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Metal-Metal-Bonded Complexes of the Early Transition Metals. 7. The Ditungsten Tetracarboxylate Story[1]

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Tetrakis(trifluoroacetato)ditungsten(II), $W_2(O_2CCF_3)_4$ or $W_2(TFA)_4$, has been obtained from the reaction of $W_2Cl_4(THF)_4$ and sodium trifluoroacetate in tetrahydrofuran. It is a volatile, thermally stable (<200 °C), yellow crystalline complex. $W_2(TFA)_4$ has been characterized by IR, Raman, NMR (^{19}F and ^{183}W), and mass spectroscopy. IR and ^{19}F NMR spectra are consistent with the presence of four equivalent bidentate carboxylate ligands. The W–W stretching vibration (Raman active) was observed at 310 (3) cm^{-1} for this quadruply M–M-bonded dimer. The ^{183}W NMR spectrum of $W_2(TFA)_4$ shows a single sharp resonance at δ +6760 (vs. 2 M Na_2WO_4 in D_2O). X-ray crystal structures of two axial adducts, $W_2(TFA)_4\cdot{}^2/_3$digly (digly = diglyme) and $W_2(TFA)_4\cdot 2PPh_3$, have been obtained. The $W_2(TFA)_4$ units in both structures have idealized D_{4h} symmetry and mean W–W bond lengths of 2.209 [2] and 2.242 [2] Å, respectively. A Raman band at 280 (3) cm^{-1} has been assigned as the W–W stretching vibration in the triphenylphosphine adduct. The diglyme and triphenylphosphine adducts both form triclinic crystals (space group $P\bar{1}$, $Z = 3$ for the former and space group $P\bar{1}$, $Z = 2$ for the latter) with unit cell dimensions (at −160 °C) in order as follows: a (Å) = 23.046 (36), 14.655 (5); b (Å) = 9.108 (9), 18.573 (7); c (Å) = 9.222 (10), 9.008 (3); α (deg) = 99.64 (6), 98.29 (2); β (deg) = 59.45 (5), 106.34 (2); γ (deg) = 103.55 (6), 71.99 (2). The structures refined to residuals of R_F = 0.047, 0.043 and R_{wF} = 0.046, 0.043.

The molybdenum(II) carboxylates, $Mo_2(O_2CR)_4$, are the most important class of compounds that contain molybdenum–molybdenum quadruple bonds.[3] Literally hundreds of complexes that contain the Mo_2^{4+} core are derived from the carboxylate dimers, which, in turn, are obtained by variants of essentially a single route (reaction 1), originally developed

$$2Mo(CO)_6 + 4HO_2CR \xrightarrow{\Delta} Mo_2(O_2CR)_4 + 12CO + 2H_2 \quad (1)$$

by Wilkinson and co-workers in the early 1960s.[4] Ever since the true nature of Wilkinson's molybdenum(II) carboxylates was established,[5] efforts have been made to prepare tungsten analogues in the hope that they would play a similar role in the development of W_2^{4+} chemistry. Attempts to mimic the original Wilkinson synthesis by substituting $W(CO)_6$ for $Mo(CO)_6$ gave disappointing results vis-à-vis the primary objective.[6] Tungsten hexacarbonyl reacts with acetic acid or other carboxylic acids to give only the trinuclear tungsten(IV) species, e.g., $[W_3O_2(O_2CMe)_6(H_2O)_3]^{2+}$, without any indication that $W_2(O_2CR)_4$ compounds are ever formed.[7] Metathetical reactions between preformed quadruply bonded complexes (e.g., $[Li(THF)]_4W_2Me_8$[8] and $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$[9,10]) and carboxylic acids have also failed to provide $W_2(O_2CR)_4$ compounds. Only by the treatment of $W_2Cl_4(THF)_4$ with sodium trifluoroacetate under nonacidic (i.e., nonoxidizing) conditions was the preparation of the first tungsten(II) carboxylate, $W_2(O_2CCF_3)_4$ or $W_2(TFA)_4$, finally achieved. The details of this reaction, the physicochemical properties of $W_2(TFA)_4$, and the structures of two adducts are reported here. Some of this work has been described in a preliminary communication.[11]

Results and Discussion

Synthesis. In their report on the quadruply M–M-bonded $W_2Cl_4(PR_3)_4$ compounds, Sharp and Schrock[9] noted that THF suspensions of polymeric tungsten tetrachloride could be reduced with sodium amalgam in the absence of phosphine. One-electron reduction of $[WCl_4]_x$ yielded $W_2Cl_6(THF)_4$, and a subsequent two-electron reduction of isolated yellow-green $W_2Cl_6(THF)_4$ in THF yielded an intense blue solution containing (presumably) $W_2Cl_4(THF)_4$. The latter decomposes slowly at 0 °C and more rapidly at room temperature, but if sodium trifluoroacetate (4 equiv) is added to the cold blue tungsten(II) solution, it rapidly turns yellow-brown, signaling the formation of $W_2(TFA)_4$ (yellow) and as yet unidentified light brown side products (reaction 2). $W_2(TFA)_4$ is isolated from these yellow-brown solutions by solvent removal and sublimation of the residue. Since neither $W_2Cl_6(THF)_4$ nor $[WCl_4]_x$ react with NaTFA under the prevailing experimental conditions, a more convenient synthesis (reaction 3) has replaced the original one.[12] Sodium trifluoroacetate is added to a suspension of $[WCl_4]_x$ in cold (0 °C) THF followed by the requisite amount of sodium amalgam. The mixture is stirred vigorously for 2 h and then worked up as noted above. In either case, yields of $W_2(TFA)_4$ in the range of 50–60%, based on $[WCl_4]_x$, have been obtained.

$$W_2Cl_6(THF)_4 + 2Na/Hg \xrightarrow{THF} [W_2Cl_4(THF)_4] \xrightarrow{4NaTFA} W_2(TFA)_4 \quad (2)$$

$$[WCl_4]_x + 2NaTFA + 2Na/Hg \rightarrow 0.5W_2(TFA)_4 + 4NaCl \quad (3)$$

The choice of sodium trifluoroacetate for our synthesis was based on the premise that we would be able to sublime $W_2(TFA)_4$ out of the crude reaction mixture. This turned out to be the case, but the method (reaction 2) is not limited to $W_2(TFA)_4$ alone. Appropriate modifications in the workup

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[12] We are grateful to Professor R. A. Andersen (Berkeley) for suggesting this modification.

Table I. Crystal Data for $W_2(TFA)_4$ Adducts

	$W_2(TFA)_4 \cdot {}^2/_3$digly	$W_2(TFA)_4 \cdot 2PPh_3$
mol formula	$W_2F_{12}O_8C_8 \cdot {}^2/_3C_6H_{14}O_3$	$W_2P_2F_{12}O_8C_{44}H_{30}$
color	yellow	yellow-orange
cryst dimens, mm	0.08 × 0.08 × 0.02	0.11 × 0.09 × 0.08
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
a, Å	23.046 (36)[a]	14.655 (5)[b]
b, Å	9.108 (9)	18.573 (7)
c, Å	9.222 (10)	9.008 (3)
α, deg	99.64 (6)	98.29 (2)
β, deg	59.45 (5)	106.34 (2)
γ, deg	103.55 (6)	71.99 (2)
molecules/cell	3	2
cell V, Å^3	1617.85	2233.04
d(calcd), g cm^{-3}	2.799	1.999
λ, Å	0.71069	0.71069
mol wt	909.22	1344.34
linear abs coeff, cm^{-1}	110.35	54.29
min abs	0.234	
max abs	0.504	
2θ range, deg	5–50	6–45
no. of data with $F_o > 2.33\sigma(F_o)$	3592	4561
no. of unique data	4244	5854
final residuals		
R_F	0.0465	0.0433
R_{wF}	0.0462	0.0425
goodness of fit, last cycle	1.122	1.105
max Δ/σ, last cycle	0.05	0.05

[a] At −162 °C; 24 reflections. [b] At −163 °C; 42 reflections.

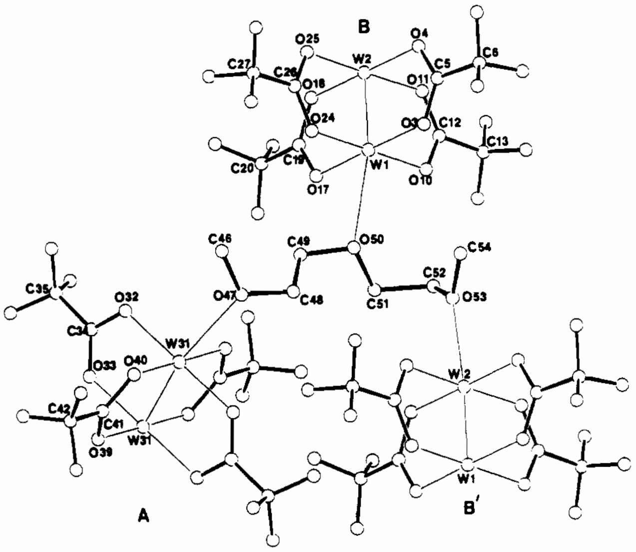

Figure 1. ORTEP drawing of $W_2(TFA)_4 \cdot {}^2/_3$digly showing the partial contents of two unit cells (see text).

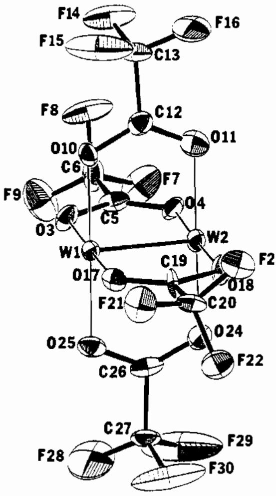

Figure 2. ORTEP drawing of one of the crystallographically independent dimers (B) in the structure of $W_2(TFA)_4 \cdot {}^2/_3$digly.

procedure will provide other members of the tungsten(II) carboxylate family, e.g., $W_2(O_2C\text{-}t\text{-}Bu)_4$ and $W_2(O_2C\text{-}n\text{-}Pr)_4$, in good to excellent yield. Future papers in this series will provide synthetic, structural, and spectroscopic data on these dimers.[13]

Immediately following the successful isolation and physical characterization (vide infra) of $W_2(TFA)_4$, we began what turned out to be a frustrating search for crystals of the pure dimer that were suitable for X-ray crystallography. Neither vacuum sublimation nor sublimation in an inert-gas stream[14] provided X-ray quality crystals despite numerous attempts by three different investigators. $W_2(TFA)_4$ crystallizes nicely from cold toluene, but the clear yellow needles turn opaque soon after removal from the mother liquor. Faced with these difficulties, we turned our attention to the synthesis of adducts.

The diglyme adduct, $W_2(TFA)_4 \cdot {}^2/_3$digly (digly = diglyme) was obtained by recrystallization of $W_2(TFA)_4$ from benzene/diglyme and a subsequent sublimation of the crude product. A second adduct, $W_2(TFA)_4 \cdot 2PPh_3$, was obtained in high yield by adding triphenylphosphine to concentrated toluene solutions of the parent (reaction 4). It forms beautiful, clear yellow-orange crystals from hot hexane. The structures of both of the aforementioned adducts are described below. Both are axial or class I adducts.

$$W_2(TFA)_4 + 2PPh_3 \xrightarrow{PhCH_3} W_2(TFA)_4 \cdot 2PPh_3 \quad (4)$$

We may note here that it is also possible to prepare equatorial or class II adducts of $W_2(TFA)_4$ in reactions with small, basic, tertiary phosphines (e.g., PMe_3, PEt_3, PMe_2Ph). These complexes will be discussed in detail elsewhere.[13] We mention them here only to indicate that, insofar as Lewis base chemistry is concerned, the reactivity of $W_2(TFA)_4$ apparently parallels that of $Mo_2(TFA)_4$.[16] Only when potential oxidizing agents (e.g., aqueous HCl[11]) are present do we see a divergence in the chemistry of these homologues. We will discuss this point further after first describing the crystal structures of our two adducts.

Solid-State Structures. Crystal data for the $W_2(TFA)_4 \cdot {}^2/_3$digly and $W_2(TFA)_4 \cdot 2PPh_3$ complexes are given in Table I. Positional and isotropic thermal parameters for the former adduct are given in Table II, and selected interatomic distances and angles are presented in Table III (supplementary material). Positional and isotropic thermal parameters for $W_2(TFA)_4 \cdot 2PPh_3$ are presented in Table IV, and selected interatomic distances and angles are given in Table V (supplementary material). Finally, in Table VI, we have collected the mean values of important interatomic distances and angles in the two structures.

A view of the structure of $W_2(TFA)_4 \cdot {}^2/_3$digly is shown in Figure 1. This particular view shows the partial contents of two unit cells and nicely illustrates the tridentate nature of the polyether which stitches $W_2(TFA)_4$ units together in the

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(13) Santure, D. J.; Huffman, J. C.; Sattelberger, A. P., to be submitted for publication.

(14) This method was used to grow crystals of $Mo_2(TFA)_4$[15] and has been reproduced in our laboratory albeit with low recovery and extensive decomposition. $W_2(TFA)_4$ decomposed without providing any crystalline sublimate.

(15) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161–172.

(16) For a discussion of class I and class II adducts of quadruply M–M-bonded molybdenum carboxylate complexes see: Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805–810.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(TFA)_4 \cdot {}^2/_3$digly[a]

atom	x	y	z	B_{iso}, Å^2
W(1)	1888.7 (3)	3068 (1)	9642 (1)	15
W(2)	1616.5 (3)	5297 (1)	9874 (1)	17
O(3)	1511 (5)	2254 (11)	7945 (13)	22
O(4)	1245 (5)	4517 (11)	8186 (13)	21
C(5)	1247 (7)	3176 (18)	7678 (19)	20
C(6)	947 (9)	2475 (19)	6484 (24)	32
F(7)	956 (6)	3592 (13)	5666 (15)	49
F(8)	309 (5)	1894 (14)	7422 (14)	52
F(9)	1268 (6)	1483 (13)	5376 (14)	48
O(10)	929 (5)	2345 (11)	11645 (12)	18
O(11)	646 (5)	4600 (13)	11895 (13)	27
C(12)	532 (8)	3279 (17)	12332 (19)	21
C(13)	−186 (8)	2666 (21)	13785 (21)	29
F(14)	−555 (5)	1806 (15)	13156 (14)	54
F(15)	−142 (6)	1860 (20)	14738 (15)	77
F(16)	−499 (6)	3755 (15)	14688 (18)	87
O(17)	2224 (5)	3852 (11)	11406 (12)	19
O(18)	1958 (5)	6108 (11)	11623 (13)	20
C(19)	2191 (8)	5175 (16)	11989 (18)	17
C(20)	2428 (8)	5759 (19)	13299 (20)	24
F(21)	2541 (5)	4673 (11)	13850 (12)	35
F(22)	3017 (5)	6767 (11)	12566 (12)	32
F(23)	1982 (5)	6519 (11)	14593 (11)	29
O(24)	2847 (5)	3759 (12)	7614 (13)	23
O(25)	2574 (5)	6047 (12)	7867 (13)	24
C(26)	2957 (7)	5099 (19)	7188 (18)	20
C(27)	3674 (8)	5566 (19)	5662 (22)	26
F(28)	3971 (9)	4513 (19)	4777 (24)	151
F(29)	3672 (6)	6392 (24)	4694 (18)	103
F(30)	4081 (6)	6379 (20)	6193 (16)	85
W(31)	4855.5 (3)	247 (1)	9103 (1)	13
O(32)	5246 (5)	2539 (11)	9288 (11)	18
O(33)	5534 (5)	2016 (11)	11079 (12)	17
C(34)	5509 (8)	2949 (16)	10257 (17)	16
C(35)	5742 (7)	4584 (17)	10474 (17)	15
F(36)	5262 (4)	5182 (10)	11885 (11)	28
F(37)	6300 (4)	4838 (10)	10621 (11)	25
F(38)	5877 (5)	5398 (10)	9234 (11)	29
O(39)	3905 (5)	590 (11)	11121 (12)	17
O(40)	4196 (5)	110 (11)	12955 (11)	17
C(41)	3782 (7)	437 (15)	12566 (18)	26
C(42)	3093 (7)	709 (18)	14044 (18)	20
F(43)	3027 (5)	676 (13)	15522 (11)	40
F(44)	2993 (5)	2093 (12)	13967 (13)	44
F(45)	2596 (4)	223 (13)	13932 (13)	41
C(46)	4554 (8)	1470 (18)	6209 (18)	22
O(47)	4201 (5)	525 (11)	7685 (12)	17
C(48)	3511 (8)	−44 (17)	8187 (20)	22
C(49)	3093 (7)	1218 (17)	9283 (19)	19
O(50)	2392 (5)	690 (11)	9684 (12)	18
C(51)	2021 (9)	−228 (19)	11184 (19)	26
C(52)	1327 (8)	−1012 (19)	11313 (21)	28
O(53)	1416 (5)	−2133 (11)	9959 (13)	22
C(54)	1443 (11)	−1576 (21)	8561 (22)	36

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(TFA)_4 \cdot 2PPh_3$[a]

atom	x	y	z	B_{iso}, Å^2
W(1)	706.5 (3)	155.6 (2)	194.5 (5)	12
P(2)	2749 (2)	175 (2)	258 (3)	13
O(3)	495 (5)	777 (4)	2256 (8)	16
O(4)	923 (5)	−457 (4)	−1891 (8)	16
C(5)	−268 (8)	778 (6)	2653 (13)	18
C(6)	−474 (8)	1233 (6)	4144 (12)	16
F(7)	195 (5)	1605 (4)	4799 (7)	26
F(8)	−1354 (4)	1756 (4)	3831 (7)	26
F(9)	−467 (5)	787 (3)	5162 (7)	26
O(10)	−60 (5)	1135 (4)	−1003 (8)	15
O(11)	1465 (5)	−820 (4)	1401 (8)	14
C(12)	−983 (8)	1258 (6)	−1534 (12)	15
C(13)	−1582 (8)	1998 (6)	−2301 (13)	21
F(14)	−2014 (5)	2499 (4)	−1303 (7)	27
F(15)	−2297 (4)	1886 (3)	−3503 (7)	23
F(16)	−1031 (5)	2318 (4)	−2778 (7)	24
C(17)	2942 (8)	−55 (6)	−1685 (12)	16
C(18)	3629 (7)	−678 (6)	−2101 (12)	17
C(19)	3695 (9)	−836 (6)	−3617 (13)	24
C(20)	3057 (9)	−384 (7)	−4746 (13)	27
C(21)	2341 (9)	265 (7)	−4375 (14)	25
C(22)	2279 (8)	429 (6)	−2849 (12)	19
C(23)	3758 (8)	−527 (6)	1424 (12)	16
C(24)	3713 (8)	−1262 (6)	1275 (12)	19
C(25)	4428 (8)	−1816 (6)	2174 (13)	21
C(26)	5194 (8)	−1630 (6)	3210 (14)	23
C(27)	5280 (8)	−893 (7)	3446 (13)	24
C(28)	4561 (8)	−343 (6)	2528 (12)	16
C(29)	3075 (7)	1065 (6)	897 (12)	16
C(30)	2709 (8)	1498 (6)	2127 (12)	19
C(31)	2959 (9)	2165 (6)	2682 (14)	26
C(32)	3526 (8)	2417 (6)	2014 (15)	26
C(33)	3870 (8)	1993 (6)	781 (13)	20
C(34)	3652 (8)	1326 (6)	224 (12)	17
W(1A)	4260.6 (3)	4923.7 (2)	9941.3 (5)	12
P(2A)	2206 (2)	5021 (2)	9880 (3)	14
O(3A)	3583 (5)	5935 (4)	8783 (8)	17
O(4A)	4942 (5)	3906 (4)	11063 (8)	15
C(5A)	4121 (8)	6299 (6)	8534 (12)	15
C(6A)	3588 (8)	7012 (6)	7746 (13)	20
F(7A)	2990 (5)	6884 (3)	6370 (7)	22
F(8A)	3017 (5)	7502 (4)	8591 (8)	31
F(9A)	4199 (5)	7350 (4)	7478 (8)	30
O(10A)	4272 (5)	5535 (4)	12066 (8)	15
O(11A)	4253 (5)	4309 (4)	7813 (7)	14
C(12A)	5015 (8)	5799 (6)	12718 (12)	16
C(13A)	4980 (8)	6252 (6)	14252 (13)	21
F(14A)	5020 (6)	5820 (4)	15340 (8)	41
F(15A)	5706 (5)	6568 (4)	14763 (8)	39
F(16A)	4137 (5)	6805 (4)	14103 (8)	32
C(17A)	2078 (7)	4859 (5)	11773 (11)	12
C(18A)	1696 (8)	4305 (6)	11967 (13)	20
C(19A)	1670 (8)	4189 (6)	13466 (14)	23
C(20A)	2012 (8)	4645 (7)	14720 (12)	23
C(21A)	2391 (8)	5206 (7)	14535 (12)	21
C(22A)	2431 (8)	5328 (6)	13040 (13)	21
C(23A)	1771 (7)	4278 (6)	8559 (11)	13
C(24A)	2456 (8)	3568 (6)	8479 (12)	20
C(25A)	2194 (10)	2987 (6)	7516 (13)	26
C(26A)	1236 (8)	3117 (6)	6567 (13)	21
C(27A)	546 (8)	3813 (7)	6639 (13)	25
C(28A)	812 (8)	4398 (6)	7644 (12)	17
C(29A)	1240 (8)	5896 (6)	9281 (12)	16
C(30A)	1252 (8)	6205 (6)	7957 (12)	18
C(31A)	564 (9)	6876 (7)	7438 (15)	27
C(32A)	−129 (8)	7267 (7)	8257 (14)	25
C(33A)	−125 (8)	6975 (6)	9582 (14)	23
C(34A)	552 (8)	6293 (6)	10096 (14)	22

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

solid state. Dimers A (which lie on the crystallographic center of inversion) and B are crystallographically independent and in the same unit cell as the diglyme. The symmetry-related partners of dimer B and the diglyme are not shown in Figure 1. Dimer B′ is related to B by a unit translation. A blowup of dimer B is shown in Figure 2. Each of the independent dimers has idealized D_{4h} symmetry with the tungsten atoms bridged by trifluoroacetate ligands. The W–W bond lengths in dimers A and B are 2.211 (2) and 2.207 (2) Å, respectively. These distances fall within the range of known W–W quadruple-bond lengths, i.e., 2.155 (2)–2.375 (1) Å.[17] There are

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(17) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 3880–3886 and references therein.

Table VI. Comparison of Mean[a] Dimensions in $W_2(TFA)_4$ Adducts

	$W_2(TFA)_4 \cdot {}^2/_3$digly	$W_2(TFA)_4 \cdot 2PPh_3$
	Distances (Å)	
W-W	2.209 [2]	2.242 [2]
W-O	2.087 [4]	2.091 [3]
C-O	1.257 [5]	1.266 [4]
C-C	1.53 [1]	1.51 [1]
C-F	1.308 [8]	1.329 [3]
W···O	2.56 [7]	
W···P		2.97 [2]
	Angles (deg)	
W-W-O	90.4 [2]	90.0 [4]
O-W-O (cis)	90.0 [4]	90.0 [2]
W-O-C	116.7 [5]	117.7[4]
O-C-O	125.7 [8]	124.6 [5]
C-C-F	111.4 [6]	111.3 [3]
W-W···O	169 [3]	
W-W···P		167 [3]

[a] A number in brackets is equal to $[\Sigma_m \Delta_i^2/m(m-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value in a set of *m* such values from the arithmetic mean.

three different W···O intermolecular contacts with diglyme oxygens, and the mean value is 2.56 [7] Å. Since the corresponding molybdenum analogue is presently unknown, we can only compare our data with that obtained for $Mo_2(TFA)_4$.[15] This is reasonable since there is an intermolecular Mo···O contact (2.72 (1) Å) between the nearest neighbors in the crystal structure of this dimer. Here the Mo–Mo bond length is 2.090 (4) Å or ca. 0.1 Å shorter than the W–W separation found in the diglyme adduct. Such differences between homologues or closely similar molybdenum and tungsten compounds with multiple bonds are typical and, given the near-equivalence of metal radii, are taken as indications of weaker M–M bonding in the tungsten dimers.[18]

We turn now to the crystal structure of $W_2(TFA)_4 \cdot 2PPh_3$. There are two crystallographically independent dimers in the unit cell, each with a crystallographic center of inversion. A view of one of the independent dimers is shown in Figure 3. The only significant differences between the two independent molecules are in the tungsten–phosphorus interactions. In one dimer, the W···P distance and W–W–P angle are 2.989 (3) Å and 164.8 (1)°, while in the other dimer (Figure 3), these values are 2.945 (3) Å and 169.8 (1)°. The different disposition of PPh_3 ligands appears to be a consequence of packing forces, and the W–W distances in both dimers are essentially equal (2.240 (1) vs. 2.243 (1) Å). Although the structure of $Mo_2(TFA)_4 \cdot 2PPh_3$ has not been published,[19,20] the structure of a closely related, axially ligated molybdenum complex has. In $Mo_2(TFA)_4 \cdot 2PPh_2Me$,[21] the Mo···P distances and Mo–Mo–P angles are very close to the analogous quantities reported here. The Mo–Mo distance at 2.128 (1) Å is, again, ca. 0.1 Å *shorter* than the mean W–W separation, 2.242 [2] Å, in the PPh_3 adduct.

The increases of ca. 0.03 Å in the W–W bond length from $W_2(TFA)_4 \cdot {}^2/_3$digly to $W_2(TFA)_4 \cdot 2PPh_3$ and ca. 0.04 Å in the Mo–Mo bond length from $Mo_2(TFA)_4$ to $Mo_2(TFA)_4 \cdot 2PPh_2Me$, though not very large, are most likely indications of stronger M–L σ-bonding and weaker M–M σ-bonding in the phosphine adducts relative to that in the oxygen adducts.[22] Note also that a comparison of the molybdenum dimers or tungsten dimers (Table VI) reveals no substantive differences in the $M_2(TFA)_4$ units except for changes in metal–metal bond length.

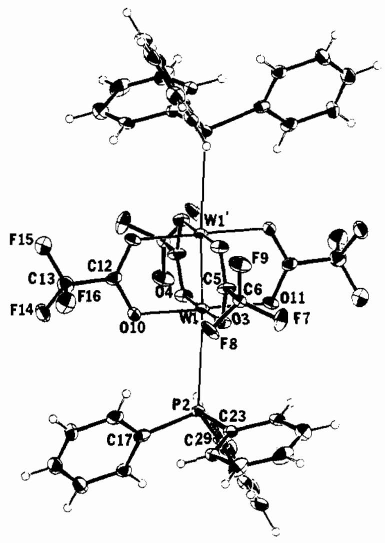

Figure 3. ORTEP drawing of one of the crystallographically independent adducts in the structure of $W_2(TFA)_4 \cdot 2PPh_3$.

Physicochemical Properties. $W_2(TFA)_4$ is an air-sensitive, bright yellow complex. It is much more air sensitive than its molybdenum analogue,[15] turning black within seconds after exposure to laboratory air. The dimer is thermally quite stable, decomposing at ca. 200 °C in a sealed evacuated capillary, and can be sublimed in vacuo at temperatures between 100 and 130 °C and pressures of $\leq 10^{-4}$ torr. A strong parent ion multiplet was observed in the mass spectrum and affords conclusive evidence for the existence of the complex in the vapor phase. The isotopic distribution pattern, which is uniquely characteristic of the W_2 unit, and the mass numbers themselves were in excellent agreement with the calculated pattern.

The fragmentation pattern of $W_2(TFA)_4$ is very reminiscent of that of $Mo_2(TFA)_4$.[15] The molecule breaks down by successive loss of CF_2CO_2 units, and the third fluorine from the carboxylate ligand becomes bound to tungsten in each fragmentation process. When the unit $W_2F_3(O_2CCF_3)^+$ is reached, the breakdown becomes less systematic, resulting finally in the fragments WOF_2^+, WOF^+, and WO^+. The W_2^+ ion was not observed.

The volatility of $W_2(TFA)_4$ makes it an attractive candidate for other vapor-phase studies in addition to mass spectroscopy. In collaboration with Professor G. M. Bancroft of the Department of Chemistry, University of Western Ontario, we were able to obtain the UV photoelectron spectrum of this material. The results of this study and our interpretation of the spectrum have already been published.[1] The δ ionizations of $Mo_2(TFA)_4$ andd $W_2(TFA)_4$ appear at 8.76 and 7.39 eV, respectively. The difference in these first ionization potentials, 1.37 eV, is the largest yet observed between molybdenum and tungsten homologues.[24] The destabilization of the δ orbital

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(18) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040–4045.

(19) The structure of the axial adduct, $Mo_2(TFA)_4 \cdot 2PPh_3$, is mentioned in a recent paper by Cotton and Lay[20] but "full refinement was not achieved". An Mo···P distance of 3.07 ± 0.05 Å is quoted therein.

(20) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935–940.

(21) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1982**, *21*, 1318–1321. The Mo···P distances are 2.964 (1) and 3.012 (1) Å, and the Mo–Mo–P angles are 166.31 (2) and 165.99 (2)°.

(22) Similar conclusions, albeit with theoretical backing from SCF–Xα–SW calculations, have been reached in the case of $Rh_2(O_2CH)_4 \cdot 2H_2O$ vs. $Rh_2(O_2CH)_4 \cdot 2PH_3$.[23]

(23) Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042–3048.

(24) The δ ionizations in $Mo_2(mhp)_4$ and $W_2(mhp)_4$ are observed[25] at 5.89 and 5.30 eV, respectively (Δ = 0.59 eV), and the δ ionizations of $Mo_2Cl_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$ are observed[26] at 6.44 and 5.81 eV, respectively (Δ = 0.63 eV).

(25) Bursten, B. E.; Cotton, F. A.; Cowley, A. H.; Hanson, B. E.; Lattman, M.; Stanley, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 6244–6249.

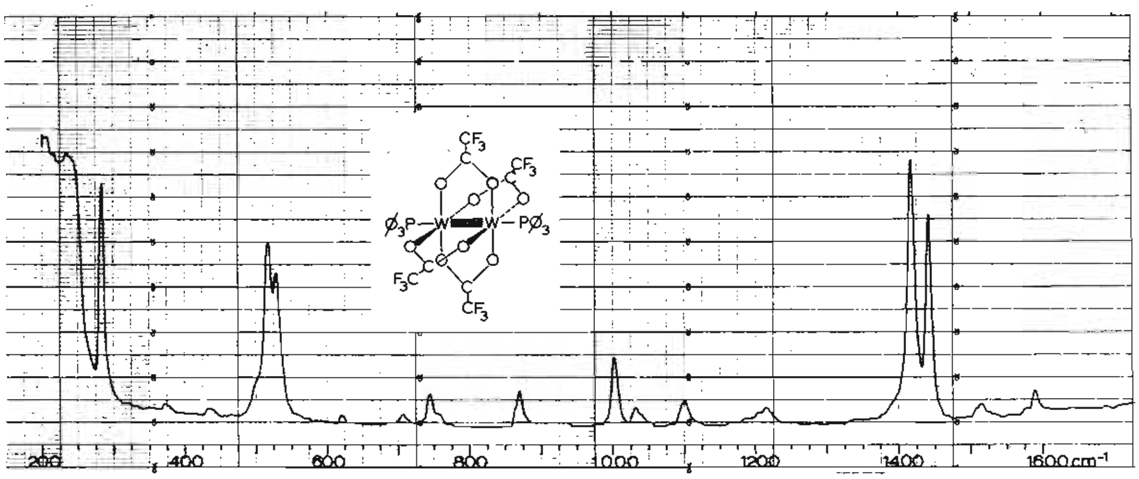

Figure 4. Raman spectrum of crystalline $W_2(TFA)_4 \cdot 2PPh_3$ obtained with 6328-Å exciting radiation.

in the tungsten dimer makes it much more susceptible to oxidation[27] *and* oxidative-addition reactions[11] than its molybdenum counterpart and eliminates H^+ as a reagent for carboxylate removal in reactions whose goal is to preserve the W_2^{4+} core. In retrospect, it is not very surprising that the tungsten hexacarbonyl/carboxylic acid reactions or metathesis reactions with carboxylic acids (vide supra) failed to produce $W_2(O_2CR)_4$ compounds. The tungsten(II) carboxylates, if they are even formed in these latter reactions, could not survive the inherent oxidizing conditions.

The vibrational spectra of $W_2(TFA)_4$ and its PPh_3 adduct have been investigated by IR and Raman spectroscopy (characterization of the diglyme adduct beyond its crystal structure was not pursued). Both complexes give infrared spectra characteristic of bidentate carboxylate ligands. The asymmetric CO_2 vibration in the parent appears, as a doublet, at 1559 and 1542 cm^{-1}; in the adducts we observed a broad singlet centered at 1552 cm^{-1} and assigned it as the same mode. In $Mo_2(TFA)_4$ and $Mo_2(TFA)_4 \cdot 2PPh_2Me$ (axial isomer), the asymmetric CO_2 vibrations are observed at 1592, 1572 (parent),[15] and 1598 cm^{-1} (adduct).[21]

The most interesting feature of the vibrational spectra of quadruply bonded complexes is the vibration that corresponds mainly to $M\overset{4}{-}M$ stretching, $\nu(M-M)$. This totally symmetric vibration is Raman active and was observed in the Raman spectra of $W_2(TFA)_4$ and $W_2(TFA)_4 \cdot 2PPh_3$. The W–W stretching mode in the parent appears at 310 (3) cm^{-1}. In Figure 4, we present the Raman spectrum of the PPh_3 adduct. It is quite similar to the spectrum of the parent except that the W–W stretching mode has shifted some 30 cm^{-1} to 280 (3) cm^{-1}. The magnitude and the direction of the shift in $\nu(M-M)$ were anticipated from earlier work with $Mo_2(TFA)_4$[15] and $Mo_2(TFA)_4 \cdot 2py$.[29] The Mo–Mo bond lengths (Mo–Mo stretching frequencies) in these two complexes are 2.090 (4) Å (397 cm^{-1}) and 2.129 (2) Å (363 cm^{-1}), respectively. An *increase* in bond length of 0.04 Å corresponds to a *decrease* of 34 cm^{-1} in the Mo–Mo stretching frequency. Using this information, we can reasonably predict that the W–W bond length in pure $W_2(TFA)_4$ is in the range 2.20–2.21 Å.

The ^{19}F NMR spectra of $W_2(TFA)_4$ and $W_2(TFA)_4 \cdot 2PPh_3$ show single, sharp resonances at δ −70.1 and δ −70.0 (vs. $CFCl_3$, δ 0.0), respectively, consistent with the presence of bidentate TFA ligands for both complexes in solution.[30] The $^{31}P\{^1H\}$ NMR spectrum of the adduct shows a single resonance 12.26 ppm downfield from the resonance position of the free ligand in the same solvent (benzene-d_6). No tungsten-183 ($I = ^1/_2$, natural abundance 14.4%) satellites were observed in the spectrum. The latter observation suggests that PPh_3 is only weakly coordinated in solution, consistent with the rather long W···P separation observed in the solid-state structure.

The ^{183}W NMR spectrum of $W_2(TFA)_4$ (ca. 1 M in THF or ca. 0.28 M in tungsten-183) was also obtained as part of our characterization of this complex. A single, sharp (fwhm $\cong$ 1 Hz) resonance line was observed at δ +6760 (vs. 2 M Na_2WO_4 in D_2O, δ 0.0[31]). This shift is outside the range of all previously reported tungsten-183 chemical shifts by some 4500 ppm.[32] No chemical shift data are currently available on other multiply M–M-bonded tungsten compounds for comparison, but the ^{183}W chemical shift in the single M–M-bonded dimer $[CpW(CO)_3]_2$ is δ −4040[33] (i.e., 10 800 ppm upfield of $W_2(TFA)_4$!), and mononuclear tungsten(II) complexes of the type $CpW(CO)_3X$ (X = Cl, Br, H, Me, etc.) have shifts in the range δ −2400 to −4000. Chemical shift data on other quadruply bonded tungsten compounds are currently being collected and will be reported in future publications.

Summary. The following are the principal results and conclusions of this investigation.

(i) A simple route to the *first* quadruply M–M-bonded tungsten(II) carboxylate, $W_2(O_2CCF_3)_4$, has been achieved.

(ii) Mean W–W bond lengths of 2.209 [2] and 2.242 [2] Å have been established for the axial-diglyme and -triphenylphosphine adducts of $W_2(O_2CCF_3)_4$.

(iii) W–W stretching vibrations of 310 (3) and 280 (3) cm^{-1} have been observed for $W_2(TFA)_4$ and $W_2(TFA)_4 \cdot 2PPh_3$.

(iv) The Lewis base chemistry of $W_2(TFA)_4$ apparently mimics the Lewis base chemistry of $Mo_2(TFA)_4$.

(v) The first ^{183}W NMR spectrum of a multiply metal–metal-bonded tungsten dimer has been obtained. The tung-

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(26) Cotton, F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *104*, 679–686.

(27) Cotton and co-workers[25] have correlated δ ionization potentials with reversible one-electron oxidation potentials for the $M_2(mhp)_4$ dimers (M_2 = Mo_2, W_2, MoW, CrMo; mhp = anion of 2-hydroxy-6-methylpyridine). $E_{1/2}$ values (vs. SCE) for the Mo_2 and W_2 dimers were 0.20 and −0.35 V, respectively. The $E_{1/2}$ values for the $M_2(TFA)_4$ dimers are presently unknown, but the electrochemical behavior of these species is under investigation.[28]

(28) Haushalter, R., private communication.

(29) Cotton, F. A.; Norman, J. G., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5697–5702.

(30) Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 446–451. For a discussion of the application of ^{19}F NMR to quadruply bonded molybdenum trifluoroacetate complexes see ref 16.

(31) Gansow, O. A.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, *187*, C27–C31. Chemical shifts to the high-frequency side of the reference are assigned positive values.

(32) Harris, R. K. Mann, B. E. "NMR and the Periodic Table"; Academic Press: New York, 1979; Chapter 8, pp 215–217.

(33) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616–1622. We have converted the chemical shifts reported in this paper to the Gansow–Klemperer scale.[31]

sten-183 chemical shift of $W_2(TFA)_4$ was located at δ +6760, far removed from all previously reported tungsten chemical shifts.

Experimental Section

Reagents. Tungsten hexacarbonyl (Pressure Chemical), tungsten hexachloride (99.9%, Great Western Inorganics), triphenylphosphine (Orgmet), and trifluoroacetic acid (Aldrich) were used without further purification. Sodium trifluoroacetate was either purchased (Aldrich) or synthesized from trifluoroacetic acid and freshly prepared sodium methoxide in methanol. In either case, the salt was dried by azeotropic distillation with benzene.

Diglyme, THF, benzene, toluene, and ether were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, and sodium or potassium. Hexane was distilled from a solution of the solvent and *n*-butyllithium. Chlorobenzene was distilled from a suspension of the solvent plus P_4O_{10} immediately before use. Solvents (except PhCl) were stored in 500-mL bottles inside the drybox.

$[WCl_4]_x$ was prepared from the reaction $2WCl_6 + W(CO)_6$ in refluxing chlorobenzene[34] and stored in the drybox. $W_2Cl_6(THF)_4$ was prepared from $[WCl_4]_x$ by the method of Sharp and Schrock.[9]

Physical and Analytical Measurements. Elemental analyses and molecular weight measurements were performed by Galbraith Laboratories, Knoxville, TN.

Infrared measurements were obtained from Nujol mulls between KBr plates with a Perkin-Elmer Model 1330 infrared spectrophotometer.

Raman spectra were obtained on a Spex Ramalog system equipped with a Spectra-Physics Model 125 helium/neon laser, which served as a source of 6328-Å radiation. Solid samples were sealed in evacuated melting point capillaries. Peak positions are accurate to ± 3 cm^{-1}.

NMR spectra were obtained on a JEOL-FX90Q spectrometer. ^{19}F, ^{31}P, and ^{183}W NMR spectra were recorded at 84.26, 36.20, and 3.73 MHz, respectively. Benzene-d_6 was used as a lock solvent for ^{19}F and ^{31}P NMR. ^{183}W NMR spectra were run on external lock. Chemical shifts (δ) are reported in ppm relative to external $CFCl_3$, 85% H_3PO_4 and 2 M Na_2WO_4 in D_2O, all of which are assignedd a δ value of 0.0. Negative chemical shifts are assigned to lines at lower frequency (higher field) than the reference.

Mass spectra were obtained on a Finnegan mass spectrometer by the method of direct insertion. Probe temperatures of 100–200 °C and ionizing voltages of 40–70 eV were employed. Isotope patterns were calculated by using a program written by Steve Werness of the University of Michigan, Chemistry Department.

General Procedures. Due to the highly reactive nature of tungsten halides and $W_2(TFA)_4$ and its derivatives, all preparations and operations were carried out under dry and oxygen-free conditions with use of Schlenk or drybox techniques. The drybox is a Vacuum Atmospheres HE 43-2 model equipped with a high-capacity purifier (MO-40V) and a Dry-Cold freezer operating at −40 °C.

$W_2(TFA)_4$. Method A. Inside the drybox $W_2Cl_6(THF)_4$ (2.0 g, 2.3 mmol) was added to 75 mL of THF in a 200-mL Schlenk flask. Sodium amalgam (21.5 g of 0.5% amalgam, 4.7 mmol of Na) was added and the flask removed from the drybox with minimal agitation of the contents. The flask was connected to a Schlenk line and placed in a −20 °C bath (ethanol/dry ice). The reactants were stirred *vigorously* for 1 h at −20 °C, and the solution color changed from yellow-green to deep blue. As rapidly as possible, the deep blue solution was poured (under a countercurrent of argon) into a second Schlenk flask containing powdered sodium trifluoroacetate (1.4 g, 10.3 mmol) precooled to −20 °C. The blue solution quickly changed to yellow-brown and was allowed to warm to room temperature over a 2-h period. The flask containing the product was returned to the drybox and the solution filtered through Celite to remove NaCl and any mercury that might have been transferred. The THF was stripped from the yellow-brown filtrate, providing a similarly colored solid. (If the residue is tacky, hexane (ca. 20 mL) is added and the solvent stripped again.) The latter was scraped from the walls of the filter flask and placed in a conventional sublimator. Glass wool was placed atop the crude product to prevent contamination of the sublimate. The sublimator was attached to a source of high vacuum (at least 10^{-4} torr[35]) and the residue thoroughly dried for 1 h at 50 °C. The temperature was slowly raised to 130 °C and held at this value until all of the yellow sublimate was collected (8–10 h). Inside the drybox, the yellow microcrystalline $W_2(TFA)_4$ was scraped off the walls of the sublimator and weighed; yield ca. 1.0 g, 53%. An analytical sample was obtained by recrystallization from hot hexane. Anal. Calcd for $W_2(O_2CCF_3)_4$: C, 11.72; F, 27.81; mol wt, 820. Found: C, 11.56; F, 27.53; mol wt, 805. ^{19}F NMR (ppm, C_6D_6, 84.26 MHz): −70.1 (s). ^{183}W NMR (ppm, THF, 3.733 MHz): 6760 (s). IR (Nujol mull, KBr plates, cm^{-1}): 1559, 1542 ($\nu(CO_2)_{asym}$).

Method B. WCl_4 (20 g, 61.4 mmol) and NaO_2CCF_3 (34 g, 250 mmol) were added to 500 mL of cold (0 °C) THF in a 1-L Morton flask. Sodium amalgam (565 g of 0.5% amalgam, 123 mmol of Na) was added, and the mixture was stirred *vigorously* with an overhead mechanical stirrer for 2 h. The solution first turns green ($W_2Cl_6(THF)_4$) and finally yellow-brown. The reaction mixture was worked up as in method A; yield 13 g, 52%.

$W_2(TFA)_4 \cdot {}^2/_3$digly. $W_2(TFA)_4$ (1.0 g, 1.2 mmol) was dissolved in benzene (20 mL), and diglyme (0.32 g, 2.4 mmol) was added with stirring. No obvious color change was observed. The solvent was stripped, and the yellow residue was washed with a small amount of hexane. The solid was loaded into a glass tube that was subsequently evacuated (10^{-4} torr, 1 h) and sealed off. The glass tube was placed in a conventional tube furnace with the solid resting in the center and the clean end projecting out of the furnace. The temperature in the center of the furnace was adjusted to 70 °C, and the tube was left undisturbed for 1 week. Approximately 15–20 well-formed yellow crystals were observed near the end of the tube. These were sealed off from the remaining solid and sent to the Molecular Structure Center, Indiana University, for X-ray analysis (vide infra).

$W_2(TFA)_4 \cdot 2PPh_3$. $W_2(TFA)_4$ (1.0 g, 1.2 mmol) was dissolved in 15 mL of hot (ca. 80 °C) toluene. Triphenylphosphine (0.639 g, 2.4 mmol) was dissolved in a minimal amount of toluene and added, in one portion, to the yellow tungsten solution, which rapidly turned yellow-orange. As the solution cooled, a yellow-orange solid precipitated. The suspension was placed in the freezer (2 h, −40 °C) to complete the precipitation. The solid was collected by filtration, washed (3 × 2 mL) with hexane, and dried in vacuo; yield 1.5 g, 90%. Anal. Calcd for $W_2(TFA)_4 \cdot 2PPh_3$ ($W_2C_{44}H_{30}F_{12}O_8P_2$): C, 39.31; H, 2.25; F, 16.96. Found: C, 39.49, H, 2.34; F, 16.71. ^{31}P NMR (ppm, C_6D_6, 36.20 MHz, ^1H decoupled): +5.26 (s). ^{19}F NMR (ppm, C_6D_6, 84.26 MHz): −70.0 (s). IR (Nujol mull, KBr plates, cm^{-1}): 1552 ($\nu(CO_2)_{asym}$).

X-ray quality crystals (yellow-orange blocks) of $W_2(TFA)_4 \cdot 2PPh_3$ were obtained by slow cooling of hot, concentrated hexane solutions.

X-ray Structure Determinations. General procedures were as described previously.[36]

$W_2(TFA)_4 \cdot {}^2/_3$digly. One of the sublimed yellow plates was mounted on a glass fiber with silicon grease inside a nitrogen-filled drybag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer. Diffraction data were collected at −162 ± 4 °C, and the structure was solved by a combination of direct methods and Patterson techniques. An absorption correction was applied (see Table I) and the structure refined by full-matrix least-squares refinement techniques. All atoms, with the exception of diglyme hydrogens, were located and their positional and thermal parameters (anisotropic for W, C, O, and F) refined. The final thermal parameters for atoms in the CF_3 groups are in several cases unreasonably large, particularly the fluorines (F(28)–F(30)) attached to C(27). We thought that this might be due to inaccuracies in the absorption correction, but attempts to recalculate the latter, using slightly different crystal dimensions, led to larger uncertainties and residuals. Careful examination of the Fourier and difference-Fourier maps indicated that disorder might be present, but attempts to resolve the disorder were unsuccessful. Our conclusion is that the CF_3 group in question is undergoing large vibratory motion which may or may not be disorder. Similar problems with refinement of CF_3 groups have been encountered by other workers.[15,20,29]

$W_2(TFA)_4 \cdot 2PPh_3$. Inside a nitrogen-filled drybag, a suitable fragment was cleaved from a large crystal of the adduct and mounted

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(34) McCarley, R. E., private communication.

(35) The importance of a good vacuum cannot be overemphasized. Both the yield and the quality of the sublimate suffer drastically if the vacuum falls below 10^{-4} torr.

(36) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

on a glass fiber with silicon grease. The sample was handled as above, and diffraction data were collected at −163 ± 4 °C. The structure was solved by direct methods, difference-Fourier, and full-matrix least-squares refinement techniques. No absorption correction ($\mu = 54.29$ cm^{-1}) was attempted. All atoms, with the exception of phenyl protons, were located and their positional and thermal parameters (anisotropic for W, C, O, and F) refined. Hydrogen atoms were included as fixed-atom contributors in the final stages of refinement. Two independent molecules were located, each with a crystallographic center of symmetry. A final difference Fourier was featureless, the largest peak being 1.2 e Å^{-3} located near W(1A). The final thermal parameters for atoms in the CF$_3$ groups were quite reasonable.

Acknowledgment. The authors are grateful to the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE 82-06169) for support of our work on metal–metal-bonded complexes. We wish to thank Steve Werness (mass spectra and computer simulations) and Melvin Luetkens (tungsten-183 NMR) for their expert technical assistance and the Marshall H. Wrubel Computing Center, Indiana University, for a generous gift of computer time. A.P.S wishes also to thank Professors R. A. Andersen (Cal-Berkeley) and F. A. Cotton (Texas A&M) for helpful discussions and preprints of their work on tungsten dimer chemistry.

Registry No. $W_2(TFA)_4$, 77479-85-7; $W_2(TFA)_4 \cdot {}^2/_3$(diglyme), 77479-87-9; $W_2(TFA)_4 \cdot 2PPh_3$, 77494-64-5; $W_2Cl_6(THF)_4$, 77479-88-0; W, 7440-33-7.

Supplementary Material Available: Tables of selected distances and angles, anisotropic thermal parameters, and observed and calculated structure factors for $W_2(TFA)_4 \cdot {}^2/_3$digly (Tables III, VII, and VIII) and $W_2(TFA)_4 \cdot 2PPh_3$ (Tables V, IX, and X) and derived hydrogen positional parameters for the latter complex (Table IV supplemental) (73 pages). Ordering information is given on any current masthead page. The complete structural reports (diglyme adduct, MSC-8046; PPh$_3$ adduct, MSC 82906) are available in microfiche form only from the Chemistry Library, Indiana University.

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Mononuclear Three-Coordinate Copper(I) Complexes: Synthesis, Structure, and Reaction with Carbon Monoxide[1]

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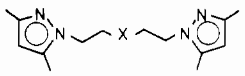
The new ligands bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (pza), bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether (pze), and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] sulfide (pzs) form three-coordinate, T-shaped Cu(I) derivatives in the solid state, typified by the structure determined for Cu(pze)BF$_4$. Reaction of the copper complexes with carbon monoxide in nitromethane solution results in the formation of carbonyl adducts with ν(CO) = 2082, 2106, and 2123 cm^{-1}, respectively. Measured binding constants of CO for all three compounds reveal that Cu(pze)BF$_4$ reacts much more weakly with carbon monoxide than do the others, suggesting stabilization of the decarbonylated form because of the ligand. Crystal data for Cu(pze)BF$_4$: monoclinic, $a = 11.286$ (4) Å, $b = 13.456$ (5) Å, $c = 12.051$ (4) Å, $\beta = 99.269$ (25)°, $V = 1806.2$ (1.9) Å^3, space group $P2_1/n$, $Z = 4$.

Investigation of the reaction chemistry of coordinatively unsaturated copper(I) complexes is prerequisite to understanding the reaction mechanisms by which dioxygen-activating copper proteins function. Two- or three-coordination for the cuprous form of those enzymes[2] would appear to be compulsory for interaction of the dioxygen molecule with the metal ion prior to oxidation of substrate.

The paucity of well-characterized Cu(I) complexes[3] has deterred a detailed study of their chemistry. One reason for that is the spectroscopic "invisibility" of the d^{10} cuprous ion, which hinders structural characterization of the complex in solution. One way to circumvent this problem is to allow the copper center to interact with a spectroscopically observable ligand and to observe the effects of the complex on the spectral properties of that ligand. In our studies of Cu(I) complexes, we have chosen initially to use carbon monoxide as the spectral probe and the reasons for this are threefold: (1) carbonyl complexes of metal ions, including copper,[4] are reasonably well understood, and unusual bonding modes are unlikely; (2) spectroscopic analysis of the carbonyl adducts is straightforward and confined to a normally blank portion of the infrared region; (3) carbonyl derivatives have been characterized for several copper proteins including hemocyanin[5,6] and cytochrome oxidase,[7] and understanding the interaction of CO with simple complexes might give us clues to the structures of those systems.

This paper reports the synthesis of a new series of ligands, **1–3**, having two pyrazolyl groups in addition to a third, neutral, donor, as well as the preparation and characterization of their cuprous derivatives. These results thus add to our understanding of Cu(I) chemistry by expanding the range of stable, characterized cuprous complexes and by demonstrating one facet of their reactivity, namely their reaction with carbon monoxide.



1, X = NH (pza)
2, X = O (pze)
3, X = S (pzs)

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(1) Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; see Abstract INOR 182.

(2) Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; Chapter 2.

(3) We limit this statement to those Cu(I) complexes that are well-defined, mono- or binuclear molecular entities, ligated by "innocent" N, O, or S ligands. See: Osterberg, R. *Coord. Chem. Rev.* **1974**, *12*, 309–347.

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