

Reactivity of $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ ($\text{Mo}=\text{Mo}$) toward Iodine and Chalcogens. Crystal Structure of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})]_2$

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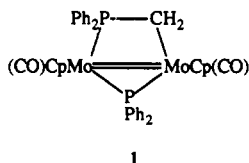
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Elemental iodine, sulfur, and selenium insert into the $\text{Mo}=\text{Mo}$ bond present in the compound $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) to give $[(\mu\text{-E})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})]^{n+}$ ($\text{E} = \text{I}$, $n = 1$; $\text{E} = \text{S}$, Se , $n = 0$). Reaction with oxygen leads instead to the decarbonylation product $(\text{O})\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{MoCp}(\text{CO})$ and to the tetranuclear compound $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})]_2$, the latter resulting from decarbonylation and insertion of oxygen into $\text{Mo}=\text{Mo}$ and $\text{Mo}-\text{PPh}_2$ bonds, and further condensation. CO substitution by oxygen is prevented by using a CO/O_2 mixture, which leads to $(\mu\text{-O})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-OPPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$. The stereochemistry of the new compounds is analyzed in the light of IR and (^1H , ^{13}C , ^{31}P) NMR data. The structure of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})]_2$ was determined by X-ray diffraction. The compound crystallizes in the space group $P2_1/n$ ($a = 16.113$ (2) Å, $b = 19.487$ (6) Å, $c = 11.686$ (3) Å, $\beta = 101.63$ (1)°, $V = 3594$ (2) Å³, $Z = 2$). The structure was refined to $R = 0.045$ ($R_2 = 0.053$) for 5092 reflections with $I \geq 3\sigma(I)$. The centrosymmetric molecule consists of two dimolybdenum moieties jointed by a linear oxygen bridge. Inside each moiety, the metal atoms ($\text{Mo}(1)-\text{Mo}(2) = 2.9688$ (5) Å) are asymmetrically bridged by an oxygen atom, and by $C,P\text{-CH}_2\text{PPh}_2$, and $O,P\text{-OPPh}_2$ ligands. The latter two ligands could not be differentiated in this study, both appearing as essentially identical XPPH_2 groups, X having intermediate electronic density between C and O. Each molybdenum atom bears one cyclopentadienyl ligand, and either the oxo ligand bridging both binuclear moieties ($\text{Mo}(1)$) or one CO ($\text{Mo}(2)$).

Introduction

During our studies on the reactivity of the dppm -bridged compound $(\mu\text{-dppm})\text{Mo}_2\text{Cp}_2(\text{CO})_4$, ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$),¹ we found that a clean $\text{P}-\text{C}(\text{sp}^3)$ bond cleavage occurs by gentle heating at 60 °C, leading to $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (**1**) which formally contains an $\text{Mo}=\text{Mo}$ bond.²



In addition to the carbonyl ligands, compound **1** contains three potential reactive centers of interest, i.e.: the $\text{Mo}=\text{Mo}$, $\text{Mo}-\text{CH}_2$, and $\text{Mo}-\text{PPh}_2$ bonds. Organome-

tallic compounds containing $\text{Mo}=\text{Mo}$ bonds are relatively scarce and their reactivity has been little explored,³ although they are not expected to display as wide reactivity as the triple bonded $\text{Mo}_2\text{Cp}_2(\text{CO})_4$.⁴ On the other hand, insertion reactions on metal-alkyl bonds are well known,⁵ and some examples of reactivity at phosphido bridges began to appear in the 1980s.⁶ Thus, it was of interest to determine the most reactive sites in compound **1**, since

(3) (a) Cotton, F. A.; Walton, R. A. *Multiple bonds between metal atoms*; Wiley & Sons: New York, 1982; pp 291-296. (b) Benson, I. B.; Killops, S. D.; Knox, S. A. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1980, 1137. (c) Endrich, K.; Korswagen, R.; Zahn, T.; Zeigler, M. L. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 919. (d) Herrmann, W. A.; Bell, L. K.; Ziegler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* 1983, 247, 39. (e) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solís, H. E.; Barceló, I. D.; Butler, W. M. *J. Am. Chem. Soc.* 1987, 109, 3603. (f) Kuhn, N.; Zander, E.; Bose, R.; Bläser, D. *J. Chem. Soc., Dalton Trans.* 1988, 2171. (g) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, R. R. *J. Chem. Soc., Dalton Trans.* 1989, 1555.

(4) (a) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. *A.C.S. Symp. Ser.* 1981, 155, 221. (b) Curtis, M. D. *Polyhedron* 1987, 6, 759. (c) Winter, M. J. *Adv. Organomet. Chem.* 1989, 29, 101.

(5) Crabtree, R. H. *The Organometallic Chemistry of the Transition Elements*; Wiley & Sons: New York, 1988; Chapter 7.

(6) See for example: (a) Geoffrey, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* 1984, 106, 1519. (b) Yu, Y.-F.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* 1986, 5, 47. (c) Klingert, B.; Rheingold, A. L.; Werner, H. *Inorg. Chem.* 1988, 27, 1354. (d) Conole, G.; McPartlin, M.; Mays, M. J.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* 1990, 2359.

(1) (a) Riera, V.; Ruiz, M. A.; Villafaña, F.; Jeannin, Y.; Bois, C. *J. Organomet. Chem.* 1988, 345, C4. (b) Riera, V.; Ruiz, M. A.; Villafaña, F.; Boise, C.; Jeannin, Y. *J. Organomet. Chem.* 1990, 382, 407. (c) Riera, V.; Ruiz, M. A.; Villafaña, F. *Organometallics* 1992, 11, 2854.

(2) (a) Riera, V.; Ruiz, M. A.; Villafaña, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* 1989, 375, C23. (b) Decarbonylation studies on $(\mu\text{-P-P})\text{M}_2\text{Cp}_2(\text{CO})_4$, ($\text{P-P} = \text{dppm}$, dmpm , tedip ; $\text{M} = \text{Mo}$, W): Álvarez, M. A.; García, E.; Riera, V.; Ruiz, M. A.; Villafaña, F.; Bois, C.; Jeannin, Y. Unpublished results.

Table I. IR and $^{31}\text{P}\{^1\text{H}\}$ NMR Data for the Compounds Described in this Work

	IR ^a	$^{31}\text{P}\{^1\text{H}\}$ NMR ^b		
		chemical shifts		J_{PP}
		downfield	highfield	
$[(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2]\text{I}$ (2)	1960 m, 1903 s	151.4	-1.1	14
$(\mu\text{-S})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (3)	1899 m, 1836 s	90.7	27.6	60
$(\mu\text{-Se})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (4)	1885 m, 1842 s	96.2 ^c	21.5 ^d	50
$(\text{O})\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{MoCp}(\text{CO})$ (5)	1780	201.6	36.1	3
$(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})]_2$ (6)	1815	108.7*	60.0	129
$(\mu\text{-O})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-OPPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (7)	1979 vs, 1827 s	110.3*	56.7	173

^a Data in cm^{-1} , CH_2Cl_2 solution. ^b Data in ppm; all signals are doublets, J_{PP} in Hz; the spectra were recorded at 121.44 MHz at rt. Solvent was CDCl_3 for compounds 2, 3, 6, and 7, and C_6D_6 for 4 and 5. The downfield signals are assigned to $\mu\text{-PPh}_2$, except those marked with an asterisk, assigned to $\mu\text{-OPPh}_2$; the highfield signals are assigned always to $\mu\text{-CH}_2\text{PPh}_2$. ^c $J_{\text{SeP}} = 25$ Hz. ^d $J_{\text{SeP}} = 39$ Hz.

the presence of all these three reaction centers in the same species has no precedent in the literature.

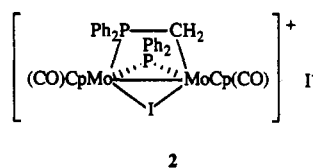
The present paper describes the behavior of 1 toward iodine and chalcogens. Compound 1 is extremely air sensitive, and by controlling the oxidation processes, several oxocompounds could be isolated in moderate yields. This feature is not uncommon in the synthesis of organometallic oxo complexes, which so far has been based more often on serendipitous discoveries than on planned synthesis. However, the chemistry of these species is currently the object of intensive studies, as shown by the appearance of two excellent reviews in 1988.⁷ Organometallic oxo compounds may be considered as a link between the purely inorganic solids, to which they are related by some structural features, and the low-valent organometallic complexes. They have been proposed as intermediates in the metal oxide catalyzed oxidations of organic substrates and olefin metathesis.^{7a} Their importance in bioinorganic chemistry has also been recognized.^{7b,8} In particular, molybdenum oxo compounds have been proposed as intermediates in the oxidation of organic species,⁹ and as theoretical link between homogeneous and heterogeneous catalysts in syngas processes.¹⁰

A preliminary account of this work has already appeared.^{2a}

Results and Discussion

1. Reactivity toward Iodine, Sulfur, and Selenium.

The addition of an equimolar amount of iodine to a solution of 1 in diethyl ether at room temperature (rt) leads to the immediate precipitation of $[(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2]\text{I}$ (2).



The spectroscopic data for compound 2 (Table I and the Experimental Section) reveal that the diphenylphosphido and (diphenylphosphino)methyl bridges, as well as the two cyclopentadienyl and terminal carbonyl ligands present in 1, remain unaltered after the reaction. The electrical conductivity of 2 in nitrobenzene solution

- (7) (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* 1988, 28, 339.
 (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1297.
 (8) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kuesthardt, U.; Okuda, J. *Polyhedron* 1987, 6, 1165.
 (9) Almond, M. J.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* 1988, 809.
 (10) Sapienza, R.; Seigeir, W.; Mahajan, D. *Polyhedron* 1986, 5, 249.

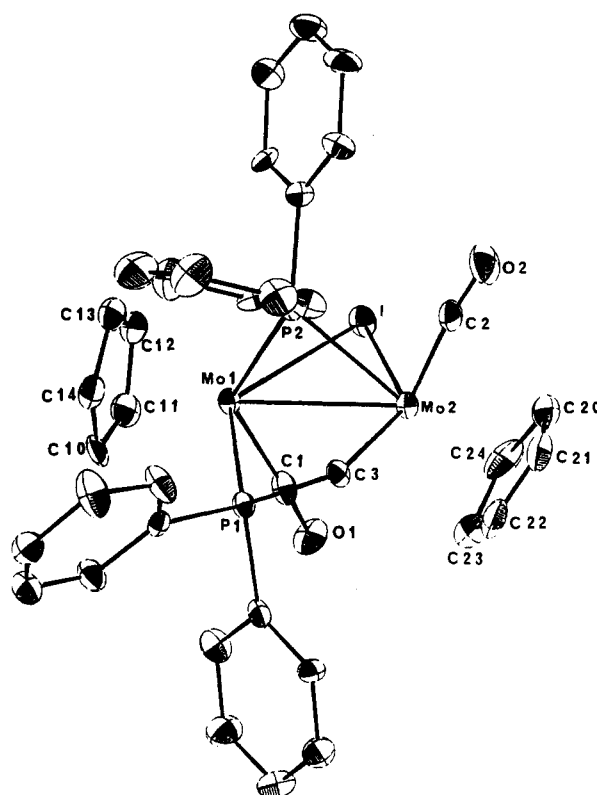


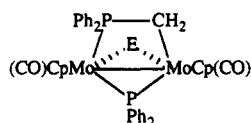
Figure 1. Crystal structure of the cation $[(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2]^+$ (2).^{2a} Labels for phenyl carbon atoms are omitted for clarity.

corresponds to an 1/1 electrolyte, indicating that only one iodine atom is bonded to the bimetallic center probably in a bridging position, whereas the second iodine atom remains as a iodide counterion. An X-ray study carried out on the cation $[(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2]^+$ (Figure 1)^{2a} confirmed the above proposals, and the molecule can be viewed as the result of the addition of an "I⁺" fragment to the Mo=Mo bond present in 1.

Furthermore, NMR data for 2 indicate that the main structural features found in the solid state are retained in solution. Thus, the cis arrangement of the phosphorus donor ligands (angle P(1)-Mo(1)-P(2) = 84.8 (1)°) is reflected in a low P-P coupling constant (14 Hz) in the phosphorus NMR spectrum. The carbonyl ligands give rise to two distinct ^{13}C resonances at δ 237.3 (dd, J_{PC} 15 and 4 Hz), and 241.5 ppm (d, J_{PC} 41 Hz). The first signal is assigned to C(1) (trans to P(2) and cis to P(1)), and the second is assigned to C(2) (cis to P(2)). Since $^2J_{\text{PC}}$ couplings have been found to be larger for cis than for trans arrangements in cyclopentadienyl derivatives of group 6 metals,¹¹ the unusually high value found in 2 is

probably a consequence of the rather low angle C(2)–Mo(2)–P(2) (68.8 (5)°). In fact, this gives rise to a local geometry around Mo(2) very different from the four-legged piano-stool geometries commonly found on related cyclopentadienyl carbonyl complexes. At this moment we have no explanation for this unusual structural feature.

Since chalcogens are isoelectronic with the "I⁺" cation, it was decided to explore the reactivity of compound 1 toward sulfur and selenium. The addition of equimolar amounts of these elements to solutions of 1 in toluene at rt yields the compounds (μ -E)(μ -CH₂PPh₂)(μ -PPh₂)Mo₂Cp₂(CO)₂, 3 (E = S) and 4 (E = Se).



3 (E = S), 4 (E = Se)

The similarity of the spectroscopic data for 3 and 4 (Table I and the Experimental Section) suggests the same geometry for both species. The values of the ⁷⁷Se–³¹P coupling constants detected in the ³¹P{¹H} NMR spectrum of 4 (25 Hz for the phosphide and 39 Hz for the phosphinomethyl ligand) are consistent with the geometry proposed and rule out the possible presence of any " μ -SePPh₂" moiety. The insertion of selenium into metal-phosphide bonds is known to result in much higher ⁷⁷Se–³¹P (one bond) coupling.¹² A strong deshielding in the phosphorus involved, also observed when S is the inserted atom, is another effect found.^{6c,13} The IR spectrum of 3 shows two C–O stretching absorptions (1910 (s) and 1830 (vs) cm⁻¹ in KBr), and allows the presence of any Mo=S bond to be ruled out, since no bands in the 480–490-cm⁻¹ range are apparent.¹⁴ However, the presence of a bridging S atom cannot be inferred from this spectrum as the 425–460-cm⁻¹ region, where the Mo–S–Mo asymmetric stretching bands are expected to appear,¹⁴ also contains absorptions due to C–O bending modes. On the other hand, the possibility of insertion of chalcogen into the Mo–CH₂ bond in 1 can be ruled out by considering the ¹H and ¹³C resonances due to the CH₂ group in compounds 3 and 4. Thus, the ¹H chemical shifts and P–H couplings are analogues to those shown by compound 2, and the resonance of the methylenic carbon atom in 4 appears at –2.9 ppm, exhibiting a normal one-bond P–C coupling of 26 Hz. This chemical shift is within the range expected for Mo–C(sp³) bonds, whereas values in the range +30 to +50 ppm would have been expected in the case of Se insertion,¹⁵ which would have generated a Mo–P–CH₂–Se–Mo chain. All together, these data suggest that both 3 and 4 contain a single chalcogen atom, most probably bridging the metal–metal bond. This is also consistent with the mass spectrum of 3, and elemental analysis for both 3 and 4. The selective addition of a single chalcogen

atom to the dimetal center in the unsaturated precursor 1 is somewhat surprising, as both sulfur and selenium are known to react with dimetallic substrates forming small chains of two or more chalcogen atoms in many instances.¹⁶

Our proposal of a relative *trans* arrangement for the phosphido and phosphinomethyl ligands in 3 and 4 is based on ¹H and ³¹P NMR data. Thus, their ¹H spectra display two distinct cyclopentadienyl resonances, the higher field signal appearing as a triplet (*J* = 2 Hz), due to coupling with two mutually *trans* phosphorus atoms. As will be discussed later, this situation is also found for complexes 6 (*J*_{PH} = 2 Hz, P–Mo–P = 137.24 (4)°) and 7 and in the related (μ -CH₂)(μ -PPh₂)(μ -OPPh₂)Mo₂Cp₂(CO)₂ (*J*_{PH} = 2 Hz, P–Mo–P = 121.28 (8)°)¹⁷. Incidentally, such relatively large P–H couplings are also found for *trans*-dicarbonyl MoCp(CO)₂PL complexes (P = phosphorus donor ligand, L = ligand)¹⁸ or *trans*-MoCp(CO)(PPh₂)₂Cl.¹¹ The second indication of a *trans* arrangement of the phosphorus-donor ligands is provided by the ³¹P{¹H} NMR spectra, which show P–P couplings much larger than that found for 2. Interestingly, these couplings seem to follow an order opposite to that for the bridging atom size:

$$\begin{array}{l} \text{size} \quad [\mu\text{-I}]^+ (2) > \mu\text{-Se} (4) > \mu\text{-S} (3) \\ J_{PP} \quad 14 (2) \ll 50 (4) < 60 (3) \end{array}$$

Thus, the size of the bridging atom might exert a decisive influence on the geometry of the complex. The presence of a large atom, such as iodine, could force the phosphorus-donor ligands to adopt a *cis* arrangement, whereas they could coordinate in a more distant position (*trans*) for smaller bridging atoms, such as Se and S.

As a corollary of this apparent relationship, it might be predicted that a hypothetical oxygen analogue to the sulfur and selenium compounds 3 and 4 would also display the same *trans* geometry. Unfortunately, we have not been able to confirm this prediction, as no oxygen analogue of compounds 3 and 4 has been detected in the reactions of oxygen with 1. Instead, more complex transformations in the original substrate are observed in these processes, and they are treated separately.

2. Reactivity toward Oxygen. As indicated before, compound 1 is highly oxygen sensitive. Not only the presence of air, but traces of oxygen present in the gases normally used in the laboratory (such as nitrogen or carbon monoxide), or water, led to the formation of several oxo derivatives of compound 1. Although these reactions always gave mixtures of oxo compounds, their relative amounts were sensitive to the experimental conditions, and some selectivity could be achieved.

Bubbling nitrogen (containing 10 ppm of oxygen) through a toluene solution of 1 leads, after 18 h at rt, to the formation of the purple oxo compound (O)CpMo(μ -CH₂PPh₂)(μ -PPh₂)MoCp(CO) (Mo=Mo) (5) as the major product, which can be isolated in a ca. 30% yield.

The IR spectrum of 5 shows a new absorption at 905 cm⁻¹ (KBr), which is not observed in the compounds previously described in this work. This is assigned to the

(11) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* 1978, 154, 151.

(12) Verkade, J. G.; Mosbo, J. A. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 13.

(13) Werner, H.; Luxenburger, G.; Hoffmann, W.; Nadvornik, N. *J. Organomet. Chem.* 1987, 323, 161.

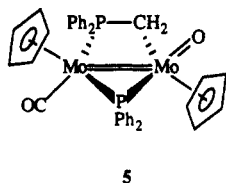
(14) (a) Bruce, A. E.; Tyler, D. R. *Inorg. Chem.* 1984, 23, 3433. (b) Tanner, L. D.; Haltiwanger, R. C.; Noordik, J.; DuBois, M. R. *Inorg. Chem.* 1988, 27, 1736.

(15) Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

(16) (a) Brunner, H.; Wachter, J.; Wintergart, H. *J. Organomet. Chem.* 1982, 235, 77. (b) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* 1982, 1, 1107. (c) Chen, W.; Goh, L. Y.; Sinn, E. *Organometallics* 1988, 7, 2020. (d) Wachter, J. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1613.

(17) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. Unpublished results. Supplementary information about this crystal structure can be obtained from the authors.

(18) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* 1970, 92, 5852.



$\text{M}=\text{O}$ stretching mode, its frequency being in the range characteristic of oxo ligands terminally bonded to molybdenum.^{14a,19} A single C–O stretching band at 1770 cm^{-1} is also observed, suggesting the replacement of a carbonyl ligand in the parent compound 1 by a terminal oxygen atom, presumably with concomitant CO_2 elimination. The single CO ligand gives rise to a $^{13}\text{C}\{^1\text{H}\}$ NMR resonance at δ 231.5 ppm (dd, $^2J_{\text{PC}} = 11$ and 6 Hz), which indicates that both phosphorus-donor atoms and the carbonyl ligand are bonded to the same molybdenum atom. Both the chemical shift and the coupling constants are similar to those of related systems.^{3g} The resonance due to the methylenic carbon (δ 0.6 ppm, $^1J_{\text{PC}} = 10$ Hz) is very similar to that found for the parent compound 1 (δ 1.0 ppm, $^1J_{\text{PC}} = 8$ Hz).^{2a} However, the hydrogen atoms of the methylenic group are influenced by the presence of an oxo ligand bonded to the same molybdenum atom, since the ^1H NMR spectrum shows a ca. 1-ppm deshielding compared to compound 1,^{2a} as expected for an increase in the metal's oxidation state, now formally a Mo(IV) center.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 5 shows two doublets ($J_{\text{PP}} = 3$ Hz) at δ 201.6 and 36.1 ppm, corresponding to the phosphido and phosphinomethyl bridging ligands, respectively. Comparing these chemical shifts with those of 1 (δ 92.1 and 46.8 ppm),^{2a} a high deshielding (ca. 110 ppm) effect is observed on the phosphido resonance upon replacement of CO by O (i.e. from 1 to 5). A similar deshielding effect (ca. 80 ppm) has been reported for the complex $(\text{O})\text{CpMo}(\mu\text{-PPh}_2)_2\text{MoCp}(\text{CO})$,^{3g} isoelectronic with 5. By contrast, this effect is not observed for the phosphinomethyl ligand, since the phosphorus atom of this group and the oxo ligand are bonded to different metal centers. These data are in accordance with the structure proposed for 5, which in fact is very similar to those crystallographically determined for the above diphosphido complex,^{3g} and the phosphido vinyl compound $(\text{O})\text{-CpMo}(\mu\text{-}\sigma,\pi\text{-CH=CHPh})(\mu\text{-PPh}_2)\text{MoCp}(\text{CO})$,^{3c} all containing two three-electron donor bridging ligands. The local geometry of these binuclear species may be visualized as a pseudotetrahedral coordination around each molybdenum atom, if the cyclopentadienyl ligands are assumed to occupy one coordination position. The P–P coupling constant measured in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 5 is unexpectedly low. An almost complete mutual cancellation of the two- and three-bond contributions,²⁰ perhaps due to the presence of the double metal–metal bond, may explain this feature. The possibility of both phosphorus

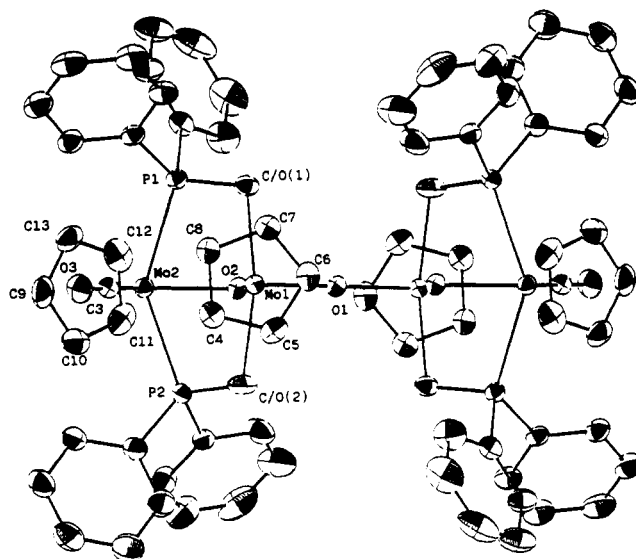
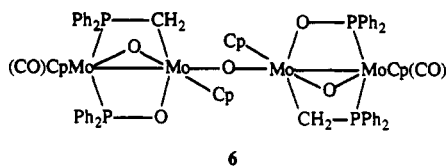


Figure 2. Crystal structure of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2$ (6). Labels for phenyl carbon atoms are omitted for clarity.

atoms being coordinated in a cis relative arrangement similar to that found for 2, where the P–Mo–P angle is ca. 80° , can be excluded not only on steric grounds, but also because this would probably lead to quite dissimilar $^3J_{\text{PH}}$ couplings for the methylenic protons (for example, 2 and 14 Hz for 2). The reason for this is the well-known Karplus-type dependence of the $^3J_{\text{PH}}$ couplings on the dihedral angle defined by the atoms involved.²² By contrast, a relative arrangement of these phosphorus ligands as proposed for 5, or the complexes 3 and 4 would probably lead to similar $^3J_{\text{PH}}$ couplings for each of the methylenic protons, as is observed experimentally (0 and 2 Hz for 3; 0 and 4 Hz for 5).

Taken together, the above data are fully consistent with the structure proposed for 5. However, there is one feature we cannot distinguish from these data, namely, whether the cyclopentadienyl ligands are on the same side or different sides relative to the $\text{Mo}_2\text{P}_2\text{C}(\text{H}_2)$ pseudoplane. Unfortunately, all attempts to grow suitable crystals of 5 for X-ray diffraction were unsuccessful.

In addition to 5, the reaction of 1 with nitrogen (containing 10 ppm of oxygen) yields ca. 5% of the blue compound $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2$ (6).



The crystal structure of this oxo compound has been solved by an X-ray diffraction study. A view of the molecule is depicted in Figure 2, and Table II collects the most relevant bond distances and angles. The CH_2PPh_2 and OPPh_2 bridging ligands could not be distinguished from each other in this study, since their positions are exchanged throughout the crystal. The corresponding

(19) (a) Adam, G. J. S.; Green, M. L. H. *J. Organomet. Chem.* 1981, 208, 299. (b) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* 1988, 340, 59.

(20) The observed coupling constant must be mainly due to the 3-bond and 2-bond contributions, since generally $^3J_{\text{PP}} \geq ^2J_{\text{PP}} \gg ^4J_{\text{PP}}$. However, $^3J_{\text{PP}}$ and $^2J_{\text{PP}}$ are commonly opposite in sign,²¹ and this can lead to small values. In compounds 2–5, the existence of two possible 3-bond pathways (i.e.: P–Mo–C–P, and P–Mo–Mo–P) makes the observed values for the P–P coupling constant relatively small (<60 Hz). For complexes 6–8, the 3-bond pathways no longer exist, and we can assume that the observed J_{PP} value is mainly due to the contribution of $^2J_{\text{PP}}$, since $^4J_{\text{PP}}$ must be much lower.

(21) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 6.

(22) (a) Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 11. (b) Carreño, R.; Riera, V.; Ruiz, M. A. *J. Organomet. Chem.* 1991, 419, 163.

Table II. Selected Distances (Å) and Angles (deg) for $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2]_2$ (6)^a

Mo(1)–Mo(2)	2.9688 (5)	O(3)–C(3)	1.175 (6)
Mo(1)–O(1)	1.8788 (4)	Mo(2)–C(3)	1.918 (5)
Mo(1)–O(2)	1.860 (3)	Mo(2)–O(2)	2.056 (3)
Mo(1)–C/O(1)	2.241 (3)	Mo(2)–P(1)	2.528 (1)
Mo(1)–C/O(2)	2.235 (4)	Mo(2)–P(2)	2.510 (1)
Mo(1)–C(4)	2.345 (4)	Mo(2)–C(12)	2.338 (5)
Mo(1)–C(5)	2.438 (4)	Mo(2)–C(13)	2.332 (5)
Mo(1)–C(6)	2.523 (4)	Mo(2)–C(9)	2.368 (5)
Mo(1)–C(7)	2.446 (4)	Mo(2)–C(10)	2.338 (5)
Mo(1)–C(8)	2.354 (4)	Mo(2)–C(11)	2.334 (5)
P(1)–C/O(1)	1.658 (4)	P(2)–C/O(2)	1.634 (4)
Mo(1)–Cp(1)	2.11	Mo(2)–Cp(2)	2.02
O(1)–Mo(1)–Mo(2)	130.89 (2)	Mo(1)–O(2)–Mo(2)	98.5 (1)
O(1)–Mo(1)–O(2)	87.65 (8)	P(1)–Mo(2)–P(2)	137.25 (4)
O(1)–Mo(1)–C/O(1)	91.9 (1)	C/O(1)–Mo(1)–C/O(2)	154.6 (1)
O(1)–Mo(1)–C/O(2)	93.8 (1)	O(2)–Mo(1)–C/O(1)	77.2 (1)
C(3)–Mo(2)–Mo(1)	79.3 (1)	O(2)–Mo(1)–C/O(2)	78.2 (1)
C(3)–Mo(2)–O(2)	117.6 (1)	O(2)–Mo(2)–P(1)	74.58 (8)
C(3)–Mo(2)–P(1)	86.4 (1)	O(2)–Mo(2)–P(2)	71.33 (8)
C(3)–Mo(2)–P(2)	87.2 (1)	O(2)–Mo(2)–Mo(1)	38.30 (7)
P(1)–C/O(1)–Mo(1)	104.4 (2)	P(2)–C/O(2)–Mo(1)	107.1 (2)
Cp(1)–Mo(1)–O(2)	167.97	Cp(2)–Mo(2)–O(2)	126.36

^a Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings.

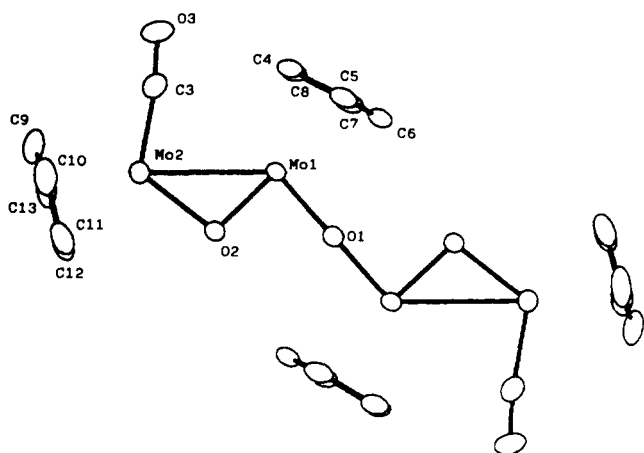


Figure 3. Projection of the molecular structure of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2]_2$ (6) on the Mo_4O_3 plane. CH_2PPh_2 and OPPh_2 groups are omitted for clarity.

carbon (methylene) or oxygen atoms in these ligands have been therefore labeled C/O(1) and C/O(2) (see Figure 2 and the Experimental Section). This centrosymmetric molecule is formed by two equivalent dimolybdenum moieties bonded by a linear oxo bridge O(1), which is placed at the inversion center. Each moiety contains two molybdenum atoms, bearing respective cyclopentadienyl ligands, which are bridged by mutually trans CH_2PPh_2 and OPPh_2 ligands ($\text{P}(1)\text{-Mo}(2)\text{-P}(2) = 137.25$ (4)°, $\text{C/O}(1)\text{-Mo}(1)\text{-C/O}(2) = 154.6$ (1)°, and by an oxygen atom O(2) bonded in a significantly asymmetric manner. Finally, Mo(2) bears a carbonyl ligand.

The Mo_4O_3 unit is planar (maximum deviation from the least-squares plane is 0.002 Å), and Figure 3 shows a projection of the molecule on that plane (phosphorus ligands are excluded for clarity). As shown in Figures 2 and 3, the coordination geometry around Mo(2) is of the "four-legged piano-stool" type, whereas that around Mo(1) is not, as was found for complex 2 (Figure 1). Although in the latter compound this feature had no immediate explanation, in compound 6 this might be a steric requirement for the appropriate approaching of the two molybdenum units around O(1). The Mo(2)–O(2) distance

is 2.056 (3) Å, in the range expected for a single bond. However, the values found for the Mo(1)–O(2) and Mo(1)–O(1) bonds (1.860 (3) and 1.8788 (4) Å, respectively) are significantly shorter. The latter distances are intermediate between the single-bonded Mo(2)–O(2) and that expected for an Mo=O bond, found consistently around 1.70 Å, both for purely inorganic or organometallic molybdenum compounds containing terminal oxo ligands.^{7a} Such relatively short metal–oxygen distances are common in cyclopentadienyl dimers containing linear M–O–M linkages (for example 1.864 (1) Å for $(\mu\text{-O})\text{Mo}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{(O)}_4$),^{19b} and they have been interpreted as a reflection of substantial π -bonding between lone pairs of oxygen and empty d orbitals in the metal atoms.^{7a,19b} In compound 6, this interpretation can be extended to the short molybdenum–O(2) bond. This would follow from the high formal oxidation state of Mo(1) ("5+" compared to "2+" for Mo(2)), which would make this metal center a powerful electron acceptor.

As a consequence of the strong binding of O(2) to Mo(1), a significant lengthening is observed in the Mo–C distances corresponding to cyclopentadienyl carbon atoms trans to O(2) (maximum distance for C(6) = 2.523 (4) Å, minimum for C(4) or C(8) = 2.345 (4) and 2.354 (4) Å). This trans lengthening is even higher than that found for $(\text{O})\text{CpMo}(\mu\text{-PPh}_2)_2\text{MoCp}(\text{CO})$,^{3e} which contains a terminal oxo ligand, and comparable to those for cyclopentadienyl rhenium complexes with $\text{Re}=\text{O}$ bonds.^{7b} On the other hand, the effect of O(2) on the cyclopentadienyl ligand bonded to Mo(2) is almost negligible, because only the Mo(2)–C(9) distance (C(9) being the most trans positioned) is slightly longer than others by ca. 0.03 Å. This feature cannot be explained on geometrical grounds as, for example, the O(2)–Mo(2)–C(9) angle (ca. 156.4°) is similar to O(2)–Mo(1)–C(6) (ca. 163.8°), experiencing the larger trans lengthening. Therefore, the origin of this observation might be electronic, since π contribution to the Mo(2)–O(2) bond, which is generally a necessary condition for the trans influence,^{7a} must be very small, as previously discussed.

The coordination sphere around the metal centers in 6 is completed by the CH_2PPh_2 and OPPh_2 bridging ligands. As a consequence of the disorder found in the crystal, the corresponding structural parameters have averaged values. Thus, the P(1)–C/O(1) and P(2)–C/O(2) distances (ca. 1.64 Å) are intermediate between the expected for a phosphinomethyl bridge (such as 1.81 (1) Å in $2,^{2a}$ 1.75 (2) Å in $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\mu\text{-dmpm})\text{Fe}_2(\text{CO})_4$,²³ or 1.787 (6) Å in $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Fe}_2(\text{NO})_4$)²⁴ and those corresponding to a phosphinite ligand (1.548 (6) Å for $(\mu\text{-CH}_2)(\mu\text{-OPPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$,¹⁷ or 1.526 (3) Å for $(\mu\text{-OP}(\text{OMe})_2)_2[\text{Mo}_2(\text{CO})_2(\text{CF}_3\text{CO}_2)\text{P}(\text{OMe})_3]_2$).²⁵ The same applies for the P–C/O–Mo angles.

Finally, the intermetallic interaction in compound 6 deserves some comments. The usual conventions lead to the assignment of an oxidation state of "2+" (d^4) to Mo(2), and "5+" (d^1) to Mo(1). Consequently, there is no way of explaining the diamagnetism observed for this tetrametallic species by supposing that both dimetallic moieties are independent. Therefore, it is necessary to postulate

(23) Doherty, N. M.; Hogart, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1986, 540.

(24) Chau, C.-N.; Yu, Y.-F.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *Organometallics* 1987, 6, 308.

(25) Arabi, S.; Berthelot, C.; Barry, J. P.; Taylor, N. J.; Chaudret, B. *Polyhedron* 1986, 5, 1785.

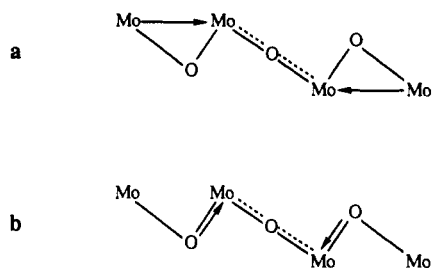


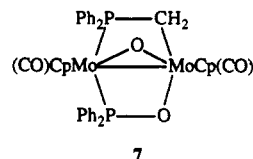
Figure 4. Schematic pictures of the main contributions to the bonding in the Mo_2O_3 core of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2]$ (**6**).

an (antiferromagnetic) intermetallic interaction²⁶ through the linear Mo–O–Mo bridge so as to remove the presence of unpaired electrons. This phenomenon is quite common in molybdenum(V) dimers containing the linearly oxygen bridged $\text{Mo}_2\text{O}_3^{4+}$ moiety.²⁷ The requirement seems to be the feasibility of a π -type three-center bonding interaction (positive overlap) between d orbitals of both metals and a p orbital of the linear oxo bridge.²⁸ In fact, the planarity of the Mo_2O_3 framework in compound **6** makes this possible and leads to an overall formal order of 1.5 for the Mo(1)–O(1) bond, in agreement with the experimental interatomic distance. In terms of electron counting, this is equivalent to admit O(1) as a six-electron donor atom (considered as O^{2-}) and leads to a number of 18 electrons around Mo(2), and 16 around Mo(1), if we ignore the Mo(1)–Mo(2) interaction. Therefore, in order to fulfill the EAN rule, it seems reasonable to postulate an essentially donor-acceptor bond between the “electron-rich” Mo(2) and the “electron-deficient” Mo(1) (Figure 4a). The presence of a bonding interaction between the molybdenum atoms in **6** is compatible with the experimental Mo(1)–Mo(2) distance of 2.9688 (5) Å, which is comparable with that found for the Mo(III) dimer **2** (3.001 (2) Å)^{2a} or even for the Mo(II)–Mo(IV) oxo complexes $(\text{O})\text{CpMo}(\mu\text{-PPh}_2)_2\text{MoCp}(\text{CO})$,^{3g} and $(\text{O})\text{CpMo}(\mu\text{-}\sigma,\pi\text{-CH}=\text{CHPh})(\mu\text{-PPh}_2)\text{MoCp}(\text{CO})$ ^{3c} (2.942 (1) Å and 2.885 (1) Å, respectively), which contain formally Mo=Mo bonds. However, as discussed above and in order to account for the relatively short Mo(1)–O(2) distance, a significant π -donation from O(2) to Mo(1) must also be postulated, in detriment of the intermetallic bond (Figure 4b). Therefore, a combination of both extreme descriptions seems to be a more realistic way of conciliating the structural data for **6**.

Spectroscopic data in solution of **6** are consistent with the structure found in the crystal. The trans arrangement of the phosphorus atoms around Mo(2) is reflected in the appearance of the high-field cyclopentadienyl protons as a triplet ($J_{\text{PH}} = 2$ Hz) in the ^1H NMR spectrum and in the large P–P coupling ($J_{\text{PP}} = 129$ Hz) observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The latter value is also derived from the elimination of the three-bond contribution to the coupling constant,²⁰ due to the insertion of an oxygen atom into the Mo–phosphido bond present in the parent compound **1**. The presence of this oxygen atom in the phosphinite ligand also removes the three-bond P–H coupling of the methylenic protons, which now displays couplings ($^2J_{\text{PH}}$) with

only one phosphorus atom in the ^1H NMR spectrum (see the Experimental Section).

One of the processes leading to the formation of **5** and **6**, i.e. substitution of a CO ligand in the parent compound **1** by an oxygen atom, can be avoided by the use of a mixture CO/O_2 (in fact, carbon monoxide containing 10 ppm of oxygen). The product thus obtained can be viewed as the result of the two other processes occurring in the formation of **6**: insertion of oxygen into the Mo=Mo and Mo–phosphido bonds. Thus, when carbon monoxide (contaminated with oxygen) is bubbled through a solution of **1** in diethyl ether, at rt for 1 h, the dark-yellow compound $(\mu\text{-O})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-OPPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (**7**) can be isolated in ca. 45% yield.



The strong similarity of the $^{31}\text{P}\{^1\text{H}\}$ NMR data for **6** and **7** (Table I) leads to the assumption that the “ $(\mu\text{-O})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-OPPh}_2)\text{Mo}_2$ ” core is common for both species. Thus, the high value of the P–P coupling constants would be indicative, not only of the trans arrangement of the phosphorus-donor ligands, but also of the presence of the phosphinite ligand.²⁰ On the other hand, the chemical shifts of the phosphinite resonances indicate that the insertion of an oxygen atom into the Mo–phosphido bond does not cause significant changes in the chemical shift of the phosphorus atom involved, as it has been reported before for group 9 phosphido complexes.^{6c,29} The presence of a bridging oxo ligand in the molecule is confirmed by the presence in the IR spectrum of **7** of an absorption at 635 cm^{-1} (KBr), in the range of Mo–O–Mo asymmetric stretching bands described.³⁰ Two C–O stretching absorptions (Table I) are also evident in the terminal carbonyl region. It should be noted that the difference between these two bands is ca. 150 cm^{-1} , whereas that is $40\text{--}60\text{ cm}^{-1}$ in all other dicarbonyl complexes reported here (**2–4**). This is probably a consequence of the strong electronic asymmetry of this mixed valence Mo(II)–Mo(IV) complex. Moreover, the low-energy band shows a frequency comparable to that of complex **6** (Table I), in agreement with their similar Mo(II) environments. Finally, in the ^1H NMR spectrum of **7**, the high-field cyclopentadienyl resonance appears as a triplet ($J_{\text{PH}} = 2$ Hz), as expected for a trans arrangement of the phosphorus-donor ligands. The presence of the phosphinite ligand is also denoted in this spectrum by the absence of $^3J_{\text{PH}}$ couplings in the methylenic protons (see the Experimental Section).

Although the use of carbon monoxide formally suppresses any decarbonylation in compound **1**, allowing the synthesis of the dicarbonyl complex **7**, the exact role of CO in this reaction is by no means clear. When **1** was treated with CO at 1 atm in a closed Schlenck no reaction was observed. At slightly higher pressures (ca. 2 atm), a new pink compound was detected, but it could not be characterized, since it decomposed rapidly in the absence of carbon monoxide atmosphere. Therefore, the first step in the process leading to **7** (just as in the formation of **5**

(26) Kahn, O. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 834.

(27) (a) Garner, C. D.; Charnock, J. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 3, Sect. 36.4.3.5.2. (b) Stiefel, E. I. *Prog. Inorg. Chem.* 1977, 22, 1.

(28) Blake, A. B.; Cotton, F. A.; Wood, J. S. *J. Am. Chem. Soc.* 1964, 86, 3024.

(29) Klingert, B.; Werner, H. *J. Organomet. Chem.* 1983, 252, C47.

(30) Heberhold, H.; Kemnitz, W.; Razavi, A.; Schllhorn, H.; Thewalf, U. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 601.

and 6) seems to be the reaction of 1 with oxygen and only after that does the nature of the oxygen carrier gas (either nitrogen or carbon monoxide) affect the course of the reaction.

The low reactivity of 1 toward CO is unexpected, given the formal unsaturation of this complex. This behavior cannot be steric in origin, since 1 easily adds large atoms, such as iodine. Then, the high electron density at the dimetal center in the parent compound 1, apparent from the reactions previously discussed, seems to be the factor preventing the reaction with a not very strong base, such as CO.

Conclusions

The reactions of $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ with iodine, sulfur, and selenium lead to the insertion of "I", or one chalcogen atom into the Mo=Mo bond present in the parent compound. The reactions with oxygen are strongly dependent on the conditions used. When decarbonylation is favored (traces of oxygen in nitrogen), the major product obtained is the result of the substitution of the carbonyl ligand present in the "MoCp(CH₂)" fragment by an oxygen atom. Instead, in the presence of carbon monoxide, elemental oxygen inserts not only into the Mo=Mo bond (as for S and Se), but also into the Mo-phosphide bond. The tetranuclear diamagnetic compound $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2]$, also obtained in these reactions, is the result of all three processes and further condensation. In all the above reactions, the "MoCpP₂(CO)" fragment of the parent compound remained unaltered, as well as the Mo-CH₂ bond at the second metal center. The latter, however, turned out to contain the most reactive sites, since both decarbonylation and insertion into the Mo-phosphide bond occurred specifically at this side of the molecule. Therefore, the carbon atom of the phosphinomethyl ligand seems to have a pronounced labilizing influence on the carbonyl and phosphido ligands of the molecule.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures,³¹ distilled, and purged with nitrogen prior to use. The compounds $(\mu\text{-dppm})\text{Mo}_2\text{Cp}_2(\text{CO})_4$ ^{1c} and $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ ^{2a} were prepared as reported before. All other reagents were obtained from the usual commercial suppliers and used as received. Gases used in this work contained traces of oxygen and water in the following proportions (maximum values in ppm): nitrogen, O₂ (10), H₂O (10); carbon monoxide, O₂ (10), H₂O (5).

The progress of the reactions was monitored by solution IR spectra in the 2100–1700-cm⁻¹ region. Filtrations were carried out on dry Celite under nitrogen. Column chromatographies were carried out under nitrogen in alumina IV, prepared from aluminum oxide, neutral (Brockmann I, 150 mesh, 58 Å), and deactivated with water. The products were recrystallized at -20 °C.

Infrared spectra were obtained using Perkin-Elmer 599 or 833 apparatus, in NaCl windows for solutions and for Nujol emulsions or in KBr pellets. NMR spectra were recorded on a Bruker AC-300 instrument at rt, unless otherwise indicated. TMS was used as internal reference for carbon and proton NMR spectra, and 85% aqueous H₃PO₄ was used for phosphorus NMR spectra, as external reference. ³¹P and ¹³C NMR spectra were carried out with complete ¹H decoupling. The mass spectrum of compound

3 was obtained using a Hewlett-Packard 5987A mass spectrometer operating at 70 eV. Masses were correlated with the following isotopes: ¹H, ¹²C, ¹⁶O, ³¹P, ³²S, and ¹⁸⁰Mo, ¹⁹²Mo, or ⁹⁸Mo. The electrical conductivity measurement of compound 2 was carried out at rt with a Crison 522 conductivitymeter using a 5 × 10⁻⁴ M solution. The range of molar conductivity for 1/1 electrolytes is 20–30 S cm² mol⁻¹ in nitrobenzene solutions.³² Elemental analysis were performed on a Perkin-Elmer 240B microanalyzer. Solution IR bands in the carbonyl region and ³¹P{¹H} NMR data for the new compounds are given in Table I.

Synthesis of $(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (2). A solution of 0.052 g (0.2 mmol) of I₂ in 10 mL of Et₂O was added dropwise to a solution of 0.114 g (0.15 mmol) of $(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (1) in 15 mL of Et₂O. A pale brown solid precipitated immediately, and the mixture was stirred for a period of 30 min at rt, once the addition had finished. The pale pink solution was syringed off, and the solid was washed with Et₂O (5 × 10 mL) and dried in vacuo. Recrystallization of the solid from CH₂Cl₂/Et₂O yielded 0.134 g (0.132 mmol, 88%) of 2 as orange microcrystalline solid. Conductivity: (C₆H₅NO₂): 32 S cm² mol⁻¹. IR (KBr, cm⁻¹): 3020 vw, 1955 m, 1895 s, 1470 w, 1430 m, 1420 msh, 1300 vw, 1175 vw, 1150 vw, 1090 m, 1010 w, 995 w, 920 vw, 845 w, 830 w, 740 m, 695 m, 520 m, 490 m. ¹H NMR (300 MHz, CDCl₃): δ 7.9–6.5 (m, Ph, 20 H), 5.80 (d, *J*_{PH} = 2 Hz, C₆H₅, 5 H), 5.42 (s, C₆H₅, 5 H), 1.54 (ddd, ²*J*_{HH} = 14 Hz, *J*_{PH} = 10 and 2 Hz, CH₂, 1 H), 0.91 (ddd, ²*J*_{HH} = 14 Hz, *J*_{PH} = 19 and 14 Hz, CH₂, 1 H). ¹³C{¹H} NMR (75.4 MHz, THF/C₆D₆): δ 241.5 (d, ²*J*_{PC} = 41 Hz, MoCO), 237.3 (dd, ²*J*_{PC} = 15 and 4 Hz, MoCO), 138.1–127.8 (Ph), 97.9 (s, C₆H₅), 91.7 (s, C₆H₅), -21.4 (br, MoCH₂P). Anal. Calcd for C₃₇H₃₂I₂Mo₂O₂P₂: C, 43.72; H, 3.18. Found: C, 44.03; H, 3.36.

Synthesis of $(\mu\text{-S})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (3). Sulfur (0.007 g, 0.22 mequiv) was added to a solution of 0.153 g (0.2 mmol) of 1 in 10 mL of toluene. After the mixture had been stirred for 10 min at rt, the brown solution obtained was filtered. The addition of 10 mL of hexane and cooling to -20 °C gave dark red crystals, which were separated from the solution, washed with hexane (3 × 3 mL), and dried in vacuo, yielding 0.065 g (0.082 mmol, 41%) of 3. IR (KBr, cm⁻¹): 3015 vw, 2955 vw, 2915 vw, 1920 s, 1830 vs, 1585 w, 1570 vw, 1480 w, 1430 m, 1425 wsh, 1305 vw, 1160 vw, 1095 m, 1070 w, 1030 vw, 1020 vw, 1005 vw, 915 w, 895 w, 840 msh, 830 m, 810 m, 740 m, 700 s, 530 s, 505 w, 485 vw, 461 m, 410 vw, 360 vw, 335 vw. ¹H NMR (300 MHz, CDCl₃): δ 7.9–7.1 (m, Ph, 20 H), 5.20 (s, C₆H₅, 5 H), 4.44 (t, *J*_{PH} = 2 Hz, C₆H₅, 5 H), 1.82 (dd, ²*J*_{HH} = 10 Hz, ²*J*_{PH} = 10 Hz, CH₂, 1 H), 1.66 (ddd, ²*J*_{HH} = 10 Hz, *J*_{PH} = 4 and 2 Hz, CH₂, 1 H). Mass spectrum (EI), *m/z* (relative intensity): 739, 737 (M⁺ - 2CO, 4), 555, 553 (Mo₂Cp₂(CH₂PPh₂)SH⁺, 2), 476, 474 (Mo₂Cp₂Ph⁺ - H, 1), 385 (Ph₂PCH₂PPh₂⁺, 1), 232 (SPPPh₂CH₃⁺, 48), 217 (SPPPh₂⁺, 46), 215 (SPPPh₂⁺ - 2H, 95), 201 (PPh₂CH₂H⁺, 89), 200 (PPh₂-CH₃⁺, 89), 183 (PPh₂⁺, 100), 153 (Ph₂⁺ - H, 26). Anal. Calcd for C₃₇H₃₂Mo₂O₂P₂S: C, 55.93; H, 4.07. Found: C, 56.11; H, 3.98.

Synthesis of $(\mu\text{-Se})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (4). Black selenium (0.018 g, 0.23 mequiv) was added to a solution of 0.153 g (0.2 mmol) of 1 in 10 mL of toluene, and the mixture was stirred for 1 h at rt. Workup as for 3 yielded 0.070 g (0.083 mmol, 42%) of 4 as brown-red crystals. IR (Nujol, cm⁻¹): 3020 vw, 1875 s, 1815 vs, 1570 w, 1425 m, 1170 w, 1150 vw, 1080 m, 1060 m, 995 m, 905 vw, 830 msh, 820 m, 810 msh, 740 s, 695 s. ¹H NMR (300 MHz, C₆D₆): δ 7.9–6.9 (m, Ph, 20 H), 4.83 (d, *J*_{PH} = 1 Hz, C₆H₅, 5 H), 4.31 (t, *J*_{PH} = 2 Hz, C₆H₅, 5 H), 1.98–1.88 (unresolved ABMX system, CH₂, 2 H). ¹³C{¹H} NMR (75.4 MHz, CH₂Cl₂/C₆D₆): δ 246.4 (m, MoCO), 237.4 (d, ²*J*_{PC} = 3 Hz, MoCO), 146.7–117.1 (Ph), 92.7 (s, C₆H₅), 89.7 (s, C₆H₅), -2.9 (d, ¹*J*_{PC} = 26 Hz, MoCH₂P). Anal. Calcd for C₃₇H₃₂Mo₂O₂P₂Se: C, 52.81; H, 3.54. Found: C, 53.06; H, 3.77.

Synthesis of $(\text{O})\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)\text{MoCp}(\text{CO})$ (5) and $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{MoCp}(\text{CO})_2]$ (6). A 100-mL Schlenk flask equipped with a magnetic stirring bar and an inlet glass tube which allowed bubbling of

(31) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

(32) Geary, W. *Coord. Chem. Rev.* 1971, 7, 81.

Table III. Experimental Data for the Crystallographic Analysis of $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{-MoCp}(\text{CO})]_2\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$ (6)

formula	$\text{C}_{73}\text{H}_{68}\text{Cl}_2\text{Mo}_4\text{O}_8\text{P}_4$
molecular weight	1651.9
crystal system	monoclinic
space group	$P2_1/n$
a , Å	16.113 (2)
b , Å	19.487 (6)
c , Å	11.686 (3)
β , deg	101.63 (1)
V , Å ³	3594 (2)
z	2
ρ_{calcd} , g cm ⁻³	1.52
reflections for lattice parameters: number	25
range	17–18
$F(000)$	1664
μ , cm ⁻¹	8.8
T , °C	18
crystal size, mm ³	0.65 × 0.40 × 0.20
diffractometer	Phillips PW1100
radiation	Mo $K\alpha$
monochromator	graphite
scan type	$\omega\text{-}2\theta$
scan width	1.2 + 0.34 tan θ
θ range, deg	1–25
standard reflections	2, measured every 2 h
no. of observed reflections	5967
no. of reflections used, $I \geq 3\sigma(I)$	5092
min–max height in final $\Delta\rho$, e Å ⁻³	–0.6 to 1.9
no. of refined parameters	419
$R = [\sum \Delta F /\sum F_o]$	0.045
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.053

$a_w = w\{1 - [(F_o - F_c)/6\sigma(F_o)]^2\}$. $w' = 1/\sum_{(r=1,3)} A_r T_r(X)$, with three coefficients 3.90, 1.31, and 2.86 for the Chebyshev polynomial $T_r(X)$ with $X = F_o/F_o(\text{max})$.

nitrogen through the solution was charged with 0.572 g (0.75 mmol) of 1 and 30 mL of toluene. After the mixture had been stirred for 18 h under a gentle stream of nitrogen, the black solution obtained was chromatographed at 10 °C on alumina IV prepared in hexane. Elution with toluene gave a purple band containing (O)CpMo($\mu\text{-CH}_2\text{PPh}_2$)($\mu\text{-PPh}_2$)MoCp(CO) (5). Concentration in vacuo of the solution and cooling to –20 °C gave purple black crystals, which were separated from the solution, washed with hexane (3 × 3 mL), and dried in vacuo, yielding 0.200 g (0.237 mmol, 32%) of 5-C₆H₅CH₃. IR (Nujol, cm⁻¹): 3040 vw, 1770 vs, 1600 vw, 1580 vw, 1570 vw, 1500 w, 1440 m, 1355 vw, 1300 vw, 1180 vw, 1160 vw, 1100 w, 1085 vw, 1020 vw, 1000 w, 920 vw, 905 m, 840 m, 835 wsh, 805 w, 795 m, 740 m, 700 m, 665 vw. ¹H NMR (300 MHz, C₆D₆): δ 7.8–7.0 (m, Ph, 20 H), 5.14 (s, C₆H₅), 4.62 (s, C₆H₅, 5 H), 3.23 (ddd, ²J_{HH} = 11 Hz, J_{PH} = 11 and 4 Hz, CH₂, 1 H), 2.34 (dd, ²J_{HH} = 11 Hz, ²J_{PH} = 6 Hz, CH₂, 1 H). ¹³C{¹H} NMR (75.4 MHz, THF/C₆D₆, –20 °C): δ 235.1 (dd, ²J_{PC} = 11 and 6 Hz, MoCO), 150.0–126.0 (Ph), 107.4 (s, C₆H₅), 87.6 (s, C₆H₅), 0.6 (d, ¹J_{PC} = 10 Hz, MoCH₂P). Anal. Calcd for C₄₈H₄₀Mo₂O₂P₂ (5-toluene): C, 62.29; H, 4.79. Found: C, 62.16; H, 4.67.

Elution with CH₂Cl₂/toluene gave a small red band, which was discarded. Further elution with CH₂Cl₂/THF (1/1, v/v) gave a blue band containing $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{-MoCp}(\text{CO})]_2$ (6). The solvent was removed in vacuo, and the dark residue was recrystallized from CH₂Cl₂/hexane, yielding 0.030 g (0.019 mmol, 5%) of 6, as a dark blue microcrystalline solid. IR (KBr, cm⁻¹): 3050 w, 2920 vw, 1820 vsbr, 1585 vw, 1575 vw, 1480 m, 1440 m, 1370 vw, 1310 vw, 1275 vw, 1180 w, 1160 vw, 1100 m, 1070 m, 1030 w, 1020 w, 1000 w, 970 mbr, 840 msh, 830 m, 805 w, 740 s, 700 s, 640 w, 580 w, 560 msh, 540 s, 500 msh, 490 m, 440 w, 370 vw. ¹H NMR (300 MHz, CDCl₃): δ 7.7–7.2 (m, Ph, 40 H), 6.54 (s, C₆H₅, 10 H), 4.72 (t, J_{PH} = 2 Hz, C₆H₅, 10 H), 2.19 (t, ²J_{HH} = 11 Hz, ²J_{PH} = 11 Hz, CH₂, 2 H), 1.88 (dd, ²J_{HH} = 11 Hz, ²J_{PH} = 7 Hz, CH₂, 2 H). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 251.9 (m, MoCO), 148.1–127.5 (Ph), 109.8 (s, C₆H₅), 95.0 (s, C₆H₅), 22.8 (d, ¹J_{PC} = 10 Hz, MoCH₂P). Anal. Calcd for C₇₂H₆₄Mo₄O₇P₄: C, 55.82; H, 4.17. Found: C, 56.09; H, 4.24.

Table IV. Atomic Coordinates and Thermal Parameters for $(\mu\text{-O})[\text{CpMo}(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-O})(\mu\text{-OPPh}_2)\text{-MoCp}(\text{CO})]_2$ (6)

atom	x/a	y/b	z/c	$U(\text{eqv})^a$
Mo(1)	–0.10405 (2)	0.04008 (2)	0.01147 (3)	0.0296
Mo(2)	–0.20615 (2)	0.14782 (2)	–0.13203 (3)	0.0352
P(1)	–0.25071 (6)	0.02857 (5)	–0.20478 (9)	0.0358
P(2)	–0.09614 (7)	0.20048 (5)	0.02638 (9)	0.0380
O(1)	0.00000	0.00000	0.00000	0.0343
O(2)	–0.0954 (2)	0.0932 (1)	–0.1179 (2)	0.0343
O(3)	–0.3193 (2)	0.1291 (2)	0.0497 (3)	0.0582
C/O(1)	–0.1740 (2)	–0.0227 (2)	–0.1379 (3)	0.0427
C/O(2)	–0.0441 (3)	0.1358 (2)	0.0955 (3)	0.0499
C(3)	–0.2725 (3)	0.1327 (2)	–0.0153 (4)	0.0420
C(4)	–0.1618 (3)	0.0468 (3)	0.1799 (4)	0.0439
C(5)	–0.0803 (3)	0.0185 (3)	0.2211 (4)	0.0454
C(6)	–0.0791 (3)	–0.0477 (3)	0.1736 (4)	0.0442
C(7)	–0.1579 (3)	–0.0594 (2)	0.1013 (4)	0.0437
C(8)	–0.2098 (3)	–0.0018 (2)	0.1058 (4)	0.0424
C(9)	–0.3084 (4)	0.2320 (3)	–0.2086 (6)	0.0648
C(10)	–0.2291 (4)	0.2631 (3)	–0.1848 (6)	0.0626
C(11)	–0.1794 (4)	0.2347 (3)	–0.2573 (6)	0.0616
C(12)	–0.2281 (5)	0.1843 (3)	–0.3264 (5)	0.0649
C(13)	–0.3081 (4)	0.1818 (3)	–0.2932 (5)	0.0616
C(20)	–0.2634 (3)	0.0102 (2)	–0.3620 (4)	0.0444
C(21)	–0.1920 (4)	0.0180 (4)	–0.4104 (5)	0.0730
C(22)	–0.1981 (6)	0.0048 (5)	–0.5279 (7)	0.0881
C(23)	–0.2735 (7)	–0.0149 (4)	–0.5974 (5)	0.0784
C(24)	–0.3438 (5)	–0.0226 (3)	–0.5501 (5)	0.0690
C(25)	–0.3378 (4)	–0.0104 (3)	–0.4325 (4)	0.0567
C(30)	–0.3494 (3)	–0.0072 (2)	–0.1742 (3)	0.0398
C(31)	–0.4194 (3)	0.0337 (3)	–0.1742 (5)	0.0528
C(32)	–0.4949 (3)	0.0039 (4)	–0.1532 (5)	0.0627
C(33)	–0.4985 (4)	–0.0650 (4)	–0.1328 (5)	0.0630
C(34)	–0.4287 (4)	–0.1056 (3)	–0.1330 (5)	0.0634
C(35)	–0.3553 (3)	–0.0775 (3)	–0.1537 (4)	0.0520
C(40)	–0.0182 (3)	0.2556 (2)	–0.0222 (4)	0.0437
C(41)	–0.0262 (3)	0.3261 (3)	–0.0292 (6)	0.0593
C(42)	0.0328 (5)	0.3646 (4)	–0.0724 (7)	0.0776
C(43)	0.0989 (5)	0.3350 (5)	–0.1070 (6)	0.0843
C(44)	0.1078 (5)	0.2650 (5)	–0.0995 (9)	0.0921
C(45)	0.0495 (4)	0.2256 (4)	–0.0563 (8)	0.0767
C(50)	–0.1249 (3)	0.2536 (2)	0.1414 (4)	0.0491
C(51)	–0.2068 (3)	0.2765 (3)	0.1385 (5)	0.0590
C(52)	–0.2241 (4)	0.3171 (3)	0.2298 (6)	0.0666
C(53)	–0.1621 (5)	0.3347 (4)	0.3211 (5)	0.0733
C(54)	–0.0804 (5)	0.3145 (4)	0.3244 (6)	0.0827
C(55)	–0.0614 (4)	0.2736 (4)	0.2344 (5)	0.0716
Cl(1)	–0.0684 (5)	–0.2369 (4)	–0.5450 (7)	0.091 (1)*
Cl(2)	–0.0582 (6)	–0.2314 (5)	–0.5911 (8)	0.091 (1)*
Cl(3)	0.0257 (6)	–0.1041 (5)	–0.5227 (8)	0.091 (1)*
Cl(4)	–0.0825 (8)	–0.1350 (7)	–0.441 (1)	0.091 (1)*
Cl(5)	–0.0301 (9)	–0.2102 (7)	–0.626 (1)	0.091 (1)*
O(W)	–0.0972 (5)	–0.1242 (4)	–0.2584 (7)	0.069 (2)*

^a Asterisks denote U values that are isotropic.

Synthesis of $(\mu\text{-O})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-OPPh}_2)\text{Mo}_2\text{Cp}_2(\text{CO})_2$ (7). A 100-mL Schlenk flask equipped with a magnetic stirring bar and an inlet glass tube which impinges above the liquid level was charged with 0.114 g (0.15 mmol) of 1 and 30 mL of Et₂O. The mixture was vigorously stirred at rt, with a stream of carbon monoxide sweeping through the system. After 1 h, the solvent was removed in vacuo from the resulting black solution, affording a brown oil to which charcoal was added. Extraction of this mixture with toluene and filtration gave a dark yellow solution, which after concentration in vacuo and cooling to –20 °C yielded 0.050 g (0.063 mmol, 42%) of 7 as black crystals. IR (KBr, cm⁻¹): 3060 w, 2920 w, 1980 vs, 1840 vs, 1590 w, 1575 w, 1485 m, 1440 s, 1335 w, 1315 w, 1280 vw, 1270 vw, 1190 w, 1160 w, 1105 m, 1075 w, 1030 msh, 1010 m, 1000 m, 850 msh, 830 m, 810 m, 750 s, 705 s, 635 m. ¹H NMR (300 MHz, CDCl₃): δ 7.7–7.0 (m, Ph, 20 H), 4.91 (s, C₆H₅, 5 H), 4.87 (t, J_{PH} = 2 Hz, C₆H₅, 5 H), 2.10 (dd, ²J_{HH} = 12 Hz, ²J_{PH} = 7 Hz, CH₂, 1 H), –0.28 (t, ²J_{HH} = 12 Hz, ²J_{PH} = 12 Hz, CH₂, 1 H). ¹³C{¹H} NMR (75.4 MHz, C₆D₆): δ 252.4 (dd, ²J_{PC} = 16 and 12 Hz, MoCO), 243.4 (s, MoCO), 148.4–127.5 (Ph), 97.9 (s, C₆H₅), 94.7 (s, C₆H₅), 3.43 (d, ¹J_{PC} = 4 Hz, MoCH₂P).

Anal. Calcd for $C_{37}H_{32}Mo_2O_4P_2$: C, 55.93; H, 4.07. Found: C, 55.74; H, 4.21.

X-ray Crystallographic Analysis of $(\mu-O)[CpMo(\mu-CH_2-PPh_2)(\mu-O)(\mu-OPPh_2)MoCp(CO)]_2$ (6). Suitable crystals of 6 were grown by slow diffusion of a concentrated dichloromethane solution of the complex into hexane at rt. These crystals were found to contain one dichloromethane and one water molecule per molecule of complex. The latter may be due to traces of water accidentally present in the solvents employed.

Details of data collection and refinements are given in Table III. Structure was solved by direct methods and subsequent Fourier maps. An empirical absorption correction was applied with the program DIFABS³³ from CRYSTALS.³⁴ Secondary extinction correction was not necessary. The structure consists of a tetranuclear entity, one part being related to the other through an oxygen atom O(1), located on an inversion center. So there are two molybdenum atoms in the asymmetric unit, bridged by an oxygen atom O(2), and two identical X-PPh₂ groups, X appearing with an electronic density intermediate between C and O. This can be explained by a disorder: in one-half of the dimer there is one CH₂-PPh₂ bridge and one O-PPh₂ bridge. The other part of the dimer is centrosymmetric, except for O and CH₂, which have exchanged their position, so each site is occupied by half C and half O. We tried to refine these four noncentrosymmetric atoms in the group P1, but we did not succeed in

differentiating them. They have been called C/O(1) and C/O(2). Almost all hydrogen atoms were found on difference maps (except naturally those of CH₂ groups) but not refined.

Important spurious peaks in the final difference Fourier synthesis were attributed to the chlorine atoms of a disordered CH₂Cl₂ molecule, the carbon atom of which was not found; there is one CH₂Cl₂ for one tetranuclear unit, so the sum of the occupancy factor of chlorine atoms is 1. There was also one water molecule O(W) of multiplicity 0.5. It is in the vicinity of CH₂Cl₂, but cannot be another chlorine, because it was too near the bridging C/O atoms. The greatest peaks in the last difference map are in the vicinity of the disordered CH₂Cl₂.

Figure 2 is an ORTEP drawing of the tetranuclear entity with the numbering scheme, and Figure 3 is a projection on the plane containing the metal and oxo atoms, excluding the X-PPh₂ groups, omitted for clarity. Atomic coordinates for refined atoms are given in Table IV, and selected bond lengths and angles are collected in Table II.

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Supplementary Material Available: Drawing of the molecular structure of compound 6 showing the numbering for all atoms and tables of atomic coordinates and thermal parameters for hydrogen atoms, anisotropic thermal parameters, and additional bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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(33) Walker, N.; Stuart, D. *Acta Crystallogr.* 1983, A39, 158.

(34) Carruthers, J. R.; Watkin, D. W. *CRYSTALS, an Advanced Crystallographic Computer Program*; Chemical Crystallography Laboratory, Oxford University: Oxford, 1985.