Manganese Complexes with S_2CPEt_3 Ligands. *X*-Ray Crystal Structures of *cis-trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ and *cis-trans*-$[Mn(CO)_2(PEt_3)_2(S_2CH)]$†

Daniel Miguel and Victor Riera *
Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain
Jesús A. Miguel and Fernando Diego
Laboratorio de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain
Claudette Bois and Yves Jeannin
Laboratoire de Chimie des Métaux de Transition, UA-CNRS 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

A variety of manganese(I) carbonyl complexes containing triethylphosphine and monodentate or chelate triethylphosphoniodithiocarboxylato ligands can be obtained by substitution reactions either under mild conditions or by thermal or photochemical methods. The products resulting from the thermal reactions between bromo carbonyls and S_2CPEt_3 are very different from those obtained with $S_2CP(C_6H_{11})_3$ under similar conditions, and this can be attributed to the difference in electronic and steric properties of the phosphines concerned. The *X*-ray structure of *cis,trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ has been determined. Reduction of this compound with $NaBH_4$ affords the neutral dithioformate complex *cis,trans*-$[Mn(CO)_2(PEt_3)_2(S_2CH)]$ which has been characterized by spectroscopic methods and by *X*-ray crystallography.

The study of the chemistry of complexes containing trialkylphosphoniodithiocarboxylato ligands, S_2CPR_3, has been an active field in the last twenty years, and a great number of compounds have been reported in which these ligands co-ordinate a wide variety of transition metals of the Groups 6—11.[1–19] Some of these complexes have been synthesized by insertion of CS_2 into a metal–phosphine bond,[1–5] or by nucleophilic attack of a phosphine on the carbon atom of a previously co-ordinated CS_2 group.[6,7] However, the usual procedure is to treat a suitable metal complex with a stable, previously formed, S_2CPR_3 adduct (R = alkyl).[9–19] From the literature on the preparation of S_2CPR_3 complexes of a wide range of metals, it is noticeable that very little has been reported about the effect of a change in the substituent R on the stoicheiometry, stereochemistry, or reactivity of the resulting compounds. This lack of information can be attributed to several reasons: in some cases a wide range of substituents R in the S_2CPR_3 ligands has been used in reactions which can be considered as kinetically controlled or under highly selective conditions. Thus, the work of Usón *et al.*[8–10] on the preparation of complexes of Pd^{II}, Pt^{II}, Au^{I}, and Au^{III} with S_2CPR_3 ligands [$R_3 = Bu_3$, $(C_6H_{11})_3$, Et_3, or Me_2Ph] is based mainly on the displacement of weakly bonded ligands such as perchlorate or tetrahydrothiophene at room temperature. In other cases, the preparation of S_2CPR_3 complexes, though achieved by means of more drastic and less-selective conditions (*i.e.* thermal or photochemical reactions), has been restricted to only one type of ligand. Notably, most of the great amount of work reported by Bianchini[7,11–19] and co-workers was made exclusively with S_2CPEt_3.

We have recently reported the preparation of a variety of mononuclear[20] and binuclear[21] complexes with the $S_2CP(C_6H_{11})_3$ (C_6H_{11} = cyclohexyl) adduct acting as a two-electron monodentate, four-electron chelate, or eight-electron bridging ligand. As an extension of this work, we have found that on changing the very bulky $P(C_6H_{11})_3$ group to the smaller PEt_3 some qualitative changes are induced in the chemistry of the S_2CPR_3 complexes, especially when thermal reactions are involved. In this paper we report the preparation of manganese carbonyl complexes with triethylphosphoniodithiocarboxylato ligands, and discuss the similarities and differences with the chemistry of the previously reported $S_2CP(C_6H_{11})_3$[20] complexes.

Results and Discussion

The reactions leading to complexes containing S_2CPEt_3 ligands are summarized in Scheme 1, and can be classified into three types which are discussed in different paragraphs: (*a*) thermal reactions [(*i*), (*iv*), and (*v*)] of the S_2CPEt_3 adduct with $[Mn(CO)_5Br]$ (**1**) or other substituted bromo carbonyls such as (**3**) or (**4**); (*b*) reactions [(*vi*)—(*viii*), (*x*), and (*xiv*)] in which S_2CPEt_3 displaces a weakly co-ordinated ligand such as perchlorate or acetone, at room temperature, to give complexes (**5**)—(**8**), (**12**), and (**13**) containing S_2CPEt_3 bonded to the metal in a monodentate fashion; and (*c*) reactions [(*ix*), (*xi*), and (*xii*)] of intramolecular carbonyl displacement in which a monodentate S_2CPEt_3 ligand becomes a chelate. Some reactions of S_2CPEt_3 complexes with $NaBH_4$ are discussed in paragraph (*d*). Spectroscopic data for all the complexes prepared are collected in Table 1.

(*a*) *Thermal Reactions of Bromo Carbonyl Derivatives with* S_2CPEt_3.—The thermal reactions carried out on $[Mn(CO)_5Br]$ (**1**) with S_2CPR_3 adducts (R = C_6H_{11} or Et) are summarized in Scheme 2 for a better comparison. Heating $[Mn(CO)_5Br]$ with $S_2CP(C_6H_{11})_3$ in CS_2 at reflux temperature gave deep blue

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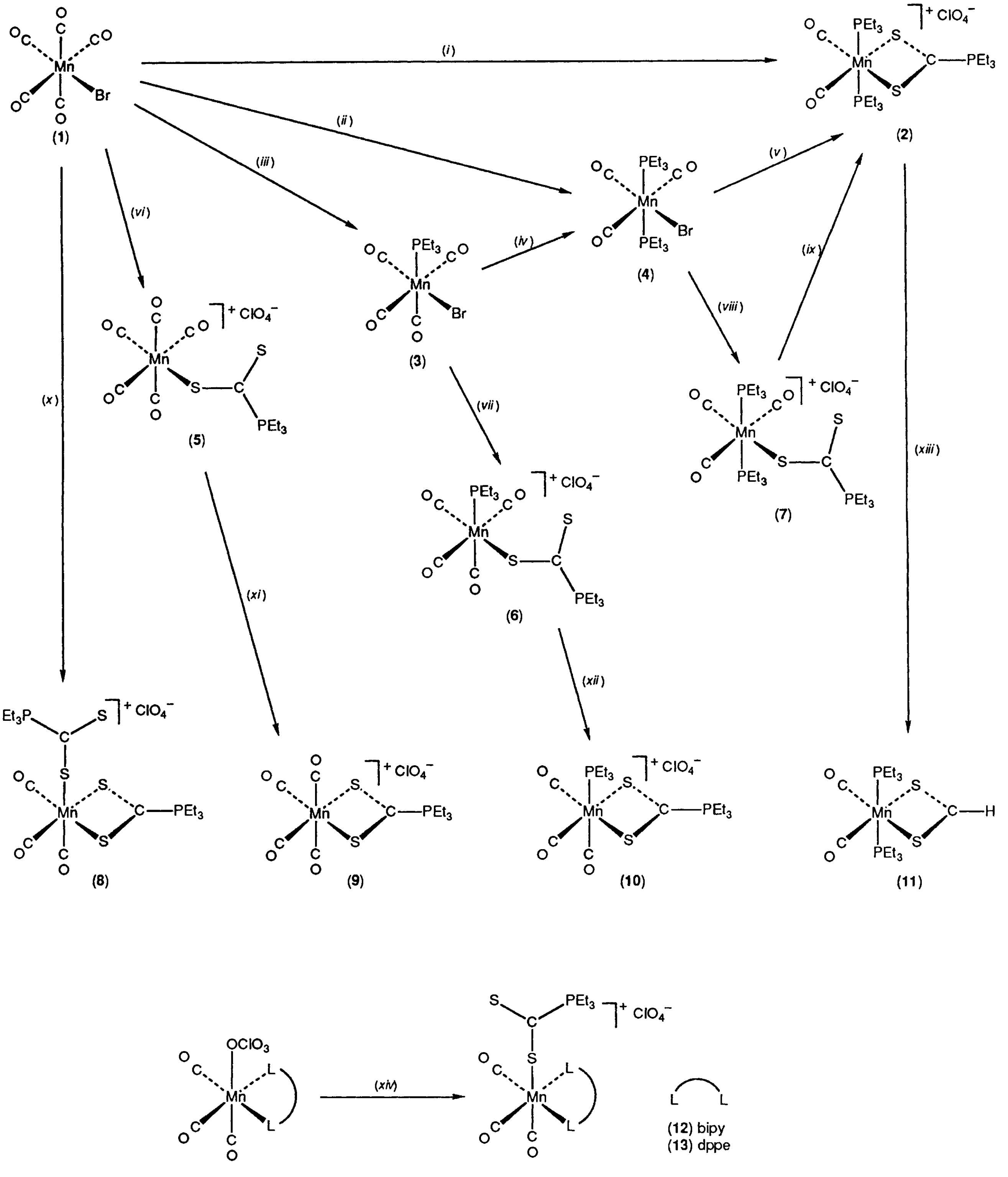
† Dicarbonylbis(triethylphosphine)(triethylphosphoniocarbodithiolate-κ^2S) manganese perchlorate and dicarbonyl(dithioformato-κ^2S)-bis(triethylphosphine)manganese.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme 1. (*i*) $3S_2CPEt_3$ in toluene–CS_2, reflux, 10 h; $AgClO_4$ in CH_2Cl_2, room temperature (r.t.), 30 min; (*ii*) $2PEt_3$, toluene, reflux, 1.5 h; (*iii*) PEt_3, $CHCl_3$, reflux, 1 h; (*iv*) PEt_3, toluene, reflux, 1 h; (*v*) S_2CPEt_3 in benzene–CS_2, reflux, 1 h; $AgClO_4$, 0.5 h, r.t.; (*vi*) $AgClO_4$ in CH_2Cl_2, 3 h, r.t., filtration; S_2CPEt_3, 30 min, r.t.; (*vii*) $AgClO_4$ in CH_2Cl_2, r.t., 2.5 h, filtration; S_2CPEt_3, r.t., 30 min; (*viii*) $AgClO_4$ in CH_2Cl_2, r.t., 3 h, filtration; S_2CPEt_3, r.t., 2 h; (*ix*) $CHCl_3$, reflux, 3 h; or u.v. irradiation, r.t., 10 min; (*x*) $AgClO_4$ in acetone, r.t., 2 h, filtration; $2S_2CPEt_3$, r.t., 30 min; (*xi*) $CHCl_3$, reflux, 3 h; (*xii*) Me_3NO, in CH_2Cl_2, r.t., 5 min; or u.v. irradiation, r.t., 30 min; (*xiii*) $NaBH_4$ in CH_2Cl_2–EtOH (2:1), r.t., 1.5 h; (*xiv*) S_2CPEt_3 in CH_2Cl_2, r.t.; 30 min for (**12**), 4 h for (**13**)

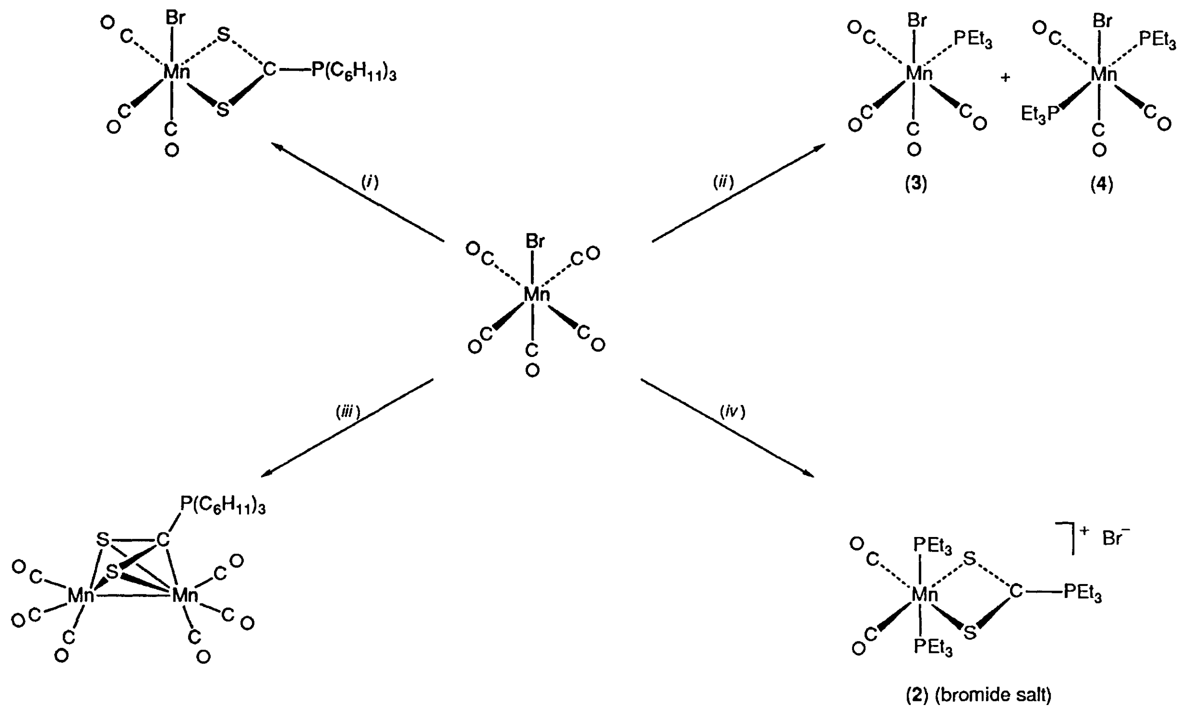
fac-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}Br]$ in 80% yield. When S_2CPEt_3 was used under the same conditions *cis*-$[Mn(CO)_4(PEt_3)Br]$ (**3**) was produced, and the use of an excess of S_2CPEt_3 produced mixtures of the tetracarbonyl (**3**) together with *mer,trans*-$[Mn(CO)_3(PEt_3)_2Br]$ (**4**).

On the other hand, heating the bromopentacarbonyl (**1**) and

Table 1. Spectroscopic data for the new compounds

Compound	I.r. ν(CO)/cm^{-1} (CH_2Cl_2 solution)	^{31}P-{^1H} N.m.r.[a] ($CDCl_3$ solution): S_2CP	^{31}P-{^1H} N.m.r.[a] ($CDCl_3$ solution): Other
(**2**) *cis, trans*-[$Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$	1 940s, 1 874s	27.3 [t, ^4J(PP) = 12.2]	53.1 (d, 2 P, Mn–PEt_3)[b]
(**3**) *cis*-[$Mn(CO)_4(PEt_3)Br$]	2 078w, 1 995vs, 1 945s		32.4(s)
(**4**) *mer,trans*-[$Mn(CO)_3(PEt_3)_2Br$]	2 034w, 1 945s, 1 900s		43.1(s)
(**5**) [$Mn(CO)_5\{SC(S)PEt_3\}]ClO_4$	2 142m, 2 061vs, 2 041(sh)	47.4(s)	
(**6**) *cis*-[$Mn(CO)_4(PEt_3)\{SC(S)PEt_3\}]ClO_4$	2 084m, 2 015(sh), 1 995vs, 1 975s	43.4 [d, ^4J(PP) = 3.5]	34.7 (br, Mn–PEt_3)
(**7**) *mer,trans*-[$Mn(CO)_3(PEt_3)_2\{SC(S)PEt_3\}]ClO_4$	2 032w, 1 947vs, 1 925s	38.5 [t, ^4J(PP) = 4.2]	42.5 (br, 2 P, Mn–PEt_3)
(**8**) *fac*-[$Mn(CO)_3(S_2CPEt_3)\{SC(S)PEt_3\}]ClO_4$	2 032s, 1942s (br)	37.8(s), 33.0(s)	
(**9**) *cis*-[$Mn(CO)_4(S_2CPEt_3)]ClO_4$	2 100m, 2 024vs, 1 992s	42.6(s)	
(**10**) *fac*-[$Mn(CO)_3(PEt_3)(S_2CPEt_3)]ClO_4$	2 024s, 1 960s, 1 935s	35.5 [d, ^4J(PP) = 9.8]	43.4 (br, Mn–PEt_3)
(**11**) *cis,trans*-[$Mn(CO)_2(PEt_3)_2(S_2CH)$]	1 919s, 1 853s		47.2 (br, Mn–PEt_3)
(**12**) *fac*-[$Mn(CO)_3(bipy)\{SC(S)PEt_3\}]ClO_4$	2 037s, 1 942s	36.9(s)	
(**13**) *fac*-[$Mn(CO)_3(dppe)\{SC(S)PEt_3\}]ClO_4$	2 020s, 1 953s, 1 937s	39.5 [t, ^4J(PP) = 3.9]	74.3 [br, $(CH_2PPh_2)_2$]

[a] δ (ppm) from external H_3PO_4 (aqueous, 85%), *J* in Hz. [b] In CD_2Cl_2 solution at −90 °C.



Scheme 2. (*i*) $S_2CP(C_6H_{11})_3$, CS_2 reflux; (*ii*) S_2CPEt_3, CS_2 reflux; (*iii*) $S_2CP(C_6H_{11})_3$, toluene reflux; (*iv*) S_2CPEt_3 (excess), toluene reflux

$S_2CP(C_6H_{11})_3$ in refluxing toluene produces a dinuclear red manganese(0) compound [$Mn_2(CO)_6\{\mu$-$S_2CP(C_6H_{11})_3\}$] in which the dithio ligand forms an asymmetric bridge, donating 8e.[21] When S_2CPEt_3 was used instead of $S_2CP(C_6H_{11})_3$ a dark blue solution was produced, from which a deep blue, unstable solid (**2**) (bromide salt) could be isolated. Its i.r. spectrum showed two ν(CO) maxima (1 940s and 1 874s cm^{-1}) corresponding to a *cis*-dicarbonyl unit, and conductivity measurements showed a 1:1 electrolyte suggesting that the bromine atom may have been displaced from the co-ordination sphere of the manganese, therefore remaining as a counter anion. This was confirmed by treating the salt with $AgClO_4$, which resulted in precipitation of AgBr without altering the position of the ν(CO) maxima in the i.r. spectrum. After filtration, the deep blue *cis*-dicarbonyl was isolated as the very stable crystalline perchlorate salt (**2**). The ^{31}P-{^1H} n.m.r. spectrum of (**2**) at room temperature consists of a sharp, well resolved triplet at δ 27.28 p.p.m. which can be assigned to the phosphorus atom of the S_2CPEt_3 adduct, and a broad signal at δ 53.13 p.p.m., attributed to the phosphines co-ordinated to manganese. A low-temperature (−90 °C) spectrum resolved the latter broad signal as a sharp doublet due to coupling with the phosphorus of the S_2CPEt_3 group [^4J(P–P) = 12.2 Hz]. This shows the equivalence of the two phosphines, which have therefore to be in mutually *trans* positions, since the two carbonyl ligands occupy *cis* positions as shown by the i.r. spectrum. An *X*-ray structure determination was carried out to confirm this and the resulting ORTEP picture can be seen in Figure 1. Crystallographic details are collected in Table 2, final atomic co-ordinates in Table 3, and selected bond lengths and angles in Table 4.

The cation [$Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]^+$ exhibits a slightly distorted octahedral co-ordination around the manganese atom, the most important deviation from ideal geometry being induced by the small bite of the S_2CPEt_3 chelate [S(2)–Mn–S(1) 72.82(3)°]. The two phosphine ligands are *trans* to each other, the P(2)–Mn–P(1) [174.84(3)°] arrangement being slightly bent towards the carbonyl ligands which are

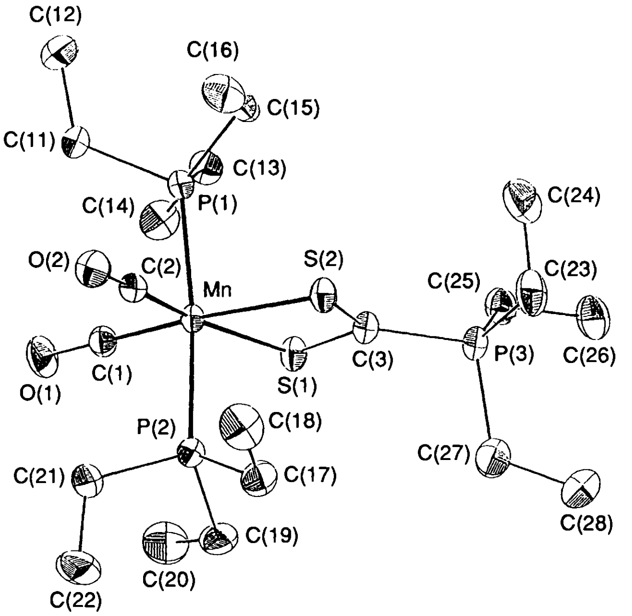


Figure 1. Perspective drawing of the cation *cis,trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]^+$ in compound (**2**), showing the atom numbering

Table 2. Crystallographic details for compounds (**2**) and (**11**)[a]

Compound	(**2**)	(**11**)
Formula	$C_{21}H_{45}ClMnO_6P_3S_2$	$C_{15}H_{31}MnO_2P_2S_2$
M	641.02	424.42
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$[b]	$C2cb$[c]
a/Å	21.197(1)	11.230(4)
b/Å	8.526(3)	13.499(6)
c/Å	19.181(3)	14.192(2)
β/°	114.42(1)	90
U/Å	3 156.4(2)	2 151(2)
D_c/g cm^{-3}	1.35	1.31
F(000)	1 352	896
Crystal colour	Dark blue	Red
size (mm)	0.65 × 0.45 × 0.30	0.55 × 0.50 × 0.45
μ/cm^{-1}	7.9	9.3
θ range/°	1—25	1—26
No. of reflections	5 276	1 225
No. used in refinement [$I \geqslant 3\sigma(I)$]	4 310	1 043
No. of parameters	310	147
Absorption correction	Empirical (ψ scan)	None (flat ψ scan)
Transmission factors (minimum, maximum)	1.00, 1.12	—
R	0.0412	0.0310
R'	0.0545	0.0323

[a] Details in common: $Z = 4$; Philips PW1100 diffractometer; λ(Mo-K_α) 0.710 69 Å; scan mode ω—2θ. [b] Non-standard setting of $P2_1/c$ (no. 14). [c] Non-standard setting of $Aba2$ (no. 41).

mutually *cis* and *trans* to the sulphur atoms. The Mn–S [2.375(1) and 2.354(1) Å] and C–S [1.680(3) and 1.677(3) Å] distances are close to those found in $[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}_2]ClO_4$.[20] The C–S distances are little affected by co-ordination, being very close to those found in the free S_2CPEt_3 adduct [1.68(3) and 1.71(3) Å][22] and in other S_2CPEt_3 complexes.[11,12] On the other hand, the angle S–C–S decreases from 127(2)° in the free adduct to 113.5(2)° in the chelate, this being the main structural effect induced in the S_2CPEt_3 group by co-ordination to a metal centre.

Table 3. Atomic co-ordinates for *cis,trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ (**2**)

Atom	x	y	z
Mn	0.752 89(2)	0.018 38(5)	0.679 81(2)
S(1)	0.819 14(4)	−0.045 29(8)	0.810 55(4)
S(2)	0.769 55(4)	0.252 45(8)	0.750 30(4)
P(1)	0.851 92(4)	0.056 66(8)	0.659 75(4)
P(2)	0.649 96(4)	−0.031 06(9)	0.689 31(4)
P(3)	0.845 76(4)	0.221 85(9)	0.924 64(4)
O(1)	0.740 7(1)	−0.295 4(3)	0.611 2(2)
O(2)	0.671 0(1)	0.153 0(3)	0.528 1(1)
C(1)	0.747 0(2)	−0.172 7(4)	0.639 9(2)
C(2)	0.703 6(1)	0.102 3(3)	0.587 8(2)
C(3)	0.813 9(1)	0.145 8(3)	0.828 9(1)
C(11)	0.839 5(2)	−0.001 6(4)	0.562 5(2)
C(12)	0.898 9(2)	0.028 3(5)	0.539 3(2)
C(13)	0.930 5(2)	−0.050 3(4)	0.722 3(2)
C(14)	0.921 8(2)	−0.225 5(5)	0.724 0(2)
C(15)	0.885 8(2)	0.256 7(4)	0.668 4(2)
C(16)	0.835 4(2)	0.371 0(4)	0.610 9(3)
C(17)	0.605 4(2)	0.135 2(5)	0.710 7(2)
C(18)	0.585 6(2)	0.266 0(5)	0.651 7(3)
C(19)	0.650 5(2)	−0.172 3(5)	0.762 2(2)
C(20)	0.676 6(3)	−0.334 5(6)	0.755 0(3)
C(21)	0.584 2(2)	−0.112 3(5)	0.600 0(2)
C(22)	0.513 5(2)	−0.145 7(8)	0.598 7(3)
C(23)	0.844 6(2)	0.430 1(4)	0.921 4(2)
C(24)	0.894 0(4)	0.499 1(6)	0.893 0(3)
C(25)	0.930 4(2)	0.143 4(4)	0.978 5(2)
C(26)	0.964 4(2)	0.193 8(5)	1.062 8(2)
C(27)	0.784 7(2)	0.146 8(6)	0.963 7(2)
C(28)	0.792 3(3)	0.211 4(7)	1.038 1(3)
Cl	0.083 85(5)	0.261 3(1)	0.898 31(5)
O(3)	0.096 7(3)	0.226 4(5)	0.975 2(2)
O(4)	0.108 2(2)	0.414 2(4)	0.895 6(2)
O(5)	0.120 5(3)	0.155 6(5)	0.872 5(3)
O(6)	0.013 7(2)	0.244 7(7)	0.852 9(3)

The *cis*-dicarbonyl (**2**) appears to be the most thermodynamically stable product in the system $Mn/CO/PEt_3/CS_2$ since heating any product from (**3**) to (**10**), at high temperatures (refluxing benzene or toluene), in the presence of excess of CS_2 leads to the formation of (**2**) (as the Br or ClO_4 salt), in variable yields depending on the ratio Mn/PEt_3. In the Experimental section we describe the reaction of the tricarbonyl (**4**) with S_2CPEt_3 as a better route to the preparation of (**2**).

I.r. monitoring of the reaction [(*i*) in Scheme 1] of the pentacarbonyl (**1**) with an excess of S_2CPEt_3 in refluxing benzene or toluene shows that there is sequential substitution of carbonyl groups giving the tetracarbonyl (**3**) and the tricarbonyl (**4**), and then attack of the S_2CPEt_3 group occurs giving compound (**2**) with displacement of one CO and the bromine atom. Thus, reaction (*i*) is, in fact, an overall process involving successively steps (*ii*)—(*v*), which can be performed separately. These facts suggest the existence of two competitive reactions: replacement of CO by phosphine *versus* replacement of CO by S_2CPEt_3 adduct, and the results of the reactions can be explained in terms of the steric features of the phosphines involved. Since the electronic properties of PEt_3 are not significantly different from those of $P(C_6H_{11})_3$, it can be assumed that the donor abilities of the sulphur atoms are similar in both adducts, and also the dissociation equilibrium $S_2C + PR_3 \rightleftharpoons S_2CPR_3$ is not greatly affected on changing $P(C_6H_{11})_3$ to PEt_3. The only significant difference between the two systems is the better co-ordinating ability of PEt_3 derived from its smaller size [cone angle of 132° against 170° for $P(C_6H_{11})_3$[23]]. Thus, the phosphine complexes (**3**) and (**4**) are favoured even in the case when the solvent is CS_2 and the

Table 4. Selected bond distances (Å) and angles (°) for *cis,trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ **(2)**

Around manganese			
Mn–P(1)	2.308(1)	Mn–P(2)	2.302(1)
Mn–S(1)	2.375(1)	Mn–S(2)	2.354(1)
Mn–C(1)	1.783(3)	Mn–C(2)	1.788(3)
S(1)–Mn–P(1)	91.54(3)	S(2)–Mn–P(1)	92.59(3)
S(2)–Mn–S(1)	72.82(3)	P(2)–Mn–S(2)	91.82(3)
P(2)–Mn–P(1)	174.84(3)	P(2)–Mn–S(1)	92.32(3)
C(1)–Mn–S(1)	98.7(1)	C(1)–Mn–P(1)	88.0(1)
C(1)–Mn–S(2)	171.5(1)	C(1)–Mn–P(2)	88.1(1)
C(2)–Mn–P(1)	88.81(9)	C(2)–Mn–S(1)	169.5(1)
C(2)–Mn–S(2)	96.64(9)	C(2)–Mn–P(2)	88.02(9)
C(2)–Mn–C(1)	91.9(1)		
Carbonyl ligands			
C(1)–O(1)	1.163(4)	C(2)–O(2)	1.148(3)
O(1)–C(1)–Mn	177.1(3)	O(2)–C(2)–Mn	178.4(3)
S_2CPEt_3 ligand			
S(1)–C(3)	1.680(3)	C(3)–S(2)	1.677(3)
C(3)–P(3)	1.795(3)	P(3)–C(23)	1.777(4)
P(3)–C(25)	1.789(3)	P(3)–C(27)	1.856(4)
C(3)–S(1)–Mn	86.47(9)	C(3)–S(2)–Mn	87.2(1)
P(3)–C(3)–S(1)	122.4(2)	S(2)–C(3)–S(1)	113.5(2)
P(3)–C(3)–S(2)	123.9(2)		
Perchlorate			
Cl–O(3)	1.416(4)	Cl–O(4)	1.411(3)
Cl–O(5)	1.406(4)	Cl–O(6)	1.385(4)
O(4)–Cl–O(3)	108.4(2)	O(5)–Cl–O(3)	109.6(3)
O(6)–Cl–O(3)	109.1(4)	O(5)–Cl–O(4)	108.4(2)
O(6)–Cl–O(4)	112.6(3)	O(6)–Cl–O(5)	108.6(3)

dissociation equilibrium should be displaced towards the formation of the adduct. Moreover, reactions using $S_2CPPr^i_3$ (cone angle of PPr^i_3 160°[23]) show the same behaviour as those described for the adduct of $P(C_6H_{11})_3$. On the other hand, heating *cis*-$[Mn(CO)_4\{P(C_6H_{11})_3\}Br]$ in CS_2 leads to *fac*-$[Mn(CO)_3\{S_2CP(C_6H_{11})_3\}Br]$,[20] *via* insertion of CS_2 into the Mn–P bond, while no insertion of this kind is produced in the Mn–PEt_3 complexes **(3)** or **(4)**. This can be explained by assuming that the Mn–$P(C_6H_{11})_3$ bond is somewhat labilized by the steric hindrance due to the cyclohexyl groups.

(*b*) *Reactions leading to Monodentate* S_2CPEt_3 *Ligands*.— Reactions (*vi*)—(*viii*) and (*x*), in Scheme 1, involve an overall exchange of a bromine atom by a sulphur atom of the S_2CPEt_3 ligand, promoted by silver perchlorate as halogen abstractor. This is a very well known method, widely employed in the preparation of cationic complexes of manganese(I)[20,24] and of other metals.[8–10] In this case, since silver perchlorate is known to react with S_2CPEt_3 to give $[Ag_2(S_2CPEt_3)_4][ClO_4]_2$,[16] it is convenient to split the reaction into two successive steps. First, the bromo carbonyl $[Mn(CO)_{5-n}(PEt_3)_n(Br)]$ [n = 0, **(1)**; 1, **(3)**; or 2, **(4)**] is treated with $AgClO_4$ in CH_2Cl_2 at room temperature to obtain a solution of the perchlorato derivative $[Mn(CO)_{5-n}(PEt_3)_n(OClO_3)]$ (for reaction times and i.r. spectra of these solutions see Experimental section). After filtering to eliminate the precipitate of AgBr, addition of S_2CPEt_3 results in smooth displacement of the perchlorato ligand to give the phosphoniodithiocarboxylato complexes **(5)**—**(7)**, respectively. Analytical (see Experimental section) and spectroscopic data (see Table 1) are in good agreement with the structures assigned in Scheme 1. Conductivity data fall in the range expected for 1:1 electrolytes.

A special case is reaction (*x*), in which the first step is conducted in acetone. Under such conditions acetone is known to displace the perchlorato ligand and two CO groups, to give *fac*-$[Mn(CO)_3(OCMe_2)_3]ClO_4$.[24] After filtering, addition of 2 equivalents of S_2CPEt_3 results in displacement of the weakly bonded acetone ligands to give compound **(8)** containing two S_2CPEt_3 groups. I.r. and ^{31}P n.m.r. spectra of **(8)** are quite similar to those of the analogous compound we had reported with $S_2CP(C_6H_{11})_3$, the structure of which was confirmed by *X*-ray crystallography[20] as having one chelate and one monodentate S_2CPR_3 group.

Compounds containing monodentate S_2CPEt_3 together with other ligands such as 2,2′-bipyridine (bipy) **(12)** or $Ph_2PCH_2CH_2PPh_2$ (dppe) **(13)** can be obtained *via* perchlorate displacement on the appropriate precursors [reaction (*xiv*) in Scheme 1].

All the reactions leading to monodentate S_2CPEt_3 ligands are quite similar to those previously reported for $S_2CP(C_6H_{11})_3$. Since these reactions are conducted at room temperature, dissociation of the adduct and therefore the attack by free phosphine are inhibited. Under such conditions the most important factor in the reaction is the donor ability of the adduct, which should not be greatly affected on changing $P(C_6H_{11})_3$ to PEt_3. An indirect proof of that can be obtained from the ν(CO) frequencies of compounds **(5)**, **(9)**, **(12)**, and **(13)**, which appear in the same positions (within a few cm^{-1}) to those of the similar compounds containing the adduct of $P(C_6H_{11})_3$.[20]

(*c*) *Reactions of Intramolecular Displacement of* CO.— Compounds **(5)**—**(7)**, containing monodentate S_2CPEt_3 ligands, easily undergo intramolecular CO displacement by the unco-ordinated sulphur [reactions (*ix*), (*xi*), and (*xii*), in Scheme 1] giving, respectively, complexes **(9)**, **(10)**, and **(2)**, in which the adduct acts as a chelate. Analytical and spectroscopic data support the structures proposed for **(9)** and **(10)**, while the product of the decarbonylation of (7) is identical to **(2)**, described above. Decarbonylations of **(6)** and **(7)** are cleanly achieved by u.v. irradiation [or with Me_3NO in the case of **(6)**], while decarbonylation of **(5)**, thermally induced [reaction (*xi*)] leads to some decomposition and the production of some **(10)** due to phosphine attack on compound **(9)**.

The dicarbonyl **(2)** can be obtained in good yield from **(4)** by a method combining reactions (*viii*) and (*ix*) (see Experimental section). Thus, treatment of *mer,trans*-$[Mn(CO)_3(PEt_3)_2(OClO_3)]$ [made from **(4)** and $AgClO_4$ as described above] with S_2CPEt_3 in refluxing chloroform for 30 min gives **(2)** in 79% yield.

(*d*) *Reactions of* S_2CPEt_3 *Complexes with* $NaBH_4$.—Hydride attack on the central carbon of co-ordinated S_2CPR_3 complexes is known to produce either simple addition to give $S_2C(H)PR_3^-$ ligands,[14] or nucleophilic displacement of the phosphine leading to dithioformate, S_2CH^-,[12,13,15,18] compounds. The final result depends on the electronic and steric features of the starting complex. We have recently reported[25] the reaction of *cis*-$[Mn(CO)_4\{S_2CP(C_6H_{11})_3\}]ClO_4$ with $NaBH_4$ to give the neutral dinuclear compound $[Mn_2(CO)_6\{\mu\text{-}S_2C(H)P(C_6H_{11})_3\}_2]$ containing the tricyclohexylphosphine adduct of dithioformate acting as a five-electron bridging ligand.

Sodium tetrahydroborate reacts with compound **(2)** [reaction (*xiii*), Scheme 1] to give a red, neutral complex **(11)** which exhibits ν(CO) absorptions at frequencies (1 919s and 1 853s cm^{-1}) considerably lower than those of the parent compound (1 940s and 1 874s cm^{-1}). The ^{13}P n.m.r. spectrum

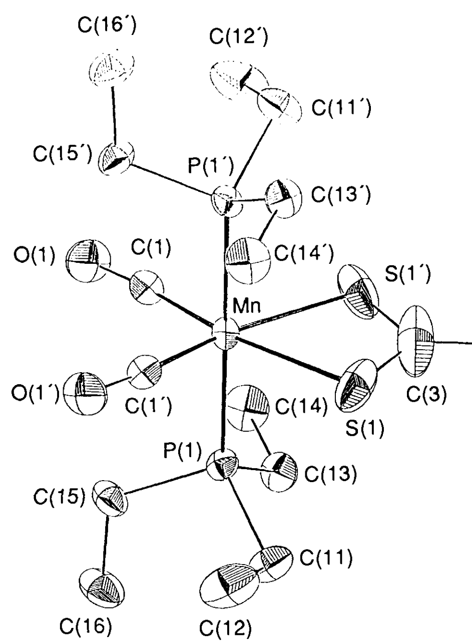


Figure 2. Perspective drawing of compound *cis,trans*-[Mn(CO)$_2$(PEt$_3$)$_2$(S$_2$CH)] (**11**) showing the atom numbering

Table 5. Atomic co-ordinates for *cis,trans*-[Mn(CO)$_2$(PEt$_3$)$_2$(S$_2$CH)] (**11**)

Atom	*x*	*y*	*z*
Mn	0.0000	0.0000	0.0000
P(1)	−0.000 7(2)	−0.122 72(7)	0.112 28(7)
S(1)	0.176 1(2)	0.071 3(2)	0.071 6(2)
O(1)	−0.188 5(5)	−0.103 2(3)	−0.102 1(3)
C(1)	−0.109 0(5)	−0.064 1(4)	−0.064 6(4)
C(3)	0.254(1)	0.0000	0.0000
C(11)	0.066 8(7)	−0.094 2(6)	0.227 7(5)
C(12)	0.013(1)	−0.005 4(8)	0.278 3(6)
C(13)	0.075 2(5)	−0.240 8(4)	0.085 5(5)
C(14)	0.029 8(7)	−0.294 1(5)	0.000 9(6)
C(15)	−0.152 0(5)	−0.163 5(4)	0.143 6(4)
C(16)	−0.159 9(8)	−0.239 6(5)	0.222 2(6)
H(3)	0.366(4)	0.0000	0.0000

Table 6. Selected bond distances (Å) and angles (°) for *cis,trans*-[Mn(CO)$_2$(PEt$_3$)$_2$(S$_2$CH)] (**11**)

Mn–P(1)	2.299(1)	Mn–C(1)	1.758(6)
Mn–S(1)	2.422(2)		
P(1)–Mn–P(1′)	179.5(1)	C(1)–Mn–P(1)	90.2(2)
S(1)–Mn–S(1′)	70.6(1)	C(1)–Mn–S(1′)	98.9(2)
S(1)–Mn–P(1)	89.94(7)	C(1)–Mn–S(1)	169.5(2)
S(1)–Mn–P(1′)	90.44(7)	C(1)–Mn–C(1′)	91.7(3)
C(1)–Mn–P(1′)	89.4(2)		
Carbonyl ligands			
O(1)–C(1)	1.166(7)	O(1)–C(1)–Mn	174.1(5)
Dithioformate ligand			
S(1)–C(3)	1.651(7)	C(3)–S(1)–Mn	86.7(4)
C(3)–H(3)	1.25(5)	S(1)–C(3)–S(1′)	115.9(8)
		H(3)–C(3)–S(1)	122.0(4)

of (**11**) shows only one signal (δ 47.2 p.p.m.) attributable to PEt$_3$ bonded to manganese, and the ^{1}H n.m.r. spectrum displays one triplet at δ 10.64 [^4J(PH) = 7.3 Hz], in the range expected for the proton of the S$_2$CH group.[5,26] These data suggest the structure proposed in Scheme 1, and it has been confirmed by an *X*-ray diffraction study. Crystallographic details are summarized in Table 2, final atomic parameters are given in Table 5, and selected bond distances and angles are in Table 6. An ORTEP view of the molecule is shown in Figure 2.

Although two compounds containing dithioformate ligands bonded to manganese in a monodentate fashion are known,[27] (**11**) is, as far as we know, the first reported to contain the dithioformate group as a bidentate chelate ligand towards manganese. A very similar rhenium compound, [Re(CO)$_2$(PPh$_3$)$_2$(S$_2$CH)], has been prepared by insertion of CS$_2$ into a Re–H bond,[28] and its structure determined by *X*-ray crystallography.[29]

Compound (**11**) displays a fairly regular octahedral co-ordination of the manganese, the main distortion being induced, as in the structure of (**2**), by the small bite of the chelating dithioformate [S(1)–Mn–S(1′) 70.6(1)°] which is smaller than that induced by the S$_2$CPEt$_3$ ligand in (**2**). Since the Mn and C(3) atoms lie on a binary axis, the two halves of the molecular are symmetry related. The C–S distances, and the S–C–S angle, are close to those found in other structures containing chelate S$_2$CH ligands such as [Fe(depe)$_2$(S$_2$CH)]BPh$_4$[12] (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$) and [Re(CO)$_2$(PPh$_3$)$_2$(S$_2$CH)].[29]

Mn–S distances are slightly longer, and the S–C distances are slightly shorter, in compound (**11**) (see Table 6), than those found in (**2**) (Table 4). This suggests a stronger interaction between the manganese atom and the dithio ligand in the case of (**2**), which may result from a greater delocalization of electron density from the manganese towards the S$_2$CPEt$_3$ ligand which thus behaves as a better π acceptor than S$_2$CH, due to the presence of the phosphine at the carbon atom. However, this feature is not reflected in the Mn–C and C–O distances, which are virtually identical in the two compounds.

Reaction of tetracarbonyl (**9**) with NaBH$_4$ produces a yellow solution with ν(CO) bands at 2 010s, 1 990vs, 1 910vs, and 1 884(sh) cm^{-1}, attributable to the formation of the dinuclear compound [Mn$_2$(CO)$_6${μ-S$_2$C(H)PEt$_3$}], analogous to that obtained from the P(C$_6$H$_{11}$)$_3$ derivative.[25] In this case, however, the dinuclear compound was not stable and could not be isolated, the work-up of its solutions leading to mixtures in which the *cis,trans* derivative (**11**) was present. Compound (**11**) is also the final product of the reaction of the tricarbonyl (**7**) and NaBH$_4$.

^{13}C-{^{1}H} *N.M.R. Spectra of* S$_2$CPEt$_3$ *and* S$_2$CH *Complexes.*—Despite the great number of compounds containing S$_2$CPR$_3$ ligands reported, very few ^{13}C n.m.r. data are available. We have recorded ^{13}C-{^{1}H} n.m.r. spectra for three representative compounds; (**7**) (with a monodentate S$_2$CPEt$_3$), (**2**) (with a chelating S$_2$CPEt$_3$), and (**11**) (containing a S$_2$CH ligand). The data and the assignments are in Table 7. The signals of the central carbons of the S$_2$CPEt$_3$ adducts appear close to the carbonyl region as a sharp doublet due to coupling to the phosphorus, and are shifted to lower fields when compared with the values reported for the free adduct,[30] the shift being bigger for the chelate adduct in (**2**) than for the monodentate one in (**7**). It was not possible to observe, in these signals, the coupling to the two P atoms bonded to manganese. The signal of the carbon of the S$_2$CH ligand in (**11**) was identified as a C–H resonance in a distortionless enhancement of polarization transfer (DEPT) experiment, and appears at δ 232.14 p.p.m., as a sharp triplet due to coupling to the two equivalent P atoms of the PEt$_3$ ligands [^3J(P–C) 10.5 Hz]. It is shifted 30.17 p.p.m. downfield from the resonance of the S$_2$CPEt$_3$ ligand in the parent compound (**2**).

Experimental

All reactions were carried out in dry solvents under a nitrogen

Table 7. $^{13}C-\{^1H\}$ N.m.r. data for some S_2CX complexes[a]

Compound	S_2C	S_2C-PEt_3	$Mn-PEt_3$	Carbonyl groups
(**2**)	201.97 [d, $^1J(PC)$ 41.3]	13.49 [d, 3CH_2, $^1J(PC)$ 49.1] 5.72 (s, 3 CH_3)	19.58 [d, 6CH_2, $^1J(PC)$ 34.9] 7.72 (s, 6CH_3)	227.35 (s, br, 2 CO)
(**7**)	223.07 [d, $^1J(PC)$ 52.3]	15.57 [d, 3CH_2, $^1J(PC)$ 48.2] 6.14 [d, 3CH_3, $^2J(PC)$ 4.7]	19.95 (m, 6CH_2) 7.80 (s, 6CH_3)	221.96 (s, br, 1CO) 217.54 (s, br, 2CO)
(**11**)	232.14 [t, $^3J(PC)$ 10.5]		18.12 (m, 6CH_2) 7.87 (s, 6CH_3)	227.51 (s, br, 2CO)
S_2CPEt_3[b]	229.51 [d, $^1J(PC)$ 43.95]	14.10 [d, 3CH_2, $^1J(PC)$ 48.83] 4.74 (s, 3CH_3)		

[a] In $CDCl_3$ solutions at room temperature; δ (p.p.m.) from internal $SiMe_4$. J in Hz. [b] Taken from ref. 30.

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 salts or 2,2′-bipyridine were performed in darkness. Filtrations were done through a Celite pad unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotomer, ^1H (300.13 MHz, $CDCl_3$ solution, δ to higher frequencies from internal $SiMe_4$], $^{31}P-\{^1H\}$ [121.50 MHz, $CDCl_3$ solution, δ (p.p.m.) to higher frequencies from external 85% H_3PO_4], and $^{13}C-\{^1H\}$ [75.47 MHz, $CDCl_3$ solution, δ (p.p.m.) to internal $SiMe_4$] n.m.r. spectra on a Bruker AC-300. Elemental analyses were carried out on a Perkin-Elmer 240 B analyser.

cis,trans-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ (**2**).—(*a*) A mixture of compound (**1**)[31] (0.2 g, 0.726 mmol), S_2CPEt_3 (0.423 g, 2.178 mmol), and CS_2 (2 cm^3) in toluene (20 cm^3) was refluxed for 10 h and then the solvents were evaporated *in vacuo*. The dark residue was washed with hexane (3 × 10 cm^3) and then dissolved in CH_2Cl_2. To this solution was added $AgClO_4$ (0.174 g, 0.835 mmol), and the mixture was stirred in the dark for 30 min. After filtration, the solvent was evaporated *in vacuo* to give a dark solid which was recrystallized from CH_2Cl_2–Et_2O. Yield 0.258 g, 55%.

(*b*) A mixture of compound (**4**) (0.2 g, 0.438 mmol), S_2CPEt_3 (0.085 g, 0.438 mmol), and CS_2 (1 cm^3) in benzene (20 cm^3) was heated under reflux for 5 h. The solvents were evaporated *in vacuo*, and the dark residue was washed with hexane (3 × 20 cm^3) and then dissolved in CH_2Cl_2 (20 cm^3). To this solution was added $AgClO_4$ (0.114 g, 0.55 mmol) and the mixture was stirred in the dark for 30 min. Filtration and evaporation of the solvent *in vacuo* produced a dark blue solid which was recrystallized from CH_2Cl_2–Et_2O. Yield 0.171 g, 61%.

(*c*) A mixture of compound (**4**) (0.2 g, 0.439 mmol) and $AgClO_4$ (0.136 g, 0.876 mmol) in CH_2Cl_2 (20 cm^3) was stirred in the dark for 4 h and then filtered to obtain a yellow solution of *mer,trans*-$[Mn(CO)_3(PEt_3)_2(OClO_3)]$ [ν(CO) at 2 040w, 1 950s, and 1 905s cm^{-1}], and then the solvent was evaporated *in vacuo*, giving a yellow oil. To this were added $CHCl_3$ (20 cm^3), CS_2 (1 cm^3), and S_2CPEt_3 (0.085 g, 0.438 mmol), and the mixture was refluxed for 30 min. The resulting deep blue solution was filtered and concentrated *in vacuo*. Addition of Et_2O produced deep blue crystals of compound (**2**). Yield 0.222 g, 79%.

(*d*) A solution of compound (**7**) (0.1 g, 0.149 mmol) in CH_2Cl_2 (20 cm^3) was irradiated with u.v. light for 10 min. The colour changed from red to deep blue. Evaporation of the solvent *in vacuo* and addition of Et_2O (10 cm^3) gave (**2**) as a deep blue microcrystalline solid. Yield 0.079 g, 82% (Found: C, 39.60; H, 7.40. Calc. for $C_{21}H_{45}ClMnO_6P_3S_2$: C, 39.35; H, 7.10%).

Crystal Structure Determination of cis,trans-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]ClO_4$ (**2**).—Relevant crystallographic details are given in Table 2. The structure was solved by direct methods with SHELX[32] and subsequent Fourier maps. Some hydrogen atoms were found in a difference map and others were geometrically positioned. Least-squares refinements were made in three blocks, with anisotropic thermal parameters for all non-hydrogen atoms. Anomalous dispersion effects were introduced. All computations were carried out with CRYSTALS.[33]

cis-$[Mn(CO)_4(PEt_3)Br]$ (**3**).—Compound (**1**) (0.5 g, 1.81 mmol) and PEt_3 (0.27 cm^3, 1.81 mmol) were refluxed in $CHCl_3$ (15 cm^3) for 1.5 h. Evaporation of the solvent *in vacuo* gave an orange solid which was recrystallized from CH_2Cl_2–EtOH. Yield 0.61 g, 90% (Found: C, 33.05; H, 4.20. Calc. for $C_{10}H_{15}BrMnO_4P$: C, 32.90; H, 4.15%).

mer,trans-$[Mn(CO)_3(PEt_3)_2Br]$ (**4**).—Compound (**1**) (0.825 g, 3 mmol) and PEt_3 (0.8 cm^3, *ca.* 7 mmol) were heated in toluene (30 cm^3) at reflux temperature for 1.5 h. The solvent was evaporated *in vacuo* and the orange residue was pumped off for 1 h to eliminate the excess of PEt_3. The residue was then dissolved in CH_2Cl_2 (10 cm^3), EtOH (5 cm^3) was added, and after filtration the solution was concentrated to *ca.* 5 cm^3 and left overnight in a refrigerator (−10 °C) to obtain orange-red crystals of compound (**4**). Yield 1.053 g, 77% (Found: C, 39.60; H, 6.95. Calc. for $C_{15}H_{30}BrMnO_3P_2$: C, 39.60; H, 6.65%).

$[Mn(CO)_5\{SC(S)PEt_3\}]ClO_4$ (**5**).—A mixture of compound (**1**) (0.5 g, 1.81 mmol) and $AgClO_4$ (0.565 g, 2.72 mmol) in CH_2Cl_2 (20 cm^3) was stirred in the dark for 3 h and then filtered through Celite. To the resulting yellow solution {containing *ca.* 1.81 mmol of $[Mn(CO)_5(OClO_3)]$, ν(CO) at 2 154w, 2 070s, and 2 020m, cm^1}[24] was added S_2CPEt_3 (0.35 g, 1.81 mmol) and the mixture was stirred in the dark for 30 min. Evaporation of the solvent *in vacuo* gave an oil which was stirred with Et_2O (2 × 15 cm^3) to obtain a brown solid. Recrystallization from CH_2Cl_2 produced orange-brown crystals of (**5**). Yield 0.7 g, 78% (Found: C, 29.95; H, 3.30. Calc. for $C_{12}H_{15}ClMnO_9PS_2$: C, 29.50; H, 3.10%).

cis-$[Mn(CO)_4(PEt_3)\{SC(S)PEt_3\}]ClO_4$ (**6**).—Compound (**3**) (0.3 g, 0.82 mmol) and $AgClO_4$ (0.25 g, 1.23 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 2.5 h, and then filtered to obtain a solution of *cis*-$[Mn(CO)_4(PEt_3)(OClO_3)]$ [ν(CO) at 2 105w, 2 025s, and 1 962s cm^{-1}]. To the clear solution was added S_2CPEt_3 (0.16 g, 0.82 mmol) and the mixture was stirred in the dark for 0.5 h. Filtration and evaporation of the solvent afforded brown crystals of compound (**6**). Yield 0.33 g, 68% (Found: C, 35.30; H, 5.40. Calc. for $C_{17}H_{30}ClMnO_8PS_2$: C, 35.25; H, 5.20%).

mer,trans-$[Mn(CO)_3(PEt_3)_2\{SC(S)PEt_3\}]ClO_4$ (**7**).—A filtered solution of *mer,trans*-$[Mn(CO)_3(PEt_3)_2(OClO_3)]$ was prepared from compound (**4**) (0.2 g, 0.438 mmol) and $AgClO_4$ (0.136 g, 0.438 mmol), as described above in the preparation of compound (**2**), method (*c*). To this solution was added S_2CPEt_3 (0.085 g, 0.439 mmol) and the mixture was stirred in the dark for 2 h. The resulting red solution, very light-sensitive, was filtered, and the solvent was evaporated *in vacuo* to give a red residue which was washed with Et_2O (3 × 10 cm^3) and recrystallized from CH_2Cl_2–Et_2O. Yield 0.24 g, 83% (Found: C, 39.25; H, 7.00. Calc. for $C_{22}H_{45}ClMnO_7P_3S_2$: C, 39.50; H, 6.80%).

fac-$[Mn(CO)_3(S_2CPEt_3)\{SC(S)PEt_3\}]ClO_4$ (**8**).—Compound (**1**) (0.1 g, 0.36 mmol) and $AgClO_4$ (0.113 g, 0.514 mmol) were stirred in acetone (20 cm^3) for 2 h and then filtered through Celite to obtain a yellow solution of *fac*-$[Mn(CO)_3(Me_2CO)_3]ClO_4$ [ν(CO) in acetone at 2 023s and 1 935s (br) cm^{-1}].[24] To this solution was added S_2CPEt_3 (0.13 g, 0.67 mmol) and the mixture was stirred for 30 min and then filtered. After evaporation of the solvent *in vacuo* the residue was washed with Et_2O (3 × 10 cm^3) and recrystallized from CH_2Cl_2–Et_2O. Yield 0.18 g, 79% (Found: C, 33.30; H, 5.00. Calc. for $C_{17}H_{30}ClMnO_7PS_2$: C, 32.55; H, 4.80%).

cis-$[Mn(CO)_4(S_2CPEt_3)]ClO_4$ (**9**).—Compound (**5**) (0.5 g, 1.09 mmol) was dissolved in $CHCl_3$ (25 cm^3) and the solution was heated under reflux for 3 h. After cooling to room temperature the solution was filtered, and the solvent was evaporated *in vacuo*. The resulting oil was stirred with Et_2O (3 × 20 cm^3) to give an orange-red solid which was recrystallized from CH_2Cl_2. Yield 0.2 g, 42%. I.r. monitoring of the reaction progress is necessary to determine the final point of the reaction since further heating of complex (**9**) results in decomposition and formation of *fac*-$[Mn(CO)_3(PEt_3)(S_2CPEt_3)]ClO_4$ (**10**) [Found: C, 35.30; H, 5.40. Calc. for $C_{11}H_{15}ClMnO_8PS_2$, (**9**): C, 35.25; H, 5.20%].

fac-$[Mn(CO)_3(PEt_3)(S_2CPEt_3)]ClO_4$(**10**).—(*a*) To a solution of compound (**6**) (0.1 g, 0.18 mmol) in CH_2Cl_2 (15 cm^3) was added Me_3NO (0.018 g, 0.24 mmol) and the mixture was stirred for 5 min. The solution turned from deep brown to violet. Filtration and evaporation of the solvent produced a violet residue which was washed with hexane (3 × 15 cm^3) and recrystallized from CH_2Cl_2–Et_2O. Yield (0.081 g, 85%) (Found: C, 34.65; H, 5.50. Calc. for $C_{16}H_{30}ClMnO_7PS_2$: C, 34.90; H, 5.50%).

(*b*) U.v. irradiation of a solution of compound (**6**) (0.1 g, 0.18 mmol) in CH_2Cl_2 (20 cm^3) produced (**10**) in 30 min. The same effect was obtained by irradiation with natural light for 8 h. The work-up of the resulting solution to isolate (**10**) was done as described in method (*a*), and the yield was similar (0.077g, 82%)

cis,trans-$[Mn(CO)_2(PEt_3)_2(S_2CH)]$ (**11**).—A solution of $NaBH_4$ (0.059 g, 1.56 mmol) in EtOH (10 cm^3) was added with a syringe to a stirred solution of compound (**2**) (0.2 g, 0.31 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 1.5 h, the reaction mixture turned from deep blue to bright red. The solvent was then evaporated *in vacuo* and the residue was pumped off for 1 h to eliminate the free phosphine. The red solid was extracted with hexane (3 × 10 cm^3) and the extracts were filtered. Addition of EtOH (2 cm^3) and slow evaporation *in vacuo* gave red crystals of compound (**11**). Yield 0.2 g, 90% (Found: C, 42.25; H, 7.50. Calc. for $C_{15}H_{31}MnO_2P_2S_2$: C, 42.45; H, 7.35%).

Crystal Structure Determination of cis,trans-$[Mn(CO)_2(PEt_3)_2(S_2CH)]$ (**11**).—Relevant crystallographic details are given in Table 2. The structure was solved by Patterson analysis and subsequent Fourier maps. Hydrogen atoms were found from a difference map and refined with an overall isotropic parameter. All non-hydrogen atoms were anisotropically refined by full-matrix least-squares methods with unit weights. All computations were carried out with CRYSTALS.[33]

fac-$[Mn(CO)_3(bipy)\{SC(S)PEt_3\}]ClO_4$ (**12**).—A solution of *fac*-$[Mn(CO)_3(bipy)(OClO_3)]$[34] (0.1 g, 0.25 mmol) and S_2CPEt_3 (0.049 g, 0.25 mmol) in CH_2Cl_2 (15 cm^3) was stirred in the dark for 30 min. The solution was then filtered, the solvent was evaporated *in vacuo*, and the resulting oily residue was washed with Et_2O (2 × 10 cm^3) to give an orange-red solid which was recrystallized from CH_2Cl_2–Et_2O. Yield 0.105 g, 70% (Found: C, 40.50; H, 3.90; N, 4.80. Calc. for $C_{20}H_{23}ClMnN_2O_7PS_2$: C, 40.80; H, 3.95; N, 4.75%).

fac-$[Mn(CO)_3(dppe)\{SC(S)PEt_3\}]ClO_4$ (**13**).—A mixture of *fac*-$[Mn(CO)_3(dppe)(OClO_3)]$[35] (0.272 g, 0.430 mmol), S_2CPEt_3 (0.083 g, 0.430 mmol), and CS_2 (1 cm^3) in CH_2Cl_2 (25 cm^3) was stirred in the dark for 4 h. The mixture was then filtered, and the solvents were evaporated *in vacuo*. The orange residue was washed with hexane (2 × 15 cm^3) and recrystallized from CH_2Cl_2–hexane. Yield 0.234 g, 73% (Found: C, 52.25; H, 4.70. Calc. for $C_{36}H_{39}ClMnO_7P_3S_2$: C, 52.05; H, 4.75%).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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