In memory of S. M. Nelson and T. A. Stephenson

The Reaction of $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(R)=CHR\}(\mu\text{-}PPh_2)(CO)_7]$ (R = H or Ph) with Nucleophiles: *X*-Ray Crystal Structures of $[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6]$, $[Mn_2\{PPh_2C(Ph)=CHPh\}(CO)_9]$, $[Mn_2(\mu\text{-}PPh_2CH=CH_2)(CO)_8]$, $[Mn_2\{\mu\text{-}C(O)C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$, $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$, and $[Mn(\mu\text{-}PPh_2CH=CH_2)(CO)_7(PEt_3)]$†

Kim Henrick and Mary McPartlin
Department of Chemistry, Polytechnic of North London, Holloway Road, London N7 8DB
Jonathan A. Iggo, Alan C. Kemball, Martin J. Mays,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW

The reaction of $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(R)=CHR\}(\mu\text{-}PPh_2)(CO)_7]$ (R = H or Ph) with the nucleophiles H^-, CO, Bu^tNC, and PEt_3 have been studied and the structures of six of the products of these reactions have been determined by *X*-ray diffraction. In all of the products the nucleophile is bound to the metal but the course of a given reaction is highly sensitive both to the nature of the nucleophile and to the substituents on the μ-vinyl group. With H^- as the nucleophile and R = Ph the principal product is the μ-acyl complex $[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6]$ in which the Mn–Mn distance of 2.813(1) Å indicates the presence of a metal–metal bond. With CO as the nucleophile a P–C coupling reaction between the μ-PPh_2 and the μ-vinyl ligand is induced (R = H or Ph) leading *via* $[Mn_2\{\mu\text{-}PPh_2C(R)=CHR\}(CO)_8]$ to the final product $[Mn_2\{PPh_2C(R)=CHR\}(CO)_9]$ which results from the addition of a second molecule of the nucleophile. The structures of both of these P–C linked complexes have been determined by *X*-ray diffraction, the former for R = H and the latter for R = Ph. The Mn–Mn separations for these two complexes are 2.957(1) and 2.941(1) Å, respectively. With Bu^tNC as the nucleophile and R = Ph a μ-acyl complex, $[Mn_2\{\mu\text{-}C(O)C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$, is also obtained as the principal product but the *X*-ray diffraction study reveals an Mn–Mn separation of 3.820(2) Å indicating the absence of a metal–metal interaction. A second product obtained in this reaction has been shown by an *X*-ray diffraction study to be the Bu^tNC-substituted vinyl derivative $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$ in which the Mn–Mn distance is 2.758(1) Å. With phosphines as the nucleophiles, complex mixtures of products are, in general, obtained and these products have not all been characterised. With PEt_3 and R = H, however, the principal product is the P–C linked complex $[Mn_2(\mu\text{-}PPh_2CH=CH_2)(CO)_7(PEt_3)]$ and this has been isolated and structurally characterised by an *X*-ray diffraction study which shows that the Mn–Mn distance is 2.989(3) Å. Finally, with Bu^tNC as the nucleophile and R = H a compound is formed which is tentatively assigned a structure analogous to that obtained with PEt_3 as the nucleophile. Some reaction pathways which account for the formation of the major products in the above reactions are proposed and discussed.

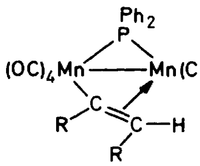
The reactions of μ-η^2-acetylide ligands with nucleophiles in dinuclear and polynuclear transition metal complexes have been studied extensively, particularly by Carty.[1,2] The ligand is a highly electrophilic site and the reactions most frequently give products in which the nucleophile has become attached to the α- or β-carbon atoms of the acetylide group, although CO substitution at a metal centre is sometimes also observed.[2]

The corresponding reactions of complexes containing a μ-η^2-vinyl ligand have received less attention, although certain organophosphines (PR_3, R = alkyl or aryl) react with $[Os(\mu\text{-}H)(\mu\text{-}\sigma:\eta^2\text{-}CH=CH_2)(CO)_{10}]$ at the β-carbon atom of the vinyl group to give $[Os(\mu\text{-}H)(\mu\text{-}CHCHPR_3)(CO)_{10}]$, containing a heteropolar ylide ligand.[3,4] In contrast, the reaction of PR_3 with $[Re_2(\mu\text{-}H)(\mu\text{-}\sigma:\eta^2\text{-}CH=CH_2)(CO)_8]$ leads to elimination of ethene and the formation of $[Re_2(CO)_8(PR_3)_2]$. For R = Me, however, an intermediate of the form $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}CH(PR_3)=CH_2\}(CO)_8]$ resulting from attack of PR_3 on the α-carbon atom of the vinyl group was isolated.[5]

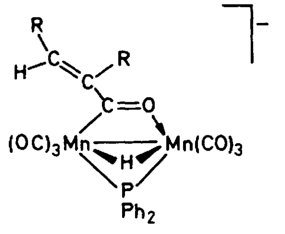
---

† Bis(triphenylphosphine)iminium 1,1,1,2,2,2-hexacarbonyl-μ-[2′,3′-diphenylacryloyl-*C*(Mn^1)*O*(Mn^2)]-μ-diphenylphosphido-μ-hydrido-dimanganate(*Mn–Mn*), 1,1,1,1,1,2,2,2,2-nonacarbonyl-2-[(1′,2′-diphenylvinyl)diphenylphosphine-*P*]dimanganese (*Mn–Mn*), 1,1,1,1,-2,2,2,2-octacarbonyl-μ-[diphenyl(vinyl)phosphine-*C*^{1,2}(Mn^1)*P*-(Mn^2)]-dimanganese (*Mn–Mn*), 1,1,1,2,2,2-hexacarbonyl-μ-[2′,3′-diphenylacryloyl-*C*(Mn^1)*O*(Mn^2)]-μ-diphenylphosphido-1,2-bis(t-butyl-isocyanide)dimanganese, 1,1,1,2,2,2-hexacarbonyl-μ-diphenylphosphido-μ-[σ:η^2-1′,2′-diphenylvinyl-*C*^{1,2}(Mn^2)*C*^{1}(Mn^1)]-1-t-butyl-isocyanide dimanganese (*Mn–Mn*), and 1,1,1,2,2,2,2-heptacarbonyl-μ-[diphenyl(vinyl)phosphine-*C*^{1,2}(Mn^1)*P*(Mn^2)]-1-(triethylphosphine) dimanganese (*Mn–Mn*) respectively.

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



(1a), R = H
(1b), R = Ph



(2a), R = H
(2b), R = Ph

We have prepared a series of μ-η^2-vinyl complexes of manganese, $[Mn_2\{\mu-\sigma:\eta^2-C(R)=CHR\}(\mu-PPh_2)(CO)_7]$, from the reaction of $[Mn_2(\mu-H)(\mu-PPh_2)(CO)_8]$ with alkynes[6] and, in this paper, we report the reactions of two of these complexes [R = H (**1a**) or Ph (**1b**)] with a wide range of nucleophiles. These reactions invariably lead to products in which the nucleophile is bound to one or both of the metal atoms rather than to the vinyl group. Addition of the nucleophile in this way usually results in transformations of the vinyl ligand, involving CO insertion into the Mn–C σ bond or coupling of this ligand with the μ-PPh_2 group. The identity of the products obtained in a given reaction is highly sensitive both to the nature of the nucleophile and to the substituents on the μ-vinyl ligand. A preliminary account of part of this work has been published.[7]

Results and Discussion

(*a*) *Reactions of* (**1a**) *and* (**1b**) *with Hydride Donors*.—Reaction of the deep red vinyl complexes (**1a**) or (**1b**) with excess $NaBH_4$ in thf or acetonitrile solution at 20 °C affords, after metathesis with $[N(PPh_3)_2]Cl$ and work-up, the bright red μ-acyl complexes $[N(PPh_3)_2][Mn_2(\mu-H)\{\mu-C(O)C(R)=CHR\}(\mu-PPh_2)(CO)_6]$ [R = H (**2a**) or Ph (**2b**)]. Formation of these μ-acyl complexes is presumably initiated by nucleophilic attack of H^- at one of the metal centres, this then inducing the insertion of a co-ordinated CO group into the metal–carbon σ bond of the co-ordinated vinyl ligand. In accordance with this suggestion the reaction of (**1b**) with $NaBD_4$ gives (**2b**) containing a μ-D group but does not result in the incorporation of deuterium elsewhere in the molecule.

The molecular structure of (**2b**) has been determined by a single-crystal *X*-ray diffraction study and is shown in Figure 1. Table 1 lists selected bond lengths and interbond angles. The structure consists of discrete molecular ions separated by normal van der Waals distances. The CO group of the acyl ligand spans the two manganese atoms bonding through carbon to Mn(2) and oxygen to Mn(1). The geometry of the Mn–C–O–Mn ring is comparable with that found in similar systems[8,9] [Mn(1)–O(1) 2.048(3), Mn(2)–C(1) 2.008(4), C(1)–O(1) 1.266(5) Å]. The Mn(1)–Mn(2) distance of 2.813(1) Å is within the expected range[10] for the Mn–Mn single bond which is required in order for (**2b**) to satisfy the effective atomic number (e.a.n.) rule. Bond lengths in the carbon chain of the acyl ligand correspond closely to those expected for $C(sp^3)$–$C(sp^3)$ single bonds (adjacent to C=O) [C(1)–C(2) 1.506(6) Å] and $C(sp^2)$–$C(sp^2)$ double bonds [C(2)–C(3) 1.346(7) Å][11] indicating that there is little delocalisation of the π-bonding electrons in the 'unsaturated' system.

The phenyl ring bonded to the terminal carbon of the acyl side-chain is disordered with occupancy factors of 49% and 51% for the two sites. The hydride ligand was not located in the difference map but is proposed, on the basis of its chemical shift (δ −11.59 p.p.m.) and the folded geometry of the Mn(1)–P(1)–Mn(2)–C(1)–O(1) ring, to occupy a bridging site *trans* to C(13) and C(22). The co-ordination of the manganese atoms is then approximately octahedral if the other metal atom is ignored. The Mn–C(carbonyl) distances show the expected variation with π-acid properties of the *trans* ligand; thus the Mn(1)–C(11) (*trans* to P) distance [1.817(5) Å] is longer than both the Mn(1)–C(12) [*trans* to O(1)] [1.789(4) Å] and Mn(1)–C(13) (*trans* to H) [1.784(5) Å] distances. A similar pattern is seen in the manganese–carbonyl distances around Mn(2). There is a slight asymmetry in the phosphido bridge [Mn(1)–P(1) 2.283(1), Mn(2)–P(1), 2.273(1) Å] which is not unexpected in view of the asymmetry in the molecule as a whole.

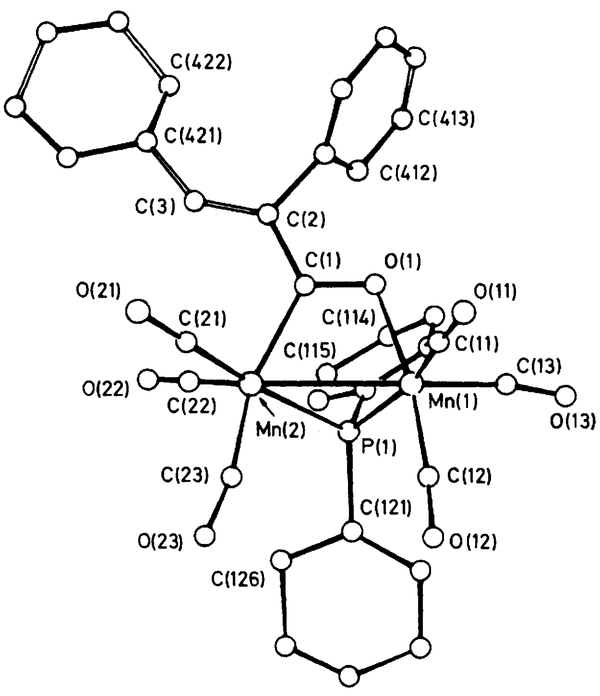


Figure 1. Molecular structure of $[N(PPh_3)_2][Mn_2(\mu-H)\{\mu-C(O)C(Ph)=CHPh\}(\mu-PPh_2)(CO)_6]$ (**2b**) including the atom numbering scheme

Complex (**2a**) could not be isolated in a pure state from the reaction mixture giving rise to it and was identified by comparison of its i.r. [ν(CO)] and ^1H n.m.r. spectra with those of (**2b**) (Table 2), although the ^1H n.m.r. resonances of the $CH=CH_2$ group could not be distinguished from signals due to other species present in the reaction mixture. These included the anions $[Mn_2(\mu-PPh_2)(CO)_8]^-$ [12] and $[Mn_2(\mu-H)_2(\mu-PPh_2)(CO)_6]^-$. This latter anion was isolated as its $[N(PPh_3)_2]^+$ salt (**3**) and its spectroscopic properties are reported in Table 2.

(*b*) *Reactions of* (**1a**) *and* (**1b**) *with* CO.—Reaction of (**1a**) or (**1b**) in refluxing n-heptane or n-octane respectively gives the complexes $[Mn_2\{PPh_2C(R)=CHR\}(CO)_9]$ [R = H (**4a**) or Ph (**4b**)]. The formation of these complexes from (**1a**) and (**1b**) respectively may be rationalised in terms of a P–C coupling reaction induced by the addition of a molecule of CO followed by displacement of the η^2-bonded vinyl group by a second molecule of CO. That the reaction may take place in these two stages is suggested by the reaction of (**1a**) with MeCN. Thus a solution of (**1a**) in MeCN turns from purple-red to yellow on being stirred for 2 h at room temperature and, on treatment of this yellow solution with CO, the complex $[Mn_2(\mu-PPh_2CH=CH_2)(CO)_8]$ (**5a**) was isolated. Complex (**5a**) is converted rapidly to (**4a**) on further treatment with CO in refluxing hexane solution.

Table 1. Selected bond parameters for $[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6]$ (**2b**)

Bond lengths (Å)

Mn(1)–Mn(2)	2.813(1)	Mn(1)–O(1)	2.048(3)	Mn(2)–C(22)	1.810(4)	Mn(2)–C(23)	1.780(5)
Mn(1)–C(11)	1.817(5)	Mn(1)–C(12)	1.789(4)	Mn(2)–P(1)	2.273(1)	O(1)–C(1)	1.266(5)
Mn(1)–C(13)	1.784(5)	Mn(1)–P(1)	2.283(1)	C(1)–C(2)	1.506(6)	C(2)–C(3)	1.346(7)
Mn(2)–C(1)	2.008(4)	Mn(2)–C(21)	1.808(5)	C(2)–C(411)	1.497(6)	C(3)–C(421)	1.474(8)

Bond angles (°)

Mn(2)–Mn(1)–O(1)	68.6(1)	Mn(2)–Mn(1)–C(11)	114.9(1)	C(1)–Mn(2)–C(22)	166.3(2)	C(1)–Mn(2)–C(23)	97.7(2)
Mn(2)–Mn(1)–C(12)	102.6(2)	Mn(2)–Mn(1)–C(13)	145.9(2)	C(1)–Mn(2)–P(1)	82.1(1)	C(21)–Mn(2)–C(22)	89.7(2)
Mn(2)–Mn(1)–P(1)	51.7(1)	O(1)–Mn(1)–C(11)	171.9(2)	C(21)–Mn(2)–C(23)	96.3(2)	C(21)–Mn(2)–P(1)	169.8(2)
O(1)–Mn(1)–C(12)	98.5(2)	O(1)–Mn(1)–P(1)	82.0(1)	C(22)–Mn(2)–P(1)	93.2(2)	C(22)–Mn(2)–P(1)	93.2(2)
C(11)–Mn(1)–P(1)	88.7(2)	C(11)–Mn(1)–C(13)	98.8(2)	C(23)–Mn(2)–P(1)	93.2(2)	Mn(1)–O(1)–C(1)	108.2(2)
C(11)–Mn(1)–P(1)	166.6(1)	C(12)–Mn(1)–C(13)	90.0(2)	Mn(2)–C(1)–O(1)	116.6(3)	Mn(2)–C(1)–C(2)	130.1(3)
C(12)–Mn(1)–P(1)	94.2(2)	C(13)–Mn(1)–P(1)	96.4(2)	O(1)–C(1)–C(2)	113.3(3)	C(1)–C(2)–C(3)	118.9(4)
Mn(1)–Mn(2)–C(1)	66.4(1)	Mn(1)–Mn(2)–C(21)	117.8(2)	C(1)–C(2)–C(411)	118.5(4)	C(3)–C(2)–C(411)	122.6(4)
Mn(1)–Mn(2)–C(22)	100.6(2)	Mn(1)–Mn(2)–C(23)	142.1(2)	C(2)–C(3)–C(421)	130.7(4)	Mn(1)–P(1)–Mn(2)	76.3(1)
Mn(1)–Mn(2)–P(2)	52.0(1)	C(1)–Mn(2)–C(21)	92.9(2)				

Table 2. Infrared and ^1H n.m.r. data for the new complexes

	Compound	$\nu_{CO}{}^a$/cm^{-1}	^1H N.m.r.^{b,c}
(**2a**)	$[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)CH{=}CH_2\}(\mu\text{-}PPh_2)(CO)_6]^d$	1 999m, 1 966s, 1 903s, 1 876m	−12.06 [d, ^2J(PH) 33.7, Mn_2H]
(**2b**)	$[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6]$	1 998m, 1 966s, 1 904s, 1 876m	−11.59 [d, ^2J(PH) 32.1, Mn_2H], 6.30 [dd, ^5J(PH) 1.6, ^5J(HH) 7.8, CPh=C*H*Ph]^e
(3)	$[N(PPh_3)_2][Mn_2(\mu\text{-}H)_2(\mu\text{-}PPh_2)(CO)_6]^d$	2 005m, 1 972s, 1 894 (sh), 1 889s	−17.52 [d, ^2J(PH) 49.7, Mn_2H_2]
(**4a**)	$[Mn_2(PPh_2CH{=}CH_2)(CO)_9]$	2 090m, 2 011m, 1 994s, 1 972m, 1 939m	5.32 [ddd, ^3J(PH) 19.5, $^3J(H_\alpha H_\beta)$ 17.8, $^2J(H_\beta H_{\beta'})$ 1, 1 H, *trans* CH=CH_2], 6.25 [ddd, ^3J(PH) 38.3, $^3J(H_\alpha H_{\beta'})$ 12.0, 1 H, *cis* CH=CH_2], 6.85 [ddd, ^2J(PH) 24.2, 1 H, C*H*=CH_2]^e
(**4b**)	$[Mn_2\{PPh_2C(Ph){=}CHPh\}(CO)_9]$	2 091m, 2 011m, 1 996s, 1 974m, 1 938m	6.62 [d, ^3J(PH) 8.0, 1 H, CPh=C*H*Ph]^e
(**5a**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_8]$	2 070s, 2 016vs, 2 006w, 1 987 (sh), 1 983vs, 1 970s, 1 961m, 1 941m	2.10 [ddd, ^2J(PH) 18, 1 H, C*H*=CH_2], 2.19 [dd, ^3J(PH) 11.5, $^3J(H_\alpha H_\beta)$ 14, 1 H, *cis*-CH=CH_2], 3.16 [dd, ^3J(PH) 9.5, $^3J(H_\alpha H_\beta)$ 2.12, 1 H, *trans* CH=CH_2]
(**5b**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(CNBu^t)]^f$	2 041s, 1 995s, 1 984m, 1 969s, 1 955s, 1 948m, 1 924w, 1 916m	1.00 (s, 9 H, $CNBu^t$), 1.66, 1.86, 2.88 (each m, 1 H, CH=CH_2)
(**5c**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PEt_3)]$	2 048s, 1 981m, 1 975m, 1 965s, 1 937m, 1 906m	1.10 [dt, ^3J(PH) 14.8, ^3J(HH), 14.8, 9 H, CH_2CH_3], 1.24 (m, 1 H, CH=CH_2), 1.92 [qnt, ^2J(PH) 7.8, 6 H, CH_2CH_3], 2.09, 2.50 (each m, 1 H, CH=CH_2)
(**5d**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7\{P(OMe)_3\}]$	2 052m, 1 991m, 1 986 (sh), 1 978m, 1 966s, 1 940m, 1 923w	3.82 [d, ^3J(PH) 10.8, 9 H, OMe]
(**5e**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PMe_2Ph)]$	2 043m, 1 980m, 1 965s, 1 957s, 1 926m, 1 912m, 1 903m, 1 895 (sh)	1.85—2.05 (m, 6 H, Me), 2.2 (m, CH=CH_2), 2.95 (m, CH=CH_2)
(**5f**)	$[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PPh_3)]^d$	2 069m, 2 045m, 2 014m, 2 004 (sh), 1 979s, 1 963s, 1 935 (sh)	*g*
(6)	$[Mn\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]^h$	2 020s, 1 999vs, 1 952s, 1 920vs	0.91 (s, 9 H, $CNBu^t$), 1.09 (s, 9 H, $CNBu^t$), 6.46 (s, 1 H, CPh=C*H*Ph)
(7)	$[Mn_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]^i$	2 028m, 2 001s, 1 964m, 1 954m, 1 941m, 1 929 (sh)	1.08 (s, 9 H, $CNBu^t$), 4.94 [d, ^4J(PH) 8.7, 1 H, CPh=C*H*Ph]^j
(8)	$[Mn_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_5(CNBu^t)_2]^k$	2 007, 1 958s, 1 950s, 1 927m, 1 909m	1.03 (s, 9 H, $CNBu^t$), 1.12 (s, 9 H, $CNBu^t$), 4.5 [d, ^4J(PH) 9.7, 1 H, CPh=C*H*Ph]^j
(9)	$[Mn_2\{C(Ph){=}CHPh\}(PPh_2)(CO)_n(PMe_2Ph)]$ (*n* could be 6 or 7)	2 018m, 1 986m, 1 949s, 1 943 (sh), 1 934m, 1 929 (sh), 1 919w	1.25 [dd, ^2J(PH) 84.3, ^4J(HH) 9.1, 6 H, Me], 4.39 [d, ^4J(PH) 9.4, 1 H, CPh=C*H*Ph]

[a] Infrared spectrum recorded in cyclohexane solution unless otherwise indicated. [b] Recorded in CD_2Cl_2 solution; phenyl resonances are not given. [c] Coupling constants in Hz, s = singlet, d = doublet, t = triplet, qnt = quintet, m = multiplet. [d] Infrared spectrum recorded in CH_2Cl_2 solution. [e] Recorded in $(CD_3)_2CO$ solution. [f] ν_{CNR} = 2 139w cm^{-1}. [g] Broad lines lost in noise. [h] ν_{CNR} = 2 176m, 2 156m cm^{-1}. [i] ν_{CNR} = 2 161m cm^{-1}. [j] Recorded in $CDCl_3$ solution at 243 K; ^1H noise or gated decoupled; phenyl resonances are not given. [k] ν_{CNR} = 2 155m, 2 121m cm^{-1}.

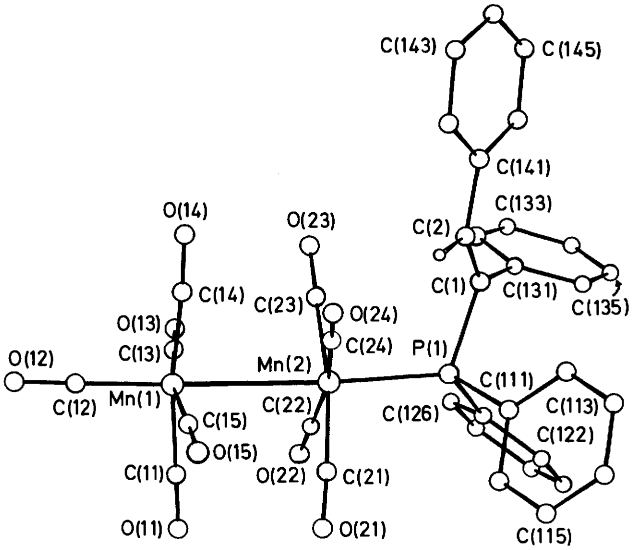


Figure 2. Molecular structure of $[Mn_2\{PPh_2C(Ph)=CHPh\}(CO)_9]$ (**4b**) including the atom numbering scheme

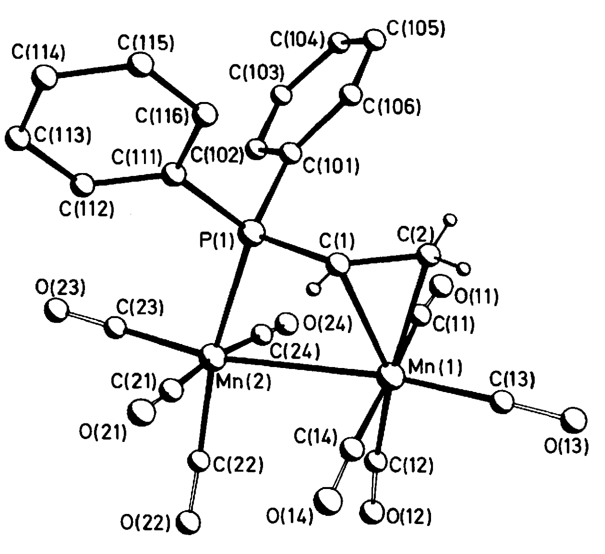
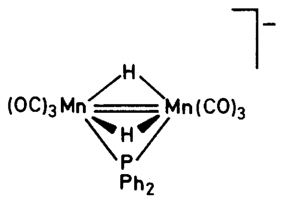
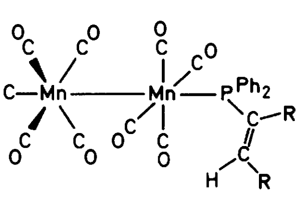


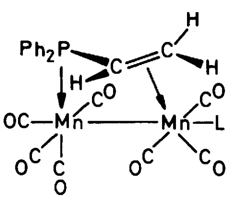
Figure 3. Molecular structure of $[Mn_2(\mu\text{-}PPh_2CH=CH_2)(CO)_8]$ (**5a**) including the atom numbering scheme



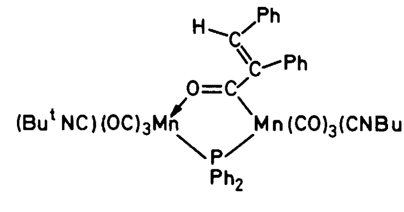
(3)



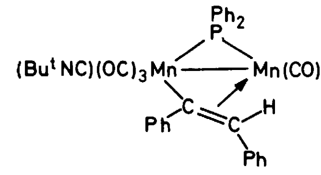
(4a), R = H
(4b), R = Ph



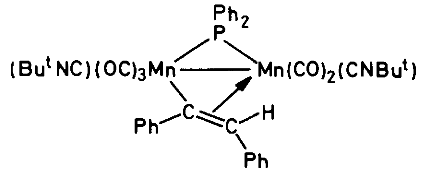
(5a), L = CO
(5b), L = CNBu^t
(5c), L = PEt$_3$
(5d), L = P(OMe)$_3$
(5e), L = PMe$_2$Ph
(5f), L = PPh$_3$



(6)



(7)



(8)

The molecular structures of complexes (**4b**) and (**5a**) have been determined by single-crystal *X*-ray diffraction studies and are shown in Figures 2 and 3 respectively. Tables 3 and 4 list selected final bond lengths and interbond angles for (**4b**) and (**5a**) respectively. The structure of (**4b**) is closely similar to those of other $[Mn_2(PR_3)(CO)_9]$ type complexes which have been determined previously.[13] Thus the manganese atoms are approximately octahedrally co-ordinated by the second metal atom and by either five CO ligands [Mn(1)] or by four CO ligands and the phosphine [Mn(2)]. The phosphine occupies an axial site and the equatorial CO groups adopt a staggered configuration thus minimising their steric interactions. The metal–metal [2.941(1) Å], metal–carbonyl [av. 1.839(7) Å], and metal–phosphorus [2.303(1) Å] bond lengths are typical. The olefinic bond is not co-ordinated to either of the metal centres.

The ^1H and ^{13}C n.m.r. spectra of (**4a**) and (**4b**) (Tables 2 and 5) show that both complexes have the same structure in solution as found for (**4b**) in the solid state. Thus the ^1H n.m.r. spectrum of (**4a**) shows three resonances (doublets of double doublets) at δ 6.85, 6.25, and 5.32 p.p.m. which may be assigned to the vinyl protons. The values of $J(^1H^{31}P)$ for these resonances are several times larger than those for the corresponding vinyl protons in (**1a**), which is consistent with the vinyl moiety being directly bonded to phosphorus in (**4a**). The ^{13}C n.m.r. spectrum of (**4a**) shows only one resonance due to the carbonyl groups over the temperature range 213—273 K indicating complete scrambling of these groups between the two metal atoms and between axial and equatorial sites. The absence of a bridging phosphido group clearly lowers the activation energy for the scrambling process since, for example, (**1a**) exhibits a 'frozen-out' ^{13}C spectrum at 213 K and only a localised scrambling of the CO groups on each metal atom at 273 K.[6]

The structure of (**5a**) is related to that of (**4b**) but the phosphorus atom is equatorially rather than axially bonded and the vinyl group is co-ordinated to the second manganese atom in place of one of the equatorial CO groups. The equatorial carbonyl ligands on the two metal atoms adopt a staggered configuration and the metal atom separation [2.957(1) Å] is consistent with the presence of a single bond.[10]

Table 3. Selected bond parameters for $[Mn_2\{PPh_2C(Ph){=}CHPh\}(CO)_9]$ **(4b)**

Bond lengths (Å)

Mn(2)–Mn(1)	2.941(1)	C(11)–Mn(1)	1.849(9)	C(24)–Mn(2)	1.836(7)	C(23)–Mn(2)	1.827(7)
C(12)–Mn(1)	1.811(5)	C(13)–Mn(1)	1.847(7)	C(121)–P(1)	1.839(6)	C(11)–P(1)	1.845(4)
C(14)–Mn(1)	1.851(8)	C(15)–Mn(1)	1.836(6)	C(2)–C(1)	1.347(8)	C(1)–P(1)	1.875(6)
P(1)–Mn(2)	2.303(1)	C(21)–Mn(2)	1.833(7)	C(141)–C(2)	1.492(9)	C(131)–C(1)	1.491(7)
C(22)–Mn(2)	1.852(7)						

Bond angles (°)

C(11)–Mn(1)–Mn(2)	86.6(2)	C(12)–Mn(1)–Mn(2)	178.3(3)	C(22)–Mn(2)–C(21)	86.3(3)	C(23)–Mn(2)–Mn(1)	86.5(1)
C(12)–Mn(1)–C(11)	94.9(3)	C(13)–Mn(1)–Mn(2)	84.4(2)	C(23)–Mn(2)–P(1)	90.8(1)	C(23)–Mn(2)–C(21)	171.6(2)
C(13)–Mn(1)–C(11)	89.6(3)	C(13)–Mn(1)–C(12)	94.9(3)	C(23)–Mn(2)–C(22)	90.6(3)	C(24)–Mn(2)–Mn(1)	85.4(1)
C(14)–Mn(1)–Mn(2)	85.6(2)	C(14)–Mn(1)–C(11)	172.1(2)	C(24)–Mn(2)–P(1)	92.7(1)	C(24)–Mn(2)–C(21)	90.8(3)
C(14)–Mn(1)–C(12)	92.9(3)	C(14)–Mn(1)–C(13)	89.0(3)	C(24)–Mn(2)–C(22)	170.6(2)	C(24)–Mn(2)–C(23)	91.1(3)
C(15)–Mn(1)–Mn(2)	85.6(2)	C(15)–Mn(1)–C(11)	88.0(3)	C(111)–P(1)–Mn(2)	117.1(1)	C(121)–P(1)–Mn(2)	116.0(1)
C(15)–Mn(1)–C(12)	95.2(3)	C(15)–Mn(1)–C(13)	169.8(2)	C(121)–P(1)–C(111)	102.1(2)	C(1)–P(1)–Mn(2)	113.4(1)
C(15)–Mn(1)–C(14)	92.0(3)	P(1)–Mn(2)–Mn(1)	176.6(1)	C(1)–P(1)–C(111)	104.3(2)	C(1)–P(1)–C(121)	101.9(2)
C(21)–Mn(2)–Mn(1)	85.4(1)	C(21)–Mn(2)–P(1)	97.4(1)	C(2)–C(1)–P(1)	114.7(4)	C(131)–C(1)–P(1)	117.5(4)
C(22)–Mn(2)–Mn(1)	85.5(2)	C(22)–Mn(2)–P(1)	96.5(2)	C(131)–C(1)–C(2)	127.8(5)	C(141)–C(2)–C(1)	129.2(5)

Table 4. Selected bond parameters for $[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_8]$ **(5a)**

Bond lengths (Å)

Mn(2)–Mn(1)	2.957(1)	C(1)–Mn(1)	2.244(3)	C(21)–Mn(2)	1.846(3)	C(22)–Mn(2)	1.822(3)
C(2)–Mn(1)	2.237(4)	C(11)–Mn(1)	1.865(4)	C(23)–Mn(2)	1.795(3)	C(24)–Mn(2)	1.837(3)
C(12)–Mn(1)	1.808(4)	C(13)–Mn(1)	1.802(4)	C(101)–P(1)	1.824(3)	C(111)–P(1)	1.846(3)
C(14)–Mn(1)	1.853(4)	P(1)–Mn(2)	2.277(1)	C(1)–P(1)	1.790(3)	C(2)–C(1)	1.372(4)

Bond angles (°)

C(1)–Mn(1)–Mn(2)	73.8(1)	C(2)–Mn(1)–Mn(2)	106.7(1)	C(22)–Mn(2)–C(21)	97.2(1)	C(22)–Mn(2)–P(1)	168.2(1)
C(2)–Mn(1)–C(1)	35.7(1)	C(11)–Mn(1)–Mn(2)	89.7(1)	C(22)–Mn(2)–C(21)	89.5(1)	C(23)–Mn(2)–Mn(1)	169.4(1)
C(11)–Mn(1)–C(1)	97.2(1)	C(11)–Mn(1)–C(2)	83.9(2)	C(23)–Mn(2)–P(1)	99.1(1)	C(23)–Mn(2)–C(21)	95.8(1)
C(12)–Mn(1)–Mn(2)	78.3(1)	C(12)–Mn(1)–C(1)	151.7(1)	C(23)–Mn(2)–C(22)	92.1(1)	C(24)–Mn(2)–Mn(1)	83.9(1)
C(12)–Mn(1)–C(2)	169.9(2)	C(12)–Mn(1)–C(11)	87.4(2)	C(24)–Mn(2)–P(1)	95.0(1)	C(24)–Mn(2)–C(21)	172.6(1)
C(13)–Mn(1)–Mn(2)	173.0(1)	C(13)–Mn(1)–C(1)	112.6(2)	C(24)–Mn(2)–C(22)	88.6(1)	C(24)–Mn(2)–C(23)	91.4(1)
C(13)–Mn(1)–C(2)	80.3(2)	C(13)–Mn(1)–C(11)	92.0(2)	C(101)–P(1)–Mn(22)	119.9(1)	C(111)–P(1)–Mn(2)	119.1(1)
C(13)–Mn(1)–C(12)	95.0(2)	C(14)–Mn(1)–Mn(1)	87.0(1)	C(111)–P(1)–C(101)	103.5(1)	C(1)–P(1)–Mn(2)	102.0(1)
C(14)–Mn(1)–C(1)	85.6(1)	C(14)–Mn(1)–C(2)	100.8(1)	C(1)–P(1)–C(101)	109.2(1)	C(1)–P(1)–C(111)	101.4(1)
C(14)–Mn(1)–C(11)	174.9(2)	C(14)–Mn(1)–C(2)	88.1(2)	P(1)–C(1)–Mn(1)	101.0(1)	C(2)–C(1)–Mn(1)	71.9(2)
C(14)–Mn(1)–C(13)	90.8(2)	P(1)–Mn(2)–Mn(1)	72.0(1)	C(2)–C(1)–P(1)	132.9(3)	C(1)–C(2)–Mn(1)	72.4(2)
C(21)–Mn(2)–Mn(1)	89.3(1)	C(21)–Mn(2)–P(1)	85.5(1)				

Table 5. Selected ^{13}C and ^{31}P n.m.r. data (δ)* for the new complexes

Complex	
(2b)	^{13}C: 309.3 [d, ^2J(PC) *ca.* 10, >C=O], 229.2, 227.3, 226.0, 222.7 (each 1 CO), 224.2 (2 CO)
(4a)	^{13}C: 224.0 [d, J(PC) 11.7, 9 CO]. ^{31}P: −76.1 (s, $Ph_2PCH{=}CH_2$)
(6)	^{13}C: 323.2 (s, >C=O), 224.9 [d, ^2J(PC) 16.4, 1 CO], 221.2, 218.9 (each s, 2 CO), 216.5 [d, ^2J(PC) 18, 1 CO], 29.7, 29.4 (each s, CN*Bu*^{t}). ^{31}P: −60.4 (s, μ-PPh_2)
(7)	^{31}P: −129.4 (s, μ-PPh_2)
(9)	^{13}C: 193.3 (s, *C*Ph=CHPh), 87.9 [d, J(CH) 154.4, CPh=*C*HPh], 18.1 [d, J(PC), 24.9, Me], 11.5 [d, J(PC) 24.9, Me]. ^{31}P: 11.9 (s, μ-PPh_2), −153.1 (s, PMe_2Ph)

* Recorded in $CDCl_3$ solution at 243 K, ^{1}H noise or gated decoupled; phenyl resonances are not given; s = singlet, d = doublet. δ Values are in p.p.m. relative to $SiMe_4$ (^{13}C) or $P(OMe)_3$ (^{31}P) with upfield shifts negative. ^{13}C N.m.r. data for vinyl group carbon atoms were only obtained for **(9)**.

The co-ordination of the vinyl group in **(5a)** to the metal atom is maintained in solution as evidenced by the ^{1}H n.m.r. spectrum of **(5a)** which shows the resonances due to the vinyl group shifted upfield by *ca.* 3 p.p.m. compared to their positions in the spectrum of **(4b)**.

(*c*) *Reactions of* **(1a)** *and* **(1b)** *with* Bu^{t}NC.—The reactions of complexes **(1)** with H^- and CO are not apparently sensitive to the nature of the R groups (R = H or Ph) on the vinyl ligand. This is not the case, however, with the more bulky nucleophile Bu^{t}NC, which reacts differently with **(1a)** and **(1b)**. Thus **(1a)** reacts with Bu^{t}NC at room temperature in hexane solution to give a mixture of two products proposed on the basis of ^{1}H n.m.r. and i.r. [ν(CO) and ν(CNR)] spectroscopy and microanalysis to be isomeric forms of $[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(CNBu^t)]$ **(5b)** in *ca.* 50% yield, a reaction which is analogous to the proposed first stage in the reaction of **(1a)** with CO. Complex **(1b)**, however, does not react with Bu^{t}NC at room

Table 6. Selected bond parameters for $[Mn_2\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (**6**)

Bond lengths (Å)

Mn(1)–P(1)	2.391(2)	Mn(1)–C(1)	2.031(6)	Mn(2)–C(42)	1.805(5)	Mn(2)–C(43)	1.775(6)
Mn(1)–C(28)	1.931(5)	Mn(1)–C(38)	1.786(6)	P(1)–C(121)	1.876(5)	P(1)–C(111)	1.868(6)
Mn(1)–C(39)	1.801(5)	Mn(1)–C(40)	1.820(9)	O(1)–C(1)	1.235(6)	C(1)–C(2)	1.518(8)
Mn(2)–P(1)	2.375(2)	Mn(2)–O(1)	2.055(4)	C(2)–C(15)	1.494(7)	C(2)–C(3)	1.345(7)
Mn(2)–C(33)	1.927(5)	Mn(2)–C(41)	1.812(8)				

Bond angles (°)

P(1)–Mn(1)–C(1)	88.1(1)	P(1)–Mn(1)–C(28)	90.4(2)	O(1)–Mn(2)–C(42)	89.6(2)	O(1)–Mn(2)–C(43)	178.1(2)
P(1)–Mn(1)–C(38)	177.9(3)	P(1)–Mn(1)–C(39)	90.0(2)	C(33)–Mn(2)–C(41)	88.0(3)	C(33)–Mn(2)–C(42)	172.6(3)
P(1)–Mn(1)–C(40)	90.7(2)	C(1)–Mn(1)–C(28)	82.7(2)	C(33)–Mn(2)–C(43)	95.2(2)	C(41)–Mn(2)–C(42)	91.7(3)
C(1)–Mn(1)–C(38)	94.0(3)	C(1)–Mn(1)–C(39)	87.7(3)	C(41)–Mn(2)–C(43)	87.0(3)	C(42)–Mn(2)–C(43)	92.1(2)
C(1)–Mn(1)–C(40)	178.6(2)	C(28)–Mn(1)–C(38)	89.9(2)	Mn(1)–P(1)–C(121)	113.8(2)	Mn(1)–P(1)–C(111)	111.9(2)
C(28)–Mn(1)–C(39)	170.4(3)	C(28)–Mn(1)–C(40)	96.6(3)	Mn(2)–P(1)–C(121)	112.5(2)	Mn(2)–P(1)–C(111)	113.6(2)
C(38)–Mn(1)–C(39)	90.0(2)	C(38)–Mn(1)–C(40)	87.2(3)	C(121)–P(1)–C(111)	98.6(3)	Mn(2)–O(1)–C(1)	130.7(4)
C(39)–Mn(1)–C(40)	93.0(3)	P(1)–Mn(2)–O(1)	86.6(1)	Mn(1)–C(1)–O(1)	127.3(4)	Mn(1)–C(1)–C(1)	120.4(3)
P(1)–Mn(2)–C(33)	92.0(2)	P(1)–Mn(2)–C(41)	178.7(2)	O(1)–C(1)–C(2)	112.2(5)	C(1)–C(2)–C(15)	115.8(4)
P(1)–Mn(2)–C(42)	88.1(2)	P(1)–Mn(2)–C(43)	94.3(2)	C(1)–C(2)–C(3)	118.9(5)	C(15)–C(2)–C(3)	125.3(5)
O(1)–Mn(2)–C(33)	83.1(2)	O(1)–Mn(2)–C(41)	92.1(3)	Mn(1)–P(1)–Mn(2)	106.5(1)		

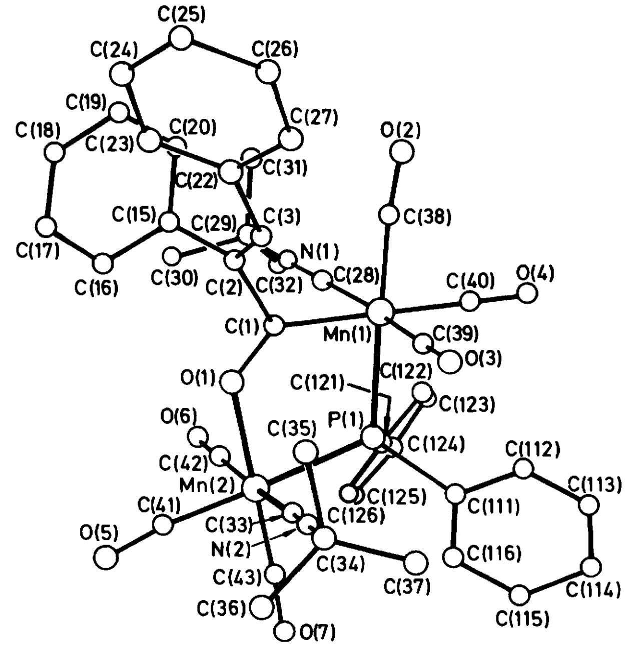


Figure 4. Molecular structure of $[Mn_2\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (**6**) including the atom numbering scheme

temperature although, on refluxing the solution, reaction does occur to give a mixture of the acyl complex $[Mn_2\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (**6**) and the substituted vinyl complex $[Mn_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$ (**7**).

Running the reaction of (**1b**) with Bu^{t}NC under an atmosphere of CO suppresses decomposition reactions and the formation of (**7**), giving an enhanced yield of (**6**).

The molecular structures of (**6**) and (**7**) have been determined by single-crystal *X*-ray diffraction and are shown in Figures 4 and 5 respectively. Tables 6 and 7 list selected bond lengths and angles. The molecular structure of (**6**) reveals that, as in (**2b**), the acyl ligand bridges the Mn–Mn vector, bonding through C(1) to Mn(1) and through O(1) to Mn(2). The metal atoms in (**6**), however, are not within bonding distance, the separation being 3.820(2) Å as compared to 2.813(1) Å in (**2b**). This difference can be accounted for in terms of the e.a.n. rule which requires a formal single Mn–Mn bond in (**2b**) but not in (**6**). The fact that (**2b**) and (**6**) nevertheless both contain a μ-acyl and a μ-phosphido group illustrates the flexibility with respect to bite angle of both these ligands.

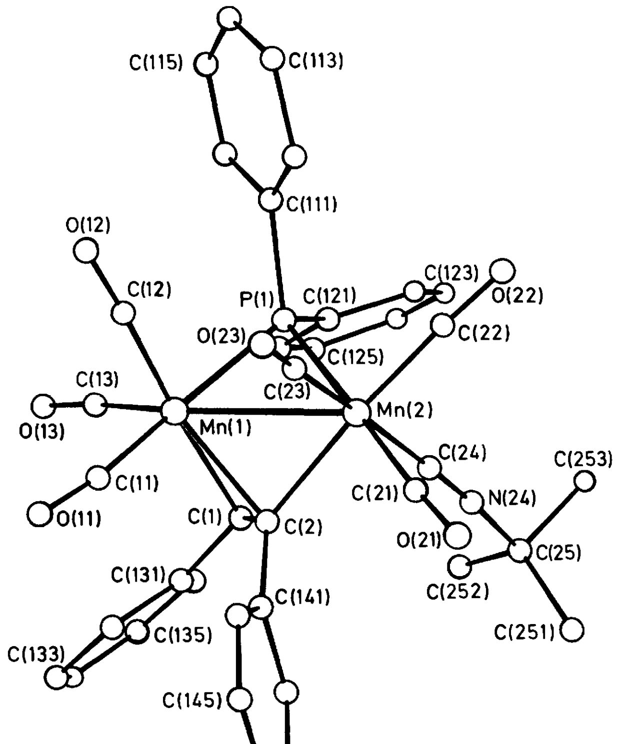


Figure 5. Molecular structure of $[Mn_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$ (**7**) including the atom numbering scheme

Table 7. Selected bond parameters for $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$ (**7**)

Bond lengths (Å)

Mn(2)–Mn(1)	2.758(1)	P(1)–Mn(1)	2.274(2)	C(23)–Mn(2)	1.832(7)	C(24)–Mn(2)	1.980(8)
C(11)–Mn(1)	1.819(8)	C(12)–Mn(1)	1.809(7)	C(2)–Mn(2)	2.156(6)	C(111)–P(1)	1.826(7)
C(13)–Mn(1)	1.809(8)	C(1)–Mn(1)	2.253(6)	C(121)–P(1)	1.844(6)	C(2)–C(1)	1.415(9)
C(2)–Mn(1)	2.104(6)	P(1)–Mn(2)	2.348(2)	C(131)–C(1)	1.497(9)	C(14)–C(2)	1.494(9)
C(21)–Mn(2)	1.843(8)	C(22)–Mn(2)	1.815(8)				

Bond angles (°)

P(1)–Mn(1)–Mn(2)	54.6(1)	C(11)–Mn(1)–Mn(2)	114.6(2)	C(22)–Mn(2)–C(21)	92.7(3)	C(23)–Mn(2)–Mn(1)	73.6(2)
C(11)–Mn(1)–P(1)	165.4(2)	C(12)–Mn(1)–Mn(2)	105.8(2)	C(23)–Mn(2)–P(1)	95.8(2)	C(23)–Mn(2)–C(21)	85.3(3)
C(12)–Mn(1)–P(1)	87.8(2)	C(12)–Mn(1)–C(11)	86.1(3)	C(23)–Mn(2)–C(22)	95.2(3)	C(24)–Mn(2)–Mn(1)	110.2(2)
C(13)–Mn(1)–Mn(2)	148.5(2)	C(13)–Mn(1)–P(1)	101.0(3)	C(24)–Mn(2)–P(1)	90.8(2)	C(24)–Mn(2)–C(21)	88.0(3)
C(13)–Mn(1)–C(11)	92.5(3)	C(13)–Mn(1)–C(12)	91.3(3)	C(24)–Mn(2)–C(22)	88.5(3)	C(24)–Mn(2)–C(23)	173.3(3)
C(1)–Mn(1)–Mn(2)	74.3(2)	C(1)–Mn(1)–P(1)	84.7(2)	C(2)–Mn(2)–Mn(1)	48.8(2)	C(2)–Mn(2)–P(1)	87.9(2)
C(1)–Mn(1)–C(111)	102.4(3)	C(1)–Mn(1)–C(12)	170.7(3)	C(2)–Mn(2)–C(21)	91.7(3)	C(2)–Mn(2)–C(22)	166.7(3)
C(1)–Mn(1)–C(13)	84.7(3)	C(2)–Mn(1)–Mn(2)	50.5(2)	C(2)–Mn(2)–C(23)	100.4(3)	C(2)–Mn(2)–C(24)	79.1(2)
C(2)–Mn(1)–P(1)	91.2(2)	C(2)–Mn(1)–C(11)	87.1(3)	Mn(2)–P(1)–Mn(1)	73.3(1)	C(2)–C(1)–Mn(1)	65.4(3)
C(2)–Mn(1)–C(12)	148.4(3)	C(2)–Mn(1)–C(13)	119.8(3)	C(131)–C(2)–Mn(1)	118.3(4)	C(131)–C(1)–C(2)	127.4(6)
C(12)–Mn(1)–C(1)	37.7(2)	P(2)–Mn(2)–Mn(1)	52.1(1)	Mn(2)–C(2)–Mn(1)	80.7(2)	C(1)–C(2)–Mn(1)	76.9(4)
C(21)–Mn(2)–Mn(1)	128.2(2)	C(21)–Mn(2)–P(1)	178.8(2)	C(1)–C(2)–Mn(2)	116.0(4)	C(141)–C(2)–Mn(1)	129.6(4)
C(22)–Mn(2)–Mn(1)	133.9(2)	C(22)–Mn(2)–P(1)	87.4(3)	C(141)–C(2)–Mn(2)	118.4(4)	C(141)–C(2)–C(1)	122.1(5)

It is interesting to compare the geometries of the Mn–Mn–O(1)–C(1) rings in (**2b**) and (**6**). Thus the longer metal–metal distance in (**6**) is accommodated with remarkably little change in the other bond lengths within the ring [values for (**2b**) in parentheses]: Mn–C(1) 2.031(6) [2.008(4)], Mn–O(1) 2.055(4) [2.048(3)], C(1)–O(1) 1.235(6) [1.266(5) Å]. The similarity of these distances in the two complexes requires the acyl ligand to lie closer to the metal–metal vector in (**6**) than in (**2b**) and this is reflected in the interbond angles. The Mn–C–O angle increases from 116.6(3)° in (**2b**) to 127.3(4)° in (**6**) and the Mn–O–C angle from 108.2(2)° to 130.7(4)°. Obviously the angles subtended by the μ-acyl ligand at the two metal centres are more flexible than the metal–ligand bond distances and this is also true of the μ-phosphido group. Thus the average metal–phosphorus bond length increases by only *ca.* 0.11 Å, from 2.278(4) Å in (**2b**) to 2.384(4) Å in (**6**), whereas the Mn(1)–P(1)–Mn(2) bond angle increases from 76.3(1) to 106.5(1)°, an increase of 40% in the bond angle and only 5% in the average metal–ligand bond length.

The Mn(1)–C(1)–O(1)–Mn(2)–P(1) ring in (**6**) adopts an essentially planar configuration rather than the folded arrangement found in (**2b**). This is accompanied by a rotation of the acyl side-chain through *ca.* 70° about the C(1)–C(2) bond in one structure as compared to the other (Figures 1 and 4), presumably to minimise the net steric interactions within the acyl ligand and between this ligand and the other ligands on the two metal atoms in each case. As in (**2b**) the bond lengths within the acyl side-chain indicate that there is little, if any, π-delocalisation of electrons within the unsaturated system [C(1)–C(2) 1.518(8), C(2)–C(3) 1.345(7) Å]. Other complexes containing both μ-PPh_2 and μ-acyl ligands have been structurally characterised and the geometric features of such complexes closely resemble those of (**2b**) or of (**6**) according to whether a metal–metal bond is[14] or is not[15] present as judged by the intermetallic separation and conformity to the e.a.n. rule.

Spectroscopic data for complexes (**6**) and (**7**) (Tables 2 and 5) are in accord with the structures found in the solid state being maintained in solution. Thus the vinyl proton in (**7**) shows a doublet resonance [*J*(PH) 8.7 Hz] whereas the corresponding proton in (**6**), which is more remote from the phosphorus atom, gives rise to a singlet. The acyl carbon atom in (**6**) shows a ^{13}C n.m.r. resonance at 323.2 p.p.m.

The empirical formula of (**6**) differs from that of (**7**) only in that (**6**) contains an extra molecule of CO and of the nucleophile, Bu^tNC. The possibility arises, therefore, that (**7**) is an intermediate in the formation of (**6**). That this is not the case is shown by the fact that the reaction of (**7**) with Bu^tNC requires more vigorous conditions (n-heptane, reflux) than does that of (**1b**) (hexane, reflux). Furthermore, reaction of (**7**) with Bu^tNC under these conditions gives only trace quantities of (**6**). The major products were a red complex, which could not be obtained pure but was identified from its ^1H n.m.r. spectrum as $[Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_5(CNBu^t)_2]$ (**8**), and a green complex of unknown composition (see below). Heating (**6**) alone in refluxing heptane showed that these red and green complexes were not products of the decomposition of (**6**) at the higher temperatures. In order to confirm the identity of the red complex (**8**) it was synthesised in a pure state in a separate experiment from $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ and C_2Ph_2 (see Experimental section).

(*d*) *Reactions of* (**1a**) *and* (**1b**) *with Phosphines and Phosphites*.—These nucleophiles again react differently with (**1a**) and with (**1b**). Thus PEt_3 reacts with (**1a**) in hexane solution at room temperature in an analogous fashion to Bu^tNC to give the P–C linked complex, $[Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PEt_3)]$ (**5c**). In contrast there is no reaction between (**1b**) and PEt_3 at room temperature and, at higher temperatures (70—100 °C) in aliphatic hydrocarbon solvents, only unidentified decomposition products which did not move on t.l.c. plates were obtained.

There is an unstable intermediate in the reaction of (**1a**) with PEt_3 which elutes faster than (**1a**) on a t.l.c. plate. Although dilute solutions of this intermediate could be obtained by column chromatography on Florisil the solutions rapidly gave (**5c**) on standing.

Suitable crystals of (**5c**) for an *X*-ray structure determination were obtained on cooling warm hexane solutions to which one drop of chloroform had been added. Three crystals of (**5c**) were required to collect a complete data set due to crystal decomposition during data acquisition. The structure of (**5c**) is shown in Figure 6. Table 8 lists selected bond lengths and interbond angles. The molecular structure of (**5c**) is analogous to that determined by *X*-ray analysis for (**5a**). The PEt_3 ligand occupies an axial site on the manganese atom to which the vinyl group is

Table 8. Selected bond parameters for [$Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PEt_3)$] (**5c**)

Bond lengths (Å)

Mn(1)–Mn(2)	2.989(3)	Mn(1)–P(2)	2.290(5)	Mn(2)–C(22)	1.780(16)	Mn(2)–C(23)	1.741(17)
Mn(1)–C(11)	1.786(17)	Mn(1)–C(12)	1.812(17)	C(1)–C(2)	1.424(21)	C(1)–P(2)	1.789(15)
Mn(1)–C(13)	1.776(16)	Mn(1)–C(14)	1.719(16)	P(1)–C(111)	1.876(16)	P(1)–C(121)	1.819(16)
Mn(2)–C(1)	2.229(15)	Mn(2)–C(2)	2.237(15)	P(1)–C(131)	1.821(17)	P(2)–C(211)	1.826(14)
Mn(2)–P(1)	2.291(5)	Mn(2)–C(21)	1.776(16)	P(2)–C(221)	1.827(16)		

Bond angles (°)

P(2)–Mn(1)–Mn(2)	70.1(1)	C(11)–Mn(1)–Mn(2)	99.3(5)	C(22)–Mn(2)–C(1)	98.2(6)	C(22)–Mn(2)–C(2)	95.6(6)
C(11)–Mn(1)–P(2)	169.3(5)	C(12)–Mn(1)–Mn(2)	87.8(5)	C(22)–Mn(2)–P(1)	89.2(5)	C(22)–Mn(2)–C(21)	176.2(7)
C(12)–Mn(1)–P(2)	94.1(6)	C(12)–Mn(1)–C(11)	86.7(7)	C(23)–Mn(2)–C(2)	76.2(5)	C(23)–Mn(2)–C(1)	150.0(7)
C(13)–Mn(1)–Mn(2)	85.5(5)	C(13)–Mn(1)–P(2)	87.3(5)	C(23)–Mn(2)–C(2)	171.7(7)	C(23)–Mn(2)–P(1)	90.5(6)
C(13)–Mn(1)–C(11)	90.5(7)	C(13)–Mn(1)–C(12)	172.2(7)	C(23)–Mn(2)–C(21)	87.9(8)	C(23)–Mn(2)–C(22)	88.4(8)
C(14)–Mn(1)–Mn(2)	167.7(6)	C(14)–Mn(1)–P(2)	97.6(6)	C(2)–C(1)–Mn(2)	71.7(9)	P(2)–C(1)–Mn(2)	99.7(7)
C(14)–Mn(1)–C(11)	93.1(7)	C(14)–Mn(1)–C(12)	92.9(7)	P(2)–C(1)–C(2)	134(1)	C(1)–C(2)–Mn(2)	71.1(9)
C(14)–Mn(1)–C(13)	94.5(7)	C(1)–Mn(2)–Mn(1)	74.7(4)	C(111)–P(1)–Mn(2)	115.0(5)	C(121)–P(1)–Mn(2)	116.0(5)
C(2)–Mn(2)–Mn(1)	109.3(4)	C(2)–Mn(2)–C(1)	37.2(5)	C(121)–P(11)–C(111)	96.7(7)	C(131)–P(1)–Mn(2)	115.3(6)
P(1)–Mn(2)–Mn(1)	166.7(2)	P(1)–Mn(2)–C(1)	118.6(4)	C(131)–P(1)–C(111)	104.6(7)	C(131)–P(1)–C(121)	107.2(8)
P(1)–Mn(2)–C(2)	83.7(4)	C(21)–Mn(2)–Mn(1)	91.4(5)	C(1)–P(2)–Mn(1)	103.8(5)	C(211)–P(2)–Mn(1)	118.6(5)
C(21)–Mn(2)–C(1)	85.6(6)	C(21)–Mn(2)–C(2)	98.0(6)	C(211)–P(2)–C(1)	112.1(7)	C(221)–P(2)–Mn(1)	119.2(5)
C(21)–Mn(2)–P(1)	89.7(5)	C(22)–Mn(2)–Mn(1)	88.8(5)	C(221)–P(2)–C(1)	101.4(7)	C(221)–P(2)–C(211)	100.8(17)

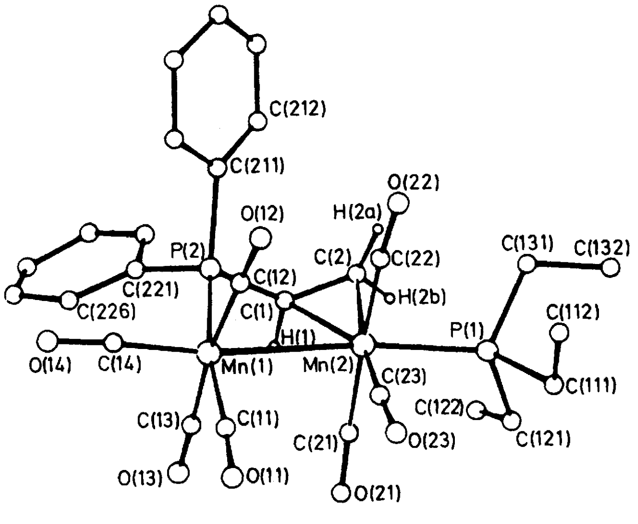


Figure 6. Molecular structure of [$Mn_2(\mu\text{-}PPh_2CH{=}CH_2)(CO)_7(PEt_3)$] (**5c**) including the atom numbering scheme

also co-ordinated. The structural parameters are otherwise closely similar to those for the unsubstituted complex (**5a**).

Other phosphorus-donor ligands such as $P(OMe)_3$, PMe_2Ph, and PPh_3 also react at room temperature with (**1a**) to give products which were deduced from their i.r. and ^1H n.m.r. spectra in solution (Table 2) to be analogous to (**5a**)—(**5c**). These products decompose more rapidly in solution than (**5a**)—(**5c**), however, and could not be obtained pure in the solid state.

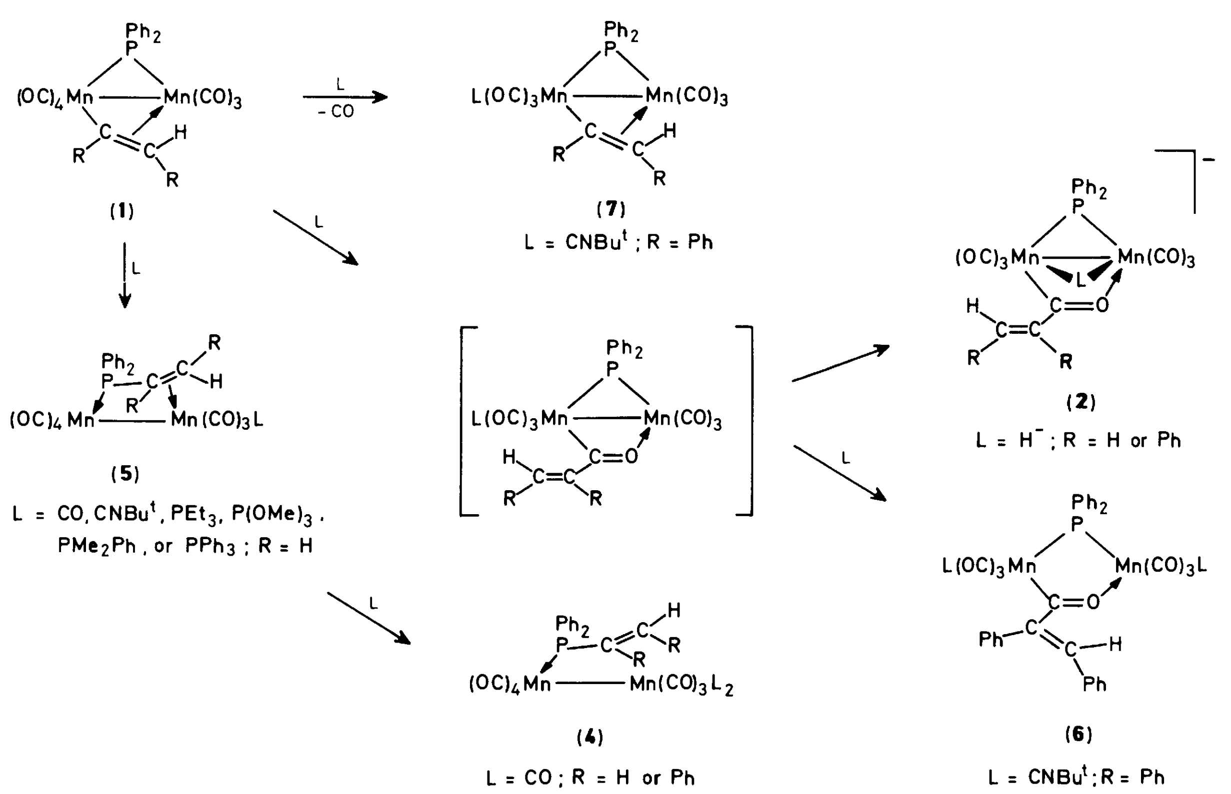
None of the phosphorus-donor ligands which we have found to react with (**1a**) at room temperature does so under these conditions with (**1b**). At 70—100 °C PPh_3 still shows no reaction whilst PEt_3 and $P(OMe)_3$ give the decomposition products already referred to. On the other hand, PMe_2Ph in hexane under reflux gives, after work-up, a green product [all the other complexes (**1**)—(**8**) are yellow, orange, or red] with the empirical formula (from elemental analysis) [$Mn_2\{C(Ph){=}CHPh\}(PPh_2)(CO)_n(PMe_2Ph)$] (**9**) (*n* could be 6 or 7). Optimum yields of this complex (*ca.* 30%) were obtained when the reaction was run under a carbon monoxide atmosphere. Complex (**9**) is readily soluble in polar solvents but only slightly soluble in hydrocarbon solvents. Its i.r. and ^1H n.m.r. spectra (Table 2) are not compatible with the formulation of (**9**) either as an acyl, a P–C linked, or a zwitterionic product of the type which is formed in other systems by the attack of the phosphorus nucleophile at the β-carbon atom of a bridging vinyl group,[3,4] and the identity of the complex remains unknown.

(*e*) *A Possible Reaction Scheme.*—It is not possible on the basis of the available evidence to propose a unified reaction system for the reactions of (**1a**) and (**1b**) with nucleophiles. However, the Scheme shows some pathways which account for all the observed major products.

The initial step is presumably attack of the nucleophile at one of the metal centres, rather than at the β-carbon atom of the vinyl group as in the attack of nucleophiles on [$Os_3(\mu\text{-}H)(\mu\text{-}\sigma{:}\eta^2\text{-}CHCH_2)(CO)_{10}$] and other related complexes.[3,4] This is suggested both by the lack of H/D exchange in the reaction of (**1b**) with $NaBD_4$ and by the fact that the nucleophile is bound to one or both manganese centres in all the characterised products of every reaction studied. The initial co-ordination of the nucleophile to the metal must be accompanied, if the effective atomic number rule is not to be violated, by (*i*) CO loss, (*ii*) loss of the metal–metal bond, (*iii*) a CO-insertion reaction into the σ bond between the metal and the vinyl group, (*iv*) detachment of the η^2 bonding of the vinyl group to the second metal centre, or (*v*) a P–C coupling reaction. Related systems provide examples of each of these processes[16–20] but the range of products obtained in the dimanganese system is unprecedented and suggests that in this particular case the activation energies for all the possible steps (*i*)—(*v*) are comparable.

Experimental

All reactions were performed under dry, oxygen-free nitrogen in nitrogen-saturated solvents. Solvents other than tetrahydrofuran (thf) were dried over 4Å molecular sieves unless otherwise stated; thf was dried by distillation from sodium benzophenone ketyl. Spectroscopic instrumentation was the same as previously used.[6]



Scheme. Suggested routes to the major products formed in the reactions of (**1a**) and (**1b**) with nucleophiles. The proposed intermediate shown in square brackets was not isolated

Reaction of [$Mn_2\{\mu$-$\sigma:\eta^2$-C(Ph)=CHPh$\}(\mu$-$PPh_2)(CO)_7$] (**1b**) *with Sodium Tetrahydroborate*.—Solid $NaBH_4$ (0.004 g, 0.1 mmol) was added to a stirred solution of (**1b**) (0.033 g, 0.05 mmol) in thf (5 cm^3). The mixture was stirred until no (**1b**) remained (spot t.l.c., *ca.* 30 min). The resulting solution was taken to dryness (high vacuum), the residue redissolved in $CHCl_3$ (10 cm^3), [$N(PPh_3)_2$]Cl (0.029 g, 0.05 mmol) added, and the solution then filtered through Celite under N_2. The volatiles were removed under reduced pressure and the solid residue extracted with EtOH (1 cm^3). The remaining solid was redissolved in the minimum quantity of $CHCl_3$ and red crystalline blocks of [$N(PPh_3)_2$][$Mn_2(\mu$-H)$\{\mu$-C(O)C(Ph)=CHPh$\}(\mu$-$PPh_2)(CO)_6$] (**2b**) (0.034 g, 57%) were then obtained by slow diffusion of hexane into this solution (Found: C, 67.8; H, 4.3; N, 1.2; P, 6.6. $C_{69}H_{52}Mn_2NO_7P_2$ requires C, 68.4; H, 4.3; N, 1.2; P, 7.7%).

The complex [$N(PPh_3)_2$][$Mn_2(\mu$-$H)_2(\mu$-$PPh_2)(CO)_6$] (**3**) was obtained as purple crystalline blocks (0.007 g, 14%) from the EtOH extract above by removal of the solvent followed by crystallisation of the residue by slow diffusion of EtOH into a concentrated $CHCl_3$ solution at 0 °C (Found: C, 63.1; H, 4.2; P, 8.5. $C_{54}H_{41}Mn_2NO_6P_3$ requires C, 64.6; H, 3.6; P, 9.3%).

Solutions of [$N(PPh_3)_2$][$Mn_2(\mu$-H)$\{\mu$-C(O)CH=CH$_2\}(\mu$-$PPh_2)(CO)_6$] (**2a**) and (**3**) can be prepared from (**1a**) in an analogous procedure to that described above for (**2b**). The only products isolated after crystallisation, however, were the known anion of [$N(PPh_3)_2$][$Mn_2(\mu$-$PPh_2)(CO)_8$][6] (51%) and (**3**) contaminated with this anion (combined yield *ca.* 25%).

Reaction of (**1a**) *and* (**1b**) *with Carbon Monoxide*.—A solution of (**1a**) (0.104 g, 0.2 mmol) in heptane (25 cm^3) was refluxed with passage of CO. After 45 min the reaction was stopped, the yellow solution taken to dryness, and the reaction products separated by preparative t.l.c. using hexane–CH_2Cl_2 (10:1) as eluant. A single yellow band eluted which, on evaporation to dryness, gave yellow crystals of [$Mn_2(PPh_2CH=CH_2)(CO)_9$] (**4a**), 0.17 g (95%) (Found: C, 48.4; H, 2.5; P, 5.0. $C_{23}H_{13}Mn_2O_9P$ requires C, 48.1; H, 2.3; P, 5.4%). The complex [$Mn_2\{PPh_2C(Ph)$=CHPh$\}(CO)_9$] (**4b**) was prepared by an analogous procedure using (**1b**) (0.067 g, 0.1 mmol) and octane as the solvent. Yield (decreasing R_f values): (**4b**) (0.020 g, 27%), (**1b**) (0.015 g, 22%).

Reaction of (**1a**) *with Acetonitrile*.—A solution of (**1a**) (0.025 g, 0.05 mmol) in MeCN (10 cm^3) was stirred for 1 h during which time the colour changed from purple-red to yellow. Carbon monoxide was then passed through the solution for 3 h. The volatiles were removed under reduced pressure and the product purified by t.l.c. on silica using hexane–CH_2Cl_2 (3:1) as eluant. Yield of [$Mn_2(\mu$-$PPh_2CH=CH_2)(CO)_8$] (**5a**): 0.041 g, 53% (Found: C, 47.9; H, 2.4; P, 4.8. $C_{22}H_{13}Mn_2O_8P$ requires C, 48.3; H, 2.4; P, 5.6%).

Reaction of (**1a**) *with* Bu^{t}NC.—A solution of (**1a**) (0.026 g, 0.05 mmol) in hexane (7 cm^3) was stirred with Bu^{t}NC (0.006 cm^3, *ca.* 10% excess) for 2.5 h during which time the colour of the solution paled to orange-red. A further quantity of Bu^{t}NC (0.006 cm^3) was then added resulting in an immediate colour change to bright orange. The volatiles were removed under reduced pressure and the residue chromatographed [preparative t.l.c., hexane–CH_2Cl_2 (5.5:1) as eluant]. Only one major yellow band eluted and this was evaporated to dryness to give yellow crystals of [$Mn_2(\mu$-$PPh_2CH=CH_2)(CO)_7(CNBu^t)$] (**5b**). Yield: 0.015 g, 50% (Found: C, 51.5; H, 3.7; N, 2.2; P, 5.3. $C_{26}H_{22}Mn_2NO_7P$ requires C, 51.9; H, 3.7; N, 2.3; P, 5.2%).

Reaction of (**1b**) *with* Bu^{t}NC.—A solution of (**1b**) (0.067 g, 0.1 mmol) and Bu^{t}NC (0.024 cm^3, 0.2 mmol) in hexane (30 cm^3)

Table 9. Data for crystal structure analysis

	(2b)	**(4b)**	**(5a)**	**(6)**	**(7)**	**(5c)**
Molecular formula	$C_{69}H_{52}Mn_2NO_7P_3$	$C_{36}H_{21}Mn_2O_9P$	$C_{22}H_{13}Mn_2O_8P$	$C_{43}H_{39}Mn_2N_2O_7P$	$C_{37}H_{30}Mn_2NO_6P$	$C_{27}H_{28}Mn_2N_2O_7P_2$
M	1 209.87	726.4	546.17	836.65	694.5	636.34
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Crystal colour	Red	Yellow	Yellow	Orange	Orange	Red
Crystal dimensions (mm)	0.35 × 0.37 × 0.40	0.32 × 0.25 × 0.23	0.02 × 0.02 × 0.61	0.23 × 0.41 × 0.45	0.18 × 0.26 × 0.35	0.25 × 0.30 × 0.33
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	10.129(3)	12.839(4)	9.917(1)	10.609(1)	18.141(5)	15.459(4)
b/Å	17.533(5)	13.610(4)	14.542(1)	10.844(3)	19.059(5)	16.355(4)
c/Å	17.446(5)	11.204(4)	16.500(1)	20.426(2)	10.290(3)	11.735(3)
α/°	98.05(4)	110.68(3)		87.04(2)		
β/°	101.95(4)	91.60(3)	105.96(1)	82.80(1)	92.92(3)	93.67(4)
γ/°	93.02(4)	114.10(3)		65.05(2)		
U/Å^3	2 990.6	1 637.6	2 287.8	2 113.8	3 553.1	2 960.9
Z	2	2	4	2	4	4
D_c/g cm^{-3}	1.36	1.47	1.59	1.44	1.30	1.43
F(000)	1 248	708	1 096	808	1 488	1 248
Radiation	Mo	Mo	Mo	Cu	Mo	Mo
λ/Å	0.710 69	0.710 69	0.710 69	1.5418	0.710 69	0.710 69
μ/cm^{-1}	5.06	8.07	11.38	55.24	7.42	9.31
Diffractometer	PW1100	PW1100	Stoe	Syntex $P2_1$	PW1100	PW1100
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ Range (°)	6—50	6—50	5—50	3—125		
Method of absorption correction	None	None	Numerical face index	Empirical azimuthal scans	None	None
Transmission factors			0.75—0.89	0.35—0.85		
No. unique data	6 375	3 848	4 029	6 564	4 142	1 873
No. observed data	6 160	3 741	3 376	5 046	3 629	1 725
Criteria (n) for observed [$F > n\sigma(F)$]	6	6	4	5	6	6
Solution method	Patterson	Patterson	Direct	Direct	Patterson	Patterson
Method of refinement	Blocked cascade	Blocked full-matrix	Blocked full-matrix	Blocked cascade	Blocked full-matrix	Blocked full-matrix
No. parameters refined	738	425	310	452	425	183
Anisotropic atoms	C, Mn, N, O, P	C, Mn, O, P	C, Mn, P, O	C, N, O, P, Mn	Mn, P, C, N, O	Mn, P
Final R	0.0521	0.0512	0.0378	0.074	0.0717	0.0748
Final R'	0.0566	0.0535	0.0408	0.087	0.0704	0.0738
Max. final electron density difference (e Å^{-3})	0.50	0.68	0.32	0.72	0.10	0.85

Table 10. Atomic co-ordinates (× 10^4) for $[N(PPh_3)_2][Mn_2(\mu\text{-}H)\{\mu\text{-}C(O)C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_6]$ (**2b**)

Atom	*x*	*y*	*z*
Mn(1)	1 504(1)	3 162(1)	1 862(1)
Mn(2)	1 540(1)	1 665(1)	2 269(1)
O(1)	2 991(3)	3 115(2)	2 844(2)
C(1)	2 991(4)	2 423(3)	2 976(2)
C(2)	4 119(4)	2 301(3)	3 648(3)
C(3)	4 428(5)	1 575(3)	3 731(3)
C(411)	4 885(5)	2 997(3)	4 184(3)
C(412)	4 302(6)	3 394(3)	4 759(3)
C(413)	4 999(8)	4 004(4)	5 274(4)
C(414)	6 270(9)	4 248(4)	5 248(4)
C(415)	6 865(6)	3 875(3)	4 679(4)
C(416)	6 183(5)	3 241(3)	4 125(3)
C(421)	5 510(7)	1 289(3)	4 296(3)
C(422)	6 265(6)	1 676(3)	4 976(4)
C(423)	7 289(7)	1 330(4)	5 463(4)
C(424)	7 224(12)	510(7)	5 368(7)
C(425)	6 108(16)	102(9)	4 920(10)
C(426)	5 162(13)	454(8)	4 341(8)
C('24)	7 933(13)	802(8)	5 170(9)
C('25)	7 537(20)	487(11)	4 417(13)
C('26)	6 325(17)	753(9)	3 874(10)
C(11)	2 709(4)	3 387(3)	1 270(3)
O(11)	3 389(3)	3 539(2)	851(2)
C(12)	189(5)	3 040(3)	983(3)
O(12)	−626(4)	2 959(3)	405(2)
C(13)	1 089(5)	4 128(3)	2 116(3)
O(13)	759(4)	4 744(2)	2 236(2)
C(21)	2 753(5)	1 047(3)	1 941(3)
O(21)	3 470(3)	617(2)	1 731(2)
C(22)	220(5)	1 151(3)	1 475(3)
O(22)	−576(4)	817(2)	948(2)
C(23)	1 189(5)	1 124(2)	3 005(3)
O(23)	942(4)	769(2)	3 479(2)
P(1)	196(1)	2 604(1)	2 587(1)
C(111)	324(4)	3 012(3)	3 629(3)
C(112)	874(6)	3 740(3)	3 943(3)
C(113)	941(7)	4 030(4)	4 752(4)
C(114)	497(6)	3 580(5)	5 221(4)
C(115)	−50(7)	2 862(4)	4 933(3)
C(116)	−152(6)	2 565(3)	4 129(3)
C(121)	−1 633(4)	2 429(2)	2 233(3)
C(122)	−2 381(5)	2 987(3)	1 954(4)
C(123)	−3 764(5)	2 865(4)	1 695(4)
C(124)	−4 425(5)	2 173(3)	1 688(4)
C(125)	−3 684(6)	1 598(3)	1 997(4)
C(126)	−2 291(5)	1 730(3)	2 261(4)
P(2)	3 969(1)	6 434(1)	1 605(1)
P(3)	5 088(1)	8 058(1)	1 739(1)
N	4 839(4)	7 155(2)	1 465(2)
C(211)	3 259(4)	5 839(2)	670(3)
C(212)	2 171(5)	5 292(3)	597(3)
C(213)	1 675(5)	4 813(3)	−119(3)
C(214)	2 257(6)	4 878(3)	−751(3)
C(215)	3 333(6)	5 405(3)	−687(3)
C(216)	3 849(5)	5 893(3)	25(3)
C(221)	2 579(5)	6 649(2)	2 071(3)
C(222)	1 400(5)	6 885(3)	1 628(3)
C(223)	349(5)	7 084(3)	1 985(4)
C(224)	455(6)	7 054(3)	2 793(4)
C(225)	1 602(6)	6 820(3)	3 223(3)
C(226)	2 683(5)	6 618(3)	2 883(3)
C(231)	5 047(4)	5 850(2)	2 194(2)
C(232)	4 508(5)	5 174(3)	2 401(3)
C(233)	5 355(5)	4 696(3)	2 804(3)
C(234)	6 715(6)	4 882(3)	2 980(3)
C(235)	7 285(6)	5 543(3)	2 786(3)
C(236)	6 437(5)	6 027(3)	2 386(3)
C(311)	5 904(5)	8 476(3)	1 065(3)
C(312)	5 842(5)	9 267(3)	1 011(3)
C(313)	6 636(6)	9 601(4)	559(4)
C(314)	7 441(6)	9 168(4)	168(3)
C(315)	7 462(6)	8 389(4)	193(3)
C(316)	6 706(5)	8 041(3)	639(3)
C(321)	3 555(5)	8 527(3)	1 754(3)
C(322)	3 205(5)	8 860(3)	2 450(3)
C(323)	1 972(5)	9 156(3)	2 419(3)
C(324)	1 081(5)	9 138(3)	1 714(3)
C(325)	1 422(5)	8 816(3)	1 015(3)
C(326)	2 646(5)	8 507(3)	1 029(3)
C(331)	6 242(5)	8 296(3)	2 694(3)
C(332)	6 019(5)	7 974(3)	3 336(3)
C(333)	6 923(5)	8 124(3)	4 060(3)
C(334)	8 043(5)	8 567(3)	4 145(3)
C(335)	8 312(5)	8 872(3)	3 523(3)
C(336)	7 422(5)	8 733(3)	2 795(3)

Table 11. Atomic co-ordinates (× 10^5 for Mn, × 10^4 for other atoms) for $[Mn_2\{PPh_2C(Ph){=}CHPh\}(CO)_9]$ (**4b**)

Atom	*x*	*y*	*z*
Mn(1)	−11 608(6)	26 185(6)	6 520(9)
Mn(2)	−25 106(5)	4 914(5)	−17 182(8)
P(1)	−35 508(9)	−12 383(9)	−35 119(14)
C(11)	−1 129(5)	3 457(4)	−346(7)
O(11)	−1 097(4)	3 982(4)	−960(6)
C(12)	316(4)	3 903(5)	2 129(7)
O(12)	197(3)	4 706(3)	3 085(5)
C(13)	115(5)	2 459(5)	65(7)
O(13)	892(3)	2 358(4)	−287(6)
C(14)	−1 294(5)	1 596(5)	1 441(7)
O(14)	−1 327(5)	1 020(4)	1 975(5)
C(15)	−2 575(5)	2 574(4)	947(7)
O(15)	−3 451(3)	2 582(4)	1 127(5)
C(21)	−3 354(4)	1 253(4)	−1 916(6)
O(21)	−3 808(4)	1 788(3)	−2 019(6)
C(22)	−1 489(5)	1 271(5)	−2 578(7)
O(22)	−874(4)	1 777(4)	−3 086(5)
C(23)	−1 502(4)	−57(4)	−1 354(6)
O(23)	−884(3)	−413(3)	−1 154(5)
C(24)	−3 426(5)	−46(4)	−642(6)
O(24)	−3 995(4)	−375(4)	31(5)
C(111)	−5 146(3)	−1 791(3)	−3 872(5)
C(112)	−5 921(3)	−2 931(4)	−4 101(5)
C(113)	−7 112(4)	−3 315(4)	−4 428(6)
C(114)	−7 537(4)	−2 573(4)	−4 546(6)
C(115)	−6 786(4)	−1 440(4)	−4 321(7)
C(116)	−5 589(4)	−1 043(4)	−3 993(6)
C(121)	−3 166(4)	−1 244(3)	−5 082(5)
C(122)	−4 003(4)	−1 671(4)	−6 195(5)
C(123)	−3 641(5)	−1 690(5)	−7 366(6)
C(124)	−2 490(5)	−1 321(5)	−7 442(7)
C(125)	−1 663(5)	−900(5)	−6 353(7)
C(126)	−1 992(4)	−850(4)	−5 174(6)
C(1)	−3 344(3)	−2 503(3)	−3 438(5)
C(2)	−3 636(4)	−2 748(4)	−2 395(5)
C(131)	−2 849(3)	−3 089(3)	−4 491(5)
C(132)	−1 665(4)	−2 804(4)	−4 264(7)
C(133)	−1 198(5)	−3 302(5)	−5 289(8)
C(134)	−1 892(6)	−4 067(6)	−6 485(8)
C(135)	−3 047(6)	−4 374(5)	−6 705(6)
C(136)	−3 534(4)	−3 876(4)	−5 710(5)
C(141)	−3 531(4)	−3 644(4)	−1 993(5)
C(142)	−3 219(4)	−4 517(4)	−2 702(6)
C(143)	−3 133(5)	−5 277(4)	−2 185(6)
C(144)	−3 348(5)	−3 169(5)	−967(7)
C(145)	−3 666(5)	−4 319(5)	−244(7)
C(146)	−3 773(4)	−3 561(4)	−763(6)
H(2)	−4 005	−2 257	−1 705

Table 12. Atomic co-ordinates (× 10^4) for [Mn_2(μ-$PPh_2CH{=}CH_2$)$(CO)_8$] (**5a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	5 841(1)	384(1)	7 165(1)	C(11)	6 189(4)	388(3)	6 110(2)
Mn(2)	8 884(1)	559(1)	7 977(1)	O(11)	6 313(3)	446(2)	5 451(2)
P(1)	8 432(1)	−932(1)	7 571(1)	C(12)	6 077(4)	1 618(3)	7 180(2)
C(101)	8 668(3)	−1 323(2)	6 568(2)	O(12)	6 153(4)	2 400(2)	7 149(2)
C(102)	9 762(3)	−955(2)	6 299(2)	C(13)	3 972(4)	424(3)	6 700(3)
C(103)	9 995(4)	−1 236(2)	5 547(2)	O(13)	2 781(3)	463(3)	6 428(2)
C(104)	9 146(4)	−1 898(3)	5 066(2)	C(14)	5 595(4)	473(2)	8 235(2)
C(105)	8 082(4)	−2 290(2)	5 337(2)	O(14)	5 412(3)	568(2)	8 884(2)
C(106)	7 854(4)	−2 011(2)	6 094(2)	C(21)	8 586(3)	192(2)	8 984(2)
C(111)	9 236(3)	−1 858(2)	8 312(2)	O(21)	8 420(2)	−29(2)	9 610(1)
C(112)	10 510(3)	−1 725(2)	8 908(2)	C(22)	8 869(4)	1 754(2)	8 305(2)
C(113)	11 100(4)	−2 423(3)	9 465(2)	O(22)	8 926(4)	2 505(2)	8 506(2)
C(114)	10 416(4)	−3 248(3)	9 430(2)	C(23)	10 763(4)	506(2)	8 333(2)
C(115)	9 159(4)	−3 392(2)	8 845(3)	O(23)	11 962(3)	504(2)	8 539(2)
C(116)	8 561(4)	−2 700(2)	8 283(2)	C(24)	8 940(3)	967(2)	6 933(2)
C(1)	6 623(3)	−1 043(2)	7 546(2)	O(24)	9 031(3)	1 255(2)	6 307(1)
C(2)	5 414(4)	−1 112(3)	6 898(2)				

Table 13. Atomic co-ordinates (× 10^4) for [Mn_2{μ-C(O)C(Ph)=CHPh}(μ-PPh_2)$(CO)_6(CNBu^t)_2$] (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	4 356(1)	2 938(1)	2 014	C(20)	3 353(5)	−38(5)	862(2)
Mn(2)	3 557(1)	1 579(1)	3 703	C(3)	1 243(6)	2 750(6)	1 537(2)
P(1)	4 854(1)	2 715(1)	3 135(1)	C(22)	255(5)	2 814(4)	1 081(2)
C(121)	6 769(5)	1 838(5)	3 230(3)	C(23)	−38(5)	1 727(4)	935(2)
C(122)	7 754(5)	1 966(5)	2 744(3)	C(24)	−1 001(5)	1 901(4)	493(2)
C(123)	9 179(5)	1 259(5)	2 803(3)	C(25)	−1 671(5)	3 162(4)	196(2)
C(124)	9 620(5)	424(5)	3 347(3)	C(26)	−1 377(5)	4 250(4)	342(2)
C(125)	8 635(5)	295(5)	3 833(3)	C(27)	−414(5)	4 076(4)	784(2)
C(126)	7 210(5)	1 002(5)	3 775(3)	C(28)	5 773(6)	1 120(5)	1 825(2)
C(22A)	7 750(7)	1 571(12)	2 698(5)	N(1)	6 577(6)	21(5)	1 691(2)
C(23A)	9 164(7)	973(12)	2 793(5)	C(29)	7 585(7)	−1 345(6)	1 504(3)
C(24A)	9 554(7)	732(12)	3 431(5)	C(30)	6 951(9)	−2 317(7)	1 816(4)
C(25A)	8 531(7)	1 089(12)	3 974(5)	C(31)	7 669(10)	−1 486(8)	766(3)
C(26A)	7 117(7)	1 687(12)	3 879(5)	C(32)	8 937(9)	−1 578(9)	1 736(6)
C(111)	4 470(6)	4 393(5)	3 506(3)	C(33)	1 854(6)	3 225(7)	3 768(3)
C(112)	5 302(6)	5 053(5)	3 248(3)	N(2)	759(6)	4 140(7)	3 791(3)
C(113)	4 955(6)	6 384(5)	3 439(3)	C(34)	−652(9)	5 184(10)	3 793(4)
C(114)	3 777(6)	7 056(5)	3 887(3)	C(35)	−1 149(10)	5 083(12)	3 124(4)
C(115)	2 945(6)	6 395(5)	4 145(3)	C(36)	−1 548(10)	4 874(12)	4 355(5)
C(116)	3 292(6)	5 064(5)	3 954(3)	C(37)	−604(12)	6 500(9)	3 870(6)
C(12A)	4 894(20)	4 261(14)	4 203(8)	C(38)	4 024(7)	3 137(6)	1 170(3)
C(13A)	4 533(20)	5 463(14)	4 547(8)	O(2)	3 830(6)	3 331(6)	615(2)
C(14A)	4 036(20)	6 709(14)	4 218(8)	C(39)	2 836(7)	4 500(6)	2 218(3)
C(15A)	3 900(20)	6 752(14)	3 546(8)	O(3)	1 842(5)	5 488(4)	2 321(3)
C(16A)	4 262(20)	5 549(14)	3 202(8)	C(40)	5 492(7)	3 808(7)	1 804(3)
O(1)	2 961(4)	1 418(4)	2 803(2)	O(4)	6 143(6)	4 421(6)	1 650(3)
C(1)	3 120(5)	1 940(5)	2 266(2)	C(41)	2 560(7)	703(7)	4 118(3)
C(2)	2 329(6)	1 689(5)	1 756(2)	O(5)	1 950(6)	201(6)	4 444(2)
C(15)	2 862(5)	252(5)	1 528(2)	C(42)	5 088(6)	−2(6)	3 543(3)
C(16)	2 844(5)	−783(5)	1 958(2)	O(6)	6 044(5)	−1 017(4)	3 452(2)
C(17)	3 317(5)	−2 107(5)	1 724(2)	C(43)	4 012(6)	1 750(6)	4 489(3)
C(18)	3 808(5)	−2 397(5)	1 059(2)	O(7)	4 294(5)	1 810(5)	5 009(2)
C(19)	3 826(5)	−1 362(5)	628(2)				

were refluxed under an atmosphere of CO for 45 min with exclusion of light. The reaction products were separated by preparative t.l.c. using hexane–ethyl acetate (10:1) as eluant to give (decreasing R_f values): (**1b**) (trace), [Mn_2{μ-C(O)C(Ph)=CHPh}(μ-PPh_2)$(CO)_6(CNBu^t)_2$] (**6**) (0.040 g, 53%), and [Mn_2{μ-σ:η^2-C(Ph)=CHPh}(μ-PPh_2)$(CO)_6(CNBu^t)$] (**7**) (0.005 g, 7%) [Found for (**6**): C, 61.2; H, 4.8; N, 3.4. $C_{43}H_{39}Mn_2N_2O_7P$ requires C, 61.7; H, 4.7; N, 3.3%. Found for (**7**): C, 61.5; H, 4.5; P, 5.0. $C_{37}H_{30}Mn_2NO_6P$ requires C, 61.2; H, 4.1; P, 4.3%].

Repeating the reaction under an atmosphere of N_2 afforded (**1b**) (0.020 g, 30%), (**6**) (0.014 g, 19%), and (**7**), (0.008 g, 11%).

Complex (**7**) may be obtained in higher yield from the reaction of [Mn_2(μ-H)(μ-PPh_2)$(CO)_7(CNBu^t)$]^6 with C_2Ph_2. Thus a solution of this complex (0.115 g, 0.2 mmol) and C_2Ph_2 (tenfold excess) in hexane (15 cm^3) was irradiated with u.v. light (Hanovia medium-pressure lamp) for 2 h. The products were separated by preparative t.l.c. using hexane–ethyl acetate (20:1) as eluant (decreasing R_f values): [Mn_2(μ-H)(μ-PPh_2)$(CO)_7$-$(CNBu^t)$] (0.015 g, 13%), (**7**) (0.085 g, 74%).

Reaction of (**1a**) *with* PEt_3.—Solutions of (**1a**) (0.026 g, 0.05 mmol) and PEt_3 (0.007 cm^3, 0.05 mmol) in hexane (5 cm^3) were stirred together for 20 min. The resulting bright red solution

Table 14. Atomic co-ordinates (× 10^4) for [$Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)$] (**7**)

Atom	*x*	*y*	*z*
Mn(1)	1 124(1)	2 663(1)	−1 884(1)
Mn(2)	608(1)	1 489(1)	−653(1)
P(1)	806(1)	1 632(1)	−2 874(2)
C(11)	1 498(1)	3 339(4)	−793(7)
O(11)	1 788(3)	3 789(3)	−226(6)
C(12)	2 072(4)	2 471(4)	−2 218(7)
O(12)	2 683(3)	2 389(3)	−2 425(6)
C(13)	1 042(4)	3 263(4)	−3 246(8)
O(13)	984(3)	3 664(3)	−4 068(6)
C(21)	432(4)	1 377(4)	1 083(8)
O(21)	361(3)	1 274(4)	2 167(6)
C(22)	709(4)	551(4)	907(8)
O(22)	759(3)	−39(3)	−1 051(7)
O(23)	1 578(4)	1 588(4)	−94(7)
O(23)	2 162(3)	1 595(3)	369(6)
C(24)	−466(4)	1 380(3)	−1 040(6)
N(24)	−1 082(3)	1 307(3)	−1 177(6)
C(25)	−1 871(4)	1 273(5)	−1 315(9)
C(251)	−2 164(6)	1 310(10)	−10(15)
C(252)	−2 096(5)	1 759(11)	−2 373(14)
C(253)	−2 041(7)	549(8)	−1 970(17)
C(1)	−103(3)	2 822(3)	−1 785(6)
C(2)	252(3)	2 567(3)	−623(6)
C(111)	1 541(3)	1 170(3)	−3 671(8)
C(112)	2 050(4)	747(4)	−2 979(9)
C(113)	2 639(4)	446(5)	−3 679(12)
C(114)	2 708(5)	590(6)	−4 977(13)
C(115)	2 215(5)	1 006(5)	−5 619(10)
C(116)	1 627(4)	1 299(4)	−5 025(8)
C(121)	20(3)	1 467(4)	−4 041(7)
C(122)	−281(4)	795(4)	−4 118(7)
C(123)	−876(4)	653(4)	−4 993(8)
C(124)	−1 162(4)	1 183(5)	−5 798(8)
C(125)	−862(4)	1 845(5)	−5 715(8)
C(126)	−273(4)	1 986(4)	−4 826(7)
C(131)	−409(3)	3 542(3)	−2 033(6)
C(132)	−415(4)	4 155(3)	−1 467(7)
C(133)	−406(7)	4 806(4)	−1 841(8)
C(134)	−1 153(4)	5 265(4)	−3 155(10)
C(135)	−1 235(4)	4 259(4)	−3 419(9)
C(136)	−962(4)	3 602(4)	−3 050(7)
C(141)	152(3)	2 907(3)	665(7)
C(142)	−536(3)	3 159(4)	989(7)
C(143)	−659(4)	3 455(4)	2 198(8)
C(144)	−78(4)	3 504(4)	3 123(8)
C(145)	601(4)	3 246(4)	2 824(7)
C(146)	721(3)	2 958(4)	1 669(7)

Table 15. Atomic co-ordinates (× 10^4) for [$Mn_2(\mu\text{-}PPh_2CH=CH_2)(CO)_7(PEt_3)$] (**5c**)

Atom	*x*	*y*	*z*
Mn(1)	2 940(1)	−224(1)	3 439(2)
Mn(2)	1 369(1)	824(1)	3 003(2)
P(1)	−2(2)	1 356(3)	2 783(4)
P(2)	3 263(2)	870(3)	2 325(3)
C(1)	2 489(10)	1 628(9)	2 671(12)
C(2)	1 734(10)	1 957(9)	2 081(13)
C(11)	2 495(10)	−986(10)	4 337(14)
O(11)	2 257(7)	−1 485(7)	4 936(10)
C(12)	2 546(10)	−848(10)	2 241(14)
O(12)	2 296(7)	−1 267(7)	1 500(10)
C(13)	3 176(9)	416(10)	4 642(13)
O(13)	3 352(7)	805(7)	5 475(9)
C(14)	3 945(10)	−676(10)	3 505(13)
O(14)	4 634(8)	−1 014(7)	3 621(10)
C(21)	1 474(9)	1 219(10)	4 415(14)
O(21)	1 513(7)	1 422(8)	5 396(11)
C(22)	1 217(9)	377(10)	1 622(14)
O(22)	1 033(7)	60(7)	730(11)
C(23)	963(10)	−71(11)	3 569(14)
O(23)	643(7)	−658(7)	3 967(9)
C(111)	−899(10)	609(9)	2 997(14)
C(112)	−964(12)	−79(12)	2 136(16)
C(121)	−293(10)	2 085(9)	3 866(13)
C(122)	234(11)	2 876(11)	3 938(15)
C(131)	−286(10)	1 819(11)	1 398(14)
C(132)	−1 243(13)	2 080(13)	1 229(18)
C(211)	3 290(8)	719(9)	785(11)
C(212)	3 005(9)	1 300(10)	−5(12)
C(213)	3 092(9)	1 127(10)	−1 176(13)
C(214)	3 446(10)	480(11)	−1 532(16)
C(215)	3 771(11)	−107(11)	−751(15)
C(216)	3 682(10)	19(10)	422(14)
C(221)	4 282(10)	1 417(10)	2 631(13)
C(222)	4 391(13)	2 184(12)	2 153(16)
C(223)	5 191(14)	2 616(14)	2 345(18)
C(224)	5 836(14)	2 272(14)	3 033(17)
C(225)	5 762(15)	1 485(15)	3 403(19)
C(226)	4 967(12)	1 067(13)	3 256(16)
H(1)	26 110	19 360	34 430
H(2a)	14 970	17 300	13 120
H(2b)	13 792	24 432	24 068

was then applied to the top of a chromatography column (10 × 1.5 cm) packed with Florisil (60—100 mesh). Elution of the column with N_2-saturated hexane–ethyl acetate (10:1) afforded two bands. Crystallisation from the minimum of warm hexane (to which one drop of $CHCl_3$ had been added) of the dried residue from the more slowly eluting band afforded bright red blocks of [$Mn_2\{\mu\text{-}PPh_2CH=CH_2\}(CO)_7(PEt_3)$] (**5c**) (0.017 g, 53%) (Found: C, 50.8; H, 4.3; P, 9.4. $C_{27}H_{28}Mn_2O_7P_2$ requires C, 50.9; H, 4.4; P, 9.7%).

Preparation of [$Mn_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Ph)=CHPh\}(\mu\text{-}PPh_2)(CO)_5(CNBu^t)_2$] (**8**).—A solution of [$Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2$] (0.035 g, 0.05 mmol) and C_2Ph_2 (ten-fold excess) in hexane (50 cm^3) was irradiated with u.v. light whilst the solvent was evaporated by passing a rapid stream of N_2 over the solution (4 h). The products were separated by preparative t.l.c. using hexane–ethyl acetate (10:1) as eluant (decreasing R_f values): [$Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2$](0.012 g, 34%), (**8**) (0.014 g, 32%).

Crystal Structure Determination and Refinements.—Suitable single crystals of the complexes were mounted on glass fibres with epoxy-resin. Details of the data-collection procedures, structure solution and refinements are presented in Table 9; in each case data were collected for a unique volume of reciprocal space. For complexes (**2b**), (**4b**), (**7**), and (**5c**) reflections for which $I > 3\sigma(I)$ were rejected after a prescan and were not recorded.

During the refinements it was found that in both (**2b**) and (**6**) the phenyl groups were positionally disordered in two sites, related by an approximate two-fold axis passing through the pivot carbon and the one *trans* to it in the ring. In each case, both orientations were refined with occupancies k and $(1 - k)$; k refined to 0.506(5) for (**2b**), and to 0.561(6) and 0.601(5) for the two rings in (**6**). All phenyl groups in (**6**) were refined as rigid bodies with C–C fixed at 1.395 Å, and C–C–C at 120°. In all the structures phenyl, methylene, and methyl hydrogens were placed in idealised positions, and allowed to ride 1.08 Å from the relevant C atom. Each type of hydrogen was assigned a common isotropic thermal parameter. In complexes (**5a**) and (**5c**) the olefinic hydrogens were allowed to refine freely with constrained thermal parameters. The hydride in the structure of (**2b**) was not located.

All the structures were refined to convergence. Weighting schemes were applied, and analyses of the variations of the sum of $w\Delta^2$ $[\Delta = (F_o - |F_c|)]$ according to $|F_o|$ and $\sin\theta$ indicated that the schemes were appropriate. The final residuals were calculated on the basis $R = \Sigma|F_o - |F_c||/\Sigma F_o$, $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||$, $w = 1/[\sigma^2(F_o) + gF_o^2]$, where $\sigma(F_o)$ is the estimated standard deviation in F_o from counting statistics. The final atomic co-ordinates for the non-hydrogen atoms of all the structures are listed in Tables 10—15. All atoms were assigned complex neutral-atom scattering factors taken from ref. 21. Calculations were performed on the Polytechnic of North London DEC 10 computer, and the University of Cambridge IBM 3081 mainframe computer using modified versions of SHELX 76.[22]

Acknowledgements

We wish to thank the S.E.R.C., BP Chemicals Ltd. (Hull Division), and BP p.l.c. for financial support and Drs. J. E. Hamlin and D. Pippard for valuable discussion.

References

1 A. J. Carty, *Adv. Chem. Ser.*, 1982, **196**, 163.
2 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.
3 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **112**, C39.
4 B. G. DeBoer, M. R. Churchill, J. B. Keister, and J. R. Shapley, *J. Am. Chem. Soc.*, 1976, **98**, 2357.
5 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 1984, **106**, 644.
6 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1983, 205.
7 K. Henrick, J. A. Iggo, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1984, 209.
8 G. N. Mott, R. Gransby, S. A. MacLaughlin, N. J. Taylor, and A. J. Carty, *Organometallics*, 1983, **2**, 189.
9 J. R. Blickensdorf, H. D. Kaesz, and C. B. Nobler, *J. Am. Chem. Soc.*, 1975, **97**, 2686; R. Szostak, C. E. Strouse, and H. D. Kaesz, *J. Organomet. Chem.*, 1980, **191**, 243; B. F. G. Johnson, T. I. Odiaka, and P. R. Raithby, *ibid.*, 1981, **216**, C56.
10 M. Creswick, I. Bernal, B. Reiter, and W. A. Herrmann, *Inorg. Chem.*, 1982, **21**, 645.
11 'Molecular Structures and Dimensions,' eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. G. Petterson, and W. G. Town, N. V. A. Oosthoek, Utrecht, 1972, vol. A1, p. 52.
12 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 633.
13 M. Laing, E. Singleton, and R. Reimann, *J. Organomet. Chem.*, 1973, **56**, C21.
14 Y. F. Yu, J. Gallucci, and A. Wojcicki, *J. Am. Chem. Soc.*, 1983, **105**, 4826; G. N. Nott, R. Granby, S. A. MacLaughlin, N. J. Taylor, and A. J. Carty, *Organometallics*, 1983, **2**, 189; J. C. Jeffery and J. G. Lawrence-Smith, *J. Chem. Soc., Chem. Commun.*, 1985, 275.
15 R. P. Rosen, J. B. Hoke, R. R. Whittle, G. L. Geoffroy, J. P. Hutchinson, and J. A. Zubieta, *Organometallics*, 1984, **3**, 846.
16 R. Regragui, P. H. Dixneuf, N. J. Taylor, and A. J. Carty, *Organometallics*, 1984, **3**, 814.
17 G. L. Geoffroy, S. Rosenberg, P. M. Shulman, and R. R. Whittle, *J. Am. Chem. Soc.*, 1984, **106**, 1519.
18 J. Ros, X. Solans, M. Font-Altaba, and R. Mathieu, *Organometallics*, 1984, **3**, 1014.
19 J. Ros, G. Commenges, R. Mathieu, X. Solans, and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1985, 1087.
20 T. Adatia, K. Henrick, A. D. Horton, M. J. Mays, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1986, 1206.
21 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
22 G. M. Sheldrick, SHELX 76, crystal structure determination package, University of Cambridge, 1976.

Received 11*th February* 1987; *Paper* 7/249