Synthesis of Platinum–Manganese and –Rhenium Complexes with Bridging Thiocarbonyl Ligands; Crystal Structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ †

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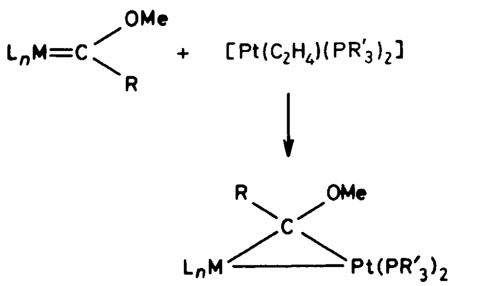
Addition of the compounds $[M(CO)_2(CS)(\eta\text{-}C_5H_5)]$ (M = Mn or Re) to the species $[Pt(C_2H_4)(PR_3)_2]$ in light petroleum at 0 °C affords the dimetal complexes $[MPt(\mu\text{-}CS)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (M = Mn, PR_3 = PMe_2Ph or $PMePh_2$; M = Re, PR_3 = PMe_2Ph). The structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ has been established by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell with a = 16.655(4), b = 9.684(3), c = 21.409(5) Å, β = 114.57(2)°. The structure was refined to *R* 0.043 (*R'* 0.043) for 4 358 independent absorption-corrected intensities with $2.9 \leqslant 2\theta \leqslant 50°$ (Mo-K_α *X*-radiation) collected at room temperature. The Pt–Mn bond [2.641(1) Å] is bridged by the CS ligand [C–Mn 1.878(8), C–Pt 2.015(8) Å] and strongly semi-bridged by a CO group [Mn–C–O 154.0(8)°; C–Mn 1.798(8), C–Pt 2.220(9) Å]. Variable-temperature n.m.r. studies revealed that the compounds $[MPt(\mu\text{-}CS)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ undergo dynamic behaviour in solution, and possible mechanisms for site exchange of PR_3 and CO ligands are discussed. Treatment of $[MnPt(\mu\text{-}CS)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ with $[OMe_3][BF_4]$ gave the salt $[MnPt(\mu\text{-}CSMe)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ containing the μ-CSMe thiocarbyne ligand.

ZEROVALENT platinum compounds $[Pt(C_2H_4)(PR_3)_2]$ readily combine with the alkylidene metal complexes prepared by Fischer *et al.*[1] to give species with bonds between platinum and other metals, and bridging alkylidene ligands (Scheme 1).[2] These results suggested that nucleophilic platinum compounds would add to other carbon–metal bonds which are multiple in character, thereby affording a range of heteronuclear dimetal complexes in which the metal–metal bonds are supported by



SCHEME 1 ML_n = $M(CO)_5$ (M = Cr, Mo, or W) or $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Mn or Re); R and R' = alkyl or aryl

bridging carbon atoms. Indeed, reactions which have been observed [3] between zerovalent platinum compounds and co-ordinatively saturated metal carbonyls, the products of which are cluster compounds with heteronuclear metal–metal bonds, may involve as the first step complexation of a co-ordinatively unsaturated platinum species $Pt(PR_3)_2$ or $Pt(CO)(PR_3)$ with a terminal M≡CO group. These observations prompted a study of reactions between the compounds $[Pt(C_2H_4)(PR_3)_2]$ and complexes containing terminal M–CS groups. Addition of the fragments $Pt(PR_3)_2$ to mononuclear metal thiocarbonyl complexes could lead to the formation of the first heteronuclear dimetal compounds with bridging CS ligands. Homonuclear dimetal compounds with thiocarbonyl bridges are now well established.[4-6] A preliminary account of our work has been given.[7]

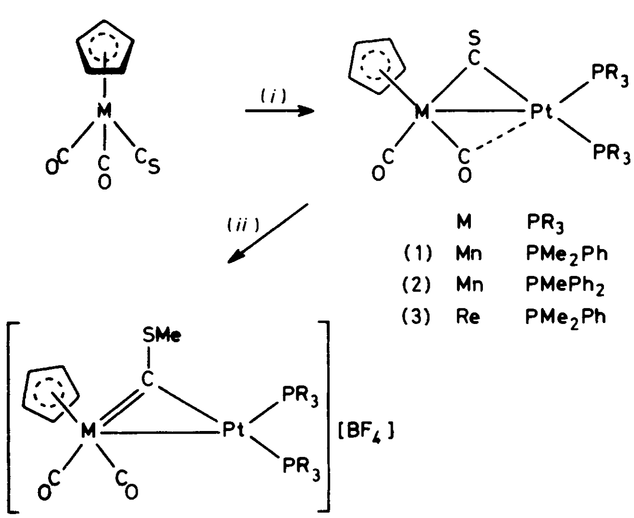
† *d*-μ-Carbonyl-*e*-carbonyl-*f*-(η-cyclopentadienyl)-*a*,*b*-bis(methyldiphenylphosphine)-*c*-μ-thiocarbonyl-platinum-manganese (*Pt–Mn*).

RESULTS AND DISCUSSION

Addition of $[Mn(CO)_2(CS)(\eta\text{-}C_5H_5)]$ [8] to $[Pt(C_2H_4)(PMe_2Ph)_2]$ in light petroleum at room temperature (Scheme 2) affords a yellow compound formulated as $[MnPt(\mu\text{-}CS)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (1) on the basis of microanalysis, and i.r. and n.m.r. data. A similar reaction employing $[Pt(C_2H_4)(PMePh_2)_2]$ gave a related complex (2).

Compound (1) showed two CO stretching bands (1 927 and 1 797 cm^{-1}) in its i.r. spectrum; the low-frequency absorption can be assigned to a semi-bridging or bridging carbonyl group. *X*-Ray diffraction studies have been carried out recently on the species $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [2d] and $[MnPt(SC_6H_4Me\text{-}4)\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ [2e] revealing that the former contains a semi-bridging CO ligand [Mn–C–O 157(1)°] and the latter a fully bridging CO group [Mn–C–O 146(1)°]. For these two complexes the lowest frequency CO stretches are at 1 829 and 1 730 cm^{-1}, respectively.

Reaction between $[Re(CO)_2(CS)(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PMe_2Ph)_2]$, under similar conditions to those which gave compounds (1) and (2), yielded the platinum–rhenium complex (3). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the three compounds were similar, and moreover, revealed that the complexes underwent dynamic behaviour in solution. Thus at ambient temperatures only one ^{31}P resonance was observed but on cooling solutions to *ca.* −60 °C two signals are seen, corresponding to PR_3 groups *transoid* and *cisoid* to the metal–metal bonds. It was thus important to establish the structure in the solid state for at least one of the compounds (1)—(3). Fortunately, for an *X*-ray diffraction study, it was possible to grow a good quality crystal of (2). The results of the *X*-ray diffraction study are summarised in Tables 1—3,



(4) M = Mn, $PR_3 = PMe_2Ph$

SCHEME 2 (*i*) $[Pt(C_2H_4)(PR_3)_2]$, (*ii*) $[OMe_3][BF_4]$

and the molecular structure with the atom-numbering scheme is shown in Figure 1.

The molecule has a Mn–Pt bond bridged by a CS group, and one of the CO ligands is semi-bridged to the platinum atom. This is in accord with the previously discerned preference for the CS group to occupy the bridging position in competition with CO in homonuclear dimetal complexes,[5,6] and provides the basis of our interpretation of the dynamic behaviour of the complexes in solution, discussed later.

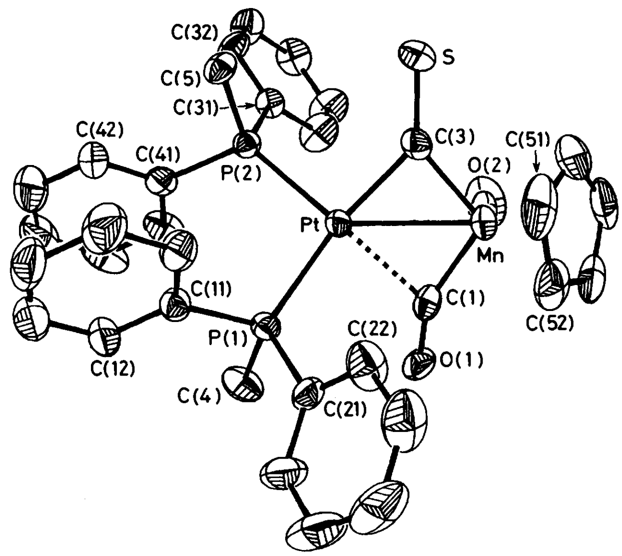
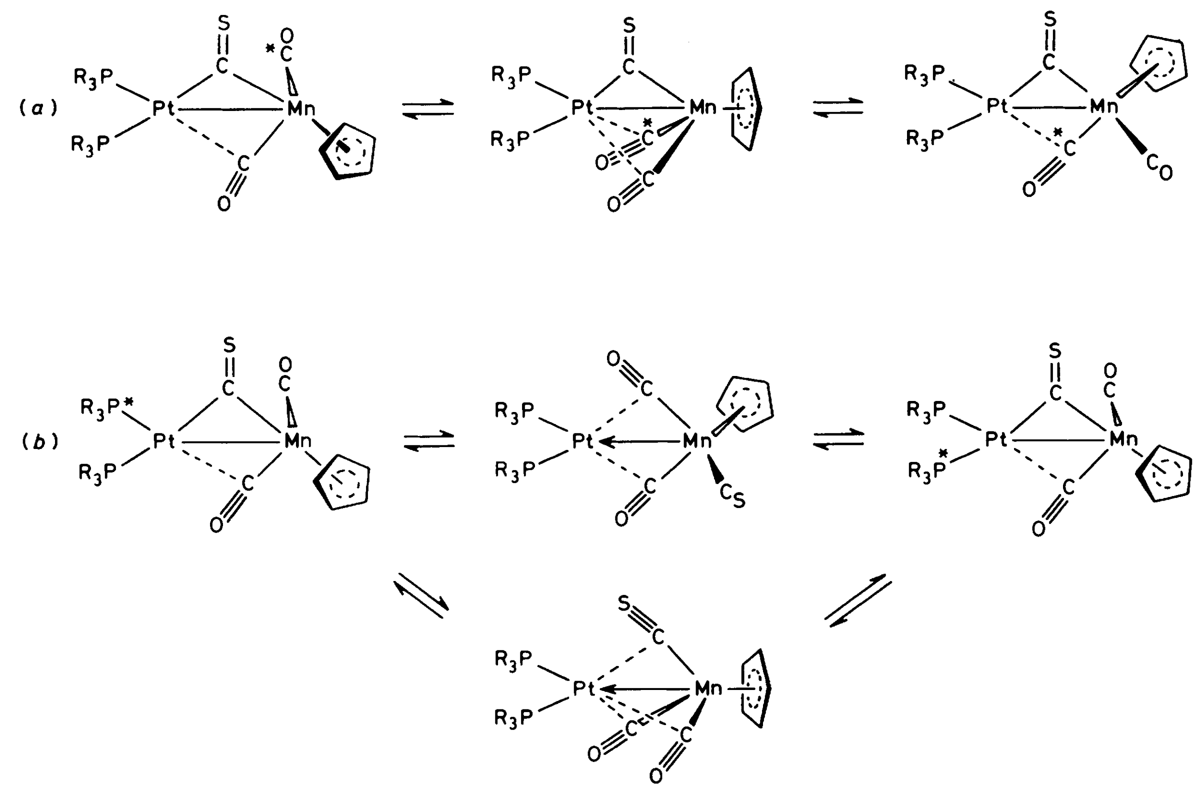


FIGURE 1 Molecular structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (2), with the crystallographic numbering

The Mn–Pt separation [2.641(1) Å] is typical of that found in other complexes containing a $\overline{Mn(\mu\text{-}C)Pt}$ ring system and may be compared with those found in $[MnPt(\mu\text{-}C_4H_5O)(CO)_4(PMe_3)_2]$ [two forms, Mn–Pt 2.691(1)



SCHEME 3 Dynamic behaviour of complexes (1)—(3): (*a*) CO site exchange, (*b*) PR_3 site exchange

and 2.659(2) Å],[2b] $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [2.628(1) Å],[2d] and $[MnPt(SC_6H_4Me\text{-}4)\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ [2.626(1) Å].[2e]

TABLE 1

Atomic positional parameters (fractional co-ordinates) for complex (2), with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.238 35(2)	1.057 56(3)	0.111 46(1)
Mn	0.182 97(8)	1.223 54(14)	0.003 87(6)
P(1)	0.264 29(14)	1.128 68(22)	0.222 44(10)
P(2)	0.279 59(14)	0.828 77(22)	0.132 45(11)
C(1)	0.247 17(54)	1.280 20(94)	0.090 47(45)
O(1)	0.284 47(43)	1.365 18(61)	0.133 63(33)
C(2)	0.278 21(58)	1.211 9(11)	−0.013 15(48)
O(2)	0.338 86(53)	1.204 2(11)	−0.025 99(42)
C(3)	0.178 97(53)	1.030 19(83)	0.008 93(39)
S	0.137 99(24)	0.898 96(29)	−0.041 06(13)
C(4)	0.376 27(61)	1.190 7(13)	0.278 17(49)
C(5)	0.190 70(53)	0.702 06(84)	0.109 79(44)
C(16)	0.153 27(38)	0.934 68(68)	0.234 54(26)
C(15)	0.122 62(38)	0.838 06(68)	0.267 81(26)
C(14)	0.173 20(38)	0.806 11(68)	0.336 67(26)
C(13)	0.254 44(38)	0.870 79(68)	0.372 26(26)
C(12)	0.285 09(38)	0.967 41(68)	0.338 99(26)
C(11)	0.234 51(38)	0.999 36(68)	0.270 13(26)
C(21)	0.191 75(38)	1.266 12(59)	0.225 81(31)
C(22)	0.110 61(38)	1.283 57(59)	0.169 76(31)
C(23)	0.051 35(38)	1.383 12(59)	0.172 05(31)
C(24)	0.073 23(38)	1.465 21(59)	0.230 39(31)
C(25)	0.154 37(38)	1.447 75(59)	0.286 43(31)
C(26)	0.213 63(38)	1.348 21(59)	0.284 14(31)
C(31)	0.346 76(35)	0.775 29(54)	0.087 89(30)
C(32)	0.363 24(35)	0.635 61(54)	0.082 35(30)
C(33)	0.421 42(35)	0.596 07(54)	0.053 94(30)
C(34)	0.463 13(35)	0.696 20(54)	0.031 05(30)
C(35)	0.446 65(35)	0.835 88(54)	0.036 58(30)
C(36)	0.388 47(35)	0.875 42(54)	0.065 00(30)
C(41)	0.353 93(35)	0.780 64(62)	0.219 70(23)
C(42)	0.332 66(35)	0.678 04(62)	0.256 01(23)
C(43)	0.392 69(35)	0.642 66(62)	0.322 18(23)
C(44)	0.473 99(35)	0.709 87(62)	0.352 05(23)
C(45)	0.495 27(35)	0.812 47(62)	0.315 74(23)
C(46)	0.435 24(35)	0.847 86(62)	0.249 56(23)
C(51)	0.042 24(45)	1.249 52(96)	−0.031 47(55)
C(52)	0.084 61(45)	1.374 74(96)	−0.000 67(54)
C(53)	0.131 15(45)	1.424 62(96)	−0.038 58(54)
C(54)	0.117 56(45)	1.330 22(96)	−0.092 81(54)
C(55)	0.062 60(45)	1.222 00(96)	−0.088 42(54)

Particular interest centres on the Mn, Pt, C(3)S, C(1)-O(1) bridge system. The C(3)-Mn separation [1.878(8) Å] is relatively short, being comparable with the Mn=C(carbene) distance [1.88 Å] in $[Mn\{C(COPh)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$.[9] Moreover, C(3)-Mn is only marginally longer than the μ-C-Mn linkage in $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [1.829(8) Å] which is formally a C=Mn bond.[2d] The μ-C-Mn distances in $[Mn_2(\mu\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2]$ [1.97(1) Å],[10] $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ [2.026(1) Å],[11] and $[MnPt(SC_6H_6Me\text{-}4)\{\mu\text{-}C(PMe_3)C_6H_6Me\text{-}4\}(\mu\text{-}CO)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ [2.047(9) Å][2e] are all significantly longer than C(3)-Mn in (2). These data suggest that the latter linkage has some multiple bond character. In contrast, the C(3)-Pt distance [2.015(8) Å] is normal, being in the middle of the range (1.99—2.15 Å) generally associated with μ-C-Pt bridge bonds,[2d] and close to that in $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [1.997(9) Å].[12]

TABLE 2

Bond lengths (Å) and angles (°) for $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (2), with estimated standard deviations in parentheses

(a) Bond lengths *

Pt–Mn	2.641(1)	Pt–P(1)	2.335(2)
Pt–P(2)	2.308(2)	Pt–C(1)	2.220(9)
Pt–C(3)	2.015(8)	Mn–C(1)	1.798(8)
Mn–C(2)	1.77(1)	Mn–C(3)	1.878(8)
Mn–C(51)	2.157(7)	Mn–C(52)	2.169(9)
Mn–C(53)	2.170(9)	Mn–C(54)	2.16(1)
Mn–C(55)	2.151(7)	P(1)–C(4)	1.847(9)
P(1)–C(11)	1.810(7)	P(1)–C(21)	1.819(7)
P(2)–C(5)	1.826(9)	P(2)–C(31)	1.821(8)
P(2)–C(41)	1.821(5)	C(1)–O(1)	1.20(1)
C(2)–O(2)	1.15(2)	C(3)–S	1.618(8)

(b) Interbond angles

P(1)–Pt–Mn	123.9(1)	P(2)–Pt–Mn	136.2(1)
C(1)–Pt–Mn	42.3(2)	C(3)–Pt–Mn	45.2(2)
P(2)–Pt–P(1)	99.8(1)	C(1)–Pt–P(1)	85.4(3)
C(3)–Pt–P(1)	161.2(3)	C(1)–Pt–P(2)	158.8(3)
C(3)–Pt–P(2)	93.3(2)	C(3)–Pt–C(1)	87.2(3)
C(1)–Mn–Pt	56.2(3)	C(2)–Mn–Pt	97.1(3)
C(3)–Mn–Pt	49.5(2)	C(51)–Mn–Pt	108.1(3)
C(52)–Mn–Pt	115.7(3)	C(53)–Mn–Pt	147.7(3)
C(54)–Mn–Pt	168.9(2)	C(55)–Mn–Pt	130.6(3)
C(2)–Mn–C(1)	91.8(4)	C(3)–Mn–C(1)	105.4(4)
C(51)–Mn–C(1)	114.8(4)	C(52)–Mn–C(1)	87.4(4)
C(53)–Mn–C(1)	96.9(4)	C(54)–Mn–C(1)	133.6(4)
C(55)–Mn–C(1)	151.2(4)	C(3)–Mn–C(2)	90.3(5)
C(51)–Mn–C(2)	150.4(4)	C(52)–Mn–C(2)	139.2(4)
C(53)–Mn–C(2)	101.8(4)	C(54)–Mn–C(2)	88 3(4)
C(55)–Mn–C(2)	112.5(4)	C(51)–Mn–C(3)	94.4(4)
C(52)–Mn–C(3)	129.1(4)	C(53)–Mn–C(3)	154.3(3)
C(54)–Mn–C(3)	121.1(3)	C(55)–Mn–C(3)	90.2(3)
C(52)–Mn–C(51)	38.3(1)	C(53)–Mn–C(51)	64.1(2)
C(54)–Mn–C(51)	64.3(2)	C(55)–Mn–C(51)	38.5(1)
C(53)–Mn–C(52)	38.2(1)	C(54)–Mn–C(52)	64.1(2)
C(55)–Mn–C(52)	64.3(2)	C(54)–Mn–C(53)	38.3(2)
C(55)–Mn–C(53)	64.2(2)	C(55)–Mn–C(54)	38 5(2)
C(4)–P(1)–Pt	117.6(4)	C(11)–P(1)–Pt	113.1(2)
C(21)–P(1)–Pt	114.3(2)	C(11)–P(1)–C(4)	107.5(4)
C(21)–P(1)–C(4)	104.2(4)	C(21)–P(1)–C(11)	98.1(3)
C(5)–P(2)–Pt	116.8(3)	C(31)–P(2)–Pt	111.6(2)
C(41)–P(2)–Pt	117.8(2)	C(31)–P(2)–C(5)	106.0(4)
C(41)–P(2)–C(5)	103.3(3)	C(41)–P(2)–C(31)	99.3(3)
Mn–C(1)–Pt	81.4(3)	O(1)–C(1)–Pt	124.5(7)
O(1)–C(1)–Mn	154.0(8)	O(2)–C(2)–Mn	178.3(8)
Mn–C(3)–Pt	85.3(3)	S–C(3)–Pt	134.8(5)
S–C(3)–Mn	139.5(5)	C(16)–C(11)–P(1)	115.7(2)
C(12)–C(11)–P(1)	124.2(2)	C(22)–C(21)–P(1)	118.4(2)
C(26)–C(21)–P(1)	121.5(2)	C(32)–C(31)–P(2)	120.4(2)
C(36)–C(31)–P(2)	119.4(2)	C(42)–C(41)–P(2)	122.1(2)
C(46)–C(41)–P(2)	117.8(2)	C(52)–C(51)–Mn	71.3(3)
C(55)–C(51)–Mn	70.5(3)	C(51)–C(52)–Mn	70.4(2)
C(53)–C(52)–Mn	70.9(3)	C(52)–C(53)–Mn	70.8(3)
C(54)–C(53)–Mn	70.4(3)	C(53)–C(54)–Mn	71.3(3)
C(55)–C(54)–Mn	70.5(2)	C(51)–C(55)–Mn	71.0(3)
C(54)–C(55)–Mn	71.1(3)		

* The phenyl and cyclopentadienyl rings were included as rigid hexagonal or pentagonal groups with C–C (C_6H_5) 1.395, C–C (C_5H_5) 1.420, and C–H (C_6H_5, C_5H_5) 0.960 Å.

The atoms MnPtC(3)S are coplanar (Table 3), and the Mn(μ-CS)Pt moiety is relatively symmetric, as evidenced by the similarity of the angles Mn-C(3)-S [139.5(5)°] and Pt-C(3)-S [134.8(5)°]. The carbonyl group C(1)O(1) is semi-bridging [Mn-C(1)-O(1) 154.0(8)°], a property likely to be related to the ligand site-exchange processes observed in solution, and discussed further below. The angle of 154° is slightly more than half-way between that expected for a terminal Mn-C-O linkage and that for a symmetrical CO bridge.[13] This results in a relatively short C(1)–Pt distance [2.220(9) Å] which is comparable with that found [2.21(3) Å] for the semi-bridging CO groups in $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$.[14] Evidently, the semi-bridging C(1)O(1) ligand in (2) provides a mechanism for the electron-rich $Pt(PMePh_2)_2$ group to transfer electron density back to the $Mn(CO)_2(\eta\text{-}C_5H_5)$ moiety.

The Pt atom is essentially coplanar with its ligated atoms, and the dihedral angle between the planes defined by P(1)PtP(2) and MnPtC(3) is only 24° (Table 3). As is customarily observed in complexes containing Pt(μ-C)M ring systems, the P(1)–Pt distance [2.335(2) Å] *transoid* to the μ-C(3) atom is longer than the P(2)–Pt distance [2.308(2) Å] *cisoid* to this atom.

TABLE 3

Some least-squares planes * for the complex (2); distances (Å) of atoms from the planes are given in square brackets

Plane (i): Mn, Pt, C(3), S
$$16.559x - 0.900y - 9.894z = 1.903$$
[Mn −0.01, Pt −0.01, C(3) 0.05, S −0.02]

Plane (ii): Pt, P(1), P(2)
$$15.900x + 2.385y - 5.245z = 5.727$$

Plane (iii): Mn, Pt, C(1), O(1)
$$16.297x - 1.660y - 10.943z = 0.910$$
[Mn −0.001, Pt −0.001, C(1) 0.004, O(1) −0.002]

Plane (iv): Pt, Mn, P(1), P(2), C(3), S
$$16.553x + 1.066y - 8.654z = 4.001$$
[Pt 0.11, Mn 0.30, P(1) −0.35, P(2) 0.36, C(3) −0.02, S −0.40]

Dihedral angles (°) between the least-squares planes:

(i)—(ii)	24	(ii)—(iii)	30
(i)—(iii)	6		

* *x*, *y*, and *z* are fractional crystal co-ordinates.

Having established the molecular structure of (2) by the *X*-ray diffraction study, and by implication the structures of (1) and (3) also, since the spectral properties of all three compounds are very similar, it was possible to interpret the dynamic n.m.r. data.

At temperatures below *ca.* −60 °C the ^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$ spectra of (1)—(3) reflect the structure found for (2) in the solid state, except that even at the low-temperature experimental limit the ^{13}C spectra show only one CO ligand signal. Site exchange of the two non-equivalent CO groups could occur *via* a transition state with mirror symmetry having two semi-bridging carbonyl ligands, Scheme 3(*a*). The ^{13}C spectra show μ-CS resonances which are highly deshielded, ranging from δ 386.5 p.p.m. for (1) to 353.4 p.p.m. for (3). These resonances occur as doublets due to ^{13}C–^{31}P coupling with the *transoid* PR_3 groups. The spectrum of (3) (−70 °C) was of sufficiently good quality to show ^{195}Pt satellite peaks [*J*(PtC) 806 Hz]. Interestingly, the μ-CS chemical shifts are even more deshielded than in the precursors $[M(CO)_2(CS)(\eta\text{-}C_5H_5)]$, thus for M = Mn, δ(CS) 335 p.p.m., and for M = Re, δ(CS) 289 p.p.m.[15] A similar increase in deshielding is observed [2d] for the contact carbon of the carbyne ligand in the complexes $[MPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (M = Mn or Re) compared with the resonances in the mononuclear metal cationic species $[M\{\equiv C(C_6H_4Me\text{-}4)\}(CO)_2(\eta\text{-}C_5H_5)]^+$.

As mentioned earlier, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra show only a single resonance at ambient temperatures, with the limiting spectrum of two resonances being observed at *ca.* −40 to −60 °C. The data for (1) were the better quality and are discussed here. At the low-temperature limit, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consists of two doublet signals at δ 12.03 p.p.m. [*J*(PP) 16, *J*(PtP) 4 213 Hz] and −2.19 p.p.m. [*J*(PP) 16, *J*(PtP) 2 647 Hz] (Figure 2). The resonance at 12.03 p.p.m. may be assigned to the PMe_2Ph ligand *transoid* to the Mn–Pt bond on account of the large ^{195}Pt–^{31}P coupling.[2] On warming from −60 °C, the PMe_2Ph ligands evidently undergo site exchange since at ambient temperatures a single peak with ^{195}Pt satellites is seen. From the coalescence temperature (268 K) the activation energy ($\Delta G_{T_c}^{\ddagger}$) for the process is estimated to be 53 kJ mol^{-1}. The dynamic behaviour of the phosphine ligands is also apparent from the ^1H n.m.r. data which reveal one MeP signal at 25 °C and two resonances at −80 °C, with appropriate ^{31}P and ^{195}Pt couplings.

The apparently equivalent PMe_2Ph group environments at ambient temperatures can be explained by a mechanism closely similar to that proposed for CO exchange at −60 °C. Thus, rapid exchange on the n.m.r. time-scale between the bridging CS ligand and a terminal CO group could give a transition state with mirror symmetry in which the PMe_2Ph ligands are equivalent, Scheme 3(*b*). However, it might be unreasonable to propose a transition state in which the CS ligand adopts a purely terminal site.[5] A plausible alternative is shown in which the CS and two CO ligands are all semi-bridging. Rotation of the $Pt(PMe_2Ph)_2$ group in the ' socket ' formed by the CO and CS groups could lead to the observation of a single ^{31}P n.m.r. resonance at 25 °C. Such an intermediate is attractive for two reasons. Firstly, $[Mn(CO)_3(\eta\text{-}C_5H_5)]$, and presumably the analogue $[Mn(CO)_2(CS)(\eta\text{-}C_5H_5)]$, has its highest occupied molecular orbital (h.o.m.o.) centred on the metal,[16] allowing donation of an electron pair to another metal as in $[(\eta\text{-}C_5H_5)(OC)_3Mn\rightarrow Rh(CO)(\eta\text{-}C_5Me_5)]$.[17] Hence the ' semi-triply ' bridged intermediate [Scheme 3(*b*)] is reasonable. Secondly, in the tetranuclear metal complexes $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ [18] a low-energy dynamic process may occur involving rotation of the Pt(CO)(PR_3) fragment in the socket formed by the Os_3 triangle. In the hypothetical molecule $[Fe_3Pt(CO)_{10}(PH_3)]^{2-}$ the barrier for rotation of the Pt(CO)(PH_3) group is estimated [19] to be only *ca.* 25 kJ mol^{-1}. Thus, in (1) in solution rotation of the $Pt(PR_3)_2$ fragments about an axis through the platinum and manganese atoms and the centre of the C_5H_5 ring seems possible, although whatever the mechanism the activation energy (*ca.* 53 kJ mol^{-1}) is evidently higher than that estimated for rotation of a platinum atom in a socket formed by a triangle of metal atoms.

It is interesting to relate the formation of (1)—(3) to that of the bridged alkylidene compounds of Scheme 1. The carbon–metal bonding in Fischer's[1] mononuclear metal alkylidene complexes is predominantly ylide-like in character with the electrophilic centre at the carbon atom. Hence it has been proposed[2a,12] that the attack of the nucleophilic $Pt(PR_3)_2$ fragments occurs at the

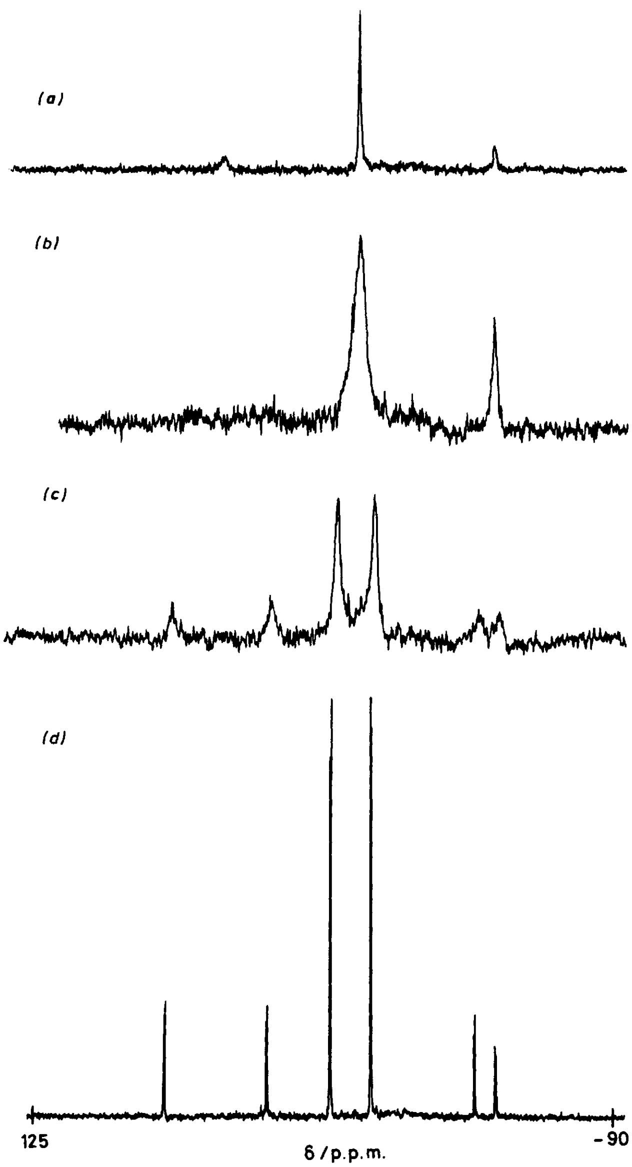


FIGURE 2 Proton-decoupled ^{31}P n.m.r. spectra of complex (1) measured at (*a*) 25, (*b*) 0, (*c*) −20, and (*d*) −60 °C

carbon atoms of the alkylidene–metal compounds affording dipolar species $[L_n\overset{\delta-}{M}\{C(OMe)R\}\overset{\delta+}{Pt}(PR_3)_2]$ which collapse forming the metal–metal bonds. If a similar mechanism operates in the reaction of the compounds $[Pt(C_2H_4)(PR_3)_2]$ with the species $[M(CO)_2(CS)(\eta\text{-}C_5H_5)]$ the dipolar intermediate would be expected to be of the form $[(\overset{\delta-}{SC})M\{(CO)_2(\eta\text{-}C_5H_5)\}\overset{\delta+}{Pt}(PR_3)_2]$, so that the metal–metal bond forms in the first step. This is because in mononuclear metal thiocarbonyl complexes there is a build-up of electron density at the carbon centre,[20,21] in contrast to the situation with Fischer's alkylidene metal complexes. Nevertheless, although the CS ligand when bonded to a single metal centre leaves the metal with a greater positive charge, mononuclear metal thiocarbonyl complexes in certain reactions undergo nucleophilic attack at the apparently electron-rich ligated carbon atom. To account for this reactivity pattern it has been proposed[21] that the reactivity of the M–CS group is frontier orbital controlled rather than charge controlled. Hence we would favour a mechanism for the formation of (1)—(3) in which the homo *xz* orbital of the $Pt(PR_3)_2$ group[22,23] interacts with the lowest unoccupied molecular orbital (l.u.m.o.) of the complex, the π^* (CS) orbital. This combination would destroy the multiple-bond character in the M–CS bond, giving the observed products.

The reactions of Scheme 1 may also be frontier orbital controlled, rather than proceeding *via* dipolar intermediates. Because of the isolobal relationship between $Pt(PR_3)_2$ and CH_2 groups, combination of the former species with $L_nM{=}C(OMe)R$ complexes may involve similar orbital interactions[24] to those which account for the addition of CH_2 or $Pt(PR_3)_2$ groups to the electrophilic molecule $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.[25] Hence the reactions of Schemes 1 and 2, and formation of the platinumdirhodium compounds $[PtRh_2(\mu\text{-}CO)_2L_2(\eta\text{-}C_5Me_5)_2]$ [L = CO or PPh_3, L_2 = cyclo-octa-1,5-diene (cod)], may have the common feature of being orbital controlled by interaction of the filled b_2 orbital of a $Pt(PR_3)_2$ species with the l.u.m.o. of the substrate molecule, the platinum fragment being produced by ethylene dissociation from the complexes $[Pt(C_2H_4)(PR_3)_2]$.

Alkylation of (1) with $[OMe_3][BF_4]$ affords the salt (4) with a bridging thiocarbyne ligand. Related di-iron species $[Fe_2(\mu\text{-}CSR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]^+$ have been previously reported,[26] but complex (4) is the first example of a heteronuclear dimetal compound with a bridging CSR ligand. In contrast to (1)—(3), compound (4) does not show dynamic behaviour for the PMe_2Ph ligands, although the appearance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of only one CO signal implies carbonyl group site exchange. At room temperature the $^{31}P\text{-}\{^1H\}$ spectrum shows two doublet signals at δ 2.82 p.p.m. [*J*(PP) 11, *J*(PtP) 3 917 Hz] and −7.65 p.p.m. [*J*(PP) 11, *J*(PtP) 2 631 Hz]; the latter resonance with the smaller ^{195}Pt–^{31}P coupling may be assigned to the PMe_2Ph ligand *transoid* to the μ-CSMe group. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the resonance for the μ-*C*SMe group is highly deshielded, δ 384.3 p.p.m., and appears as the expected doublet [*J*(PC) 72 Hz] with ^{195}Pt satellites [*J*(PtC) 812 Hz].

EXPERIMENTAL

The various reactions were carried out using Schlenk-tube techniques and under an atmosphere of oxygen-free nitrogen. Solvents were dried and distilled prior to use, and light petroleum refers to that fraction of b.p. 40—60 °C. The n.m.r. measurements were made with JEOL–JNM-

FX90Q and FX200 instruments, and i.r. spectra were recorded in dichloromethane with a Perkin-Elmer 257 spectrometer. Bis(cyclo-octa-1,5-diene)platinum [27] and the compounds $[M(CO)_2(CS)(\eta-C_5H_5)]$ (M = Mn or Re) [8,28] were prepared by methods described elsewhere.

Reactions of $[Mn(CO)_2(CS)(\eta-C_5H_5)]$ *with the Compounds* $[Pt(C_2H_4)(PR_3)_2]$.—(*a*) $[Pt(cod)_2]$ (0.41 g, 1 mmol) was slowly dissolved in an ethylene-saturated solution of light petroleum (20 cm^3) at 0 °C. The solution was then treated with PMe_2Ph (0.28 g, 2 mmol) so as to generate *in situ* $[Pt(C_2H_4)(PMe_2Ph)_2]$. The compound $[Mn(CO)_2(CS)(\eta-C_5H_5)]$ (0.22 g, 1 mmol) was then added, and the mixture stirred (48 h). Filtration afforded yellow *microcrystals of* $[MnPt(\mu-CS)(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)]$ (1) (0.52 g, 75%) (Found: C, 41.4; H, 4.1. $C_{24}H_{27}MnO_2P_2PtS$ requires C, 41.7; H, 4.0%); m.p. 95—98 °C (decomp.); $\nu_{max.}$(CO) at 1 927s and 1 797w cm^{-1}. N.m.r. ([$^2H_2$]dichloromethane): ^1H (25 °C), δ 1.6 [d, 12 H, MeP, *J*(PH) 10, *J*(PtH) 29 Hz], 4.54 (s, 5 H, C_5H_5), 7.27 (s br, 10 H, Ph); ^1H (−80 °C), δ 1.48 [d, 6 H, MeP, *J*(PH) 9, *J*(PtH) 21], 1.78 [d, 6 H, MeP, *J*(PH) 11, *J*(PtH) 42 Hz], 4.60 (s, 5 H, C_5H_5), 7.27 (s br, 10 H, Ph); $^{31}P-\{^1H\}$ (25 °C), δ [to high frequency of 85% H_3PO_4 (external)] 3.74 p.p.m. [s, *J*(PtP) 3 456 Hz]; $^{31}P-\{^1H\}$ (−60 °C), δ 12.03 [d, P *transoid* to μ-CO, *J*(PP) 16, *J*(PtP) 4 213], −2.19 p.p.m. [d, P *transoid* to μ-CS, *J*(PP) 16, *J*(PtP) 2 647 Hz]; $^{13}C-\{^1H\}$ (−50 °C), δ 386.5 [d, μ-CS, *J*(PC) 71], 233.9 [d, CO, *J*(PC) 4, *J*(PtC) 77], 138—128 (Ph), 88.0 (C_5H_5), 14.1 [d, MeP, *transoid* to CS, *J*(PC) 24, *J*(PtC) 31], 10.5 p.p.m. [d, MeP, *transoid* to μ-CO, *J*(PC) 34, *J*(PtC) 49 Hz].

(*b*) A light petroleum (40 cm^3) solution of $[Pt(C_2H_4)(PMePh_2)_2]$ {0.5 mmol, prepared *in situ* from $[Pt(cod)_2]$ (0.21 g, 0.5 mmol) and $PMePh_2$ (0.14 g, 1 mmol)} at 0 °C was treated with $[Mn(CO)_2(CS)(\eta-C_5H_5)]$ (0.11 g, 0.5 mmol), and the mixture stirred (48 h). Filtration gave yellow *microcrystals* of $[MnPt(\mu-CS)(CO)_2(PMePh_2)_2(\eta-C_5H_5)]$ (2) (0.32 g, 80%) (Found: C, 49.8; H, 4.1. $C_{34}H_{31}MnO_2P_2PtS$ requires C, 50.1; H, 3.9%); m.p. 159—162 °C (decomp.); $\nu_{max.}$(CO) at 1 929s and 1 809s cm^{-1}. N.m.r.: ^1H ([$^2H_2$]dichloromethane, 25 °C), δ 1.7—2.1 (m br, 6 H, MeP), 4.38 (s, 5 H, C_5H_5), 7.18 (s, br, 20 H, Ph); $^{31}P-\{^1H\}$ ([$^2H_2$]dichloromethane–CH_2Cl_2, 25 °C), δ 16.51 p.p.m. [s, *J*(PtP) 3 623 Hz]; $^{31}P-\{^1H\}$ (−70 °C), δ 25.2 [d, P *transoid* to μ-CO, *J*(PP) 24, *J*(PtP) 4 404], 7.4 [d, P *transoid* to μ-CS, *J*(PP) 24, *J*(PtP) 2 776 Hz]; $^{13}C-\{^1H\}$ ([$^2H_2$]dichloromethane–CH_2Cl_2, −60 °C), δ 379.4 (μ-CS), 232.6 [CO, *J*(PtC) 73 Hz], 136—127 (Ph), 88.5 (C_5H_5), 8.1 p.p.m. (m br, MeP).

(*c*) In a similar manner, a light petroleum (40 cm^3) solution of $[Pt(C_2H_4)(PMe_2Ph)_2]$ {from $[Pt(cod)_2]$ (0.37 g, 0.9 mmol) and PMe_2Ph (0.25 g, 1.8 mmol)} was treated with $[Re(CO)_2(CS)(\eta-C_5H_5)]$ (0.32 g, 0.9 mmol), and the mixture stirred (24 h). Removal of product by filtration afforded pink *microcrystals* of $[PtRe(\mu-CS)(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)]$ (3) (0.46 g, 64%) (Found: C, 35.3; H, 3.5. $C_{24}H_{27}O_2PtReS$ requires C, 35.0; H, 3.3%); m.p. 120—122 °C (decomp.); $\nu_{max.}$(CO) at 1 929s and 1 847m cm^{-1}. N.m.r.: ^1H ([$^2H_2$]dichloromethane, 25 °C), δ 1.6—1.7 (m, 12 H, MeP), 5.18 (s, 5 H, C_5H_5), 7.12 (m br, 10 H, Ph); ^1H (−70 °C), δ 1.50 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 20], 1.80 [d, 6 H, MeP, *J*(PH) 10, *J*(PtH) 45 Hz], 5.18 (s, 5 H, C_5H_5), 7.22 (m br, 10 H, Ph); $^{31}P-\{^1H\}$ ([$^2H_2$]dichloromethane, 25 °C), δ 1.98 p.p.m. [s, *J*(PtP) 3 726 Hz]; $^{31}P-\{^1H\}$ (−70 °C), δ 10.63 [d, P *transoid* to μ-CO, *J*(PtP) 22, *J*(PtP) 4 558], −3.17 p.p.m. [d, P *transoid* to μ-CS, *J*(PP) 22, *J*(PtP) 2 512 Hz]; $^{13}C-\{^1H\}$ ([$^2H_2$]dichloromethane–CH_2Cl_2, −70 °C), δ 353.4 [d, CS, *J*(PC) 70, *J*(PtC) 806], 205.0 (br, CO), 139—127 (Ph), 87.9 (C_5H_5), 13.8 [d, MeP, *J*(PC) 19], 10.1 p.p.m. [d, MeP, *J*(PC) 34, *J*(PtC) 49 Hz].

Methylation of $[MnPt(\mu-CS)(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)]$ (1).—Solid $[OMe_3][BF_4]$ (0.49 g, 3.3 mmol) was added to a stirred dichloromethane (20 cm^3) solution of (1) (0.5 g, 0.7 mmol) at room temperature. After 1.5 h the mixture was filtered, and solvent was removed *in vacuo* from the filtrate to give dark red *microcrystals* of the salt $[MnPt(\mu-CSMe)(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)][BF_4]$ (4) (0.40 g, 66%) (Found: C, 36.5; H, 4.2. $C_{25}H_{30}BF_4MnO_2P_2PtS$ requires C, 36.4; H, 3.7%); $\nu_{max.}$(CO) at 1 979s and 1 859s cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), δ 1.83 [d, 6 H, MeP, *J*(PH) 10], 1.93 [d, 6 H, MeP, *J*(PH) 12 Hz], 3.20 (s, 3 H, MeS), 5.04 (s, 5 H, C_5H_5), 7.49 (m br, 10 H, Ph); $^{31}P-\{^1H\}$ ([$^2H_2$]dichloromethane–CH_2Cl_2) δ 2.82 [d, *J*(PP) 11, *J*(PtP) 3 917], −7.65 p.p.m. [d, *J*(PP) 11, *J*(PPt) 2 631 Hz]; $^{195}Pt-\{^1H\}$ (CH_2Cl_2), δ (Ξ 21.4 MHz, in a field where $SiMe_4$ is 100 MHz) 300.2 p.p.m. [d of d, *J*(PPt) 3 917 and 2 631 Hz]; $^{13}C-\{^1H\}$ ([$^2H_2$]dichloromethane–CH_2Cl_2), 384.3 [d, μ-*C*SMe, *J*(PC) 72, *J*(PtC) 812], 223.7 (CO), 134.5 [d, C^1 (C_6H_5), *J*(PC) 24], 133.5 [d, C^1 (C_6H_5), *J*(PC) 21], 131—120 (Ph), 86.5 (C_5H_5), 32.5 (SMe), 16.3 [d, MeP, *J*(PC) 34], 14.5 p.p.m. [d, MeP, *J*(PC) 31 Hz].

Crystal Structure Determination of $[MnPt(\mu-CS)(CO)_2(PMePh_2)_2(\eta-C_5H_5)]$ (2).—Prolonged cooling (−20 °C) of a saturated solution of (2) in dichloromethane–light petroleum (1 : 10) eventually afforded a good quality prism (*ca.* 0.40 × 0.24 × 0.13 mm) showing developed faces of the type ⟨010⟩ and ⟨101⟩. Diffracted intensities were recorded at room temperature for $2.9 \leqslant 2\theta \leqslant 50°$ on a Nicolet *P3m* four-circle diffractometer. Of the total 7 265 independent recorded intensities, only 4 358 had $(F_o) \geqslant 5\sigma(F_o)$, where $\sigma(F_o)$ is the standard deviation based on counting statistics, and these were used in the final refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption.

Crystal data. $C_{34}H_{31}MnO_2P_2PtS$, *M* = 815.7, Monoclinic, *a* = 16.655(4), *b* = 9.684(3), *c* = 21.409(5) Å, β = 114.57(2)°, *U* = 3 140(2) Å^3, *Z* = 4, D_c = 1.66 g cm^{-3}, *F*(000) = 1 600, space group $P2_1/c$, μ(Mo-K_α) = 50.8 cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å.

Structure solution and refinement. The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. The phenyl and cyclopentadienyl rings were treated as rigid groups [C–C (C_6H_5) 1.395, C–C (C_5H_5) 1.420, and C–H 0.960 Å], the hydrogen atoms being given a common refined isotropic temperature factor. All non-hydrogen atoms were refined with anisotropic temperature factors. Refinement by blocked-cascade least squares led to *R* 0.043 (*R'* 0.043), and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.001|F_o|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >1.0 e Å^{-3} except in the immediate neighbourhood of the Pt atom where several peaks of *ca.* 1.5 e Å^{-3} occurred. Scattering factors were from ref. 29 for C, O, and S, ref. 30 for H, and ref. 31 for Mn and Pt. All computations were carried out within the Laboratory on an 'Eclipse' Data General Minicomputer with the 'SHELXTL' system of programs.[32] The results are summarised in Tables 1—3. Observed and calculated structure factors, hydrogen atom co-ordinates, and all thermal parameters are listed in Supplementary Publication No. SUP 23316 (30 pp.).*

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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