Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 9.[1] Reactivity of the Cations $[MPt(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)]^+$ (M = Mn or Re, $PR_3 = PMe_3$ or PMe_2Ph) towards Tertiary Phosphines and the Toluene-*p*-thiolate Anion; *X*-Ray Crystal Structures of $[MnPt\{\mu-C(PMe_3)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$ * and $[MnPt(SC_6H_4Me-4)\{\mu-C(PMe_3)C_6H_4Me-4\}(\mu-CO)(CO)(PMe_3)(\eta-C_5H_5)]$ †

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The salts $[MPt(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$ (M = Mn or Re, $PR_3 = PMe_3$ or PMe_2Ph), in which a tolylidyne group bridges the metal–metal bond, readily add a molecule of tertiary phosphine to form adducts, the ^{31}P n.m.r. spectra of which suggest the formulation $[MPt\{\mu-C(PR_3)C_6H_4Me-4\}(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$. This was confirmed by a single-crystal *X*-ray diffraction study on the compound M = Mn and $PR_3 = PMe_3$, crystals of which are triclinic, with space group $P\bar{1}$ and $Z = 2$ in a unit cell of dimensions $a = 10.877(2)$, $b = 10.230(2)$, $c = 13.917(4)$ Å, $\alpha = 92.80(2)$, $\beta = 95.28(2)$, and $\gamma = 90.08(2)°$. The structure has been determined by heavy-atom methods from automated diffractometer data for $2.9 \leqslant 2\theta \leqslant 50°$, and refined to *R* 0.031 (*R′* 0.034) for 4 845 reflections. The Mn–Pt bond [2.645(1) Å] is bridged by a $C(PMe_3)C_6H_4Me-4$ group, and semi-bridged by one CO ligand [MnCO 162.0(7)°]. In the three-membered ring Mn(μ-C)Pt the Mn–C separation of 2.107(5) Å is as expected for a σ bond and is thus significantly longer than the corresponding distance [1.829(8)Å] in the precursor $[MnPt(\mu-CC_6H_4Me-4)(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$ which formally contains a C=Mn linkage. In the PMe_3 adduct the platinum atom is in an essentially planar environment [with Pt–μ-C 2.078(5) Å], while the plane Mn(μ-C)Pt is almost perpendicular to the plane defined by the atom μ-C and its ligated P and C atoms. Whereas the salt $[PtRe(\mu-CC_6H_4Me-4)(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)][BF_4]$ reacts with $Na[SC_6H_4Me-4]$ to give the expected product $[PtRe\{\mu-C(SC_6H_4Me-4)C_6H_4Me-4\}(CO)_2(PMe_2Ph)_2(\eta-C_5H_5)]$, the salts $[MnPt(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$ ($PR_3 = PMe_3$ or PMe_2Ph) undergo an unusual reaction with this reagent to afford the compounds $[MnPt(SC_6H_4Me-4)\{\mu-C(PR_3)C_6H_4Me-4\}(\mu-CO)(CO)(PR_3)(\eta-C_5H_5)]$. The structures of the latter species were revealed by their spectroscopic properties (i.r. and ^{31}P n.m.r.) and confirmed by a single-crystal *X*-ray diffraction study on the compound with $PR_3 = PMe_3$. Crystals are orthorhombic, space group $Pca2_1$ and $Z = 4$ in a unit cell of dimensions $a = 19.482(4)$, $b = 12.827(4)$, and $c = 11.649(2)$ Å. The structure has been refined to *R* 0.031 (*R′* 0.032) for 2 846 reflections ($2.9 \leqslant 2\theta \leqslant 55°$) measured at room temperature. The platinum atom is in a planar environment with distances $Pt-PMe_3$ 2.319(2), $Pt-SC_6H_4Me$ 2.365(3), Pt–μ-C 2.132(8), and Pt–Mn 2.626(1) Å. The latter bond is bridged by a CO ligand which is essentially *trans* to the S atom [C–Pt–S 170.3(3)°], while μ-C is *trans* to PMe_3 on platinum [μ-C–Pt–P 168.6(3)°]. Within the Mn(μ-C)Pt ring, the Pt–μ-C separation [2.132(8) Å] is significantly longer and the Mn–μ-C separation [2.047(9) Å] shorter than the corresponding distances in $[MnPt\{\mu-C(PMe_3)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$.

TREATMENT of the dimetallacyclopropane ring compounds $[(\eta-C_5H_5)(OC)_2M\{\mu-C(OMe)C_6H_4Me-4\}Pt(PR_3)_2]$ (M = Mn, $PR_3 = PMe_3$; M = Re, $PR_3 = PMe_3$ or PMe_2Ph) with $[OMe_3][BF_4]$ affords the salts $[(\eta-C_5H_5)(OC)_2M(\mu-CC_6H_4Me-4)Pt(PR_3)_2][BF_4]$ which contain a tolylidyne group bridging the metal–metal bond.[2] These salts react quantitatively with sodium methoxide in methanol to regenerate the neutral dimetalla-complexes with bridging $C(OMe)C_6H_4Me-4$ groups, thereby demonstrating that the alkylidyne carbon atoms in the cations are susceptible to nucleophilic attack. Hence, treatment of the salts with nucleophiles other than OMe^- could give a variety of new compounds based on the reactivity of the electrophilic carbon atoms at the dimetal centres. In this paper we describe reactions of the salts with tertiary phosphines and with the toluenethiolate anion, chosen to exemplify a neutral and an anionic nucleophile respectively.

RESULTS AND DISCUSSION

Reaction of trimethylphosphine in light petroleum with a dichloromethane solution of the salt $[MnPt(\mu-CC_6H_4Me-4)(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$ gave a deep red solution, from which a red crystalline compound (1) was isolated on addition of diethyl ether. The product was characterised by microanalysis, and by i.r. and n.m.r. spectroscopy (Tables 1 and 2). The data were in accord with (1) being the PMe_3 adduct $[MnPt\{\mu-C(PMe_3)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$. The ^{31}P n.m.r. spectrum was especially informative since it showed two resonances characteristic of a *cis*-$Pt(PMe_3)_2$ group [2] with a third signal at low field as expected for a phosphonium cation.[3]

Compounds (2)—(4) were prepared in a similar manner to (1), by adding the appropriate tertiary phosphine to the salts $[MPt(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$

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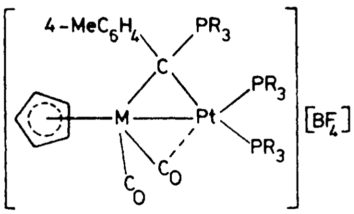
* 2,2-Dicarbonyl-2-η-cyclopentadienyl-μ-[*p*-tolyl(trimethylphosphonio)methanide-*C*]-1,1-bis(trimethylphosphine)platinummanganese(*Pt–Mn*) tetrafluoroborate.

† μ-Carbonyl-2-carbonyl-2-η-cyclopentadienyl-1-toluene-*p*-thiolato-μ-[*p*-tolyl(trimethylphosphonio)methanide-*C*]-1-(trimethylphosphine)platinum-manganese(*Pt–Mn*).

(M = Mn or Re). It was evident from the spectroscopic properties of (2)—(4) (Tables 1 and 2) that their structures were similar to that of (1). For each compound the ^{31}P n.m.r. spectrum showed three resonances, as expected for the proposed structures, with the low-field signal being assigned to the phosphonium group. Moreover, the two resonances in each spectrum due to the *cis*-$Pt(PR_3)_2$ groups are readily identified by their characteristic ^{195}Pt–^{31}P coupling constants, the larger (*ca.* 3 800 Hz) being associated with the PR_3 ligand *transoid* to the metal–metal bond.[2] The i.r. spectra of (1)—(4) show two CO stretching bands, that in each spectrum at lowest frequency (Table 1) being indicative of a semi-bridging CO ligand.



	M	PR_3
(1)	Mn	PMe_3
(2)	Mn	PMe_2Ph
(3)	Re	PMe_3
(4)	Re	PMe_2Ph

In order to confirm the structural identities of (1)—(4) an *X*-ray diffraction study was carried out on (1) for which suitable single crystals were available. The results are summarised in Tables 3—5, and the cation is shown in Figure 1 with the atomic numbering scheme. It will be seen immediately that a PMe_3 group is bonded to the carbon atom bridging the metal–metal bond, as was indicated by the ^{31}P n.m.r. spectrum.

The $Mn[\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4]Pt$ ring system present in (1) is very similar to that previously found in the ylide derivative $[(OC)_4Re\{\mu\text{-}C(PMe_3)C_6H_5\}(\mu\text{-}CO)W(CO)_4]$, prepared by adding PMe_3 to $[(OC)_5Re\text{–}W(\equiv CC_6H_5)(CO)_4]$.[4] Whereas this rhenium–tungsten compound has a bridging CO group, in (1) one of the CO ligands is semi-bridging [MnC(1)O(1) 162.0(7)°], the other being terminally bound to manganese [MnC(2)O(2) 172.6(6)°]. The Pt–C(1) distance [2.332(7) Å] may be compared with those found for the semi-bridging carbonyls in $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ [2.21(3) Å] [5] and in $[MnPt(\mu\text{-}CC_6H_4Me)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [2.31(1) Å].[2]

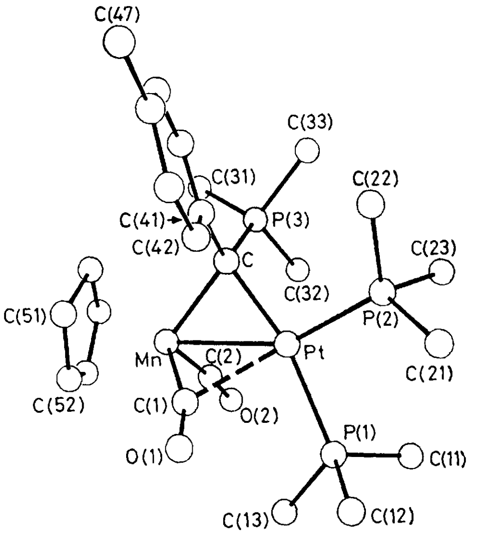


FIGURE 1 Crystal structure of the cation of complex (1), showing the atomic numbering scheme

Addition of PMe_3 to the bridging alkylidyne carbon atom of $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ to give the compound (1) produces significant changes in

TABLE 1

Analytical [a] and physical data for the dimetal complexes

Compound	M.p. (θ_c/°C) [b]	Colour	ν(CO) [c]/ cm^{-1}	Yield (%)	Analysis (%) C	Analysis (%) H
(1) $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}Pt(PMe_3)_2][BF_4]$	55—60	Dark red	1 909s, 1 811m	83	33.0 (34.3)	5.0 (4.7)
(2) $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(PMe_2Ph)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2][BF_4]$	66—70	Dark red	1 917s, 1 813w	82	45.3 (45.2)	4.5 (4.9)
(3) $[(\eta\text{-}C_5H_5)(OC)_2Re\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}Pt(PMe_3)_2][BF_4]$	148—150	Yellow	1 931s, 1 860m	80	31.0 (31.3)	4.1 (4.3)
(4) $[(\eta\text{-}C_5H_5)(OC)_2Re\{\mu\text{-}C(PMe_2Ph)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2][BF_4]$	120—122	Yellow	1 930s, 1 861	82	42.8 (42.3)	4.7 (4.1)
(5) $[(\eta\text{-}C_5H_5)(OC)Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(\mu\text{-}CO)Pt(SC_6H_4Me\text{-}4)(PMe_3)]$	120	Dark orange	1 861s, 1 730m	75	43.8 (44.8)	5.0 (5.0)
(6) $[(\eta\text{-}C_5H_5)(OC)Mn\{\mu\text{-}C(PMe_2Ph)C_6H_4Me\text{-}4\}(\mu\text{-}CO)Pt(SC_6H_4Me\text{-}4)(PMe_2Ph)]$	135—137	Dark orange	1 880s, 1 745s	54	51.1 (50.4)	5.0 (4.6)
(7) $[(\eta\text{-}C_5H_5)(OC)_2Re\{\mu\text{-}C(SC_6H_4Me\text{-}4)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$		Yellow	1 933s, 1 848s [d]	63	44.7 (45.4)	4.4 (4.1)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In dichloromethane. [d] In cyclohexane.

TABLE 2

Phosphorus-31 and ^{1}H n.m.r. data [a]

Complex	^{31}P (δ/p.p.m.) [b]	^{1}H (τ)
(1)	16.3 [d, *J*(PP) 25, *J*(PtP) 2 492], 15.8 [d of d, *J*(PP) 25 and 4, *J*(PtP) 3 819], −16.2 [d, *J*(PP) 4, *J*(PtP) 65]	2.6—3.2 (m, 4 H, C_6H_4), 5.70 (s, 5 H, C_5H_5), 7.80 (s, 3 H, MeC), 8.0—9.1 (m, 27 H, MeP)
(2)	7.2 [d, *J*(PP) 26, *J*(PtP) 2 498], 3.7 [d, *J*(PP) 26, *J*(PtP) 3 778], −13.7 [s, *J*(PtP) 73]	2.5—3.0 (m, 19 H, C_6H_4 and Ph), 5.84 (s, 5 H, C_5H_5), 7.75 (s, 3 H, MeC), 8.1—8.7 (m, 18 H, MeP)
(3)	42.0 [d of d, *J*(PP) 26 and 5, *J*(PtP) 3 928], 37.3 [d of d, *J*(PP) 26 and 4, *J*(PtP) 2 626], −40.2 [d of d, *J*(PP) 5 and 4, *J*(PtP) 41]	3.1 (m, 4 H, C_6H_4), 5.13 (s, 5 H, C_5H_5), 7.77 (s, 3 H, MeC), 8.05 [d, 9 H, MeP, *J*(PH) 12], 8.29 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 22] 8.36 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 37]
(4)	15.2 [d, *J*(PP) 24, *J*(PtP) 3 904], 13.3 [d, *J*(PP) 24, *J*(PtP) 2 528], −21.7 [s, *J*(PtP) 55]	2.4—3.0 (m, 19 H, C_6H_4 and Ph), 5.17 (s, 5 H, C_5H_5), 7.72 (s, 3 H, CMe), 7.73 [d, 3 H, MeP, *J*(PH) 11], 7.92 [d, 3 H, MeP, *J*(PH) 11], 8.38 [d, 3 H, MeP, *J*(PH) 5, *J*(PtH) 18], 8.46 [d, 3 H, MeP, *J*(PH) 5, *J*(PtH) 18], 8.76 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 37], 8.96 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 37]
(5)	12.6 [d, *J*(PP) 2, *J*(PtP) 2 974], −15.8 [d, *J*(PP) 2, *J*(PtP) 15]	2.5—3.5 (m, 8 H, C_6H_4), 5.8 (s, 5 H, C_5H_5), 7.80 (s, 6 H, MeC), 8.22 [d, 9 H, MeP, *J*(PH) 12], 8.60 [d, 9 H, MeP, *J*(PH) 9]
(6)	5.9 [s, *J*(PtP) 2 983], −17.3 (s)	2.8—3.3 (m, 18 H, C_6H_4 and Ph), 5.26 (s, 5 H, C_5H_5), 7.84 (s, 6 H, MeC), 8.32—9.2 (m, 12 H, MeP)
(7)	20.7 [s, *J*(PtP) 4 185], 12.8 [s, *J*(PtP) 2 585]	2.50—3.20 (m, 18 H, C_6H_4 and Ph), 5.02 (s, 5 H, C_5H_5), 7.69 (s, 3 H, MeC), 7.77 (s, 3 H, MeC), 8.42 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 22], 8.59 [d, 3 H, MeP, *J*(PH) 11, *J*(PtH) 41], 8.72 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 22], 9.01 [d, 3 H, MeP, *J*(PH) 11, *J*(PtH) 41]

[a] Spectra measured in [$^{2}H_1$]chloroform, coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. as positive to low frequency (high field) of 85% H_3PO_4 (external).

TABLE 3

Atomic positional (fractional co-ordinates) parameters for complex (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.164 2(1)	0.087 8(1)	0.246 2(1)
Mn	0.402 6(1)	0.039 4(1)	0.243 1(1)
P(1)	0.044 3(2)	−0.101 2(2)	0.232 0(2)
P(2)	0.002 5(1)	0.223 8(1)	0.253 1(1)
P(3)	0.332 8(2)	0.281 2(1)	0.392 0(1)
C	0.312 1(5)	0.217 8(4)	0.269 3(4)
C(1)	0.295 1(7)	−0.030 4(6)	0.151 0(5)
O(1)	0.251 7(6)	−0.083 4(6)	0.076 8(5)
C(2)	0.364 0(6)	−0.053 7(6)	0.338 5(5)
O(2)	0.350 6(6)	−0.122 5(5)	0.402 4(5)
C(11)	−0.067(1)	−0.110 9(9)	0.323 4(9)
C(12)	−0.048(1)	−0.141(1)	0.120 2(8)
C(13)	0.132(1)	−0.252 7(7)	0.247(1)
C(21)	−0.136 4(7)	0.176 2(8)	0.174 3(6)
C(22)	0.027 5(7)	0.387 7(6)	0.213 0(7)
C(23)	−0.056 4(8)	0.252 3(8)	0.373 1(6)
C(31)	0.491 0(7)	0.315 0(7)	0.443 8(5)
C(32)	0.275 0(8)	0.170 4(7)	0.474 3(5)
C(33)	0.253 6(7)	0.435 3(6)	0.414 1(5)
C(41)	0.326 0(5)	0.318 9(4)	0.196 6(3)
C(42)	0.271 6(6)	0.298 1(5)	0.101 9(4)
C(43)	0.281 4(6)	0.390 2(6)	0.032 4(4)
C(44)	0.341 0(6)	0.510 1(5)	0.055 2(4)
C(45)	0.398 0(6)	0.530 1(5)	0.148 0(4)
C(46)	0.390 5(6)	0.436 2(5)	0.216 3(4)
C(47)	0.348 2(8)	0.612 8(6)	−0.019 0(5)
C(51)	0.593 8(6)	0.054 8(7)	0.299 9(6)
C(52)	0.573 5(7)	−0.067 9(7)	0.248 3(7)
C(53)	0.535 4(7)	−0.042 6(8)	0.154 1(7)
C(54)	0.530 5(7)	0.096 8(7)	0.142 3(6)
C(55)	0.567 8(6)	0.155 9(6)	0.233 6(6)
B	9.729 8(8)	0.566 1(6)	0.301 6(5)
F(1)	0.834 3(4)	0.586 6(4)	0.365 6(3)
F(2)	0.628 1(5)	0.620 3(5)	0.339 8(4)
F(3)	0.708 0(5)	0.438 0(4)	0.283 0(4)
F(4)	0.743 1(7)	0.626 3(6)	0.218 3(4)

the dimensions of the $\overline{\text{Mn}(\mu\text{-C})\text{Pt}}$ ring system. For the former species internuclear separations are Mn–Pt 2.628(1), Mn–C 1.829(8), and Pt–C 1.967(8) Å.[2] In (1) the corresponding distances are all longer (Table 4), especially Mn–C 2.107(5) Å. The latter separation corresponds closely to that found for various manganese–carbon σ bonds.[6] These differences are to be expected since the cation of (1) contains a dimetallacyclopropane ring, whereas its precursor $[\text{MnPt}(\mu\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$ has a dimetallacyclopropene ring with formally a C=Mn bond.

The P–Pt distances in (1) are close to those measured in related structures with $\text{Pt}(\text{PMe}_3)_2$ groups, those *trans* to the bridging carbon atoms being *ca.* 0.08 Å longer than those *trans* to the metal–metal bonds.[2,7] The platinum atom in (1) is in an essentially planar environment with respect to P(1), P(2), C, and Mn, since the dihedral angle between the planes defined by P(1)P(2)Pt and CMnPt is only 7°. The plane defined by the atoms P(3)CC(41) is almost perpendicular to the dimetallacyclopropane ring $\overline{\text{MnCPt}}$ (Table 5). A similar configuration for the bridging carbon atom and its four ligated atoms has been found [7] in molecules containing the group $\overline{\text{W}[\mu\text{-C(OMe)R}]\text{Pt}}$ (R = Ph or C_6H_4Me-4). However, although this geometry suggests sp^3 hybridisation for the μ-C atom the bond angles at this atom deviate markedly from tetrahedral due to the constraints of the ring angle MnCPt of 78.4(2)°.

We have also studied reactions of the salts $[\text{MPt}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with $\text{Na}[\text{SC}_6\text{H}_4$-

TABLB 4

Bond lengths (Å) and angles (°) for complex (1)

$[(\eta\text{-}C_5H_5)(OC)_2\overline{Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}Pt}(PMe_3)_2][BF_4]$

(*a*) Distances			
Pt–Mn	2.645(1)		
Pt–C	2.078(5)	Mn–C	2.107(5)
Pt–P(1)	2.321(2)	Pt–P(2)	2.250(2)
Mn–C(1)	1.775(7)	Mn–C(2)	1.753(7)
C(1)–O(1)	1.199(8)	C(2)–O(2)	1.179(8)
Pt–C(1)	2.332(7)	C–C(41)	1.499(6)
C(41)–C(42)	1.401(7)	C(42)–C(43)	1.393(8)
C(43)–C(44)	1.395(8)	C(44)–C(45)	1.386(8)
C(45)–C(46)	1.392(7)	C(46)–C(41)	1.392(7)
C(44)–C(47)	1.516(8)	P(1)–C(11)	1.84(1)
P(1)–C(12)	1.80(1)	P(1)–C(13)	1.831(9)
P(2)–C(21)	1.834(8)	P(2)–C(22)	1.820(6)
P(2)–C(23)	1.853(8)	P(3)–C(31)	1.829(7)
P(3)–C(32)	1.803(6)	P(3)–C(33)	1.824(6)
P(3)–C	1.791(5)	Mn–C(51)	2.158(7)
Mn–C(52)	2.157(7)	Mn–C(53)	2.135(7)
Mn–C(54)	2.165(7)	Mn–C(55)	2.172(6)
C(51)–C(52)	1.42(1)	C(52)–C(53)	1.37(1)
C(53)–C(54)	1.45(1)	C(54)–C(55)	1.41(1)
C(55)–C(51)	1.43(1)	B–F (mean)	1.37(1)
(*b*) Angles			
P(1)–Pt–Mn	112.8(1)	P(2)–Pt–Mn	152.6(1)
P(2)–Pt–P(1)	94.6(1)	C–Pt–Mn	51.3(1)
C–Pt–P(1)	163.1(1)	C–Pt–P(2)	101.6(1)
C(1)–Pt–Mn	41.2(2)	C(1)–Pt–P(1)	85.0(2)
C(1)–Pt–P(2)	148.1(2)	C(1)–Pt–C	83.9(2)
C–Mn–Pt	50.3(1)	C(51)–Mn–Pt	153.8(2)
C(51)–Mn–C	109.9(2)	C(52)–Mn–Pt	159.9(2)
C(52)–Mn–C	148.0(3)	C(52)–Mn–C(51)	38.5(3)
C(53)–Mn–Pt	142.7(3)	C(53)–Mn–C	140.0(3)
C(53)–Mn–C(51)	63.3(3)	C(53)–Mn–C(52)	37.3(3)
C(54)–Mn–Pt	130.0(2)	C(54)–Mn–C	101.0(2)
C(54)–Mn–C(51)	64.3(3)	C(54)–Mn–C(52)	64.7(3)
C(54)–Mn–C(53)	39.3(3)	C(55)–Mn–Pt	135.7(2)
C(55)–Mn–C	86.6(2)	C(55)–Mn–C(51)	38.6(3)
C(55)–Mn–C(52)	64.4(3)	C(55)–Mn–C(53)	63.8(3)
C(55)–Mn–C(54)	37.8(3)	C(1)–Mn–Pt	59.9(2)
C(1)–Mn–C	98.8(2)	C(1)–Mn–C(51)	146.3(3)
C(1)–Mn–C(52)	110.2(3)	C(1)–Mn–C(53)	83.3(3)
C(1)–Mn–C(54)	93.7(4)	C(1)–Mn–C(55)	130.7(3)
C(2)–Mn–Pt	78.0(2)	C(2)–Mn–C	102.6(3)
C(2)–Mn–C(51)	92.6(3)	C(2)–Mn–C(52)	86.8(3)
C(2)–Mn–C(53)	116.6(3)	C(2)–Mn–C(54)	151.4(3)
C(2)–Mn–C(55)	128.5(3)	C(2)–Mn–C(1)	98.3(4)
C(11)–P(1)–Pt	114.4(3)	C(12)–P(1)–Pt	119.2(4)
C(12)–P(1)–C(11)	103.5(5)	C(13)–P(1)–Pt	114.5(3)
C(13)–P(1)–C(11)	102.5(6)	C(13)–P(1)–C(12)	100.6(5)
C(21)–P(2)–Pt	115.7(3)	C(22)–P(2)–Pt	115.1(2)
C(22)–P(2)–C(21)	100.1(4)	C(23)–P(2)–Pt	116.5(2)
C(23)–P(2)–C(21)	103.3(4)	C(23)–P(2)–C(22)	104.1(4)
C(32)–P(3)–C(31)	103.4(4)	C(33)–P(3)–C(31)	103.4(3)
C(33)–P(3)–C(32)	105.1(4)	C–P(3)–C(31)	117.3(3)
C–P(3)–C(32)	112.1(3)	C–P(3)–C(33)	114.3(3)
Mn–C–Pt	78.4(2)	P(3)–C–Pt	112.0(3)
P(3)–C–Mn	114.6(2)	C(41)–C–Pt	118.4(3)
C(41)–C–Mn	115.2(3)	C(41)–C–P(3)	113.7(3)
Mn–C(1)–Pt	78.9(2)	O(1)–C(1)–Pt	118.5(5)
O(1)–C(1)–Mn	162.0(7)	O(2)–C(2)–Mn	172.6(6)
C(42)–C(41)–C	119.8(4)	C(46)–C(41)–C	124.3(4)
C(46)–C(41)–C(42)	115.9(5)	C(43)–C(42)–C(41)	121.5(5)
C(44)–C(43)–C(42)	121.5(5)	C(45)–C(44)–C(43)	117.3(5)
C(47)–C(44)–C(43)	121.9(5)	C(47)–C(44)–C(45)	120.8(5)
C(46)–C(45)–C(44)	120.8(5)	C(45)–C(46)–C(41)	122.8(5)
C(52)–C(51)–Mn	70.7(4)	C(55)–C(51)–Mn	71.2(4)
C(55)–C(51)–C(52)	108.1(7)	C(51)–C(52)–Mn	70.8(4)
C(53)–C(52)–Mn	70.4(4)	C(53)–C(52)–C(51)	107.4(7)
C(52)–C(53)–Mn	72.2(4)	C(54)–C(53)–Mn	71.5(4)
C(54)–C(53)–C(52)	110.2(7)	C(53)–C(54)–Mn	69.2(4)
C(55)–C(54)–Mn	71.4(4)	C(55)–C(54)–C(53)	106.0(7)
C(51)–C(55)–Mn	70.2(4)	C(54)–C(55)–Mn	70.8(4)
C(54)–C(55)–C(51)	108.3(6)	F(2)–B–F(1)	110.3(5)
F(3)–B–F(1)	111.0(6)	F(3)–B–F(2)	108.2(6)
F(4)–B–F(1)	110.1(6)	F(4)–B–F(2)	106.9(6)
F(4)–B–F(3)	110.2(6)		

TABLE 5

Some least-squares planes for complex (1) in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal co-ordinates; distances (Å) of atoms from the planes are given in square brackets

Plane (i): Pt, Mn, P(1), P(2), C

$$-0.279x - 1.259y + 13.848z = 3.277$$

[Pt −0.02, Mn −0.07, P(1) 0.05, P(2) −0.05, C 0.10, C(1) −1.24, C(2) 1.38]

Plane (ii): Pt, Mn, C(1), O(1)

$$1.688x + 8.618y - 7.910z = -0.916$$

[Pt 0.003, Mn 0.01, C(1) −0.04, O(1) 0.02]

Plane (iii): P(3), C, C(41)

$$10.652x - 2.066y - 0.768z = 2.663$$

Plane (iv): Mn, Pt, C

$$-0.271x - 2.182y + 13.696z = 3.135$$

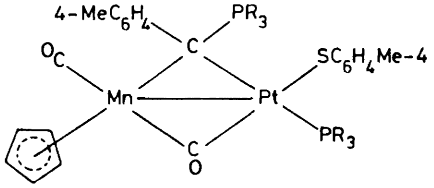
Plane (v): Pt, P(1), P(2)

$$-0.180x - 0.935y + 13.865z = 3.301$$

Angles (°) between the planes:

(i)—(ii)	128	(i)—(iii)	89
(iii)—(iv)	88	(iv)—(v)	7

Me-4] as a possible route to dimetal complexes having the as yet unknown μ-C(SR)R ligand. Addition of solid $Na[SC_6H_4Me\text{-}4]$ to a dichloromethane solution of $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ at room temperature afforded a dark orange crystalline compound (5). It was immediately obvious from the ^{31}P n.m.r. spectrum that (5) did not have the anticipated structure with $Pt(PMe_3)_2$ and $\mu\text{-}C(SC_6H_4Me\text{-}4)C_6H_4Me\text{-}4$ groups present. The spectrum (Table 2) showed the presence of a $Pt(PMe_3)$ group, the value of $J(^{195}Pt\text{-}^{31}P)$ being such as to indicate that the PMe_3 ligand was *cisoid* to the Pt–Mn bond and *transoid* to the μ-C atom. Moreover, the second resonance at δ −15.8 p.p.m., with J(PtP) only 15 Hz, is that of a phosphonium group of the type established in (1). This unexpected result suggested the structure shown, with the $SC_6H_4Me\text{-}4$ ligand attached to platinum causing a PMe_3 group to migrate to the bridging carbon atom. A compound (6) of evidently similar structure was prepared by treating $Na[SC_6H_4Me\text{-}4]$ with $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$. The ^{31}P n.m.r. spectrum of this product also showed one of its two signals to low field. Both (5) and (6) have a band in their i.r. spectra corresponding to a bridging CO group.



	PR_3
(5)	PMe_3
(6)	PMe_2Ph

In order to confirm the molecular structures of these complexes an X-ray diffraction study was carried out on (5) for which suitable crystals were available. The

TABLE 6

Atomic positional (fractional co-ordinates) parameters for complex (5), with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.001 6(1)	0.310 6(1)	0.000 0 *
Mn	0.131 6(1)	0.319 3(1)	0.058 6(2)
P(1)	−0.068 8(1)	0.456 0(2)	−0.013 6(2)
P(2)	0.063 3(1)	0.088 5(2)	0.084 8(2)
S	−0.075 8(1)	0.192 7(2)	−0.087 2(3)
C	0.079 8(4)	0.194 6(6)	−0.008 5(11)
C(1)	0.133 1(4)	0.277 5(8)	0.202(1)
O(1)	0.138 1(4)	0.262 7(7)	0.300 2(7)
C(2)	0.062 0(4)	0.409 5(8)	0.103 7(8)
O(2)	0.047 7(3)	0.482 9(6)	0.158 7(6)
C(11)	−0.141 3(5)	0.454 2(8)	−0.113 9(9)
C(12)	−0.108 5(5)	0.506(1)	0.118(1)
C(13)	−0.021 0(6)	0.567 5(9)	−0.067(1)
C(21)	0.025 7(5)	−0.022 5(8)	0.016(1)
C(22)	0.005 2(5)	0.118(1)	0.198(1)
C(23)	0.136 9(5)	0.032 2(8)	0.156(1)
C(31)	0.099 7(4)	0.159 2(7)	−0.127 7(8)
C(32)	0.146 3(5)	0.075 2(8)	−0.147 9(9)
C(33)	0.166 0(5)	0.047 7(8)	−0.257(1)
C(34)	0.142 9(4)	0.099 2(7)	−0.353 4(9)
C(35)	0.098 1(5)	0.184 5(8)	−0.335 2(9)
C(36)	0.076 9(5)	0.212 7(8)	−0.225 5(8)
C(37)	0.165 1(6)	0.069 0(9)	−0.472 1(8)
C(41)	−0.158 4(5)	0.210 3(7)	−0.027 9(8)
C(42)	−0.171 6(5)	0.249 7(9)	0.078 0(9)
C(43)	−0.237 1(5)	0.266 3(9)	0.119(1)
C(44)	−0.294 1(5)	0.244 2(8)	0.052(1)
C(45)	−0.282 2(5)	0.199 4(9)	−0.057(1)
C(46)	−0.216 3(4)	0.181 2(8)	−0.097(1)
C(47)	−0.366 6(5)	0.261 8(9)	0.094(1)
C(51)	0.215 9(5)	0.422(1)	0.088(1)
C(52)	0.241 4(5)	0.323(1)	0.056(2)
C(53)	0.219 6(5)	0.297(1)	−0.052(1)
C(54)	0.181 0(5)	0.380(1)	−0.096(1)
C(55)	0.178 4(5)	0.457 1(8)	−0.008(2)

* Co-ordinate fixed at 0.000.

TABLE 7

Bond lengths (Å) and angles (°) for (5) $[(\eta\text{-}C_5H_5)(OC)Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(\mu\text{-}CO)Pt(SC_6H_4Me\text{-}4)(PMe_3)]$ *

(*a*) Distances

Pt–Mn	2.626(1)	Pt–P(1)	2.319(2)
Pt–S	2.365(3)	Pt–C	2.132(8)
Pt–C(2)	2.110(9)	Mn–C	2.047(9)
Mn–C(1)	1.76(1)	Mn–C(2)	1.859(9)
Mn–C(51)	2.13(1)	Mn–C(52)	2.139(9)
Mn–C(53)	2.16(1)	Mn–C(54)	2.18(1)
Mn–C(55)	2.13(1)	P(1)–C(11)	1.83(1)
P(1)–C(12)	1.83(1)	P(1)–C(13)	1.82(1)
P(2)–C	1.77(1)	P(2)–C(21)	1.79(1)
P(2)–C(22)	1.78(1)	P(2)–C(23)	1.81(1)
S–C(41)	1.766(9)	C–C(31)	1.51(2)
C(1)–O(1)	1.16(1)	C(2)–O(2)	1.17(1)
C(31)–C(32)	1.43(1)	C(32)–C(33)	1.37(2)
C(33)–C(34)	1.38(2)	C(34)–C(35)	1.41(1)
C(35)–C(36)	1.39(1)	C(36)–C(31)	1.40(1)
C(34)–C(37)	1.50(1)	C(41)–C(42)	1.36(1)
C(42)–C(43)	1.38(1)	C(43)–C(44)	1.39(2)
C(44)–C(45)	1.41(2)	C(45)–C(46)	1.39(1)
C(46)–C(41)	1.44(1)	C(44)–C(47)	1.52(1)
C(51)–C(52)	1.42(2)	C(52)–C(53)	1.37(2)
C(53)–C(54)	1.40(2)	C(54)–C(55)	1.42(2)
C(55)–C(51)	1.41(2)		

(*b*) Angles

TABLE 7 (*continued*)

P(1)–Pt–Mn	123.7(1)	P(2)–Pt–P(1)	160.9(1)
S–Pt–Mn	138.9(1)	S–Pt–P(1)	96.2(1)
C–Pt–Mn	49.6(2)	C–Pt–P(1)	168.6(3)
C–Pt–S	89.4(2)	C(2)–Pt–Mn	44.6(2)
C(2)–Pt–P(1)	83.4(3)	C(2)–Pt–S	170.3(3)
C(2)–Pt–C	92.7(4)	C–Mn–Pt	52.5(2)
C(1)–Mn–Pt	104.5(3)	C(1)–Mn–C	97.7(5)
C(2)–Mn–Pt	52.8(3)	C(2)–Mn–C	103.5(4)
C(2)–Mn–C(1)	86.1(4)	C(51)–Mn–Pt	144.2(3)
C(51)–Mn–C	157.4(4)	C(51)–Mn–C(1)	91.4(5)
C(51)–Mn–C(2)	97.7(4)	C(52)–Mn–Pt	164.1(5)
C(52)–Mn–C	120.2(4)	C(52)–Mn–C(1)	90.1(5)
C(52)–Mn–C(2)	136.2(5)	C(52)–Mn–C(51)	38.7(5)
C(53)–Mn–Pt	127.1(3)	C(53)–Mn–C	93.5(4)
C(53)–Mn–C(1)	121.1(5)	C(53)–Mn–C(2)	145.8(5)
C(53)–Mn–C(51)	64.2(5)	C(53)–Mn–C(52)	37.2(6)
C(54)–Mn–Pt	103.1(3)	C(54)–Mn–C	100.6(5)
C(54)–Mn–C(1)	152.4(4)	C(54)–Mn–C(2)	109.3(4)
C(54)–Mn–C(51)	64.5(5)	C(54)–Mn–C(52)	62.8(5)
C(54)–Mn–C(53)	37.5(5)	C(55)–Mn–Pt	110.6(3)
C(55)–Mn–C	136.0(6)	C(55)–Mn–C(1)	126.3(6)
C(55)–Mn–C(2)	84.2(4)	C(55)–Mn–C(51)	38.5(6)
C(55)–Mn–C(52)	63.4(5)	C(55)–Mn–C(53)	63.4(5)
C(55)–Mn–C(54)	38.4(6)	C(11)–P(1)–Pt	119.3(3)
C(12)–P(1)–Pt	118.2(4)	C(12)–P(1)–C(11)	102.2(4)
C(13)–P(1)–Pt	110.7(4)	C(13)–P(1)–C(11)	100.7(5)
C(13)–P(1)–C(12)	103.3(6)	C(21)–P(2)–C	114.4(6)
C(22)–P(2)–C	113.9(6)	C(22)–P(2)–C(21)	103.9(6)
C(23)–P(2)–C	116.4(4)	C(23)–P(2)–C(21)	102.2(5)
C(23)–P(2)–C(22)	104.6(5)	C(41)–S–Pt	109.3(3)
Mn–C–Pt	77.8(3)	P(2)–C–Pt	112.2(5)
P(2)–C–Mn	117.1(6)	C(31)–C–Pt	115.8(7)
C(31)–C–Mn	117.3(6)	C(31)–C–P(2)	112.3(6)
O(1)–C(1)–Mn	171(1)	Mn–C(2)–Pt	82.6(4)
O(2)–C(2)–Pt	131.5(6)	O(2)–C(2)–Mn	145.9(7)
C(32)–C(31)–C	122.7(8)	C(36)–C(31)–C	121.2(8)
C(36)–C(31)–C(32)	115.9(9)	C(33)–C(32)–C(31)	121.6(9)
C(34)–C(33)–C(32)	122.7(9)	C(35)–C(34)–C(33)	116.6(9)
C(33)–C(34)–C(37)	122.3(9)	C(37)–C(34)–C(35)	121.1(9)
C(36)–C(35)–C(34)	121.5(9)	C(35)–C(36)–C(31)	121.6(9)
C(42)–C(41)–S	125.2(7)	C(46)–C(41)–S	117.5(7)
C(46)–C(41)–C(42)	117.3(8)	C(43)–C(42)–C(41)	123.3(9)
C(44)–C(43)–C(42)	121(1)	C(45)–C(44)–C(43)	117.5(9)
C(47)–C(44)–C(43)	122(1)	C(47)–C(44)–C(45)	121(1)
C(46)–C(45)–C(44)	122(1)	C(45)–C(46)–C(41)	119(1)
C(52)–C(52)–Mn	70.9(7)	C(55)–C(51)–Mn	70.9(6)
C(55)–C(51)–C(52)	106(1)	C(51)–C(52)–Mn	70.4(6)
C(53)–C(52)–Mn	72.4(6)	C(53)–C(52)–C(51)	110(1)
C(52)–C(53)–Mn	70.4(7)	C(54)–C(53)–Mn	71.9(7)
C(54)–C(53)–C(52)	109(1)	C(53)–C(54)–Mn	70.6(7)
C(55)–C(54)–Mn	69.0(7)	C(55)–C(54)–C(53)	107(1)
C(51)–C(55)–Mn	70.6(8)	C(54)–C(55)–Mn	72.6(6)
C(54)–C(55)–C(51)	109(1)		

* Methyl hydrogen atoms were refined as rigid methyl groups with C(sp^3)–H 1.08 Å and H–C–H 109.5°. Aromatic hydrogen atoms were included in calculated positions with C(sp^2)–H 1.08Å.

TABLE 8

Some least-squares planes for complex (5) in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal co-ordinates; distances (Å) of atoms from the planes are given in square brackets

Plane (i): Pt, Mn, C
$-4.592x - 3.880y + 10.759z = 1.213$
[P(1) −0.37, S −0.13, C(2) 0.46]

Plane (ii): Pt, Mn, C(2), O(2)
$-3.647x - 7.490y + 9.202z = -2.334$
[Pt 0.00, Mn 0.001, C(2) 0.005, O(2) 0.002]

Plane (iii): P(2), C, C(31)
$18.747x - 0.125y + 3.169z = 1.445$

Plane (iv): Pt, Mn, P(1), S, C, C(2)
$-6.370x - 4.021y + 10.386z = -1.308$
[Pt 0.049, Mn −0.21, P(1) −0.23, S 0.11, C −0.07, C(2) 0.34]

Plane (v): Pt, S, P(1)
$-7.621x - 2.717y + 10.433z = -0.856$

Angles (°) between the planes:

(i)—(ii)	162	(i)—(iii)	88
(i)—(v)	10	(iii)—(iv)	94

results are summarised in Tables 6—8, and the molecular structure with the atomic numbering scheme is shown in Figure 2. It will be seen that in (5) a $C(PMe_3)C_6H_4Me$-4 group bridges the manganese–platinum bond, in an arrangement similar to that found in (1). The Mn–Pt bonds in the two compounds are very similar in length. In (5), however, the Pt–μ-C separation is significantly longer and the Mn–μ-C separation shorter than the corresponding distances in (1). A CO ligand in (5) is fully bridging [MnC(2)O(2) 145.9(7)°, Pt–C(2) 2.110(9) Å] in contrast with the semi-bridging CO in (1) [MnC(1)O(1) 162.0(7)° and Pt–C(1) 2.332(7) Å]. Even the second CO ligand in (5) shows a greater deviation from MnCO linearity than that in (1).

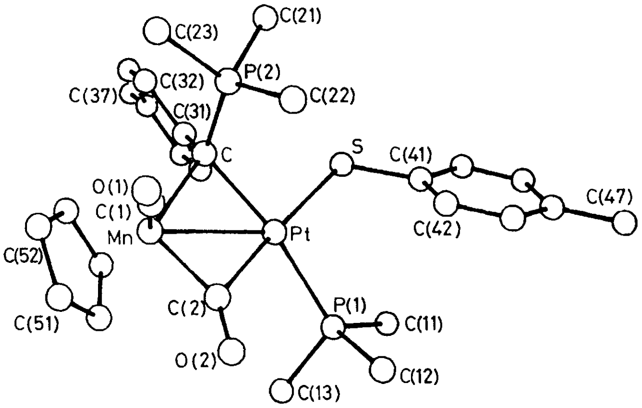


FIGURE 2 Crystal structure of complex (5), showing the atomic numbering scheme

The Pt atom in (5) is bonded to PMe_3 and to SC_6H_4Me-4 groups, with the former ligand *trans* to the bridging carbon atom [P(1)PtC 168.6(3)°] and the latter *cis* [SPtC 89.4(2)°], as was indicated by the *J*(PtP) value from the ^{31}P n.m.r. spectrum, mentioned above. The P(1)–Pt separations in (1) and (5) are the same within experimental error. The Pt–S bond in (5) [2.365(3) Å] is very similar in length to that found in several complexes containing Pt–SR groups, *e.g.* *trans*-$[Pt(SPh)_2(PBu^n{}_3)_2]$ [2.355(8) Å],[8] (*E*)-$[Pt(SPh)\{C(SO)SPh\}(PPh_3)_2]$ [2.379(4) Å],[9] and $[PtCl(SC_6F_5)\{C_6H_4(CH{=}CH_2)NMe_2\text{-}1,2\}]$ [2.304(4) Å].[10] In (5) the Pt atom is in an essentially planar environment, the dihedral angle between the two planes PtSP(1) and PtMnC being only 10°.

The geometry at the bridging carbon atom in (5) is very similar to that in (1). In particular, the plane of the dimetallacyclopropane ring in (5) is at 88° to that of the plane P(2)CC(31); the corresponding dihedral angle in (1) is also 88°. The bond angles at C in the two molecules are very similar (Tables 4 and 7).

In contrast with the behaviour of the manganese salts, the rhenium salt $[PtRe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ reacted with $Na[SC_6H_4Me\text{-}4]$ to give a compound $[PtRe\{\mu\text{-}C(SC_6H_4Me\text{-}4)C_6H_4Me\text{-}4\}(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (7), in which the toluenethiolate group is attached to the bridging carbon atom. Evidence for this structure is firmly based on the spectroscopic properties. There is no band in the i.r. spectrum of (7) corresponding to a bridging CO ligand. Moreover, the ^{31}P n.m.r. spectrum (Table 2) establishes the presence of a *cis*-$Pt(PMe_2Ph)_2$ group with the expected ^{31}P–^{195}Pt *J* values.

Whereas the formation of (7) is readily understandable, since it parallels the behaviour of the cation $[PtRe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]^+$ towards OMe^- ion, where attack on the bridging alkylidyne carbon atom also occurs, the isolation of complexes with structures (5) and (6) is unexpected. There is insufficient evidence to establish a mechanism for the synthesis of (5) and (6), but during the reaction between $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ and $Na[SC_6H_4Me\text{-}4]$, bands were observed in the i.r. spectrum at 1 915 and 1 813 cm^{-1}, which are very similar to those observed in the spectrum of (7). This might be consistent with the presence of an intermediate $[MnPt\{\mu\text{-}C(SC_6H_4Me\text{-}4)C_6H_4Me\text{-}4\}(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ which subsequently undergoes exchange of PMe_2Ph and SC_6H_4Me-4 between μ-C and Pt bonded sites.

EXPERIMENTAL

Instrumentation used and experimental techniques employed were as described earlier.[2,7] Light petroleum refers to that fraction of b.p. 40—60 °C. Analytical data and yields for the new compounds are given in Table 1.

The complex $[MnPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$, required as a precursor to complexes (2) and (6) *via* the salt $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$, was prepared as follows. Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was dissolved in light petroleum (40 cm^3) saturated with ethylene at 0 °C, and PMe_2Ph (2 mmol) was added to generate $[Pt(C_2H_4)(PMe_2Ph)_2]$ *in situ*. The solution was then treated with $[Mn\{C(OMe)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]$ (0.31 g, 1 mmol), and the mixture stirred for 48 h. The precipitate was removed by filtration affording yellow *microcrystals* of $[MnPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (0.52 g, 66%), m.p. 162—163 °C (Found: C, 49.0; H, 4.9. $C_{32}H_{37}MnO_3P_2Pt$ requires C, 49.2; H, 4.8%); $\nu_{max.}$ (CH_2Cl_2) at 1 861s and 1 797s cm^{-1}. The ^1H n.m.r. spectrum (in $[^2H_1]$chloroform) showed resonances at τ 2.39—3.32 (m, 14 H, C_6H_5 and C_6H_4), 5.77 (s, 5 H, C_5H_5), 6.53 (s, 3 H, OMe), 7.71 (s, 3 H, Me-4), and 8.32—9.32 (m, 12 H, MeP). The ^{31}P-$\{^1H\}$ n.m.r. spectrum (in $[^2H_1]$chloroform) showed resonances at δ 6.2 [d, *J*(PP) 9, *J*(PtP) 4 714] and 11.6 p.p.m. [d, *J*(PP) 9, *J*(PtP) 2 641 Hz].

Synthesis of the Complexes $[MPt\{\mu\text{-}C(PR_3)C_6H_4Me\text{-}4\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$.—(*a*) A solution of PMe_3 (0.023 g, 0.30 mmol) in light petroleum (10 cm^3) was added to the salt $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ [2] (0.22 g, 0.30 mmol) in dichloromethane (10 cm^3). The deep red solution was stirred (3 h) and then concentrated *in vacuo* to *ca.* 3 cm^3. Slow addition of diethyl ether (10 cm^3) afforded red *crystals* of $[MnPt\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (1) (0.2 g).

A similar method was used to isolate *crystals* of $[MnPt\{\mu\text{-}C(PMe_2Ph)C_6H_4Me\text{-}4\}(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ (2) (0.66 g). For this synthesis the hitherto unreported salt $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ was prepared as oily red *microcrystals* [i.r. (CH_2Cl_2), ν_{CO} (max.)

at 1 995vs and 1 839s cm^{-1}. N.m.r. ([^{2}H$_2$]dichloromethane): ^{31}P-{^{1}H}, δ 2.2 and -5.8 p.p.m. [J(PtP) 4 119 and 2 639 Hz]; ^{13}C-{^{1}H}, δ 422 [μ-C, J(PC) 70 Hz], 226 (CO), 157 (C^1 of C$_6$H$_4$), 139.6, 130.6, 129.3, 128.3, 127.6, 119 (Ph), 89.5 (C$_5$H$_5$), 20.1 (CH$_3$C$_6$), 12.7, 12.2, 11.6, 11.4, and 11.0 (Me) p.p.m.] by treating [MnPt{μ-C(OMe)C$_6$H$_4$Me}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] (0.5 mmol) in acetonitrile (10 cm^3) with [OMe$_3$][BF$_4$] (2.5 mmol).

(*b*) Solid [OMe$_3$][BF$_4$] (0.049 g, 0.33 mmol) was added to a dichloromethane (20 cm^3) solution of [PtRe{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] [2] (0.24 g, 0.30 mmol), and the mixture stirred (2 h) at room temperature. After filtration the solution was evaporated to afford a red solid which was washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. The solid was dissolved in dichloromethane (20 cm^3) and PMe$_3$ (0.6 mmol) in light petroleum (10 cm^3) was added. The mixture was stirred (1 h) and then filtered. The filtrate was evaporated *in vacuo* to *ca*. 5 cm^3. Addition of diethyl ether (15 cm^3) gave yellow *microcrystals* of [PtRe{μ-C(PMe$_3$)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (3) (0.22 g).

The compound [PtRe{μ-C(PMe$_2$Ph)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)][BF$_4$] (4) (0.27 g) was similarly prepared by adding PMe$_2$Ph (0.3 mmol) to the salt [PtRe(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.3 mmol) in dichloromethane (30 cm^3).

Reactions of Na[SC$_6$H$_4$Me-4] *with the Salts* [MPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (M = Mn *or* Re).—(*a*) A solution of [MnPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.216 g, 0.304 mmol) in dichloromethane (20 cm^3) was treated with solid Na[SC$_6$H$_4$Me-4] (0.088 g, 0.6 mmol). The deep red solution was stirred (4 h), gradually turning orange in colour. Solvent was removed *in vacuo* and the residue dissolved in toluene and chromatographed on alumina. Elution with toluene afforded a single orange-red band which was collected and concentrated *in vacuo* to *ca*. 1 cm^3. Addition of light petroleum afforded dark orange *crystals* of [(η-C$_5$H$_5$)(OC)$\overline{\mathrm{Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(\mu\text{-}CO)Pt}}$(SC$_6H_4$Me-4)(PMe$_3$)] (5) (0.17 g, 75%).

A similar method was used to prepare [MnPt(SC$_6$H$_4$Me-4){μ-C(PMe$_2$Ph)C$_6$H$_4$Me-4}(μ-CO)(CO)(PMe$_2$Ph)(η-C$_5$H$_5$)] (6).

(*b*) To a suspension of the complex [PtRe{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] (0.26 g, 0.3 mmol) in methanol (10 cm^3) was added solid [OMe$_3$][BF$_4$] (0.48 g, 0.33 mmol). The yellow suspension immediately dissolved affording a deep red solution of the salt [PtRe(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)][BF$_4$].[2] Solvent was removed *in vacuo* and the residue was extracted with CH$_2$Cl$_2$ (15 cm^3) and filtered. Solid Na[SC$_6$H$_4$Me-4] (0.24 g, 1.5 mmol) was added to the resulting clear red solution which immediately became yellow. Solvent was removed *in vacuo* and the residue was chromatographed on alumina. Elution with dichloromethane–hexane (1 : 1) afforded a single yellow band which on concentration and addition of hexane afforded yellow *crystals* of [PtRe{μ-C(SC$_6$H$_4$Me-4)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] (7) (0.19 g).

Crystal Structure Determinations.—Compound (1). Crystals were grown by slow evaporation of CH$_2$Cl$_2$–MeOH–Et$_2$O solutions, and that used for data collection was a thin dark red parallelepiped of dimensions 0.63 × 0.20 × 0.08 mm. Diffracted intensities were recorded (room temperature, $2.9 \leqslant 2\theta \leqslant 50°$) on a Nicolet *P*3 four-circle diffractometer. Of the total 5 447 unique recorded intensities, 4 845 had $|F| \geqslant 5\sigma(F)$, where $\sigma(F)$ 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. Computations were carried out with the 'SHELX' system of programs.[11]

Crystal data. C$_{24}$H$_{39}$BF$_4$MnO$_2$P$_3$Pt, $M = 789.3$, Triclinic, $a = 10.877(2)$, $b = 10.230(2)$, $c = 13.917(4)$ Å, $\alpha = 92.80(2)$, $\beta = 95.28(2)$, $\gamma = 90.08(2)°$, $U = 1\,540.1(6)$ Å^3, D_m not measured, $Z = 2$, $D_c = 1.70$ g cm^{-3}, $F(000) = 776$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 49.3 cm^{-1}, space group $P\bar{1}$.

Compound (5). Crystals were grown by slow evaporation of CH$_2$Cl$_2$–Me$_2$CO solutions, and that used for data collection was a dark orange parallelepiped of dimensions 0.15 × 0.09 × 0.45 mm. Data were collected at room temperature for $2.9 \leqslant 2\theta \leqslant 55°$. Of the total 3 956 unique recorded intensities, 2 846 had $|F| \geqslant 5\sigma(F)$ and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption. Computations were made with the 'SHELX' system of programs.[11]

Crystal data. C$_{28}$H$_{37}$MnO$_2$P$_2$PtS, $M = 749.6$, Orthorhombic, $a = 19.482(4)$, $b = 12.827(4)$, $c = 11.649(2)$ Å, $U = 2\,911(1)$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 1\,480$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 52.1 cm^{-1}, space group $Pca2_1$.

Structure solution and refinement. The data for the two compounds were treated by similar methods, those for (5) being given in square brackets. Structures were solved by heavy-atom methods using the 'SHELX' system [11] of programs. All atoms, except hydrogens, were located by successive electron-density difference syntheses. For (5) the hydrogen atoms were included at positions calculated for rigid group atoms, and only common temperature factors for chemically equivalent hydrogen atoms were refined. For (1) the hydrogen atoms were not included in the refinement. Refinement converged at R 0.031 (R' 0.034) [R 0.031 (R' 0.032)], with a mean shift-to-error ratio in the final cycle of 0.15 [0.10]. Satisfactory weighting schemes were of the form $w^{-1} = 0.901[\sigma^2(F) + 0.001|F_o|^2]$ $[0.862\{\sigma^2(F) + 0.001|F_o|^2\}]$ where $\sigma(F)$ is the estimated error based on counting statistics only. The final electron-density difference synthesis showed no peaks >1.2 or < -1.2 [> 1.5 or < -1.5] e Å^{-3}. Scattering factors were from ref. 12 for C, O, P, and S, ref. 13 for hydrogen, and ref. 14 for Mn and Pt, including corrections for the effects of anomalous dispersion. Observed and calculated structure factors, anisotropic temperature factors for all non-hydrogen atoms, and hydrogen-atom positional parameters for compound (5) are listed in Supplementary Publication No. SUP 23152 (40 pp.).*

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