



Synthesis, characterization and chemistry of platinum complexes derived from bicyclic cyclopropanes
by John Ole Hoberg

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 Zeise's dimer ($Pt\pi$) with cyclopropyl methyl ketal. An insoluble precipitate was formed that could be solubilized by reaction with pyridine or bipyridine ligands. Hydrolysis of the ketal producing acetyl platinum(IV)cyclobutanes were achieved in excellent yields.

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Reaction of 1-alkoxybicyclo[X.1.0]systems with catalytic Zeise's dimer yielded methylated cyclic ketones in good yields. A mechanism on the formation of the ketones was postulated from labelling studies that were performed. Platinum(II) olefin complexes were prepared from the reaction of Zeise's dimer with 1-alkoxybicyclo[4.1.0]hept-3-ene. This led to the insertion of Pt(II) into a tetra substituted cyclopropane (7-methyl-1-methoxybicyclo [4.1.0]hept-3-ene).

A platinum(II) complex was also prepared from the reaction of bicyclo[4.1.0]hept-2-ene and Zeise's dimer. Reaction with pyridine, PPh, and other ligands produced novel platinum complexes. Furthermore, organic molecules could be produced in good yields and excellent regio- and stereoselectivity. This was achieved by the reaction of the initial complex with ROH, AcOH, H₂O followed by H₂, PPh₃ or CO. Bicyclo[3.1.0]hex-2-ene and bicyclo[5.1.0]oct-2-ene produced similar results on reaction with Pt(II).

SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF
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John Ole Hoberg

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in

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APPROVAL

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John Ole Hoberg

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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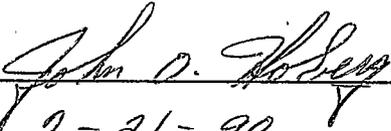
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TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	ix
ABSTRACT	xiv
INTRODUCTION	1
Platinum Carbonyl Complexes	2
Structure and Bonding	2
Formation and Characterization of Pt-Carbonyl Complexes	3
Reaction Involving Pt-Carbonyls	5
Platinum-Olefin Complexes	9
Structure and Bonding	9
Characterization of Pt-Olefins	11
Reactions of Pt(II)-Olefins	14
Platinum π -Allyls	16
Structure and Bonding	16
Formation and Reaction	18
Platinum Olefin Isomerization	19
Alkene Hydrogenation	22
Platina(IV)cyclobutane Complexes	23
Structure and Bonding	23
Characterization of Platinacyclic Compounds	27
Formation of Platinacycles	34
Isomerization of Platinacyclobutanes	40
Platinacyclobutane Chemistry	43
Reactions of Norbornyl Platinacyclobutanes	47
Bicyclo Platinacyclobutane Chemistry	49
History of Vinyl Cyclopropanes in Organometallic Chemistry	52
RESULTS AND DISCUSSION	55
Statement of Problem	55

Formation and Characterization of Platinacyclobutanes	56
Complexes from Cyclopropane 22	56
On the Mechanism of the Norbornyl Ring Expansion Reaction	70
Synthesis and Reaction of 8-Phenyl-exo-tricyclo[3.2.1.0 ^{2,4}]	
oct-6-ene	82
Substituted Bicyclo[X.1.0] Systems: Ether Substituents	89
Saturated Ether Systems	89
Unsaturated Ether Systems	94
Mechanism for the Formation of 1-Methylcyclohexanone	110
Bicyclo[X.1.0] Hydrocarbons: Vinyl Cyclopropanes	116
Reaction of Bicyclo[4.1.0]hept-2-ene with Pt(II)	116
Reaction of Ligands with Complex 115	122
Organic Transformations using Complex 115	141
Expansion of the Bicyclo-vinylcyclopropane System	154
EXPERIMENTAL	161
General	161
Formation of Platinacyclobutanes	162
Mechanistic Studies on the Norbornyl Ring Expansion Reaction	163
Bicyclo System: Ether Substituents	167
Bicyclo System: Vinyl Cyclopropanes	175
REFERENCES	186
APPENDICES	194
Appendix A: NMR and MS Data for 37, 38, 39, 40, 57, 70, 72	
and unlabelled 37 and 40	195
Appendix B: ¹³ C NMR Shifts for Norbornyl Platinacyclobutanes	200
Appendix C: Chloro-Norbornyl Platinacyclobutane	202
Appendix D: Postulation of a Novel Platinacyclobutane-Olefin Complex	205
Appendix E: NMR Assignments for Compounds 101, 114, 137, 138, 139, 149	208
Appendix F: Reaction of 115 with Ethylene-CO, Amines and Formic Acid ..	212
Appendix G: X-RAY Data for Complex 100	216
Appendix H: Structures	220

LIST OF TABLES

Table	Page
1. C-O Stretching Frequencies (cm^{-1}) in some Pt(II) Carbonyls.	4
2. C-C Stretching Frequencies of Pt(II)-Olefins.	12
3. Pt-Olefin Stretching Frequencies.	12
4. Platinum(II)-Olefin ^{13}C Resonances and Coupling Constants.	13
5. NMR Data for Equations 5 and 6 in ppm.	14
6. Stretching Frequencies for Platinacyclobutanes.	28
7. ^{13}C NMR Shifts and ^1J Constants for Various Complexes.	31
8. Pt(IV) NMR Shifts Relative to 1M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C	32
9. Pt(II) NMR Shifts Relative to 1M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C	33
10. NMR Data for Compound 24.	62
11. NMR Data for Compound 25.	64
12. NMR Data for Complex 26.	67
13. NMR Data for Complex 27.	67
14. NMR Data for Complex 28.	68
15. NMR Data for Complex 66.	84
16. NMR Data for Complex 67.	84
17. NMR Data for Complex 93.	104
18. NMR Data for Complex 97	104
19. NMR Data for Complex 100	105
20. CP/MAS ^{13}C Resonances for 115.	117

21. Solution NMR Data for 115	118
22. NMR Data for Complex 117	123
23. NMR Data for Complex 118	129
24. NMR Data for Complex 119	130
25. NMR Data for Complex 120	131
26. ¹³ C NMR Data for 121	134
27. ¹ H and ¹³ C NMR Data for Complex 122	134
28. ¹ H and ¹³ C NMR Data for Complex 123	135
29. ¹ H and ¹³ C NMR Data for Complex 117 in Benzene.	140
30. NMR Data for Complex 159	155
31. ¹ H and ¹³ C NMR Data for Complex 161	157
32. ¹ H and ¹³ C NMR Data for Complex 162	158
33. ¹ H and ¹³ C NMR Data for Complex 164	160
34. NMR Data for Compound 37	196
35. ¹³ C NMR Data for Compound 39	196
36. NMR Data for Compound 38 and Compound 40	197
37. NMR Data for Compound 57	197
38. ¹ H NMR Data for Compound 70	198
39. NMR Data for Compound 72	198
40. NMR Data for Compound 37 -nonlabelled.	199
41. NMR Data for Compound 40 -nonlabelled.	199
42. ¹³ C NMR Data for Unsaturated Norbornyl Platinacyclobutane.	201
43. ¹³ C NMR Data for Cyclopropyl Norbornyl Platinacyclobutane.	201
44. NMR Data for 8-chloro-tricyclo[3.2.1.0 ^{2,4}]oct-6-ene.	203
45. NMR Data for Chloro-Norbornyl Platinacyclobutane.	203

46.	NMR Data for Platinacyclobutane-Olefin Complex.	206
47.	NMR Assignments for 101 and 114.	209
48.	NMR Assignments for 137, 138 and 139.	210
49.	NMR Assignments for 149.	211
50.	NMR Data for 165.	213
51.	Atomic Coordinates ($\times 10^3$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with Standard Deviations in Parenthesis.	217
52.	Bond Angles (deg).	218
53.	Bond Lengths (\AA).	218
54.	Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with Standard Deviations.	219

LIST OF FIGURES

Figure	Page
1. Pt-CO Bonding Scheme.	3
2. Migratory Insertion Mechanim.	5
3. Reversible CO Insertion.	5
4. Palladium Catalyzed Reaction Pathways.	7
5. Proposed Pathways to Ester Formation.	8
6. Palladium Catalyzed Lactone Formation.	8
7. Carboalkoxylation of Ethylene.	9
8. Bonding Scheme between Platinum and an Olefin.	10
9. Amine Attack on a Pt(II)-Olefin.	15
10. Nucleophilic Attack on a Platinum-chelated Olefin.	16
11. Pt- π -allyl Bonding Scheme.	17
12. Nucleophilic Attack on Pt- η -allyl.	17
13. C-C Coupling Reaction of Methallyl and Acetylacetonate Ligands.	18
14. Mechanism of C-C Coupling.	19
15. Alkene Isomerization Mechanisms.	20
16. Hydride-Generating Reactions.	21
17. Hydrogenation Mechanism of an Alkene by Oxidative Addition of H ₂	22
18. The Walsh-basis.	23
19. The (F.C.M.)-basis.	24
20. McGinnety Platinacyclobutane Bonding Scheme.	26

21. McQuillin Platinacyclobutane Orbital Model.	27
22. CP/MAS Resonances of a Platinacyclobutane.	29
23. ^{13}C NMR Resonance Ranges in PPM.	30
24. π -Allyl Formation from Norcarane and Pt(II).	35
25. 2,3,3-Trisubstituted Platinacyclobutane.	38
26. 2,3,4-Trisubstituted Platinacyclobutane.	38
27. Proposed Mechanisms for the Puddephatt Rearrangement.	42
28. Comparison of $\text{LCl}_2\text{Pt}(\text{C}_3\text{H}_6)$ to the Nonclassical Carbonium Ion.	43
29. α -Elimination Mechanism.	45
30. β -Elimination Mechanism.	45
31. Pathways in Olefin Formation from the β -Mechanism.	46
32. Reaction of CO with Norbornyl Platinacyclobutanes.	47
33. Ring Expansion with DMSO.	47
34. Proposed Ring Homologation Mechanism.	48
35. Rhodium Ring Expansion and Mechanism.	48
36. Olefin Formation via Diazo Compounds.	49
37. Olefin Formation from the Bicyclo[4.1.0] System.	50
38. Mechanistic Pathway with Deuterium Results.	52
39. Effects of Ketal Protection on Platinum Insertion.	57
40. Reaction of Pt(II) with Cyclopropyl Methyl Ketone.	57
41. Synthetic Pathway to Norbornyl Platinum Complexes.	58
42. Synthetic Pathway to Platinacyclobutane Acetyl Complexes.	59
43. ^{13}C NMR Spectrum of 24.	61
44. Gated and BB ^{13}C NMR Spectra of 25.	63
45. ^{13}C NMR Spectra of 26 and 27.	66

46.	^{13}C NMR Spectrum of 26.	69
47.	Ring Homologation of Norbornyl IPC's.	70
48.	Synthesis of 29, 30, 31 and 32.	71
49.	Formation and Reaction of IPC's 33, 34, 35 and 36.	72
50.	^2H NMR Spectrum of 38.	73
51.	Proposed Mechanism for Ring Expansion of 30 and 32.	74
52.	^{13}C NMR Spectrum of 39.	75
53.	Proposed Mechanism for Formation of 37 and 39.	77
54.	Alternative Pathway for Formation of 51, Path C.	78
55.	Isomerization of 46 to 52.	79
56.	Postulated Products from Paths A and B.	80
57.	Expected Product from Alternative Mechanism.	81
58.	Ring Homologation of 64 and 65.	85
59.	Expanded ^1H NMR Spectrum of 57 and 70.	86
60.	^{13}C Labelling Results on 71 and 73.	87
61.	Mechanism for Ring Homologation in Unsaturated Norbornyl Systems.	88
62.	Formation of a Bicyclo Platinacyclobutane.	89
63.	Initially Proposed Mechanism for 1-Methylcyclohexanone Formation.	91
64.	Synthesis of 76 from 84 and 85.	92
65.	Alternative Formation of 76.	93
66.	Effect of Ring Size on Platinum Insertion.	94
67.	Reaction of 91 with Platinum.	95
68.	CPD ^{13}C NMR Spectrum of 93.	96
69.	Deuterium Labelled Platinum Complex.	97
70.	CP/MAS ^{13}C NMR Spectrum of 92.	99

71. Alkene Isomerization Alternatives.	100
72. 2-Dimensional (COSY) ^1H NMR Spectrum of 97	102
73. CPD ^{13}C NMR Spectrum of 97	103
74. Pt(II) Insertion into a Tetra-Substituted Cyclopropane.	105
75. X-ray Crystal Structure for Complex 100	106
76. Reaction of 101 with Pt(II).	108
77. Reaction of 102 and 103 with Pt(II).	109
78. Formation of 6-Methyl-2-cyclohexenone.	109
79. Possible Mechanisms in the Formation of 76	111
80. Mechanism for the Synthesis of 1-Methylcyclohexanone.	114
81. CP/MAS ^{13}C NMR Spectrum of 115	117
82. Mechanism for the Formation of 115	119
83. ^{195}Pt NMR Spectrum of 115 in CDCl_3	120
84. ^{195}Pt NMR Spectrum of Zeise's Dimer in CDCl_3	121
85. Proposed Isomers of Complex 115	121
86. CPD ^{13}C NMR Spectrum of 117	124
87. ^1H - ^1H Correlated (COSY) Spectrum of 117	125
88. ^1H - ^{13}C Correlated (XHCORR) Spectrum of 117	126
89. CPD ^{13}C NMR Spectrum of 118	128
90. CPD ^{13}C NMR Spectrum of 120-d₇	132
91. Formation of Complex 122	134
92. Mechanism for Formation of 120	136
93. Expected Results for Alpha and Beta Pathways.	137
94. Deuterium Results in the Reaction of 129 with $(\text{MeO})_3\text{P}$	138
95. Mechanistic Pathway for the Formation of 114 and 127	139

96. Formation of 132 and 133	142
97. Mechanism for the Formation of 131-133	142
98. Formation of 134-136	144
99. Mechanism for the Formation of 134	145
100. Formation of 137-139 by Esterification of 115	146
101. Esterification of 115 using Ethanol.	147
102. Proposed Mechanism for the Formation of 137, 138 and 139	148
103. Formation of 143, 144, 145 and 146	149
104. Proposed Mechanism for the Formation of 143-146	150
105. Formation of 147 and 148	151
106. Mechanism for the Formation of 149	152
107. Formation of Acids 150-152	153
108. CPD ¹³ C NMR Spectrum of 159	156
109. CPD ¹³ C NMR Spectrum of 162	159
110. CPD ¹³ C NMR Spectrum of Chloro-Norbornyl Platinacyclobutane.	204
111. BB ¹³ C NMR Spectrum of Platinacyclobutane-Olefin Complex.	207
112. Possible Products in the Reaction of 115 with CO, C ₂ H ₄ and MeOH.	214
113. Reaction of 115 with Isopropyl Amine.	215

ABSTRACT

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INTRODUCTION

Transition metal organometallic chemistry has been growing immensely since its inception in the 1950's. The chemistry that has developed has led to new methods of organic synthesis as well as a number of unique organometallic molecules. A number of industrial processes, such as the Ziegler Natta catalysis, have employed transition metals in catalytic synthesis. Also the long-sought after molecule, cyclobutadiene, was formed by stabilization with metals. Not only have novel complexes been made but surprising mechanisms have been discovered in the study of transition metal chemistry.

When defining organometallic chemistry it is important to note that a metal-carbon bond must exist, by either a σ or π bond. Metal complexes having ligands such as amines and halides do not "qualify" as organometallic compounds. Transition metal ions are also Lewis acids, which means that they can bind to the lone pairs of ligands. Carbon monoxide is an example of a ligand that bonds with its pair of electrons and produces an organometallic compound, while water also bonds with a pair of electrons it is not classified as an organometallic compound.

The area of organometallic chemistry which this author has undertaken is organoplatinum chemistry. Starting in the late 1960's, a number of articles were reported on highly strained organic molecules rearranging upon exposure to a transition metal. Platinum is particularly adept at this when the organic molecule is a cyclopropane. Quite an interest was taken in this chemistry until most felt that it had run its course and was finished. P.W. Jennings revived the area in the early 1980's with the norbornyl system and has since expanded the platinum cyclopropane area. Platinum also undergoes chemistry

other than that with cyclopropanes. It has long been used as a hydrogenation catalyst and is particularly good at complexing with sites of unsaturation, especially olefins.

The material in the introduction has been covered to familiarize the reader (and author) with basic bonding, mechanisms, reactions and history that is needed to help understand the research presented in the discussion. Usually each section of the introduction will begin with a very brief history of platinum in that specific area and some basic bonding concepts using frontier molecular orbitals. This is most often followed by known reactions using either platinum or another transition metal that will serve as an analogy. Structure determination of known platinum complexes will also be presented to add precedence to structures presented in the discussion.

Platinum Carbonyl Complexes

Structure and Bonding

The discovery of the first organotransition-metal compound, $K^+[(C_2H_4)PtCl_3]EtOH$ was first reported by Zeise in 1827¹. Forty years later Schutzenberger² prepared the first metal carbonyl, $[PtCl_2(CO)_2]$, and since then a whole host of platinum pi complexes have been prepared. By virtue of the C-O multiple bond, CO is an unsaturated ligand. Known as a soft ligand because of its capability of accepting metal d_π electrons, CO is called a π acceptor or π acid. Sigma bonding between platinum and CO consists of the donation of a lone electron pair on the carbon, shown in Figure 1, to an empty hybrid metal orbital. The CO ligand having empty π^* orbitals interact and accept electrons from the filled metal d orbitals. This delocalization of electron density from the metal to the carbonyl ligand, known as back bonding, compensates for excess electron density donated to the metal. A composite picture is shown at the bottom of Figure 1.

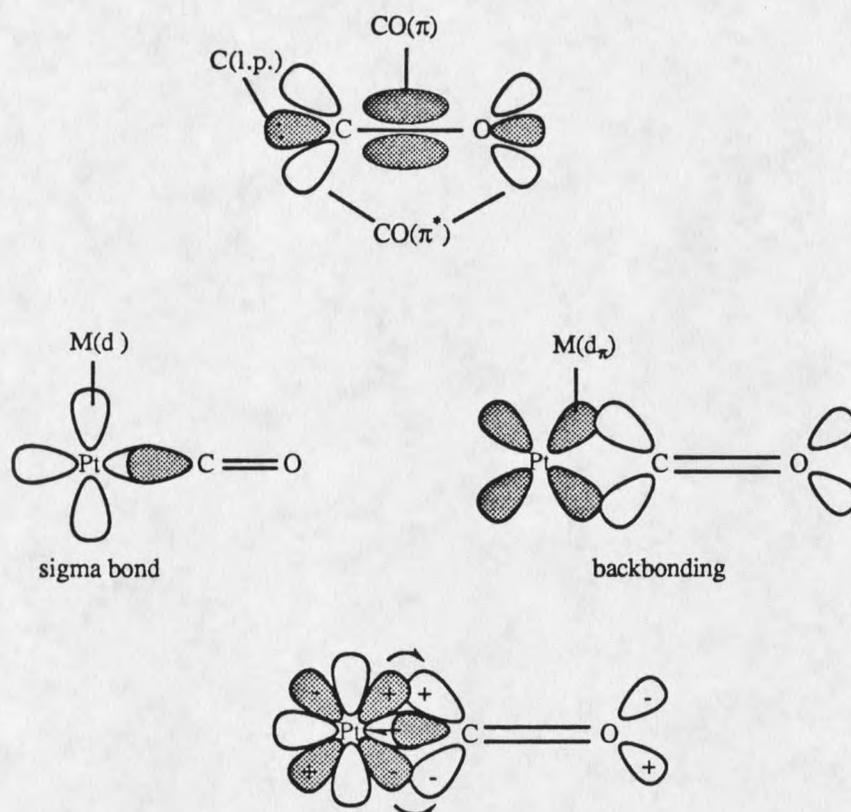


Figure 1. Pt-CO Bonding Scheme (bottom). The shading represents occupied orbitals and the plus and minus signs the phasing. Only one of the two π orbitals is shown in the structure of CO (top).

Formation and Characterization of Pt-Carbonyl Complexes

The presence of electrons in the antibonding orbitals of CO causes weakening of the C-O bond. This weakening causes a shift in the C-O stretching frequency due to CO resembling an electronically excited state. Free CO has a resonance frequency in the infrared spectrum at 2155 cm^{-1} . Table 1 shows the CO stretching frequencies of some Pt compounds. As the electronegativity of the halogen decreases so does the frequency reflecting the increase of back-donation from Pt(II) to CO.

The electronic effects that ligands in Pt complexes have on $^1J_{\text{Pt,C}}$ and ^{13}CO NMR chemical shifts have also been studied. Changes in both the cis and trans ligands relative to the CO can have a marked affect on the chemical shift and Pt-C coupling. For complexes

such as trans-[PtX(CO)L₃]BF₄ (X = H, C₆H₄Cl, CH₂Ph, NCS, NO₃, Cl, Br or I) ¹³C measurements have been made. If X has a high trans influence, the platinum carbon (CO) coupling is between 960-990 Hz but if X has a low trans influence, the range is between 1660 and 1820 Hz¹⁰.

Table 1. C-O Stretching Frequencies (cm⁻¹) in some Pt(II) Carbonyls

	Cl	Br	I
cis-[Pt(CO)X ₃]	2132	2112	2088
[PtX ₂ (CO) ₂]	2152	2130	2112
[Pt(bipy)(CO)X]	2145	2132	2120
cis-[(PEt ₃)PtX ₂ (CO)]	2100	2094	2085

In recent years, extensive chemical studies have been made on platinum(II) carbonyls. Preparative routes to simple platinum carbonyls are as follows⁹: (a) Displacement of a chlorine ligand in a solution containing a counter ion resulting in the formation of cationic carbonyl complexes, Equation 1. Similar reactions also go in the presence of silver nitrate which abstracts a chloride. (b) Olefins and acetylenes can also be displaced by carbon monoxide to form complexes as shown in Equation 2. (c) Chlorine bridged compounds can also be cleaved by carbon monoxide, Equation 3. When CO is passed through solutions of halogen-bridged platinum-olefin complexes in carbon tetrachloride, mixed complexes containing olefins are formed.



Reactions Involving Pt-Carbonyls

CO shows a strong tendency to insert into metal alkyl bonds. With Pd^4 , pressures as low as 1 atmosphere will insure insertion. Platinum on the other hand needs much higher pressures such as 70 atmospheres⁵. The actual mechanism for the reaction is thought to be migration of the alkyl group to a cis CO. Evidence for this migration can be seen in experiments using ^{13}C labelled CO. After the migration, an empty site develops at the metal, Figure 2⁶. When the incoming ligand is ^{13}CO , the observed product contains only one labelled ^{13}CO . This shows that the methyl group migrates to a coordinated CO, instead of free CO inserting into the metal-methyl bond. By using microscopic reversibility, the reverse reaction also sheds light on the mechanism, Figure 3. Elimination of CO from $\text{Me}^{13}\text{COMn}(\text{CO})_5$ followed by migration of methyl showed the ^{13}CO was cis to the methyl group.

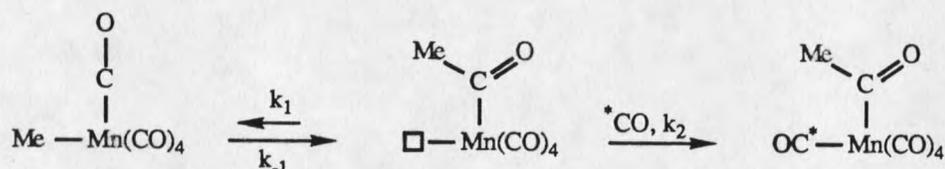


Figure 2. Migratory Insertion Mechanism (squares indicate vacant sites).

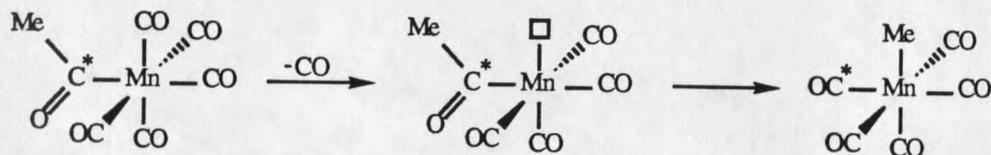


Figure 3. Reversible CO Insertion.

