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Synthesis of dimanganese complexes containing mixed bridging phosphido ligands; crystal structures of $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ and $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$

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Abstract

The synthesis of a number of dimanganese complexes each containing two different bridging phosphido ligands is reported. The complex $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhH)(CO)_8]$ (**1**) is prepared by the reaction of $[Mn_2(CO)_{10}]$ firstly with PPh_2H followed by reaction with $PPhH_2$ in decalin. The reaction of **1** with CCl_4 gives $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhCl)(CO)_8]$ (**2**) and deprotonation of **1** with *n*-BuLi followed by reaction of the deprotonated species with RX (X = halide) or $[Mn(CO)_5Br]$ gives the complexes $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhR)(CO)_8]$ (R = Me(**3a**), Et(**3b**), CH_2COMe(**3c**) or CO_2Et(**3d**)) and $[Mn(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (**4**). The deprotonation of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ with one equivalent of *n*-BuLi and subsequent reaction with MeCOCl gives $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (**5**) which exists in solution as a mixture of isomers. The structures of $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (**4**) and of *trans*-$[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (**5**) have been determined by single-crystal X-ray studies. All the complexes have been characterized spectroscopically and by elemental analysis.

Keywords: Manganese; Phosphido; Crystal structure; Bridging ligand

1. Introduction

Dinuclear transition metal complexes containing bis-phosphido bridging ligands ($\mu\text{-}PR_2$) were first synthesized over 34 years ago [1,2] and a wide range of such species have since been prepared [3]. Most of the reported complexes are homodinuclear, although more recently a significant number of heterodinuclear complexes have been prepared [4–11]. The examples of complexes containing two different types of phosphido ligand, i.e. where the R groups on each phosphido group are dissimilar, are considerably fewer [12], and indeed with dimanganese complexes are to our knowledge, limited to the complex $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhMe)(CO)_8]$ [13]. This scarcity may be attributable to the fact that the methods employed in making complexes containing the $Mn(\mu\text{-}PR_2)_2Mn$ unit are not generally applicable to bis-phosphido-bridged complexes in which the bridging groups are not identical.

Our interest in the reactivity of phosphido-bridged dimanganese complexes [14–17] has led us to prepare a range of complexes of this metal containing two different bridging phosphido ligands, and these are described in this paper (Scheme 1 and Table 1) together with the crystal and molecular structures of two representative compounds.

2. Results and discussion

The reaction of the known dimanganese complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ [16] with an equimolar quantity of the primary phosphine $PhPH_2$ in decalin at 433 K gave $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhH)(CO)_8]$ (**1**). It is not necessary to isolate $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ in the

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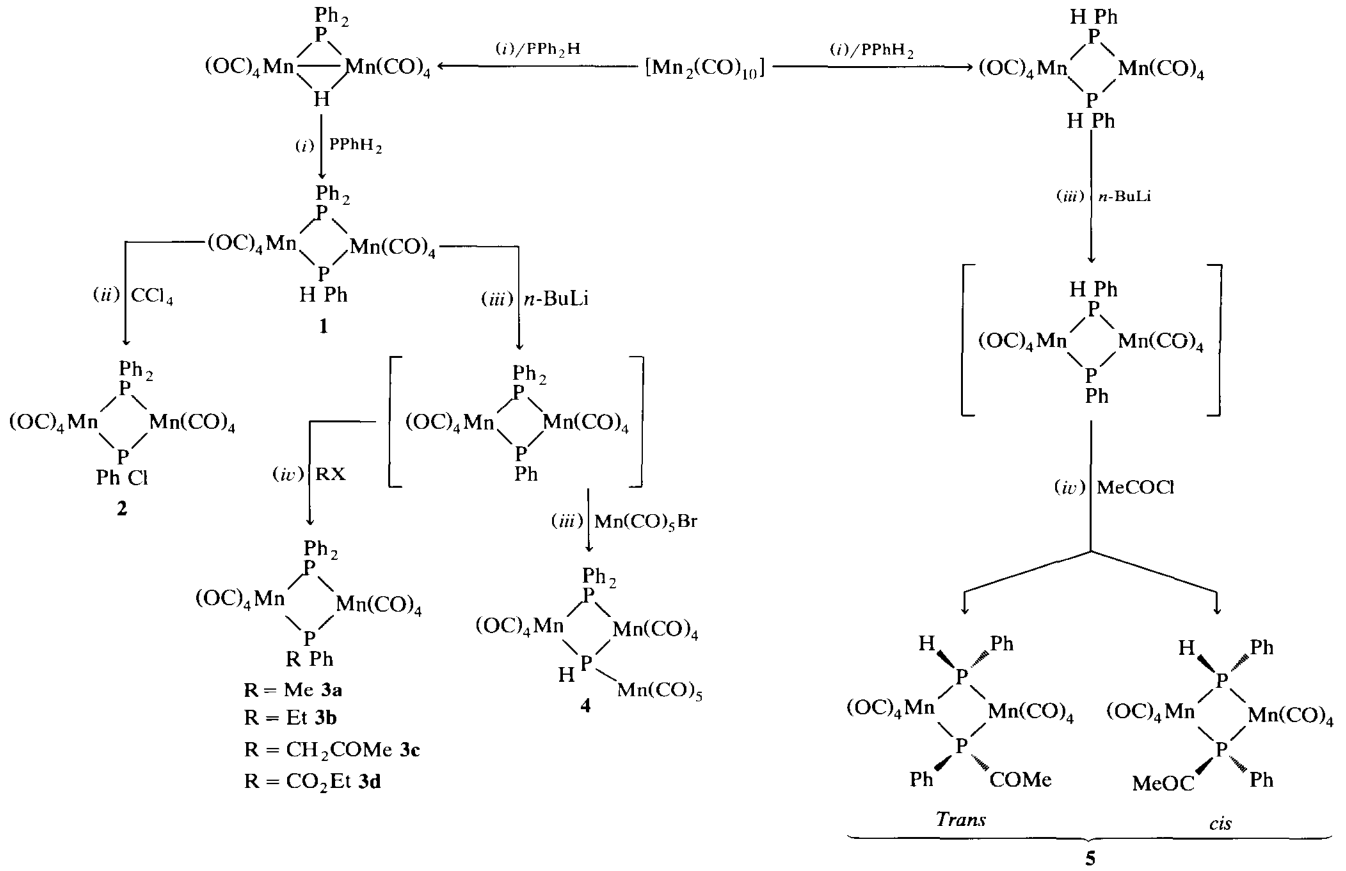
preparative reaction, and **1** is most conveniently made directly by the successive addition of one equivalent each of Ph_2PH and $PhPH_2$ to a heated decalin solution of $[Mn_2(CO)_{10}]$.

Several workers have reported the exchange of halogen for hydrogen in μ-phosphido complexes containing P–H bonds [18–20] and, when **1** was treated with CCl_4 at 343 K for 17 h, $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhCl)(CO)_8]$ (**2**) was obtained with a good yield. Deprotonation of **1** by the addition of *n*-BuLi to a toluene solution of the complex at 195 K took place readily, with a colour change of the solution from yellow to red. The anion $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPh)(CO)_8]$, which was not isolated, reacts with a range of organic halides RX to give complexes of the type $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhR)(CO)_8]$ (R = Me(**3a**), Et(**3b**), CH_2COMe(**3c**) or CO_2Et(**3d**)). The anion also reacts with the manganese carbonyl halide, $[Mn(CO)_5Br]$, to give the trimetallic complex $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (**4**). Although **4** may be regarded as an analogue of **3**, with a metallophosphido bridge, it may alternatively be regarded as a phosphinidene-capped trinuclear cluster with two "missing" metal–metal bonds. Similar phosphinidene-capped complexes have been prepared both directly and by deprotonation from species containing μ-PRH ligands [21].

The molecular structure of **4** is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2 and fractional atomic coordinates in Table 3.

The geometry about the bis-phosphido-bridged manganese atoms Mn(1) and Mn(2) in **4** is approximately octahedral (four carbonyl groups and two phosphorus atoms). The Mn(1)–P(1)–Mn(2) and Mn(1)–P(2)–Mn(2) bond angles of 98.0(1) and 102.8(1)° respectively, although considerably smaller than the Mn(1)–P(1)–Mn(3) and Mn(2)–P(1)–Mn(3) angles of 118.1(1) and 121.8(1)°, are in the range expected for phosphido-bridged complexes in which there is no metal–metal bond between the two metal centres concerned [22]. The Mn(1)–Mn(2) distance of 3.726(1) Å is significantly longer than that in related complexes in which a metal–metal single bond is present [23]. The manganese–phosphorus bonds to the bridging metallophosphido ligand (Mn(1)–P(1), 2.462(2) Å; Mn(2)–P(1), 2.474(2) Å) are significantly longer than the corresponding bonds to the diphenylphosphido ligand



Scheme 1. Preparation of the new dimanganese complexes **1**–**5**: (*i*) decalin, 433 K; (*ii*) room temperature; (*iii*) tetrahydrofuran, 195 K, 1:1 ratio of reactants; (*iv*) tetrahydrofuran, 195 K, excess of halide.

(Mn(1)–P(2), 2.396(2) Å; Mn(2)–P(2), 2.372(2) Å), suggesting perhaps that the metallophosphido ligand is a poorer donor than the diphenylphosphido ligand to the two remaining manganese centres. In mono-substituted chromium carbonyl complexes of the type $LCr(CO)_5$ (L = triorganophosphine) a short Cr–P bond and a long *trans* Cr–C bond are associated with enhanced π-electron-accepting ability of the phosphine [24]. In **4**, however, the Mn–C bond lengths for the CO groups *trans* to the PPh_2 bridge (Mn(1)–C(4), 1.812(7) Å; Mn(2)–C(8), 1.814(7) Å) are not significantly different from those *trans* to the metallophosphido bridge (Mn(1)–C(3), 1.812(7) Å; Mn(2)–C(5), 1.810(7) Å), suggesting that this is not the explanation here. All the four Mn–C bonds above are significantly shorter than the Mn–C bonds to the axial carbonyl ligands on Mn(1) and Mn(2) (*trans* to each other), as would be expected on the basis of the reduced π acidity of the phosphido bridges relative to CO. The geometry around Mn(3) is approximately octahedral.

We have previously reported that the double deprotonation of $[Mn_2(\mu\text{-PPhH})_2(CO)_8]$ with two equivalents of *n*-BuLi, followed by treatment of the dianion with organic halides RX gives the complexes $[Mn_2(\mu\text{-PPhR})_2(CO)_8]$ [25]. It was of interest to determine whether deprotonation of $[Mn_2(\mu\text{-PPhH})_2(CO)_8]$ with one equivalent of *n*-BuLi would give the monoanion $[Mn_2(\mu\text{-PPhH})(\mu\text{-PPh})(CO)_8]^-$, which could then be treated with RX to give complexes of the type $[Mn_2(\mu\text{-PPhH})(\mu\text{-PPhR})(CO)_8]$. A previous IR spectroscopy study of the reaction of $[Fe_2(\mu\text{-PPhH})_2(CO)_8]$ with one equivalent of *n*-BuLi had revealed only the presence of the dianion $[Fe_2(\mu\text{-PPh})_2(CO)_8]^{2-}$ and unchanged starting material [26]; IR spectroscopy studies of a 1 : 1 mixture of $[Mn_2(\mu\text{-PPhH})_2(CO)_8]$ and n-BuLi were similarly inconclusive [27]. Nevertheless, addition of an excess of MeCOCl to such a 1 : 1 mixture gave $[Mn_2(\mu\text{-PPhH})(\mu\text{-PPhCOMe})(CO)_8]$ (**5**) (28% yield) and unchanged $[Mn_2(\mu\text{-PPhH})_2(CO)_8]$ (48% yield), suggesting that the monoanion was present in at least

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

Compound	ν (CO) [a] (cm^{-1})	^1H NMR, δ [b] (ppm)	^{31}P NMR, δ [c] (ppm)
1 $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhH})(CO)_8]$	2075vw, 2053m, 1991s, 1962m	7.8–7.3 (m, 15H, *Ph*), 4.05 (dd, $^1J(PH) = 308.8$ Hz, $^3J(PH) = 1.1$ Hz, 1H, *Ph*)	−187.2 (s, μ-*P*Ph$_2$), −231.5 (s, μ-*P*PhH)
2 $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhCl})(CO)_8]$	2082w, 2060m, 1998s, 1971m	8.0–7.0 (m, 15H, *Ph*)	[d]
3a $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhMe})(CO)_8]$	2073vw, 2050m, 1988s, 1957m	7.8–7.3 (m, 15H, *Ph*), 2.03 (d, $^2J(PH) = 7.2$ Hz, 3H, *Me*)	−182.8 (s, μ-*P*Ph$_2$), −210.6 (s, μ-*P*PhMe)
3b $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhEt})(CO)_8]$	2073vw, 2050m, 1986s, 1957m	7.9–7.2 (m, 15H, *Ph*), 2.47 (m, 2H, C*H*$_2$), 0.90 (dt, $^3J(PH) = 16.3$ Hz, $^3J(HH) = 7.4$ Hz, 3H, *Me*)	−181.2 (s, μ-*P*Ph$_2$), −192.3 (s, μ-*P*PhEt)
3c $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhCH}_2\text{COMe})(CO)_8]$	2075vw, 2053m, 1991s, 1961s, 1706m	7.9–7.2 (m, 15H, *Ph*), 3.41 (d, $^2J(PH) = 4.6$ Hz, 2H, C*H*$_2$), 1.47 (s, 3H, *Me*)	−182.5 (s, μ-*P*Ph$_2$ and μ-*P*PhCH$_2$COMe)
3d $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhCO}_2\text{Et})(CO)_8]$	2078vw, 2057m, 1995s, 1965m, 1692m	7.9–7.2 (m, 15, Ph), 4.27 (q, $^3J(HH) = 7.1$ Hz, 2H, C*H*$_2$), 1.25 (t, $^3J(HH) = 7.1$ Hz, 3H, *Me*)	−181.4 (s, μ-*P*Ph$_2$), −153.2 (s, μ-*P*PhCO$_2$Et)
4 $[Mn_2(\mu\text{-PPh}_2)(\mu\text{-PPhMn(CO)}_5)(CO)_8]$	2015m, 2082w, 2056vw, 2047m, 2030s, 1996s, 1955m	8.1–6.6 (m, 15H, *Ph*)	[d]
5 $[Mn_2(\mu\text{-PPhH})(\mu\text{-PPhCOMe})(CO)_8]$	2078w, 2056m, 1994s, 1966m, 1972w	*trans* isomer; 7.9–7.3 (m, 10H, *Ph*), 3.98 (dd, $^1J(PH) = 308.9$ Hz, $^3J(PH) = 2.1$ Hz, 1H, P*H*), 2.09 (s, 3H, CO*Me*) *cis* isomer; 7.9–7.3 (m, 10H, *Ph*), 3.94 (dd, $^1J(PH) = 310.0$ Hz $^3J(PH) = 1.3$ Hz, 1H, P*H*), 2.09 (s, 3H, CO*Me*)	−231.5 (s, μ-*P*PhH), −152.7 (s, μ-*P*PhCOMe)

[a] Recorded in CH_2Cl_2 solution unless otherwise indicated.
[b] Recorded in $CDCl_3$ solution at 293 K.
[c] Recorded in $CDCl_3$ solution at 293 K; chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative.
[d] Not recorded

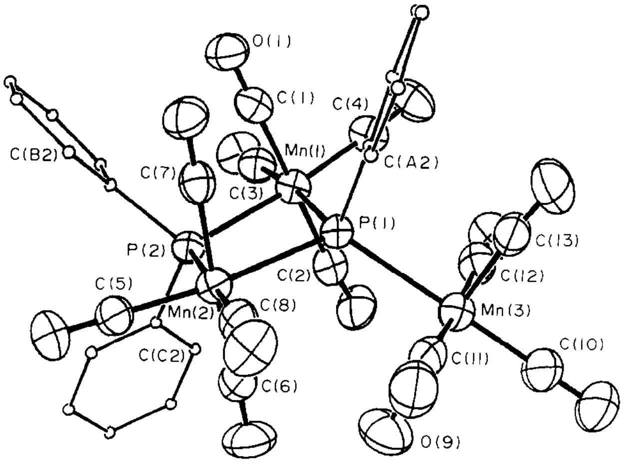


Fig. 1. A view of the molecular structure of $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (4). In the carbonyl ligands the oxygen atoms are labelled by the same numbers as the carbon atoms to which they are bonded, and the C(9) atom is obscured by C(11) and O(11). In the phenyl rings the atoms are numbered cyclically, C(n1)–C(n6), and the C(n1) atom is attached to phosphorus; only the C(n2) atoms are labelled, for clarity (n ≡ A, B or C).

kinetically significant concentrations. Although there were three other minor products of the reaction which were not identified, none of these had an IR spectrum corresponding to that of $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$, which is the major product of the reaction of MeCOCl with a 1:2 mixture of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ and n-BuLi [25].

The ^1H NMR spectrum of a sample of $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (5), obtained by thin layer chromatography (TLC) separation of the reaction mixture above, shows two sets of signals for the PPh*H* protons in approximately equal intensity, indicating the presence of isomers. Crystallization of this sample of 5 from CH_2Cl_2-propan-2-ol by the diffusion method with CH_2Cl_2 as the lower layer gave crystals which, on dissolution in $CDCl_3$, gave only one set of PPh*H* NMR signals, suggesting that one of the isomers crystallizes preferentially from solution and is configurationally stable in $CDCl_3$ at room temperature.

In order to determine the molecular structure of this isomer a single-crystal X-ray analysis was undertaken. The molecular structure is shown in Fig. 2, and Table 4 lists selected bond lengths and angles. Fractional atomic coordinates are given in Table 5.

The geometry about each of the manganese atoms is approximately octahedral and the phenyl groups of the bridging phosphido groups are mutually *trans*. The molecular structure of 5 is closely similar to those of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ and $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$, in which the phenyl groups are also in a mutually *trans* arrangement [25].

The structure of the isomeric complex of 5, identified from ^1H NMR, is assumed to be one in which the phenyl groups of the bridging phosphido groups are mutually *cis* (Scheme 1).

3. Experimental details

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative TLC was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230

Table 2
Selected bond lengths (Å) and angles (°) in $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (4)

Bond lengths			
Mn(1)–P(1)	2.462(2)	Mn(1)–P(2)	2.396(2)
Mn(1)–C(1)	1.846(7)	Mn(1)–C(2)	1.830(7)
Mn(1)–C(3)	1.812(7)	Mn(1)–C(4)	1.812(7)
Mn(2)–P(1)	2.474(2)	Mn(2)–P(2)	2.372(2)
Mn(2)–C(5)	1.810(7)	Mn(2)–C(6)	1.837(7)
Mn(2)–C(7)	1.845(7)	Mn(2)–C(8)	1.814(7)
Mn(3)–P(1)	2.563(2)	Mn(3)–C(9)	1.861(8)
Mn(3)–C(10)	1.816(8)	Mn(3)–C(11)	1.828(8)
Mn(3)–C(12)	1.854(8)	Mn(3)–C(13)	1.849(8)
P(1)–C(A1)	1.893(6)	P(2)–C(B1)	1.871(7)
P(2)–C(C1)	1.867(7)		
Bond angles			
P(1)–Mn(1)–P(2)	79.2(1)	P(1)–Mn(1)–C(1)	89.4(3)
P(1)–Mn(1)–C(2)	88.7(3)	P(1)–Mn(1)–C(3)	172.9(3)
P(1)–Mn(1)–C(4)	97.2(3)	P(2)–Mn(1)–C(1)	83.4(3)
P(2)–Mn(1)–C(2)	95.6(3)	P(2)–Mn(1)–C(3)	94.2(3)
P(2)–Mn(1)–C(4)	172.4(3)	C(1)–Mn(1)–C(2)	178.0(4)
C(1)–Mn(1)–C(3)	92.3(3)	C(1)–Mn(1)–C(4)	90.0(3)
C(2)–Mn(1)–C(3)	89.5(3)	C(2)–Mn(1)–C(4)	90.9(3)
C(3)–Mn(1)–C(4)	89.7(3)	P(1)–Mn(2)–P(2)	79.4(1)
P(1)–Mn(2)–C(5)	169.7(3)	P(1)–Mn(2)–C(6)	92.0(3)
P(1)–Mn(2)–C(7)	84.3(2)	P(1)–Mn(2)–C(8)	100.3(2)
P(2)–Mn(2)–C(5)	90.8(2)	P(2)–Mn(2)–C(6)	88.2(3)
P(2)–Mn(2)–C(7)	92.5(3)	P(2)–Mn(2)–C(8)	178.3(3)
C(5)–Mn(2)–C(6)	90.9(3)	C(5)–Mn(2)–C(7)	93.0(3)
C(5)–Mn(2)–C(8)	89.6(3)	C(6)–Mn(2)–C(7)	176.0(3)
C(6)–Mn(2)–C(8)	90.2(3)	C(7)–Mn(2)–C(8)	89.1(3)
P(1)–Mn(3)–C(9)	92.2(3)	P(1)–Mn(3)–C(10)	176.0(3)
P(1)–Mn(3)–C(11)	85.3(3)	P(1)–Mn(3)–C(12)	89.7(3)
P(1)–Mn(3)–C(13)	90.5(3)	C(9)–Mn(3)–C(10)	89.5(4)
C(9)–Mn(3)–C(11)	91.4(4)	C(9)–Mn(3)–C(12)	90.8(4)
C(9)–Mn(3)–C(13)	177.1(3)	C(10)–Mn(3)–C(11)	91.0(4)
C(10)–Mn(3)–C(12)	93.9(4)	C(10)–Mn(3)–C(13)	87.8(4)
C(11)–Mn(3)–C(12)	174.6(4)	C(11)–Mn(3)–C(13)	89.9(4)
C(12)–Mn(3)–C(13)	88.2(3)	Mn(1)–P(1)–Mn(2)	98.0(1)
Mn(1)–P(1)–Mn(3)	118.1(1)	Mn(1)–P(1)–C(A1)	112.1(3)
Mn(2)–P(1)–Mn(3)	121.8(1)	Mn(2)–P(1)–C(A1)	108.0(2)
Mn(3)–P(1)–C(A1)	99.0(2)	Mn(1)–P(2)–Mn(2)	102.8(1)
Mn(1)–P(2)–C(B1)	109.8(3)	Mn(1)–P(2)–C(C1)	119.3(2)
Mn(2)–P(2)–C(B1)	115.9(3)	Mn(2)–P(2)–C(C1)	112.4(3)
C(B1)–P(2)–C(C1)	97.4(4)		

Table 3
Fractional atomic coordinates and isotropic thermal parameters (Å^2) (for [Mn_2 (μ-PPh_2){μ-PPhMn$(CO)_5$}$(CO)_8$] (**4**)

Atom	*x*	*y*	*z*	*U* [a] (Å^2)
Mn(1)	−0.13678(11)	0.30773(7)	0.31783(5)	0.042
Mn(2)	0.06671(11)	0.17264(7)	0.15777(5)	0.040
Mn(3)	0.25229(12)	0.15695(9)	0.41952(6)	0.053
P(1)	0.02348(18)	0.15496(12)	0.29528(9)	0.035
P(2)	−0.06420(18)	0.33169(12)	0.19265(9)	0.036
O(1)	−0.4193(6)	0.1416(4)	0.1933(3)	0.064
O(2)	0.1403(7)	0.4720(4)	0.4460(3)	0.071
O(3)	−0.3078(6)	0.5068(4)	0.3363(3)	0.071
O(4)	−0.2561(7)	0.2490(4)	0.4569(3)	0.079
O(5)	0.0740(6)	0.2174(4)	−0.0069(3)	0.068
O(6)	0.3730(6)	0.3397(5)	0.2398(3)	0.083
O(7)	−0.2337(6)	−0.0061(4)	0.0813(3)	0.060
O(8)	0.2372(6)	−0.0209(4)	0.1126(3)	0.066
O(9)	0.4362(8)	0.3877(5)	0.4209(4)	0.099
O(10)	0.5209(7)	0.1394(6)	0.5532(3)	0.096
O(11)	0.3898(7)	0.0208(5)	0.2909(3)	0.090
O(12)	0.0919(7)	0.2817(4)	0.5438(3)	0.076
O(13)	0.0923(7)	−0.0683(4)	0.4383(3)	0.086
C(1)	−0.3094(8)	0.2030(5)	0.2404(4)	0.050
C(2)	0.0388(9)	0.4083(5)	0.3931(4)	0.053
C(3)	−0.2421(8)	0.4287(5)	0.3265(4)	0.050
C(4)	−0.2046(8)	0.2700(5)	0.4042(4)	0.053
C(5)	0.0709(7)	0.2013(5)	0.0571(4)	0.047
C(6)	0.2553(8)	0.2773(6)	0.2105(4)	0.050
C(7)	−0.1214(8)	0.0641(5)	0.1115(4)	0.046
C(8)	0.1720(8)	0.0536(5)	0.1332(4)	0.048
C(9)	0.3633(9)	0.3002(7)	0.4170(4)	0.067
C(10)	0.4171(9)	0.1491(7)	0.5028(4)	0.067
C(11)	0.3335(8)	0.0746(7)	0.3377(4)	0.059
C(12)	0.1515(9)	0.2357(6)	0.4952(4)	0.056
C(13)	0.1480(8)	0.0160(6)	0.4277(4)	0.055
C(A1)	−0.0944(8)	0.0014(4)	0.2769(3)	0.038(1)
C(A2)	−0.0470(4)	−0.0950(4)	0.2321(3)	0.051(2)
C(A3)	−0.1309(7)	−0.2079(3)	0.2183(4)	0.056(2)
C(A4)	−0.2621(7)	−0.2245(4)	0.2492(3)	0.057(2)
C(A5)	−0.3094(5)	−0.1281(4)	0.2940(3)	0.061(2)
C(A6)	−0.2256(9)	−0.0152(4)	0.3079(5)	0.046(2)
C(B1)	−0.2440(6)	0.3323(8)	0.1100(4)	0.041(1)
C(B2)	−0.3054(8)	0.2408(5)	0.0363(5)	0.048(2)
C(B3)	−0.4488(9)	0.2386(5)	−0.0177(3)	0.063(2)
C(B4)	−0.5307(6)	0.3279(6)	0.0021(4)	0.079(2)
C(B5)	−0.4692(8)	0.4194(4)	0.0759(5)	0.079(2)
C(B6)	−0.3258(10)	0.4216(6)	0.1298(3)	0.063(2)
C(C1)	0.0540(9)	0.4763(5)	0.1961(3)	0.045(2)
C(C2)	0.1299(7)	0.5643(4)	0.2710(2)	0.091(3)
C(C3)	0.2182(11)	0.6663(6)	0.2706(3)	0.118(4)
C(C4)	0.2445(8)	0.6802(4)	0.1951(3)	0.088(3)
C(C5)	0.1756(8)	0.5922(5)	0.1201(3)	0.084(3)
C(C6)	0.0804(12)	0.4903(7)	0.1206(3)	0.075(2)

[a] For Mn, P, O and C(1)–C(13) atoms, *U* is equivalent isotropic thermal parameter defined as $U = \frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{i=1}^{3}U_{ij}a_i^*a_j^*(\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

mesh) or (230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously [15]. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification.

3.1. Preparations

The new complexes were prepared as follows.

3.1.1. [Mn_2(μ-PPh_2)(μ-PPhH)$(CO)_8$] (1)

A solution of [$Mn_2(CO)_{10}$] (0.520 g, 1.33 mmol) in 50 cm^3 of undried decalin (99% as received from the suppliers Aldrich) was heated to 433 K and PPh_2H (240 μl, 1.38 mmol) was added. The solution was stirred at 433 K for 2.25 h and a further quantity of $PPhH_2$ (150 μl, 1.36 mmol) was then added. After stirring at 433 K for a further hour, CO was bubbled through the solution, which changed colour immediately from orange to yellow. The solvent was removed under reduced pressure and the residue was redissolved in the minimum quantity of CH_2Cl_2. TLC on silica with CH_2Cl_2 : hexane (3 : 7) as eluent gave five yellow bands, of which the first two, in order of decreasing R_f values, were shown to contain [Mn_2(μ-$PPhH)_2(CO)_8$] [25] (0.045 g (6%)) and [Mn_2(μ-PPh_2)(μ-PPhH)$(CO)_8$] (**1**) (0.168 g (20%)), respectively. The remaining three bands gave low yields of products that could not be characterized. Anal. Found; C, 49.5; H, 2.8. $C_{26}H_{16}Mn_2O_8P_2$ calc.: C, 49.7; H, 2.8%. Mass spectrum: *m/z* 600 ($M^+ -$ CO) and $M^+ - n$(CO) (n = 1–4).

3.1.2. [Mn_2(μ-PPh_2)(μ-PPhCl)$(CO)_8$] (2)

A solution of [Mn_2(μ-PPh_2)(μ-PPhH)$(CO)_8$] (**1**) in CCl_4 (25 cm^3) was heated to 343 K for 17 h and the

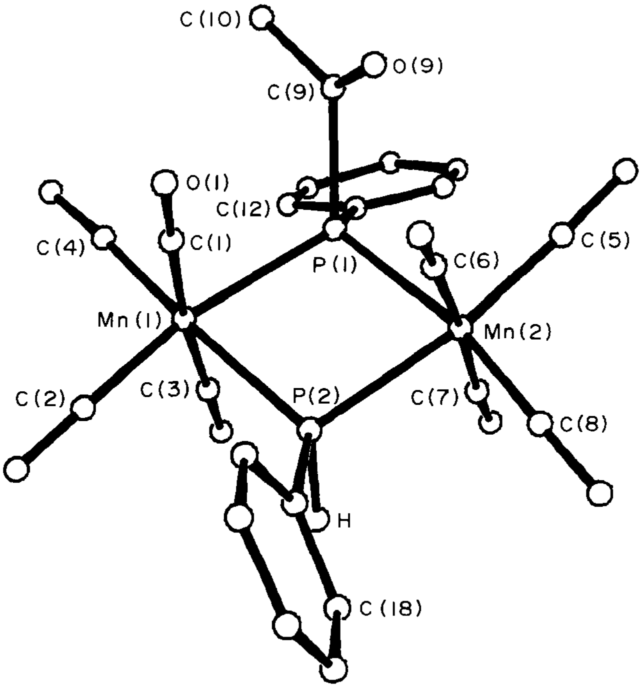


Fig. 2. A view of the structure of [Mn_2(μ-PPhH)(μ-PPhCOMe)$(CO)_8$] (**5**). In the phenyl rings the carbon atoms are numbered progressively, C(*n*), C(*n* + 1),...,C(*n* + 5), with the C(*n*) atom bonded to phosphorus; only the C(*n* + 1) atoms are labelled, for clarity.

solvent was then removed under reduced pressure. Separation of the residue by TLC with CH_2Cl_2 : hexane (2 : 3) as eluent gave one yellow band, which gave microcrystalline [Mn_2(μ-PPh_2)(μ-PPhCl)$(CO)_8$] (**2**) (0.20 g (76%)) on evaporation of the solvent. Anal. Found: C, 46.7; H, 2.5. $C_{26}H_{15}ClMn_2O_8P_2$ calc.: C, 47.1; H, 2.3%. Mass spectrum: *m/z* 662 (M^+) and $M^+ - CO$.

3.1.3. *[Mn_2(μ-PPh_2(μ-PPhMe)$(CO)_8$] (3a)*

A solution of [Mn_2(μ-PPh_2)(μ-PPhH)$(CO)_8$] (**1**) (0.025 g, 0.040 mmol) in tetrahydrofuran (THF) (15 cm^3) was cooled to 195 K and *n*-BuLi (16 μl of a 2.5 M solution, 0.040 mmol) was added, causing the colour of the solution to change immediately from yellow to red. After 5 min an excess (1 cm^3) of CH_3I was added resulting in an instant colour change from red to yellow. The solution was stirred for 10 min at 195 K and then for a further 1 h at room temperature. The THF was removed under vacuum and the residue separated by TLC with CH_2Cl_2 : hexane (2 : 3) as eluent. One yellow band was obtained and gave microcrystalline [Mn_2(μ-PPh_2)(μ-PPhMe)$(CO)_8$] (**3a**) on evaporation of the solvent. Anal. Found: C, 50.0; H, 2.9. $C_{27}H_{18}Mn_2O_8P_2$ calc.: C, 50.5; H, 2.8%. Mass spectrum: *m/z* 614 ($M^+ - CO$) and $M^+ - n(CO)$ ($n = 1$–4).

Table 4
Selected bond lengths (Å) and angles (°) in [Mn_2(μ-PPhH)(μ-PPhCOMe)$(CO)_8$] (**5**)

Bond lengths			
Mn(1)–P(1)	2.368(6)	Mn(1)–P(2)	2.346(6)
Mn(1)–C(1)	1.78(2)	Mn(1)–C(2)	1.77(2)
Mn(1)–C(3)	1.77(2)	Mn(1)–C(4)	1.75(3)
Mn(2)–P(1)	2.365(7)	Mn(2)–P(2)	2.349(6)
Mn(2)–C(5)	1.78(3)	Mn(2)–C(6)	1.81(2)
Mn(2)–C(7)	1.79(2)	Mn(2)–C(8)	1.72(3)
P(1)–C(9)	1.91(3)	P(1)–C(11)	1.77(2)
P(2)–C(17)	1.78(2)	O(9)–C(9)	1.25(3)
C(9)–C(10)	1.46(3)		
Bond angles			
P(1)–Mn(1)–P(2)	76.7(2)	P(1)–Mn(1)–C(1)	85.8(6)
P(1)–Mn(1)–C(2)	168.6(6)	P(1)–Mn(1)–C(3)	89.3(7)
P(1)–Mn(1)–C(4)	98.6(7)	P(2)–Mn(1)–C(1)	92.1(6)
P(2)–Mn(1)–C(2)	91.9(6)	P(2)–Mn(1)–C(3)	84.4(7)
P(2)–Mn(1)–C(4)	174.1(7)	C(1)–Mn(1)–C(2)	94.9(8)
C(1)–Mn(1)–C(3)	174.5(9)	C(1)–Mn(1)–C(4)	91.1(9)
C(2)–Mn(1)–C(3)	89.4(9)	C(2)–Mn(1)–C(4)	92.7(9)
C(3)–Mn(1)–C(4)	92.1(9)	P(1)–Mn(2)–P(2)	76.7(2)
P(1)–Mn(2)–C(5)	96.4(7)	P(1)–Mn(2)–C(6)	92.1(6)
P(1)–Mn(2)–C(7)	88.0(7)	P(1)–Mn(2)–C(8)	169.0(7)
P(2)–Mn(2)–C(5)	171.6(7)	P(2)–Mn(2)–C(6)	86.7(6)
P(2)–Mn(2)–C(7)	88.5(7)	P(2)–Mn(2)–C(8)	92.6(7)
C(5)–Mn(2)–C(6)	88.8(8)	C(5)–Mn(2)–C(7)	96.1(9)
C(5)–Mn(2)–C(8)	94.5(9)	C(6)–Mn(2)–C(7)	175.1(9)
C(6)–Mn(2)–C(8)	89.3(9)	C(7)–Mn(2)–C(8)	89.7(9)
Mn(1)–P(1)–Mn(2)	102.4(3)	Mn(1)–P(1)–C(9)	113.2(7)
Mn(1)–P(1)–C(11)	115.8(7)	Mn(2)–P(1)–C(9)	112.0(8)
Mn(2)–P(1)–C(11)	116.6(7)	C(9)–P(1)–C(11)	97(1)
Mn(1)–P(2)–Mn(2)	103.5(3)	Mn(1)–P(2)–C(17)	112.5(7)
Mn(2)–P(2)–C(17)	114.8(7)	P(1)–C(9)–O(9)	115(2)
P(1)–C(9)–C(10)	121(2)	O(9)–C(9)–C(10)	121(2)

Table 5
Fractional atomic coordinates and isotropic thermal parameters in [Mn_2(μ-PPhH)(μ-PPhCOMe)$(CO)_8$] (**5**)

Atom	*x*	*y*	*z*	*U* [a] (Å)
Mn(1)	0.2783(2)	0.2883(3)	0.1521(1)	0.041
Mn(2)	0.2582(2)	−0.0596(3)	0.0918(1)	0.039
P(1)	0.3363(3)	0.0793(6)	0.1431(2)	0.036
P(2)	0.2066(3)	0.1571(5)	0.0929(2)	0.031
O(1)	0.2323(7)	0.1541(14)	0.2467(5)	0.065(4)
O(2)	0.1864(7)	0.5218(16)	0.1465(5)	0.071(5)
O(3)	0.3274(7)	0.3932(14)	0.0541(5)	0.064(4)
O(4)	0.3792(8)	0.4459(16)	0.2176(6)	0.077(5)
O(5)	0.3315(7)	−0.3214(15)	0.1094(6)	0.073(5)
O(6)	0.1855(7)	−0.1319(14)	0.1834(5)	0.064(4)
O(7)	0.3198(7)	0.0227(15)	−0.0032(6)	0.071(5)
O(8)	0.1499(7)	−0.1824(16)	0.0215(6)	0.073(5)
O(9)	0.3297(9)	−0.0958(19)	0.2251(7)	0.114(7)
C(1)	0.2799(9)	0.2089(21)	0.2093(7)	0.044(6)
C(2)	0.2230(10)	0.4286(20)	0.1499(7)	0.039(5)
C(3)	0.3076(10)	0.3510(21)	0.0929(8)	0.054(7)
C(4)	0.3384(12)	0.3788(23)	0.1931(9)	0.057(7)
C(5)	0.3023(10)	−0.2179(22)	0.1007(7)	0.047(6)
C(6)	0.2178(10)	−0.1023(19)	0.1502(8)	0.045(6)
C(7)	0.2936(10)	−0.0047(12)	0.0333(8)	0.052(6)
C(8)	0.1938(10)	−0.1316(20)	0.0515(8)	0.049(6)
C(9)	0.3664(12)	−0.0045(26)	0.2102(9)	0.074(8)
C(10)	0.4133(14)	0.0650(28)	0.2487(11)	0.117(9)
C(11)	0.4135(10)	0.0966(21)	0.1188(8)	0.051(6)
C(12)	0.4502(11)	0.2131(24)	0.1236(8)	0.067(7)
C(13)	0.5115(13)	0.2224(28)	0.1054(9)	0.094(8)
C(14)	0.5434(12)	0.1081(27)	0.0868(9)	0.085(8)
C(15)	0.5046(14)	−0.0053(31)	0.0796(11)	0.109(9)
C(16)	0.4427(13)	−0.0148(25)	0.0976(9)	0.084(8)
C(17)	0.1214(10)	0.1498(20)	0.0977(8)	0.044(6)
C(18)	0.0754(12)	0.1372(22)	0.0551(8)	0.061(7)
C(19)	0.0104(14)	0.1200(28)	0.0604(11)	0.099(9)
C(20)	−0.0093(12)	0.1123(26)	0.1062(11)	0.084(9)
C(21)	0.0297(14)	0.1233(26)	0.1505(10)	0.086(9)
C(22)	0.0976(12)	0.1424(24)	0.1472(9)	0.083(8)

[a] For Mn and P atoms, *U* is equivalent isotropic thermal parameters defined as $U = \frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^* a_j^*(\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

3.1.4. *[Mn_2(μ-PPh_2)(μ-PPhEt)$(CO)_8$] (3b)*

In a procedure analogous to that in Section 3.1.3, a solution of **1** (0.025 g, 0.40 mmol) in THF (15 cm^3) was treated with *n*-BuLi (16 μl of a 2.5 M solution, 0.040 mmol) and the resulting mixture was reacted with an excess (1 cm^3) of EtI. Separation of the residue as Section 3.1.3 gave, in order of decreasing R_f values, yellow [Mn_2(μ-PPh_2)(μ-PPhEt)$(CO)_8$] (**3b**) (0.008 g (31%) and a second yellow band which was not characterized. Anal. Found: C, 50.5; H, 3.4. $C_{28}H_{20}Mn_2O_8P_2$ calc.: C, 51.2; H, 3.0%. Mass spectrum: *m/z* 628 ($M^+ - CO$), $M^+ - n(M^+ - CO)$($n = 1$–5).

3.1.5. *[Mn_2(μ-PPh_2){μ-PPh(CH_2COMe)}$(CO)_8$] (3c)*

In a procedure analogous to that in Section 3.1.3, a solution of **1** (0.025 g, 0.040 mmol) in THF (15 cm^3)

was treated with *n*-BuLi (16 μl of a 2.5 M solution, 0.040 mmol) and the resulting mixture was treated with an excess (1 cm^3) of $MeCOCH_2Cl$. Separation of the residue by TLC gave (decreasing R_f values) unreacted **1** (0.003 g), a red band which was not characterized, and yellow $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh(CH_2COMe)\}(CO)_8]$ (**3c**) (0.009 g (34%)). Anal. Found: C, 51.2; H, 3.0. $C_{29}H_{20}Mn_2O_9P_2$ calc.: C, 50.9; H, 2.9%. Mass spectrum: *m/z* 628 ($M^+ - 2CO$) and $M^+ - n(CO)$ ($n = 2$–6).

3.1.6. $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}PPhCO_2Et)(CO)_8]$ (3d)

This was prepared as in Section 3.1.3 using **1** (0.025 g, 0.050 mmol) in THF (15 cm^3), *n*-BuLi (16 μl of a 2.5 M solution, 0.040 mmol) and an excess of $EtCO_2Cl$ (1 cm^3). TLC separation with CH_2Cl_2 : hexane (2 : 3) as eluent gave **1** (0.002 g), an unidentified red band and yellow $[Mn_2(\mu\text{-}PPh)(\mu\text{-}PPhCO_2Et)(CO)_8]$ (**3d**) (0.009 g (33%)). Anal. Found: C, 49.6; H, 2.8. $C_{29}H_{20}Mn_2O_{10}P_2$ calc.: C, 49.7; H, 2.9%. Mass spectrum: *m/z* 672 ($M^+ - CO$) and $M^+ - 2CO$.

3.1.7. $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (4)

This was prepared as in Section 3.1.3 using **1** (0.050 g, 0.080 mmol) in THF (30 cm^3), and *n*-BuLi (32 μl of a 2.5 M solution, 0.080 mmol). The resulting red solution was treated with $[Mn(CO)_5Br]$ (0.022 g, 0.080 mmol) and, after removal of solvent, the residue was separated by TLC with CH_2Cl_2 : hexane (2 : 3) as eluent. The three bands eluted were identified as **1** (0.015 g), yellow $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (**4**) (0.021 g (32%)) and $[Mn(CO)_5Br]$ (0.004 g). Anal. Found: C, 44.6; H, 45.3. $C_{30}H_{15}Mn_3O_{12}P_2$ calc.: C, 45.3; H, 1.9%. Mass spectrum: *m/z* 794 ($M^+ - CO$), $M^+ - n(CO)$ ($n = 1$–4).

3.1.8. $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (5)

A solution of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ [25] (0.200 g, 0.362 mmol) in THF (15 cm^3) was treated with *n*-BuLi (145 μl of a 2.5 M solution, 0.362 mmol) as in Section 3.1.3, and the resulting red solution was treated with an excess of MeCOCl (1 cm^3). Separation of the reaction residue by TLC with CH_2Cl_2 : hexane (35 : 65) as eluent gave five bands. The first band (decreasing R_f values) yielded $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ (0.095 g) and the third band the yellow $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (**5**) (0.060 g (28%)). The other bands did not yield sufficient material to permit characterization. Anal. Found: C, 44.4; H, 2.5. $C_{22}H_{14}Mn_2O_9P_2$ calc.: C, 44.4; H, 2.4%. Mass spectrum: *m/z* 594 (M^+) and $M^+ - n(CO)$ ($n = 1, 2$).

3.2. Crystal structure analysis of 4 and 5

Table 6
Crystallographic data and for the complexes $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}PPhMn(CO)_5\}(CO)_8]$ (**4**) and $[Mn_2(\mu\text{-}PPhH)(\mu\text{-}PPhCOMe)(CO)_8]$ (**5**)

	4	**5**
Formula	$C_{31}H_{15}Mn_3O_{13}P_2$	$C_{22}H_{14}Mn_2O_9P_2$
M	822.21	594.17
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	8.852(1)	20.63(1)
b (Å)	11.886(1)	9.652(5)
c (Å)	16.790(2)	25.11(1)
α (°)	103.90(1)	90
β (°)	102.64(1)	96.43(4)
γ (°)	97.87(1)	90
U (Å^3)	1639.4	4968.5
Z	2	8
D_c (g cm^{-3})	1.666	1.589
F(000)	820	2384
μ (cm^{-1})	12.52	11.50
θ range (°)	2–25	2–20
Number of reflections measured	6955	2744
Number of unique reflections	5751	2302
Number of unique reflections with $I \geqslant f\sigma(I)$	3588 ($f = 3$)	1040 ($f = 2$)
R_{int}	0.025	0.057
R	0.049	0.063
R_w	0.064	0.069
$(\Delta\rho)_{max}$ electron Å^{-3}	0.86	0.56

Crystallographic measurements were made at 295 K with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and on an Enraf–Nonius CAD4 diffractometer. The crystal of **4** was an orange–red prism of 0.08 × 0.32 × 0.44 mm and that of **5** was a thin yellow plate of 0.01 × 0.80 × 0.80 mm^3.

For each compound the unit-cell dimensions (Table 6) were determined by a least-squares treatment of diffractometeric setting angles for 23 reflections. The intensity data were measured by continuous ω–2θ scans, with the width in ω of 0.60° for **4** and 0.80° for **5**. For each compound, two standard reflections were remeasured every 2 h during data collection and they showed no significant variation in intensity. The integrated intensities of all reflections, derived in the usual manner ($q = 0.03$) [28], were corrected for Lorentz, polarization and absorption effects. The latter correction, made by an empirical method [29], led to transmission factors on *F* of 0.76–1.13 for **4** and 0.75–1.49 for **5**. Of measured reflections (Table 6) only the unique reflections with $I \geqslant f\sigma(I)$, of which there were 3588 ($f = 3$) for **4** and 1040 ($f = 2$) for **5**, were used in the structure analyses.

The structures were solved by Patterson and difference Fourier methods. They were refined to convergence ($\Delta/\sigma \leqslant 0.06$) by full-matrix least-squares method based on *F* ($W = \sigma^{-2}(F_o)$). All calculations were performed using the GX program package [30], and the neutral atom scattering factors and anomalous dispersion corrections were taken from [31].

In the refinement of **4** the carbon atoms of the phenyl groups were allowed isotropic displacement parameters and the remaining non-hydrogen atoms anisotropic displacement parameters. The phenyl rings were treated as rigid bodies constrained to D_{6h} symmetry; C–C, 1.38 Å; C–H, 0.96 Å; $U(\mathrm{H}) = 1.2U(\mathrm{C})$. In the structural model of **5** the manganese and phosphorus atoms were assigned anisotropic displacement parameters, and oxygen and carbon atoms isotropic displacement parameters. The hydrogen atoms were initially placed in calculated positions (P–H, 1.40; C–H, 0.96 Å), the orientation of the methyl groups being obtained from a small-angle difference synthesis. They were allowed to ride on the carbon atoms to which they are bonded, with an isotropic displacement parameter fixed at $U = 0.10$ Å^2. The residual electron density in the final difference synthesis showed no chemically significant features for either compound.

Tables of H-atom coordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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