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SOME CHEMISTRY OF PLATINUM(II) HYDRIDES
AND RELATED COMPOUNDS

by

William John Jacobs

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario

London, Canada

July, 1969

To my wife
Jeannie

ABSTRACT

The platinum hydride trans-[PtHCl(PPh₃)₂] reacts with tetrafluoroethylene in moist benzene at 120° in a glass vessel to give two vinylic compounds, trans-[PtCl(CF=CF₂)(PPh₃)₂] and trans-[PtCl(C{CF₂H}=CF₂)(PPh₃)₂], and a carbonyl salt, trans-[PtCl(CO)(PPh₃)₂][BF₄]. The same reaction at 80° gives the two vinylic complexes along with a low yield of a halogen-bridged diplatinum tetrafluoroborate salt, [Pt₂Cl₂(PPh₃)₄][BF₄]₂. Reaction of the hydride trans-[PtHCl(PEt₃)₂] with tetrafluoroethylene in dry benzene in a stainless steel autoclave gives the addition product trans-[PtCl(CF₂CF₂H)(PEt₃)₂].

The dimeric salts [Pt₂X₂(PR₃)₄][BF₄]₂ were prepared for R = phenyl and X = Cl, Br and I and R = ethyl and X = Cl and Br by the reaction of the corresponding compound cis-[PtX₂(PR₃)₂] with boron trifluoride. These dimeric salts reacted with carbon monoxide to give the platinum carbonyl fluoroborate salt, trans-[PtX(CO)(PR₃)₂][BF₄] with the rates of reaction following the order X = I > Br > Cl and R = ethyl > phenyl. This reaction with carbon monoxide was more rapid in chloroform solution than nitromethane. The carbonyl salts trans-[PtX(CO)(PPh₃)₂][BF₄] reacted with methanol and ethanol to give

alkoxycarbonyl compounds, $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ (R = methyl or ethyl) with X = Cl, Br and I. The carbonyl salts trans- $[\text{PtX}(\text{CO})(\text{PEt}_3)_2]$ $[\text{BF}_4]$ reacted with water under reflux to give the corresponding hydrides trans- $[\text{PtHX}(\text{PEt}_3)_2]$ and carbon dioxide. The mechanism of this reaction was investigated by following the carbonyl stretching mode in the infra-red. The reaction does not proceed via hydroxyl attack but probably by an initial attack by water which gives an intermediate capable of undergoing slow decarboxylation to give the hydride.

The alkoxycarbonyl compounds, $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$, also reacted with water at 130° to give the corresponding hydrides, trans- $[\text{PtHX}(\text{PPh}_3)_2]$, and carbon dioxide. Alcohols (methanol for R = methyl and ethanol for R = ethyl) were also obtained as products. These reactions were catalyzed by halide salts and the function of this salt was investigated.

The general nature of the reaction of transition metal alkoxy-carbonyls with water to give the hydride was tested by reaction of the alkoxycarbonyls $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COOCH}_3)]$, $[\text{Mn}(\text{CO})_5(\text{COOC}_2\text{H}_5)]$ and $[\text{Ir}(\text{CO})_2(\text{COOCH}_3)(\text{PPh}_3)_2]$ with water. Hydrolysis of the first two compounds gave good yields of the hydrides $[\text{FeH}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2]$ and $[\text{MnH}(\text{CO})_5]$. For the iridium complex the reaction with water yielded an unstable solid tentatively identified as $[\text{IrH}(\text{CO})_2(\text{PPh}_3)_2]$

ACKNOWLEDGEMENTS

I am greatly indebted to Professor Howard C. Clark for his guidance, patience and encouragement throughout this work.

I wish to thank the members of this research group, especially Dr. K. R. Dixon, for many hours of lively discussion.

Thanks also go to Professor H. W. Baldwin for his assistance on the section on kinetic studies.

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CHAPTER I

GENERAL INTRODUCTION

In the 1930's the discovery of the unstable and reactive carbonyl hydrides of iron and cobalt by Hieber and co-workers (1) was met with great curiosity by chemists. These metal hydrides were naively considered uniquely different from any bonding systems known at the time and Hieber himself regarded the hydrogens as being buried deep in the electron core of the metal. A more sophisticated approach was taken to this metal hydride question after the discovery of the stable platinum hydride, trans-[PtHCl(PEt₃)₂], by Chatt, Duncanson and Shaw in 1957 (2) and the more detailed preparation of complexes of the type trans-[PtHX(PR₃)₂] (3). A variety of preparatory methods were extended to most of the other transition metals in the years after this and the unique status attributed to the bonding in hydrido-systems was soon lost to the extent that M. L. H. Green and D. J. Jones in their review (4) define transition metal hydrides as "those discrete complexes which contain one or more hydrogen atoms bonded directly to a transition metal by an essentially covalent, two-electron bond".

Many hydrides prepared had high thermal stability and chemical character that allowed comparison of the hydride ligand with halides or alkyl species. The advances in spectroscopic methods, including nuclear magnetic resonance spectroscopy, enabled more revealing studies to be made on the various hydride systems.

Transition metal hydrides exhibit sharp metal-hydride stretching absorptions in the infra-red regions ranging from near 2200 cm^{-1} for the phosphine hydrides, where the hydrogen is considered anionic in character, to below 1800 cm^{-1} for the carbonyl hydrides, considered to have a hydrogen ligand cationic in character. The characteristic high-field chemical shifts for the transition metal hydrides in proton magnetic resonance studies have allowed facile examination of these hydrides without interference from solvent protons. These easy methods of study are perhaps a main reason for the rapid development in the chemistry of metal hydrides. The ability to follow their action as catalysts in solution may well encourage a more complete study of this function.

The importance of transition metal hydrides in the field of catalysis is well known and studies of the role of these hydrides as intermediates in hydroformylations, isomerizations of olefins and polymerizations have been made. Recently much work has

been done on homogeneous hydrogenation of olefins and transition metal hydrides have been shown to be involved as intermediates in this catalytic process. Wilkinson and co-workers (5) have studied the hydrogenation reactions of various olefins in solutions containing the rhodium complex $[\text{RhCl}(\text{PPh}_3)_3]$. They detected high field lines in the n. m. r. spectra attributed to $[\text{RhH}_2\text{Cl}(\text{PPh}_3)_2]$ in hydrogen-saturated solutions of $[\text{RhCl}(\text{PPh}_3)_3]$ and suggested this as an intermediate which reacts with the olefin with regeneration of the rhodium complex $[\text{RhCl}(\text{PPh}_3)_3]$. Similar catalytic reactivity has been found with Vaska's compound $[\text{IrX}(\text{CO})(\text{PPh}_3)_2]$ (6) and the suggested hydride intermediate $[\text{IrH}_2\text{X}(\text{CO})(\text{PPh}_3)_2]$ has been isolated and identified spectroscopically.

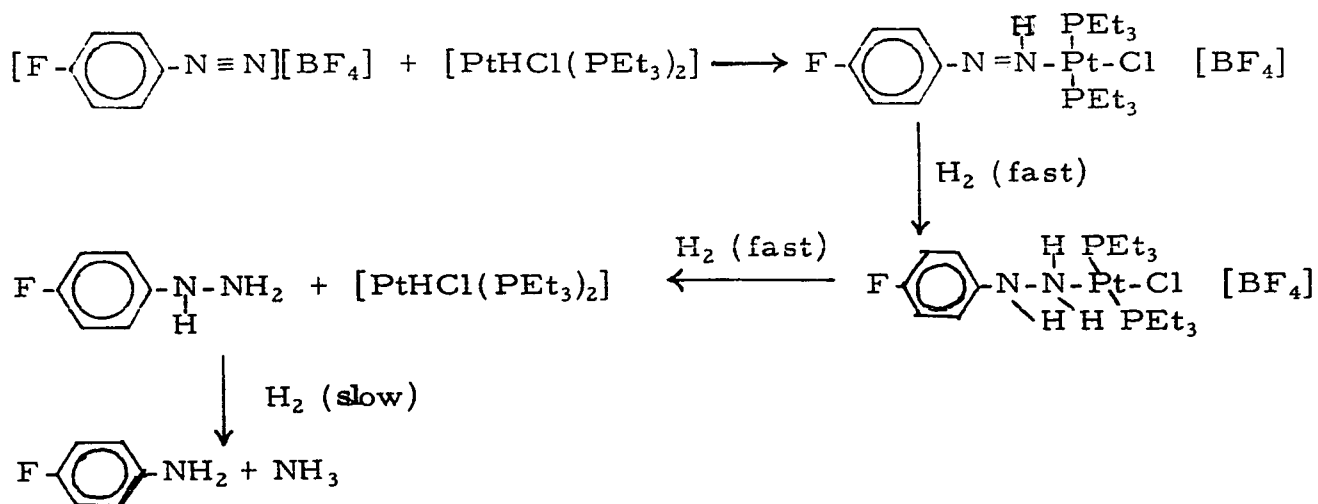
Because fluorocarbon derivatives of transition metals generally show greater thermal and oxidative stabilities than their alkyl counterparts, it is believed that an investigation of reactions of metal hydrides with fluoro-olefins may be of use in the study of the mechanisms involved in the catalytic activity of the hydrides. Stone and co-workers (7, 8) have done much work on the reactions of various transition metal hydrides with fluoro-olefins. The reversible addition of ethylene to the platinum hydride trans- $[\text{PtHCl}(\text{PEt}_3)_2]$ has prompted similar studies on fluoro-olefins with trans- $[\text{PtHCl}(\text{PEt}_3)_2]$. The effects of changes in the

surrounding ligands on the reactivity of the hydride have, as yet, not been studied and such investigations are discussed in this text.

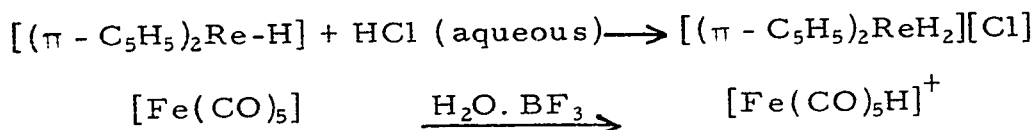
Recently there has been great interest in nitrogen-fixed transition metal complexes, not only because of the novelty of molecular nitrogen as a ligand, but also because an inorganic model system for duplication of "nitrogen-fixing" in legume plants might be possible. The importance of studying this process whereby certain plants can convert gaseous nitrogen to ammonia is evident. Recently biochemists (10) have adopted theories that suggest ammonia production in plants involves reaction of a nitrogen-fixed transition metal complex, contained in the enzyme called Nitrogenase, with a hydride of a transition metal (perhaps molybdenum or iron), found in another enzyme termed Hydrogenase.

Volpin and Shur (11) have done much work in attempting to discover an efficient ammonia-producing inorganic system and have met with partial success. Brintzinger (12) has suggested a bridged titanium hydride, $\left[\text{Cp}_2\text{Ti} \begin{array}{c} \diagup \text{H} \diagdown \\ \diagdown \text{H} \diagup \end{array} \text{TiCp}_2 \right]$, as an intermediate in one Volpin-Shur system and suggests reaction of the hydrido- compound with nitrogen gas in acid media yields ammonia.

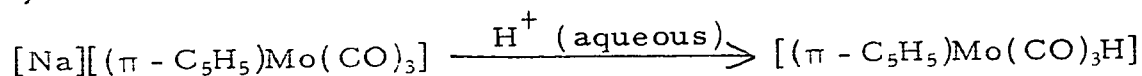
Parshall (13) has used a platinum hydride for reaction with an aryl diazonium tetrafluoroborate as a model system for ammonia production. He suggests the scheme below:



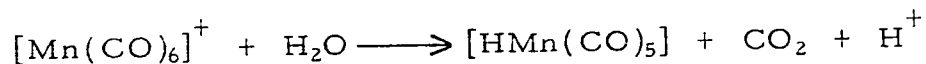
If transition metal hydrides are involved in the biological ammonia-producing process, then a study of preparations of such hydrides under biological conditions is important. Few transition metal hydrides have been produced under truly biological conditions but some hydrolysis reactions have produced hydrido-compounds. Protonation with strong acids in aqueous solution have been reported (14, 15) :



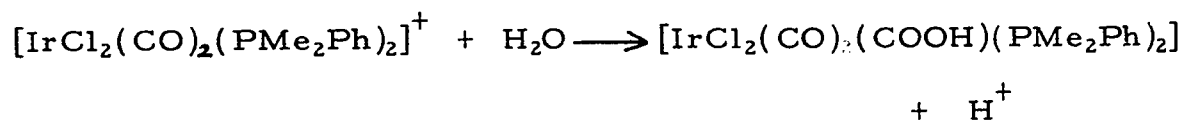
The hydrolysis of alkali metal salts of complex carbonyls to give hydrides is well known (16) :



Hieber and co-workers (17) have reported the reaction of the cationic manganese hexacarbonyl with water to give a hydride:



Very recently Deeming and Shaw (18) have reported the facile reaction of an iridium cationic carbonyl with water to give a carboxylate compound, the first stable transition metal complex of its kind:



This novel compound underwent thermal decomposition to give the hydride $[\text{IrHCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, with evolution of carbon dioxide.

It was along this direction of work that studies of the reactions of cationic platinum carbonyls with water were undertaken in an attempt to form hydrides from water under very mild, indeed biological, conditions.

CHAPTER II

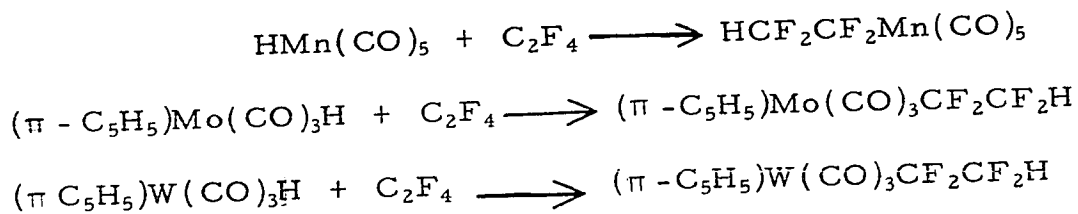
REACTION OF

HYDRIDOCHLOROBIS(TRIALKYLPHOSPHINE)PLATINUM(II)

WITH TETRAFLUOROETHYLENE

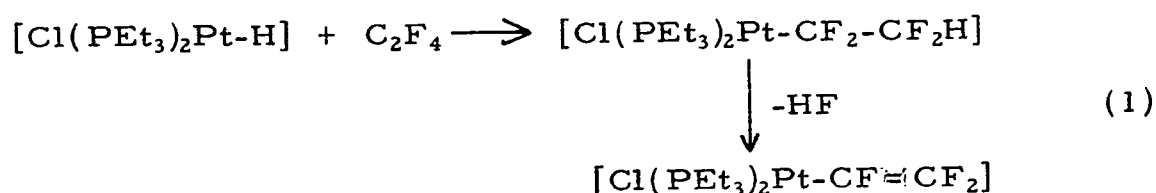
(a) Introduction

As part of an effort to study the mechanisms of catalytic hydrogenation of olefinic compounds by transition metals, much work has been done on reactions of various transition metal hydrides with fluoro-olefins. The products of such reactions demonstrate greater thermal and oxidative stability than their alkyl counterparts. F.G.A. Stone and co-workers (7, 8) have found that reactions of various transition metal hydrides with tetrafluoroethylene lead to addition of the fluoro-olefin across the metal-hydrogen bond:



However, Clark and Tsang (9) found that the hydride trans-[PtHCl(PEt₃)₂] reacted with perfluoroethylene in a Pyrex vessel to give unexpected products. Mixtures of two fluorovinyllic

compounds, trans-[PtCl(CF=CF₂)(PEt₃)₂] and trans-[PtCl{C(CF₂H)=CF₂}(PEt₃)₂], were obtained together with a third complex formulated as a π-complexed C₂F₄ adduct of the platinum hydride. The former vinylic compound was thought to be produced by hydrogen fluoride elimination from the expected fluoroalkyl product:

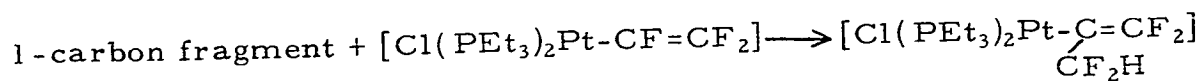
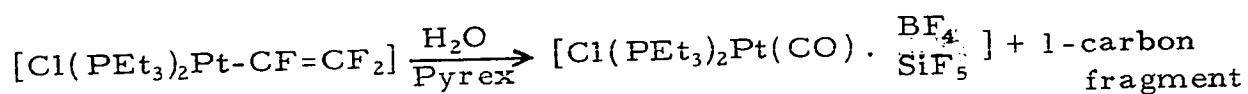


The source of the three-carbon vinylic compound was unknown. A π-bonded perfluoroethylene transition metal hydride had been suggested as an intermediate in the reaction of tetrafluoroethylene with metal hydrides. It appeared that the third compound was this intermediate since analysis, spectral data, and conductivity were consistent.

In 1966 Ibers et al (19) working on an X-ray diffraction study of the compound showed this formulation to be incorrect. They indicated the presence of a carbonyl group and a fluoroborate anion. Further work by Clark and Dixon (20) confirmed these findings. The compound was actually a cationic carbonyl of platinum, trans-[PtCl(CO)(PEt₃)₂]⁺ stabilized by a mixture of the counterions BF₄⁻ and the new pentacoordinate SiF₅⁻ anion. The salt was characterized by ¹⁹F and ¹H n. m. r. spectroscopy, infra-red

spectroscopy, mass spectroscopy, and analysis. The reaction of the hydride trans-[PtHCl(PEt₃)₂] with C₂F₄ in a silica tube gave similar results except that the carbonyl complex formed was isolated as the pure salt trans-[PtCl(CO)(PEt₃)₂][SiF₅]. Other work by Clark and Dixon (21) gave a more rational preparation of salts containing the SiF₅⁻ anion.

The suggested reaction scheme involved water as well as acid attack on the surface of the reaction vessel. Initially, the production of a fluoroalkyl intermediate was suggested which could eliminate hydrogen fluoride giving the vinyl compound observed, as in equation 1. Attack by hydrogen fluoride on the vessel walls, and attack of water (present in small amounts) on the vinylic compound could result in the formation of the observed carbonyl cation stabilized by a mixture of BF₄⁻ and SiF₅⁻ anions. The one-carbon fragment species could also react with another vinyl compound to give the second observed vinylic species:



This scheme was confirmed when it was found that the reaction of trans-[PtCl(PEt₃)₂(CF=CF₂)] with water and SiF₄

gave the products trans-[Pt(CO)Cl(PEt₃)₂][SiF₅] and [PtCl{C(CF₂H)=CF₂}(PEt₃)₂] as predicted.

It was appropriate at this point to attempt the reaction of the hydride trans-[PtHCl(PEt₃)₂] with C₂F₄ in an unreactive vessel with more carefully dried solvents in an attempt to isolate the expected addition product [PtCl(CF₂CF₂H)(PEt₃)₂]. We also carried out reactions with the analogous compound trans-[PtHCl(PPh₃)₂] in an attempt to examine the effect of the triphenylphosphine ligand on this highly reactive system.

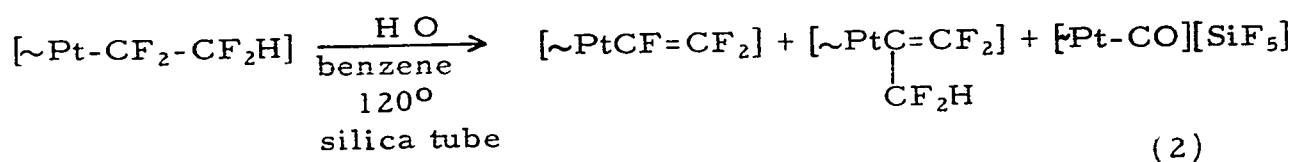
(b) Results and Discussion

(I) Reaction of trans-[PtHCl(PEt₃)₂] with tetrafluoroethylene in an autoclave.

Trans-[PtHCl(PEt₃)₂] was heated at 120° with C₂F₄ and dried benzene in a stainless steel autoclave giving a good yield of the expected addition product trans-[PtCl(CF₂CF₂H)(PEt₃)₂]. The ¹H and ¹⁹F n. m. r. spectra and C-F absorption patterns of the infra-red spectrum are similar to those observed in other compounds containing an M-CF₂CF₂H grouping (7, 8). The n. m. r. spectrum is described in the experimental section. While this product was suggested as an intermediate in the formation of the vinyl complex [PtCl(CF=CF₂)(PEt₃)₂], it was not isolated previously because HF was readily eliminated and attacked the reactive surface of the Pyrex or silica reaction tubes. On providing an unreactive

surface, however, the Pt-CF₂-CF₂H group did not eliminate HF and no vinyl compound was isolated. Hence, although the initial step in the reaction of this hydride with C₂F₄ gave results similar to those of other transition metal hydrides, the platinum system showed a marked inclination to further reaction. The unusual products isolated in the glass and silica reaction tubes illustrate the surprising ability of the vinylic compound [PtCl(CF=CF₂)(PEt₃)₂] to react with water to give a carbonyl cation. The counter ions of this cation must be the products of attack by HF on the reaction vessel surface.

These conclusions are supported by the further reaction (20) of the perfluoroethylene addition product under moist conditions in a silica vessel giving the two vinylic compounds and the carbonyl salt as described in equation 2 :



(II) Reaction of Trans-[PtHCl(PPh₃)₂] with C₂F₄

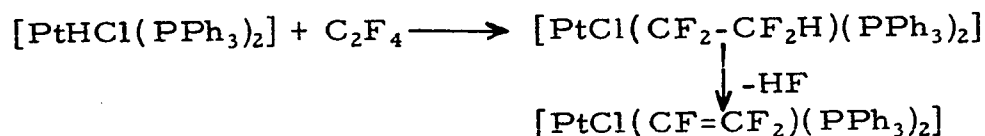
The reaction of trans-[PtHCl(PPh₃)₂] with C₂F₄ in a glass vessel in moist benzene at 120° gave similar results to the triethylphosphine analogue. A mixture of [PtCl{C(CF₂H)=CF₂}(PPh₃)₂] and [PtCl(CF=CF₂)(PPh₃)₂] was obtained, each compound characterized by infra-red spectroscopy and analysis. Although their solu-

bilities were too low for ^{19}F n. m. r. studies, the patterns of C-F infra-red absorptions are similar and the absorptions due to stretching vibrations appear at the expected region in the infra-red spectra. A third compound identified as trans-[PtCl(CO)(PPh₃)₂][BF₄] was also isolated. Unlike the triethylphosphine analogue this salt contained ~~only~~ BF₄⁻ as the counter anion and no traces of absorptions due to the SiF₅⁻ anion could be detected in the infra-red spectra (20).

When the above reaction was carried out in a silica tube under similar conditions only the vinylic compounds were formed and no carbonyl salt was isolated. Apparently the larger size of the cation with its bulkier triphenylphosphine ligands is a limitation on its ability to stabilize the SiF₅⁻ anion. However, it then seems surprising that the SiF₆²⁻ anion is not formed as a counter ion, although perhaps the formation of the doubly charged anion is energetically unfavourable.

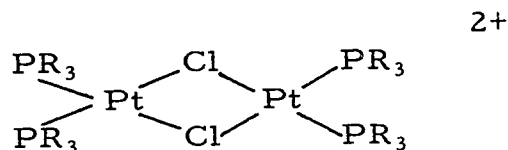
The above reaction was carried out in a stainless steel autoclave at 120°. Unlike the triethylphosphine analogue no addition product was obtained, although the vinylic compounds [PtCl(CF=CF₂)(PPh₃)₂] and a trace of [PtCl{C(CF₂H)CF₂}(PPh₃)₂] were isolated from the reaction products. Hence it appears that the stability of [PtCl(CF₂CF₂H)(PPh₃)₂] is low and HF elimination

takes place readily to give the vinylic compound $[\text{PtCl}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2]$:



(III) Reaction of trans- $[\text{PtHCl}(\text{PR}_3)_2]$ with C_2F_4 at 80°

Reaction of the hydrides trans- $[\text{PtHCl}(\text{PR}_3)_2]$ (for both R = ethyl and phenyl) with C_2F_4 in undried benzene at 80° in a glass tube gave somewhat different results from high temperature reactions. Again the two vinylic compounds were isolated but no carbonyl salt was obtained for R = phenyl and only a trace for R = ethyl. Instead a chloro-bridged cationic dimeric species shown below was formed:



This had, as counter ion, the fluoroborate anion for the case of R = phenyl while the anion was either BF_4^- or SiF_5^- for R = ethyl. Although it appears that these dimeric species are only the result of a side reaction, perhaps the disproportionation of the hydrides, the compounds are of interest and will be fully discussed in the next chapter.

In conclusion, it can be said that the hydride with trans

triphenylphosphine ligands did not demonstrate great differences in reactivity from its triethylphosphine analogue. The larger size of the phosphine probably reduced the stability of the SiF_5^- salt, and the addition product $[\text{PtCl}(\text{CF}_2\text{CF}_2\text{H})(\text{Ph}_3\text{P})_2]$ was not isolated. The instability of the addition product could have been due to steric hindrance of the phenyl groups although this seems rather unlikely. Differences in electron withdrawal ability of the phosphine groups may have effected the Pt-C bond explaining the difference in reactivity.

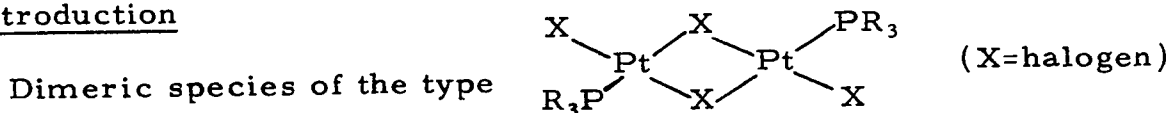
CHAPTER III

PREPARATION AND REACTIONS OF

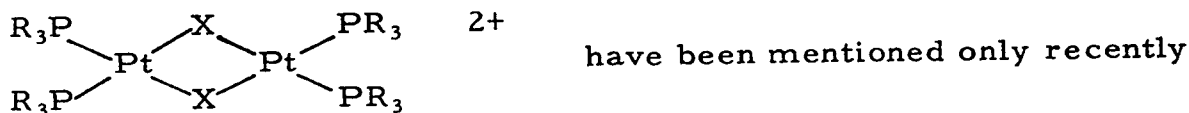
TETRAKIS(TRIALKYLPHOSPHINE)- μ, μ' -DIHALODIPLATINUM(II)

FLUOROBORATE

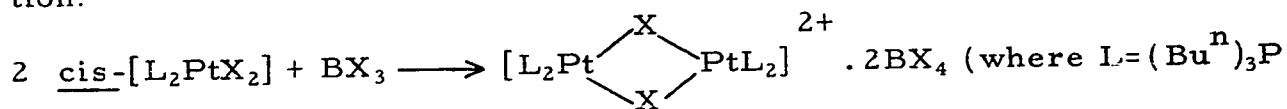
(a) Introduction



are well known and much work has been done on their preparation and reactions (22, 23, 24). In contrast cationic dimers of the type'

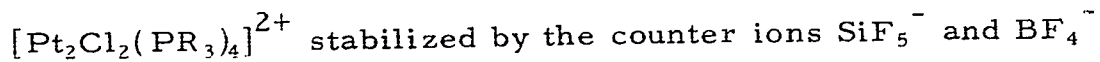


by M. F. Lappert and co-workers (25) who have reported the reaction:

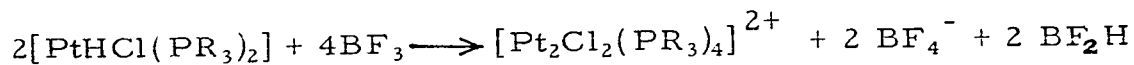


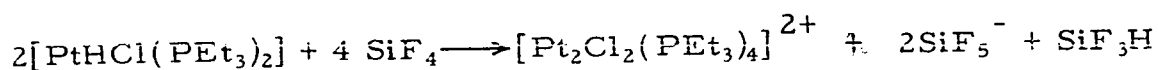
and $\text{X} = \text{Cl}$ or Br).

As mentioned in the last chapter, the reaction of the hydride trans- $[\text{PtHCl}(\text{PR}_3)_2]$ (for $\text{R} = \text{ethyl}$ or phenyl) with C_2F_4 gave low yields of the cationic chloro-bridged diplatinum compound



for $\text{R} = \text{ethyl}$, and by BF_4^- only, for $\text{R} = \text{phenyl}$. Since these anions are probably formed during the reaction by attack on the glass by hydrofluoric acid (20), the reactions might be described as:



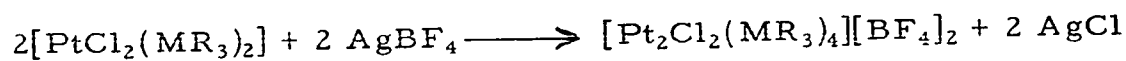


At this point it seemed appropriate to attempt preparations of these cationic dimers by a more rational method and to study any changes in reactivity with changes in the halogen and phosphine type.

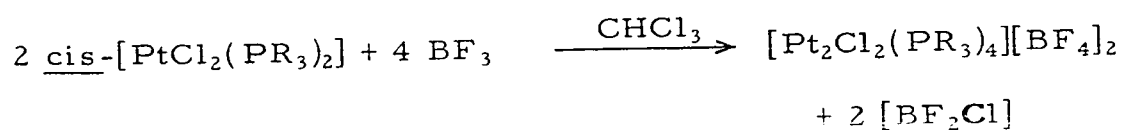
(b) Results and Discussion

(I) Preparation of $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4][\text{BF}_4]_2$

The hydrides trans- $[\text{PtHCl}(\text{PR}_3)_2]$ (R=ethyl or phenyl) were heated with boron trifluoride in benzene giving good yields of the dimeric diplatinum cations with BF_4^- as the anion. The compounds were characterized by infra-red spectroscopy and analysis. Very recent work (26, 27) indicates that reaction of the dichloride $[\text{PtCl}_2(\text{MR}_3)_2]$ (M=P, As, or Sb) with silver fluoroborate leads readily to the dimeric species and silver chloride :



The method of Lappert and co-workers (25) also gave the halo-bridged cation under mild conditions. In chloroform the dichloride $[\text{PtCl}_2(\text{PR}_3)_2]$ (R=ethyl or phenyl) reacted with boron trifluoride to give $[\text{Pt}_2\text{Cl}_2(\text{PR}_3)_4][\text{BF}_4]_2$ nearly quantitatively. The reaction apparently followed the scheme:



This reaction of the dihalo- complex with boron trifluoride was found to be general for X = Cl, Br and I with R=phenyl and for X = Cl and Br for R=ethyl. The ease of reaction decreased in the order Cl > Br > I. For X = Cl the reaction proceeded at room temperature for both the triethylphosphine and triphenylphosphine complexes. For the bromo- analogues even temperatures of 70° gave lower yields of the bromo- bridged dimer. Cis-[PtI₂(PPh₃)₂] reacted with boron trifluoride to give low yields of [Pt₂I₂(PPh₃)₄][BF₄]₂ only at 130° while the triethylphosphine analogue could not be prepared by this method.

Since the breaking of a platinum - halogen bond may be involved in the initial step of the reaction, the strength of this bond might be the factor determining the ease of reaction. The trans-weakening ligands, triethylphosphine and triphenylphosphine, labilize the chloride and since they are thought to be near each other on the "trans effect" scale (28), they would have approximately the same labilizing effect on the trans halide. The lability of the platinum - halogen bond is generally conceded to follow the order Cl < Br < I (29, 30) and thus the chloro- system should undergo reaction under mildest conditions followed by the bromo- and iodo- analogues. This order is consistent with the experimental results.

(II) Physical properties of the compound $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4][\text{BF}_4]_2$

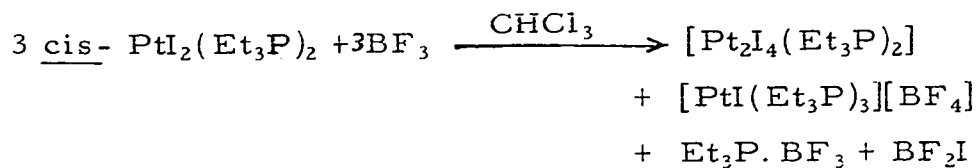
The salts of these dimeric cations are air-stable, non-hygroscopic, crystalline solids. For $\text{X} = \text{Cl}$ or Br and $\text{R} = \text{ethyl}$ or phenyl the compounds are white but the iodo-triphenylphosphine analogue is a yellow solid. The conductivities of the two chloro-analogues in nitromethane are of the order expected for 2:1 electrolytes (see experimental). The cis position of the triethylphosphine ligands relative to each other is shown by the presence of two bands in the infra-red Pt-P stretching region at about 440 and 425 cm^{-1} for both the bromo- and chloro- analogues. This region is masked by phenyl absorption modes in the triphenylphosphine analogues.

The ^1H n. m. r. absorptions of the methyl protons in the triethylphosphine analogues give a 1:2:2:2:1 quintet. This is attributed to ^{31}P coupling ($\underline{J}_{\text{P-H}} = 16$ c. p. s.) of the near phosphorus nucleus and further splitting by the two methylene protons ($\underline{J}_{\text{H-H}} = 8$ c. p. s.) to give two overlapping triplets and the observed multiplet. This is consistent with a cis configuration of the two phosphine groups. The trans configuration would give a 1:4:6:4:1 quintet arising from virtual coupling of the two phosphorus nuclei with the methylene protons. Such a system is thoroughly characterized elsewhere (31, 32, 33, 34).

A main feature of the infra-red spectra of these compounds is the stretching absorptions of the Pt-Cl-Pt bridges of the two chloro- species. These stretching absorptions (280 cm^{-1} for R=ethyl and 300 cm^{-1} for R=phenyl) are broadened relative to the corresponding cis- $[\text{PtCl}_2(\text{PR}_3)_2]$ compounds (305 and 280 cm^{-1} for R=ethyl, and 310 and 280 cm^{-1} for R=phenyl) but are not significantly lowered in frequency. Lappert and co-workers (25) have suggested that the decrease in frequency expected for a bridged rather than a terminal Pt-Cl bond is counter-balanced by the increase in changing from uncharged to bipoisitive platinum.

(III) Reaction of cis- $[\text{PtI}_2(\text{PEt}_3)_2]$ with BF_3

The reaction of cis- $[\text{PtI}_2(\text{PEt}_3)_2]$ with boron trifluoride at 70° gives entirely different products from those described above for analogous compounds. Low yields of the previously described (23) uncharged iodo-bridged dimer $[\text{Pt}_2\text{I}_4(\text{PEt}_3)_2]$ and of the new compound iodotris(triethylphosphine)platinum(II) tetrafluoroborate, $[\text{PtI}(\text{PEt}_3)_3][\text{BF}_4]$, are obtained. The scheme of the reaction can be written as :

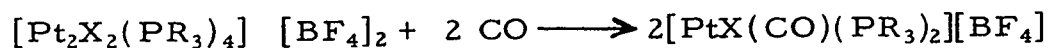


This anomolous reaction is puzzling and because of its

complicated nature will not be discussed at length. Possibly the change in reactivity can be attributed to the ability of the iodide to compete more efficiently than the other halogens with the triethylphosphine for the platinum electrons in the filled non-bonding d-orbitals of the metal, thus labilizing the triethylphosphine group.

(IV) The reaction of $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4] [\text{BF}_4]_2$ with Carbon Monoxide

The ability of carbon monoxide to cleave a halo-bridged diplatinum(II) compound is well known (22) for the series $[\text{Pt}_2\text{X}_4(\text{PR}_3)_2]$. Hence, the analogous facile reaction of carbon monoxide with the cationic dimeric species, $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4] [\text{BF}_4]_2$ is not surprising. In chloroform solution the dimeric cations react in minutes with carbon monoxide at one atmosphere pressure.



For $\bar{X} = \text{Cl}$ or Br and $\text{R} = \text{ethyl}$ or phenyl the equilibrium lies to the right and the carbonyl can be isolated as an air-insensitive crystalline solid. For $\text{X} = \text{I}$, and $\text{R} = \text{phenyl}$, the equilibrium lies to the right for carbon monoxide-saturated chloroform solutions. However, in the absence of carbon monoxide, the dimeric salt rapidly precipitates. The rates of reaction of these cationic dimers with carbon monoxide has been studied qualitatively by measuring carbon monoxide uptake via a capillary manometer. Nitromethane and chloroform solutions of equimolar amounts of the dimers

$[\text{Pt}_2\text{X}_2(\text{PR}_3)_4]$ $[\text{BF}_4]_2$ (X = Cl, Br or I with R = phenyl and X=Cl or Br with R=ethyl) were stirred at 22° under one atmosphere pressure of carbon monoxide. The rates of reactions were generally found to be much faster than the rates of carbonylation of the uncharged dimers $[\text{Pt}_2\text{X}_4(\text{PR}_3)_2]$ (22) and were functions of halogen type, phosphine type and reaction solvent (see Figures 1 and 2).

While in nitromethane as solvent the rates of reaction are generally slower than in chloroform, the same order of reactivity is observed. In fact the effect of the halogen type is more emphasized in nitromethane. This is best illustrated by the chloro-analogues which will not take up carbon monoxide in this solvent at room temperature.

Fig.1 Carbon Monoxide Uptake by Dimers in Chloroform Solution

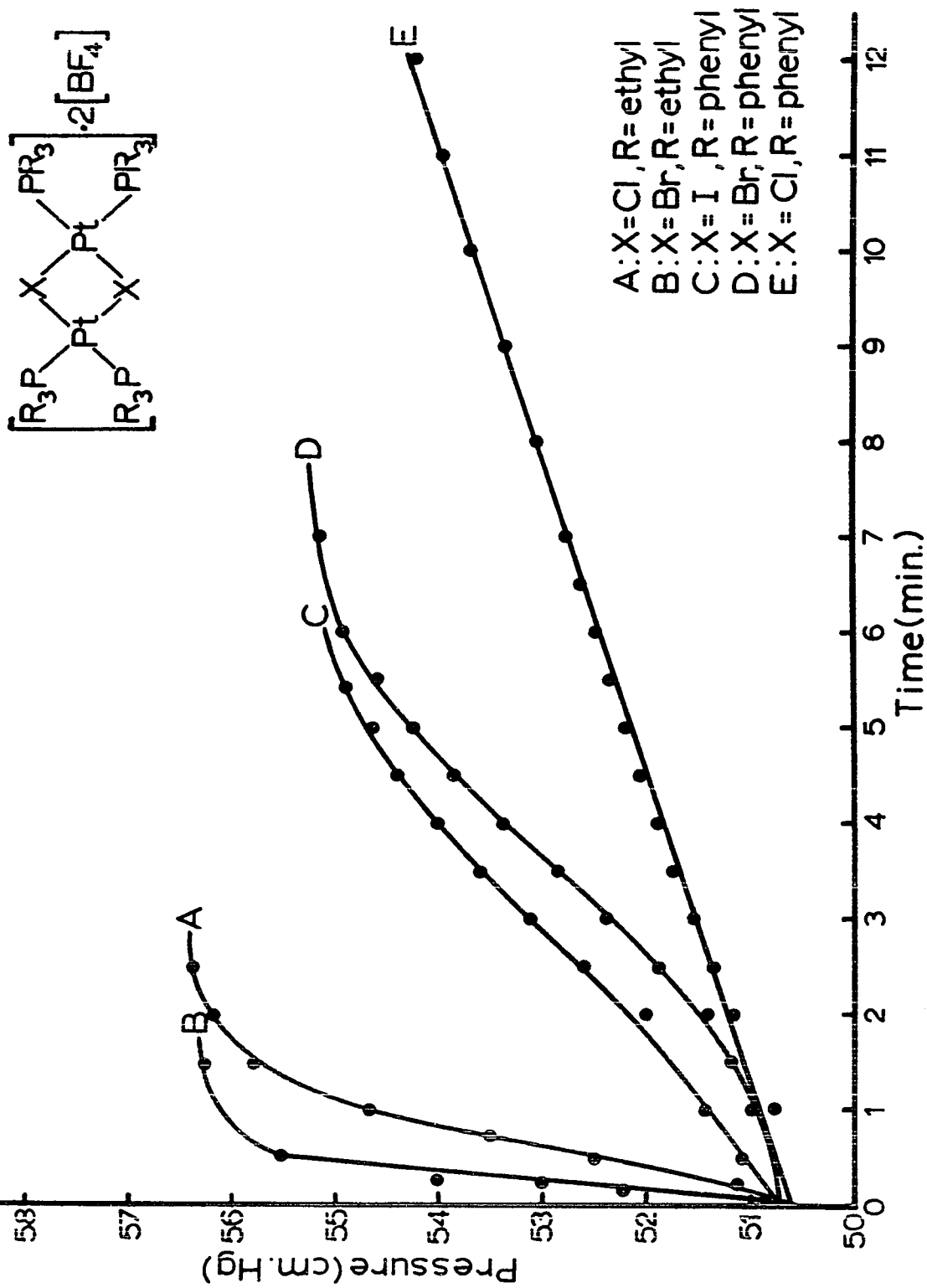
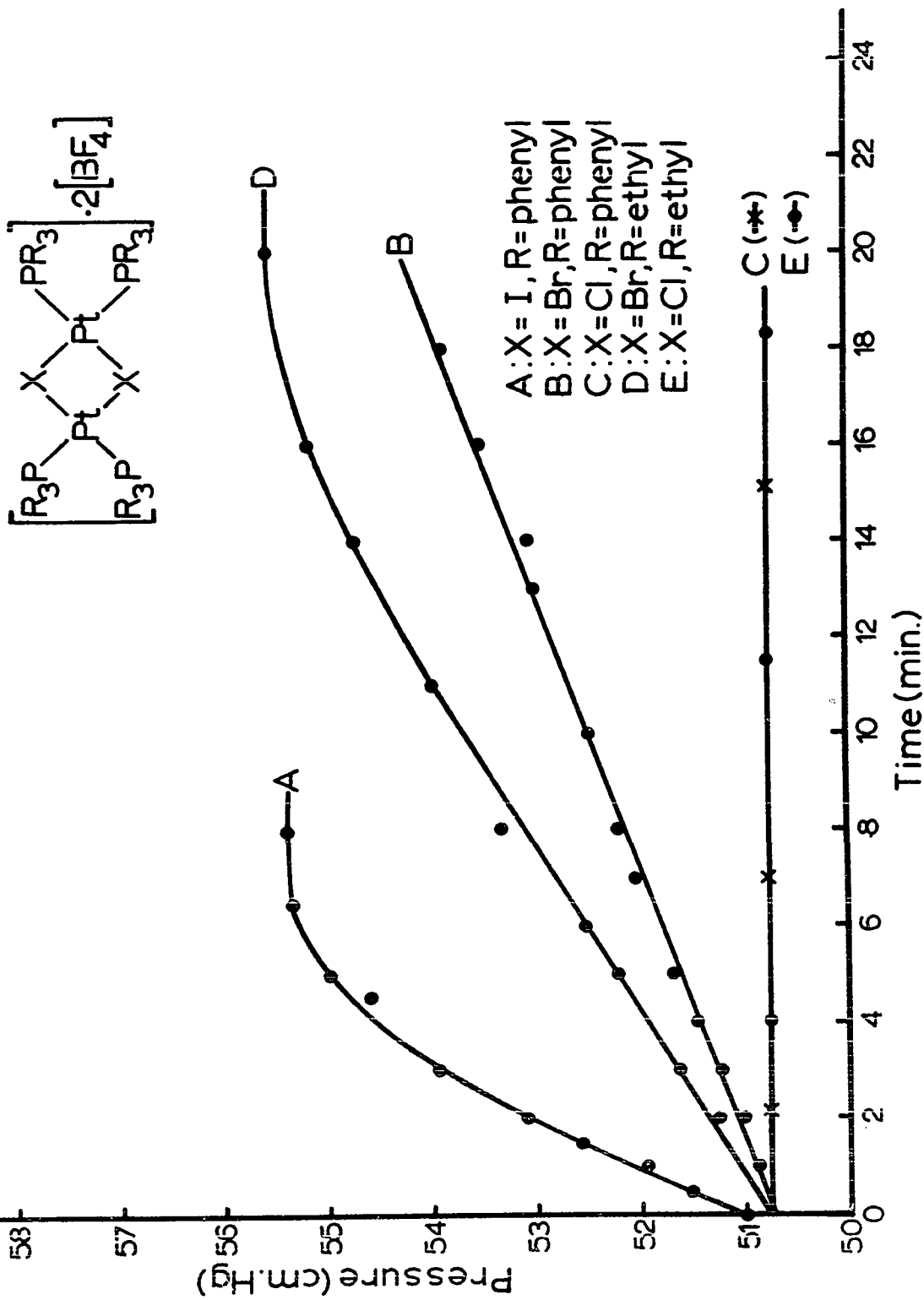
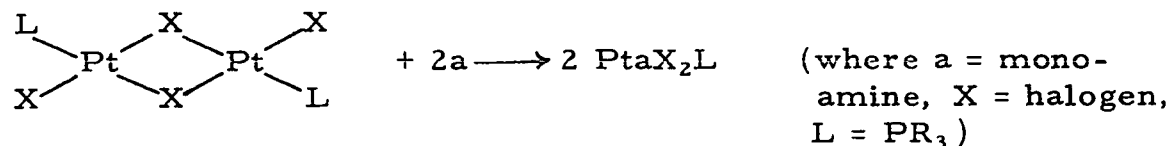


Fig.2 Carbon Monoxide Uptake by Dimers in Nitromethane Solution

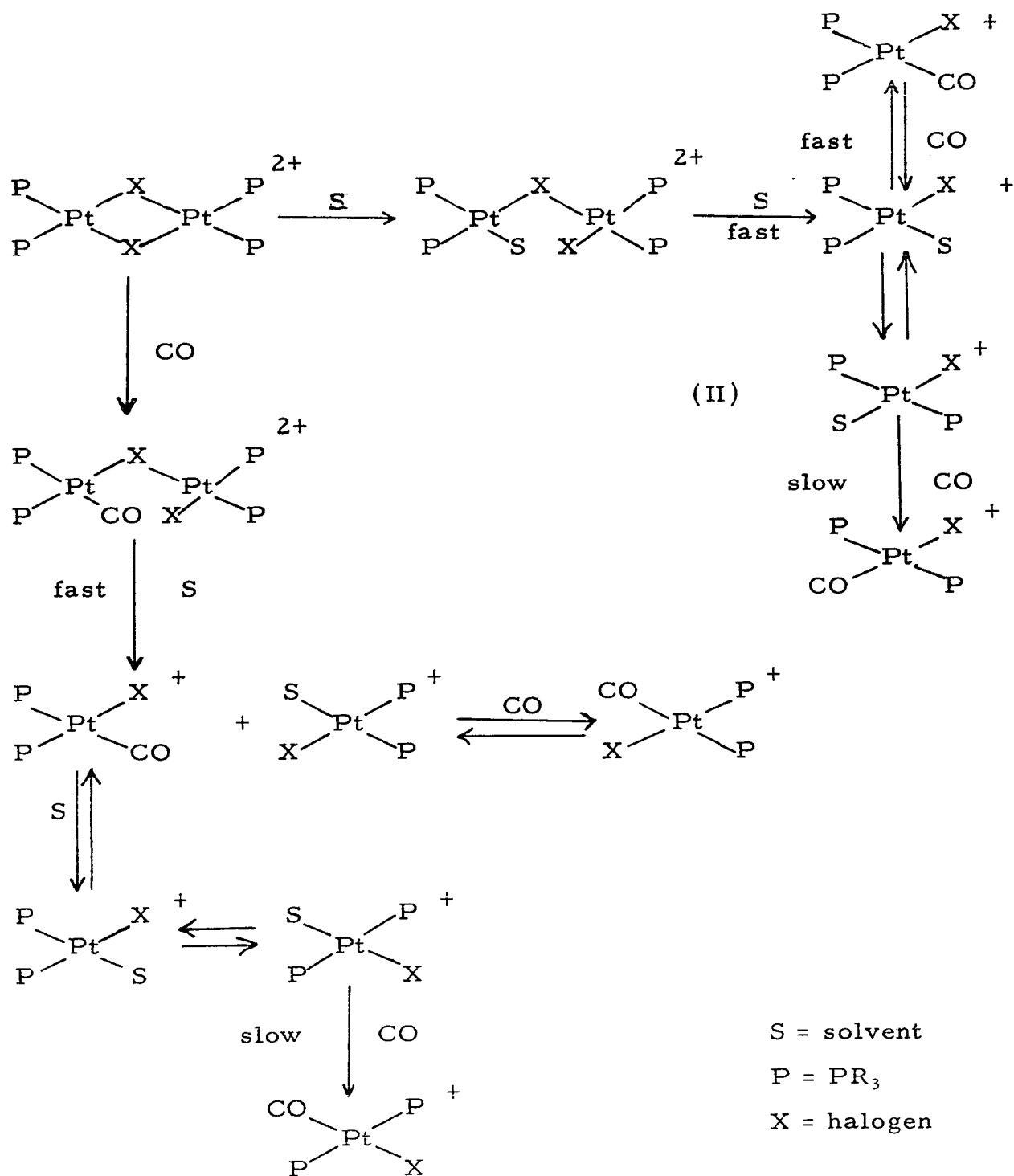


Pearson and Muir (29) have recently described a kinetic study of the cleavage of various halogen-bridged complexes of platinum(II) by monoamines :



They found the reaction mechanism follows two different paths. The first is a direct attack on the bridged species by an amine followed by an immediate further reaction of the mono-bridged transition state with a solvent molecule and final exchange of the solvent by another amine. The second path involves the initial attack by a solvent molecule and immediate further reaction with a second solvent molecule. These workers feel that the remaining unstable halogen bridge is immediately broken. They suggest that the absence of any platinum(II) complexes containing a single halogen bridge is evidence of this instability. The rate of cleavage of the various halo-bridges was found to decrease in the order $\text{Cl} > \text{Br} > \text{I}$. It was suggested that this order indicated the initial breaking of the bridge by the amine or solvent molecule is the rate-determining step of the two mechanisms. Since the order of metal-halogen bond lability increases as $\text{Cl} < \text{Br} < \text{I}$, then the chloro-bridged species should react at the most rapid rate, followed by the bromo- and then iodo-analogues. No large solvent effects were reported in the various solvents attempted.

Such a mechanism may well hold for the carbonylation of the



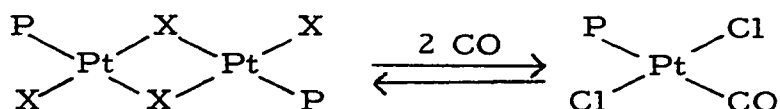
Possible Mechanisms of Reaction of Carbon Monoxide With Cationic
Halo-bridged Dimers.

of the cationic dihalo-bridged dimers. The large effect of the solvent indicates an important role for the solvent molecules. If only a direct reaction with carbon monoxide were occurring, such solvent effects would be less marked. However if, as Pearson points out, the initial cleavage of the halide bridge is the rate determining step then the order of increasing rates of reaction would be $I < Br < Cl$. Also since nitromethane is a better coordinating solvent than chloroform the expected solvent effect on the rate of reaction would be $CHCl_3 < CH_3NO_2$. Finally, the two ligands trans to the halogen are expected to labilize this halogen in the order $PEt_3 < PPh_3$ and this effect should be borne out in observed rates of reaction. In fact the observed relative rates for this system are in opposition to all the values expected for the cleavage step to be the rate-determining step.

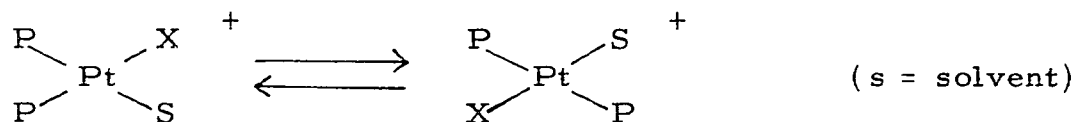
If the reaction of the solvated species II (see reaction scheme) with carbon monoxide were the rate-determining step, then a reverse halogen effect would be observed. The rate of reaction would increase with increased trans-labilizing effect; that is $I > Br > Cl$. The better coordinating solvent nitromethane would give a slower reaction rate than the chloroform. Finally the different phosphines in their cis positions to the leaving solvent group would show no appreciable differences in observed rates.

These rationalizations are in fact consistent with the observed results.

As seen in the reaction scheme (see page 25), the cleavage of the bridged species leads to either $[\text{PtX}(\text{S})(\text{PR}_3)_2]$ or $[\text{PtX}(\text{CO})(\text{PR}_3)_2]$ both of which are in the cis form. However, the final product is isolated only in the trans form. Chatt and Shaw (22) point out that, in their system, although the equilibrium



may be set up, the equilibrium would lie to the left-hand side because both phosphine and carbon monoxide are strongly π -bonding ligands and the competition for the platinum non-bonded electrons would not favour the production of the isomer. Similarly for the cationic dimeric species, although reaction to give the species cis- $[\text{PtX}(\text{CO})(\text{PR}_3)_2]^+$ would be possible, it would not be the most favourable product. Isomerizations of the type:



would be expected in solution and it is these species that could react with carbon monoxide to give the observed final product.

A more sophisticated explanation of the reaction scheme may be made invoking 5-coordinate species but the rationalizations

would remain basically unchanged. Although the halogen effects on reaction rates differ from those observed by Pearson and Muir (29), a similar series of steps may be occurring with differing slow steps determining the reactivity observed.

CHAPTER IV

A STUDY OF THE COMPOUNDS trans-[PtX(CO)(PR₃)₂][BF₄]

(R=ethyl or phenyl)

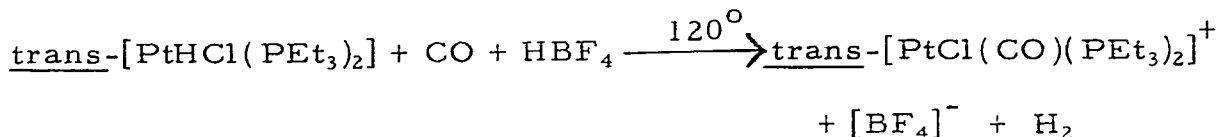
(I) Introduction

As mentioned in chapter II the platinum(II) carbonyl cations [PtCl(CO)(PR₃)₂]⁺ (R=ethyl or phenyl) were formed from the unexpected reaction involving attack of water on a fluorovinylplatinum(II) compound. The fluoroborate salt of this cation was found to be very stable and attempts at a rational preparation of the salt seemed worthwhile. Because the compound was isoelectronic with Vaska's compound, [IrCl(CO)(PR₃)₂] (R=alkyl or aryl) (6), and its rhodium analogue, [RhCl(PPh₃)₃] (5), it seemed logical to determine whether the platinum analogue has the same reactivity.

(II) Results and Discussions

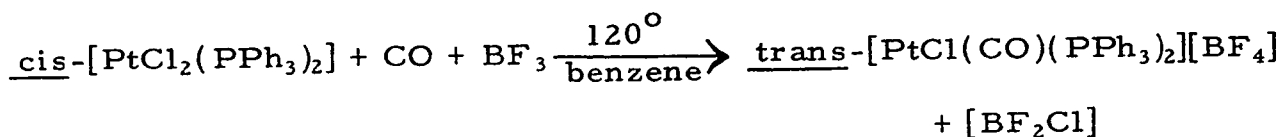
(i) Preparation of trans-[PtX(CO)(PR₃)₂][BF₄] (R=ethyl or phenyl and X=halogen).

Initially trans-[PtCl(CO)(PEt₃)₂][BF₄] was prepared (20) by reaction of trans-[PtHCl(PEt₃)₂] in benzene with aqueous 48% fluoroboric acid in an autoclave under a pressure of 5 atmospheres of carbon monoxide.



The analogous reaction with trans-[PtHCl(PPh₃)₂] is more complex. A lower yield of trans-[PtCl(CO)(PPh₃)₂][BF₄] is obtained and there are other products which are difficult to separate and have not been fully characterized. The difference in the behaviour of the triphenyl- and triethylphosphine complexes may be due to the greater reducing power of the former ligand.

The compound trans-[PtCl(CO)(PPh₃)₂][BF₄] can be prepared more readily by reaction of cis-[PtCl₂(PPh₃)₂] with gaseous boron trifluoride and carbon monoxide in benzene solution :



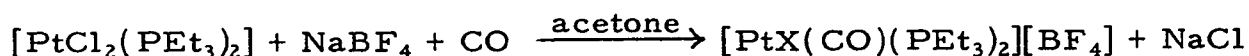
The reaction probably proceeds via the halo-bridged dimeric cation and its solvated cations discussed in the previous chapter. This preparation can be extended to trans-[PtX(CO)(PR₃)₂][BF₄] with X = Br or I with R=phenyl, and X = Cl or Br with R=ethyl.

As mentioned in the previous chapter, these carbonyl salts can be prepared by simple carbonylation in solution of the dimeric species, [Pt₂X₂(PR₃)₄][BF₄]₂, at one atmosphere of carbon monoxide pressure.

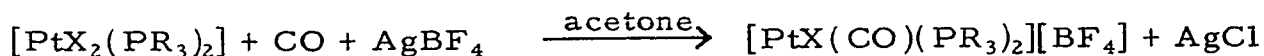
The acidification of the alkoxy-carbonyls [PtX(COOR)(PPh₃)₂] (R=methyl or ethyl and X = Cl, Br or I), discussed later in this chapter, with aqueous fluoroboric acid gives quantitative yields of

the carbonyl salts trans-[PtX(CO)(PPh₃)₂][BF₄].

Church and Mays (35, 36) have reported the facile reaction of cis- or trans-[PtCl₂(PEt₃)₂] with sodium perchlorate and carbon monoxide to give the carbonyl cation stabilized by the perchlorate anion. A similar reaction with sodium fluoroborate was found to give analogous results with the production of the fluoroborate salt at 25° :



As yet the most general preparation of the carbonyl salt is the reaction of silver fluoroborate with the compound cis-[PtX₂(PR₃)₂] (X = Cl or Br and R=ethyl or phenyl). The driving force of this reaction is probably the formation of the insoluble silver salt which forces the equilibrium well to the right:



Such reactions have been extended to analogous arsine and stibine systems (27).

(ii) Physical Properties of trans-[PtX(CO)(PR₃)₂][BF₄]

The compounds trans-[PtX(CO)(PR₃)₂][BF₄] (X = Cl, Br and I with R=phenyl and X = Cl or Br with R=ethyl) are crystalline solids, soluble in polar organic solvents such as chloroform or acetone but sparingly soluble in benzene and insoluble in cyclohexane or pentane. They are non-hygroscopic and stable in air

for about a month, although after longer storage in air there is evidence of slight decomposition. The conductivities of both chloro-analogues in nitromethane are of the order expected for 1:1 electrolytes (see experimental). The salts with triphenylphosphine ligands all decompose about 200° but the two triethylphosphine analogues have definite melting points. (for X = Cl, m. p. = $168-171^{\circ}$ and for X = Br, m. p. = $158 - 160^{\circ}$)

The carbonyl stretching frequencies appear between 2120 and 2098 cm^{-1} in the infra-red (see table 3). No correlation of carbonyl stretching frequencies with changing X or R could be made but the observed frequencies did correspond well with the reported value (22) of 2100 cm^{-1} for cis- $[\text{PtCl}_2(\text{CO})(\text{PEt}_3)]$, which also has the carbonyl trans to chloride. Single crystal x-ray studies (19) show the cation $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2]^+$ to have the expected square planar configuration about platinum and confirm the trans configuration for the two phosphine ligands. ^1H n. m. r. spectra of the methyl protons indicate a multiplet characteristic of that obtained for the trans phosphine configuration for four-coordinate platinum(II) complexes (31, 33).

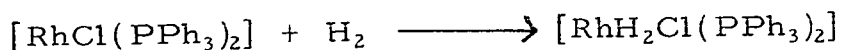
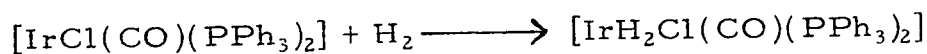
(iii) Reactions of trans- $[\text{PtX}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$

(a) Comparison of reactivity with isoelectronic compounds.

Wilkinson has intensively studied the ability of the compound

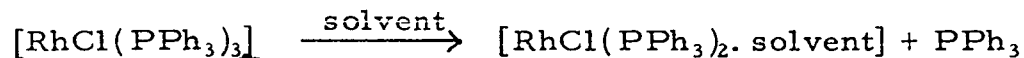
$[\text{RhCl}(\text{PPh}_3)_3]$ (5, 37) to act as a catalyst for the hydrogenation of various olefins. Analogous reactivity has been demonstrated for Vaska's compound $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (38). This iridium compound also demonstrates a remarkable ability to form a complex with molecular nitrogen (39). Because the platinum carbonyl cation $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2]^+$ is isoelectronic with these reactive compounds and, especially since the iridium complex has similar surrounding ligands, analogous reactivity might be expected. No such reactivity was found. Neither salts of triethylphosphine (20) nor triphenylphosphine analogues of $[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ combine with hydrogen gas or dry hydrogen chloride at atmospheric pressure at 25° . No reaction with perfluoroethylene was observed for the two chloro-

The absence of such reactivity can be rationalized quite easily. Four-coordinate platinum(II) complexes are less able to undergo oxidative addition to give six-coordinate platinum(IV) complexes compared to analogous iridium or rhodium systems which readily go to the formal oxidation state of three from the oxidation state of one as below (40).



Such complexes are suggested intermediates in olefin-hydrogenation reactions (5). The rhodium complex easily dissociates to a

solvated species shown below :



This solvated species can easily react with hydrogen to give the dihydro-complex. The platinum salt $[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ is unlikely to undergo such facile dissociation, nor is it likely to easily oxidatively add H_2 to give a six-coordinate compound.

Wilkinson (5) writes that with decreasing electron density on the metal atom, the promotional energy required to form two or more bonds (for H_2 addition) increases. If this is the case, the positively charged platinum cation would be greatly inhibited from reaction with molecular hydrogen. Hence, it can be concluded that, because of the cationic nature of the complex, the high $\text{Pt}(\text{II}) \rightarrow \text{Pt}(\text{IV})$ oxidation potential, and the absence of easily available sites of coordination, that the compounds $[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ (R= ethyl or phenyl) will not readily undergo olefin-hydrogenation reactions.

Vaska's compound $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ undergoes reaction with benzoyl azide to give the complex with molecular nitrogen coordinated to the iridium (39). The platinum carbonyls do not react with benzoyl azide. However, since so little is known about the reactions of transition metal complexes with molecular nitrogen (41), differences in reactivity cannot be rationalized.

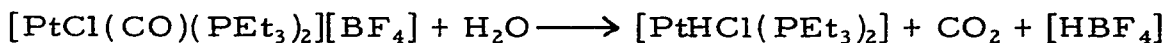
(b) Reactions with Halide Ion

If the compounds $[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ (R=ethyl or phenyl) are dissolved in a solution of a chloride salt such as NEt_4Cl ,

effervescence takes place and the carbonyls rapidly react to give the dichloride compounds cis-[PtCl₂(PR₃)₂] (R=ethyl or phenyl) apparently with liberation of carbon monoxide.

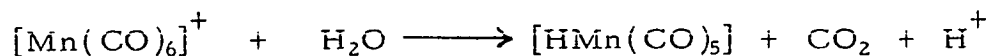
(c) Reactions of [PtX(CO)(PR₃)₂][BF₄] with Water.

Although catalytic reactivity like that shown by isoælectronic iridium and rhodium compounds is not present in the platinum carbonyl cations, they do undergo two unexpected reactions. The first is the reaction with water. Under reflux for 30 minutes in water the compound [PtCl(CO)(PEt₃)₂][BF₄] gives quantitative yields of carbon dioxide and trans-[PtHCl(PEt₃)₂]

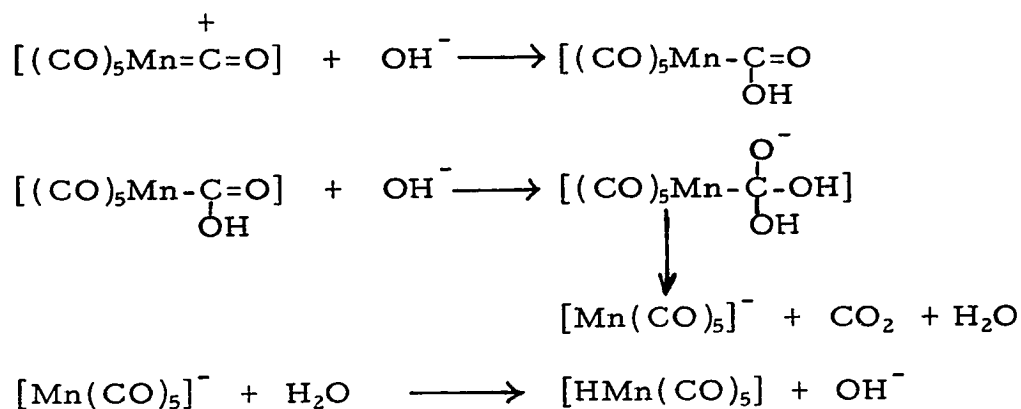


Trans-[PtCl(CO)(PPh₃)₂][BF₄] was not converted to the hydride as readily as the triethylphosphine analogue. Low yields of the hydride [PtHCl(PPh₃)₂] were obtained at 130° in water but the bulk of the residues consisted of uncharacterized decomposition products. Perhaps the lower solubility of the triphenylphosphine analogue prevents convenient reaction or the greater electron withdrawing ability of these phosphine ligands sufficiently effects the reactivity of the carbonyl carbon to prevent facile reaction.

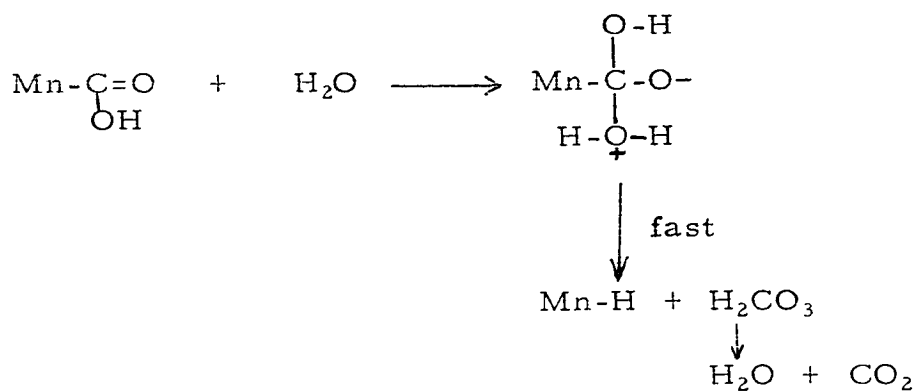
Similar reactivity has been recently reported for transition metal carbonyl cations. The reaction of hexacarbonylmanganese(I) cation with water follows the scheme :



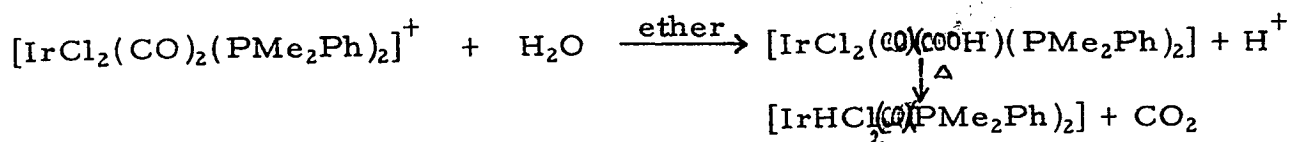
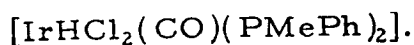
Hieber and Kruck (17) suggested that this reaction proceeds through the attack of an hydroxyl group to form a short-lived carboxylic acid. They suggest that further attack by hydroxide gives the manganese pentacarbonyl anion which then could abstract a proton from water.



The formation of a carboxylate compound $[\text{Mn}(\text{CO})_5(\text{COOH})]$ seems a reasonable initial step in the reaction; however, the reaction need not proceed through a manganese pentacarbonyl anion. Further reaction of the $\text{Mn}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}=\text{O}$ group with water could form the hydride along with carbon dioxide and water via a route such as :



pyrolysis at 160 - 180° good yields of CO₂ and the hydride

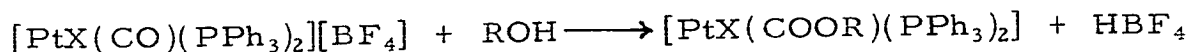


With L = PMe₃ reaction of the dicarbonyl cation with moist ether gave CO₂ and the hydride [IrHCl₂(CO)(PMe₃)₂] directly and no carboxylate was isolated.

The reaction is a close parallel to that of the platinum system and may aid in the study of the mechanism of the reaction of the cationic carbonyl, [PtCl(CO)(PEt₃)₂][BF₄] with water. Further discussion of the mechanism of the reaction is given in chapter V.

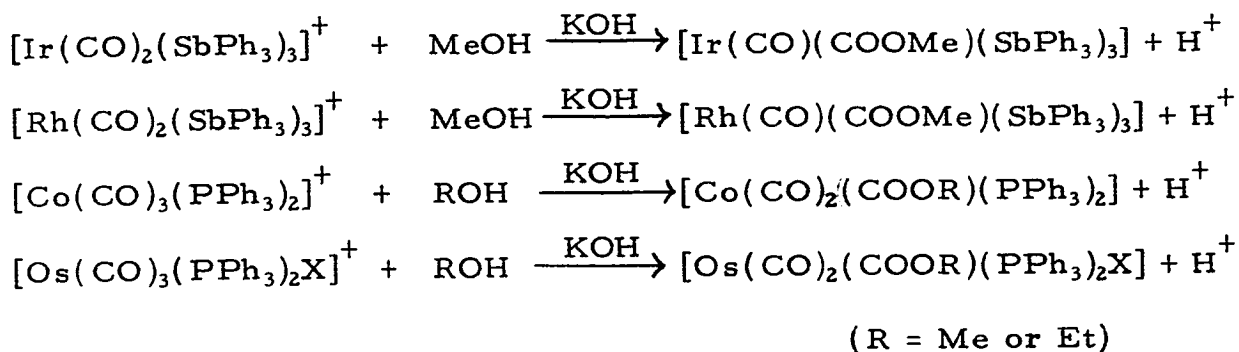
(d) Reaction of [PtX(CO)(PR₃)₂][BF₄] with Alcohols.

The second surprising reaction of the carbonyl cation was that with neat methanol or ethanol to give the corresponding alkoxy-carbonyls, [PtX(COOR)(PPh₃)₂] (R=methyl or ethyl and X = Cl, Br or I).

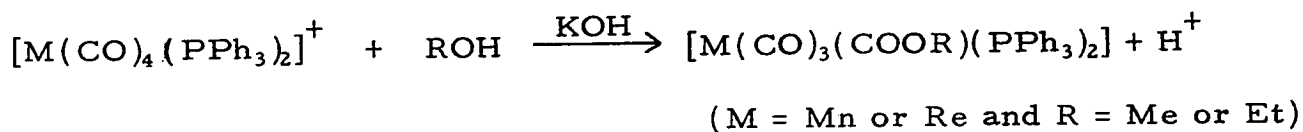


The remarkable ability of the alkoxide ion to attack the carbonyl carbon of cationic metal carbonyls has been described for a wide range of central transition metals with a number of different surrounding ligands. Hieber and co-workers (43, 44, 45)

have reacted alcoholic KOH with various cationic carbonyls to give neutral alkoxy-carbonyls



Kruck and Noack (46) have described closely related reactions with similar manganese and rhenium compounds.



Malatesta et al (47) have found similar reactivity for an iridium carbonyl cation :



Unlike these above reactions where a basic medium must be provided by ammonia or alkali metal hydroxide, the platinum carbonyl cation trans- $[\text{PtX}(\text{CO})(\text{PPh}_3)_2]^+$ (X = Cl, Br or I) is capable of reaction at neutral pH and room temperature to give the alkoxy-carbonyls, $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ (R = methyl or ethyl). Reaction with both methanol and ethanol is rapid (see experimental) but reversible in acidic solutions. The reaction of the triethylphosphine analogue trans- $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2][\text{BF}_4]$ with carefully dried methanol gives the expected methoxycarbonyl compound

$[\text{PtCl}(\text{COOMe})(\text{PEt}_3)_2]$ at refluxing temperature but the product is very unstable. In undried refluxing methanol the reaction with water is preferred to that with alcohol and only the hydride trans- $[\text{PtHCl}(\text{PEt}_3)_2]$ is formed. These platinum(II) alkoxy-carbonyls will be discussed more fully in chapter VI.

(e) Conclusions.

The platinum(II) carbonyl salt $[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ (R=ethyl or phenyl) did not demonstrate reactivity similar to the isoelectronic iridium complex $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ or the rhodium compound $[\text{RhCl}(\text{PPh}_3)_3]$. The platinum system was unable to undergo oxidative addition with simple reagents such as HCl or H_2 . However, the complex does show remarkable reactivity at the carbonyl carbon. Reactions of water or alcohols with these platinum complexes probably all involve attack at the carbonyl carbon at some stage of the reaction. With the wide range of transition metal alkoxy carbonyls now prepared from the reaction of cationic carbonyls with alcohols, it appears that such reactions are fairly general.

CHAPTER V

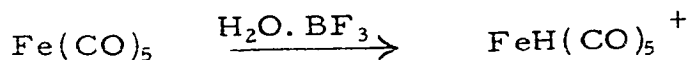
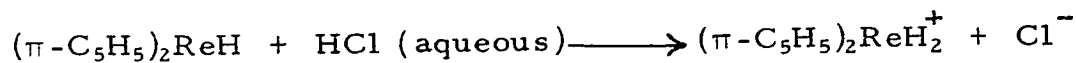
KINETIC STUDIES OF THE HYDROLYSIS OF trans-[PtCl(CO)(PEt₃)₂] (BF₄)]

(a) Introduction

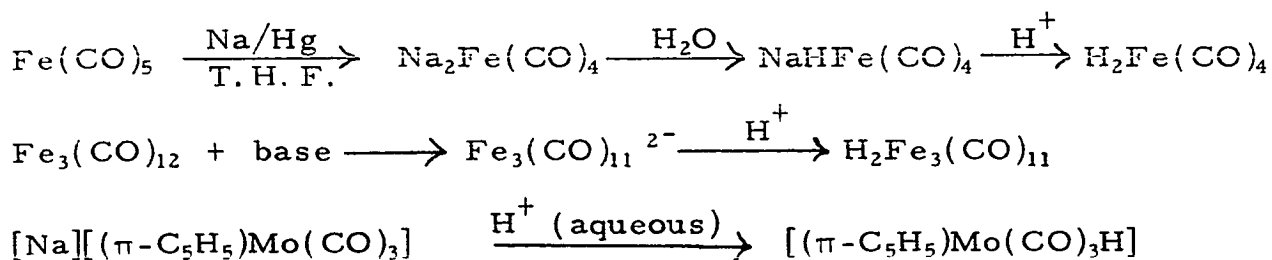
Transition metal hydrides have been prepared by a variety of methods (4), but most of the standard methods require vigorous forcing conditions (see chapter I). Direct hydrogenation at high pressure, reduction with hydride complexes of group III metals or hydrazine and reductions with alkaline refluxing alcohols are all widely used in the preparation of hydrides.

However, few transition metal hydrides have been synthesized in aqueous media with the water hydrogen as the source of the hydrido- group attached to the metal.

Reactions involving protonation of neutral complexes to give cationic hydrides have been reported (14, 15, 48, 49):



Many transition metal carbonyl hydrides may be prepared by the hydrolysis of alkali metal salts. Three examples are given below (50, 16, 51):



In the above three cases the reaction to give a hydride involves the protonation of an anionic transition metal species.

Very few reactions of cationic transition metal carbonyls with water to give neutral hydrides have been reported. Hieber and co-workers (17) have reported the reaction of $[\text{Mn}(\text{CO})_6]^+$ with water but suggested that the mechanism involves OH^- attack to give the $[\text{Mn}(\text{CO})_5]^-$ anion before final reaction with water to give $[\text{HMn}(\text{CO})_5]$. If the suggested mechanism is correct then this reaction is similar to the above reactions of anionic transition metal complexes with protons and is not actually an attack of water on a cationic carbonyl complex. Recently, Deeming and Shaw (18) reported the reaction of the cationic species $[\text{IrCl}_2(\text{CO})_2\text{L}_2]^+$ ($\text{L}=\text{PMe}_2\text{Ph}$ or AsMe_2Ph) with water to give the compound $[\text{IrCl}_2(\text{CO})(\text{COOH})\text{L}_2]$ with a carboxylate group bonded to the metal. This complex decarboxylates easily at $160\text{-}180^\circ$ to give the hydride $[\text{IrHCl}_2(\text{CO})\text{L}_2]$ and carbon dioxide. With $\text{L}=\text{PMe}_3$ the reaction of the carbonyl cation with water gives carbon dioxide and the hydride $[\text{IrHCl}_2(\text{CO})(\text{PMe}_3)_2]$. The expected intermediate

$[\text{IrCl}_2(\text{COOH})(\text{CO})(\text{PMe}_3)_2]$ was not isolated for this trimethylphosphine analogue.

The facile reaction of platinum(II) carbonyl cation $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2]^+$ with water (see chapter IV) may well be the first example of a transition metal carbonyl cation giving a neutral hydride via simple hydrolysis. Since so little information on such hydrolysis reactions is available, it seemed appropriate to attempt a detailed study of the mechanism involved in the reaction by examining the kinetics.

(b) Results and Discussion

(I) Initial Equilibrium of trans- $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2][\text{BF}_4]$ in Aqueous Media.

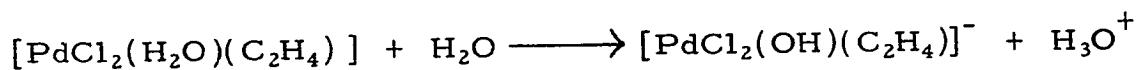
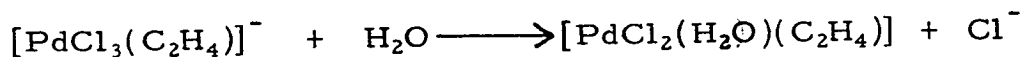
The carbonyl salt $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2][\text{BF}_4]$ was found to partially dissociate in aqueous media giving uncharacterized hydrolysis products, one of which is an acidic species. Since the original carbonyl salt can be isolated quantitatively by the removal of the solvents, an equilibrium must be involved in this hydrolysis. Because of the acidic nature of these hydrolysis products, the degree of dissociation could be estimated by pH measurements as indicated below:

SALT CONCENTRATION	WATER CONCENTRATION IN ACETONE	DEGREE OF DISSOCIATION CALCULATED FROM pH
0.08 N	14 N	9 %
0.04 N	14 N	13 %
0.02 N	14 N	23 %

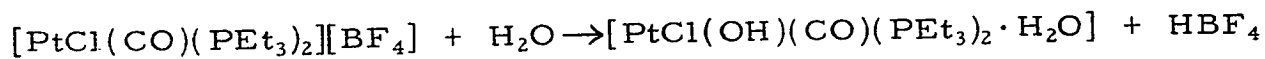
Several suggestions as to the identity of these hydrolysis products can be made. Because of its position trans to the trans-labilizing carbon monoxide ligand, the chloride might be replaced by an hydroxide ion in aqueous solution:



A similar equilibrium has been suggested by Henry (52) in his kinetic studies of palladium oxidation of olefins. He suggests an hydroxyl ion replacement of a chloride ion of the square planar palladium (II) anion $[\text{PdCl}_3(\text{C}_2\text{H}_4)]^-$:



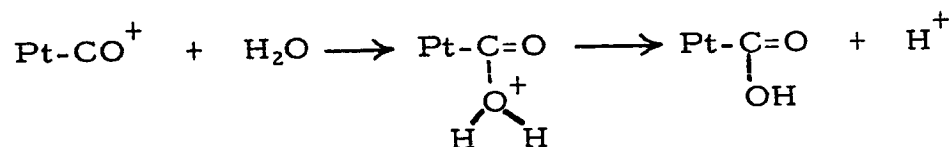
The platinum species in question might be a 5-coordinate hydroxy-platinum compound with solvent molecules in the sixth position of coordination:



The empty d_{z^2} orbital of platinum is available for bonding with nucleophiles and the cationic nature of the complex increases the chances of attack by a nucleophile.

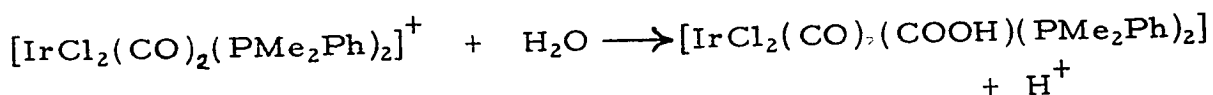
However, attack of water at the platinum is not the only possible source of the observed acidity. The carbonyl carbon can be considered as being somewhat positive in nature since the

positively charged metal will tend to retain electron density from the carbon. Hence attack by water or hydroxyl ion at the carbon would not be unexpected :



No experimental evidence for such a carboxylate group could be found since characteristic infra-red absorptions of this group would be masked by the solvent.

Deeming and Shaw (18) have isolated such a carboxylate of an iridium complex as the product of reaction of water with an iridium carbonyl cation :



As mentioned previously this carboxylate was reported to undergo thermal decomposition to give the corresponding hydride $[\text{IrHCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2]$ and carbon dioxide. Such a parallel in reactivity with the platinum system suggests that the third rationalization for the equilibrium deserves serious consideration.

(II) A Possible Reaction Mechanism

Several statements concerning the mechanism of the hydrolysis can be made from the general chemistry of the system and the

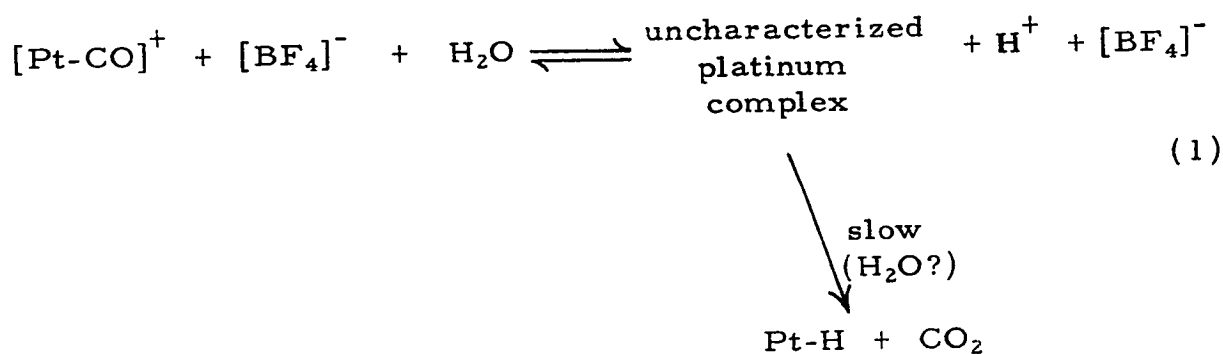
kinetic studies carried out and these are outlined below.

The reaction probably does not involve the attack by hydroxide ions. Slow hydrolysis was observed even at starting acidities of $[H^+] = 0.35$ and $0.09N$ (see figure 4), while at $[H^+] = 7 \times 10^{-3}N$, the reaction had a half-life of about 20 minutes at 64° . The hydroxide concentration at these high acid concentrations is too low to consider OH^- attack as a possible step in the reaction.

The source of the hydrogen for the platinum hydride appears to be the water hydrogens. Qualitative studies indicate that the rate of formation of the compound $PtDCl(PEt_3)_2$ is faster than the rate of exchange of $PtHCl(PEt_3)_2$ in refluxing D_2O . The only other source of hydrogen is from the triethylphosphine groups but, if this was a source of the hydrogen, one triethylphosphine group would be chemically changed or at least have a deuterium in one C_2H_5 group. 1H n. m. r. spectra of the product, $PtDCl(PEt_3)_2$, indicate the multiplets for the trans triethylphosphine groups to have no peculiarities.

As the acidity of the solution is increased the hydrolysis rate decreases. This would suggest that protonation is unlikely to be involved in the rate-determining step. If the uncharacterized platinum product formed from the equilibrium reaction with water and carbonyl cation is involved in the reaction to give the hydride,

either by further reaction with water or simple intramolecular reaction, the overall rate of reaction will depend on the concentration of this species. If the reaction of this unidentified species is the rate-determining step of the reaction, then a rate equation may be set up in terms of the carbonyl cation concentration and acid concentration.



The rate of reaction can be written as:

$$\text{Rate} = -\frac{d[\mathbf{x}]}{dt} = k[\mathbf{x}] \quad \mathbf{x} = \begin{array}{c} \text{uncharacterized} \\ \text{platinum complex} \end{array}$$

and k may or may not involve a term of water concentration, which can be assumed to remain constant in value. Using equilibrium 1, \mathbf{x} may be expressed in terms of the carbonyl cation and acid concentrations:

$$[\mathbf{x}][\text{H}^+] = K [\text{PtCO}^+][\text{H}_2\text{O}]$$

$$[\mathbf{x}] = K^1 \frac{[\text{PtCO}^+]}{[\text{H}^+]} \quad K^1 = K[\text{H}_2\text{O}]$$

The rate of disappearance of the intermediate \mathbf{x} can be approximated to the rate of reaction of the platinum carbonyl cation and

hence the rate of reaction can be written :

$$\text{Rate} = \frac{-d[x]}{dt} = \frac{-d[\text{PtCO}^+]}{dt} = \frac{kK^1 [\text{PtCO}^+]}{[\text{H}^+]} \quad (2)$$

As a rough approximation the acid concentration can be written in terms of the amount of carbonyl complex consumed :

$$[\text{H}^+]^{t=t} = [\text{PtCO}^+]^{t=0} - [\text{PtCO}^+]^{t=t}$$

Hence the rate equation becomes

$$\frac{-d[\text{PtCO}^+]}{dt} = k^1 [\text{PtCO}^+] / [\text{PtCO}^+]^{t=0} - [\text{PtCO}^+]^{t=t} \quad K^1 = kK^1$$

Integration gives the final rate equation

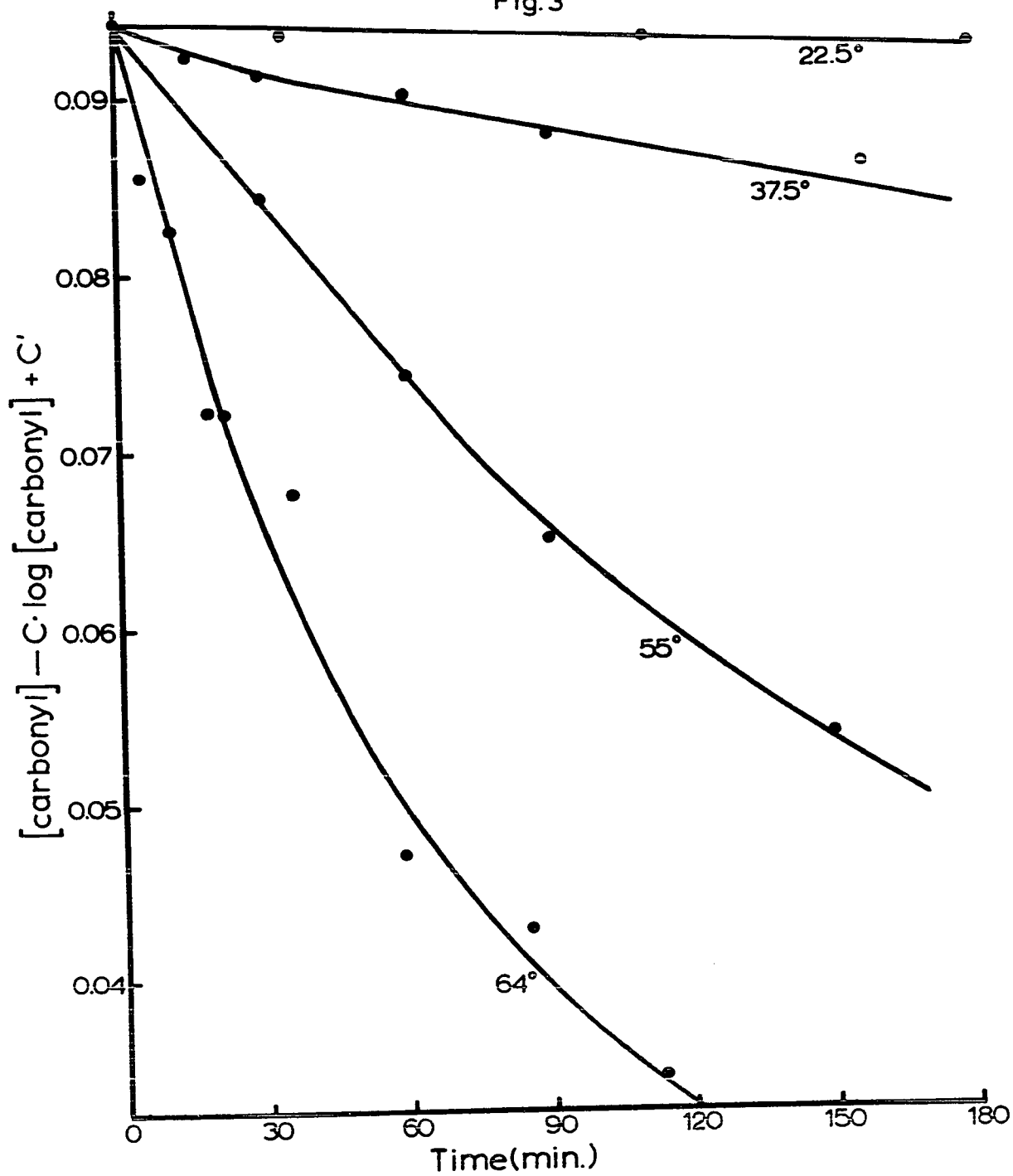
$$[\text{PtCO}^+] - k^* \log[\text{PtCO}^+] = k^1 t + C \quad (3)$$

$$k^* = 2.3 [\text{PtCO}^+]^{t=0}$$

C = constant of integration

This equation can be explained in terms of the actual chemistry involved. A simple first order reaction of the reactant x expressed in terms of the platinum carbonyl concentration gives the logarithmic term above. However, as the reaction proceeds the concentration of the acid increases and effectively acts to lower the concentration of the reactant x by driving the equilibrium I to the left. Hence the direct concentration term represents an expression for the retarding effect of the acid produced in the reaction. Plots were made of $[\text{PtCO}^+] - k^* \log[\text{PtCO}^+]$ versus time and good straight lines were obtained for the first half-life of the hydrolysis reaction for temperatures ranging from 22.5 to 64° (see diagram 3).

Fig.3



C' = A constant to adjust baseline

$C = 2.303 [\text{carbonyl}]^{t=0}$

$[\text{carbonyl}]^{t=0} = 0.084 \text{ Molar}$

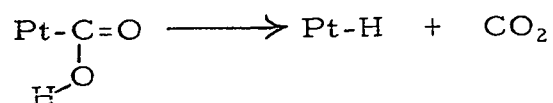
The rate equation was tested by adding sufficient acid at the beginning of the reaction so that the acid concentration throughout the reaction could be assumed constant. Hence equation 2 simplifies to :

$$\frac{-d[\text{PtCO}^+]}{dt} = k[\text{PtCO}^+]$$

and pseudo-first order kinetics must be followed. Plots of $\log [\text{PtCO}^+]$ versus time at high acid concentrations gave good straight lines (see diagram 4) as expected, although the rates were much slower than the runs at low acid concentrations.

Using the rate constants derived from equation 3, an Arrhenius plot (53) was obtained from which the overall heat of activation, ΔH_a , was measured to be approximately 20 Kcal. mole⁻¹ (see diagram 5).

The mechanism of the rate-determining step is unclear, since the postulated reactant is uncharacterized, but several suggestions can be made. If the reacting species is a carboxylate, a possible rate-determining step is the decarboxylation of a Pt-COOH group with the concerted formation of a hydride.



Such a mechanism is likely in the thermal decomposition of the iridium carboxylate previously discussed (18).

A more likely mechanism for such a system in aqueous solution (54) would be the reaction to give carbonic acid, since this involves direct reaction with water.

Fig.4

Reaction of $[\text{Pt}(\text{CO})\text{Cl}(\text{PEt}_3)_2][\text{BF}_4]$ with Water at Varying Temperatures and Hydrogen Ion Concentration

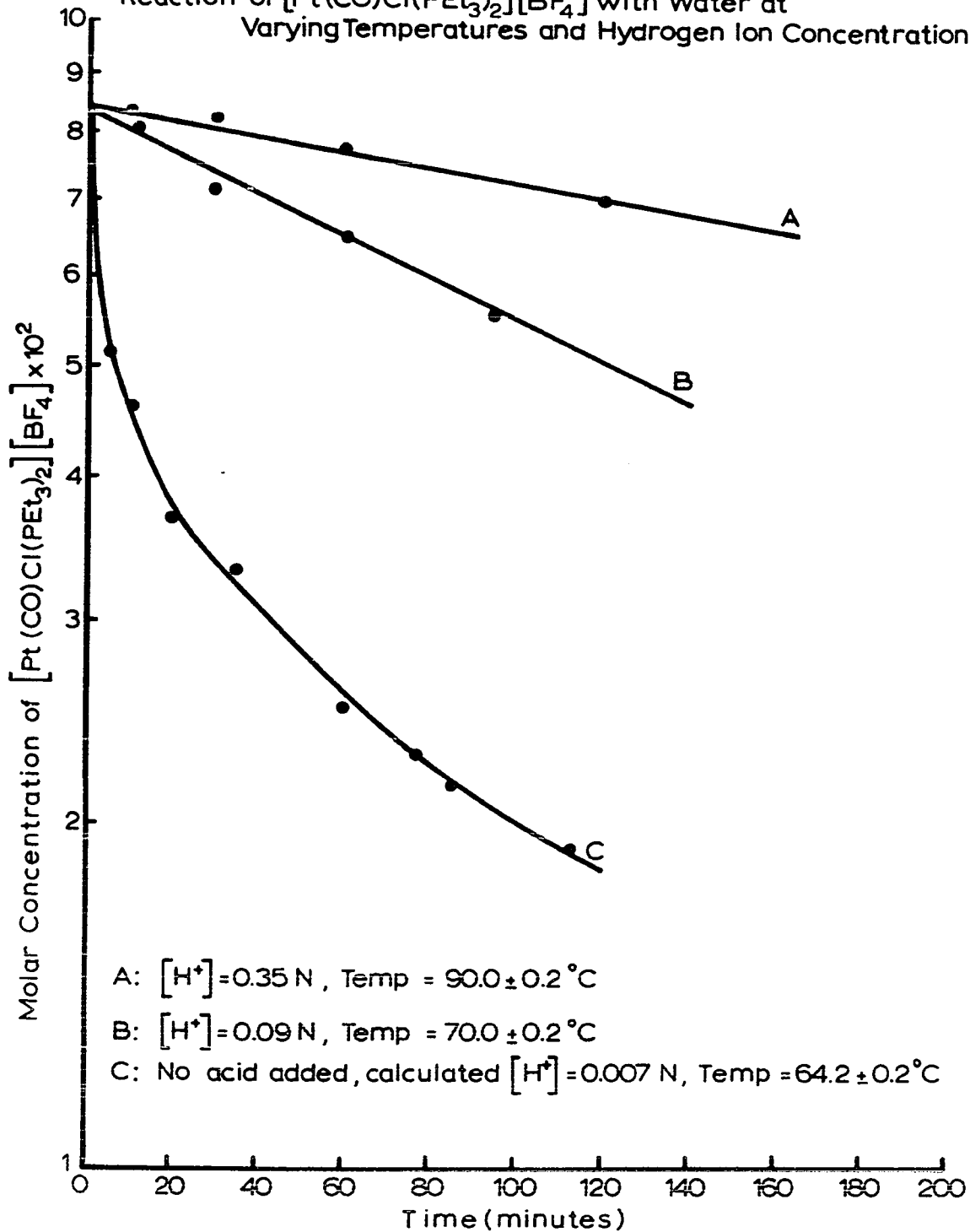
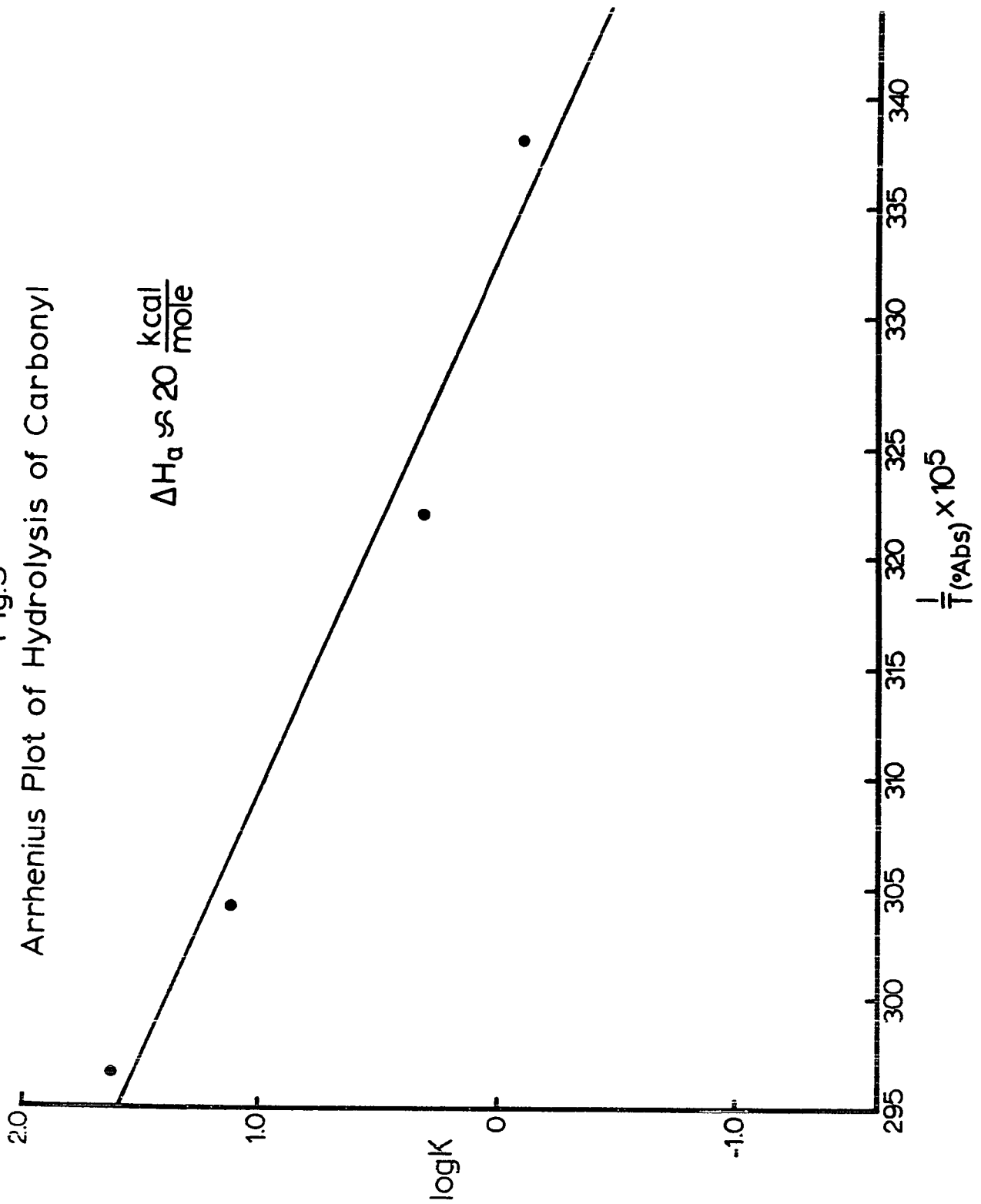
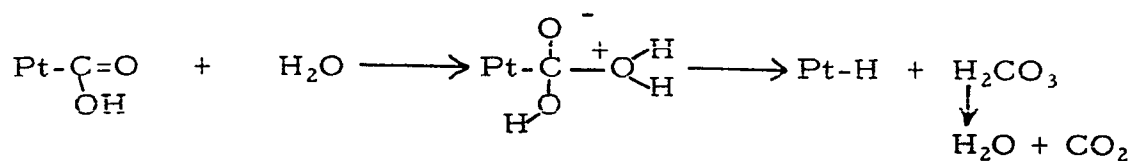
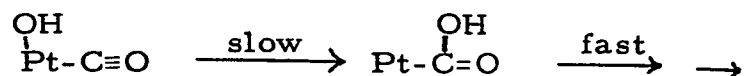


Fig.5
Arrhenius Plot of Hydrolysis of Carbonyl

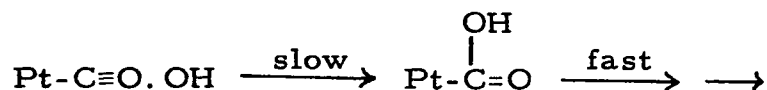




If the reacting species is a hydroxy- platinum carbonyl, existing either as an ion pair or with the hydroxyl ion bonded directly to the platinum, then reaction might occur to give a short-lived carboxylate :



or



Such reactions might well involve water molecules assisting the formation of the carboxylate compound.

(III) Conclusions

The overall mechanism that has been postulated here is only one possible scheme and others may be suggested. However, the acid effects, the evidence of an equilibrium in water, and the rate equation derived from this postulated path all fit the experimental findings. Several possible intermediates have been described for the reaction but it must be emphasized that others could be suggested.

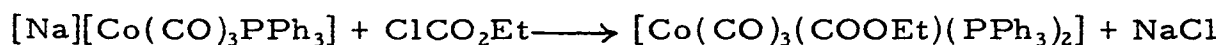
CHAPTER VI

THE CHEMISTRY OF HALOBIS(TRIPHENYLPHOSPHINE)ALKOXY-CARBONYL PLATINUM(II)

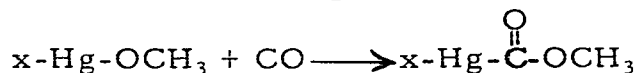
(a) Introduction

Transition metal complexes with the alkoxy carbonyl groups (-COOR) have been recently prepared by alkoxide attack on various cationic carbonyl complexes. Such reactions have been carried out with Ir(47), Co(44), Rh(43), Os(45), Mn(55) and Re(55) as central metals (see chapter IV).

Another method for the preparation of these metal alkoxy carbonyls is the reaction of chloroformate esters with sodium salts of anionic transition metal complexes (46):

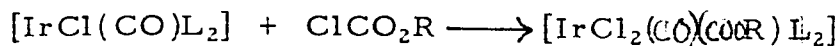


The reaction of carbon monoxide with a mercury alkoxide has been reported (56) to give a mercury alkoxy carbonyl compound with carbon monoxide inserting between the mercury-oxygen bond.



(x= acetate or chloride)

Recently Deeming and Shaw (18) have prepared alkoxy carbonyls with iridium as the central metal by the oxidative addition of chloroformates to iridium(I) complexes:

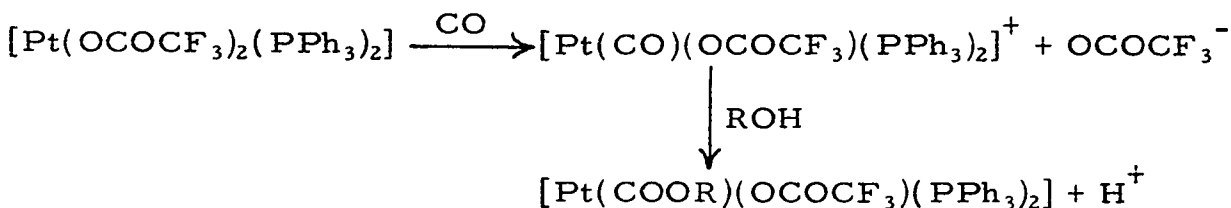


For L=PMe₂Ph, R=methyl, ethyl
or phenyl

For L=AsMe₂Ph, R=methyl or ethyl

For L=PMe₃, R=methyl

Very recently Kemmitt and co-workers (73) have reacted the platinum(II) compound [Pt(OCOCF₃)₂(PPh₃)₂] with carbon monoxide in alcoholic solution and obtained the alkoxy carbonyl compound [Pt(OCOCF₃)(COOR)(PPh₃)₂] (R=methyl or ethyl). The reaction may well have proceeded through a cationic carbonyl intermediate as shown below :



The system appears analogous to the platinum(II) system described in this text.

In chapter IV the reaction of the platinum carbonyl cation, [PtCl(CO)(PPh₃)₂]⁺, with neat methanol or ethanol was described. This chapter will be concerned with the reactivity of the platinum alkoxy-carbonyls, [PtX(COOR)(PPh₃)₂], formed from this reaction, and the analogous reactivity of iron, iridium and manganese alkoxy-carbonyls. Some interesting spectral properties of the platinum alkoxy-carbonyls will also be discussed.

(b) Results and Discussion

(I) Physical properties

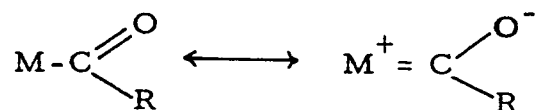
The compounds $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ (R=methyl or ethyl and X = Cl, Br or I) are air-stable crystalline compounds of high melting point (above 200°) and range in colour from white for X = Cl to pale yellow for X = I. These compounds are soluble in chloroform and methylene chloride, slightly soluble in alcohols, but insoluble in light petroleum or diethyl-ether.

(II) Infra-red Studies

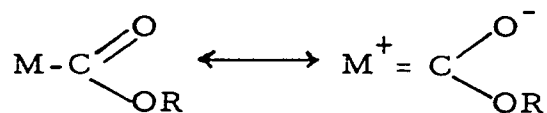
The stretching frequency of the carboxylic C=O group in the infra-red for the platinum esters are all near 1638 cm^{-1} in chloroform solution. This figure is essentially unchanged for the spectra of ethoxycarbonyls, $[\text{PtX}(\text{COOEt})(\text{PPh}_3)_2]$, run as Nujol mulls. However the methoxy- analogues, $[\text{PtX}(\text{COOMe})(\text{PPh}_3)_2]$, show a general shift to a value about 30 cm^{-1} higher as Nujol mulls. This discrepancy may be due to some crystal packing effect in the methoxycarbonyl analogue.

The stretching frequency of the C=O group in the infra-red for the various other transition metal alkoxycarbonyls are generally near the values obtained for the platinum system (see table 1). These values are generally lower than for the organic analogues (e.g. HCOOR) by about 100 cm^{-1} . Treichel et al. (57) have

attributed the lowering of $\nu(\text{C}=\text{O})$ in metal-acyl compounds compared to the organic analogue to contribution of some $d_{\pi}-p_{\pi}$ interaction between the metal and carbonyl carbon, thus lowering the C=O bond order :



Such interaction can be postulated for the transition metal alkoxy-carbonyl compounds. The apparent lowering of the C=O bond order suggests some $d_{\pi}-p_{\pi}$ bonding may be occurring thus increasing the M-C bond order :



The first x-ray study on such a compound has been recently reported by Albano et al (58). These workers have examined the compound diiodocarbomethoxycarbonyl(2,2'-bipyridyl)iridium, $[\text{IrI}_2(\text{CO})(\text{COOCH}_3)(\text{C}_{10}\text{H}_8\text{N}_2)]$. They found the ketonic C=O of the ethoxycarbonyl group to be coplanar with the square of carbon monoxide and bidentate nitrogen ligands, in good position for possible $d_{\pi}-p_{\pi}$ interaction between the metal and the ketonic carbon but attribute this position mainly to hydrogen bonding with the dipyridyl ligand. They conclude that the Ir-C bond distance (2.05 \AA°) of the iridium-methoxycarbonyl group indicates an

Table 1.

Infra-red Data on Transition Metal Alkoxycarbonyls and Organic Esters

Compound	Reference	C=O Stretching Frequency (cm^{-1})	
		Solution	Nujol Mull
$\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2$	-	1637 ^a	1664
$\text{PtBr}(\text{COOMe})(\text{PPh}_3)_2$	-	1637 ^a	1665
$\text{PtI}(\text{COOMe})(\text{PPh}_3)_2$	-	1648 ^a	1655
$\text{PtCl}(\text{COOEt})(\text{PPh}_3)_2$	-	1638 ^a	1638
$\text{PtBr}(\text{COOEt})(\text{PPh}_3)_2$	-	1638 ^a	1638
$\text{PtI}(\text{COOEt})(\text{PPh}_3)_2$	-	1638 ^a	1638
$\text{PtCl}(\text{COOMe})(\text{AsPh}_3)_2$	(27)	1639 ^a	1658
$\text{PtCl}(\text{COOEt})(\text{AsPh}_3)_2$	(27)	1636 ^a	1632
$\text{Mn}(\text{CO})_5(\text{COOEt})$	(46)	1644 ^b	-
$\text{Mn}(\text{CO})_3(\text{COOMe})(\text{PPh}_3)_2$	(46)	1612 ^b	-
$\text{Fe}(\text{CO})_2\text{Cp}(\text{COOMe})$	(62)	1665 ^c	-
$\text{IrCl}_2(\text{CO})(\text{COOMe})\text{L}_2^{\text{d}}$	(18)	1675 ^a	1677
HCOOMe	(61)	1725	-
HCOOEt	(61)	1725	-

a: chloroform solution

b: benzene solution

c: cyclohexane solution

d: L = PMe_2Ph

Ir-C linkage via a pure σ -bond and that very little $d_{\pi}-p_{\pi}$ interaction takes place. However, they base this conclusion on a comparison of the measured Ir-C length with that of the sum of the covalent radius of iridium ($r_{\text{Ir}} \cong 1.35 \text{ \AA}$) and an sp^2 -hybridized carbon ($r_{\text{C}} = 0.74 \text{ \AA}$) and also compare the measured Ir-C length with that found (59, 60) for the metal-carbon lengths of methyl platinum compounds. This interpretation of the Ir-C bond order must be classified as questionable since no good estimate of the length of a solely σ -bonded linkage of metal to acyl carbon can be made. Thus in spite of the conclusions of these workers, the lowering of the C=O stretching frequencies and hence of the bond order must strongly suggest $d_{\pi}-p_{\pi}$ interaction of the metal with the acyl carbon.

(III) Nuclear Magnetic Resonance Studies

The nuclear magnetic resonance spectra of the platinum alkoxy-carbonyls $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ (R=methyl or ethyl) were somewhat surprising. The chloromethoxycarbonyl $[\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2]$ had a methyl resonance ($\tau = 7.6$) at a chemical shift expected for such compounds (see table 2). However this resonance was split in a 1:4:1 triplet. This was attributed to a long-range coupling of the methyl protons by ^{195}Pt (34% abundance

and $l=1/2$). The possibility of this splitting being due to the ^{31}P nuclei of the phosphine ligands can be eliminated since a 1:2:1 triplet would be obtained from such a system. The measured $^{195}\text{Pt-H}$ coupling constant of 7 c. p. s. is remarkably large since this coupling is taking place through four bonds.

The ethoxycarbonyl compound $[\text{PtCl}(\text{COOEt})(\text{PPh}_3)_2]$ showed similar long-range coupling of platinum with the protons. The methylene protons are coupled with the three methyl protons ($J_{\text{H-H}} = 7.5$ c. p. s.) to give a quartet. This quartet is further complicated by ^{195}Pt coupling with the methylene protons ($J_{\text{Pt-H}} = 7$ c. p. s.) giving the multiplet illustrated in figure 7.

This long-range platinum coupling is even more surprising in the light of recent work by Cherwinski and Clark (27). They report the analogous alkoxy-carbonyls with triphenylarsine replacing the triphenylphosphine ligands, $[\text{PtCl}(\text{COOR})(\text{AsPh}_3)_2]$ ($\text{R}=\text{methyl or ethyl}$), and indicate that no long-range platinum coupling to the methyl protons of the $-\text{COOMe}$ group or the methylene protons of the $-\text{COOCH}_2\text{CH}_3$ group is observed (see figures 6 and 7).

This difference in the platinum-hydrogen coupling constant must be explained in terms of the change in ligands from triphenylphosphine to triphenylarsine. Both these ligands function as bases, donating electron density via a σ -bond to the central metal.

However they also act as π -bond acceptors (28). The empty 3d-orbitals of the phosphorus atoms overlap with filled non-bonding d-orbitals of the transition metal. The empty arsenic 4d-orbitals might be expected to be even more capable of overlap with the filled d-orbitals of the metal since they are more similar in size to the metal d-orbitals. The triarylphosphines are generally accepted to have greater coordinating affinities than the arsines (28, 63) probably because they are

Table 2

Proton NMR of Alkoxy-carbonyls

Compound	Reference	Solvent	Chemical Shifts (τ) of Alkoxy-carbonyls		Coupling Constant (c. p. s.)	$\frac{J}{\nu_{\text{Pt-H}}}$
			CH ₃	CH ₂		
PtCl(COOMe)(PPh ₃) ₂	-	CH ₂ Cl ₂	7.6(t) ^a	-	7	-
PtBr(COOMe)(PPh ₃) ₂	-	CH ₂ Cl ₂	7.6(t) ^a	-	7	-
PtCl(COOEt)(PPh ₃) ₂	-	CH ₂ Cl ₂	-	7.3(m) ^b	7	7.5
			9.5(t)	-	<1	7.5
PtCl(COOMe)(PEt ₃) ₂	-	C ₆ H ₆	7.1(t) ^a	-	7	-
PtCl(COOMe)(AsPh ₃) ₂	(27)	CH ₂ Cl ₂	7.5(s)	-	<1	-
PtCl(COOEt)(AsPh ₃) ₂	(27)	CH ₂ Cl ₂	-	7.1(q)	<1	7.5
			9.5(t)	-	0	7.5
IrCl ₂ (CO)(COOMe)L ₂ ^c	(18)	-	6.8(s)	-	-	-
IrCl ₂ (CO)(COOEt)L ₂	(18)	-	-	6.3(q)	-	7.2
			9.0(t)	-	-	7.2
Fe(CO) ₂ Cp(COOMe)	(62)	CS ₂	6.6(s)	-	-	-
Mn(CO)(NO)Cp(COOMe)	(62)	CS ₂	6.5(s)	-	-	-

s=singlet a) The methyl protons are split by ¹⁹⁵Pt (34% abundance) with I=1/2 into a 1:4:1 triplet.

t=triplet

q=quartet

m=multiplet

c) L=PMe₂Ph

Fig.6

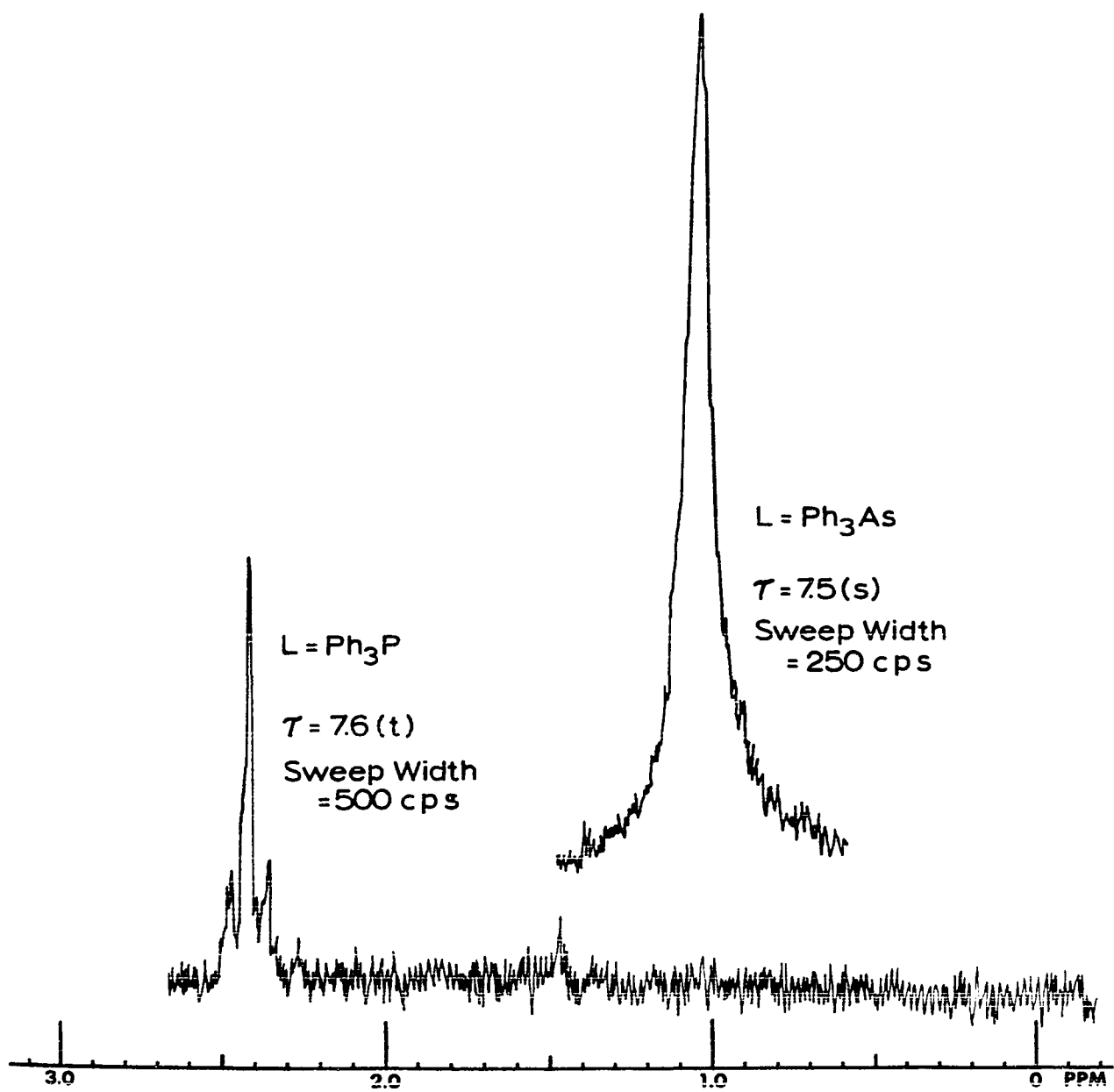
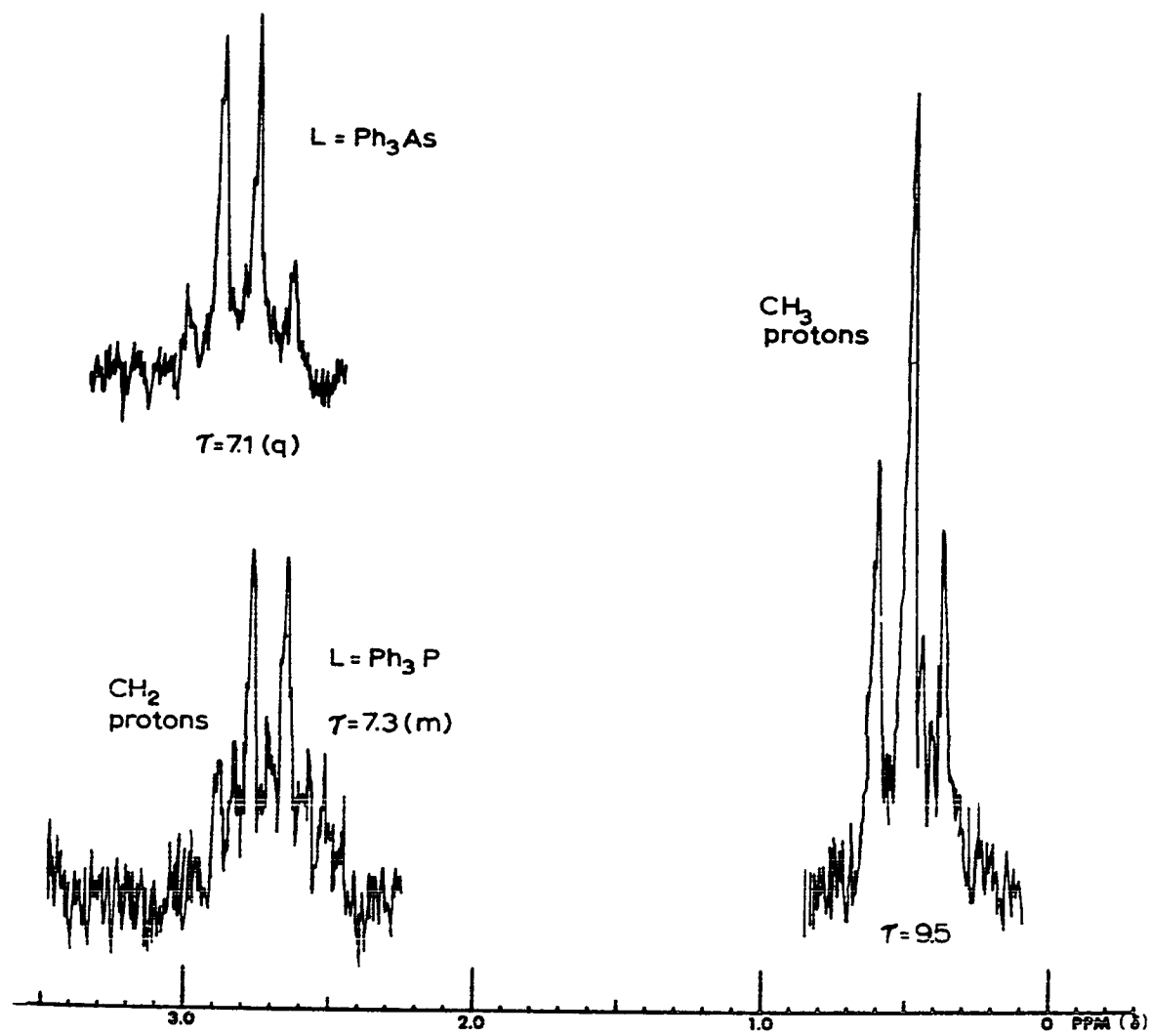
 ^1H N.M.R. : $\text{trans} - [\text{PtCl}(\text{COOMe})\text{L}_2]$ 

Fig.7 ^1H N.M.R. : $\text{trans} - [\text{PtCl}(\text{COOEt})\text{L}_2]$ 

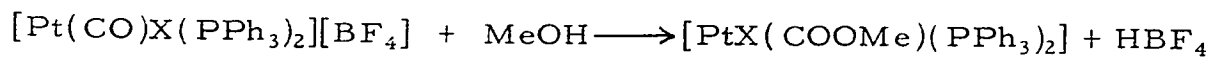
better σ -donors and less capable π -acceptors. Hence in this platinum system, the triphenylarsine ligands would be expected to leave the platinum with a lower net electron density than the triphenylphosphine ligands. This depletion of electron density must be used to explain the lesser ability of the platinum to couple with the methyl protons of the methoxycarbonyl moiety for the compound $[\text{PtCl}(\text{COOMe})(\text{AsPh}_3)_2]$ compared to its triphenylphosphine analogue. This drop in coupling constant is remarkably large and is a dramatic indication of the differences of electron density at the platinum with differing surrounding ligands.

(IV) Reactions of $[\text{PtX}(\text{COOR})\text{PPh}_3)_2]$ (X=Cl, Br or I and
R=methyl or ethyl)

(i) Reaction with Aqueous Acids

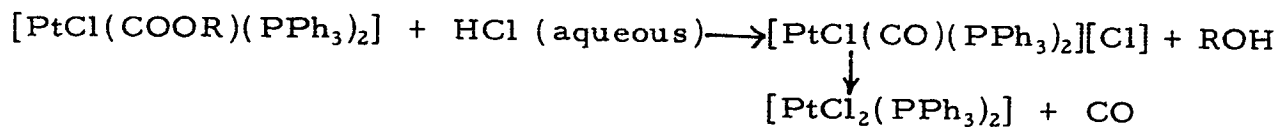
The compounds $[\text{PtX}(\text{COOMe})(\text{PPh}_3)_2]$ (X = Cl, Br or I) reacted with 48% aqueous fluoroboric acid to give the carbonyl cation $[\text{PtX}(\text{CO})(\text{PPh}_3)_2]^+$ stabilized by the fluoroborate anion.

Methanol was also characterized in the reaction product. This acidification reaction is the reverse of the original reaction of methanol with the carbonyl cation to give the methoxycarbonyl:



Similar results were obtained for the ethoxy- analogue, with the cationic carbonyl and ethanol being produced on treatment with aqueous fluoroboric acid. Aqueous HCl could be used instead of HBF_4 . The final products isolated were the alcohols and the

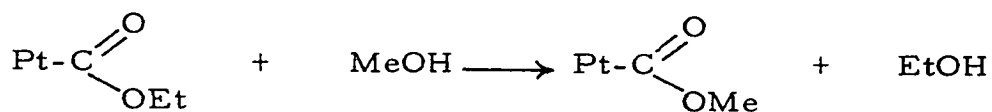
dichloro-compound $[\text{PtCl}_2(\text{PPh}_3)_2]$. Apparently this reaction proceeded via a carbonyl cation to the dichloride with a chloride ion replacing the carbon monoxide ligand :



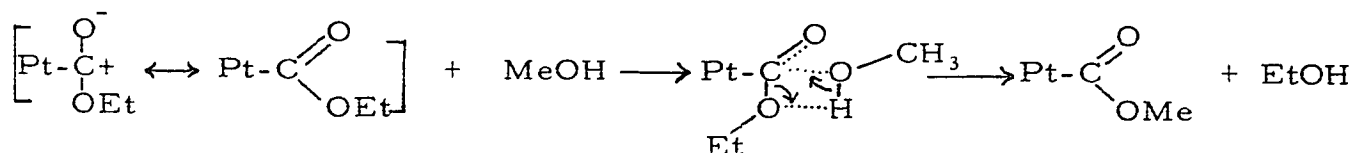
The production of cationic carbonyls by acidification of the alkoxy-carbonyl metal complexes is a general reaction for most transition metal alkoxy-carbonyls (46, 47, 18) .

(ii) Reaction of $[\text{PtCl}(\text{COOEt})(\text{PPh}_3)_2]$ with Methanol

The ethoxycarbonyl $[\text{PtCl}(\text{COOEt})(\text{PPh}_3)_2]$ was heated at 65° for 12 hours with methanol. Reaction occurred and the ethoxy-group was replaced by the methoxy ion

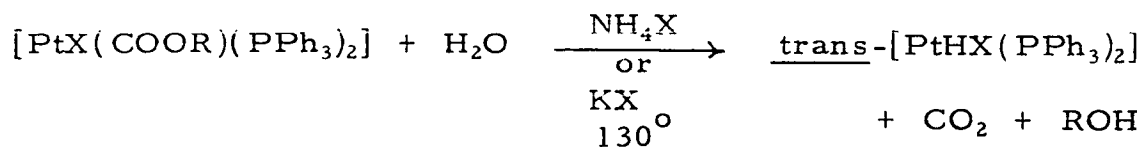


Such reactivity can best be explained in terms of a methanol attack at the electro-positive acyl carbon :



(iii) Reaction of $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ with Water (X=Cl, Br or I and R=methyl or ethyl)

The platinum alkoxy-carbonyl compounds undergo a novel reaction with water :



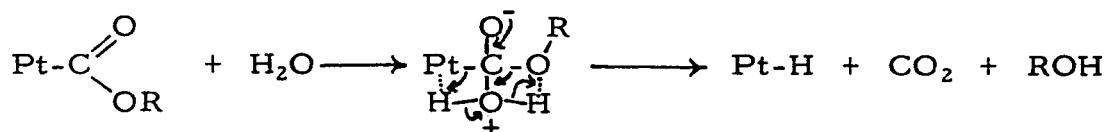
For X = Cl the products of this reaction have been separated and near quantitative yields of carbon dioxide and platinum hydride, $[\text{PtHCl}(\text{PPh}_3)_2]$, were isolated and the alcohols methanol (if R = methyl) or ethanol (if R=ethyl) were characterized by n. m. r. and infra-red spectroscopy. The reaction was catalyzed by the chloride salts KCl, NH_4Cl and NMe_4Cl and for R = methyl no reaction was observed unless a salt was present. For R=ethyl the reaction required somewhat less vigorous conditions (100°) and the effect of the salt was less marked. Although best yields of the hydride were obtained with the salt present, lower yields of the hydride were obtained along with uncharacterized decomposition materials without the salt present.

For X = Br or I the yields of hydride from the hydrolysis were much lower even in the presence of halide salts, and more decomposition occurred than in the chloro- analogue.

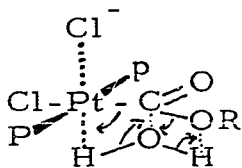
Such hydrolysis reactions can be understood when two other facts are also considered :

- 1) The alkoxy group of the platinum alkoxy carbonyl exchanges with other alkoxy groups.

2) Trans-[PtCl(CO)(PEt₃)₂][BF₄] reacts directly with water to give the hydride, possibly via a short-lived carboxylic acid. The lability of the alkoxy group towards exchange with other alcohols suggests that a similar exchange could occur with water giving a short-lived carboxylate which might then decarboxylate to give a hydride. Possibly a concerted reaction of the alkoxy-carbonyl with water leads directly to the platinum hydride, carbon dioxide and the alcohol :

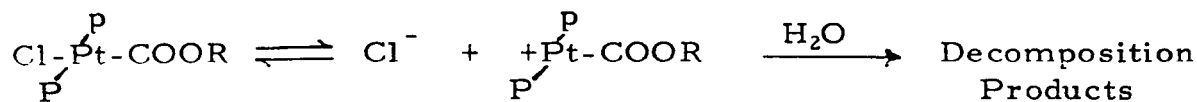


The function of the halide salt is uncertain. While catalysis may be due to the cation fulfilling a role similar to that of a proton in the acid-catalysed hydrolysis of organic esters, the fact that X⁻ is the common species strongly favours anionic catalysis. Coordination of X⁻ to the platinum of the alkoxy-carbonyl may well facilitate both decarboxylation and hydride formation through a transition state such as :



The salt might function merely to stabilize the compound at high temperatures. If an equilibrium exists with the halide ion as shown below then the dissociated platinum species might further

react leading to decomposition at high temperature in the non-homogeneous water mixture.

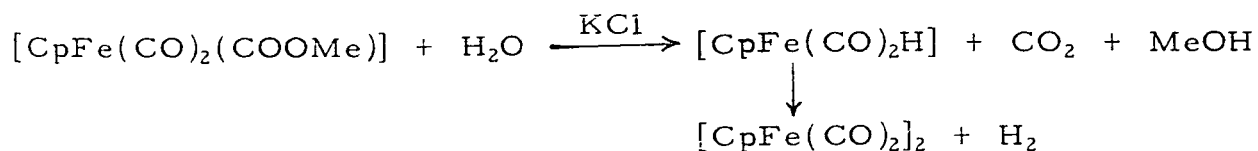


The presence of excess halide would drive the equilibrium to the left preventing decomposition and enabling an attack of water at a site which would lead to hydride production.

At this point it seemed worthwhile to attempt this hydrolysis reaction on alkoxycarbonyls of other transition metals to see if such reactivity was general for the M-COOR group.

(V) Reactions of Alkoxycarbonyls of Iron, Iridium and Manganese With Water

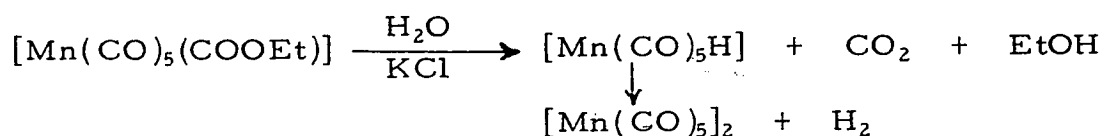
The iron methoxycarbonyl $[\text{CpFe}(\text{CO})_2(\text{COOMe})]$ (62) reacted completely with water at 45° in 20 minutes. The products consisted of the hydride $[\text{CpFe}(\text{CO})_2\text{H}]$ (obtained in 50% yield), the dimeric compound $[\text{CpFe}(\text{CO})_2]_2$, carbon dioxide and methanol. A trace of methyl formate was also isolated. The scheme of reaction probably was :



The iron hydride $[\text{CpFe}(\text{CO})_2\text{H}]$ is reported (74) to decompose to the dimer $[\text{CpFe}(\text{CO})_2]_2$ at temperatures used in the experiment,

thus accounting for its formation. Carbon dioxide was collected nearly quantitatively suggesting almost complete initial reaction to the hydride. The reaction was repeated without the salt catalyst and no differences were observed in the reaction.

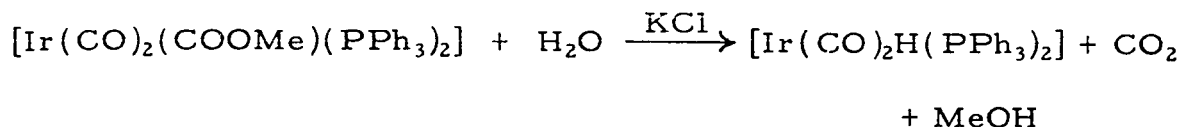
The manganese ethoxycarbonyl $[\text{Mn}(\text{CO})_5(\text{COOEt})]$ was reacted with a KCl solution of water for 5 hours at 75° . The manganese hydride $[\text{Mn}(\text{CO})_5\text{H}]$ was obtained in approximately 60% yield along with its decomposition product $[\text{Mn}(\text{CO})_5]_2$. Carbon dioxide was isolated near quantitatively and ethanol was identified as a product by infra-red and n. m. r. spectroscopy. A trace of ethyl formate was also isolated. The reaction apparently follows the scheme :



The reaction was repeated without the salt catalyst and somewhat higher yields of ethyl formate were observed but the reaction was basically unchanged.

The iridium methoxycarbonyl $[\text{Ir}(\text{CO})_2(\text{COOMe})(\text{PPh}_3)_2]$ was heated at 130° for 18 hours with saturated KCl- H_2O solution. Carbon dioxide, methanol and an unstable solid, tentatively assigned as $[\text{Ir}(\text{CO})_2\text{H}(\text{PPh}_3)_2]$ ($\nu_{\text{Ir-H}} = 2105 \text{ cm}^{-1}$ and $\delta_{\text{Ir-H}} = 815 \text{ cm}^{-1}$), were isolated. A reaction scheme similar to those above can be

suggested for the iridium methoxycarbonyl hydrolysis.



However, similar reactions in dilute KCl solution or salt-free water yielded only uncharacterized decomposition products. No reaction was observed in saturated KCl solutions at 90° for 18 hours.

(VI) Conclusions

It appears that the reaction of transition metal alkoxy-carbonyls with water to give hydrides is quite general. Reaction has occurred for transition metals in differing oxidation states, with a variety of surrounding ligands, and differing coordination numbers. Because of the general nature of the hydrolysis, the most likely position of attack of water is at the alkoxy-carbonyl group and specifically at the acyl carbon. Attack of water at the various central metals seems unlikely since the metals with different oxidation states and surrounding ligands would be unlikely to all act similarly as a site for water attack.

The function of the salt remains uncertain but as the ease of hydrolysis increases the salt effect is less marked. Only in the platinum and iridium systems is the salt necessary for hydrolysis and it is not possible at this stage to differentiate between several possible explanations of its function.

CHAPTER VII
EXPERIMENTAL SECTION

1. Apparatus and Techniques

Standard high-vacuum techniques (71) were used. Reactions were performed in silica or thick-walled Pyrex glass carius tubes. All reactions not involving sealed tubes were carried out under a nitrogen atmosphere unless otherwise stated.

Infra-red spectra were recorded with Beckman IR 10 and IR 7 spectrometers with spectra recorded from 4000 to 250 cm^{-1} with cesium iodide optics and calibrated against polystyrene film. For the work on kinetics (see section VII, 9) spectra were recorded with Beckman IR-tran solution cells. ^1H and ^{19}F nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100 and DP-60 spectrometers. Chemical shifts were reported relative to tetramethylsilane and Freon 11 (CFCl_3).

Melting points were recorded by capillary methods and were corrected unless otherwise stated. Conductance measurements were made with a dip-type cell of constant 0.1 cm^{-1} connected to a conductivity bridge, Model RC 18, Industrial Instruments Inc.

Microanalyses were carried out by Dr. A. B. Gygli, Toronto, and the Schwarzkopf Microanalytical Laboratory, Inc., New York, N. Y.

2. Preparation of Starting Materials

a) Preparation of trans-[PtHCl(PEt₃)₂]

(i) Preparation of triethylphosphine

Triethylphosphine was prepared by a modification of the method of H. Hibbert (64) and all steps were carried out under nitrogen. A Grignard reagent was made from magnesium turnings (130 g., 5.4 moles) and ethyl bromide (544 g., 5.0 moles) in 1.5 litres of anhydrous diethyl ether. Phosphorus trichloride (115 g., 0.84 moles) in 250 ml. of anhydrous ether was added dropwise at temperatures between -30 and -40^o. The mixture was then allowed to warm to room temperature. A saturated aqueous solution of ammonium chloride (1.5 litres) was added dropwise with stirring and the ether layer was removed from the aqueous layer via a separatory funnel. Fractional distillation of the ether layer gave triethylphosphine (70 g., 75% yield).

(ii) Preparation of cis-[PtCl₂(PEt₃)₂]

The method of K. A. Jensen was used for this preparation (65). Potassium chloroplatinite (4.6 g., 11 mmoles) in 55 ml.

of water was shaken for one hour with triethylphosphine (2.6 g., 22 mmoles). A reddish-brown precipitate of $[\text{Pt}(\text{PEt}_3)_4][\text{PtCl}_4]$ was formed and on heating for 10 minutes at 100° changed to a grey solid. The solid was filtered, washed with water and dried. It was then extracted with diethyl ether and the residue recrystallized from alcohol giving white crystals of cis- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (2.8 g., 5.6 mmoles). The ether was evaporated from the yellow extract giving yellow crystals of trans- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (1.5 g., 3.0 mmoles).

(iii) Preparation of trans- $[\text{PtHCl}(\text{PEt}_3)_2]$

The method of Chatt and Shaw (2) was used for this preparation. 1.0 ml. of 85% hydrazine hydrate solution was added to a suspension of cis- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (2.8 g., 5.6 mmoles) in 22 ml. water. The mixture was heated on a steam bath for one hour. A grey precipitate formed and was filtered and dried. Recrystallization from light petroleum ether gave white needles of trans- $[\text{PtHCl}(\text{PEt}_3)_2]$ (1.9 g., 4.1 mmoles).

Infra-red Spectrum: $\nu_{(\text{Pt-H})} = 2210$, $\delta_{(\text{Pt-H})} = 835 \text{ cm}^{-1}$

b) Preparation of trans- $[\text{PtHCl}(\text{PPh}_3)_2]$

(i) Preparation of cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$

The method of Bailar (66) was used for this preparation.

A solution of potassium chloroplatinite (2.0 g., 4.8 mmoles) in 25 ml. water was added dropwise with stirring to a boiling solution of triphenylphosphine (2.5 g., 9.6 mmoles) in 30 ml. of ethanol. The mixture was stirred for 2 hours at 60° and the white crystals of cis-[PtCl₂(PPh₃)₂] (3.6 g., 4.6 mmoles) were filtered and washed with hot water, hot ethanol and diethyl ether.

(ii) Preparation of trans-[PtHCl(PPh₃)₂]

The method of Bailar (66) was used for this preparation. To a solution of cis-[PtCl₂(PPh₃)₂] (3.6 g., 4.6 mmoles) in 90 ml. ethanol, 2.6 g. of 85% hydrazine hydrate solution was added. The mixture was refluxed for 5 minutes and then 2.2 g. acetic acid, 36 ml. water and 20 ml. ethanol were added. The white crystals formed were filtered and recrystallized from a 1:2 mixture of benzene and ethanol giving trans-[PtHCl(PPh₃)₂] (2.4 g., 3.2 mmoles).

Infra-red Spectrum : $\nu_{(\text{Pt-H})} = 2200$, $\delta_{(\text{Pt-H})} = 830 \text{ cm}^{-1}$

c) The preparation of cis-[PtBr₂(PPh₃)₂]

To a solution of potassium chloroplatinite (0.50 g., 1.2 mmoles) in 50 ml. water, 50 ml. of a saturated aqueous solution of sodium bromide was added. The mixture was stirred for one

hour at 90° and the solution became deep brown in colour. A solution of triphenylphosphine (0.63 g., 2.4 mmoles) in 50 ml. ethanol was added dropwise with stirring and the mixture warmed at 40° for one hour. The precipitate was filtered and washed with alcohol, diethyl ether, and light petroleum ether leaving pale yellow crystals of cis-[PtBr₂(PPh₃)₂] (0.97 g., 1.1 mmoles).

d) The preparation of cis-[PtI₂(PPh₃)₂]

The procedure of 2c was followed except that sodium iodide was used instead of sodium bromide. A near quantitative yield of the bright yellow compound, cis-[PtI₂(PPh₃)₂], was obtained.

e) The preparation of cis-[PtBr₂(PEt₃)₂]

A solution of 3.0 g. sodium bromide in 50 ml. water was added dropwise to a solution of potassium chloroplatinite (1.0 g., 2.3 mmoles) in 25 ml. water. The solution was stirred at 40° for 2 hours. Triethylphosphine (0.54 g., 4.6 mmoles) was added and the mixture refluxed for 15 minutes. The yellow precipitate was filtered and washed with water, dried and extracted with light petroleum ether. The white solid residue was recrystallized from ethanol giving white crystals of cis-[PtBr₂(PEt₃)₂] (0.5 g., 0.8 mmoles).

The petroleum ether was evaporated from the yellow extract giving yellow crystals of trans-[PtBr₂(PEt₃)₂] (0.6 g., 1.0 mmoles).

f) Preparation of cis-[PtI₂(PEt₃)₂]

The method of Jensen (65) was used for this preparation. A solution of 2.0 g. sodium iodide in 10 ml. water was added to a solution of cis-[PtCl₂(PEt₃)₂] (0.19 g., 0.37 mmoles) in 10 ml. ethanol. The mixture was stirred at 25° for 30 minutes. The yellow solid formed was filtered, washed with an ethanol-water mixture and dried. The compound cis-[PtI₂(PEt₃)₂] (0.23 g., 0.34 mmoles) was not recrystallized.

Infra-red : $\nu_{(\text{Pt-P})} = 415 \text{ and } 435 \text{ cm}^{-1}$

g) Preparation of tetrafluoroethylene

Teflon chips in a silica tube were heated under vacuum at 500°. The volatile products were fractionated through traps at -96, -125 and -196°. The trap at -196° contained perfluoroethylene and a trace of silicon tetrafluoride, identified by the sharp Si-F stretch in the infrared region at 1020 cm⁻¹. The silicon tetrafluoride was removed by several condensations of the mixture over moist potassium fluoride. The remaining volatile product was spectroscopically pure tetrafluoroethylene (67).

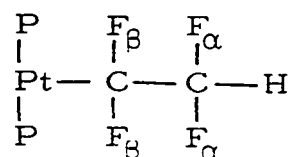
3. Reactions of trans-[PtHCl(PEt₃)₂] with Tetrafluoroethylene

(i) Reaction in Stainless Steel Autoclave

Trans-[PtHCl(PEt₃)₂] (0.6 g.) in 10 ml. benzene was heated with C₂F₄ (1.5 g.) at 120° for 48 hours in a stainless steel autoclave. After removal of excess C₂F₄ the benzene solution was evaporated and the resulting yellow oil extracted with methanol. Evaporation of the methanol extract gave an oil which slowly formed white crystals of trans-[PtCl(PEt₃)₂(CF₂CF₂H)]. These were washed with very small volumes of methanol, collected (0.42 g., 58% yield) and recrystallized from methanol, using a seed crystal to aid crystallization. The product was extremely soluble in light petroleum ether, benzene, or chloroform but rather less soluble in methanol, mp 78-79°. Anal. Calcd for C₁₄H₃₁ClF₄P₂Pt : C, 29.6; H, 5.5; F, 13.4. Found: C, 29.6; H, 5.6; F, 13.7.

The infra-red absorptions (Table 5) due to C-F vibrations are similar to those observed in other compounds containing an M-C₂F₄H grouping (7, 8). In addition to the expected ethyl proton resonance, the ¹H nmr spectrum in deuteriochloroform solution consisted of a 1:2:1 triplet (J = 56 cps) centered at -5.43 ppm, each component of which was split into a 1:2:1 triplet (5 cps). The integrated intensities of the triplets and the ethyl resonance

were in the ratio 0.9:30. The ^{19}F nmr spectrum in CFCl_3 solution consisted of two multiplets of equal intensity centered at +72.3 and +126.3 ppm. The high-field resonance was a broad doublet ($J = 55.5$ cps; width at half-height, 11 cps) whose ^{195}Pt (33% abundance) satellites (coupling constant, 106 cps) overlapped the main peaks producing a 1:4:4:1 quartet. The low-field resonance was a 1:2:1 triplet (coupling constant, 23.2 cps) with ^{195}Pt satellites (coupling constant, 470 cps). Each component of the triplet was split into a doublet (coupling constant, 4.8 cps) and again into overlapping triplets (coupling constant, 4.5 cps) producing a 1:3:3:1 quartet. These spectra are consistent with the following interpretation.



The high-field resonance is due to the α fluorine atoms and the low-field resonance to the β fluorine atoms. The coupling constants are $J_{\text{H-F}_\alpha} = 55.5$, $J_{\text{H-F}_\beta} = 4.8$, $J_{\text{F}_\alpha\text{-F}_\beta} = 4.5$, $J_{\text{Pt-F}_\alpha} = 106$, $J_{\text{Pt-F}_\beta} = 470$, $J_{\text{P-F}_\beta} = 23.2$ cps. $J_{\text{Pt-H}}$ was not observed because of poor signal-to-noise ratio, but all other coupling constants are less than 2 cps. The magnitudes of the various coupling constants and the assignments of the spectra are in agreement with previous

results on other compounds containing an M-CF₂CF₂H grouping (7, 8).

(ii) Reaction in Pyrex Glass at 80°

Trans-[PtHCl(PEt₃)₂] (1.0 g.) in 20 ml. of undried benzene was heated with C₂F₄ (1.0 g.) at 80° for 48 hours in a Pyrex tube. Insoluble crystals of [Pt₂Cl₂(PEt₃)₄][BF₄]₂ (0.06 g., 5% yield) were filtered from the benzene solution and characterized as in section 5(a).

The benzene solution was evaporated to about 5 ml. and an equal volume of cyclohexane added. A white precipitate formed and was filtered giving trans-[PtCl(CO)(PEt₃)₂][SiF₅] and its [BF₄]⁻ analogue (0.1 g.). The characterization of this compound has been described (20). Evaporation of the benzene-cyclohexane solution gave a mixture of trans-[PtCl(PEt₃)₂(CF=CF₂)] and trans-[PtCl(PEt₃)₂(C{CF₂H}=CF₂)] (0.5 g.) in approximately 3:1 ratio. The characterizations of these fluorovinylplatinum(II) compounds have been previously described (9).

4. Reactions of trans-[PtHCl(PPh₃)₂] with Tetrafluoroethylene

(i) Reaction in glass vessel at 120°

Trans-[PtHCl(PPh₃)₂] (0.7 g.) in 25 ml. of benzene was

heated with tetrafluoroethylene (0.5 g.) at 120° for 48 hours in a Pyrex tube. The gaseous products were examined by infra-red spectroscopy and contained the starting material C_2F_4 and another volatile product tentatively identified as SiF_4 from its characteristic Si-F vibration at 1020 cm^{-1} . The benzene solution was evaporated and the residues were extracted with chloroform, leaving 0.005 g. of white residue showing infra-red absorptions characteristic of SiF_6^{2-} and BF_4^{-} . Fractional precipitation by addition of light petroleum ether to the chloroform extract gave 0.15 g. (yield 19%) of trans- $[PtCl(CO)(PPh_3)_2][BF_4]$ as the first precipitate. This product was recrystallized from benzene as white crystals, insoluble in light petroleum but soluble in chloroform or methanol, mp $278-282^{\circ}$ (with decomp.)

Anal. Calcd for $C_{37}H_{30}BClF_4OP_2Pt$: C, 51.2; H, 3.5; B, 1.24. Found: C, 51.2; H, 3.7; B, 1.29. In addition to absorptions due to the cation (Table 5), the infrared spectrum of this product had absorptions characteristic of BF_4^{-} at $1090(s)$ and $1050(vs, b)\text{ cm}^{-1}$. The molar conductivity of a $1.0 \times 10^{-3}M$ solution in nitromethane was $74\text{ ohm}^{-1}\text{ cm}^2$ at 25° .

Evaporation of the chloroform-petroleum filtrate gave 0.45 g. of an approximately 3:1 mixture of trans- $[PtCl(PPh_3)_2(CF=CF_2)]$ and trans- $[PtCl(PPh_3)_2(C\{CF_2H\}=CF_2)]$. These products were

separated by chromatography on Florisil using 50% benzene in chloroform as eluent and recrystallized from an ethanol-chloroform mixture as white needles, insoluble in light petroleum, slightly soluble in benzene, and soluble in chloroform, mp 253-255^o and 248-250^o respectively.

Anal. Calcd for C₃₈H₃₀ClF₃P₂Pt: C, 54.5; H, 3.6; F, 6.8. Found: C, 55.0; H, 3.8; F, 7.6. Calcd for C₃₉H₃₁ClF₄P₂Pt: C, 54.0; H, 3.6. Found: C, 53.9; H, 3.5. The patterns of C-F absorptions (Table 5) are similar to those reported previously (9) for their triethylphosphine analogues. Their solubilities were too low for ¹⁹F nmr studies. The above reaction was repeated with heating at 120^o for 48 hours in a silica tube to which a few grams of chromatographic silica gel (previously dried at 800^o in a muffle furnace) had been added. Trans-[PtCl(PPh₃)(CF=CF₂)] and trans-[PtCl(PPh₃)₂(C{CF₂H}=CF₂)] were formed, but no salts of trans-[PtCl(CO)(PPh₃)₂]⁺ were detected.

(ii) Reaction at low temperature

The above reaction was repeated with heating at 80^o for 48 hours. Again the vinylic compounds trans-[PtCl(CF=CF₂)(PPh₃)₂] and trans-[PtCl(C{CF₂H}=CF₂)(PPh₃)₂] were isolated in the same proportions as above. However, no carbonyl complex as described

above was isolated. A low yield (20%) of the benzene-insoluble salt $[\text{Pt}_2\text{Cl}_2(\text{PPh}_3)_4][\text{BF}_4]_2$ was filtered from the benzene solution and characterized as in section 5a(iii).

(iii) Reaction in a Stainless Steel Autoclave

Trans- $[\text{PtHCl}(\text{PPh}_3)_2]$ (1.0 g.) in 20 ml. benzene was heated with C_2F_4 (1.5 g.) at 120° for 48 hours in a stainless steel autoclave. The solution obtained was filtered and the benzene evaporated. An infra-red spectrum of the crude products indicated no absorption at 2100 cm^{-1} assigned to the carbonyl cation $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+$ isolated in the identical reaction in glass (see 4(i)). Work up of the residues in a manner identical to that of 4(i) gave solely the two vinyl complexes trans- $[\text{PtCl}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2]$ (0.5 g.) and trans- $[\text{PtCl}(\text{C}\{\text{CF}_2\text{H}\}=\text{CF}_2)(\text{PPh}_3)_2]$ (0.15 g.). No other products were isolated.

5. Preparation of the compounds $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4][\text{BF}_4]_2$

a) Reaction of cis- $[\text{PtX}_2(\text{PR}_3)_2]$ with Boron Trifluoride

(i) Reaction of cis- $[\text{PtCl}_2(\text{PEt}_3)_2]$

Cis- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (0.175 g., 0.35 mmoles) in 5 ml. dry chloroform was shaken with dry boron trifluoride (0.3 g., 4 mmoles) at 25° in a silica tube. An almost colourless oil

precipitated at once, but shaking was continued for 15 hours. The products were evaporated to dryness under vacuum and the residue extracted with nitromethane. Evaporation of the extract to small bulk, followed by addition of diethyl ether and light petroleum ether, gave $[\text{Pt}_2\text{Cl}_2(\text{PEt}_3)_4][\text{BF}_4]_2$ (0.18 g., 1.6 mmoles) as a white precipitate, insoluble in benzene or chloroform but soluble in methanol and nitromethane. The compound had no sharp melting point but decomposed at about 250° . It was recrystallized by solution in the minimum volume of methanol or nitromethane and addition of an equal volume of diethyl ether followed by light petroleum ether to the cloud point; crystallization then occurred. Anal. Calcd for $\text{C}_{24}\text{H}_{60}\text{B}_2\text{Cl}_2\text{F}_8\text{P}_4\text{Pt}_2$: C, 26.0; H, 5.5; Cl, 6.4. Found: C, 25.8; H, 5.6; Cl, 6.2. The molar conductivity of a $0.3 \times 10^{-3}\text{M}$ solution in nitromethane was $170 \text{ ohm}^{-1}\text{cm}^2$ at 25° .

In addition to absorptions due to the cation (see Table 5), the infra-red spectrum of this product had absorptions characterized of BF_4^- at $1090(\text{sh})$, $1050(\text{vs, b})$, and $515(\text{m}) \text{ cm}^{-1}$.

(ii) Reaction of cis- $[\text{PtBr}_2(\text{PEt}_3)_2]$

The procedure similar to 5a(ii) was used in this reaction.

Cis- $[\text{PtBr}_2(\text{PEt}_3)_2]$ (0.29 g.) and boron trifluoride (0.25 g.) heated at 50° for 12 hours in chloroform, gave white crystalline $[\text{Pt}_2\text{Br}_2(\text{PEt}_3)_4][\text{BF}_4]_2$ (0.19 g., 75%).

Anal. Calcd for $C_{24}H_{60}B_2Br_2F_8P_4Pt_2$: C, 24.1; H, 5.1.

Found: C, 24.7; H, 5.2. The residue, insoluble in methanol-diethyl ether mixture was identified spectroscopically as trans- $[PtBr_2(PEt_3)_2]$ (0.10 g.).

(iii) Reaction of cis- $[PtCl_2(PPh_3)_2]$

Cis- $[PtCl_2(PPh_3)_2]$ (0.32 g.) in 40 ml. chloroform was shaken with boron trifluoride (0.3 g.) at 25° in a silica tube. A yellowish oil precipitated at once, but shaking was continued for 12 hours before evaporation of the products under vacuum. The residue was washed with small volumes of methanol leaving $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.3 g., 85% yield) as a white powder, insoluble in light petroleum and slightly soluble in chloroform or methanol. The product was recrystallized as described above for the triethylphosphine analogue. Anal. Calcd for $C_{72}H_{60}B_2Cl_2F_8P_4Pt_2$: C, 51.3; H, 3.6; Cl, 4.2. Found: C, 50.5; H, 3.6; Cl, 3.7. The molar conductivity of a $0.5 \times 10^{-3}M$ solution in nitromethane was $174 \text{ ohm}^{-1}\text{cm}^2$ at 25° . In addition to absorptions due to the cation (see Table 5), the infra-red spectrum of this product had absorptions characteristic of BF_4^- at $1080(s, b)$ and $1045(vs, b)$ cm^{-1} .

(iv) Reaction of cis-[PtBr₂(PPh₃)₂]

Cis-[PtBr₂(PPh₃)₂] (0.34 g.) and boron trifluoride (0.4 g.) in 10 ml. chloroform were heated at 70° in a silica tube for 12 hours and gave pale yellow crystals of [Pt₂Br₂(PPh₃)₄][BF₄]₂ (0.29 g.). Recrystallization was from a nitromethane-petroleum ether-diethyl ether mixture. Anal. Calcd for C₇₂H₆₀B₂Br₂F₈P₄Pt₂: C, 48.8; H, 3.4. Found: C, 49.4; H, 3.7.

(v) Reaction of cis-[PtI₂(PPh₃)₂] (2.30 g.) and boron trifluoride (0.5 g.) after 48 hours at 130° in a 1:1 chloroform-benzene solution, gave [Pt₂I₂(PPh₃)₄][BF₄]₂ (0.77 g., 35%). Anal. Calcd for C₇₂H₆₀B₂I₂F₈P₄Pt₂: C, 46.3; H, 3.2. Found: C, 46.0; H, 3.1.

b) Reaction of trans-[PtHCl(PR₃)₂] with Boron Trifluoride (R = ethyl or phenyl)

Trans-[PtHCl(PEt₃)₂] (0.1 g.) in 5 ml. dried benzene was heated with dry BF₃ (0.3 g.) at 40° for one hour in a silica tube. A brownish oil precipitated. A procedure identical with that in 5a(i) gave [Pt₂Cl₂(PEt₃)₄][BF₄]₂ (0.1 g., 86% yield). Very little reaction was observed when the reaction was repeated at 25° for 20 hours.

The above reaction was repeated with trans-[PtHCl(PPh₃)₂] with heating at 80° for 12 hours. Similar work-up to that described

in 5a(iii) gave $[\text{Pt}_2\text{Cl}_2(\text{PPh}_3)_4][\text{BF}_4]_2$ in 70% yield.

6. Reaction of cis- $[\text{PtI}_2(\text{PEt}_3)_2]$ with Boron Trifluoride

Cis- $[\text{PtI}_2(\text{PEt}_3)_2]$ (1.0 g.) was heated at 70° for 28 hours in a sealed tube with boron trifluoride (0.3 g.) and chloroform (3 ml.). Removal of the volatiles under vacuum, extraction with methanol, followed by recrystallization at 25° from a chloroform-diethyl ether mixture, gave yellow plates of $[\text{PtI}(\text{PEt}_3)_3][\text{BF}_4]$ (0.20 g.). Anal. calcd for $\text{C}_{18}\text{H}_{45}\text{BF}_4\text{IP}_3\text{Pt}$: C, 28.3; H, 6.1. Found: C, 28.3; H, 6.0. M.p. $148-150^\circ$. Further extraction of the residue with chloroform gave trans- $[\text{PtI}_2(\text{PEt}_3)_2]$ (0.52 g.) identified spectroscopically. Recrystallization of the remaining residue from acetone-methylene chloride gave orange crystals of $[\text{Pt}_2\text{I}_4(\text{PEt}_3)_2]$ (0.23 g.). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{I}_4\text{P}_2\text{Pt}_2$: C, 12.7; H, 2.7. Found: C, 13.7; H, 2.6. This compound has already been described (22). The new compound $[\text{PtI}(\text{PEt}_3)_3][\text{BF}_4]$ can also be identified by characteristic infra-red absorptions due to $\nu(\text{Pt-P})$ at $425(\text{m})$ with weak shoulders at 410, and 440 cm^{-1} .

7. Preparation of trans- $[\text{PtX}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$

a) Reaction of $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4][\text{BF}_4]_2$ with Carbon Monoxide.

Typically for X = Cl, Br and I and R=phenyl and for X = Cl and Br and R=ethyl, the compound $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4][\text{BF}_4]_2$

(0.25 mmoles) in 20 ml. degassed chloroform or nitromethane solution was stirred at constant rate in a closed system at 23^o under one atmosphere of carbon monoxide. The course of the reaction was followed by measuring the carbon monoxide uptake on a capillary monometer. The uptake of the carbon monoxide due to solubility in the solvent was rapid (complete within two minutes) and blank runs were made in solvent alone to determine a correction for calculating carbon monoxide uptake attributed solely to reaction with the dimeric salt. Plots of carbon monoxide uptake as a function of time for the various compounds in chloroform and nitromethane are illustrated in figures 1 and 2.

For the carbonylation reactions with chloroform as solvent, the products were isolated and purified. For X = Cl or Br, and R=ethyl or phenyl, the chloroform was removed under vacuum and the residue recrystallized as shown in Table 3. For X = I and R=phenyl, work-up was carried out in a carbon monoxide atmosphere by the addition of the chloroform solution to a carbon monoxide-saturated diethyl ether-petroleum ether mixture. The resulting yellow solid was not recrystallized. Further details on each specific reaction are shown in Table 3.

Table 3. Properties of Halocarbonyl Platinum(II) Salts
Formed From Reaction of Dimeric Halogen-Bridged
Salts with Carbon Monoxide

Compound	Percentage Yield from carbonylation reaction †	Melting Point	Recrystallization Solvents	Carbonyl Stretching Frequency (as chloroform solution cm ⁻¹)	Anal. Calcd.	Found	C% H% N% in CHCl ₃ in CH ₃ NO ₂	Time For Complete Carbonylation (in minutes)
[PtCl(CO)(Ph ₃ P) ₂][BF ₄]	85	slow decomposition above 200°C; with liquifaction near 270°C.	Benzene	2120	51.2	51.2	3.5 3.7 3.7	20 -*
[PtBr(CO)(Ph ₃ P) ₂][BF ₄]	80		Benzene	2111	48.6	49.0	3.3 3.5 3.5	8 25
[PtI(CO)(Ph ₃ P) ₂][BF ₄]	50		-	2120	46.2	45.4	3.2 3.4 3.4	7 6
[PtCl(CO)(Et ₃ P) ₂][BF ₄]	89	168-171°C with decom.	ethyl acetate	2098	26.0	25.8	5.5 5.6 5.6	2.5 2.5 -*
[PtBr(CO)(Et ₃ P) ₂][BF ₄]	85	158-160°C with decom.	ethyl acetate	2112	24.9	25.0	4.8 4.6 4.6	2.5 20

* No reaction was observed.

† Yields represent first crop of crystals except for [PtI(CO)(Ph₃P)₂][BF₄]

b) Reactions of trans-[PtHCl(PPh₃)₂] with Tetrafluoroboric Acid
and Carbon Monoxide

Trans-[PtHCl(PPh₃)₂] (1.0 g., 1.3 mmoles) was heated at 120^o for 48 hours in a stainless steel autoclave with 20 ml. benzene and 5 drops aqueous 48% tetrafluoroboric acid solution under 8 atmospheres of carbon monoxide pressure. The volatile products were removed under vacuum and the oily residue was extracted with chloroform. Careful addition of a diethyl ether-petroleum ether mixture gave small crystals of trans- [PtCl(CO)(PPh₃)₂][BF₄] (0.4 g., 0.5 mmole). The solvents were removed from the remaining solution leaving an oily yellow solid with absorptions in the infra-red region at 2030 and 2050 cm⁻¹. These products could not be purified and remained uncharacterized.

c) Reaction of cis-[PtCl₂(PR₃)₂] with Boron Trifluoride and
Carbon Monoxide. (R=ethyl or phenyl)

Cis-[PtCl₂(PPh₃)₂] (0.89 g., 1.1 mmoles) in 15 ml. chloroform was heated with boron trifluoride (2.4 g.) under a pressure of 15 atmospheres of carbon monoxide at 110^o for 36 hours in a stainless steel autoclave. All volatile materials were removed under vacuum and the residue recrystallized from benzene giving white needles of trans-[PtCl(CO)(PPh₃)₂][BF₄] (0.6 g., 61% yield).

The characterization of this compound has been described in section 4(i).

The above reaction was repeated with cis-[PtCl₂(PEt₃)₂] as starting material. Similar procedure gave trans-[PtCl(CO)(PEt₃)₂][BF₄] (80% yield) which was recrystallized from ethyl acetate. The characterization of this salt has been described elsewhere (20).

d) Reaction of cis-[PtCl₂(PEt₃)₂] with Sodium Tetrafluoroborate
and Carbon Monoxide

Through a solution of cis-[PtCl₂(PEt₃)₂] (1.0 g., 2.0 mmoles) and sodium tetrafluoroborate (0.22 g., 2.0 mmoles) in 20 ml. acetone carbon monoxide was bubbled through for 4 hours. A white precipitate formed and was filtered off and the solution evaporated leaving white crystals of trans-[PtCl(CO)(PEt₃)₂][BF₄] which were recrystallized from ethyl acetate (1.0 g., 1.7 mmoles).

e) Reaction of cis-[PtX₂(PR₃)₂] with Silver Tetrafluoroborate
and Carbon Monoxide (X = Cl or Br, and R = Et or Ph)

Carbon monoxide was bubbled through a solution of cis-[PtCl₂(PPh₃)₂] (1.0 g., 1.3 mmoles) and silver tetrafluoroborate (0.25 g., 1.3 mmoles) in 20 ml. acetone for 2 hours. The precipitate of silver chloride was filtered from the solution by fluted filter paper. The acetone was evaporated leaving a yellow oil which

on cooling from a hot benzene solution gave white crystals of $\text{trans-}[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ (1.0 g., 1.2 mmoles).

The above reaction was repeated for $\text{cis-}[\text{PtX}_2(\text{PR}_3)_2]$ with X = Br and R=phenyl and X = Cl or Br and R=ethyl. Good yields were obtained in all cases.

8. Reactions of $\text{trans-}[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{BF}_4]$ (R=ethyl or phenyl)

a) Reaction with Chloride Ion

$\text{Trans-}[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ was dissolved in chloroform with an approximately equimolar quantity of Et_4NCl . Slight effervescence was observed to occur. The chloroform was evaporated, the residue extracted with water, and the water solution evaporated under vacuum. The white solid residue had absorptions in the infra-red spectrum characteristic of both Et_4N^+ and BF_4^- and was tentatively identified as the salt Et_4NBF_4 . The water-insoluble fraction was identified by infra-red spectroscopy as $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$.

b) Reaction with Hydrogen

A sample of $\text{trans-}[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ was stirred in chloroform solution for 18 hours under one atmosphere of hydrogen. No reaction was detected and the sample was recovered unchanged.

c) Reaction with C_2F_4

Samples with trans- $[PtCl(CO)(PPh_3)_2][BF_4]$ and its triethylphosphine analogue were reacted with benzene and C_2F_4 in sealed tubes. No reaction was detected for either case.

d) Reaction with dry HCl

Trans- $[PtCl(CO)(PPh_3)_2][BF_4]$ was reacted with dry benzene and dry HCl at 25° for 18 hours. No change was observed in the starting material.

e) Reaction with Benzoyl Azide

Trans- $[PtCl(CO)(PPh_3)_2][BF_4]$ was dissolved in chloroform containing a one molar excess of benzoyl azide (68). The infrared spectrum of the solution initially showed strong bands at 2135 and 2120 cm^{-1} due to azide and carbonyl respectively. No change was observed over a period of 5 hours. The solution was then heated at 55° for 18 hours. The band at 2135 cm^{-1} had disappeared but the carbonyl band at 2120 cm^{-1} was still present. Hence reaction did not occur even at temperatures sufficiently high for decomposition of the benzoyl azide.

f) Reaction of trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ with Water

(i) Trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ (0.155 g., 0.27 mmoles)

was heated at 110° for 18 hours in degassed 1:1 methanol-water solution (2 ml.) in an evacuated Pyrex tube. A white crystalline solid formed on cooling. The volatile products were fractionated under vacuum through -78° , -120° and -196° traps. Carbon dioxide (0.011 g., 0.25 mmoles) was collected and identified by infra-red spectroscopy. The residue was extracted with water affording a white solid (0.030 g.) with infra-red absorptions characteristic of SiF_6^{2-} and BF_4^- anions. The residual solid was trans- $[\text{PtHCl}(\text{PEt}_3)_2]$ (0.122 g., 0.26 mmoles), characterized by its melting point ($80-82^{\circ}$), proton n. m. r. spectroscopy, and infra-red spectroscopy.

(ii) The above reaction was repeated with water alone as solvent. Although the reaction was not homogeneous and some reduction to metallic platinum occurred, the yields of carbon dioxide and trans- $[\text{PtHCl}(\text{PEt}_3)_2]$ were nearly quantitative after one hour refluxing in a nitrogen atmosphere.

(iii) The above reaction was repeated using D_2O (98% pure) in place of water. The reaction was complete within one hour giving carbon dioxide and trans- $[\text{PtDCl}(\text{PEt}_3)_2]$. The latter product was identified by infra-red spectroscopy ($\nu(\text{Pt-D}) = 1595$, $\delta(\text{Pt-D}) = 580 \text{ cm}^{-1}$).

(iv) Trans-[PtCl(CO)(PEt₃)₂][BF₄] (0.3 g.) was refluxed in D₂O (2 ml.) for 15 minutes. The mixture was cooled for one minute at 0° and the solid filtered and dried under vacuum. An infra-red spectrum of the solid (as a Nujol mull) indicated that the reaction to the platinum deuteride [PtDCl(PEt₃)₂] was about 80% complete.

Trans-[PtHCl(PEt₃)₂] (0.3 g.) was refluxed for 15 minutes in D₂O (2 ml.) containing a drop of 48% aqueous fluoroboric acid. The mixture was cooled for one minute at 0° and the solid filtered and dried under vacuum. An infra-red spectrum of the solid (as a Nujol mull) indicated that the reaction to the platinum deuteride compound [PtDCl(PEt₃)₂] was about 30% complete.

g) Reaction of trans-[PtCl(CO)(PPh₃)₂][BF₄] with Water

Trans-[PtCl(CO)(PPh₃)₂][BF₄] (0.10 g.) was shaken at 110° for 12 hours with water (2 ml.). The volatile products were removed under vacuum and carbon dioxide and carbon monoxide were identified spectroscopically in the infra-red region. The residue was extracted with methylene chloride which on slow evaporation afforded trans-[PtHCl(PPh₃)₂] (0.01 g.), identified by infra-red spectroscopy (66). Further evaporation of the methylene chloride solution afforded an oil which remained uncharacterized.

9. A study of the Kinetics of the Hydrolysis of trans-[PtCl(CO)(PEt₃)₂]
[BF₄]

a) Calculation of Extent of Dissociation of [PtCl(CO)(PEt₃)₂]⁺
In Water.

The cation of the salt trans-[PtCl(CO)(PEt₃)₂][BF₄] was found to partially dissociate in aqueous media giving uncharacterized hydrolysis products, one of which is acidic. The extent of this dissociation was studied by measuring the pH of an acetone-water solution of the salt. The pH of acetone-water solutions of known added acid concentrations were measured to calibrate the pH meter. Results are tabulated below:

[HCl] (N)	[H ₂ O] in acetone(N)	pH observed	Theoretical pH	Correction
0.005	14	1.95	2.30	+ 0.35
0.010	14	1.70	2.00	+ 0.30
0.025	14	1.30	1.60	+ 0.30
0.100	14	0.72	1.00	+ 0.28

The pH values of solutions of varying concentrations of the carbonyl salt in the water-acetone mixture were then measured, and adjusted using the calibrations above. The H⁺ concentration and hence the percentage dissociation of the cation was calculated as shown below:

Initial Conc. of Carbonyl Salt (molar)	Observed pH	Calculated pH (after applying correction)	$[H^+]$ (Molar)	% Dissociation
0.020	2.05	2.35	0.0045	23
0.040	1.95	2.30	0.0050	13
0.082	1.85	2.15	0.0071	9

b) Kinetic study of Hydrolysis of trans-[PtCl(CO)(PEt₃)₂][BF₄]

The progress of the reaction of water with the carbonyl cation in acetone solution of 14 N water concentration was followed by infra-red spectroscopy by observing the disappearance of the carbonyl peak, $\nu(C\equiv O)$, at 2100 cm^{-1} . Identical samples of 0.50 ml. of the reacting stock solution were placed in Pyrex tubes of 1.0 ml. capacity via a ground-glass syringe of 0.5 ml. capacity. The tubes were heated in a constant temperature oil bath. Tubes ready to be examined were cooled in liquid nitrogen to quench the reaction, then the volatile products were removed under vacuum at 0° . 0.50 ml. chloroform was added to the solid residue and the solution ~~examined~~ examined by infra-red spectroscopy with a 0.1 mm solution cell. A calibration of peak size versus concentration of the carbonyl salt was made and this calibration allowed a direct translation of peak size in the spectra to concentration of the reactant carbonyl.

The peak height at time = ∞ was always = 0 and as a result any terms involving carbonyl concentration at time = ∞ could be dropped from the calculations.

The two reactions that were run at specified starting acid concentrations, had aqueous fluoroboric acid added to the stock solution at the beginning of the experiment.

The Arrhenius plot was made from measurements of slopes in the first half-life of the reactions shown in Fig. 5.

Table 4. Some Properties of Platinum Alkoxy-carbonyls formed from reaction of the Carbonyl Cation with Alcohols.

Compound	Colour	M. P. ^a (°C)	Reaction ^b Time(min)	Analysis Calcd		Results Found	
				%C	%H	%C	%H
PtCl(COOMe)L ₂ ^c	white	222-227	2	56.1	4.1	55.8	4.2
PtBr(COOMe)L ₂	cream	226-231	2	53.2	3.9	53.0	4.0
PtI(COOMe)L ₂	light yellow	226-229	2	50.4	3.7	50.3	3.9
PtCl(COOEt)L ₂	white	215-217	40	56.6	4.3	56.5	4.2
PtBr(COOEt)L ₂	white	226-231	10	53.7	4.0	53.8	4.0
PtI(COOEt)L ₂	light yellow	221-229	5	51.0	3.8	51.1	3.8
PtCl(COOMe)L ₂ ^d	white	--	360	-	-	-	-

a: All compounds softened and discoloured above 180°

b: Time for complete reaction of cationic carbonyl with appropriate alcohol; qualitative estimate only. Reactions were run at 25° except for the last compound which was run at 60°.

c: L = triphenylphosphine

d: L' = triethylphosphine

10. Reactions of trans-[PtX(CO)(PPh₃)₂][BF₄] with Alcohols

- a) Preparation of [PtX(COOR)(PPh₃)₂] (X = Cl, Br or I; R = CH₃
or C₂H₅)

Typically, for R = CH₃, trans-[PtX(CO)(PPh₃)₂][BF₄] (X = Cl, Br or I) was stirred in methanol at 25° for one hour. The fine precipitate was filtered, washed with water and a small volume of methanol, and dried under vacuum. Evaporation of the methanol mother liquor gave a further crop of the product and an oil which had absorptions in the infra-red region characteristic of the fluoroborate anion. For R=ethyl, the same procedure was followed except ethanol replaced methanol as both reactant and wash solvent, and the reaction was carried out for 12 hours. Both sets of compounds were soluble in chloroform and methylene chloride and only slightly soluble in alcohols and benzene. Yields were essentially quantitative. All these alkoxy carbonyl compounds could be recrystallized by the addition of light petroleum ether and diethyl ether to saturated solutions of the platinum compounds in chloroform or dichloromethane. These white or pale yellow crystalline compounds (Table 4) were characterized by analyses, infra-red spectroscopy, proton n.m.r. spectroscopy, (see Table 2), and chemical reactions (see section 11(a), (b)). Infrared absorptions for the methoxycarbonyl compounds at 1660 cm⁻¹ (Nujol mull)

were assigned to the C=O stretching vibration, and strong broad peaks centered at 1060 cm^{-1} were assigned to OMe. Similar absorptions appeared at about 1635 and 1080 cm^{-1} for the ethoxy analogues. The infra-red spectra also contained absorptions typical of the triphenylphosphine ligand. Further information on the experimental details for specific compounds is given in Table 4.

b) Reaction of trans-[PtCl(CO)(PEt₃)₂][BF₄] with dry Methanol

Trans-[PtCl(CO)(PEt₃)₂][BF₄] (0.10 g.) was heated with 2 ml. dried methanol for 18 hours at 60° in a dried evacuated Pyrex tube. The volatile products were removed under vacuum leaving a white oily solid. Characterization of this residue was incomplete because of its instability. However, infra-red and proton n.m.r. spectroscopy indicate a compound analogous to the products of reaction 10 (a), *i. e.*, trans-[PtCl(COOMe)(PEt₃)₂] : infrared absorptions (cm^{-1}), $\nu(\text{C=O}) = 1600$, $\nu(\text{Pt-P}) = 410$ (br), $\nu(\text{Pt-Cl}) = 270$ (w); n.m.r. methyl absorptions, triplet at $\tau = 7.1$, $\frac{J}{\nu_{\text{Pt-H}}} = 7$ cps.

11. Reactions of the compounds [PtX(COOR)(PPh₃)₂] (R = Me or Et)

a) Reaction of [PtCl(COOR)(PPh₃)₂] with Fluoroboric Acid.

[PtCl(COOMe)(PPh₃)₂] (0.12 g., 0.15 mmoles) was shaken

at 25° for one hour with dichloromethane (5 ml.) and 48% aqueous fluoroboric acid (1 ml.). After separation of the two layers, n. m. r. spectra of the water layer showed a singlet at 3.4 ppm assigned to the methyl protons of methanol. Light petroleum ether was added to the dichloromethane solution affording $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ (0.12 g., 0.14 mmole) identified by infra-red spectroscopy.

A similar reaction with $[\text{PtCl}(\text{COOEt})(\text{PPh}_3)_2]$ gave trans- $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ in good yield. Proton n. m. r. spectroscopy indicated ethanol as the other hydrolysis product.

Similar acid hydrolysis reactions occurred for the bromo- and iodo- analogues.

Hydrochloric acid could be used in place of fluoroboric acid for the above hydrolysis. However, the product was the dichloride cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$.

b) Reaction of $[\text{PtCl}(\text{COOC}_2\text{H}_5)(\text{PPh}_3)_2]$ with Methanol

$[\text{PtCl}(\text{COOC}_2\text{H}_5)(\text{PPh}_3)_2]$ (0.01 g.) was heated with methanol at 63° for 12 hours in an evacuated sealed tube. The solid product was filtered and identified from infra-red spectroscopy as $[\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2]$ (0.008 g.): for $[\text{PtCl}(\text{COOC}_2\text{H}_5)(\text{PPh}_3)_2]$, $\nu(\text{C}=\text{O}) = 1638 \text{ cm}^{-1}$ (Nujol mull); for $[\text{PtCl}(\text{COOCH}_3)(\text{PPh}_3)_2]$, $\nu(\text{C}=\text{O}) = 1665 \text{ cm}^{-1}$ (Nujol mull).

c) Reactions of $[\text{PtX}(\text{COOCH}_3)(\text{PPh}_3)_2]$ with Water (X = Cl, Br or I)

(i) Trans- $[\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2]$ (0.17 g., 0.21 mmole) was heated at 130° for 18 hours in an evacuated Pyrex tube containing degassed saturated water-potassium chloride solution (3.0 ml.). The volatile products were fractionated under vacuum through -78° , -120° , and -196° traps. Carbon dioxide (0.0073 g., 0.17 mmole) was collected and identified by infra-red spectroscopy. The -120° trap contained methanol identified by infra-red and n. m. r. spectroscopy. The residue was extracted with water, dried, then extracted with methylene chloride affording trans- $[\text{PtHCl}(\text{PPh}_3)_2]$ (0.15 g., 0.20 mmole) identified by melting point ($216-221^\circ$) and infra-red spectroscopy (66). An uncharacterized insoluble compound (0.015 g.) was left as residue.

The above reaction was repeated with D_2O (98% pure) instead of water. Carbon dioxide and trans- $[\text{PtDCl}(\text{PPh}_3)_2]$ were formed, both identified by infra-red spectroscopy ($\nu_{(\text{Pt-D})} = 1585 \text{ cm}^{-1}$).

Trans- $[\text{PtHCl}(\text{PPh}_3)_2]$ was heated in a sealed tube at 110° for 12 hours in D_2O (98% pure). The starting material was obtained quantitatively and no exchange had occurred.

(ii) Reactions under conditions identical with the chloro-analogue were carried out with $[\text{PtX}(\text{COOCH}_3)(\text{PPh}_3)_2]$ in saturated

H₂O-KX solution (X = Br or I). For X = Br, trans-[PtHBr(PPh₃)₂] was isolated in 65% yield and the remainder of the product was starting material. For X = I, only a trace of trans-[PtHI(PPh₃)₂] was obtained.

d) Reactions of [PtX(COOC₂H₅)(PPh₃)₂] with Water

(i) [PtCl(COOC₂H₅)(PPh₃)₂] (0.16 g., 0.19 mmole) was heated for 18 hours at 110^o in an evacuated Carius tube containing a degassed saturated potassium chloride-water solution (2 ml.). The volatile products were fractionated through -78^o, -120^o and -196^o traps. Carbon dioxide (0.0075 g., 0.17 mmole) was collected and identified by infra-red spectroscopy. Ethanol was also identified as a volatile product by proton n. m. r. spectroscopy. The solid residue was extracted with dichloromethane affording trans-[PtHCl(PPh₃)₂] (0.14., 0.19 mmole) characterized by melting point (217-220^o) and infra-red spectroscopy. Further extraction of the residue afforded 0.004 g., of unidentified solid. The water-soluble, white residue which remained was assumed to be potassium chloride.

(ii) Similar reactions were carried out with [PtX(COOEt)(PPh₃)₂]-KX-H₂O systems for X = Br or I. For [PtBr(COOEt)(PPh₃)₂] as starting material, trans-[PtHBr(PPh₃)₂]

was obtained in 90% yield. For the iodo- analogue only trace reaction was observed.

e) Reactions of $[\text{PtX}(\text{COOR})(\text{PPh}_3)_2]$ with Water and No Salt Catalyst

For $\text{X} = \text{Cl}$ and $\text{R} = \text{methyl}$, it was found that reaction to give the platinum hydrido- compound from the ester species did not occur in the absence of a salt. However, NH_4Cl and NMe_4Cl could replace KCl as the salt catalyst.

For $\text{X} = \text{Cl}$ and $\text{R} = \text{ethyl}$, best yields of the hydride $[\text{PtHCl}(\text{PPh}_3)_2]$ were obtained with a chloride salt present, although the hydride was isolated in lower yields even in the absence of a salt.

Table 5. Characteristic^a Infra-red Absorptions (cm^{-1}) of some Platinum(II) Phosphine Complexes.

Compound ^b	Pt-Cl stretch	C-F stretch	Others
A	very weak	1240(s), 1065(s), 985(vs), 970(w, sh)	ν (C=C) 1734(m)
B	very weak	1330(w), 1240(vw), 1120(m), 1070(m), 990(m), 950(m)	ν (C=C) 1665(s)
C	325(w, b)	1355(w), 1165(s), 1140(m), 1080(vs), 965(s), 950(s), 845(vw), 790(m)	640(w), 595(m), 545(m), 520(vw) ν (Pt-P) 410(m)
D	300(w, b)		ν (B-F) 1080(s, b) 1045(vs, b)
E	280(w, b)		ν (B-F) 1090(sh), 1050(vs), 515(m); ν (Pt-P) 440(m), 420(m)
F	335(w)		ν (C=O) 2100(s), ν (¹³ C=O) 2050(vw), ν (B-F) 1090(s), 1050(vs, b)
G	not visible		ν (C=O) 1660(s) ν (C-O) 1065(s, b)
H	not visible		ν (C=O) 1635(s) ν (C-O) 1060(s, b)

^a Absorptions due to the phosphine ligands are omitted and all spectra are run as Nujol mulls

^b A = trans-[PtCl(PPh₃)₂(CF=CF₂)], B = trans-[PtCl(PPh₃)₂(C{CF₂H}=CF₂)], C = trans-[PtCl(PEt₃)₂(CF₂CF₂H)].

D = [Pt₂Cl₂(PPh₃)₄][BF₄]₂, E = [Pt₂Cl₂(PEt₃)₄][BF₄]₂, F = trans-[PtCl(CO)(PPh₃)₂][BF₄]

G = [PtCl(COOCH₃)(PPh₃)₂], H = [PtCl(COOCH₂CH₃)(PPh₃)₂]

12. Reaction of Iron, Manganese and Iridium Alkoxycarbonyls
with Water

a) Reaction of $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COOCH}_3)]$ with Water

(i) Preparation of $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COOCH}_3)]$

The method of R. B. King and co-workers (62) was used in this preparation. Sodium (5 g.) and mercury (500 g.) in 300 ml. of dried tetrahydrofuran were stirred for 18 hours with the iron dimer, $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2]_2$, (8.8 g., 50 mmoles). The brown solution obtained was decanted from the mercury and stirred with dimethylcarbonyl chloride (5.0 g., 50 mmoles) for 12 hours. The tetrahydrofuran was removed under vacuum and the residues refluxed in reagent methanol for 2 hours. The methanol was removed under vacuum and the brown oil residue was recrystallized from cooled hexane solution giving yellow-brown needles. The crystalline product was sublimed at 80° and 0.1 mm Hg pressure giving yellow needles of $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COOCH}_3)]$ (2.0 g., 8.4 mmoles), (M. P. = $32\text{-}34^\circ$), which slowly decomposed on standing in air.

Infra-red (Nujol mull): $\nu_{(\text{C}=\text{O})} = 1630 \text{ cm}^{-1}$

(ii) Reaction with Water

$[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COOMe})]$ (0.25 g., 1.1 mmoles) was

shaken at 45° for 20 minutes in degassed water (1 ml.) containing KCl (1.0 g.) in an evacuated Pyrex tube. Effervescence was observed during the reaction and a deep red liquid, immiscible in water, and a black solid were obtained. The volatile products were distilled under vacuum through traps at -25°, -96° and -196° traps. The trap at -196° contained carbon dioxide (0.036 g., 0.8 mmole) identified by infra-red spectroscopy. Two less volatile products were isolated; one characterized as methanol by infra-red and n. m. r. spectroscopy, and another tentatively identified by infra-red spectroscopy as methyl formate (70). The trap at -25° contained water and a red liquid identified (75) as $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ (0.09 g., 0.52 mmole) by infra-red and ¹H n. m. r. spectroscopy (hydride chemical shift, $\tau = 21$ in CHCl_3). The nonvolatile products were extracted with chloroform and the chloroform extract contained the dimer $[\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ (0.08 g., 0.44 mmoles) identified by infra-red spectroscopy. The residue, a white solid, was assumed to be KCl. On exposure of the hydrido-compound to the atmosphere, reaction to the black dimer was complete within one minute.

The above reaction was repeated without the salt. Similar reaction occurred and the identical products were isolated.

b) Reaction of $[\text{Mn}(\text{CO})_5(\text{COOC}_2\text{H}_5)]$ with Water(i) Preparation of $[\text{Mn}(\text{CO})_5(\text{COOC}_2\text{H}_5)]$

The method of Kruck and Noack (46) was used for this preparation. $[\text{Mn}_2(\text{CO})_{10}]$ (2.0 g., 10 mmoles) was stirred for 3 hours in 25 ml. dried tetrahydrofuran with an amalgam of sodium (0.5 g.) and mercury (50 g.). The tetrahydrofuran solution was decanted from the mercury and the solvent removed under vacuum. The brown residue was stirred for 18 hours with chloromethyl formate (1.0 g., 14 mmoles) and 10 ml. diethyl ether. The solvent was removed under vacuum and the brown oily residue sublimed at 25° to a -20° coldfinger under 0.01 mm Hg pressure. White needles of $[\text{Mn}(\text{CO})_5(\text{COOC}_2\text{H}_5)]$ were collected (0.8 g., 3 mmoles),

$$\text{Infra-red (Nujol mull)} : \nu_{(\text{C}=\text{O})} = 1625 \text{ cm}^{-1}$$

(ii) Reaction with Water

$[\text{Mn}(\text{CO})_5(\text{COOC}_2\text{H}_5)]$ (0.28 g., 1.0 mmole) was shaken at 75° in a Pyrex tube for 12 hours with KCl (1.0 g.) and 4 ml. water. A viscous oil, immiscible in water, was left after reaction. The volatile products were distilled through traps at -25° , -96° and -196° . The trap at -196° contained carbon dioxide (0.039 g., 0.9 mmole) identified by infra-red spectroscopy.

The other traps contained water and ethanol, characterized by infra-red and proton n.m.r. spectroscopy, and a yellow liquid

identified as $\text{Mn}(\text{CO})_5\text{H}$ (0.12 g., 0.6 mmole) and characterized by infra-red (72) and n.m.r. spectroscopy (72) (hydride chemical shift, $\tau = 18$ in CHCl_3). The non-volatile products contained a yellow solid, identified by infra-red spectroscopy as the dimeric compound $[\text{Mn}_2(\text{CO})_{10}]$ (0.06 g., 0.3 mmoles), and a white water-soluble solid assumed to be KCl .

The above reaction was repeated without potassium chloride and, although trace amounts of ethyl formate were isolated in the volatile products, the reaction was basically unchanged.

c) Reaction of $[\text{Ir}(\text{CO})_2(\text{COOCH}_3)(\text{PPh}_3)_2]$ with Water

(i) Preparation of $[\text{Ir}(\text{CO})_2(\text{COOCH}_3)(\text{PPh}_3)_2]$

The preparation of this compound was carried out using several steps which are outlined below.

Preparation of Vaska's Compound $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$.

The preparation of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ was made by the method of Vaska and diLuzio (6). Iridium trichloride (1.0 g., 3.0 mmoles) (Alpha Chemicals) was refluxed with 100 ml. diethylene glycol and triphenylphosphine (15 g., 57 mmoles) for 2 hours. The solution turned dark green and yellow crystals formed on cooling. The mixture was extracted with benzene and the addition of light petroleum and diethyl ether gave yellow crystals of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (2.0 g., 2.7 mmoles).

Preparation of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2][\text{ClO}_4]$

$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (2.0 g., 2.7 mmoles) was added to 25 ml. methanol containing $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.5 g., 3.6 mmoles) and carbon monoxide was bubbled through for 5 hours. The white precipitate that formed was tentatively identified as $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2][\text{ClO}_4]$ and reacted further in situ.

Preparation of $[\text{Ir}(\text{CO})_2(\text{COOCH}_3)(\text{PPh}_3)_2]$

The methanol mixture of the iridium salt was made alkaline to pH = 9 by dropwise addition of methanolic potassium hydroxide and stirred for 3 hours under a carbon monoxide atmosphere. The grey precipitate formed was filtered and extracted with acetone. The acetone solution was treated with light petroleum and diethyl ether yielding slightly yellow crystals of $[\text{Ir}(\text{CO})_2(\text{COOCH}_3)(\text{PPh}_3)_2]$ (1.3 g., 1.7 mmole).

Infra-red (Nujol mull) : $(\text{C}=\text{O}) = 1630 \text{ cm}^{-1}$

(ii) Reaction with Water

$[\text{Ir}(\text{CO})_2(\text{COOMe})(\text{PPh}_3)_2]$ (0.09 g., 0.12 mmole) was shaken in a Pyrex tube at 130° for 18 hours with 1 ml. water saturated with potassium chloride. The volatile products were fractionally distilled under vacuum through -25° , -96° and -196° traps. The trap at -196° contained carbon dioxide (0.002 g., 0.05 mmole).

The non-volatile residues were washed with water leaving a white solid tentatively assigned as $[\text{Ir}(\text{CO})_2\text{H}(\text{PPh}_3)_2]$. The solid had sharp infra-red absorptions at 2105 and 815 cm^{-1} , assigned to $\nu_{(\text{Ir}-\text{H})}$ and $\delta_{(\text{Ir}-\text{H})}$ respectively. Further work-up of this solid yielded uncharacterized decomposition products.

The above reaction was repeated at 90° and the starting material was recovered quantitatively.

The above reaction was again repeated at 130° in water without salt present. Only uncharacterized decomposition products were obtained. Similar results were found in reactions in dilute potassium chloride solutions.

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