Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 5.[1] Synthesis and Crystal Structure of [MnPt(μ-I)($COCH_2CH_2CH_2$)$(CO)_4$(PBu^t_2Me)] †

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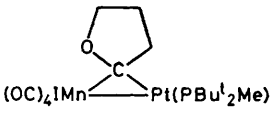
The mononuclear manganese–carbene complex [MnI($COCH_2CH_2CH_2$)$(CO)_4$] reacts with [Pt$(C_2H_4)_2$(PBu^t_2Me)] to afford a mixture of the triplatinum compounds [{Pt(μ-CO)(PBu^t_2Me)}$_3$] and a dimetalla-complex of composition [MnPtI(C_4H_6O)$(CO)_4$(PBu^t_2Me)]. A ^{13}C n.m.r. study of the latter suggested that the 2-oxacyclopentylidene ligand was terminally bonded to the platinum and was not bridging the metal–metal bond. In order to establish the molecular structure, a single-crystal *X*-ray diffraction study was carried out. Crystals are orthorhombic, with space group *Pbca* and $Z = 8$ in a unit cell of dimensions $a = 14.634(5)$, $b = 19.546(18)$, and $c = 16.325(5)$ Å. The structure has been determined by heavy-atom methods from automated diffractometer data collected at 200 K for $2.9 \leqslant 2\theta \leqslant 65°$ and refined to R 0.036 (R' 0.036) for 3 197 reflections. A manganese–platinum bond is bridged by an iodo-ligand [Mn–Pt 2.603(1), Mn–I 2.689(2), Pt–I 2.662(1) Å]. The carbene ligand is terminally bonded to the platinum [C–Pt 1.889(8) Å] such that the $COCH_2CH_2CH_2$ group is essentially *trans* to the iodine atom, while the PBu^t_2Me group is *trans* to the metal–metal bond [P–Pt–Mn 167.8(1)°]. The CO ligands adopt four octahedral positions around the manganese atom. (Ethylene)bis(trimethylphosphine)platinum reacts with [MnI($COCH_2CH_2CH_2$)$(CO)_4$] to give [MnI$(CO)_4$(PMe_3)] and the previously reported complex [$(OC)_4$Mn{μ-(1-σ,1—2-η-C=CHCH$_2$CH$_2$O)}Pt$(PMe_3)_2$]. The latter species was also produced, together with [MnI$(CO)_3$$(PMe_3)_2$], by reacting [$(OC)_4$Mn($\mu$-I)Pt($COCH_2CH_2CH_2$)($PBu^t_2Me$)] with an excess of trimethylphosphine.

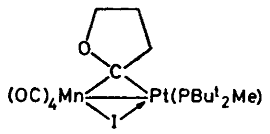
IN Part 2 of this series we showed [2] that the mononuclear manganese carbene complex [Mn{C(OMe)Ph}$(CO)_2$(η-C_5H_5)] reacted with the zerovalent platinum compounds [Pt$(C_2H_4)(PMe_3)_2$] and [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) to give stable dimetal compounds [(η-C_5H_5)$(OC)_2$Mn{μ-C(OMe)Ph}PtL_2] (L_2 = 2 PMe_3 or cod). In a parallel study of the reaction of [Mn{C(OMe)Ph}$(CO)_2$(η-C_5H_5)] with the bis(ethylene)platinum complex [Pt$(C_2H_4)_2$(PBu^t_2Me)] it was observed [1] that no stable manganese–platinum complex was formed, instead the triplatinum compound [Pt_3{μ-C(OMe)Ph}$_2$(μ-CO)(PBu^t_2Me)$_3$] was produced. This result, involving transfer of a carbene ligand from manganese to platinum, led us to investigate a reaction between [Pt$(C_2H_4)_2$(PBu^t_2Me)] and another mononuclear manganese carbene complex, *viz.* [MnI{$COCH_2CH_2CH_2$}$(CO)_4$] [3] with the results herein described.

RESULTS AND DISCUSSION

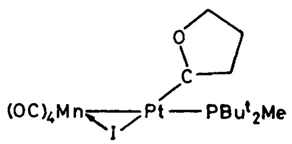
The compound [Pt$(C_2H_4)_2$(PBu^t_2Me)], generated *in situ* from [Pt(cod)$_2$] and PBu^t_2Me, reacted at room temperature with [MnI($COCH_2CH_2CH_2$)$(CO)_4$] in light petroleum–tetrahydrofuran mixtures to give two products separated by chromatography. The first compound eluted from the column was characterised as the triplatinum complex [Pt_3(μ-CO)$_3$(PBu^t_2Me)$_3$] (1), by analysis and by i.r. and ^1H n.m.r. spectroscopy. The i.r. spectrum (cyclohexane) of (1) showed $\nu_{max.}$ (CO) at 1 833s and 1 773vs cm^{-1}, frequencies very similar to those observed [4] (1 827s and 1 760vs cm^{-1}) in the spectrum of [Pt_3(μ-CO)$_3$(PBu^t_2Ph)$_3$]. The second product was an orange air-stable crystalline compound, (2), which on the basis of microanalysis, the i.r. spectrum in the CO region, and a parent ion observed in the mass spectrum, can be formulated as the manganese-platinum compound [MnPtI($COCH_2CH_2CH_2$)$(CO)_4$(PBu^t_2Me)]. A possible structure is (2a). However, formulation (2a) involves three-co-ordinate Pt^{II}, an unusual co-ordination for this oxidation state. Structure (2b), involving a bridging iodo-ligand, circumvents this difficulty but examination of the ^{13}C n.m.r. spectrum of (2) revealed features which suggested that (2b) was also not the structure of the compound. Thus the ^{13}C (^1H-decoupled) n.m.r. spectrum of (2) showed a resonance at 261 p.p.m. characteristic [5] of the ligating carbon atom of a carbene ligand but at a sigificantly downfield chemical shift compared with that observed [6]



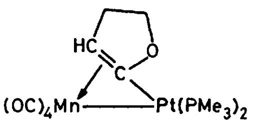
(2a)



(2b)



(2c)



(3)

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† *defg*-Tetracarbonyl-*c*-μ-iodo-*a*-(methyldi-t-butylphosphine)-*b*-(2-oxacyclopentylidene)platinummanganese (*Pt–Mn*).

(194 p.p.m.) for the bridging carbene-carbon atom in $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)(C_6H_4Me\text{-}p)\}Pt(PMe_3)_2]$. Generally the resonance for a carbene-carbon atom bridging two metal atoms experiences an upfield chemical shift compared with that for the ligated carbene-carbon atom in a mononuclear metal complex.[7] Moreover, the resonance in the ^{13}C spectrum of (2) at 261 p.p.m. showed platinum-195 satellite peaks with $J(PtC) = 1\,704$ Hz. The magnitude of this coupling was higher than those observed in the spectra of all other molecules containing the $M\{\mu\text{-}C(OMe)R\}Pt$ structure which we have so far prepared. For example, in the complex $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)Ph\}Pt\}(cod)]$, $J(Pt\text{-}\mu\text{-}C)$ is 975 Hz.[2] These ^{13}C n.m.r. results strongly suggested that (2) had a structure in which the $=COCH_2CH_2CH_2$ ligand was bonded only to the platinum atom, and did not bridge the Mn–Pt bond. The ^{31}P n.m.r. spectrum of (2) was not structurally informative apart from confirmation of the presence of the $Pt\text{-}PBu^t_2Me$ group through the observation of a singlet resonance at δ −61.5 p.p.m. (to low frequency of 85% H_3PO_4 external) with platinum satellites [$J(PPt)$ 2 968 Hz].

TABLE 1

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

Atom	x	y	z
Mn	0.125 08(9)	0.102 35(7)	0.127 59(8)
Pt	0.009 19(2)	0.203 33(2)	0.125 69(2)
I	0.184 02(4)	0.230 27(4)	0.157 16(5)
P	−0.066 7(1)	0.306 9(1)	0.130 1(1)
C(1)	0.126 4(6)	0.123 3(5)	0.016 4(6)
O(1)	0.125 6(5)	0.134 5(4)	−0.051 7(4)
C(2)	0.229 4(7)	0.053 1(5)	0.137 6(5)
O(2)	0.293 2(5)	0.019 4(4)	0.146 1(5)
C(3)	0.085 6(7)	0.097 5(5)	0.234 4(6)
O(3)	0.059 1(6)	0.091 0(5)	0.299 8(4)
C(4)	0.053 1(6)	0.031 9(5)	0.103 9(5)
O(4)	0.006 8(4)	−0.014 2(4)	0.088 6(4)
C(5)	−0.092 3(5)	0.146 7(5)	0.103 1(6)
C(6)	−0.150 6(7)	0.110 7(6)	0.161 7(7)
C(7)	−0.217 8(14)	0.069 0(14)	0.112 5(14)
C(8)	−0.198 9(8)	0.083 8(9)	0.028 7(12)
O(5)	−0.121 0(4)	0.133 6(4)	0.027 9(5)
C(31)	−0.189 7(5)	0.292 3(5)	0.126 2(6)
C(11)	−0.051 4(6)	0.354 7(5)	0.228 9(5)
C(12)	−0.048 3(7)	0.300 5(5)	0.297 3(5)
C(13)	−0.131 7(7)	0.402 5(6)	0.246 9(7)
C(14)	0.037 2(6)	0.395 7(5)	0.229 8(6)
C(21)	−0.046 2(6)	0.361 4(5)	0.037 6(5)
C(22)	−0.058 5(6)	0.371 5(6)	0.023 7(6)
C(23)	−0.083 0(8)	0.320 3(6)	−0.035 2(5)
C(24)	−0.090 8(8)	0.432 4(5)	0.042 7(7)

In order to resolve the structure of (2) a single-crystal X-ray diffraction study was carried out, and the results are summarised in Tables 1—3. Figure 1 shows a view of the molecule and also indicates the atomic numbering system. The contents of the orthorhombic unit cell are shown in Figure 2.

As was deduced from the ^{13}C n.m.r. study, the carbene ligand is terminally bonded to the platinum, *i.e.* the the molecule can be represented as (2c). The Pt–C(5) bond length [1.889(8) Å] compares with that found [1.92(1) Å] for the Pt–C(carbene) distance in *cis*-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$,[8] and as expected, is somewhat shorter than generally found (1.99—2.15 Å) for platinum–carbon σ-bond distances.[9] The plane defined

TABLE 2

Bond lengths and angles for the complex $[MnPt(\mu\text{-}I)(COCH_2CH_2CH_2)(CO)_4(PBu^t_2Me)]$ (2)

(*a*) Distances (Å)			
Pt–Mn	2.603(1)		
Pt–I	2.662(1)	Mn–I	2.689(2)
Pt–C(5)	1.889(8)	Pt–P	2.310(2)
Mn–C(1)	1.86(1)	C(1)–O(1)	1.13(1)
Mn–C(2)	1.81(1)	C(2)–O(2)	1.15(1)
Mn–C(3)	1.84(1)	C(3)–O(3)	1.14(1)
Mn–C(4)	1.78(1)	C(4)–O(4)	1.15(1)
C(5)–O(5)	1.32(1)		
C(5)–C(6)	1.46(1)	C(6)–C(7)	1.51(2)
C(7)–C(8)	1.42(2)	C(8)–O(5)	1.50(1)
P–C(11)	1.876(9)	P–C(21)	1.873(9)
P–C(31)	1.823(8)	C(11)–C(12)	1.54(1)
C(11)–C(13)	1.53(1)	C(11)–C(14)	1.53(1)
C(21)–C(22)	1.56(1)	C(21)–C(23)	1.53(1)
C(21)–C(24)	1.54(1)		
(*b*) Angles (°)			
Pt–I–Mn	58.2(1)	Mn–Pt–P	167.8(1)
Mn–Pt–I	61.4(1)	I–Mn–Pt	60.4(1)
I–Mn–C(1)	88.2(3)	I–Mn–C(2)	102.0(3)
I–Mn–C(3)	88.8(3)	I–Mn–C(4)	161.9(3)
P–Pt–I	106.4(1)	P–Pt–C(5)	98.2(3)
C(5)–Pt–I	155.4(3)	C(5)–Pt–Mn	94.0(3)
Mn–C(1)–O(1)	178.2(8)	Mn–C(2)–O(2)	176.5(9)
Mn–C(3)–O(3)	176.2(10)	Mn–C(4)–O(4)	179.6(6)
C(1)–Mn–C(2)	101.3(4)	C(1)–Mn–C(3)	159.9(4)
C(1)–Mn–C(4)	88.0(4)	C(2)–Mn–C(3)	98.8(4)
C(2)–Mn–C(4)	96.2(4)	C(3)–Mn–C(4)	88.8(4)
C(1)–Mn–Pt	80.1(3)	C(2)–Mn–Pt	162.3(3)
C(3)–Mn–Pt	81.1(3)	C(4)–Mn–Pt	101.5(3)
O(5)–C(5)–Pt	123.0(7)	C(6)–C(5)–Pt	127.8(8)
O(5)–C(5)–C(6)	109.2(8)	C(5)–C(6)–C(7)	106.9(11)
C(6)–C(7)–C(8)	106.0(12)	C(7)–C(8)–O(5)	106.8(12)
C(8)–O(5)–C(6)	111.0(10)		
C(11)–P–Pt	113.9(3)	C(1)–P–C(31)	103.1(4)
C(11)–P–C(21)	113.0(4)	C(21)–P–C(31)	102.6(4)
C(21)–P–Pt	113.3(3)	C(31)–P–Pt	109.6(3)
C(12)–C(11)–C(13)	107.6(8)	C(12)–C(11)–C(14)	109.3(8)
C(13)–C(11)–C(14)	109.2(8)	P–C(11)–C(12)	106.5(7)
P–C(11)–C(13)	112.2(7)	P–C(11)–C(14)	111.8(6)
C(22)–C(21)–C(23)	107.4(8)	C(22)–C(21)–C(24)	108.1(8)
C(23)–C(21)–C(24)	111.5(8)	P–C(21)–C(22)	110.3(6)
P–C(21)–C(23)	105.7(7)	P–C(21)–C(24)	113.7(7)

TABLE 3

Some least-squares planes 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, I

$$-2.480x - 2.546y + 15.947z = 1.464$$

Plane (ii): C(5), C(6), C(7), C(8), O(5)

$$-9.357x + 15.016y + 0.5038z = 3.138$$

[C(5) −0.02, C(6) 0.02, C(7) −0.01, C(8) 0.00, O(5) 0.01]

Plane (iii): C(5), Pt, P, I, Mn

$$-2.399x - 2.424y + 15.976z = 1.501$$

[C(5) 0.01, Pt −0.01, Mn −0.01, I 0.01, P −0.01]

Plane (iv): Pt, I, Mn, C(2), C(4)

$$2.606x - 2.558y + 15.921z = 1.445$$

[Pt 0.01, I −0.01, Mn 0.00, C(2) 0.01, C(4) −0.01]

Angles (°) between planes

(i)—(ii) 87.8 (ii)—(iii) 87.7

by the ring atoms of the 2-oxacyclopentylidene ligand is inclined at 87.8° to the Pt–I–Mn plane (Table 3).

The Pt–Mn bond [2.602(1) Å] is discernibly shorter than that [2.628(1) Å] in the cation $[\mathrm{MnPt}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}p)(\mathrm{CO})_2(\mathrm{PMe_3})_2(\eta\text{-}\mathrm{C_5H_5})]^+$ (ref. 6). The metal–metal bond is bridged by the iodine atom which is essentially *trans* to the carbene-carbon atom C(5) [C(5)–Pt–I, 155.4(3)°] and to the C(4)O(4) ligand on the manganese [I–Mn–C(4), 161.9(3)°]. The co-ordination around the manganese is distorted octahedral since the Pt–Mn–I angle is only 60.4°, and this is probably responsible for a widening of the C(2)–Mn–C(4) angle to 96.2(4)°. It is of interest that the angle C(1)–Mn–C(3) [159.9(4)°] departs so much from linearity, but the Mn–C(1)–O(1) and Mn–C(3)–O(3) angles and the Pt–C(1) and Pt–C(3) distances (2.93 Å) reflect no semi-bridging to platinum character. This is in contrast to what is observed[6] in $[\mathrm{MnPt}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}p)(\mathrm{CO})_2(\mathrm{PMe_3})_2(\eta\text{-}\mathrm{C_5H_5})]^+$, which also contains a three-electron bridging group.

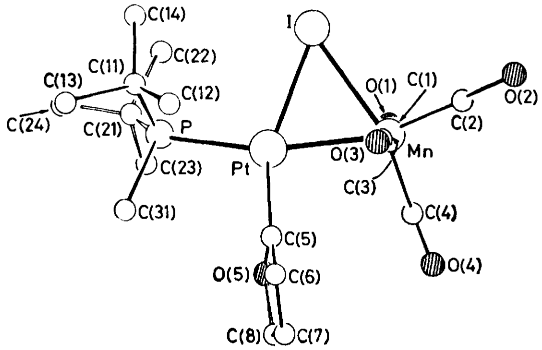

Figure 1 The molecular structure of $[\mathrm{MnPt}(\mu\text{-I})(\overline{\mathrm{COCH_2CH_2CH_2}})(\mathrm{CO})_4(\mathrm{PBu^t_2Me})]$ (2) showing the crystallographic numbering system

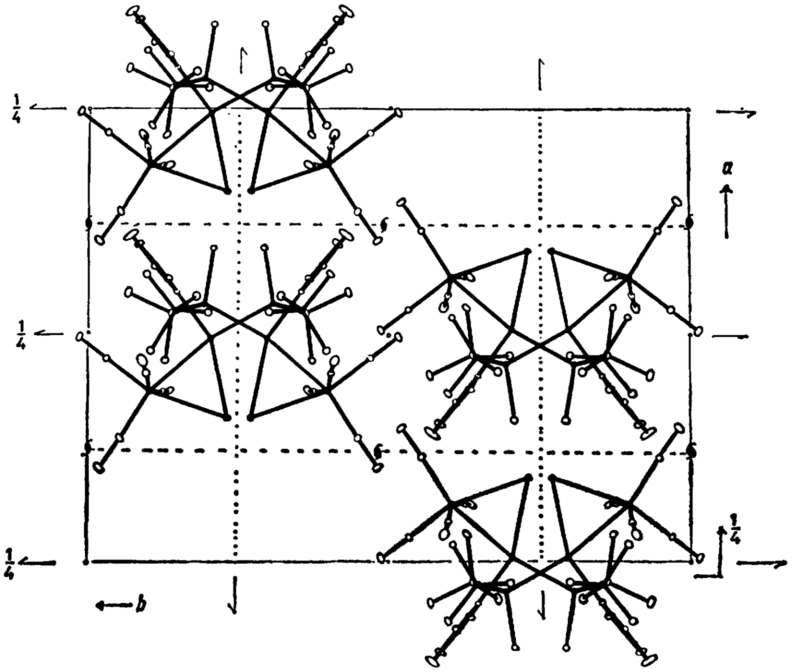

Figure 2 Contents of the orthorhombic unit cell viewed down *c* towards the origin

Although the platinum atom is essentially co-planar with respect to the atoms P, I, Mn, and C(5) [Table 3, plane (iii)], these ligands are not disposed at the corners of a square since the angle I–Pt–Mn is only 61.4°. Consequently the angles P–Pt–I and P–Pt–C(5) are greater than 90°, at 106.4(1)° and 98.2(3)° respectively.

The Pt–I distance [2.662(1) Å] is longer than in *trans*-$[\mathrm{PtI_2(PMe_3)_2}]$ [2.599(2) Å],[10] reflecting the greater *trans* influence of the carbene ligand in (2c) over that of iodine in the di-iodide. The Pt–P distance [2.310(2) Å] agrees well with the average found for $\mathrm{Pt^{II}}$–P bond lengths.[9c,11]

The formation of (2c) by reaction of $[\mathrm{Pt(C_2H_4)_2(PBu^t_2Me)}]$ with $[\mathrm{MnI}(\overline{\mathrm{COCH_2CH_2CH_2}})(\mathrm{CO})_4]$ is of interest in the context of earlier studies. Fischer and Beck[12] found that the mononuclear carbene complex $[\mathrm{Mo\{C(OMe)Ph\}(CO)(NO)}(\eta\text{-}\mathrm{C_5H_5})]$ reacted with $[\mathrm{Ni(CO)_4}]$ to give $[\mathrm{Ni_3}\{\mu\text{-}\mathrm{C(OMe)Ph}\}_3(\mathrm{CO})_3]$ and $[\mathrm{Mo(CO)_2(NO)}(\eta\text{-}\mathrm{C_5H_5})]$. Presumably the molybdenum-to-nickel carbene transfer occurs *via* an intermediate species containing a $[\overline{\mathrm{Mo}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Ni}}]$ group, and that as the carbene ligand passes on to the nickel the metal–metal bond breaks. In complex (2c) the iodo-ligand probably stabilises the metal–metal bond, so that a complex $[\mathrm{Pt_3}(\mu\text{-}\mathrm{COCH_2CH_2CH_2})_3(\mathrm{PBu^t_2Me})_3]$ does not form by trimerisation of $[\mathrm{Pt(COCH_2CH_2CH_2)(PBu^t_2Me)}]$ following elimination of $[\{\mathrm{MnI(CO)_4}\}_2]$. An *X*-ray crystallographic study[13] of the compound $[\mathrm{PtW}\{\mu\text{-}\mathrm{C(OMe)Ph}\}(\mathrm{CO})_5(\mathrm{PMe_3})_2]$ showed that the bridging C(OMe)Ph group was asymmetrically disposed across the metal–metal bond, being closer to the platinum. A similar asymmetry in the chromium analogue may presage the observed ready decomposition in toluene at 80 °C into $[Cr(CO)_5(PMe_3)]$, $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PMe_3)_3]$, and $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PMe_3)_3]$.[1]

The mononuclear manganese carbene complex $[MnI(COCH_2CH_2CH_2)(CO)_4]$ reacted with $[Pt(C_2H_4)(PMe_3)_2]$ at 0 °C to give a mixture of $[MnI(CO)_4(PMe_3)]$ and the previously fully characterised compound (3).[2] The expected product of this reaction was $[(OC)_4IMn(\mu\text{-}COCH_2CH_2CH_2)Pt(PMe_3)_2]$, based on the formation of $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ from $[Mn\{C(OMe)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PMe_3)_2]$.[2] Evidently a very complex reaction sequence occurs to afford (3). The latter was also formed, together with $[MnI(CO)_3(PMe_3)_2]$, when compound (2c) was reacted with an excess of trimethylphosphine. Reaction of (2c) in diethyl ether with carbon monoxide at 1 atm * afforded compound (1), and no manganese containing complex was identified. The triplatinum complex (1) was also produced in the reaction of $[Pt(C_2H_4)_2(PBu^t{}_2Me)]$ with the dimanganese carbene compound $[Mn_2(CO)_9(COCH_2CH_2CH_2)]$.

EXPERIMENTAL

The instrumentation used was as described in earlier Parts of this series.[13] Light petroleum refers to that fraction of b.p. 30—40 °C. Hydrogen-1, ^{31}P, and ^{13}C (^{1}H-decoupled) n.m.r. spectra were measured at 100, 40.48, and 25.15 MHz respectively. For ^{31}P spectra chemical shifts are in p.p.m. relative to 85% H_3PO_4 (external) with shifts to low frequency taken as positive. For ^{13}C spectra chemical shifts are in p.p.m. relative to $SiMe_4$ with positive values to high frequency. The complexes $[MnI(COCH_2CH_2CH_2)(CO)_4]$ [3] and $[Mn_2(CO)_9(COCH_2CH_2CH_2)]$ [14] were prepared as described elsewhere.

Reactions of $[MnI(COCH_2CH_2CH_2)(CO)_4]$.—(a) *With bis(ethylene)(methyldi-t-butylphosphine)platinum.* Bis(cycloocta-1,5-diene)platinum [15] (0.411 g, 1 mmol) was dissolved portion-wise in light petroleum (40 cm³) at 0 °C saturated with ethylene, and $PBu^t{}_2Me$ (1 mmol) was added. To the resulting solution of $[Pt(C_2H_4)_2(PBu^t{}_2Me)]$ was added $[MnI(COCH_2CH_2CH_2)(CO)_4]$ (0.364 g, 1 mmol) in tetrahydrofuran (40 cm³) to dissolve the manganese compound. The mixture was stirred (4 h) at room temperature, and then the solvent was removed *in vacuo*. The resulting brown oil was dissolved in toluene and transferred to an alumina column. Elution with a mixture (10 : 1) of light petroleum and diethyl ether gave a red solution. Evaporation and crystallisation from light petroleum gave red *crystals* of $[Pt_3(\mu\text{-}CO)_3(PBu^t{}_2Me)_3]$ (1) (60 mg, 21%) (Found: C, 31.0; H, 5.6. Calc. for $C_{30}H_{63}O_3P_3Pt_3$: C, 31.3; H, 5.5%); $\nu_{max.}$ (hexane) CO at 1 827s and 1 760vs cm⁻¹; ^{1}H n.m.r. ($[^{2}H_6]$benzene): τ 8.10 [d, 4 H, Bu^t, J(PH) 12] and 8.75 [d, 9 H, Me, J(PH) 8, J(PtH) 22 Hz]. Elution of a yellow band from the column with diethyl ether gave, after evaporation of solvent, an orange residue. Crystallisation from light petroleum at −78 °C afforded orange *crystals* of the complex $[MnPt(\mu\text{-}I)(COCH_2CH_2CH_2)(CO)_4(PBu^t{}_2Me)]$ (2c) (270 mg, 38%), m.p. 128 °C [Found: C, 28.5; H, 3.9%. *M*(mass spec.), 719. Calc. for $C_{17}H_{27}IMnO_5PPt$: C, 28.4; H, 3.8%. *M*, 719]; $\nu_{max.}$ (hexane), 2 031m, 1 961s, 1 951s, and 1 900s cm⁻¹ (CO), $\nu_{max.}$ (Nujol), 2 033s, 1 939s br, 1 915s br, 1 879s br, 1 420w, 1 403w, 1 367m, 1 291w, 1 281w, 1 212s, 1 189s br, 1 080m, 1 039vw, 1 018w, 935w, 890s, 879m, 871w, 838w br, 809w br, 774vw br, 729m, 666s, 647s, 630s, 576w br, 564w, 529w, 472m, 451w, and 420w br cm⁻¹. N.m.r.: ^{1}H ($[^{2}H_6]$benzene), τ 5.93 (m, 2 H, OCH_2), 6.41 (m, 2 H, CH_2), 8.72 [d, 3 H, MeP, J(PH) 8, J(PtH) 35], and 9.00 [d, br, 20 H, CH_2 and Bu^t, J(PH) 15 Hz]; ^{31}P ($[^{2}H_6]$benzene), δ −61.5 p.p.m. [J(PtP) 2 968 Hz]; ^{13}C [($[^{2}H_2]$dichloromethane), δ 261 [$COCH_2CH_2CH_2$, J(PtC) 1 704], 231, 223 [CO, J(PtC) 22], 217 [CO, J(PtC) 70], 82 [OCH_2, J(PtC) 118], 54 [CCH_2, J(PtC) 229], 35.5 [d, CMe_3, J(PC) 17, J(PtC) 50], 29 [d, CCH_3, J(PC) 5], 21.5 [$CH_2CH_2CH_2$, J(PtC) 35], and 12 p.p.m. [d, CH_3P, J(PC) 24, J(PtC) 65 Hz].

(b) *With (ethylene)bis(trimethylphosphine)platinum.* A solution of $[Pt(C_2H_4)(PMe_3)_2]$ (1 mmol) in light petroleum (40 cm³) at 0 °C was treated with $[MnI(COCH_2CH_2CH_2)(CO)_4]$ (1 mmol) in tetrahydrofuran (40 cm³). The mixture was stirred (3 h) and then the solvent was evaporated *in vacuo*. The oily residue was dissolved in toluene (10 cm³) and chromatographed on alumina. Elution with light petroleum–diethyl ether (4 : 1) gave a yellow solution. Evaporation and crystallisation from light petroleum gave orange *crystals* of $[MnI(CO)_4(PMe_3)]$ (60 mg, 16%) (Found: C, 22.6; H, 2.6. Calc. for $C_7H_9IMnO_4P$: C, 22.7; H, 2.4%); $\nu_{max.}$ (hexane) CO at 2 073s, 2 011s, and 1 953s cm⁻¹. ^{1}H n.m.r. ($[^{2}H_6]$benzene), τ 8.99 [d, 3 H, J(PH) 10 Hz]. Further elution of the column with light petroleum–diethyl ether (1 : 1) gave, after evaporation of solvent, yellow *crystals* of $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{—}2\text{-}\eta\text{-}C{=}CHCH_2CH_2O)\}Pt(PMe_3)_2]$ (3) (96 mg, 17%), identified spectroscopically by comparison with an authentic sample.[2]

Reaction of $[Mn_2(CO)_9(COCH_2CH_2CH_2)]$ *with Bis(ethylene)(methyldi-t-butylphosphine)platinum.*—A light petroleum (40 cm³) solution of $[Pt(C_2H_4)_2(PBu^t{}_2Me)]$ (1 mmol) was treated at 0 °C with $[Mn_2(CO)_9(COCH_2CH_2CH_2)]$ (0.5 mmol). After stirring for 6 h, solvent was removed *in vacuo* and the residue dissolved in toluene and chromatographed on alumina. Elution with light petroleum gave unreacted $[Mn_2(CO)_9(COCH_2CH_2CH_2)]$. Elution with a diethyl ether–light petroleum (1 : 10) mixture gave, after evaporation of solvent, red *crystals* of $[Pt_3(\mu\text{-}CO)_3(PBu^t{}_2Me)_3]$ (130 mg, 34%), identified by i.r. and n.m.r. (see above).

Reaction of Complex (2c) *with Trimethylphosphine.*—Compound (2c) (0.14 g, 0.2 mmol) was dissolved in a 1 : 1 mixture of light petroleum–diethyl ether (40 cm³). Trimethylphosphine (0.8 mmol) in light petroleum (1 cm³) was added drop-wise, the mixture turning from orange to pale yellow. Volatile material was removed *in vacuo* giving a yellow residue. The latter was dissolved in toluene and chromatographed on alumina. Elution with light petroleum–diethyl ether (5 : 1) gave a yellow solution from which was obtained orange *crystals* of $[MnI(CO)_3(PMe_3)_2]$ (15 mg, 18%) (Found:

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* Throughout this paper: 1 atm = 101 325 Pa.

C, 25.6; H, 4.5. Calc. for $C_9H_{18}IMnO_3P_2$: C, 25.8; H, 4.3%); $\nu_{max.}$ (hexane) CO at 2 023m, 1 945s, and 1 908s cm^{-1}, ^{1}H n.m.r. ([$^2H_6$]benzene), τ 8.66 [d, 18 H, J(PH) 8 Hz]. Elution of the column with a 1 : 1 mixture of diethyl ether–light petroleum gave the compound (3) (10 mg, 9%), identified spectroscopically.

Crystal-structure Determination of [MnPt(μ-I)-($COCH_2CH_2CH_2$)(CO)$_4$(PBu$^t_2$Me)].—Crystals of (2c) grow as orange plates; that for data collection was of dimensions 0.18 × 0.14 × 0.03 mm, and diffracted intensities were recorded at 200 K for $2.9 \leqslant 2\theta \leqslant 65°$ on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[16] Of the total of 5 501 recorded independent intensities, 3 197 had $|F| \geqslant 5\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics, and only 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 programmes.[17]

Crystal data. $C_{17}H_{27}IMnO_5PPt$, $M = 719$, Orthorhombic, $a = 14.634(5)$, $b = 19.546(18)$, $c = 16.325(5)$ Å, $U = 4\,669.5$ Å^3, $D_m = 1.96$ (flotation), $Z = 8$, $D_c = 2.04$ g cm^{-3}, $F(000) = 2\,872$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 75.9 cm^{-1}, space group *Pbca*.

Structure solution and refinement. The structure was solved by the heavy-atom method and all atoms (except hydrogen) were located by successive electron-density difference syntheses. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included at positions calculated for rigid group atoms and only common temperature factors for chemically equivalent hydrogen atoms were refined. Refinement for the structure converged at R 0.036 (R' 0.036) with a mean shift-to-error ratio in the final cycle of refinement being 0.03 : 1 with a maximum of 0.36 : 1. A weighting scheme of the form $w = 1.585\,7\ (\sigma^2F + 0.001\ F^2)^{-1}$, 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 > 0.85 e Å^{-3} or less than -1.0 e Å^{-3}. Scattering factors were from ref. 18 for C, O, and P, ref. 19 for hydrogen, and ref. 20 for Mn, Pt, and I, including corrections for the effects of anomalous dispersion for 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), and I ($\Delta f'$ −0.726, $\Delta f''$ 1.812). Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2, and some least-squares planes in Table 3. Packing of the unit cell is shown in Figure 2. Observed and calculated structure factors, all thermal parameters, and parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22782 (20 pp.).*

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

REFERENCES

[1] Part 4, T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, preceding paper.

[2] M. Berry, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Dalton*, 1980, 1601.

[3] C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 351.

[4] T. Yoshida and S. Otsuka, *J. Amer. Chem. Soc.*, 1977, **99**, 2134.

[5] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

[6] J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1979, 1170.

[7] T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Dalton*, 1980, 1609.

[8] G. K. Anderson, R. J. Cross, L. Manojlović-Muir, K. W. Muir, and R. A. Wales, *J.C.S. Dalton*, 1979, 684.

[9] (*a*) M. R. Truter and R. C. Watling, *J. Chem. Soc.* (*A*), 1967, 1955; (*b*) R. Mason, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc.* (*A*), 1976, 535; (*c*) G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1978, 1839.

[10] P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J.C.S. Dalton*, 1977, 2038.

[11] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J.C.S. Dalton*, 1978, 46.

[12] E. O. Fischer and H. J. Beck, *Angew. Chem. Internat. Edn.*, 1970, **9**, 72.

[13] T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J.C.S. Dalton*, 1980, 1593.

[14] C. P. Casey, *Chem. Comm.*, 1970, 1220; C. P. Casey and R. L. Anderson, *J. Amer. Chem. Soc.*, 1971, **93**, 3554.

[15] J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213; M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[16] P. Woodward and A. Modinos, *J.C.S. Dalton*, 1974, 2065.

[17] G. M. Sheldrick, Cambridge University, 1976.

[18] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[19] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[20] ' International Tables for X-Ray Crystallography ' Kynoch Press, Birmingham, 1975, vol. 4.