



Preparation and reactions of platinum(IV) cyclobutanes and the first platinum(IV)-bound olefin from bicyclo[n.1.0]hydrocarbons
by Edith Jane Parsons

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:

Platinum(IV)cyclobutanes were prepared by the reaction of platinum(II) in the form of Zeise's dimer with bicyclo-[4.1.0]heptane, bicyclo [6.1.0] nonane, and bicyclo [6.1.0]non-4-ene. The bicycloalkanes formed insoluble polymeric platinumcyclobutanes which were solubilized upon conversion to monomeric species with pyridine or bipyridine ligands. The bicycloheptane complex was much less stable than the corresponding bicyclononane complex. Reaction of these platinumcyclobutanes with soft ligands KCN, PΦ, DMSO, and THF reproduced the original cyclopropanes or yielded olefinic products. The platinumcycles also rearranged thermally to one or more olefinic compounds.

The platinumcyclobutane from bicyclononene formed as a dimeric platinum(II)-platinum(IV) species wherein the platinum(IV) was incorporated into a 2,4-disubstituted platinumcyclobutane. This complex also contained the first reported platinum (IV)-olefin bond and was characterized by X-ray crystallography. The reactivity of the complex was dominated by reductive elimination of the original cyclopropane, although the nucleophiles H⁻ and EtO⁻ were induced to attack the platinum (IV)-bound olefin.

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APPROVAL

of a thesis submitted by

Edith Jane Parsons

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	viii
ABSTRACT	xii
INTRODUCTION	1
Platinum(II)-Olefin Complexes	1
Nucleophilic Attack on Pt(II)-Olefin Complexes	7
π -Allyl Formation From Pt(II)-Olefin Complexes	11
Platinum Catalyzed Rearrangement of Olefins	13
Platinum(IV)-Olefin Complexes	16
Bridged, Binuclear Platinum Complexes	16
Platinum Carbonyl Complexes	17
Platina(IV)cyclobutane Complexes	19
Platinacyclobutane Structure and Bonding	19
Analysis of Platinacyclobutanes	24
Formation of Platinacyclobutanes	28
Platinacyclobutane Rearrangement	33
Chemistry of Platinacyclobutanes	39
Platinacyclobutane Decomposition	40
Additions to Platinacyclobutanes	47
Reactions of Norbornyl Platinacyclobutanes	47
RESULTS AND DISCUSSION	52
Statement of Problem	52
Formation of Platinacyclobutanes	53
Complexes from Cyclopropane 21	53
Complexes from Cyclopropane 25	58

TABLE OF CONTENTS-Continued

	Page
Complexes from Cyclopropane 32	62
Chemistry of the Platinacyclobutanes	75
Reactions with KCN, DMSO, and $P\phi_3$	75
Thermal Decomposition of 23 and 48.	80
Reactions of 22 and 37 with THF and CO.	104
Thermal Rearrangement of IPCs 22 and 29.	111
Reaction of 23 and 37 with CH_2N_2	126
Reaction of 37 with nucleophiles.	129
EXPERIMENTAL	134
General	134
Synthesis of Substrates and Standards	135
Formation of Platinacyclobutanes	138
X-ray Diffractometry on Platinacyclobutane 37	143
Reactions of Platinacyclobutanes	144
Kinetic Measurements	156
Olefin Isomerizations Catalyzed by Platinum	158
REFERENCES	162
APPENDICES	171
Appendix A: NMR and Mass Spectral Data for Cyclo- propanes, Olefins, and Platinum-Olefin Complexes	172
Appendix B: X-ray Data for Complex 37	181
Appendix C: Structures	186

LIST OF TABLES

Table	Page
1. Representative Platinum(II)-Olefin Infrared Carbon-Carbon Stretching Frequencies.	4
2. Representative Platinum(II)-Olefin Infrared Metal-Carbon Stretching Frequencies.	5
3. Range of Platinum(II)-Olefin ^{13}C NMR Resonances	5
4. Infrared Bands of Cyclopropane and its Platina-cyclobutanes.	25
5. ^{195}Pt NMR Resonances of Monomeric Platinacyclobutanes, With Respect to $1.0\text{M Na}_2\text{Pt}(\text{CN})_4$ in D_2O	29
6. Cyclopropanes Which Form Platinacyclobutanes.	31
7. Norbornylcyclopropanes Which Form Platina-cyclobutanes.	32
8. Cyclopropanes Which Do Not Form Platinacyclobutanes.	33
9. Platinacyclobutane 22 Solid State ^{13}C NMR Resonances.	54
10. NMR Resonances for Compounds 23 (L = py) and 24 (L = bipy).	55
11. NMR Resonances for Compounds 30 (L = py) and 31 (L = bipy).	61
12. NMR Resonances for Compounds 36, 37, and 48.	65
13. ^{195}Pt and ^{13}C NMR Resonances for Compound 43.	71
14. ^1H and ^2H NMR Resonances for Olefins 49 and 56.	83
15. Average Rate Constants for the Decomposition of Complex 23.	85

LIST OF TABLES-Continued

Table	Page
16. Average Rate Constants for the Decomposition of Complex 55.	87
17. Corrected Rate Constants for the Decomposition of Complex 55.	89
18. Kinetic Isotope Effects for the Decomposition of Complexes 23 and 55.	90
19. Product Yields From the Decomposition of 22 With Time.	113
20. Variation in Relative Concentrations of Olefins 49-51 Upon Heating With Platinum.	115
21. NMR and MS Data for Cyclopropanes 21, 25 and 32.	173
22. NMR and MS Data for Olefins 28, 51, 88, 91 and 96.	174
23. NMR and MS Data for Olefins 26, 27, 81 and 82.	175
24. NMR and MS Data for Dienes 83, 84 and 85.	176
25. NMR and MS Data for Olefins 49, 50 and 51.	177
26. NMR Data for Platinum-Olefin Complexes 63, 80 and 97.	178
27. NMR Data for Platinum-Olefin Complexes 54, 62 and 98.	179
28. NMR Data for Platinum-Olefin Complexes 99 and 100.	180
29. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{A}^2 \times 10^3$).	182
30. Bond lengths (A).	182
31. Bond Angles ($^\circ$):	183
32. Anisotropic Thermal Parameters ($\text{A}^2 \times 10^3$).	183

LIST OF FIGURES

Figure	Page
1. Bonding Between Platinum(II) and an Olefin.	3
2. Situation of a Platinum-Bound Olefin with Respect to the Ligand Plane.	3
3. Rotation of a Platinum Coordinated Olefin.	7
4. Mechanisms for Nucleophilic Attack on Platinum(II) Bound Olefins.	8
5. Activation of Platinum(II)-Olefins.	8
6. Stereochemistry of Amine Attack on a Platinum(II) Olefin.	9
7. Reaction of Amines with Platinum-Ethylene.	10
8. Mechanism for Palladium Insertion into an Allylic Carbon-Hydrogen Bond.	12
9. Possible Transition States in Platinum Insertion into an Alkane Carbon-Hydrogen Bond.	13
10. Platinum Catalyzed Olefin Isomerization Mechanisms.	14
11. Possible Platinum Hydride-Generating Reactions and Their Analogues.	15
12. Binuclear Platinum(0)-Platinum(II) Complexes.	18
13. Binuclear Platinum(II)-Platinum(IV) Complexes.	18
14. Walsh Cyclopropane Orbitals.	20
15. Proposed Tetrameric Platinacyclobutane Structures.	22
16. McGinnety Platinacyclobutane Orbitals.	23

LIST OF FIGURES-Continued

Figure	Page
17. Platinacyclobutane ^{13}C NMR Resonance Ranges With all Values in ppm.	26
18. Proposed Puddephatt Rearrangement Mechanisms.	35
19. Mechanism Proposed for the Puddephatt Rearrange- ment by Analogy to the Cyclobutyl Cation.	37
20. Initial Ligand Dissociation From a Platinacyclo- butane.	40
21. Mechanisms Proposed for the Rearrangement of Platinacyclobutanes to Olefins.	42
22. Pi-allyl ^1H NMR Resonance Ranges.	46
23. Mechanism Proposed for the Reaction of Diazo- methane with Platinacyclobutanes.	48
24. Reactions of Norbornyl Platinacyclobutanes with DMSO.	49
25. Reactions of Norbornyl Platinacyclobutanes with CO.	49
26. Cationic Mechanisms Proposed for the Reactions of Norbornyl Platinacyclobutanes with CO.	50
27. Thermolysis of Norbornyl Platinacyclobutanes.	51
28. Proposed Mechanism for Formation of Diolefins from Norbornyl Platinacyclobutane Thermolysis.	51
29. Solid State ^{13}C NMR Spectrum of 22.	54
30. Reactions of Platinacyclobutanes 22 and 35 With DMSO.	77
31. Reactions of Platinacyclobutanes 37 and 48 With DMSO.	79
32. Thermal Reactions of Platinacyclobutanes 48 and 53.	80
33. Platinacyclobutane Decomposition Mechanisms as Differentiated by Deuterium Labelling.	82

LIST OF FIGURES-Continued

Figure	Page
34. Possible Isotopomers in the Decomposition of 55.	88
35. Decomposition of Platinacyclobutane 22 with one or two Pyridines.	93
36. Possible Mechanisms for Producing Olefin Mixtures From Platinacyclobutanes.	94
37. Thermal Decompositions of 23 Involving Isomerization of Olefin 54.	95
38. Species Not Responsible for the Isomerization of Olefins 49 and 50.	96
39. Possible Mechanisms for the Isomerization of Olefin 49.	98
40. Reactions of Olefins 49 and 50 With Platinum(II).	100
41. Formation of Pi-Allyls 66 and 67 From Decomposition of 23 in Methanol:	102
42. Possible Mechanisms For the Formation of a Pi-Allyl From Olefin Complex 54 Following Loss of a Pyridine Ligand.	103
43. Possible Mechanisms for the Reaction of Platinacyclobutanes with CO.	107
44. Deuterium Labelling to Distinguish Between the Possible Mechanisms in the Reaction of 22 with CO.	109
45. Reaction of Complex 37 with CO.	110
46. Thermal Decomposition of 22 Followed by Treatment with KCN.	112
47. Possible Relationships Affecting the Relative Product Yields in the Thermal Decomposition of 22.	116
48. A Possible Mechanism for the Formation of Diolefin 83 by Thermal Decomposition of 29.	124
49. GC Peaks for Compounds 25, and 78-85.	125

LIST OF FIGURES-Continued

Figure	Page
50. Precedence for Possible Products from the Reactions of 22 and 37 with CH_2N_2	127
51. Possible Products and Mechanisms for the Reactions of 22 and 37 with CH_2N_2	127
52. Illustration of the Similarity of CO and CH_2 as Ligands.	129
53. Proton NMR Resonance Assignments for 21 and 93.	131
54. Proposed Mechanism for the Reaction of 37 With H^-	132
55. Reaction of 37 with Nucleophiles.	132
56. Computer-Generated View of the Non-Hydrogen Atoms For Complex 37.	184
57. Computer-Generated View of the Platinacyclobutane Ring and Dichlorodiplatinum Ring System with Corresponding Bond Lengths for Complex 37.	185

ABSTRACT

Platina(IV)cyclobutanes were prepared by the reaction of platinum(II) in the form of Zeise's dimer with bicyclo[4.1.0]heptane, bicyclo[6.1.0]nonane, and bicyclo[6.1.0]non-4-ene. The bicycloalkanes formed insoluble polymeric platinacyclobutanes which were solubilized upon conversion to monomeric species with pyridine or bipyridine ligands. The bicycloheptane complex was much less stable than the corresponding bicyclononane complex. Reaction of these platinacyclobutanes with soft ligands KCN, $P\phi_3$, DMSO, and THF reproduced the original cyclopropanes or yielded olefinic products. The platinacycles also rearranged thermally to one or more olefinic compounds.

The platinacyclobutane from bicyclononene formed as a dimeric platinum(II)-platinum(IV) species wherein the platinum(IV) was incorporated into a 2,4-disubstituted platinacyclobutane. This complex also contained the first reported platinum(IV)-olefin bond and was characterized by X-ray crystallography. The reactivity of the complex was dominated by reductive elimination of the original cyclopropane, although the nucleophiles H^- and EtO^- were induced to attack the platinum(IV)-bound olefin.

INTRODUCTION

Platinum(II)-Olefin Complexes

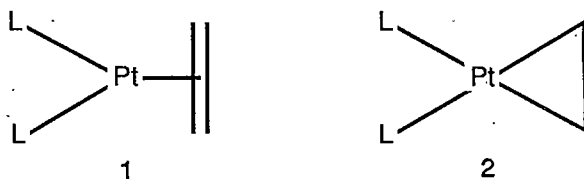
The first metal π -complex to be recognized was Zeise's salt, $K[C_2H_4PtCl_3] \cdot H_2O$ ¹. This complex was made by W. C. Zeise and was published (in Latin) in 1830. Since then, a tremendous variety of olefin complexes of Pt(II) have been prepared and identified.

Mono-olefin complexes of Pt(II) can be separated into two main classes. The first group is comprised of four general forms², where X can be a halogen, an alkoxide, or a hydride and L is a neutral ligand:

- a) Dimeric, bridged complexes $[Pt(olefin)X_2]_2$;
- b) Salts of an olefin-containing anion $M^+[Pt(olefin)-X_3]^-$
- c) Salts of an olefin-containing cation $[Pt(olefin)-XL_2]^+A^-$
- d) Neutral mononuclear complexes, $[Pt(olefin)X_2L]$,

where L can be an olefin $[Pt(olefin)_2X_2]$.

The second class, illustrated by complexes 1 and 2, may be regarded as Pt(0) or as Pt(II). In the latter case, the Pt(II) and olefin carbons are connected by σ bonds and form a platinacyclopropane ring. The two possibilities represent bonding extremes.



Bonding between Pt(II) and an olefin consists of one σ - and one π -bond. The σ -bond is formed when the olefin's filled π -orbital donates electron density to an empty dsp^2 orbital on the platinum. The π bond then results from back donation of electron density from a filled platinum d orbital to the vacant olefin π^* orbital³. As shown in Figure 1, these bonds act synergistically. A platinacyclopropane ring is formed when back bonding from the platinum to the olefin becomes greatly enhanced.

X-ray analyses of Zeise's salt⁴ and other Pt-olefin complexes⁵ have shown that platinum and its non-olefin ligands define a plane coincident with the platinum dsp^2 plane. The olefin lies perpendicular to this plane, as shown in Figure 2. The olefinic hydrogen atoms probably form a plane which is displaced slightly from co-planarity with the carbon atoms but is parallel to the ClZCl plane. The carbon-carbon bond length in the olefin is about 1.4 \AA ⁶, which is slightly elongated from that of uncomplexed olefins ($\approx 1.3 \text{ \AA}$).

Figure 1. Bonding Between Platinum(II) and an Olefin.

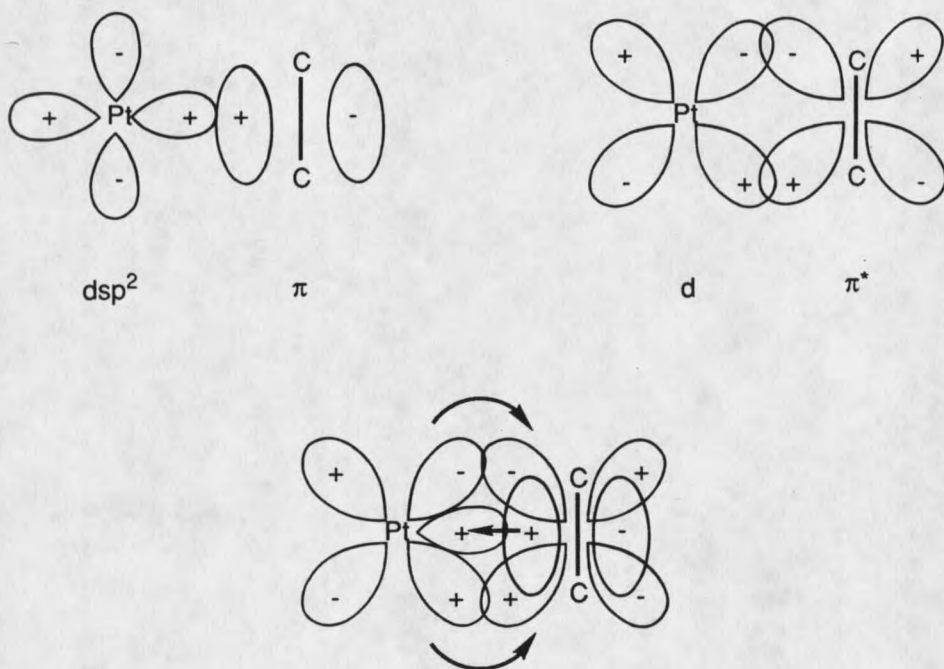
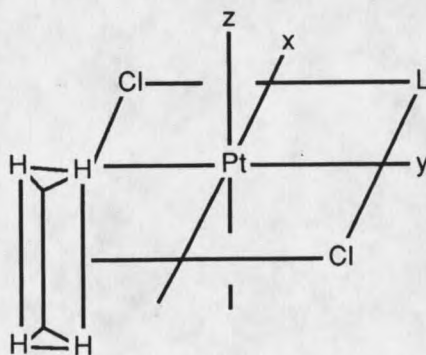


Figure 2. Situation of a Platinum-Bound Olefin with Respect to the Ligand Plane.



Infrared and Raman spectroscopies provide a useful qualitative picture of Pt-olefin π -bonding⁷⁻⁹. Generally, the C-C stretching frequency moves to lower wave numbers with increasing Metal-olefin bond strength. Some examples are shown in Table 1. As a quantitative tool for determining Pt-olefin bond strength, however, this frequency must be used with caution. The C-C stretching frequency can couple with other modes to lead to complex results. A better diagnostic tool for bond strength is the Pt-olefin stretching frequency. This vibration normally comes between 410 and 380 cm^{-1} , as illustrated in Table 2.

Table 1. Representative Platinum(II)-Olefin Infrared Carbon-Carbon Stretching Frequencies.

	cm^{-1}
$\text{H}_2\text{C}=\text{CHCH}_2$	1647
$\text{H}_2\text{C}=\text{CH}_2$ (gas)	1623 (Raman)
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$	1506
$[\text{Pt}(\text{C}_3\text{H}_6)\text{Cl}_2]_2$	1504
$\text{K}_2[\text{Pt}(\text{C}_4\text{H}_6)\text{Cl}_3]_2$	1413
$\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$	1516
$t-[\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2]$	1521
$t-[\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Br}_2]$	1517
$\text{K}[\text{Pt}(\text{C}_3\text{H}_6)\text{Cl}_3]\text{H}_2\text{O}$	1504

Table 2. Representative Platinum(II)-Olefin Infrared Metal-Carbon Stretching Frequencies.

	cm ⁻¹
K[Pt(C ₂ H ₄)Cl ₃]H ₂ O	407
K[Pt(C ₂ H ₄)Br ₃]H ₂ O	395
K[Pt(C ₃ H ₆)Cl ₃]	393
K[Pt(t-C ₄ H ₈)Cl ₃]	387
K[Pt(c-C ₄ H ₈)Cl ₃]	405
t-[Pt(C ₂ H ₄)(NH ₃)Cl ₂]	383

Platinum is particularly useful as an NMR marker. Its 195 isotope (33.8% natural abundance) is NMR active with spin $\frac{1}{2}$ and receptivity 19.1 (relative to carbon). This allows platinum coupling to the ¹H and ¹³C nuclei to be observed¹⁰. By ¹³C NMR spectroscopy, Pt-bound olefinic carbons always appear upfield relative to the free olefins. Resonances have been reported from 67 to 6130, as listed in Table 3, with trans-Pt(C₂H₄)pyCl₂ appearing at about midrange¹¹.

Table 3. Range of Platinum(II)-Olefin ¹³C NMR Resonances.

	ppm
Pt(C ¹ H ₂ =C ² H ₂ HCN)Me(HBpz ₃)	C ² = 7.4
Pt(t-NCCH=CHCN)Me(HBpz ₃)	C _{olef} = 7.8
[Pt(cod)(C ₈ H ₁₃)] ⁺	C _{olef} = 126.9
t-Pt(C ₂ H ₄)pyCl ₂	C _{olef} = 75.0

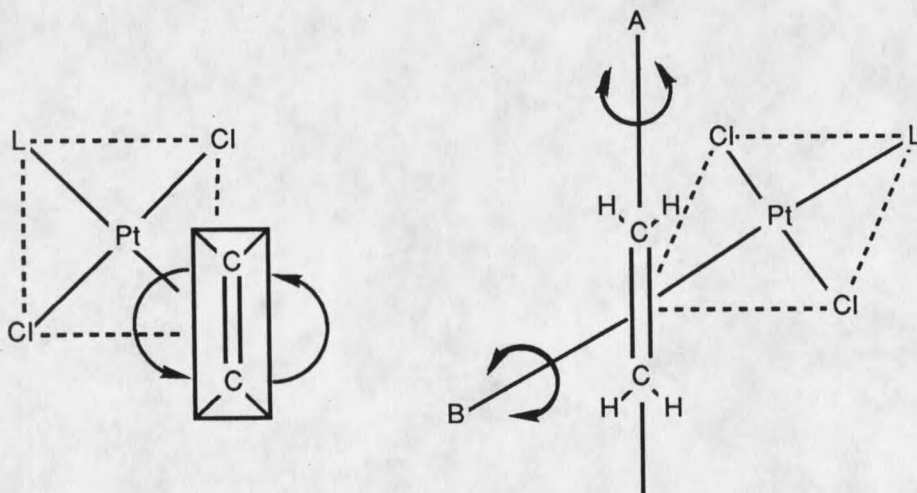
Although $^1J_{Pt,c}$ depends mainly on carbon hybridization, Pregosin has observed that platinum coupling to the directly bound olefinic carbons indicates the strength of the platinum-olefin bond^{1,2}. This coupling ranges from 40 to 400 Hz, and generally decreases with increasing trans influence in the ligand trans to the olefin. However, olefin geometry, at least for non-strained olefins, does not appear to affect the constant.

Proton NMR shifts are dependent on complicated shielding effects, making it difficult to predict changes upon binding to the platinum. Generally platinum is thought to shield the protons. However, ligand effects and various other incompletely characterized effects may move the resonance downfield. Platinum bonding to other remote functionality in the olefinic molecule may also result in a change in the chemical shift of the olefinic protons.

Platinum to olefinic proton couplings in the range of 10 to 83 Hz have been observed, however this coupling is not always indicative of bond strength. Often, Pt-H coupling is not observed at all; instead broad olefinic resonances are obtained. This may be due to the platinum-bound olefin exchanging with free olefin in the solution. In most cases the exchange is very rapid, but can be halted at low temperatures. Alternately, broadening may be the result of a propeller-like rotation of the coordinated olefin, shown in Figure 3. This internal, hindered rotation ranges from 10-20

kcal/mole and increases with decreasing platinum-olefin bond strength and lower steric hinderance. In a non-symmetrical complex the motion makes the protons equivalent, but can be halted at low temperatures. Rotation about axis A also appears to occur, but does not affect the solution NMR spectrum¹³.

Figure 3. Rotation of a Platinum Coordinated Olefin.



Nucleophilic Attack on Pt(II)-Olefin Complexes

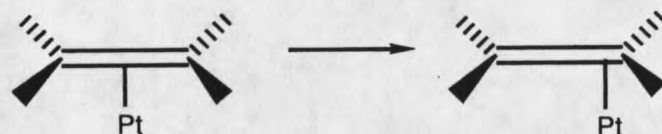
Platinum(II) bound olefins are known to undergo nucleophilic attack¹⁴⁻²⁵. The two mechanisms illustrated in Figure 4 have been postulated for this attack. The olefin and nucleophile may both coordinate to platinum, followed by

cis attack of the nucleophile on the olefin. Alternatively, the olefin may bond to the platinum followed by external nucleophilic attack, or trans-addition. In either case, the olefin is probably activated by a slippage of the platinum²⁴, as shown in Figure 5.

Figure 4. Mechanisms for Nucleophilic Attack on Platinum(II) Bound Olefins.



Figure 5. Activation of Platinum(II)-Olefins.



Monoolefins bound to other platinum-group metals appear to react via prior nucleophile coordination and cis-attack. However, in 1970, Panunzi¹⁴ reported a stereochemical study of amine attack on (+)-cis-dichloro[(S)-1-butene] [(S)- α -methylbenzylamine] platinum(II). The results, shown in Figure 6, clearly demonstrated that the nucleophile did not coordinate to the platinum. In other studies involving Pt(II)-monoolefin complexes, no attempt was made to determine stereochemistry¹⁵⁻¹⁸.

