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 \( \pi \)-bonded hydrocarbon ligands and stabilise carbonium ions in the reactions of \( \sigma \)-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 KPtCl₅(C₂H₅)₂H₂O (I), PtMe₅ (X) (2) and Chugaev’s salt [PtC₆H₁₅N₅]ₓClₓ (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 0, 2⁺ and 4⁺.

(ii) For a given valence state platinum shows a well-defined coordinated chemistry. Pt(0) compounds are either three or four coordinate. 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 \(^{195}\text{Pt}\), 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 \( \pi \)-bonded hydrocarbon ligands and may stabilise carbonium ions in the reactions of \( \sigma \)-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 \( \text{trans-PtCH₃(un)L}_2 \text{PF}_6^- \), I, where un = an unsaturated hydrocarbon and L = a tertiary phosphine or arsine, according to reaction A below.

\[
\text{A \: PtCH₃(Cl)L}_2 \text{un} + \text{AgPF}_6^- \xrightarrow{\text{solvent}} \text{trans-PtCH₃(un)L}_2 \text{PF}_6^- + \text{AgCl}
\]

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≡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 ν(C≡C) for the methylplatinum group in I, where un = RC≡CR, with related values observed for methylplatinum(2+) cations trans-[PtCH(CH3)2L2]+, where L' = a neutral donor ligand, the following trans-influence series may be formulated: (27)

\[
\begin{align*}
\text{OR} & > \text{PR}_3 > \text{CO} \approx \text{CNR} \approx \text{As(CH}_3)_2 > \text{py} > \text{RC} \equiv \text{CR} > \text{RCN} > \text{acetone}
\end{align*}
\]

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

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 = CH3C≡CCH3. ν(C≡C) which occurs at ∼ 2200 cm⁻¹ in free 2-butyne is reduced only 100 cm⁻¹ on coordination to the methylplatinum(2+) cation. In contrast, coordination to zerovalent platinum as in \((\text{P(C}_6\text{H}_5)_2\text{Pt})_2(\text{CH}_3\text{C} \equiv \text{CCH}_3)\) causes a much greater reduction in this stretching frequency. Indeed the value of ν(C≡C) is lowered to a value comparable to that observed for cis-2-butene. Similarly the \(^{13}\text{C}\) shieldings of the acetylenic carbons (see the Table) reveal the very different nature of the metal-acetylene bond in trans-[PtCH3(CH3C≡CCH3)L2]⁺ and \((\text{P(C}_6\text{H}_5)_2\text{Pt})_2(\text{CH}_3\text{C} \equiv \text{CCH}_3)\).

A single crystal X-ray determination on trans-[PtCH3(CH3C≡CCH3)(P(CH3)2CH2)₂]⁺PF6⁻ revealed (29) a C≡C bond length of 1.22Å, c.f. (30), 1.21 Å for free 2-butyne, and an average C≡C-C angle of 168°.

In summary all available spectroscopic data suggests that, based on the original Dewar (31)-Chatt-Duncanson (32) pictorial descriptions of metal-acetylene bonding below,
platinum or acetylene $\pi^*$ 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 sizable degree of cyclopropenoid character. The primary mode of bonding in $I$, un = RC=CR, appears to be a $\sigma$-interaction involving donation from filled $\pi$-acetylenic orbitals to vacant platinum hybrid orbitals.

Although dialkyl and diaryl acetylenes did yield $I$ according to A, the reaction of terminal acetylenes, RC=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 complex $II$.

$$\text{B trans-PtCH}_3(\text{Cl})\text{L}_2 + \text{RC} = \text{CH} + \text{AgPF}_6 \rightarrow \text{trans-PtCH}_3(\text{CH}_2\text{R})\text{L}_2\text{PF}_6^- + \text{AgCl}$$

**Scheme 1**

Some reactions of trans-[PtMe(R'C=CR'R')L]'Z-(L = PMe, Ph or AsMe; Z = PF$_6$ or Cl) (I) [Z = PF$_6$, R = alkyl or aryl], (II) (L = PMe, Ph, R = alkyl or aryl), (III) (L = PMe, Ph, R = H or aryl), (IV) (L = PMe, Ph, R = H or alkyl), (V) (Z = PF$_6$, R = H or alkyl), (VI) (Z = Cl, L = PMe, Ph, R = H or Me), (VII) (Z = PF$_6$, L = AsMe, R = Ph), (VIII) (Z = PF$_6$, L = AsMe, R' = PPh)$_3$, (IX) (Z = PF$_6$, L = PMe, Ph, L' = PPh$_3$, AsR$_3$, CO, RCN, olefins, allene, acetone), (X) and (XI) (Z = PF$_6$, L = PMe, Ph). The ligands L have been omitted in the scheme for brevity.

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\( \pi \)-vinyl ether complex, which then by hydride shift yields the alkoxy-carbene ligand. However, we were subsequently able to isolate cationic methylplatinum \( \pi \)-vinyl ether complexes (21). These were stable below \(+80^\circ\text{C}\) 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 \( \text{un} \); this has the effect of inducing carbonium ion reactivity. Specifically for acetylenes co-ordinated to platinum(2 +) cations this can be pictured by the resonance shown below. Insertion into a group already bound to platinum leading to cis-vinyl 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-methylcyclobutadiene complex [PtCF3(C4H4(CH3)2)P(CH3)2 C6H5]PF6- (35, 36).

Another reaction in organoplatinum chemistry which is consistent with the platinum
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 \(RCECH\) 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 \(CH_3OD\) showed \((21)\) that the acetylenic hydrogen was not lost to the solvent but rather was incorporated on the \(\equiv\)-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 deprotonation) and irreversible. The exact role of platinum in facilitating this hydride shift is not clear and the intermediacy of a platinum-hydrde 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, \(HC\equiv CH\), gives the alkoxy (methyl) carbene ligand we prefer to believe in the \(H^-\) shift mechanism. Of course, a \(^{13}\)C 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
(iii) with HPF₄ in methanol to give quantitative formation of the methoxycarbene complex

\[
\text{trans-PtCl} \left( \text{C} \right) \left( \text{P(CH₃)₂C₆H₅} \right) \left( \text{OCH₃} \right) \right] \text{PF₄}^- \]

where R = H, CH₃ and C₆H₅. Addition of a one molar equivalent of LiCl to an acetone solution of

\[
\text{trans-PtCl} \left( \text{C} \right) \left( \text{P(CH₃)₂C₆H₅} \right) \left( \text{OCH₃} \right) \right] \text{PF₄}^- \]

leads to quantitative formation of trans-PtCl \left( \text{COCH₃} \right) \left( \text{P(CH₃)₂C₆H₅} \right) 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

\[
\text{trans-PtCl} \left( \text{C} \right) \left( \text{P(CH₃)₂C₆H₅} \right) \left( \text{OCH₃} \right) \right] \text{Cl}^- \]

which readily eliminates CH₃Cl 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 hydrido-alkynylplatinum(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 alkoxy-carbene ligands according to C.
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≡CH)L$_2$, in which either the $\alpha$ or $\beta$ acetylenic carbon is specifically labelled, could form the basis for ascertaining the intermediacy of a cationic $\pi$-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 LnM provides an electron-rich metal site.

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

where R = H, CH$_3$ and C$_6$H$_5$ and L = P(CH$_3$)$_2$, C$_6$H$_5$.

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.

(ii) Reaction of PtBr(CCl=C(H)R)L$_2$ with AgPF$_6$ in MeOH gives only the chloro-platinum complex

\[ \text{trans-PtCl(CCl=C(H)R)L}_2 \rightarrow \text{trans-PtCl (C \text{OMe}) (L}_2)^{+} \text{PF}_6^{-} \]

(Analysis showed <0.1 per cent Br).

(iii) Reaction in MeOD shows that the vinyl 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≡CMc)L$_2$ and NH$_4$Cl.

(v) trans-PtCl(CCl=C(II)Me)c)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** \( \text{Pt} - C = C \)

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

\[
\text{trans-PtX(L}_2\text{)}C = C
\]

is sensitive to the nature of the **trans**-ligand X. This is indicated by the following (42):

1. **trans-PtCH₃(Cl)L₂** reacts with AgPF₆ and HC≡CH in MeOD to give

\[
\text{trans-PtCl(C=CH)₂L₂}\rightarrow \text{PF₆}^-
\]

in which both acetylenic hydrogens are incorporated in the \( \alpha \)-carbene methyl group.

2. **trans-Pt(C≡CH)L₂** reacts with DPF₆ in MeOD to give

\[
\text{trans-PtCl(C≡CH)L₂}\rightarrow \text{PF₆}^-
\]

in which the acetylenic H/D ratio is \( \sim 2:1 \) and the methyl H/D ratio is less than 1:6.

3. The reaction of DPF₆ in MeOD with

\[
\text{trans-PtCl(C≡CH)L₂}\rightarrow \text{PF₆}^-
\]

and the reaction of

\[
\text{trans-PtCl(Cl=CH)₂L₂}\rightarrow \text{AgCl}
\]

in MeOD both yield

\[
\text{trans-PtCl(C≡CH)₂L₂}\rightarrow \text{AgCl}
\]

The above reactions indicate that the relative rates of H⁺ elimination versus carbene formation from

\[
\text{trans-PtX(C=CH)L₂}\rightarrow \text{PF₆}^-
\]

is sensitive to the nature of X. H⁺ elimination is favoured \( X = \text{Cl} > \text{C≡CH} > \text{CH}_2 \).

**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 PtL₄, \( L = \text{PMePh₃} \), was stereospecific in giving

\[
\text{trans-PtCl(C≡C=Cl)L₂}\rightarrow \text{Cl}
\]

However, upon treatment with anhydrous HCl the apparent thermodynamic equilibrium
distribution of vinylic isomers was obtained as indicated below.

\[
\begin{align*}
&L\text{-Pt-C}=\text{C}-\text{Cl} \\
&\text{Cl-L} & \xrightarrow{\text{HCl}} & \text{Cl-L}\text{-Pt-C}=\text{C}-\text{H} \\
&30\% & \xrightarrow{\text{Cl-I}} & 70\%
\end{align*}
\]

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.

\[
\begin{align*}
&L\text{-Pt-C}=\text{C}-\text{Cl} \\
&\text{Cl-L} & \xrightarrow{\text{HCl}} & \text{Cl-L}\text{-Pt-C}=\text{C}-\text{H} \\
&II & & III
\end{align*}
\]

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 diminution 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: CF₃COOH, HPF₆ and HSO₃F/SbF₅ to CD₃Cl₂ solutions of

\[
\text{trans-PtCl}(\text{C}=\text{C}=\text{Cl})\text{L}_2
\]

These observations lead us to believe that a simple protonation-deprotonation sequence involving the platinum-stabilised carbonium ion trans-PtCl(ÇCl—CH₂Cl)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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**References**

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 1,611,052; 1,335,619; 1,262,845; U.S. Patent 3,635,874); General Electric (U.S. Patents 3,539,539; 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 (Japanese Kokai 74,67,933; 74,67,934; 74,67,935).