Chemistry of Phosphido-bridged Dimolybdenum Complexes. Part 1. High-yield Synthesis of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ and its Reactions with Organophosphorus Ligands: *X*-Ray Crystal Structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$†

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The thermal reaction of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ with PPh_2H in toluene or decalin gives $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (**1a**) in high yield. An analogous reaction with $PPhH_2$ affords $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_4]$ (**1b**). The photolytic reaction of (**1a**) with organophosphorus ligands, L, gives the monosubstituted complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3L]$ [L = $P(OMe)_3$, $P(OPh)_3$, PPh_3, $P(C_6H_4Me\text{-}m)_3$, PEt_2Ph, or dppm-*P* (dppm = $Ph_2PCH_2PPh_2$)]. ^1H N.m.r. spectroscopy reveals that each of the monosubstituted products exists as an equilibrium mixture of two isomers in solution, the position of the equilibrium depending on the ligand L and on the solvent. The structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ in the solid state has been determined by a single-crystal *X*-ray analysis.

Complexes such as $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Re_2(\mu\text{-}H)_2(dppm)(CO)_6]$ [dppm = bis(diphenylphosphino)methane] react readily under mild conditions with two-electron donor ligands (*e.g.* organophosphines) to form 1:1 adducts in which one of the bridging hydride ligands becomes terminally bonded to one metal centre.[1—3] This pattern of reactivity has also been observed for $[Co_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]PF_6$[4] but other μ-hydrido μ-phosphido complexes such as $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$[5] and $[MoMn(\eta^5\text{-}C_5H_5)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$[6,7] give substituted derivatives on treatment with two-electron donor ligands without there being any evidence for intermediate adduct formation.[5]

The range of μ-hydrido μ-phosphido complexes which have been prepared in yields which are adequate to permit detailed studies of their reactivity is very narrow and, in order to extend this range, we now describe a high-yield route to the dimolybdenum complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPhR)(CO)_4]$ [R = Ph (**1a**) or H (**1b**)] together with an investigation of the reactions of (**1a**) with organophosphines.

Results and Discussion

(*a*) *Synthesis and Fluxional Behaviour of* (**1a**) *and* (**1b**).—Complex (**1a**) has been previously synthesised by Treichel *et al.*[8] in 13.5% yield from the reaction of $[Mo(\eta^5\text{-}C_5H_5)Br(CO)_2(PPh_2H)]$ with $LiBu^n$. Direct reaction of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ with PPh_2H in toluene or decalin at 383 K, however, affords (**1a**) in 75% yield. An analogous reaction in toluene at 368 K using $PPhH_2$ in place of PPh_2H gives the new complex (**1b**) in 67% yield. Similar procedures have been used previously to form related complexes of Mn,[5,9] Fe,[10] and Co.[11]

Complexes (**1a**) and (**1b**) have been characterised on the basis of mass spectrometry and microanalysis and by comparison of their i.r. and ^1H n.m.r. spectra with published data for (**1a**)[8] and $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ (**1c**)[12] (see Experimental section). The ^1H n.m.r. spectrum of (**1b**) in $CDCl_3$ at 293 K shows, in addition to the sharp phenyl, hydrogen on phosphorus, and metal–hydride resonances, two broad cyclopentadienyl peaks. These peaks, which are sharp and of equal intensity at 228 K, gradually broaden as the temperature is raised, coalesce at *ca.* 314 K and form a single sharpening peak at 336 K. Over the same temperature range the ^1H n.m.r. spectrum of (**1a**) is invariant.

The structures of (**1a**) and (**1b**) in solution may be assumed to be similar to that found for (**1c**) in the solid state by *X*-ray[13] and neutron[14] structural analysis (Figure 1); the two cyclopentadienyl groups adopted a relative *trans* orientation with respect to the Mo–Mo vector. It is clear that in (**1a**) the two cyclopentadienyl groups have identical environments and, as expected, only one cyclopentadienyl resonance is observed, even at low temperatures. In (**1b**), however, the two cyclopentadienyl groups have different environments in accord with the low-temperature ^1H n.m.r. spectrum. A possible mechanism to explain the fluxional behaviour observed for (**1b**) at higher temperatures is shown in Figure 2. The two enantiomers, (**A**) and (**B**), interconvert *via* a change of geometry at the Mo centres from square pyramidal in (**A**) and (**B**) (if the Mo–Mo bond is ignored) to trigonal bipyramidal in (**C**). The fluxional process results in no overall change in the environments of the phenyl group or metal hydride ligand. A similar process has been invoked by Casey and Bullock[15,16] to explain the fluxional behaviour of $[MoFe(\eta^5\text{-}C_5H_5)(\mu\text{-}AsMe_2)(CO)_6]$[15] and $[MoMn(\eta^5\text{-}C_5H_5)(\mu\text{-}H)\{\mu\text{-}P(C_6H_4Me\text{-}p)_2\}(CO)_6]$.[16] It should be noted that the interconversion of the two enantiomers, (**A**) and (**B**), may equally well occur in stages, involving successive rather than the simultaneous square planar–trigonal bipyramidal geometry changes at the two Mo centres shown in Figure 2.

The ^{13}CO n.m.r. spectrum of (**1a**) at 223 K exhibits two resonances, a doublet [^2J(PC) 23.9 Hz] and a singlet. Todd *et al.*[17] have shown that in square-pyramidal complexes of the type $[Mo(\eta^5\text{-}C_5H_5)X(PR_3)(CO)_2]$ (X = halogen, methyl, or acetyl), ^2J(PC) couplings are in the range *ca.* 20—30 Hz for carbonyls *cis* to the phosphine and *ca.* 5 Hz for the *trans* carbonyls. On this basis the doublet and singlet resonances observed for (**1a**) are assigned respectively to the two equivalent

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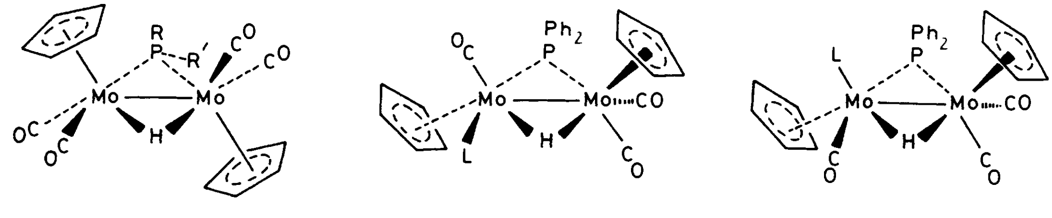
† 1,1,2-Tricarbonyl-1,2-bis(η-cyclopentadienyl)-μ-diphenylphosphido-μ-hydrido-2-(trimethyl phosphite)dimolybdenum(II) (*Mo–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

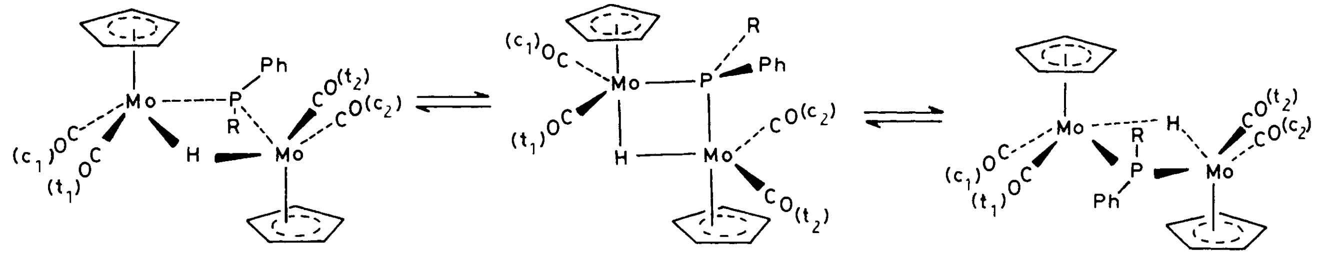


Isomer (I) Isomer (II)

(**1a**) R = R′ = Ph
(**1b**) R = H,R′ = Ph
(**1c**) R = R′ = Me (refs.13,14)

(**2a**) L = $P(OMe)_3$
(**2b**) L = $P(OPh)_3$
(**2c**) L = PPh_3
(**2d**) L = $P(C_6H_4Me\text{-}m)_3$
(**2e**) L = PEt_2Ph
(**2f**) L = dppm-*P*

Figure 1. Proposed structures for the new complexes



(**A**) (**C**) (**B**)

Figure 2. Possible mechanism for enantiomer interconversion in (**1a**) (R = Ph) and (**1b**) (R = H): c and t indicate *cis* and *trans* to the bridging PPhR group

cis and *trans* CO groups. All four CO groups in (**1b**) are inequivalent and the two doublet and two singlet resonances observed in the ^{13}C n.m.r. spectrum at 200 K are correspondingly assigned as being due respectively to *cis* and *trans* CO ligands at each of the Mo centres.

The fluxional process invoked to account for the high-temperature ^1H n.m.r. spectrum of (**1b**) would be expected to lead to equivalence of all four CO groups in (**1a**) and of the pairs c_1,t_2 and c_2,t_1 in (**1b**) (Figure 2). However, although the carbonyl resonances in (**1a**) and (**1b**) collapse over the range 220—330 K, no high-temperature limiting spectrum was observed in either case.

(*b*) *Substitution Reactions of* (**1a**) *with Organophosphines*.—U.v. irradiation of (**1a**) with organophosphines in hexane–benzene solution results in the formation of the monosubstituted products $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3L]$ [L = $P(OMe)_3$ (**2a**), $P(OPh)_3$ (**2b**), PPh_3 (**2c**), $P(C_6H_4Me\text{-}m)_3$ (**2d**), PEt_2Ph (**2e**), or dppm-*P* (**2f**)]. Attempted thermal substitution reactions using $P(OMe)_3$ or PPh_3 led only to slow decomposition. The substituted complexes have been characterised by i.r. and ^1H n.m.r. spectroscopy, mass spectrometry, and microanalysis; complex (**2a**) has also been characterised by ^{13}C and ^{31}P n.m.r. spectroscopy and by *X*-ray analysis.

The ^1H n.m.r. spectra of the substitution products reveal the presence of two isomers, (**I**) and (**II**), in a ratio strongly dependent on the ligand, L, and the solvent. Thus for each complex two pairs of cyclopentadienyl resonances and two metal hydride resonances are observed. The latter are each a doublet of doublets due to coupling to two phosphorus nuclei [^2J(PH) *ca.* 30—60 Hz]; the hydride resonance of the major isomer (**I**) is, in each case, *ca.* 0.5 p.p.m. downfield from that of the minor isomer (**II**). The observation in the ^{13}C n.m.r. spectrum of three ^{13}CO resonances due to the major isomer of (**2a**) confirms that monosubstitution has occurred. On the basis of the study by Todd *et al.*[17] of ^2J(PC) coupling constants in square-pyramidal molybdenum complexes the two upfield ^{13}CO resonances, a singlet and a doublet [^2J(PC) 21.1 Hz], may be assigned respectively to the carbonyls *trans* and *cis* to the μ-PPh_2 group on the unsubstituted metal centre. The downfield doublet of doublets [^2J(PC) 35.1, 23.3 Hz] is similarly assigned to a carbonyl *cis* to both the $P(OMe)_3$ and μ-PPh_2 groups. The proposed structure of isomer (**I**) of (**2a**), consistent with the n.m.r. evidence, is shown in Figure 1; the most probable structure of the minor isomer, (**II**), for which no ^{13}CO peaks could be observed, is also given.

(*c*) X-*Ray Analysis of* (**2a**).—Suitable crystals of (**2a**) were obtained by slow evaporation of a hexane–CH_2Cl_2 (3:1) solution at 273 K. The molecular structure of (**2a**) is shown in Figure 3 and Table 1 lists the atomic co-ordinates; selected bond lengths and interbond angles are given in Table 2.

The crystal structure shows that the $P(OMe)_3$ ligand in (**2a**) occupies the position proposed in the major isomer (**I**) in solution. The overall configuration of ligands around the metals is similar to that found previously for $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ (**1c**).[13,14] The Mo–Mo bond length of 3.254(1) Å is slightly shorter than that in (**1c**), 3.267(2) Å. The Mo(1)–P(1)-(μ-PPh_2) bond at 2.412(3) Å, is significantly shorter than the corresponding bond involving Mo(2), 2.441(3) Å. This presumably reflects a greater degree of π back-bonding from Mo(1) to the bridging group due to a reduced π-acid character of $P(OMe)_3$ on Mo(1) compared to CO on Mo(2). The mean Mo–P(μ-PPh_2) bond length of 2.427(3) Å in (**2a**) is, however, equal within experimental error to the corresponding average length of 2.422(3) Å in (**1c**) and, this, together with the relatively

Table 1. Fractional atomic co-ordinates for $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ (**2a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	0.112 75(2)	−0.022 04(8)	0.012 27(5)	C(25)	0.170 3(4)	0.295 4(13)	−0.102 7(9)
Mo(2)	0.104 99(3)	0.234 33(8)	−0.111 30(5)	O(21)	0.166 9(3)	−0.217 6(9)	−0.074 9(6)
P(1)	0.113 0(1)	0.214 7(2)	0.038 3(1)	O(22)	0.203 1(3)	−0.187 0(10)	0.072 2(6)
P(2)	0.170 0(1)	−0.105 4(3)	−0.006 6(2)	O(23)	0.201 5(3)	−0.003 6(10)	−0.012 4(6)
C(16)	0.151 3(3)	−0.012 3(9)	0.127 0(6)	C(211)	0.148 3(5)	−0.175 5(18)	−0.158 9(11)
C(26)	0.072 9(3)	0.109 1(11)	−0.196 8(7)	C(222)	0.192 1(3)	−0.302 4(11)	0.104 0(7)
C(27)	0.050 6(4)	0.277 3(11)	−0.125 4(7)	C(223)	0.240 2(5)	−0.045 8(18)	−0.016 0(11)
O(16)	0.172 0(2)	−0.012 2(8)	0.196 2(5)	C(111)	0.158 6(3)	0.291 9(9)	0.113 5(6)
O(26)	0.052 9(3)	0.041 6(9)	−0.251 0(5)	C(112)	0.157 9(3)	0.390 1(10)	0.170 7(6)
O(27)	0.178 8(2)	0.300 5(10)	−0.136 4(6)	C(113)	0.192 8(3)	0.441 7(11)	0.228 8(7)
C(11)	0.084 5(4)	−0.218 4(14)	0.029 0(9)	C(114)	0.228 8(3)	0.399 8(12)	0.229 9(8)
C(12)	0.065 8(4)	−0.120 1(13)	0.057 4(9)	C(115)	0.230 5(3)	0.302 9(11)	0.172 4(7)
C(13)	0.045 1(4)	−0.042 8(14)	−0.005 2(9)	C(116)	0.195 4(3)	0.250 9(11)	0.115 8(7)
C(14)	0.047 1(4)	−0.090 3(15)	−0.079 4(10)	C(121)	0.075 9(3)	0.287 4(9)	0.078 3(6)
C(15)	0.071 6(4)	−0.194 2(14)	−0.062 1(9)	C(122)	0.061 8(3)	0.414 3(10)	0.054 2(6)
C(21)	0.153 4(4)	0.406 5(13)	−0.079 6(9)	C(123)	0.037 5(3)	0.475 9(11)	0.092 1(7)
C(22)	0.119 4(4)	0.445 5(15)	−0.148 0(9)	C(124)	0.026 8(3)	0.407 7(11)	0.151 0(7)
C(23)	0.115 6(4)	0.362 4(13)	−0.215 2(9)	C(125)	0.041 7(3)	0.280 1(11)	0.175 8(7)
C(24)	0.147 8(4)	0.267 5(13)	−0.184 7(8)	C(126)	0.066 3(3)	0.220 1(10)	0.138 4(6)

Table 2. Selected bond lengths (Å) and angles (°) for (**2a**)

Mo(1)–Mo(2)	3.254(1)	Mo(1)–C(11)	2.275(14)
Mo(1)–C(12)	2.305(16)	Mo(1)–C(13)	2.344(15)
Mo(1)–C(14)	2.398(13)	Mo(1)–C(15)	2.318(13)
Mo(1)–P(1)	2.412(3)	Mo(1)–P(2)	2.341(3)
Mo(1)–C(16)	1.927(9)	Mo(2)–C(21)	2.366(13)
Mo(2)–C(22)	2.314(15)	Mo(2)–C(23)	2.312(16)
Mo(2)–C(24)	2.318(16)	Mo(2)–C(25)	2.372(15)
Mo(2)–P(1)	2.441(3)	Mo(2)–C(26)	1.941(10)
Mo(2)–C(27)	1.926(13)	C(11)–C(12)	1.373(22)
C(11)–C(15)	1.454(21)	C(12)–C(13)	1.302(19)
C(13)–C(14)	1.365(24)	C(14)–C(15)	1.326(20)
C(21)–C(22)	1.395(17)	C(21)–C(25)	1.388(21)
C(22)–C(23)	1.373(21)	C(23)–C(24)	1.436(18)
C(24)–C(25)	1.353(18)	P(1)–C(111)	1.836(8)
P(1)–C(121)	1.844(11)	P(2)–O(21)	1.584(11)
P(2)–O(22)	1.640(9)	P(2)–O(23)	1.551(10)
C(16)–O(16)	1.132(11)	C(26)–O(26)	1.154(13)
C(27)–O(27)	1.144(16)	O(21)–C(211)	1.394(19)
O(22)–C(222)	1.390(16)	O(23)–C(223)	1.470(21)
P(1)–Mo(1)–Mo(2)	48.3(1)	P(2)–Mo(1)–Mo(2)	94.0(1)
P(2)–Mo(1)–P(1)	115.5(1)	C(16)–Mo(1)–Mo(2)	117.8(3)
C(16)–Mo(1)–P(1)	79.3(3)	C(16)–Mo(1)–P(2)	79.1(3)
C(26)–Mo(2)–Mo(1)	81.7(3)	C(26)–Mo(2)–P(1)	122.1(4)
C(27)–Mo(2)–Mo(1)	95.8(4)	C(27)–Mo(2)–P(1)	83.0(3)
Mo(2)–P(1)–Mo(1)	84.2(1)	C(111)–P(1)–Mo(1)	118.9(3)

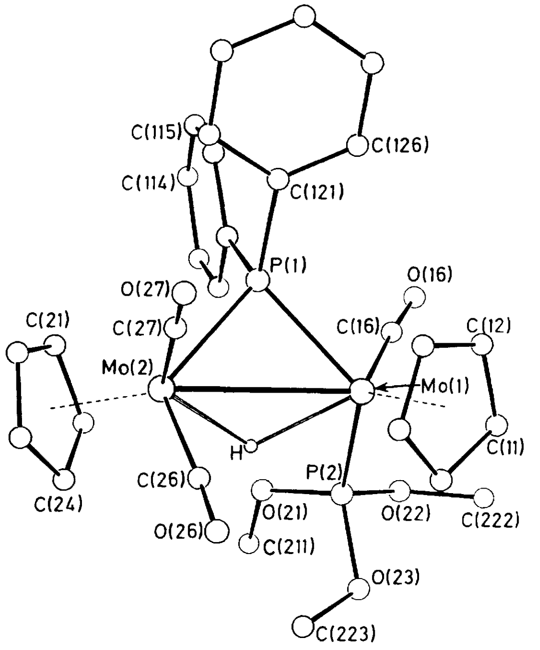


Figure 3. Molecular structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ (**2a**) showing the crystallographic numbering

similar Mo–Mo bond lengths in the two complexes, results in similar phosphido group bridging angles [Mo(1)–P(1)–Mo(2)] of 84.2(1)° in (**2a**) and 84.8(1)° in (**1c**).

The location of the carbonyls in (**2a**) is somewhat different from that in (**1c**); the largest difference in the Mo–Mo–CO angles is seen for CO(27) at 95.8(4)° compared to 112.0(1)° for the mean Mo–Mo–CO (*cis* to PMe_2) angle in (**1c**). Such a large change for a carbonyl remote from the site of PR_3 substitution is surprising, particularly as the smaller angle is associated with the more bulky bridging group. The reduction in the mean Mo–CO bond distance to 1.931(13) Å in (**2a**), compared to 1.960(3) Å in (**1c**), although of low significance, may again reflect the weaker π-acid character of $P(OMe)_3$ as compared to CO.

The position of substitution of the phosphorus ligand in (**2a**) is different to that in a recently reported structure by Kyba *et al.*[18] of the complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)\{\mu\text{-}P(Ph)C_6H_4\text{-}PPhH\text{-}o\}(CO)_3]$. In the latter, however, the terminally substituting phosphorus atom is constrained by its linkage to the μ-phosphido group to occupy a site *cis* to this group. The slightly longer Mo–Mo distance of 3.282(1) Å in this complex compared to 3.254(1) Å in (**2a**) may reflect increased steric crowding.

(*d*) *Isomerisation of the Substituted Products*.—The variations in the isomer ratio (**I**):(**II**) with changes in the substituting ligand and with solvent are summarised in Table 3. The variation with solvent shows that the two isomers interconvert in solution, but the observation in the ^1H n.m.r. spectrum of sharp resonances due to each indicates that this interconversion is slow on the n.m.r. time-scale. Warming a solution of (**2c**) in toluene over the range 303—377 K resulted in gradual broadening of the cyclopentadienyl and metal hydride

Table 3. Variation in the isomer ratio for (**2a**)—(**2f**) with solvent and with the Tolman electronic parameter and cone angle[19] of the ligand

Complex	Ligand(L)	Isomer ratio [(**I**):(**II**)][a]	Electronic parameter ν/cm^{-1} [b]	Cone angle Θ/°
(**2a**)	$P(OMe)_3$	13.3	2 079.5	107
		3.8 (acetone)		
(**2b**)	$P(OPh)_3$	6.1	2 085.3	128
(**2c**)	PPh_3	4.9	2 068.9	145
		7.3 (toluene)		
		1.2 (acetone)		
(**2d**)	$P(C_6H_4Me\text{-}m)_3$	6.7	2 067.2	145
(**2e**)	PEt_2Ph	1.1	2 063.7	136
		1.6 (benzene)		
(**2f**)	dppm-*P*	1.1	—	121

[a] In $CDCl_3$ solution unless otherwise indicated; (**I**) = major isomer, (**II**) = minor isomer. [b] $\nu_{max.}(CO)(A_1)$ of $[Ni(CO)_3L]$ in $CDCl_3$ (cm^{-1}).

resonances. However no coalescence took place and, at the upper end of the temperature range, a number of decomposition peaks appeared. On cooling the sample the decomposition peaks remained but the peaks due to (**2c**) sharpened up again.

The mechanism of isomer interconversion is presumably similar to that which has already been put foward (Figure 2) to account for the fluxional behaviour of (**1b**). This process would interconvert isomers (**I**) and (**II**) and the existence of such a facile interconversion process lends some support to the structural proposals.

Table 3 also relates the ratio of the two isomers of complexes (**2a**)—(**2f**) to the Tolman electronic parameter[19] and the ligand cone angle[19] for the organophosphines. The Tolman electronic parameter, ν, is a measure of the electron donor–acceptor properties of a phosphine and the cone angle, Θ, of the steric bulk of the phosphine at a metal centre. For the series of ligands $P(OMe)_3$, PPh_3, and PEt_2Ph (in $CDCl_3$) a decrease in ν, indicating a decrease in the π-acid character of the ligand, is coincident with a decrease in the (**I**):(**II**) ratio from 13.1:1 to 4.9:1 to 1.1:1. However, the dependence of the isomer ratio on other factors, such as the steric bulk of the organophosphine, is illustrated by the similarity in the isomer ratio for (**2b**) and (**2d**) despite the large difference in ν. Faller and Anderson[20] have observed a similar dependence of isomer ratio on a balance between electronic and steric factors in the related complexes $[Mo(\eta^5\text{-}C_5H_5)X(PR_3)(CO)_2]$ (X = H, D, Me, CH_2Ph, Cl, Br, or I; R = Ph, Bu^n, OMe, or OPh).

Experimental

All reactions were carried out with magnetic stirring under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Ultraviolet irradiation was carried out in a glass photolysis vessel using a water- or ethanol-cooled Hanovia 125W medium-pressure immersion lamp in a quartz inner tube.

Work-up procedures were generally performed in air. Preparative thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25-mm layer of silica, or on 1-mm silica plates prepared in the Department (Cambridge); products are presented in order of decreasing R_f value. Column chromatography was performed on silica (Merck Kieselgel 60, 70—230, or 230—400 mesh) or alumina (grade UGI) as specified, under a positive pressure of N_2.

Infrared spectra were recorded in solution in 0.5-mm NaCl cells using a Perkin-Elmer 983 instrument. Mass spectra were recorded on an AEI MS 12 instrument using tris(perfluoroheptyl)-*s*-triazine as reference. N.m.r. spectra were recorded on Bruker WP 80, WM 250, or AM 400 spectrometers using the solvent as reference for ^1H and ^{13}C and external $P(OMe)_3$ for ^{31}P spectra. The ^{13}C and ^{31}P spectra are ^1H-gated decoupled. Proton and ^{13}C chemical shifts are given in δ (p.p.m.) relative to $SiMe_4$ (0.0 p.p.m.). The ^{31}P shifts are given relative to $P(OMe)_3$ (0.0 p.p.m.) with upfield shifts negative. The chemical shift of 85% H_3PO_4 on this scale is -141 p.p.m. Elemental analyses were performed by the Microanalytical Department, University Chemical Laboratory, Cambridge.

The complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ was prepared by the method of King.[21] All other chemicals were obtained from commercial suppliers and used without further purification.

(*i*) *Synthesis of* $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (**1a**).—$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (10.3 g, 21.0 mmol) was dissolved in toluene (600 cm^3) and PPh_2H (3.65 cm^3, 21.0 mmol) added. The mixture was stirred at 383 K for 1.25 h during which time the colour of the solution changed from dark red to dark orange. Further PPh_2H (0.26 cm^3, 1.5 mmol) was added and the mixture stirred again at 110 °C for 45 min. The solvent was removed on a rotary evaporator and the orange residue, having been dissolved in the minimum quantity of CH_2Cl_2, was adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–CH_2Cl_2 (3:1) gave a trace of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ followed by (**1a**) as an intense orange band. Following the removal of solvent this was further purified by recrystallisation from hexane–CH_2Cl_2 (3:1) to give dark orange crystals of (**1a**) (9.5 g, 75%) (Found: C, 50.2; H, 3.3; P, 5.0. $C_{26}H_{21}Mo_2O_4P$ requires C, 50.3; H, 3.4; P, 5.0%); mass spectrum: *m*/*e* 620 (M^+), $M^+ - n$CO (n = 0—4); $\nu_{max.}$(CO) at 1 945s and 1 882s cm^{-1}. N.m.r.: ^1H (303 K), δ 7.4—7.2 (m, 10 H, Ph), 4.88 (s, 10 H, C_5H_5), and -11.81 [d, ^2J(PH) 38.2, 1 H, Mo(μ-H)Mo]; ^{13}C (233 K), δ 243.4 [d, ^2J(PC) 23.9, 2CO(*cis*)], 235.7 [s, 2CO(*trans*)], 143.0—127.7 (m,Ph), and 92.0 (s, C_5H_5); ^{31}P (293 K), δ 39.9 (s, μ-PPh_2). Further elution of the column, first with hexane–CH_2Cl_2 (1:1) and then with hexane–acetone (4:1) gave respectively dark green crystalline $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (0.4 g, 2.5%) and dark red $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(O)(CO)]$ (0.18 g, 1.1%). These two complexes have been prepared in much higher yield by an alternative route and their characterisation and properties will be described elsewhere.[22]

(*ii*) *Synthesis of* $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_4]$ (**1b**).—$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (5.0 g, 10.2 mmol) and $PPhH_2$ (1.12 cm^3, 10.2 mmol) were stirred in toluene (600 cm^3) at 368 K for 3.5 h. An additional quantity of $PPhH_2$ (0.25 cm^3, 2.3 mmol) was added and the mixture stirred for a further 1 h at 368 K. A similar purification procedure to that in (*i*) was then used except that hexane–toluene (3:1) was employed as the eluant for column chromatography. Orange crystals of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_4]$ (**1b**) (3.7 g, 67%) were obtained as the only major product (other weak bands which eluted gave species which were too unstable to characterise) (Found: C, 43.5; H, 3.1; P, 5.4. $C_{20}H_{17}Mo_2O_4P$ requires C, 44.2; H, 3.1; P, 5.7%); mass spectrum: *m*/*e* 544 (M^+), $M^+ - n$CO (n = 0—4); $\nu_{max.}$(CO) at 1 948s, 1 891s, and 1 885m cm^{-1}. N.m.r.: ^1H (228 K), δ 7.4—7.2 (m, 5 H, Ph), 6.56 [d, J(PH) 351, 1 H, PH], 5.20 (s, 5 H, C_5H_5), 5.05 (s, 5 H, C_5H_5), and -12.01 [d, ^2J(PH) 37.5, 1 H, Mo(μ-H)Mo]; at 336 K one resonance at 5.12 (s, 10 H, C_5H_5) replaces the two resonances at 5.20 and 5.05 observed at the lower temperature; ^{13}C (220 K), δ 242.8 [d, ^2J(PC) 24.5, 1CO(*cis*)], 241.8 [d, ^2J(PC) 19.8, 1CO(*cis*)], 236.2 [s, 1CO(*trans*)], 234.7 [s, 1CO(*trans*)], 140.2—128.1 (m, Ph), 91.5 (s, C_5H_5)], and 90.5 (s, C_5H_5); at 330 K one resonance at 90.9 (s, C_5H_5) replaces the two resonances at 91.5 and 90.5 observed at the lower temperature; ^{31}P (293 K), δ -14.0 (s, μ-PPh_2).

(*iii*) *Substitution Reactions of* (**1a**) *with Organophosphines*.—(*a*) *With* $\mathrm{P(OMe)_3}$. Complex (**1a**) (0.52 g, 0.85 mmol) and $\mathrm{P(OMe)_3}$ (0.18 cm^3, 1.5 mmol) were dissolved in hexane (250 cm^3) in a glass photolysis vessel. A quartz vessel containing the u.v. filament was placed into the vessel and the solution was irradiated with u.v. light for 24 h; the solution was cooled by a flow of ethanol through the quartz vessel from a temperature-controlled ethanol reservoir. At the conclusion of the reaction the hexane was removed on a rotary evaporator and the residue, having been redissolved in the minimum of cyclohexane–$\mathrm{CH_2Cl_2}$ (3:1) was added to the top of a silica column. Elution with the same solvent mixture gave (**1a**) (0.13 g, 25%) followed by an intense red band which, on evaporation of the solvent, gave red crystals of $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}}]$ (**2a**) (0.3 g, 50%) (Found: C, 46.2; H, 4.3; P, 9.0. $\mathrm{C_{28}H_{30}Mo_2O_6P_2}$ requires C, 46.9; H, 4.2; P, 8.7%); mass spectrum: *m/e* 716 (M^+), $M^+ - n\mathrm{CO}$ (n = 0—3); $\nu_{\mathrm{max.}}$(CO) at 1 940s and 1 867s cm^{-1}. N.m.r.: ^{1}H (303 K), major isomer (93%), δ 7.5—7.2 (m, 10 H, Ph), 4.80 (s, 5 H, $\mathrm{C_5H_5}$), 4.63 (s, 5 H, $\mathrm{C_5H_5}$), 3.75 [d, ^3J(PH) 11.6, 9 H, OMe], and −11.97 [dd, ^2J(PH) 43.4, 39.0, 1 H, Mo(μ-H)Mo]; minor isomer (7%), δ 5.11 (s, 5 H, $\mathrm{C_5H_5}$), 4.76 (s, 5 H, $\mathrm{C_5H_5}$), 3.70 [d, ^3J(PH) 11, 9 H, OMe], and −12.53 [dd, ^2J(PH) 43.2, 38.6, 1 H, Mo(μ-H)Mo]; ^{13}C (293 K), δ 248.9 [dd, ^2J(PC) 35.1, 23.3, 1CO(*cis*)], 245.5 [d, ^2J(PC) 21.1, 1CO(*cis*)], 238.5 [s, 1CO(*trans*)], 145.4—127.1 (m, Ph), 92.2 (s, $\mathrm{C_5H_5}$), 90.7 (s, $\mathrm{C_5H_5}$), and 51.8 [q (^{1}H noise decoupled spectrum), J(CH) 145.3, OMe]; ^{31}P (293 K), δ 59.5 [s, $\mathrm{P(OMe)_3}$] and 35.5 (s, μ-$\mathrm{PPh_2}$).

The reaction of (**1a**) (0.062 g, 0.1 mmol) with $\mathrm{P(OMe)_3}$ (0.1 cm^3, 0.85 mmol) was also carried out thermally in refluxing hexane (50 cm^3) for 18 h. Unchanged (**1a**) (0.05 g, 81%) was the only product recovered.

(*b*) *With* $\mathrm{P(OPh)_3}$. Complex (**1a**) (0.35 g, 0.56 mmol) and $\mathrm{P(OPh)_3}$ (0.25 cm^3, 0.95 mmol) were photolysed as in (*a*) to give, by an analogous procedure, (**1a**) (0.21 g, 60%) and red crystalline $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OPh)_3\}}]$ (**2b**) (0.154 g, 30%) (Found: C, 57.4; H, 4.0; P, 5.9. $\mathrm{C_{43}H_{36}Mo_2O_6P_2}$ requires C, 57.2; H, 4.0; P, 6.9%); mass spectrum: *m/e* 780 (M^+ − PhOH − CO), M^+ − PhOH − nCO (n = 2 or 3); $\nu_{\mathrm{max.}}$(CO) at 1 954(sh), 1 942s, 1 878(sh), 1 868s, and 1 857(sh) cm^{-1}. N.m.r.: ^{1}H (303 K), major isomer (86%), δ 7.6—7.0 (m, 25 H, Ph), 4.83 (s, 5 H, $\mathrm{C_5H_5}$), 3.95 (s, 5 H, $\mathrm{C_5H_5}$), and −11.93 [dd, ^2J(PH) 42.4, 40.0, 1 H, Mo(μ-H)Mo]; minor isomer (14%), δ 4.78 (s, 5 H, $\mathrm{C_5H_5}$), 4.09 (s, 5 H, $\mathrm{C_5H_5}$), −12.07 [dd, ^2J(PH) 43.8, 41.1, Mo(μ-H)Mo].

(*c*) *With* $\mathrm{PPh_3}$. Complex (**1a**) (0.05 g, 0.08 mmol) and $\mathrm{PPh_3}$ (0.024 g, 0.092 mmol) were photolysed as in (*a*) to give, by an analogous procedure (**1a**) (0.015 g, 30%) and red crystalline $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3(PPh_3)}]$ (**2c**) (0.025 g, 37%) (Found: C, 60.5; H, 4.3; P, 7.6. $\mathrm{C_{43}H_{36}Mo_2O_3P_2}$ requires C, 60.4; H, 4.2; P, 7.3%); mass spectrum: 720 (M^+ − PhH − 2CO), 692 (M^+ − PhH − 3CO); $\nu_{\mathrm{max.}}$(CO) at 1 953(sh), 1 938s, 1 863s, and 1 832s cm^{-1}. N.m.r.: ^{1}H (303 K), major isomer (83%), δ 7.6—7.0 (m, 25 H, Ph), 4.38 (s, 5 H, $\mathrm{C_5H_5}$), 4.37 (s, 5 H, $\mathrm{C_5H_5}$), −11.45 [dd, ^2J(PH) 49.3, 33.2, 1 H, Mo(μ-H)Mo], minor isomer (17%), δ 4.91 (s, 5 H, $\mathrm{C_5H_5}$), 4.48 (s, 5 H, $\mathrm{C_5H_5}$), −12.06 [dd, ^2J(PH) 47.8, 35.5, 1 H, Mo(μ-H)Mo]. Attempted thermal substitution with $\mathrm{PPh_3}$ in refluxing hexane led only to very small amounts of decomposition after 18 h.

(*d*) *With* $\mathrm{P(C_6H_4Me\text{-}}m)_3$. Complex (**1a**) (0.2 g, 0.32 mmol) and $\mathrm{P(C_6H_4Me\text{-}}m)_3$ (0.12 g, 0.39 mmol) were photolysed as in (*a*) to give, by an analogous procedure (**1a**) (0.07 g, 35%) and red crystalline $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(C_6H_4Me\text{-}}m)_3\}]$ (**2d**) (0.092 g, 32%) (Found: C, 61.7; H, 4.8; P, 7.0. $\mathrm{C_{46}H_{42}Mo_2O_3P_2}$ requires C, 61.7; H, 4.8; P, 7.0%); mass spectrum: 776 (M^+ − $\mathrm{PhCH_3}$ − CO), M^+ − $\mathrm{PhCH_3}$ − nCO (n = 2 or 3); $\nu_{\mathrm{max.}}$(CO) at 1 955(sh), 1 936s, 1 861s, and 1 831s cm^{-1}. N.m.r.: ^{1}H (303 K), major isomer (87%), δ 7.5—7.1 (m, 22 H, Ph and $\mathrm{C_6}H_4\mathrm{Me}$-*m*), 4.37 (s, 5 H, $\mathrm{C_5H_5}$), 4.34 (s, 5 H, $\mathrm{C_5H_5}$), 2.35 (s, 9 H, $\mathrm{C_6H_4}Me$-*m*), and −11.38 [dd, ^2J(PH) 48.2, 32.2, 1 H, Mo(μ-H)Mo]; minor isomer (13%), δ 4.89 (s, 5 H, $\mathrm{C_5H_5}$), 4.46 (s, 5 H, $\mathrm{C_5H_5}$), 2.29 (s, 9 H, $\mathrm{C_6H_4}Me$-*m*), and −12.03 [dd, ^2J(PH) 49.0, 35.2, 1 H, Mo(μ-H)Mo].

(*e*) *With* $\mathrm{PEt_2Ph}$. Complex (**1a**) (0.2 g, 0.32 mmol) and $\mathrm{PEt_2Ph}$ (0.075 cm^3, 0.49 mmol) were photolysed as in (*a*) to give, by an analogous procedure (**1a**) (0.04 g, 20%) and red crystalline$[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3(PEt_2Ph)}]$(**2e**) (0.113 g, 48%) (Found: C, 55.7; H, 5.3; P, 8.4. $\mathrm{C_{35}H_{36}Mo_2O_3P_2}$ requires C, 55.4; H, 4.8; P, 8.2%); mass spectrum: 758 (M^+), 730 (M^+ − CO); $\nu_{\mathrm{max.}}$(CO) at 1 956m, 1 943s, 1 864s, 1 839(sh), and 1 829s cm^{-1}. N.m.r.: ^{1}H (303 K), major isomer (53%), δ 7.8—6.0 (m, 15 H, Ph), 4.69 (s, 5 H, $\mathrm{C_5H_5}$), 4.35 (s, 5 H, $\mathrm{C_5H_5}$), 2.5—0.8 (m, 10 H, PEt_2Ph), and −11.70 [dd, ^2J(PH) 58.5, 36.5, 1 H, Mo(μ-H)Mo]; minor isomer (47%), δ 5.02 [d, ^3J(PH) 1.0, 5 H, $\mathrm{C_5H_5}$], 4.66 (s, 5 H, $\mathrm{C_5H_5}$), −12.38 [dd, ^2J(PH) 45.9, 36.3, 1 H, Mo(μ-H)Mo].

(*f*) *With dppm*. Complex (**1a**) (0.186 g, 0.3 mmol) and dppm (0.173 g, 0.45 mmol) were photolysed as in (*a*) to give by an analogous procedure (**1a**) (0.081 g, 44%) and red crystalline $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3(dppm\text{-}}P)]$ (**2f**) (0.102 g, 35%) (Found: C, 62.1; H, 5.1. $\mathrm{C_{50}H_{43}Mo_2O_3P_2}$ requires C, 61.5; H, 4.4%); $\nu_{\mathrm{max.}}$(CO) at 1 957m, 1 945m, 1 940(sh), 1 862s, 1 832m, and 1 822w cm^{-1}. N.m.r.: ^{1}H (303 K) major isomer (52%), δ 7.9—6.2 (m, 30 H, Ph), 4.78 (d, 5 H, $\mathrm{C_5H_5}$), 4.38 (s, 5 H, $\mathrm{C_5H_5}$), 3.5—3.2 (m, 2 H, $\mathrm{CH_2}$), and −11.4 [dd, ^2J(PH) 55.7, 34.7, 1 H, Mo(μ-H)Mo]; minor isomer (48%), δ 4.80 (s, 5 H, $\mathrm{C_5H_5}$), 4.54 (s, 5 H, $\mathrm{C_5H_5}$), and −12.14 [dd, ^2J(PH) 47.8, 39.6, Mo(μ-H)Mo].

Crystal Data for (**2a**).—$\mathrm{C_{28}H_{30}Mo_2O_6P_2}$, M = 715.36, monoclinic, a = 35.835(7), b = 10.016(2), c = 16.862(2) Å, β = 111.34(2)°, U = 5 637.2 Å^3, space group $C2/c$, Z = 8, D_c = 1.57 g cm^{-3}, $F(000)$ = 2 928. Crystal size 0.24 × 0.18 × 0.12 mm; μ(Mo-K_α) = 9.33 cm^{-1}.

Data Collection.—Data were collected on a Phillips PW1100 diffractometer in the range θ 3—25°, with a scan width of 0.70°, using the technique described previously.[23] Lorentz polarisation corrections were applied, and equivalent reflections were merged to give 3 346 data with $I/\sigma(I) > 3.0$.

Structure Solution and Refinement.[24]—The co-ordinates of the metal atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. A difference-Fourier calculation using data with sinθ < 0.35 revealed maxima that appeared to correspond to some but not all the hydrogen atoms. The 'best' hydrogen atom for each methyl group was included in structure factor calculations to define the orientation. The remaining hydrogen atoms were included in calculated positions and were constrained to 'ride' on the relevant carbon atoms. The hydrogen atoms were given a common isotropic thermal parameter of 0.08 Å^2 which was not refined. A peak attributable to the hydrogen atom attached to the metal was located at *ca.* 1.9 Å from both metals and has been included in Figure 3, but not in the refinement. The molybdenum, phosphorus, oxygen, and carbonyl carbon atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at R 0.061 and R' 0.066, with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, intermolecular distances, and remaining bond length and angles.

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