Scheme II

$$An_4Sn \xrightarrow{SnCl_4} An_2SnCl_2 \xrightarrow[NpMgBr]{MeMgI +} MeAn_2SnNp$$

$$MeAn_2SnNp \xrightarrow[\substack{PhCl-MeOH \\ -70°}]{HCl}$$

$$MeAnNpSnCl \xrightarrow{LiAlH_4} MeAnNpSnH$$

with Me-*i*-PrPhSnBr which can be transformed into a series of racemic tetraorganotins Me-*i*-PrPhSnR.

Optically Active Tetraorganotins. In order to synthesize optically active tetraorganotin compounds, it was advisable to put two different aryl groups on tin. This is why we started from the very reactive tetra-*p*-anisyltin since the *p*-anisyl group is cleaved much faster than the other aromatic groups; see Table VI.[6,12] We used Scheme II (in which An stands for *p*-anisyl and Np for 1-naphthyl) to prepare and isolate the first optically active tin derivative in which the metal is the only chiral center.[32] The addition of this racemic triorganotin hydride to (−)-methyl acrylate yields two diastereoisomers which can be distinguished by nmr and separated. One of these, with [α]D −24°, reacted with methylmagnesium iodide to give the corresponding chiral alcohol MeAnNpSnCH₂CH₂CMe₂OH, [α]D +9°,[6] which is optically stable, as expected.[33,34]

Optical Stability of Organotin Compounds. Optically active organotin compounds containing a chiral tin atom might normally be expected to be of

some use for the study of the stereochemistry of SN2 reactions at the metal atom, much as in organosilicon or organogermanium chemistry.[4,35] However, it has been shown by the coalescence of diastereotopic signals that triorganotin halides are not optically stable.[33,34] Their ready conversion[36] into stereochemically nonrigid[37,38] pentacoordinate structures might account for this optical instability. This means that the study of the stereochemistry at tin in the halogen cleavage of carbon–tin bonds will be very difficult, if one does not find a way to reduce the optical instability of RR'R''SnX compounds. To do this, one may either try to slow down the formation of pentacoordinate complexes or the stereomutation processes by which they interconvert, or introduce constraints into the chemical system to avoid at least those stereomutations which are responsible for their optical instability, and which are best visualized on topological (graphical or matrix) representations.[4,37,38] This is the reason why we started several studies on sterically hindered organotin compounds[39] and on stannetanes,[40] which, we hope, will make it possible to obtain optically stable triorganotin halides[41] and hydrides.[42]

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Some Aspects of Organoplatinum Chemistry. Significance of Metal-Induced Carbonium Ions

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Malcolm H. Chisholm received both his B.Sc. and his Ph.D. degrees from Queen Mary College of the University of London, the latter in 1969 with Professor D. C. Bradley. After 3 years as a postdoctoral fellow at the University of Western Ontario with Howard C. Clark, he was then appointed Assistant Professor of Chemistry at Princeton University.

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The commercial importance of homogeneous and heterogeneous transition-metal-catalyzed reactions of olefins and acetylenes has generated tremendous interest in the activation of unsaturated molecules by transition-metal complexes. Noteworthy examples are (a) the hydroformylation of olefins to aldehydes, catalyzed by cobalt tetracarbonyl hydride,[1] (b) the hydrogenation of olefins catalyzed by [P(C₆H₅)₃]₃RhCl,[2] and (c) the oxidation of ethylene to acetal-

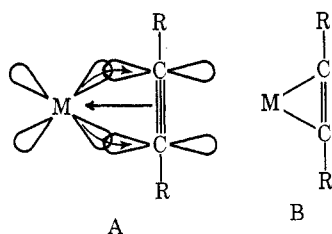(1) D. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960).

Figure 1. The Dewar–Chatt–Duncanson model of transition-metal–acetylene bonding.

dehyde in a continuous process catalyzed by $PdCl_2$–$CuCl_2$.[3]

Research into homogeneous catalysis has been stimulated by the belief that homogeneous catalysts can be "designed" which are more efficient than their heterogeneous counterparts. However, the role of a homogeneous catalyst is in many cases obscured by the very nature of the catalytic reaction: they are either very fast or very complex, usually both, and their reactive intermediates are normally inaccessible to direct or reliable observation.[4] The bonding in simple olefin and acetylene adducts with transition-metal complexes is therefore of particular interest since an understanding of the factors which lead to "stability" also illuminates the factors which produce "reactivity."

The original Dewar[5]–Chatt–Duncanson[6] model suggested that the bonding may be described as a combination of a σ interaction, olefin or acetylene π to metal "dsp," and a π interaction, metal "d" to olefin or acetylene π^* (Figure 1A) or in its extreme form as involving two metal–carbon σ bonds with complete rehybridization of the carbon atoms (Figure 1B).

For some complexes, e.g., $RhCl[P(C_6H_5)_3]_2C_4F_6$, X-ray structural determinations have led to the conclusion that the bonding is that of A in Figure 1 while for others, e.g., $Pt[P(C_6H_5)_3]_2C_4F_6$, bonding as in B is regarded as more appropriate. The concept of the synergic effect which is implicit in A is still accepted, although considerable debate has evolved concerning the relative magnitudes of σ and π interactions, the choice of metal orbitals employed in this bonding, and thus the coordination number and formal valency state of the metal.[4-14]

The sensitivity of σ- and π-bonding contributions to changes in the relative energies of the metal va-

lence orbitals and the acetylene–olefin π and π^* molecular orbitals is clearly seen in the model of Maitlis,[8] et al. They consider that, for acetylene complexes, five situations could reasonably be postulated to occur, A → E, in which the energy of the metal valence electrons decreases relative to the acetylene π and π^* orbitals. Their case D was compared to the bonding described in A in Figure 1, and they predicted weak interaction between the metal and the acetylene, the bonding orbitals having mostly metal character and the antibonding orbital mostly acetylene. The pair of electrons originally on the acetylene is thus transferred to the metal.

If the relative magnitudes of the σ and π contributions differ, the polar nature of the metal–acetylene-olefin bond should facilitate reaction by an ionic mechanism. It has been suggested that fluoro olefins and fluoroacetylenes, which are strong π acids (i.e., strong acceptors of metal d electrons into olefin or acetylene π^* orbitals) because of their electron-withdrawing substituents, react with low-valent electron-rich metal complexes via anionic or carbanion mechanisms.[15-18] Similarly, in the reactions of acetylenes with Pd(0)[19] and members of the cobalt triad,[20-24] which lead to benzenoid trimers and metallocyclopentadienes, the metal acts as a nucleophilic "catalyst." Indeed, this type of reaction is not limited to transition metals but is shared by other Lewis bases such as tertiary phosphines.[25]

On the other hand, olefin and acetylene complexes of higher valent and more electrophilic metals, in which bonding is dominated by the olefin–acetylene π to metal dsp contribution, have been predicted to be (i) unstable and (ii) susceptible to nucleophilic attack at the unsaturated carbon atoms.[8] It is this type of reaction which is discussed in detail in this Account, with special reference to the behavior of organoplatinum compounds. However, a third mode of reaction, involving free-radical formation, should also be recognized. Thus, the activation of unsaturated hydrocarbons may be compared with the activation of molecular hydrogen[26] or of alkyl halides[27] by transition-metal complexes and may occur by any one of these three mechanisms depending on the

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particular system being examined and on the particular reaction conditions.

Certain aspects of the chemistry of organoplatinum compounds make them ideally suited to the consideration of these problems, namely[28] (a) the observance of well-defined oxidation states 0, +2, +4; (b) well-defined coordination numbers (three and four for Pt(0), four for Pt(2+) and six for Pt(4+)) in organoplatinum compounds; (c) their thermodynamic stability (and inertness to oxygen and water) and generally convenient rates of reaction; and (d) their suitability for the application of a variety of spectroscopic techniques.

In regard to points a and b, numerous illustrative compounds are known, e.g., $[(C_6H_5)_3P]_2Pt(un)$ where un = olefin or acetylene,[29] $[(C_6H_5)_3P]_2Pt(CH_3)_2$, and $[(C_6H_5)_3P]_2Pt(CH_3)Cl$ and $[(C_6H_5)_3]_2Pt(CH_3)_nCl_{4-n}$ where n = 1-4.[29] While the assignment of the coordination number of platinum in $[(C_6H_5)_3P]_2Pt(un)$ is arbitrary, deviations from four-coordinate Pt(2+) and six-coordinate Pt(4+) are very rare, and in such cases the metal always attains an 18-electron valence shell e.g., $Pt(SnCl_3)_5^-$,[30] $(\pi-C_5H_5)Pt[(C_6H_5)_3P]_2^+$,[31] CF_3-$[P(CH_3)_2C_6H_5]_2PtC_4(CH_3)_4^+$,[32] and $(\pi-C_5H_5)Pt(CH_3)_3$.[33] Their stability is indicated by the isolation of $[(CH_3)_3PtCl]_4$, which was one of the first organometallic compounds to be discovered;[34] this compound requires treatment with bromine to cleave the Pt–CH$_3$ bonds. Finally, examination of organoplatinum compounds and their reactions by the nmr method is particularly fruitful; the presence of ^{195}Pt (33% abundance, $I = \frac{1}{2}$) and hence the measurement of couplings between ^{195}Pt and other nuclei prove to be an invaluable tool in the understanding of trans influences[35] and chemical bonding.

Organoplatinum(2+) Cations

An unexpected product from the reaction of tetrafluoroethylene with $(R_3P)_2PtHCl$ in a glass container was[36,37] the cation $[(R_3P)_2PtCl(CO)]^+$, which is isoelectronic with the so-called Vaska's compound,[4,38] $(R_3P)_2IrCl(CO)$, and is similarly related to Wilkinson's[39] active catalyst, $(R_3P)_3RhCl$. This prompted us to prepare, and examine with respect to their catalytic activity, the related olefinic and acetylenic organoplatinum cations.

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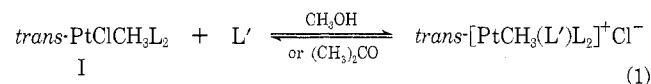
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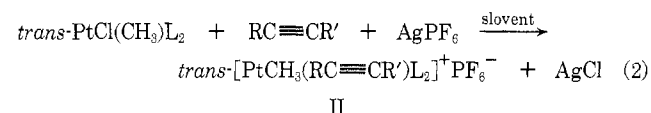(38) (a) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970); (b) J. P. Collman, *ibid.*, 1, 136 (1968).

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The chloride ligand in trans-$PtCl(CH_3)L_2$ (where L = tertiary phosphine or arsine), I, is labile due to the high trans influence of the trans methyl group.[40,41] Hence the addition of a neutral donor ligand, L', to I gives rise to equilibrium 1, for example when L' = pyridine.[42] The addition of a silver salt of a nonpolarizable anion allows the isolation[40] of cationic platinum(2+) complexes for a variety of neutral ligands L'.
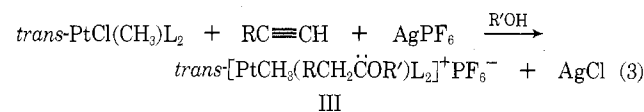
$$\text{trans-}PtClCH_3L_2 + L' \underset{\text{or (CH}_3)_2CO}{\overset{CH_3OH}{\rightleftharpoons}} \text{trans-}[PtCH_3(L')L_2]^+Cl^-$$
$$\text{I} \tag{1}$$

Acetylenic Platinum(2+) Cations

With the hope of isolating methylplatinum acetylenic cations, trans-$[PtCH_3(RC\equiv CR')L_2]^+PF_6^-$ (II), we studied reaction 2. However, the products ob-

$$\text{trans-}PtCl(CH_3)L_2 + RC\equiv CR' + AgPF_6 \xrightarrow{\text{slovent}}$$
$$\text{trans-}[PtCH_3(RC\equiv CR')L_2]^+PF_6^- + AgCl \tag{2}$$
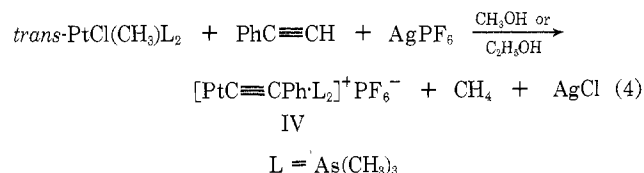$$\text{II}$$

tained from (2) showed a marked dependence on (i) the substituents of the acetylene, R and R', (ii) the ligands on platinum, L, (iii) the solvent, and (iv) the reaction conditions.
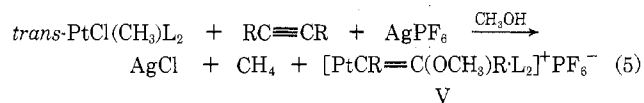
The reaction of dialkyl- or diarylacetylenes in methanol or acetone did in many instances yield[42,43] II, while monoalkyl acetylenes, $RC\equiv CH$, in methanol or ethanol gave[42,44] cationic alkoxycarbene complexes (III) according to eq 3.

$$\text{trans-}PtCl(CH_3)L_2 + RC\equiv CH + AgPF_6 \xrightarrow{R'OH}$$
$$\text{trans-}[PtCH_3(RCH_2COR')L_2]^+PF_6^- + AgCl \tag{3}$$
$$\text{III}$$

Similarly, phenylacetylene gave[44] a benzylalkoxycarbene complex (III) when L = $P(CH_3)_2C_6H_5$, but when L = $As(CH_3)_3$ only acetylide formation occurred[42] as shown in (4). Reactions of monoalkyl acetylenes in aprotic polar solvents, such as tetrahydrofuran, also gave[45] acetylide formation as in (4).

$$\text{trans-}PtCl(CH_3)L_2 + PhC\equiv CH + AgPF_6 \xrightarrow{\substack{CH_3OH \text{ or} \\ C_2H_5OH}}$$
$$[PtC\equiv CPh\cdot L_2]^+PF_6^- + CH_4 + AgCl \tag{4}$$
$$\text{IV}$$
$$L = As(CH_3)_3$$

Disubstituted acetylenes $RC\equiv CR'$ containing electron-withdrawing groups R and R' produced[43] σ vinyl ether complexes in methanol (see 5), while in

$$\text{trans-}PtCl(CH_3)L_2 + RC\equiv CR + AgPF_6 \xrightarrow{CH_3OH}$$
$$AgCl + CH_4 + [PtCR\equiv C(OCH_3)R\cdot L_2]^+PF_6^- \tag{5}$$
$$\text{V}$$

aprotic polar solvents insertion into the methylplatinum bond occurred,[46] as in (6). In reactions 5 and 6 addition to the acetylenic triple bond leads to the

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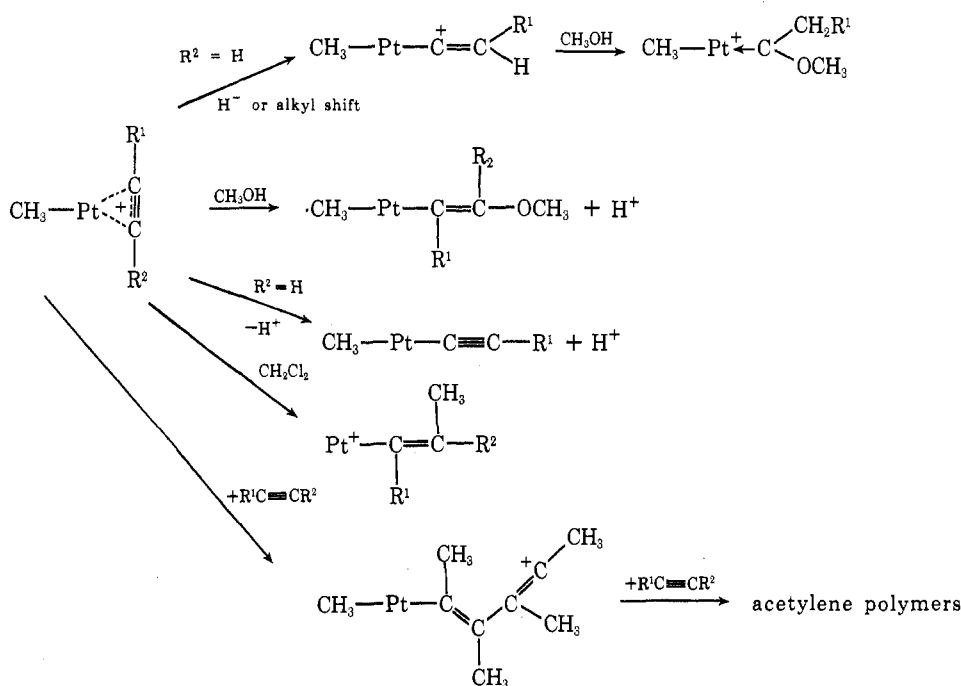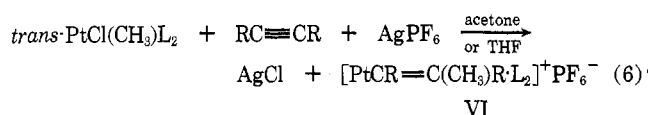
Figure 2.

$$trans\text{-}PtCl(CH_3)L_2 + RC\equiv CR + AgPF_6 \xrightarrow[\text{or THF}]{\text{acetone}}$$

$$AgCl + [PtCR=C(CH_3)R\cdot L_2]^+PF_6^- \quad (6)$$
$$\text{VI}$$

stereospecific formation of trans and cis vinyl isomers respectively.[46]

## The Carbonium Ion Model in Organoplatinum Chemistry

The products of reactions 3 to 6 are derived from the initial formation of cationic acetylenic platinum complexes (II) which show reactivity characteristic of carbonium ions (II') and hence lead to products interpretable in terms of intramolecular rearrangements and/or nucleophilic addition.[46,47]
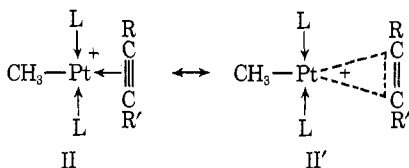
Reactions 2 to 6 led us to predict[46] that the carbonium ion reactivity of an acetylene $RC\equiv CR'$ coordinated to a platinum cation $[PtX \cdot Q_2]^+$ would be dependent on (i) the substituents on the acetylene, R and R', (ii) the ligands on platinum, X and L, and (iii) the availability and nature of a nucleophile, which may be the solvent. Reactions 3 to 6 are explainable on this basis as shown in Figure 2. Thus, carbene formation (reaction 3) only occurs with terminal acetylenes in a protic solvent. In a polar but aprotic solvent, proton elimination or abstraction by solvent takes place to give acetylides. Moreover, the acidity of the acetylenic proton in the metal-induced carbonium ion is also influenced by the other ligands on platinum, as shown by the occurrence of both reactions 3 and 4 for phenylacetylene.[46]

Both cationic carbene complex formation and cationic acetylide complex formation prevent the isolation of cationic acetylenic complexes II, although such complexes have been isolated for dialkyl- or diarylacetylenes. The latter complexes are only slowly attacked by a nucleophilic protic solvent such as methanol to give methyl vinyl ether complexes (reaction 5), although on increasing the electrophilic character of the acetylene (e.g., $HOCH_2C\equiv C\text{-}CH_2OH$, or $CH_3OOCC\equiv CCOOCH_3$), this reaction proceeds more rapidly. In the absence of a nucleophilic protic solvent, these electrophilic acetylenes react with the formation of insertion products (reaction 6). Indeed, in the absence of any nucleophile other than excess acetylene, polymerization is favored, as shown in Figure 2. Clearly, then, the choice of solvent and the ratio of reactants are critical in determining the course of these reactions.

Although many alkoxycarbene complexes of transition metals are now known,[48] reaction 3 is surprising and the mechanism deserves further comment. Initially we considered that the formation of the alkoxycarbene complexes III could be represented by (7), in which the cationic acetylenic complex II reacts with the solvent to produce a cationic vinyl ether complex, which then by hydride shift gives III.
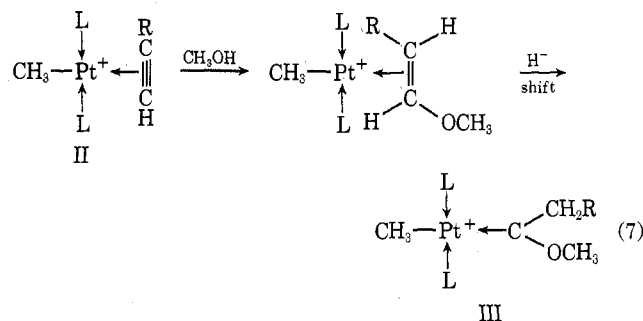
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However, substitution of methyl (or ethyl) vinyl ether for the acetylene in reaction 3 led to the isolation of a stable methyl (or ethyl) vinyl ether cationic complex, which did not decompose in solution below 80°.[46] It should be noted that a carbonium ion mechanism involving H^- migration of a vinylic hydrogen is not favorable due to the orthogonality of the π cloud. This fact may be responsible for the inability of this π-coordinated vinyl ether to rearrange to give the alkoxycarbene ligand. Thus the formation of the platinum-stabilized carbonium ion, $CH_3PtC^+=$ CHR (VII) is essential for conversion to the alkoxycarbene ligand. The formation of VII can occur either by a hydride shift of II' or by proton elimination (Figure 3). Deuterium-labeling studies[46] are consistent with the intramolecular mechanism involving hydride migration. Moreover, the formation[49] of Pt(4+) carbene complexes from cationic Pt(4+) acetylenic intermediates suggests that an oxidative addition–reductive elimination mechanism is not operative.

Other than the above reactions, many other aspects of organoplatinum chemistry clearly illustrate the generality of this carbonium ion model. For example, substitution of the methyl group attached to Pt in II 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*-$[PtCF_3(RC\equiv CR)L_2]^+$. Although we have been unable to isolate such simple dialkylacetylene cations, they are reactive intermediates in the polymerization of acetylenes, a process which occurs much faster than for II in the absence of a polar protic solvent. A terminating step in the polymerization of dimethylacetylene is the formation[46,49] of the cationic tetramethylcyclobutadiene complex, $[PtCF_3\{C_4\text{-}(CH_3)_4\}L_2]^+PF_6^-$, shown in reaction 8. Incidentally,

(8)

ligands L omitted for brevity
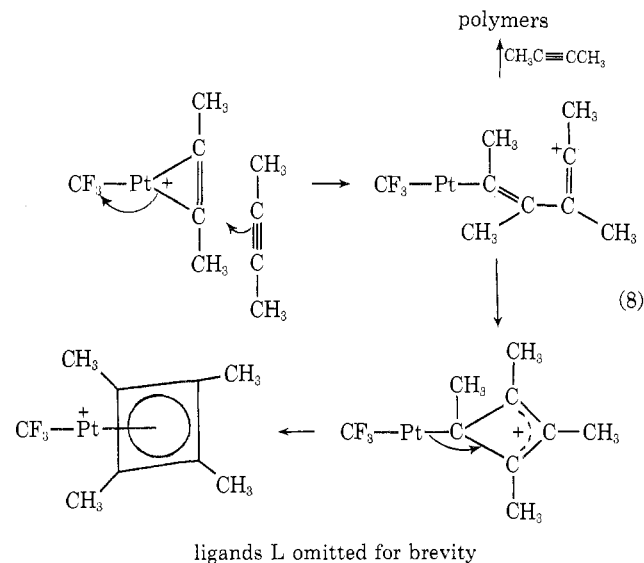
the geometry of this cation—pseudotetrahedral— is unusual for a Pt(2+) complex; moreover, its nmr parameters are consistent with fluxional behavior in solution.[32]

Another reaction in organoplatinum chemistry which is consistent with the carbonium ion model is

(49) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 1484 (1971).
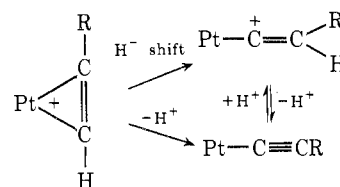
Figure 3.

the formation of an alkoxycarbeneplatinum(4+) cation *via* a cationic acetylenic Pt(4+) intermediate.[49]

$$[Pt(CH_3)_2CF_3(CH\equiv CCH_2CH_2OH)L_2]^+ \longrightarrow$$

$$[Pt(CH_3)_2CF_3(\overline{CH_2CH_2O\ddot{C}CH_2})L_2]^+$$
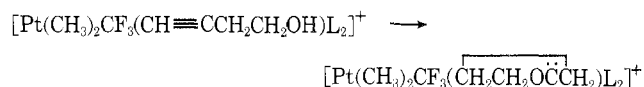
Data from ^{13}C nmr spectroscopy again illustrate the electron-deficient nature of the carbene carbon atom in these alkoxycarbene complexes.[50] By comparison with purely organic analogs, the ^{13}C shieldings of the carbene carbons are comparable to those of trialkylcarbonium ions.[51] Indeed, these platinum complexes could alternatively be considered as platinum-stabilized alkoxycarbonium ions, a nomenclature which more closely reflects their chemical behavior than does the name "alkoxycarbene." For example, carbenoid complexes undergo reactions with nucleophiles such as amines.[48] Likewise, we have found[45] that *trans*-$[PtCl\{\ddot{C}(OCH_3)CH_3\}L_2]^+$ reacts with pyridine to give neutral *trans*-$[PtCl(COCH_3)L_2]$, and the *N*-methylpyridine cation, a reaction which is the reverse of the well-known formation of cationic metal–carbene complexes from acyl derivatives.[48]
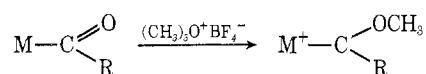
The role of platinum-induced carbonium ions is not limited to reactions described by eq 2; they are the reactive intermediates in the formation of neutral σ vinyl ether (eq 9), acyl (eq 10), and σ vinyl derivatives[52] (eq 11), shown below, which proceed *via* cationic acetylenic intermediates *trans*-$[PtCH_3-(RC\equiv CR)L_2]^+Cl^-$.

trans-$PtCl(CH_3)L_2$ + $RC\equiv CR$ + CH_3OH $\longrightarrow$

   trans-$PtCl(CR=C(OCH_3)R)L_2$ + CH_4 (9)

trans-$PtCl(CH_3)L_2$ + $RC\equiv CH$ + $2CH_3OH$ $\longrightarrow$

   trans-$PtCl(COCH_2R)L_2$ + CH_4 + $(CH_3)_2O$ (10)

trans-$PtCl(CH_3)L_2$ + $RC\equiv CR$ + cat. $\xrightarrow[\text{solvent}]{CH_2Cl_2}$

   trans-$Pt(CR=C(CH_3)R)\cdot Cl\cdot L_2$ (11)

   cat. = trace of $[PtCH_3(acetone)Q_2]^+PF_6^-$
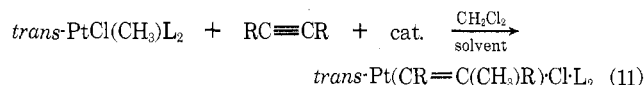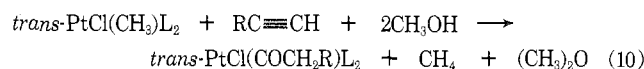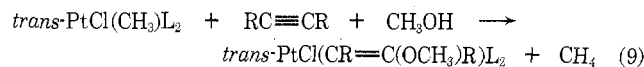
Thus, the formation of methyl vinyl ether complexes in (5) and (9) is stereospecific, giving only the trans vinylic (*i.e.*, trans with respect to C=C) isomer; it is thus analogous to the stereospecific bromination of an acetylene in methanol, which is traditionally regarded[53] as proceeding *via* a carbonium ion mechanism.

(50) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

(51) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

(52) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 11, 1269 (1972).
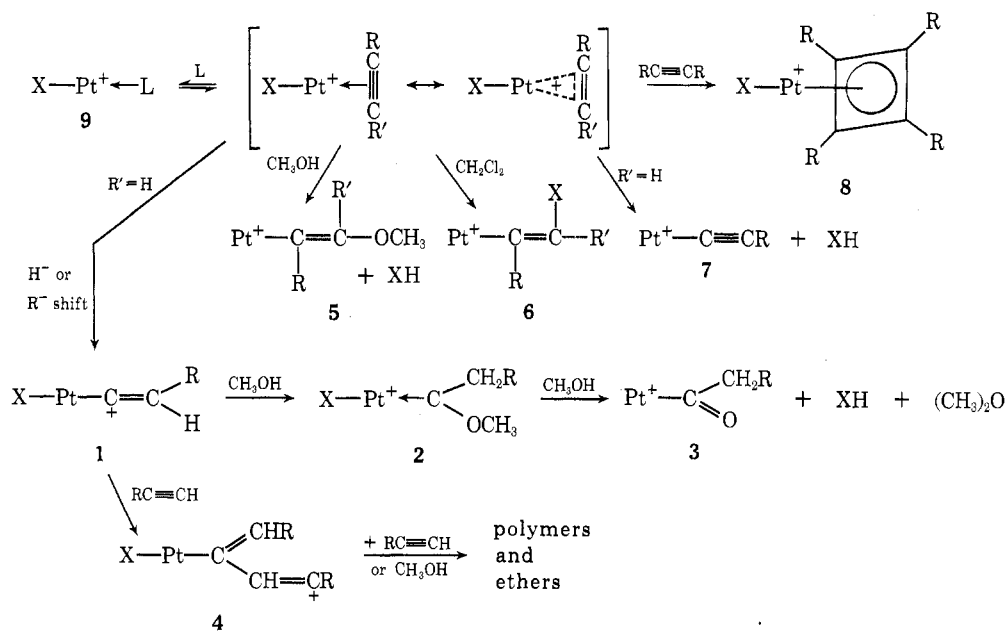
Figure 4. Some reactions of *trans*-[PtX(RC≡CR')Q_2]$^+$Z$^-$. Q = P(CH_3)_2C_6H_5 omitted from the figure for brevity. Z = PF_6 or Cl, except 8 = PF_6 only; X = CH_3 or CF_3 and R = alkyl or aryl for 1-4. X = CH_3, R = R' = alkyl, COOCH_3, COOH, CH_2OH for 5; X = CH_3, R = R' = COOCH_3, CF_3 for 6; X = CH_3, R = phenyl or alkyl, solvent = THF or acetone for 7; X = CF_3, R = CH_3 for 8; X = CH_3 or CF_3, L = PR_3, py, CO, acetone, etc., for 9.

Moreover, reactions 5 and 9 are analogous to a multitude of nucleophilic addition reactions of olefins in the presence of metal salts. The oxymercuration of simple unstrained olefins has long been known to be stereospecific in trans addition.[54] This was first predicted by Lucas, Hepner, and Winstein in 1939 by analogy to the behavior of the bromonium ion.[55] Similarly, platinum (II)- and palladium(II)-diolefin complexes of dicyclopentadiene, norbornadiene, and bicyclo[2.2.2]octadiene yield metal–carbon-bonded σ complexes with the methoxy group in the exo configuration on treatment with alkaline methanol.[56-60] Acyl formation, reaction 10, which occurs on prolonged contact with methanol, is considered to arise from further nucleophilic attack by the methanol on the electron-deficient carbene ligand,[46] e.g., as in (12), and may be compared to the
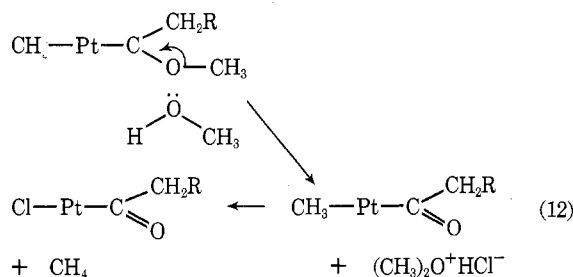
reaction of the methoxymethyl carbene ligand and pyridine discussed earlier.

Reaction 11 provides an excellent illustration of the importance of the choice of solvent.[52] For R = CF_3, in a nonpolar solvent such as benzene, I gives[61] a relatively stable 1:1 adduct of known geometry[62] and ultimately *trans*-PtCl[C(CF_3)=C(CF_3)CH_3]L_2, Pt(C_4F_6)L_2, and PtCl_2(CH_3)_2L_2.

In contrast, in dichloromethane solution, I plus hexafluorobut-2-yne, with a trace of *trans*-[PtCH_3-(acetone)L_2]$^+$ as halide abstractor, rapidly gives[52] *only* the above vinylic product. This reaction may be represented by the catalyzed sequence 13.

(i)   *trans*-[PtCH_3(acetone)L_2]$^+$PF_6$^-$ + CF_3C≡CCF_3 $\xrightarrow{CH_2Cl_2}$

     [L_2PtCCF_3=C(CH_3)CF_3]$^+$PF_6$^-$ + acetone

(ii)   [L_2PtCCF_3=C(CH_3)CF_3]$^+$PF_6$^-$ + *trans*-PtClCH_3L_2 ⇌

     cis-PtCl(CCF_3=C(CH_3)CF_3)L_2 + [PtCH_3Q_2]$^+$PF_6$^-$

(iii)   [PtCH_3L_2]$^+$PF_6$^-$ + CF_3C≡CCF_3 ⟶

     [L_2PtCCF_3=C(CH_3)CF_3]$^+$PF_6$^-$ (13)
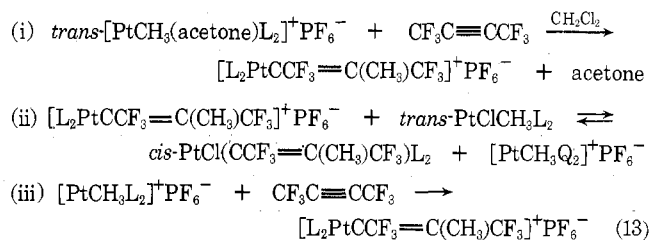
Such activation of acetylenes as we have described above is not limited to methylplatinum compounds; it has also been observed[45,63,64] for a variety of other organoplatinum derivatives where the organic moiety bound to platinum is alkyl, phenyl, vinyl, or alkynyl, all of which exert a high trans influence. The reactions of acetylenes and their products are summarized in Figure 4. Nor is such activation limited to acetylenes. Other unsaturated ligands, un, in cationic complexes–intermediates [PtX(un)L_2]$^+$ are activated toward (i) insertion into the Pt–X bond, (ii) isomerization, and (iii) nucleophilic attack; un =

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(63) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970); *Inorg. Chem.*, **9**, 2670 (1970).

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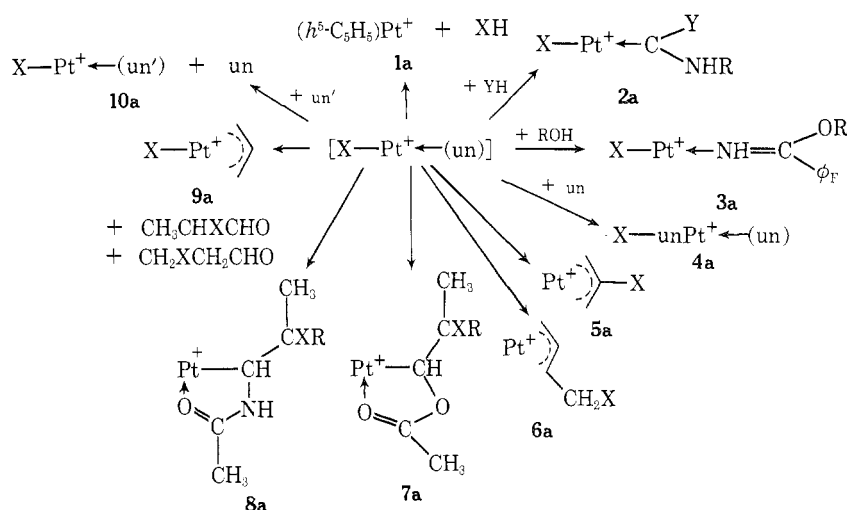
Figure 5. Some reactions of *trans*-[PtX(un)Q$_2$]$^+$Z$^-$. Q = PMe$_2$Ph PMePh$_2$, or PPh$_3$—omitted from figure for brevity. Z = PF$_6$, BF$_4$, ClO$_4$ or NO$_3$; 1a, X = CH$_3$, un = cyclopentadiene; 2a, X = Cl, un = RNC, Y = OCH$_3$, OC$_2$H$_5$, SR, NR$_2$ and NHR; 3a, X = CH$_3$, CF$_3$, un = ϕ_FC≡N where ϕ_F is a perfluoroaryl group, R = CH$_3$ or C$_2$H$_5$; 4a, X = H, un = CH$_2$=CH$_2$, CH$_3$CH=CH$_2$, CH$_3$CH$_2$CH=CH$_2$; 5a, X = H, CH$_3$, un = CH$_2$=C=CH$_2$; 6a, X = H, un = CH$_2$=CH—CH=CH$_2$; 7a, X = H, un = CH$_2$=CH—CH$_2$OCOCH$_3$; 8a, X = un = CH$_2$= CHCH$_2$NHCO—CH$_3$; 9a, X = H, un = (CH$_2$=CHCH$_2$)$_2$O; 10a, X = D, un = CH$_2$=CHCH$_2$OCH$_3$, CH$_2$=CHCH$_2$OC$_6$H$_5$, CH$_3$CH$_2$-CH=CH$_2$, un' = CH$_3$CH=CHOCH$_3$, CH$_3$CH=CHOC$_6$H$_5$, and CH$_3$CH=CHCH$_3$, respectively, accompanied by D scrambling.

olefins, dienes, allenes, vinyl ethers, allyl alcohols, allylamines, allyl ethers, allyl esters, cyanides, and isocyanides.[47,64-76] These reactions are summarized in Figure 5.

Pt-C vs. Pt-H Insertion Reactions

The induced formation of cationic species in polar solvents can thus activate a wide variety of unsaturated compounds. Although the precise nature of the solvated cation and of the role of the solvent and counteranion are unknown, the attainment of the fourth coordination position trans to the ligand of high trans influence (*e.g.*, CH$_3$, H, C$_6$H$_5$, etc.) is clearly essential for activation. Thus, even in Pt-H or Pt-CH$_3$ insertion reactions, attainment of this position by un is a prerequisite. For example, the reaction of allene[47,75] with *trans*-[PtCH$_3$(acetone)L$_2$]$^+$ gives below 0° the *trans*-[PtCH$_3$(π-allene)L$_2$]$^+$ cation, which at higher temperatures leads to Pt(π-C$_4$H$_7$)L$_2$$^+$, where π-C$_4H_7$ = π-2-methallyl. Similarly, the reaction of *trans*-[PtH(acetone)L$_2$]$^+$ with ethylene[74] at −78° gives *trans*-[PtH(π-C$_2$H$_4$)L$_2$]$^+$ which at higher temperature leads to the *trans*-[Pt(C$_2$H$_5$)(π-C$_2$H$_4$)L$_2$]$^+$ derivative. The mechanism by which such insertions proceed following attainment by un of that fourth coordination position is not clear, and the roles of the solvent and counteranion may well be critical.

It is instructive to compare the reactivities of [CH$_3$PtL$_2$]$^+$ and [HPtL$_2$]$^+$ cations. Firstly, the hydride cations [HPtL$_2$]$^+$ are the more reactive toward insertion; this may be partly attributable to the thermodynamic properties of the Pt-H bond compared with those of the Pt-C bond in either the [CH$_3$PtL$_2$]$^+$ cation or in the products. Secondly, the difference in reactivity may relate to the availability of alternative reaction mechanisms. Thus, reactions involving [CH$_3$PtL$_2$]$^+$ proceed in a Markovnikov manner by electrophilic attack of Pt$^+$: for example, as mentioned above, Pt(π-2-methallyl)L$_2$$^+$ is formed from allene and *trans*-[PtCH$_3$(acetone)L$_2$]$^+$, whereas the analogous butadiene cation does not lead[75] to a π-allylic derivative by Pt-CH$_3$ insertion. In contrast, [HPtL$_2$]$^+$ can react either by Markovnikov or anti-Markovnikov mechanisms,[74] *i.e.*, Pt$^+$ or H$^+$ attack. A consequence of this apparent versatility is the formation[70,74] of π-allylic complexes from both allenes and 1,3-dienes with [HPtL$_2$]$^+$; moreover, this versatility is responsible for the characteristic isomerization and H-D exchange reactions of olefins with platinum hydrides.[77]

It is now generally accepted[78-80] that metal–carbon and metal–hydrogen insertion reactions form the basis of transition-metal-catalyzed polymerization and hydrogenation reactions of unsaturated hydrocarbons, respectively. The catalytic activity of d^8 transition metals has been attributed to their ability to expand their coordination spheres, and five-coordinate π complexes have been invoked[61,81-88] as the reactive intermediates in such reactions.

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While insertion may occur *via* the intramolecular rearrangement of such five-coordinate species, little direct evidence to establish this is yet available. Other possibilities, such as bimolecular or free-radical processes involving the five-coordinate species, may well need to be kept in mind. All of our present evidence would suggest that acetylenes are activated toward (i) rearrangements, (ii) Pt–C insertion, and (iii) nucleophilic attack, by coordination to a relatively electron-deficient metal atom as in [PtX(RC≡CR')L₂]⁺. In contrast, coordination to a relatively electron-rich metal as in the five-coordinate π complex with I activates the acetylene to a much smaller extent and may indeed deactivate it toward such reactions.

Conclusions

In considering the generality of the metal-induced carbonium ion model, one must recognize that such reactions are not limited to those of cationic transition-metal complexes with unsaturated compounds. All that is required is that the metal be effectively acidic and capable of leading to a dipole-induced reaction. For example, the platinum–methyl insertion reactions with acetylenes, which proceed rapidly when the acetylene attains the fourth coordination position, may be compared with analogous insertion reactions involving aluminum trialkyls where kinetic data show[89] that the reactive species is R₃Al(RC≡CR). On the other hand, formal positive charge on an organometallic cation does not always lead to acidic or electrophilic interaction with unsaturated compounds. For example, low-valent transition-metal cations may be relatively electron rich. The cationic Ir(+) acetylene complex [Ir(CO)₂(PR₃)₂(H₃COOCC≡CCOOCH)]⁺[90] may be com-

pared with the neutral Pt(2+) formed from I and the same acetylene; in both cases, the metal is acting as a strong nucleophile.

Certainly many organometallic- and transition-metal-catalyzed reactions can be considered to proceed *via* metal-induced or -stabilized carbonium ions. In particular, examples may be drawn from the following classes of reactions: metalation reactions,[54] proton-addition and hydride-abstraction reactions,[91] electrophilic substitution reactions of metallocenes.[92,93] Lewis acid cocatalyzed polymerization of olefins, dienes and acetylenes,[79,94] and metal-catalyzed σ rearrangements of strained alkanes.[95-97] Of these, the Ziegler–Natta process (involving a Lewis acid and an organohalo derivative of any early transition metal as cocatalysts) is of the greatest commercial significance, and its characteristic feature shows a close similarity to that of the organoplatinum systems discussed above. Both require the creation of a vacant and electrophilic coordination site,[98] and their differences result from the different thermodynamic properties of Ti–C and Pt–C σ bonds. Thus, many of the reactions of organoplatinum compounds described above serve as models for those which occur in more complex systems.

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(98) For example, in the TiCl₄–(CH₃)₂AlCl system (which is a typical Ziegler–Natta catalyst) the active complex is CH₃TiCl₃–CH₃AlCl₂. On the basis of solvent studies, the following ionic solvated structure has been ascribed to the active species [CH₃TiCl₂]⁺[Al(CH₃)Cl₃]⁻, which allows formation of cationic olefinic intermediates (ref 92, p 130, and references therein).

$$\left[\begin{array}{c} \overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{Cl-Ti\leftarrow\|}} \overset{CH_2}{\underset{CH_2}{}} \end{array} \right]^+$$

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Study of the Interfacial Properties of Water by Gas Chromatography

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Arleigh Hartkopf worked with Professor Karger, receiving his Ph.D. in 1970. He is presently an assistant professor at Wayne State University.

In recent years, interest in the nature of water at or near interfaces has increased markedly. The controversy over anomalous water[1] attracted a good deal of attention and promoted much theoreti-

(1) B. V. Deryaguin, *Sci. Amer.* 223 (5), 52 (Nov 1970).