

PYROLYSIS AND HYDROLYTIC CLEAVAGE OF VINYL- AND ALLYLSILANE  
PLATINUM(II) COMPLEXES

THESIS

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By

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## Chapter I

### INTRODUCTION

#### A. Historical Background

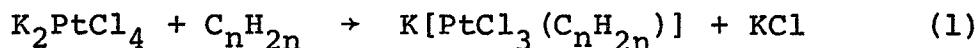
The subject of organotransition metal chemistry as a distinct area of chemistry is less than twenty years old. It was of relatively little interest before 1950, even though the Danish chemist, Zeise, synthesized the salt,  $K[PtCl_3(C_2H_4)]$ , in 1827.<sup>1</sup> Significant interest in olefin-metal compounds did not develop until the structure of ferrocene was determined in 1952.<sup>2</sup> It was subsequently realized that the transition metals possessed the capability of forming a wide variety of stable olefin-metal compounds. Many attempts to synthesize these compounds were unsuccessful because the stabilities of these complexes depend on the particular ligands complexed to the metal.<sup>3</sup> Unfortunately, stable combinations were not initially found.

Considerable industrially-oriented work on the use of transition metals in catalytic organic reactions has prompted extensive investigations on the nature of the metal-olefin bond. Apart from this technical motivation, the  $\pi$ -olefin-metal complexes are of considerable academic interest, because of the bonding involved and the unusual reactions the complexes undergo. Consequently, investigation and review of the latest ideas about  $\pi$ -olefin-platinum(II) complexes has been intensified.

### B. Synthesis and Properties of Olefin-Platinum(II) Complexes

Preparation- There are several methods of preparing olefin-platinum(II) complexes; however, only two methods are herein described.

Method I - Olefinic compounds react directly with potassium tetrachloroplatinate(II) by displacement of one chloride ion from the co-ordinated complex (see equation 1).<sup>4</sup>



In the older method, the reaction proceeded at room temperature in aqueous-alcoholic solution, and it was slow owing to the insolubility of potassium tetrachloroplatinate(II) in alcohol. In this laboratory, however, 4% aqueous HCl solution was used as a solvent in the preparation of Zeise's salt,  $K[PtCl_3(C_2H_4)]$ . The HCl must be present to inhibit oxidative hydrolysis, and high pressure is applied to shift the equilibrium to the right and to increase the rate of the reaction. The stability of the ethylenetrichloroplatinate(II) ion is so high that Zeise's salt may be crystallized unchanged in the presence of hydrochloric acid.<sup>4</sup>

Method II - The most striking and significant mode of synthesis of olefin-platinum(II) complexes is by direct replacement of one olefin by the other.<sup>5</sup> Co-ordinated olefins such as ethylene in Zeise's salt may be displaced by less

volatile ligands if they are added in excess (see equation 2).



Vigorous reaction takes place, and ethylene is liberated quantitatively. The factor involved is not solely the relative stability of the salts but also the relative volatility of the olefins.

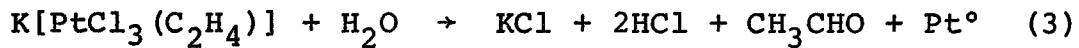
Properties.--The physical properties of olefin-platinum(II) complexes are very well established. Zeise's salt and its analogues are usually yellow crystalline compounds. The ionic complexes are soluble in water, alcohol and acetone, whereas the neutral complexes, except for the tetrameric allylchloroplatinum(II),<sup>6</sup> are soluble in most organic solvents.<sup>4</sup>

The olefin-platinum(II) complexes decompose over a wide range of temperatures without melting. The shelf-life varies considerably from one compound to the other. Zeise's salt and the dipentene complex seem to be stable over a period of several months in air.<sup>7</sup> However, vinyl- and allylsilane platinum(II) complexes have a comparatively short shelf-life because they are sensitive to moisture and light, as has been observed in this laboratory.

The chemical properties of these complexes are not as well established as their physical properties. Olefin-platinum(II) complexes undergo a variety of chemical reactions. The olefins in these complexes normally undergo nucleophilic attack.<sup>8</sup>

Olefin-platinum(II) salts are not readily oxidized but undergo oxidative hydrolysis when exposed to moisture.<sup>9</sup>

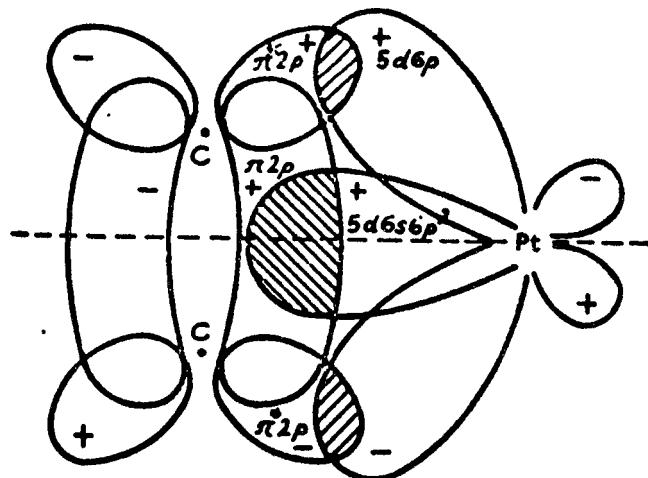
Zeise's salt is oxidatively hydrolysed as shown in equation 3.<sup>10</sup>



On the other hand, the tetrmeric allylchloroplatinum(II) complex has been observed in this laboratory to be very unreactive as well as stable and insoluble in water and aqueous KCl solution.

### C. Metal-Olefin Bonding

A concise description of the bonding in  $\pi$ -olefin-transition metal complexes is presented by Coates, Wade and Green.<sup>11</sup> In their description, which is basically that postulated by Chatt and Duncanson,<sup>12</sup> the olefin is attached to the metal by two types of bonds, the  $\sigma$ - and  $\pi$ -type bonds illustrated in Figure 1.



Bond in  $\text{C}_2\text{H}_4\text{PtCl}_3^-$

Figure 1. Chatt-Dewar-Duncanson Bonding Model<sup>12</sup>

The  $\sigma$ -type bond is formed by the overlap of the filled  $\pi$ 2p orbital of the olefin with an empty  $d$ sp<sup>2</sup> hybrid orbital of platinum. The  $\pi$ -type bond is formed by the overlap of the vacant antibonding  $\pi^*$ 2p orbital of the olefin with a filled d orbital of the platinum. This  $\pi$ -type of bonding is called backbonding. The shift of electrons in backbonding lowers the potentially unfavorable high electron density around the platinum ion caused by the  $\sigma$ -bonding. In addition, the shift of electrons from the olefin to the metal gives the olefinic carbons a partial positive charge.<sup>13</sup> Furthermore, the backbonding interaction is reported to have a net effect of lowering the carbon-carbon double bond order.<sup>3</sup> Support of this bonding effect is obtained from the analysis of infrared spectra of olefin-platinum(II) complexes. Lowering of the bond order weakens the carbon-carbon double bond and lowers the stretching force constant of the bond. The infrared stretching frequency of complexed olefins is observed to be lowered as much as  $150\text{cm}^{-1}$ , or more, for strongly backbonded olefins.<sup>3</sup> Complexed acetylenes also show a downward shift of the triple-bond stretching frequency from that in the free acetylene by about  $200\text{cm}^{-1}$ .<sup>3</sup>

Another type of olefin-metal bond is that of a four-electron donor system such as that encountered in the  $\pi$ -allyl-metal complexes. The metal-allyl bond is effectively described by R. F. Heck<sup>3</sup> and is illustrated in Figure 2. The allyl group may also bond as a two electron donor, in which case it is  $\sigma$ -bonded.

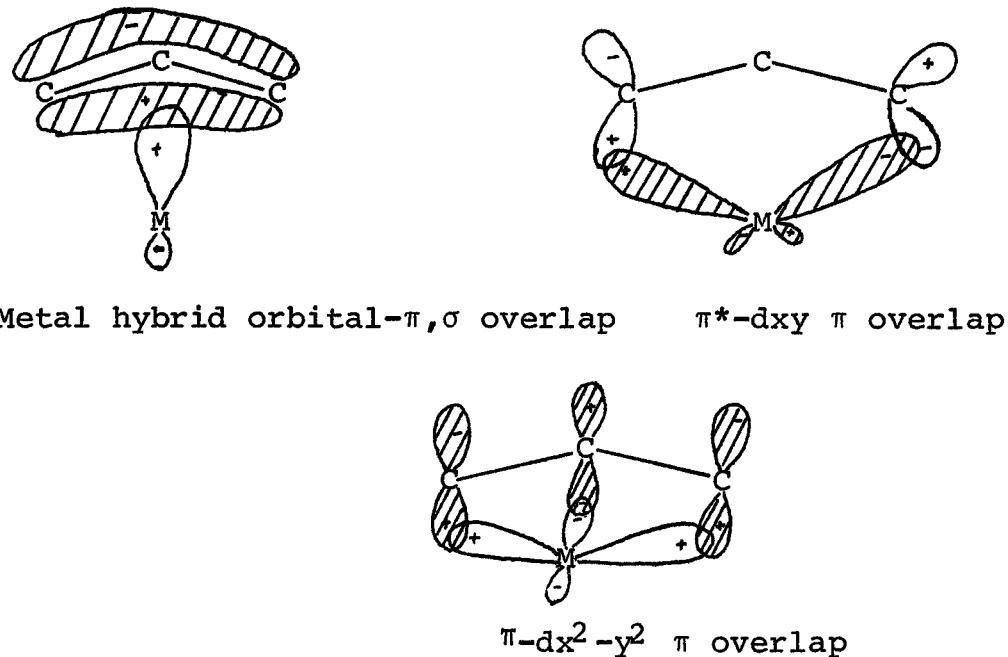


Figure 2. Bonding of  $\pi$ -Allyl groups<sup>3</sup>

#### D. Physical Methods of Investigating the Structure of Olefin-Platinum Complexes

Many physical methods have been used to study the nature and structure of metal-olefin complexes. Infrared and nuclear magnetic resonance spectroscopy as well as X-ray crystallography have been fruitfully applied to resolve these problems. These methods are herein described.

X-Ray Investigations.--Structure determinations for Zeise's salt,<sup>2, 4</sup> Zeise's dimer<sup>13</sup> and related simple ethylene complexes of platinum are reported extensively in the literature. X-ray diffraction techniques have been used in the structure determinations of Zeise's salt<sup>14</sup> and dichloro-(dipentene)platinum(II)<sup>15</sup> (Figure 3). X-ray determination of the structure of Zeise's salt gives the best confirmation of

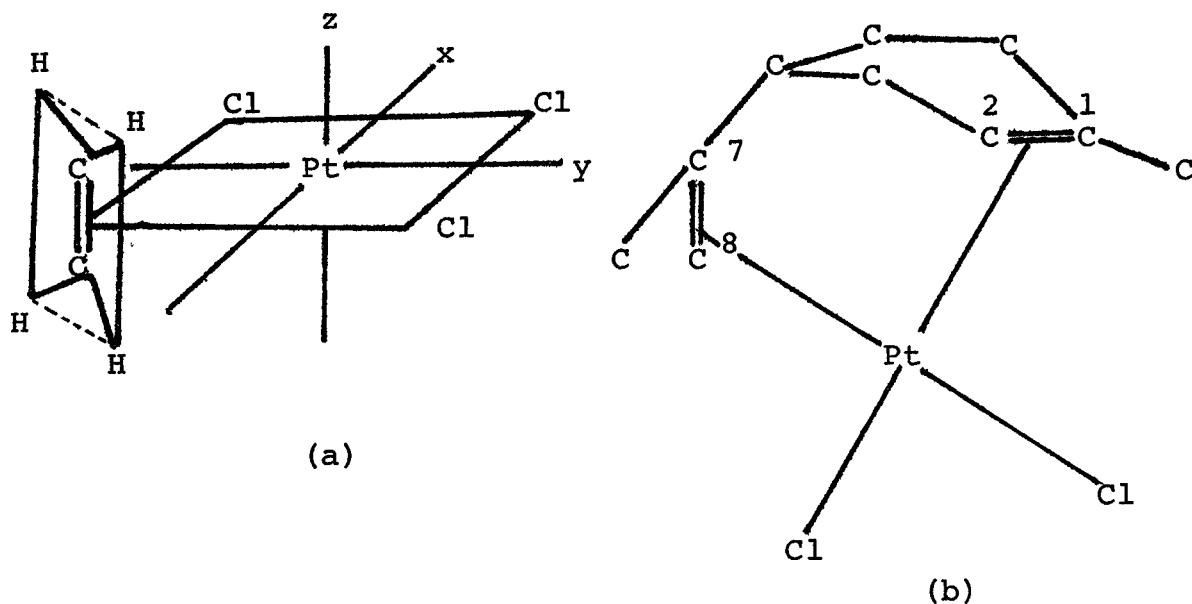


Figure 3. X-ray Structures of (a) Potassium Trichloro(ethylene)platinate(II)<sup>14</sup> and (b) Dichloro(dipentene)-platinum(II)<sup>15</sup>

the bonding scheme postulated by Chatt and Duncanson.<sup>12</sup> However, the first attempt in structure determination of Zeise's salt led to controversy about the exact bond lengths. Large atoms such as platinum scatter X-rays strongly and thus give inaccurate data on the location of the lighter atoms such as carbon and chlorine.<sup>14</sup> There is, however, a general agreement that the plane of the olefin bond is perpendicular to the metal-olefin bond<sup>12</sup>, except in special cases where strain exists such as in dichloro(dipentene)-platinum(II) (Figure 3b). X-ray studies of dichloro(dipentene)platinum(II) shows that, because of internal strain, the double bonds are not parallel to each other. As indicated in Figure 3, one double bond ( $C_1=C_2$ ) is perpendicular to the plane containing the  $PtCl_2$  group, whereas the other double bond ( $C_7=C_8$ ) is at an angle of  $62.1^\circ$ .<sup>15</sup> It may be

concluded, therefore, that the perpendicular orientation of the carbon-carbon double bond is favored, but it is apparently not essential for bond formation.

X-ray studies of allylic complexes indicate that in symmetrical complexes the terminal carbons are equidistant from the metal, and the middle carbon is also close enough to be bonded strongly. The three carbons of the allylic group and the five substituents are approximately coplanar with the metal.<sup>3</sup>

Infrared Investigations.--Several detailed studies on the infrared (IR) spectrum of Zeise's salt and Zeise's dimer have been reported.<sup>13,16</sup> Reports as early as 1953 confirmed the lowering of the carbon-carbon double bond stretching frequency upon co-ordination with the platinum metal. The earliest systematic IR studies of Zeise's salt and its analogues were performed by Chatt and Duncanson.<sup>17</sup> They concentrated on the  $1500\text{cm}^{-1}$  region and found that the carbon-carbon double bond vibrational frequency was lowered by 60 to  $150\text{cm}^{-1}$ . However, they were unable to detect any absorption in this region in the spectrum of Zeise's salt. A wider range of frequencies was studied by Powell and Sheppard.<sup>18</sup> They compared vibrational frequencies of the ethylene in Zeise's salt with those of ethylene sulfide,  $\overline{\text{CH}_2\text{SCH}_2}$ , and free ethylene. They came to the conclusion that the co-ordinated ethylene in Zeise's salt gave rise to frequencies only a little different from those in free

ethylene with the former having its stretching frequency shifted furthest.

This finding was, however, contested by a group of Russian workers<sup>19</sup> who assigned the vibration at 1500cm<sup>-1</sup> to the deformation of CH<sub>2</sub>, and suggested a great similarity with the IR spectrum of a compound,  $\text{CH}_2\overline{\text{OCH}}_2$ . This report was again, by and large, discredited by the findings of Adams and Chatt,<sup>17</sup> and Powell and Sheppard.<sup>16</sup> The former two investigators found a small isotopic shift in the 1500cm<sup>-1</sup> band in K[PtCl<sub>3</sub>(CH<sub>2</sub>=CH-CH<sub>3</sub>)].H<sub>2</sub>O and its fully deuterated analogue,<sup>20</sup> while the later found a band at 1505cm<sup>-1</sup> in the cis-2-butene complex, K[PtCl<sub>3</sub>(cis-CH<sub>3</sub>CH=CHCH<sub>3</sub>)].

Furthermore, Sheppard<sup>21</sup> and Hartley<sup>22</sup> have made detailed calculations to show that the two bands at 1500cm<sup>-1</sup> and at 1200cm<sup>-1</sup>, whose assignment is in dispute, must be assigned together to the strongly coupled vibrations  $\nu(\text{C}=\text{C})$  and  $\delta(\text{CH}_2)$  of ethylene in Zeise's salt. In addition Hartley<sup>22</sup> has demonstrated that contrary to the general assertion, no correlation exists between the carbon double bond stretching frequency of coordinated olefins and the metal-olefin bond strength.

Comparative studies of Zeise's salt and Zeise's dimer have been made, and the assignments of the ethylene peaks were virtually identical.<sup>13</sup> A normal co-ordinate analysis has also indicated that a band at 408cm<sup>-1</sup> is due to the stretching modes of the platinum-ethylene bond. The band at 364cm<sup>-1</sup> was assigned to the platinum-terminal chlorine

stretching mode.<sup>23</sup> This is in good agreement with an independent assignment of similar stretching modes in a number of platinum(II)-bridged chloro-complexes.<sup>19</sup>

Nuclear Magnetic Resonance Investigations.--Nuclear magnetic resonance (NMR) studies have been used in conjunction with infrared spectroscopy to give evidence of the structure of metal-olefin complexes. In particular, NMR has been a powerful tool in distinguishing between the olefinic and allylic complexes and in the investigation of the stereochemistry of these complexes.

Detailed studies of several metal-olefin complexes have been reported in recent reviews.<sup>24</sup> The studies of the NMR spectrum of Zeise's salt are consistent with the planar configuration of the hydrogen atoms of the co-ordinated ethylene molecule.<sup>25</sup> However, an accurate estimate of the inter-hydrogen distances in the molecule cannot be made due to apparent rotational oscillations of the co-ordinated ethylene.<sup>24</sup>

The high resolution NMR spectrum of the  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  ion in deuterium oxide shows a strong singlet attributed to the ethylenic protons. This result is in agreement with a symmetrically co-ordinated ethylene molecule.<sup>16</sup> Infrared arguments also indicate symmetrical co-ordination.<sup>18</sup>

Recent NMR studies have indicated that molecular orbital treatments of metal-olefin complexes have adopted a model which is too rigid.<sup>26</sup> Ethylene in Zeise's salt undergoes rotational oscillations about the platinum-ethylene bond.<sup>27</sup>

The molecular orbital scheme can be made less rigid if the  $\pi$ -backdonation to the olefin antibonding orbital can occur from both the  $d_{yz}$  and  $d_{xz}$  orbitals of metal or a linear combination of these.<sup>27</sup>

#### E. Cleavage Reactions of the Carbon-Silicon Bond

During the past 26 years, research in the field of organosilicon chemistry has undergone an intensive development directed especially towards the production of organosilicon commercial products - silicones. These products have been used extensively because of their resistance toward thermal and oxidative decomposition.<sup>28</sup>

Silicon is markedly less electronegative than carbon, and for this reason the carbon-silicon bond has a 12% ionic character.<sup>8</sup> This bond is somewhat facile and can be made to undergo heterolytic fission when attacked by either electrophiles or nucleophiles.

Cleavage of Vinyl and Allylsilanes.--Unsaturated groups at the  $\alpha$  or  $\beta$  position from a silicon atom are cleaved more readily than alkyl groups when attacked by nucleophilic or electrophilic reagents.<sup>29</sup> Electrophilic reagents such as strong acids cleave the vinyl group from the silicon atom. A typical example is the reaction of sulfuric acid with vinyltrimethylsilane as shown in equation 4. The



protonation occurs at the  $\alpha$  carbon atom owing to the electron

deficiency created at the  $\beta$  carbon by the (p-d) $\pi$ -interaction<sup>30</sup> shown in Figure 4.

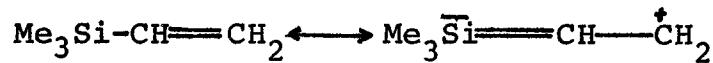
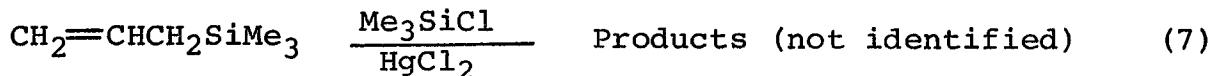
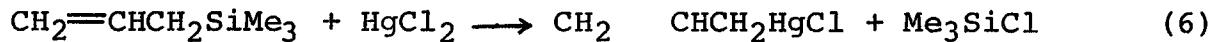


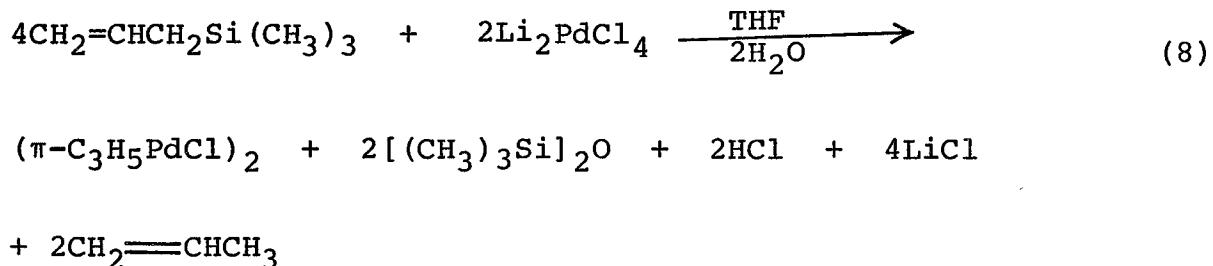
Figure 4. Bond Polarization in Vinyltrimethylsilane

Vinyl groups are cleaved from silicon atoms by nucleophilic reagents with relative difficulty. It is necessary to use high concentrations of alkali metal hydroxides or alkoxides, and elevated temperatures.<sup>31</sup> Comparatively, allyl and alkynyl groups are split from silicon more easily by means of several nucleophilic reagents.<sup>33</sup> However, alkenyl groups with the double bond in more remote positions from silicon are comparable to the alkyl groups with respect to cleavage from silicon.<sup>22</sup>

Cleavage of the C—Si Bond by Transition Metal Compounds.-- Several recent reports have described the kinetics and the mechanisms of cleavage reactions of vinyl and allylsilanes catalyzed by transition metal salts. In these reactions the unsaturated organosilanes usually react with the transition metal to form initially an intermediate  $\pi$ -complex.<sup>31</sup> In a recent paper, Roberts reported the kinetics of the mercury(II) salt catalyzed cleavage of allyltrimethylsilane.<sup>32</sup> The products detected in this case were chlorotrimethylsilane and allylmercuric chloride as shown in equations 6 and 7.

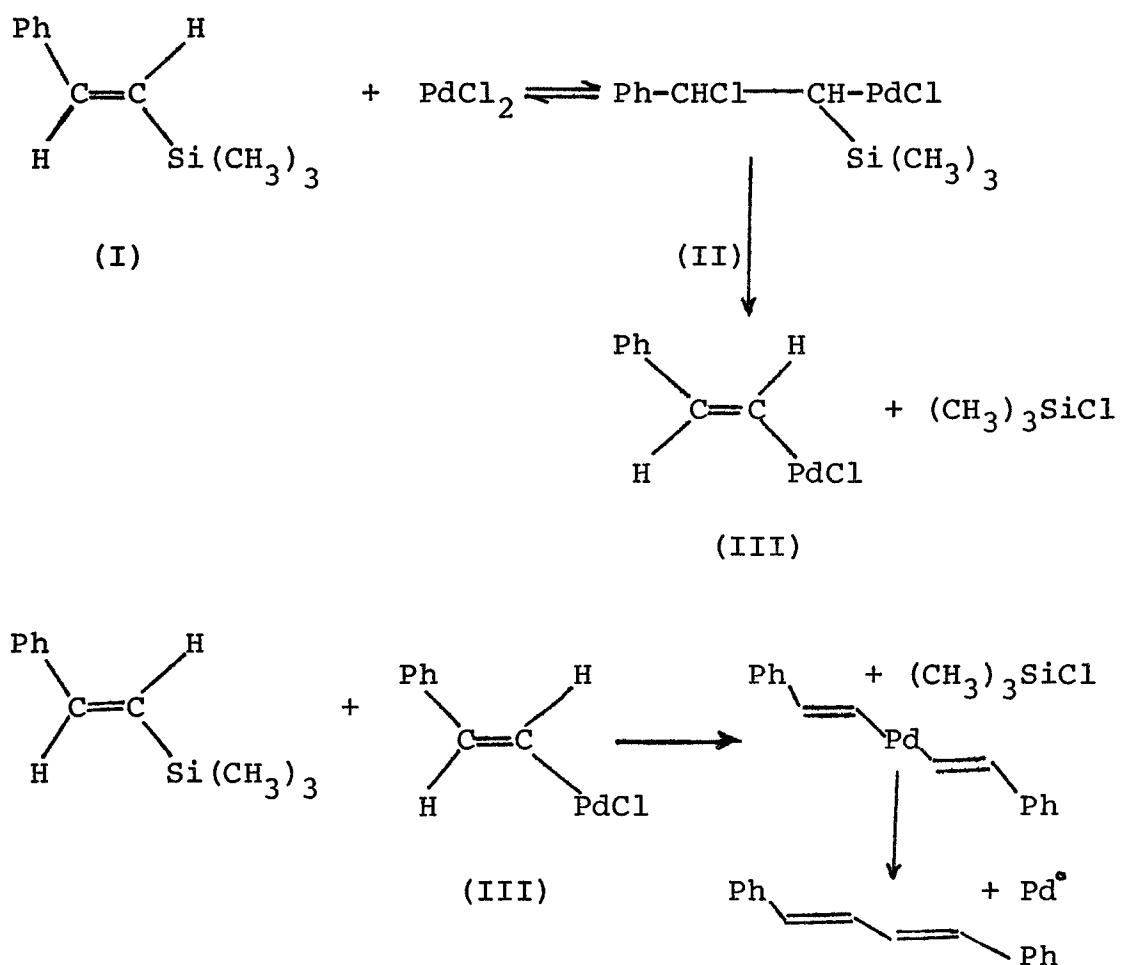


At about the same period, Poist and Kraihanzel<sup>33</sup> reported that platinum(II) halides catalyze the cleavage of the alkynyl group from silicon in ethanol at 40° to give ethoxytrimethylsilane, gaseous products and platinum residues that contained alkyne bonds. They found that allyltrimethylsilane also reacts with platinum(II) halides, but they did not completely identify the products. Furthermore, Kriegman<sup>34</sup> has reported that palladium(II) salts cleave allylsilanes in an extremely rapid reaction in water and methanol solution as shown in equation 8. He proposed a



mechanism in which the stoichiometric cleavage gives a π-allylpalladium(II) complex and chlorotrimethylsilane which immediately reacts with water to form hexamethyl-disiloxane. It is noteworthy that his data disproved the general assertion that this type of reaction is catalytic in palladium. On the contrary he noted and verified that the reaction is catalytic in HCl generated from the cleavage reaction.

Weber et al.<sup>35</sup> have also recently reported on the reaction of vinylsilanes with palladium salts. They found that the reaction products can be explained in terms of vinyl palladium intermediates. A typical reaction of  $\beta$ -styryltrimethylsilane with  $PdCl_2$  in methanol formed trans,trans-1,4-diphenyl-1,3-butadiene in high yield. This compound was thought to form from the dimerization of two styryl fragments. Significantly, they advanced a versatile mechanism generally thought to occur in reactions of this nature. The mechanism is illustrated in Figure 5.



**Figure 5.** Mechanism for the Reaction  $\beta$ -Styryl-trimethylsilane with Palladium Chloride

In this mechanism the first step is the reaction of  $\text{PdCl}_2$  with (I) to form a  $\pi$  complex which subsequently rearranges to intermediate (II). Chlorotrimethylsilane is formed as a result of a known facile  $\beta$ -elimination, and a transient  $\sigma$ -styrylpalladium complex (III) is formed at the same time. The intermediate (III) reacts with another molecule of (I) to form a bis- $\beta$ -Styrylpalladium(II) intermediate which finally forms the product by oxidative coupling of the two styryl fragments.

F. Recently Observed Reactions of Vinyl and Allyl-silanes in this Laboratory.

Although intermediates involving  $\pi$ -complexes of vinylsilanes<sup>35</sup> and allylsilanes<sup>31</sup> have been suggested in several of the reactions discussed, they have not to our knowledge been isolated and studied in detail. As a matter of fact, these reactions seem to imply that it is not practically feasible to isolate stable  $\pi$ -complexes containing vinyl- or allylsilanes as ligands. However, Fitch and co-workers have recently successfully isolated stable vinylsilane<sup>36</sup> and allylsilane<sup>37</sup> platinum(II) complexes as well as vinylsilane copper(I)<sup>38</sup> complexes in this laboratory.

The stability of these vinylsilane complexes is attributed to the possible overlap of the silicon d orbital with the d orbital of the transition metal (Figure 6). However, the bonding and stability of the allylsilane in platinum(II) complexes is thought to be similar to that observed in regular olefins albeit the complexes are very reactive.

The extent of the silicon d orbital participation in the bonding in vinylsilane platinum(II) complexes is not well established.

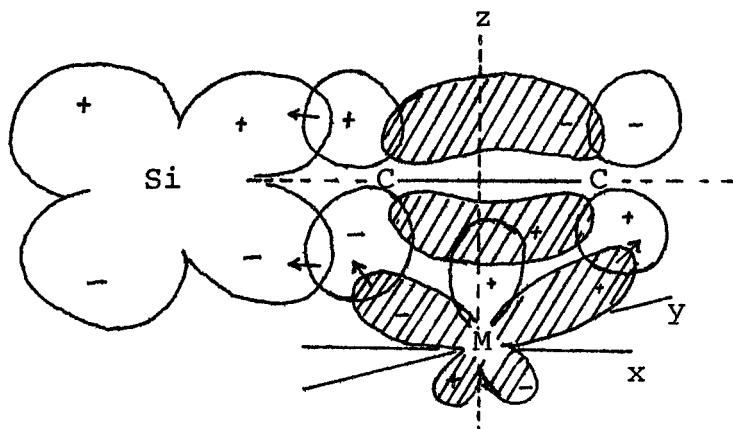


Figure 6. Proposed Bonding in Transition Metal-Vinylsilane Complexes<sup>12</sup>

The cleavage reactions described above and similar unsuccessful attempts in this laboratory to isolate various vinylsilane and allylsilane platinum(II) complexes are considered important. In this paper the C—Si bond cleavage in these newly synthesized complexes will be discussed. If the mechanism of the carbon-silicon bond cleavage reaction is understood, one can perhaps establish a criterion for the synthesis of more inert platinum(II) complexes of both vinyl and allylsilanes. These stable complexes could then be studied with respect to the perturbation in bonding caused by the presence of the silicon atom.

## Chapter II

### EXPERIMENTAL

#### A. Purification of Solvents

Pentane.--Unsaturated hydrocarbon impurities were removed by washing with concentrated sulfuric acid. Excess sulfuric acid was removed from the pentane layer by washing it with a dilute solution of sodium bicarbonate. The pentane was then washed with water several times and then dried over magnesium sulfate. It was further dried by distillation from calcium hydride after which it was stored over Linde Molecular Sieves, Type 4A, 1/16".

Benzene and Tetrahydrofuran.--Trace amounts of water were removed from benzene or tetrahydrofuran by refluxing the compound for three to five hours over calcium hydride. The dry compound was then distilled from calcium hydride and stored over Linde Molecular Sieves, Type 4A, 1/16".

Acetone.--Reagent acetone was dried by allowing it to percolate through a two foot long column packed with 1/16" pellets of 4A Linde Molecular Sieve.<sup>39</sup> The acetone was then distilled from a small amount of powdered Linde Molecular Sieves, Type 4A, 1/16", and it was used immediately after distillation.

Carbon Tetrachloride.--Trace amounts of water were removed by drying carbon tetrachloride over calcium sulfate for twenty four hours. The solvent was then distilled and stored over Linde Molecular Sieves, Type 4A, 1/16".

#### B. Analytical Procedures

Melting Point.--Melting points of all compounds were determined on a Unit-melt Capillary Melting Point Apparatus, A. H. Thomas Company.

Infrared Analysis.--All infrared (IR) spectra were determined on a Beckman IR-10 Spectrometer. Spectra of solid samples were either recorded in Nujol mulls or as KBr wafers. Spectra of liquid samples were obtained on either neat samples or in carbon tetrachloride solutions. Spectra of gases or gaseous products were recorded in a 10cm gas cell. All spectra were calibrated with polystyrene.

Nuclear Magnetic Resonance Analysis.--Nuclear magnetic resonance (NMR) spectra of compounds were recorded on a Perkin-Elmer R-12A Spectrometer. Solvents used were carbon tetrachloride and deuterated benzene, chloroform, acetone, and dimethylsulfoxide. The standard internal reference used was tetramethylsilane (TMS) and/or the non-deuterated impurities of the solvents after calibration with TMS.

Carbon and Hydrogen Analysis.--All carbon and hydrogen analyses were determined by Galbraith Laboratories, Knoxville,

Tennessee. Samples were submitted in evacuated, sealed ampoules or in sealed, nitrogen-filled ampoules.

Gas Chromatography.--All reactions involving cleavage of the carbon-silicon bond were monitored on a Gow-Mac Series 550 Gas Chromatograph using thermal conductivity detectors.

Thermal Analysis.--Thermogravimetric analyses were performed on a Cahn, "Little Gem" system with a model RM-2 Electrobalance which was calibrated with copper sulfate pentahydrate.

### C. Preparation of Reagents

Vinyltrimethylsilane and allyltrimethylsilane.--Vinyltrimethylsilane and allyltrimethylsilane were commercially available and were purchased from PCR Incorporated, Gainesville, Florida. These reagents were used without further purification. The IR spectra appearing in Appendix I are as follows: vinyltrimethylsilane (No. 1); allyltrimethylsilane (No. 2).

Preparation of  $\beta$ -styryltrimethylsilane.-- $\beta$ -styryltrimethylsilane was prepared by a standard, described method.<sup>40</sup> In a typical preparation, a 3000 ml flask, equipped with a stirrer, reflux condensor, and dropping funnel was charged with dry magnesium powder (24.6 g, 1.02 g-atom). The apparatus was evacuated and then flushed with nitrogen. The magnesium was covered with 1050 ml of anhydrous ethyl ether and stirred. A solution of methyl iodide (2 ml in 150 ml

tetrahydrofuran) was added drop-wise to initiate the reaction.

$\beta$ -Bromostyrene (203.4 g, 1.11 mol, in 300 ml tetrahydrofuran) was added drop-wise from the dropping funnel over a period of 45 minutes. The reaction started after 30 minutes of warming. The mixture was refluxed for 15 hours, and it turned brown during the refluxing period. After the reaction mixture had been cooled, dry benzene (300 ml) was added into the flask, and chlorotrimethylsilane (123.0 g, 1.14 mol) was added cautiously from the dropping funnel because the reaction is exothermic. At the end of this addition period the mixture had turned murky and was refluxed for 32 hours. It was then cooled to room temperature and hydrolysed with a saturated solution of ammonium chloride. The layers were separated, and the organic layer was dried over magnesium sulfate for 24 hours. The solvent was then removed in vacuo at room temperature.

The high-boiling point product,  $\beta$ -styryltrimethylsilane, was purified from the residue by fractional distillation (the  $\beta$ -styryltrimethylsilane distilled at 56 - 58°/0.8 mm Hg). The product obtained weighed 75.0 g (38% yield). The product was identified by its IR and NMR spectra which were compared with authentic spectra. The synthesized product was identified as the trans-isomer (99.9% purity) by its observed J-value (19 Hz) which is in accord with literature values<sup>35</sup> for the vinylic hydrogens.

The IR and NMR spectra can be seen in Appendix I spectrum No. 3 and Appendix II spectrum No. 1 respectively.

Anal. Calcd. for  $C_{11}H_{16}Si$ : C = 74.90%, H = 9.08%.  
Found: C = 75.07%, H = 9.12%.

Potassium Trichloro(ethylene)platinum(II).--Potassium trichloro(ethylene)platinum(II) (Zeise's salt) and precursors to Zeise's salt were prepared by literature methods.<sup>41,42</sup> The procedure by Kauffman and Cowan was used for the reduction of potassium hexachloroplatinate(IV) ( $K_2PtCl_6$ ) to potassium tetrachloroplatinate(II) ( $K_2PtCl_4$ ).<sup>43,44</sup>

In a typical preparation, the platinum metal (16.36 g, 83.9 mmol) was digested in 100 ml aqua regia (3 ml HCl : 1 ml  $HNO_3$ ). The reaction mixture was digested on a steam bath until all platinum metal was in solution. The solution was then concentrated on a low-temperature hotplate (150°). Concentrated HCl (100 ml) was then added, and the solution was again concentrated until the total volume was 25 ml. Upon cooling, orange crystals of hexachloroplatinic(II) acid ( $H_2PtCl_6 \cdot H_2O$ ) precipitated.

The precipitate was dissolved in 155 ml of water, and a solution of KCl (6.65 g, 0.089 mol in 125 ml of water) was added to the solution of the complex. Immediately, a yellow precipitate of potassium hexachloroplatinate(IV) was observed. An equal volume of ethyl alcohol was added, and the mixture was cooled in an ice bath to insure complete crystallization.

The yellow crystals of  $K_2PtCl_6$  (15.59 g, 32.1 mmol) were suspended in 150 ml of water. To effect reduction of  $K_2PtCl_6$ , half the equivalent amount of hydrazine chloride (1.69 g, 16.6 mmol) was added slowly to the stirred solution. The mixture was quickly warmed to 60° at which time the reaction occurred, and the solution turned deep red with the evolution of nitrogen gas. The solution was then heated to 60° for ten minutes to complete the reaction. Trace amounts of deposited elemental platinum were removed by filtration. The solution was concentrated by heating on a hot plate (125°) until crystals of  $K_2PtCl_4$  were observed.

To precipitate  $K_2PtCl_4$  a two liter mixture of two parts of acetone and one part of ethyl ether was added to the deep red-brown solution of  $K_2PtCl_4$ . Light pink crystals of  $K_2PtCl_4$  immediately precipitated and were collected by filtration.

To prepare Zeise's salt,  $K_2PtCl_4$  (6.29 g, 15.2 mmol) was dissolved in 60 ml of a 4% HCl-water mixture. The solution was transferred into a glass pressure bottle, charged with ethylene gas (50 p.s.i.), and allowed to shake for 48 hours in a Parr Pressure Reaction Apparatus. At the end of this period, the color of the solution had changed from dark red to yellow. The solution was filtered to remove trace amounts of elemental platinum that had formed. The filtrate, Zeise's salt in solution, was dried in a desiccator containing concentrated sulfuric acid and potassium

hydroxide pellets. After the salt had dried, it was dissolved in dry acetone to separate it from KCl and unreacted  $K_2PtCl_4$ . The acetone solution of Zeise's salt was evaporated under reduced pressure to yield a solid yellow product (3.4 g, 9.21 mmol, 60.86% yield). Infrared and NMR spectra of the product appear in Appendix I (No. 4) and Appendix II (No. 2) respectively.

Potassium Trichloro(vinyltrimethylsilane)platinate(II).--Potassium trichloro(vinyltrimethylsilane)platinate(II) was prepared by a described method.<sup>36</sup> Zeise's salt (1.02 g, 2.6 mmol) was placed in a Schlenk tube which was then evacuated. Acetone (15 ml) was added against the countercurrent of nitrogen to dissolve the salt. Evolution of gas was observed as excess vinyltrimethylsilane (3.0 ml, 20.7 mmol) was added to the Zeise's salt solution. At the end of a 30 minute period the color of the solution had changed from light yellow to orange. At this point the murky reaction mixture was filtered. The clear orange filtrate was evaporated under reduced pressure to yield a dull yellow product which was subsequently dried in vacuo in a desiccator containing phosphorus pentoxide. The product (1.04 g, 92.3% yield) decomposed at 107°. The IR and NMR spectra of the complex were identical to those of known samples. IR and NMR spectra appear in Appendix I (No. 5) and Appendix II (No. 3) respectively.

Potassium Trichloro(allyltrimethylsilane)platinum(II).--Potassium trichloro(allyltrimethylsilane)platinum(II) was prepared by the reaction of Zeise's salt (3.37 g, 9.1 mmol) with allyltrimethylsilane (2.0 ml, 12.0 mmol) in acetone (15 ml).<sup>37</sup> Evolution of ethylene gas was observed after the ligand was added. The mixture was allowed to react for one hour during which time the color changed from yellow to deep orange. At the end of the reaction period the mixture was filtered to remove insoluble impurities. Excess ligand and acetone were removed from the filtrate under reduced pressure. The solid product was washed with dry pentane and dried in vacuo. The product (3.76 g, 90%) decomposed at 160-165° without melting. The IR and NMR spectra of the product were identical with those of a known sample. The IR and NMR spectra appear in Appendix I (No. 6) and Appendix II (No. 4) respectively.

Di- $\mu$ -Chlorodichlorobis(ethylene)platinum(II)  
Zeise's dimer).--Zeise's dimer<sup>45</sup> was prepared by adding Zeise's salt to a 250 ml Erlenmeyer flask which contained HCl (2.5 ml concentrated HCl in 50 ml absolute alcohol). The mixture was vigorously stirred for 15 minutes. The mixture was murky and was, therefore, filtered to remove potassium chloride. The absolute alcohol was removed by simple distillation to reduce the volume to half the original.

The remaining absolute alcohol and HCl were removed by evaporation under reduced pressure. To crystallize the initially oily product it was necessary to pump hard on the oil. The product was recrystallized from boiling toluene. The Zeise's dimer (0.22 g, 49% yield) obtained was dull orange. It was wrapped with aluminum foil and stored in vacuo in a desiccator containing phosphorus pentoxide. The IR spectrum of the product was identical to that of a known sample of Zeise's dimer.

Di- $\mu$ -Chlorodichlorobis(allyltrimethylsilane)platinum(II) (Allyl Dimer).--Allyl dimer was prepared by the literature method.<sup>37</sup> Zeise's dimer (1.79 g, 3.0 mmol) was added to a Schlenk tube, which was then evacuated. Dry purified pentane was next introduced against a counter-current of nitrogen. Finally, allyltrimethylsilane (3.4 ml, 21.0 mmol) was injected into the suspension in the Schlenk tube and a brisk evolution of ethylene gas was observed. The color of the mixture changed from orange to light yellow. The mixture was stirred for 45 minutes, after which it was filtered under a nitrogen blanket, dried and then stored in vacuo. The light yellow product (2.1 g, 92.0%) decomposed without melting at 116-120°. The product was characterized by comparing its IR spectrum with that of a known sample.

$\pi$ -Acetylacetonechloroacetylacetona platinum(II).-- $\pi$ -Acetylacetonechloroacetylacetona platinum(II), was prepared by the method described in the literature,<sup>45</sup> except

that the chlorobis(acetylacetonato)platinum(II) intermediate was by-passed. In a typical preparation, potassium tetrachloroplatinate(II) (6.04 g, 14.5 mmol) was dissolved in 50 ml of water in a round-bottomed flask, and potassium hydroxide (4.15 g, dissolved in 10 ml of water) was added. The 2,4-pentanedione (11.0 ml, 0.107 mol) was then injected into the mixture.

The reaction was stirred vigorously and heated to 55-60° for 1.5 hours. After the mixture had cooled it was chilled in an ice bath and filtered. When the filtrate was acidified with 6N HCl a bright yellow precipitate formed immediately. The mixture was cooled and then filtered. The product was dried in vacuo, and its IR spectrum was identical to that of a known sample. No further analysis was performed on the product.

Acetylacetonatochloro(ethylene)platinum(II).--

$\pi$ -Acetylacetonechloroacetylacetonatoplatinum(II) (11.25 g, 26.0 mmol) was dissolved in dry benzene (200 ml), and ethylene was then bubbled through the solution for 45 minutes. The solution, which turned light orange, was allowed to stand for 1.5 hours. The benzene was removed by evaporation under reduced pressure, and the dingy yellow product was dried and stored in vacuo. The IR of the product was identical to that of a known sample.

Anal. Calcd. for  $\text{PtCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_2\text{H}_4)$  : C = 23.47%, H = 3.09%. Found: C = 23.93%, H = 3.29%.

Acetylacetonatochloro(allyltrimethylsilane)platinum(II).--Acetylacetonatochloro(ethylene)platinum(II) (0.59 g, 1.3 mmol) was dissolved in a Schlenk tube containing dry benzene (22 ml) with a nitrogen atmosphere. Excess allyltrimethylsilane (3.0 ml, 18.9 mmol) was injected, and the mixture was stirred for one hour. Evolution of ethylene gas was observed, and the solution turned bright yellow. Excess ligand and benzene were removed by evaporation under reduced pressure. The residue was washed with purified pentane dried and stored in vacuo. The bright yellow product (0.49 g, 85.0%) decomposed at 94-98° without melting. The IR spectrum (No.1) of the product was recorded and appears in Appendix I.

Anal. Calcd. for  $\text{PtCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3)$  :  
 $\text{C} = 29.76\%$ ,  $\text{H} = 4.77\%$ . Found:  $\text{C} = 30.09\%$ ,  $\text{H} = 4.69\%$ .

#### D. Reactions of Vinylsilanes

Reaction of Vinyltrimethylsilane with Acetylacetanatochloro(ethylene)platinum(II).--Acetylacetanatochloro(ethylene)platinum(II) (0.46 g, 1.28 mmol) was added into a Schlenk tube which was then evacuated and back filled with nitrogen. The sample was dissolved in dry benzene (15 ml), and vinyltrimethylsilane (2.0 ml, 5.2 mmol) was added against a counter-current of nitrogen. Decomposition occurred in 10 minutes. The reaction was allowed to continue for an additional 20 minutes. The mixture turned dark brown, and evolution of a gas was observed during the reaction.

After the reaction period, the dark mixture was filtered to remove elemental platinum, but the filtrate was still dark brown. Celite was added to the filtrate to remove colloidal platinum and it was filtered again. The filtrate was, however, still quite brown. Excess ligand and solvent were then removed by evaporation under reduced pressure. The IR and NMR spectra of the isolated brown residue were unsatisfactory.

The experiment was repeated, but this time reaction was allowed to take place at 0° in an ice bath for 30 minutes. Evolution of ethylene gas was observed. The solution did not show any decomposition during the reaction, but immediate decomposition occurred on attempted isolation of the product. No further analysis was made on the dark brown residue.

Reaction of  $\beta$ -Styryltrimethylsilane with Acetylacetatochloro(ethylene)platinum(II).--Acetylacetatochloro(ethylene)platinum(II) (1.28 g, 3.57 mmol) was placed in a Schlenk tube which was then evacuated and back filled with nitrogen. Dry benzene (15 ml) was added as solvent.  $\beta$ -styryltrimethylsilane (1.1 ml, 5.5 mmol) was injected into the solution of the complex against a nitrogen counter-current. Bubbles of ethylene gas were observed to evolve after addition of the ligand. The solution turned light brown immediately and dark brown after 45 minutes. Celite was added to the dark solution which was then filtered.

The filtrate was dark brown. The solvent and excess ligand were removed by evaporation under reduced pressure. The dark brown residue was dissolved in dry benzene to remove insoluble impurities, but the residue was completely soluble and left no solid elemental platinum. The NMR spectrum of the residue obtained was not satisfactory. Gas chromatographic analysis of the distillate indicated the presence of chlorotrimethylsilane and hexamethyldisiloxane.

Reaction of  $\beta$ -Styryltrimethylsilane with Zeise's salt.--Zeise's salt (1.21 g, 3.13 mmol) was added to a fritted flask. The fritted flask was evacuated and back filled with nitrogen. This was repeated three times to ensure complete removal of traces of water in the apparatus. Acetone (10 ml), dried immediately before use, was added as solvent against a counter-current of nitrogen, and finally  $\beta$ -styryltrimethylsilane (2.0 ml, 10.5 mmol) was injected into the fritted flask. The solution was stirred for 45 minutes, and evolution of ethylene gas was observed during the reaction. After 15 minutes the solution turned dark, and the reaction was allowed to continue for 20 hours.

The black solution was filtered and evaporated under reduced pressure to remove the solvent and volatile products. The gas chromatographic analysis of the distillate indicated the presence of only chlorotrimethylsilane. The dark brown residue was washed with purified pentane to remove excess

$\beta$ -styryltrimethylsilane. The pentane washings were evaporated to a small volume after which tan crystals were observed to form on the side of the container. The mixture was then filtered, and the tan crystals (0.21 g, 65%) were obtained and analysed. The IR and NMR spectra of this product appear in Appendix I (No. 8) and Appendix II (No. 5) respectively. Its observed melting point was 150-151° (literature<sup>35</sup> m.pt. 150-151°). The product was identified as trans,trans-1,4-diphenyl-1-3-butadiene.

#### E. Hydrolytic Cleavage of Vinylsilane and Allyl-silane Platinum(II) Complexes

Hydrolysis of Potassium Trichloro(vinyltrimethylsilane)platinate(II) with Methanol.--Potassium trichloro(vinyltrimethylsilane)platinate(II) (1.24 g, 30.6 mmol) was placed in a test tube, and methanol (10 ml) was added. The test tube was stoppered and allowed to stand for a week. The solution turned black because of deposition of elemental platinum. The solution was filtered to remove the black residue, and an orange filtrate was obtained. The methanol and volatile products were distilled under reduced pressure into a trap immersed in a dry ice-ethanol bath. The yellow product isolated was identified as Zeise's salt by its NMR spectrum (No. 6) in Appendix II which was identical to that of a known sample. The volatile products were injected into the gas chromatograph, and the analysis of the gas

chromatogram indicated the presence of methoxytrimethylsilane and a small amount of HCl which was also detected by pH paper.

Hydrolysis of Potassium Trichloro(vinyltrimethylsilane)platinate(II) with Wet Acetone.--Potassium trichloro(vinyltrimethylsilane)platinate(II) (1.04 g, 2.68 mmol) was mixed with acetone (10 ml of the reagent directly from the bottle) in a test tube, stoppered, and allowed to stand for a week. Decomposition of the solution was observed. The solution was filtered, and the filtrate was evaporated under reduced pressure. A yellow residue was obtained and was identified by the NMR spectrum as Zeise's salt. The NMR spectrum (No. 7) of the product appears in Appendix II. The distillate was injected into the gas chromatograph, and the analysis of the gas chromatogram indicated the presence of hexamethyldisiloxane.

The experiment was repeated in deuteroacetone, and the decomposition was monitored by NMR. A concentrated solution of potassium trichloro(vinyltrimethylsilane)-platinate(II) in deuteroacetone was placed into an NMR tube. The successive decomposition stages were monitored by running the NMR spectrum at intervals. The NMR spectrum obtained at the end of the hydrolysis was identical to that of an authentic sample of Zeise's salt.

Hydrolysis of Potassium Trichloro(allyltrimethylsilane)platinate(II) with Pure Water and Aqueous Solutions of Potassium Chloride.--Potassium trichloro(allyltrimethyl-

silane)platinate(II) (0.6 g, 1.30 mmol) was added to each of four test tubes. Distilled water (25 ml) was added to test tube 1, and 25 ml of potassium chloride (0.5M, 2M, and saturated) was added to each of the remaining three test tubes. The complex was found to be slightly soluble in the aqueous solvents. Immediately after the addition of each solvent, a pH sensitive electrode was placed into the solution to measure the amount of HCl generated from the hydrolysis of the complex. The data were plotted in the graph which appears in Figure 7.

Each of the four test tubes was allowed to stand for 24 hours to complete the slow hydrolysis. Insoluble orange-yellow crystals were observed to form during the hydrolysis. After the 24 hour period, the insoluble orange-yellow crystals were isolated by filtration, washed with distilled water, and then small amounts of acetone. The products were dried in vacuo in a desiccator over phosphorus pentoxide. The yellow filtrate was evaporated under reduced pressure to give orange-yellow crystals which were washed with acetone and distilled water to remove the expected propene complex<sup>40</sup> and potassium chloride. The products were dried in vacuo in the presence of phosphorus pentoxide.

The washings described above were evaporated under reduced pressure, and the residues were washed with distilled water to remove potassium chloride. This third crop of crystals was obtained in very small quantities.

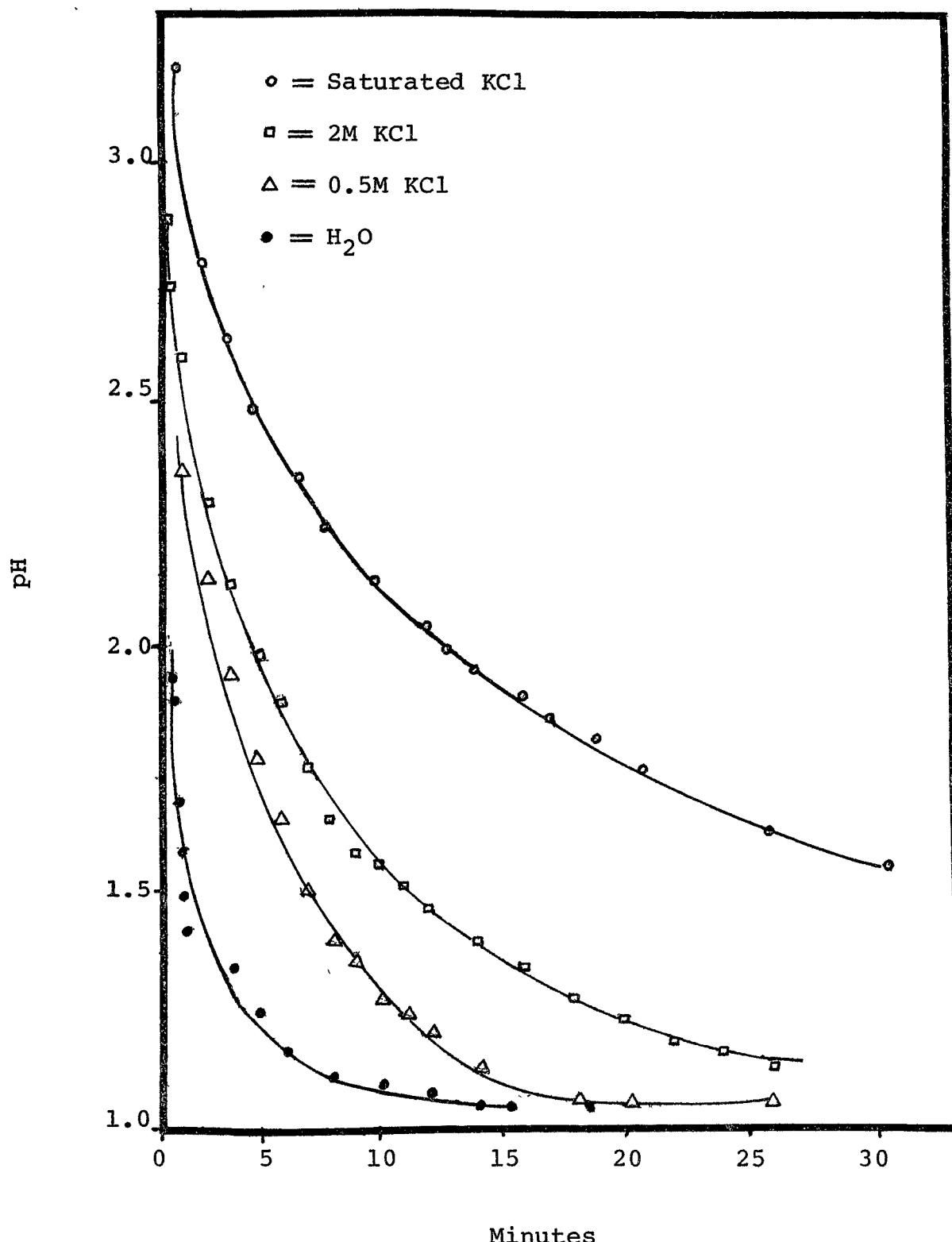


Figure 7. Hydrolysis of Potassium Trichloro-(allyltrimethylsilane)platinate(II)

The IR spectra of all isolated products were obtained. However, the NMR spectra were obtained only in deuteriodimethylsulfoxide because the complexes are insoluble in all other solvents tested. The IR and NMR spectra of the product obtained from the water hydrolysis appear in (Appendix I, No. 9) and (Appendix II, No. 8) respectively.

Anal. Calcd. for  $(C_3H_5PtCl)_x$ : C = 13.25%, H = 1.85%.  
Found: C = 13.71%, H = 1.93%.

The hydrolysis in the potassium chloride solutions gave identical solid products. IR spectrum (No. 10) (only one is shown since the complexes gave identical IR spectra) is shown in Appendix I and NMR spectrum (No. 9) in Appendix II are typical.

Anal. Calcd. for  $(C_3H_5PtCl)_4$ : C = 13.25%, H = 1.85%.  
Found: C = 13.34%, H = 1.86%.

The complexes obtained from the hydrolysis in potassium chloride solutions were tentatively identified as tetrameric allylchloroplatinum(II). However, the complex from the hydrolysis in pure water was different and was tentatively identified as  $(C_3H_5PtCl)_x$ . The experimental data from these reactions are summarized in Table I.

Hydrolysis of Di- $\mu$ -Chlorodichlorobis(allyltrimethylsilane)platinum(II) With Pure Water and Aqueous Potassium Chloride Solution.--Di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II) (0.6 g, 0.79 mmol) was added to each of

Table I

Analytical Data on Hydrolysis Products of Potassium  
Trichloro(allyltrimethylsilane)platinate(II)

Sample No.	1	2	3	4
Reagent used	water	saturated KCl	2M KCl	0.5M KCl
Complex used	1.3 mmol	1.3 mmol	1.3 mmol	1.3 mmol
Total yield	0.35 g (98%)	0.25 g (71%)	0.28 g (79%)	0.34 g (96%)
Decomposition point	150-156°	159-170°	159-170°	150-165°
Solubility in regular solvents	insoluble	insoluble	insoluble	insoluble
Solubility in dimethylsulfoxide*	soluble	soluble	soluble	soluble

\*Solubility in dimethylsulfoxide involves solvent-ligand exchange reaction.

three test tubes. Distilled water (25 ml) was added to one of the test samples, and potassium chloride was added to the other two samples. The rest of the experimental procedure was performed as described in the preceding experiment. The generation of HCl as a function of time after addition of each solution is shown in Figure 8.

The IR spectra of the complexes isolated from the hydrolyses with potassium chloride solutions and water were identical to the spectra of a tetramer,  $(C_3H_5PtCl)_4$ , and its isomer,  $(C_3H_5PtCl)_x$ , respectively. The other analytical data are summarized in Table 2.

Reaction of Acetylacetonatochloro(allyltrimethylsilane)platinum(II) With Wet Acetone.--Acetylacetonato-chloro(allyltrimethylsilane)platinum(II) (0.46 g, 1.04 mmol) was added to a test tube, and wet reagent grade acetone (10 ml) was added to the sample. The test tube was stoppered and allowed to stand for a week. Initially, a small amount of a green precipitate formed, but finally, an orange product precipitated. The orange crystals were obtained by filtration and were dried in vacuo. The complex decomposed at 155-158° without melting. The IR spectrum (No. 11) of the product appears in Appendix I. The product was identified as  $(C_3H_5PtCl)_4$  by correlation of the IR spectrum with that of a known sample.

Anal. Calcd. for  $(C_3H_5PtCl)_4$  : C = 13.25%, H = 1.85%.  
Found: C = 13.80%, H = 1.86%.

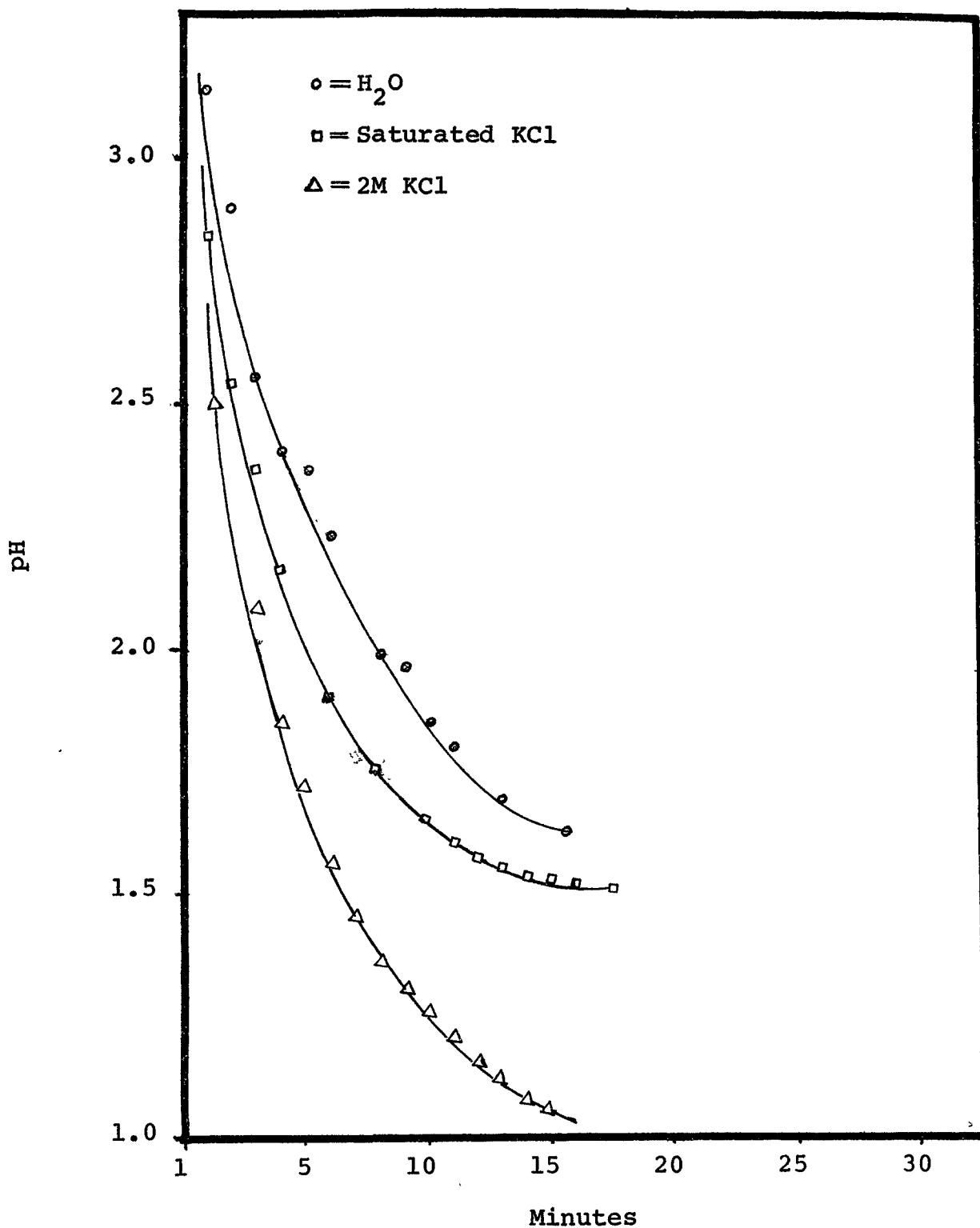


Figure 8. Hydrolysis of Di- $\mu$ -chlorodichloro-(allyltrimethylsilane)platinum(II)

Table II

Analytical Data on Hydrolysis Products of Di- $\mu$ -Chloro-dichloro(allyltrimethylsilane)platinum(II)

Sample No.	1	2	3
Reagent used	water	2M KCl	saturated KCl
Amount of Complex used	0.79 mmol	0.79 mmol	0.79 mmol)
Total yield	0.38 g (44%)	0.38 g (44%)	0.40 g (46%)
Decomposition point	150-156°	159-165°	159-165°
Solubility in regular solvents	insoluble	insoluble	insoluble
Solubility in dimethylsulfoxide*	soluble	soluble	soluble

\* Solubility in dimethylsulfoxide involves solvent-ligand exchange reaction.

The filtrate was evaporated under reduced pressure, and the distillate was captured in a trap cooled with a dry ice-ethanol bath. Analysis of the distillate by gas chromatography revealed the presence of free acetylacetone and hexamethyldisiloxane.

#### F. Pyrolytic Cleavage Reactions

General Procedure.--All pyrolytic decomposition reactions were performed in an apparatus as shown in Figure 7. A known quantity of a sample under investigation was placed in a Schlenk tube which was connected to a trap whose other outlet was closed. The apparatus was evacuated, and the trap was placed in the dry ice-ethanol bath. The complex was heated in a silicon oil bath to its decomposition point, and the volatile products were collected in the trap.

The trap was warmed to room temperature and then connected to an evacuated 10cm IR gas cell. The volatile products were swept with dry nitrogen into the gas cell after which the IR spectrum of the product(s) was obtained.

Pyrolysis of Potassium Trichloro(vinyltrimethylsilane)platinate(II).--In a typical reaction, potassium trichloro(vinyltrimethylsilane)platinate(II) (0.19 g, 0.47 mmol) was placed in a Schlenk tube connected to a trap. The whole assembly (Figure 9) was evacuated. The trap was then placed in a dry ice-ethanol bath, and the sample was

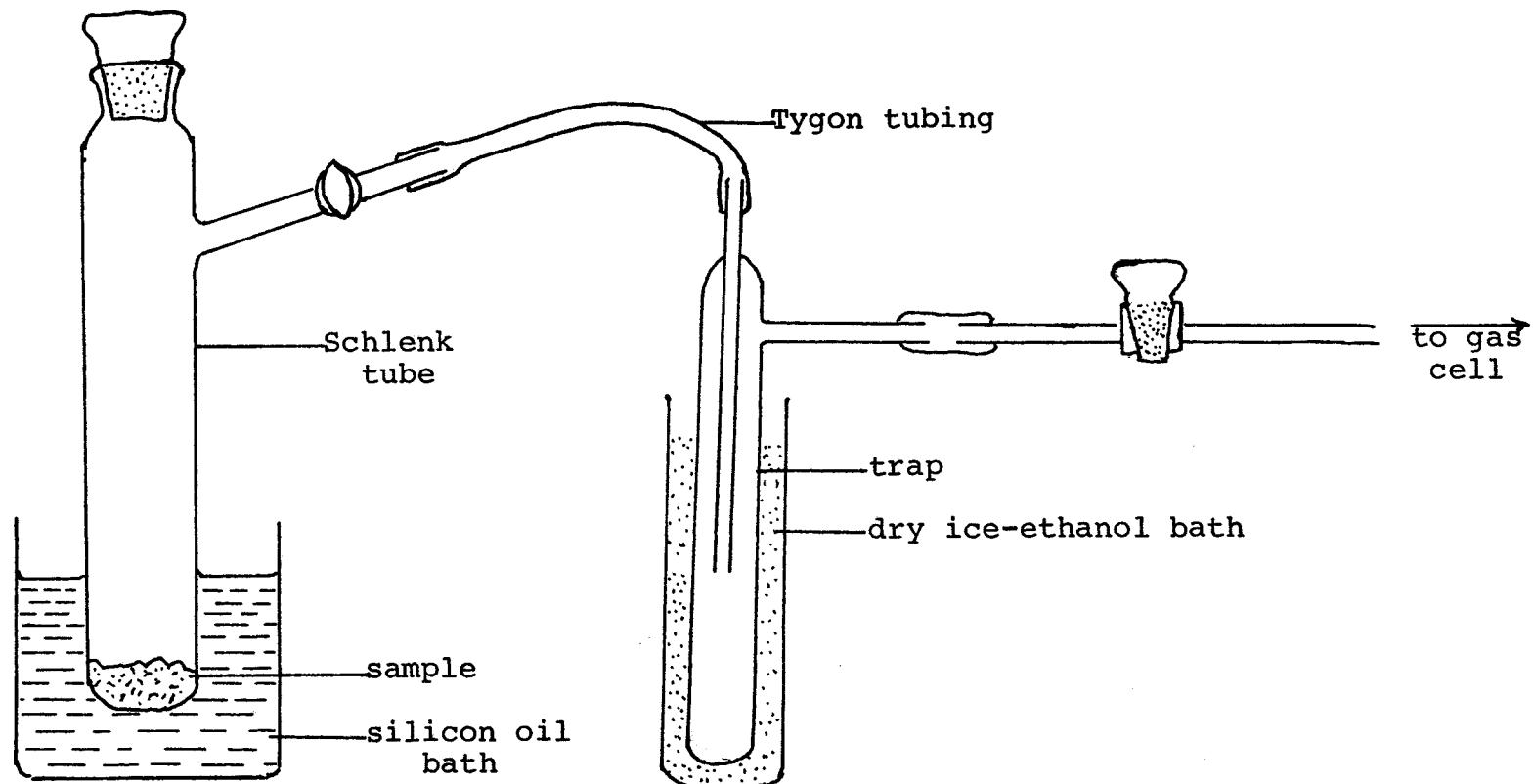


Figure 9. General Pyrolysis Apparatus

heated in a silicon oil bath at 185°. The temperature was maintained at 185° for 30 minutes to insure complete decomposition into a black residue.

At the end of the pyrolysis, the trap containing volatile products was allowed to warm to room temperature. An evacuated gas cell was then connected to the trap. The volatile products were swept into the gas cell with dry nitrogen and an IR spectrum (No. 12 in Appendix I) was obtained. The IR spectrum of the products was identical to the IR spectrum of a known sample of chlorotrimethylsilane. The product in the trap fumed in air and was acidic.

Pyrolysis of Potassium Trichloro(allyltrimethylsilane)platinate(II).--Potassium trichloro(allyltrimethylsilane)platinate(II) (0.95 g, 2.0 mmol) was placed into a Schlenk tube, connected to a trap, and the apparatus was evacuated. The trap was then placed in dry ice-ethanol bath, and the sample was maintained at a maximum temperature of 210° for 15 minutes.

The trap was allowed to warm to room temperature, and the volatile products were characterized. The IR (gas cell) and NMR spectra of the volatile products are shown in Appendix I (No. 13) and Appendix II (No. 10), respectively. The volatile products in the trap were dissolved in a minimum amount of benzene. The gas chromatographic analysis of the solution indicated the presence of hexamethyldisiloxane, chlorotrimethylsilane, acetone and a small amount of the ligand.

Pyrolysis of Di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II).--In a typical decomposition reaction, di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II) (0.92 g, 1.20 mmol) was pyrolysed by the method described in the preceding experiments. The sample was maintained at a maximum temperature of 210° for 5 hours. The IR (gas cell) and NMR spectra of the volatile products appear in Appendix I (No. 14) and Appendix II (No. 11), respectively. Gas chromatography indicated the presence of hexamethyldisiloxane, chlorotrimethylsilane, acetone and the ligand, allyltrimethylsilane.

Pyrolysis of Acetylacetonatochloro(allyltrimethylsilane)platinum(II).--Acetylacetonatochloro(allyltrimethylsilane)platinum(II) (0.17 g, 0.38 mmol) was also pyrolysed by the general method described above. The sample was maintained at a maximum temperature of 180° for 2 hours. The IR spectrum (No. 15) of the volatile products is shown in Appendix I. The gas chromatographic analysis indicated the presence of chlorotrimethylsilane.

#### G. Thermogravimetric Analyses under Nitrogen

Thermogravimetric Analysis of Potassium Trichloro(vinyltrimethylsilane)platinate(II).--Potassium trichloro(vinyltrimethylsilane)platinate(II) (9.21 mg) was analysed for weight loss upon heating. The complex gave an initial weight loss of 0.41 mg (4.4%) at 90°. A second weight loss

of 2.1 mg (22.8%) was observed at 110°. Further weight loss beyond 270° was also observed. The thermogravimetric curve is graphically shown in Figure 10.

Thermal Analysis of Potassium Trichloro(allyl-trimethylsilane)platinate(II).--Thermogravimetric analysis of the allyltrimethylsilane complex (8.55 mg) gave an initial weight loss of 2.2 mg (25.7%) at 200°. Further weight loss was observed beyond this temperature. The thermogravimetric curve of the complex appears in Figure 11.

Thermal Analysis of Di- $\mu$ -chlorodichlorobis(allyl-trimethylsilane)platinum(II).--The thermogravimetric analysis of the dimeric allyltrimethylsilane complex (7.5 mg) gave an initial weight loss of 1.9 mg (25%) within the temperature range of 108-132° and a second weight loss of 1.38 mg (18.4%) from 132° to 160°. The thermogravimetric curve is shown in Figure 12.

Thermal Analysis of Acetylacetonatochloro(allyl-trimethylsilane)platinum(II).--Thermogravimetric analysis of the sample (9.34 mg) gave an initial weight loss of 3.7 mg (41%) and a second weight loss of about 0.96 mg (10%). The thermogravimetric curve is shown in Figure 13. Decomposition occurred between temperatures of 93° and 183°.

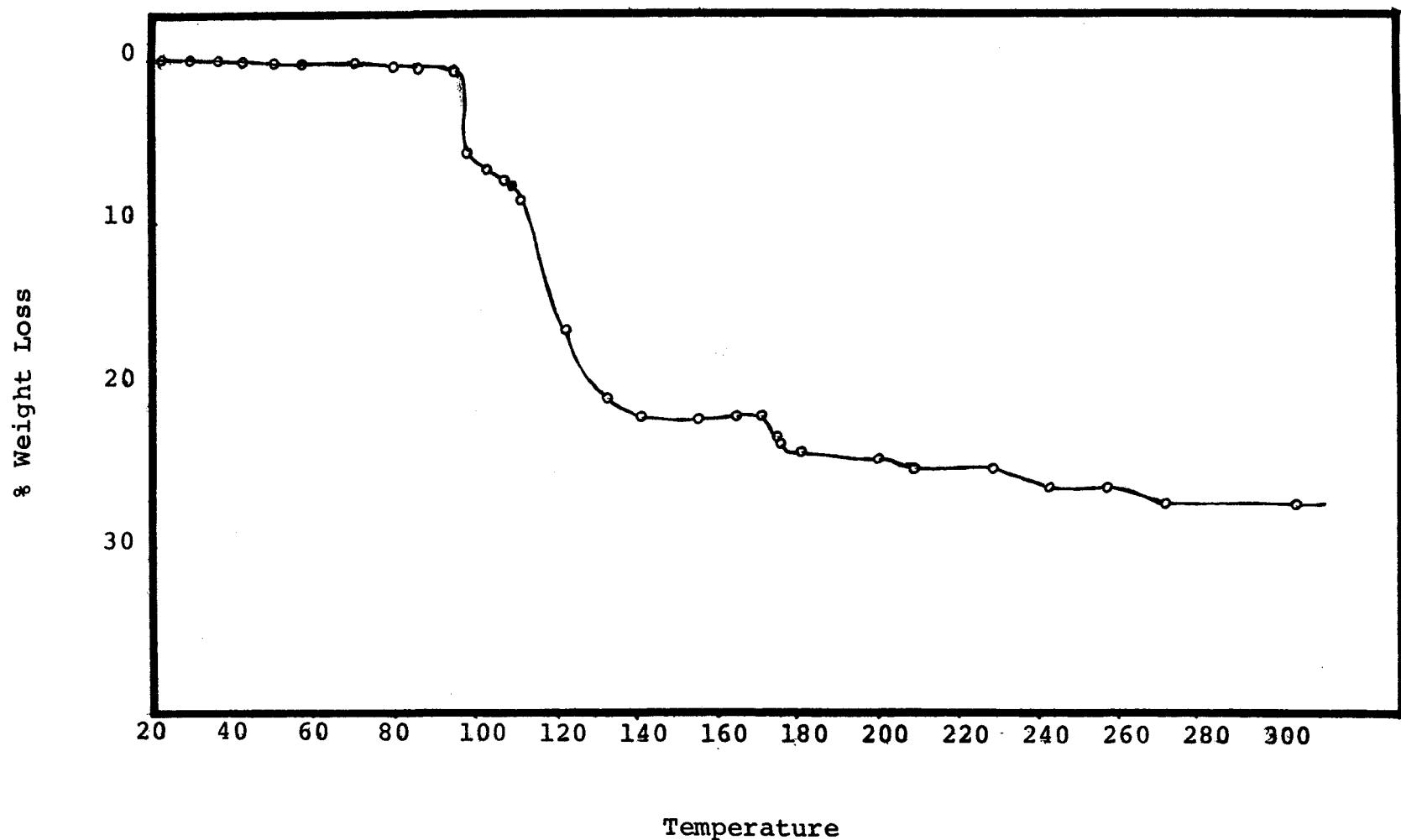


Figure 10. Thermogravimetric Analysis of Vinyltrimethylsilane Complex

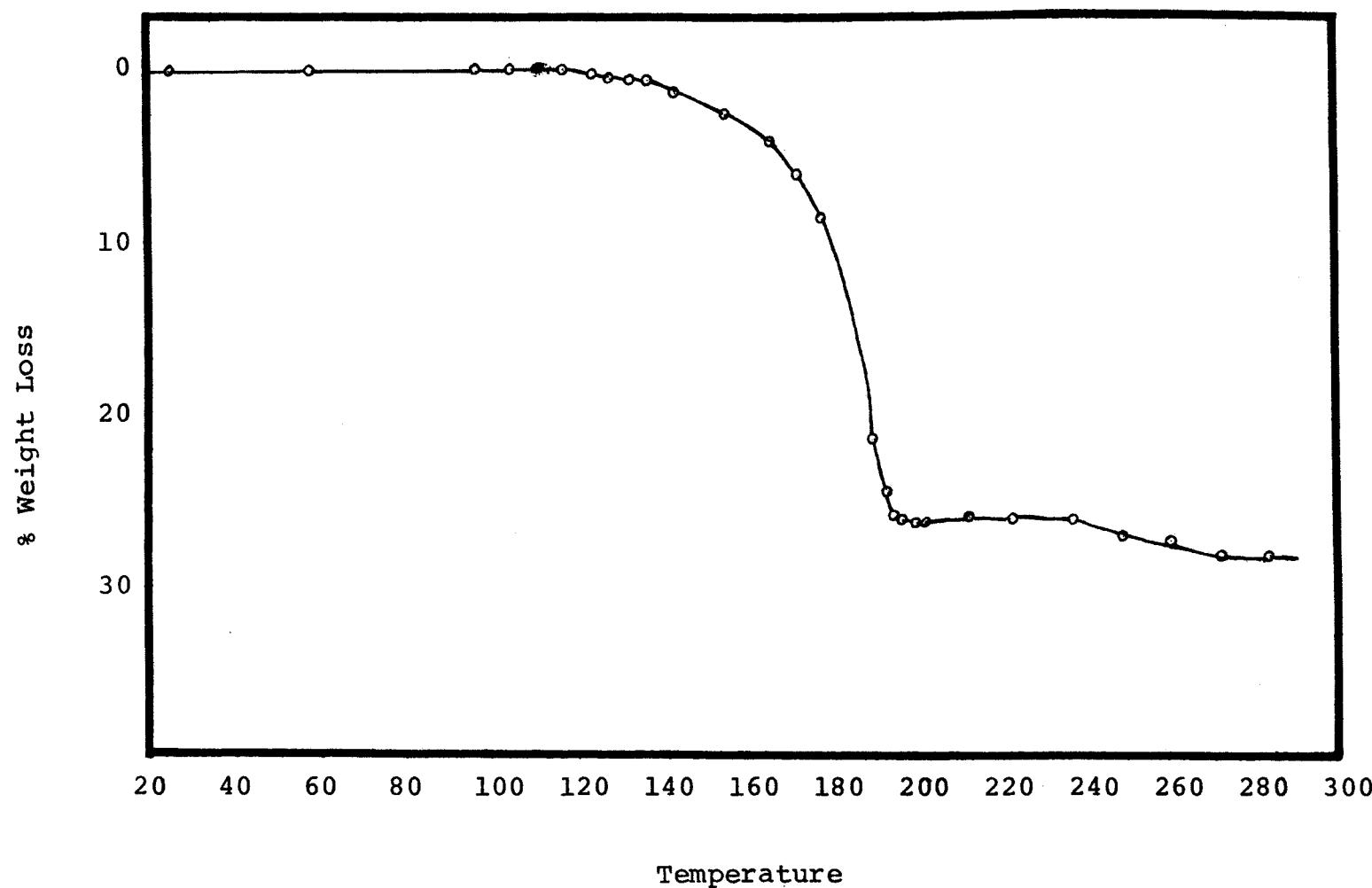


Figure 11. Thermogravimetric Analysis of Potassium  
Trichloro(allyltrimethylsilane)platinate(II)

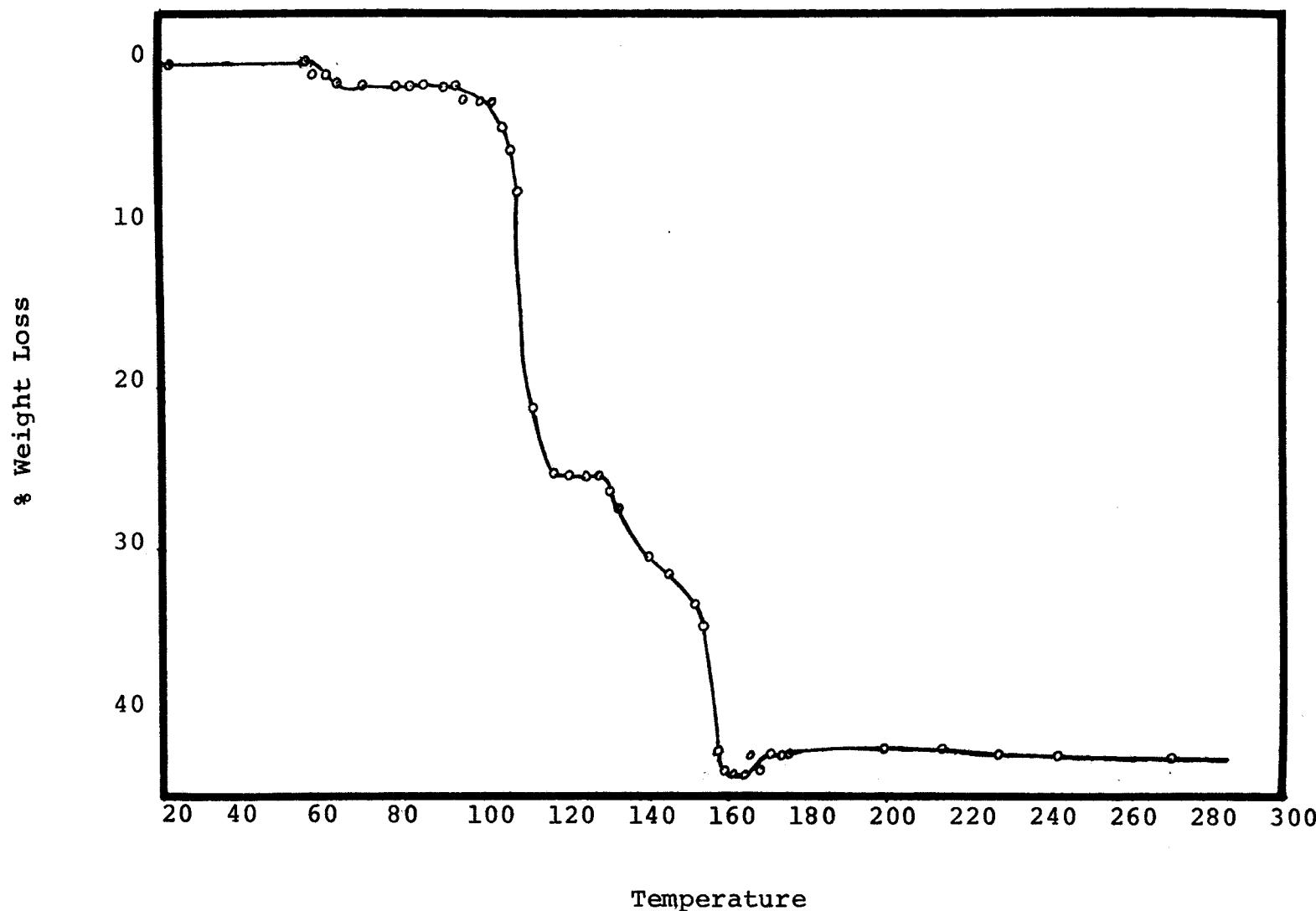


Figure 12. Thermogravimetric Analysis of Di- $\mu$ -chlorodichloro-(allyltrimethylsilane)platinum(II)

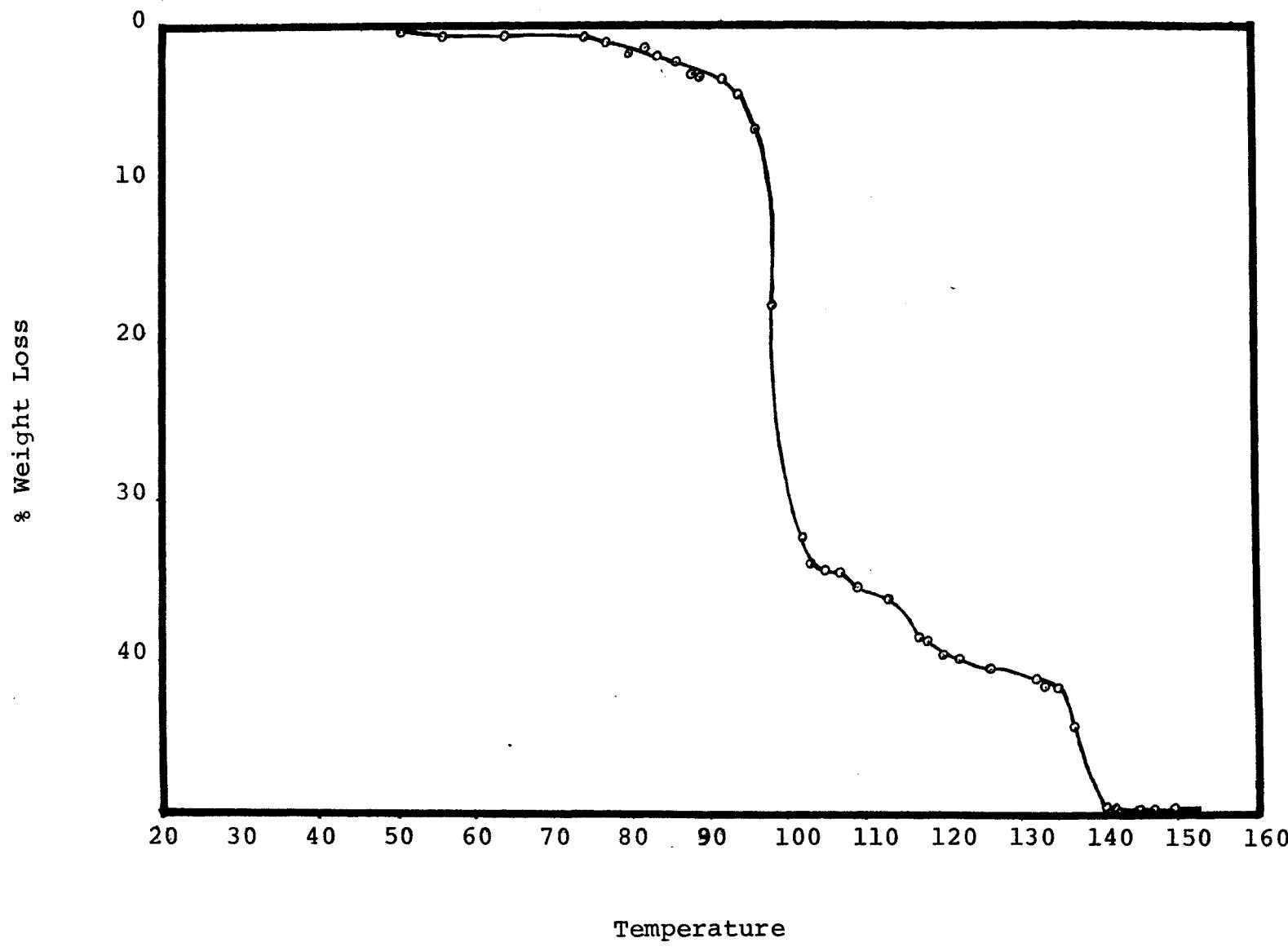


Figure 13. Thermogravimetric Analysis of Acetylacetonatochloro-(allyltrimethylsilane) platinum(II)

## Chapter III

### DISCUSSION

#### A. Introduction

While the cleavage of the alkynyl carbon-silicon bond can be accomplished by several nucleophiles including hydroxide<sup>47</sup> and fluoride ions,<sup>48</sup> the corresponding cleavage of the vinyl carbon-silicon bond by nucleophilic displacement at silicon is rare.<sup>49</sup> Thus vinyltrimethylsilane is stable toward potassium fluoride in refluxing ethanol,<sup>48</sup> and the compound  $\text{CH}_3\text{CH}=\text{CHSiH}_3$  is not cleaved by hot aqueous alkali.<sup>50</sup>

Furthermore, Becker and Tsutsui<sup>18</sup> have also reported that vinyl groups are cleaved from silicon by means of nucleophilic agents only with relative difficulty. For example it is necessary to use severe conditions such as very concentrated solutions of bases or alkoxides and high temperatures.<sup>51</sup> Allyl groups, in contrast, are cleaved under less severe conditions by reagents such as aqueous alcoholic solutions of bases<sup>50</sup> or potassium carbonate.<sup>52</sup> Furthermore, both vinyl and allyl groups are cleaved from the silicon atom at low temperatures by strong nucleophiles such as concentrated sulfuric acid.<sup>49</sup>

Recent investigations of cleavage reactions have indicated that vinylsilanes are easily cleaved at the vinyl carbon-silicon bond by both platinum(II)<sup>33</sup> and palladium(II)<sup>35</sup> halides. Similarly, the cleavage of the allyl carbon-silicon bond in allyltrimethylsilane by several compounds of the transition metals has been the subject of a few reports. Reactions of allyltrimethylsilane with Zeise's salt in refluxing ethanol,<sup>33</sup> mercury(II) chloride in acetonitrile,<sup>32</sup> and lithium tetrachloroplatinate(II) in methanol have conclusively indicated that the trimethylsilyl group is removed from the allyl carbon. In addition, the reaction with tetrachloropalladate(II) ion yielded the stable compound  $\pi$ -allylpalladium chloride.<sup>34</sup>

Fitch, Haschke and Quick have also reported similar cleavage reactions in which the trimethylsilyl group is removed from allyltrimethylsilane by potassium tetrachloroplatinate(II) in 4% hydrochloric acid solution.<sup>37</sup> Fitch and Haschke have also recently reported the cleavage of the carbon-silicon bond of co-ordinated vinyltrimethylsilane.<sup>36</sup> These cleavage reactions as well as several pyrolysis reactions have been further studied and are herein reported.

## B. Hydrolytic Cleavage Reactions

Hydrolysis of Potassium Trichloro(vinyltrimethylsilane)platinate(II) in Methanol.--The hydrolysis of potassium trichloro(vinyltrimethylsilane)platinate(II),  $K[PtCl_3C_2H_3Si(CH_3)_3]$ , gave the products expected according to a four centered attack at silicon by methanol as shown in Figure 14. The isolation of Zeise's salt from this

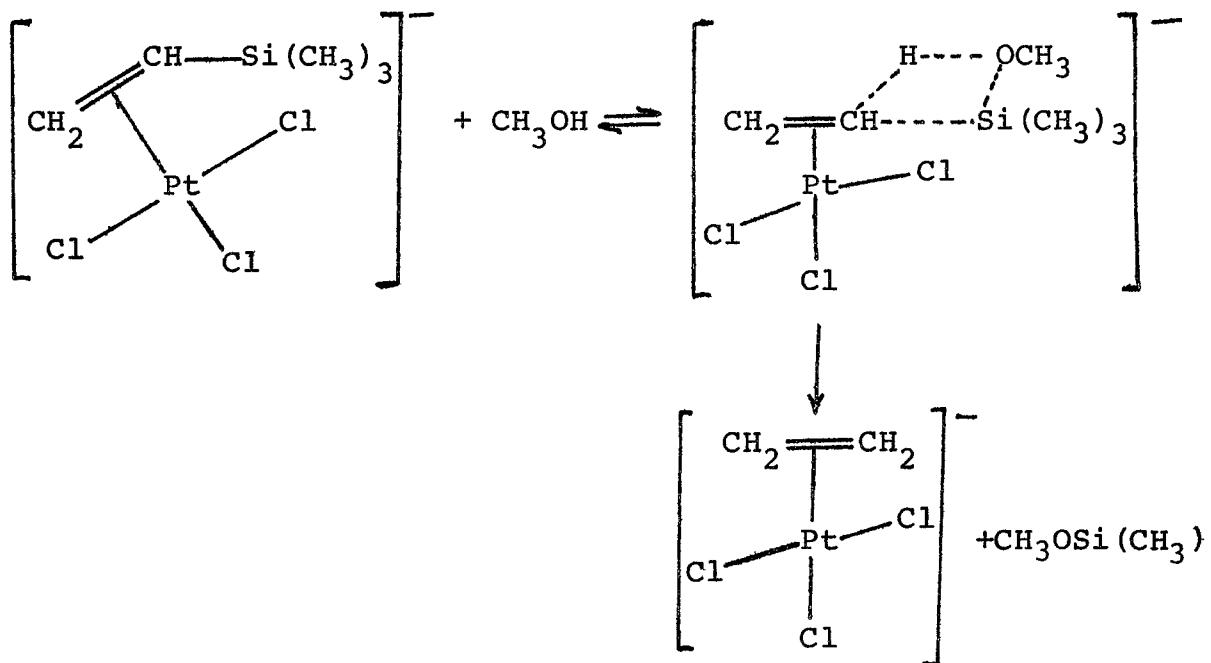


Figure 14. Postulated Mechanism for Methanol Attack on Silicon in Potassium Trichloro(vinyltrimethylsilane)platinate(II)

reaction suggests that the cleavage of the vinyl carbon-silicon bond is due to nucleophilic attack on the silicon by methanol. When the methanol was evaporated from the filtered reaction mixture and subjected to gas chromatographic analysis, it was found to contain methoxytrimethyl-

silane as required by the suggested mechanism. However, the evaporated volatile components from the reaction mixture were observed to be slightly acidic. This observation could be explained by a competing mechanism involving chloride ion attack on silicon which might lead to some decomposition of the complex. Indeed, decomposition was indicated by the brown color of the reaction mixture. The yellow residue obtained from the evaporated filtrate gave an NMR spectrum identical to that of a known sample of Zeise's salt. This spectrum contained a sharp singlet peak at  $5.76\tau$  and symmetrically spaced satellite peaks ( $J = 64$  cps) on both sides of the main singlet peak. The main singlet peak at  $5.75\tau$  was attributed to ethylenic protons, and the satellites arise from  $^1\text{H}^{195}\text{Pt}$  coupling ( $^{195}\text{Pt}$  has a 33.7% natural abundance).

A second mechanism assumes an intermediate containing co-ordinated methanol. The mechanism is shown in Figure 15. The first step involves the reversible displacement of chloride ion from the vinylsilane complex, I, to form a neutral intermediate complex II. Complex III is then formed upon deprotonation of II after which methoxide could attack the  $\beta$ -carbon of the co-ordinated vinylsilane to give intermediate IV. IV can then undergo  $\beta$ -elimination of methoxytrimethylsilane to give, ultimately, Zeise's salt, or it can decompose and give a variety of products. Alternatively, the co-ordinated methoxide ion could attack silicon directly.

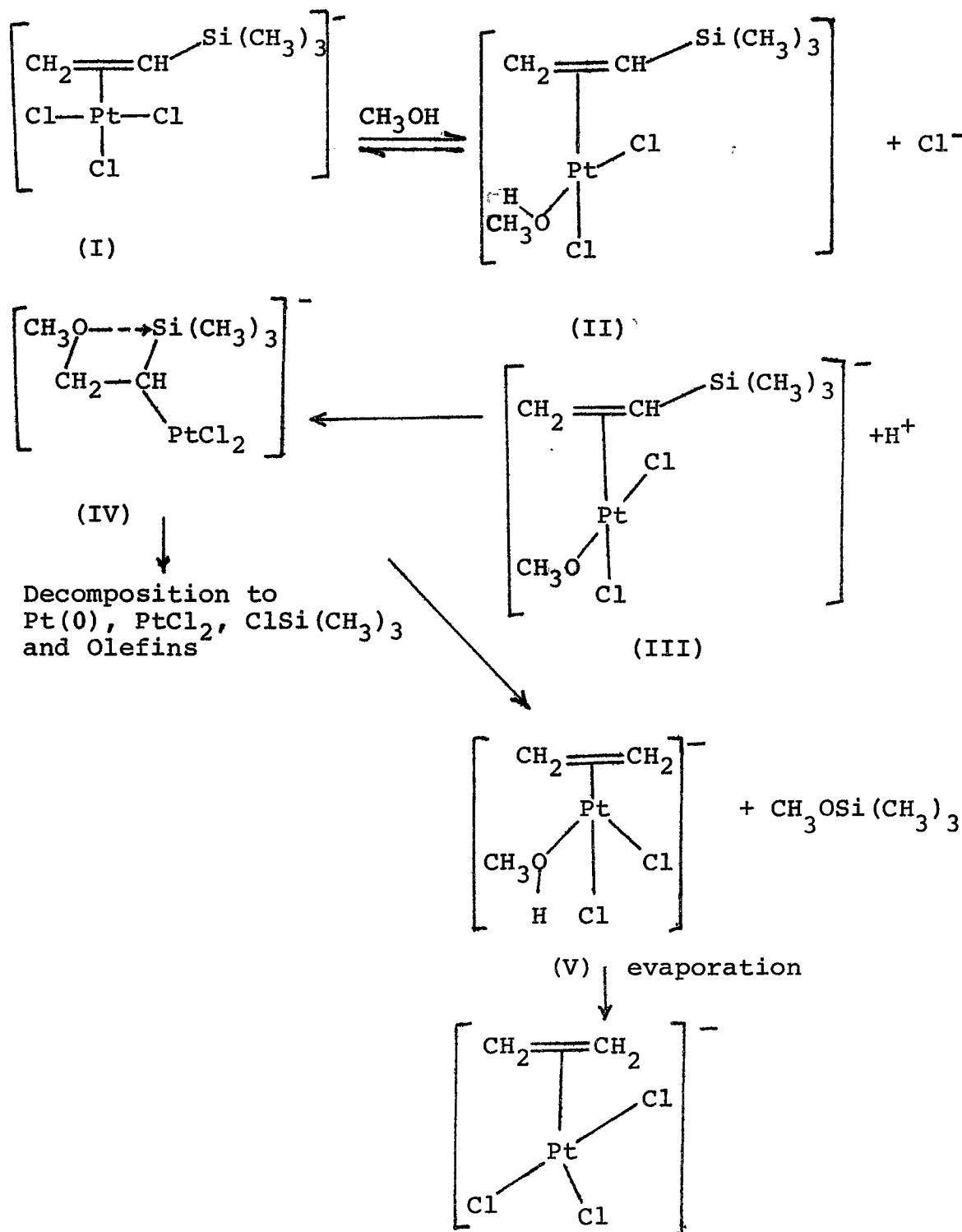


Figure 15, Proposed Mechanism for Silicon-Carbon Bond Cleavage in Methanol Solution of Potassium Trichloro(vinyltrimethylsilane)platinate(II)

Weber and co-workers<sup>35</sup> have proposed a mechanism in the reaction of  $PdCl_2$  with  $\beta$ -styryltrimethylsilane which is similar to that shown in Figure 15. Chlorotrimethylsilane is obtained according to their mechanism by  $\beta$ -elimination from an intermediate formed from formal addition of a Pd-Cl moiety across the styrene double bond. However, the intermediate was not isolated.

Hydrolysis of Potassium Trichloro(vinyltrimethylsilane)-platinate(II).--The hydrolysis of this complex in wet acetone was studied next. The yellow residue obtained after evaporating the filtered reaction mixture to dryness gave an NMR spectrum identical to that of a known sample of Zeise's salt. Gas chromatographic analysis of the distillate indicated the presence of only hexamethyldisiloxane.

Two mechanisms involving nucleophilic attack on silicon by water can be postulated. The first mechanism, which seems unlikely, involves direct attack on the silicon by water in a manner similar to that shown in Figure 14 for attack by methanol.

The second mechanism similar to that previously described for the methanolysis of the vinyltrimethylsilane complex is illustrated in Figure 16. It involves the equilibrium displacement of chloride ion by water to form a neutral intermediate aquo complex, II, which subsequently

deprotonates to form a hydroxo complex ion, III. The hydroxide ion then cleaves the vinyl carbon-silicon bond in the presence of water to form complex, IV, and hexamethyl-disiloxane. The transient  $\sigma$ -vinyl platinum complex, IV, then could undergo two competitive reactions. The first reaction would be Pt-C bond fission leading to decomposition with formation of elemental platinum. The second reaction, which likely predominates, involves the attack by a proton at the carbon-platinum  $\sigma$  bond to generate co-ordinated ethylene (complex V). V is converted to Zeise's salt when the solution is evaporated.

The hydrolysis of the vinyltrimethylsilane complex was next conducted in wet acetone-d<sub>6</sub> and monitored by NMR. The product obtained was confirmed to be Zeise's salt. Attempts to examine the hydrolysis of potassium trichloro(vinyltrimethylsilane)platinate(II) in pure water failed because of extensive decomposition in this medium which resulted in the deposition of black residues and the generation of acidic solutions.

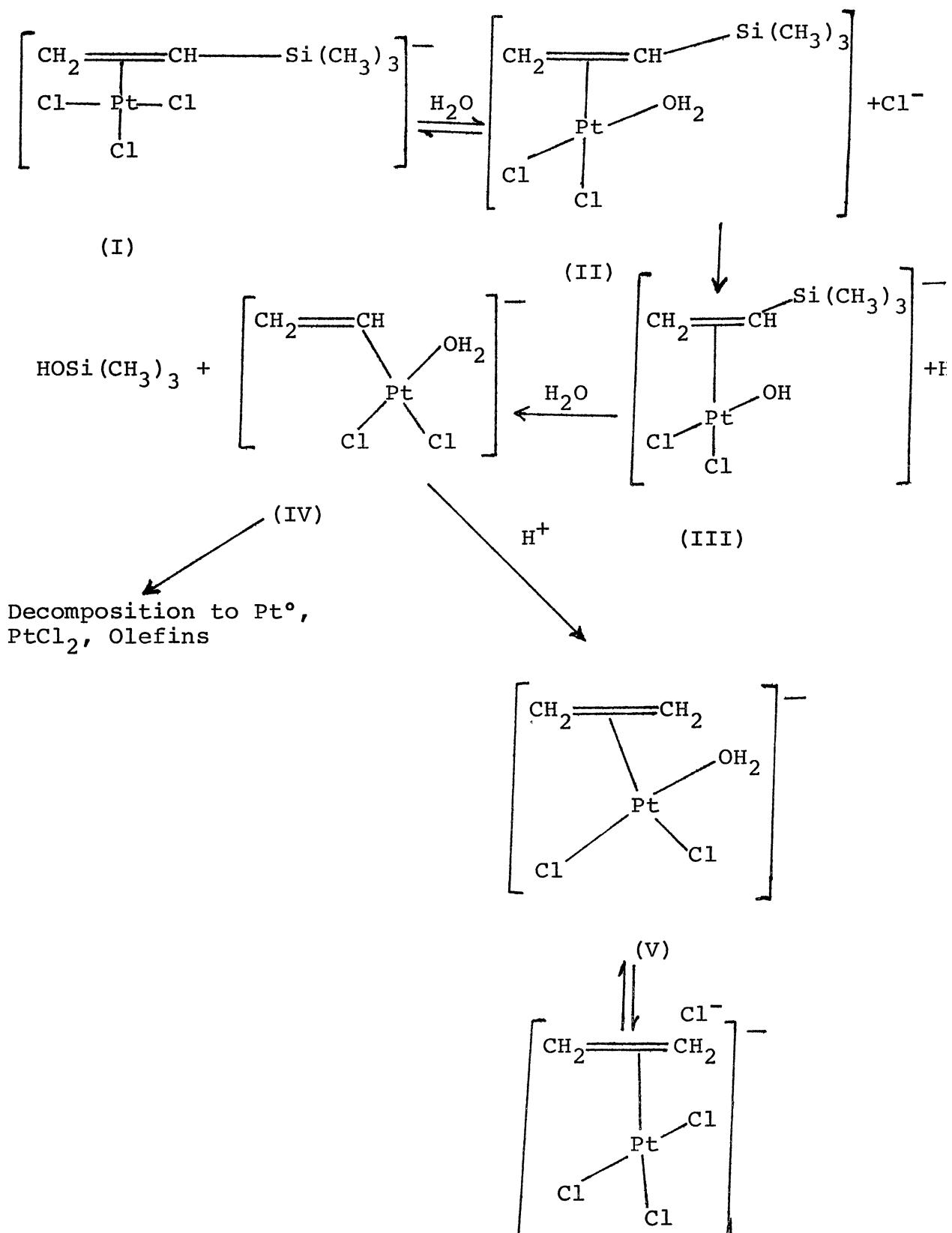


Figure 16. Proposed Mechanism for the Attack of Silicon in Potassium Trichloro(vinyltrimethylsilane)platinate(II)

### C. Reaction of $\beta$ -Styryltrimethylsilane with Zeise's Salt

An attempt was made next to prepare the  $\beta$ -styryltrimethylsilane complex of platinum(II) in order to examine further the mechanism and stereochemistry of the hydrolysis of vinylsilane platinum(II) complexes. However, attempts to isolate this complex at room temperature under a nitrogen atmosphere were unsuccessful. Repeated experiments were performed using the freshly distilled and dried solvents, acetone, acetonitrile, benzene, and tetrahydrofuran. In each case there was massive decomposition immediately after the addition of the ligand,  $\beta$ -styryltrimethylsilane. However, the complex appears to be stable at 0° or lower temperatures but decompose instantly at room temperature. The fact that a brisk evolution of ethylene was observed after the addition of the ligand, suggests that the complex was formed although it decomposed immediately at room temperature. These observations therefore suggest that the  $\beta$ -styryltrimethylsilane platinum(II) complex is very unstable.

The decomposed mixture was filtered to removed the black residue which was presumed to be mainly elemental platinum. The filtrate was evaporated to dryness, and the residue was washed with pentane several times. The pentane washings were evaporated to dryness, and crystals of a product identified as trans,trans-1,4-diphenyl-1,3-butadiene were formed. This compound had IR and NMR spectra superimposable with those of

a known sample. The volatile product was gas chromatographically identified as chlorotrimethylsilane.

Weber *et al.* performed a similar experiment in which they also obtained trans, trans-1,4-diphenyl-1,3-butadiene from the reaction of  $\beta$ -styryltrimethylsilane with palladium chloride in methanol.<sup>35</sup> A possible mechanism, illustrated in Figure 17, is basically that proposed by Weber and co-workers for palladium complexes and studied by Tsuji.<sup>54,55</sup>

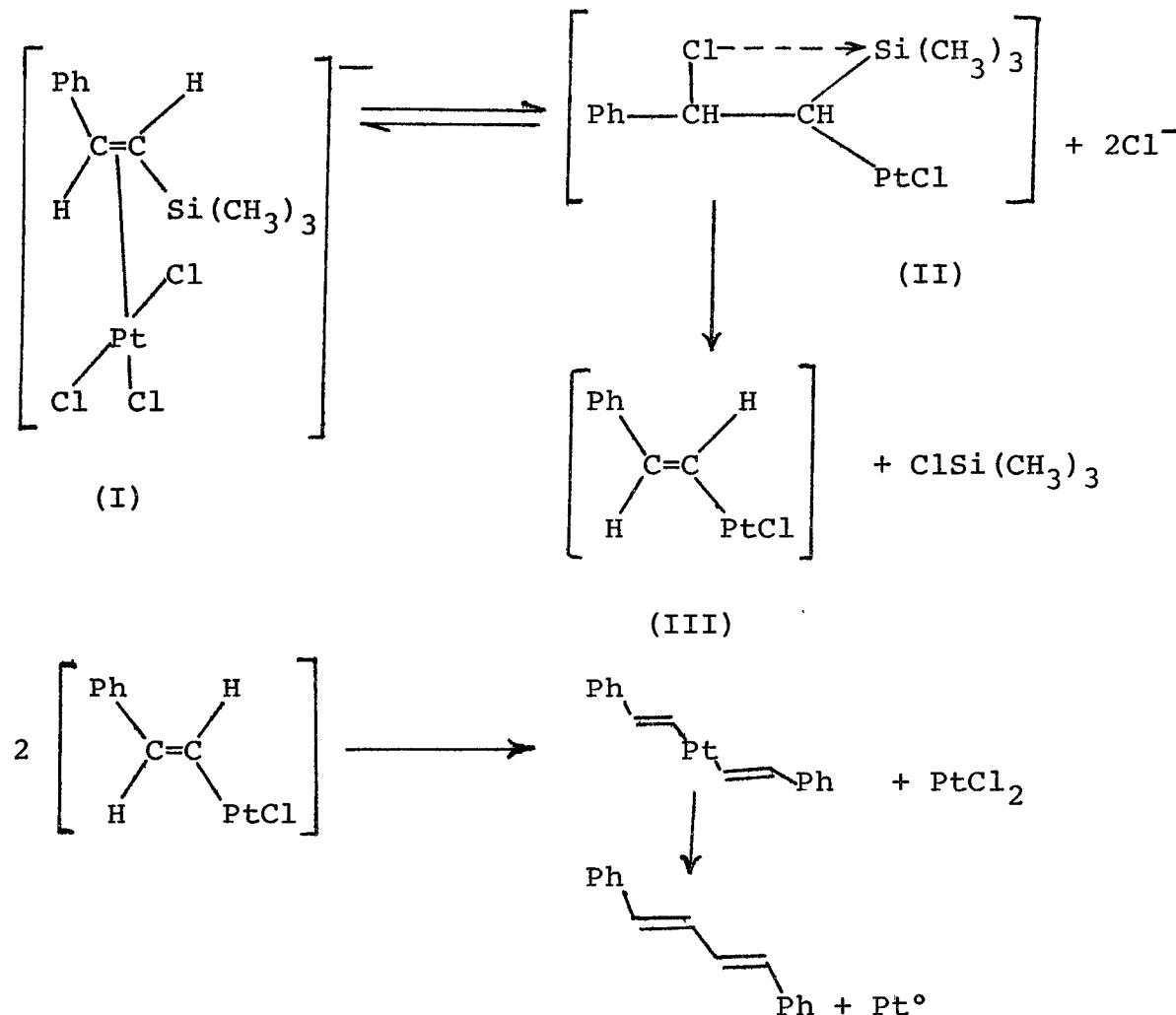


Figure 17. Proposed Cleavage Mechanism of  $\beta$ -Styryltrimethylsilane Platinum(II) Complex

The instability of the complex, potassium trichloro-( $\beta$ -styryltrimethylsilane)platinate(II), may be accounted for by steric effects resulting from the substitution in the vinyl group at both ends in the  $\beta$ -styryltrimethylsilane. Anderson reported that in general the effects of substitution in vinyl groups is to lower greatly the stability of their complex salts.<sup>4</sup>

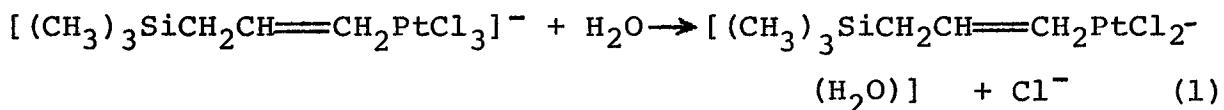
#### D. Hydrolysis of Allyltrimethylsilane Platinum(II) Complexes

Qualitative kinetic experiments on the hydrolysis of potassium trichloro(allyltrimethylsilane)platinate(II) with both pure water and potassium chloride solutions were performed to determine if the chloride ion is a catalyst for this reaction. The HCl generated in the hydrolyses of these complexes was monitored by a pH-sensitive electrode. The amount of hydrogen chloride generated was plotted against time, and the graph appears in Figure 7 of the experimental section.

The graph indicates that the rate of hydrolysis increases in direct proportion to the dilution factor. That is, the hydrolysis with saturated KCl solution was slower than the hydrolysis with a 2M KCl solution which was in turn slower than that of a 0.5M KCl solution. Furthermore, all hydrolyses in the presence of potassium chloride were slower than the hydrolysis in pure water. This inhibition of hydrolysis by potassium chloride solutions can be explained by a common ion effect.

If the first step in the mechanism of this hydrolysis involves the displacement of the co-ordinated chloride ion by

water, then this reaction would be inhibited by added chloride ion (see equation 1, below).



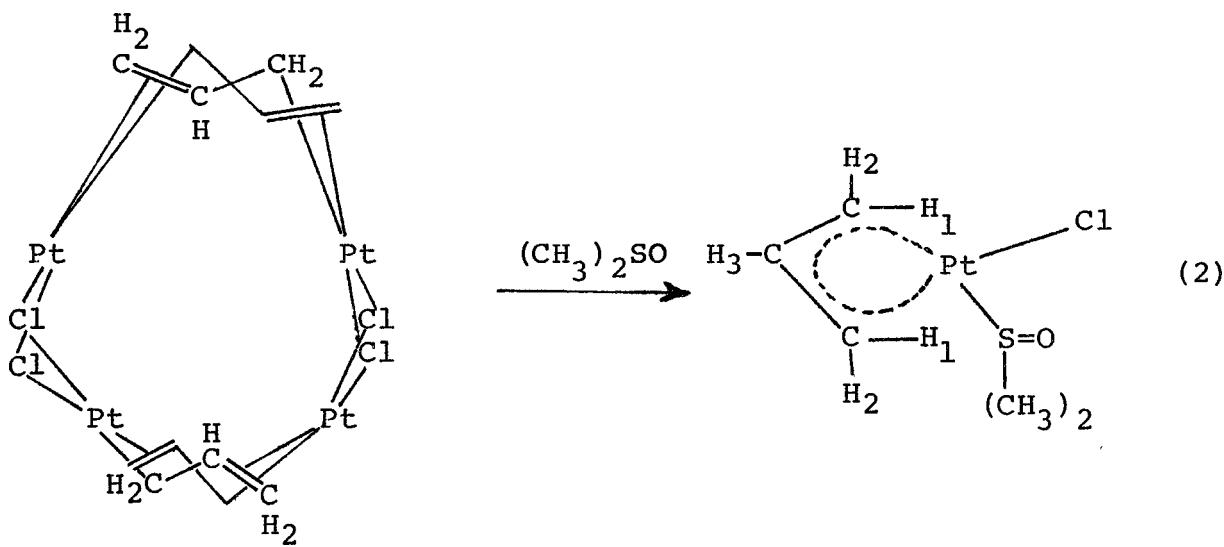
However, the results of this experiment are of somewhat limited value because of the slight solubility of the complex in aqueous solutions. Because of this low solubility the hydrolysis was conducted heterogeneously and allowed to continue for 24 hours to ensure complete reaction.

The yellow insoluble hydrolysis products were isolated by filtration and identified by their IR spectra as the tetrakis[allylchloroplatinum(II)] complex,  $(\text{C}_3\text{H}_5\text{PtCl})_4$ . The IR spectrum (No. 10 in Appendix I) of the insoluble product (1) isolated from the hydrolysis in potassium chloride solution was identical to the IR spectrum of a known sample of tetrakis[allylchloroplatinum(II)] prepared by a described method.<sup>56</sup> However, the insoluble yellow product (2) isolated from the hydrolysis in pure water gave an IR spectrum (No. 9 in Appendix I) which is different from the IR spectrum of product (1).

The IR spectra of both complexes showed a strong band at  $1480\text{cm}^{-1}$  attributed to  $\nu(\text{C}=\text{C})$  by Mann, Shaw and Shaw.<sup>6</sup> Complex (1) shows four weak bands in the region 2860 to 3000  $\text{cm}^{-1}$  while complex (2) shows only one weak band at  $2965\text{cm}^{-1}$  and a medium band at  $2918\text{cm}^{-1}$ . Complex (2) shows another sharp band at  $1374\text{cm}^{-1}$  which is very weak in complex (1).

Again the region 1080 to  $1200\text{cm}^{-1}$  has weak bands for complex (2), and two sharp bands for complex (1). Very different spectra appear in the region 350 to  $550\text{cm}^{-1}$  where complex (1) shows three medium bands at  $365\text{cm}^{-1}$ ,  $410\text{cm}^{-1}$  and  $475\text{cm}^{-1}$  respectively, while complex (2) shows only two medium bands at  $410\text{cm}^{-1}$  and  $548\text{cm}^{-1}$ .

Although the NMR spectra of many allylic complexes of transition metals have been studied,<sup>57,58</sup> the tetrameric allylchloroplatinum(II) complexes are insoluble in most organic solvents and hence not suitable for an NMR spectral characterization. Nevertheless, NMR spectra were obtained in dimethylsulfoxide- $d_6$ , which is known to react with  $\pi$ -allyl palladium(II) complexes.<sup>57</sup> Hartley has reported that bis[ $\pi$ -allylchloropalladium(II)] reacts with dimethylsulfoxide with cleavage of the halogen-bridge to give a monomeric  $\pi$ -allyl system.<sup>59</sup> A similar reaction is suggested for tetrakis[allylchloroplatinum(II)] as shown in equation 2.



Complexes (1) and (2) in dimethylsulfoxide-d<sub>6</sub> gave similar NMR spectra (Nos. 9 and 8 in Appendix II respectively). Three broad peaks arising from the proton bound to the central carbon atom (H<sub>3</sub>), the terminal anti protons (H<sub>2</sub>) and the terminal syn protons (H<sub>1</sub>) were observed. Typical  $\tau$  values are 4.9, 6.0, and 7.45, for (H<sub>3</sub>), (H<sub>2</sub>) and (H<sub>1</sub>) respectively, and these peaks have an area ratio of 1: 2: 2. These  $\tau$  values are in fair agreement with the corresponding  $\tau$  values, 4.19, 5.71 and 7.01 at -20° of  $\pi$ -allylpalladium(II) chloride-DMSO-d<sub>6</sub> adduct in chloroform-d<sub>1</sub> solution which were reported by Ramey and Statton.<sup>58</sup> Additional information concerning the allylplatinum(II) chloride complex and its equilibrium in DMSO-d<sub>6</sub> could be obtained from the temperature dependence of the NMR spectrum since it is not sharply resolved at room temperature, and this probably indicates fluxional motion.

However, the NMR and IR spectra in conjunction with elemental analysis indicate that an allylchloroplatinum(II) complex is indeed formed by hydrolysis in pure water and potassium chloride solutions. The difference between the two isomeric complexes (1) and (2) observed in the IR spectra may be attributed to different crystal orientations or degree of polymerization. X-ray diffraction studies of these complexes could certainly resolve the problem in structural determination for these complexes.

At least two mechanisms, both of which are in accord with the observed products and experimental data, can be advanced in these reactions. The first mechanism is shown in Figure 18. This mechanism postulates a direct intramolecular attack on the silicon by the chloride ion to form an

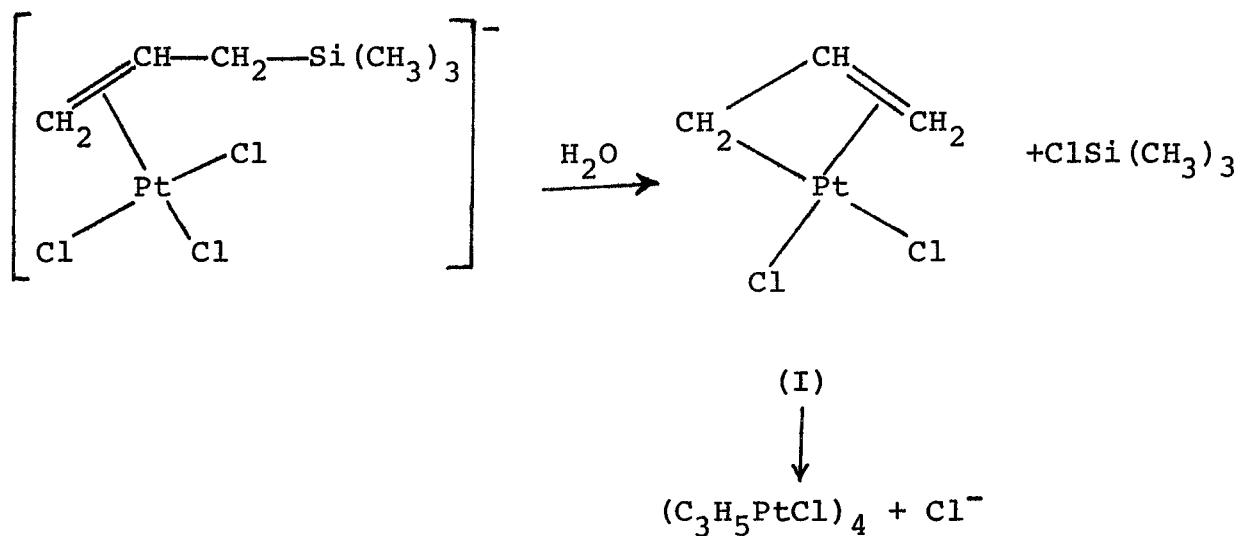


Figure 18. Proposed Mechanism for the Hydrolysis of Potassium Trichloro(allyltrimethylsilane) platinate(II)

intermediate I and chlorotrimethylsilane, which instantly hydrolyses in the presence of water to form hydrochloric acid and hexamethyldisiloxane. The intermediate I forms the tetrakis[allylchloroplatinum(II)] complex by expulsion of chloride ion.

The second mechanism illustrated in Figure 19, is the most likely. In this mechanism, the first step involves the equilibrium displacement of co-ordinated chloride ion by water<sup>53</sup> to form a neutral aquo complex, I. The aquo complex

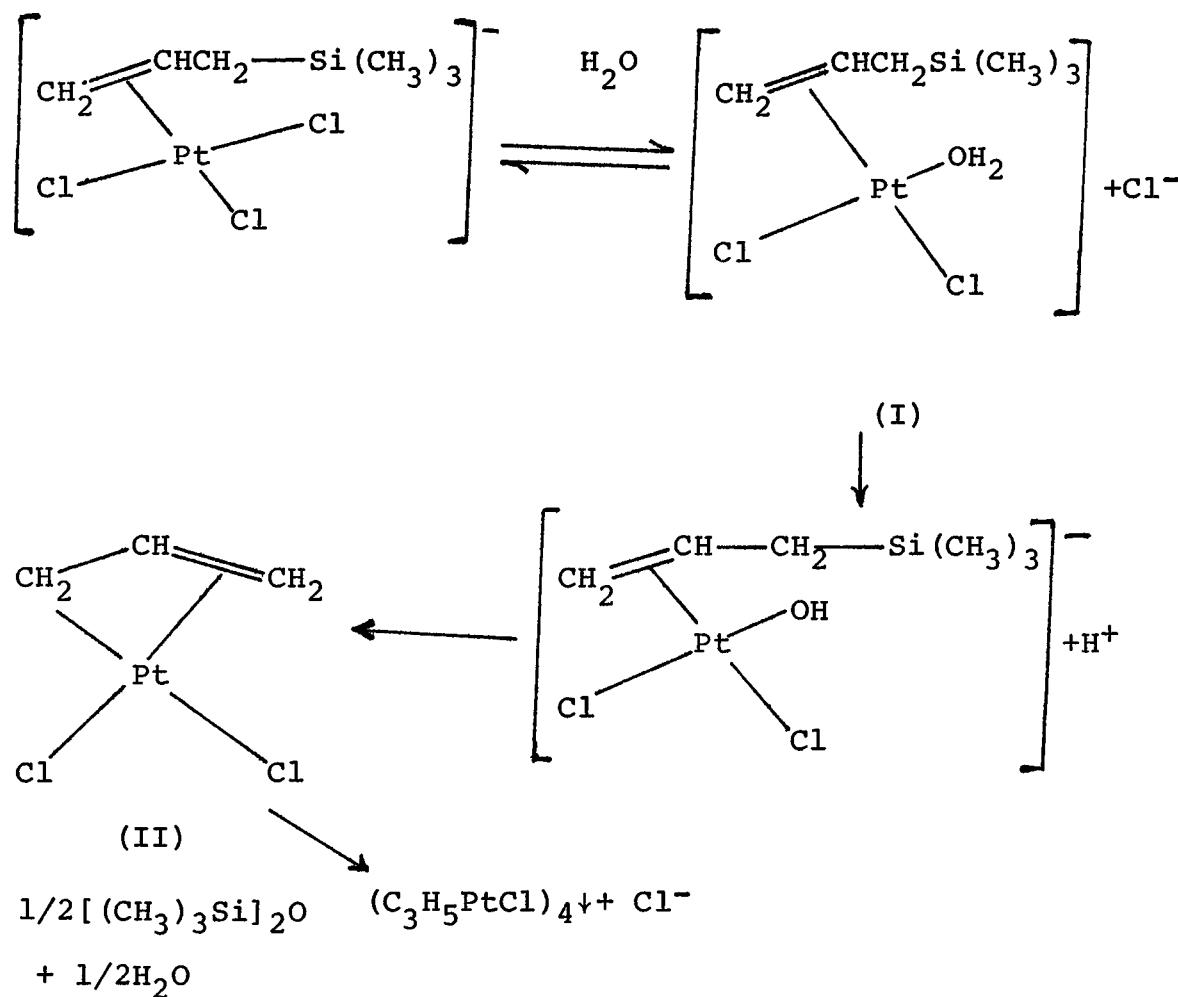


Figure 19. Proposed Mechanism for the Hydrolysis of Potassium Trichloro(allyltrimethylsilane)platinate (II)

then deprotonates to form an intermediate hydroxo complex II, which undergoes an intramolecular attack at the silicon by hydroxide ion. The displaced allyl group rearranges to form a  $\sigma$ -allyl platinum chloride intermediate complex, III. The chloride ion is then expelled from this complex to give the isolated product, allylchloroplatinum(II). This mechanism is in agreement with predictions based on the spectrochemical series in which water is suggested to be a better ligand than the chloride ion and therefore will displace it in aqueous solution.

Since the rate of hydrolysis decreases with increasing potassium chloride concentration as shown in the graph in Figure 7 (in the experimental section) potassium chloride does not catalyse the hydrolysis of the allyltrimethylsilane platinum(II) complex. The mechanism cannot, therefore, involve the attack on the silicon atom by a chloride ion from potassium chloride. On the contrary, the presence of potassium chloride most probably inhibits the first step of the hydrolysis through a simple common ion effect (see Figure 19).

Table 1 on page 3 presents data which also support the second proposed mechanism. It shows decreasing percentage yields (98%, 96%, 79%, and 71%) in water, 0.5M 2M and saturated KCl solutions respectively. These data further confirm the suggestion that the hydrolyses in potassium chloride solutions are indeed hindered, while in pure water the reaction goes nearly to completion. Further support of the above view is found from the observation that all of the insoluble yellow product from the hydrolysis in water was isolated by filtering the original mixture. The filtrate was not found to yield any additional complex. On the other hand, two portions of identical material were obtained separately from the hydrolyses in potassium chloride solutions. The first portion of the insoluble product was isolated by

filtering the mixture, and the second portion was obtained by evaporation of the filtrate to dryness. Both products were shown by their IR spectra to be tetrakis[allylchloroplatinum(II)]. The fact that a second product was obtained from the filtrate (recalling that the tetramer is insoluble in aqueous solution) indicate that the yellow filtrate must have contained a precursor of the tetramer.

Hydrolysis of Di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II).--Di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II) was hydrolyzed in a parallel experiment in pure water and potassium chloride solutions as described above. Tetrakis[allylchloroplatinum(II)] was isolated from the hydrolyses, and the mechanism is postulated to be similar to the second mechanism described previously.

However, an important difference between the hydrolyses of potassium trichloro(allyltrimethylsilane)platinate(II) and di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II) is the observation that the rates of hydrolyses were reversed (see graphs on page 33 and 37). That is, the rate of hydrolysis of the dimer in potassium chloride solutions was faster than that in pure water. This observation may be attributed to the fact that the bridging chloro groups cleave readily in potassium chloride solution and hence facilitate the hydrolysis simply because of improved solubility of the resulting salt.

### E. Hydrolysis of Acetylacetonatochloro(allyltrimethylsilane)platinum(II) in Wet Acetone

When acetylacetonatochloro(allyltrimethylsilane)-platinum(II) was allowed to hydrolyse in wet acetone, it did not yield the known complex, di- $\mu$ -allylbis(acetylacetonato)-diplatinum(II),<sup>6</sup> as was anticipated. On the contrary, insoluble yellow crystals precipitated and were subsequently identified as the tetramer, allylchloroplatinum(II), from IR spectral (No. 11 in Appendix I) and elemental analysis. The volatile reaction products were identified chromatographically as free acetylacetone and hexamethyldisiloxane.

A possible mechanism for this hydrolysis reaction is illustrated in Figure 20. The fact that no HCl was detected in solution by pH paper, coupled with the observation that a chloride ion remains in the hydrolysis product, allylchloroplatinum(II), strongly suggest that the chloride ion is not the attacking nucleophile. Significantly, therefore, this experiment suggests that the chloride ion does not attack the silicon atom in any of the hydrolysis reactions considered previously. On the other hand, water probably displaces the chloride ion prior to its attack at the electropositive silicon atom.

An experiment was next performed in which acetylacetonatochloro(allyltrimethylsilane)platinum(II) was allowed to decompose in the non-polar solvent, benzene-d<sub>6</sub>. The decomposition was periodically monitored by NMR spectroscopy for

one month. During this time the NMR spectra showed the appearance of a second resonance signal (singlet at  $9.70\tau$ ) which grew at the expense of the original peak at  $9.95\tau$  (attributed to the methyl protons in the co-ordinated allyltrimethylsilane). The peak at  $9.70\tau$  likely arises from the methyl protons in chlorotrimethylsilane which is a decomposition product.

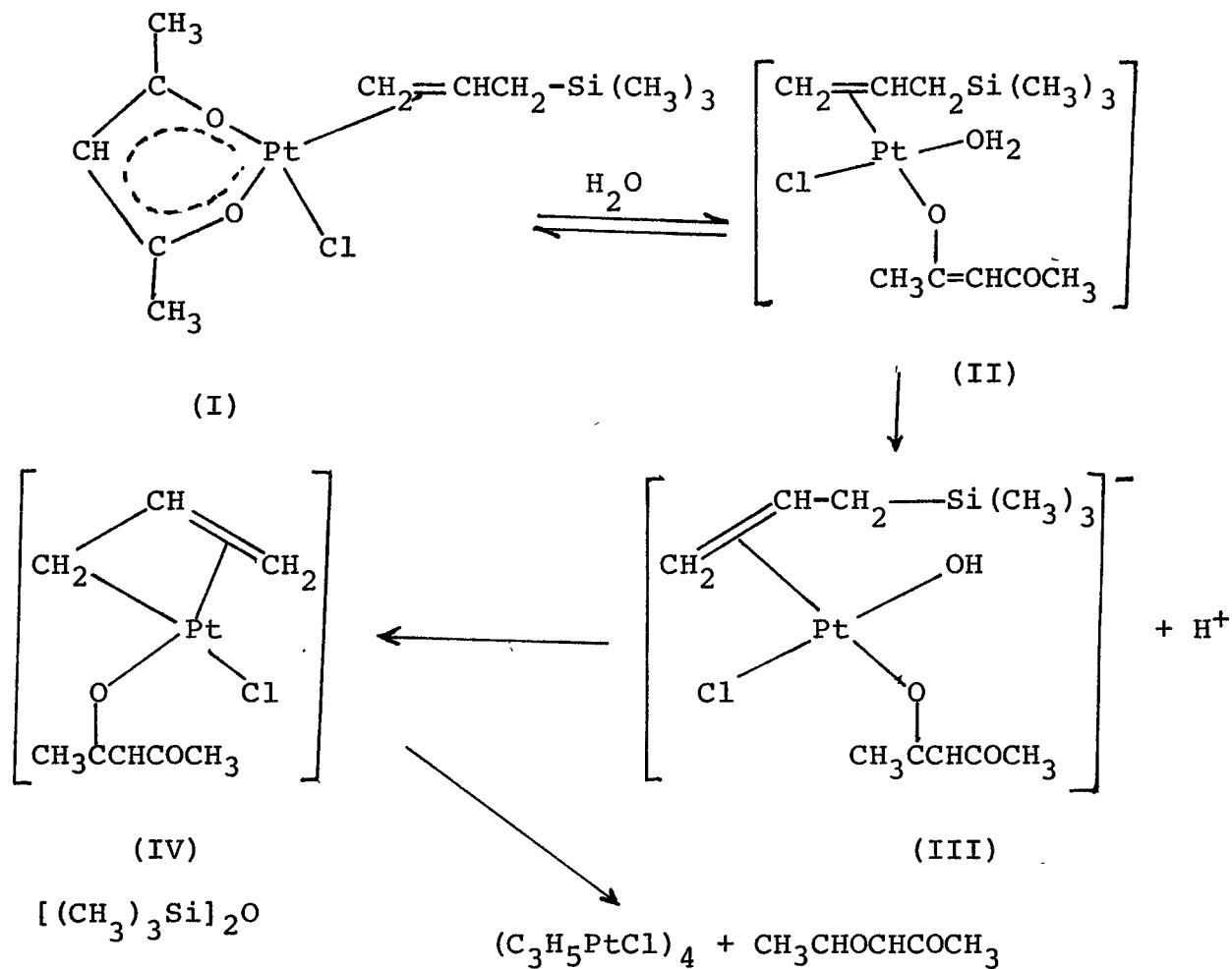


Figure 20. Proposed Mechanism for the Hydrolysis of Acetylacetonatochloro(allyltrimethylsilane)platinum(II)

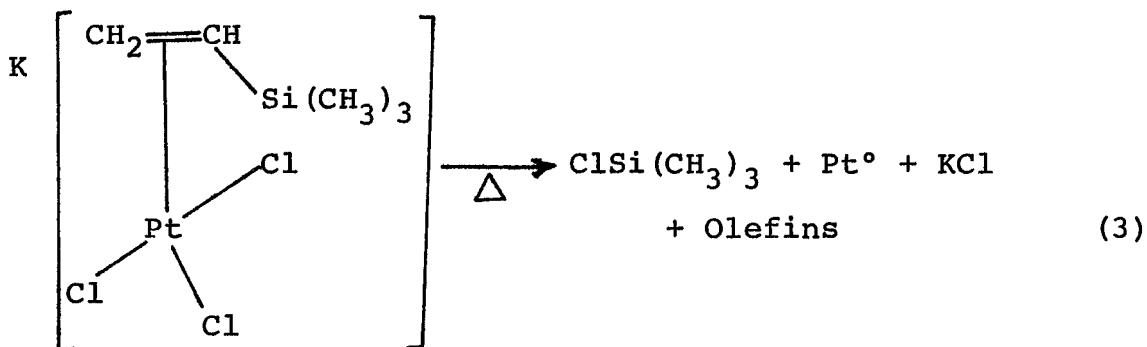
This is a significant observation because it indicates that the chloride ion can attack the silicon atom directly from within the complex. Therefore, it may be concluded that in the absence of better nucleophiles the chloride ion will cleave the facile carbon-silicon bond. This conclusion is further supported by the results of the pyrolysis experiments as indicated in the following sections. Free acetylacetone was also observed in the NMR spectrum, but no peak was assignable to the allyl group after complete decomposition had occurred. Presumably the allyl groups formed gaseous products which escaped the NMR tube.

#### F. Thermal Decomposition

Since the experimental procedure used resulted in complete thermal decomposition of the complexes all analytical work was performed on the volatile components. Volatile products were analysed by IR, NMR, and gas chromatography.

Pyrolysis of potassium trichloro(vinyltrimethylsilane)-platinate(II), (3) gave mainly chlorotrimethylsilane identified by IR (gas cell), (spectrum No. 12 in Appendix I). The IR spectrum showed a medium band at  $2960\text{cm}^{-1}$  arising from stretching vibrations of C-H of the methyl groups and three sharp bands at  $1258\text{cm}^{-1}$ ,  $1068\text{cm}^{-1}$  and  $840\text{cm}^{-1}$  all arising from the symmetric deformation vibrations and rocking of  $\text{Si}-\text{CH}_3$ . The IR spectrum was identical to that of a known sample of chlorotrimethylsilane. However, no olefin bands

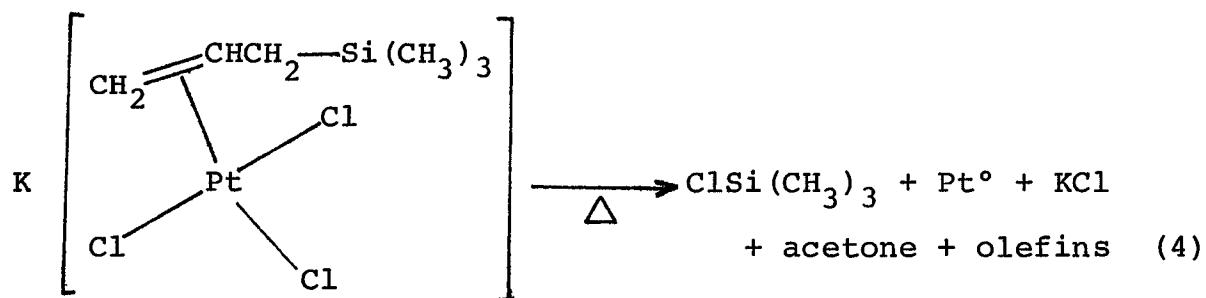
were observed. The decomposition reaction is illustrated in equation 3.



Thermogravimetric analysis (TGA) of compound (3) gave an initial weight loss of 0.41 mg (4.4%) at 90° which was attributed to a theoretical percentage weight loss of 3.9% for water. A second weight loss of 2.1 mg (22.8%) at 110° corresponds to the theoretical weight loss of chlorotrimethylsilane. The TGA curve in Figure 10 confirms the products obtained in the pyrolysis of complex (3) in a closed system. The presence of water, indicated above, shows that the complex contains water of "hydration", which is difficult to remove. This is also confirmed by the IR (nujol) spectrum of (3) which contains a broad band at 3600cm<sup>-1</sup>. This water is not believed to be primarily co-ordinated.

Pyrolysis of potassium trichloro(allyltrimethylsilane)-platinate(II) (4) is illustrated in equation 4. Chlorotrimethylsilane was found to be the main volatile product chromatographically. The NMR spectrum (No. 10 in Appendix II) and gas chromatogram of the volatile products indicated the presence of chlorotrimethylsilane, hexamethyldisiloxane, acetone and a small amount of the free ligand, allyltrimethyl-

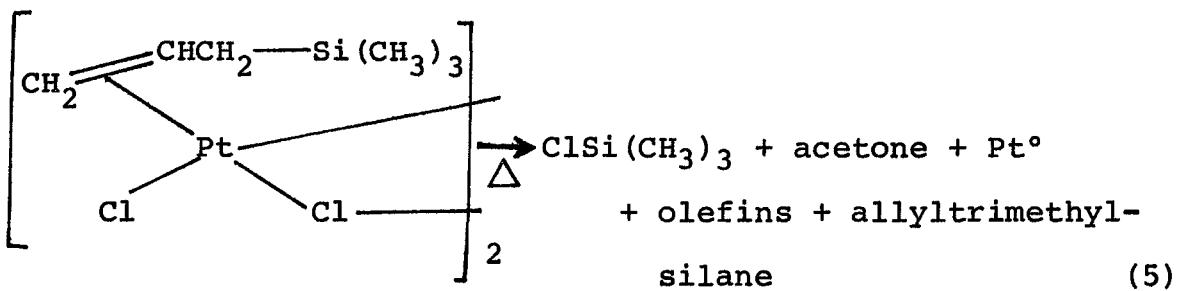
silane. The IR spectrum (No. 13 in Appendix I) indicated



mainly chlorotrimethylsilane and acetone (indicated by the carbonyl band at  $1700\text{cm}^{-1}$ ). The weak bands at  $3080\text{cm}^{-1}$ ,  $3020\text{cm}^{-1}$  and at  $940\text{cm}^{-1}$  and  $910\text{cm}^{-1}$  suggest the presence of olefins. The formation of acetone can be explained by the fact that the complex has water of "hydration", which oxidizes the allyl group.

The TGA of complex (4) indicated an initial weight loss of 2.2 mg (25.7%) from  $125^\circ$  to  $200^\circ$  which corresponds to a theoretical weight loss of 26.8% for water (in a monohydrate complex) and chlorotrimethylsilane. These products cleaved at about the same time, and thus it was not possible to see distinct steps in the TGA curve (Figure 11). The water detected here helps to explain the formation of acetone in the above pyrolysis experiment of complex (4).

Pyrolysis of di- $\mu$ -chlorodichlorobis(allyltrimethylsilane)platinum(II) (5) is illustrated in equation 5. The volatile products were analysed by their IR and NMR spectra and chromatographically. The IR spectrum (No. 14 in Appendix I) indicated the presence of mainly chlorotrimethylsilane and olefins indicated by bands at  $3020\text{cm}^{-1}$ ,  $901\text{cm}^{-1}$  and  $980\text{cm}^{-1}$ .

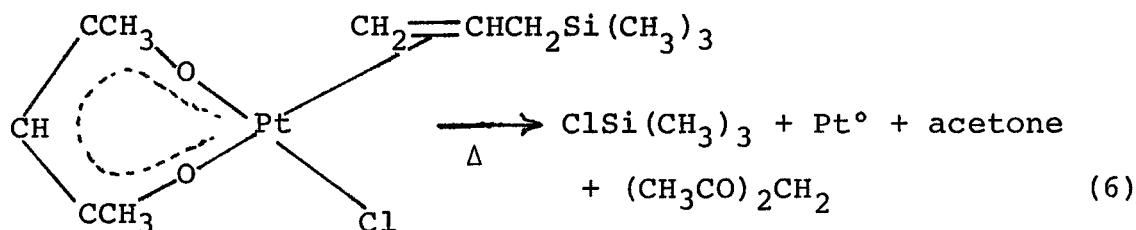


However, the NMR spectrum (No. 11 in Appendix II) and gas chromatography indicate the presence of chlorotrimethylsilane ( $9.60\tau$ ), hexamethyldisiloxane ( $9.98\tau$ ), acetone ( $7.88\tau$ ) and a small amount of free allyltrimethylsilane (broad peaks at  $5.0\tau$  and  $8.4\tau$ ).

A thermogravimetric analysis (Figure 11) of the allyltrimethylsilane dimer, complex (6), shows an initial weight loss of 1.9 mg (25%) at  $108^\circ$  which correspond to the theoretical percentage weight loss of 28.6% for chlorotrimethylsilane. The second weight loss of 1.38 mg (18.4%) may be due to acetone and free allyltrimethylsilane. The TGA curve is rather difficult to analyse qualitatively. The pyrolysis of the neutral dimeric complex (6) and the allyltrimethylsilane salt complex (5) were performed with the idea to contrast their cleavage reactions and mechanism. The analytical data seem to show that the mechanism is the same in both cases.

Pyrolysis of acetylacetatochloro(allyltrimethylsilane)platinum(II), is illustrated in equation 6. This experiment was performed to investigate the possibility of synthesizing a known complex, di- $\mu$ -allylbis(acetylacet-

tonato)platinum(II)<sup>6</sup>, through the pyrolysis route. The pyrolysis was performed in dry benzene solution at 80° for 5 hours. The experiment was repeated; in each case decomposition occurred, but the anticipated complex was not



identified. The IR spectrum of the residue indicated incomplete decomposition; however, the gas chromatographic analysis of the evaporated volatile products indicated the presence of chlorotrimethylsilane, acetone and the free ligands, allyltrimethylsilane and acetylacetone.

The thermogravimetric analysis of the complex indicated a total weight loss of 4.5 mg (51%), which is attributed to the cleavage of acetylacetone, chlorotrimethylsilane and the allyl group in the decomposition reaction. These data confirm the pyrolysis data described above because the same products were obtained in both decomposition reactions.

## G. Summary

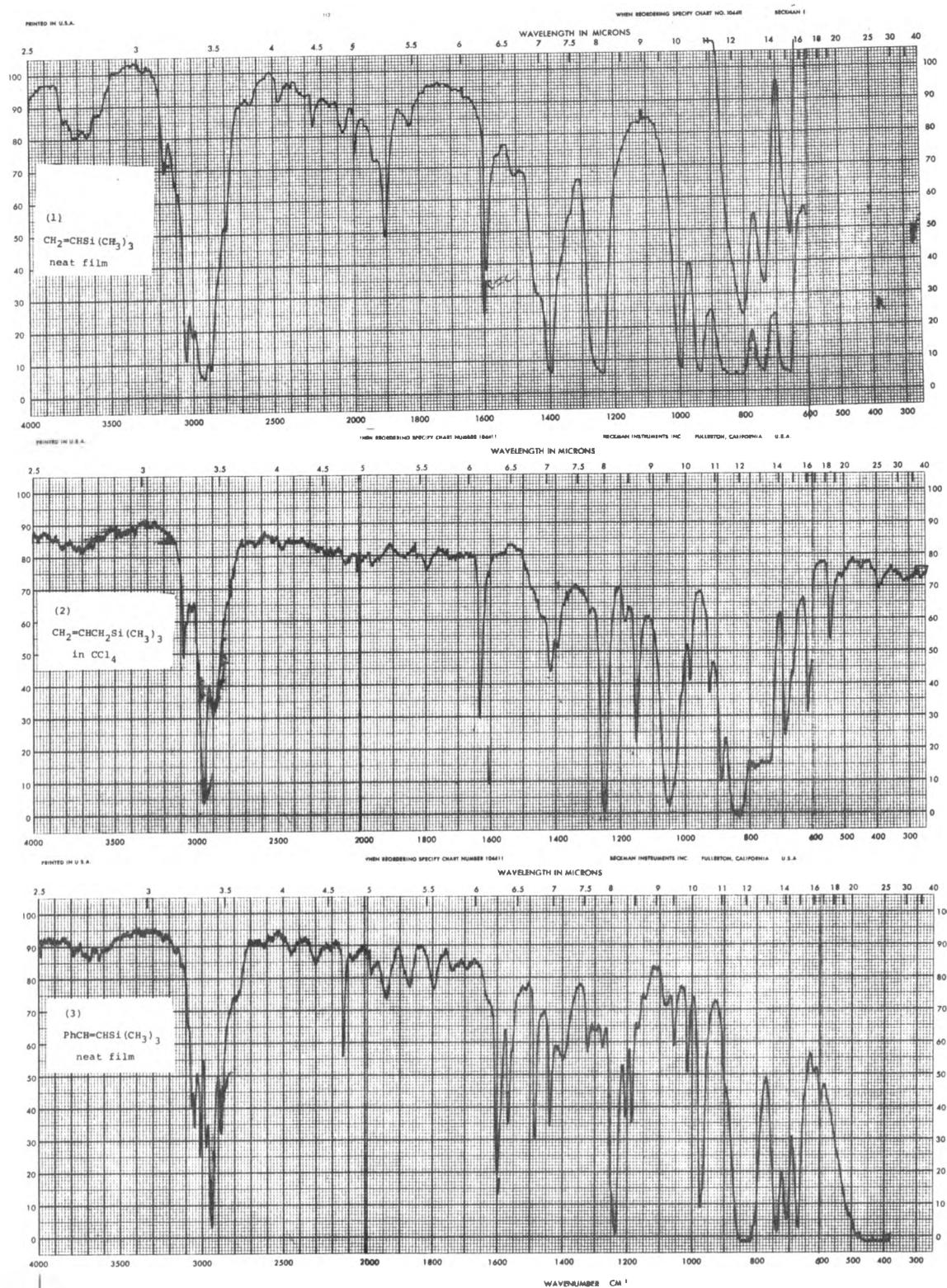
The findings of this study of the pyrolytic and hydrolytic cleavages of vinyl- and allylsilane platinum(II) complexes are compatible with a published report that the

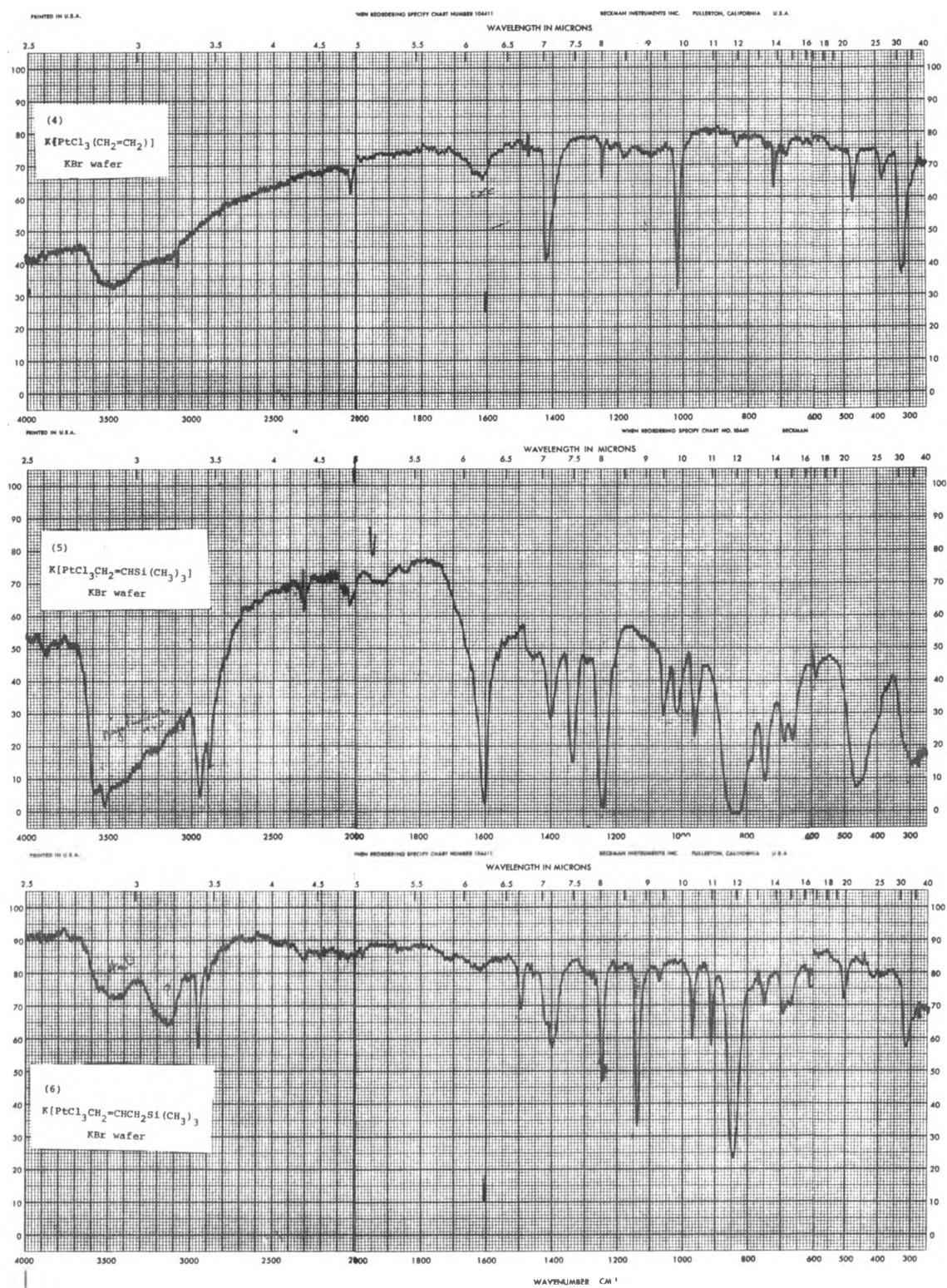
carbon-silicon bond is highly polarized.<sup>26</sup> The high polarity of the carbon-silicon bond makes heterolytic fission of the bond likely.

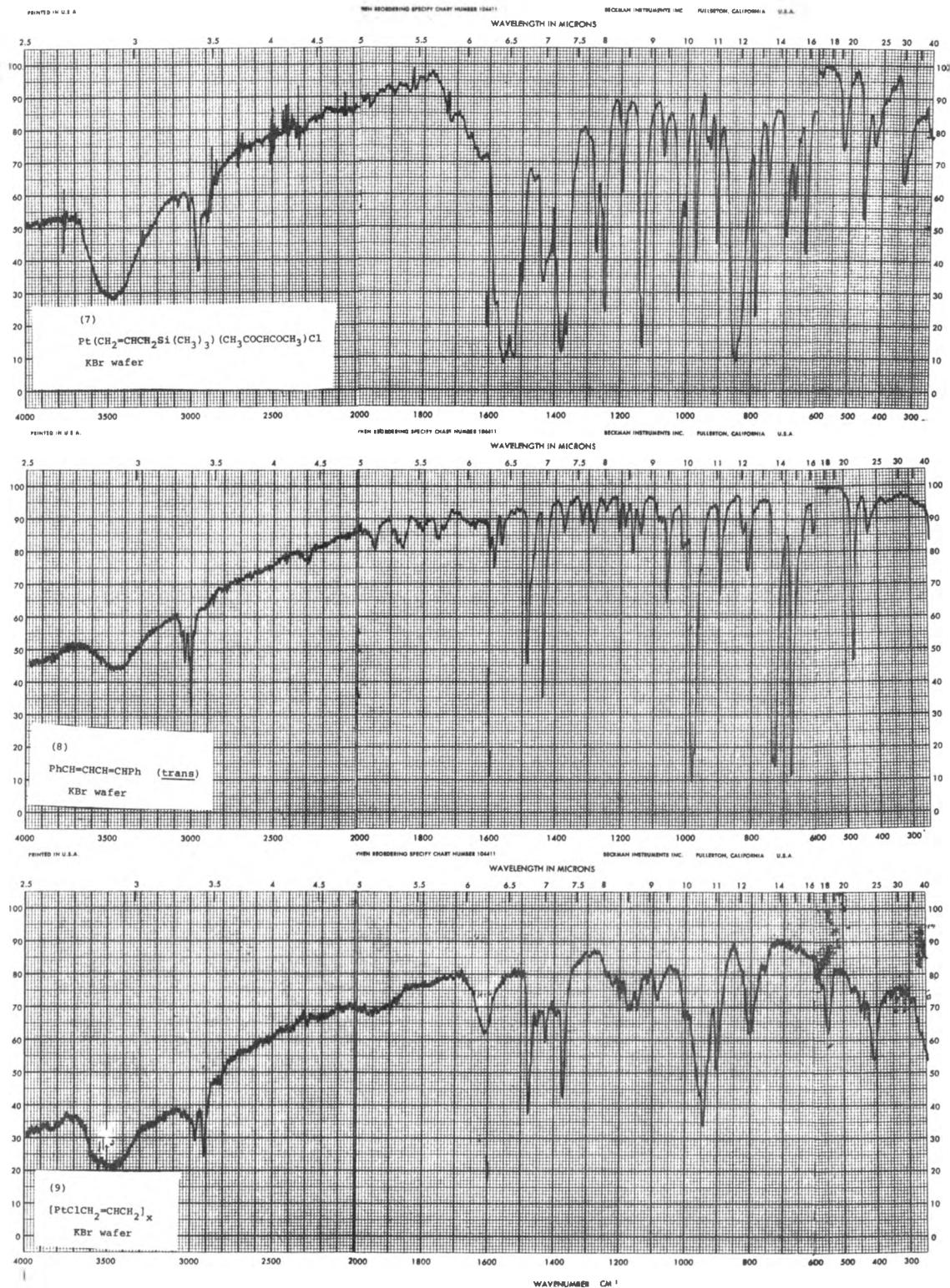
The study further shows the dramatic effect of co-ordination on the chemistry of these silanes. Each complex studied was observed to undergo hydrolysis which resulted in C-Si bond cleavage. Furthermore, the mechanism of hydrolytic cleavage is best interpreted in terms of a model postulating the attack on the silicon by co-ordinated water or hydroxide ion. Consequently an earlier incomplete report by Poist and Kraihanzel<sup>33</sup> concerning the ability of Zeise's salt to catalyse the de-silylation of unsaturated silanes may now be substantiated by the mechanism and models shown herein.

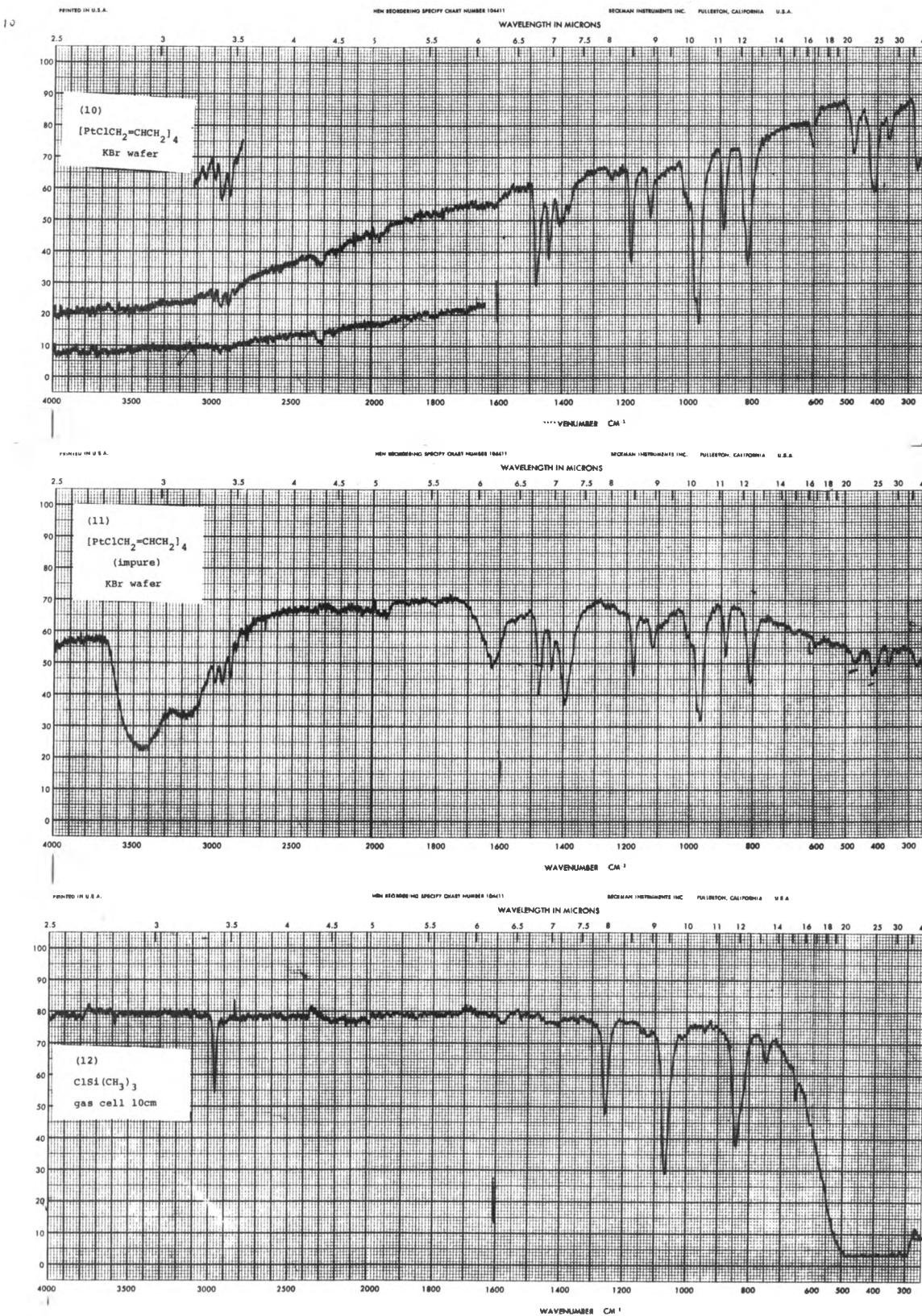
Thermal analysis of these complexes has shown them to be of a rather low order of stability. Furthermore, all complexes were found to liberate, invariably, chlorotrimethylsilane as the main volatile product in the initial decomposition. Thus one may come to the conclusion that in the absence of a better nucleophile (such as water), even chloride ion will attack the silicon atom and effect cleavage of the facile C-Si bond.

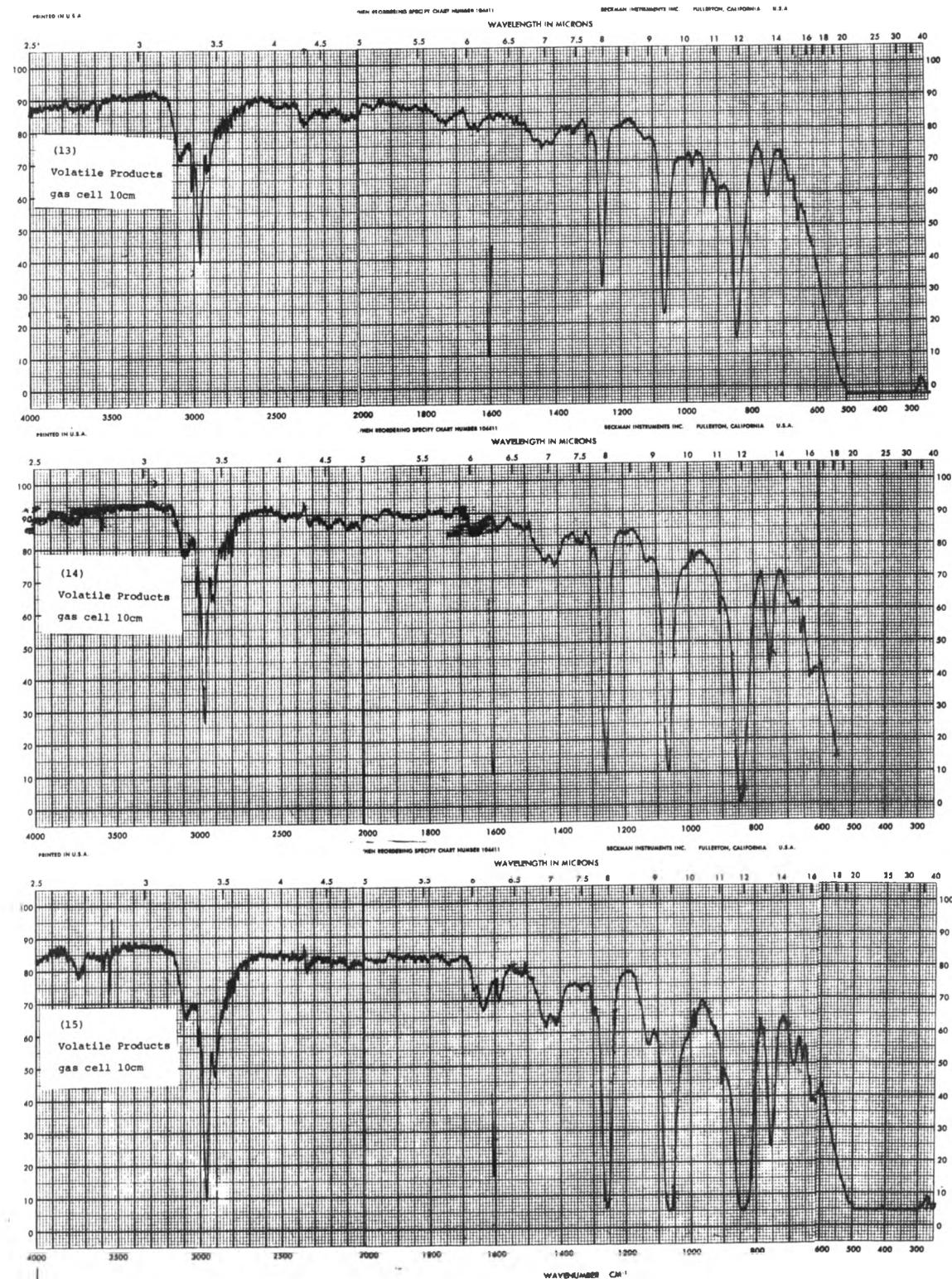
**APPENDIX I**  
**INFRARED SPECTRA**



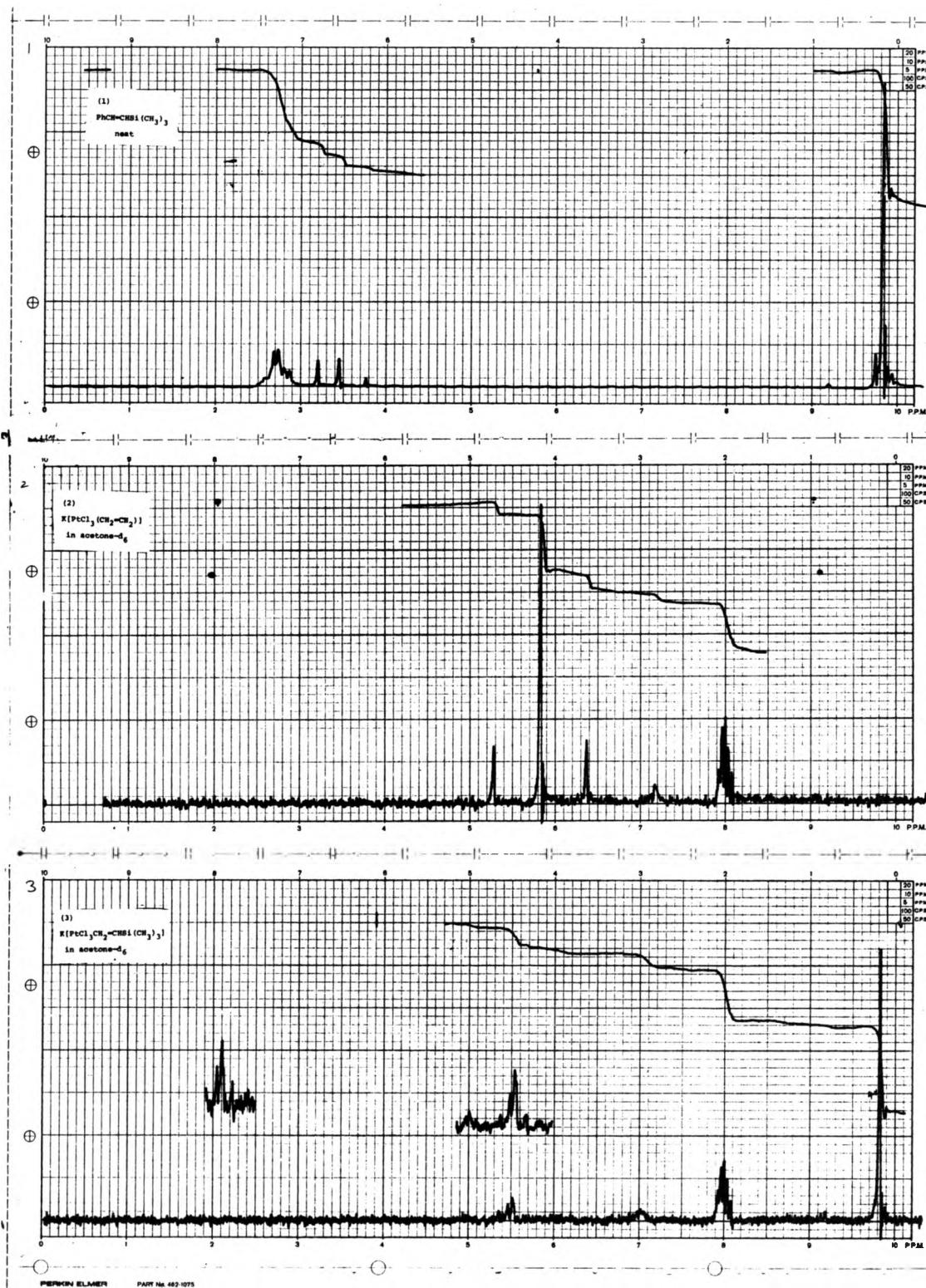


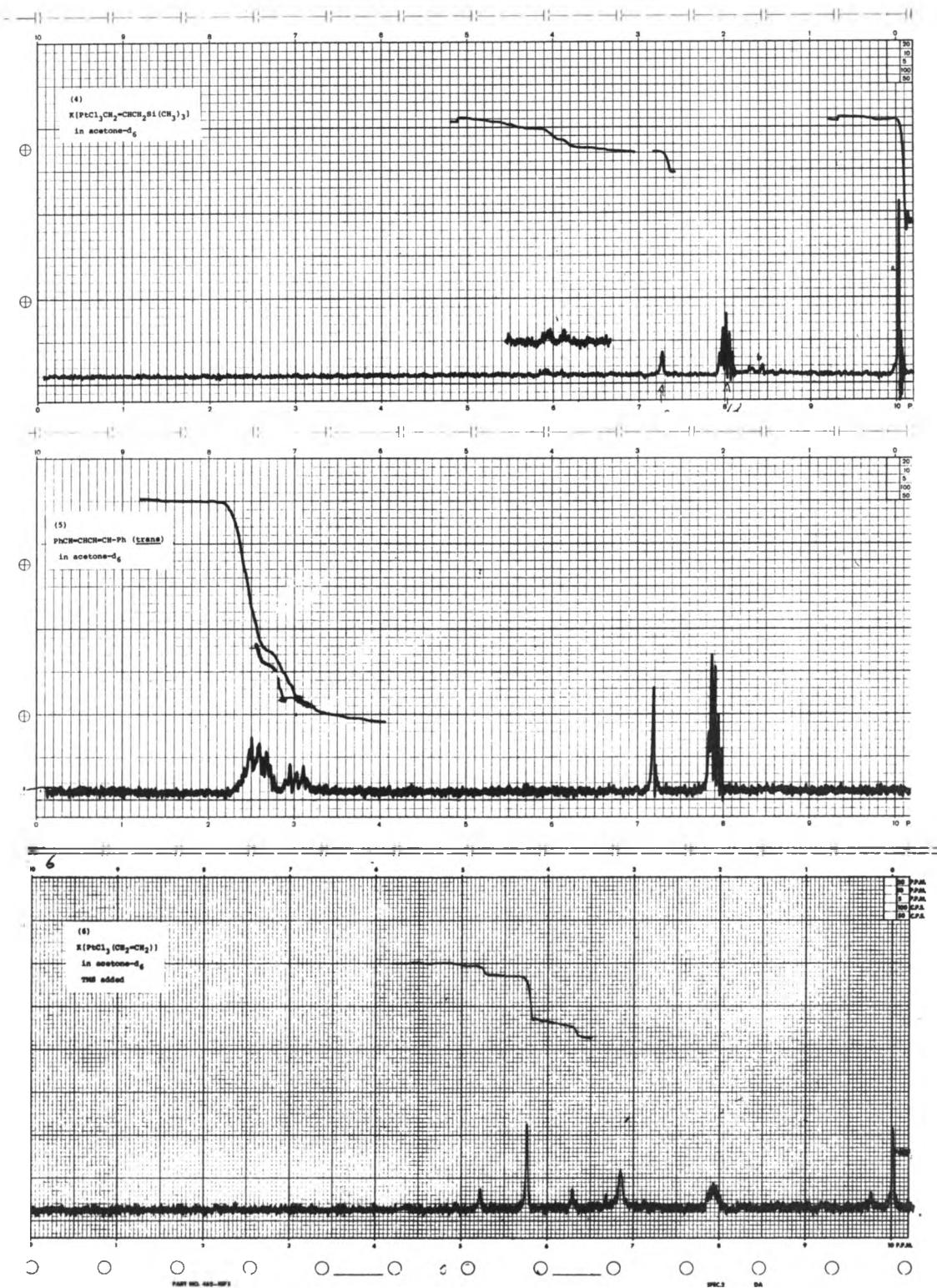


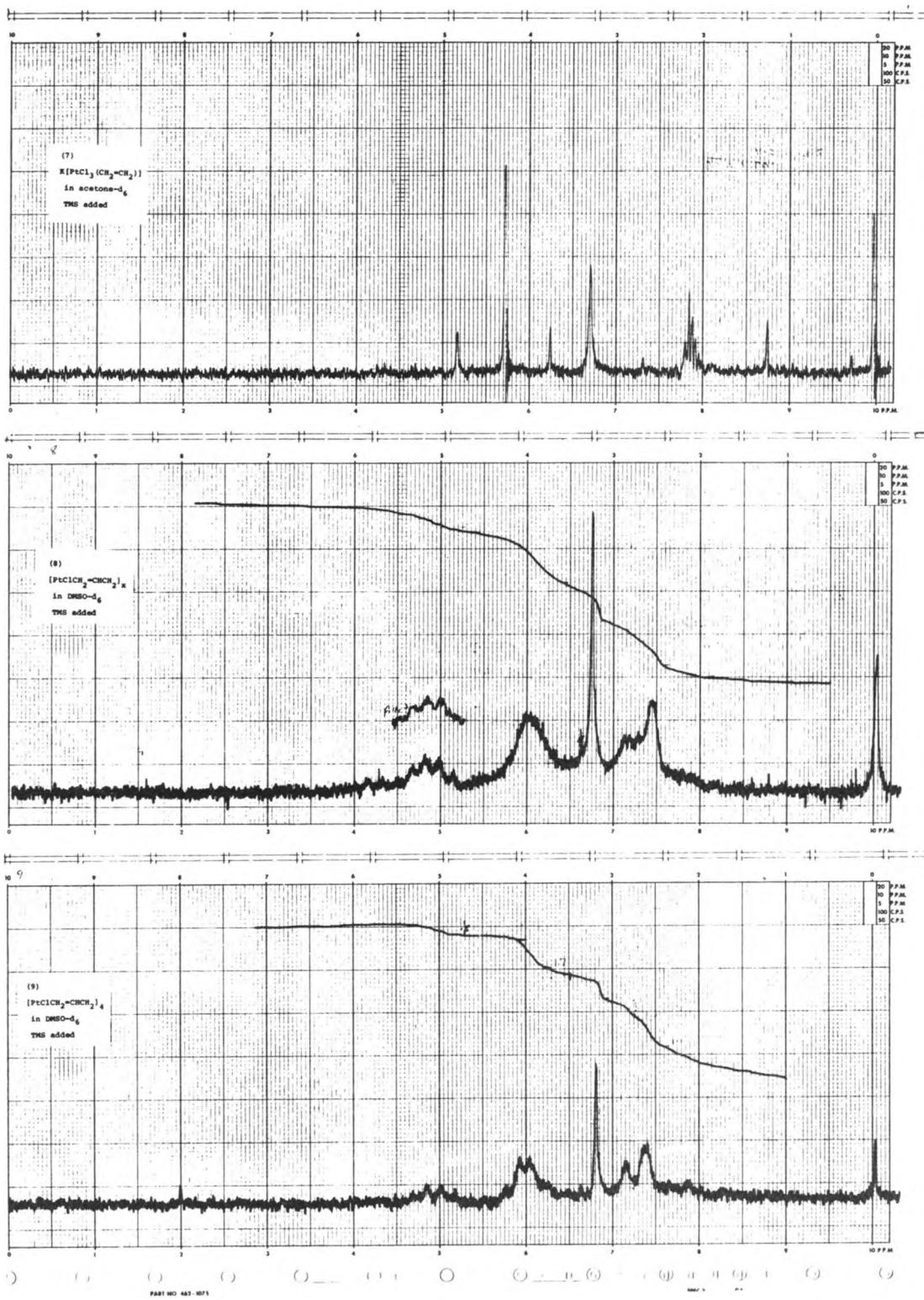


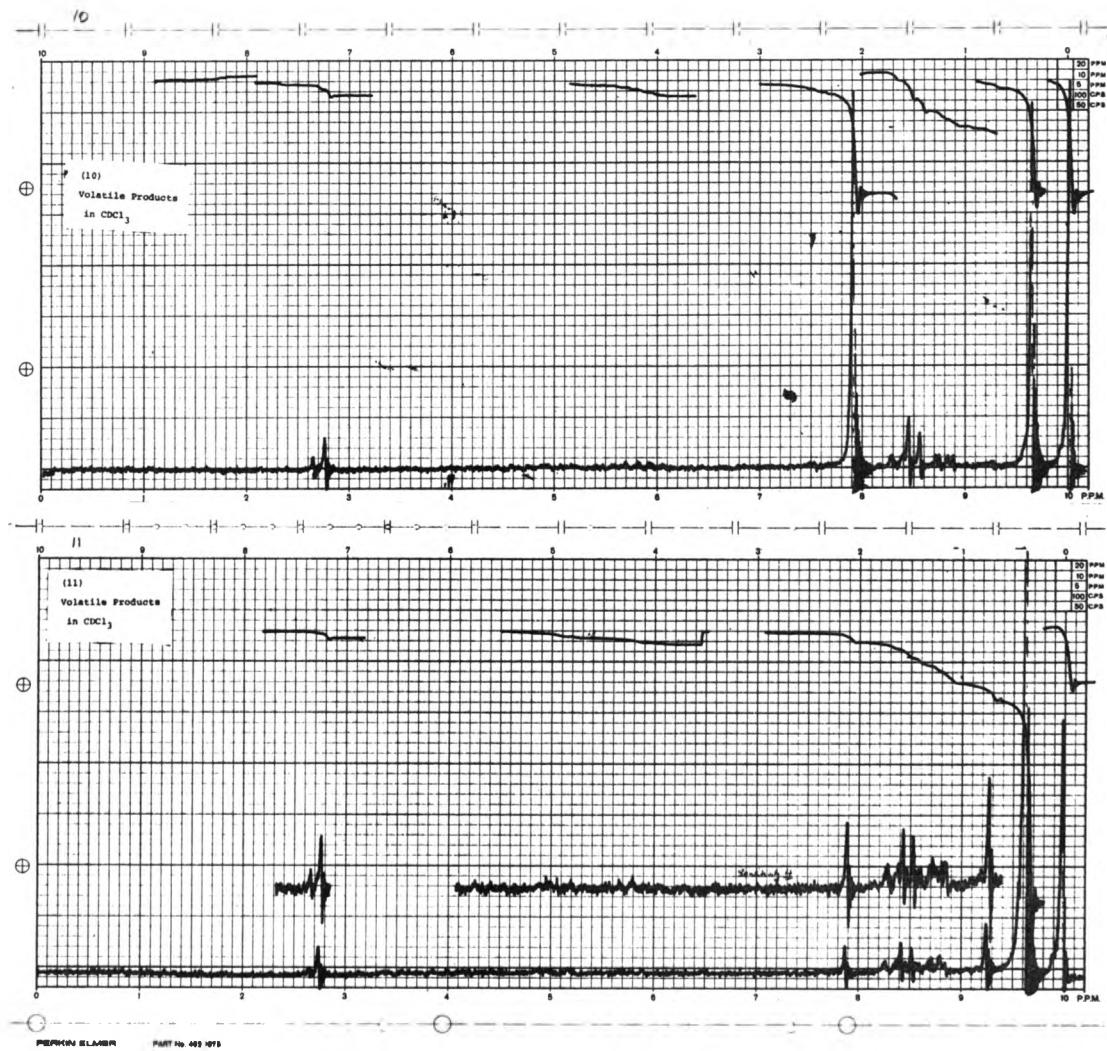


APPENDIX II  
NUCLEAR MAGNETIC RESONANCE SPECTRA









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