# Reactions of Alkynyl- and Alkenylplatinum(II) Compounds. 2.[1] Study of the Reaction between Anhydrous Hydrogen Chloride and Diethynylbis(dimethylphenylphosphine)platinum(II). Evidence for Platinum-Stabilized Vinyl Cations

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trans-Pt(C≡CH)$_2$L$_2$, I, reacts with anhydrous HCl (1 equiv) in the solvents CDCl$_3$ and CD$_2$Cl$_2$ to give *trans*-PtCl(C≡CH)L$_2$, V, and acetylene by way of a sequence of reactions involving *trans*-Pt(C≡CH)(CCl=CH$_2$)L$_2$, II, *trans*-Pt(CCl=CH$_2$)$_2$L$_2$, III, and *trans*-PtCl(CCl=CH$_2$)L$_2$, IV, where L = PMe$_2$Ph. I and III exist in equilibrium with II: 2II ⇌ I + III, $K \simeq$ 1. *trans*-Pt(CCl=CH$_2$)$_2$L$_2$, III, decomposes slowly, both in solution and in the melt, to give *trans*-PtCl(CCl=CH$_2$)L$_2$, IV, and acetylene. These reactions involve platinum(II)-promoted HCl addition–elimination processes. III and IV react with the tertiary amines Me$_3$N and proton sponge to give I and V, respectively. The rates of elimination of HCl from II–IV in benzene are approximately zeroth order in base concentration and show an isotope ratio $k_H/k_D \simeq 3$. The rate of HCl elimination from the CCl=CH$_2$ moiety is greatly dependent on the solvent, C$_6$H$_5$NO$_2$ > CDCl$_3$ ~ CD$_2$Cl$_2$ >> C$_6$D$_6$ ~ CCl$_4$, and is dependent on the nature of the [XPt] moiety to which it is bound: PtC≡CH ~ PtCCl=CH$_2$ > PtCl >> Pt$^+$C(Me)OMe. Elimination of HCl from the chlorovinyl ligands PtCCl=C(D(H))H(D) proceeds with no apparent stereochemical preference; elimination of HCl from PtCCl=C(Me(H))H(Me) occurs preferentially from the *trans*-PtC≡CH isomer. *trans*-Pt(CCl=CH$_2$)$_2$L$_2$ reacts with MeOD to give *trans*-[Pt(CCl=CH$_2$)(C(CD$_3$)OMe)L$_2$]$^+$ which has been isolated as a hexafluorophosphate salt. A stepwise addition–elimination sequence involving the platinum-stabilized vinyl cation PtC$^+$=CH$_2$ is proposed to account for all of these observations

$$Pt-\overset{\vert}{\underset{Cl}{C}}=CH_2 \rightleftarrows Pt-\overset{+}{C}=CH_2 \;\; Cl^- \rightleftarrows Pt-C\equiv CH + HCl$$
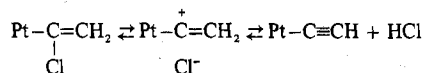
The molecular structure of III deduced from x-ray studies reveals a long vinylic C–Cl bond distance, 1.809 (6) Å, and a large Pt–C–C angle, 133.5°. The decomposition of III to give IV and acetylene occurs much faster in CD$_2$Cl$_2$ and CDCl$_3$ than in benzene. The reaction III → IV + HC≡CH is slow relative to HCl elimination from III, irrespective of the solvent. A mixture of III and III-d_4 decomposes in the melt and in solution to give a mixture of acetylene-d_0, -d_1, and -d_2. An isotope ratio $k_H/k_D \simeq 1.9$ has been found for the reaction III → IV + acetylene. A number of mechanisms which could yield acetylene in the above reaction are discussed. These findings are compared to solvolysis and elimination reactions of aryl-substituted vinyl compounds, Ar(X)C=CH$_2$, where X = Cl, Br, or CF$_3$SO$_3$. Platinum(II) is thus shown to greatly activate the σ-coordinated unsaturated organic ligand.

Introduction

We have previously proposed[1–4] that a number of organic reactions occurring within the coordination sphere of platinum can be interpreted in terms of a carbonium ion model. In the preceding paper[1] the formation of cationic alkoxycarbene complexes was discussed. Platinum(II)-stabilized vinyl cations, PtC$^+$=CHR, formed from (i) protonation of platinum(II) acetylides, (ii) cationic π-acetylenic platinum(II) intermediates, and (iii) solvolysis reactions of α-chlorovinylplatinum(II) compounds, were proposed to be reactive intermediates

$$Pt-\overset{+}{C}=CHR + R'OH \rightarrow Pt^+-C\overset{\displaystyle OR'}{\underset{\displaystyle CH_2R}{\big\langle}}$$
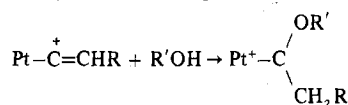
However, the above reactions have no simple analogues in organic chemistry. Our proposal that platinum(II) can stabilize a vinyl cation PtC$^+$=CHR can only be evaluated more precisely in situations where there exist closely related organic and organometallic reactions. In this paper we describe our studies of the reaction between *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$ and anhydrous HCl (1 equiv) which gives *trans*-PtCl(C≡CH)(PMe$_2$Ph)$_2$ and acetylene in solvents such as dichloromethane and benzene. This seemingly trivial organometallic reaction proceeds via a sequence of platinum(II)-promoted addition–elimination reactions

$$Pt-C\equiv CH + HCl \rightleftarrows Pt-CCl=CH_2$$
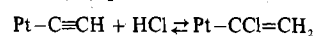
A direct comparison with analogous organic reactions is now possible. Preliminary accounts of this work have been reported.[5,6]

Results and Discussion

Syntheses. In the preceding paper[1] the preparations of *trans*-Pt(C≡CH)$_2$L$_2$, I, *trans*-Pt(CCl=CH$_2$)$_2$L$_2$, III, and *trans*-PtCl(CCl=CH$_2$)L$_2$, IV, where L = PMe$_2$Ph, were reported. *trans*-PtCl(C≡CH)L$_2$, V, is best prepared by the addition of an amine to a solution of *trans*-PtCl(CCl=CH$_2$)L$_2$, IV, in a polar solvent such as dichloromethane. The compounds I, III, IV, and V have been characterized by elemental analyses and a number of spectroscopic methods. This work is concerned with the solution chemistry of these compounds and ^{1}H NMR spectroscopy has been used extensively as an analytical probe.

^{1}H NMR Spectra. For a solution containing all four compounds, I, III, IV, and V, it is possible to identify each species and estimate its relative concentration by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of I and III are shown in Figures 1 and 2, respectively.

For all four compounds the phosphine methyl proton resonances appear as 1:2:1 triplets due to the virtual coupling of two mutually trans phosphorus nuclei (^{31}P, $I = {}^1/_2$, 100% natural abundance) and are flanked by satellites of one-fourth intensity due to coupling to ^{195}Pt (^{195}Pt, $I = {}^1/_2$, 34% natural abundance).[7]

The acetylenic protons in I (see Figure 1) and V also appear as 1:2:1 triplets due to coupling to two equivalent phosphorus nuclei (a four-bond coupling) and are flanked by satellites due to coupling to ^{195}Pt. The magnitude of the latter coupling constant, $^3J_{Pt–H}$, is markedly different in I (45 Hz) and in V (71.6 Hz) reflecting the very different trans influence[8] of the trans ligands: C≡CH > Cl.
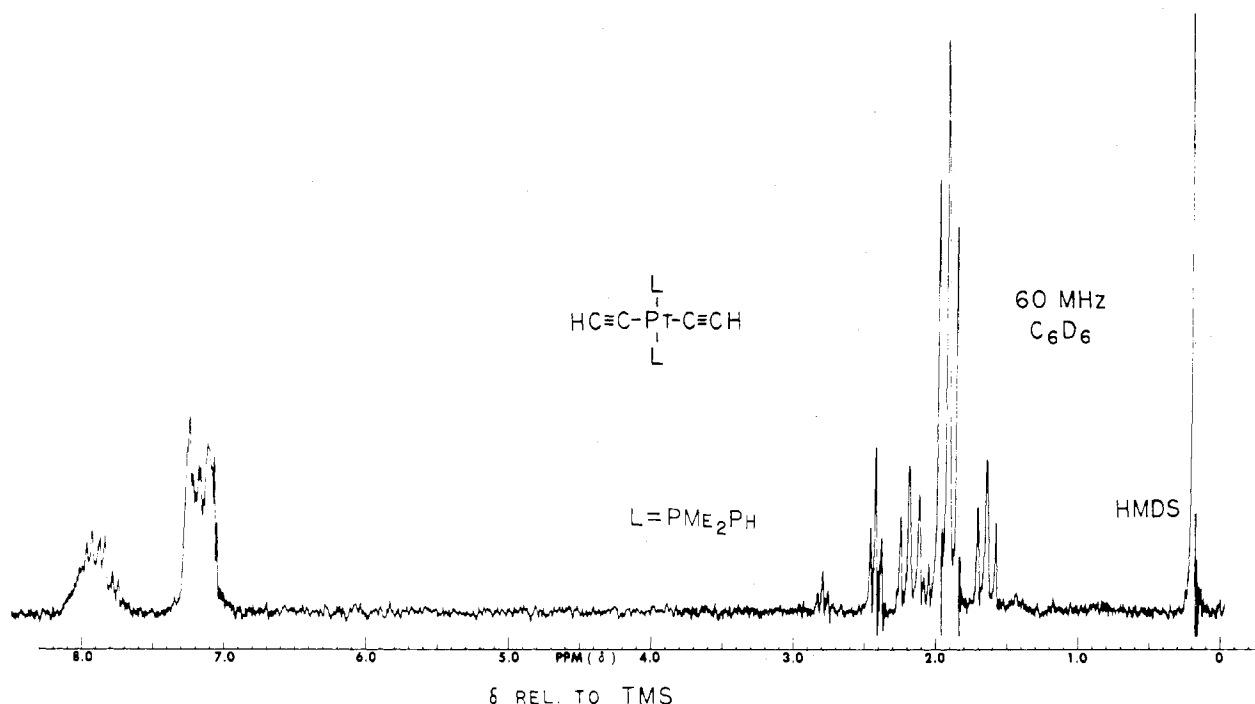
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Figure 1. ¹H NMR spectrum of *trans*-Pt(C≡CH)₂(PMe₂Ph)₂ recorded in C₆D₆ at 60 MHz, 35 °C. Assignments are given in Table I.

Table I. ¹H NMR Characterization Data for Acetylide- and α-Chlorovinyl–Platinum(II) Compounds[a]

| | P methyls | | | Acetylide H | | | Vinylic protons | | | | | | | |
| | | | | | | | *cis*-PtCCH | | | *trans*-PtCCH | | | |
Compd[b]	δ	J^c	J^d	δ	J^e	J^d	δ	J^e	J^d	δ	J^e	J^d	J^d
PtL₂(C≡CH)₂	2.05	7.8	33	2.13	2.3	45							
PtL₂(C≡CH)(CCl=CH₂)	1.94	7.6	33.6	2.07	2.3	41.6	4.82	1.6	25.5	5.92	1.85	68	<0.6
PtL₂(CCl=CH₂)₂	1.84	7.6	34				4.71	1.9	24	5.82	2.2	64	g
PtL₂Cl(CCl=CH₂)	1.86	7.6	43.2				4.92	1.7	43.2	5.93	1.5	114	1.0
PtL₂Cl(C≡CH)	1.90	8.05	31.4	2.12	2.3	71.6							

[a] Chemical shifts (δ) in ppm relative to TMS; coupling constants (*J*) in Hz; spectra recorded in benzene-*d₆* at ca. 35 °C; phosphine phenyl proton resonances were observed. [b] L = PMe₂Ph. [c] $^2J + {}^4J_{PH}$. [d] $^3J_{PtH}$. [e] $^4J_{PH}$. [f] J_{HH}, geminal coupling. [g] Ca. 0.0 Hz.

The vinylic protons in III (Figure 2) and IV also appear as sets of 1:2:1 triplets due to coupling to two equivalent phosphorus nuclei and ¹⁹⁵Pt. The magnitudes of the coupling constants ³J_{PtH} are very different for III and IV reflecting the trans influence of the ligands: CCl=CH₂ > Cl. For both III and IV the chemical shifts of the cis and trans vinylic protons (defined with respect to Pt) are well separated (ca. 1 ppm). The magnitude of ³J_{PtH} (*trans*-PtC=CH) is much greater than ³J_{PtH} (*cis*-PtC=CH). The ratio ³J_{PtH}(*trans*-PtC=CH):³J_{PtH}(*cis*-PtC=CH) is ca. 2.5:1. This phenomenon has been well documented previously.[8,9] Pertinent ¹H NMR characterization data for I, III, IV, and V are given in Table I.

Infrared Spectroscopy. Infrared spectroscopy is also useful in identifying the various species present in mixtures of these compounds. For the acetylides I and V the values of ν(C—H) and ν(C≡CH) are significantly different. For the deuterated compounds *trans*-Pt(C≡CD)₂L₂, I-*d₂*, *trans*-Pt(CCl= CD₂)₂L₂, III-*d₄*, *trans*-PtCl(CCl=CD₂)L₂, IV-*d₂*, and *trans*-PtCl(C≡CD)L₂, V-*d₁*, the values of ν(C—D), ν(C≡CD), and ν(C=CD₂) are similarly diagnostic. These characteristic infrared bands, which are sharp and quite intense, are given in Table II.

trans-Pt(C≡CH)₂(PMe₂Ph)₂ + HCl. General Procedures. The reaction between I and HCl was followed by ¹H NMR and infrared spectroscopy. Compound I (ca. 30 mg, 0.05 mmol) was dissolved in the solvent of choice (0.5 ml) in an NMR tube. Anhydrous HCl was added using a calibrated vacuum line and the sample was sealed in vacuo. The various

Table II. Infrared Characterization Data for Acetylide- and Vinyl–Platinum(II) Compounds

Compd[a]	ν(C≡C)[b]	ν(C–H/D)[b]	ν(C=C)[b]
Pt(C≡CH)₂L₂	1968	3278	
Pt(C≡CD)₂L₂	1852	2542	
Pt(C≡CH)(CCl=CH₂)L₂	1973	3288	1565
Pt(C≡CD)(CCl=CD₂)L₂	1855	2550	1518
Pt(CCl=CH₂)₂L₂			1565
Pt(CCl=CD₂)₂L₂			1518
PtCl(CCl=CH₂)L₂			1565
PtCl(CCl=CD₂)L₂			1518
PtCl(C≡CH)L₂	1987	3278	
PtCl(C≡CD)L₂	1877	2560	

[a] L = PMe₂Ph. [b] ν in cm⁻¹; values accurate to ±2 cm⁻¹.

platinum compounds present in solution were identified and an estimate of their relative concentrations was obtained from the ¹H NMR data (Table I). In a number of studies the reactions were quenched after a certain time by freezing the samples in liquid nitrogen. The NMR tubes were then opened under vacuum and the gaseous products (acetylene and vinyl chloride) were separated and analyzed by ¹H NMR and mass spectroscopy. The platinum-containing solids were examined by infrared spectroscopy.

Reactions in CDCl₃ and CD₂Cl₂. Addition of anhydrous HCl (1 equiv) to I in CDCl₃ or CD₂Cl₂ caused an apparently instantaneous reaction, even at −60 °C, and gave a mixture of I, *trans*-Pt(C≡CH)(CCl=CH₂)L₂, II, and III in the concentration ratio ca. 1:2:1, respectively.
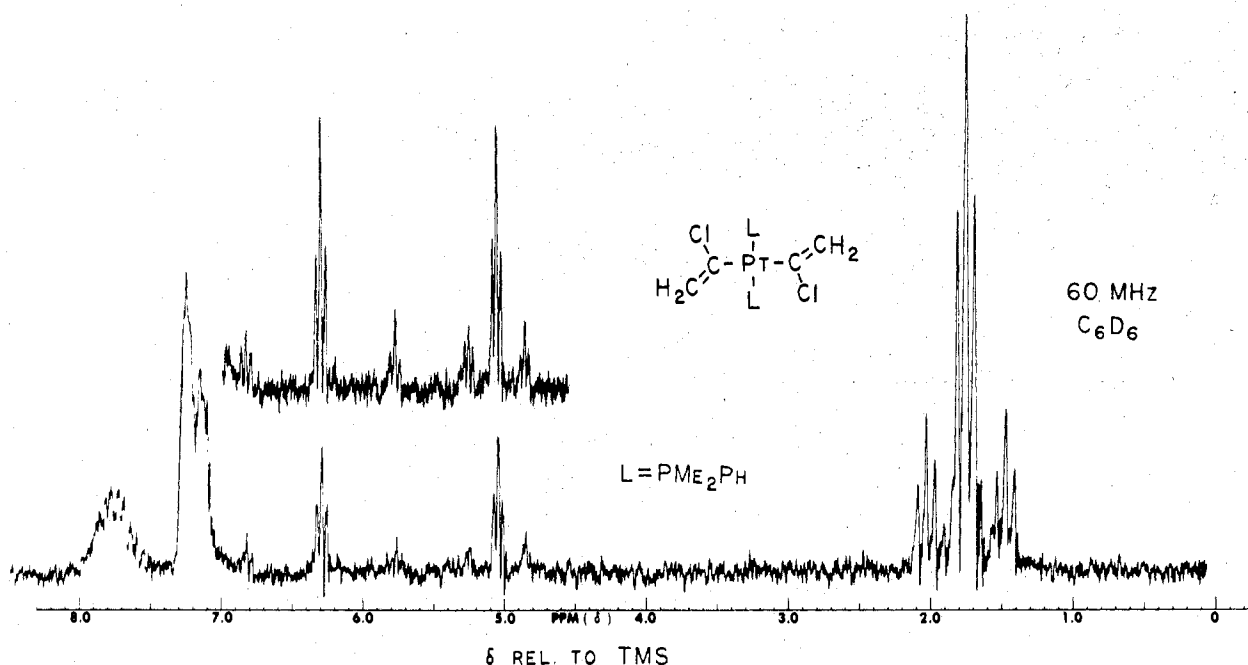
Figure 2. ^{1}H NMR spectrum of *trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$ recorded in benzene-d_6 at 60 MHz, 35 °C. Vinylic proton resonances are also shown at higher spectrum amplitude. Assignments are given in Table I.

II has not been isolated as a pure compound (free from I and III) but the characterization data shown in Tables I and II leave no doubt concerning the identity of this species in solutions of I and III. The values of $^3J_{PtH}$ for the acetylenic and vinylic protons demonstrate the high and comparable trans influence of the groups –C≡CH and –CCl=CH$_2$.

The initial very fast reaction between I and HCl (1 equiv) to give the ca. 1:2:1 mixture of I, II, and III, was followed by a slower reaction. After 12 h at 25 °C, a ca. 1:1 mixture of I and IV was present in solution. Analysis of the volatile organic products showed that at $t \approx 5$ min (immediately after adding the HCl) only a trace of acetylene was present and that at $t = 12$ h acetylene was present in almost 50% yield based on added HCl. Only a trace of vinyl chloride was detected at $t = 12$ h, and no V was detected either in the ^{1}H NMR spectra recorded during the course of reaction or in the infrared spectrum of the $t = 12$ h platinum-containing solids. The initial reaction between I and HCl (1 equiv) can be represented by eq 1.

$$4I + 4HCl \rightarrow I + 2II + III \rightarrow 2I + 2IV + 2HC≡CH \qquad (1)$$
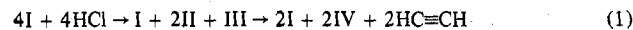
When equimolar quantities of I and III were dissolved in CD$_2$Cl$_2$, the ^{1}H NMR spectrum showed that the formation of the ca. 1:2:1 mixture of I, II, and III, respectively, was achieved within ca. 5 min at 30 °C. When equimolar quantities of I and III-d_4 were dissolved in CD$_2$Cl$_2$, the ^{1}H NMR spectrum recorded at $t \approx 5$ min showed that formation of I, II, and III was accompanied by complete H/D scrambling of the vinylic protons. (To be precise the ratio of signal intensities of the vinylic protons (III:II) was as expected for the ca. 1:2:1 mixture of I, II, and III.) The infrared spectrum of the platinum-containing solids showed the presence of both PtC≡CH and PtC≡CD moieties for I and II.

These observations demonstrate that I and III exist in equilibrium with II, eq 2. Furthermore the position of

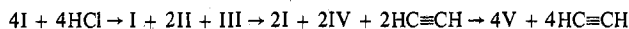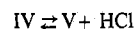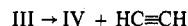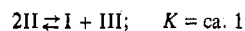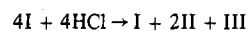$$I + III \rightleftarrows 2II \qquad K \approx 1 \qquad (2)$$

equilibrium in (2) is readily attained due to facile HCl exchange between α-chlorovinyl and ethynyl ligands as shown in eq 3. The reaction between I and III-d_4 shows that (3)

$$Pt–C≡CH + Pt'–CCl=CH_2 \rightleftarrows Pt–CCl=CH_2 + Pt'–C≡CH \qquad (3)$$
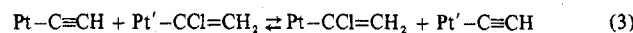
occurs by HCl exchange and not by ligand exchange reactions

Scheme I

$$4I + 4HCl \rightarrow I + 2II + III$$

$$2II \rightleftarrows I + III; \qquad K = ca. 1$$

$$III \rightarrow IV + HC≡CH$$

$$IV \rightleftarrows V + HCl$$

$$4I + 4HCl \rightarrow I + 2II + III \rightarrow 2I + 2IV + 2HC≡CH \rightarrow 4V + 4HC≡CH$$

of the type Pt–L + Pt'–L' ⇌ PtL' + Pt'–L where L and L' are ethynyl and chlorovinyl ligands, respectively.

The compound *trans*-Pt(CCl=CH$_2$)$_2$L$_2$, III, is best prepared by the reaction between I and HCl (2 equiv) in benzene or toluene. It may similarly be prepared in CDCl$_3$ or CD$_2$Cl$_2$ but in these solvents III decomposes to give IV and acetylene quite rapidly. Addition of HCl (1 equiv) to III in CDCl$_3$ or CD$_2$Cl$_2$ gives IV and vinyl chloride. The compound *trans*-PtCl(CCl=CH$_2$)L$_2$, IV, is stable with respect to elimination of vinyl chloride in the presence of excess anhydrous HCl. Thus IV is the sole product obtained by the reaction of I with excess anhydrous HCl in CDCl$_3$ and CD$_2$Cl$_2$ solvents. However, IV is not the ultimate product in the reaction between I and HCl (1 equiv) since IV is labile toward the elimination of HCl. Consequently the 1:1 mixture of I and IV, which was formed in the reaction between I and HCl (1 equiv) after 12 h, slowly reacts further to give V and acetylene. Formation of V in this manner is exceedingly slow. The overall reaction between I and HCl (1 equiv) to give V and acetylene is summarized by the reactions shown in Scheme I. Each of the α-chlorovinyl compounds, II–IV, is kinetically labile toward elimination of HCl.

V is best prepared by taking advantage of the facts that (i) IV is readily prepared from I and HCl (3 equiv) and (ii) IV is labile toward elimination of HCl. Thus treating a solution of IV with NMe$_3$ or proton sponge gives V and the respective amine hydrochloride.

Reactions in C$_6$D$_6$ and C$_6$D$_5$CD$_3$. Addition of HCl (1 equiv) to a frozen solution of I in benzene-d_6 gave, upon melting, a 1:1 mixture of I and III. Over a period of 24 h at 25 °C this reacted to give the ca. 1:2:1 mixture of I, II, and III, respectively. Further reaction to give I, IV, and acetylene, eq 1, was very slow requiring ca. 4 weeks at 25 °C.
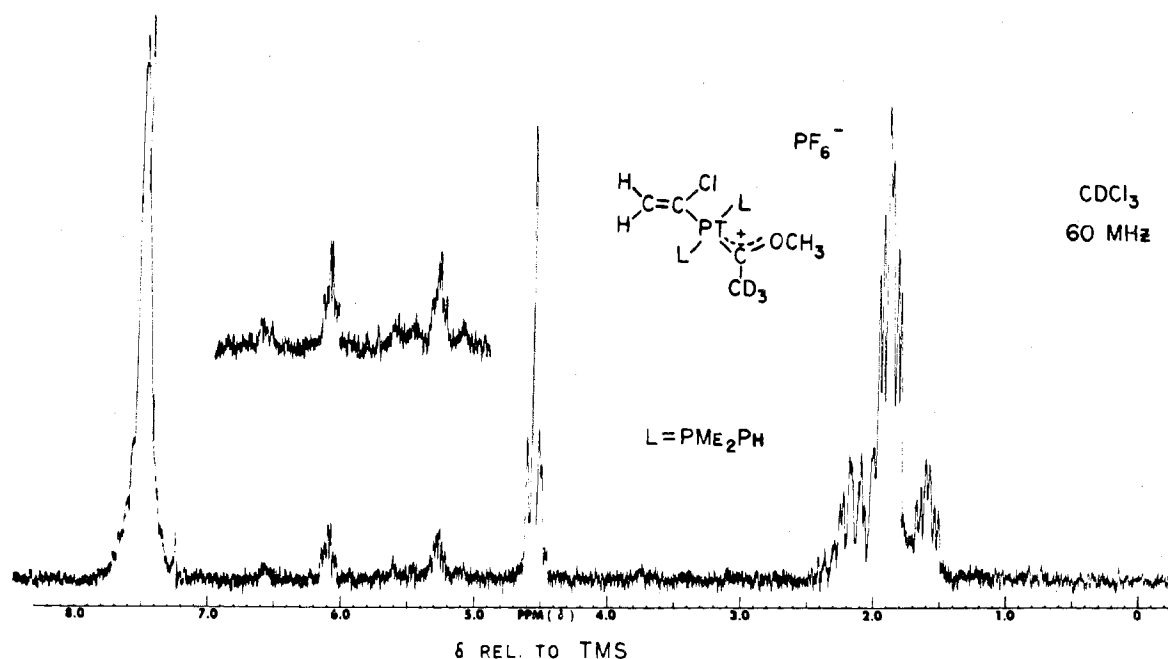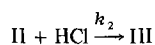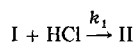
Figure 3. ^{1}H NMR spectrum of trans-[Pt(CCl=CH$_2$)(C(CD$_3$)OMe)(PMe$_2$Ph)$_2$]$^+$PF$_6$$^-$ obtained from the reaction between trans-Pt-(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$ and AgPF$_6$ (1 equiv) in CH$_3$OD. Spectrum recorded in CDCl$_3$ (35 °C) at 60 MHz.

Addition of HCl (1 equiv) to a solution of I in toluene-d_8 at ca. −78 °C gave within 5 min a 1:1 mixture of I and III. During 12 h at 25 °C this reacted to give the ca. 1:2:1 mixture of I, II, and III, respectively.

The initial formation of the 1:1 mixture of I and III in C$_6$D$_6$ and C$_6$D$_5$CD$_3$ solvents contrasts with the reactions in CDCl$_3$ and CD$_2$Cl$_2$ described above. Two factors could readily account for such a solvent dependence: (1) The formation of III could be kinetically favored in the reaction sequence

$$I + HCl \xrightarrow{k_1} II$$

$$II + HCl \xrightarrow{k_2} III$$

if $k_2 \gg k_1$. Since the back-reactions determined by k_{-1} and k_{-2} are slow in benzene and toluene, the 1:1 mixture of I and III would be the kinetically favored products in the reaction between I and HCl (1 equiv). (2) HCl may exist as [HCl]$_n$ in the solvents benzene and toluene.[10] The reaction between I and [HCl]$_n$ could then give III and [HCl]$_{n-2}$. The same situation could hold for reactions in CD$_2$Cl$_2$ and CDCl$_3$ but in these solvents the back-reactions (k_{-1}, k_{-2}) are facile leading to rapid attainment of the thermodynamic equilibrium mixture of I, II, and III.

We have found that benzene solutions of II and III eliminate HCl at comparable rates (see later); it may therefore be expected that I and II react with HCl at comparable rates to give II and III, respectively. Thus we believe that the 1:1 mixture of I and III initially formed in the reaction between I and HCl (1 equiv) in C$_6$D$_6$ and C$_6$D$_5$CD$_3$ arises from the aggregated nature of anhydrous HCl in these solvents.

Addition of anhydrous HCl (2 equiv) to I in benzene or toluene gives virtually quantitative formation of III. III reacts with HCl to give IV and vinyl chloride in these solvents. However, the latter reaction is relatively slow: addition of HCl to III-d_4 in toluene-d_8 led to rapid H/D scrambling of the vinylic protons of III with subsequent formation of IV and vinyl chloride. It is the fact that III reacts only relatively slowly with HCl to give IV and vinyl chloride which accounts for the observation that I + HCl (1 equiv) gives I and III.

III is relatively stable in C$_6$D$_6$ and C$_6$D$_5$CD$_3$. The reactions (i) III → II + HCl and (ii) III → IV + HC≡CH are both slow but, as is seen in the following, (i) occurs more rapidly

than (ii). A mixture of III and III-d_4 reacted in benzene and in the melt to give IV and acetylene-d_0, -d_1, and -d_2. The acetylene liberated in these reactions was analyzed by mass spectroscopy. In both instances acetylene-d_1 was the major constituent, a finding which can only be accounted for by the fact that reversible HCl elimination from III is faster than the reaction of III which gives IV and acetylene.

trans-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$ + MeOH. III dissolves in methanol to give trans-[Pt(CCl=CH$_2$)(C(Me)OMe)-(PMe$_2$Ph)$_2$]$^+$Cl$^-$, which in the presence of AgPF$_6$ (1 equiv) gives the air-stable, white crystalline compound trans-[Pt-(CCl=CH$_2$)(C(Me)OMe)(PMe$_2$Ph)$_2$]$^+$PF$_6$$^-$. The analogous reaction in MeOD led to trans-[Pt(CCl=CH$_2$)(C(CD$_3$)-OMe)(PMe$_2$Ph)$_2$]$^+$PF$_6$$^-$. Significantly only one of the α-chlorovinyl groups reacted with MeOD: this is clearly evident from the fact that the vinylic protons of the PtCCl=CH$_2$ moiety in the carbene complex are not exchanged with deuterium atoms of the solvent. The ^{1}H NMR spectrum of the labeled compound trans-[Pt(CCl=CH$_2$)(C(CD$_3$)-OMe)(PMePh)$_2$]$^+$PF$_6$$^-$ is shown in Figure 3: note the geminal coupling of the vinylic protons.

Structure of trans-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$. The molecular structure of III has been deduced by single-crystal x-ray studies. Full details of this study are reported[11] elsewhere but certain features of the structure warrant attention in the context of this work.

The phosphine phenyl groups and vinylic chlorine atoms are directed above and below the coordination plane of platinum. The molecule is centrosymmetric; the platinum atoms reside on centers of symmetry and thus the coordination plane about platinum is rigorously planar. With the P–Pt–C$_\alpha$ angle equal to 87.85°, the coordination geometry is nearly ideal. Figure 4 gives a view of the molecule slightly above the P–Pt–P axis. The phosphine methyl and phenyl groups are omitted in Figure 4 in order to reveal more clearly the bonding parameters of interest. The C$_\alpha$–C$_\beta$ bond distance is normal for a carbon–carbon double bond but the C$_\alpha$–Cl distance and the interatomic angles about C$_\alpha$ are quite unusual.[12] Vinyl chloride is reported to have a C–Cl bond length of 1.728 (7) Å[13] and the similar bond in 2-chloropropene is 1.727 Å.[14] The average C–Cl bond distance in (π-C$_2$Cl$_4$)Pt(PPh$_3$)$_2$ is 1.75 (3) Å.[15] The long C$_\alpha$–Cl bond distance in III, 1.809 (6) Å, is similar to the

Figure 4. ORTEP view of *trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$ showing important bond angles and bond distances; the phosphine methyls and phenyl are omitted for clarity. Atom ellipsoids represent equiprobability surfaces of thermal displacement and contain 50% of the probability distribution.

C$_{sp^3}$–Cl bond distance found in *tert*-butyl chloride: 1.807 (4),[16] 1.828 (5) Å.[17] The observed Pt–C$_\alpha$–Cl bond angle is smaller than expected while the Pt–C$_\alpha$–C$_\beta$ angle is expanded, in opposition to what would be expected from steric considerations.

Elimination of HCl from α-Chlorovinyl Ligands. III reacted with anhydrous NH$_3$ (1 equiv) in CD$_2$Cl$_2$ to give an immediate precipitate of NH$_4$Cl and a ca. 1:2:1 mixture of I, II, and III respectively. With 2 equiv of anhydrous NH$_3$, III reacted to give I. These reactions also occurred rapidly when the aprotic amines NMe$_3$ and proton sponge [1,8-bis(dimethylamino)-naphthalene] were used. Under similar conditions IV reacted to give V. The rate of elimination of HCl from II, III, and IV was very dependent on the nature of the solvent. At ca. 25 °C when III was reacted with proton sponge (1 equiv) the ca. 1:2:1 mixture of I, II, and III, respectively, was obtained within 5 min in nitrobenzene, ca. 30 min in CDCl$_3$ and CD$_2$Cl$_2$, and ca. 24 h in C$_6$D$_6$. Elimination of HCl in benzene-d_6 was sufficiently slow that these reactions were amenable to kinetic studies.

The reactions between each of III, III-d_4, IV, and IV-d_2 and NMe$_3$ or proton sponge in varying concentrations (1–3 equiv) were followed by ^{1}H NMR spectroscopy. Typically ca. 30 mg of the α-chlorovinylplatinum compound under study was dissolved in benzene-d_6 (ca. 0.5 ml) and a measured quantity of the tertiary amine was added. (NMe$_3$ was added using a calibrated vacuum line and proton sponge was added in known amount from a stock solution in benzene-d_6.) With time a precipitate of the amine hydrochloride formed. This was repeatedly centrifuged to the bottom of the NMR tube. The rate of HCl elimination was monitored by the diminution of the methyl proton resonance of the amine. The relative concentration of the amine was calibrated against an internal reference, TMS or hexamethyldisiloxane, whose concentration remained constant during the course of the reaction. For a number of reasons the measurement of peak height may not provide a totally accurate measure of concentration. However, this method is considered sufficiently accurate for the purposes at hand. The methyl resonances of NMe$_3$ and proton sponge appear as sharp singlets and are well separated from other resonances. One equivalent of HCl corresponds to 9 and 12 proton equiv of NMe$_3$ and proton sponge, respectively.

Kinetic data for HCl elimination from III, II, and IV are reported in Table III. The rate was found to be first order in the α-chlorovinylplatinum complex and zeroth order in amine concentration in the concentration range studied. The observed rate was very similar for both NMe$_3$ and proton sponge.[18] We conclude that elimination of HCl does not occur by an E2 mechanism of the type shown in eq 4, which is

$$\text{Pt} \quad \overset{\frown}{\text{H}} \text{ :B}$$
$$\overset{\text{\textbackslash}}{\underset{/}{\text{C}}}=\overset{/}{\underset{\text{\textbackslash}}{\text{C}}} \quad \rightarrow \text{BH}^+\text{Cl}^- + \text{Pt}-\text{C}{\equiv}\text{CH} \qquad (4)$$
$$\quad \text{Cl} \quad \text{H}$$

Compd[a]	Amine (equiv)[b]	k_{obsd}, s^{-1}	Correln coeff
IV	NMe$_3$ (1)	2.14 (4) × 10^{-6}	0.997
IV	PS (1)	1.25 (2) × 10^{-6}	0.999
IV-d_2	PS (1)	5.0 (2) × 10^{-7}	0.994
III	NMe$_3$ (1)	1.02 (8) × 10^{-5}	0.991
III	NMe$_3$ (1) + PMe$_2$Ph (1)	1.02 (5) × 10^{-5}	0.995
III	NMe$_3$ (3)	1.1 (1) × 10^{-5}	0.96
III	PS (1)	3.4 (2) × 10^{-6}	0.99
III	PS (3)	3.9 (1) × 10^{-6}	0.995
III-d_2	PS (1)	1.16 (6) × 10^{-6}	0.99

[a] IV = *trans*-PtCl(CCl=CH$_2$)(PMe$_2$Ph)$_2$; IV-d_2 = *trans*-PtCl(CCl=CD$_2$)(PMe$_2$Ph)$_2$; III = *trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$; III-d_4 = *trans*-Pt(CCl=CD$_2$)$_2$(PMe$_2$Ph)$_2$. [b] PS = proton sponge, 1,8-bis(dimethylamino)naphthalene.

common for simple organic vinyl halides.[19]

When III was treated with R$_3$N (3 equiv), the formation of I via II was clearly evident from the ^{1}H NMR spectra. Good straight-line plots were obtained when the data were analyzed (see Experimental Section) which means that in the sequential reaction

$$\text{III} \overset{k_1}{\longrightarrow} \text{II} + \text{HCl}; \quad \text{II} \overset{k_2}{\longrightarrow} \text{I} + \text{HCl}$$

the rate constants k_1 and k_2 must be very similar. The observed rate of HCl elimination from IV in benzene was significantly slower than that from III and II. As noted previously the cationic carbene complex *trans*-[Pt(CCl=CH$_2$)(C(CD$_3$)OMe)(PMe$_2$Ph)$_2$]$^+$PF$_6^-$ did not exchange its vinylic protons with deuterium atoms in CH$_3$OD solution. Thus even in methanol HCl elimination from the PtCCl=CH$_2$ moiety in this complex must be exceedingly slow. The observed rate of HCl elimination from the –CCl=CH$_2$ moiety is dependent on the trans ligand X and in the order X = C≡CH ~ CCl=CH$_2$ > Cl >> C$^+$(CH$_3$)OMe.

The observed rate of DCl elimination from the deuterated compounds III-d_4 (II-d_3) and IV-d_2 was markedly slower than HCl elimination from the corresponding protio compound: $k_H/k_D \simeq 3.0$.

Addition of PMe$_2$Ph (1 equiv) to a solution of III in benzene-d_6 at ca. 35 °C caused the phosphine methyl proton resonances to collapse to a singlet. The vinylic protons lost their coupling to phosphorus but maintained their coupling to platinum-195. This is expected when exchange between free and coordinated phosphine is rapid on the NMR time scale. Previous studies of phosphine-exchange reactions involving platinum(II) complexes, e.g.,[20] *trans*-PtCl(H)(PEt$_3$)$_2$, have shown that exchange occurs by an associative process

$$\text{PtH(Cl)(PEt}_3\text{)}_2 + \text{PEt}_3 \rightleftarrows \text{PtH(Cl)(PEt}_3\text{)}_3$$

When NMe$_3$ (1 equiv) was added to a benzene-d_6 solution of III + PMe$_2$Ph (1 equiv), the rate of HCl elimination (monitored by consumption of NMe$_3$) was essentially unchanged from that observed in the absence of added PMe$_2$Ph. When all of the NMe$_3$ had reacted to give Me$_3$NH$^+$Cl$^-$, a further reaction to give I and PhMe$_2$PH$^+$Cl$^-$ occurred. The phosphonium salt was precipitated from the benzene-d_6 solution. Presumably the phosphonium salt formed in the presence of NMe$_3$ is rapidly deprotonated by the amine.

When V was reacted with DCl (1 equiv) in benzene, a mixture of isotopically labeled compounds was formed: IV, IV-d_1, and IV-d_2. A similar mixture is formed by treating IV with DCl (2 equiv). IV-d_1 is favored statistically in the above mixtures and is seen to be the major protio species present by ^{1}H NMR spectroscopy: IV-d_1 shows no geminal coupling, $J_{HD} \approx 0$, whereas in IV geminal $J_{HH} = 1.0$ Hz.

The ^{1}H NMR spectrum of the mixture of IV, IV-d_1, and IV-d_2 showed that the concentrations of *cis*-PtC=CH and

trans-PtC≡CH protons were approximately equal (within the limits of integration). Thus VI and VII must also be present

$$
\begin{array}{cc}
\underset{\substack{\text{Cl} \quad \text{D} \\ \text{VI}}}{\overset{\substack{\text{Pt} \quad \text{H} \\ \diagdown \diagup}}{\text{C=C}}} &
\underset{\substack{\text{Cl} \quad \text{H} \\ \text{VII}}}{\overset{\substack{\text{Pt} \quad \text{D} \\ \diagdown \diagup}}{\text{C=C}}}
\end{array}
$$

in at least approximately equal concentrations.

When NMe₃ is added to a benzene solution containing IV, IV-d_1, and IV-d_2, HCl is eliminated preferentially; k_H/k_D = ca. 3. Since the half-lives of the reactions IV + NMe₃ → V + Me₃NH⁺Cl⁻ ($t_{1/2}$ = 8 days) and IV-d_2 + NMe₃ → V-d_1 + Me₃ND⁺Cl⁻ ($t_{1/2}$ = 20 days) are long in benzene-d_6 at 20 °C, one might expect to observe a stereochemical preference in the elimination of HCl from IV-d_1. Thus preferential elimination of HCl from VI would lead to a relative increase in the concentration of VII as monitored by the *cis*- and *trans*-PtC≡CH proton resonances. However, no apparent stereochemical preference for elimination of HCl from IV-d_1 was observed: the relative concentrations of *cis*- and *trans*-PtC≡CH protons, corresponding to VI and VII, respectively, remained at least approximately equal throughout the slow reaction.

In a similar experiment *trans*-PtCl(CCl=C(H)Me)-(AsMe₃)₂ was reacted with proton sponge (3 equiv) in benzene-d_6. The *trans*-PtCl(CCl=C(H)Me)(AsMe₃)₂ used in this reaction was prepared from the reaction between *trans*-Pt(C≡CMe)₂(AsMe₃)₂ and anhydrous HCl (>2 equiv) and was a thermodynamic mixture of *cis*- and *trans*-PtC≡CH isomers in the ratio ca. 1:2, respectively. During the reaction with proton sponge to give *trans*-PtCl(C≡CMe)(AsMe₃)₂ the composition of the mixture of *cis*- and *trans*-PtC≡CH isomers was displaced in favor of the cis isomer. The *trans*-PtC≡CH isomer was thus found to eliminate HCl more rapidly. In this reaction the CCl=C(H)*Me* resonances were monitored.

Acetylene Formation. As noted previously the formation of acetylene in the reaction between I and HCl (1 equiv) arises from the decomposition of III. In the presence of excess HCl, I reacts to give IV and vinyl chloride. The reaction of III to give IV and acetylene is quite solvent dependent following the order CDCl₃ ∼ CD₂Cl₂ ($t_∞$ = ca. 24 h) > *p*-dioxane-d_8 ∼ C₆H₅NO₂ ($t_∞$ = ca. 6 days) > C₆D₆ ($t_∞$ > 6 weeks) at 20 °C.

During the course of the reaction III → IV + acetylene the only platinum-containing compounds identified by ¹H NMR and infrared spectroscopy were III and IV.

The rate of acetylene formation in benzene-d_6 was monitored by following the appearance of the acetylenic proton resonance, δ 1.98 ppm (relative to TMS), in a manner similar to that described for reactions involving NMe₃ or proton sponge. At least an approximate value for the observed rate of acetylene formation may be obtained in this manner. The formation of acetylene was found to be first order in III. The formation of acetylene-d_2 from III-d_4 was also followed by ¹H NMR spectroscopy. Of course it was not possible to detect acetylene-d_2 directly but the formation of IV could be followed in the phosphine methyl region of the spectrum. A reasonable estimate of $t_{1/2}$, [III] = [IV], can be made in this way. We observed a k_H/k_D ratio of ca. 1.8 for the reaction leading to acetylene. While the error in this ratio is quite large, the ratio is significantly smaller than that found for HCl elimination from III and IV (k_H/k_D = ca. 3).

Significantly when III was dissolved in benzene in the presence of proton sponge (3 equiv), I was formed quantitatively. No acetylene or vinyl chloride was detected in the volatiles and no V was detected in the platinum-containing solids (which consisted of I). (See Table IV for kinetic data.)

Mechanistic Considerations. HCl Elimination. A possible reaction sequence leading to HCl elimination from the

Table IV. Kinetic Data for Acetylene Formation from III and III-d_4

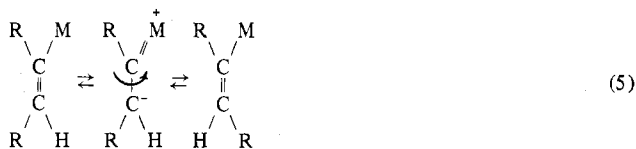| Compd	Temp, °C	Solvent	k_{obsd}, s⁻¹	Correln coeff
III	20	CD₂Cl₂	1.28 (4) × 10⁻⁵	0.996
III-d_4	20	CD₂Cl₂	6.8 (6) × 10⁻⁶	0.986
III	20	C₆D₆	2.19 (5) × 10⁻⁷	0.997
III	40	C₆D₆	4.00 (9) × 10⁻⁶	0.997
III-d_4	40	C₆D₆	2.5 (1) × 10⁻⁶	0.989

Scheme II
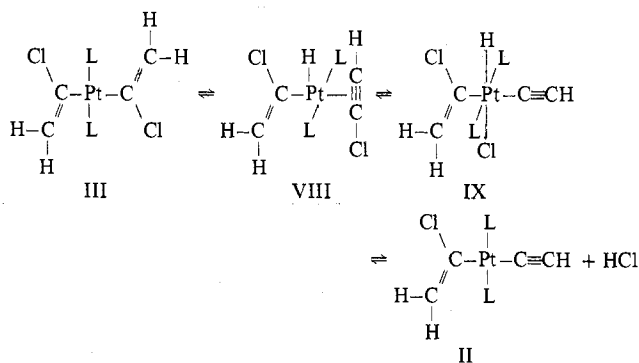
PtCCl=CH₂ moiety is shown in Scheme II for the reaction III → II + HCl. In this scheme β-hydrogen elimination from the α-chlorovinyl ligand gives a hydrido(α-chlorovinyl)(π-chloroacetylene)platinum(II) intermediate, VIII. This intermediate, VIII, then reacts to give a hydrido(chloro)(α-chlorovinyl)(σ-acetylide)platinum(IV) intermediate, IX, which by reductive elimination of HCl yields II. Each of these steps has precedent in organometallic chemistry. (1) β-Hydrogen elimination from a σ-vinyl ligand to generate a metal hydride and an acetylene has been observed directly[21] and is merely the microscopic reverse of metal hydride insertion involving acetylenes. The latter is well documented in the chemistry of hydridoplatinum(II) chemistry.[22] (2) Haloacetylenes have been found to react with zerovalent platinum complexes to give alkynylplatinum(II) derivatives, e.g.,[23] Pt(PPh₃)₄ + PhC≡CBr → *trans*-PtBr(C≡CPh)(PPh₃)₂. To our knowledge, however, such an addition to platinum(II) is not known. (3) Reductive elimination of HCl from Pt(H)₂(Cl)₂(PEt₃)₂ has been observed directly.[24]

Although there are precedents for the individual steps of Scheme II, we believe there are good, if not unequivocal, reasons to reject this reaction sequence.

1. We know of no example where β-hydrogen elimination has been shown to proceed from other than the cis position. In the thermal decomposition of vinyliridium(I) and -rhodium(I) complexes, when a cis β hydrogen was not present acetylene elimination was not observed.[21] Thus in Scheme II cis ⇌ trans isomerization of the vinylic ligand must occur faster than β-hydrogen elimination in order to account for our stereochemical observations concerning HCl elimination from IV-d_1.
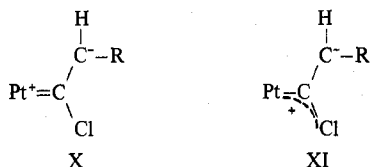
A dipolar isomerization mechanism shown in eq 5 has been

$$
\begin{array}{ccccc}
\underset{\substack{\text{C} \\ \| \\ \text{C} \\ \diagup \diagdown \\ \text{R} \quad \text{H}}}{\overset{\substack{\text{R} \quad \text{M} \\ \diagdown \diagup}}{}} & \rightleftarrows &
\underset{\substack{\text{C}^- \\ \diagup \diagdown \\ \text{R} \quad \text{H}}}{\overset{\substack{\text{R} \quad \overset{+}{\text{M}} \\ \diagdown \| \diagup}}{\text{C}}} & \rightleftarrows &
\underset{\substack{\text{C} \\ \| \\ \text{C} \\ \diagup \diagdown \\ \text{H} \quad \text{R}}}{\overset{\substack{\text{R} \quad \text{M} \\ \diagdown \diagup}}{}}
\end{array}
\qquad (5)
$$

suggested[25,26] to account for the formation of *trans*-MC≡CH products in certain insertion reactions involving metal hydrides and acetylenes RC≡CR.[25-29] Rotation about the C–C double bond is promoted by metal to ligand back-bonding which in turn is favored by electron-rich metal centers and by strongly electron-withdrawing vinylic substituents, e.g., R = COOMe,

Scheme III[a]
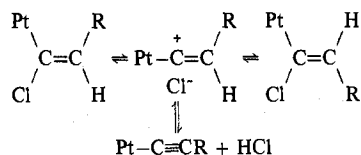
[a] R = H or Me.

CN, and CF_3. For α-chlorovinylplatinum compounds resonance structures X and XI might be considered to allow *cis*-

$\rightleftharpoons$ *trans*-PtC=CH isomerization.

We prefer to discount a dipolar isomerization mechanism, eq 5, involving X or XI, for the following reasons.

(i) The substituents on C_β, R = H, or Me are not electron withdrawing or π accepting.

(ii) The structure of III (Figure 4) reveals a normal $C_\alpha-C_\beta$ bond distance and an abnormally long $C_\alpha-Cl$ bond distance. If X and XI contributed significantly to the bonding in the PtCCl=CH_2 moiety, we would expect the opposite.[30]

Of course none of the above objections rule out the possibility of *cis-* $\rightleftharpoons$ *trans*-PtC=CH isomerization by a dipolar mechanism. However, our observation that elimination of HCl occurs more rapidly from the *trans*-PtC=CH isomer of *trans*-PtCl(CCl=C(H)Me)(AsMe$_3$)$_2$ implies that if Scheme II is operative, then trans β-hydrogen elimination must occur more rapidly than cis β-hydrogen elimination, a notion we find quite unacceptable and totally without precedent.

2. The thermal decomposition of the platinum(II) alkyls *trans*-PtBr(CD$_2$CH$_3$)(PEt$_3$)$_2$,[31] *cis*-Pt(CD$_2$CH$_2$CH$_2$CH$_3$)$_2$-(PPh$_3$)$_2$,[32] and *cis*-Pt(CH$_2$CD$_2$CH$_2$CH$_3$)$_2$(PPh$_3$)$_2$[32] has been shown to proceed via a β-hydrogen elimination mechanism. However, these compounds are quite stable at 20 °C in solution and do not scramble their deuterium labels. The rate of β-hydrogen elimination from the PtCCl=CH_2 moiety would have to be faster than that from the Pt–alkyl moiety. We feel this to be unlikely.[33]

3. Finally we note a number of closely related vinylplatinum(II) compounds can be prepared in one isomeric form. They appear indefinitely stable in solvents such as benzene and dichloromethane at room temperature. However, addition of acids such as HCl readily causes isomerization to a thermodynamic mixture of isomers. A compound of this type is *trans*-PtCl(CCl=C(H)Cl)(PMePh$_2$)$_2$.[34] Therefore these compounds do not (i) eliminate HCl, (ii) isomerize by a dipolar mechanism of the type shown in eq 5, or (iii) undergo isomerization by a reversible cis–trans β-hydrogen elimination sequence.

For these reasons we reject the reaction sequence shown in Scheme II. We propose that elimination of HCl from the PtCCl=CH_2 moiety proceeds via the reaction sequence shown in Scheme III.

$C_\alpha-Cl$ heterolytic bond cleavage to form a tight ion pair may be followed by either elimination of HCl or ion recombination. The latter could yield cis–trans isomerization of the vinylic ligand. We would expect the free platinum vinyl cation PtC$^+$=CH_2 to adopt a linear Pt–C–C ground-state geometry because (i) this is favored by the resonance-stabilized form Pt$^+$=C=CH_2 and (ii) theoretical and experimental evidence suggests that simple organic vinyl cations adopt a linear geometry RC$^+$=CH_2.[35,36] Of course under the influence of solvent and counteranion (nucleophile) the free existence of

such an intermediate is not achieved. In the present situation we are clearly not dealing with a free PtC$^+$=CH_2 entity.

A number of factors are consistent with an E1 mechanism: rate-determining $C_\alpha-Cl$ bond heterolysis. (1) The rate of HCl elimination is very dependent on the solvent and correlates with dielectric constant:[37] C$_6$H$_5$NO$_2$ (34.82) > CD$_2$Cl$_2$ (9.08) > C$_6$H$_6$ (2.27). (2) The rate is dependent on the Pt–X moiety and follows the order PtC≡CH ~ PtCCl=CH_2 > PtCl >> Pt$^+$C(Me)OMe. (3) The long $C_\alpha-Cl$ bond distance and large Pt–$C_\alpha-C_\beta$ angle are suggestive of an unusually weak vinylic C–Cl bond, one that might be particularly labile toward C–Cl bond heterolysis. (4) The kinetics of HCl elimination are zeroth order in amine concentration. (5) The observed preferential cis HCl elimination from the PtCCl=C(H)Me ligand shows that vinyl isomerization by ion recombination must be slower than HCl elimination. In fact we have no evidence that vinyl isomerization by ion recombination or any other mechanism ever occurs. That cis HCl elimination from the PtCCl=C(H)Me moiety occurs preferentially can be attributed to the differing rates of formation of the vinyl cation generated from

$$\begin{array}{c} Me \\ | \\ Pt-C=C-H \\ | \\ Cl \end{array}$$

as opposed to

$$\begin{array}{c} H \\ | \\ Pt-C=C-Me \\ | \\ Cl \end{array}$$
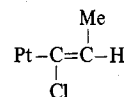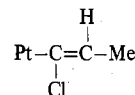
The only experimental piece of data which might appear contrary to the notion that $C_\alpha-Cl$ bond heterolysis is rate determining is an observed isotope effect of ca. 3.0. As isotope effects for organometallic systems are far from well understood, it is not possible to extrapolate with any accuracy from known organic systems for the purpose of rationalizing such effects in organometallic compounds. Analogies drawn from the organic systems mentioned below should be applied with caution.

If $C_\alpha-Cl$ bond breaking were rate determining, this ratio would have to be a secondary isotope effect. Secondary isotope effects are generally quite small. For example, formation of carbonium ions from PhCHBrCH$_3$ and PhCHBrCD$_3$ showed $k_H/k_D = 1.22$.[38] Similarly for C–Cl heterolysis in (CH$_3$)$_3$C–Cl and (CH$_3$)$_2$(CD$_3$)C–Cl k_H/k_D was found to be 1.33.
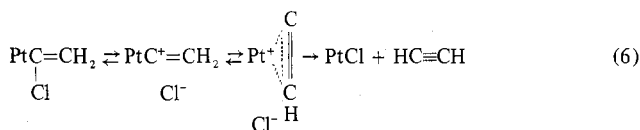
For an E1 or S$_N$1 mechanism we would expect k_H/k_D to be larger in the unsaturated vinylic systems than in saturated (C$_{sp^3}$) systems since (i) in the transition state the C–H bond is ideally positioned for overlap with the developing vacant p orbital and (ii) the C–C bond distance is shorter than in saturated systems and thus closer to the developing vacant p orbital.[36] Typically k_H/k_D = ca. 1.4 has been found for S$_N$1 solvolysis reactions involving vinyl cations generated from Ar(X)C=CHR, where X = halide or CF$_3$SO$_3$ and R = H or Me.[36] Larger k_H/k_D values have been attributed to a small degree of E2 elimination (with solvent acting as base) superimposed on the dominant S$_N$1 mechanism. An E2 mechanism (eq 5) would yield a primary kinetic deuterium isotope effect for which k_H/k_D could range from 2 to 7. In the present case it is difficult to conceive of benzene (but not NMe$_3$ or proton sponge) acting as an effective base. Thus our observed k_H/k_D ratio (ca. 3), difficult to rationalize with the other observations, remains to be accounted for.

Acetylene Formation. A likely route to acetylene formation in the reaction between I and HCl is by reductive elimination (of acetylene) from a hydrido(chloro)platinum(IV) intermediate, such as IX shown in Scheme II. In the decomposition of III to give IV and acetylene, IX could arise either from HCl

Scheme IV

$$II + HCl \xrightarrow{k_1} III$$

$$II + HCl \xrightarrow{k_2} IV + HC{\equiv}CH$$

$$k_1 > k_2$$
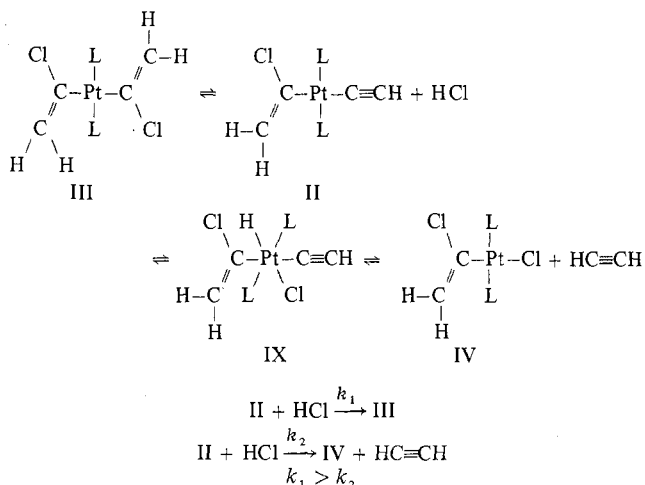
oxidative addition to II (II and HCl being generated by Scheme III) or by the β-hydrogen elimination route shown in Scheme II. An alternative route to acetylene generation is shown in eq 6. This route involves a $\sigma \rightleftarrows \pi$ rearrangement

$$PtC{=}CH_2 \rightleftarrows PtC^+{=}CH_2 \rightleftarrows Pt^+ \overset{C}{\underset{Cl^-}{\Vert}} \rightarrow PtCl + HC{\equiv}CH \qquad (6)$$

of the platinum vinyl cation followed by chloride ion displacement of the π-bonded acetylene. (The π to σ rearrangement involving a hydride shift has been proposed in the formation of alkoxycarbene ligands from π-coordinated acetylenes in alcohol solvents.[1])

Reductive elimination of acetylene from IX formed by the β-hydrogen elimination mechanism, Scheme II, and formation of acetylene according to eq 6 would both compete with HCl elimination from the PtCCl=CH$_2$ moiety. Thus, even in the presence of an HCl trap such as amine, some acetylene formation would always occur. The relative rates of HCl to acetylene elimination from III are ca. 10:1 in benzene-d_6. We believe our observation that III and proton sponge react in benzene to give I in the absence of detectable quantities of V and acetylene is significant. HCl elimination from III must occur before acetylene may be formed. Acetylene formation could arise from the sequence shown in Scheme IV. Kinetically II and HCl preferentially react to give III. This, of course, says nothing about the relative rates of oxidative addition to give IX or reductive elimination from IX (either HCl or acetylene). A similar scheme could apply to the reaction of I and HCl to give II

$$I + HCl \xrightarrow{k_1} II; \quad I + HCl \xrightarrow{k_2} V + HC{\equiv}CH$$
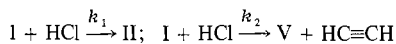
where $k_1 > k_2$.

Comparison with Organic Analogues. The observation that the PtC≡CH moiety readily reacts with anhydrous HCl under mild conditions in solvents such as benzene and dichloromethane clearly indicates the activating influence of platinum(II). Acetylene and HCl do not react under comparable conditions[40] and vinyl chloride is similarly stable with regard to the elimination of HCl. The unreactivity of simple alkylvinyl halides, even in the presence of AgNO$_3$, is diagnostic.[41] This lack of reactivity has been attributed to both the low stability of the vinyl cation and the very strong halogen to carbon bond.[36] The high strength of the vinylic C–X bond compared to C_{sp^3}–X bonds in alkyl halides has been ascribed to a partial double-bond character due to the resonance form, $C^-{-}C{=}X^+$, coupled with increased σ-bond strength due to

differences in carbon hybridization. However over the last decade vinyl cations have become respectable members of the carbonium ion community.[35,36]

The earliest evidence for the intermediacy of vinyl cations came from work by Jacobs and Drenth and their co-workers on the acid-catalyzed hydration of alkynyl ethers[42–46] and alkynyl thioethers.[47–49] The rate-determining step was shown to be protonation to give the vinyl cation RHC=C$^+$—XR, where X = O or S. These vinyl cations are uniquely stabilized in the sense that they have a resonance form in which the positive charge resides on the heteroatom
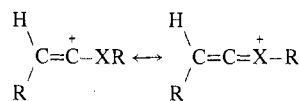
The situation is analogous to the behavior of ordinary carbonium ions generated by solvolysis, where α-halo ethers are some 10^6 times more reactive than unsubstituted halides.[50] One might expect that electron-rich transition metals capable of strong dπ to pπ bonding could also stabilize the electron-deficient α carbon by the similar resonance
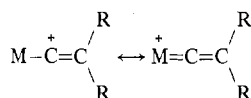
The ability of transition metals to stabilize electron-deficient carbon atoms is well exemplified in the recent work of Schrock[51] and Fischer[52] and their co-workers, who have characterized compounds containing M–CH$_2$ and M–CR moieties. The structural characterization of these compounds reveals a uniquely short M–C bond distance indicating the significant metal–carbon π bonding, M=CH$_2$ and M≡CR. Very recently Nesmeyanov et al. have characterized a compound CpMn(CO)$_2$(C=C(H)Ph), which contains an
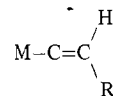
moiety.[53] Early work of King et al. had demonstrated the existence of compounds containing the MC=C(CN)$_2$ moiety.[54] Rather interestingly the latter were generated from reactions involving Cl$_2$C=C(CN)$_2$ and electron-rich metal complexes and the ultimate formation of the MC=C(CN)$_2$ arose from MC(Cl)=C(CN)$_2$ intermediates which in many ways parallel this work.

A compound containing an MC=CR$_2$ moiety has been called a vinylidene–metal complex; cf.[55] transition metal-carbene complexes. If the metal complex carries a positive charge it could be called either a cationic vinylidene complex or metal-stabilized vinyl cation. The distinction is moot and should merely reflect the relative significance of the resonance forms which place the positive charge on the metal or on the α carbon.

In the present work the reactions of the [PtC=CH$_2$]$^+$ moiety closely parallel reactions of vinyl cations. The solvolysis reactions of the PtCCl=CH$_2$ moiety may be compared to studies of Grob[56] on the solvolytic behavior of substituted α-bromostyrenes, p-XC$_6$H$_4$CBr=CH$_2$. The latter where X = NH$_2$, CH$_3$CONH, or CH$_3$O were found to react in 80% aqueous ethanol to give the corresponding acetophenone. The rates were found to be first order in styrene, were found to increase with solvent polarity as well as with addition of Ag$^+$, but were independent of added amine. The rates were very sensitive to the nature of the para X substituent: p-NH$_2$C$_6$H$_4$CBr=CH$_2$ reacted 10^8 times faster than C$_6$H$_5$C-Br=CH$_2$, while p-NO$_2$C$_6$H$_4$CBr=CH$_2$ failed to react even at 190 °C. These observations led Grob to suggest an S_N1 mechanism leading to the vinyl carbonium ion XC$_6$H$_4$C$^+$=

CH_2. Since that time numerous studies on related systems have supported this contention.

The reactions of $PtCCl=CH_2$ have many analogies to those above. For example *trans*-$PtCl(CCl=CH_2)L_2$ reacts with water to give *trans*-$PtCl(C(CH_3)=O)L_2$, where L = PMe_2Ph or $AsMe_3$. *trans*-$PtCl(CCl=CH_2)L_2$ complexes react in alcohols ROH to give *trans*-$[PtCl(C(CH_3)OR)L_2]^+Cl^-$ complexes which in the presence of RO^- give *trans*-$PtCl-(C(OR)=CH_2)L_2$.[1] There is, however, a considerable difference in relative reactivity between the two systems. For the reaction of $C_6H_5CBr=CH_2$ in 80% aqueous ethanol at 100 °C k_{obsd} = 4.2 × 10^{-9} s^{-1}.[56] *trans*-$PtCl(CCl=CH_2)(PMe_2Ph)_2$ reacts apparently instantaneously with methanol or H_2O at room temperature. Indeed even for the elimination of HCl in *benzene* at 25 °C $k_{obsd} \approx 10^{-7}$ s^{-1}. Clearly platinum has a pronounced labilizing influence, as would be expected if the $Pt^+=C=CH_2$ resonance contributed significantly to the stability of the vinyl cation.

Conclusion

Platinum(II) has been shown to promote both addition and elimination of HCl from σ-coordinated ligands, $PtC≡CH + HCl ⇌ PtCCl=CH_2$. This reversible process leads to an intricate sequence in the reaction of *trans*-$Pt(PMe_2Ph)_2$-$(C≡CH)_2$ with HCl (1 equiv) to give *trans*-$PtCl-(PMe_2Ph)_2(C≡CH)$, involving isolable platinum α-chlorovinyl intermediates. Numerous observations concerning the reactivity of the $PtCCl=CH_2$ moiety indicate that it is labile toward C–Cl bond heterolysis in an S_N1 or E1 manner. This results from the ability of platinum to stabilize the vinyl cation, $PtC^+=CH_2$. This stabilization is far greater than that observed for simple organic analogues, e.g., α-halostyrenes, and thus results in enhanced reactivity of the vinylic C–X bond.

Experimental Section

General Information. Proton magnetic resonance (^1H NMR) spectra were obtained on a Varian A-60A spectrometer. Infrared measurements were taken on either a Perkin-Elmer 257 or a Beckman IR-12 spectrometer. Gas mass spectra were obtained on a Consolidated Engineering Corp. mass spectrometer, Model 21-620. NMR solvents (dried over molecular sieves) were from Aldrich; DCl was from Merck Sharp and Dohme. Analysis was performed by Atlantic Microlab, Inc., Atlanta, Ga.

The preparations of I–V and their deuterated analogues were reported in the previous paper.[1]

I + HCl. On a calibrated vacuum manifold dry HCl (0.08 mmol) was condensed into each of two evacuated NMR tubes containing a frozen (liquid N_2) mixture of I (40 mg) and CDCl$_3$ (0.4 ml). Tubes were sealed by torch and allowed to warm to room temperature. After 5 min, the ^1H NMR spectrum indicated formation of a mixture of I–II–III in the concentration ratio 1:2:1, respectively. This was apparent from the PMe_2Ph resonances (Table I).

t = **5 min.** At this time one tube was quenched in liquid N_2. Subsequently volatiles were collected and sealed in an empty NMR tube via the vacuum manifold. Inspection by ^1H NMR disclosed only a trace (<5% based on added HCl) of acetylene ($\delta \sim 1.8$) and no vinyl chloride ($\delta \sim 5.5, 6.3$). Inspection of the platinum-containing solids by IR (Nujol mull) indicated I ($\nu(C≡CH)$ 1968 cm^{-1}, $\nu(C—H)$ 3278 cm^{-1}), II ($\nu(C≡C—H)$ 3288 cm^{-1}), and III ($\nu(C=C)$ 1565 cm^{-1}) but no apparent V ($\nu(C≡CH)$ 1987 cm^{-1}).

t = ∞ **(24 h).** The second tube was allowed to react for 24 h during which time the ^1H NMR spectra indicated the appearance of C_2H_2 and IV, with the concomitant disappearance of the 1:2:1 distribution of I, II, and III. After this time the reaction was quenched (liquid N_2) and the volatiles transferred and sealed in another NMR tube. Inspection by ^1H NMR indicated C_2H_2 in almost 50% yield based on I (as measured by integration with respect to an internal TMS standard) and only a trace of vinyl chloride (<5%). Infrared examination of the Pt-containing solids indicated I ($\nu(C≡C)$ 1968 cm^{-1}) and a vinyl stretch ($\nu(C=C)$ 1565 cm^{-1}) but no II ($\nu(C≡C)$ 1973 cm^{-1}). Similar results were obtained with CD_2Cl_2.

I + III in CD_2Cl_2. Equimolar amounts of I (19 mg) and III (22 mg) were dissolved in CD_2Cl_2 in an NMR tube. After 5 min at 40

°C, the ^1H NMR spectrum showed a 1:2:1 mixture of I, II, and III respectively, identical with that observed for I + HCl, *t* = 5 min.

I + III-d_4 in CD_2Cl_2. The ^1H NMR spectrum of the reaction between I and III-d_4 showed the appearance of vinyl resonances ($\delta \sim 4.8$ and 5.8) and the diminution of the acetylide H ($\delta \sim 2.1$) to about one-third its original peak height. After 5 min no further change was observed. After 15 min solvent was removed by vacuum and the Pt-containing solids were examined by IR spectroscopy. Deuterated I ($\nu(C≡CD)$ 1852 cm^{-1}, $\nu(C—D)$ 2542 cm^{-1}) and protonated vinyl absorptions ($\nu(C=CH_2)$ 1565) were clearly evident.

III + HCl in $CDCl_3$. Dry HCl (0.06 mmol) was condensed and sealed in an NMR tube containing III (35 mg) and $CDCl_3$ using the vacuum-manifold technique previously described. Upon warming to room temperature the ^1H NMR indicated almost quantitative formation of IV and vinyl chloride.

III + 5HCl in $CDCl_3$. A fivefold excess of HCl (0.35 mmol) was similarly sealed with III (35 mg) in $CDCl_3$. Although vinyl chloride was again formed upon warming to room temperature, IV was apparently stable to HCl as no *cis*-PtL_2Cl_2 was observed (no phosphine methyl doublets). After 30 min the solvent was removed under vacuum and the solids, redissolved in $CDCl_3$, were identified as pure IV.

I + HCl in C_6D_6. Similar reactions of HCl (0.06 mmol) with III (35 mg) in benzene-d_6 and toluene-d_8 resulted initially in 1:1 mixtures of I and III, identified by their ^1H NMR spectra. Over a period of approximately 24 h these mixtures reacted to form the I–II–III mixture (concentration ratio ca. 1:2:1). Further reaction to give IV and acetylene was monitored by NMR spectroscopy. This was a slow reaction requiring >4 weeks at 25 °C.

III-d_4 + HCl in Toluene-d_8. Reaction of HCl (0.05 mmol) with III-d_4 (30 mg) in toluene-d_8 (NMR tube) indicated rapid vinylic H/D scrambling as noted by the appearance of broadened vinyl resonances with no alteration of the phosphine methyl signal. The formation of vinyl chloride was observed to occur slowly (~ 1 h) with concomitant formation of IV.

III + III-d_4 (+Δ) → acetylene + IV. Equimolar amounts of III (45 mg) and III-d_4 (45 mg) in a vessel connected to an evacuated vacuum manifold were heated (oil bath) to 150 °C for 0.5 h. The gas evolved, acetylene with a trace of air, was analyzed by mass spectroscopy for deuterium content. A distribution of C_2H_2, C_2HD, and C_2D_2 (4:3:1) was observed indicating intermolecular HCl transfer occurs in the melt. The variance of this distribution from that statistically anticipated (1:2:1 or 1:0:1, depending on decomposition mechanism) may be due to incomplete deuteration in III-d_4. A sample of III-d_4 was pyrolyzed under the same conditions and the analyzed acetylene-d_0, -d_1, and -d_2 were in the ratio 1:4:5. As no exchange of acetylene, once formed, is observed, the large amount of C_2HD relative to C_2D_2 in the decomposition of III + III-d_4 must be rationalized through an HCl-exchange process.

III + III-d_4 (in $CDCl_3$) → IV + acetylene. A mixture of III (50 mg) and III-d_4 (50 mg) was allowed to react in $CDCl_3$ for 24 h. The mass spectrum of the gas evolved showed an acetylene distribution similar to that observed above (pyrolysis).

III + AgPF$_6$/MeOH → $[H_2C=ClCPt(L)_2C(Me)OMe]^+PF_6^-$. III (148 mg) was dissolved in methanol (5 ml). One equivalent of AgPF$_6$ (63 mg) dissolved in methanol (1 ml) was added. The AgCl precipitate was removed by centrifugation. The volume of the solution was reduced to ca. 2 ml on a rotary evaporator and CH_2Cl_2 (2 ml) was added. A small amount of diethyl ether was added dropwise until the originally clear solution became slightly cloudy. Cooling (5 °C) for 12 h yielded 140 mg of yellow crystals (77%), mp 117–118 °C. Anal. Calcd: C, 34.26; H, 4.07; halide, 4.82. Found: C, 34.13; H, 4.10; halide, 4.73.

III + NH_3/CD_2Cl_2. One equivalent of ammonia (0.05 mmol) was condensed and sealed in an evacuated NMR tube containing a frozen mixture of III (30 mg) and CD_2Cl_2 (0.4 ml). After ~ 5 min at 40 °C, the ^1H NMR exhibited the I:II:III distribution of ca. 1:2:1 seen in the reaction of I + HCl in CD_2Cl_2.

Similar reaction with 2 equiv of ammonia led to quantitative formation of I as identified by NMR and by IR ($\nu(C≡CH)$ 1968 cm^{-1}).

IV + NH_3 in CD_2Cl_2. Similar reaction of 1 equiv of ammonia (0.07 mmol) with IV (40 mg) in CD_2Cl_2 led to quantitative formation of V as verified by IR ($\nu(C≡CH)$ 1987 cm^{-1}).

III + NR_3 as a Function of Solvent. Proton sponge (11 mg, 1 equiv) was added to and sealed in a series of NMR tubes containing III (30 mg) and the solvents (0.4 ml) $C_6H_5NO_2$, $CDCl_3$, CD_2Cl_2, C_6D_6, and

CCl$_4$. Reaction was monitored by ^{1}H NMR by the disappearance of the amine methyl groups as a function of time. Approximate reaction times (t_∞) are as follows: C$_6$H$_5$NO$_2$, ~5 min; CDCl$_3$ and CD$_2$Cl$_2$, ~30 min; C$_6$D$_6$ and CCl$_4$, >24 h.

III + NR$_3$ in C$_6$D$_6$: Kinetic Studies. The reaction of III with trimethylamine was monitored by ^{1}H NMR via the disappearance of the amine methyl resonance as a function of time. As this signal is sharp and well separated from others (δ ~3.1) in the spectrum the assumption that peak height is proportional to amine concentration is justifiable. An internal standard (TMS) was used to correct for variations in instrument performance. A plot of ln [A/S] vs. time, where A = amine peak height and S = TMS standard peak height, yielded a linear relationship indicating first-order dependence on III. In a similar fashion data were collected for III-d_4 and IV.

Samples were prepared by condensing trimethylamine into evacuated frozen mixtures of III (~30 mg) in C$_6$D$_6$ (0.3 ml) via a calibrated vacuum manifold as previously described. These samples, sealed by torch, were kept at 20 (±0.2) °C in a constant-temperature bath. The NMR spectrometer probe temperature was cooled to 20 °C for each measurement. Probe temperature, checked by the methanol methyl–hydroxyl separation (96 Hz/20 °C), was monitored prior to and after each set of measurements. As the reaction proceeded, insoluble ammonium salts precipitated from the benzene solution. Sample tubes were centrifuged prior to measurement.

Data were subjected to linear least-squares analysis and correlation coefficients calculated. Reactions were typically monitored for more than 2 half-lives. A sample of data is given as follows for the reaction IV + NMe$_3$ in C$_6$D$_6$: time in s $\times$ 10^{-5} (relative peak height/standard peak height): 0.0054 (24.25), 0.126 (23.14), 0.616 (21.43), 1.03 (18.5), 1.47 (16.4), 1.93 (14.38), 2.30 (13.97), 2.80 (12.86), 3.20 (11.3), 3.54 (10.63), 4.10 (10.06), 5.00 (8.00), 5.86 (6.55), 7.06 (5.86), 7.84 (3.91), 8.64 (3.97), 10.7 (2.20), 12.0 (1.66).

III + PS (Proton Sponge) in C$_6$D$_6$: Kinetics. A similar procedure to that described above was used for the reactions of III, III-d_4, IV, and IV-d_2 with proton sponge. As this base is a stable solid at room temperature, standard solutions in C$_6$D$_6$ were readily prepared (108 mg/3 ml). This method has several advantages over trimethylamine. First, dilution improves accuracy. Second, complete transfer of base into the NMR tube is ensured. Third, proton sponge (four methyl groups) has a stronger methyl resonance per mole than trimethylamine. Base concentrations were varied by a factor of 3 with no significant effect on reaction rate.

III + 3PS in C$_6$D$_6$. The plot of ln [A/S] vs. t remained linear beyond the point at which one proton sponge had been consumed. Therefore II must be reacting to produce HCl at very nearly (within experimental error) the same rate as III.

Synthesis of trans-[PtCl(AsMe$_3$)$_2$(CCl=CHCH$_3$)]. Dry HCl (4 mmol) was condensed from a calibrated vacuum manifold into an evacuated flask (50 ml) containing a frozen mixture of trans-[Pt-(AsMe$_3$)$_2$(C≡CCH$_3$)$_2$] (500 mg) and benzene (10 ml). The solution was allowed to warm to room temperature and stand for 1 h. Volume was reduced by vacuum to 5 ml and the concentrate was passed through a short Florisil column to remove polymerization products. It was subsequently pumped to dryness under vacuum to yield a yellowish semicrystalline product (400 mg, 75%), mp 82 °C. ^{1}H NMR indicated a trans-PtC=CH to cis-PtC=CH ratio of 2:1 as the equilibrium mixture of the isomeric vinyls. Stereochemical assignment was based on the vinyl protons (trans-PtC=CH, δ 6.27, $^3J_{Pt-H}$ = 85 Hz; cis-PtC=CH, δ 5.46). Isomeric ratios were verified by the ratio of vinylic methyl doublets (trans-PtC=CCH$_3$, δ 1.70; cis-PtC=CCH$_3$, δ 1.85, $^3J_{H-H}$ = 7 Hz).

Formation of a 5:1 Trans–Cis PtC=CH Mixture. Extraction of the equilibrium mixture above with pentane (≈5 ml) yielded a solution enriched in the trans-PtC=CH isomer (~5:1). This nonequilibrium mixture is stable in the solid state.

IV + DCl. Dry DCl (0.1 mmol) was condensed into an evacuated NMR tube containing a frozen mixture of V (50 mg) in CDCl$_3$. Upon warming, the ^{1}H NMR spectrum of the product indicated a pure compound (single set of phosphine methyl resonances) but an H/D mixture in the vinylic resonances (integration of the vinylic protons indicated ca. one proton as expected). A similar mixture may be obtained by the reaction of IV with 2 DCl in CDCl$_3$. IV is stable with respect to loss of vinyl chloride and thus DCl serves to scramble the vinylic protons.

IV–H/D + NR$_3$ in C$_6$D$_6$. Trimethylamine (0.07 mmol) was condensed into an evacuated NMR tube containing a frozen mixture

of IV–H/D (40 mg) and CDCl$_3$ (0.4 ml). After warming to room temperature the reaction was monitored by ^{1}H NMR spectroscopy over a period of 4 days. A progressive decrease of both vinylic resonances was noted but no preferential loss was observed. This reaction was later duplicated with IV–H/D (49 mg) and proton sponge (25 mg) with similar results.

ClPt(AsMe$_3$)$_2$CCl=CHCH$_3$ cis- ⇌ trans-PtC=CH Isomerization in C$_6$D$_6$. The isomerization of the trans-PtC=CH-enriched vinyl mixture (35 mg) was monitored by ^{1}H NMR in C$_6$D$_6$ (0.4 ml) at 20 °C. Temperature was maintained by a constant-temperature bath. As observed fron the vinyl methyl doublets, the mixture returned to the 2:1 (trans:cis) equilibrium over a period of 3 h during which time spectra were recorded every 20 min.

trans-PtC=CH-Enriched PtCl(AsMe$_3$)$_2$(CCl=C(H)CH$_3$) + 3PS in C$_6$D$_6$. In a similar reaction to the above the enriched vinyl mixture (35 mg) was treated with 3 equiv of proton sponge (40 mg) in C$_6$D$_6$ (0.4 ml) and monitored by ^{1}H NMR at 20 °C. In the presence of base, slow disappearance of the trans-PtC=CH isomer was observed. However no resulting increase in the cis isomer was apparent. This reaction was monitored every 12 h for 5 days, during which time the trans:cis ratio decreased to a value of 3:1.

PtCl(AsMe$_3$)$_2$(CCl=CHCH$_3$) + PS. A sample of the equilibrium mixture (35 mg) was treated with proton sponge (40 mg, 3.5 equiv) in C$_6$D$_6$ (0.4 ml) and the reaction was monitored by ^{1}H NMR. To increase the rate of reaction the temperature was maintained at 35 °C. Over a period of 36 h the ratio of vinylic methyl doublets decreased from the original 2:1 to less than 1:1 indicating marked displacement from the equilibrium mixture of trans- to cis-PtC=CH isomers.

III → IV + C$_2$H$_2$ Kinetics. The kinetics of the decomposition of III in CD$_2$Cl$_2$ and C$_6$D$_6$ to yield IV and acetylene were monitored by ^{1}H NMR. Reaction progress was monitored by the appearance of the acetylene singlet (δ ~1.8). Similar to the previously described kinetics procedure acetylene concentration was assumed to be proportional to peak height as corrected by an internal TMS standard. High concentration values (t approaching ∞) were discarded as slow acetylene polymerization was observed under these conditions. III-d_4 could not be monitored in this manner due to unobservable C$_2$D$_2$. In this case a comparison of phosphine methyl resonances (δ 1.84, 1.86) and their ^{195}Pt satellites (III vs. IV) gave an assessment of reaction progress. Also by this method, $t_{1/2}$ is readily apparent yielding an alternate measurement of reaction rate. Data were subjected to linear least-squares analysis. Rates and correlation coefficients are listed in Table IV.

III → IV + C$_2$H$_2$ in Various Solvents. To qualitatively assess the effects of solvent on these reactions, samples of III (30 mg) were sealed in NMR tubes with the appropriate solvent (0.3 ml) and monitored by ^{1}H NMR. Values for t_∞ varied from 24 h for CDCl$_3$ and CD$_2$Cl$_2$ to approximately 6 days for p-dioxane-d_8 and C$_6$H$_5$NO$_2$ to greater than 6 weeks for C$_6$D$_6$ at 20 °C.

III + PS in C$_6$D$_6$ (65 °C). III (35 mg) was treated with 3 equiv of proton sponge (40 mg) in C$_6$D$_6$ (0.4 ml) sealed in an NMR tube. To hasten reaction completion, the tube was kept at 65 °C. After 6 h the NMR indicated only the presence of I and precipitated ammonium salts were evident. After 12 h the volatiles were transferred and sealed in a second NMR tube via the vacuum manifold. The ^{1}H NMR spectrum showed no indication of acetylene or vinyl chloride. The Pt-containing solids, examined by IR, showed only the presence of I (ν(C≡C) 1968 cm^{-1}) with no apparent V (ν(C≡C) 1987 cm^{-1}).

Registry No. I, 60314-10-5; I-d_2, 61426-25-3; II, 60293-83-6; II-d_3, 61426-26-4; III, 60293-84-7; III-d_4, 61426-27-5; IV, 60293-85-8; IV-d_2, 61426-28-6; V, 60293-86-9; V-d_1, 61426-29-7; trans-[Pt(CCl=CH$_2$)(C(CD$_3$)OMe)(PMe$_2$Ph)$_2$]PF$_6$, 61426-31-1; [H$_2$C=ClCPt-(PMe$_2$Ph)$_2$C(Me)OMe]PF$_6$, 61055-92-3; trans-[PtCl(AsMe$_3$)$_2$-(CCl=CHCH$_3$)], 61394-75-0.

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