

TABLE V  
 MELTING POINTS, YIELDS, COLORS, AND ANALYTICAL RESULTS

Compd	Mp, °C	Yield, %	Color	% calcd			% found		
				C	H	Cl	C	H	Cl
Cl <sub>3</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	155 dec	55	White	14.25	0.13	14.00	14.20	0.16	14.40
Cl <sub>3</sub> SiDR <sub>2</sub> (CO) <sub>9</sub>	154–155 dec	50	White	14.20	0.27	13.97	14.63	0.36	14.47
C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	130–132	50	White	22.49	0.75	8.84	22.67	0.96	8.42
CH <sub>3</sub> Cl <sub>2</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	108–110	35	White	16.25	0.55	9.59	16.48	0.73	9.70
HRe <sub>3</sub> (CO) <sub>14</sub> <sup>a</sup>	...	50	Yellow	17.66	0.11	...	17.50	0.25	...

<sup>a</sup> Infrared and mass spectra were in agreement with those reported in ref 4 and 11.

bonyl (1.44 g, 2.20 mmol) and methylchlorosilane (2.0 g, 18 mmol) was irradiated with the 450-W source for 12 hr. Carbon monoxide pressure was released every 2 hr. Unreacted methylchlorosilane was distilled off on a vacuum system and the residual solid was sublimed at 55° to remove unreacted rhenium carbonyl. Three recrystallizations from *n*-hexane afforded white crystals (0.60 g) of the pure product.

Hyrido(phenyldichlorosilyl)nonacarbonylirhenium, C<sub>6</sub>H<sub>5</sub>-Cl<sub>2</sub>SiHRe<sub>2</sub>(CO)<sub>9</sub>.—A solution of rhenium carbonyl (1.10 g, 1.70 mmol) and phenyldichlorosilane (1.0 g, 5.6 mmol) in 50 ml of cyclohexane was irradiated for 4.5 hr with the 140-W source. The solution was maintained at *ca.* 15° during the irradiation. Solvent and starting materials were then removed by evaporation at reduced pressure and sublimation at 50°. Unsublimed

solid was recrystallized twice from *n*-hexane to yield 0.40 g of the product.

Hydridotetradecacarbonyltrirhenium, HRe<sub>3</sub>(CO)<sub>14</sub>.—Eighteen hours of irradiation (140-W source) of a solution of rhenium carbonyl (1.58 g, 2.4 mmol) and triphenylsilane (0.70 g, 2.7 mmol) in 50 ml of benzene gave a yellow solution. Benzene was evaporated at reduced pressure and the residue was sublimed at 60° (0.01 mm) to remove unreacted starting materials. The unsublimed yellow solid was recrystallized from dichloromethane-*n*-hexane to afford yellow crystals of the product (0.70 g).

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## Cationic Acetylenic Platinum(II) Compounds and Their Derivatives.

### IV. Displacement Reactions

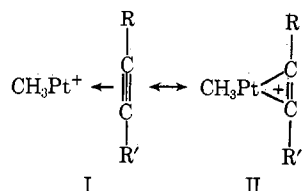
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The equilibrium reaction  $trans-[PtCH_3(L)Q_2]^+PF_6^- + L' \rightleftharpoons trans-[PtCH_3(L')Q_2]^+PF_6^- + L$ , where  $Q = P(CH_3)_2C_6H_5$ , has been studied for a variety of neutral ligands,  $L'$ , to give a displacement series. The comparison of this series with the trans-influence series, obtained from nmr data, demonstrates the importance of Pt-L  $\pi$  bonding. The dependence of these displacement reactions on the choice of solvent, when  $L'$  is an unsaturated ligand, further indicates the importance of a cationic mechanism in which  $L'$  must occupy the fourth coordination position of the  $[CH_3PtQ_2]^+$  plane, before carbonium ion reactivity is achieved.

#### Introduction

We have previously described<sup>1,2</sup> the preparation and properties of the cationic complexes  $trans-[PtCH_3-(RC\equiv CR')Q_2]^+PF_6^-$  (I), where  $Q = P(CH_3)_2C_6H_5$  or  $As(CH_3)_3$  and R, R' = alkyl or aryl groups. When R and R' were other than alkyl or aryl groups, cationic acetylide,<sup>1</sup> alkoxy-carbene,<sup>3</sup> or vinyl ether complexes<sup>2</sup> were obtained. These products are believed to be derived from the initial formation of cationic acetylene complexes I which show reactivity characteristic of carbonium ions (II) and hence lead to products inter-



pretable in terms of intramolecular rearrangements

- (1) M. H. Chisholm and H. C. Clark, *J. Chem. Soc. D*, 763 (1970).
- (2) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 2557 (1971).
- (3) M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 1711 (1971).

and/or nucleophilic addition.<sup>4,5</sup> The addition to the triple bond of the complexed acetylene in the formation of methyl vinyl ether complexes gives<sup>6</sup> only the trans vinylic isomer as predicted from the carbonium ion II. However, depending on the nature of the nucleophile, nucleophilic attack may occur at platinum and thus produce displacement of the acetylene.<sup>4</sup> In this paper we examine the factors influencing the directional course of this nucleophilic attack (attack at platinum *vs.* attack at the triple bond) since this determines the reactivity of an unsaturated ligand when coordinated to the cation  $[CH_3PtQ_2]^+$ .

#### Results and Discussion

Values of  $J(Pt-C-H)$  for the platinum methyl group and  $J(Pt-P-C-H)$  for the phosphine methyl groups for a series of cationic methylplatinum complexes  $trans-[PtCH_3(L)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$  (III) are given in Table I. These platinum-hydrogen coupling con-

(4) M. H. Chisholm, H. C. Clark, and D. H. Hunter, *J. Chem. Soc. D*, 809 (1971).

(5) Part III: M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972).

TABLE I<sup>a</sup>  
 $J(\text{Pt}-\text{C}-\text{H})$  AND  $J(\text{Pt}-\text{P}-\text{C}-\text{H})$  FOR  
 $\text{trans}[\text{PtCH}_3(\text{L})\text{Q}_2]^+ \text{PF}_6^-$  ( $\text{Q} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ )

L	$J(\text{Pt}-\text{C}-\text{H})$ , Hz	$J(\text{Pt}-\text{P}-\text{C}-\text{H})$ , Hz
$\text{CH}_2\text{CH}_2\text{OCCH}_2^b$	51	34
$\text{Sb}(\text{C}_6\text{H}_5)_3$	55	29
$\text{P}(\text{C}_6\text{H}_5)_3$	57	30
$\text{P}(\text{C}_6\text{H}_5)_3$	58	30
CO	63	33
$\text{C}_2\text{H}_5\text{NC}^d$	63.6	33.2
$\text{As}(\text{C}_6\text{H}_5)_3$	67	29
Pyridine	74	32
$\text{CH}_2=\text{CH}_2^e$	74.2	29.5
$\text{NH}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5^e$	76.4	30.6
$\text{CH}_3\text{C}\equiv\text{CCH}_3^e$	77	29
$\text{CH}_3\text{CN}$	80	32
$(\text{CH}_3)_2\text{CO}^f$	88	32.4
$\text{CH}_3\text{OH}^f$	88	32.4

<sup>a</sup> Trans-influence,  $\sigma$ -donor strength decreases down the series

$\text{CH}_2\text{CH}_2\text{OCCH}_2 \rightarrow \text{CH}_3\text{OH}$ .  $\pi$ -Acceptor properties are in the order  $\text{Sb}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3 \sim \text{As}(\text{C}_6\text{H}_5)_3 \sim \text{CH}_2=\text{CH}_2 \sim$

$\text{CH}_3\equiv\text{CCH}_3 > \text{CO} \sim \text{pyridine} \sim \text{C}_2\text{H}_5\text{NC} \sim \text{CH}_2\text{CH}_2\text{OCCH}_2 \sim$  acetone,  $\text{CH}_3\text{OH}$ . All values are previously reported in ref 6 except where noted differently. <sup>b</sup> Reference 3. <sup>c</sup> Reference 2. <sup>d</sup> Part II: H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 503 (1972). <sup>e</sup> Part I: H. C. Clark and L. E. Manzer, *ibid.*, **10**, 2699 (1971). <sup>f</sup> This work. <sup>g</sup> Part V: M. H. Chisholm and H. C. Clark, submitted for publication in *Inorg. Chem.*

stants may be used to evaluate the trans-influence<sup>3,6</sup> and  $\pi$ -acceptor properties<sup>2</sup> of the neutral ligand L, and so by arranging the ligands in descending order of their  $\sigma$ -donor and/or  $\pi$ -acceptor strength we obtain the trans-influence and  $\pi$ -acceptor series shown in Table I. Although the theoretical basis for the formulation of a trans-influence series and a  $\pi$ -acceptor series based on platinum-hydrogen coupling constants is not rigorous,<sup>7-10</sup> it should be noted that this series is consistent with that found by many other spectroscopic and X-ray crystallographic studies on platinum(II) compounds, e.g., the comparison of alkoxy- and amino-carbene ligands with tertiary phosphines and isocyanide ligands.<sup>11-15</sup> (N. B. This trans-influence series is a static or ground-state effect arising only from the  $\sigma$ -donor properties of the ligand.<sup>16</sup>) Similarly it is reasonable that acetylenes and olefins should be better  $\pi$  acceptors than nitriles and pyridines, and, on the basis of Mössbauer studies, Bancroft, *et al.*,<sup>17</sup> have suggested that carbon monoxide is a stronger  $\pi$  acceptor than isocyanide ligands. However, it is interesting to note the high position held by  $\text{Sb}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{C}_6\text{H}_5)_3$ , and  $\text{As}(\text{C}_6\text{H}_5)_3$  in this  $\pi$ -acceptor series. Venanzi<sup>18</sup> questioned the existence of such Pt-P  $\pi$  back-bonding in platinum(II) complexes on the grounds that though

(6) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1229 (1970).

(7) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1938 (1970).

(8) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(9) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(10) G. W. Smith, *ibid.*, **39**, 2031 (1963); **42**, 435 (1965).

(11) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *J. Chem. Soc. D*, 1322 (1969).

(12) E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc. A*, 21 (1971).

(13) B. Crociani and T. Boschi, *J. Organometal. Chem.*, **24**, C1 (1970).

(14) B. Crociani, T. Boschi, and V. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

(15) F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *J. Organometal. Chem.*, **25**, 255 (1970).

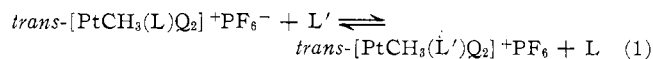
(16) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(17) (a) G. M. Bancroft, M. J. Mays, and B. E. Praters, *ibid.*, 1938 (1970); (b) G. M. Bancroft, personal communication.

(18) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968).

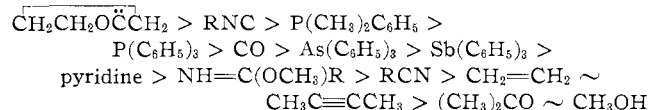
symmetry may allow the formation of  $\pi$  bonds, this need not be taken as an indication (a) that such bonds are formed and (b) that, if formed, they play a major role in determining physical and chemical properties of compounds in which such bonds can be postulated.

In order to determine the relative affinity of neutral donor ligands toward the cation  $[\text{CH}_3\text{PtQ}_2]^+$  we studied the equilibrium reaction



where  $\text{Q} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ .

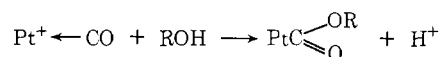
By arranging the neutral ligands L in the order of their ability to displace and not to be displaced, we have obtained the displacement series (where  $\ddot{\text{C}}$  is the carbene carbon atom bound to platinum)



This displacement series arranges the cationic complexes III in order of their thermodynamic stability; e.g., the conversion of III (L = acetone) to III (L =  $\text{CH}_2\text{CH}_2\text{OCCH}_2$ ) is exothermic<sup>19</sup> and very favorable. Ignoring entropy changes and steric considerations (see later) this displacement series arranges the ligands L in descending order of their nucleophilicity with respect to the cation  $[\text{CH}_3\text{PtQ}_2]^+$ . If this electrophilic platinum cation were hard (incapable of  $\pi$  back-bonding to the ligand L), then the displacement series would follow the trans-influence series, i.e.,  $\sigma$ -donor properties of the ligand. Although there is some similarity to the trans-influence series, many changes are evident, notably with ligands that we have suggested are acting as strong  $\pi$  acceptors. This shows (i) that  $\pi$  bonding can occur in the Pt<sup>+</sup>-L bond and (ii) that the bonding destabilizes the cationic complex III. (The position of a ligand in the displacement series does not necessarily reflect Pt<sup>+</sup>-L bond strength but simply the relative energy of the cationic complex III.)

The ability of isocyanide ligands to displace tertiary phosphine and stibine ligands, which are higher in the trans-influence series (see Table I), indicates significant Pt-L  $\pi$  bonding; furthermore, since phosphine and arsine ligands displace stibines, the  $\pi$ -bonding order must be  $\text{L} = \text{Sb}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3$ . Similarly the ready displacement of CO by RNC confirms the predictions<sup>17</sup> that  $\text{CO} > \text{RNC}$  in  $\pi$ -acceptor properties since their  $\sigma$ -donor properties are comparable.

On the other hand, the high position of CO in the displacement series shows that the platinum "d" to carbonyl " $\pi^*$ " bonding is relatively small in III, and therefore the carbonyl ligand is acting primarily as a  $\sigma$ -donor ligand. This is consistent with the high value of  $\nu_{\text{str}}(\text{C}\equiv\text{O})$ , ca. 2100  $\text{cm}^{-1}$ , and the susceptibility of the carbonyl carbon atom toward nucleophilic attack, e.g.<sup>20-22</sup>



(19) Calorimetric studies are being undertaken.

(20) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **91**, 1346 (1969).

(21) W. J. Cherwinski and H. C. Clark, *Can. J. Chem.*, **47**, 2665 (1969).

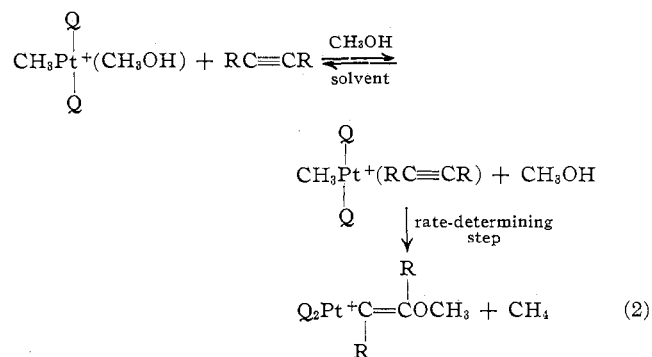
(22) J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 1634 (1971).

The addition of trace quantities of EtNC to III ( $L = \overline{\text{CH}_2\text{CH}_2\text{O}\ddot{\text{C}}\text{CH}_2}$ ) in dichloromethane solution gives rise to rapid exchange of the  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  groups and loss of both platinum and phosphorus coupling to the phosphine methyl protons in the nmr. If the quantity of EtNC is increased to 1 mol, low-temperature spectra ( $-80^\circ$ ) indicate that the complex  $[\text{Pt}(\overline{\text{CH}_3(\text{CH}_2\text{CH}_2\text{O}\ddot{\text{C}}\text{CH}_2)(\text{EtNC})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}})]^+\text{PF}_6^-$  is formed in which the alkoxy-carbene ligand is trans to the platinum methyl group. This demonstrates the strong nucleophilic properties of the alkoxy-carbene ligand and is consistent with our earlier view<sup>2</sup> that the alkoxy-carbene ligand in III is acting primarily as a  $\sigma$  donor with relatively little Pt "d"  $\rightarrow$  carbene "p<sub>z</sub>"  $\pi$  bonding. Thus, although only zero-, mono-, and divalent metal-alkoxy-carbene complexes are known at present, we would expect that these carbene ligands are capable of stabilizing metals in higher valency states.<sup>23</sup> On the other hand, the ready displacement of dialkylacetylenes and ethylene by a weaker  $\sigma$  donor such as an alkyl-nitrile shows that platinum-acetylene and/or -olefin  $\pi$  back-bonding is far from insignificant.

**Steric Factors.**—If the ligand L in III causes severe steric interaction with the dimethyl(phenyl)phosphine ligands, substitution by a less bulky ligand will be favorable and so may cause the order of the ligands in the displacement series to deviate from the order of nucleophilicity. However, molecular models of III suggest that this is not normally an important factor except when L is a substituted olefin which must  $\pi$  bond to the  $\text{CH}_3\text{Pt}^+\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  unit, and due to the planar geometry of the olefinic double bond, this causes severe steric repulsion with the dimethyl(phenyl)phosphine ligands; *cf.* disubstituted acetylenes where the substituents are collinear with the acetylenic triple bond. Thus the ready displacement of propylene by ethylene and our inability to isolate olefin complexes of *cis*- and *trans*-but-2-ene and -stilbene are probably entirely due to steric factors.

*trans*- $[\text{PtCH}_3(\text{solvent})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{X}^-$  ( $\text{X} = \text{PF}_6$  or  $\text{SbF}_6$ ; Solvent = Acetone or  $\text{CH}_3\text{OH}$ ).—Previously we reported<sup>2</sup> that the nmr spectra of the cationic acetylenic complexes I in acetone solution showed appreciable amounts of free acetylene and the presence of a platinum methyl group with an unprecedentedly large value of  $J(\text{Pt}-\text{C}-\text{H})$ . Tentatively this was assigned to the cation *trans*- $[\text{PtCH}_3(\text{acetone})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+$ , and subsequently, by careful crystallization, we were able to isolate this cation as white, air-stable salts of the large anions  $\text{PF}_6^-$  and  $\text{SbF}_6^-$ .<sup>5</sup> These compounds show  $J(\text{Pt}-\text{C}-\text{H}) = 88$  Hz and  $\nu_{\text{str}}(\text{Pt}-\text{C}) 568$   $\text{cm}^{-1}$  for the platinum methyl group consistent with the very weak *trans*-influence,  $\sigma$ -donor properties of the acetone. The nmr spectrum of I ( $L = \text{CH}_3\text{C}\equiv\text{CCH}_3$ ) 0.2 M in methanol at  $31^\circ$  shows that 50% displacement of the acetylene has occurred with the formation of III ( $L = \text{CH}_3\text{OH}$ ). However, we have been unable to isolate this methanol complex as a stable crystalline product. The dissociation of I in methanol as solvent suggests that the formation of methyl vinyl ether complexes should be represented as

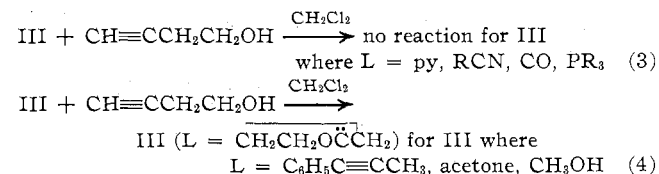
in (2).<sup>24</sup> The rate-determining step in the nucleophilic



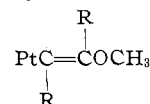
attack on the acetylenic triple bond depends on the carbonium ion contribution to the resonance  $\text{I} \leftrightarrow \text{II}$ , and so electron-withdrawing substituents on the acetylene should increase the rate of vinyl ether formation. Although this is generally the case observed, reactions involving  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  gave<sup>2</sup> only  $[\text{PtCH}_3\text{Q}_2]^+\text{PF}_6^-$  derived from the decomposition of *trans*- $[\text{PtCH}_3(\text{CH}_3\text{OH})\text{Q}_2]^+\text{PF}_6^-$ . This may be interpreted in terms of the displacement series since an increase in the electron-withdrawing properties of the substituents R and R' on the acetylene increases the  $\pi$ -acceptor properties of the acetylene and so lowers the acetylene in the displacement series (decreases the nucleophilicity of the acetylene). Thus in methanol solvent equilibrium 2 may be so far to the left that the formation of I becomes the rate-determining step. This we believe to be the situation in the reaction of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  previously described.<sup>2</sup> The isolation of III ( $L = \text{acetone}$ ) allows us (i) to study the reactions of acetylenes in non-nucleophilic solvents such as dichloromethane and (ii) to obtain III ( $L = \text{acetylenes, olefins, and other unsaturated ligands}$ ) which cannot be isolated from reactions in nucleophilic solvents (*e.g.*, methanol and acetone) because of the unfavorable equilibrium 2. The latter are discussed in part V of this series.

### Displacement Reactions

**Alkoxy-carbene Formation.**—Although the formation of III ( $L = \text{RCH}_2\ddot{\text{C}}\text{OCH}_3$ ) is thermodynamically favorable and, once formed, the carbene ligand is not readily displaced, the formation of the alkoxy-carbene ligand only occurs if the acetylene can achieve the fourth coordination site of the  $\text{CH}_3\text{Pt}^+\text{Q}_2$  plane; *i.e.*, alkoxy-carbene formation is limited by the position of  $\text{RC}\equiv\text{CH}$  in the displacement series. This is easily seen from reactions 3 and 4. Alkoxy- and amino-



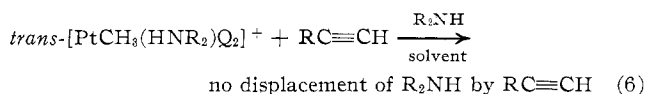
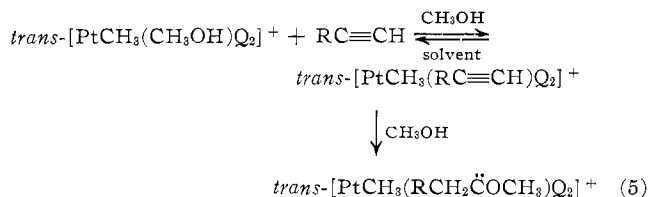
(24) Since only the *trans* vinylic isomer



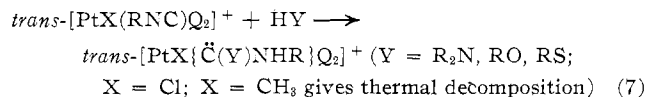
is formed,<sup>5</sup> we can eliminate the possibility of a mechanism involving the reaction of the acetylene and methanol in a five-coordinate platinum intermediate; *cf.* the esterification of alkyl alcohols by Pt(II) salts: F. Hartley, *Chem. Rev.*, 799 (1969), and references therein.

(23) We have now been able to isolate cationic platinum(IV)-alkoxy-carbene complexes: M. H. Chisholm and H. C. Clark, *J. Chem. Soc. D*, 1484 (1971).

carbene ligands show very similar coordination properties,<sup>11-15,25-27</sup> and therefore we would expect the formation of III (L = RCH<sub>2</sub>C̈NR<sub>2</sub>) from III (L = RC≡CH) to be thermodynamically very favorable. However, the relative order of nucleophilicity with respect to the [CH<sub>3</sub>PtQ<sub>2</sub>]<sup>+</sup> cation is R<sub>2</sub>NH > RC≡CH > CH<sub>3</sub>OH and so aminocarbene complexes are not obtained from reactions of RC≡CH in amine solvents. See (5) and (6).



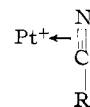
We should expect that amino- and alkoxycarbene ligands should be obtained from reaction 7 since the



relative order of nucleophilicity is RNC ≫ R<sub>2</sub>NH > ROH and therefore (7) should be both thermodynamically and kinetically favorable. This expectation is not realized for the cationic methylplatinum compounds III (L = RNC) which readily decompose<sup>27</sup> under the refluxing conditions necessary to convert the isocyanide to a carbene ligand, but other cationic platinum isocyanide complexes do show this reaction.<sup>27-29</sup>

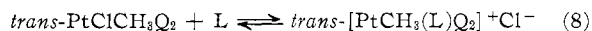
The mechanism for the conversion of a coordinated isocyanide to a carbene ligand is of considerable interest. Richards, *et al.*,<sup>12</sup> suggested that the nitrogen might be activated toward electrophilic attack by a proton, but since amines react faster than alcohols, it seems more reasonable that the rate-determining step must involve nucleophilic attack at the electron-deficient isocyanide carbon.<sup>27</sup> Furthermore the conversion Pt-CNR + HY → PtC(Y)NHR, where Y = NR<sub>2</sub>, SR, or OR, is slower for cationic Pt(II) than for neutral Pt(II) complexes. We believe the most plausible mechanism involves nucleophilic attack on an activated isocyanide ligand which is π bonded to the metal (*cf.* the conversion of a coordinated acetylene to an alkoxy-carbene ligand). This formalization explains the rate of reactivity with respect to both the nucleophile YH [R<sub>2</sub>NH > ROH] and the electrophilicity of metal [Pt(II) < Pt<sup>+</sup>(II)], since the more electrophilic the metal, the greater the energy of activation required to form such a π-bonded complex.

**Nitrile and Imino Ether Complexes.**—Nitrile ligands, RCN, can coordinate to the cation [CH<sub>3</sub>PtQ<sub>2</sub>]<sup>+</sup> as either N-bonded Pt<sup>+</sup>←NCR or π-bonded

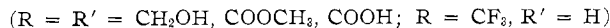
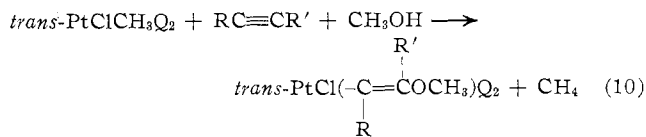
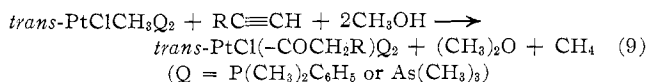


ligands. Normally the N-bonded complexes III are formed, but when R is a perfluoroaromatic group, the π-bonded form appears to be equally stable.<sup>30,31</sup> In the latter case the nitrile ligand is activated to nucleophilic attack and in methanol solvent leads to imino ether complexes, III (L = NH=C(OCH<sub>3</sub>)R). Although the thermodynamic stability of III is greater for L = NH=C(OCH<sub>3</sub>)R than for L = NCR (from the displacement series), the formation of NH=C(OCH<sub>3</sub>)R from a coordinated nitrile ligand is limited by the nucleophilic properties of the nitrile ligand, σ-NCR > π-RCN, and only when the π-bonded form is accessible, is the conversion to the imino ether ligand possible.<sup>30,31</sup>

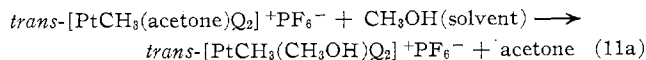
**Acyl and Vinyl Ether Formation.**—The chloride ligand in *trans*-PtClCH<sub>3</sub>Q<sub>2</sub> is labile due to the high trans influence of the methyl group,<sup>6</sup> and the addition of a neutral ligand L may give rise to the equilibrium<sup>32</sup>



The position of this equilibrium depends on the nucleophilicity of L and on the solvent. It appears that acetylenes may displace Cl<sup>-</sup> in polar solvents such as methanol and that reactions of RC≡CR' with *trans*-PtClCH<sub>3</sub>Q<sub>2</sub> may proceed *via* III (L = RC≡CR').<sup>5</sup> This we believe to be the case in the formation of acyl and vinyl ether complexes



The substituents on the acetylene, R and R', affect equilibrium 8 since they change the nucleophilicity of the acetylene. Thus reactions involving CF<sub>3</sub>C≡CH<sup>33</sup> are reluctant to give methyl vinyl ether formation, eq 10, compared to reactions of CH<sub>3</sub>C≡CH,<sup>5</sup> eq 9. Consequently the reaction of *trans*-PtClCH<sub>3</sub>Q<sub>2</sub> with CF<sub>3</sub>C≡CH in methanol, eq 10, is normally carried out<sup>33</sup> under the forcing conditions of a sealed-tube reaction where a high concentration (excess) is easily maintained. However, we find that this cationic mechanism may be enhanced by the addition of a catalytic amount of III (L = acetone) to a methanolic solution of *trans*-PtClCH<sub>3</sub>Q<sub>2</sub>. This has the effect of labilizing the Cl<sup>-</sup> ligand and thus promoting a cationic mechanism involving reaction of *trans*-[PtCH<sub>3</sub>(RC≡CR)-Q<sub>2</sub>]<sup>+</sup>. The reaction may be represented by the sequence



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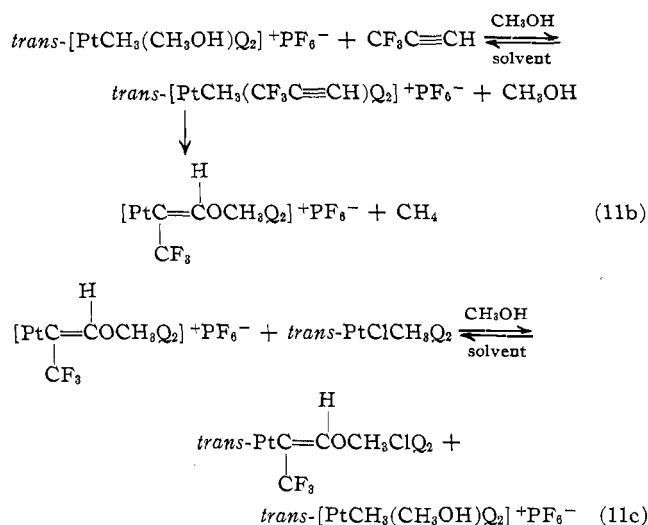
(29) H. C. Clark and L. E. Manzer, *ibid.*, **30**, C89 (1971).

(30) H. C. Clark and L. E. Manzer, *J. Chem. Soc. D*, 387 (1971).

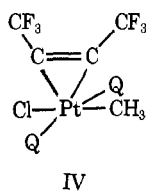
(31) Part I: H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971).

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

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**Methylplatinum Insertions. Vinyl Formation.**— Electron-withdrawing substituents on the acetylene increase the  $\pi^*$ -acceptor properties of the acetylene, and reactions of strong  $\pi$  acids, such as  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ , with  $\text{trans-PtClCH}_3\text{Q}_2$  have been shown<sup>34-36</sup> to proceed *via* initial formation of  $\pi$  complexes (IV) which may be

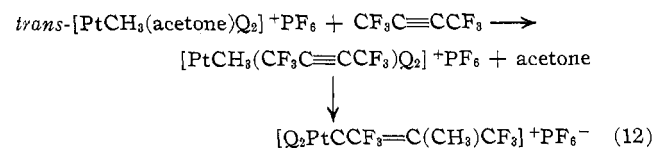


considered to arise from electrophilic attack on  $\text{trans-PtClCH}_3\text{Q}_2$  (*cf.* reactions of type (8) where the acetylene is acting primarily as a nucleophile). Subsequent decomposition of IV leads to the formation of  $\text{trans-PtCl}\{-\text{CCF}_3=\text{C}(\text{CH}_3)\text{CF}_3\}\text{Q}_2$  (V),  $\text{Pt}(\text{C}_4\text{F}_6)\text{Q}_2$ , and  $\text{PtCl}_2(\text{CH}_3)_2\text{Q}_2$ . The formation of platinum vinyl derivatives (V), in which *cis* addition to the acetylenic triple bond occurs, is of considerable interest since this type of reaction (initial coordination of an unsaturated molecule followed by insertion into a metal-carbon bond) is believed to form the basis of transition metal catalyzed polymerizations of olefins and acetylenes,<sup>37</sup> and the isolation of the  $\pi$  complex IV may be considered as an intermediate in this process. However, either a concerted, free-radical or ionic mechanism could account for the subsequent insertion into the methyl-platinum bond,  $\text{IV} \rightarrow \text{V}$ , and the formation of  $\text{Pt}(\text{C}_4\text{F}_6)\text{Q}_2$  and  $\text{PtCl}_2(\text{CH}_3)_2\text{Q}_2$  suggests that the decomposition of IV is complex.

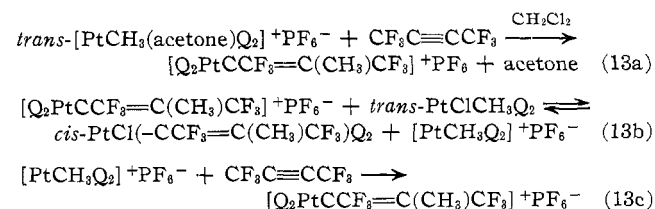
We now find that insertion into the methyl-platinum bond is greatly facilitated by a cationic mechanism. The reaction of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  with III (L = acetone) in dichloromethane at room temperature gives quantitative and rapid formation of the complex  $[\text{Q}_2\text{PtCCF}_3=\text{C}(\text{CH}_3)\text{CF}_3]^+\text{PF}_6^-$  and the addition of a neutral ligand, such as CO, allows the isolation of  $\text{trans-[Pt}\{-\text{CCF}_3=\text{C}(\text{CH}_3)\text{CF}_3\}(\text{CO})\text{Q}_2]^+\text{PF}_6^-$ . This insertion to the methyl-platinum bond gives only the *cis* vinyl isomer

as would be expected from an intramolecular rearrangement. Below  $-30^\circ$ ,  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  does not react with III (L = acetone) in dichloromethane solution, and above this temperature only the insertion product is detectable in the nmr spectra. Consequently we have not been able to isolate or detect spectroscopically III (L =  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ). The reaction of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  (1 mol) with III (L =  $\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3$ ) in dichloromethane solution at room temperature gave only 25% insertion into the methyl-platinum bond over a period of 5 days, and, with III (L = pyridine or CO) no evidence of methyl-platinum insertion was observed over a period of 1 month at room temperature, even in the presence of a large excess of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ .

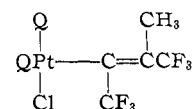
We conclude that this insertion into the methyl-platinum bond proceeds as in (12) and that the rate-



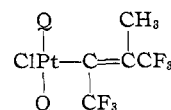
determining step is the formation of the cationic acetylenic intermediate III (L =  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ). Since the nucleophilicity of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  is very low, the nucleophilicity of the solvent, acetone  $\sim \text{CH}_3\text{OH} \gg \text{CH}_2\text{Cl}_2$ , is critical in the formation of  $\text{trans-[PtCH}_3(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2]^+\text{PF}_6^-$  (see (2) previously discussed). This facile insertion into the methyl-platinum bond suggested that the reaction of  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  with  $\text{trans-PtClCH}_3\text{Q}_2$  could be catalyzed by the addition of trace quantities of III (L = acetone), and indeed this is the case observed. The conditions of this reaction (see Experimental Section) contrast dramatically with the more vigorous conditions required in the absence of III (L = acetone).<sup>35</sup> Furthermore, this catalyzed reaction proceeds without the formation of the by-products  $\text{Pt}(\text{C}_4\text{F}_6)\text{Q}_2$  and  $\text{PtCl}_2(\text{CH}_3)_2\text{Q}_2$  previously obtained.<sup>35</sup> The reaction may be represented by



It may be noted that the *cis* isomer of V



is formed in reaction 13 and this contrasts with the *trans* isomer



(34) H. C. Clark and R. J. Puddephatt, *J. Chem. Soc. D*, 92 (1970).

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previously obtained.<sup>35</sup> However, little significance can be derived from this since *cis*-*trans* isomerism is a function of solvent and may be catalyzed by a trace of excess phosphine. Only the product of a single insertion is obtained by reactions 12 and 13, even in the presence of excess  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ , and, in this respect, these reactions are analogous to many well-documented insertion reactions of fluoroolefins and -acetylenes with metal hydrides and alkyls.<sup>34,35,38-42</sup>

#### Olefin Insertion into Platinum-Hydrogen Bonds.—

The reversible addition of ethylene to *trans*- $\text{PtClH}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$  to give *trans*- $\text{PtClC}_2\text{H}_5\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$  is well established<sup>43</sup> and it has been accepted<sup>44,45</sup> that this reaction proceeds *via* a five-coordinate  $\pi$ -olefinic complex (similar to IV). Recently we have shown<sup>46</sup> that this type of platinum-hydride insertion is facilitated by a cationic mechanism and may be catalyzed by trace quantities of  $[\text{PtH}(\text{acetone})_2]^+$  in a similar manner to (13).

#### Conclusion

Reactions 2-13 demonstrate that an unsaturated ligand has to attain the fourth coordination position of the  $[\text{CH}_3\text{PtQ}_2]^+$  plane before carbonium ion reactivity is achieved. Thus the choice of an appropriate solvent and/or the addition of a chloride ion abstractor as a catalyst greatly facilitates the cationic reaction of *trans*- $\text{PtClCH}_3\text{Q}_2$  with acetylenes.

#### Experimental Section

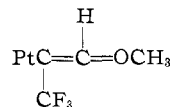
General methods have been described previously.<sup>3</sup> *trans*- $\text{PtClCH}_3\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  was prepared by the method of Ruddick and Shaw.<sup>47</sup> The preparations of the methylplatinum cationic complexes *trans*- $[\text{PtCH}_3(\text{L})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{Z}^-$  (III), where  $\text{Z} = \text{BF}_4, \text{PF}_6, \text{or B}(\text{C}_6\text{H}_5)_4$  and  $\text{L} = \text{Sb}(\text{C}_6\text{H}_5)_3, \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5, \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{pyridine, or CH}_3\text{CN}$ , have been described in ref 6;  $\text{L} = \text{CH}_3\text{C}\equiv\text{CCH}_3$  complexes, in ref 2;  $\text{L} = \text{CH}_2\text{CH}_2\text{OCCCH}_3$  and, in general,  $\text{RCH}_2\text{C}\equiv\text{OCH}_3$  complexes, in ref 3;  $\text{L} = \text{R}(\text{CH}_3\text{O})\text{C}=\text{NH}$  and  $\text{RCN}$  complexes, in ref 31; and  $\text{L} = \text{RNC}$  complexes, in ref 27. They may, however, be easily prepared from III ( $\text{L} = \text{acetone}$ ) by the addition of the neutral ligand  $\text{L}$  (in the cases where the ligand is stable).

*trans*- $[\text{PtCH}_3(\text{CH}_3\text{OH})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$ .—All attempts to prepare III ( $\text{L} = \text{methanol}$ ) from methanol solvent by the method previously described<sup>3</sup> for the acetone complex failed to yield a crystalline product other than  $[\text{PtCH}_3\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$  derived from decomposition.<sup>2</sup> When *trans*- $[\text{PtCH}_3(\text{acetone})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{SbF}_6^-$  ( $\sim 0.2$  g) was dissolved in methanol (2 ml) and pentane (5 ml) was added, a cloudy solution was formed. After leaving this solution in a refrigerator at  $-15^\circ$  for 7 days (with periodic shaking of the solution) a sticky white solid formed. The mother liquid was decanted, and the crystals were washed with ether and air-dried on a sintered-glass filter. This gave a sticky solid, which the infrared spectra suggested was III ( $\text{L} = \text{methanol}$ ) contaminated with excess methanol. However, on drying *in vacuo* at  $25^\circ$  decomposition occurred. The nmr data given in Table I for *trans*- $[\text{PtCH}_3$ -

$(\text{CH}_3\text{OH})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$  were obtained from the air-dried product.

**The Displacement Series.**—Equilibrium 1 was studied by nmr spectroscopy with 0.1-0.2 *M* concentrations of III in chloroform, dichloromethane, and acetone solutions. No solvent dependence was observed except for III ( $\text{L} = \text{RC}\equiv\text{CR}$  or olefins) in acetone. The reaction was followed by examination of  $\delta(\text{CH}_3)$  and  $J(\text{Pt}-\text{C}-\text{H})$  of the platinum methyl group. Only III ( $\text{L} = \text{CO}$  and  $\text{C}_2\text{H}_5\text{NC}$ ) show very similar values of  $J(\text{Pt}-\text{C}-\text{H})$ . However, the addition of  $\text{C}_2\text{H}_5\text{NC}$  to III ( $\text{L} = \text{CO}$ ) causes an immediate and irreversible evolution of CO. At  $31^\circ$  the equilibrium 1 is reached in a few minutes; this was checked by also making the inverse addition of the ligands; e.g., (i)  $\text{P}(\text{C}_6\text{H}_5)_3$  (1 mol) was added to III ( $\text{L} = \text{Sb}(\text{C}_6\text{H}_5)_3$ ) and (ii)  $\text{Sb}(\text{C}_6\text{H}_5)_3$  (1 mol) was added to III ( $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ).

*trans*- $\text{PtCl}\{-\text{CCF}_3=\text{C}(\text{OCH}_3)\text{H}\}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$ .—*trans*- $\text{PtClCH}_3\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  (0.260 g, 0.5 mmol) and *trans*- $[\text{PtCH}_3(\text{acetone})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$  (0.014 g, 0.02 mmol) were dissolved in methanol (20 ml) in a round-bottomed two-necked flask (25 ml) fitted with a magnetic stirring bar.  $\text{CF}_3\text{C}\equiv\text{CH}$  was bubbled through this solution for 2 min. The solution, thus saturated with  $\text{CF}_3\text{C}\equiv\text{CH}$ , was stirred for 2 hr before solvent was removed under reduced pressure. This gave a pale yellow gum which was dried *in vacuo* ( $10^{-3}$  cm,  $35^\circ$ ) for 15 min. The gum was extracted with benzene, and the pale yellow solution so obtained was passed through a short Florisil column eluting with benzene. This removed any cationic or poly(fluoro-vinyl) products. The nmr spectrum of this solution showed the absence of a platinum methyl group (indicating that all of the *trans*- $\text{PtClCH}_3\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  had reacted) and gave a good spectrum of the known product<sup>33</sup> *trans*- $\text{PtCl}\{-\text{CCF}_3=\text{C}(\text{OCH}_3)\text{H}\}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$ , notably the

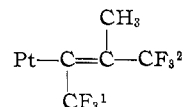


group which shows  $\delta(\text{CF}_3)$  40.96 ppm from  $\text{CFCl}_3$ ,  $J(\text{PtF}) = 131$  Hz,  $\delta(\text{OCH}_3) - 3.20$  ppm from TMS,  $\delta(=\text{CH}) - 4.99$  ppm from TMS,  $^3J(\text{PtH}) = 56.0$  Hz, and  $^4J(\text{PH}) = 1.8$  Hz.

Crystallization from benzene-pentane gave *trans*- $\text{PtCl}\{-\text{CCF}_3=\text{C}(\text{OCH}_3)\text{H}\}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  (0.25 g, 80% based on (10)) identical (nmr, ir, and mixture melting point) with an analyzed sample.

To determine the catalytic effect of the addition of *trans*- $[\text{PtCH}_3(\text{acetone})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$  a blank reaction was carried out: *trans*- $\text{PtClCH}_3\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2$  (0.241 g) was treated with  $\text{CF}_3\text{C}\equiv\text{CH}$  in methanol as before and was recovered in  $\sim 80\%$  yield (0.205 g). The nmr spectrum of the crude product showed very little ether formation had occurred.

**Reactions of Hexafluorobut-2-yne.**  $[\text{PtCCF}_3=\text{C}(\text{CH}_3)\text{CF}_3]\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$ .—*trans*- $[\text{PtCH}_3(\text{acetone})\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]^+\text{PF}_6^-$  (0.45 mmol) was dissolved in dichloromethane (1 ml) and placed in a thick-walled nmr tube.  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  (0.5 mmol) and  $\text{CFCl}_3$  (0.1 ml) were condensed into this tube and cooled in liquid nitrogen. The tube was sealed *in vacuo* and placed in the probe of a Varian HA-100 nmr spectrometer at  $-60^\circ$ . The  $^{19}\text{F}$  spectrum showed only a single absorption due to  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  and a doublet due to  $\text{PF}_6^-$ . The temperature was slowly raised and above  $-30^\circ$  two new resonances appeared at  $\delta$  49.55 and 60.10 ppm from  $\text{CFCl}_3$ . These two peaks grew rapidly at the expense of the  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  resonance but no other resonance was observed. The  $^{19}\text{F}$  spectrum at  $31^\circ$  was consistent with the formation of the vinyl group



Nmr data are as follows:  $\delta(\text{CF}_3^1)$  49.55 ppm from  $\text{CFCl}_3$ ,  $^3J(\text{PtF}) = 155$  Hz,  $J(\text{F}^1\text{F}^2) = 15.0$  Hz,  $J(\text{HF}^1) = 2.0$  Hz,  $\delta(\text{CH}_3^2)$  60.10 ppm from  $\text{CFCl}_3$ ,  $J(\text{F}^2\text{F}^1) = 15.0$  Hz,  $J(\text{PtF}^2) = 6.0$  Hz. The  $^1\text{H}$  nmr spectrum of this solution showed the absence of the methylplatinum group and only a singlet for the phosphine methyl protons—consistent with the vinyl cation rapidly undergoing exchange with the solvent. Carbon monoxide was bubbled through this solution, followed by the addition of ether. This gave a pale yellow oil which on cooling

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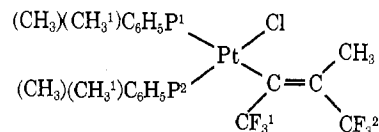
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in the refrigerator gave pale yellow crystals. Recrystallization from dichloromethane-ether gave *trans*-[PtCCF<sub>3</sub>=C(CH<sub>3</sub>)CF<sub>3</sub>(CO)]{P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>+PF<sub>6</sub><sup>-</sup> as a white crystalline solid, mp 176–178°, characterized by comparison with an authenticated sample.<sup>5</sup>

*cis*-PtCl{-CCF<sub>3</sub>=C(CH<sub>3</sub>)CF<sub>3</sub>}{P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>.—*trans*-PtCl-CH<sub>3</sub>{P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub> (0.258 g, 0.5 mmol) and *trans*-[PtCH<sub>3</sub>(acetone)]{P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>+PF<sub>6</sub><sup>-</sup> (0.014 g, 0.02 mmol) were dissolved in dichloromethane (15 ml) in a two-necked round-bottomed flask (25 ml) fitted with a magnetic stirring bar. CF<sub>3</sub>C≡CCF<sub>3</sub> was bubbled through the solution for 2 min. The solution was then stirred for 3 hr before removing the solvent under reduced pressure. This gave a pale yellow sticky solid which was extracted with benzene and passed through a short Florisil column eluting with benzene to remove any cationic platinum and poly(fluorovinyl) derivatives. Crystallization from benzene-pentane solution gave *cis*-PtCl(-CCF<sub>3</sub>=C(CH<sub>3</sub>)CH<sub>3</sub>){P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub> as a white crystalline compound, mp 155°. *Anal.* Calcd for PtP<sub>2</sub>F<sub>6</sub>ClC<sub>21</sub>H<sub>25</sub>: C, 36.90; H, 3.69; F, 16.69; Cl, 5.20. Found: C, 37.15; H, 3.76; F, 17.07; Cl, 5.66.

The nmr data recorded in dichloromethane solution at 31° and at 100 MHz are interpreted according to the stereochemistry



Chemical shifts,  $\delta$ , measured from TMS or CFCl<sub>3</sub> internal reference are as follows: P<sup>1</sup> methyls:  $\delta$ (CH<sub>3</sub>) -1.55, -1.51 ppm, <sup>3</sup>J(PtH) = 14.0 Hz, J(PH) = 10.4 Hz; P<sup>2</sup> methyls:  $\delta$ (CH<sub>3</sub>) -1.65, -1.60 ppm, <sup>3</sup>J(PtH) = 44.4 Hz, J(PH) = 10.4 Hz; vinyl methyl:  $\delta$ (CH<sub>3</sub>) -2.35 ppm (b), <sup>4</sup>J(PtH) = ca. 13 Hz; trifluoromethyls:  $\delta$ (CF<sub>3</sub><sup>1</sup>) 48.00 ppm, <sup>3</sup>J(PtF<sup>1</sup>) = 98.5 Hz, <sup>4</sup>J(PF<sup>1</sup>) = 9.1 Hz, J(F<sup>1</sup>F<sup>1</sup>) = 15.0 Hz, J(HF<sup>1</sup>) = 2.2 Hz;  $\delta$ (CF<sub>3</sub><sup>2</sup>) 61.48 ppm, <sup>4</sup>J(PtF<sup>2</sup>) = 5 Hz, <sup>5</sup>J(PF<sup>2</sup>) = 2.0 Hz, J(F<sup>1</sup>F<sup>2</sup>) = 15.0 Hz.

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## Chemistry of Metal Hydrides. XII. The Role of Cationic Intermediates in Olefin Insertions into the Platinum-Hydrogen Bond

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*trans*-PtHX(PR<sub>3</sub>)<sub>2</sub> (X = Cl or Br) reacted with ethylene in the presence of AgBF<sub>4</sub> or AgPF<sub>6</sub> in acetone-CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature and atmospheric pressure for PR<sub>3</sub> = PPh<sub>3</sub>, PPh<sub>2</sub>Me, or PMe<sub>2</sub>Ph and in boiling acetone solution (1 atm) for PR<sub>3</sub> = PEt<sub>3</sub>, giving ethylplatinum compounds. Similar reactions occurred between *trans*-PtH(NO<sub>3</sub>)(PPh<sub>2</sub>Me)<sub>2</sub> and ethylene or *trans*-PtHX(PPh<sub>2</sub>Me)<sub>2</sub>-AgBF<sub>4</sub> and propene or butene-1. Some  $\pi$ -allylplatinum(II) phosphine complexes were prepared by a similar reaction of *trans*-PtHX(PR<sub>3</sub>)<sub>2</sub> with allene or butadiene in the presence of AgPF<sub>6</sub>. These facile olefin insertion reactions into the Pt-H bond are interpreted in terms of an intermediate four-coordinate cationic complex, *trans*-[PtH(PR<sub>3</sub>)<sub>2</sub>(olefin)]<sup>+</sup>.

### Introduction

The catalytic homogeneous hydrogenation, isomerization, and polymerization of olefins and acetylenes have been the subject of many studies, particularly for those cases where transition metal complexes are the most effective catalysts. It has generally been accepted that the formation of the metal-hydrido bond and its reaction with unsaturated compounds are the key steps in the overall reactions.<sup>1</sup> Thus, some hydridophosphine complexes of platinum(II) have been shown to undergo insertion reactions toward simple olefins such as ethylene and propene<sup>2,3</sup> as well as several dienes,<sup>4</sup> tetrafluoroethylene,<sup>5</sup> and phosphine-substituted styrene.<sup>6</sup> The first example was reported by Chatt and Shaw,<sup>2</sup> who observed the reversible reaction

of *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub> with ethylene to give *trans*-PtEtCl(PEt<sub>3</sub>)<sub>2</sub> under rather vigorous conditions (95° and 80 atm)



Cramer and Lindsey reported<sup>7</sup> that the above equilibrium is established within 30 min at 25° and 1 atm in the presence of 1 mol % of tin(II) chloride ( $K_{\text{eq}} = 35 \text{ l}^{-1} \text{ mol}$ ), although they did not describe the detailed experimental procedure. The suggestions have been accepted<sup>8,9</sup> that both forward and reverse reactions proceed *via* five-coordinate  $\pi$ -olefinic hydrido complexes and that the strong trans influence and good  $\pi$ -acceptor property of the SnCl<sub>3</sub><sup>-</sup> ligand<sup>9,10</sup> may cause both the weakening of the Pt-H bond and the greater interaction of ethylene with platinum. On the other hand, the reactivity of RhHCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>10</sup> or HCo(CO)<sub>4</sub><sup>11</sup>

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