Synthesis and Co-ordination Chemistry of a New Tripodal Phosphine Alcohol†

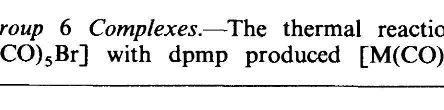
Tung-Ying Hsieh, Ming-Chu Cheng, Shie-Ming Peng and Shiuh-Tzung Liu*
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

The tripodal phosphine alcohol $CH_3C(CH_2PPh_2)_2(CH_2OH)$ (dpmp) was prepared and its co-ordination chemistry towards Group 6 metal carbonyls and a manganese(I) complex studied. In $[M(CO)_4(dpmp\text{-}P,P')]$ (M = Cr, Mo or W), the tripodal ligand behaves as a bidentate ligand with the hydroxyl site unco-ordinated. Reaction of dpmp with $[Mn(CO)_5Br]$ gave a stereoisomeric mixture of products, *anti,fac*-$[Mn(CO)_3Br(dpmp\text{-}P,P')]$ **4a** and *syn,fac*-$[Mn(CO)_3Br(dpmp\text{-}P,P')]$ **4b**. Treatment of **4a** or **4b** with silver hexafluorophosphate yielded a facial complex *fac*-$[Mn(CO)_3(dpmp\text{-}P,P',O)]PF_6$ **6**. Complex **6** reacted with the anions X^- (X = Br, I, N_3 or SCN) stereospecifically to give *syn,fac*-$[Mn(CO)_3X(dpmp\text{-}P,P')]$ (X = Br **4b**, I **5b**, N_3 **8b** or NCS **9b**). X-Ray crystal structures of complexes **4b**, **6** and **9b** were determined. The crystal structure of complex **9b** is the first of a manganese thiocyanate complex containing carbonyl ligands. Both the bond angles [Mn–N–C 170.4(5), N–C–S 175.0(6)°] and the distances [C–N 1.143(8), S–C 1.637(7) Å] of **9b** clearly demonstrated the nature of the Mn–NCS bond, which is consistent with spectral data. Comparison of the co-ordination chemistry of dpmp with $CH_3C(CH_2PPh_2)_2(CH_2OCH_3)$ is discussed.

Multidentate ligands containing 'hybrid' donor atoms with consequent modified reactivity of the metal ion have received much attention, especially those containing both soft and hard donors. Among them, ligands with a combination of phosphorus and oxygen donors have been intensively investigated, due to the lability of the ether–metal interaction.[1–15] We have shown that the tripodal ligand 2,2-bis(diphenylphosphinomethyl)propyl methyl ether (dpmpme) behaves in only a bidentate mode towards various metal ions, due to the co-ordinating nature of the ether.[14,15] In order to investigate the properties of the oxygen donor in this tripodal system the ether site in dpmpme was replaced by a hydroxyl function to alter its capability. Herein we report the results of the co-ordination chemistry of the tripodal ligand 2,2-bis(diphenylphosphinomethyl)propan-1-ol (dpmp) and compare it with that of dpmpme.

Results and Discussion

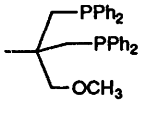
The desired tripodal compound dpmp was prepared by the reaction of 3-methyloxetan-3-ylmethyl methanesulfonate with excess of diphenylphosphide anion according to equation (1).



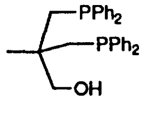
(1)

It was isolated as an air-stable white solid and its structure was confirmed by spectral and elemental analyses. A broad absorption at 3378 cm^{-1} in the IR spectrum clearly indicated the existence of a hydroxyl group and the ^{31}P NMR spectrum showed a single signal at δ −25.05 which is a shift typical of a tertiary phosphine.

Group 6 *Complexes*.—The thermal reaction of $[NEt_4][M(CO)_5Br]$ with dpmp produced $[M(CO)_4(dpmp\text{-}P,P')]$



dpmpme



dpmp

(M = Cr **1**, Mo **2** or W **3**). In all instances, the dpmp tripodal ligand acts in a bidentate manner, essentially similar to that of dpmpme in the analogous complexes $[M(CO)_4(dpmpme\text{-}P,P')]$ (M = Cr, Mo or W).[14] Attempts to prepare the tridentate complexes using $[M(CO)_3(MeCN)_3]$ or $[M(CO)_3(C_7H_8)]$ as starting materials failed. The structural analyses of complexes **1**–**3**, by analogy with $[M(CO)_4(dpmpme\text{-}P,P')]$ (M = Cr, Mo or W),[14] were confirmed by IR and NMR spectroscopy (Table 1).

Manganese(I) *Complexes*.—The substitution reaction of $[Mn(CO)_5Br]$ by dpmp in equimolar proportions in refluxing chloroform yielded a mixture of stereoisomers, *anti,fac*-$[Mn(CO)_3Br(dpmp\text{-}P,P')]$ **4a** and *syn,fac*-$[Mn(CO)_3Br(dpmp\text{-}P,P')]$ **4b** in a 1 : 1 ratio [equation (2)]. The isomeric forms of **4a** and **4b** arise from the non-equivalent orientations of the bromide ligand and the unco-ordinating hydroxyl function along the chelate ring. Complex **4b** was obtained in pure form by recrystallization from tetrahydrofuran (thf)–hexane. Both complexes exhibit identical chemical shifts (δ 29.7) in their ^{31}P NMR spectra and carbonyl absorptions (2029s, 1963m and 1904m cm^{-1}) in their IR spectra, but these two complexes are easily differentiated by their ^1H NMR spectra. The chemical shift of the methyl group in the *syn* isomer **4b** is upfield from that of the *anti* isomer **4a** by 0.7 ppm, whereas the trend of the chemical shifts of the methylene units adjacent to oxygen in **4a** and **4b** are the opposite (*cf.* δ 3.30 **4b** and 2.86 **4a**). This outcome is consistent with that previously observed for $[Mn(CO)_3Br(dpmpsp\text{-}P,P')]$ [dpmpsp = 2,2-bis(diphenylphosphinomethyl)-1-(phenylsulfanyl)propane].[16] The assignment of **4b** as the *syn,fac* stereoisomer is confirmed by X-ray crystallography (Fig. 1). The analogous iodide complexes **5a** and **5b** were obtained in a similar manner using $[Mn(CO)_5I]$ and characterized by spectral methods.

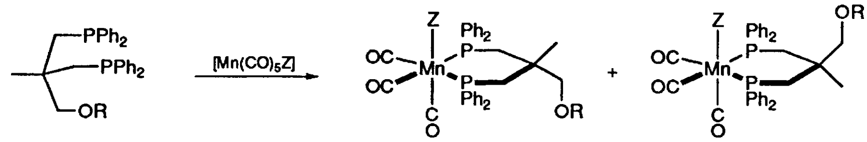
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Partial ^{1}H NMR, ^{31}P NMR and IR data of the complexes

Complex	$\delta(^1H)$	$\delta(^{31}P)$	$\Delta\delta(^{31}P)^a$	$\tilde{\nu}(CO)/cm^{-1}$
1	0.71 ($-CH_3$) 3.27 ($-CH_2-O-$)	40.3	65.3	2004m, 1947w 1918s, 1885s
2	0.71 ($-CH_3$) 3.35 ($-CH_2-O-$)	18.9	43.9	2017m, 1957m 1896s, 1809m
3	0.73 ($-CH_3$) 3.34 ($-CH_2-O-$)	−0.4	24.6	2013m, 1948w 1916s, 1882s
[Cr(CO)$_4$(dpmpme)]^b	0.75 ($-CH_3$) 2.76 ($-CH_2-O-$)	41.1	66.2	2006m, 1999m 1917m, 1882s
[Mo(CO)$_4$(dpmpme)]^b	0.75 ($-CH_3$) 2.83 ($-CH_2-O-$)	19.6	40.7	2017m, 1919m 1892s
[W(CO)$_4$(dpmpme)]^b	0.76 ($-CH_3$) 2.82 ($-CH_2-O-$)	0.01	25.1	2014m, 1913m 1892s
4a	1.01 ($-CH_3$) 2.86 ($-CH_2-O-$)	29.7	54.7	2029s, 1963m 1904m
4b	0.26 ($-CH_3$) 3.30 ($-CH_2-O-$)	29.7	54.7	2029s, 1963m 1904m
5a	1.08 ($-CH_3$) 2.78 ($-CH_2-O-$)	26.4	51.4	2023s, 1961m 1905m
5b	0.16 ($-CH_3$) 3.34 ($-CH_2-O-$)	26.4	51.4	2023s, 1961m 1905m
6	1.34 ($-CH_3$) 3.71 ($-CH_2-O-$)	34.8	59.8	2040s, 1973m 1923m
7a	1.12 ($-CH_3$) 3.12 ($-CH_2-O-$)	30.2	54.8	2030s, 1966m 1907m
7b	0.46 ($-CH_3$) 3.27 ($-CH_2-O-$)	29.2	53.8	2030s, 1966m 1907m
8b	0.42 ($-CH_3$) 3.23 ($-CH_2-O-$)	32.7	57.7	2009s, 1999m, 1948m, 1903m
9b	0.45 ($-CH_3$) 3.35 ($-CH_2-O-$)	33.4	58.4	2036s, 1968m, 1926m

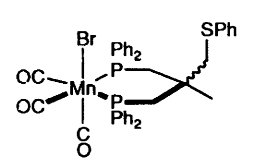
^{a} $\Delta\delta$ = δ(complex) − δ(free ligand) in ppm. ^{b} Ref. 14.



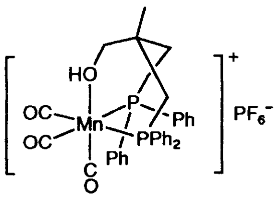
(2)

	R	Z
4a	H	Br
5a	H	I
7a	Me	Br

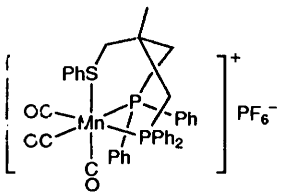
	R	Z
4b	H	Br
5b	H	I
7b	Me	Br



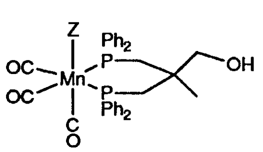
[Mn(CO)$_3$Br(dpmpsp-*P, P′*)]



6



[Mn(CO)$_3$(dpmpsp-*P, P′,S*)] PF$_6$



8b Z = N$_3$
9b Z = NCS

A mixture of **4a** and **4b** was readily converted into the complex *fac*-[Mn(CO)$_3$(dpmp-*P,P′,O*)]PF$_6$ **6** on treatment with silver hexafluorophosphate, the dpmp ligand now co-ordinating in a tridentate, rather than bidentate manner. Complex **6** was isolated as an air-stable, yellow crystalline solid and its structure was confirmed by single-crystal X-ray crystallography (Fig. 2). The ^{1}H NMR resonance of the methyl group at δ 1.34 in complex **6** is relatively deshielded compared with that in the other tripodal $CH_3C(CH_2PPh_2)_2(CH_2OR)$ (R = H or Me) complexes (Table 1), a trend which is consistent with other known systems.[18,19]

The ligand dpmpme behaved similarly to dpmp towards [Mn(CO)$_5$Br] to give a mixture of products **7a** and **7b**. Upon treatment with AgPF$_6$, neither **7a** nor **7b** led to the fomation of a tridentate-mode complex, indicating that the co-ordinating ability of the ether function is weaker towards the manganese(I) complex than that of the hydroxyl.

Ligand-substitution Reactions of Complex **6**.—Reaction of complex **6** with tetrabutylammonium bromide proceeded in thf at room temperature by displacement of the co-ordinated oxygen donor to give *syn,fac*-[Mn(CO)$_3$Br(dpmp-*P,P′*)] **4b** exclusively. The incoming bromide evidently co-ordinates at the position that the oxygen donor occupied. Stereospecificity of this kind in a ligand-substitution reaction is relevant to the previously reported system, [Mn(CO)$_3$(dpmpsp-*P,P′,S*)]PF$_6$. Moreover, complex **6** reacted with iodide, azide or thiocyanate

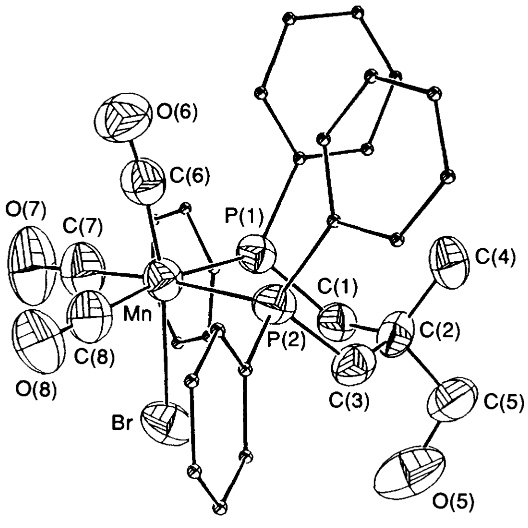


Fig. 1 ORTEP[17] plot of *syn,fac*-[Mn(CO)$_3$Br(dpmp-*P,P'*)] **4b**

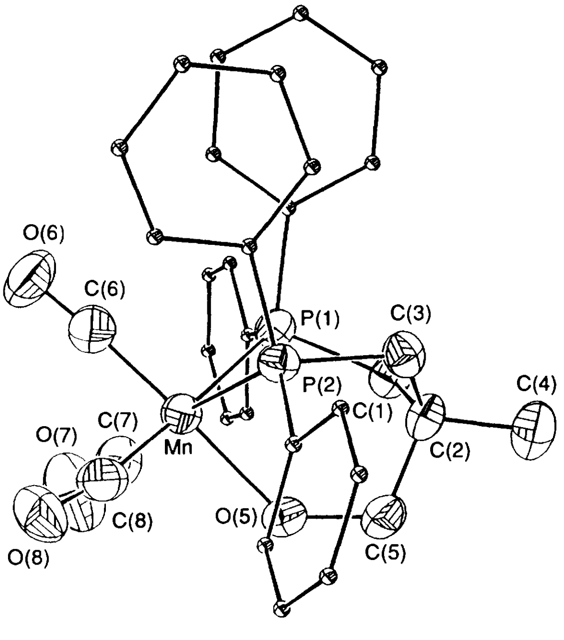


Fig. 2 ORTEP[17] plot of the [Mn(CO)$_3$(dpmp-*P,P',O*)]$^+$ cation of **6**

stereospecifically to give the corresponding *syn* products **5b**, [Mn(CO)$_3$(N$_3$)(dpmp-*P,P'*)] **8b** or [Mn(CO)$_3$(NCS)(dpmp-*P,P'*)] **9b** respectively. Both complexes **8b** and **9b** were characterized by spectral and elemental analyses and the stereochemistry of **9b** was confirmed by X-ray structural analysis (Fig. 3).

Crystal Structure Analysis.—The structures of complexes **4b**, **6** and **9b** were determined by single-crystal X-ray diffraction and are shown in Figs. 1–3. Selected bond distances and angles are listed in Table 2 and atomic coordinates in Tables 3–5, respectively. These structural determinations demonstrate that each complex consists of an octahedrally co-ordinated manganese atom with three carbonyl ligands arranged in a facial fashion. In complex **6**, all three donors (two phosphorus and one oxygen atoms) of the tripodal ligand form another facial plane around the metal centre. The metal to phosphorus distances are all within normal ranges [2.329(2)–2.371(2) Å]. As expected for the *trans* influence of ligands, the M–C distances *trans* to the phosphines are slightly larger than those *trans* to the bromine, oxygen or nitrogen donor. The deviation of P(1)–Mn–C(6) from 90° in both **4b** and **9b** is due to steric interaction of the phenyl ring in the phosphorus and carbonyl ligand [C(6)–O(6)].

Table 2 Selected bond distances (Å) and angles (°)

	4b (X = Br)	**6** [X = O(5)]	**9b** (X = N)
Mn–P(1)	2.340(2)	2.348(2)	2.359(2)
Mn–P(2)	2.371(2)	2.329(2)	2.346(3)
Mn–X	2.543(1)	2.102(3)	2.015(5)
Mn–C(6)	1.762(7)	1.767(5)	1.783(7)
Mn–C(7)	1.816(7)	1.812(5)	1.810(7)
Mn–C(8)	1.809(7)	1.813(5)	1.823(7)
C(6)–O(6)	1.152(8)	1.145(6)	1.157(8)
C(7)–O(7)	1.131(8)	1.136(6)	1.152(8)
C(8)–O(8)	1.142(8)	1.156(6)	1.143(8)
S–C	—	—	1.637(7)
C–N	—	—	1.143(8)
P(1)–Mn–P(2)	88.2(2)	87.03(6)	87.70(8)
P(1)–Mn–X	87.87(6)	85.0(1)	86.1(2)
P(2)–Mn–X	88.33(6)	82.8(1)	84.0(2)
P(1)–Mn–C(6)	100.9(2)	94.2(2)	98.5(2)
P(1)–Mn–C(7)	90.7(2)	92.4(2)	90.0(2)
P(1)–Mn–C(8)	171.0(2)	177.6(2)	174.7(2)
P(2)–Mn–C(6)	95.8(2)	98.8(2)	93.3(2)
P(2)–Mn–C(7)	174.3(2)	173.2(2)	176.4(2)
P(2)–Mn–C(8)	91.0(2)	91.8(2)	92.7(2)
C(6)–Mn–C(7)	89.9(3)	88.0(2)	89.8(3)
C(6)–Mn–C(8)	88.1(3)	84.0(2)	86.7(3)
C(7)–Mn–C(8)	89.3(3)	89.1(2)	89.4(3)
Mn–N–C	—	—	170.4(5)
N–C–S	—	—	175.0(6)

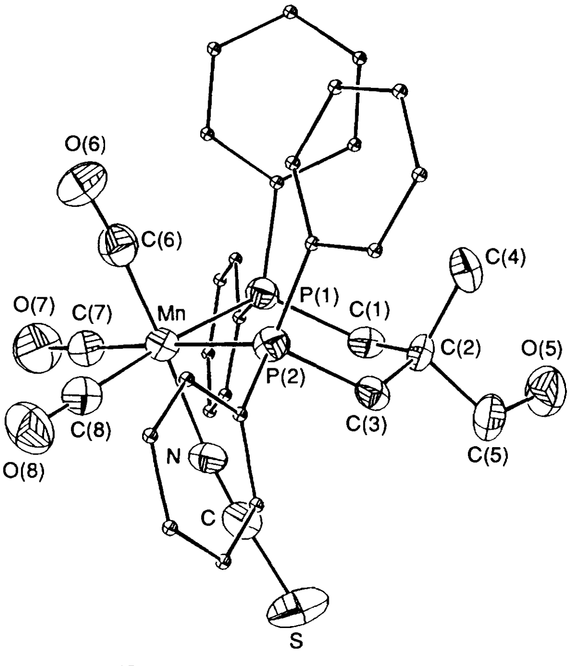


Fig. 3 ORTEP[17] plot of *syn,fac*-[Mn(CO)$_3$(NCS)(dpmp-*P,P'*)] **9b**

The crystal structure of **9b** is the first of a manganese thiocyanate compound containing π-acceptor ligands. The Mn–N–C [170.4(5)°] and N–C–S [175.0(6)°] angles imply that the co-ordinating thiocyanate ligand is linear, similar to that in *trans*-[Mn(H$_2$O)$_4$(NCS)$_2$] (171.9 and 178.5° respectively).[20] The C–N [1.143(8) Å] and S–C [1.637(7) Å] bond distances, which are essentially identical to those of *trans*-[Mn(H$_2$O)$_4$(NCS)$_2$] (N–C 1.146, S–C 1.637 Å), indicate triple and single bonds respectively. This observation is clearly considered indicative of Mn–NCS bonding, which is consistent with the IR absorption at 2105 cm^{-1} for the CN of the thiocyanato-*N* complex **9b**.[21,22] The bands at 2036, 1968 and 1926 cm^{-1} (carbonyl stretches) support the structure of **9b** in which all the carbonyl ligands are *cis*.

Table 3 Atomic coordinates for complex **4b**

Atom	*x*	*y*	*z*
Mn	0.769 13(9)	0.512 81(6)	0.277 02(5)
Br	0.576 34(7)	0.580 28(5)	0.213 69(4)
P(1)	0.676 06(15)	0.392 72(10)	0.235 07(9)
P(2)	0.692 08(16)	0.500 74(10)	0.385 36(9)
C(1)	0.524 4(5)	0.383 8(4)	0.251 4(3)
C(2)	0.499 3(5)	0.389 7(4)	0.331 1(3)
C(3)	0.537 4(5)	0.469 1(4)	0.367 8(3)
C(4)	0.548 9(6)	0.322 2(4)	0.380 9(3)
C(5)	0.362 5(6)	0.383 9(5)	0.321 2(4)
O(5)	0.308 0(4)	0.453 1(4)	0.283 2(3)
C(6)	0.914 2(6)	0.481 1(4)	0.319 0(4)
O(6)	1.012 5(4)	0.466 0(3)	0.344 1(3)
C(7)	0.814 2(7)	0.525 4(4)	0.188 1(4)
O(7)	0.845 1(6)	0.536 0(3)	0.134 2(3)
C(8)	0.817 7(6)	0.611 3(4)	0.302 6(4)
O(8)	0.848 9(5)	0.673 9(3)	0.315 7(3)
C(11A)	0.648 0(5)	0.381 6(4)	0.132 1(3)
C(12A)	0.550 2(6)	0.412 5(4)	0.085 4(3)
C(13A)	0.532 7(6)	0.404 7(4)	0.007 9(3)
C(14A)	0.612 7(7)	0.366 3(4)	−0.022 5(3)
C(15A)	0.712 5(7)	0.335 4(5)	0.022 6(4)
C(16A)	0.729 8(6)	0.341 7(4)	0.100 8(3)
C(11B)	0.750 9(5)	0.299 8(4)	0.264 3(3)
C(12B)	0.686 8(6)	0.230 6(4)	0.263 0(4)
C(13B)	0.745 1(7)	0.160 8(4)	0.282 2(4)
C(14B)	0.867 2(7)	0.158 7(4)	0.302 3(4)
C(15B)	0.932 6(6)	0.225 7(4)	0.302 7(4)
C(16B)	0.873 2(6)	0.295 3(4)	0.283 9(4)
C(21A)	0.685 2(6)	0.594 8(4)	0.431 9(3)
C(22A)	0.586 8(6)	0.643 7(4)	0.412 3(4)
C(23A)	0.586 9(7)	0.714 9(4)	0.448 8(4)
C(24A)	0.681 4(7)	0.736 9(4)	0.502 8(4)
C(25A)	0.780 0(7)	0.690 0(4)	0.522 4(4)
C(26A)	0.782 6(6)	0.618 9(4)	0.487 4(4)
C(21B)	0.763 8(5)	0.440 9(4)	0.465 5(3)
C(22B)	0.722 6(6)	0.444 9(4)	0.531 9(4)
C(23B)	0.771 5(6)	0.400 4(4)	0.592 9(3)
C(24B)	0.862 5(6)	0.351 3(4)	0.589 7(4)
C(25B)	0.904 0(6)	0.345 6(4)	0.524 4(4)
C(26B)	0.854 7(6)	0.390 0(4)	0.462 8(3)
O(31)	0.212 8(9)	0.446 2(8)	0.081 6(6)
C(32)	0.186 9(14)	0.433 9(9)	0.141 6(6)
C(33)	0.090 3(13)	0.399 4(10)	0.146 6(7)
C(34)	0.096 1(16)	0.357 1(7)	0.090 0(9)
C(35)	0.101 6(14)	0.412 0(11)	0.039 3(7)

Table 6 lists all the torsional angles around the six-membered chelate ring of the complexes, which facilitates their comparison. The conformations of the chelate rings in **4b** and **9b** adopt the chair forms according to the characteristic $+g$, $-g$ alternations of the torsional angles along the chelate rings. In contrast, all three 'fused' rings in **6** are forced into twist-boat forms because of the geometric limitation of the tripodal frame.

Conclusion

In this work we investigated the co-ordination behaviour of tripodal ether and hydroxyl phosphines towards some transition-metal ions. Even through a chelation effect, the oxygen atoms in both tripodal ligands (dpmp and dpmpme) are unable to co-ordinate to metal ions of Group 6 carbonyls, but the hydroxyl function of dpmp becomes a donor towards Mn^I in the formation of *fac*-[Mn(CO)$_3$(dpmp-*P*,*P′*,*O*)]PF$_6$. This complex undergoes ligand-substitution reactions with halide or pseudo-halide ligands stereospecifically to provide *syn,fac*-[Mn(CO)$_3$X(dpmp-*P*,*P′*)] (X = Br, I, NCS or N$_3$). The first X-ray crystal structure determination of a manganese(I) thiocyanate compound containing carbonyl ligands, *syn,fac*-[Mn(CO)$_3$(NCS)(dpmp-*P*,*P′*)], accommodates accurately the Mn–NCS bonding mode.

Table 4 Atomic coordinates for complex **6**

Atom	*x*	*y*	*z*
Mn	0.512 64	0.465 36(7)	0.372 30
P(1)	0.467 80(7)	0.372 27(13)	0.459 71(8)
P(2)	0.600 81(7)	0.548 69(14)	0.480 34(8)
C(1)	0.446 01(23)	0.512 2(5)	0.510 1(3)
C(2)	0.492 02(25)	0.635 8(5)	0.525 8(3)
C(3)	0.568 09(24)	0.598 9(5)	0.555 3(3)
C(4)	0.479 8(3)	0.724 4(6)	0.588 2(3)
C(5)	0.470 1(3)	0.721 8(5)	0.451 6(3)
O(5)	0.464 04(16)	0.643 1(3)	0.385 12(18)
C(6)	0.550 9(3)	0.313 5(5)	0.360 1(3)
O(6)	0.574 16(21)	0.217 2(4)	0.346 64(24)
C(7)	0.438 5(3)	0.418 4(6)	0.288 9(3)
O(7)	0.395 61(21)	0.387 8(5)	0.233 31(23)
C(8)	0.550 44(25)	0.533 2(5)	0.306 8(3)
O(8)	0.574 75(21)	0.556 9(4)	0.261 64(21)
C(11A)	0.520 41(23)	0.257 2(5)	0.533 3(3)
C(12A)	0.555 1(3)	0.155 8(6)	0.514 0(3)
C(13A)	0.593 6(3)	0.062 1(6)	0.567 2(4)
C(14A)	0.598 6(3)	0.070 1(6)	0.642 3(3)
C(15A)	0.563 3(3)	0.170 2(6)	0.663 4(3)
C(16A)	0.525 5(3)	0.261 9(6)	0.609 7(3)
C(11B)	0.387 64(23)	0.283 6(5)	0.418 2(3)
C(12B)	0.379 4(3)	0.150 6(5)	0.435 7(3)
C(13B)	0.317 0(3)	0.088 3(6)	0.400 1(4)
C(14B)	0.263 5(3)	0.156 8(6)	0.350 3(3)
C(15B)	0.270 7(3)	0.286 6(6)	0.334 3(3)
C(16B)	0.332 2(3)	0.351 2(5)	0.367 4(3)
C(21A)	0.671 88(23)	0.436 0(5)	0.526 0(3)
C(22A)	0.705 10(23)	0.388 6(5)	0.479 4(3)
C(23A)	0.758 6(3)	0.300 6(6)	0.506 4(3)
C(24A)	0.779 9(3)	0.257 5(6)	0.581 5(3)
C(25A)	0.748 2(3)	0.304 3(6)	0.629 7(3)
C(26A)	0.694 9(3)	0.397 0(6)	0.602 5(3)
C(21B)	0.641 42(23)	0.705 3(5)	0.467 3(3)
C(22B)	0.701 1(3)	0.744 0(6)	0.523 7(3)
C(23B)	0.732 0(3)	0.864 7(6)	0.517 8(3)
C(24B)	0.702 0(3)	0.945 0(6)	0.453 7(3)
C(25B)	0.641 9(3)	0.906 8(5)	0.397 1(3)
C(26B)	0.611 02(25)	0.789 6(5)	0.402 3(3)
P	0.243 41(9)	0.730 85(17)	0.268 66(10)
F(1)	0.269 39(24)	0.847 3(4)	0.229 3(3)
F(2)	0.310 55(18)	0.738 8(6)	0.340 98(23)
F(3)	0.276 7(3)	0.625 6(4)	0.233 1(3)
F(4)	0.216 54(21)	0.615 9(4)	0.305 91(24)
F(5)	0.177 62(19)	0.724 5(4)	0.195 81(23)
F(6)	0.211 79(21)	0.838 6(4)	0.306 7(3)
C(30)	0.414 2(3)	0.877 7(6)	0.225 2(3)
O(31)	0.435 19(20)	0.768 7(4)	0.250 24(23)
C(32)	0.419 3(4)	0.990 9(8)	0.276 5(5)
C(33)	0.380 9(3)	0.896 7(8)	0.141 6(4)

Experimental

Proton ^{13}C and ^{31}P NMR spectra were measured on a Bruker AC-E 200 or AM-300WB spectrometer. Chemical shifts are given in ppm relative to SiMe$_4$ and 85% H_3PO_4 for ^1H and ^{31}P NMR spectra in CDCl$_3$ respectively, unless otherwise noted. Infrared spectra were obtained on Perkin-Elmer 983G and Bio-Rad FT-IR instruments. Elemental analyses were performed on a Perkin-Elmer 240C instrument.

Syntheses.—*2,2-Bis(diphenylphosphinomethyl)propan-1-ol (dpmp)*. Diphenylphosphide anion, which was prepared by the addition of a hexane solution (1.6 mol dm^{-3}) of *n*-butyllithium (27 cm^3, 43.2 mmol) to a thf solution of diphenylphosphine (5.5 g, 29 mmol) at ice temperature, was added to a thf (50 cm^3) solution of 3-methyloxetan-3-ylmethyl methanesulfonate[9] (2.5 g, 13.9 mmol) with stirring. The resulting mixture was heated to reflux for 6 h and degassed water (10 cm^3) was added to quench the reaction. The organic portion was separated, dried and concentrated. The residue was chromatographed on silica (80 g) with ethyl acetate–hexane (1:3) as eluent. The eluate was collected and concentrated to give the desired product as a white solid (3.34 g, 53%) (Found: C, 76.10; H, 6.70. Calc. for $C_{29}H_{30}OP_2$: C, 76.30; H, 6.65%), m.p. 96–98 °C. IR (KBr): ν(OH) 3378 cm^{-1}. NMR: ^1H, δ 7.57–7.36 (m, 20 H), 3.60 (s, 2 H), 2.52 (t, 4 H) and 1.09 (s, 3 H); ^{31}P, δ −25.05.

Table 5 Atomic coordinates for complex **9b**

Atom	*x*	*y*	*z*
Mn	0.141 34(11)	0.690 03(9)	0.325 48(8)
P(1)	0.197 94(18)	0.866 47(16)	0.266 86(13)
P(2)	0.334 81(19)	0.598 92(16)	0.208 61(13)
S	−0.081 3(3)	0.789 72(22)	0.039 96(17)
C	−0.024 7(7)	0.759 9(6)	0.145 4(5)
N	0.024 1(5)	0.740 4(5)	0.215 3(4)
C(1)	0.239 4(7)	0.899 0(6)	0.132 7(5)
C(2)	0.352 2(7)	0.808 7(6)	0.067 4(4)
C(3)	0.333 0(6)	0.686 0(6)	0.086 3(5)
C(4)	0.511 0(7)	0.795 4(6)	0.070 1(5)
C(5)	0.322 8(8)	0.858 9(6)	−0.038 4(5)
O(5)	0.348 9(5)	0.967 1(5)	−0.077 3(4)
C(6)	0.248 3(7)	0.631 2(6)	0.421 8(5)
O(6)	0.309 3(6)	0.587 4(5)	0.488 2(4)
C(7)	−0.012 1(7)	0.768 0(6)	0.409 5(4)
O(7)	−0.106 9(5)	0.814 3(5)	0.466 3(4)
C(8)	0.085 2(7)	0.558 9(6)	0.363 2(5)
O(8)	0.048 6(6)	0.477 5(5)	0.388 6(4)
C(11A)	0.044 2(6)	1.003 0(6)	0.287 9(5)
C(12A)	0.053 5(7)	1.087 9(6)	0.335 0(5)
C(13A)	−0.064 7(8)	1.191 7(6)	0.348 5(6)
C(14A)	−0.190 7(7)	1.211 2(6)	0.315 6(5)
C(15A)	−0.201 8(7)	1.127 1(7)	0.270 4(6)
C(16A)	−0.085 6(7)	1.024 1(6)	0.256 2(5)
C(11B)	0.337 6(6)	0.882 8(5)	0.319 9(5)
C(12B)	0.330 5(7)	0.856 8(7)	0.421 2(5)
C(13B)	0.435 6(8)	0.864 7(7)	0.464 9(6)
C(14B)	0.549 5(8)	0.898 2(7)	0.409 8(6)
C(15B)	0.556 3(7)	0.926 8(7)	0.312 1(6)
C(16B)	0.449 3(7)	0.922 5(6)	0.265 6(5)
C(21A)	0.527 5(6)	0.551 1(6)	0.222 0(5)
C(22A)	0.571 7(7)	0.589 7(6)	0.289 8(5)
C(23A)	0.719 3(7)	0.566 2(7)	0.288 7(6)
C(24A)	0.821 0(7)	0.505 4(7)	0.219 5(6)
C(25A)	0.776 9(7)	0.463 6(7)	0.152 9(6)
C(26A)	0.631 8(7)	0.485 8(6)	0.153 9(5)
C(21B)	0.316 5(7)	0.463 5(6)	0.190 1(5)
C(22B)	0.372 4(8)	0.358 5(6)	0.252 4(6)
C(23B)	0.346 5(9)	0.255 8(7)	0.247 6(7)
C(24B)	0.265 9(9)	0.258 4(7)	0.180 6(7)
C(25B)	0.210 9(8)	0.360 1(7)	0.119 3(6)
C(26B)	0.233 9(7)	0.462 7(6)	0.123 6(5)

[M(CO)$_4$(dpmp-*P*,*P′*)] (M = Cr **1**, Mo **2** *or* W **3**). The carbonyl complex [NEt_4][M(CO)$_5$Br] and dpmp in equimolar proportions in thf were heated to reflux for 3 h. Filtration and concentration of the reaction mixture gave the crude product as a brown viscous liquid. The pure product was obtained by chromatography on silica gel with acetone as the eluent.

[2,2-Bis(diphenylphosphinomethyl)propan-1-ol-*P*,*P′*]tetracarbonylchromium(0) **1**. Yellow solid (96%) (Found: C, 63.65; H, 4.95. Calc. for $C_{33}H_{30}CrO_5P_2$: C, 63.85; H, 4.85%), m.p. 160–164 °C (decomp.). IR (benzene): ν_{CO} 2004, 1947, 1918 and 1885 cm^{-1}. NMR: ^1H, δ 7.82–7.75 (m, 4 H), 7.54–7.34 (m, 16 H), 3.27 (d, J_{P-H} = 1, 2 H), 2.69 (dd, *J* = 17, 11, 2 H), 2.60 (dd, *J* = 15, 3 Hz, 2 H), 1.40 (br, 1 H) and 0.71 (s, 3 H); ^{31}P, δ 40.3.

[2,2-Bis(diphenylphosphinomethyl)propan-1-ol-*P*,*P′*]tetracarbonylmolybdenum(0) **2**. White solid (96%) (Found: C, 59.55; H, 4.65. Calc. for $C_{33}H_{30}MoO_5P_2$: C, 59.65; H, 4.55%), m.p. 155–158 °C. IR (benzene): ν_{CO} 2017, 1957, 1896 and 1809 cm^{-1}. NMR: ^1H, δ 7.87–7.80 (m, 4 H), 7.52–7.32 (m, 16 H), 3.35 (s, 2 H), 2.86 (dd, *J* = 15, 12, 2 H), 2.57 (dd, *J* = 15, 3.8 Hz, 2 H), 1.40 (br, 1 H) and 0.71 (s, 3 H); ^{31}P, δ 18.9.

[2,2-Bis(diphenylphosphinomethyl)propan-1-ol-*P*,*P′*]tetracarbonyltungsten(0) **3**. Light yellow solid (97%) (Found: C, 52.55; H, 4.00. Calc. for $C_{33}H_{30}O_5P_2W$: C, 52.65; H, 4.00%), m.p. 168–173 °C. IR (benzene): ν_{CO} 2013, 1948, 1916 and 1886 cm^{-1}. NMR: ^1H, δ 7.85–7.79 (m, 4 H), 7.52–7.34 (m, 16 H), 3.34 (s, 2 H), 2.94 (dd, *J* = 17, 15, 2 H), 2.66 (dd, *J* = 15, 5 Hz, 2 H), 1.39 (br, 1 H) and 0.73 (s, 3 H); ^{31}P, δ − 0.4 (J_{P-W} = 224 Hz).

anti,fac- *and* syn,fac-[2,2-*Bis*(*diphenylphosphinomethyl*)-*propan*-1-*ol*-P,P′]*bromotricarbonylmanganese*(I) **4a** *and* **4b**. A mixture of [Mn(CO)$_5$Br] (527.9 mg, 1.92 mmol) and dpmp (875.6 mg, 1.19 mmol) in anhydrous thf (60 cm^3) was heated to reflux for 2 h. The reaction mixture was concentrated and the residue filtered through silica gel (20 g) with acetone as the eluent. The filtrate was concentrated to give an orange-yellow solid (1281 mg, 99%), which was a mixture of **4a** and **4b**. Recrystallization from thf–hexane gave **4b** as an orange solid (620 mg) (Found: C, 57.15; H, 4.40. Calc. for $C_{32}H_{30}BrMnO_4P_2$: C, 56.90; H, 4.50%), m.p. 183–186 °C (decomp.). IR ($CDCl_3$): ν_{CO} 2029s, 1963m and 1904m cm^{-1}. NMR: $^1H[(CD_3)_2CO]$, δ 7.88–7.82 (m, 4 H), 7.61–7.45 (m, 16 H), 4.23 (br, 1 H), 3.30 (s, 2 H), 2.74 (dd, *J* = 14, J_{P-C-H} = 3.3, 2 H), 2.59 (dd, *J* = 14, J_{P-C-H} = 8.7 Hz, 2 H) and 0.26 (s, 3 H); ^{31}P, δ 29.7. **4a**. IR ($CDCl_3$): ν_{CO} 2029s, 1963m and 1904m cm^{-1}. NMR: $^1H[(CD_3)_2CO]$, δ 7.80–7.78 (m, 4 H), 7.69–7.65 (m, 4 H), 7.54–7.37 (m, 12 H), 3.96 (br, 1 H), 3.06 (dd, *J* = 14, J_{P-C-H} = 4.2, 2 H), 2.86 (s, 2 H), 2.68 (dd, *J* = 14, J_{P-C-H} = 6.5 Hz, 2 H) and 1.01 (s, 3 H); ^{31}P, δ 29.7.

Table 6 Torsional angles (°) along the chelate ring

Complex **4b** Mn–P(1)–C(1)–C(2)–C(3)–P(2)		Complex **9b** Mn–P(1)–C(1)–C(2)–C(3)–P(2)	
Mn–P(1)–C(1)–C(2)	−58.8(3)	Mn–P(1)–C(1)–C(2)	−51.5(4)
P(1)–C(1)–C(2)–C(3)	60.4(4)	P(1)–C(1)–C(2)–C(3)	50.9(5)
C(1)–C(2)–C(3)–P(2)	−61.2(4)	C(1)–C(2)–C(3)–P(2)	−56.5(5)
C(2)–C(3)–P(2)–Mn	61.2(3)	C(2)–C(3)–P(2)–Mn	63.8(4)
C(3)–P(2)–Mn–P(1)	−43.7(2)	C(3)–P(2)–Mn–P(1)	−48.1(3)
P(2)–Mn–P(1)–C(1)	42.4(2)	P(2)–Mn–P(1)–C(1)	42.5(3)

Complex **6**

Mn–P(1)–C(1)–C(2)–C(3)–P(2)		Mn–P(1)–C(1)–C(2)–C(5)–O(5)		Mn–P(2)–C(3)–C(2)–C(5)–O(5)	
Mn–P(1)–C(1)–C(2)	−34.0(2)	Mn–P(1)–C(1)–C(2)	−34.0(2)	Mn–P(2)–C(3)–C(2)	−24.9(2)
P(1)–C(1)–C(2)–C(3)	−43.5(2)	P(1)–C(1)–C(2)–C(5)	81.6(3)	P(2)–C(3)–C(2)–C(5)	−42.3(2)
C(1)–C(2)–C(3)–P(2)	80.5(3)	C(1)–C(2)–C(5)–O(5)	−49.7(3)	C(3)–C(2)–C(5)–O(5)	75.5(4)
C(2)–C(3)–P(2)–Mn	−24.9(2)	C(2)–C(5)–O(5)–Mn	−28.0(2)	C(2)–C(5)–O(5)–Mn	−28.0(2)
C(3)–P(2)–Mn–P(1)	−36.1(1)	C(5)–O(5)–Mn–P(1)	58.2(2)	C(5)–O(5)–Mn–P(2)	−29.4(2)
P(2)–Mn–P(1)–C(1)	63.8(1)	O(5)–Mn–P(1)–C(1)	−19.2(2)	O(5)–Mn–P(2)–C(3)	49.3(2)

Table 7 Crystal data for complexes **4b**, **6** and **9b**[a]

Compound	**4b**·thf	**6**·Me$_2$CO	**9b**
Formula	$C_{36}H_{38}BrMnO_5P_2$	$C_{35}H_{36}F_6MnO_5P_3$	$C_{33}H_{30}MnNO_4P_2S$
M	747.47	798.54	653.55
Crystal system	Monoclinic	Monoclinic	Triclinic
Crystal size/mm	0.40 × 0.50 × 0.50	0.35 × 0.35 × 0.35	0.15 × 0.20 × 0.2
Space group	$P2_1/c$	Cc	$P\bar{1}$
a/Å	11.488(2)	21.293(8)	9.981(5)
b/Å	17.171(3)	9.939(5)	12.228(4)
c/Å	18.209(8)	18.520(9)	14.198(7)
α/°	—	—	77.25(3)
β/°	102.56(2)	111.62(4)	77.00(4)
γ/°	—	—	68.23(4)
U/Å^3	3506(1)	3627(3)	1550(1)
Z	4	4	2
D_c/g cm^{-3}	1.416	1.463	1.401
μ/mm^{-1}	1.61	0.54	0.61
2θ range/°	19.06–22.20	18.7–28.60	19.06–23.04
F(000)	1536	1640	676
T/K	298	298	298
Scan width[b]	0.8 + 0.35 tan θ	0.7 + 0.35 tan θ	0.75 + 0.35 tan θ
Transmission range	0.92–1.00	0.97–1.00	0.71–1.00
2θ_{max}/°	45.0	50.0	45.0
No. of unique reflections	4597	3187	3766
No. of reflections observed [$I > 2\sigma(I)$]	2785	2596	2142
No. of parameters	407	454	380
R	0.042	0.034	0.040
R'	0.039	0.024	0.034
S	1.95	1.80	1.31

[a] Details in common: θ–2θ scan mode, Mo-Kα radiation (λ = 0.710 69 Å); weighting scheme $w^{-1} = \sigma^2(F)$. [b] The stationary counting for background is applied.

anti,fac- *and* syn,fac-[2,2-*Bis(diphenylphosphinomethyl)-propan*-1-*ol*-P,P′]*tricarbonyliodomanganese*(I) **5a** *and* **5b**. Complexes **5a** and **5b** were obtained in a similar procedure to that described for **4a** and **4b**. **5a**. IR (CDCl$_3$): ν_{CO} 2023s, 1961m and 1905m cm^{-1}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 7.76–7.74 (m, 4 H), 7.72–7.70 (m, 4 H), 7.49–7.35 (m, 12 H), 3.75 (br, 1 H), 3.25 (dd, J = 14, $J_{P\text{-}C\text{-}H}$ = 3.3, 2 H), 2.84 (dd, J = 14, $J_{P\text{-}C\text{-}H}$ = 6.5 Hz, 2 H), 2.78 (s, 2 H) and 1.08 (s, 3 H); ^{31}P, δ 26.4. **5b** (Found: C, 52.80; H, 4.65. Calc. for $C_{32}H_{30}IMnO_4P_2$: C, 53.20; H, 4.20%), m.p. 184–189 °C (decomp.). IR (CDCl$_3$): ν_{CO} 2023s, 1961m and 1905m cm^{-1}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 7.93–7.88 (m, 4 H), 7.56–7.51 (m, 4 H), 7.49–7.35 (m, 12 H), 4.38 (br, 1 H), 3.65 (dd, J = 14, $J_{P\text{-}C\text{-}H}$ = 3.3, 2 H), 3.34 (s, 2 H), 2.63 (dd, J = 14, $J_{P\text{-}C\text{-}H}$ = 8.8 Hz, 2 H) and 0.16 (s, 3 H); ^{31}P, δ 26.4.

fac-[2,2-*Bis(diphenylphosphinomethyl)propan*-1-*ol*-P,P′,O]-*tricarbonylmanganese*(I) *hexafluorophosphate* **6**. To a flask containing AgPF$_6$ (355.5 mg, 1.41 mmol) was added a solution of a mixture of **4a** and **4b** (948.9 mg, 1.41 mmol) in thf (30 cm^3). After stirring for 0.5 h, the reaction mixture was filtered through silica gel (20 g) and washed with acetone. The filtrate was concentrated and the residue was recrystallized from thf–hexane to give the desired complex as a yellow crystalline solid (1030 mg, 90%) (Found: C, 52.00; H, 4.45. Calc. for $C_{32}H_{30}F_6MnO_4P_3$: C, 51.90; H, 4.10%), m.p. 163–167 °C (decomp.). IR (CDCl$_3$): ν_{CO} 2040s, 1973m and 1923m cm^{-1}. NMR [(CD$_3$)CO]: ^{1}H, δ 7.54–7.51 (m, 16 H), 7.36–7.31 (m, 4 H), 7.07 (br, 1 H), 3.71 (s, 2 H), 3.03 (dd, J = 16, $J_{P\text{-}C\text{-}H}$ = 5.7, 2 H), 2.53 (dd, J = 16, $J_{P\text{-}C\text{-}H}$ = 4.7 Hz, 2 H) and 1.34 (s, 3 H); ^{31}P, δ 34.8.

anti,fac- *and* syn,fac-[2,2-*Bis(diphenylphosphinomethyl)-propyl methyl ether*-P,P′]*bromotricarbonylmanganese*(I) **7a** *and* **7b**. These complexes were prepared according to a similar procedure to that described for complexes **4a** and **4b**. **7a** (Found: C, 57.45; H, 4.70. Calc. for $C_{33}H_{32}BrMnO_4P_2$: C, 57.50; H, 4.70%). IR (CHCl$_3$): ν_{CO} 2030s, 1966m and 1907m cm^{-1}. NMR: ^{1}H, δ 7.68–7.64 (m, 8 H), 7.42–7.33 (m, 12 H), 3.12 (d, J = 14, 2 H), 2.57 (s, 3 H), 2.51 (dt, J = 14, $J_{P\text{-}C\text{-}H}$ = 7.1 Hz, 2 H), 2.31 (s, 2 H) and 1.12 (s, 3 H); ^{31}P, δ 30.2. **7b**, m.p. 190–193 °C (decomp.). IR (CHCl$_3$): ν_{CO} 2030s, 1966m and 1907m cm^{-1}. NMR: ^{1}H (CDCl$_3$), δ 7.68–7.64 (m, 8 H), 7.42–7.33 (m, 12 H), 3.27 (d, J = 14, 2 H), 2.97 (s, 5 H), 2.28 (dt, J = 14, $J_{P\text{-}C\text{-}H}$ = 7.5 Hz, 2 H) and 0.46 (s, 3 H); ^{31}P, δ 29.2.

Ligand-substitution reactions of complex **6** *by halides and pseudo-halides*. To a solution of complex **6** in anhydrous thf or acetone was added NBu$_4$X (X = Br or SCN), KI or NaN$_3$ at room temperature. After stirring for 30 min, the solvent was removed and the residue was dissolved in CDCl$_3$ to measure the ^{1}H NMR spectrum. Complexes **4b** and **5b** were identified by spectral methods, whereas complexes **8b** and **9b** were isolated by recrystallization from thf–hexane.

syn,fac-Azido[2,2-bis(diphenylphosphinomethyl)propan-1-ol-*P,P′*]tricarbonylmanganese(I) **8b**. Yellow solid (Found: C, 59.90; H, 4.90; N, 6.30. Calc. for $C_{32}H_{30}MnN_3O_4P_2$: C, 60.30; H, 4.75; N, 6.60%), m.p. 152–155 °C. IR: ν(N=N) 2053; ν(CO) 2009s, 1999m, 1948m and 1903m cm^{-1}. NMR: ^{1}H[(CD$_3$)CO], δ 7.86–7.80 (m, 4 H), 7.55–7.43 (m, 16 H), 4.20 (br, 1 H), 3.23 (s, 2 H), 2.92 (dd, J = 14.6, 3.5, 2 H), 2.41 (dd, J = 14.6, 7.9 Hz, 2 H) and 0.42 (s, 3 H); ^{31}P, δ 32.7.

syn,fac-[2,2-Bis(diphenylphosphinomethyl)propan-1-ol-*P,P′*]tricarbonyl(thiocyanato-*N*) manganese(I) **9b**. Light yellow solid (Found: C, 60.50; H, 4.75; N, 2.10. Calc. for $C_{33}H_{30}MnNO_4P_2S$: C, 60.65; H, 4.65; N, 2.15%), m.p. 186–189 °C (decomp.). IR: ν(NCS) 2105, ν(CO) 2036s, 1968m and 1926m cm^{-1}. NMR: ^{1}H, δ 7.88–7.82 (m, 4 H), 7.61–7.45 (m, 16 H), 4.23 (br, 1 H), 3.35 (s, 2 H), 2.74 (dd, J = 14, 3.3, 2 H), 2.59 (dd, J = 14, 8.7 Hz, 2 H) and 0.45 (s, 3 H); ^{31}P, δ 33.4.

X-Ray Crystallography.—Crystals of **4b**, **6** and **9b** were obtained in suitable forms for X-ray analysis. Cell parameters were measured and data collected on a CAD4 diffractometer. Scattering factors were taken from ref. 23 and the NRCC SDP VAX program was used for the calculations.[24] Details of the crystal parameters, data collection and structure refinement for complexes **4b**, **6** and **9b** are summarized in Table 7. Complex **6** crystallized in a monoclinic space group with a C centre and c glide; the intensity distribution favoured the non-centric one. The space group Cc was assumed and confirmed by the successful solution and refinement of the structure.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the National Science Council of the Republic of China (NSC83-0208-M-002-63) for financial support.

References

1 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
2 M. R. Mason, Y. Su, R. A. Jacobson and J. G. Verkade, *Organometallics*, 1991, **10**, 2335; M. R. Mason and J. G. Verkade, *Organometallics*, 1992, **11**, 1514.
3 V. V. S. Reddy, A. Varshney and G. M. Gray, *J. Organomet. Chem.*, 1990, **391**, 259; A. Varshney, M. L. Webster and G. M. Gray, *Inorg. Chem.* 1992, **31**, 2580.
4 E. Lindner and R. Speidel, *Z. Naturforsch., Teil B*, 1989, **44**, 437; E. Lindner, H. Rothfuß, R. Fawzi and W. Hiller, *Chem. Ber.*, 1992, **125**, 541.
5 J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658.
6 G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.
7 S. J. Chen and K. R. Dunbar, *Inorg. Chem.*, 1990, **29**, 588.
8 N. W. Alcock, J. M. Brown and J. C. Jeffrey, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.
9 A. J. McAlees, R. McCrindle and A. R. Woon-Fat, *Inorg. Chem.*, 1976, **15**, 1065.
10 H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.
11 D. Harry, M. W. Thewissen, K. Timmer, J. G. Noltes and J. W. Marsman, *Inorg. Chim. Acta*, 1985, **97**, 143.
12 U. Klabunde and S. D. Ittel, *J. Mol. Catal.*, 1987, **41**, 123.
13 J. Ipaktschi and W. Sulzbach, *J. Organomet. Chem.*, 1992, **434**, 287.
14 S.-T. Liu, G.-J. Liu, C.-H. Yieh, M.-C. Cheng and S.-M. Peng, *J. Organomet. Chem.*, 1990, **387**, 83.
15 S.-T. Liu, C.-H. Yieh and H.-J. Lu, *Phosphorus Sulfur*, 1989, **44**, 261.
16 S.-T. Liu, H.-E. Wang, L.-M. Yiin, S.-C. Tsai, K.-J. Liu, Y.-M. Wang, C.-M. Cheng and S.-M. Peng, *Organometallics*, 1993, **12**, 2277.
17 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
18 S.-C. Tsai, H.-E. Wang, C.-T. Huang, L.-M. Yiin, C.-M. Cheng, S.-M.Peng and S.-T. Liu, *Chem. Ber.*, in the press.
19 H.-E. Wang, M.-C. Cheng, G.-H. Lee, S.-M. Peng and S.-T. Liu, *J. Organomet. Chem.*, 1993, **445**, 171.
20 B. Beagley, C. A. McAuliffe, A. G. Mackie and R. G. Pritchard, *Inorg. Chim. Acta*, 1984, **89**, 163.
21 M. J. Coyer, R. H. Herber, J. Chen, M. Croft and S. P. Szu, *Inorg. Chem.*, 1994, **33**, 716.
22 J. L. Burmeister, *Coord. Chem. Rev.*, 1990, **105**, 77.
23 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
24 E. J. Gabe and F. L. Lee, *Acta Crystallogr., Sect. A*, 1981, **37**, S339.

Received 27th April 1994; *Paper* 4/02495H