on each of the three ring nitrogen atoms. There is a close, hydrogen-bonded contact made by each of these N–H groups with an adjacent chlorine atom, at distances of 2.2–2.4 Å. We have previously observed such bonds in $[Mo_2(O_2CC_5H_4NH)_4Cl_2]Cl_2 \cdot nH_2O$, where the (N–H)···Cl distance is 2.22 (4) Å.[21] The average bond distances for the three Hmhp ligands are summarized in Figure 4. These results do not distinguish between the reasonable resonance contributors to the electronic structure, D, E, E′, and probably all three are contributors.

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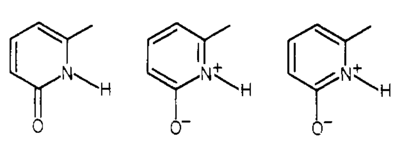
D E E′

Registry No. $V_2O_2Cl_4(\mu\text{-Hmhp})_3 \cdot CH_2Cl_2$, 83801-80-3; $VCl_3 \cdot 3THF$, 19559-06-9.

Supplementary Material Available: Tables of observed and calculated structure factors, thermal parameters (Table IIB), hydrogen atom parameters (Tables IIC and IV), and torsion angles (Table V) (19 pages). Ordering information is given on any current masthead page.

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[21] Cotton, F. A.; Roth, W. J., unpublished results.

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Preparation and Structure of Crystalline Tetrakis(D-mandelato)dimolybdenum(II) Bis(tetrahydrofuranate)

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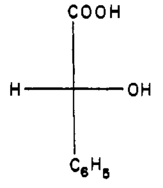
The preparation and structural characterization of the quadruply bonded, chiral dimolybdenum complex $Mo_2(C_8H_7O_3)_4$ are reported. Reaction of an aqueous solution of the Mo_2^{4+} unit with an aqueous solution of D-mandelic acid yielded the yellow product, which was recrystallized from a mixture of tetrahydrofuran and hexane. The crystals were found to be orthorhombic, in space group $P2_12_12_1$, with unit cell dimensions a = 13.199 (3) Å, b = 22.302 (9) Å, c = 27.289 (6) Å, V = 8033 (7) Å^3, and Z = 8. The asymmetric unit consists of two molecules of the molybdenum dimer and four uncoordinated molecules of tetrahydrofuran (THF, C_4H_8O). The two independent molecules are almost identical, with Mo$\overset{4}{-}$Mo distances of 2.104 (1) and 2.101 (1) Å. A network of hydrogen bonds connects the extended structure. The absolute configuration has been determined and is in agreement with previous conformational analyses of mandelic acid by chemical means.

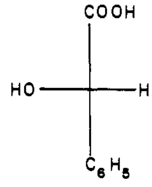
Introduction

The preparation and study of compounds in which chiral ligands are coordinated to the Mo_2^{4+} unit traces back to work done several years ago in this laboratory on substances in which the ligands were amino acids.[2-4] The two compounds that have previously been subjected to X-ray crystallographic study are $[Mo_2(\text{L-leu})_4]Cl_2(CH_3C_6H_4SO_3)_2 \cdot 2H_2O$[3] and $[Mo_2(\text{L-isoleu})_2(NCS)_4] \cdot 4^1/_2H_2O$.[4] More recently, as the result of work by G. Snatzke and co-workers,[5-7] there has been a new impetus for the study of such substances, involving chiral ligands in general and not just amino acids. They have shown that chiral carboxylic acids as well as other chiral organic molecules with functionalities capable of coordinating to the Mo_2^{4+} unit can give rise to conveniently measurable CD and ORD spectra in the visible region when small amounts of $Mo_2(O_2CCH_3)_4$ are added to their solutions. Presumably, partial replacement of CH_3CO_2 takes place and the chirality of the replacing ligand imposes the observed Cotton effects on the Mo_2^{4+} chromophore. It has even been possible to develop empirical quadrant rules for correlating the signs of the observed CD and ORD effects with absolute configurations. However, an explicit and fundamental examination of these effects using well-defined Mo_2^{4+}-containing molecules is lacking.

We have been engaged in such a fundamental investigation, and we provide here our first report, which deals with the preparation and structural characterization of a compound containing the D-mandelate anion (I). This was one of the chiral substances covered by Snatzke's survey, and the mandelate ion has also been mentioned in a recent Russian publication.[8] However, the latter paper is largely if not entirely concerned with racemic mandelic acid and it does not,



I (R)



II (S)

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in any case, provide information on either the structure or the optical activity of complexes.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of oxygen-free argon. Organic solvents, with the exception of ethanol, were distilled from a Na–K alloy immediately before use and transferred by syringe. Oxygen-free water and ethanol were prepared either by alternate freezing and thawing in vacuo or by prolonged boiling under an argon atmosphere. $K_4Mo_2(SO_4)_4$ was made according to the published procedure.[9] $Ba(OH)_2{\cdot}8H_2O$, trifluoromethanesulfonic acid (HTFMS), and D-mandelic acid were used as supplied.

Preparation of an Aqueous Solution of Mo_2^{4+}. A solution 0.10 M in $Ba(TFMS)_2$ and 1 M in HTFMS was prepared in water. A stoichiometric amount (1:4 mole ratio) was added to 0.20 g of $K_4Mo_2(SO_4)_4$ (0.27 mmol). After 1 h of stirring at room temperature, the resulting bright red aqueous solution was separated by filtration from the precipitate of $BaSO_4$.

Preparation of Mo_2(D-man)$_4$·2THF (D-man = D-mandelato). A 5-mL portion of the aqueous solution of Mo_2^{4+} (0.11 mmol) was added to 0.20 g of D-mandelic acid (1.3 mmol) dissolved in 5 mL of water. The color changed immediately to yellow, and a precipitate formed. The yellow solid was filtered and quickly washed with small portions of cold water, ethanol, and ether. It was then dried under vacuum, dissolved in THF, and layered with hexane to produce crystals suitable for X-ray diffraction.

X-ray Data Collection and Reduction. A yellow, block-shaped crystal of approximate dimensions 0.5 × 0.4 × 0.3 mm was sealed inside a glass capillary tube, under an atmosphere of dry argon. All geometrical and intensity data were gathered from this crystal, by a computer-controlled four-circle X-ray diffractometer (Enraf-Nonius CAD-4) equipped with a molybdenum X-ray tube and a graphite monochromator.

A preliminary rotation photograph indicated that the crystal was of good quality. The automatic search procedure of the diffractometer was used to find 25 reflections for use in defining the unit cell. This was followed by a preliminary data collection, which was used to verify the Laue class (*mmm*) and to locate strong reflections for refinement of the unit-cell parameters. The latter were determined accurately by a least-squares fit to the goniometer positions of 25 accurately located reflections in the range $22° < 2\theta < 30°$. The unit-cell dimensions and other pertinent data are summarized in Table I.

A 2θ–ω motion was used to scan 10 048 possible data points in the range $2.5° \le 2\theta \le 50.0°$. Three standard reflections, scanned after every $^1/_2$ h of X-ray exposure, decreased in intensity by an average of 17.5% over the 152 h of beam time; a decay correction was included in the data reduction. Three orientation standards were checked after every 100 data scans. In addition, Friedel opposites were measured for approximately one-eighth of the reflections in a unique octant of the Laue class. Throughout data collection, the scan range in ω was calculated as $(0.90 + 0.35 \tan \theta)°$, and the speed of the ω motion was variable in the range 1.5–20.1°/min. The data were gathered in two stages—all measurements above 36° in 2θ were made first, followed by the lower-angle data. Azimuthal scans of several reflections with Eulerian angle χ near 90° indicated that an absorption correction was not necessary.

The data were processed by standard computer programs.[10] Lorentz and polarization corrections were applied, and structure factors were derived in the usual way. A decay correction was applied, and equivalent data were merged, leaving 6569 data (5384 with $F_o^2 \ge 3\sigma(F_o^2)$), which included 817 Friedel pairs (650 pairs with both members above 3σ). Systematic absences identified the space group as $P2_12_12_1$. Reflections $h0l$, $l = 2n + 1$ were systematically weak—but not absent—indicating the presence of pseudosymmetry.[11]

Structure Solution and Refinement. Most of the prominent peaks on the three-dimensional Patterson map had z coordinates of either 0 or $^1/_2$, a further indication of pseudosymmetry. On a Patterson map made from reflections with $2\theta > 35°$ (i.e., the self-convolution of the Mo pattern), 22 of the top 25 peaks had z coordinates of 0 or $^1/_2$. Correct positions were derived for the four unique molybdenum atoms and their sixteen coordinated carboxy oxygen atoms. While inclusion of these atoms brought the least-squares residual to about 25%, refinement of parameters for them led to chemically unreasonable results, and no further development of the structure occurred.

Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for Mo_2(D(−)-man)$_4$·2THF

formula	$Mo_2(C_8H_7O_3)_4{\cdot}2(C_4H_8O)$
fw	940.66 for $Mo_2C_{40}H_{44}O_{14}$
space group	$P2_12_12_1$
a, Å	13.199 (3)
b, Å	22.302 (9)
c, Å	27.289 (6)
V, Å^3	8033 (7)
Z	8
d_{calcd}, g/cm^3	1.56
cryst size, mm	0.5 × 0.4 × 0.3
μ(Mo Kα), cm^{-1}	6.87
data collection instrument	Enraf-Nonius CAD-4
radiation	Mo Kα (graphite-monochromated); $\lambda_{\bar{\alpha}} = 0.710\,73$ Å
scan method	2θ–ω
data collection range, deg	$2.5 \leqslant 2\theta \leqslant 50$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	5384
no. of parameters refined	829 (see text)
R^a	0.0496
$R_w{}^b$	0.0589
quality-of-fit indicator^c	1.485
largest shift/esd, final cycle	0.40

^{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 is equal to $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

The direct-methods program set MULTAN80 was used to find coordinates of a sufficient number of atoms to lead to successful development of the structure. The automatic phase-determination procedure was not successful, since the enantiomorph-defining reflection and one of the origin-fixing reflections were not used until over 100 phases had been assigned. A starting set was picked in such a way as to minimize the effects of this evident bifurcation in the phase-extension pathway. In addition, a statistically weighted tangent formula was used in phase determination.[12] This led to successful location of some 30 atoms; a sequence of alternate least-squares refinements and difference Fourier maps led to the identification of the remainder of the 112 non-hydrogen atoms in the crystallographic asymmetric unit.

Because of computer memory limitations, the final refinement was done in blocks. The two independent molybdenum dimers consist of 46 atoms each, and all of these were refined with anisotropic thermal parameters. The four THF molecules add another 20 non-hydrogen atoms, each with an isotropic temperature factor. The blocking of the final refinement was done as follows: First molecule 1 and the four THF's were refined to convergence, to account for possible correlation among their respective parameters. Then molecule 2 and the THF's were similarly refined to convergence. Finally the two dimers were refined together.

One of the THF molecules in the lattice refined with rather unreasonable bond lengths and angles. In addition, some bond distances and angles in the other THF molecules and in a few of the phenyl rings were not ideal after the final refinement. Attempts to refine several disordered models for the poorly defined THF led to unsatisfactory results. In the end, the atoms in question were allowed to refine freely to a chemically imperfect result, in order that their covariance-related effects on the other, chemically more interesting, parts of the structure would not be lost.

The final refinement of molecules 1 and 2 involved 92 atoms and a total of 829 parameters, which were fitted to 5384 reflections with $F_o^2 \ge 3\sigma(F_o^2)$. A set of 650 Friedel opposites in the data were treated as unique reflections, since anomalous dispersion effects would make

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(9) (a) Cotton, F. A.; Frenz, B. A; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391. (b) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287.

(10) Computing was done on a PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the Enraf-Nonius Structure Determination Package.

(11) A genuine glide plane here would have put the crystal in the impossible class $2m2$.

(12) Hull, S. E.; Irwin, M. J. *Acta Crystallogr., Sect. A* **1978**, *A34*, 863.

Table II. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(D(-)\text{-man})_4 \cdot 2THF^a$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.27856 (8)	0.58204 (4)	0.27189 (3)	2.64 (2)	C(33)	0.734 (1)	0.3252 (5)	0.1399 (4)	3.0 (2)
Mo(2)	0.16823 (8)	0.51410 (4)	0.26831 (4)	2.73 (2)	C(34)	0.727 (1)	0.3283 (5)	0.0836 (4)	4.7 (3)
O(1)	0.2635 (7)	0.6012 (3)	0.1966 (3)	3.8 (2)	O(21)	0.7996 (9)	0.2863 (5)	0.0647 (4)	7.4 (3)
O(2)	0.3945 (6)	0.5195 (3)	0.2533 (3)	3.1 (2)	C(35)	0.750 (1)	0.3913 (6)	0.0640 (4)	4.7 (4)
O(3)	0.2948 (6)	0.5719 (3)	0.3490 (3)	3.4 (2)	C(36)	0.672 (1)	0.4328 (6)	0.0680 (5)	5.7 (4)
O(4)	0.1632 (6)	0.6476 (3)	0.2856 (3)	2.7 (1)	C(37)	0.685 (2)	0.4883 (7)	0.0472 (6)	7.3 (5)
O(5)	0.1414 (7)	0.5287 (3)	0.1929 (3)	3.5 (2)	C(38)	0.768 (2)	0.5033 (8)	0.0265 (7)	9.0 (6)
O(6)	0.2750 (6)	0.4483 (3)	0.2483 (3)	3.1 (2)	C(39)	0.855 (2)	0.464 (1)	0.0237 (8)	10.2 (7)
O(7)	0.1800 (7)	0.4972 (3)	0.3449 (3)	3.8 (2)	C(40)	0.842 (2)	0.4075 (8)	0.0424 (6)	8.2 (5)
O(8)	0.0500 (6)	0.5750 (4)	0.2840 (3)	3.2 (2)	C(41)	0.5737 (9)	0.2289 (5)	0.2156 (4)	2.9 (2)
C(1)	0.193 (1)	0.5712 (5)	0.1733 (4)	4.1 (3)	C(42)	0.491 (1)	0.1880 (5)	0.1981 (5)	4.2 (3)
C(2)	0.175 (1)	0.5872 (5)	0.1204 (5)	4.7 (3)	O(22)	0.5261 (7)	0.1272 (4)	0.2075 (3)	4.1 (2)
O(9)	0.2564 (9)	0.6242 (5)	0.1030 (3)	6.5 (3)	C(43)	0.484 (1)	0.1970 (5)	0.1395 (5)	4.8 (3)
C(3)	0.073 (1)	0.6204 (5)	0.1151 (5)	4.6 (3)	C(44)	0.382 (1)	0.2101 (8)	0.1261 (7)	9.4 (5)
C(4)	0.056 (1)	0.6715 (8)	0.1465 (7)	7.4 (5)	C(45)	0.376 (1)	0.2186 (8)	0.0739 (8)	10.0 (5)
C(5)	−0.035 (1)	0.7057 (7)	0.1397 (9)	9.1 (6)	C(46)	0.462 (2)	0.2130 (7)	0.0421 (7)	8.8 (5)
C(6)	−0.104 (2)	0.6906 (9)	0.1010 (9)	11.4 (8)	C(47)	0.561 (2)	0.2010 (7)	0.0599 (6)	8.0 (5)
C(7)	−0.092 (2)	0.632 (1)	0.0741 (9)	13.0 (8)	C(48)	0.568 (1)	0.1898 (6)	0.1105 (5)	5.4 (4)
C(8)	0.011 (2)	0.602 (1)	0.0760 (8)	11.2 (7)	C(49)	0.694 (1)	0.2869 (5)	0.3350 (5)	4.0 (3)
C(9)	0.366 (1)	0.4663 (5)	0.2419 (5)	4.2 (3)	C(50)	0.678 (1)	0.2792 (5)	0.3888 (4)	5.3 (4)
C(10)	0.439 (1)	0.4240 (5)	0.2165 (4)	3.5 (3)	O(23)	0.7625 (9)	0.2507 (5)	0.4132 (3)	6.3 (3)
O(10)	0.5419 (7)	0.4353 (4)	0.2322 (3)	4.2 (2)	C(51)	0.575 (1)	0.2377 (7)	0.3936 (5)	6.2 (4)
C(11)	0.421 (1)	0.4317 (6)	0.1610 (4)	3.9 (3)	C(52)	0.556 (2)	0.1976 (9)	0.3534 (9)	9.8 (7)
C(12)	0.420 (1)	0.3803 (5)	0.1339 (5)	4.5 (3)	C(53)	0.472 (2)	0.159 (1)	0.363 (1)	16 (1)
C(13)	0.399 (1)	0.3865 (7)	0.0836 (6)	5.7 (4)	C(54)	0.412 (2)	0.160 (1)	0.402 (1)	18 (1)
C(14)	0.395 (1)	0.4408 (8)	0.0609 (5)	6.6 (4)	C(55)	0.430 (2)	0.2038 (9)	0.4465 (9)	16.5 (7)
C(15)	0.405 (1)	0.4920 (7)	0.0882 (6)	6.4 (4)	C(56)	0.521 (2)	0.244 (1)	0.4364 (9)	15.7 (7)
C(16)	0.418 (1)	0.4871 (6)	0.1396 (6)	5.0 (4)	C(57)	0.8685 (9)	0.3892 (5)	0.2666 (4)	3.5 (3)
C(17)	0.237 (1)	0.5328 (5)	0.3695 (4)	3.8 (3)	C(58)	0.9420 (9)	0.4310 (5)	0.2902 (4)	3.0 (3)
C(18)	0.231 (1)	0.5289 (6)	0.4249 (5)	6.0 (4)	O(24)	1.0429 (6)	0.4235 (3)	0.2725 (3)	3.2 (2)
O(11)	0.299 (1)	0.5711 (6)	0.4444 (4)	9.6 (4)	C(59)	0.9314 (9)	0.4245 (5)	0.3457 (4)	2.9 (2)
C(19)	0.250 (1)	0.4678 (7)	0.4451 (5)	6.2 (4)	C(60)	0.926 (1)	0.3698 (7)	0.3647 (5)	5.1 (4)
C(20)	0.177 (2)	0.4335 (8)	0.4593 (8)	9.6 (6)	C(61)	0.917 (1)	0.3639 (7)	0.4183 (5)	5.6 (4)
C(21)	0.200 (2)	0.3733 (9)	0.4791 (7)	10.3 (7)	C(62)	0.913 (1)	0.4191 (7)	0.4455 (6)	6.1 (4)
C(22)	0.294 (2)	0.3577 (9)	0.4809 (7)	11.3 (7)	C(63)	0.926 (1)	0.4731 (7)	0.4243 (5)	5.9 (4)
C(23)	0.360 (2)	0.393 (2)	0.462 (1)	25 (2)	C(64)	0.931 (1)	0.4766 (6)	0.3746 (5)	4.8 (3)
C(24)	0.347 (2)	0.451 (1)	0.446 (1)	20 (1)	O(25)	0.451 (1)	0.6865 (7)	0.6423 (6)	13.1 (5)*
C(25)	0.0756 (9)	0.6298 (5)	0.2902 (5)	3.3 (3)	C(65)	0.467 (2)	0.622 (1)	0.6509 (9)	12.4 (8)*
C(26)	−0.0053 (9)	0.6721 (5)	0.3054 (4)	3.1 (3)	C(66)	0.398 (2)	0.5880 (9)	0.6126 (7)	8.7 (5)*
O(12)	0.0245 (7)	0.7313 (4)	0.2956 (3)	4.2 (2)	C(67)	0.380 (2)	0.6316 (9)	0.5734 (7)	8.9 (5)*
C(27)	−0.021 (1)	0.6638 (5)	0.3617 (4)	3.5 (3)	C(68)	0.385 (2)	0.6897 (9)	0.5996 (8)	10.2 (6)*
C(28)	0.060 (1)	0.6690 (6)	0.3935 (5)	4.3 (3)	O(26)	0.1492 (9)	0.3265 (5)	0.3046 (4)	7.1 (3)*
C(29)	0.050 (1)	0.6604 (6)	0.4444 (5)	5.7 (4)	C(69)	0.198 (1)	0.2920 (8)	0.2647 (7)	8.2 (5)*
C(30)	−0.042 (1)	0.6464 (7)	0.4633 (6)	6.2 (4)	C(70)	0.298 (2)	0.276 (1)	0.2889 (9)	11.1 (7)*
C(31)	−0.124 (1)	0.6384 (7)	0.4335 (6)	7.3 (4)	C(71)	0.322 (2)	0.316 (1)	0.3273 (9)	11.3 (7)*
C(32)	−0.117 (1)	0.6453 (6)	0.3791 (6)	5.9 (4)	C(72)	0.208 (1)	0.3436 (7)	0.3442 (6)	7.1 (4)*
Mo(3)	0.66771 (8)	0.34317 (4)	0.23976 (3)	2.56 (2)	O(27)	0.659 (1)	0.5361 (6)	0.2010 (6)	11.3 (4)*
Mo(4)	0.77758 (8)	0.27513 (4)	0.23640 (4)	2.50 (2)	C(73)	0.716 (2)	0.5181 (9)	0.1645 (9)	10.7 (7)*
O(13)	0.6790 (7)	0.3590 (3)	0.1631 (3)	3.5 (2)	C(74)	0.819 (2)	0.536 (1)	0.179 (1)	13.4 (9)*
O(14)	0.5475 (6)	0.2831 (3)	0.2226 (3)	3.2 (2)	C(75)	0.812 (2)	0.586 (1)	0.217 (1)	13.4 (9)*
O(15)	0.6435 (6)	0.3272 (3)	0.3145 (3)	3.7 (2)	C(76)	0.703 (2)	0.589 (1)	0.229 (1)	17 (1)*
O(16)	0.7752 (6)	0.4070 (3)	0.2601 (3)	3.1 (2)	O(28)	0.577 (2)	0.5446 (9)	0.3514 (8)	18.8 (8)*
O(17)	0.7932 (6)	0.2875 (3)	0.1594 (3)	3.4 (2)	C(77)	0.610 (3)	0.548 (1)	0.398 (1)	19 (1)*
O(18)	0.6626 (6)	0.2102 (3)	0.2222 (3)	3.3 (2)	C(78)	0.622 (3)	0.481 (2)	0.420 (1)	23 (2)*
O(19)	0.7615 (7)	0.2566 (3)	0.3122 (3)	3.3 (2)	C(79)	0.656 (2)	0.462 (1)	0.3757 (9)	13.0 (8)*
O(20)	0.8952 (6)	0.3358 (3)	0.2548 (3)	3.3 (2)	C(80)	0.527 (2)	0.481 (1)	0.356 (1)	15 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

it undesirable to average them. The final cycle of least squares did not shift any parameter by more than 0.40 times its estimated standard deviation. The residuals (for the enantiomorph chosen, vide infra) were as follows: $R = 0.0496$; $R_w = 0.0589$; quality-of-fit indicator, 1.485. (These are summarized and defined in Table I.) A difference map at the end of refinement had no peak above 0.85 e/Å^3; the top peaks were near either a molybdenum atom or one of the THF molecules that had previously shown signs of disorder.

Positional parameters and isotropic-equivalent thermal parameters are given in Table II. Tables III and IV list the more important bond distances and bond angles, respectively. Tables of observed and calculated structure factors, anisotropic thermal parameters, and all bond lengths and angles are available as supplementary material. Figure 1 shows the atom-labeling scheme for molecules 1 and 2.

Determination of Absolute Configuration. The enantiomers of mandelic acid, represented by the Fischer projections I and II, have been distinguished by chemical means,[13,14] but there has not previously been a diffraction study of an optically pure mandelate moiety.[15] Our results are in agreement with the previous assignment[13] of D-mandelic acid to enantiomer I.

The absolute configuration was determined by an application of Hamilton's significance test[16] to the least-squares residuals from independent refinements of both enantiomorphs. The refinements involved fitting 829 parameters to 5384 data, thus giving 4555 degrees

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Table III. Important Bond Lengths (in Angstroms) and Their Estimated Standard Deviations for $Mo_2(D(-)\text{-man})_4{\cdot}2THF^a$

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo(1)	Mo(2)	2.104 (1)	Mo(3)	Mo(4)	2.101 (1)
Mo(1)	O(1)	2.108 (7)	Mo(3)	O(13)	2.126 (7)
Mo(1)	O(2)	2.132 (7)	Mo(3)	O(14)	2.129 (8)
Mo(1)	O(3)	2.126 (7)	Mo(3)	O(15)	2.094 (8)
Mo(1)	O(4)	2.145 (7)	Mo(3)	O(16)	2.085 (7)
Mo(2)	O(5)	2.114 (7)	Mo(4)	O(17)	2.130 (7)
Mo(2)	O(6)	2.106 (7)	Mo(4)	O(18)	2.133 (7)
Mo(2)	O(7)	2.128 (7)	Mo(4)	O(19)	2.121 (7)
Mo(2)	O(8)	2.113 (7)	Mo(4)	O(20)	2.119 (7)
O(1)	C(1)	1.309 (14)	O(13)	C(33)	1.229 (12)
O(2)	C(9)	1.285 (12)	O(14)	C(41)	1.271 (12)
O(3)	C(17)	1.291 (13)	O(15)	C(49)	1.255 (13)
O(4)	C(25)	1.229 (12)	O(16)	C(57)	1.307 (13)
O(5)	C(1)	1.283 (13)	O(17)	C(33)	1.261 (12)
O(6)	C(9)	1.273 (14)	O(18)	C(41)	1.258 (13)
O(7)	C(17)	1.281 (13)	O(19)	C(49)	1.274 (14)
O(8)	C(25)	1.278 (12)	O(20)	C(57)	1.282 (12)
C(1)	C(2)	1.508 (15)	C(33)	C(34)	1.541 (14)
C(2)	O(9)	1.44 (2)	C(34)	O(21)	1.434 (15)
C(2)	C(3)	1.54 (2)	C(34)	C(35)	1.53 (2)
C(9)	C(10)	1.523 (15)	C(41)	C(42)	1.50 (2)
C(10)	O(10)	1.440 (13)	C(42)	O(22)	1.455 (13)
C(10)	C(11)	1.544 (15)	C(42)	C(43)	1.61 (2)
C(17)	C(18)	1.516 (15)	C(49)	C(50)	1.49 (2)
C(18)	O(11)	1.41 (2)	C(50)	O(23)	1.45 (2)
C(18)	C(19)	1.49 (2)	C(50)	C(51)	1.65 (2)
C(25)	C(26)	1.485 (15)	C(57)	C(58)	1.491 (15)
C(26)	O(12)	1.403 (12)	C(58)	O(24)	1.427 (12)
C(26)	C(27)	1.560 (15)	C(58)	C(59)	1.528 (14)

^{a} Estimated standard deviations are given in parentheses for the least significant digits.

of freedom. The weighted R factors (R_w, defined in Table I) were 0.0589 for enantiomer I and 0.0599 for enantiomer II. The ratio of the two residuals, $R_w(\text{II})/R_w(\text{I}) = 1.017$, is larger than the relevant 1% significance point[17] ($R_{1,4555,0.01} = 1.0007$), and so enantiomer I is established at the 99% confidence level.

Least-squares residuals from the refinements of the two enantiomorphs are summarized in Table V; these include residuals based only on Friedel pairs and show an indisputable trend toward structure I.

The refinements of the two enantiomorphs, while giving significantly different R factors, did not result in any noteworthy differences in the refined or derived parameters. Both refinements converged with no parameter shift greater than 0.40.

Figure 2, a stereoscopic view of both independent dimers, shows clearly the conformations about all of the chiral α-carbon atoms.

Discussion of the Structure.

The two independent dinuclear complexes, with Mo–O bonds eclipsed and with Mo–Mo distances of 2.104 (1) and 2.101 (1) Å, have the well-known structure of quadruply bonded dimers.[18] Table VI, which summarizes average bond distances and angles in the coordination shells, shows that there are no unusual features involving these units.

The complexes are grouped into pairs bound by contacts between oxygen atoms of one complex and a molybdenum atom of the second and by hydrogen bonds between the two.

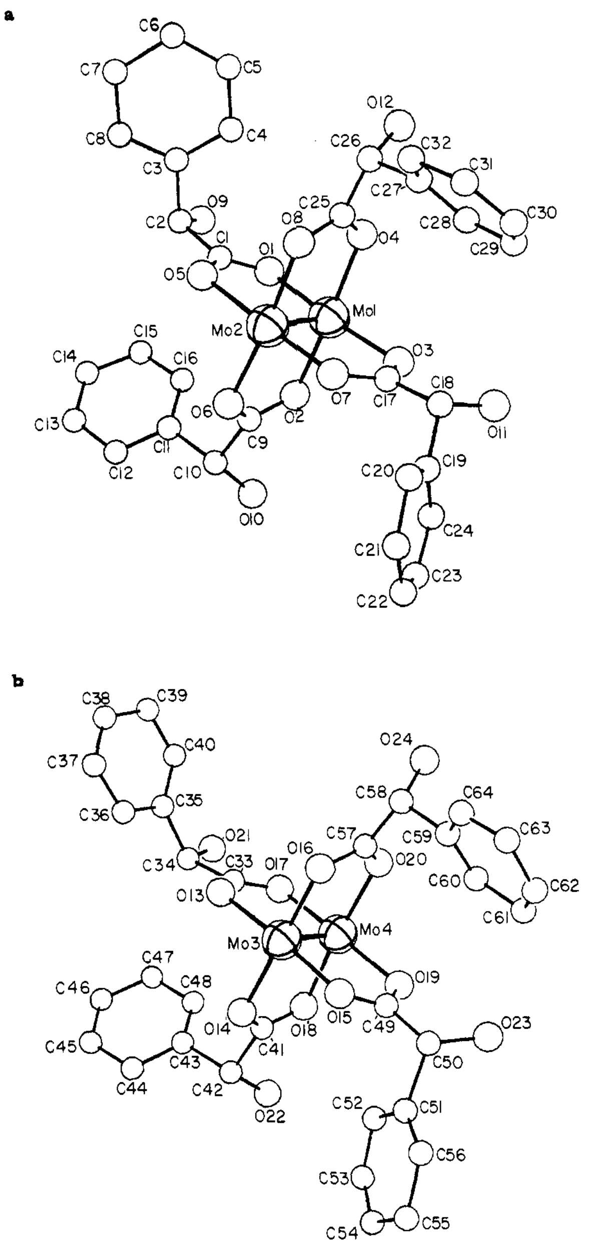

Figure 1. Molecular geometry and atom-labeling scheme for (a) molecule 1 and (b) molecule 2.

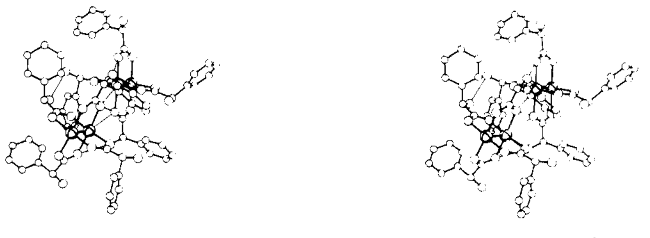

Figure 2. Stereoscopic view of the two independent dimers. Molecule 1 is drawn with shaded bonds.

Figure 2 shows one such pair of molecules. While several examples exist in which coordinated oxygen atoms of quadruply bonded units take part in weak axial interactions with adjacent molecules,[19] the present structure involves bifurcated interactions, in which two oxygen atoms have weak, quasi-axial

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[17] In line with Hamilton's procedure, a change of enantiomorph was treated as a one-dimensional hypothesis. The significance point $R_{1,4555,0.01}$ was calculated from the formula (Hamilton's eq 24):

$$R_{b,n-m,\alpha} = \left(\frac{b}{n-m}F_{b,n-m,\alpha} + 1\right)^{1/2}$$

Here, b is the dimension of the hypothesis, $n - m$ is the number of degrees of freedom, α is the confidence limit, and $F_{b,n-m,\alpha}$ is the analysis-of-variance ratio. The value of $F_{1,4555,0.01}$ was obtained by harmonic interpolation of the values in a standard compilation: Keeping, E. S. "Introduction to Statistical Inference"; Van Nostrand: Princeton, NJ, 1962.

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Table IV. Important Bond Angles (in Degrees) for Mo_2(D(−)-man)$_4$·2THF[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(2)	Mo(1)	O(1)	92.0 (2)	Mo(4)	Mo(3)	O(13)	91.7 (2)
Mo(2)	Mo(1)	O(2)	90.8 (2)	Mo(4)	Mo(3)	O(14)	92.9 (2)
Mo(2)	Mo(1)	O(3)	92.2 (2)	Mo(4)	Mo(3)	O(15)	91.4 (2)
Mo(2)	Mo(1)	O(4)	90.4 (2)	Mo(4)	Mo(3)	O(16)	92.0 (2)
O(1)	Mo(1)	O(2)	88.2 (3)	O(13)	Mo(3)	O(14)	86.6 (3)
O(1)	Mo(1)	O(3)	174.5 (3)	O(13)	Mo(3)	O(15)	175.2 (3)
O(1)	Mo(1)	O(4)	88.0 (3)	O(13)	Mo(3)	O(16)	95.8 (3)
O(2)	Mo(1)	O(3)	95.4 (3)	O(14)	Mo(3)	O(15)	89.6 (3)
O(2)	Mo(1)	O(4)	176.0 (3)	O(14)	Mo(3)	O(16)	174.5 (3)
O(3)	Mo(1)	O(4)	88.4 (3)	O(15)	Mo(3)	O(16)	87.8 (3)
Mo(1)	Mo(2)	O(5)	92.9 (2)	Mo(3)	Mo(4)	O(17)	90.9 (2)
Mo(1)	Mo(2)	O(6)	92.9 (2)	Mo(3)	Mo(4)	O(18)	90.4 (2)
Mo(1)	Mo(2)	O(7)	91.8 (2)	Mo(3)	Mo(4)	O(19)	91.7 (2)
Mo(1)	Mo(2)	O(8)	92.2 (2)	Mo(3)	Mo(4)	O(20)	92.0 (2)
O(5)	Mo(2)	O(6)	88.1 (3)	O(17)	Mo(4)	O(18)	88.7 (3)
O(5)	Mo(2)	O(7)	174.4 (3)	O(17)	Mo(4)	O(19)	176.2 (3)
O(5)	Mo(2)	O(8)	88.5 (3)	O(17)	Mo(4)	O(20)	94.6 (3)
O(6)	Mo(2)	O(7)	94.7 (3)	O(18)	Mo(4)	O(19)	88.5 (3)
O(6)	Mo(2)	O(8)	174.0 (3)	O(18)	Mo(4)	O(20)	176.0 (3)
O(7)	Mo(2)	O(8)	88.2 (3)	O(19)	Mo(4)	O(20)	88.1 (3)
Mo(1)	O(1)	C(1)	115.9 (7)	Mo(3)	O(13)	C(33)	116.6 (7)
Mo(1)	O(2)	C(9)	116.6 (8)	Mo(3)	O(14)	C(41)	115.4 (7)
Mo(1)	O(3)	C(17)	116.2 (7)	Mo(3)	O(15)	C(49)	118.3 (7)
Mo(1)	O(4)	C(25)	117.7 (6)	Mo(3)	O(16)	C(57)	118.0 (6)
Mo(2)	O(5)	C(1)	115.4 (7)	Mo(4)	O(17)	C(33)	116.3 (7)
Mo(2)	O(6)	C(9)	116.4 (6)	Mo(4)	O(18)	C(41)	117.7 (7)
Mo(2)	O(7)	C(17)	116.6 (7)	Mo(4)	O(19)	C(49)	116.2 (7)
Mo(2)	O(8)	C(25)	116.5 (7)	Mo(4)	O(20)	C(57)	116.8 (7)
O(1)	C(1)	O(5)	124 (1)	O(13)	C(33)	O(17)	123.9 (9)
O(1)	C(1)	C(2)	117 (1)	O(13)	C(33)	C(34)	117 (1)
O(5)	C(1)	C(2)	119 (1)	O(17)	C(33)	C(34)	119.3 (9)
C(1)	C(2)	O(9)	109 (1)	C(33)	C(34)	O(21)	106.6 (9)
C(1)	C(2)	C(3)	110 (1)	C(33)	C(34)	C(35)	112.2 (9)
O(9)	C(2)	C(3)	110.3 (9)	O(21)	C(34)	C(35)	110 (1)
O(2)	C(9)	O(6)	122 (1)	O(14)	C(41)	O(18)	123 (1)
O(2)	C(9)	C(10)	119 (1)	O(14)	C(41)	C(42)	115 (1)
O(6)	C(9)	C(10)	118 (1)	O(18)	C(41)	C(42)	122 (1)
C(9)	C(10)	O(10)	111.0 (9)	C(41)	C(42)	O(22)	106.1 (9)
C(9)	C(10)	C(11)	106 (1)	C(41)	C(42)	C(43)	106 (1)
O(10)	C(10)	C(11)	115 (1)	O(22)	C(42)	C(43)	108 (1)
O(3)	C(17)	O(7)	122.5 (9)	O(15)	C(49)	O(19)	122 (1)
O(3)	C(17)	C(18)	120 (1)	O(15)	C(49)	C(50)	116 (1)
O(7)	C(17)	C(18)	117 (1)	O(19)	C(49)	C(50)	121 (1)
C(17)	C(18)	O(11)	108 (1)	C(49)	C(50)	O(23)	113 (1)
C(17)	C(18)	C(19)	114 (1)	C(49)	C(50)	C(51)	105 (1)
O(11)	C(18)	C(19)	111 (1)	O(23)	C(50)	C(51)	110.6 (9)
O(4)	C(25)	O(8)	123 (1)	O(16)	C(57)	O(20)	120 (1)
O(4)	C(25)	C(26)	119.9 (9)	O(16)	C(57)	C(58)	119 (1)
O(8)	C(25)	C(26)	117 (1)	O(20)	C(57)	C(58)	121 (1)
C(25)	C(26)	O(12)	110.1 (9)	C(57)	C(58)	O(24)	112.8 (9)
C(25)	C(26)	C(27)	107.2 (9)	C(57)	C(58)	C(59)	108.0 (9)
O(12)	C(26)	C(27)	109.6 (9)	O(24)	C(58)	C(59)	114.2 (9)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

Table V. Summary of Least-Squares Residuals in the Refinement of Mo_2(D(−)-man)$_4$·2THF

	enantiomorph I[a]	enantiomorph II
no. of parameters refined	829	829
no. of data used	5384	5384
R^b	0.0496	0.0503
$R_w{}^b$	0.0589	0.0599
quality-of-fit indicator[b]	1.485	1.510
R (on 650 Friedel pairs)	0.0507	0.0518
R_w (on 650 Friedel pairs)	0.0573	0.0586

[a] See text for definition of enantiomers. [b] Quantity defined in Table I.

Table VI. Average Bond Distances (Angstroms) and Angles (Degrees) for Mo_2(D(−)-man)$_4$·2THF[a]

	Distances		
Mo-Mo	2.103 [2]	C-C(α)	1.51 [1]
Mo-O(coord)	2.119 [4]	C(α)-C(β)	1.56 [2]
O(coord)-C	1.273 [6]	C(α)-O(H)	1.43 [1]
	Angles		
Mo-Mo-O(coord)	91.8 [2]	O-C-C(α)	119 [1]
cis-O-Mo-O	90.0 [8]	C-C(α)-O(H)	110 [1]
trans-O-Mo-O	175.1 [3]	C-C(α)-C(β)	109 [1]
Mo-O-C	116.7 [2]	(H)O-C(α)-C(β)	111 [1]
O-C-O	123 [1]		

[a] The quantity in brackets is calculated as $[\Sigma_n \Delta_i^2/n(n-1)]^{1/2}$: Δ_i is the deviation of the ith (of n) values from the arithmetic mean of the n values.

contacts with a molybdenum atom. Atom Mo(1) has contacts of 2.967 (7) and 2.825 (8) Å, respectively, with coordinated oxygen atom O(18) and hydroxyl oxygen atom O(22) of molecule 2 (at $1 - x$, $^1/_2 + y$, $^1/_2 - z$); these two oxygen atoms subtend an angle of 53.6 (2)° at Mo(1). The angles Mo(2)–Mo(1)–O(18) and Mo(2)–Mo(1)–O(22) have values of 151.4 (2) and 153.9 (2)°, respectively. Similarly, Mo(4) has contacts of 3.010 (6) and 2.922 (8) Å with O(4) and O(12), respectively, which subtend an angle of 52.6 (2)° at Mo(4). Each molecule also has a shorter, conventional axial interaction

Table VII. Axial Contacts to Mo and Noncovalent O-O Contacts for $Mo_2(D(-)\text{-}man)_4 \cdot 2THF$

atom 1	atom 2	dist, Å	atom 2 coord
Mo(1)	O(18)	2.967 (7)	$1-x, {}^1/_2+y, {}^1/_2-z$
	O(22)	2.825 (8)	$1-x, {}^1/_2+y, {}^1/_2-z$
Mo(2)	O(24)	2.613 (6)	$-1+x, y, z$
Mo(3)	O(10)	2.650 (7)	x, y, z
Mo(4)	O(4)	3.010 (6)	$1-x, -{}^1/_2+y, {}^1/_2-z$
	O(12)	2.922 (8)	$1-x, -{}^1/_2+y, {}^1/_2-z$
O(2)	O(22)	2.831 (10)	$1-x, {}^1/_2+y, {}^1/_2-z$
O(4)	O(18)	2.699 (10)	$1-x, {}^1/_2+y, {}^1/_2-z$
O(9)	O(23)	2.867 (14)	$1-x, {}^1/_2+y, {}^1/_2-z$
O(10)	O(27)	2.858[a]	x, y, z
O(12)	O(17)	2.978 (12)	$1-x, {}^1/_2+y, {}^1/_2-z$
O(12)	O(20)	2.906 (10)	$1-x, {}^1/_2+y, {}^1/_2-z$
O(12)	O(25)	2.678[a]	$-{}^1/_2+x, {}^3/_2-y, 1-z$
O(22)	O(28)	2.799[a]	$1-x, -{}^1/_2+y, {}^1/_2-z$
O(24)	O(26)	2.723[a]	$1+x, y, z$

[a] Since THF molecules were not refined in the last cycle, these esd's are omitted.

at its opposite end: the hydroxyl oxygen O(24) of molecule 2 (at $-1 + x, y, z$) is 2.613 (6) Å from Mo(2) (Mo(1)-Mo(2)-O(24) = 173.1 (2)°); Mo(3) and O(10) are 2.650 (7) Å apart, with the angle Mo(4)-Mo(3)-O(10) equal to 171.6 (2)°.

Table VII is a list of intermolecular contacts. As it shows, the quasi-axial contacts to two of the molybdenum atoms are accompanied by similarly bifurcated interactions centered at the oxygen atoms involved. It can be seen from Figure 2 that the noncovalent contacts form a zigzag pattern beginning with O(12)-O(20) (2.906 (10) Å) and continuing down along the interface of the two molecules, to the short (2.831 (10) Å) contact between coordinated oxygen atom O(2) of molecule 1 and hydroxyl oxygen O(22) of molecule 2.

In accommodation of this array of nonbonded interactions, the mandelate ligands are arranged so that their four alcoholic oxygen atoms are roughly in the coordination plane of one of the molybdenum atoms. The plane of Mo(1) and its respective oxygen atoms (O(1), O(2), O(3), O(4), O(9), O(10), O(11), O(12)) in molecule 1 is nearly parallel to the analogous plane (Mo(4), O(17), O(18), ..., O(24)) of molecule 2. (The dihedral angle is 4.3°.)

Hydrogen bonding allows the identification of the oxygen atom in each of the THF molecules. Although not all of these moieties were refined well, each has a single close contact to one of the mandelate oxygen atoms (Table VII).

Acknowledgment. We are grateful to the Robert A. Welch Foundation and the National Science Foundation for financial support.

Registry No. $Mo_2(D\text{-}man)_4 \cdot 2THF$, 83944-23-4.

Supplementary Material Available: Complete tables of bond distances and bond angles, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Reactions of $Mo_2(O\text{-}i\text{-}Pr)_6$ with *trans*-$WBr(CO)_4(CPh)$ and Pyridine. Structural Characterizations of $WBr(CO)_2(py)_2(CPh)$ and $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$

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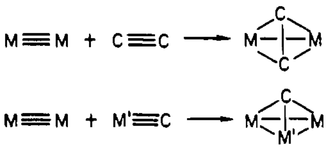
Received June 8, 1982

An attempt to form an addition product of $Mo_2(O\text{-}i\text{-}Pr)_6$ with *trans*-$WBr(CO)_4(CPh)$ by reaction in the presence of pyridine led instead to $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ (**1**) and $WBr(CO)_2(py)_2(CPh)$ (**2**); both are new compounds that have been characterized by X-ray crystallography. It has been shown that **1** may be obtained by reaction of $Mo_2(O\text{-}i\text{-}Pr)_6(CO)$ with pyridine alone and **2** by reaction of *trans*-$WBr(CO)_4(CPh)$ with pyridine alone. Compound **1** crystallizes in space group $C2/c$ with four molecules in a cell of the following dimensions: $a = 10.674$ (10) Å, $b = 18.502$ (13) Å, $c = 18.238$ (14) Å, $\beta = 91.50$ (7)°; $V = 3600$ (5) Å^3. The structure of **1** was solved and refined, showing that the $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ molecule is simply the bis(pyridine) adduct of the O-*i*-Pr homologue of the previously characterized $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$ molecule. It is a confacial bioctahedron with the two O-*i*-Pr and the CO as bridging groups. The Mo=Mo distance is 2.487 (1) Å. The bridging and terminal Mo-O distances are 2.104 [7] and 1.908 [2] Å. The Mo-C and Mo-N distances are 2.045 (3) and 2.341 (4) Å. Compound **2** crystallizes in space group $P2_1/n$ with $Z = 4$ and the following unit cell dimensions: $a = 10.298$ (6) Å, $b = 13.372$ (5) Å, $c = 16.861$ (9) Å, $\beta = 98.35$ (4)°. The molecular structure is derived from an octahedron with Br and CPh trans and the pairs of CO groups and py groups cis. The metal-ligand distances are as follows: W-CPh, 1.84 (2) Å; W-Br, 2.696 (2) Å; W-CO, 2.00 (2), 2.01 (2) Å; W-N, 2.26 (1), 2.28 (1) Å.

Introduction

trans-Bromo(tetracarbonyl)(phenylcarbyne)tungsten has been found to be a synthon for trinuclear clusters.[1] It is isolobal with alkynes and expected to add across metal-metal multiple bonds analogously, i.e.



The expected products are alkylidyne-capped trinuclear clusters. We have demonstrated earlier that $Cp_2Mo_2(CO)_4$ and *trans*-$WBr(CO)_4(CPh)$ form a benzylidyne capped heteronuclear trimer.[1] Although $Mo_2(O\text{-}i\text{-}Pr)_6$ has been observed to react with *trans*-$WBr(CO)_4(CPh)$, no defined addition

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[1] Cotton, F. A.; Schwotzer, W. *Angew. Chem.* **1982**, *94*, 652; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 629. We have been informed by Prof. F. G. A. Stone that he has used the closely related *trans*-$WBr(CO)_4CC_6H_4CH_3$ carbyne to synthesize trinuclear clusters capped by $CC_6H_4CH_3$.

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