MASS SPECTRAL STUDY OF 2-ALLYLPYRIDINE AND SOME OF ITS METAL COMPLEXES AND SALTS

by

Doris Zimmerman

Submitted in Partial Fulfillment of the Requirement

for the Degree of

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in the

Chemistry

Program

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Adviser — Date

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THESIS

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ABSTRACT

MASS SPECTRAL STUDY OF 2-ALLYLPYRIDINE AND SOME OF ITS METAL COMPLEXES AND SALTS

Doris Zimmerman

Master of Science

Youngstown State University, 1989

Electron-ionization mass spectra of 2-allylpyridine and its compounds with hydrogen chloride, picric acid, platinum(II), and palladium(II) are reported. The acid compounds give the same spectrum as the 2-allylpyridine. The palladium complex did not show palladium in its mass spectrum. These spectra are compared with those of analogous compounds from chemical literature, and proposed structures of some fragment ions are given. The results tend to support and extend previous research in the field of mass spectral studies of substituted pyridines and organometallic complexes of platinum(II) and palladium(II).

ACKNOWLEDGEMENTS

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INTRODUCTION

Statement of Problem

Mass spectrometry is a multi-faceted tool used for the identification and structural analysis of compounds. Based on the detection of ionized molecules and atoms in the vaporized state, mass spectrometry is able to provide both qualitative information, identification of ions, which is based on mass to charge ratios (m/z), and quantitative information, which is number or abundance of ions; and it can be used to determine molecular weights.

Pyridine, C_5H_5N, is a heterocyclic compound with a six-membered ring. A heterocyclic compound is one that contains a ring made up of more than one kind of atom. Pyridine is classified as aromatic because of its unsaturation and stability with the delocalization of π electrons. Like arenes, pyridine has σ bonds formed from sp^2 hybrid orbitals between the atoms in the ring and π bonds formed from unhybridized p orbitals. The pyridine molecule is planar with the ring angles being equal to 120^o and the bond lengths within the ring being approximately equal to 1.36 Å. Pyridine is a constituent of coal tar and a water soluble base. Pyridine derivatives include vitamins, tuberculosis treatment drugs,[1] nicotine, and chemotherapy drugs.[2]

Many substituted pyridines, mostly alkyl substituted, have been analyzed by mass spectrometry and reported in the literature, but there are no reports of a mass spectral analysis of any allyl substituted pyridines. Allyl substitution would be unsaturated, but not conjugated to the ring. The substituted pyridines that have been analyzed are as follows: ethylpyridines, methylethylpyridines, and 2-(4-heptyl)pyridine;[3] 4-propylpyridine;[4] 2-alkylpyridines;[5] methylpyridines (picolines), dimethylpyridines, and 2-methyl-5-

ethenylpyridine;[6] butylpyridines;[7] 2-propylpyridine and 2-methyl-5-ethylpyridine;[8] 3-methyl-5-propylpyridine and 2-vinylpyridine.[9]

2-Allylpyridine, (a pyridine ring with $-CH_2-CH=CH_2$ attached to the ring carbon adjacent to the nitrogen) C_8H_9N, can be a bidentate ligand with a metal, but there has been no report of this, except by Yingst[10] and Heaton and McCaffrey[11] for the complexes of 2-allylpyridine with Cu(I), Ag(I), and Pt(II). There are no reports of dichloro(2-allylpyridine)palladium(II) in the chemical literature. Some platinum(II) and palladium(II) complexes have been studied by mass spectrometry as follows: $M(C_3H_5)_2$ where M = Ni, Pd, Pt;[12] vic-dioximate complexes of Ni, Pd, Pt;[13] $[(\pi\text{-}C_3H_5)PdCl]_2$;[14] and $[(C_3H_6)PtCl_2]_n$.[15]

The purpose of this work is two-fold. First, the mass spectrum of 2-allylpyridine is to be obtained for verification of synthesis and comparison to those of other substituted pyridines. Possible mechanisms for the dissociative ionization of 2-allylpyridine are to be formulated based upon its structure. Secondly, the mass spectrum of the free ligand is to be compared with the mass spectra of its salts, 2-allylpyridinium chloride and 2-allylpyridinium picrate, and its complexes, dichloro(2-allylpyridine)platinum(II) and dichloro(2-allylpyridine)palladium(II). The identities of the complexes are to be verified and structures are to be proposed.

Since "organometallic chemistry has become one of the most exciting and active areas in the chemical sciences", [16] this is a current field of research. Because very little research has been done in the field of olefinic substitution of pyridine, this also is an area of needed research. Also the molecular weight previously obtained by osmometry for the platinum(II) complex was not identical to that for the proposed structure.[10] In mass spectrometry the molecular ion, the ion corresponding to the loss of an electron from the molecule, is usually the ion of greatest m/z value in the mass spectrum; it is used to determine the molecular weight.

History

The development of mass spectrometry dates back to the late nineteenth century with the discovery of positive rays by Goldstein (1886). He discovered these rays in a low-pressure electrical discharge tube. These rays were deflected in both magnetic and electric fields by Wein (1898). Wein also showed that they were actually positive ions which were created in a gaseous discharge at low pressures. J. J. Thomson in 1897 showed the existence of electrons, with negative charge. Thomson also established the fact that the positive ray particles were the fragments remaining after a neutral molecule had lost one or more electrons. He discovered two isotopic forms of neon, the first isotopes discovered for a nonradioactive element.

In 1919, F. W. Aston devised an instrument that he called the mass spectrograph. This instrument focused as well as analyzed the positive rays. He determined the atomic masses of the isotopes of chlorine, mercury, nitrogen, and the noble gases. It was called a spectrograph since it used a photographic plate in the same plane as the focused ions. In 1918, A. J. Dempster used a semicircular instrument with both electrical and magnetic fields to focus the positive rays to determine the isotopic masses of magnesium, lithium, potassium, calcium, and zinc. These positive ions were produced from a salt coated on a hot filament. In 1930, Bainbridge added a Wein velocity filter, which is a device for producing a velocity dispersion, to Dempster's mass spectrometer so that a monoenergetic ion source was not needed. Bainbridge's work provided the first experimental proof of the mass-energy relationship proposed by Einstein. In 1934, Herzog and Mattauch proposed focusing equations for use in electric and magnetic fields which made possible the design of high resolution, double focusing mass spectrometers. With the development of vacuum technology by Nier in 1935, precise determinations of atomic masses were made possible. Commercial mass spectrometers were available in 1950 using both electrical and magnetic fields.[3,17] The first industrial use of mass spectrometry as an analytical tool was in the

petroleum industry to quantitatively determine the amount of various compounds that were present in the volatile samples.[18] In the late 1950's, W. Paul and his group at Bonn University introduced the quadrupole mass spectrometer.[17]

Instrumentation

The mass spectrometer used for the analysis of 2-allylpyridine and its complexes and salts is the Finnigan 1020B GC/MS. GC/MS stands for gas chromatograph/mass spectrometer. The main components of a mass spectrometer are an inlet, an ion source, a mass analyzer, and a collector. In the Finnigan 1020B there are two methods of introducing the sample for analysis. One is by means of the gas chromatograph (GC). The GC separates the components of a mixture of gases or volatile compounds by their differences in eluting times through a column. The sample is carried through the capillary column by an inert gas, in this case, helium. The wall of the 15-m long capillary tube serves as a support for the stationary liquid phase. If the individual components of the sample have different distribution coefficients between the two phases (carrier gas and the liquid phase), separation is achieved from repeated absorption/desorption as the sample is transported by the gas. This leads to different eluting times, or separation. The sample is injected onto the column, which has a split/splitless injector, with a 10-μL syringe. The GC oven temperature is microprocessor controlled and can be programmed from 50° to greater than 400° C at ramp rates from 0.1 to 39.9° C/min, in increments of 0.1° C/min; or the GC can be run isothermally. GC parameters that can be programmed are as follows: zone temperature, initial temperature, final temperature, initial time, temperature ramp rate, final time, separator temperature, manifold temperature, split/sweep valve time, and filament/multiplier off time. There is a direct connection between the outlet of the GC and the MS.[19]

The other method of introducing the sample into the mass spectrometer is by solid probe. The solid sample is dissolved in a solvent and placed in a 10-μL pyrex tube, where the solvent is allowed to evaporate, leaving the solid adhering to the walls of the tube. The tube is then placed in the solid probe for insertion into the ion source of the mass spectrometer. The solid probe can be heated to a maximum temperature of 400° C at a ramp rate of 15, 30, 60, or 120° C/min.

The second component of the mass spectrometer is the ion source, pictured in Figure 1, which is the site of electron bombardment and subsequent ionization of the sample molecules. The electrons are produced by thermionic emission from an electrically heated rhenium filament and are accelerated to 70 eV.[19] An energy of approximately 10 eV is required to ionize an organic molecule or to break a covalent bond[8], but an energy of 70 eV is used because maximum ion yield has been noted near this value.[20] This energy is sufficient to remove an electron from the sample molecule to produce a molecular ion. This electron may have originated from one of three sources as follows: i) a lone pair of electrons on a heteroatom such as oxygen, sulfur, nitrogen, or a metal; ii) a pair of electrons in the π orbital of a multiple bond; iii) a pair of electrons in the σ orbital of a single bond. The molecular ion which results is represented as $[M]^{+\cdot}$ since it has a positive charge and an unpaired electron remaining.[21]

Molecular ions formed in electron impact mass spectrometry are usually radical-cations, with an odd electron. Radical cations are known in solution chemistry to be reactive species and the molecular ions formed in mass spectrometry frequently decompose by ejection of a radical to form an even-electron charged species.[20] Many of the ions formed occur at odd m/z value which signifies an even-electron ion, except in the case of an odd number of nitrogen atoms, when an even m/z value corresponds to an even-electron species.[20] The charged particles resulting in greatest abundance from the ionization are those requiring the lowest amount of energy. So therefore, the weakest bonds are cleaved or rearrangement (the breaking and forming of bonds) may occur so that the most stable

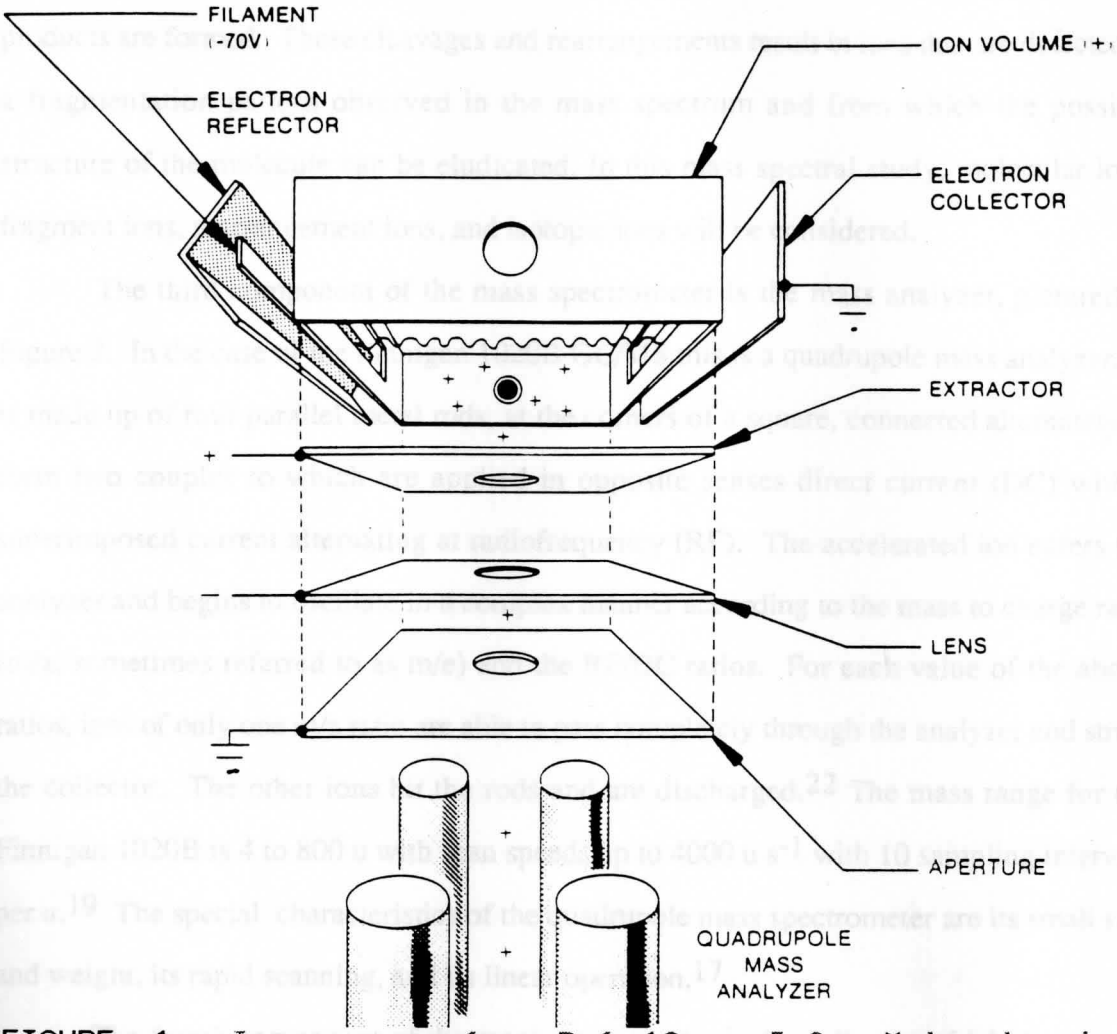


FIGURE 1. Ion source, from Ref. 19. p. 5-8. Molecules in the ion volume are bombarded by electrons emitted from the rhenium filament. The resulting ions are extracted from the ion volume, focused, and accelerated down the axis of the quadrupole mass analyzer.

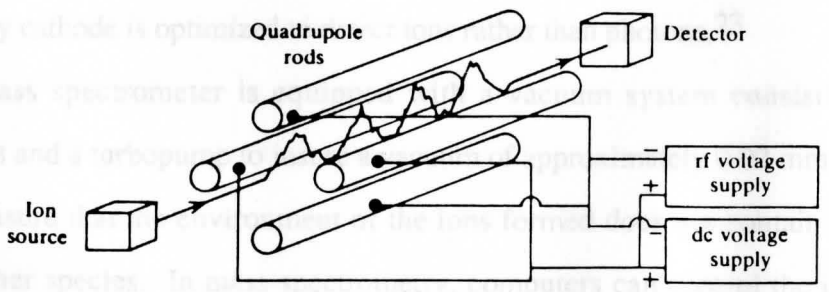


FIGURE 2. Quadrupole, from Ref. 20. p. 32. Arrangement of the quadrupole mass filter, showing the complex flight path of a focussed ion. Ions that are not focussed collide with the rods.

products are formed. These cleavages and rearrangements result in ions that are detected in a fragmentation pattern observed in the mass spectrum and from which the possible structure of the molecule can be eludicated. In this mass spectral study, molecular ions, fragment ions, rearrangement ions, and isotopic ions will be considered.

The third component of the mass spectrometer is the mass analyzer, pictured in Figure 2. In the case of the Finnigan 1020B GC/MS this is a quadrupole mass analyzer. It is made up of four parallel metal rods, at the corners of a square, connected alternately to form two couples to which are applied in opposite senses direct current (DC) with a superimposed current alternating at radiofrequency (RF). The accelerated ion enters the analyzer and begins to oscillate in a complex manner according to the mass to charge ratio (m/z, sometimes referred to as m/e) and the RF/DC ratios. For each value of the above ratios, ions of only one m/z ratio are able to pass completely through the analyzer and strike the collector. The other ions hit the rods and are discharged.[22] The mass range for the Finnigan 1020B is 4 to 800 u with scan speeds up to 4000 u s^{-1} with 10 sampling intervals per u.[19] The special characteristics of the quadrupole mass spectrometer are its small size and weight, its rapid scanning, and its linear operation.[17]

The fourth component of the mass spectrometer is the collector which detects the ions. In the Finnigan 1020B GC/MS, the collector is a continuous dynode electron multiplier.[19] The electron multiplier is operationally the same as a photomultiplier, except that the primary cathode is optimized to detect ions rather than photons.[23]

The mass spectrometer is equipped with a vacuum system consisting of two external pumps and a turbopump to insure a vacuum of approximately 0.02 mm Hg, which is needed to insure that the environment of the ions formed does not contain significant amounts of other species. In mass spectrometry, computers can control the instrument, acquire the data, and compare the data to that of known substances.[24] The hardware supplied for the Finnigan 1020B consists of a 32-K, 16-bit word, Nova 4C/5 minicomputer with a foreground/background, priority-interrupt operating system for

simultaneous data acquisition and processing and a 10 megabyte dual fixed/removable disk drive. The software controls and monitors the instrument and processes the data.[19]

Tuning

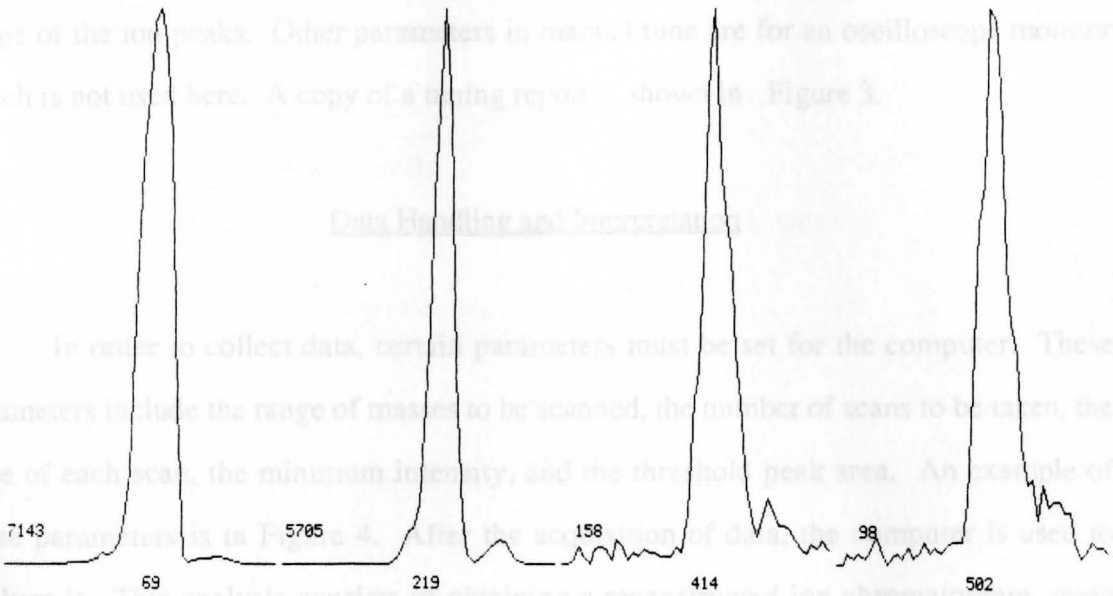
The mass spectrometer has to be tuned daily to achieve maximum efficiency and reproducibility. Tuning optimizes the conditions of the ion source. Parameters that can be varied include electron multiplier voltage, ion energy, filament, ion program, lens, extractor, resolution, electrometer zero, and electrometer range. Electron multiplier voltage is set at a high negative value to attract the ions as they exit the mass analyzer. Ion energy is the positive potential applied to the ion volume (walls of the ion source) to propel positive ions out of the ion source. This primarily affects low m/z values. The filament generates electrons that ionize the sample molecule and is operated by a toggle switch through the software. By ion program, one determines the ramp of the velocity of the ions. The negative potential that is applied to the lens serves to focus the ion beam. This affects the peak shape in the graph of ion intensity to m/z, as shown in Figure 3. The positive potential that is applied to the extractor influences the shape of the ion beam. This potential affects the shape and amplitude of the peak. Resolution is a measure of the degree of separation of adjacent peaks or intensities. One wishes to achieve unit resolution, which results when the signal returns to the baseline between adjacent integer mass peaks. The "resolution high" control adjusts the resolution for mainly high masses, while the "resolution low" adjusts all mass resolutions. The electrometer zero is used to control the no-signal or zero level on the electrometer. The electrometer range control amplifies the signal from the electron multiplier.[19]

The goal of tuning is to achieve maximum intensity and optimum resolution of the relative amounts of the ions formed for the calibration gas. Perfluorotributylamine $(C_4F_9)_3N$ (PFTBA or FC43) is used as the calibration gas. Four masses, 69, 219, 414,

CALIBRATION REPORT:
18 = LOWEST PEAK IN REFERENCE TABLE FOUND
614 = HIGHEST PEAK IN REFERENCE TABLE FOUND
21 OF 21 REFERENCE PEAKS WERE FOUND
1 % OF PEAK WIDTH = RMS FIT ERROR

SCAN A4 ON LINEAR DSPLY DV:CL CG:ON 30 AUG 88 13:47:52 5-WAY
EM UPPER LIMIT 2500 SMOOTHING FACTOR 1

1 ELECTRON MULT SW	ON	9 EXTRACTOR	1.88
2 ELECT MULT VOLTS	-2070.59	10 ELECTROMETR RNG	8.00
3 RESOLUTION HIGH	134.00	11 SCOPE SWEEP SW	OFF
4 RESOLUTION LOW	128.00	12 SCOPE SWP SPEED	1.00
5 ION ENERGY	1.57	13 ELECTROMTR ZERO	-0.92
6 FILAMENT SW	ON	14 SCOPE 1ST MASS	100.39
7 ION PROGRAM	10.98	15 SCOPE MASS RNG	0.00
8 LENS VOLTAGE	-64.31	16 SCOPE SENSITVTY	0.50



AUTOMATIC TUNE RATIO REPORT 08/30/88

MASS	INTENSITY	% OF 69	TARGET %
69	85247.	100.00	100.00
219	41599.	48.79	30.00- 60.00
414	1289.	1.51	1.40- 2.00
502	811.	0.95	0.80- 2.00

ISOTOPE RATIO REPORT

MASSES	% ISOTOPE	TARGET %
69/ 70	1.21	0.80- 1.30
219/220	4.10	3.50- 5.20
414/415	12.24	7.20-10.80
502/503	13.79	8.10-12.10

FIGURE 3. Tuning report, including calibration report, mass spectrum of calibration gas, parameters selected, ratios of intensities, and isotope ratios.

and 502, are used with their target intensities listed in Figure 3. Isotope ratios showing proper zeroing of the detector are also listed in Figure 3. The operator wishes to achieve good peak shape and amplitude. Before proceeding with manual tuning, one must adjust the electron-collimating magnet using the magnet adjust program. The operator then zeros the electrometer using the EZ program, before entering the manual tune (MT) program. Within MT, one can adjust the electron multiplier voltage, the ion energy, the ion program, lens voltage, extractor, electrometer range, and the high and low resolution to optimize the shape of the ion peaks. Other parameters in manual tune are for an oscilloscope monitor which is not used here. A copy of a tuning report is shown in Figure 3.

Data Handling and Interpretation

In order to collect data, certain parameters must be set for the computer. These parameters include the range of masses to be scanned, the number of scans to be taken, the time of each scan, the minimum intensity, and the threshold peak area. An example of these parameters is in Figure 4. After the acquisition of data, the computer is used to analyze it. This analysis consists of obtaining a reconstructed ion chromatogram, mass chromatograms, mass spectra, and mass lists. The latter two may include averaging and background subtraction.

The reconstructed ion chromatogram (RIC) is a graph of total ion intensity vs. scan number or time. (See Figure 5) A pure sample should produce one RIC peak. Mass chromatograms are graphs similar to the RIC, but show the intensity at only one m/z value versus time. If mass chromatograms have similar shapes, it can be assumed that the corresponding ions are formed from the same compound. A mass spectrum is a display of the ion intensity for each m/z value in a given mass range. In this study, the mass spectra of metal-containing compounds contained clusters of peaks at neighboring m/z values

```
 5/17/88     20:42:15              SCAN 1 OF 70
      ACQ STARTED
RUN:  0:ALPYPT11

SAMPLE:  5UL OFO.0023G IN 10 ML BENZENE EI SOURCE
SUBMITTED BY:  DLZ
ANALYST:  DLZ
COMMENTS:  REPEAT 11 40 TO 300 @120

GC BYPASSED
INJ.  MODE:CAP.
   0 SEC = SPLIT/SWEEP VALVE TIME
   1 SEC = FIL./MULT.  OFF TIME
FIL/MUL MODE:AUTO.

SCAN FROM  40 AMU TO 800 AMU IN  2.0 SEC.


 5/17/88     20:44:40
      ACQUISITION COMPLETED
```

FIGURE 4. Acquisition parameters for solid probe injection

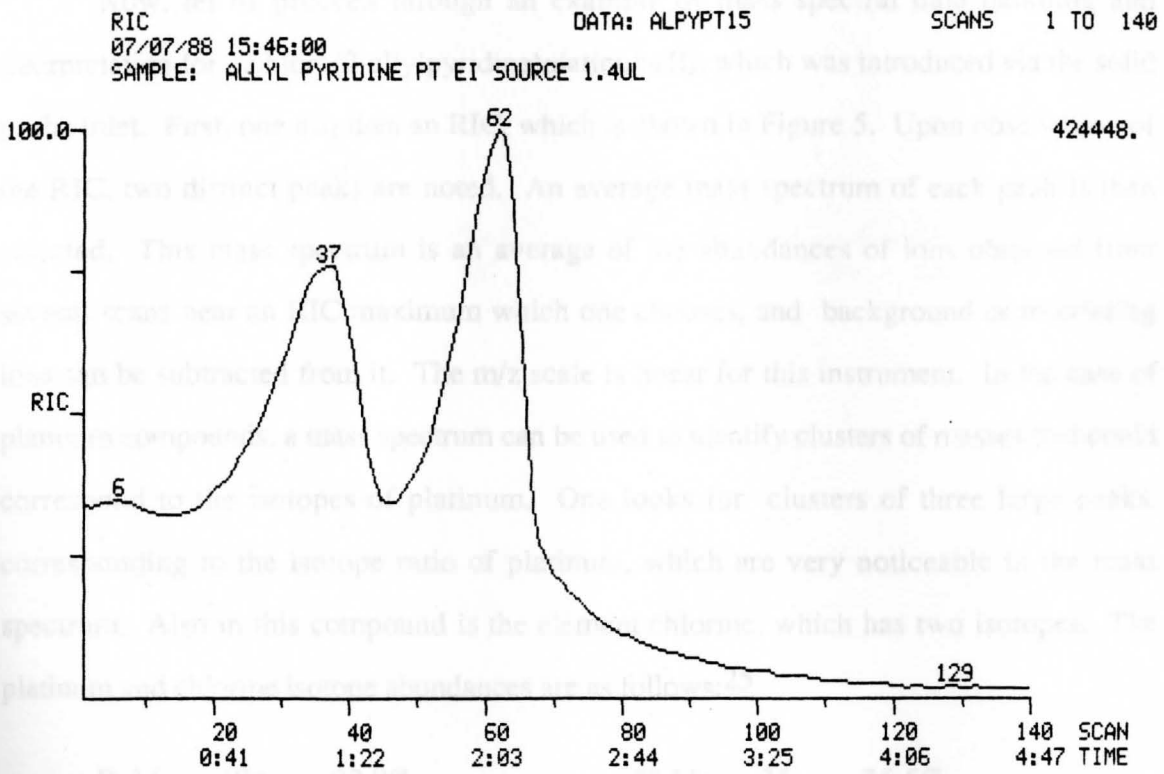


FIGURE 5. RIC of supposed dichloro(2-allylpyridine) platinum(II) showing two peaks, one at scan #37 and the other at scan #62, indicating the presence of at least two compounds.

because palladium and platinum are polyisotopic. Mass lists give numerical values for ion abundance and are used for mathematical calculations to determine the ions present in the sample at each m/z value. The mass lists obtained in this study are located in the Appendix.

Now, let us proceed through an example of mass spectral data handling and interpretation for dichloro(2-allylpyridine)platinum(II), which was introduced via the solid probe inlet. First, one acquires an RIC, which is shown in Figure 5. Upon observation of the RIC, two distinct peaks are noted. An average mass spectrum of each peak is then selected. This mass spectrum is an average of the abundances of ions obtained from several scans near an RIC maximum which one chooses, and background or interfering ions can be subtracted from it. The m/z scale is linear for this instrument. In the case of platinum compounds, a mass spectrum can be used to identify clusters of masses that could correspond to the isotopes of platinum. One looks for clusters of three large peaks, corresponding to the isotope ratio of platinum, which are very noticeable in the mass spectrum. Also in this compound is the element chlorine, which has two isotopes. The platinum and chlorine isotope abundances are as follows:[25]

Pt Mass	194	-	32.9%	Cl Mass	35	- 75.5%
	195	-	33.8%		36	- 0.0%
	196	-	25.3%		37	- 24.5%
	197	-	0.0%			
	198	-	7.2%			

The mass spectrum (Figure 6) is supposedly that of dichloro(2-allylpyridine)platinum(II), formula $C_8H_9NPtCl_2$. The next procedure in experimental interpretation is to demonstrate that each of the ions observed in the mass spectrum is actually an ion of that particular compound. This procedure involves checking mass chromatograms for each m/z value on the mass list that corresponds to the mass spectrum average. In Figure 7 is shown the mass chromatograms for m/z 383 to 389 which would correspond to the molecular ion of dichloro(2-allylpyridine)platinum(II). In Figure 7, the top left number of each chromatogram is the maximum relative ion abundance, and the

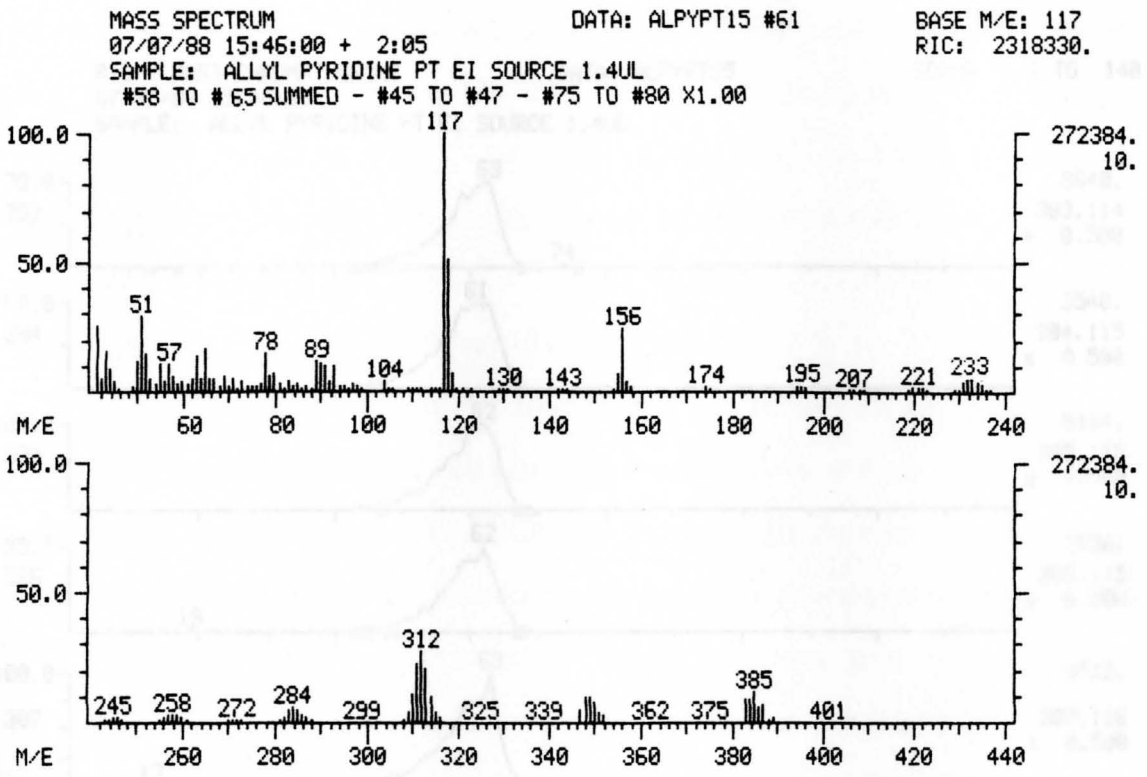


FIGURE 6. Mass spectrum of $C_8H_9NPtCl_2$.

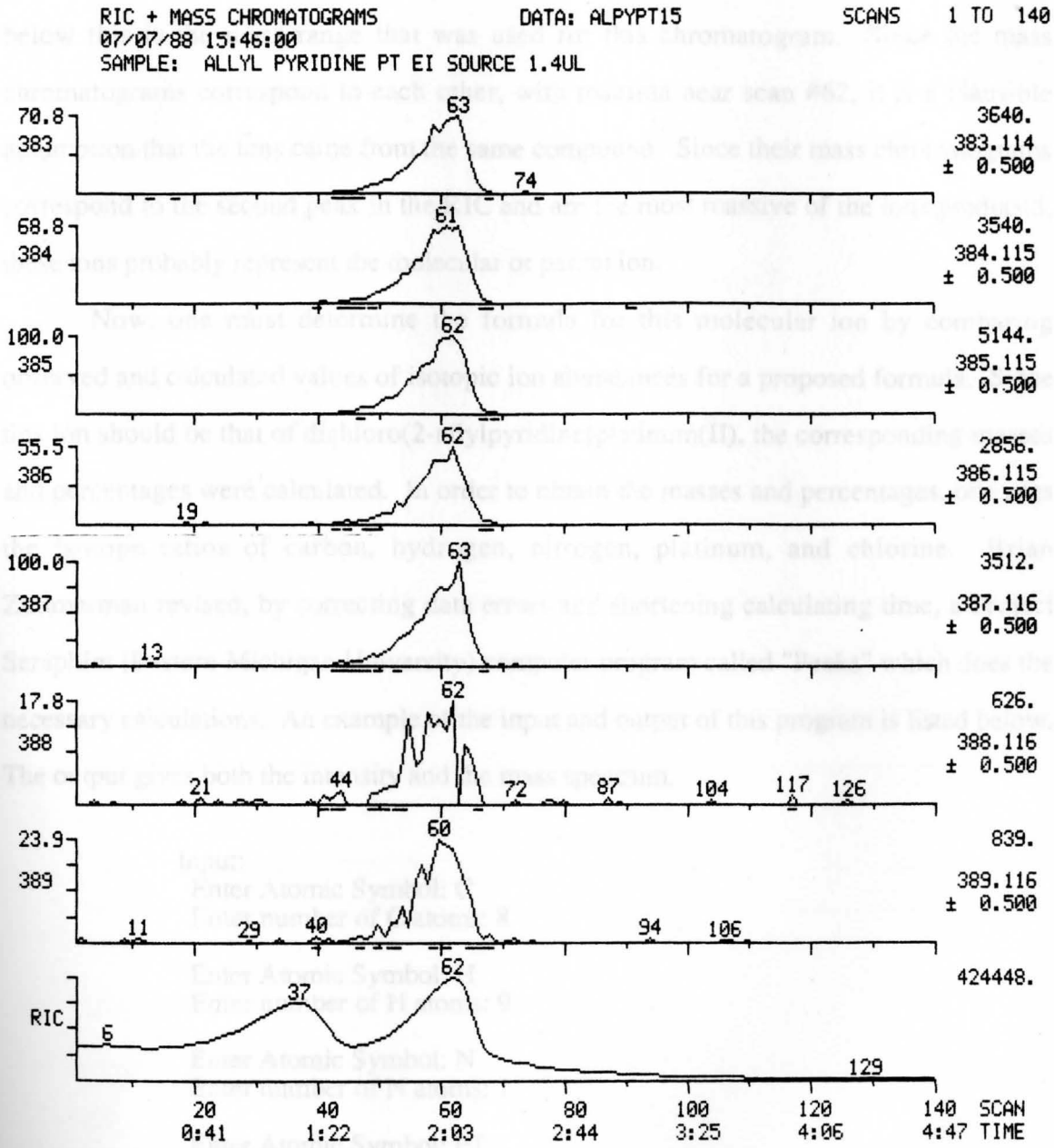


FIGURE 7. Mass chromatograms for molecular ion of $C_8H_9NPtCl_2$.

number below this is the m/z of this chromatogram. The top right number of each chromatogram is the maximum ion current in arbitrary units for this m/z, and the number below this is the mass range that was used for this chromatogram. Since the mass chromatograms correspond to each other, with maxima near scan #62, it is a plausible assumption that the ions came from the same compound. Since their mass chromatograms correspond to the second peak in the RIC and are the most massive of the ions produced, these ions probably represent the molecular or parent ion.

Now, one must determine the formula for this molecular ion by comparing observed and calculated values of isotopic ion abundances for a proposed formula. Since this ion should be that of dichloro(2-allylpyridine)platinum(II), the corresponding masses and percentages were calculated. In order to obtain the masses and percentages, one uses the isotope ratios of carbon, hydrogen, nitrogen, platinum, and chlorine. Brian Zimmerman revised, by correcting data errors and shortening calculating time, a Project Seraphim (Eastern Michigan University) computer program called "Peeks" which does the necessary calculations. An example of the input and output of this program is listed below. The output gives both the intensity and the mass spectrum.

Input:
Enter Atomic Symbol: C
Enter number of C atoms: 8

Enter Atomic Symbol: H
Enter number of H atoms: 9

Enter Atomic Symbol: N
Enter number of N atoms: 1

Enter Atomic Symbol: PT
Enter number of Pt atoms: 1

Enter Atomic Symbol: CL
Enter number of Cl atoms: 2

Enter Atomic Symbol: END

Calculating for C 8 H 9 N 1 Pt 1 Cl 2

Is this the correct formula? Y

Calculating. . .

Output:

For : C 8 H 9 N 1 Pt 1 Cl 2

Mass	Abund	PCT	
379	.0001	0.024	
380	.0000	0.002	
381	.0041	1.582	
382	.0004	0.150	
383	.1740	66.902	**********
384	.1926	74.030	**********
385	.2601	100.000	**********
386	.1363	52.406	**********
387	.1518	58.371	**********
388	.0317	12.205	**
389	.0400	15.381	***
390	.0037	1.406	
391	.0040	1.544	
392	.0004	0.142	
393	.0000	0.006	
394	.0000	0.000	

Comparison of the observed values and the calculated values is given in Table 1.

TABLE 1. COMPARISION OF ABUNDANCE FOR $[C_8H_9NPtCl_2]^{+\cdot}$

m/z	Observed Average Abundance (%)	Calculated Abundance (%)	Error
383	70.4	66.9	3.5
384	74.3	74.0	0.3
385	100.0	100.0	---
386	52.2	52.4	-0.2
387	57.8	58.4	-0.6
388	11.6	12.2	-0.6
389	17.0	15.4	1.6

The average absolute error, the difference between the observed and the calculated values, is 1.1. The agreement of the larger, more intense, ion populations with calculated values is to be expected if these are the isotope peaks for the molecular ion only. The less intense ions are more apt to include significant interference from background and thus have a higher error. As one can notice in Figure 7, the shapes of the mass chromatograms that have more ion intensity appear closer to the shape of the RIC. The agreement of the percentages indicates that the formula $[C_8H_9NPtCl_2]^{+\cdot}$ is very likely, with no significant interference in this m/z range from ions corresponding to any other formula.

Following the above procedure, it is now a matter of calculation to account for the other platinum-containing ions that showed clusters in the mass spectrum. Often it is not possible to explain a series of m/z values with only one formula. Let us look at another example, that of m/z 308 to 316. Mass chromatograms for this cluster are shown in Figure 8. The proposed ions will be fragment ions resulting from cleavage of the Pt-Cl bonds and loss of $H^{\cdot}$. The proposed ions for these m/z values are $[C_8H_8NPt]^+$, resulting from the loss of HCl and $Cl^{\cdot}$ from the molecular ion; $[C_8H_7NPt]^{+\cdot}$ from the loss of 2HCl; $[C_8H_6NPt]^+$ from the loss of 2HCl and $H^{\cdot}$; $[C_8H_5NPt]^{+\cdot}$ from the loss of 2HCl and H_2; and $[C_8H_4NPt]^+$ from the loss of 2HCl, H_2 and $H^{\cdot}$. These ions were proposed since there is no ion with m/z 317, which would correspond to the loss from the molecular ion of $2Cl^{\cdot}$ or Cl_2; and there is no ion with m/z 307, which would correspond to the loss from the molecular ion of 2HCl and $2H_2$. The process used above for the molecular ion is now repeated five times for this sequence. The calculated values for the ions are shown in Table 2.

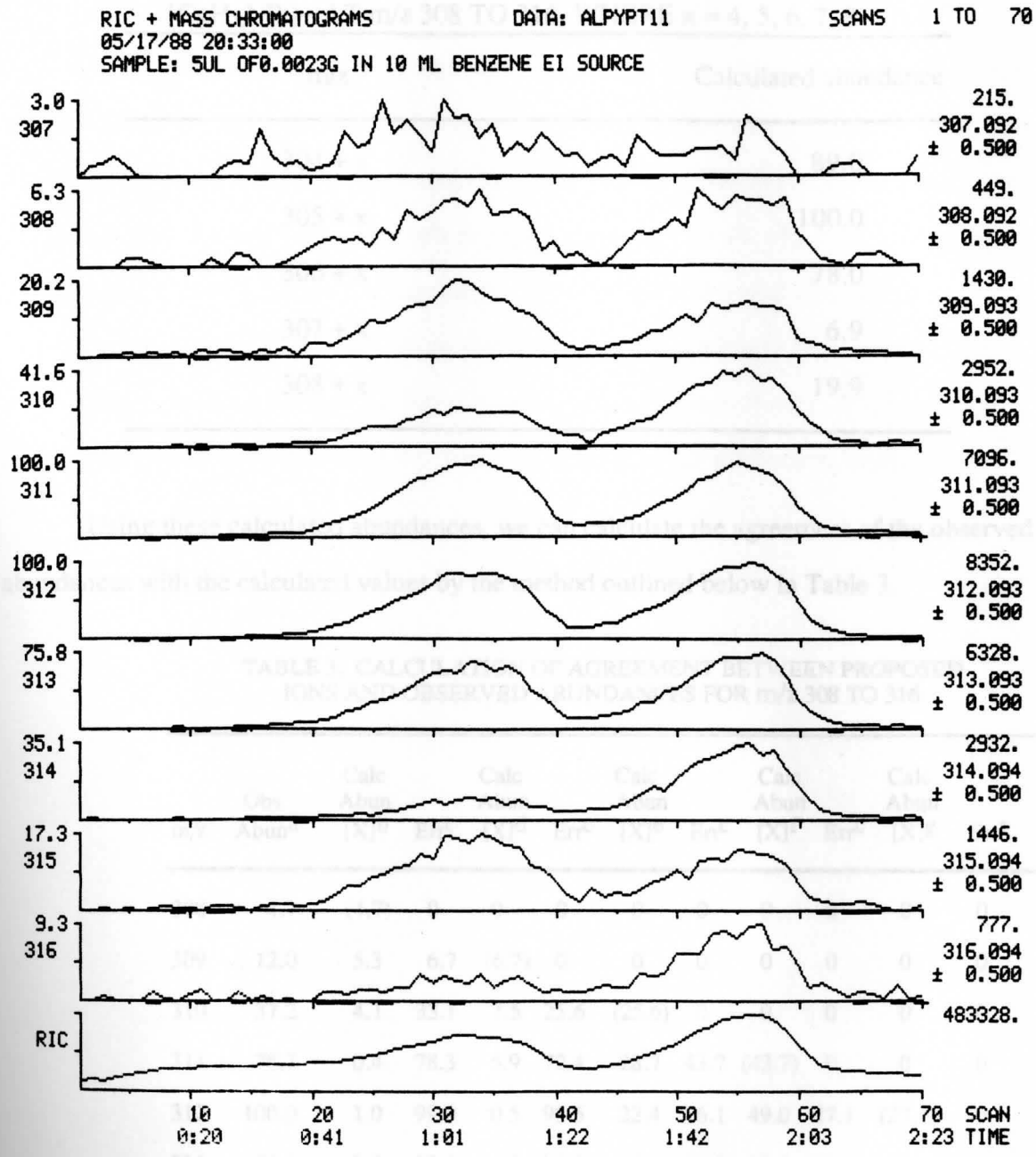


FIGURE 8. Mass chromatograms for $C_8H_9NPtCl_2$ fragment ions of m/z 307 to 316.

TABLE 2. CALCULATED ISOTOPE RATIOS FOR PROPOSED $[C_8H_xNPt]+$ AT m/z 308 TO 316, WHERE x = 4, 5, 6, 7, 8

m/z	Calculated abundance
304 + x	89.0
305 + x	100.0
306 + x	78.0
307 + x	6.9
308 + x	19.9

Using these calculated abundances, we can calculate the agreement of the observed abundances with the calculated values by the method outlined below in Table 3.

TABLE 3. CALCULATION OF AGREEMENT BETWEEN PROPOSED IONS AND OBSERVED ABUNDANCES FOR m/z 308 TO 316

m/z	Obs Abun[a]	Calc Abun [X][b]	Err[c]	Calc Abun [X][d]	Err[c]	Calc Abun [X][e]	Err[c]	Calc Abun [X][f]	Err[c]	Calc Abun [X][g]	Err[c]
308	4.7	(4.7)	0	0	0	0	0	0	0	0	0
309	12.0	5.3	6.7	(6.7)	0	0	0	0	0	0	0
310	37.2	4.1	33.1	7.5	25.6	(25.6)	0	0	0	0	0
311	78.7	0.4	78.3	5.9	72.4	28.7	43.7	(43.7)	0	0	0
312	100.0	1.0	99.0	0.5	98.5	22.4	76.1	49.0	27.1	(27.1)	0
313	73.8	0.0	73.8	1.5	72.3	2.0	70.3	38.3	32.0	30.4	1.6
314	35.6	0.0	35.6	0.0	35.6	5.7	29.9	3.4	26.5	23.7	2.8
315	12.9	0.0	12.9	0.0	12.9	0.0	12.9	9.8	3.1	2.1	1.0
316	8.0	0.0	8.0	0.0	8.0	0.0	8.0	0.0	8.0	6.1	1.9

[a] Observed Abundance(%) [b] Calculated Abundance(%) $[C_8H_4NPt]^+$ [c] Error
[d] Calculated Abundance(%) $[C_8H_5NPt]^{+\cdot}$ [e] Calculated Abundance(%) $[C_8H_6NPt]^+$
[f] Calculated Abundance(%) $[C_8H_7NPt]^{+\cdot}$ [g] Calculated Abundance(%) $[C_8H_8NPt]^+$

Values in parentheses are forced into agreement with observed values, and other abundances in the same column are calculated in proportion to those in Table 2. The errors are the differences between the preceding two columns. The average error in the last column is 1.8. As one may note, this is rather good agreement, but it took five ions to explain this cluster. Since the agreement between the observed abundances and the calculated abundances is good, the proposed ions most likely account for these m/z values.

After working through an interpretation of mass spectral data, it is very easy to agree with McLafferty that "the approach is similar to an arithmetic brain-teaser."[26]

CHAPTER II

EXPERIMENTATION

Preparation of compounds analyzed

The complexes of 2-allylpyridine that were analyzed with the Finnigan 1020B GC/MS had been prepared by Dr. Ralph E. Yingst[10] using the following procedure. 2-Allylpyridine was prepared by the reaction of allylmagnesium bromide with 2-bromopyridine.[27,28] The addition of 2-allylpyridine to a solution of picric acid produced the yellow picrate of 2-allylpyridine. Potassium tetrachloroplatinate(II) was added to 2-allylpyridine. This was acidified to produce dichloro(2-allylpyridine)platinum(II), which was reported to be an orange solid after vacuum sublimation. A yellow palladium(II) complex was synthesized using 2-allylpyridine and $PdCl_4^{-2}$.[27]

For the present study, the picrate was converted to 2-allylpyridine by the following procedure. The picrate was dissolved in 6-M HCl to form an aqueous solution of picric acid and 2-allylpyridinium chloride. The picric acid was extracted with benzene until there was no yellow color remaining in the aqueous phase. Aqueous sodium hydroxide was added to the 2-allylpyridinium chloride solution, until the latter was basic, to form 2-allylpyridine. The 2-allylpyridine was then extracted into diethyl ether. The water in this extraction was removed by mixing with anhydrous $CaCl_2$.

Mass Spectral Analysis

All mass spectral analyses of the compounds were done using the Finnigan 1020B GC/MS with the electron impact ionization source.

A 0.5-μL sample of the ether extract of 2-allylpyridine was introduced through the septum into the capillary column of the gas chromatograph. A scan of m/z 40 to 400 was taken every second. The acquisition of data took 2.6 minutes. The following GC parameters were used:

220 deg. = zone temperature
55 deg. = initial temperature
200 deg. = final temperature
1 min. = initial time before ramping
20 deg./min.= ramp rate
3 min. = final time
220 deg. = separator temperature
80 deg. = manifold temperature
injection mode is capillary
10 sec. = split/sweep valve time
(This means that after 10 seconds gases remaining in the injector are vented.)
40 sec. = filament/multiplier off time
(This means analysis by mass spectrometry will not start for 40 seconds after injection)
filament/multiplier mode is automatic

The hydrochloride salt of 2-allylpyridine was also analyzed using the mass spectrometer. 2-Allylpyridinium picrate was dissolved in HCl, and the picric acid formed was extracted with benzene. Three μL of the remaining aqueous solution was heated in a 10-μL pyrex tube until all the water had evaporated. The pyrex tube was then inserted into the ion source by use of the solid probe. The initial temperature of the probe was set at 40° C with a ramping rate of 120° C/min to a final temperature of 330° C. A scan of m/z 40 to 400 was taken every 2 seconds, and the acquisition of data took 2.5 minutes.

2-Allylpyridinium picrate, picric acid, dichloro(2-allylpyridine)platinum(II), and dichloro(2-allylpyridine)palladium(II) were analyzed by mass spectrometry using the same

conditions for solid probe injection as those of the 2-allylpyridinium chloride. Picric acid and 2-allylpyridinium picrate were evaporated from ethanol solutions to introduce approximately 300 ng of solid. 1.4 μL of a benzene solution of dichloro(2-allylpyridine)platinum(II) (2.3 mg in 10 mL) was used for the analysis of this complex. 2.5 μL of a chloroform solution of dichloro(2-allylpyridine)palladium(II) (0.6 mg in 2 mL) was used for the analysis of this complex, but the scan limit was increased to m/z 600 because of the belief that this complex may be a dimer; while the platinum(II) complex was a monomer. In both complexes, it is supposed that the ligand is coordinated through both the pyridyl nitrogen and the olefinic group.[27]

The compounds submitted for study have the following colors: 2-allylpyridinium picrate is a yellow solid, the palladium(II) complex is a yellow solid, and the platinum(II) complex is an orange and yellow-brown solid. The platinum(II) complex was pulverized but still produced two colors.

An attempt to separate manually the two crystalline forms of the platinum(II) complex was done. Mass spectral analysis was done on each crystal form, but this showed only enhancement of one form of the crystal over the other, rather than complete separation.

Additional Analytical Methods

Other methods used to assist in the identification and interpretation of the mass spectral results were melting points, differential scanning calorimetry (DSC), scanning electron microscopy with energy dispersive x-ray spectrometry (SEM), and infrared spectrometry (IR).

Whenever a material undergoes a change in physical state, heat is either absorbed or given off. Differential scanning calorimeters are designed for use in determining these enthalpies of physical change by measuring the difference in heat flow required for the

sample and an inert reference material. Thermograms can be either endothermic showing possible melting points or exothermic showing possible decomposition of the sample.[23] Determination of the thermal history of 2-allylpyridinium picrate and of dichloro(2-allylpyridine)palladium(II) was done using a Perkin-Elmer DSC-2 differential scanning calorimeter. The melting points of the two complexes of platinum were also determined.

An analysis of the surface of the 10-μL pyrex tube, after use for injection of dichloro(2-allylpyridine)palladium(II) into the mass spectrometer, was done to determine possible decomposition products using the Cambridge Model S-200 scanning electron microscope. A photograph can be taken of the sample under microscopic analysis. The x-ray spectrum indicates x-ray emission, which can be used to identify an element. Each element has a characteristic x-ray emission which is dependent upon its electronic structure.[23] The Tracor Northern T/N 5500 energy dispersive X-ray microanalyzer was used to obtain an x-ray spectrum.

Infrared spectra arise from a molecule's different modes of vibration and rotation. Since many of the peaks occurring in the IR spectrum are characteristic of specific groups of atoms in the molecule, information about molecular structure can be deduced.[29] A sample of dichloro(2-allylpyridine)platinum(II) was mixed with potassium bromide and pressed under vacuum to form a salt plate that was analyzed using a Perkin-Elmer 1750 infrared Fourier-transform spectrometer. A background spectrum was taken with a potassium bromide salt plate for subtraction purposes. A spectrum was obtained from wavenumbers of 3100 to 950 cm^{-1} and from 1000 to 250 cm^{-1}.

Liquid chromatography can be used for the separation of the components of a mixture by the difference in retention time in a column as is observed with gas chromatography. In the column there is a stationary phase and a mobile phase. In this work the mobile phase was benzene. Molecular absorption in the ultraviolet and visible regions of the spectrum (100 - 700 nm) is dependent upon the electronic structure of a molecule and can indicate, among other things, chromophores for organic molecules, and

unfilled d subshells for transition metals.[22] Benzene solutions of the platinum(II) complex that were used for MS study were analyzed by a Waters 6000 pumping system with a wisp autosampler liquid chromatograph with a Whatman reversed phase C-18, 4.6 by 250 mm column, using a Waters 990 diode array spectrophotometer as detector; and spectra were obtained in the region of 280 to 800 nm. Below 280 nm, benzene shows absorbance and this region could not be analyzed.

CHAPTER III

ANALYSIS OF 2-ALLYLPYRIDINE

Summary of Previously Reported Results

Some mass spectral work on pyridine and substituted pyridines has been reported. Heterocyclic molecules such as furan, pyrrole, pyridine, and indole show an intense molecular ion peak as does benzene.[30] This shows the stability of the aromatic ring, with its rich stock of π-electrons. The removal of a π-electron requires only a very small amount of energy in comparison with the energy needed to break the ring system for further fragmentation.[31] Primary rupturing of the ring of a nitrogen-containing heterocyclic molecule usually involves the loss of nitrogen in a neutral molecule, such as HCN, preceded by hydrogen scrambling,[32] meaning all hydrogens in the molecule have an equal opportunity to combine with the carbon. Electron density is greatest for position 3 on the pyridine ring, followed by position 4, and lowest for position 2.[32] Substituted heterocyclic molecules also tend to lose the substituent or part of it before cleavage of the ring, as cleavage of the ring usually requires more energy.[3] These substituents preferentially fragment in the β-position with respect to the ring, leaving the charge on the π-electron system of the ring.[30] Olefinic substituents tend to lose neutral species such as H_2, $CH_3^{\cdot}$, C_2H_4, etc.[33]

The ionization of pyridine produces two abundant ions, the molecular ion and the ion formed from the loss of HCN by the molecular ion[34] following the fragmentation scheme[35] and mechanism[36] shown in Figure 9. The ion at m/z 78 can be explained as the well-stabilized dehydropyridinium cation.[35]

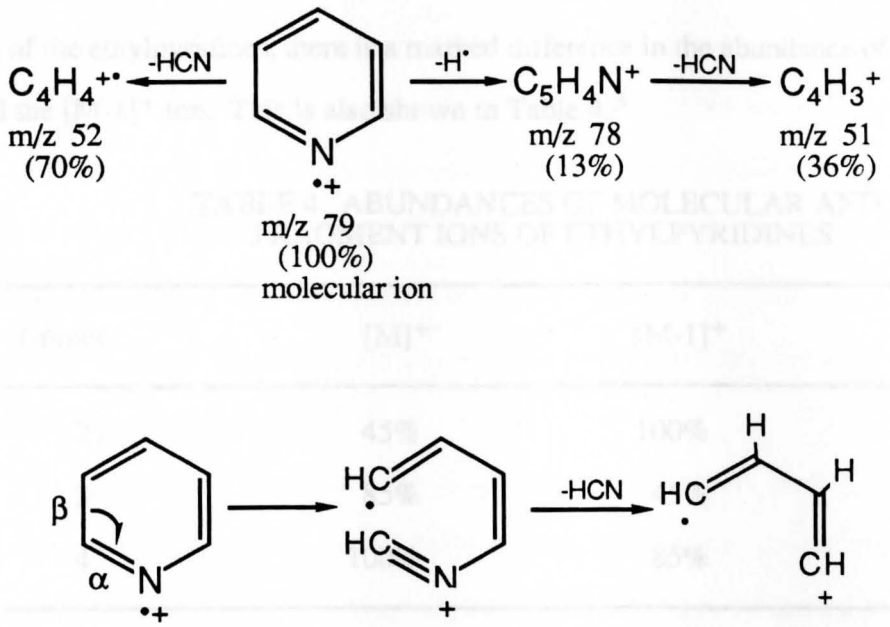


FIGURE 9. Fragmentation mechanism of pyridine, from Ref. 35 and 36.

Previous research on substituted pyridines has shown similar fragmentation patterns which can be used to identify isomers. The mass spectrum of 2-(4-heptyl)pyridine (m.w. 177) shows that the molecule first loses, by rearrangement, an olefin molecule, propylene, with a change in the arrangement of the double bonds in the pyridine ring to form a double bond between the substituent and the ring. This is followed by the loss of an ethyl radical to form an ion of m/z 106.[3] The mass spectra of 2-ethylpyridine, 3-ethylpyridine, and 4-ethylpyridine show marked differences in the first fragmentation occurring in the side chain, which is the loss of the methyl radical, as shown in Table 4. The explanation for the low intensity of the $[M-15]^+$ or m/z 92 ion is that a possible resonance form created from the 2-ethylpyridine molecule, but not from the other isomers, would have the positive charge located at a nitrogen atom with only six electrons, resulting in an energetically unfavorable configuration. Some isomers can be distinguished, as the above example illustrates, with the $[M-15]^+$ peak in the mass spectrum. Also, in the mass

spectra of the ethylpyridines, there is a marked difference in the abundance of the molecular ion and the $[M-1]^+$ ion. This is also shown in Table 4.[3]

TABLE 4 ABUNDANCES OF MOLECULAR AND FRAGMENT IONS OF ETHYLPYRIDINES

Isomer	$[M]^{+\cdot}$	$[M-1]^+$	$[M-15]^+$
2	45%	100%	5%
3	85%	45%	100%
4	100%	85%	50%

Another example of isomeric differences in the mass spectra of heterocyclic molecules is the case of 3-ethyl-4-methylpyridine, 3-ethyl-5-methylpyridine, and 2-ethyl-6-methylpyridine, which is illustrated in Table 5.[3]

TABLE 5 ABUNDANCES OF MOLECULAR AND FRAGMENT IONS OF ETHYLMETHYLPYRIDINES

Isomer	$[M]^{+\cdot}$	$[M-1]^+$	$[M-15]^+$
3,4	70%	25%	100%
3,5	85%	60%	100%
2,6	50%	100%	0%

The mass spectra of 2-,3-,and 4-methylpyridines also show isomeric differences with the $[M-1]^+$ ion being most abundant for the 3-methyl isomer, while the $[M-15]^+$ ion is most abundant for the 2-methyl isomer.[20]

The mass spectra of two isomeric alkylpyridines, 2-propylpyridine and 2-methyl-5-ethylpyridine show fragmentation patterns that can be used for identification of the side chains. The base peak or most abundant ion in the 2-propylpyridine is accounted for by fragmentation β to the aromatic ring, followed by migration of the hydrogen atom and a loss of neutral ethylene. This ion also occurs in the ionization of 2-methyl-5-ethylpyridine, but to a lesser extent. The base peak in the spectrum of 2-methyl-5-ethylpyridine results from the loss of a methyl radical.[8]

Butyl-substituted pyridines were another series of isomers studied. The base peak of the 2- and 4-butylpyridine is due to the ion resulting from the loss of propylene, while the base peak for 3-butylpyridine is at m/z 92, not 93. The m/z 93 shows an abundance of 90% in the 3-isomer. An azatropylium ion[35] or methylene attached to the pyridinium ion [37] are possible explanations for m/z 93. The molecular ion is also intense in the 3- and 4-butylpyridine spectra and quite small in the 2-butylpyridine mass spectrum. Ions resulting from the loss of $C_2H_5^{\cdot}$ and $CH_3^{\cdot}$ were more abundant in the mass spectrum of 2-butylpyridine.[7]

The mass spectrum of 4-propylpyridine also has isomeric similarities corresponding to the mass spectrum of 2-propylpyridine. The mass spectra of these substituted pyridines have a base peak of 93, with the 4-isomer producing the more abundant molecular ion.[4]

Isomeric differences in substituted groups were also noted in hydroxy pyridines.[38] Loss of substituent groups before ring cleavage was also noted in $C_{11}H_{15}N(OH)_2$ and its acetyl derivative.[39]

The carbon-carbon bond in the side chain of 2-substituted pyridines undergoes β cleavage and participates in an interesting intermediary ion. This ion is proposed to be a two-ring or spiro type ion (See Figure 10). This can happen in the 2-position since the

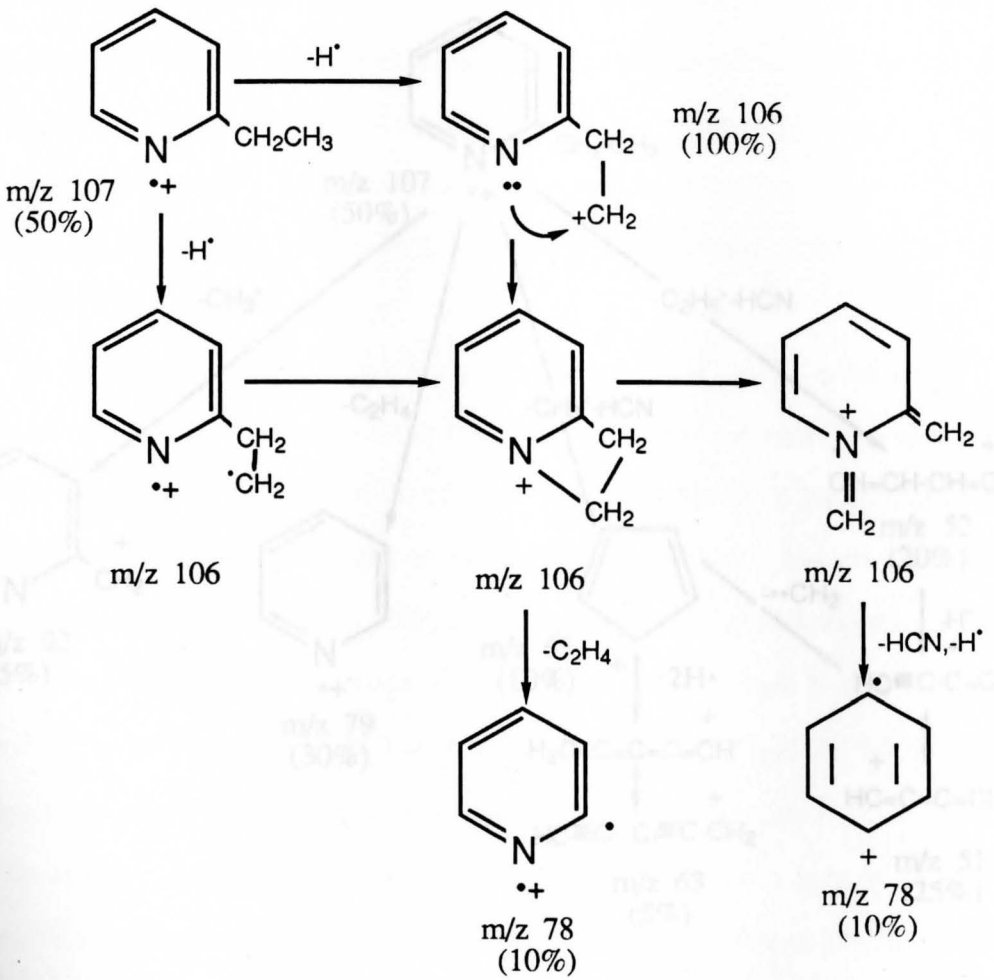


FIGURE 10. Fragmentation mechanism of 2-ethylpyridine from Ref. 9, p. 569.

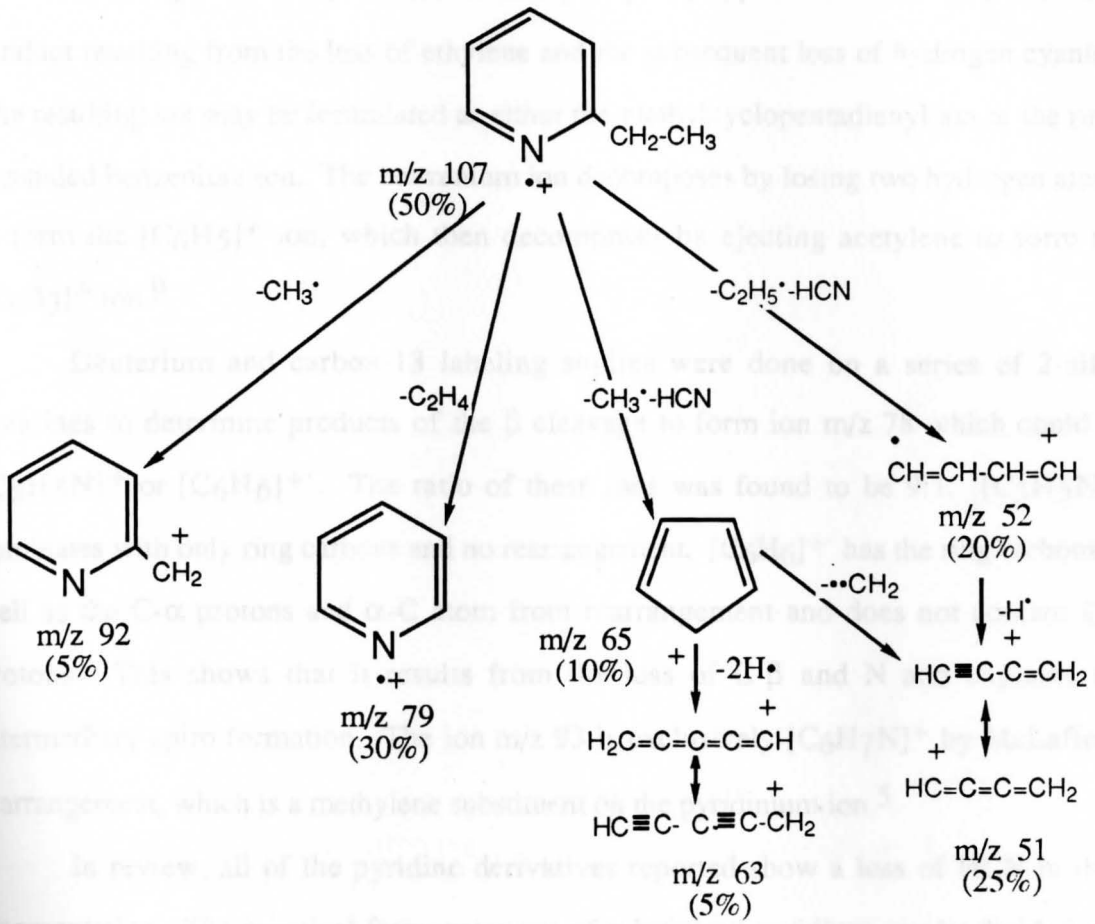


FIGURE 10. Continued.

charge on the nitrogen atom in the pyridine ring can attract the electron on the terminal hydrogen on the side chain due to its proximity.[5,40]

The fragmentation pattern of 5-methyl-3-propyl-pyridine shows the β-cleavage product resulting from the loss of ethylene and the subsequent loss of hydrogen cyanide. The resulting ion may be formulated as either the methylcyclopentadienyl ion or the ring-expanded benzenium ion. The benzenium ion decomposes by losing two hydrogen atoms to form the $[C_6H_5]^+$ ion, which then decomposes by ejecting acetylene to form the $[C_4H_3]^+$ ion.[9]

Deuterium and carbon-13 labeling studies were done on a series of 2-alkyl pyridines to determine products of the β cleavage to form ion m/z 78 which could be $[C_5H_5N]^+$ or $[C_6H_6]^{+\cdot}$. The ratio of these ions was found to be 9:1. $[C_5H_5N]^+$ dominates with only ring carbons and no rearrangement. $[C_6H_6]^{+\cdot}$ has the ring carbons as well as the C-α protons and α-C atom from rearrangement and does not contain C-β protons. This shows that it results from the loss of C-β and N and explains the intermediary spiro formation. The ion m/z 93 is exclusively $[C_6H_7N]^+$ by McLafferty rearrangement, which is a methylene substituent on the pyridinium ion.[5]

In review, all of the pyridine derivatives reported show a loss of HCN in their fragmentation. The principal fragmentations of substituted pyridines can be divided into four types:

1. β-cleavage. An example of this is the loss of a methyl radical from the ethylpyridines.
2. γ-cleavage. This is favored in 2-substituted pyridines. For example, the $[M-1]^+$ peak in the mass spectrum of 2-ethylpyridine exceeds the $[M]^{+\cdot}$ peak in intensity.
3. McLafferty rearrangement. An example of this is found in the mass spectrum of 2-propylpyridine, with the fragment resulting from the loss of ethylene.

4. α-cleavage with hydrogen rearrangement. An example of this is the ion resulting from the elimination of ethylene in the mass spectrum of 2-ethylpyridine.

An example of the different cleavages is shown in the mechanism for 2-ethylpyridine in Figure 10.[3] McLafferty rearrangement can be shown in the fragmentation of 2-(4-heptyl)pyridine[3] located in Figure 11.

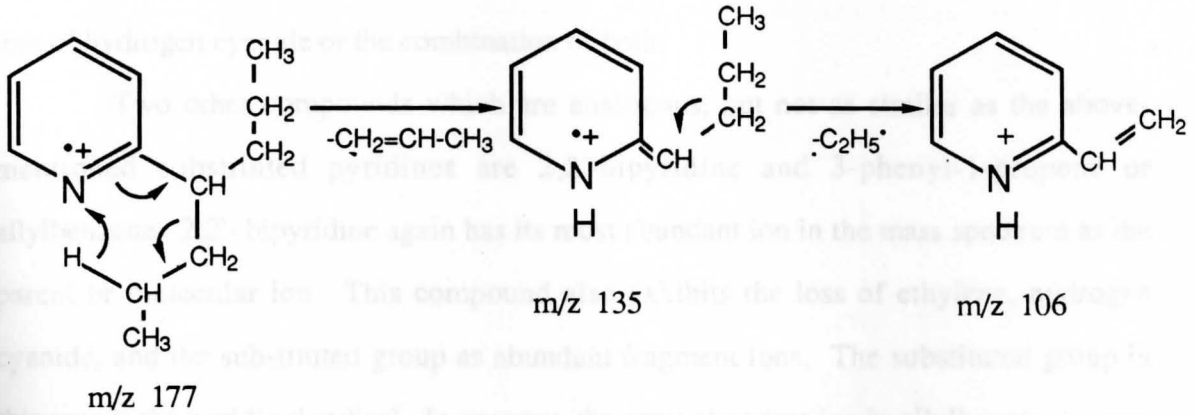


FIGURE 11. McLafferty rearrangement in the fragmentation of 2-(4-heptyl)pyridine, from Ref. 9, p. 570.

Using data from the *Catalog of Mass Spectral Data*[6], a comparison of the fragmentation of some analogs of 2-allylpyridine shows similiarities to the mass spectrum obtained for 2-allylpyridine. The fragment ions of pyridine are those showing the cleavage of the ring with the loss of hydrogen cyanide. The ring cleavage ions are those of m/z 50, 51, 52, and 53, with formulas of $[C_4H_2]^{+\cdot}$, $[C_4H_3]^+$, $[C_4H_4]^{+\cdot}$, and $[C_4H_5]^+$.[6]

The mass spectra of the methyl-substituted pyridines also show the most abundant ion to be the molecular ion. Other abundant ions in these spectra are $[M-1]^+$, $[M-15]^+$ from the loss of the methyl radical, $[M-27]^+$ from the loss of hydrogen cyanide, $[M-28]^{+\cdot}$

from the loss of ethylene, $[M-30]^{+\cdot}$ from the loss of the ethane, and $[M-42]^{+\cdot}$ or $[C_4H_3]^+$ from the loss of hydrogen cyanide and the methyl group. The mass spectra of the dimethyl substituted pyridines also show the most abundant ion to be the molecular ion, with similar fragmentation patterns as noted for the monomethyl substituted pyridines; i.e., the loss of the methyl radical, ethylene, the ethyl radical, hydrogen cyanide, and both the methyl radical and hydrogen cyanide. In the mass spectrum of 2-methyl-5-ethenyl-pyridine, the most abundant ion is also the molecular ion. Abundant fragment ions are also found as noted for the methyl-substituted pyridines with the loss of the substituted groups and the loss of hydrogen cyanide or the combination of both.

Two other compounds which are analogous, but not as similar as the above-mentioned substituted pyridines are 2,2'-bipyridine and 3-phenyl-1-propene or allylbenzene. 2,2'- bipyridine again has its most abundant ion in the mass spectrum as the parent or molecular ion. This compound also exhibits the loss of ethylene, hydrogen cyanide, and the substituted group as abundant fragment ions. The substituted group in this case is the pyridinyl radical. In contrast, the most abundant ion in allylbenzene's mass spectrum is $[M-1]^+$. This mass spectrum reflects the loss of the substituted group and the cleavage of the aromatic ring to form fragment ions. These abundant fragment ions are $[M-15]^+$ from the loss of $CH_3^{\cdot}$, $[M-27]^+$ from the loss of $C_2H_3^{\cdot}$, $[M-40]^{+\cdot}$ from the loss of C_3H_4, $[M-53]^+$ from the loss of $C_4H_5^{\cdot}$, and $[M-55]^+$ from the loss of $C_4H_7^{\cdot}$.

For each of these compounds, Table 6 shows the principal types of fragmentations with the abundances and m/z values for the resulting ions from the *Catalog of Mass Spectral Data*.[6]

Compound A = pyridine
Compound B = 2-methylpyridine
Compound C = 3-methylpyridine
Compound D = 4-methylpyridine
Compound E = 2,4-dimethylpyridine
Compound F = 2,6-dimethylpyridine
Compound G = 2-methyl-5-ethenylpyridine
Compound H = 2,2'-bipyridine
Compound I = 3-phenyl-1-propene (allylbenzene)

TABLE 6. DATA FROM THE *CATALOG OF MASS SPECTRAL DATA*

Cpd	$[C_4H_2]^{+\bullet}$ (50)	$[C_4H_3]^+$ (51)	$[C_4H_4]^{+\bullet}$ (52)	$[C_4H_5]^+$ (53)	[M-42]$^{+\bullet}$	[M-30]$^{+\bullet}$	[M-28]$^{+\bullet}$	[M-27]$^+$	[M-15]$^+$	[M-2]$^{+\bullet}$	[M-1]$^+$	[M]$^{+\bullet}$	
A	31[a]	40	76	9							12 (78)	100 (79)	
B	12	19	11	6 (51)	19 (63)	8 (65)	17 (66)	42 (78)	19 (91)	1 (92)	12 (93)	100	
C	8	11	8	4 (51)	11 (63)	11 (65)	29 (66)	46 (78)	5 (91)	3 (92)	31 (93)	100	
D	9	13	7	7 (51)	13 (63)	10 (65)	26 (66)	42 (78)	5 (91)	3 (92)	24 (93)	100	
E	8	6	8	7 (65)	15 (77)	9 (79)	22 (80)	7 (92)	18 (105)	4 (106)	38 (107)	100	
F	6	7	6	5 (65)	18 (77)	6 (79)	9 (80)	(92) 4 (105)	18 (106)	4 (107)	29	100	
G	13	21	13	4 (77)	8		(92)	6 (104)	10 (117)	9 (118)	25 (119)	100	
H	8	14	6	1		(128)	19 (129)	15		(155)	32 (156)	100	
I	8	17	4	1		(91)	41[b] (103)	8	(117)	100 (118)	81		

[a] numbers not in parentheses are relative abundances; numbers in parentheses are m/z values. (*Data from Catalog of Mass Spectra*).[6] [b] this is loss of $C_2H_3^{\cdot}$

TABLE 7 ADDITIONAL ABUNDANT IONS FROM THE *CATALOG OF MASS SPECTRAL DATA*

Cpd	M-	m/z	loss of	abundance
E	41	66	CH_3CN	10.4
	44	63	$CH_3^{\cdot}$,HCN,H_2	6.8
F	41	66	CH_3CN	22.0
	44	63	$CH_3^{\cdot}$,HCN,H_2	9.3
G	26	93	C_2H_2	4.0
	28	91	$H^{\cdot}$,HCN	35.4
	41	78	C_2H_2,CH_3[a]	6.0
	44	75	$CH_3^{\cdot}$,HCN,H_2	1.7
	54	65	$C_2H_3^{\cdot}$,HCN	11.9
	56	63	$C_2H_5^{\cdot}$,HCN	10.1
H	78	78	$C_5H_4N^{\cdot}$	15.0
I	40	78	C_3H_4	10.2
	53	65	$C_4H_5^{\cdot}$	14.0
	55	63	$C_4H_7^{\cdot}$	7.8

[a] This ion is formed differently than $[M-41]^+$ for compounds 5 and 6, as there is a larger substituent group and it is not necessary to break the ring at this point in the fragmentation.

Analysis of 2-Allylpyridinium Picrate and Picric Acid

The DSC of 2-allylpyridininum picrate showed a melting range of 155 and 163° C, which is in good agreement with the reported 157-161° C.[27] Since a sample of 2-allylpyridine was not originally available, a scheme was devised to infer indirectly the mass spectrum of this compound. Mass spectra of 2-allylpyridinium picrate, picric acid, and the common solvent, ethanol, were obtained. The proposal was that the mass spectrum of 2-allylpyridinium picrate in an ethanol solution should contain all the ions formed in the ionization of 2-allylpyridine, picric acid, and ethanol. Sometimes the solvent does not totally evaporate and may appear in the mass spectrum. If the spectral contributions of the

ions of picric acid and possibly ethanol are subtracted from those of the ions of 2-allylpyridinium picrate, the resulting spectrum should be that of 2-allylpyridine.

The mass spectrum of 2-allylpyridinium picrate contained peaks at m/z 41, 46, 50, 51, 52, 53, 59, 61, 62, 63, 64, 65, 66, 77, 78, 79, 80, 89, 90, 91, 92, 93, 104, 105, 117, 118, 119, 199, and 229. A molecular ion for 2-allylpyridinium picrate at m/z 348 does not appear; therefore, the compound must decompose upon heating into 2-allylpyridine and picric acid with molecular ions of 119 and 229 respectively.

The mass spectrum of picric acid indicated fragments at m/z 46, 50, 51, 53, 61, 62, 63, 77, 80, 91, 105, 199, 229, 230, and 231 as being abundant ions. This is in good agreement with published results[41] which note m/z values of 50, 51, 53, 61, 62, 63, 77, 80, 91, 199, and 229, in excess of 10% abundance.

By eliminating m/z values characteristic of only the picric acid from those of the picrate, it may be assumed that fragments at m/z 41, 52, 59, 64, 65, 66, 78, 79, 89, 90, 92, 93, 104, 117, 118, and 119, are characteristic of 2- allylpyridine. Fragments with m/z 46, 53, 61, 77, 105, 199, 229 are characteristic of picric acid. Both picric acid and 2-allylpyridine could have fragments at m/z values of 50, 51, 62, 63, 80, and 91. Figure 12 is the mass spectrum of 2-allylpyridinium picrate at the top with that of picric acid at the bottom.

"A very intriguing rearrangement" is that involving the loss of neutral nitric oxide from an ion. Many organic nitro compounds eliminate NO· from their molecular ion. This loss is facilitated by the stability of the NO· radical and the resulting even-electron ion produced.[42] The loss of NO· is proposed for the ion at m/z 199 and for other fragment ions together with the loss of hydrocarbons. The picric acid ions formed are listed in Table 8.

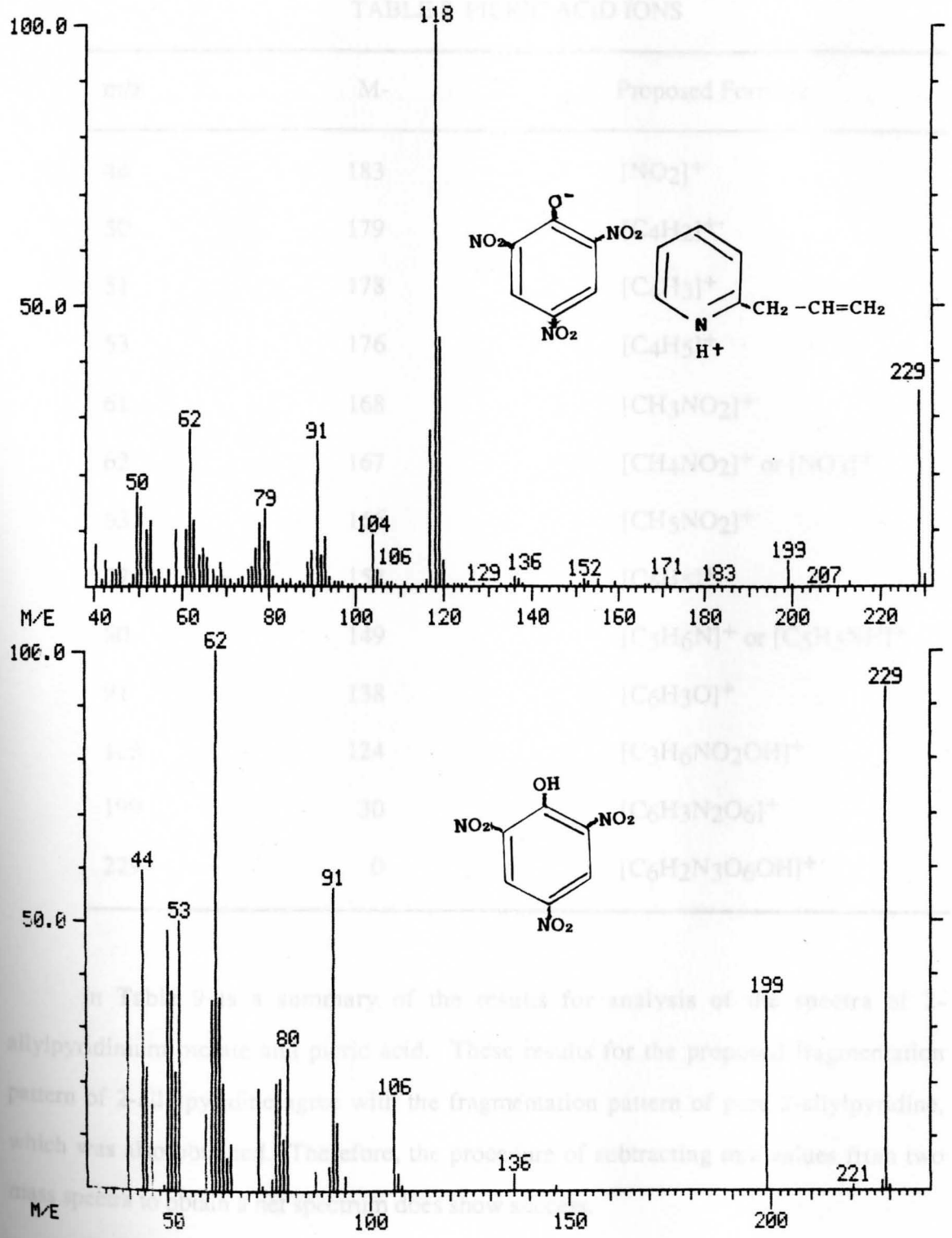


FIGURE 12. Mass spectra of 2-allylpyridinium picrate (top) and picric acid (bottom).

TABLE 8 PICRIC ACID IONS

m/z	M-	Proposed Formula
46	183	$[NO_2]^+$
50	179	$[C_4H_2]^{+\cdot}$
51	178	$[C_4H_3]^+$
53	176	$[C_4H_5]^+$
61	168	$[CH_3NO_2]^{+\cdot}$
62	167	$[CH_4NO_2]^+$ or $[NO_3]^+$
63	166	$[CH_5NO_2]^{+\cdot}$
77	152	$[C_6H_5]^+$
80	149	$[C_5H_6N]^+$ or $[C_5H_5NH]^+$
91	138	$[C_6H_3O]^+$
105	124	$[C_3H_6NO_2OH]^{+\cdot}$
199	30	$[C_6H_3N_2O_6]^+$
229	0	$[C_6H_2N_3O_6OH]^{+\cdot}$

In Table 9 is a summary of the results for analysis of the spectra of 2-allylpyridinium picrate and picric acid. These results for the proposed fragmentation pattern of 2-allylpyridine agree with the fragmentation pattern of pure 2-allylpyridine, which was also obtained. Therefore, the procedure of subtracting m/z values from two mass spectra to obtain a net spectrum does show success.

TABLE 9 m/z VALUES FOR 2-ALLYLPYRIDINIUM PICRATE AND PICRIC ACID.

m/z	2-Allylpyridinium Picrate	Picric Acid	2-Allylpyridine Proposed	2-Allylpyridine Actual
41	VW		x	VW
46	VW	W		
50	M	M	x	VW
51	M	W	x	W
52	W		x	VW
53	W	M		
59	VW		x	VW
61	W	W		
62	S	S	x	VW
63	W	W	x	W
64	VW			x
	VW			
65	VW		x	VW
66	VW		x	VW
77	VW	W		
78	W		x	VW
79	W		x	W
80	VW	W	x	VW
89	VW		x	VW
90	VW		x	VW
91	S	S	x	W
92	VW		x	VW
93	VW		x	VW
104	VW		x	VW
105	VW	VW		
117	S		x	S
118	S*		x	S*
119	S		x	S-P
120	VW-I		x	VW-I
199	VW	M		
229	S	S*-P		
230	VW-I	VW-I		
231	VW-I	VW-I		

P is parent or molecular ion; I is isotope ion; * is most abundant ion; VW is very weak intensity less than 10; W is weak intensity from 10 to 15; M is moderate intensity from 16 to 25; S is strong intensity from 26 to 100.

Other successes of this procedure have been reported in the literature, in that several other amine picrates also show the mass spectrum of picric acid superimposed on that of the free amine.[41]

Interpretation of Mass Spectrum of 2-allylpyridine

In Figure 13 is shown the mass spectrum of 2-allylpyridine using GC/MS, which agrees very well with one proposed for this compound by subtracting the mass spectrum of picric acid from that of 2-allylpyridinium picrate. In Table 10 are shown the m/z ratios, the proposed formulas, and the abundances of the most important ions in the spectrum of 2-allylpyridine.

A mass spectrum of 2-allylpyridinium chloride was also obtained, shown in Figure 14. This salt should have a spectrum similar to that of 2-allylpyridine as with the picrate salt. The HCl produced would give ions below m/z 40 and would not be observed here. These two mass spectra are in good agreement. It appeared that these salts of 2-allylpyridine have the same mass spectrum as 2-allylpyridine, which they should if they vaporize as free acid and base. There were no complications within the spectrum because of the initial decomposition of the salt prior to ionization.

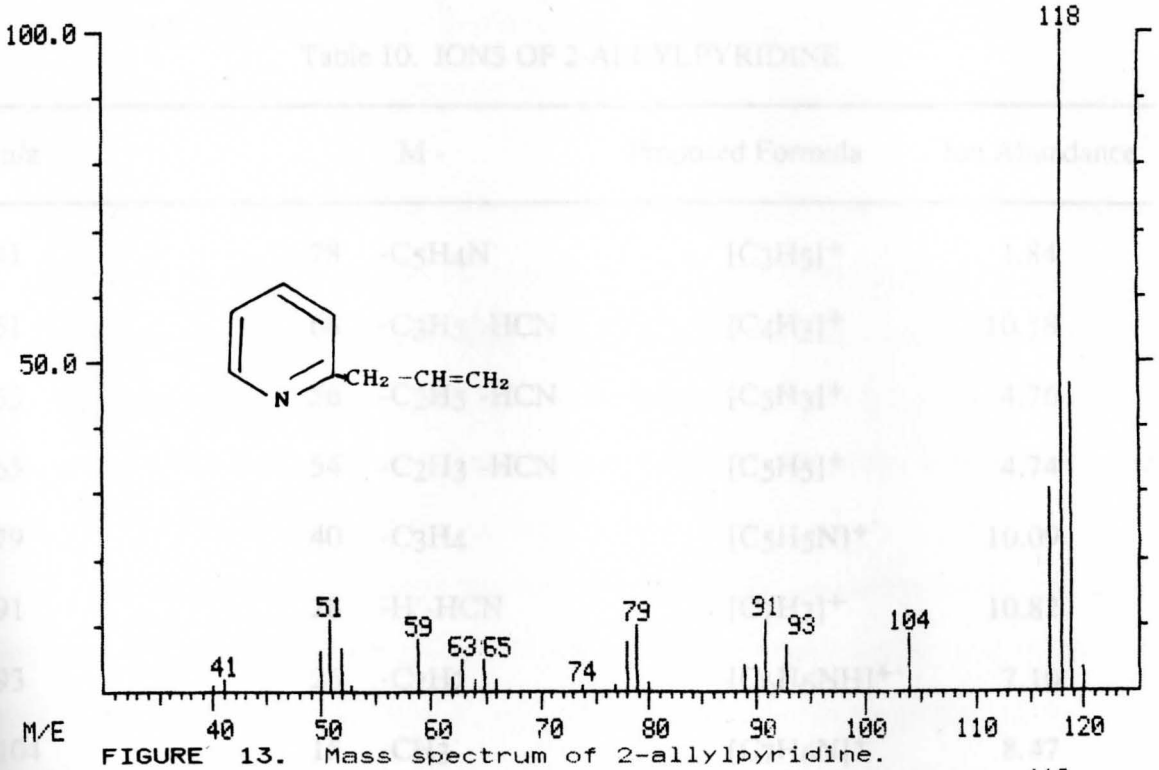


FIGURE 13. Mass spectrum of 2-allylpyridine.

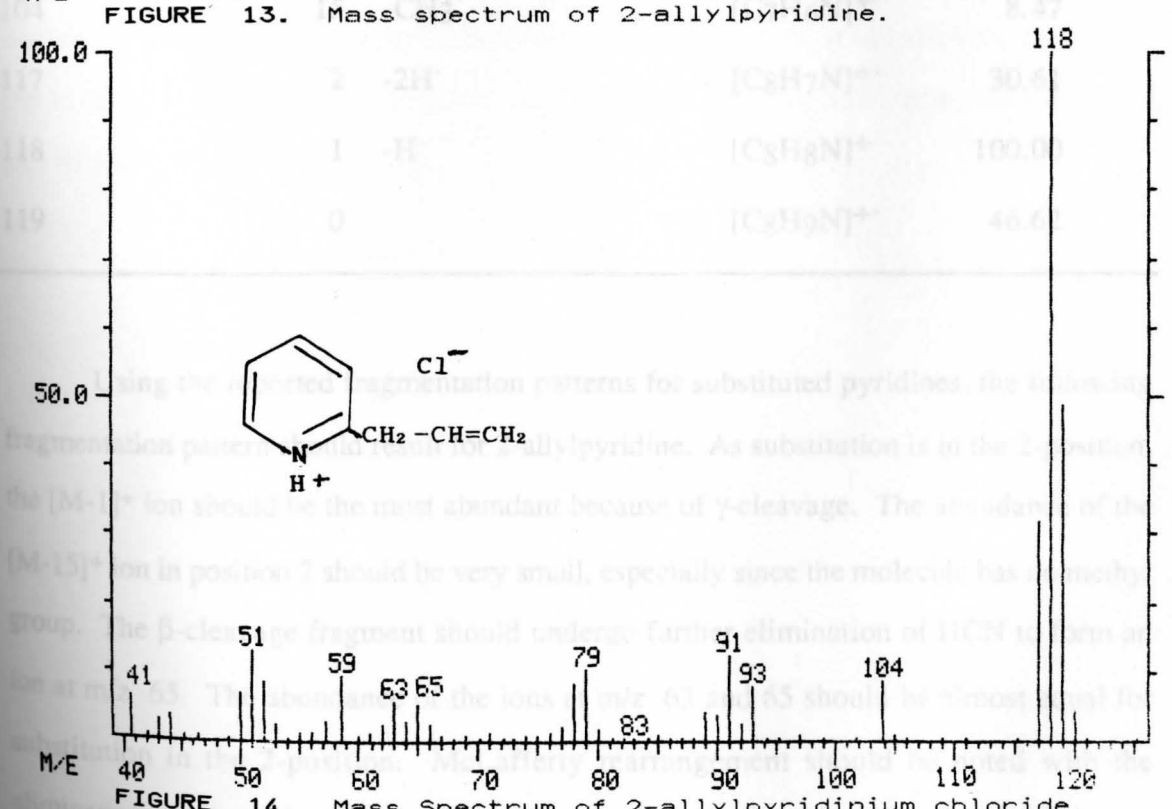


FIGURE 14. Mass Spectrum of 2-allylpyridinium chloride.

Table 10. IONS OF 2-ALLYLPYRIDINE

m/z	M -		Proposed Formula	Ion Abundance
41	78	$-C_5H_4N^{\cdot}$	$[C_3H_5]^+$	1.84
51	68	$-C_3H_5^{\cdot}$-HCN	$[C_4H_3]^+$	10.58
63	56	$-C_2H_5^{\cdot}$-HCN	$[C_5H_3]^+$	4.76
65	54	$-C_2H_3^{\cdot}$-HCN	$[C_5H_5]^+$	4.74
79	40	$-C_3H_4$	$[C_5H_5N]^{+\cdot}$	10.09
91	28	$-H^{\cdot}$-HCN	$[C_7H_7]^+$	10.82
93	26	$-C_2H_2$	$[C_6H_6NH]^{+\cdot}$	7.10
104	15	$-CH_3^{\cdot}$	$[C_7H_6N]^+$	8.47
117	2	$-2H^{\cdot}$	$[C_8H_7N]^{+\cdot}$	30.61
118	1	$-H^{\cdot}$	$[C_8H_8N]^+$	100.00
119	0		$[C_8H_9N]^{+\cdot}$	46.62

Using the reported fragmentation patterns for substituted pyridines, the following fragmentation pattern should result for 2-allylpyridine. As substitution is in the 2-position, the $[M-1]^+$ ion should be the most abundant because of γ-cleavage. The abundance of the $[M-15]^+$ ion in position 2 should be very small, especially since the molecule has no methyl group. The β-cleavage fragment should undergo further elimination of HCN to form an ion at m/z 65. The abundance of the ions at m/z 63 and 65 should be almost equal for substitution in the 2-position. McLafferty rearrangement should be noted with the elimination of acetylene. In the case of an allyl substituent, in place of an alkyl substituent,

acetylene instead of ethylene should be lost to obtain an ion of m/z 93, which is reported for vinylpyridine.[9] There should be a series of ions with m/z 50, 51, 52, and 53 which is characteristic of all pyridine compounds, with the ion at m/z 51 being the most abundant in this group.

The above predictions and the obtained mass spectrum of 2-allylpyridine are in very good agreement. Most of the ions are formed by elimination of unsaturated hydrocarbons and hydrogen cyanide. There is no abundant ion at m/z 77, which would be formed from the loss of the methyl radical and HCN. The unsaturation in the allyl group may account for the lack of the loss of the methyl radical and its replacement by the ethyl radical. The peaks at m/z 74 and 59 are from the solvent.

The proposed mechanisms for the formation of the important ions in the mass spectrum of 2-allylpyridine are given in Figure 15. The spiro intermediary and subsequent loss of $H^{\cdot}$ to form m/z 117 are shown. The m/z 93 ion can be explained by three tautomeric ions: one with methyl substitution, one with methylene substitution, and the last the azatropylium ion. The m/z 91 ion can be explained as the stable tropylium ion. The m/z 41 ion is the allyl carbocation.

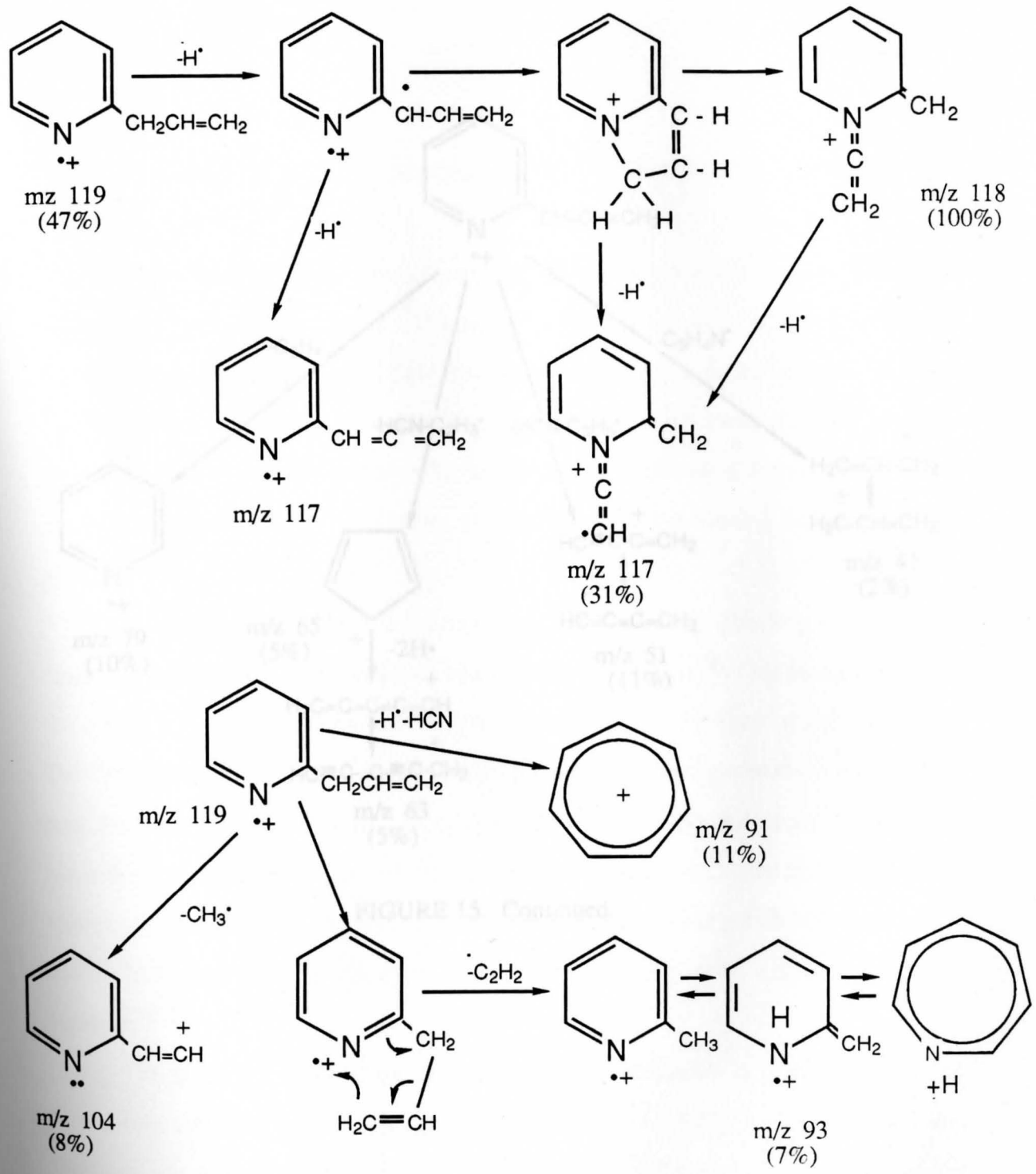


FIGURE 15. Proposed mechanism for fragmentation of 2-allypyridine.

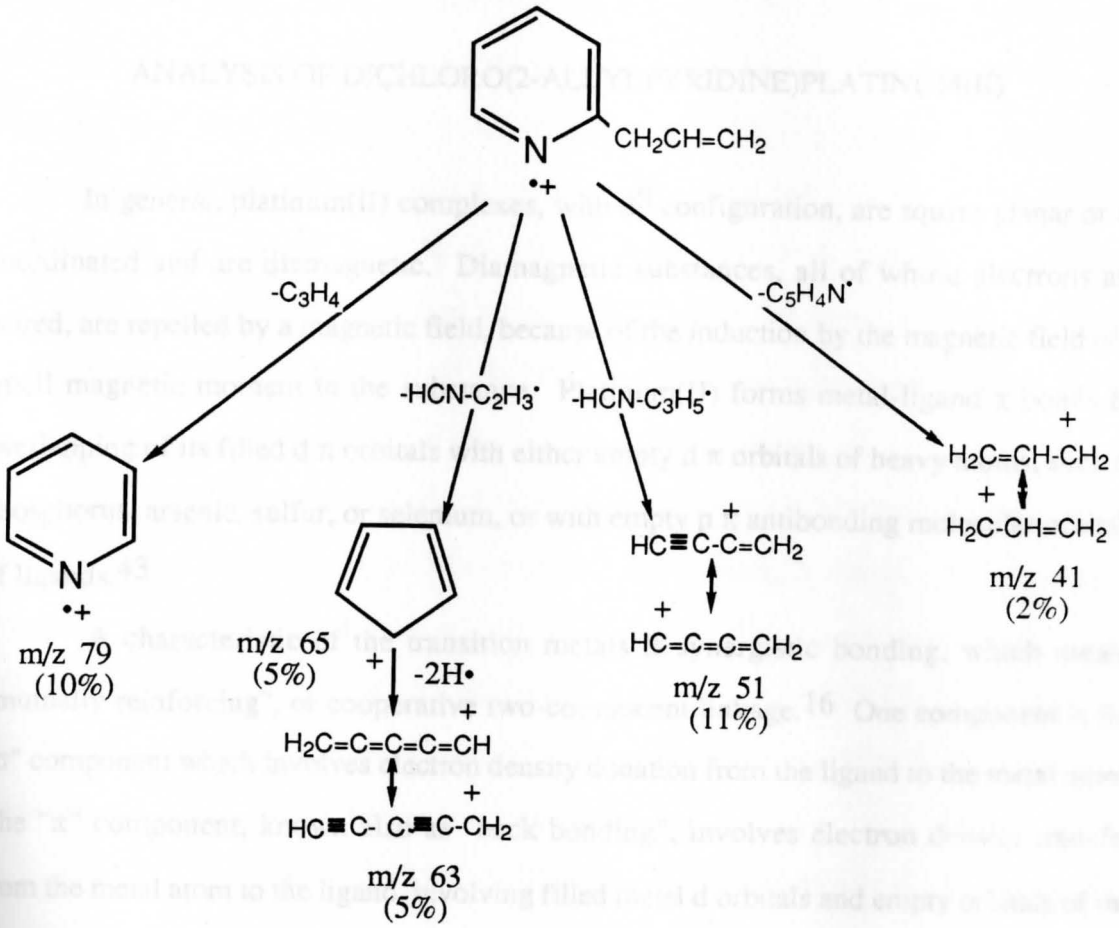


FIGURE 15. Continued.

CHAPTER IV

ANALYSIS OF DICHLORO(2-ALLYLPYRIDINE)PLATINUM(II)

In general, platinum(II) complexes, with d^8 configuration, are square planar or 4-coordinated and are diamagnetic. Diamagnetic substances, all of whose electrons are paired, are repelled by a magnetic field, because of the induction by the magnetic field of a small magnetic moment in the substance. Platinum(II) forms metal-ligand π bonds by overlapping of its filled d π orbitals with either empty d π orbitals of heavy atoms, such as phosphorus, arsenic, sulfur, or selenium, or with empty p π antibonding molecular orbitals of ligands.[43]

A characteristic of the transition metals is synergistic bonding, which means "mutually reinforcing", or cooperative two-component linkage.[16] One component is the "σ" component which involves electron density donation from the ligand to the metal atom. The "π" component, known also as "back bonding", involves electron density transfer from the metal atom to the ligand, involving filled metal d orbitals and empty orbitals of the same symmetry of the ligand.[16] It has been proposed that 2-allylpyridine forms a monomeric platinum(II) complex $[PtCl_2L]$ (L=2-allylpyridine) in which both the nitrogen and the olefinic group of 2-allylpyridine are bonded to platinum by a type of synergistic bonding.[10,11]

The $[C_3H_3]^+$ in the mass spectra of π-allyl complexes is proposed to be the cyclopropenium ion. Loss of allyl groups and elimination of allyl halides are two other important processes of fragmentation.[44] Some mass spectral reports on π-allyl complexes show ion formation by ring closure involving the allyl group which lost the hydrogen forming a ring π bonded to the metal atom. Others suggest ion formation by ring expansion occurring to form the fragment ion.[33]

EI mass spectra of bis-π-allyl complexes of $M(C_3H_5)_2$ (M = Ni, Pd, or Pt) contained hydrocarbon decomposition products and metal-containing ions. Considerable fragmentation of the low intensity molecular ion was observed. These complexes gave abundant ions derived from the successive losses of the allyl radicals. The loss of hydrogen atoms from these various ions occurred readily and notably complicated the isotope pattern. In the bis-π-allylplatinum, the prominent fragmentation was the loss of propylene. In the mass spectrum of $(C_3H_5)_2Pt(PPh_3)_2$, ions of $[Pt(C_3H_5)_2]^+$, $[Pt(C_3H_5)]^+$, $[C_3H_5]^+$, $[Pt(C_3H_4)]^+$, and Pt^+ were observed in addition to the phosphine fragmentation ions. The stability of the Pt-C bond was also noted.[12]

In the mass spectral analysis of (allyl ether) platinum(II) chloride, $C_6H_{10}OPtCl_2$, the molecular ion cluster was noted at m/z 362-368 showing it likely to be monomeric. Fragmentations noted were the loss of HCl and the loss of allyl chloride from the molecular ion. Other important platinum containing ions were $[C_3H_5PtCl]^+$, $[C_5H_8Pt]^+$, $[(C_2H_4)_2Pt]^+$, $[C_3H_5Pt]^+$, and $[C_2H_4Pt]^+$. Losses of hydrogen from the fragment ions were noted as in the mass spectrum of allyl ether.[45]

Tipper's compound, $[PtCl_2(C_3H_6)]_n$, is a tetramer (n=4) and shows a molecular ion of m/z 1232. Intense peaks due to the thermal decomposition product, platinum(II) chloride were also noted. The dimer ion $[PtCl_2(C_3H_6)]_2^+$ was also observed in the mass spectrum. Ions resulting from the loss of $:CH_2$, $Cl^{\cdot}$, $CH_2Cl^{\cdot}$, Cl_2, CH_2Cl_2, $Cl_3^{\cdot}$, and $CH_2Cl_3\cdot$ were also noted.[15]

In the π-cyclopentadienyl complex of platinum, $(CH_3)_3PtC_5H_5$, the molecular ion can fragment either by loss of the cyclopentadienyl ring forming $[(CH_3)_3Pt]^+$ or by the loss of methyl groups forming $[CH_3PtC_5H_5]^+$ and $[C_5H_5Pt]^+$. A group of fragment ions, $[C_7H_9Pt]^+$, $[C_7H_7Pt]^+$, $[C_6H_7Pt]^+$, and $[C_6H_5Pt]^+$, arise from dehydrogenation of the methyl groups with the possible insertion of the carbon atoms of the methyl groups into the ring. Metal-free ions with six, seven, and eight carbon atoms were also observed.

The normal ions in the fragmentation of π-cyclopentadienyl derivatives were also noted, $[C_5H_6]^+$ and $[C_3H_3]^+$.[46]

The sample that was received appeared to consist of two compounds as noted previously. This was confirmed by the RIC showing two peaks. The first peak appeared at a temperature in the solid probe around 172° C. The second compound was vaporized at approximately 268° C. The presence of two compounds suggested that they were either formed concurrently, or one was a decomposition product formed since the original synthesis of the metal complex, or that the vaporization or sublimation of the sample created the two compounds. The molecular weight of the first compound was 376 and of the second, 384. (Molecular weight determinations were calculated using 12 for carbon, 1 for hydrogen, 14 for nitrogen, 195 for platinum, and 35 for chlorine.) Molecular weights were confirmed by methane chemical ionization (CI) mass spectrometry of the platinum(II) complex. The first compound (orange color) hereafter will be referred to as the X complex; the second compound (yellow-brown color) with the molecular weight of 384 will be referred to as the Y complex.

A benzene solution of predominantly orange sample was analyzed by mass spectrometry and showed enhancement of the RIC of the compound vaporizing first in the RIC of the mixture. An enhanced sample of this complex X melted from 188 to 190° C. The RIC of the compound vaporizing last in the mixture agreed with the RIC of a benzene solution that was saturated with the yellow-brown sample. This complex Y melted from 176 to 179° C.

An IR spectrum of the complex was obtained to verify the constancy of the composition of the complex since its synthesis. The IR spectrum of the sample which contained both complex X and Y showed agreement with the one reported by Yingst and by Heaton and McCaffrey, in the following absorbances:[10,11]

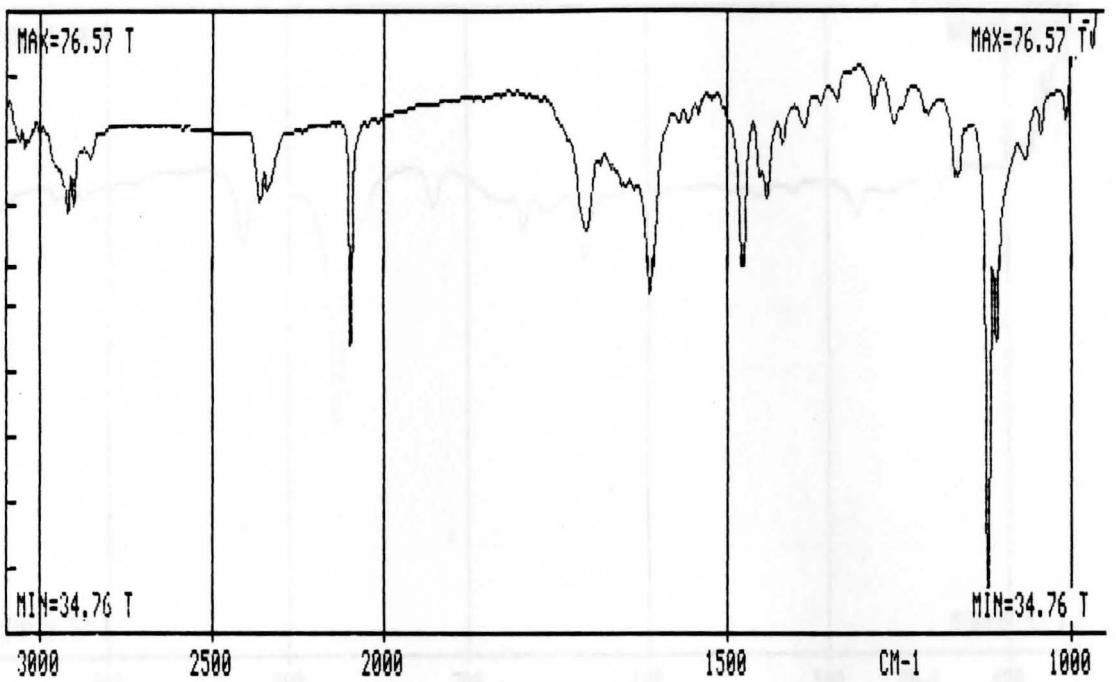
IR BANDS cm^{-1}	ASSIGNMENT
3047	ν (=CH2)
2910,2099	ν (-CH2-)
1613,1570,1478	ν (ring CC, CN)
1419,1340	β (=CH2)
1287,1168,1122	β (ring CH)
826	γ (=CH)
774	γ (ring CH)

ν, stretching vibration; β, in-plane deformation; γ, out-of-plane deformation.

The IR spectrum is shown in Figures 16 and 17. The wavenumbers in cm^{-1} are given on the left side of each column and the percent transmittance is given on the right side of each column.

Liquid chromatography followed by UV/VIS spectrometry was performed on saturated benzene solutions of complex X and complex Y. These same solutions were analyzed by mass spectrometry to show which complex was prominent in which solution. The chromatograms obtained in the range studied were inconclusive since one soluton (X) showed only absorbance at 400 nm and the other solution (Y) showed no absorbance at any wavelength. Mass spectra were obtained for both solutions.

The molecular weight for complex Y was determined to be 384 which agrees with the proposed formula of dichloro(2-allylpyridine)platinum(II), $C_8H_9NPtCl_2$. The mass spectrum of complex Y is shown in Figure 18. A summary of the other platinum clusters is shown in Table 11. The clusters are numbered to correspond to the original mass spectrum for this second peak in the RIC with the mass range below the number of the cluster. In the second column is given the m/z value for the principal isotopes of the proposed ion. In the third column is shown the molecular ion's loss of mass. The proposed formula of the ion is given in the fourth column. The ion of m/z 117 is the most abundant in the mass spectrum, and in column 5 is the abundance of the identified ion with respect to the ion of m/z 117 being 100%. The sixth column is the m/z for the strongest



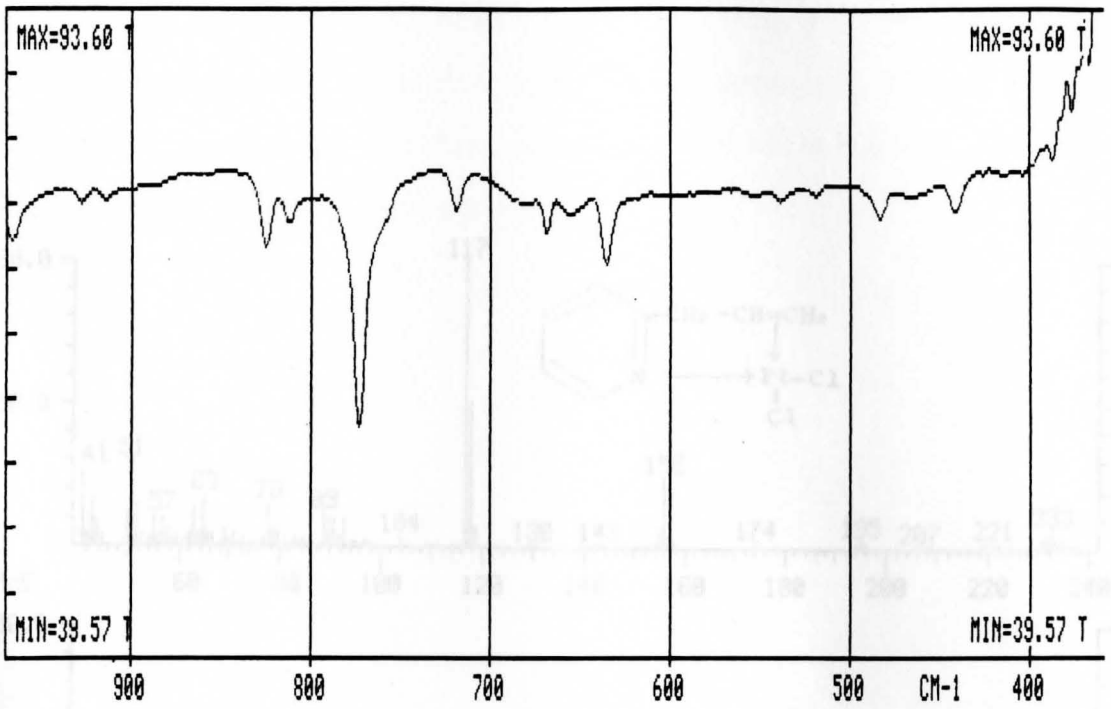
X: 2151 3100 - 950 1.00 35.89 77.97 T F AC20

REF: 4000 100.0 2000 100.0

3062	68.0	3047	67.8	2922	63.5	2905	63.8	2359	64.2
2341	64.9	2099	53.0	1707	62.3	1613	56.3	1570	69.2
1558	69.3	1478	58.8	1443	64.5	1419	67.9	1387	69.0
1340	70.8	1287	70.3	1257	69.3	1206	69.9	1163	65.8
1122	35.9	1109	52.5	1065	67.0	1042	68.5	1006	69.5
966	74.2								

END 26 PEAK(S) FOUND

FIGURE 16. Absorption spectrum of platinum(II) complexes from wavenumbers 3100 to 950 cm^{-1}. The first number in each column refers to the wavenumber cm^{-1} and the second number refers to the percent transmittance.



Z: 751 1000 - 250 1.00 -51060.7851054.53T AC20

REF: 4000 100.0 2000 100.0

966	74.4	920	77.5	825	73.9	812	75.8	774	58.6
719	76.9	669	74.8	656	76.4	636	72.3	539	77.5
484	76.3	441	76.7	387	80.9	376	85.0	366	88.6
348	101.4	343	4.4	338	0.0	330	0.0	327	11.4
323	0.0	316	0.0	310	0.0	307	67.7	296	51.8
286	42.9	273	41.8	268	32.4	263	38.0	253	28.2

END 30 PEAK(S) FOUND

FIGURE 17. Absorption spectrum of platinum(II) complexes from wavenumbers 1000 to 250 cm^{-1}. The first number in each column refers to the wavenumber cm^{-1} and the second number refers to the percent transmittance.

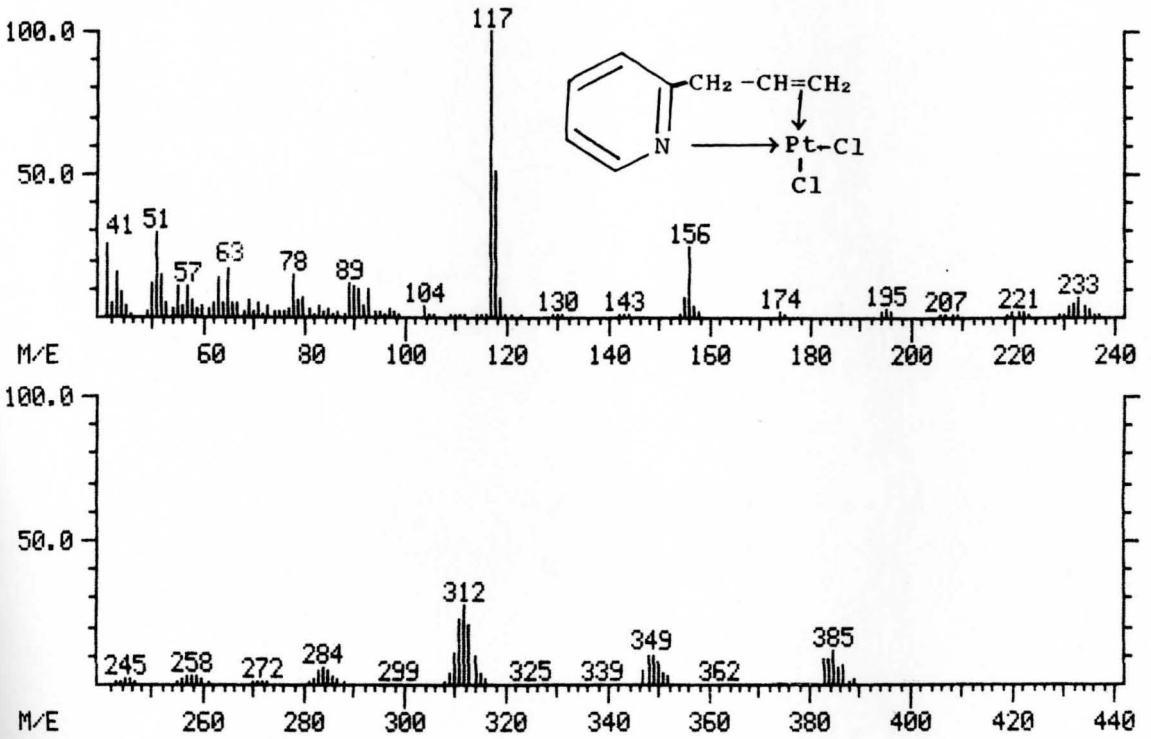


FIGURE 18. Mass spectrum of platinum complex Y.

peak in each cluster. Column 7 is the average absolute error or difference between the observed abundance of the ions of the cluster and the calculated value for the abundance of these ions. The abundances of the metallic ions are very small in comparison to those of ions that are formed without the platinum atom. The last column is the reference number to the proposed structure of the most abundant metallic ions given in Figure 19. A summary of the clusters and possible formation follows:

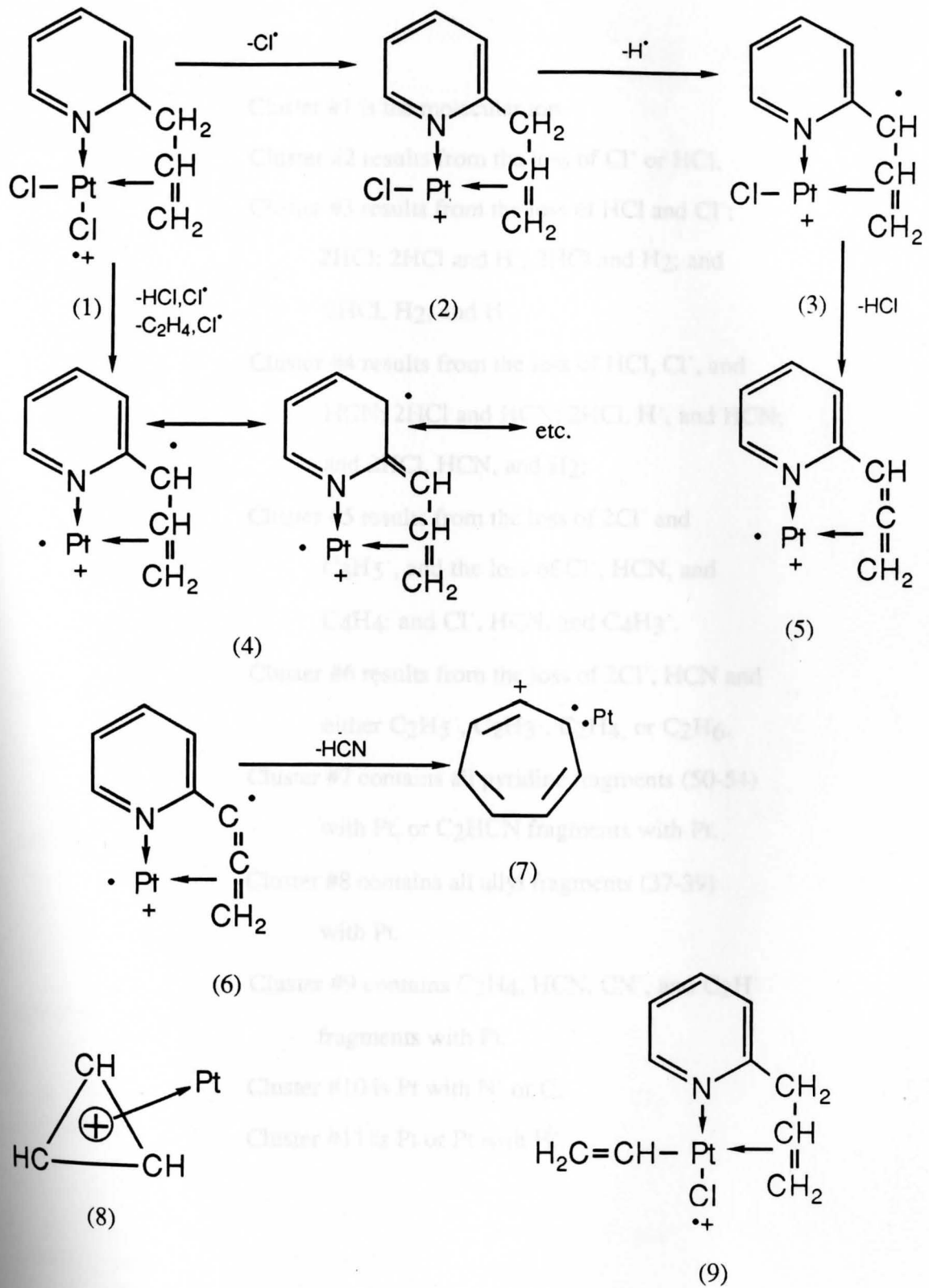


FIGURE 19. Proposed structures of the most abundant ions of complexes X and Y. Refer to Tables 11 and 13.

Cluster #1 is the molecular ion

Cluster #2 results from the loss of $Cl^{\cdot}$ or HCl.

Cluster #3 results from the loss of HCl and $Cl^{\cdot}$;
2HCl; 2HCl and $H^{\cdot}$; 2HCl and H_2; and
2HCl, H_2, and $H^{\cdot}$.

Cluster #4 results from the loss of HCl, $Cl^{\cdot}$, and
HCN; 2HCl and HCN; 2HCl, $H^{\cdot}$, and HCN;
and 2HCl, HCN, and H_2;

Cluster #5 results from the loss of $2Cl^{\cdot}$ and
$C_3H_5^{\cdot}$, and the loss of $Cl^{\cdot}$, HCN, and
C_4H_4; and $Cl^{\cdot}$, HCN, and $C_4H_3^{\cdot}$.

Cluster #6 results from the loss of $2Cl^{\cdot}$, HCN and
either $C_2H_5^{\cdot}$, $C_2H_3^{\cdot}$, C_2H_4, or C_2H_6.

Cluster #7 contains all pyridine fragments (50-54)
with Pt, or C_2HCN fragments with Pt.

Cluster #8 contains all allyl fragments (37-39)
with Pt.

Cluster #9 contains C_2H_4, HCN, $CN^{\cdot}$, and $C_2H^{\cdot}$
fragments with Pt.

Cluster #10 is Pt with $N^{\cdot}$ or C.

Cluster #11 is Pt or Pt with $H^{\cdot}$.

TABLE 11 PLATINUM COMPLEX Y

Cluster	m/z	M-	Proposed Formula	Ion Abund	Most Abund	Relative Error	Proposed Structure
1	384	0	$[C_8H_9NPtCl_2]^{+\cdot}$	6.8	385	1.7	1
(383-389)							
2	349	35	$[C_8H_9NPtCl]^+$	3.5	349	2.3	2
(347-354)	348	36	$[C_8H_8NPtCl]^{+\cdot}$	2.7			3
3	313	71	$[C_8H_8NPt]^+$	3.8	312	1.8	4
(308-316)	312	72	$[C_8H_7NPt]^{+\cdot}$	6.2			5
	311	73	$[C_8H_6NPt]^+$	3.6			6
	310	74	$[C_8H_5NPt]^{+\cdot}$	0.9			
	309	75	$[C_8H_4NPt]^+$	0.7			
4	286	98	$[C_7H_7Pt]^+$	0.5	284	3.6	
(282-288)	285	99	$[C_7H_6Pt]^{+\cdot}$	0.6			
	284	100	$[C_7H_5Pt]^+$	1.1			7
	283	101	$[C_7H_4Pt]^{+\cdot}$	0.8			
5	273	111	$[C_5H_4NPt]^+$	0.2	272	4.0	
(269-274)	271	113	$[C_3H_5PtCl]^{+\cdot}$	0.04			
	270	114	$[C_3H_4PtCl]^+$	0.2			
6	260	124	$[C_5H_5Pt]^+$	0.5	258	20.0	
(255-261)	259	125	$[C_5H_4Pt]^{+\cdot}$	0.3			
	258	126	$[C_5H_3Pt]^+$	0.4			
	257	127	$[C_5H_2Pt]^{+\cdot}$	0.7			
7	248	136	$[C_4H_5Pt]^+$, $[C_3H_3NPt]^{+\cdot}$	0.1	245	8.3	
(243-248)	247	137	$[C_4H_4Pt]^{+\cdot}$, $[C_3H_2NPt]^+$	0.2			
	246	138	$[C_4H_3Pt]^+$, $[C_3HNPt]^{+\cdot}$	0.3			
	245	139	$[C_4H_2Pt]^{+\cdot}$, $[C_3NPt]^+$	0.2			
	244	140	$[C_4HPt]^+$	0.4			
8	234	150	$[C_3H_3Pt]^+$	1.8	233	14.5	8
(229-235)	233	151	$[C_3H_2Pt]^{+\cdot}$	0.6			
	232	152	$[C_3HPt]^+$	1.8			
9	223	161	$[C_2H_4Pt]^{+\cdot}$	0.1	221	1.1	
(219-224)	222	162	$[CHNPt]^{+\cdot}$	0.5			
	221	163	$[CNPt]^+$	0.5			
	220	164	$[C_2HPt]^+$	0.4			
10	210	174	$[NHPt]^{+\cdot}$	0.1	207	4.2	
(206-211)	208	176	$[CHPt]^+$	0.3			
	207	177	$[CPt]^{+\cdot}$	0.4			
11	196	188	$[HPt]^+$	0.1	195	2.1	
(194-198)	195	189	$[Pt]^{+\cdot}$	1.8			

The nonmetallic ions produced in the fragmentation of complex Y are the same as the ions produced in the fragmentation of 2-allylpyridine and in the same relative abundance, with some exceptions. The most abundant ion is at m/z 117. This is accounted for by the unsaturation due to the loss of a hydrogen atom occurring in the allyl chain rather than a rearrangement with additional bonding to the pyridine ring. Also, there are abundant fragment ions with m/z 143, 155, and 156. The ion of m/z 143 could correspond to the addition of acetylene to the base ion (the most abundant ion in a mass spectrum.) The ions of m/z 155 and 156 could correspond to the addition of C_3H_3 and C_3H_2 to the base ion. These ions could be formed from interaction between a molecule of complex Y and the base ion, with the allyl chain or part of it being removed from the complex. The ion at m/z 89 is more prominent in the ionization of the complex than in the ionization of 2-allylpyridine. This ion can be explained by the loss of HCN and H_2 from the latter.

In the analysis of complex X, which gives the first peak obtained in the RIC of the mixed platinum sample, the molecular ion occurred at m/z 376. Platinum-containing ions were also observed in the mass spectrum of complex X, but they contain only one atom of chlorine according to isotopic ratios. Let us compare the molecular ion isotopes with those for a composition which may account for this molecular ion, Table 12.

TABLE 12 COMPARISON OF VALUES FOR $[C_{10}H_{12}NPtCl]^{+\cdot}$

m/z	Observed Average Abundance (%)	Calculated Abundance (%) $[C_{10}H_{12}NPtCl]^{+\cdot}$	Error
375	84.7	82.5	2.2
376	93.9	93.8	0.1
377	100.0	100.0	---
378	38.4	38.0	0.4
379	43.3	42.1	1.2

The average error, the difference between the observed and the calculated values, is 0.98 for $[C_{10}H_{12}NPtCl]^{+\cdot}$. A summary of the other platinum clusters is given in Table 13, with clusters #4 (281-287), #7 (243-248), #8 (229-237), #9 (219-224), and #11 (194-198) being very similar for both complex X and complex Y. The last column gives the reference number to the proposed structure of the most abundant metallic ions given in Figure 19. The format of this table is the same as the one given for Table 11. The possible formations for the other fragment ions which are not similar to the fragments of complex Y are as follows:

Cluster #1 is the molecular ion.

Cluster #2 results from the loss of C_2H_4.

Cluster #3 results from the loss of HCl and C_2H_4, and HCl and C_2H_2.

Cluster #5 is not being analyzed since the abundance is very low and agreement with calculated values was very poor.

Cluster #6 results from the loss of HCN, HCl, and C_5H_6; HCN, HCl, and $C_5H_7^{\cdot}$; C_7H_8 and HCN; and $C_7H_9^{\cdot}$ and HCN.

Cluster #10 is Pt with $N^{\cdot}$, CH, or CH_2.

The nonmetallic ions produced in the fragmentation of complex X are also the same as the ions produced in the fragmentation of 2-allylpyridine and in the same relative abundances, with the same exceptions as were noted for the nonmetallic ions of complex Y. Another noted difference in the abundance of nonmetallic ions for complex X is the ratio between the abundance at m/z 63 and m/z 65, which is 4:1. An ion of m/z 170 was also produced in this fragmentation which may be accounted for by the ion $[C_5H_4NC_4H_3C_3H_5]^+$ which is 2-allylpyridine and $C_4H_3^{\cdot}$. The mass spectrum for complex X is in Figure 20.

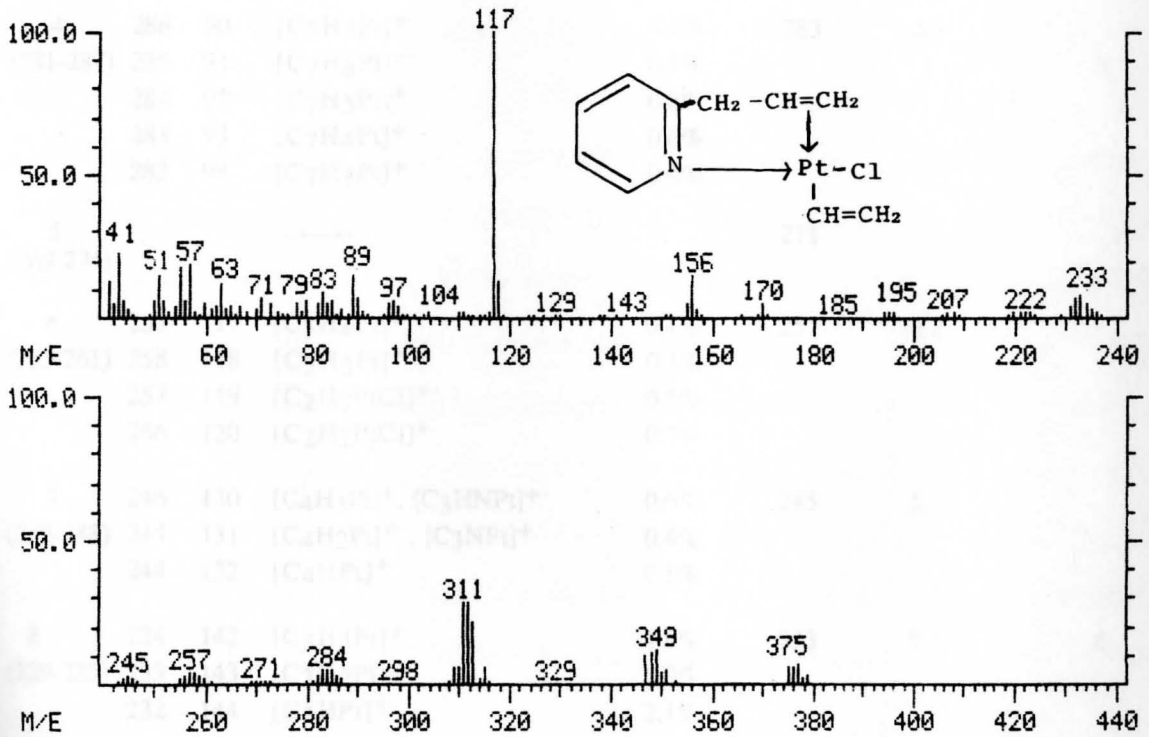


FIGURE 20. Mass spectrum of platinum complex X.

TABLE 13 PLATINUM COMPLEX X

Cluster	m/z	M-	Proposed Formula	Ion Abund	Most Abund	Relative Error	Proposed Structure
1	376	0	$[C_{10}H_{12}NPtCl]^{+\cdot}$	3.8%	377	1.0	9
(375-379)							
2	348	28	$[C_8H_8NPtCl]^{+\cdot}$	5.7%	349	1.8	3
(347-354)							
3	312	64	$[C_8H_7NPt]^{+\cdot}$	12.5%	312	2.5	5
(307-316)	310	62	$[C_8H_5NPt]^{+\cdot}$	2.5%			
4	286	90	$[C_7H_7Pt]^{+}$	0.4%	283	2.1	
(281-287)	285	91	$[C_7H_6Pt]^{+\cdot}$	0.4%			7
	284	92	$[C_7H_5Pt]^{+}$	0.8%			
	283	93	$[C_7H_4Pt]^{+\cdot}$	0.6%			
	282	94	$[C_7H_3Pt]^{+}$	0.4%			
5			--------		271		
(269-274)							
6	259	117	$[C_5H_4Pt]^{+\cdot}$	0.4%	257	6.2	
(255-261)	258	118	$[C_5H_3Pt]^{+}$	0.3%			
	257	119	$[C_2H_3PtCl]^{+\cdot}$	0.5%			
	256	120	$[C_2H_2PtCl]^{+}$	0.7%			
7	246	130	$[C_4H_3Pt]^{+}$, $[C_3HNPt]^{+\cdot}$	0.6%	245	5.1	
(243-248)	245	131	$[C_4H_2Pt]^{+\cdot}$, $[C_3NPt]^{+}$	0.4%			
	244	132	$[C_4HPt]^{+}$	0.5%			
8	234	142	$[C_3H_3Pt]^{+}$	1.9%	233	9.7	8
(229-237)	233	143	$[C_3H_2Pt]^{+\cdot}$	1.0%			
	232	144	$[C_3HPt]^{+}$	2.1%			
9	223	153	$[C_2H_4Pt]^{+\cdot}$	0.5%	222	3.3	
(219-224)	222	154	$[CHNPt]^{+\cdot}$	0.3%			
	221	155	$[CNPt]^{+}$	0.3%			
	220	156	$[C_2HPt]^{+}$	0.4%			
10	209	166	$[CH_2Pt]^{+\cdot}$	0.1%	207	5.7	
(206-210)	208	168	$[CHPt]^{+}$	0.3%			
	207	169	$[CPt]^{+\cdot}$	0.6%			
11	196	180	$[HPt]^{+}$	0.1%	195	3.5	
(194-198)	195	181	$[Pt]^{+\cdot}$	1.9%			

It should be noted that the loss of hydrogen to form fragment ions in the complexes of platinum was quite common, as many ions differing by one mass unit were needed to

explain the observed abundances. These two platinum complexes, as indeed there are two, have different properties, but also show some similiarities. The main similarity is that they both have 2-allylpyridine as a bidentate ligand. Fragments were formed which had platinum bonded to a nitrogen-containing group, and platinum was also in ions containing carbon but not nitrogen.

Two different 2-allylpyridine complexes of platinum(II) exist. One of these complexes, Y, appears to be dichloro(2-allylpyridine)platinum(II). Complex X contains platinum(II), 2-allylpyridine and one chlorine, and has a molecular mass of 376. Subtracting the masses of these known constituents from the molecular mass leaves a mass of 27, corresponding to C_2H_3. A fragment ion of complex X, $[M-28]^{+\cdot}$, is observed in the mass spectrum. Loss of C_2H_4 would account for this ion. Attempts to explain the 27 mass units in the molecular weight, plus the fragment ion showing a loss of 28 were made using various combinations of carbon, nitrogen, oxygen, and hydrogen, but none of these fits the pattern. If oxygen were present, then PtO^+ or $PtCO^+$ would be expected in the spectrum. No ion of m/z 211 or 233, which would verify the presence of oxygen, was observed, thus, eliminating CO as a possible substituent. A possible nitrogen-containing ligand with 27 mass units is HCN, but this would require the unlikely loss of H_2CN to account for the loss of 28.

C_2H_4 (m/z 28) is a stable molecule that is lost in fragmentation of many organic compounds. Also, a platinum complex involving a C_2H_3 ligand has been reported by Cardin and Muir,[47] trans-chlorobis(diethylphenylphosphine)(vinyl)platinum(II) or trans - $[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$. In this complex, the platinum coordination is square planar and the Pt-C=C angle is 127°. Very little research has been done on transition metal-alkenyl compounds. Most of this has been on substituted vinyls, which show the occurrence of C_2H_3 as a stable ligand.[47] This provides a precedent for the structure of complex X proposed here.

In the CI analysis of the supposed dichloro(2-allylpyridine)platinum(II), the only fragment ion formed was that accounted for by the loss of HCl from $[MH]^+$ for complexes X and Y. There was also an ion formed from ion-molecule reaction whose proposed formula is $[2M-Cl]^+$ for complex X.

There are similarities between the mass spectra of these platinum(II) complexes and ones that were previously studied. The loss of hydrogen atoms from various ions occurred readily. Formation of cyclopropenium ion was noted and its metal-containing ion was abundant. Also, loss of stable alkyl and alkenyl radicals or the formation of ions with these radicals was noted. The stability of the Pt-C bond and the formation of Pt^+ were observed. Hydrocarbon decomposition products, along with metal-containing ions, are in low intensity. The many metal-containing, low intensity ions and the fragment ions of the ligand make up the mass spectra of the platinum(II) complexes.

CHAPTER V

ANALYSIS OF DICHLORO(2-ALLYLPYRIDINE)PALLADIUM(II)

The organometallic chemistry of palladium is dominated by its formation of synergistic metal-unsaturated hydrocarbon bonds. Many palladium(II) complexes also have square planar geometry.[16] π- Allyl complexes of palladium are similar to those of platinum.[12] Palladium(II) complexes are somewhat less stable, both thermodynamically and kinetically, than their platinum(II) analogs[43], even though they are quite similar in other respects.

The parent ion in the mass spectrum of $C_3H_5PdC_5H_5$ shows fragmentation either by loss of the π-allyl group as allene, giving $[C_5H_6Pd]^+$, or by the loss of the π-cyclopentadienyl group, giving $[C_3H_5Pd]^+$. The ion $[C_5H_5Pd]^+$ was not present in any significant amount. The presence of metal-free ions of six and seven carbons in the mass spectrum indicated that the π-allyl carbons may bond to the ring carbons to form complex hydrocarbon fragments. In the mass spectrum of $(C_{10}H_{12}OCH_3)PdC_5H_6$ the most abundant palladium-containing ion is that of $[C_5H_5PdOCH_3]^+$ resulting from the loss of $C_{10}H_{12}$. The only other palladium-containing ions are $[C_{10}H_{11}OCH_3Pd]^+$, $[C_5H_6Pd]^+$, $[C_5H_5Pd]^+$, $[C_{10}H_{12}Pd]^+$, $[C_{10}H_{11}Pd]^+$, and $[C_3H_3Pd]^+$. Metal-free ions of $[C_{10}H_{11}OCH_3]^+$, $[C_{10}H_{10}OCH_3]^+$, $[C_{10}H_{12}]^+$, $[C_{10}H_{10}]^+$, $[C_5H_5OCH_3]^+$ and ions typical of cyclopentadienyl derivatives are present.[46]

In the mass spectrum of $(C_3H_5PdCl)_2$, the molecular ion appears to lose one chlorine atom followed by a stepwise loss of two allyl groups to give $[Pd_2Cl]^+$. The only other abundant palladium ion is that of $[C_3H_5Pd]^+$. Many hydrocarbon ions are observed as well as chlorine-containing ions, $[C_3H_5Cl]^+$, $[CH_2Cl]^+$, and $[HCl]^+$.[48]

Lupin and Cais[14] reported that the mass spectra of many palladium complexes show no peaks containing palladium, but showed only peaks derived from the organic ligand. This was probably because of thermal decomposition upon introducing the sample into the spectrometer,[14] and the palladium not entering the ion source. They studied the following complexes: bis(triphenylphosphine)dichloropalladium(II), hexa-1,5-dienedichloropalladium(II), bicyclo[2,2,0]hepta-1,5-dienedichloropalladium(II), di-μ-chlorodicyclohexenyldipalladium-(II), di-μ-chlorodi-(4-methoxy-1-methylpent-2-enyl)dipalladium(II) and several other methoxyallylic palladium complexes. Only two of these complexes showed significant peaks containing both palladium and chlorine, di-μ-chlorodiallyldipalladium(II) and di-μ-chlorodi-(4-methoxy-2-methylbut-2-enyl)dipalladium(II). In this first complex, several fragments contained the Pd_2Cl unit, which indicates its great stability. The second complex showed only three very weak clusters of palladium-containing ions, the molecular ion, $[M\text{-}HCl]^+$ fragment, which then loses $C_6H_{11}OCl$ giving $[C_6H_{10}OPd_2]^+$. The base peak is that of the $[L\text{-}H]^+$ ion, as it is with all the complexes that did not show any palladium-containing ions.

In the analysis of dichloro(2-allylpyridine)palladium(II), four RIC peaks were observed. The mass spectrum of the first RIC peak matches that of chloroform, which was the solvent used for this organometallic complex. The spectrum of the second RIC peak matches that of 2-allylpyridine (Figure 13). The mass spectrum of this second RIC peak is located in Figure 21. The third RIC peak was rounded with a spiked peak on top of it. The mass spectrum of the third RIC also matched the mass spectrum of 2-allylpyridine. The spiked peak is an indication of the possible presence of palladium and chlorine with clusters of ions. The palladium and chlorine isotope ratios are as follows:[25]

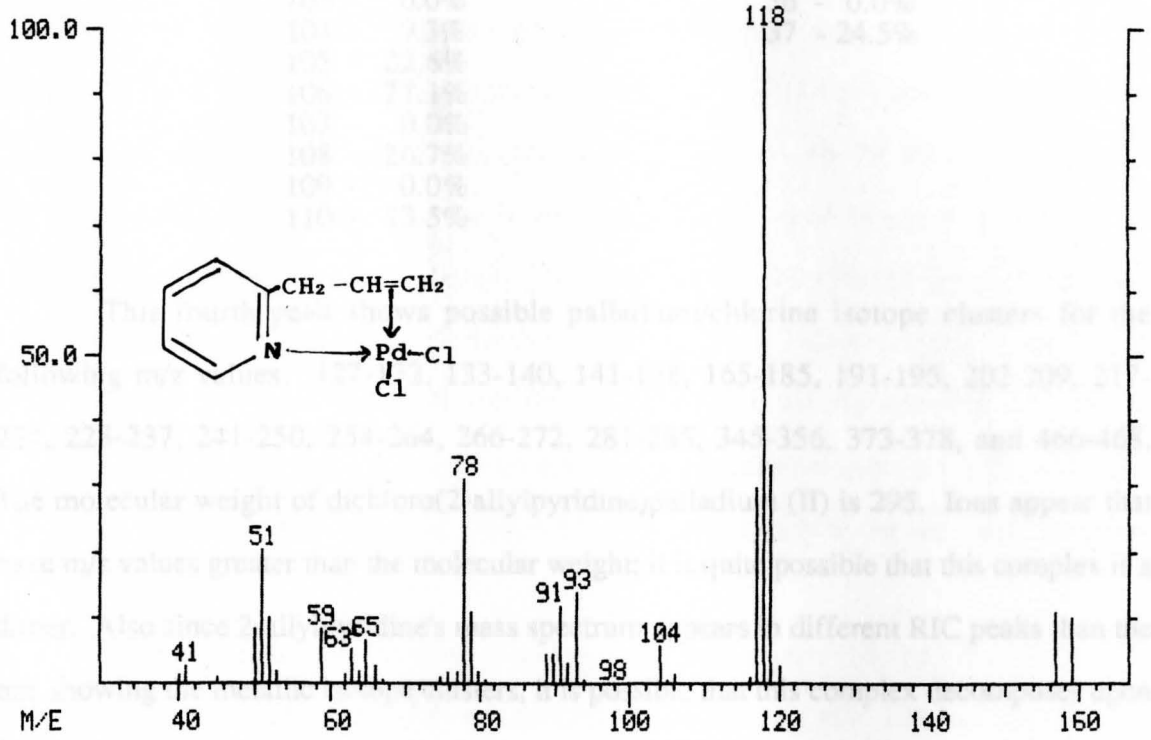


FIGURE 21. Mass spectrum of second RIC peak of palladium(II) complex, which is similar to the mass spectrum of 2-allylpyridine.

Pd		Cl	
Mass	102 - 0.8%	Mass	35 - 75.5%
	103 - 0.0%		36 - 0.0%
	104 - 9.3%		37 - 24.5%
	105 - 22.6%		
	106 - 27.1%		
	107 - 0.0%		
	108 - 26.7%		
	109 - 0.0%		
	110 - 13.5%		

This fourth peak shows possible palladium/chlorine isotope clusters for the following m/z values: 127-132, 133-140, 141-158, 165-185, 191-195, 202-209, 217-221, 228-237, 241-250, 254-264, 266-272, 281-285, 345-356, 373-378, and 466-468. The molecular weight of dichloro(2-allylpyridine)palladium (II) is 295. Ions appear that have m/z values greater than the molecular weight; it is quite possible that this complex is a dimer. Also since 2-allylpyridine's mass spectrum appears in different RIC peaks than the one showing the metallic isotope clusters, it is possible that this complex decomposes upon heating.

The observed abundances in the clusters did not match any calculated abundances, which were obtained for various combinations of palladium and chlorine, from one to six atoms of each. Not even the stable fragment ions $[Pd_2Cl]^+$, m/z 247, or $[Pd_2Cl_2]^+$, m/z 364, which some palladium(II) chlorine complexes produce, were observed in the mass spectrum of this palladium(II) complex. The stability of the $[Pd_2Cl]^+$ has been attributed to a new stronger bond being formed between the two palladium atoms after one of the bridging bonds in the molecular ion is broken.[14]

The analysis by differential scanning calorimetry showed an exotherm at 167° C, which indicated decomposition. The reported value of decomposition is 153-157° C.[27] The analysis by scanning electron microscopy also showed the presence of palladium in the 10-μL sample tube. Characteristic x-ray emission of palladium was observed in the spectrum. The photograph shows white dots which represent the palladium on the glass.

This analysis is in Figure 22. Therefore, the palladium complex had decomposed and the ions that had reached the mass analyzer were combinations of C, H, N, and Cl.

The base ion of the mass spectrum of this spiked peak is at m/z 93, which can be accounted for as being the azatropylium ion, $[C_6H_7N]^{+\cdot}$. This mass spectrum also shows the fragment ions of 2-allylpyridine at m/z 41, 51, 52, 63, 65, 78, 79, 89, 90, 92, 93, 104, 117, 118, and 119. The ratio of the intensity of m/z 63 to 65 is equal to one, which indicates substitution at the 2-position. The ratio of m/z 117:118:119 is 2:2:1, which is different from the ratio of these ions for the fragmentation of 2-allylpyridine. There is also an abundant ion at m/z 106 which may be $[C_7H_8N]^+$. In ten reproducible runs of two different samples of this complex, abundant ions were found at m/z 130, 143, 144, 154, 156, 169, 180, 195, 207, 219, 232, 245, 258, 269, 347, and 349, in the mass spectrum of this spiked peak.

In greater than 10% relative abundance are ions at m/z 130, 143, 144, 154, 156, and 169. The ion at m/z 130 could be $[C_9H_8N]^+$; the ones with m/z 154 and 156 could be $[C_4Cl_3H]^+$ and $[C_4Cl_3H_3]^+$; and the ions at m/z 143 and 144 could be $[C_{10}H_9N]^+$ and $[C_{10}H_8N]^+$. The other abundant ions with m/z greater than 180 may be rationalized by combinations of C, N, H, and Cl. The patterns seem to indicate the Cl isotopes; but by comparing calculated abundances for various hydrocarbons with varying numbers of Cl, no close match was obtained using as many as three different combinations of Cl with the hydrocarbon and using five proposed ions. An interesting note is that the ion at m/z 232 has approximately two times the mass of 2-allylpyridine, and the ion at m/z 349 has approximately three times this mass. An ion of m/z 237 was also observed in CI and no palladium clusters were present in the CI mass spectrum of the palladium complex. As noted in the literature, many palladium complexes do not produce palladium-containing ions in their mass spectra. They also tend to have a base peak of $[L\text{-}H]^+$. Both of these statements are true for the palladium(II) complex presently studied.

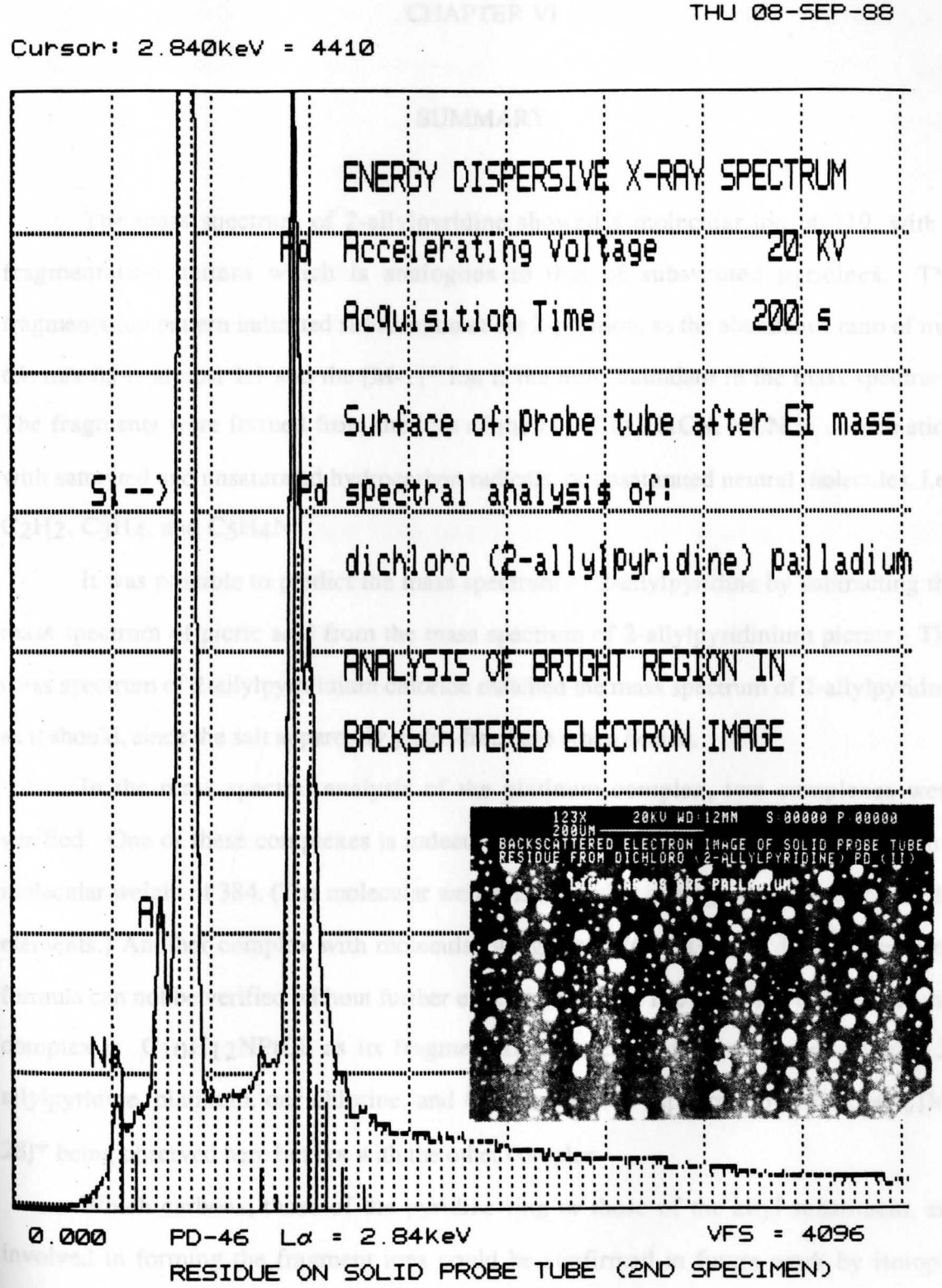


FIGURE 22. Energy dispersive x-ray spectrum of pyrex tube used for Pd complex. Photograph of microscopic observation with scanning electron microscope.

CHAPTER VI

SUMMARY

The mass spectrum of 2-allylpyridine showed a molecular ion of 119, with a fragmentation pattern which is analogous to that of substituted pyridines. The fragmentation pattern indicated substitution at the 2-position, as the abundance ratio of m/z 63: m/z 65 is almost 1:1 and the $[M-1]^+$ ion is the most abundant in the mass spectrum. The fragments were formed from the loss of the $H^{\cdot}$, $CH_3^{\cdot}$, HCN, HCN in combination with saturated and unsaturated hydrocarbon radicals, or unsaturated neutral molecules, i.e., C_2H_2, C_3H_4, and C_5H_4N.

It was possible to predict the mass spectrum of 2-allylpyridine by subtracting the mass spectrum of picric acid from the mass spectrum of 2-allylpyridinium picrate. The mass spectrum of 2-allylpyridinium chloride matched the mass spectrum of 2-allylpyridine as it should, since the salt apparently yields free base when heated.

In the mass spectral analysis of the platinum complex, two complexes were verified. One of these complexes is indeed dichloro(2-allylpyridine)platinum(II) with a molecular weight of 384. (The molecular weight is 385 using average atomic weights of the elements.) Another complex with molecular weight of 376 was found, but its structural formula can not be verified without further experimentation. The proposed formula for this complex is $C_{10}H_{12}NPtCl$, as its fragmentation pattern indicates the presence of 2-allylpyridine, platinum, one chlorine, and C_2H_3, which is supported by a fragment $[M-28]^+$ being observed here but not with the other complex.

Which carbons, those of the pyridine ring or those of the allyl substituent, are involved in forming the fragment ions could be confirmed in future work by isotopic labeling using carbon-13. This would also lend confirmation of a bidentate ligand. The location of hydrogens in the ions could be identified by using deuterium. The easiest

approach would be to have the isotopes located in the allyl chain. Isotopic substitution in the allyl group would result in shifts in mass of every fragment which contained this group. Comparison of this mass spectrum with the mass spectrum of the unlabeled molecule would show which peaks have shifted and provide evidence for the fragmentation pattern.[21]

The palladium(II) complex of 2-allylpyridine could not be analyzed by the Finnigan 1020B GC/MS, as the complex decomposed upon heating. The mass spectrum of this complex was used to denote the presence of 2-allylpyridine and chlorine. The presence of palladium in the pyrex sample tube was an indication that the complex had contained palladium.

There are other methods of mass spectral analysis which can be used for nonvolatile compounds. Among these methods is that of field desorption. The sample is coated directly onto a removable emitter and is ionized directly from the solid state. [21] Direct chemical ionization or direct "in-beam" electron bombardment can also be used.[26] A fast heavy ion can volatilize and ionize some non-volatile organic compounds deposited on a metal surface. [49]

The mass spectral analysis of all of the compounds, both metal complexes and salts, showed the presence of 2-allylpyridine. Analysis of mass spectra of metallic complexes also showed low abundances of metallic ions and the easy loss of hydrogen from the ions formed. In Table 14 is shown the comparison of m/z values for the mass spectrum of 2-allylpyridine with the mass spectrum of each of the compounds for the non-metal-containing ions. The free allylpyridine and the chloride salt give identical spectra.

TABLE 14 COMPARISON OF Pd AND Pt COMPLEXES WITH 2-ALLYLPYRIDINE

m/z	Pd(II) Complex	Pt(II) Complex Y	Pt(II) Complex X	Cl^- Salt of 2-Allylpyridine	2-Allyl-pyridine
41	VW	S	W	VW	VW
50	M	W	VW	W	VW
51	S	S	W	W	W
52	S	W	VW	VW	VW
59	VW	VW	VW	VW	VW
62	VW	VW	VW	VW	VW
63	W	W	W	VW	W
64	VW	VW	VW	VW	VW
65	W	M	VW	VW	VW
66	VW	VW	VW	VW	VW
78	M	W	VW	VW	VW
79	S	VW	VW	W	W
80	VW	VW	VW	VW	VW
89	VW	W	W	VW	VW
90	VW	W	VW	VW	VW
91	W	VW	VW	W	W
92	VW	VW	VW	VW	VW
93	S	VW	VW	VW	VW
104	W	VW	VW	VW	VW
117	S	S*	S*	S	S
118	S*	S	W	S*	S*
119	S	S	VW	S	S-P
120	VW-I	VW	VW	VW-I	VW-I

P is parent or molecular ion; I is isotope ion; * is most abundant ion; VW is very weak intensity less than 10; W is weak intensity from 10 to 15; M is moderate intensity from 16 to 25; S is strong intensity from 26 to 100.

In this study, the mass spectrum of 2-allylpyridine was obtained and the proposed mechanisms for its fragmentation pattern were given, and could be enhanced with further study of other olefinic-substituted pyridines. This mass spectrum was compared with those of its salts, 2-allylpyridinium chloride and 2-allylpyridinium picrate, and its complexes, dichloro(2-allylpyridine)platinum(II) and dichloro(2-allylpyridine)-palladium(II). It was noted that the spectra were the same for the salts and the

palladium(II) complex, that decomposed upon vaporization, releasing the free ligand. The molecular weight of the dichloro(2-allylpyridine)platinum(II) was confirmed at 384. A fragmentation pattern of this complex was proposed, as was that of an additional platinum(II) complex of 2-allylpyridine with the proposed formula, $C_{10}H_{12}NPtCl$, and molecular weight 376.

APPENDIX

Mass Lists

MASS LIST OF 2-ALLYLPYRIDINE

MASS LIST DATA: ALPY11 # 173 BASE M/E: 118
08/30/88 19:24:00 + 3:02 RIC: 40640.
SAMPLE: ETHER EXTRACT OF ALLYLPYRIDINE SAT 1.0 UL
#172 TO #175 SUMMED

40 0.00 MINIMA MIN INTEN: 0. MAX INTEN: 14192.
120 # 0 MAXIMA

MASS	% RA
40	0.65
41	1.84
50	6.16
51	10.58
52	6.50
53	0.94
59	7.55
61	0.16
62	2.10
63	4.76
64	1.61
65	4.74
66	1.60
74	0.70
76	0.21
77	0.85
78	7.17
79	10.09
80	1.18
89	3.71
90	3.92
91	10.82
92	1.92
93	7.10
104	8.47
117	30.61
118	100.00
119	46.62
120	3.57

MASS LIST OF PICRIC ACID

MASS LIST DATA: ALPA02 # 41 BASE M/E: 62
08/30/88 20:12:00 + 1:24 RIC: 28096.
SAMPLE: PICRIC ACID A. 200NG EVAPORATED FROM ALCOHOL
#39 TO #43 SUMMED - #20 TO #24 - #58 TO #60 X1.00

40 0.00 MINIMA MIN INTEN: 0. MAX INTEN: 3312.
230 # 0 MAXIMA

MASS	% RA
40	36.29
44	59.66
45	22.77
46	16.06
49	0.75
50	48.13
51	37.08
52	22.16
53	49.88
60	14.07
61	35.45
62	100.00
63	35.63
64	19.78
65	6.19
66	8.45
73	19.08
74	0.94
76	2.36
77	19.72
78	20.83
79	9.51
80	26.18
87	3.62
90	4.23
91	56.10
92	12.29
94	2.48
106	17.21
107	2.81
108	1.00
136	2.93
147	0.94
152	0.06
199	35.57
221	0.72
228	1.78
229	93.24
230	0.69

MASS LIST OF DICHLORO(2-ALLYLPYRIDINE)PLATINUM(II)
COMPLEX Y

MASS LIST DATA: ALPYPT15 # 61 BASE M/E: 117
07/07/88 15:46:00 + 2:05 RIC: 2318330.
SAMPLE: ALLYL PYRIDINE PT EI SOURCE 1.4UL
#58 TO #65 SUMMED - #45 TO #47 - #75 TO #80 X1.00

41 0.00 MINIMA MIN INTEN: 593. MAX INTEN: 272384.
402 # 0 MAXIMA

MASS	% RA	MASS	% RA	MASS	% RA	MASS	% RA
41	25.19	91	9.61	154	0.63	264	0.47
42	4.86	92	4.26	155	6.85	265	0.38
43	15.44	93	9.72	156	24.30	266	0.30
44	8.42	94	1.52	157	3.60	267	0.37
45	4.24	95	2.39	158	2.20	268	0.30
46	1.31	96	1.22	161	0.23	269	0.40
47	0.37	97	2.87	171	0.27	270	0.49
48	0.33	98	2.04	174	2.41	271	0.63
49	1.54	99	0.83	175	0.87	272	0.84
50	11.82	100	0.34	176	0.25	273	0.78
51	28.95	101	0.48	194	2.08	274	0.48
52	14.92	102	0.47	195	2.48	280	0.28
53	4.83	103	0.43	196	1.74	281	0.54
54	2.51	104	3.46	197	0.26	282	1.63
55	10.77	105	0.70	198	0.37	283	4.59
56	3.67	106	0.70	206	0.59	284	5.50
57	11.14	107	0.48	207	1.18	285	5.06
58	5.49	108	0.36	208	1.11	286	3.22
59	3.16	109	1.12	209	0.57	287	1.85
60	3.94	110	0.67	210	0.34	288	0.65
61	2.58	111	1.17	211	0.24	297	0.22
62	4.96	112	0.93	219	0.62	298	0.24
63	14.07	113	0.39	220	1.61	299	0.32
64	5.28	114	0.72	221	2.15	308	1.06
65	17.01	115	1.16	222	1.77	309	3.50
66	5.32	116	0.58	223	0.94	310	10.47
67	4.52	117	100.00	224	0.38	311	22.18
68	1.94	118	51.41	229	0.76	312	27.54
69	5.67	119	7.23	230	0.79	313	20.63
70	1.83	120	0.95	231	4.08	314	9.74
71	5.08	121	0.52	232	5.19	315	3.58
72	0.60	122	0.36	233	6.79	316	2.03
73	3.95	123	0.59	234	4.04	339	0.41
74	1.81	124	0.23	235	2.54	340	0.28
75	1.66	125	0.30	236	1.03	341	0.33
76	2.02	129	0.69	237	0.67	347	4.42
77	3.24	130	0.69	243	0.89	348	9.41
78	14.97	131	0.50	244	1.34	349	10.26
79	5.90	132	0.34	245	2.06	350	7.65
80	6.63	134	0.27	246	1.53	351	4.24
81	3.24	135	0.44	247	0.88	352	2.65
82	1.46	137	0.46	248	0.37	353	0.48
83	4.20	141	0.42	255	1.12	354	0.40
84	2.24	142	0.55	256	2.10	383	8.38
85	3.32	143	1.07	257	2.86	384	8.59
86	1.18	144	0.69	258	3.11	385	11.83
87	1.88	149	0.23	259	2.69	386	6.05
88	0.79	151	0.48	260	1.76	387	6.99
89	12.22	152	0.32	261	0.81	388	1.17
90	10.59	153	0.25	262	0.48	389	1.82

MASS LIST OF COMPLEX X

MASS LIST DATA: ALPYPT15 # 35 BASE M/E: 117
07/07/88 15:46:00 + 1:12 RIC: 1712120.
SAMPLE: ALLYL PYRIDINE PT EI SOURCE 1.4UL
#30 TO #40 SUMMED - #10 TO #15 - #45 TO #47 X1.00

41 0.00 MINIMA MIN INTEN: 344. MAX INTEN: 241664.
399 # 0 MAXIMA

MASS	% RA	MASS	% RA	MASS	% RA	MASS	% RA
41	12.82	99	1.18	183	0.18	262	0.19
42	4.56	100	0.54	185	0.29	264	0.25
43	22.54	101	1.36	194	2.39	267	0.15
44	5.65	102	0.19	195	2.38	268	0.42
45	2.46	103	0.57	196	1.85	269	0.66
46	0.50	104	2.08	197	0.19	270	0.55
49	0.50	108	0.20	198	0.36	271	1.11
50	5.95	109	0.45	199	0.24	272	0.93
51	14.99	110	1.85	206	0.81	273	0.67
52	5.44	111	2.32	207	1.55	274	0.19
53	1.88	112	0.85	208	1.51	278	0.17
54	3.63	113	0.89	209	0.76	279	0.30
55	17.51	114	0.86	210	0.29	280	0.56
56	5.59	115	1.39	211	0.25	281	0.98
57	18.17	116	1.93	213	0.15	282	3.12
58	2.12	117	100.00	219	0.69	283	5.22
59	1.21	118	12.55	220	1.56	284	5.38
60	5.01	119	1.42	221	2.04	285	4.75
61	3.22	123	0.17	222	2.44	286	2.54
62	4.32	124	0.92	223	1.62	287	1.74
63	11.51	125	0.61	224	0.84	288	0.18
64	3.19	126	0.33	225	0.21	296	0.14
65	3.44	127	0.53	227	0.20	297	0.17
66	1.42	128	0.35	229	0.62	298	0.17
67	3.93	129	1.36	230	0.34	307	0.38
68	2.08	130	0.57	231	4.38	308	1.19
70	3.40	138	0.65	232	7.04	309	5.56
71	7.07	139	0.66	233	7.67	310	6.18
73	4.96	140	0.28	234	5.03	311	28.55
74	1.83	141	0.50	235	2.77	312	28.07
75	0.99	142	0.24	236	2.26	313	21.61
76	1.27	143	1.42	237	0.91	314	1.71
78	5.05	144	0.22	239	0.27	315	6.09
79	2.43	148	0.24	241	0.16	316	0.66
80	5.61	151	0.62	242	0.19	340	0.20
82	4.49	152	1.10	243	1.09	341	0.19
83	8.63	153	0.48	244	1.97	345	0.22
84	4.72	154	0.49	245	2.64	347	10.24
85	5.44	155	4.69	246	1.93	348	11.10
86	1.44	156	14.30	247	0.70	349	11.36
87	3.20	157	3.08	248	0.25	350	3.93
88	0.94	158	0.74	250	0.30	351	4.72
89	14.78	166	0.51	254	0.32	352	0.34
90	7.20	169	0.75	255	1.80	353	0.66
91	2.17	170	5.36	256	3.43	375	5.48
92	0.53	171	0.87	257	4.34	376	6.18
95	1.01	172	0.34	258	3.73	377	6.40
96	4.71	174	0.44	259	2.78	378	2.32
97	6.01	179	0.18	260	1.52	379	2.64
98	3.53	180	0.17	261	0.68	381	0.24

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