Manganese(I) Complexes with (Tricyclohexylphosphonio)dithiocarboxylate as Chelate and Unidentate Ligand. *X*-Ray Crystal Structure of *fac*-[Mn(CO)$_3${S$_2$CP(C$_6$H$_{11}$)$_3$}$_2$]ClO$_4$·H$_2$O†

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[Mn(CO)$_5$Br] reacts with S$_2$CP(C$_6$H$_{11}$)$_3$ (C$_6$H$_{11}$ = cyclohexyl) in refluxing CS$_2$ to give *fac*-[Mn(CO)$_3${S$_2$CP(C$_6$H$_{11}$)$_3$}Br] (**1**) which can be also obtained by refluxing *cis*-[Mn(CO)$_4${P(C$_6$H$_{11}$)$_3$}Br] in CS$_2$. Halide abstraction from (**1**) with AgClO$_4$, and subsequent treatment with neutral ligands L affords *fac*-[Mn(CO)$_3$L{S$_2$CP(C$_6$H$_{11}$)$_3$}]ClO$_4$ with L = CO, P(OMe)$_3$, P(C$_6$H$_{11}$)$_3$, S$_2$CP(C$_6$H$_{11}$)$_3$. In the case of L = S$_2$CP(C$_6$H$_{11}$)$_3$ an *X*-ray structure determination shows that the resulting compound *fac*-[Mn(CO)$_3${S$_2$CP(C$_6$H$_{11}$)$_3$}$_2$]ClO$_4$ contains one S$_2$CP(C$_6$H$_{11}$)$_3$ acting as a chelate (*SS'*) ligand and another acting in a unidentate σ-(*S*) fashion. Compounds [Mn(CO)$_5${S$_2$CP(C$_6$H$_{11}$)$_3$}]ClO$_4$ and *fac*-[Mn(CO)$_3$(L–L){S$_2$CP(C$_6$H$_{11}$)$_3$}]ClO$_4$ (L–L = Ph$_2$PCH$_2$PPh$_2$ or 2,2'-bipyridyl) containing unidentate S$_2$CP(C$_6$H$_{11}$)$_3$ ligands can be obtained by displacement of OClO$_3^-$ from perchlorate complexes.

Many transition metal complexes containing carbon disulphide adducts of tertiary phosphines S$_2$CPR$_3$ as ligand have been reported in recent years.[1–8] The synthetic routes for the preparation of these complexes can be classified into two main types depending on the properties of both the phosphines and the precursors involved. Since trialkylphosphines give stable S$_2$CPR$_3$ compounds, the usual procedures to form (trialkylphosphonio)dithiocarboxylate complexes are reactions of suitable substrates with the previously formed S$_2$CPR$_3$ adduct[4] or the insertion of CS$_2$ into a metal–trialkylphosphine bond.[2] On the contrary, triarylphosphines do not form stable adducts with CS$_2$ and, in these cases, nucleophilic attack of the triarylphosphine on the carbon atom of a previously co-ordinated CS$_2$ group has been suggested for the formation of complexes like [Ir(CO)(PPh$_3$)$_2$(S$_2$CPPh$_3$)]BPh$_4$.[1]

In the case of manganese complexes, the reaction of [Mn(CO)$_2$(η^5-C$_5$H$_5$)(thf)] (thf = tetrahydrofuran) with S$_2$CPEt$_3$ has been reported to give [Mn(CO)$_2$(η^5-C$_5$H$_5$)(S$_2$CPEt$_3$)],[4] this being the only manganese compound with a S$_2$CPR$_3$ ligand described to date. On the other hand, a number of manganese and rhenium complexes with anionic bidentate PS- and SS-donor ligands (L–L) have been recently prepared[9,10] and one hydrometallation reaction of CS$_2$ with [M(CO)$_3$H(L–L)] [M = Mn or Re; L–L = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm)] giving [M(CO)$_3${Ph$_2$P(CH$_2$)$_n$P(CHS$_2$)Ph$_2$-*PSS'*}] (*n* = 1 or 2)[11] has been reported.

Here we report the use of the adduct of tricyclohexylphosphine and carbon disulphide, S$_2$CP(C$_6$H$_{11}$)$_3$, in the preparation of octahedral manganese complexes containing the tricyclohexylphosphoniodithiocarboxylate ligand in chelate (*SS'*) and unidentate σ-(*S*) fashion.

Results and Discussion

Reaction of [Mn(CO)$_5$Br] with S$_2$CP(C$_6$H$_{11}$)$_3$ in refluxing CS$_2$ [reaction (*i*), Scheme] for 4 h produces a deep blue precipitate of *fac*-[Mn(CO)$_3${S$_2$CP(C$_6$H$_{11}$)$_3$}Br] (**1**) in 80% yield. This product is moderately soluble in CH$_2$Cl$_2$, insoluble in Et$_2$O and hydrocarbons, and can be obtained as a deep blue air-stable crystalline solid by slow evaporation of a CH$_2$Cl$_2$ solution. Compound (**1**) is indefinitely stable in solution under an N$_2$ atmosphere, but it decomposes slowly on contact with air giving a small amount of *fac*-[Mn(CO)$_3${P(C$_6$H$_{11}$)$_3$}{S$_2$CP(C$_6$H$_{11}$)$_3$}]-Br.

The i.r. spectrum of (**1**) in CH$_2$Cl$_2$ consists of three strong bands at 2 024s, 1 939s, and 1 917s cm^{-1} in the ν(CO) region (Table 1), a typical pattern for a *fac*-tricarbonyl arrangement. The ^{31}P-{^{1}H} n.m.r. spectrum of (**1**) displays a sharp singlet at δ 20.1 p.p.m. Alternatively compound (**1**) can also be obtained in 79% yield by refluxing *cis*-[Mn(CO)$_4${P(C$_6$H$_{11}$)$_3$}Br] in CS$_2$ for 7 h [reaction (*ii*), Scheme].

Although the intimate mechanisms of these reactions have not been studied, reaction (*i*) appears to be a simple substitution of two CO groups for the previously formed S$_2$CP(C$_6$H$_{11}$)$_3$ ligand, while reaction (*ii*) is a formal insertion of CS$_2$ into a phosphine–metal bond with a simultaneous loss of CO. Since no evidence has been found in these or other reactions for the formation of a CS$_2$ complex, the other possible pathway for the reaction (attack on the carbon of a co-ordinated CS$_2$ molecule) would be unlikely in these manganese compounds.

The reaction [(*iii*), Scheme] of (**1**) with AgClO$_4$ in CH$_2$Cl$_2$ for 2 h produces a purple solution. Its i.r. spectrum (CH$_2$Cl$_2$) shows ν(CO) bands at 2 030s, 1 950s, and 1 935s cm^{-1} suggesting the formation of the perchlorato complex *fac*-[Mn(CO)$_3$(OClO$_3$){S$_2$CP(C$_6$H$_{11}$)$_3$}]. Unfortunately several attempts to isolate such species as a solid gave mixtures of decomposition products. However the purple solution thus obtained can be immediately used to prepare cationic complexes by displacement of the weakly co-ordinated perchlorate ion by CO [(**2**)], P(OMe)$_3$ [(**3a**)], P(C$_6$H$_{11}$)$_3$ [(**3b**)], or S$_2$CP(C$_6$H$_{11}$)$_3$ [(**4**)]. Orange-red *cis*-[Mn(CO)$_4${S$_2$CP(C$_6$H$_{11}$)$_3$}]ClO$_4$ (**2**) is obtained in 81% yield by bubbling

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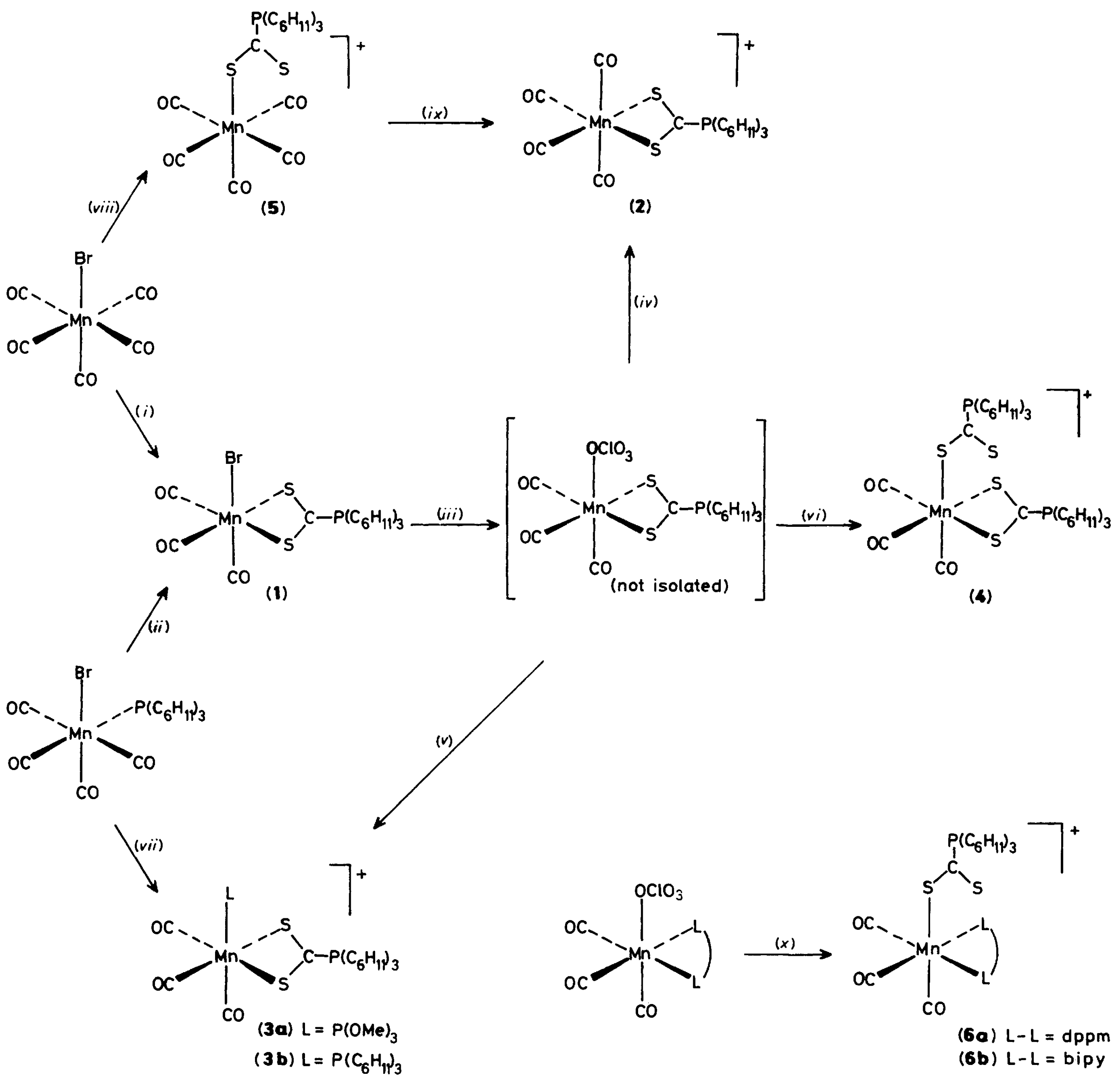
† *fac*-Tricarbonyl[(tricyclohexylphosphonio)dithiocarboxylate-*S*]-[(tricyclohexylphosphonio)dithiocarboxylate-*SS'*]manganese(I) perchlorate–hydrate (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme. Reactions were in CH_2Cl_2 solution at room temperature unless otherwise stated. (*i*) CS_2, $S_2CP(C_6H_{11})_3$, reflux, 4 h; (*ii*) CS_2, reflux, 7 h; (*iii*) $AgClO_4$, 2 h; (*iv*) CO, 3 h; (*v*) L, 45 min; (*vi*) $S_2CP(C_6H_{11})_3$, 1 h; (*vii*) $AgClO_4$, 2 h; then L, 3.5 h; (*viii*) $AgClO_4$, $S_2CP(C_6H_{11})_3$, 30 min; (*ix*) $CHCl_3$, reflux, 2.5 h; (*x*) $S_2CP(C_6H_{11})_3$, 4 h for (**6a**) and 1 h for (**6b**)

CO through a mixture of (**1**) and $AgClO_4$ in CH_2Cl_2 [reaction (*iv*), Scheme]. The i.r. spectrum of (**2**) in CH_2Cl_2 solution displays three bands in the ν(CO) region (2 104m, 2 027vs, 1 988s cm^{-1}) in a pattern consistent with a *cis*-tetracarbonyl disposition, and the analytical data (Table 1) are in good agreement with the proposed formulation. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**2**) in $CDCl_3$ shows a sharp singlet at δ 36.1 p.p.m. downfield 16 p.p.m. from the signal of compound (**1**). The strong deshielding of phosphorus is consistent with the decrease of electronic density around the metal when changing a bromide for a CO ligand.

Cationic *fac*-tricarbonyl complexes of formula *fac*-$[Mn(CO)_3L\{S_2CP(C_6H_{11})_3\}]ClO_4$ [L = $P(OMe)_3$, (**3a**); L = $P(C_6H_{11})_3$, (**3b**)] are produced by treating the purple solution of *fac*-$[Mn(CO)_3(OClO_3)\{S_2CP(C_6H_{11})_3\}]$ with the appropriate P-donor ligand [reaction (*v*), Scheme]. After evaporation of solvent *in vacuo*, addition of diethyl ether gives yellow-orange (**3a**) in 85% yield, or dark purple (**3b**) in 82% yield as air-stable crystalline solids. Alternatively compound (**3b**) can also be prepared by treating *cis*-$[Mn(CO)_4(OClO_3)\{P(C_6H_{11})_3\}]$ with $S_2CP(C_6H_{11})_3$ in CH_2Cl_2 solution [reaction (*vii*), Scheme], by displacement of perchlorate with simultaneous loss of CO.

The i.r. spectra of these compounds exhibit three absorption bands in the ν(CO) region [(**3a**), 2 046s, 1 978s, 1 948s; (**3b**), 2 027s, 1 956s, 1 935s cm^{-1}] with the pattern expected for *fac* arrangements of three carbonyls. The $^{31}P-\{^1H\}$ n.m.r. spectra of compounds (**3a**) and (**3b**) in $CDCl_3$ at room temperature consist of two signals (Table 1). The signal at high field is in both cases a

Table 1. Melting points, analytical, i.r. and $^{31}P-\{^1H\}$ n.m.r. data

Compound	Analysis[a] (%) C	H	M.p.[b] (°C)	$\nu(CO)^c/cm^{-1}$	$^{31}P-\{^1H\}$ N.m.r.[d] $S_2CP(C_6H_{11})_3$	Other
(1) *fac*-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}Br]$	45.65 (45.90)	6.00 (5.80)	164	2 024s, 1 939s, 1 917s	[e] 20.1 (s)	
(2) *cis*-$[Mn(CO)_4\{S_2CP(C_6H_{11})_3\}]ClO_4$	44.05 (44.35)	5.45 (5.35)	154	2 104m, 2 027vs, 1 988s	36.1 (s)	
(3a) *fac*-$[Mn(CO)_3\{P(OMe)_3\}\{S_2CP(C_6H_{11})_3\}]$-$ClO_4$	42.05 (41.75)	5.90 (5.90)	160[f]	2 046s, 1 978s, 1 948s	30.1 [d, $^4J(P-P)$ = 13.7 Hz]	161[br, Mn-$P(OMe)_3$]
(3b) *fac*-$[Mn(CO)_3\{P(C_6H_{11})_3\}\{S_2CP(C_6H_{11})_3\}]$-$ClO_4\cdot CH_2Cl_2$	51.25 (51.30)	7.25 (7.15)	188	2 027s, 1 956s, 1 935s	29.1 [d, $^4J(P-P)$ = 8 Hz]	66.2 [br, Mn-$P(C_6H_{11})_3$]
(4) *fac*-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]ClO_4\cdot H_2O$	50.35 (50.80)	7.25 (7.05)	182	2 027s, 1 945s	25.9 (s), 31.7 (s)	
(5) $[Mn(CO)_5\{S_2CP(C_6H_{11})_3\}]ClO_4$	44.05 (44.30)	5.15 (5.10)	134	2 139m, 2 056vs, 2 038 (sh)	41.7 (s)	
(6a) *fac*-$[Mn(CO)_3(dppm)\{S_2CP(C_6H_{11})_3\}]ClO_4$	57.30 (57.65)	5.65 (5.65)	167	2 025s, 1 961s, 1 944s	32.7 [t, $^4J(P-P)$ = 3.7 Hz]	16.3 [br, $CH_2(PPh_2)_2$]
(6b) *fac*-$[Mn(CO)_3(bipy)\{S_2CP(C_6H_{11})_3\}]ClO_4$[g]	51.25 (51.15)	5.55 (5.50)	166	2 032s, 1 942s br	31.8 (s)	

[a] Calculated values given in parentheses. [b] With decomposition. [c] CH_2Cl_2 solution. [d] $CDCl_3$ solution unless otherwise stated; external 85% H_3PO_4 as reference; positive sign for δ denotes signals downfield from H_3PO_4. [e] CD_2Cl_2 solution. [f] Change of aspect in the solid can be observed at *ca.* 90 °C. [g] Analysis: N, 4.00 (3.75)%.

Table 2. Intramolecular bond distances (Å) and angles (°)

Manganese co-ordination			
Mn–C(3)	1.800(8)	Mn–S(1)	2.383(2)
Mn–C(4)	1.806(7)	Mn–S(2)	2.361(3)
Mn–C(5)	1.819(12)	Mn–S(3)	2.349(2)
C(3)–Mn–C(4)	89.4(3)	C(4)–Mn–S(2)	89.5(4)
C(3)–Mn–C(5)	91.8(5)	C(4)–Mn–S(3)	176.7(4)
C(3)–Mn–S(1)	168.2(4)	C(5)–Mn–S(1)	99.9(3)
C(3)–Mn–S(2)	94.9(4)	C(5)–Mn–S(2)	173.3(3)
C(3)–Mn–S(3)	90.9(2)	C(5)–Mn–S(3)	91.9(2)
C(4)–Mn–C(5)	91.4(4)	S(1)–Mn–S(2)	73.37(9)
C(4)–Mn–S(1)	91.5(3)	S(1)–Mn–S(3)	87.53(6)
S(2)–Mn–S(3)	87.27(8)		
Carbonyl ligands			
C(3)–O(3)	1.14(1)	Mn–C(3)–O(3)	176.7(6)
C(4)–O(4)	1.13(1)	Mn–C(4)–O(4)	178.9(9)
C(5)–O(5)	1.12(2)	Mn–C(5)–O(5)	174.8(5)
Phosphoniodithiocarboxylates			
Ligand A		Ligand B	
P(1)–C(1)	1.815(9)	P(2)–C(2)	1.848(6)
P(1)–C(11)	1.829(6)	P(2)–C(41)	1.825(6)
P(1)–C(21)	1.833(11)	P(2)–C(51)	1.832(9)
P(1)–C(31)	1.822(6)	P(2)–C(61)	1.827(11)
S(1)–C(1)	1.660(10)	S(3)–C(2)	1.689(7)
S(2)–C(1)	1.673(7)	S(4)–C(2)	1.648(9)
S(1)–C(1)–S(2)	116.4(5)	S(3)–C(2)–S(4)	129.5(3)
S(1)–C(1)–P(1)	121.9(4)	S(3)–C(2)–P(2)	114.3(5)
S(2)–C(1)–P(1)	121.6(6)	S(4)–C(2)–P(2)	116.0(4)
C(1)–P(1)–C(11)	107.7(3)	C(2)–P(2)–C(41)	108.3(3)
C(1)–P(1)–C(21)	106.0(4)	C(2)–P(2)–C(51)	106.9(3)
C(1)–P(1)–C(31)	107.5(4)	C(2)–P(2)–C(61)	109.2(4)
C(11)–P(1)–C(21)	109.0(4)	C(41)–P(2)–C(51)	108.3(4)
C(11)–P(1)–C(31)	109.9(3)	C(41)–P(2)–C(61)	114.7(4)
C(21)–P(1)–C(31)	116.4(4)	C(51)–P(2)–C(61)	109.1(4)
Average C–C (cyclohexyl) distance			1.51(2)
Average C–C–C (cyclohexyl) angle			110.9(8)

sharp doublet [(**3a**), δ 30.1 p.p.m. $^4J(P-P)$ = 13.7 Hz; (**3b**), δ 29.1 p.p.m., $^4J(P-P)$ = 8.0 Hz] assigned to the phosphorus atom of the $S_2CP(C_6H_{11})_3$ ligand. The broad low-field signal [(**3a**), δ 161 p.p.m. for Mn–$P(OMe)_3$; (**3b**), δ 66.2 p.p.m. for Mn–$P(C_6H_{11})_3$] is assigned to the phosphorus atom of ligand L directly bound to manganese. The broadening of these signals is attributable to the quadrupole moment of the manganese nucleus and precludes the observation of the expected doublet due to the small value of the coupling constants.

Under similar conditions to those above, purple *fac*-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]ClO_4$ (**4**) is obtained by treating *fac*-$[Mn(CO)_3(OClO_3)\{S_2CP(C_6H_{11})_3\}]$ with an equimolar amount of $S_2CP(C_6H_{11})_3$ [reaction (*vi*), Scheme]. The i.r. spectrum (Table 1) of compound (**4**) reveals a *fac*-tricarbonyl unit and the $^{31}P-\{^1H\}$ n.m.r. spectrum in CD_2Cl_2 shows two sharp peaks at δ 25.9 p.p.m. and δ 31.7 p.p.m., both assigned to the resonances of phosphorus atoms of two different $S_2CP(C_6H_{11})_3$ ligands. The long distance (six bonds) between the two phosphorus atoms precludes coupling between them thus explaining the signals appearing as two singlets. Chemical analyses are in good agreement with the proposed stoicheiometry and conductivity measurements support the formulation of (**4**) as a 1:1 electrolyte.

All these experimental data, together with the great tendency of Mn^I towards octahedral co-ordination, strongly suggest a structure for (**4**) with one $S_2CP(C_6H_{11})_3$ group acting as a (*SS'*) chelating ligand and the other acting in a unidentate σ-(*S*) fashion. That structure has been confirmed by an *X*-ray structural determination carried out on a crystal of (**4**) (Figure). The bond lengths and angles are given in Table 2, final atomic co-ordinates are in Table 3. Calculations showed that (**4**) crystallized with one molecule of water, possibly taken from the solvent during the work-up. It was found that crystals can be obtained free of water under strict anhydrous conditions; then the ^1H n.m.r. spectrum and analysis (C, H) indicated the presence of one molecule of CH_2Cl_2.

Some structures of mononuclear complexes with chelate[2] and σ-unidentate[4,12] S_2CPR_3 ligands have been reported, and also one structure in which S_2CPEt_3 adducts act as chelate and bridging ligands in a dinuclear silver complex;[3] however, as far as we know, this is the first structure determination of a complex

Table 3. Final atomic co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn	0.717 54(9)	0.128 13(8)	0.100 64(6)	C(46)	1.339 1(8)	0.549 1(6)	−0.200 0(5)
S(1)	0.873 9(2)	0.288 0(1)	0.130 9(1)	C(51)	1.046 4(7)	0.323 1(5)	−0.290 3(4)
S(2)	0.815 0(2)	0.078 3(1)	0.163 0(1)	C(52)	0.929 3(9)	0.199 7(7)	−0.262 2(6)
S(3)	0.912 3(2)	0.184 8(1)	−0.043 2(1)	C(53)	0.861(1)	0.173 3(8)	−0.321 8(8)
S(4)	0.965 1(2)	0.405 0(2)	−0.069 6(1)	C(54)	0.804 3(9)	0.237 6(9)	−0.315 9(7)
P(1)	1.020 5(2)	0.258 7(1)	0.215 3(1)	C(55)	0.918(1)	0.358 8(8)	−0.345 1(6)
P(2)	1.133 2(2)	0.356 8(1)	−0.221 6(1)	C(56)	0.993 2(9)	0.389 7(8)	−0.290 1(6)
C(1)	0.904 3(6)	0.208 8(5)	0.167 3(4)	C(61)	1.201 9(7)	0.277 6(6)	−0.232 3(4)
C(2)	0.996 4(6)	0.315 0(5)	−0.101 5(4)	C(62)	1.275 3(8)	0.296 3(7)	−0.177 0(6)
C(11)	0.914 6(7)	0.234 1(5)	0.337 7(4)	C(63)	1.303 1(9)	0.211 0(7)	−0.178 2(6)
C(12)	0.795(1)	0.112 5(7)	0.387 7(5)	C(64)	1.392 0(9)	0.217 0(8)	−0.273 0(6)
C(13)	0.716(1)	0.098 9(9)	0.488 3(6)	C(65)	1.324(1)	0.202 9(9)	−0.329 6(7)
C(14)	0.661 1(9)	0.165 8(9)	0.507 4(6)	C(66)	1.295(1)	0.286 8(8)	−0.331 2(5)
C(15)	0.777(1)	0.283 2(9)	0.458 2(6)	C(3)	0.613 3(8)	−0.004 7(7)	0.084 9(5)
C(16)	0.858 4(9)	0.302 3(8)	0.355 9(5)	C(4)	0.571 9(8)	0.082 4(6)	0.214 1(5)
C(21)	1.082 6(7)	0.173 5(6)	0.198 9(4)	C(5)	0.656 5(7)	0.182 8(6)	0.052 8(5)
C(22)	1.169 4(9)	0.193 9(8)	0.243 7(7)	O(3)	0.542 4(6)	−0.090 4(5)	0.079 2(5)
C(23)	1.189(1)	0.103 9(8)	0.241 0(7)	O(4)	0.479 2(6)	0.052 9(5)	0.284 8(4)
C(24)	1.257(1)	0.098 2(8)	0.145 2(7)	O(5)	0.609 7(6)	0.208 9(6)	0.025 5(5)
C(25)	1.176(1)	0.085 2(8)	0.099 1(7)	Cl	0.258 0(2)	0.422 7(2)	0.421 1(1)
C(26)	1.157 2(9)	0.175 0(7)	0.099 5(5)	O(11)	0.128(1)	0.338(1)	0.431 4(6)
C(31)	1.155 7(6)	0.406 1(5)	0.160 4(4)	O(12)	0.288(1)	0.404(1)	0.483 3(8)
C(32)	1.234 8(8)	0.463 1(6)	0.211 3(5)	O(13)	0.268(2)	0.512(1)	0.455(1)
C(33)	1.333 5(8)	0.586 2(6)	0.169 3(5)	O(14)	0.372 9(9)	0.462(1)	0.331 3(6)
C(34)	1.433 3(8)	0.617 1(7)	0.068 7(6)	O(15)	0.224(2)	0.500(2)	0.419(1)
C(35)	1.356 5(9)	0.558 4(7)	0.018 8(6)	O(16)	0.290(3)	0.473(3)	0.481(2)
C(36)	1.256 5(8)	0.434 8(6)	0.059 7(5)	O(17)	0.136(3)	0.402(3)	0.426(2)
C(41)	1.265 8(7)	0.506 0(5)	−0.256 6(4)	O(18)	0.259(2)	0.346(2)	0.484(1)
C(42)	1.373 3(8)	0.552 2(7)	−0.358 6(5)	O(19)	0.342(3)	0.410(3)	0.330(2)
C(43)	1.464 2(9)	0.678 3(7)	−0.383 6(6)	O(20)	0.384(4)	0.505(4)	0.338(2)
C(44)	1.533 4(8)	0.724 6(7)	−0.326 4(5)	O(21)	0.156(3)	0.307(2)	0.421(2)
C(45)	1.427 2(8)	0.672 9(6)	−0.224 8(6)	W	0.113(1)	0.050 2(9)	0.516 9(6)

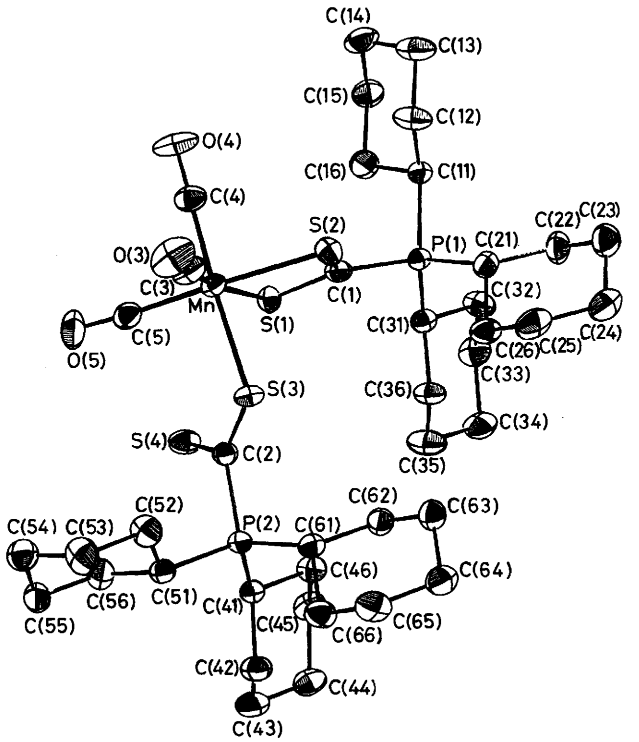


Figure. Structure of the cation $[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]^+$ with the atom labelling scheme; atoms are depicted as 30% probability ellipsoids

containing both chelate and σ-unidentate S_2CPR_3 ligands bound to the same central atom.

The structure consists of a mononuclear cation, $[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]^+$, the co-ordination around manganese being distorted octahedral with the three carbonyls in a facial arrangement. One of the $S_2CP(C_6H_{11})_3$ groups acts as a bidentate chelate ligand, while the other is bound by only one sulphur atom [S(3)], the distance from manganese to the non-bonded S(4) atom being 3.74 Å. The three Mn–C distances are equivalent within experimental error. The Mn–S distances are in the range 2.349—2.383 Å, comparable to those found in the manganese dithiocarbamate complex $[Mn(CO)_3(PPh_3)(S_2CNMe_2)]$ (2.37—2.38 Å).[13]

The most important distortion from C_{3v} symmetry is related to the angle S(1)–Mn–S(2) [73.37(9)°]. Of interest is the small value of S(1)–C(1)–S(2) [116.4(5)°] compared with the S–C–S angles in other S_2CPR_3 chelating ligands: 126.5(4)° in $[Ag_2(S_2CPEt_3)_4][ClO_4]_2$,[3] 123.5(5)° in $[Cu(PPh_3)_2(S_2CPEt_3)]BPh_4$,[2] and 119.0(3)° in *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$.[14] The angle S(3)–C(2)–S(4) [129.5(3)°] in the unidentate $S_2CP(C_6H_{11})_3$ ligand is close to those measured in $[Cr(CO)_5(S_2CPEt_3)]$ [130.8(7)°],[4] $[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)]ClO_4$ [129.4(9)°],[12] and $[Pt(C_6F_5)_2(CO)\{S_2CP(C_6H_{11})_3\}]$ [128.8(4)°].[14]

The four C–S distances are not very different, including that between C(2) and non-bonded S(4), and fall in the range 1.648(9)—1.689(7) Å, very close to the similar distances in other chelate or unidentate S_2CPR_3 complexes mentioned above. The small differences between the two C–S bond lengths is a consequence of electron delocalization within the S_2C moiety.[12]

Other cationic complexes containing $S_2CP(C_6H_{11})_3$ acting as a unidentate ligand can be prepared by displacement of weakly co-ordinated perchlorate under mild conditions. Thus treatment of $[Mn(CO)_5(OClO_3)]$ with $S_2CP(C_6H_{11})_3$ in CH_2Cl_2 solution affords yellow-orange $[Mn(CO)_5\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(5)** in 60% yield (analytical data in Table 1). The i.r. spectrum [v(CO) at 2 139m, 2 056vs, 2 038 (sh) cm^{-1}, in CH_2Cl_2] and ^{31}P-$\{^1H\}$ n.m.r. spectrum [δ 41.7 p.p.m. (s)] confirm the structure shown in the Scheme. Additional support comes from the fact that heating **(5)** in $CHCl_3$ for 2.5 h [reaction (*ix*), Scheme] produces the tetracarbonyl **(2)** in 73% yield *via* an intramolecular CO displacement.

Tricarbonyl compounds *fac*-$[Mn(CO)_3(L\text{-}L)\{S_2CP(C_6H_{11})_3\}]ClO_4$ [L–L = bis(diphenylphosphino)methane(dppm), **(6a)**; L–L = 2,2′-bipyridyl (bipy), **(6b)**] are produced by reaction of the appropriate perchlorato complex *fac*-$[Mn(CO)_3(L\text{-}L)(OClO_3)]$ with one equivalent of $S_2CP(C_6H_{11})_3$ in CH_2Cl_2. The air-stable crystalline solids show i.r. spectra in the v(CO) region [CH_2Cl_2 solution; **(6a)**, 2 025s, 1 961s, 1 944s; **(6b)**, 2 032s, 1 942s br cm^{-1}] which are typical for *fac*-tricarbonyl complexes. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of **(6a)** in $CDCl_3$ shows two signals as expected for one AX_2 pattern. The broad high-field signal at δ 16.3 p.p.m. can be assigned to the two equivalent phosphorus atoms of the dppm ligand directly bound to manganese. The downfield signal appears at δ 32.7 p.p.m. as a sharp triplet [^4J(P–P) = 3.7 Hz]. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of compound **(6b)** consists of only one sharp singlet at δ 31.8 p.p.m.

Experimental

All reactions were carried out in dry solvents under a nitrogen atmosphere. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated. Reactions involving silver(I) salts or 2,2′-bipyridyl compounds were performed in darkness. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer, ^{31}P-$\{^1H\}$ n.m.r. spectra ($CDCl_3$ or CD_2Cl_2 solutions, external 85% H_3PO_4 as reference) were recorded at room temperature on a Varian FT 80 A instrument. Elemental analyses were carried out on a Perkin-Elmer 240 B analyzer.

fac-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}Br]$ **(1)**.—*Method* (*a*). $[Mn(CO)_5Br]$[15] (0.55 g, 2 mmol) and $S_2CP(C_6H_{11})_3$ (0.713 g, 2 mmol) were stirred in CS_2 (30 cm^3) at reflux temperature for 4 h. The deep blue precipitate of **(1)** was collected on a frit and washed with diethyl ether (2 × 30 cm^3) and recrystallized from CH_2Cl_2. Yield: 0.92 g, 80%.

Method (*b*). *cis*-$[Mn(CO)_4\{P(C_6H_{11})_3\}Br]$[16] (0.2 g, 0.38 mmol) was stirred in CS_2 for 7 h. The deep blue precipitate of **(1)** was worked-up as in the preceding reaction. Yield: 0.173 g, 79%.

cis-$[Mn(CO)_4\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(2)**.—*Method* (*a*). A slow stream of CO (*ca.* 1 bubble per second) was passed through a stirred mixture of **(1)** (0.2 g, 0.35 mmol) and $AgClO_4$ (0.108 g, 0.52 mmol) in CH_2Cl_2 (40 cm^3) for 3 h in darkness. The AgBr precipitate was then filtered off and the clear orange-red solution was concentrated *in vacuo*. Addition of diethyl ether gave orange-red crystals of **(2)** (0.175 g, 81%).

Method (*b*). A solution of **(5)** (0.2 g, 0.31 mmol) in $CHCl_3$ (20 cm^3) was heated under reflux for 2.5 h. After filtering the reaction mixture and after evaporating the solvent *in vacuo*, addition of diethyl ether gave **(2)** as an orange-red crystalline solid. Yield: 0.14 g, 73%.

fac-$[Mn(CO)_3\{P(OMe)_3\}\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(3a)**.—Silver(I) perchlorate (0.09 g, 0.43 mmol) and **(1)** (0.2 g, 0.35 mmol) in CH_2Cl_2 (35 cm^3) were stirred in darkness for 2 h. The AgBr precipitate was filtered off and the purple solution was collected in a flask containing $P(OMe)_3$ (0.04 cm^3, 0.35 mmol) and stirred for 45 min. The colour of the solution changed from purple to orange-red. Evaporation of solvent *in vacuo* gave an oil which was stirred with diethyl ether (30 cm^3) affording **(3a)** as an orange-yellow microcrystalline solid. Yield: 0.214 g, 85%.

fac-$[Mn(CO)_3\{P(C_6H_{11})_3\}\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(3b)**.—*Method* (*a*). The first step of the reaction was as described for **(3a)** using $AgClO_4$ (0.09 g, 0.43 mmol) and **(1)** (0.2 g, 0.35 mmol) in CH_2Cl_2 (35 cm^3). After filtering off the AgBr precipitate, the resulting solution was stirred with $P(C_6H_{11})_3$ (0.097 g, 0.35 mmol) for 30 min. Evaporation of solvent *in vacuo* and treatment of the resulting oil with diethyl ether (30 cm^3) affords compound **(3b)** as a dark purple solid. Yield: 0.25 g, 82%. It was recrystallized by slow addition of diethyl ether to a concentrated CH_2Cl_2 solution giving dark purple crystals.

Method (*b*). *cis*-$[Mn(CO)_4\{P(C_6H_{11})_3\}Br]$[16] (0.2 g, 0.38 mmol) and $AgClO_4$ (0.098 g, 0.47 mmol) were stirred in darkness for 2 h. After filtering off AgBr, $S_2CP(C_6H_{11})_3$ (0.135 g, 0.38 mmol) was added to the resulting solution and the mixture was stirred for 3.5 h. The colour changed from yellow to deep purple. Evaporation of CH_2Cl_2 *in vacuo* followed by addition of diethyl ether gave **(3b)** as a dark purple solid. Yield: 0.25 g, 75%.

fac-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]ClO_4$ **(4)**.—The first step of the reaction was as described for **(3a)** using $AgClO_4$ (0.09 g, 0.43 mmol) and **(1)** (0.3 g, 0.35 mmol) in CH_2Cl_2 (35 cm^3). After removing the AgBr precipitate by filtration, $S_2CP(C_6H_{11})_3$ (0.136 g, 0.35 mmol) was added to the solution and the mixture was stirred for 1 h. Evaporation of solvent *in vacuo* and addition of diethyl ether gave **(4)** as a purple microcrystalline solid. Yield: 0.29 g, 88%.

$[Mn(CO)_5\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(5)**.—The compound $S_2CP(C_6H_{11})_3$ (0.26 g, 0.76 mmol) was added to a filtered $[Mn(CO)_5(OClO_3)]$[17] solution in CH_2Cl_2 prepared from $[Mn(CO)_5Br]$ (0.2 g, 0.73 mmol) and $AgClO_4$ (0.226 g, 1.1 mmol). The mixture was stirred in darkness for 30 min. Evaporating the solvent *in vacuo* and stirring the resulting oil with diethyl ether (25 cm^3) gave **(5)** as a yellow-orange solid. Yield: 0.29 g, 60%. Recrystallization was from CH_2Cl_2–Et_2O as described for **(3a)**.

fac-$[Mn(CO)_3(dppm)\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(6a)**.—The complex *fac*-$[Mn(CO)_3(dppm)(OClO_3)]$[18] (0.2 g, 0.32 mmol) and $S_2CP(C_6H_{11})_3$ (0.114 g, 0.32 mmol) were stirred in CH_2Cl_2 (30 cm^3) for 4 h, in darkness.. The solvent was evaporated *in vacuo* and the residue stirred with diethyl ether giving **(6a)** as a microcrystalline orange solid. Yield: 0.22 g, 71%.

fac-$[Mn(CO)_3(bipy)\{S_2CP(C_6H_{11})_3\}]ClO_4$ **(6b)**.—The reaction was performed under similar conditions as for **(6a)** using *fac*-$[Mn(CO)_3(bipy)(OClO_3)]$[19] (0.2 g, 0.51 mmol) in CH_2Cl_2 (30 cm^3); the mixture was stirred for 1 h. The work-up was as described for **(6a)**, affording **(6b)** as orange-red crystals. Yield: 0.29 g, 77%.

Crystal Structure Determination of fac-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]ClO_4\cdot H_2O$ **(4)**.—Crystals were grown by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of **(4)**. A dark purple prism (0.35 × 0.30 × 0.30 mm) was mounted in a sealed capillary tube.

Crystal data. $C_{41}H_{66}ClMnO_7P_2S_4$, M = 951.6, triclinic, a = 13.102(4), b = 15.180(4), c = 16.878(5) Å, α = 91.48(3), β = 64.63(3), γ = 123.58(3)°, U = 2 425(5) Å^3 (by least-squares refinement on setting angles of 25 automatically centred reflections), $\lambda = 0.710\,69$ Å, space group $P\bar{1}$, $Z = 2$, $D_c = 1.30$ g cm^{-3}.

Data collection and processing. CAD4 Enraf-Nonius diffractometer, $\omega/2\theta$ mode with ω-scan width of $1.3 + 0.35\tan\theta$; graphite-monochromated Mo-K_α radiation; 5 535 reflections measured at room temperature with $1.5 < \theta < 25°$ (hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$); 4 193 reflections with $F > 3\sigma(F)$ used for computations; no absorption correction (small value of $\mu = 5.7$ cm^{-1} and flat ψ scan); two standard reflections measured every 2 h.

Structure analysis and refinement. Direct methods with MULTAN;[20] full-matrix refinements in two blocks with SHELX.[21] Hydrogen atoms were found on a difference-Fourier map and were refined with one overall thermal parmeter [4.9(3) Å^2].

The perchlorate anion is not part of the co-ordination group; it presented an unsolved oxygen disorder problem. The difference map showed several diffuse peaks around the chlorine atoms. Four major peaks correspond to an approximate tetrahedral environment; however such a tetrahedron does not refine well and other peaks still appeared on a difference map. These lower peaks did not clearly show an alternative orientation for the tetrahedron. Occupation factors were then refined, arbitrarily, for 11 positions, all partially occupied by oxygen atoms, the sum of which converged to 4.2. Oxygen isotropic thermal parameters ranged from 3.8 to 7.5 Å^2, and Cl–O distances ranged from 1.33 to 1.60 Å. The Fourier map also revealed one additional peak near the inversion centre; this was refined as a water molecule. A refinement without this solvent molecule led to $R = 0.082$; when this water molecule was included, refinement converged to $R = 0.057$ and $R' = 0.049$, with $w = 1/[\sigma^2(F) + 0.0005(F)]$ where σ was evaluated from counting statistics. In the final cycle no parameter change was higher than 0.03, shift/e.s.d.

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