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Reactions of Alkynyl- and Alkenylplatinum(II) Compounds. 3. Reactions of α-Chlorovinylplatinum(II) Compounds with Protic Acids

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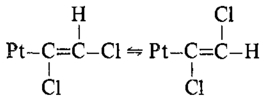
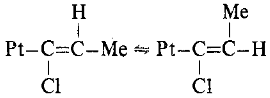
trans-PtCl(CCl═C(H)Cl)L_2, Ia, where L = $PMePh_2$, reacts with acids HX to give an equilibrium mixture of vinylic isomers



$$\mathrm{Pt-\underset{Cl}{C}=\overset{H}{C}-Cl \rightleftharpoons Pt-\underset{Cl}{C}=\overset{Cl}{C}-H}$$

Ia Ib

The rate of isomerization is a function of X, $X^- = SO_3F^- \cdot SbF_5 > PF_6^- > Cl^- > CF_3COO^- >> CH_3COO^-$, for which isomerization does not occur. Isomerization occurs much faster in CD_2Cl_2 than in benzene. Reaction of Ia with DCl results in H/D exchange at the β-carbon atom at a rate which is faster than apparent isomerization. A similar vinylic isomerization occurs for *trans*-PtCl(CCl═CHMe)$(AsMe_3)_2$, II, in the presence of HCl

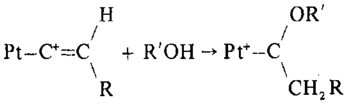


$$\mathrm{Pt-\underset{Cl}{C}=\overset{H}{C}-Me \rightleftharpoons Pt-\underset{Cl}{C}=\overset{Me}{C}-H}$$

trans-PtCl(CCl═CH_2)$(PMe_2Ph)_2$, III, reacts reversibly and rapidly (on the ^1H NMR time scale) with HCl at the vinylic moiety. In contrast, addition of HCl to *trans*-PtCl(CH═C(H)Cl)$(PMePh_2)_2$ results in rapid and quantitative formation of *cis*-PtL_2Cl_2 and vinyl chloride. The stability of the α-chlorovinyl ligand toward cleavage by protic acids and their acid-catalyzed isomerization reactions are rationalized in terms of the generation of the $PtC^+(Cl)R$ moiety, which may be viewed as a stabilized carbonium ion or as a cationic platinum–chlorocarbene intermediate.

Introduction

Prior to this work we have suggested[1-3] that a number of reactions occurring within the coordination sphere of platinum(II) may be interpreted in terms of a carbonium ion model. For example, platinum(II)-stabilized vinyl cations, PtC^+═CHR, formed from the reactions of (i) cationic π-acetylenic platinum(II) intermediates, (ii) protonation of platinum(II) acetylides, and (iii) solvolysis reactions of α-chlorovinylplatinum compounds are the proposed intermediates in the formation of cationic alkoxycarbene complexes[4]



$$\mathrm{Pt-C^{+}{=}C{\begin{smallmatrix}H\\R\end{smallmatrix}} + R'OH \rightarrow Pt^{+}-C{\begin{smallmatrix}OR'\\CH_2R\end{smallmatrix}}}$$

In the reaction between *trans*-Pt(C≡CH)$_2(PMe_2Ph)_2$ and HCl (1 equiv) in inert solvents such as dichloromethane we found that the formation of *trans*-PtCl(C≡CH)$(PMe_2Ph)_2$ is preceded by a sequence of reactions involving the reversible addition of HCl to the acetylenic triple bond[5]

$$\mathrm{Pt-C{\equiv}CH + HCl \rightleftarrows Pt-CCl{=}CH_2}$$

Detailed studies of this reaction,[6] the structural parameters of *trans*-Pt(CCl═CH_2)$_2(PMe_2Ph)_2$, and its reaction with MeOD to give the *trans*-Pt(CCl═CH_2)(C(CD_3)OMe)-$(PMe_2Ph)_2^+$ cation[6,7] all pointed to the significance of the Pt—C^+═CH_2 moiety.

Electron-deficient carbon atoms directly bonded to a transition metal (C–M σ) may be stabilized by metal-to-carbon π bonding. The recent structural characterizations of compounds containing carbene, CH_2,[8] vinylidene, C═CHR,[9] and carbyne, CR,[10] ligands bonded directly to the metal provide unequivocal evidence for metal dp to carbon p π bonding. Thus we believe that there should be an extensive class of organometallic reactions involving reactive intermediates which may be described as metal-stabilized carbonium ions.[11] Further to this open-ended view, we describe a number of reactions of α-chlorovinylplatinum(II) compounds with protic acids, HX. We suggest that these reactions are members of this class of organometallic reactions.

Results and Discussion

Stereochemistry of Alkenylplatinum(II) Compounds. Central to the discussion of acid-promoted reactions of alkenylplatinum(II) compounds is the stereochemistry of the compounds themselves. For compounds of the type PtX(alkenyl)L_2, where L = PMe_3, PMe_2Ph, or $PMePh_2$, the stereochemistry about the metal may generally be deduced from the appearance of the phosphine methyl proton resonances. Mutually trans phosphine methyl protons appear as 1:2:1 triplets due to the virtual coupling (^2J + $^4J_{PH}$) while cis phosphine methyls appear as 1:1 doublets.[12] Application of this observation, originally noted by King[13] and Shaw,[14] is now common in the stereochemical assignment of square-planar complexes of the type $MXYL_2$, where L = tertiary phosphine ligand, $PMeR_2$. (The appearance of 1:1 doublets or 1:2:1 triplets is, of course, a limiting situation.[12]) In addition, a plane of symmetry, either real or apparent, containing the MP_2 plane may be probed by the use of ligands such as PMe_2Ph or $AsMe_2Ph$.[15]

In addition a number of criteria for stereochemical assignments about the vinylic ligand are generally accepted, although not conclusively established.[16]

From organic chemistry the magnitude of J_{HH} coupling constants in vinylic compounds is generally found to follow the order[17,18] trans > cis > geminal. Further for platinum–alkenyl compounds like PtX(alkenyl)L_2, where L = PR_3, (1) the magnitude of J_{PH} is larger to the α-vinylic proton than to the β-vinylic protons, (2) vinylic proton chemical shifts are usually further downfield for *trans*-PtC═CH hydrogens than for *cis*-PtC═CH hydrogens, and (3) the magnitude of $^3J_{^{195}PtH}$ (*trans*-PtC═CH) is approximately twice as large as that of $^3J_{^{195}PtH}$ (*cis*-PtC═CH); both are larger than $^2J_{^{195}PtH}$ (*gem*-PtCH═C). The ^1H NMR data for the compound *trans*-PtBr(CH═CH_2)$(PPh_3)_2$ well exemplifies the assignments for the $PtCH^1$═$C(H^3)H^2$ moiety:[19] $\delta(H^1)$ 6.25, $^2J_{PtH} = 8.0$, $J_{H^1H^2} = 10.2$, $J_{H^1H^3} = 17.75$; $\delta(H^2) = 5.21$, $J_{PtH} = 148$, $J_{H^1H^2} = 10.2$, $J_{H^2H^3} = 1.4$; $\delta(H^3)$ 4.26, $J_{PtH} = 78$, $J_{H^1H^3} = 17.5$, $J_{H^2H^3} = 1.4$ (δ in ppm relative to TMS, J in Hz).

***trans*-PtCl(CCl═CHCl)$(PMePh_2)_2$.** In 1974, Lewis and co-workers[20] reported the synthesis and properties of a number

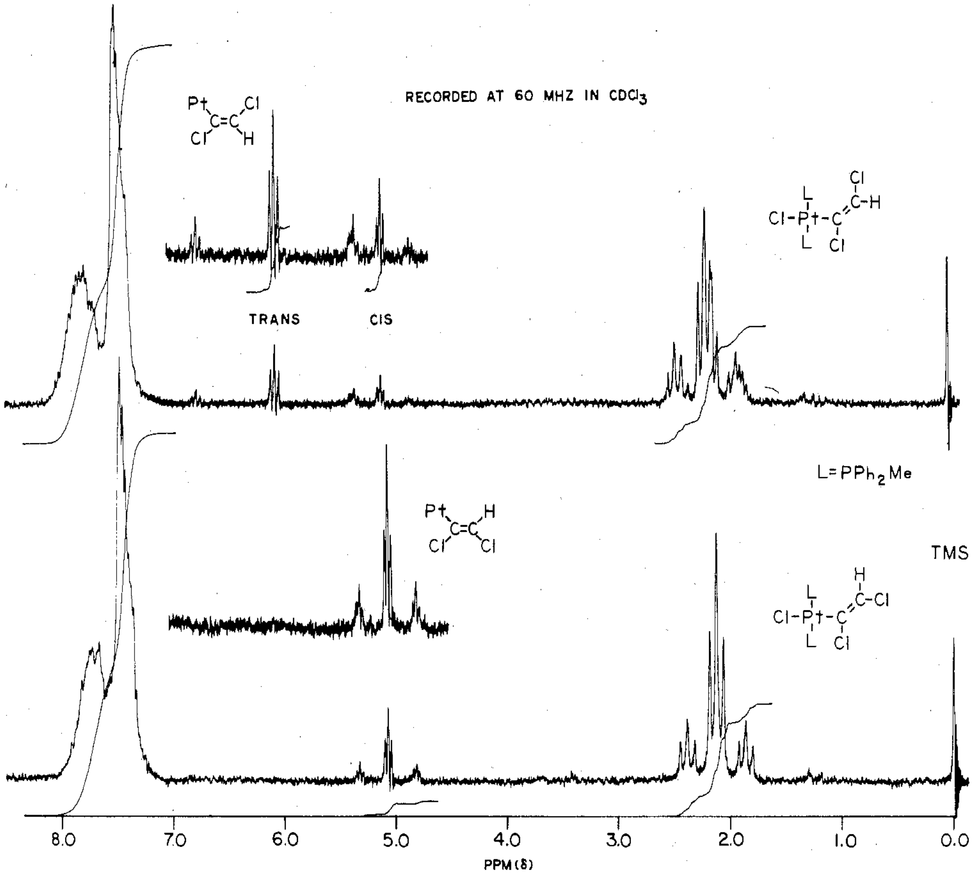
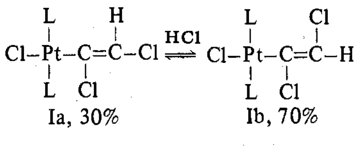


Figure 1. ^{1}H NMR spectra recorded in $CDCl_3$ (35 °C) at 60 MHz: bottom, *trans*-$PtCl(CCl{=}C(H)Cl)(PMe_2Ph)_2$, Ia; top, equilibrium mixture of Ia and *trans*-$PtCl(CCl{=}C(Cl)H)(PMe_2Ph)_2$, Ib.

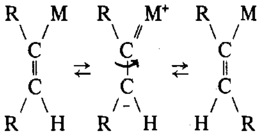
of platinum(II) and palladium(II) vinylic complexes. The reaction of zerovalent metal complexes ML_4, where M = Pd or Pt and L = $PMePh_2$, with the chlorinated olefins tetrachloroethylene, trichloroethylene, and *trans*-1,2-dichloroethylene yielded *trans*-$MCl(vinyl)L_2$ compounds.[20] (Previously oxidative addition of vinyl halides to zerovalent platinum compounds had also been noted.[21,22]) Lewis et al.[20] noted that the reaction between trichloroethylene and PtL_4 led to the stereospecific formation of *trans*-$PtCl(CCl{=}CHCl)(PMePh_2)_2$, Ia, which in the presence of HCl isomerized to a mixture of Ia (ca. 30%) and Ib (ca. 70%) according to eq 1. Assignment of the stereochemistries of Ia and Ib follows



$$\mathrm{Cl{-}\overset{L}{\underset{L}{Pt}}{-}\underset{Cl}{C}{=}\overset{H}{C}{-}Cl} \overset{HCl}{\rightleftharpoons} \mathrm{Cl{-}\overset{L}{\underset{L}{Pt}}{-}\underset{Cl}{C}{=}\overset{Cl}{C}{-}H} \qquad (1)$$

Ia, 30% Ib, 70%

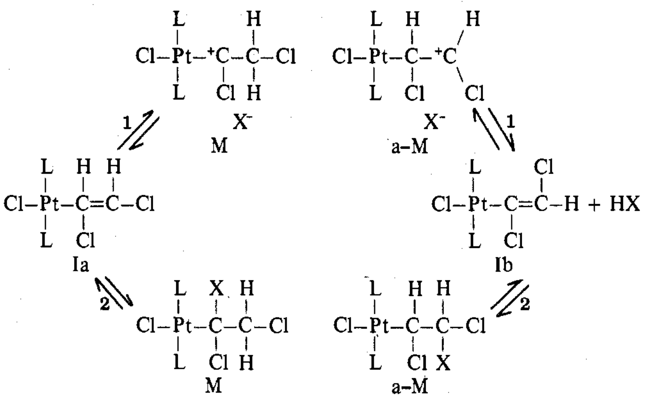
from the criteria mentioned above: *cis*-$PtC{=}CH$, δ 5.0, J_{PtH} = 31 Hz; *trans*-$PtC{=}CH$, δ 6.0, J_{PtH} = 84 Hz. We have confirmed these observations: see Figure 1. The reaction between $Pt(PMePh_2)_4$ and trichloroethylene is stereospecific in yielding Ia which appears indefinitely stable in solvents such as $CDCl_3$ and CD_2Cl_2. This observation coupled with the knowledge that Ib is the thermodynamically favored isomer precludes isomerization by a mechanism involving charge separation of the type shown in eq 2 which has been



$$\begin{array}{c} R\quad M \\ C \\ \| \\ C \\ R\quad H \end{array} \rightleftarrows \begin{array}{c} R\quad M^+ \\ C \\ | \\ C^- \\ R\quad H \end{array} \rightleftarrows \begin{array}{c} R\quad M \\ C \\ \| \\ C \\ H\quad R \end{array} \qquad (2)$$

suggested[23,24] for certain metal–alkenyl complexes containing electron-withdrawing substituents, e.g., R = CF_3, COOMe, CN, and electron-rich metals. Moreover it shows that elimination of HCl from the $PtCCl{=}CHCl$ ligand cannot occur to any significant extent; cf.[5,6] HCl elimination from the $PtCCl{=}CH_2$ ligand in the compounds *trans*-$Pt(CCl{=}CH_2)_2(PMe_2Ph)_2$ and *trans*-$PtCl(CCl{=}CH_2)(PMe_2Ph)_2$.

Scheme I[a]



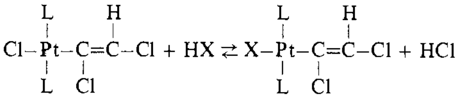
[a] M = Markownikov; a-M = anti-Markownikov.

The isomerization reaction 1 could occur by a carbonium ion mechanism, involving protonation–deprotonation of the vinyl ligand, or by a reversible addition–elimination sequence involving a reactive $Pt{-}C_2Cl_3H_2$ moiety. Moreover reaction could occur in either a Markownikov or anti-Markownikov manner. These possibilities are shown in Scheme I. Rotation about the carbon–carbon single bond produced by either protonation or addition would allow for the isomerization Ia ⇄ Ib.

In order to distinguish between Markownikov and anti-Markownikov reactions we reacted Ia with DCl (1 equiv). If an anti-Markownikov reaction occurred, either protonation or addition, then isomerization would occur prior to H/D exchange of vinyl hydrogens. Indeed the vinylic hydrogens of Ia and Ib would never be exchanged with deuteriums if an anti-Markownikov reaction was exclusive. Experimentally we observed that H/D exchange occurred at a faster rate than apparent isomerization. (We could not, of course, detect the formation of the PtCCl═CDCl ligand by ^{1}H NMR spectroscopy directly.) Specifically we observed diminution of the vinylic proton resonances of Ia followed by the appearance of the downfield vinylic proton resonances of Ib which increased in signal intensity until the thermodynamic equilibrium (eq 1) was attained. Integration of the t_∞ spectrum of the mixture of Ia and Ib obtained in this reaction indicated the presence of approximately a 0.5 proton equiv for the vinyl hydrogens relative to the phosphine methyl hydrogens. We conclude that the reaction between Ia and HCl occurs predominantly, if not exclusively, in a Markownikov manner.

In an attempt to distinguish between a carbonium ion mechanism and the addition–elimination sequence, routes 1 and 2, respectively, in Scheme I, Ia was reacted with each of the following acids: magic acid ($HSO_3F{\cdot}SbF_5$), hexafluorophosphoric acid (HPF_6), trifluoroacetic acid, and acetic acid. With the exception of acetic acid case, isomerization was observed.

There is the possibility that acids HX could react with Ia to generate HCl according to an equilibrium reaction of type 3. Equilibrium 3 could be achieved by a reversible oxidative



$$\mathrm{Cl{-}\overset{L}{\underset{L}{Pt}}{-}\underset{Cl}{C}{=}\overset{H}{C}{-}Cl + HX \rightleftarrows X{-}\overset{L}{\underset{L}{Pt}}{-}\underset{Cl}{C}{=}\overset{H}{C}{-}Cl + HCl}$$

(3)

addition–reductive elimination sequence of the type demonstrated in the reaction between *trans*-$PtH(Cl)(PEt_3)_2$ and HCl.[25] If this were the case, then the isomerization reaction induced by HPF_6 and $HSO_3F{\cdot}SbF_5$ would actually proceed by HCl catalysis. However, a comparison of the rates of isomerization of Ia in the presence of HCl and an equivalent amount of magic acid discounts this possibility. The rate of isomerization induced by magic acid was at least 3 orders of magnitude greater than that for HCl.

We also noted that the rate of isomerization was highly solvent dependent. Equivalent amounts of HCl isomerized Ia over 100 times faster in CD_2Cl_2 than in benzene-d_6.

The observation that the acids HX, where X^- is noncoordinating (PF_6^- and $SO_3F{\cdot}SbF_5^-$), can induce the isomerization reaction 1 at rates faster than that for HCl supports Markownikov protonation to give *trans*-$PtCl(^+CCl{-}CH_2Cl)L_2$, shown in Scheme I. HCl-induced isomerization may also occur in this manner but we cannot rule out a Markownikov addition–elimination sequence.

Although magic acid very rapidly isomerizes Ia to the 30:70 mixture of Ia–Ib respectively, a further slow reaction occurs yielding *cis*-1,2-dichloroethylene and an uncharacterized platinum compound (quite probably $[Pt_2L_2Cl_2]^{2+}(SO_3F{\cdot}SbF_5^-)_2$). It is interesting that only *cis*-1,2-dichloroethylene is liberated from the thermodynamic mixture of Ia and Ib. *cis*- rather than *trans*-1,2-dichloroethylene is the thermodynamically favored olefin, but by only 0.45 kcal mol^{-1}.[26] Isomerization of the free olefin does not occur subsequent to its formation since we found *trans*-1,2-dichloroethylene to be stable with respect to isomerization by magic acid under the reaction conditions.

***trans*-PtCl(CCl═CHMe)(AsMe$_3$)$_2$.** The reaction of *trans*-$PtCl(C{\equiv}CMe)(AsMe_3)_2$ with HCl ($\geq$1 equiv) or *trans*-$Pt(C{\equiv}CMe)_2(AsMe_3)_2$ with HCl ($\geq$2 equiv) leads to *trans*-$PtCl(CCl{=}CHMe)(AsMe_3)_2$, II, as a mixture of *trans*-PtC═CH and *cis*-PtC═CH vinylic isomers in the ratio ca. 3:2, respectively.[6] We have not separated these vinylic isomers but have found that washing the equilibrium mixture with cold pentane preferentially removes the *trans*-PtC═CH isomers into pentane solution. Evaporation of the pentane solution yields a nonthermodynamic mixture, *trans*-PtC═CH:*cis*-PtC═CH = ca. 5, which is stable in the solid state. However, when dissolved in benzene-d_6 at 20 °C, this nonequilibrium trans–cis mixture of vinylic isomers reacted to restore the equilibrium concentrations of vinylic isomers (trans:cis = ca. 3:2) within approximately 3 h. Isomerization of II is achieved by HCl catalysis. This is evident from the observation that addition of HCl to the *trans*-PtC═CH-enriched sample of II in benzene immediately restored the ca. 3:2 trans:cis vinylic ratio. In the absence of added HCl, the catalysis occurs by HCl elimination from the vinyl ligand

$$\mathrm{PtCCl{=}CHMe \rightleftarrows PtC{\equiv}CMe + HCl}$$

This reaction has previously been discussed.[6] Thus for the *trans*-PtCCl═CHMe moiety isomerization may occur (i) by elimination of HCl to give PtC≡CMe and HCl, which may react to generate either the *cis*- or *trans*-PtC═CH isomer, and (ii) by direct reaction of HCl with the PtCCl═CHMe moiety, which is analogous to the HCl-catalyzed reactions Ia ⇄ Ib described above.

***trans*-PtCl(CCl═CH$_2$)(PMe$_2$Ph)$_2$ + HCl.** We noted previously[6] that when *trans*-$Pt(CCl{=}CD_2)_2(PMe_2Ph)_2$ was treated with HCl in toluene-d_8 H/D scrambling at the vinylic β carbon occurred much faster than the reaction leading to *trans*-$PtCl(CCl{=}CH_{2-n}D_n)(PMe_2Ph)_2$ and vinyl chloride (n = 0, 1, 2). Indeed the compound *trans*-$PtCl(CCl{=}CH_2)(PMe_2Ph)_2$, III, is stable toward elimination of vinyl chloride in the presence of anhydrous HCl. However, a reaction does occur.

When anhydrous HCl is added to III in CD_2Cl_2, changes are observed in the ^{1}H NMR spectra. These changes affect the vinylic proton resonances of III and are dependent both on temperature and on the relative concentration of HCl.

^{1}H NMR spectra recorded at various temperatures are shown in Figure 2 for the reaction between III and 1 equiv of anhydrous HCl. At +30 °C two broadened resonances at δ ca. 5 and 6 ppm relative to TMS correspond to *cis*- and *trans*-PtC═CH protons, respectively. Coupling to neither phosphorus-31 nor platinum-195 is apparent. There is also a broad resonance at δ ca. 3 ppm. The phosphine methyl proton resonances (not shown in Figure 2 at 30 °C) appear as well resolved 1:2:1 triplets ($^2J + {}^4J_{PH} = 7$ Hz) with satellites of one-fourth relative intensity ($^3J_{PtH} = 32$ Hz). On lowering the temperature the vinylic resonances sharpen and at −80 °C coupling to ^{195}Pt is clearly resolved. However, coupling to ^{31}P is still not apparent. (In the absence of added HCl the vinylic protons appear as well resolved 1:2:1 triplets due to coupling to two equivalent phosphorus nuclei, $^4J_{PH}$ = ca. 2 Hz, similar to the vinylic proton resonances shown in Figure 1.) The broad resonance at δ ca. 3 ppm at +30 °C shifts to lower field, sharpens on cooling, and at −80 °C appears as a singlet, δ ca. 4 ppm.

^{1}H NMR spectra recorded at various temperatures monitoring the reaction between III and 2 equiv of anhydrous HCl are shown in Figure 3. At 30 °C the only signal, other than those attributable to the dimethyl(phenyl)phosphine ligand, is a very broad resonance at δ ca. 2.6 ppm. On lowering the temperature this resonance shifts downfield and sharpens to a broad singlet at δ ca. 3.2 ppm at −70 °C. At this temperature two broadened resonances at δ ca. 5 and 6 ppm are also evident. Significantly the phosphine methyl resonances retain the appearance that they have in the absence of added HCl; in particular $^3J_{PtH}$ = 32 Hz.

These observations demonstrate that reaction is occurring at the vinylic ligand. HCl may also be reversibly adding to

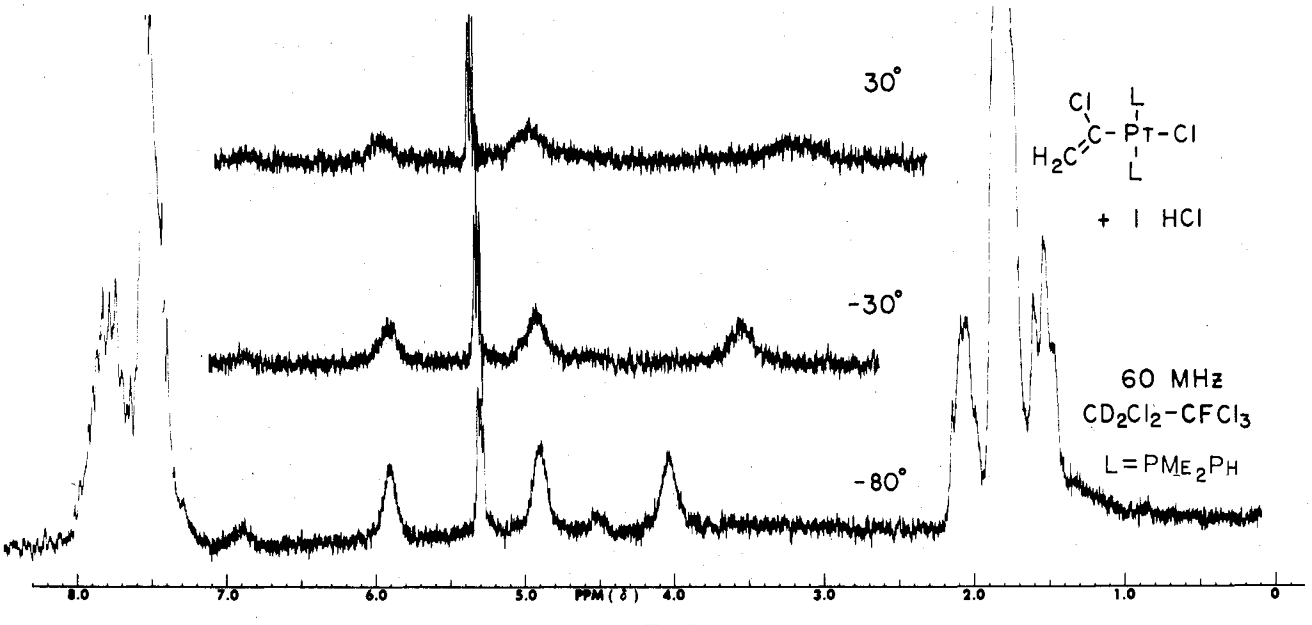


Figure 2. ^{1}H NMR spectra of *trans*-PtCl(CCl=CH$_2$)(PMe$_2$Ph)$_2$ + HCl recorded in CD$_2$Cl$_2$/CFCl$_3$, 60 MHz, at various temperatures. The 1:1:1 triplet at δ ca. 5.3 ppm corresponds to the CHDCl$_2$ impurity in the solvent.

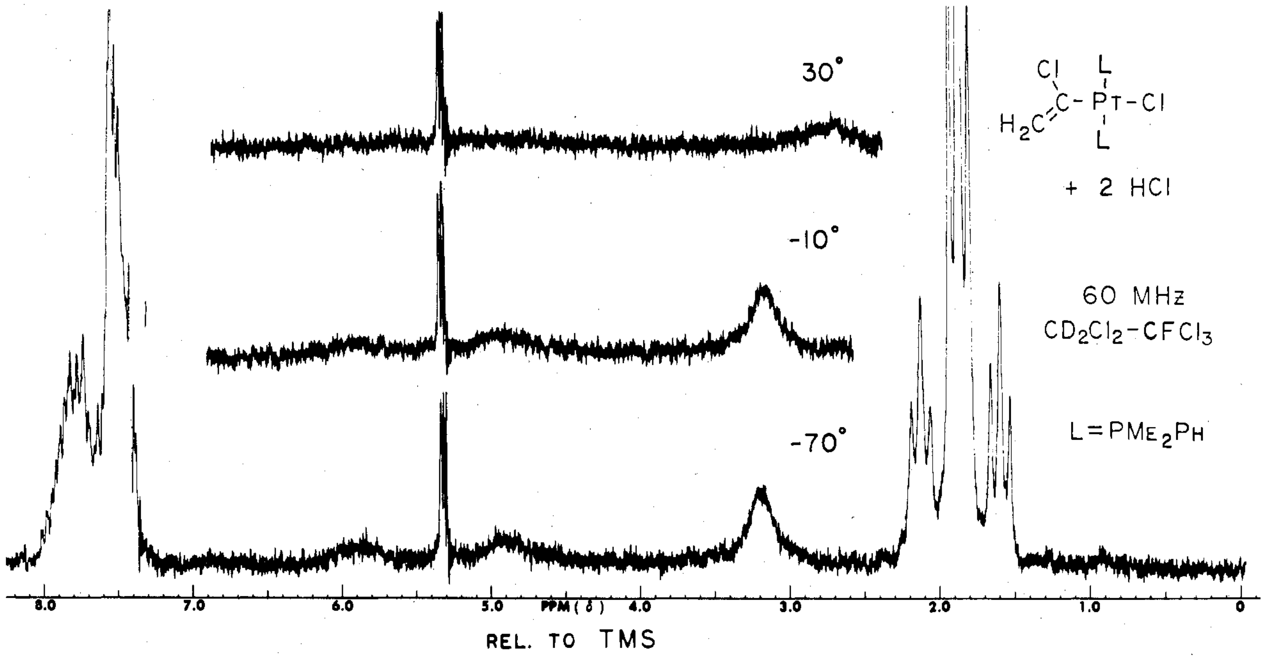


Figure 3. ^{1}H NMR spectra of *trans*-PtCl(CCl=CH$_2$)(PMe$_2$Ph)$_2$ + 2HCl recorded in CD$_2$Cl$_2$/CFCl$_3$, 60 MHz, at various temperatures. The 1:1:1 triplet at δ ca. 5.3 ppm corresponds to the CHDCl$_2$ impurity in the solvent.

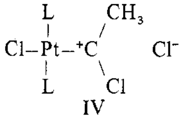
platinum but *not* to yield any significant concentration of a hydridoplatinum(IV) intermediate (e.g., Pt(H)(Cl)$_2$(CCl=CH$_2$)(PMe$_2$Ph)$_2$) since this would result in a change in the appearance of the phosphine methyl resonances. Typically $^3J_{PtH}$ to the phosphine methyl protons in compounds of the type *trans*-PtMe(Cl)(X)(Y)(PMe$_2$Ph)$_2$ is ca. 20 Hz, i.e., approximately two-thirds the value of that in the related platinum(II) complex as expected for a coupling constant dominated by the Fermi contact term (Pt^{II}(sp^{2}d) vs. Pt^{IV}(sp^{3}d^2)).[27]

The reaction between III and HCl appears to be entirely reversible and removal of HCl under vacuum regenerates III. Only after an extended period of time (100 h) in the presence of a large excess of HCl (5 equiv) did III begin to show any evidence of the irreversible formation of vinyl chloride and *cis*-PtCl$_2$(PMe$_2$Ph)$_2$. The spectral changes (Figures 2 and 3) may be interpreted in terms of the equilibrium reaction 4.

$$\text{III} + \text{HCl} \rightleftarrows \text{adduct} \quad K = \text{ca. } 1 \tag{4}$$

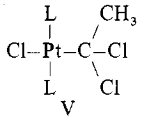
At −80 °C the reaction I + HCl ⇄ adduct (Figure 2) is almost frozen out on the NMR time scale and III and its HCl adduct are present in approximately equal concentrations. At +30 °C (Figures 2 and 3) the rate of HCl exchange is sufficiently fast that the coalescence temperature is being approached. In the fast-exchange limit we would expect a single resonance, the chemical shift of which would be dependent on the relative concentrations of III and HCl and the equilibrium constant *K*.

At present we can only speculate as to the nature of the adduct. It could be formulated either as the ionic species IV or as the dichloroethylplatinum complex V. It is certain that reaction occurs predominantly, if not exclusively, in a Mar-



$\mathrm{Cl{-}\overset{L}{\underset{L}{Pt}}{-}{}^{+}C(CH_3)(Cl)\quad Cl^-}$

IV



$\mathrm{Cl{-}\overset{L}{\underset{L}{Pt}}{-}C(CH_3)(Cl){-}Cl}$

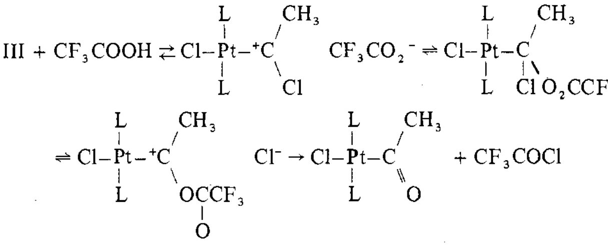
V

kownikov manner since addition of DCl (excess) leads to the apparently instantaneous formation of *trans*-$\mathrm{PtCl(CCl{=}CD_2)(PMe_2Ph)_2}$.[6] Of course, addition of HCl to III might lead to both IV and V as shown in (5). This point remains

$$\mathrm{III + HCl \rightleftarrows IV \rightleftarrows V} \qquad (5)$$

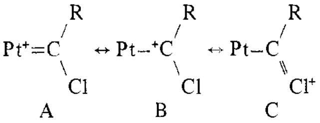
to be investigated.

Similar reactions were attempted with trifluoroacetic acid. Vinyl resonances were perturbed as in the reaction between III and HCl, but a resonance in the vicinity of δ 3 ppm was not observed. Over a period of hours the reaction produced *trans*-$\mathrm{PtCl(C(CH_3){=}O)(PMe_2Ph)_2}$ as the sole platinum-containing compound. This could have arisen from hydrolysis of III[4] or by elimination of trifluoroacetyl chloride from a trifluoroacetoxycarbene intermediate by the sequence of reactions shown in (6). Elimination of trifluoroacetyl chloride from a trifluoroacetoxycarbene intermediate in (6) has parallel in the known reactions of cationic alkyl(alkoxy)carbene complexes, $\mathrm{PtC^+(R')OR}$, which readily generate alkyl chlorides, RCl, and acylplatinum compounds, $\mathrm{PtC(R'){=}O}$, in the presence of $\mathrm{Cl^-}$.[4,28] Regrettably we have not elaborated further on the origin of the acylplatinum compound at present.



$$\mathrm{III + CF_3COOH \rightleftarrows Cl{-}\overset{L}{\underset{L}{Pt}}{-}{}^{+}C(CH_3)(Cl)\ \ CF_3CO_2^- \rightleftharpoons Cl{-}\overset{L}{\underset{L}{Pt}}{-}C(CH_3)(Cl)(O_2CCF_3) \rightleftharpoons Cl{-}\overset{L}{\underset{L}{Pt}}{-}{}^{+}C(CH_3)(OC(O)CF_3)\ \ Cl^- \rightarrow Cl{-}\overset{L}{\underset{L}{Pt}}{-}C(CH_3){=}O + CF_3COCl} \qquad (6)$$

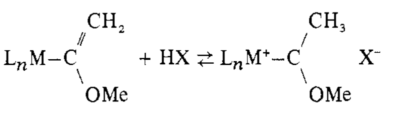
The prime purpose of this paper is to draw attention to a number of reactions of α-chlorovinylplatinum(II) compounds with acids HX which may best be interpreted by protonation at the β carbon yielding the carbonium ion B which is stabilized by platinum, A, and the chlorine atom, C, as shown in the resonance forms



$$\mathrm{\underset{A}{Pt^+{=}C(R)Cl} \leftrightarrow \underset{B}{Pt{-}{}^{+}C(R)Cl} \leftrightarrow \underset{C}{Pt{-}C(R){=}Cl^+}}$$

Fischer[29] and Lappert[30] and their co-workers have recently isolated stable metal complexes containing dialkylamino(chloro)carbene ligands, $\mathrm{L_nMC(Cl)NR_2}$. Undoubtedly the stabilizing influence of the $\mathrm{NR_2}$ group is of paramount importance. However, even the electronegative chlorine atom may contribute to the overall stabilization through π donation as in resonance form C.

Our proposal also finds a parallel in the chemistry of α-methoxyvinyl compounds which react reversibly with acids HX to give cationic alkoxycarbene complexes as in



$$\mathrm{L_nM{-}C({=}CH_2)(OMe) + HX \rightleftarrows L_nM^+{-}C(CH_3)(OMe)\quad X^-} \qquad (7)$$

E.g., $\mathrm{L_nM = (CO)_5Cr}$,[31] $\mathrm{C_6Cl_5Ni(PMe_2Ph)_2}$,[32] or $\mathrm{XPt(PMe_2Ph)_2}$.[4] The position of equilibrium in 7 is dependent on the nature of both $\mathrm{L_nM}$ and the conjugate base $\mathrm{X^-}$.[4]

In the absence of a stabilizing group in the α position alkenylplatinum(II) compounds react with HCl (and other acids) to liberate the alkene.[33] For example, *trans*-$\mathrm{PtCl(CH{=}C(H)Cl)(PMePh_2)_2}$, which is closely related to III, reacts with HCl (1 equiv), rapidly and quantitatively, to give *cis*-$\mathrm{PtCl_2(PMePh_2)_2}$ and vinyl chloride.

Experimental Section

^{1}H NMR spectra were recorded on a Varian A-60 spectrometer fitted with a variable-temperature probe. NMR solvents were from Aldrich; DCl gas was from Merck Sharp and Dohme. HCl gas was from Matheson.

Details of the syntheses of *trans*-$\mathrm{PtL_2Cl(CCl{=}CHCl)}$ and *trans*-$\mathrm{PtL_2Cl(CH{=}CHCl)}$ are given in ref 20. A Fisher-Porter bottle was used during this procedure to contain the volatile chlorinated alkenes. The preparation of *trans*-$\mathrm{PtCl(CCl{=}CH_2)(PMe_2Ph)_2}$ was also previously described.[4]

Ia in $\mathrm{CDCl_3}$. Ia (40 mg) was dissolved in $\mathrm{CDCl_3}$ (0.4 ml) in an NMR tube and sealed by torch. The ^{1}H NMR spectra, observed over 4 days, showed only a single vinyl resonance. Similar results were obtained in $\mathrm{CD_2Cl_2}$.

Ia + DCl in $\mathrm{CDCl_3}$. Ia (45 mg) was dissolved in $\mathrm{CDCl_3}$ (0.3 ml) in an NMR tube and frozen in liquid nitrogen, and the system was evacuated. On a calibrated vacuum manifold DCl (0.06 mmol) was condensed into the tube and sealed by torch. The tube was warmed to room temperature and the ^{1}H NMR spectra were recorded at 15-min intervals for 6 h. Initially the concentration of the *cis*-PtC=CH proton, as measured by integration, showed a slow decrease. After about 1 h the *trans*-PtC=CH proton resonance began to appear. When the 30:70 equilibrium mixture was attained, no further decrease in either resonance was observed. Total integration of both resonances corresponded to ~0.6 proton equiv.

Ia + Magic Acid. Ia (80 mg) was dissolved in $\mathrm{CDCl_3}$ (0.3 ml) in an NMR tube. Magic acid (13.3 μl) was microsyringed into the solution and the ^{1}H NMR spectrum was recorded immediately which disclosed the 70:30 *trans*- + *cis*-PtC=CH equilibrium mixture. In the course of a few minutes a small resonance (δ 6.45) appeared. After 1 h the volatile products were transferred via vacuum manifold to a second NMR tube. One-half equivalent of *trans*-1,2-dichloroethylene (5 μl) was added. ^{1}H NMR clearly indicated that only the *cis*-1,2-dichloroethylene had been formed and in ca. 40% yield based on added acid. Similar reactions demonstrated that the *cis*-1,2-dichloroethylene yield was almost quantitatively based on acid concentration when the reaction was allowed to proceed to completion.

Ia + $\mathrm{H^+PF_6^-}$ in $\mathrm{CDCl_3}$. Ia (80 mg) was dissolved in $\mathrm{CDCl_3}$ (0.4 ml) containing 1 equiv of $\mathrm{H^+PF_6^-}$, formed by reaction of HCl gas (0.11 mmol) with $\mathrm{AgPF_6}$ (28 mg) in $\mathrm{CDCl_3}$. The solution was centrifuged to remove AgCl. NMR spectra were taken over a period of 30 min during which time the Ia vinylic proton decreased and the Ib vinylic proton rose to the equilibrium 30:70 ratio.

Ia + HCl in $\mathrm{CDCl_3}$. HCl gas (0.11 mmol) was condensed into an evacuated NMR tube containing a frozen mixture of 1 equiv of Ia (80 mg) and $\mathrm{CDCl_3}$ (0.3 ml). The tube was sealed via torch and allowed to warm to room temperature. NMR spectra, recorded at 20-min intervals, indicated isomerization was complete in ~1 h. Similar results were obtained in $\mathrm{CD_2Cl_2}$.

Ia + TFA in $\mathrm{CDCl_3}$. In similar fashion to the magic acid reaction, trifluoroacetic acid (8 μl) was microsyringed into a solution of 1 equiv of Ia (80 mg) in $\mathrm{CDCl_3}$ (0.3 ml). ^{1}H NMR spectra disclosed that isomerization was complete in approximately 6 h.

Ia + Magic Acid vs. Ia + HCl: Relative Rates of Isomerization. To Ia (80 mg) in $\mathrm{CD_2Cl_2}$ (0.3 ml) was added 15 mol % of magic acid (2 μl) via microsyringe. ^{1}H NMR spectra indicated isomerization was complete in less than 1 min.

To Ia (80 mg) in $\mathrm{CD_2Cl_2}$ (0.3 ml) frozen by liquid $\mathrm{N_2}$ was added via a calibrated vacuum manifold 25 mol % of HCl (0.028 mmol). ^{1}H NMR spectra indicated isomerization was complete in ca. 24 h.

Ia + HCl in $\mathrm{C_6D_6}$ vs. $\mathrm{CD_2Cl_2}$. HCl gas (0.11 mmol) was condensed into an evacuated NMR tube containing a frozen mixture of 1 equiv of Ia (80 mg) and $\mathrm{C_6D_6}$ (0.3 ml). The tube was sealed by torch and allowed to warm to room temperature. NMR isomerization was complete in ~8 days. T_{isom} for $\mathrm{CD_2Cl_2}$, already reported, was ~1 h.

II in $\mathrm{C_6D_6}$ (5:1 trans:cis); II (5:1) + HCl. The synthesis and characterization of the 5:1 trans:cis (PtC=CH) nonequilibrium mixture of II has been described previously.[6] The mixture (35 mg) dissolved in $\mathrm{C_6H_6}$ (0.3 ml) isomerizes to the equilibrium 2:1 ratio in about 3 h at 20 °C. A similar sample indicated immediate isomerization when treated with 25 μl of a benzene/HCl solution (dry HCl bubbled through benzene).

trans-1,2-Dichloroethylene + Magic Acid. Magic acid (13.3 μl) was microsyringed into an NMR tube containing *trans*-1,2-dichloroethylene (8.5 μl) and $CDCl_3$ (0.4 ml). The sealed tube was monitored by ^1H NMR spectroscopy for 3 days during which time it showed only *trans*-1,2-dichloroethylene and no evidence of the thermodynamically favored cis isomer.

trans-$PtCl(PMePh_2)_2(CH{=}C(H)Cl)$ + HCl in $CDCl_3$. One equivalent of dry HCl gas (0.14 mmol) was condensed from a calibrated vacuum manifold into a frozen mixture of the Pt complex (80 mg) and $CDCl_3$ (0.3 ml). The ^1H NMR spectrum of the sealed tube indicated immediate and quantitative formation of vinyl chloride ($\delta \sim 5.4$, 5.5, 6.3; J_{HH}: geminal, 1.4 Hz; cis, 7.2; trans, 14.9) and *cis*-PtL_2Cl_2.

III + HCl (Variable Temperature). As above, HCl was condensed into NMR tubes containing III (40 mg) and $CDCl_3$ (0.3 ml). HCl concentration ranged from 1 (0.07 mmol) to 5 equiv (0.35 mmol). As shown in Figures 2 and 3 the ^1H NMR spectra were temperature dependent, producing sharpened vinyl resonances with decreasing temperature. Only after 4 days did the most concentrated (5 equiv) solution show indications of decomposition to PtL_2Cl_2 and vinyl chloride.

III + TFA. One equivalent of trifluoroacetic acid (5.2 μl) was syringed into an NMR tube containing III (40 mg) in $CDCl_3$ (0.3 ml). The ^1H NMR spectrum showed broadening and diminution in the vinyl resonances as seen with HCl + III but for TFA no resonance at $\delta \sim 3$ was observed. After about 24 h a new triplet began to appear in the phosphine methyl region ($\delta \sim 1.9$). Upon further investigation of the Pt-containing solids of the reaction by IR spectroscopy this proved to be[4] *trans*-$PtClL_2(COCH_3)$, $\nu(C{=}O)$ 1630 cm^{-1}.

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Registry No. Ia, 52554-21-9; Ib, 52611-09-3; II, 61394-75-0; III, 60293-85-8; *trans*-$PtCl(PMePh_2)_2CH{=}C(H)Cl$, 61473-85-6.

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(34) One referee suggested we should comment on why the L group is different for the three complexes studied (I, L = $PMePh_2$; II, L = $AsMe_3$; III, L = PMe_2Ph). It is our opinion that the reactivity of the chlorovinyl ligand in compounds of the type *trans*-$PtCl(CCl{=}CHR)L_2$ is little affected by the nature of L: the carbonium ion model is equally applicable to tertiary phosphine and tertiary arsine compounds. This view is well exemplified in our studies of the formation of alkoxycarbene ligands within the coordination sphere of platinum(II): part 1 of this series.[4] In the present case the use of L = $PMePh_2$, PMe_2Ph, and $AsMe_3$ simply follows historically. The Cambridge workers used L = $PMePh_2$[24] while we have traditionally used L = PMe_2Ph and $AsMe_3$.