Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 2.[1] Formation of Manganese–Platinum, –Palladium, and –Nickel Compounds, and the Crystal Structures of Two Forms of $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{—}2\text{-}\eta\text{-}C{=}CH\text{-}CH_2\text{-}CH_2\text{-}O)\}Pt(PMe_3)_2]$ †

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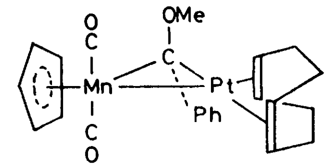
The mononuclear manganese–carbene complex $[Mn\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$ reacts with the compound $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) to give the dimetal complex $[(OC)_2(\eta\text{-}C_5H_5)Mn\{\mu\text{-}C(OMe)Ph\}Pt(cod)]$. Similarly, $[Pt(C_2H_4)_3]$, $[Pd(dba)_2]$ (dba = dibenzylideneacetone), and $[Ni(cod)_2]$, each treated with 2 mol of PMe_3, react with the mononuclear manganese compound to yield heteronuclear dimetal complexes $[(OC)_2(\eta\text{-}C_5H_5)Mn\{\mu\text{-}C(OMe)Ph\}M(PMe_3)_2]$ (M = Ni, Pd, or Pt). The PMe_3 ligand *trans* to the μ-C(OMe)Ph group in the palladium and platinum compounds is readily replaced by $CNBu^t$. The binuclear manganese–carbene complex $[(OC)_5Mn\text{–}Mn(C\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}O)(CO)_4]$ reacts with $[Pt(C_2H_4)_3]$, treated with 2 mol of PMe_3, to form two crystalline forms of a compound $[(OC)_4Mn(\mu\text{-}C_4H_5O)Pt(PMe_3)_2]$. Single-crystal *X*-ray diffraction studies have been carried out (200 K) on these geometrical isomers. The red form is monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with lattice parameters $a = 9.357(5)$, $b = 12.844(10)$, $c = 15.989(9)$ Å, and $\beta = 98.14(4)°$. The structure has been refined to R 0.023 (R' 0.030) for 3 274 reflections to $2\theta \leqslant 50°$ (Mo-K_α *X*-radiation). The yellow form is triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 9.429(5)$, $b = 12.113(4)$, $c = 9.729(6)$ Å, $\alpha = 93.97(14)$, $\beta = 115.45(4)$, and $\gamma = 98.83(3)°$. The structure has been refined to R 0.055 (R' 0.073) for 3 350 reflections to $2\theta \leqslant 50°$ (Mo-K_α *X*-radiation). In both isomers a cyclic $1\text{-}\sigma,1\text{—}2\text{-}\eta\text{-}C{=}CH\text{–}CH_2\text{–}CH_2\text{–}O$ ligand bridges a platinum–manganese bond such that the manganese atom is η^2-co-ordinated by the C=CH group, which is σ-bonded to the platinum. The two forms differ in the relative orientation of some least-squares planes involving various groups of atoms comprising the molecules and in the Mn–Pt distances [2.6909(7) Å red form, 2.659(2) Å yellow form]. The ^1H, ^{13}C, and ^{31}P n.m.r. spectra of the various compounds are discussed.

In Part 1[1] of this series we described heteronuclear dimetal compounds $[(OC)_5M\{\mu\text{-}C(OMe)Ph\}PtL_2]$ (M = Cr, Mo, or W; L = PR'_3, L_2 = cod = cyclo-octa-1,5-diene) with bridging ' carbene ' ligands. These species were prepared by treating the zerovalent platinum compounds $[Pt(C_2H_4)(PR'_3)_2]$ (PR'_3 = PMe_3 or PMe_2Ph) or $[Pt(cod)_2]$ with the carbene complexes $[M\{C(OMe)Ph\}(CO)_5]$. In this paper we describe reactions between d^{10} compounds of platinum, palladium, and nickel and the mononuclear manganese–carbene complex $[Mn\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$. In addition, a novel product from the reaction of $[Pt(C_2H_4)(PMe_3)_2]$ with $[(OC)_5Mn\text{–}Mn(C\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}O)(CO)_4]$ is reported. These studies were carried out in order to extend our knowledge of heteronuclear dimetal species with bridging carbene ligands. This class of compound could well serve as precursors to other types of complex and, therefore, the scope of the synthetic route, namely reaction of a low-valent metal species with a mononuclear metal–carbene complex, requires establishment. A preliminary account of this work has appeared.[2]

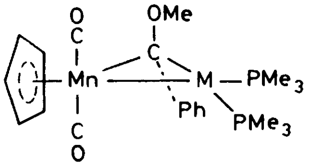
It may be noted in passing that homonuclear dimanganese complexes with bridging carbene ligands have been reported by Herrmann and co-workers.[3]

RESULTS AND DISCUSSION

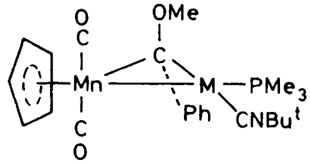
Reaction between $[Pt(cod)_2]$[4] and $[Mn\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$[5] in light petroleum at 0 °C afforded an air-stable black crystalline complex (1), formulated as



(1)



M
(2) Pt
(3) Pd
(4) Ni



M
(5) Pt
(6) Pd

shown on the basis of analysis and spectroscopic properties (Tables 1 and 2). The ^{13}C n.m.r. spectrum

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† μ-2-σ:2—3-η-(4,5-Dihydro-2-furyl)-[bis(trimethylphosphine)-platinum][tetracarbonylmanganese] (*Mn–Pt*)

TABLE 1

Analytical[a] and physical data for the complexes

	Complex	M.p. (θ_c/°C)	Colour	Yield (%)	ν(CO)/[b] cm^{-1}	Analysis (%) C	Analysis (%) H
(1)	$\mathrm{[(cod)Pt\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$ [c]	128	Black	47	1 893s, 1 824m,br	46.1 (46.1)	4.2 (4.4)
(2)	$\mathrm{[(Me_3P)_2Pt\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$ [d]	151	Orange	63	1 871s, 1 814s	39.1 (39.2)	5.0 (4.8)
(3)	$\mathrm{[(Me_3P)_2Pd\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$	124	Orange	24	1 870s, 1 817s	45.4 (45.5)	5.7 (5.6)
(4)	$\mathrm{[(Me_3P)_2Ni\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$	80 (decomp.)	Purple	32	1 863s, 1 806s	49.2 (49.7)	6.4 (6.1)
(5)	$\mathrm{[(Me_3P)(Bu^tNC)Pt\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$ [e]	111	Red	38	1 884s, 1 830s	42.6 (42.5)	4.8 (4.8)
(6)	$\mathrm{[(Me_3P)(Bu^tNC)Pd\{\mu\text{-}C(OMe)Ph\}Mn(\eta\text{-}C_5H_5)(CO)_2]}$ [f]	98 (decomp.)	Orange	44	1 883s, 1 828s	49.2 (49.2)	5.5 (5.8)
(7)	$\mathrm{[(Me_3P)_2Pt\{\mu\text{-}C_4H_5O\}Mn(CO)_4]}$	122 (decomp.)	Yellow Red [g]	15	2 011s, 1 937s 1 913s, 1 903s	28 9 (28.8)	4.1 (4.0)

[a] Calculated values are given in parentheses. [b] In hexane. [c] M(mass spectrometric) 599 (calc. 599). [d] *M* 643 (643). [e] $\nu_{\max.}$(NC) at 2 140s,br cm^{-1}; N, 2.2 (2.2%). [f] $\nu_{\max.}$(NC) at 2 165 cm^{-1}; N, 2.9 (2.4%). [g] See text.

(Experimental section) revealed a resonance at 198 p.p.m. with $J(^{195}\mathrm{Pt}\text{–}^{13}\mathrm{C}) = 975$ Hz. The chemical shift and coupling constant are as expected for the bridging carbon atom of the carbene ligand. Thus for $\mathrm{[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(cod)]}$ [1] the contact carbene-carbon atom gives a signal at 197 p.p.m. with $J(^{195}\mathrm{Pt}\text{–}^{13}\mathrm{C}) = 1\,367$ Hz. The higher value of *J*(PtC) for the tungsten compound may be due to asymmetric carbene bridging.[1]

In accord with the dimetallacyclopropane ring structure of (1), with Ph and OMe substituents above and below the ring, the cod ligand gives rise in the ^{13}C spectrum to four distinct signals for the CH groups and four for the CH$_2$ groups. The relative magnitudes of the $J(^{195}\mathrm{Pt}\text{–}^{13}\mathrm{C})$ values suggest that the signals at 93 and 91 p.p.m. [$J(^{195}\mathrm{Pt}\text{–}^{13}\mathrm{C})$ 181 and 170 Hz, respectively] be assigned to the two CH groups *trans* to the Mn–Pt bond, while the resonances at 113 and 111 p.p.m. [$J(^{195}\mathrm{Pt}\text{–}^{13}\mathrm{C})$ 61 and 55

TABLE 2

Hydrogen-1 and i.r. data for the new complexes

Complex	N.m.r. chemical shifts (τ) [a]	I.r. bands (cm^{-1}) [b]
(1)	2.76—3.11 (m, 5 H, Ph), 4.53 (m, 2 H, cod), 5.77 (s, 7 H, C$_5$H$_5$ and cod), 6.45 (s, 3 H, OMe), 7.71 (m, 8 H, CH$_2$)	3 052w,br, 1 586w, 1 484m, 1 439m, 1 428m, 1 338w, 1 309w,br, 1 200w, 1 170m, 1 150 (sh), 1 100m,br, 1 081m, 1 032w, 1 013w, 1 003w,br, 968m,br, 929m, 852m, 843m, 829 (sh), 810m, 786w, 760w, 703s, 669m,br, 636m, 620m,br, 587m, 525m, 503m, 446w,br
(2)	2.62—3.30 (m, 5 H, Ph), 5.91 (s, 5 H, C$_5$H$_5$), 6.76 (s, 3 H, OMe) 8.41 [d, 9 H, *cis*-Me$_3$P–Pt–Mn, *J*(PH) 8, *J*(PtH) 20], 8.70 [d, 9 H, *trans*-Me$_3$P–Pt–Mn, *J*(PH) 11, *J*(PtH) 33]	3 082w,br, 3 054w,br, 1 587m, 1 564w, 1 482m. 1 440m, 1 422 (sh), 1 417m, 1 307 (sh), 1 301w, 1 289m, 1 283m, 1 212w,br, 1 178w, 1 165m, 1 152w, 1 112w, 1 091m, 1 080 (sh), 1 054w, 1 029w, 1 010w, 1 001w, 965m, 944s,br, 916 (sh), 890w, 859 (sh), 852w, 841w, 830w, 819m, 768w, 733m, 725m, 711s, 671m, 657s, 634m, 622 (sh), 615m, 593m, 581m, 494m
(3)	2.52—3.25 (m, 5 H, Ph), 5.94 (s, 5 H, C$_5$H$_5$), 6.55 (s, 3 H, OMe), 8.64 [d, 9 H, MeP, *J*(PH) 7], 8.99 [d, 9 H, MeP, *J*(PH) 9]	1 584w, 1 417m, 1 284w, 1 280w, 1 165w, 1 089m, 1 080 (sh), 963m, 945s, 915 (sh), 841w, 829w, 818w, 769w, 730w, 723w, 710s, 660s, 636w, 623m, 617m, 593w, 497m
(4) [c]	2.04—3.05 (m, 5 H, Ph), 5.71 (s, 5 H, C$_5$H$_5$), 6.38 (s, 3 H, OMe), 8.87 (br, 9 H, MeP), 9.14 (br, 9 H, MeP)	
(5)	2.64—3.31 (m, 5 H, Ph), 5.93 (s, 5 H, C$_5$H$_5$), 6.81 (s, 3 H, OMe), 8.43 (s, 9 H, Bu^t) 8.66 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 43]	1 584w, 1 481m, 1 420m, 1 370m,br, 1 302w,br, 1 284m, 1 277w,br, 1 202m,br, 1 180w, 1 167w, 1 094m, 1 061w, 1 041w, 1 001w, 970s, 954s, 913w,br, 887w, 853w, 842w, 824m, br,739w,br, 701s, 683w, 655s, 634w, 619s,br, 593m, 585 (sh), 507m, 456w,br
(6)	2.44—3.09 (m, 5 H, Ph), 5.87 (s, 5 H, C$_5$H$_5$), 6.49 (s, 3 H, OMe), 8.41 (s, 9 H, Bu^t), 8.95 [d, 9 H, MeP, *J*(PH) 9]	1 281w, 1 205w,br, 1 179w, 1 165w, 1 093m, 1 079 (sh), 1 060w,br, 1 032w, 963m, 951m, 913w,br, 879w, 855w, 848w, 842w, 823w, 815 (sh), 732w, 719w,br, 699m, 659m, 637w, 623w, 619w, 591w, 582w, 505w
(7) [d]	5.84—6.19 (m, 2 H, OCH$_2$), 6.29 (m, 1 H, CH), 7.81 (m, 2 H, CH$_2$), 8.70 [d, 9 H, *cis*-Me$_3$P–Pt–Mn, *J*(PH) 9, *J*(PtH) 24], 8.87 [d, 9 H, *trans*-Me$_3$P–Pt–Mn, *J*(PH) 10, *J*(PtH) 32]	1 415m,br, 1 303w, 1 282m, 1 163w, 1 061m, 1 045m, 965m, 949m, 919w, 855 (sh), 849m, 842 (sh), 784w,br, 732w, 722w, 673w, 662s, 643s, 589w, 566w,br, 533w, 489w,br

[a] In [^{2}H$_6$]acetone. Coupling constants in Hz. [b] In Nujol. For CO and NC bands see Table 1. [c] Infrared bands not measured due to decomposition. [d] Infrared bands refer to yellow crystals. In Nujol, bands due to red crystals show slight variation from those of yellow form.

Hz, respectively] are due to the two CH groups *trans* to the C(OMe)Ph moiety.

Reactions of the manganese compound [Mn{C(OMe)Ph}(η-C_5H_5)$(CO)_2$] with either [Pt$(C_2H_4)_3$], [Pd$(dba)_2$] (dba = dibenzylideneacetone), or [Ni$(cod)_2$], all treated with 2 mol of PMe_3 gave the crystalline compounds (2), (3), and (4), respectively. The nickel compound was found to be very air sensitive. However, the palladium compound was only slightly air sensitive and the platinum complex not at all, thereby allowing more detailed spectroscopic study. Thus the ^{31}P spectrum of (2) showed two doublet resonances [*J*(PP) 12 Hz] at 16.3 and 22.3 p.p.m., as expected for the non-equivalent PMe_3 ligands in the structure proposed. Moreover, the signal at 22.3 p.p.m. had *J*(PPt) = 4 663 Hz, a value greater than that [*J*(PPt) = 2 451 Hz] for the resonance at 16.3 p.p.m. The former signal may be assigned, therefore, to the PMe_3 group in the *trans*-Me_3P–Pt–Mn configuration, and the latter to the *cis*-Me_3P–Pt–Mn group. Complex (2) afforded a well defined mass spectrum showing a parent ion followed by peaks corresponding to the loss of two CO ligands.

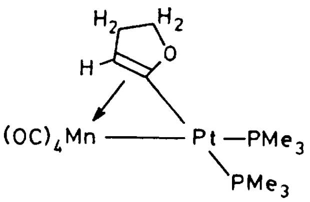
The ^{31}P n.m.r. spectrum of (3) also showed non-equivalent PMe_3 ligands at 27.3 and 29.0 p.p.m. [AB quartet, *J*(PP) 8 Hz], and the ^{13}C spectrum revealed the usual resonances, including a signal characteristic for the contact carbon atom of the μ-C(OMe)Ph group at 211 p.p.m. The ^1H n.m.r. spectrum was as expected (Table 2).

Complexes (2) and (3) were treated with t-butyl isocyanide to establish whether or not this reagent might insert into either the Mn-C or the Pt-C bonds of the Mn{μ-C(OMe)Ph}Pt group. Reactions occurred at room temperature, but the products were the complexes (5) and (6) in which $CNBu^t$ has replaced a PMe_3 ligand *trans* to the C(OMe)Ph group. This stereochemistry follows from the ^{31}P n.m.r. spectrum of (5) in which the resonance due to the single PMe_3 ligand has platinum satellites with *J*(PtP) = 4 430 Hz. This high value accords with an arrangement in which the phosphorus nucleus is *trans* to the metal–metal bond rather than the platinum–carbon bond. We have previously referred to the two *J*(PtP) values of 2 451 and 4 663 Hz measured from the spectrum of (2). The i.r. spectra of (5) and (6) both show a band due to an NC stretch in addition to two CO bands (Table 1).

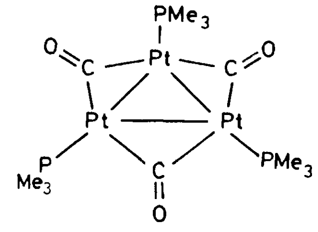
Formation of (5) and (6) from (2) and (3) is perhaps not unexpected in view of the strong *trans*-directing influence of σ-bonded carbon atoms.[6] We have previously reported[1] that the reaction between Bu^tNC and [$(OC)_5$-Cr{μ-C(OMe)Ph}Pt$(PMe_3)_2$] affords a complex [$(OC)_5$-Cr{μ-C(OMe)Ph}Pt($CNBu^t$)(PMe_3)] in which the isocyanide ligand is *trans* to the μ-C(OMe)Ph group. Reaction of (2) in diethyl ether with a stream of CO gas resulted in cleavage of the Mn–Pt bond and formation of [Mn(η-C_5H_5)$(CO)_3$] and the triplatinum compound [Pt_3{μ-C(OMe)Ph}$_2$(μ-CO)$(PMe_3)_3$].[7]

Some years ago King[8] investigated the reaction between sodium pentacarbonylmanganate(–I) and either 1,3-dibromopropane or 4-chlorobutyryl chloride and obtained a product which was subsequently shown by Casey[9] to be the dimanganese–carbene complex [$(OC)_5$Mn–Mn(C–CH_2–CH_2–CH_2–O)$(CO)_4$]. We have investigated the reaction of this compound with [Pt$(C_2H_4)_3$], treated with 2 mol of PMe_3, in the expectation that the Pt$(PMe_3)_2$ moiety thereby generated would add to give a dimanganese–platinum complex in which the cyclic carbene group bridged the manganese–platinum bond of a trimetallic Mn–Mn–Pt system.

Reaction readily occurred to give a complex mixture of products which after chromatography on alumina afforded an air-stable yellow crystalline product associated with a few red crystals (7), and a brown microcrystalline substance (8). The latter did not contain manganese and analysed for [{Pt(CO)(PMe_3)}$_n$]. The i.r. spectrum [ν(CO) at 1 821w,br and 1 745,br cm^{-1}] and the ^{31}P n.m.r. spectrum, which had one signal at –16.0 p.p.m. (broad with ^{195}Pt satellites), suggested that (8) was the triplatinum complex shown. This type of complex is well known with other tertiary phosphine ligands.[10-12] Indeed the i.r. spectrum of [{Pt(μ-CO)-[$PPh_2(CH_2Ph)$]}$_3$][10] in the carbonyl-stretching region, with ν(CO) at 1 852w and 1 789s cm^{-1}, is very similar to that of (8).



(7)



(8)

The yellow and red crystals (7) were separated by hand. In solution their i.r. and ^1H n.m.r. spectra were identical. However, when the i.r. bands were measured in Nujol slight differences were observed. The mass spectra were identical showing the highest peak at *m/e* 583, followed by peaks corresponding to the loss of only four CO ligands. These observations implied that the yellow and red crystals were two forms of the same compound, and analysis established that in the synthesis of (7) an Mn$(CO)_5$ group had been lost from the carbene–dimanganese precursor. The ^1H n.m.r. spectrum was informative in showing a different pattern from that anticipated for a Mn{μ-C–CH_2–CH_2–CH_2–O}Pt bridging group. Thus the resonances observed for the organic ligand corresponded in relative intensity to five rather than six protons. In particular, a signal at τ 6.29 corresponded to a unique proton. The ^{13}C n.m.r. spectrum was difficult to measure due to the relative insolubility of (7), but in [$^2H_1$]chloroform several resonances were observed, and a signal at 226 p.p.m. seemed likely to be due to a carbon atom bridging platinum and manganese. Unfortunately the spectrum was too weak for $^{195}Pt-^{13}C$ coupling to be detected.

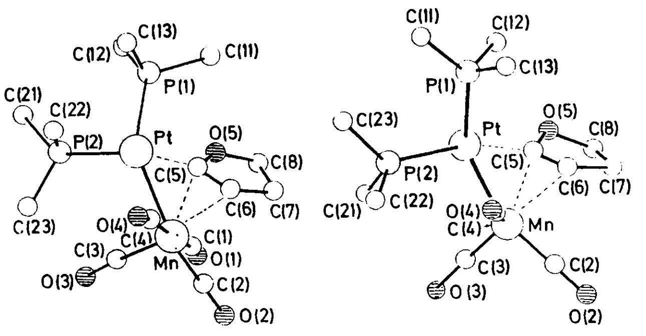
In order to resolve the nature of (7) *X*-ray diffraction studies were carried out on both a yellow and a red single crystal. The molecular configurations are shown together in Figure 1, which also shows the atomic numbering scheme. It will be seen that in both molecules a cyclic 1-σ,1-2-η-$\overline{C=CH-CH_2-CH_2-O}$ ligand bridges a platinum–manganese bond. The diffraction studies, made at 200 K, located all the hydrogen atoms and it is evident that during the formation of (7) from $[(OC)_5Mn-Mn(\overline{C-CH_2-CH_2-CH_2-O})(CO)_4]$ the CH_2 group attached to the carbene-carbon atom has lost a hydrogen atom, thus explaining the appearance in the ^1H n.m.r. spectrum of a multiplet signal at τ 6.29 due to a single proton.

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex(7)

	red			yellow		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pt	0.096 48(2)	0.092 11(1)	0.018 524(1)	0.012 70(5)	0.237 14(4)	0.100 80(5)
Mn	−0.134 34(8)	0.199 43(5)	0.111 28(4)	0.165 8(2)	0.326 7(1)	0.396 9(2)
Trimethylphosphine ligands [a]						
P(1)	0.318 5(1)	0.026 0(1)	0.176 7(1)	0.030 4(4)	0.185 1(2)	−0.118 5(3)
C(11)	0.373 8(7)	0.035 3(6)	0.072 7(4)	−0.135(2)	0.158(1)	−0.307(1)
C(12)	0.466 6(6)	0.091 4(5)	0.241 8(4)	0.124(2)	0.062(1)	−0.115(1)
C(13)	0.351 4(7)	−0.111 5(4)	0.199 5(4)	0.170(2)	0.293(1)	−0.142(2)
P(2)	0.066 8(1)	0.021 6(1)	0.314 9(1)	−0.252 0(4)	0.244 2(3)	0.027 5(4)
C(21)	0.214 5(7)	0.041 8(5)	0.400 1(3)	−0.337(2)	0.162(1)	0.133(2)
C(22)	0.043 5(9)	−0.119 0(5)	0.314 4(5)	−0.295(2)	0.382(1)	0.057(2)
C(23)	−0.084 6(9)	0.064 1(8)	0.365 3(5)	−0.403(2)	0.189(2)	−0.165(2)
Bridging ligand [b]						
C(5)	0.079 5(5)	0.168 0(4)	0.075 2(3)	0.242(2)	0.234(1)	0.236(1)
C(6)	−0.019 1(6)	0.148 5(4)	0.003 8(3)	0.367(1)	0.325(1)	0.325(1)
H(6)	−0.058(7)	0.082(4)	−0.010(4)	0.358	0.384	0.306
C(7)	0.012 0(7)	0.218 7(5)	−0.067 3(3)	0.516(1)	0.283(1)	0.417(1)
H(71)	−0.061(6)	0.261(4)	−0.088(3)	0.600	0.235	0.405
H(72)	0.046(6)	0.168(4)	−0.118(3)	0.553	0.330	0.543
C(8)	0.146 6(9)	0.277 2(6)	−0.027 4(4)	0.451(2)	0.157(1)	0.396(2)
H(81)	0.125(7)	0.349(5)	−0.024(4)	0.430	0.130	0.500
H(82)	0.246(9)	0.234(6)	−0.054(4)	0.498	0.109	0.358
O(5)	0.174 4(4)	0.246 8(3)	0.061 4(2)	0.292 6(9)	0.132 5(7)	0.264 6(9)
Carbonyl ligands						
C(1)	−0.082 3(6)	0.336 3(4)	0.101 9(3)	0.145(2)	0.186(1)	0.453(1)
O(1)	−0.058 6(5)	0.423 2(3)	0.094 8(3)	0.124(2)	0.102(1)	0.492(1)
C(2)	−0.303 1(6)	0.218 0(4)	0.042 2(3)	0.317(1)	0.400(1)	0.578(1)
O(2)	−0.410 0(4)	0.230 0(5)	−0.000 5(3)	0.414(1)	0.445(1)	0.700(1)
C(3)	−0.190 8(6)	0.236 8(4)	0.209 6(3)	0.005(1)	0.350(1)	0.440(1)
O(3)	−0.277 4(5)	0.264 0(3)	0.271 7(2)	−0.093(1)	0.367(1)	0.468(1)
C(4)	−0.169 9(6)	0.060 0(4)	0.134 3(3)	0.130(2)	0.444(1)	0.282(1)
O(4)	−0.212 1(4)	−0.020 8(3)	0.146 7(2)	0.113(1)	0.521(1)	0.220(1)

[a] Positional parameters for hydrogen atoms of these ligands are in Appendix 1 of SUP 22758. [b] For the yellow form hydrogen atoms were not refined in final cycles, therefore, no estimated standard deviations are given.



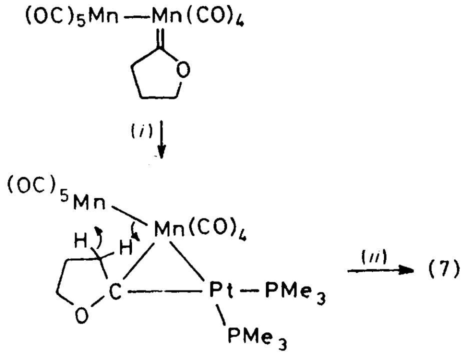
(a) (b)

FIGURE 1 Molecular structures of (*a*) the red form and (*b*) the yellow form of the complex $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{—}2\text{-}\eta\text{-}\overline{C=CH-CH_2-CH_2-O})\}Pt(PMe_3)_2]$ (7) projected on to the Pt, Mn, C(5), C(6) planes

The two crystalline forms of (7) are shown projected on to the $\overline{O(5)-C(5)-C(6)-C(7)-C(8)}$ planes in Figure 2, and the results of the *X*-ray diffraction studies which compare and contrast the data obtained are given in Tables 3—5. Figure 2 emphasizes the differences between the two conformations. The Pt–Mn separation in the red form [2.690 9(7) Å] is somewhat longer than that in the yellow [2.659(2) Å], and there are appreciable differences in the distances Mn–C(5) and Mn–C(6) (Table 4). There is an obvious variation in the relative orientations of the $Mn(CO)_4$ moieties with respect to both the Mn–Pt bond vectors and the five-membered rings (Figure 2). The latter is emphasized by the difference in the dihedral angles, 12.3 and 26.3° respectively, between the planes defined by Mn–C(5)–C(6) and C(2)–Mn–C(3) in the red and yellow forms (Table 5). Moreover, there is *ca.* 12° difference in the orientation of the P(1)PtP(2) planes with respect to the planes of O(5), C(5)—C(8), and the angles P(1)PtP(2) in the two forms are also significantly different (Table 4). The angles Mn–C–O for the two isomers are very similar except for Mn–C(4)–O(4) which is 170° in the red form and 176° in the yellow. This may reflect some tendency for C(4) to semi-bridge to the platinum in the red crystal.

For both structures the shortest intermolecular contacts occur between the hydrogen atoms of the phosphine ligands and between the carbonyl oxygen atoms on adjacent molecules but these distances are greater than the sum of the van der Waals radii.

The *X*-ray crystallographic studies reveal why both forms show similar spectral properties in solution, when the differences observed in the crystalline states would be removed. The mode of formation of (7) from $[(OC)_5Mn{-}Mn(\overline{C{-}CH_2{-}CH_2{-}CH_2{-}O})(CO)_4]$ is not known but a reasonable pathway is *via* release of $[MnH(CO)_5]$ from an initially formed trimetal complex (Scheme).



SCHEME (*i*)$[Pt(C_2H_4)(PMe_3)_2]$; (*ii*) $-[MnH(CO)_5]$

EXPERIMENTAL

The instrumentation used was as described in Part 1.[1] All reactions were carried out under nitrogen using carefully dried solvents. Light petroleum refers to that fraction of b.p. 30—40 °C. Analytical data, yields of products, *etc.* are given in Table 1. Table 2 summarises ^1H n.m.r. and i.r. measurements.

Reactions of Dicarbonyl(η-*cyclopentadienyl*)(1-*methoxy*-1-*phenylmethylene*)*manganese*.—(*a*) *With bis*(*cyclo-octa*-1,5-*diene*)*platinum*. The complex $[Mn\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$ (148 mg, 0.5 mmol) in toluene (4 cm^3) was added to a light petroleum (40 cm^3) solution of $[Pt(cod)_2]$ (206 mg, 0.5 mmol) which had been saturated with ethylene at 0 °C.

TABLE 4

Bond lengths (Å) and angles (°) for complex (7) [a]

	Red form	Yellow form
(*a*) Distances		
Pt–Mn	2.690 9(7)	2.659(2)
Pt–P(1)	2.266(1)	2.265(4)
Pt–P(2)	2.315(1)	2.301(4)
Pt–C(5)	1.998(5)	1.996(12)
Mn–C(5)	2.197(5)	2.275(15)
Mn–C(6)	2.251(5)	2.292(17)
Mn–C(1)	1.837(6)	1.83(1)
Mn–C(2)	1.811(5)	1.78(1)
Mn–C(3)	1.794(6)	1.80(2)
Mn–C(4)	1.868(6)	1.85(1)
Bridging ligand		
C(5)–C(6)	1.385(7)	1.39(1)
C(5)–O(5)	1.384(6)	1.39(1)
O(5)–C(8)	1.461(7)	1.46(1)
C(8)–H(81)	0.94(6)	1.17(2)
C(8)–H(82)	1.21(8)	0.94(2)
C(7)–C(8)	1.527(10)	1.52(2)
C(7)–H(71)	0.90(5)	1.09(2)
C(7)–H(72)	1.11(5)	1.22(2)
C(6)–C(7)	1.511(8)	1.49(2)
C(6)–H(6)	0.94(6)	0.76(1)
Carbonyl ligands		
C(1)–O(1)	1.146(7)	1.13(2)
C(2)–O(2)	1.139(7)	1.16(1)
C(3)–O(3)	1.149(7)	1.12(2)
C(4)–O(4)	1.138(7)	1.14(2)
Trimethylphosphine ligands [b]		
P(1)–C(11)	1.813(7)	1.79(1)
P(1)–C(12)	1.816(6)	1.84(2)
P(1)–C(13)	1.821(6)	1.81(2)
P(2)–C(21)	1.817(6)	1.82(2)
P(2)–C(22)	1.819(7)	1.81(2)
P(2)–C(23)	1.810(9)	1.79(1)
(*b*) Angles		
P(1)–Pt–P(2)	97.73(5)	106.2(1)
P(1)–Pt–Mn	148.33(4)	147.4(1)
P(2)–Pt–Mn	113.79(4)	105.1(1)
Pt–C(5)–Mn	79.6(2)	76.7(5)
Pt–C(5)–C(6)	126.7(4)	128.5(9)
Pt–Mn–C(5,6) [c]	60.6	61.6
C(5)–C(6)–Mn	69.7(3)	71.6(9)
C(6)–Mn–Pt	75.2(1)	76.1(3)
C(1)–Mn–C(2)	92.4(2)	97.7(6)
C(1)–Mn–C(3)	86.0(2)	88.2(7)
C(1)–Mn–C(4)	172.3(2)	161.3(5)
C(2)–Mn–C(3)	99.2(2)	93.5(6)
C(2)–Mn–C(4)	94.7(2)	100.8(6)
C(3)–Mn–C(4)	90.1(2)	88.3(7)
C(2)–Mn–Pt	155.8(2)	162.0(5)
C(3)–Mn–C(6)	168.3(2)	170.5(5)
C(3)–Mn–C(5,6) [c]	150.5	163.7
C(2)–Mn–C(5,6) [c]	110.0	102.6
C(3)–Mn–Pt	94.0(2)	102.7(4)
C(4)–Mn–Pt	64.9(2)	72.2(4)
C(1)–Mn–Pt	108.7(2)	90.8(4)
Bridging ligand		
C(5)–C(6)–H(6)	124(3)	118(1)
C(5)–C(6)–C(7)	109.6(5)	110(1)
H(6)–C(6)–C(7)	118(4)	129(1)
C(6)–C(7)–C(8)	102.4(4)	101(1)
H(71)–C(7)–H(72)	111(4)	117(1)
C(7)–C(8)–O(5)	107.2(5)	107(1)
H(81)–C(8)–H(82)	130(5)	115(2)
C(8)–O(5)–C(5)	108.7(4)	108(1)
Carbonyl ligands		
Mn–C(1)–O(1)	175.8(5)	175(2)
Mn–C(2)–O(2)	179.2(5)	177(1)
Mn–C(3)–O(3)	177.8(5)	178(1)
Mn–C(4)–O(4)	170.0(5)	176(1)
Trimethylphosphine ligands		
Pt–P(1)–C(11)	114.4(2)	124.2(6)
Pt–P(1)–C(12)	115.1(2)	114.5(5)
Pt–P(1)–C(13)	118.8(2)	109.8(5)
C(11)–P(1)–C(12)	101.6(3)	102.9(7)
C(12)–P(1)–C(13)	103.9(3)	100.8(8)
C(11)–P(1)–C(13)	100.7(3)	101.6(7)
Pt–P(2)–C(21)	116.1(2)	112.7(5)
Pt–P(2)–C(22)	114.5(2)	116.5(6)
Pt–P(2)–C(23)	118.8(3)	121.1(7)
C(21)–P(2)–C(22)	102.9(3)	102.7(9)
C(21)–P(2)–C(23)	100.6(3)	98.9(8)
C(22)–P(2)–C(23)	101.6(4)	102.1(8)

[a] Estimated standard deviations are in parentheses. [b] C–H distances in trimethylphosphine ligands are in Appendix 2 of SUP 22758. [c] C(*n,m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*).

The mixture was stirred (24 h), precipitating a red-brown solid. Solvent was removed *in vacuo* and the residue extracted with diethyl ether and light petroleum (1 : 1). The extract was filtered through an alumina pad (2 × 1 cm^2), concentrated, and cooled to −78 °C giving black crystals of $[MnPt\{\mu\text{-}C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2(cod)]$ (1) (140 mg). Carbon-13 n.m.r. {in $[^2H_2]$dichloromethane, δ (^{1}H-decoupled; chemical shifts relative to $SiMe_4$, positive values to high frequency)}: 235 (CO), 230 (CO), 198 [*C*(OMe)Ph, *J*(PtC) 975], 158 [C^1 (Ph), *J*(PtC) 52], 126, 124 (Ph), 113 [CH(cod), *J*(PtC) 61], 111 [CH(cod), *J*(PtC) 55], 93 [CH(cod), *J*(PtC) 181], 91 [CH(cod), *J*(PtC) 170], 89 (C_5H_5), 60 [OMe, *J*(PtC) 29], 33 [CH_2(cod), *J*(PtC) 24], 31 [CH_2(cod)], 29 [CH_2(cod), *J*(PtC) 21 Hz], and 27 [CH_2(cod)] p.p.m.

TABLE 5

Some least-squares planes for complex (7) in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal coordinates; distances (Å) from the planes are given in square brackets

		Red crystal	Yellow crystal
Plane (i):	Mn, C(5), C(6)	$0.999x + 12.240y - 4.732z = 1.780$ [Pt −1.43]	$-2.055x + 8.712y - 5.971z = 0.135$ [Pt 1.30]
Plane (ii):	C(5), C(6), C(7), C(8), O(5)	$-6.121x + 9.054y + 5.815z = 1.490$ [C(5) −0.02, C(6) −0.01, C(7) 0.02, C(8) −0.04, O(5) 0.03, Pt −0.17]	$-6.532x + 0.319y + 9.226z = 0.654$ [C(5) 0.02, C(6) 0.05, C(7) −0.09, C(8) 0.11, O(5) −0.08]
Plane (iii):	Pt, P(1), P(2)	$3.356x + 10.442y + 6.450z = 2.480$	$1.052x + 11.624y - 2.672z = 2.500$
Plane (iv):	Mn, C(2), C(3)	$2.618x + 12.164y - 3.120z = 1.727$	$0.302x + 10.987y - 4.695z = 1.776$
Plane (v):	Mn, C(1), C(4)	$-7.612x + 3.577y + 9.921z = 2.840$ [O(1) 0.06, O(4) 0.16]	$8.544x - 4.008y - 6.794z = -2.589$ [O(1) −0.10, O(4) −0.03]
Dihedral angles (°) between least-squares planes:			
	(i)–(ii)	58.4	66.6
	(i)–(iii)	46.9	42.9
	(i)–(iv)	12.3	26.3
	(i)–(v)	88.1	85.7
	(ii)–(iii)	89.1	76.6

(*b*) *With ethylenebis(trimethylphosphine)platinum.* A solution of $[Pt(cod)_2]$ (822 mg, 2 mmol) in light petroleum (60 cm^3) was saturated with ethylene at 0 °C and treated with PMe_3 (4 mmol) in light petroleum (5 cm^3). To this mixture was added $[Mn\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$ (592 mg, 2 mmol) in toluene (5 cm^3). The orange solution was stirred (60 h), evaporated, and the residue extracted with diethyl ether and filtered through an alumina pad. Solvent was partially removed *in vacuo* affording at −78 °C orange *crystals* of $[MnPt\{\mu\text{-}C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)_2(PMe_3)_2]$ (2) (800 mg). Phosphorus-31 n.m.r. {in $[^2H_6]$benzene, δ [^{1}H-decoupled, chemical shifts to low frequency of 85% H_3PO_4 (external)]}: 16.3 [d, *J*(PP) 12, *J*(PtP) 2 451] and 22.3 p.p.m. [d, *J*(PP) 12, *J*(PtP) 4 663 Hz].

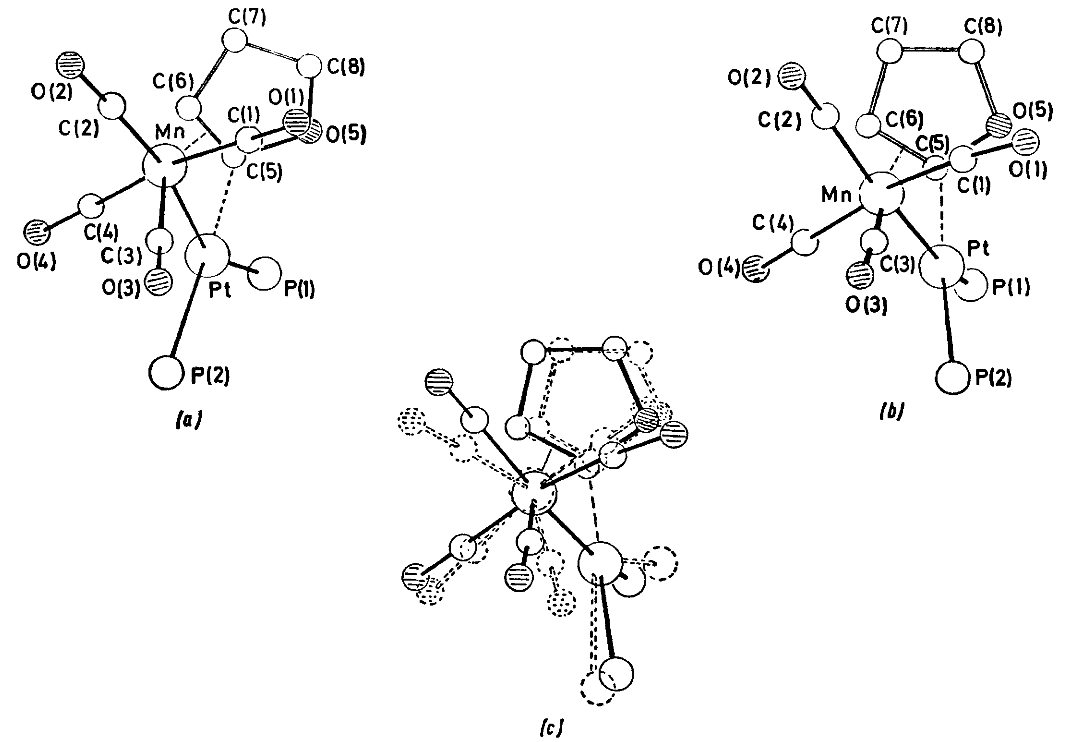


FIGURE 2 Views of the molecular structures of (*a*) the red form and (*b*) the yellow form of complex (7) projected on to the O(5), C(5), C(6), C(7), C(8) planes. Composite projection in (*c*)

(*c*) *With bis(dibenzylideneacetone)palladium*[13] *and trimethylphosphine*. The complex [Mn{C(OMe)Ph}(η-C_5H_5)$(CO)_2$] (269 mg, 1 mmol) in toluene (4 cm^3) was added to [Pd$(dba)_2$] (574 mg, 1 mmol) in tetrahydrofuran (60 cm^3) to which PMe_3 (2 mmol) in light petroleum (2 cm^3) had been added. The mixture was stirred (2 d), and solvent removed *in vacuo* giving an orange-green oil. The latter was extracted with light petroleum (70 cm^3) and the solution cooled (−20 °C) crystallising out dba. The recovered solution was evaporated, extracted with diethyl ether–light petroleum, and filtered through an alumina pad. The filtrate was concentrated and chilled to give slightly air-sensitive orange *crystals* of [MnPd{μ-C(OMe)Ph}(η-C_5H_5)$(CO)_2(PMe_3)_2$] (3) (130 mg). N.m.r.: ^{13}C (in [$^2H_2$]dichloromethane), δ 237, 235 (CO), 211 [*C*(OMe)Ph], 161 [C^1 (Ph)], 127 (br), 123 (Ph), 87 (C_5H_5), 59 (OMe), and 17 p.p.m. (MeP); ^{31}P (in [$^2H_6$]benzene), δ 27.3 and 29.0 p.p.m. [AB quartet, *J*(PP) 8 Hz].

By treating the alumina pad with acetone it was possible to isolate orange *needles* of [Pd(dba)$(PMe_3)_2$] (78 mg, 16%), m.p. 101 °C (Found: C, 55.9; H, 6.3. Calc. for $C_{23}H_{32}OP_2Pd$: C, 55.9; H, 6.9%). N.m.r.: ^1H (in [$^2H_6$]acetone), τ 2.65—2.84 (m, C_6H_5CH), 4.19 (m br, 4 H, CH_2), 8.75 [d, 9 H, MeP, *J*(PH) 7], and 8.95 [d, 9 H, MeP, *J*(PH) 6 Hz]; ^{31}P (in [$^2H_6$]benzene), δ 22.4 and 25.8 p.p.m. [AB quartet, *J*(PP) 10 Hz].

(*d*) *With bis(cyclo-octa-*1,5-*diene)nickel and trimethylphosphine*. Bis(cyclo-octa-1,5-diene)nickel (275 mg, 1 mmol) in diethyl ether (60 cm^3) was treated with PMe_3 (2 mmol) in light petroleum (2 cm^3) followed by [Mn{C(OMe)-Ph}(η-C_5H_5)$(CO)_2$] (296 mg, 1 mmol) in toluene (4 cm^3). The mixture was stirred (17 h) during which time it turned deep red. Solvent was removed *in vacuo* and the residue extracted with diethyl ether and light petroleum (1 : 1). The filtrate was passed through an alumina pad, concentrated, and cooled to give purple air-sensitive *crystals* of [NiMn{μ-C(OMe)Ph}(η-C_5H_5)$(CO)_2(PMe_3)_2$] (4) (130 mg).

Reactions of the Complexes (2) *and* (3) *with t-Butyl Isocyanide*.—An excess of Bu^tNC was added to (1) (100 mg, 0.16 mmol) in diethyl ether (40 cm^3). After 1 h solvent was removed *in vacuo* and the residue extracted with light petroleum to give an orange solution The latter was concentrated and cooled to give red *crystals* of [MnPt{μ-C(OMe)-Ph}(η-C_5H_5)$(CO)_2$($CNBu^t$)(PMe_3)] (5) (40 mg). Phosphorus-31 n.m.r. (in [$^2H_6$]benzene): δ 18.7 p.p.m. [s, *J*(PPt) 4 430 Hz].

The microcrystalline air-sensitive complex [MnPd{μ-C(OMe)Ph}(η-C_5H_5)$(CO)_2$($CNBu^t$)(PMe_3)] (6) (45 mg) was similarly prepared from compound (3) (100 mg, 0.18 mmol) and excess of Bu^tNC.

Reaction of Ethylenebis(trimethylphosphine)platinum with the Complex [$(OC)_5Mn$–Mn($\overline{C{-}CH_2{-}CH_2{-}CH_2{-}O}$)$(CO)_4$].—Bis(cyclo-octa-1,5-diene)platinum (411 mg, 1 mmol) was dissolved in light petroleum (40 cm^3) and saturated with ethylene at 0 °C. Trimethylphosphine (2 mmol) in light petroleum (2 cm^3) was added. The mixture was treated with the complex [$Mn_2(CO)_9$($\overline{C{-}CH_2{-}CH_2{-}CH_2{-}O}$)] (432 mg, 1 mmol). The solution turned purple and after 1 h solvent was removed *in vacuo* and the residual oil was extracted with toluene and chromatographed on alumina. Elution with light petroleum afforded some unreacted dimanganese complex (117 mg). Further elutions from the column were carried out with mixtures of light petroleum and diethyl ether in ratios of 10 : 1, 5 : 1, and 1 : 1. The last afforded a yellow solid which was rechromatographed. The solution afforded yellow *needles* together with a few red crystals of (7) (90 mg). N.m.r.: ^{13}C (in [$^2H_1$]chloroform), δ 226 (μ-C), 222 202, 198 (CO), 69 [O–CH_2, *J*(PC) 3, *J*(PtC) 55], 59 [CH, *J*(PC) 10, *J*(PtC) 98], 31 (CH_2), 19, 18 p.p.m. (MeP); ^{31}P (in [$^2H_6$]benzene), δ 10.8 [d, *J*(PP) 12, *J*(PtP) 3 022] and 21.3 p.p.m. [d, *J*(PP) 12, *J*(PtP) 2 617 Hz]. Further elution of the alumina column with a 1 : 1 diethyl ether–light petroleum mixture gave purple crystals of [{Pt(μ-CO)(PMe_3)}$_3$] (8) (55 mg, 18%), m.p. >300 °C (decomp.) (Found: C, 16.1; H, 3.0. Calc. for $C_{12}H_{27}O_3P_3Pt_3$: C, 16.1; H, 3.0%). I.r.: ν(CO) at 1 821w,br and 1 745s,vbr cm^{-1}. N.m.r.: ^1H (in [$^2H_6$]benzene), τ 8.60 (br with ^{195}Pt satellites); ^{31}P, δ −16.0 p.p.m, at −60 °C this resonance sharpens and shows a complex pattern of ^{195}Pt satellites.

Crystal-structure Determinations.—The collection of reflection intensities and the solution and refinement of the structures of the red and yellow forms of (7) followed similar lines, and are therefore described for the red form only. Data in braces correspond to those for the yellow crystal.

The crystals grow as rectangular prisms {plates}; that for data collection was of dimensions 0.10 × 0.10 × 0.40 mm {0.05 × 0.075 × 0.40 mm} and diffracted intensities were recorded at 200 K {200 K} for $2\theta \leqslant 50°$ on a Syntex $P2_1$ four-circle diffractometer.[14] Of the total 3 581 {3 709} recorded intensities, 3 274 {3 350} had $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, 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 carried out with the '*X*-RAY' system of programs[15] available for the CDC 7600 at the London Computing Centre.

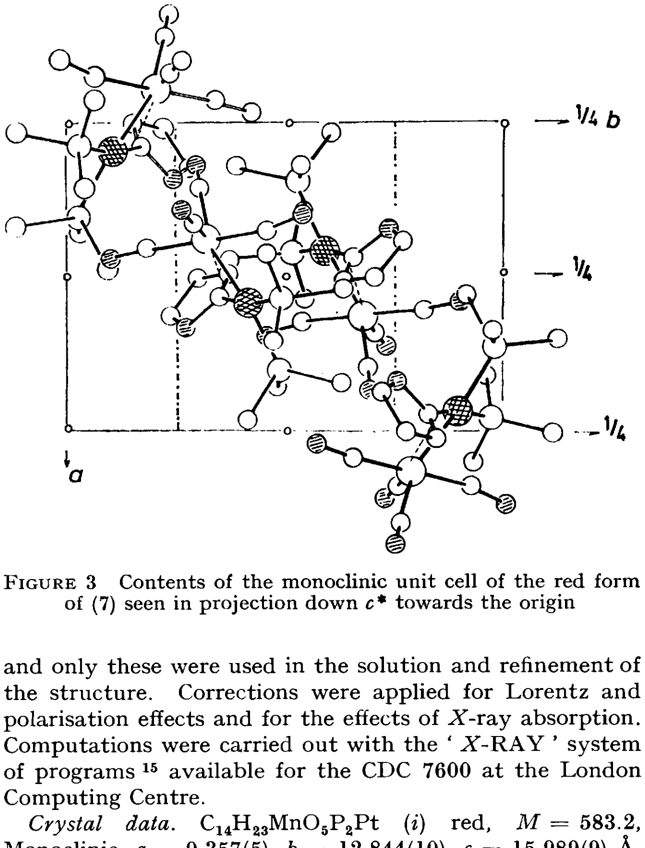


FIGURE 3 Contents of the monoclinic unit cell of the red form of (7) seen in projection down *c** towards the origin

Crystal data. $C_{14}H_{23}MnO_5P_2Pt$ (*i*) red, *M* = 583.2, Monoclinic, *a* = 9.357(5), *b* = 12.844(10), *c* = 15.989(9) Å, β = 98.14(4)°, space group $P2_1/n$, *U* = 1 902.0 Å^3, D_m = 2.04 (flotation), *Z* = 4, D_c = 2.05 g cm^{-3}, *F*(000) = 1 124, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 86.1 cm^{-1}; (*ii*) yellow, *M* = 583.2, Triclinic,

$a = 9.429(5)$, $b = 12.113(4)$, $c = 9.729(6)$ Å, $\alpha = 93.97(14)$, $\beta = 115.45(4)$, $\gamma = 98.83(3)°$, space group $P\bar{1}$, $U = 980.0$ Å^3, $D_m = 1.98$ (flotation), $Z = 2$, $D_c = 1.96$ g cm^{-3}, $F(000) = 562$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 83.6 cm^{-1}.

Structure solution and refinement. The platinum, manganese, and phosphorus atoms were located from a Patterson synthesis, and all the remaining atoms (including hydrogen for the red form) by successive electron-density difference synthesis. For the yellow form some hydrogen atoms were incorporated in calculated positions. The structures were refined by block-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were refined individually for the red form only. Refinement converged at R 0.023 (R' 0.030) {R 0.055 (R' 0.073)} with a mean shift-to-error ratio in the last cycle of 0.05 {0.007}. A weighting scheme of the form $1/w = \sigma(F) + \alpha(F) + \beta(F)^2$, with $\alpha = 0.025$ and $\beta = 0.0$ {$\alpha = 0.0$ and $\beta = 0.004$} and where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 0.4 or < -0.5 e Å^{-3} {> 0.9 or < -0.7 e Å^{-3}} except in the vicinity of the metal atoms. Scattering factors were from ref. 16 for C, O, and P, ref. 17 for H, and ref. 18 for Pt and Mn, including corrections for the effects of anomalous dispersion (Pt $\Delta f' = -2.352$, $\Delta f'' = 8.388$; Mn $\Delta f' = 0.295$, $\Delta f'' = 0.729$; P $\Delta f' = 0.090$, $\Delta f'' = 0.095$). Atomic positional parameters are in Table 3, interatomic distances in Table 4, and some least-squares planes in Table 5. Packings of the red and yellow forms in the unit cells are shown in Figures 3 and 4. Observed and calculated structure factors, all thermal parameters, and parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22758 (34 pp.).*

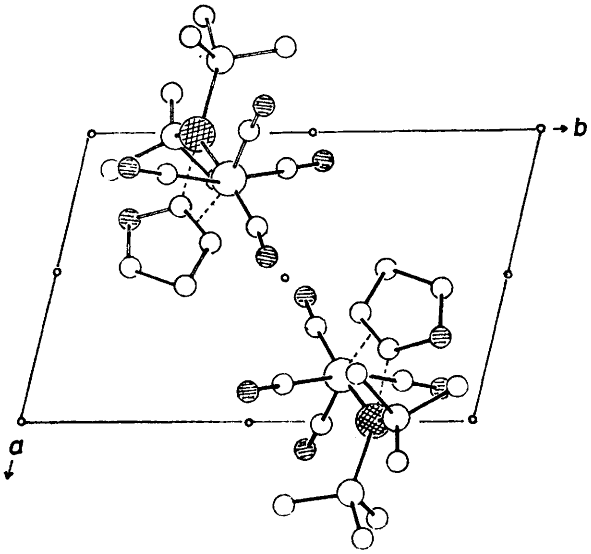


FIGURE 4 Contents of the triclinic unit cell of the yellow form of (7) seen in projection down c^* towards the origin

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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