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The Tungsten–Tungsten Triple Bond. 8.[1] Dinuclear Alkoxides of Tungsten(III) and Structural Characterization of Hexaisopropoxybis(pyridine)ditungsten, the First Compound with Four-Coordinated Tungsten Atoms United by a Triple Bond

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$W_2(NMe_2)_6$ reacts with *t*-BuOH and Me_3SiOH to yield the crystalline compounds $W_2(OBu\text{-}t)_6$ and $W_2(OSiMe_3)_6(HNMe_2)_2$, respectively. The tungsten compounds, unlike their molybdenum analogues, are thermally unstable and cannot be sublimed in vacuo. The thermal decomposition which occurs in vacuo appears to be autocatalytic and not stoichiometric. The reaction between $W_2(NMe_2)_6$ and the less bulky alcohols *i*-PrOH and Me_3CCH_2OH leads to polynuclear products; this is in contrast to the analogous reactions involving $Mo_2(NMe_2)_6$ which yield $(RO)_3Mo{\equiv}Mo(OR)_3$ compounds. In pyridine solution $W_2(NMe_2)_6$ reacts with *i*-PrOH to give the black crystalline compound $W_2(OPr\text{-}i)_6(py)_2$, which has been characterized by IR, NMR, and mass spectroscopy and a single-crystal X-ray diffraction study. In the crystalline state the molecular structure contains two $W(OPr\text{-}i)_3py$ units linked by a W–W triple bond with a length of 2.332 (1) Å. The rotational conformation is roughly halfway between staggered and eclipsed, and the two pyridine ligands are adjacent to each other. Low-temperature ^{13}C NMR spectra support the view that this structure is also present in solution. The crystallographic data are space group $P2_1$, $a = 10.022$ (2) Å, $b = 17.839$ (4) Å, $c = 11.946$ (2) Å, $\beta = 125.57$ (1)°, $V = 1737.1$ (6) Å^3, and $Z = 2$.

Introduction

Prior work has shown the existence of isostructural M_2X_6 compounds containing nonbridged triple bonds between the metal atoms for M = Mo and W and X = NMe_2[3,4] and CH_2SiMe_3.[5,6] The reaction between $Mo_2(NMe_2)_6$ and alcohols has been shown to lead to the structurally related compounds $(RO)_3Mo{\equiv}Mo(OR)_3$, where R = *t*-Bu, *i*-Pr, Me_3CCH_2, and Me_3Si.[7] We herein report studies of the reactions between $W_2(NMe_2)_6$ and alcohols aimed at the preparation and characterization of analogous dinuclear alkoxides of tungsten(III).[8] For a given alkoxy ligand, tungsten is shown to have a marked preference, relative to molybdenum, for increasing its coordination number either by oligomerization, $M_2(OR)_6 \rightarrow [M(OR)_3]_n$, or by coordination with neutral donor ligands as in the stabilization of the W≡W unit by coordination of pyridine in the $W_2(OPr\text{-}i)_6(py)_2$ molecule.

Results and Discussion

Syntheses. Hydrocarbon solutions of $W_2(NMe_2)_6$ react readily with *tert*-butyl alcohol and trimethylsilanol at room temperature to form the crystalline compounds $W_2(OBu\text{-}t)_6$ and $W_2(OSiMe_3)_6(HNMe_2)_2$, respectively. These compounds are extremely oxygen and moisture sensitive and very soluble in hydrocarbon solvents. The spectroscopic properties of these tungsten compounds were virtually identical with those of their molybdenum analogues. Moreover, $W_2(OBu\text{-}t)_6$ reacts reversibly with carbon dioxide to give $W_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$. Thus we believe that these tungsten compounds are isostructural with the previously characterized compounds $(RO)_3Mo{\equiv}Mo(OR)_3$,[7] $(Me_2NH)(Me_3SiO)_3Mo{\equiv}Mo(OSiMe_3)_3(HNMe_2)$,[9] and $(OBu\text{-}t)_2Mo{\equiv}Mo(\mu\text{-}O_2COBu\text{-}t)_2(OBu\text{-}t)_2$.[10] The tungsten compounds differ in only one notable way from their molybdenum analogues, namely, in their thermal stability. Neither $W_2(OBu\text{-}t)_6$ nor $W_2(OSiMe_3)_6(HNMe_2)_2$ may be purified by vacuum sublimation; both compounds appear to undergo an autocatalytic and nonstoichiometric decomposition.

$W_2(OBu\text{-}t)_6$ decomposes at ca. 100 °C (10^{-4} cmHg) with the evolution of isobutylene, *tert*-butyl alcohol, and water. The tungsten residue has a gray metallic appearance but is evidently not a pure oxide since analyses always show small, but significant, quantities of carbon and hydrogen.

$W_2(OSiMe_3)_6(HNMe_2)_2$ when heated under vacuum, >80 °C (10^{-4} cmHg), evolves $HNMe_2$ and $(Me_3Si)_2O$. Again, however, the thermolysis is not clean since the nonvolatile tungsten residue contains small quantities of carbon and hydrogen.

Though neither $W_2(OBu\text{-}t)_6$ nor $W_2(OSiMe_3)_6(HNMe_2)_2$ may be purified by sublimation, they do give $W_2(OR)_6^+$ and many other W_2-containing ions in the mass spectrometer.

Hydrocarbon solutions of $W_2(NMe_2)_6$ react rapidly at room temperature with *i*-PrOH and Me_3CCH_2OH to give black, solid products which, on the basis of elemental analyses, have the empirical formula $W(OR)_3$. These alkoxides are also thermally unstable and in vacuo yield alkenes, alcohols, and trace amounts of water. Cryoscopic molecular weight determinations in benzene suggest that both the isopropoxide and neopentoxide are tetrameric, $[W(OR)_3]_4$, in solution. A black crystalline isopropoxide, obtained from the above reaction, has been the subject of a single-crystal X-ray study and found to be a tetranuclear complex of tungsten(IV) resulting from oxidative addition of a PrO–H bond across the W-to-W triple bond. This is the subject of continuing investigations.[11] At this time we emphasize the marked difference between the chemistry of molybdenum and tungsten alkoxides since molybdenum forms thermally stable dinuclear compounds $Mo_2(OR)_6$, where R = *i*-Pr and Me_3CCH_2.

By the reaction of $W_2(NMe_2)_6$ and *i*-PrOH in pyridine as solvent, it has been possible to isolate a black crystalline dinuclear isopropoxide as a pyridine adduct, $W_2(OPr\text{-}i)_6(py)_2$. The compound is again thermally unstable and liberates pyridine, isopropyl alcohol, and propene at 80 °C (10^{-4} cmHg). In the mass spectrometer a weak molecular ion, $W_2(OPr\text{-}i)_6(py)_2^+$, is observed, followed by loss of two py ligands to give a strong $W_2(OPr\text{-}i)_6^+$ ion.

Because of the reactivity of the ditungsten alkoxy compounds, which is quite different from that of their Mo analogues, we considered it important to determine the structures and other properties of the reaction products. We describe here the results for the pyridine adduct.

Solid-State Structure of $W_2(OPr\text{-}i)_6(py)_2$. In the space group $P2_1$ with $Z = 2$, the entire molecule is the asymmetric unit, and no crystallographic symmetry is imposed on it. The positional and thermal parameters for the atoms constituting one molecule are listed in Table I. Interatomic distances and

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.0885 (1)	0.0000 (0)	0.35863 (9)	3.47 (3)	5.80 (5)	2.72 (3)	−0.41 (5)	1.85 (2)	−0.52 (5)
W(2)	−0.0855 (1)	−0.05622 (7)	0.14348 (10)	4.06 (3)	4.65 (4)	3.60 (3)	−0.52 (5)	2.46 (2)	−0.30 (5)
O(1)	−0.050 (2)	0.057 (1)	0.382 (2)	2.4 (5)	10 (1)	4.0 (6)	2.5 (7)	0.2 (4)	−3.6 (7)
O(2)	0.147 (2)	−0.081 (1)	0.495 (2)	10 (1)	3.8 (8)	2.8 (6)	1.4 (8)	3.2 (5)	1.8 (6)
O(3)	0.297 (2)	−0.020 (1)	0.396 (2)	1.4 (5)	12 (1)	4.0 (7)	2.0 (7)	0.0 (5)	−2.4 (8)
O(5)	−0.064 (2)	−0.001 (1)	0.023 (1)	6.3 (6)	5.2 (8)	4.1 (5)	−2.1 (7)	3.3 (4)	0.9 (6)
O(6)	0.043 (3)	−0.147 (1)	0.153 (2)	9 (1)	4.5 (9)	8 (1)	1.9 (9)	5.0 (7)	2.4 (8)
O(7)	−0.212 (2)	−0.125 (1)	0.183 (1)	6.9 (5)	5.6 (9)	5.9 (5)	−3.9 (6)	5.3 (3)	−2.7 (6)
N(1)	0.087 (2)	0.107 (1)	0.261 (2)	5.2 (7)	7 (1)	6.5 (8)	−0.8 (9)	4.2 (5)	1.9 (9)
N(2)	−0.284 (5)	0.029 (2)	0.092 (3)	20 (2)	6 (1)	7 (2)	7 (1)	4 (2)	3 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.173 (3)	0.106 (2)	0.209 (3)	4.8 (6)	C(51)	−0.085 (7)	−0.033 (4)	−0.114 (5)	12.9 (18)
C(2)	0.191 (4)	0.170 (2)	0.149 (3)	6.7 (8)	C(52)	0.044 (5)	−0.000 (3)	−0.110 (4)	10.3 (13)
C(3)	0.094 (4)	0.233 (2)	0.136 (3)	7.3 (9)	C(53)	−0.251 (6)	−0.002 (3)	−0.223 (5)	11.1 (15)
C(4)	−0.005 (4)	0.232 (2)	0.184 (4)	8.2 (10)	C(61)	0.193 (3)	−0.182 (2)	0.254 (3)	5.0 (7)
C(5)	−0.008 (3)	0.163 (2)	0.254 (3)	5.5 (7)	C(62)	0.161 (4)	−0.265 (2)	0.252 (3)	7.2 (9)
C(11)	−0.018 (3)	0.062 (2)	0.528 (3)	5.4 (7)	C(63)	0.303 (4)	−0.168 (2)	0.209 (3)	7.7 (10)
C(12)	−0.183 (4)	0.078 (2)	0.498 (3)	7.9 (10)	C(71)	−0.328 (5)	−0.183 (3)	0.078 (4)	10.1 (13)
C(13)	0.113 (4)	0.123 (2)	0.609 (3)	6.7 (8)	C(72)	−0.395 (5)	−0.225 (3)	0.149 (4)	9.3 (12)
C(21)	0.086 (3)	−0.156 (1)	0.499 (2)	3.7 (5)	C(73)	−0.430 (6)	−0.167 (3)	−0.058 (5)	12.1 (16)
C(22)	−0.052 (4)	−0.147 (2)	0.521 (3)	6.8 (9)	C(81)	−0.366 (5)	0.009 (2)	0.143 (4)	9.1 (11)
C(23)	0.231 (4)	−0.196 (2)	0.613 (3)	5.9 (7)	C(82)	−0.501 (4)	0.076 (2)	0.095 (4)	8.4 (10)
C(31)	0.444 (3)	0.007 (2)	0.524 (3)	5.8 (7)	C(83)	−0.525 (5)	0.125 (3)	0.013 (4)	9.4 (12)
C(32)	0.527 (4)	0.059 (3)	0.478 (4)	8.8 (11)	C(84)	−0.422 (4)	0.138 (2)	−0.035 (4)	8.4 (11)
C(33)	0.549 (9)	−0.067 (4)	0.622 (7)	18.6 (28)	C(85)	−0.299 (3)	0.083 (2)	0.006 (3)	6.2 (8)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

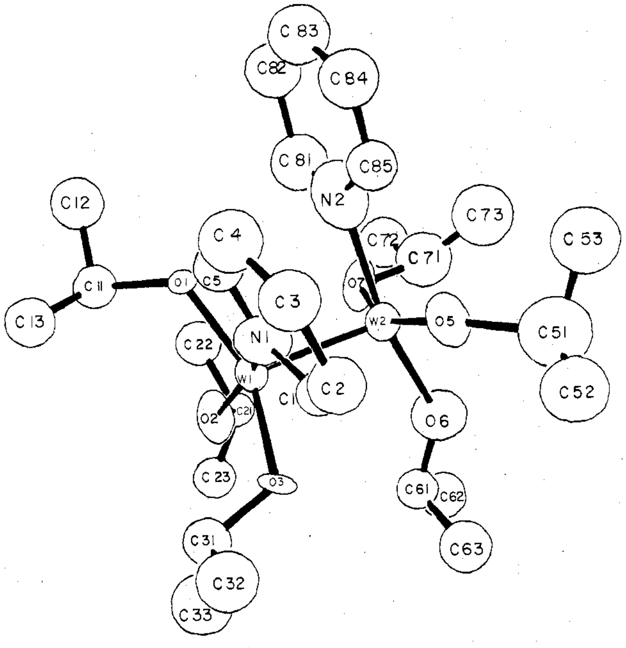

Figure 1. View of the $W_2(OCHMe_2)_6(py)_2$ molecule. Projections of thermal ellipsoids and spheres are drawn at the 50% probability level.

angles are given in Table II. An ORTEP drawing of the molecule, in which the atom numbering scheme is defined, is shown in Figure 1.

The errors on almost all the bond distances and angles not involving the tungsten atoms and the thermal parameters of several of the light atoms are rather large. There are two likely reasons for this, one being the quality of the empirical absorption correction. As this crystal was rather irregular, the correction may be accurate only to a first approximation. However, as this crystal did not have well-defined faces (nor did any other one we could see) and was embedded in epoxy resin, making measurement of its boundary faces impossible, an empirical correction is the best that could be done. Second, there is the domination of the scattering by the tungsten atoms. With just these two atoms anisotropically refined, the value of R_1 was about 0.08. The standard deviations are therefore large for light-atom positions since the differences used in the least-squares refinement are insensitive to shifts in the light-atom parameters. During refinement several of the light atoms with large temperature factors were removed and replaced with atoms in positions suggested by new electron density maps. In each case the atom parameters slowly returned to the former values. The high-temperature parameters for some atoms in the isopropoxide ligands are not without precedent. In the structure of dinitrosylhexaisopropoxydimolybdenum,[7] where absorption was quite small, isotropic thermal parameters for the carbon atoms ranged from 7.7 to 23.8 Å^3.

The molecule consists of two $W(OCHMe_2)_3py$ units linked by a W–W bond length of 2.332 (1) Å. This is slightly longer than any previously found in a X_3WWX_3-type compound where the range is from 2.255 (2) to 2.301 (2) Å with the average being about 2.29 Å.[12] The comparison is quite similar to that between the distance of 2.241 (1) Å found in both $Mo_2(OSiMe_3)_6(NHMe_2)_2$[9] and $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$[10] and the distances of 2.16–2.22 Å found in X_3MoMoX_3-type compounds.[12]

The W–O distances range from 1.86 (2) to 2.04 (3) Å. In view of the large esd's it is questionable whether there is any real pattern involved, although the average of the two W–O bond lengths trans to W–N is 2.02 ± 0.02 Å while the average of the other four is 1.91 ± 0.05 Å. The W–N bonds do seem to be longer and weaker than the W–O bonds since the grand average of all W–O bond lengths is 1.95 ± 0.07 Å while the two W–N bond lengths average 2.26 ± 0.03 Å. This is quite analogous to the situation in $Mo_2(OSiMe_3)_6(NHMe_2)_2$ where the mean Mo–O distance is 1.95 ± 0.02 Å and the mean Mo–N distance is 2.282 ± 0.004 Å.

The W–O–C angles show a clear pattern. The four isopropoxide groups that are trans to each other have angles averaging 121 ± 2° while the two that are trans to the pyridine ligands have angles of 137 ± 1°. The reason for this difference cannot be stated with certainty.

The rotational conformation is intermediate between eclipsed and fully staggered. Because of irregularities in the ar-

Table II. Interatomic Distances (Å) and Angles (deg) for $W_2(OCHMe_2)_6(py)_2$

Distances

W(1)-W(2)	2.332 (1)		
W(1)-O(1)	1.86 (2)	W(2)-O(5)	1.86 (2)
W(1)-O(2)	2.00 (2)	W(2)-O(6)	2.04 (3)
W(1)-O(3)	1.90 (2)	W(2)-O(7)	2.01 (2)
W(1)-N(1)	2.23 (3)	W(2)-N(2)	2.28 (4)
O(1)-C(11)	1.59 (4)	O(5)-C(51)	1.63 (7)
O(2)-C(21)	1.47 (3)	O(6)-C(61)	1.40 (4)
O(3)-C(31)	1.45 (4)	O(7)-C(71)	1.52 (6)
N(1)-C(1)	1.33 (4)	N(2)-C(81)	1.32 (7)
C(1)-C(2)	1.41 (5)	C(81)-C(82)	1.63 (6)
C(2)-C(3)	1.45 (5)	C(82)-C(83)	1.24 (6)
C(3)-C(4)	1.40 (6)	C(83)-C(84)	1.47 (6)
C(4)-C(5)	1.49 (5)	C(84)-C(85)	1.42 (5)
C(5)-N(1)	1.35 (4)	C(85)-N(2)	1.35 (5)
C(11)-C(12)	1.50 (5)	C(51)-C(52)	1.39 (10)
C(11)-C(13)	1.55 (5)	C(51)-C(53)	1.50 (9)
C(21)-C(22)	1.55 (4)	C(61)-C(67)	1.51 (5)
C(21)-C(23)	1.48 (4)	C(61)-C(63)	1.50 (5)
C(31)-C(32)	1.53 (5)	C(71)-C(72)	1.54 (7)
C(31)-C(33)	1.68 (9)	C(71)-C(73)	1.36 (7)

Angles

W(2)-W(1)-O(1)	104.7 (6)	W(1)-W(2)-O(5)	106.1 (7)
-O(2)	105.3 (7)	-O(6)	103.8 (9)
-O(3)	101.2 (7)	-O(7)	99.8 (6)
-N(1)	91.0 (8)	-N(2)	89 (1)
O(1)-W(1)-O(2)	99 (1)	O(5)-W(2)-O(6)	97 (1)
-O(3)	151 (1)	-O(7)	152 (1)
-N(1)	80 (1)	-N(2)	85 (2)
O(2)-W(1)-O(3)	85 (1)	O(6)-W(2)-O(7)	88 (1)
-N(1)	163 (1)	-N(2)	166 (2)
O(3)-W(1)-N(1)	87 (1)	O(7)-W(2)-N(2)	84 (2)
W(1)-O(1)-C(11)	120 (2)	W(2)-O(5)-C(51)	126 (3)
W(1)-O(2)-C(21)	138 (2)	W(2)-O(6)-C(61)	136 (2)
W(1)-O(3)-C(31)	119 (2)	W(2)-O(7)-C(71)	120 (2)
W(1)-N(1)-C(1)	115 (2)	W(2)-N(2)-C(81)	112 (3)
W(1)-N(1)-C(5)	118 (2)	W(2)-N(2)-C(85)	112 (4)
C(1)-N(1)-C(5)	127 (3)	C(81)-N(2)-C(85)	136 (5)
N(1)-C(1)-C(2)	122 (3)	N(2)-C(81)-C(82)	105 (4)
C(1)-C(2)-C(3)	114 (3)	C(81)-C(82)-C(83)	122 (5)
C(2)-C(3)-C(4)	123 (4)	C(82)-C(83)-C(84)	124 (5)
C(3)-C(4)-C(5)	119 (3)	C(83)-C(84)-C(85)	116 (4)
C(4)-C(5)-N(1)	114 (3)	C(84)-C(85)-N(2)	116 (4)
O(1)-C(11)-C(12)	105 (2)	O(5)-C(51)-C(52)	104 (4)
-C(13)	106 (3)	-C(53)	100 (5)
C(12)-C(11)-C(13)	115 (3)	C(52)-C(51)-C(53)	115 (5)
O(2)-C(21)-C(22)	110 (2)	P(6)-C(61)-C(62)	107 (3)
-C(23)	105 (2)	-C(63)	105 (3)
C(22)-C(21)-C(23)	113 (3)	C(62)-C(61)-C(63)	110 (3)
O(3)-C(31)-C(32)	105 (3)	O(7)-C(71)-C(72)	104 (4)
-C(33)	108 (4)	-C(73)	122 (5)
C(32)-C(31)-C(33)	118 (4)	C(72)-C(71)-C(73)	120 (5)

Torsional Angles

O(1)-W(1)-W(2)-N(2)	16.9	N(1)-W(1)-W(2)-N(2)	63.4
N(1)-W(1)-W(2)-O(5)	21.2	O(1)-W(1)-W(2)-O(7)	67.0
O(3)-W(1)-W(2)-O(6)	35.0	O(2)-W(1)-W(2)-O(6)	53.1
O(2)-W(1)-W(2)-O(7)	37.3	O(3)-W(1)-W(2)-O(5)	66.1

rangement of the four ligand atoms about each tungsten atom, the four smallest independent torsional angles (Table II and Figure 2) are quite disparate; their average value is 28°. It is interesting that the py groups are in adjacent positions, only 63° apart; in this respect the structure differs from that of $Mo_2(OSiMe_3)_6(NHMe_2)_2$. It should be kept in mind that the rotational conformations observed in crystals may be due as much to intermolecular forces as intramolecular forces, though as shown below, there is evidence to support the existence of this conformer in solution.

NMR Studies of $W_2(OPr\text{-}i)_6(py)_2$. $W_2(OPr\text{-}i)_6(py)_2$ is soluble in hydrocarbon solvents. Unfortunately, however, the compound slowly decomposes with the liberation of pyridine and the formation of as yet unidentified isopropoxides of tungsten. The most reliable NMR spectroscopic data were consequently obtained by working with freshly prepared samples at low temperatures.

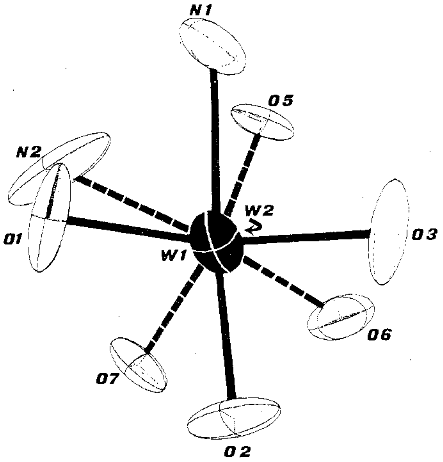

Figure 2. Coordination and rotational conformations as viewed conformation down the W–W axis. Thermal ellipsoids are drawn at the 50% proability level.

At 100 MHz and −80 °C, the three pyridine carbon signals were broad, almost embedded in the base line. We attribute this broadening to restricted rotation about the W–N bonds, comparable to that involved in the proximal ⇌ distal exchange in $M_2(NMe_2)_6$ compounds (M = Mo, W).

The methylene carbon resonances appeared as three sharp signals in the integral ratio 1:1:1. This is exactly what would be expected for the structure found in the solid state. The $W_2O_6N_2$ skeleton has virtual C_2 symmetry (see Figure 2) which leads to the pairwise equivalence of oxygen atoms and their respective methylene carbon atoms in the following manner: (O1, O5), (O3, O7) and (O2, O6).

The methyl carbon signals are not resolved. This is not surprising since for the $W_2N_2O_6$ conformer with C_2 symmetry there are a total of six different pairs of methyl carbon atoms some of which may appear magnetically degenerate because they are well removed from the dinuclear center.

At +60 °C and 100 MHz, the three pyridine carbon resonances are sharp; there is a single methylene carbon resonance and a single methyl carbon resonance. Evidently some fluxional process readily leads to the equivalence of all isoproxy groups on the NMR time scale at this temperature.

Comparisons and Conclusions

The great majority of compounds containing metal–metal triple bonds[12] of the X_3MMX_3 type where X is a monodentate ligand (including some where the ligand atoms are not all the same) have perfectly, or almost perfectly, staggered ethane-like rotational conformations. The great majority of compounds containing metal–metal quadruple bonds[13,14] are of the type X_4MMX_4 (again including those where more than one type of ligand is present) and have essentially eclipsed rotational conformations. The relatively few exceptions to each of these generalizations are of interest because they provide further insight into the nature of metal–metal multiple bonds.

Among molecules with M–M triple bonds, those unusual ones which have four ligands bound to each metal atom are of special interest with respect to the research described here. The case of $La_4Re_2O_{10}$[15] is exceptional since eclipsed stereochemistry is enforced by the crystal packing. $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$[16] is also more or less in a class by itself. In addition to these there is a class of compounds in which the triple bond results from cancellation of the δ^2 component of bonding by a δ^{*2} antibonding component. Two structurally characterized representatives of this class are $Re_2(PEt_3)_4Cl_4$[17] and $Re_2(Ph_2PCH_2CH_2PPh_2)_2Cl_4$.[18]

There are, so far, only a few well-characterized representatives of the class of triply bonded X_4MMX_4 species in which the triple bond is due, simply, to a $\sigma^2\pi^4$ configuration. The only three whose structures have been reported are $Mo_2(OSiMe_3)_6(NHMe_2)_2$,[9] $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$,[10] and $[Mo_2(HPO_4)_4]^{2-}$.[19] In the first, the rotational configuration (by use of the method of mean torsional angle introduced in earlier papers[20,21]) is 24° from eclipsed. In the second, where the two alkylcarbonato ligands favor an eclipsed configuration, the angle of twist is only 8°. In the phosphato-bridged anion the eclipsed configuration is found, but this may be attributed to the steric preference of the bridging groups. In $W_2(OPr\text{-}i)_6(py)_2$ an intermediate conformation with a mean torsional angle of 28° is seen again.

It seems clear from this work that tungsten, relative to molybdenum, shows a greater tendency to increase its coordination number in compounds containing a central $(M{\equiv}M)^{6+}$ moiety. $Mo_2(OPr\text{-}i)_6$ does not react with amines or pyridine to form the stable adducts $Mo_2(OPr\text{-}i)_6L_2$ whereas $W_2(OPr\text{-}i)_6$ is reactive in at least three ways: (i) formation of an adduct of the type $W_2(OPr\text{-}i)_6(py)_2$ in the presence of a donor ligand; (ii) oligomerization, which presumably occurs via the formation of W–OR–W bridges; (iii) attack by RO–H via oxidative addition across $W{\equiv}W$ to give a hydride-bridged $W{=}W$ bond.[11]

Experimental Section

General procedures including the purification and drying of alcohols and Me_3SiOH have been previously described.[7]

$W_2(NMe_2)_6$ was prepared from the reaction between WCl_4 and $LiNMe_2$.[4]

Preparation of $W_2(OBu\text{-}t)_6$. $W_2(NMe_2)_6$ (2.175 g) was dissolved in benzene (50 mL) in a round-bottomed 100-mL flask containing a magnetic Teflon spin bar. To this yellow solution was added the *tert*-butyl alcohol–benzene azeotrope (40 mL) which contains 36.6% by weight *tert*-butyl alcohol. The solution turned deep red and was stirred for 6 h at room temperature. The solvent was stripped. Hexane (40 mL) was added: the red solids dissolved at 40 °C. The flask was then set aside in a large water bath at 40 °C which was slowly cooled to room temperature. The flask was then slowly cooled to 0 °C and finally placed in the refrigerator at −15 °C for 12 h. The resulting dark red crystals were filtered, and the filtrate was concentrated and treated in the manner described above to obtain a second crop of red needlelike crystals of $W_2(OBu\text{-}t)_6$. Anal. Calcd for $W_2C_{24}H_{54}O_6$: C, 35.75; H, 6.75. Found: C, 35.3; H, 6.07.

Thermal Decomposition of $W_2(OBu\text{-}t)_6$. $W_2(OBu\text{-}t)_6$ (471.9 mg, 0.585 mmol) was placed in a pear-shaped flask, and this was attached to a vacuum line. The sample was heated in vacuo to 110 °C at which temperature trace quantities of a red sublimate formed. When the temperature was raised to 120 °C, there was a sudden increase in pressure, and both the bulk sample and the small quantity of sublimate were turned to a black powder which had a metallic sheen. The volatiles were collected in the vacuum line (199.8 mg) and were found to be a mixture of isobutylene, *tert*-butyl alcohol, and water by NMR and GC analysis. The nonvolatiles (266.3 mg) showed small quantities of carbon and hydrogen: C, 1.76%; H, 0.35%. In this reaction, $W_2(OBu\text{-}t)_6$ (1 mol) yielded isobutylene (4.0 mol), *tert*-butyl alcohol (1.3 mol), and water (0.9 mol). Similar experiments yielded similar but not identical results. The differences occurred in (i) the temperature at which decomposition occurred which ranged from 100 to 140 °C and (ii) the molar equivalents of isobutylene, *tert*-butyl alcohol and water. The range of the latter, $(CH_3)_2C{=}CH_2$:$(CH_3)_3C(OH)$:H_2O, was (4.0 ± 0.2):(1.2 ± 0.2):(0.9 ± 0.2).

Preparation of $W_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$. $W_2(OBu\text{-}t)_6$ (0.341 g) was dissolved in toluene (15 mL) in a round-bottomed flask (25 mL). CO_2 (2.54 mmol, 6 equiv) was added by use of a calibrated vacuum manifold. The solution darkened (red → brown) over a period of ca. 1 h. The flask was placed under 1 atm of CO_2 and left in the refrigerator at ca. −10 °C. After 12 h the solution was dark green, and dark green crystals had formed. The latter were collected by filtration (Schlenk technique) and dried in vacuo at room temperature to yield $W_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$, ca. 100 mg. Anal. Calcd for $C_{26}H_{54}O_{10}W_2$: C, 34.92; H, 6.09. Found: C, 34.9; H, 6.16. Although $W_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ is stable at room temperature in the solid state, it readily loses CO_2 to give $W_2(OBu\text{-}t)_6$ in solution in the absence of excess CO_2. Moreover, in the mass spectrometer the ion of highest mass corresponds to $W_2(OBu\text{-}t)_6^+$.

Preparation of $[W(OPr\text{-}i)_3]_n$. $W_2(NMe_2)_6$ (3.989 g, 6.31 mmol) was dissolved in benzene (100 mL) in a 250-mL round-bottomed flask fitted with a magnetic follower. To this magnetically stirred solution isopropyl alcohol (15 mL, ca. 200 mmol) was added. The solution immediately darkened to reddish black. The solution was stirred for 12 h at room temperature. The solvent was stripped, and the residual black solid was dried at 40–45 °C (10^{-4} cmHg) for 3 h. Hexane (50 mL) was then added; all the solids dissolved. The black hexane solution was warmed to ca. 45 °C, concentrated to ca. 30 mL, and then left to cool slowly, first to room temperature and then to −10 °C. Black crystals (1.5 g) formed in this way were collected by filtration and dried in vacuo. Anal. Calcd for $C_9H_{21}O_3W$: C, 29.93; H, 5.86. Found: C, 30.28; H, 5.96.

A cryoscopic molecular weight determination in benzene gave $M_r = 1460 \pm 60$; for a tetramer, $[W(OPr\text{-}i)_3]_4$, M_r would be 1440.

Preparation of $[W(OCH_2CMe_3)_3]_n$. The preparation followed the same procedure as that described above except that neopentyl alcohol was added in place of isopropyl alcohol. Black crystals of $[W(OCH_2CMe_3)_3]_n$ were obtained. Anal. Calcd for $C_{15}H_{33}O_3W$: C, 40.46; H, 7.47. Found: C, 40.2; H, 7.28.

Preparation of $W_2(OPr\text{-}i)_6(py)_2$. $W_2(NMe_2)_6$ (470 mg, 0.744 mmol) was dissolved in pyridine (20 mL). Isopropyl alcohol (10 mL) was syringed into the flask; the solution turned reddish black and was left stirring at room temperature for 12 h. The volume of the solution was reduced to ca. 10 mL and the flask stored in the refrigerator (ca. −5 °C) for ca. 12 h. Black crystals formed which were collected by Schlenk filtration and dried in vacuo, yielding $W_2(OPr_2)_6(py)_2$ (260 mg, 0.295 mmol). Anal. Calcd for $C_{28}H_{52}O_6N_2W_2$: C, 38.2; H, 5.95; N, 3.18. Found: C, 39.2; H, 6.17; N, 3.10. IR data obtained from a Nujol mull between CsI plates in the region 4000–200 cm^{-1}: 1602 (w), 1338 (m), 1262 (m), 1216 (m), 1162 (m), 1114 (s, br), 1041 (m), 992 (s), 980 (s), 969 (s), 845 (w), 835 (m), 825 (m), 805 (m), 755 (m), 696 (m), 603 (m, br), 535 (m), 400 (w, br), 325 (w, br). ^{13}C NMR data were recorded at 100 MHz in toluene-d_8. At 25 °C the single methyl carbon resonance was δ 27.5, the single broad methyne carbon resonance was δ 75.6, and the py carbon resonances were δ 150.5, 135.1, and 122.5 in the intensity ratio 2:1:2, respectively. At −80 °C the broad methyl carbon signals were at δ 29, 28.1, and 25.4 (of unequal intensity), the methyne carbon resonances were at δ 79.7, 71.25, and 70.3 (of equal intensity), and the py carbon resonances were broad centered at δ 149.8, 135.3, and 121.7.

X-ray Crystallography. Data Collection. A very irregular crystal approximately 0.5 × 0.3 × 0.2 mm was placed in a soft glass capillary immersed in a drop of expoxy resin. The crystal was mounted and data were collected on a Syntex $P\bar{1}$ automated diffractometer using crystallographic procedures previously described.[21,22] All operations were performed at 22 ± 1 °C wtih Mo Kα radiation monochromated by a graphite crystal in the incident beam. The cell dimensions based on a least-squares fit of 15 centered reflections in the range $15 < 2\theta < 27°$ were $a = 10.022$ (2) Å, $b = 17.839$ (4) Å, $c = 11.946$ (2) Å, $\beta = 125.57$ (1)°, $V = 1737.1$ (6) A^3, $Z = 2$, and $d_{calcd} = 1.457$ g/cm^3.

A total of 1671 reflections were measured by using the θ–2θ scan technique in the range $0 < 2\theta \leq 45°$. A data-collection program was used which does not collect data for reflections whose intensity during a rapid prescan is below a preselected threshold. No record is made in the output file for these weak reflections. Variable scan rates from 4 to 24° min^{-1} were used for the collected reflections, depending on their intensities, and the scan width extended from 0.9° below Mo Kα_1 to 0.9° above Mo Kα_2. Three standard reflections were checked after every 97 prescanned reflections and displayed about a 10% reduction during data collection. A decay correction was applied to the data.

Solution and Refinement of the Structure. All calculations were performed with the Enraf-Nonius structure-determination package on the PDP11/45 computer located at Molecular Structure Corp., College Station, TX. The absorption coefficient of 70.33 cm^{-1} made an absorption correction necessary. An empirical correction based on five sets of ψ scans ($\psi = 0$–360° at 10° intervals) at a χ of 90° was used because of the irregular shape of the crystal. Absences in the data appeared to indicate the space group $P2_1/c$. For this space group with $Z = 2$, the molecules must lie on inversion centers.

Structure refinement was begun in $P2_1/c$ by using only those 1446 reflections having $F_o^2 > 3\sigma(F_o^2)$. The Patterson map appeared to be consistent with the chosen space group and yielded coordinates for the tungsten atom. After three cycles of least-squares refinement the discrepancy indices were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.132$$

$$R_2 = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2} = 0.184$$

The function minimized during all least-squares cycles was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w equals $4F_o/\sigma(F_o^2)^2$. A value of 0.07 was used for the "ignorance parameter", ρ, in the calculation[21] of σ. The difference Fourier map based on this phasing displayed mainly peaks within 1 Å of the tungsten atom. Therefore, this atom was refined anisotropically which lowered the indices to $R_1 = 0.084$ $R_2 = 0.138$. The Fourier maps then indicated eight possible ligand atoms around each tungsten atom. This indication of pseudosymmetry caused us to reconsider our choice of space group in favor of one with lower symmetry. A Howell–Phillips–Rogers plot was made and it strongly indicated an acentric space group.

Reexamination of the data set showed that while the conditions for the screw axis ($0k0$, $k = 2n$) were never violated, the conditions for the c glide ($h0l$, $l = 2n$) were. The reflections 001 and 101 were both present though weak. Refinement was therefore begun again in $P2_1$. Attempts to leave the tungsten atoms with the same coordinates as in $P2_1/c$ caused their positions to shift drastically. This was probably because of correlation. Direct methods were then run to obtain new positions for these atoms. Solution and refinement then proceeded without problems. During the last least-squares cycle no atom moved by more than 0.03 Å. A final difference Fourier map displayed no peak greater than 0.63 e Å^{-3}. The final discrepancy indices were $R_1 = 0.040$ and $R_2 = 0.053$ and the goodness-of-fit index was 1.19. Two least-squares refinement cycles were then run on the enantiomorph of the chosen cell. The discrepancy indices were unchanged so the original cell is reported here.

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Registry No. $W_2(OBu\text{-}t)_6$, 57125-20-9; $W_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$, 70178-76-6; $[W(OPr\text{-}i)_3]_4$, 70160-64-4; $[W(OCH_2CMe_3)_3]_4$, 70160-65-5; $W_2(O\text{-}Pr\text{-}i)_6(py)_2$, 70178-75-5; $W_2(NMe_2)_6$, 54935-70-5; $W_2(OSiMe_3)_6(HNMe_2)_2$, 57157-52-5.

Supplementary Material Available: A table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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