Substitution and Insertion Reactions of the Dinuclear Manganese μ-Hydride Complex $[M_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$; Crystal Structures of the Complexes $[Mn_2(\mu\text{-}\sigma{:}\eta^2\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$ and $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ †

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$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1) has been synthesised in 80% yield from $[Mn_2(CO)_{10}]$ and $PHPh_2$. Reaction of (1) with RCN, RNC, PPh_3, $P(OMe)_3$, or $(EtO)_2POP(OEt)_2$ gives substitution products of general formulae $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7L]$ [L = NCMe (2a); NCPh (2b); $CNBu^t$ (2c); $CNCH_2Ph$ (2d); PPh_3 (2e); $P(OMe)_3$ (2f); $P(OEt)_3$ (2g)], $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6L_2]$ [L = $CNBu^t$ (3a); $L_2 = (EtO)_2POP(OEt)_2$ (3b)], and $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4\{(EtO)_2POP(OEt)_2\}_2]$ (4). Reaction of (1) with alkynes gives the complexes $[Mn_2(\mu\text{-}\sigma{:}\eta^2\text{-}CR{=}CHR')(\mu\text{-}PPh_2)(CO)_7]$ [R = R' = H (5a); R = Ph, R' = H (5b); R = H, R' = Ph (5c); R = R' = Ph (5d); R = R' = CF_3 (5e)] which are derived from (1) by insertion of the alkyne into a Mn–H bond together with loss of a CO group. Complexes (3a) and (5a) have been characterised by *X*-ray structure analysis by conventional heavy-atom methods using room-temperature diffractometer data. Crystals of (3a) are triclinic, space group $P\bar{1}$, with $a = 17.686(3)$, $b = 10.063(2)$, $c = 9.231(3)$ Å, $\alpha = 96.92(4)$, $\beta = 99.40(4)$, $\gamma = 104.34(5)°$, and $Z = 2$. 3 047 Reflections with $I \geqslant 3\sigma(I)$ [$3 \leqslant \theta \leqslant 25°$] refined to $R = 0.044$ and $R' = 0.043$. The complex (5a) crystallises in space group $P\bar{1}$ with $a = 10.301(4)$, $b = 10.320(4)$, $c = 24.359(11)$ Å, $\alpha = 92.70(3)$, $\beta = 92.17(3)$, $\gamma = 123.59(3)°$, and $Z = 4$. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked-cascade least squares to $R = 0.047$ for 6 036 diffractometer data. Structures are proposed for the other new complexes and the mechanism of formation of the complexes (5) from (1) is discussed.

There is now considerable interest in dinuclear and polynuclear complexes containing μ-phosphido and other bridging phosphorus ligands, since these ligands appear to inhibit the fragmentation of such complexes to lower nuclearity species on reaction, *e.g.* with electron-donor ligands such as CO, PR_3, RNC, and alkynes.[1-3] Thus, whereas $[Re_2(\mu\text{-}H)_2(CO)_8]$ reacts instantaneously with PPh_3 at room temperature to give $[ReH(CO)_4(PR_3)]$, $[Re_2(\mu\text{-}H)_2(CO)_6(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) reacts without fragmentation with PR_3 to give 1 : 1 adducts and with RNC or RCN to give products resulting from insertion of these ligands into a Re–H bond.[4]

Dinuclear manganese complexes are also stabilised with respect to fragmentation into mononuclear species by the presence of bridging phosphorus ligands [5,6] but, apart from a recent report on the reduction of $[Mn_2(\mu\text{-}H)(CO)_6(dppm)_2]^+$ by $Li[BHEt_3]$ which, it is claimed, may proceed *via* a dinuclear metal formyl complex,[7] there have been no studies on the reactivity of dinuclear complexes of this metal containing μ-hydrido-ligands. We have therefore sought to prepare complexes of this type to compare their reactivity with the rhenium complexes we have previously studied and, in this paper, we report a high yield synthesis of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1) from $[Mn_2(CO)_{10}]$ and $PHPh_2$, and present an account of its reactions with two-electron-donor ligands and with alkynes. Such reactions have led to the synthesis of new substitution products and, with alkynes, to products derived from the parent compound by insertion of the alkyne into a Mn–H bond. Simple insertion reactions of this kind involving polynuclear transition metal complexes with μ-H ligands have previously only been well documented for a small group of second and third row transition-metal complexes such as $[Os_3H_2(CO)_{10}]$ and $[Re_2(\mu\text{-}H)_2(CO)_8(dppm)]$ which formally require multiple metal–metal bonds to achieve 18-electron configurations at the metal centres.[4,8,9]

Results and Discussion

(*a*) *Preparation.*—Complex (1) was first prepared by Green and Moelwyn-Hughes [10] in 2% yield from the reaction of PPh_2Cl with $[Mn(CO)_5]^-$ and has been subsequently synthesised by Hayter [11,12] in 12% yield from the reaction of $[Mn_2(CO)_{10}]$ with P_2Ph_4. We now find that treatment of $[Mn_2(CO)_{10}]$ in undried decalin at 150 °C with one equivalent of $PHPh_2$ affords (1) in 80% yield. This is the first reported high yield synthesis of a complex of this type. Complex (1) was characterised by mass spectrometry and microanalysis (Table 1) and comparison of its i.r. and ^1H n.m.r. spectra (Table 2) with published data.[10] If pre-dried decalin is used in the preparation of (1) a lower yield is obtained suggesting that, at least in part, the hydride ligand is derived from the solvent. Presumably in the previously reported preparation of (1) from $[Mn_2(CO)_{10}]$ and P_2Ph_4 the solvent is also the source of the hydride ligand.[11]

(*b*) *Substitution Reactions.*—Reaction of (1) with organophosphines, nitriles, or isonitriles in refluxing cyclohexane or on u.v. irradiation in pentane solution results in the formation of substitution products of general formulae $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7L]$ [L = NCMe (2a); NCPh (2b); $CNBu^t$ (2c); $CNCH_2Ph$ (2d); PPh_3 (2e); $P(OMe)_3$ (2f); $P(OEt)_3$ (2g)],

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† 1,1,1,2,2,2-Heptacarbonyl-μ-diphenylphosphido-μ-σ:1'-2'-η-vinyl(*C*¹–*Mn*¹)-dimanganese(*Mn*–*Mn*) and μ-diphenylphosphido-μ-hydrido-bis[tricarbonyl(t-butyl isocyanide)manganese](*Mn*–*Mn*).

Supplementary data available (No. SUP 23469, 68 pp.): observed and calculated structure factors, hydrogen atom co-ordinates, isotropic and anisotropic thermal parameters, least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 atm = 101 325 Pa.

Table 1. Mass spectroscopic and microanalytical data for μ-phosphido-dimanganese complexes

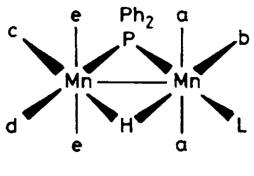
	Compound	Mass spectra		Analysis (%) [a]			Yield (%) [b,c]
		M	Fragmentation	C	H	P	
(1)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$	520	$M - n$CO (n = 0—8)	46.3 (46.0)	2.1 (2.1)		
(2a)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(NCMe)]$ [d]						43(4)
(2b)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(NCPh)]$ [d]						
(2c)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(CNBu^t)]$	575	$M - n$CO (n = 0—2, 7)	50.0 (50.1)	3.6 (3.5)	5.3 (5.6)	71(38)
(2d)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(CNCH_2Ph)]$	609	$M - n$CO (n = 0, 2—5, 7)				55(32)
(2e)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(PPh_3)]$	754	$M - n$CO (n = 0—3, 4)	58.4 (58.7)	3.4 (3.4)	7.9 (8.2)	76(76)
(2f)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7\{P(OMe)_3\}]$	616	$M - n$CO (n = 0, 1, 3—7)	42.6 (42.9)	3.3 (3.3)	10.2 (10.1)	72(55)
(2g)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7\{P(OEt)_3\}]$	658	$M - n$CO (n = 0, 3—7)				4(3)
(3a)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$	630	$M - n$CO (n = 0, 2, 3, 6)	52.9 (53.3)	4.7 (4.6)	*e*	21(10)
(3b)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6L_2]$ [f]	722	$M - n$CO (n = 0—6)	43.0 (43.2)	4.2 (4.3)	13.1 (12.9)	21(16)
(4)	$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4L_4]$ [f]	924	$M - n$CO (n = 0—4)				9(7)
(5a)	$[Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$	518	$M - n$CO (n = 0—7)	48.5 (48.7)	2.9 (2.5)	6.0 (6.0)	99(17)
(5b)	$[Mn_2(\mu\text{-}CPh{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$ }	594	$M - n$CO (n = 0—7)	55.0 (54.6)	3.0 (2.9)	5.8 (5.2)	73(22)
(5c)	$[Mn_2(\mu\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)(CO)_7]$ }						
(5d)	$[Mn_2(\mu\text{-}CPh{=}CHPh)(\mu\text{-}PPh_2)(CO)_7]$	670	$M - n$CO (n = 0—7)	59.1 (58.8)	3.1 (3.0)	4.6 (4.8)	46(15)
(5e)	$[Mn_2\{\mu\text{-}C(CF_3){=}CHCF_3\}(\mu\text{-}PPh_2)(CO)_7]$	645	$M - n$CO (n = 0, 3, 7)	42.4 (42.2)	1.9 (1.7)	4.7 (4.7)	48(2.2)

[a] Calculated values are given in parentheses. [b] Based on % of (1) consumed. [c] Yields based on (1) added to reaction mixture are given in parentheses. [d] Satisfactory mass spectroscopic and microanalytical data for (2a) and (2b) were not obtained (identified by ^{1}H n.m.r. and i.r. spectroscopy). [e] N analysis: 4.5(4.4%). [f] L_2 = $(EtO)_2POP(OEt)_2$.

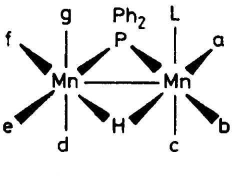
$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6L_2]$ [L = CNBu^t (3a); L_2 = $(EtO)_2POP(OEt)_2$ (3b)], and $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4\{(EtO)_2POP(OEt)_2\}_2]$ (4). Mass spectroscopic and analytical data for these new complexes are given in Table 1, and i.r. and ^{1}H n.m.r. data are in Table 2. Complex (2g) was isolated from the reaction of (1) with $(EtO)_2POP(OEt)_2$ and its formation is presumably due to the presence of $P(OEt)_3$ as an impurity in the $(EtO)_2POP(OEt)_2$ used.

The ^{1}H n.m.r. spectra of the complexes (2a)—(2d) and (3a) show a doublet resonance around δ − 16 p.p.m. which may be assigned to the μ-H ligand coupled to the phosphorus of the μ-PPh_2 ligand [^2J(PH) *ca.* 34—37 Hz]. These values are comparable to those for the parent complex (1). For the other new substitution products the phosphorus atom of the substituent causes a further splitting of the metal hydride resonance which is essentially identical in magnitude in each case to the splitting caused by the μ-PPh_2 ligand. Thus the μ-H ligand in (2e) gives rise to a triplet at δ − 15.82 p.p.m. [^2J(PH) 30.8 Hz] and that in (3b) gives a quartet at −17.11 p.p.m. [^2J(PH) 28.9 Hz].

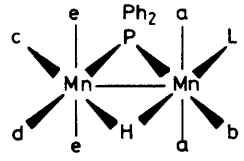
There are three possible isomers for the monosubstitution products and these are shown below. The similarities in PH coupling constants for coupling of the μ-PPh_2 and PR_3 ligands to the bridging metal hydride suggest that both these ligands are *cis* to the hydride, favouring isomers (A) or (B). The ^{13}C n.m.r. spectrum of (2e) (data in Table 3) shows five peaks which may be assigned to CO resonances in an approximate intensity ratio of 2 : 2 : 1 : 1 : 1 as required for isomer (A), whereas for isomer (B) all the CO ligands are inequivalent. A similar ^{13}CO spectrum is observed for (2f) suggesting that isomer (A) represents the correct structure for both of these monosubstituted derivatives. The ^{13}CO spectrum of (2c), however, shows seven resonances of equal intensity which is as required for isomer (B) in which the CNBu^t ligand is *cis* to both the PR_2 and hydride ligands. It seems likely that the CNBu^t ligands in the disubstituted derivative (3a) will each have a similar orientation but this leaves open the question as to whether the CNBu^t ligands are mutually *cis* or *trans* and these two possibilities cannot be distinguished on the basis of ^{13}C n.m.r. data. An *X*-ray diffraction study of (3a) was therefore undertaken. Suitable crystals for such a study were obtained by recrystallisation of (3a) from hexane–chloroform (1 : 5) solution.



Isomer (A)



Isomer (B)



Isomer (C)

The structure of (3a) is shown in Figure 1 and a line diagram of this structure is shown below. Tables 4 and 5 list the final bond lengths and interbond angles respectively. Each Mn atom is approximately octahedrally co-ordinated by three carbonyl groups, an isonitrile group, and the μ-H and μ-PPh_2 ligands. The CNBu^t ligands adopt a mutually *trans*

Table 2. Infrared and ^{1}H n.m.r. data (δ/p.p.m.) for the μ-phosphido-dimanganese complexes

Compound	ν(CO)/cm^{-1}	^{1}H n.m.r.[a]
(1)	2 093m, 2 064m, 2 011s, 2 000m, 1 966s	7.93 (m, 10 H, Ph), −16.18 [d, ^2J(PH) 35.5, 1 H, MnH]
(2a)	2 074m, 2 020s, 2 000s, 1 974s, 1 953s, 1 947m, 1 927m	7.46 (m, 10 H, Ph), 4.29 (m, 3 H, Me), −15.06 [d, ^2J(PH) 34.9, 1 H, MnH]
(2b)	2 074m, 2 019s, 1 998s, 1 979s, 1 952s, 1 929s	8.18—6.97 (m, 15 H, Ph), −14.85 (d, ^2J(PH) 34.4, 1 H, MnH]
(2c)	2 072m, 2 017s, 1 998s, 1 980s, 1 959m, 1 951s, 1 934s	7.65 (m, 10 H, Ph), 0.99 (s, 9 H, Bu^t), −16.42 [d, ^2J(PH) 33.9, 1 H, MnH]
(2d)	2 073m, 2 020s, 1 999s, 1 978s, 1 953m, 1 943s, 1 938s	7.55 (m, 15 H, Ph), 4.38 (m, 2 H, CH_2), −16.40 [d, ^2J(PH) 33.0, 1 H, MnH]
(2e)	2 073m, 2 023m, 1 989s, 1 953s, 1 940m, 1 917m	7.78 (m, 25 H, Ph), −15.82 [t, ^2J(PH) 30.8, 1 H, MnH]
(2f)	2 075m, 2 034m, 1 992s, 1 950s, 1 926m	7.70 (m, 10 H, Ph), 3.89 [d, ^3J(PH) 12.0, 9 H, OMe], −16.46 [t, ^2J(PH) 30.6, 1 H, MnH]
(2g)	2 074m, 2 011s, 1 990(sh), 1 944m	7.69 (m, 10 H, Ph), 4.36 (m, 15 H, OEt), −16.38 [t, ^2J(PH) 32, 1 H, MnH]
(3a)	2 016m, 2 004s, 1 950s, 1 944w, 1 924s	7.67 (m, 10 H, Ph), 0.99 (s, 18 H, Bu^t), −16.36 [d, ^2J(PH) 36.6, 1 H, MnH]
(3b)	2 034s, 2 003s, 1 959m, 1 925s	7.89 (m, 10 H, Ph), 4.11 (m, 20 H, Et), −17.11 [q, ^2J(PH) 28.9, 1 H, MnH]
(4)	2 075m, 2 029m, 1 989vs, 1 945s, 1 929 (sh)[b]	7.69 (m, 10 H, Ph), 4.22 (m, 40 H, Et), −16.72 (m, 1 H, MnH)
(5a)	2 066m, 2 019s, 2 005s, 1 981s, 1 965m, 1 957m, 1 941m	7.44 (m, 10 H, Ph), 9.27 [ddd, J_{12} 14.6, J_{13} 9.27, ^3J(PH) 8.05, 1 H, H^1], 4.35 [dd, $J_{23} \approx 0$, ^4J(PH) 6.84, 1 H, H^2], 3.82 [dd, ^4J(PH) 6.10, 1 H, H^3][c]
(5b)	2 063m, 2 017s, 2 005s, 1 978s, 1 963m, 1 953m, 1 941m[d]	7.41 (m, 15 H, Ph), 3.88 [dd, J(HH) 1.7, ^4J(PH) 10.6, 2 H, H^{2,3}], 3.58 [dd,^{4} J(PH) 8.8, 1 H, H^{2,3}][c]
(5c)		7.41 (m, 15 H, Ph), 9.32 [dd, J_{13} 14.5, ^3J(PH) 8.3, 1 H, H^1], 5.47 [dd, ^4J(PH) 4.9, 1 H, H^3][c]
(5d)	2 058m, 2 013s, 2 003s, 1 977s, 1 962m, 1 947m, 1 942m	7.33 (m, 20 H, Ph), 5.24 [d, ^4J(PH) 8.79, 1 H, H^3][c]
(5e)	2 081m, 2 037s, 2 025s, 1 997s, 1 986 (sh), 1 982s, 1 971m	7.61 (m, 10 H, Ph), 3.51 [dq, ^4J(PH) 9.9, ^3J(FH) 8.6, 1 H, CH]

[a] Recorded at 298 K in CD_2Cl_2 solution for (1)—(3), $CD_3C(O)CD_3$ solution for (4) and (5). J Values are in Hz; d = doublet, t = triplet, q = quartet, m = multiplet. [b] Recorded in CH_2Cl_2 solution. [c] See text for numbering scheme. [d] I.r. spectrum of isomeric mixture of (5b) and (5c).

Table 3. Carbon-13 n.m.r. data (δ/p.p.m.)[a] for the μ-phosphido-dimanganese complexes

Compound	^{13}CO resonances	Other ^{13}C resonances
(1)	218.2 [d, ^2J(PC) 10.5, 2 CO], 216.3 (s, 2 CO), 209.0 [d, ^2J(PC) 14.0, 4 CO]	140.1—128.4 (m, Ph)
(2c)	222.1 (m, 1 CO), 220.3 (m, 1 CO), 219.4 (m, 1 CO), 218.0 (m, 1 CO), 214.0 (m, 1 CO), 210.8 (m, 1 CO), 209.1 (m, 1 CO)	153.3 (s, *C*NBu^t), 141.4—127.1 (m, Ph), 57.1 (s, CN*C*Me$_3$), 29.2 [q, J(CH) 127.4, CNC*Me*$_3$]
(2e)	223.5 (m, 1 CO), 219.2 (m, 1 CO), 217.2 (m, 1 CO), 214.2 (m, 2 CO), 209.8 (m, 2 CO)	141.7—128.2 (m, Ph)
(2f)	222.0 (m, 1 CO), 219.4 (m, 1 CO), 218.2 (m, 1 CO), 212.4 (m, 2 CO), 209.7 (m, 2 CO)	141.5—128.1 (m, Ph), 52.1 [q, J(CH) 147.5, OMe]
(5a)	219.7 (m, 1 CO), 217.8 (m, 1 CO), 216.6 (m, 1 CO), 214.9 (m, 1 CO), 214.2 (m, 2 CO), 212.0 (m, 1 CO)	178.3 [d, J(CH) 160.2, 1 C, *C*HCH$_2$], 140.5—127.6 (m, Ph), 83.7 [t, J(CH) 160.2, 1 C, CH*C*H$_2$]
(5a)[b]	217.7 (s, 4 CO), 215.6 (s, 3 CO)	178.3 [d, J(CH) 160.2, 1 C, *C*HCH$_2$], 140.5—127.6 (m, Ph), 83.7 [t, J(CH) 160.2, 1 C, CH*C*H$_2$]

[a] Recorded in $CDCl_3$ solution at 213 K; J values in Hz; s = singlet, t = triplet, m = multiplet; relative intensities are approximate. [b] Recorded at 298 K.

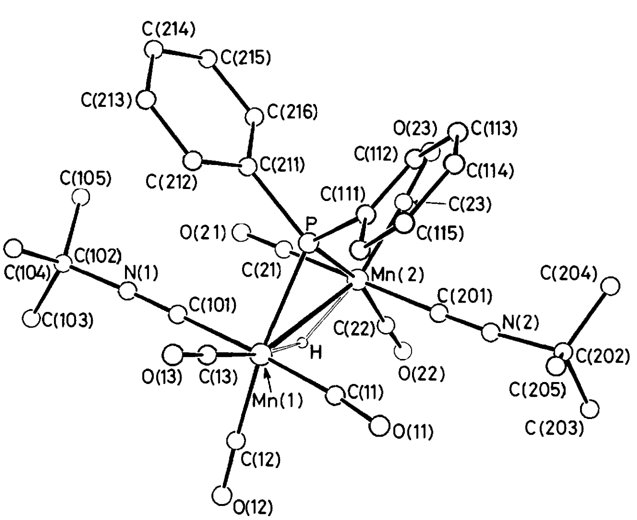
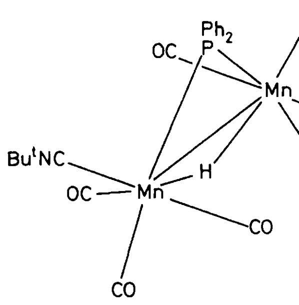


Figure 1. Molecular structure of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (3a) including the atom numbering scheme



(3a)

configuration, thus minimising their steric interaction and are each *cis* to the phosphido-bridge. Bond lengths and bond angles of the other ligands are only slightly perturbed by the substitution of two carbonyl groups by CNBu^t groups as compared with (1).[13] Thus the Mn–Mn bond distance of 2.959(1) Å is only marginally longer than in (1) [2.937(5) Å] and the average Mn–C(carbonyl) distance is unchanged at 1.81 Å. The μ-PPh$_2$ group symmetrically bridges the metal-metal bond in both (3a) and (1) with Mn–P distances of 2.280(2) Å and 2.284(2) Å respectively. This determination of the molecular structure of (3a) confirms the orientation of the CNBu^t ligands with respect to the μ-PR$_2$ and metal hydride ligands deduced from the ^{13}C data and provides strong support for the proposed structures of the monosubstituted complexes given earlier and derived on a similar basis.

(c) *Insertion Reactions with Alkynes.*—The reaction of alkynes with $[Os_3H_2(CO)_{10}]$ gives complexes of the type $[Os_3(\mu\text{-}H)(\mu\text{-}\sigma{:}\eta^2\text{-}CR{=}CHR')(CO)_{10}]$ (R = R′ = H; R = H, R′ = Ph)[14] which, it has been suggested,[15] are derived by initial co-ordination of an alkyne to give $[Os_3(\mu\text{-}H)_2(CO)_{10}(alkyne)]$ followed by insertion of the alkyne into an Os–H bond. The ease with which this reaction takes place is almost certainly associated with the ability of $[Os_3H_2(CO)_{10}]$ to co-ordinate an additional two-electron-donor ligand.[8,9] The reaction of co-ordinatively saturated complexes containing μ-H ligands is less well documented and requires more forcing conditions. $[Os_4H_4(CO)_{12}]$ does react with C_2H_2 under photolytic conditions to give $[Os_4H_3(\mu\text{-}CH{=}CH_2)(CO)_{11}]$[15,16] but other complexes which have been studied appear not to give simple insertion products. Thus the photolytic reaction of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ with PhC≡CPh gives dimeric substitution products, formulated as $[Re_2H_2(CO)_7(PhC{\equiv}CPh)_2]$ and $[Re_2H_2(CO)_5(PhC{\equiv}CPh)_3]$ but these have not been fully characterised,[17] while the reaction of $[FeRu_3(\mu\text{-}H)_2(CO)_{13}]$ with RC≡CR′ gives $[FeRu_3(CO)_{12}(RC{\equiv}CR')]$ with elimination of molecular hydrogen.[18]

Table 4. Bond lengths (Å) for (3a) *

Mn(1)–Mn(2)	2.959(1)	Mn(1)–H	1.67
Mn(1)–P	2.280(2)	Mn(1)–C(11)	1.812(4)
Mn(1)–C(12)	1.816(6)	Mn(1)–C(13)	1.780(6)
Mn(1)–C(101)	1.932(4)	Mn(2)–H	1.63
Mn(2)–P	2.284(2)	Mn(2)–C(21)	1.821(5)
Mn(2)–C(22)	1.819(6)	Mn(2)–C(23)	1.781(7)
Mn(2)–C(201)	1.951(4)	P–C(111)	1.839(5)
P–C(211)	1.834(5)	C(11)–O(11)	1.151(5)
C(12)–O(12)	1.145(8)	C(13)–O(13)	1.152(8)
C(21)–O(21)	1.140(6)	C(22)–O(22)	1.138(8)
C(23)–O(23)	1.148(9)	C(101)–N(1)	1.148(6)
N(1)–C(102)	1.477(7)	C(102)–C(103)	1.536(14)
C(102)–C(104)	1.518(13)	C(102)–C(105)	1.409(16)
C(102)–C(303)	1.71(5)	C(102)–C(304)	1.55(6)
C(102)–C(305)	1.38(6)	C(201)–N(3)	1.148(6)
N(2)–C(202)	1.449(6)	C(202)–C(203)	1.512(10)
C(202)–C(204)	1.504(9)	C(202)–C(205)	1.503(11)
C(111)–C(112)	1.375(8)	C(111)–C(116)	1.385(8)
C(112)–C(113)	1.389(7)	C(113)–C(114)	1.373(10)
C(114)–C(115)	1.364(9)	C(115)–C(116)	1.398(7)
C(211)–C(212)	1.385(8)	C(211)–C(216)	1.374(9)
C(212)–C(213)	1.394(8)	C(213)–C(214)	1.365(11)
C(214)–C(215)	1.343(10)	C(215)–C(216)	1.390(9)

* Estimated standard deviations are in parentheses in Tables 4—9 .

The reaction of (1) with RC≡CR′ does, however, give simple insertion products of general formula $[Mn_2(\mu\text{-}\sigma{:}\eta^2\text{-}CR{=}CHR')(\mu\text{-}PPh_2)(CO)_7]$ [R = R′ = H (5a); R = Ph, R′ = H (5b); R = H, R′ = Ph (5c); R = R′ = Ph (5d); R = R′ = CF$_3$ (5e)]. Using the same reaction conditions as for the substitution reactions described earlier these insertion products are formed in good to near quantitative yield based on complex (1) consumed (Table 1). Conversion factors are, however, low, typically 3—20% for both the thermal and photolytic reactions. The conversion of reactants to products can be increased by using a large excess of the alkyne but at the expense of lowering the overall yield. Thus in the reaction of (1) with PhC≡CPh, the conversion of (1) (Table 1) using a ten-fold excess of alkyne was 42%. Prolonged reaction times or higher reaction temperatures lead to the formation of uncharacterised brown products. Similar brown products are obtained from reaction of the complexes (5) with further amounts of the same or different alkynes or with Bu^{t}NC.

In order to determine the structure of the complexes (5) a single-crystal *X*-ray analysis of (5a) was undertaken. Suitable crystals were obtained by recrystallisation from hexane. The asymmetric unit of the crystallographic unit cell contains two independent but structurally similar molecules which are enantiomers. Views of molecules 1 and 2 are shown in Figures 2 and 3, respectively. Tables 6 and 7 list the final bond lengths and interbond angles. The vinyl group is π-bonded to Mn(1) [Mn(3) in molecule 2] and σ-bonded to Mn(2) [Mn(4)] *via* C(1) [C(3)]. This ligand does not take up a *trans* (with respect to the midpoint of the Mn–Mn vector) orientation to the phosphido-bridge as does the μ-H ligand in (1) but adopts a *cisoid* configuration with an angle between the Mn(1)Mn(2)-C(1) [Mn(3)Mn(4)C(3)] and Mn(1)Mn(2)P(1) [Mn(3)Mn(4)-

Table 5. Bond angles (°) for (3a)

H-Mn(1)-Mn(2)	26	P-Mn(1)-Mn(2)	49.7(1)
P-Mn(1)-H	75	C(11)-Mn(1)-Mn(2)	90.3(2)
C(11)-Mn(1)-H	83	C(11)-Mn(1)-P	92.4(2)
C(12)-Mn(1)-Mn(2)	117.4(2)	C(12)-Mn(1)-H	92
C(12)-Mn(1)-P	167.0(2)	C(12)-Mn(1)-C(11)	88.5(2)
C(13)-Mn(1)-Mn(2)	146.6(2)	C(13)-Mn(1)-H	169
C(13)-Mn(1)-P	97.0(2)	C(13)-Mn(1)-C(11)	90.5(2)
C(13)-Mn(1)-C(12)	96.0(3)	C(101)-Mn(1)-Mn(2)	91.1(2)
C(101)-Mn(1)-H	98	C(101)-Mn(1)-P	89.8(2)
C(101)-Mn(1)-C(11)	177.7(3)	C(101)-Mn(1)-C(12)	89.3(2)
C(101)-Mn(1)-C(13)	89.3(2)	H-Mn(2)-Mn(1)	27
P-Mn(2)-Mn(1)	49.5(1)	P-Mn(2)-H	76
C(21)-Mn(2)-Mn(1)	91.9(2)	C(21)-Mn(2)-H	97
C(21)-Mn(2)-P	93.2(2)	C(22)-Mn(2)-Mn(1)	113.7(2)
C(22)-Mn(2)-H	88	C(22)-Mn(2)-P	163.2(2)
C(22)-Mn(2)-C(21)	88.7(2)	C(23)-Mn(2)-Mn(1)	148.6(2)
C(23)-Mn(2)-H	172	C(23)-Mn(2)-P	99.1(2)
C(23)-Mn(2)-C(21)	89.5(3)	C(23)-Mn(2)-C(22)	97.7(3)
C(201)-Mn(2)-Mn(1)	92.2(2)	C(201)-Mn(2)-H	87
C(201)-Mn(2)-P	89.0(2)	C(201)-Mn(2)-C(21)	175.9(3)
C(201)-Mn(2)-C(22)	90.2(2)	C(201)-Mn(2)-C(23)	86.7(2)
Mn(2)-H-Mn(1)	127	Mn(2)-P-Mn(1)	80.8(1)
C(111)-P-Mn(1)	118.8(2)	C(111)-P-Mn(2)	118.5(2)
C(211)-P-Mn(1)	120.5(2)	C(211)-P-Mn(2)	121.0(2)
C(211)-P-C(111)	98.8(2)	O(11)-C(11)-Mn(1)	176.0(5)
O(12)-C(12)-Mn(1)	177.4(5)	O(13)-C(13)-Mn(1)	178.2(5)
O(21)-C(21)-Mn(2)	174.7(6)	O(22)-C(22)-Mn(2)	178.1(5)
O(23)-C(23)-Mn(2)	178.5(6)	N(1)-C(101)-Mn(1)	176.2(5)
C(102)-N(1)-C(101)	174.3(6)	C(103)-C(102)-N(1)	107.2(1)
C(104)-C(102)-N(1)	107.5(6)	C(104)-C(102)-C(103)	104.2(8)
C(105)-C(102)-N(1)	110.0(8)	C(105)-C(102)-C(103)	108(1)
C(105)-C(102)-C(104)	119(1)	C(303)-C(102)-N(1)	102(1)
C(304)-C(102)-N(1)	103(2)	C(304)-C(102)-C(303)	106(3)
C(305)-C(102)-N(1)	115(2)	C(305)-C(102)-C(303)	99(3)
C(305)-C(102)-C(304)	128(3)	N(2)-C(201)-Mn(2)	174.7(5)
C(202)-N(2)-C(201)	176.9(6)	C(203)-C(202)-N(2)	108.7(5)
C(204)-C(202)-N(2)	107.6(5)	C(204)-C(202)-C(203)	111.8(5)
C(205)-C(202)-N(2)	107.0(5)	C(205)-C(202)-C(203)	110.3(6)
C(205)-C(202)-C(204)	111.2(6)	C(112)-C(11)-P	121.7(4)
C(116)-C(111)-P	119.3(4)	C(116)-C(111)-C(112)	119.0(4)
C(113)-C(112)-C(111)	120.3(6)	C(114)-C(113)-C(112)	120.8(6)
C(115)-C(114)-C(113)	119.1(5)	C(116)-C(115)-C(114)	120.9(6)
C(115)-C(116)-C(111)	119.9(5)	C(212)-C(211)-P	121.1(4)
C(216)-C(211)-P	120.7(4)	C(216)-C(211)-C(212)	118.2(5)
C(213)-C(212)-C(211)	119.8(6)	C(214)-C(213)-C(212)	121.1(6)
C(215)-C(214)-C(213)	119.0(6)	C(216)-C(215)-C(214)	121.3(7)
C(215)-C(216)-C(211)	120.6(6)		

P(2)] planes of 125.7° [123.6°]. The C(1)-C(2) [C(3)-C(4)] bond length [average 1.371(7) Å] is similar to the value of 1.396(4) Å in [$Os_3(\mu\text{-}H)(\mu\text{-}\sigma{:}\eta^2\text{-}CH{=}CH_2)(CO)_{10}$],[19] and shows the expected increase in length of the formal C=C double bond upon co-ordination to a metal. Although the complex (5a) obeys the overall 18-electron rule assuming a single, non-dative Mn-Mn bond, Mn(1) [Mn(3)] is electron poor and Mn(2) [Mn(4)] electron rich. This imbalance is partially counteracted by the presence of an incipient bridging carbonyl group. The orientation of the $Mn(CO)_3$ unit is twisted with respect to the $Mn(CO)_4$ unit in (5a) unlike the approximately eclipsed arrangement of the ligands in (3a). This twisting brings a carbonyl group on Mn(2) [Mn(4)] closer to the Mn(1) [Mn(3′)] atom. The Mn(1) ··· C(21) and Mn(3) ··· C(41) distances of 2.733 and 2.663 Å respectively, together with a reduction in the Mn(2)-C(21)-O(21) and Mn(4)-C(41)-O(41) angles to 168.9(5) and 168.5(4)° respectively, are in agreement with assignment of an incipient bridge bond. The remaining carbonyl groups are essentially linear. The electron imbalance between the two Mn atoms is also reflected in the asymmetric bridging of the Mn-Mn bond by the phosphido-ligand. The P-Mn(1) [P-Mn(3)] distance is *ca.* 0.11 Å shorter than the P-Mn(2) [P-Mn(4)] distance so that the stronger donation is to the electron-poor metal atom. This contrasts with the symmetric bridging of the phosphido-ligand in (1) [13] and in (3a). The average Mn-Mn distance of 2.774(4) Å is in the range observed for Mn-Mn single bonds but is *ca.* 0.2 Å shorter than that found in either (1) or (3a). This may be correlated with the absence of a bridging hydride ligand in (5a) since such ligands usually lengthen metal-metal bonds.[20] If the metal-metal bond is ignored the Mn(2) [Mn(4)] atom displays a distorted octahedral co-ordination geometry. The Mn-C(carbonyl) distances for the axial groups on Mn(2) [Mn(4)] average 1.849(9) Å, while Mn-C(carbonyl) *trans* to P average 1.833(8) Å, and Mn-C(carbonyl) *trans* to C(1) [C(3)] average 1.832(7) Å. The longer axial Mn-C bonds is in keeping with the π-acceptor properties of two competing carbonyls. Again, ignoring the Mn-Mn bond, Mn(1) [Mn(3)] may be considered pseudo-five-co-ordinate with the π-bound vinyl occupying one site. The average of the Mn-C(carbonyl) bond

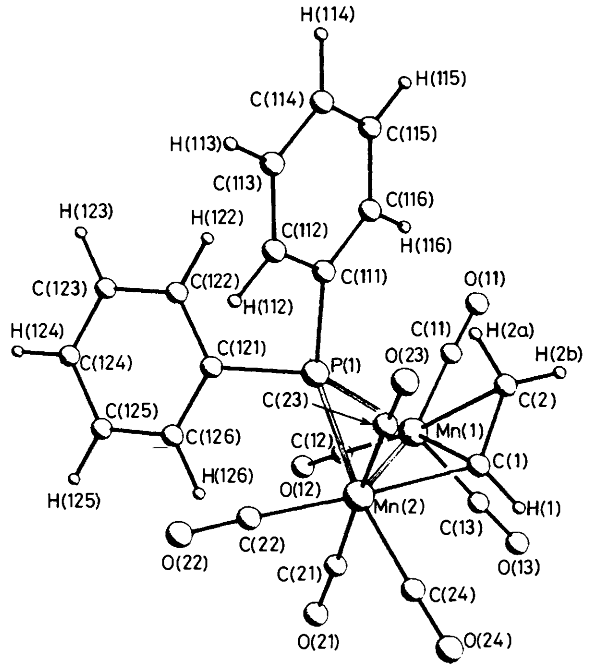


Figure 2. Molecular structure of $[Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$ (5a) including the numbering scheme, molecule 1

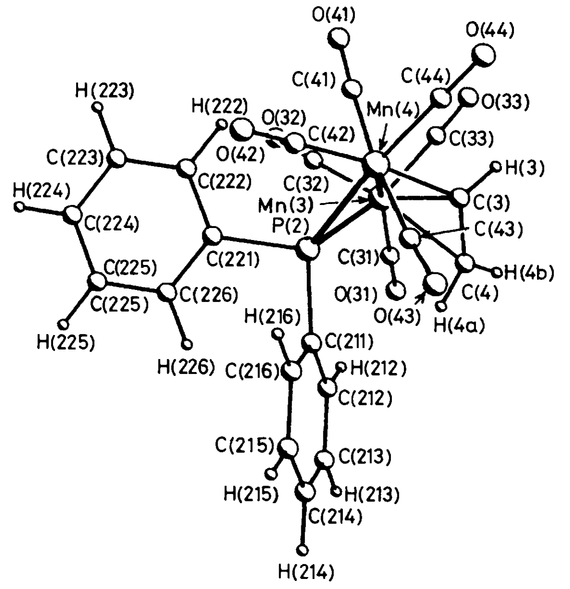


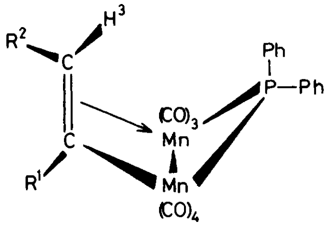
Figure 3. Molecular structure of $[Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$ (5a) including the numbering scheme, molecule 2

Table 6. Bond lengths (Å) for (5a)

Mn(1)-Mn(2)	2.750(2)	Mn(3)-Mn(4)	2.738(2)
Mn(1)-P(1)	2.253(2)	Mn(3)-P(2)	2.257(1)
Mn(1)-C(1)	2.086(3)	Mn(3)-C(3)	2.102(7)
Mn(1)-C(2)	2.263(4)	Mn(3)-C(4)	2.264(7)
Mn(1)-C(11)	1.777(5)	Mn(3)-C(31)	1.791(4)
Mn(1)-C(12)	1.816(4)	Mn(3)-C(32)	1.815(7)
Mn(1)-C(13)	1.825(6)	Mn(3)-C(33)	1.826(6)
Mn(2)-P(1)	2.369(1)	Mn(4)-P(2)	2.365(1)
Mn(2)-C(1)	2.057(6)	Mn(4)-C(3)	2.053(6)
Mn(2)-C(21)	1.846(4)	Mn(4)-C(41)	1.856(5)
Mn(2)-C(22)	1.832(7)	Mn(4)-C(42)	1.832(6)
Mn(2)-C(23)	1.850(4)	Mn(4)-C(43)	1.844(6)
Mn(2)-C(24)	1.842(4)	Mn(4)-C(44)	1.823(7)
P(1)-C(111)	1.833(3)	P(2)-C(211)	1.830(3)
P(1)-C(212)	1.838(3)	P(2)-C(221)	1.830(4)
C(1)-H(1)	0.939(44)	C(3)-H(3)	0.909(49)
C(1)-C(2)	1.372(7)	C(3)-C(4)	1.370(6)
C(2)-H(2a)	1.031(44)	C(4)-H(4a)	1.016(46)
C(2)-H(2b)	0.929(54)	C(4)-H(4b)	0.864(49)
C(11)-O(11)	1.156(7)	C(31)-O(31)	1.144(5)
C(12)-O(12)	1.136(5)	C(32)-O(32)	1.134(8)
C(13)-O(13)	1.138(8)	C(33)-O(33)	1.131(8)
C(21)-O(21)	1.150(5)	C(41)-O(41)	1.141(6)
C(22)-O(22)	1.130(10)	C(42)-O(42)	1.126(8)
C(23)-O(23)	1.136(5)	C(43)-O(43)	1.135(7)
C(24)-O(24)	1.130(5)	C(44)-O(44)	1.136(9)

lengths pseudo-*trans* to P is 1.826(6) Å and the carbonyl distances pseudo-*trans* to the vinyl average 1.816(4) Å. These distances are significantly longer than the Mn(1)–C(11) [Mn(3)–C(31)] bond [average 1.784(8) Å] which is apparently not competing strongly with other ligands for back donation from a particular metal orbital.

The products (5) are red both in the solid state and in solution whereas (1) and the substitution products (2), (3), and (4) are yellow. Hydrogen-1 n.m.r. spectra of the complexes (5) in $[^2H_6]$acetone (Table 2) suggest that they all possess the structure found for (5a) in the solid state. Thus the spectrum of (5a) exhibits a doublet of double doublets centred at δ 9.27 p.p.m. which may be assigned to H^1 (see below) and two sets of double doublets centred at δ 4.35 and δ 3.82 p.p.m. due respectively to H^2 and H^3. These assignments were confirmed and the various $^1H-^1H$ and $^{31}P-^1H$ coupling constants determined (Table 2) from $^1H\text{-}\{^{31}P\}$ n.m.r. spectra and by selective ^1H decoupling experiments. The ^1H n.m.r. spectrum of the product with phenylacetylene suggests that two isomers are present in acetone solution, since two sets of signals of unequal intensity were observed. The more intense signals are seen as two double doublets centred at δ 3.58 and δ 3.88 p.p.m. which, on the basis of the $^1H-^1H$ coupling constant, determined as for (5a), may be assigned to (5b) in which the phenyl group is on the carbon atom σ-bonded to Mn(1). The less intense signals, two double doublets centred at δ 9.32 and δ 5.47 p.p.m., may be assigned on the basis of chemical shift and coupling constant data respectively to protons H^1 and H^3 of (5c). The ratio of the concentrations (5b) : (5c) was estimated from the ^1H n.m.r. spectrum of the mixture to be



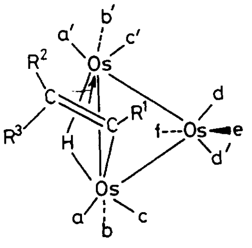
	R^1	R^2
(5a)	H^1	H^2
(5b)	Ph	H^2
(5c)	H^1	Ph
(5d)	Ph	Ph
(5e)	CF_3	CF_3

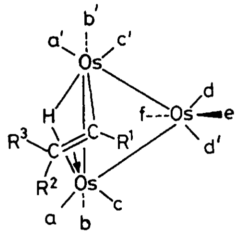
Table 7. Bond angles (°) for (5a)

Mn(2)-Mn(1)-P(1)	55.5(1)	Mn(4)-Mn(3)-P(2)	55.5(1)
Mn(2)-Mn(1)-C(1)	48.0(2)	Mn(4)-Mn(3)-C(3)	48.0(1)
P(1)-Mn(1)-C(1)	88.7(2)	P(2)-Mn(3)-C(3)	87.7(2)
Mn(2)-Mn(1)-C(2)	74.0(2)	Mn(4)-Mn(3)-C(4)	74.3(1)
P(1)-Mn(1)-C(2)	85.7(2)	P(2)-Mn(3)-C(4)	84.6(2)
C(1)-Mn(1)-C(2)	36.5(2)	C(3)-Mn(3)-C(4)	36.3(2)
Mn(2)-Mn(1)-C(11)	148.6(1)	Mn(4)-Mn(3)-C(31)	150.3(2)
P(1)-Mn(1)-C(11)	103.4(2)	P(2)-Mn(3)-C(31)	104.7(2)
C(1)-Mn(1)-C(11)	116.7(2)	C(3)-Mn(3)-C(31)	116.8(3)
C(2)-Mn(1)-C(11)	82.0(2)	C(4)-Mn(3)-C(31)	82.6(2)
Mn(2)-Mn(1)-C(12)	109.2(2)	Mn(4)-Mn(3)-C(32)	111.5(1)
P(1)-Mn(1)-C(12)	90.7(2)	P(2)-Mn(3)-C(32)	92.7(2)
C(1)-Mn(1)-C(12)	150.2(2)	C(3)-Mn(3)-C(32)	152.7(2)
C(2)-Mn(1)-C(12)	172.5(2)	C(4)-Mn(3)-C(32)	170.7(2)
C(11)-Mn(1)-C(12)	92.4(2)	C(31)-Mn(3)-C(32)	89.5(3)
Mn(2)-Mn(1)-C(13)	109.3(2)	Mn(4)-Mn(3)-C(33)	105.5(2)
P(1)-Mn(1)-C(13)	163.2(2)	P(2)-Mn(3)-C(33)	159.7(1)
C(1)-Mn(1)-C(13)	84.1(2)	C(3)-Mn(3)-C(33)	82.6(3)
C(2)-Mn(1)-C(13)	97.3(2)	C(4)-Mn(3)-C(33)	97.8(3)
C(11)-Mn(1)-C(13)	93.4(3)	C(31)-Mn(3)-C(33)	95.7(2)
C(12)-Mn(1)-C(13)	88.0(2)	C(32)-Mn(3)-C(33)	87.9(3)
Mn(1)-Mn(2)-P(1)	51.6(1)	Mn(3)-Mn(4)-P(2)	51.9(1)
Mn(1)-Mn(2)-C(1)	48.9(1)	Mn(3)-Mn(4)-C(3)	49.6(2)
P(1)-Mn(2)-C(1)	86.3(1)	P(2)-Mn(4)-C(3)	86.0(2)
Mn(1)-Mn(2)-C(21)	69.8(2)	Mn(3)-Mn(4)-C(41)	67.7(1)
P(1)-Mn(2)-C(21)	96.3(1)	P(2)-Mn(4)-C(41)	96.0(2)
C(1)-Mn(2)-C(21)	96.1(2)	C(3)-Mn(4)-C(41)	95.4(2)
Mn(1)-Mn(2)-C(22)	133.7(1)	Mn(3)-Mn(4)-C(42)	131.0(2)
P(1)-Mn(2)-C(22)	93.2(1)	P(2)-Mn(4)-C(42)	90.6(2)
C(1)-Mn(2)-C(22)	175.2(2)	C(3)-Mn(4)-C(42)	173.9(2)
C(21)-Mn(2)-C(22)	88.7(2)	C(41)-Mn(4)-C(42)	90.1(2)
Mn(1)-Mn(2)-C(23)	112.5(2)	Mn(3)-Mn(4)-C(43)	114.9(1)
P(1)-Mn(2)-C(23)	86.9(1)	P(2)-Mn(4)-C(43)	89.9(2)
C(1)-Mn(2)-C(23)	84.1(2)	C(3)-Mn(4)-C(43)	83.0(2)
C(21)-Mn(2)-C(23)	176.7(2)	C(41)-Mn(4)-C(43)	173.8(3)
C(22)-Mn(2)-C(23)	91.1(2)	C(42)-Mn(4)-C(43)	91.8(3)
Mn(1)-Mn(2)-C(24)	123.0(2)	Mn(3)-Mn(4)-C(44)	123.3(2)
P(1)-Mn(2)-C(24)	170.8(2)	P(2)-Mn(4)-C(44)	173.8(2)
C(1)-Mn(2)-C(24)	85.0(2)	C(3)-Mn(4)-C(44)	87.7(3)
C(21)-Mn(2)-C(24)	87.6(2)	C(41)-Mn(4)-C(44)	84.8(3)
C(22)-Mn(2)-C(24)	95.3(3)	C(42)-Mn(4)-C(44)	95.6(3)
C(23)-Mn(2)-C(24)	89.2(2)	C(43)-Mn(4)-C(44)	89.2(3)
Mn(1)-P(1)-Mn(2)	73.0(1)	Mn(3)-P(2)-Mn(4)	72.6(1)
Mn(1)-P(1)-C(111)	125.2(1)	Mn(3)-P(2)-C(211)	124.4(1)
Mn(2)-P(1)-C(111)	117.8(1)	Mn(4)-P(2)-C(211)	118.9(1)
Mn(1)-P(1)-C(121)	120.8(1)	Mn(3)-P(2)-C(221)	121.3(1)
Mn(2)-P(1)-C(121)	119.9(1)	Mn(4)-P(2)-C(221)	117.6(1)
C(111)-P(1)-C(121)	100.3(1)	C(211)-P(2)-C(221)	101.5(1)
P(1)-C(111)-C(112)	119.8(1)	P(2)-C(211)-C(212)	118.5(1)
P(1)-C(111)-C(116)	119.8(1)	P(2)-C(211)-C(216)	121.2(1)
P(1)-C(121)-C(122)	119.4(1)	P(2)-C(221)-C(222)	119.5(1)
P(1)-C(121)-C(126)	120.4(1)	P(2)-C(221)-C(226)	120.3(1)
Mn(1)-C(1)-Mn(2)	83.1(2)	Mn(3)-C(3)-Mn(4)	82.4(3)
Mn(1)-C(1)-H(1)	115.0(20)	Mn(3)-C(3)-H(3)	116.7(26)
Mn(2)-C(1)-H(1)	119.6(31)	Mn(4)-C(3)-H(3)	116.3(22)
Mn(1)-C(1)-C(2)	78.8(2)	Mn(3)-C(3)-C(4)	78.3(4)
Mn(2)-C(1)-C(2)	123.8(4)	Mn(4)-C(3)-C(4)	124.2(5)
H(1)-C(1)-C(2)	116.3(31)	H(3)-C(3)-C(4)	119.2(24)
Mn(1)-C(2)-C(1)	64.7(2)	Mn(3)-C(4)-C(3)	65.4(4)
Mn(1)-C(2)-H(2a)	102.4(19)	Mn(3)-C(4)-H(4a)	106.5(32)
C(1)-C(2)-H(2a)	121.8(29)	C(3)-C(4)-H(4a)	123.8(21)
Mn(1)-C(2)-H(2b)	121.1(21)	Mn(3)-C(4)-H(4b)	113.0(31)
C(1)-C(2)-H(2b)	123.5(24)	C(3)-C(4)-H(4b)	121.5(30)
H(2a)-C(2)-H(2b)	111.8(37)	H(4a)-C(4)-H(4b)	112.8(38)
Mn(1)-C(11)-O(11)	176.3(3)	Mn(3)-C(31)-O(31)	179.5(7)
Mn(1)-C(12)-O(12)	177.0(6)	Mn(3)-C(32)-O(32)	175.0(4)
Mn(1)-C(13)-O(13)	177.2(5)	Mn(3)-C(33)-O(33)	178.2(5)
Mn(2)-C(21)-O(21)	168.9(5)	Mn(4)-C(41)-O(41)	168.5(4)
Mn(2)-C(22)-O(22)	178.3(4)	Mn(4)-C(42)-O(42)	179.5(6)
Mn(2)-C(23)-O(23)	176.9(4)	Mn(4)-C(43)-O(43)	176.7(6)
Mn(2)-C(24)-O(24)	178.2(5)	Mn(4)-C(44)-O(44)	177.7(5)

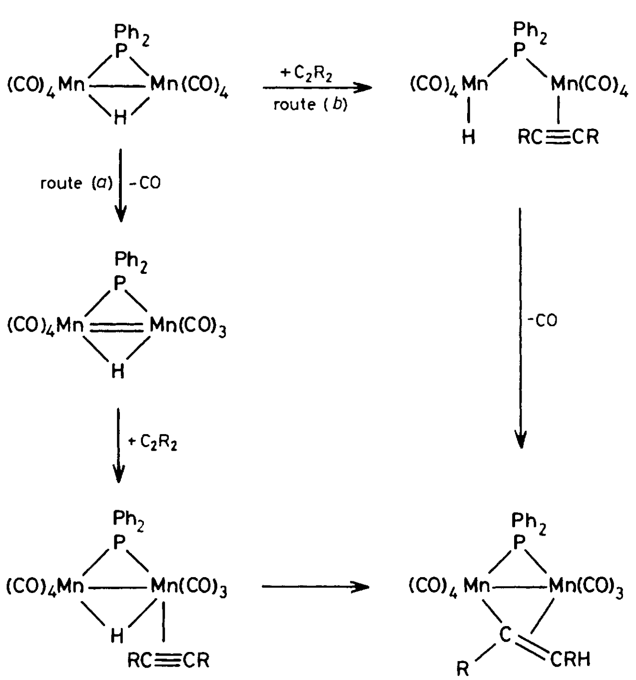
approximately 4 : 1. The ^{1}H n.m.r. spectra of (5d) and (5e) are also consistent with the structures shown above. For (5e) a double quartet is observed with $^{3}J(^{19}F^{1}H) = 8.6$ Hz which is comparable with other $^{3}J(^{19}F^{1}H)$ coupling constants in similar systems.[21] The fluorine atoms attached to the σ-bonded carbon atom are presumably too remote from H^{3} to couple with it.

Shapley *et al.*[22] have previously shown that the vinyl ligand in $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ is fluxional at room temperature with the σ and π bonds to the cluster alternating rapidly between the two μ-H bridged Os atoms on the n.m.r. time-scale, as shown below. This process was apparent only from ^{13}C n.m.r. spectra and it was therefore of interest to investigate the ^{13}C n.m.r. spectra of the complexes (5). Of course the complexes (5) differ from $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ in that the two bridged manganese atoms possess an unequal number of CO ligands and any fluxionality of the vinyl ligand must presumably be accompanied by the transfer of a CO group from one metal atom to the other. At 213 K the ^{13}C-{^{1}H} spectrum of (5a) in the carbonyl region (Table 3) shows 6 peaks with an approximate intensity ratio of 1 : 1 : 1 : 1 : 2 : 1. This is as required for the ' frozen out ' spectrum of (5a) if an accidental degeneracy of two of the ^{13}CO peaks is assumed. This spectrum collapses at 243 K and at temperatures above 273 K two peaks of approximate intensity ratio 4 : 3 are observed. This spectrum is difficult to reconcile with the transfer of a CO group between Mn(1) and Mn(2) together with a fluxionality of the vinyl ligand analogous to that shown for the osmium complex. A more likely explanation is that a localised rotation of the CO groups on each Mn atom is taking place, and that CO transfer (and, in consequence, vinyl fluxionality) is sterically inhibited by the bridging PPh_2 ligand. Such a localised rotation of CO groups is not observed, however, in the ^{13}CO n.m.r. spectra of (1) or (2e) (Table 3) which remain essentially unchanged over the temperature range 213—323 K although for (2e) the resolution achieved at 323 K is very poor, perhaps due to quadrupole broadening by the manganese atoms.





There are two alternative pathways which can be conceived for the insertion reactions leading to the products (5), and these are shown in the Scheme. Route (*a*) involves initial loss of a CO ligand to give the unsaturated species $[Mn_2H(\mu\text{-}PPh_2)(CO)_7]$ which can then react with the alkyne in the same manner as proposed for $[Os_3H_2(CO)_{10}]$. Route (*b*) involves initial co-ordination of the alkyne without CO loss, which presumably requires the concomitant breaking of the Mn–Mn bond if 20 e intermediates are not to be invoked. Of course routes (*a*) and (*b*) represent extreme situations, and routes involving co-ordination of the alkyne with simultaneous weakening of the Mn–Mn bond and/or partial dissociation of a CO ligand cannot be excluded. In order to determine whether it is possible to co-ordinate an additional two-electron-donor ligand and break the Mn–Mn bond in (1), a solution of (1) in heptane was treated with CO (50 atm) in a high-pressure i.r. cell. At temperatures up to 200 °C no changes were observed in the i.r. spectrum of (1) in the ν(CO) region such as would have been expected for an associative reaction. On the other hand, photolysis of (1) in donor or hydrocarbon solvents in the presence of a stream of N_2 to drive off any dissociated CO causes no change either in the i.r. spectrum or in the colour of the solution and subsequent addition of C_2Ph_2 gives none of the insertion product (5d). Nevertheless, photolysis does induce both the substitution and insertion reactions of (1) which we have described earlier, and a plausible explanation is that an excited state of (1) is generated reversibly which can then co-ordinate alkynes or two-electron-donor ligands prior to CO loss. Once the alkyne is co-ordinated it must undergo insertion rapidly, since no simple alkyne adducts (as shown in the Scheme) were isolated from reaction with any of the alkynes studied, but it is impossible to say whether this occurs before or after CO loss. $[Os_3H_2(CO)_{10}]$ similarly undergoes insertion with alkynes rapidly at room temperature but it was not possible to demonstrate the intermediate formation of $[Os_3H_2(CO)_{10}(alkyne)]$ adducts.[8,9]



Scheme.

With small unsaturated molecules other than alkynes the tendency of (1) to give insertion products is clearly less than that of $[Os_3H_2(CO)_{10}]$. Thus while this latter molecule gives insertion products quite readily with isonitriles, $PhCH_2NC$ and $Bu^{t}NC$ on reaction with (1) give only the simple substitution products (2c), (2d), and (3a). Nevertheless, this work, along with a recent report of the insertion of RNC into the μ-H–metal bonds present in $[Fe_3H(CO)_{11}]^-$,[23] does suggest that this type of reaction may be quite general for saturated hydrido-bridged complexes of first-row transition metals, particularly if an additional bridging ligand is present to inhibit fragmentation into lower nuclearity species.

Experimental

All reactions were performed under dry, oxygen-free nitrogen in nitrogen-saturated solvents. Solvents were dried over 4-Å molecular sieves unless otherwise stated.

Infrared spectra were recorded in cyclohexane solution

Table 8. Fractional atomic co-ordinates for (3a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn(1)	0.175 02(4)	0.185 31(7)	0.018 84(9)	C(201)	0.164 5(3)	0.014 3(5)	−0.353 3(6)
Mn(2)	0.246 01(4)	0.182 52(7)	−0.250 01(9)	N(2)	0.121 0(2)	−0.087 1(4)	−0.419 9(5)
P	0.265 13(7)	0.074 78(13)	−0.048 35(15)	C(202)	0.069 1(3)	−0.215 6(5)	−0.509 0(7)
C(11)	0.091 3(3)	0.041 0(5)	−0.077 3(6)	C(203)	0.008 8(4)	−0.180 9(7)	−0.623 9(8)
O(11)	0.035 3(2)	−0.047 1(4)	−0.134 2(4)	C(204)	0.029 7(4)	−0.301 0(6)	−0.405 2(8)
C(12)	0.106 0(3)	0.290 6(5)	0.034 7(7)	C(205)	0.120 8(4)	−0.287 7(7)	−0.584 2(8)
O(12)	0.060 7(2)	0.353 1(4)	0.046 8(6)	C(111)	0.238 1(3)	−0.116 5(4)	−0.077 9(5)
C(13)	0.169 0(3)	0.123 0(6)	0.190 3(7)	C(112)	0.184 1(3)	−0.191 8(5)	−0.006 4(6)
O(13)	0.165 3(3)	0.079 4(4)	0.299 5(5)	C(113)	0.165 9(4)	−0.336 2(6)	−0.029 0(7)
C(21)	0.325 8(3)	0.338 4(6)	−0.164 6(7)	C(114)	0.201 8(4)	−0.406 1(6)	−0.121 9(7)
O(21)	0.376 6(2)	0.437 3(4)	−0.121 9(5)	C(115)	0.254 6(3)	−0.332 0(6)	−0.194 6(7)
C(22)	0.208 7(3)	0.281 8(5)	−0.383 5(7)	C(116)	0.272 8(3)	−0.186 8(5)	−0.174 7(6)
O(22)	0.187 5(3)	0.346 3(4)	−0.466 5(5)	C(211)	0.364 1(3)	0.110 1(5)	0.070 3(6)
C(23)	0.312 0(3)	0.123 4(6)	−0.352 0(7)	C(212)	0.432 6(3)	0.156 8(6)	0.015 6(7)
O(23)	0.355 4(3)	0.084 6(5)	−0.414 8(5)	C(213)	0.507 0(4)	0.174 7(8)	0.105 7(9)
C(101)	0.261 4(3)	0.343 0(5)	0.123 6(6)	C(214)	0.513 7(4)	0.148 7(7)	0.248 2(8)
N(1)	0.310 2(3)	0.437 5(5)	0.191 8(5)	C(215)	0.447 3(4)	0.105 4(8)	0.301 8(7)
C(102)	0.370 7(4)	0.554 1(7)	0.293 1(8)	C(216)	0.372 3(3)	0.087 1(7)	0.215 1(7)
C(103)	0.450 5(6)	0.562 7(15)	0.244 3(15)	C(303)	0.407 0(27)	0.656 8(47)	0.171 4(50)
C(104)	0.382 9(7)	0.512 5(11)	0.446 0(11)	C(304)	0.319 5(29)	0.630 8(53)	0.373 1(53)
C(105)	0.351 2(10)	0.680 1(12)	0.278 8(23)	C(305)	0.439 6(31)	0.523 5(47)	0.353 0(62)

with 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer using CO gas as calibrant. Mass spectra were obtained on an A.E.I. MS 12 instrument using Fomblin (a perfluoropolyether) as reference. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates CFT20 spectrometer unless otherwise stated in the text and ^{13}C n.m.r. spectra were recorded on a Bruker WM250 spectrometer. Both were calibrated relative to $SiMe_4$ using the solvent resonances as internal standards. Microanalyses were carried out at the Chemical Laboratory, University of Cambridge.

Preparative t.l.c. was performed on silica using hexane–dichloromethane (10 : 1) as eluant unless otherwise stated.

(*i*) *Preparation of* $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1).—$[Mn_2(CO)_{10}]$ (3.12 g, 8.0 mmol) was dissolved in undried decalin (400 cm^3) and heated to 150 °C, then $PHPh_2$ (1.44 cm^3, 8.0 mmol) was added. The mixture was stirred at 150 °C for 1 h, and the solution turned dark orange. The solvent was removed under vacuum at 60 °C. The orange residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and applied to the top of a chromatography column (Keisel gel 60, 70—230 mesh). The column was then eluted with hexane–dichloromethane (10 : 1). Complex (1) eluted first as a yellow band (yield 3.32 g). Complex (1) could be further purified by recrystallisation from hot hexane.

(*ii*) *Substitution Reactions of* (1).—(*a*) *With* MeCN. Complex (1) (0.104 g, 0.20 mmol) and MeCN (excess) were irradiated in pentane solution (25 cm^3) for 1 h; the solution turned orange and an orange precipitate of (2a) formed. The solution was filtered and the precipitate washed with hexane and dried (yield 0.046 g).

(*b*) *With* PhCN. In a procedure analogous to that in (*a*) the complex (1) (0.104 g, 0.20 mmol) and PhCN (excess) were used. The solution turned orange and an orange precipitate was observed. The i.r. spectrum of the solution showed absorptions that were assigned to (2b).

(*c*) *With* Bu^{t}NC. The complex (1) (0.268 g, 0.52 mmol) and Bu^{t}NC (60 µl, 0.50 mmol) were refluxed in cyclohexane (80 cm^3) for 90 min, then more Bu^{t}NC (30 µl, 0.25 mmol) was added and the solution refluxed for a further 90 min. The cyclohexane was removed on a rotary evaporator, the residue redissolved in the minimum of CH_2Cl_2, and the products were separated by preparative t.l.c. The order of elution was (decreasing R_f values, yields in parentheses): (1) (0.127 g), (2c) (0.113 g), and (3a) (0.034 g).

Alternatively, (1) (0.104 g, 0.2 mmol) and Bu^{t}NC (24 µl, 0.2 mmol) were used in a procedure analogous to (*a*) above. Yield: (1) (0.018 g); (2c) (0.029 g); (3a) (0.006 g).

(*d*) With $PhCH_2NC$. In a procedure analogous to that in (*c*) above, (1) (0.104 g, 0.2 mmol) and $PhCH_2NC$ (25 µl, 0.2 mmol) were used and the products separated by preparative t.l.c. The order of elution was (decreasing R_f values, yields in parentheses): (1) (0.044 g), (2d) (0.039 g).

(*e*) *With* PPh_3. Complex (1) (0.052 g, 0.01 mmol) and PPh_3 (0.026 g, 0.1 mmol) were used in an analogous procedure to (*c*) above. Preparative t.l.c. gave (2e) (0.057 g).

(*f*) *With* $P(OMe)_3$. In a procedure analogous to (*e*) above (1) (0.360 g, 0.69 mmol) and $P(OMe)_3$ (82 µl, 0.69 mmol) were used. The products were separated by preparative t.l.c. (decreasing R_f values, yields in parentheses): (1) (0.160 g), (2f) (0.170 g).

(*g*) *With* $(EtO)_2POP(OEt)_2$. The complex (1) (0.208 g, 0.4 mmol) and $(EtO)_2POP(OEt)_2$ (145 µl, excess) were refluxed in cyclohexane, redistilled off CaH_2 (20 cm^3) for 6 h. The solution was taken to dryness, the residue redissolved in the minimum quantity of CH_2Cl_2, and the products separated by preparative t.l.c. using hexane–dichloromethane (3 : 1) as eluant. The order of elution was (decreasing R_f values, yields in parentheses): (1) (0.051 g), (2g) (0.008 g), (3b) (0.045 g), (4) (0.026 g).

(*iii*) *Insertion Reactions of* (1).—(*a*) *With* C_2H_2. Complex (1) (0.052 g, 0.1 mmol) was dissolved in cyclohexane (50 cm^3). C_2H_2 was passed through the solution and it was refluxed for 4 h, when it turned red-gold. The solution was taken to dryness and the products separated by preparative t.l.c. (in order of decreasing R_f, yields in parentheses): (1) (0.043 g), (5a) (0.009 g).

Alternatively, (1) (2.59 g, 5 mmol) was dissolved in pentane (200 cm^3) in a quartz vessel and irradiated with u.v. light for 90 min whilst C_2H_2 was bubbled through the solution. The solvent was removed on a rotary evaporator and the residue column chromatographed using hexane–dichloromethane (4 : 1) (Kieselgel 60, 60—230 mesh). Complexes (1) and (5a)

Table 9. Atom co-ordinates (× 10^4) for (5a)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mn(1)	6 798(1)	2 234(1)	8 557(1)	Mn(3)	−577(1)	−2 660(1)	6 373(1)
Mn(2)	9 773(1)	2 900(1)	8 524(1)	Mn(4)	2 071(1)	301(1)	6 474(1)
P(1)	7 775(1)	1 172(1)	9 078(1)	P(2)	1 561(1)	−1 882(1)	5 908(1)
C(111)	8 187(3)	1 525(3)	9 828(1)	C(211)	1 612(2)	−1 766(3)	5 161(1)
C(112)	9 365(3)	1 421(3)	10 077(1)	C(212)	339(2)	−2 954(3)	4 823(1)
C(113)	9 568(3)	1 515(3)	10 650(1)	C(213)	402(2)	−2 983(3)	4 251(1)
C(114)	8 593(3)	1 713(3)	10 974(1)	C(214)	1 738(2)	−1 825(3)	4 019(1)
C(115)	7 415(3)	1 817(3)	10 725(1)	C(215)	3 011(2)	−637(3)	4 357(1)
C(116)	7 212(3)	1 722(3)	10 152(1)	C(216)	2 947(2)	−608(3)	4 929(1)
C(121)	6 593(3)	−930(3)	8 991(1)	C(221)	2 793(3)	−2 616(3)	6 044(1)
C(122)	6 326(3)	−1 832(3)	9 437(1)	C(222)	3 274(3)	−2 621(3)	6 587(1)
C(123)	5 583(3)	−3 448(3)	9 366(1)	C(223)	4 130(3)	−3 268(3)	6 697(1)
C(124)	5 467(3)	−4 161(3)	8 849(1)	C(224)	4 504(3)	−3 911(3)	6 265(1)
C(125)	6 094(3)	−3 259(3)	8 403(1)	C(225)	4 024(3)	−3 906(3)	5 722(1)
C(126)	6 837(3)	−1 644(3)	8 474(1)	C(226)	3 168(3)	−3 258(3)	5 612(1)
C(1)	8 991(5)	4 336(5)	8 649(2)	C(3)	−212(6)	−475(6)	6 266(2)
C(2)	8 354(5)	4 433(5)	9 121(2)	C(4)	−1 022(6)	−1 303(7)	5 778(2)
C(11)	5 328(5)	2 118(5)	8 953(2)	C(31)	−2 148(6)	−4 300(7)	5 954(2)
O(11)	4 432(4)	2 119(4)	9 225(1)	O(31)	−3 158(5)	−5 341(5)	5 686(2)
C(12)	5 423(5)	350(5)	8 185(2)	C(32)	−317(5)	−3 980(6)	6 755(2)
O(12)	4 527(4)	−802(4)	7 943(2)	O(32)	−268(5)	−4 865(5)	6 998(2)
C(13)	6 423(6)	3 135(5)	8 000(2)	C(33)	−1 783(6)	−2 697(7)	6 911(2)
O(13)	6 127(5)	3 667(5)	7 659(2)	O(33)	−2 498(5)	−2 706(6)	7 253(2)
C(21)	8 652(5)	1 957(5)	7 854(2)	C(41)	1 679(6)	−648(6)	7 131(2)
O(21)	8 167(5)	1 383(4)	7 413(1)	O(41)	1 620(5)	−985(5)	7 573(1)
C(22)	10 565(6)	1 693(6)	8 468(2)	C(42)	4 136(6)	998(6)	6 580(2)
O(22)	11 072(6)	966(5)	8 422(2)	O(42)	5 401(5)	1 416(6)	6 645(2)
C(23)	10 991(5)	3 924(5)	9 174(2)	C(43)	2 433(6)	1 400(6)	5 859(2)
O(23)	11 794(4)	4 596(4)	9 559(1)	O(43)	2 645(5)	2 125(5)	5 496(2)
C(24)	11 285(6)	4 484(5)	8 144(2)	C(44)	2 247(7)	1 916(6)	6 888(2)
O(24)	12 220(4)	5 483(4)	7 922(2)	O(44)	2 307(7)	2 889(5)	7 151(2)

eluted as a yellow band, turning to blood-red. The products were separated by fractional recrystallisation from hexane solution [yield: (1) 1.45 g, (5a) 0.61 g].

(*b*) *With* Ph≡CH. Complex (1) (0.104 g, 0.2 mmol) and PhC≡CH (24 μl, 0.2 mmol) were dissolved in pentane (25 cm^3) and the solution irradiated as above. The solvent was removed on a rotary evaporator and the products separated by preparative t.l.c. (in order of decreasing R_f, yields in parentheses): (1) (0.67 g), (5b) + (5c) 0.03 g.

(*c*) *With* C_2Ph_2. In an analogous procedure to (*b*) above, (1) (0.104 g, 0.2 mmol) and C_2Ph_2 (0.037 g, 0.2 mmol) were used. The products were separated by preparative t.l.c. and recrystallisation gave (1) 0.07 g and (5d) 0.02 g.

(*d*) *With* $CF_3C{\equiv}CCF_3$. Complex (1) (0.11 g, 0.21 mmol) and $CF_3C{\equiv}CCF_3$ (*ca*. 0.4 mmol) were irradiated with u.v. radiation in a sealed quartz vessel for 1 h. The solution was taken to dryness and the products separated by preparative t.l.c. (in order of decreasing R_f values, yields in parentheses): (1) (0.105 g), (5e) (0.003 g).

Crystal Data.—*For* (3a). $C_{28}H_{29}Mn_2N_2O_6P$, $M = 630.3$, Triclinic, space group $P\bar{1}$, $a = 17.686(3)$, $b = 10.063(2)$, $c = 9.231(3)$ Å, $\alpha = 96.92(4)$, $\beta = 99.40(4)°$, $\gamma = 104.34(5)$, $U = 1\,547.9$ Å^3, $Z = 2$, $D_c = 1.352$ g cm^{-3}, $F(000) = 648$, μ(Mo-K_α) = 8.47 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

For (5a). $C_{21}H_{13}Mn_2O_7P$, $M = 581.16$, Triclinic, space group $P\bar{1}$, $a = 10.301(4)$, $b = 10.320(4)$, $c = 24.359(11)$ Å, $\alpha = 92.70(3)$, $\beta = 92.17(3)$, $\gamma = 123.59(3)°$, $U = 2\,148.3$ Å^3, $Z = 4$, $D_c = 1.602$ g cm^{-3}, $F(000) = 1\,040$, μ(Mo-K_α) = 12.07 cm^{-1}, λ(Mo-K_α) 0.710 69 Å.

Intensity Measurements.—*For* (3a). Data were collected with a crystal of dimensions *ca*. 0.13 × 0.13 × 0.12 mm on a Philips PW1100 four-circle diffractometer with Mo-K_α radiation from a graphite monochromator. A θ—2θ scan mode was used with a constant scan speed of 0.5° s^{-1}, a scan width of 0.7°, and reflections with $3.0 \leqslant \theta \leqslant 25.0$ were examined, using the technique previously described.[24] The variance of the intensity (I) was calculated as $\{[\sigma_c(I)]^2 + (0.04I)^2\}^{\frac{1}{2}}$, where $[\sigma_c(I)]$ is the variance due to counting statistics, and the term in I^2 was introduced to allow for other sources of error.

For (5a). A single crystal (*ca*. 0.34 × 0.27 × 0.25 mm) was mounted on a glass fibre, and cell dimensions and space group determined photographically. The crystal was transferred to a Syntex P2$_1$ four-circle diffractometer and accurate cell dimensions were determined from the centring of 15 reflections in the range $15 < 2\theta < 25°$. On the diffractometer a pseudo-monoclinic C centred cell was obtained but the α and γ angles showed rather greater deviations from 90.0° than could be accounted for from the estimated standard deviations. When reflections that should be equivalent in the monoclinic space group were measured, considerable variations in intensity were noted and the data collection proceeded assuming that the crystal system was triclinic, in keeping with the photographically determined cell. 7 537 Reflections were measured in the range $3.0 < 2\theta < 55.0°$ using Mo-K_α radiation and a 96-step ω/2θ scan technique. The scan width ranged from 1° below Mo-K_{α_1} ($\lambda_{\alpha_1} = 0.702\,69$ Å) to 1° above Mo-K_{α_2} ($\lambda_{\alpha_2} = 0.713\,54$ Å) and the scan speed varied from 2.0 to 29.3° min^{-1} depending on the intensity of a 1-s prescan; reflections with intensities <8 counts s^{-1} were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation. A semi-empirical absorption correction based on a pseudo-ellipsoid model and 438 azimuthal scan data from 27 independent reflections was applied. Transmission factors ranged from 0.728 to 1.000 for the full data set. Lorentz polarisation corrections were applied and equivalent reflections averaged to give 6 036 unique observed data [$F > 3\sigma(F)$].

Structure Solution and Refinement.—For (3a). The Mn atoms were located from a Patterson synthesis, the remaining non-hydrogen atoms were found from subsequent difference syntheses. The hydride atom position was located from a difference map and included in the structure factor calculations but not refined; the remaining H atom positions were estimated geometrically (C–H 1.08 Å). One of the t-butyl groups was found to be disordered over two sites with occupation factors of 0.801(15) and 0.119(15) for atoms C(103), C(104), C(105) and atoms C(303),C(304),C(305) respectively. Except for the last three named atoms the non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of refinement in which the reflections were weighted as $1/\sigma_2(F_o)$.

For (5a). The four independent Mn and the two independent P atoms were located by multisolution Σ_2 sign expansion and all the remaining atoms from subsequent electron-density difference syntheses. The structure was refined by blocked-cascade least squares with the Mn, P, O, and carbonyl C atoms assigned anisotropic thermal parameters. The phenyl C atoms were assigned independent isotropic temperature factors and were refined as rigid bodies with C–C fixed at 1.395 Å and C–C–C at 120.0°; phenyl H atoms were placed in geometrically idealised positions (C–H 1.08 Å, C–C–H 120.0°) and were constrained to ride on the relevant C atom, all being assigned a common isotropic thermal parameter. The vinyl H atoms were located directly and their positions allowed to refine freely; they were assigned a common isotropic temperature factor. In the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F_o) + 0.0003|F_c|^2]$ was introduced.

For (3a), the final R and R' were 0.044 and 0.043 and for (5a), 0.047 and 0.051, where $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$. For both structures, final difference maps calculated showed no regions of significant electron density.

Complex neutral-atom scattering factors [25] were employed throughout both structure solutions and refinements. Computations for both structures were performed using programs written by Professor G. M. Sheldrick. The molecular plots were drawn by ORTEP 2 (3a) and PLUTO (5a) (written by Dr. D. S. Motherwell).

The final atomic co-ordinates are given in Tables 8 and 9 for compounds (3a) and (5a) respectively; bond lengths and angles are in Tables 4—7.

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