Synthesis, Structure and Isomerism of $[Mn_2(\mu\text{-}PPhR)_2(CO)_8]$ (R = H, alkyl, acyl or carboxylate); Crystal Structures of *trans*-$[Mn_2(\mu\text{-}PPhR)_2(CO)_8]$ (R = H or COMe) †

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The thermal reaction of $[Mn_2(CO)_{10}]$ with $PPhH_2$ in undried decalin at 150 °C gives $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ as a *cis–trans* mixture of isomers. Recrystallisation enables the *trans* isomer to be separated from this mixture and the structure of this isomer has been determined by X-ray diffraction analysis. The *trans* isomer is configurationally stable in toluene at room temperature but isomerises in more polar solvents or on heating. Possible mechanisms for this isomerisation are investigated. Deprotonation of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ followed by treatment with a range of organic halides, RX, gives the complexes $[Mn_2(\mu\text{-}PPhR)_2(CO)_8]$ which also exhibit *cis–trans* isomerism in solution. Recrystallisation of one of these complexes, $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$, gives the *trans* isomer, the structure of which has also been determined by X-ray analysis.

The preparation of the dinuclear iron complex $[Fe_2(\mu\text{-}PPhH)_2(CO)_6]$ was first reported by Treichel *et al.*,[1] who obtained it from the reaction of $[Fe_2(CO)_9]$ with $PPhH_2$ at room temperature. A better high-yield procedure involving reaction of $PPhH_2$ with $[Fe(CO)_5]$ in octane at 100–105 °C was later developed by Stelzer and co-workers.[2] The complex contains a non-planar Fe_2P_2 core and exists in solution as a mixture of three possible isomers (Fig. 1) which proved impossible to separate, although there is reference to an unpublished X-ray crystal-structure determination of the axial, axial diphenyl species.[1] The isomers are configurationally stable in solution at room temperature.[3]

We are interested in the chemistry of phosphido-bridged dimanganese complexes[4–6] and in this paper report the synthesis of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1**, and a study of the isomerism of this complex. We also describe the synthesis and isomerism of $[Mn_2(\mu\text{-}PPhR)_2(CO)_8]$ **2** (R = Me, **2a**; Et, **2b**; Pr^n, **2c**; COMe, **2d**; CH_2COMe, **2e**; or CO_2Et, **2f**) obtained by deprotonation of **1** and subsequent reaction of the deprotonated species with the appropriate halide, RX. If, as expected, the complexes **1** and **2** have a planar Mn_2P_2 core[7] then two isomers are possible in each case which may or may not be separable and configurationally stable.

Results and Discussion

Synthesis, Isomerism and Reactivity of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$.—Reaction of $[Mn_2(CO)_{10}]$ with 2 equivalents of $PPhH_2$ in undried decalin at 150 °C gives $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1** in *ca.* 56% yield together with $[Mn_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_8]$ **3** in *ca.* 3% yield. The ^1H NMR spectrum of **1** (see below) showed that a mixture of two isomers was present in $CDCl_3$ solution at room temperature. Although these isomers could not be separated by TLC, crystallisation of **1** from CH_2Cl_2–hexane by the diffusion method gave crystals which were subjected to X-ray analysis and shown to consist exclusively of the *trans* isomer **1a**. The molecular structure of **1a** is shown in Fig.2. Selected bond lengths and bond angles are listed in Table 1 and fractional coordinates in Table 2.

The molecule has an inversion centre (in the crystals); the geometry about each of the manganese atoms is approximately

Table 1 Selected bond lengths (Å) and angles (°) for $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$

Mn(1)–P(1)	2.354(2)	P(1)–Mn(1)–P(1*)	77.0(1)
Mn(1)–P(1*)	2.358(2)	Mn(1)–P(1)–Mn(1*)	103.1(1)
P(1)–H(1)	1.26(3)	Mn(1)–P(1)–H(1)	109(1)
P(1)–C(11)	1.830(3)	Mn(1)–P(1)–C(11)	121.0(1)
Mn–C	1.821(4)–1.842(3)	H(1)–P(1)–C(11)	98(1)
C–O	1.134(4)–1.141(5)		
C–C	1.338(6)–1.382(6)		
C–H	0.89(3)–0.95(3)		

* Symmetry equivalent atoms at $-x, -y, -z$.

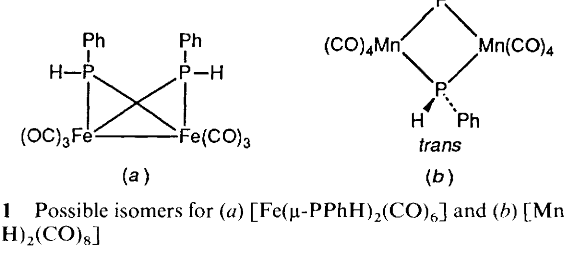

Fig. 1 Possible isomers for (*a*) $[Fe(\mu\text{-}PPhH)_2(CO)_6]$ and (*b*) $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$

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† *trans*-Bis(μ-phenylphosphido)- and *trans*-bis(μ-acetylphenylphosphido)-bis(tetracarbonylmanganese).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

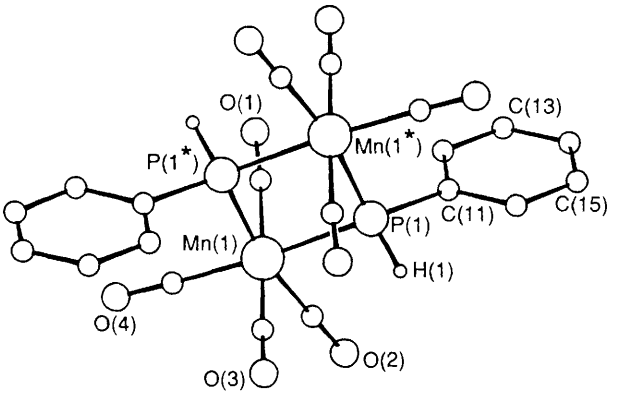


Fig. 2 Molecular structure of *trans*-$[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1a** showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

Table 2 Fractional atomic coordinates for $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$

Atom	*x*	*y*	*z*
Mn(1)	0.0839(1)	0.1212(1)	0.1068(1)
P(1)	0.1651(1)	0.0524(1)	−0.1315(1)
C(1)	−0.0580(4)	0.2811(4)	0.0320(4)
O(1)	−0.1524(4)	0.3779(3)	−0.0063(3)
C(2)	0.2915(4)	0.2526(4)	0.0493(4)
O(2)	0.4233(3)	0.3313(3)	0.0113(3)
C(3)	0.2069(4)	−0.0529(4)	0.1837(3)
O(3)	0.2854(4)	−0.1595(3)	0.2277(3)
C(4)	−0.0043(4)	0.1483(4)	0.3019(4)
O(4)	−0.0623(4)	0.1670(4)	0.4232(3)
H(1)	0.3077(40)	−0.0257(35)	−0.1361(34)
C(11)	0.2463(4)	0.2039(3)	−0.3205(3)
C(12)	0.1768(6)	0.3483(4)	−0.3551(4)
C(13)	0.2367(7)	0.4560(5)	−0.5023(5)
C(14)	0.3654(6)	0.4198(5)	−0.6163(4)
C(15)	0.4379(7)	0.2756(6)	−0.5858(5)
C(16)	0.3802(6)	0.1689(5)	−0.4375(4)
H(12)	0.0959(45)	0.3785(37)	−0.2808(38)
H(13)	0.1931(44)	0.5511(40)	−0.5237(37)
H(14)	0.4090(44)	0.4867(39)	−0.7143(40)
H(15)	0.5322(42)	0.2508(36)	−0.6652(39)
H(16)	0.4418(42)	0.0878(40)	−0.4101(39)

octahedral (four carbonyl groups and two phosphorus atoms). The Mn–C bond distances show the expected variation with the π acidity of the *trans* ligand.[8–10] Thus the Mn–C bond lengths of 1.840(4) Å and 1.842(3) Å for the axial carbonyls (*trans* to CO) are longer than those [1.828(4) and 1.821(4) Å] for the equatorial carbonyls (*trans* to PPhH). The Mn–P bond distances [2.354(2) and 2.358(2) Å] are significantly shorter than those in $[Mn_2(\mu\text{-}PPh_2)_2(CO)_8]$ of 2.383(2), 2.389(2), 2.386(2) and 2.394(2) Å,[11] perhaps reflecting the lower steric bulk of the μ-PPhH as compared to the $\mu\text{-}PPh_2$ ligand. They are, however, slightly longer than the Mn–P bond distances in $[Mn_2(\mu\text{-}PMe_2)_2(CO)_8]$.[7] The P–H bonds in **1a** are *trans* and the dihedral angle between the H and the phenyl groups on P(1) is 98(1)°, which is rather larger than the angles between the two phenyl groups in $[Mn_2(\mu\text{-}PPh_2)_2(CO)_8]$ (77 and 82°). The Mn–P–Mn angle of 103.1(1)° may be compared with those of 101.4(1) and 101.0(1)° in the diphenylphosphido complex and angles of this magnitude are normally associated with the absence of any significant interaction between the two metal centres.[12] In $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ where the effective atomic number rule requires such an interaction the Mn–P–Mn angle is 78.7(1)°.[5]

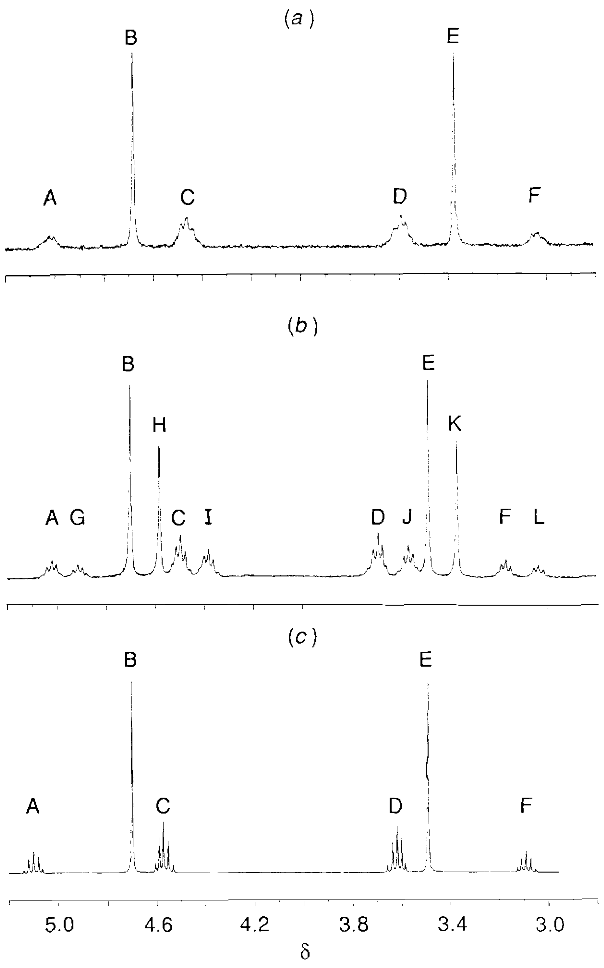
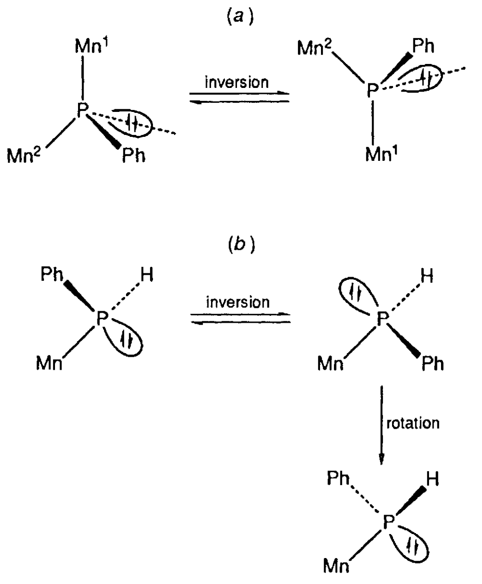


Fig. 3 Proton NMR spectrum in the PH region of (*a*) *trans*-$[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1a** (*b*) the *cis–trans* mixture of **1a** and **1b** obtained in the original synthesis and (*c*) the simulated spectrum for **1a**

The ^1H NMR spectrum of *trans*-$[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1a** in $CDCl_3$ solution in the PPh*H* region is shown in Fig. 3(*a*) and is a second-order AA′XX′ spectrum. The H–P–P–H spin system should show a maximum of 10 lines, comprising a doublet with intensity 2 separated by ${}^1J_{PH} + {}^3J_{PH}$ and two AB subspectra. The latter have effective AB chemical shifts of $\pm\frac{1}{2}({}^1J_{PH} - {}^3J_{PH})$ and coupling constants equal to $(J_{PP} + J_{HH})$ and $(J_{PP} - J_{HH})$ respectively.[13] Although the spectrum has the expected general features (a sharp doublet flanked by AB subspectra) there are five rather than two subspectra. Decoupling experiments show that this additional structure is due to coupling with *o*-phenyl protons.

At first sight it is surprising that coupling to other nuclei splits the AB subspectra and not the sharp doublet. However it is not the protons that are coupled to the phenyl group but the phosphorus nuclei. The sharp doublet in the proton spectrum arises from molecules in which both phosphorus atoms have the same spin quantum number (both in state α or both β). The two lines in the proton spectrum arising from these phosphorus spin states are unaffected by any other coupling to the phosphorus nuclei. However, the AB subspectra arise from molecules in which the phosphorus nuclei are in different spin states (one α and one β). These subspectra are altered if the phosphorus spins are not in symmetrically equivalent environments. In isomers **1a** and **1b** the environment of each phosphorus spin depends on the spin state (m_z = 1, 0 or −1) of the pair of *o*-protons on the adjacent phenyl group. The quintuplet of AB subspectra observed for these compounds correspond to the five ways in which the spin states on the two phenyl groups can differ (Δm = 2, 1, 0, −1 or −2). The simulated spectrum for **1a** is shown in Fig. 3 along with the observed spectra for **1a** and for the *cis–trans* mixture of **1a** and **1b** (see below).

The ^1H NMR spectrum of $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ prior to recrystallisation showed in the P–*H* region [Fig. 3(*b*)] a set of peaks (G–L) in addition to those attributable to the *trans*



Scheme 1 Inversion at phosphorus leading to the isomerisation of complex **1a** to **1b** following (*a*) deprotonation of **1a** or (*b*) Mn–P bond cleavage

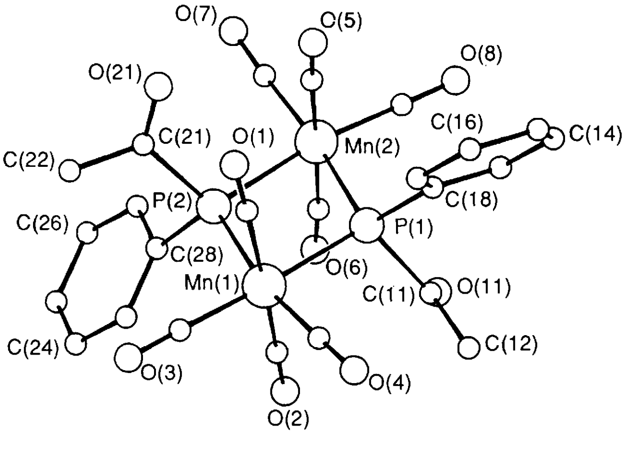


Fig. 4 Molecular structure of *trans*-$[Mn_2(\mu\text{-PPhCOMe})_2(CO)_8]$ **2d** showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

isomer **1a** (A–F). This set of peaks was assigned to the P–*H* resonances of the *cis* isomer **1b**.

The mother-liquor after recrystallisation of complex **1a** at room temperature from CH_2Cl_2–propan-2-ol by the diffusion method was shown by ^1H NMR spectroscopy to contain **1a** and **1b** in comparable amounts. On cooling to -40 °C more crystals were obtained which were a mixture of **1a** and **1b**. The ^1H NMR spectrum of the remaining mother-liquor, however, then showed only the peaks G–L assigned to the *cis* isomer **1b**.

In order to examine the configurational stability of **1a** the ^1H NMR spectrum of this complex in a variety of solvents and at different temperatures was studied. After 24 h at room temperature (r.t.) in either $CDCl_3$ or deuteriated toluene solution no isomerisation of **1a** to **1b** had taken place. A spectrum of a deuteriated acetonitrile solution of **1a** recorded immediately after dissolution of the complex also showed only one isomer to be present but after leaving the solution in the NMR tube for approximately 23 h a *ca.* 1:1 mixture of isomers had formed which showed no further change in composition after 3 d. The spectrum of **1a** in $[^2H_6]$acetone and in $[^2H_8]$tetrahydrofuran at r.t. showed a *ca.* 1:1 mixture of isomers to be present immediately after dissolution of the complex. There was no change in the spectrum of the latter solution after 24 h but a slight increase in the relative concentration of the *cis* isomer **1b** in the former solution after the same time. Isomerisation of **1a** to an isomer mixture of **1a** and **1b** was also effected by heating **1a** in $[^2H_8]$toluene to 110 °C for 24 h but there was no isomerisation in benzene at 70 °C after the same period.

There are two plausible mechanisms for the conversion of complex **1a** to a *cis–trans* mixture of isomers. The first [mechanism (*a*)] involves deprotonation of the complex to form $[Mn_2(\mu\text{-PPhH})(\mu\text{-PPh})(CO)_8]^-$ or $[Mn_2(\mu\text{-PPh})_2(CO)_8]^{2-}$ or both, followed by inversion of configuration at the deprotonated phosphorus atom (Scheme 1) with subsequent reprotonation. The alternative mechanism [(*b*)] involves breaking of a manganese–phosphorus bond and inversion at the phosphorus atom of the terminal phosphido ligand thus formed (Scheme 1). Rotation about the unbroken Mn–P bond and reformation of the broken bond would then give the other isomer.

That isomerisation of complex **1a** takes place more readily at r.t. in polar solvents such as acetone and thf than in non-polar solvents such as toluene provides evidence in favour of the deprotonation mechanism. On the other hand the fact that it also isomerises in toluene at 110 °C but not at r.t. suggests that Mn–P bond breaking [mechanism (*b*)] may also be important. To explore this possibility further the behaviour of **1a** in the acidic solvent CD_3CO_2D was studied. No isomerisation took place at r.t. but after 24 h at 110 °C a *ca.* 1:1 mixture of **1a** and **1b** was present in solution. Significantly there had been no significant incorporation of deuterium into either **1a** or **1b** although such incorporation would have been expected if the deprotonation mechanism were operative. It seems likely, therefore, that both mechanisms (*a*) and (*b*) are involved in the isomerisation process but that the former provides a more rapid pathway in polar solvents. This was confirmed by the fact that if **1a** in toluene is deprotonated by addition of $LiBu^n$ and immediately reprotonated with CH_3CO_2H a *ca.* 1:1 mixture of isomers is obtained even at r.t.

Several workers have reported the exchange of halogen for hydrogen in μ-phosphido complexes containing P–H bonds.[3,14,15] It was of interest to determine whether the exchange would take place in the dimanganese complexes **1a** and **1b**. When an isomer mixture of **1a** and **1b** was treated with CCl_4 at 70 °C for 18 h the complex $[Mn_2(\mu\text{-PPhCl})_2(CO)_8]$ **4** was indeed obtained in essentially quantitative yield. The ^{31}P NMR spectrum of **4** showed only one singlet resonance and it was not possible to determine from the spectroscopic data whether one or more than one isomer was present.

Synthesis and Isomerism of $[Mn_2(\mu\text{-PPhR})_2(CO)_8]$.—Treatment of the isomer mixture of **1** in tetrahydrofuran (thf) at -78 °C with 2 equivalents of $LiBu^n$ followed by the relevant halide, RX, gave the complexes $[Mn_2(\mu\text{-PPhR})_2(CO)_8]$ **2** in moderate yields (26–56% depending on R) (R = Me, **2a**; Et, **2b**; Pr^n, **2c**; COMe, **2d**; CH_2COMe, **2e**; or CO_2Et, **2f**. Proton NMR spectra of complexes **2** in $CDCl_3$ solution revealed two sets of resonances, indicating the presence of two isomers in a concentration ratio of *ca.* 3:2 for all except **2d**. It seems likely that **2d** is also present in solution as two isomers but that the signals due to the methyl protons of each isomer are coincident.

Crystals of complex **2d** were grown by diffusion using dichloromethane as the lower layer and propan-2-ol as the upper layer and subjected to X-ray diffraction analysis. The molecular structure is shown in Fig. 4 and selected bond lengths and bond angles are given in Table 3 and fractional coordinates in Table 4. The structures of **2d** is very similar to that of **1a** with the acetyl groups in a mutually *trans* arrangement just as the phosphorus-bound hydrogen atoms are in **1a**. The Mn–P–Mn bite angles in **2d** are 102.5(1) and 102.1(1)° compared to 103.1(1)° for **1a**. One interesting feature for which there is no obvious explanation is that the Mn(1)–P bond lengths at 2.370(3) and 2.377(3) Å are significantly longer than the Mn(2)–P bond lengths at 2.344(3) and 2.349(3) Å.

Crystals of $[Mn_2(\mu\text{-PPhR})_2(CO)_8]$ (R = Pr^n, CH_2COMe, or CO_2Et) were obtained in the same manner as the crystals of **2d**

Table 3 Selected bond lengths (Å) and angles (°) for *$[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$*

Mn(1)–P(1)	2.370(3)	P(1)–Mn(1)–P(2)	77.1(1)
Mn(1)–P(2)	2.377(3)	P(1)–Mn(2)–P(2)	78.1(1)
Mn(2)–P(1)	2.344(3)	Mn(1)–P(1)–Mn(2)	102.5(1)
Mn(2)–P(2)	2.349(3)	Mn(1)–P(2)–Mn(2)	102.1(1)
P(1)–C(11)	1.895(9)	C(11)–P(1)–C(18)	96.7(3)
P(1)–C(18)	1.840(6)	C(21)–P(2)–C(28)	96.8(3)
P(2)–C(21)	1.872(9)	P(1)–C(11)–O(11)	119.9(7)
P(2)–C(28)	1.825(5)	P(1)–C(11)–C(12)	119.0(5)
C(11)–O(11)	1.19(1)	O(11)–C(11)–C(12)	121.1(8)
C(11)–C(12)	1.50(1)	P(2)–C(21)–O(21)	121.2(8)
C(21)–O(21)	1.16(1)	P(2)–C(21)–C(21)	119.6(6)
C(21)–C(22)	1.46(1)	O(21)–C(21)–C(22)	119.1(8)
Mn–C	1.82(1)–1.85(1)		
MnC–O	1.12(1)–1.14(1)		

Table 4 Fractional atomic coordinates for $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$

Atom	*x*	*y*	*z*
Mn(1)	0.2649(1)	0.3119(1)	0.0942(1)
Mn(2)	0.2173(1)	0.1955(1)	0.4175(1)
P(1)	0.1712(1)	0.2325(2)	0.2021(2)
P(2)	0.3132(1)	0.2646(2)	0.3072(2)
C(1)	0.2433(4)	0.4244(6)	0.1836(9)
O(1)	0.2329(4)	0.4934(5)	0.2380(7)
C(2)	0.2894(4)	0.1948(6)	0.0294(8)
O(2)	0.3048(3)	0.1219(4)	−0.0094(6)
C(3)	0.3419(5)	0.3679(7)	0.0236(10)
O(3)	0.3892(3)	0.4040(5)	−0.0239(8)
C(4)	0.2124(4)	0.3400(6)	−0.0547(9)
O(4)	0.1786(3)	0.3539(5)	−0.1475(7)
C(5)	0.1843(5)	0.3138(7)	0.4684(10)
O(5)	0.1612(3)	0.3835(5)	0.4989(8)
C(6)	0.2527(4)	0.0804(6)	0.3560(9)
O(6)	0.2784(3)	0.0129(4)	0.3168(8)
C(7)	0.2601(4)	0.1862(6)	0.5840(9)
O(7)	0.2845(3)	0.1834(6)	0.6902(6)
C(8)	0.1385(5)	0.1371(7)	0.4779(12)
O(8)	0.0905(3)	0.0984(7)	0.5169(10)
C(11)	0.1439(4)	0.1241(6)	0.0997(10)
O(11)	0.1547(4)	0.0463(5)	0.1434(8)
C(12)	0.1097(4)	0.1383(6)	−0.0367(10)
C(13)	0.0283(3)	0.2355(3)	0.2383(7)
C(14)	−0.0377(3)	0.2763(3)	0.2412(7)
C(15)	−0.0462(3)	0.3725(3)	0.2098(7)
C(16)	0.0113(3)	0.4280(3)	0.1757(7)
C(17)	0.0773(3)	0.3873(3)	0.1728(7)
C(18)	0.0858(3)	0.2910(3)	0.2042(7)
C(21)	0.3492(4)	0.3678(6)	0.4053(11)
O(21)	0.3163(4)	0.4073(6)	0.4866(9)
C(22)	0.4194(4)	0.4021(6)	0.3754(10)
C(23)	0.4350(2)	0.1937(4)	0.1849(4)
C(24)	0.4994(2)	0.1485(4)	0.1885(4)
C(25)	0.5220(2)	0.1045(4)	0.3084(4)
C(26)	0.4801(2)	0.1056(4)	0.4247(4)
C(27)	0.4156(2)	0.1508(4)	0.4211(4)
C(28)	0.3931(2)	0.1948(4)	0.3012(4)

and it seems likely that all of these have the *trans* configuration. In $CDCl_3$ solution the ^1H NMR spectra of these crystals correspond to the major component of the isomer mixture and, on this basis, the more intense set of signals observed for each of the isomer mixtures prior to recrystallisation are tentatively assigned to the *trans* isomer.

In the ^1H NMR spectrum of $[Mn_2(\mu\text{-}PPhMe)_2(CO)_8]$ **2a** the resonances due to the methyl groups of each isomer are seen as triplets. Similar triplets are seen in the spectra of $[Fe_2(\mu\text{-}PPhMe)_2(CO)_6]$,[16] $[Mn_2(\mu\text{-}PMe_2)(CO)_8]$,[17] $[Mo_2(\mu\text{-}PMe_2)_2(CO)_4(\eta\text{-}C_5H_5)_2]$[18] and $[Ni_2(\mu\text{-}PMe_2)_2(CO)_8]$.[18] Such triplets are the result of strong phosphorus–phosphorus coupling[16,17] and the triplet splittings give the average P–H coupling of the methyl protons to the two phosphorus atoms. In the present work coupling of this type is seen for **2e** as well as for **2a**.

Experimental

Details of experimental procedures and the instrumentation used to obtain spectroscopic data have been described previously.[5a] Infrared spectra were recorded in CH_2Cl_2 solution and NMR spectra in $CDCl_3$ solution. The ^{31}P NMR data are ^1H noise decoupled and values for δ are relative to $P(OMe)_3$ as external reference with upfield shifts negative. Proton NMR spectra were recorded at 303 K and ^{31}P spectra at 293 K. All reagents were obtained from the normal commercial suppliers and used without further purification.

Preparations.—$[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$. The compound $[Mn_2(CO)_{10}]$ (5.070 g, 13.0 mmol) was added to undried decalin (99%, as received from the suppliers, Aldrich) (500 cm^3). The mixture was heated to 150 °C and $PPhH_2$ (2.86 cm^3, 27.8 mmol) was added.[5b] The reaction solution was heated at 150 °C for 3.75 h and the solvent was then removed under vacuum. The residue was dissolved in CH_2Cl_2 and adsorbed on silica which was then dried on a rotary evaporator and added to the top of a silica chromatography column. The column was then eluted with hexane to give, in order of elution, yellow $[Mn_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_8]$ **3** (0.152 g, 3%), and yellow $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1** (4.030 g, 56%). Recrystallisation of **1** by the diffusion method at r.t. with dichloromethane as the lower layer and either hexane or (more reliably) propan-2-ol as the upper layer gave crystals of *trans*-$[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1a**. After removal of a further crop of crystals at −40 °C, shown by ^1H NMR spectroscopy to consist of a *cis–trans* mixture, the remaining mother-liquor contained almost exclusively the *cis* isomer **1b** {Found for **3**: C, 37.1; H, 2.3. $C_{14}H_7Mn_2O_8P$ requires C, 37.8; H, 1.6%); *m/z* 444 (M^+); $\nu_{max}(CO)$ at 2093w, 2062m, 2004s and 1969m cm^{-1}; $\delta(^1H)$ 7.81–7.34 (m, 10 H, Ph), 5.47 [d, $^1J(PH)$ 347.7, 1 H, PH], and −17.30 [d, $^2J(PH)$ 33.8 Hz, 1 H, MnH]; $\delta(^{31}P)$ −65.6 (s, μ-PPhH)} {Found for **1**: C, 43.0; H, 2.3. $C_{20}H_{12}Mn_2O_8P_2$ requires C, 43.5; H, 2.2%); *m/z* 552 (M^+) and 524 ($M^+ - CO$); $\nu_{max}(CO)$ at 2073vw, 2052m, 1988s and 1969m cm^{-1}; $\delta(^1H)$, *trans* isomer **1a**, 7.75–7.36 (m, 10 H, Ph), 4.10 [m, $^1J(PH)$ 304.0 ± 0.5, $^4J(PH)$ −1.6 ± 0.5, $^2J(PP)$ 130.0 ± 0.5, $^3J(PH)$ (*o*-phenyl) 10 ± 2]; *cis* isomer **1b**, 7.86–7.29 (m, 10 H, Ph), 3.97 [m, $^1J(PH)$ 303.7 ± 0.5, $^4J(PH)$ − 1.6 ± 0.5, $^2J(PP)$ 130.0 ± 0.5, $^3J(PH)$ (*o*-phenyl) 10 ± 2]; $\delta(^{31}P)$ − 240.3 (s, μ-PPhH)}.

$[Mn_2(\mu\text{-}PPhCl)_2(CO)_8]$ **4**. The compound $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ (0.150 g, 0.272 mmol) was added to CCl_4 (50 cm^3). The mixture was heated at 70 °C for 18 h and the CCl_4 was then removed under vacuum to leave yellow $[Mn_2(\mu\text{-}PPhCl)_2(CO)_8]$ **4** (0.164 g, 97%) as the only product (Found: C, 38.3; H, 1.9. $C_{20}H_{10}Cl_2Mn_2O_8P_2$ requires C, 38.6; H, 1.6%); *m/z* 622 (M^+) and 594 ($M^+ - CO$); $\nu_{max}(CO)$ at 2089w, 2067m, 2008s and 1984m cm^{-1}. NMR: ^1H, δ 8.14–7.30 (m, 10 H, Ph); ^{31}P, δ 1.3 (s, μ-PPhCl).

$[Mn_2(\mu\text{-}PPhR)_2(CO)_8]$ **2**. (*a*) R = Me, **2a**. Complex **1** (0.200 g, 0.362 mmol) was dissolved in thf (15 cm^3) and the solution cooled to 295 K using a solid CO_2–Pr^iOH slush bath. Butyllithium (290 μl of a 2.5 mol dm^{-3} solution, 0.725 mmol) was added whereupon the yellow solution changed to red. After 5 min a large excess (1 cm^3) of MeI was added and the colour of the solution changed immediately back from red to yellow. After a further 5 min the slush bath was removed and, after stirring the solution for 1 h, the thf and excess of MeI were removed under vacuum. The residue was separated by TLC using CH_2Cl_2–hexane (30:70) as eluent. A yellow band, which eluted first, was removed from the TLC plates and extracted with CH_2Cl_2. Evaporation of the solvent gave $[Mn_2(\mu\text{-}PPhMe)_2(CO)_8]$ **2a** (0.105 g, 50%) (Found: C, 45.5; H, 3.2.

$C_{22}H_{16}Mn_2O_8P_2$ requires C, 45.5; H, 2.8%); *m/z* 580 (M^+) and 552 ($M^+ - CO$); ν_{max}(CO) at 2070vw, 2046m, 1983s and 1956m cm^{-1}. NMR: ^{1}H, major isomer, δ 7.87–7.33 (m, 10 H, Ph) and 1.93 [t, $J(PH)_{av}$ 4.2, 3 H, Me); minor isomer, δ 7.87–7.33 (m, 10 H, Ph) and 2.04 [t, $J(PH)_{av}$ 4.2 Hz, 3 H, Me); ^{31}P, δ −215.8 (s, μ-PPhMe). A faint red band on the TLC plate which eluted more slowly than the yellow band was not characterised.

(*b*) R = Et, **2b**. This was synthesised as for **2a** from complex **1** (0.050 g, 0.091 mmol) and LiBu^n (70 μl of a 2.5 mol dm^{-3} solution, 0.175 mmol) with addition of excess (0.5 cm^3) of EtI. Separation by TLC using CH_2Cl_2–hexane (40:60) as eluent gave $[Mn_2(\mu\text{-}PPhEt)_2(CO)_8]$ **2b** (0.014 g, 26%) (Found: C, 48.3; H, 3.7. $C_{24}H_{20}Mn_2O_8P_2$ requires C, 47.4; H, 3.3%); *m/z* 608 (M^+) and $M^+ - nCO$ (n = 1 or 2); ν_{max}(CO) at 2069vw, 2046m, 1983s and 1954m cm^{-1}. NMR: ^{1}H, major isomer, δ 7.86–7.29 (m, 10 H, Ph), 2.33 [dq, ^2J(PH) 2.4, ^3J(HH) 7.2, 2 H, CH_2] and 0.91 (m, 3 H, Me); minor isomer, δ 7.86–7.29 (m, 10 H, Ph), 2.51 [dq, ^2J(PH) 2.4, ^3J(HH) 7.2 Hz, 2 H, CH_2] and 0.91 (m, 3 H, Me); ^{31}P, δ −189.7 (s, μ-PPhEt).

(*c*) R = $CH_2{}^aCH_2{}^bCH_3{}^c$ **2c**. This was synthesised as for complex **2a** from **1** (0.050 g, 0.091 mmol) and LiBu^n (70 μl of a 2.5 mol dm^{-3} solution, 0.175 mmol) with addition of excess (0.5 cm^3) Pr^{n}Br. Separation by TLC using CH_2Cl_2–hexane (40:60) as eluent gave $[Mn_2(\mu\text{-}PPhPr^n)_2(CO)_8]$ **2c** (0.032 g, 56%) (Found: C, 48.9; H, 3.9. $C_{26}H_{24}Mn_2O_8P_2$ requires C, 49.1; H, 3.8%); *m/z* 636 (M^+) and $M^+ - nCO$ (n = 1–4); ν_{max}(CO) at 2069vw, 2046m, 1983s and 1954m cm^{-1}. NMR: ^{1}H, major isomer, δ 7.82–7.32 (m, 10 H, Ph), 2.27 (m, 2 H, $CH_2{}^a$), 1.22 (m, 2 H, $CH_2{}^b$) and 0.87 [t, $^3J(H^bH^c)$ 7.2, 3 H, Me^c]; minor isomer, δ 7.82–7.32 (m, 10 H, Ph), 2.45 (m, 2 H, $CH_2{}^a$), 1.22 (m, 2 H, $CH_2{}^b$) and 0.96 [t, $^3J(H^bH^c)$ 7.1 Hz, 3 H, Me^c]; ^{31}P, δ −196.5 (s, μ-PPhPr^n).

(*d*) R = COMe **2d**. This was synthesised as for complex **2a** from **1** (0.075 g, 0.136 mmol) and LiBu^n (105 μl of a 2.6 mol dm^{-3} solution, 0.273 mmol) with addition of excess of MeCOCl (0.5 cm^3). Separation by TLC using CH_2Cl_2–hexane (40:60) gave $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$ **2d** (0.029 g, 34%) (Found: C, 44.9; H, 3.1. $C_{24}H_{16}Mn_2O_{10}P_2$ requires C, 45.3; H, 2.5%); *m/z* 608 ($M^+ - CO$) and $M^+ - nCO$ (n = 1–4); ν_{max}(CO) at 2081vw, 2061m, 2006s, 1965m and 1673m cm^{-1}. NMR: ^{1}H, δ 7.79–7.50 (m, 10 H, Ph) and 2.1 (s, 3 H, Me); ^{31}P, δ −145.7 (s, μ-PPhCOMe).

(*e*) R = CH_2COMe **2e**.—This was synthesised as for complex **2a** (0.075 g, 0.136 mmol) and LiBu^n (105 μl of a 2.6 mol dm^{-3} solution, 0.273 mmol) with addition of excess (0.5 cm^3) of $MeCOCH_2Cl$. Separation by TLC using CH_2Cl_2–hexane (40:60) gave $[Mn_2(\mu\text{-}PPhCH_2COMe)_2(CO)_8]$ **2e** (0.025 g, 28%) (Found: C, 46.8; H, 3.3. $C_{26}H_{20}Mn_2O_{10}P_2$ requires C, 47.1; H, 3.0%); *m/z* 664 (M^+) and $M^+ - nCO$ (n = 1–6); ν_{max}(CO) at 2076vw, 2053m, 1991s, 1964m and 1712m cm^{-1}. NMR: ^{1}H, major isomer, δ 7.90–7.35 (m, 10 H, Ph), 3.40 (m, 2 H, CH_2) and 1.43 (s, 3 H, Me); minor isomer, δ 7.90–7.35 m, 10 H, Ph), 3.28 (m, 2 H, CH_2) and 1.41 (s, 3 H, Me); ^{31}P, δ −179.6 (s, μ-$PPhCH_2COMe$).

(*f*) R = CO_2Et **2f**. This was synthesised as for complex **2a** from **1** (0.075 g, 0.136 mmol) and LiBu^n (105 μl of a 2.6 mol dm^{-3} solution, 0.273 mmol) with addition of excess of $ClCO_2Et$ (0.5 cm^3). Separation by TLC using CH_2Cl_2–hexane (30:70) gave $[Mn_2(\mu\text{-}PPhCO_2Et)_2(CO)_8]$ (0.033 g, 35%) (Found: C, 45.0; H, 3.0. $C_{26}H_{20}Mn_2O_{12}P_2$ requires C, 44.8; H, 2.9%); *m/z* 696 (M^+) and 668 ($M^+ - CO$); ν_{max}(CO) at 2084vw, 2062m, 2000s, 1974m and 1695m cm^{-1}. NMR: ^{1}H, major isomer, δ 7.87–7.38 (m, 10 H, Ph), 4.26 (m, 2 H, CH_2) and 1.23 [t, ^3J(HH) 7.2, 3 H, Me]; minor isomer, δ 7.87–7.38 (m, 10 H, Ph), 4.26 (m, 2 H, CH_2) and 1.29 [t, ^3J(HH) 7.1 Hz, 3 H, Me]; ^{31}P, δ −168.8 (s, μ-$PPhCO_2Et$).

Crystallographic Data Collection and Processing.—(*a*) $[Mn_2(\mu\text{-}PPhH)_2(CO)_8]$ **1a**. Stoe four-circle diffractometer, 24-step ω–θ scan, with step width 0.04°, scan speed 0.5–2.0 s per step, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); 1830 reflections measured ($5.0 \leqslant 2\theta \leqslant 47.5^\circ$, $\pm h, +k, \pm l$), 1704 unique [merging $R = 0.015$ after numerical absorption correction (maximum, minimum transmission factors 0.962, 0.651)], giving 1468 unique with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity during data collection.

Crystal data. $C_{20}H_{12}Mn_2O_8P_2$, M = 552.0, triclinic, space group $P\bar{1}$, a = 7.515(1), b = 8.801(1), c = 9.151(1) Å, α = 73.89(1), β = 75.28(1), γ = 89.24(1)°, U = 561.3 Å^3 (by least squares refinement of 54 reflections in range $20 < 2\theta < 30^\circ$), Z = 1, D_c = 1.63 g cm^{-3}, $F(000)$ = 276, μ(Mo-Kα) = 12.6 cm^{-1}. Crystal dimensions were *ca.* 0.030 × 0.342 × 0.418 mm.

The Mn and P atoms were found by the Patterson method and the remaining atoms (including H) were found from Fourier difference maps (SHELX).[19] All non-hydrogen atoms were assigned anisotropic thermal parameters and the H atoms were assigned a fixed isotropic thermal parameter (U = 0.05 Å^2). No constraints were placed on positional parameters. On least-squares refinement, the structure converged at R and R' values of 0.030 and 0.033, respectively, for all 1468 reflections. The weighting scheme $w = 1/[\sigma^2(F) + 0.0058F^2]$ gave satisfactory agreement analysis. The final electron-density difference map showed no peaks >0.25 or < −0.22 e Å^{-3}.

(*b*) $[Mn_2(\mu\text{-}PPhCOMe)_2(CO)_8]$ **2d**. Stoe STADI-2 two-circle diffractometer, 4691 reflections measured ($5 < 2\theta > 50^\circ$), 2795 unique. No absorption correction was applied.

Crystal data. $C_{24}H_{16}Mn_2O_{10}P_2$, M = 636.16, orthorhombic, space group $P2_12_12_1$, a = 19.27(7), b = 14.032(5), c = 9.78(1) Å, U = 2644.6 Å^3 (by least-squares refinement on diffractometer angles for 16 centred reflections), Z = 4, D_m = 1.63 g, cm^{-3}, D_c = 1.60 g cm^{-3}, $F(000)$ = 1280, μ(Mo-Kα) = 10.88 cm^{-1}. Crystal dimensions were *ca.* 0.6 × 0.5 × 0.3 mm.

The Mn and P atoms were found by the Patterson method and the remaining non-hydrogen atoms were found from Fourier difference maps (SHELX).[19] The Mn, P and O atoms were assigned anisotropic thermal parameters. The phenyl ring C atoms were constrained to idealised geometry (C–C 1.395 Å) and H atoms were placed in calculated positions (C–H 1.08 Å) and allowed to ride on their respective C atoms. The H atoms of the methyl groups were placed in calculated positions and assigned a fixed thermal parameter (0.05 Å^2). On full-matrix refinement the structure converged at R and R' values of 0.051 and 0.052, respectively, for 2002 reflections with $F > 6\sigma(F)$. The absolute configuration was not established. The weighting scheme $w = 1/[\sigma^2(F) = 0.000\,49F^2]$ gave satisfactory agreement analysis. The final electron-density difference map showed no peaks >0.49 or < −0.43 e Å^{-3}.

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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