New Bonding Mode of Tricyclohexylphosphoniodithiocarboxylate (S_2CPCy_3) as an Eight-electron Donor. Synthesis, Reactivity, and *X*-Ray Crystal Structure of [$Mn_2(CO)_6(S_2CPCy_3)$]

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The reaction of $Mn_2(CO)_{10}$ with the tricyclohexylphosphine–carbon disulphide adduct S_2CPCy_3 in refluxing toluene affords the dinuclear complex [$Mn_2(CO)_6(S_2CPCy_3)$] (1) in good yield, the structure of which, determined by *X*-ray crystallography, shows a new mode of co-ordination of the S_2CPCy_3 ligand which is bonded to an Mn atom by two sulphur atoms and to the other Mn atom by two sulphur and one carbon atom donating 8 electrons; thermal reactions of (1) with neutral monodentate ligands L yield [$Mn_2(CO)_5(S_2CPCy_3)(L)$] *via* CO displacement.

Many transition metal complexes have been synthesised recently with the trialkylphosphine–carbon disulphide adducts S_2CPR_3 as ligands.[1—4] In these complexes the phosphoniodithiocarboxylato ligand may be co-ordinated in various ways (Figure 1), the chelate η^2,4e (b)[1] and monodentate σ,2e (a)[2,3] forms being the most common; there are only a few examples of bridging forms η^2,4e (c),[4] and only one of the unsymmetrically bridged η^3,σ,6e form (d).[2] Herein we report a new co-ordination mode (e) for the adduct S_2CPCy_3 as an unsymmetrical η^2,η^3 bridging ligand donating 8 electrons (Cy = cyclohexyl).

$Mn_2(CO)_{10}$ reacts with S_2CPCy_3 in refluxing toluene affording red crystals of [$Mn_2(CO)_6(S_2CPCy_3)$] (**1**) in good yield. The i.r. spectrum† of (**1**) in tetrahydrofuran (THF) shows five bands in the ν(CO) region at 2022s, 1980vs, 1928s, 1918s, and 1900m cm^{-1} and the $^{31}P\{^1H\}$ n.m.r. spectrum (in CD_2Cl_2) exhibits only one sharp peak at δ 30.9 p.p.m. The analytical data are in agreement with the formulation as a dimanganese hexacarbonyl complex with only one S_2CPCy_3 ligand. An *X*-ray diffraction study‡ of (**1**) established the structure shown in Figure 2. The molecule consists of a $Mn_2(CO)_6$ unit bridged by an S_2CPCy_3 ligand. The Mn(1)–Mn(2) distance of 2.737(1) Å is shorter than the Mn–Mn distance in $Mn_2(CO)_{10}$ [2.923(3) Å],[5] and falls well in the range (2.50—3.23 Å)[6] of Mn–Mn distances in compounds with an assumed bond order of 1. Distances between the core

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† Selected spectroscopic data, [$^{31}P\{^1H\}$ chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4 (external); coupling constants in Hz]. Compound (**1**), ν(CO) (THF) 2022s, 1980vs, 1928s, 1918s, and 1900m cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 30.9 (s, P–CS_2). (**2a**), ν(CO) (CH_2Cl_2) 1992vs, 1933s, 1889m, and 1869w cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 186.8 (br., P–O) and 30.16 (s, P–CS_2). (**2b**), ν(CO) (CH_2Cl_2) 1995vs, 1943s, 1902m, and 1875w (sh) cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 186.8 (br., P–O) and 29.99 (s, P–CS_2). (**2c**), ν(CO) (CH_2Cl_2) 1985s, 1912vs, 1908(sh), and 1835w cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 59.19 (br., PEt_3) and 29.64 (d, P–CS_2, $^4J_{PP}$ 4.9). (**2d**), ν(CO) (CH_2Cl_2) 1985s, 1928vs, 1900m, and 1861w; ν(CN) 2114w cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 30.12 (s, P–CS_2). (**3**), ν(CO) (CH_2Cl_2) 1923w, 1898vs, and 1841m cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 60.88—59.46 (m, br., dppm) and 29.92 (br, m, P–CS_2). (**4a**), ν(CO) (CH_2Cl_2) 2024vs, 1939vs, and 1917vs cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 20.10 (s, P–CS_2). (**4b**), ν(CO) (CH_2Cl_2) 2028vs, 1934vs, and 1917vs cm^{-1}; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 20.35 (s, P–CS_2).

‡ *Crystal data*, compound (**1**): $C_{25}H_{33}Mn_2O_6PS_2$, M = 634.5 triclinic space group, $P\bar{1}$, a = 11.652(4), b = 11.368(4), c = 10.973(3) Å, α = 85.76(2), β = 77.29(2), γ = 86.00(2)°, U = 1412(1) Å^3, D_c = 1.492 g cm^{-3}, Z = 2, $F(000)$ = 656, λ(Mo-K_α) = 0.71069 Å, graphite monochromator, μ(Mo-K_α) = 11.75 cm^{-1}, room temperature. Red tabular crystal (0.15 × 0.15 × 0.10 mm). Intensities were collected on a Phillips PW-1000 four-circle diffractometer using the ω-scan technique, with scan width 1° and scan speed 0.03° s^{-1}, 3621 independent reflections were measured in the range $2 \leqslant \theta \leqslant 25°$; 3492 with $I \geqslant 2.5\sigma(I)$ were assumed observed. Lorentz-polarization but not absorption corrections were applied. Mn atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms by DIRDIF.[9] The structure was refined by full-matrix least-squares using SHELX-76.[10] The position of H-atoms was computed and refined with an overall isotropic thermal parameter; the remaining atoms were refined anisotropically. The final R was 0.061 (R_w 0.064). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

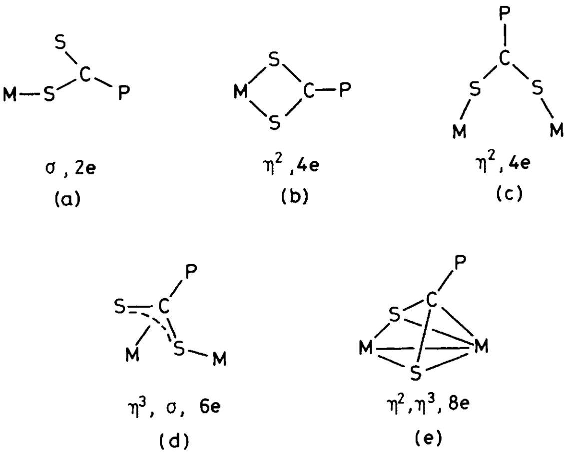


Figure 1. Co-ordination modes of S_2CPR_3 adducts.

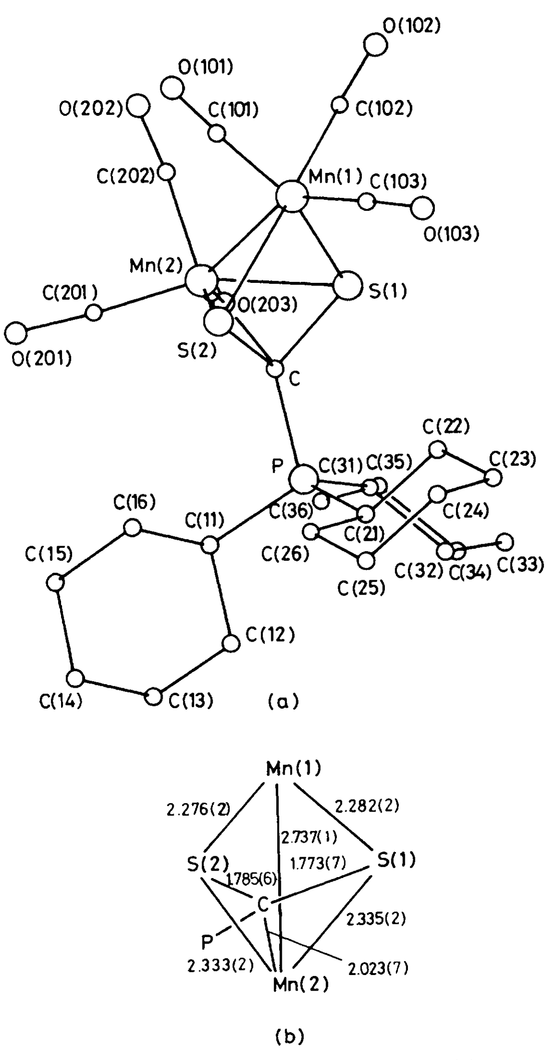
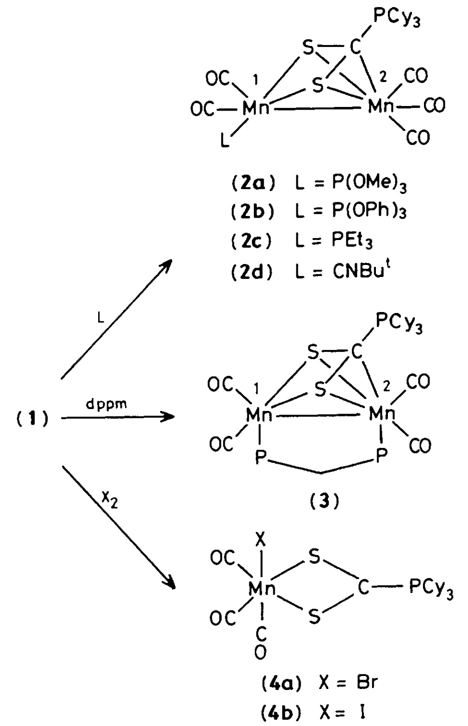


Figure 2. (a) Structure of (**1**) and the numbering system. (b) Schematic drawing of the core atoms with some relevant distances. Other distances (Å) and angles (°) are: C–P 1.787(7), Mn(1)–C(101) 1.820(9), Mn(1)–C(102) 1.818(7), Mn(1)–C(103) 1.773(9), Mn(2)–C(201) 1.816(8), Mn(2)–C(202) 1.800(8), Mn(2)–C(203) 1.798(9); S(2)–C–S(1) 103.7(3), S(1)–Mn(1)–S(2) 75.7(1), S(2)–Mn(2)–S(1) 73.6(1), S(2)–Mn(2)–C 47.7(2), S(1)–Mn(2)–C 47.3(2), P–C–Mn(2) 139.6(4), P–C–S(1) 126.2(4), P–C–S(2) 121.4(4).



Scheme 1

atoms are shown in Figure 2(b). The whole core is fairly symmetrical with respect to the plane defined by Mn(1), C, and Mn(2), whereas both sulphur atoms are closer to Mn(1) than to Mn(2) while the central carbon atom of the CS_2 group is within bonding distance to Mn(2) [2.023(7) Å] and much further away from Mn(1) (2.906 Å). In this way, the S_2CPCy_3 adduct can be regarded as acting like a chelating η^2-(S,S) ligand towards Mn(1) and like a pseudo π-allylic η^3-(S,C,S) ligand towards Mn(2). It is remarkable that the Mn(1)–S average lengths (2.279 Å) are shorter than those found in previously known manganese complexes containing dithiocarbamates acting as η^2-(S,S) chelate ligands, 2.37—2.38 Å in $[Mn(CO)_3(PPh_3)(S_2CNMe_2)]$,[7] and even the longer S–Mn(2) distances [average 2.334(2), Å] are slightly shorter than the range found in the dithiocarbamate complex. The C–Mn(2) distance of 2.023(7) Å is significantly shorter than the distance between the central carbon and the manganese atom [2.114(15) Å] in the π-allyl complex $[Mn(\eta^3\text{-}C_3H_5)(CO)_2\text{-}P(OMe)_3 2]$.[8] All these facts point to the existence of a very strong interaction between the S_2CPCy_3 ligand and the $Mn_2(CO)_6$ unit in compound (**1**) which accounts reasonably well for its thermal and chemical stability.

When compound (**1**) is heated in toluene or chloroform with a neutral ligand L, substitution of one carbonyl group occurs, affording stable crystalline compounds which can be formulated as $[Mn_2(CO)_5(S_2CPCy_3)(L)]$ [L = $P(OMe)_3$ (**2a**), $P(OPh)_3$ (**2b**), PEt_3 (**2c**), or CNBuᵗ (**2d**)] on the basis of analytical and spectroscopic data (Scheme 1). The $^{31}P\{^1H\}$ n.m.r. spectra of compounds (**2a**—**d**) show the signal for the P atom of the S_2CPCy_3 ligand in the range 29.64—30.96 p.p.m., very close to the chemical shift of the P atom in the parent compound (**1**) (30.90 p.p.m.). This suggests that the chemical and electronic environment within the S_2CPCy_3 ligand is not changed very much on going from (**1**) to the carbonyl substituted complexes (**2a**—**d**) and supports the structures in Scheme 1. The low values of the P–P coupling constants (when appreciable) in compounds (**2a**—**c**) suggest that the entering ligand L becomes attached to the Mn(1) atom, thus giving four-bond P–P coupling, rather than to Mn(2) which would produce larger three-bond coupling constants.

Treatment of (**1**) with dppm ($Ph_2PCH_2PPh_2$) in refluxing xylene gave compound (**3**), formulated as $[Mn_2(CO)_4(S_2CPCy_3)(dppm)]$ on the basis of analytical and spectroscopic data. Again the $^{31}P\{^1H\}$ n.m.r. spectrum of (**3**) shows a signal for the P atom of S_2CPCy_3 with a chemical shift of δ 29.92 p.p.m. suggesting that the co-ordination in the adduct is not appreciably altered.

Attempted oxidation with elemental halogens led to cleavage of the dimetallic unit, yielding *fac*-$[Mn(CO)_3(S_2CPCy_3)X]$ [X = Br (**4a**), I (**4b**)]. The i.r. spectra for these compounds show three bands in the ν(CO) region with a typical pattern for *fac*-tricarbonyl grouping in mononuclear complexes. The analytical data are in accordance with the proposed stoicheiometry. The $^{31}P\{^1H\}$ n.m.r. spectra of these compounds display only one sharp singlet [(**4a**), δ 20.10 p.p.m.; (**4b**), δ 20.35 p.p.m.] for the P atom of the S_2CPCy_3 ligand. These chemical shifts are quite different from that of the parent compound (**1**) reflecting the drastic change of electron distribution due to the change in the co-ordination mode. The reactivity of (**1**) with other nucleophiles and with reducing agents is now being studied.

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References

1 C. Bianchini, A. Meli, and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4161; C. Bianchini, C. A. Ghilarrdi, A. Meli, and A. Orlandini, *ibid.*, 1983, **22**, 2188.
2 C. Bianchini, C. A. Ghilardi, A. Meli, S. Midolini, and A. Orlandini, *Organometallics*, 1982, **1**, 778.
3 R. Uson, J. Fornies, R. Navarro, M. A. Uson, M. P. García, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1984, 345.
4 C. Bianchini, C. A. Ghilardi, A. Meli, A. Orlandini, and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1983, 1969; H. Werner, *Coord. Chem. Rev.*, 1982, **43**, 165.
5 L. F. Dahl and R. F. Rundle, *Acta Crystallogr.*, 1963, **16**, 419.
6 I. Bernal, M. Creswick, and W. A. Herrmann, *Z. Naturforsch., Teil B.*, 1979, **34**, 1345.
7 W. K. Dean and J. W. Moncrief, *J. Coord. Chem.*, 1976, **6**, 107.
8 B. J. Brisdon, D. A. Edwards, J. W. White, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1980, 2129.
9 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. van der Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, and V. Parthasarathi, DIRDIF, An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors, Tech. Rep. 1981/2, Univ. of Nijmegen, The Netherlands, 1981.
10 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.