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Novel Products in the Carbonylation of the Triply Bonded Ditungsten Hexaisopropoxide Dipyridine Adduct. 2. Preparation and Structure of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$, a Molecule Containing Two Atoms of the Same Metallic Element with Oxidation Numbers Differing by Six Units

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Abstract: Short exposure of $W_2(O\text{-}i\text{-}Pr)_6py_2$ to approximately 2 molar equiv of CO gas in toluene led to the isolation of two crystalline products, $[W_2(O\text{-}i\text{-}Pr)_6(CO)py]_2$ (**1**) and $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ (**2**). The preparation and properties of **1** have already been described elsewhere,[1] and we now report the structural characterization of **2**. This compound crystallizes in the space group $P2_1/n$ with the following cell dimensions: a = 9.729 (8) Å, b = 31.622 (19) Å, c = 10.601 (9) Å, β = 111.67 (8)°, V = 3031 (5) Å^3, Z = 4. The crystals consist of an ordered array of discrete molecules. Molecular dimensions and IR data favor a description as a dinuclear complex in which a $W(O\text{-}i\text{-}Pr)_6$ molecule serves as a chelating bidentate ligand to a $W(CO)_4$ moiety. In the $W(O\text{-}i\text{-}Pr)_6$ moiety, the four W-O bonds to nonbridging O-*i*-Pr groups have an average length of 1.86 (2) Å while those to bridging O-*i*-Pr groups average 1.96 (1) Å. The (μ-*i*-PrO)-$W(CO)_4$ bond lengths average 2.25 (1) Å. The $(RO)_2W(CO)_4$ moiety is essentially octahedral, with the M-CO distances trans and cis to the W-O bonds being 1.89 (1) and 1.97 (3) Å, respectively. The interaction between the W atoms is repulsive, and the W-W distance is 3.410 (1) Å. The structure was refined to reliability indices of R = 0.048 and R_w = 0.058.

Cleavage of the intermetallic triple bond in $M_2(OR)_6$ (M = Mo, W) by carbon monoxide is known to proceed in several steps.[2] In all reported cases the primary intermediate is formed by addition of one CO molecule across the metal-metal bond.[2-4] The reaction mixture, after exhaustive carbonylation, contains in the case of $Mo_2(O\text{-}i\text{-}Pr)_6$ predominantly $Mo(CO)_6$ and $Mo_2(O\text{-}i\text{-}Pr)_8$.[3] For the analogous reaction with $W_2(O\text{-}i\text{-}Pr)_6py_2$ only $W(CO)_6$ has so far been positively identified, although there is IR and NMR evidence for intermediates.

We now report that there are conditions under which carbonylation of $W_2(O\text{-}i\text{-}Pr)_6py_2$ leads to a novel binuclear compound that is of interest from a mechanistic as well as structural point of view. This compound formally results from the addition of four CO molecules with accompanying extrusion of pyridine. It is a binuclear complex with the tungsten atoms in formal oxidation states VI and 0 and a repulsive interaction between the metal atoms. Its crystal structure has been determined, and the above interpretation is supported by IR data. $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ can be viewed as the last binuclear species within a complex reaction scheme. It decomposes in solution without a supply of CO to $W(CO)_6$ and tungsten compounds of higher oxidation states which have so far not been identified.

Experimental Section

General procedures, including the preparation of $W_2(O\text{-}i\text{-}Pr)_6py_2$, have been reported.[5]

Preparation of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$. A weighted amount (300 mg; 0.342 mmol) of $W_2(O\text{-}i\text{-}Pr)_6py_2$ was placed in a Schlenk flask. Toluene (ca. 15 mL) was added up to a predetermined level so as to leave a gas volume of 30 mL. The solution was frozen in liquid N_2, and the gas volume was evacuated and backfilled with CO gas. The reaction mixture was allowed to reach room temperature under stirring. The gas volume was then purged with argon, and the flask was sealed and placed into a −20 °C cold room. The first crystals to appear were red plates of $[W_2(O\text{-}i\text{-}Pr)_6(CO)py]_2$[1] (after 24 h). Black prismatic crystals of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ started growing after 36 h. Product yields depend critically on the reaction conditions; typically a 3:2 ratio in favor of the monocarbonyl adduct was observed, with an approximately 80% combined yield. Once the crystals of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ are formed, they are scarcely soluble in hexane or tetrachloroethane whereas the monocarbonyl adduct exhibits a limited solubility in both of these solvents.

Table I. Crystallographic Data

formula	$W_2(O\text{-}i\text{-}Pr)_6(CO)_4$; $W_2O_{10}C_{22}H_{42}$
formula weight	834.3
space group	$P2_1/n$
a, Å	9.729 (8)
b, Å	31.622 (19)
c, Å	10.601 (9)
β, deg	111.67 (8)
V, Å^3	3031. (5)
Z	4
d_{calcd}, g/cm^3	1.828
cryst size, mm	0.4 × 0.4 × 0.15
μ (Mo Kα), cm^{-1}	77.9
data collection instrument	Syntex P$\bar{1}$
radiation	Mo Kα
scan method	$\omega/2\theta$
data collection range	4°-50° (2θ)
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	2637
no. of parameters refined	307
R^a	0.048
$R_w{}^b$	0.058
quality-of-fit indicator^c	1.077
largest shift/esd, final cycle	0.29
decay during data collection 49.6% (isotropic), corrected	
absorption correction semiempirical (ψ scan)	

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

X-ray Crystallography. A black prismatic crystal of approximate dimensions 0.4 × 0.4 × 0.15 mm was wedged into a glass capillary, which was afterwards sealed at both ends. All dimensions were determined on a Syntex P$\bar{1}$ diffractometer from 15 centered reflections with $2\theta \geq 24°$. The space group $P2_1/n$ is uniquely determined by the systematic absences. During data collection the three standard reflections that were monitored after every 100 data suffered a 49.6% isotropic decay. For

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Table II. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
W(1)	0.22563 (7)	0.37039 (2)	0.72709 (7)	2.59 (1)
W(2)	0.30520 (9)	0.39318 (3)	1.06103 (8)	3.56 (2)
O(1)	0.345 (1)	0.4057 (4)	0.673 (1)	4.0 (3)
O(2)	0.101 (1)	0.3306 (4)	0.762 (1)	3.9 (3)
O(3)	0.293 (1)	0.3249 (4)	0.653 (1)	4.4 (3)
O(4)	0.073 (1)	0.3885 (4)	0.576 (1)	3.8 (3)
O(5)	0.383 (1)	0.3643 (4)	0.906 (1)	3.5 (3)
O(6)	0.175 (1)	0.4111 (4)	0.843 (1)	3.4 (3)
O(7)	0.523 (2)	0.3585 (6)	1.331 (2)	6.9 (5)
O(8)	0.152 (2)	0.4390 (7)	1.230 (2)	12.8 (6)
O(9)	0.086 (2)	0.3235 (6)	1.077 (2)	9.7 (5)
O(10)	0.499 (2)	0.4743 (7)	1.138 (2)	10.6 (8)
C(1)	0.359 (2)	0.4291 (5)	0.561 (2)	4.6 (5)
C(2)	0.279 (3)	0.4720 (8)	0.547 (3)	7.9 (8)
C(3)	0.524 (2)	0.4308 (9)	0.582 (2)	7.6 (7)
C(4)	0.047 (3)	0.2876 (7)	0.726 (3)	6.1 (7)
C(5)	0.147 (3)	0.2594 (9)	0.840 (3)	8.2 (9)
C(6)	−0.112 (3)	0.288 (1)	0.727 (4)	11 (1)
C(7)	0.375 (2)	0.3133 (8)	0.579 (2)	5.9 (6)
C(8)	0.459 (3)	0.2700 (9)	0.638 (3)	8.9 (9)
C(9)	0.283 (3)	0.3049 (9)	0.431 (2)	7.6 (8)
C(10)	−0.081 (2)	0.3820 (8)	0.495 (2)	5.8 (7)
C(11)	−0.087 (3)	0.3471 (9)	0.386 (3)	8.0 (8)
C(12)	−0.145 (3)	0.425 (1)	0.422 (3)	9.0 (9)
C(13)	0.535 (2)	0.3517 (9)	0.926 (2)	6.1 (7)
C(14)	0.567 (3)	0.3110 (8)	1.017 (3)	8.6 (8)
C(15)	0.643 (2)	0.389 (1)	0.987 (3)	8.1 (8)
C(16)	0.068 (2)	0.4463 (6)	0.797 (2)	4.1 (5)
C(17)	0.140 (3)	0.4886 (8)	0.869 (3)	8.3 (8)
C(18)	−0.068 (2)	0.4317 (8)	0.838 (3)	6.9 (7)
C(19)	0.436 (2)	0.3706 (8)	1.227 (2)	5.3 (5)
C(20)	0.213 (2)	0.4216 (8)	1.165 (2)	5.8 (6)
C(21)	0.163 (2)	0.3483 (9)	1.056 (2)	6.3 (6)
C(22)	0.428 (3)	0.4446 (8)	0.094 (3)	7.5 (8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

this reason the data set used to solve and refine the structure was one in which the outer shell ($35° \leq 2\theta \leq 50°$) was collected first. Data were afterwards corrected for linear decay and also absorption by using a semiempirical, ψ-scan method. The positions of the tungsten atoms were determined from a three-dimensional Patterson map. The rest of the non-hydrogen atoms were located by a combination of least-squares and Fourier techniques. Refinement proceeded uneventfully. Data pertaining to crystallographic measurements and structure refinement are given in Table I.

IR Measurements. A crystalline sample (approximately 50 mg) of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ was carefully washed with hexane to remove all traces of $W_2(O\text{-}i\text{-}Pr)_6(CO)py$ and was dissolved in dry, air-free CH_2Cl_2. Spectra were recorded on a Perkin-Elmer 283B IR spectrometer.

Results and Discussion

The reaction of carbon monoxide with $W_2(O\text{-}i\text{-}Pr)_6py_n$ can take a number of different courses depending on conditions. When $n = 0$, i.e., when $W_2(O\text{-}i\text{-}PR)_6$ itself is the reactant, a rather complex and not fully characterized product is obtained.[6] At the other extreme, when $n = 2$ and an excess of pyridine is present, one obtains, initially, a simple, binuclear monocarbonyl product, $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CO)py_2$,[3] which has a molybdenum analogue.[3,4] When $W_2(O\text{-}i\text{-}Pr)_6py_2$ is used with no additional pyridine present, the course of the reaction is dependent on the contact time between the CO and the starting complex.

We find that the dimeric monocarbonyl adduct **1** is reasonably stable with respect to CO attack and can be isolated in pure form and high yields provided that the contact time is limited to a few minutes and that a suitable solvent system is chosen.[1] At the other extreme, long reaction times such as 12 h lead to a complex mixture of products from which we were only able to isolate $W(CO)_6$ in pure form. The conditions leading to $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ involve a contact time of ca. 20 min at room temperature, subsequent purging of the gas volume with argon (but not degassing of the solution), and crystallization at −20 °C. The properties of **2**, i.e., its insolubility in nonpolar solvents and its instability in solution, suggest that it may be formed and thereafter trapped in crystalline form in the cold, either by reaction of **1** with dissolved carbon monoxide or by disproportionation of **1**. Thus, **2** could be regarded as a true intermediate, achieving only a steady-state concentration at higher temperatures even with a substoichiometric supply of carbon monoxide.

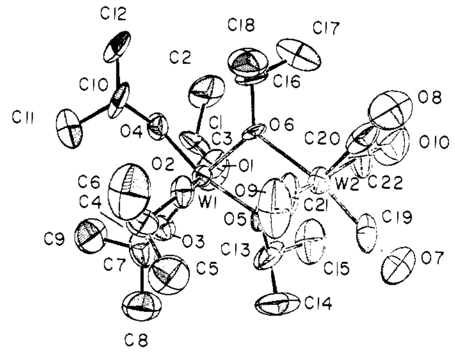

Figure 1. ORTEP view of the $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ molecule, defining the atom labeling scheme. Each atom is represented by its ellipsoid of thermal vibration scaled at the 40% level. W(1) is in the $W(O\text{-}i\text{-}Pr)_6$ moiety and W(2) in the $W(CO)_4$ moiety.

Table III. Relevant Bond Lengths and Angles for $W_2(O\text{-}i\,Pr)_6(CO)_4$

	Bond Lengths, Å		
W(1)-W(2)	3.410 (1)	W(2)-C(19)	1.89 (3)
-O(1)	1.852 (11)	-C(20)	1.89 (3)
-O(2)	1.876 (12)	-C(21)	1.97 (2)
-O(3)	1.873 (12)	-C(22)	1.97 (3)
-O(4)	1.826 (15)	O(7)-C(19)	1.18 (3)
-O(5)	1.955 (12)	O(8)-C(20)	1.19 (3)
-O(6)	1.967 (12)	O(9)-C(21)	1.16 (3)
W(2)-O(5)	2.239 (12)	O(10)-C(22)	1.16 (3)
-O(6)	2.258 (12)		
	Bond Angles, deg		
O(1)-W(1)-O(2)	172.8 (6)	O(6)-W(2)-C(19)	168.1 (8)
-O(3)	88.5 (6)	-C(20)	105.6 (8)
-O(4)	86.5 (6)	-C(21)	91.7 (8)
-O(5)	90.3 (6)	-C(22)	93.0 (8)
-O(6)	97.6 (6)	C(19)-W(2)-C(20)	86. (1)
O(2)-W(1)-O(3)	85.5 (6)	-C(21)	89. (1)
-O(4)	90.6 (6)	-C(22)	89. (1)
-O(5)	94.1 (6)	C(20)-W(2)-C(21)	83. (1)
-O(6)	89.0 (6)	-C(22)	84. (1)
O(3)-W(1)-O(4)	99.9 (6)	C(21)-W(2)-C(22)	166. (1)
-O(5)	93.5 (6)	W(1)-O(5)-W(2)	108.6 (3)
-O(6)	167.1 (6)	-O(6)-W(2)	107.4 (4)
O(4)-W(1)-O(5)	166.1 (6)	W(2)-C(19)-O(7)	176. (1)
-O(6)	91.8 (5)	-C(20)-O(8)	179. (1)
O(5)-W(1)-O(6)	75.2 (5)	-C(21)-O(9)	169. (1)
-W(2)-O(6)	64.3 (4)	-C(22)-O(10)	168. (1)
-W(2)-C(19)	103.8 (8)		
-C(20)	169.9 (8)		
-C(21)	96.5 (9)		
-C(22)	97.0 (8)		

Structural Characterization. The crystal structure of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ consists of a well-ordered array of discrete molecules (Figure 1). Atomic coordinates with equivalent isotropic temperature factors are listed in Table II. Relevant bond lengths and angles are in Table III. An overall description of the geometry is that of two edge-sharing octahedra. The coordination sphere of W(1) consists exclusively of isopropoxide residues. There are four shorter bonds between W(1) and the terminal OR groups (1.83 (2) to 1.88 (1) Å) and two somewhat longer bonds to the bridging ones, ca. 1.96 Å. The latter are, however, significantly shorter than the W–O distances typical for symmetrically bridging

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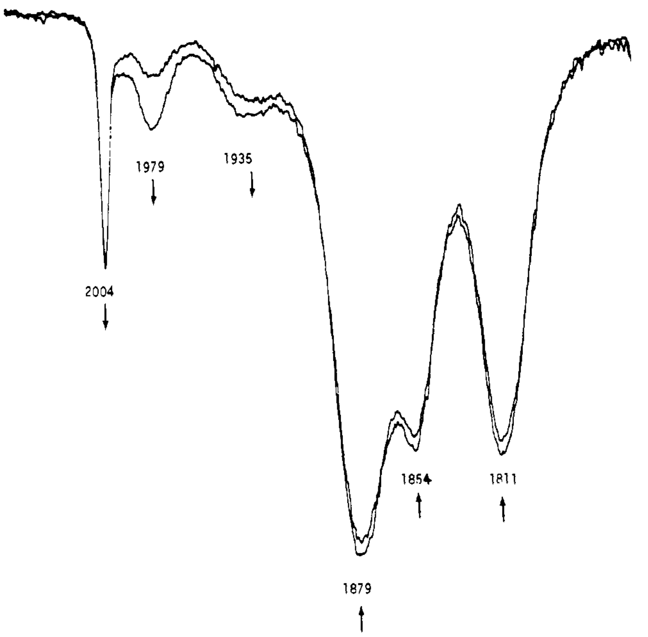

Figure 2. Infrared spectrum of $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ in the CO-stretching region. (a) Upper curve recorded 5 min after dissolving the sample in CH_2Cl_2. (b) Lower curve recorded after 10 min.

alkoxide groups, e.g., 2.012 (14) and 2.075 (14) Å in $W_2(O\text{-}i\text{-}Pr)_6(CO)$.[1]

The $W(CO)_4$ group—aside from having another W atom as a neighbor—to a large extent resembles the $W(CO)_4$ group in a conventional disubstituted tungsten carbonyl compound ($L_2W(CO)_4$). Although the differences are not statistically significant, there appear to be shorter W–C distances for the CO ligands trans to the bridging alkoxides as compared to their cis counterparts. Simultaneously the CO bond lengths are both longer in the trans CO groups.

The W–W distance, 3.410 (1) Å, is clearly outside the range of W–W single bonds. It was noted before[7] that when two octahedra are joined without distortion on a common element, face or edge, the metal atoms make a contact that is repulsive in the absence of M–M bond formation. This will cause them to move away from each other, thus causing various angle distortions in the structure. This effect can clearly be observed in the (μ-O)–W–(μ-O) angles 75.2 (5)°, 64.3 (4)°), which are decreased, and the W–(μ-O)–W angles (108.6 (3)°, 107.4 (4)°), which are increased. The W–W distance is longer than that expected for a rectangular bridged system, viz., about 3.00 Å.

We find that the totality of the structural evidence supports a formulation of the compound as a substituted tungsten carbonyl in which two cis CO groups have been replaced by donor atoms of the bidentate neutral ligand $W(O\text{-}i\text{-}Pr)_6$. This conclusion is fully supported by the infrared spectrum in the CO-stretching region, shown in Figure 2a. The four observed peaks at 2004, 1879, 1854, and 1811 cm^{-1} can be assigned to A_1, B_1, A_1, and B_2 vibrations, as in numerous other cis-disubstituted group 6 hexacarbonyls.[8] The pattern of intensities as well as the actual frequencies are very similar to the main features of the spectra for conventional *cis*-$W(CO)_4L_2$ complexes such as $W(CO)_4$en, in which the frequencies are 2006, 1867, 1852, and 1809 cm^{-1}.[8] It can thus be concluded that the $W(O\text{-}i\text{-}Pr)_6$ moiety is serving essentially as a bidentate ligand with no significant π-acceptor ability.

The binuclear compound is unstable in CH_2Cl_2, and its decomposition can be followed in the infrared spectrum. A broad peak (already noticeable in Figure 2a) around 1935 cm^{-1} appears within 5 min after the solution is made. After about 5 more min, another peak begins to appear at 1980 cm^{-1} These results can be seen in Figure 2b. The peak at 1935 cm^{-1} can plausibly be assigned to a $LW(CO)_5$ species and the one at 1980 cm^{-1} could well be assigned to $W(CO)_6$. The former peak seems to reach a steady-state intensity, while the latter continues to grow. Evidently, a decomposition process in which carbonyl groups are transferred to generate, successively, a pentacarbonyl intermediate and then $W(CO)_6$ is suggested by our observations.

Perhaps the most extraordinary thing about $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$ is that it contains two atoms of the same element in different oxidation states that differ by *six* units. We know of no prior example of such an enormous difference, and there are few examples of differences that even approach it. The closest case we have been able to find is the compound $(\eta\text{-}C_5H_5)_2W(\mu\text{-SPh})W(CO)_4$[9] where the metal atoms have oxidation states of IV and 0.

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Registry No. 2, 86350-17-6; $W_2(O\text{-}i\text{-}Pr)_6Py_2$, 70178-75-5.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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