Stabilised Carbonium Ions in the Organic Chemistry of Platinum

THE EVIDENCE FOR THEIR EXISTENCE

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This account of research on the organometallic chemistry of platinum summarises work which indicates that platinum may induce carbonium ion reactivity in π-bonded hydrocarbon ligands and stabilise carbonium ions in the reactions of σ-bonded unsaturated hydrocarbons. It is based on a lecture at the Chemical Society annual meeting held at York in April.

Historically, platinum has played a prominent role in organometallic chemistry. The compounds $KPtCl_3(C_2H_4)H_2O$ (1), $PtMe_3$ (X) (2) and Chugaev's salt $[PtC_8H_{15}N_6]_xCl_x$ (3, 4) present some of the first examples of stable metal-olefin, metal-alkyl and metal-carbene complexes, although ironically the nature of the bonding in these compounds was not immediately recognised. In the study of organometallic reaction mechanisms platinum has also been in the forefront, for example, in studies of the decomposition pathways of metal-alkyls (5, 6); oxidative-addition reactions (7–9); C-C and C-H reductive-elimination reactions (10–14); and M-H and M-C insertion reactions (15–22).

Certain aspects of the organometallic chemistry of platinum are well suited for the study of organic reactions occurring at metal centres (23):

(i) There exists a diverse organometallic chemistry for platinum in its well-defined valence states o, 2+ and 4+.

(ii) For a given valence state platinum shows a well-defined coordinated chemistry. Pt(o) compounds are either three or four co-ordinate. Pt(2+) compounds show a remarkable preference for a four coordinate square planar geometry; five coordination is comparatively rare. Compounds of Pt(4+) are almost invariably six coordinate.

(iii) Platinum-carbon bonds are stable to oxygen, water and thermolysis. This stability results from a combination of thermodynamic and kinetic factors.

(iv) Platinum compounds are well suited to a wide variety of spectroscopic techniques. In particular the presence of ^{195}Pt, $I=\frac{1}{2}$, 34 per cent natural abundance, provides a useful mechanistic probe in n.m.r. studies of organoplatinum compounds.

This account summarises work in our laboratories which indicates that platinum may induce carbonium ion reactivity in π-bonded hydrocarbon ligands and may stabilise carbonium ions in the reactions of σ-bonded unsaturated hydrocarbons.
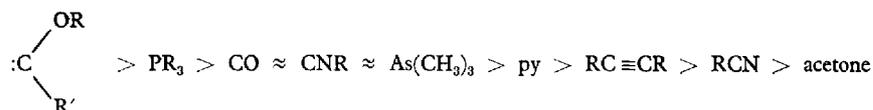
Organoplatinum Cations

By taking advantage of the high *trans*-influence (24) of the methyl ligand we set out to synthesise a series of cationic methyl-platinum compounds *trans*-$[PtCH_3(un)L_2]^+$ PF_6^-, *I*, where un = an unsaturated hydrocarbon and L = a tertiary phosphine or arsine, according to reaction **A** below.

A *trans*-$PtCH_3(Cl)L_2$ + un + $AgPF_6$ $\xrightarrow{\text{solvent}}$
trans-$[PtCH_3(un)L_2]^+PF_6^-$ + $AgCl$
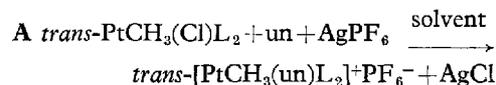
Compounds *I* were considered ideal for detailed studies of the bonding and reactivity

of the unsaturated ligand un. However, the products derived from **A** were found to be dependent on the nature of the unsaturated hydrocarbon, the ligands on platinum, the solvent, and the reaction conditions. Reactions involving dialkyl or diaryl acetylenes, un = $RC \equiv CR$, in acetone solvent did lead to the isolation of cationic methylplatinum(2+) acetylenic compounds as white air stable crystalline salts (25, 26). From a comparison of $\nu_{str}(Pt\text{-}C)$, $^2J_{195Pt\text{-}H}$ and $^1J_{195Pt\text{-}13C}$ for the methylplatinum group in I, where un = $RC \equiv CR$, with related values observed for methylplatinum(2+) cations $trans\text{-}[PtCH_3(L')L_2]^+$, where L' =a neutral donor ligand, the following $trans$-influence series may be formulated: (27)

platinum(2+) cation. In contrast, co-ordination to zerovalent platinum as in $(P(C_6H_5)_3)_2Pt(CH_3C \equiv CCH_3)$ causes a much greater reduction in this stretching frequency. Indeed the value of $\nu_{str}(C \equiv C)$ is lowered to a value comparable to that observed for cis-2-butene. Similarly the ^{13}C shieldings of the acetylenic carbons (see the Table) reveal (28) the very different nature of the metal-acetylene bond in $trans\text{-}[PtCH_3(CH_3C \equiv CCH_3)L_2]^+$ and $(P(C_6H_5)_3)_2Pt(CH_3C \equiv CCH_3)$. A single crystal X-ray determination on $trans\text{-}[PtCH_3(CH_3C \equiv CCH_3)(P(CH_3)_2C_6H_5)_2]^+PF_6^-$ revealed (29) a $C \equiv C$ bond length of 1.22Å, c.f. (30), 1.21 Å for free 2-butyne, and an average $C \equiv C\text{-}C$ angle of 168°.

$$\underset{R'}{\overset{OR}{:C}} \quad > PR_3 > CO \approx CNR \approx As(CH_3)_3 > py > RC \equiv CR > RCN > acetone$$

This series shows that the acetylenic triple bond exerts a relatively weak $trans$-influence, somewhere between the nitrogen donor ligands pyridine and alkylnitriles.

Further insight into the nature of the platinum-acetylene bond in I can be obtained from a consideration of the data shown in the Table. This pertains specifically to I, un = $CH_3C \equiv CCH_3$. $\nu_{str}(C \equiv C)$ which occurs at $\sim$ 2200 cm^{-1} in free 2-butyne is reduced only 100 cm^{-1} on coordination to the methyl-

In summary all available spectroscopic data suggests that, based on the original Dewar (31)-Chatt-Duncanson (32) pictorial descriptions of metal-acetylene bonding below,
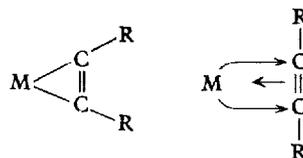
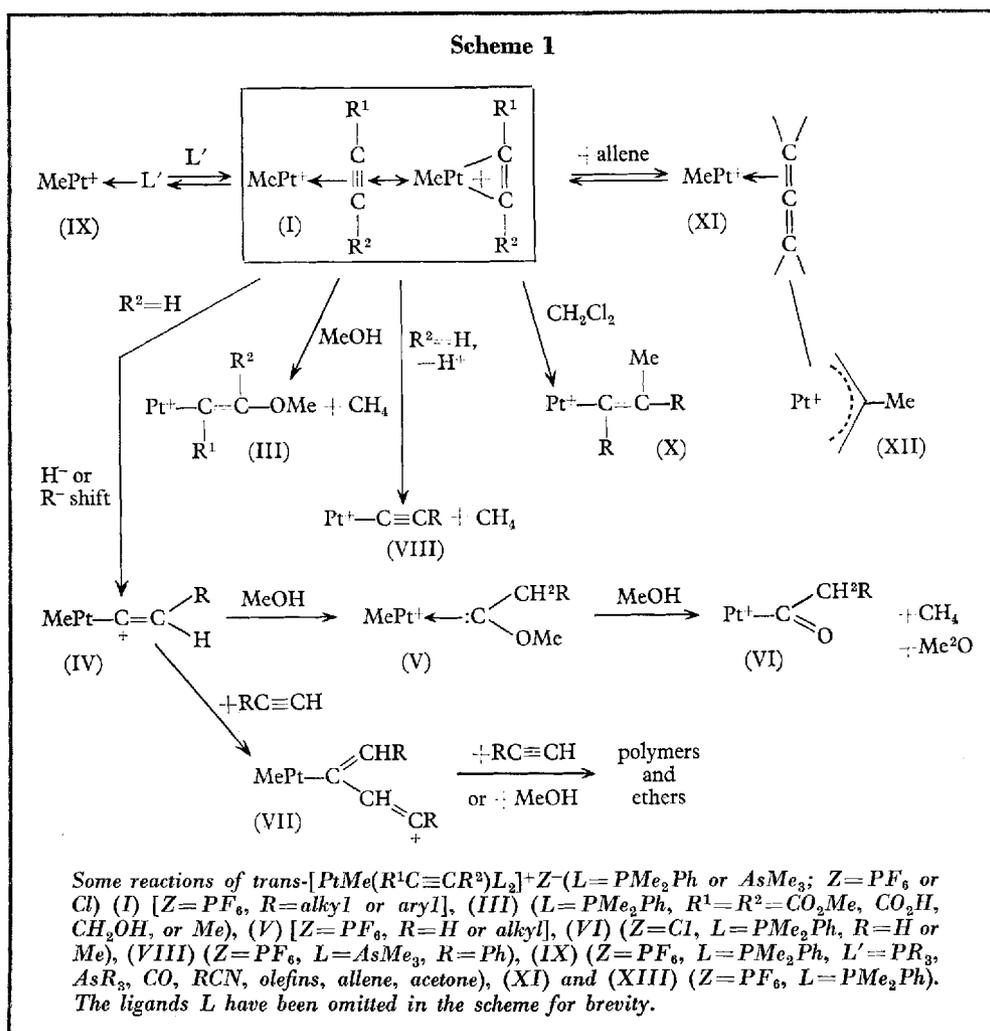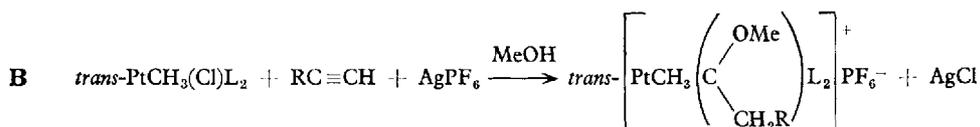| Compound	$\nu_{str}(C \equiv C)$ cm^{-1}	$\delta(C)^a$
$CH_3C \equiv CCH_3$	~2200	73.9
$PtL_2(CH_3C \equiv CCH_3)$	1750	122.8
$[PtCH_3(CH_3C \equiv CCH_3)L_2]^+$	2100	69.5
$cis\text{-}CH_3CH = CHCH_3$	~1650	124.3

^{a}sp or sp^2-carbon; p.p.m. downfield from TMS; data from ref. 28

platinum or acetylene π^* bonding is of minor importance in I. This is in marked contrast to the bonding in zero valent platinum acetylene compounds which may be considered to show a sizeable degree of cyclopropenoid character. The primary mode of bonding in I, $un=RC\equiv CR$, appears to be a σ-interaction involving donation from filled π-acetylenic orbitals to vacant platinum hybrid orbitals.

Although dialkyl and diaryl acetylenes did yield I according to **A**, the reaction of terminal acetylenes, $RC\equiv CH$, in methanol solvent gave cationic methylplatinum methoxy-carbene complexes according to **B** (25,33). Analogous reactions in ethanol gave the appropriate ethoxy-carbene complexes. This formation of the alkoxy-carbene ligand in **B** was unexpected and requires specific comment.

Initially we proposed (25, 33) a mechanism in which a cationic acetylenic complex I reacts with the solvent to produce a cationic

$$\textbf{B} \quad \textit{trans-}PtCH_3(Cl)L_2 + RC\equiv CH + AgPF_6 \xrightarrow{\text{MeOH}} \textit{trans-}\left[PtCH_3\left(C\begin{array}{c}OMe\\ \diagup \\ \diagdown \\ CH_2R\end{array}\right)L_2\right]^+ PF_6^- + AgCl$$

Scheme 1

Some reactions of trans-$[PtMe(R^1C\equiv CR^2)L_2]^+Z-(L=PMe_2Ph$ or $AsMe_3$; $Z=PF_6$ or $Cl)$ (I) $[Z=PF_6,\ R=alkyl$ or $aryl]$, (III) $(L=PMe_2Ph,\ R^1=R^2=CO_2Me,\ CO_2H,\ CH_2OH,$ or $Me)$, (V) $[Z=PF_6,\ R=H$ or $alkyl]$, (VI) $(Z=Cl,\ L=PMe_2Ph,\ R=H$ or $Me)$, $(VIII)$ $(Z=PF_6,\ L=AsMe_3,\ R=Ph)$, (IX) $(Z=PF_6,\ L=PMe_2Ph,\ L'=PR_3,$ $AsR_3,\ CO,\ RCN,\ olefins,\ allene,\ acetone)$, (XI) and $(XIII)$ $(Z=PF_6,\ L=PMe_2Ph)$. The ligands L have been omitted in the scheme for brevity.

π-vinyl ether complex, which then by hydride shift yields the alkoxy-carbene ligand. However, we were subsequently able to isolate cationic methylplatinum π-vinyl ether complexes (21). These were stable below +80°C and did not rearrange to give alkoxy-carbene derivates. This observation together with many other reactions of cationic acetylenic platinum complexes, summarised in Scheme 1, led us to propose a general carbonium ion model for the activation of unsaturated ligands in organoplatinum cations trans-[PtR (un)L₂]⁺ (21, 34).

The Carbonium Ion Model

We proposed (21, 34) that activation occurs by delocalisation of the positive charge from platinum to the unsaturated moiety un; this has the effect of inducing carbonium ion reactivity. Specifically for acetylenes coordinated to platinum(2+) cations this can be pictured by the resonance shown below.

Scheme 2
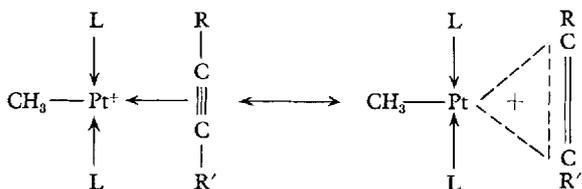
The carbonium ion reactivity of the coordinated acetylene is thus dependent on the nature of the substituents of the acetylene, R and R′; the ligands on platinum, X and L, since these determine the electrophilicity of the platinum cation; the solvent; and the nature and availability of a nucleophile.
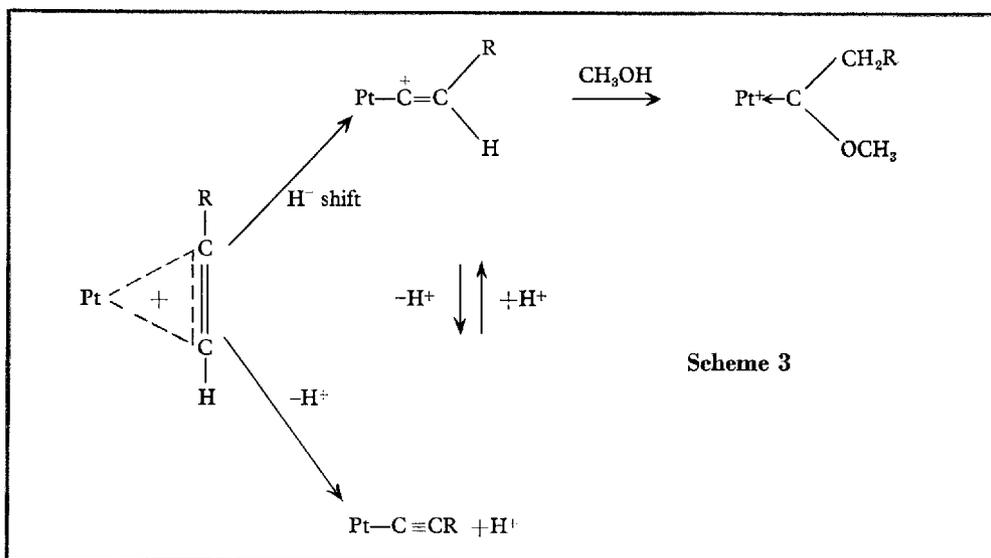
Thus most of the reactions shown in Scheme 1 may be reduced to three fundamental types of reactions shown in Scheme 2. These are (i) nucleophilic attack on the coordinated acetylene leading to trans-vinylic products, (ii) proton elimination or abstraction by the solvent when R=H (this is favoured in polar aprotic solvents), and (iii)
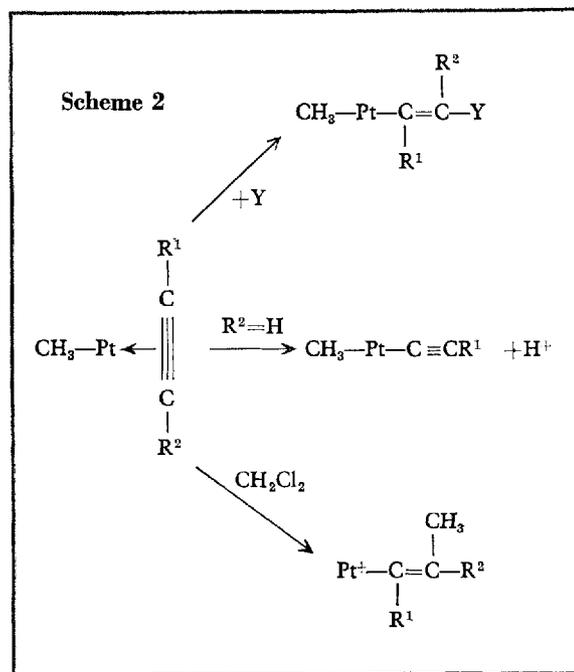
insertion into a group already bound to platinum leading to cis-vinylic products.

Aside from these three types of reactions (Scheme 2) many other aspects of organoplatinum chemistry illustrate the generality of this platinum induced carbonium ion model. For example, substitution of the methyl group bound to platinum in I by the more electron withdrawing trifluoromethyl group increases the electrophilicity of the organoplatinum cation and hence increases the carbonium ion reactivity of the acetylene in trans-[PtCF₃(RC≡CR′)L₂]⁺ relative to I. Although we have been unable to isolate such simple dialkylacetylene cations, they are the reactive intermediates in the polymerisation of acetylenes, a process which occurs much faster than for I in the absence of a polar protic solvent. A terminating step in the polymerisation of dimethylacetylene is the formation of the cationic tetra-methyl-cyclobutadiene complex [PtCF₃(C₄(CH₃)₄) (P(CH₃)₂ C₆H₅)₂]⁺PF₆⁻ (35, 36).

Another reaction in organoplatinum chemistry which is consistent with the platinum

Scheme 3:

$$Pt—\overset{+}{C}=C\overset{\diagup R}{\diagdown H} \xrightarrow{CH_3OH} Pt^+\leftarrow C\overset{\diagup CH_2R}{\diagdown OCH_3}$$

H⁻ shift

$$Pt<\ +\ \begin{matrix}R\\|\\C\\\|\|\\C\\|\\H\end{matrix}$$

−H⁺ ↓↑ +H⁺

−H⁺

Pt—C≡CR +H⁺

Scheme 3

induced carbonium ion model is the formation of an alkoxy-carbene ligand from a platinum (4+) cationic acetylenic intermediate (35).

Mechanism of Formation of the Carbene Ligand

The mechanism for the formation of the alkoxy-carbene ligand from the elements of RC≡CH and R'OH deserves specific comment. The proposed mechanism, based on the carbonium ion model, is shown in Scheme 3. The essential feature of this mechanism involves the intermediacy of a platinum vinyl carbonium ion which, once formed, reacts with the alcohol solvent to yield the alkoxy-carbene ligand. A platinum vinyl carbonium ion may be formed by one of two routes; (i) an intramolecular mechanism involving an H⁻ shift or (ii) an intermolecular mechanism involving deprotonation (abstraction of H⁺ by solvent) to give a platinum acetylide followed by protonation of the triple bond. Reactions carried out in CH₃OD showed (21) that the acetylenic hydrogen was not lost to the solvent but rather was incorporated on the α-carbene carbon. This demonstrates that the intramolecular mechanism is operative and furthermore shows that the reaction of the vinyl carbonium ion with alcohol solvent is fast (at least relative to deprotona-

tion) and irreversible. The exact role of platinum in facilitating this hydride shift is not clear and the intermediacy of a platinum-hydride cannot be excluded. However, in the reaction of cationic acetylenic intermediates of Pt(4+), which also yield the carbene ligand (35), formation of a platinum-hydride intermediate seems most unlikely since this would be formally a hydride of Pt(6+). Finally, it should be recognised that an alkyl shift rather than a hydride shift could be operative. Based on the relative migratory aptitudes of H⁻ and R⁻, and the fact that acetylene, HC≡CH, gives the alkoxy (methyl) carbene ligand we prefer to believe in the H⁻ shift mechanism. Of course, a ¹³C labelling experiment involving the specific labelling of one of the acetylenic sp-carbons could distinguish between these two possibilities. However, the salient feature of the proposed mechanism involves the intermediacy of a vinyl carbonium ion and is thus independent of which group migrates.

The concept of a platinum stabilised vinyl carbonium ion is an interesting one since simple vinyl carbonium ions are rather reactive species (37), indeed it is only recently that they have become respectable intermediates in the carbonium ion community (38). However metal vinyl carbonium ions

$$L_nM \overset{+}{-\!}C \overset{\cdots}{=} C \overset{H}{\underset{R}{<}} \quad \longleftrightarrow \quad L_nM^{\overset{+}{\cdots}} = C = C \overset{H}{\underset{R}{<}}$$
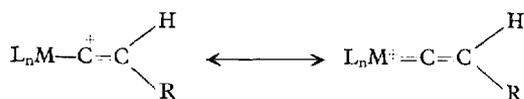
could be stabilised by a metalloallene resonance form as shown above.

σ-Routes to Platinum Stabilised Carbonium Ions

If organoplatinum cations can induce carbonium ion reactivity in a π-bonded unsaturated hydrocarbon ligand and at the same time show evidence of stabilising the carbonium ion so formed, it is reasonable to expect that this carbonium ion stabilisation should be reflected in the reactions of σ-bonded unsaturated hydrocarbons.

We have now examined some reactions of divalent platinum acetylides of the type $trans$-Pt(C≡CR)$_2$L$_2$ and $trans$-PtCl(C≡CR) L$_2$ where R—H, CH$_3$, CF$_3$ and C$_6$H$_5$, and L = P(CH$_3$)$_2$C$_6$H$_5$). These reactions are also of interest since they allow a direct comparison with the chemistry of organo-platinum compounds PtR$_2$L$_2$ and PtCl(R)L$_2$ where R— alkyl or phenyl, and the presence of a four coordinate d^8 metal and a coordinated alkynyl ligand provides the opportunity to compare the reactivity of inorganic and organic sites of unsaturation. Our initial findings show (39, 40) that these compounds exhibit a very intricate chemistry based on reaction at either the metal or the triple bond.

The reactions involving protic acids are particularly pertinent to the carbonium ion model outlined previously. For example $trans$-PtCl(C≡CR)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$ reacts:

(i) with anhydrous HCl to give almost quantitative formation of the vinylic product $trans$-PtCl(CCl=C(H)R)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$; (addition of HCl to the triple bond gives a mixture of cis- and $trans$-vinylic isomers but is specific in giving $only$ the α-chlorovinylic isomer PtCCl=C(H)R);

(ii) with anhydrous HCl in methanol to give $trans$-PtCl(COCH$_2$R)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$ and methylchloride;

(iii) with HPF$_6$ in methanol to give quantitative formation of the methoxycarbene complex

$$trans\text{-}\left[PtCl\left(C \overset{OCH_3}{\underset{CH_2R}{<}} \right)\left(P(CH_3)_2C_6H_5 \right)_2 \right]^+ PF_6^-$$
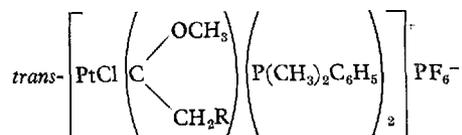
where R—H, CH$_3$ and C$_6$H$_5$. Addition of a one molar equivalent of LiCl to an acetone solution of

$$trans\text{-}\left[PtCl\left(C \overset{OCH_3}{\underset{C_2H_5}{<}} \right)\left(P(CH_3)_2C_6H_5 \right)_2 \right]^+ PF_6^-$$
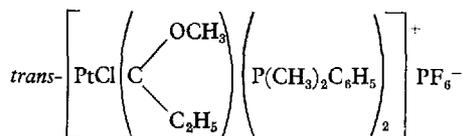
leads to quantitative formation of $trans$-PtCl (COC$_2$H$_5$)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$ with the formation of methyl chloride. Consequently we consider that propionyl formation in the reaction involving anhydrous HCl in methanol proceeds via initial formation of

$$trans\text{-}\left[PtCl\left(C \overset{OCH_3}{\underset{C_2H_5}{<}} \right)\left(P(CH_3)_2C_6H_5 \right)_2 \right]^+ Cl^-$$
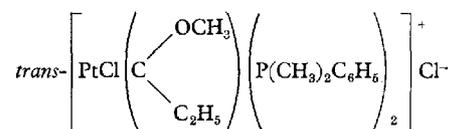
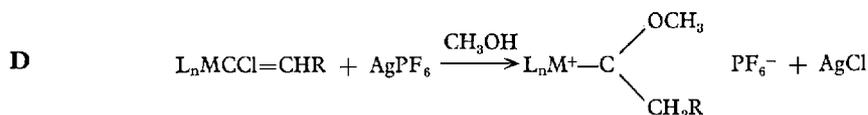which readily eliminates CH$_3$Cl irreversibly.

These reactions provide further evidence for the intermediacy of platinum vinyl carbonium ions. However, the initial or preferential site of protonation is uncertain and again we must recognise the possible intermediacy of hydridoplatinum(4+) cations. Scheme 4 overleaf shows possible equilibria which may, either directly or indirectly, lead to platinum vinyl carbonium ions. Our work thus far has clearly demonstrated the existence of certain of these pathways. For example, cationic acetylenic intermediates yield alkoxy-carbene and acetylide complexes in alcohols and THF respectively. However, the intermediacy of hydrido-alkynylplatinum species remains a possibility. This potential route to metal vinyl carbonium ions leads us to predict a new synthetic route to alkoxycarbene ligands according to C.

C $\qquad$ $L_nM(H)(Cl)(C\equiv CR) + AgPF_6 \xrightarrow{\text{CH}_3\text{OH}} L_nM^+\!\!-\!C\!\!\begin{smallmatrix}\diagup OCH_3\\[4pt]\diagdown CH_2R\end{smallmatrix} \quad PF_6^- + AgCl$
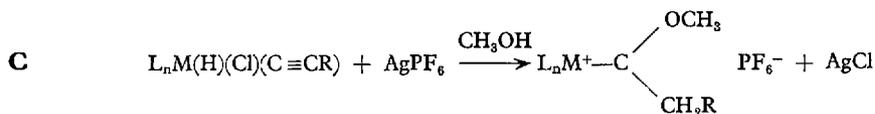
<table>
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Complexes suited to this type of reductive rearrangement could well involve Co, Rh and Ir.

Finally we note that the reaction of HPF_6 in methanol with *trans*-$PtX(C\equiv CH)L_2$, in which either the α or β acetylenic carbon is specifically labelled, could form the basis for ascertaining the intermediacy of a cationic π-acetylenic complex in this route to alkoxy-carbene complexes.

As a further test of our hypothesis that low valent metals can stabilise vinyl carbonium ions we predict a direct solvolytic route to alkoxy-carbene ligands as in **D** where L_nM provides an electron-rich metal site.

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Scheme 4

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D $\qquad$ $L_nMCCl{=}CHR + AgPF_6 \xrightarrow{\text{CH}_3\text{OH}} L_nM^+\!\!-\!C\!\!\begin{smallmatrix}\diagup OCH_3\\[4pt]\diagdown CH_2R\end{smallmatrix} \quad PF_6^- + AgCl$

This type of solvolysis reaction is unprecedented in the reactions of simple organic vinyl halides but should be possible when the metal can assist in stabilising the vinyl carbonium ion as a metalloallene cation described previously.
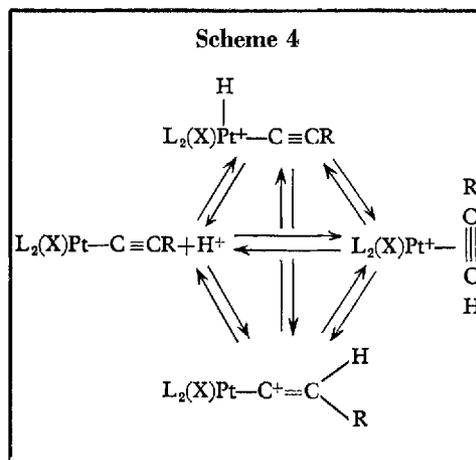
While reactions **C** and **D** are hypothetical we have recently shown (41) that alkoxy-carbene ligands can be generated quantitatively according to **E**
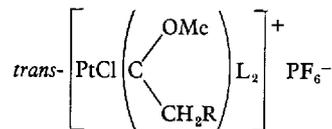
(ii) Reaction of $PtBr(CCl{=}C(H)R)L_2$ with $AgPF_6$ in MeOH gives only the chloro-platinum complex

$$trans\text{-}\left[PtCl\left(C{\begin{smallmatrix}\diagup OMe\\[6pt]\diagdown CH_2R\end{smallmatrix}}\right)L_2\right]^+ PF_6^-$$

(Analysis showed <0.1 per cent Br).

E $\quad$ *trans*-$PtCl(CCl{=}C(H)R)L_2 + AgPF_6 \xrightarrow{\text{CH}_3\text{OH}} trans\text{-}\left[PtCl\left(C{\begin{smallmatrix}\diagup OCH_3\\[6pt]\diagdown CH_2R\end{smallmatrix}}\right)L_2\right]^+ PF_6^- + AgCl$

where $R=H$, CH_3 and C_6H_5 and $L=P(CH_3)_2C_6H_5$.

Several observations indicate that reaction **E** proceeds via the mechanism shown in Scheme 5 (opposite page):

(i) Alcoholysis reactions of $PtX(CCl{=}C(H)R)L_2$ only occur when the Pt-X bond is labile towards Pt^+X^- solvolytic heterolysis e.g. $X=Cl$, Br and I.

(iii) Reaction in MeOD shows that the vinylic hydrogen is lost to the solvent.

(iv) *trans*-$PtCl(CCl{=}C(H)Me)L_2$ dissolves in MeOH saturated with anhydrous NH_3 to give *trans*-$PtCl(C\equiv CMe)L_2$ and NH_4Cl.

(v) *trans*-$PtCl(CCl{=}C(H)Me)L_2$ does not react with anhydrous NH_3 in benzene; cf. (iv) above.

The observations (i)–(v) above demonstrate the importance of Pt-Cl heterolysis and that H^+ is abstracted by the solvent. We cannot distinguish between a concerted or a stepwise elimination of the elements of HCl.

H^+ Elimination

from $Pt-C^+=C\diagdown^H_R$
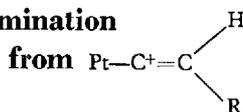
Subtle changes in the ligands bound to a metal often provide the basis for important modifications of catalytic processes. In this regard it is interesting to note that the reactivity of

$$trans\text{-}PtX(L_2)C^+=C\diagdown^H_R$$
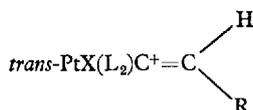
is sensitive to the nature of the $trans$-ligand X. This is indicated by the following (42): (1) $trans\text{-}PtCH_3(Cl)L_2$ reacts with $AgPF_6$ and $HC\equiv CH$ in MeOD to give

$$trans\text{-}\left[PtCH_3\left(C\diagup^{OMe}_{CH_2D}\right)L_2\right]^+ PF_6^-$$
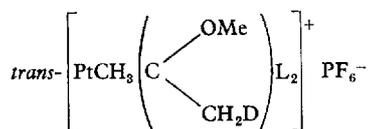
in which both acetylenic hydrogens are incorporated in the α-carbene methyl group. (2) $trans\text{-}Pt(C\equiv CH)_2L_2$ reacts with DPF_6 in MeOD to give

$$trans\text{-}\left[Pt\left(C\equiv CH/D\right)\left(C\diagup^{OMe}_{C(H/D)_3}\right)L_2\right]^+ PF_6^-$$
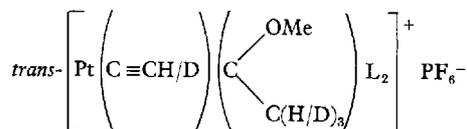
in which the acetylenic H/D ratio is ~ 2:1 and the methyl H/D ratio is less than 1:6. (3) The reaction of DPF_6 in MeOD with $trans\text{-}PtCl(C\equiv CH)L_2$ and the reaction of $trans\text{-}PtCl(CCl=CH_2)L_2$ with $AgPF_6$ in MeOD both yield

Scheme 5

$$trans\text{-}\left[PtCl\left(C\diagdown^{OMe}_{CD_3}L_2\right)\right]^+ PF_6^-$$
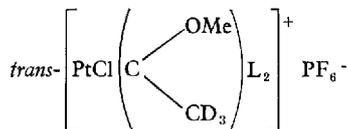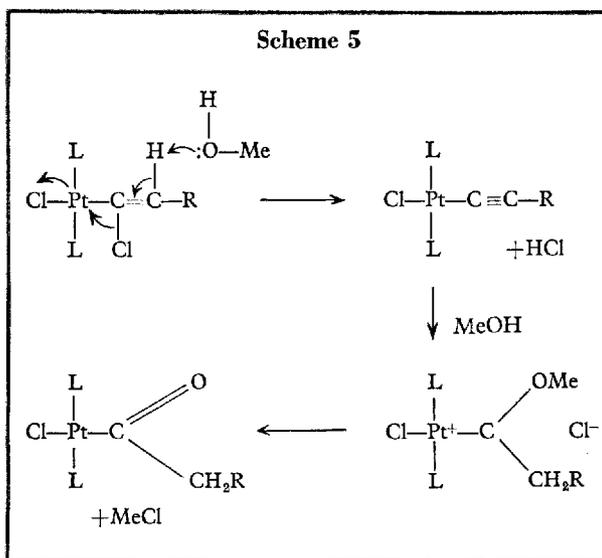
The above reactions indicate that the relative rates of H^+ elimination versus carbene formation from

$$trans\text{-}PtX\left(C^+=C\diagdown^H_H\right)L_2$$
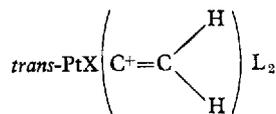
is sensitive to the nature of X. H^+ elimination is favoured $X=Cl>C\equiv CH>CH_3$.

H^+ Catalysed Isomerisations of Vinylic Ligands

In a study of halovinyl complexes of platinum(II) Lewis and co-workers (43) noted that the reaction between trichloroethylene and PtL_4, $L=PMePh_2$, was stereospecific in giving

$$trans\text{-}PtCl\left(C=C\diagdown^{Cl}_{Cl}-Cl\atop H\right)L_2$$
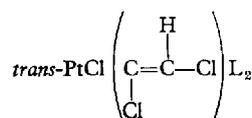
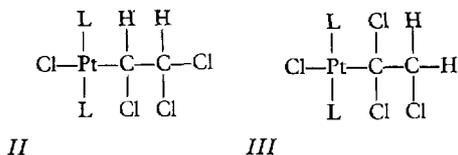However, upon treatment with anhydrous HCl the apparent thermodynamic equilibrium

distribution of vinylic isomers was obtained as indicated below.


30%   70%
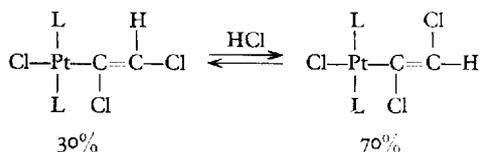
Two plausible mechanisms were suggested (43) to account for this isomerisation—an addition-elimination sequence or a carbonium ion mechanism. Addition of HCl could occur to give either *II* or *III*.

II   *III*

Based on our concepts of platinum-stabilised carbonium ions we felt that the kinetically controlled mode of addition should lead to *III*. Consistent with this expectation was our observation (42) that the DCl catalysed isomerisation was accompanied by immediate vinyl-H/D scrambling as evidenced by the diminuation of the vinylic proton nmr signals. This observation does not rule out that addition of HCl may occur to give *II* but indicates that it is not the kinetically favoured mode of addition.

We have also found (42) that this vinylic isomerisation can be catalysed by the addition of each of the following acids: CF_3COOH, HPF_6 and HSO_3F/SbF_5 to CD_2Cl_2 solutions of
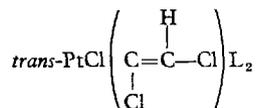
These observations lead us to believe that a simple protonation-deprotonation sequence involving the platinum-stabilised carbonium ion *trans*-$PtCl(\overset{+}{C}Cl—CH_2Cl)L_2$ provides the basis for vinyl isomerisation.

Conclusions

In attempting to describe the organic reactions that occur within the coordination sphere of a metal it has often been implicitly assumed and sometimes explicitly stated (44) that the ability of a metal to act either as a source or a sink of electrons makes the common organic reactive intermediates carbonium ions and carbanions unfavourable. Contrary to this view there is now, in our opinion, a good deal of evidence to support the view that platinum may either induce or stabilise carbonium ion intermediates within its coordination sphere. Consequently we believe that the concept of metal-induced stabilised carbonium ions should be valuable both in interpreting and designing many organometallic reactions. Of course, there exists a certain fundamental problem in terminology. The reactivity of a metal-stabilised carbonium ion may be far removed from its simple organic analogue. In the extreme this may be compared to the dramatic difference in reactivity often observed for a carbene bonded to a metal (45–47) relative to its free organic existence (48). However, in regard to the reactions of organoplatinum complexes described above the carbonium ion terminology seems quite appropriate.

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Fire-resistant Silicone Rubber

A continuing and increasing interest in the use of platinum or platinum-containing compounds for the production of fire-resistant silicone rubbers is shown by the patents being filed on this subject.

Specialised rubbers used where fire resistance is particularly desirable may have their fire retardant properties improved by the addition of very small amounts of platinum in a variety of forms, probably together with other materials such as silica fillers, sulphur-free carbon black or Group II metal oxides.

Suggested applications for such rubbers include the insulation of electrical conductors, transformer encapsulants, heater ducts, and window gaskets. With the performance and safety of ships and aircraft depending largely on the correct functioning of electrical devices and wiring it is clearly advantageous for the insulation employed to be flame resistant.

Patents include those held by Dow Corning (*British Patents* 1,161,052; 1,335,619; 1,262,845; *U.S. Patent* 3,635,874); General Electric (*U.S. Patents* 3,539,530; 3,514,424; 3,711,520; *French Patent* 2,016,946; *British Patent* 1,380,323); Shinetsu Chemical (*British Patent* 1,389,393), and Toshiba Silicone (*Japan Kokai* 74 67,933; 74 67,934; 74 67,935).