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High Oxidation State Dinitrogen Complexes. Synthesis and Crystal Structure of $[W(C_6H_5C{\equiv}CC_6H_5)(CH_3OCH_2CH_2OCH_3)Cl_2]_2(\mu\text{-}N_2)\cdot0.5CH_3OCH_2CH_2OCH_3$

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$W(C_2Ph_2)(OCMe_3)_4$ in toluene reacts with 0.5 equiv of hydrazine to produce brown $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$ (**1**) in high yield. Addition of 4 equiv of HCl to **1** in pentane in the presence of 1,2-dimethoxyethane (dme) yields purple $[W(C_2Ph_2)(dme)Cl_2]_2(\mu\text{-}N_2)$ (**2**). Crystals of the 2:1 solvate, $[W(C_2Ph_2)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot0.5$dme, belong to the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15), with unit cell parameters as follows: $a = 36.016$ (15) Å, $b = 14.131$ (6) Å, $c = 16.650$ (6) Å, $\beta = 96.23$ (3)°, $V = 8424$ (6) Å^3, D(calcd) = 1.69 g cm^{-3} for $Z = 8$. Diffraction data (Mo Kα, $2\theta = 4.0$–$50.0°$) were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was solved via a combination of direct methods, difference-Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 5.7\%$ and $R_{wF} = 4.8\%$ for all 3684 independent reflections and $R_F = 4.8\%$ and $R_{wF} = 4.7\%$ for those 3276 reflections with $|F_o| > 3\sigma(|F_o|)$. The dme of solvation lies on a C_2 axis, but no crystallographic symmetry is imposed upon the dinuclear tungsten complex (which nevertheless has approximate C_2 symmetry). The coordination geometry about each tungsten is approximately octahedral with the acetylene in a position cis to the N_2 ligand and chloride ligands trans to one another. The W_2N_2 system is essentially linear, and the N–N bond length [1.292 (16) Å] is long relative to the N–N bond length in all other simple μ-N_2 complexes except those containing tantalum. It can be argued that **1** contains an N_2^{4-} ligand on the basis of the long N–N bond and hydrolysis to give hydrazine essentially quantitatively.

Introduction

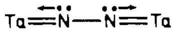
Research directed toward elucidating how the iron- and molybdenum-containing nitrogenase enzyme reduces molecular nitrogen has been proceeding on several fronts in the past two decades.[2] According to one theory, perhaps that which is most often proposed, at least one end of the dinitrogen molecule bonds to molybdenum at the beginning of, and perhaps throughout, the reduction sequence. The only evidence is circumstantial, e.g., the large number of transition-metal complexes that contain molecular nitrogen.[3] However, a fundamental problem is that dinitrogen in general is found only in relatively low-valent "electron-rich" metal complexes—in group 6 the most common are those of the type $ML_4(N_2)_2$ (M = Mo, W; L = a phosphine ligand)—while all evidence suggests that a relatively high oxidation state of molybdenum, perhaps Mo(IV), is the pivotal oxidation state in the enzyme.[2]

In the first reported dinitrogen complexes of Nb or Ta, the dinitrogen ligand was found to be of the μ-N_2 variety (eq 1 and 2).[4] X-ray crystallographic studies of the μ-dinitrogen

$$2Nb(CHCMe_3)(THF)_2Cl_3 + PhCH{=}N{-}N{=}CHPh \rightarrow [Nb(THF)_2Cl_3]_2(\mu\text{-}N_2) \quad (1)$$

$$2Ta(CHCMe_3)(PMe_3)_4Cl + N_2 \rightarrow [Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2) \quad (2)$$

complexes $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[5a] and $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$[5b] (Bz = $CH_2C_6H_5$) reveal that in the Ta(μ-N_2)Ta core the tantalum–nitrogen distances are short (1.837 (8)–1.842 (8) and 1.796 (5) Å (twice), respectively) and the nitrogen–nitrogen distances rather long (1.298 (12) and 1.282 (6) Å, respectively) compared to N–N bond distances in other simple μ-N_2 complexes. Therefore, it was suggested that these species are formally tantalum(V) complexes of the N_2^{4-} ion, i.e.


$$Ta{=}N{-}N{=}Ta$$

This suggestion is supported by the synthesis of related organoimido complexes of tantalum,[4b] a structural study of the species *mer*-Ta(NPh)(THF)(PEt$_3$)Cl$_3$ in which Ta═N = 1.765 (5) Å,[6] and the reaction of both the imido and μ-N_2 complexes with acetone to give $Me_2C{=}NPh$ and $Me_2C{=}N{-}N{=}CMe_2$, respectively.

We thought it should be possible to prepare related Mo(IV) or W(IV) μ-N_2 complexes. Unfortunately, we have not been able to find routes analogous to those shown in eq 1 and 2. In our search for an alternative source of "N_2^{4-}", we turned to hydrazine itself, reasoning that under the proper circumstances it should be deprotonated by alkyl, alkoxide, or amido ligands to yield (ultimately) the desired $M_2(\mu\text{-}N_2)$ complex. One of our first attempts consisted of the reaction between $W[\eta^5\text{-}C_5Me_4(CMe_3)](CCMe_3)I_2$ and hydrazine. The product was the μ-1,2-$N_2H_2^{2-}$ complex $[W[\eta^2\text{-}C_5Me_4(CMe_3)](CCMe_3)I]_2(\mu\text{-}N_2H_2)$.[7] We then turned to the recently discovered diphenylacetylene complex, $W(C_2Ph_2)(OCMe_3)_4$.[8a] In this case, deprotonation of hydrazine is complete. Here we report some of the details of this chemistry along with a crystal structure of one of the μ-N_2 complexes. Some of these results have been reported in preliminary form.[8b]

Results and Discussion

Yellow $W(C_2Ph_2)(OCMe_3)_4$[8] reacts smoothly in toluene with 0.5 equiv of hydrazine to produce a single product in high yield (eq 3) if the reaction is worked up relatively quickly. The

$$2W(C_2Ph_2)(OCMe_3)_4 \xrightarrow[-4Me_3COH]{N_2H_4} \underset{\mathbf{1}}{[W(C_2Ph_2)(OCMe_3)_2]_2(N_2)} \quad (3)$$

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Table I. Interatomic Distances (Å) and Esd's for $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot0.5dme$

(A) Distances from Tungsten Atoms			
W(1)-N(1)	1.776 (11)	W(2)-N(2)	1.735 (11)
W(1)-Cl(11)	2.432 (4)	W(2)-Cl(21)	2.414 (4)
W(1)-Cl(12)	2.420 (4)	W(2)-Cl(22)	2.442 (4)
W(1)-O(11)	2.299 (10)	W(2)-O(21)	2.265 (9)
W(1)-O(12)	2.245 (10)	W(2)-O(22)	2.251 (9)
W(1)-C(11)	2.032 (15)	W(2)-C(31)	2.053 (13)
W(1)-C(21)	2.050 (14)	W(2)-C(41)	2.063 (14)
(B) Nitrogen-Nitrogen Distance			
N(1)-N(2)	1.292 (16)		
(C) Distances within $MeOCH_2CH_2OMe$ Ligands			
C(1)-C(2)	1.453 (25)	C(5)-C(6)	1.506 (23)
C(1)-O(11)	1.459 (19)	C(5)-O(21)	1.434 (18)
C(2)-O(12)	1.479 (20)	C(6)-O(22)	1.442 (19)
O(11)-C(3)	1.502 (21)	O(21)-C(7)	1.450 (19)
O(12)-C(4)	1.443 (29)	O(22)-C(8)	1.468 (19)
(D) Distances within PhC≡CPh Ligands			
C(11)-C(21)	1.255 (21)	C(31)-C(41)	1.267 (19)
C(11)-C(12)	1.506 (24)	C(31)-C(32)	1.483 (19)
C(12)-C(13)	1.416 (29)	C(32)-C(33)	1.349 (21)
C(13)-C(14)	1.354 (36)	C(33)-C(34)	1.445 (22)
C(14)-C(15)	1.278 (38)	C(34)-C(35)	1.341 (24)
C(15)-C(16)	1.302 (34)	C(35)-C(36)	1.291 (26)
C(16)-C(17)	1.548 (32)	C(36)-C(37)	1.435 (24)
C(17)-C(12)	1.274 (29)	C(37)-C(32)	1.404 (21)
C(21)-C(22)	1.484 (20)	C(41)-C(42)	1.469 (20)
C(22)-C(23)	1.368 (21)	C(42)-C(43)	1.381 (20)
C(23)-C(24)	1.398 (24)	C(43)-C(44)	1.407 (23)
C(24)-C(25)	1.343 (24)	C(44)-C(45)	1.365 (25)
C(25)-C(26)	1.381 (25)	C(45)-C(46)	1.343 (25)
C(26)-C(27)	1.411 (25)	C(46)-C(47)	1.394 (24)
C(27)-C(22)	1.365 (22)	C(47)-C(42)	1.359 (21)
(E) Distances within the $MeOCH_2CH_2OMe$ Solvent Molecule[a]			
CS(2)-CS(2′)	1.43 (5)		
CS(2)-OS(1)	1.68 (5)	CS(2′)-OS(1′)	1.68 (5)
OS(1)-CS(1)	1.46 (5)	OS(1′)-CS(1′)	1.46 (5)

[a] The solvent molecule is defined sequentially by the following atoms: CS(1)-OS(1)-CS(2)-CS(2′)-OS(2′)-CS(1′).

brown complex can be crystallized with difficulty from pentane in the form of dense, smooth, brown nodules. It is not stable for long at 25 °C in solution in the presence of 2-methyl-2-propanol, and it is extremely sensitive to water, even in the solid state. Its IR spectrum shows an absorption at 1665 cm^{-1} characteristic of an acetylene complex of a d^2 metal,[8,9,10] but no *obvious* absorption characteristic of a $\mu\text{-}N_2$ ligand analogous to that at ~850 cm^{-1} in recently discovered Nb(V) and Ta(V) "$\mu\text{-}N_2^{4-}$" complexes.[4]

Addition of 4 equiv of HCl to **1** in pentane in the presence of 1,2-dimethoxyethane (dme) yields a purple-brown product that can be recrystallized from a mixture of dichloromethane and ether in the form of purple needles. Elemental analysis and IR and NMR spectra suggest that the product be formulated as $[W(C_2Ph_2)(dme)Cl_2]_2(N_2)$, although again we see no obvious absorption in the IR spectrum attributable to the $\mu\text{-}N_2$ ligand. The crystal of $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)$ selected for the X-ray study contained 0.5 equiv of additional dme. This amount is too small to be detected definitively by elemental analysis. However, since free dme does not exchange with coordinated dme at a rate of the order of the NMR time scale, we can show by ^1H NMR that the average amount of dme of crystallization in a typical bulk sample is much less than 0.5 equiv.

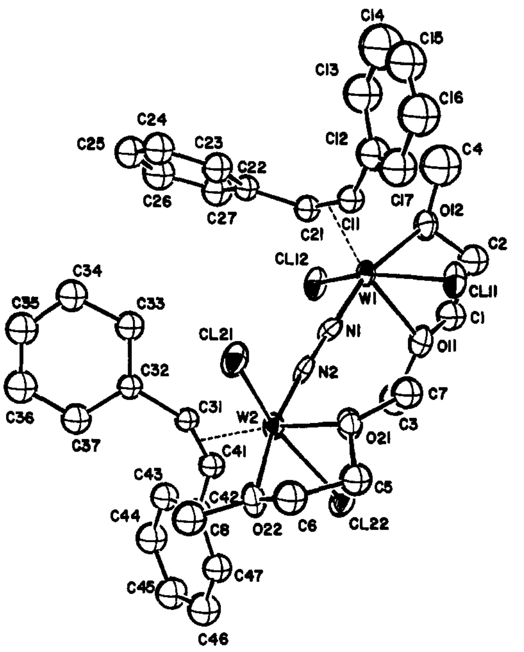

Figure 1. Labeling of atoms in $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot0.5dme$. Hydrogen atoms are omitted for the sake of clarity (ORTEP II diagram; 30% probability contours).

Table II. Selected Interatomic Angles (deg)

(A) Angles around Tungsten Atoms			
Cl(11)-W(1)-Cl(12)	152.8 (1)	Cl(21)-W(2)-Cl(22)	153.5 (1)
Cl(11)-W(1)-O(11)	77.5 (3)	Cl(21)-W(2)-O(21)	75.3 (3)
Cl(11)-W(1)-O(12)	82.2 (3)	Cl(21)-W(2)-O(22)	81.8 (3)
Cl(11)-W(1)-N(1)	92.5 (4)	Cl(21)-W(2)-N(2)	96.5 (4)
Cl(11)-W(1)-C(11)	84.2 (4)	Cl(21)-W(2)-C(31)	83.0 (4)
Cl(11)-W(1)-C(21)	119.8 (4)	Cl(21)-W(2)-C(41)	116.8 (4)
Cl(12)-W(1)-O(11)	77.6 (3)	Cl(22)-W(2)-O(21)	79.1 (3)
Cl(12)-W(1)-O(12)	80.5 (3)	Cl(22)-W(2)-O(22)	83.8 (3)
Cl(12)-W(1)-O(12)	98.8 (4)	Cl(22)-W(2)-N(2)	92.5 (4)
Cl(12)-W(1)-C(11)	116.7 (4)	Cl(22)-W(2)-C(31)	120.5 (4)
Cl(12)-W(1)-C(21)	83.4 (4)	Cl(22)-W(2)-C(41)	84.8 (4)
O(11)-W(1)-O(12)	73.4 (4)	O(21)-W(2)-O(22)	72.1 (3)
O(11)-W(1)-N(1)	91.6 (4)	O(21)-W(2)-N(2)	94.9 (4)
O(11)-W(1)-C(11)	157.0 (5)	O(21)-W(2)-C(31)	156.0 (4)
O(11)-W(1)-C(21)	160.2 (5)	O(21)-W(2)-C(41)	155.7 (5)
O(12)-W(1)-N(1)	164.8 (5)	O(22)-W(2)-N(2)	166.9 (4)
O(12)-W(1)-C(11)	90.6 (5)	O(22)-W(2)-C(31)	95.1 (4)
O(12)-W(1)-C(21)	98.2 (5)	O(22)-W(2)-C(41)	88.3 (5)
N(1)-W(1)-C(11)	103.1 (6)	N(2)-W(2)-C(31)	97.7 (5)
N(1)-W(1)-C(21)	96.9 (5)	N(2)-W(2)-C(41)	104.0 (5)
C(11)-W(1)-C(21)	35.8 (6)	C(31)-W(2)-C(41)	35.9 (5)
(B) Angles in the $W(\mu\text{-}N_2)W$ System			
W(1)-N(1)-N(2)	176.4 (10)	W(2)-N(2)-N(1)	175.6 (10)
(C) Angles within dme Ligands			
W(1)-O(11)-C(1)	112.1 (9)	W(2)-O(21)-C(5)	115.0 (8)
O(11)-C(1)-C(2)	109.2 (13)	O(21)-C(5)-C(6)	106.4 (12)
C(1)-C(2)-O(12)	108.2 (13)	C(5)-C(6)-O(22)	108.5 (13)
C(2)-O(12)-W(1)	113.0 (9)	C(6)-O(22)-W(2)	115.1 (8)
W(1)-O(11)-C(3)	119.5 (9)	W(2)-O(21)-C(7)	121.5 (8)
C(1)-O(11)-C(3)	113.9 (11)	C(5)-O(21)-C(7)	114.8 (11)
W(1)-O(12)-C(4)	123.7 (12)	W(2)-O(22)-C(8)	121.6 (8)
C(2)-O(12)-C(4)	113.4 (14)	C(6)-O(22)-C(8)	110.4 (11)
(D) Selected Angles within the PhC≡CPh Ligands			
C(21)-C(11)-C(12)	139.8 (15)	C(41)-C(31)-C(32)	142.8 (13)
C(11)-C(21)-C(22)	138.0 (14)	C(31)-C(41)-C(42)	140.0 (14)
W(1)-C(11)-C(12)	147.2 (12)	W(2)-C(31)-C(32)	144.6 (10)
W(1)-C(21)-C(22)	148.0 (11)	W(2)-C(41)-C(42)	148.3 (10)
W(1)-C(11)-C(21)	72.9 (9)	W(2)-C(31)-C(41)	72.5 (9)
W(1)-C(21)-C(11)	71.3 (9)	W(2)-C(41)-C(31)	71.7 (9)

The structure of $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot0.5dme$ is shown in Figure 1. The dme molecules of crystallization lie on crystallographic C_2 axes. Interatomic distances and angles are collected in Tables I and II, respectively. Although

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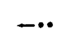
no crystallographic symmetry is imposed upon the dinuclear complex, it does, nevertheless, have a symmetry that approaches C_2, i.e., the two ends twisted by 90° relative to one another. This is true also in $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[5a] but not in $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$[5b] (Bz = $CH_2C_6H_5$).

The bond lengths and angles in the $W_2(\mu\text{-}N_2)$ system resemble those in $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$ in every way; i.e. (i) the W═N—N═W system is essentially linear [W(1)-N(1)-N(2) = 176.4 (10), W(2)-N(2)-N(1) = 175.6 (10)°]; (ii) the W-N bond lengths are short [W(1)-N(1) = 1.776 (11), W(2)-N(2) = 1.735 (11) Å], and (iii) the N-N bond length is long relative to that in linear μ-N_2 complexes of more reduced metals[3] [N(1)-N(2) = 1.292 (16) Å]. On this basis, and the fact that the μ-N_2 ligand in this type of molecule can be protonated readily (see below), we must conclude that the μ-N_2 ligand is best described as being fully reduced, i.e., μ-N_2^{4-}.

The geometry about each tungsten center is significantly distorted from octahedral as indicated by the trans Cl-W-Cl angles on each tungsten atom [Cl(11)-W(1)-Cl(12) = 152.8 (1), Cl(21)-W(2)-Cl(22) = 153.5 (1)°] and by the trans N-W-O angles [N(1)-W(1)-O(12) = 164.8 (5), N(2)-W(2)-O(22) = 166.9 (4)°]. Some of this distortion appears to be in response to the steric bulk of the diphenylacetylene ligand; i.e. at W(1) all four cis atoms [N(1), Cl(12), O(12), Cl(11)] are bent away from C(11) and C(12). However, some distortion might result from the relatively small bite angle of the dimethoxyethane ligand. The individual tungsten–chlorine bond distances range from 2.414 (4) through 2.442 (4) Å, averaging normal 2.427 Å. If one assumes r(Cl) = 0.99 Å,[11] the covalent radius of tungsten becomes 1.44 Å. Therefore, a W-N *single* bond should be ~2.14 Å (r(N) = 0.70 Å[11]). The tungsten–oxygen distances range from 2.245 (10) through 2.299 (10) Å; those trans to diphenylacetylene ligands [W(1)-O(11) = 2.299 (10), W(2)-O(21) = 2.265 (9) Å] appear to be marginally longer than those trans to the μ-dinitrogen ligand [W(1)-O(12) = 2.245 (10), W(2)-O(22) = 2.251 (9) Å].

It is important to look closely at the diphenylacetylene ligands in this complex. We first note that each acetylene ligand is found in a position cis to the W-N bond. One would expect it in this position if the μ-N_2 ligand utilizes two of the three d_π orbitals to form what can be viewed as a



$$\mathrm{W}\overset{\longleftarrow}{=\!=}\ddot{\mathrm{N}}-$$

bond. The remaining d_π orbital (δ with respect to the W-N bond) is then best used to form the π-type bond between it and a π^* acetylene orbital. Therefore, both the location *and* the orientation of the acetylene ligand are fixed and are what one would predict *if* a pseudo triple bond between W and N is invoked. The diphenylacetylene ligands take up the usual cis-bent geometry with C≡C—Ph angles as follows: C(21)-C(11)-C(12) = 139.8 (15), C(11)-C(21)-C(22) = 138.0 (14), C(41)-C(31)-C(32) = 142.8 (13), C(31)-C(41)-C(42) = 140.0 (14)°. The tungsten–carbon(acetylene) distances are rather short (W-C(11) = 2.032 (15), W-C(21) = 2.050 (14), W-C(31) = 2.053 (13), W-C(41) = 2.063 (14) Å], similar to those in $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$[12] and $W(\eta^2\text{-}CH{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$[13] [W-C(av) = 2.014 and 2.022 Å, respectively]. However, the acetylene carbon–carbon bonds in the present complex [C(11)-C(21) = 1.255 (21), C(31)-C(41) = 1.267 (19) Å] are closer to that expected for a normal-coordinated acetylene than one of the "strongly bound" variety [cf., C≡C = 1.312 (10) Å in $W[\eta^5\text{-}C_5Me_4(t\text{-}Bu)](\eta^2\text{-}MeC{\equiv}CMe)Cl_2$[12] and 1.316 (6) Å in $W(\eta^2\text{-}CH{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$[13]]. Therefore, it would seem that the acetylene in this complex, on the basis of the C-C bond length at least, is *not* one of the highly reduced type, i.e., a $[PhC{=}CPh]^{2-}$ ligand, and that the metal is therefore W(IV), rather than W(VI). But one can argue that the C-C bond length is a function of how "reduced" the acetylene ligand is only up to a point and that the very long C-C bonds largely are the result of π donation of electron density from the C═C π bond in a "tungstacyclopropene" ring into a d_π tungsten orbital. But, we have already argued that both of the d_π orbitals that could accept electrons from the C═C π bond are already involved in W-N bonding while the W-C lengths are still relatively short, characteristic of a tungstacyclopropene description. Therefore, the oxidation state of the metal is ambiguous. The fact remains, however, that the μ-N_2 ligand is essentially μ-N_2^{4-}, as we had observed in the tantalum complexes mentioned earlier, and that the metal must be in a relatively high oxidation state. We are continuing to search for $W_2(\mu\text{-}N_2)$ complexes in which the oxidation state of tungsten is convincingly W(VI).

Table III. Data for the X-ray Diffraction Study of $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot 0.5dme$

(A) Crystallographic Parameters

cryst syst: monoclinic	β = 96.23 (3)°
space group: $C2/c$	V = 8424 (6) Å^3
a = 36.016 (15) Å	Z = 8
b = 14.131 (6) Å	T = 23 °C
c = 16.650 (6) Å	D(calcd) = 1.69 g cm^{-3}

(B) Data Collection

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented graphite, equatorial geometry, 2θ(mono) = 12.2°
reflcns measd: $h,k,\pm l$ for 2θ = 4–50°
scan type: coupled θ(cryst)-2θ(counter)
scan width: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
scan speed: 2.0°/min (in 2θ)
bkgd measurements: stationary crystal, stationary counter at beginning and end of 2θ scan; each for half of total scan time
std reflcns: 3 remeasured after each 97 reflections; no decay observed
no. of reflcns collcd: 4391 total; merged to 3684 unique data [WNFR file name]
μ(Mo Kα): 60.6 cm^{-1}; empirical correction applied

Experimental Section

Collection of X-ray Diffraction Data. A single crystal of approximate dimensions 0.27 × 0.21 × 0.17 mm was sealed into a thin-walled glass capillary under an argon atmosphere. The crystal was aligned with its extended direction coincident with the ϕ axis of the Syntex P2$_1$ diffractometer. Accurate cell dimensions were based upon a least-squares analysis of the automatically centered setting angles of 25 reflections, well separated in reciprocal space, and all having 2θ values between 25 and 30°. Data collection was carried out as described previously;[14] specific details appear in Table III.

The systematic absences [hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$ ($h = 2n + 1$)] are consistent with space groups $C2/c$ [No. 15] or Cc [No. 9]. The former, centrosymmetric possibility was selected on the basis of (a) there being 8 molecules per unit cell, (b) intensity statistics, and (c) the successful solution of the structure in this higher symmetry space group.

All data were corrected for the effects of absorption (relative transmission factors varying from 1.00 down to 0.70) and for Lorentz

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(11) Covalent radii are taken from: Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-2, p 224.

(12) See especially Table VII: Churchill, M. R.; Wasserman, H. J. *Organometallics* **1983**, *2*, 755.

(13) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1983**, *22*, 41. (b) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766.

(14) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

Table IV. Final Positional Parameters for $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)\cdot0.5dme$

atom	x	y	z	B_{iso}, Å^2
W(1)	0.43228 (2)	0.30834 (4)	0.55686 (4)	
W(2)	0.33961 (2)	0.51923 (4)	0.42908 (4)	
Cl(11)	0.45996 (11)	0.29683 (32)	0.43033 (24)	
Cl(12)	0.43358 (10)	0.35198 (31)	0.69765 (23)	
Cl(21)	0.29773 (11)	0.39745 (30)	0.37214 (23)	
Cl(22)	0.38611 (10)	0.64368 (28)	0.42100 (24)	
O(11)	0.47659 (26)	0.42604 (75)	0.56971 (56)	
O(12)	0.48626 (26)	0.23973 (79)	0.60568 (65)	
O(21)	0.35843 (25)	0.48916 (69)	0.30615 (56)	
O(22)	0.30492 (24)	0.60865 (72)	0.33751 (56)	
N(1)	0.39745 (32)	0.38868 (81)	0.51526 (66)	
N(2)	0.37182 (32)	0.44378 (84)	0.48095 (63)	
C(1)	0.51095 (48)	0.3957 (12)	0.6172 (10)	5.50 (40)
C(2)	0.51930 (48)	0.2989 (13)	0.5956 (10)	5.81 (41)
C(3)	0.46509 (48)	0.5254 (13)	0.5872 (10)	5.95 (42)
C(4)	0.49339 (70)	0.1396 (19)	0.6004 (15)	10.77 (70)
C(5)	0.34768 (45)	0.5589 (11)	0.24551 (94)	4.86 (37)
C(6)	0.30769 (45)	0.5841 (12)	0.2543 (10)	5.35 (39)
C(7)	0.39361 (45)	0.4422 (11)	0.29777 (91)	4.85 (37)
C(8)	0.26647 (47)	0.6358 (12)	0.3486 (10)	5.46 (40)
C(11)	0.41007 (41)	0.1799 (11)	0.52465 (89)	4.19 (34)
C(12)	0.40898 (49)	0.0974 (13)	0.4671 (11)	6.25 (44)
C(13)	0.40998 (59)	0.0078 (16)	0.5053 (12)	8.18 (55)
C(14)	0.40934 (73)	−0.0716 (20)	0.4597 (18)	11.52 (76)
C(15)	0.40571 (62)	−0.0582 (17)	0.3833 (15)	8.90 (60)
C(16)	0.40371 (64)	0.0165 (18)	0.3374 (14)	9.41 (61)
C(17)	0.40552 (56)	0.1066 (15)	0.3905 (13)	7.84 (52)
C(21)	0.39663 (39)	0.2047 (10)	0.58784 (86)	3.79 (32)
C(22)	0.36497 (39)	0.1778 (10)	0.63321 (85)	3.61 (31)
C(23)	0.33440 (46)	0.1372 (11)	0.5908 (10)	5.02 (37)
C(24)	0.30313 (47)	0.1109 (12)	0.6285 (10)	5.64 (40)
C(25)	0.30281 (47)	0.1293 (12)	0.7076 (10)	5.70 (41)
C(26)	0.33290 (51)	0.1721 (13)	0.7517 (11)	6.27 (44)
C(27)	0.36476 (47)	0.1961 (12)	0.7136 (10)	5.51 (40)
C(31)	0.30254 (35)	0.52571 (94)	0.51428 (74)	2.78 (28)
C(32)	0.27149 (38)	0.4760 (10)	0.54819 (79)	3.24 (29)
C(33)	0.27169 (42)	0.3810 (11)	0.55660 (88)	4.36 (35)
C(34)	0.24027 (46)	0.3369 (11)	0.5888 (10)	5.18 (38)
C(35)	0.21249 (47)	0.3915 (13)	0.6101 (10)	5.57 (40)
C(36)	0.21183 (49)	0.4827 (13)	0.6044 (10)	5.75 (40)
C(37)	0.24215 (44)	0.5306 (11)	0.57259 (89)	4.72 (36)
C(41)	0.32104 (38)	0.6022 (10)	0.51853 (80)	3.48 (31)
C(42)	0.32489 (37)	0.6897 (10)	0.56630 (80)	3.29 (29)
C(43)	0.32095 (41)	0.6858 (11)	0.64782 (91)	4.48 (35)
C(44)	0.32431 (47)	0.7682 (13)	0.6955 (10)	5.74 (41)
C(45)	0.33132 (47)	0.8524 (13)	0.6600 (10)	5.84 (41)
C(46)	0.33467 (49)	0.8579 (13)	0.5806 (11)	6.22 (43)
C(47)	0.33159 (43)	0.7756 (11)	0.53412 (92)	4.67 (36)
OS(1)	0.46248 (74)	0.1676 (20)	0.1792 (16)	20.0
CS(1)	0.4376 (11)	0.2473 (32)	0.1588 (24)	20.0
CS(2)	0.4901 (12)	0.0759 (27)	0.2104 (20)	20.0
H(13)	0.41108 (0)	0.00343 (0)	0.56243 (0)	6.0
H(14)	0.41144 (0)	−0.13312 (0)	0.48286 (0)	6.0
H(15)	0.40413 (0)	−0.11563 (0)	0.35345 (0)	6.0
H(16)	0.40147 (0)	0.01586 (0)	0.28003 (0)	6.0
H(17)	0.40408 (0)	0.16766 (0)	0.36647 (0)	6.0
H(23)	0.33441 (0)	0.12668 (0)	0.53444 (0)	6.0
H(24)	0.28249 (0)	0.08050 (0)	0.59881 (0)	6.0
H(25)	0.28153 (0)	0.11258 (0)	0.73357 (0)	6.0
H(26)	0.33214 (0)	0.18546 (0)	0.80743 (0)	6.0
H(27)	0.38580 (0)	0.22446 (0)	0.74362 (0)	6.0
H(33)	0.29193 (0)	0.34417 (0)	0.54176 (0)	6.0
H(34)	0.23931 (0)	0.27013 (0)	0.59489 (0)	6.0
H(35)	0.19197 (0)	0.36121 (0)	0.63063 (0)	6.0
H(36)	0.19148 (0)	0.51759 (0)	0.62113 (0)	6.0
H(37)	0.24237 (0)	0.59762 (0)	0.56814 (0)	6.0
H(43)	0.31593 (0)	0.62691 (0)	0.67193 (0)	6.0
H(44)	0.32173 (0)	0.76523 (0)	0.75166 (0)	6.0
H(45)	0.33388 (0)	0.90813 (0)	0.69199 (0)	6.0
H(46)	0.33908 (0)	0.91714 (0)	0.55633 (0)	6.0
H(47)	0.33427 (0)	0.77975 (0)	0.47809 (0)	6.0
H(1)	0.50783 (0)	0.39865 (0)	0.67310 (0)	6.0
H(1′)	0.53091 (0)	0.43593 (0)	0.60626 (0)	6.0
H(2)	0.54024 (0)	0.27640 (0)	0.62985 (0)	6.0
H(2′)	0.52464 (0)	0.29663 (0)	0.54097 (0)	6.0
H(5)	0.36312 (0)	0.61333 (0)	0.25373 (0)	6.0
H(5′)	0.34967 (0)	0.53374 (0)	0.19325 (0)	6.0
H(61)	0.29201 (0)	0.53154 (0)	0.23940 (0)	6.0
H(62)	0.30027 (0)	0.63650 (0)	0.22051 (0)	6.0

and polarization effects. Data were placed on an approximate absolute scale by means of a Wilson plot.

Solution and Refinement of the Structure. All computations were performed on the Syntex XTL system as modified at SUNY–Buffalo. The positions of the two tungsten atoms were quickly and unambiguously located by using direct methods (MULTAN[15]); all remaining non-hydrogen atoms in the $[W(PhC{\equiv}CPh)(dme)Cl_2]_2(\mu\text{-}N_2)$ molecule were located via a series of difference-Fourier syntheses. Full-matrix least-squares refinement of positional and thermal parameters minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $1/w = [\sigma(|F_o|)]^2 + [0.015|F_o|]^2$, and with hydrogen atoms included in calculated positions with d(C–H) = 0.95 Å[16] led to convergence with[17] R_F = 6.0%, R_{wF} = 5.7%, and GOF = 1.95.

A difference-Fourier map revealed a set of weak, diffuse peaks arranged about the C_2 axis. They were interpreted as the six non-hydrogen atoms of a 1,2-dimethoxyethane molecule of solvation. After a number of unsuccessful attempts to refine occupancy and/or thermal parameters of atoms of this system, we finally set the occupancy factors to unity and assigned isotropic thermal factors of B = 20 Å^2 for each atom. Refinement of positional parameters of the solvent molecule, along with all other previously refined parameters of the dinuclear tungsten complex, led to final convergence with R_F = 5.7%, R_{wF} = 4.8%, and GOF = 1.64. [Discrepancy indices for those 3276 data with $|F_o| > 3\sigma(|F_o|)$ were R_F = 4.8%, R_{wF} = 4.7%, and GOF = 1.71.]

An analysis of the function $\sum w(|F_o| - |F_c|)^2$ showed no unusual trends as a function of Miller indices, $|F_o|$, $(\sin\theta)/\lambda$, or sequence number. No correction for secondary extinction was required. A final difference-Fourier synthesis showed no significant features. Final positional and thermal parameters are collected in Tables IV and IV-S (supplementary material), respectively.

All calculations are based upon the analytical form of the scattering factor of the appropriate neutral atom, corrected for both the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[18]

Preparations. $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$. Hydrazine (122 μL, 3.82 mmol) was added to a cold (−40 °C) solution of 5.0 g of $W(C_2Ph_2)(OCMe_3)_4$ (7.69 mmol) in 50 mL of toluene. The solution turned dark red-brown upon slowly being warmed to room temperature. The solvent was removed in vacuo, and the oily residue was dissolved in pentane. After the solution was allowed to stand for at least 1 day at ∼−30 °C, 3.27 g of brown, brittle, dense "nodules" were collected: yield 82%; ^1H NMR (C_6D_6) δ 8.02 (m, 4, Ph), 7.27 (t, 4, Ph), 7.10 (m, 2, Ph), 1.32 (s, 18, $OCMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 202.5 (C_2Ph_2), 141.0 (C_{ipso}), 130.7, 128.7 (Ph), 81.6 ($O\mathit{C}Me_3$), 32.5 ($OC\mathit{Me}_3$); IR (Nujol) 1665 cm^{-1} ($\nu_{C\equiv C}$). Samples of $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$ analyzed approximately correctly for C, H, and N, but the results were erratic. We blame the poor analyses on the extreme sensitivity of this molecule to water.

$[W(C_2Ph_2)(dme)Cl_2]_2(\mu\text{-}N_2)$. $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$ (3.24 g, 3.10 mmol) was dissolved in 20 mL of pentane. 1,2-Dimethoxyethane (4 mL) was added, and the solution was cooled to 0 °C. Gaseous HCl (295 mL, 12.24 mmol) was added to this solution via syringe. The resulting purple-brown precipitate was filtered off and dried for 2 h in vacuo to yield 2.9 g of product, yield 87%. The crude product could be recrystallized from a mixture of dichloromethane and ether as purple needles: ^1H NMR (CD_2Cl_2) δ 7.58 (m, 4, Ph), 7.38 (t, 4, Ph), 7.24 (m, 2, Ph), 4.23 (br s, 3, MeO), 4.07 (br m, 2, $MeOC\mathit{H}_2$), 3.91 (br m, 2, $MeOC\mathit{H}_2$), 3.29 (br s, 3, MeO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 184.4 (C_2Ph_2), 139.6 (C_{ipso}), 130.7, 128.6, 128.2 (Ph), 74.6, 71.3, 66.3, 65.2 (dme). Anal. Calcd for $W_2C_{36}H_{40}Cl_4N_2O_4$:

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(15) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

(16) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(17) $R_F = [\sum(|F_o| - |F_c|)/\sum|F_o|] \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2]^{1/2} \times 100$ (%); GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

(18) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

4476 *Inorg. Chem.* **1984**, *23*, 4476-4486

C, 40.25; H, 3.75; N, 2.61; Cl, 13.20. Found: C, 40.04; H, 3.58; N, 2.64; Cl, 12.91.

Protonation of $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$. $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$ (108 mg, 0.103 mmol) was dissolved in 5 mL of ether. To this solution was added an ether solution of HCl (5 mL, 1.76 M, 85 equiv). A precipitate formed immediately. Deionized water (10 mL) was added, and the ether was pumped away in vacuo. The mixture was filtered through a layer of Celite, and the Celite was washed twice with water. The filtrate and washes were combined and analyzed for hydrazine by the usual colorimetric method.[19] The result of that determination suggested that 0.100 (5) mmol of hydrazine had been produced.

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table IV-S) and observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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[19] Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006.

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Degenerate Framework Rearrangement in a Capped-Square-Pyramidal Metal-Carbon Cluster and Its Conversion to a Capped-Trigonal-Bipyramidal Cluster. Crystal Structures of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(\mu_3\text{-}CC_6H_4CH_3)_2H$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu_3\text{-}CC_6H_4CH_3)_2H$[1a]

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The compound $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)H$ (**1**) ($Cp = \eta^5\text{-}C_5H_5$; $Tol = p\text{-}C_6H_4CH_3$) is one of the products (together with 1 equiv of $CpW(CO)_3H$) from the reaction of $H_2Os_3(CO)_{10}$ and $CpW(CO)_2(CTol)$. Variable-temperature ^1H and ^{13}C NMR spectra of $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ show that the compound in solution undergoes a degenerate framework rearrangement that interchanges the two alkylidyne moieties. This can be interpreted as breaking and making hydrogen-bridged metal-metal bonds. In refluxing toluene $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ is converted to $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**2**) by loss of a carbonyl ligand. The latter has been isolated as a crystalline solid and has been characterized by spectroscopic (infrared, mass, ^1H and ^{13}C NMR) data. Molecular structures of both tetrametallic dialkylidyne complexes have been determined by single-crystal X-ray diffraction studies. Crystals of $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ belong to the monoclinic space group $P2_1/n$ (C_{2h}^5, No. 14) with $a = 10.610$ (4) Å, $b = 16.000$ (3) Å, $c = 19.394$ (6) Å, $\beta = 104.33$ (2)°, $V = 3189$ (2) $Å^3$, and $\rho(\text{calcd}) = 2.72$ g cm^{-3} for $Z = 4$ and molecular weight 1307. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer using Mo $K\alpha$ radiation, and the structure was refined to $R_F = 7.1\%$ and $R_{wF} = 5.1\%$ for all 3001 reflections with $2\theta = 3.0\text{-}40°$. The four metal atoms adopt a "butterfly" configuration. The dihedral angle between Os(1)-Os(2)-W and Os(3)-Os(2)-W planes is 98.7°. The molecule contains two μ_3-CTol ligands. One occupies a normal position on the outside of the Os(2)-Os(3)-W triangle; the other takes up an unusual position, bridging the "hinge" tungsten atom and the two "wing-tips" of the butterfly. The $WOs_3(\mu_3\text{-}C)_2$ fragment defines a capped square pyramid (base defined by Os(1)-Os(2)-Os(3)-C(11) and principal apex by W). $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}, No. 14) with $a = 19.067$ (3) Å, $b = 16.828$ (3) Å, $c = 19.947$ (3) Å, $\beta = 98.62$ (1)°, $V = 6327$ (2) $Å^3$, and $\rho(\text{calcd}) = 2.68$ g cm^{-3} for $Z = 8$ and molecular weight 1279. Diffraction data were collected as described above, and the structure was refined to $R_F = 5.4\%$ and $R_{wF} = 5.1\%$ for 6169 reflections with $2\theta = 3.5\text{-}45°$ and $I > 1.5\sigma(I)$. There are two equivalent molecules (A and B) in the crystallographic asymmetric unit. The tetrametallic cluster adopts a tetrahedral geometry and contains two μ_3-CTol ligands, which are located in almost equivalent environments on opposing sides of the pseudo plane of symmetry. Os(1), a unique osmium atom, and W are bonded to both alkylidyne fragments, and the Os(1)-W vector is almost coincident with the pseudo plane of symmetry. Molecules A and B have similar stereochemistry with the exception of the conformation of the carbonyl ligands surrounding Os(3). A terminal hydride on the tungsten atom was located from a difference-Fourier synthesis only in molecule B.

Introduction

We have previously reported that the reaction of $H_2Os_3(CO)_{10}$ and $CpW(CO)_2(CTol)$ ($Cp = \eta^5\text{-}C_5H_5$; $Tol = p\text{-}C_6H_5CH_3$) yields three products, $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$, $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$, and $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$.[2] The crystal structure of $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$ has been presented elsewhere.[3] The crystal structure and an NMR spectroscopic study of $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ also have been discussed separately.[2b] For the third product, $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ (**1**), variable-temperature ^1H and ^{13}C NMR studies show that it undergoes a degenerate rearrangement of the cluster framework in solution. Furthermore, the capped-square-pyramidal cluster **1** is cleanly converted to a new capped-trigonal-bipyramidal cluster, $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**2**), by loss of a carbonyl ligand in refluxing toluene. This paper describes these spectroscopic and chemical results together with the X-ray structural analyses of the dialkylidyne

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[1] (a) Part 29 of the series "Structural Studies on Polynuclear Osmium Carbonyl Hydrides". For Part 28, see: Churchill, M. R.; Bueno, C.; Park, J. T.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 1017. (b) University of Illinois. (c) SUNY—Buffalo.

[2] (a) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7385. (b) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579.

[3] Churchill, M. R. Bueno, C.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 640.