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A New Cyclotetramolybdenum Diyne, $Mo_4Cl_8[P(OCH_3)_3]_4$

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The tetranuclear complex $Mo_4Cl_8[P(OCH_3)_3]_4$, containing a metallacyclobutadiyne ring, has been prepared in >90% yield by the reaction of $K_4Mo_2Cl_8$ with $P(OCH_3)_3$, and it also forms spontaneously from $Mo_2Cl_4[P(OMe)_3]_4$ in CH_2Cl_2 solution. It has a molecular structure generally comparable to those of other such compounds that have been discovered and characterized by R. E. McCarley and co-workers. The molecule resides on a crystallographic center of symmetry, and the planar Mo_4 ring has bond lengths of 2.226 (1) Å (triple) and 2.878 (1) Å (single). The arrangement of the Cl and $P(OCH_3)_3$ ligands about the central $Mo_4(\mu\text{-Cl})_4$ group is such as to give C_{2h} symmetry, as previously found in $Mo_4Cl_8[P(C_2H_5)_3]_4$, whereas in $W_4Cl_8[P(C_4H_9)_3]_4$ the ligand arrangement gave rise to D_2 symmetry. The title compound crystallizes in space group $P2_1/n$ with a = 10.429 (3) Å, b = 14.523 (4) Å, c = 12.835 (5) Å, β = 106.36 (3)°, V = 1865 (2) Å^3, and Z = 2. Final values of the usual unit weighted (R_1) and statistically weighted (R_2) reliability indices are 0.037 and 0.050, respectively.

Introduction

Several years ago McCarley and co-workers announced the fascinating and important discovery that compounds containing $M\overset{4}{-}M$ (quadruple) bonds, with M = Mo[1,2] or W,[2] could undergo [2 + 2] cycloaddition reactions to produce tetrametallacyclodiynes. Recently, a very detailed report on the molybdenum compounds, describing a number of preparative routes, has appeared.[3] The compound reported here was discovered accidently because it forms spontaneously under conditions that had been expected to lead only to the recrystallization of $Mo_2Cl_4[P(OCH_3)_3]_4$. Subsequently, we have found that it can be prepared deliberately in high yield (ca. 90%) by a one-pot reaction between $K_4Mo_2Cl_8$ and $P(OMe)_3$.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry, oxygen-free argon. Dichloromethane and hexane were dried by refluxing with phosphorus pentoxide and sodium–potassium amalgam, respectively. Both solvents were freshly distilled under argon before use.

Preparation. $Mo_2Cl_4[P(OCH_3)_3]_4$ was prepared according to the published procedure.[4] The title compound was first obtained as follows. The dinuclear compound, $Mo_2Cl_4[P(OCH_3)_3]_4$ (0.15 g), was dissolved in 10 mL of dichloromethane to give a blue-green solution. This solution was carefully layered with 25 mL of hexane in a large Schlenk tube. The color of the original solution slowly changed from blue-green to yellow-brown, and yellow-brown crystals formed along the sides of the tube. After 12 h, all liquid was removed by syringe and the air-sensitive crystals were placed in deoxygenated mineral oil.

A more direct method of preparation, in which yields of ca. 90% are obtained, is by addition of a slightly more than stoichiometric quantity of trimethyl phosphite to a suspension of $K_4Mo_2Cl_8$ in methanol. During this reaction the purple color of $[Mo_2Cl_8]^{4-}$ first changes to blue-green (indicating, probably, intermediate formation of $Mo_2Cl_4[P(OCH_3)_3]_4$) and then the yellow-brown product begins to precipitate. If a large excess (e.g., eightfold) of the phosphite is used and the slurry in methanol is refluxed for 10 h, both the blue-green dinuclear compound and the yellow-brown Mo_4 compound are formed, in a mole ratio of ca. 6:1.

The title compound can also be conveniently prepared from $Mo_2Cl_4[P(OCH_3)_3]_4$ be refluxing it (0.2 g) in methanol (30 mL) for 6 h. Conversion under these conditions is essentially quantitative.

The electronic absorption spectrum of $Mo_4Cl_8[P(OCH_3)_3]_4$ dissolved in CH_2Cl_2 has a peak in the visible region at 415 nm with a molar extinction coefficient of ca. 10^3.

X-ray Crystallography. A well-formed crystal, obtained from the initial preparation, measuring 0.2 × 0.4 × 0.5 mm was coated with epoxy cement and sealed in a thin-walled glass capillary. Routine data collection was carried out at room temperature on a Syntex P$\bar{1}$ four-circle diffractometer employing graphite-monochromated Mo Kα radiation. Pertinent crystallographic parameters are summarized in Table I. Three standard reflections, measured after every 100 reflections, displayed an average loss of intensity of 7.5% in 80 h of exposure time, and an appropriate decay correction was applied. Lorentz and polarization corrections were also applied, but no absorption correction was deemed necessary. Only the reflections with $I \geq 3\sigma(I)$ were retained as observed.

Table I. Crystallographic Data and Data Collection Parameters

formula	$Mo_4Cl_8[P(OCH_3)_3]_4$
fw	1163.7
space group	$P2_1/n$
a, Å	10.429 (3)
b, Å	14.523 (4)
c, Å	12.835 (5)
β, deg	106.36 (3)
V, Å^3	1865 (2)
Z	2
d_{calcd}, g/cm^3	2.072
cryst size, mm	0.2 × 0.4 × 0.5
μ(Mo Kα), cm^{-1}	20.763
data collection instrument	Syntex P$\bar{1}$
radiation	Mo Kα (graphite monochromated); $\lambda_{\bar{\alpha}}$ = 0.71073 Å
scan method	$2\theta-\omega$
data collection range, deg	$2\theta \leq 50$
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	2074
no. of parameters refined	181
R^a	0.0366
$R_w{}^b$	0.0500
quality-of-fit indicator^c	1.128
largest shift/esd, final cycle	0.03

^{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 = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

The structure was solved and refined in space group $P2_1/n$ with the use of standard computer programs.[5] The two independent molybdenum atom positions for the centrosymmetric molecule were determined from a three-dimensional Patterson function. The remaining non-hydrogen atoms were located through subsequent least-squares refinements and difference Fourier maps. After complete anisotropic refinement, the residuals were R = 0.0366 and R_w = 0.0500, and the quality-of-fit indicator had a value of 1.128. A final difference Fourier map revealed no peaks above 0.90 e/Å^3.

Final atomic positional parameters and isotropic-equivalent thermal parameters are given in Table II. Tables III and IV list important bond distances and angles within the molecule. Tables of observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material.

(1) McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900.
(2) McCarley, R. E.; Ryan, T. R.; Torardi, C. C. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 41.
(3) Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072.
(4) San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140.
(5) All calculations were 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.

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Table II. Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters for $Mo_4Cl_8[P(OCH_3)_3]_4$

atom	x	y	z	B, Å²
Mo(1)	0.07306 (6)	−0.09067 (4)	−0.06380 (4)	2.70 (1)
Mo(2)	0.04021 (6)	−0.03300 (4)	0.14170 (4)	2.77 (1)
Cl(1)	0.0349 (2)	−0.2291 (1)	−0.1693 (2)	4.76 (5)
Cl(2)	−0.0409 (2)	−0.0996 (1)	0.2813 (1)	4.92 (5)
Cl(3)	0.2377 (2)	−0.0265 (1)	0.0849 (1)	3.84 (4)
Cl(4)	−0.0823 (2)	−0.1565 (1)	0.0272 (1)	3.66 (4)
P(1)	0.2619 (2)	−0.0740 (1)	−0.1475 (2)	3.97 (4)
P(2)	0.1881 (3)	0.0495 (2)	0.3023 (2)	4.83 (5)
O(11)	0.3388 (6)	0.0199 (4)	−0.1227 (4)	5.2 (1)
O(12)	0.3673 (5)	−0.1508 (4)	−0.0887 (5)	5.7 (1)
O(13)	0.2444 (6)	−0.0839 (4)	−0.2730 (4)	6.3 (1)
O(21)	0.1175 (7)	0.1003 (5)	0.3797 (4)	6.6 (2)
O(22)	0.2801 (7)	0.1259 (5)	0.2693 (5)	8.5 (2)
O(23)	0.288 (1)	−0.0142 (7)	0.3873 (6)	11.7 (3)
C(11)	0.397 (1)	0.0741 (7)	−0.1932 (8)	7.0 (2)
C(12)	0.5022 (9)	−0.1587 (8)	−0.0999 (9)	7.5 (3)
C(13)	0.217 (1)	−0.1678 (8)	−0.3375 (8)	8.4 (3)
C(21)	0.158 (2)	0.112 (1)	0.4926 (8)	14.7 (6)
C(22)	0.340 (2)	0.201 (1)	0.328 (1)	12.1 (5)
C(23)	0.345 (2)	−0.093 (1)	0.378 (1)	11.0 (4)

Table III. Bond Distances (Å) for $Mo_4Cl_8[P(OCH_3)_3]_4$

Mo(1)-Mo(1)′	3.653 (1)	P(1)-O(11)	1.569 (6)
-Mo(2)	2.878 (1)	-O(12)	1.598 (6)
-Mo(2)′	2.226 (1)	-O(13)	1.575 (6)
-Cl(1)	2.394 (2)	P(2)-O(21)	1.577 (6)
-Cl(3)	2.370 (2)	-O(22)	1.600 (8)
-Cl(4)	2.443 (2)	-O(23)	1.577 (8)
-P(1)	2.507 (2)	O(11)-C(11)	1.46 (1)
Mo(2)-Mo(2)′	3.624 (1)	O(12)-C(12)	1.46 (1)
-Cl(2)	2.391 (2)	O(13)-C(13)	1.46 (1)
-Cl(3)	2.373 (2)	O(21)-C(21)	1.40 (1)
-Cl(4)	2.439 (2)	O(22)-C(22)	1.37 (1)
-P(2)	2.505 (2)	O(23)-C(23)	1.31 (2)

Table IV. Bond Angles (deg) for $Mo_4Cl_8[P(OCH_3)_3]_4$

Mo(2)-Mo(1)-Mo(2)′	89.53 (2)	Cl(2)-Mo(2)-Cl(4)	85.33 (7)
-Cl(1)	135.97 (5)	-P(2)	80.94 (8)
-Cl(3)	52.68 (5)	Cl(3)-Mo(2)-Cl(4)	101.35 (6)
-Cl(4)	53.82 (4)	-P(2)	81.20 (7)
-P(1)	132.49 (5)	Cl(4)-Mo(2)-P(2)	160.78 (7)
Mo(2)′-Mo(1)-Cl(1)	116.15 (6)	Mo(1)-Cl(3)-Mo(2)	74.74 (6)
-Cl(3)	102.53 (5)	Mo(1)-Cl(4)-Mo(2)	72.26 (5)
-Cl(4)	101.00 (5)	Mo(1)-P(1)-O(11)	114.5 (2)
-P(1)	96.39 (5)	-O(12)	104.4 (2)
Cl(1)-Mo(1)-Cl(3)	138.89 (7)	-O(13)	123.4 (3)
-Cl(4)	85.11 (6)	O(11)-P(1)-O(12)	105.5 (3)
-P(1)	82.18 (7)	-O(13)	101.1 (3)
Cl(3)-Mo(1)-Cl(4)	101.34 (6)	O(12)-P(1)-O(13)	106.6 (4)
-P(1)	80.14 (7)	Mo(2)-P(2)-O(21)	117.0 (3)
Cl(4)-Mo(1)-P(1)	161.72 (7)	-O(22)	113.0 (3)
Mo(1)-Mo(2)-Mo(1)′	90.47 (2)	-O(23)	114.9 (4)
-Cl(2)	136.70 (6)	O(21)-P(2)-O(22)	105.3 (4)
-Cl(3)	52.58 (4)	-O(23)	99.9 (5)
-Cl(4)	53.92 (4)	O(22)-P(2)-O(23)	105.3 (6)
-P(2)	133.53 (6)	P(1)-O(11)-C(11)	128.5 (6)
Mo(1)′-Mo(2)-Cl(2)	114.07 (6)	P(1)-O(12)-C(12)	124.2 (6)
-Cl(3)	103.10 (5)	P(1)-O(13)-C(13)	127.3 (6)
-Cl(4)	101.58 (5)	P(2)-O(21)-C(21)	130.6 (9)
-P(2)	96.29 (6)	P(2)-O(22)-C(22)	128.4 (8)
Cl(2)-Mo(2)-Cl(3)	140.14 (7)	P(2)-O(23)-C(23)	132.6 (9)

Results

The $Mo_4Cl_8[P(OMe)_3]_4$ molecule resides on a crystallographic center of inversion. However, as can be seen from Figures 1 and 2, which show, respectively, the whole molecule and the $Mo_4Cl_8P_4$ core only, the molecule has idealized C_{2h} symmetry. The mirror plane would be defined by the four bridging chlorine atoms and the twofold axis would pass through the centers of the two Mo≡Mo (triple) bonds, Mo(1)–Mo(2)′ and Mo(1)′–Mo(2).

The set of four Mo atoms is rigorously planar but not precisely rectangular, as may be seen from the dimensions in

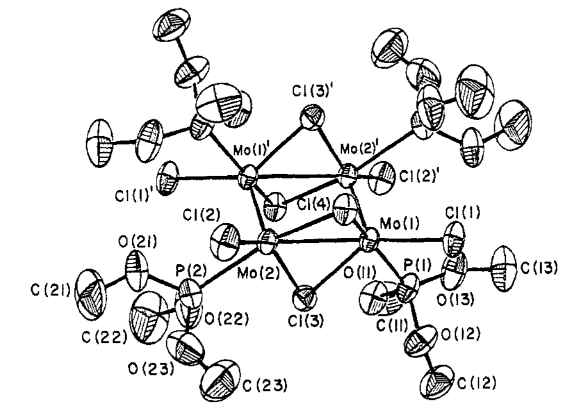

Figure 1. Complete molecular geometry and atom-labeling scheme for $Mo_4Cl_8[P(OCH_3)_3]_4$.

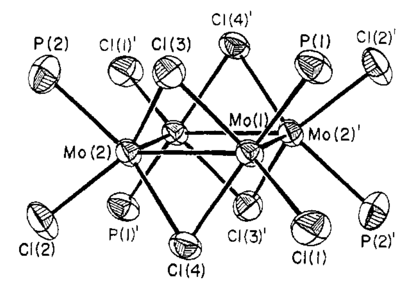

Figure 2. View of only the central portion of the molecule.

Table V. Selected Average Bond Distances (Å) and Angles (deg) for $Mo_4Cl_8[P(OCH_3)_3]_4$[a] and $Mo_4Cl_8(PEt_3)_4$[b]

	$Mo_4Cl_8[P(OCH_3)_3]_4$	$Mo_4Cl_8(PEt_3)_4$
short Mo-Mo	2.226 (1)[c]	2.211 (3)
long Mo-Mo	2.878 (1)	2.901 (2)
Mo-Cl(terminal)	2.392 [2]	2.423 [2]
Mo-Cl(bridging)[d]	2.372 [2]	2.424 [2]
	2.441 [2]	2.377 [4]
Mo-P	2.506 [1]	2.557 [1]
Mo-Mo-Mo	90.0 [5]	90.0 [6]
$Mo-Cl_b-Mo$	74 [1]	74.4 [8]

[a] This paper. [b] Reference 1. [c] A number in parentheses is an esd for a given value while a number in brackets is equal to $[\Sigma_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith of n values from the arithmetic mean of the n values. [d] The first values correspond to chlorine atoms cis to phosphorus and the second to chlorine atoms trans to P.

Tables III and IV. Thus, the two diagonals, Mo(1)–Mo(1)′ and Mo(2)–Mo(2)′, differ by 0.029 (2) Å and the Mo(1)–Mo(2)–Mo(1)′ and Mo(2)–Mo(1)–Mo(2)′ angles are 90.47 (2) and 89.53 (2)°, respectively.

The bridging chlorine atoms show evidence of the different trans bond weakening tendencies of $P(OCH_3)_3$ and Cl. The Mo–(μ-Cl) bonds trans to $P(OCH_3)_3$ groups are, on the average, 0.069 (3) Å longer than those trans to terminal chlorine atoms.

As in the compounds McCarley has described, the four Mo atoms define a rectangle whose long, Cl-bridged sides have lengths, 2.878 (1) Å, that are consistent with the existence of Mo–Mo single bonds and whose short sides have lengths, 2.226 (1) Å, consistent with the assumption that there are Mo≡Mo triple bonds in these positions. These and other bond lengths in $Mo_4Cl_8[P(OMe)_3]_4$ are compared with bond lengths in McCarley's $Mo_4Cl_8[P(C_2H_5)_3]_4$ in Table V.

Discussion

The ease with which $Mo_4Cl_8[P(OCH_3)_3]_4$ is formed from the dinuclear precursor, i.e., directly and fairly quickly, is interesting because the preparation of similar compounds in which there are trialkylphosphines seems to require more deliberate or forcing measures such as the use of a specially reactive intermediate or the use of a reagent intended to remove some PR_3 ligands. Much remains to be learned about the factors influencing reaction 1 but it appears, tentatively, that the more π acidic the phosphorus ligand the more the reaction tends to go to the right.

$$2Mo_2X_4(PY_3)_4 \rightleftharpoons Mo_4Cl_8(PY_3)_4 + 4PY_3 \qquad (1)$$

The other point worthy of discussion has to do with the fact that the $M_4X_8(PY_3)_4$ molecules are known to exist in either of two geometrically isomeric forms, **1** and **2**, with D_2 and C_{2h} symmetry, respectively. Previously[2] the molybdenum compound $Mo_4Cl_8[P(C_2H_5)_3]_4$ was known to have structure **2** while only the tungsten compound, $W_4Cl_8[P(C_4H_9)_3]_4$, had been found to have structure **1**. The new molybdenum compound also has the C_{2h} structure (**2**). The fact that $P(C_2H_5)_3$ and $P(OCH_3)_3$ are very similar sterically but rather different electronically would seem to suggest, tentatively, that the relative stabilities of structures **1** and **2** may be more sensitive to steric than to electronic influences.

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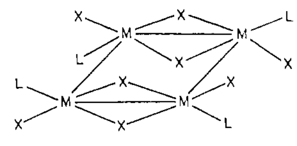
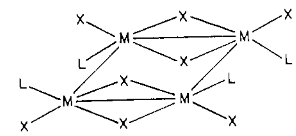


1



2

Registry No. $Mo_4Cl_8[P(OCH_3)_3]_4$, 84454-20-6; $Mo_2Cl_4[P(OCH_3)_3]_4$, 38832-74-5; $K_4Mo_2Cl_8$, 25448-39-9; Mo, 7439-98-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Carbon-Rich Metallacarboranes. 12.[1] Synthesis and Structures of Chromium(III) Complexes with "Nonconforming" Cage Geometries

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The reaction of the $(C_2H_5)_4C_4B_8H_8^{2-}$ dianion with $CrCl_2$ and NaC_5H_5 in cold tetrahydrofuran (THF) gave primarily red, paramagnetic $(\eta^5\text{-}C_5H_5)Cr(C_2H_5)_4C_4B_8H_8$ (I). Column chromatography of the product mixture under N_2 gave also purple II, an unstable species isomeric with I. Air oxidation of solutions of I over prolonged periods gave yellow, unstable $(\eta^5\text{-}C_5H_5)Cr(C_2H_5)_4C_4B_7H_7$ (III); products II and III were characterized only from mass spectra. On workup of the product mixture in air, a small quantity of green IV, isomeric with III, was obtained together with I (the major product) and III. Compounds I and IV were structurally characterized by X-ray diffraction studies and were shown to have respectively 13-vertex nido and 12-vertex nido cage geometries; each of these structures is a formal $(2n + 1)$-electron system and appears to violate the Wade electron-count scheme, which requires $2n + 4$ electrons for nido geometry. However, if the deficiency of three electrons is localized in the metal nonbonding orbitals (rendering chromium a 15-electron atom), then both I and IV can be viewed as $(2n + 4)$-electron cage systems in conformity with their observed structures. Crystal data for I: $CrC_{17}B_8H_{33}$; mol wt 376.94; space group $P\bar{1}$; $Z = 2$; $a = 8.637$ (8), $b = 8.664$ (5), $c = 16.484$ (8) Å; $\alpha = 99.19$ (5), $\beta = 92.06$ (4), $\gamma = 118.66$ (7)°; $V = 1059$ Å^3; $R = 0.102$ for 2101 independent reflections having $F_o^2 > 3\sigma(R_o^2)$. Crystal data for IV: $CrC_{17}B_7H_{32}$; mol wt 364.12; space group $Pna2_1$; $Z = 4$; $a = 14.763$ (8), $b = 10.828$ (4), $c = 12.348$ (2) Å; $V = 1974$ Å^3; $R = 0.026$ for 1820 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

A principal focus of interest in the four-carbon $R_4C_4B_8H_8$ carboranes and their metallacarborane derivatives[3,4] (indeed, our main objective in studying these molecules) is the intricate relationship between their cage structures and skeletal electron populations. Collectively, this family of compounds provides an excellent means of examining electronic influence on bonding in large covalent clusters. The $R_4C_4B_8H_8$ species (R = alkyl) have 28 framework electrons and are "electron rich" relative to the 26 required for 12-vertex closo cages such as the icosahedral $R_2C_2B_{10}H_{10}$ carboranes.[4] The $R_4C_4B_8H_8$ cages in which R is CH_3, C_2H_5, or $n\text{-}C_3H_7$ are fluxional in solution,[3,5] alternating between pseudoicosahedral geometry and more open arrangements that reflect the "nido" character expected[6] for $(2n + 4)$-electron polyhedra, where n is the number of vertices. So sensitive is the cage geometry to electronic influence that the choice of alkyl substituent on carbon has major consequences in the observed stereochemistry.[5c]

(1) This article continues the "Tetracarbon Metallacarborane" series under a new, more general title. For paper 11 in this series, see: Maynard, R. B.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 3858.
(2) (a) Present address: RCA Picture Tube Division, Lancaster, PA 17604. (b) Visiting scholar from the Institute of Chemistry, Academica Sinica, Beijing, China, 1981–1983.
(3) For a recent review see: Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*.
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