

Reactions of Bis(phosphido)-bridged Dimanganese Complexes with Alkynes and Allene*

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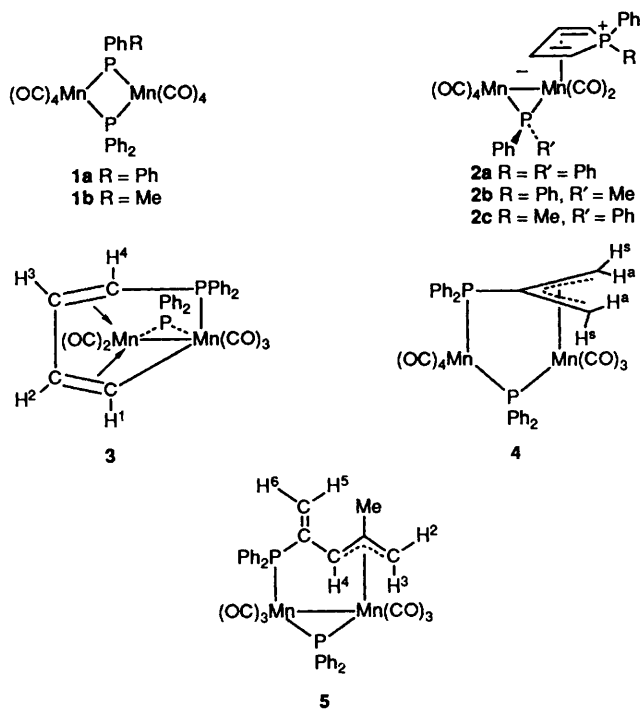
The photolytic reactions of $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhR})(\text{CO})_8]$ ($\text{R} = \text{Ph}$ **1a** or Me **1b**) with acetylene and of **1a** with allene have been studied. Although they are highly non-specific, a number of products have been isolated and characterised which contain new ligands derived from the combination of one of the bridging phosphido groups with acetylene or with allene. The reactions can involve the breaking of one or both of the bonds between the metal atoms and the bridging group. Thus the complexes $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhR})(\mu\text{-PPhR}')(\text{CO})_6]$ ($\text{R} = \text{R}' = \text{Ph}$ **2a**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ **2b**; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ **2c**), containing quaternised phosphole ligands, and $[\text{Mn}_2(\mu\text{-}\sigma\text{:}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **3** are obtained in the reactions of **1a** and **1b** with acetylene. The complexes $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_7]$ **4** and $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **5**, containing ligands derived respectively from the combination of one and two allene molecules with a phosphido group, are obtained in the reaction of **1a** with allene. Single-crystal X-ray analyses of the molecular structures of **2c**, **4** and **5** have been performed, and some reaction pathways are proposed and discussed.

Bridging phosphido ligands can inhibit the fragmentation of di- and poly-nuclear metal complexes in the reactions of such species with unsaturated organic molecules.¹ On the other hand phosphido bridges are by no means always inert and can participate in reactions of this type themselves, often with phosphorus-carbon bond formation.²⁻⁹ We have previously investigated the reactivity of phosphido-bridged dimanganese complexes and have observed phosphorus-carbon bond formation in some of the products arising from the reactions of $[\text{Mn}_2(\mu\text{-CRCHR})(\mu\text{-PPh}_2)(\text{CO})_7]$ ($\text{R} = \text{Ph}$ or H) with nucleophiles.¹⁰ A phosphorus-carbon bond is also formed in one of the products obtained from the reaction of $[\text{Mn}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_8]$ with buta-1,3-diene.¹¹

In order to focus upon this particular type of reaction in manganese chemistry we have now examined the reactions with alkynes and with allene of the dinuclear complexes $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhR})(\text{CO})_8]$ ($\text{R} = \text{Ph}$ or Me) which contain phosphido groups as the only bridging ligands, since if other bridging ligands are present they are usually the more reactive centres.^{12,13} A preliminary account of part of this work has been given.¹⁴

Results and Discussion

(a) Reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhR})(\text{CO})_8]$ ($\text{R} = \text{Ph}$ **1a** or Me **1b**) with C_2H_2 .—The passage of a slow stream of acetylene gas through a toluene solution of $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ **1a** for 15 h at 363 K did not result in any reaction and **1a** was recovered in quantitative yield. On the other hand the UV irradiation of a CH_2Cl_2 solution of **1a** for 5 h at room temperature gave at least nine products, all in low yield, and no starting material remained. It has proved possible to characterise only two of these products, $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **2a** (13% yield) and $[\text{Mn}_2(\mu\text{-}\sigma\text{:}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_5]$ **3** (22% yield). Infrared, ¹H and ³¹P NMR spectra for them are given in Table 1; their molecular structures have been determined by single crystal X-ray analyses and were



reported in the preliminary communication.¹⁴ The formation of $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **2a** in the reaction is significant in that it represents the only reported case in manganese chemistry in which both metal-phosphorus bonds of a bridging phosphido group are cleaved in a chemical reaction. A related dinuclear cobalt complex, $[\text{Co}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_4(\text{CO}_2\text{Me})_4\text{PPh}_2\}(\mu\text{-PPh}_2)(\text{CO})_4]$, is formed in the thermal reaction of $[\text{Co}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$ with dimethyl acetylenedicarboxylate.¹⁴

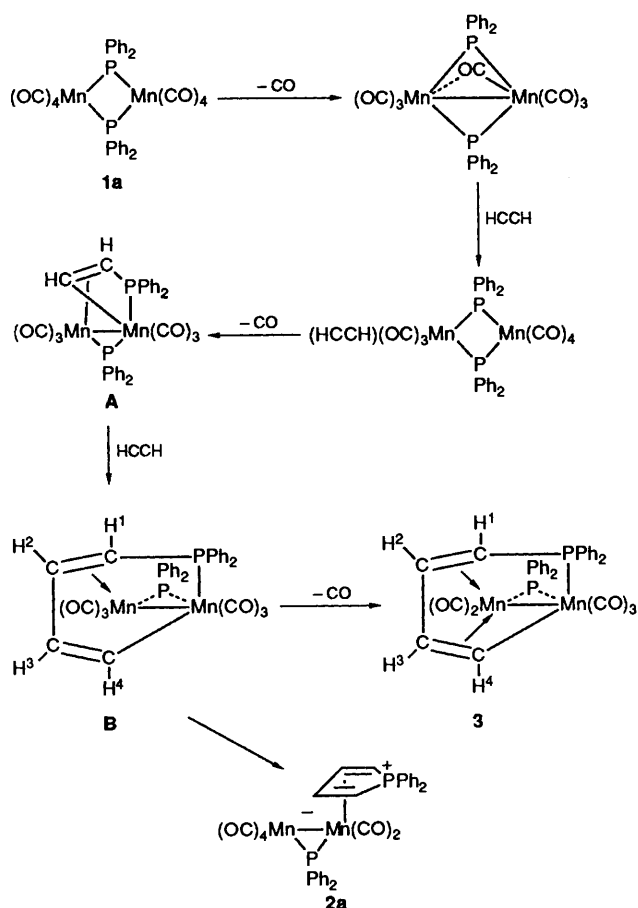
The $\mu\text{-}\sigma\text{:}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$ ligand in complex **3** is presumably formed by a double insertion of acetylene into a metal-phosphorus bond of one of the bridging phosphido groups in **1**.

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

Table 1 Infrared and ^1H and ^{31}P NMR data for the dimanganese complexes

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	^1H NMR ^b	^{31}P NMR
2a $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$	2047s, 1973(sh), 1953(br), 1933(sh)	7.9–7.1 (m, 20 H, Ph), 4.60 [dd, $^3J(\text{PH})$ 18.6, $^3J(\text{HH})$ 2.4, 2 H, CHCHPPh_2], 2.00 [dd, $^2J(\text{PH})$ 19.1, 2 H, CHCHPPh_2]	58.9 (s, $\mu\text{-PPh}_2$), –103.1 (s, $\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$)
2b $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPhMe})(\text{CO})_6]$	2047, 1995(sh), 1972(sh), 1952(br), 1932(sh)	7.9–7.3 (m, 15 H, Ph), 4.64 [dd, $^3J(\text{PH})$ 17.7, $^3J(\text{HH})$ 1.3, 2 H, CHCHPPh_2], 1.66 [dd, $^2J(\text{PH})$ 20.5, 2 H, CHCHPPh_2], 1.34 [d, $^2J(\text{PH})$ 10.7, 3 H, Me]	54.2 (s, $\mu\text{-PPhMe}$), –99.9 (s, $\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$)
2c $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhMe})(\mu\text{-PPh}_2)(\text{CO})_6]$	2047s, 1972(sh), 1952(br), 1933(sh), 1905w	7.7–7.3 (m, 15 H, Ph), 5.08 [dd, $^3J(\text{PH})$ 17.3, $^3J(\text{HH})$ 0.9, 2 H, CHCHPPhMe], 2.60 [dd, $J(\text{PH})$ 13.7, 3 H, Me], 1.5 (m, 1 H, CHCHPPhMe)	52.0 (s, $\mu\text{-PPh}_2$), –106.1 (s, $\eta^4\text{-C}_4\text{H}_4\text{PPhMe}$)
3 $[\text{Mn}_2(\mu\text{-}\sigma\text{-}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_5]$	2019m, 1956s, 1895m	10.80 [dd, $^3J(\text{H}^3\text{H}^4)$ 8.1, $^3J(\text{PH})$ 2.0, 1 H, H^4], 8.02–6.76 (m, 22 H, Ph, H^2 , H^3), 3.07 [d, $^2J(\text{P}^*\text{H})$ 9.2, 1 H, H^1]	111.5 (s, $\mu\text{-PPh}_2$), –83.7 (s, $\mu\text{-}\sigma\text{-}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$)
4 $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_7]$	2070w, 1994s, 1984(sh), 1968(sh), 1925m, 1905m	7.8–7.3 (m, 20 H, Ph), 3.35 [m, $^3J(\text{PH}^*)$ 9.6, 2 H, H^*], 2.44 [m, $^3J(\text{PH}^*)$ 20.3, 2 H, H^*]	–51.2(s), –99.5(s)
5 $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$	2052w, 2031w, 1990m, 1957s, 1912w, 1894m	8.1–7.3 (m, 20 H, Ph), 5.70 [d, $^3J(\text{PH})$ 27.9, 1 H, H^5], 4.79 [d, $^3J(\text{PH})$ 14.9, 1 H, H^6], 3.53 (s, 1 H, H^2), 2.86 [d, $^3J(\text{PH})$ 4.0, 1 H, H^4], 2.06 (s, 3 H, Me), 1.96 (s, 1 H, H^3)	64.6 (s, $\mu\text{-PPh}_2$), –86.3 (s, $\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2$)

^a Recorded in CH_2Cl_2 solution. ^b Recorded in CDCl_3 solution; chemical shifts (δ), coupling constants in Hz.

**Scheme 1** Possible steps in the formation of complexes **2a** and **3**

Such multiple insertions have been observed previously, for example in the reaction of $[\text{RuCo}(\mu\text{-PPh}_2)(\text{CO})_7]$ with Ph_2C_2 to give $[\text{RuCo}\{\mu\text{-PhCCPhC}(\text{O})\text{PPh}_2\}(\text{CO})_5]$ ³ and in the reaction of $[\text{Fe}_2(\mu\text{-CCBu}^t)(\mu\text{-PPh}_2)(\text{CO})_7]$ with R_2C_2 .⁷

The $\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$ quaternised phosphole ligand in complex **2a** could be formed from the $\mu\text{-}\sigma\text{-}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2$ ligand in **3** via ring closure, with addition of a molecule of CO to complex **3** to enable **2a** to comply with the effective atomic number (e.a.n.) rule. Alternatively, the ligand in **3** could be formed from the ligand in **2a** via phosphorus–carbon bond cleavage and loss of a molecule of CO. Complex **3**, however, was recovered unchanged after UV irradiation (125 W UV lamp) for 1.5 h of a CO-saturated CH_2Cl_2 solution, and no trace of **2a** could be detected. Similarly the UV irradiation of a CH_2Cl_2 solution of **2a** gave only unchanged starting material. Accordingly it is perhaps more likely that **2a** and **3** are formed irreversibly from a common intermediate and a tentative reaction scheme starting from **1a** is shown in Scheme 1. The light-induced loss of CO from $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ in dichloromethane solution to give the metal–metal bonded heptacarbonyl species $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_7]$, which is postulated as the first step, has been documented previously¹⁵ and the colour change from yellow to red which accompanies this CO loss is also observed in the early stages of the reaction of **1a** with acetylene under photolytic conditions. Stable complexes with bridging Ph_2PCHCH ligands analogous to that in intermediate **A** are well known¹⁶ and the insertion of CO into the M–CH bond in such complexes has also been documented.¹⁷ The insertion of $\text{HC}\equiv\text{CH}$ (Scheme 1) which is postulated to give **B** from **A** is therefore not unreasonable and could be followed either by CO loss to give **3** or by ring closure and rearrangement of the CO ligands to give **2a**. The feasibility of the suggested rearrangement of the CO ligands between the metal centres is supported by the presence of a semibringing carbonyl group in **2a** as revealed by the X-ray determination.¹⁴

In order to explore the scope of the reaction of complexes of type **1** with alkynes we have studied the reaction of **1a** with $\text{EtC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CH}$ and $\text{PhC}\equiv\text{CPh}$. The reactions of the unsymmetrical alkynes were even less specific than the reaction of acetylene itself with **1a** and we were not able to characterise any of the low-yield products obtained. Diphenylacetylene did not react at all. We have also studied the reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhMe})(\text{CO})_8]$ **1b** with acetylene in the hope of ascertaining which type of bridging phosphido group would react more readily with the organic substrate. Again, however, the reaction is non-specific and only two of the nine or more

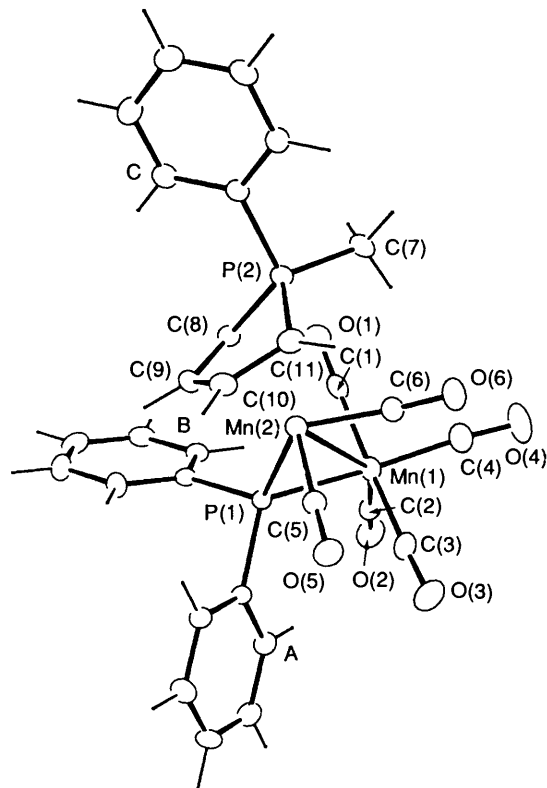


Fig. 1 A view of the structure of $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhMe})(\mu\text{-PPh}_2)(\text{CO})_6]$ **2c**. Here, and in Figs. 2 and 3, 20% displacement ellipsoids are shown for non-hydrogen atoms, whereas hydrogen atoms are represented by small spheres of arbitrary radius; phenyl rings are numbered cyclically C(n1)–C(n6), with C(n1) attached to phosphorus, and the ring label, *n*, is placed adjacent to C(n2)

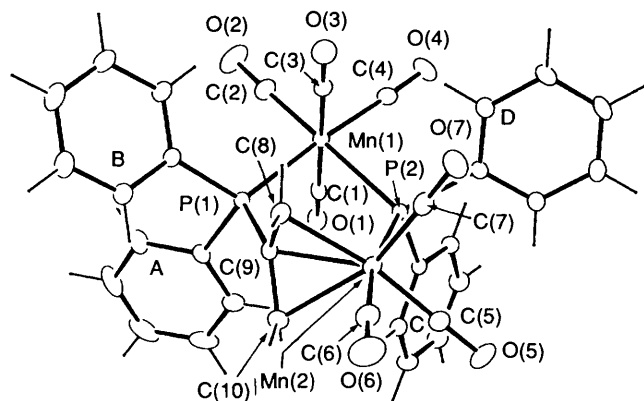


Fig. 2 A view of the structure of $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_7]$ **4**

low-yield products seen on the TLC plate could be isolated. The slowest-moving band gave an orange complex in 4% yield which has been characterised as $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhMe})(\mu\text{-PPh}_2)(\text{CO})_6]$ **2c** by an X-ray diffraction study. The molecular structure is illustrated in Fig. 1. Table 2 lists selected bond distances and angles.

The $\text{C}_4\text{H}_4\text{PPhMe}$ ligand in complex **2c** is η^4 bonded, through C(8), C(9), C(10) and C(11), to Mn(2), with the Me and Ph groups oriented respectively towards and away from the second metal centre. The phosphole C_4 unit is planar [maximum C-atom displacement 0.006(6) Å], with the P atom 0.647(2) Å above this plane on the opposite side to the metal atoms. The bond lengths and angles in the molecule as a whole are in good agreement with those in the molecular structure of the closely related **2a**¹⁴ and a semibringing carbonyl group

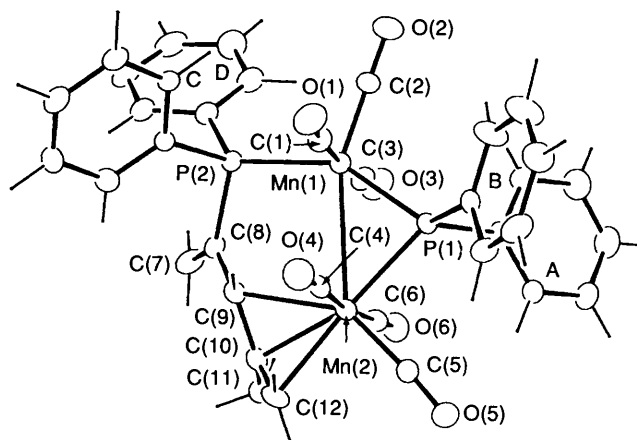


Fig. 3 A view of the structure of $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **5**

$[\text{Mn}(2)\text{-C}(6)\text{-O}(6)$ 162.1(5)° and $\text{Mn}\cdots\text{C}(6)$ 2.60 Å] is again present.

The other product isolated in low yield (3%) from the reaction of complex **1b** with acetylene shows the same molecular ion peak in its mass spectrum as **2c**. On this basis and on the basis of its spectroscopic properties (Table 1) the complex is formulated as $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPhMe})(\text{CO})_6]$ **2b**, although it is not possible from the available data to rule out entirely an alternative formulation of the complex as $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhMe})(\mu\text{-PPh}_2)(\text{CO})_6]$, an isomer of **2c** which could differ in structure from **2c** only in that the other face of the quaternised phosphole is co-ordinated to the metal.

(b) *Reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ **1a** with Allene.*—The UV irradiation of a CH_2Cl_2 solution of complex **1a** with allene leads to the formation of at least fifteen products of which two, $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_7]$ **4** (5% yield) and $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ **5** (12% yield), have been characterised, both by single-crystal X-ray analyses.

The molecular structure of complex **4** is shown in Fig. 2. Table 3 lists selected bond distances and angles. The two manganese atoms are bridged by a PPh_2 ligand and a $\text{C}_3\text{H}_4\text{PPh}_2$ ligand which is σ bonded to Mn(1) via the phosphorus atom and η^3 bonded to Mn(2) via the C_3H_4 grouping. The Mn(1) atom is additionally ligated by four terminal CO groups, completing an approximately octahedral arrangement, while Mn(2) is also co-ordinated by three terminal CO groups. The Mn–P–Mn angle associated with the bridging phosphido group of 117.6(1)° may be compared with the corresponding Mn–P–Mn angle of 78.3(1)° in **2c** and is in the range associated with the absence of any significant interaction between the two metal centres.¹⁸ The Mn···Mn non-bonded distance is 4.125(1) Å. The two carbon–carbon distances within the allyl ligand are equal within experimental error [1.404(6) and 1.406(5) Å] and the C–C–C angle at 120.9(4)° is typical of that expected for an allyl group η^3 bonded to a metal atom.¹⁹ The two Mn–P bonds to the bridging phosphido group are unequal in length [Mn(1)–P(2) 2.438(1), Mn(2)–P(2) 2.385(1) Å], perhaps reflecting the fact that this group needs to donate two electrons to Mn(2) and only one to Mn(1) in order for the e.a.n. rule to be obeyed at each metal centre.

The molecular structure of complex **5** is shown in Fig. 3. Table 4 lists selected bond distances and angles. The two manganese atoms are bridged by a PPh_2 ligand and by a $\text{C}_6\text{H}_8\text{PPh}_2$ ligand which is derived from one of the PPh_2 groups in **1a** and 2 equivalents of allene. One of the allene molecules is linked through its central carbon atom to phosphorus and through a terminal carbon atom to the central carbon atom of the other allene. A hydrogen atom has migrated from the linking

terminal carbon atom of the first allene molecule to the terminal carbon atom C(11) of the second. This ligand is bonded through phosphorus to Mn(1) and *via* an η^3 -allyl linkage to Mn(2). In contrast to the allyl ligand in **4** the carbon-carbon bond lengths in the allyl group in **5** are not the same [C(9)-C(10) 1.421(9), C(10)-C(12) 1.389(10) Å] and the C-C-C angle is a little

smaller [117.7(6)°]. As expected, the unco-ordinated carbon-carbon double bond, C(7)-C(8), is considerably shorter [1.308(10) Å] than the carbon-carbon bonds within the allyl group or the single bonds C(8)-C(9) and C(10)-C(11) [1.471(9) and 1.498(10) Å respectively]. The Mn-P-Mn angle of the bridging phosphido group is 82.7(1)° and angles of this magnitude are normally associated with some degree of direct interaction between the two metal centres.¹⁸ The Mn(1)-Mn(2) distance [2.986(2) Å] is indeed in the range expected for an Mn-Mn single bond.²⁰ The two Mn-P distances to the bridging phosphido group [Mn(2)-P(1) 2.323(2), Mn(1)-P(1) 2.196(2) Å] differ by a wider margin than the corresponding Mn-P distances in **4**. Again the shorter bond is to the manganese atom [Mn(1)] which requires the donation of two electrons to satisfy the e.a.n. rule. Each Mn atom is additionally co-ordinated by three terminal CO groups.

Complex **4** represents, to our knowledge, the first example of the insertion of allene into a metal-phosphorus bond of a bridging phosphido group. It seems probable that **5** is formed *via* the further reaction of **4** with allene, although the yields of **4** and **5** are such that we have not been able to verify this experimentally. One possible pathway for the formation of **5** *via* this route is shown in Scheme 2. Hydrogen-atom migrations similar to that required to convert intermediate **B** into complex **5** have been observed previously in photolytic reactions of related dimanganese and molybdenum-manganese complexes.¹³

The dimerisation of allene at transition-metal centres is a well known process and can take place in several different ways.²¹ Coupling of the two central carbon atoms is most commonly observed although there is at least one known example of terminal-central carbon coupling.²² The hydrogen migration and phosphorus-carbon bond formation which accompany this process in the formation of **5** are, however, to our knowledge unique.

Experimental

All reactions were carried out under a nitrogen atmosphere in N₂-saturated solvents distilled from the appropriate drying agent and stored over 4 Å molecular sieves. Ultraviolet irradiation was carried out in a glass photolysis vessel using Hanovia 4 W or 125 W medium-pressure immersion lamps in a water- or ethanol-cooled quartz inner tube.

Table 2 Selected bond lengths (Å) and angles (°) in complex **2c**

Mn(1)-Mn(2)	2.858(2)	Mn(1)-P(1)	2.264(2)
Mn(1)-C(1)	1.841(6)	Mn(1)-C(2)	1.776(6)
Mn(1)-C(3)	1.825(6)	Mn(1)-C(4)	1.806(7)
Mn(2)-P(1)	2.263(2)	Mn(2)-C(5)	1.749(6)
Mn(2)-C(6)	1.797(7)	Mn(2)-C(8)	2.217(6)
Mn(2)-C(9)	2.117(6)	Mn(2)-C(10)	2.082(6)
Mn(2)-C(11)	2.128(6)	P(1)-C(A1)	1.857(6)
P(1)-C(B1)	1.860(6)	P(2)-C(7)	1.791(6)
P(2)-C(8)	1.729(5)	P(2)-C(11)	1.768(6)
P(2)-C(C1)	1.822(6)	O(1)-C(1)	1.152(7)
O(2)-C(2)	1.153(8)	O(3)-C(3)	1.150(8)
O(4)-C(4)	1.155(9)	O(5)-C(5)	1.169(7)
O(6)-C(6)	1.167(8)	C(8)-C(9)	1.439(7)
C(9)-C(10)	1.388(8)	C(10)-C(11)	1.429(8)
Mn(2)-Mn(1)-P(1)	50.8(1)	Mn(2)-Mn(1)-C(1)	83.8(2)
Mn(2)-Mn(1)-C(2)	149.9(2)	Mn(2)-Mn(1)-C(3)	88.7(2)
Mn(2)-Mn(1)-C(4)	115.6(3)	P(1)-Mn(1)-C(1)	90.9(2)
P(1)-Mn(1)-C(2)	99.4(2)	P(1)-Mn(1)-C(3)	87.7(2)
P(1)-Mn(1)-C(4)	166.1(3)	C(1)-Mn(1)-C(2)	93.4(3)
C(1)-Mn(1)-C(3)	171.3(3)	C(1)-Mn(1)-C(4)	90.3(3)
C(2)-Mn(1)-C(3)	95.3(3)	C(2)-Mn(1)-C(4)	94.3(3)
C(3)-Mn(1)-C(4)	89.1(3)	Mn(1)-Mn(2)-P(1)	50.9(1)
Mn(1)-Mn(2)-C(5)	99.6(2)	Mn(1)-Mn(2)-C(6)	63.2(2)
Mn(1)-Mn(2)-C(8)	103.7(2)	Mn(1)-Mn(2)-C(9)	130.7(2)
Mn(1)-Mn(2)-C(10)	169.0(2)	Mn(1)-Mn(2)-C(11)	142.5(2)
P(1)-Mn(2)-C(5)	90.4(2)	P(1)-Mn(2)-C(6)	112.7(2)
C(5)-Mn(2)-C(6)	87.9(3)	Mn(1)-P(1)-Mn(2)	78.3(1)
Mn(1)-P(1)-C(A1)	118.9(2)	Mn(1)-P(1)-C(B1)	119.7(2)
Mn(2)-P(1)-C(A1)	120.4(2)	Mn(2)-P(1)-C(B1)	121.0(2)
C(A1)-P(1)-C(B1)	99.7(3)	C(7)-P(2)-C(8)	116.4(3)
C(7)-P(2)-C(11)	117.8(3)	C(7)-P(2)-C(C1)	103.1(3)
C(8)-P(2)-C(11)	89.7(3)	C(8)-P(2)-C(C1)	117.7(3)
C(11)-P(2)-C(C1)	112.7(3)	Mn(1)-C(1)-O(1)	179.0(6)
Mn(1)-C(2)-O(2)	178.8(6)	Mn(1)-C(3)-O(3)	178.5(6)
Mn(1)-C(4)-O(4)	174.6(7)	Mn(2)-C(5)-O(5)	176.5(5)
Mn(2)-C(6)-O(6)	162.1(5)	P(2)-C(8)-C(9)	107.6(4)
C(8)-C(9)-C(10)	112.2(5)	C(9)-C(10)-C(11)	112.0(5)
P(2)-C(11)-C(10)	106.7(4)		

Table 3 Selected bond lengths (Å) and angles (°) in complex **4**

Mn(1)-P(1)	2.324(1)	Mn(1)-P(2)	2.438(1)	P(1)-C(A1)	1.836(4)	P(1)-C(B1)	1.837(4)
Mn(1)-C(1)	1.857(4)	Mn(1)-C(2)	1.816(4)	P(2)-C(C1)	1.858(4)	P(2)-C(D1)	1.849(4)
Mn(1)-C(3)	1.839(4)	Mn(1)-C(4)	1.839(4)	O(1)-C(1)	1.129(5)	O(2)-C(2)	1.127(6)
Mn(2)-P(2)	2.385(1)	Mn(2)-C(5)	1.795(4)	O(3)-C(3)	1.144(5)	O(4)-C(4)	1.117(5)
Mn(2)-C(6)	1.810(5)	Mn(2)-C(7)	1.799(4)	O(5)-C(5)	1.155(5)	O(6)-C(6)	1.151(6)
Mn(2)-C(8)	2.164(4)	Mn(2)-C(9)	2.129(3)	O(7)-C(7)	1.140(5)	C(8)-C(9)	1.404(6)
Mn(2)-C(10)	2.237(4)	P(1)-C(9)	1.862(4)	C(9)-C(10)	1.406(5)	Cl(S)-C(S)	1.703(5)
P(1)-Mn(1)-P(2)	85.9(1)	P(1)-Mn(1)-C(1)	90.3(2)	C(7)-Mn(2)-C(10)	155.7(2)	Mn(1)-P(1)-C(9)	115.2(2)
P(1)-Mn(1)-C(2)	94.7(2)	P(1)-Mn(1)-C(3)	88.1(2)	Mn(1)-P(1)-C(A1)	114.8(2)	Mn(1)-P(1)-C(B1)	117.2(2)
P(1)-Mn(1)-C(4)	174.8(2)	P(2)-Mn(1)-C(1)	88.7(2)	C(9)-P(1)-C(A1)	107.1(2)	C(9)-P(1)-C(B1)	98.6(2)
P(2)-Mn(1)-C(2)	176.9(2)	P(2)-Mn(1)-C(3)	90.0(2)	C(A1)-P(1)-C(B1)	101.9(2)	Mn(1)-P(2)-Mn(2)	117.6(1)
P(2)-Mn(1)-C(4)	89.0(2)	C(1)-Mn(1)-C(2)	88.3(2)	Mn(1)-P(2)-C(C1)	105.5(2)	Mn(1)-P(2)-C(D1)	109.6(2)
C(1)-Mn(1)-C(3)	177.9(2)	C(1)-Mn(1)-C(4)	90.7(2)	Mn(2)-P(2)-C(C1)	113.4(2)	Mn(2)-P(2)-C(D1)	109.1(2)
C(2)-Mn(1)-C(3)	93.1(2)	C(2)-Mn(1)-C(4)	90.4(2)	C(C1)-P(2)-C(D1)	100.2(2)	Mn(1)-C(1)-O(1)	177.8(4)
C(3)-Mn(1)-C(4)	90.8(2)	P(2)-Mn(2)-C(5)	84.7(2)	Mn(1)-C(2)-O(2)	176.3(4)	Mn(1)-C(3)-O(3)	177.8(4)
P(2)-Mn(2)-C(6)	168.7(2)	P(2)-Mn(2)-C(7)	87.5(2)	Mn(1)-C(4)-O(4)	178.1(4)	Mn(2)-C(5)-O(5)	177.0(4)
P(2)-Mn(2)-C(8)	103.3(2)	P(2)-Mn(2)-C(9)	87.6(1)	Mn(2)-C(6)-O(6)	176.4(4)	Mn(2)-C(7)-O(7)	176.6(4)
P(2)-Mn(2)-C(10)	102.9(2)	C(5)-Mn(2)-C(6)	85.2(2)	Mn(2)-C(9)-P(1)	125.7(2)	Mn(2)-C(9)-C(8)	72.3(2)
C(5)-Mn(2)-C(7)	97.4(2)	C(5)-Mn(2)-C(8)	170.0(2)	Mn(2)-C(9)-C(10)	75.4(3)	P(1)-C(9)-C(8)	113.9(3)
C(5)-Mn(2)-C(9)	138.3(2)	C(5)-Mn(2)-C(10)	105.3(2)	P(1)-C(9)-C(10)	125.2(3)	C(8)-C(9)-C(10)	120.9(4)
C(6)-Mn(2)-C(7)	88.7(2)	C(6)-Mn(2)-C(8)	87.2(2)	Cl(S)-C(S)-Cl(S)	113.2(5)		
C(6)-Mn(2)-C(9)	103.3(2)	C(6)-Mn(2)-C(10)	84.7(2)				
C(7)-Mn(2)-C(8)	88.9(2)	C(7)-Mn(2)-C(9)	123.2(2)				

Table 4 Selected bond lengths (Å) and angles (°) in complex **5**

Mn(1)–Mn(2)	2.986(2)	Mn(1)–P(1)	2.196(2)	P(2)–C(C1)	1.819(6)	P(2)–C(D1)	1.816(7)
Mn(1)–P(2)	2.266(2)	Mn(1)–C(1)	1.788(7)	O(1)–C(1)	1.167(8)	O(2)–C(2)	1.160(8)
Mn(1)–C(2)	1.747(7)	Mn(1)–C(3)	1.805(7)	O(3)–C(3)	1.155(9)	O(4)–C(4)	1.156(9)
Mn(2)–P(1)	2.323(2)	Mn(2)–C(4)	1.823(7)	O(5)–C(5)	1.158(8)	O(6)–C(6)	1.153(9)
Mn(2)–C(5)	1.778(7)	Mn(2)–C(6)	1.820(7)	C(7)–C(8)	1.308(10)	C(8)–C(9)	1.471(9)
Mn(2)–C(9)	2.319(6)	Mn(2)–C(10)	2.188(7)	C(9)–C(10)	1.421(9)	C(10)–C(11)	1.498(10)
Mn(2)–C(12)	2.197(7)	P(1)–C(A1)	1.831(6)	C(10)–C(12)	1.389(10)		
P(1)–C(B1)	1.826(6)	P(2)–C(8)	1.836(6)				
Mn(2)–Mn(1)–P(1)	50.5(1)	Mn(2)–Mn(1)–P(2)	96.7(1)	C(5)–Mn(2)–C(9)	145.5(3)	C(5)–Mn(2)–C(10)	111.0(3)
Mn(2)–Mn(1)–C(1)	92.3(3)	Mn(2)–Mn(1)–C(2)	157.9(3)	C(5)–Mn(2)–C(12)	81.4(3)	C(6)–Mn(2)–C(9)	94.3(3)
Mn(2)–Mn(1)–C(3)	91.9(2)	P(1)–Mn(1)–P(2)	147.2(1)	C(6)–Mn(2)–C(10)	82.1(3)	C(6)–Mn(2)–C(12)	104.0(3)
P(1)–Mn(1)–C(1)	89.6(2)	P(1)–Mn(1)–C(2)	107.4(3)	Mn(1)–P(1)–Mn(2)	82.7(1)	Mn(1)–P(1)–C(A1)	120.5(2)
P(1)–Mn(1)–C(3)	91.0(2)	P(2)–Mn(1)–C(1)	92.9(2)	Mn(1)–P(1)–C(B1)	118.5(3)	Mn(2)–P(1)–C(A1)	117.1(3)
P(2)–Mn(1)–C(2)	105.4(3)	P(2)–Mn(1)–C(3)	89.2(2)	Mn(2)–P(1)–C(B1)	118.4(3)	C(A1)–P(1)–C(B1)	100.7(3)
C(1)–Mn(1)–C(2)	85.7(3)	C(1)–Mn(1)–C(3)	175.1(3)	Mn(1)–P(2)–C(8)	104.0(2)	Mn(1)–P(2)–C(C1)	118.4(2)
C(2)–Mn(1)–C(3)	89.5(3)	Mn(1)–Mn(2)–P(1)	46.8(1)	Mn(1)–P(2)–C(D1)	122.0(3)	C(8)–P(2)–C(C1)	103.6(3)
Mn(1)–Mn(2)–C(4)	84.7(2)	Mn(1)–Mn(2)–C(5)	137.9(3)	C(8)–P(2)–C(D1)	107.3(3)	C(C1)–P(2)–C(D1)	100.0(3)
Mn(1)–Mn(2)–C(6)	88.6(2)	Mn(1)–Mn(2)–C(9)	76.5(2)	Mn(1)–C(1)–O(1)	174.3(6)	Mn(1)–C(2)–O(2)	178.1(6)
Mn(1)–Mn(2)–C(10)	110.5(2)	Mn(1)–Mn(2)–C(12)	139.3(2)	Mn(1)–C(3)–O(3)	175.5(6)	Mn(2)–C(4)–O(4)	176.2(6)
P(1)–Mn(2)–C(4)	87.5(2)	P(1)–Mn(2)–C(5)	91.1(3)	Mn(2)–C(5)–O(5)	175.8(6)	Mn(2)–C(6)–O(6)	178.4(6)
P(1)–Mn(2)–C(6)	85.5(2)	P(1)–Mn(2)–C(9)	123.3(2)	P(2)–C(8)–C(7)	123.0(5)	P(2)–C(8)–C(9)	109.6(5)
P(1)–Mn(2)–C(10)	154.5(2)	P(1)–Mn(2)–C(12)	167.9(2)	C(7)–C(8)–C(9)	127.4(6)	C(8)–C(9)–C(10)	127.9(6)
C(4)–Mn(2)–C(5)	92.5(3)	C(4)–Mn(2)–C(6)	172.5(3)	C(9)–C(10)–C(11)	122.9(6)	C(9)–C(10)–C(12)	117.7(6)
C(4)–Mn(2)–C(9)	87.4(3)	C(4)–Mn(2)–C(10)	103.4(3)	C(11)–C(10)–C(12)	119.5(6)		
C(4)–Mn(2)–C(12)	83.3(3)	C(5)–Mn(2)–C(6)	90.3(3)				

Table 5 Crystallographic data and refinement details for the complexes **2c**, **4** and **5**

Compound	2c	4	5
Formula	C ₂₉ H ₂₂ Mn ₂ O ₆ P ₂	C ₃₄ H ₂₄ Mn ₂ O ₇ P ₂ ·0.5CH ₂ Cl ₂	C ₃₆ H ₂₈ Mn ₂ O ₆ P ₂
<i>M</i>	638.31	758.85	728.44
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	12.231(2)	35.291(5)	34.679(5)
<i>b</i> /Å	9.637(2)	9.537(1)	9.697(2)
<i>c</i> /Å	23.774(3)	21.529(3)	20.430(3)
β/°	94.27(1)	115.17(1)	99.86(1)
<i>U</i> /Å ³	2794.5(7)	6558(2)	6769(2)
<i>Z</i>	4	8	8
<i>D</i> _c /g cm ⁻³	1.517	1.537	1.429
<i>F</i> (000)	1296	3080	2976
μ/cm ⁻¹	10.5	9.6	8.5
Crystal size/mm	0.18 × 0.08 × 0.40	1.1 × 0.88 × 0.40	0.48 × 0.24 × 0.04
θ/°	2–22	2–27	2–22
<i>h</i>	0–12	0–45	0–36
<i>k</i>	0–10	0–12	0–10
<i>l</i>	–25 to 25	–27 to 27	–21 to 21
Reflections measured	4504	7586	4037
Unique reflections	3395	7089	3964
Observed reflections	2068	5049	2236
<i>R</i> _{int}	0.022	0.025	0.029
<i>R</i>	0.031	0.043	0.036
<i>R</i> '	0.039	0.057	0.041
Parameters	316	436	415
Δρ /e Å ⁻³	0.30	0.60	0.42

Work-up procedures were generally performed in air. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica; products are presented in order of decreasing *R_f* values.

The instrumentation used to obtain spectroscopic data has been described previously.²³ Phosphorus-31 NMR chemical shifts are given relative to P(OMe)₃ with upfield shifts negative. All NMR spectra were recorded at 293 K. The complex [Mn₂(μ-PPh₂)₂(CO)₈]²⁴ was prepared in high yield from the reaction of [Mn₂(CO)₁₀] with PPh₂H (see below) and the complex [Mn₂(μ-PPh₂)(μ-PPhMe)(CO)₈] in 53% yield from the deprotonation and subsequent methylation with MeI of [Mn₂(μ-PPh₂)(μ-PPhH)(CO)₈].²⁵ All other reagents were

obtained from the usual commercial suppliers and used without further purification.

(i) *Synthesis of [Mn₂(μ-PPh₂)₂(CO)₈] 1a*.—A solution of [Mn₂(CO)₁₀] (1.040 g, 2.67 mmol) in undried decalin (200 cm³) (used as obtained from the commercial suppliers)²⁶ was heated to 423 K and PPh₂H (0.990 cm³, 5.69 mmol) was then added. The mixture was stirred at 423 K for 4 h after which CO was bubbled through the solution for 2 min. The decalin was removed under vacuum to leave a yellow residue to which CH₂Cl₂ (50 cm³) was added to form a slurry. This slurry was filtered through a Whatman No. 1 filter-paper to yield [Mn₂(μ-PPh₂)₂(CO)₈] **1a** (1.380 g). A further 0.372 g of

Table 6 Fractional coordinates for non-hydrogen atoms**(a) [Mn₂(η⁴-C₄H₄PPhMe)(μ-PPh₂)(CO)₆] 2c**

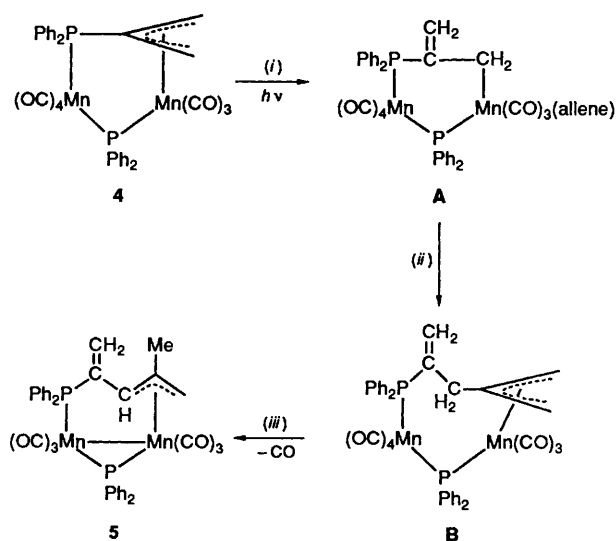
Atom	x	y	z	Atom	x	y	z
Mn(1)	0.202 56(7)	0.130 57(9)	-0.072 32(3)	C(11)	-0.036 4(4)	0.383 4(6)	-0.199 8(2)
Mn(2)	0.114 11(6)	0.307 53(9)	-0.160 81(3)	C(A1)	0.406 3(4)	0.273 2(4)	-0.154 5(3)
P(1)	0.283 41(10)	0.308 69(15)	-0.115 39(5)	C(A2)	0.489 0(3)	0.190 2(5)	-0.130 5(1)
P(2)	-0.076 67(11)	0.445 69(16)	-0.134 57(5)	C(A3)	0.581 8(2)	0.166 2(6)	-0.158 6(2)
O(1)	0.091 2(3)	0.327 1(5)	0.002 3(1)	C(A4)	0.591 9(3)	0.225 3(3)	-0.210 9(2)
O(2)	0.376 3(4)	0.062 6(5)	0.014 8(2)	C(A5)	0.509 2(3)	0.308 3(5)	-0.234 9(2)
O(3)	0.283 4(4)	-0.057 4(5)	-0.159 4(2)	C(A6)	0.416 4(3)	0.693 2(6)	-0.206 8(3)
O(4)	0.063 7(5)	-0.102 6(6)	-0.039 3(2)	C(B1)	0.333 8(5)	0.461 6(5)	-0.073 3(2)
O(5)	0.194 4(3)	0.168 2(4)	-0.258 5(1)	C(B2)	0.338 3(3)	0.459 9(3)	-0.015 1(2)
O(6)	-0.023 5(3)	0.060 2(5)	-0.153 8(2)	C(B3)	0.374 1(3)	0.575 6(5)	0.015 1(1)
C(1)	0.134 6(4)	0.252 4(7)	-0.026 6(2)	C(B4)	0.405 3(4)	0.632 0(5)	-0.012 8(2)
C(2)	0.308 5(5)	0.090 6(6)	-0.019 6(2)	C(B5)	0.400 7(2)	0.694 6(4)	-0.071 0(2)
C(3)	0.253 4(5)	0.016 4(6)	-0.125 8(2)	C(B6)	0.364 9(4)	0.578 9(6)	-0.101 2(1)
C(4)	0.113 6(6)	-0.007 5(7)	-0.052 2(3)	C(C1)	-0.178 3(4)	0.583 9(6)	-0.142 8(3)
C(5)	0.1655(4)	0.224 2(6)	-0.186 6(2)	C(C2)	-0.148 9(3)	0.720 0(7)	-0.131 6(2)
C(6)	0.039 1(5)	0.151 5(6)	-0.148 4(2)	C(C3)	-0.226 2(5)	0.824 0(5)	-0.138 9(2)
C(7)	-0.138 1(4)	0.324 9(7)	-0.089 1(2)	C(C4)	-0.332 9(3)	0.791 9(5)	-0.157 4(2)
C(8)	0.057 5(4)	0.492 3(6)	-0.115 6(2)	C(C5)	-0.362 2(4)	0.655 9(6)	-0.168 6(2)
C(9)	0.108 3(4)	0.526 7(6)	-0.166 5(2)	C(C6)	-0.284 9(5)	0.551 9(4)	-0.161 3(2)
C(10)	0.054 5(4)	0.466 5(6)	-0.213 9(2)				

(b) [Mn₂(μ-η³-C₃H₄PPh₂)(PPh₂)(CO)₇] 4

Mn(1)	0.143 87(2)	0.298 69(5)	-0.005 04(2)	C(A4)	0.245 67(15)	-0.075 47(50)	-0.096 17(32)
Mn(2)	0.096 19(2)	-0.062 26(5)	0.040 04(2)	C(A5)	0.242 60(14)	-0.085 48(44)	-0.035 28(27)
P(1)	0.130 18(3)	0.102 66(9)	-0.075 38(4)	C(A6)	0.207 95(12)	-0.031 15(41)	-0.028 94(21)
P(2)	0.139 70(3)	0.139 64(8)	0.080 47(4)	C(B1)	0.092 63(12)	0.123 59(38)	-0.165 50(17)
O(1)	0.235 81(8)	0.244 44(29)	0.051 60(12)	C(B2)	0.081 21(13)	0.005 41(44)	-0.207 06(19)
O(2)	0.155 37(11)	0.494 22(37)	-0.101 33(16)	C(B3)	0.055 64(14)	0.015 39(51)	-0.275 47(20)
O(3)	0.051 87(9)	0.350 33(34)	-0.062 78(14)	C(B4)	0.039 46(14)	0.142 66(53)	-0.304 29(20)
O(4)	0.159 12(9)	0.535 01(28)	0.091 42(15)	C(B5)	0.049 56(14)	0.259 08(50)	-0.263 75(20)
O(5)	0.141 45(9)	-0.170 06(33)	0.180 97(13)	C(B6)	0.076 39(13)	0.250 69(45)	-0.194 60(19)
O(6)	0.046 37(11)	-0.321 25(34)	0.021 79(19)	C(C1)	0.194 81(11)	0.097 10(35)	0.139 07(16)
O(7)	0.030 17(8)	0.088 75(33)	0.061 40(14)	C(C2)	0.211 85(11)	-0.031 89(38)	0.138 67(17)
C(1)	0.200 91(12)	0.262 14(35)	0.030 29(17)	C(C3)	0.254 12(13)	-0.057 41(43)	0.177 52(21)
C(2)	0.150 07(13)	0.416 82(41)	-0.066 24(19)	C(C4)	0.279 52(12)	0.045 43(48)	0.218 54(20)
C(3)	0.087 03(12)	0.328 02(37)	-0.040 18(17)	C(C5)	0.263 22(12)	0.173 63(45)	0.221 03(19)
C(4)	0.153 37(11)	0.444 21(37)	0.055 80(18)	C(C6)	0.221 34(12)	0.199 88(39)	0.181 54(18)
C(5)	0.124 71(11)	-0.126 50(38)	0.125 86(18)	C(D1)	0.124 00(11)	0.238 35(37)	0.139 69(17)
C(6)	0.064 88(13)	-0.219 25(42)	0.026 81(20)	C(D2)	0.094 03(14)	0.340 06(47)	0.117 48(20)
C(7)	0.056 68(11)	0.032 60(41)	0.054 65(17)	C(D3)	0.082 94(16)	0.417 13(52)	0.162 54(24)
C(8)	0.061 82(12)	-0.022 43(43)	-0.068 72(18)	C(D4)	0.102 15(15)	0.387 90(51)	0.231 79(22)
C(9)	0.104 32(10)	-0.045 51(34)	-0.052 15(15)	C(D5)	0.131 42(14)	0.285 43(46)	0.255 24(20)
C(10)	0.123 74(13)	-0.172 88(38)	-0.022 75(19)	C(D6)	0.142 25(12)	0.209 12(42)	0.209 22(18)
C(A1)	0.175 99(11)	0.030 38(37)	-0.083 80(19)	Cl(S)	0.025 06(6)	0.681 74(20)	-0.177 95(10)
C(A2)	0.180 31(13)	0.045 85(47)	-0.145 40(20)	C(S)	0.000 0	0.716 1(9)	-0.250 0
C(A3)	0.215 43(16)	-0.008 74(56)	-0.150 12(27)				

(c) [Mn₂(μ-η⁴-C₆H₈PPh₂)(PPh₂)(CO)₆] 5

Mn(1)	0.129 48(2)	0.224 68(9)	0.088 32(4)	C(A2)	0.183 12(19)	-0.067 97(68)	0.261 51(30)
Mn(2)	0.106 20(3)	-0.070 17(9)	0.097 66(4)	C(A3)	0.217 67(22)	-0.092 94(78)	0.305 64(34)
P(1)	0.128 67(4)	0.096 56(15)	0.176 69(7)	C(A4)	0.243 22(22)	0.012 00(101)	0.321 97(39)
P(2)	0.119 10(4)	0.237 00(16)	-0.024 08(7)	C(A5)	0.235 44(23)	0.139 64(99)	0.295 34(43)
O(1)	0.051 24(15)	0.330 80(48)	0.100 30(25)	C(A6)	0.200 73(24)	0.163 43(74)	0.251 32(39)
O(2)	0.154 41(14)	0.498 65(50)	0.135 47(24)	C(B1)	0.096 86(18)	0.147 93(66)	0.235 03(27)
O(3)	0.212 52(15)	0.157 36(52)	0.086 83(26)	C(B2)	0.069 77(21)	0.062 48(64)	0.257 10(34)
O(4)	0.025 29(14)	0.036 20(47)	0.093 64(23)	C(B3)	0.045 44(22)	0.111 60(79)	0.298 02(39)
O(5)	0.095 80(14)	-0.274 49(47)	0.199 17(23)	C(B4)	0.047 65(24)	0.242 92(91)	0.320 14(36)
O(6)	0.190 01(15)	-0.148 08(48)	0.109 09(22)	C(B5)	0.074 62(28)	0.328 16(85)	0.300 38(43)
C(1)	0.081 25(18)	0.284 18(64)	0.093 14(29)	C(B6)	0.099 17(23)	0.281 41(76)	0.257 96(38)
C(2)	0.144 89(18)	0.389 48(66)	0.115 88(30)	C(C1)	0.071 33(17)	0.293 39(62)	-0.066 80(28)
C(3)	0.179 75(20)	0.178 09(60)	0.087 11(30)	C(C2)	0.056 51(19)	0.418 06(62)	-0.048 43(30)
C(4)	0.057 19(20)	-0.000 89(62)	0.096 20(28)	C(C3)	0.021 57(20)	0.468 83(64)	-0.080 53(34)
C(5)	0.100 90(18)	-0.191 39(65)	0.160 83(31)	C(C4)	-0.000 38(20)	0.394 98(78)	-0.129 87(38)
C(6)	0.157 46(20)	-0.117 78(63)	0.103 68(30)	C(C5)	0.013 09(23)	0.273 08(81)	-0.149 25(35)
C(7)	0.143 62(23)	0.017 11(68)	-0.093 55(33)	C(C6)	0.048 94(22)	0.220 77(68)	-0.117 42(35)
C(8)	0.121 92(18)	0.056 91(58)	-0.050 62(28)	C(D1)	0.150 50(19)	0.337 65(65)	-0.068 43(34)
C(9)	0.097 06(18)	-0.029 65(60)	-0.015 84(28)	C(D2)	0.183 17(21)	0.403 48(73)	-0.035 16(36)
C(10)	0.101 90(19)	-0.171 56(64)	0.000 98(30)	C(D3)	0.206 97(23)	0.481 52(85)	-0.068 60(46)
C(11)	0.134 59(23)	-0.257 28(64)	-0.016 53(29)	C(D4)	0.198 75(28)	0.489 79(86)	-0.136 50(51)
C(12)	0.074 65(22)	-0.231 71(63)	0.034 62(32)	C(D5)	0.166 19(29)	0.429 26(85)	-0.170 86(40)
C(A1)	0.174 08(17)	0.059 06(66)	0.234 05(28)	C(D6)	0.141 87(22)	0.352 27(72)	-0.137 19(37)



Scheme 2 Possible steps in the formation of complex 5 from 4. (i) allene; (ii) insertion; (iii) H-atom migration

material with the same infrared spectrum, identical to that reported in the literature for $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$,²⁴ was obtained on evaporation of the filtrate. The combined yield was 93%.

(ii) *Reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ 1a with C_2H_2 .*—A solution of complex 1a (0.100 g, 0.142 mmol) in CH_2Cl_2 (85 cm^3) with acetylene bubbling through was irradiated with a 4 W UV lamp at room temperature for 5 h. After removal of the solvent on a rotary evaporator the residue was redissolved in the minimum of CH_2Cl_2 and separated by preparative TLC using dichloromethane–hexane (35:65) as eluent. Nine bands were eluted of which the ninth, orange in colour, was the only one to give a product in greater than ca. 1–2% yield. This band contained $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ 2a (0.13 g, 13%). The fifth band, red-brown in colour, gave $[\text{Mn}_2(\mu\text{-}\sigma\text{-}\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_5]$ 3 (0.002 g, 2%). The other seven bands did not yield sufficient quantities of material to permit characterisation. Complex 2a (Found: C, 58.2; H, 3.7. $\text{C}_{34}\text{H}_{24}\text{Mn}_2\text{O}_6\text{P}_2$ requires C, 58.3; H, 3.4%); m/z 644 ($M^+ - 2\text{CO}$) and 616 ($M^+ - 3\text{CO}$). Complex 3: m/z 672 (M^+) and $M^+ - n\text{CO}$ ($n = 1-5$).

(iii) *Reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhMe})(\text{CO})_8]$ 1b with C_2H_2 .*—The complex $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PPhMe})(\text{CO})_8]$ 1b (0.075 g, 0.119 mmol) in CH_2Cl_2 (85 cm^3) was irradiated with a 4 W UV lamp at room temperature for 12.75 h with acetylene bubbling through the solution. After removal of the CH_2Cl_2 on a rotary evaporator the reaction residue was separated by TLC using CH_2Cl_2 –hexane (2:3) as eluent. Nine bands were eluted of which the ninth, orange in colour, gave $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPh}_2)(\mu\text{-PPhMe})(\text{CO})_6]$ 2b (0.002 g, 3%). The eighth, also orange in colour, gave $[\text{Mn}_2(\eta^4\text{-C}_4\text{H}_4\text{PPhMe})(\mu\text{-PPh}_2)(\text{CO})_6]$ 2c (0.003 g, 4%). None of the other bands gave products in yields sufficient to permit their characterisation. Complex 2b: m/z 638 (M^+) and $M^+ - n\text{CO}$ ($n = 1$ or 2). Complex 2c (Found: C, 52.9; H, 3.4. $\text{C}_{29}\text{H}_{22}\text{Mn}_2\text{O}_6\text{P}_2$ requires C, 54.5; H, 3.4%); m/z 638 (M^+).

(iv) *Reaction of $[\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ 1a with Allene.*—Complex 1a (0.250 g, 0.355 mmol) in CH_2Cl_2 (85 cm^3) was irradiated with a 125 W UV lamp at 258 K for 25 min while allene was bubbled slowly through the solution. After removal of the CH_2Cl_2 on a rotary evaporator the reaction residue was separated by TLC using CH_2Cl_2 –hexane (3:7) as eluent. Twelve bands were eluted of which band seven (decreasing R_f

values), orange in colour, gave $[\text{Mn}(\mu\text{-}\eta^3\text{-C}_6\text{H}_8\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_6]$ 5 (0.032 g, 12%). Band six was rechromatographed using ethyl acetate–hexane (1:5) as eluent. Four bands were eluted of which band two gave orange $[\text{Mn}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_4\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_7]$ 4 (0.014 g, 5%). None of the other bands gave products in sufficient yield to permit their characterisation. Complex 4 (Found: C, 55.4; H, 3.3. $\text{C}_{34}\text{H}_{24}\text{Mn}_2\text{O}_7\text{P}_2$ requires C, 57.0; H, 3.4%); m/z 688 ($M^+ - \text{CO}$) and $M^+ - n\text{CO}$ ($n = 1-7$). Complex 5 (Found: C, 58.7; H, 4.2. $\text{C}_{36}\text{H}_{28}\text{Mn}_2\text{O}_6\text{P}_2$ requires C, 59.3; H, 3.8%); m/z 672 ($M^+ - 2\text{CO}$) and $M^+ - n\text{CO}$ ($n = 2-6$).

Crystal Structure Analysis of Complexes 2c, 4 and 5.—Similar experimental and computational methods were used in all three structure analyses (Table 5). Measurements were made at 295 K with Mo-K α X-rays, $\lambda = 0.71069$ Å, on an Enraf-Nonius CAD4 diffractometer fitted with a graphite monochromator. Cell dimensions were obtained from least-squares treatments of the setting angles of 21–25 high-angle reflections. Intensities were determined from ω – 2θ scans of 0.70 – 0.80° in ω and were corrected for Lorentz polarisation and absorption²⁷ effects. The structures were solved by Patterson and Fourier methods. They were then refined on F with $w = 1/\sigma(F^2)$ to convergence ($\Delta/\sigma \geq 0.50$) by the method of full-matrix least squares using reflections with $I \geq k\sigma(I)$ ($k = 2$ for 2c, $k = 3$ for 4 and 5). With the exceptions noted below, anisotropic displacement parameters were refined for non-hydrogen atoms and allowance was made for the scattering of the hydrogen atoms. Hydrogen atoms were initially positioned to give conventional stereochemistry at their parent carbon atoms, the orientations of each methyl group being derived from a difference synthesis, and were then constrained to ride on their parent carbon atoms with C–H 0.96 Å and with fixed isotropic displacement parameters $U(\text{H}) = 1.2U(\text{C})$. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 28 and the calculations were performed on a SEL 3227 computer with the GX program package.²⁹

The phenyl rings in complex 2c were refined as rigid hexagons of side 1.38 Å. The positional and isotropic displacement parameters of the allyl hydrogen atoms in 4 were refined without constraints. Crystals of 4 contain a loosely held dichloromethane solvent molecule which lies on a diad axis and which may be disordered; its hydrogen atoms were not included in the calculations. For 4 and 5 different sets of parameters were refined in alternate cycles because of constraints on the size of the normal matrix. For all three structures final atomic coordinates are presented in Table 6.

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

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