



Mechanisms of platinum(II) and palladium(II) catalyzed organic transformations : hydration of alkynes and the cope rearrangement
by William Charles Hiscox

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:

Mechanisms of the platinum (II) catalyzed hydration of alkynes and the palladium (II) catalyzed Cope rearrangement of 2-methyl-3-phenyl-1,5-heptadiene were studied using nuclear magnetic resonance spectrometry (NMR). Kinetic studies were done for both reactions. For both reactions the rate determining steps were found to be ligand substitution reactions of the respective substrates on the active catalysts. The reactions are shown to proceed through metallacycle intermediates.

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AND THE COPE REARRANGEMENT

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Advisor: Reed A. Howald, Ph.D.

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Signature *Nellie C. Mirer*

Date September 15, 1993

This thesis is dedicated to the memory of Marjorie Nichols, one of the first women ever admitted to a college chemistry course, and the one responsible for my interest in science.

TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. PLATINUM(II) CATALYZED HYDRATION OF ALKYNES AND RELATED REACTIONS	3
Background	5
Experimental Section	13
General	13
Preparation of Zeise's Dimer	14
di-(4,4-dimethyl-2-pentyne)-dichloro-di- μ - dichloroplatinum(II)	15
General Method for Hydration of Alkynes- Illustrated for 1-Hexyne	16
Recycling of Platinum	18
Monitoring of Reactions by ^1H NMR	19
Effect of p-toluenesulfonic acid on reaction rate	20
Effect of D_2O vs H_2O	20
Rate of Reaction with 4,4-dimethyl-2-pentyne dimer vs Zeise's Dimer	21
Michaelis-Menten kinetics	22
Reaction of Zeise's Dimer with 4-Octyne in CHCl_3	23
Dichloroplatinum(II)-tetraalkylcyclobutadienes ...	24
Methanol Addition to 1-alkynes	31
Results and Discussion	36
Mechanistic Studies	43
Exchange experiments on Zeise's Dimer	48
The Role of the Ethylene Ligand in the Catalyst	51
Kinetics Experiments- ^1H NMR	56
Michaelis-Menten Catalyst Model	62
Evaluation of Possible Mechanisms	63
Addition of Methanol to 1-Alkynes	72
Cyclobutadienes	78
Summary	85
3. PALLADIUM CATALYZED COPE REARRANGEMENT OF 2-METHYL-3-PHENYL-1,5-HEPTADIENE	86
Background	89
Mechanism of Thermal Cope Rearrangements	91
Palladium(II) Catalyzed Cope Rearrangements	98

TABLE OF CONTENTS-continued

	page
Experimental Section	102
General	102
Synthesis of Starting Materials	103
Thermal Rearrangement of trans-2-methyl-3-phenyl-1,5-heptadiene	109
Molecular Modeling	109
bis-Acetonitriledichloropalladium(II)	110
Palladium Catalyzed Cope Rearrangement of trans-2-methyl-3-phenyl-1,5-heptadiene in Tetrahydrofuran	111
Separation of Cis and Trans Isomers of 2-methyl-3-phenyl-1,5-heptadiene and of their Cope Rearrangement Products, Cis and Trans-2,4-dimethyl-1-phenyl-1,5-hexadiene	112
Characterization of diene II	113
Kinetics- Monitoring of Reactions by ¹ H NMR	114
Reactions of purified Cope Products	116
Data Handling, Analysis	116
Viability of the Catalyst at Long Reaction Times	118
Effect of Added Acetonitrile	118
Double-bond Isomerization of 3-heptene	119
Results	121
Collecting the Data: Preliminary Results	128
Reactions of Purified Dienes	130
Modeling the Palladium(II) Catalyzed Cope Rearrangement as a Set of Concurrent First Order Reactions	135
Effect of Added Acetonitrile	139
Molecular Modeling Studies	142
Details of Analysis of the Kinetic Data	143
Kinetic Runs at 308K	155
Thermodynamic Activation Parameters	155
Discussion	159
Summary	164
4. CONCLUSION	166
REFERENCES CITED	168
APPENDIX Data From Kinetic Runs in Chapter 3	176

LIST OF TABLES

Table	page
1. Data for Michaelis-Menten Graph	61
2. Thermodynamic Activation Parameters	156

LIST OF FIGURES

Figure	page
1. Hydration of 4-Octyne	4
2. Chatt-Dewar-Duncanson Model for olefin-metal bonding	9
3. Synergistic Bonding of Orthogonal π_{\perp} and π_{\perp}^* Acetylene Orbitals to Platinum	11
4. Correlation Diagram for Acetylene Backbonding to Platinum	12
5. Hydration of Dialkylalkynes	37
6. Explanation for Regioselectivity	38
7. ^{13}C and ^1H NMR of 2-Heptanone from Hydration of 1-Heptyne	40
8. Structure of Zeise's Dimer	44
9. NMR Spectra for D ₂ O Monomer of Zeise's Dimer	45
10. ^{13}C and ^1H NMR Spectra of Zeise's Dimer in CD ₃ OD....	46
11. Zeise's Dimer in CD ₃ CN	47
12. ^1H NMR Spectra for Catalytic Reaction in Tetrahydrofuran-d ₈	49
13. ^1H NMR Spectra for Ethylene Displacement in Chloroform-d	50
14. Top: di-(4,4-dimethyl-2-pentyne)-dichloro-di-m-dichlorodiplatinum(II). Bottom: Addition of 4-octyne and water to the complex.....	54
15. Detailed Mechanism of Platinum(II) Catalyzed Hydration of Alkynes Showing the Michaelis-Menten Constants	57
16. First Order Plots at Several Initial Concentrations of Alkyne	58
17. Saturation Kinetics	59
18. Michaelis-Menten Graph	60
19. Cis-Addition of Water and Methanol to an Osmium(II)-Alkyne Complex	67
20. Addition of Protonic Acids to a Platinum(0)-Alkyne Complex	68
21. Mechanism of Hydroxypalladation	70

LIST OF FIGURES-continued

Figure	page
22. Evidence for External Attack of Water on the Coordinated Ethylene of Zeise's Dimer	71
23. ^{13}C , ^1H and Mass Spectra of 2,2-dimethoxyheptane....	75
24. Top: HETCORR of 2,2-dimethoxyheptane. Bottom: Vinyl Ether?	76
25. Tetrapropylcyclobutadienedichloroplatinum(II)	79
26. ORTEP Plots of (tetrapropylcyclobutadiene)dichloroplatinum(II) ...	80
27. Mechanism of formation of tetrapropylcyclobutadienedichloroplatinum(II)	81
28. Other Cyclobutadiene Complexes	84
29. The Cope Rearrangement	86
30. Four Products of Palladium(II) Catalyzed Cope Rearrangement of 3-phenyl-2-methyl-1,5- heptadiene	88
31. Stereospecificity in the Claisen Rearrangement	91
32. Six Atom versus Four Atom Overlap	93
33. Argument Against Separated Allyl Fragments	95
34. Support for Minor Boat Transition State in the Thermal Cope Rearrangement	96
35. Rearrangement of cis,trans-1,5-cyclooctadiene on Palladium(II)	99
36. Palladium Catalyzed Cope Rearrangements of Substituted 3-phenyl-1,5-dienes	99
37. Analysis of Best Chair for the Rearrangement of (3R, 5E)-2,3-dimethyl-3-phenyl-1,5-heptadiene	101
38. Autoprogram KINET11.AU.....	114
39. Autoprogram FTPKINT.AU.....	117
40. Synthesis of Cope Starting Materials	120
41. Spectra for Compound I	122
42. Spectra for Compound II	123
43. ^1H Spectrum of Compound III	124
44. Nuclear Overhauser Effect in Compound II	125
45. Attempted Rearrangement of Geranyl Compounds	127
46. Summary of Reactions on the Dienes	129
47. Stacked Plot for Reaction of III→I	132
48. Graph of Integrals for the reaction III→I	133
49. Chromatograph of Cope Product Mixture	134
50. Associative Rate Law	140
51. The Palladium(II) Catalyzed Cope Rearrangement Cycle	141
52. Relative Stabilities of the Products from Molecular Modeling	142
53. Output for Rate Constant Matrix at 298K	145

LIST OF FIGURES-continued

Figure	page
54. Fit of Calculated Line to Experimental Line for Compound I	146
55. Fit of Calculated Line to Experimental Line for Compound II	147
56. Fit of Calculated Line to Experimental Line for Compound III	148
57. Output for the Rate Constant Matrix at 308K.....	152
58. Fit of Calculated Lines at 308K	153
59. Energy Diagrams for Formation of Three Products from Compound I	158
60. Predicted Stereochemical Outcome Through the Possible Boat and Chair Transition States	160
61. Structure of (η^4 -1,5-hexadiene)palladium dichloride	162
62. Summary	163

ABSTRACT

Mechanisms of the platinum(II) catalyzed hydration of alkynes and the palladium(II) catalyzed Cope rearrangement of 2-methyl-3-phenyl-1,5-heptadiene were studied using nuclear magnetic resonance spectrometry (NMR). Kinetic studies were done for both reactions. For both reactions the rate determining steps were found to be ligand substitution reactions of the respective substrates on the active catalysts. The reactions are shown to proceed through metallacycle intermediates.

CHAPTER 1

INTRODUCTION

Platinum and palladium are important strategic metals, and are used as catalysts for a wide variety of organic transformations. Knowledge of the mechanisms of these reactions is essential to the successful design of new catalysts. The work described here focuses on mechanisms of catalytic reactions of platinum(II) and palladium(II). The organic transformations which were studied are the platinum(II) catalyzed hydration of alkynes and the palladium(II) catalyzed Cope rearrangement of 2-methyl-3-phenyl-1,5-heptadiene.

Several related reactions were discovered during this study, including the formation of platinum(II)cyclobutadiene complexes from Zeise's Dimer and alkynes, which proceed through a platinacyclopentadiene intermediate. The study of platinacyclobutanes and pentanes was originally undertaken because of the proposed intermediacy of metallacycles in transition metal catalyzed olefin metathesis and other reactions. Several platinum mediated organic transformations

have recently been proposed to involve platinacycle intermediates. It will be shown that the reactions discussed here also proceed through platinacycle and palladacycle intermediates.

CHAPTER 2

**PLATINUM(II) CATALYZED HYDRATION OF ALKYNES
AND RELATED REACTIONS**

The hydration of alkynes is of great importance in organic synthesis, and for the functionalization of this hydrocarbon resource on an industrial scale. Alternatives to classical mercury catalyzed processes are becoming ever more important, due to the toxicity of mercury compounds and the increasing regulations on their use. Recent studies on addition of water and methanol to the carbon-carbon triple bond of alkynes coordinated to osmium(II) complexes¹, and new results on the mechanisms of Wacker type processes², among others, have dramatically changed the way mechanisms of late transition metal catalysis are described. With respect to organoplatinum chemistry, nucleophilic addition to alkynes is a long standing problem.

The hydration of alkynes, using Zeise's Dimer as the platinum(II) catalyst precursor, was first reported in 1989 (figure 1)³. This has been developed into an efficient method

for the transformation of dialkylalkynes and 1-alkynes into their corresponding ketones. The complete reaction of these alkynes requires less than 1mol% catalyst in water/tetrahydrofuran solutions, with no added protonic acid, at room temperature, to proceed without side products. The ketones are isolable by direct distillation from the reaction flask.

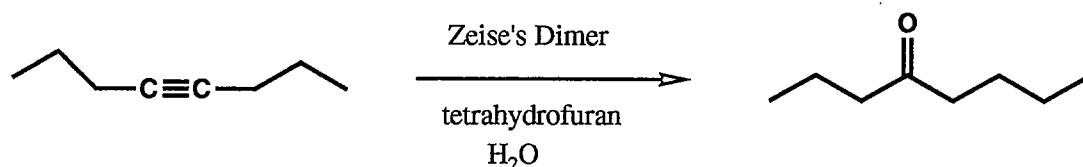


Figure 1 Hydration of 4-Octyne

Several fundamental questions arose upon the initial, serendipitous, observation that platinum(II) had catalyzed the hydration of 4-octyne in diethylether. What ligands are bonded to platinum in the active catalyst, and what is their geometry about the metal center? What is the fate of the ethylene on Zeiese's Dimer after reaction with an alkyne? Does Zeise's Dimer remain in the dimeric form during the reaction? More importantly, how does the active catalyst "activate" the substrate, and what role do its resident

ligands play in this step? Can methanol or other nucleophiles be added to an alkyne using this catalyst? These are the questions that will be addressed.

Background

Little mention is made of platinum catalyzed hydration of alkynes in the literature, except for the observation by Chatt and Duncanson⁴, that hydration of several alkynes was observed in the presence of platinum, which they believed had been reduced to the zero oxidation state during their attempted synthesis of platinum(II)-alkyne complexes in ethanol solvent. For the most part, such complexes could not be isolated, with the exception of those formed from dialkylacetylenes bearing at least one tertiary butyl group. The importance of these complexes will be discussed later.

Palladium(II) catalysts have been used for the hydration of alkynes⁵. However, complex mixtures result from the hydration of terminal acetylenes, such as methyl acetylene⁶, in strong acid solutions of the metal. Utimoto and coworkers⁷ have developed a hydration scheme for alkynones such as 5-heptyn-2-one, which employs palladium(II) catalysts, but relies upon intramolecular

assistance by the carbonyl oxygen of the alkynone for the reaction to proceed. Simple alkynes are not hydrated under the same conditions. Although palladium(II) is an excellent catalyst for the oxidation of olefins, its reactivity with alkynes is different from platinum. It is known more for its use in cyclotrimerizations of alkynes to make benzenes, for instance⁸.

Mercury(II) catalysis is the classical method of hydrating alkynes⁹, and the mechanism of the reaction is still actively studied. The reaction is usually run in concentrated acid solutions of mercury(II). Most of the current literature focuses on specific cases, such as the hydration of alkynes with other functionality, and recently on Nafion-H supports for mercury catalysts¹⁰. Mercury has traditionally been used to hydrate terminal alkynes to the corresponding ketones, in accord with Markovnikov's rules. However, polymers are often formed in the reaction, as well as mercuration products of the acetylene¹¹. Large amounts of mercury are used because the catalyst is easily poisoned, and workup is also inefficient. The mercury by-products, including metallic mercury and assorted organomercury compounds, are highly toxic. These products constitute a serious environmental hazard, and contamination by these compounds is widespread. Mercury is insidious because it accumulates in the fatty tissues of animals, and moves up

the food chain. It will be shown that for simple alkylalkynes, platinum(II) hydration catalysts have more longevity than mercury catalysts, can be used in truly catalytic amounts, and can be recycled easily without environmental degradation.

Previous attempts at alkyne hydration by platinum(II) catalysts have not been fruitful. Trogler has developed platinum(II) hydration catalysts for nitriles¹² and alkenes¹³, and has proposed their use for the hydration of alkynes. However, success in this last area has not been reported to date. The catalysts developed by Trogler are hydrido-hydroxo platinum(II) complexes formed via the photolysis of bis-triphenylphosphineplatinum(0) in the presence of water.

Hydrido-hydroxotransition metal complexes, in general, can be prepared by oxidative addition of protic compounds to low valent transition metals¹⁴. Oxidative addition of water to a transition metal should give a species with the general formula HMOH, disregarding the other ligands. In fact, reaction of water with $\text{Os}_3(\text{CO})_{12}$ gives $\text{Os}_3(\text{H})(\text{OH})(\text{CO})_{10}$ ¹⁵ and, likewise, $[\text{Rh}(\text{en})_2]^+$ gives $[\text{Rh}(\text{H})(\text{OH})(\text{en})_2]^+$ ¹⁶. An earlier, but thorough, investigation of the catalytic properties of platinum hydridohydroxy complexes was carried out by Otsuka and company.¹⁷ They studied both deuteration reactions and hydration reactions facilitated by these

catalysts. It was shown that the addition of water to $\text{Pt}[\text{P}(\text{i-pr})_3]_2$ gives $\text{trans-Pt}(\text{H})(\text{OH})[\text{P}(\text{i-pr})_3]_2$, while $\text{Pt}[\text{P}(\text{i-pr})_3]_3$ gives $[\text{Pt}(\text{H})\text{L}_3]\text{OH}$ ($\text{L} = \text{P}(\text{i-pr})_3, \text{P}(\text{Et})_3, \text{solvent}$). These catalysts, when generated in-situ, efficiently catalyzed the hydration of both olefins and nitriles.

For the platinum(II) catalyzed hydration of alkynes it is possible that coordinated water is "split" by platinum in a very fast step, resulting in the addition of the elements of water to the alkyne substrate. It will be shown that the rate of aquo-exchange on platinum(II)-alkyne complexes must be fast with respect to the rate determining step. Rates of Aquo-exchange on Platinum Complexes in aqueous solution have been measured by Steve Dunham and Edwin Abbott¹⁸. They found that the rate of water exchange on platinum(III) in the form of $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)\text{Cl}_2]^{4-}$ was greater than 10^4s^{-1} ! Platinum(IV) complexes had much slower exchange rates, on the order of 10^{-6}s^{-1} . They did not investigate platinum(II) complexes. By the Chatt-Dewar-Duncanson model, one extreme of platinum-olefin bonding is described as the metallacyclopropane extreme. One can look at this as a formal oxidative addition of alkyne across the platinum center in a 1,2 sense, thereby increasing the oxidation state of platinum over platinum(II), the active catalyst precursor.

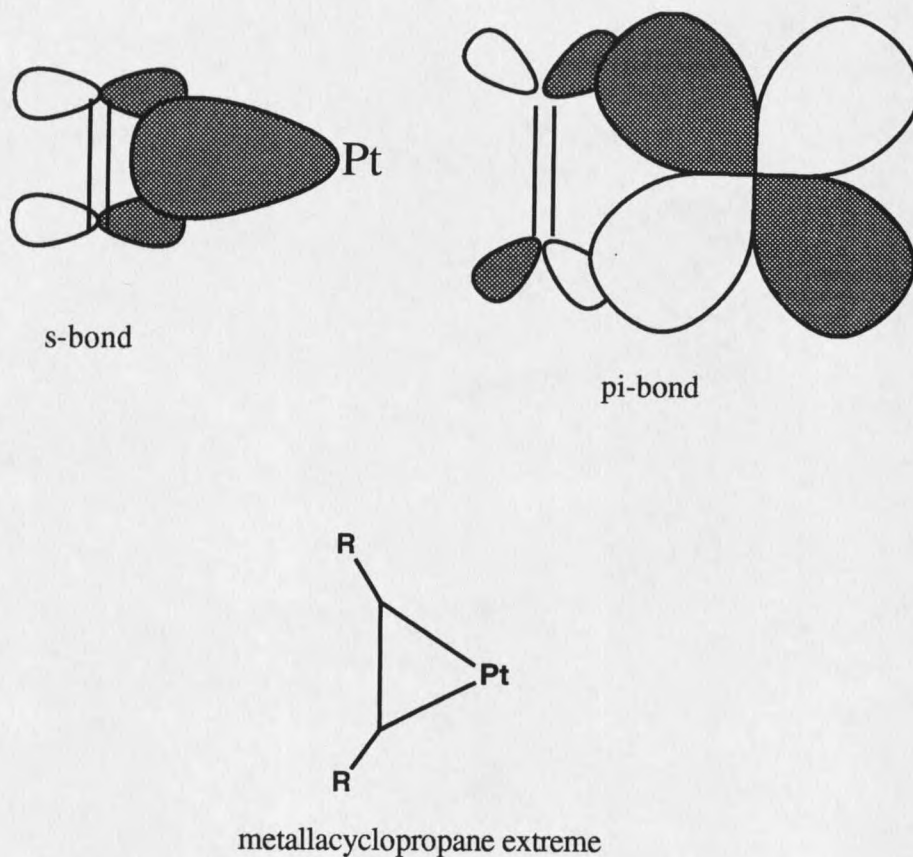


Figure 2 Chatt-Dewar-Duncanson Model for Olefin-Metal Bonding

The Chatt-Dewar-Duncanson¹⁹ model for olefin and acetylene-transition metal bonding is an excellent template on which to base predictions of structure, reactivity and stability of platinum(II) complexes of unsaturated organic ligands. The model (figure 2) recognizes two types of bonding: sigma donation from the filled pi orbitals on the olefin to empty metal d-orbitals forms the sigma component of the bond, and back donation of electrons from filled metal d-orbitals to the antibonding orbitals of the olefin

forms the pi component. The two components together form a "dative double bond". The picture for alkynes is much the same with regard to ligand-metal bonding, except for the extra set of bonding and antibonding orbitals on the alkyne. The orthogonal π_{\perp} and π_{\perp}^* orbitals of acetylenes may also interact with orbitals on the metal²⁰. This "synergistic" bonding is usually weak, however, due to the marginal overlap of the orbitals involved. Nevertheless, this interaction is important in the molecular orbital picture, because the mixing of these orbitals changes the LUMO of the complex. The bonding picture is illustrated in figure 3. The mixing of the orthogonal acetylene orbitals with orbitals on the metal results in an additional set of molecular orbitals, of which the antibonding orbital is now the LUMO of the complex. As shown in the correlation diagram in figure 4, this is where nucleophilic attack should occur.

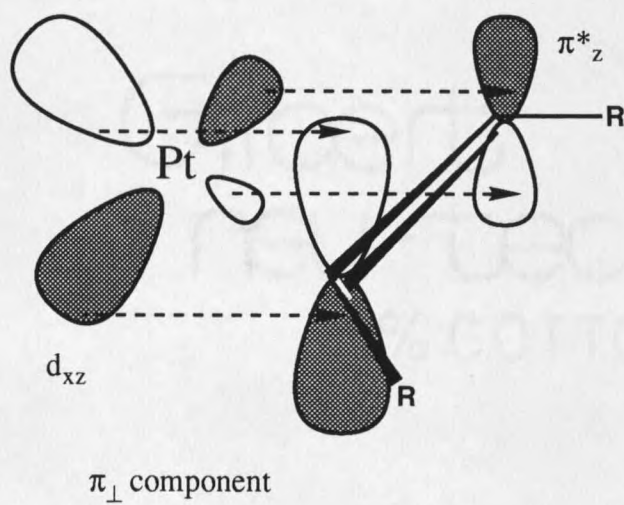
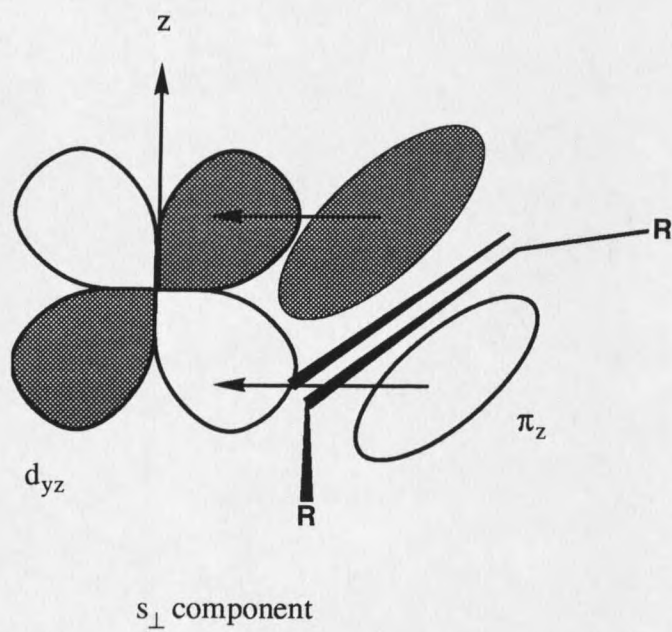


Figure 3 Synergistic Bonding of Orthogonal π_{\perp} and π_{\perp}^* Acetylene Orbitals to Platinum

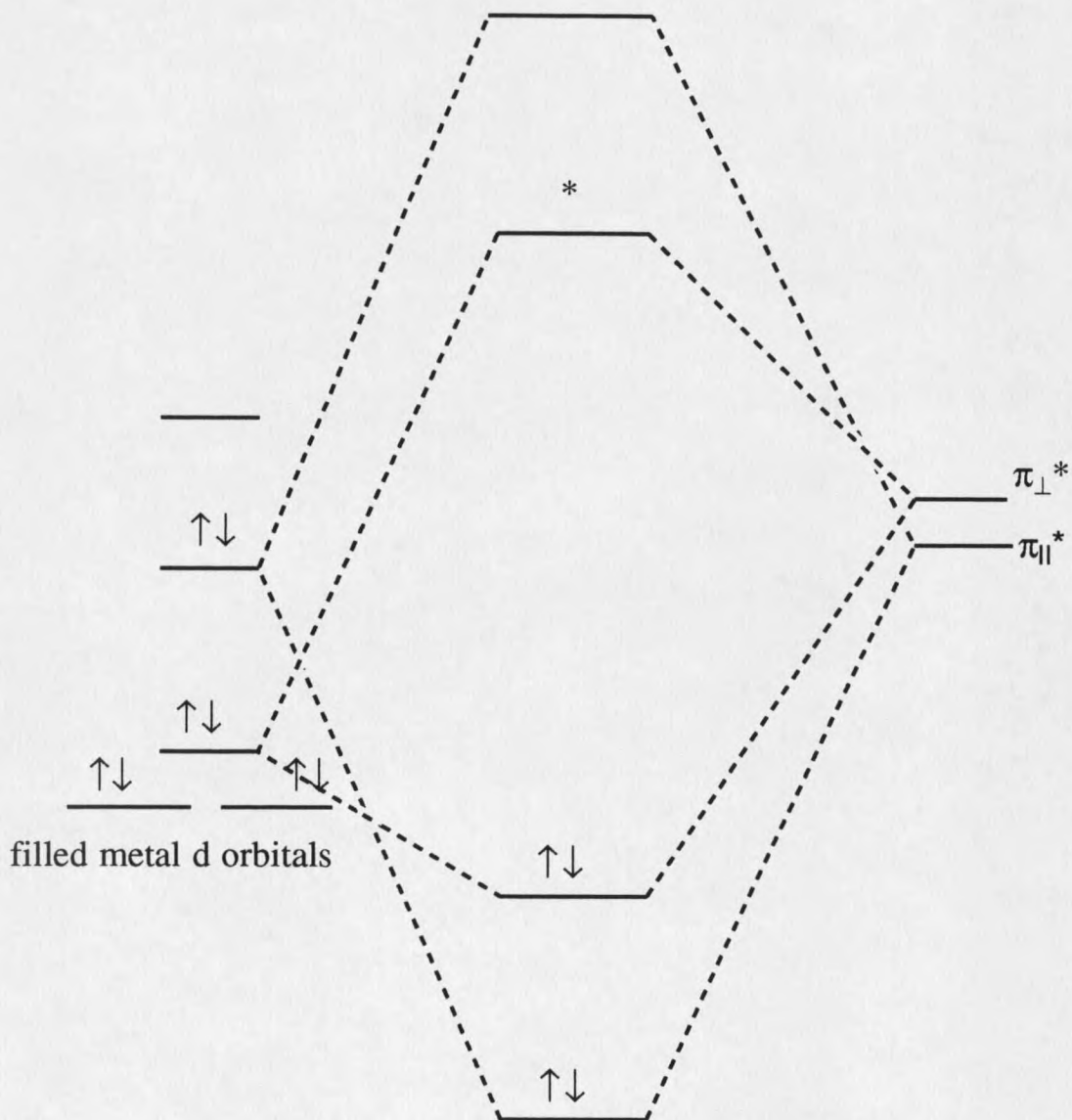


Figure 4 Correlation Diagram for Acetylene Backbonding to Platinum

Experimental Section

General

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. Chloroform was distilled from anhydrous calcium chloride. d_8 -THF (99.8% D), $CDCl_3$ (99% D), CD_3OD and CD_3CN were purchased from Cambridge Isotope Laboratories and used as received. Alkynes were purchased from Aldrich Chemical Company and Farchan Chemical Company, and used without further purification. Cyclic diynes were provided graciously by Bruce King, of the University of Georgia Chemistry Department.

NMR spectra were referenced to the solvent, except for platinum-195 NMR spectra, which were externally referenced to K_2PtCl_6 in D_2O . 1H , and ^{13}C nuclear magnetic resonance data were collected on 250, 300, and 500MHz Bruker fourier transform instruments. ^{195}Pt spectra were obtained on the 250MHz instrument equipped with a broadband probe.

Preparation of Zeise's Dimer

Zeise's Dimer was prepared by dissolving K_2PtCl_4 (5g) in a 3% HCl solution (100ml). This was transferred to a glass Parr reaction vessel which had been fitted with a magnetic stir-bar. The Parr vessel was sealed, then pressurized to 90psi of ethylene and maintained at this pressure with stirring for approximately 24 hours until the solution had turned bright yellow. At this time the solution was transferred to a 250ml round bottom flask, and the solvent removed by rotary evaporation. The resulting solids were extracted with 100ml of a 1% HCl in ethanol solution, the extracts were filtered and evaporated under vacuum. Finally, toluene was added to the residue and again evaporated under vacuum to co-distill any remaining water. From this process was isolated very bright, orange crystals of Zeise's Dimer (~3.5-4 grams). 300MHz 1H NMR ($CDCl_3$) δ 4.9 (anti, s, =CH₂, $J_{Pt-H} = 70Hz$) ppm. ^{13}C NMR (75MHz, $CDCl_3$) δ 71.9 (anti, s, $J_{Pt-C} = 205Hz$), 71.7 (syn, s, $J_{Pt-C} = 193Hz$) ppm. 1H NMR (d_8 -THF) δ 4.25 (s, $J_{Pt-H} = 68.7Hz$) ppm. ^{13}C NMR (75MHz, CD_3CN) δ 74.3 (s, $J_{Pt-C} = 172Hz$) ppm. 1H NMR (D_2O , 4.65 ppm) δ 4.36 (s, br, $J_{Pt-H} = 70.3Hz$), 4.52 (s, br, minor peak unidentified) ppm. ^{13}C NMR (D_2O) δ 68.3 (s, sharp, $J_{Pt-C} = 213.6Hz$), 72.5 (br, $J_{Pt-C} = 160.8Hz$) ppm. 1H NMR (CD_3OD , 3.34 ppm) δ 2.81 (s, br, $J_{Pt-H} = 73.0Hz$) ppm. ^{13}C NMR (CD_3OD ,

49.9 ppm) δ 62.5 (s, sharp, $J_{\text{Pt-C}} = 232\text{Hz}$) ppm. ^{195}Pt NMR (CDCl₃, K₂PtCl₆ in D₂O external standard) δ -2516.58 ppm.

di-(4,4-dimethyl-2-pentyne)-dichloro-di- μ -dichloroplatinum(II). 4,4-Dimethyl-2-pentyne (1ml) was added to a stirring chloroform (5ml) solution of Zeise's Dimer (200mg). After several seconds an orange precipitate began to form. The resulting mixture was allowed to stir at room temperature for several hours. The precipitate was isolated by vacuum filtration, washed twice with 1 ml of pentane, then placed under high vacuum overnight. ^1H NMR (CDCl₃) δ 2.23 (anti, s, br, CH₃, $J_{\text{Pt-H}} = 53\text{Hz}$), 2.18 (syn, d, CH₃), 1.48 (anti, s, br, (CH₃)₃), 1.45 (syn, d, (CH₃)₃) ppm. ^{13}C NMR (CDCl₃) δ 79.8 (anti, $J_{\text{Pt-C}} = 205\text{Hz}$), 79.6 (syn, $J_{\text{Pt-C}} = 205\text{Hz}$), 70.2 (anti, $J_{\text{Pt-C}} = 205\text{Hz}$), 70.0 (syn, $J_{\text{Pt-C}} = 205\text{Hz}$), 30.1 (br, (CH₃)₃), 26.9 (syn, quaternary), 26.5 (anti, quaternary), 7.91 (br, CH₃) ppm. ^1H NMR (d₈-THF) δ 2.08 (s, 3H, CH₃, $J_{\text{Pt-H}} = 37.2\text{Hz}$), 1.42 (s, 9H, (CH₃)₃) ppm. ^{13}C NMR (d₈-THF) δ 57.0 ($J_{\text{Pt-C}} = 201\text{Hz}$), 46.9 ($J_{\text{Pt-C}} = 199\text{Hz}$), 30.1, 25.9, 7.3 ppm.

General Method for Hydration of Alkynes-Illustrated for 1-Hexyne

2-Hexanone. A 250ml round bottom flask was fitted with a magnetic stir bar and placed into a heating mantel over a stir plate, and 150ml of tetrahydrofuran and 5ml of distilled water were introduced. Zeise's Dimer (0.100g, 0.34mmol Pt(II)) was added to the solution and stirred for a few minutes. The reaction flask was fitted with a claisen adaptor, to which was fitted both a reflux condenser and a 50ml addition funnel. To the addition funnel was added a solution of 1-hexyne (2.14g, 26.0mmol) in tetrahydrofuran to make 50 milliliters. The Zeise's Dimer solution was heated to mild reflux, and then the 1-hexyne solution was added slowly over 30 minutes. When the addition was complete, the homogeneous red solution was allowed to reflux for 2 hours, after which the reaction had gone to completion by ^1H NMR. Most of the tetrahydrofuran was removed by careful distillation, and the remaining solution was cooled to room temperature, then extracted three times with 50ml portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The product was isolated by distillation of the solvent, followed by vacuum distillation of the product (5torr, 30°C), to yield 2-hexanone (2.46g, 94% yield). ^1H NMR: δ 2.32 (t, 2H, CH_2),

2.01 (s, 3H, CH₃), 1.45 (m, 2H, CH₂), 1.20 (m, 2H, CH₂), 0.80 (t, 3H, CH₃) ppm. ¹³C NMR: δ 209, 43.8, 29.9, 26.0, 22.2, 13.8 ppm.

2-Heptanone: ¹H NMR (CDCl₃) δ 2.37 (t, 2H, CH₂), 2.08 (s, 3H, CH₃), 1.52 (m, 2H, CH₂), 1.24 (m, 4H, CH₂), 0.83 (tr, 3H, CH₃) ppm. ¹³C NMR (75MHz, CDCl₃) δ 209.2, 43.7, 31.3, 29.7, 23.5, 22.4, 13.8 ppm.

4-Octanone: 300MHz ¹H NMR (CDCl₃) δ 2.35 (m, 4H, CH₂), 1.55 (m, 4H, CH₂), 1.30 (m, 2H, CH₂), 0.87 (dt, 6H, CH₃) ppm. ¹³C NMR (75MHz, CDCl₃) δ 210.3 (C=O), 44.5 (CH₂), 42.3 (CH₂), 25.8 (CH₂), 22.4 (CH₂), 17.2 (CH₃), 13.6 (CH₃) ppm. Mass spectrum m/z 128 (m⁺, TIC = 28%), 85 (75), 71 (100), 57 (89), 43 (97).

2,2-Dimethyl-3-pentanone: ¹H NMR (CDCl₃) δ 2.36 (q, 2H, CH₂), 1.00 (s, 3H CH₃), 0.88 (tr, 3H, CH₃) ppm.

4,4-Dimethyl-2-pentanone: ¹H NMR (CDCl₃) δ 2.18 (s, 2H, CH₂), 1.99 (s, 3H, CH₃), 0.84 (s, 3H, CH₃) ppm.

3-Hexanone: ¹H NMR (CDCl₃) δ 2.38 (t, 4H, CH₂), 1.53 (m, 2H, CH₂), 0.99 (t, 3H, CH₃), 0.87 (t, 3H, CH₃) ppm.

2-Pentanone: ^1H NMR (CDCl_3) δ 2.37 (t, 2H, CH_2), 2.09 (s, 3H, CH_3), 1.57 (m, 2H, CH_2), 0.88 (t, 3H, CH_3) ppm.

3-Pentanone: ^1H NMR (CDCl_3) δ 2.40 (q, 4H, CH_2), 1.02 (t, 6H, CH_3) ppm.

Recycling of Platinum

The typical method for recycling platinum after use in reactions involves collection of platinum containing waste, and distillation of the organics from the solid waste to leave a cake of platinum containing sludge. This is ignited in a crucible and heated by a Meeker burner for several days, until only a grey ash is left. The ash is washed with water several times to remove unwanted inorganic salts, and re-ashed. The fine powder obtained contains reduced platinum which is then digested in boiling aqua-regia. The platinum salts obtained from this process are used as starting material for the synthesis of Zeise's Dimer and other products. **Caution:** Mixing of incompatible chemicals or very reactive chemicals in the waste collection jar is to be avoided. Distillation of unknown mixtures of organics, possibly including inorganics, should be considered very hazardous, and a blast shield should be used during this

process. Avoid vapors from this process and from the ashing process. Boiling aqua-regia is extremely hazardous. Thick rubber gloves and eye protection are minimal protection for all of these procedures.

Monitoring of Reactions by ^1H NMR

For the purpose of monitoring reactions under controlled conditions, reactions were run in matched 5mm ultraprecision thin walled NMR tubes, which were sealed from the surrounding environment with tight fitting plastic caps. For ligand exchange studies, reaction solutions in deuterated solvents were monitored by ^1H and ^{13}C NMR throughout the course of reaction, and monitoring was continued over a period of days to ensure the identity of the equilibrium products.

Kinetics studies were performed with a Bruker 250MHz NMR spectrometer, using an automated data collection routine which collected ^1H spectra periodically (5 or 10 minute intervals). Machine integration was used, and the relative peak areas for the product and reactant were used to determine the extent of reaction at each acquisition time during a run.

Effect of p-toluenesulfonic acid on reaction rate

Three identical NMR tubes were prepared in the following way for three side by side experiments. Zeise's Dimer in d_8 -THF solution (0.40ml) was added to two of the NMR tubes. To sample 1 was added 5ul H_2O . To sample 2 was added 5ul of a p-toluenesulfonic acid solution ($3 \times 10^{-4}g$, $4 \times 10^{-3}M$ solution in THF sample). A third NMR tube was prepared without Zeise's Dimer, adding only the acid solution (5ul) to the measured amount of tetrahydrofuran. 4-Octyne was injected into each of the NMR tubes at approximately the same time. The contents were mixed thoroughly and 1H NMR spectra were taken at several reaction times over a period of six hours. Throughout the experiment there was no evidence of significant rate difference between the two samples including Zeise's Dimer catalyst. The sample that did not have Zeise's Dimer showed no reaction.

Effect of D_2O vs H_2O

Two identical samples were prepared in matched 5mm NMR tubes. 4,4-dimethyl-2-pentyne (100 μ l) was delivered to each tube by syringe. H_2O (40 μ l) was added to one tube and D_2O (40 μ l) was added to the other. Aliquots of Zeise's Dimer in

d_8 -THF were delivered to each test tube forcefully to mix the components. The two reactions were monitored periodically by ^1H NMR. No difference in the extent of reaction was noted throughout the period in which the reactions were monitored.

Rate of Reaction with 4,4-dimethyl-2-pentyne dimer vs Zeise's Dimer

Two kinetic runs were performed to compare the rate of hydration of 4-octyne with Zeise's Dimer catalyst to the rate with the 4,4-dimethyl-2-pentyne analog as catalyst. For each experiment an NMR tube was prepared by adding 4-octyne (10 μ l) and H_2O (10 μ l) by syringe. In the first experiment a solution of di-(4,4-dimethyl-2-pentyne)-dichloro-di- μ -dichloroplatinum(II) (0.06M Pt) in d_8 -THF was added to the NMR tube by syringe forcefully, mixing the components thoroughly before starting the acquisition. Data were collected in the usual way. The run for Zeise's Dimer was performed in the same way with the same molar amount of catalyst. First order plots of the data showed the rate constant for the 4,4-dimethyl-2-pentyne analog was $2.72 \times 10^{-4} \text{s}^{-1}$, while Zeise's Dimer gave a rate constant of $8.12 \times 10^{-5} \text{s}^{-1}$.

Michaelis-Menten Kinetics

4-Octyne was used as substrate in all of the kinetic runs taken for the purpose of generating the Michaelis-Menten graph. A stock solution (5 ml) of Zeise's Dimer in d_8 -THF (0.08M Pt) was prepared immediately before the kinetics runs were started, and this solution was delivered to the NMR tubes by syringe. Distilled water (10.0ul) and an aliquot (5.0-50.0ul) of 4-octyne were placed in an NMR tube, and an aliquot of the Zeise's Dimer solution (0.25ml) was injected forcefully into the NMR tube, which was immediately capped and inverted several times to ensure complete mixing. The sample was placed in the magnetic field of the instrument, which had been shimmed to another sample of similar composition, and the kinetic run was started immediately after the deuterium lock was established. In this way, data collection was started within one minute of mixing, in most cases. Five data sets were collected for five different concentrations of 4-octyne.

The initial rate of each reaction was taken from the first four data points generated in each kinetics run. The Michaelis-Menten plot was generated by plotting the reciprocal of the initial rate (s/M) vs. the reciprocal of the initial alkyne concentration ($1/M$). The initial concentration of alkyne was adjusted using the extent of

