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Zerovalent Platinum Chemistry. Part X*. Cluster Compounds of Platinum with Triphenylphosphine as Ligand and their Reactions with Carbon Monoxide

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A series of cluster compounds of platinum with triphenylphosphine as ligand is presented and their properties, notably the reactions with carbon monoxide, which have led to the identification of new carbonyl phosphine platinum(0) species, are described.

Introduction

Since the discovery of the first zerovalent platinum compounds $Pt\{P(C_6H_5)_3\}_{3,4}$[1] there has been developed a large bank of information on their reactions[2], particularly those in which phosphines are substituted by anionic ligands to give platinum(II) products, or by neutral unsaturated molecules, *e.g.* oxygen or olefins, which give π-complexes of formally platinum(0) although the actual oxidation state of the metal seems to vary between 0 and +2.[2,3] In addition to these monomeric compounds several oligomeric carbonylphosphines of platinum(0) have been reported.[4] The chemistry of the oligomeric derivatives of platinum(0) containing only phosphine ligands is much less well documented. Information on this type of compound is limited to the preliminary communication[5] from Gillard *et al.* describing $[Pt(PPh_3)_2]_3$ and $[Pt(PPh_3)]_4$, the brief comments on these formulations given[6] by Glocking *et al.*, the report[7] by Chini and Longoni of the preparation of $Pt_3(PPh_3)_4$, and the very recent report[8] of the structures of $[Pt_2(PPh_3)_2(PPh_2)_2]\cdot C_6H_6$ and $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]\cdot C_6H_6$.

In view of the obviously interesting nature of the compounds themselves and because of their relationship to the rather better characterised carbonyl phosphine oligomers of platinum(0), we now present further details of their preparations and properties which allow for better characterisation than was possible at the time of the earlier report.[5] We also report the reactions of these species with carbon monoxide which have led to the identification of two new carbonyl phosphine platinum(0) clusters.

Results

Oligomeric platinum phosphine compounds can be prepared by several methods starting from monomeric platinum(0) or platinum(II) species. These reactions are shown in Schemes 1a and 1b in which the compounds which form the main subject of this paper are numbered I–V.

When tri- or tetrakis-triphenylphosphineplatinum(0) is melted under nitrogen, subsequent cooling produces a red solid.

In the earlier note[5], this compound was tentatively assigned the trimeric structure shown in Figure 1. We still believe this structure to be most reasonable, but a more complex structure in which metallation or some more complicated transformation of the phosphines has taken place[9] cannot be excluded; the molecular weight recorded for I would in fact be consistent with its formulation as $[Pt_2(PPh_3)_2(PPh_2)_2]_2\cdot C_6H_6$[8]. However, our material reacts easily with oxygen and could not be crystallised which thus supports the original[5] trimeric formulation. The ready reaction of I with oxygen produces $OPPh_3$ and a red–orange material, II, which can be recrystallised from benzene. Molecular weight and analyses are consistent with formulae [Pt

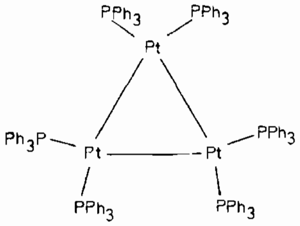

Figure 1. Suggested structure of (I).

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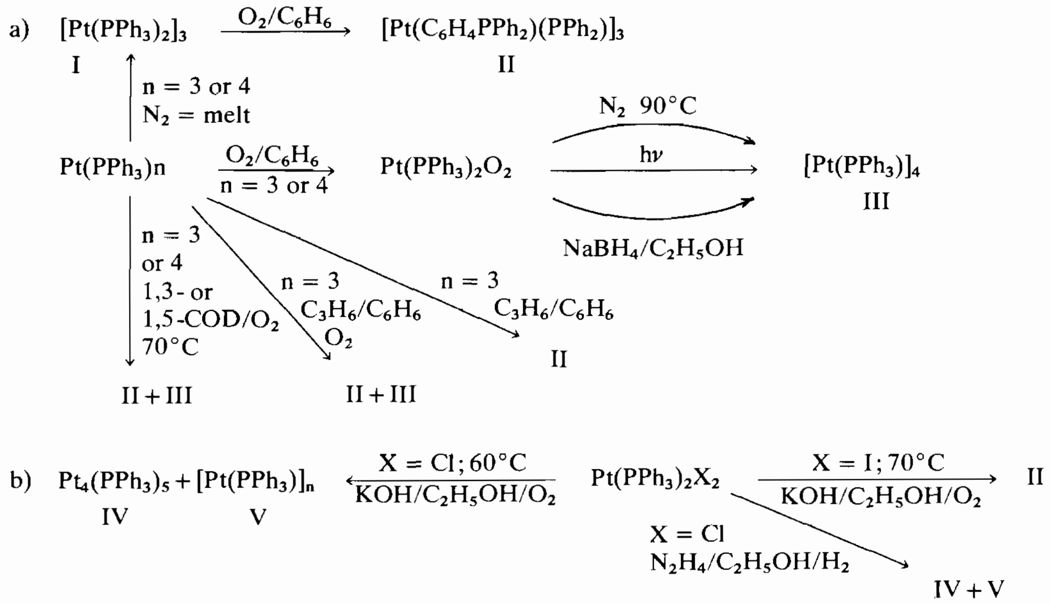
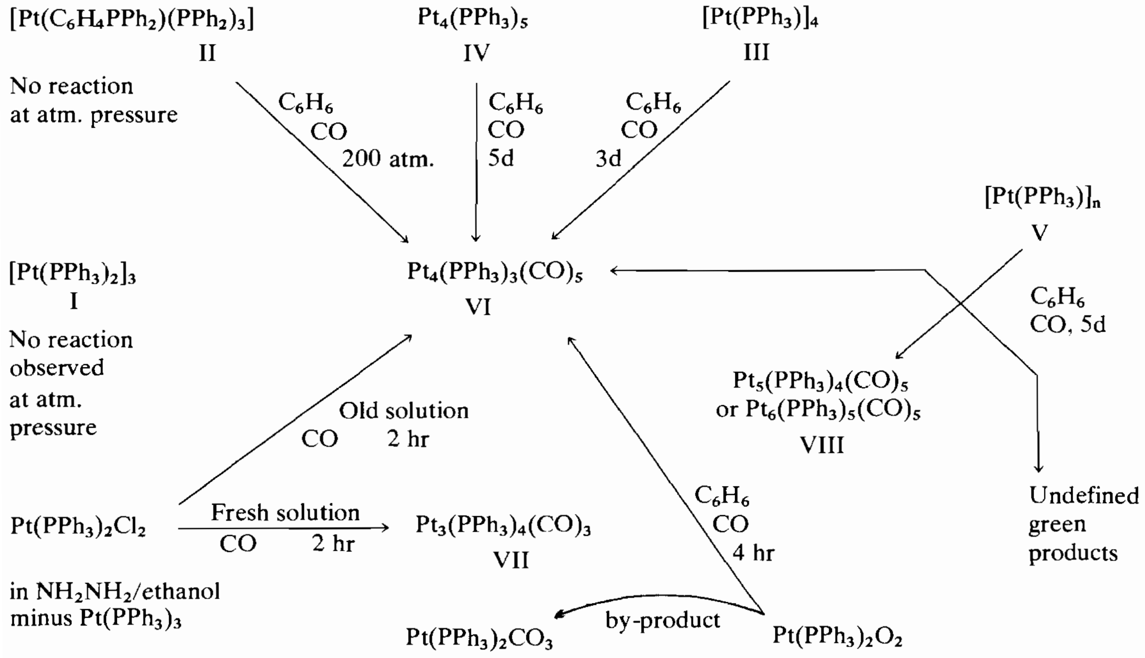
* Part IX: M. Keubler, R. Ugo, S. Cenini and F. Conti, *J.C.S. Dalton,* 1081 (1975).



Scheme 1. Methods of preparation of platinum phosphine oligomers.



Scheme 2. Reactions of platinum phosphine compounds I–V with carbon monoxide.

$(C_6H_4PPh_2)(PPh_2)]_3$ (Figure 2a), which has been given[6] by Glockling *et al.* for one of the products of pyrolysis of Pt(*m*-$FC_6H_4)_2(PPh_3)_2$, or $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]\cdot C_6H_6$ (Figure 2b) which has been obtained by prolonged refluxing of $Pt(PPh_3)_4$ in benzene and for which the crystal structure is known[8].

Consistent with both formulations reaction of II with cyanide produces both *tri*- and *di*phenylphosphine. Al-

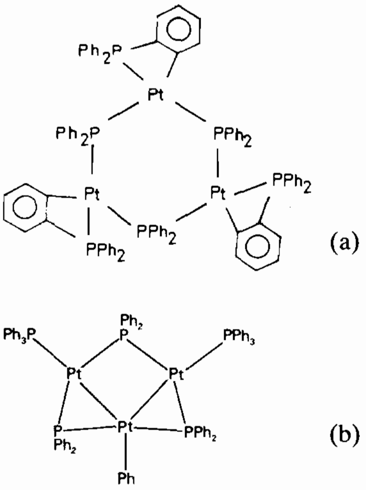


Figure 2. Possible structures for (II).

though the infrared spectrum of II shows a strong band at 730 cm^{-1}, indicative of an orthometallated phenyl group[10], definite assignment of bands in this region is impossible since even the monomers $Pt(PPh_3)_n$ have an abundance of bands in this region.

However, the X-ray powder pattern of II (*d* values: 14.2, 11.9, 11.2, 10.5, 9.1, 8.3, 7.6, 7.0, 6.5, 5.6, 5.0, 4.5, 4.3, 3.3, 3.2, 2.8, 2.1, 2.0) is not fully consistent with the X-ray data[8] for $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]\cdot C_6H_6$ so that we suggest that II, with structure 2a, is a different compound than depicted as 2b, although we cannot rule out the possibility that the powder lines which are incompatible with the reported structure[8] may be due to impurity. Attempts to obtain ^{31}P nmr spectra of I and II (and of all the other compounds presented here) have been unsuccessful due to too low solubilities, probably further aggravated by an extensive splitting of the signals which is to be expected for both structures 2a and 2b or even similar related ones.

It is quite clear that II and the obviously related $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]\cdot C_6H_6$ are produced by thermal transformation of bis-triphenylphosphine species which occur readily both in solution and in the solid state. This has been indirectly reported already by Glockling *et al.*[6] and by other groups of workers. Some of us[11] and Tolman *et al.*[12] observed a reddening of solutions of $Pt(PPh_3)_2C_2H_4$ as ethylene is eliminated. Durkin and Schram[13] have reported that pyrolysis of the products obtained from addition of Lewis acids (*e.g.* SiF_4, BCl_3) to $Pt(PPh_3)_3$ and of $Pt(PPh_3)_3$ itself, produces red "residues". These "residues" were not discussed in detail but the infrared data given[13] are fully consistent with that observed by us for II. In agreement with the above observation[10,11] we have now isolated II from solutions of $Pt(PPh_3)_{3,4}$ in 1,3- or 1,5-cyclooctadiene (COD) and from $Pt(PPh_3)_3$ in benzene/cyclopropane. In the absence of oxygen, II can be obtained in up to 60% yields. The presence of $Pt(PPh_3)_2$ as an active intermediate in these oligomerisations is particularly strongly indicated by our observation that using C_6H_6/C_3H_6 and $Pt(PPh_3)_n$ reaction only occurs to give II when n = 3 and when cyclopropane is present in quantity. Thus the reactions occurring are probably:

$$Pt(PPh_3)_n + C_3H_6 \underset{C_6H_6}{\overset{1}{\rightleftharpoons}} Pt(PPh_3)_2C_3H_6^{*} + (n-2)\,PPh_3$$

$$C_6H_6 \;\Big\updownarrow\; 2$$

$$C_3H_6 + \underset{\text{"active"}}{Pt(PPh_3)_2} \rightarrow II + C_6H_6$$

in which equilibrium 1 is only favourable for further reaction to produce II when the free phosphine concentration is minimal (*i.e.* n = 3) and when the C_3H_6 concentration is high. A similar scheme can be drawn for the COD reaction in which case COD is used as solvent and hence in great excess so that equilibrium 1 lies to the right irrespective of the value of n. In the presence of oxygen the reactions of $Pt(PPh_3)_{3,4}$ with COD and cyclopropane are more complicated and the products are II and $[Pt(PPh_3)]_4$ (III) which can be separated by chromatography when III is obtained as a benzene adduct, $[Pt(PPh_3)]_4\cdot C_6H_6$.

Since oxygen is the factor which causes the COD and C_3H_6 reactions to follow courses leading to III as well as II, it seemed that III is produced by thermal decomposition of the oxygen complex $Pt(PPh_3)_2O_2$. In order to prove this we have heated $Pt(PPh_3)_2O_2$ under nitrogen and indeed obtain the brown material III, with triphenylphosphine oxide as by-product. Elimination of oxygen (and $OPPh_3$) can also be achieved by irradiation of $Pt(PPh_3)_2O_2$ with u.v. light or by treatment with sodium borohydride in alcohol.

In the earlier note[5] the formulation of III as a tetramer having only PPh_3 as ligand (Figure 3) was based on molecular weight measurement and on its spectroscopic characteristics. Further support for this formulation is provided by a detailed comparison of its infrared spectrum with that of the monomer Pt $(PPh_3)_4$ which shows that the observed vibrations are very similar indeed.

In addition to its preparation from platinum(0) monomers, II can be obtained by treating $Pt(PPh_3)_2X_2$ (X = I) with alcoholic KOH at *ca.* 70°C. When X = Cl two materials can be isolated by chromatography

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[*] This cyclopropane adduct intermediate and related species with rhodium(I) and iridium(I) are to be discussed in a later paper.

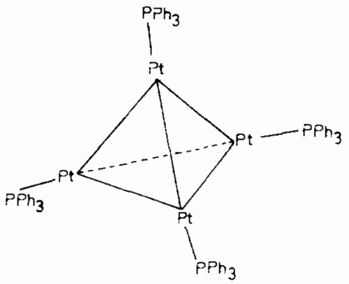

Figure 3. Suggested structure of $[Pt(PPh_3)]_4$ (III).

of the reaction mixture. They analyse as $Pt_4(PPh_3)_5$ (IV) (as a C_6H_6 adduct) and a black material $[Pt(PPh_3)]_n$ (V). The major product is the dark-brown IV, but the amount of black polymeric material V increases as the reaction time is increased. As is well known, in the reaction of $Pt(PPh_3)_2Cl_2$ with hydrazine in alcohol $Pt(PPh_3)_3$ is precipitated[1]; by bubbling hydrogen through the mother liquor for *ca.* 2 days a mixture of IV and V is also obtained. Chromatography, melting point consistency and sharpness, as well as consistent analyses suggest that IV is a pure compound. This is further endorsed by its relatively clean reaction with carbon monoxide (see below). By reaction of IV with cyanide the formation of a certain amount of diphenylphosphine has been detected; however, by reaction with 1,2-diphenylphosphinethane (DPE) the well known zerovalent $Pt(DPE)_2$ is formed. These contradictory results would support the presence of both zero- and divalent platinum in an irregular structure of low symmetry (*cf.* Figure 2b) and in which both PPh_2 bridges and PPh_3 terminal ligands occur. These observations and the odd stoichiometry (which from analyses might also be $Pt_3(PPh_3)_4$ or even $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]$ without benzene of crystallisation, see Discussion) does not allow for any suggestion of structure and we have so far been unable to grow reasonable crystals for an X-ray study.

Reactions of I–V with Carbon Monoxide

The reactivities of the present platinum systems towards carbon monoxide serve as a useful indication of formal oxidation state of the metal and also of the degree of oligo- or polymerisation. Thus whilst species containing zerovalent platinum are known to be carbonylated rather easily,[2, 11] platinum(II) compounds with phosphine should show relative inertness to CO.

Indeed II, which we formulate as a platinum(II) species, only reacts with CO und 200 atmosphere pressure whilst III, IV and V react, although slowly, even at atmospheric pressure. Although we formulate I as containing platinum(0) we have observed no reaction with CO. As mentioned above, however, even traces of oxygen in the reaction system would cause immediate reaction to II and this would readily explain the observed inertness. The carbonylation reactions are summarised in Scheme 2.

Carbonylation of III gives a single brown product which analyses as $Pt_4(PPh_3)_3(CO)_n$ (VI). n is probably 5 since CO evolution measurements give values indicating $4<n<5$ although oxygen analyses show $5<n<6$. This same compound can be obtained from $Pt(PPh_3)_2O_2$ by bubbling CO through its solution in benzene; $Pt(PPh_3)_2CO_3$ is obtained as by-product.

Carbonylation of IV proceeds only very slowly at atmospheric pressure and the main product of a mixture is again VI, as is also produced in very low yields at 200 atmospheres CO from II. After purification by chromatography VI is obtained as a benzene adduct, $Pt_4(PPh_3)_3(CO)_5 \cdot 1.5\ C_6H_6$. VI can also be prepared by bubbling CO through the solution of *cis*-$Pt(PPh_3)_2Cl_2$ in hydrazine/ethanol from which precipitated $Pt(PPh_3)_3$ has been filtered off and which has stood for some days. $Pt_3(PPh_3)_4(CO)_3$ (VII), which has already been reported,[4] is also obtained from this reaction and is the only product when a fresh hydrazine/ethanol solution of *cis*-$Pt(PPh_3)_2Cl_2$ is used.

The black material V also reacts only slowly with atmospheric pressure of CO to give a mixture of products. This would support the view that this material is not a single pure compound, although the major component is probably a cluster of high nuclearity which analyses as $[Pt(PPh_3)]_n$. After separation of the carbonylated mixture by chromatography a violet compound VIII and a brown material have been obtained. This latter is predominantly VI although it is impure due to the presence of very small amounts of two further green carbonyl species which have not been investigated further. The violet VIII has a molecular weight which, coupled with the analyses fit $Pt_5(PPh_3)_4(CO)_5$ although other formulations, *e.g.* $Pt_6(PPh_3)_5(CO)_5$, would also be possible (see Experimental). The infrared spectrum of VIII shows that it contains both bridging and terminal carbonyl groups.

Discussion and Conclusion

The present results provide evidence in substantiation of the earlier report[5] of the existence of zerovalent platinum phosphine cluster compounds $[Pt(PPh_3)_2]_3$ and $[Pt(PPh_3)]_4$. In addition another compound which analyses as $Pt_4(PPh_3)_5$ has been identified. Evidence that the first two compounds are platinum(0) species is provided by: 1) their reaction with DPE to give $Pt(DPE)_2$, 2) the fact that they can be carbonylated under relatively mild conditions, at least in the case of $[Pt(PPh_3)]_4$, and 3) their reaction with KCN gives PPh_3 and no $HPPh_2$.

The trimeric cluster I is not very well characterised, a result of its ready reaction to give II, but the recent characterisation of a trimeric cluster of formula $Pt_3(t\text{-}BuNC)_6$[14] is in support of our formulation.

The easy reaction to give II is particularly interesting in view of the fact that the trimeric Pt(0)–CO–phosphine clusters[4] are very stable. The stabilisation which carbonyl groups give to low oxidation state metal complexes is well known as is also the fact that systems containing phenylphosphine but no carbon monoxide ligands can undergo intramolecular reaction to give oxidised species, containing orthometallated phenyl groups, as exemplified by the fact that Vaska's compound $IrCl(CO)(PPh_3)_2$ is very stable whilst the related $IrCl(PPh_3)_3$ complex can be easily transformed into $Ir(C_6H_4PPh_2)(PPh_3)_2(H)Cl$.[10] The present I→II oligomer transformation is clearly a related phenomenon, although the mechanism apparently involves monomeric species as intermediates.

To support our view we have evidence that $Pt(PPh_3)_2$ itself undergoes orthometallation. n-BuLi + $Pt(PPh_3)_2(H)Cl$ at –40°C gives $Pt(PPh_3)_2$.[11] At high temperature, *e.g.* –10°C, the product is pale cream and although pure samples have not been obtained (those obtained always contain the above $Pt(PPh_3)_2$ species and unreacted $Pt(PPh_3)_2(H)Cl$) analyses indicate a stoichiometry $[Pt(C_6H_4PPh_2)(PPh_2)]_n$; with n = 2, this would correspond to the product reported[15] by Blake and Nyman and to the dimer obtained by Glockling *et al.*[6]

The compound IV ($Pt_4(PPh_3)_5$) has analyses which would also be consistent with a $Pt_3(PPh_3)_4$ or a $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)]$ formulation. Its preparation by the reaction: $Pt(PPh_3)_2Cl_2 + N_2H_4/H_2$ in ethanol is obviously analogous to that from which Chini and Longoni[7] obtained the product which they formulated as $Pt_3(PPh_3)_4$. The contradictory results with respect to the oxidation state of the metal, discussed above, do not allow any further comment to be made. The tetrameric formulation is supported only by its carbonylation to produce a tetrameric compound VI, $Pt_4(PPh_3)_3(CO)_5$.

This new carbonyl $Pt_4(PPh_3)_3(CO)_5$ (VI) is particularly interesting when compared with some of the tetrameric platinum carbonyls already known. The present compound is obviously related to $Pt_4L_4(CO)_5$ (L = various phosphines or $AsPh_3$) which exhibits two structural forms and $Pt_4(AsPh_3)_3(CO)_5$[4d]. The infrared spectrum of the present VI shows the presence of both bridging and terminal CO groups as is found for the above arsine compound of analogous stoichiometry. Indeed the infrared spectra of these two compounds are very similar in the CO regions, as shown in Table I. On the basis of these results we suggest that $Pt_4(PPh_3)_3(CO)_5$ is isostructural with its arsine analogue, having the structure shown in Figure 4.

TABLE I. Carbonyl Region Infrared Bands (Nujol mull) reported[4d] for *a*, $Pt_4(AsPh_3)_3(CO)_5$ and observed in the present work for *b*, $Pt_4(PPh_3)_3(CO)_5$.

a	1995(s)	1875(w)	1865(m)	1800(s)	1775(s)	1720(w)
b	1990(s)	1889(w)	1845(m)	1805(s)	1780(s)	

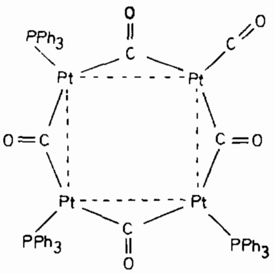

Figure 4. Suggested structure of $Pt_4(PPh_3)_3(CO)_5$; *cf.* $Pt_4(AsPh_3)_3(CO)_5$.[4d]

The clean reaction of $[Pt(PPh_3)]_4$ (III) with CO to give the above compound VI is, in addition to the molecular weight and infrared characteristics, further evidence for its tetrameric character.

It appears from our investigations that the formation of highly unsaturated monomeric species of platinum(0) (*e.g.* "$Pt(PPh_3)_2$" or "$Pt(PPh_3)$") is the required condition to produce phosphine cluster compounds of platinum. In this respect reagents such as oxygen (or air) or borohydride favour the formation of the unsaturated species since phosphine can be readily displaced as $OPPh_3$ or $BH_3 \cdot PPh_3$.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 621 grating spectrophotometer as nujol mulls or KBr discs. Melting points were determined on a Leitz Heiztischmikroskop and are uncorrected. Molecular weights were measured on a Mechrolab Osmometer. Column chromatography was done on 50 cm columns of alkali free alumina, deactivated by water (10% unless otherwise stated). Thin layer chromatography was done on 20 cm × 20 cm layers of silica gel (1 mm thickness). Benzene was used as eluent unless otherwise stated.

$Pt(PPh_3)_{3,4}$[16], $Pt(PPh_3)_2X_2$ (X = Cl,[17] I[1]) and $Pt(PPh_3)_2O_2$[18] were prepared by literature methods.

The analytical results and other properties of the compounds I–VIII are given in Table II.

$[Pt(PPh_3)_2]_3$, I

$Pt(PPh_3)_3$ (2 g) was melted under nitrogen at 200°C in an oil bath. The red solid obtained on cooling was dissolved in nitrogen-degassed benzene and purified by column chromatography under nitrogen. The red fraction eluted with benzene was evaporated to dryness and washed with n-hexane. Yield: 1.2 g.

TABLE II. Analytical Results (required values in parentheses) and Carbonyl Stretching Frequencies of Platinum Cluster Compounds.

	Compound	Colour	M.P.	C	H	O	P	Pt	MW[a]	νCO[b]
I	$[Pt(PPh_3)_2]_3$	Bright Red	–	59.6 (60.1)	4.2 (4.2)	–	8.5 (8.6)	26.7 (27.1)	1460 (2157)	–
II	$[Pt(C_6H_4PPh_2)(PPh_2)]_3$	Red–Orange	244–248	56.1 (56.2)	4.1 (3.7)	–	8.0 (9.7)	29.7 (30.4)	1615 (1923)	–
III	$[Pt(PPh_3)]_4$	Brown	142–145	47.7 (47.3)	3.4 (3.3)					
III	$[Pt(PPh_3)]_4 \cdot C_6H_6$	Brown	195	48.7 (49.1)	3.7 (3.5)	–	6.4 (6.5)	40.5 (40.9)	1770–2016 (1906)	–
IV	$[Pt_4(PPh_3)_5] \cdot C_6H_6$[e]	Brown–Black	174	53.4 (53.1)	3.9 (3.7)	–	7.2 (7.1)	34.8 (35.9)	1600–2010 (2168)	–
V	$[Pt(PPh_3)]_n$	Black	–	48.1 (47.2)	3.5 (3.3)	–	6.8 (6.8)	41.0 (42.7)	1940–2200 (–)	–
VI	$[Pt_4(PPh_3)_3(CO)_5] \cdot 1.5C_6H_6$[c]	Brown	146	44.8 (44.8)	3.1 (2.9)	5.3 (4.4)	5.0 (5.1)	41.2 (42.7)	1960 (1823)	1990(s) 1889(w) 1845(m) 1805(s) 1780(s)
VII	$[Pt_3(PPh_3)_4(CO)_3] \cdot C_6H_6$	Red	180[d] dec.	54.3 (54.2)	3.6 (3.7)	–	7.1 (6.9)	–	1310 (1795)	1845(w) 1799(s) 1782(s)
VIII	$Pt_5(PPh_3)_4(CO)_5$ or $Pt_6(PPh_3)_5(CO)_5$	Violet	210 dec.	42.6 (42.7) (43.5)	3.1 (2.8) (2.9)	3.6–4.6 (3.7) (3.0)	5.1 (5.7) (5.9)	45.2 (45.1) (44.7)	2060–2170 (2163) (2620)	2012(s) 1990(s) 1819(sh m) 1785(s)

[a] Benzene solution. [b] cm^{-1}; Nujol mull. [c] CO: 4.5–4.7 mol per mol of complex. [d] Lit.[4] 179–182. [e] Analytical data are satisfactory for formulations as $Pt_3(PPh_3)_4$ or $[Pt_3(PPh_3)_2(PPh_2)_3Ph]$.

$[Pt(C_6H_4PP_2)(PPh_2)]_3$, II

i) By dissolving I in benzene in air an easy oxidation of one mol of phosphine to triphenylphosphine oxide per mol of complex takes place. In some cases reaction with carbon dioxide occurs and white $Pt(PPh_3)_2CO_3$ is precipitated. After filtering this off, the red benzene solution was purified by column chromatography and the red fraction evaporated to dryness and washed with n-hexane. Yield: ~80%.

ii) $Pt(PPh_3)_3$ (0.5 g) was dissolved in 20 ml nitrogen-degassed benzene in a 75 ml ampoule into which was condensed *ca.* 20 ml liquid cyclopropane before sealing. The reaction solution was kept at 70°C for 48 hr during which time it became bright red. This was then stored at –5°C for *ca.* 2 weeks after which time red crystals of the product had precipitated. These were filtered off and washed with n-hexane. Yield: ~60%. Using less cyclopropane the yields were correspondingly lower and when non-degassed benzene was used the product was mixed with *ca.* 50% $[Pt(PPh_3)]_4$ (III).

iii) See III iv below.

iv) $Pt(PPh_3)_2I_2$ (2 g) and KOH (0.5 g) were added to ethanol (*ca.* 50 ml). The suspension was stirred for 24 hr at 70°C in air. After cooling the red–orange solid was filtered off, washed with water until the filtrates were free of inorganic material, ethanol/water and n-hexane. The solid was purified by column chromatography as in i). Yield: 0.5 g. By increasing the temperature, the reaction time and the amount of KOH, the same mixture of compounds as described in IV i was obtained.

$[Pt(PPh_3)]_4$, III

i) $Pt(PPh_3)_2O_2$ (1 g) was heated slowly to 90°C in a nitrogen atmosphere and held at this temperature for 6 hr, during which time the flesh coloured starting material had become dark brown. In some experiments the oxygen evolved was collected in a burette; its volume corresponded to 1/2 mol O_2 per mol of starting complex. The brown solid was extracted with hot diethyl ether for several hours in order to remove triphenylphosphine oxide. The product analysed as $[Pt(PPh_3)]_4$. Yield: *ca.* 100%. When dissolved in benzene and purified by column chromatography on alumina deactivated with 6% water, using benzene + 10% ethanol as eluent, the brown product analysed as $[Pt(PPh_3)]_4 \cdot C_6H_6$.

ii) $Pt(PPh_3)_2O_2$ (2 g) was dissolved in absolute ethanol (40 ml). Excess 0.1*N* sodium borohydride in water was added slowly to cause precipitation of the brown product which was purified as above. Yield: ~80%.

iii) $Pt(PPh_3)_2O_2$ (1 g) in benzene (100 ml) was irradiated with u.v. light for *ca.* 3 hr. The resulting brown solution was evaporated to dryness and the product purified as above. Yield: ~80%.

iv) $Pt(PPh_3)_n$ (n = 3 or 4,5 g) dissolved in peroxide free 1,3- or 1,5-cyclooctadiene (50 ml) was heated at 70°C for 1 week in air. The yellow solution turned red. After evaporation to dryness and washing with n-hexane the solid was dissolved in benzene and purified by column chromatography. Elution with benzene produced a fraction from which (II) was isolated (1.3 g). Elution with benzene +10% ethanol gave a second product, which after extraction with hot diethyl ether in order to remove triphenylphosphine oxide, was isolated as $[Pt(PPh_3)]_4 \cdot C_6H_6$. Yield: 0.4 g.

By conducting the reaction under the same conditions using cyclooctadiene which had stood for some time the yield of III increased (to 1 g) at the expense of II (0.4 g). In some cases an unidentified orange product, insoluble in the reaction medium, was also obtained.

$Pt_4(PPh_3)_5$ *or* $Pt_3(PPh_3)_4$ *or* $[Pt_3(PPh_3)_2(PPh_2)_3Ph]$, *IV*

i) A solution of KOH (1.4 g) in ethanol (70 ml) was added to *cis*-$Pt(PPh_3)_2Cl_2$ (4 g) and the suspension was stirred for 2 hr at 60°C. The resulting brown solution was evaporated to dryness. The residue, smelling of organic materials, was washed with water until the filtrate was at pH = 7 and then with n-hexane. It was then purified by column chromatography. The brown fraction was evaporated to dryness to give the product. Yield: 1.2 g. The benzene could be eliminated by stirring this product in boiling n-hexane, filtering and drying under vacuum. The infrared spectrum showed the absence of the 670 cm^{-1} band of benzene but the presence of n-hexane was detected by ^1H nmr.

ii) See V ii below.

$[Pt(PPh_3)]_n$, *V*

i) After elution of $[Pt_4(PPh_3)_5] \cdot C_6H_6$ from the chromatography column as in IV i above, with benzene, the column was eluted with benzene + 10% ethanol and a brown–black fraction was collected. After evaporation to dryness it was extracted with hot diethyl ether to eliminate $OPPh_3$ (solvents like ethanol which readily dissolve the oxide also dissolve the product). The solid residue (*ca.* 100 mg) analysed as $[Pt(PPh_3)]_n$. By increasing the reaction time of IV i to three days the amount of V increased to *ca.* 500 mg with the yield of IV decreasing to *ca.* 500 mg. At the same time, brown–black intractable oils were also produced. These were partially eliminated by filtration of the benzene solutions before chromatography, but black residues which could not be eluted were always observed at the top of the column.

ii) *cis*-$Pt(PPh_3)_2Cl_2$ (0.5 g) suspended in ethanol (15 ml) was treated with 85% aqueous hydrazine solution dropwise with stirring until a clear pale yellow solution was obtained. This was then boiled to reflux causing precipitation of $Pt(PPh_3)_3$. After filtration the solution was stored and after repeated preparations, *ca.* 250 ml was collected. By bubbling hydrogen through this solution for 24 hr at room temperature the colour changed through brown to black. After concentration by evaporation under vacuum (15 mm) a brown product was collected which was washed with water and n-hexane before dissolving in benzene. Chromatography of this solution gave two fractions of compound IV (1.2 g) and $[Pt(PPh_3)]_n$ (2 g). As above, black residues were found at the top of the column.

$Pt_4(PPh_3)_3(CO)_5$, *VI*

i) $[Pt(PPh_3)]_4$ (III) (0.1 g) was dissolved in benzene (40 ml) and CO bubbled through the stirred solution for 3d. Additional benzene was occasionally added to maintain the solution at constant volume. The product solution was reduced to 10 ml and purified by column chromatography. A brown fraction was collected, evaporated to dryness and washed with n-hexane to give the solvated product $[Pt_4(PPh_3)_3(CO)_5] \cdot 1.5C_6H_6$. Yield: 30 mg.

ii) $Pt(PPh_3)_2O_2$ (1 g) was suspended in benzene (70 ml) and CO bubbled through the stirred mixture for 4 hr. A white insoluble compound, identified as $Pt(PPh_3)_2CO_3$, was filtered off. The brown filtrate was concentrated to 20 ml and purified by column chromatography to give the solvate as above. Yield: 0.2 g. This compound is air-stable, but slowly loses CO even in an inert atmosphere.

iii) Compound (IV) (1 g) dissolved in benzene (40 ml) was treated with CO at atmospheric pressure for 5 d. After concentration of the solution to 10 ml it was chromatographed on the column and the carbonyl containing fraction further purified by t.l.c. to give $[Pt_4(PPh_3)_3(CO)_5] \cdot 1.5C_6H_6$ as the main product.

iv) (II) (1 g) was dissolved in benzene (15 ml) and treated with 200 atm. CO in an autoclave for 12 hr. The initially red solution became yellow but rapidly reverted to red as the CO pressure was lifted. The solution was concentrated to 5 ml and chromatographed on the column. After further purification by t.l.c., $Pt_4(PPh_3)_3(CO)_5$ was isolated as the main product as its benzene adduct.

$Pt_3(PPh_3)_4(CO)_3$, *VII*

CO was bubbled through the pale yellow solution (200 ml) prepared as in V ii for 1 hr. A red mixture precipitated which was filtered off, washed with water, ethanol and n-hexane. Carbonylated species (*ca.* 2 g) were separated from other products by column chromatography and were then further purified by t.l.c. in 60–80 mg batches. A large portion of the material did not move on the plate, but after 1–1.5 hr a grey compound was isolated in small quantities (this has not been investigated further other than recording its infrared spectrum: νCO = 1830(s) and 1800(s) cm^{-1})

followed by the brown compound VI. Red $[Pt_3(PPh_3)_4(CO)_3]\cdot C_6H_6$ was removed from the middle of the plate.

By carbonylating a freshly prepared solution from V ii, the precipitate was VII free of impurities and was thus obtained in good yield. A further batch of pure product was isolated by evaporation of the solution.

$Pt_5(PPh_3)_4(CO)_5$ or $Pt_6(PPh_3)_5(CO)_5$, VIII

$[Pt(PPh_3)]_n$ (V) (1.5 g) was dissolved in benzene (80 ml) and CO bubbled through the stirred solution for 5 d. Additional benzene was occasionally added to maintain a constant volume. The solution was concentrated to 20 ml and the carbonylated products separated from other materials by column chromatography. Further concentration of this fraction, followed by repeated column chromatography resulted in the separation of two fractions, *a*, brown and *b*, violet. Evaporation to dryness of *b* produced VIII (50 mg).

On evaporation of *a* and the intermediate between *a* and *b*, 60–80 mg of solid were obtained. This was dissolved in benzene and purified by t.l.c. Part of the product did not move on the plate indicating partial decomposition. After 1–1.5 hr, two green materials were collected from the top of the plate, but the quantities were too low to allow for further investigation. Brown VI (*ca.* 20 mg) was isolated as a middle fraction, followed by the violet VIII (*ca.* 40 mg).

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