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ORGANOMETALLIC COMPLEXES WITH METAL—METAL BONDS

XVI *. SYNTHESIS OF NEW TRI- AND TETRAMETALLIC PLATINUM-MANGANESE COMPLEXES. CRYSTAL STRUCTURES OF $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(CO)(\mu_2\text{-}PPh_2)Mn}(CO)_4$, $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}H(\mu_2\text{-}PPh_2)_2Mn(CO)_4$ AND $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(\mu_2\text{-}PPh_2)_2Pt(\mu_2\text{-}PPh_2)Mn}(CO)_4$ **

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Summary

Reaction of *cis*-$PtCl_2(PPh_2Cl)_2$ with $NaMn(CO)_5$ in tetrahydrofuran yields new tri- and tetrametallic platinum-manganese complexes. The substitution of the Pt—Cl and P—Cl bonds is accompanied by a redox reaction, a labilization of the Pt—P bonds as exemplified by the isolation of complexes in which such bonds have been broken or created, and the rupture of one Mn—CO bond.

The various complexes were separated by column chromatography and the following tri- and tetrametallic complexes were characterized: $Pt(CO)_2[Mn(CO)_5]_2$, I, which is most likely to possess a linear Mn—Pt—Mn arrangement; $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(CO)(\mu_2\text{-}PPh_2)Mn}(CO)_4$, II, which was shown by X-ray diffraction to have a chiral $PtMn_2P_2$ framework with two Pt—Mn bonds (average 2.744(1) Å) forming an angle of 159.54(6)°, and two PPh_2 groups spanning these bonds; $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}H(\mu_2\text{-}PPh_2)_2Mn(CO)_4$, III, which possesses one Pt—Mn bond (2.847(2) Å) spanned by a PPh_2 ligand, whereas the other Pt—Mn

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[*] Part XV: see Ref. 1.

[**] Dedicated to the memory of Professor Paolo Chini.

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separation (3.618(2) Å) does not correspond to a metal—metal bond, the metals being only connected by two PPh_2 ligands; $(OC)_4Mn(\mu_2\text{-}PPh_2)Pt(\mu_2\text{-}PPh_2)_2Pt(\mu_2\text{-}PPh_2)Mn(CO)_4$, IV, which is a centrosymmetric molecule characterized by the first planar heterotetrametallic chain (with Pt(1)Pt(1)′ = 2.669(1) Å and Pt(1)Mn(1) = 2.717(2) Å and Mn(1)Pt(1)Pt(1)′ = 146.11(8)°), and by one bridging PPh_2 group on each Pt—Mn bond and two PPh_2 bridges on the Pt—Pt bond. Almost planar pentacoordination is found for platinum in II and IV, and is most likely for III, but the hydrogen atom in the latter was not located by X-ray diffraction.

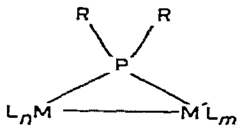
The synthetic method used in this work appears promising for the preparation of novel heteropolymetallic complexes, although a detailed reaction mechanism cannot be proposed.

Introduction

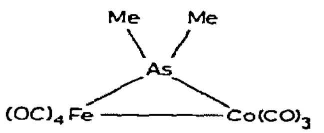
The attention recently focused on phosphido- or arsenido-bridged organometallic clusters is mainly due to the expectation that the bridging ligands will prevent the clusters from fragmenting into mononuclear moieties when treated with organic reagents. This is highly desirable in view of the current search for new homogeneous catalysts of the cluster type. In a unit such A, which may be a bimetallic complex or part of a larger cluster, the possible metal—metal bond functionality, its heteronuclear nature, and the great flexibility of the M—P—M′ angle, can give rise to unusual reactivity. Recent examples illustrating these points include:

(1) The catalytic activity of B for the homogeneous dimerization of norbornadiene into Binor-S, shown to preceed by opening of the iron—cobalt bond [2];

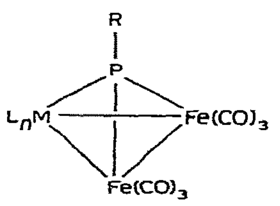
(2) The first demonstration that clusters can reversibly add CO with opening of metal—metal bond(s), achieved with complexes of type C [3];



(A)



(B)



(C)

L_nM = $(CO)_5Cr$, $(CO)_2CpMn$

R = alkyl, aryl

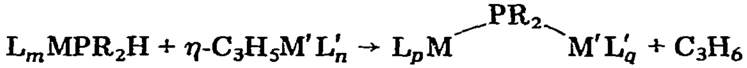
(3) The reduction of $Fe_2(CO)_6(\mu_2\text{-}PPh_2)_2$ to $[Fe_2(CO)_6(\mu_2\text{-}PPh_2)]^{2-}$ with considerable change in the Fe_2P_2 core geometry and its reaction with alkyl halides yielding aldehydes quantitatively after protonation [4];

(4) The ability of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2$, stabilized by the capping P—Ph bridges to act as an hydroformylation catalyst [5].

The syntheses of heteronuclear phosphido- (or arsenido-) bridged complexes mainly involve four different approaches:

(1) Propene elimination resulting from the reaction of a π-allyl complex with

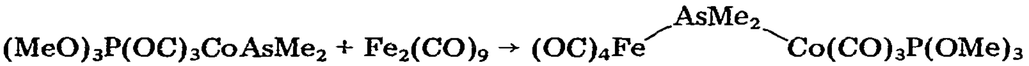
coordinated PR_2H:



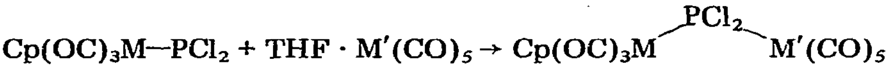
$$L_mMPR_2H + \eta\text{-}C_3H_5M'L'_n \rightarrow L_pM\overset{PR_2}{\diagup\ \diagdown}M'L'_q + C_3H_6$$

This method, first reported by Thomson et al. [6], has been largely used and extended by Vahrenkamp to produce bridged systems with or without metal—metal bonds [7].

(2) Reaction of mononuclear phosphido (or arsenido) complexes with neutral metal carbonyls, e.g. [8]:

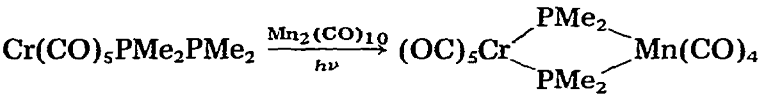
(a) 

$$(MeO)_3P(OC)_3CoAsMe_2 + Fe_2(CO)_9 \rightarrow (OC)_4Fe\overset{AsMe_2}{\diagup\ \diagdown}Co(CO)_3P(OMe)_3$$

(b) 

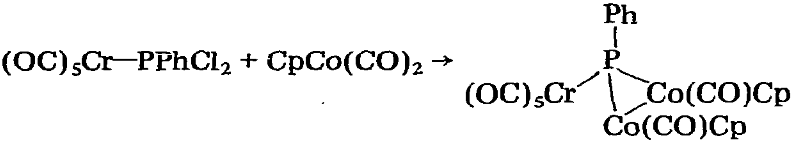
$$Cp(OC)_3M\text{—}PCl_2 + THF \cdot M'(CO)_5 \rightarrow Cp(OC)_3M\overset{PCl_2}{\diagup\ \diagdown}M'(CO)_5$$

(3) Cleavage of the coordinated Me_2PPMe_2 ligand, e.g. [9]:

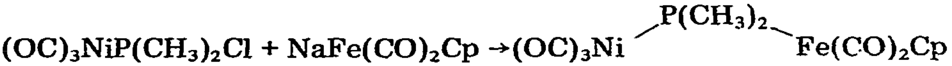


$$Cr(CO)_5PMe_2PMe_2 \xrightarrow[h\nu]{Mn_2(CO)_{10}} (OC)_5Cr\underset{PMe_2}{\overset{PMe_2}{\lessgtr\ \gtrless}}Mn(CO)_4$$

(4) Chloride substitution from a coordinated chlorophosphine, e.g. [10,11]:

(a) 

$$(OC)_5Cr\text{—}PPhCl_2 + CpCo(CO)_2 \rightarrow (OC)_5Cr\text{—}P(Ph)[Co(CO)Cp]_2$$

(b) 

$$(OC)_3NiP(CH_3)_2Cl + NaFe(CO)_2Cp \rightarrow (OC)_3Ni\overset{P(CH_3)_2}{\diagup\ \diagdown}Fe(CO)_2Cp$$

In general, these reactions are limited either by the availability of the precursors or by the low yields arising from secondary reactions.

The type of reaction we have previously used for the preparation of platinum-mixed metal clusters, which is based on chloride substitution in $PtCl_2(PR_3)_2$ complexes by carbonylmetallates, e.g. $Co(CO)_4^-$ [12], $Mo(CO)_3Cp^-$, $W(CO)_3Cp^-$ [13], failed with $Mn(CO)_5^-$. With the latter no mixed platinum-manganese cluster could be isolated, but instead the pentametallic $Pt_5(CO)_6(PR_3)_4$ cluster was obtained [14]. This was surprising since we had shown that Pt—Mn bonds are intrinsically strong enough to allow the isolation of trimetallic open $(OC)_5MnPt(L)_2Mn(CO)_5$ complexes [15] (L = pyridine, isonitrile). This observation led us to envisage the use of a bridge-assisted metal—metal bond formation method which, to our knowledge, had not previously been investigated with platinum. The reaction of pentacarbonylmanganate with *cis*-$PtCl_2(Ph_2PCl)_2$ does, indeed, permit isolation of new Pt—Mn complexes containing the diphenylphosphido bridging ligand, and is the subject of this paper.

Experimental

The reaction was performed in a Schlenk-type flask under dry nitrogen. Solvents were distilled under nitrogen from sodium benzophenone-ketyl prior to use, except for dichloromethane which was dried over and distilled from P_2O_5. Nitrogen (Air Liquide R grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. Chromatography was performed using a silica gel column (Kieselgel 60, Merck). Elemental C and H analyses were performed by the Service Central de Microanalyses du C.N.R.S. Infrared spectra were recorded on a Perkin-Elmer 398 spectrophotometer with KBr pellets in the region 4000—400 cm^{-1} and on a Polytec FIR 30 FT-Interferometer with polythene discs in the region 420—50 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra were recorded at 36.43 MHz on a FT Bruker WH-90 instrument. Positive phosphorus chemical shifts are downfield relative to external H_3PO_4. The ^1H NMR spectrum was recorded at 250 MHz on a Cameca instrument.

Mass spectra for compounds I and II were measured on a Thompson THN Mass Spectrometer, E.I., 70 eV, 8 kV by Dr. G. Teller (Université Louis Pasteur). Those of compounds III and IV were measured on a Varian 311 A spectrometer, E.I., 115 eV, 2.6 kV and F.D. conditions, respectively, by Dr. T. Würminghausen (Paderborn, West Germany).

Preparation of complexes

$NaMn(CO)_5$ was prepared by literature methods [16]. *cis*-$PtCl_2(Ph_2PCl)_2$ was prepared by adding a solution of freshly distilled Ph_2PCl (2.32 g, 10.5 mmol) in toluene (20 ml) dropwise to a stirred suspension of $PtCl_2(PhCN)_2$ (2.36 g, 5 mmol) in toluene (250 ml). After 15 h stirring, the white product was filtered off, washed with pentane, and dried under vacuum.
Anal. Found: C, 40.68; H, 2.80. Calcd. for $C_{24}H_{20}Cl_4P_2Pt$: C, 40.76; H, 2.85%. Far IR: 322s, 298vs cm^{-1}.

Preparation of $PtMn_2(CO)_{12}$ (I)

To a stirred suspension of *cis*-$PtCl_2(Ph_2PCl)_2$ (1.41 g, 2 mmol) in THF (50 ml) was added at 0°C a tetrahydrofuran solution (40 ml) of $NaMn(CO)_5$, prepared from $Mn_2(CO)_{10}$ (1.60 g, 4 mmol). The resulting dark red mixture was stirred for 2 h at room temperature then filtered, and the solvent was removed under vacuo. The residue was chromatographed at —15°C on a silica gel column. Elution with pentane gave first a yellow solution of $Mn_2(CO)_{10}$ (trace amount, characterized by IR), then a red solution of I, affording claret-colored needles on crystallization at —78°C (0.04 g, 3% based on Pt).
Anal. Found: C, 22.09; H, $\simeq$0. Calcd. for $C_{12}Mn_2O_{12}Pt$; C, 22.48%. Mass spectrum: 641 (*M*), 501 ($M - 5$ CO), 473 ($M - 6$ CO), 445 ($M - 7$ CO), 417 ($M - 8$ CO), 389 ($M - 9$ CO), 361 ($M - 10$ CO), 332 ($M - 11$ CO), 305 ($M - 12$ CO — Mn), m.p. 78°C (dec.), IR: ν(CO) 2066s. 2046s, 2022s, 1994(sh), 1984vs, 1967vs cm^{-1} far IR bands: 171s, 98 vs cm^{-1}.

Preparation of $PtMn_2(\mu_2\text{-}PPh_2)_2(CO)_9$ (II)

After elution of complex I in the previous reaction, further elution with pentane gave a concentrated red solution from which orange-red crystals of II were obtained at —10°C (0.20 g, 11% based on Pt).
Anal. Found: C, 42.77; H, 2.09. Calcd. for $C_{33}H_{20}Mn_2O_9P_2Pt$: C, 42.74; H, 2.17%. Mass spectrum: 927 (*M*), 899 (M — CO), 815 ($M - 4$ CO), 787 ($M - 5$

CO), 703 ($M - 8$ CO), 675 ($M - 9$ CO). m.p. 171–172°C. IR: ν(CO) 2069s, 2050s, 2000(sh), 1990vs, 1970vs, 1945vs cm^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 161 ppm (with ^{195}Pt satellites, ^{1}J(PPt) = 2265 Hz).

Preparation of $PtMn_2H(\mu_2\text{-}PPh_2)_3(CO)_8$ *(III)*

This complex was obtained during the reaction described above which gave I and II. Chromatography with a 1/2 toluene/pentane mixture gave a yellow solution of III. Recrystallization from toluene/pentane afforded III as yellow single crystals (0.08 g, 4% based on Pt).
Anal. Found: C, 48.60; H, 2.77. Calcd. for $C_{44}H_{31}Mn_2O_8P_3Pt$: C, 48.68; H, 2.88%. Mass spectrum: 1057 ($M - $ CO), 973 ($M - 4$ CO), 945 ($M - 5$ CO), 889 ($M - 7$ CO), 861 ($M - 8$ CO), 784 ($M - 8$ CO $- C_6H_5$). m.p. >195°C. IR: ν(CO) 2060s, 1992vs, 1982vs, 1955vs, 1951vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −11.15 (ddd, ALMNX spin system with L, M, N = P, X = Pt, ^{2}J(LH) = 55.7 Hz, ^{2}J(NH) = 18.3 Hz, ^{2}J(MH) = 6.9 Hz, ^{1}J(PtH) = 526 Hz) ppm. ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 124 (P(1), d with ^{195}Pt satellites, ^{2}J(P(1)P(2)) = 238 Hz, ^{2}J(P(1)P(3)) = 0 Hz, ^{1}J(P(1)Pt) = 1755 Hz), ≃−84 ppm (center of a broad signal, P(3)), ≃−102 (center of a broad doublet, P(2)) ppm.

Preparation of $Pt_2Mn_2(\mu_2\text{-}PPh_2)_4(CO)_8$ *(IV)*

This compound was obtained during the reaction described above. Chromatography with a 4/1 toluene/pentane mixture gave an orange-yellow solution. The solvent was removed and the brick-red residue was recrystallized from CH_2Cl_2/pentane, to give IV as red crystals (0.18 g, 12% based on Pt). Anal. Found: C, 45.85; H, 2.63. Calcd. for $C_{56}H_{40}Mn_2O_8P_4Pt_2$: C, 45.94; H, 2.75%. Mass spectrum: 1463.647 (calcd. M: 1463.972). m.p. >200°C (dec.). IR: ν(CO) = 2029s, 1967(sh), 1952vs, 1930(sh), 1927(sh), 1925(ms cm^{-1}. ^{31}P NMR (CD_2Cl_2). Two groups of signals were identified, centered at 273 ppm and 162 ppm, respectively: the first one showed sharp lines and was tentatively assigned to Pt(μ-PPh_2)$_2$Pt, while the second group showed broad lines (because of ^{55}Mn quadrupole broadening) and was assigned to Pt(μ-PPh_2)Mn moieties. The quality of the spectrum did not allow detailed analysis.

Collection of the X-ray data and structure determinations

The X-ray and molecular structures of compounds II and III were determined by O. Bars, M. Louër and D. Grandjean, that of compound IV by J. Fischer and A. Mitschler. Suitable single crystals of compound II were obtained from a pentane solution at −10°C. When crystallization of II was carried out in toluene/pentane (1/10) mixture another crystalline variety was obtained: monoclinic, a: 16.848(6), b: 11.595(5), c: 18.773(8) Å, β: 111.85(4)°, V = 3404 Å^3, Z = 2, space group: $P2_1/n$.

The molecular structure was found to be identical with that described below, the only difference being a slight variation in the stacking of the molecules.

Cell constants and other pertinent data are presented in Table 1. For IV, the space group was checked in precession photographs and precise lattice parameters were obtained by standard Enraf-Nonius and Philips least-squares methods using 25 carefully selected reflections. Intensity data were collected on automatic diffractometers. No intensity decay was observed during the data collec-

TABLE 1

CRYSTAL DATA AND INTENSITY COLLECTION DETAILS FOR II, III AND IV

Compound	$PtMn_2(\mu_2\text{-}PPh_2)_2(CO)_9$ (II)	$PtMn_2H(\mu_2\text{-}PPh_2)_3(CO)_8$ (III)	$Pt_2Mn_2(\mu_2\text{-}PPh_2)_4(CO)_8$ (IV)
Formula	$PtMn_2P_2O_9C_{33}H_{20}$	$PtMn_2P_3O_8C_{44}H_{31}$	$Pt_2Mn_2P_4O_8C_{56}H_{40}$
Molecular weight	927.09	1085.61	1464.89
Crystal system	triclinic	triclinic	monoclinic
a (Å)	10.240(5)	10.941(2)	24.106(8)
b (Å)	10.812(4)	19.740(5)	12.002(4)
c (Å)	17.483(8)	10.720(2)	20.841(7)
α (deg.)	94.89(3)	96.13(2)	20 841(7)
β (deg.)	101.41(5)	105.08(2)	93.39(2)
γ (deg.)	112.14(3)	105.22(2)	
V (Å^3)	1730	2118	6019
Z	2	2	4
Density obs. (calcd.)	1.78 ± 0.02 (1.77)	1.70 ± 0.02 (1.71)	1.60 ± 0.02 (1.62)
Crystal dimension (mm)		0.08 × 0.08 × 0.15	sphere Φ = 0.35 ± 0.01
Space Group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
F_{000} (e^-)	896	1064	2824
Diffractometer	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4	Philips PW 1100/16
Radiation	Mo-K_α (graphite monochromated)	Mo-K_α (graphite monochromated)	Mo-K_α (graphite monochromated)
Linear absorption coefficient (cm^{-1})	23	42.5	54.6
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan range (deg.)	1.2 + 035 tg θ	1.0 + 0.35 tg θ	1.0 + 0.35 tg θ
Scan speed (deg. min^{-1})			1.44
θ limits (deg.)	1—30	2—25	2—25
Data collected	7419	7614	11787
Unique data used	4861	3353	6415 $I > 3\sigma(I)$
$R = \Sigma\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_0\rvert$	0.043	0.041	0.045
$R_w = (\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma w F_0{}^2)^{1/2}$	0.048	0.053	0.066
Standard error of an unit weight observation (e^-)	1.28	1.04	1.28
Fudge factor	0.03	0.025	0.08

tion. The crystal structures were solved using the heavy atom method and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located on difference maps, and introduced by their computed coordinates in structure factor calculations. The final difference maps showed no significant maxima. The refinement results are given in Table 1. Tables of observed and calculated structure factors may be obtained from the authors.

The molecular structures of complexes II, III, IV are shown in Figs. 1—3, which also illustrate the numbering of atoms used throughout. Fractional atomic coordinates are given in Tables 2—4. Anisotropic thermal parameters are presented in Tables 5—7. Interatomic distances and bond angles are given in Tables 8—10, least-squares planes in Tables 11—13. Estimated standard deviations are in parenthesis throughout.

Results and discussion

The chloride substitutions occurring in reactions between square planar Pt^{II} substrates $PtCl_2L_2$ and metal carbonyl anions have been shown to be complex reactions, often affording unexpected products [12—14]. Although we could not isolate complexes with Pt—Mn bonds on reacting $PtCl_2L_2$ ($L = PPh_3$, PEt_3) with $Na[Mn(CO)_5]$ we expected that the use of $L = PPh_2Cl$ would lead to production of phosphido-bridged Pt—Mn bonds.

The reaction of carbonylmetallates with coordinated chlorophosphines has been used in the past [11], but not in platinum chemistry. A further extension in the present work was to use as precursor a complex with two such reactive chlorophosphines. In view of the number of Pt—Cl and P—Cl bonds in $PtCl_2(PPh_2Cl)_2$ the variety of structural types observed in the reaction was not surprising.

Reaction of *cis*-$PtCl_2(PPh_2Cl)_2$ with $Na[Mn(CO)_5]$ in THF at a Pt/Mn ratio of 1/4 (in order to ensure complete replacement of the chloride ligands) even at —20° C gave a large number of compounds, of which I—IV could be separated by column chromatography (see Experimental section). Complexes I, II and IV are red, complex III is yellow-brown. Their IR spectra in the carbonyl region showed only terminal carbonyl absorption bands (see Experimental section). Complex I was identified by IR spectroscopy and by its mass spectrum, which showed the stepwise loss of 12 carbonyls. Its formation involves the loss of the two phosphine ligands attached to the platinum in the substrate, and their replacement by two carbonyl groups originally on manganese. These ligand exchange reactions have frequently been used in synthesis of platinum clusters [12—14], possibly because of increased lability of the Pt—P bond when the metal becomes more electron-rich; substitution of Cl^- by $Mn(CO)_5^-$ at Pt—Cl and/or P—Cl bonds will render the platinum more electron rich. The structure of I is most likely to be analogous to that of the isoelectronic $(OC)_5Mn—Pt(RNC)_2—Mn(CO)_5$ molecules [15b], which have a linear arrangement of the three metal atoms, and which were among the first reported complexes containing a platinum—manganese bond [15a]. The ν_{as}(Pt—Mn) vibration was found in I at 171 cm^{-1} ($k = 0.60$ mdyn/Å) and indicates a strengthening of the metal—metal bond compared with, e.g. *trans*-$Pt[Mn(CO)_5]_2$(*tert*-$BuNC)_2$

TABLE 2

ATOMIC COORDINATES OF II [a]

Atom	*X*	*Y*	*Z*
Pt	0.42527(5)	0.20671(5)	0.25330(3)
Mn(1)	0.2881(2)	0.1237(2)	0.0951(1)
Mn(2)	0.4841(2)	0.2045(2)	0.4133(1)
P(1)	0.6400(3)	0.3285(3)	0.3479(2)
P(2)	0.4599(4)	0.3296(3)	0.1512(2)
C(1)	0.2639(11)	0.1306(10)	−0.0083(6)
C(2)	0.1430(11)	0.1831(11)	0.0998(6)
C(3)	0.1599(11)	−0.0490(11)	0.0891(6)
C(4)	0.4266(11)	0.0560(9)	0.0933(6)
C(5)	0.4102(9)	0.3331(9)	0.4265(6)
C(6)	0.3225(10)	0.0858(9)	0.4372(5)
C(7)	0.5385(10)	0.0644(9)	0.3932(6)
C(8)	0.6055(11)	0.2632(10)	0.5112(6)
C(9)	0.2680(9)	0.0478(9)	0.2600(5)
C(10)	0.7841(8)	0.2737(8)	0.3366(5)
C(11)	0.8834(10)	0.2752(10)	0.4033(6)
C(12)	0.9901(12)	0.2264(13)	0.3976(8)
C(13)	0.9921(13)	0.1741(14)	0.3250(9)
C(14)	0.8976(14)	0.1708(14)	0.2587(8)
C(15)	0.7891(11)	0.2203(10)	0.2635(6)
C(16)	0.7269(9)	0.5127(7)	0.3648(5)
C(17)	0.6426(10)	0.5873(8)	0.3636(5)
C(18)	0.7094(12)	0.7300(9)	0.3730(6)
C(19)	0.8548(13)	0.7926(10)	0.3812(7)
C(20)	0.9397(12)	0.7210(10)	0.3843(7)
C(21)	0.8766(9)	0.5801(8)	0.3759(6)
C(22)	0.4134(9)	0.4740(8)	0.1711(5)
C(23)	0.3393(17)	0.6893(13)	0.2082(8)
C(24)	0.4737(13)	0.5918(10)	0.1410(6)
C(25)	0.3179(10)	0.4670(9)	0.2185(6)
C(26)	0.4323(18)	0.6991(12)	0.1611(8)
C(27)	0.2792(13)	0.5750(12)	0.2359(7)
C(28)	0.6338(9)	0.4001(8)	0.1269(5)
C(29)	0.7486(10)	0.5151(9)	0.1733(6)
C(30)	0.8838(11)	0.5600(11)	0.1561(7)
C(31)	0.9058(12)	0.4953(13)	0.0924(8)
C(32)	0.7949(13)	0.3822(12)	0.0463(7)
C(33)	0.6560(11)	0.3320(10)	0.0621(6)
O(1)	0.2497(10)	0.1364(9)	0.0741(5)
O(2)	0.0465(9)	0.2136(9)	0.0983(5)
O(3)	0.0761(9)	−0.1603(8)	0.0823(5)
O(4)	0.5068(9)	0.0056(7)	0.0911(5)
O(5)	0.3572(8)	0.4070(7)	0.4367(5)
O(6)	0.2237(8)	0.0122(7)	0.4549(5)
O(7)	0.5684(9)	−0.0256(7)	0.3801(5)
O(8)	0.6850(9)	0.2962(8)	0.5717(4)
O(9)	0.1728(8)	−0.0494(7)	0.2635(4)

[a] In this and subsequent tables, estimated standard deviations in the last place of figures are given in parentheses.

(ν_{as}(Pt—Mn) = 164 cm^{-1}, k = 0.56 mdyn/Å). This is due to the better π-acceptor properties of CO vs. RNC [15b].

Complex II is one of the main products (yield ca. 10%, based on Pt). Although the mass spectrum and the elemental analysis allowed an unambiguous formula-

TABLE 3

ATOMIC COORDINATES OF III

Atom	*X*	*Y*	*Z*
Pt	0.63940(6)	0.73382(4)	0.87603(6)
Mn(1)	0.7781(2)	0.6659(1)	0.7380(2)
Mn(2)	0.4509(2)	0.8524(1)	0.9378(2)
P(1)	0.8216(4)	0.6995(2)	0.9617(4)
P(2)	0.4762(4)	0.7794(2)	0.7636(4)
P(3)	0.5845(3)	0.7862(2)	1.0471(4)
C(1)	0.9009(17)	0.6184(9)	0.7395(16)
O(1)	0.9753(13)	0.5881(7)	0.7458(20)
C(2)	0.7043(17)	0.6486(9)	0.5562(18)
O(2)	0.6670(15)	0.6381(9)	0.4482(12)
C(3)	0.6581(16)	0.5820(10)	0.7442(16)
O(3)	0.5799(14)	0.5330(8)	0.7438(14)
C(4)	0.8990(18)	0.7496(11)	0.7311(16)
O(4)	0.9754(12)	0.7990(7)	0.7238(18)
C(5)	0.6008(14)	0.9180(9)	0.9274(14)
O(5)	0.6922(11)	0.9576(6)	0.9159(11)
C(6)	0.3423(13)	0.8948(9)	0.8258(16)
O(6)	0.2745(11)	0.9218(7)	0.7746(12)
C(7)	0.4624(14)	0.9046(7)	1.0918(16)
O(7)	0.4752(10)	0.9384(6)	1.1904(11)
C(8)	0.3009(14)	0.7825(9)	0.9337(13)
O(8)	0.2085(10)	0.7377(6)	0.9273(10)
C(9)	0.8252(13)	0.6290(7)	1.0523(13)
C(10)	0.7289(14)	0.6024(8)	1.1127(14)
C(11)	0.7259(16)	0.5450(10)	1.1787(16)
C(12)	0.8283(16)	0.5151(8)	1.1885(15)
C(13)	0.9261(14)	0.5387(9)	1.1315(15)
C(14)	0.9229(13)	0.5934(9)	1.0622(13)
C(15)	0.9644(12)	0.7724(9)	1.0564(13)
C(16)	0.9715(14)	0.8412(10)	1.0272(15)
C(17)	1.0702(16)	0.8991(9)	1.0965(17)
C(18)	1.1726(16)	0.8924(11)	1.1929(17)
C(19)	1.1727(14)	0.8276(12)	1.2286(17)
C(20)	1.0683(14)	0.7686(8)	1.1544(14)
C(21)	0.5312(12)	0.8336(7)	0.6486(12)
C(22)	0.4473(14)	0.8632(8)	0.5663(13)
C(23)	0.4997(17)	0.9087(9)	0.4877(16)
C(24)	0.6330(16)	0.9270(8)	0.4993(14)
C(25)	0.7160(17)	0.8966(10)	0.5822(17)
C(26)	0.6666(14)	0.8518(8)	0.6549(15)
C(27)	0.3260(12)	0.9109(8)	0.6544(12)
C(28)	0.2026(11)	0.7238(8)	0.6033(13)
C(29)	0.1007(15)	0.6686(11)	0.5216(17)
C(30)	0.1079(18)	0.6013(11)	0.4880(15)
C(31)	0.2259(17)	0.5879(8)	0.5402(14)
C(32)	0.3359(14)	0.6415(8)	0.6251(13)
C(33)	0.7312(11)	0.8358(7)	1.1892(12)
C(34)	0.7932(14)	0.7961(8)	1.2701(15)
C(35)	0.9065(15)	0.8301(11)	1.3705(14)
C(36)	0.9619(15)	0.9033(11)	1.3923(16)
C(37)	0.8978(16)	0.9424(9)	1.3164(15)
C(38)	0.7824(13)	0.9089(7)	1.2137(13)
C(39)	0.4875(11)	0.7220(7)	1.1225(12)
C(40)	0.4700(13)	0.7442(7)	1.2389(13)
C(41)	0.3931(15)	0.6991(9)	1.3006(14)
C(42)	0.3278(14)	0.6300(10)	1.2321(16)
C(43)	0.3425(14)	0.6053(7)	1.1141(14)
C(44)	0.4192(12)	0.6516(7)	1.0568(13)

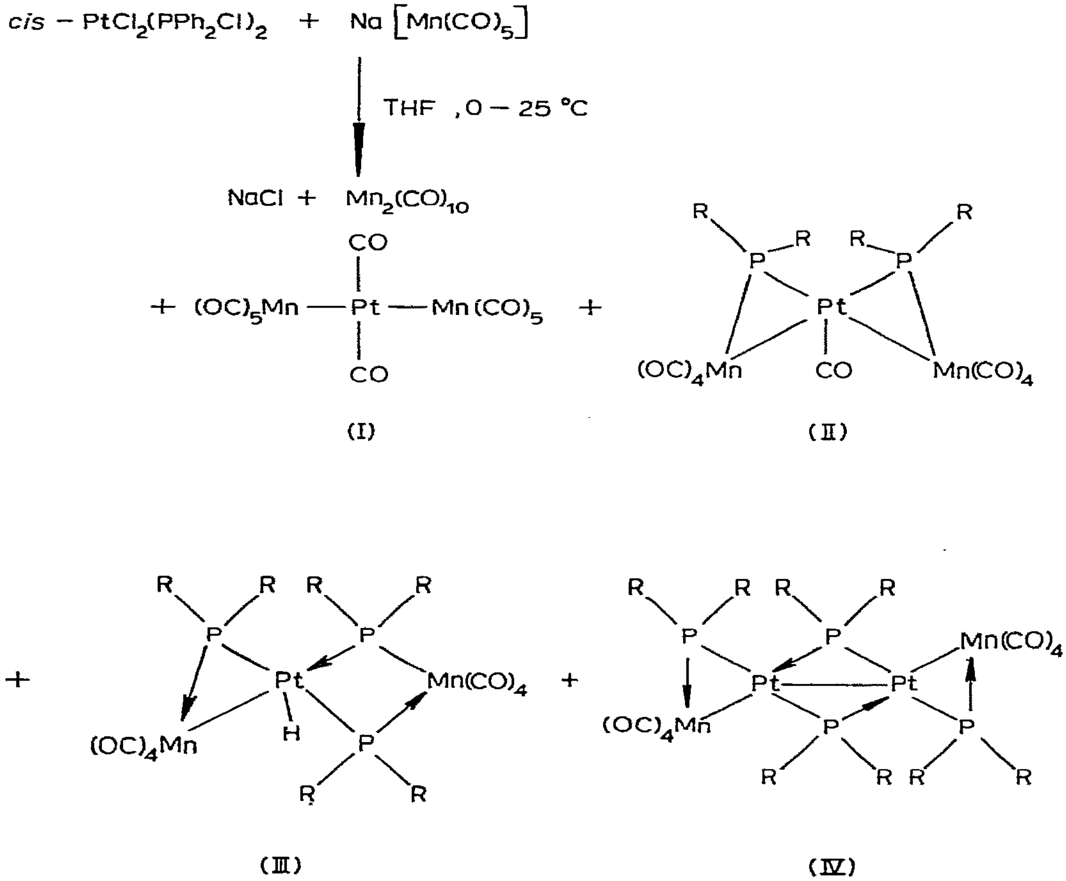
TABLE 4

ATOMIC COORDINATES OF IV

Atom	*X*	*Y*	*Z*
Pt(1)	0.04950(2)	0.03724(4)	0.02268(2)
Pt(2)	0.45501(2)	−0.56023(4)	0.01073(2)
Mn(1)	0.15003(8)	−0.0175(2)	0.07986(10)
Mn(2)	0.39019(8)	−0.7367(2)	−0.02505(9)
P(1)	0.1245(1)	0.1493(3)	0.0396(2)
P(2)	−0.0184(1)	0.1419(3)	−0.0274(2)
P(3)	0.5155(1)	−0.5940(3)	−0.0671(2)
P(4)	0.6282(1)	−0.3927(3)	−0.0482(2)
O(1)	0.2648(4)	0.0203(9)	0.1223(6)
O(2)	0.1140(5)	0.0482(9)	0.2084(5)
O(3)	0.1399(5)	−0.2474(8)	0.1258(5)
O(4)	0.1857(5)	−0.0907(9)	−0.0473(6)
O(5)	0.4537(5)	−0.8789(8)	−0.1146(5)
O(6)	0.2887(4)	−0.8784(9)	−0.0243(6)
O(7)	0.4518(5)	−0.8671(9)	0.0819(5)
O(8)	0.3440(5)	−0.5944(9)	−0.1329(5)
C(1)	0.2214(6)	0.004(1)	0.1074(7)
C(2)	0.1259(6)	0.026(1)	0.1584(7)
C(3)	0.1427(6)	−0.160(1)	0.1071(7)
C(4)	0.1725(7)	−0.063(1)	0.0034(6)
C(5)	0.4302(6)	−0.822(1)	−0.0836(6)
C(6)	0.3271(6)	−0.826(1)	−0.0252(7)
C(7)	0.4286(6)	−0.819(1)	0.0455(7)
C(8)	0.3620(6)	−0.646(1)	−0.0920(6)
C(9)	0.1247(5)	0.269(1)	0.0958(6)
C(10)	0.0782(6)	0.342(1)	0.0918(7)
C(11)	0.0800(7)	0.432(1)	0.1352(8)
C(12)	0.1226(7)	0.452(1)	0.1763(8)
C(13)	0.1690(7)	0.381(1)	0.1772(8)
C(14)	0.1700(6)	0.285(1)	0.1383(7)
C(15)	0.1532(5)	0.210(1)	−0.0310(6)
C(16)	0.1842(6)	0.307(1)	−0.0275(7)
C(17)	0.2053(6)	0.345(1)	−0.0824(9)
C(18)	0.1960(6)	0.296(1)	−0.1429(8)
C(19)	0.1660(7)	0.205(2)	−0.1458(7)
C(20)	0.1427(6)	0.159(1)	−0.0900(8)
C(21)	−0.0022(5)	0.200(1)	−0.1047(6)
C(22)	0.0188(6)	0.307(1)	−0.1129(7)
C(23)	0.0347(6)	0.341(1)	−0.1730(7)
C(24)	0.0284(7)	0.271(2)	−0.2244(8)
C(25)	0.0078(8)	0.164(2)	−0.2166(8)
C(26)	−0.0068(6)	0.132(1)	−0.1567(7)
C(27)	−0.0498(5)	0.245(1)	0.0196(6)
C(28)	−0.0688(6)	0.346(1)	−0.0003(7)
C(29)	−0.0935(7)	0.421(1)	0.0361(8)
C(30)	−0.1005(7)	0.393(1)	0.0982(10)
C(31)	−0.0826(7)	0.291(1)	0.1238(8)
C(32)	−0.0542(6)	0.218(1)	0.0835(7)
C(33)	0.5598(5)	−0.714(1)	−0.0636(6)
C(34)	0.5966(6)	−0.738(1)	−0.1078(7)
C(35)	0.6341(8)	−0.827(1)	−0.0970(9)
C(36)	0.6334(8)	−0.890(1)	−0.0456(9)
C(37)	0.5986(7)	−0.863(1)	−0.0010(9)
C(38)	0.5609(5)	−0.778(1)	−0.0083(7)
C(39)	0.4920(5)	−0.572(1)	−0.1485(6)
C(40)	0.4754(6)	−0.466(1)	−0.1636(7)
C(41)	0.4561(8)	−0.441(1)	−0.2278(8)
C(42)	0.4543(8)	−0.525(2)	−0.2749(8)

TABLE 4 (continued)

Atom	*X*	*Y*	*Z*
C(43)	0.4714(7)	−0.630(1)	−0.2581(7)
C(44)	0.4891(6)	−0.653(1)	−0.1934(7)
C(45)	0.6825(5)	−0.498(1)	−0.0359(6)
C(46)	0.7287(5)	−0.499(1)	−0.0707(6)
C(47)	0.7678(6)	−0.575(1)	−0.0598(8)
C(48)	0.7631(6)	−0.650(1)	−0.0199(9)
C(49)	0.7199(7)	−0.657(1)	0.0197(8)
C(50)	0.6769(6)	−0.578(1)	0.0102(7)
C(51)	0.6358(5)	−0.353(1)	−0.1309(6)
C(52)	0.6637(6)	−0.258(1)	−0.1462(6)
C(53)	0.6730(7)	−0.234(1)	−0.2093(8)
C(54)	0.6539(8)	−0.306(1)	−0.2585(7)
C(55)	0.6241(8)	−0.401(1)	−0.2455(7)
C(56)	0.6154(7)	−0.420(1)	−0.1794(7)



R = Ph

TABLE 5

ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS FOR II

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00765(6)	0.00559(5)	0.00255(2)	0.00252(4)	0.00066(3)	0.00048(2)
Mn(1)	0.0114(3)	0.0100(3)	0.0030(1)	0.0032(2)	0.0006(1)	0.0002(1)
Mn(2)	0.0105(3)	0.0071(2)	0.0029(1)	0.0028(2)	0.0010(1)	0.0006(1)
P(1)	0.0084(4)	0.0068(3)	0.0032(2)	0.0034(3)	0.0009(2)	0.0007(2)
P(2)	0.0107(5)	0.0080(4)	0.0028(2)	0.0039(3)	0.0010(2)	0.0010(2)
C(1)	0.0087(10)	0.0093(9)	0.0041(4)	0.0047(8)	0.0011(5)	0.0016(5)
C(2)	0.0148(14)	0.0204(14)	0.0049(5)	0.0110(12)	0.0012(7)	0.0014(7)
C(3)	0.0165(17)	0.0298(21)	0.0071(7)	0.0163(17)	0.0023(9)	0.0036(10)
C(4)	0.0203(20)	0.0316(24)	0.0083(8)	0.0199(19)	0.0038(10)	0.0041(10)
C(5)	0.0271(23)	0.0336(24)	0.0067(8)	0.0214(20)	0.0051(11)	0.0002(11)
C(6)	0.0157(15)	0.0195(14)	0.0045(5)	0.0108(12)	0.0032(7)	0.0017(7)
C(7)	0.0117(12)	0.0069(8)	0.0029(3)	0.0026(8)	0.0005(5)	0.0004(4)
C(8)	0.0151(14)	0.0082(9)	0.0041(4)	0.0053(10)	0.0024(6)	0.0013(5)
C(9)	0.0231(19)	0.0081(10)	0.0055(5)	0.0070(11)	0.0022(8)	0.0010(6)
C(10)	0.0191(19)	0.0080(13)	0.0079(6)	−0.0010(13)	0.0004(8)	0.0010(7)
C(11)	0.0157(18)	0.0107(13)	0.0077(6)	−0.0001(13)	0.0010(9)	0.0009(7)
C(12)	0.0095(11)	0.0076(10)	0.0061(5)	0.0010(8)	−0.0003(6)	0.0006(6)
C(13)	0.0148(13)	0.0102(10)	0.0033(4)	0.0080(10)	0.0009(6)	0.0014(5)
C(14)	0.0439(31)	0.0188(19)	0.0073(7)	0.0230(21)	0.0009(11)	−0.0002(9)
C(15)	0.0307(23)	0.0138(12)	0.0049(5)	0.0135(14)	0.0037(8)	0.0034(6)
C(16)	0.0189(15)	0.0142(13)	0.0041(4)	0.0106(12)	0.0015(6)	0.0002(6)
C(17)	0.0512(33)	0.0146(17)	0.0076(7)	0.0199(21)	0.0050(12)	0.0049(9)
C(18)	0.0281(22)	0.0199(16)	0.0062(6)	0.0181(17)	0.0019(9)	−0.0004(8)
C(19)	0.0126(12)	0.0098(10)	0.0035(4)	0.0044(9)	0.0020(5)	0.0019(5)
C(20)	0.0136(14)	0.0128(12)	0.0051(5)	−0.0001(10)	0.0027(7)	0.0016(6)
C(21)	0.0141(16)	0.0202(17)	0.0056(6)	−0.0025(13)	0.0031(8)	0.0017(8)
C(22)	0.0142(18)	0,0265(20)	0.0076(7)	0.0004(15)	0.0061(9)	0.0012(10)
C(23)	0.0204(20)	0.0205(18)	0.0064(6)	0.0046(16)	0.0063(9)	0.0004(9)
C(24)	0.0181(16)	0.0127(13)	0.0052(5)	0.0044(12)	0.0045(8)	0.0012(6)
C(25)	0.0150(15)	0.0157(14)	0.0036(5)	0.0070(12)	0.0018(7)	0.0008(6)
C(26)	0.0135(15)	0.0176(15)	0.0035(4)	0.0064(13)	0.0004(6)	−0.0004(6)
C(27)	0.0170(16)	0.0128(13)	0.0040(5)	0.0032(12)	0.0009(7)	0.0010(6)
C(28)	0.0158(16)	0.0097(11)	0.0034(4)	0.0048(11)	0.0017(6)	0.0005(5)
C(29)	0.0089(11)	0.0092(10)	0.0043(4)	0.0032(9)	0.0020(6)	0.0003(5)
C(30)	0.0114(13)	0.0101(10)	0.0034(4)	0.0023(10)	0.0009(6)	0.0005(5)
C(31)	0.0138(14)	0.0084(10)	0.0045(5)	0.0049(10)	0.0010(6)	0.0023(5)
C(32)	0.0158(15)	0.0121(12)	0.0034(4)	0.0051(11)	0.0005(7)	0.0005(6)
C(33)	0.0105(12)	0.0085(10)	0.0035(4)	0.0022(9)	0.0011(6)	0.0006(5)
O(1)	0.0306(17)	0.0298(16)	0.0033(3)	0.0152(14)	0.0031(6)	0.0027(6)
O(2)	0.0159(12)	0.0284(15)	0.0072(5)	0.0116(12)	0.0010(6)	−0.0003(7)
O(3)	0.0247(14)	0.0139(10)	0.0068(5)	−0.0036(10)	0.0017(6)	−0.0001(5)
O(4)	0.0261(15)	0.0165(10)	0.0063(4)	0.0139(11)	0.0039(6)	0.0020(5)
O(5)	0.0162(11)	0.0143(9)	0.0068(4)	0.0079(9)	0.0042(6)	0.0006(5)
O(6)	0.0172(11)	0.0136(9)	0.0062(4)	−0.0018(8)	0.0043(6)	0.0017(5)
O(7)	0.0267(15)	0.0115(9)	0.0078(5)	0.0117(10)	0.0029(7)	0.0022(5)
O(8)	0.0209(13)	0.0224(13)	0.0038(4)	0.0085(11)	−0.0021(5)	−0.0003(5)
O(9)	0.0187(12)	0.0124(9)	0.0049(4)	−0.0015(8)	0.0023(5)	0.00009(5)

The form of the anisotropic thermal parameter is:

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

tion, an X-ray diffraction study was required to reveal its structural features. Its metallic frame is made of a triatomic bent chain in which each of the two metal—metal bonds is bridged by a PPh_2 group. It remains unclear whether the

TABLE 6

ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS FOR III

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00558(6)	0.00167(2)	0.00606(6)	0.00123(3)	0.00209(4)	0.00094(3)
Mn(1)	0.0103(3)	0.0027(1)	0.0086(3)	0.0025(1)	0.0042(2)	0.0013(1)
Mn(2)	0.0075(2)	0.0021(9)	0.0091(3)	0.0017(1)	0.0034(2)	0.0013(1)
P(1)	0.0079(4)	0.0021(2)	0.0084(5)	0.0023(2)	0.0033(4)	0.0015(2)
P(2)	0.0062(4)	0.0023(2)	0.0070(4)	0.0013(2)	0.0021(3)	0.0014(2)
P(3)	0.0063(4)	0.0019(1)	0.0072(4)	0.0013(2)	0.0017(3)	0.0010(2)
C(1)	0.0153(24)	0.0041(8)	0.0139(22)	0.0057(11)	0.0078(19)	0.0046(11)
O(1)	0.0233(20)	0.0063(6)	0.0230(20)	0.0100(9)	0.0142(17)	0.0075(9)
C(2)	0.0176(26)	0.0045(8)	0.0086(22)	0.0055(11)	0.0042(21)	0.0005(11)
O(2)	0.0286(26)	0.098(8)	0.0080(14)	0.0082(12)	0.0042(17)	0.0001(9)
C(3)	0.0080(20)	0.0036(8)	0.0129(22)	0.0010(9)	0.0002(10)	−0.0007(10)
O(3)	0.0162(20)	0.0042(7)	0.0245(22)	−0.0001(6)	0.0045(17)	0.0006(8)
C(4)	0.0098(21)	0.0045(8)	0.0124(21)	0.0044(11)	0.0073(17)	0.0040(11)
O(4)	0.0139(16)	0.0044(6)	0.0226(18)	0.0005(7)	0.0116(14)	0.0031(8)
C(5)	0.0102(18)	0.0023(6)	0.0105(19)	0.0025(9)	0.0053(16)	0.0010(9)
O(5)	0.0143(15)	0.0028(5)	0.0182(17)	−0.0007(6)	0.0089(13)	0.0019(6)
C(6)	0.0066(19)	0.0022(7)	0.0139(22)	−0.0005(9)	0.0039(16)	0.0026(10)
O(6)	0.0131(16)	0.0038(6)	0.0177(17)	0.0028(7)	−0.0004(10)	0.0036(7)
C(7)	0.0084(17)	0.0018(6)	0.0117(20)	0.0013(8)	0.0050(16)	0.0006(8)
O(7)	0.0140(14)	0.0038(5)	0.0122(15)	0.0036(6)	0.0070(12)	0.0017(7)
C(8)	0.00633(16)	0.00391(7)	0.0073(16)	0.0011(8)	0.0019(13)	−0.0002(8)
O(8)	0.0091(12)	0.0042(5)	0.0153(15)	0.0013(6)	0.0052(11)	0.0020(6)
C(9)	0.0106(17)	0.0012(5)	0.0076(16)	0.0011(8)	0.0034(14)	0.0021(7)
C(10)	0.0102(18)	0.0012(5)	0.0111(18)	0.0002(8)	0.0053(15)	0.0014(8)
C(11)	0.0138(22)	0.0028(7)	0.0114(21)	0.0013(10)	0.0064(18)	0.0016(10)
C(12)	0.0154(22)	0.0016(6)	0.0116(19)	0.0021(9)	0.0044(17)	0.0029(8)
C(13)	0.0105(18)	0.0023(6)	0.0100(17)	0.0023(8)	0.0021(14)	0.0024(8)
C(14)	0.0080(17)	0.0023(6)	0.0093(16)	0.0027(8)	0.0018(13)	0.0023(8)
C(15)	0.0050(14)	0.0030(7)	0.0103(18)	0.0011(8)	0.0040(13)	0.0022(9)
C(16)	0.0066(17)	0.0037(7)	0.0099(20)	0.0015(9)	0.0006(15)	0.0006(9)
C(17)	0.0093(19)	0.0025(7)	0.0141(22)	0.0007(9)	0.0034(17)	0.0015(10)
C(18)	0.0083(22)	0.0041(8)	0.0147(24)	0.0006(11)	0.0046(19)	−0.0004(10)
C(19)	0.0039(16)	0.0046(9)	0.0168(24)	0.0009(10)	−0.0003(15)	0.0011(10)
C(20)	0.0094(16)	0.0029(6)	0.0103(17)	0.0039(9)	0.0014(14)	0.0014(8)
C(21)	0.0084(15)	0.0012(5)	0.0051(14)	0.0010(7)	0.0016(12)	0.0002(6)
C(22)	0.0125(20)	0.0030(6)	0.0039(14)	0.0025(9)	0.0005(13)	0.0016(7)
C(23)	0.0112(22)	0.0034(7)	0.0118(20)	0.0014(9)	0.0024(18)	0.0028(10)
C(24)	0.0158(22)	0.0022(6)	0.0099(18)	0.0013(9)	0.0076(16)	0.0013(8)
C(25)	0.0143(24)	0.0036(8)	0.0159(23)	0.0045(11)	0.0078(20)	0.0024(10)
C(26)	0.0115(20)	0.0031(6)	0.0133(20)	0.0023(8)	0.0075(16)	0.0030(9)
C(27)	0.0081(15)	0.0024(6)	0.0065(15)	0.0006(8)	0.0016(12)	0.0028(8)
C(28)	0.0034(13)	0.0043(7)	0.0106(17)	0.0011(8)	0.0008(12)	0.0026(9)
C(29)	0.0071(20)	0.0055(9)	0.0126(24)	−0.0021(12)	−0.0023(17)	0.0032(13)
C(30)	0.0159(26)	0.0052(9)	0.0066(18)	−0.0025(13)	0.0015(17)	0.0002(10)
C(31)	0.0135(22)	0.0041(8)	0.0071(18)	−0.0028(10)	−0.0007(16)	0.0001(9)
C(32)	0.0141(21)	0.0023(6)	0.0078(18)	0.0020(9)	0.0016(15)	0.0016(9)
C(33)	0.0056(14)	0.0020(6)	0.0074(15)	0.0007(5)	0.0031(12)	0.0012(8)
C(34)	0.0124(20)	0.0032(7)	0.0112(19)	0.0026(10)	0.0047(16)	0.0017(9)
C(35)	0.0113(20)	0.0061(9)	0.0074(18)	0.0044(11)	−0.0037(15)	−0.0024(11)
C(36)	0.0089(20)	0.0068(9)	0.0096(21)	0.0021(12)	0.0015(17)	−0.0037(12)
C(37)	0.0137(23)	0.0043(8)	0.0093(20)	−0.0014(11)	0.0003(10)	−0.0018(10)
C(38)	0.0088(17)	0.0013(6)	0.0111(18)	−0.0004(7)	0.0033(14)	−0.0003(8)
C(39)	0.0071(15)	0.0020(6)	0.0062(16)	0.0008(7)	0.0033(12)	−0.0007(7)
C(40)	0.0138(19)	0.0016(6)	0.0108(17)	0.0017(8)	0.0063(15)	0.0016(8)
C(41)	0.0138(20)	0.0029(7)	0.0118(21)	0.001(9)	0.0064(17)	0.0004(10)
C(42)	0.0126(21)	0.0057(9)	0.0112(22)	0.0028(11)	0.0070(18)	0.0029(11)
C(43)	0.0157(22)	0.0013(6)	0.0111(20)	−0.0003(9)	0.0036(17)	0.0024(8)
C(44)	0.0096(17)	0.0013(5)	0.0095(18)	0.0008(8)	0.0012(13)	0.0006(8)

The form of the anisotropic thermal parameter is:

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

TABLE 7

ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS FOR IV

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt(1)	0.00129(1)	0.00481(3)	0.00210(1)	−0.00004(3)	0.00075(2)	0.000026(3)
Pt(2)	0.00130(1)	0.00473(3)	0.00147(1)	−0.00005(3)	0.00046(1)	−0.00009(3)
Mn(1)	0.00155(4)	0.0054(1)	0.00244(5)	0.0007(1)	0.00069(7)	0.0001(1)
Mn(2)	0.00176(4)	0.0050(1)	0.00192(5)	−0.0004(1)	−0.00003(7)	0.0000(1)
P(1)	0.00143(6)	0.0051(2)	0.00237(9)	0.0000(2)	0.0008(1)	−0.0003(2)
P(2)	0.00154(6)	0.0053(2)	0.00224(8)	0.0001(2)	0.0006(1)	0.0007(2)
P(3)	0.00138(6)	0.0049(2)	0.00170(7)	0.0000(2)	0.0004(1)	−0.0005(2)
P(4)	0.00139(6)	0.0054(2)	0.00188(8)	−0.0001(2)	0.0004(1)	0.0005(2)
O(1)	0.0014(2)	0.0110(10)	0.0060(5)	0.0008(7)	0.0001(5)	0.0004(12)
O(2)	0.0036(3)	0.0112(10)	0.0029(3)	0.0017(9)	0.0016(5)	−0.0012(9)
O(3)	0.0031(2)	0.0070(7)	0.0035(3)	0.0015(7)	0.0001(5)	0.0014(8)
O(4)	0.0038(3)	0.0109(9)	0.0040(3)	0.0049(9)	0.0023(5)	−0.0014(10)
O(5)	0.0038(3)	0.0095(8)	0.0025(3)	0.0023(8)	0.0012(5)	−0.0034(8)
O(6)	0.0022(2)	0.0095(9)	0.0064(5)	−0.0042(7)	−0.0020(5)	0.0009(11)
O(7)	0.0041(3)	0.0128(10)	0.0029(3)	0.0052(9)	−0.0012(5)	0.0038(10)
O(8)	0.0037(3)	0.0095(8)	0.0021(3)	0.0022(8)	−0.0007(5)	0.0024(8)
C(1)	0.0017(3)	0.0073(10)	0.0036(5)	0.0010(9)	0.0005(6)	0.0018(12)
C(2)	0.0017(3)	0.0070(10)	0.0024(3)	0.0003(9)	0.0006(5)	0.0015(10)
C(3)	0.0022(3)	0.0052(9)	0.0030(4)	0.0018(9)	−0.0002(6)	−0.0002(11)
C(4)	0.0036(4)	0.0065(10)	0.0021(3)	0.0011(11)	0.0024(6)	0.0007(11)
C(5)	0.0021(3)	0.0075(10)	0.0016(3)	−0.0012(9)	−0.0015(5)	0.0007(10)
C(6)	0.0025(3)	0.0060(10)	0.0033(4)	0.0008(10)	−0.0006(7)	0.0002(12)
C(7)	0.0022(3)	0.0072(10)	0.0033(4)	−0.0014(9)	0.0015(6)	−0.0043(11)
C(8)	0.0020(3)	0.0069(10)	0.0020(3)	−0.0001(9)	−0.0004(5)	−0.0010(10)
C(9)	0.0018(2)	0.0051(9)	0.0025(3)	0.0002(8)	0.0017(5)	−0.0005(9)
C(10)	0.0023(3)	0.0069(10)	0.0028(4)	0.0012(10)	0.0015(6)	0.0001(11)
C(11)	0.0039(4)	0.0064(11)	0.0036(5)	0.0023(12)	0.0027(7)	0.0015(12)
C(12)	0.0035(4)	0.0086(12)	0.0030(4)	0.0022(12)	0.0005(7)	−0.0042(12)
C(13)	0.0035(4)	0.0111(13)	0.0028(4)	−0.0060(12)	−0.0020(7)	0.0013(14)
C(14)	0.0025(3)	0.0078(11)	0.0022(4)	−0.0023(10)	−0.0002(6)	−0.0022(11)
C(15)	0.0018(3)	0.0060(9)	0.0019(3)	0.0012(8)	0.0004(5)	0.0003(9)
C(16)	0.0021(3)	0.0057(9)	0.0036(4)	−0.0009(8)	0.0021(5)	0.0036(10)
C(17)	0.0022(3)	0.0097(14)	0.0055(6)	−0.0016(12)	0.0026(7)	0.0008(16)
C(18)	0.0019(3)	0.0142(17)	0.0041(5)	−0.0018(12)	0.0022(6)	0.0037(15)
C(19)	0.0029(3)	0.0179(20)	0.0027(4)	0.0030(14)	0.0033(6)	−0.0012(15)
C(20)	0.0023(3)	0.0068(11)	0.0039(5)	0.0011(10)	0.0001(7)	−0.0020(13)
C(21)	0.0015(2)	0.0065(9)	0.0021(3)	0.0004(8)	0.0006(5)	0.0009(10)
C(22)	0.0020(3)	0.0077(11)	0.0034(4)	0.0002(10)	0.0012(6)	0.0010(12)
C(23)	0.0021(3)	0.0092(12)	0.0042(5)	−0.0005(10)	0.0020(6)	0.0059(12)
C(24)	0.0033(4)	0.0145(18)	0.0031(5)	−0.0020(15)	0.0018(7)	0.0021(16)
C(25)	0.0035(4)	0.0157(18)	0.0027(4)	−0.0053(14)	0.0021(7)	−0.0010(16)
C(26)	0.0028(3)	0.0106(13)	0.0022(4)	−0.0030(11)	0.0007(6)	0.0014(12)
C(27)	0.0013(2)	0.0077(10)	0.0020(3)	0.0003(8)	0.0006(4)	−0.0011(10)
C(28)	0.0020(3)	0.0076(11)	0.0027(4)	0.0017(10)	0.0005(5)	0.0004(11)
C(29)	0.0035(4)	0.0061(10)	0.0039(5)	0.0028(11)	0.0004(8)	−0.0029(12)
C(30)	0.0026(4)	0.0108(14)	0.0065(7)	0.0019(12)	−0.0024(9)	−0.0091(15)
C(31)	0.0027(4)	0.0137(17)	0.0038(5)	−0.0015(13)	0.0026(7)	−0.0038(16)
C(32)	0.0019(3)	0.0110(13)	0.0031(4)	0.0017(11)	0.0007(6)	−0.0024(13)
C(33)	0.0018(3)	0.0056(9)	0.0020(3)	0.0007(8)	0.0006(5)	0.0010(9)
C(34)	0.0021(3)	0.0092(12)	0.0031(4)	0.0027(10)	0.0012(6)	−0.0001(12)
C(35)	0.0037(4)	0.0094(13)	0.0049(6)	0.0021(13)	0.0032(8)	−0.0036(15)
C(36)	0.0038(5)	0.0081(13)	0.0050(6)	0.0012(13)	0.0010(9)	0.0027(16)
C(37)	0.0024(3)	0.0095(13)	0.0051(6)	0.0017(12)	0.0004(8)	0.0036(16)
C(38)	0.0015(3)	0.0070(10)	0.0036(4)	0.0008(9)	0.0002(6)	0.0028(12)
C(39)	0.0018(2)	0.0061(9)	0.0015(3)	−0.0004(8)	0.0007(4)	−0.0003(9)
C(40)	0.0026(3)	0.0083(12)	0.0022(4)	0.0014(10)	0.0006(6)	−0.0004(11)
C(41)	0.0034(4)	0.0091(13)	0.0035(5)	0.0020(13)	0.0002(8)	0.0033(14)
C(42)	0.0043(5)	0.0143(18)	0.0021(4)	0.0017(17)	−0.0010(8)	−0.0018(15)

TABLE 7 (continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(43)	0.0038(4)	0.0076(12)	0.0025(4)	—0.0006(12)	0.0004(7)	—0.0013(12)
C(44)	0.0021(3)	0.0097(12)	0.0024(4)	0.0004(11)	—0.0001(6)	—0.0018(12)
C(45)	0.0016(2)	0.0053(8)	0.0020(3)	0.0000(8)	0.0008(5)	—0.0005(9)
C(46)	0.0016(2)	0.0079(10)	0.0024(3)	0.0022(8)	0.0014(5)	0.0007(11)
C(47)	0.0023(3)	0.0080(11)	0.0039(5)	0.0011(10)	0.0024(6)	0.0023(13)
C(48)	0.0020(3)	0.0102(14)	0.0059(7)	0.0030(11)	0.0015(7)	—0.0013(17)
C(49)	0.0023(3)	0.0091(13)	0.0047(6)	0.0008(11)	—0.0016(7)	0.0047(14)
C(50)	0.0023(3)	0.0072(11)	0.0026(4)	0.0007(10)	—0.0007(6)	—0.0002(11)
C(51)	0.0013(2)	0.0078(10)	0.0017(3)	—0.0003(8)	0.0010(4)	0.0006(10)
C(52)	0.0024(3)	0.0080(11)	0.0022(3)	—0.0020(10)	0.0010(6)	—0.0004(11)
C(53)	0.0025(3)	0.0111(14)	0.0036(5)	—0.0024(12)	0.0009(7)	0.0037(14)
C(54)	0.0048(5)	0.0115(15)	0.0020(4)	—0.0004(15)	0.0017(7)	0.0039(13)
C(55)	0.0039(5)	0.0127(16)	0.0018(4)	—0.0012(15)	0.0008(7)	—0.0005(14)
C(56)	0.0026(3)	0.0120(14)	0.0018(3)	—0.0012(12)	0.0008(6)	0.0012(12)

The form of the anisotropic thermal parameter is:

$\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl.$

two phosphorous atoms originate from the same platinum since the existence of compounds I and III suggests the formation during the course of the reaction of "$Ph_2PMn(CO)_n$" (n = 4 or 5) which should be very reactive. The ^{31}P NMR chemical shift (δ = 161 ppm, $^1J(PPt)$ = 2265 Hz) is in keeping with a PPh_2 unit bridging a metal—metal bond [17]. With a total of 48 electrons, this molecule shows the expected two metal—metal bonds, with one 16-electron platinum and two 18-electron manganese atoms.

Complex III, obtained in low yields, was characterized by its mass spectrum, elemental analysis and ^1H and ^{31}P NMR. The presence of the hydrogen atom bonded to the platinum was revealed by the ^1H NMR signal at δ = —11.1 ppm ($^1J(PtH)$ = 526 Hz). This hydride is probably formed by the reaction of an unsaturated species with a solvent molecule or with the residual water present in the silica gel used for chromatography. The different chemical shift values of the ^{31}P NMR signals suggested the presence of two types of PPh_2 bridges, one spanning a metal—metal bond (signal at low field) the other connecting two non-bonded metal centers (signals at high field). This was found to be the case, as revealed by the X-ray diffraction study which indicates only one metal—metal bond as expected for this 50-electron molecule.

Complex IV (yield ca. 12%) was formulated as $Pt_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8$ on the basis of its mass spectrum, elemental analysis and IR spectrum. Although the ^{31}P NMR data are poor, there are good indications of the presence of PtPMn or PtPPt triangles (large downfield ^{31}P NMR shifts). Complex IV is a 62-electron molecule and if 16- or 18-electron platinum atoms are assumed, two structures can be envisaged. Although several complexes with a b type structure are known (butterfly [12a] or planar-type [13] structure) all of them contain 16-electron platinum atoms. For this reason we favoured the chain type structure a, and this was confirmed by X-ray diffraction.

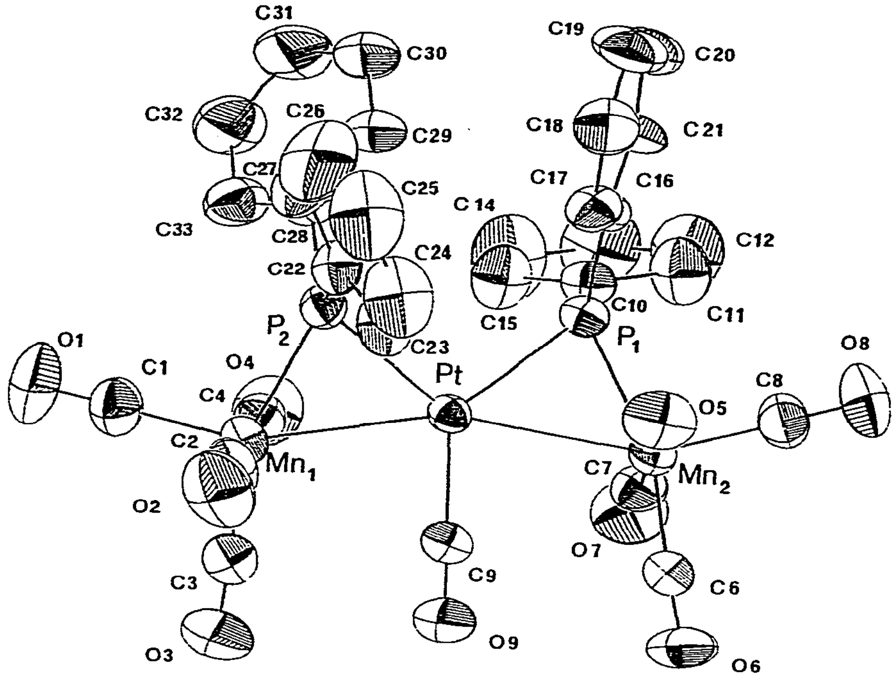


Fig. 1. ORTEP view of $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(CO)(\mu_2\text{-}PPh_2)Mn}(CO)_4$, II.

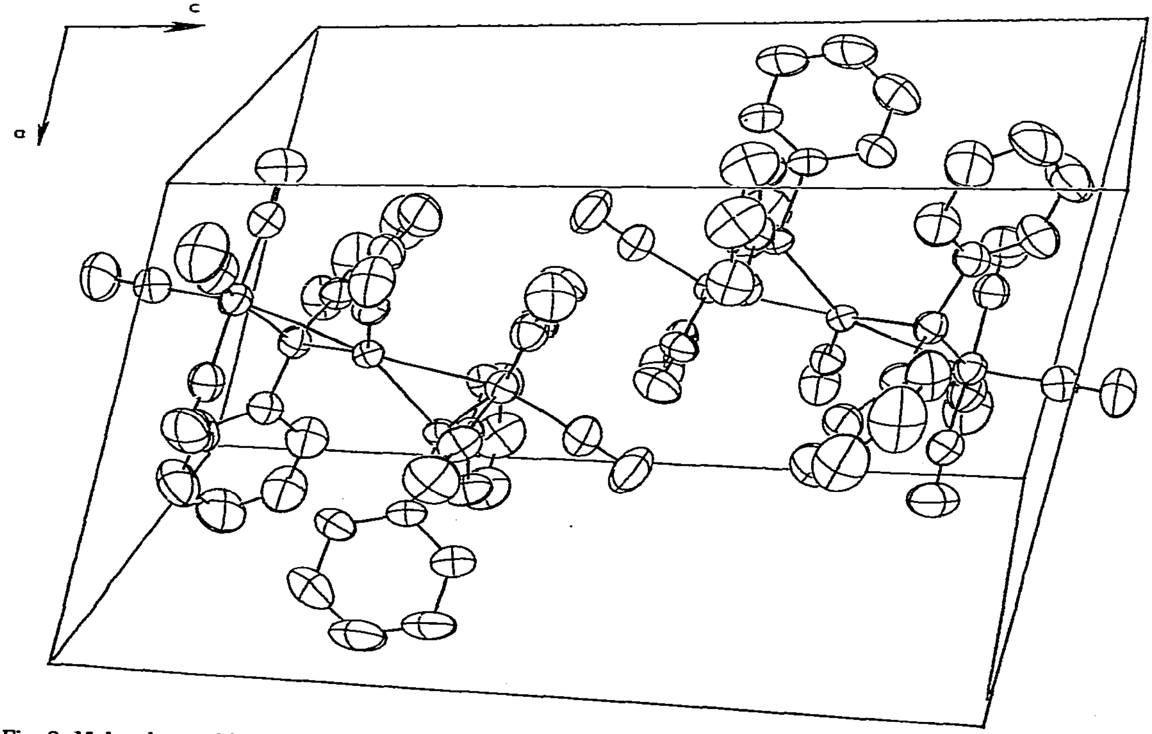


Fig. 2. Molecular packing of II.

TABLE 8

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg.) FOR $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(CO)(\mu_2\text{-}PPh_2)Mn}(CO)_4$ (II)

Pt—Mn(1)	2.741(1)	2.744(1)	Mn(1)—Pt—Mn(2)	159.54(6)
Pt—Mn(2)	2.747(1)			
Pt—P(1)	2.305(2)	2.312(2)	P(1)—Pt—P(2)	101.08(11)
Pt—P(2)	2.319(3)			
Mn(1)—P(2)	2.237(2)	2.239(2)	Mn(1)—Pt—P(2)	51.65(8)
			Mn(2)—Pt—P(1)	51.77(8)
Mn(2)—P(1)	2.241(3)			
Mn(1)—Mn(2)	5.401(2)			
Pt—C(9)	1.893(7)		Pt—C(33)—O(9)	179.26(77)
C(9)—O(9)	1.149(10)			
Mn(1)—C(1)	1.787(10)	1.820(3)	Mn(1)—C(1)—O(1)	179.26(95)
Mn(1)—C(2)	1.840(13)		Mn(1)—C(2)—O(2)	175.35(45)
Mn(1)—C(3)	1.813(9)		Mn(1)—C(3)—O(3)	177.57(72)
Mn(1)—C(4)	1.829(12)		Mn(1)—C(4)—O(4)	175.75(35)
Mn(2)—C(5)	1.835(11)		Mn(2)—C(5)—O(5)	175.32(40)
Mn(2)—C(6)	1.823(9)		Mn(2)—C(6)—O(6)	177.67(67)
Mn(2)—C(7)	1.831(11)		Mn(2)—C(7)—O(7)	178.00(77)
Mn(2)—C(8)	1.804(9)		Mn(2)—C(8)—O(8)	176.72(48)
C(1)—O(1)	1.140(13)	1.146(5)		
C(2)—O(2)	1.150(16)			
C(3)—O(3)	1.164(11)			
C(4)—O(4)	1.149(16)			
C(5)—O(5)	1.142(14)			
C(6)—O(6)	1.145(11)			
C(7)—O(7)	1.144(14)			
C(8)—O(8)	1.134(11)			
P(1)—C(10)	1.823(11)	1.817(5)	P(1)—C(10)—C(11)	119.37(37)
P(1)—C(16)	1.818(8)		P(1)—C(10)—C(15)	121.40(71)
P(2)—C(22)	1.822(10)		C(22)—P(2)—C(28)	104.88(42)
P(2)—C(28)	1.807(9)			
C(10)—C(11)	1.382(13)		C(10)—P(1)—C(16)	104.65(45)
C(11)—C(12)	1.397(19)		C(10)—C(11)—C(12)	121.30(99)
C(12)—C(13)	1.352(21)		C(11)—C(12)—C(13)	118.31(94)
C(13)—C(14)	1.344(19)		C(12)—C(13)—C(14)	122.25(150)
C(14)—C(15)	1.416(21)		C(13)—C(14)—C(15)	120.00(84)
C(15)—C(10)	1.375(15)		C(14)—C(15)—C(10)	119.10(73)
			C(15)—C(10)—C(11)	119.02(65)
C(16)—C(17)	1.385(15)		C(16)—C(17)—C(18)	119.64(58)
C(17)—C(18)	1.411(11)		C(17)—C(18)—C(19)	119.80(66)
C(18)—C(19)	1.355(16)		C(18)—C(19)—C(20)	121.27(107)
C(19)—C(20)	1.361(19)		C(19)—C(20)—C(21)	119.84(68)
C(20)—C(21)	1.386(12)		C(20)—C(21)—C(16)	120.47(73)
C(21)—C(16)	1.391(11)		C)21)—C(16)—C(17)	118.92(57)
C(22)—C(23)	1.388(14)		C(22)—C(23)—C(24)	121.58(94)
C(23)—C(24)	1.395(18)		C(23)—C(24)—C(25)	119.03(76)
C(24)—C(25)	1.338(18)		C(24)—C(25)—C(26)	120.83(117)
C(25)—C(26)	1.358(24)		C(25)—C(26)—C(27)	122.23(141)
C(26)—C(27)	1.417(20)		C(26)—C(27)—C(22)	116.89(110)
C(27)—C(22)	1.389(12)		C(27)—C(22)—C(23)	119.39(60)
C(28)—C(29)	1.392(9)		C(28)—C(29)—C(30)	102.08(65)
C(29)—C(30)	1.388(14)		C(29)—C(30)—C(31)	121.07(98)
C(30)—C(31)	1.365(18)		C(30)—C(31)—C(32)	119.76(75)

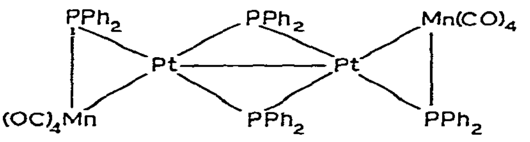
TABLE 8 (continued)

C(31)—C(32)	1.363(13)	C(31)—C(32)—C(33)	121.14(106)
C(32)—C(33)	1.412(16)	C(32)—C(33)—C(28)	118.75(68)
C(33)—C(28)	1.401(14)	C(33)—C(28)—C(29)	119.18(59)
mean C=C	1.382(3)		
		C(1)—Mn(1)—C(2)	91.06(51)
		C(1)—Mn(1)—C(3)	99.26(49)
		C(1)—Mn(1)—C(4)	91.11(49)
		C(2)—Mn(1)—C(3)	89.59(50)
		C(3)—Mn(1)—C(4)	87.32(48)
		C(2)—Mn(1)—C(4)	176.47(48)
		C(5)—Mn(2)—C(6)	86.95(43)
		C(5)—Mn(2)—C(8)	92.62(47)
		C(6)—Mn(2)—C(7)	89.05(44)
		C(6)—Mn(2)—C(8)	99.40(46)
		C(7)—Mn(2)—C(8)	92.68(48)
		C(5)—Mn(2)—C(7)	173.82(45)
		P(1)—C(16)—C(17)	119.69(34)
		P(1)—C(16)—C(21)	121.35(63)
		Mn(2)—P(1)—Pt	74.31(9)
		C(10)—P(1)—C(16)	104.65(45)
		Mn(2)—P(1)—C(10)	115.51(31)
		Mn(2)—P(1)—C(16)	125.65(23)
		Pt—P(1)—C(10)	112.42(25)
		Pt—P(1)—C(16)	122.33(28)
		Mn(1)—P(2)—Pt	73.97(12)
		C(22)—P(2)—C(28)	104.88(42)
		Mn(1)—P(2)—C(22)	121.29(27)
		Mn(1)—P(2)—C(28)	123.53(28)
		Pt—P(2)—C(22)	108.21(24)
		Pt—P(2)—C(28)	122.22(28)

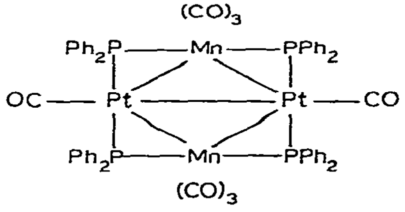
Description of the structures

$(OC)_4M\overline{n(\mu_2\text{-}PPh_2)Pt(CO)(\mu_2\text{-}PPh_2)M}n(CO)_4$ (II)

Atomic coordinates and thermal parameters are given in Tables 2 and 5, interatomic distances and bond angles in Table 8, and least squares planes in Table 11. The molecular structure is shown in Fig. 1 and the packing in Fig. 2. The framework of II is a trimetallic MnPtMn bent chain with an angle between the two Pt—Mn bonds of 159°5. The two Pt—Mn distances (average value 2.743 Å) are comparable to the values found in the linear $(OC)_5MnPt(py)_2Mn(CO)_5$ molecule [15a]. The almost planar arrangement around the pentacoordinated platinum of P(1), P(2), Mn(1), Mn(2) and C(9) is reminiscent of that found in some Pt^0-olefin complexes [18]. The geometry adopted by this molecule probably minimises the repulsive interactions [19] between the carbonyl ligands C(3)O(3), C(9)O(9) and C(6)O(6). The stereochemistry around each manganese



IVa (16e Pt)



IVb (18e Pt)

TABLE 9

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg) FOR $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}H(\mu_2\text{-}PPh_2)_2Mn(CO)_4$, III

Pt—Mn(1)	2.847(2)		Mn(1)—Pt—Mn(2)	157.26(6)
Pt—Mn(2)	3.618(2)		Mn(1)—Pt—P(1)	52.09(10)
Pt—P(1)	2.273(4)		Mn(1)—Pt—P(2)	120.52(10)
Pt—P(2)	2.325(4)		P(1)—Pt—P(3)	108.27(14)
Pt—P(3)	2.299(4)		P(3)—Pt—P(2)	69.06(14)
Mn(1)—P(1)	2.306(4)	2.347(2)	P(1)—Mn(1)—Pt	51.04(6)
Mn(2)—P(2)	2.355(4)		P(1)—Mn(1)—C(9)	99.02(48)
Mn(2)—P(3)	2.379(4)		P(1)—Mn(1)—C(2)	164.30(47)
Mn(1)—C(1)	1.827(21)	1.836(6)	P(1)—Mn(1)—C(3)	88.61(47)
Mn(1)—C(2)	1.860(17)		P(1)—Mn(1)—C(4)	91.65(52)
Mn(1)—C(3)	1.843(17)		Pt—Mn(1)—C(1)	149.55(38)
Mn(1)—C(4)	1.849(18)		Pt—Mn(1)—C(2)	113.26(37)
Mn(2)—C(5)	1.841(15)		Pt—Mn(1)—C(3)	85.00(39)
Mn(2)—C(6)	1.829(17)		Pt—Mn(1)—C(4)	95.46(40)
Mn(2)—C(7)	1.807(16)		C(1)—Mn(1)—C(2)	96.54(82)
Mn(2)—C(8)	1.833(14)		C(1)—Mn(1)—C(3)	89.31(81)
P(1)—C(9)	1.782(15)		C(1)—Mn(1)—C(4)	90.34(85)
P(1)—C(15)	1.796(12)		C(2)—Mn(1)—C(3)	89.48(41)
P(2)—C(21)	1.833(14)		C(2)—Mn(1)—C(4)	91.12(64)
P(2)—C(27)	1.842(10)		C(3)—Mn(1)—C(4)	179.61(84)
P(3)—C(33)	1.855(10)		P(2)—Mn(2)—P(3)	76.63(15)
P(3)—C(39)	1.828(13)		P(2)—Mn(2)—C(5)	85.13(42)
C(1)—O(1)	1.122(26)	1.127(7)	P(2)—Mn(2)—C(6)	96.70(44)
C(2)—O(2)	1.100(21)		P(2)—Mn(2)—C(7)	167.86(41)
C(3)—O(3)	1.109(21)		P(2)—Mn(2)—C(8)	89.74(42)
C(4)—O(4)	1.130(23)		P(3)—Mn(2)—C(5)	89.90(41)
C(5)—O(5)	1.141(18)		P(3)—Mn(2)—C(6)	172.94(44)
C(6)—O(6)	1.139(22)		P(3)—Mn(2)—C(7)	91.96(41)
C(7)—O(7)	1.143(20)		P(3)—Mn(2)—C(8)	89.94(41)
C(8)—O(8)	1.136(18)		C(5)—Mn(2)—C(6)	91.85(74)
C(9)—C(10)	1.395(22)		C(5)—Mn(2)—C(7)	90.80(71)
C(10)—C(11)	1.395(22)		C(5)—Mn(2)—C(8)	174.76(71)
C(11)—C(12)	1.384(27)		C(6)—Mn(2)—C(7)	94.85(72)
C(12)—C(13)	1.370(24)		C(6)—Mn(2)—C(8)	87.69(73)
C(13)—C(14)	1.378(24)		C(7)—Mn(2)—C(8)	94.44(70)
C(14)—C(9)	1.413(23)		Pt—P(1)—Mn(1)	76.87(15)
C(15)—C(16)	1.413(27)		Pt—P(1)—C(15)	113.50(38)
C(16)—C(17)	1.333(19)		Mn(1)—P(1)—C(15)	121.11(42)
C(17)—C(18)	1.358(24)		Pt—P(1)—C(9)	125.31(36)
C(18)—C(19)	1.373(32)		Mn(1)—P(1)—C(9)	114.98(49)
C(19)—C(20)	1.388(20)		C(9)—P(1)—C(15)	104.53(70)
C(20)—C(15)	1.356(19)		Pt—P(2)—Mn(2)	101.26(15)
C(21)—C(22)	1.390(21)		Pt—P(2)—C(21)	112.14(36)
C(22)—C(23)	1.409(23)		Pt—P(2)—C(27)	114.32(36)
C(23)—C(24)	1.376(24)		Mn(2)—P(2)—C(21)	110.03(36)
C(24)—C(25)	1.399(25)		Mn(2)—P(2)—C(27)	117.33(35)
C(25)—C(26)	1.340(25)		C(21)—O(2)—C(27)	102.10(68)
C(26)—C(21)	1.411(20)		Pt—P(3)—Mn(2)	101.30(15)
C(27)—C(28)	1.419(19)		Pt—P(3)—C(33)	113.12(37)
C(28)—C(29)	1.359(18)		Pt—P(3)—C(39)	113.72(36)
C(29)—C(30)	1.367(31)		Mn(2)—P(3)—C(33)	117.61(36)
C(30)—C(31)	1.373(27)		Mn(2)—P(3)—C(39)	109.63(38)
C(31)—C(32)	1.397(17)		C(33)—P(3)—C(39)	101.94(58)
C(32)—C(27)	1.410(22)		Mn(1)—C(1)—O(1)	176.62(81)
C(33)—C(34)	1.396(22)		Mn(1)—C(2)—O(2)	176.18(65)
C(34)—C(35)	1.364(17)		Mn(1)—C(3)—O(3)	175.71(64)
C(35)—C(36)	1.380(88)		Mn(1)—C(4)—O(4)	176.81(91)
C(36)—C(37)	1.368(28)		Mn(2)—C(5)—O(5)	177.34(95)
C(37)—C(38)	1.388(17)		Mn(2)—C(6)—O(6)	178.55(140)

TABLE 9 (continued)

C(38)—C(33)	1.371(19)	Mn(2)—C(7)—O(7)	177.16(87)
C(39)—C(40)	1.355(19)	Mn(2)—C(8)—O(8)	177.42(99)
C(40)—C(41)	1.400(22)	C(14)—C(9)—C(10)	114.95(128)
C(41)—C(42)	1.383(21)	C(9)—C(10)—C(11)	124.00(133)
C(42)—C(43)	1.371(24)	C(10)—C(11)—C(12)	117.33(157)
C(43)—C(44)	1.379(20)	C(11)—C(12)—C(13)	121.63(160)
C(44)—C(39)	1.400(16)	C(12)—C(13)—C(14)	119.50(94)
		C(13)—C(14)—C(9)	122.48(152)
		C(20)—C(15)—C(16)	115.62(153)
		C(15)—C(16)—C(17)	122.00(168)
		C(16)—C(17)—C(18)	119.99(119)
		C(17)—C(18)—C(19)	121.60(181)
		C(18)—C(19)—C(20)	116.57(187)
		C(19)—C(20)—C(15)	123.31(143)

TABLE 10

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg) FOR $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}(\mu_2\text{-}PPh_2)_2\overline{Pt(\mu_2\text{-}PPh_2)Mn}(CO)_4$, IV [a]

Pt(1)—Pt(1)′	2.669(1)	2.668(1)		
Pt(2)—Pt(2)′	2.667(1)			
Pt(1)—Mn(1)	2.717(2)	2.713(2)		
Pt(2)—Mn(2)	2.710(2)		Mn(1)—Pt(1)—Pt(1)′	146.11(8)
Pt(1)—P(1)	2.265(3)	2.273(2)	Mn(2)—Pt(2)—Pt(2)′	147.04(8)
Pt(2)—P(4)	2.266(3)		Mn(1)—Pt(1)—P(2)	159.5(1)
Pt(1)—P(2)	2.268(3)		Mn(2)—Pt(2)—P(3)	158.7(1)
Pt(1)—P(2)′	2.280(3)		Mn(1)—Pt(1)—P(2)′	92.3(1)
Pt(2)—P(3)	2.280(3)		Mn(2)—Pt(2)—P(3)′	92.7(1)
Pt(2)—P(3)′	2.283(3)		Mn(1)—Pt(1)—P(1)	52.5(1)
Mn(1)—P(1)	2.242(4)	2.241(3)	Mn(2)—Pt(2)—P(4)	52.6(1)
Mn(2)—P(4)	2.241(4)		P(2)—Pt(1)—P(2)′	108.1(1)
Mn(1)—C(1)	1.80(1)	1.855(5)	P(3)—Pt(2)—P(3)′	108.5(1)
Mn(1)—C(2)	1.84(1)		P(1)—Pt(1)—P(2)	106.9(1)
Mn(1)—C(3)	1.81(1)		Mn(1)—Pt(1)—P(2)′	92.3(1)
Mn(1)—C(4)	1.80(1)		Pt(1)—P(1)—Mn(1)	74.1(1)
Mn(2)—C(5)	1.90(1)		Pt(2)—P(4)—Mn(2)	73.9(1)
Mn(2)—C(6)	1.86(1)		Pt(1)—P(2)—Pt(1)′	71.8(1)
Mn(2)—C(7)	1.96(1)			
Mn(2)—C(8)	1.87(1)		C(1)—Mn(1)—C(2)	91.3(6)
C(1)—O(1)	1.09(1)	1.118(5)	C(1)—Mn(1)—C(3)	98.2(6)
C(2)—O(2)	1.13(1)		C(1)—Mn(1)—C(4)	89.6(7)
C(3)—O(3)	1.12(1)		C(2)—Mn(1)—C(3)	87.1(6)
C(4)—O(4)	1.17(1)		C(2)—Mn(1)—C(4)	178.5(6)
C(5)—O(5)	1.12(1)		C(3)—Mn(1)—C(4)	91.6(6)
C(6)—O(6)	1.12(1)			
C(7)—O(7)	1.08(1)		Mn(1)—C(1)—O(1)	177(1)
C(8)—O(8)	1.12(1)		Mn(1)—C(2)—O(2)	175(1)
P(1)—C(9)	1.85(1)		Mn(1)—C(3)—O(3)	177(1)
P(1)—C(15)	1.82(1)		Mn(1)—C(4)—O(4)	178(1)
P(2)—C(21)	1.82(1)			
P(2)—C(27)	1.78(1)			
Mean P—C	1.808(4)			
Mean $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$	1.375(3)			

[a] The prime indices indicate the atoms deduced by inversion center within a molecule. The second molecule is characterized by Pt(2)Mn(2)P(3)P(4) (see text).

TABLE 11

LEAST-SQUARES PLANES FOR II

Plane No.	Atoms	Distance from plane (Å)
1	P(1)[a]	—0.120(3)
	C(10)	—0.004(10)
	C(11)	0.004(10)
	C(12)	—0.005(10)
	C(13)	0.007(13)
	C(14)	—0.005(14)
	C(15)	0.005(14)
2	P(1)[a]	0.101(3)
	C(16)	0.007(8)
	C(17)	—0.001(8)
	C(18)	—0.011(10)
	C(19)	0.017(12)
	C(20)	—0.006(10)
	C(21)	—0.005(12)
3	P(2)[a]	—0.031(3)
	C(22)	0.001(8)
	C(23)	0.002(11)
	C(24)	—0.004(9)
	C(25)	0.011(12)
	C(26)	0.002(15)
	C(27)	—0.012(15)
4	P(2)[a]	—0.115(3)
	C(28)	—0.001(8)
	C(29)	0.005(9)
	C(30)	—0.010(11)
	C(31)	0.009(13)
	C(32)	—0.001(12)
	C(33)	—0.002(10)
5	Pt	
	Mn(1)	
	Mn(2)	
	P(1)[a]	0.589(3)
	P(2)[a]	—0.363(3)
	C(9)[a]	—0.112(9)
	O(9)[a]	—0.168(8)
6	Pt	
	Mn(1)	
	P(2)	
	Mn(2)[a]	—0.191(2)
	P(1)[a]	0.797(3)
	C(9)[a]	—0.482(10)
	O(9)[a]	—0.763(9)
7	Pt	
	Mn(2)	
	P(1)	
	Mn(1)[a]	0.311(2)
	P(2)[a]	—0.722(3)
	C(9)[a]	0.496(9)
	O(9)[a]	0.809(8)

Dihedral angles between the planes

Planes	angle (deg)		
1—2	102	5—6	11.5
3—4	123	5—7	19
		6—7	30

TABLE 11 (continued)

Equations of the planes of the form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.3393	0.9365	−0.0891	3.0600
2	0.0884	0.1001	−0.9910	−5.3368
3	−0.5379	−0.2210	−0.8135	−4.2037
4	−0.4217	0.6896	−0.5888	−0.6240
5	0.8741	−0.4737	−0.1076	1.2282
6	0.9457	−0.2905	−0.1459	1.4930
7	0.6690	−0.7279	−0.1506	0.1708

[a] These atoms were not used in defining the plane.

deviates from the usual octahedral arrangement; the small PtMnP bite angles (mean value 54.15 (5)°) induce an opening of the C(6)Mn(2)C(8) and C(1)Mn(1)C(3) angles (mean value 99.3 (3)°) corresponding to the equatorial carbonyls. There is no crystallographic element of symmetry in this molecule, for which the chirality is inherent in the $PtMn_2P_2$ framework.

An analogous chirality was found in the cationic $Rh[Fe(PPh_2)(CO)_2(\eta\text{-}CH_3C_5H_4)]_2^+$ [20]. Hetero-trimetallic bent chain complexes containing a Pt atom were previously unknown [21].

$(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}H(\mu_2\text{-}PPh_2)_2Mn(CO)_4$ *(III)*

Atomic coordinates and thermal parameters are given in Tables 3 and 6, interatomic distances and bond angles in Table 9, least squares planes in Table 12. The molecular structure in shown in Fig. 3 and the packing in Fig. 4. As in compound II, the platinum atom is bonded to manganese Mn(1) and this bond is bridged by a PPh_2 unit. In contrast to II, the second manganese atom is not bonded to the platinum, as shown by the Pt—Mn(2) distance of 3.618(2) Å, greater by about 0.77 Å than Pt—Mn(1); Pt and Mn(2) are linked by two PPh_2 groups.

As in II the observed coordination about the platinum atom of III is almost planar (Table 12). The observation of the coupling ^1J(PtH), together with the linearity of the carbonyl ligands and no anomalous distortion around the manganese atoms indicate that the H atom is terminally bonded to the platinum. Although it is likely to be located within the angle of largest size, i.e. Mn(1)-PtP(2) (120°), we were unable to locate it crystallographically. Thus the platinum atom in III is five coordinated as in II and has a 16-electron configuration, the manganese atoms keeping their usual 18-electron configuration. The Pt—Mn(1) bond is ca. 0.1 Å longer than in II because of a more electron rich platinum atom in III; three phosphorus atoms are coordinated to the platinum which bears no carbonyl group (as in II) for electron density release. The tetracarbonyl manganese fragments also are slightly distorted from the usual octahedral geometry. As in II, the P(1)Mn(1)Pt bite angle (51.04°) causes an opening of the C(1)Mn(1)C(2) equatorial angle (96.54°). Because of the absence of a PtMn(2) bond, the octahedron around Mn(2) is more regular: P(2)Mn(2)P(3) = 76.6°(2), C(6)Mn(2)C(7) = 94.8°(7).

Interestingly, this complex contains two types of PPh_2 bridges, each bonded to platinum and to an $Mn(CO)_4$ moiety. The PPh_2 group spanning the Mn(1)Pt bond gives a PtP(1)Mn(1) angle of 76.9°, whereas the other two PPh_2 groups

TABLE 12

LEAST-SQUARES PLANES FOR III

Plane no.	atoms	distance from plane (Å)
1	Pt	0.046(1)
	Mn(1)	−0.213(2)
	Mn(2)	−0.232(2)
	P(1)	−0.400(4)
	P(2)	0.171(4)
	P(3)	0.083(4)
	C(1)[a]	−0.326(20)
	O(1)[a]	−0.361(14)
	C(2)[a]	0.037(18)
	O(2)[a]	0.151(16)
	C(6)[a]	−0.369(17)
	O(6)[a]	−0.456(13)
	C(7)[a]	−0.630(15)
	O(7)[a]	−0.922(12)
2	Pt	
	Mn(1)	
	P(1)	
	Mn(2)[a]	0.802(2)
	P(2)[a]	0.340(4)
	P(3)[a]	0.023(5)
	C(1)[a]	−0.196(19)
	O(1)[a]	−0.355(14)
	C(2)[a]	−0.014(18)
	O(2)[a]	0.002(16)
3	Pt	−0.006(1)
	Mn(2)	−0.057(2)
	P(2)	0.193(4)
	P(3)	0.180(4)
	Mn(1)[a]	−0.457(3)
	P(1)[a]	−0.539(4)
	C(6)[a]	−0.146(17)
	O(6)[a]	−0.202(13)
	C(7)[a]	−0.348(15)
	O(7)[a]	−0.575(12)
4	C(9)	−0.009(13)
	C(10)	−0.007(15)
	C(11)	0.021(16)
	C(12)	−0.008(15)
	C(13)	−0.012(15)
	C(14)	0.019(14)
	P(1)[a]	0.039(4)
5	C(15)	−0.010(14)
	C(16)	0.014(16)
	C(17)	−0.017(18)
	C(18)	0.020(18)
	C(19)	−0.019(17)
	C(20)	0.012(15)
	P(1)[a]	−0.061(4)
6	C(21)	0.001(13)
	C(22)	−0.013(14)
	C(23)	0.025(16)
	C(24)	−0.016(15)
	C(25)	0.004(17)
	C(26)	0.004(15)
	P(2)[a]	−0.171(4)

TABLE 12 (continued)

Plane no.	atoms	distance from plane (Å)
7	C(27)	0.017(12)
	C(28)	−0.013(13)
	C(29)	0.002(18)
	C(30)	0.010(17)
	C(31)	0.001(16)
	C(32)	−0.015(14)
	P(2)	0.039(4)
8	C(33)	0.014(12)
	C(34)	−0.009(16)
	C(35)	−0.012(16)
	C(36)	0.026(17)
	C(37)	−0.011(18)
	C(38)	−0.008(14)
	P(3) [a]	0.140(4)
	C(39)	−0.013(12)
	C(40)	0.014(14)
	C(41)	−0.012(16)
	C(42)	0.012(17)
	C(43)	−0.012(15)
	C(44)	0.014(14)
	P(3) [a]	0.093(4)

Dihedral angles between the planes

Planes	angle (deg)	planes	angle (deg)
1—2	168		
1—3	176		
1—4	126	4—5	114
1—5	70	5—6	130
1—6	120	7—8	149
1—7	58		
1—8	66		
1—9	100		
2—3	166		

Equations of the planes of the form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	−0.5468	−0.8330	−0.0842	−11.4401
2	0.4010	0.9157	−0.0260	11.3206
3	−0.5952	−0.8021	−0.0476	−10.7199
4	−0.1920	−0.4993	−0.8449	−14.5371
5	0.7570	−0.0145	−0.6532	−4.4604
6	0.1937	−0.6468	−0.7377	−14.3903
7	0.4567	0.4098	−0.7896	−1.1232
8	0.7843	0.0327	−0.6195	−6.7799
9	−0.8043	0.3666	−0.4677	0.1627

[a] These atoms were not used in defining the plane.

between the non-bonded metals give PtPMn(2) angles of 101.2 and 101.3°, closer to the expected values for tetrahedral phosphorus. Similar features have recently been observed in homo-trinuclear platinum complexes [22]. A precedent for a planar arrangement of three mixed metals and three bridging phosphorus atoms is to be found in $Fe_2M(\mu\text{-}PMe_2)_3(CO)_4(NO)_2L$ (M = Fe, L = NO, M = Co, L = CO), which, however, contain two metal—metal bonds [7].

TABLE 13

LEAST-SQUARES PLANES FOR IV

Plane No.	Atoms	Distances from plane (Å)
1	Pt(1)	
	Pt(1)'	
	P(2)	
	P(2)'	
	Mn(1) [a]	0.089(2)
	P(1) [a]	0.202(3)
2	Pt(1)	
	Mn(1)	
	P(1)	
	P(2) [a]	0.000(1)
	C(1) [a]	0.05(1)
	C(3) [a]	−0.13(1)
	Pt(1)' [a]	
3	Pt(2)	
	Pt(2)'	
	P(3)	
	P(3)'	
	Mn(2) [a]	0.021(2)
	P(4) [a]	0.225(3)
4	Pt(2)	
	Mn(2)	
	P(4)	

Dihedral angles between the planes

Planes	angle (deg)
1—2	5.3
3—4	6.8

Equations of the planes of the form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.4305	−0.1909	−0.8822	0
2	0.3749	−0.2654	−0.8822	−0.1009
3	−0.5106	0.5792	−0.6355	−9.6298
4	−0.4248	0.5556	−0.7147	−8.5489

[a] The atoms were not used in defining the plane.

$(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(\mu_2\text{-}PPh_2)_2Pt(\mu_2\text{-}PPh_2)Mn}(CO)_4$ (IV)

Atomic coordinates and thermal parameters are given in Tables 4 and 7, interatomic distances and bond angles in Table 10, and least-squares planes in Table 13. The molecular structure is shown in Fig. 5.

In the asymmetric unit of the cell, there are two PtMn units around different inversion centers, leading to two centrosymmetric Pt_2Mn_2units. One is referred to as Pt(1)Pt(1)'Mn(1)Mn(1)', the other one as Pt(2)Pt(2)'Mn(2)Mn(2)' with P(3) bridging Pt(2)Pt(2)' and P(4) bridging Mn(2)Pt(2). Each platinum atom is bonded to one manganese atom and to an equivalent platinum atom; the platinum—manganese bonds are bridged by a PPh_2 unit and the platinum—platinum bond by two such units, thus the four metal atoms form a planar

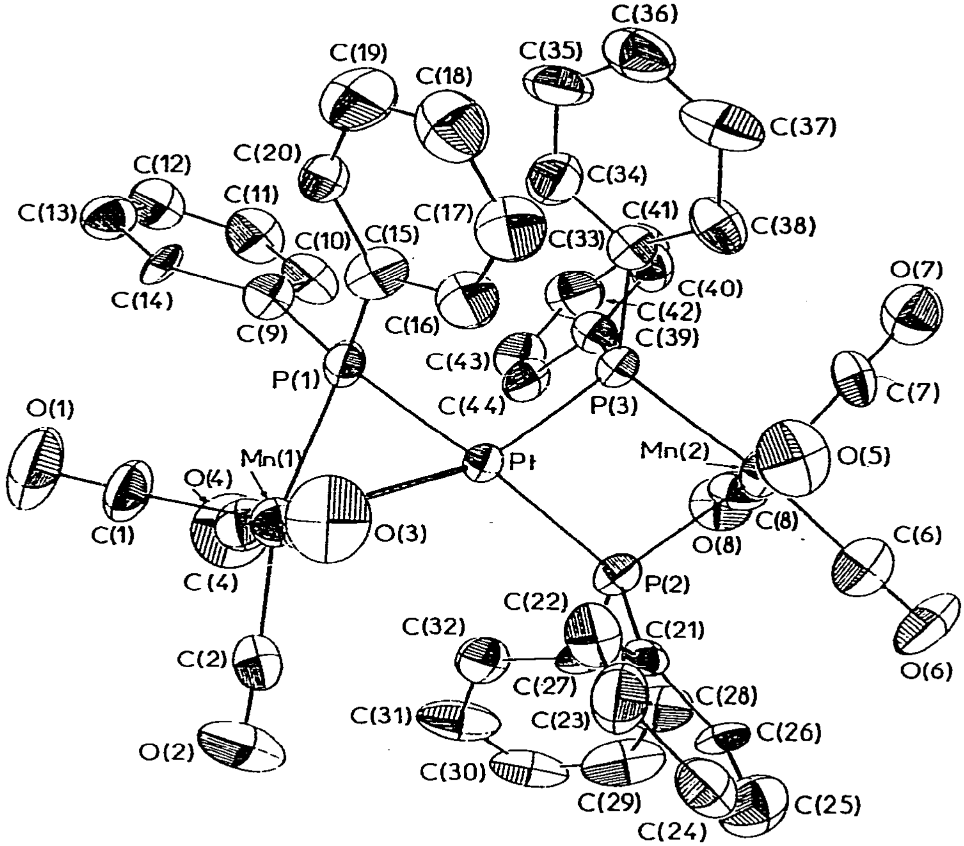


Fig. 3. ORTEP view of $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt}H(\mu_2\text{-}PPh_2)_2Mn(CO)_4$, III. The hydrogen atom bonded to the platinum is not shown.

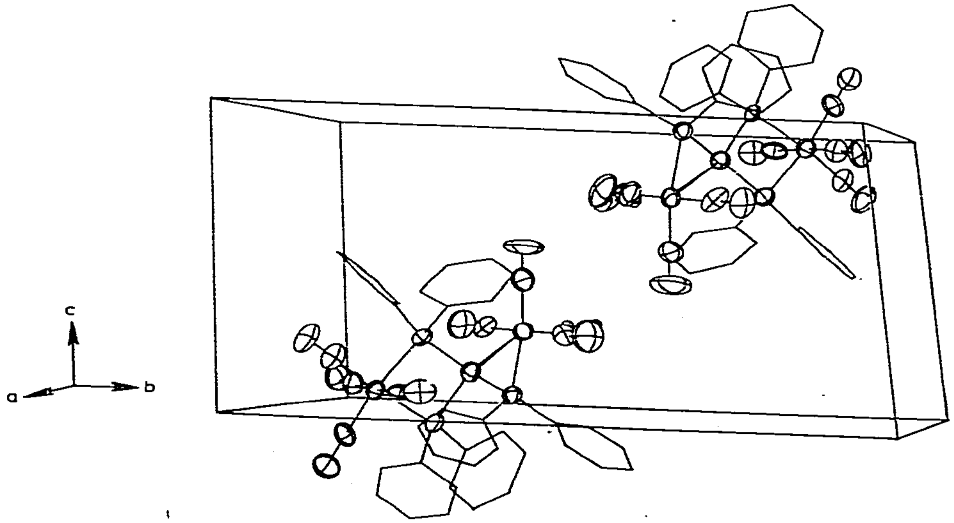


Fig. 4. Molecular packing of III.

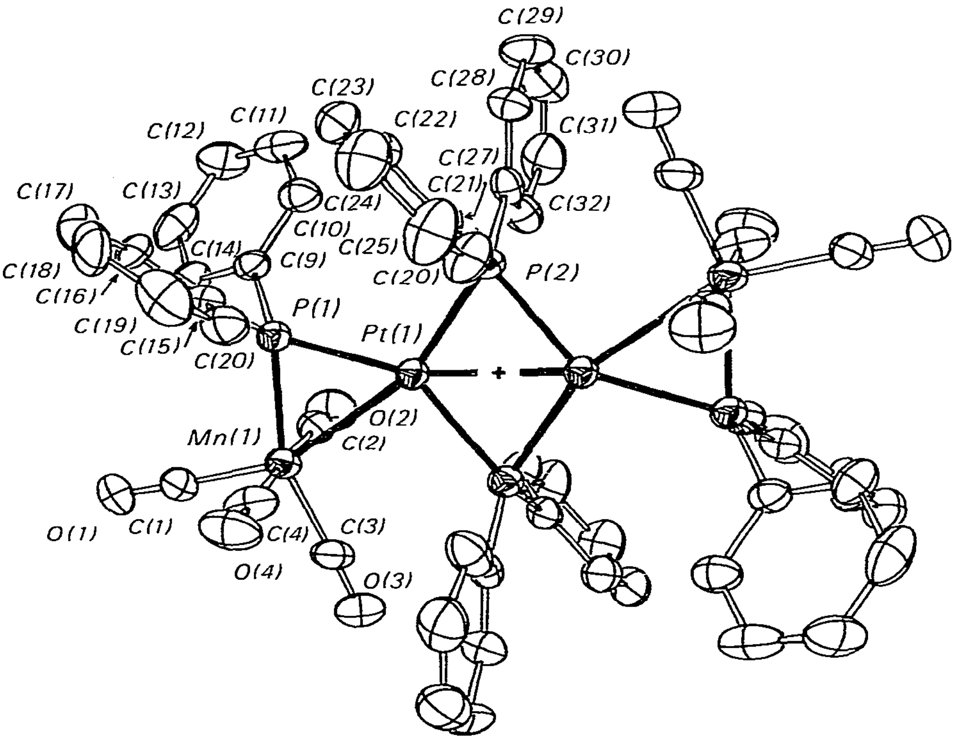


Fig. 5. ORTEP view of $(OC)_4\overline{Mn(\mu_2\text{-}PPh_2)Pt(\mu_2\text{-}PPh_2)_2Pt(\mu_2\text{-}PPh_2)Mn}(CO)_4$, IV. The molecule possesses an inversion center represented by the cross in the middle of the Pt(1)—Pt(1)′ bond.

broken line. This is the first structure, to our knowledge, in which such an arrangement of metal atoms is found *.

The four metal atoms and the four phosphorus atoms are not exactly in the same plane: the Mn(1) and Mn(2) atoms are out of the mean planes Pt(1)-Pt(1)′P(2)P(2)′ and Pt(2)Pt(2)′P(3)P(3)′ by 0.089(2) and 0.021(2) Å, respectively. As in complexes II and III, the platinum atoms are five coordinated, but in contrast, their chemical environment is different: three phosphorus atoms, one manganese and an other platinum atom. The Pt—Pt bond distance of 2.744(1) Å is in the range found in platinum clusters (from 2.668(1) to 2.916(1) Å in $Pt_5(CO)(\mu_2\text{-}CO)_5(PPh_3)_4$ for example [14]). The Pt—P bond lengths, with a mean value of 2.273(2) Å, are also in the range of those found in compounds II and III. The arrangements around the manganese atoms are distorted octahedrons as in II and II (see Table 10).

The family of complexes II, III and IV is of interest as involving different structural units combined to each other. Using the approach developed by R. Hoffmann et al., which establishes the isolobal character of PPh_2 with CH_2^- and $Mn(CO)_4$ with CH_2^+ [23,24], our complexes II, III and IV become II′, III′ and IV′, respectively:

The structural analogy between II and Pt^0 olefin complexes has been mentioned above, and it should be added that in both cases the geometry around the platinum atom is not strictly planar, since a slight tilt-angle is observed

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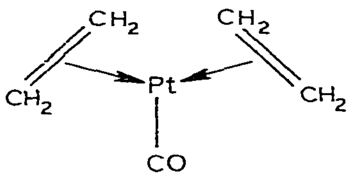
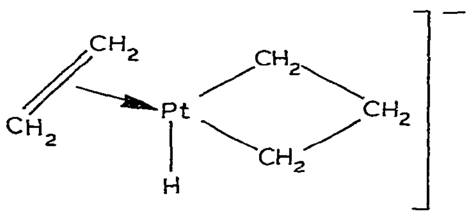
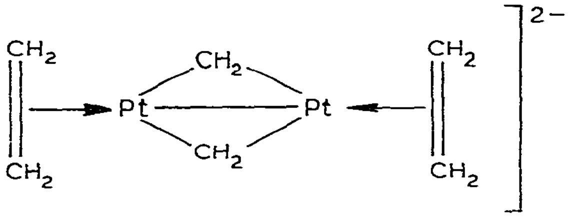
* Note added in proof: Since the submission of this paper, details of two structures have appeared with linear Mn—Rh—Rh—Mn [28] and bent Sn—Mn—Hg—Mn [29] frameworks.



(II′)



(III′)



(IV′)

between the two olefins [18] and between the $Ph_2PMn(CO)_4$ fragments. On the other hand, III′ and IV′ would represent prototypes for the rapidly growing class of metallacyclobutane [25] and bridging methylene complexes [26], respectively. There is also a nice analogy between IV′ and the complexes of the type

$R_3P \rightarrow Pt - Pt \leftarrow R_3P$

shown recently by Werner et al. [27] to contain two η^3-allyl ligands bridging the metal—metal bond.

Conclusion

The reaction of *cis*-$PtCl_2(PPh_2Cl)_2$ with $NaMn(CO)_5$ has been shown to give new platinum-manganese complexes with metal—metal bonds. Separation of the reaction products by column chromatography allowed us to isolate tri- and tetrametallic mixed complexes with characteristic linear or bent frameworks: linear $PtMn_2$ with two metal—metal bonds in I, bent $PtMn_2$ with two PPh_2 bridges and two metal—metal bonds in the chiral II, bent $PtMn_2$ with three PPh_2 bridges and only one metal—metal bond in III, and a planar zig-zag $MnPt_2Mn$ chain with four PPh_2 bridges and three metal—metal bonds in IV. The structure of the latter complex appears to be the first example of such a framework.

The structures of II, III and IV have many points in common, such as the presence of pentacoordinated 16-electron platinum in an almost planar environment, the PPh_2 bridges forming closed PtPMn or PtPPt triangles or open PtPMn ones and $Mn(CO)_4$ fragments with octahedral coordination more or less distorted depending upon the geometric contraints imposed by the bridges. Although the reaction of carbonylmetallates with a single coordinated chlorophosphine has been used previously, we have extended it to platinum and to a situation where two coordinated PPh_2Cl ligands are available for reaction. The latter feature, together with the unexpected lability of the phosphido ligand during the reaction, which facilitates CO migration from Mn to Pt, may account for the complexity and the variety of the products.

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