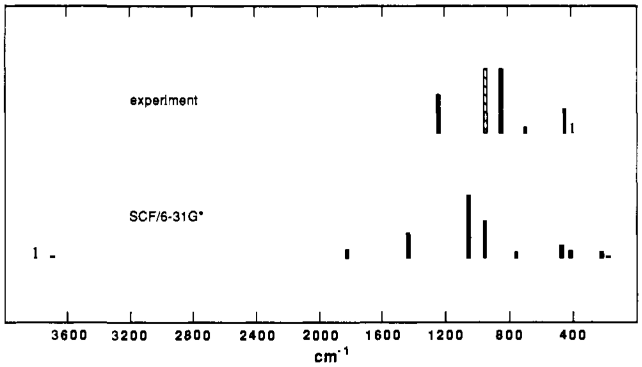


Figure 1. Experimental and theoretical spectra of I. Ault did not report a relative intensity for the open bar shown in the experimental spectrum.

Initially I–III were optimized by using the SCF/3-21G basis set with the following symmetry constraints: I with C_s symmetry (it converged to a C_{3v} structure); II with the F_1–Si–F_2 plane (this plane also contains the nitrogen atom) held perpendicular to the F_3–Si–F_4 plane; III with C_{4v} symmetry of the SiF_4 skeleton. Vibrational analyses gave all real frequencies for I, but a single imaginary frequency was found for both II (67*i*) and III (151*i*), which indicates that I is a minimum and II and III are transition structures on the potential surface. Examination of the normal mode of the imaginary frequency in both II and III indicates that these transition structures may involve fluorine scrambling.

Therefore further calculations were carried out on I to determine if it corresponds to the structure isolated by Ault. An SCF/6-31G* geometry optimization (energy of the optimized structure = −743.148 408 au) was performed for I with a C_{3v} symmetry constraint (the hydrogens attached to nitrogen were staggered with respect to those bound to silicon; $R_{\text{Si-F(axial)}} = 1.591$ Å, $R_{\text{Si-F(equat)}} = 1.584$ Å, $R_{\text{Si-N}} = 2.146$ Å, $R_{\text{N-H}} = 1.004$ Å, $\angle_{\text{Si-N-H}} = 111.0°$, $\angle_{\text{N-Si-F(equat)}} = 81.9°$, $\angle_{\text{F(equat)-Si-F(equat)}} = 118.0°$, $\angle_{\text{H-N-H}} = 107.9°$), and a subsequent vibrational analysis with the same basis set again gave all real frequencies. The computed frequencies and IR intensities for I are given in Table I along with their symmetries. In Figure 1 are plotted the computed infrared spectrum of I (those bands with a relative intensity >0.00) and the experimental spectrum reported by Ault for the 1:1 adduct of ammonia and silane. It is immediately seen that there is a very good correspondence between the computed and observed spectra[3] (Ault reported the spectrum only in the region of 380–1260 cm^{-1}). This is strong evidence that the structure of the adduct is indeed I as suggested. Furthermore Ault's symmetry assignments of the observed bands are in agreement with those calculated.[5]

Also given in Table I are the computed frequencies and intensities of the isotopomers $SiF_4{\cdot}{}^{15}NH_3$ and $SiF_4{\cdot}ND_3$. Comparison with the frequencies reported by Ault for these isotopomers

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[1] Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.
[2] Lorenz, T. J.; Ault, B. S. *Inorg. Chem.* **1982**, *21*, 1758.
[3] Ault, B. S. *Rev. Chem. Intermed.* **1988**, *9*, 233.
[4] Marsden, C. J. *Inorg. Chem.* **1983**, *22*, 3177.

[5] The 456-cm^{-1} absorption should have been assigned in ref 1 as an A_1 rather than an E mode (Ault, B. S., private communication).

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