Trialkylphosphine–Carbon Disulfide Adducts as Eight-Electron Bridging Ligands. X-ray Structures of $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ and $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$

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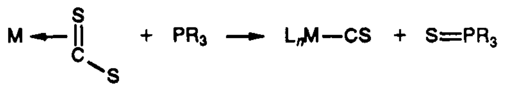
Carbon disulfide adducts of bulky trialkylphosphines, such as PCy_3 or PPr^i_3, react with $Mn_2(CO)_{10}$ to give dimanganese hexacarbonyl complexes $[Mn_2(CO)_6(S_2CPR_3)]$. An X-ray determination of the structure of the derivative with S_2CPCy_3 (**1a**, triclinic, space group $P\bar{1}$, $a = 11.652$ (4) Å, $b = 11.368$ (3) Å, $c = 10.973$ (3) Å, $\alpha = 85.76$ (2)°, $\beta = 77.29$ (2)°, $\gamma = 86.00$ (2)°, $Z = 2$, $R = 0.061$, $R_w = 0.064$) showed that the ligand adopted a new bonding mode, which can be described as $\eta^2(S,S')$ chelate to one manganese and $\eta^3(S,C,S')$ pseudoallyl to the other manganese, thus bridging unsymmetrically the Mn–Mn bond and donating 8 e to the metals. The analysis of the bond distances within the Mn_2S_2C core suggests a strong interaction between the S_2C group and the metal atoms. This is confirmed by the high thermal stability of the 8e bridge, which permits the preparation of a variety of derivatives $[Mn_2(CO)_5(L)(\mu\text{-}S_2CPR_3)]$ and $[Mn_2(CO)_4(L)_2(\mu\text{-}S_2CPR_3)]$ by carbonyl substitution reactions requiring high temperatures. Thus, the thermal robustness of the 8e bridge has been proved by the X-ray structure determination of the derivative $[Mn_2(CO)_4(\mu\text{-dppm})(S_2CPCy_3)]$ (**4e**), which has to be prepared by heating the parent hexacarbonyl (**1a**) and dppm in refluxing xylene for 30 h. (**4a** is triclinic, space group $P\bar{1}$, $a = 16.403$ (4) Å, $b = 14.927$ (3) Å, $c = 11.903$ (3) Å, $\alpha = 116.48$ (3)°, $\beta = 106.46$ (3)°, $\gamma = 81.49$ (2)°, $Z = 2$, $R = 0.039$, $R_w = 0.044$). ^{13}C NMR spectra display the signal of the central carbon of the S_2CPR_3 ligand in the range δ 79.19–85.51 ppm, being therefore a very useful tool for the characterization of this type of bridge. A close inspection of the structures suggests an alternative view of the bonding, consisting of a nearly planar $\eta^4\text{-}\overline{\text{Mn–S–C–S}}$ ring which donates (formally) 5 electrons to the second manganese atom. A comparison of the structural parameters of the molecules with those known for cymantrene, cymantrene-like, and η^3-allyl compounds is given.

Introduction

The study of the chemistry of 1,1-dithiolato ligands has attracted the interest of several research groups for many years, giving rise to a great number of literature references.[1] Apart from the great amount of work carried out in the more classical coordination chemistry, there has been a renewed interest in CS_2 and related complexes that has been motivated, in part, by the connections of their chemistry with CS_2 (and CO_2) activation.[2] Thus, complexes containing trialkylphosphinedithiocarboxylato ligands, S_2CPR_3, have been considered as intermediates[3] in the desulfurization reaction



$$M \leftarrow S_2C + PR_3 \longrightarrow L_nM\text{—}CS + S\text{=}PR_3$$

and this has stimulated the synthesis of many compounds[4-13] in which these ligands display a great variety of coordination modes (see Chart I) acting as 2-, 4-, and

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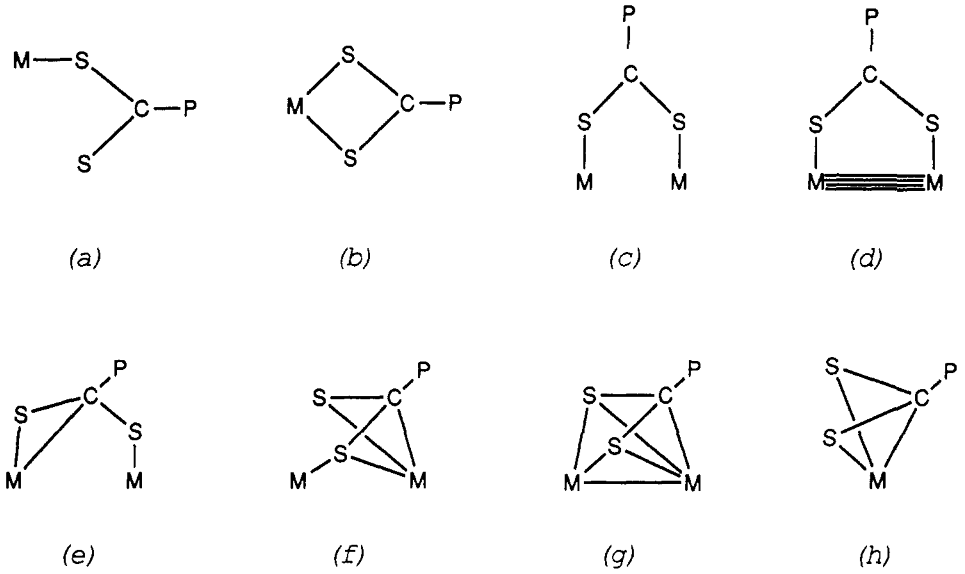
Chart I



(a) (b) (c) (d)

(e) (f) (g) (h)

6e donors. Monodentate (a)[5,6a,11] and chelate (b)[6b-f,7-10] modes are the most commonly found, while there are only a few examples of the bridging forms c,[5a,6d] d,[12] e,[7b] and f.[6a]

We have found that some trialkylphosphinedithiocarboxylato ligands bearing bulky phosphines such as PCy$_3$ or PPr$^i_3$ are able to form very stable dimanganese complexes in which the S$_2$CPR$_3$ adduct exhibits a new coordination mode as an unsymmetrically bridging η^2-(*S*,*S′*), η^3-(*S*,*C*,*S′*) ligand of type g donating 8 e. In this paper we describe the preparation and characterization of complexes [Mn$_2$(CO)$_6$(μ-η^2,η^3-S$_2$CPR$_3$)] and of a variety of their derivatives, containing η^2,η^3-S$_2$CPR$_3$ bridges of 8 e, which have been obtained by substitution reactions at high temperatures. A preliminary account of part of this work has been published.[13] Two mononuclear molybdenum complexes containing η^3-S$_2$CPMe$_3$ ligands of type h have been reported recently.[14]

Experimental Section

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. Infrared spectra were recorded on a Perkin-Elmer FT1720-X instrument. ^{1}H NMR spectra [79.54 MHz, δ (ppm) to higher frequencies from internal TMS] were recorded on a Varian FT80 spectrometer; ^{31}P{^{1}H} [125.50 MHz, δ (ppm) to higher frequencies from external 85% H$_3$PO$_4$] and ^{13}C{^{1}H} [75.47 MHz, δ (ppm) to higher frequencies from internal TMS] NMR spectra were recorded on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240B analyzer.

[Mn$_2$(CO)$_6$(μ-S$_2$CPCy$_3$)] (1a). (a) [Mn(CO)$_5$Br][15] (0.550 g, 2.0 mmol) and S$_2$CPCy$_3$[16] (0.713 g, 2.0 mmol) were refluxed in a mixture of toluene (15 mL) and CS$_2$ (1 mL) for 1.5 h. The solvents were evaporated in vacuo, and the residue was extracted with CH$_2$Cl$_2$ (25 mL) and filtered. Addition of hexane (30 mL) to the solution and slow evaporation of the solvents gave 1a as a red microcrystalline solid (0.381 g, 30%).

(b) Mn$_2$(CO)$_{10}$ (0.300 g, 0.769 mmol) and S$_2$CPCy$_3$ (0.274 g, 0.769 mmol) were refluxed in a mixture of toluene (20 mL) and CS$_2$ (1 mL) for 2 h. The mixture was then allowed to cool down to room temperature and then stored overnight in a refrigerator (−10 °C). This produced red crystals of 1a, which were collected in a frit and dried in vacuo (0.313 g, 64%). The mother liquors were evaporated to dryness, and the dark brown residue was dissolved in CH$_2$Cl$_2$ and chromatographed on alumina (activity II, 2.5 × 10 cm column). Elution with CH$_2$Cl$_2$/hexane (1:1) gave a yellow band containing small amounts of manganese–phosphine complexes. Further elution with CH$_2$Cl$_2$ gave a red band containing compound 1a. This band was collected and evaporated in vacuo to obtain 1a as a red, microcrystalline solid (0.083 g, 17%). Overall yield was 81%, based on Mn$_2$(CO)$_{10}$. Suitable crystals for an X-ray study were grown by slow diffusion of hexane into a concentrated CH$_2$Cl$_2$ solution at room temperature. Anal. Calcd for C$_{25}$H$_{33}$Mn$_2$O$_6$PS$_2$: C, 47.32; H, 5.24. Found: C, 47.06; H, 5.36.

[Mn$_2$(CO)$_6$(μ-S$_2$CPPr$^i_3$)] (1b). A mixture of Mn$_2$(CO)$_{10}$ (0.500 g, 1.282 mmol), PPr$^i_3$ (0.205 g, 1.282 mmol), and CS$_2$ (2 mL) was refluxed in toluene (20 mL) for 2 h. The solvents were then evaporated in vacuo giving a dark red residue. This was dissolved in CH$_2$Cl$_2$ (20 mL), and the resulting solution was filtered. Addition of hexane (30 mL) and concentration of the solution in vacuo produced red crystals of **1b**. Yield: 0.607 g, 92%. Anal. Calcd for C$_{16}$H$_{21}$Mn$_2$O$_6$PS$_2$: C, 37.37; H, 4.12. Found: C, 37.52; H, 4.38.

{Mn$_2$(CO)$_5$(μ-S$_2$CPCy$_3$)[P(OMe)$_3$]} (2a). A mixture of 1a (0.100 g, 0.158 mmol) and P(OMe)$_3$ (0.159 g, 1.6 mmol) was refluxed in toluene (20 mL) for 1 h. The solvent was then evaporated in vacuo, and the oily residue was washed with hexane (3 × 10 mL) to obtain a red solid. Recrystallization from CH$_2$Cl$_2$/hexane gave red needles of compound **2a**. Yield: 0.093 g, 81%. Anal. Calcd for C$_{27}$H$_{42}$Mn$_2$O$_8$P$_2$S$_2$: C, 44.29; H, 5.79. Found: C, 44.51; H, 5.89.

{Mn$_2$(CO)$_5$(μ-S$_2$CPCy$_3$)[P(OPh)$_3$]} (2b). **1a** (0.100 g, 0.158 mmol) and P(OPh)$_3$ (0.489 g, 1.6 mmol) were refluxed in toluene (20 mL) for 5 h. The workup was as for **2a**. Yield: 0.116 g, 80%. Anal. Calcd for C$_{42}$H$_{48}$Mn$_2$O$_8$P$_2$S$_2$: C, 55.02; H, 5.28. Found: C, 55.12; H, 5.33.

[Mn$_2$(CO)$_5$(μ-S$_2$CPCy$_3$)(PEt$_3$)] (2c). **1a** (0.100 g, 0.158 mmol) and PEt$_3$ (0.185 g, 1.6 mmol) were refluxed in CHCl$_3$ (15 mL) for 5 h. The workup was as for **2a**. Yield: 0.083 g, 72%. Anal. Calcd for C$_{42}$H$_{48}$Mn$_2$O$_8$P$_2$S$_2$: C, 50.01; H, 6.82. Found: C, 49.72; H, 6.68.

[Mn$_2$(CO)$_5$(μ-S$_2$CPCy$_3$)(CNBu^t)] (2d). **1a** (0.100 g, 0.158 mmol) and CNBu^t (0.017 g, 1.6 mmol) were refluxed in CHCl$_3$ (20 mL) for 4 h. The workup was as for **2a**. Yield: 0.075 g, 69%. Anal. Calcd for C$_{29}$H$_{42}$Mn$_2$NO$_5$PS$_2$: C, 50.51; H, 6.14; N, 2.03. Found: C, 50.70; H, 6.27; N, 1.99.

{Mn$_2$(CO)$_5$(μ-S$_2$CPPr$^i_3$)[P(OEt)$_3$]} (2e). Compound **1b** (0.150 g, 0.292 mmol) and P(OEt)$_3$ (0.050 g, 0.292 mmol) were refluxed in toluene (15 mL) for 3 h. The workup was as for **2a**. Yield: 0.142 g, 74%. Anal. Calcd for C$_{21}$H$_{36}$Mn$_2$O$_8$P$_2$S$_2$: C, 38.66;, H, 5.56. Found: C, 38.28; H, 5.47.

{Mn$_2$(CO)$_5$(μ-S$_2$CPPr$^i_3$)[P(OPh)$_3$]} (2f). Compound **1b** (0.075 g, 0.146 mmol) and P(OPh)$_3$ (0.453 g, 1.46 mmol) were refluxed

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in toluene (15 mL) for 1 h. The workup was as for **2a**. Yield: 0.082 g, 71%. Anal. Calcd for $C_{33}H_{38}Mn_2O_8P_2S_2$: C, 49.76; H, 4.56. Found: C, 49.95, H, 4.46.

$\{Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)[P(OMe)_3]_2\}$ (3a). (a) Compound **1a** (0.100 g, 0.158 mmol) and $P(OMe)_3$ (0.159 g, 1.6 mmol) were refluxed in toluene (20 mL) for 14 h. The workup was as for **2a**. Yield: 0.122 g, 93%. (b) Compound **2a** (0.080 g, 0.109 mmol) and $P(OMe)_3$ (0.135 g, 1.095 mmol) were refluxed in toluene (15 mL) for 12 h. The workup was as for **2a**. Yield: 0.071 g, 89%. Anal. Calcd for $C_{29}H_{51}Mn_2O_{10}P_3S_2$: C, 42.14; H, 6.22. Found: C, 42.28; H, 6.04.

$\{Mn_2(CO)_4(\mu\text{-}S_2CPPr^i_3)[P(OEt)_3]_2\}$ (3b). (a) Compound **1b** (0.100 g, 0.194 mmol) and $P(OEt)_3$ (0.323 g, 1.94 mmol) were refluxed in toluene (20 mL) for 6 h. The workup was as for **2a**. Yield: 0.115 g, 75%. (b) Compound **2b** (0.080 g, 0.109 mmol) and $P(OEt)_3$ (0.135 g, 1.095 mmol) were refluxed in toluene (15 mL) for 5 h. The workup was as for **2a**. Yield: 0.068 g, 79%. Anal. Calcd for $C_{26}H_{51}Mn_2O_{10}P_3S_2$: C, 39.39; H, 6.32. Found: C, 39.50; H, 6.50.

$[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4a). Compound **1a** (0.200 g, 0.320 mmol) and dppm (0.121 g, 0.320 mmol) were refluxed in xylene (20 mL) for 30 h. The workup was as for **2a**. Suitable crystals for x-ray analysis were grown by slow difussion of hexane into a concentrated solution of **4a** in CH_2Cl_2 at −20 °C. Yield: 0.198 g, 60%. Anal. Calcd for $C_{48}H_{55}Mn_2O_4P_3S_2{\cdot}CH_2Cl_2$: C, 56.17; H, 5.48. Found: C, 56.07; H, 5.48.

$[Mn_2(CO)_4(\mu\text{-}S_2CPPr^i_3)(\mu\text{-dppm})]$ (4b). Compound **1b** (0.150 g, 0.292 mmol) and dppm (0.112 g, 0.292 mmol) were refluxed in toluene (20 mL) for 10 h. The workup was as for **2a**. Yield: 0.155 g, 69%. Anal. Calcd for $C_{39}H_{43}Mn_2O_4P_3S_2$: C, 55.59; H, 5.14. Found: C, 55.27; H, 5.19.

$\{Mn_2(CO)_9[SC(S)PCy_3]\}$ (5). To a solution of $Mn_2(CO)_{10}$ (0.2 g, 0.51 mmol), S_2CPCy_3 (0.183 g, 0.51 mmol), and CS_2 (1 mL) in CH_2Cl_2 (20 mL) was added $ONMe_3$ (0.058 g, 0.71 mmol); the mixture was stirred at room temperature for 30 min and evaporated to dryness in vacuo. The residue was dissolved in a mixture of CH_2Cl_2/hexane (1:1, 5 mL) and chromatographed in alumina (activity III, 2 × 15 cm column). Elution with hexane gave first a pale yellow band which was discarded. Further elution with CH_2Cl_2/hexane (1:4) gave a red band which was collected. Slow evaporation of the solvents gave compound **5** as a red crystalline solid. Yield: 0.128 g, 35%. Anal. Calcd for $C_{28}H_{33}Mn_2O_9PS_2$: C, 46.80; H, 4.63. Found: C, 47.07; H, 4.72.

$[Mn(CO)_3(S_2CPCy_3)(I)]$ (6b). To a stirred solution of **1a** (0.05 g, 0.079 mmol) and S_2CPCy_3 (0.028 g, 0.079 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of iodine (0.020 g, 0.079 mmol) in CH_2Cl_2 (10 mL). When the addition was completed, the mixture was stirred for 15 min and then the solvent was evaporated in vacuo. The dark residue was washed with hexane (3 × 10 mL) to give a deep green solid. Recrystallization from CH_2Cl_2/hexane gave **6b** as a deep green microcrystalline solid. Yield: 0.073 g, 74%. Anal. Calcd for $C_{22}H_{33}IMnO_3PS_2$: C, 42.45; H, 5.34. Found: C, 42.17; H, 5.35.

X-ray Diffraction Studies of 1a and 4a. Relevant crystallographic details are given in Table II. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. During the data collection (see details in Table II), three reflections were measured every 2 h as orientation and intensity control. Significant decay was not observed. For the structure of **1a**, heavy atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms by DIRDIF.[17] The structure of **4a** was solved by direct methods with MULTAN[18] and subsequent Fourier maps. Full-matrix least-squares refinements for both structures were made with SHELX.[19] Scattering factors, *f*, *f* ′, and *f* ″ were taken from ref 20. Hydrogen atoms were geometrically positioned and refined with an overall isotropic temperature factor. All non-hydrogen atoms were refined isotropically. Final residues for all observed reflections were, for **1a**, $R = 0.061$ ($R_w = 0.064$) and, for **4a**, $R = 0.039$ ($R_w = 0.044$). Drawings shown in Figures 1 and 2 were made with PLUTO.[21] Torsion angles, least-squares planes, and other calculations were made with PARST.[22]

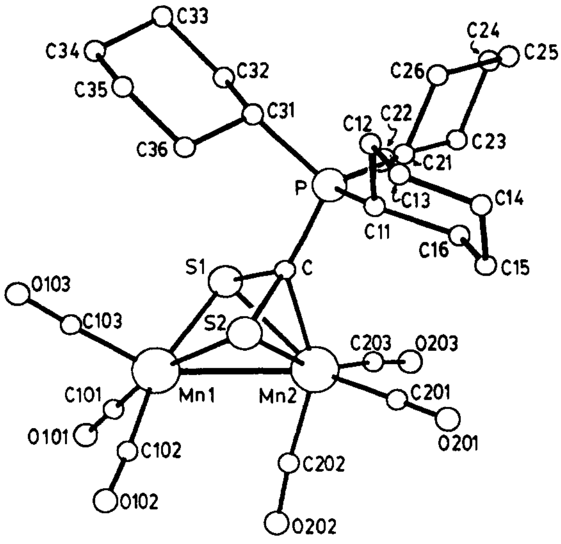

Figure 1. Perspective view of the structure of $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**1a**), showing the atom numbering.

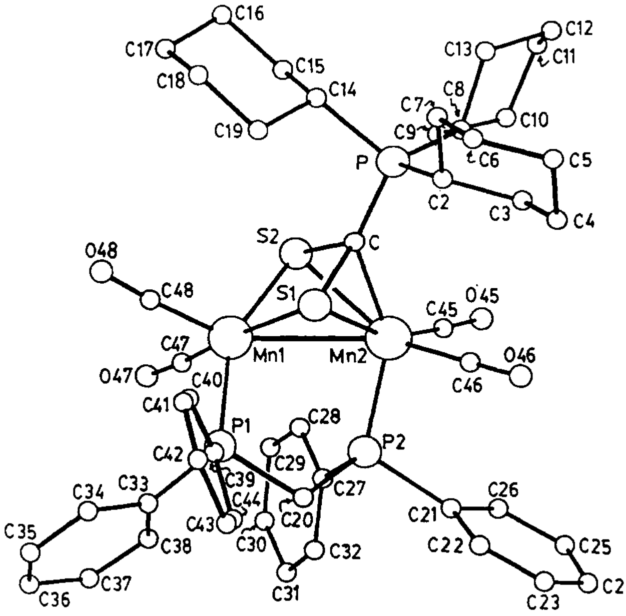

Figure 2. Perspective view of the structure of $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (**4a**), showing the atom numbering.

Results and Discussion

Reaction of $[Mn(CO)_5(Br)]$ with S_2CPCy_3 in refluxing toluene affords a red solution from which compound **1a** can be isolated as a bright red crystalline solid in low yield (30%). The IR spectrum of **1a** in toluene showed five bands in the *ν*(CO) region (see Table I), suggesting the formation of a polynuclear complex, and its $^{31}P\{^1H\}$ NMR

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Table I. IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR Data for the New Complexes

compd	ν(CO), cm^{-1} [a]	^1H NMR,[b] ppm	$^{31}P\{^1H\}$ NMR,[c] ppm	
			S_2CPR_3	other
1a	2024 (s), 1982 (vs), 1934 (s), 1921 (s), 1903 (m)	2.35–1.26 [m, br, $P(C_6H_{11})_3$]	30.91 (s)	
1b	2025 (s), 1983 (vs), 1933 (s), 1921 (s), 1905 (m)	1.62 [m, 3 H, $P[CH(CH_3)_2]$], 0.68 [dd, 18 H, J(PH) = 15, J(HH) = 7, $P[CH(CH_3)_2]$]	41.23 (s)	
2a	1995 (vs), 1938 (vs), 1906 (s), 1861 (m)	3.68 [d, 9 H, J(PH) = 1, $P(OCH_3)_3$], 2.41–1.36 [m, br, 33 H, $P(C_6H_{11})_3$]	30.16 (s)	209.8 [s, br $P(OCH_3)_3$]
2b	1995 (vs), 1943 (vs), 1902 (s), 1875 (sh)	3.68 [d, 15 H, $P(OC_6H_5)_3$], 2.37–1.31 [m, br, 33 H, $P(C_6H_{11})_3$]	29.92 (s)	186.8 [s, br, $P(OC_6H_5)_3$]
2c	1985 (vs), 1928 (vs), 1897 (sh), 1834 (m)	2.16–1.08 [m, br, 33 H, $P(C_6H_{11})_3$], 1.59 [m, 6 H, $P(CH_2CH_3)_3$], 1.03 [m, 9 H, $P(CH_2CH_3)_3$]	29.64 [d, J(PP) = 5 Hz]	59.2 [s, br, $P(CH_2CH_3)_3$]
2d	1985 (vs), 1928 (vs), 1900 (s), 1861 (m)	2.39–1.24 [m, br, 33 H, $P(C_6H_{11})_3$], 1.41 [s, 9 H, $CNC(CH_3)_3$]	30.12 (s)	
2e	1992 (vs), 1944 (s), 1900 (s), 1862 (m)	4.04 [m, 6 H, $P(OCH_2CH_3)_3$], 2.65 [m, 3 H, $P[CH(CH_3)_2]_3$], 1.48 [dd, 18 H, J(PH) = 15, J(HH) = 7, $P[CH(CH_3)_2]_3$], 1.31 [t, 9 H, J(HH) = 7, $P(OCH_2CH_3)_3$]	40.19 (s)	205.2 [s, br, $P(OCH_2CH_3)_3$]
2f	1998 (vs), 1949 (s), 1904 (s), 1879 (sh)	7.28, 7.15 [m, br, 15 H, $P(OC_6H_5)_3$], 2.47 [m, 3 H, $P[CH(CH_3)_2]$], 1.34 [dd, 18 H, J(PH) = 15 J(HH) = 7, $P[CH(CH_3)_2]_3$]	39.74 (s)	195.5 [s, br, $P(OC_6H_5)_3$]
3a	1947 (s), 1909 (vs), 1865 (s), 1819 (m)	3.69 [m, br, 18 H, 2 $P(OCH_3)_3$], 2.32–1.35 [m, br, 33 H, $P(C_6H_{11})_3$]	31.25 (s)	216 [s, v br, $P_A(OCH_3)_3$], 202.6 [s, br, $P_B(OCH_3)_3$]
3b	1945 (s), 1907 (vs), 1863 (s), 1845 (m)	4.20 [m, 12 H, 2 $P(OCH_2CH_3)_3$], 2.15 [m, 3 H, $P[CH(CH_3)_2]_3$], 1.34, 1.25, 1.18, 1.09, 0.99, 0.90 [m, 36 H, $P[CH(CH_3)_2]_3$, and 2 $P(OCH_2CH_3)_3$]	40.66 (s)	211 [s, v br, $P_A(OCH_2CH_3)_3$], 196.6 [s, br, $P_B(OCH_2CH_3)_3$]
4a	1927 (w), 1904 (vs), 1849 (vs)	7.67, 7.31, 7.23 [m, br, 20 H, $CH_2[P(C_6H_5)_2]_2$], 3.52 [m, br, 2 H, $CH_2[P(C_6H_5)_2]_2$], 2.36–1.32 [m, br, 33 H, $P(C_6H_{11})_3$]	30.30 (s)	61.82 [d, J(PP) = 64, $P_A(C_6H_5)_2$] 59.24 [d, J(PP) = 64, $P_B(C_6H_5)_2$]
4b	1927 (m), 1903 (vs), 1849 (vs)	7.53–7.10 [m, br, 20 H, $CH_2[P(C_6H_5)_2]_2$], 3.57 [m, br, 2 H, $CH_2[P(C_6H_5)_2]_2$], 2.02 [m, 3 H, $P[CH(CH_3)_2]_3$], 0.92 [dd, 18 H, J(PH) = 15, J(HH) = 7, $P[CH(CH_3)_2]_3$]	39.54 (s)	62.47 [d, J(PP) = 66, $P_A(C_6H_5)_2$] 59.01 [d, J(PP) = 66, $P_B(C_6H_5)_2$]
5	2079 (w), 2013 (m), 1982 (vs) 1955 (m), 1922 (m)	2.90–1.27 [m, br, $P(C_6H_{11})_3$]	28.42 (s)	
6b	2028 (s), 1934 (s), 1917 (s)[d]	2.15–1.85 [m, br, $P(C_6H_{11})_3$]	20.35 (s)	

[a] In toluene solution unless otherwise stated. [b] In $CDCl_3$ solutions, δ from internal TMS. [c] In $CDCl_3$ solutions, δ from external 85% H_3PO_4. [d] In CH_2Cl_2 solution.

spectrum displayed only one sharp signal at δ 30.9 ppm. It was soon found that the reaction of $Mn_2(CO)_{10}$ and S_2CPCy_3 in refluxing toluene produces the same compound **1a** in good yield (81%). Analytical data for **1a** were in agreement with its formulation as a dimanganese hexacarbonyl complex with only one S_2CPCy_3 ligand. However, since on the basis of these data it was not possible to establish a correct formulation for the compound, an x-ray diffraction study was necessary to ascertain its structure. Crystallographic details are given in Table II, atomic coordinates in Table III, and selected bond lengths and angles in Table IV. A perspective drawing of the molecule is shown in Figure 1. The molecule can be viewed as a $Mn_2(CO)_6$ unit bridged by a S_2CPCy_3 ligand. The Mn(1)–Mn(2) distance [2.737 (1) Å] is shorter than the Mn–Mn distance in $Mn_2(CO)_{10}$ [2.923 (3) Å], and falls well into the range (2.50–3.23 Å)[23] of Mn–Mn distances in complexes with an assumed metal–metal bond order of 1. Both sulfur atoms are closer to Mn(1) than to Mn(2), while the central carbon atom is within bonding distance to Mn(2) [2.023 (7) Å] and much further away from Mn(1) [2.899 (6) Å]. Thus, the S_2CPCy_3 adduct could be regarded as acting like a η^2-(S,S') chelate toward Mn(1) and like a η^3-(S,C,S') pseudoallylic ligand toward Mn(2). Further aspects of the structure of **1a** will be discussed below, in connection with the structure of its derivative **4a**.

The formation of complex **1a** from $Mn_2(CO)_{10}$ can be considered as the result of a thermally induced substitution of four carbonyl groups by the S_2CPCy_3 ligand, and this has therefore to donate 8 e to the dimanganese moiety to satisfy the EAN rule. Thus, compound **1a** constitutes the first example of a new bonding mode of the S_2CPR_3 group acting as a η^2-(S,S'), η^3-(S,C,S'), 8e bridging ligand.

On the other hand, the reaction of $[Mn(CO)_5(Br)]$ with S_2CPCy_3 to give **1a** must involve some more complexity since the overall result is the production of a Mn(0) complex from the starting Mn(I) bromocarbonyl. This formal reduction of manganese is probably achieved through a disproportionation process such as

$$4[Mn(I)] \rightarrow [Mn(0)]_2 + 2[Mn(II)]$$

and this would account for the low yield of the reaction. In fact, a considerable amount of insoluble material, probably consisting of Mn(II) salts, is produced.

Treatment of the mononuclear Mn(I) complex $[Mn(CO)_3(S_2CPCy_3)(Br)]$ with $NaBH_4$ in CH_2Cl_2/EtOH at room temperature produces small amounts (10–15%) of **1a** together with the dimeric Mn(I) complex $[Mn_2(CO)_6(\mu\text{-}S_2C(H)PCy_3)_2]$ which contains a dithioformate–PCy_3 adduct, $S_2C(H)PCy_3^-$ acting as an asymmetric bridge between two $Mn(CO)_3$ units without metal–metal interaction.[24] It seems therefore that high temperatures, rather than strictly reducing conditions are determinant in the mechanism that leads to the formation of **1a** from the starting mononuclear Mn(I) complexes. Additional work is in progress in an attempt to shed some light on the mechanism of these reactions.

Several attempts to prepare compounds analogous to **1a** bearing other S_2CPR_3 adducts produced different results depending on the phosphines employed. Thus, heating $Mn_2(CO)_{10}$ with $S_2CPPr^i_3$ (prepared in situ from PPr^i_3 and excess CS_2) led to the formation of $[Mn_2(CO)_6(\mu\text{-}S_2CPPr^i_3)]$ (**1b**) in 92% yield, while the use of S_2CPR_3 adducts of smaller[25] phosphines such as PEt_3 or PMe_2Ph produced extensive decomposition and the formation of a mixture of yellow products containing direct Mn–P bonds, even when those reactions were performed with excess of CS_2. A similar result was obtained with a bulky but less basic

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[24] Miguel, D.; Miguel, J. A.; Riera, V.; Solâns, X. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1014.

[25] Cone angles (deg) for the phosphines employed: PCy_3 170, PBz_3 165, PPr^i_3 160, PPh_3 145, PEt_3 132, and PMe_2Ph 122. Values taken from: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table II. Crystal Data and Refinement Details for $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (1a) and $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4a)

	1a	4a
formula	$C_{25}H_{33}Mn_2O_6PS_2$	$C_{48}H_{55}Mn_2O_4P_3S_2.CH_2Cl_2$
mol wt	634.51	1047.82
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	11.652 (4)	16.403 (4)
b, Å	11.368 (4)	14.927 (3)
c, Å	10.973 (3)	11.903 (3)
α, deg	85.76 (2)	116.48 (3)
β, deg	77.29 (2)	106.46 (3)
γ, deg	86.00 (2)	81.49 (2)
V, Å^3	1412 (1)	2501 (2)
molecules/cell	2	2
d(calcd), g cm^{-3}	1.49	1.39
F(000)	656	1088
diffractometer	PHILIPS PW1100	PHILIPS PW1100
cryst color	red	red
cryst size, mm	0.15 × 0.15 × 0.1	0.1 × 0.1 × 0.8
μ, cm^{-1}	11.75	8.12
λ(Mo Kα radiation, graphite monochromator), Å	0.170 69	0.710 69
method of collcn	ω scan	ω scan
scan width, deg	1	0.8
scan speed, deg s^{-1}	0.03	0.03
θ range, deg	$2 \leq \theta \leq 25$	$2 \leq \theta \leq 25$
no. of reflns, measd	3621	5624
in refinement, $I \geq 2.5\sigma(I)$	3492	4815
no. of params	424	821
data to param ratio	8.23	5.86
abs corrn	none	empirical
transm factors: max, min		0.94, 0.89
weight, g^a	0.018	0.013
final R, R_w	0.061, 0.064	0.039, 0.044

[a] Minimized function: $w||F_o| - |F_c||^2$, applied weighting: $(\sigma^2(F_o) + g|F_o|^2)^{-1}$.

Table III. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (1a) (Mn × 10^5)

	x	y	z
Mn(1)	20077 (9)	12679 (9)	24902 (9)
Mn(2)	29872 (9)	32730 (9)	12888 (9)
S(1)	3623 (2)	1320 (2)	879 (2)
C	2807 (6)	2220 (6)	−58 (6)
S(2)	1370 (1)	2365 (2)	924 (2)
P	3019 (2)	2244 (2)	−1723 (2)
C(11)	1819 (6)	3231 (7)	−2123 (6)
C(12)	1290 (6)	2882 (6)	−3195 (7)
C(13)	175 (6)	3689 (6)	−3274 (7)
C(14)	441 (7)	4978 (6)	−3456 (8)
C(15)	1025 (8)	5320 (7)	−2412 (8)
C(16)	2123 (7)	4539 (6)	−2347 (8)
C(21)	4436 (7)	2819 (6)	−2489 (7)
C(22)	5519 (6)	2369 (7)	−1958 (6)
C(23)	6580 (6)	3063 (6)	−2611 (7)
C(24)	6835 (7)	2986 (7)	−4013 (8)
C(25)	5766 (7)	3434 (7)	−4541 (8)
C(26)	4672 (6)	2758 (7)	−3917 (6)
C(31)	2866 (6)	765 (6)	−2178 (6)
C(32)	3967 (6)	−74 (5)	−2183 (7)
C(33)	3803 (6)	−1280 (6)	−2620 (8)
C(34)	2699 (9)	−1808 (6)	−1792 (11)
C(35)	1610 (7)	−992 (7)	−1778 (9)
C(36)	1769 (6)	228 (6)	−1362 (7)
C(101)	2808 (7)	784 (7)	3705 (7)
O(101)	3283 (6)	479 (6)	4493 (6)
C(102)	704 (7)	1662 (7)	3667 (8)
O(102)	−130 (6)	1854 (7)	4413 (6)
C(103)	1463 (7)	−134 (7)	2400 (8)
O(103)	1105 (6)	−1024 (5)	2296 (8)
C(201)	2401 (7)	4725 (7)	846 (7)
O(201)	2014 (5)	5633 (5)	572 (6)
C(202)	2776 (7)	3577 (7)	2913 (7)
O(202)	2720 (6)	3828 (6)	3916 (5)
C(203)	4464 (7)	3752 (7)	1030 (7)
O(203)	5406 (5)	4086 (6)	943 (7)

phosphine such as PPh_3. This suggests that both a basic character and a big size are required on the phosphine to form the 8e bridge. As a confirmation, similar reactions with the adduct of tribenzylphosphine, S_2CPBz_3, did produce $\{Mn_2(CO)_6[\mu\text{-}S_2CPBz_3]\}$ (**1c**), albeit in low yield.[26] The reason for this behavior may be due to the fact that small, basic phosphines, have a strong tendency to get attached to the metal, as shown by the reaction of $[Mn(CO)_5Br]$ with an excess of S_2CPEt_3, which leads sequentially (via subsubstitution of CO) to the manganese-phosphine complexes *cis*-$[Mn(CO)_4(PEt_3)(Br)]$ and *mer,trans*-$[Mn(CO)_3(PEt_3)_2(Br)]$, and only then is the adduct able to coordinate, giving *cis–trans*-$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]Br$ as the final product.[27] On the other hand, bulky but less basic triarylphosphines are not nucleophilic enough to form a stable adduct with CS_2. Only in the case of bulky *and* basic phosphines such as PCy_3, PPr^i_3, or PBz_3, may the direct coordination to the metal be somewhat difficult by their size and, in the balance, the reaction is driven toward the coordination of the S_2CPR_3 adduct.

A closer inspection to the structure of **1a** reveals that there is a very strong interaction between the $Mn_2(CO)_6$ moiety and the CS_2 grouping. Thus the Mn(1)–S [2.282 (2) and 2.276 (2) Å] and even the longer Mn(2)–S [2.335 (2) and 2.332 (2) Å] distances are significantly shorter than those found in complexes such as $[Mn(CO)_3(S_2CPCy_3)_2]ClO_4$ [Mn–S, 2.383 (2) and 2.361 (3) Å][11] or $[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]$ [Mn–S, 2.375 (1) and 2.354 (2) Å],[27] in which the S_2CPR_3 ligands act as a chelate. In addition to that, the Mn(2)–C distance (2.023 (7) Å) is shorter than the Mn–C(allyl) distances found in genuine η^3-allyl manganese complexes such as $\{Mn(\eta^3\text{-}C_3H_5)(CO)_2[P(OMe)_3]_2\}$ [Mn–C(terminal), 2.229 (13) and 2.223 (17) Å; Mn–C(central, 2.114 (15) Å].[28]

The strong interaction between the S_2C group and the $Mn_2(CO)_6$ unit accounts very well for the high stability of the complexes containing the S_2CPR_3 bridge of 8 e. Compounds **1a,b** are obtained in refluxing toluene and can be refluxed in this solvent for several hours without any significant decomposition. This stability of the 8e bridge allows the preparation of a number of derivatives by thermally promoted substitution of CO by other ligands (reaction ii in Scheme I), to give pentacarbonyl complexes $[Mn_2(CO)_5(\mu\text{-}S_2CPR_3)(L)]$ [R = Cy, L = $P(OMe)_3$ (**2a**),

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[26] (a) $[Mn(CO)_5Br]$ (0.248 g, 0.452 mmol), PBz_3 (0.125 g, 0.452 mmol), and CS_2 (2 mL) were refluxed in toluene (20 mL) for 3 h. Workup was as described for **1a** (method a) in the Experimental Section. Yield: 0.077 g, 26%. (b) $Mn_2(CO)_{10}$ (0.200 g, 0.512 mmol), PBz_3 (0.142 g, 0.512 mmol), and CS_2 (2 mL) were refluxed in toluene (15 mL) for 4 h. Workup was as described for **1a** (method b) in the Experimental Section. Yield: 0.108 g, 32%. The samples of $[Mn_2(CO)_6(\mu\text{-}S_2CPBz_3)]$ (**1c**) obtained from both reactions rendered the same spectroscopic properties. IR ν(CO) (toluene): 2026 (s), 1984 (vs), 1937 (m), 1925 (m), 1908 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$; δ, ppm): 7.97–6.96 (m, 15 H, 3 C_6H_5), 3.19 [d, J(PH) = 14 Hz, 6 H, 3 PCH_2]. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ, ppm): 29.1 (s).

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Table IV. Selected Bond Lengths (Å) and Angles (deg) for $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (1a)

Coordination around Mn Atoms			
Mn(2)–Mn(1)	2.737 (1)	S(1)–Mn(2)	2.335 (2)
S(1)–Mn(1)	2.282 (2)	C–Mn(2)	2.023 (7)
S(2)–Mn(1)	2.276 (2)	S(2)–Mn(2)	2.333 (2)
C(101)–Mn(1)	1.820 (9)	C(201)–Mn(2)	1.816 (8)
C(102)–Mn(1)	1.818 (7)	C(202)–Mn(2)	1.800 (8)
C(103)–Mn(1)	1.773 (9)	C(203)–Mn(2)	1.798 (9)
S(1)–Mn(1)–Mn(2)	54.5 (1)	S(2)–Mn(2)–Mn(1)	52.6 (1)
S(2)–Mn(1)–Mn(2)	54.5 (1)	S(2)–Mn(2)–S(1)	73.6 (1)
S(2)–Mn(1)–S(1)	75.7 (1)	S(2)–Mn(2)–C	47.7 (2)
C(101)–Mn(1)–Mn(2)	107.5 (3)	C(201)–Mn(2)–Mn(1)	134.4 (2)
C(101)–Mn(1)–S(1)	96.0 (2)	C(201)–Mn(2)–S(1)	152.1 (3)
C(101)–Mn(1)–S(2)	161.9 (3)	C(201)–Mn(2)–C	105.4 (3)
C(102)–Mn(1)–Mn(2)	109.8 (3)	C(201)–Mn(2)–S(2)	91.9 (3)
C(102)–Mn(1)–S(1)	164.2 (3)	C(202)–Mn(2)–Mn(1)	77.5 (3)
C(102)–Mn(1)–S(2)	93.6 (3)	C(202)–Mn(2)–S(1)	113.6 (3)
C(102)–Mn(1)–C(101)	90.7 (4)	C(202)–Mn(2)–C	150.7 (3)
C(103)–Mn(1)–Mn(2)	148.9 (3)	C(202)–Mn(2)–S(2)	110.9 (3)
C(103)–Mn(1)–S(1)	103.0 (2)	C(202)–Mn(2)–C(201)	93.7 (3)
C(103)–Mn(1)–S(2)	102.4 (3)	C(203)–Mn(2)–Mn(1)	131.0 (2)
C(103)–Mn(1)–C(101)	95.1 (4)	C(203)–Mn(2)–S(1)	93.2 (2)
C(103)–Mn(1)–C(102)	90.5 (4)	C(203)–Mn(2)–S(2)	159.0 (3)
S(1)–Mn(2)–Mn(1)	52.8 (1)	C(203)–Mn(2)–C	111.4 (3)
C–Mn(2)–Mn(1)	73.3 (2)	C(203)–Mn(2)–C(201)	92.8 (3)
C–Mn(2)–S(1)	47.3 (2)	C(203)–Mn(2)–C(202)	89.2 (4)
Phosphoniodithiocarboxylate Ligand			
C–S(1)	1.773 (7)	C(11)–P	1.839 (7)
S(2)–C	1.785 (6)	C(21)–P	1.821 (8)
P–C	1.787 (7)	C(31)–P	1.820 (7)
Mn(2)–S(1)–Mn(1)	72.7 (1)	P–C–Mn(2)	139.6 (4)
C–S(1)–Mn(1)	90.3 (2)	P–C–S(1)	126.2 (4)
C–S(1)–Mn(2)	57.0 (2)	P–C–S(2)	121.4 (4)
S(1)–C–Mn(2)	75.6 (3)	Mn(2)–S(2)–Mn(1)	72.9 (1)
S(2)–C–Mn(2)	75.3 (2)	C–S(2)–Mn(1)	90.2 (2)
S(2)–C–S(1)	103.7 (3)	C–S(2)–Mn(2)	57.0 (2)
Carbonyl Ligands			
O(101)–C(101)	1.147 (11)	O(201)–C(201)	1.144 (10)
O(102)–C(102)	1.143 (10)	O(202)–C(202)	1.145 (10)
O(103)–C(103)	1.144 (11)	O(203)–C(203)	1.168 (11)
O(101)–C(101)–Mn(1)	178.2 (7)	O(201)–C(201)–Mn(2)	178.9 (7)
O(102)–C(102)–Mn(1)	176.7 (8)	O(202)–C(202)–Mn(2)	174.3 (7)
O(103)–C(103)–Mn(1)	177.3 (8)	O(203)–C(203)–Mn(2)	175.5 (7)

$P(OPh)_3$, (**2b**), PEt_3 (**2c**), $CNBu^t$ (**2d**); R = Pr^i, L = $P(OEt)_3$ (**2e**), $P(OPh)_3$ (**2f**)]. In some cases, it is possible to achieve the substitution of two CO groups by two monodentate ligands (reactions iv and v) or by bis(diphenylphosphine)methane, dppm (reaction vi) to obtain tetracarbonyl complexes $[Mn_2(CO)_4(\mu\text{-}S_2CPR_3)(L)_2]$ [R = Cy, L = $P(OMe)_3$ (**3a**); R = Pr^i, L = $P(OEt)_3$ (**3b**)] or $[Mn_2(CO)_4(\mu\text{-}S_2CPR_3)(\mu\text{-dppm})]$ [R = Cy (**4a**), Pr^i(**4b**)]. Analytical and spectroscopic data (Table I) are consistent with the structures proposed for these derivatives in Scheme I. Their ^{31}P NMR spectra exhibit the signal of the phosphorus on the S_2CPR_3 ligand in the ranges δ 29.64–31.25 ppm for the derivatives of PCy_3 (**2a–d**, **3a**, **4a**) and δ 39.54–40.66 ppm for those with PPr^i_3 (**2e**,**f**, **3b**, **4b**), very close to those of the parent compounds (δ 30.91 for **1a** and 41.23 for **1b**). This suggest that the chemical environment within the S_2CPR_3 ligand is not very much changed and the S_2CPR_3 bridge has been maintained in the product of the substitution reaction.

Additionally, ^{13}C NMR spectra have proved to be a very useful tool in the characterization of this type of bridge. The signal of the central carbon in S_2CPR_3 appears in a very narrow range of chemical shifts (δ 79.19–85.51 ppm) for all the derivatives (Table V), very far from the region (δ 220–230 ppm) where the same signals occur for the monodentate or chelate ligands. Although not enough ^{13}C NMR data of coordinate S_2CPR_3 groups are available to make a safe correlation, the appearance of the signal of the central carbon around δ 80 ppm could be used as an indication of the presence of $\eta^3(S,C,S')$-bonded S_2CPR_3 ligands. Thus, for the mononuclear complexes $\{Mo(NO)(Cl)[S_2CPMe_3\text{-}S,C,S'](PMe_3)_2\}$ and $\{Mo(NO)(S_2CNMe_2)[S_2CPMe_3\text{-}S,C,S'](PMe_3)\}$, those signals have been reported[14] to be placed at δ 82.75 and 82.9 ppm, respectively. In complexes **1b**–**4b**, these signals are observed as characteristic doublets, the $^1J(PC)$ constants ranging from 41 to 48 Hz. Smaller couplings with P atoms of the other ligands were not observed, probably due to the broadening effect of the quadrupole moment of the Mn atoms. The same effect could be responsible for the broad shape of the signals of the carbonyl groups, which gave little structural information.

On the other hand the coupling between the P atom in the S_2CPR_3 ligand to the other P atoms bonded to manganese were not observed, even when the spectra were recorded at low temperature (at -90 °C for **2a** and **4a**). Only the compound **2c** (L = PEt_3) does the signal corresponding to the S_2CPR_3 ligand appear as a narrow doublet ($J(PP)$ = 5 Hz), while the signal of PEt_3 appears as a broad singlet due to the quadrupole effect of the Mn atom. At the beginning, this led us to conclude that the entering ligand would be attached to the hexacoordinate manganese, thus giving a small (as in **2c**) or unobservable (as in the other pentacarbonyls) four-bond PP coupling. However, this argument loses its validity since the three-bond coupling in tetracarbonyls **3a**,**b** and **4a**,**b** (expected to be somewhat stronger) could not be observed either. Therefore, the actual position of the monodentate L ligands in the pentacarbonyls **2a–f**, and in the tetracarbonyls **3a**,**b** remains unconfirmed, and the structures depicted for them in Scheme I must be considered as tentatively proposed, mainly on the grounds of steric factors. This appears to be reasonable since the compounds are obtained at high temperatures, and the thermodinamically favored isomers are to be expected. In the case of pentacarbonyls **2a–f**, the position proposed for the ligand L appears to be both the less sterically congested and also the kinetically predicted due to the cis-labilizing properties of the sulfur atoms.

Although no quantitative study of the kinetics of the substitution reactions has been made, qualitative observations show that the first substitution in **1a**,**b**, to give the pentacarbonyls **2a–f**, can be achieved somewhat easily, while the second substitution (when possible) takes much longer refluxing times, even in the presence of great excess of the entering ligand. This is consistent both with a different CO lability in the two metal centers and also with the fact that the first substitution of CO by a less π-acceptor ligand increases the electron density in the resulting pentacarbonyl, and this reduces the lability of the remaining CO groups. Accordingly, when the pentacarbonyl **2c**, where L is the electron-rich PEt_3 ligand, is refluxed in toluene in the presence of great excess of PEt_3 for more than 12 h, no significant amount of the corresponding tetracarbonyl is detected by IR monitoring of the reaction mixture.

In the reactions of the hexacarbonyls **1a**–**b** with the bidentate dppm ligand, the successive IR spectra of the reaction mixtures show the formation of the tetracarbonyls **4a**,**b**, simultaneous to the dissappearance of the starting hexacarbonyls, but no bands attributable to the expected pentacarbonyl intermediate (bearing a monodentate dppm ligand) can be observed. This suggests that, in this case, the second substitution of CO is much faster than the first one, being favored by its intramolecular character.

An X-ray determination was carried out on **4a**, to confirm the presence of the 8e bridge. Crystallographic details

Scheme I

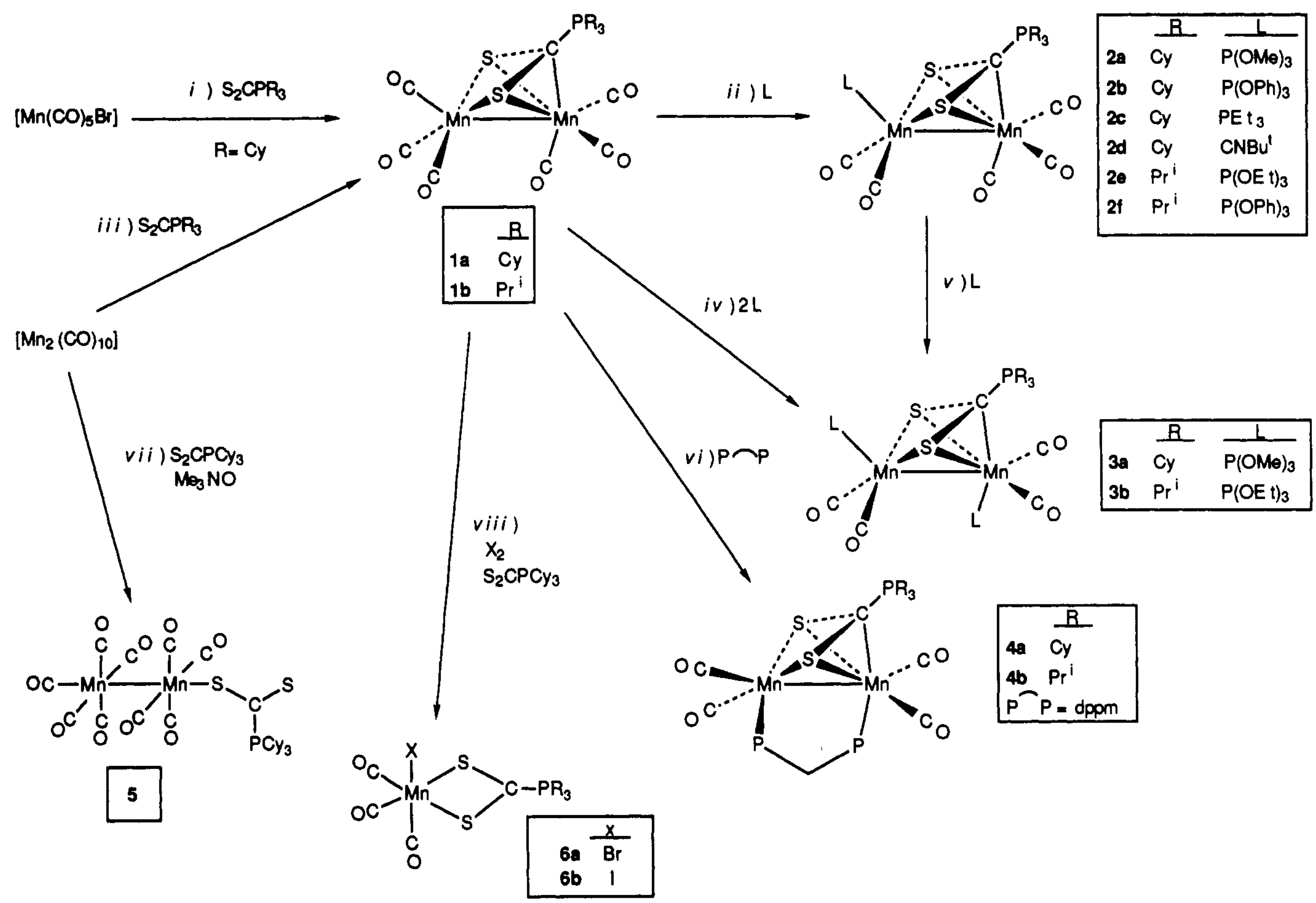

Table V. $^{13}C\{^1H\}$ NMR Data for the New Complexes[a]

compd	S_2CPR_3	R	S_2CPR_3	L		CO
1a	*b*	Cy	33.68 (d, 42, C^1), 27.87 (C^3, C^5), 27.17 (d, 12, C^2, C^6), 25.96 (C^4)			*b*
1b	84.18 (d, 41)	Pr^i	23.76 (d, 44, CH), 17.48 (2 CH_3)			223.96 222.18
2a	83.65 (d, 47)	Cy	33.36 (d, 42, C^1), 27.53 (d, 3.8, C^3, C^5), 27.01 (d, 12, C^2, C^6), 25.65 (C^4)	$P(OMe)_3$	51.65 (d, 4, OCH_3)	226.15 (br), 225.57 (br)
2b	85.50 (d, 45)	Cy	33.91 (d, 42.0, C^1), 27.56 (d, 3, C^3, C^5), 26.97 (d, 12, C^2, C^6), 25.65 (C^4)	$P(OPh)_3$	152.13 (d, 8, C^1), 129.71 129.63, 121.75 (C^2–C^6)	224.94 (br)
2c	85.29 (d, 44)	Cy	33.48 (d, 43, C^1), 27.51 (C^3, C^5), 26.87 (d, 13, C^2, C^6), 25.62 (C^4)	PEt_3	20.63 (d, 22, CH_2), 7.87 (CH_3)	232.16 (br), 225.76 (br)
2d	84.14 (d, 43)	Cy	33.21 (d, 40, C^1), 27.32 (C^3, C^5), 26.84 (C^2, C^6), 25.83 (C^4)	$C{\equiv}NC(CH_3)_3$	172.24 (br, $C{\equiv}NC$), 57.86 ($CNC(CH_3)_3$), 30.91 $(CH_3)_3$	225.34 (br), 223.87 (br)
2e	81.47 (d, 49)	Pr^i	23.44 (d, 44, CH), 17.53 (d, 2, CH_3)	$P(OEt)_3$	60.30 (d, 4, OCH_2), 16.32 (OCH_2CH_3)	226.04 (d, 34), 225.37 (br)
2f	83.95 (d, 48)	Pr^i	23.90 (d, 44, CH), 17.56 (d, 2, CH_3)	$P(OPh)_3$	151.83 (d, 8, C^1), 129.40 (C^3, C^5), 124.21 (C^4), 121.6 (d, 4, C^2, C^6)	224.97 (br)
3a	80.78 (d, 46)	Cy	33.61 (d, 43, C^1), 27.81 (C^3, C^5), 27.27 (d, 11, C^2, C^6), 25.84 (C^4)	$2P(OMe)_3$	51.87 (d, 3) and 51.23 (d, 3) ($2OCH_3$)	228.86 (d, 34), 225.78 (d, 31)
3b	79.19 (d, 40)	Pr^i	23.44 (d, 44, CH), 17.53 (d, 2, CH_3)	$2P(OEt)_3$	60.34 (d, 3) and 50.0 (2 OCH_2), 16.41 and 16.3 (2 OCH_2CH_3)	228.60 (d, 34), 226.41 (d, 32)
4a	85.51 (d, 58)	Cy	33.65 (d, 43, C^1), 27.61 (C^3, C^5), 26.93 (d, 11, C^2, C^6), 25.69 (C^4)	dppm	48.85 (dd, 20 and 11, PCH_2P), 138.63 (d, 35, br, 4 C^1 (C_6H_5)), 131.76, 128.86, 128.53, 128.41, and 127.76 (4 (C^2–C^6) (C_6H_5)	228 (vbr)
4b	84.96 (d, 46)	Pr^i	24.09 (d, 44, CH), 17.74 (d, 2, CH_3)	dppm	48.62 (dd, 19 and 14, PCH_2P), 138.62 (d, br, 35, 4 C^1 (C_6H_5)), 131.73, 129.22, 128.20, 128.09, 127.91, and 127.79 (4 (C^2–C^6) (C_6H_5))	231 (vbr)
5	215.10 (d, 44)	Cy	33.22 (d, 38, C^1), 27.04 (d, 11, C^2, C^6), 26.77 (C^3, C^5), 25.52 (C^4)			226.3, 222.6, 218.63

[a] In $CDCl_3$ solutions, chemical shifts in δ (ppm) from TMS. Multiplicity: d = doublet, dd = doublet of doublets. $J(PC)$, in Hz, given in parentheses. [b] Not observed due to the low solubility of compound **1a**.

are given in Table II, atomic coordinates in Table VI, and selected bond distances and angles in Table VII. A perspective view of the molecule is shown in Figure 2. In the structure of **4a**, the geometry of the Mn_2S_2C core is virtually the same as that found in the parent compound **1a**, and both structures will be compared below in more

Table VI. Atomic Coordinates (×10⁴) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4a) (Mn, S, and P ×10⁵)

	x	*y*	*z*
Mn(1)	27863 (2)	37421 (2)	50982 (3)
Mn(2)	17584 (2)	20174 (2)	39028 (3)
P(1)	40522 (4)	29370 (6)	52379 (5)
P(2)	28146 (4)	15563 (4)	52029 (5)
P	4377 (3)	30043 (4)	17573 (5)
S(1)	23650 (3)	27337 (4)	29068 (5)
S(2)	13719 (3)	37502 (4)	47049 (5)
C	1269 (1)	2937 (2)	3023 (2)
C(2)	690 (1)	2055 (2)	217 (2)
C(3)	343 (2)	1032 (2)	−211 (2)
C(4)	632 (2)	270 (2)	−1399 (3)
C(5)	362 (2)	578 (2)	−2537 (2)
C(6)	716 (2)	1600 (2)	−2086 (2)
C(7)	404 (2)	2385 (2)	−884 (2)
C(8)	−565 (1)	2692 (2)	1855 (2)
C(9)	−751 (2)	3177 (2)	3230 (2)
C(10)	−1542 (2)	2682 (2)	3170 (3)
C(11)	−2308 (2)	2790 (3)	2144 (3)
C(12)	−2146 (2)	2466 (3)	771 (3)
C(13)	−1343 (1)	2914 (2)	870 (2)
C(14)	391 (1)	4250 (2)	1803 (2)
C(15)	36 (2)	5048 (2)	2886 (2)
C(16)	19 (2)	6075 (2)	2810 (2)
C(17)	896 (2)	6335 (2)	2876 (3)
C(18)	1237 (2)	5552 (2)	1795 (3)
C(19)	1269 (1)	4521 (2)	1850 (3)
C(20)	3897 (1)	1695 (2)	5101 (2)
C(21)	2787 (1)	210 (2)	4810 (2)
C(22)	3224 (2)	−571 (2)	3923 (3)
C(23)	3121 (2)	−1535 (2)	3633 (3)
C(24)	2598 (2)	−1851 (2)	4055 (3)
C(25)	2148 (2)	−1145 (2)	4821 (4)
C(26)	2230 (2)	−134 (2)	5208 (3)
C(27)	2904 (1)	2106 (2)	6959 (2)
C(28)	2365 (2)	2869 (2)	7511 (2)
C(29)	2423 (2)	3278 (2)	8836 (2)
C(30)	3042 (2)	2879 (3)	9589 (3)
C(31)	3581 (2)	2116 (2)	9060 (2)
C(32)	3501 (2)	1760 (2)	7779 (3)
C(33)	4904 (1)	3471 (2)	6660 (2)
C(34)	5554 (2)	3965 (2)	6648 (3)
C(35)	6189 (2)	4410 (2)	7780 (3)
C(36)	6189 (2)	4404 (2)	8892 (3)
C(37)	5555 (2)	3892 (2)	8897 (3)
C(38)	4914 (2)	3434 (2)	7821 (2)
C(39)	4595 (1)	2649 (2)	3974 (2)
C(40)	4461 (2)	3191 (2)	3260 (3)
C(41)	4885 (2)	2984 (3)	2255 (3)
C(42)	5466 (2)	2301 (3)	2012 (3)
C(43)	5662 (2)	1645 (4)	2750 (4)
C(44)	5238 (2)	1847 (3)	3734 (3)
O(46)	1673 (1)	−7 (1)	1809 (2)
O(45)	426 (1)	1534 (1)	4761 (2)
O(47)	3077 (1)	4863 (2)	7925 (2)
O(48)	3271 (2)	5509 (2)	5011 (2)
C(45)	984 (1)	1730 (2)	4438 (2)
C(46)	1709 (1)	778 (2)	2634 (2)
C(47)	2960 (2)	4390 (2)	6829 (2)
C(48)	3113 (2)	4837 (2)	5089 (2)
CL(1)	4259 (1)	−676 (1)	11359 (1)
CL(2)	3094 (1)	79 (1)	9647 (2)
C(60)	3625 (4)	278 (5)	11145 (6)

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4a)

Coordination around Mn Atoms			
Mn(1)–Mn(2)	2.855 (1)	C(46)–Mn(2)	1.787 (2)
P(2)–Mn(2)	2.224 (1)	S(2)–Mn(1)	2.232 (1)
S(2)–Mn(2)	2.379 (1)	S(1)–Mn(1)	2.309 (1)
S(1)–Mn(2)	2.378 (1)	P(1)–Mn(1)	2.242 (1)
C–Mn(2)	2.026 (3)	C(47)–Mn(1)	1.798 (2)
C(45)–Mn(2)	1.752 (3)	C(48)–Mn(1)	1.800 (3)
P(2)–Mn(2)–Mn(1)	80.4 (1)	C(46)–Mn(2)–S(1)	95.5 (1)
S(2)–Mn(2)–Mn(1)	49.5 (1)	C(46)–Mn(2)–C	105.9 (1)
S(2)–Mn(2)–P(2)	116.4 (1)	C(46)–Mn(2)–C(45)	90.1 (1)
S(1)–Mn(2)–Mn(1)	51.4 (1)	S(2)–Mn(1)–Mn(2)	54.1 (1)
S(1)–Mn(2)–P(2)	107.9 (1)	S(1)–Mn(1)–Mn(2)	53.6 (1)
S(1)–Mn(2)–S(2)	72.4 (1)	S(1)–Mn(1)–S(2)	76.4 (1)
C–Mn(2)–Mn(1)	71.0 (1)	P(1)–Mn(1)–Mn(2)	97.1 (1)
C–Mn(2)–P(2)	150.6 (1)	P(1)–Mn(1)–S(2)	150.6 (1)
C–Mn(2)–S(2)	47.2 (1)	P(1)–Mn(1)–S(1)	91.3 (1)
C–Mn(2)–S(1)	47.8 (1)	C(47)–Mn(1)–Mn(2)	115.0 (1)
C(45)–Mn(2)–Mn(1)	129.5 (1)	C(47)–Mn(1)–S(2)	95.2 (1)
C(45)–Mn(2)–P(2)	92.4 (1)	C(47)–Mn(1)–S(1)	168.4 (1)
C(45)–Mn(2)–S(2)	93.2 (1)	C(47)–Mn(1)–P(1)	92.5 (1)
C(45)–Mn(2)–S(1)	158.7 (1)	C(48)–Mn(1)–Mn(2)	150.5 (1)
C(45)–Mn(2)–C	110.9 (1)	C(48)–Mn(1)–S(2)	110.0 (1)
C(46)–Mn(2)–Mn(1)	139.5 (1)	C(48)–Mn(1)–S(1)	101.1 (1)
C(46)–Mn(2)–P(2)	91.2 (1)	C(48)–Mn(1)–P(1)	98.5 (1)
C(46)–Mn(2)–S(2)	152.0 (1)	C(48)–Mn(1)–C(47)	89.2 (1)
Phosphoniodithiocarboxylato ligand			
C–P	1.752 (2)	C(14)–P	1.826 (3)
C(2)–P	1.866 (2)	C–S(2)	1.793 (2)
C(8)–P	1.823 (3)	C–S(1)	1.813 (2)
C(2)–P–C	106.8 (1)	Mn(1)–S(1)–Mn(2)	75.1 (1)
C(8)–P–C	110.4 (1)	C–S(1)–Mn(2)	55.9 (1)
C(8)–P–C(2)	108.8 (1)	C–S(1)–Mn(1)	89.2 (1)
C(14)–P–C	109.5 (1)	S(1)–C–P	121.7 (1)
C(14)–P–C(2)	109.3 (1)	S(1)–C–S(2)	102.3 (1)
C(14)–P–C(8)	111.9 (1)	P–C–Mn(2)	140.7 (1)
Mn(1)–S(2)–Mn(2)	76.5 (1)	S(2)–C–Mn(2)	76.8 (1)
C–S(2)–Mn(2)	56.0 (1)	S(2)–C–P	124.9 (1)
C–S(2)–Mn(1)	92.2 (1)	S(1)–C–Mn(2)	76.3 (1)
Carbonyl Ligands			
C(46)–O(46)	1.141 (2)	C(47)–O(47)	1.146 (3)
C(45)–O(45)	1.203 (4)	C(48)–O(48)	1.119 (4)
O(47)–C(47)–Mn(1)	175.2 (3)	O(45)–C(45)–Mn(2)	177.2 (2)
O(48)–C(48)–Mn(1)	175.2 (2)	O(46)–C(46)–Mn(2)	178.9 (3)

detail. Since **4a** is obtained in 60% yield by heating **1a** with dppm in refluxing xylene (ca. 140 °C) for 30 h, the maintenance of the 8e bridge in **4a** is good proof of the remarkable thermal stability of this bonding mode of the S_2CPR_3 ligand.

In contrast, the stability of the 8e bridge appears to be rather sensitive to other factors such as the electronic density in the metallic centers or the separation between them. Several attempts to cleave the Mn–Mn bond in compound **1a** with halogens led also to the cleavage of the bridge. Thus, treatment of **1a** with bromine or iodine produced mixtures from which the mononuclear Mn(I) compounds *fac*-$[Mn(CO)_3(S_2CPCy_3)(X)]$ [X = Br (**6a**) or I (**6b**)] were isolated in low yields (25–35%) as the only stable products. When the reaction with halogen was made in the presence of 1 equiv of S_2CPCy_3 (reaction viii, Scheme I), the same mononuclear tricarbonyls **6a** (X = Br) or **6b** (X = I), were obtained in good yield (64 and 72%, respectively). Complexes **6a**,**b** were easily identified by comparing their analytical and spectroscopic data with those known for the bromo derivative **6a**, previously prepared by other methods.[11] It seems that the longer metal–metal distance induced by the cleavage of the Mn–Mn bond is not appropriate to maintain the η^2-(*S*,*S*′), η^3-(*S*,*C*,*S*′) interaction between the S_2C group and the two Mn atoms, and the dinuclear molecule is unsymmetrically broken, giving *fac*-$[Mn(CO)_3(S_2CPCy_3)(X)]$ together with the unstable fragment "$Mn(CO)_3(X)$", which is able to coordinate S_2CPCy_3 as a chelating ligand to form a second molecule of the final product. IR monitoring of reaction viii in the carbonyl stretching region, shows that **1a** is converted instantaneously into **6a** (or **6b**) upon addition of the halogen, indicating that the possible binuclear Mn(I) intermediate (with the S_2CPCy_3 bridge, but no Mn–Mn bond), if formed, must be rather unstable and short-lived to be detected.

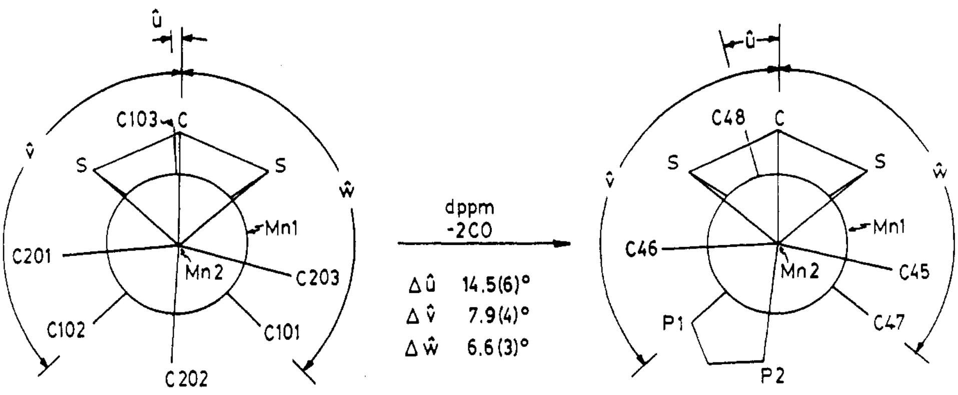

Figure 3. Schematic view of molecules of **1a** and **4a**, projected in a plane perpendicular to the Mn(1)-Mn(2) bond. *û*, *v̂*, and *ŵ* are the torsion angles defined as follows: molecule of **1a** *û* = C(103)-Mn(1)-Mn(2)-C, *v̂* = C(102)-Mn(1)-Mn(2)-C, *ŵ* = C(101)-Mn(1)-Mn(2)-C; molecule of **4a** *û* = C(48)-Mn(1)-Mn(2)-C, *v̂* = P(1)-Mn(1)-Mn(2)-C, *ŵ* = C(47)-Mn(1)-Mn(2)-C. Δ*û*, Δ*v̂*, and Δ*ŵ* are taken as absolute values (i.e. Δ*û* = ||*û*(**1a**)| − |*û*(**4a**)||, etc.). $\sigma(\Delta\hat{u})$ has been estimated as $\sigma(\Delta\hat{u}) = \{\sigma^2[\hat{u}(\mathbf{1a})] + \sigma^2[\hat{u}(\mathbf{4a})]\}^{1/2}$. $\sigma(\Delta\hat{v})$ amd $\sigma(\Delta\hat{w})$ have been estimated in a similar way.

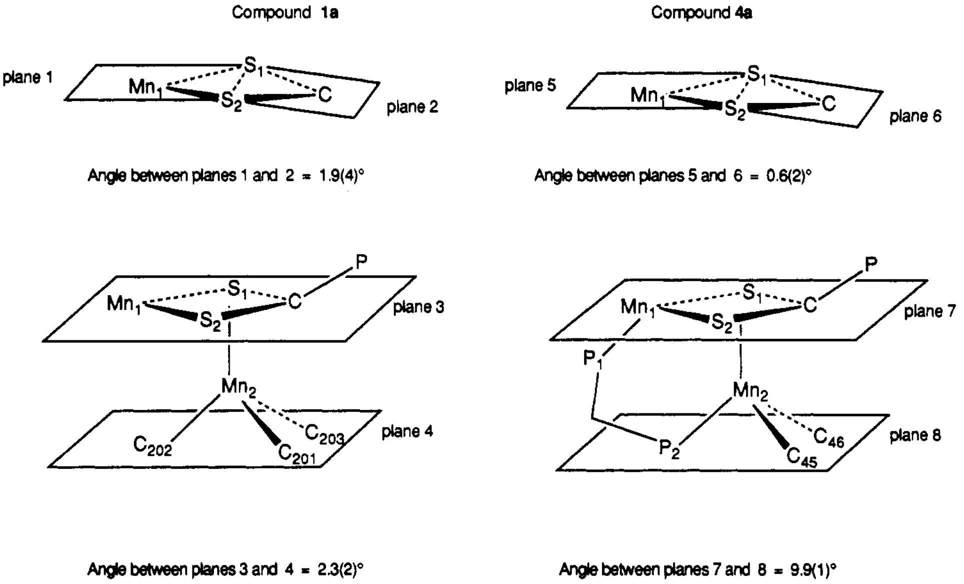

Figure 4. Dihedral angles between least-squares planes in **1a** and **4a**, showing the coordination of the Mn(1)-S(1)-C-S(2) ring to Mn(2).

Since complexes **1a,b** are obtained from $Mn_2(CO)_{10}$ by substitution of four CO groups in refluxing toluene (ca. 110 °C), several attempts were made to study the reaction between $Mn_2(CO)_{10}$ and S_2CPCy_3 at lower temperatures, searching for the existence of less substituted products that could be intermediates in the formation of the 8e S_2CPR_3 bridge. Thus, when the reaction was carried out in refluxing THF/CS_2 (10:1), the IR spectra of the reaction mixture in the ν(CO) region showed the slow disappearance of the bands of $Mn_2(CO)_{10}$ and the simultaneous formation of **1a**. No other bands were detected that could be assigned to an intermediate (less substituted than **1a**) compound. The use of lower temperatures (refluxing CH_2Cl_2/CS_2) only lowered the speed of the conversion from $Mn_2(CO)_{10}$ to **1a**.

On the other hand, $Mn_2(CO)_{10}$ reacts at room temperature with S_2CPCy_3 and Me_3NO (reaction viii in Scheme I) to give the purple-red compound $[Mn_2(CO)_9(S_2CPCy_3)]$ (**5**), which was characterized by analytical and spectroscopic methods. The $^{31}P\{^1H\}$ NMR signal for the P atom on **5** appears as a sharp singlet at δ 28.4 ppm, and the central carbon of the S_2CPCy_3 ligand appears, in the $^{13}C\{^1H\}$ NMR spectrum, as a doublet at δ 215.10 ppm (J(PC) = 44 Hz), both signals being in the regions expected for a monodentate or chelate S_2CPCy_3 group. On the other hand, the IR spectrum of **5** shows five ν(CO) absorptions, in a pattern consistent with its formulation as a dimanganese nonacarbonyl complex with the substituent in the axial position (effective symmetry C_{4v}), as depicted in Scheme I. The isomer bearing the S_2CPCy_3 ligand in the equatorial position (effective symmetry C_s) would display a more complex spectrum (nine ν(CO) bands). As a confirmation, both the pattern and the positions of the ν(CO) bands of **5** are very similar to those found in analogous complexes such as $[Mn_2(CO)_9(SC(NMe_2)_2)]$.[29]

Heating compound **5** in toluene/CS_2 (10:1) produced only minor amounts of **1a** (ca. 10%), together with mixtures of yellow products containing direct Mn-P bonds ($^{31}P\{^1H\}$ NMR signals at $\delta > 60$ ppm) which were not isolated. Nonacarbonyl **5**, therefore, can not be considered as an intermediate in the formation of the hexacarbonyl **1a**, since the direct reaction of $Mn_2(CO)_{10}$ and S_2CPCy_3 produces **1a** in much better yield.

X-ray Structures of $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (1a) and $[Mn_2(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4a). The main features concerning the geometry of the bridging S_2CPCy_3 ligand in **1a** have been described above, and it has also been pointed out that the distances and angles within the

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[29] Carriedo, C.; Sanchez, M. V.; Carriedo, G. A.; Riera, V.; Solans, X.; Valin, M. L. *J. Organomet. Chem.* **1987**, *331*, 53.

Mn_2S_2C core are not very much changed in the dppm derivative **4a**. However, the substitution of two CO groups by the bridging diphosphine leads to significant changes in the relative orientation of the coordination spheres of the manganese atoms. Thus, the molecular geometry of **1a** can be approximated to C_s, the atoms directly bonded to the metals being positioned in a fairly symmetrical arrangement on both sides of the plane defined by Mn(1), Mn(2), C, and P (see Figure 3). When the structure of **4a** is compared with that of **1a**, it can be noticed that the orientation of the substituents on Mn(2) relative to the S_2CPR_3 bridge remains unaltered, while the three substituents on Mn(1) have been rotated to permit the formation of the dppm bridge. This rotation, however, does not apply equally to the three substituents on Mn(1), as can be observed in Figure 3.

It has been pointed out above that the S_2CPCy_3 in compound **1a** can be considered as acting like a chelating η^2-(S,S') ligand toward Mn(1) and as a η^3-(S,C,S') pseudoallylic ligand toward Mn(2), and the same can be said for the derivative **4a** and all the other complexes from **1b** to **4b**. However, a detailed inspection of the X-ray structures of **1a** and **4a** suggests another way to consider the bonding within these molecules. Calculations of several least-squares planes in the structure of **1a**, which have been summarized in Figure 4, revealed some interesting features. On one hand, the $\overline{\mathrm{Mn(1)-S(1)-C-S(2)}}$ ring is very close to planarity (see Figure 4), the larger deviation from the weighted mean plane affecting to the C atom (at 0.033 Å). On the other hand, the dihedral angle between the planes defined by the ring $\overline{\mathrm{Mn(1)-S(1)-C-S(2)}}$ (plane 3) and the three carbon atoms of the carbonyl groups attached to Mn(2), [C(201), C(202), and C(203), plane 4] gives a very small value, 2.3 (2)°, planes 3 and 4 thus being nearly parallel. If we make the reasonable assumption that the 8e S_2CPCy_3 ligand donates 4 e to Mn(1), to which it is bonded as a η^2-(S,S') chelate, then it has to donate the remaining 4 e to Mn(2), and this atom would receive a total donation of 5 e from the ring. From the point of view of the atom Mn(2), the whole molecule could be regarded as a pseudo-cymantrene in which the cyclopentadienyl is replaced by a nearly planar, four-membered manganadithiabutene ring donating (formally) 5 e. Some other parameters hold well the comparison with those of cymantrene and related heterosubstituted cymantrene-like molecules. Thus, the distance from Mn(2) to the ring plane 3 (1.853 (1) Å) compares well with the corresponding distances found in cymantrene (1.80 Å) and in the derivative with a phosphole ring {[η^5-$PC_4H(CH_3)_2(COC_6H_5)$]-$Mn(CO)_3$} (1.757 (1) Å),[30] especially when it is taken into account that in the $\overline{\mathrm{Mn(1)-S(1)-C-S(2)}}$ ring, three out of the four atoms are considerably heavier than carbon and the bond distances from those atoms to Mn(2) should be longer than in cymantrene or related compounds. Consistently, the distance Mn(2)–C [2.023 (7) Å] is even shorter than the average Mn–C(ring) distance found in cymantrene or in the derivative with the phosphole ring [respectively, 2.165 (25) and 2.169 (4) Å].[30] Although distorted by the coordination of the dppm bridge, similar features are found again in the structure of **4a**, as can be seen in Figure 4.

This analysis of the structures of **1a** and **4a** could be pursued even further. Thus, the $(CO)_3Mn(1)$ moiety could be regarded in **1a** as being bonded to an S(1)–Mn(2)–S(2) grouping analogous to a pseudoallylic system which would donate 5 e [2 e from each S plus 1 e from Mn(2)].[31]

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Supplementary Material Available: Figure 5 and discussion as mentioned in ref 31 and tables of anisotropic thermal parameters, bond distances and angles, atomic coordinates for hydrogen atoms, torsion angles, and least-squares planes for both structures (22 pages); listings of observed and calculated structure factor amplitudes for both complexes (44 pages). Ordering information is given on any current masthead page.

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(30) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 2129.

(31) A schematic view of both molecules, together with the pertinent data, has been included in the supplementary material.