$(Cp)(L)_2(NO)]$ (L = $^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) complexes appear to be stable in solution, we will isolate these complexes and further study their reactivity with molecular oxygen.

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Notes

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X-ray Structure of $\{HB(Me_2pz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(Me_2pz)_3\}$, a Molecule Containing Rare *cis*-$[WO(CO)]^{2+}$ and *syn*-$[W^{VI}W^{IV}O_3(\mu\text{-}O)]^{2+}$ Moieties [$HB(Me_2pz)_3^-$ = Hydrotris(3,5-dimethyl-1-pyrazolyl)borate]

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The study of high-valent organometallic oxo complexes has intensified in recent years, and a timely review by Bottomley and Sutin has appeared.[2] Interest in this area stems from the extensive use of metal oxides as catalysts for organic reactions and the likely involvement of organometallic oxo intermediates in these reactions.[3] The majority of known species are polynuclear cyclopentadienyl and alkyl complexes of oxophilic early transition metals or cluster μ_3-oxo carbonyls of the group 8 and 9[4] metals.[2] In contrast, noncluster oxo carbonyl complexes are extremely rare. In the early 1980s *trans*-$MO_2(CO)_4$ (M = Mo, W),[5,6] and $MO_2(CO)_2$ (M = Cr, Mo, W)[6,7] were identified by matrix isolation techniques and $CrO_2(CO)_3$[8] was obtained in the gas phase. Later that decade the stable oxo carbonyl–W(IV) complex $WOCl_2(CO)(PMePh_2)_2$, formed by reaction of $WOCl_2(PMePh_2)_3$ with CO[9] or oxidative addition of CO_2 to $WCl_2(PMePh_2)_4$,[10] was reported by Mayer and co-workers. In addition to their relevance to catalysis, complexes containing such electronically disparate ligands are of intrinsic interest. Mixed-valence compounds also attract considerable current interest and early-transition-metal compounds of this type have been exhaustively reviewed.[11] Approximately 18 dinuclear mixed-valence complexes of tungsten are known, but only the complexes $L_2W^{IV}(\mu\text{-}S)_2W^{VI}S_2$ (L = $C_5H_5^-$ or $MeC_5H_4^-$)[12] contain the metal in oxidation states of +4 and +6. We report here the synthesis and X-ray structure of the mixed-valence oxocarbonyl complex $\{HB(Me_2pz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(Me_2pz)_3\}$ [**1**; $HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate], formed upon oxidative hydrolysis of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$.

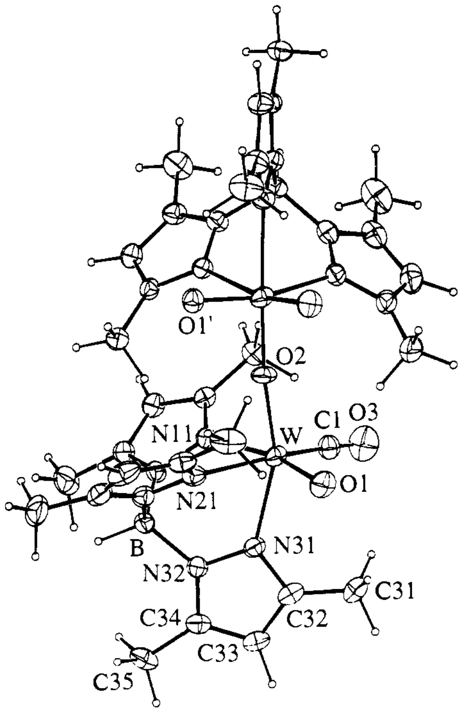

Figure 1. Molecular structure of $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$ showing the atom-labeling scheme. The carbonyl and O(1′) ligands are disordered and each have an occupancy of 0.5 at the two sites. The numbering of atoms in the pyrazolyl rings containing N(11) and N(21) parallels that shown for the ring containing N(31). Thermal ellipsoids are plotted at the 30% probability level, and hydrogen atoms are represented by small spheres.

Results and Discussion

Recrystallization of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ from acetonitrile/water, according to the method described by Trofimenko,[13] results in the slow development of a red coloration in the mother liquor upon standing. This coloration is due to the formation of the title compound, which precipitates as red microcrystals. The formation of **1** requires the presence of both water and oxygen, but the mechanism of the reaction involved has not been established. Exhaustive decarbonylation with concomitant oxidation is a useful route to cyclopentadienylmetal oxo compounds and hydrolysis is a common route to organometallic group 4 oxo complexes.[2] The infrared spectrum of the insoluble, diamagnetic complex exhibits bands typical of $HB(Me_2pz)_3^-$ (ν(BH) = 2550 cm^{-1}), a single strong ν(CO) band at 1950 cm^{-1}, three bands of medium to strong intensity assigned to ν(W=O) (955, 940, and 890 cm^{-1}) and a strong band due to ν(WOW) at 820 cm^{-1}. Fast atom bombardment mass spectrometry revealed a strong [M –

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H]$^-$ parent ion at *m/e* 1053. The insolubility of the complex prevented other physical and spectroscopic measurements. The structure of the complex has been determined by X-ray crystallography. Special conditions were necessary for the growth directly from the reaction mixture of crystals suitable for X-ray crystallography (see Experimental Section).

An ORTEP drawing of the molecule, along with the atomic labeling scheme, is given in Figure 1. The dinuclear complex is composed of distorted octahedral *fac*-$[\{HB(Me_2pz)_3\}W^{VI}O_2]^+$ and *fac*-$[\{HB(Me_2pz)_3\}W^{IV}O(CO)]^+$ moieties linked by a near-linear oxo ligand bridge (W-O(2) = 1.912(1) Å; W-O(2)-W angle = 169.2(2)°). As the molecules are sited on 2-fold rotation axes, the structure is disordered and the complex possesses pseudo-C_2 symmetry. The terminal oxo ligands O(1) exhibit a short W-O(1) distance of 1.708(4) Å and are *syn* disposed with a twist angle between the W-O(1) vectors of 2.2(2)°. On one tungsten atom, a carbonyl ligand is bound cis to terminal O(1) and bridging O(2) oxo ligands; this unusual feature has only one structurally characterized precedent, *cis*-$WOCl_2(CO)(PMePh_2)_2$.[10] On the adjacent tungsten atom a terminal oxo ligand O(1′) is bound cis to terminal O(1) and bridging O(2) oxo ligands. Disorder at the site occupied by the carbonyl carbon C(1) and terminal oxo ligand O(1′) prevented the determination of accurate bond lengths and angles for these ligands. The W—C(1)/O(1′) distance of 1.841 (6) Å is very close to the average distance of the W=O (1.689 (6) Å) and W—CO (2.029 (9) Å) bond distances observed in *cis*-$WOCl_2(CO)(PMePh_2)_2$.[10] The C(1)/O(1′)-O(3) distance and W-C(1)/O(1′)-O(3) angle are 1.13 (2) Å and 170 (1)°, respectively. The slightly shorter W-C(1) distance and lower ν(CO) of **1** compared to that in $WOCl_2(CO)(PMePh_2)_2$ (ν(CO) = 2006 cm^{-1}) is consistent with stronger π-back-bonding to the carbonyl ligand in **1**. The O(1)-W-C(1)/O(1′) angle is 98.0 (2)°. The cis disposition of the oxo (orientated along the *z* axis) and carbonyl ligands in both **1** and $WOCl_2(CO)(PMePh_2)_2$ allows π-back-bonding between the filled d_{xy} and π^* CO orbitals. The *cis*-dioxo-W(VI) moiety observed in **1** is a common feature in W(VI) chemistry.[14] The $HB(Me_2pz)_3^-$ ligand adopts its usual *facial* coordination mode at both tungsten centers. The W-N bond distances in **1** range from 2.197 (5) to 2.306 (4) Å, the longest being trans to the terminal oxo as observed in oxo-Mo complexes of $HB(Me_2pz)_3^-$.[15-18] The angles between the cis and trans donor atoms in the coordination sphere are within the ranges 77.8 (2)-103.6 (2) and 159.5 (2)-168.5 (2)°, respectively. There are no unusually short intermolecular contacts between molecules of **1**.

The *syn*-$[W^{VI}W^{IV}O_3(\mu\text{-}O)]^{2+}$ fragment is an unprecedented feature of the molecule. While dinuclear mixed-valence compounds of tungsten having integral and half-integral oxidation states ranging from +5.5 to +2, with the exception of +4, have been reported,[11] few oxo complexes are known and none have been isolated. The blue W^VW^{VI} complex $[W_2O_4(\mu\text{-}O)(Me_3tcn)_2]^+$ (Me_3tcn = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane) has been prepared by reduction of $[W_2O_4(\mu\text{-}O)(Me_3tcn)_2]^{2+}$ and is likely to possess a corner-shared bioctahedral structure related to **1**.[19] Complexes of the type $L_2W(\mu\text{-}S)_2WS_2$ (L = $C_5H_5^-$ or $MeC_5H_4^-$),[12] which formed upon reaction of $[WS_4]^{2-}$ and L_2WCl_2 and are the only previously known $W^{VI}W^{IV}$ complexes, possess structures unrelated to that of **1**. The structure of the *syn*-$[W_2O_2(\mu\text{-}O)]^{4+}$ core of **1** is closely related to fragments of the structure established for the $W^V{}_2W^{VI}{}_2$ complex $[W_4O_4(\mu\text{-}O)_4(NCS)_{12}]^{6-}$ reported by Launay et al.[20] The W=O and W—O(bridge) distances in this complex are in the ranges 1.53 (4)-1.83 (4) and 1.82 (3)-1.93 (3) Å, respectively. The W-O-W angles vary from 167 (2) to 176 (2)°. The only other structurally characterized $[W_2O_2(\mu\text{-}O)]^{n+}$ fragment is that found in $W_2O_3(CH_2CMe_3)_6$ but in this case a linear O=W—O—W=O fragment with average W=O and W—O bond distances of 1.71 and 1.95 Å, respectively, was observed.[21]

Table I. Crystal Data for $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$

$C_{31}H_{44}B_2N_{12}O_5W_2$	space group: $C2/c$ ($C2h$; No. 15)
fw = 1054.10	T = 295 (1) K
a = 28.046 (3) Å	λ = 0.71069 Å
b = 9.551 (1) Å	ρ_{obsd} = 1.82 (1) g cm^{-3}
c = 15.856 (2) Å	ρ_{calcd} = 1.822 g cm^{-3}
β = 115.25 (1)°	μ = 61.41 cm^{-1}
V = 3842 (1) Å^3	R = 0.027
Z = 4	R_w = 0.035

Dinuclear complexes of the $HB(Me_2pz)_3^-$ ligand are also quite rare. Indeed, this sterically encumbered ligand has been employed to prevent dinucleation, especially in model studies of the mononuclear active sites of oxo-type molybdoenzymes.[15-18,22] A necessary requirement for the formation of dinuclear complexes is a large separation of the metal centers; examples include $[\{HB(Me_2pz)_3\}MoO_2]_2(\mu\text{-}O)$,[23] $[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$,[18] and $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2(\mu\text{-}S)$[24] reported by Enemark and co-workers.

These results provide further evidence of the ability of d^2 metal centers to stabilize *cis*-oxocarbonyl ligands,[9,10] and combined with the capacity of the $HB(Me_2pz)_3^-$ ligand to stabilize otherwise reactive ligands,[22] they have encouraged us to plan further studies of $[MO(L)]^{n+}$ (M = Mo, W; L = CO, CH_2CH_2) complexes of $HB(Me_2pz)_3^-$.

Experimental Section

Potassium hydrotris(3,5-dimethylpyrazolyl)borate[25] and $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$[13] were prepared by the methods of Trofimenko, and the tungsten complex was recrystallized from hot acetonitrile before use. Infrared spectra were recorded on the compounds as KBr disks by using a Perkin-Elmer 1430 spectrophotometer, and microanalyses were performed by Atlantic Microlabs. Mass spectra were recorded on a JEOL JMS-DX303 mass spectrometer with fast atom bombardment ion source and negative ion detection.

Synthesis of 1. A solution of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ (0.1 g, 0.14 mmol) in boiling acetonitrile (2 mL) was slowly treated with water (2 mL) and the mixture refluxed for a further 5 min. The reaction vessel was then placed in a Dewar of hot water and allowed to cool slowly in contact with air. After 3-4 days the red air-stable crystals were isolated (yield = 15%). These crystals were suitable for X-ray crystallography.

Anal. Calcd for $C_{31}H_{44}B_2N_{12}O_5W_2$: C, 35.32; H, 4.21; N, 15.95. Found: C, 35.8; H, 4.3; N, 16.4. IR data (cm^{-1}): 2940 w; ν(BH) 2550 w; ν(CO) 1950 s; 1540 m, 1450 m, 1420 m, 1380 m, 1370 m, 1200 m, 1070 m, 1045 w; ν(W=O) 955 m, 940 m, 890 s; 910 w, 865 w; ν(WOW) 820 s; 695 w, 650 w, 470 w, 380 w.

X-ray Crystallographic Studies

Crystal data and experimental details are reported in Table I. Cell constants and an orientation matrix were obtained from least-squares refinement, using setting angles of 25 reflections in the range 30° ≤ 2θ ≤ 47°. Data were recorded at 295 (1) K on an Enraf-Nonius CAD-4F diffractometer using graphite-monochromated Mo Kα radiation. During data collection, four monitored reflections showed no variation in intensity. The data were corrected for Lorentz and polarization effects and for absorption. Absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%.[26a,27] No correction for

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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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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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