

# The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 6.\* The Reaction of Carbon Disulphide with Dihalophosphinemanganese(II) and Dihalophosphinebis(tetrahydrofuran)manganese(II) Complexes to Form Dimeric Carbon Disulphide-bridged Complexes $[\{Mn(PR_3)_2X_2\}_2CS_2]$ and $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$

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Received May 9, 1984

## Abstract

The  $Mn(PR_3)_2X_2$  and  $Mn(PR_3)_2X_2(THF)_2$  complexes ( $PR_3 = PPh_3$ ,  $PBu_3$ ,  $PPhMe_2$ ,  $PPhEt_2$ ,  $PPhPr_2$ ;  $X = Cl, Br, I$ ) react with carbon disulphide in diethylether to form the insoluble  $[\{Mn(PR_3)_2X_2\}_2CS_2]$  and  $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$  complexes. Electron paramagnetic and electronic spectra are consistent with pseudotetrahedral and pseudo-octahedral co-ordination geometries, respectively, for the carbon disulphide complexes. The infrared spectra are consistent with bridging  $CS_2$  ligands. The carbon disulphide moieties are bound strongly; heating  $[\{Mn(PR_3)_2X_2\}_2CS_2]$  *in vacuo* at 80 °C for long periods does not displace the  $CS_2$ . Heating  $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$  displaces the tetrahydrofuran and  $[\{Mn(PR_3)_2X_2\}_2CS_2]$  are formed. The  $CS_2$  ligands cannot be displaced by dioxygen, but dioxygen is displaced from  $[Mn(PR_3)_2X_2(O_2)]$  by carbon disulphide to form  $[\{Mn(PR_3)_2X_2\}_2CS_2]$ .

## Introduction

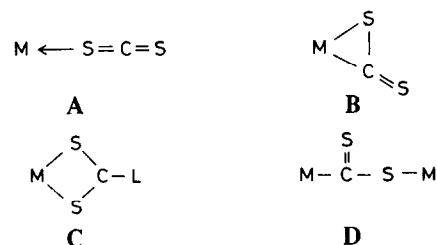
Carbon disulphide has been shown to form adducts with a large number of transition metal complexes and, in doing so, exhibits various types of bonding (A–D) [2, 3]. Relatively few examples of

one site with no change in the oxidation state of the metal. The characteristic  $\nu(S-C-S)$  vibration occurs in the region of  $1500\text{ cm}^{-1}$ , identical to that of liquid  $CS_2$ . An example of this is the  $Cr(AlCl_3)_2(CS_2)_2$ , which exhibits this band at  $1490\text{ cm}^{-1}$  [4]. The formation of  $\pi$ -bonded  $CS_2$  adducts, (B), generally involves either oxidative addition to the metal, or ligand replacement reactions in which some formally unsaturated ligand (e.g. a coordinated alkyne) is replaced by carbon disulphide. This mode of coordination is readily characterised by infrared bands in the  $955\text{--}1235\text{ cm}^{-1}$  and  $632\text{--}653\text{ cm}^{-1}$  regions, being assigned as non-ring  $\nu(C=S)$  and in-ring  $\nu(C-S)$  vibrations, respectively; an example of such a compound is  $Pt(PPh_3)_2(CS_2)$  [5–7]. Type (C) coordination occurs when carbon disulphide inserts into a variety of  $M-L$  bonds, and this reaction has been reviewed in detail by Butler and Fenster [2]. Finally, type (D) bonding has been reported for a number of systems, but no general infrared correlations have been made [3, 8, 9].

The affinity of  $Mn(PR_3)_2X_2$  complexes [10] for a range of small molecules has been demonstrated [11–13]. We here describe studies of the reaction of some  $Mn(PR_3)_2X_2$  complexes with carbon disulphide.

## Results and Discussion

The manganese complexes (where  $PR_3 = PPh_3$ ,  $PBu_3$ ,  $PPhMe_2$ ,  $PPhEt_2$ ,  $PPhPr_2$  and  $X = Cl, Br, I$ ) react with excess carbon disulphide ( $CS_2$ ) in solution to give insoluble solid products containing manganese and  $CS_2$  in the ratio 2:1 (Tables I and II). When tetrahydrofuran (THF) was used as solvent, the products also contained solvent molecules and had the formula  $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$  (Table II). Alternatively the solvento-complexes  $Mn(PR_3)_2X_2(THF)_2$  could be preformed and subsequently reacted with carbon disulphide to yield  $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$ .



$CS_2$  complexes in which the ligand is bound to the metal solely through a sulphur atom are known. These  $\sigma$ -bonded  $CS_2$  complexes, (A), coordinate at

\*See ref. [1].

TABLE I. Physical and Analytical Data for  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  Complexes.

Compound	Colour	$\mu_{\text{eff}}$	mp/ $^{\circ}\text{C}^{\text{a}}$	%C <sup>b</sup>	%H	%P	%S	%X	%Mn
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{Cl}_2\}_2\text{CS}_2]$	off-white	5.70	210	34.8(35.2)	6.0(6.5)	9.5 (9.6)	10.0 (9.9)	22.0(21.9)	17.7(16.9)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{Cl}_2\}_2\text{CS}_2]$	off-white	5.75	224	41.4(40.9)	7.2(7.4)	8.0 (8.5)	9.0 (8.7)	19.0(19.4)	15.4(15.0)
$[\{\text{Mn}(\text{PPhMe}_2)\text{Cl}_2\}_2\text{CS}_2]$	off-white	5.69	225	34.5(33.8)	4.0(3.6)	10.0(10.3)	11.0(10.6)	23.1(23.5)	17.4(18.2)
$[\{\text{Mn}(\text{PPhEt}_2)\text{Cl}_2\}_2\text{CS}_2]$	off-white	5.72	240	37.5(38.2)	4.2(4.0)	9.5 (9.4)	10.2 (9.7)	22.4(21.5)	16.2(16.7)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{Cl}_2\}_2\text{CS}_2]$	off-white	5.72	200	42.4(41.9)	5.5(5.3)	8.2 (8.7)	9.0 (8.9)	20.0(19.8)	14.9(15.4)
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	buff	5.84	188	28.0(27.6)	5.0(5.1)	7.0 (7.5)	8.0 (7.7)	39.5(38.7)	12.5(13.3)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	buff	5.85	190	33.5(32.9)	6.1(5.9)	7.0 (6.8)	7.0 (7.0)	34.5(35.1)	11.9(12.1)
$[\{\text{Mn}(\text{PPhMe}_2)\text{Br}_2\}_2\text{CS}_2]$	buff	5.80	210	26.5(26.1)	3.5(2.8)	7.4 (7.9)	8.5 (8.2)	41.5(40.9)	12.8(14.1)
$[\{\text{Mn}(\text{PPhEt}_2)\text{Br}_2\}_2\text{CS}_2]$	buff	5.88	238	28.9(30.1)	4.0(3.6)	7.0 (7.4)	8.0 (7.6)	39.5(38.2)	12.6(13.1)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	buff	5.84	222	34.0(33.6)	4.0(4.3)	7.0 (6.9)	7.8 (7.2)	36.2(35.8)	11.0(12.3)
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	brown	5.88	224	23.0(22.5)	4.5(4.1)	5.5 (6.1)	7.0(6.3)	50.6(50.1)	9.4(10.8)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	brown	5.92	186	28.0(27.3)	5.0(4.9)	5.7 (5.6)	6.0 (5.8)	45.5(46.3)	9.8(10.0)
$[\{\text{Mn}(\text{PPhMe}_2)\text{I}_2\}_2\text{CS}_2]$	brown	5.95	220	21.7(21.0)	2.5(2.3)	6.0 (6.4)	7.0 (6.6)	53.0(52.4)	10.0(11.3)
$[\{\text{Mn}(\text{PPhEt}_2)\text{I}_2\}_2\text{CS}_2]$	brown	5.90	170	25.0(24.6)	3.2(2.9)	5.5 (6.0)	6.8 (6.2)	50.8(49.5)	8.9(10.7)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	brown	5.88	194	28.0(27.7)	4.0(3.5)	5.2 (5.7)	6.0 (5.9)	46.0(47.0)	10.8(10.2)

<sup>a</sup>All compounds decompose. <sup>b</sup>Found (calculated).TABLE II. Physical and Analytical Data for  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  Complexes.

Compound	Colour	$\mu_{\text{eff}}$	mp/ $^{\circ}\text{C}^{\text{a}}$	%C <sup>b</sup>	%H	%P	%S	%X	%Mn
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{Cl}_2(\text{THF})_2\}_2\text{CS}_2]$	cream	5.69	210	41.0(40.9)	7.5(7.3)	8.0(7.8)	7.5(8.1)	17.4(17.9)	13.4(13.9)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{Cl}_2(\text{THF})_2\}_2\text{CS}_2]$	cream	5.69	224	44.7(45.2)	7.4(8.0)	6.5(7.1)	8.0(7.3)	15.8(16.2)	11.5(12.6)
$[\{\text{Mn}(\text{PPhMe}_2)\text{Cl}_2(\text{THF})_2\}_2\text{CS}_2]$	cream	5.72	225	41.0(40.1)	5.4(5.1)	7.9(8.3)	8.0(8.6)	20.0(19.0)	13.9(14.7)
$[\{\text{Mn}(\text{PPhEt}_2)\text{Cl}_2(\text{THF})_2\}_2\text{CS}_2]$	cream	5.70	240	40.0(43.3)	6.0(5.7)	8.0(7.7)	7.5(8.0)	18.2(17.7)	13.0(13.7)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{Cl}_2(\text{THF})_2\}_2\text{CS}_2]$	cream	5.72	200	47.1(46.0)	7.0(6.3)	6.9(7.2)	6.8(7.4)	17.0(16.5)	11.9(12.8)
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{Br}_2(\text{THF})_2\}_2\text{CS}_2]$	buff	5.88	188	34.0(33.4)	5.8(6.0)	6.0(6.4)	5.9(6.6)	32.9(32.9)	10.8(11.3)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{Br}_2(\text{THF})_2\}_2\text{CS}_2]$	buff	5.79	190	38.2(37.6)	7.1(6.6)	6.2(5.9)	5.5(6.1)	30.5(30.3)	9.9(10.4)
$[\{\text{Mn}(\text{PPhMe}_2)\text{Br}_2(\text{THF})_2\}_2\text{CS}_2]$	buff	5.82	210	33.0(32.4)	5.0(4.1)	6.6(6.7)	6.0(6.9)	35.2(34.5)	11.0(11.9)
$[\{\text{Mn}(\text{PPhEt}_2)\text{Br}_2(\text{THF})_2\}_2\text{CS}_2]$	buff	5.84	238	37.1(35.5)	4.0(4.7)	5.5(6.3)	7.0(6.5)	34.0(32.6)	10.4(11.2)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{Br}_2(\text{THF})_2\}_2\text{CS}_2]$	buff	5.80	222	39.0(38.2)	6.0(5.2)	5.5(6.0)	5.8(6.2)	31.5(30.8)	11.0(10.6)
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{I}_2(\text{THF})_2\}_2\text{CS}_2]$	brown	5.91	224	28.5(27.9)	4.7(5.0)	4.9(5.4)	4.9(5.5)	45.0(43.9)	8.9(9.5)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{I}_2(\text{THF})_2\}_2\text{CS}_2]$	brown	5.92	186	30.0(31.9)	6.0(5.6)	5.4(5.0)	4.8(5.2)	41.0(40.9)	7.8(8.9)
$[\{\text{Mn}(\text{PPhMe}_2)\text{I}_2(\text{THF})_2\}_2\text{CS}_2]$	brown	5.90	220	28.0(26.9)	3.0(3.4)	6.0(5.6)	5.5(5.7)	44.0(45.6)	9.0 (9.9)
$[\{\text{Mn}(\text{PPhEt}_2)\text{I}_2(\text{THF})_2\}_2\text{CS}_2]$	brown	5.95	170	30.9(29.7)	4.5(3.9)	5.0(5.3)	6.0(5.5)	42.9(43.4)	10.0 (9.4)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{I}_2(\text{THF})_2\}_2\text{CS}_2]$	brown	5.90	194	33.0(32.3)	4.0(4.4)	4.5(5.1)	5.9(5.2)	41.0(41.4)	9.9 (9.0)

<sup>a</sup>All compounds decompose. <sup>b</sup>Found (calculated).

The solid state electron paramagnetic resonance spectra of the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  complexes all exhibit bands in the region  $g_{\text{eff}} = 4$  and 2 consistent with high spin manganese(II) in a tetrahedral environment. This contrasts with the spectra of the THF-containing adducts which suggest octahedral geometry around the Mn, exhibiting bands at  $g_{\text{eff}} = 6$  and 2. All the spectra consist of only broad bands with no hyperfine coupling being observed. The EPR data for the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  complexes are

listed in Table III and the data for the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  adducts in Table IV.

The very low solubility of the complexes in the common organic solvents has prevented the recording of electron paramagnetic resonance, electronic or infrared spectra in solution, and this insolubility has also precluded the determination of molecular weights for any of the adducts.

The room temperature magnetic moments of the complexes are in the range 5.7–5.90 B.M. (Tables I

TABLE III. EPR data for  $\{[Mn(PR_3)_2X_2]_2CS_2\}$  Complexes.

Complex	Line Positions/G
$\{[Mn(PPr_3^n)Cl_2]_2CS_2\}$	1600(m), 3350(s), 4550(w)
$\{[Mn(PBu_3^n)Cl_2]_2CS_2\}$	1540(m), 3400(s), 4400(w)
$\{[Mn(PPhMe_2)Cl_2]_2CS_2\}$	1650(m), 3450(s), 4500(w)
$\{[Mn(PPhEt_2)Cl_2]_2CS_2\}$	1650(m), 3500(s), 4500(w)
$\{[Mn(PPhPr_2^n)Cl_2]_2CS_2\}$	1650(m), 3500(s), 4500(w)
$\{[Mn(PPr_3^n)Br_2]_2CS_2\}$	1500(m), 3300(s), 4400(w)
$\{[Mn(PBu_3^n)Br_2]_2CS_2\}$	1500(m), 3300(s), 4500(w)
$\{[Mn(PPhMe_2)Br_2]_2CS_2\}$	1550(w), 3300(s), 4400(w)
$\{[Mn(PPhEt_2)Br_2]_2CS_2\}$	1550(w), 3300(s), 4500(w)
$\{[Mn(PPhPr_2^n)Br_2]_2CS_2\}$	1600(w), 3400(s), 4400(w)
$\{[Mn(PPr_3^n)I_2]_2CS_2\}$	1600(w), 3310(s), 4450(w)
$\{[Mn(PBu_3^n)I_2]_2CS_2\}$	1600(w), 3340(s), 4500(w)
$\{[Mn(PPhMe_2)I_2]_2CS_2\}$	1650(w), 3300(s), 4400(w)
$\{[Mn(PPhEt_2)I_2]_2CS_2\}$	1650(m), 3300(s), 4400(w)
$\{[Mn(PPhPr_2^n)I_2]_2CS_2\}$	1650(m), 3320(s), 4400(w)

TABLE IV. EPR Data for  $\{[Mn(PR_3)_2X_2(THF)_2]_2CS_2\}$  Complexes.

Complex	Line Positions/G
$\{[Mn(PPr_3^n)Cl_2(THF)_2]_2CS_2\}$	900(w), 1500(w), 3400(s), 5400(w)
$\{[Mn(PBu_3^n)Cl_2(THF)_2]_2CS_2\}$	850(w), 1400(vw), 3400(s), 5500(w)
$\{[Mn(PPhMe_2)Cl_2(THF)_2]_2CS_2\}$	925(w), 1500(vw), 3400(s), 5500(w), 8000(w)
$\{[Mn(PPhEt_2)Cl_2(THF)_2]_2CS_2\}$	950(w), 1500(vw), 3400(s), 5400(w), 7900(w)
$\{[Mn(PPhPr_2^n)Cl_2(THF)_2]_2CS_2\}$	950(w), 1500(vw), 3400(s), 5500(w)
$\{[Mn(PPr_3^n)Br_2(THF)_2]_2CS_2\}$	1100(w), 1400(vw), 3300(s), 5350(w)
$\{[Mn(PBu_3^n)Br_2(THF)_2]_2CS_2\}$	1200(w), 1400(vw), 3300(s), 5400(w)
$\{[Mn(PPhMe_2)Br_2(THF)_2]_2CS_2\}$	1150(w), 1400(vw), 3300(s), 5400(w)
$\{[Mn(PPhEt_2)Br_2(THF)_2]_2CS_2\}$	1150(w), 1450(vw), 3300(s), 5350(w)
$\{[Mn(PPhPr_2^n)Br_2(THF)_2]_2CS_2\}$	1150(w), 1450(vw), 3300(s), 5350(w)
$\{[Mn(PPr_3^n)I_2(THF)_2]_2CS_2\}$	950(w), 1350(vw), 3350(s), 5350(w)
$\{[Mn(PBu_3^n)I_2(THF)_2]_2CS_2\}$	1000(w), 1350(w), 3300(s), 5400(w)
$\{[Mn(PPhMe_2)I_2(THF)_2]_2CS_2\}$	1050(w), 1350(w), 3350(s), 5400(w)
$\{[Mn(PPhEt_2)I_2(THF)_2]_2CS_2\}$	950(w), 1350(vw), 3300(s), 5350(w)
$\{[Mn(PPhPr_2^n)I_2(THF)_2]_2CS_2\}$	950(w), 1350(vw), 3300(s), 5350(w)

TABLE V. Infrared Data for  $\{[Mn(PR_3)_2X_2]_2CS_2\}$  Complexes ( $cm^{-1}$ ).<sup>a</sup>

Complex	$\nu(C=S)$	$\nu(C-S)$	$\nu(Mn-C)$	$\nu(Mn-S)$	$\nu(Mn-P)$	$\nu(Mn-X)$
$\{[Mn(PPr_3^n)Cl_2]_2CS_2\}$	1120(m,sh)	825(m)	590(mw)	330(w,br)	390(s,sh)	310(s,br)
$\{[Mn(PBu_3^n)Cl_2]_2CS_2\}$	1118(m,sh)	830(m,sh)	585(w)	330(m,br)	385(m,sh)	305(s,br)
$\{[Mn(PPhMe_2)Cl_2]_2CS_2\}$	1120(m,sh)	830(m)	590(w)	325(m,br)	390(m,sh)	310(s,br)
$\{[Mn(PPhEt_2)Cl_2]_2CS_2\}$	1122(m)	835(w,sh)	585(w,br)	325(m,br)	385(s,sh)	305(s,br)
$\{[Mn(PPhPr_2^n)Cl_2]_2CS_2\}$	1119(m,sh)	830(m)	585(mw,br)	325(m,br)	390(s,sh)	310(s,br)

(continued overleaf)

and II) and close to the spin-only value of 5.92 B.M. expected for a high-spin  $d^5$  system. These values are not inconsistent with the EPR data and clearly confirm the presence of manganese(II) in all the complexes. The slight lowering of the values can be attributed to some spin-pairing presumably brought about by bridging between two or more manganese centres.

The infrared spectra of the complexes were recorded as nujol mulls and are listed in Tables V and VI. All the complexes exhibit bands attributable to coordinated  $CS_2$  in the region *ca.* 1110  $cm^{-1}$ , 800–830  $cm^{-1}$ , 580  $cm^{-1}$  and 330  $cm^{-1}$ . In addition, the  $\{[Mn(PR_3)_2X_2(THF)_2]_2CS_2\}$  complexes have bands at *ca.* 1040  $cm^{-1}$  and 880  $cm^{-1}$  due to coordinated THF [14, 15] (Table VI). Bands which can be assigned to Mn–P and terminal Mn–X linkages can also be identified, and there is no evidence for bridging Mn–X–Mn linkages in any of the complexes studied [16].

The diffuse reflectance spectra of the  $\{[Mn(PR_3)_2X_2]_2CS_2\}$  complexes (Table VII) have been assigned

TABLE V. (continued)

Complex	$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{S})$	$\nu(\text{Mn}-\text{C})$	$\nu(\text{Mn}-\text{S})$	$\nu(\text{Mn}-\text{P})$	$\nu(\text{Mn}-\text{X})$
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	1105(m)	790(m,sh)	574(m,br)	331(m,br)	380(s,sh)	230(s,br)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	1108(m,sh)	794(w,sh)	575(m,sh)	335(w,br)	380(s)	228(s,br)
$[\{\text{Mn}(\text{PPhMe}_2)\text{Br}_2\}_2\text{CS}_2]$	1110(mw,sh)	800(m)	580(mw)	328(m)	385(s,sh)	228(s,br)
$[\{\text{Mn}(\text{PPhEt}_2)\text{Br}_2\}_2\text{CS}_2]$	1108(m,sh)	795(mw)	578(m,br)	326(br)	384(s,sh)	229(s,br)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{Br}_2\}_2\text{CS}_2]$	1109(m,sh)	796(m)	580(w,br)	329(w,br)	388(s,sh)	232(s,br)
$[\{\text{Mn}(\text{PPr}_3^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	1108(mw)	800(w)	587(m,br)	329(m)	390(m,sh)	196(s,br)
$[\{\text{Mn}(\text{PBu}_3^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	1105(mw)	802(m)	590(w)	325(mw,br)	390(m,sh)	200(s,sh)
$[\{\text{Mn}(\text{PPhMe}_2)\text{I}_2\}_2\text{CS}_2]$	1105(m)	800(m)	585(mw)	330(m,sh)	385(s,sh)	195(s,sh)
$[\{\text{Mn}(\text{PPhEt}_2)\text{I}_2\}_2\text{CS}_2]$	1108(w,sh)	779(w,br)	590(w)	328(m,sh)	390(m,sh)	199(vs,sh)
$[\{\text{Mn}(\text{PPhPr}_2^{\text{n}})\text{I}_2\}_2\text{CS}_2]$	1110(mw)	798(w,sh)	589(w,br)	327(m,br)	391(s,sh)	202(vs,sh)

<sup>a</sup>s = strong, m = medium, w = weak, sh = sharp, br = broad.

on the basis of essentially  $T_d$  symmetry according to the suggestions of Figgis [17] and in accord with the geometry implied from their EPR spectra. The  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  complexes exhibit almost identical spectra to the  $[\text{Mn}(\text{PR}_3)\text{X}_2]_2\text{CS}_2$  complexes (Table VIII). This is not surprising since both tetrahedral and octahedral manganese(II) have the same  $^6A_1$  ground state [17].

From the infrared evidence it is clear that the  $\text{Mn}-\text{CS}_2$  complexes exhibit bands assignable to both  $(\text{C}=\text{S})$  and  $(\text{C}-\text{S})$  moieties (Tables V and VII) [2, 3]. The adducts cannot, therefore, be  $\sigma$ -bonded, nor can they be insertion products as the infrared spectra are inconsistent with either of these two types of adduct. This therefore implies that the  $\text{CS}_2$  must be either  $\pi$ -bonded or bridging.

The microanalytical data (Tables I and II) show the  $\text{Mn}:\text{CS}_2$  ratio as 2:1. For the adducts to be  $\pi$ -bonded, oxidative addition or ligand replacement would have to have occurred at a manganese centre. The magnetic moment and EPR measurements show that the manganese is present as  $\text{Mn(II)}$  and so oxidative addition appears to be ruled out. It is possible that a rearrangement has occurred in solution and that the adducts are of the type  $\text{MnX}_4[\text{Mn}(\text{PR}_3)_2(\text{CS}_2)]$ .

A formulation of this type is not inconsistent with the majority of physical data available. However, a compound of this type might be expected to be readily soluble in polar solvents and, as has already been stated the complexes are virtually insoluble in all common organic solvents, which would tend to imply some other structure. More importantly, complexes with the formation above would be 1:1 electrolytes, and all the adducts are non-conductors in dichloromethane solution. This observation clearly rules out any type of anion-cation complex of the sort suggested above.

From all the available data it can be postulated with a good degree of certainty that the  $\text{Mn}-\text{CS}_2$

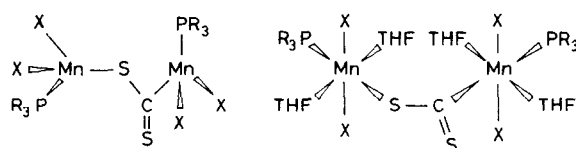


Fig. 1. Proposed structures of the carbon disulphide complexes.

complexes contain bridging  $\text{CS}_2$  moieties. Figure 1 shows likely structures for the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  and the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  complexes based on all the physical data.

Studies on the reversibility of  $\text{CS}_2$  adduct formation have also been undertaken. Heating the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  adducts *in vacuo* at  $80^\circ\text{C}$  for up to 12 h resulted in no significant changes in the spectroscopic properties of the solids. The magnetic moments of the complexes also remained unchanged. These observations clearly show that  $\text{CS}_2$  is irreversibly bonded to the  $\text{Mn}(\text{PR}_3)\text{X}_2$  complexes.

Similar heat-treatment of the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  complexes gave different results. After heating *in vacuo* for several hours the spectral properties of the complexes changed significantly. The bands assigned to co-ordinated THF decreased in intensity under heat treatment. After prolonged heating, *i.e.* in the region of 24 h, the THF bands were completely lost. In addition, the EPR spectra changed from characteristic octahedral-type signals in the region  $g_{\text{eff}} = 6$  and 2, to a spectrum characteristic of a tetrahedral species with bands at  $g_{\text{eff}} = 4$  and 2.

During these heat treatments, the bands due to co-ordinated  $\text{CS}_2$  were not diminished, indicating that the carbon disulphide is irreversibly bound. It seems that the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2\}_2\text{CS}_2]$  complexes can be converted to the  $[\{\text{Mn}(\text{PR}_3)\text{X}_2\}_2\text{CS}_2]$  compounds by heating *in vacuo*. Indeed, as can be

TABLE VI. Infrared Data for  $\{[Mn(PR_3)_2X_2(THF)_2]_2CS_2\}$  Complexes ( $cm^{-1}$ ).

Complex	$\nu(THF)$	$\nu(C=S)$	$\nu(C-S)$	$\nu(Mn-C)$	$\nu(Mn-S)$	$\nu(Mn-P)$	$\nu(Mn-X)$
$\{[Mn(PPR_3^n)Cl_2(THF)_2]_2CS_2\}$	1040(s,sh)	1120(m,sh)	825(m)	590(m,w)	330(m,br)	390(s,sh)	310(s,br)
$\{[Mn(PBu_3^n)Cl_2(THF)_2]_2CS_2\}$	1040(s,sh)	1120(m,sh)	830(m,br)	585(mw)	325(m,br)	388(s,sh)	305(s,sh)
$\{[Mn(PPhMe_2)Cl_2(THF)_2]_2CS_2\}$	1042(s,sh)	1118(m,sh)	830(m)	590(m)	330(m,sh)	385(s,sh)	310(s,sh)
$\{[Mn(PPhEt_2)Cl_2(THF)_2]_2CS_2\}$	1040(s,sh)	1115(m)	825(mw)	585(m)	330(mw,sh)	390(m,sh)	310(s,sh)
$\{[Mn(PPhPr_2^n)Cl_2(THF)_2]_2CS_2\}$	1038(s,sh)	1115(m,sh)	830(mw,br)	590(w,sh)	325(m,br)	390(s,sh)	305(s,sh)
$\{[Mn(PPR_3^n)Br_2(THF)_2]_2CS_2\}$	1045(s,sh)	1105(m,sh)	790(m,br)	575(w,sh)	325(m,br)	380(s,br)	230(s,sh)
$\{[Mn(PBu_3^n)Br_2(THF)_2]_2CS_2\}$	1045(s,sh)	1108(m,sh)	795(w,sh)	580(m,br)	330(m,br)	380(s,sh)	225(s,sh)
$\{[Mn(PPhMe_2)Br_2(THF)_2]_2CS_2\}$	1045(s,sh)	1110(m,sh)	788(m,br)	578(w,sh)	322(m,sh)	384(m,sh)	225(s,sh)
$\{[Mn(PPhEt_2)Br_2(THF)_2]_2CS_2\}$	1040(s,sh)	1105(m,sh)	785(m,sh)	575(m)	330(m,br)	380(s,br)	230(s,sh)
$\{[Mn(PPhPr_2^n)Br_2(THF)_2]_2CS_2\}$	1040(s,sh)	1110(m,sh)	785(m,sh)	580(mw,sh)	330(m,br)	380(s,sh)	225(s,sh)
$\{[Mn(PPR_3^n)I_2(THF)_2]_2CS_2\}$	1035(s,sh)	1110(m,sh)	800(m,sh)	590(m,br)	329(w,br)	390(s,br)	195(s,sh)
$\{[Mn(PBu_3^n)I_2(THF)_2]_2CS_2\}$	1035(s,sh)	1105(m,sh)	795(mw,sh)	588(w,sh)	325(m,br)	390(m,sh)	200(s,sh)
$\{[Mn(PPhMe_2)I_2(THF)_2]_2CS_2\}$	1035(s,sh)	1105(m,sh)	800(m,sh)	590(w,br)	320(m,br)	385(s,sh)	190(s,sh)
$\{[Mn(PPhEt_2)I_2(THF)_2]_2CS_2\}$	1040(s,sh)	1110(m,sh)	790(w,sh)	585(m,sh)	325(s,sh)	385(s,sh)	195(s,sh)
$\{[Mn(PPhPr_2^n)I_2(THF)_2]_2CS_2\}$	1035(s,sh)	1110(mw,sh)	795(w,br)	590(m,sh)	325(m,sh)	385(m,sh)	195(s,sh)

TABLE VII. Diffuse Reflectance Spectra for  $\{[Mn(PR_3)_2X_2]_2CS_2\}$  Complexes (nm).

Complex	${}^6A_1 \rightarrow 4T_1(G)$	${}^6A_1 \rightarrow 4T_2(G)$	${}^6A_1 \rightarrow 4A_1, 4E(G)$	${}^6A_1 \rightarrow 4T_2$
$\{[Mn(PPR_3^n)Cl_2]_2CS_2\}$	530	450	420	370
$\{[Mn(PBu_3^n)Cl_2]_2CS_2\}$	525	460	420	370
$\{[Mn(PPhMe_2)Cl_2]_2CS_2\}$	530	460	415	365
$\{[Mn(PPhEt_2)Cl_2]_2CS_2\}$	525	450	420	365
$\{[Mn(PPhPr_2^n)Cl_2]_2CS_2\}$	530	460	415	370
$\{[Mn(PPR_3^n)Br_2]_2CS_2\}$	540	462	430	377
$\{[Mn(PBu_3^n)Br_2]_2CS_2\}$	540	460	425	380
$\{[Mn(PPhMe_2)Br_2]_2CS_2\}$	535	460	430	375
$\{[Mn(PPhEt_2)Br_2]_2CS_2\}$	534	460	426	369
$\{[Mn(PPhPr_2^n)Br_2]_2CS_2\}$	532	458	429	374
$\{[Mn(PPR_3^n)I_2]_2CS_2\}$	535	450	400	385
$\{[Mn(PBu_3^n)I_2]_2CS_2\}$	532	454	395	380
$\{[Mn(PPhMe_2)I_2]_2CS_2\}$	535	455	390	380
$\{[Mn(PPhEt_2)I_2]_2CS_2\}$	534	452	402	384
$\{[Mn(PPhPr_2^n)I_2]_2CS_2\}$	535	450	395	380

TABLE VIII. Diffuse Reflectance Spectra for  $[\{Mn(PR_3)_2X_2(THF)_2\}_2CS_2]$  Complexes (nm).

Complex	${}^6A_1 \rightarrow 4T_1(G)$	${}^6A_1 \rightarrow 4T_2(G)$	${}^6A_1 \rightarrow 4A_1, 4E(G)$	${}^6A_1 \rightarrow 4T_2$
$[\{Mn(PPr_3^n)Cl_2(THF)_2\}_2CS_2]$	540	465	420	390
$[\{Mn(PBu_3^n)Cl_2(THF)_2\}_2CS_2]$	540	460	418	395
$[\{Mn(PPhMe_2)Cl_2(THF)_2\}_2CS_2]$	544	465	422	395
$[\{Mn(PPhEt_2)Cl_2(THF)_2\}_2CS_2]$	540	460	420	395
$[\{Mn(PPhPr_2^n)Cl_2(THF)_2\}_2CS_2]$	540	460	420	395
$[\{Mn(PPr_3^n)Br_2(THF)_2\}_2CS_2]$	545	455	425	390
$[\{Mn(PBu_3^n)Br_2(THF)_2\}_2CS_2]$	545	460	425	390
$[\{Mn(PPhMe_2)Br_2(THF)_2\}_2CS_2]$	545	455	428	392
$[\{Mn(PPhEt_2)Br_2(THF)_2\}_2CS_2]$	545	455	428	390
$[\{Mn(PPhPr_2^n)Br_2(THF)_2\}_2CS_2]$	545	460	430	390
$[\{Mn(PPr_3^n)I_2(THF)_2\}_2CS_2]$	550	470	420	400
$[\{Mn(PBu_3^n)I_2(THF)_2\}_2CS_2]$	550	465	418	395
$[\{Mn(PPhMe_2)I_2(THF)_2\}_2CS_2]$	550	470	415	400
$[\{Mn(PPhEt_2)I_2(THF)_2\}_2CS_2]$	548	465	420	395
$[\{Mn(PPhPr_2^n)I_2(THF)_2\}_2CS_2]$	552	470	420	400

seen from Tables I and II the melting points of the  $[Mn(PR_3)_2X_2]_2CS_2$  and their THF containing analogues are the same. This suggests that the THF is liberated before the complexes melt.

Attempts to displace the co-ordinated  $CS_2$  by reacting the adducts with dioxygen proved unsuccessful. Stirring either toluene or THF suspensions of  $CS_2$  adducts under an atmosphere of pure dioxygen for 24 h led to no change in the spectroscopic properties (infrared, EPR and diffuse reflectance). It was also found that stirring the dioxygen adducts  $Mn(PR_3)_2X_2(O_2)$  in either toluene or THF with excess  $CS_2$  resulted in precipitation of solids which were spectroscopically identical to the materials obtained by reaction of  $CS_2$  with  $Mn(PR_3)_2X_2$  complexes.

## Conclusion

From the data presented above it is clear that carbon disulphide binds irreversibly with  $Mn(PR_3)_2X_2$  complexes forming bridging adducts with a  $Mn-CS_2$  ratio of 2:1. Furthermore it has been shown that  $CS_2$  is capable of displacing, and is bound more strongly than, co-ordinated dioxygen.

## Experimental

### Synthesis of Manganese Complexes

The successful synthesis of the  $Mn(PR_3)_2X_2$  complexes was crucially dependent upon the use of rigorously anhydrous, dioxygen-free conditions. All reactions unless otherwise stated, were carried out under a dry argon atmosphere using dry, freshly

distilled solvents. All solid materials were, wherever possible, handled in a dry box under argon.

### $Mn(PR_3)_2X_2$ Complexes

The same general method was used for the synthesis of all the  $Mn(PR_3)_2X_2$  complexes, namely the reaction of equimolar quantities of manganese(II) halide and tertiary phosphine under an inert atmosphere in an appropriate solvent or solvent mixture. Three different solvent systems were employed and the toluene/dichloromethane solvent system is illustrated. Other solvent systems were diethylether and n-pentane.

#### Toluene/Dichloromethane

This method is best suited to the synthesis of the complexes  $Mn(PR_3)_2X_2$  where  $PR_3 = PPr_3^n$ ,  $PBu_3^n$ ,  $PPhMe_2$ ,  $PPhEt_2$  and  $PPhPr_2^n$  and where  $X = Cl$ ,  $Br$ , or  $I$ . A typical example is the synthesis of  $Mn(PPhMe_2)Br_2$ .

A 250 cm<sup>3</sup> round bottom flask equipped with a side arm with a ground glass tap is dried in an oven for 2 h at 130 °C prior to use. The flask was then removed and the apparatus, flask, tap, magnetic stirrer and ground glass stopper were allowed to cool in an argon atmosphere. Once cool the apparatus was assembled and connected to a vacuum line, the flask evacuated and heated with a bunsen flame to ensure no traces of moisture were present. The vacuum was then let down under argon and the flask charged with 0.86 g (4 mmol) of  $MnBr_2$  and subsequently flushed several times with argon. The solvent mixture, 50 cm<sup>3</sup> toluene followed by 50 cm<sup>3</sup> dichloromethane, was then introduced into the flask by means of a syringe (oven dried prior to use) and

the flask again flushed several times with argon. The dimethylphenylphosphine  $0.56 \text{ cm}^3$  (4 mmol) was then added and the flask again flushed with argon. The mixture was then allowed to stir under an argon atmosphere for 5 days at room temperature. The volume of solution was then reduced to *ca.*  $25 \text{ cm}^3$  by application of a vacuum (heat was not applied) and the resultant slurry filtered in a Schlenk apparatus. The solid product was then washed with small portions of dichloromethane ( $3 \times 10 \text{ cm}^3$ ) and finally dried *in vacuo*. The solid complex could then be stored in dry argon filled glass ampoules, yield greater than 90%.

#### *Mn(PR<sub>3</sub>)X<sub>2</sub>(THF)<sub>2</sub> Complexes*

The manganese(II) halides were found to react with tertiary phosphines in both non-coordinating solvent and tetrahydrofuran. In the latter solvent, the solids recovered would be induced to contain, in addition to the phosphine ligand, two molecules of THF per Mn atom. The synthesis of these compounds is given generally here. A  $250 \text{ cm}^3$  round bottom flask with side arm, ground glass top and magnetic stirrer bar was dried by the normal procedure. The flask was then charged with 0.63 g (5 mmol) of anhydrous manganese(II) chloride and the phosphine (5 mmol). Dry tetrahydrofuran ( $50 \text{ cm}^3$ ) was then distilled into the flask under argon and the mixture stirred for 10 d. After this time the THF was removed by application of a vacuum, dry pentane ( $50 \text{ cm}^3$ ) was then added and the mixture stirred vigorously for 1 h. The resulting slurry was then filtered in a Schlenk apparatus and the solid complex dried *in vacuo* for 6 h. Yields approx. quantitative.

#### *Synthesis of [Mn(PR<sub>3</sub>)X<sub>2</sub>]<sub>2</sub>CS<sub>2</sub>] Complexes*

The same method was employed for the synthesis of all the  $[\text{Mn}(\text{PR}_3\text{X})_2]_2\text{CS}_2$  complexes as typified by the isolation of  $[\text{Mn}(\text{PPhMe}_2)\text{Br}_2]_2\text{CS}_2$ : a  $250 \text{ cm}^3$  side arm flask was dried by the usual procedure and charged with 0.5 g (1.42 mmol) of  $\text{Mn}(\text{PPhMe}_2)\text{Br}_2$  solid in a dry box. The flask was then sealed and removed from the dry box and attached to the diethylether distillation apparatus. Approximately  $50 \text{ cm}^3$  of dry solvent were then distilled onto the dry solid and the flask was then removed from the still, placed on an oil bath and equipped with a reflux condenser and argon flow. Excess  $\text{CS}_2$  was then added and the mixture refluxed gently under a blanket of argon for 48 h. The mixture was then allowed to cool to room temperature under argon and the resulting slurry filtered in a Schlenk apparatus.

The solid was then washed with small portions of ether ( $3 \times 10 \text{ cm}^3$ ) and finally dried *in vacuo* for 6 h at room temperature. The  $[\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2]_2\text{CS}_2$  complexes were similarly synthesised from  $\text{Mn}(\text{PR}_3)\text{X}_2(\text{THF})_2$  and  $\text{CS}_2$ .

#### Acknowledgement

We are grateful to Dr. M. H. Jones for his initial experimental data on this system, and the UMIST for the award of a Part Time Teaching Assistantship (DSB).

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