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

F. Albert Cotton* and Rinaldo Poli

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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 ($\lambda_{\bar{\alpha}}$ = 0.71073 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 ($\bar{\lambda}$ = 0.71073 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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Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $MoI_2(CO)(dmpm)_2 \cdot C_7H_8$[a]

atom	x	y	z	B
Mo	0.7850 (1)	0.7945 (1)	0.64885 (2)	2.96 (3)
I1	0.9963 (1)	0.9509 (1)	0.62495 (6)	4.94 (3)
I2	0.7305 (1)	0.9239 (1)	0.75590 (5)	4.76 (3)
P1	0.9833 (4)	0.6960 (4)	0.6831 (2)	3.6 (1)
P2	0.7433 (5)	0.6116 (4)	0.7010 (2)	3.8 (1)
P3	0.6816 (5)	0.9570 (5)	0.5959 (2)	4.5 (1)
P4	0.5465 (5)	0.7732 (5)	0.6354 (2)	4.5 (1)
C1	0.815 (2)	0.717 (2)	0.5777 (8)	4.5 (5)
O1	0.828 (2)	0.669 (1)	0.5349 (5)	7.0 (4)
C2	0.912 (2)	0.557 (2)	0.7059 (9)	5.1 (5)
C3	1.075 (2)	0.743 (2)	0.7486 (8)	4.6 (4)
C4	1.109 (2)	0.657 (2)	0.6292 (8)	4.9 (5)
C5	0.656 (2)	0.491 (2)	0.6670 (9)	5.1 (5)
C6	0.689 (2)	0.609 (2)	0.7768 (9)	6.5 (6)
C7	0.511 (2)	0.917 (2)	0.6076 (9)	5.2 (5)
C8	0.702 (3)	0.960 (2)	0.5166 (8)	7.8 (6)
C9	0.696 (2)	1.109 (2)	0.6150 (9)	6.3 (6)
C10	0.485 (2)	0.681 (2)	0.5775 (9)	6.7 (6)
C11	0.431 (2)	0.753 (2)	0.6954 (9)	6.0 (6)
C20	0.473 (3)	1.167 (3)	0.419 (1)	12 (1)*
C21	0.424 (2)	1.196 (2)	0.474 (1)	7.9 (7)*
C22	0.471 (2)	1.292 (2)	0.501 (1)	8.7 (7)*
C23	0.443 (3)	1.337 (3)	0.559 (1)	11.1 (9)*
C24	0.352 (3)	1.264 (3)	0.585 (1)	12 (1)*
C25	0.320 (3)	1.157 (3)	0.563 (1)	12 (1)*
C26	0.340 (3)	1.120 (3)	0.508 (1)	10.4 (9)*

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

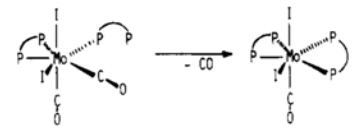
2040 s, 1975 vs, and 1920 s cm^{-1} of $MoI_2(CO)_3dppm$[4]) and those at 1920 m and 1855 m cm^{-1} to $MoI_2(CO)_2(dmpm)_2$ (cf. 1946 s and 1870 s cm^{-1} of $MoI_2(CO)_2(dppm)_2$[4,6]). The average difference in position for corresponding bands, as one goes from the dppm to the dmpm derivatives, is about 23 cm^{-1} and is in accord with the higher Lewis basicity of the methyl-substituted diphosphine. $MoI_2(CO)_2(dppm)_2$ has been structurally characterized[6] and shown to contain one chelating and one monodentate diphosphine in a distorted-capped-octahedral arrangement of the donor atoms; the geometry of $MoI_2(CO)_2(dmpm)_2$ is therefore expected to be similar. The presence, in our reaction mixture, of an ionic species such as $[MoI(CO)_2(dmpm)_2]I$, similar to the corresponding yellow dppm complex prepared by Colton and Howard, $[MoI(CO)_2(dppm)_2]I$,[7] cannot be ruled out, since small amounts of a yellow precipitate were actually observed (see Experimental Section).

However complex the room-temperature reaction mixture is, subsequent reflux gives rise to a less complicated solution from which $Mo_2I_4(dmpm)_2$ (**1**) and $MoI_2(CO)(dmpm)_2$ (**2**) can be easily crystallized. Compound **1** was the major product when a dmpm/Mo ratio close to 1 was used. The relative amount of compound **2** could be increased upon raising the dmpm/Mo ratio to 2, but a certain amount of compound **1** was nevertheless recovered from the final crop of crystals.

Compound **1** is a dinuclear molybdenum(II) compound with a quadruple bond between the two metal centers. This is clearly shown by the characteristic visible $\delta \rightarrow \delta^*$ absorption at 14 400 cm^{-1} (cf. 14 100 cm^{-1} for $Mo_2I_4(dppm)_2$). Also the rest of the UV–visible spectrum is similar to that of the dppm compound, for which the structure is known,[4] and we therefore suggest that the two complexes have the same arrangement of the ligands; namely, the two dmpm ligands bridge the two metals in a relative trans arrangement with a torsional angle around the metal–metal bond close to 0°.

The very low wavenumber of the CO stretching vibration in compound **2**, 1794 cm^{-1}, denotes the high electron density on the molybdenum atom, despite the formal +II oxidation state. This is certainly due to the presence of four strongly basic phosphorus atoms in the coordination sphere.

Scheme I



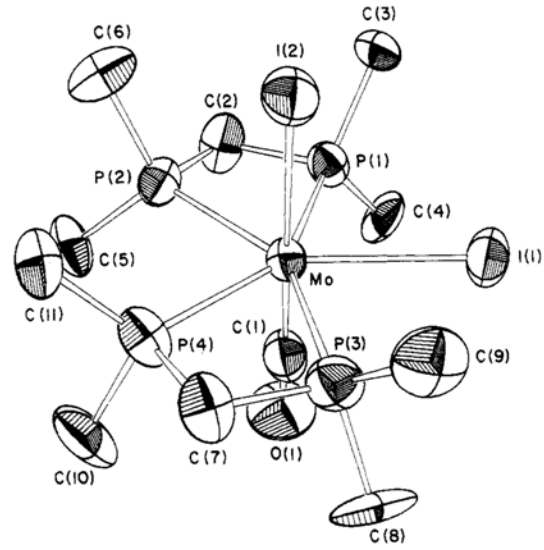


Figure 1. ORTEP view of the $MoI_2(CO)(dmpm)_2$ molecule.

The formation of compound **2** can be envisaged to occur via the supposed $MoI_2(CO)_2(dmpm)_2$ intermediate. This would in turn have one CO ligand replaced by the dangling phosphorus atom of the monodentate phosphine (see Scheme I).

We might simply rationalize the formation of the two products by stating that decarbonylation of $MoI_2(CO)_3dmpm$ leads to the formation of **1**, while decarbonylation of $MoI_2(CO)_2(dmpm)_2$ affords compound **2**; the relative amount of the two final products of the high-temperature reaction would therefore be solely determined by the initial dmpm/Mo ratio. We cannot, however, rule out the possibility that compound **2** slowly decomposes with elimination of CO *and* one diphosphine to convert itself to **1**. This idea is supported by the observation[8] that $MoI_2(CO)_2(dppm)_2$ thermally decomposes to a green product, which we believe to be the known[3,4,9] quadruply bonded dimer $Mo_2I_4(dppm)_2$. The substitution of a CO ligand by the dangling phosphorus in $MoI_2(CO)_2(dppm)_2$ might be prevented by the high steric demand of the phenyl groups in a structure like that of compound **2** so that, following CO release, a dppm ligand is also lost to provide a route to the formation of the stable quadruply bonded dimolybdenum(II) unit. Compound **2**, on the other hand, is expected to be more stable, and it is in fact by far the major product after a 24-h reflux when the reaction is conducted with a dmpm/Mo ratio of 2.

We wish to stress the fact that, although other authors have investigated several reactions of $Mo_2X_4(CO)_8$ complexes with phosphines[1,10] and diphosphines,[11] none of them reported on the formation of quadruply bonded molybdenum(II) dimers.

Complex **2** appears to be the first structurally characterized molybdenum(II) compound containing two diphosphines both

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Table III. Selected Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $MoI_2(CO)(dmpm)_2 \cdot C_7H_8$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	I1	2.903 (2)	P1	C2	1.86 (2)	P3	C8	1.84 (2)
Mo	I2	2.946 (2)	P1	C3	1.86 (2)	P3	C9	1.84 (2)
Mo	P1	2.480 (5)	P1	C4	1.85 (2)	P4	C7	1.84 (2)
Mo	P2	2.495 (5)	P2	C2	1.86 (2)	P4	C10	1.83 (2)
Mo	P3	2.501 (5)	P2	C5	1.86 (2)	P4	C11	1.84 (2)
Mo	P4	2.496 (5)	P2	C6	1.83 (2)	C1	O1	1.14 (2)
Mo	C1	1.90 (2)	P3	C7	1.85 (2)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
I1	Mo	I2	88.68 (5)	P2	Mo	P4	78.6 (2)	C5	P2	C6	104 (1)
I1	Mo	P1	74.6 (1)	P2	Mo	C1	91.8 (6)	Mo	P3	C7	98.3 (6)
I1	Mo	P2	139.8 (1)	P3	Mo	P4	66.1 (2)	Mo	P3	C8	116.6 (8)
I1	Mo	P3	75.4 (1)	P3	Mo	C1	90.9 (6)	Mo	P3	C9	126.0 (7)
I1	Mo	P4	141.5 (2)	P4	Mo	C1	90.4 (6)	C7	P3	C8	105 (1)
I1	Mo	C1	90.9 (6)	Mo	P1	C2	99.8 (6)	C7	P3	C9	107 (1)
I2	Mo	P1	97.6 (1)	Mo	P1	C3	122.8 (7)	C8	P3	C9	102 (1)
I2	Mo	P2	90.5 (1)	Mo	P1	C4	118.6 (6)	Mo	P4	C7	98.6 (6)
I2	Mo	P3	86.2 (1)	C2	P1	C3	103.4 (9)	Mo	P4	C10	119.6 (8)
I2	Mo	P4	88.1 (1)	C2	P1	C4	104.6 (9)	Mo	P4	C11	124.0 (7)
I2	Mo	C1	177.0 (6)	C3	P1	C4	104.8 (9)	C7	P4	C10	103 (1)
P1	Mo	P2	65.7 (2)	Mo	P2	C2	99.2 (6)	C7	P4	C11	104 (1)
P1	Mo	P3	149.6 (2)	Mo	P2	C5	122.6 (7)	C10	P4	C11	104 (1)
P1	Mo	P4	143.9 (2)	Mo	P2	C6	121.7 (8)	Mo	C1	O1	177 (2)
P1	Mo	C1	85.1 (6)	C2	P2	C5	102.8 (9)	P1	C2	P2	93.2 (9)
P2	Mo	P3	144.6 (2)	C2	P2	C6	103 (1)	P3	C7	P4	95.2 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

chelating the metal to form four-membered rings. Other molybdenum(II) seven-coordinate complexes containing two such diphosphines are known,[12] but in these only one diphosphine chelates, while the other is monodentate. Compound **2** crystallizes with a toluene molecule of solvation; the structure of the $MoI_2(CO)(dmpm)_2$ molecule is shown in Figure 1. The geometry around the metal center is close to that of an ideal pentagonal bipyramid, the two axial ligands being I2 and the carbonyl group. The equatorial plane is defined by I1 and the four phosphorus atoms, and the largest deviation from it is 0.127 (5) Å for P1; the molybdenum atom is off the plane by only 0.005 (1) Å. The two bonds with the axial ligands form angles of 85.4° (I2) and 88.4° (C1) with the least-squares equatorial plane.

It is worth noting that, although the pentagonal bipyramid (pb) is a fairly common polyhedron in seven-coordination chemistry, it is not as common[12a] for carbonyl derivatives of d^4 metals; the capped octahedron (co) or the capped trigonal prism (ctp) have commonly been found in such cases.[12b] We suggest that the choice of the pb arrangement for compound **2** is favored by the chelation of *two* dmpm ligands. In fact, the dmpm ligand requires a fairly small angle between the two M–P vectors (angles of 65.7 (2) and 66.1 (2)° are found in compound **2** for P1–Mo–P2 and P3–Mo–P4, respectively). An ideal co geometry exhibits an L_c–M–L_{cf} angle (we use the Drew nomenclature[12b] here) of 74.1°; the angles between any other pair of M–L vectors are higher (76.6° for $(L_{cf}\text{–M–}L_{uf})_{cis}$, 89.6° for L_{uf}–M–L_{uf}, and 112.8° for L_{cf}–M–L_{cf}).[12b] The same thing happens for the ctp geometry, where there is one 71.5° angle (L_c–M–L_c), while the others are at least 78.7°.[12b] The ideal pb geometry, on the other hand, shows angles of 72° between any pair of cis-equatorial ligands.[12b] A single chelating dmpm would presumably be accommodated in a distorted co or ctp structure as well as in a distorted tb structure, and a few structures of complexes with related ligands such as $MoBr_2(CO)_2(dpam)_2$,[11a] $MoCl_2(CO)_2(dpam)_2$,[11b] $WI_2(CO)_3dpam$[13] (dpam = bis(diphenylarsino)methane), $MoCl_2(CO)_2(dppm)_2$,[11b] and $MoI_2(CO)_2(dppm)_2$[6] have indeed been best described as capped octahedra. When two chelating dmpm ligands have to be accommodated, however, only the tb geometry provides two independent low-angle sites.

The two molybdenum–iodine distances, 2.903 (2) and 2.946 (2) Å for Mo–I1 and Mo–I2, respectively, are somewhat longer than those commonly found for terminal Mo–I bonds in 18-electron molybdenum(II) carbonyl derivatives, e.g. 2.855 (2) Å in $Mo_2I_4(CO)_8$,[2] 2.833 (4), 2.845 (4), and 2.836 (4) Å in the cation and the dinuclear anion, respectively, of $[MoI(CO)_3(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][Mo_2I_5(CO)_6]$,[14] 2.835 (2), 2.860 (3), 2.846 (2), and 2.855 (1) Å in the cation and the anion, respectively, of $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$,[14] 2.822 (2) Å in $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_5$,[15] and 2.807 (3), 2.854 (3) and 2.865 (3) Å in the cation and anion, respectively, of $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_2(I_3)(CO)_4]$.[15] The electronic influence of the phosphines in compound **2** might be responsible for this effect. The Mo–I distances in $MoI_2(CO)_2(dppm)_2$,[6] electronically more similar to our compound **2**, are 2.846 (1) and 2.904 (1) Å, while those in $MoI_2(CO)_3$(*meso*-dimas) and in $MoI_2(CO)_3$(*rac*-dimas) (dimas = *o*-phenylenebis(methylphenylarsine))[16] are in the 2.854 (3)–2.877 (3) Å range.

It is interesting to note that these distances seem to be sensitive to the electronic situation on the metal. They are longest (ca. 2.9 Å) in the phosphine-substituted 18-electron complexes, while they are in the 2.80–2.85-Å range for 18-electron carbonyl derivatives without phosphines, and they are even shorter in quadruply bonded dimers (2.762 (1) and 2.756 (1) Å in $Mo_2I_4(PMe_3)_4$[3] and 2.751 (1) and 2.735 (1) Å in $Mo_2I_4(dppm)_2$[4]) where the number of electrons on the metal is formally 16.

The Mo–P distances in complex **2** are in the narrow range from 2.480 (5) to 2.501 (5) Å and agree well with the values found for other similar compounds.

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Registry No. **1**, 103904-45-6; **2**, 103933-02-4; $MoI_2(CO)_3dmpm$, 103904-46-7; $MoI_2(CO)_2(dmpm)_2$, 103904-47-8; $Mo_2I_4(CO)_8$, 22547-54-2.

Supplementary Material Available: Full tables of bond distances and angles and a listing of anisotropic displacement parameters (4 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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