Halo Carbonyls of the Group 4 Elements. Synthesis and Structural Characterization of $Hf(CO)_2(Me_2PCH_2CH_2PMe_2)_2I_2$, the First Stable Derivative of the Unknown $Hf(CO)_6I_2$[†]

John E. Ellis,* Scott R. Frerichs, and Kai-Ming Chi

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received May 8, 1990

Summary: Treatment of $HfI_4(Me_2PCH_2CH_2PMe_2)_2$ with potassium naphthalenide at −60 °C in 1,2-dimethoxyethane followed by a low-temperature, atmospheric pressure carbonylation provided $Hf(CO)_2(dmpe)_2I_2$ in 60–70% yield as a yellow-green crystalline substance. This material represents the first stable derivative of the unknown $Hf(CO)_6I_2$ and has been characterized by a single-crystal X-ray structure. The latter establishes the eight-coordinate nature of the hafnium in the complex. Much less thermally stable compounds, presumed to be $Hf(CO)_2(dmpe)_2Cl_2$ and $Zr(CO)_2(dmpe)_2I_2$, have also been prepared by analogous procedures and are formulated on the basis of their infrared spectra in the ν(CO) region.

Hafnium carbonyl chemistry remains poorly explored and has been limited to compounds containing at least one tridentate ligand such as the cyclopentadienyl,[1] pentamethylcyclopentadienyl,[1] indenyl,[2] 1,3,5-tri-*tert*-butylbenzene,[3] or 1,1,1-tris[(dimethylphosphino)methyl]ethane groups.[4] Now we report on the synthesis, isolation, and characterization of a new type of hafnium carbonyl, $Hf(CO)_2(dmpe)_2I_2$, which is stabilized only by the bidentate ligand 1,2-bis(dimethylphosphino)ethane (dmpe) and iodide groups and may be considered to be the first stable derivative of the unknown $Hf(CO)_6I_2$. Equation 1 summarizes the procedure employed for the synthesis of this and an analogous zirconium complex. Conditions: (i)

$$HfI_4(dmpe)_2 + 2KC_{10}H_8 \xrightarrow{(i)} \xrightarrow{(ii)} Hf(CO)_2(dmpe)_2I_2 + 2KI + 2C_{10}H_8 \quad (1)$$

argon, −60 °C, 1,2-dimethoxyethane, 30 min; (ii) CO (1 atm of pressure), −60 to +20 °C, 12 h.

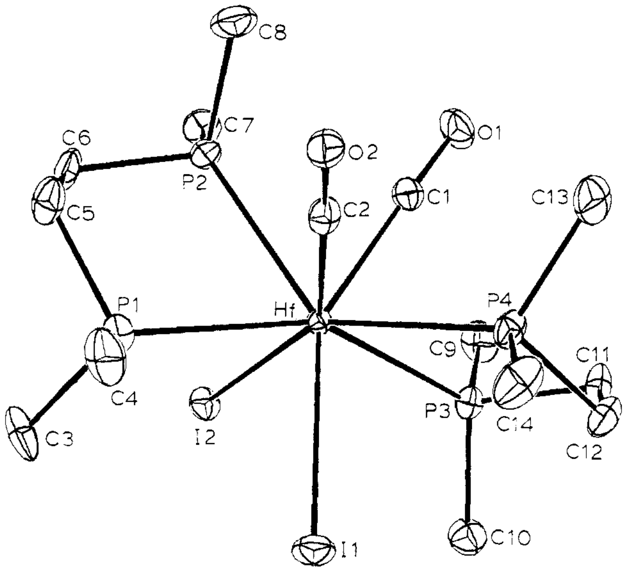

Figure 1. ORTEP plot of $Hf(CO)_2(dmpe)_2I_2$ drawn with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Hf-I(1) = 2.986 (1), Hf-I(2) = 3.028 (1), Hf-C(1) = 2.153 (7), Hf-C(2) = 2.138 (7), Hf-P(1) = 2.749 (2), Hf-P(2) = 2.748 (2), Hf-P(3) = 2.752 (2), Hf-P(4) = 2.748 (2), C(1)-O(1) = 1.146 (9), C(2)-O(2) = 1.159 (9), P-C (av) = 1.82 (2), C-C (av) = 1.53 (1), Hf-C(1)-O(1) = 175.5 (6), Hf-C(2)-O(2) = 176.4 (6), I(1)-Hf-C(1) = 148.9 (2), I(1)-Hf-C(2) = 104.6 (2), I(2)-Hf-C(2) = 149.2 (2), I(2)-Hf-C(1) = 104.1 (2), I(1)-Hf-I(2) = 86.11 (2), C(1)-Hf-C(2) = 81.6 (3), P(1)-Hf-P(2) = 73.17 (6), P(3)-Hf-P(4) = 72.76 (6).

In a typical synthesis, treatment of a cold (−60 °C) yellow solution of $HfI_4(dmpe)_2$[5,6] (2.2 mmol) in 70 mL of 1,2-dimethoxyethane (DME) with $KC_{10}H_8$ (4.5 mmol) in 100 mL of DME under argon provided within minutes a dark red-brown intermediate, presumed to be a naphthalene complex. After exchange of argon by purified carbon monoxide (1 atm of pressure), the reaction mixture was stirred for 12 h and slowly warmed to room temperature. During this time, the solution gradually turned green. Following filtration, solvent was removed in vacuo and pentane was added to yield a yellowish-green solid. Recrystallization from toluene–pentane gave a 70% yield (1.25 g) of yellow-green crystals, which provided satisfactory elemental analyses for the composition $Hf(CO)_2(dmpe)_2I_2$.[7] Corresponding reductive carbonylations of $ZrI_4(dmpe)_2$[5] and $HfCl_4(dmpe)_2$[6] gave green solutions of products believed to be $Zr(CO)_2(dmpe)_2I_2$ and $Hf(CO)_2(dmpe)_2Cl_2$.[8] However, these compounds were too thermally unstable to isolate as pure substances and could only be characterized on the basis of their infrared spectra in the ν(CO) region. The latter consisted of two bands of approximately the same positions, shapes, and relative intensities as corresponding bands of $Hf(CO)_2(dmpe)_2I_2$. The analogous $Hf(^{13}CO)_2(dmpe)_2I_2$ (ν(CO) in DME: 1841

[†] Dedicated to Professor J. Doyle Britton on the occasion of his 60th birthday.

(1) (a) Sikora, D. J.; Moriarty, K. J.; Rausch, M. D. *Inorg. Synth.* **1986**, *24*, 147 and references cited therein. (b) Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Orgnomet. Chem.* **1986**, *25*, 317 and references cited therein. (c) Palmer, G. T.; Brooks, F.; Kool, L. B.; Rausch, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 4417. (d) Frerichs, S. R.; Ellis, J. E. *J. Organomet. Chem.* **1989**, *359*, C41. (e) Wielstra, Y.; Gambarotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* **1988**, *7*, 2177 and references cited therein.

(2) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E.; Samuel, E. *J. Organomet. Chem.* **1987**, *327*, 39.

(3) Cloke, F. G. N.; Lappert, M. F.; Lawless, G. A.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1667.

(4) Blackburn, D. W.; Chi, K.-M.; Frerichs, S. R.; Tinkham, M. L.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 437.

(5) To our knowledge, $HfI_4(dmpe)_2$ has *not* been reported previously but was prepared by essentially the same method used to obtain $HfCl_4(dmpe)_2$.[6] In a typical synthesis, 5.0 g of HfI_4 (7.3 mmol) and 3.0 mL (16 mmol) of dmpe were combined in 150 mL of toluene. After the slurry was stirred at 40 °C for 30 min, most material dissolved to provide a light yellow solution. Following filtration and solvent removal, 100 mL of pentane was added to precipitate all product from the filtrate. The pale yellow solid was collected on a glass frit, washed with 2 × 20 mL of pentane, and dried in vacuo. A 92% yield (6.6 g) of $HfI_4(dmpe)_2$, which provided satisfactory elemental analyses, was thereby obtained: Anal. Calcd for $C_{12}H_{32}I_4P_4Hf$: C, 14.61; H, 3.27; P, 12.56. Found: C, 14.85, H, 3.20; P, 12.65. $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C) δ −18.1 (s) ppm. The previously unreported $ZrI_4(dmpe)_2$ was obtained in 78% yield by the same procedure. Anal. Calcd for $C_{12}H_{32}I_4P_4Zr$: C, 16.03; H, 3.59. Found: C, 16.05; H, 3.41; $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C) δ −18.5 (s) ppm.

(6) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 53.

(7) Anal. Calcd for $C_{14}H_{32}I_2O_2P_4Hf$: C, 21.32; H, 4.09; P, 15.71. Found: C, 21.06; H, 4.10; P, 15.45. IR (DME) ν (CO) 1884 m, 1775 s cm^{-1}.

(8) $Hf(CO)_2(dmpe)_2Cl_2$: IR (DME) ν(CO) 1872 m, 1760 s cm^{-1}. $Zr(CO)_2(dmpe)_2I_2$: IR (DME) ν(CO) 1890 m, 1783 s cm^{-1}.

0276-7333/90/2309-2858$02.50/0

m, 1734 s cm^{-1}) was prepared by the same procedure with 99% ^{13}CO. Like the previously reported $(C_5Me_5)Hf(CO)_2(dmpe)Cl$,[9] solutions of $Hf(CO)_2(dmpe)_2I_2$ (1) slowly decomposed in toluene or THF at room temperature unless they were stored under an atmosphere of CO.

The X-ray structure of 1 is shown in Figure 1 and establishes the eight-coordinate nature of the hafnium in the complex.[10] Inspection of the coordination core of 1 suggests that the geometry about hafnium is perhaps better described as a distorted square antiprism (SAP) than a distorted dodecahedron (DD), but the choice is not distinct.[11,12] Selected interatomic distances and angles for 1 are given in Figure 1. The average Hf–C(CO) and C–O bond distances (2.15 (3) and 1.15 (4) Å, respectively) are similar to corresponding values found for $Cp_2Hf(CO)_2$ and $Cp^*{}_2Hf(CO)_2$,[1] but the C(1)–Hf–C(2) angle (81.6 (3)°) is smaller than those of the hafnocene dicarbonyls, perhaps due to the presence of the bulky dmpe ligands.[13,14] Hf–P bond lengths (average = 2.75 (3) Å) are about the same as those in $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ (average Hf–P = 2.760 (6) Å),[9] while they are significantly longer than those present in the less crowded $Hf(\eta\text{-}C_4H_6)_2(dmpe)$ (average Hf–P = 2.69 (2) Å),[15] which contains six- rather than eight-coordinate hafnium.

The ^{31}P NMR spectrum of $Hf(CO)_2(dmpe)_2I_2$ contains two resonances of the same intensity (–4.4 and –12.4 ppm) due to coordinated dmpe at room temperature. It is consistent with the solid-state structure, which shows two chemically inequivalent phosphorus environments; i.e., P(1) and P(3) are in equivalent positions that are closer to the two iodine atoms than those of P(2) and P(4), which in turn are in equivalent positions that are closer to the two carbonyl groups. (See Figure 1.) The ^{13}C NMR spectrum of the isotopically labeled compound, $Hf(^{13}CO)_2(dmpe)_2I_2$, exhibits a binomial pentet carbonyl resonance at 288.2 ppm with a ^{31}P–^{13}C coupling constant of 11.2 Hz.[16] Thus, despite the inequivalence of the phosphorus atoms, the P–C coupling constants appear to be the same. Unfortunately, the poor thermal stability of this material in solution has obviated attempts to observe corresponding NMR spectra at elevated temperatures.

An original objective of this study was to synthesize Zr and Hf analogues of the quite useful titanium complexes, $Ti(CO_3)(dmpe)_2$[17] and $Ti(CO)_5(dmpe)$.[18] While this goal has not yet been achieved, a new type of divalent hafnium carbonyl has been obtained from readily available precursors. This compound promises to be a useful reagent in the study of the chemistry of hafnium carbonyls in the absence of carbocyclic ligands, a virtually unexplored area of chemistry.

Acknowledgment. Financial support for this work was provided by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are indebted to Professor Doyle Britton of the University of Minnesota for the crystal structure determination.

Supplementary Material Available: Details on the X-ray structural analysis and tables of final positional and thermal parameters, interatomic distances and angles, anisotropic thermal parameters, and least-squares planes (11 pages); a table listing observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

---

(9) Stein, B. K.; Frerichs, S. R.; Ellis, J. E. *Organometallics* **1987**, *6*, 2017.

(10) Single crystals of $Hf(CO)_2(dmpe)_2I_2$ were slowly grown from pentane–toluene at 0 °C over a 2-day period. Data collection was carried out at –90 °C on an Enraf-Nonius CAD 4 automated diffractometer using Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/a$ (nonstandard setting of No. 14) and has the cell parameters a = 15.731 (7) Å, b = 10.169 (8) Å, c = 16.902 (11) Å, β = 109.84 (5) °, V = 2543 (5) Å^3, and Z = 4. Intensity data were collected for 5190 reflections of which 4368 were unique and measured $F_o^2 \geq 1.0\sigma F_o^2$ and were used for structure solution and refinement by using Enraf-Nonius CAD 4-SDP programs. The last cycle of least-squares refinement gave residuals of R = 0.036 and R_w = 0.040 and a GOF of 0.964 for a fit of 209 variables to 4368 observations. Complete details of the refinement and tables of data are available as supplementary material.

(11) For example, I(1), P(1), C(2), P(4) and I(2), P(2), C(1), P(3) provide an approximately square antiprismatic array of atoms about hafnium, but the ligands are sufficiently different in character that the angles subtended by the eight metal–ligand bonds and the pseudo-4-fold axis of the SAP passing through the hafnium vary from 52 to 60°. For a given undistorted SAP complex, these angles should have the same value of about 57°.[12] Similarly, one can identify two approximately orthogonal trapezial least-squares planes (dihedral angle = 89.1°) of a dodecahedron in 1. These are defined by Hf, P(1), P(2), C(1), I(1) and Hf, P(3), P(4), C(2), I(2). Although the observed dihedral angle is close to that required for a bona fide DD complex,[12] the positions of the carbonyl carbon, phosphorus, and iodine atoms deviate substantially (0.16–0.35 Å) from the trapezial planes.

(12) Kepert, D. L *Prog. Inorg. Chem.* **1978**, *24*, 179.

(13) Related seven-coordinate compounds of the general formula $Nb(CO)_2(dmpe)_2X$, X = Cl or I, have remarkably acute C–M–C angles of 70° or less and corresponding short nonbonded carbonyl contacts of 2.24–2.30 Å.[14] While the carbonyl groups in these Nb(I) species are likely to be involved in a form of incipient reductive coupling,[14] the carbonyls in our Hf(II) complex have a much longer nonbonded carbonyl contact of 2.82 (2) Å and appear to be more or less normal despite the higher coordination number of this compound.

(14) Bianconi, P. A.; Vrtis, R. N.; Ras, C. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968.

(15) Wreford, S. S.; Whiteney, J. F. *Inorg. Chem.* **1981**, *20*, 3918.

(16) Similar very downfield ^{13}C carbonyl chemical shifts have been reported for other hafnium species: $(C_5Me_5)Hf(CO)_2(dmpe)Cl$, δ 283 ppm;[9] $Hf(CO)_4(trmpe)$, δ 282 ppm;[4] and $[(C_5R_5)Hf(CO)_4]^-$, δ 291 (R = H), 296 (R = Me) ppm.[1d]

(17) Domaille, P. J.; Warlow, R. L.; Wreford, S. S. *Organometallics* **1982**, *1*, 935.

(18) Chi, K.-M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. B.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 163.