Rearranging

$$C = KA_0B/(1 + K'B)$$

but since

$$C'/C = B'/B$$

$$dB'/dt = KC' = kK'A_0B'/(1 + K'B)$$

Since A_0 is constant, this rate expression integrates to a first-order expression, where

$$k_{obsd} = kK'A_0/(1 + K'B)$$

Inverting we have

$$1/k_{obsd} = 1/kK'A_0 + B/kA_0$$

Thus a plot of $1/k_{obsd}$ *vs.* B should be a straight line with $1/kK'A_0$ as intercept and $1/kA_0$ as slope. This treatment is an approximation in that it does not consider the equilibrium represented by eq 2. However, this approximation is not serious, since under the reaction conditions of Figure 2, 95% of the Pd(II) is in the form of dimer. In any case, this equilibrium would cause the plot to curve downward.

Rate data for the allylic esters other than allyl propionate from which the values of K_2, k', and k'' in Table IV were calculated are listed in Table V.

Ultraviolet Spectra Study. The procedure was the same as described previously.[6] The computer program which treated the earlier data was altered to simultaneously include equilibria such as that represented by eq 5 and 8.

Absorbancies were determined at wavelengths of 245, 255, 269, 280, and 340 nm for 34 solutions in which $[Pd(II)]_t$ was varied from 0.00112 to 0.012 *M*, $[Cl]_t$ from 0.029 to 0.4 *M*, and allyl propionate from 0.05 to 2.0 *M*. Absorbancies at all five wavelengths were used in the nonlinear regression program simultaneously. The value of K for eq 5 was calculated to be $0.26 \cdot M^{-1}$ with correlation coefficients of 0.02 to 0.08, while the K for eq 8 was found to give a very poor fit to the data. If the data are calculated assuming that both eq 5 and 8 are occurring simultaneously, a value of 0.11 M^{-1} is obtained for K_2, while the value for K_3 is about 0.08. However, the nature of the equilibria is such that the monomeric π complex is in at least fivefold excess over **1** under all experimental conditions. In any case, little reliance can be placed on these results. A much more detailed study would be required to determine if K_3 is large enough to be calculated, and even then, the reliability of the data in such a complicated system would be doubtful.

Acknowledgments. The author gratefully acknowledges helpful discussions with Professors H. Taube and H. Goering, and is grateful to the following who aided in the experimental work: Mr. Orin Marks, who wrote the computer programs; Miss Kathleen Matarese, who made the spectral measurements; and Mr. F. J. Kriss, for his excellent technical assistance.

Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. III. Reactions of Platinum(II) Stabilized Carbonium Ions

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Abstract: Cationic acetylenic platinum complexes show reactivity characteristic of carbonium ions and are the reactive intermediates in the formation of acetylide, acyl, alkoxy-carbene, vinyl, vinyl ether, and cyclobutadiene complexes. The carbonium ion reactivity of the coordinated acetylene is dependent on (i) the substituents on the acetylene, (ii) the ligands on the platinum cation, and (iii) the availability of a nucleophile. Similar mechanisms involving transition metal induced carbonium ions may provide a general explanation for many transition metal catalyzed reactions of acetylenes and olefins.

Our interest in both acetylenic[1-3] and cationic[4] complexes of platinum(II) initiated a study of reaction A, which might lead to cationic acetylenic complexes II.

$$\underset{\text{I}}{trans\text{-}PtClCH_3Q_2} + RC\equiv CR' + AgPF_6 \xrightarrow{\text{solvent}}$$

$$\underset{\text{II}}{trans\text{-}[PtCH_3(RC\equiv CR')Q_2]^+PF_6^-} + AgCl \quad \text{(A)}$$

$$Q = P(CH_3)_2C_6H_5 \text{ or } As(CH_3)_3$$

Although such complexes of platinum(II) are not unknown [*e.g.*, $\{PtX(en)(ac)\}_n^+$ where n = 1 or 2, X = Cl, Br, or I, ac = $(CH_3)_2OHCC\equiv CC(CH_3)_2OH$ and en = ethylenediamine[5]], the complexes II are ideally suited for spectroscopic studies valuable in the elucidation of both the trans influence of the acetylene and the nature of the platinum–acetylene bond. However, it soon became apparent that the products obtained from (A) were dependent on the nature of the acetylene, the ligands Q, the solvent, and the reaction conditions.

The reaction of dialkyl or diaryl acetylenes in methanol or acetone solvent did in many instances yield II,[6,7] while monoalkyl acetylenes, $RC\equiv CH$, in methanol gave[6,8] cationic alkoxy-carbene complexes III according to (B).

Similarly, phenylacetylene gave a benzyl alkoxy-carbene complex, III, when Q = $P(CH_3)_2C_6H_5$, but

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(1) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).

(2) H. C. Clark and R. J. Fuddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

(3) H. C. Clark and R. J. Puddephatt, *ibid.*, 10, 18 (1971).

(4) H. C. Clark and J. D. Ruddick, *ibid.*, **9**, 1226 (1970).

(5) P. Kong and T. Theophanides, *Can. J. Chem.*, **45**, 3193 (1967).

(6) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970).

(7) Part II: M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 2557 (1971).

(8) Part I: M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 1711 (1971).

$$trans\text{-}\mathrm{PtClCH_3Q_2}\ (\mathrm{I}) + \mathrm{RC{\equiv}CH} + \mathrm{AgPF_6} \xrightarrow{\mathrm{R'OH}} trans\text{-}[\mathrm{PtCH_3(RCH_2COR')Q_2}]^+\mathrm{PF_6}^-\ (\mathrm{III}) + \mathrm{AgCl} \quad \mathrm{(B)}$$

$$\mathrm{Q = P(CH_3)_2C_6H_5 \text{ or } As(CH_3)_3 \text{ and } R' = CH_3 \text{ or } C_2H_5}$$

when $\mathrm{Q = As(CH_3)_3}$ only acetylide formation occurred[6] as shown in (C).

$$trans\text{-}\mathrm{PtClCH_3Q_2} + \mathrm{C_6H_5C{\equiv}CH} + \mathrm{AgPF_6} \xrightarrow[\text{or } \mathrm{C_2H_5OH}]{\mathrm{CH_3OH}} [\mathrm{Pt(C{\equiv}CC_6H_5)Q_2}]^+\mathrm{PF_6}^- + \mathrm{CH_4} + \mathrm{AgCl} \quad \mathrm{(C)}$$

$$\mathrm{Q = As(CH_3)_3}$$

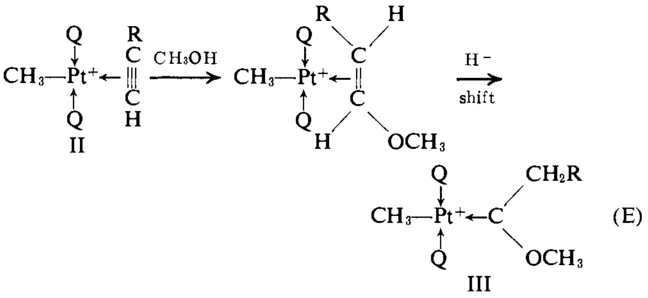
Disubstituted acetylenes, $\mathrm{RC{\equiv}CR'}$, containing electron-withdrawing groups, R and R′, produced[7] vinyl complexes as shown in (D). Even in the absence of

$$trans\text{-}\mathrm{PtClCH_3Q_2} + \mathrm{RC{\equiv}CR'} + \mathrm{AgPF_6} \xrightarrow{\mathrm{CH_3OH}} [\mathrm{PtCR{=}C(OCH_3)R'.Q_2}]^+\mathrm{PF_6}^- + \mathrm{CH_4} + \mathrm{AgCl} \quad \mathrm{(D)}$$

$$\mathrm{Q = P(CH_3)_2C_6H_5;\ R = R' = COOH, COOCH_3, CH_2OH,}$$
$$\mathrm{and\ R = CF_3, R' = H}$$

silver hexafluorophosphate the reaction of methanolic solutions of I with these acetylenes gave[7] platinum–vinyl ether complexes, *trans*-$\mathrm{PtCl\{CR{=}C(OCH_3)R'\}Q_2}$.

Initially we considered[6,8] that the formation of the alkoxy-carbene complexes III could be represented by (E), 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. However, substitution of ethyl vinyl ether for the acetylene, $\mathrm{RC{\equiv}CH}$, in reaction A did not yield[8] the ethyl ethoxy-carbene complex predicted by (E). Furthermore the anti-Markovnikov addition of the alcohol to the acetylene in the formation of III warrants further comment. In this paper we propose a general mechanism which explains all of these results and may also account for many other reactions of coordinated acetylenes.

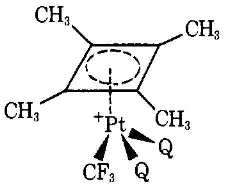
Results

The following new compounds are reported where $\mathrm{Q = P(CH_3)_2C_6H_5}$ unless otherwise stated: *trans*-$[\mathrm{PtCH_3(acetone)Q_2}]^+\mathrm{X}^-$ where $\mathrm{X = PF_6}$ or $\mathrm{SbF_6}$; *trans*-$[\mathrm{PtCH_3(CH_2{=}CHOCH_3)Q_2}]^+\mathrm{PF_6}^-$; *trans*-$\mathrm{PtCl\{CCH_3{=}C(OCH_3)CH_3\}\{P(CH_3)_3\}_2}$; *trans*-$[\mathrm{Pt\{CCF_3{=}C(CH_3)CF_3\}(CO)Q_2}]^+\mathrm{PF_6}^-$; *trans*-$\mathrm{PtCl(COCH_2R)Q_2}$ where R = H or $\mathrm{CH_3}$ and $\mathrm{Q = P(CH_3)_2C_6H_5}$ or $\mathrm{As(CH_3)_3}$; *trans*-$[\mathrm{PtCF_3(acetone)Q_2}]^+\mathrm{PF_6}^-$; $[\mathrm{PtCF_3\{C_4(CH_3)_4\}Q_2}]^+\mathrm{PF_6}$ where $\mathrm{C_4(CH_3)_4}$ is tetramethylcyclobutadiene; and $[\mathrm{Pt(CH_3)_2(CF_3)(\overline{CH_2CH_2OCC}H_2)Q_2}]^+\text{-}\mathrm{PF_6}^-$.

These compounds have been characterized by analysis, infrared, Raman, and ^{1}H and ^{19}F nmr spectroscopy. Relevant data are recorded in the Experimental Section. Only the fact that these compounds have been formed and isolated is pertinent to the discussion in this paper and therefore we defer a detailed discussion of their chemistry and spectroscopic properties except for the following points.

1. *trans*-$[\mathrm{PtCH_3(CH_2{=}CHOCH_3)Q_2}]^+\mathrm{PF_6}^-$ shows similar spectroscopic properties to the compounds, *trans*-$[\mathrm{PtCH_3(olefin)Q_2}]^+\mathrm{PF_6}^-$, in particular coupling of the olefinic protons to ^{195}Pt, and J(Pt–C–H) for the platinum–methyl group.[9] We conclude that methyl vinyl ether is π bonded to platinum and not coordinated *via* the oxygen.

2. The only cyclobutadiene complexes of platinum previously reported are $[\mathrm{Pt\{C_4(C_6H_5)_4\}X_2}]$ where X = Cl, Br, or I.[10] Evidence for the tetramethyl cyclobutadiene ligand in $[\mathrm{PtCF_3\{C_4(CH_3)_4\}Q_2}]^+\mathrm{PF_6}^-$ is based on (a) analytical data, (b) infrared spectra,[11] and (c) ^{1}H and ^{19}F nmr spectra. The latter contrast dramatically with the nmr spectra of square-planar cationic platinum(II) complexes[12] by showing values of ^3J(Pt–H) for the phosphine methyl protons and ^2J(Pt–F) for the trifluoromethyl fluorines which are comparable to those associated with organoplatinum(IV) compounds, *e.g.*, $\mathrm{Pt(CH_3)_2(CF_3)IQ_2}$.[13] Furthermore no phosphorus coupling to the trifluoromethyl fluorines is observed. This results from the stereochemistry of this platinum cation (shown below) which is necessary to allow stable bonding between platinum and the cyclobutadiene ring.[14]



3. The cationic platinum(IV) complex $[\mathrm{Pt(CH_3)_2(CF_3)(\overline{CH_2CH_2OCC}H_2)Q_2}]^+\mathrm{PF_6}$ is the first example of a carbene ligand coordinated to a metal in a higher valency state than two. Its isolation also further demonstrates the strong nucleophilic character of the alkoxy-carbene ligand and the relative insignificance of metal "d" → carbene "$\mathrm{p_z}$" π bonding.[7,8]

Discussion

The bonding in transition metal olefin and acetylene complexes has long been a source of interest to chemists. The original Dewar[15]–Chatt–Duncanson[16] model predicted that the bonding consists of a σ interaction, acetylene "π" → metal "dsp", and a π interaction, metal "d" → acetylene "π*." The concept of this synergic effect is still accepted, and most of the subsequent debate has been devoted to an appraisal of the

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[9] M. H. Chisholm and H. C. Clark, unpublished results.

[10] F. Canziani, P. Chini, A. Quarta, and A. Dimartino, *J. Organometal. Chem.*, **26**, 285 (1971).

[11] Compare assignments for $[\mathrm{C_4(CH_3)_4NiCl_2}]_2$: H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 260 (1964).

[12] (a) *trans*-$[\mathrm{PtCH_3(L)Q_2}]^+$, see ref 4; (b) *trans*-$[\mathrm{PtCF_3(L)Q_2}]^+$, see T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, in press.

[13] H. C. Clark and J. D. Ruddick, *ibid.*, **9**, 2556 (1970).

[14] F. A. Cotton in "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1964, p 180.

[15] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

[16] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

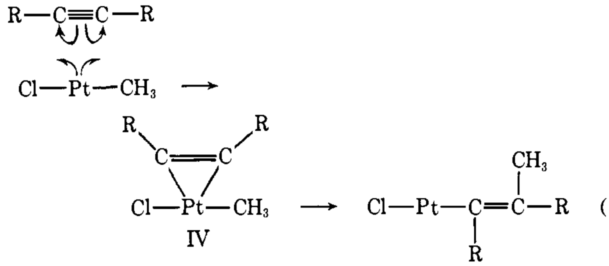
Table I. Reactions of Methanolic Solutions of *trans*-$PtClCH_3Q_2$ (I) with Acetylenes[a]

Reaction	Comments
1. $I + RC{\equiv}CH + AgPF_6 \rightarrow$ *trans*-$[PtCH_3\{C(OCH_3)CH_2R\}Q_2]PF_6 + AgCl$	$R = H, CH_3, C_2H_5, C_3H_7{}^n, C_4H_9{}^n, C_5H_{11}{}^n, C_6H_{11}{}^{cyclo}$, and C_6H_5; reactions in ethanol lead to ethoxycarbenes
2. $I + C_6H_5C{\equiv}CH + AgPF_6 \rightarrow [Pt(C{\equiv}CC_6H_5)Q_2]PF_6 + AgCl + CH_4$	For $Q = As(CH_3)_3$ only
3. $I + RC{\equiv}CR' + AgPF_6 \rightarrow$ *trans*-$[PtCH_3(RC{\equiv}CR')Q_2]PF_6 + AgCl$	$Q = P(CH_3)_2C_6H_5$; $RC{\equiv}CR' = CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CC_2H_5$, $C_2H_5C{\equiv}CC_2H_5$, $CH_3C{\equiv}CC_6H_5$, and $C_6H_5C{\equiv}CC(C_6H_5)_2OH$; $Q = As(CH_3)_3$; $RC{\equiv}CR' = C_6H_5C{\equiv}CC_6H_5$ and $C_6H_5C{\equiv}CC(C_6H_5)_2OH$; other dialkyl and diaryl acetylene complexes may be obtained in solution
4. $I + RC{\equiv}CR' + AgPF_6 \rightarrow [PtCR{=}C(OCH_3)R'.Q_2]PF_6 + AgCl + CH_4$	$Q = P(CH_3)_2C_6H_5$; $R = R' = COOCH_3, CH_2OH, COOH$, and $R = CF_3$, $R' = H$
5. $I + CF_3C{\equiv}CCF_3 + AgPF_6 \rightarrow [PtCH_3Q_3]PF_6 + Pt(0) + AgCl$	
6. $I + RC{\equiv}CH \xrightarrow[\text{1 atm}]{\text{12 hr, 30°}}$ *trans*-$PtCl(COCH_2R)Q_2 + CH_4$	$R = H$ and CH_3
7. $I + C_6H_5C{\equiv}CH \xrightarrow{\text{1 hr, 30°}}$ *trans*-$PtCl(C{\equiv}CC_6H_5)Q_2 + CH_4$	
8. $I + RC{\equiv}CR' \rightarrow$ *trans*-$PtCl\{CR{=}C(OCH_3)R'\}Q_2 + CH_4$	$Q = P(CH_3)_2C_6H_5$; $R = R' = COOCH_3, CH_2OH$, and $R = CF_3$, $R' = H$
9. $I + RC{\equiv}CH \xrightarrow[\text{3 hr}]{\text{30°}} Pt(0) +$ "polymerization" $+ CH_4$	$R = CH_2OH$ and CH_2CH_2OH, $RC{\equiv}CH$ in excess of 1 mol ratio
10. $I + CF_3C{\equiv}CCF_3 \rightarrow$ 1:1 adduct $\rightarrow PtCl\{CF_3C{=}C(CH_3)CF_3\}Q_2$ $\downarrow$ $Pt\{CF_3C{\equiv}CCF_3\}Q_2 + Pt(CH_3)_2Cl_2Q_2$	
11. $I + RC{\equiv}CR' \rightarrow$ no reaction; 12 hr, 30°, 1 atm	$R = R' = CH_3$ and C_2H_5

[a] $Q = P(CH_3)_2C_6H_5$ or $As(CH_3)_3$; all reactions involved 1:1 molar ratio of $RC{\equiv}CR'$:I.

relative magnitudes of the σ and π interactions and to the choice of metal orbitals employed in this bonding.[17-23] The sensitivity of the σ- and π-bonding contributions to changes in the relative energies of the metal valence orbitals and the acetylene π and π^* orbitals is clearly seen in the Maitlis model.[18] The reactivity of transition metal coordinated acetylenes and olefins, which leads to a wide variety of products ranging from "thick brown soups" to "organometallic exotica,"[24] is inherently related to the nature of this bonding. The attack of a transition metal complex by an acetylene may be considered to be electrophilic or nucleophilic in origin depending on the relative σ donor/π^* acceptor contribution to the bonding in the adduct. We believe that many reactions of *trans*-$PtClCH_3Q_2$ with acetylenes can be classified in this manner and that the products reflect the nature of the initial attack.

Some reactions of methanolic solutions of I with acetylenes are summarized in Table I. Reactions 7 and 10 are solvent independent and have been shown[1-3] to proceed *via* initial neutral π-complex formation as in (F).



(F)

The π complex IV, which in turn leads to the insertion product, is formed only by acetylenes with electron-withdrawing substituents such as CF_3 and $COOCH_3$, *viz.*, strong π acids [similarly with the olefins C_2F_4 and $C_2(CN)_4$]. No reaction is observed between monoalkyl or dialkyl acetylenes and benzene or chloroform solutions of I, nor is there any nmr spectroscopic evidence for the formation of IV. Furthermore the formation of IV is dependent on the ligands Q in I, and for *trans*-$PtClCF_3Q_2$, where the methyl group has been replaced by the more electron-withdrawing trifluoromethyl group, no reaction or formation of IV is observed.[25] Consequently we consider that the formation of IV results from electrophilic attack of the acetylene on I and that the most important factor stabilizing (IV) is the metal "d" → acetylene "π^*" bonding.

The chloride ligand in I is labile due to the high trans influence of the *trans*-methyl group.[4,26] Hence the addition of a neutral donor ligand, L, to I gives rise to the equilibrium G, for example, when L = pyridine.[26] Similarly, the addition of a strong σ donor such as an isonitrile, RNC, to I gives only *trans*-$[PtCH_3(CNR)Q_2]^+Cl^-$, even in dichloromethane

$$\textit{trans}\text{-}PtClCH_3Q_2 + L \underset{\text{or }(CH_3)_2CO}{\overset{CH_3OH}{\rightleftharpoons}} \textit{trans}\text{-}[PtCH_3(L)Q_2]^+Cl^- \quad (G)$$

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(18) E. O. Greaves, C. J. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(19) F. R. Hartley, *Chem. Rev.*, 799 (1969), and references cited therein.

(20) J. H. Nelson, K. S. Wheelock, L. C. Casachs, and H. B. Jonassen, *Chem. Commun.*, 1019 (1969).

(21) J. H. Nelson, K. S. Wheelock, L. C. Casachs, and J. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969).

(22) K. S. Wheelock, J. H. Nelson, L. C. Casachs, *ibid.*, **92**, 5110 (1970).

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(24) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, 3rd ed, Methuen, London, 1968, p 288.

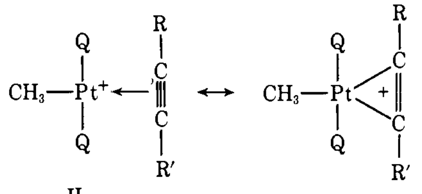
(25) T. G. Appleton, M. H. Chisholm, and H. C. Clark, unpublished results.

(26) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

solution.[27] We therefore believe that acetylenes with electron-releasing substituents may react *via* nucleophilic attack on I, and, in the presence of polar solvents, cause nucleophilic displacement of Cl^-, as in (G). While the equilibrium probably lies well to the left, the addition of silver hexafluorophosphate allows the isolation of cationic acetylenic complexes II, as in reaction 3 of Table I, or cationic complexes derived from their reaction with methanol, as in 1 and 4, depending on the nature of the acetylene. Even in the absence of silver hexafluorophosphate it appears that the reaction of certain acetylenes with methanolic solutions of I proceeds *via* cationic intermediates, as in 6 and 8 of Table I (see Experimental Section). Alternative mechanisms which do not involve the lability of the chloride ligand are considered less likely since *cis*-$Pt(CH_3)_2Q_2$ does not react with $CH_3C{\equiv}CH$ in methanol under the conditions of 6 (see Experimental Section). Similarly reactions of $CF_3C{\equiv}CH$ with methanolic solutions of *cis*-$Pt(CH_3)_2Q_2$ show no sign of methyl vinyl ether formation,[28] in marked contrast to 8.

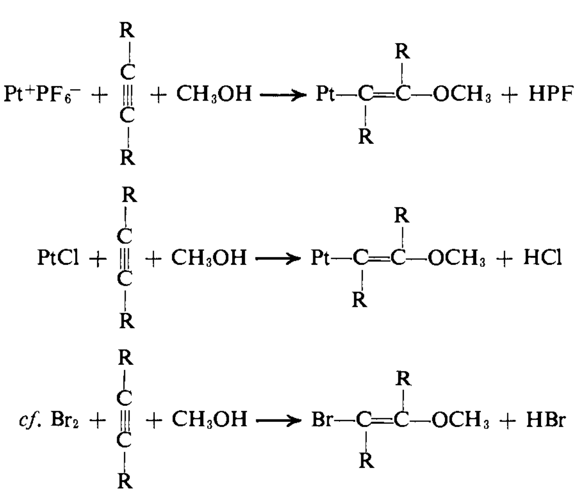
For certain acetylenes, $RC{\equiv}CR'$, one might expect that the reaction with I would proceed by electrophilic attack, F, or nucleophilic attack, G, depending on the nature of the solvent. We find[25] that when $R = R' = COOCH_3$, and $R = CF_3$, $R' = H$, the reaction proceeds *via* IV, as in F, in benzene or chloroform; whereas in methanol it proceeds as in G (reaction 8 of Table I).

The products of reactions 1–4, 6, 8, and 9, which involve a cationic mechanism, are derived from the reaction of the carbonium ion V, formed by electrophilic attack of the platinum on the acetylenic triple bond.



II V

Recognition of the fact that a metal-stabilized carbonium ion is involved leads to a general explanation that readily accounts for both the stereochemistry and the nature of the products of these reactions.



$$Pt^+PF_6^- + \begin{array}{c}R\\|\\C\\|||\\C\\|\\R\end{array} + CH_3OH \longrightarrow Pt{-}\underset{R}{C}{=}\overset{R}{C}{-}OCH_3 + HPF_6$$

$$PtCl + \begin{array}{c}R\\|\\C\\|||\\C\\|\\R\end{array} + CH_3OH \longrightarrow Pt{-}\underset{R}{C}{=}\overset{R}{C}{-}OCH_3 + HCl \qquad (H)$$

$$cf.\ Br_2 + \begin{array}{c}R\\|\\C\\|||\\C\\|\\R\end{array} + CH_3OH \longrightarrow Br{-}\underset{R}{C}{=}\overset{R}{C}{-}OCH_3 + HBr$$

Reactions of V

1. Nucleophilic Addition. Methyl Vinyl Ether Formation. The formation of methyl vinyl ether complexes (reactions 4 and 8 of Table I) may be compared to the reaction of halogens with unsaturated hydrocarbons in methanol. See reactions in (H).

In the preparation of the methyl vinyl ether complex, *trans*-$PtCl\{CCH_3{=}C(OCH_3)CH_3\}Q_2$, outlined in (I) below, *only* the vinylic trans isomer,[29] $Pt(CH_3)C{=}C(CH_3)OCH_3$, is formed (see Experimental Section). While the vinylic trans isomer is predicted from V, it is not obvious from II where the positive charge is formally on the platinum; furthermore this contrasts to the cis addition to the triple bond produced[2,30] by reactions of type F.

$$I + CH_3C{\equiv}CCH_3 + AgPF_6 \xrightarrow{CH_3OH} trans\text{-}[PtCH_3(CH_3C{\equiv}CCH_3)Q_2]^+PF_6^- + AgCl$$

$$\Big\downarrow {\scriptstyle CH_3OH,\ 12\ hr,\ 30°}$$

$$[PtCCH_3{=}C(OCH_3)CH_3Q_2]^+PF_6^- + CH_4 \xrightarrow{NaCl} trans\text{-}PtCl\{CCH_3{=}C(OCH_3)CH_3\}Q_2 + NaPF_6 \qquad (I)$$

$$Q = P(CH_3)_3$$

The formation of platinum–vinyl ether complexes in reactions 4 and 8 is 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.[31] This was first predicted by Lucas, Hepner, and Winstein in 1939 by analogy to the behavior of the bromonium ion.[32] 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.[33–37]

2. H^- Migrations. Alkoxy-carbene and Acyl Formation. Our initial suggestion that alkoxy-carbene formation proceeds *via* cationic vinyl ether intermediates, as in (E), must be rejected since *trans*-$[PtCH_3(CH_2{=}CHOCH_3)Q_2]^+PF_6^-$ has now been isolated as a white crystalline air-stable solid.[38]

The anti-Markovnikov addition of CH_3OH to $RC{\equiv}CH$ in the formation of RCH_2COCH_3 is considered to arise by a rearrangement of V to $Pt{-}C^+{=}CHR$ (VI). Since only acetylene and monoalkyl or

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(27) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, in press.

(28) T. G. Appleton, H. C. Clark, and R. J. Puddephatt, *ibid.*, in press.

(29) Compare, *e.g.*, B. E. Mann, B. L. Shaw, and M. I. Tucker, *Chem. Commun.*, 1333 (1970); ref 2 and 24.

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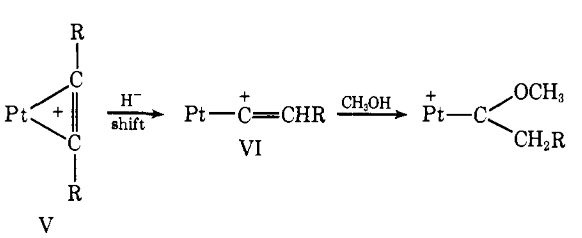
(35) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

(36) C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.*, 7, 181 (1967).

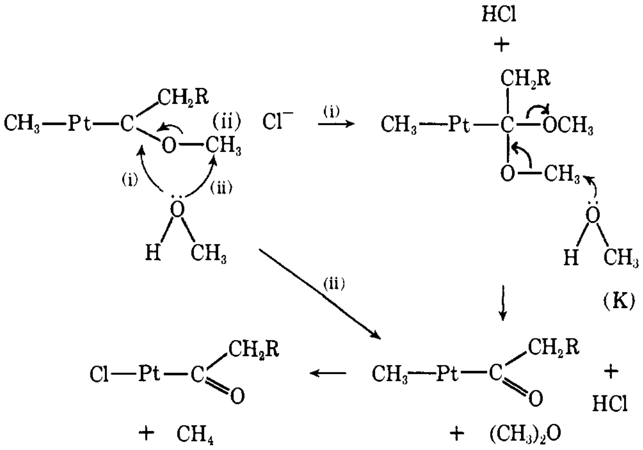
(37) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

(38) 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 alkoxy-carbene ligand.

-aryl acetylenes give carbene formation, and the migratory aptitudes of R groups are normally R = H > aryl > alkyl,[39] we believe the conversion V → VI proceeds *via* H^- migration. Therefore we suggest that alkoxy-carbene formation (reaction 1 of Table I) may be represented by (J). Acyl formation (reaction 6 of Table I), which occurs on prolonged contact with methanol, is considered to arise from further nucleophilic attack by the methanol on the electron-deficient carbene ligand,[40] *e.g.*, as in (K) below.



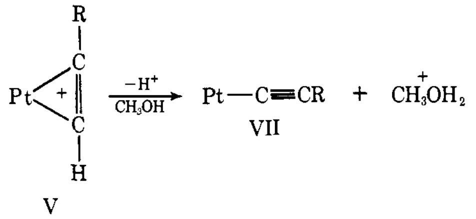
(J)



(K)

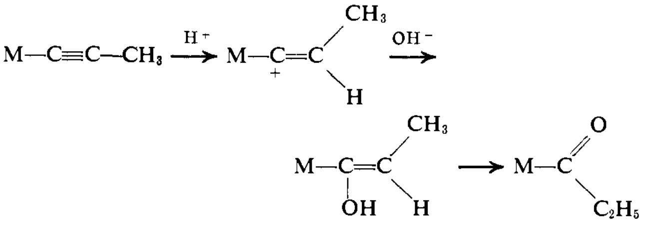
It is interesting to note that in the reaction of I with fluoroolefins in methanol and ethanol (which react *via* alkoxy insertion), dimethyl ether and diethyl ether are formed respectively.[28]

3. H^+ Loss (Abstraction by CH_3OH). Acetylide Formation. Acetylide formation, as in reaction 2 of Table I, may arise because the acidity of the acetylenic proton in RC≡CH is greater for R = C_6H_5 than for R = alkyl,[41] and, therefore, proton loss (abstraction by CH_3OH) is favored over H^- migration.



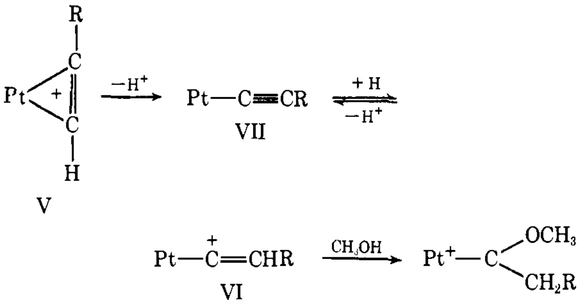
When Q = $P(CH_3)_2C_6H_5$ and $As(CH_3)_3$ alkoxy-carbene formation and acetylide formation occur respectively. This strongly suggests that the stability and/or formation of VI is dependent on the ligands stabilizing the platinum cation.

H^- Migration *vs.* H^+ Loss. A "vinylidene carbene complex" or "metal-stabilized vinyl cation," equivalent to the platinum-stabilized carbonium ion VI, has been proposed[42] as the reactive intermediate in the reaction shown below.



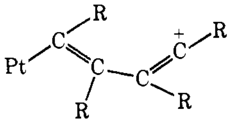
M = π-$C_5H_5Fe(CO)_2$

The isolation of $M(CH_3COO)C{=}C(CH_3)H$ from the reaction of $MC{\equiv}CCH_3$ with anhydrous acetic acid was suggested as evidence of VI. Similarly certain platinum acetylides are known to react with HCl to give the vinyl group $PtCCl{=}CHR$[43] and therefore probably proceed *via* VI. It was suggested[44] on the basis of the above reactions and the isolation of acetylide (reaction 2 of Table I) that alkoxy-carbene formation more likely occurred as in (L). We had dismissed this mechanism since methyl–platinum(II) complexes are very susceptible to protic attack to give methane and loss of the methyl platinum group (*e.g.*, as in reactions 4 and 8 of Table I). To clarify this point we carried out reaction 1 of Table I with C_2H_2 and CH_3OD as solvent. Mechanism J, hydride shift, can only lead to CH_2DCOCH_3 in contrast to L, H^+ scrambling, which would yield mostly CD_3COCH_3. ^1H nmr showed the methoxy to α-carbene proton ratio was 3:2 and therefore substantiates the hydride migration mechanism J in the formation of III.

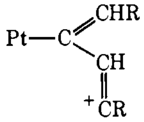


(L)

4. Electrophilic Attack on Another Acetylene. Excess acetylene (≫1 molar ratio) in reaction A greatly reduces the yields of II or III but produces a substantial increase in organic "tars" (see also reaction 9 of Table I). We consider that excess acetylene provides an alternative nucleophile for reaction with V or VI and polymerization occurs *via* VIII or IX.



VIII



IX

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[39] J. March in "Advanced Organic Chemistry: Reaction, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968.

[40] The susceptibility of transition metal-alkoxy-carbene complexes to nucleophilic attack allows their conversion to amino- or thiocarbene complexes on treatment with amines and thiols, respectively. See U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, **89**, 7141 (1967), and J. A. Connor and E. O. Fischer, *J. Chem. Soc. A*, 578 (1969).

[41] (a) A. E. Streitwieser and D. M. E. Reuben, *ibid.*, **93**, 1794 (1971); (b) D. J. Cram in "Fundamentals of Carbanion Ion Chemistry," Academic Press, New York, N. Y., 1965, p 59.

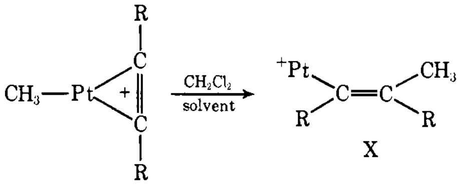
[42] P. W. Jolly and R. Pettit, *J. Organometal. Chem.*, **12**, 491 (1968).

[43] M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc. A*, 356 (1968).

[44] We thank the referee for raising this point.

5. Intramolecular Rearrangement. Methyl–Platinum Insertion. The isolation of *trans*-[PtCH$_3$(acetone)Q$_2$]$^+$PF$_6^-$ has allowed us to study the reactions of V in nonnucleophilic solvents, such as dichloromethane, since acetone is readily displaced by acetylenes.

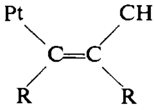
Acetylenes, RC≡CR, with strongly electron-withdrawing groups R, such as CF$_3$, react *via* insertion into the methyl–platinum bond to give platinum vinyl compounds X.



X

V

Only the cis-vinylic isomer



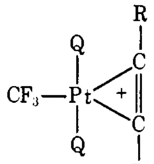
is obtained as would be expected from an intramolecular rearrangement, consistent with a concerted 1,2-CH$_3^-$ shift from Pt to C$_2$.

The Carbonium Ion Model

These reactions of V (1–5) demonstrate that the carbonium ion reactivity of an acetylene coordinated to a platinum cation is dependent on (i) the substituents on the acetylene, (ii) the ligands on the platinum, and (iii) the availability and nature of a nucleophile.

The generality of this carbonium ion concept is indicated by the following.

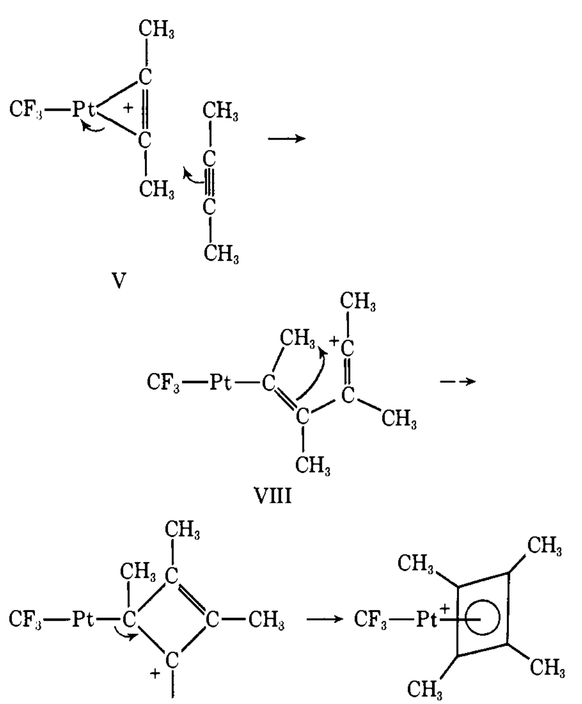
1. Substitution of the methyl group in II by the more electron-withdrawing trifluoromethyl group should increase the electrophilicity of the platinum cation. Therefore, the carbonium ion V, shown below, should be more reactive (more electrophilic) than the methyl platinum analog.



V

This is indeed the case observed, and, even by the reaction of *trans*-[PtCF$_3$(acetone)Q$_2$]$^+$PF$_6^-$ with RC≡CR in a nonnucleophilic solvent such as dichloromethane, we have been unable to isolate simple dialkyl acetylene complexes analogous to II. In the presence of excess acetylene polymerization occurs much faster than for II. The formation of the cyclobutadiene ligand in [PtCF$_3${C$_4$(CH$_3$)$_4$}Q$_2$]$^+$PF$_6^-$ is considered to arise from cyclization of a single trans addition VIII, as indicated in (M) below.

2. Platinum(IV) Carbonium Ions. No π-coordinated acetylenic complexes of tetravalent platinum are known. This is presumably due to the inadequacy of platinum(IV) "d" → acetylenic "π*" bonding.[45]



V

VIII

(M)

Therefore we would not expect to be able to isolate stable cationic complexes of the form [Pt(CH$_3$)$_2$(CF$_3$)(RC≡CR′)Q$_2$]$^+$PF$_6^-$. Our model predicts that they would be reactive carbonium intermediates. We find that the cation [Pt(CH$_3$)$_2$(CF$_3$)Q$_2$]$^+$ very readily polymerizes acetylenes and in acetone solution reacts with the acetylene CH≡CCH$_2$CH$_2$OH to give the alkoxycarbene cation

$$[\mathrm{Pt(CH_3)_2(CF_3)(\overline{CH_2CH_2OC}CH_2)Q_2}]^+$$

Many reactions of unsaturated organic ligands with transition metal complexes can be interpreted in terms of metal induced/stabilized carbonium ion mechanisms. These will be discussed elsewhere.

Experimental Section

General methods have been outlined previously.[8]

trans-PtClCH$_3$Q$_2$ and *cis*-Pt(CH$_3$)$_2$Q$_2$ where Q = P(CH$_3$)$_2$C$_6$H$_5$, P(CH$_3$)$_3$, or As(CH$_3$)$_3$ were prepared by the method of Ruddick and Shaw[46,47] and *trans*-PtCF$_3$IQ$_2$ and Pt(CH$_3$)$_2$(CF$_3$)(I)Q$_2$ by the method of Clark and Ruddick.[13]

Acyl Derivatives. *trans*-PtCl(COR)Q$_2$ where R = CH$_3$ or C$_2$H$_5$ and Q = P(CH$_3$)$_2$C$_6$H$_5$ or As(CH$_3$)$_3$ were all prepared in a similar manner, and so we describe only one preparation in detail.

trans-PtCl(COC$_2$H$_5$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$. *trans*-PtClCH$_3${P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.244 g) was dissolved in methanol (30 ml) in a two-necked 100-ml round-bottomed flask containing a magnetic stirring bar. Propyne was bubbled through the solution for 2 min and then the solution was stirred (magnetically) under an atmosphere of propyne for 12 hr during which time it turned pale yellow. Solvent was removed under reduced pressure and the resultant yellow gum dried under high vacuum (10^{-4} cm) at 20° for 30 min. The gum was dissolved in benzene (5 ml) and passed through a short Florisil column eluting with benzene. A pale yellow solution was obtained and, after reducing the volume to *ca.* 5 ml, the addition of pentane initiated crystallization. After cooling in the refrigerator for 3 hr the off-white crystalline product was collected by filtration, washed with pentane, and dried *in vacuo*. Further chromatography (benzene–Florisil) and recrystallization (chloroform–ether) gave *trans*-PtCl(COC$_2$H$_5$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (0.145 g, 60% theory, based on Pt) as fine white needles, mp 134–136°. *Anal.* Calcd for PtP$_2$ClO-

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(45) *E.g.*, cases D and E of the Maitlis model, ref 18.

(46) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

(47) J. D. Ruddick and B. L. Shaw, *ibid.*, 2964 (1969).

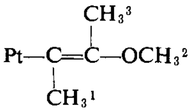
$\mathrm{C_{19}H_{27}}$: C, 40.45; H, 4.83; Cl, 6.30. Found: C, 40.55; H, 4.70; Cl, 6.52.

trans-$\mathrm{PtCl(COCH_3)\{P(CH_3)_2C_6H_5\}_2}$ was prepared as above using acetylene in place of propyne. The use of a large excess of acetylene was avoided since this led to a considerable increase in organic tars at the expense of the acyl derivative and also made purification by chromatography and crystallization more tedious. *Anal.* Calcd for $\mathrm{PtP_2ClOC_{18}H_{25}}$: C, 39.31; H, 4.59; Cl, 6.46. Found: C, 39.78; H, 4.66; Cl, 6.76.

All our acyl derivatives show an intense infrared absorption in the region 1640–1630 cm^{-1} characteristic of ν_{str}(C═O) in platinum(II) acyl compounds.[48,49] The trans stereochemistry is readily apparent from the phosphinemethyl proton magnetic resonances which appear as 1:2:1 triplets, $^2J + {}^4J$(P–H)[50] = 7.5 Hz, with platinum satellites, $J(^{195}\mathrm{Pt{-}H})$ = 37.7 Hz, characteristic of mutually *trans*-phosphinemethyl protons in square-planar platinum(II) complexes.[46]

Reaction of *cis*-$\mathrm{Pt(CH_3)_2\{P(CH_3)_2C_6H_5\}_2}$ with $\mathrm{CH_3C{\equiv}CH}$ in Methanol. *cis*-$\mathrm{Pt(CH_3)_2\{P(CH_3)_2C_6H_5\}_2}$ (0.173 g) was dissolved in methanol (25 ml) in a two-necked 100-ml round-bottomed flask fitted with a magnetic stirring bar. Propyne was bubbled through for 2 min and the solution was then stirred under an atmosphere of propyne for 12 hr. Evaporation of the methanol solvent under reduced pressure gave a cream solid. *cis*-$\mathrm{Pt(CH_3)_2\{P(CH_3)_2C_6H_5\}_2}$ (0.155 g) was recovered (90%) by recrystallization from benzene–pentane solution.

***trans*-$\mathrm{PtCl\{CCH_3{=}C(OCH_3)CH_3\}\{P(CH_3)_3\}_2}$.** *trans*-$\mathrm{PtClCH_3\{P(CH_3)_3\}_2}$ (0.086 g) was dissolved in methanol (0.5 ml) in a centrifuge tube. $\mathrm{AgPF_6}$ (0.042 g) in methanol (0.5 ml) was added causing a thick precipitate of AgCl. After centrifugation the clear colorless solution of *trans*-$\mathrm{[PtCH_3(CH_3OH)\{P(CH_3)_3\}_2]^+PF_6^-}$ was pipetted into an nmr tube. To the solution but-2-yne (10 μl, 1 molar ratio) was added giving *trans*-$\mathrm{[PtCH_3(CH_3C{\equiv}CCH_3)\{P(CH_3)_3\}_2]^+PF_6^-}$. The solution was maintained at 30° in the probe of a Varian T60 nmr spectrometer, and the slow loss of the platinum-methyl group with the liberation of methane was followed spectroscopically. After 12 hr this was complete and evaporation of the resultant yellow solution gave a yellow gum. This was treated with a methanolic solution of NaCl (excess) at 60° for 5 min. After evaporation to dryness the residue was extracted with dichloromethane to give a yellow solution, which was chromatographed (Florisil–benzene) yielding a clear colorless solution. Addition of pentane to a reduced volume of the latter (~2 ml) gave white crystals. Recrystallization from chloroform–ether gave white needles of *trans*-$\mathrm{PtCl\{CCH_3{=}C(OCH_3)CH_3\}\{P(CH_3)_3\}_2}$ (0.080 g, 80% yield based on I), mp 161–163°. *Anal.* Calcd for $\mathrm{C_{11}H_{27}OClP_2Pt}$: C, 28.30; H, 5.82; Cl, 7.59. Found: C, 28.49; H, 5.71; Cl, 7.76. The proton nmr data (100 MHz) recorded in chloroform at 30° is shown below and is consistent with formation of *only* the vinylic trans isomer.[29]



$$\mathrm{Pt{-}C(CH_3{}^{1}){=}C(CH_3{}^{3}){-}OCH_3{}^{2}}$$

$\delta(\mathrm{CH_3{}^1})$ −1.86 ppm, J(Pt–H) = 54 Hz, J(P–H) = 1.3 Hz, $J(\mathrm{H^1H^3})$ = 1.3 Hz; $\delta(\mathrm{CH_3{}^2})$ −3.42 ppm, singlet; $\delta(\mathrm{CH_3{}^3})$ −1.94 ppm; J(Pt–H) = 8.5 Hz, $J(\mathrm{H^3H^1})$ = 1.3 Hz; $\delta(\mathrm{PCH_3})$ −1.46 ppm, J(Pt–H) = 31.0 Hz, $^2J + {}^4J$(P–H) = 7.4 Hz. A medium intensity peak in the infrared and Raman spectra at 1620 cm^{-1} is assigned to ν_{str} (C═C).

***trans*-$\mathrm{[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$.** *trans*-$\mathrm{PtClCH_3\{P(CH_3)_2C_6H_5\}_2}$ (0.358 g) was dissolved in acetone (15 ml) in a round-bottomed flask (25 ml) fitted with a magnetic stirring bar. $\mathrm{AgPF_6}$ (0.173 g, 1 molar ratio) in acetone (5 ml) was added with vigorous stirring. A thick white precipitate of AgCl formed instantaneously. The solution was stirred for 5 min to ensure complete chloride abstraction from *trans*-$\mathrm{PtClCH_3\{P(CH_3)_2C_6H_5\}_2}$ and to allow the coagulation of the precipitate. After centrifugation, to remove all the AgCl, the resultant clear solution was evaporated under reduced pressure to a small volume (~5 ml). This solution was kept cool (~0°) to avoid decomposition and pentane (5 ml) was added with shaking. The solution turned cloudy and crystals slowly formed together with a colorless oil. Ether (10 ml) was added slowly with shaking and this promoted faster crystallization from the oil. The solution was left in a refrigerator at −15° for 6 hr after which time the solution was decanted and the white crystalline product washed with ether and dried *in vacuo* at 25°. (Heating the solid causes decomposition.) This gave *trans*-$\mathrm{[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$ (0.375 g, 75% theory) as a white crystalline solid, mp 110–115° dec. *Anal.* Calcd for $\mathrm{PtP_3F_6C_{20}H_{31}}$: C, 34.83; H, 4.53. Found: C, 34.46; H, 4.46. Nmr data recorded at 31° in $\mathrm{CHCl_3}$ solution at 100 MHz (δ in parts per million from TMS internal references): $\delta\{\mathrm{(CH_3)_2C{=}O}\}$ −2.02 ppm, broad; $\delta(\mathrm{PCH_3})$ −1.70 ppm, J(Pt–H) = 32.4 Hz, $^2J + {}^4J$(P–H)[50] = 7.0 Hz; $\delta(\mathrm{Pt{-}CH_3})$ −0.64 ppm, J(Pt–H) = 88.0 Hz, J(P–H) = 7.6 Hz.

***trans*-$\mathrm{[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+SbF_6^-}$** was prepared as above using $\mathrm{AgSbF_6}$. Crystallization from acetone–pentane–ether gave a white crystalline solid, mp 100–110° dec. *Anal.* Calcd for $\mathrm{PtP_2SbF_6C_{20}H_{31}}$: C, 30.77; H, 4.01. Found: C, 30.73; H, 3.92.

***trans*-$\mathrm{[PtCF_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$** was prepared from the reaction of *trans*-$\mathrm{Pt(CF_3)I\{P(CH_3)_2C_6H_5\}_2}$ with $\mathrm{AgPF_6}$ in acetone solvent by the above procedure. Crystallization from acetone–pentane–ether gave white sticky crystals of *trans*-$\mathrm{[PtCF_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$ which decomposes *in vacuo* and slowly decomposes in air or in chlorinated solvents. *Anal.* Calcd for $\mathrm{PtP_3F_9OC_{20}H_{28}}$: C, 32.30; H, 3.80. Found: C, 31.29; H, 3.90.

***trans*-$\mathrm{[PtCH_3(CH_2{=}CHOCH_3)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$.** Methyl vinyl ether was bubbled through a solution of *trans*-$\mathrm{[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$ (0.245 g) in dichloromethane (5 ml). Pentane (*ca.* 5 ml) was added dropwise until the solution turned opaque. The solution was set aside and fine needle-shaped crystals formed. Ether (2 ml) was added and the solution cooled in a refrigerator at −15°. The white crystalline product was filtered, washed with ether, and dried in a stream of air (slow decomposition due to loss of $\mathrm{CH_2{=}CHOCH_3}$ occurs *in vacuo*). This gave *trans*-$\mathrm{[PtCH_3(CH_2{=}CHOCH_3)\{P(CH_3)_2(C_6H_5\}_2]^+PF_6^-}$, mp 118–120°. *Anal.* Calcd for $\mathrm{PtP_3F_6C_{20}H_{31}}$: C, 34.83; H, 4.53. Found: C, 34.85; H, 4.57. The ^{1}H nmr recorded in $\mathrm{CHCl_3}$ at 31° and at 100 MHz showed (for the platinum methyl group) $\delta(\mathrm{CH_3})$ −0.64 ppm, ^2J(Pt–H) = 71.0 Hz and J(P–H) = 7.0 Hz; (for the phosphine-methyl protons) $\delta(\mathrm{CH_3})$ −1.81 ppm, ^3J(Pt–H) = 29.0 Hz and $^2J + {}^4J$(P–H)[50] = 7.0 Hz; (for the methoxy protons) $\delta(\mathrm{CH_3})$ −3.71 ppm (singlet); and (for the vinyl protons) $\delta(\mathrm{CH{=}CH_2})$ *ca.* −3.40 ppm, broad unresolved multiplet (due to HH′ and J(P–H) coupling) with J(Pt–H) ~ 38 Hz. Chemical shifts δ relative to TMS internal reference.

***trans*-$\mathrm{[PtCH_3(CH_2DCOCH_3)\{As(CH_3)_3\}_2]^+PF_6^-}$.** The reaction of *trans*-$\mathrm{PtClCH_3\{As(CH_3)_3\}_2}$ (0.2015 g) with $\mathrm{AgPF_6}$ (0.104 g) in $\mathrm{CH_3OD}$ (15 ml), by the procedure given in part I,[8] gave *trans*-$\mathrm{[PtCH_3(CH_2DCOCH_3)\{As(CH_3)_3\}_2]^+PF_6^-}$ (0.145 g after purification and recrystallization, 60% theory) as a white crystalline solid (mp 180°). ^{1}H nmr spectra in chloroform showed that the ratio of the methoxy (δ −4.86 ppm), the α-carbene methyl (δ −2.55 ppm), and the platinum-methyl protons (δ −0.11 ppm) was 1.0:0.7:1.1.

***trans*-$\mathrm{[Pt\{CCF_3{=}C(CH_3)CF_3\}(CO)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$.** *trans*-$\mathrm{[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$ (0.201 g) was dissolved in dichloromethane (5 ml) and $\mathrm{CF_3C{\equiv}CCF_3}$ was bubbled through the solution for 2 min. The solution turned pale yellow. CO was then bubbled through this solution and ether (10 ml) was added dropwise. A pale yellow precipitate formed which was collected by filtration, purified by chromatography (Florisil–$\mathrm{CH_2Cl_2}$), and finally recrystallized from $\mathrm{CH_2Cl_2{-}Et_2O}$. This gave *trans*-$\mathrm{[Pt\{CCF_3{=}C(CH_3)CF_3\}(CO)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-}$ (0.195 g, 85% theory) as a white crystalline solid, mp 176–178°. *Anal.* Calcd for $\mathrm{PtP_3F_{12}C_{22}H_{25}}$: C, 31.39; H, 2.99; F, 27.11. Found: C, 31.90; H, 2.73; F, 27.13. The infrared spectrum (Nujol mull) showed ν_{str}(C≡O) 2110 cm^{-1} (vs) and ν_{str} (C═C) 1610 cm^{-1} (w). Other absorptions due to $\mathrm{P(CH_3)_2C_6H_5}$ and $\mathrm{PF_6^-}$ were also observed.[7,8] The nmr spectrum recorded in dichloromethane at 31° showed (for the phosphine–methyl protons) $\delta(\mathrm{CH_3})$ −2.18 and −2.10 ppm from TMS, ^3J(Pt–H) = 32.0 Hz, and $^2J + {}^4J$(P–H) = 8.0 Hz; (for the vinylic methyl group) $\delta(\mathrm{CH_3})$ −1.52 ppm from TMS as a broad resonance with ^4J(Pt–H) ~ 15 Hz and J(HF) = 2.0 Hz; (for the trifluoromethyl groups; see structure on following page) $\delta(\mathrm{CF_3{}^1})$ 46.02 ppm from $\mathrm{CFCl_3}$, $^3J(\mathrm{Pt{-}F^1})$ = 107.5 Hz, $J(\mathrm{HF^1})$ = 2.0 Hz, $\delta(\mathrm{CF_3{}^2})$ 60.26 ppm from $\mathrm{CFCl_3}$, $^4J(\mathrm{Pt{-}F^2})$ ~ 6.0 Hz, $^5J(\mathrm{P{-}F^2})$ = 3.0 Hz and $J(\mathrm{F^1F^2})$ = 15.0 Hz.

The overlapping sets of 1:2:1 triplets for the phosphine–methyl proton resonances arise from virtual coupling of mutually *trans*-

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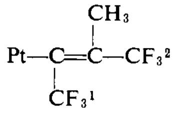
(48) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

(49) J. G. Oliver and I. J. Worrall, *ibid.*, 845 (1970).

(50) R. K. Harris, *Can. J. Chem.*, 42, 2275 (1964).



$Pt-C(CF_3^{1})=C(CH_3)-CF_3^{2}$

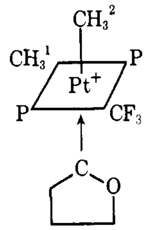
phosphine ligands containing inequivalent methyl groups, $P(CH_3)(CH_3^1)$.[2,46] The latter arise from the presence of the $Pt-CCF_3=C(CH_3)CF_3$ group which destroys the symmetry plane of the P_2Pt-CO unit.

The stereochemistry of the $Pt-CCF_3=C(CH_3)CF_3$ group follows from a comparison of J(Pt–F), J(Pt–H), J(FF), and J(HF) with other platinum fluorovinyl derivatives.[2,30]

$[PtCF_8\{C_4(CH_3)_4\}\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$. *trans*-$[PtCF_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ (0.299 g) was dissolved in dichloromethane (2 ml) and $CH_3C\equiv CCH_3$ (0.5 ml, ≫1 molar excess) was added. The solution slowly turned from yellow to green. Ether (5 ml) was slowly added and the solution was cooled in an ice bath. Fine crystals slowly formed and the solution was transferred to a refrigerator (−15°) for 24 hr. The mother liquor was then decanted and the sticky crystals (contaminated with a green-brown gum) were washed with benzene and ether and then dried *in vacuo*. Dichloromethane (2 ml) was added to give a green-brown solution which was passed through a short Florisil column eluting with dichloromethane. This process gave a pale yellow-green solution which yielded fine yellow-green crystals on the addition of ether, $[PtCF_3\{C_4(CH_3)_4\}\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ (0.175 g, 60% theory), mp 165° dec. *Anal.* Calcd for $PtP_3F_9C_{25}H_{34}$: C, 37.83; H, 4.32; F, 21.56. Found: C, 37.87; H, 4.37; F, 21.49. The nmr spectrum in CDCl at 30° and 100 MHz showed (for the tetramethylcyclobutadiene) $\delta(CH_3)$ −1.52 ppm from TMS,[51] J(Pt–H) = 12.7 Hz, J(F–H) = 0.8 Hz, J(P–H), not resolved; (for the phosphine methyls) $\delta(CH_3)$ −1.90 ppm from TMS, ^3J(Pt–H) = 20.0 Hz, and ^2J(P–H) = 10.0 Hz; and the phosphine phenyl protons appeared as a multiplet *ca.* −7.50 ppm from TMS. Integration of phenyl, phosphine–methyl, and cyclobutadiene–methyl protons showed the ratio 10:12:12 as predicted for $[PtCF_3\{C_4(CH_3)_4\}\{P(CH_3)_2C_6H_5\}]^+PF_6^-$: $\delta(CF_3)$ 9.86 ppm from $CFCl_3$; ^3J(Pt–F) = 496 Hz, J(P–F), not observed, and J(HF), not resolved. The infrared spectrum (KBr disk) showed the characteristic absorptions of the groups $P(CH_3)_2C_6H_5$, PF_6^-,[7,8] and $Pt-CF_3$,[12b] and bands at 1540 (m), 1445 (vs), 1360 (m), 1070 (s), and 1000 cm^{-1} (vs) may be assigned to the tetramethylcyclobutadiene ligand.[11]

$[Pt(CH_3)_2(CF_3)(CH_2CH_2OCCH_2)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$. $Pt(CH_3)_2(CF_3)(I)\{P(CH_3)_2C_6H_5\}_2$ (0.210 g) was dissolved in acetone (15 ml) in a round-bottomed flask fitted with a magnetic stirring bar. $AgPF_6$ (0.0775 g, 1 molar ratio) in acetone (5 ml) was added with vigorous stirring. A thick yellow precipitate of AgI formed and, after stirring the solution for 5 min (to allow complete abstraction of iodide and coagulation of the precipitate), this was removed by centrifugation. But-1-yn-4-ol, $CH\equiv CCH_2CH_2OH$ (40 μl, 20% excess of 1 molar ratio), was added to the clear solution obtained after centrifugation, and this caused the solution to change from colorless to yellow, to pink, and finally to brown (within 1 min). The volume of the solution was reduced to *ca.* 5 ml under reduced pressure and on the addition of ether a brown precipitate formed. The solution was cooled in the refrigerator at −15° for 6 hr after which time the precipitate was collected by filtration, washed with ether, and dried *in vacuo* (10^{-4} cm, 25°, 15 min). This gave a brown powdery solid which was dissolved in dichloromethane and was passed through a short chromatography column (Florisil–CH_2Cl_2). The addition of ether to the pale pink solution so obtained gave a pale pink crystalline product. The chromatography/recrystallization was repeated twice more to yield $[Pt(CH_3)_2(CF_3)(CH_2CH_2OCCH_2)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ as a white powdery solid (0.140 g, 65% theory), mp 175–180° dec. *Anal.* Calcd for $PtP_3F_9OC_{23}H_{34}$: C, 35.11; H, 4.37; F, 21.78. Found: C, 35.28; H, 4.36; F, 21.47. The nmr data obtained from a dichloromethane solution at 31°, 100 MHz, showed (for the phosphine–methyl protons) $\delta(CH_3)$ −1.78 and −2.03 ppm, ^3J(Pt–H) = 20.5 Hz, $^2J + {}^4J$(P–H)[50] = 8.0 Hz; (for the platinum–methyl groups) $\delta(CH_3^1)$ −0.44 ppm, ^2J(Pt–H) = 46.0 Hz, ^3J(P–H) = 7.7 Hz, and $\delta(CH_3^2)$ −0.22 ppm, ^2J(Pt–H) = 44.0 Hz, ^3J(P–H) = 6.3 Hz; (for the cyclic carbene ligand $CH_2^{\beta}CH_2^{\alpha}OCCH^{\gamma}_2$) $\delta(H^{\alpha})$ −4.63 ppm, $^4J(Pt-H^{\alpha})$ = 5.0 Hz, $J(H^{\alpha}H^{\beta})$ = 8.0 Hz; $\delta(H^{\beta})$ −0.88 ppm (pentet), $J(H^{\beta}H^{\alpha\gamma})$ = 8.0 Hz; $\delta(H^{\gamma})$ −2.16 ppm, $J(Pt-H^{\gamma})$, not resolved, $J(H^{\beta}H^{\gamma})$ = 8.0 Hz; (for the trifluoromethyl fluorines) $\delta(CF_3)$ 18.94 ppm, ^2J(Pt–F) = 249 Hz, ^3J(P–F) = 7.2 Hz.

^1H and ^{19}F chemical shifts are relative to TMS and $CFCl_3$, respectively. The nmr data are assigned to the stereochemistry shown below, for the following reasons.



$P = P(CH_3)_2C_6H_5$

1. The phosphine–methyl proton resonances appear as two sets of 1.2.1 triplets and thus indicate the presence of mutually *trans*-phosphine ligands[46] and the absence of a plane of symmetry containing the P–Pt–P axis,[7] $P(CH_3)(CH_3^1)C_6H_5$.
2. The platinum-methyl groups also appear as two sets of 1.2.1 triplets and therefore show that they are inequivalent (*i.e.*, mutually cis) and that they are flanked by mutually *trans*-phosphine ligands.
3. The assignment of the platinum-methyl groups CH_3^1 and CH_3^2 is speculative but is suggested since (a) the CH_3^2 protons show broadening probably due to coupling to the fluorines of the trifluoromethyl group,[13] (b) platinum-methyl resonances trans to alkoxy-carbene ligands appear at high field,[8] and (c) we expect the trans influence $CH_2CH_2OCCH_2 > CF_3$ and therefore assign ^2J(Pt–H) = 44.0 Hz to the group $Pt-CH_3^2$.

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(51) Compare $\delta(CH_3)$ = −1.73 ppm for $C_4(CH_3)_4Fe(CO)_3$: R. Bruce, K. Moseley, and P. M. Maitlis, *ibid.*, **45**, 2011 (1967).