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Photochemistry of ring-coupled group VI bimetallic compounds I: phosphine substitution without disproportionation. The molecular structures of $Mo_2(CO)_5[P(C_6H_5)_3](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$ and $Mo_2(CO)_4[P(CH_3)_3]_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$[1]

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Abstract

Solution photolysis of ring-coupled bimetallic compounds of the formula $M_2(CO)_6(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$, where M = Mo or W and R = H or CH_3, in the presence of triphenylphosphine or trimethylphosphine yields simple substitution derivatives $M_2(CO)_5L(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$ or $M_2(CO)_4L_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$. The compounds have been fully characterized by IR and NMR spectroscopy and elemental analysis. Phosphine ligands are found to occupy positions trans to the M–M bond. No evidence was found for disproportionation processes such as those found for similar reactions of the non-ring-coupled species. The molecular structures of two compounds have been determined: $(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)Mo_2(CO)_5(PPh_3)$: monoclinic, $P2_1/c$, $a = 22.871(8)$, $b = 16.415(6)$, $c = 15.957(9)$ Å, $\beta = 94.29(3)°$, $V = 5974(4)$ Å^3, $Z = 8$, $R(F) = 8.87\%$; $(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)Mo_2(CO)_4(PMe_3)_2$: monoclinic, $P2_1/c$, $a = 9.843(5)$, $b = 15.343(7)$, $c = 31.514(6)$ Å, $\beta = 97.28(3)°$, $V = 4720(4)$ Å^3, $Z = 8$, $R(F) = 4.38\%$.

Keywords: Photolysis; Bi metallic compounds; Substitution reactions; Phosphines

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1. Introduction

The photochemistry of $Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2$ in the absence of ligands is now well understood to involve both radical and carbonyl-loss pathways as summarized in Scheme 1 [1]. Some years ago Turaki and Huggins [2] established that the carbonylation of triply bonded $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ to give $Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2$ (and its microscopic reverse) proceeded by a mechanism in which the metal–metal bond was retained, precluding a radical involvement in this important reaction.

In the presence of a potential ligand, such as a phosphine or phosphite, either the 17-electron (17-e) radical, $M(CO)_3(\eta^5\text{-}C_5H_5)$, or the electron deficient intermediate, $Mo_2(CO)_5(\eta^5\text{-}C_5H_5)_2$, could react with the ligand. A number of investigations have established that the ultimate products in these reactions are strongly dependent upon the electronic donor ability and the cone angle of the phosphine or phosphite [3]. Tyler has proposed a mechanism for these reactions, Scheme 2, in which a $M(CO)_3(\eta^5\text{-}C_5H_5)$, 17-e radical reacts with a ligand to give $M(CO)_2L(\eta^5\text{-}C_5H_5)$. Subsequent reaction of this 17-e species with a second ligand forms a highly reducing 19-e species, $M(CO)_2L_2(\eta^5\text{-}$

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[1] In honor of our friend and colleague Prof. R. Bruce King on the occasion of his 60th birthday.

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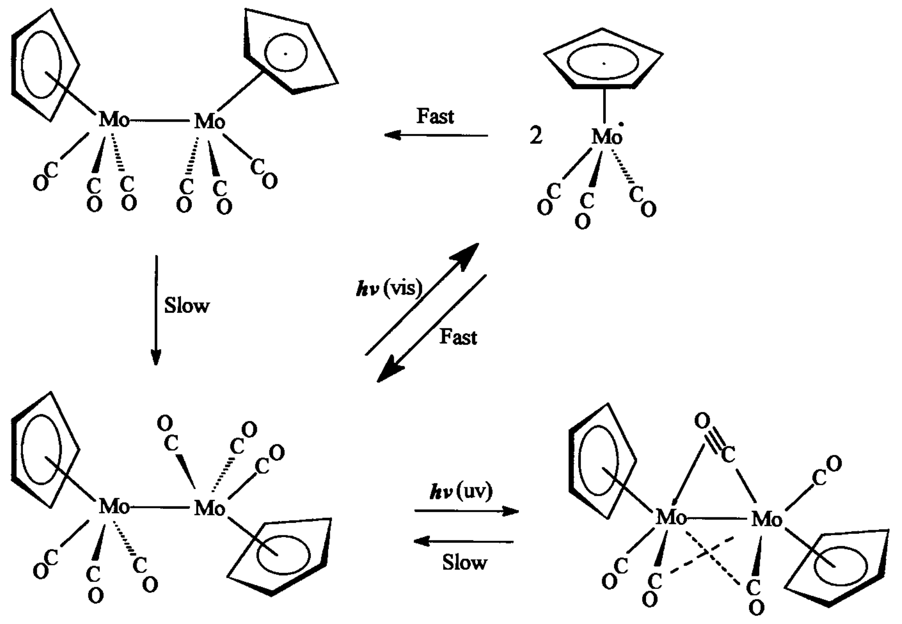


Scheme 1.

C_5H_5). The rate dependence of the reaction on the cone angle of the ligand is attributed to the step in which the second ligand molecule reacts with $M(CO)_2L(\eta^5\text{-}C_5H_5)$ since formation of a bis(ligand) species would be inhibited by bulky ligands.

An alternative mechanism that is also consistent with the observed data is shown in Scheme 3. In this mechanism $Mo_2(CO)_5L(\eta^5\text{-}C_5H_5)_2$, formed by either carbonyl loss or radical routes, undergoes photochemical disproportionation to yield $[M(CO)_2L(\eta^5\text{-}C_5H_5)]^+$ and $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$. Reaction of $[M(CO)_2L(\eta^5\text{-}C_5H_5)]^+$ with a second molecule of L yields the bis(ligand) cation. Since in this mechanism, L is competing with $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$ for reaction with $[M(CO)_2L(\eta^5\text{-}C_5H_5)]^+$, disproportionation will be favored for all but the largest cone angles.

We have previously reported the synthesis and matrix photochemistry of ring-coupled compounds of the general formula $M_2(CO)_6(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_4)$, where M = Mo or W and R = H or CH_3 [4]. Photolysis of these compounds in inert gas matrices [5] and in frozen Nujol [6] indicate that a single carbon monoxide is lost upon photolysis. Unlike the parent species, $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, there is no evidence for loss of a second carbon monoxide to form a triply bonded species when the compounds are photolyzed in the absence of potential ligands, nor is there any evidence for the formation of metal-based radicals upon photolysis. In order to evaluate the consequences of ring-coupling on the reaction chemistries of these Group VI compounds, we have examined the simple photochemical ligand substitution chemistry with phosphines. The results of these studies are reported in this paper.

2. Results and discussion

Broad band photolysis of the red bimetallic compounds **1**–**3**, Scheme 4, in the presence of triphenylphosphine ligand or photolysis of **1** with trimethylphosphine in degassed benzene afforded dark purple reaction mixtures. After removal of solvent, the reaction mixtures were cleanly separable by medium pressure column chromatography to give three bands. Characterization of these bands, vide infra, established them to be monosubstituted phosphine derivatives, disubstituted phosphine derivatives and unreacted starting material. The proportions of the three bands were dependent upon the ratio of the bimetallic compound and phosphine in the initial reaction mixture. Insufficient quantities of $[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4]Mo_2(CO)_5(PMe_3)$ were isolated for full characterization.

Monosubstituted compounds, $Mo_2(CO)_5PPh_3(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$, **4**, $W_2(CO)_5PPh_3(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$, **5**, and $Mo_2(CO)_5PPh_3(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CMe_2\text{–}C_5H_4)$, **6**, were isolated as red–purple powders. The IR spectra of all three compounds are very

$$Cp_2Mo_2(CO)_6 \rightarrow CpMo(CO)_3 \quad \text{(photolysis)}$$

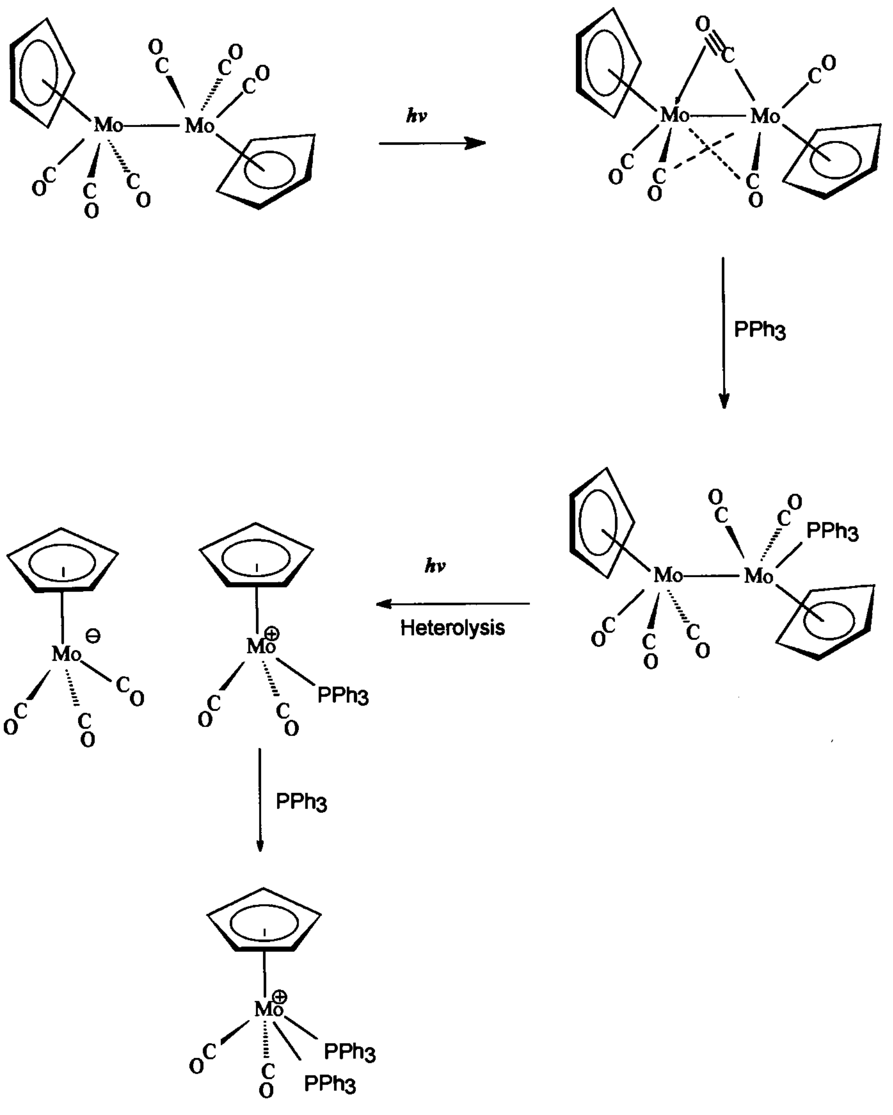
$$CpMo(CO)_3 + L \rightarrow CpMo(CO)_2L + CO$$

$$CpMo(CO)_2L + L \rightarrow CpMo(CO)_2L_2 \quad \text{(19-electron intermediate)}$$

$$CpMo(CO)_2L_2 + Cp_2Mo_2(CO)_6 \rightarrow [CpMo(CO)_2L_2]^{+1} + [Cp_2Mo_2(CO)_6]^{-1}$$

$$[Cp_2Mo_2(CO)_6]^{-1} \rightarrow CpMo(CO)_3 + [CpMo(CO)_3]^{-1}$$

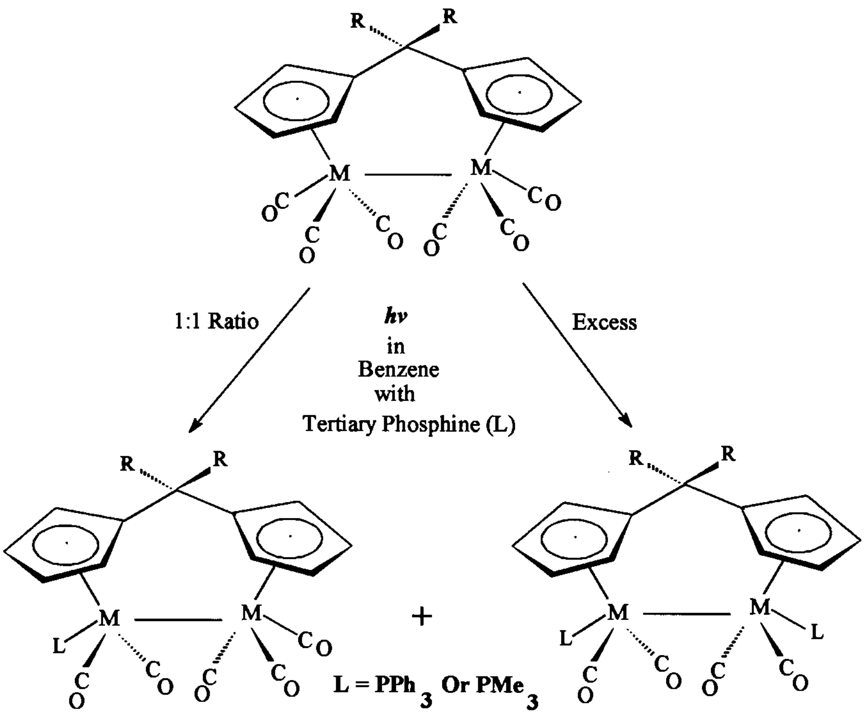
Scheme 2.



Scheme 3.

similar and contain four carbonyl stretching bands in the terminal region, shifted about 50–70 cm^{-1} to lower energy relative to the parent compounds reflecting the lower π-acid character of triphenylphosphine relative to carbon monoxide. The room temperature (r.t.) ^{1}H-NMR spectra of **4** and **5** show a complex envelope associated with the triphenylphosphine group, a well-defined AB pattern for the methylene group, and eight cyclopentadienyl ring proton resonances. The spectrum of **6** differs only in that two methyl resonances were observed for the CMe_2 linkage between the cyclopentadienyl rings. The observed patterns require that all three compounds have C_1 symmetry in solution. The ^{13}C-NMR spectra are also consistent with monosubstitutition to yield an asymmetric molecule. The carbon spectra of **4** and **5** cleanly resolve five carbonyl resonances, ten cyclopentadienyl ring resonances (two distinct *ipso* resonances were resolved) and a resonance for the methylene carbon. The spectrum for **6** was identical to those of **4** and **5** except that two methyl resonances and a quaternary carbon resonance were observed for the CMe_2 linkage. The *ortho* phenyl carbon resonances of the triphenylphosphine ligand were broadened and split into two broad resonances having an integration of ca. 2:1. No coupling was resolved between the single *para* carbon resonance and the phosphorus atom, and the *ipso* resonances were very broadened when observed. We attribute the unusual spectral pattern of the triphenylphosphine phenyl groups to hindered or slowed rotation about the P–Mo bond creating two magnetically distinct environments for the phenyl groups.

X-ray quality crystals of **4** were obtained by vapor diffusion of petroleum ether into a dichloromethane solution of **4** in the cold. The ORTEP diagram of **4** is presented in Fig. 1. Crystallographic data for compounds **4** and **11** are summarized in Table 1, and selected bond lengths and angles for **4** are presented in



Scheme 4.

Tables 2 and 3. The structure of **4** was solved in the $P2_1/c$ space group with two independent, but chemically equivalent, molecules in the asymmetric unit. One of these molecules resolved well, but the other was found to be statistically disordered over two positions. As a consequence, the *R* factor of 8.87% is somewhat higher than is typical for this class of compounds.

The core structures of **4** and **1**, i.e. $Mo_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}C_5H_4)$, are virtually identical with a C_2 rotation about an axis running between the bridging carbon and the midpoint of the Mo–Mo bond. The triphenylphosphine ligand in **4** occupies a position *trans* to the M–M bond. The Mo–Mo bond length of **1** is 3.140 Å while that of **4** is 3.173 Å. The bond lengthening observed in the phosphine derivative may be attributable to either the reduced π-acid character of triphenylphosphine relative to carbon monoxide, or to an indirect effect of the steric bulk of the phosphine.

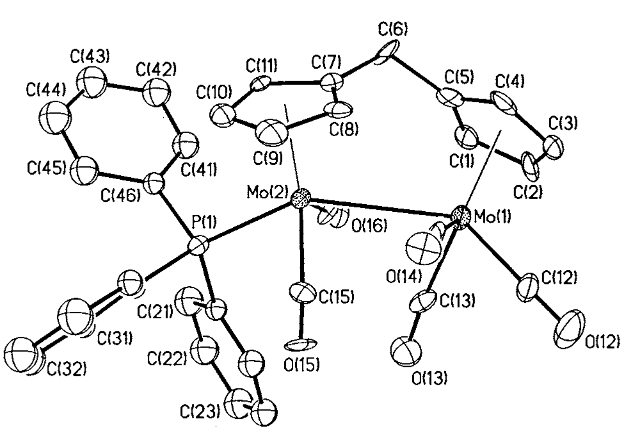


Fig. 1. Molecular structure of $(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}C_5H_4)Mo_2(CO)_5(PPh_3)$.

Variable temperature NMR spectral studies of **1** demonstrate that this compound undergoes a twisting motion about the C_2 axis that averages the magnetic environment of the ring protons. At r.t. two ring proton resonances are observed and these split upon cooling to give four resonances, consistent with the frozen out C_2 structure. In the case of **4**, the r.t. ^{1}H-NMR spectrum exhibits five resonances (three resonances were shown by integration to result from the accidental overlap of two hydrogen resonances) for ring protons, while ten separate ring resonances were observed in the ^{13}C-NMR spectrum. This is consistent with the C_1 symmetry established by the molecular structure. Apparently the phosphine ligand serves to lock the molecule into the twisted structure as found for **4**, increasing the barrier to twisting. The NMR and IR spectra of compound **5** and **6** were similar to those of **4**, thus all of the mono-phosphine compounds in the series are assumed to have similar structures.

Photolysis of **1**, **2** and **3** in the presence of excess triphenylphosphine in degassed benzene afforded good yields of dark purple colored products. Three broad carbonyl bands were observed for each of these compounds. The r.t. ^{1}H-NMR spectra of **7** and **8** show broad envelopes of resonances associated with the triphenylphosphine ligands, a singlet for the methylene group linking the cyclopentadienyl rings, and four cy-

Table 1
Crystallographic data for $(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)Mo_2(CO)_5(PPh_3)$, **4** and $(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)Mo_2(CO)_4(PMe_3)_2$, **11**

	4	**11**
Formula	$C_{34}H_{25}Mo_2O_5P$	$C_{21}H_{28}Mo_2O_4P_2$
Formula weight	736.39	598.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Crystal data		
a (Å)	22.871(8)	9.843(5)
b (Å)	16.415(6)	15.343(7)
c (Å)	15.957(9)	31.514(6)
β (°)	94.29(3)	97.28(3)
V (Å^3)	5974(4)	4720(4)
Z	8	8
Crystal color, habit	Red block	Red block
D_{calc} (g cm^{-3})	1.638	1.683
μ(Mo–K$_\alpha$) (cm^{-1})	9.35	12.22
T (K)	233	244
Diffractometer	Siemens P4	Siemens P4
Radiation	Mo–K$_\alpha$ (λ = 0.71073 Å)	Mo–K$_\alpha$ (λ = 0.71073 Å)
2θ scan range (°)	4–42	4–50
Reflections collected	7911	10692
Independent reflections	6404	8321
$R(F)$ (%)[a]	8.87	4.38
$R(wF^2)$ (%)[a]	17.98	9.23
$\Delta\rho$ (e Å^{-3})	0.81	0.95
N_o/N_v	9.8	15.9
GOF	1.49	1.03

[a] Quantity minimized $= R(wF^2) - \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{\frac{1}{2}}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2
Selected bond lengths of **4** in angstroms

Atoms	Bond length (Å)	
	Molecule A	Molecule B
Mo(1)–Mo(2)	3.173(2)	3.190(4)
Mo(1)–C(12)	1.93(2)	1.93(3)
Mo(1)–C(13)	2.00(2)	2.02(4)
Mo(1)–C(14)	1.92(2)	1.94(4)
Mo(2)–C(15)	1.99(2)	2.04(3)
Mo(2)–C(16)	1.96(2)	1.87(3)
C(12)–O(12)	1.17(2)	1.15(3)
C(13)–O(13)	1.16(2)	1.14(4)
C(14)–O(14)	1.23(2)	1.18(4)
C(16)–O(16)	1.14(2)	1.29(4)
C(15)–O(15)	1.12(2)	1.09(3)
Mo(2)–P(1)	2.477(4)	2.462(8)

Table 3
Selected bond angles of **4** in degrees

Atoms	Angle (°)	
	Molecule A	Molecule B
C(7)–C(6)–C(5)	112.1	115.0(2)
C(12)–Mo(2)–C(13)	76.1	96.1(13)
C(12)–Mo(1)–C(14)	81.6	80.0(13)
C(16)–Mo(2)–C(15)	105.1	104.0(13)
C(15)–Mo(2)–P(1)	82.0	79.7(9)
C(16)–Mo(2)–P(1)	77.0	77.7(8)

clopentadienyl ring protons resonances. The spectrum of **9** differs only in that a singlet resonance is observed for the two methyl groups on the CMe_2 linkage. The spectra indicate that these molecules have C_2 symmetry in solution. ^{13}C-NMR spectra are also consistent with a C_2 symmetry for these molecules. The ^{13}C spectra of **7** and **8** show two sets of phosphorus coupled carbonyl resonances, five cyclopentadienyl ring resonances (including the *ipso*) and a resonance for the methylene carbon. The triphenylphosphine phenyl resonances were similar to those observed for the mono-substituted derivatives indicating some degree of hindered rotation about the M–triphenylphosphine bond. The ^{13}C spectrum of **9** substitutes a methyl resonance and quaternary carbon resonance for that of the methylene group, but is otherwise identical. ^{13}P-NMR spectra of all three compounds show a single phosphorus resonance.

X-ray quality crystals could not be obtained for these compounds, but it is reasonable to assume that the phosphine ligands are located *trans* to the M–M bonds as found for **6**.

As noted above, only a small quantity of mono-substituted trimethylphosphine, **10**, was isolated and this material was characterized by comparison with the IR spectra of **4**, **5**, and **6**.

Upon photolysis of $[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4]Mo_2(CO)_6$ in the presence of an excess of the trimethylphosphine ligand and subsequent chromatographic work-up, a dark purple product, **11**, was recovered. The IR spectra of **11** contains three terminal carbonyl stretching bands that are, almost, identical in position to those of $Mo_2Fv(CO)_4(PMe_3)_2$ reported by Vollhardt and coworkers [7]. The r.t. ^{1}H- and ^{13}C-NMR spectra of **11** are similar to those of **7** with the substitution of trimethylphosphine resonances for those of triphenylphosphine.

X-ray quality crystals of **11** were grown by vapor diffusion of petroleum ether into a saturated solution of **11** in dichloromethane in the cold. The structure was solved in the $P2_1/c$ space group and both of the independent, but chemically equivalent molecules in the asymmetric unit were well resolved. The ORTEP diagram of **11** is presented in Fig. 2. Tables 4 and 5 present selected bond lengths and angles, respectively. Comparison of the Mo–Mo bond length of **11** with that of the parent compound indicates that considerable metal–metal bond shortening has resulted from the substitution of two carbonyl ligands by two trimethylphosphine ligands. This may be attributed to

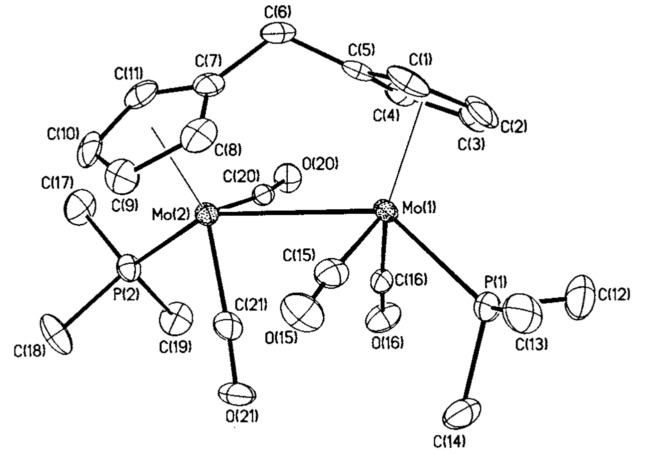


Fig. 2. Molecular structure of (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_4(PMe_3)_2$.

the strong σ-donating and weak π-accepting character of trimethylphosphine relative to carbon monoxide. The same effect on Mo–Mo bond length was observed for (μ-η^5,η^5-C_5H_4–C_5H_4)$Mo_2(CO)_4(PMe_3)_2$ (see Table 6 for a comparison of Mo–Mo bond lengths).

3. Conclusions

Photolysis of the ring-linked compounds (μ-η^5,η^5-C_5H_4–CR_2–C_5H_4)$M_2(CO)_6$, where M = Mo or W, and R = H or Me, with either triphenylphosphine or trimethylphosphine gives good yields of mono and disubstituted products. No evidence was found for disproportionation products such as those exclusively isolated when the analogous non-ring-linked compounds are photolyzed with triphenylphosphine. Since it is not reasonable that the ring-linkages should significantly alter the accessible electronic states of the M–M bonds, it appears that the role of the linkage may be to suppress the radical and disproportionation pathways by facilitating rapid recombination of any radicals or ionic species that might be formed. In essence, the linkage creates an artificial cage from which the metal fragments cannot escape. We are continuing to pursue an understanding of the mechanism of the disproportion reaction of the non-ring coupled Group VI compounds.

Table 4
Selected bond lengths for **11** in angstroms

Atoms	Bond lengths (Å)	
	Molecule A	Molecule B
Mo(1)–Mo(2)	3.1341(12)	3.1200(13)
Mo(1)–C(15)	1.951(7)	1.959(6)
Mo(1)–C(16)	1.942(6)	1.934(7)
Mo(1)–P(1)	2.405(2)	2.409(2)
Mo(2)–C(20)	1.919(7)	1.962(6)
Mo(2)–C(21)	1.96137(7)	1.937(7)
Mo(2)–P(2)	2.410(2)	2.402(2)
C(15)–O(15)	1.177(7)	1.156(7)
C(16)–O(16)	1.166(7)	1.171(7)
C(20)–O(20)	1.183(7)	1.163(7)
C(21)–O(21)	1.157(7)	1.165(7)

Table 5
Selected bond angles for **11** in degrees

Atoms	Angles (°)	
	Molecule A	Molecule B
C(7)–C(6)–C(5)	115.6(5)	116.2(6)
C(16)–Mo(1)–C(15)	102.7(2)	102.4(2)
C(15)–Mo(1)–P(1)	76.3(2)	78.4(2)
C(16)–Mo(1)–P(1)	80.3(2)	76.5(2)
C(20)–Mo(2)–P(2)	79.6	78.0(2)
C(21)–Mo(2)–P(2)	77.9	76.8(2)
C(20)–Mo(2)–C(21)	99.4(2)	102.0(2)

4. Experimental

All synthesis were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All purification chromatography was performed using reagent grade solvents, neutral alumina provided by CAMAG or silica gel (Fisher Scientific). Medium pressure chromatography was carried out using an Altex medium pressure column packed with 40 micron silica gel. All preparative solvents were dried and distilled under nitrogen.

^1H-, ^{13}C- and ^{13}P-NMR spectra were recorded on an Bruker NR-300 spectrometer (UI) or a QE-300 spectrometer (USNA). Chemical shifts were recorded in ppm relative to tetramethylsilane using appropriate solvent resonances as internal standards. IR spectra were obtained using a Bio-Rad Qualimatic FTIR spectrometer. HPLC analyses were conducted using a Gow-Mac HPLC with a 254 nm fixed wavelength detector. The stationary phase for HPLC was a Whatman Parasil PXS 10/25 silica gel column and the solvent system was 70:30 mixture of petroleum ether and THF. Elemental

Table 6
Comparisons of M–M bond lengths (Å) among related compounds

Compound	Mo–Mo bond length
(μ-η^5,η^5-C_5H_4–C_5H_4)$Mo_2(CO)_6$	3.371 [7]
(μ-η^5,η^5-C_5H_4–C_5H_4)$Mo_2(CO)_4(Pme_3)_2$	3.220 [8]
(μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_6$	3.140 [9]
(μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_4(PMe_3)_2$	3.1341

analysis were performed by Desert Analysis of Tucson, Arizona. Dr Gary Knerr conducted fast atom bombardment mass spectrometry on a VG 7070-HS GC/MS.

1, **2**, and **3** were prepared by the procedures of Bitterwolf ([4]b) and Feirro ([4]a).

4.1. General procedures for photochemical synthesis

Group VI bimetallic compounds and an appropriate phosphine were charged into a 400 ml Ace quartz irradiation vessel and the apparatus was flushed with dinitrogen. Air-free, dry benzene was added and the solution was stirred while nitrogen was bubbled through via a syringe. A medium pressure mercury lamp was used for broad band irradiation of the reaction mixture. During photolysis, the color of the solution changed from dark red to dark purple. The photolysis was stopped when IR spectra showed the absence of starting material. The reaction mixture was concentrated with a rotary evaporator and the resulting solution was placed on a silica gel column and chromatographed with petroleum ether or heptane as an eluant to remove unreacted phosphine ligand. The material remaining on the column was stripped from the column by benzene. After removal of the benzene solvent, the resulting solid was taken up in a 60:40 mixture of benzene and heptane (or 20:80 for compound **11**) and chromatographed using a medium pressure column eluting with the same mixture. In all cases, three bands were eluted from the column which were shown to be the mono-substituted derivative, the di-substituted derivative, and unreacted starting material, respectively. The yields of products are cited relative to starting material.

4.2. (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_5(PPh_3)$, 4

Compound **1**, (0.52g, 1.0 mmol) and triphenylphosphine (0.26g, 1.0 mmol) were placed in the quartz irradiation vessel. The reaction mixture was photolyzed for 110 min and the reaction mixture worked-up according to the general procedure described above (Section 4.1). Result: red–purple crystals, m.p. 223–226°C, yield 28%. IR (CH_2Cl_2): 1979, 1910, 1882 and 1830 cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.35 (br, 15H, triphenylphosphine), 5.5 (m, 2H, Cp), 5.1 (br, 2H, Cp), 4.57 (s, 1H, Cp), 4.17 (m, 2H, Cp), 3.95(s, 1H, Cp), 3.33 and 3.73 (AB quartet, $J_{A-B} = 14.5$ Hz, 2H, CH_2) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 230 (d, $J_{P-C} = 16.6$ Hz, Mo–CO), 223.8 (d, $J_{P-C} = 17.8$ Hz, Mo–CO), 223, 218.6 and 214.4 (Mo–CO), 133 (broad d, *o*-Ph, about 2:1), 130 (s, *p*-Ph), 128 (d, $J_{C-P} = 7$ Hz, *m*-Ph), 116 (*ipso*-Cp), 105 (*ipso*-Cp), 98, 94, 89, 88, 87, 85, 84 and 83 (Cp), 27 (CH_2) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 74.5 (Mo–PPh_3) ppm. Anal. Calc. $C_{34}H_{25}O_5Mo_2P_2$: C, 55.45; H, 3.43; P, 4.21%. Found: C, 55.26; H, 3.28; P, 4.02%.

4.3. (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$W_2(CO)_5(PPh_3)$, 5

Compound **2** and triphenylphosphine were irradiated for 30 min and the procedure described in Section 4.1 was followed. Result: red–purple crystals, m.p. 245–250°C, yield 25%. IR (CH_2Cl_2): 1976, 1902, 1876 and 1820 cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.39 (br, 15H, triphenylphosphine), 5.65 (m, 2H, Cp), 5.3 (m, 2H, Cp), 5.1 (s, 1H, Cp), 4.18 (m, 2H, Cp), 4.05(s, 1H, Cp), 4.44 and 3.33 (AB quartet, $J_{A-B} = 14.0$ Hz, 2H, CH_2) ppm. ^{13}C-NMR: (δ, $CDCl_3$), 230 (d, $J_{C-P} = 16.7$ Hz, W–CO), 224 (d, $J_{C-P} = 17.85$ Hz, W–CO), 223, 218 and 214.4 (W–CO), 135 (broad d, $J_{P-C} = 60$ Hz, *ipso*-Ph) 133 (broad d about 2:1, *o*-Ph), 130 (s, *p*-Ph), 128 (d, $J_{P-C} = 9$ Hz, *m*-Ph), 116 (*ipso*-Cp), 105 (*ipso*-Cp), 98, 94, 89, 88, 87, 85, 84 and 83 (Cp), 27 (CH_2) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 44.5 (W–PPh_3) ppm. Anal. Calc. $C_{34}H_{25}O_5W_2P$: C, 44.77; H, 2.77%. Found: C, 44.42; H, 2.47%.

4.4. (μ-η^5,η^5-C_5H_4–CMe_2–C_5H_4)$Mo_2(CO)_5(PPh_3)$, 6

See procedure (Section 4.1). Result: red–purple crystals, m.p. 234–236°C, yield 20%. IR (CH_2Cl_2): 1978, 1908, 1883 and 1828 cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.35 (br, 15H, triphenylphosphine), 5.55 (m, 2H, Cp), 5.1 (br, 2H, Cp), 4.2 (br, 2H, Cp), 3.8 (s, 2H, Cp), 1.5 (s, 3H, CH_3), 1.18 (s, 3H, CH_3) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 133 (d, $J_{C-P} = 10$ Hz, *o*-Ph), 130 (s, *p*-Ph), 128 (d, $J_{C-P} = 7$ Hz, *m*-Ph), 119 (s, *ipso*-Cp), 98, 95.1, 94, 93(br), 89, 87 (d, $J_{C-P} = 7.5$ Hz), 86 (d, $J_{C-P} = 10$ Hz), 85 and 83.5 (br, Cp), 36 (C, bridging CMe_2), 30 (s, CH_3), 28 (s, CH_3) ppm. Metal carbonyl resonances were not resolved. ^{31}P-NMR: (δ, $CDCl_3$) 74.9 (Mo–PPh_3) ppm. Anal. Calc. $C_{36}H_{29}O_5Mo_2P_2$: C, 56.56; H, 3.82%. Found: C, 55.43; H, 3.97%.

*4.5. (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_4(PPh_3)_2$, **7***

See procedure (Section 4.1). Result: red–purple crystals, m.p. 323–326°C, yield 35%. IR (CH_2Cl_2): 1918(m), 1832 and 1800(s) cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.35 (br, 30H, triphenylphosphine), 5.62 (m, 2H, Cp), 4.55 (br, 2H, Cp), 4.28 (m, 4H, Cp), 3.38 (s, 2H, CH_2) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 241 (d, $J_{C-P} = 10$ Hz, CO, Mo–CO), 234 (d, $J_{C-P} = 10$ Hz, CO, Mo–CO), 137 (broad, *ipso*-Ph), 133 (broad d, *o*-Ph), 129 (s, *p*-Ph), 128 (d, *m*-Ph), 110 (*ipso*-Cp), 97.5, 89, 88 and 86 (s, Cp), 28 (s, CH_2) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 79.25 (Mo–PPh_3) ppm. Anal. Calc. $C_{51}H_{40}O_4Mo_2P_2$: C, 63.10; H, 4.16; P, 6.39%. Found: C, 63.02; H, 4.60; P, 4.29%

4.6. (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$W_2(CO)_4(PPh_3)_2$, 8

See procedure (Section 4.1). Result: red–purple crystals, m.p. 263–270°C, yield 30%. IR (CH_2Cl_2): 1911(m), 1824 and 1792(s) cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.38 (br, 30H, triphenylphosphine), 5.65 (s, 2H, Cp), 4.60 (s, 2H, Cp), 4.36 (s, 2H, Cp), 4.21 (d, 2H, Cp), 3.71 (s, 2H, CH_2) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 229 (d, $J_{C-P} = 10$ Hz, CO, W–CO), 225 (d, $J_{C-P} = 10$ Hz, CO, W–CO),137 (broad, *ipso*-Ph), 133 (broad s, *o*-Ph), 129 (s, *p*-Ph), 128 (d, *m*-Ph), 110 (*ipso*-Cp), 96, 87, 86.8 and 86 (Cp), 27.8 (CH_2) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 42 (W–PPh_3) ppm. Anal. Calc. $C_{51}H_{40}O_4W_2P_2$: C, 53.45; H, 3.53; P, 5.58%. Found: C, 53.95; H, 4.26; P, 5.12%

4.7. (μ-η^5,η^5-C_5H_4–CMe_2–C_5H_4)$Mo_2(CO)_4(PPh_3)_2$, 9

See procedure (Section 4.1). Result: red–purple crystals, m.p. 323–326°C. IR (CH_2Cl_2): 1917(m), 1832 and 1798(s) cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 7.37 (br, 30H, triphenylphosphine), 5.71 (s, 2H, Cp), 4.50 (s, 2H, Cp), 4.25 (s, 4H, Cp), 1.36 (s, 6H, CH_3) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 241 (d, $J_{C-P} = 24.3$ Hz, CO, Mo–CO), 234 (d, $J_{C-P} = 24.3$ Hz, CO, Mo–CO), 133 (d, $J_{C-P} = 10$ Hz, *o*-Ph), 129 (s, *p*-Ph), 128 (d, $J_{C-P} = 7$ Hz, *m*-Ph), 95.3 (s, *ipso*-Cp), 88.2, 87.7 and 84.3 (Cp), 31 (CH_3) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 79.8 (Mo–PPh_3) ppm. Anal. Calc. $C_{53}H_{44}O_4Mo_2P_2$: C, 63.73; H, 4.45; P, 6.2%. Found: C, 63.15; H, 5.08; P, 5.98%.

4.8. (μ-η^5,η^5-C_5H_4–CH_2–C_5H_4)$Mo_2(CO)_4(PMe_3)_2$, 11

See procedure (Section 4.1). Result: red–purple crystals, m.p. 250–252°C, yield 35%. IR (CH_2Cl_2): 1907(m), 1817 and 1784(s) cm^{-1}. ^{1}H-NMR: (δ, $CDCl_3$) 5.36 (m, 2H, Cp), 5.05 (m, 2H, Cp), 4.58 (m, 4H, Cp), 3.38 (s, 2H, CH_2), 1.55(d, 18H, PMe_3) ppm. ^{13}C-NMR: (δ, $CDCl_3$) 240 (d, $J_{C-P} = 25.3$ Hz, CO, Mo–CO), 233 (d, $J_{C-P} = 25.3$ Hz, CO, Mo–CO), 109.5 (*ipso*-Cp), 97, 87, 85 and 84 (Cp), 28 (CH_2), 21 (d, $J_{C-P} = 29.9$ Hz, PMe_3) ppm. ^{31}P-NMR: (δ, $CDCl_3$) 32.6 (Mo–PMe_3) ppm. MS: 600 (M^+, 13%), 544 ($M^+ - 2CO$, 32%), 149 (100%). Anal. Calc. $C_{21}H_{28}O_4Mo_2P_2$: C, 42.16; H, 4.73; P, 10.35%. Found: C, 41.93; H, 4.49; P, 10.66%.

5. Crystallographic structure determinations

Crystallographic data are collected in Table 1. Crystals of both **4** and **11** were obtained as red blocks and found to possess monoclinic symmetry. The space group for both was unambiguously determined from systematic absences in the data. Only small variations in azimuthal scan intensities were seen ($<10\%$) and corrections for absorption were ignored. The structures were solved by direct methods. In both cases, the asymmetric unit contains two independent, but chemically similar, molecules. In **4**, one of the two independent molecules is disordered in two positions in an approximately equal occupation; we were able to resolve all atoms of the two sites except for one of the bridging CH_2 groups. In **4**, cyclopentadienyl and phenyl rings were rigidly constrained and carbon atoms of the distorted molecule were isotropically refined. Otherwise, all non-hydrogen atoms in both structures were anisotropically refined. Hydrogen atoms were treated as idealized contributions except for those in the disordered molecule of **4** where they were ignored. All computations used SHELXTL software (version 5.03, G. Sheldrick, Siemens XRD, Madison, WI).

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