3700 *Inorg. Chem.* **1986**, *25*, 3700–3703

Notes

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Synthesis and Molecular Structure of $Mo_2I_4(dppm)_2 \cdot 2C_7H_8$ (dppm = Bis(diphenylphosphino)methane)

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Received March 11, 1986

Although many studies have been carried out on dinuclear molybdenum(II) compounds of general formula $Mo_2X_4L_4$ or $Mo_2X_4(LL)_2$ (X = Cl, Br; L = monodentate ligand, LL = bidentate ligand),[1-6] little work has been done on the corresponding complexes where X is iodine. This is presumably due to a lack of convenient synthetic routes to dimolybdenum(II) iodide derivatives.[7-9]

We have recently developed two new methods for the preparation of iodide derivatives of molybdenum(II). The first is the decarbonylation of molybdenum(II) carbonyl iodides.[10] The second is the reaction of $Mo_2(OAc)_4$ with Me_3SiI in the presence of the desired ligand, which is an adaptation of the method already applied to the synthesis of the corresponding chlorides[2] and bromides.[5] These two methods have been successfully applied to the preparation of $Mo_2I_4(dppm)_2$, and we now report the synthetic details and the single-crystal X-ray structure of this complex. The synthesis by method 1 has been the subject of a preliminary communication.[10]

Experimental Section

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods and distilled under dinitrogen. $Mo_2I_4(CO)_8$[11] and $Mo_2(OAc)_4$[12] were prepared according to literature procedures. Iodotrimethylsilane was purchased from Aldrich Chemical Co., and bis(diphenylphosphino)methane (dppm) was purchased from Strem Chemicals. Both were used without further purification.

Preparation of $MoI_2(CO)_3(dppm)$ (2). $Mo_2I_4(CO)_8$ (0.50 g, 0.54 mmol) was treated with dppm (0.43 g, 1.11 mmol) in 30 mL of toluene. Vigorous gas evolution was observed. The resulting orange solution was quickly filtered and set aside at room temperature without stirring. Red-orange crystals formed after several hours. They were filtered off, washed with hexane, and dried in vacuo; yield 0.54 g (61%). Anal. Calcd for $C_{28}H_{22}I_2MoO_3P_2$: C, 41.1; H, 2.7; I, 31.0. Found: C, 41.7; H, 2.9; I, 30.2. IR (toluene): 2040 s, 1975 vs, 1920 s cm^{-1}.

Table I. Crystal Data for $Mo_2I_4(dppm)_2 \cdot 2C_6H_5CH_3$

formula	$C_{57}H_{52}I_4Mo_2P_4$
fw	1560.44
space group	$P2_1/n$
systematic absences	$h0l$, $h + l \neq 2n$
a, Å	11.789 (6)
b, Å	13.108 (5)
c, Å	20.319 (6)
α, deg	90
β, deg	103.55 (1)
γ, deg	90
V, $Å^3$	3052 (2)
Z	2
d_{calcd}, g/cm^3	1.698
cryst size, mm	0.4 × 0.4 × 0.3
μ(Mo Kα), cm^{-1}	25.389
data collecn instrument	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)
orientation reflecns: no., range (2θ)	15, 10–30
temp, °C	5
scan method	ω–2θ
data collecn range, 2θ, deg	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3957
no. of parameters refined	422
transmission factors: max, min	99.96, 96.11
R^a	0.0262
R_w^b	0.0385
quality of fit indicator[c]	0.868
largest shift/esd, final cycle	0.46
largest peak, e/$Å^3$	0.515

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

Preparation of $Mo_2I_4(dppm)_2 \cdot 2C_7H_8$ (1). Method 1. $Mo_2I_4(CO)_8$ (0.47 g, 0.51 mmol) was treated with dppm (0.41 g, 1.06 mmol) in 20 mL of toluene. Gas evolution occurred, and the resulting orange solution was refluxed for ca. 12 h, during which time the product precipitated as a dark green microcrystalline solid. This was filtered off, washed with toluene, and dried in vacuo; yield 0.73 g (86%). The product possesses IR and UV–visible spectroscopic properties that are identical with those of the fully characterized sample obtained from method 2 (vide infra). The green product **1** can also be prepared by taking the isolated monomeric species, $MoI_2(CO)_3(dppm)$ (**2**), and refluxing it in toluene.

A single crystal suitable for the X-ray diffraction study was grown directly from the reaction solution obtained by treating $Mo_2I_4(CO)_8$ with 2 equiv of dppm and refluxing for 10 min. The hot solution was filtered and slowly cooled to room temperature.

Method 2. An aliquot of iodotrimethylsilane (0.3 mL, 2.1 mmol) was added to 30 mL of toluene containing $Mo_2(OAc)_4$ (0.20 g, 0.47 mmol) and dppm (0.40 g, 1.04 mmol). The solution was refluxed for 1 h, during which time the color changed from yellow to olive green with the deposition of a green microcrystalline solid. The solution was then stirred at room temperature for an additional 30 min. After this, the reaction solution was reduced in volume to ca. 10 mL and then chilled to −20 °C for 24 h. Subsequent filtration yielded a crop of green crystals that were washed with several aliquots of toluene and dried in vacuo; yield 0.65 g (94%). Anal. Calcd for $C_{64}H_{60}I_4Mo_2P_4$: C, 46.52; H, 3.66; I, 30.72. Found: C, 45.83; H, 3.62; I, 31.04. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm): 13.43 s. Visible spectrum (λ_{max}, nm (ϵ)): 707 (4108), 438 (8280).

X-ray Crystallography. Data Collection. A single crystal of approximate dimensions 0.3 × 0.4 × 0.4 mm was selected and mounted on the tip of a glass fiber. Data collection was carried out at 5 °C with the use of an automated Syntex P$\bar{1}$ diffractometer equipped with monochromated Mo Kα radiation ($\bar{\lambda}$ = 0.71073 Å). No significant change of intensity was observed for three standards monitored throughout the 122.3 h of data collection. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections[13] based on azimuthal (ψ)

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Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $Mo_2I_4(dppm)_4 \cdot 2C_7H_8$[a]

atom	x	y	z	B
I1	0.14220 (3)	0.22032 (3)	1.00690 (2)	3.100 (7)
I2	−0.24669 (3)	0.03815 (3)	0.89935 (2)	3.078 (7)
Mo	−0.02796 (3)	0.07259 (3)	0.97809 (2)	1.963 (7)
P1	0.0379 (1)	0.04517 (9)	0.86862 (6)	2.21 (2)
P2	−0.0944 (1)	0.1630 (1)	1.08136 (6)	2.54 (2)
C1	0.0144 (4)	−0.0899 (4)	0.8448 (2)	2.41 (9)
C11	0.1860 (4)	0.0654 (4)	0.8571 (2)	2.6 (1)
C12	0.2820 (4)	0.0557 (4)	0.9106 (3)	3.1 (1)
C13	0.3937 (5)	0.0578 (5)	0.8982 (3)	4.1 (1)
C14	0.4075 (5)	0.0672 (5)	0.8332 (3)	4.8 (1)
C15	0.3123 (5)	0.0767 (5)	0.7812 (3)	4.8 (1)
C16	0.2026 (4)	0.0770 (5)	0.7927 (3)	3.6 (1)
C21	−0.0499 (4)	0.1217 (4)	0.8009 (2)	2.56 (9)
C22	−0.1162 (5)	0.0832 (4)	0.7415 (3)	3.9 (1)
C23	−0.1814 (5)	0.1471 (5)	0.6927 (3)	4.3 (1)
C24	−0.1813 (5)	0.2480 (5)	0.7031 (3)	4.2 (1)
C25	−0.1141 (7)	0.2875 (5)	0.7614 (3)	5.6 (2)
C26	−0.0491 (6)	0.2248 (4)	0.8105 (3)	4.8 (2)
C31	−0.2448 (4)	0.1775 (4)	1.0900 (3)	2.9 (1)
C32	−0.3315 (5)	0.1982 (4)	1.0321 (3)	3.7 (1)
C33	−0.4432 (5)	0.2206 (5)	1.0375 (3)	4.9 (1)
C34	−0.4698 (5)	0.2220 (6)	1.0997 (4)	5.8 (2)
C35	−0.3844 (6)	0.2040 (6)	1.1570 (3)	5.4 (2)
C36	−0.2722 (5)	0.1825 (5)	1.1523 (3)	3.8 (1)
C41	−0.0511 (4)	0.2955 (4)	1.1009 (3)	2.8 (1)
C42	−0.0960 (6)	0.3676 (4)	1.0519 (3)	4.8 (2)
C43	−0.0735 (6)	0.4706 (5)	1.0639 (4)	5.7 (2)
C44	−0.0086 (6)	0.5018 (4)	1.1242 (4)	5.2 (2)
C45	0.0372 (6)	0.4315 (5)	1.1731 (3)	5.3 (2)
C46	0.0152 (5)	0.3267 (4)	1.1621 (3)	3.7 (1)
C51	0.4342 (9)	0.3933 (8)	0.8721 (4)	10.3 (3)
C52	0.4969 (8)	0.3242 (7)	0.8455 (4)	8.2 (2)
C53	0.615 (1)	0.3321 (9)	0.8545 (5)	11.2 (3)
C54	0.674 (1)	0.407 (1)	0.8942 (5)	13.2 (3)
C55	0.607 (1)	0.4818 (9)	0.9213 (5)	17.8 (5)
C56	0.488 (2)	0.4721 (9)	0.9095 (5)	15.8 (5)
C60	0.308 (1)	0.384 (1)	0.8622 (6)	16.7 (5)
H1	−0.069 (4)	−0.104 (4)	0.840 (2)	3 (1)*
H2	0.033 (4)	−0.111 (4)	0.801 (3)	5 (1)*
H12	0.277 (4)	0.047 (3)	0.954 (2)	3 (1)*
H13	0.461 (5)	0.051 (5)	0.933 (3)	6 (2)*
H14	0.467 (4)	0.076 (4)	0.828 (3)	5 (1)*
H15	0.326 (4)	0.094 (4)	0.743 (3)	5 (1)*
H16	0.150 (3)	0.084 (3)	0.763 (2)	1.4 (8)*
H22	−0.121 (4)	0.013 (4)	0.730 (2)	3 (1)*
H23	−0.243 (6)	0.095 (6)	0.648 (4)	9 (2)*
H24	−0.236 (4)	0.283 (4)	0.671 (2)	3 (1)*
H25	−0.130 (4)	0.340 (4)	0.773 (3)	5 (1)*
H26	−0.006 (5)	0.235 (5)	0.858 (3)	7 (2)*
H32	−0.313 (4)	0.187 (4)	0.989 (3)	4 (1)*
H33	−0.5027	0.2363	0.9976	4*
H34	−0.530 (5)	0.225 (4)	1.106 (3)	5 (1)*
H35	−0.4032	0.2062	1.2003	4*
H36	−0.214 (4)	0.168 (4)	1.190 (2)	3 (1)*
H42	−0.134 (6)	0.354 (6)	1.021 (4)	9 (2)*
H43	−0.097 (4)	0.521 (4)	1.028 (3)	4 (1)*
H44	0.010 (5)	0.574 (5)	1.130 (3)	6 (2)*
H45	0.070 (4)	0.448 (4)	1.205 (3)	4 (1)*
H46	0.042 (4)	0.276 (4)	1.195 (2)	3 (1)*

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

scans of nine reflections having an Eulerian angle χ near 90° were applied. Pertinent crystallographic parameters are summarized in Table I.

Structure Solution and Refinement. Axial photographs and systematic absences from the data indicate that the crystal belongs to the monoclinic $P2_1/n$ space group. The structure was solved and refined by using the Enraf-Nonius Structure Determination Package. The positions of the heavy atoms were determined by Patterson and direct methods. Full-matrix least-squares refinement followed by a difference Fourier map revealed the positions of all the other non-hydrogen atoms. The structure was refined further with all atoms anisotropic, to an R_1 value of 0.030. A subsequent Fourier map revealed the positions of all the hydrogen atoms of the $Mo_2I_4(dppm)_2$ molecule, but not those of the toluene solvent molecule. These were included in the subsequent cycles of refinement. The toluene hydrogen atoms were placed at calculated positions with a C–H distance of 0.95 Å, but they could not be refined well and were therefore excluded again. Also, two hydrogen atoms of the $Mo_2I_4(dppm)_2$ molecule, H33 and H35, could not be refined well. These were reset at the calculated positions, and all the parameters of the hydrogen atoms were fixed during the last cycles of refinement. Convergence was achieved with $R_1 = 0.0267$ and $R_2 = 0.0382$. Table II contains positional and thermal parameters for compound **1**. Selected bond distances and angles are reported in Table III.

Table III. Selected Bond Distances and Angles for $Mo_2I_4(dppm)_2 \cdot 2C_7H_8$

(a) Bond Lengths (Å)			
Mo–Mo′	2.139 (1)	P1–C1	1.839 (5)
Mo–I1	2.751 (1)	P1–C11	1.834 (5)
Mo–I2	2.735 (1)	P1–C21	1.818 (5)
Mo–P1	2.548 (1)	P2–C1	1.843 (6)
Mo–P2	2.682 (1)	P2–C31	1.832 (6)
		P2–C41	1.826 (5)
(b) Bond Angles (deg)			
I1–Mo–I2	141.38 (2)	Mo–P1–C21	110.3 (2)
I1–Mo–Mo′	113.55 (3)	Mo–P2–C1	102.7 (2)
I1–Mo–P1	85.91 (3)	Mo–P2–C31	126.0 (2)
I1–Mo–P2	81.62 (3)	Mo–P2–C41	118.1 (2)
I2–Mo–Mo′	104.66 (3)	C1–P1–C11	101.2 (3)
I2–Mo–P1	84.52 (3)	C1–P1–C21	107.9 (3)
I2–Mo–P2	97.05 (3)	C11–P1–C21	102.3 (2)
P1–Mo–Mo′	96.36 (4)	C1–P2–C31	107.3 (3)
P2–Mo–Mo′	100.70 (4)	C1–P2–C41	104.7 (3)
P1–Mo–P2	161.84 (5)	C31–P2–C41	96.2 (3)
Mo–P1–C1	107.9 (2)	P1–C1–P2	105.7 (3)
Mo–P1–C11	125.8 (2)		

Results and Discussion

Synthetic Methods. The title compound has been prepared by two different routes (see eq 1 and 2).

$$Mo_2I_4(CO)_8 + 2dppm \xrightarrow[\text{reflux}]{\text{toluene}} Mo_2I_4(dppm)_2 + 8CO \quad (1)$$

$$Mo_2(OAc)_4 + 4Me_3SiI + 2dppm \xrightarrow[\text{reflux}]{\text{toluene}} Mo_2I_4(dppm)_2 + 4MeCOOSiMe_3 \quad (2)$$

The complex $Mo_2I_4(dppm)_2$ has also recently been reported by Walton and co-workers[9a] as an acetone solvate by halide exchange from the corresponding chloride (see eq 3).

$$Mo_2Cl_4(dppm)_2 + 4NaI \xrightarrow{\text{acetone}} Mo_2I_4(dppm)_2 + 4NaCl \quad (3)$$

Our methods (eq 1 and 2) afford compound **1** in very high yields and have the advantage of being single-step procedures using readily available starting materials.

The products isolated from the reaction mixtures of methods 1 and 2 exhibit identical spectroscopic properties and are undoubtedly the same compound. These results, however, are not in complete accord with the data reported by Walton et al. for the species isolated from acetone (eq 3).[9a] The origin of these discrepancies is currently under investigation.[9b]

The synthetic approach taken in eq 2 is an exploitation of results first described by McCarley et al., who reported that the action of Me_3SiX (X = Cl, Br, I) upon quadruply bonded dimers results in condensation to form tetranuclear cluster complexes.[14] A subsequent study by Green and co-workers revealed that $Mo_2(OAc)_4$ reacts with Me_3SiCl in the presence of donor ligands to yield dinuclear products.[15] The general utility of the latter

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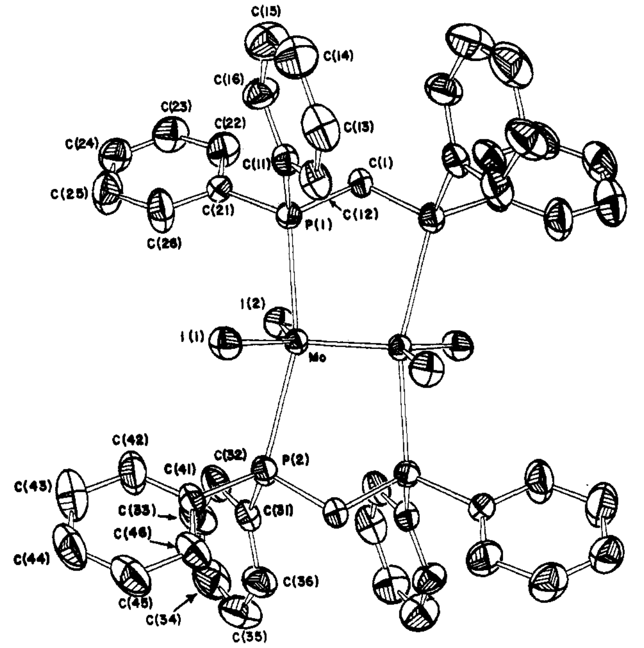

Figure 1. ORTEP view of the $Mo_2I_4(dppm)_2$ molecule in compound **1**.

reaction was further demonstrated by Agaskar and Cotton, who used this method to prepare complexes of the type $Mo_2X_4(dppe)_2$ (X = Cl, Br; dppe = bis(diphenylphosphino)ethane).[2,5] The use of Me_3SiI, like the corresponding chloride and bromide reagents, in a reaction involving $Mo_2(OAc)_4$ and a bidentate phosphine leads to a clean production of $Mo_2I_4(LL)_2$ (LL = dppm, dppe[16]).

The primary product of the reaction between $Mo_2I_4(CO)_8$ and dppm is the mononuclear tricarbonyl complex $MoI_2(CO)_3dppm$ (**2**) (see eq 4), which can be readily isolated from the reaction mixture. It exhibits three strong absorptions in the carbonyl

$$\mathrm{Mo_2I_4(CO)_8} + 2\mathrm{dppm} \xrightarrow[\text{room temp}]{\text{toluene}} 2\mathrm{MoI_2(CO)_3dppm} + 2\mathrm{CO} \qquad (4)$$

stretching region at 2040 s, 1975 vs, and 1920 s cm^{-1} (cf. 2050 s, 1975 vs, and 1925 s cm^{-1} for the corresponding bromide, $MoBr_2(CO)_3dppm$).[17] The same type of compound is obtained from $Mo_2Br_4(CO)_8$[17] or $W_2I_4(CO)_8$[18] and dppm at room temperature, and a large number of tricarbonyl derivatives of the $MX_2(CO)_3L_2$ type (M = Mo, W; X = Cl, Br, I) have also been prepared in a similar way from the corresponding $M_2X_4(CO)_8$.[19]

When the room-temperature reaction was carried out with a slight excess of dppm, two more bands at 1946 and 1870 cm^{-1} were detectable in the final solution. These are due to the mononuclear dicarbonyl $MoI_2(CO)_2(dppm)_2$ (**3**), containing a chelating and a monodentate diphosphine. This complex has also been obtained by reacting $[MoI_3(CO)_4]^-$ with dppm and has been structurally characterized.[20] When compound **2** is refluxed, product **1** is finally obtained. It is remarkable that while quite a few molybdenum(II) tricarbonyl derivatives of the type $MoI_2(CO)_3L_2$ have been subjected to high temperature, the only observed decarbonylation products have been the mononuclear 16e dicarbonyls[21] $MX_2(CO)_2L_2$ or the corresponding 18e dimers[21f]

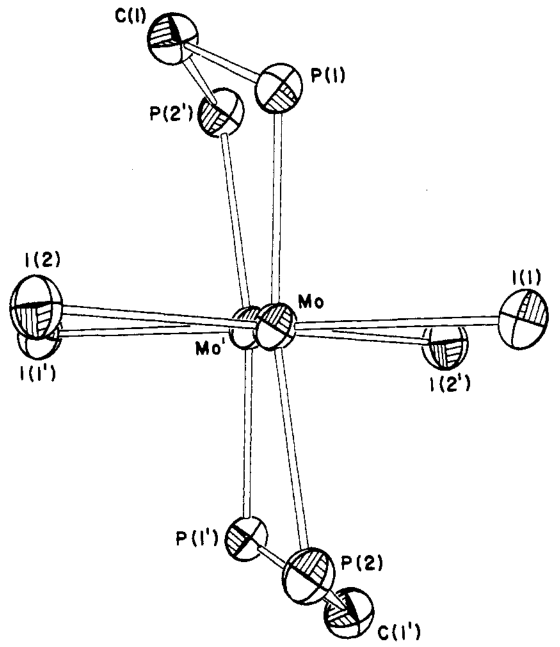

Figure 2. Central portion of the $Mo_2I_4(dppm)_2$ molecule viewed along a direction close to the Mo–Mo' axis.

$[MX_2(CO)_2L_2]_2$. In our system, however, complete decarbonylation occurs with production of the quadruply bonded dimer **1**. This result is possibly due to the forcing conditions employed and to the chelating effect of the ligand, although the latter is probably not so important, since we observed the formation of the Mo–Mo quadruple bond also with monodentate phosphines.[10]

Crystal Structure. Compound **1** crystallizes in the centrosymmetric monoclinic $P2_1/n$ space group. The dimer (see Figure 1) resides on a crystallographic inversion center, and the toluene molecules occupy general positions. Compound **1** is isostructural with $Mo_2Br_4(dppm)_2{\cdot}2THF$,[3] and both differ from $Mo_2Cl_4(dppm)_2{\cdot}2C_3H_6O$,[22] the latter crystallizing in the $C2/c$ space group. All three dimers, however, reside on an inversion center and have the same molecular geometry. The rotational conformation around the Mo–Mo' bond in compound **1** (see Figure 2) is strictly eclipsed with zero average torsional angle. The two independent torsional angles are 5.7 and 6.2°, which may be compared with 6.2 and 8.1° in the bromide[3] and 2.6 and 6.1° in the chloride.[22] With the exception of the Mo–I distances, all the structural parameters are very similar to the corresponding ones in the other two halides.[3,22] Most notably, the Mo–Mo' distance is statistically the same in the three compounds, in agreement with previous findings concerning the effect of the halide on metal–metal bond length.[23] The Mo–I distances, 2.751 (1) and 2.735 (1) Å, compare with those found in $Mo_2I_4(PMe_3)_4{\cdot}2THF$[10] (2.762 (1) and 2.756 (1) Å) and with those found in the $[Mo_2I_6(H_2O)_2]^{2-}$ anion[24] (average 2.790 (1) Å).

Comparison of the $\delta \rightarrow \delta^*$ Transitions in $Mo_2X_4(dppm)_2$ (X = Cl, Br, I). Recently, efforts in this group have been directed toward studying the spectroscopic and structural properties of compounds of the type $M_2X_4(LL)_2$, where LL is a bridging bidentate ligand such as $R_2P(CH_2)_nPR_2$.[2-6] Specifically, the correlation has been studied of Mo–Mo quadruple-bond length with the degree of internal rotation about the Mo–Mo axis. In addition to lengthening the M–M distance, internal twist makes the chromophore chiral and also decreases the $\delta \rightarrow \delta^*$ transition energy. The latter phenomenon was discussed with use of data for 10 compounds of the type $Mo_2X_4(LL)_2$, where X = Cl, Br.[4] Included in this study were the compounds $Mo_2X_4(dppm)_2$ (X = Cl, Br), which

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have an average torsional twist of 0°. The present study of the iodo derivative presents an opportunity to further compare the energy of the $\delta \rightarrow \delta^*$ transition as a function of the halide. This comparison is believed to be particularly meaningful since the three complexes exhibit practically identical structural parameters (see previous section). These absorptions occur at 15 600, 15 300, and 14 100 cm^{-1} for the chloro, bromo, and iodo derivatives, respectively. These values are taken from spectra recorded as Nujol mulls on solid samples. An earlier comparison of the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition energy for three other related chloro and bromo complexes led to an average energy difference of 600 cm^{-1}.[4] Our work shows that the transition for $Mo_2I_4(dppm)_2$ is considerably red-shifted from those of the chloro and bromo analogoues. Presumably there are interactions between the halogen pπ and dπ orbitals and the metal–metal δ and δ^* orbitals, and these differ on going from chloride to bromide and then to iodide.

Acknowledgment. We are grateful to Prof. R. A. Walton for helpful discussions and for sending us a copy of his manuscript prior to publication. We also thank the National Science Foundation for support.

Supplementary Material Available: Full tables of bond distances and angles and a listing of anisotropic displacement parameters (5 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Products of the Reaction between $Mo_2I_4(CO)_8$ and Bis(dimethylphosphino)methane (dmpm). X-ray Crystal Structure of $MoI_2(CO)(dmpm)_2 \cdot C_7H_8$

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Received April 7, 1986

The molybdenum(II) diiodide tetracarbonyl dimer, $Mo_2I_4(CO)_8$,[1] whose synthesis has been recently[2] made possible on a large scale, has been found to react with monodentate[3] and bidentate[3,4] phosphines to afford quadruply bonded dimolybdenum(II) derivatives. Tricarbonyl and dicarbonyl mononuclear intermediates were isolated or detected in the bis(diphenylphosphino)methane (dppm) reaction. In order to acquire further information on the mechanism of this metal–metal bond formation, we carried out a similar reaction with bis(dimethylphosphino)methane (dmpm), the results of which are herein reported.

Experimental Section

All the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods and distilled under dinitrogen. $Mo_2I_4(CO)_8$ was prepared as described elsewhere.[2] The dmpm ligand was purchased from Strem Chemicals and dissolved in toluene to give a 1.2 M solution, which was then used directly. Spectrometers: UV-visible, Cary 17; IR, Perkin-Elmer 783. Solution IR spectra were recorded on an expanded abscissa scale and calibrated with both CO(g) and water vapor.

Reaction of $Mo_2I_4(CO)_8$ with dmpm. $Mo_2I_4(CO)_8$ (0.41 g, 0.44 mmol) was dissolved in 25 mL of toluene and treated at room temperature with 0.96 mmol of dmpm. An immediate reaction took place with evident gas evolution and formation of a flocculent yellow solid suspended in an orange solution. The solution had IR bands at 2070 vw, 2016 w, 1939 s, 1920 m, 1898 ms, and 1855 m cm^{-1}. The mixture was refluxed for 24 h and then filtered hot and cooled to room temperature. Further cooling to −20 °C gave, over a period of 24 h, a mixture of emerald green and red crystals. A red crystal from this crop was used for the X-ray diffraction study. The two compounds were separated by handpicking.

Table I. Crystal Data for $MoI_2(CO)(dmpm)_2 \cdot C_7H_8$

formula	$C_{18}H_{36}I_2MoOP_4$
fw	742.13
space group	$P2_12_12_1$
systematic absences	$h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$
a, Å	10.331 (3)
b, Å	11.725 (1)
c, Å	22.997 (5)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2785 (2)
Z	4
d_{calcd}, g/cm^3	1.77
cryst size, mm	0.1 × 0.2 × 0.5
μ(Mo Kα), cm^{-1}	28.877
data collecn instrument	CAD4
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)
orientation reflecns: no., range (2θ)	25, 18–33
temp, °C	20
scan method	ω
data collecn range, 2θ, deg	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1483
no. of parameters refiend	201
transmission factors: max, min	99.98, 90.52
R^a	0.0406
R_w^b	0.0466
quality-of-fit indicator^c	1.128
largest shift/esd, final cycle	0.08
largest beak, e/Å	0.480

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

Green compound (**1**): UV–visible spectroscopic properties (CH_2Cl_2, λ_{max}, cm^{-1} (ϵ)) 14 400 (1610), 23 900 (7240). Red compound (**2**): IR (toluene) 1794 cm^{-1}.

X-ray Crystallography for $MoI_2(CO)(dmpm)_2 \cdot C_7H_8$. Data Collection. A single crystal of approximate dimensions 0.1 × 0.2 × 0.5 mm was mounted in a capillary in the presence of a small amount of its saturated toluene solution. Data collection was carried out at room temperature with the use of an automated CAD-4 diffractometer equipped with monochromated Mo Kα radiation (λ = 0.710 73 Å). No significant change of intensity was observed for three standard reflections monitored throughout the data collection. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections[5] based on azimuthal (ψ) scans of nine reflections having an Eulerian angle χ near 90° were applied. Pertinent crystallographic parameters are summarized in Table I.

Structure Solution and Refinement. Axial photographs and systematic absences from the data uniquely determined the space group as the orthorhombic $P2_12_12_1$. The structure was solved and refined by using the Enraf-Nonius Structure Determination Package. The positions of the heavy atoms were determined by direct methods, and full-matrix least-squares refinement followed by a difference Fourier map revealed the positions of all the other non-hydrogen atoms. Subsequent anisotropic refinement was carried out independently on both enantiomers. The one reported here is the one that converged to the lowest R value. The hydrogen atoms were not included in the refinement. Table II contains positional and thermal parameters for compound **2**. Selected bond distances and angles are reported in Table III.

Results and Discussion

The reaction of $Mo_2I_4(CO)_8$ with dmpm is very fast at room temperature; CO evolution occurs, and carbonyl products are formed, among which $MoI_2(CO)_3$dmpm and $MoI_2(CO)_2(dmpm)_2$ have been recognized. Their identification is based on the comparison of the CO stretching vibrations of the resulting toluene solution (see Experimental Section) with those of the corresponding dppm compounds. The bands at 2016 w, 1939 s, and 1898 ms cm^{-1} are therefore assigned to the $MoI_2(CO)_3$dmpm species (cf.

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