SYNTHESIS, MOLECULAR STRUCTURE AND SPECTROSCOPIC CHARACTERIZATION OF $M_0(CO)_2I_2(\eta^2-dppm)(\eta^1-dppm)$

F. ALBERT COTTON* and MAREK MATUSZ

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, U.S.A.

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Abstract—A new, high-yield method has been developed for the preparation of $Mo(CO)_2I_2(\eta^2$ -dppm)(η^1 -dppm). The title compound was prepared by the reaction of $[Et_4N][Mo(CO)_4I_3]$ with dppm in benzene in 95% yield. It has been characterized by a single-crystal X-ray study. The crystallographic data are as follows: monoclinic, space group $P2_1/n$, a = 19.023(4) Å, b = 14.439(3) Å, c = 20.141(5) Å, $\beta = 100.45(2)^\circ$, V = 5440(2) Å³, Z = 4. The geometry around the central metal atom could be considered as either a distortion from a capped octahedron with a carbonyl in a capping position or from a trigonal prism with the iodine capping a rectangular face. The solution behavior of $Mo(CO)_2I_2(dppm)_2$ was examined with ³¹P NMR, which showed it to be fluxional.

Recently we have been investigating the possibility of forming multiply bonded heteroatomic dimers. One of the designed approaches would be to have a bidentate, dangling ligand on one metal atom. The dangling ligand might then coordinate to a second metal atom, bringing it close enough for an M—M' bond to be formed, with the dangling ligand(s) becoming a bridge spanning the dimetallic core. For such a purpose the starting material would have to meet at least the following criteria :

(1) contain a metal that easily forms multiple bonds, or

(2) have the metal already in a suitable oxidation state.

Of the possible bidentate ligands, phosphines are of the greatest practical interest, with bis(diphenylphosphino)methane (dppm) being one of the best choices.

There are only a few examples in the chemical literature of complexes with dangling diphosphines.¹⁻⁷ At first we focused our attention on Mo(II) and Mo(III) compounds, since they fulfill the above requirements. A search of the chemical literature then revealed that a promising candidate for our experiments already existed and has been

structurally characterized. $Mo(CO)_2Cl_2(dppm)_2$ was first prepared³ by Colton *et al.*, and then later structurally characterized⁷ as possessing a seven-coordinate molybdenum atom with two carbonyl groups, two chlorine atoms, one chelating diphosphine ligand and one dangling dppm ligand.

The reported synthesis of $Mo(CO)_2Cl_2(dppm)_2$ utilized the following reactions:

$$Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4Cl_2,$$
$$Mo(CO)_4Cl_2 + 2dppm \rightarrow Mo(CO)_2Cl_2(dppm)_2$$

In our hands the first step, i.e. the oxidative halogenation of molybdenum hexacarbonyl, has proved to be unreliable. In view of recent structural characterization of other $M_2(CO)_8X_4$ type dimers^{8,9} it is possible that dimeric $Mo_2(CO)_8Cl_4$ instead of monomeric $Mo(CO)_4Cl_2$ is the product of chlorination of $Mo(CO)_6$, and that this may lead to poor yields of $Mo(CO)_2Cl_2(dppm)_2$.

We turned our attention to the corresponding bromo and iodo compounds. We found that $Mo(CO)_2I_2(dppm)_2$ (1) had been prepared by the following procedure:¹⁰

 $Mo(CO)_6 + dppm \rightarrow Mo(CO)_4 dppm$

$$\stackrel{I_2}{\rightarrow} \alpha, \beta Mo(CO)_3 I_2 dppm$$
$$\stackrel{dppm}{\longrightarrow} Mo(CO)_2 I_2(dppm)_2.$$

^{*}Author to whom correspondence should be addressed.

This method gives not only the molecular compound $Mo(CO)_2I_2(dppm)_2$, but also the *cis* and *trans* isomers of $[Mo(CO)_2I(dppm)_2]I$, which have to be separated. We therefore searched for an alternative method of preparation of 1.

After trying several reactions we found that the desired product could be synthesized in 95% yield by the following procedure:

$[R_4N][Mo(CO)_4I_3] + 2dppm$

$$\rightarrow Mo(CO)_2 I_2(dppm)_2 + R_4 NI.$$

The starting material, $[R_4N][Mo(CO)_4I_3]$, can be easily prepared in a high-yield, one-pot synthesis from Mo(CO)₆. Compound 1 had not been structurally characterized, and some unusual stereochemistry might be found in a relatively crowded, presumably seven-coordinate molecule. The molecular structure was therefore determined by singlecrystal X-ray studies.

During the routine spectroscopic characterization we discovered that the ³¹P NMR spectrum was temperature-dependent, indicating fluxional behavior of $Mo(CO)_2I_2(dppm)_2$ in solution. The low-temperature ³¹P spectrum is in accord with the observed solid-state structure.

EXPERIMENTAL

General

Standard Schlenk tube techniques were employed throughout. All solvents were dried and freshly distilled prior to use. Tetraethylammonium iodide was purchased from Aldrich Chemical Co. and used as received.

Formation of [Et₄N][Mo(CO)₄I₃]¹¹

Molybdenum hexacarbonyl (9.08 g, 0.0344 mol) and Et₄NI (9.19 g, 0.0359 mol) were charged into a 500-cm³, round-bottom flask. 100 cm³ of THF was added and the reaction mixture was refluxed for 1.5 h. After that time the color of the reaction mixture was bright yellow, indicating the formation of [Et₄N][Mo(CO)₅I], which can be isolated by adding ether and refrigerating. If any unreacted Mo(CO)₆ is still present, the reaction mixture should be filtered while still hot. The bright yellow solution was cooled and 8.7 g (0.0344 mol) of elemental iodine was added from an addition finger during a period of 5 min. The reaction mixture was stirred vigorously during that time. Addition of each portion of iodine was accompanied by evolution of carbon monoxide. After all the iodine was added, the reaction mixture was stirred for an additional 15 min. It was dark orange at this time. 100 cm³ of diethyl ether was added to initiate precipitation and the reaction mixture was refrigerated overnight. The crystalline product was filtered, washed with ether and vacuum dried. The yield was 18.1 g (73%) of dark yellow crystals. An additional 2.4 g of the product could be recovered from the mother liquor, bringing the yield to 83%.

 $Mo(CO)_2I_2(dppm)_2$ (1)

[Et₄N][Mo(CO)₄I₃] (1.0 g, 1.40 mmol), 1.6 g (6.1 mmol) of dppm and 40 cm³ of benzene were stirred at room temperature. The reaction proceeded with CO evolution and an orange precipitate was deposited. After 6 h of stirring the reaction mixture was brought to a boil and filtered hot. Remaining solids were treated with an additional 40 cm^3 of hot benzene and filtered. A white solid (Et₄NI) remained on the filter stick. The combined filtrates were treated with 100 cm³ of hexane and refrigerated. The product was filtered, washed with hexane and vacuum dried, to give a yield of 1.55 g (95%) of orange-red crystalline material. The complex is air-stable in the solid state, but it is light-sensitive both in the solid state and in solution. Found: C, 55.5; H, 4.1%. Calc. for $M_0(CO)_2 I_2(dppm)_2 \cdot C_6 H_6$: C, 55.6; H, 4.0%. IR spectrum (Nujol mull): v(CO) = 1930(s) and 1850(s) cm⁻¹. Solution spectra (chloroform and toluene) were essentially identical. Electronic spectrum (chloroform solution): $\lambda_{\text{max}} = 450 \text{ nm}$ (sh), and 350 nm (sh).

Measurements

Elemental analyses were performed by Galbraith Laboratories Inc. IR spectra were recorded on a Perkin–Elmer 785 spectrophotometer. The electronic spectra were recorded on a chloroform solution using a Cary 17D spectrophotometer. ³¹P–{¹H} NMR spectra were recorded on a Varian XL 200 spectrometer at an operating frequency of 80.98 MHz in CDCl₃ solutions. 85% H₃PO₄ was used as an external standard. For the variabletemperature measurements the sample was referenced to H₃PO₄ at room temperature.

X-ray crystallographic procedures

Single crystals of 1 were grown by layering hexane on top of a benzene solution of the complex. The diffraction data were collected on a P3 autodiffractometer. Lorentz, polarization and absorption corrections were applied to the data. Standard

Formula	MoI ₂ P ₄ O ₂ C ₅₈ H ₅₀
Formula weight	1252.69
Space group	$P2_1/n$
Systematic absences	$h0l: h+l \neq 2n; 0k0: k \neq 2n$
a (Å)	19.023(4)
$b(\mathbf{A})$	14.439(3)
$c(\mathbf{A})$	20.141(5)
α (°)	90.0
β (°)	100.45(2)
ν (°)	90.0
$V(Å^3)$	5440(2)
Z	4
$d_{\rm mb} ({\rm g}{\rm cm}^{-3})$	1.529
Crystal size (mm)	$0.2 \times 0.3 \times 0.6$
μ (Mo-K ₋) (cm ⁻¹)	15.128
Data collection instrument	Р3
Radiation (monochromated in	
incident beam)	Mo- K_{π} ($\lambda_{\pi}^{-} = 0.71073$ Å)
Orientation reflections	
[number, range (2θ) (°)]	25, $16 < 2\theta < 25$
Temperature (°C)	27
Scan method	2θ-ω
Data collection range (2θ) (°)	4-45
Number of unique data, total	
with $F_a^2 > 3\sigma(F_a^2)$	5469, 4354
Number of parameters refined	569
Transmission factors (max, min)	0.9987, 0.8640
R ^a	0.0416
R_{w}^{b}	0.0555
Quality-of-fit indicator ^c	1.17
Largest shift/esd (final cycle)	0.84
Largest peak ($e \text{ Å}^{-3}$)	0.60

Table 1. Crystal data for $Mo(CO)_2I_2(dppm)_2 \cdot C_6H_6$

 ${}^{a} R = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|.$ ${}^{b} R_{w} = [\sum w(|F_{o}| - |F_{c}|)^{2} \sum w|F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|).$ ${}^{c} \text{ Quality of fit} = [\sum w(|F_{o}| - |F_{c}|)^{2} / (N_{obs} - N_{oarameters})]^{1/2}.$

procedures were used to process the data.^{12*} The solution of the structure was initiated by placing the Mo atom at a position obtained from the $Mo(CO)_2Cl_2(dppm)_2 \cdot C_6H_6$ structure⁷ (x- and z-coordinates were reversed). Additional atoms were located from the alternating least-squares cycles and difference Fourier maps. All the nonhydrogen atoms with the exception of the benzene molecule present as solvent of crystallization and C(44) were refined anisotropically. The structure converged to a value of R = 0.0416. The final difference Fourier map was featureless with a highest peak of 0.60 e Å⁻³. All the relevant crystallographic data are presented in Table 1.

RESULTS AND DISCUSSION

Synthesis

Preparation of 1 proceeds through the following synthetic steps:

 $Mo(CO)_6 + R_4NI \rightarrow [R_4N][Mo(CO)_5I] + CO$

 $\stackrel{I_2}{\rightarrow}$ [R₄N][Mo(CO)₄I₃]

$$\xrightarrow{\text{appm}} Mo(CO)_2 I_2(dppm)_2 + 2CO + R_4 NI.$$

The first stage entails thermal CO substitution of $Mo(CO)_6$ by tetraalkylammonium iodide. The reaction is of a general type, and has been widely used with other alkylammonium salts. The product, $[R_4N][Mo(CO_5)I]$, was not routinely isolated, but oxidized *in situ* with elemental iodine. The iodine has the advantage of being a mild oxidiz-

^{*} Calculations were done on the VAX 11/780 computer at the Department of Chemistry, Texas A&M University, College Station, Texas, with a VAX-SDP software package.

ing agent and it is easy to handle. The oxidation proceeds rapidly, with high yields. Despite the earlier reports of the extreme instability of $[R_4N][Mo(CO)_3I_3]$, we found that it can be isolated and conveniently handled. In the absence of light and air the complex could be stored for several days. The last step in the preparative procedure, the ligand substitution with dppm, gives the desired compound (1) with yields over 95%. A variety of tetralkylammonium salts have been tried (ethyl, propyl and butyl), with tetraethylammonium being the most convenient.

The preparation of 1, by the method of $Colton^{10}$ has several disadvantages, namely, lower yields, and, in addition to the desired molecular complex Mo(CO)₂I₂(dppm)₂, *cis*- and *trans*-[Mo(CO)₂I(dppm)₂]I are also formed.

Colton and coworkers also investigated reactions of $[Mo(CO)_4X_3]^-$ with dppm,¹³ but under their conditions only the ionic complex $[Mo(CO)_2I_2dppm)_2]I$ was formed.

The preparation of 1 via the route employed for the synthesis of $Mo(CO)_2Cl_2(dppm)_2$ is not feasible because diiodotetracarbonyl molybdenum is inaccessible.

Our method of preparation of 1 gives only the molecular complex, uncontaminated by the ionic isomers. $Mo(CO)_2I_2(dppm)_2$ can be recrystallized from dichloromethane-hexane, but refluxing of dichloromethane solutions of 1 or even their prolonged storage leads to the formation of ionic species.

Spectroscopy

The IR spectrum shows two strong C=O absorptions at 1947 and 1869 cm⁻¹ in toluene (1940 and 1865 cm⁻¹ in CHCl₃).

Figure 1 represents a series of variable-temperature ³¹P studies of 1 in CDCl₃ solution.

At -40° C (Fig. 1a) the spectrum consists of four groups of peaks (integration 1:1:1:1), indicating that all four phosphorus atoms are nonequivalent, which is in accord with the solid-state structure. The assignment of all the lines in the spectrum is given in Fig. 1a. There are four chemical shifts (ppm) (12.64, 7.78, -25.40 and -43.04) and four coupling constants (Hz) (30.50, 84.7, 168 and 22.3).

A large coupling constant $(J_{AD} = 168 \text{ Hz})$ is probably between P(3) and P(2), since these are the most trans phosphorus atoms. The second largest coupling is observed for P(1) and P(2) in the chelating dppm ($J_{DB} = 84.7$ Hz). Small coupling constants are observed for the two phosphorus atoms in the dangling dppm ($J_{AC} = 30.5$ Hz) and between P(3) and P(1) $(J_{AB} = 22.3 \text{ Hz})$. The doublet at -25.40 ppm is assigned to uncoordinated phosphorus. This value is consistent with that of free dppm. The coupling to the second phosphorus atom in this dppm molecule splits the signal into a doublet. One of the chelating phosphorus atoms is shifted upfield to -43.04 ppm, an unusual chemical shift, since phosphorus atoms in a five-membered ring are usually shifted downfield from the corresponding uncoordinated phosphines.

Upon warming, the resonances due to P(1) and P(2) start broadening. Also the J_{AB} coupling is "lost" in the P(3) resonance. At room temperature (Fig. 1d) the resonances of P(1) and P(2) are broad, and the fine structure of (P3) is very poorly resolved, except for the AC coupling. The dangling phosphorus P(4) is still present as a sharp doublet, suggesting that fluxionality does not involve opening of the chelating ring, and closing with an uncoordinated phosphorus P(4). There are at least two possible exchange mechanisms for 1. One is a dissociative mechanism, involving dissociation of iodide from the capping position in the trigonal prism. The trigonal prism can then rearrange to an octahedron, rendering the phosphorus atoms equivalent. Another possibility is a simple rearrangement between capped trigonal prisms¹⁴ which can be achieved easily by compressing and elongating bonds (see Fig. 2). As the temperature increases the sharp doublet assigned to the uncoordinated phosphorus atom begins to broaden as well, but it has been observed that 1 is decomposed in boiling dichloromethane or even at room temperature over a period of days.

Molecular structure

Selected bond distances and angles for 1 are listed in Table 2. Figure 3 presents a labelled ORTEP diagram of 1 along with a labelling scheme.* The molecule is seven-coordinate with the molybdenum atom bonded to two carbonyl groups, three phosphorus atoms and two iodine atoms. One of the dppm ligands is bidentate, but the second one is only monodentate. This type of structure has been postulated and observed before. The structure is distorted from a capped octahedron with CO(2) capping the P(1)-P(3)-1C(1) face and a trigonal prism with the I(1) capping the C(1)-P(2)-I(2)-

^{*} Supplementary material available. Atomic positional parameters, full listing of bond angles, bond distances, isotropic-equivalent displacement parameters, and observed and calculated structure factors (28 pp.). Copies are available from the Editor. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.



Fig. 1. Variable-temperature ${}^{31}P-{}^{1}H$ NMR studies. Referenced to H_3PO_4 as an external standard at room temperature. (a) $-40^{\circ}C$, (b) $0^{\circ}C$, (c) $10^{\circ}C$, (d) $25^{\circ}C$, and (e) $40^{\circ}C$. Peak assignment on top of Fig. 1a.



Fig. 2. Idealized capped trigonal prism geometry showing one of the possible exchange mechanisms.

Table 2. Selected bond distances (Å) and angles (°) for $Mo(CO)_2I_2(dppm)_2 \cdot C_6H_6^a$

Ato	om 1	Ato	m 2	Distance	
 Mo	b (1)	I	1)	2.846(1)	
M	n(1)	Ĩ	2)	2.904(1)	
Mo	(1)	P	-) 1)	2.491(2)	
Ma	$\dot{(1)}$	P	2)	2.589(2)	
Mo	s(1) −	P(3)	2.574(2)	
Mo	o(1)	C	(1)	1.957(10)	
Mo	b(l)	C	(2)	1.945(9)	
P(1	I)	C	(3)	1.827(8)	
P(2	2)	C	(3)	1.839(8)	
P(3	3)	C	(4)	1.850(8)	
P(4	4)	C	(4)	1.866(9)	
O(1)	С	(1)	1.136(10)	
O (2)	C	(2)	1.160(10)	
Atom 1	Ato	m 2	Atom 3	Angl	e
 I(I)	Mo	(1)	I(2)	86.77	(3)
I(1)	Mo	(1)	P(1)	145.35	(6)
$\mathbf{I}(1)$	Mo	$\dot{(1)}$	P(2)	82.98	(5)
IÌÌ	Мо	$\dot{(1)}$	P(3)	83.64	(6)
$\mathbf{I}(1)$	Mo	$\dot{(1)}$	C(1)	80.9(3	3)
IÌÌ	Мо	$\dot{(1)}$	C(2)	142.5(3)
I(2)	Мс	$\dot{(1)}$	P(1)	82.86	(5)
I(2)	Mo	$\dot{(1)}$	P(2)	86.64	(5)
I(2)	Mo	$\mathbf{x}(1)$	P(3)	83.21	(5)
I(2)	Mo	o (1)	C(1)	167.6(3)
I(2)	Мс	b (1)	C(2)	116.4(3)
P(1)	Mo	o (1)	P(2)	63.53	(7)
P(1)	Мо	o (1)	P(3)	127.40	(8)
P(1)	Mo	b (1)	C(1)	106.3(3)
P(1)	Mo	b (1)	C(2)	70.4(3)
P(2)	Mo	o (1)	P(3)	163.62	(7)
P(2)	Mo	b(1)	C(1)	89.9(3)
P(2)	Mo	b(1)	C(2)	124.9(3)
P(3)	Mo	b (1)	C(1)	97.2(3)
P(3)	Mo	b(1)	C(2)	71.4(3)
C(1)	Mo	b(l)	C(2)	75.2(4)
Mo(1)	P(]	l)	C(3)	97.8(3)
Mo(1)	P(2	2)	C(3)	94.2(3)
Mo(1)	P(3	3)	C(4)	116.6(3)
Mo(1)	C(1)	O(1)	174.8(8)
Mo(1)	C (2	2)	O(2)	174.6(8)
P(1)	C (3)	P(2)	93.7(4)
P(3)	- C(-	4)	P(4)	115.20	4)

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

Table	3.	Comparison	of	selected	bond	angles	(°)
for $Mo(CO)_2X_2(dppm)_2$							
<u> </u>							

Angle	X = Cl	$\mathbf{X} = \mathbf{I}$
P(1)—Mo—P(2)	63.5(2)	63.53(7)
P(1) - Mo - P(3)	126.4(2)	127.40(8)
P(2)—Mo—P(3)	163.1(2)	163.62(7)
X(1) - Mo - X(2)	86.7(2)	86.77(3)
C(1)—Mo—C(2)	73.5(1)	75.2(4)
X(1) - Mo - C(1)	115.5(7)	80.9(3)
X(1) - Mo - C(2)	141.5(7)	142.5(3)
X(2)-Mo-C(1)	170.4(7)	167.6(3)
X(2) - Mo - C(2)	83.9(8)	116.4(3)
X(1) - Mo - P(1)	147.8(2)	145.35(6)
X(1)—Mo—P(2)	80.0(2)	82.98(5)
X(1)—Mo—P(3)	81.2(2)	83.64(6)

P(3) rectangular face (see Fig. 2). The principal distances (in Å) in the molecule are : Mo(1)—I(1) = 2.846(1), Mo(1)—I(2) = 2.904(2), Mo(1)—P(1) = 2.491(2), Mo(1)—P(2) = 2.589(2), Mo(1)—P(3) = 2.574(2), Mo(1)—C(1) = 1.957(10), and Mo(1)—C(2) = 1.945(9). All the distances are with the normal range and require no further comment. All the angles are almost identical to those observed in the chloro analogue, Table 3, demonstrating that substitution of chlorides by iodides had almost no effect on the molecular structure.

Concluding remarks

We have developed a new synthetic method for the preparation of $Mo(CO)_2I_2(\eta_2$ -dppm)(η_1 -dppm). The title complex has been characterized by a singlecrystal X-ray diffraction. The central molybdenum atom is seven-coordinate with two iodine atoms, two carbonyl groups and three phosphorus atoms forming the immediate coordination sphere. One of the dppm ligands is chelating, the other one has one dangling phosphorus atom. The geometry around the central molybdenum atom is distorted from a capped octahedron or a capped trigonal prism. Variable-temperature ³¹P NMR studies revealed that the molecule is fluxional in solution. The reac-



Fig. 3. ORTEP drawing of Mo(CO)₂I₂(dppm)₂.

tivity of 1 in the formation of heterobimetallic dimers, as well as its photochemical behavior are currently under investigation.

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REFERENCES

- R. J. Puddephatt, Chemistry of Bis(diphenylphosphino)methane, p. 103. Chemical Society Reviews, London (1983).
- 2. E. E. Isaacs and W. A. G. Graham, Inorg. Chem. 1975, 14, 2560.
- M. W. Anker, R. Colton and I. B. Tomkins, Aust. J. Chem. 1968, 21, 1143.
- 4. M. W. Anker, R. Colton and I. B. Tomkins, Aust. J. Chem. 1968, 21, 1159.
- 5. R. L. Keiter, A. L. Rheingold, J. J. Hamerski and C. K. Castle, Organometallics 1983, 2, 1635.
- R. L. Keiter, Y. Y. Sun, J. W. Brodack and L. W. Cary, J. Am. Chem. Soc. 1979, 101, 2638.
- 7. M. G. B. Drew, A. P. Walters and I. B. Tomkins, J. Chem. Soc., Dalton Trans. 1977, 974.
- F. A. Cotton, L. R. Falvello and J. H. Meadows, *Inorg. Chem.* 1985, 24, 514.
- 9. F. Calderazzo, R. Poli and P. F. Zanazzi, manuscript in preparation.
- R. Colton and J. J. Howard, Aust. J. Chem. 1970, 23, 223.
- 11. S. N. J. Burgmayer and J. L. Templeton, *Inorg. Chem.* 1985, 24, 2224.
- (a) A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem.* 1979, 18, 3558; (b) F. A. Cotton, B. A. Frenz, G. Deganello and A. J. Shaver, *J. Organomet. Chem.* 1973, 50, 227; (c) A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Cryst.* 1968, A39, 158.
- R. Colton and J. J. Howard, Aust. J. Chem. 1969, 22, 2543.
- For a review of seven-coordinate complexes and isomerization see: M. G. B. Drew, *Prog. Inorg. Chem.* 1977, 23, 67.