SYNTHESIS AND LIGAND SUBSTITUTION CHEMISTRY OF DINUCLEAR, PHOSPHIDO-BRIDGED COMPLEXES OF MANGANESE. X-RAY CRYSTAL STRUCTURES OF $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_7(Cy_2PH)$ AND $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_6(PMe_3)_2$

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Summary

Reaction of $Mn_2(CO)_{10}$ with two equivalents of dicyclohexylphosphine in toluene at 110°C produces $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_7(PCy_2H)$ (**1**) in 60% yield. Interaction of **1** with excess trimethylphosphine produces $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_6(PMe_3)_2$ (**2**) in 90% yield. The X-ray crystal structures of **1** and **2** have been determined. Both structures contain two Mn atoms bridged by a Cy_2P group and a hydride. In each case, the metal atoms exhibit distorted octahedral geometry, with the phosphines occupying positions *trans* to the P atom of the bridging dicyclohexylphosphide. A metal–metal distance of ca. 2.9 Å separates the manganese atoms in both complexes.

Introduction

Recently there has been increased interest in the chemistry of phosphido-bridged transition metal complexes, because of the ability of bridging PR_2 units to tolerate a wide variety of metals and bond distances [1,2]. A variety of dinuclear phosphido- or arsenido-bridged complexes of manganese are known [3,4]. However, only recently has the chemistry of phosphido- and hydrido-bridged dimanganese species begun to be explored [5]. These studies have centered on species bridged by the diphenylphosphido unit, which has frequently been shown to be less stable, with respect to maintaining cluster integrity, than other bridging phosphido units [6,7]. Studies of molecular models indicate that a Cy_2P unit is slightly more sterically demanding than a Ph_2P unit. In addition, their electronic properties should be quite different. In order to assess these differences in the properties of Mn_2-bridged systems, we have undertaken the synthesis of dicyclohexylphosphide-bridged di-

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manganese species, and report here the synthesis and structural characterization of two such species: $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)(CO)_7(PCy_2H)$ (1) and $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)\text{-}$ $(CO)_6(PMe_3)_2$ (2), which appear to be more thermally stable and less reactive than similar $\mu\text{-PPh}_2$-bridged complexes. In addition, to our knowledge, 1 has no diphenylphosphido-bridged analogue.

Results and discussion

The complex, $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2H)(CO)_7(PCy_2H)(1)$, was prepared by the interaction of $Mn_2(CO)_{10}$ with two equivalents of dicyclohexylphosphine in toluene at 110°C (60% yield). Prolonged heating of 1 in toluene (110°C), or xylene (130°C) does not afford the expected di-phosphido-bridged species [8], and no reaction occurs. In spite of its thermal stability, the terminal ligands of 1 are sufficiently labile for substitution reactions to occur. Thus, interaction of 1 with an excess of PMe_3 in toluene at 110°C affords $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)(CO)_6(PMe_3)_2$ (2) cleanly and in virtually quantitative yield.

Spectroscopic data for both complexes are in accord with the structures as determined by X-ray crystallography. The solution infra-red spectra of both complexes exhibit $\nu(CO)$ absorptions in the terminal CO region: 2030, 2001, 1980, 1950, and 1915 cm^{-1} for 1, and 1930 and 1905 cm^{-1} for 2. The ^{31}P {^1H} NMR spectra of both species exhibit broadened resonances (due to ^{55}Mn coupling) well downfield, indicating phosphido groups bridging metal–metal bonds [9]. The presence of phosphine is indicated in both complexes by resonances in the phosphine region of the $^{31}P\{^1H\}$ spectrum; however, due possibly to ^{55}Mn coupling ($I = 5/2$), no phosphorus–phosphorus coupling information is observed. The ^1H NMR spectra of these complexes exhibit resonances upfield of TMS ($\delta - 16.20$ (t) (1) and $\delta - 16.50$ (q) (2)) as well as the typical, room temperature cyclohexyl spectrum in the aliphatic region.

X-Ray studies

The solid state structures of each compound were determined by single crystal X-ray diffraction studies. Crystals of 1 and 2 suitable for X-ray diffraction were obtained by slow cooling (-20°C) of toluene solutions. Table 1 lists pertinent data collection parameters for both complexes. Figure 1 shows an ORTEP [10] view of 1, with atom numbering scheme, and important bond lengths and angles are given in Tables 2 and 3, respectively. Each manganese atom exhibits roughly octahedral geometry. The phosphine (Cy_2PH) in 1 bonded to Mn (2) is *trans* to the phosphide but *cis* to the bridging hydride. Though not crystallographically imposed, the Mn atoms and the bridging P and H atoms lie on a plane which also includes P(2), C(3), C(4), C(7), O(3), O(4), and O(7). The Mn–Mn distance is 2.940(3) Å, which is well within bonding distance, [11] and this is consistent with the diamagnetism implied by the NMR spectra. The manganese–phosphido distance is 2.290(4) Å (av.) and the Mn–P(1)–Mn angle is 80.0(1)°. The manganese–hydride distance is 1.64(9) Å (av.), and the Mn(1)–H–Mn(2)angle is 128(6)°. These metal–hydride distances and angles indicate that the hydride is located significantly closer to the Mn(1)–Mn(2) vector than in the related complex $Mn_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_8$ [12]. However, it is well recognized that the location of hydrides by X-ray diffraction methods is not without a considerable degree of error, and neutron diffraction studies of 1 are

TABLE 1

CRYSTAL STRUCTURE PARAMETERS FOR $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_7(PCy_2H)$ (1), AND $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_6(PMe_3)_2$ (2)

Description of crystal	1	2
Color of crystal	yellow	yellow/orange
Habit of crystal	brick	brick
Max. crystal dimensions (mm)	$0.39 \times 0.27 \times 0.18$	$0.30 \times 0.28 \times 0.10$
Unit cell		
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (Nr. 14)	$Pnma$ (Nr. 62)
Unit cell parameters		
a	13.9563(3) Å	11.5270(1) Å
b	10.7231(4) Å	15.0220(3) Å
c	22.7189(6) Å	18.0430(3) Å
α	90°	90°
β	91.8730 (2)°	90°
γ	90°	90°
U (Å^3)	3398.16	3124.30
Molecules per unit cell	4	4
Formula	$Mn_2P_2O_7C_{31}H_{45}$	$Mn_2P_3O_6C_{24}H_{41}$
M (g mol^{-1})	701.524	628.389
Calculated density (g cm^{-3})	1.371	1.336
$\mu_{calc.}$ (cm^{-1})	8.468	9.591
Data collection		
Radiation (Å)	0.71073	0.71073
Scan technique	$\theta/2\theta$	$\theta/2\theta$
Scan width (deg.)	$0.8 + 0.35 \tan(\theta)$	$0.8 + 0.35 \tan(\theta)$
Range of indices (h, k, l)	-15 $+15$; 0 11; 0 25	0 17; 0 21; 0 13
2θ range (deg.)	3.00 to 46.00	2.00 to 50.00
No. reflections measured	5019	3114
Standard reflections		
intensity	5 4 8, 4 5 6	5 1 5, 2 10 0
orientation	3 6 4, 1 4 11	4 4 5, 6 3 4
Decay of standards	< 0.1%	2.5%
Minimum% transmission	90.23	90.46
Maximum% transmission	99.99	98.02
Average% transmission	96.90	93.35
Agreement factor for averaged refl		
(F_{obs})	0.028	
(Intensity)	0.025	
Structure determination		
No. reflections used ($I > 3\sigma(I)$)	2494	1153
No. parameters varied	387	207
Data/parameter ratio	6.444	5.570
Shift to error ratio	0.179	0.047
E.s.d. of an observation of unit weight	4.8701	5.6743
R	0.0628	0.0770
R_w	0.0712	0.0480

required to accurately locate the μ-H atom in 1 [13]. In addition the ring H atoms in both structures were not located, suggesting less reliability in the μ-H positions.

Figure 2 presents an ORTEP view of **2**, with atom numbering scheme, and

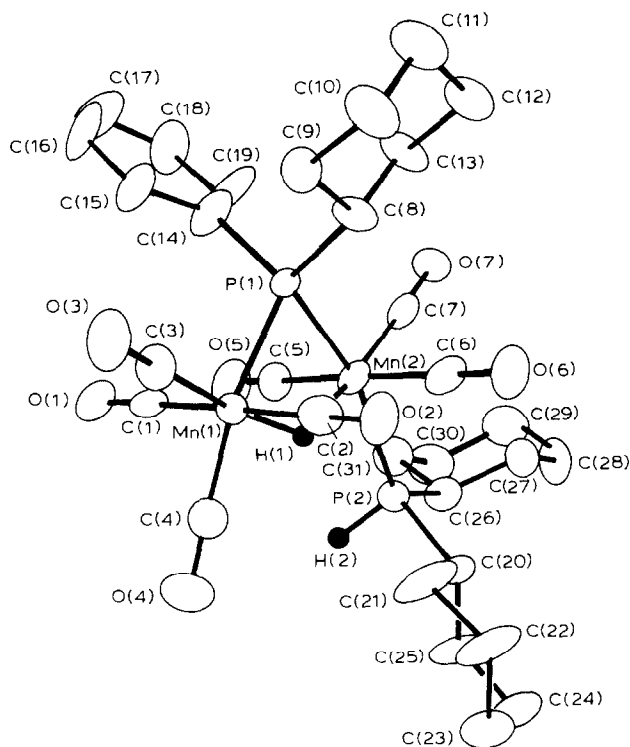Fig. 1. An ORTEP view of $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)(CO)_7(PCy_2H)$ (**1**) with atom numbering scheme.

TABLE 2

BOND DISTANCES (Å) FOR $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)(CO)_7(PCy_2H)$ (**1**) (Numbers in parentheses are estimated standard deviations in the least significant digits)

Mn(1)–Mn(2)	2.940(3)	P(2)–H(2)	1.26(9)	C(17)–C(18)	1.50(3)
Mn(1)–P(1)	2.312(4)	O(1)–C(1)	1.16(1)	C(18)–C(19)	1.50(2)
Mn(1)–C(1)	1.80(1)	O(2)–C(2)	1.14(1)	C(20)–C(21)	1.51(2)
Mn(1)–C(2)	1.84(1)	O(3)–C(3)	1.14(1)	C(20)–C(25)	1.53(2)
Mn(1)–C(3)	1.79(1)	O(4)–C(4)	1.16(2)	C(21)–C(22)	1.59(2)
Mn(1)–C(4)	1.79(1)	O(6)–C(6)	1.14(1)	C(22)–C(23)	1.54(2)
Mn(1)–H(1)	1.65(9)	C(8)–C(9)	1.56(2)	C(23)–C(24)	1.49(2)
Mn(2)–P(1)	2.267(3)	C(8)–C(13)	1.55(2)	C(24)–C(25)	1.55(2)
Mn(2)–P(2)	2.296(3)	C(9)–C(10)	1.55(2)	C(26)–C(27)	1.55(2)
Mn(2)–C(5)	1.84(1)	C(10)–C(11)	1.53(2)	C(26)–C(31)	1.54(2)
Mn(2)–C(6)	1.83(1)	C(11)–C(12)	1.56(2)	C(27)–C(28)	1.59(2)
Mn(2)–C(7)	1.75(1)	C(12)–C(13)	1.57(2)	C(28)–C(29)	1.51(2)
Mn(2)–H(1)	1.63(9)	C(14)–C(15)	1.49(2)	C(29)–C(30)	1.55(2)
P(1)–C(8)	1.89(1)	C(14)–C(19)	1.37(2)	C(30)–C(31)	1.55(2)
P(1)–C(14)	1.88(1)	C(15)–C(16)	1.54(2)		
P(2)–C(20)	1.87(1)	C(16)–C(17)	1.35(3)		
P(2)–C(26)	1.84(1)				

TABLE 3

KEY BOND ANGLES (°) FOR $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_7(PCy_2H)$ (**1**) (Numbers in parentheses are estimated standard deviations in the least significant digits)

|			
P(1)–Mn(1)–C(1)	91.0(4)	C(6)–Mn(2)–C(7)	86.7(5)
P(1)–Mn(1)–C(2)	90.2(4)	C(6)–Mn(2)–H(1)	92.(3)
P(1)–Mn(1)–C(3)	100.1(4)	C(7)–Mn(2)–H(1)	174.(3)
P(1)–Mn(1)–C(4)	163.2(4)	Mn(1)–P(1)–Mn(2)	80.0(1)
P(1)–Mn(1)–H(1)	75.(3)	Mn(1)–P(1)–C(8)	116.5(4)
C(1)–Mn(1)–C(2)	178.4(5)	Mn(1)–P(1)–C(14)	117.7(5)
C(1)–Mn(1)–C(3)	89.4(5)	Mn(2)–P(1)–C(8)	116.1(4)
C(1)–Mn(1)–C(4)	87.2(5)	Mn(2)–P(1)–C(14)	120.2(4)
C(1)–Mn(1)–H(1)	96.(3)	C(8)–P(1)–C(14)	105.4(6)
C(2)–Mn(1)–C(3)	89.4(5)	Mn(2)–P(2)–C(20)	119.8(4)
C(2)–Mn(1)–C(4)	91.9(5)	Mn(2)–P(2)–C(26)	120.1(4)
C(2)–Mn(1)–H(1)	86.(3)	Mn(2)–P(2)–H(2)	115.(4)
C(3)–Mn(1)–C(4)	96.6(6)	C(20)–P(2)–C(26)	102.9(5)
C(3)–Mn(1)–H(1)	173.(3)	C(20)–P(2)–H(2)	102.(4)
C(4)–Mn(1)–H(1)	88.(3)	C(26)–P(2)–H(2)	92.(4)
P(1)–Mn(2)–P(2)	159.5(1)	P(1)–Mn(2)–C(5)	95.0(3)
P(1)–Mn(2)–C(6)	91.3(3)	P(1)–Mn(2)–C(7)	97.9(4)
P(1)–Mn(2)–H(1)	77.(3)	P(2)–Mn(2)–C(5)	86.2(4)
P(1)–C(8)–C(9)	112.6(8)		
P(2)–Mn(2)–C(6)	89.3(3)	P(2)–Mn(2)–C(7)	102.6(3)
P(2)–Mn(2)–H(1)	83.(3)	C(5)–Mn(2)–C(6)	172.5(4)
C(5)–Mn(2)–C(7)	88.4(5)	C(5)–Mn(2)–H(1)	94.(3)
Mn(1)–H(1)–Mn(2)	128.(6)		
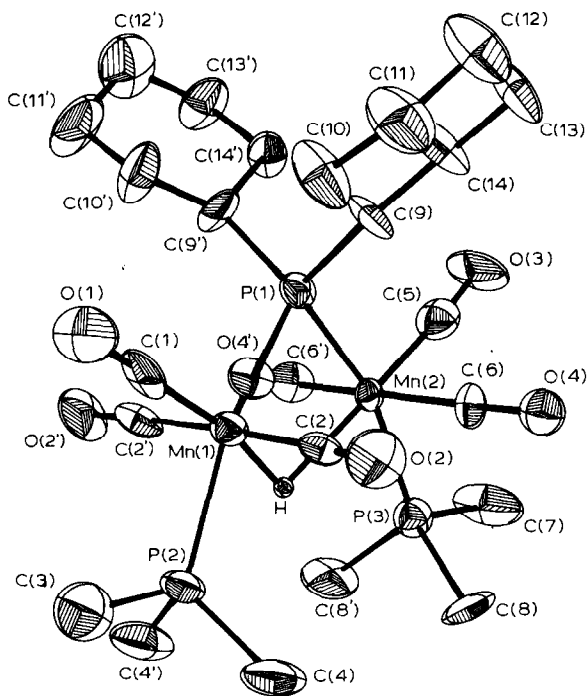
Fig. 2. An ORTEP view of $Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO_6(PMe_3)_2$ (**2**). Hydride shown in fixed position (see Experimental section).

important bond lengths and angles are given in Tables 5 and 6 respectively. Again, each Mn atom exhibits a distorted octahedral geometry, with the PMe₃ groups occupying positions *trans* to the bridging phosphide. There is a crystallographically

TABLE 4

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR (1)

Atom	x	y	z	$B(\text{Å}^2)$ [a]
Mn(1)	0.8041(1)	0.1359(2)	0.92178(7)	3.74(4)
Mn(2)	0.6321(1)	0.2531(2)	0.86745(7)	3.43(3)
P(1)	0.7884(2)	0.3059(3)	0.8596(1)	3.64(6)
P(2)	0.4992(2)	0.1436(3)	0.8945(1)	3.71(6)
O(1)	0.7999(6)	0.2948(8)	1.0278(4)	6.4(2)
O(2)	0.8181(6)	−0.0338(8)	0.8187(4)	6.0(2)
O(3)	1.0131(6)	0.122(1)	0.9353(5)	8.4(3)
O(4)	0.7610(8)	−0.0723(8)	1.0015(4)	7.6(3)
O(5)	0.4023(6)	0.5892(9)	0.0280(4)	6.8(2)
O(6)	0.6323(6)	0.1085(9)	0.7558(4)	6.6(2)
O(7)	0.4459(6)	0.5454(8)	0.2056(4)	5.8(2)
C(1)	0.7998(8)	0.235(1)	0.9853(5)	4.4(3)
C(2)	0.8110(7)	0.032(1)	0.8578(5)	4.0(3)
C(3)	0.9319(8)	0.129(1)	0.9308(5)	5.3(3)
C(4)	0.7788(9)	0.008(1)	0.9699(5)	4.8(3)
C(5)	0.6129(7)	0.350(1)	0.9328(5)	4.2(3)
C(6)	0.6348(7)	0.161(1)	0.7997(5)	4.1(3)
C(7)	0.5824(7)	0.373(1)	0.8241(5)	4.0(3)
C(8)	0.8396(8)	0.289(1)	0.7842(5)	5.1(3)
C(9)	0.9512(8)	0.280(1)	0.7864(6)	6.3(4)
C(10)	0.9844(9)	0.256(2)	0.7230(6)	7.1(4)
C(11)	0.951(1)	0.361(2)	0.6821(7)	8.5(4)
C(12)	0.839(1)	0.364(2)	0.6794(6)	8.6(5)
C(13)	0.8024(9)	0.393(1)	0.7425(6)	7.0(4)
C(14)	0.833(1)	0.461(1)	0.8879(7)	7.3(4)
C(15)	0.9337(9)	0.460(2)	0.9123(6)	7.4(4)
C(16)	0.964(1)	0.592(2)	0.9334(9)	14.2(5)
C(17)	0.905(1)	0.690(2)	0.9378(8)	13.3(5)
C(18)	0.803(1)	0.683(1)	0.9158(8)	9.6(5)
C(19)	0.770(1)	0.559(1)	0.8911(9)	11.6(5)
C(20)	0.4829(8)	−0.022(1)	0.8699(5)	4.4(3)
C(21)	0.575(1)	−0.095(1)	0.8760(9)	8.4(5)
C(22)	0.559(1)	−0.230(1)	0.8494(8)	7.9(4)
C(23)	0.483(1)	−0.296(1)	0.8855(7)	7.4(4)
C(24)	0.393(1)	−0.224(1)	0.8808(8)	8.3(4)
C(25)	0.406(1)	−0.089(1)	0.9044(6)	7.0(4)
C(26)	0.3788(7)	0.210(1)	0.8823(5)	4.1(3)
C(27)	0.3531(8)	0.223(1)	0.8155(6)	5.6(3)
C(28)	0.2464(9)	0.274(1)	0.8087(6)	7.1(4)
C(29)	0.238(1)	0.399(1)	0.8390(7)	7.4(4)
C(30)	0.265(1)	0.383(1)	0.9051(7)	7.4(4)
C(31)	0.3698(8)	0.337(1)	0.9131(6)	5.4(3)
H(1)	0.689(6)	0.144(9)	0.905(4)	5(2)*
H(2)	0.489(6)	0.135(9)	0.949(4)	4(2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

TABLE 5

BOND DISTANCES (Å) FOR $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)(CO)_6(PMe_3)_2$ (2) (Numbers in parentheses are estimated standard deviations in the least significant digits)

Mn(1)–Mn(2)	2.961(2)	P(1)–C(9)	1.88(2)	C(9)–C(10)	1.45(3)
Mn(1)–P(1)	2.280(3)	P(2)–C(3)	1.76(2)	C(9)–C(14)	1.53(2)
Mn(1)–P(2)	2.280(3)	P(2)–C(4)	1.82(2)	C(10)–C(11)	1.54(3)
Mn(1)–C(1)	1.75(2)	P(3)–C(7)	1.85(2)	C(11)–C(12)	1.52(2)
Mn(1)–C(2)	1.87(2)	P(3)–C(8)	1.85(2)	C(12)–C(13)	1.41(3)
Mn(2)–P(1)	2.276(3)	L(1)–C(1)	1.17(2)	C(13)–C(14)	1.52(3)
Mn(2)–P(3)	2.269(4)	O(2)–C(2)	1.112(9)		
Mn(2)–C(5)	1.79(2)	O(3)–C(5)	1.17(2)		
Mn(2)–C(6)	1.80(2)	O(4)–C(6)	1.15(2)		

TABLE 6

BOND ANGLES (°) FOR $Mn_2(\mu\text{-H})(\mu\text{-Cy}_2P)CO_6(PMe_3)_2$ (2) (Numbers in parentheses are estimated standard deviations in the least significant digits)

P(1)–Mn(1)–P(2)	165.8(1)	Mn(1)–P(1)–Mn(2)	81.0(3)
P(1)–Mn(1)–C(1)	96.2(4)	C(9)–P(1)–C(9')	107.1(9)
P(1)–Mn(1)–C(2)	92.5(2)	C(3)–P(2)–C(4)	102.6(8)
P(2)–Mn(1)–C(1)	97.9(4)	C(4)–P(2)–C(4')	97.(1)
P(2)–Mn(1)–C(2)	87.8(2)	C(7)–P(3)–C(8)	101.5(8)
C(1)–Mn(1)–C(2)	89.0(3)	C(8)–P(3)–C(8')	100.(1)
C(2)–Mn(1)–C(2')	174.8(5)	C(10)–C(9)–C(14)	118.(1)
P(1)–Mn(2)–P(3)	160.4(1)	C(9)–C(10)–C(11)	112.8(3)
P(1)–Mn(2)–C(5)	100.4(7)	C(10)–C(11)–C(12)	113.4(4)
P(1)–Mn(2)–C(6)	92.8(6)	C(11)–C(12)–C(13)	116.2(6)
P(3)–Mn(2)–C(5)	99.2(7)	C(12)–C(13)–C(14)	117.5(5)
P(3)–Mn(2)–C(6)	88.1(5)	C(9)–C(14)–C(13)	112.3(4)
C(5)–Mn(2)–C(6)	87.4(3)	C(6)–Mn(2)–C(6')	173.(1)
Mn(1)–P(1)–C(9)	116.2(3)	Mn(2)–P(1)–C(9)	117.4(6)
P(1)–C(9)–C(10)	118.(3)	P(1)–C(9)–C(14)	114.6(5)

imposed mirror plane that contains the heavy atoms {Mn(1),Mn(2),P(1),P(2), and P(3)}, as well as C(1), C(3), C(5), C(7), O(1), and O(3). There is some disorder in the hydride position with respect to the mirror (see Experimental section). Figure 2 shows the hydride in a fixed position, which is also in the mirror plane. The metal–metal distance is 2.961(2) Å (av.), which is slightly longer than that in 1, but still within bonding distance [11]. The manganese–phosphide distance is 2.278(3) Å (av.) and the Mn–P(1)–Mn angle is 81.0(3)°, which is similar to that observed in 1. Presumably, the steric bulk of the μ-Cy$_2$P moiety prevents the phosphine groups in 1 and 2 from occupying cis positions relative to it. Interestingly, the less sterically demanding t-BuNC groups of $Mn_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_6(t\text{-BuNC})_2$ do occupy such cis positions [5].

Further studies on the substitution chemistry of these complexes are in progress.

Experimental section

All operations were performed under dry nitrogen or under vacuum. Microanalyses were by the Schwartzkopf Microanalytical Laboratory, Woodside, NY.

Hexane was dried over sodium and distilled from sodium benzophenone under nitrogen before use. Toluene was dried over, and then distilled from sodium under nitrogen before use. Melting point determinations were carried out in a sealed tube, under 1 atm of N_2, and are uncorrected. $Mn_2(CO)_{10}$ was purchased from the Pressure Chemical Co., and used as received. Cy_2PH was purchased from Strem Chemicals Inc., and stored under nitrogen. Infrared spectra were run on a Perkin–Elmer 1330 and calibrated against a polystyrene standard. NMR spectra were run on Nicolet NT-200 (^1H, 200 MHz) and Varian FT-80 (^{31}P, 32.384 MHz) instruments. For ^1H NMR, samples were run at ambient temperature and referenced to external Me_4Si (δ 0.0). For ^{31}P NMR, samples were run at ambient temperature and referenced to external 85% H_3PO_4 (δ 0.0, positive is downfield).

$Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_7(PCy_2H)$ (1)

To a solution of $Mn_2(CO)_{10}$ (0.75 g, 1.92 mmol) in toluene (100 ml) was added two equivalents (0.843 ml, 3.85 mmol) of neat Cy_2PH. The mixture was then heated under reflux (12 h). After cooling to room temp., volatile materials were removed under vacuum, the yellow residue extracted into hexane (2 × 25 ml), and the resulting solution filtered. The solution volume was reduced under vacuum (ca. 20 ml) and cooled overnight ($-20°C$). The complex was obtained as a yellow powder which was collected and dried under vacuum. The complex is air stable in the solid state, but decomposes slowly in solution. Yield: 0.81 g (60%) M.p. 177–179°C(dec); IR (hexane soln, KBr cells): 2280wbr, 2030m, 2001m, 1980s, 1950s, 1915s (cm^{-1}). (Nujol mull, CsI plates): 2270m, 2040s, 1950s br, 1925s br, 1870s br, 1330w, 1310vw, 1290m, 1260m, 1200m, 1150m, 1090m, 1050w, 1020w, 1000w, 980m, 890w, 875m, 860vw, 830m, 810vw, 790m, 710m, 700m, 640m, 615m br, 490w, 470m, 440w, 380m, 370m (cm^{-1}); ^1H NMR (C_6D_6, 200 MHz): δ 4.41 d ($\Delta w_{1/2}$ 28 Hz, J(P–H) 325 Hz, (1H) Cy_2 PH), δ 1.77 m ($\Delta w_{1/2}$ 300 Hz (appears as distorted pentuplet) 44 H) Cy_2PH), δ – 16.20 t ($\Delta w_{1/2}$ 28 Hz, J(P–H) 26 Hz (1H) μ-H). $^{31}P\{^1H\}$NMR (C_6D_6, 32.384 MHz): δ 190.0 s ($\Delta w_{1/2}$ 55 Hz, μ-Cy_2P), δ 53.0 s ($\Delta w_{1/2}$ 85 Hz, Cy_2PH). ^{31}P NMR (C_6D_6, 32.384 MHz): δ 190.0 s br ($\Delta w_{1/2}$ 70 Hz μ-Cy_2P), δ 53.0 d ($\Delta w_{1/2}$ 64 Hz, J(P–H) 325 Hz, Cy_2PH). Analysis: Found: C, 53.10; H, 6.49. $C_{31}H_{45}Mn_2O_7P_2$ calcd.: C, 53.08; H, 6.47%.

$Mn_2(\mu\text{-}H)(\mu\text{-}Cy_2P)(CO)_6(PMe_3)_2$ (2)

To a solution of 1 (0.2439 g, 0.35 mmol) in toluene (50 ml) was added an excess of neat PMe_3 (0.30 ml, 2.95 mmol). The mixture was then heated under reflux (6 h). After cooling to room temp., volatile materials were removed under vacuum, the yellow/orange residue was extracted into hexane (2 × 20 ml), and the solution filtered. The volume was reduced (ca. 20 ml), and cooled overnight ($-20°C$). The compound was obtained as a yellow/orange micro-crystalline solid. It was collected and dried under vacuum. It is air stable in the solid state, but decomposes slowly in solution. Yield: 0.20 g (90%) M.p. 250–252°C (dec). IR (pentane soln, KBr cells): 1930s, 1905s (cm^{-1}). (Nujol mull, CsI plates): 2005m, 1990w, 1915s br, 1870s br, 1420w, 1340w, 1300w, 1280m, 1255w, 1200vw, 1170m, 1125w, 1115vw, 1070wbr, 1040w, 1020vw, 1000w, 950s, 930s, 890vw, 835m, 810vw, 720s, 640s br, 515m, 490m, 460vw, 450vw 410m, 390w, 360m, 325vw, 300w, 240w, 220m (cm^{-1}). ^1H NMR (C_6D_6, 200 MHz): δ 2.11 m ($\Delta w_{1/2}$ 297 Hz, (22H) Cy_2P), δ 1.18 d ($\Delta w_{1/2}$ 17Hz, ^2J(P–H) 11 Hz (18H) Me_3P), δ – 16.5 q ($\Delta w_{1/2}$ 20 Hz J(P–H) 24 Hz, (1H) μ-H).

$^{31}P\{^1H\}NMR$ (C_6D_6, 32.384 MHz): δ 192.0 s ($\Delta w_{1/2}$ 73 Hz, μ-Cy_2P), δ 21.5 s ($\Delta w_{1/2}$ 155 Hz, Me_3P). Analysis: Found: C, 45.90; H, 6.60. $C_{24}H_{41}Mn_2O_6P_3$ calcd.: C, 45.87; H, 6.58%.

X-Ray crystallography

General. Data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo-K_α radiation. Data were collected by the $\theta/2\theta$ scan technique at 23 ± 2°C. Details of the standard data collection methods were similar to those outlined in ref. 7j.

$Mn_2(\mu$-$H)(\mu$-$Cy_2P)(CO)_7(PCy_2H)$ (1). Crystals of 1 were grown by slow cooling of a toluene solution ($-20°C$). A suitable, yellow brick was mounted in a thin walled glass capillary and sealed under vacuum. Unit cell parameters were obtained by carefully centering 25 strong reflections having 2θ values between 24.0 and 26.0°. The monoclinic space group $P2_1/n$ (No. 14) was uniquely determined by the systematic absences ($h0l, h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Data were collected in the $\pm h$, $+k$, $+l$ quadrant between 2θ values of 3.00 and 46.00°. The data were then corrected for Lorentz and polarization effects. The check reflections showed less than a 0.1% decrease in intensity over the course of data collection, and hence no decay correction was applied. A psi scan of 4 reflections having χ values between 80 and 90° showed a minimum percent transmission of 90.23, and a maximum percent transmission of 99.99. An empirical absorption correction (Program EAC) was applied. The observed structure factors of equivalent reflections were averaged, with agreement factors of 0.028 (intensity) and 0.025 (F_{obs}). The positions of the heavy atoms were obtained by direct methods (MULTAN) [14], and the remaining non-hydrogen atoms were located by successive cycles of difference Fourier maps followed by least-squares refinement. The only hydrogen atoms located were the bridging hydride, and the hydrogen atom of the secondary phosphine (Cy_2PH). Data with intensities less than 3 σ (I) and sin θ/λ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor P of 0.05 was used in the final stages of refinement [15]. The structure was refined to final values of 0.0628 and 0.0712 for R and R_w. The highest peak in the final difference Fourier map had a height of 0.514 e/Å^3 and was located 1.141 Å from C(31). Crystal data and collection parameters are in Table 1. Positional parameters for 1 are given in Table 4. General temperature factors are available as supplementary material.

$Mn_2(\mu$-$H)(\mu$-$Cy_2P)(CO)_6(PMe_3)_2$ (2). Crystals of 2 were grown by slow cooling of a toluene solution ($-20°C$). A suitable yellow/orange brick was mounted in a thin walled glass capillary and sealed under vacuum. Unit cell parameters were obtained by carefully centering 25 strong reflections having 2θ values between 22.0 and 24.0°. Examination of the diffraction symmetry, and the systematic absences ($0kl, k + l = 2n + 1$; $hk0$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l, l = 2n + 1$; $h00$, $h = 2n + 1$ indicated a choice of the orthorhombic space groups $Pn2_1a$ or $Pnma$. The space group $Pnma$ (No. 62) was chosen to be the correct one on the basis of successful refinement of the structure. Data were collected in the $+h + k + l$ quadrant between 2θ values of 2.00 and 50.00°. The data were then corrected for Lorentz and polarization effects. The check reflections showed a 2.5% decrease in intensity over the course of data collection, and hence no correction was applied. A psi scan of 4 reflections having χ values between 80 and 90° showed minimum percent transmis-

TABLE 7

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR (2)

Atom	x	y	z	$B(\text{Å}^2)$ [a]
Mn(1)	0.9522(3)	0.250	0.5699(2)	3.14(7)
Mn(2)	0.2958(3)	0.250	0.0602(2)	2.72(7)
P(1)	0.7548(5)	0.250	0.5631(4)	2.6(1)
P(2)	0.1463(6)	0.250	0.5456(4)	4.8(2)
P(3)	0.3991(7)	0.250	0.1673(4)	4.1(2)
O(1)	0.964(2)	0.250	0.731(1)	8.8(7)
O(2)	0.967(1)	0.4479(8)	0.577(1)	7.6(4)
O(3)	0.557(2)	0.250	0.380(1)	8.5(7)
O(4)	0.284(1)	0.0547(8)	0.0736(9)	6.3(4)
C(1)	0.961(2)	0.250	0.667(2)	5.5(7)
C(2)	0.959(1)	0.374(1)	0.572(1)	4.7(4)
C(3)	1.233(5)	0.250	0.626(3)	7.3(6)
C(4)	1.208(2)	0.341(2)	0.492(2)	9.1(7)
C(5)	0.652(3)	0.250	0.402(1)	4.7(7)
C(6)	0.292(2)	0.131(1)	0.066(1)	4.4(4)
C(7)	0.813(3)	0.250	0.246(2)	12(2)
C(8)	0.999(2)	0.156(2)	0.317(1)	7.8(6)
C(9)	0.680(1)	0.150(1)	0.602(1)	5.2(4)
C(10)	0.699(2)	0.128(2)	0.679(1)	7.9(6)
C(11)	0.649(2)	0.036(2)	0.701(1)	8.8(7)
C(12)	0.528(2)	0.020(2)	0.671(2)	10.4(8)
C(13)	0.508(2)	0.045(1)	0.597(1)	7.0(6)
C(14)	0.559(1)	0.132(1)	0.570(1)	5.3(5)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos \gamma)B(1,2)+ac(\cos \beta)B(1,3)+bc(\cos \alpha)B(2,3)]$.

sion of 90.47 and maximum percent transmission of 98.02. An empirical absorption correction was applied. The positions of the heavy atoms were obtained by direct methods (MULTAN [14]), and the remaining non-hydrogen atoms were located by successive cycles of difference Fourier maps followed by least-squares refinement. Difference Fourier maps showed three peaks close together in the region expected for a bridging hydride; however, none of these were refined successfully. The hydride was fixed at 0.97165, 0.25000, 0.49121 but not refined. It appears in Fig. 2 in this position. No other hydrogen atoms were located. Data with intensities less than $3\sigma(I)$ and $\sin(\theta/\lambda)$ less than 0.10 or greater than 0.55 were exluded, and a non-Poisson contribution weighting scheme with an experimental instability factor P of 0.05 was used in the final stages of refinement [15]. The structure was refined to final values of 0.0770 and 0.0840 for R and R_w, respectively. The maximum peak in the final difference Fourier map had a height of 0.876 e/Å and was located 1.208 Å from Mn(2). Positional parameters for 2 are given in Table 7. General temperature factors are available as supplementary material. All calculations were performed on a PDP 11/44 computer using the Enraf–Nonius software package "SDP-PLUS" [16] Supplementary material is available from the authors upon request.

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