Table II. Final Atomic Positional Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms of $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$ with Esd Values in Parentheses

atom	*x/a*	*y/b*	*z/c*
W	4298.6 (1)	2652.5 (2)	2399.5 (2)
N(11)	4244 (2)	245 (5)	2288 (3)
N(12)	3862 (2)	−417 (5)	1544 (3)
C(11)	4987 (2)	−464 (6)	3790 (4)
C(12)	4538 (2)	−767 (6)	2876 (4)
C(13)	4344 (2)	−2065 (6)	2495 (4)
C(14)	3918 (2)	−1817 (6)	1659 (4)
C(15)	3550 (3)	−2828 (6)	971 (6)
N(21)	4049 (2)	2500 (5)	845 (3)
N(22)	3751 (2)	1400 (5)	338 (3)
C(21)	4520 (3)	4542 (8)	605 (5)
C(22)	4207 (2)	3225 (6)	300 (4)
C(23)	4022 (3)	2598 (7)	−548 (5)
C(24)	3741 (2)	1444 (7)	−521 (4)
C(25)	3475 (3)	310 (8)	−1228 (4)
N(31)	3449 (2)	2284 (4)	1909 (3)
N(32)	3167 (2)	1387 (4)	1183 (3)
C(31)	3257 (3)	3863 (7)	2960 (5)
C(32)	3100 (2)	2835 (6)	2202 (5)
C(33)	2614 (2)	2266 (6)	1673 (5)
C(34)	2662 (2)	1373 (6)	1042 (4)
C(35)	2248 (2)	518 (7)	300 (4)
B	3457 (2)	454 (6)	750 (4)
O(1)	4203 (2)	4421 (4)	2367 (3)
O(2)	5000	2472 (5)	2500
C(1) or O(1′)[a]	4403 (2)	2366 (5)	3614 (4)
O(3)[b]	4478 (5)	2393 (10)	4373 (8)

[a] Atoms included with nitrogen scattering curve. [b] Atom given occupancy factor of 0.5.

Table III. Bond Lengths (Å) and Angles (deg) for $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$[a]

Distances			
W–O(1)	1.708 (4)	W–O(2)	1.912 (1)
W–C(1)	1.841 (6)	W–N(11)	2.306 (4)
W–N(21)	2.262 (5)	W–N(31)	2.197 (5)
C(1)–O(3)	1.130 (15)	W···W	3.809 (4)
Angles			
W–O(2)–W	169.2 (2)	O(1)–W–O(2)	103.6 (2)
O(1)–W–C(1)	97.6 (2)	O(1)–W–N(11)	168.4 (2)
O(1)–W–N(21)	93.4 (2)	O(1)–W–N(31)	90.9 (2)
C(1)–W–O(2)	101.6 (2)	O(2)–W–N(21)	85.0 (2)
N(21)–W–N(31)	79.6 (2)	C(1)–W–N(31)	90.6 (3)
C(1)–W–N(11)	84.7 (3)	O(2)–W–N(11)	87.1 (2)
N(11)–W–N(21)	82.7 (2)	N(11)–W–N(31)	77.7 (2)
O(2)–W–N(31)	159.5 (2)	C(1)–W–N(21)	165.4 (3)
W–C(1)–O(3)	170.1 (8)		

[a] Atom C(1) becomes atom O(1′) when the carbonyl ligand is replaced by the oxo ligand.

extinction was made. The structure was solved by Patterson and Fourier methods. The structural model adopted,[28] consistent with the diffraction data and the imposed crystallographic symmetry, was disordered with carbonyl and terminal oxo ligands occupying a common site in the lattice. As an approximation for this disorder, the carbon (or oxygen) bonded to the tungsten was included with a nitrogen scattering factor. Although the hydrogen atoms were revealed on a difference map, they were included in their calculated positions apart from the hydrogen on boron whose coordinates were refined. All non-hydrogen atoms were anisotropically refined. The methyl hydrogens were assigned group isotropic temperature factors while all others were assigned individual temperature factors; all were varied in the refinement apart from those of the C(21) hydrogens (fixed). Refinement was carried out with the SHELX-76 program[27] and Figure 1 was prepared from the output of ORTEP-II.[29] Scattering curves were taken from refs 27 (H, B, C, N, O) and 26b (W), those for the non-hydrogen atoms being corrected for anomalous dispersion.[26c] Final atomic coordinates for non-hydrogen atoms are given in Table II. Selected bond distances and angles are given in Table III.

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Supplementary Material Available: Complete listings of crystallographic data, positional atomic data, thermal parameters, and bond distances and angles (6 pages); listings of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(28) Refinement of models such as $[\{HB(Me_2pz)_3\}WO(CO)]_2(\mu\text{-}O)$ (**2**) and disordered mixtures of **2** and $[\{HB(Me_2pz)_3\}WO_2]_2(\mu\text{-}O)$ was also undertaken. Structure **2** refined with $R = 0.029$ and $R_w = 0.039$, but the carbonyl oxygen O(3) was characterized by large thermal parameters (refined isotropically with $U_{11} = 0.217$ (6) Å^2). Refinement of structure **1** led to slightly lower *R* values and well-behaved anisotropic thermal parameters for all atoms.

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New Syntheses of Xenon Hexafluoride (XeF_6) and Xenon Tetrafluoride (XeF_4)

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With few exceptions, the synthesis of noble-gas fluorides have remained essentially unchanged for the past three decades.[1] For example, xenon hexafluoride, XeF_6, is still generally prepared by the 1966 method of heating a 20:1 mixture of fluorine and xenon in a sealed reactor at 300 °C for 15–17 h at a total pressure of approximately 50 atm.[2] The product mixture can be purified by complexing with sodium fluoride followed by thermal decomposition of the $NaXeF_7$, which is formed, to yield pure XeF_6.[3] However, this method must be used with extreme caution because it requires the use of fluorine at high temperatures and pressures. Irradiation of Xe and F_2 with a high-pressure UV lamp has also been used to prepare XeF_6, but with poor yields and purity.[4]

Xenon tetrafluoride is the most difficult xenon fluoride to prepare because, even under optimal conditions, XeF_2 and XeF_6 are product contaminants. Xenon tetrafluoride prepared by thermal methods results in products containing equilibrium concentrations of XeF_6 and XeF_2. The latter are separated by using metal fluorides on the basis of differing Lewis acid/base properties.[5] These separations can be difficult and time consuming. However, pure XeF_4 can be prepared photolytically in quantitative yield by reaction of xenon with excess fluorine.[6] In this report we present alternative high-yield methods for preparing high-purity XeF_6 and XeF_4 at relatively low pressures.

Experimental Section

Caution. All materials used in these experiments are potent oxidizing agents. In the presence of moisture, XeF_4 and XeF_6 will hydrolyze to

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form explosive XeO_3. The appropriate safety precautions should be observed when these materials are handled.

Materials and Apparatus. Xenon and oxygen (Matheson Gas Co.) were used as received. Dioxygen difluoride, O_2F_2, was prepared by photolysis of a 1:1 mixture of F_2 and O_2 in a copper reactor fitted with a sapphire window at −196 °C.[7] Fluorine (Matheson) was treated with NaF to remove HF before use. Volatile materials were manipulated in a stainless steel vacuum line equipped with Kel-F and stainless steel traps, Autoclave Engineers valves, and MKS and Helicoid pressure gauges. prior to use, the vacuum line was thoroughly passivated with ClF_3 and XeF_6 followed by overnight evacuation. Infrared spectra were recorded with a Perkin-Elmer 1500 Fourier transform spectrometer using a 10-cm stainless steel cell fitted with AgCl windows.

Preparation of XeF_6. A modified version of the "hot wire" reactor described by Bezmel'nitsyn and co-workers was used.[8] The reactor consists of a well-passivated stainless steel tube inside which is a resistively heated nickel filament. The reactor is immersed in liquid nitrogen, and the filament is heated to 700–800 °C by a dc power supply. The reactor is connected to a vacuum system that consists of a ballast volume and a metal bellows circulating pump (Metal Bellows Corp., Model 601). In a typical reaction, xenon (15 mmol) was condensed onto the walls of the reactor in 5-mmol increments to ensure that the xenon was evenly distributed along the complete length of the reactor as a thin coating. Fluorine was then introduced into the ballast cans (160 Torr in 22 L, 190 mmol). Following the addition of the xenon and fluorine, the power was turned on and the filament was heated electrically to 700–800 °C. After the filament had reached the desired operating temperature, the fluorine was circulated through the reactor at a nominal pressure of 50–70 Torr. After 1 h, the reactor was shut down and 2.3 g of white solid material was condensed at −78 °C into a stainless steel trap fitted with a sapphire view-point. The material was identified as pure XeF_6 by infrared spectroscopy and its room-temperature vapor pressure.[2] The 2.3 g of XeF_6 recovered represents a 62% yield based on the xenon used as a starting material. The less than quantitative yield most likely is due to layering effects and condensation of xenon in regions of the reactor that are essentially unavailable to filament-generated fluorine atoms.

Preparation of XeF_4. Xenon (3.0 mmol) and a large excess (10-fold or greater) of O_2F_2 were condensed at −196 °C into a 35-mL stainless steel reaction vessel. A −155 °C cold trap (CF_2Cl_2/liquid N_2 slush bath) was placed around the reactor, which then was allowed to warm slowly to −120 °C over a period of 2–4 h. Subsequently, the reactor was warmed to −78 °C by filling the Dewar flask with dry ice. The system was then left overnight at −78 °C, during which time the excess O_2F_2 decomposed to O_2 and F_2. The volatile material was then passed through a trap cooled to −196 °C to remove O_2 and F_2. The −196 °C trap also retained a white solid material. The −196 °C Dewar flask was replaced with one cooled to −78 °C, and the contents of the trap were pumped on for 1 h to remove CF_4, COF_2, and SiF_4 impurities. The remaining product was identified as a mixture of XeF_2 and XeF_4 (0.58 g) by its infrared spectrum.[9,10] Following a second treatment of the XeF_4/XeF_2 mixture with O_2F_2, as described above, pure XeF_4 product was isolated in quantitative yield (0.62 g, 3.0 mmol) and identified by its infrared[10] and Raman spectra.[10]

Results and Discussion

The reaction of xenon with fluorine under conditions of low pressure and high filament temperature in the "hot wire" reactor provides a useful method for the preparation of pure XeF_6. The use of an excess of fluorine (5–10 times that of xenon) is necessary, since it is likely that some of the fluorine reacts with the reactor walls and hot filament. Excess fluorine also inhibits the formation of XeF_4 and XeF_2 as side products. This reaction, like the reported photochemical reaction for preparing XeF_6, presumably occurs through formation of fluorine atoms.

Xenon tetrafluoride was prepared in quantitative yield and very high purity at low pressure and temperature. The reaction of O_2F_2 with xenon initially converts all of the xenon to a mixture of XeF_2 and XeF_4. Prolonged exposure of this mixture to excess O_2F_2 further fluorinates the remaining Xe(II) to Xe(IV). This observation is contrary to a previously published report in which only XeF_2 was observed from the fluorination of xenon with O_2F_2.[11] We found no evidence for formation of XeF_6 from the reaction of XeF_4 even with a large excess of O_2F_2 over a prolonged period of time. In contrast to hot fluorine atoms, as demonstrated by the reaction of F_2 and xenon above, apparently O_2F_2 is not sufficiently potent to oxidize Xe(IV) to Xe(VI).

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Registry No. XeF_4, 13709-61-0; XeF_6, 13693-09-9; O_2F_2, 7783-44-0; F_2, 7782-41-4; O_2, 7782-44-7; Xe, 7440-63-3.

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Solution and Solid-State Structures of the Monomeric, Piano-Stool Mono(peralkylcyclopentadienyl)vanadium(IV) Trihalides

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Low-valent organovanadium chemistry is dominated by the study of mono- and bis(cyclopentadienyl)vanadium compounds.[2,3] Less studied are compounds with ring alkylation, a derivatization that has been shown to yield reactive compounds such as the highly oxidizing $(\eta\text{-}C_5H_4Me)VCl_3$.[4] Cyclopentadienyl ring *per*alkylation has been shown to inhibit (though not completely prevent) intramolecular ring metalation in early-transition-metal chemistry. In our research in low-valent mono(peralkylcyclopentadienyl) group 5 chemistry, we were interested in preparing organo*di*vanadium(III) analogues[5] of $(\eta\text{-}C_5Me_4R)_2Ta_2X_4$[6] (R = Me, Et; X = Cl, Br) via reductive dimerization in order to examine comparative structure and reactivity[7] between first- and third-row congeners and to develop early-metal–early-metal bonded organodimetallic[8] chemistry. For such studies, a mono(peralkylcyclopentadienyl)vanadium(IV) halide precursor was needed to avoid possible C_5H_5 or C_5H_4Me metalation during reduction; this compound was expected to possess a three-legged piano-stool structure[4] rather than the nonbonded structure of the organoditantalum(IV) compounds $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_2X_4$.[9]

Previous preparations of mono(cyclopentadienyl)vanadium(IV) halides involved halogenation of $CpV(CO)_4$ with X_2[10] or $SOCl_2$[11]

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