Substitution Reactions of a Heterodimetallic Molybdenum–Manganese Complex*

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The reactions of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_7$] **1** with phosphines and with isonitriles have been studied. Less bulky phosphines give derivatives of **1** of the type [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$L], which are monosubstituted at the manganese atom [L = PPh_2H **2a**, PPh_2Me **2b**, $PPhMe_2$ **2c** or $P(OMe)_3$ **2f**] whereas more bulky phosphines substitute only at the molybdenum atom (L = PPh_3 **3a**). Phosphines of intermediate bulk give both types of derivative depending on the reaction conditions (L = PPh_2Et **2e** or **3b**, $PPh_2CH{=}CH_2$ **2d** or **3c**). Disubstituted derivatives, [MoMn(μ-$C_5H_4PPh_2$)$(CO)_5L_2$] [L = PPh_2Me **4a**, $PPh_2CH{=}CH_2$ **4b** or $P(OMe)_3$ **4c**], obtained by reaction of **1** with excess of the appropriate ligand, have one substituent on the manganese and one on the molybdenum atom. Isonitriles give derivatives [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$L] (L = $CNCH_2Ph$ **2g** or $CNBu^t$ **2h**) which are monosubstituted at the manganese atom but in a different position to the phosphine derivatives **2a–2f**. Thermolysis of the diphenylphosphine derivative **2a** gives [MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPh_2)$(CO)_5$] **5a** and thermolysis of either one of the vinylphosphine derivatives **2d** or **3c** gives a complex [MoMn(μ-$C_5H_4PPh_2$)(μ-$PPh_2CH{=}CH_2$)$(CO)_5$] **6** in which the vinylphosphine ligand is bonded through phosphorus to manganese and through the vinyl group to the molybdenum atom. Hydrogenation of **6** gives **3b** in a reaction which involves a transfer of the co-ordination of the vinylphosphine phosphorus atom from manganese to molybdenum. Addition reactions of **6** with CO and $P(OMe)_3$ involve a similar transfer to give [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$($PPh_2CH{=}CH_2$)] **3c** and [MoMn(μ-$C_5H_4PPh_2$)$(CO)_5$($PPh_2CH{=}CH_2$){$P(OMe)_3$}] **7** respectively. The structures of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$(PPh_2Et)] **3b** and [MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPh_2)$(CO)_5$] **5a** have been determined by X-ray analysis.

Heterodimetallic complexes with metal–metal bonds have been studied intensively in recent years.[1,2] A driving force for much of the work has been the hope that the presence of two different adjacent metal atoms might lead to novel and perhaps catalytic reactivity of co-ordinated substrates being observed as a result of co-operative effects between the metal centres.[3]

The polar nature of the bond between two different metal centres is such that inert bridging ligands are often required to prevent fragmentation in the reactions of heterodimetallic complexes, and a ligand which has been widely used for this purpose is the cyclopentadienylphosphine $C_5H_4PPh_2$.[4] However the majority of studies with this ligand have concentrated on the synthesis of new complexes and there have been fewer reports dealing with the relative reactivities of the metal centres.[5,6]

We have previously studied the reactivity of the heterodimetallic phosphido-bridged molybdenum–manganese complex [MoMn(μ-H)(μ-PPh_2)(η^5-C_5H_5)$(CO)_6$] and have shown that, under photolytic conditions, it reacts preferentially at the manganese atom with two-electron-donor ligands, although the molybdenum atom can also become involved.[7] A precursor to the above molybdenum–manganese complex is the cyclopentadienylphosphine-bridged species [MoMn(μ-$C_5H_4PPh_2$)$(CO)_7$] **1**, first reported by Casey *et al.*,[8] and we have now studied some substitution reactions of **1** with phosphines and with isonitriles in order to determine whether the change in the nature of the bridging ligands affects the site selectivity. Some of the substituting ligands are capable of further reaction with the metal centres and these reactions have also been investigated.

Results and Discussion

Monosubstitution of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_7$] **1** *by Phosphines at the Manganese Atom.*—The thermal reaction of **1** with one equivalent of PPh_2H or $PPhMe_2$ in refluxing toluene at 383 K or reaction with one equivalent of PPh_2H, PPh_2Me, $PPh_2CH{=}CH_2$, or PPh_2Et in refluxing hexane–toluene (5:1) at 353 K gave the orange complexes [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$L] (L = PPh_2H **2a**, PPh_2Me **2b**, $PPhMe_2$ **2c**, $PPh_2CH{=}CH_2$ **2d** or PPh_2Et **2e**), which have been shown from spectroscopic data to be monosubstituted at the manganese atom. This conclusion is supported by an X-ray structure analysis of **2a** which, although of low accuracy (*R* 0.09), clearly revealed the PPh_2H substituent to be on the manganese atom *trans* to the phosphorus atom of the $C_5H_4PPh_2$ ligand.[9] In the case of PPh_2H a second orange complex is formed, which has been identified spectroscopically and crystallographically as [MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPh_2)$(CO)_5$] **5a**. This second complex is formed in higher yield than **2a** when the reaction time is increased.

The ^1H NMR spectra of complexes **2a**–**2e** all show two signals at δ 5.3–5.4 and 4.6–4.7 which are seen either as pseudo-quartets with a coupling of *ca.* 2 Hz or as broad singlets, and these may be assigned to the cyclopentadienyl protons (Table 1). Analogous signals are observed for **1** and the presence of only two such signals supports the existence in all of the complexes of a plane of symmetry through the phosphorus–cyclopentadienyl and metal–metal bonds. Although there are two possible isomers having such a plane of symmetry (both isomers are present for **2f**) that with the substituent *trans* to the $C_5H_4PPh_2$ phosphorus atom seems the more likely for **2a**–**2e** on steric grounds. The ^{31}P-{^1H} NMR spectra of the complexes show two broad singlets at room temperature with the broadening presumably due to the quadrupolar effects of the

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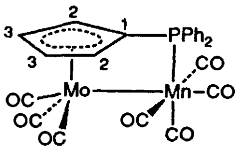
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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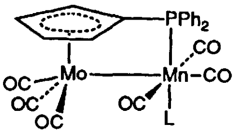
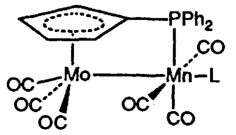
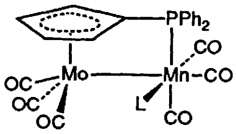


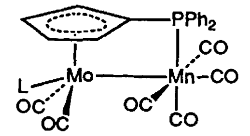
L
2a PPh_2H
2b PPh_2Me
2c $PPhMe_2$
2d $PPh_2CH{=}CH_2$
2e PPh_2Et
2f $P(OMe)_3$ (isomer A)



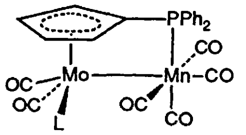
L
2f $P(OMe)_3$ (isomer B)



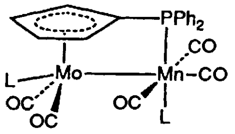
L
2g $CNCH_2Ph$
2h $CNBu^t$



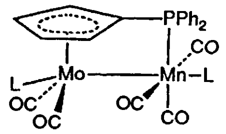
L
3a PPh_3
3b PPh_2Et
3c $PPh_2CH{=}CH_2$ (isomer A)



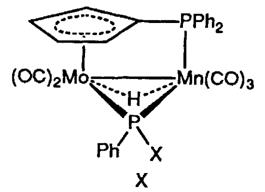
L
3c $PPh_2CH{=}CH_2$ (isomer B)



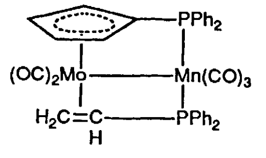
L
4a PPh_2Me
4b $PPh_2CH{=}CH_2$
4c $P(OMe)_3$ (isomer A)



L
4c $P(OMe)_3$ (isomer B)



X
5a Ph
5b H



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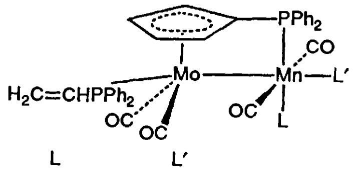


L L′
$P(OMe)_3$ **7** CO (isomer A)
CO **7** $P(OMe)_3$ (isomer B)

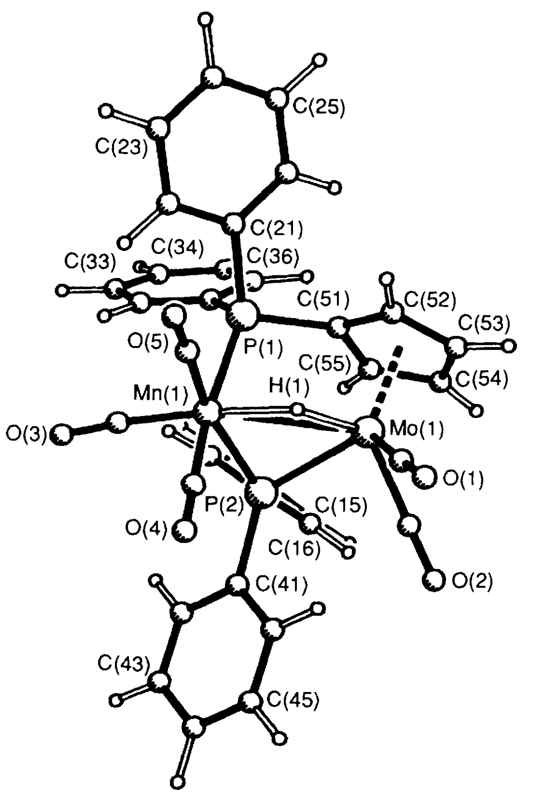


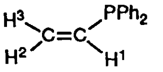
Fig. 1 Molecular structure of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}H)(CO)_5]$ **5a** showing the atom numbering scheme

^{55}Mn to which the phosphorus atoms are directly bonded. This broadening precluded the observation of phosphorus–phosphorus coupling at room temperature but on cooling to 225 K the spectrum of **2b** revealed two doublets with $^2J(PP)$ 10 Hz. The ^{13}C NMR spectrum of **2a** at 234 K shows two sharp singlet peaks in the carbonyl region at δ 232.2 and 228.5 in a 2:1 ratio, which may be assigned to the molybdenum-bound carbonyl carbon atoms, and a relatively broad singlet due to the manganese-bound carbon atoms, as expected for the proposed structure.

The reaction of **1** with one equivalent of $P(OMe)_3$ in refluxing hexane at 343 K gave $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6\{P(OMe)_3\}]$ **2f**. This complex has an infrared spectrum and NMR spectra which are quite different to those of **2a**–**2e** revealing the presence in solution of two isomers in an approximate concentration ratio of 1:1. Recrystallisation of **2f** from CH_2Cl_2–hexane (1:1) gave a 3:1 mixture of the two isomers which are not in rapid equilibrium in solution at room temperature, and this enabled the spectra due to each isomer to be identified. The major isomer after recrystallisation (isomer A) appears to correspond more closely in its spectroscopic properties to those of **2a**–**2e** and is assigned the same structure. The minor isomer (isomer B) shows only two multiplets due to cyclopentadienyl protons in its ^{1}H NMR spectrum, suggesting that it has the same plane of symmetry as the major isomer. Accordingly it is assigned a structure with the phosphite ligand *trans* to the metal–metal bond.

The formation of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a** in addition to **2a** in the reaction of **1** with PPh_2H has been referred to above. Thermolysis of **2a** at 383 K gives **5a** in good yield, suggesting that **2a** is an intermediate in its formation. The molecular structure of **5a** has been determined by X-ray analysis and is shown in Fig. 1. Table 2 lists selected bond lengths and bond angles. The Mo–Mn distance [3.004(1) Å] may be compared with those in $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$[7] [3.008(1) Å] and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$[8] [3.054(1) Å] and indicates the presence of a direct bond between the metal centres. The Mn–P and Mo–P distances to the bridging PPh_2 group in **5a** [2.282(1) and 2.447(1) Å respectively] are similar to the corresponding distances in $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ [2.294(2) and 2.435(1) Å].[7] If the metal–metal bond in **5a** is ignored then the manganese atom is co-ordinated in an approximately

Table 1 Infrared and ^{1}H NMR data for the new complexes



Compound		ν(CO)^a/cm^{-1}	^{1}H NMR^{b,c} (δ)
2a	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(PPh_2H)]	2019w, 1959s, 1942m, 1881m, 1861m	8.2–7.9 (m, 8 H, *o*-Ph), 7.6–7.4 (m, 12 H, *m*- and *p*-Ph), 7.14 [dd, *J*(PH) 360, *J*(PH) 3.8, 1 H, $PPh_2\mathit{H}$], 5.36 (pq, *J* 2, 2 H, C_5H_4P), 4.69 (pq, *J* 2, 2 H, C_5H_4P)
2b	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(PPh_2Me)]	2012w, 1938s, 1880m, 1852m^d	8.0–7.7 (m, 8 H, *o*-Ph), 7.7–7.3 (m, 12 H, *m*- and *p*-Ph), 5.35 (pq, *J* 2, 2 H, C_5H_4P), 4.69 (pq, *J* 2, 2 H, C_5H_4P), 2.24 [d, *J*(PH) 8.4, 3 H, $PPh_2\mathit{Me}$]
2c	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$($PPhMe_2$)]	2014w, 1939s, 1879m, 1847m^d	8.1–7.3 (m, 15 H, Ph), 5.36 (pq, *J* 2, 2 H, C_5H_4P), 4.64 (pq, *J* 2, 2 H, C_5H_4P), 1.99 [d, *J*(PH) 8.6, 6 H, $PPh\mathit{Me}_2$]
2d	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$($PPh_2CH{=}CH_2$)]	2011w, 1949s, 1936s, 1886m, 1858m^d	8.1–7.6 (m, 8 H, *o*-Ph), 7.5–7.1 (m, 12 H, *m*- and *p*-Ph), 6.76 [ddd, *J*(PH) 28.7, *J*(H^1H^2) 12.6, *J*(H^1H^3) 18.1, 1 H, $PPh_2C\mathit{H}{=}CH_2$, H^1], 5.91 [dd, *J*(PH) 34.4, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^2], 5.34 [pq, *J* 2, 2 H, C_5H_4P], 5.06 [t, *J*(PH) 18.1 Hz, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^3], 4.69 [pq, *J* 2, 2 H, C_5H_4P]
2e	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(PPh_2Et)]^d	2009w, 1946s, 1934s, 1880m, 1853m	8.0–7.6 (m, 8 H, *o*-Ph), 7.6–7.3 (m, 12 H, *m*- and *p*-Ph), 5.32 (br, s, 2 H, C_5H_4P), 4.67 (br, s, 2 H, C_5H_4P), 2.63 [qnt, *J*(PH) = *J*(HH) 6.3, 2 H, $PPh_2C\mathit{H}_2CH_3$], 0.94 [dt, *J*(PH) 15.1, 3 H, PPh_2, $CH_2\mathit{Me}$]
2f	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6${P(OMe)$_3$}]	2025m, 1999m (sh), 1961s, 1949s, 1899m	8.2–7.8 (m, 4 H, *o*-Ph), 7.6–7.3 (m, 6 H, *m*- and *p*-Ph), 5.33 (m, 2 H, C_5H_4P, isomers A and B), 4.60 (pq, *J* 2, 2 H, C_5H_4P, isomer A), 4.29 (pq, *J* 2, 2 H, C_5H_4, isomer B), 3.83 [d, *J*(PH) 10.9, 9 H, P(OMe)$_3$, isomer A], 3.82 [d, *J*(PH) 11.0, 9 H, P(OMe)$_3$, isomer B]
2g	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$($CNCH_2Ph$)]^e	2022s, 1969m, 1960s, 1921w, 1904m, 1879m	8.0–7.8 (m, 4 H, $C_5H_4PPh_2$, *o*-Ph), 7.5–7.1 (m, 9 H, *m*- and *p*-Ph), 6.64 [d, *J*(PH) 7.1, 2 H, $PhCH_2NC$, *o*-Ph], 5.30 (m, 1 H, C_5H_4P), 5.17 (m, 1 H, C_5H_4P), 4.39 [dd, *J*(PH) 15.9, *J*(HH) 3.5, 1 H, $PhC\mathit{H}_2NC$], 4.30 (m, 1 H, C_5H_4P), 4.21 (d, 1 H, $PhC\mathit{H}_2NC$), 3.50 (m, 1 H, C_5H_4P)
2h	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(CNBu^t)]^f	2021m, 1968m, 1960s, 1919w, 1903w, 1882m	8.1–7.9 (m, 4 H, *o*-Ph), 7.5–7.2 (m, 6 H, *m*- and *p*-Ph), 5.40 (m, 2 H, C_5H_4P), 4.34 (pq, *J* 1.5, 1 H, C_5H_4P), 4.25 (pq, *J* 1.4, 1 H, C_5H_4P), 0.95 (s, 9 H, Me_3CNC)
3a	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(PPh_3)]	2043m, 1980m, 1968s, 1927s, 1890w, 1846m	8.1–7.8 (m, 4 H, $C_5H_4PPh_2$, *o*-Ph), 7.7–7.3 (m, 21 H, $C_5H_4PPh_2$, *m*- and *p*-Ph, and PPh_3), 4.58 (pq, *J* 2, 2 H, C_5H_4P), 4.25 (m, 2 H, C_5H_4P)
3b	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$(PPh_2Et)]	2042m, 1982m, 1967s, 1926s, 1893w, 1840m	7.9–7.5 (m, 8 H, *o*-Ph), 7.4–7.3 (m, 12 H, *m*- and *p*-Ph), 4.50 (pq, *J* 2, 2 H, C_5H_4P), 4.17 (pq, *J* 2, 2 H, C_5H_4P), 2.74 [qnt, *J*(PH) = *J*(HH) 7.7, 2 H, $PPh_2C\mathit{H}_2Me$], 1.07 [dt, *J*(PH) 1.75, 3 H, $PPh_2CH_2\mathit{Me}$]
3c	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_6$($PPh_2CH{=}CH_2$)]	2042m, 1978w, 1967s, 1925s, 1897m, 1847m	8.0–7.4 (m, 8 H, *o*-Ph), 7.4–7.3 (m, 12 H, *m*- and *p*-Ph), 6.7 (m, 1 H, $PPh_2C\mathit{H}{=}CH_2$, H^1), 6.04 [dd, *J*(PH) 40.0, *J*(H^1H^2) 11.6, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^2], 5.63 [t, *J*(PH) and *J*(H^1H^3) 18.7, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^3], 4.51 (m, 2 H, C_5H_4P), 4.33 (m, 2 H, C_5H_4P); at 195 K,^{g} 7.0–5.5 (m, 3 H, $Ph_2C\mathit{H}{=}C\mathit{H}_2$, isomers A and B), 5.01 (m, 1 H, C_5H_4P, isomer B), 4.60 (m, 1 H, C_5H_4P, isomer B), 4.54 (m, 2 H, C_5H_4P, isomer A), 4.44 (m, 1 H, C_5H_4P, isomer B), 4.28 (m, 2 H, C_5H_4P, isomer A), 3.51 (m, 1 H, C_5H_4P, isomer B)
4a	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_5$(PPh_2Me)$_2$]	1930s, 1920m (sh), 1906w, 1880s, 1807w	8.1–7.5 (m, 12 H, *o*-Ph), 7.4–7.3 (m, 18 H, *m*- and *p*-Ph), 4.67 (pq, *J* 2, 2 H, C_5H_4P), 4.33 (pq, *J* 2, 2 H, C_5H_4P), 2.10 [d, *J*(PH) 8.1, 3 H, $PPh_2\mathit{Me}$], 1.91 [d, *J*(PH) 8.4, 3 H, $PPh_2\mathit{Me}$]
4b	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_5$($PPh_2CH{=}CH_2$)$_2$]	1931s, 1920m (sh), 1906w, 1883w, 1817w	8.1–7.5 (m, 12 H, *o*-Ph), 7.5–7.2 (m, 18 H, *m*- and *p*-Ph), 6.8 (m, 1 H, $PPh_2CH{=}CH_2$), 6.0 (m, 2 H, $PPh_2CH{=}CH_2$), 5.4 (m, 2 H, $PPh_2CH{=}CH_2$), 4.72 (d, *J* 2, 2 H, C_5H_4P), 4.7 (m, 1 H, $PPh_2CH{=}CH_2$), 4.35 (m, 2 H, C_5H_4P)
4c	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_5${P(OMe)$_3$}$_2$]	2006m, 1935s, 1900m, 1888m, 1846m	8.1–8.0 (m, 4 H, *o*-Ph), 7.4–7.1 (m, 6 H, *m*- and *p*-Ph), 5.01 (m, 2 H, C_5H_4P, isomers A and B), 4.52 (m, 2 H, C_5H_4P, isomer A), 4.26 (m, 2 H, C_5H_4P, isomer B), 3.79 [d, *J*(PH) 11.1, 9 H, P(OMe)$_3$, isomer B], 3.77 [d, *J*(PH) 10.8, 9 H, P(OMe)$_3$, isomer A], 3.67 [d, *J*(PH) 11.6, 9 H, P(OMe)$_3$, isomer B], 3.66 [d, *J*(PH) 11.6, 9 H, P(OMe)$_3$, isomer A]
5a	[MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPh_2)(CO)$_5$]	2017m, 1958s, 1917m, 1895m	7.8–6.9 (m, 20 H, Ph), 5.90 (m, 1 H, C_5H_4P), 5.57 (m, 1 H, C_5H_4P), 5.33 (m, 1 H, C_5H_4P), 4.30 (m, 1 H, C_5H_4P), −12.14 [dd, *J*(PH) 39.2, *J*(P′H) 14.1, 1 H, MoHMn]
5b	[MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPhH)(CO)$_5$]	2021m, 1961s, 1956m, 1924m, 1902m	8.0–7.0 (m, 15 H, Ph), 5.98 (m, 1 H, C_5H_4P), 5.33 (m, 2 H, C_5H_4P), 5.33 [d, *J*(PH) 345, 1 H, $PPh\mathit{H}$], 4.67 (m, 1 H, C_5H_4P), −12.42 [dd, *J*(PH) 37.8, *J*(P′H) 12.3, 1 H, MoHMn]
6	[MoMn(μ-$C_5H_4PPh_2$)(μ-$PPh_2CH{=}CH_2$)(CO)$_5$]	2003w, 1952s, 1924s, 1905m, 1892m	8.0–7.2 (m, 20 H, Ph), 5.46 (m, 1 H, C_5H_4P), 5.07 (m, 1 H, C_5H_4P), 5.04 (m, 1 H, C_5H_4P), 3.24 (m, 1 H, C_5H_4P), 2.98 (m, 1 H, $PPh_2C\mathit{H}{=}CH_2$, H^1), 2.67 [dd, *J*(PH) 28.8, *J*(H^1H^2) 8.6, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^2], 2.35 [dd, *J*(PH) 19.7, *J*(H^1H^3) 10.7, 1 H, $PPh_2CH{=}C\mathit{H}_2$, H^3]
7	[MoMn(μ-$C_5H_4PPh_2$)(CO)$_5$($PPh_2CH{=}CH_2$)-{P(OMe)$_3$}]	2003w, 1933s, 1890m, 1838m	8.1–7.5 (m, 8 H, *o*-Ph), 7.4–7.3 (m, 12 H, *m*- and *p*-Ph), 6.7 (m, 1 H, $PPh_2C\mathit{H}{=}CH_2$), 6.1–5.5 (m, 2 H, $PPh_2CH{=}C\mathit{H}_2$), 4.61 (m, 2 H, C_5H_4P, isomer A), 4.31 (m, 2 H, C_5H_4P, isomer B), 4.22 (m, 2 H, C_5H_4P, isomers A and B), 3.80 [d, *J*(PH) 11.1, 9 H, P(OMe)$_3$, isomer B], 3.72 [d, *J*(PH) 10.9, 9 H, P(OMe)$_3$, isomer A]

[a] Recorded in hexane solution unless otherwise indicated. [b] Abbreviations: s, singlet, d, doublet; t, triplet; qnt, quintet; pq, pseudo-quartet; m, multiplet. [c] Recorded in $CDCl_3$ solution and at 298 K unless otherwise indicated, *J* in Hz. [d] Recorded in CH_2Cl_2 solution. [e] ν(CNR) at 2149(br) cm^{-1}. [f] ν(CNR) at 2148(br) cm^{-1}. [g] Recorded in CD_2Cl_2.

Table 2 Selected bond parameters (lengths in Å, angles in °) for [MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPh_2)$(CO)_5$] **5a**

Mn(1)–Mo(1)	3.004(1)	P(1)–Mn(1)	2.353(1)
P(2)–Mo(1)	2.447(1)	P(2)–Mn(1)	2.282(1)
C(1)–Mo(1)	1.943(3)	C(3)–Mn(1)	1.793(4)
C(2)–Mo(1)	1.964(4)	C(4)–Mn(1)	1.804(3)
C(51)–Mo(1)	2.313(2)	C(5)–Mn(1)	1.819(4)
C(52)–Mo(1)	2.313(3)	C(21)–P(1)	1.830(3)
C(53)–Mo(1)	2.345(3)	C(31)–P(1)	1.835(3)
C(54)–Mo(1)	2.358(3)	C(51)–P(1)	1.822(3)
C(55)–Mo(1)	2.353(3)	C(11)–P(2)	1.832(3)
C(52)–C(51)	1.430(4)	C(41)–P(2)	1.835(3)
C(55)–C(51)	1.428(4)	C(53)–C(52)	1.420(5)
C(54)–C(53)	1.406(5)	C(55)–C(54)	1.419(5)
Mo(1)–H(1)	1.83(3)	Mn(1)–H(1)	1.76(3)
P(2)–Mo(1)–Mn(1)	48.2(1)	P(1)–Mn(1)–Mo(1)	75.6(1)
C(1)–Mo(1)–Mn(1)	97.7(1)	P(2)–Mn(1)–Mo(1)	53.0(1)
C(1)–Mo(1)–P(2)	114.0(1)	P(2)–Mn(1)–P(1)	96.0(1)
C(2)–Mo(1)–Mn(1)	121.7(1)	C(3)–Mn(1)–Mo(1)	146.9(1)
C(2)–Mo(1)–P(2)	80.1(1)	C(3)–Mn(1)–P(1)	98.6(1)
C(2)–Mo(1)–C(1)	78.3(1)	C(3)–Mn(1)–P(2)	96.3(1)
C(21)–P(1)–Mn(1)	118.1(1)	C(4)–Mn(1)–Mo(1)	97.8(1)
C(31)–P(1)–Mn(1)	125.1(1)	C(4)–Mn(1)–P(1)	169.0(1)
C(31)–P(1)–C(21)	98.7(1)	C(4)–Mn(1)–P(2)	86.7(1)
C(51)–P(1)–Mn(1)	102.9(1)	C(4)–Mn(1)–C(3)	91.7(1)
C(51)–P(1)–C(21)	104.2(1)	C(5)–Mn(1)–Mo(1)	112.2(1)
C(51)–P(1)–C(31)	105.8(1)	C(5)–Mn(1)–P(1)	87.7(1)
Mn(1)–P(2)–Mo(1)	78.8(1)	C(5)–Mn(1)–P(2)	161.6(1)
C(11)–P(2)–Mo(1)	112.1(1)	C(5)–Mn(1)–C(13)	100.1(2)
C(11)–P(2)–Mn(1)	126.4(1)	C(5)–Mn(1)–C(4)	84.6(1)
C(41)–P(2)–Mo(1)	125.4(1)	P(1)–C(51)–Mo(1)	106.3(1)
C(41)–P(2)–Mn(1)	115.4(1)	C(52)–C(51)–Mo(1)	72.0(1)
C(41)–P(2)–C(11)	100.3(1)	C(52)–C(51)–P(1)	124.3(2)
C(55)–C(51)–Mo(1)	73.7(2)	C(55)–C(51)–P(1)	125.5(2)
C(55)–C(51)–C(52)	107.8(3)	C(53)–C(52)–C(51)	107.4(3)
C(54)–C(53)–C(52)	108.6(3)	C(55)–C(54)–C(53)	108.6(3)
C(54)–C(55)–C(51)	107.5(3)	Mo(1)–H(1)–Mn(1)	114(2)

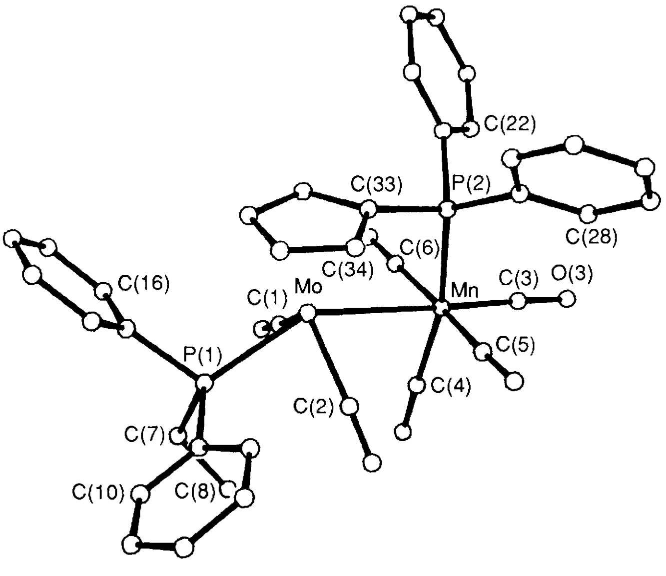


Fig. 2 Molecular structure of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$(PPh_2Et)] **3b**. In the phenyl (and cyclopentadienyl) rings the carbon atoms are numbered by progressive sequences C(*n*), C(*n* + 1), ..., C(*n* + 5), starting from the site of phosphorus substitution; only C(*n* + 1) atoms are labelled for clarity. The carbonyl oxygens are labelled by the same numbers of the carbon atoms to which they are bonded

octahedral arrangement by the three carbonyl ligands, by the phosphorus atoms of the bridging $C_5H_4PPh_2$ and PPh_2 ligands which are *cis* to each other, with a P(2)–Mn(1)–P(1) angle of 96.0(1)°, and by the hydride ligand. The Mn(1)–P(1) bond is bent towards the molybdenum atom such that the P(1)–Mn(1)–Mo(1) and P(1)–Mn(1)–C(3) angles are respectively 75.6(1) and 98.6(1)°. The hydride ligand presumably completes the octahedron around the Mn atom. The co-ordination about the Mo atom in **5a** is similar to that in [MoMn(μ-H)(μ-PPh_2)(η^5-C_5H_5)$(CO)_6$].[7]

In the reaction of **1** with $PPhH_2$ at 383 K a complex analogous to **5a**, [MoMn(μ-$C_5H_4PPh_2$)(μ-H)(μ-PPhH)$(CO)_5$] **5b**, is the only product after 6 h, although careful infrared monitoring in the initial stages of the reaction showed weak ν(CO) bands attributed to a product monosubstituted at the manganese atom by $PPhH_2$. The conversion of this product to **5b** is presumably more facile than that of **2a** to **5a**. The structure shown for **5b** is assigned on the basis of the crystallographic evidence for **5a** and the similarity of their spectroscopic properties. For example, the ^1H NMR spectra of the two complexes show peaks at δ −12.42 and −12.14 respectively which may be assigned to the bridging hydride ligands. These each appear as doublets of doublets due to coupling to the two inequivalent phosphorus atoms. Complex **5b** can, in principle, exist as either one of two isomers differing in the orientation of PPhH group relative to the other bridging ligand but it was not possible to determine from the NMR data which one was present.

Monosubstitution of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_7$] **1** *by Phosphines at the Molybdenum Atom.*—The ligand PPh_3 does not react with **1** at 353 K in refluxing hexane–toluene (5:1) to give a complex of type **2** but, on refluxing overnight in toluene at 383 K, [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$(PPh_3)] **3a** was obtained. Although this complex has the same type of molecular formula as the complexes **2** it is assigned a structure with the PPh_3 substituent on the molybdenum atom, on the basis of its spectroscopic properties. These are very similar to those of [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$(PPh_2Et)] **3b**, the structure of which has been determined by X-ray analysis. Complex **3b** is obtained in a 1:2 ratio with **2e** as an inseparable mixture when **1** and PPh_2Et are refluxed in toluene at 383 K [rather than in hexane–toluene (5:1) at 353 K which gives **2e** only]. The sample of **3b** used for the X-ray study was, however, obtained by a different route. Another complex monosubstituted at the molybdenum atom, [MoMn(μ-$C_5H_4PPh_2$)$(CO)_6$($PPh_2CH{=}CH_2$)] **3c**, was obtained as one of the products of the reaction of $PPh_2CH{=}CH_2$ with **1** in refluxing toluene.

The molecular structure of **3b**, shown in Fig. 2 and characterised by the bond lengths and angles listed in Table 3, is similar to that of **1**,[8] to which it is related by replacement of the carbonyl group attached to the molybdenum atom in the position transoid to the metal–metal bond by a PPh_2Et ligand. The Mo–Mn bond [3.073(1) Å] in **3b** is slightly longer than that in **1** [3.054(1) Å][8] and comparable with that in [MoMn(η^5-C_5H_5)$(CO)_8$] [3.08(1) Å].[10] Except for the phenyl and ethyl groups of the PPh_2Et ligand, the molecular structure of **3b** shows approximate C_s symmetry, the plane of symmetry passing through the P(1)–Mo–Mn–P(2)–C(33) linkage [as well as the carbonyl groups C(3)–O(3) and C(4)–O(4)] and bisecting the C_5H_4 ring. The asymmetrical orientation of the PPh_2Et ligand with respect to this plane, characterised by the torsion angles listed in Table 3, may reflect the steric requirements of this bulky phosphine.

In the MoMn(μ-$C_5H_4PPh_2$) fragment the cyclopentadienyl group is planar [the atomic displacements from the plane not exceeding 0.004(4) Å] and perpendicular to the ring formed by the centroid of the C_5H_4 group, Mo, and the Mn and P(2) atoms [dihedral angle 89.8(5)°]. The C(33)–P(2) bond is bent out of the C_5H_4 plane toward the manganese atom, to afford the C(33)–P(2)–Mn angle of 103.6(2)°. The Mn–P(2) bond is bent toward the molybdenum atom, resulting in the closure of the P(2)–Mn–Mo and P(2)–Mn–C(4) angles to 77.3(1) and 165.1(2)° in the distorted octahedron around the manganese centre. The Mn–Mo–C_5H_4 (centroid) angle of 101.5(1)° is much

Table 3 Selected bond parameters (lengths in Å, angles in °) for $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Et)]$ **3b**

Mo–Mn	3.073(1)	P(1)–C(15)	1.829(4)
Mo–P(1)	2.442(1)	P(2)–C(21)	1.824(4)
Mn–P(2)	2.269(2)	P(1)–C(27)	1.816(4)
Mo–C(1)	1.960(4)	P(2)–C(33)	1.797(4)
Mo–C(2)	1.960(4)	C(1)–O(1)	1.146(5)
Mn–C(3)	1.790(5)	C(2)–O(2)	1.161(5)
Mn–C(4)	1.824(5)	C(3)–O(3)	1.150(6)
Mn–C(5)	1.819(4)	C(4)–O(4)	1.143(6)
Mn–C(6)	1.838(5)	C(5)–O(5)	1.157(5)
Mo–C(33)	2.373(4)	C(6)–O(6)	1.143(6)
Mo–C(34)	2.344(4)	C(33)–C(34)	1.440(5)
Mo–C(35)	2.325(4)	C(34)–C(35)	1.399(6)
Mo–C(36)	2.332(4)	C(35)–C(36)	1.421(6)
Mo–C(37)	2.353(4)	C(36)–C(37)	1.405(6)
P(1)–C(7)	1.846(4)	C(37)–C(33)	1.415(5)
P(1)–C(9)	1.842(4)	C(7)–C(8)	1.523(7)
Mn–Mo–P(1)	145.0(1)	Mo–P(1)–C(15)	112.6(2)
Mn–Mo–C(1)	78.9(2)	C(7)–P(1)–C(9)	102.7(2)
Mn–Mo–C(2)	75.0(2)	C(7)–P(1)–C(15)	101.4(2)
P(1)–Mo–C(1)	81.3(2)	C(9)–P(1)–C(15)	100.7(2)
P(1)–Mo–C(2)	79.4(2)	Mn–P(2)–C(21)	119.7(2)
C(1)–Mo–C(2)	97.7(2)	Mn–P(2)–C(27)	119.5(2)
Mo–Mn–C(3)	175.9(2)	Mn–P(2)–C(33)	103.6(2)
Mo–Mn–P(2)	77.3(1)	C(21)–P(2)–C(27)	103.1(2)
Mo–Mn–C(4)	87.8(2)	C(21)–P(2)–C(33)	103.9(2)
Mo–Mn–C(5)	86.3(2)	C(27)–P(2)–C(33)	105.3(2)
Mo–Mn–C(6)	87.4(2)	C(37)–C(33)–C(34)	107.1(4)
P(2)–Mn–C(4)	165.1(2)	C(33)–C(34)–C(35)	107.7(4)
P(2)–Mn–C(3)	99.0(2)	C(34)–C(35)–C(36)	108.7(4)
P(2)–Mn–C(5)	87.6(2)	C(35)–C(36)–C(37)	107.7(4)
P(2)–Mn–C(6)	88.7(2)	C(36)–C(37)–C(33)	108.8(4)
C(3)–Mn–C(4)	96.0(2)	Mo–C(1)–O(1)	177.1(4)
C(3)–Mn–C(5)	91.7(2)	Mo–C(2)–O(2)	176.1(4)
C(3)–Mn–C(6)	94.5(2)	Mn–C(3)–O(3)	177.1(4)
C(4)–Mn–C(5)	92.4(2)	Mn–C(4)–O(4)	177.7(4)
C(4)–Mn–C(6)	89.6(2)	Mn–C(5)–O(5)	176.4(4)
C(5)–Mn–C(6)	173.2(2)	Mn–C(6)–O(6)	178.3(4)
Mo–P(1)–C(7)	117.9(2)	P–C(7)–C(8)	113.6(3)
Mo–P(1)–C(9)	118.8(2)		
Mn–Mo–P(1)–C(7)	−32.0(2)		
Mn–Mo–P(1)–C(9)	93.1(2)		
Mn–Mo–P(1)–C(15)	−149.5(2)		

smaller than the unconstrained Mo–Mo–C_5H_4 (centroid) angle of 117.6° in $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$.[11] The angular distortions shown here are indicative of considerable strain in the P(2)–Mn–Mo–C_5H_4 (centroid) ring and they are of equal magnitude to those observed in **1**. The co-ordination sphere around the molybdenum atom is distorted further from the idealized piano stool geometry by opening of the Mn–Mo–P(1) angle to 145.0(1)°; in **1** the corresponding Mn–Mo–C(carbonyl) angle is 141.2(2)°, reflecting the smaller steric demands of the carbonyl ligand.

The Mo–P(1) bond [2.442(1) Å] is slightly shorter than the Mo–P bonds in *trans*-$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)(COMe)]$ [2.473(3) Å][12] and in $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)I]$ [2.481(5) Å].[13] The Mn–P(2) distance [2.269(2) Å] is comparable with that of **1** [2.278(1) Å]. All the carbonyl ligands in **3b** are essentially linear, the largest deviation from linearity affording the Mo–C(2)–O(2) angle of 176.1(4)°.

The ^1H NMR spectra of **3a**–**3c** each show two pseudo-quartets or multiplets in the cyclopentadienyl region at δ 4.5–4.6 and 4.1–4.4, as expected if the plane of symmetry found in the solid-state structure of **3b** is maintained in solution for all three complexes. The ^{13}C NMR spectrum of **3c** at room temperature is also in accord with this structure, showing a single doublet in the carbonyl region at δ 234.9 with $^2J(PC)$ 23 Hz. This doublet may be assigned to the two equivalent carbonyl ligands bound to the molybdenum atom, the coupling being to the adjacent phosphine ligand. A similar signal is seen in the ^{13}C NMR spectra of *trans*-$[Mo(\eta^5\text{-}C_5H_5)(CO)_2L(X)]$ (X = halide) with $J(PC)$ 27 Hz.[14] No ^{13}C NMR signals were observed for the manganese-bound carbonyl ligands in **3c**, presumably because of quadrupole broadening by the ^{55}Mn nucleus.

A low-temperature study of the ^1H and ^{31}P NMR spectra of **3c** suggests that the above interpretation of the room-temperature spectra of **3a**–**3c** may be an oversimplification. Thus the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3c**, which consists of a sharp resonance at δ −73.0 due to the molybdenum-bound $PPh_2CH{=}CH_2$ ligand and a broad resonance at *ca.* δ 80.0 due to the manganese-bound phosphorus of the $C_5H_4PPh_2$ ligand, is modified at lower temperatures. At 200 K the peak at δ −73.0 is replaced by two peaks of approximately equal intensity and the peak at *ca.* δ −80 is considerably sharpened [Fig. 3(*a*)]. The splitting of the δ −73.0 peak at low temperatures suggests the presence of isomers in solution which are rapidly interconverting at room temperature, and this interpretation is supported by the ^1H NMR spectrum at 195 K [Fig. 3(*b*)]. The two peaks due to the cyclopentadienyl protons which are seen at room temperature are replaced by two resonances at δ 4.54 and 4.28, which may be assigned to the symmetrical isomer A found in the solid state for **3b**, and by four lower intensity resonances at δ 5.01, 4.60, 4.44 and 3.51 which may be assigned to a less symmetrical isomer B in which the vinylphosphine ligand is co-ordinated at one of the outer positions on the molybdenum atom.

A room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3c** in the presence of free $PPh_2CH{=}CH_2$ shows a sharp resonance due to the free ligand, implying that the co-ordinated vinylphosphine ligand is not dissociating rapidly on the NMR time-scale at room temperature. Accordingly the mechanism of isomer interconversion does not involve phosphine dissociation; a localised twisting process involving the two carbonyl ligands and the phosphine ligand on the molybdenum atom seems the most likely explanation.

Monosubstitution of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1** *with Isonitriles*.—The reaction of **1** with one equivalent of RNC in refluxing hexane–toluene (5 : 1) at 353 K or in refluxing toluene at 383 K gave orange complexes which are formulated on the basis of their spectroscopic properties as $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(CNR)]$ (R = CH_2Ph **2g** or Bu^t **2h**). Thus in the ^1H NMR spectrum of **2g** four signals at δ 5.30, 5.17, 4.30 and 3.50 may be assigned to the cyclopentadienyl protons, showing that this complex lacks the plane of symmetry present in **2a**–**2f**. The anomalously low chemical shift value of δ 3.50 for one of the cyclopentadienyl protons is caused possibly by its proximity to the phenyl ring of the benzyl group.[15] Similar effects have been seen in related complexes.[16] The ^{13}C NMR spectrum of **2g** shows three peaks in the carbonyl region at δ 232.4, 228.0 and 225.4 which may be assigned to molybdenum-bound carbonyl ligands. A broad peak at δ 217, similar to that reported for **1**, is assigned to the manganese-bound carbonyls.

Disubstitution of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1**.—Reaction of the complex $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)(CO)_6]$ with excess phosphine or phosphite leads to disubstitution at the manganese atom.[7] In contrast the reaction of **1** with excess PPh_2Me or $P(OMe)_3$ in refluxing toluene at 383 K gives, in addition to small quantities of the monosubstituted complexes **2**, the disubstituted complexes $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5L_2]$ [L = PPh_2Me **4a** or $P(OMe)_3$ **4c**]. These are revealed by spectroscopic evidence to have one substituent on the molybdenum and one on the manganese atom. A further disubstituted complex of the same type (L = $PPh_2CH{=}CH_2$ **4b**) is obtained as one of the low-yield products of the reaction of **1** in a 1 : 1 ratio with $PPh_2CH{=}CH_2$ in refluxing toluene. Alternatively complex **4a** may be obtained by refluxing the monosubstituted complex **2b** with excess PPh_2Me.

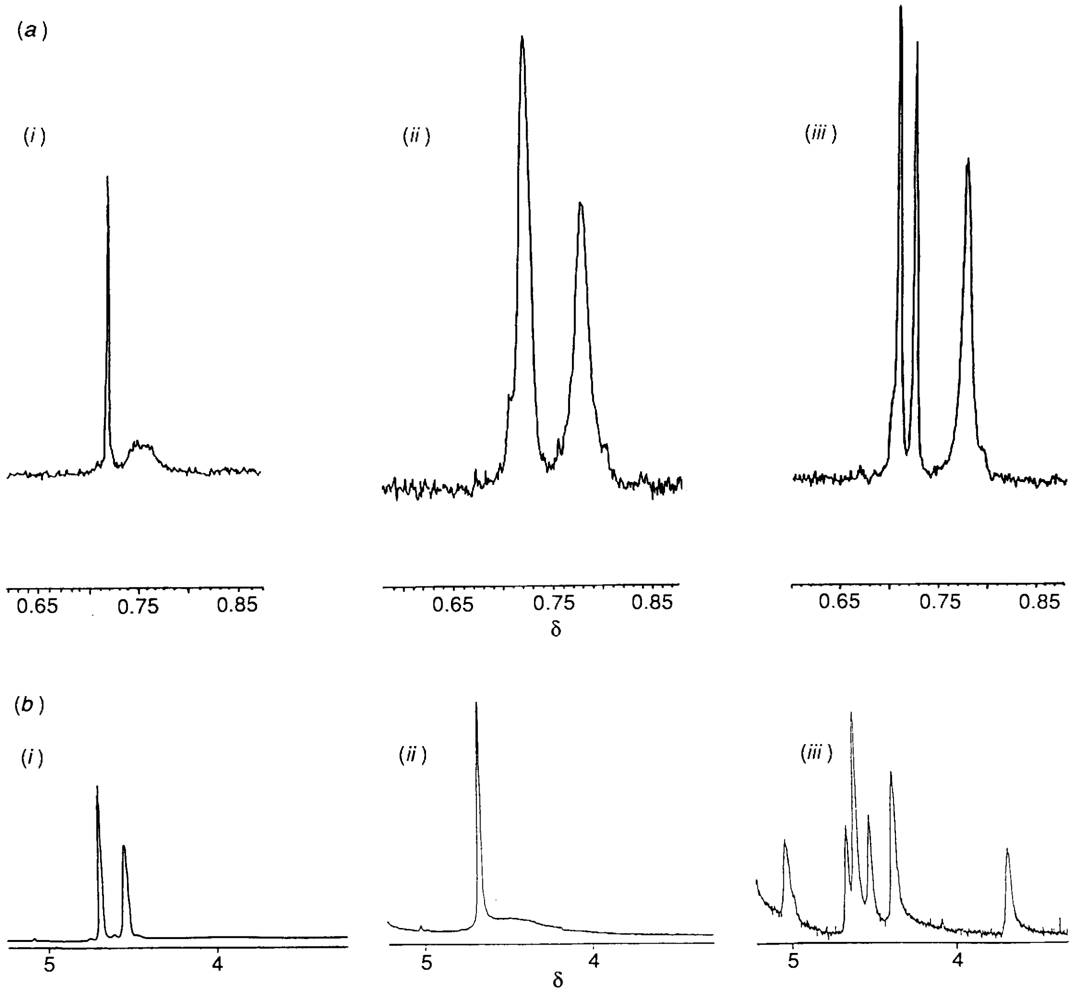


Fig. 3 (*a*) Variable temperature ^{31}P NMR spectrum of **3c** at (*i*) 294, (*ii*) 240 and (*iii*) 200 K. (*b*) Variable temperature ^{1}H NMR spectrum of **3c** at (*i*) 298, (*ii*) 237 and (*iii*) 195 K

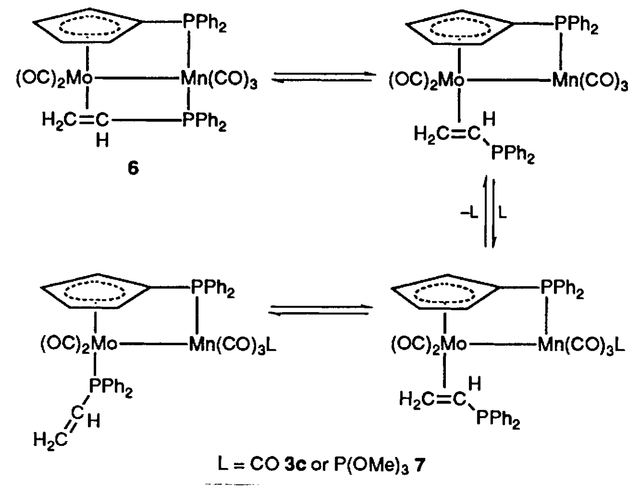
The ^{1}H NMR spectra of **4a** and **4b** each show two multiplets in the cyclopentadienyl region at *ca.* δ 4.3 and 4.7 suggesting that there is a plane of symmetry as in the complexes **2a**–**2f**. In addition, the ^{1}H NMR spectrum of **4a** shows two signals at δ 2.10 and 1.91 which may be assigned to the methyl protons of the PPh_2Me groups. The presence of two such signals, and their integrals relative to those of the cyclopentadienyl signals, confirms that disubstitution has occurred.

The ^{13}C NMR spectrum of **4a** in the carbonyl region shows a resonance at δ 238.7 which is split into a doublet by coupling to phosphorus [^{2}J(PC) 20.2 Hz] and a broad signal at δ 223. The first signal is assigned to the molybdenum-bound carbonyl ligands, and the magnitude of the phosphorus–carbon coupling strongly suggests that one of the phosphine ligands is attached to the molybdenum atom. The other signal is assigned to the manganese-bound carbonyl ligands and hence it is broad due to quadrupole relaxation. The ^{31}P NMR spectrum at 298 K shows the expected three signals.

On the basis of the above evidence and the position at which monosubstitution occurs in **2b** and **2d**, the most likely structure for **4a** and **4b** is that shown with a phosphine on manganese *trans* to the cyclopentadienyl phosphorus as in **2b** and **2d** and a phosphine attached to the molybdenum atom. The latter phosphine is shown as being on the central position on the molybdenum atom in accord with the plane of symmetry in the molecule implied by the ^{1}H NMR spectrum, and the observation of only one signal in the ^{13}C NMR spectrum for the carbonyl ligands bound to molybdenum. Fluxional behaviour, as seen in **3c**, could also account for the above observations, but the low-temperature (230 K) ^{31}P-{^{1}H} NMR spectrum of the bis(trimethyl phosphite) complex **4c** shows no sign of such behaviour.

The infrared spectrum of **4c** in the carbonyl region is substantially different from those of **4a** and **4b**. In addition the phosphite region of the ^{1}H NMR spectrum of **4c** shows four doublets, each with *J*(PH) of *ca.* 11 Hz in an intensity ratio which suggests the presence of two isomers in solution in a concentration ratio of 3:2. In the cyclopentadienyl region three multiplets are observed in an intensity ratio of 5:3:2 which can be assigned to the two isomers, with the signal of relative intensity 5 being due to two overlapping peaks of intensity 3 and 2. The ^{13}C and ^{31}P NMR spectra of **4c** can be interpreted similarly. Six signals are seen in the ^{31}P-{^{1}H} NMR spectrum at room temperature due to the three different phosphorus atoms in each isomer. Two broad peaks at δ 59.4 and 47.0 are assigned to phosphite ligands on manganese and two sharp peaks at δ 57.0 and 56.7 to phosphite ligands on molybdenum. Upon cooling to 230 K the resonances due to the manganese-bound phosphite ligands become sharper and coupling [*J*(PP) 43 Hz] between these ligands and the phosphorus of the $C_5H_4PPh_2$ ligand is observed. The signals due to the molybdenum-bound phosphorus atoms are unchanged on cooling and show no such coupling. The lack of variation with temperature of these signals suggests that the fluxional process seen in **3c** is absent in **4c**.

The observation of only two cyclopentadienyl signals for each isomer in the ^{1}H NMR spectrum of **4c** suggests that each has the



Scheme 1 Proposed mechanism for the addition reactions of **6** with CO or $P(OMe)_3$

plane of symmetry present in **2a**–**2f** and on this basis the isomers are assigned the structures shown, with the isomerism being due to the ability of the phosphite ligand to occupy two different positions at the manganese atom.

Synthesis and Reactivity of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}PPh_2CH{=}CH_2)(CO)_5]$ **6**.—The formation of complexes **3c** and **4b** in the reaction of **1** with $PPh_2CH{=}CH_2$ in refluxing toluene has already been described. A third product of this reaction, formed in 29% yield, is the complex $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}PPh_2CH{=}CH_2)(CO)_5]$ **6**. This complex is also obtained on thermolysis of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ (**2d** or **3c**) at 383 K. Although crystals of **6** suitable for an X-ray study could not be obtained the complex may be assigned the structure shown on the basis of spectroscopic evidence. The ^1H NMR spectrum of **6** shows four multiplets for the cyclopentadienyl protons, each corresponding to a single proton, implying that the ring is in an asymmetrical environment. The signal at δ 3.24 is shifted upfield as in **2g**, again presumably because of the proximity of an aromatic ring. The vinyl proton signals are observed at δ 2.98, 2.67 and 2.35, whereas in **2d** they are in the range δ 5.06–6.8, and this indicates that in **6** the vinyl group is co-ordinated to a metal atom.[17] The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **6** at room temperature shows two signals at δ −71.4 and −92.3 which confirms the presence in solution of a single isomer. By comparison with the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2d** the peak at δ −71.4 is tenatively assigned to the cyclopentadienyl phosphorus and that at −92.3 to the $PPh_2CH{=}CH_2$ phosphorus atom. A spectrum recorded at 225 K did not show phosphorus–phosphorus coupling, but the fact that both peaks appear to be broadened by the quadrupolar ^{55}Mn nucleus implies that the phosphorus atom of the vinylphosphine is attached to this metal atom. This conclusion is reinforced by the room-temperature ^{13}C NMR spectrum of **6** in the carbonyl region, which shows two sharp singlet signals at δ 229.1 and 223.6. These may be assigned to molybdenum-bound carbonyl groups and the absence of phosphorus–carbon coupling is as expected if **6** has the structure proposed. No signals due to the manganese-bound carbonyl groups were seen in the ^{13}C NMR spectrum of **6**, presumably because of quadrupole broadening.

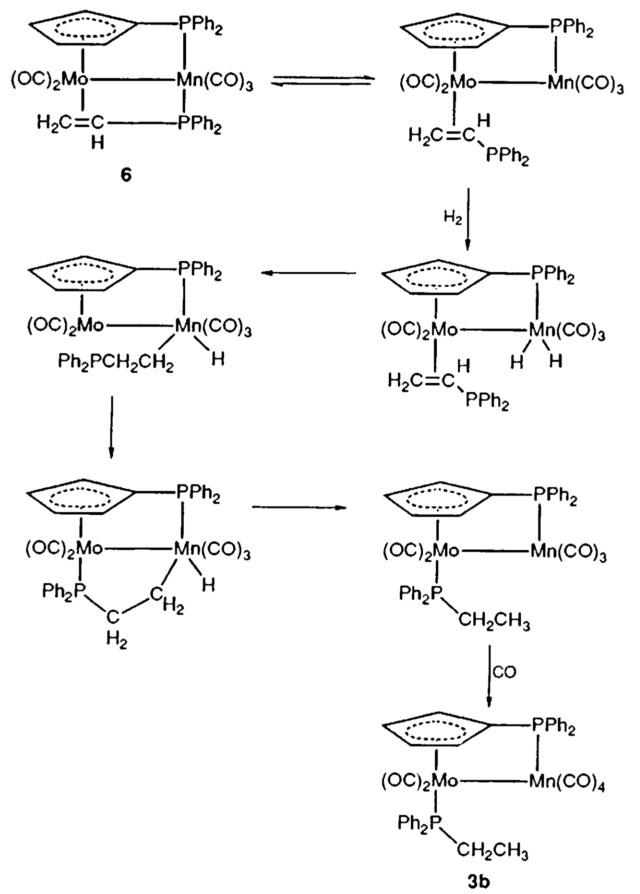
The co-ordination of the vinyl group to one of the manganese atoms in $[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_8]$ can be displaced by reaction of the complex with excess of CO.[17] In contrast, the reaction of **6** with excess of CO or H_2 at 383 K in refluxing toluene gave $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ **3c** or $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Et)]$ **3b** respectively, with the vinylphosphine ligand co-ordinated through phosphorus to the molybdenum atom, although a straightforward displacement of the co-ordinated vinyl group would have been expected to lead to the ligand remaining co-ordinated to the manganese atom as in **2d**. A similar transfer of the attachment of the vinylphosphine ligand from manganese to molybdenum takes place in the reaction of **6** with $P(OMe)_3$ under the same conditions, to give $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5(PPh_2CH{=}CH_2)\{P(OMe)_3\}]$ **7**. This complex is analgous to **4c**, apart from their differing substituents. The NMR data for **7** reveal that, as for **4c**, it exists in solution as a mixture of two isomers which differ only in the position occupied by the substituent on the manganese atom. Two broad phosphite signals are observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **7** which may be assigned to manganese-bound ligands. The two additional sharper signals due to phosphite groups seen in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4c** and assigned to molybdenum-bound ligands are of course absent in the spectrum of **7**. The $PPh_2CH{=}CH_2$ ligand in **7** gives rise to only one sharp ^{31}P signal at δ −71.7, which must be assigned as being due to coincident peaks for the two isomers, but this is not surprising since the molybdenum-bound phosphite ligands in the two isomers of **4c** also give rise to two signals which are very close together.

The above addition reactions involve in each case not only a displacement of the vinyl group from its co-ordination to the molybdenum atom but also a transfer of the attachment through phosphorus of the vinylphosphine ligand from manganese to molybdenum. Such a transfer of a vinylphosphine ligand between two metal centres has not been observed previously, although the transfer of other types of phosphines in dinuclear complexes is a known process.[18,19] A possible mechanism for the addition reactions of **6** is shown in Scheme 1. For addition of CO or $P(OMe)_3$ it is proposed that cleavage of the manganese–phosphorus bond is followed by attack of the nucleophile at the manganese atom and rearrangement of the vinylphosphine on the molybdenum atom. The proposed mechanism requires the manganese–phosphorus bond to the vinylphosphine ligand in **6** to be broken relatively easily, and this is borne out by the fact that $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6\{P(OMe)_3\}]$ **2f** is obtained when the manganese substituted complex $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Me)]$ **2b** is refluxed with $P(OMe)_3$ in toluene for 2 h. Complex **2f** prepared by this means is formed as a 3:1 mixture of the isomer with the phosphite substituent *trans* to the cyclopentadienylphosphine and the isomer with the phosphite *trans* to the metal–metal bond, whereas a 1:1 mixture is obtained when **1** is refluxed with $P(OMe)_3$.

An alternative mechanism for addition of CO or $P(OMe)_3$ could involve as a first step the breaking of the vinyl–molybdenum bond, this being followed by transfer of the phosphorus-co-ordinated vinylphosphine ligand from manganese to molybdenum and then by nucleophilic attack of the incoming ligand at the manganese atom. This seems less likely, since the unsaturated molybdenum atom postulated in the first stage of the reaction would probably react with the incoming nucleophile, leaving the vinylphosphine ligand co-ordinated to the manganese atom.

For the reaction with hydrogen we propose that the initial manganese–phosphorus bond cleavage is followed by oxidative addition of hydrogen to the manganese atom, insertion of the vinyl group into a manganese–hydrogen bond, co-ordination of the phosphine to the now unsaturated molybdenum centre and reductive elimination at manganese to give an ethylphosphine ligand, Scheme 2. The scavenging of CO from the reaction mixture is required to give the observed product, **3b**. It is tempting to propose as an alternative that **6** reacts with CO to give **3c** and that subsequent hydrogenation of the carbon–carbon double bond gives **3b**. Careful infrared monitoring of the reaction of **3c** with hydrogen shows, however, that **3c** is converted thermally to **6** before any hydrogenation takes place.

A final point which is worthy of note is that, although the conversion of **3c** to **6** may be reversed by the addition of CO, the conversion of **2d** to **6** is irreversible. This implies that **3c** is the



Scheme 2 Proposed mechanism for the addition reaction of **6** with hydrogen

thermodynamically preferred isomer, even though the formation of **2d** rather than **3c** from **1** and $PPh_2CH{=}CH_2$ is favoured kinetically.

Reactivity of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a**.—The reactions of $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ with small organic molecules lead to a variety of interesting products.[20] For this reason the reactions of **5a** with $HC{\equiv}CH$, $MeC{\equiv}CH$, $PhC{\equiv}CH$, $MeO_2CC{\equiv}CCO_2Me$ and $MeCH{=}CH_2$ were attempted under thermal and photolytic conditions. All of these reactions led merely to some decomposition and to recovery of unreacted starting material. It seems likely that the lack of reactivity of **5a** as compared to $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ with the above substrates is due to greater steric crowding round the metal–metal bond in the former complex, which presumably inhibits the approach of the organic molecules.

Conclusion

The results presented above show that, in the absence of steric constraints, the first stage in the reactions of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1** with nucleophiles is substitution of a manganese-bound carbonyl group. In the case of $P(OMe)_3$, which has the lowest cone angle,[21] monosubstitution can take place either *trans* to the metal–metal bond or *trans* to the cyclopentadienylphosphine phosphorus atom, but the rather more bulky phosphine ligands PPh_2H, PPh_2Me and $PPhMe_2$ only give the latter isomer. The ligand PPh_2Et, which has a higher cone angle, can substitute either at the manganese or the molybdenum atom depending on the reaction conditions, whereas PPh_3, which has a higher cone angle still, can only substitute at the molybdenum atom. Isonitriles, which are sterically less hindered at the donor atom than either phosphines or phosphites, substitute at manganese *trans* to a carbonyl group, as in the substitution of $[Mn_2(CO)_{10}]$ by isonitriles.[22] It is probably only the greater steric bulk of the phosphines which preclude them also from occupying this position in complexes **2a**–**2f**, since π-bonding considerations suggest that it is likely to be electronically more favourable than a position *trans* to another phosphorus atom.

The pattern of monosubstitution in **1** resembles that of the complex $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ in that substitution at the manganese atom is the preferred initial step, but differs in that for **1** a complex monosubstituted at the molybdenum atom can also be obtained. The fact that the manganese-substituted vinylphosphine complex **2d** isomerises irreversibly *via* **6** to the molybdenum-substituted complex **3c** suggests that, for this ligand at least, substitution in **1** at the molybdenum atom is thermodynamically preferred and that the initial substitution at the manganese atom is the result of kinetic control.

In the disubstitution of $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ both substituents react initially at the manganese atom,[7] whereas in **1** disubstitution results in each metal atom carrying one substituent. A similar pattern of multiple substitution taking place at more than one metal centre has been observed in other systems.[18,19]

It may be concluded from the above data that in **1** the molybdenum atom is more easily substituted, relative to the manganese atom, than in $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$. This greater relative reactivity enables both metal atoms to become involved in the reactions of **1** with ligands such as $PPh_2CH{=}CH_2$ and PPh_nH_{3-n} ($n = 1$ or 2) which, after initial co-ordination through phosphorus, are capable of further reaction with the metal centres. The transfer of a co-ordinated vinylphosphine ligand from manganese to molybdenum is a noteworthy feature of the further reactions involving this ligand.

Greater steric crowding in $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a** as compared to $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$ inhibits the reaction of the former molecule with organic substrates.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously. For the numbering of the carbon atoms see structure of compound **1**.[23] Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. Compound $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1** was prepared by a slight modification of the literature method[8] using $[Mo(CO)_3(MeCN)_3]$[24] in place of $[Mo(CO)_6]$. This modification enables the $[Li\{Mo(CO)_3(\eta^5\text{-}C_5H_4PPh_2)\}]$ intermediate to be prepared in 15 min at room temperature, rather than by overnight reflux, and gives a purer solution of the anion.

Substitution Reactions of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1**.—(*a*) With PPh_2H. (*i*) A solution of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_7]$ **1** (0.78 g, 1.31 mmol) and PPh_2H (0.23 cm^3) in toluene (60 cm^3) was heated to reflux at 383 K for 2 h. After cooling the solvent was removed under vacuum and the residue adsorbed on silica. It was then purified by column chromatography. Elution with CH_2Cl_2–hexane (1:4) gave an orange band which yielded

$[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2H)]$ **2a** (0.420 g, 42%) as an orange powder. An impurity of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a** was removed by recrystallisation of **2a** from CH_2Cl_2–hexane (1:1) to give pure **2a** (0.350 g, 35%) as orange crystals. Complex **2a** (Found: C, 55.4; H, 3.4; P, 8.4. $C_{35}H_{25}MnMoO_6P_2$ requires C, 55.7; H, 3.3; P, 8.2%). NMR: ^{13}C (CH_2Cl_2, 234 K), δ 232.2 [s, $Mo(CO)_2$], 228.5 [s, Mo(CO)], 217.2 [br, $Mn(CO)_3$], 134–127 (m, Ph), 89.1 (br s, C_5H_4P, C^2 or C^3), 88.5 [d, *J*(PC) 10.4, C_5H_4P, C^2 or C^3] and 56.4 [d, *J*(PC) 50.1 Hz, C_5H_4P, C^1]; ^{31}P ($CDCl_3$, ^1H-gated decoupled), δ −72.3 (s, $PPh_2C_5H_4$) and −80.1 (s, PPh_2H).

(*ii*) The reaction was carried out as above using **1** (0.850 g, 1.426 mmol) and PPh_2H (0.25 cm^3) in toluene (100 cm^3) except that the solution was heated to reflux for 6 h. Purification by column chromatography eluting with CH_2Cl_2–hexane (1:4) gave two orange bands which were identified as unreacted **1** (0.03 g, 4%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a** (0.495 g, 48%). Complex **5a** (Found: C, 55.8; H, 3.7; P, 6.4. $C_{34}H_{25}MnMoO_5P_2$ requires C, 56.2; H, 3.5; P, 8.5%). Mass spectrum: *m/z* 727 (M^+) and $M^+ - n$(CO) (*n* = 2–5). NMR: ^{13}C ($CDCl_3$, 298 K), δ 240.5 [d, *J*(PC) 23.0, Mo(CO)], 239.2 [s, Mo(CO)], 224.6 [br, s, Mn(CO)], 221.7 [br, s, Mn(CO)], 217 [br, s, Mn(CO)], 141–127 (m, Ph), 98.4 (br s, C_5H_4P, C^2 or C^3), 98.3 (br, s, C_5H_4P, C^2 or C^3), 94.9 (br, s, C_5H_4P, C^2 or C^3), 93.6 (br, s, C_5H_4P, C^2 or C^3) and 79.3 [d, *J*(PC), 41.5 Hz, C_5H_4P, C^2]; ^{31}P ($CDCl_3$, ^1H-gated decoupled), δ 4.2 (s, PPh_2) and −96.2 (s, $PPh_2C_5H_4$).

(*b*) *With* $PPhH_2$. The reaction was carried out as in (*a*) above using **1** (0.500 g, 0.839 mmol) and $PPhH_2$ (0.10 cm^3) in toluene (100 cm^3). The solution was heated to reflux for 6 h and, after cooling, the solvent was removed under vacuum. The residue was adsorbed on silica and then purified by column chromatography as in (*a*), eluting with CH_2Cl_2–hexane (1:2). A single orange band was obtained which yielded $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_5]$ **5b** (0.278 g, 51%) as an orange powder. Complex **5b** (Found: C, 51.8; H, 3.2; P, 8.0. $C_{28}H_{21}MnMoO_5P_2$ requires C, 51.7; H, 3.2; P, 9.5%). Mass spectrum: *m/z* 650 (M^+) and $M^+ - n$ (CO) (*n* = 1–5). NMR: ^{13}C ($CDCl_3$, 298 K), δ 237.4 [d, *J*(PC) 22.7, Mo(CO)], 236.5 [d, *J*(PC) 4.2, Mo(CO)], 217 [br, $Mn(CO)_3$], 136–127 (m, Ph), 92.4 [d, *J*(PC) 4.7, C_5H_4P, C^2 or C^3], 92.2 [d, *J*(PC) 8.0, C_5H_4P, C^2 or C^3], 89.4 [d, *J*(PC) 14.0, C_5H_4P, C^2 or C^3], 88.8 [d, *J*(PC) 15.3, C_5H_4P, C^2 or C^3] and 79.0 [d, *J*(PC) 45.0 Hz, C_5H_4P, C^1]; ^{31}P ($CDCl_3$, ^1H-gated decoupled), δ −59.5 (s, PPhH) and −86.5 (s, $PPh_2C_5H_4$).

(*c*) *With* PPh_2Me. (*i*) The reaction was carried out using **1** (0.050 g, 0.084 mmol) and PPh_2Me (0.018 cm^3, 0.084 mmol) in hexane–toluene (5:1) (15 cm^3). The solution was heated to reflux at 353 K for 16 h and, after cooling, the solvent was removed under vacuum. The residue was then purified by TLC eluting with CH_2Cl_2–hexane (3:7). The two orange bands obtained were identified as unreacted **1** (0.005 g, 10%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Me)]$ **2b** (0.02 g, 34%) as an orange powder. Complex **2b** (Found: C, 57.3; H, 3.4. $C_{36}H_{27}MnMoO_6P_2$ requires C, 56.2; H, 3.5%). NMR: ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −71.4 (s, $PPh_2C_5H_4$) and −95.4 (s, PPh_2Me); ^{31}P (CD_2Cl_2, 225 K); δ −71.6 [d, *J*(PP) 10 Hz] and −95.1 (d).

(*ii*) The reaction was carried out as in (*a*) above using **1** (0.050 g, 0.084 mmol) and PPh_2Me (0.045 cm^3, 0.242 mmol) in toluene (30 cm^3) and refluxing at 383 K for 16 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (1:4). Two orange bands were obtained which were identified as **2b** (0.005 g, 8%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5(PPh_2Me)_2]$ **4a** (0.031 g, 39%) (an orange powder). Complex **4a** (Found: C, 60.7; H, 4.2. $C_{48}H_{40}MnMoO_5P_3$ requires C, 61.3; H, 4.3%). Fast atom bombardment (FAB) mass spectrum: *m/z* 940 (M^+), and $M^+ - n$ (CO) (*n* = 1–3). NMR: ^{13}C ($CDCl_3$, 298 K), δ 238.7 [d, *J*(PC) 20.2, $Mo(CO)_2$], 223 [br, $Mn(CO)_3$], 139.8 [d, *J*(PC) 41.6, *ipso*-Ph], 136.5 [d, *J*(PC) 38.4, *ipso*-Ph], 132–127 (m, Ph), 91.5 [d, *J*(PC) 6.3, C_5H_4P, C^2 or C^3], 87.5 [d, *J*(PC) 10.2, C_5H_4P, C^2 or C^3], 61.8 [d, *J*(PC) 40 Hz, C_5H_4P, C^2] and 19.4 (m, PPh_2*Me*); ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −68.8 (br s, $PPh_2C_5H_4$), −82.6 (s, $MoPPh_2Me$) and −90.4 (br s, $MnPPh_2Me$).

(*d*) *With* $PPhMe_2$. The reaction was carried out as in (*a*) above using **1** (0.050 g, 0.084 mmol) and $PPhMe_2$ (0.015 cm^3, 0.848 mmol) in toluene (15 cm^3) and refluxing at 383 K for 16 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (3:7) to give a single orange band from which $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPhMe_2)]$ **2c** (0.012 g, 20%) was obtained as an orange powder on evaporation of the solvent.

(*e*) *With* $PPh_2CH{=}CH_2$. (*i*) The reaction was carried out as in (*a*) above using **1** (0.200 g, 0.336 mmol) and $PPh_2CH{=}CH_2$ (0.070 cm^3, 0.352 mmol) in hexane–toluene (5:1) (30 cm^3), and refluxing at 353 K for 16 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (3:7) to give two orange bands from which unreacted **1** (0.032 g, 16%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ **2d** (0.110 g, 42%) were obtained. Complex **2d**. FAB mass spectrum: *m/z* 780 (M^+). NMR: ^{13}C ($CDCl_3$, 298 K), δ 229.1 [s, $Mo(CO)_2$], 227 [s, Mo(CO)], 220 [br, $Mn(CO)_3$], 135.4 [d, *J*(PC), 40.0, *ipso*-Ph], 135.2 [d, *J*(PC) 42.1, *ipso*-Ph], 134.9 [d, *J*(PC) 30, P*C*H=CH$_2$], 133.3 [d, *J*(PC) 9.7, *o*-Ph], 131.5 [d, *J*(PC) 11.5, *o*-Ph], 130.7 (s, *p*-Ph), 129.8 (s, *p*-Ph), 128.8 [d, *J*(PC) 10.1, *m*-Ph], 128.5 (s, PCH=*C*H$_2$), 128.2 [d, *J*(PC) 9.5, *m*-Ph], 89.3 [d, *J*(PC) 10.1, C_5H_4P, C^2 or C^3], 88.8 [d, *J*(PC) 6.4, C_5H_4P, C^2 or C^3] and 60.5 [d, *J*(PC) 46.8, C_5H_4P, C^1]; ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −70.6 (s, $PPh_2C_5H_4$) and −84.4 (s, $PPh_2CH{=}CH_2$).

(*ii*) The reaction was carried out as in (*a*) above using **1** (0.200 g, 0.335 mmol) and $PPh_2CH{=}CH_2$ (0.060 cm^3, 0.302 mmol) in toluene (50 cm^3) and refluxing at 383 K for 4 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (1:2) to give three bands. The first band gave $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}PPh_2\text{-}CH{=}CH_2)(CO)_5]$ **6** (0.074 g, 29%) as a brown powder. The second and third bands, which were both orange, gave respectively $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ **3c** (0.106 g, 40%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5(PPh_2CH{=}CH_2)_2]$ **4b** (0.015 g, 5%) both as orange powders. Complex **3c** (Found: C, 55.9; H, 3.6; P, 7.6. $C_{37}H_{27}MnMoO_6P_2$ requires C, 56.9; H, 3.5; P, 7.9%). FAB mass spectrum: *m/z* 780 (M^+), and $M^+ - n$ (CO) (*n* = 1–4). NMR: ^{13}C ($CDCl_3$, 298 K), δ 234.9 [d, *J*(PC) 23.0, $Mo(CO)_2$], 137.3 [d, *J*(PC) 45.8, P*C*H=CH$_2$], 134.8 [d, *J*(PC) 43.2, *ipso*-Ph], 134.7 [d, *J*(PC) 39.9, *ipso*-Ph], 132.8 [d, *J*(PC) 10.1, *o*-Ph], 131.6 [d, *J*(PC) 12.4, *o*-Ph], 131.0 (s, *p*-Ph), 130.2 (s, PCH=*C*H$_2$), 129.9 (s, *p*-Ph), 128.9 [d, *J*(PC) 10.5, *m*-Ph], 128.3 [d, *J*(PC) 9.6, *m*-Ph], 91.8 [d, *J*(PC) 6.4, C_5H_4P, C^2 or C^3], 86.3 [d, *J*(PC) 10.4, C_5H_4P C^2 or C^3] and 57.1 [d, *J*(PC) 52.4 Hz, C_5H_4P, C^1]; ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −73.0 (s, $PPh_2CH{=}CH_2$), −79 (br, $-PPh_2C_5H_4$); ^{31}P (CD_2Cl_2, ^1H-gated decoupled, 190 K), δ 70.5 (s, $PPh_2CH{=}CH_2$, isomer A), −72.2 (s, $PPh_2CH{=}CH_2$, isomer B) and −77.6 (br, s, $PPh_2C_5H_4$). Complex **4b**. Mass spectrum: *m/z* 936 (M^+ − CO), $M^+ - n$ (CO) (*n* = 1–5). Complex **6** (Found: C, 57.3; H, 3.7; P, 8.2. $C_{36}H_{27}MnMoO_5P_2$ requires C, 57.5; H, 3.6; P, 8.2%). NMR: ^{13}C ($CDCl_3$, 298 K), δ 229.1 [s, Mo(CO)], 223.6 [s, Mo(CO)], 144.6 [d, *J*(PC) 19.6, *ipso*-Ph], 138.1 [d, *J*(PC) 44.6, *ipso*-Ph], 136.7 [d, *J*(PC) 30, *ipso*-Ph], 134.3 [d, *J*(PC) 37.3, *ipso*-Ph], 133–128 (m, Ph), 91.5 [d, *J*(PC) 10.6, C_5H_4P, C^2 or C^3], 84.8 [br, s, C_5H_4P, C^2 or C^3], 81.4 [br s, C_5H_4P, C^2 or C^3], 77.8 [d, *J*(PC) 8.6, C_5H_4P, C^2 or C^3], 54.2 [d, *J*(PC) 47.5, C_5H_4P, C^1], 33.6 [d, *J*(PC) 12.9, PCH=*C*H$_2$] and 19.8 [d, *J*(PC), 42.2 Hz, P*C*H=CH$_2$]; ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −71.4 (br, s, $PPh_2C_5H_4$) and −92.3 (br s, $PPh_2CH{=}CH_2$); ^{31}P (CD_2Cl_2, ^1H-gated decoupled, 225 K), δ −71.7 (br, s) and −92.5 (br, s).

(*f*) *With* PPh_2Et. (*i*) The reaction was carried out as in (*a*) above using **1** (0.051 g, 0.086 mmol) and PPh_2Et (0.050 cm^3, 0.25 mmol) in hexane–toluene (5:1) (30 cm^3) and refluxing at 353 K for 16 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (3:7) to give two orange bands from which unreacted **1** (0.005 g, 10%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPhEt_2)]$ **2e** (0.032 g, 48%) were obtained. Complex **2e** (Found: C, 55.5; H, 3.7. $C_{37}H_{29}MnMoO_6P_2$ requires C, 56.8; H, 3.7%).

(*ii*) The reaction was carried out as in (*a*) above using **1** (0.050 g, 0.084 mmol) and PPh_2Et (0.016 cm^3, 0.084 mmol) in toluene (20 cm^3) and refluxing at 383 K for 22 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (1:3) to give two orange bands from which unreacted **1** (0.011 g, 22%) and a 2:1 mixture (as judged by ^1H NMR spectroscopy) of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Et)]$ **2e** and **3b**, substituted respectively on the manganese and molybdenum atoms (0.015 g, 23%), was obtained.

(*g*) *With* $P(OMe)_3$. (*i*) The reaction was carried out as in (*a*) using **1** (0.200 g, 0.336 mmol) and $P(OMe)_3$ (0.040 cm^3, 0.339 mmol) in hexane (40 cm^3) and refluxing at 343 K for 3 d. After cooling, the solvent was removed by bubbling nitrogen through the reaction mixture and the residue was then purified by TLC using CH_2Cl_2–hexane (1:4) as eluent. The two orange bands obtained were unreacted **1** (0.040 g, 20%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6\{P(OMe)_3\}]$ **2f** (0.110 g, 34%). Complex **2f** (Found: C, 44.7; H, 3.0; P, 8.7. $C_{26}H_{23}MnMoO_9P_2$ requires C, 45.1; H, 3.3; P, 9.0%). Mass spectrum: *m*/*z* 692 (M^+), and $M^+ - n(CO)$ (n = 1–3). NMR: ^{13}C ($CDCl_3$, 298 K), isomer A, δ 233.8 [s, Mo(CO)], 227.9 [s, $Mo(CO)_2$], 218 [br, $Mn(CO)_3$], 135.2 [d, *J*(PC) 39.6, *ipso*-Ph], 131.5 [d, *J*(PC) 11.9, *o*-Ph], 128.8 [d, *J*(PC) 10.2, *m*-Ph], 130.9 (s, *p*-Ph), 88 (m, C_5H_4P, C^2 and C^3), 59.0 [d, *J*(PC) 48.1, C_5H_4P, C^1] and 53.0 [d, *J*(PC) 7.8 Hz, $P(OMe)_3$]; isomer B, δ 227.2 [s, $Mo(CO)_2$], 218 [br, $Mn(CO)_3$], 134.2 [d, *J*(PC) 37.8, *ipso*-Ph], 132.2 [d, *J*(PC) 12.1, *o*-Ph], 130.7 (s, *p*-Ph), 128.5 [d, *J*(PC) 10.0, *m*-Ph], 88 (m, C_5H_4P, C^2 and C^3), 55 [d, *J*(PC) 40, C_5H_4P, C^1] and 52.7 [d, *J*(PC) 6.3 Hz, $P(OMe)_3$]. ^{13}C (CD_2Cl_2, 218 K), isomer A, δ 233.7 [s, Mo(CO)], 227.7 [s, $Mo(CO)_2$], 217 [br, $Mn(CO)_3$]; isomer B, δ 231.7 [s, Mo(CO)], 227.2 [s, $Mo(CO)_2$], 217 [br, $Mn(CO)_3$]; ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), isomer A, δ −73.5 (s, $PPh_2C_5H_4$) and 40.8 [br, s, $P(OMe)_3$]; isomer B, δ −85.7 (s, $PPh_2C_5H_4$) and 57.1 [br, s, $P(OMe)_3$].

(*ii*) The reaction was carried out as in (*a*) using **1** (0.200 g, 0.336 mmol) and $P(OMe)_3$ (0.100 cm^3, 0.848 mmol) in toluene (70 cm^3) and refluxing at 383 K for 40 h. After cooling, the solvent was removed by bubbling nitrogen through the reaction mixture and the residue was then purified by TLC using CH_2Cl_2–hexane (3:7) as eluent. The two orange bands obtained were $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6\{P(OMe)_3\}]$ **2f** (0.010 g, 6%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5\{P(OMe)_3\}_2]$ **4c**. Complex **4c** (Found: C, 42.5; H, 4.1; P, 11.4. Calc. for $C_{28}H_{32}MnMoO_{11}P_3$: C, 42.6; H, 4.1, P, 11.0%). Mass spectrum: *m*/*z* 788 (M^+), and $M^+ - n(CO)$ (n = 1–5). NMR: ^{13}C ($CDCl_3$, 298 K), isomer A, δ 234 [m, $Mo(CO)_2$], 222 [br, $Mn(CO)_3$], 136.9 [d, *J*(PC) 38.4, *ipso*-Ph], 131.7 [d, *J*(PC) 6.7, *o*-Ph], 130.4 (s, *p*-Ph), 128.5 (br, s, *m*-Ph), 89.1 [d, *J*(PC) 6.9, C_5H_4P, C^2 or C^3], 86.3 [d, *J*(PC) 10.6, C_5H_4P, C^2 or C^3], 59.4 [d, *J*(PC) 49.4 Hz, C_5H_4P, C^1] and 52 [m, $P(OMe)_3$]; isomer B, δ 234 [m, $Mo(CO)_2$], 222 [br, $Mn(CO)_3$], 135.2 [d, *J*(PC) 36.0, *ipso*-Ph], 132.9 [d, *J*(PC) 6.5, *o*-Ph], 130.4 (s, *p*-Ph), 128.2 (br s, *m*-Ph), 88.5 [d, *J*(PC) 6.2, C_5H_4P, C^2 or C^3], 85.4 [d, *J*(PC) 10.0, C_5H_4P, C^2 or C^3], 56.6 [d, *J*(PC) 30.2 Hz, C_5H_4P, C^1] and 52 [m, $P(OMe)_3$]; ^{13}C (CD_2Cl_2, 225 K), isomer A, δ 234.2 [d, *J*(PC) 26.4 Hz, $Mo(CO)_2$], 230 [br, Mn(CO)] and 221 [br, $Mn(CO)_2$]; isomer B, δ 233.7 [d, *J*(PC) 29.6 Hz, $Mo(CO)_2$], 227 [br, Mn(CO)] and 221 [br, $Mn(CO)_2$]; ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ 59.4 [br s, $MnP(OMe)_3$, isomer B], 57.0 [s, $MoP(OMe)_3$, isomer A or B], 56.7 [s, $MoP(OMe)_3$, isomer A or B], 47.0 [br, s, $MnP(OMe)_3$, isomer A], −79.1 (br, s, $PPh_2C_5H_4$, isomer A), −82.8 (br, s, $PPh_2C_5H_4$, isomer B). ^{31}P (CD_2Cl_2, ^1H-gated decoupled, 230 K), δ 59.4 (br, isomer B), 57.2 (s, isomer A or B), 57.1 (s, isomer A or B), 48.0 [d, *J*(PP) 43, isomer A], −78.1 (d, isomer A), −83.0 [d, *J*(PP) 43 Hz, isomer B].

(*h*) *With* PPh_3. The reaction was carried out as in (*a*) above using **1** (0.050 g, 0.084 mmol) and PPh_3 (0.019 g, 0.084 mmol) in toluene (20 cm^3) and refluxing at 383 K for 22 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (1:3) to give two orange bands from which unreacted **1** (0.004 g, 8%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_3)]$ **3a** (0.012 g, 17%) were obtained.

(*i*) *With* $PhCH_2NC$. The reaction was carried out using **1** (0.200 g, 0.336 mmol) and $PhCH_2NC$ (0.040 cm^3, 0.328 mmol) in hexane–toluene (5:1) (40 cm^3). The solution was heated to reflux at 353 K for 40 h and, after cooling, the solvent was removed under vacuum. The residue was then purified by TLC eluting with CH_2Cl_2–hexane (1:4). The two orange bands obtained with identified as unreacted **1** (0.051 g, 25%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(CNCH_2Ph)]$ **2g** (0.051 g, 22%) as an orange powder. Complex **2g** (Found: C, 55.0; H, 4.0; N, 2.1. $C_{31}H_{21}MnNO_6P$ requires C, 54.3; H, 3.0; N, 2.0%). Mass spectrum: *m*/*z* 685 (M^+), and $M^+ - n(CO)$ (n = 3–6). NMR: ^{13}C ($CDCl_3$, 298 K), δ 232.4 [s, Mo(CO)], 228.0 [s, Mo(CO)], 225.4 [s, Mo(CO)], 217 [br, $Mn(CO)_3$], 167 (br, $PhCH_2N$*C*), 136–127 (m, Ph), 88.6 [d, *J*(PC) 6.2, C_5H_4P, C^2 or C^3], 88.5 [d, *J*(PC) 6.2, C_5H_4P, C^2 or C^3], 87.7 [d, *J*(PC) 9.8, C_5H_4P, C^2 or C^3], 87.6 [d, *J*(PC) 9.9, C_5H_4P, C^2 or C^3], 53.3 [d, *J*(PC) 48.9 Hz, C_5H_4P, C^1] and 48.3 (s, Ph*C*H_2NC); ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −77.6 (s, $PPh_2C_5H_4$).

(*j*) *With* Bu^tNC. The reaction was carried out using **1** (0.051 g, 0.086 mmol) and Bu^tNC (0.010 cm^3, 0.080 mmol) in toluene (20 cm^3). The solution was heated to reflux at 383 K for 16 h and, after cooling, the solvent was removed under vacuum. The residue was then purified by TLC eluting with CH_2Cl_2–hexane (1:4). The two orange bands obtained were identified as unreacted **1** (0.010 g, 20%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(CNBu^t)]$ **2h** (0.020 g, 37%) as an orange powder. Complex **2h** (Found: C, 52.8; H, 4.4; N, 2.0. $C_{28}H_{23}MnMoNO_6P$ requires C, 51.6; H, 3.6; N, 2.2%). Mass spectrum: *m*/*z* 651 (M^+), and $M^+ - n(CO)$ (n = 3–6).

Reaction of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Me)]$ **2b** *with Excess of* PPh_2Me.—The reaction was carried out using **2b** (0.150 g, 0.195 mmol) and PPh_2Me (0.070 cm^3, 0.377 mmol) in toluene (30 cm^3) and refluxing at 383 K for 16 h. The residue was purified by TLC eluting with CH_2Cl_2–hexane (3:7). Two orange bands were obtained which were identified as $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Me)]$ **2b** (0.013 g, 9%) and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5(PPh_2Me)_2]$ **4a** (0.095 g, 52%) as an orange powder.

Thermolysis of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2H)]$ **2a**.—A solution of **2a** (0.200 g, 0.265 mmol) in toluene (50 cm^3) was heated to reflux at 283 K for 3 h. After cooling the solvent was removed in vacuum and the residue was purified by TLC using CH_2Cl_2–hexane (1:2) as the eluent. A single orange band was obtained which yielded $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a** (0.090 g, 47%) as an orange powder.

Addition Reactions of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}PPh_2CH{=}CH_2)(CO)_5]$ **6**.—(*a*) *With* CO. Carbon monoxide was bubbled vigorously through a solution of **6** (0.015 g, 0.020 mmol) in toluene (30 cm^3) at room temperature for 5 min after which the rate of gas flow was reduced. The brown solution was then heated to reflux at 383 K for 3 h at which point the solution had changed to orange. After cooling the solvent was removed under vacuum and the residue purified by TLC using CH_2Cl_2–hexane (1:2) as eluent. A single orange band was obtained which yielded $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ **3c** (0.005 g, 32%) as an orange powder.

(*b*) *With* $P(OMe)_3$. Complex **6** (0.040 g, 0.053 mmol) was dissolved in toluene (30 cm^3) and $P(OMe)_3$ (0.01 cm^3, 0.085 mmol) was added. The reaction mixture was then heated to reflux at 383 K for 1 h. After cooling the solvent was removed under vacuum and the residue purified by TLC using CH_2Cl_2–hexane (1:1) as eluent. Two orange bands were obtained which were identified as $[MoMn(\mu\text{-}C_5H_4PPh_2)(PPh_2CH{=}CH_2)$-

$(CO)_5\{P(OMe)_3\}]$ **7** (0.016 g, 34%) as an orange powder and $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5\{P(OMe)_3\}_2]$ **4c** (0.010 g, 24%). Complex **7**. FAB mass spectrum: *m/z* 876 (M^+). NMR: ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), isomer A, δ −71.7 (s, $MoPPh_2CH{=}CH_2$), −70.5 (br s, $PPh_2C_5H_4$) and 47.1 [br s, $MnP(OMe)_3$]; isomer B, δ −71.7 (s, $MoPPh_2CH{=}CH_2$), −82.3 (br s, $PPh_2C_5H_4$) and 59.4 [br, s, $MnP(OMe)_3$].

(*c*) *With* H_2. Hydrogen gas was bubbled vigorously through a solution of **6** (0.065 g, 0.086 mmol) in toluene (40 cm^3) at room temperature for 5 min after which the rate of gas flow was reduced. The brown solution was then heated to reflux at 383 K for 2 h at which point the solution had changed to orange. After cooling the solvent was removed under vacuum and the residue purified by TLC using CH_2Cl_2–hexane (3:7) as eluent. A single orange band was obtained which yielded $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Et)]$ **3b** (0.049 g, 72%) as an orange powder. Complex **3b** (Found: C, 56.0; H, 3.6. $C_{37}H_{29}MnMoO_6P_2$ requires C, 56.8; H, 3.7%). NMR: ^{31}P ($CDCl_3$, ^1H-gated decoupled, 298 K), δ −75.0 (s, PPh_2Et) and −70 (br s, $PPh_2C_5H_4$).

Reaction of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2CH{=}CH_2)]$ **3c** *with* H_2.—Hydrogen gas was bubbled vigorously through a solution of **3c** (0.030 g, 0.038 mmol) in toluene (40 cm^3) at room temperature for 5 min, after which the rate of gas flow was reduced. The brown solution was then heated to reflux at 383 K for 0.5 h at which point infrared monitoring showed the appearance of peaks corresponding to the formation of **6** and the disappearance of peaks corresponding to **3c**. After a further 11.5 h the peaks due to **6** had disappeared and been replaced by peaks due to **3b**. After cooling the solvent was removed under vacuum and the residue purified by TLC using CH_2Cl_2–hexane (2:3) as eluent. A single orange band was obtained which yielded **3b** (0.013 g, 43%) as an orange powder.

Reaction of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_5(PPh_2Me)]$ **2b** *with* $P(OMe)_3$.—A solution of **2b** (0.080 g, 0.039 mmol) in toluene (30 cm^3) was treated with $P(OMe)_3$ (0.005 cm^3, 0.042 mmol) and the reaction mixture was refluxed for 2 h at 383 K. At this point infrared monitoring showed that no further change was taking place. After cooling, the solvent was removed under vacuum and the residue purified by TLC using CH_2Cl_2–hexane (1:4) as eluent. A single orange band was obtained which yielded $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6\{P(OMe)_3\}]$ **2f** (0.016 g, 59%).

Crystal-structure Determination of $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a**.—Suitable orange blocked-shaped crystals of **5a** were grown by slow evaporation of a CH_2Cl_2–hexane solution.

Crystal data. $C_{34}H_{25}MnMoO_5P_2$, *M* = 726.39, monoclinic, space group $P2_1/c$ (no. 14), *a* = 10.045(5), *b* = 17.926(9), *c* = 18.029(9) Å, β = 103.65(2)°, *U* = 3155(3) $Å^3$ (by least-squares refinement on diffractometer angles from 50 automatically centred reflections in the range $20 < \theta < 25°$, λ = 0.710 73 Å), *Z* = 4, D_c = 1.529 g cm^{-3}; D_m not measured, *F*(000) = 1464. Orange block, crystal dimensions (distance from faces to centre): 0.105(010, 010) × 0.228(100, 100) × 0.228 (001, 001) mm, μ(Mo-Kα) = 9.11 cm^{-1}.

Data collection and processing. Stoe four-circle diffractometer, 30 step ω–θ scan mode, ω step width 0.03°, step time 0.5–2.0 s per step, graphite-monochromated, Mo-Kα radiation; 6953 reflections measured ($5.0 < 2\theta < 50.0°$, $+h, +k, \pm l$), on-line profile fitting, 5335 unique [R_{int} = 0.018 after numerical absorption correction (transmission factors, minimum, maximum, 0.667, 0.770)], 4851 with $F > 4\sigma(F)$. Three standard reflections showed no significant variations in intensity.

Table 4 Atomic coordinates (× 10^4) for $[MoMn(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$ **5a**

Atom	*x*	*y*	*z*
Mo(1)	3 723(1)	3 320(1)	2 059(1)
Mn(1)	6 014(1)	2 906(1)	1 327(1)
H(1)	4 728(28)	3 560(15)	1 368(16)
P(1)	7 125(1)	3 289(1)	2 567(1)
P(2)	4 512(1)	2 113(1)	1 695(1)
C(1)	2 624(3)	3 881(2)	1 211(2)
O(1)	1 967(3)	4 235(2)	724(2)
C(2)	1 990(3)	2 765(2)	1 849(2)
O(2)	959(3)	2 451(2)	1 724(2)
C(3)	7 206(3)	2 204(2)	1 195(2)
O(3)	7 896(3)	1 727(2)	1 075(2)
C(4)	5 001(3)	2 782(2)	366(2)
O(4)	4 382(3)	2 744(2)	−253(1)
C(5)	6 713(3)	3 713(2)	937(2)
O(5)	7 069(3)	4 205(2)	630(1)
C(11)	4 905(3)	1 459(2)	2 499(2)
C(12)	6 236(3)	1 223(2)	2 822(2)
C(13)	6 488(5)	782(2)	3 472(2)
C(14)	5 420(5)	565(2)	3 792(2)
C(15)	4 105(5)	781(2)	3 466(2)
C(16)	3 840(4)	1 230(2)	2 821(2)
C(21)	8 245(3)	4 107(2)	2 667(2)
C(22)	9 178(3)	4 171(2)	2 208(2)
C(23)	10 069(3)	4 777(2)	2 299(2)
C(24)	10 056(4)	5 307(2)	2 841(2)
C(25)	9 154(4)	5 243(2)	3 310(2)
C(26)	8 256(3)	4 642(2)	3 232(2)
C(31)	8 206(3)	2 693(2)	3 292(2)
C(32)	9 203(3)	2 273(2)	3 066(2)
C(33)	10 096(4)	1 835(2)	3 594(3)
C(34)	9 975(5)	1 807(2)	4 342(3)
C(35)	9 019(4)	2 237(2)	4 576(2)
C(36)	8 129(3)	2 686(2)	4 054(2)
C(41)	3 545(3)	1 499(2)	945(2)
C(42)	4 054(3)	789(2)	864(2)
C(43)	3 396(4)	317(2)	285(2)
C(44)	2 188(4)	546(3)	−215(2)
C(45)	1 679(4)	1 239(3)	−147(2)
C(46)	2 355(3)	1 724(2)	427(2)
C(51)	5 711(3)	3 587(2)	2 969(1)
C(52)	4 966(3)	4 267(2)	2 775(2)
C(53)	3 728(3)	4 203(2)	3 021(2)
C(54)	3 690(3)	3 493(2)	3 352(2)
C(55)	4 912(3)	3 109(2)	3 331(2)

Structure analysis and refinement. Centrosymmetric direct methods (Mo, Mn and P atoms) followed by Fourier difference techniques (for remaining non-hydrogen atoms). Blocked full-matrix least squares with anisotropic displacement parameters for all non-hydrogen atoms. The hydride was directly located in the Fourier difference map and refined freely with an isotropic thermal parameter, and phenyl and cyclopentadienyl hydrogen atoms were placed in idealised positions (C–H 1.08 Å) and allowed to ride on the relevant carbon atom; the two types of hydrogen atoms were each refined with a common isotropic thermal parameter. The weighting scheme $1.765/[\sigma^2(F) + 0.005|F^2|]$ gave satisfactory agreement analyses. The converted residuals were *R* = 0.034 and *R′* = 0.038. A final Fourier difference map showed no residual electron density peaks above 0.5 e $Å^{-3}$. Final atomic coordinates are presented in Table 4. For the solution and refinement of the structure neutral atom scattering factors were taken from ref. 25. All computations were carried out on the University of Cambridge IBM 3081 computer using SHELX 76.[26]

Crystal-structure Determination of $[MoMn(\mu\text{-}C_5H_4PPh_2)(CO)_6(PPh_2Et)]$ **3b**.—The X-ray diffraction measurements were made on a red prismatic crystal (0.64 × 0.52 × 0.32 mm), with graphite monochromated Mo-Kα radiation and an Enraf–Nonius CAD4 diffractometer.

Crystal data. $C_{37}H_{29}MnMoO_6P_2$, *M* = 782.5, monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.674(2), *b* = 13.545(1), *c* = 17.256(1) Å, β = 96.468(8)° (by a least-squares treatment of

Table 5 Fractional atomic coordinates for [MoMn(μ-$C_5H_4PPh_2$)-$(CO)_6(PPh_2Et)$] **3b**

Atom	x	y	z
Mo	−0.241 09(2)	0.056 93(2)	0.081 25(2)
Mn	−0.171 07(3)	0.213 96(4)	0.202 08(3)
P(1)	−0.237 85(6)	−0.118 07(7)	0.047 74(5)
P(2)	0.266 85(6)	0.301 69(7)	0.115 49(5)
O(1)	−0.030 8(2)	0.030 9(2)	0.082 1(2)
O(2)	−0.266 6(2)	−0.042 2(2)	0.240 5(1)
O(3)	−0.118 8(2)	0.370 1(3)	0.316 8(2)
O(4)	−0.056 1(2)	0.059 7(2)	0.286 9(2)
O(5)	−0.332 5(2)	0.167 6(2)	0.285 5(2)
O(6)	−0.019 7(2)	0.255 9(3)	0.105 3(2)
C(1)	−0.108 1(3)	0.040 5(3)	0.083 9(2)
C(2)	−0.254 8(2)	−0.003 1(3)	0.182 7(2)
C(3)	−0.137 9(3)	0.310 2(3)	0.270 6(3)
C(4)	−0.101 6(3)	0.117 6(3)	0.253 5(2)
C(5)	−0.270 5(3)	0.183 2(3)	0.251 5(2)
C(6)	−0.078 0(3)	0.238 4(3)	0.141 9(3)
C(7)	−0.132 1(3)	−0.188 0(3)	0.078 8(3)
C(8)	−0.109 1(1)	−0.193 8(4)	0.166 9(3)
C(9)	−0.382 2(2)	−0.199 6(3)	0.077 4(2)
C(10)	−0.324 3(3)	−0.301 3(3)	0.065 6(2)
C(11)	−0.395 0(3)	−0.361 7(3)	0.842 2(2)
C(12)	−0.470 3(3)	−0.322 1(3)	0.113 8(2)
C(13)	−0.475 6(3)	−0.222 8(3)	0.125 1(2)
C(14)	−0.404 6(2)	−0.161 7(3)	0.107 3(2)
C(15)	−0.250 7(2)	−0.139 2(3)	−0.057 6(2)
C(16)	−0.179 0(3)	−0.113 6(4)	−0.099 7(3)
C(17)	−0.187 9(4)	−0.123 3(4)	−0.179 7(3)
C(18)	−0.269 2(4)	−0.158 4(4)	−0.217 9(3)
C(19)	−0.340 6(4)	−0.184 3(4)	−0.178 1(3)
C(20)	−0.331 7(3)	−0.174 1(3)	−0.097 0(2)
C(21)	−0.220 6(2)	0.398 8(3)	0.058 0(2)
C(22)	−0.146 1(3)	0.455 0(3)	0.090 3(2)
C(23)	−0.109 0(3)	0.527 9(3)	0.047 1(3)
C(24)	−0.146 0(3)	0.545 5(3)	−0.028 9(3)
C(25)	−0.221 0(3)	0.492 6(3)	−0.061 1(2)
C(26)	−0.258 1(3)	0.419 9(3)	−0.018 4(2)
C(27)	−0.368 5(2)	0.358 4(3)	0.147 2(2)
C(28)	−0.361 4(3)	0.406 2(3)	0.218 9(2)
C(29)	−0.438 5(3)	0.452 7(3)	0.244 1(3)
C(30)	−0.520 5(3)	0.499 8(3)	0.198 7(3)
C(31)	−0.528 4(3)	0.404 2(3)	0.126 9(3)
C(32)	−0.452 8(3)	0.358 8(3)	0.101 0(2)
C(33)	−0.309 1(2)	0.211 2(3)	0.044 1(2)
C(34)	−0.380 6(2)	0.140 5(3)	0.052 2(2)
C(35)	−0.375 0(3)	0.067 1(3)	−0.004 2(2)
C(36)	−0.300 6(3)	0.089 6(3)	−0.047 2(2)
C(37)	−0.260 5(3)	0.177 8(3)	−0.017 2(2)

diffractometric angles for 25 reflections with $14.0 \leqslant \theta \leqslant 17.2°$, $\lambda = 0.710\,69$ Å), $U = 3408.0(6)$ Å^3, $Z = 4$, $D_c = 1.525$ g cm^{-3}, $F(000) = 1584$, μ(Mo-Kα) = 8.51 cm^{-1}.

Data collection and processing. Intensities of 6580 reflections with $4 < 2\theta < 50.0°$ were measured by θ–2θ scans of $(0.70 + 0.35 \tan\theta)°$ in θ. The scan speeds were adjusted to give $\sigma(I)/I < 0.02$, subject to a time limit of 90 s. The intensities of two standard reflections remeasured every 2 h showed only random fluctuations not exceeding 3.3% of their mean values. Corrections for Lorentz, polarization and absorption effects[27] were introduced (transmission factors on F 0.78–1.44) and the structure amplitudes of 1187 symmetry related reflections were averaged to give 592 independent ones and R (internal) of 0.020. Of 5985 unique reflections measured, only 4385 [$I > 3\sigma(I)$] were used in the structure analysis.

Structure analysis. The crystal structure was determined by the heavy-atom method. The positions of the molybdenum and manganese atoms were obtained from a Patterson function and those of the remaining non-hydrogen atoms from the subsequent difference electron density maps. The hydrogen atoms were located in a low angle difference map, but they were included in the structural model in calculated positions (C–H 1.0 Å) and allowed to ride on the carbon atoms to which they are bonded; their individual isotropic displacement parameters were refined. All non-hydrogen atoms were assigned anisotropic displacement parameters. The structure was refined by block diagonal least squares [$w = 1/\sigma^2(|F_o|)$] to convergence at $R = 0.032$ and $R' = 0.042$, using neutral scattering factors taken from ref. 25. The highest residual electron density peak in the final Fourier difference map was 0.44 e Å^{-3}. The final atomic coordinates are shown in Table 5. All calculations were carried out using the GX program package.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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