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Reactions of Metal-Metal Multiple Bonds. 9.[1] α-Diketone Adducts of Ditungsten Hexaalkoxides: $W_2(OR)_6(O_2C_2R'_2)_2$ (M-M)

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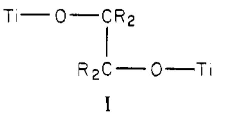
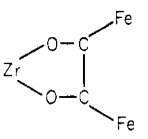
α-Diketones, R'C(O)C(O)R', where R' = Me, Ph, and *p*-tolyl, react with ditungsten hexaalkoxides in hydrocarbon solvents to give adducts $W_2(OR)_6(O_2C_2R'_2)_2$, where R = *t*-Bu and *i*-Pr. In the solid state, the compounds $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R'_2)_2$, where R' = Me and *p*-tolyl, adopt a common edge-shared bioctahedral W_2O_{10} unit with C_i symmetry. The halves of the molecule are joined by a pair of μ-O-*i*-Pr bridges and a W-W single bond of distance 2.750 (2) Å (R' = *p*-tolyl) and 2.744 (3) Å (R' = Me), the latter being averaged for two independent molecules. The W-O, C-O, and C-C distances associated with the coordinated α-diketone ligands indicate that they have been reduced to 2e ligands. These results complement recent findings of Cotton, Walton, and co-workers, who found that ketones react with $W_2Cl_4(OR)_4(HOR)_2$ (M=M) compounds to give $W_2Cl_4(OR)_2(O_2C_2R_4)_2$ (M—M) compounds, and provide further evidence of the reducing properties of W-W multiple bonds. ^1H NMR studies indicate that a number of isomers are present in solution and that at high temperatures (>80 °C), in toluene-d_8, these compounds are fluxional: bridge ⇌ terminal OR exchange and $O_2C_2R'_2$ site exchange rapidly equilibrate all isomers. These processes do not involve dissociation of the α-diketone (2e) ligands. Crystal data are as follows. For $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(C_7H_7)_2)_2$ at -162 °C: monoclinic, *a* = 20.124 (1) Å, *b* = 9.735 (1) Å, *c* = 12.651 (1) Å, β = 90.23 (5)°, space group $P2_1/a$ with *Z* = 2. For $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ at -162 °C: triclinic, *a* = 22.127 (14) Å, *b* = 9.750 (4) Å, *c* = 9.361 (4) Å, α = 76.11 (3)°, β = 64.27 (3)°, γ = 69.03 (3)°, space group $P\bar{1}$ with *Z* = 2.

Introduction

Metal-metal multiple bonds provide a reservoir of electrons for oxidations. For a metal in a given oxidation state, a dinuclear compound may, in principle, deliver twice the number of electrons available to a mononuclear species; e.g. in $(W{\equiv}W)^{6+}$-containing compounds, the six electrons of the $\sigma^2\pi^4$ W-W triple bond are available, compared to the three 5d electrons in mononuclear W^{3+} complexes. Furthermore, the presence of the dinuclear center may facilitate multielectron transfer and may provide a template effect for coordinated ligands. We were thus intrigued by the notion that the W≡W bond in hexaalkoxides of ditungsten could be used to promote carbon-carbon bond formation in an analogous manner to that found in the reactions of ketones with $TiCl_3$[2] and metal carbonyls with Zr^{2+} compounds,[3] shown schematically as I and II.



I



II

We report here our studies of the reactions of α-diketones with $W_2(OR)_6$ compounds that were prompted by the above considerations. It should be noted that Cotton, Walton, and co-workers[4] have recently reported that $W_2Cl_4(OR)_4(HOR)_2$ (M=M) compounds react with ketones to give $W_2Cl_4(OR)_2(O_2C_2R'_4)_2$ (M—M) compounds wherein C—C bond formation occurs: $2R'_2C{=}O \rightarrow R_4C_2O_2^{2-}$. Furthermore, α-diazoketone ligands have been reduced in reactions with $Cp_2Mo_2(CO)_4$ (M≡M).[5]

Results and Discussion

Syntheses and Reactions. Ketones react rapidly with $W_2(O\text{-}t\text{-}Bu)_6$[6] and $W_2(O\text{-}i\text{-}Pr)_6(py)_2$[6] in hydrocarbon solvents when the ketone contains hydrogens that are active in the enol form. No simple products have been characterized from these reactions, but 2,4-pentanedione, acacH, reacts smoothly to substitute two alkoxy ligands with the formation of $W_2(OR)_4(acac)_2$ compounds.[7] Diaryl ketones and $W_2(O\text{-}t\text{-}Bu)_6$ and $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ fail to react in hydrocarbon solvents. This could be because of the unfavorable equilibrium (eq 1) that exists between oxygen donor ligands and $M_2(OR)_6$ compounds (M = Mo and W).

$$M_2(OR)_6 + 2L \rightleftharpoons M_2(OR)_6L_2 \qquad (1)$$

We thus turned our attention to α-diketones for which the chelate effect could assist in promoting adduct formation. Benzil, 4,4'-dimethylbenzil, and diacetyl all readily react with hydrocarbon solutions of $W_2(O\text{-}t\text{-}Bu)_6$ and $W_2(O\text{-}t\text{-}Pr)_6$ at room temperature to give the adducts $W_2(OR)_6(O_2C_2R'_2)_2$, where R' = Ph, *p*-tolyl, and Me.

Physicochemical Properties of $W_2(OR)_6(O_2C_2R'_2)_2$ Compounds. The α-diketone adducts are air-sensitive, diamagnetic, black, crystalline solids. The compounds are soluble in hydrocarbon solvents. When heated to +80 °C in toluene-d_8, $W_2(O\text{-}t\text{-}Bu)_6(O_2C_2Ph_2)_2$ decomposes to as yet unknown products. The isopropoxy compounds are more thermally stable and do not decompose at +110 °C over short periods of time. In the infrared spectra, aside from bands attributable to OR ligands, each compound shows a strong band at ca. 1600 cm^{-1} originating from the coordinated α-diketone ligand. The free ligands show strong bands 60-70 cm^{-1} higher in energy, due primarily to C=O stretching vibrations. As will be seen later, upon complexation, the C—O double character decreases toward a single bond while the C—C single bond becomes a double bond. The band at ca. 1600 cm^{-1} in the coordinated ligands may therefore be predominantly ν(C=C), but with C=O mixing. The black color of these compounds arises from intense absorption throughout the visible region. For example, $W_2(O\text{-}t\text{-}Pr)_6(O_2C_2Me_2)_2$ shows very broad bands having λ_{max} at 385 nm (ε = 8595) and 520 nm (ε = 3280).

Solid-State Molecular Structures. In the solid state, the compounds $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R'_2)_2$, where R = *p*-tolyl and

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[1] Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138.

[2] Coults, R. S. P.; Wales, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145.

[3] Berry, D. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 4712.

[4] Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Walton, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 7375.

[5] Hermann, W. A.; Krechbaum, G. W.; Ziegler, M.; Pfisterer, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 707.

[6] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[7] Chisholm, M. H.; Huffman, J. C.; Ratermann, A. L. *Inorg. Chem.*, in press.

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Table I. Fractional Coordinates for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	546.7 (2)	3836.9 (4)	182.6 (4)	12
O(2)	1590 (3)	3311 (6)	−1101 (7)	18
C(3)	1927 (5)	4205 (10)	−1040 (11)	20
C(4)	1526 (5)	5262 (10)	−67 (11)	16
O(5)	838 (3)	5209 (6)	733 (7)	18
C(6)	2691 (5)	3858 (11)	−2033 (12)	26
C(7)	1695 (5)	6430 (11)	331 (12)	29
O(8)	642 (3)	2322 (6)	1886 (7)	18
C(9)	1263 (5)	1205 (9)	1929 (11)	19
C(10)	1632 (6)	1792 (12)	2544 (14)	36
C(11)	1057 (6)	−135 (11)	2935 (12)	30
O(12)	537 (3)	2522 (6)	−921 (7)	16
C(13)	825 (8)	2036 (20)	−2444 (19)	15
C(14)	1479 (6)	668 (11)	−2576 (13)	32
C(15)	236 (10)	1722 (24)	−2694 (22)	22
O(16)	−425 (3)	4590 (6)	1716 (7)	16
C(17)	−898 (5)	4360 (15)	3365 (11)	42
C(18)	−557 (8)	4447 (26)	4425 (16)	120
C(19)	−1029 (7)	2904 (20)	3585 (24)	111
C(13)′	794 (11)	946 (21)	−1204 (25)	31
C(15)′	239 (11)	607 (21)	−1522 (26)	28
W(1A)	5651.4 (2)	4250.6 (4)	9012.6 (4)	12
O(2A)	6595 (3)	4587 (6)	8273 (7)	18
C(3A)	6672 (5)	5859 (9)	7277 (11)	17
C(4A)	6137 (5)	6587 (10)	6834 (11)	19
O(5A)	5596 (3)	5962 (6)	7489 (7)	17
C(6A)	7339 (5)	6184 (12)	6810 (13)	32
C(7A)	6028 (5)	7987 (10)	5778 (11)	24
O(8A)	5963 (3)	2854 (6)	7520 (7)	20
C(9A)	6684 (5)	2104 (9)	6647 (11)	18
C(10A)	6915 (5)	2965 (11)	4993 (12)	31
C(11A)	6707 (5)	559 (11)	6528 (12)	25
O(12A)	5928 (3)	2787 (6)	10454 (7)	14
C(13A)	6331 (5)	2287 (11)	11431 (11)	24
C(14A)	5909 (6)	1516 (13)	12958 (13)	39
C(15A)	7014 (6)	1279 (12)	10549 (14)	37
O(16A)	5305 (3)	5750 (6)	10675 (7)	18
C(17A)	5647 (5)	6389 (10)	11261 (11)	26
C(18A)	5475 (5)	8034 (12)	10774 (13)	32
C(19A)	5418 (5)	6028 (12)	13054 (11)	27

Table II. Fractional Coordinates for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(p\text{-tol})_2)_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	9 717.8 (3)	487 (1)	914.6 (5)	13
O(2)	9 898 (4)	2181 (10)	1792 (8)	12
O(3)	10 545 (5)	82 (10)	1620 (8)	14
C(4)	11 270 (8)	4130 (19)	2702 (13)	24
C(5)	11 433 (8)	5369 (19)	3170 (13)	24
C(6)	10 959 (9)	6124 (18)	3715 (13)	24
C(7)	10 325 (9)	5537 (21)	3781 (15)	33
C(8)	10 200 (8)	4258 (18)	3336 (15)	26
C(9)	10 670 (7)	3533 (17)	2770 (11)	15
C(10)	10 500 (7)	2214 (19)	2254 (11)	20
C(11)	10 880 (7)	1037 (15)	2204 (12)	13
C(12)	11 519 (7)	673 (14)	2647 (11)	10
C(13)	11 886 (10)	−283 (23)	2122 (13)	36
C(14)	12 482 (9)	−767 (23)	2520 (15)	37
C(15)	12 750 (8)	−206 (22)	3459 (13)	28
C(16)	12 383 (8)	737 (18)	4000 (12)	21
C(17)	11 745 (8)	1147 (17)	3603 (13)	19
C(18)	11 086 (10)	7483 (20)	4240 (15)	33
C(19)	3 394 (9)	9288 (22)	3879 (14)	33
O(20)	9 162 (5)	−325 (11)	1984 (7)	15
C(21)	8 993 (8)	237 (15)	3000 (13)	21
C(22)	9 461 (11)	−419 (22)	3811 (15)	40
C(23)	8 280 (11)	−92 (25)	3179 (18)	46
O(24)	10 324 (5)	1356 (11)	−245 (7)	15
C(25)	10 625 (13)	2710 (22)	−413 (17)	51
C(26)	10 360 (19)	3363 (27)	−1376 (19)	81
C(27)	11 386 (15)	2523 (37)	−328 (19)	89
O(28)	9 026 (5)	1526 (12)	361 (8)	17
C(29)	8 659 (14)	2708 (31)	493 (25)	85
C(30)	8 505 (11)	3430 (36)	−491 (39)	132
C(31)	8 080 (29)	2352 (82)	983 (34)	288

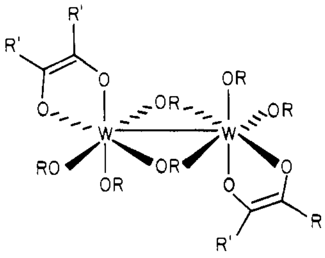
Table III. Selected Bond Distances for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ Molecule

		dist, Å	
A	B	molecule 1	molecule 2
W(1)	W(1)′	2.745 (2)	2.742 (2)
W(1)	O(2)	2.020 (6)	2.018 (6)
W(1)	O(5)	1.925 (6)	1.922 (6)
W(1)	O(8)	1.925 (5)	1.919 (6)
W(1)	O(12)	1.841 (6)	1.843 (5)
W(1)	O(16)	1.979 (6)	2.006 (6)
W(1)	O(16)′	2.097 (6)	2.097 (6)
O(2)	C(3)	1.356 (11)	1.376 (10)
O(5)	C(4)	1.389 (11)	1.372 (10)
O(8)	C(9)	1.425 (11)	1.438 (10)
O(12)	C(13)	1.408 (18)	1.434 (11)
O(16)	C(17)	1.459 (12)	1.460 (10)
C(3)	C(4)	1.332 (13)	1.327 (13)
C(3)	C(6)	1.489 (14)	1.477 (14)
C(4)	C(7)	1.485 (14)	1.490 (13)

Table IV. Selected Bond Distances for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(p\text{-tol})_2)_2$ Molecule

A	B	dist, Å	A	B	dist, Å
W(1)	W(1)′	2.750 (2)	W(1)	O(24)	2.091 (10)
W(1)	O(2)	2.020 (9)	W(1)	O(28)	1.856 (11)
W(1)	O(3)	1.926 (10)	O(2)	C(10)	1.344 (17)
W(1)	O(20)	1.928 (9)	O(3)	C(11)	1.365 (17)
W(1)	O(24)′	1.985 (10)	C(10)	C(11)	1.379 (22)

Me, adopt the centrosymmetry edge-shared bioctahedral geometry depicted in III.



III

Fractional coordinates are given in Tables I (R′ = Me) and II (R′ = p-tolyl), selected bond distances are given in Tables III (R′ = Me) and IV (R′ = p-tolyl), and selected bond angles are given in Tables V (R′ = Me) and VI (R′ = p-tolyl). ORTEP views of the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R')_2$ molecules showing the atom-numbering scheme used in the tables are given in Figures 1 (R′ = Me) and 2 (R′ = p-tolyl).

The compound $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ crystallized with two independent molecules in the unit cell. In one molecule, an isopropoxy ligand is disordered while, in the other, all atoms are well-behaved. The bond distances and bond angles associated with methyl groups of the isopropoxy ligands and the p-tolyl groups are all normal and are available as supplementary material. Most hydrogen atoms were located and were included as fixed idealized contributors in the final cycles of the refinements. Figure 3 shows two stereoviews of a superimposition of the two crystallographically independent $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ molecules. The central W_2O_{10} skeletons are essentially identical; the only significant differences in the molecules arise from orientations of the isopropyl group.

The $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R'_2)_2$ compounds can be formulated as d^1–d^1 dimers with M–M single bonds on the following grounds. (1) The W–W distance is typical of the distance

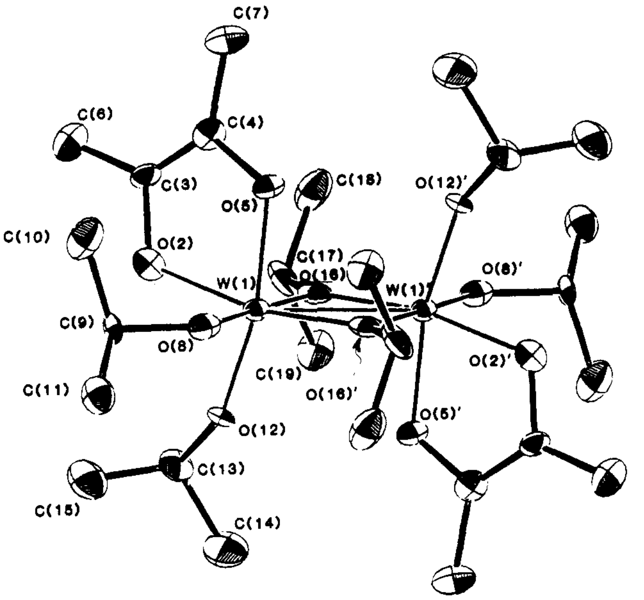


Figure 1. ORTEP view of one of the centrosymmetric $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ molecules showing the atom-numbering scheme used in the table. The numbering of the atoms in the other molecule uses the correspondence 1 to 1A, 2 to 2A, etc.

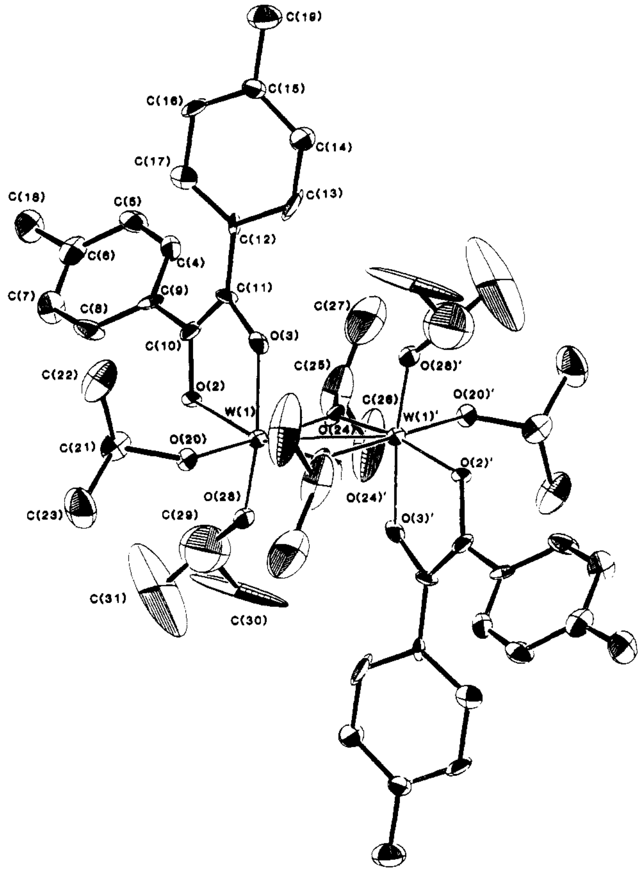


Figure 2. ORTEP view of the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(C_7H_7)_2)_2$ molecule showing the atom-numbering scheme used in the tables.

Table V. Selected Bond Angles for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ Molecule

A	B	C	angle, deg	
			molecule 1	molecule 2
W(1)'	W(1)	O(2)	132.1 (2)	130.9 (2)
W(1)'	W(1)	O(5)	87.8 (2)	86.8 (2)
W(1)'	W(1)	O(8)	134.0 (2)	133.0 (2)
W(1)'	W(1)	O(12)	98.9 (2)	100.5 (2)
W(1)'	W(1)	O(16)	45.9 (2)	46.7 (2)
O(2)	W(1)	O(5)	76.6 (2)	77.1 (2)
O(2)	W(1)	O(8)	93.2 (2)	94.9 (2)
O(2)	W(1)	O(12)	85.9 (2)	85.9 (2)
O(2)	W(1)	O(16)	87.6 (2)	85.6 (3)
O(2)	W(1)	O(16)'	166.8 (2)	167.0 (2)
O(5)	W(1)	O(8)	96.8 (2)	95.3 (2)
O(5)	W(1)	O(12)	161.1 (3)	161.2 (3)
O(5)	W(1)	O(16)	86.5 (3)	85.6 (2)
O(5)	W(1)	O(16)'	90.7 (2)	90.2 (3)
O(8)	W(1)	O(12)	91.3 (3)	91.6 (3)
O(8)	W(1)	O(16)	176.8 (2)	179.0 (2)
O(8)	W(1)	O(16)'	84.6 (2)	83.5 (2)
O(12)	W(1)	O(16)	85.7 (2)	87.6 (2)
O(12)	W(1)	O(16)'	107.1 (2)	107.0 (2)
O(16)	W(1)	O(16)'	95.4 (2)	96.2 (3)
W(1)	O(2)	C(3)	115.9 (6)	115.0 (6)
W(1)	O(5)	C(4)	119.1 (5)	118.8 (5)

Table VI. Selected Bond Angles for the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(p\text{-}tol)_2)_2$ Molecule

A	B	C	angle, deg
W(1)'	W(1)	O(2)	132.1 (3)
W(1)'	W(1)	O(3)	87.7 (3)
W(1)'	W(1)	O(20)	133.8 (3)
W(1)'	W(1)	O(24)	49.2 (3)
W(1)'	W(1)	O(28)	100.5 (3)
O(2)	W(1)	O(3)	76.1 (4)
O(2)	W(1)	O(20)	93.0 (4)
O(2)	W(1)	O(24)	87.2 (4)
O(2)	W(1)	O(24)'	168.3 (4)
O(2)	W(1)	O(28)	84.0 (4)
O(3)	W(1)	O(20)	95.4 (4)
O(3)	W(1)	O(24)	84.4 (4)
O(3)	W(1)	O(24)'	92.6 (4)
O(3)	W(1)	O(28)	158.7 (4)
O(20)	W(1)	O(24)	179.9 (4)
O(20)	W(1)	O(24)'	84.6 (4)
O(20)	W(1)	O(28)	93.0 (4)
O(24)	W(1)	O(24)'	95.2 (4)
O(24)	W(1)	O(28)	87.3 (4)
O(24)'	W(1)	O(28)	107.5 (4)
W(1)	O(2)	C(10)	114.7 (10)
W(1)	O(3)	C(11)	122.4 (8)
W(1)	O(20)	C(21)	127.7 (9)
W(1)	O(24)	W(1)	84.8 (4)
W(1)	O(24)	C(25)	135.0 (11)
W(1)	O(28)	C(29)	144.2 (16)

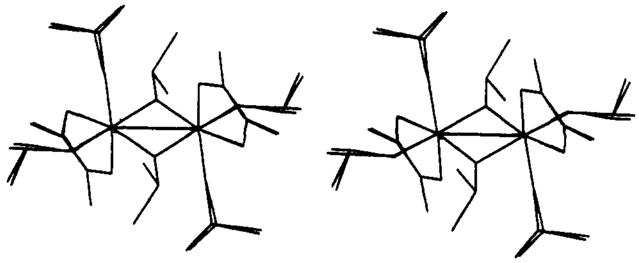


Figure 3. Two stereoviews of the best superimposition of the two $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ molecules.

associated with d^1–d^1 dimers found in $W_2Cl_4(OEt)_6$[8] and $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds, X = Cl and Br.[9] The distance is notably longer than those associated with M–M double bonds between molybdenum and tungsten atoms, e.g. W–W = 2.479 (1) Å in $W_2Cl_4(OEt)_4(HOEt)_2$ that has an edge-shared $(\mu\text{-}OEt)_2$ bioctahedral geometry,[11] and much longer

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(8) Cotton, F. A.; Walton, R. A.; DeMarco, D.; Kolthammer, B. S. W. *Inorg. Chem.* **1981**, *20*, 3048.

(9) Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1981**, *20*, 871.

(10) For a listing of M–M distances and assignments of M–M bond orders and M–OR distances in dinuclear tungsten alkoxides, see: Chisholm, M. H. *Polyhedron* **1983**, *2*, 581.

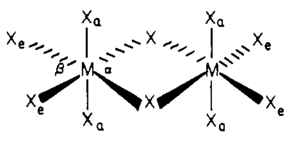
Table VII. Comparison of Certain Structural Parameters[a] in Edge-Shared Octahedral Complexes Having d^0-d^0 or d^1-d^1 M-M Interactions

compd	M-M, Å	α, deg	β, deg	M-X_a, Å	M-X_e, Å	M-(μ-X), Å	ref
$(NbCl_5)_2$	3.951 (2)	78.7 (3)	101.2 (3)	2.300 (5)	2.250 (6)	2.555 (6)	18
$(MoCl_5)_2$	3.84 (2)	81.4 (1)	96.4 (1)	2.24 (1)	2.25 (1)	2.53 (1)	15
$(WCl_5)_2$	3.815 (2)	81.5 (1)	96.3 (2)	2.243 (3)	2.243 (3)	2.519 (3)	16
$[Nb(OMe)_5]_2$	3.5	70.4 (3)	104.1 (3)	1.886 (5)	1.904 (9)	2.134 (7)	17
$Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$	2.731 (1)	94.7 (1)	85.5 (1)	1.814 (3) (Mo-O)	2.419 (2) (Mo-Cl)	2.014 (3)	9
$Mo_2(O\text{-}i\text{-}Pr)_6Br_4$	2.739 (1)	94.3 (2)	83.6 (1)	1.811 (5) (Mo-O)	2.582 (1) (Mo-Br)	2.013 (4) (Mo-O)	9
$W_2(OEt)_6Cl_4$	2.715 (1)	95.1 (2)	90.2 (1)	1.824 (4) (W-O)	2.403 (4) (W-Cl)	2.012 (4) (W-O)	8
$W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$	2.754 (2)	96.3 (2)	94.0 (2)	1.92 (1) (α-dik) 1.84 (1) (OR)	2.02 (1) (α-dik) 1.93 (1) (OR)	2.045 (6)	this work
$W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Ph_2)_2$	2.750 (2)	95.2 (4)	93.0 (4)	1.93 (1) (α-dik) 1.85 (1) (OR)	2.02 (1) (α-dik) 1.93 (1) (OR)	1.99 (1)	this work

[a] Angles are defined as α = (μ-X)-M-(μ-X) and β = X_e-M-X_e. X_a and X_e are defined in IV in the text.

than the W-W triple bond distance, 2.332 (1) Å, found in the parent compound $W_2(O\text{-}i\text{-}Pr)_6(py)_2$.[6] (2) The W-O, C-O, and central C-C bond distances associated with the α-diketone ligands imply a 2e reduction, i.e. formation of diolate ligands. A particularly pertinent comparison of these distances with those associated with *o*-quinones, semiquinones, and catecholate ligands can be made. In $MoO_2Cl_2(O_2C_{14}H_8)$, which contains the 9,10-phenanthrenequinone ligand coordinated to Mo^{6+} and is therefore a neutral, unreduced quinone ligand, the Mo-O (quinone) distances are quite long, 2.306 (3) Å, and the C-O distances, 1.234 (4) Å, are only slightly longer than those in the free ligand.[12] The C-C distance between the carbonyl carbon atoms is 1.530 (5) Å.[12] In semiquinone complexes, the C-O distances are longer and the C-C distances between the carbonyl carbons are shorter; typically these are 1.28 and 1.45 Å, respectively.[13] With a further reduction to catecholate, the C-O distances increase to ca. 1.34, which may be taken as a C_{sp^2}-O single-bond distance. The C-C distances decrease to ca. 1.40 Å; they become typical of C-C distance within an aromatic ring.[13] In the present work, the C-O distances range from 1.34 to 1.38 Å and the central C-C distances range from 1.33 to 1.38 Å, which may be taken as C-O single bonds and C-C double bonds, cf. C-C = 1.337 (5) Å in ethylene.[14] The W-O distances to the α-diketone ligands are also well within the range observed for terminal alkoxy ligands.[10]

There is therefore a consistent structural pattern implying that the ligand is reduced to a 2e ligand and that the dinuclear metal center is oxidized $(W{\equiv}W)^{6+} \rightarrow (W{-}W)^{10+}$. There is, however, one perhaps unexpected or at least not previously well-recognized aspect of the d^1-d^1 edge-shared biooctahedral geometry that should be noted. Using the general representation for an edge-shared bioctahedron shown in IV, we see that the terminal axial bonds are shorter than the terminal equatorial bonds.



IV

In order to appreciate this phenomenon, a comparison of M-X_a, M-X_e, M-(μ-X), and M-M distances, along with the angles α and β, are presented in Table VII for the d^1-d^1 dimers that contain M-M single bonds, $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R'_2)_2$, $W_2Cl_4(OEt)_6$,[8] and $Mo_2(O\text{-}i\text{-}Pr)_6X_4$[9] (X = Cl and Br), and those that do not, $(MCl_5)_2$ (M = Mo[15] and W[16]), and with related d^0-d^0 dimers such as $[Nb(OMe)_5]_2$[17] and $(NbCl_5)_2$,[18] which, of course, cannot have M-M bonds.

A number of points should be noted in examining the structural data shown in Table VII: (1) There is the now well-recognized effect that M-M bonding produces in the central $M_2(\mu\text{-}X)_2$ unit: the M-M distance decreases by ca. 0.8 Å and the α angle, (μ-X)-M-(μ-X), changes from a value of less than 90° to one greater than 90°. The angle at the μ-X ligand, M-(μ-X)-M, also changes from obtuse to acute. The β angle is little perturbed by these changes. The axial ligands bend toward the center of the molecule in the absence of M-M bonding and bend away from the center in the presence of M-M bonding. (2) There is also the general effect that M-(μ-X) distances are longer than M-X terminal distances. (3) In the absence of M-M bonding, the M-X distances are essentially the same for axial and equatorial ligands. This is seen for the $(MCl_5)_2$ compounds, where M = Nb, Mo, and W, and also for $[Nb(OMe)_5]_2$. It can also be noted that the M-X distances in the chlorides for M = Nb, Mo, and W are very similar, almost identical within the experimental error. (4) In examining the M-O (axial) and M-X (equatorial) distances for the $M_2X_4(OR)_6$ compounds, we find the M-O distances are ca. 0.1 Å shorter than those in $[Nb(OMe)_5]_2$ and the M-Cl distances are ca. 0.15 Å longer than in the $(MCl_5)_2$ compounds. In the $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2R'_2)_2$ compounds, we see that for each type of ligand, OR and $O_2C_2R'_2$, the W-O axial bonds are ca. 0.1 Å shorter than the W-O equatorial bonds. We also see that in the M-M-bonded compounds the M-(μ-O) distances to bridging alkoxy ligands are close to 2.0 Å, roughly 0.1 Å shorter than those seen in $[Nb(OMe)_5]_2$ and other compounds of molybdenum and tungsten that contain a $M_2(\mu\text{-}OR)_2$ group spanning nonbonded metal atoms, e.g. Mo-(μ-O) = 2.13 Å in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$[19] and 2.12 Å in $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$,[20] both of which contain a central edge-shared bioctahedral moiety. Thus, the formation of the M-M bonds produces a strengthening of the M-(μ-OR) bonds at the expense of the equatorial terminal bonds, at least as evidenced by metal-ligand bond distances.

Qualitatively, these changes in M-X bond distances can be related to the combined effects of M-M bonding and oxygen-to-metal π bonding. If for each metal we choose the *z* axis to be coincident with the X_a-M-X_a bonds and the *x* and

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(11) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Isley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

(12) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1977**, *16*, 2970.

(13) For a general review and lisitng of Mo-O, C-O, and C-C distances in metal catecholate and semiquinone complexes, see: Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(14) Kutchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

(15) Sands, D. E.; Zalkin, A. *Acta Crystallogr.* **1959**, *12*, 723.

(16) Cotton, F. A.; Rice, C. E. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2833.

(17) Pinkerton, A. A.; Schwarzenbach, D.; Hubert-Pfalzgraf, L. G.; Reiss, J. G. *Inorg. Chem.* **1976**, *15*, 1196.

(18) Zalkin, A.; Sands, D. D. *Acta Crystallogr.* **1958**, *11*, 615.

(19) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *Inorg. Chem.* **1980**, *19*, 2762.

(20) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

y axes to contain the X_e–M–(μ-X) bonds, then the d_{xy} orbital has the appropriate symmetry to form a M–M σ bond. Placing two electrons in the M–M σ molecular orbital derived from d_{xy}–d_{xy} interactions effectively removes this from forming π bonds with the O-donor ligands. It is therefore the d_{xz} and d_{yz} metal orbitals, which are vacant, that can interact most strongly with filled oxygen p orbitals. If we consider that in OR and $O_2C_2R'_2$ ligands the oxygen atoms are essentially sp^2 hybridized, the oxygen p_z orbital, which is active in π bonding, is perpendicular to the M–O–C plane of the ligand concerned. Inspection of the $M_2(OR)_6X_4$ and W_2(O-*i*-Pr)$_6$($O_2C_2R'_2$)$_2$ structures shows that the axial OR ligands and the bridging OR ligands have oxygen p orbitals aligned in an appropriate manner to π donate to d_{xz} or d_{yz} metal orbitals. Only in W_2(O-*i*-Pr)$_6$($O_2C_2R'_2$)$_2$ compounds do we find that one oxygen atom, namely the equatorial oxygen atom of the $O_2C_2R'_2$ ligand, has its oxygen p orbital aligned to interact with the metal d_{xy} orbital. We conclude that the marked shortening of axial bonds and lengthening of the equatorial bonds in these M–M edge-shared bioctahedral compounds can be understood qualitatively in terms of enhanced ligand-to-metal π bonding in the axial positions as a result of forming a M–M σ bond using metal d_{xy} orbitals. It may also be noted that the equatorial ligands could π donate to d_{xz} and d_{yz} orbitals, but strong and short M–X (equatorial) bonds would exert a higher trans influence,[21] thus weakening and lengthening M–(μ-X) bonds, which in turn would lengthen and weaken the M–M bond. Thus, both σ and π effects favor short axial and long equatorial M–X bonds.

NMR Studies. At −45 °C in toluene–d_8, the ^{1}H NMR spectra of W_2(O-*i*-Pr)$_6$($O_2C_2R'_2$)$_2$ compounds, where R = Me, Ph, and *p*-tolyl, indicate the presence of more than one isomer in solution. At ambient temperatures, there are broad resonances indicative of two types of O-*i*-Pr groups, roughly in the integral ratio 2:1. There are also resonances indicative of two types of R′ groups in the integral ratio 1:1. The latter is expected on the basis of the molecuar structure found in the solid state. When the temperature is raised to above 80 °C, the resonances associated with the O-*i*-Pr ligands coalesce to give a septet and a doublet indicative of one time-averaged O-*i*-Pr ligand. The methyl resonances associated with the $O_2C_2R'_2$ ligands, where R = Me or tolyl, also collapse to single resonances. Evidently the molecule is fluxional on the NMR time scale, and this rapidly equilibrates all isomers and all bioctahedral positions for the RO ligands. A large number of isomers can be envisaged for a compounds of the formula $M_2(OR)_6(\widehat{O\ O})_2$, where $\widehat{O\ O}$ represents a chelate, and further speculation about solution structures is not warranted. We do note, however, that the NMR observations do not arise because of dissociation of $O_2C_2R'_2$ ligands. Addition of diacetyl to W_2(O-*i*-Pr)$_6$($O_2C_2Me_2$)$_2$ in toluene-d_8 shows resonances due to free and coordinated $O_2C_2Me_2$ ligands even at 100 °C. Similarly, addition of benzil to W_2(O-*i*-Pr)$_6$(O_2C_2(*p*-tol)$_2$)$_2$ shows only free benzil and coordinated dimethylbenzil. Exchange between free and coordinated (reduced) α-diketone ligands is not observed.

^{13}C NMR spectra of W_2(O-*i*-Pr)$_6$($O_2C_2R'_2$)$_2$ compounds were recorded in toluene-d_8 and show signals at ca. δ 140 (relative to Me_4Si) assignable to central carbons of the reduced ligands. Significantly, these resonances are now in the region expected for olefinic carbons and are shifted upfield over 50 ppm from the free ligand values.[22] Data are given in the Experimental Section.

Experimental Section

General Procedures. All manipulations and syntheses were carried out under a dry and oxygen-free nitrogen atmosphere by using standard Schlenk techniques or a Vacuum Atmospheres Co. Dri-Lab assembly.

^{1}H NMR spectra were obtained on a Varian HR 220 spectrometer. ^{13}C NMR spectra were obtained on a Nicolet 360 spectrometer. δ are reported relative to Me_4Si.

Infrared spectra were obtained from Nujol mulls between CsI plates with a Perkin-Elmer 283 spectrometer.

UV–visible spectra were obtained from hexane solutions.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, by using drybox sampling techniques.

W_2(O-*t*-Bu)$_6$ and W_2(O-*i*-Pr)$_6$(py)$_2$ were prepared by the previously described procedure.[6] Benzil, dimethylbenzil, and diacetyl were purchased from Aldrich.

Preparation of W_2(O-*i*-Pr)$_6$($O_2C_2Ph_2$)$_2$. W_2(O-*i*-Pr)$_6$ (710 mg, 0.807 mmol) was suspended in toluene/hexane (1 mL/2 mL). A solution of benzil (3.23 mL, 0.5 M in toluene) was added by syringe. Slow cooling of the solution to −15 °C yielded black crystals that were collected by filtration and dried in vacuo. Further cooling of the filtrate yielded a second crop of crystals, yield 65%.

Anal. Calcd for W_2(O-*i*-Pr)$_6$($O_2C_2Ph_2$)$_2$: C, 48.3; H, 5.48; N, 0.00. Found: C, 48.6; H, 5.38; N, 0.04.

^{1}H NMR data, (obtained at +16 °C in toluene-d_8): O-*i*-Pr 1.28 (24 H), 1.59 (12 H), 5.42 (4 H), 5.69 (2 H); phenyl 7.16, 7.45, 7.80 (20 H) multiplets.

IR data: 2900 (s), 1590 (m), 1450 (s), 1375 (s), 1330 (w), 1261 (m), 1102 (s), 1063 (m), 990 (w), 961 (w), 930 (w), 831 (m), 795 (w), 760 (m), 721 (m), 690 (m), 653 (w), 602 (s), 460 (m) cm^{-1}.

^{13}C NMR data, δ (obtained from benzene-d_6 at +16 °C): O-*i*-Pr methyl carbons 24.1 (8 C), 25.5 (4 C); methyne carbons 76.0 (4 C), 79.5 (2) C); phenyl carbons 125.0–131.5 (20 C); O_2C_2 137.0 (2 C) and 146.0 (2 C). In benzene-d_6, $\delta(Ph_2C_2O_2)$ 194.3 for the free ligand.

W_2(O-*t*-Bu)$_6$($O_2C_2Ph_2$)$_2$ was prepared in a similar manner and yielded black crystals with toluene of inclusion that could not be removed under vacuum.

Anal. Calcd for W_2(O-*i*-Bu)$_6$($O_2C_2Ph_2$)$_2$·C_7H_8: C, 53.7; H, 6.28. Found: C, 54.2; H, 6.28.

^{1}H NMR data δ: O-*t*-Bu 1.42 (36 H), 1.84 (18 H); C_6H_5*Me* 2.11 (3 H); aromatic 7.70, 7.35, 7.00 (25 H).

IR data: 2900 (s), 1597 (m), 1460 (s), 1375 (s), 1360 (s), 1260 (w), 1238 (w), 1166 (s), 1068 (w), 1059 (m), 1021 (m), 972 (m), 938 (s), 840 (m), 765 (s), 720 (s), 691 (s), 658 (w), 618 (m), 560 (w), 540 (w), 475 (m) cm^{-1}.

W_2(O-*i*-Pr)$_6$(O_2C_2(C_7H_7)$_2$)$_2$ was prepared from the reaction between W_2(O-*i*-Pr)$_6$(py)$_2$ and 4,4′-dimethylbenzil (2 equiv) in a manner similar to that described for W_2(O-*i*-Pr)$_6$($O_2C_2Ph_2$)$_2$. The 4,4′-dimethylbenzil compound is appreciably less soluble in hydrocarbon solvents than its benzil analogue. Crystals suitable for X-ray work were grown from the mother liquor.

Anal. Calcd for W_2(O-*i*-Pr)$_6$(O_2C_2(C_7H_7)$_2$)$_2$: C, 50.1; H, 5.90. Found: C, 51.0; H, 5.90.

^{1}H NMR data, δ (toluene-d_8, +16 °C): O-*i*-Pr 1.37 (24 H), 1.62 (12 H), 5.42 (4 H), 5.69 (2 H); *p*-tolyl 2.09 (6 H), 2.14 (6 H); aromatic 6.85, 7.01, 7.41, 7.76 (16 H).

IR data: 2900 (s), 1588 (w), 1510 (m), 1498 (w), 1460 (s), 1378 (s), 1362 (m), 1328 (w), 1260 (m), 1210 (w), 1178 (w), 1161 (m), 1138 (m), 1105 (s), 1061 (s), 1018 (w), 985 (s), 932 (m), 921 (m), 858 (w), 839 (s), 820 (s), 718 (m), 690 (s), 640 (w), 612 (s), 600 (s), 530 (m), 500 (w), 489 (w), 469 (w), 401 (w) cm^{-1}.

Preparation of W_2(O-*i*-Pr)$_6$($O_2C_2Me_2$)$_2$. W_2(O-*i*-Pr)$_6$(py)$_2$ (550 mg, 0.625 mmol) was suspended in hexane (10 mL). Diacetyl (0.041 mL, 0.625 mmol) was added via microsyringe. A black precipitate formed immediately. Toluene (3 mL) was added to the suspension, and after 10 min of stirring all the precipitate had dissolved. The solution was cooled to −15 °C, slowly yielding large black crystals that were collected by filtration and dried in vacuo. These were used for X-ray and other spectroscopic studies.

Anal. Calcd for W_2(O-*i*-Pr)$_6$($O_2C_2Me_2$)$_2$: C, 34.9; H, 6.01. Found: C, 34.2; H, 5.65.

^{1}H NMR data, δ (toluene-d_8, +16 °C): O-*i*-Pr 1.12 (24 H), 1.52 (12 H), 5.45 (4 H), 5.58 (2 H); O_2C_2*Me*$_2$ 1.91 (6 H), 2.27 (6 H).

^{13}C NMR data, δ (benzene-d_6, +16 °C): O-*i*-Pr methyl carbons 23.5 (8 C), 25.2 (4 C); methyne carbons 74.5 (4 C), 78.0 (2 C);

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(21) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1972**, *10*, 335.

(22) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

Table VIII. Summary of Crystallographic Data

	I[a]	II[b]
fw	894.41	1198.80
space group	$P\bar{1}$	$P2_1/a$
a, Å	22.127 (14)	20.124 (12)
b, Å	9.750 (4)	9.735 (4)
c, Å	9.361 (4)	12.651 (7)
α, deg	76.11 (3)	
β, deg	64.27 (3)	90.23 (3)
γ, deg	69.03 (3)	
Z	2	2
V, Å	1690.13	2478.40
d(calcd), g/cm^3	1.758	1.606
cryst size, mm	0.03 × 0.03 × 0.03	0.06 × 0.12 × 0.08
cryst color	black	black
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromator	
linear abs coeff, cm^{-1}	69.92	47.90
transmission factors	no absorp corr	0.612–0.745
temp, °C	−162	−158
instrument	Picker 4-circle diffractometer locally modified and interfaced	
detector aperture	3.0 mm wide × 4.0 mm high; 22.5 cm from crystal	
sample to source dist	23.5 cm	
takeoff angle, deg	2.0	2.0
scan speed, deg/min	3.0	3.0
scan width, deg	1.8 + 0.692 tan (θ)	1.8 + 0.692 tan (θ)
bkgd counts, s	4 at each end of scan	4 at each end of scan
2θ range, deg	6–45	6–45
data collcd	3704 total	4603 total
no. of unique data	3168	3266
no. of unique data with $F_o > 3\sigma(F_o)$	3162	2768
no. of variables	362	280
$R(F)$	0.029	0.069
$R_w(F)$	0.034	0.066
goodness of fit	0.991	1.851
largest Δ/σ	0.05	0.05

[a] I = $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$. [b] II = $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(tol)_2)_2$.

$O_2C_2Me_2$ methyl carbons 16.2 (2 C), 20.0 (2 C); $O_2C_2Me_2$ 139.0 (2 C), 141.5 (2 C).

IR data: 2900 (s), 1632 (w), 1430 (s), 1375 (s), 1361 (s), 1325 (m), 1260 (w), 1222 (m), 1160 (w), 1138 (m), 1110 (s), 1005 (s), 971 (s), 928 (s), 860 (w), 834 (s), 761 (m), 610 (s), 600 (s), 550 (w), 485 (w), 465 (w), 290 (w) cm^{-1}.

UV–visible absorptions in hexane solution: λ_{max} 287 nm (ϵ 21 365), 385 (8595), 520 (3280).

X-ray Structural Determinations. General operating procedures and computational techniques have been described.[23]

Structure of $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$. Crystal and experimental data are given in Table VIII. The structure was solved by Patterson and Fourier techniques. Two independent molecules, each located at a crystallographic center of inversion, were located. One of the isopropoxy groups of one molecule was disordered, although the disorder was resolvable. Hydrogen atoms were located and included as fixed idealized contributors in the final refinement. Automated ψ scans of several reflections indicated no absorption correction was necessary. A final difference Fourier was featureless, the largest peak being 0.8 e/Å^3. Complete listings of bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors are available as supplementary data.

Structure of $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(p\text{-}tol)_2)_2$. Crystal and experimental data are given in Table VIII. All samples examined consisted of irregular clumps of thin plates, and attempts to obtain a single crystal were unsuccessful. A sample was finally located in which two distinct crystals were present, one being a minor component where diffraction was ca. 10% that of the major fragment. Data were collected on the larger crystal in the usual manner, and after processing, 23 reflections were rejected by using a procedure that examined reciprocal space for possible interference from the fragment. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and included as idealized fixed-atom contributors. A final difference Fourier was featureless, the largest peak being 1.1 e/Å^3. Complete listings of bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors are available as supplementary data.

Acknowledgment. We thank the National Science Foundation for financial support and the Marshall H. Wrubel Computing Center for computing facilities. A.L.R. is the Indiana University 1982/83 SOHIO Fellow.

Registry No. III (R = Pr-*i*, R′ = Ph), 87761-98-6; III (R = Bu-*t*, R′ = Ph), 87761-99-7; III (R = Pr-*i*, R′ = C_7H_7), 87762-00-3; III (R = Pr-*i*, R′ = Me), 87762-01-4; $W_2(O\text{-}i\text{-}Pr)_6$, 71391-16-7; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5.

Supplementary Material Available: Complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and structure factor amplitudes for $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2Me_2)_2$ and $W_2(O\text{-}i\text{-}Pr)_6(O_2C_2(C_7H_7)_2)_2$ (51 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC 82071 and 82086, are available from the Indiana University Library in microfiche form only, at $2.50 per report.

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