

Use of electron-rich η^6 -arylphosphine complexes of molybdenum(0) as ligands in group 6 metal carbonyl complexes

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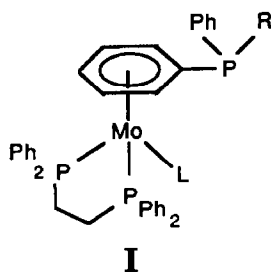
Abstract

The reactions of $M(\text{CO})_6$ $M = \text{Cr}, \text{Mo}, \text{W}$ and $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{L})$, $\text{dppe} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, $\text{L} = \text{CO}, (\text{L}_1\text{CO})$, $\text{L} = \text{PMe}_3, (\text{L}_1\text{P})$ in benzene under photolysis lead to the following dimeric species $M(\text{CO})_5(\text{L}_2\text{CO})$ and $M(\text{CO})_5(\text{L}_1\text{P})$. Here the free phosphorus of the donor complex coordinates to $M(\text{CO})_5$, without metal–metal bond formation; a Cotton–Kraihanzel force constant analysis indicates that the ordering of e-donor ability is $\text{L}_2\text{P} > \text{L}_1\text{CO} > \text{PPh}_3$. Similarly treating the new complex $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{P}(\text{OMe})_3)$, (L_2P) with $\text{Mo}(\text{CO})_6$ under photolysis gives the dimer $\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$. Heating individual solutions of complexes L_1CO , L_1P , $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{CO})$, (L_2CO) and L_2P in the presence of stoichiometric equivalents of $M(\text{CO})_4(\text{pip})_2$, $M = \text{Mo}$ or W , $\text{pip} = \text{piperidine}$ yields $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$, $\text{W}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$, $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{P})$, $\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$ and $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$. The further thermal reactions of $\text{W}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$, $\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$ and $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$ with phosphines or phosphite result in the substitution of the piperidine ligand and formation of $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$, $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$, $\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$ and $\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$. Complexes are characterised by IR, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The cone angle for L_1CO is determined to be $155 \pm 5^\circ$ by comparing the *cis/trans* equilibrium ratio for its complex $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ to literature values for other $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L})$ complexes. The bimetallics containing L_1CO or L_2CO show an irreversible one electron oxidation wave associated with the metallophosphine ligand; those containing L_1P or L_2P show one reversible oxidation at a more positive potential to that of the free metallophosphine ligands and a second irreversible oxidation.

Introduction

After developing simple, direct syntheses of complexes of molybdenum(0) containing $\eta^6\text{-C}_6\text{H}_5\text{PMePh}$ [1,2,3] or $\eta^6\text{-C}_6\text{H}_5\text{PPh}_2$ [4] ligands (Structure I), we were

interested in exploring the use of the complexes themselves as phosphorus donor ligands.



L	R	Metallophosphine ligand
CO	Ph	L ₁ CO
PMe ₃	Ph	L ₁ P
CO	Me	L ₂ CO
P(OMe) ₃	Me	L ₂ P

These metallophosphine ligands are expected to be more reducing and more basic than previous ligand complexes such as Cr(η^6 -PhPPh₂)(CO)₃ [5,6], Cr(η^6 -PhAsPh₂)(CO)₃ [7] or Mo(η^6 -tolPtol₂)(CO)₃ [8] which have several electron-withdrawing carbonyl ligands. The structure of our donor complexes allows some "tuning" of steric properties with the fragment Mo(η^6 -PhPPh₂)(dppe), L₁, being larger than Mo(η^6 -PhPMePh)(dppe), L₂, and of the electronic properties with the phosphine substituted complexes L₁P, P = PMe₃, and L₂P, P = P(OMe)₃, being more basic than carbonyl substituted complexes L₁CO and L₂CO.

Initial work demonstrated that such donor complexes I form stable bimetallic complexes with rhodium(I) [3] and transient complexes with tungsten(IV) which undergo internal redox and ligand transfer reactions to give Mo^{II}≡W^{II} quadruply-bonded dimers MoWCl₄(PR₃)₄ [9]. In this paper complexes of ligands I with group 6 metal carbonyls are synthesized and IR spectroscopy and electrochemistry are used to explore their electron-donor abilities. An objective of the work is to estimate the effective cone angles of these metallophosphines and to study the influence of the size of the ligands on substitution chemistry at the neighbouring group 6 metal centre.

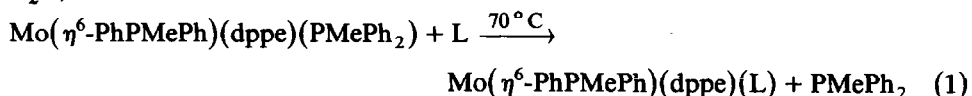
Other studies of bimetallic complexes containing, as the bridging ligand, a polyene functionalized with a tertiary phosphine or phosphido group, and also containing a group 6 carbonyl fragment are (η^5 -C₅H₅)Ti(η^7 -C₇H₆PPh₂)Mo(CO)₅ [10], Cl₂M(η^5 -C₅H₄CH₂CH₂PPh₂)₂Mo(CO)₄, M = Ti, Zr [11], Cl₂Zr(η^5 -C₅H₄PPh₂)₂Mo(CO)₄ [12], [Fe(η^5 -C₅H₄Si(CH₃)₂PPh₂)₂]₂[Mo(CO)₄]₂ [13] and Fe(η^5 -C₅H₄P(CMe₃)₂)₂Mo(CO)₄ [14]. None of these dimers contain metal-metal bonds.

Results and discussion

Synthesis

Four representative metallophosphine ligands were chosen in a study of their coordination to group 6 metal carbonyls. The metallophosphine ligand complexes

$\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{PMe}_3)$ L_1P , $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{CO})$ L_1CO , are readily prepared by substitution of the labile $\sigma\text{-PPh}_3$ group in $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{PPh}_3)$ at room temperature [4]. The $\sigma\text{-PMePh}_2$ group in $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$, less crowded than the PPh_3 analogue, only becomes labile at 70°C , and it is at this temperature that this group is substituted by CO to give $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{CO})$, L_2CO , [3] or by $\text{P}(\text{OMe})_3$ to give $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{P}(\text{OMe})_3)$, L_2P ,



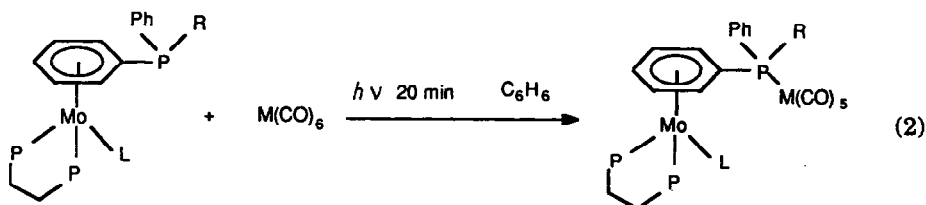
($\text{L} = \text{CO}, \text{P}(\text{OMe})_3$)

eq. 1. These metallophosphine ligands are orange, oxygen sensitive solids which are soluble in THF and benzene.

Three approaches for the synthesis of the group 6 dimeric complexes have been used (reactions 2–4). The photochemical route entails the photolysis of the η^6 -arylphosphine complex in the presence of a group 6 hexacarbonyl. A period of 20 min of irradiation in our apparatus works for all three group 6 hexacarbonyls. This method gives good yields (> 80%) of red-brown powders which are stable to oxygen for short periods. Solutions of these compounds as well as those of the other dimers synthesized in this work with THF or benzene as the solvent are air sensitive.

It is interesting that in our photochemical reactions no other products are formed. This can be contrasted with the photochemical reaction between $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_3$ and $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3$ where at least three products are isolated [6]. These are $\text{Cr}(\mu\text{-}\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_2$, $[\text{Cr}(\mu\text{-}\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_2]_2$ and $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2$. The first two products are each formed from the dimerization of two $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_3$ molecules. Thus under the conditions of this experiment a $\sigma\text{-CO}$ on $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{CO})_3$ is made labile.

Our results also differ from those of Kolodziej and Lees [15]. They report that a photochemical route similar to eq. 2 resulted in the formation of secondary products of which a major component was *cis*- $\text{M}(\text{CO})_4(\text{L})_2$, $\text{M} = \text{Cr}$ or Mo , $\text{L} = \text{pyridine}$ or a substituted pyridine, whereas prior formation of the solventpentacarbonyl followed by reaction with the ligand proved more satisfactory. In our reactions it is likely that



L_1CO : $\text{R} = \text{Ph}, \text{L} = \text{CO}$

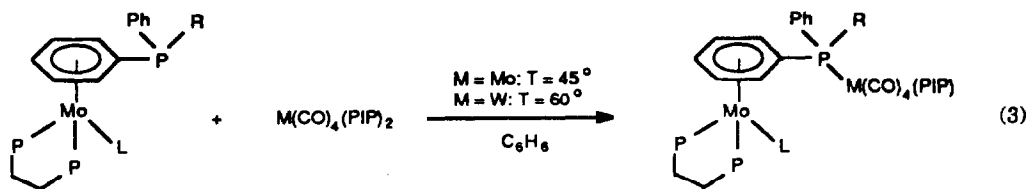
L_1P : $\text{R} = \text{Ph}, \text{L} = \text{PMe}_3$

L_2P : $\text{R} = \text{Me}, \text{L} = \text{P}(\text{OMe})_3$

$\text{M}(\text{CO})_5(\text{L}_1\text{CO})$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$

$\text{M}(\text{CO})_5(\text{L}_1\text{P})$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$

$\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$



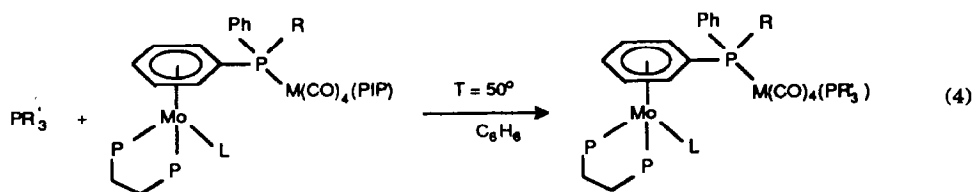
L₁CO: R = Ph, L = CO
L₁P: R = Ph, L = PMe₃
L₂CO: R = Me, L = CO
L₂P: R = Me, L = P(OMe)₃

cis-M(CO)₄(pip)(L₁CO), M = Mo, W
cis-Mo(CO)₄(pip)(L₁P)
cis-W(CO)₄(pip)(L₂CO)
cis-Mo(CO)₄(pip)(L₂P)

the steric bulk of the metallophosphine ligands prevent the formation of *cis*-Mo(CO)₄(metallophosphine)₂ complexes. The problem with the solventopentacarbonyl route in our hands was the formation of small amounts of M(CO)₄(THF)₂ during the photolysis of M(CO)₆. This resulted in inseparable mixtures consisting of the expected complex M(CO)₅(L) and the undesired by-product M(CO)₄(L)(THF) when dimer synthesis was attempted. The reactions between [M(CO)₅Cl][Et₄N], M = Cr or Mo, and metallophosphine ligands also did not yield pure monosubstituted products in contrast to the results in the literature [16,17].

A second convenient route to dimer formation consisted of thermal reactions between η⁶-arylphosphine complexes and M(CO)₄(pip)₂, M = Mo and W, pip = piperidine [18,19,20], eq. 3. The tungsten complex is substituted at a higher temperature (60 °C) than the molybdenum complex (40 °C). Orange-red powders were obtained in about 60% yield. Spectroscopic studies (see below) demonstrated that one piperidine and one metallophosphine are *cis* to each other in the tetracarbonyl products.

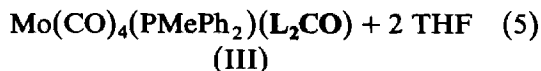
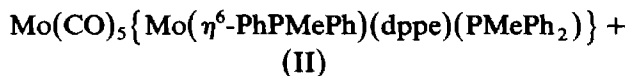
A third method is the substitution of the labile piperidine in the monopiperidine dimers of eq. 3 with small phosphine ligands (eq. 4) to give the red-orange products in about 60% yield. Here the stereochemistry of the products is *cis* when the phosphine is small (P(OMe)₃, PMe₃, Tolman's cone angle θ < 120 °). With a larger phosphine, PMe₂Ph (θ 122 °), a mixture of *cis* and *trans* isomers is obtained (see below).



W(CO)₄(pip)(L₁CO)
 W(CO)₄(pip)(L₂CO)
 Mo(CO)₄(pip)(L₂P)

cis and *trans*-W(CO)₄(PMe₂Ph)(L₁CO)
cis and *trans*-W(CO)₄(PMe₂Ph)(L₂CO)
cis-Mo(CO)₄(PR'₃)(L₂P), R' = OMe, Me

If dimer synthesis is attempted by use of the crowded complexes $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{PPh}_3)$ or $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$ as ligands in reaction 5 then inseparable mixtures result. An IR and ^{31}P NMR study of reaction 5 shows



that, apart from the expected reaction to give product II, an interesting ligand exchange reaction has taken place to give product III, $\text{Mo}(\text{CO})_4(\text{PMePh}_2)(\text{L}_2\text{CO})$. Even though the PMePh_2 ligand in $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$ is only substituted by CO at 70°C (eq. 1) to give (L_2CO) , in reaction 5 it is labilized at room temperature to give product III possibly as a result of the proximity of a coordinated $\text{M}(\text{CO})_5$ fragment.

IR spectra of these group 6 carbonyl dimers. Those complexes containing a pentacarbonyl fragment synthesized via the photochemical route, eq. 2, give rise to the characteristic A_1 stretch at $2060\text{--}2070 \text{ cm}^{-1}$ and overlapping A_1 and E vibrational modes between 1950 and 1930 cm^{-1} . For comparison the spectra of the complexes $\text{M}(\text{CO})_5(\text{PPh}_3)$, $\text{M} = \text{Cr}, \text{Mo}$ and W , were run under identical conditions.

The Cotton-Kraihanzel force constants [21], k_1 , of $\text{M}(\text{CO})_5(\text{PPh}_3)$, $\text{M} = \text{Cr}, \text{Mo}$ and W , are greater than those of the corresponding complexes $\text{M}(\text{CO})_5(\text{L}_1\text{CO})$, $\text{M} = \text{Cr}, \text{Mo}$ and W , by 0.09 , 0.02 and 0.04 mdyne/\AA respectively, Table 2. This suggests that the phosphorus donor of the L_1CO fragment is more electron-donating than PPh_3 . A similar conclusion can be made between $\text{Cr}(\eta^6\text{-PhPPh}_2)(\text{CO})_3$ and PPh_3 if one compares the corresponding IR vibrations for $\text{M}(\text{CO})_5(\text{L})$, $\text{M} = \text{group 6 metal}$, and L is either $\text{Cr}(\eta^6\text{-PhPPh}_2)(\text{CO})_3$ or PPh_3 [14]. Unfortunately the IR data for these complexes were obtained in CH_2Cl_2 and this prevents a direct comparison between the complex $\text{Cr}(\eta^6\text{-PhPPh}_2)(\text{CO})_3$ and our closely related metallophosphine ligand L_1CO .

The IR vibration for the CO ligand on L_1CO and L_2CO comes at 1840 and 1837 cm^{-1} respectively. There is no significant shift in this $\nu(\text{CO})$ vibration for L_1CO upon dimer formation in complexes $\text{M}(\text{CO})_5(\text{L}_1\text{CO})$, $\text{M} = \text{Cr}, \text{Mo}$ and W , see Table 2.

Judging from the k_1 values for the complexes $\text{M}(\text{CO})_5(\text{L}_1\text{P})$, L_1P is the most electron-donating in the series $\text{L}_1\text{P} > \text{L}_1\text{CO} > \text{PPh}_3$. This is in keeping with the greater electron-donating inductive effect of the PMe_3 group in L_1P vs. the CO group in L_1CO .

The tetracarbonyl complexes (Table 3) give spectra in keeping with a *cis* geometry; mixtures of *cis* and *trans* isomers are more readily detected by ^{31}P NMR (below) than by IR. Force constants cannot be determined unambiguously from the data in Table 3. However the characteristic A_1 vibration for $\text{Mo}(\text{CO})_4(\text{pip})(\text{L})$, $\text{L} = \text{L}_1\text{CO}, \text{L}_1\text{P}, \text{L}_2\text{P}$, reflects the electronic properties of the metallophosphine ligand in that there is a decrease in energy for this vibration in keeping with the increasing electron-donating properties of the bridging phosphorus atom in the

Table 1

Analytical data for the group 6 dimeric carbonyl complexes

Complex	Analyses (Found (Calcd.)(%))		
	C	H	N
Cr(CO) ₅ (L ₁ CO)	62.05 (61.49)	4.41 (4.03)	
Mo(CO) ₅ (L ₁ CO)	57.61 ^a (58.84)	4.05 (3.85)	
W(CO) ₅ (L ₁ CO)·0.2 C ₆ H ₆ ^b	54.66 (54.70)	3.78 (3.60)	
Mo(CO) ₄ (pip)(L ₁ CO)	58.57 ^a (60.18)	4.92 (4.68)	1.23 (1.30)
W(CO) ₄ (pip)(L ₁ CO)·0.75 C ₆ H ₆ ^b	57.45 (57.39)	4.60 (4.49)	1.19 (1.14)
W(CO) ₄ (PMe ₂ Ph)(L ₁ CO) <i>cis,trans</i> mixture	55.88 (56.18)	4.35 (4.14)	
Cr(CO) ₅ (L ₁ P)	61.87 ^a (63.81)	4.98 (5.47)	
Mo(CO) ₅ (L ₁ P)·0.3 C ₆ H ₆ ^b	59.21 (59.17)	4.76 (4.60)	
W(CO) ₅ (L ₁ P)	54.26 (54.00)	4.21 (4.18)	
Mo(CO) ₄ (pip)(L ₁ P)	59.92 (59.74)	5.19 (5.28)	1.04 (1.24)
Mo(CO) ₅ (L ₂ P)	53.76 (53.53)	4.54 (4.40)	
Mo(CO) ₄ (pip)(L ₂ P)	55.55 (55.10)	5.02 (5.17)	1.16 (1.26)
Mo(CO) ₄ (P(OMe) ₃)(L ₂ P)	51.25 (51.15)	4.80 (4.82)	
Mo(CO) ₄ (PMe ₃)(L ₂ P)· 0.3 C ₆ H ₆ ^b	54.24 (54.18)	4.97 (5.08)	
W(CO) ₄ (pip)(L ₂ CO)	53.26 (53.33)	4.63 (4.38)	1.03 (1.27)
W(CO) ₄ (PMe ₂ Ph)(L ₂ CO) <i>cis,trans</i> mixture	53.08 ^a (54.00)	5.07 (4.18)	

^a Low analyses due to silicone stopcock grease (detected by NMR). ^b Benzene solvates.

order Mo(CO)₄(pip)(L₁CO) < Mo(CO)₄(pip)(L₁P) < Mo(CO)₄(pip)(L₂P). Similar correlations have been reported in previous studies looking at the A₁ vibration for phosphine substituted metal carbonyl complexes [22]. It is noted that the substitution of the piperidine ligand by the metallophosphine leads to an increase in the energy of this CO vibration on the order of 5 cm⁻¹.

Changes in the NMR spectra of the metallophosphines when they coordinate. The assignments of ¹H NMR resonances are listed in Table 4. A typical spectrum is shown in Fig. 1 for W(CO)₄(pip)(L₂CO). Analysis of the η⁶-arene proton resonances was made possible by selective decoupling experiments on Cr(CO)₅(L₁P) and W(CO)₄(pip)(L₂CO). The similarity in patterns in the spectra of the other complexes in their arene regions allowed the assignments of those hydrogens as labeled in Table 4.

For the dimeric complexes of L₁CO and L₁P only three peaks of intensity 2/2/1 are observed in the form of a pseudo triplet (*ortho*), distorted quartet (*meta*) and

Table 2

Carbonyl stretching frequencies and C.–K. force constants for the complexes $M(\text{CO})_5(\text{PPh}_3)$, $M = \text{Cr}$, Mo and W , and $M(\text{CO})_5(\text{L})$, $\text{L} = \text{L}_1\text{CO}$, L_1P and L_2P

Complex	IR Bands in THF (cm^{-1}) ^a			Cotton–Kraihanzel force constants ($\text{mdyne}/\text{Å}$)		
	A_1	A_1	E	k_1	k_2	k_i
$\text{Cr}(\text{CO})_5(\text{PPh}_3)$	2063m		1941vs	15.41	15.81	0.30
$\text{Mo}(\text{CO})_5(\text{PPh}_3)$	2073m		1948vs	15.52	15.93	0.30
$\text{W}(\text{CO})_5(\text{PPh}_3)$	2072m		1940vs	15.41	15.84	0.32
L_1CO						
$\text{Cr}(\text{CO})_5(\text{L}_1\text{CO})$	2061m		1935vs	15.32	15.73	0.30
$\text{Mo}(\text{CO})_5(\text{L}_1\text{CO})$	2071m	1889sh	1946vs	15.50	15.90	0.30
$\text{W}(\text{CO})_5(\text{L}_1\text{CO})$	2070m		1937vs	15.37	15.80	0.32
$\text{Cr}(\text{CO})_5(\text{L}_1\text{P})$	2059m	1920sh	1939vs	15.05	15.77	0.29
$\text{Mo}(\text{CO})_5(\text{L}_1\text{P})$	2069m	1921sh	1944vs	15.07	15.88	0.31
$\text{W}(\text{CO})_5(\text{L}_1\text{P})$	2068m		1935vs	15.33	15.76	0.32
$\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$	2068m	1928sh	1942vs	15.19	15.84	0.31

^a w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. ^b $\nu(\text{CO})$ of L_1CO .

broad multiplet (*para*), respectively. This can be compared to complexes of L_2CO and L_2P containing the chiral $\eta^6\text{-PhPMePh}$ ligand. In this case five peaks of equal intensity are observed of which two are pseudo triplets (*ortho*), two are distorted quartets (*meta*) and one is a broad multiplet (*para*) of similar shapes to those observed earlier, see Fig. 1. When *cis* and *trans* isomers are present, many arene peaks are observed.

The η^6 -arene resonances shift upon coordination to the metal carbonyl, but not in a consistent fashion. In the series of dimers derived from L_1CO , the *meta* and *para* hydrogens for complexes $M(\text{CO})_5(\text{L}_1\text{CO})$, $M = \text{group 6 metal}$, are shifted upfield with respect to those of the free ligand L_1CO whereas the *ortho* protons are shifted downfield. The complexes $M(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$, $M = \text{Mo}$ and W reveal upfield shifts for *meta* and *para* H and downfield shifts for the *ortho* H.

Table 3

Carbonyl stretching frequencies for the complexes $M(\text{CO})_4(\text{pip})(\text{L})$, $M = \text{Mo}$ and W and *cis/trans*- $M(\text{CO})_4(\text{PR}_3)(\text{L})$

Complex	Bands in THF (cm^{-1}) ^a		
	A_1	A_1 or B_1 ^b	B_2 ^b
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$	2013m	1921w,1891vs	1848s
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$	2008m	1921w,1822vs	1845s
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$ ^c	2013m	1967m,1890vs	1844m
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{P})$	2010m	1944w,1890vs	1846s
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$	2008m	1931w,1890vs	1848s
$\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$	2021m	1968w,1910vs	1887s
$\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$	2011m	1940s,1896vs	1874s
L_2CO			1837s
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$	2005m	1888sh,1875vs	1848s
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ ^c	2010m	1908s,1886vs	1827m

^a w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. ^b Assuming ideal C_{2v} symmetry.

^c *Cis* and *trans* isomers can not be differentiated.

Table 4

200 MHz ^1H NMR spectra of the complexes in C_6D_6 . The values in parentheses are $^2J(\text{H},\text{P})$ couplings (Hz). The notation used for the complexes is as follows: $\text{Mo}(\eta^6\text{-PhPR}_2)(\text{dppe})(\text{L})\text{M}(\text{CO})_4(\text{L}')$

Complex	Phosphine methyl or methoxy groups		$\eta^6\text{-Arene}^a$				
	$\delta(\eta^6\text{-PCH}_3)$	$\delta(\text{L})^b$	$\delta(\text{CH}_2\text{P})\text{-dppe}$	$\delta(\text{L}')$	<i>ortho</i>	<i>meta</i>	<i>para</i>
L_1CO			1.80–2.17		4.13	4.69	4.02
$\text{Cr}(\text{CO})_5(\text{L}_1\text{CO})$			1.84–2.21		4.13	4.69	
$\text{Mo}(\text{CO})_5(\text{L}_1\text{CO})$			1.64–2.27		4.64	3.96	3.60
$\text{W}(\text{CO})_5(\text{L}_1\text{CO})$			1.70–2.27		4.64	3.96	
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$			1.65–2.27		4.66	3.97	3.54
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$			1.70–2.23		4.66	3.97	
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})^c$ (<i>cis</i>)			1.82–2.28	1.31 (7)	4.58	3.91	3.50
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})^c$ (<i>trans</i>)			1.82–2.28	1.72 (8)	4.58	3.91	
L_1P		0.56 (6.2)	1.78–2.37		4.85	4.04	3.63
$\text{Cr}(\text{CO})_5(\text{L}_1\text{P})$		0.34 (6.5)	1.52–2.08		4.85	4.04	
$\text{Mo}(\text{CO})_5(\text{L}_1\text{P})$		0.48 (6.4)	1.49–2.09		4.84	4.00	3.63
$\text{W}(\text{CO})_5(\text{L}_1\text{P})$		0.47 (6.4)	1.41–2.05		4.84	4.00	
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{P})$		0.70 (6.7)	1.60–2.10		4.84	4.00	
L_2P	1.44 (4.1)	2.79 (10.2)	1.77–2.60		4.89	4.67	4.00
$\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$	1.88 (6.7)	2.73(10.3)	1.65–2.06		4.89	4.67	
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$	2.03 (5.7)	2.87 (9.6)	1.67–2.50		4.89	4.67	
$\text{Mo}(\text{CO})_4\text{P}(\text{OMe})_3(\text{L}_2\text{P})$	2.08 (6.1)	2.76 (10.3)	1.69–2.22	3.21 (11.5)	4.89	4.67	4.00
$\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$	2.00 (5.9)	2.83 (10.0)	1.74–2.27	0.84 (6.6)	4.89	4.67	
L_2CO	1.46 (4.0)		1.91–2.24		4.89	4.67	
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$	1.98 (6.5)		1.80–2.95		4.89	4.67	
$\text{W}(\text{CO})_4\text{PMe}_2\text{Ph}(\text{L}_2\text{CO})$ (<i>cis</i>) ^c	1.88(5.8)		1.60–2.40	1.35 (7.5)	4.89	4.67	4.00
$\text{W}(\text{CO})_4\text{PMe}_2\text{Ph}(\text{L}_2\text{CO})$ (<i>trans</i>) ^c	2.23 (8.0)		1.60–2.40	1.66 (7.3)	4.89	4.67	

^a The δ positions listed are those of the mid-point of the multiplet pattern found for these peaks. ^b L is the hydrogens in the methoxy group on the $\text{P}(\text{OMe})_3$ ligand in L_1P and L_2P . ^c For these molecules the assignment of the arene protons is not conclusive due to the presence of *cis*- and *trans*-isomers.

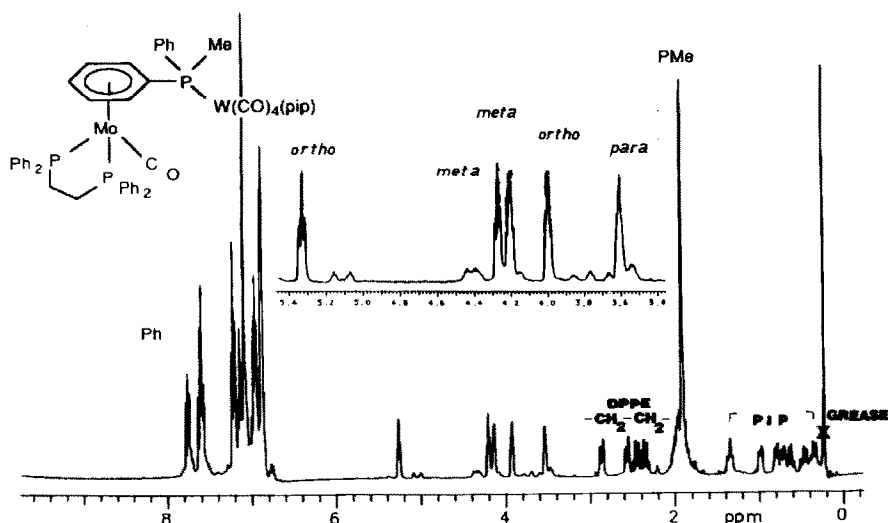


Fig. 1. The ^1H NMR spectrum at 400 MHz of *cis*- $\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$ in C_6D_6 . The η^6 -arene peaks in the region δ 3–6 (inset) have been assigned by decoupling studies. Small unassigned peaks may be due to *trans*- $\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$.

The methyl group on the “dangling” phosphorus atom in L_2P and L_2CO experiences a downfield shift upon coordination to the metal carbonyl fragment of about 0.40–0.60 ppm. Also the coupling $^2J(\text{H},\text{P})$ for this methyl group increases upon coordination. The presence of the two geometric isomers of $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$ can easily be verified in its ^1H NMR spectrum by the appearance of resonances due to the two methyl groups on the PMe_2Ph ligand in $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$ which can be *cis* and *trans* to L_1CO on the W atom. The ^1H NMR spectrum for $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ is more complex in that in the *cis* structure the methyl groups on the PMe_2Ph ligand are diastereotopic and give rise to a triplet pattern. In the *trans* structure of $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ only a doublet pattern is exhibited. The resonances for the *cis* and *trans* isomers of both $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L})$, $\text{L} = \text{L}_1\text{CO}$ or L_2CO , were differentiated on the basis of the intensities of their *cis* and *trans* peaks as the *cis* isomer is known to exist in a higher percentage.

The $^{31}\text{P}\{^1\text{H}\}$ NMR data are presented in Table 5. The ligands L_2CO and L_2P have the complicating feature that they each have a chiral centre at the “dangling” phosphorus on the η^6 -bonded ring [1]. Thus the dppe resonances for the former give an AB pattern whereas those for the latter form part of an ABX spin system.

The coordination of the “dangling” phosphorus atom onto a group 6 metal carbonyl fragment is readily apparent in the extreme downfield shift of the resonance of this phosphorus atom. The fact that only one resonance (singlet or doublet, excluding ^{183}W satellites) is observed for the bridging phosphorus atom in all of the dimers for $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$ and $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ also suggests that only one complex and isomer is formed. We believe this to be the *cis*-isomer (see below). This was also noted in the reaction with PPh_3 and $\text{W}(\text{CO})_4(\text{pip})_2$ where the *cis*-monosubstituted complex $\text{W}(\text{CO})_4(\text{pip})(\text{PPh}_3)$ formed first [18].

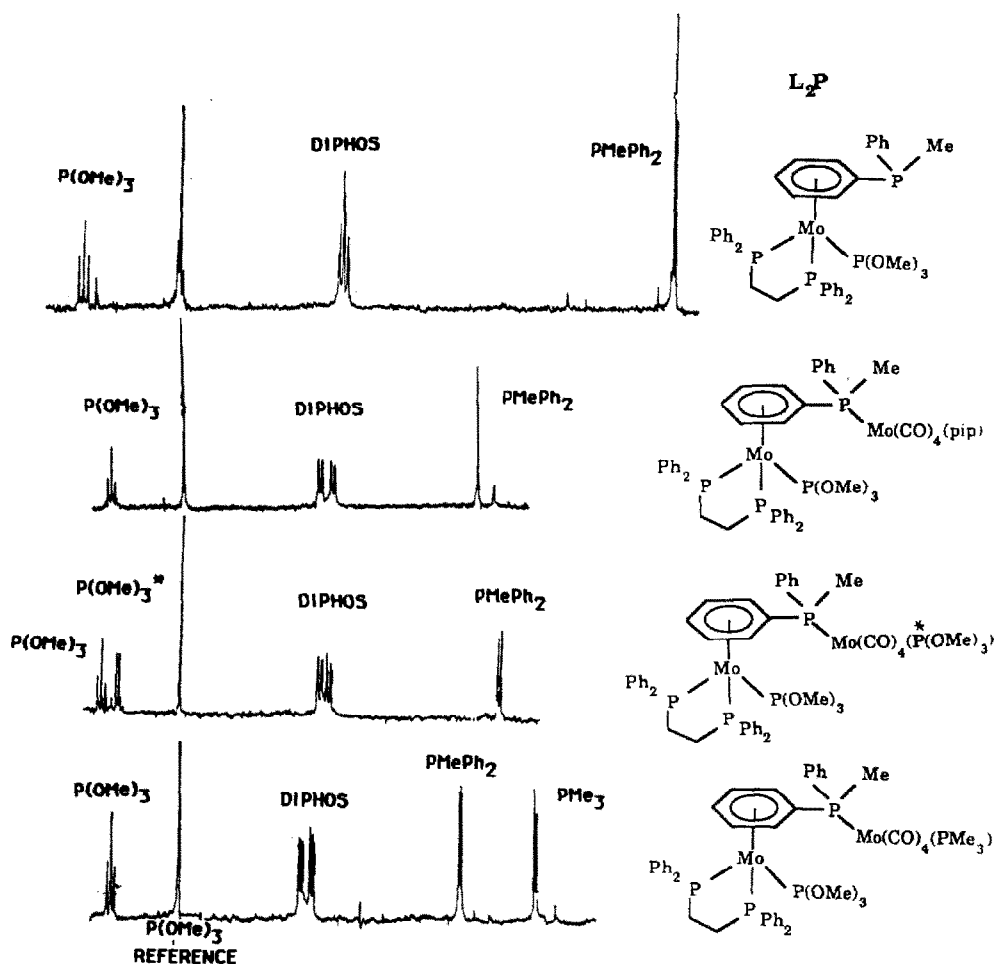


Fig. 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 81 MHz of complexes L_2P , $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$, $\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$ and $\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$ in C_6H_6 .

The chemical shift of the phosphorus atom on the phosphine or phosphite substituents on L_1CO , L_1P , L_2CO and L_2P do not change significantly when a metal carbonyl containing fragment is coordinated to the "dangling" phosphorus atom. However there is a marked difference in the positions of the two phosphorus resonances of the dppe ligand in the series of dimers $\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$, $\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$, $\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$ and $\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$ compared to L_2P (Fig. 2). The asymmetry of the magnetic field about the "dangling" phosphorus atom upon coordination is apparently accentuated in these cases.

The magnitude of the coupling constant $^2J(\text{P}_a, \text{L}')$, Table 5, for the phosphorus atoms bonded to the tetracarbonyl fragments in complexes of the form $\text{M}(\text{CO})_4(\text{P}_a)(\text{L}')$, P_a = metallophosphine, L' = phosphine or phosphite, suggests that only the *cis*-isomers are formed for complexes $\text{Mo}(\text{CO})_4(\text{L})(\text{L}_2\text{P})$, $\text{L} = \text{P}(\text{OMe})_3$ or $\text{L} = \text{PMe}_3$ [20,23]. The coupling for the *trans*-isomer is greater than twice that of the *cis*-isomers as is evident in complexes $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L})$, $\text{L} = \text{L}_1\text{CO}$ or L_2CO , see Table 5.

Table 5

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the complexes in C_6H_6 (δ in ppm referenced to H_3PO_4 , $^2J(\text{P},\text{P})$ in Hz). The notation used for some complexes is as follows: $\text{Mo}(\eta^6\text{-PhP}_a\text{R}_2)(\text{P}_b\text{P}_c)(\text{L})\text{M}(\text{CO})_4(\text{L}')$ and for all complexes $(\text{P}_b\text{P}_c) = \text{dppe}$

Complex	$\delta(\text{P}_a)^a$	$\delta(\text{L}')^a$	$^2J(\text{P}_a,\text{L}')$	$\delta(\text{L})$	$\delta(\text{P}_b,\text{P}_c)$	$^2J(\text{P}_b,\text{P}_c)$	$^2J(\text{P}_b,\text{c},\text{L})$
L_1CO	-5.1s				83.8s		
$\text{Cr}(\text{CO})_5(\text{L}_1\text{CO})$	55.9s				82.5s		
$\text{Mo}(\text{CO})_5(\text{L}_1\text{CO})$	39.3s				82.2s		
$\text{W}(\text{CO})_5(\text{L}_1\text{CO})$	22.4s				82.1s		
	(249)						
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$	43.3s				82.5s		
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$	34.3s				82.4s		
	(239)						
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$	22.8d	-25.3d	22		83.3s		
(<i>cis</i>)	(227)	(227)					
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$	30.1d	-20.1d	51		83.9s		
(<i>trans</i>)	(260)	(260)					
L_1P	-6.0s			-4.6t	82.7d		28
$\text{Cr}(\text{CO})_5(\text{L}_1\text{P})$	55.8s			-7.6t	82.0d		32
$\text{Mo}(\text{CO})_5(\text{L}_1\text{P})$	32.3s			-6.4t	81.4d		27
$\text{W}(\text{CO})_5(\text{L}_1\text{P})$	16.4s			-5.9t	81.8d		37
	(250)						
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{P})$	39.0			-6.9t	81.3d		27
L_2P	-27.6s			172.7t	85.5dd	10	49
					84.1dd	10	49
$\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$	13.9s			170.8t	84.6dd	10	49
					80.6dd	10	49
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$	21.3s			170.3t	85.4dd	10	49
					80.2dd	10	49
$\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$	15.0d	165.0d	35	171.3t	85.6dd	10	46
					81.9dd	10	46
$\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$	15.3d	-18.4d	28	170.8t	85.6dd	10	49
					80.8dd	10	49
L_2CO	-23.7s				85.0d	10	
					84.0d	10	
$\text{W}(\text{CO})_4(\text{pip})(\text{L}_2\text{CO})$	12.7s				82.8d	12	
	(234)				81.1d	12	
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$	0.5d	25.1d	22		84.1d	12	
(<i>cis</i>)	(224)	(223)			82.9d	12	
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$	6.1d	19.8d	47		83.5d	12	
(<i>trans</i>)	(264)	(266)			80.8d	12	

^a The values in parentheses are couplings $^1J(^{31}\text{P},^{183}\text{W})$.

Determination of a cone angle for L_2CO . The equilibrium *cis* to *trans* ratio for a series of complexes $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L})$ where L is a tertiary phosphine has been shown by Boyles et al. to correlate well with the Tolman's cone angle of L [20]. This experiment entailed keeping solutions of $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L})$ at 40 °C until the *cis* to *trans* ratios were established to be at equilibrium. A decrease in the *cis*/*trans* ratio was observed as the Tolman cone angle of the phosphine increased.

A solution of $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$ in a ^{31}P NMR tube was kept at 45 °C and the spectrum obtained daily to assess the *cis-trans* equilibration. After five days at this temperature the *cis* to *trans* ratio stabilized to a value of 1.0 ± 0.2 . The cone

Table 6

Electrochemical properties of the metallophosphine ligands and the dimeric complexes: $\text{Mo}_x(\eta^6\text{-PhPR}_2)(\text{dppe})(\text{L})\text{M}_y(\text{CO})_4(\text{L}')$

Complex	Mo_x $E_{1/2}(\text{ox})^a$	M_y $E_p(\text{ox})^b$	
		Observed	Calculated ^c
L_1CO	+0.15		
$\text{Cr}(\text{CO})_5(\text{L}_1\text{CO})$	+0.28 ^b		
$\text{Mo}(\text{CO})_5(\text{L}_1\text{CO})$	+0.28 ^b		
$\text{W}(\text{CO})_5(\text{L}_1\text{CO})$	+0.28 ^b		
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{CO})$	+0.18 ^b		
$\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_1\text{CO})$	+0.19 ^b		
L_1P	-0.32		
$\text{Cr}(\text{CO})_5(\text{L}_1\text{P})$	-0.13	+0.68 ^b	+0.80
$\text{Mo}(\text{CO})_5(\text{L}_1\text{P})$	-0.18	+0.62 ^b	+0.84
$\text{W}(\text{CO})_5(\text{L}_1\text{P})$	-0.18	+0.72 ^b	+0.88
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_1\text{P})$	-0.29	+0.63 ^b	
L_2P	-0.23		
$\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$	-0.11	+0.59 ^b	+0.86
$\text{Mo}(\text{CO})_4(\text{pip})(\text{L}_2\text{P})$	-0.14	+0.63 ^b	
$\text{Mo}(\text{CO})_4(\text{P}(\text{OMe})_3)(\text{L}_2\text{P})$	-0.20	+0.54 ^b	
$\text{Mo}(\text{CO})_4(\text{PMe}_3)(\text{L}_2\text{P})$	-0.18	+0.86 ^b	
L_2CO	+0.12 ^b		

^a V. vs. SCE; 22°C; solvent, THF; electrolyte, (n-Bu)₄NBF₄; scan rate, 50 mV/s. ^b $E_p(\text{ox})$, irreversible potential. ^c Calculated from the force constants in Table 2 [25].

angle for L_1CO is therefore $155 \pm 5^\circ$ according to this method. This number is larger than the Tolman cone angle for PPh_3 (θ 145°) of which L_1CO is a derivative. Our value seems reasonable considering that the metallophosphine ligand is quite asymmetrical with the large molybdenum group staying well away from the tetra-carbonyl group in the dimeric complex. Similar experiments to determine the cone angle for L_2CO were not successful as the complex $\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})(\text{L}_2\text{CO})$ is not stable at the temperatures required for equilibration.

Electrochemical properties of the metallophosphine ligands and the dimers. The electrochemical data for some of the complexes are listed in Table 6 and the voltammogram obtained for $\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$ is shown in Figure 3.

The CO substituted metallophosphine ligands L_1CO and L_2CO are much more difficult to oxidize than the phosphorus donor substituted complexes L_1P and L_2P (see $E_{1/2}(\text{ox})$ values in Table 6). This account for the better electron-donating ability of the last two as signalled by the IR spectra of CO force constants of the dimers (cf. $\text{Mo}(\text{CO})_5(\text{L}_1\text{P})$ vs. $\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$, Table 2). The ligand complexes L_1P and L_2P undergo a reversible one electron oxidation ($d^5 \leftrightarrow d^6$) whereas L_1CO and L_2CO show only partial reversibility. The mode of decomposition of the cation for the CO substituted complexes is thought to involve loss of the arene ring due to the reduction in backbonding capability of the metal.

The voltammograms for complexes $\text{Mo}(\text{CO})_5(\text{L}_1\text{CO})$, $\text{M} = \text{Cr}$, Mo and W only contained irreversible potentials at ca. 0.3 V. This oxidation originates out of the $\text{Mo}(\eta^6\text{-arene})$ centre (Mo_x) because the oxidation at the pentacarbonyl centre (m_y) would be expected at a much more positive potential [24].

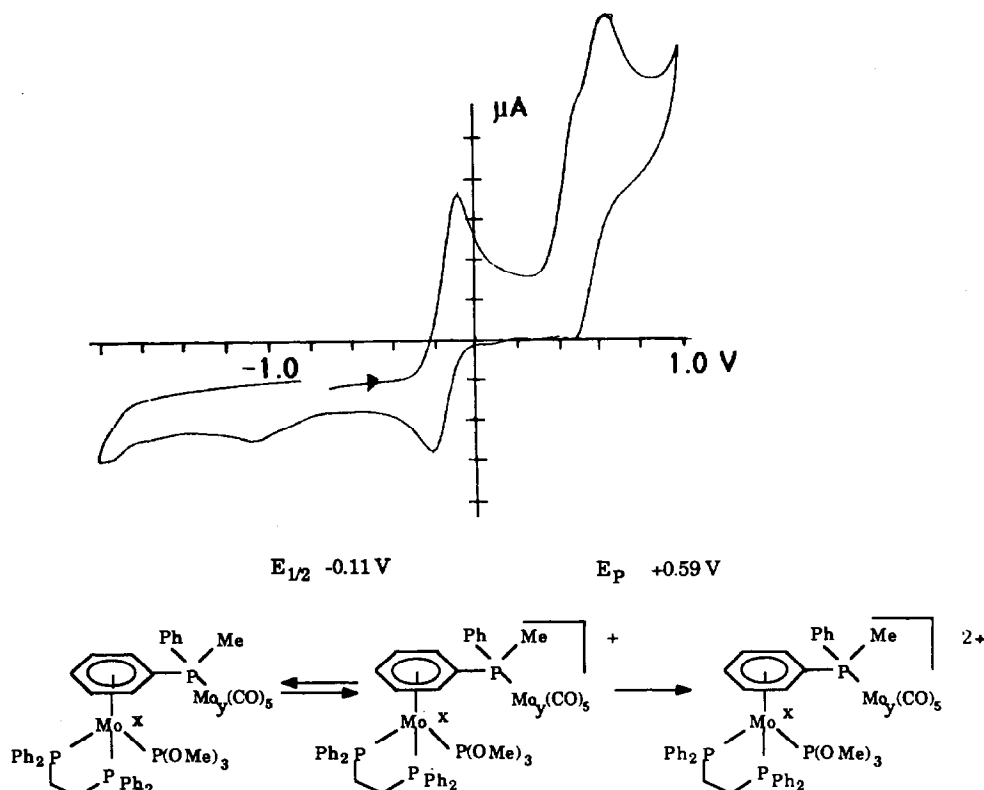


Fig. 3. The cyclic voltammogram of $\text{Mo}(\text{CO})_5(\text{L}_2\text{P})$ in $0.2 \text{ M } [\text{nBu}_4\text{N}][\text{BF}_4]$ in THF referenced to the SCE. The pseudo-reversible wave at -0.11 V is thought to involve the metal centre Mo_x whereas the irreversible wave at $+0.59 \text{ V}$ is thought to involve centre Mo_y .

The complexes of L_1P and L_2P are sufficiently electron rich so that the monocation is stable to arene loss. A second irreversible oxidation is observed in these cases. Correlations between infrared and electrochemical data suggest that at least for the pentacarbonyls the $E_{1/2}(\text{ox})$ for the Mo_y centre should be approximately 0.8 V [25]. The expected values calculated using the equation $E_{1/2}(\text{ox}) = 0.567(k_1 + k_2 + \Delta k_L) - 8.02$, $\Delta k_L = 0.3$ [25] are included in Table 6. The agreement between the potential of the predicted reversible couple and that of the observed irreversible couple is acceptable. This quasi-reversible oxidation was found to occur at 1.05 V for $\text{Mo}(\text{CO})_4(\text{dppe})$ [26]. Thus the second irreversible oxidation of our complexes could be occurring at the tetracarbonyl centre, Mo_y .

Conclusions

The best method for the preparation of these dimers containing a bridging η^6 -arylphosphine group and a pentacarbonyl fragment is to generate the $\text{M}(\text{CO})_5$ fragment by photolysis in the presence of our electron-rich arylphosphine complexes ("metallophosphine" ligands). Mixtures which cannot be separated result if one uses a metallophosphine which is too crowded ($\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$ for example) and which readily undergoes substitution of its own σ -bonded phosphine

ligand by CO. Substitution of a labile piperidine ligand in $M(\text{CO})_4(\text{pip})_2$ by the metallophosphine is a clean method of attaching a tetracarbonyl fragment to the "dangling" phosphine. Infrared and electrochemical measurements confirm the prediction that L_1P would be a more electron-donating ligand than L_1CO and similarly L_2P , more than L_2CO . From the equilibrium *cis/trans* ratio of $W(\text{CO})_4(L_1CO)(\text{PMe}_2\text{Ph})$ a cone angle for the bulky, asymmetric phosphine ligand L_1CO can be estimated to be $155 \pm 5^\circ$.

Experimental

Oxygen and water were excluded during all operations by using vacuum lines or a glove box supplied with purified nitrogen. Solvents apart from methanol were dried over and distilled from sodium-benzophenone ketyl and were degassed before use. Tetrahydrofuran (THF) was further distilled over LiAlH_4 . Methanol was dried over magnesium methoxide. Ultraviolet irradiation of solutions was conducted with a 450-W Hanovia medium-pressure mercury lamp. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer as THF solutions in 0.1 mm KBr solution cells. NMR spectra were recorded on Varian XL-400 (400 MHz for ^1H), XL-200 (200 MHz for ^1H and 81 MHz for ^{31}P NMR) or Bruker WP-80 (80 MHz for ^1H and 32.3 MHz for ^{31}P NMR) spectrometers. ^{31}P chemical shifts were measured relative to 1% $\text{P}(\text{OMe})_3$ in C_6D_6 sealed in coaxial capillaries. They are reported relative to 85% H_3PO_4 using the chemical shift difference, $\delta - 140.4$ ppm, 81 MHz; $\delta - 140.7$ ppm, 32.3 MHz. Cyclic voltammetric measurements were performed on a BAS CV 1B instrument and a Houston Instruments 100 recorder using tetrahydrofuran solutions which were 0.002 M in the complexes and 0.2 M in $(n\text{-Bu})_4\text{NBF}_4$. Voltammograms were obtained using a glassy carbon electrode referenced to a Ag/AgCl electrode but are reported relative to the Saturated Calomel Electrode (SCE). Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver. The phosphine ligands and MoCl_5 , $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were used as purchased from Strem and Morton/Thiokol-Alfa Chemicals. The preparations of the following complexes have been reported elsewhere: $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{CO}) L_1\text{CO}$ [4], $\text{Mo}(\eta^6\text{-PhPPh}_2)(\text{dppe})(\text{PMe}_3) L_1\text{P}$ [4], $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{CO}) L_2\text{CO}$ [3], $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$ [3], $M(\text{CO})_4(\text{pip})_2$, $M = \text{Mo}, \text{W}$, pip = piperidine [18].

Preparation of $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{P}(\text{OMe})_3)$, $L_2\text{P}$. Orange $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{PMePh}_2)$ (0.3 g, 0.3 mmol) was dissolved in 12 ml C_6H_6 containing $\text{P}(\text{OMe})_3$ (42 mg, 0.3 mmol). This solution was placed under vacuum, sealed and heated at 70°C for 3 h. The resulting mixture was then filtered through Celite and concentrated to 2 ml. The careful addition of CH_3OH effected the precipitation of orange crystals of $L_2\text{P}$, (150 mg, 55%).

UV irradiation method for the preparation of dimers $M(\text{CO})_5(L_1\text{CO})$, $M(\text{CO})_5(L_1\text{P})$ and $M(\text{CO})_5(L_2\text{P})$, $M = \text{Cr}, \text{Mo}, \text{W}$. Stoichiometric amounts of η^6 -arylphosphine $L_1\text{CO}$, $L_1\text{P}$ or $L_2\text{P}$ (ca. 40 mg) and hexacarbonyl $M(\text{CO})_6$, $M = \text{Cr}, \text{Mo}, \text{W}$, were dissolved in 50 ml C_6H_6 contained in a quartz flask. The solution was then subjected to photolysis while being stirred rapidly. A steady stream of N_2 or Ar through the solution always accompanied the photolysis. After 20 min in this state, the solution was filtered through Celite. Total evaporation of the solvent under vacuum usually gave analytically pure samples of the desired bimetallic complexes.

Yields were usually greater than 80%. Analytical and spectroscopic data are listed in Tables 1, 2, 4 and 5.

Attempted alternative synthesis of $W(CO)_5(L_1CO)$. A solution of $W(CO)_6$ (50 mg, 142 mmol) in ca. 50 ml THF was photolyzed for 20 min. Solid $Mo(\eta^6\text{-PhPPh}_2)(dppe)(CO)$, L_1CO (111 mg, 142 mmol) was then added and the mixture stirred for 30 min. The volume of solution was concentrated to ca. 5 ml and MeOH (10 ml) added. An orange-red precipitate formed on cooling this mixture and this was obtained by filtration (113 mg). The IR and $^{31}P\{^1H\}$ NMR of this product indicated that two products containing penta- and tetra-carbonyls were obtained. IR (nujol mull) 2068 m (pentacarbonyl), 2013 m (tetracarbonyl), 1835–1935 vs. $^{31}P\{^1H\}$ NMR (C_6H_6) $W(CO)_5(L_1CO)$ δ 22.4 (s, 1P), 82.1 (s, 2P); also a species tentatively identified as $W(CO)_4(THF)(L_1CO)$ δ 26.7 (s, 1P), 84.5 (s, 2P). These products were obtained in approximately equal quantities.

Preparation of dimers $cis\text{-}Mo(CO)_4(pip)(L)$ $L = L_1CO, L_1P, L_2P$ and $cis\text{-}W(CO)_4(pip)(L)$ $L = L_1CO, L_2CO$. The dimers were prepared by reacting the η^6 -arylphosphine complex with $M(CO)_4(pip)_2$ for 2 h in benzene at 45 °C when $M = Mo$ and 60 °C when $M = W$. In a typical reaction L_2CO (250 mg, 0.4 mmol) was dissolved in a slurry of $W(CO)_4(pip)_2$ (178 mg, 0.4 mmol) in 10 ml of C_6H_6 . This was heated for 2 h at 60 °C whereupon the solution was filtered through Celite and concentrated to 2 ml. The addition of 5 ml CH_3OH effected the precipitation of orange crystals of $W(CO)_4(pip)(L_2CO)$ (220 mg, 58%). Yields were all around 60%. Analytical and spectroscopic data are listed in Tables 1, 3–5.

Preparation of dimers $cis\text{-}Mo(CO)_4(PR_3)(L)$ $PR_3 = P(OMe)_3, PMe_3, L = L_2P$ and $cis\text{-}W(CO)_4(PMe_2Ph)(L)$ $L = L_1CO, L_2CO$. The piperidine ligand of the respective parent dimer $M(CO)_4(pip)(L)$ was substituted by addition of one equivalent of phosphorus donor in benzene at 50 °C for 1 h to yield orange solutions of these substituted dimers. In a representative preparation the complex $W(CO)_4(pip)(L_2CO)$ (150 mg, 0.1 mmol) was dissolved in 5 ml of C_6H_6 . The phosphine PMe_2Ph (19 mg, 0.1 mmol) was added and the mixture heated at 50 °C for 1 h. The resulting solution was filtered through Celite and concentrated to 1 ml. The addition of 5 ml CH_3OH effected the precipitation of red-orange crystals of $W(CO)_4(PMe_2Ph)(L_2CO)$ as a mixture of *cis* and *trans* isomers (100 mg, 64%). Analytical and spectroscopic data are listed in Tables 1, 3–5.

*Equilibrium *cis* / *trans* ratio determinations.* Approximately 20 mg of $W(CO)_4(PMe_2Ph)(L_1CO)$ was placed in 2 ml of C_6H_6 contained in a ^{31}P NMR tube. The spectrum was then obtained. The sample of $W(CO)_4(PMe_2Ph)(L_1CO)$ was heated at 45 °C for 5 days with the progress of the *cis* / *trans* equilibration monitored every day. After 5 days of heating equilibrium was achieved. The integrals of diagnostic peaks in the ^{31}P NMR spectrum were used to determine that the equilibrium *cis* to *trans* ratio was 1/1.

A determination for $W(CO)_4(PMe_2Ph)(L_2CO)$ was not possible due to extensive decomposition of the complex after 2 days of heating.

Reaction of $Mo(\eta^6\text{-PhPMePh})(dppe)(PMePh_2)$ and $Mo(CO)_5(THF)$. One equivalent of $Mo(\eta^6\text{-PhPMePh})(dppe)(PMePh_2)$ was added to $Mo(CO)_5(THF)$ which had been prepared by photolyzing 20 mg of $Mo(CO)_6$ in 20 ml THF. The solution was stirred for 1 h and evaporated to dryness. The ^{31}P NMR in C_6H_6 contained peaks assignable to the expected product $Mo(\eta^6\text{-PhP}_a\{Mo(CO)_5\}MePh)(dppe)(P_aMePh_2)$ (δ 19.0 (s, 1P_a), 28.5 (t, 1P_a, $^2J(P,P)$ 46 Hz) as well as the complex

resulting from a ligand exchange reaction $\text{Mo}(\eta^6\text{-PhP}_a\{\text{Mo}(\text{CO})_4(\text{P}_b\text{MePh}_2)\}\text{Me-Ph})(\text{P}_c\text{Ph}_2\text{CH}_2\text{CH}_2\text{P}_d\text{Ph}_2)(\text{CO})$. The latter complex was synthesized in an ^{31}P NMR tube by first reacting stoichiometric equivalents of $\text{Mo}(\eta^6\text{-PhPMePh})(\text{dppe})(\text{CO})$ and $\text{Mo}(\text{CO})_4(\text{pip})_2$ in C_6H_6 and then adding one equivalent of PMePh_2 . This is the experimental procedure for the synthesis of similar complexes as outlined above. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 14.9 (d, 1P_b , $^2J(\text{P}_a, \text{P}_b)$ 24.4 Hz), 19.3 (d, 1P_a , $^2J(\text{P}_a, \text{P}_b)$ 24.4 Hz), -83.0 (d, 1P_c , $^2J(\text{P}_c, \text{P}_d)$ 10 Hz), -84.6 (d, 1P_d , $^2J(\text{P}_c, \text{P}_d)$ 12 Hz).

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