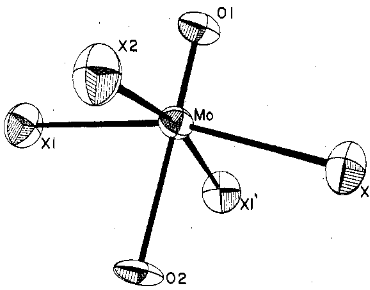

Figure 2. The $[MoOX_4(H_2O)]^-$ ions occurring in **2** (X = Br) and **3** (X = I), showing the numbering scheme. The thermal vibration ellipsoids used are those for **2** and are scaled to enclose 50% of the electron density.

Table VIII. Average Values of Distances and Angles in $[MoOX_4(H_2O)]^-$ Ions

	X		
	Cl[a]	Br	I
Mo=O, Å	1.66 ± 0.01	1.62 ± 0.02	1.65 (1)
Mo–X, Å	2.364 ± 0.005	2.53 ± 0.01	2.76 (1)
Mo–OH$_2$, Å	2.36 ± 0.03	2.32 ± 0.02	2.40 (1)
O=Mo–X, deg	98.2 ± 0.8	97.9 ± 1.1	97.8 ± 0.3
X–Mo–X, deg	89.0 ± 0.3	89.4 ± 0.4	88.9 ± 0.4

[a] See ref 3 for sources.

bromo and iodo compounds, respectively. Figure 2 shows the $[MoOX_4(H_2O)]^-$ ions.

Comparison of Structures. We now have two accurate structure determinations for the $[MoOCl_4(H_2O)]^-$ ion, three for the $[MoOBr_4(H_2O)]^-$ ion (counting the occurrence of two independent ions in compound **1**), and one for the $[MoOI_4(H_2O)]^-$ ion and it is interesting to compare the structures of the three homologous ions. In Table VIII we list the values of the important distances and angles. In each case we have averaged over all available values counting each distance or angle as many times as it actually occurs even when a given pair were required to be equal by symmetry. For the Mo═O distances in the chloro and bromo compounds the averages were calculated by weighting each individual measurement by the inverse of its own esd; in all other cases each value was given the same weight. The mean deviations from the averages are indicated by the ± interval, while figures in parentheses for the iodo compound are esd's for the single determination of that parameter.

There is a remarkable degree of regularity in the three structures. The Mo═O distance is invariant within experimental error. A value of 1.64 ± 0.02 Å can be taken as characteristic for all three compounds. Similarly, the weakly bonded water molecules are at essentially the same distance, 2.36 ± 0.04 Å in each case. What is perhaps more remarkable is the essential constancy of the O═Mo—X and X—Mo—X angles from one case to another, despite the changing size of the X atoms. There appears to be a natural explanation for this, however. The increasing van der Waals radii are accompanied by increasing Mo–X distances so that nonbonded repulsions tend to retain about the same influence on bond angles. The increasing Mo–X distances run nearly parallel to the increases in the accepted single bond radii of the halogen atoms, though not entirely. Thus, while the atomic bond radii increase by 0.15 and 0.19 Å from Cl to Br and Br to I, respectively, the bond lengths in the anions increase by 0.17 and 0.23 Å for the corresponding steps. This may be due to an overall increase in nonbonded repulsions or it may reflect a decreasing contribution from π bonding as the halogen orbitals grow too large to overlap well with the metal atom d orbitals.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. 1, 71096-99-6; **2**, 52729-41-6; **3**, 71097-01-3; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Tetrakis(dimethylphosphoniumdimethylido)dichromium and -dimolybdenum. 1. Crystal and Molecular Structures

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Received April 3, 1979

The title compounds, $[(CH_3)_2P(CH_2)_2]_4Cr_2$ (**1**) and $[(CH_3)_2P(CH_2)_2]_4Mo_2$ (**2**), have been investigated crystallographically, shown to be isomorphous, and shown to have extremely short bonds between the metal atoms. Compound **1** crystallized in space group *Pccn* with $a = 13.036$ (5) Å, $b = 13.037$ (5) Å, $c = 13.096$ (5) Å, and $Z = 4$. The structure consists of discrete molecules residing on crystallographic inversion centers but having effectively C_{4h} symmetry. The Cr–Cr distance is 1.895 (3) Å. Average values of some other molecular dimensions are as follows: Cr–C, 2.22 (1) Å; P–C, 1.80 (3) Å; ∠Cr–Cr–C, 103.3 (4)°; ∠C–Cr–C, 87.0 (6)°. Compound **2** also crystallizes in space group *Pccn* with $a = 13.122$ (3) Å, $b = 13.238$ (2) Å, $c = 13.244$ (2) Å, and $Z = 4$. The Mo–Mo distance is 2.082 (2) Å, and the average values of the other molecular dimensions are as follows: Mo–C, 2.31 (2) Å; P–C, 1.78 (2) Å; ∠Mo–Mo–C, 101.5 (8)°; ∠C–Mo–C, 88 (1)°.

Introduction

Several years ago Kurras et al. reported the preparations of the compounds $[(CH_3)_2P(CH_2)_2]_4Cr_2$[1] (**1**) and $[(CH_3)_2P(CH_2)_2]_4Mo_2$[2] (**2**). In connection with our recent discoveries of many compounds[3] containing "supershort" Cr–Cr quadruple bonds (i.e., those shorter than ca. 1.90 Å), we found it of interest to determine the bond length in **1**. As noted in a preliminary report,[4] this bond length is in the supershort range.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(CH_2)_2PMe_2]_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.0043 (2)	0.0568 (1)	0.0450 (1)	2.41 (6)	2.04 (6)	2.00 (6)	−0.1 (1)	0.0 (1)	−0.17 (8)
P(1)	−0.0034 (4)	−0.1461 (3)	0.1835 (3)	4.1 (2)	3.1 (1)	2.8 (1)	−0.1 (2)	−0.2 (3)	0.4 (1)
P(2)	0.2335 (3)	−0.0096 (3)	−0.0089 (3)	2.8 (1)	3.7 (2)	3.2 (1)	−0.1 (2)	0.3 (2)	−0.6 (1)
C(11)	−0.021 (1)	−0.0114 (9)	0.198 (1)	3.8 (9)	2.0 (5)	3.2 (6)	−0.4 (5)	0.3 (5)	0.7 (5)
C(12)	0.032 (1)	0.1883 (9)	−0.059 (1)	4.0 (7)	2.3 (5)	2.2 (6)	−0.3 (5)	0.2 (5)	0.8 (5)
C(21)	0.169 (1)	0.0605 (10)	0.084 (1)	3.2 (6)	2.5 (5)	4.1 (6)	−0.0 (6)	0.5 (6)	−1.2 (6)
C(24)	−0.158 (1)	0.1104 (9)	0.056 (1)	3.2 (6)	1.8 (5)	4.5 (7)	−0.2 (5)	−1.1 (6)	−1.0 (6)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(13)	−0.068 (1)	−0.219 (1)	0.281 (1)	4.8 (4)	C(23)	0.359 (1)	−0.055 (1)	0.036 (1)	5.1 (4)
C(22)	0.271 (1)	0.074 (1)	−0.115 (1)	4.3 (3)	C(14)	0.129 (1)	−0.179 (1)	0.212 (1)	4.5 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

In view of this, we have undertaken an extensive study of the electronic structures and spectra of both this chromium compound, **1**, and its molybdenum analogue, **2**. We shall report the results of these studies in several papers of which this is the first. We describe here, in detail, the crystal and molecular structures of both the dichromium and dimolybdenum compounds.

The structures described here are of interest in other ways as well. For the past several years there has been considerable study of the reactions of phosphonium ylides with a variety of metals,[5] and the $[(CH_3)_2P(CH_2)_2]^-$ ion has been especially interesting since it has been found to form a number of unusual types of complexes. For example, with the coinage metals, which ordinarily form rather unstable organometallic compounds, it gives quite stable complexes, such as the 1:2 adducts with copper(I) halides which are stable well above room temperature.[6]

Experimental Section

Preparation of $[(CH_3)_2P(CH_2)_2]_4Cr_2$. Trimethylphosphine methylide was prepared according to the method of Schmidbaur and Tronich from $(CH_3)_3P$ and $(CH_3)_3Si(CH_2Cl)$.[7] The lithium salt of the ylide was prepared from a stoichiometric reaction of $(CH_3)_3P{=}CH_2$ and *n*-BuLi and stored as a white powder under nitrogen.

Anhydrous chromous acetate (1.0 g, 2.9 mmol) and $(CH_3)_2P(CH_2)_2Li$ (1.1 g, 11.9 mmol) were placed in a small round-bottom flask, and 25 mL of THF, freshly distilled from sodium/potassium benzophenone, was added. The resulting mixture was stirred for 16 h and then filtered. The filtrate was reduced in volume to yield $Cr_2[(CH_2)_2P(CH_3)_2]_4$ as a yellow powder. Additional product was obtained by extracting the residue with THF. Crystals suitable for an X-ray diffraction study were obtained by slowly cooling a saturated THF solution. The mass spectrum showed no molecular ion at 160 °C and 70 eV. Peaks were observed at m/e 319, 230, and 141 corresponding to the ML_3^+, ML_2^+, and ML^+ ions. The compound melted with decomposition in the range 163–165 °C in close agreement with the value previously reported.[1]

The sample of $[(CH_3)_2P(CH_2)_2]_4Mo_2$, in the form of single crystals, was provided by Dr. E. Kurras.

Crystal Data and Structure Determinations.[8,9] In each case an approximately cubic crystal of dimensions 0.3 × 0.3 × 0.3 mm was wedged in a glass capillary under mineral oil or imbedded in epoxy. A Syntex $P\bar{1}$ diffractometer was used for preliminary X-ray examination and data collection. The crystals were found to be orthorhombic, belonging to the space group *Pccn*. ω scans of several intense reflections had peak widths at half-height of less than 0.20°. Cell constants were obtained by carefully centering on 15 reflections in the range $16° < 2\theta < 30°$. For **1** a = 13.036 (5) Å, b = 13.037 (5) Å, c = 13.096 (5) Å, and V = 2227.8 (1.5) Å^3. For **2** we found a = 13.122 (3) Å, b = 13.238 (2) Å, c = 13.244 (2) Å, and V = 2300.6 (1.2) Å^3.

Intensities were measured at 22 ± 4 °C by the θ–2θ scan technique, using Mo Kα radiation monochromated by a graphite crystal in the incident beam. For **1** there are 1425 reflections in the range $0° < 2\theta \leq 50°$ of which 766 have intensities, I, such that $I > 3\sigma(I)$, and these only were used to solve and refine the structure. The linear absorption coefficient for **1** is 13.28 cm^{-1} and absorption corrections were omitted. For **2** there are 1759 independent reflections in the range $0° < 2\theta \leq 45°$. There are 725 reflections having intensities, I, such that $I > 3\sigma(I)$ that were used in the solution and refinement of the structure.

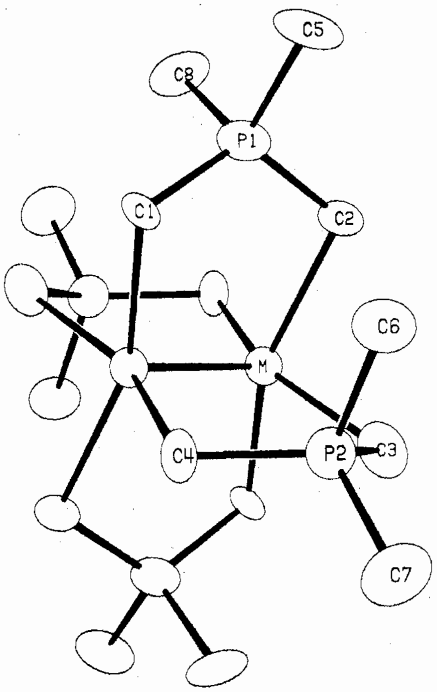


Figure 1. Structure of the $M_2[(CH_2)_2P(CH_3)_2]_4$ molecule, showing the atomic numbering scheme.

The structure of **1** was solved first. The position of the crystallographically unique Cr atom was found from the Patterson function, and the remaining ten independent, nonhydrogen atoms were found in a series of difference electron density maps, each calculated following least-squares refinement of the atoms already found. Full-matrix least-squares refinement using anisotropic thermal parameters for the chromium and phosphorus atoms and for four of the carbon atoms converged in three cycles to give final discrepancy indices of R_1 = 0.064 and R_2 = 0.089 and a goodness-of-fit parameter of 1.66.

The structure of **2** was refined by least-squares methods using the atomic positions and approximate isotropic thermal parameters found for **1** as starting values. Full-matrix anisotropic least-squares refinement on all the nonhydrogen atoms gave final discrepancy factors of R_1 = 0.048 and R_2 = 0.076 and a goodness-of-fit parameter of 1.54.

The observed and final calculated values of the structure factors are available as supplementary material.

Results

The two compounds are isotypic. With four molecules in unit cells belonging to space group *Pccn*, each molecule resides on a crystallographic inversion center. The molecules are discrete and packed with normal van der Waals contacts. The

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2[(CH_2)_2PMe_2]_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.0056 (2)	0.0611 (2)	0.0492 (2)	2.3 (1)	2.01 (9)	1.80 (9)	0.0 (2)	0.3 (2)	−0.3 (1)
P(1)	−0.0079 (10)	−0.1482 (7)	0.1850 (7)	3.5 (4)	2.9 (4)	2.6 (3)	0.3 (5)	0.4 (6)	0.6 (3)
P(2)	0.2378 (7)	−0.0142 (8)	−0.0085 (8)	2.6 (4)	3.1 (5)	2.7 (4)	−0.1 (4)	0.4 (5)	−0.2 (4)
C(1)	−0.024 (3)	−0.015 (2)	0.204 (3)	5 (2)	1 (1)	3 (1)	−1 (2)	−1 (2)	0 (1)
C(2)	0.040 (3)	0.192 (3)	−0.062 (3)	3 (1)	2 (2)	2 (2)	−0 (1)	0 (1)	1 (1)
C(3)	0.178 (3)	0.060 (3)	0.086 (3)	3 (2)	2 (2)	3 (2)	0 (2)	1 (2)	−1 (2)
C(4)	−0.161 (3)	0.115 (3)	0.057 (3)	3 (1)	2 (1)	3 (2)	−0 (1)	−0 (2)	−1 (2)
C(5)	−0.078 (4)	−0.222 (3)	0.283 (3)	7 (3)	4 (2)	3 (2)	−0 (2)	1 (2)	2 (2)
C(6)	0.273 (3)	0.069 (3)	−0.113 (3)	4 (2)	5 (2)	3 (2)	−1 (2)	1 (1)	1 (2)
C(7)	0.364 (3)	−0.064 (3)	0.035 (3)	2 (1)	6 (2)	5 (2)	1 (2)	0 (2)	−0 (2)
C(8)	0.132 (3)	−0.180 (3)	0.207 (3)	5 (2)	5 (2)	5 (2)	1 (2)	−3 (2)	1 (2)

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

Table III. Bond Distances (Å)

atoms	compd **1**	compd **2**
M–M′	1.895 (3)	2.082 (2)
M–C(1)	2.21 (1)	2.32 (2)
C(2)	2.22 (1)	2.31 (2)
C(3)	2.21 (1)	2.32 (2)
C(4)	2.23 (1)	2.30 (2)
P(1)–C(1)	1.78 (1)	1.79 (2)
C(2)′	1.77 (1)	1.78 (2)
C(5)	1.81 (1)	1.86 (2)
C(8)	1.82 (1)	1.90 (2)
P(2)–C(3)	1.74 (1)	1.77 (2)
C(4)′	1.75 (1)	1.79 (2)
C(6)	1.84 (1)	1.87 (2)
C(7)	1.83 (1)	1.83 (2)

Table IV. Bond Angles (deg)

atoms	compd **1**	compd **2**
M′–M–C(1)	103.9 (3)	101.7 (7)
C(2)	103.5 (3)	101.3 (8)
C(3)	102.6 (4)	101.3 (8)
C(4)	103.2 (3)	101.8 (8)
C(1)–M–C(2)	152.7 (4)	157 (1)
C(3)	86.9 (4)	89 (1)
C(4)	85.7 (4)	87 (1)
C(2)–M–C(3)	88.1 (4)	87 (1)
C(4)	87.1 (4)	89 (1)
C(3)–M–C(4)	154.1 (4)	157 (1)
M–C(1)–P(1)	106.5 (5)	106 (2)
M–C(2)–P(1)	107.0 (5)	107 (1)
M–C(3)–P(2)	107.3 (6)	107 (2)
M–C(4)–P(2)	105.9 (5)	106 (1)
C(1)–P(1)–C(2)	112.1 (5)	114.6 (7)
C(5)	112.9 (6)	111.1 (8)
C(8)	109.3 (6)	108.1 (9)
C(2)–P(1)–C(5)	113.2 (6)	110.5 (8)
C(8)	108.3 (6)	107.4 (8)
C(5)–P(1)–C(8)	100.2 (6)	104.5 (9)
C(3)–P(2)–C(4)	111.7 (6)	115.0 (8)
C(6)	110.1 (6)	108.1 (8)
C(7)	111.9 (6)	111.4 (9)
C(4)–P(2)–C(6)	109.0 (6)	108.4 (8)
C(7)	112.0 (6)	110.4 (8)
C(6)–P(2)–C(7)	101.7 (6)	102.8 (8)

Table V. Some Planes,[a] Dihedral Angles, and Deviations of Atoms from the Planes

	compd **1**	compd **2**
	P_1: C(1)–P(1)–C(2)	
A_1	−0.9579	−0.9558
B_1	−0.0959	−0.0729
C_1	−0.2708	−0.2850
D_1	−0.4257	−0.4559
	P_2: C(1)–M–M′–C(2)	
A_2	−0.9856	−0.9801
B_2	0.1411	0.1704
C_2	−0.0932	−0.1017
D_2	0.0036	−0.000
	P_3: C(3)–P(2)–C(4)	
A_3	0.1725	0.1798
B_3	0.8411	0.8237
C_3	−0.5126	−0.5377
D_3	0.4794	0.4668
	P_4: C(3)–M–M′–C(4)	
A_4	0.1602	0.1648
B_4	0.6147	0.6098
C_4	−0.7723	−0.7752
D_4	−0.0059	−0.000
	Dihedral Angles (deg)	
P_1/P_2	17.1	17.6
P_3/P_4	19.9	18.4
	Deviations from P_2 (Å)	
C(1)	0.004	0.040
M	0.002	0.003
M′	−0.009	0.003
C(2)	0.004	0.035
	Deviations from P_4 (Å)	
C(3)	−0.006	0.038
M	0.015	0.003
M′	0.003	0.003
C(4)	−0.006	0.037

[a] Each plane, P_n, is defined by $A_nX + B_nY + C_nZ = D_n$.

structure is shown in Figure 1 (which is drawn from the coordinates for the molybdenum compound), and the atomic numbering scheme is defined. Tables I and II give the atomic positional and thermal parameters for compounds **1** and **2**, respectively. The bond lengths for both compounds are given in Table III, the bond angles in Table IV, and some planes and dihedral angles in Table V.

The molecules have approximately C_{4h} symmetry, the descent from possible D_{4h} symmetry being caused by the bending of each five-membered ring along a line through the two carbon atoms. This is clearly shown in Figure 2 which presents a view directly down the Mo–Mo axis for a molecule of compound **2**. The dihedral angles (Table V) are in the range 17.1–19.9°.

Discussion

The metal–metal bond distances in $Cr_2[(CH_2)_2P(CH_3)_2]_4$ (**1**) and $Mo_2[(CH_2)_2P(CH_3)_2]_4$ (**2**) are 1.895 (3) and 2.082 (2) Å, respectively. For **1** the Cr–Cr quadruple bond distance is among the shortest of those that have been observed. This is significant because this very short Cr–Cr quadruple bond is found in the absence of any aromatic character on the ligand. Dichromium(II) compounds are unique among the metal–metal quadruply bonded systems in displaying a large range of metal–metal distances. The known Mo–Mo quadruple bond distances cover a range of only 0.14 Å. The longest, 2.183 (2) Å, is found in $Mo_2(C_3H_5)_4$[10] and the shortest, 2.037 (2)

Table VI. Structural Parameters in Compounds Containing the $(CH_2)_2P(CH_3)_2$ Ligand

compd	P–CH$_2$, Å	P–CH$_3$, Å	CH$_3$–P–CH$_3$, deg	CH$_2$–P–CH$_2$, deg	M–CH$_2$–P, deg	ref
$(CH_3O)_6Ti_2[(CH_2)_2P(CH_3)_2]_2$	1.75 1.71	1.80 1.82		113	118	*a*
$Cu_2[(CH_2)_2P(CH_3)_2]_2$	1.78 1.82	1.82 1.82	103.0 (9)	112.1 (8)	109.7 (7) 107.1 (9)	*b*
$Au_2[(CH_2)_2P(CH_2CH_3)_2]_2$	1.76 (3) 1.82 (3)	1.83 (3) 1.84 (2)	103 (1)	114 (1)	108 (1) 108 (1)	*c*
$Au_2[(CH_2)_2P(CH_3)_2]_2Cl_2$	1.879 (55)	1.913 (80)				*d*
$Ni_2[(CH_2)_2P(CH_3)_2]_4$	1.754 (3) 1.736 (3)	1.816 (4) 1.825 (4)	103.3 (2)	116.4 (1)	118.3 (1)	*e*
$Cr_2[(CH_2)_2P(CH_3)_2]_4$	1.76 (1) av	1.82 (1) av	100.9 (6) av	111.9 (5) av	106.7 (6) av	*f*
$Mo_2[(CH_2)_2P(CH_3)_2]_4$	1.78 (1) av	1.89 (2) av	103.6 (9) av	114.8 (8) av	107 (2)	*f*

[a] Scharf, W.; Neugebauer, D.; Schubert, W.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 601. [b] Nardin, G.; Randaccio, L.; Zangrando, E. *J. Organomet. Chem.* 1974, *74*, C23. [c] Schmidbaur, H.; Mandl, J. R.; Frank, A.; Huttner, G. *Chem. Ber.* 1976, *109*, 466. [d] Schmidbaur, H.; Mandl, J. E.; Richter, W.; Bejenke, V.; Frank, A.; Huttner, G. *Ibid.* 1977, *110*, 2236. [e] Brauer, D. J.; Kruger, C.; Roberts, P. J.; Tsay, Y. H. *Ibid.* 1974, *107*, 3706. [f] This work.

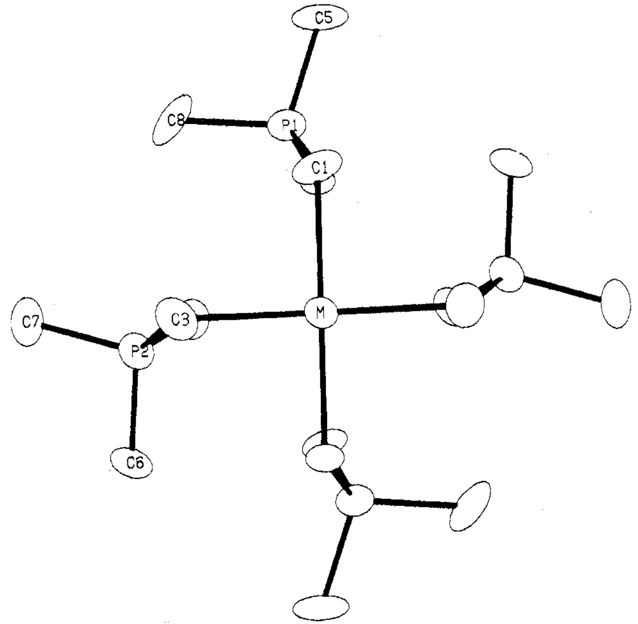
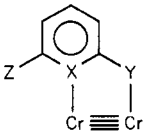


Figure 2. View of the $M_2[(CH_2)_2P(CH_3)_2]_4$ molecule looking directly along the M–M axis.

Å, in $Mo_2[(pyN)C(CH_3)O]_4$.[11] The span of Cr–Cr bond lengths, however, is 0.71 Å, ranging from a high of 2.541 (1) Å in $Cr_2(O_2CCF_3)_4(OEt_2)_2$[12] to a low of 1.830 (4) Å in $Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2\cdot 6Et_2O$.[13] The "supershort" Cr–Cr bonds (i.e., ≤1.90 Å) had, until recently, been observed only in compounds containing aromatic ligands[14] of the type



X, Y, Z = C, N, O

The occurrence of a supershort Cr–Cr quadruple bond in compound **1** where there are no aromatic rings in the ligands is therefore a point of great importance.

It should be noted also that there are no axial ligands, as has been true in every previous case of a supershort Cr–Cr quadruple bond.

The M–M bonds in these molecules are appreciably shorter than those in the $[M_2(CH_3)_8]^{4-}$ ions. For $[Cr_2(CH_3)_8]^{4-}$ the Cr–Cr distance[15] is 1.980 (5) Å and for $[Mo_2(CH_3)_8]^{4-}$ the Mo–Mo distance[16] is 2.148 (2) Å; these are 0.085 and 0.066 Å longer, respectively, than the present ones. However, the M–C distances in the corresponding pairs of compounds are essentially the same. The average Cr–C distances are 2.199 (13) Å in $[Cr_2Me_8]^{4-}$ and 2.22 (1) Å in $Cr_2[(CH_2)_2P(CH_3)_2]_4$; the Mo–C distances are 2.29 (1) and 2.31 (2) Å for the analogous molybdenum compounds.

In the $(CH_3)_2P(CH_2)_2$ ligands we find two distinctly different P–C bond lengths. The P–CH$_2$ distances average 1.75 (1) and 1.78 (2) Å for compounds **1** and **2** while the average P–CH$_3$ distances are 1.84 (1) and 1.85 (2) Å, respectively. Although statistically the differences are scarcely significant, it does seem likely that the ligand tends to retain some of the ylidic character of the P–CH$_2$ bonds when functioning as a ligand. This also appears to be the case in all of the other structures known to contain the $(CH_2)_2P(CH_3)_2$ ligand, as shown in Table VI, where the P–CH$_2$ bonds are always shorter than the P–CH$_3$ bonds.

The average CH$_2$–P–CH$_2$ angles are 111.9 (5) and 114.8 (8)° for **1** and **2**, respectively, while the CH$_3$–P–CH$_3$ angles average 106.7 (6) and 107 (2)°, respectively. These values agree well with other reported values as summarized in Table VI. Expansion of the CH$_2$–P–CH$_2$ angles is consistent with the retention of ylide character in these bonds and cannot be attributed to strain since this angle is independent of the M–C–P angle. In compounds where no M–M bonding is present, such as $Ti_2(OCH_3)_6[(CH_2)P(CH_3)_2]_2$ and $Ni_2[(CH_2)_2P(CH_3)]_4$, the M–C–P angle is 118°, but in those cases where some kind of M–M bonding is involved the M–C–P angle is 107°. In all cases, however, the CH$_2$–P–CH$_2$ angle is approximately 114°.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to Dr. E. Kurras for a sample of the molybdenum compound.

Registry No. **1**, 53237-33-5; **2**, 55467-79-3.

Supplementary Material Available: Tables of the observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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[*N*-(2-Pyridyl)acetamido-*N*,*N*′]dimolybdenum: The (New) Shortest Known Molybdenum–Molybdenum Quadruple Bond

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Received April 24, 1979

The reaction of $Mo_2(O_2CCH_3)_4$ with the anion of *N*-(2-pyridyl)acetamide gives $Mo_2[(C_5NH_4)NC(O)CH_3]_4$, a moderately air-sensitive, red, crystalline compound. An X-ray crystallographic study of this substance has shown that it has the ligands coordinated through the two nitrogen atoms. The Mo–Mo distance is 2.037 (3) Å, which makes it the shortest Mo–Mo distance known, the previously shortest one, which occurs in $Mo_2[2,6\text{-}(MeO)_2C_6H_3]_4$, having been 2.064 (1) Å. The compound crystallizes in the tetragonal system with $a = 9.050$ (1) Å, $c = 17.438$ (3) Å, and $Z = 2$. From systematic absences the possible space groups were $I4$, $I\bar{4}$, and $I4/m$, of which only the last two were consistent with the Patterson function. The structure could not be refined in $I\bar{4}$ but using a disordered model it behaved satisfactorily in $I4/m$. Each ligand is treated as having two equally populated orientations; the actual symmetry of an individual molecule thus remains unknown but is probably D_{2d}.

Introduction

Although the strength of the quadruple bond between a pair of molybdenum atoms does not vary as extravagantly as does that between chromium atoms,[1,2] there is, nonetheless, considerable variation. Thus far, the lengths of $Mo\overset{4}{-}Mo$ bonds, as observed in some 46 structures,[3] have ranged from 2.064 (1) Å in $Mo_2[2,6\text{-}(MeO)_2C_6H_3]_4$ to 2.183 (2) Å in $Mo_2(allyl)_4$. The possible causes of this moderate variability in bond length are several, of which the following have been explicitly considered: (1) axial interaction (this has been shown[4,5] to have a real effect, but a small one); (2) twist angle (this also has been found to cause a measurable change in bond length, but, again, not a large one);[6] (3) simple inductive effect (the results for $Mo_2(O_2CR)_4$ compounds, in which the electronegativity of R has been varied over the range from CF_3 through Ph, H, CH_3, to $C(CH_3)_3$, have shown that bond length is essentially unaffected by changes in this parameter[5]).

It must be admitted that despite the results of these systematic studies, we are left with the existence of many variations that have no obvious explanation. This is not to say that it is particularly surprising that a change in the set of ligands from, e.g., four SO_4^{2-} ions to four 2-oxypyridinato ions might change the Mo–Mo bond length by as much ca. 0.05 Å but simply that this change could not have been predicted and cannot now be explicitly rationalized. Our understanding of the subject is still not sufficiently refined to account for such things, let alone predict them and it is, therefore, still necessary and important to conduct experimental studies to see whether further variations may occur as still other ligands are used.

In this paper we report a new dimolybdenum compound in which there is a shorter Mo–Mo quadruple bond than any previously seen. It is shorter by a nontrivial amount, 0.027 Å, despite the fact that the ligand involved would not appear to be markedly different from others previously used.

Experimental Section

A literature method[7] for the preparation of *N*-(2-pyridyl)acetamide, by condensation of 2-aminopyridine with acetic anhydride, was used. The product was recrystallized from ethanol and its identity confirmed by ^1H NMR spectroscopy.

Preparation of the Dimolybdenum Complex. The monoanion of *N*-(2-pyridinyl)acetamide was prepared by reacting the ligand (0.27 g, 2 mmol) with 1.3 mL of 1.6 M hexane solution of *n*-butyllithium in 25 mL of THF. Since even a slight excess of *n*-BuLi results in a yellow color, the anion can be made quantitatively by a "titration". Dimolybdenum tetraacetate (0.22 g, 0.5 mmol) was added and a red color developed immediately. After 1 day a red precipitate had formed which was partly dissolved by addition of more solvent (10 mL). The mixture was filtered, and the red solution was slowly evaporated in a stream of argon, whereupon red crystals deposited on the glass wall. They were only moderately sensitive to air and proved to be suitable for X-ray crystallography.

The mass spectrum (300 °C, 10^{-6} torr) had a peak at m/e 736.033 414 while the value calculated for the principal isotopic species of $Mo_2[(C_5NH_4)NC(O)CH_3]_4$ is 736.035 260.

X-ray Crystallography. A crystal of approximate dimensions 0.25 × 0.10 × 0.20 mm was covered with epoxy cement and mounted on the end of a thin glass fiber. Rotation and oscillation photographs along with data collected in a preliminary data set (range $18° \leq 2\theta \leq 25°$) showed that the crystal had tetragonal symmetry with systematic absences $h + k + l = 2n$, indicating the possible space groups $I4$, $I\bar{4}$, or $I4/m$. The widths at half-height (ω scans) of several strong reflections were found to be <0.30°. Cell constants, obtained by carefully centering 15 reflections in the range $18° \leq 2\theta \leq 25°$, were found to be $a = 9.050$ (1) Å and $c = 17.438$ (3) Å giving a calculated volume of 1428.2 (6) $Å^3$ which is consistent with two molecules per unit cell.

The automatic centering and autoindexing procedures followed have been previously described.[8] The linear absorption coefficient for Mo Kα radiation is 18.31 cm^{-1} and absorption corrections were therefore considered unnecessary.

Intensities were measured at 22 ± 4 °C on a Syntex $P\bar{1}$ autodiffractometer by using the θ–2θ scan technique. A total of 477 independent data were measured with Mo Kα (λ 0.710 73 Å) radiation in the 2θ range from 1 to 45°. A variable scan speed of 4–24° min^{-1} was used with a scan range of $K\alpha_1 - 0.8°$ to $K\alpha_2 + 0.8°$ and a scan to background time ratio of 2. The intensities of three standard reflections were monitored throughout data collection and showed no significant decrease in intensity during the period of data collection.

Solution and Refinement.[9] The position of the crystallographically unique Mo atom was determined from a three-dimensional Patterson function which indicated that the space group is either $I\bar{4}$ or $I4/m$. Results of an NZ-test favored the space group $I\bar{4}$ but attempts to solve the structure in this space group failed. Attempts to solve the structure