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Zerovalent Platinum Chemistry. III.
Properties of Bistriphenylphosphineplatinum(0)*

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Received April 30, 1970

The cordinative reactivity and stability of the species $Pt(PPh_3)_2$ are reported; its reactivity towards small molecules is compared with that of a chemisorption center on a metal surface. The relation between the coordinative unsaturation and chemical behaviour of $Pt(PPh_3)_2$ and the carbenoid character for the platinum atom is discussed.

Introduction

In the last few years a number of workers have investigated «unsaturated» coordination compounds of transition metals in low oxidation states having mainly tertiary phosphines and carbon monoxide as ligands.[1]

The interest of this investigation is mainly due to Vaska's discovery[2] of the reactivity of the planar iridium(I) carbonyl compound which made it apparent that there is a great similarity between addition reactions and chemisorption at a transition metal surface. In the course of our work on platinum(0) chemistry, we have already described some reactions of oxidative addition[3] and of coordinative addition[4] with triphenylphosphine platinum(0) compounds having a formal d^{10} configuration; at the same time Cook and coworkers[5] have extended oxidative addition reactions of platinum(0) compounds to many other molecules, while Fitton and coworkers[6] have recently reported similar reactions with homologous palladium(0) complexes. However, the factors underlying oxidative addition reactions of d^{10} complexes are not so well defined as those of d^8 complexes; for instance the tetrakisphosphine d^{10} complexes show a facile dissociation to unsaturated trigonal planar complexes and probably to dicoordinated solvated species; at present it is not completely clear which of these unsaturated species is the reactive one.

The isolation[7] of a yellow material which analyses as $[Pt(PPh_3)_2]_x$ and which behaves as a monomer in solution has made easier the investigation of the coordinative reactivity of platinum(0) triphenylphosphine complexes. Our investigation on this material has shown that it is a very reactive species and confirms some earlier[8] and more recent[9] kinetic data on the existence in solution and reactivity of the highly unsaturated monomeric compound bistriphenylphosphineplatinum(0).

Results

Attempted syntheses of bistriphenylphosphineplatinum(0). Bistriphenylphosphineplatinum(0), $Pt(PPh_3)_2$, is always in equilibrium in solution with $Pt(PPh_3)_3$[7] or $Pt(PPh_3)_2(CH_2=CH_2)$[5] and recently the dissociation equilibrium constants of these two complexes have been reported.[9]

It follows that one method of synthesis of $Pt(PPh_3)_2$ could be that of shifting the above equilibrium by removing the ligand L from $Pt(PPh_2)_2L$. When L is volatile, as in the case of the ethylene complex, this can be slowly achieved by bubbling a stream of an inert gas into an n-hexane suspension of the ethylene adduct for several hours. Using commercial nitrogen, ethylene is slowly displaced but the solid turns' to a red material corresponding to the already known cluster $[Pt(PPh_3)_2]_3$[10] which has a completely different chemical behaviour.

It seems that the probably monomeric species $Pt(PPh_3)_2$ trimerizes on standing in the presence of oxygen. In fact with very pure nitrogen only a pale yellow material is obtained. However, as the ethylene evolution is very slow, it is rather difficult to obtain a sample which is not contaminated with the starting material.

A different method involves the oxidation of the excess of triphenylphosphine, although the method would be complicated by the simultaneous oxidation of $Pt(PPh_3)_2$ to $Pt(PPh_3)_2O_2$. However in some preparations of $Pt(PPh_3)_3$ to the air by the following method:

$$[PtH(PPh_3)_3]HSO_4 + KOH \xrightarrow{\text{ethanol}} Pt(PPh_3)_3 + KHSO_4 + H_2O$$

(*) Note I and II of this series must be considered references 3 and 4 respectively.

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(2) L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, *84*, 4970 (1962); L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, *83*, 2784 (1961).

(3) P. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, *5*, 1120 (1966).

(4) F. Cariati and R. Ugo, *Chimica e Industria*, *48*, 1288 (1966).

(5) C. D. Cook and G. S. Jauhal, *Canad. J. Chem.*, *45*, 301 (1967); *Inorg. Nuclear Chem. Letters*, *3*, 31 (1967); *J. Amer. Chem. Soc.*, *90*, 1464 (1968).

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(7) R. Ugo, F. Cariati, and G. La Monica, *Chem. Comm.*, 868 (1966).

(8) A. D. Allen and C. D. Cook, *Canad. J. Chem.*, *42*, 1063 (1964).

(9) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, *90*, 4491 (1968).

(10) R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Comm.*, 869 (1966).

an insoluble yellow powder which analysed between $Pt(PPh_3)_3$ and $Pt(PPh_3)_2$ separated quickly. This powder did not show any distinctive absorption in the infrared spectrum in the region 800-900 cm^{-1} which could be ascribed to the presence of the $Pt(PPh_3)_2O_2$ species and a variable amount of phosphine oxide was always recovered from the ethanol solution. Better analysis and a greater amount of phosphine oxide were obtained by bubbling oxygen during the addition of KOH so that probably a reduction by KOH and ethanol of $Pt(PPh_3)_2O_2$ to $Pt(PPh_3)_2$ occurred. However, preformed $Pt(PPh_3)_2O_2$ did not react easily at room temperature with alcoholic KOH and only in boiling ethanol did it quickly transform into a brown material, probably a platinum(0) cluster.[10] This confirmed that $Pt(PPh_3)_2$, when in solution, has the tendency to form clusters in the presence of oxygen and it can be used mainly *in situ*, as discovered by Cook and Jauhal.[5] In fact the yellow material, obtained by us, turned slowly red-brown on standing for some hours in ethanol suspension and in the presence of oxygen.

Carrying out the above reaction in the presence of calculated quantities of H_2O_2 a similar material was obtained. Also in this case triphenylphosphine oxide was found in the ethanol and the isolated yellow powder did not show in its infrared spectrum any absorptiosn which could be assigned to ν_{OH} or ν_{O-O}. The same powder was obtained by allowing a suspension of $Pt(PPh_3)_3$ in ethanol with H_2O_2 to stand for a few minutes. In this case, increasing the reaction time ,a more complex reaction took place and a clear pale-yellow solution was obtained.[11]

A third method of synthesis could be that of removing HX from *trans*–$PtHX(PPh_3)_2$.[3] This reaction takes place easily with KOH in the presence of an excess of PPh_3, when X=Cl, Br *etc.*, but the product is $Pt(PPh_3)_3$. The excess of triphenylphosphine is necessary in order to form an ionic hydride species which can be easily deprotonated.[3] However, with X = CN it is possible, without an excess of PPh_3, to obtain a clear yellow ethanolic solution from a suspension of $PtHCN(PPh_3)_2$ just by addition of excess KOH at about 60°C. After slight concentration a mixture of platinum(0) and the starting hydrido platinum(II) compounds was obtained; in some preparations, however, a yellow compound, which analysed as $Pt(PPh_3)_3$, separated. HX can be removed in a cleaner way by addition of n-butyllithium to a dry hexane suspension of $PtHCl(PPh_3)_2$ at about –10°C; a yellow powder, which after washing with acetone, analyses correctly as $Pt(PPh_3)_2$, was obtained. The infrared spectrum and the reactivity of this product (see later) have confirmed that it is a zerovalent platinum species.

Further, the characterisation of this material as $Pt(PPh_3)_2$ is not only based on analytical data, but also on its easy reaction with ethylene to form $Pt(PPh_3)_2(C_2H_4)$. This reaction, in fact, does not take place (see later) in the presence of free phosphine (for instance with $Pt(PPh_3)_3$). We think that the reaction with ethylene is the most characteristic of the probable coordinatively unsaturated species $Pt(PPh_3)_2$.

Reactivity of bistriphenylphosphineplatinum(0). As we have already reported[7] $Pt(PPh_3)_2$ reacts easily with with small molecules such as HCl, CH_3J, C_2H_2, C_2H_4, O_2, CO giving place to adducts, some of which are already known; however the reactivity is rather different with different molecules. While the reaction with HCl and CH_3J also proceeds in the presence of an excess of triphenylphosphine[3,12] the reaction with acetylene, ethylene, and carbon monoxide is greatly affected by the presence of free triphenylphosphine. Indeed the position of the equilibrium:

$$Pt(PPh_3)_2L + PPh_3 \rightleftharpoons Pt(PPh_3)_3 + L$$

$(L = C_2H_2,\ C_2H_4)$

is different with ethylene or acetylene.

Ethylene is weakly bound and it is impossible to isolate the ethylene adduct from $Pt(PPh_3)_3$ solutions or suspensions even in the presence of an excess of ethylene. On the other hand a cream acetylene adduct is easily obtained from $Pt(PPh_3)_3$ solutions, that is from $Pt(PPh_3)_2$ doped with PPh_3. It follows that acetylene is more strongly bound than ethylene to $Pt(PPh_3)_2$. The kinetic behaviour of the ethylene and acetylene adducts is also rather different. The presence in solution of a small quantity of free triphenylphosphine changes the p.m.r. spectrum of the ethylene coordinated to platinum, which is a well defined broad singlet with satellites due to the coupling with ^{195}Pt, into a very broad absorption. This behaviour, which can be explained by a fast exchange between the free and coordinated ethylene, appears only in the presence of free phosphine; with an excess of ethylene but without an excess of phosphine two distinct signals were always detected.

The acetylene adduct is less labile, and in the presence of excess phosphine the signal of free acetylene is a sharp peak at $\tau = 8.15$ (the signal of the coordinated acetylene being probably under the phenyl signals).[13] It follows that the exchange of the acetylenic moiety is not so rapid in these conditions as that of the ethylenic one.

The carbon monoxide and oxygen adducts are very stable; $Pt(PPh_3)_2O_2$ can be also obtained from solutions of either tristriphenylphosphineplatinum(0) or bistriphenylphosphineplatinum(0) adducts with ethylene and acetylene. The oxygen molecule, as was found by other authors,[5,14] is irreversibly coordinated and can be only slowly released, with decomposition, between 90 and 110°C. The reaction with carbon monoxide, which we have already briefly investigated in the heterogeneous phase,[4], takes place either with tristriphenylphosphineplatinum(0) or with bistriphenylphosphineplatinum(0) or related adducts with ethylene or acetylene. By following the reaction using infrared spectroscopy, it is possible to show that with tristriphenylphosphineplatinum(O) the first compound formed in solution is $Pt(PPh_3)_2CO$* the presence in solution of free triphenylphosphine makes the formation of $Pt(PPh_3)_2(CO)_2$[4] more difficult, the

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[11] R. Ugo and G. La Monica, unpublished results.

(*) Carrying out the reaction in heterogeneous phase $Pt(PPh_3)_3CO$ is obtained, however this compound dissociates completely in solution in to $Pt(PPh_3)_2CO$ and free phosphine.[4].

[12] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[13] C. D. Cook, personal communication.

[14] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 6, 92 (1967).

product slowly appearing. The second molecule of carbon monoxide is very labile and in the presence of free phosphine this second molecule can be released by merely bubbling nitrogen through the solution.

The first carbon monoxide molecule is more strongly held to the platinum atom and can only be slowly released, in a nitrogen atmosphere, by boiling in benzene. With a material analysing as bistriphenylphosphineplatinum(0) or with the related ethylene or acetylene adducts, $Pt(PPh_3)_2(CO)_2$ is easily formed. On bubbling nitrogen through this solution an irreversible transformation into carbonyl cluster compounds of platinum(0)[15] takes place.

Hydrogen seems to be rather inert towards zerovalent platinum phosphine complexes.[16] Bubbling hydrogen through a $CHCl_3$ solution of $Pt(PPh_3)_2(C_2H_4)$, a pale-yellow mixture, which analyses approximately for $Pt(PPh_3)_2$, is obtained. The mixture shows weak absorptions at 2257 cm^{-1} and at 858 cm^{-1} which could due to ν_{Pt-H} and δ_{Pt-H} respectively. In $CDCl_3$ a very weak triplet at $\tau = 26.3$ ($J_{^{31}P-^{1}H} = 13.5$ c.p.s.) appears in the p.m.r. spectrum; this signal however corresponds to some *trans*–$PtHCl(PPh_3)_2$ which is probably formed in the solution. In fact this signal did not appear when the solvent (chloroform) was not stabilised with alcohol. This suggests that a weak interaction takes place between H_2 and triphenylphosphine zerovalent platinum complexes. A weak interaction is also suggested by the recent discovery that the *ortho* hydrogens of the phosphine ligands in platinum(0) triphenylphosphine compounds exchange with gaseous deuterium.[17]

Discussion and conclusions.

The relative chemical stability of bistriphenylphosphineplatinum(0) adducts is clearly related to the equilibrium

$$Pt(PPh_3)_2L \leftrightarrows Pt(PPh_3)_2 + L \qquad L = O_2,\ CO,\ C_2H_4,\ etc.$$

The exchange reactions of the ligand L always proceed a dissociative mechanism[8,18] in the case of d^{10} zerovalent complexes. The order of stability, obtained by displacement reactions and taking into account properties of SO_2 adducts described by other authors,[19] is roughly as follows:

$$O_2 > CO > SO_2 \gg CH\equiv CH \sim PPh_3 > CH_2=CH_2 \gg H_2 > N_2$$

which agrees fairly well with the known strength of chemisorption of group VIII metal surfaces,[20] while Vaska in his quantitative studies on similar adducts with Ir^{I} and Rh^{I} phosphine complexes has found that hydrogen does not coordinate as expected[21,22] in these complexes.

The interesting point here is that $Pt(PPh_3)_3$ can be really considered from many aspects of the above reported reactivity as $Pt(PPh_3)_2$ « poisonded » with phosphine. In many cases the presence of phosphine hinders the coordination of the small molecules or decreases greatly the stability of the adducts (as in the case of carbon monoxide, for instance). Such behaviour is very similar to that of metal surface which are poisoned by molecules with donor atoms like tertiary phosphines.[18]

Chemisorption and coordinative addition in transition metal complexes have very similar electronic processes. With this assumption a chemisorption centre on a metal surface must be considered, to a first approximation, as a localised monoatomic centre similar to a monomeric metal complex.[23,24] The rather good correlation between chemisorption and coordination, which was found by us in the case of platinum(0) complexes and by Vaska and coworkers in a more complete way for rhodium(I) and iridium(I) complexes,[21,22] seems to strongly support this assumption.

It has been proposed[1] that metal complexes with d^8 configurations should give place to more stable adducts* than complexes with a d^{10} configuration. On the contrary the bistriphenylphosphinoplatinum(0) adducts are more stable than the analogous adducts of Vaska's compound. Only by substituting chlorine with iodine in Vaska's compounds is it possible for instance to obtain an oxygen adduct which can be compared in stability with the related platinum(0) adduct. This fact confirms that care must be used in comparing the energy data of the gaseous ions or metals, because the ligands play an important role which cannot be easily defined when the complexes have different types and numbers of ligands and a different stereochemistry.[21,22]

Finally, it is interesting to consider the proposed similarity[25] between the reactivity of carbene R_2C: and the reactivity of $Pt(PPh_3)_2$ or similar low oxidation state complexes. This similarity, which has been found in many other carbenoid species,[26] is also supported by some methods of formation of several platinum complexes; in fact the withdrawl of HX from $PtHX(PPh_3)_2$ with alkoxides or with lithium alkyls is similar to the formation of $:CCl_2$ from $CHCl_3$ with alcoholic KOH[27] or of $:CHCl$ from CH_2Cl_2 with lithium alkyls.[28] There are, however, some important differences in reactivity between carbenes and low-valent metal complexes. For instance carbenes, and halocarbenes particularly, behave mainly as electrophilic species (for instance they show a preference for reactions with olefins containing electron-donating substituents[29]) while low oxidation state complexes behave more as nucleophilic species (for instance they show a preference for reactions with olefins containing electron-acceptor substituents[30]).

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[22] L. Vaska, *Accounts Chem. Res.*, *1*, 335 (1968).

(*) Stability is considered as stability to adducts dissociation.

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Dihalocarbenes are less reactive with acetylenes[31] than with olefins while low valent transition metal complexes behave in the reverse manner.[32] These facts suggest that the proposed similarity is more apparent than real.

Experimental Section

Starting materials were prepared as described in other papers.[3]

Melting points were determined on a Leitz Heitztischmikroskop and were not corrected. Analyses were carried out in the analytical laboratory of Milan University.

Infrared spectra were recorded using a Perkin-Elmer 621 (grating) spectrometer or a Perkin-Elmer 237 instrument. ^1H n.m.r. spectra were recorded in $CDCl_3$ using a Varian-100 instrument and a Perkin-Elmer R-10 instrument operating at 60 Mc, with tetramethylsilane as internal standard.

Attempted syntheses of bistriphenylphosphinoplatinum(0). A) A stream of dry and very pure nitrogen was bubbled through an ethanolic suspension (30 ml) of $Pt(PPh_3)_2(C_2H_4)$ (1 mmole) for several hours. The colour of the insoluble material changed from cream to pale yellow. The infrared spectrum of this material showed the presence of some of the unchanged starting complex.[5] The same results were obtained in n-hexane and other hydrocarbon solvents.

When the nitrogen was impure the colour of the solution and of the suspended material changed to brown-red, due to oxygen, and the insoluble complex had an i.r. spectrum and analysis similar to that of $[Pt(PPh_3)_2]_3$.[10]

B) Oxygen was bubbled through an ethanolic solution (30 ml) of $[Pt(PPh_3)_3H]HSO_4$ (2 mmoles) and an ethanolic solution of KOH (8 mmoles) was slowly added. A yellow compound separated quickly, it was filtered and washed with warm water followed by cold methanol and dried under vacuum for several hours. m.p. 150-160°C (dec). Found: C, 61.0; H ,4.42; P, 8.77; Pt, 27.17. M.W. 520 (benzene solution). Calcd. for $C_{36}H_{30}P_2Pt$: C, 60.3; H, 4.17; P, 8.62; Pt, 27.1; M.W. 719. $C_{54}H_{45}P_3Pt$ requires: C, 66.0; H, 4.59; P, 9.48; Pt, 19.8; M.W. 981.

C) H_2O_2 (120 vol) (0.05 ml) was added, with stirring, to an ethanolic solution (30 ml) of $[Pt(PPh_3)_3H]HSO_4$ (0.215 g). After a few minutes an ethanolic solution of KOH (0.032 g) was slowly added. A yellow compound precipitated; it was separated by filtration, washed with ethanol and warm water (until no sulphate ion was detected in the filtrate), finally with ethanol and dried under vacuum; yellow air-unstable crystals were obtained. m.p. 150-160°C (dec). Found: C, 60.51; H, 4.39; P, 8.75; Pt, 27.4.

This reaction was repeated several times under the same conditions and yellow materials were obtained (m.p. around 140 and 155°C) which analysed as follows: C, 64.29, 63.15, 65.61, 54.43; H, 4.36, 4.34, 4.66, 4.41.

D) H_2O_2 (120 vol) (2 ml) was added with stirring to a suspension of $Pt(PPh_3)_3$ (1 g) in ethanol (40 ml). After a few minutes the yellow compound was filtered, washed with ethanol followed by n-hexane and dried under vacuum. Found: C, 63.85, 63.34; H, 4.43, 4.55.

E) To a suspension of *trans*–$PtHCN(PPh_3)_2$ (0.2 mmoles), in absolute ethanol (15 ml), at room temperature an ethanolic solution of KOH (0.4 mmoles) was added, with stirring, under nitrogen. The temperature, was then rised to 65°C. A clear yellow solution was obtained. After a few minutes a yellow precipitate was formed. It was filtered washed with water, followed by ethanol and n-hexane and dried under vacuum. Found: C, 65.56, 65.43; H, 4.46, 4.40.

F) A solution of butyl lithium (3 mmoles) in n-hexane was added to a suspension of *trans*–$PtHCl(PPh_3)_2$ (1 mmole) in absolutely dry n-hexane (30 ml), mantained at –10°C with stirring under nitrogen. The suspended white solid became slowly yellow. After 60 minutes it was filtered, washed several times with n-hexane and then with methanol which dissolves an air-unstable by-product which contaminates the precipitate.

The methanolic solution became brown when the filtration was carried out in the open atmosphere. The yellow powder was washed with acetone, in order to remove the unreacted $PtHCl(PPh_3)_2$, and finally with n-hexane and then dried under vacuum (1 mm). Found: C, 61.5; H, 4.42; M.W., 440, 500 (benzene solution).

Reactivity of $Pt(PPh_3)_2$ towards C_2H_4, C_2H_2, O_2, CO. A) The material, prepared as described in F) (previous section) was suspended in ethanol (previously deoxygenated with a stream of C_2H_4) and C_2H_4 was bubbled through with stirring. After 15 minutes the yellow suspended solid became white. The compound was filtered and dried under vacuum. Its i.r. spectrum was identical to that of $Pt(PPh_3)_2(C_2H_4)$ prepared as described elsewhere.[5]

B) The interaction with C_2H_2 was carried out as described in A). The white-cream product was identical to $Pt(PPh_3)_2(C_2H_2)$ already described.[32]

C) The zerovalent platinum complex obtained as in F) (previous section) was dissolved in benzene and O_2 was bubbled through the solution for 10 minutes. A pale-cream compound precipitated. It was filtered and dried under vacuum. Its i.r. spectrum was identical to that of $Pt(PPh_3)_2O_2$.[5]

D) The zerovalent platinum complex obtained as in F) (previous section) was suspended in n-hexane and CO was bubbled through the solution with stirring. After a few minutes a white compound was collected by filtration; its i.r. spectrum was identical to that of $Pt(PPh_3)_2(CO)_2$.[4]

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(31) T. A. Dyakonow and L. Danilkina, *Zhur. Obshchei. Khim.*, *32*, 1008 (1962).

(32) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, *89*, 844 (1967); S. Cenini, R. Ugo, and G. LaMonica, *J. Chem. Soc. (A)*, following paper of this series.

Reactivtiy of $Pt(PPh_3)_2(C_2H_4)$ towards C_2H_2, CO, O_2, H_2. A) C_2H_2 wa bubbled through a xylene solution of $Pt(PPh_3)_2(C_2H_4)$. On cooling to −20°C and by adding petroleum ether a white-cream compound precipitated. Its i.r. spectrum was identical to that of $Pt(PPh_3)_2(C_2H_2)$.[32]

B) $Pt(PPh_3)_2(C_2H_4)$ was suspended in n-hexane and CO was bubbled through with stirring. After 30 minutes a white compound was collected by filtration; its i.r. spectrum was identical to that of $Pt(PPh_3)_2(CO)_2$.[4]

The same reaction was carried out in $CHCl_3$ solution. After a few minutes the i.r. spectrum showed the presence of $Pt(PPh_3)_2(CO)_2$.

C) $Pt(PPh_3)_2(C_2H_4)$ was dissolved in benzene and O_2 was bubbled through the solution. After 10 minutes a pale-cream compound precipitated. Its i.r. spectrum confirmed the formation of $Pt(PPh_3)_2O_2$.[5]

D) $Pt(PPh_3)_2(C_2H_4)$ suspended in degassed ethanol or dissolved in stabilised chloroform, was stirred under hydrogen (1 atm) at room temperature. After 3 hours a white solid material was recovered by filtration (ethanol) or evaporation to dryness (chloroform). The material was clearly a mixture of the starting complex and other products. It showed weak infrared absorptions at 2257 and 858 cm^{-1}. Attempts at recrystallisation were unsuccessful.

Reactivity of $Pt(PPh_3)_2(C_2H_2)$ towards O_2 and CO. The reactivity of $Pt(PPh_3)_2(C_2H_2)$ towards O_2 and CO gave the same products as were obtained by reacting $Pt(PPh_3)_2(C_2H_4)$ with the same molecules under the same experimental conditions. $Pt(PPh_3)_2(C_2H_2)$ did not react, in the same conditions, with ethylene and hydrogen.

Reactivity of $Pt(PPh_3)_3$ towards C_2H_4, C_2H_2, CO. A) $Pt(PPh_3)_3$ suspended in ethanol did not show any appreciable interaction with ethylene and the yellow starting material was recovered unreacted.

B) By bubbling acetylene through a saturated xylene solution of $Pt(PPh_3)_3$, the solution became pale-yellow. On cooling to −75°C a white-cream compound precipitated. It was collected and its i.r. spectrum was identical to that reported for $Pt(PPh_3)_2(C_2H_2)$.[33]

C) $Pt(PPh_3)_3$ was dissolved in pure chloroform and carbon monoxide was bubbled through the solution whilst the reaction was followed by infrared spectroscopy. The first material formed was $Pt(PPh_3)_2(CO)$[4] which changed quickly into $Pt(PPh_3)_2(CO)_2$.[4] Passing nitrogen through this final solution the spectrum reverted into that of $Pt(PPh_3)_2CO$, which corresponds to that of $Pt(PPh_3)_3(CO)$[4] in solution.

Acknowledgments. We wish to thank the Italian C.N.R. for financial support.

(33) C. D. Cook, personal communication.