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THE COORDINATIVE REACTIVITY OF PHOSPHINE COMPLEXES OF PLATINUM(0), PALLADIUM(0) AND NICKEL(0)

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CONTENTS

A. INTRODUCTION

During the last few years interest has turned to the investigation of the coordinative reactivity of small molecules to transition metal complexes in low oxidation states.

This approach is prompted by the attempt to rationalise the chemi-adsorption of molecules on the surfaces of transition metals in terms of coordination to the individual metal atoms which lie on the surfaces. This supposes that coordination and chemi-adsorption can be related by similar electronic interactions[1] and that the behaviour in solution of some metal complexes in low oxidation states is essentially that of solvated metal atoms.

In their pioneer work[2] Vaska and coworkers pointed out that some square planar complexes of Ir^I combine easily with molecules such as H_2, O_2, SO_2, H_2S etc. sometimes in a reversible way. More recently Wilkinson and coworkers[3] in the case of Rh^I complexes and Collman and coworkers[4] in the case of Ir^I and Ru^0 complexes suggested a variety of working models in an attempt to rationalise and to predict the coordinative chemistry of a d^8 configuration.

All the d^8 complexes which have been taken as models show the following general features: they are coordinatively unsaturated (or they can be transformed by dissociation in solution into unsaturated species) and have a variable number of "soft" ligands such as phosphines, arsines (sometimes together with carbon monoxide) bound to the metal. These "soft" ligands generate a ligand-field such that a very polarisable electronic density is directionally localized on the non-bonding or slightly bonding metal orbitals; the strength of the coordinative reactivity can be related to the availability of this electronic density[1].

B. ELECTRONIC PROPERTIES OF d^{10} ZEROVALENT DERIVATIVES

Recently it was shown that some complexes of Pt^0 and Pd^0 with phosphine and related ligands, synthezised by Malatesta and coworkers[5,6] in 1957–58, undergo many similar coordination reactions, while more recently it was found that phosphine and related complexes of Ni^0 behave in the same way.

These d^{10} systems, have a great tendency to stabilize coordinatively unsaturated species (sometimes even in the solid state) and, as a consequence of the phosphine ligands, should have a localized electronic density on the metal[7].

It is surprising that these d^{10} complexes have hardly been used as models of the active centers of transition metal surfaces.

Indeed it is much more reasonable to compare a metal atom on a metal surface with a neutral d^{10} atom than a formally positively charged d^8 atom (though in d^8 ruthenium(0) complexes the metal atom is neutral).

The Pt^0 and Pd^0 phosphine derivatives have been forgotten for nearly ten years. Their real nature had been called into question for some years, it being felt that these complexes could not be so stable because of the very high ionisation potential of gaseous platinum and palladium atoms.

Once it was demonstrated that Malatesta's complexes were true zerovalent derivatives[8] it was supposed that a d^{10} configuration was not particularly apt to coordinative reactions.

The coordination of a molecule to the transition metal can be considered, to a first approximation, as a charge-transfer from the molecule to the metal (σ bond) and from the metal to the molecule (π bond).

It is not yet completely clear which of the two processes is the more important in stabilising the bond between the coordinated molecule and the metal, however it seems that with "soft" coordinating molecules (molecules with one or more low lying excited states) the charge transfer from the metal to the molecule is very important[1]. If the ionisation potentials of gaseous Ni, Pd and Pt atoms in their d^{10} valence state[9,10] are taken into account, it follows that Pd and Pt complexes should not be apt to give place to a reasonable strong π interaction because of their very high ionisation potentials (nearly 8.3 eV). On the other hand nickel complexes, on account of their lower ionisation potential (5.8 eV), should display a greater coordinating power. This is not the case; although the nickel complexes do seem to react easier than their palladium and platinum homologous, the coordinative reactivity of nickel(0), palladium(0) and platinum(0) triphenylphosphine complexes is often very similar.

The use in an absolute way of the ionisation potentials of the gaseous metals or ions is often somewhat unreliable when the metals are in low oxidation complexes.

Indeed, in complexes of low oxidation state where the formal negative charge on the central metal atom in generally high, there is a decrease in the effective nuclear charge and a consequent decrease in the ionisation potentials.

The decrease should be similar for all three metals, so that Pt and Pd should still have a higher ionisation potential than Ni.

The presence of "soft" ligands" (such as phosphines or related ligands which generally stabilise low oxidation states) sinergically increases the "softness" of the metal atom[12] and consequently the availability of its electronic density for charge transfer to the coordinated molecule.

However "softness" has less to do with ionisation potentials than with electric polarizability and density of adjacent excited states.

It follows that, as pointed out by Nyholm[10], the use of promotion energies is more valuable than that of ionisation potentials.

Many authors[1,3,7,10] have pointed out that the coordinative reactivity can be related to a first approximation to the promotion of $(n-1)$ d electrons to np orbitals.

The promotion energies $(n-1)d^{10} \rightarrow (n-1)d^9\,np$ (Ni 1.72 eV, Pd 4.23 eV, Pt 3.28 eV)[10] are lower than the ionisation potentials $(n-1)d^{10} \rightarrow (n-1)d^9$ and are more reliably related to the energies involved in the coordination reactions.

It is clear now why a closed zerovalent d^{10} shell can act as a "soft" center towards coordinating molecules that is as the surface of a bulk metal. It is well known that bulk transition metals are typical "soft" centers because the metallic state involves a crowded distribution of states corresponding to the wave functions of the continuum.

C. SYNTHESIS AND GENERAL BEHAVIOUR OF Pt^0, Pd^0 AND Ni^0 PHOSPHINE COMPLEXES

Zerovalent derivatives of Pt^0 and Pd^0 with tertiary aromatic phosphines and related ligands were obtained in 1957–58 by reduction of Pt^{II} or Pd^{II} phosphine complexes with hydrazine, alcoholic KOH[5,6] or excess of phosphine.

In the same period, hydrido phosphine complexes of platinum(II) were obtained using the same reduction conditions[13]. This fact and the peculiar stabilities of the presumed zerovalent complexes to decomposition and oxidation led to the supposition that these compounds were in reality hydrido complexes of Pt^{II} with unusual coordination numbers[14].

Later many authors independently[8,15,16] demonstrated, without any doubt, that the compounds described by Malatesta and coworkers were true zerovalent compounds. However one problem was still unresolved. Why was it possible to obtain, using the same reduction conditions, different reaction products? Recently we have undertaken[17] systematic research in order to explain this point.

With triphenylphosphine complexes it is now clear that the first stage of the reduction is the formation of an hydrido complex of Pt^{II}; in the second stage the reducing agents, which incidentally are also strong bases, dehydrogenate the species.

$$\textit{cis}\ \mathrm{PtCl_2(PPh_3)_2} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{KOH}} \textit{trans}\ \mathrm{PtHCl(PPh_3)_2} \xrightarrow[\mathrm{PPh_3}]{\mathrm{KOH}} \mathrm{Pt(PPh_3)}_n$$

$$\textit{cis}\ \mathrm{PtCl_2(PPh_3)_2} \xrightarrow{\mathrm{N_2H_4}} \textit{cis}\ \text{and}\ \textit{trans}\ \mathrm{PtHCl(PPh_3)_2} \rightarrow$$

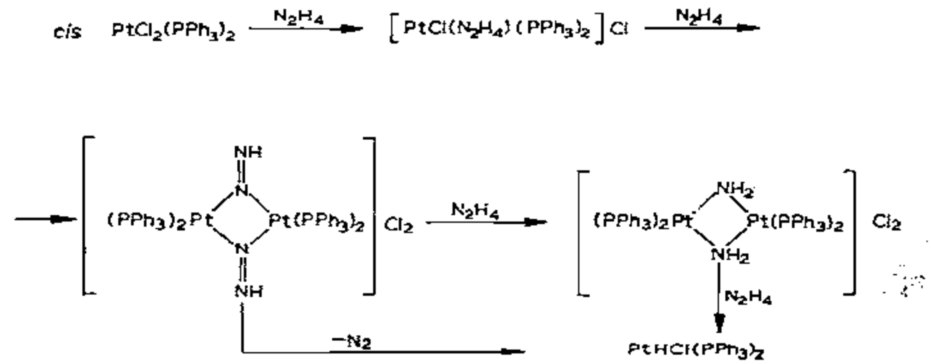
$$\xrightarrow[\mathrm{PPh_3}]{\mathrm{N_2H_4}} \mathrm{Pt(PPh_3)}_n \qquad (n = 3, 4)$$

It follows that isolation either of hydrido complexes of Pt^{II} or of complexes of Pt^0 depends not only on the temperature or the concentration of the reducing agents, but also on the reaction time. The nature of the tertiary phosphine plays a very important, though not completely understood role.

With the more basic phosphines it is very difficult to obtain zerovalent derivatives, while with the less basic phosphines (*e.g.* with tris-*p*-fluorophenylphosphine) it is possible to obtain very stable zerovalent complexes. The detailed mechanism of both types of reduction is complex. With KOH either the alcohol or the excess of phosphine can act as reducing agents while with hydrazine some interesting labile intermediates have recently been isolated[18]. It appears that the first stage of the reduction follow the scheme indicated below.

The corresponding nickel(0) complexes have been obtained by using different reducting agents such as trialkyl aluminium compounds[19], sodium tetrahydridoborate or sodium naphthalenide[20].

These methods of reduction are also suitable in the case of platinum or palladium compounds.



A new and useful method of obtaining zerovalent compounds, is the reaction of bis-π-allyl compounds with phosphine[21].

All the zerovalent compounds dissociate in solution giving place to coordinatively unsaturated species:

$$M(PR_3)_4 \rightleftharpoons M(PR_3)_3 \rightleftharpoons M(PR_3)_2 \rightleftharpoons [MPR_3]_n$$
$$(M = Ni, Pd, Pt)$$

Many stable tricoordinated species were isolated and described in the solid state (particularly with Pd and Pt).[5,6]. The dicoordinated species $M(PPh_3)_2$ was isolated only in the case of Pt[22].

However the existence, in solution, of palladium(0) and nickel(0) dicoordinated species is without doubt. The molecular weights found for the tri-coordinated and tetracoordinated species are much lower than the calculated values[6,23]. Very recently a compound of formula $Pd(PPh_3)_2$ has been reported[24] but little is known of its properties.

The existence of a monomeric monocoordinated species (which should be highly solvated) could be deduced from molecular weight measurements. A compound of formula $Pt(PPh_3)$ was recently described[25] but it is a cluster tetrameric molecule and does not dissociate in solution into a monomeric species.

The coordinative reactivity is attributed to the existence of coordinatively unsaturated species, such as bis(triphenylphosphine)platinum(0) which are, in solution, very reactive solvated centers.

The unusual stabilities of the coordinatively unsaturated species demonstrate that there is an excess of negative charge on the zerovalent metal. Indeed it appears that with a d^{10} configuration this negative charge is much better dissipated by π-back-donation to the ligands when the coordination number is low. Some authors claim that in a trigonal or linear coordination there are stronger π bonds than in a tetrahedral one[26]. However even without use of the π-back-donation hypothesis, which has been criticised in the case of phosphine complexes[27], the existence of an excess of negative charge on the zerovalent metals is clearly demonstrated by the small tendency of these complexes to increase their coordination sphere;

this could arise *via* an electrostatic repulsion of the σ electron pair of the entering ligands by the non-bonding electrons on the metal.

D. GENERAL FEATURES OF THE COORDINATIVE REACTIVITY OF ZEROVALENT d^{10} PHOSPHINE COMPLEXES

The coordinative reactivity, that is the addition of neutral molecules to low oxidation transition metal complexes like zerovalent d^{10} compounds, can be summarized by two types of reactions; the coordinative dissociation and the coordinative addition.

In the first case there is dissociation of the coordinating molecule with oxidation ($d^{10} \rightarrow d^8$) of the metal:

$$M(PPh_3)_2 + XY \rightleftharpoons M(PPh_3)_2(X)(Y) \qquad (M = Ni, Pd, Pt)$$

In the second case the coordinating molecule does not dissociate so that the formal oxidation state of the metal does not change:

$$M(PPh_3)_2 + XY \rightleftharpoons M(PPh_3)_2(XY) \qquad (M = Ni, Pd, Pt)$$

These reactions have similar electronic features[1]. The first step, the coordination of the entering molecule, requires a partially empty metal p or sp hybrid orbital which can interact with the entering molecule and form a σ bond. During this stage it is possible to transfer to the coordinating molecule some of the electronic density, which, as was pointed out above, is on the metal.

When the coordinating molecule has no antibonding orbitals of low enough energy (*e.g.* H_2, HCl, etc.) then dissociation takes place. The d electronic density of the metal is transferred to the more electronegative molecule (or atom).

This increase of electronic density (which in some way populates the antibonding orbitals of the coordinating molecule) favours the dissociation.

On the other hand addition takes place when the coordinated molecule has low lying antibonding orbitals, in this case the d electronic density of the metal can be transferred to the molecule *via* a π-mechanism.

The important electronic features which favour coordinative reactivity have been discussed in detail for the d^8 configuration[1]. The conclusions can be extended to the d^{10} configuration. The predominant electronic factor favouring coordinative reactivity, is the energy separation between the occupied slightly bonding $(n-1)d_{z^2}$ orbital and the empty np_z orbital.

This energy separation seems to be higher for a d^{10} configuration than for d^8. Indeed coordinative reactions have been described for metals in a d^8 configuration in which the metals are zerovalent [Ru^0 (ref. 4), Fe^0 (ref. 28)], monovalent [Co^I (ref. 29), Rh^I (ref. 3), Ir^I (ref. 2)] and bivalent [Pt^{II} (ref. 7)], while for metals in a d^{10} configuration only zerovalent metals (Ni^0, Pd^0, Pt^0) seem to be apt. Cu^I, Ag^I, and Au^I do not exhibit any evident addition reactions.

Owing to the increase of the $(n-1)d_{z^2} \rightarrow np_z$ energy gap with increasing formal charge on the metal, it is clear that the d^8 system is less sensitive than the d^{10} configuration to variation of the formal charge on the metal. This means that the promotion energy in Ru^0 or Fe^0 must be much lower than in Pt^0 or Ni^0. Unfortunately there are no data available for comparing a d^8 configuration with a d^{10} configuration; however it is possible to compare a d^9 configuration with a d^{10} configuration.

Indeed if the $d^9 \rightarrow d^8p$ or $d^{10} \rightarrow d^9p$ promotion energies[9,10] are considered, we have the following values (in eV):

	Co^0	Ni^I	Cu^{II}
$d^9 \rightarrow d^8p$	0.85	2.90	6.01
	Pt^0	Au^I	Hg^{II}
$d^{10} \rightarrow d^9p$	3.28	7.83	12.8

It seems reasonable to conclude from this data that the promotion energies for +1 and +2 states of d^8 configuration ions will be fairly small.

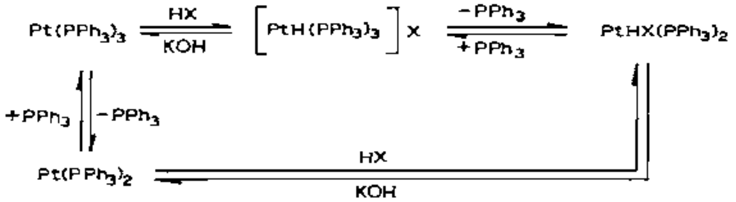
The coordinative reactivity of d^{10} Pt^0 systems has been extensively studied, but those of Ni^0 and Pd^0 have been somewhat neglected. This is because, unlike those of Pt^0, the starting materials and products involving Ni^0 and Pd^0 are generally unstable and air sensitive.

E. REACTIONS INVOLVING COORDINATIVE DISSOCIATION

(i) Reaction with acids

The interaction of inorganic acids with zerovalent d^{10} phosphine complexes[7] was the first reported example of a coordinative reaction of the dissociative type with d^{10} complexes.

Inorganic acids react with platinum(0)triphenylphosphine compounds in the following way:



Tris or bistriphenylphosphine derivatives both add, in a dissociative way, a molecule of an inorganic acid and yield hydrido complexes of platinum(II); ionic hydrido complexes can be isolated with $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$ when the anion X^- is not too nucleophilic, *i.e.* when $X^- = ClO_4^-, HSO_4^-, BF_4^-$, while nonionic *trans*-hydrido complexes are obtained when X = CN^-, NCS^-. With hydrogen chloride it is possible to isolate both ionic and covalent hydrido derivatives according to the reaction conditions; polar solvents favour the formation of the ionic hydride while non-polar or polarisable solvents favour the formation of the covalent hydride.

Only the covalent hydride is obtained with $Pt(PPh_3)_2$. The addition of acids is reversible; $Pt(PPh_3)_3$ can be quantitatively obtained by treating any ionic hydride with alcoholic KOH or NaOH under nitrogen. However $Pt(PPh_3)_2$ can only be obtained in reasonable yields from covalent hydrides[22] when X = CN^-.

Zerovalent palladium and nickel phosphine compounds react with acids, but no stable hydride formation was likely here. In every case hydrogen was slowly evolved. It is reasonable to suppose that in this case there is also a dissociative addition with formation of hydrido complexes which are known to be unstable thermally and also unstable towards excess of acids.

The mechanism of the reaction is probably as follows:

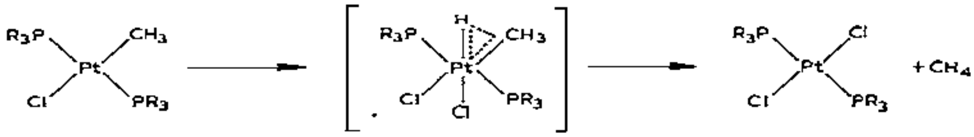
$$M(PPh_3)_3 + HX \rightleftharpoons MHX(PPh_3)_2 + $$
$$+ HX \rightleftharpoons [MH_2X_2(PPh_3)_2] \rightarrow H_2 + MX_2(PPh_3)_2$$

(M = Ni, Pd)

The formation, of a bishydrido tetravalent derivative can be supposed. In the case of platinum(II) hydrido complexes, a similar equilibrium reaction was found:

$$PtHCl(PPh_3)_2 \underset{-\,HCl}{\overset{+\,HCl}{\rightleftharpoons}} PtH_2Cl_2(PPh_3)_2$$

A recent kinetic investigation on the electrophilic reaction of carbon–metal bonded platinum complexes[30] confirmed the following mechanism:



It is not yet clear if the acid addition to $Pt(PPh_3)_2$ is *cis* or *trans*. From the reaction products only *trans* hydrido compounds were isolated. (Though sometimes traces of the *cis* species could be detectable in the infrared spectrum of the reaction mixtures.)

However, these results do not necessarily demonstrate that the addition is *trans* because it is known that the *cis* hydrido compounds isomerize very quickly in solution to the *trans* species[31].

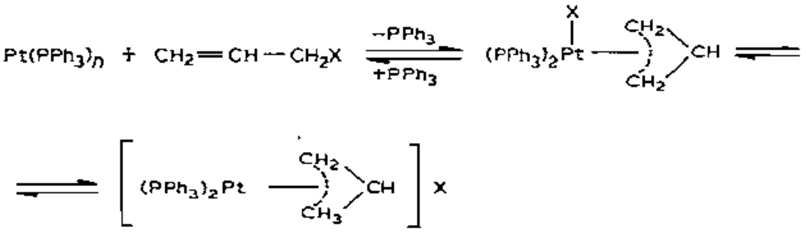
A *cis* addition is more likely since this would parallel similar reactions of d^8 complexes[3,32].

(ii) Reaction with alkyl halides

Methyl iodide reacts readily with $Pt(PPh_3)_n$ ($n = 2,3,4$) yielding the σ organometallic[22,23] compound $Pt(CH_3)I(PPh_3)_2$. This type of reaction can be extended to many alkyl halides[34] and is very useful for synthezising *cis* platinum(II) monoalkyl complexes.

For instance, by this method, it is easy to obtain[35] perfluoroalkyl derivatives of the type $Pt(R_F)I(PPh_3)_2$. Similar palladium derivatives can be obtained by reacting $Pd(PPh_3)_4$ with alkyl halides[36], but a *trans* stereochemistry was suggested for these compounds.

However the *trans* configuration of the palladium products does not illuminate the stereochemistry of the oxidative addition. The *cis* isomers are generally the less stable in the palladium series and isomerization is easy particularly in the presence of excess triphenylphosphine. More interesting are the reactions with allyl isothiocyanate and allyl halides[37]. In this case an oxidative addition also takes place, but π-allyl compounds of Pt^{II} are obtained:



$n = 2,3$; $X = SCN^-$, C^- , Br^-

The i.r. evidence confirms that the reaction products, in the solid state, are pentacoordinated π-allyl complexes; the absence of absorption in the region *ca.* 1610 cm^{-1} (in Nujol mull) suggests that the allyl group is not σ-bonded. The presence of absorption at 2047 cm^{-1} (when $X = NCS$) (which can be attributed to a coordinated SCN^- anion) and at 265 cm^{-1} (when $X = Cl$) (which can be attributed to ν Pt-Cl), confirms the formal pentacoordination of the platinum atom. This coordination persists in some solvents but in others such as nitrobenzene the compounds dissociate into square planar ionic species which are still π-allyl complexes.

At low temperature, the n.m.r. spectrum in $CDCl_3$ is consistent with a π-allyl complex, although the spectrum at room temperature indicated rapid exchange of the *syn* and *anti* protons[38].

The addition of methallylchloride to $Pd(PPh_3)_4$ yields a compound of special interest[36] of formula $PdCl(C_4H_7)(PPh_3)_2$. This compound shows a Pd-Cl stretching frequency at 282 cm^{-1}. The n.m.r. spectrum in $CDCl_3$ does not show any coupling between the allylic protons and the phosphorous nuclei. The integration of the singlets at 3.62 (4 protons) and 1.88 p.p.m. (3 protons) and the absence of coupling is consistent with a σ-bonded methallylic ligand undergoing rapid isomerisation as follows:

(iii) Reaction with acyl, aroyl and sulfonyl halides

Addition of slight excess of acyl or aroyl chloride to a benzene solution of $Pt(PPh_3)_3$ or $Pt(PPh_3)_2$ results in the following addition reaction[34,37]:

$$Pt(PPh_3)_n + RCOCl \rightarrow Pt(COR)Cl(PPh_3)_2 + (n-2)PPh_3$$
$(R = Ph, CH_3)$

The acyl and aroyl complexes are stable, both thermally and to air oxidation, and in the region around 1610–1650 cm^{-1} show i.r. absorption characteristic of the C=O group. They can be smoothly decarbonylated and this behaviour is a strong indication that the acyl derivative is a *cis* isomer.

Indeed the greater lability of the *cis* compared with the *trans* derivatives is to be expected if strict reversibility of the carbonylation reaction is assumed; *trans* $Pt^{I}CH_3(PPh_3)_2$ does not carbonylate at all.

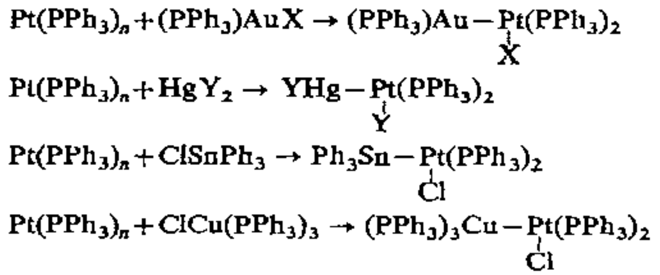
Sulphonyl halides also add smoothly to $Pt(PPh_3)_n$ (n = 2,3,4). The following scheme illustrates two procedures which permit alkyl and aryl groups to be bonded to platinum:

$$\begin{tikzcd}
 & PtCl(COR)(PPh_3)_2 \arrow[r, "heat", "-CO"'] & PtCl(R)(PPh_3)_2 \\
Pt(PPh_3)_n \arrow[ur, "RCOCl"] \arrow[dr, "R'SO_2Cl"'] & & \\
 & PtCl(SO_2R')PPh_3)_2 \arrow[r, "heat", "-SO_2"'] & PtCl(R')(PPh_3)_2
\end{tikzcd}$$

The addition of acetyl chloride to $Pd(PPh_3)_4$ yielding *trans* $PdCl(COCH_3)(PPH_3)_2$ has been recently reported[36].

(iv) Reaction with metal halide derivatives

A convenient method for the preparation of covalent metal–metal bonds between a transition metal and a post-transition metal involves the reaction of a complex of the former metal in a low oxidation state with a halide derivative of the post-transition metal (*e.g.*, $(PPh_3)AuCl$ or $HgCl_2$.) Compounds having covalent Pt-Au, Pt-Hg, Pt-Sn and Pt-Cu have been obtained by this method[39]. Triphenylphosphine platinum(0) complexes react as follows:



$$\mathrm{Pt(PPh_3)_n + (PPh_3)AuX \rightarrow (PPh_3)Au-\underset{\underset{\displaystyle X}{|}}{Pt}(PPh_3)_2}$$

$$\mathrm{Pt(PPh_3)_n + HgY_2 \rightarrow YHg-\underset{\underset{\displaystyle Y}{|}}{Pt}(PPh_3)_2}$$

$$\mathrm{Pt(PPh_3)_n + ClSnPh_3 \rightarrow Ph_3Sn-\underset{\underset{\displaystyle Cl}{|}}{Pt}(PPh_3)_2}$$

$$\mathrm{Pt(PPh_3)_n + ClCu(PPh_3)_3 \rightarrow (PPh_3)_3Cu-\underset{\underset{\displaystyle Cl}{|}}{Pt}(PPh_3)_2}$$

$X = Cl, Br; Y = Cl, I; n = 2,3,4.$

However, though this type of oxidative addition is very easy, metal–metal bonds are not always formed. For example with R_3SiCl or R_3PbCl, only $Pt(PPh_3)_2Cl_2$ was obtained[40].

Through the same type of reaction it is possible to prepare compounds with Pt-Pt and Pt-Ni bonds *e.g.* by treating $Pt(PPh_3)_n$ with $Pt(PPh_3)_2I_2$ and $Ni(PPh_3)_2I_2$ respectively[39].

F. REACTIONS INVOLVING COORDINATIVE ADDITION

(i) Reaction with olefins

Olefins add to coordinatively unsaturated zerovalent platinum(0) and nickel(0) phosphine complexes $M(PPh_3)_2$ yielding compounds of formula $[M(PPh_3)_2(\text{olefin})]$ (M = Pt, Ni) as follows:

$$M(PPh_3)_2 + \text{Olefin} \rightleftharpoons M(PPh_3)_2(\text{Olefin})$$

With activated olefins such as tetracyanoethylene[41], tetrachloroethylene[42] or perfluoroolefins[35] it is possible to obtain stable complexes from $Pt(PPh_3)_4$ or $Pt(PPh_3)_3$ *i.e.* in the presence of an excess of phosphine.

In this case it is clear that the equilibrium

$$Pt(PPh_3)_n + \text{olefin} \rightleftharpoons Pt(PPh_3)_2(\text{olefin}) + (n-2)PPh_3$$

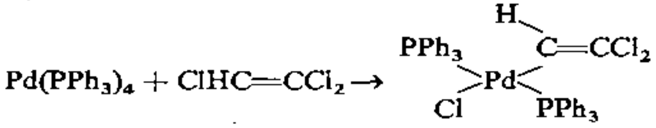
is completely shifted to the right side.

A tetrafluoroethylene complex of nickel was similarly obtained[43] from $Ni(PPh_3)_4$.

With less activated olefins, such as acrylonitrile or maleic anhydride[44] or with completely non-activated olefins[45] such as ethylene it is better and sometimes necessary to use coordinatively unsaturated species such as $Pt(PPh_3)_2$.

These species can be prepared sometimes "*in situ*" (as in the case of ethylene platinum or nickel complexes.) Examples of coordinative addition of activated olefins to phosphine palladium(0) complexes, have been recently reported[47].

The olefin palladium complexes seem to be very similar to related platinum complexes, however with perchloro-olefins a dissociative reaction takes place and σ vinyl compounds are obtained:



$$Pd(PPh_3)_4 + ClHC{=}CCl_2 \rightarrow \underset{Cl}{\overset{PPh_3}{>}}Pd\underset{PPh_3}{\overset{C(H){=}CCl_2}{<}}$$

In the case of platinum similar behaviour was found only with a perfluorochloro-olefin[35].

It is interesting to point out that in the case of the ethylene platinum compound and probably also of the nickel one, the exchange reaction

$$M(PPh_3)_3 + \text{olefin} \rightleftharpoons M(PPh_3)_2(\text{olefin}) + PPh_3 \qquad (M = Pt, Ni)$$

is fast[41].

Indeed by bubbling ethylene into a benzene solution of a mixture of $Pt(PPh_3)_2$ and $Pt(PPh_3)_3$ it is not possible to isolate any pure ethylene complex. The n.m.r. spectrum of this solution at room temperature shows a very broad signal due to the ethylenic protons with a chemical shift which is dependent on olefin concentration and the temperature. This behaviour is typical of a very fast exchange of the olefin with another ligand.

The easy dissociation of the coordinated olefin is confirmed by determination of the molecular weight of the species $Pt(PPh_3)_2$(olefin). When the olefin is stilbene or styrene, the values observed are much lower than those calculated[40]. However, with more activated olefins dissociation was not detected[44].

All this data confirms that the interaction between the zerovalent metal and the olefin is much easier when the olefin is activated by electro-negative groups, that is when there is a low energy antibonding orbital present.

There are two ways of viewing the metal–olefin bonding: the first considers the olefin as a di-carbanion functioning as a bidentate ligand with two σ-bonds to the platinum (which should therefore be platinum(II)) such that a three-membered ring ("platinacyclopropane" structure) (Fig. 1) is extant.

Some physical evidence supports this view. The C—C stretching frequency shifts more than the usual 100–150 cm^{-1} observed in typical olefin complexes and no infrared absorption corresponding to a coordinated double bond is observed.

Moreover, in some perfluoroolefin complexes[35] (Fig. 2) two important points emerge from the ^{19}F n.m.r. spectra. When $X = CF_3$ there are four groups of bands centered at 66.5, 107.1, 120.2 and 200 p.p.m. (relative to CCl_3F, increasing to high field) with a geminal F,F coupling constant of 200 c/sec. This value is of the order observed in saturated fluorocarbons.

When $X = F$ the spectrum of the complex shows the spectrum of an $AA'X_2X'_2$ system centered at 131.1 p.p.m. Similar data were obtained in perfluoroolefin nickel complexes[43]. The spectra are field and temperature invariant.

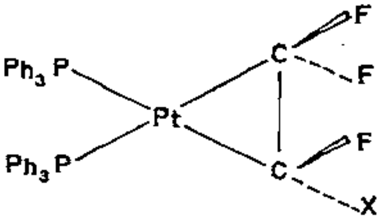


Fig. 1. The "platinacyclopropane" structure.

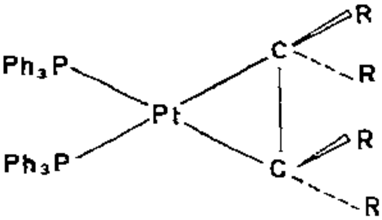
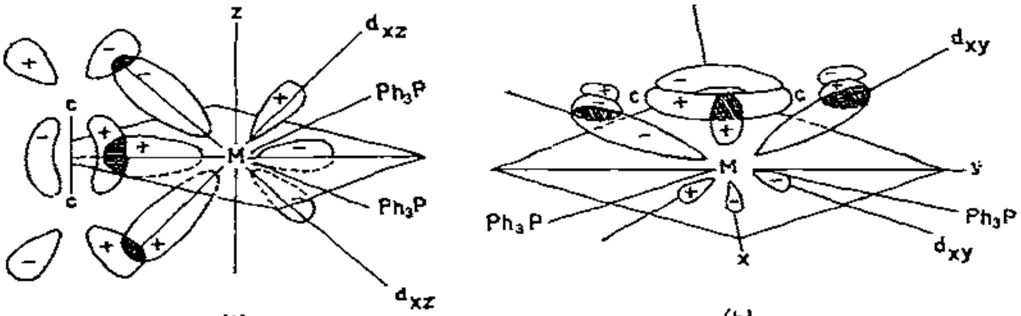


Fig. 2. The perfluoroolefin-platinum(0) complexes.

These observations are consistent with a rigid square-planar three membered ring.

However, the bonding may alternatively be interpreted in the context of the Dewar–Chatt–Duncanson model of metal–olefin bonding[48].

The compounds could be trigonal complexes of zerovalent metals with the olefin occupying one coordination position and bound in a manner similar to ethylene in Zeise's salt (Fig. 3). The electrons of the π bonding orbital of the ethylenic ligand are donated into a sp^2 hydrid orbital of the metal to form a σ bond with simultaneous back donation from the filled (case (a)) d_{xz} (or d_{xz}, p_z hydrid) or from the filled (case (b)) d_{xy} orbitals of the metal to the π^* antibonding orbital of the olefin. In the case (a) the π back-donation is perpendicular to the



(a) (b)

Fig. 3. The Dewar–Chatt–Duncanson model of metal–olefin bonding.

trigonal plane, while in the case (b) the π back-donation is in the plane. In-plane π bonding has recently been suggested as an explanation of the low barrier to rotation of coordinated ethylene in rhodium(I) complexes[49]. The Dewar–Chatt–Duncanson type of bonding is strongly suggested by the chemical behaviour of the complexes; the coordinated olefin has some tendency to dissociate, as does any π-bound olefin, and the most stable compounds of this class are formed when the olefin has a low lying π^* antibonding orbital, when the influence of π back-donation from the metal to the olefin is very apparent.

Such a picture of the bonding could also explain the unusual lowering of the νC=C frequency and the values of the F,F or H,H geminal coupling constants.

Indeed when π back-donation, in a Dewar–Chatt–Duncanson picture of the bonding, is very strong, the electronic density flows from the metal to the olefin, and the π^* antibonding orbital of the olefin becomes appreciably populated.

This process corresponds to a molecular geometry of the coordinated olefin very near to that of the first excited state[50]. The olefin molecule should no longer be planar and the carbon–carbon bond order would be reduced.

A recent X-ray structural investigation[51] supports this interpretation of the bonding quite well: the structure of the compound of formula $Pt(PPh_3)_2TCE$ (TCE = tetracyanoethylene) (Fig. 4) confirms that the bonding between the olefin and the platinum atom can be interpreted in the molecular orbital approach as a negligible σ olefin to metal bond and strong π metal to olefin bond.

The C=C distance is 1.54 Å, which is 0.23 Å longer than the same distance in tetracyanoethylene itself, and the olefin is no longer planar.

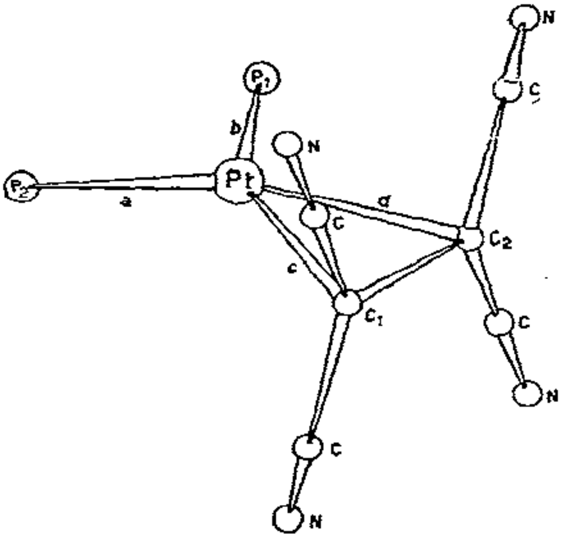


Fig. 4. The molecular structure of $Pt(PPh_3)_2TCE$
(a = 2.29 Å; b = 2.30 Å; c = 2.10 Å; d = 2.11 Å; e = 1.54 Å.
ab = 101°; cd = 42°; ac = 110°; bd = 104°).

It is noteworthy that the platinum coordination is not strictly planar, the dihedral angle between the planes P_1PtP_2 and C_1PtC_2 being 10°. This suggests that the bonding situation is between the case (a) and (b) of Fig. 3.

The source of this distortion is not yet clear but a similar dihedral angle of 12° was found in the structure of $Ni(PPh_3)_2$(ethylene)[52].

In the ethylene nickel(0) complex the $C=C$ distance is 1.46 ± 0.02 Å only 0.13 Å longer that in ethylene itself. These results are consistent with the above representation of the bonding; indeed back-donation from the metal must be lower in the ethylene complex which unlike tetracyanoethylene does not have a low enough lying π^* antibonding orbital. Incidentally this molecular orbital approach of the interaction of the zerovalent metal with the olefin (with a σ and π bond) is equivalent, mathematically, to two equivalent bent bonds[53]. However the molecular orbital approach is preferable because of its flexibility in treating intermediate cases where both olefin to metal σ bonding and metal to olefin π bonding are important in the overall bonding scheme.

The conclusion reached from the above discussion is that the acceptor properties of the olefins are more important than their donor properties in determining the strength of the interaction with metal. The metal acts as a base towards the olefin.

Following this point of view, it is reasonable to suppose that strong π acids should interact easily with phosphine zerovalent d^{10} compounds. Indeed quinones add easily to $Pt(PPh_3)_2$ or $Pt(PPh_3)_3$ yielding very stable compounds of formula $Pt(PPh_3)_2$(quinone)[54].

It is interesting that in these addition complexes the quinone moiety does not dissociate and that both double honds are involved in bonding with the platinum atom.

(ii) Reaction with alkynes

Alkynes add to zerovalent phosphine complexes more easily than olefins yielding compounds of formula $M(PPh_3)_2$(alkyne)[46,55,56] ($M = $ Ni, Pd, Pt). The metal–alkyne bonding is much more stable than metal–olefin bonding. Indeed ethylene, in common with all other olefins investigated thus far, is displaced from nickel(0) or platinum(0) phosphine complexes by treatment with alkynes.

The acetylenic moiety unlike the olefinic one does not exchange fast; by bubbling acetylene into a benzene solution of a mixture of $Pt(PPh_3)_2$ and $Pt(PPh_3)_3$ it is possible to isolate the acetylene complex (which however disappears if nitrogen is passed through the solution).

The n.m.r. spectrum of this solution shows two well separated signals; the one at higher field can be assigned to the free acetylene, while the other at lower field to the coordinated hydrocarbon. This confirms that the exchange is slow.

The exchange reaction between two different alkynes has been kinetically investigated and the following dissociative mechanism was proposed[57]:

$$\mathrm{Pt(PPh_3)_2(alkyne} \xrightleftharpoons[\text{slow}]{-\text{alkyne}} \mathrm{Pt(PPh_3)_2} \xrightleftharpoons[\text{fast}]{+\text{alkyne*}} \mathrm{Pt(PPh_3)_2(alkyne^*)}$$

(alkyne = $p\mathrm{RC_6H_4C_2H}$)

It was found that the reaction rate decreases as the electron-withdrawing power of the R groups in *para* position increases. It follows that, as in the case of the olefin complexes, the metal–alkyne bonding is stronger when electronegative groups are bound to the acetylenic group. Therefore in metal–alkyne bonding, π back-donation from the metal to the π^* antibonding system of the alkyne ligand is also a very important electronic factor.

The recent X-ray investigation[58] of the structure of bis(triphenylphosphine)-diphenylacetylene platinum(0) (Fig. 5) confirms that considerable electronic density is localized on the π^* antibonding orbital of the acetylenic moiety. The benzene rings of the alkyne are bent at angles of 40° from linear (that is with a C—C—Ph bond angle averaging 140°) and the carbon–carbon distance is 1.32 ± 0.09 Å. Very recently Mason[50] pointed out that this geometry is very similar to that of a *cis*-bent excited state of acetylene which has a bond angle of 142° and a carbon–carbon length of 1.38 Å. This confirms that the wave function describing the metal–alkyne bonding in these complexes will contain functions representing *excited* states of both the metal and the alkyne. In this structure there is a dihedral angle of 14° between the PPtP and the CPtC planes.

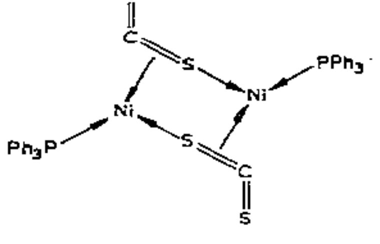
(iii) Reaction with $>\!C{=}S$ and $>\!C{=}O$ bonds

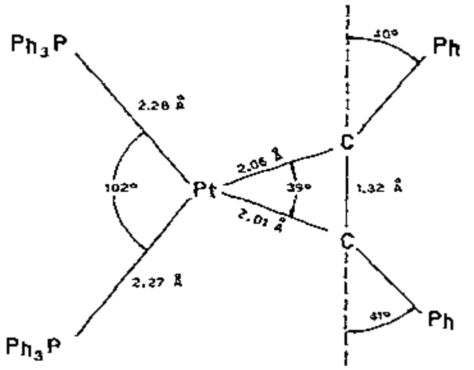
When a suspension of $\mathrm{Pt(PPh_3)_3}$ or $\mathrm{Pt(PPh_3)_2}$ in refluxing diethylether is treated with carbon disulphide an addition compound is formed[59]:

$$\mathrm{Pt(PPh_3)_n + CS_2 \rightarrow Pt(PPh_3)_2CS_2 + (n-2)PPh_3}$$

The strong C=S stretching frequency at 1157 cm^{-1} suggests a π interaction of one C=S bond with the platinum atom; an X-ray investigation[60] confirms this suggestion (Fig. 6), A similar palladium compound is obtained from $\mathrm{Pd(PPh_3)_4}$, while a nickel compound of formula $\mathrm{Ni(PPh_3)CS_2}$ is obtained by reacting $\mathrm{Ni(CO)_2(PPh_3)_2}$ with $\mathrm{CS_2}$.

The structure of this compound, which is dimeric in chloroform, could be the following:





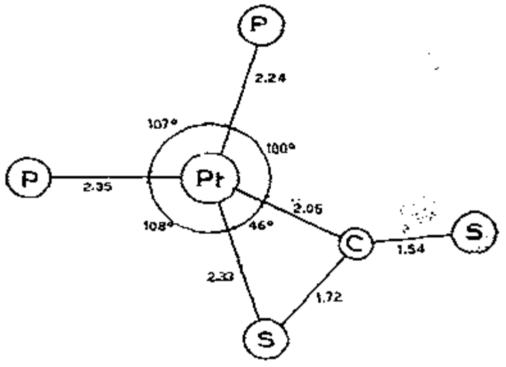
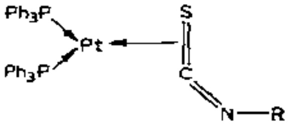


Fig. 5. The molecular structure of $Pt(PPh_3)_2(Ph{-}C{\equiv}C{-}Ph)$.

Fig. 6. The molecular structure of $Pt(PPh_3)_2CS_2$.

Structurally related platinum "π addition complexes" are obtained from carbonylsulphide (where the C=S bond is interacting with the platinum atom) and alkyl and aryl isothiocyanates.

By analogy with the structure of the carbon disulphide complexes the isothiocyanate group is presumably π-coordinated through the C=S bond as follows:

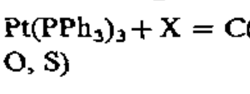


In support of this structure the infrared spectra in CH_2Cl_2 solution have rather broad bands centered at 1643 cm^{-1} (R = Ph) and at 1653 cm^{-1} ($R = CH_3$) which can be attributed to $\nu_{C=N}$.

Perfluorothioacetone[59] and perfluoroacetone[35] react with $Pt(PPh_3)_3$ giving place to interesting addition compounds:

$$Pt(PPh_3)_3 + X = C(CF_3)_2 \rightarrow Pt(PPh_3)_2(CF_3)_2C{=}X$$
(X = O, S)

Both compounds appear to be π-bound to the platinum atom through the C=S and C=O bonds as follows:



X = O, S

The infrared spectra of these complexes do not show bands assignable to the free C=X bond. Moreover, the ^{19}F n.m.r. spectra show a triplet of doublets centered at 55.8 p.p.m. ($X = S$) and at 67.8 p.p.m. ($X = O$). The complexity of the ^{19}F n.m.r. spectra is due to coupling with ^{195}Pt ($J\ ^{195}Pt-^{19}F = 71.5$ c/sec ($X{=}O$) and 39.0 c/sec ($X = S$)) and with ^{31}P.

This coupling confirms that the carbon atom of the $>C = X$ bond is directly bound to the platinum atom.

The nature of the bonding between the zerovalent metal and the coordinated molecule is not very different from that in the olefin complexes. Indeed the structural analysis of $Pt(PPh_3)_2CS_2$ (Fig. 6) shows the carbon disulphide, whicb is π-bound to the platinum, to be non-linear, the S—C—S bond angle being 136°; the mean C—S bond length in the coordinated molecule is 1.63 Å.

The lowest excited state ($^3A_2$) of CS_2 is bent, the angle being 135° and the main C—S bond length 1.64 Å. These values are identical, within experimental error, to those found in the platinum complex and confirm that the electronic density of the metal populate the antibonding levels of the CS_2 molecule through a π back-donation mechanism.

This also explains why only the presence of electronegative CF_3 groups can activate the $>C{=}O$ bond.

In fact, owing to the higher electronegativity of the oxygen atom, the $>C{=}O$ bond is not polarisable enough, consequently there is not a low enough lying antibonding orbital.

Only the presence of electronegative groups can lower the energy of the antibonding orbital and increase the "softness" of the π system of the $>C{=}O$ bond.

(iv) Reaction with sulphur donor molecules

$Pt(PPh_3)_n$ ($n = 3,4$) reacts instantly with sulphur dioxide to give a dark purple addition product as follows:

$$Pt(PPh_3)_n + SO_2 \underset{\text{heat}}{\overset{C_6H_6}{\rightleftharpoons}} Pt(PPh_3)_xSO_2(C_6H_6)_{1\cdot 5} + (n{-}x)PPh_3$$

The exact formulation of this product is uncertain because the number of phosphine bound to the platinum atom is equal to three according to some authors[60,61], and two, according to others[39].*

This dark purple compound readily loses benzene on washing with diethyl ether and transforms itself into a more stable, benzene-free, red-brown compound.

On heating in vacuo at 100–120° this compound slowly loses sulphur dioxide to yield a triphenylphosphine-platinum(0) compound.

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* Recently a green air stable platinum sulphur dioxide adduct of formula $Pt(PPh_3)_2SO_2$ was obtained by the following reaction[62]:

$$Pt(PPh_3)_2(CH_2{=}CH_2) + SO_2 \rightarrow Pt(PPh_3)_2SO_2 + CH_2{=}CH_2.$$

$Pd(PPh_3)_4$ reacts in the same way with sulphur dioxide[61] affording a purple-red addition product of formula $Pd(PPh_3)_3SO_2$.

Both platinum and palladium sulphur dioxide complexes react with oxygen giving place to sulphato-complexes $M(SO)_4(PPh_3)_2$ (M = Pt, Pd). This reaction indirectly supports the view that catalytic oxidation of sulphur dioxide at platinum surfaces involves chemisorption of the gas on the metal.

It is reasonable to suppose that in these complexes the metal–sulphur dioxide coordination occurs through the sulphur atom, as was established for a similar Ir^I compound[63].

Indeed the infrared spectrum of the platinum–sulphur dioxide complex shows two bands at 1195 and 1045 cm^{-1}, which can be assigned, as in similar rhodium and iridium complexes[64], to the asymmetrical and symmetrical S=O stretching frequencies.

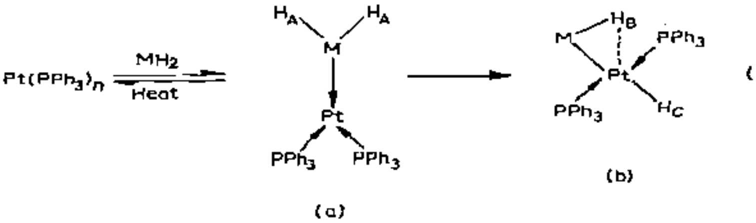
The addition reactions of molecules such as H_2S or H_2Se (which usually poison platinum surfaces) to $Pt(Ph_3)_2$ or $Pt(PPh_3)_3$[65] have been studied in order to find a model for the poison mechanism.

H_2S and H_2Se react with $Pt(PPh_3)_n$ (n = 2,3) in the following way:

$$Pt(PPh_3)_n + MH_2 \rightleftharpoons Pt(PPh_3)_2MH_2 + (n-2)PPh_3$$

(M = S, Se)

H n.m.r. studies in solution at different temperatures and infrared studies in the solid state suggest the following equilibria:



The complex (a) shows a broad low-field peak (which can be attributed to the H_A proton) which is temperature dependent. This signal lies at a lower field than the peak of pure MH_2.

The complex (b) shows two high-field (higher than tetramethylsilane) peaks which can be attributed to H_B and H_C protons respectively.

The chemical shift of the H_C proton (τ = 18.8 M=Se; τ = 19.2 M=S) has the normal high value for a σ-hydrido compound, while the H_B proton shows a peak at a lower field (τ = 14.2 M=Se; τ = 11.4 M=S). Its value seems to indicate that H_B is not a σ-bonded hydridic hydrogen. Indeed the coupling constant J ($^{195}Pt-H_B$) is unusually low showing that the platinum to hydrogen interaction is of a different type.

The coupling constant J($^{195}Pt-H_C$) has a normal high value typical for σ-hydrido compounds.

The complex (a) is formed first when MH_2 is bubbled into a degassed solution of $Pt(PPh_3)_2$ or $Pt(PPh_3)_3$, while the complex (b) is slowly formed subsequently. However by dissolving $Pt(PPh_3)_2$ or $Pt(PPh_3)_3$ in benzene previously saturated with MH_2 only the (b) complex is detectable.

It seems that the mechanism of interchange of the complexes (a) and (b), which on the grounds of the exchange with D_2O, is slow at room temperature, needs the presence of an excess of MH_2. The role played by this excess is not yet clear.

It is noteworthy that molecules like MH_2 first add to the metal atom and only later does the M—H bond dissociate.

It is possible that the poisoning mechanism of a platinum surface goes through this hydrogen abstraction of the MH_2 species bonded to the surface. The poisoning could then be due to the presence of species like Pt-MH or Pt-M formed on the surfaces and which are not reactive. To support this hypothesis we have studied the interaction of sulphur and selenium with $Pt(PPh_3)_n$ ($n = 2,3$) in our laboratory[66]. With sulphur a coordinative reaction takes place with the following stoichiometry:

$$m\mathrm{Pt(PPh_3)}_n + m\mathrm{S} \rightarrow [\mathrm{Pt(PPh_3)_2S}]_m + m(n-2)\mathrm{PPh_3}$$

The addition compound, which is probably dimeric, is very unreactive. It does not react with oxygen, carbon monoxide and similar related ligands.

However HCl reacts easily with the sulphur adduct in the following way:

$$[\mathrm{Pt(PPh_3)_2S}]_m + 2m\mathrm{HCl} \rightarrow mPt\mathrm{Cl_2(PPh_3)_2} + m\mathrm{H_2S}$$

Methyl iodide and allyl halides also react with the sulphur adduct yielding addition compounds which can often be obtained in two different forms. The two forms differ in the bonding of the alkyl moiety which can be bound to the platinum or to the sulphur.

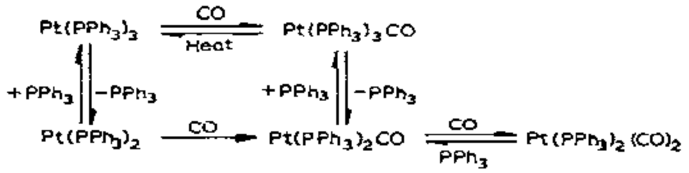
The coordinative addition of selenium to $Pt(PPh_3)_2$ has been briefly investigated. A rather unstable red compound of formula $Pt(PPh_3)_2Se$ has been isolated, but owing to its instability, its behaviour and reactivity have not been examined in detail.

Similar triphenylphosphine Ni^0 and Pd^0 H_2M or S adducts can be obtained but they are unstable.

(v) Reaction with carbon monoxide

The coordinative reactivity of carbon monoxide towards $Pt(PPh_3)_n$ ($n = 3,4$) species was first studied by Malatesta and Cariello[5]. Later[67] more detailed research was undertaken.

Carbon monoxide reacts with platinum(0) phosphine complexes according to the following scheme:



The addition of the second molecule of carbon monoxide is more difficult, particularly if free triphenylphosphine is present in the reaction mixture. $Pt(PPh_3)_2(CO)_2$ loses the second molecule of carbon monoxide when nitrogen is bubbled through the solution. On the other hand $Pt(PPh_3)_3CO$ only loses its coordinated carbon monoxide molecule on heating.

The species $Pt(PPh_3)_2CO$ seems to be more stable (although its formulation is not certain[68]) and this could be explained by a better π back-donation to carbon monoxide in a tricoordinated species than in a tetracoordinated one.

The relative instability, in these carbonyl complexes, of the coordinated carbon monoxide molecules, could be explained by assuming that the Pt—C bonds are weak because of poor π-back-donation. However the Pt—C and C=O stretchings frequencies (388 cm^{-1} and 1908 cm^{-1} respectively for $Pt(PPh_3)_3CO$ and 398,363 cm^{-1} and 1982,1950 cm^{-1} for $Pt(PPh_3)_2(CO)_2$ all in Nujol mulls) are not very different from those of the related nickel carbonyl complexes, which are very stable towards carbon monoxide dissociation.

Although it would be better to compare the force constants, it seems that the strength of the Pt—C and Ni—C bonds are not very different.

It is not yet clear why platinum(0) carbonyl complexes so easily lose carbon monoxide.

The only reasonable explanation can be found in the higher stability of the tricoordinated species in the case of platinum(0) compared to nickel(0). The reaction of carbon monoxide with palladium(0) phosphine complexes has not been described, while with nickel(0) the well known derivatives of $Ni(CO)_4$ are obtained[69].

(vi) Reaction with oxygen

Phosphine complexes of Ni^0, Pd^0 and Pt^0 react with oxygen to give addition compounds as follows[70,71,45]:

$$M(PPh_3)_n + \frac{n}{2} O_2 \rightarrow M(PPh_3)_2O_2 + (n-2)OPPh_3$$

($M = Ni, Pd, Pt; n = 3, 4$)

The nickel and palladium oxygen adducts are rather unstable and decompose at a temperature higher than −35° for the nickel compound and 20° for the palladium one[70].

The platinum oxygen adduct is much more stable but decomposes[72] at nearly 120° in the following way*:

$$Pt(PPh_3)_2O_2 \rightarrow \tfrac{1}{4}[Pt(PPh_3)_4]+\tfrac{1}{2}\,O_2+OPPh_3$$

It is interesting to point out that oxygen adds very easily to zerovalent phosphine complexes.

The reaction

$$Pt(PPh_3)_2+O_2 \rightarrow Pt(PPh_3)_2O_2$$

proceeds at a rate one hundred times faster than the corresponding reaction with Vaska's compound $IrCl(CO)(PPh_3)_2$.

However the activation energy in benzene solution is not very different[73], (nearly 10 Kcal $mole^{-1}$).

The oxygen molecule coordinated to the zerovalent metal seems to be very reactive. The oxygen adducts catalyse the oxidation of phosphine to phosphine oxide and of isonitrile to isocyanate[70,71]. The mechanism of the catalysis is probably as follows:

$$M(PPh_3)_4+O_2 \rightarrow M(PPh_3)_2O_2+2\,OPPh_3$$
$$M(PPh_3)_2O_2+2\,PPh_3 \rightarrow M(PPh_3)_2+2\,OPPh_3$$
$$M(PPh_3)_2+O_2 \rightarrow M(PPh_3)_2O_2$$

(M = Ni, Pd, Pt)

It was proposed that the coordinated oxygen is peroxidic on the basis of the increased oxygen–oxygen bond length[74] and of the formation of hydrogen peroxide upon protonation[70,75]. The above catalytic reactions can be easily explained by this assumption.

However the catalysis of autoxidation of cyclohexene to cyclohexen-3-one and cyclohexene oxide[76] by $Pt(PPh_3)_2O_2$ seems to proceed as any usual autoxidation process[77], which means that 3-cyclohexenehydroperoxide is the intermediate of the reaction *via* a free-radical mechanism. It follows that it is probable that a prerequisite for this oxidation is only prior coordination of molecular oxygen which favours the formation of radicals as in any bulk metal.

These characteristics of $Pt(PPh_3)_2O_2$ prompted investigation, under homogeneous conditions, of those reactions in which platinum has traditionally served as a heterogeneous catalyst.

Passage of SO_2, NO_2 (ref. 62) and NO (ref. 76) into a solution of $Pt(PPh_3)_2O_2$ at room temperature results in the formation of the corresponding sulphato, dinitrato and dinitro platinum(II) complexes as follows:

(*) Some authors claimed[70] that the oxygen adducts decompose as follows:

$$M(PPh_3)_2O_2 \rightarrow M+2\,OPPh_3\ (M{=}Ni,\ Pd,\ Pt)$$

This does not appear to be so in the case of the platinum adduct.

$$Pt(PPh_3)_2O_2+SO_2 \rightarrow Pt(PPh_3)_2SO_4$$
$$Pt(PPh_3)_2O_2+2\ NO_2 \rightarrow Pt(PPh_3)_2(NO_3)_2$$
$$Pt(PPh_3)_2O_2+2\ NO \rightarrow Pt(PPh_3)_2(NO_2)_2$$

$Pt(PPh_3)_2O_2$ reacts with CO_2 (ref. 79) yielding a compound[14] previously described as $PtH_2(PPh_3)_2$. The compound is actually the carbonato complex[79,80] $Pt(PPh_3)_2(CO_3)$.

Particularly interesting are some addition compounds of $Pt(PPh_3)_2O_2$ with acetone, CS_2, maleic anhydride and related compounds[81]. Their structures are under investigation by X-ray diffraction methods.

G. CONCLUSION

Some general conclusions can be reached about the coordinative reactivity of zerovalent d^{10} phosphine complexes.

Firstly there is quite a good mutual relationship between the coordination on unsaturated molecules like $M(PPh_3)_2$ (M = Pt, Pd, Ni) and the chemisorption on Pt, Pd or Ni surfaces[82]. In fact the relative strength of the coordinative bonding of molecules like $CH_2{=}CH_2$, $CH{\equiv}CH$, H_2S, CO, O_2 can be qualitatively correlated with the relative strength of their chemisorption bonding.

Secondly the coordinated molecules change their properties and their chemical behaviour in a drastic way, if a dissociation process takes place, and in a more subtle way if only a coordinative addition takes place. This has been supposed for many chemisorption process and any catalytic properties of metal surfaces must be attributed to the change of reactivity of the chemisorbed molecules.

It seems reasonable to compare molecules like $Pt(PPh_3)_2$ to "chemisorption centers" of metal surfaces. However it seems more difficult to compare these molecules to "active centers" of metal surfaces. Indeed many authors clearly demonstrated, as we have recently[1] pointed out, that the "active centers" in metal surfaces are generally those "chemisorption centers" which are topologically in points of defects or dislocations of the surfaces.

This discrimination is not possible in metal complexes. Indeed d^{10} platinum(0) and palladium(0) phosphine complexes do not particularly activate (from a catalytic point of view) the coordinated molecules.

However there must be more experimentation with these complexes in the area of catalysis before we have a clear answer to this point.

It appears clear therefore that we still need a more detailed approach to coordinative reactivity.

Only by investigating the electronic features (*e.g.* comparing the reactivity of triphenylphosphine platinum(0) complexes with those of related *p*-fluorotriphenylphosphine or *p*-methoxytriphenylphosphine compounds) or by undertaking kinetic and thermochemical studies it will be possible to have a series of quantitative data to support any hypothesis.

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