Synthesis and Substitution Reactions of a Heterodimetallic Molybdenum–Manganese Complex, $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$; *X*-Ray Crystal Structure of $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4(dppm\text{-}PP')]$†

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The photolytic reaction of $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ with PPh_2H gives $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ (**1**) and $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$ as the major products. Complex (**1**) reacts photolytically with two-electron donor ligands, L, to give the substituted complexes $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5L]$ [L = $P(OMe)_3$ (**2a**), PPh_3 (**2b**), or $CNCH_2Ph$ (**2c**)], $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4L_2]$ [L = $P(OMe)_3$ (**3a**), L_2 = dppm-*PP'* (**3b**) (dppm = $Ph_2PCH_2PPh_2$), or L = $CNCH_2Ph$ (**3c**)], and $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}L)(\eta^5\text{-}C_5H_5)(CO)_4]$ [L = dppm-*PP'* (**4**)]. An n.m.r. study reveals that the ligands L in complexes (**2**) and (**3**) have replaced respectively one or two carbonyl groups on the manganese atom. This has been confirmed for (**3b**) by *X*-ray analysis. Complex (**4**), an isomer of (**3b**) in which the dppm ligand adopts a bridging rather than a chelating bonding mode, is formed irreversibly from (**3b**) on photolysis.

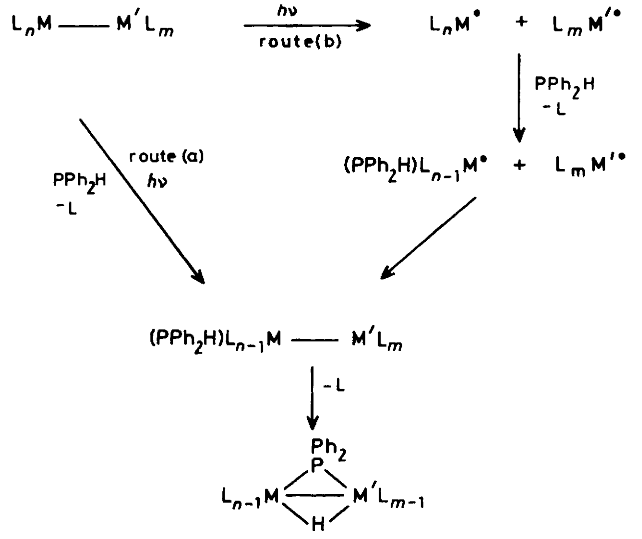
Despite their potentially interesting chemistry relatively few studies of the reactivity of heterodinuclear hydrido-bridged transition-metal complexes have been undertaken.[1–8] This is due in part to the small number of complexes of this type which have been synthesised in adequate yields.

An efficient method of synthesis of homodinuclear transition-metal complexes containing bridging hydrido and phosphido ligands involves the oxidative addition of a secondary phosphine, PR_2H, to a dinuclear carbonyl complex.[9–13] The direct synthesis of corresponding heterodinuclear complexes by this method has not been reported, although Powell *et al.*[3,4] have successfully employed the oxidative addition of a metallophosphine complex, $[M(PR_2H)]$ [M = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, or $(\eta^5\text{-}C_5H_5)Re(CO)(NO)^+$] to a second mononuclear complex to prepare complexes of this type.

In this paper we report the synthesis in *ca.* 40% yield of a μ-hydrido-μ-phosphido-molybdenummanganese complex, $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ (1) from the reaction of PPh_2H with the unbridged heterodinuclear complex $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$[14] and describe the substitution reactions of (1) with some two-electron donor ligands. A preliminary account of part of this work has appeared.[8] A complex closely related to (1), $[MoMn(\mu\text{-}H)\{\mu\text{-}P(C_6H_4Me\text{-}p)_2\}(\eta^5\text{-}C_5H_5)(CO)_6]$, has recently been synthesised in *ca.* 20% yield by Casey and Bullock[15] but the route employed is significantly longer and less convenient than the preparation based on the direct reaction of $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ and PPh_2H. Apart from this complex, the few other known examples of μ-hydrido μ-phosphido heterodimetallic complexes include $[CoIr(\mu\text{-}H)(\mu\text{-}PF_2)(PF_3)_6]$,[16] $[FeMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5]$,[17] and a series of neutral[3] and cationic[4,6] mixed-metal platinum-containing species.

Results and Discussion

Preparation and Fluxional Behaviour of Complex (1).—Reaction of $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ with a slight excess of PPh_2H in hexane–benzene (4:3) solution under u.v. irradiation affords (1) and $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$[18] in approximately equal yield. A number of minor products obtained in the reaction included some unreacted starting material and a trace of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$.[8] Complex (1) has been characterised by i.r., ^1H, ^{13}C, and ^{31}P n.m.r., mass spectroscopy, and microanalysis (see Experimental section) and its structure in the solid state has been determined by *X*-ray diffraction.[8]



Scheme 1. Alternative initial steps in the photochemical synthesis of complex (1)

As shown in Scheme 1 two alternative routes may be proposed for the initial step in the photochemical synthesis of complex (1). Route (a) involves direct substitution of CO by PPh_2H in the dinuclear precursor; route (b) involves homolytic metal–metal bond cleavage and CO substitution by PPh_2H in one of the radicals, followed by radical recombination. Loss of CO from the PPh_2H-substituted heterodinuclear complex and oxidative addition of the P–H bond to the second metal centre are the most probable subsequent steps leading to the formation of (1).

It is known that u.v. irradiation of $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ results in the formation of an equilibrium mixture of the starting

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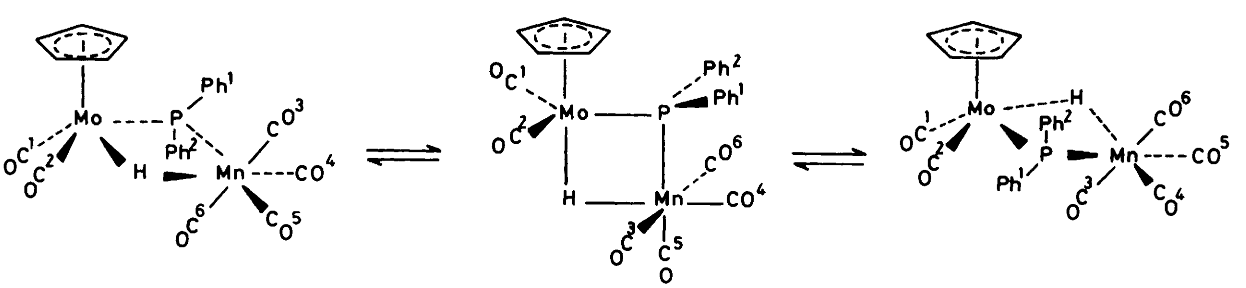
† 1-[Bis(diphenylphosphino)methane-*PP'*]-1,1,2,2-tetracarbonyl-2-η-cyclopentadienyl-μ-diphenylphosphido-μ-hydrido-manganesemolybdenum (*Mn–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.



Scheme 2. Fluxional process responsible for variations with temperature of the ^{1}H and ^{13}C n.m.r. spectra of complex (1)

complex and $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ and $[Mn_2(CO)_{10}]$ *via* a mechanism involving homolytic metal–metal bond cleavage.[14] The facile radical generation under the reaction conditions, combined with the ease of associative ligand substitution in such radicals,[19,20] supports (b) as the major route to (**1**). On the other hand, route (a) cannot be entirely discounted in the formation of (**1**), since recent studies indicate that direct CO dissociation and metal–metal bond homolysis are competitive photoprocesses for both $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ and $[Mn_2(CO)_{10}]$.[19]

Irradiation of a 1:1:2 mixture of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$, $[Mn_2(CO)_{10}]$, and PPh_2H gave less than 5% yield of complex (**1**), the major products of this latter reaction being $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (*ca.* 60%) and unreacted $[Mn_2(CO)_{10}]$ (*ca.* 80%). The much greater yield of (**1**) obtained on irradiation of the mixed-metal dimer is presumably due to the more facile generation of $[Mn(CO)_5]^{\bullet}$ radicals from this species, as expected from the order of lability of the metal–metal bonds concerned [Mo–Mo > Mo–Mn > Mn–Mn].[21]

The ^{1}H n.m.r. spectrum of complex (**1**) at room temperature shows, in addition to a sharp singlet and doublet due to the cyclopentadienyl and metal hydride ligands respectively, very broad resonances in the phenyl region. The phenyl and carbonyl group resonances in the $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum at room temperature are also very broad. At 219 K five ^{13}CO resonances are observed. Of these the two at lowest field may be assigned to two carbonyl ligands on Mo on the basis of the similarity in chemical shifts to those of the CO groups in $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$;[22] the three upfield resonances in a *ca.* 2:1:1 intensity ratio are ^{55}Mn quadrupole broadened and are assigned to the four carbonyl ligands on Mn. At 331 K the two resonances due to the carbonyl ligands on Mo coalesce to give a single resonance, as do the two upfield resonances of relative intensity one. On the other hand the broad resonance of relative intensity two remains unchanged over the range of 219—331 K. Seven ^{13}C phenyl resonances are observed at 219 K, one of which is due to two superimposed resonances; at 331 K, however, four sharp resonances are seen with chemical shifts the average of those for pairs of low-temperature resonances.

The above changes in the $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum of complex (**1**) with temperature can be understood in terms of the fluxional process shown in Scheme 2 which has also been invoked by Casey and Bullock for the corresponding $\mu\text{-}P(C_6H_4Me\text{-}p)_2$[15] complex and for $[MoFe(\mu\text{-}AsMe_2)(\eta^5\text{-}C_5H_5)(CO)_6]$.[23] It involves a change in geometry at Mo from square pyramidal (if the Mo–Mn bond is ignored) to trigonal bipyramidal in the postulated intermediate. Such a process results in the exchange of the environment of the two phenyl groups, of the two carbonyl ligands on Mo, and of the two axial groups, CO^3 and CO^6, on Mn. The temperature-invariant ^{13}CO resonance must then be assigned as being degenerate and due to the two equatorial CO groups on Mn, the environments of which are not interconverted in the fluxional process. The above explanation assumes that there is no localised rotation of the carbonyl ligands on the Mn atom; this has been shown to be the case in the related homonuclear complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$.[24]

Substitution Reactions of Complex (**1**).—Reactions between donor ligands and bridge-stabilised heterodinuclear complexes may lead to addition products[1,25] either with[3,26—28] or without[27] metal–metal bond cleavage. Alternatively simple substitution reactions may be observed[3,29—31] although these may sometimes involve associative intermediates.[32]

The reaction of complex (**1**) with two-electron donor ligands, L, under u.v. irradiation in hexane–benzene solution results in the formation of substitution products of general formula $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5L]$ [L = $P(OMe)_3$ (**2a**), PPh_3 (**2b**), or $CNCH_2Ph$ (**2c**)], $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4L_2]$ [L = $P(OMe)_3$ (**3a**), L_2 = dppm-*PP'* (**3b**), or L = $CNCH_2Ph$ (**3c**)], and $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}L)(\eta^5\text{-}C_5H_5)(CO)_4]$ (L = μ-dppm-*PP'* (**4**); dppm = $Ph_2PCH_2PPh_2$). The yield of the monosubstituted products (**2**) in relation to the disubstituted products (**3**) may be maximised by using a minimum quantity of hexane as the reaction solvent rather than hexane–benzene (9:1); the monosubstituted product then precipitates from solution. The reactions do not proceed in the absence of u.v. irradiation at room temperature and, after prolonged stirring of (**1**) in the dark with either $P(OMe)_3$ or PPh_3, the starting complex was recovered in almost quantitative yield.

The complexes (**2**)—(**4**) have been characterised by i.r. and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy, mass spectrometry, and microanalysis (see Experimental section) and the structure of (**3b**) has been confirmed by a single-crystal *X*-ray analysis.

The observation of five absorption bands in the i.r. (ν_{CO}) spectra of (**2a**)—(**2c**) is consistent with monosubstitution having taken place in these complexes. This is supported for (**2c**) by the single i.r. ν(CNR) band. Furthermore five ^{13}C n.m.r. resonances are observed in the carbonyl region for both (**2a**) and (**2b**). On the basis of similar chemical shifts and $^{31}P\text{-}^{13}C$ coupling constants to those for corresponding resonances of complex (**1**), the two sharp downfield resonances are assigned in each case to two carbonyl ligands on Mo. The three broad upfield resonances may each be assigned to a carbonyl group bonded to manganese, with the fourth group present on manganese in complex (**1**) having been replaced by the substituent. The broadening is presumably due to the manganese quadrupole and to coupling to one or both of the phosphorus atoms.

The ^{1}H n.m.r. spectra of (**2a**)—(**2c**) are consistent with each complex being present in solution as a single isomer. Of the several possibilities some are unlikely on the basis of the n.m.r. data. Thus the bridging metal hydride resonance in (**2a**) and (**2b**) shows coupling to two phosphorus nuclei with coupling constants in the range 21—33 Hz. *cis* $^{31}P\text{-}^{1}H$ Two-bond coupling constants for manganese complexes have previously been reported to lie in the range 25—60 Hz.[33] Corresponding data for complexes of Mn containing *trans* metal hydride and

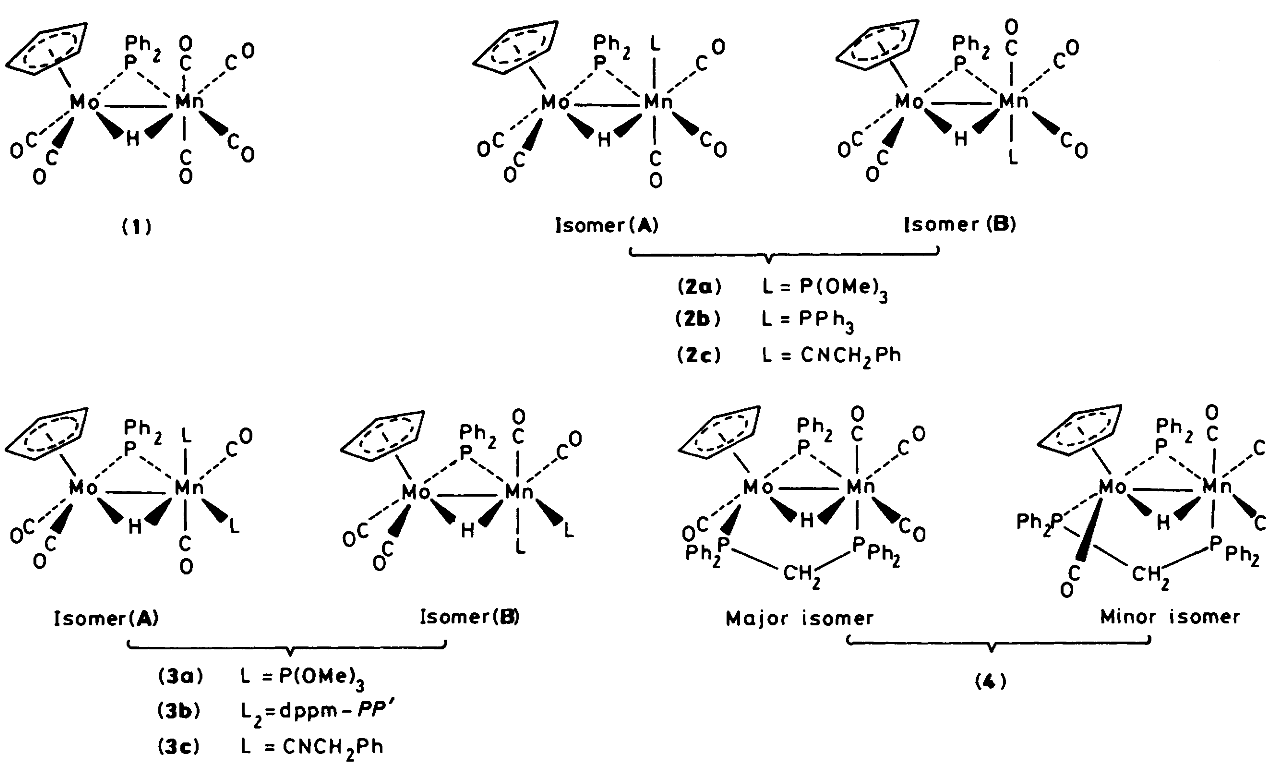


Figure 1. Proposed structures for the new complexes. Three isomers of complex (**3c**) are present in solution which may include (**A**) and/or (**B**)

phosphorus ligands are not available, but they would almost certainly be larger in comparable complexes and the fact that coupling constants for (**2a**) and (**2b**) are at the lower end of the range for *cis* complexes suggests that the metal hydride ligand in (**2a**) and (**2b**) is *cis* to both the μ-PPh_2 and the PR_3 ligands. The lack of any resolved ^{31}P–^{31}P coupling in the ^{31}P-$\{^1H\}$ n.m.r. spectra of (**2a**) and (**2b**) indicates that the two phosphorus nuclei are also mutually *cis*, since a *trans* orientation would result in a large coupling constant.

On the basis of these data it is proposed that complexes (**2a**) and (**2b**) adopt one of the two geometries shown in Figure 1. Although the data do not permit a distinction to be made, the steric crowding involving the cyclopentadienyl and phosphine ligands is minimised in (**B**). The close similarity between the i.r. (ν_{CO}) spectrum of (**2c**) and those of (**2a**) and (**2b**) suggests that (**2c**) has the same solution structure as the other two.

Unlike the series of monosubstituted products (**2a**)—(**2c**), the i.r. (ν_{CO}) spectra of complexes (**3a**) and (**3b**) are significantly different from each other. However, the ^{13}C n.m.r. spectra of the two complexes in the carbonyl region are similar in form. The two sharp downfield resonances may be assigned to two carbonyl ligands on Mo on the basis of their similarity to corresponding resonances of (**1**), (**2a**), and (**2b**). The two upfield resonances, which are again broad, are assigned to two carbonyl ligands on Mn. The observation for (**3a**) of three ^{31}P n.m.r. resonances, two of which may be assigned to inequivalent $P(OMe)_3$ ligands, confirms that disubstitution has occurred. The metal hydride resonance in the ^1H n.m.r. spectra of (**3a**) and (**3b**) shows coupling to all three phosphorus nuclei with ^{31}P–H coupling constants in the range 17—34 Hz for (**3a**) and 17—52 Hz for (**3b**). The magnitude of these coupling constants suggests that the hydride ligand adopts a *cis* orientation relative to the three phosphorus nuclei. Furthermore, the resonance due to the μ-PPh_2 ligand in the ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**3a**) is a well resolved doublet [$^2J(PP)$ 41.2 Hz]. These n.m.r. data can be explained for (**3a**) in terms of isomer (**A**) or (**B**) (Figure 1) being present, with the μ-PPh_2 ligand showing coupling to the *trans* but not the *cis* $P(OMe)_3$ group. The ^{31}P resonances due to the $P(OMe)_3$ groups themselves are too broad to allow any coupling to be resolved.

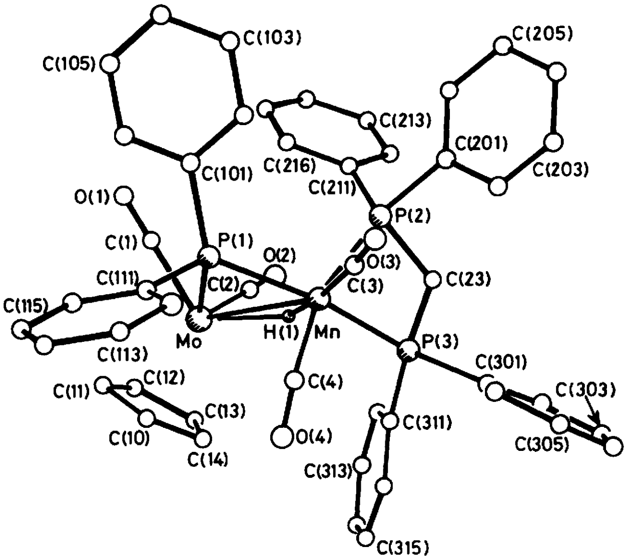


Figure 2. Molecular structure of $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4(dppm\text{-}PP')]$ (**3b**) showing the crystallographic numbering

In the ^{31}P-$\{^1H\}$ n.m.r. spectrum of complex (**3b**), only one of the dppm resonances, at δ −128.5, shows resolved coupling to the μ-PPh_2 ligand [$^2J(PP)$ 29.7 Hz]; the other, at δ −99.5, is coupled only to the other dppm phosphorus [$^2J(PP)$ 44.2 Hz]. The dppm resonances at δ −128.5 and −99.5 may therefore be assigned respectively to phosphorus *trans* and *cis* to μ-PPh_2. These data are again in accord with either of the isomers in Figure 1. In order to distinguish between these possibilities, at least in the solid state, a single-crystal *X*-ray diffraction study of

Table 1. Selected bond lengths (Å) and angles (°) for [MoMn(μ-H)(μ-PPh_2)(η^5-C_5H_5)$(CO)_4$(dppm-*PP′*)] (**3b**)

Mn–Mo	3.092(1)	H(1)–Mn	1.80(6)
H(1)–Mo	1.81(5)	P(1)–Mn	2.234(2)
P(1)–Mo	2.482(2)	P(2)–Mn	2.376(3)
C(10)–Mo	2.374(12)	P(3)–Mn	2.254(2)
C(11)–Mo	2.317(9)	C(3)–Mn	1.779(8)
C(12)–Mo	2.298(10)	C(4)–Mn	1.778(11)
C(13)–Mo	2.352(12)	C(101)–P(1)	1.840(11)
C(14)–Mo	2.396(12)	C(111)–P(1)	1.831(8)
C(1)–Mo	1.954(10)	C(23)–P(2)	1.858(8)
C(2)–Mo	1.950(9)	C(201)–P(2)	1.842(8)
		C(211)–P(2)	1.815(8)
		C(23)–P(3)	1.833(10)
		C(301)–P(3)	1.833(6)
		C(311)–P(3)	1.819(10)

H(1)–Mo–Mn	31(2)	H(1)–Mn–Mo	31(2)
P(1)–Mo–Mn	45.6(1)	P(1)–Mn–Mo	52.6(1)
P(1)–Mo–H(1)	75(2)	P(1)–Mn–H(1)	82(2)
C(1)–Mo–Mn	115.0(2)	P(2)–Mn–Mo	100.2(1)
C(1)–Mo–H(1)	121(3)	P(2)–Mn–H(1)	81(3)
C(1)–Mo–P(1)	81.4(2)	P(2)–Mn–P(1)	106.3(1)
C(2)–Mo–Mn	94.5(2)	P(3)–Mn–Mo	105.6(1)
C(2)–Mo–H(1)	67(2)	P(3)–Mn–H(1)	77(2)
C(2)–Mo–P(1)	118.9(3)	P(3)–Mn–P(1)	158.0(1)
Mn–H(1)–Mo	118(3)	P(3)–Mn–P(2)	72.1(1)
Mn–P(1)–Mo	81.8(1)	C(3)–Mn–Mo	149.6(2)
C(23)–P(2)–Mn	92.9(3)	C(3)–Mn–H(1)	170(3)
C(201)–P(2)–Mn	120.6(3)	C(3)–Mn–P(1)	97.1(2)
C(201)–P(2)–C(23)	102.8(3)	C(3)–Mn–P(2)	90.4(3)
C(211)–P(2)–Mn	128.7(2)	C(3)–Mn–P(3)	104.8(2)
C(211)–P(2)–C(23)	103.9(4)	C(4)–Mn–Mo	88.9(2)
P(3)–C(23)–P(2)	95.2(3)	C(4)–Mn–H(1)	100(3)
C(23)–P(3)–Mn	97.7(2)	C(4)–Mn–P(1)	91.6(2)
C(301)–P(3)–Mn	123.9(2)	C(4)–Mn–P(2)	162.0(2)
C(301)–P(3)–C(23)	107.6(3)	C(4)–Mn–P(3)	90.7(3)
C(311)–P(3)–Mn	118.7(2)	C(4)–Mn–C(3)	89.3(4)
C(311)–P(3)–C(23)	108.9(4)		

(**3b**) was undertaken. Suitable crystals were grown by slow cooling of a hexane–dichloromethane (1:1) solution.

The molecular structure of complex (**3b**) is shown in Figure 2 and Table 1 lists selected bond lengths and bond angles. The dppm ligand is bonded as a chelate to the manganese centre, which is approximately octahedrally co-ordinated by this ligand, two carbonyl ligands, and the phosphido and hydrido ligands (the hydride was located in the *X*-ray study) if the metal–metal bond is ignored. One of the dppm phosphorus atoms is in the equatorial plane [as defined by Mo, P(1), Mn, P(3)] and the other in the axial plane. The most significant deviation from the geometry of complex (**1**)[8] is of this axial dppm phosphorus atom, P(2); the (PPh_2)–Mn–P(2) angle of 106.3(1)° compares to an average of 91.6(2)° for the axial carbonyl ligands in (**1**). The 'bending back' of P(2) is related to the requirement of the chelating ligand for a small bite angle [P(2)–Mn–P(3)] at manganese of 72.1(1)°. The P(3)–Mn–(PPh_2) angle of 158.0(1)° is also narrower than that of 167.3(2)° in (**1**). The two carbonyl ligands and the phosphido group at Mn are close to orthogonal. The replacement of two carbonyl ligands on Mn in (**1**) by the poorer π-acid dppm ligand in (**3b**) results in reduced Mn–CO bond distances from 1.849(6) Å in (**1**) to 1.778(11) Å (CO *trans* to dppm) in (**3b**) and from 1.811(5) to 1.779(8) Å (CO *trans* to H). Similarly, the Mn–P (dppm, *trans* to CO) bond distance of 2.376(3) Å is longer than the Mn–P (dppm, *trans* to PPh_2) distance of 2.254(2) Å as a result of the greater π-acid character of CO compared to the μ-PPh_2 group. The reduction in the Mn–(PPh_2) bond distance from 2.294(2) Å in complex (**1**) to 2.234(2) Å in (**3b**), as a result of the *trans* dppm ligand, is accompanied by an increase in the Mo–(PPh_2) distance from 2.435(2) to 2.482(2) Å. The similar Mo–Mn bond distance of 3.092(1) Å in (**3b**) compared to 3.088(1) Å in (**1**), and similar average M–(PPh_2) distances in the two complexes, results in a similar bite angle at the phosphido bridge of 81.8(1)° in (**3b**) compared to 81.5(0)° in (**1**). The Mn–Mo distance in (**3b**) lies close to the high end of the range of values [2.963(2)—3.088(1) Å] for Mn–Mo 'single' bonds in other bimetallic complexes, the metal separation being sensitive to the nature of the bridging ligands.[8,34] The geometry of the ligands at the molybdenum centre in (**3b**) is very close to that in complex (**1**) with Mo–CO and average Mo–C(cyclopentadienyl) distances equal within error limits and differences of 2° in the Mn–Mo–CO interbond angles.

The above structure determination shows that isomer (**B**) (Figure 1) is favoured for (**3b**) in the solid state and it seems most likely that this isomer is also favoured for (**3a**). This can be accounted for in terms of a reduced steric interaction of the bulky dppm and cyclopentadienyl ligands in (**B**) as compared to (**A**).

The axial co-ordination of one of the dppm phosphorus nuclei in complex (**3b**) is consistent with the suggestion, discussed above, that the monosubstituted complexes (**2a**)—(**2c**) are formed on loss of an axial carbonyl ligand from the manganese atom. Attempted synthesis of the presumed intermediate in the formation of (**3b**), a dppm analogue of (**2a**)—(**2c**), was unsuccessful despite the use of short u.v. irradiation times. It is clear that chelation occurs rapidly after monosubstitution. Potential steric crowding may explain the non-formation of an alternative chelation product, involving substitution of two carbonyl ligands *cis* to the phosphido group. It may also explain why PPh_3 does not give a disubstituted derivative analogous to that obtained with the less sterically demanding ligand $P(OMe)_3$. However, the likely decreased lability of the carbonyl ligands on Mn in complex (**2b**), compared to (**2a**), due to the reduced π-acid character of PPh_3 compared to $P(OMe)_3$, may also hinder disubstitution by PPh_3.

The greater π-acidity of $PhCH_2NC$ compared to PPh_3, together with its reduced steric bulk, might be expected to favour the substitution of more than one CO group in complex (**1**) and the mass spectrum of (**3c**), a major product of the reaction of (**1**) with $PhCH_2NC$, contains a parent molecular ion peak at *m/e* 748, indicating that disubstitution has occurred. Furthermore the i.r. (ν_{CO}) spectrum of (**3c**) is very similar to that of (**3a**) and, in addition, two broad bands are seen in the ν(CNR) region. However, the ^{1}H n.m.r spectrum of (**3c**) shows the presence of three isomers in solution, each giving a cyclopentadienyl and a metal hydride resonance, in a ratio of *ca.* 1.6:1.1:1.0. The i.r. similarity between (**3a**) and (**3c**), together with the pattern of substitution by $P(OMe)_3$, suggests that all three isomers involve disubstitution at Mn. However, even with the further assumption that one ligand is axially substituted, there are still five possible isomeric structures for (**3c**) and it is not possible to infer from the spectroscopic data which three are present.

U.v. irradiation of a hexane–benzene solution of (**1**) and dppm gives, in addition to (**3b**), a second major product, [MoMn(μ-H)(μ-PPh_2)(μ-dppm)(η^5-C_5H_5)$(CO)_4$] (**4**) the yield of which, in relation to that of (**3b**), increases as the reaction time is increased. Complex (**4**) is also rapidly formed, with a conversion factor of 67% on u.v. irradiation of a solution of (**3b**).

The formulation of (**4**) as a μ-dppm complex is based on its ^{1}H and ^{13}C n.m.r. spectra. Thus the ^{1}H n.m.r. spectrum indicates that two isomers are present in solution in a ratio of *ca.* 7:3. Each shows resonances due to phenyl groups, a cyclopentadienyl ligand, a dppm methylene group, and a hydride ligand. In both isomers the hydride ligand is coupled to three non-equivalent phosphorus atoms. The $^{13}C-\{^1H\}$ n.m.r. spectrum at room temperature shows signals due to the cyclopentadienyl ligands in each of the isomers, but only the resonances due to the carbonyl ligands in the major isomer were resolved. Of these the three broad upfield resonances are assigned to CO groups on Mn and the sharp low-field doublet of doublets at δ 251.4 [^2J(PC) 25.2, 19.8 Hz] to the CO on the Mo atom. This resonance is similar in position to that observed for the CO on the phosphine-substituted Mo atom in $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_3\{P(OMe)_3\}]$ at δ 248.9 [^2J(PC) 35.1, 23.3 Hz].[22] The most likely structure for the major isomer of (**4**), based on a comparison of coupling-constant data with those for complexes (**2**) and (**3**) and the above dimolybdenum complex, in which the carbonyl ligand giving rise to the resonance at δ 248.9 is *cis* to both the $P(OMe)_3$ and $\mu\text{-}PPh_2$ ligands, is shown in Figure 1. A more tentative proposal as to the structure of the minor isomer is also given. In both isomers the requirement for the dppm ligand to bridge the Mo–Mn bond constrains the dppm to be axially co-ordinated at Mn. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**4**), which exhibits three resonances each for the major and minor isomers, is consistent with these proposals.

The only other reported example of a heterodimetallic complex containing both $\mu\text{-}PPh_2$ and μ-dppm ligands is $[RuCo(\mu\text{-}PPh_2)(\mu\text{-}dppm)(CO)_7]$.[35] This may be obtained on heating the isomeric cobalt–ruthenium complex $[RuCo(\mu\text{-}PPh_2)(dppm\text{-}PP')(CO)_7]$, in which the dppm ligand chelates the Ru atom, with 1 equivalent of dppm. In the absence of excess of dppm the isomerisation does not proceed.

Mechanism of Reactions of Complex (**1**) *with Donor Ligands*.—It is clear that the reactions of the heterodinuclear complex, (**1**), with organophosphines and benzyl isocyanide follow a pattern similar to that observed previously for the analogous homodinuclear manganese complex.[10] There is no evidence for the formation of simple 1:1 addition products with concomitant metal–metal bond breaking. Instead, substitution of one or two carbonyl ligands occurs. The formation of complexes (**2**) and (**3**) clearly shows that the carbonyl ligands on Mn are more labile than those on Mo. However the conversion of (**3b**) into (**4**) on u.v. irradiation indicates that the kinetically favoured product is not necessarily also the thermodynamically most stable.

At least three non-radical mechanisms can be envisaged for the photochemical substitution reactions of complex (**1**): (*i*) photochemical loss of CO, followed by co-ordination of the incoming ligand, as observed by Geoffroy and co-workers[36] in substitution reactions of $[FeRu_3H_2(CO)_{13}]$ with PR_3; (*ii*) co-ordination of the ligand with concomitant metal–metal bond cleavage followed by (photochemical) loss of CO, similar to the thermal substitution reactions of $[(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3]$, carried out by Langenbach and Vahrenkamp;[32] (*iii*) reversible photochemical generation of an excited state of (**1**), which may co-ordinate a ligand prior to CO loss, as suggested by Iggo *et al.*[10] to explain the substitution and insertion reactions of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$.

Prolonged u.v. irradiation of a N_2-purged solution of complex (**1**) resulted in slow decomposition and no change in the i.r. spectrum of the solution. On stirring the irradiated solution with $P(OMe)_3$ in the dark no substitution products were obtained and there is therefore no evidence for mechanism (*i*). Stirring a solution of (**1**), either with a large excess of $P(OMe)_3$ in the dark, or under 60 atm (*ca.* 6 × 10^6 Pa) CO, does not result in the formation of addition products, as judged by the i.r. spectrum of the final reaction mixture in each case and there is also therefore a lack of evidence for mechanism (*ii*). It thus appears that a photochemically generated excited state of (**1**), similar to that proposed in the photochemical reactions of the related Mn_2 complex,[10] is most likely to be involved.

Experimental

All reactions were carried out under a nitrogen atmosphere in N_2-saturated solvents distilled from an appropriate drying agent and stored over 4A molecular sieves. The instrumentation used to obtain spectroscopic data has been previously described.[37] Phosphorus-31 n.m.r. chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. Preparative thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25-mm layer of silica. The complex $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ was prepared by the literature method.[14] Photolysis experiments were conducted in a glass vessel with a quartz inner tube containing a Hanovia medium-pressure u.v. lamp (125 W).

Synthesis of $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ (**1**).—A mixture of $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ (6.2 g, 14.1 mmol) and PPh_2H (2.70 cm^3, 15.5 mmol) was dissolved in hexane–benzene (4:3, 700 cm^3) and irradiated with u.v. light for 7.5 h, during which time the colour of the solution changed from orange to dark red-orange. The solvent was removed on a rotary evaporator and the residue, after being 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 3 cm × 30 cm chromatography column (Kieselgel 60, 70—230 mesh). Elution with hexane–toluene (3:1) gave (decreasing R_f values) a trace of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$,[10] $[MoMn(\eta^5\text{-}C_5H_5)(CO)_8]$ (0.3 g, 5%), $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ (**1**) (3.0 g, 37%), $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$[18] (1.66 g, 38%), and several air-unstable yellow and orange complexes in low yield which were not characterised. Recrystallisation from hexane–dichloromethane (1:1) gave (**1**) as bright orange crystals (Found: C, 48.2; H, 2.7; P, 5.1. $C_{23}H_{16}MnMoO_6P$ requires C, 48.4; H, 2.8; P, 5.4%); mass spectrum, *m/e* 570 (M^+), $M^+ - n$CO (n = 1—6); $\nu_{max.}$(CO) (n-hexane) at 2 072m, 2 001m, 1 979s, 1 964s, and 1 903m cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 8.0—6.9 (m, 10 H, Ph), 5.03 (s, 5 H, C_5H_5), and −13.98 [d, 1 H, ^2J(PH) 32.4, Mo(μ-H)Mn]; ^{13}C($CDCl_3$, 220 K, ^{1}H gated decoupled), δ 242.2 [d, ^2J(PC) 25.9, 1Mo(CO)(*cis*)], 234.8 [s, 1Mo(CO)(*trans*)], 218.6 [m, 2Mn(CO)], 211.2 [d, ^2J(PC) 12.2, 1Mn(CO)], 208.3 [d, ^2J(PC) 12.6, 1Mn(CO)], 140.3 [d, ^1J(PC) 33.0, PC], 139.9 [d, ^1J(PC) 34.1, PC], 134.7 [d, ^2J(PC) 7.7, *o*-Ph], 131.9 [d, ^2J(PC) 10.0, *o*-Ph], 130.1 (s, *p*-Ph), 128.9 [d, ^3J(PC) 8.3, *m*-Ph], 128.8 (s, *p*-Ph), 128.1 [d, ^3J(PC) 10.7, *m*-Ph], and 92.0 (s, C_5H_5); at 331 K, δ 237.7 [m, 2Mo(CO)], 218.2 [m, 2Mn(CO)], 210.2 [m, 2Mn(CO)], 140.9 [d, ^1J(PC) 33.1, PC], 133.3 (s, *o*-Ph), 129.2 (s, *p*-Ph), 128.2 [d, ^3J(PC) 9.6 Hz, *m*-Ph], and 92.0 (s, C_5H_5); ^{31}P($CDCl_3$, ^{1}H gated decoupled), δ 17.5 (s, $\mu\text{-}PPh_2$).

Substitution Reactions of Complex (**1**).—(*a*) *With* $P(OMe)_3$. A solution of complex (**1**) (0.114 g, 0.2 mmol) and $P(OMe)_3$ (0.047 cm^3, 0.4 mmol) in hexane–benzene (9:1, 50 cm^3) was irradiated with u.v. light for 1.5 h. The colour of the solution changed from orange to bright red during this time. The solvent was removed on a rotary evaporator and the residue, after being dissolved in the minimum of CH_2Cl_2, was applied to the base of t.l.c. plates. Elution with hexane–dichloromethane (3:1) and evaporation of the solvent gave yellow crystalline $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5\{P(OMe)_3\}]$ (**2a**) (0.031 g, 23%) and orange crystalline $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4\{P(OMe)_3\}_2]$ (**3a**) (0.112 g, 73%). The yield of (**2a**) relative to (**3a**) can be increased by the use of a 1:1 ratio of (**1**) and $P(OMe)_3$ and by the use of 100% hexane as solvent, which leads to the precipitation of (**2a**) from solution as it is formed (Found:

Table 2. Atomic co-ordinates (× 10^4) for complex (**3b**)

Atom	x	y	z	Atom	x	y	z
Mo	693(1)	6 354(1)	1 045(1)	C(216)	2 063(3)	6 031(5)	791(4)
Mn	1 837(1)	7 201(1)	2 224(1)	C(211)	2 479(3)	5 818(4)	1 479(3)
H(1)	1 427(27)	6 267(36)	1 833(31)	C(302)	3 083(3)	5 954(5)	4 493(4)
P(1)	1 195(1)	7 684(1)	1 161(1)	C(303)	3 440(4)	6 171(7)	5 184(4)
C(102)	2 030(4)	8 189(5)	869(4)	C(304)	3 505(4)	6 968(7)	5 399(4)
C(103)	2 214(4)	8 469(6)	451(5)	C(305)	3 214(4)	7 577(6)	4 913(4)
C(104)	1 799(5)	8 579(7)	−254(5)	C(306)	2 853(4)	7 384(5)	4 218(4)
C(105)	1 208(5)	8 411(6)	−535(5)	C(301)	2 778(3)	6 576(4)	4 008(3)
C(106)	1 023(4)	8 135(5)	−118(4)	C(312)	1 635(4)	4 801(5)	2 898(4)
C(101)	1 435(3)	8 018(4)	595(4)	C(313)	1 236(5)	4 324(6)	2 963(5)
C(112)	986(4)	9 239(5)	1 514(4)	C(314)	985(5)	4 637(8)	3 298(5)
C(113)	650(4)	9 926(5)	1 443(5)	C(315)	1 118(4)	5 405(8)	3 574(5)
C(114)	72(5)	9 973(6)	903(5)	C(316)	1 519(4)	5 869(5)	3 525(4)
C(115)	−183(4)	9 352(6)	430(5)	C(311)	1 781(3)	5 587(5)	3 192(4)
C(116)	148(3)	8 660(5)	503(4)	C(10)	8(4)	6 960(5)	1 260(5)
C(111)	742(3)	8 585(4)	1 052(4)	C(11)	−305(4)	6 624(6)	582(5)
P(2)	2 572(1)	6 456(1)	2 173(1)	C(12)	−214(4)	5 756(6)	653(5)
C(23)	2 682(3)	5 701(4)	2 835(4)	C(13)	150(4)	5 564(6)	1 365(5)
P(3)	2 260(1)	6 290(1)	3 101(1)	C(14)	275(4)	6 303(6)	1 725(4)
C(202)	3 623(4)	7 218(5)	3 204(4)	C(1)	596(3)	6 367(4)	148(4)
C(203)	4 204(4)	7 518(6)	3 511(4)	O(1)	523(3)	6 329(4)	−390(3)
C(204)	4 492(4)	7 470(5)	3 178(5)	C(2)	1 095(3)	5 332(5)	1 093(4)
C(205)	4 198(4)	7 150(6)	2 523(5)	O(2)	1 294(3)	4 695(4)	1 098(3)
C(206)	3 613(4)	6 851(5)	2 210(4)	C(3)	2 312(4)	8 078(5)	2 549(4)
C(201)	3 325(3)	6 884(4)	2 553(4)	O(3)	2 607(3)	8 661(4)	2 727(3)
C(212)	2 815(3)	5 107(5)	1 612(4)	C(4)	1 412(4)	7 626(5)	2 526(4)
C(213)	2 733(4)	4 626(5)	1 073(4)	O(4)	1 164(3)	7 892(4)	2 759(3)
C(214)	2 318(4)	4 842(5)	400(4)	Cl(1)	615(2)	−97(3)	3 036(2)
C(215)	1 981(4)	5 541(5)	255(4)	C(100)	0	−783(13)	2 500

C, 44.4; H, 3.9; P, 8.1. $C_{25}H_{25}MnMoO_8P_2$ requires C, 45.1; H, 3.8; P, 9.3%); mass spectrum, *m/e* 666 (M^+), $M^+ - n$CO (n = 1—4); $\nu_{max.}$(CO) (n-hexane) at 2 033w, 1 959s, 1 950m, 1 934m, and 1 883m cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$, δ 8.0—6.8 (m, 10 H, Ph), 5.00 (s, 5 H, C_5H_5), 3.85 [d, ^3J(PH) 11.4, 9 H, OMe], and −14.05 [dd, 1 H, ^2J(PH) 30.4, 30.4, Mo(μ-H)Mn]; ^{13}C (CDCl$_3$, ^{1}H gated decoupled, 233 K), δ 243.5 [d, ^2J(PC) 24.5, 1Mo(CO) (*cis*)], 237.1 [s, 1Mo(CO) (*trans*)], 221.5 [m, 1Mn(CO)], 214.0 [m, 1Mn(CO)], 211.8 [m, 1Mn(CO)], 142.4—127.3 (m, Ph), 91.4 (s, C_5H_5), and 52.0 [d, ^2J(PC) 2.9 Hz, OMe]; ^{31}P (CDCl$_3$, ^{1}H gated decoupled, 263 K), δ 51.0 [m, P(OMe)$_3$] and 23.0 (m, μ-PPh$_2$).

Complex (**3a**) (Found: C, 42.3; H, 4.5; P, 11.1. $C_{27}H_{34}MnMoO_{10}P_3$ requires C, 42.5; H, 4.5; P, 12.2%): mass spectrum, *m/e* 762 (M^+); $\nu_{max.}$(CO) (n-hexane) at 1 945s, 1 909s, and 1 869m cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), δ 8.1—6.9 (m, 10 H, Ph), 4.88 (s, 5 H, C_5H_5), 3.85 [d, 9 H, ^2J(PH) 10.8, OMe], 3.40 [d, 9 H, ^3J(PH) 10.8, OMe], and −14.74 [ddd, 1 H, ^2J(PH) 33.8, 33.8, 17.4, Mo(μ-H)Mn]; ^{13}C (CDCl$_3$, ^{1}H gated decoupled, 233 K), δ −246.3 [d, ^2J(PC) 22.3, 1Mo(CO) (*cis*)], 239.2 [s, 1Mo(CO) (*trans*)], 217.3 [m, 1Mn(CO)], 215.4 [m, 1Mn(CO)], 145.4—126.1 (m, Ph), 91.6 (s, C_5H_5), and 51.9 [d, ^2J(PC) 4.9, OMe]; ^{31}P (CDCl$_3$, ^{1}H gated decoupled, 243 K), δ 53.9 [m, P(OMe)$_3$], 50.2 [m, P(OMe)$_3$], and 20.2 [d, $^2J(P_\mu\text{–}P_{trans})$ 41.2 Hz, μ-PPh$_2$].

(*b*) *With* PPh$_3$. A solution of complex (**1**) (0.114 g, 0.2 mmol) and PPh$_3$ (0.105 g, 0.4 mmol) in hexane–benzene (9:1, 50 cm^3) was treated as in (*a*) to give unreacted (**1**) (0.004 g) and yellow crystalline (**2b**) (0.145, 90%) (Found: C, 58.5; H, 3.9. $C_{40}H_{31}MnMoO_5P_2$ requires C, 59.7; H, 3.9%); $\nu_{max.}$(CO) (n-hexane) at 2 027m, 1 954s, 1 940s, 1 916s, and 1 884s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), δ 8.0—7.0 (m, 25 H, Ph), 4.53 (s, 5 H, C_5H_5), and −14.06 [dd, 1 H, ^2J(PH) 32.3, 21.1, Mo(μ-H)Mn]; ^{13}C (CDCl$_3$, ^{1}H gated decoupled, 293 K), δ 243.6 [d, ^2J(PC) 24.7 Hz, 1Mo(CO) (*cis*)], 237.1 [s, 1Mo(CO) (*trans*)], 223.8 [m, 1 Mn(CO)], 217.3 [m, 1Mn(CO)], 213.7 [m, 1Mn(CO)], 142.6—127.3 (m, Ph), and 91.4 (s, C_5H_5); ^{31}P (CDCl$_3$, ^{1}H gated decoupled, 243 K), δ 27.0 (s, μ-PPh$_2$) and −70.1, (s, PPh$_3$).

(*c*) *With* PhCH$_2$NC. A solution of complex (**1**) (0.114 g, 0.2 mmol) and PhCH$_2$NC (0.073 cm^3, 0.6 mmol) in hexane–benzene (9:1, 50 cm^3) was treated as in (*a*) to give unreacted (**1**) (0.002 g), yellow crystalline (**2c**) (0.03 g, 23%), orange microcrystalline (**3c**) (0.03 g, 20%), and an uncharacterised orange complex (0.01 g). Complex (**2c**) (Found: C, 53.6; H, 3.6; N, 2.1. $C_{30}H_{23}MnMoNO_5P$ requires C, 54.6; H, 3.5; N, 2.1%): mass spectrum, *m/e* 659 (M^+), $M^+ - n$CO (n = 2—4); $\nu_{max.}$(CO) (n-hexane) at 2 015s, 1 955s, 1 949s, 1 939s, 1 881m; ν(CNR) at 2 175br cm^{-1}. Proton n.m.r. (CDCl$_3$): δ 8.0—7.0 (m, 15 H, Ph), 5.02 (s, 5 H, C_5H_5), 4.41 (m, 2 H, CNC*H*$_2$Ph), and −13.80 [d, 1 H, ^2J(PH) 33.6 Hz, Mo(μ-H)Mn]. Complex (**3c**) (Found: C, 57.9; H, 4.1; N, 4.2. $C_{37}H_{30}MnMoN_2O_4P$ requires C, 59.4; H, 4.0; N, 4.1%): mass spectrum, *m/e* 748 (M^+), $M^+ - n$CO (n = 2 or 3); $\nu_{max.}$(CO) (n-hexane) at 1 945s, 1 913m, 1 871m; ν(CNR) at 2 160br and 2 010br cm^{-1}. Proton n.m.r. (CDCl$_3$): δ 8.0—6.9 (m, 20 H, Ph), 4.95 [s, 5 H, C_5H_5, isomer 3 (27%)], 4.92 [s, 5 H, C_5H_5, isomer 1 (43%)], 4.83 [s, 5 H, C_5H_5, isomer 2 (30%)], 4.52 (m, 4 H, CNC*H*$_2$Ph), −13.54 [d, 1 H, ^2J(PH) 33.1, Mo(μ-H)Mn, isomer 1], −14.05 [d, 1 H, ^2J(PH) 35.5, Mo(μ-H)Mn, isomer 2], and −14.84 [d, 1 H, ^2J(PH) 34.3 Hz, Mo(μ-H)Mn, isomer 3]. Use of a three-fold excess of PPh$_3$ in the reaction did not alter the product yields.

(*d*) *With dppm*. A solution of complex (**1**) (0.12 g, 0.21 mmol) and dppm (0.08 g, 0.21 mmol) in hexane–benzene (9:1, 50 cm^3) was treated as in (*a*) above to give (**1**) (0.005 g), orange crystalline (**3b**) (0.02 g, 10%), orange microcrystalline (**4**) (0.13 g, 67%), and an uncharacterised grey complex (0.01 g). The yield of (**3b**) relative to (**4**) was increased on reduced reaction times or by the use of 100% hexane as solvent. Complex (**3b**): mass spectrum, *m/e* 898 (M^+), $M^+ - n$CO (n = 1—4); $\nu_{max.}$(CO) (n-hexane) 1 948w, 1 941w, 1 926s, 1 874s, and 1 864m cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), δ 8.1—6.5 (m, 30 H, Ph), 4.77 (s, 5 H, C_5H_5), 4.52 (m, 2 H, CH$_2$), and −10.78 [ddd, 1 H, ^2J(PH) 41.7, 21.2, 17.3, Mo(μ-H)Mn]; ^{13}C(CDCl$_3$, ^{1}H gated decoupled, 233 K), δ 246.4 [d, ^2J(PC) 21.1 Hz, 1Mo(CO) (*cis*)], 241.1 [s, 1Mo(CO) (*trans*)], 228.2 [m, 1Mn(CO)], 225.4 [m, 1Mn(CO)], 146.8—127.4 (m, Ph), 92.4 (s, C_5H_5), and 50.4 (m, CH$_2$). Complex (**4**) (Found: C, 60.5; H, 4.4; P, 8.5. $C_{46}H_{38}MnMoO_4P_3$ requires C, 61.5; H, 4.4; P, 10.4%); mass spectrum, *m/e* 870 ($M^+ -$ CO), $M^+ - n$CO (n = 1 or 3); $\nu_{max.}$(CO) (n-hexane) at 1 998s, 1 929s, 1 911s, 1 871m, and 1 861(sh) cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), major isomer (68%), δ 8.0—6.3 (m, 30 H, Ph), 4.85 (s, 5 H, C_5H_5), 3.63 [ddd, 1 H, ^2J(PH) 11.6, 11.6, J_{ab} 11.6, CH^aH^b], 2.38 [ddd, 1 H, ^2J(PH) 11.6, CH^aH^b], and -12.56 [ddd, 1 H, ^2J(PH) 49.7, 31.1, 21.0, Mo(μ-H)Mn]; minor isomer (32%), δ 4.66 (s, 5 H, C_5H_5), 3.80 [ddd, 1 H, ^2J(PH) 10.2, 10.2, J_{ab} 10.2, CH^aH^b], 2.94 [ddd, 1 H, ^2J(PH) 10.2, CH^aH^b], and -10.55 [ddd, 1 H, ^2J(PH) 76.7, 50.1, 26.6, Mo(μ-H)Mn; ^{13}C (CDCl$_3$, ^{1}H gated decoupled, 233 K), major isomer, δ 251.4 [dd, ^2J(PC) 25.2, 19.8, 1Mo(CO)], 225.5 [m, 1Mn(CO)], 222.2 [m, 1 Mn(CO)], 218.0 [m, 1Mn(CO)], 145.4—126.2 (m, Ph), 90.9 (s, C_5H_5), and 41.5 (m, CH$_2$); minor isomer, δ 89.5 (s, C_5H_5); ^{31}P(CDCl$_3$, ^{1}H gated decoupled, 323 K), major isomer, δ 12.9 [d, $^2J(P_\mu-P_{Mn})$ 26.8, μ-PPh$_2$], -65.1 [d, ^2J(PP, dppm) 77.1, MoPPh$_2$CH$_2$–], and -92.4 [dd, MnPPh$_2$CH$_2$–]; minor isomer, δ 15.3 [d, $^2J(P_\mu-P_{Mo})$ 11.4, μ-PPh$_2$], -71.7 [dd, ^2J(PP, dppm) 74.4 Hz, MoPPh$_2$CH$_2$–], and -73.0 (m, MnPPh$_2$CH$_2$–).

Crystal Structure Determination of [MoMn(μ-H)(μ-PPh$_2$)(η^5-C_5H_5)(CO)$_4$(dppm-*PP′*)]·0.5 CH$_2$Cl$_2$ (**3b**).—Orange platelets of complex (**3b**) were grown by slow cooling of a hexane–dichloromethane (1:1) solution, and a suitable crystal was mounted on a glass fibre with epoxy-resin.

Crystal data. $C_{46}H_{38}MnMoO_4P_3 \cdot 0.5CH_2Cl_2$, M = 941.02, monoclinic, a = 26.907(4), b = 16.240(2), c = 23.248(5) Å, β = 123.51(1)°, U = 8 469.8 Å^3 (by least-squares refinement on diffractometer angles for 52 automatically centred reflections, λ = 0.71069 Å), space group *C*2/*c* (no. 15), Z = 8, D_c = 1.475 g cm^{-3}, F(000) = 3 832. Orange platelets. Crystal dimensions (distance to faces from centre): 0.0703 (100, $\bar{1}$00) × 0.0646 (001, 00$\bar{1}$) × 0.057 (10$\bar{1}$, $\bar{1}$01) × 0.304 (010, 0$\bar{1}$0) mm, μ(Mo-K_α) = 7.54 cm^{-1}.

Data collection and processing. Stoe-Siemens diffractometer, 24-step ω—θ mode with ω scan step-width = 0.04°, ω scan speed 0.01—0.04° s^{-1}, graphite-monochromated Mo-K_α radiation. 11 801 Reflections measured ($5.0 \leqslant 2\theta \leqslant 45.0°$, $\pm h$, $+k$, $\pm l$), 5 333 unique [merging R = 0.044 after absorption correction (maximum, minimum transmission factors = 0.915, 0.859)], giving 4 406 with $F > 4\sigma(F)$. No significant decomposition during data collection.

Structure analysis and refinement.[38] Random start tangent refinement direct methods (Mo, Mn, and P atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement (in two blocks for final, anisotropic cycles) with all non-hydrogen atoms anisotropic, except for solvent C atom, hydride H refining freely, and other hydrogens in calculated positions, with overall thermal parameters for each type of hydrogen. The weighting scheme $w = 5.14/[\sigma^2(F_o) + 0.007F_o{}^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values are 0.056, 0.055 for 515 refined parameters. Maximum and minimum residuals in final difference synthesis: 0.78 and -8.80 e Å^{-3}. Programs and computers used and sources of scattering factor data are given in ref. 38. Final atomic co-ordinates are listed in Table 2.

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References

1 M. I. Bruce, *J. Organomet. Chem.*, 1985, **283**, 339.
2 G. L. Geoffroy, *Acc. Chem. Res.*, 1980, **13**, 469.
3 J. Powell, M. R. Gregg, and J. F. Sawyer, *J. Chem. Soc., Chem. Commun.*, 1983, 1149.
4 J. Powell, J. F. Sawyer, and M. V. R. Stainer, *J. Chem. Soc., Chem. Commun.*, 1985, 1314.
5 H. Lehner, A. Musco, L. M. Venanzi, and A. Albinati, *J. Organomet. Chem.*, 1981, **213**, C46.
6 J. Powell, J. F. Sawyer, and S. J. Smith, *J. Chem. Soc., Chem. Commun.*, 1985, 1312.
7 P. A. Tooley, L. W. Arndt, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1985, **107**, 2422.
8 A. D. Horton, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1985, 247.
9 P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, 1972, **11**, 1609.
10 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1983, 205.
11 R. B. King, W-K. Fu, and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1984, 1439.
12 B. E. Hanson, P. E. Fanwick, and J. S. Mancini, *Inorg. Chem.*, 1982, **21**, 3811.
13 E. P. Kyba, J. D. Mather, K. L. Hassett, J. S. McKennis, and R. E. Davis, *J. Am. Chem. Soc.*, 1984, **106**, 5371.
14 D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, 1975, **97**, 4908.
15 C. P. Casey and R. M. Bullock, *Organometallics*, 1984, **3**, 1100.
16 T. Kruck, G. Sylvester, and I-P. Kunau, *Z. Naturforsch., Teil B*, 1973, **28**, 38.
17 R. P. Rosen, J. B. Hoke, R. R. Whittle, G. L. Geoffroy, J. P. Hutchinson, and J. A. Zubieta, *Organometallics*, 1984, **3**, 846.
18 P. M. Treichel, W. K. Dean, and W. M. Douglas, *J. Organomet. Chem.*, 1972, **42**, 145.
19 N. N. Turaki and J. M. Huggins, *Organometallics*, 1985, **4**, 1766 and refs. therein.
20 A. E. Steigman, M. Steiglitz, and D. R. Tyler, *J. Am. Chem. Soc.*, 1983, **105**, 6032.
21 H. B. Abrahamson and M. S. Wrighton, *J. Am. Chem. Soc.*, 1977, **99**, 5510.
22 A. D. Horton, Ph.D. Thesis, University of Cambridge, 1986.
23 C. P. Casey and R. M. Bullock, *J. Organomet. Chem.*, 1981, **218**, C47.
24 J. A. Iggo, Ph.D. Thesis, University of Cambridge, 1983.
25 D. A. Roberts and G. L. Geoffroy, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, London, 1982, ch. 40.
26 W. C. Mercer, R. R. Whittle, E. W. Burkhardt, and G. L. Geoffroy, *Organometallics*, 1985, **4**, 68.
27 D. A. Roberts, G. R. Steinmetz, M. J. Breen, P. M. Shulman, E. D. Morrison, M. R. Duttera, C. W. DeBrosse, R. R. Whittle, and G. L. Geoffroy, *Organometallics*, 1984, **2**, 846.
28 M. J. Breen, P. M. Shulman, G. L. Geoffroy, A. L. Rheingold, and W. C. Fultz, *Organometallics*, 1984, **3**, 782.
29 E. D. Morrison, A. D. Harley, M. A. Marcelli, G. L. Geoffroy, A. L. Rheingold, and W. C. Fultz, *Organometallics*, 1984, **3**, 1407.
30 H. C. Foley, W. C. Finch, C. G. Pierpoint, and G. L. Geoffroy, *Organometallics*, 1982, **1**, 1379.
31 S. Guesmi, G. Suss-Fink, P. H. Dixneuf, N. J. Taylor, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1984, 1606.
32 H-J. Langenbach and H. Vahrenkamp, *Chem. Ber.*, 1979, **112**, 3390.
33 J. Ellerman and H. A. Lindner, *Z. Naturforsch., Teil B*, 1979, **34**, 799; M. Laing, E. Singleton, and G. Kruger, *J. Organomet. Chem.*, 1973, **54**, C30.
34 T. Adatia, K. Henrick, A. D. Horton, M. J. Mays, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1986, 1206.
35 S. Guesmi, P. H. Dixneuf, N. J. Taylor, and A. J. Carty, *J. Organomet. Chem.*, 1986, **303**, C47.
36 J. R. Fox, W. L. Gladfelter, T. G. Wood, J. A. Smegal, T. K. Foreman, G. L. Geoffroy, I. Tavanaiepour, V. W. Day, and C. S. Day, *Inorg. Chem.*, 1981, **20**, 3214.
37 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 633.
38 B. F. G. Johnson, J. Lewis, P. R. Raithby, S. N. A. B. Syed-Mustaffa, M. J. Taylor, K. H. Whitmire, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1984, 2111.

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