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The Tungsten–Tungsten Triple Bond. 19.[1] Preparation and Characterization of W_2^{6+}-Containing Compounds Supported by Amide/Alkoxide and Trifluoromethanesulfonate Ligands

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The compound $W_2(NMe_2)_4(OTf)_2$ (I), where OTf is the trifluoromethanesulfonate anion, $O_3SCF_3^-$, has been prepared from the reaction between $W_2(NMe_2)_6$ and Me_3SiOTf (2 equiv) in hexane at room temperature (22 °C). Compound I is also formed in the reaction between $W_2Cl_2(NMe_2)_4$ and AgOTf (2 equiv) in THF but in lower yield. Crystal data for I at −153 °C: $a = 7.650$ (2) Å, $b = 18.012$ (5) Å, $c = 8.849$ (2) Å, $\beta = 109.33$ (1)°, $Z = 2$, $d_{calcd} = 2.43$ g cm^{-3}, and space group $P2_1/n$. Compound I contains an *anti*-$W_2O_2N_4$ core with W–W = 2.292 (2) Å, W–O = 2.07 (1) Å, W–N = 1.92 (1) Å (average), W–W–O = 102.0 (4)°, and W–W–N = 101.2 (5)° (average). Compound I and PMe_3 (2–4 equiv) react in toluene to give $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ (II) and $W_2(NMe_2)_6$ by ligand redistribution reactions. Crystal data for II at −172 °C: $a = 14.097$ (3) Å, $b = 14.651$ (3) Å, $c = 11.752$ (2) Å, $\alpha = 107.48$ (1)°, $\beta = 93.61$ (1)°, $\gamma = 91.27$ (1)°, $Z = 2$, $d_{calcd} = 1.98$ g cm^{-3}, and space group $P\bar{1}$. The molecular structure of II contains roughly square planar WON_2P and WO_2NP units united by a W≡W bond of length 2.324 (1) Å. The $W_2O_3N_3P_2$ unit is staggered. The W–O distance, 2.205 (9) Å, is longer when supported by two attendant NMe_2 ligands, W–N = 2.00 (1) Å (average). Conversely, the shorter W–O distances, 2.13 (1) Å (average), associated with the $W(NMe_2)(OTf)_2(PMe_3)$ moiety are supported by a shorter W–N bond, 1.92 (1) Å. Attempts to prepare $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2$ from the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and Me_3SiOTf (2 equiv) at room temperature yield a green crystalline compound that we formulate as $[W(O\text{-}t\text{-}Bu)_2(OTf)]_n$, where n = even. The latter compound is thermally unstable at room temperature and decomposes slowly in solution at −25 °C. Addition of PMe_3 (2–4 equiv) to the compound $[W(O\text{-}t\text{-}Bu)_2(OTf)]_n$ yields $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ (III) in high yields. Compound III is soluble in THF, very sparingly soluble in toluene, and insoluble in hexane. Compound III crystallizes with molecules of THF in the lattice. The molecular structure contains two roughly square planar WO_3P units, W–O(OTf) and 2.19 (2) and 2.21 (1) Å, W–O(O-*t*-Bu) = 1.88 (2) Å (average), W–P = 2.46 (1) Å (average), and W–W = 2.421 (1) Å. Crystal data for III at −176 °C: $a = 15.226$ (2) Å, $b = 21.562$ (2) Å, $c = 15.689$ (2) Å, $Z = 4$, $d_{calcd} = 1.70$ g cm^{-3}, and space group $P2_12_12_1$.

Introduction

There is now an extensive chemistry of dinuclear M_2^{6+}-containing compounds where M = Mo and W.[2] The vast majority of these compounds are neutral and are supported by covalent bonds, e.g. $M_2(NMe_2)_6$ and $M_2(OR)_4(R')_2$. There are also some anionic compounds, mostly involving halide ligands, e.g. the well-known cofacial bioctahedral $M_2X_9^{3-}$ anions, where X = Cl and Br,[3] and $W_2Cl_7(THF)_2^-$.[4] Notably absent, however, are cationic complexes. No compound such as $M_2X_5L^+$, for example, is known where X = amide, alkoxide, etc. and L = a neutral donor ligand. Since the metal atoms in M_2X_6 compounds are weak Lewis acids and π-bases to π-acceptor ligands, we were interested to see what enhanced Lewis acidity might yield in terms of reactivity. This paper describes our initial attempts to prepare cationic amido and alkoxide W_2^{6+} containing complexes along with the synthesis and characterization of a number of trifluoromethanesulfonate derivatives.

Results

Attempts to prepare cationic complexes failed but trifluorosulfonate derivates were prepared as described in the following section. The structural characterizations of $W_2(NMe_2)_4(OTf)_2$, $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$, and $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ were completed successfully. The crystallographic and structural parameters are reported in Table I–IV, and diagrams of the molecular structures are shown in Figures 1–4. Comparisons with other structures and descriptions of solution behavior are also described in the following section.

Discussion

Syntheses. Reactions between $W_2Cl_2(NMe_2)_4$ and $Ag^+PF_6^-$ (1–2 equiv) in THF (THF = tetrahydrofuran) do yield AgCl, but the formation of a rubbery, highly elastic solid, presumed to be poly-THF, is rapid. Possibly the polymerization is caused by the generation of Lewis acidic cationic tungsten centers, but this has not been proven. Attention was turned to developing a system wherein a labile and good leaving group was introduced to the ditungsten center. In this regard we chose the trifluoromethanesulfonate anion, OTf^-, which is known to coordinate relatively weakly in either the η^1 or η^2 mode and is an excellent leaving group.[5]

$W_2(NMe_2)_6$ dissolved in toluene was found to react with Me_3SiOTf according to eq 1. $W_2(NMe_2)_4(OTf)_2$ (I) is insoluble in

$$W_2(NMe_2)_6 + 2Me_3SiOTf \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2(NMe_2)_4(OTf)_2 + 2Me_3SiNMe_2 \quad (1)$$

hexane but soluble in benzene and toluene and may be readily crystallized from the latter as yellow crystals. If reaction 1 is carried out in hexane, yellow microcrystalline I precipitates as it is formed giving isolated yields of ca. 75–95%. An alternative

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Table I. Summary of Crystal Data

	I[a]	II[b]	III[c]
empirical formula	$C_{10}H_{24}F_6N_4$-$O_6S_2W_2$	$C_{36}H_{60}F_9N_3$-$O_9P_2S_3W_2$	$C_{36}H_{72}F_6$-$O_{13}P_2S_2W_2$
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
temp (°C)	−153	−172	−176
a (Å)	7.650 (2)	14.097 (3)	15.226 (2)
b (Å)	18.012 (5)	14.651 (3)	21.562 (2)
c (Å)	8.849 (2)	11.752 (2)	15.689 (2)
α (deg)		107.48 (1)	
β (deg)	109.33 (1)	93.61 (7)	
γ (deg)		91.27 (1)	
Z (molecules/cell)	2	2	4
V ($Å^3$)	1150.51	2308.42	5150.59
calcd density (g/cm^3)	2.431	1.983	1.703
λ (Å)	0.710 69	0.710 69	0.710 69
MW	842.13	1375.70	1320.71
μ (cm^{-1})	104.602	53.840	47.707
2θ range (deg)	6–45	6–45	6–45
R (F_o or F_o^2)[d]	0.0514	0.0577	0.0601
R_w (F_o or F_o^2)[e]	0.0484	0.0573	0.0634

[a] I = $W_2(NMe_2)_4(OTf)_2$. [b] II = $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$. [c] III = $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$. [d] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [e] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Selected Bond Distances (Å) and Angles (deg) for the $W_2(NMe_2)_4(OTf)_2$ Molecule

	Distances		
W(1)–W(1)′	2.2915 (16)	S(3)–O(2)	1.490 (14)
W(1)–O(2)	2.066 (12)	S(3)–O(4)	1.412 (13)
W(1)–N(10)	1.910 (16)	S(3)–O(5)	1.421 (14)
W(1)–N(13)	1.929 (15)	S(3)–C(6)	1.796 (20)
	Angles		
W(1)′–W(1)–O(2)	102.0 (4)	O(4)–S(3)–C(6)	105.1 (8)
W(1)′–W(1)–N(10)	101.7 (5)	O(5)–S(3)–C(6)	106.5 (9)
W(1)′–W(1)–N(13)	100.6 (5)	W(1)–O(2)–S(3)	124.3 (8)
O(2)–W(1)–N(10)	116.3 (6)	W(1)–N(10)–C(11)	116.2 (12)
O(2)–W(1)–N(13)	119.1 (5)	W(1)–N(10)–C(12)	133.0 (12)
N(10)–W(1)–N(13)	113.0 (6)	C(11)–N(10)–C(12)	109.6 (14)
O(2)–S(3)–O(4)	111.7 (8)	W(1)–N(13)–C(14)	135.2 (13)
O(2)–S(3)–O(5)	111.6 (7)	W(1)–N(13)–C(15)	114.8 (12)
O(2)–S(3)–C(6)	101.4 (8)	C(14)–N(13)–C(15)	109.9 (15)
O(4)–S(3)–O(5)	118.7 (9)		

preparation of I involves the reaction between $W_2Cl_2(NMe_2)_4$ and AgOTf (2 equiv) in THF. However, this reaction proceeds with extensive decomposition, possibly because Ag^+ is acting as an oxidant.

The preparation of $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2$ was attempted according to the reaction shown in eq 2. The color of a solution

$$W_2(O\text{-}t\text{-}Bu)_6 + 2Me_3SiOTf \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2(O\text{-}t\text{-}Bu)_4(OTf)_2 + 2Me_3SiO\text{-}t\text{-}Bu \quad (2)$$

of $W_2(O\text{-}t\text{-}Bu)_6$ changes from red to brown-green, and when the volume of the mother liquor is reduced and the solution is cooled to −25 °C, green needles are formed. This compound is thermally unstable at room temperature both in the solid state and in solution. We formulate this compound as $[W(O\text{-}t\text{-}Bu)_2(OTf)]_n$, where n = 2 or 4, on the basis of its reactivity with PMe_3 described later. The multiple peaks in the ^1H spectrum for the O-*t*-Bu ligands could be a result of any of the following: (a) a mixture of *anti*- and *gauche*-ethane-like rotamers that are slowly interconverting on the NMR time scale; (b) the presence of $W_2(O\text{-}t\text{-}Bu)_4(\eta^2\text{-}O_2S(O)CF_3)_2$ isomers; (c) the existence of bridged tetranuclear compounds analogous to $Mo_4F_4(O\text{-}t\text{-}Bu)_6$[6] or $Mo_4F_2(O\text{-}i\text{-}Pr)_{10}$,[7] which have bisphenoidal and rectangular M_4 units, respectively.

Table III. Selected Bond Distances (Å) and Angles (deg) for the $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ Molecule

	Distances		
W(1)–W(2)	2.3235 (14)	S(3)–O(21)	1.407 (11)
W(1)–P(6)	2.478 (4)	S(3)–C(41)	1.827 (16)
W(1)–O(17)	2.205 (9)	S(4)–O(18)	1.493 (10)
W(1)–N(26)	2.010 (11)	S(4)–O(22)	1.425 (12)
W(1)–N(27)	1.997 (12)	S(4)–O(23)	1.413 (10)
W(2)–P(7)	2.508 (4)	S(4)–C(42)	1.803 (16)
W(2)–O(18)	2.121 (9)	S(5)–O(19)	1.487 (10)
W(2)–O(19)	2.138 (10)	S(5)–O(24)	1.415 (12)
W(2)–N(28)	1.923 (13)	S(5)–O(25)	1.411 (12)
S(3)–O(17)	1.473 (10)	S(5)–C(43)	1.818 (18)
S(3)–O(20)	1.418 (11)		
	Angles		
W(2)–W(1)–P(6)	93.78 (10)	O(21)–S(3)–C(41)	105.6 (8)
W(2)–W(1)–O(17)	107.95 (26)	O(18)–S(4)–O(22)	111.9 (6)
W(2)–W(1)–N(26)	109.2 (3)	O(18)–S(4)–O(23)	112.9 (6)
W(2)–W(1)–N(27)	105.0 (3)	O(18)–S(4)–C(42)	99.3 (7)
P(6)–W(1)–O(17)	158.06 (27)	O(22)–S(4)–O(23)	119.3 (7)
P(6)–W(1)–N(26)	85.9 (3)	O(22)–S(4)–C(42)	104.2 (7)
P(6)–W(1)–N(27)	85.4 (4)	O(23)–S(4)–C(42)	106.5 (7)
O(17)–W(1)–N(26)	89.7 (4)	O(19)–S(5)–O(24)	113.2 (7)
O(17)–W(1)–N(27)	86.0 (4)	O(19)–S(5)–O(25)	111.3 (7)
N(26)–W(1)–N(27)	145.2 (5)	O(19)–S(5)–C(43)	99.4 (7)
W(1)–W(2)–P(7)	94.98 (9)	O(24)–S(5)–O(25)	120.2 (7)
W(1)–W(2)–O(18)	104.24 (27)	O(24)–S(5)–C(43)	105.1 (7)
W(1)–W(2)–O(19)	105.81 (27)	O(25)–S(5)–C(43)	104.8 (8)
W(1)–W(2)–N(28)	101.6 (4)	W(1)–O(17)–S(3)	146.7 (7)
P(7)–W(2)–O(18)	159.6 (3)	W(2)–O(18)–S(4)	138.5 (6)
P(7)–W(2)–O(19)	83.8 (3)	W(2)–O(19)–S(5)	139.6 (6)
P(7)–W(2)–N(28)	85.1 (4)	W(1)–N(26)–C(35)	114.4 (9)
O(18)–W(2)–O(19)	84.4 (4)	W(1)–N(26)–C(36)	134.0 (9)
O(18)–W(2)–N(28)	97.5 (4)	C(35)–N(26)–C(36)	110.5 (11)
O(19)–W(2)–N(28)	151.2 (5)	W(1)–N(27)–C(37)	134.3 (10)
O(17)–S(3)–O(20)	113.4 (6)	W(1)–N(27)–C(38)	113.8 (9)
O(17)–S(3)–O(21)	114.1 (6)	C(37)–N(27)–C(38)	111.8 (12)
O(17)–S(3)–C(41)	99.3 (7)	W(2)–N(28)–C(39)	139.3 (10)
O(20)–S(3)–O(21)	117.5 (7)	W(2)–N(28)–C(40)	108.8 (9)
O(20)–S(3)–C(41)	104.2 (7)	C(39)–N(28)–C(40)	111.9 (12)

Table IV. Selected Bond Distances (Å) and Angles (deg) for the $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ Molecule

	Distances		
W(1)–W(2)	2.4208 (10)	S(3)–O(15)	1.498 (15)
W(1)–P(5)	2.462 (5)	S(3)–O(16)	1.409 (18)
W(1)–O(13)	1.836 (17)	S(3)–O(17)	1.403 (17)
W(1)–O(14)	1.855 (13)	S(3)–C(45)	1.861 (12)
W(1)–O(15)	2.185 (14)	S(4)–O(20)	1.444 (12)
W(2)–P(6)	2.458 (5)	S(4)–O(21)	1.430 (15)
W(2)–O(18)	1.908 (13)	S(4)–O(22)	1.457 (17)
W(2)–O(19)	1.905 (15)	S(4)–C(46)	1.858 (22)
W(2)–O(20)	2.209 (11)		
	Angles		
W(2)–W(1)–P(5)	93.19 (13)	O(19)–W(2)–O(20)	87.6 (7)
W(2)–W(1)–O(13)	108.4 (4)	O(15)–S(3)–O(16)	114.2 (10)
W(2)–W(1)–O(14)	100.4 (4)	O(15)–S(3)–O(17)	113.0 (11)
W(2)–W(1)–O(15)	106.9 (4)	O(15)–S(3)–C(45)	100.9 (9)
P(5)–W(1)–O(13)	91.4 (5)	O(16)–S(3)–O(17)	120.2 (11)
P(5)–W(1)–O(14)	88.8 (5)	O(16)–S(3)–C(45)	103.1 (10)
P(5)–W(1)–O(15)	159.6 (4)	O(17)–S(3)–C(45)	101.9 (10)
O(13)–W(1)–O(14)	151.2 (6)	O(20)–S(4)–O(21)	113.4 (9)
O(13)–W(1)–O(15)	85.2 (6)	O(20)–S(4)–O(22)	114.1 (10)
O(14)–W(1)–O(15)	84.8 (7)	O(20)–S(4)–C(46)	102.5 (9)
W(1)–W(2)–P(6)	93.32 (11)	O(21)–S(4)–O(22)	119.2 (9)
W(1)–W(2)–O(18)	109.4 (4)	O(21)–S(4)–C(46)	101.7 (10)
W(1)–W(2)–O(19)	100.9 (5)	O(22)–S(4)–C(46)	102.8 (10)
W(1)–W(2)–O(20)	105.9 (3)	W(1)–O(13)–C(29)	136.5 (12)
P(6)–W(2)–O(18)	89.8 (5)	W(1)–O(14)–C(33)	146.3 (13)
P(6)–W(2)–O(19)	88.0 (6)	W(1)–O(15)–S(3)	153.5 (9)
P(6)–W(2)–O(20)	160.8 (3)	W(2)–O(18)–C(37)	138.6 (12)
O(18)–W(2)–O(19)	149.6 (5)	W(2)–O(19)–C(41)	147.4 (14)
O(18)–W(2)–O(20)	84.6 (6)	W(2)–O(20)–S(4)	156.2 (8)

Compound I reacts readily with PMe_3 in toluene, and orange crystals of $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ (II) are obtained upon reducing the volume of the solution and cooling to ca. −25 °C.

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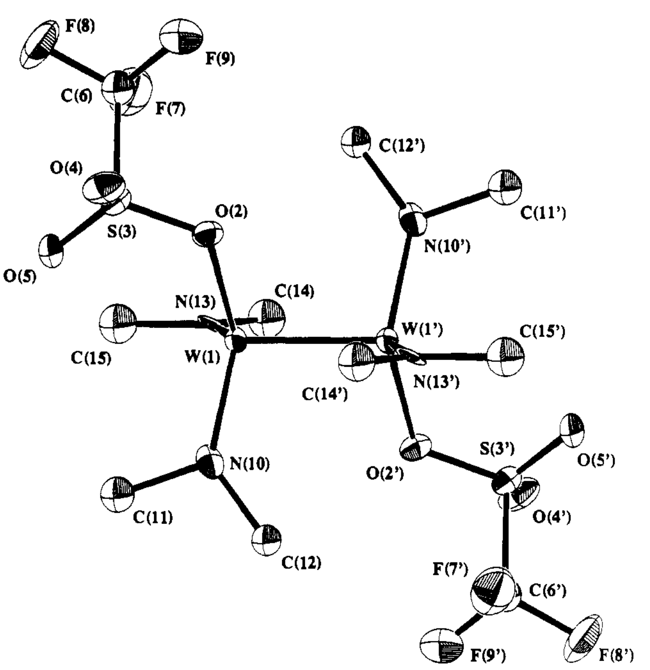

Figure 1. ORTEP drawing of the $W_2(NMe_2)_4(OTf)_2$ molecule viewed perpendicular to the M–M bond, giving the atom number scheme used in the tables. Atoms are drawn at the 50% probability level.

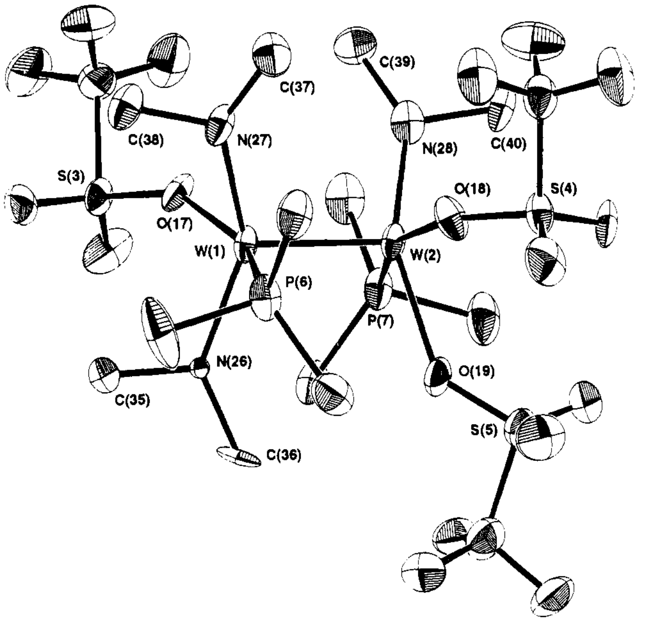

Figure 2. ORTEP drawing of the $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ molecule, showing the atom number scheme used in the tables. Atoms are drawn at the 50% probability level.

Consistent with a ligand redistribution in the formation of II, the supernatant contains $W_2(NMe_2)_6$. This type of reaction was seen previously in the preparation of $W_2Cl_3(NMe_2)_3(PMe_3)_2$[8] from $W_2Cl_2(NMe_2)_4$ and PMe_3. Similar to that shown in earlier studies, this ligand redistribution reaction is proposed to proceed via an amine-catalyzed mechanism.[8]

Addition of PMe_3 (2–4 equiv) to a toluene solution of $[W(O\text{-}t\text{-}Bu)_2(OTf)]_n$ at 22 °C yields a red solution from which red microcrystals are formed: $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ (III). Compound III is insoluble in hexane, sparingly soluble in toluene, but soluble in THF. Crystals suitable for an X-ray study were grown slowly from a THF solution.

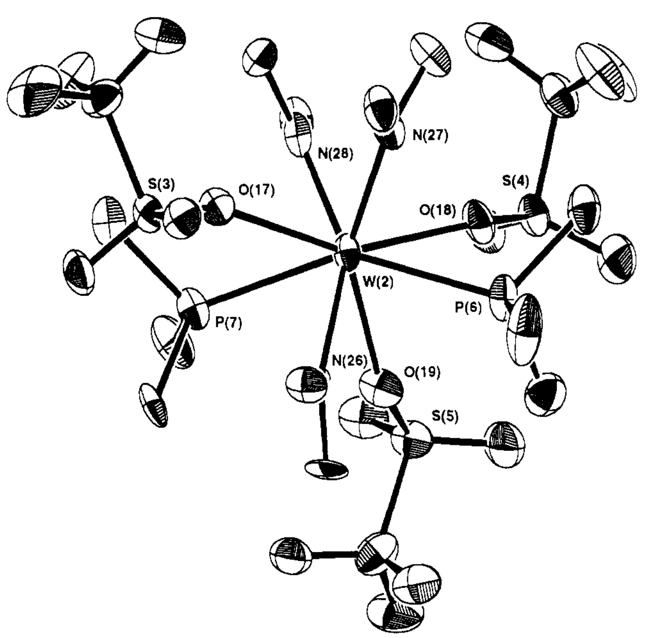

Figure 3. ORTEP drawing of the $W_2(NMe_2)_3(OTf)_3P(Me_3)_2$ molecule, viewed down the W–W bond.

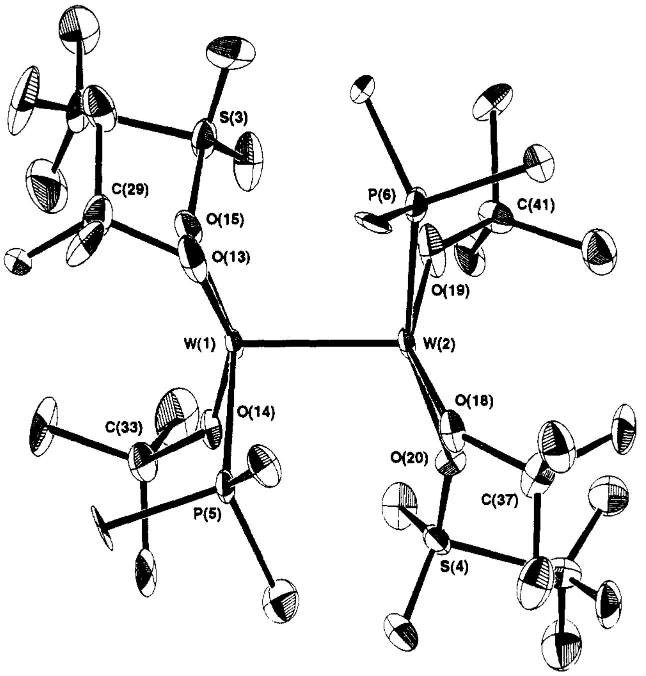

Figure 4. ORTEP drawing of the $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ molecule, showing the atom number scheme used in the tables. Atoms are drawn at the 50% probability level.

Molecular and Solid-State Structures. A summary of crystal data is given in Table I.

$W_2(NMe_2)_4(OTf)_2$ (I). In the space group $P2_1/n$, there is one unique centrosymmetric molecule. A view of the molecule showing the atom number scheme is given in Figure 1. The *anti*-$W_2N_4O_2$ core is typical of many $W_2X_4Y_2$ ($M{\equiv}M$) compounds. The W–W distance of 2.292 (2) Å is unexceptional, but the W–N distances, 1.92 (1) Å (average), are notably shorter than in $W_2(NMe_2)_6$, 1.98 (1) Å (average).[9] The W–N bond shortening presumably reflects the great N-p_π-to-W-d_π bonding in I relative to $W_2(NMe_2)_6$ where three NMe_2 ligands compete for two W d_π orbitals at each metal center. The alignment of the $-NC_2$ blades along the W–W axis (as can be seen from inspection of Figure

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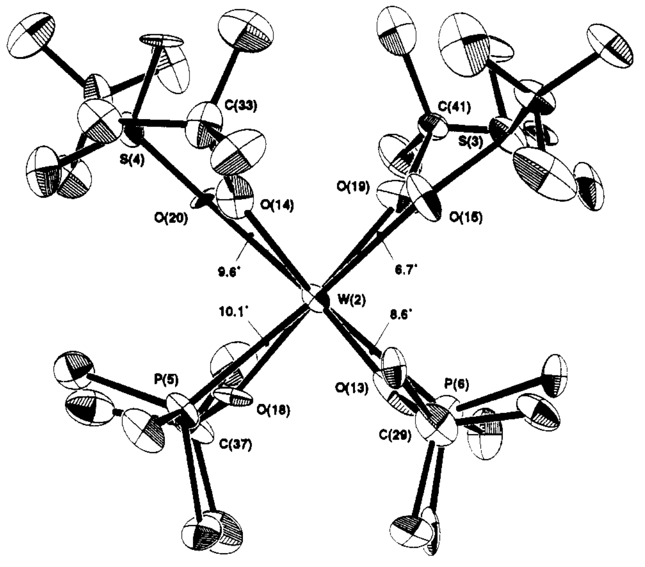

Figure 5. ORTEP drawing of the $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ molecule, viewed down the W–W bond. Torsion angles (deg) are shown.

1) allows for maximum Me_2N-p_π-to-W-d_π bonding. The OTf ligand is η^1-bound, and the W–O distance of 2.07 (1) Å is much longer than those seen for alkoxides, c.f. W–O = 1.88 (1) Å in $W_2(O\text{-}i\text{-}Pr)_6$.[10] Listings of pertinent bond distances and angles are given in Table II.

$W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ (II). Compound II crystallizes with three molecules of toluene in the space group $P\bar{1}$. A view of the molecule giving the atom number scheme is shown in Figure 2. Selected bond distances and bond angles are given in Table III.

Each tungsten is coordinated to four ligands in a roughly square planar manner. The central $W_2N_3O_3P_2$ moiety is staggered as is shown in Figure 3. One tungsten is ligated by two trans-NMe_2 groups, one OTf ligand, and one PMe_3 ligand. Here the W–N distances are long, 2.00 (1) Å (average), as the two NMe_2 ligands compete for one W-d_π orbital. The other tungsten has one NMe_2 ligand with a short W–N distance of 1.92 (1) Å, indicative of a W–N double bond. The W–O(OTf) distances span a range 2.12–2.21 Å with the longest bond being the one associated with the tungsten bound by two NMe_2 ligands. Of further interest is the fact that the W–P distance, 2.478 (4) Å, to the tungsten bound by two NMe_2 ligands is actually shorter than that W–P distance, 2.508 (4) Å, to the tungsten bearing two OTf ligands. Perhaps this is a consequence of the relative binding of PMe_3 to hard and soft W centers. Cotton, Walton, and co-workers have noted Re–P distances in $Re_2Cl_4(PMe_3)_4{}^{n+}$ complexes, where $n = 0$, 1, and 2, increase as the oxidation state of the metal increases, whereas the Re–Cl distances decrease in the same order.[11] Perhaps we see here a related phenomenon.

$W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$. In the space group $P2_12_12_1$, there is one unique molecule in the unit cell. A view of the molecule giving the atom number scheme is given in Figure 4, and a view down the M–M bond is shown in Figure 5. Selected bond distances and angles are given in Table IV.

The molecule has virtual C_2 symmetry and most remarkably a near-eclipsed $W_2O_6P_2$ skeleton. The dihedral angles range from 6.7 to 10.1° and are shown in Figure 5. The W–W distance of 2.421 (1) Å is the longest we have found for a $W_2{}^{6+}$-containing compound supported by a group of eight ligands and may be compared to W–W = 2.362 (2) Å seen in $W_2(OCH_2\text{-}t\text{-}Bu)_6(PMe_3)_2$.[12] The W–O(OTf) distances, 2.185 (14) and 2.209 (11) Å, are the longest of the three ditungsten triflate complexes reported here, and the W–O–S angles, 156.2 (8) and 153.5 (9)°, are notably larger than those in II (139–147°) and I (124°). Perhaps this is a reflection of the steric crowding and potentially an indication of lability of the OTf ligands toward dissociation. By contrast the W–O(alkoxide) distances are in the range 1.84–1.91 Å, just over 0.3 Å shorter than the W–OTf bond distances.

NMR Solution Behavior. The ^1H NMR spectrum of $W_2(NMe_2)_4(OTf)_2$ (I) in toluene-d_8 is consistent with the presence of the anti rotamer and shows restricted rotation about the W–N bonds. The activation energy for the interconversion of proximal and distal NMe_2 groups is estimated to be 14.7 (2) kcal mol^{-1} from the coalescence of the NMe_2 resonances. This is roughly 1 kcal mol^{-1} higher than that of the analogous chloro compound $W_2Cl_2(NMe_2)_4$.[13] The ^{19}F NMR spectrum reveals a single resonance for the CF_3 fluorine atoms as expected.

The ^1H NMR spectrum of $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ (II) in toluene-d_8 at 22 °C reveals frozen out proximal and distal NMe groups, and furthermore, some of the NMe_2 signals show small couplings to ^{31}P nuclei. In addition there are two distinct PMe_3 groups which appear as doublets due to ^{31}P–^1H coupling, 10.5 Hz.

In the $^{31}P\{^1H\}$ NMR there are two ^{31}P signals assignable to the two types of PMe_3 ligands. Each signal appears as a doublet due to ^{31}P–^{31}P coupling, which presumably is transmitted through the W≡W bond, $^3J_{^{31}P-^{31}P} = 13.4$ Hz. Each signal is also flanked with satellites due to coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance $^1J_{^{183}W-^{31}P} = 440$ and 379 Hz.

In the ^{19}F NMR spectrum there are three fluorine signals as expected for II, which has three different OTf ligands. Two of the signals appear as quartets, and this presumably arises from a small through-space ^{19}F–^{19}F coupling, $J = 3.1$ Hz, associated with the two OTf ligands that are bound to the same tungsten atom, W(2) in Figure 2.

The ^1H NMR spectra for $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ (III) in THF-d_8 are as expected for a molecule with C_2 symmetry: there are two O-*t*-Bu signals in the ratio 1:1 and one broad signal for the PMe_3 protons at room temperature. Upon lowering of the temperature, the broad PMe_3 signal splits into three sets of two doublets. This indicates that at low temperatures there must be restricted rotation about W–P bonds on the NMR time scale leading to two rotamers in roughly equal concentration. The O-*t*-Bu signals are broadened at low temperature but remain as two singlets in a 1:1 ratio.

The ^{31}P NMR spectrum in THF-d_8 shows a single resonance flanked by ^{183}W satellites, $J_{^{183}W-^{31}P} = 457$ Hz, and in the ^{19}F NMR spectrum there is a single resonance as expected on the basis of the solid-state structure.

Concluding Remarks. Though we have been unable to prepare cationic W≡W-containing compounds, the triflate derivatives reported here show very long W–O distances, particularly when compared to the W–O distances of alkoxides, and as such may prove to be labile ligands in reactions with various substrates. Further studies are in progress.

Experimental Section

General Procedures. Standard Schlenk procedures and Vacuum Atmospheres Co. Dri-Lab Systems were used for all syntheses and sample manipulations. All solvents were distilled under N_2 from Na/benzophenone ketyl and stored over 4-Å molecular sieves. ^1H NMR spectra were recorded in dry and deoxygenated benzene-d_6, toluene-d_8, or tetrahydrofuran-d_8 on a Varian XL300 (300 MHz) spectrometer. The data were calibrated against the residual protio impurities of the deuterated solvents. ^{31}P and ^{19}F NMR spectra were recorded on a Nicolet NT-360 spectrometer at 146.2 and 339.72 MHz, respectively, using dry and deoxygenated benzene-d_6, toluene-d_8, or tetrahydrofuran-d_8. ^{31}P spectra were calibrated against an external H_3PO_4 (85%) standard set at 0.0 ppm. ^{19}F

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spectra were calibrated against an external CF_3CO_2H (100%) standard set at −78.45 ppm. The IR spectra were obtained from Nujol mulls between CsI plates using a Nicolet 510P FT-IR spectrometer.

Elemental analyses were performed by Oneida Research Services.

Chemicals. $W_2(NMe_2)_6$,[9] $W_2Cl_2(NMe_2)_4$,[13] and $W_2(O\text{-}t\text{-}Bu)_6$[14] were prepared according to previously described procedures. Trimethylphosphine was synthesized from $P(OPh)_3$ and CH_3MgBr and purified by distillation.[15] $Me_3SiO_3SCF_3$ was purchased commercially and used without further purification.

$W_2(NMe_2)_4(OTf)_2$. Method A. To a stirring hexane (30 mL) solution of $W_2(NMe_2)_6$ (0.800 g, 1.27 mmol) was added slowly via syringe $Me_3SiO_3SCF_3$ (0.489 mL, 2.54 mmol). The mixture was left to stir for 12 h, during which time a yellow precipitate formed. The yellow precipitate was collected by filtration through a medium-porosity frit followed by a hexane wash (yield 1.01 g, 95%). Recrystallization from toluene solutions at −25 °C produced single crystals suitable for an X-ray diffraction study.

Method B. To a stirring toluene (15 mL) solution of 1,2-$W_2Cl_2(NMe_2)_4$ (0.500 g, 0.814 mmol), cooled to −40 °C in a CH_3CN/N_2 bath, was added in the dark a toluene (20 mL) solution of $Ag(O_3SCF_3)$ (0.420 g, 1.64 mmol). A precipitate formed immediately upon addition of the silver salt. The reaction mixture was stirred an additional 20 min at −40 °C and was then warmed to 22 °C. Upon exposure to light, the precipitate darkened. The reaction mixture was filtered through Celite. The volume of the orange supernatant was reduced to ca. 5 mL and stored at −25 °C. Clusters of yellow crystals were isolated by filtration and dried in vacuo (yield 0.105 g, 15%). Anal. Calcd for $C_{10}H_{24}F_6O_6N_4S_2W_2$: C, 14.26; H, 2.87; N, 6.65. Found: C, 14.41; H, 2.94; N, 6.62.

^1H NMR (22 °C, benzene-d_6): δ 4.15 (br s, 12 H, N(CH_3)), 2.20 (br s, 12 H, N(CH_3)). ^{19}F NMR (22 °C, benzene-d_6): δ −75.3 (s, 6 F, O_3SCF_3).

IR (Nujol, cm^{-1}): 1360 s, 1237 m, 1198 s, 1159 m, 1040 w, 961 m, 939 s, 766 w, 631 m, 612 w, 571 w, 540 w, 515 w.

$W_2(NMe_2)_3(OTf)_3(PMe_3)_2$. To a toluene (50 mL) solution of $W_2(NMe_2)_4(OTf)_2$ (0.300 g, 0.356 mmol) was added PMe_3 (0.147 mL, 1.42 mmol) via μL syringe. The volume was then reduced in vacuo to ≈25 mL while being warmed gently. The reaction mixture was then placed in a freezer at −25 °C. After 3 days orange crystals were collected by removing the mother liquor and washing with hexane (yield 0.308 g, 55%). Anal. Calcd for $C_{15}H_{36}F_9N_3O_9P_2S_3W_2$: C, 16.39; H, 3.30; N, 3.82. Found: C, 17.99; H, 3.38; N, 3.62. A good analysis was precluded because toluene could not be completely removed from the crystal lattice. Anal. Calcd for $W_2(NMe_2)_3(OTf)_3(PMe_3)_2\cdot{}^1/_4C_7H_8$ ($C_{16.75}H_{38}F_9N_3O_9P_2S_3W_2$): C, 17.93; H, 3.41; N, 3.74.

^1H NMR (22 °C, benzene-d_6): δ 4.45 (d, 3 H, J_{H-P} = 4.2 Hz, N(CH_3)), 4.27 (d, 3 H, J_{H-P} = 1.2 Hz, N(CH_3)), 3.75 (s, 3 H, N(CH_3)), 2.36 (d, 3 H, J_{H-P} = 2.4 Hz, N(CH$_3$)), 2.30 (d, 3 H, J_{H-P} = 0.60 Hz, N(CH_3)), 2.19 (s, 3 H, N(CH_3)), 1.25 (d, 9 H, J_{H-P} = 10.5 Hz, P(CH_3)$_3$), 1.00 (d, 9 H, J_{H-P} = 10.5 Hz, P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (22 °C, benzene-d_6): δ 7.22 (d, 1 P, $^1J_{W-P}$ = 440 Hz, $^3J_{P-P}$ = 13.4 Hz, P(CH$_3$)$_3$), 3.82 (d, 1 P, $^1J_{W-P}$ = 379 Hz, $^3J_{P-P}$ = 13.4 Hz, P(CH$_3$)$_3$). ^{19}F NMR (22 °C, benzene-d_6): δ −77.0 (q, 3 F, J_{FF} = 3.1 Hz, O_3SCF_3), −77.2 (q, 3 F, J_{FF} = 3.1 Hz, O_3SCF_3), −77.4 (s, 3 F, O_3SCF_3).

IR (Nujol, cm^{-1}): 1314 m, 1294 m, 1233 s, 1194 s, 1169 s, 1017 s, 997 s, 974 s, 959 s, 926 s, 857 w, 764 w, 723 m, 631 m, 519 m, 590 w, 569 w, 507 w.

$[W_2(O\text{-}t\text{-}Bu)_4(OTf)_2]_n$. To a stirring hexane (10 mL) solution of $W_2(O\text{-}t\text{-}Bu)_6$ (0.200 g, 0.248 mmol) was added $Me_3SiO_3SCF_3$ (0.096 mL, 0.496 mmol) via syringe. Over the course of 5 h the reaction mixture turned from orange to green-brown. The solvent was then removed in vacuo. The green-brown solid was redissolved in toluene, and the solution was placed in a freezer at −25 °C overnight. Green crystals were isolated and washed with hexane (yield 0.115 g).

^1H NMR (22 °C, benzene-d_6): δ (OC(CH_3)$_3$) 2.19, 2.11, 1.85, 1.69, 1.45, 1.35, 1.32, 1.23, 1.11, and 1.06. ^{19}F NMR (22 °C, benzene-d_6): δ (O_3SCF_3) −77.8.

IR (Nujol, cm^{-1}): 1610 w, 1300 s, 1225 s, 1160 s, 1021 s, 723 m, 631 m.

$W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$. To $W_2(O\text{-}t\text{-}Bu)_6$ (0.200 g, 0.248 mmol) dissolved in toluene (7 mL) was added $Me_3SiO_3SCF_3$ (96 μL, 0.496 mmol) via syringe. The mixture was left to stir at 22 °C for 4 h. PMe_3 (103 μL, 0.992 mmol) was then added to the green-brown reaction mixture. A maroon precipitate formed immediately as PMe_3 was added. Solvent was then removed in vacuo. THF was added to dissolve the maroon powder. The solution was filtered, and solvent was removed in vacuo (yield 0.241 g, 88%). Crystals suitable for X-ray analysis were isolated from −25 °C THF solutions. A satisfactory analysis was not obtained.

^1H NMR (22 °C, THF-d_8): δ 1.57 (s, 9 H, OC(CH_3)$_3$), 1.38 (s, 9 H, OC(CH_3)$_3$, 1.97 (br, 18 H, P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (22 °C, THF-d_8): δ 6.09 (s, $^1J_{W-P}$ = 457 Hz, P(CH$_3$)$_3$). ^{19}F NMR (22 °C, THF-d_8): δ −78.0 (s, 6 F, O_3SCF_3).

IR (Nujol, cm^{-1}): 1333 s, 1287 m, 1233 s, 1208 s, 1175 s, 1076 w, 1017 s, 959 s, 920 s, 905 s, 845 w, 781 m, 673 w, 627 m, 577 w, 521 w, 505 w, 486 w.

Crystallographic Studies. General operating procedures and listings of programs have been given previously.[16] A summary of crystal data is given in Table I.

$W_2(NMe_2)_4(OTf)_2$ (I). Because of the anticipated heavy-atom structure, a very small crystal was selected for study. The compound is extremely reactive. Even though it was handled in a nitrogen-atmosphere glovebag, the amber-colored sample became noticeably darker when removed from its original container. The crystal was coated with silicone grease as quickly as possible, and this seemed to slow down the reaction. The crystal was then mounted and transferred to a goniostat where it was cooled to −153 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed intensities with Laue symmetry and systematic absences which were consistent with space group $P2_1/n$, which was later proven correct by the successful solution of the structure. Following complete intensity data collection, data processing gave a residual of 0.055 for the averaging of 372 unique intensities which had been observed more than once. Four standards measured every 300 data showed no significant trends. An attempt to correct for absorption was unsuccessful, probably due to errors in trying to accurately measure a very small crystal.

The tungsten atom in the asymmetric unit was located using a Patterson map. The remaining non-hydrogen atoms were located in a subsequent difference Fourier map. Hydrogen atoms were included in calculated positions as fixed contributors. Hydrogen thermal parameters were fixed at 1 plus the isotropic thermal parameter of the atom to which they were bonded.

In the final cycles of least-squares refinement, the atoms heavier than carbon were varied with anisotropic thermal parameters and the carbon atoms were varied with isotropic thermal parameters to a final $R_w(F)$ = 0.051. The largest peak in the final difference Fourier was a tungsten residual of 1.68 e/Å^3.

The center of the molecule, i.e., the midpoint of the W–W bond, is at a crystallographic center of symmetry.

$W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ (II). A crystal of suitable size was mounted using silicone grease and was transferred to a goniostat where it was cooled to −172 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. An initial choice of space group $P\bar{1}$ was confirmed by the successful solution of the structure. No absorption correction was made.

The structure was solved by a usual combination of direct methods (MULTAN78) and Fourier techniques. The W atom positions were obtained from an initial E-map, and the remainder of the non-hydrogen atoms were found in subsequent iterations of least-squares refinement and difference Fourier calculations. After partial refinement of the non-hydrogen atoms, a difference Fourier revealed some of the hydrogen atoms. All but the hydrogen atoms of the disordered solvent molecules were included in the calculated positions.

The unique cell contains three molecules of toluene solvent. Two of them lie on the different centers of symmetry and, therefore, are disordered.

$W_2(O\text{-}t\text{-}Bu)_4(OTf)_2(PMe_3)_2$ (III). The properties of the sample (it was very air and water sensitive and desolvated extremely fast) made it difficult to choose a good crystal. Nevertheless, a crystal was mounted using silicone grease and transferred to a goniostat where it was cooled to −176 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed symmetry and systematic absences corresponding to the orthorhombic space group $P2_12_12_1$.

The structure was solved by a usual combination of direct methods (MULTAN78) and Fourier techniques. The W atom positions were

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obtained from an initial *E*-map, and the remainder of the non-hydrogen atoms were found in subsequent iterations of least-squares refinement and difference Fourier calculations. Hydrogen atoms were introduced in calculated positions and were not refined. In the final cycles of refinement 46 non-hydrogen atoms of the molecule were varied anisotropically and THF atoms isotropically to an $R(F) = 0.060$. Overall 476 parameters were refined using 3770 reflections.

The compound crystallizes in a chiral space group, but as the quality of data was not very good, an absorption correction was not performed. We could not choose the right enantiomorph. They were indistinguishable.

The final difference map was rather "noisy", but the highest 10 peaks (4–1.2 e/Å^3) were in the vicinity of tungsten atoms.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Listings of crystal data, anisotropic thermal parameters, and complete bond distances and angles and VERSORT stereodrawings (17 pages). Ordering information is given on any current masthead page.

Registry No. I, 143294-64-8; II, 143294-66-0; II·3C_7H_8, 143344-36-9; III, 143294-67-1; III·3THF, 143344-37-0; $W_2(NMe_2)_6$, 54935-70-5; 1,2-$W_2Cl_2(NMe_2)_4$, 63301-81-5; $W_2(O\text{-}t\text{-}Bu)_4(OTf)_2$, 143294-65-9; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; W, 7440-33-7.