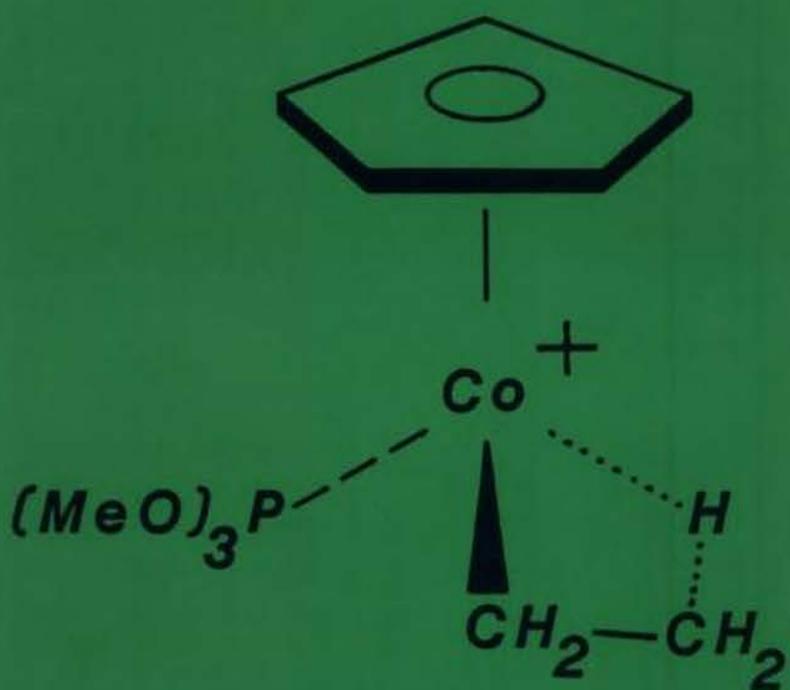


**PROBLEMS AND SOLUTIONS  
IN  
ORGANOMETALLIC  
CHEMISTRY**



*SUSAN E. KEGLEY and ALLAN R. PINHAS*

# **Problems and Solutions in Organometallic Chemistry**

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## PREFACE

Although quite a few textbooks dealing with transition metal organometallic chemistry have recently been published, there seems to be a general lack of problems to reinforce the principles discussed in these books. The aim of this book is to fill this void by providing real problems from the recent literature, complete with solutions and references. Additionally, we feel that it would be helpful to the practicing organometallic chemist to have a readily accessible compilation of IR and NMR spectral data for a variety of organometallic compounds, and to have descriptions of NMR techniques frequently used as tools in the spectroscopic characterization of organometallic compounds. Chapter 1 is such a source and Chapter 4 provides some practice problems related to dynamic NMR spectroscopy and fluxional processes. Chapter 2 deals with structure and bonding in organometallic compounds, while Chapters 3 and 5-8 cover the basic reaction types in organometallic chemistry: ligand substitution, oxidative-addition, reductive-elimination, migratory insertion, nucleophilic and electrophilic attack on coordinated ligands. Chapters 9, 10, and 11 on metallacycles, transition metal alkyls and hydrides, and catalytic reactions require the student to apply the principles learned in Chapters 3-8 to specific topics. Chapter 12 emphasizes the applications of organometallics to organic synthesis, and Chapter 13 is a collection of additional problems that require the student to use all facets of his or her knowledge of organometallic chemistry.

When designing problems, we chose to take a mechanistic approach. We feel that it is quite important to know why a reaction occurs and how to prove mechanistic hypotheses, rather than just know that the reaction does occur. For this reason, there are certain areas that are not covered as thoroughly as others, e.g. applications to organic synthesis and catalytic reactions, where for many systems, mechanistic information is largely unknown. We hope that exposure to a few of the known systems will be educational.

It should be kept in mind that for many problems, particularly those that require the student to propose experiments that would prove a mechanistic hypothesis, there is certainly more than one correct answer. The answers given in the book represent what has actually been done and published by workers in the field.

This book is intended to match the subject material covered in the second edition of Collman, Hegedus, Norton, and Finke's "Principles and Applications of Organotransition Metal Chemistry", thus the general chapter headings in the problem book are similar to those in the text; however, we feel that the problems in this book will be useful to any student of organometallic chemistry.

Susan E. Kegley

Allan R. Pinhas

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We are extremely grateful to those who have assisted in the production of the camera-ready copy. For help with the drawings, we thank Chris Staats, Diane Copeland, Ebbe Hartz, Lisa Schmeichel, Brigid Nicholson, Gail Byers, and Jeff Kelly. The computer program to produce many of the drawings was skillfully written by Kipley Olson. For help with the typing and assembly of the manuscript, we thank Shevaun Mackie, Chris Staats, and Mrs. Joyce McAllister. The people at the Middlebury College computer center and in the Middlebury College Science Library were extremely helpful in this endeavor, particularly Tom Copeland and Sharon Strassner.

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Thanks y'all!

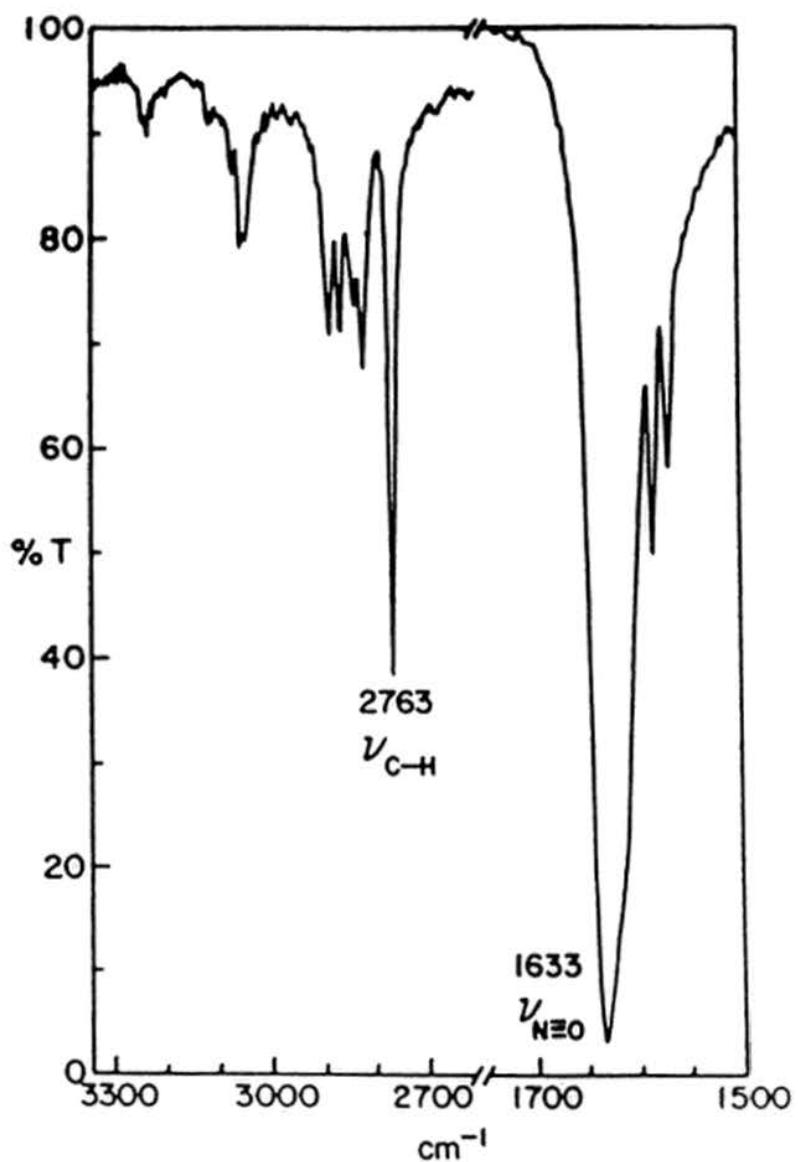
## ABBREVIATIONS

acac	acetylacetone anion
AIBN	azoisobutyronitrile
Ar	aryl
n-Bu	n-butyl, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
t-Bu	t-butyl, $-\text{C}(\text{CH}_3)_3$
CIDNP	chemically induced dynamic nuclear polarization
$\text{cm}^{-1}$	wave number
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
Cp	$\eta^5$ -cyclopentadienyl, $\eta^5\text{-C}_5\text{H}_5$
Cp*	$\eta^5$ -pentamethylcyclopentadienyl, $\eta^5\text{-C}_5\text{Me}_5$
d	doublet (NMR)
dd	doublet of doublets (NMR)
dt	doublet of triplets (NMR)
dq	doublet of quartets (NMR)
diphos	bis-1,2-diphenylphosphinoethane (dppe)
dmpe	bis-1,2-dimethylphosphinoethane
dppe	bis-1,2-diphenylphosphinoethane (diphos)
dtc <sup>-</sup>	dithiocarbamate anion, $[(\text{H}_2\text{N})\text{CS}_2]^-$
Et	ethyl, $-\text{CH}_2\text{CH}_3$
Fp	$\text{CpFe}(\text{CO})_2$
HOMO	highest occupied molecular orbital
Hz	hertz, $\text{sec}^{-1}$
IR	infrared
L	a generic unidentate ligand
LUMO	lowest unoccupied molecular orbital

m	medium (IR), multiplet (NMR)
M	a generic metal
Me	methyl, $-\text{CH}_3$
MO	molecular orbital
NMR	nuclear magnetic resonance
$^-\text{OAc}$	acetate anion, $[\text{OCOCH}_3]^-$
$^-\text{OTf}$	triflate anion, $[\text{OSO}_2\text{CF}_3]^-$
$\text{PPN}^+$	bis(triphenylphosphine)iminium, $(\text{Ph}_3\text{P})_2\text{N}^+$
Ph	phenyl, $-\text{C}_6\text{H}_5$
$\text{Ph}_3\text{P}$	triphenylphosphine, $\text{P}(\text{C}_6\text{H}_5)_3$
n-Pr	n-propyl, $-\text{CH}_2\text{CH}_2\text{CH}_3$
i-Pr	iso-propyl, $-\text{CH}(\text{CH}_3)_2$
p-tol	para-tolyl, p- $\text{C}_6\text{H}_4\text{-CH}_3$
q	quartet (NMR)
R	a generic alkyl group
rds	rate-determining step
RT	room temperature
s	strong (IR), singlet (NMR)
sh	shoulder (IR)
SST	spin saturation transfer
t	triplet (NMR)
THF	tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$
tos	toluenesulfonyl, $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2^-$
TMS	trimethylsilyl, $\text{Me}_3\text{Si}$ ; tetramethylsilane, $\text{SiMe}_4$ (NMR)
UV	ultraviolet
w	weak (IR)
x	a halogen

## 1

# Methods for the Identification of Organometallic Complexes



## 1: METHODS FOR THE IDENTIFICATION OF ORGANOMETALLIC COMPLEXES

### INTRODUCTION

A variety of techniques are now employed in the characterization of organometallic complexes, and it is therefore useful to have a general feel for the significance of the analytical data obtained by these techniques in the study of new complexes. Many methods are available for the characterization of organometallics, including nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, X-ray diffraction, neutron diffraction, mass spectroscopy, elemental analysis, electrochemistry, and UV-visible spectroscopy. Typically, the identification of a new organometallic compound involves the use of a combination of these techniques, with the most common being NMR spectroscopy and IR spectroscopy.

Definitive proof of structure is possible by the use of X-ray crystallographic analysis of a single crystal of the substance, accompanied by an elemental analysis. X-ray diffraction is a very powerful tool that can provide concrete evidence of atomic interactions that can only be hinted at by other analytical methods; however, it gives no information about any dynamic behavior of the molecule in solution, and it is limited by the requirement for single crystals and by the fact that the expertise and instrumentation are not always readily available. A collection of crystal structures of many organometallic compounds can be found in the series "Comprehensive Organometallic Chemistry" [1(a)].

Neutron diffraction [1(b)] is useful when it is necessary to specifically locate hydrogen atoms in a crystal structure. Typically, larger crystals are necessary for neutron diffraction than for X-ray diffraction, and there are only a few facilities in the U.S. where this analysis can be carried out, specifically at Argonne, Brookhaven, and Los Alamos National Laboratories.

Information about the electrochemical properties [2a,b] and the UV-visible spectrum of a compound is useful for specific applications, but these techniques are not routinely used for the characterization of organometallic complexes. Mass spectroscopic analysis [2c-f] is an important tool for determining the molecular weight of a compound, and knowledge of the fragmentation patterns for organometallic molecules can be of assistance in assigning a structure to a new compound.

The detailed information about molecular structure provided by NMR spectroscopy has made it a very popular technique and has led to a great demand for better and more easily used NMR spectrometers. This demand has been met successfully by manufacturers of NMR instrumentation and it is now common for a practicing organometallic chemist to have "hands-on" access to a high-field NMR spectrometer. Infrared spectrometers have long been readily available because of their inherent simplicity of design. This chapter will thus focus on the characterization of organometallic compounds by IR and NMR spectroscopy. The structure of a new organometallic compound can often be ascertained by comparison of its NMR and IR data to that of complexes of known structure, aided by a knowledge of the reaction chemistry of the particular complex; thus, it is useful to have a

collection of spectral data with which to compare. The purpose of this chapter is to provide a central location for the practicing organometallic chemist to turn to when in pursuit of general trends for the NMR and IR spectral data of organometallic complexes. Additionally, there are a number of NMR techniques frequently used by organometallic chemists that will be described briefly, specifically variable temperature NMR and spin saturation transfer experiments as applied to the clarification of the fluxional behavior of organometallic molecules and the determination of the energy barriers involved. Although there are many interesting magnetically active nuclei, the contents of this chapter will be confined to carbon-13 and proton NMR data of mono- and dinuclear complexes. The reader is referred to other sources for information on other magnetically active nuclei (see Tables 1 and 2).

#### GENERAL INFORMATION: NMR SPECTROSCOPY

A number of excellent books have been written that present specific information on NMR and Fourier Transform (FT) NMR spectroscopy. Some are quite theoretical and very detailed [3], while others are written for the beginning NMR spectroscopist [4]. Books that address the more practical aspects of NMR, including hardware and software are also available [5]. In this chapter, it is assumed that the reader has a working knowledge of the basic principles of NMR spectroscopy and a feel for the location of organic proton and carbon resonances for strictly organic compounds.

There are many magnetically active nuclei that are relevant to organometallic chemistry, as listed in Tables 1 and 2 (data in these tables are taken largely from reference 5b, pp. 2-5). Table 1 contains the nuclei that have a spin quantum number ( $I$ ) of  $1/2$ , and therefore produce sharp lines in their NMR spectra. NMR spectra of nuclei with  $I > 1/2$  (see Table 2) can also be obtained; however, because of higher nuclear spin quantum numbers and nuclear quadrupole moments, the NMR spectra of these elements typically produce broader lines than those nuclei with  $I = 1/2$ , with the amount of broadening dependent on the value of the quadrupole moment and the efficiency of quadrupolar relaxation for that particular nucleus. While NMR spectra of all magnetically active nuclei can be useful, the higher resolution obtainable for elements with  $I = 1/2$  often makes NMR studies on molecules containing these elements more informative. More information on each nucleus is given in the references listed. The references are not meant to be comprehensive; instead, recent reviews are cited, which should provide a place to start looking for more information on NMR spectroscopy of that particular nucleus.

#### Practical Considerations

##### Solvents

When choosing a solvent for an NMR sample, several factors should be taken into consideration. The first and most obvious is that the solvent should dissolve the complex and not react with it. If variable temperature NMR spectroscopy is being carried out, the freezing point or boiling point of the solvent must be compatible with the temperatures to

TABLE 1: Magnetic Properties of Nuclei with  $I = 1/2$ 

Isotope	Natural Abundance	Frequency(MHz) for a 23.5 kG field	Relative Sensitivity <sup>a</sup>	Reference
$^1\text{H}$	99.985	100.00	1.0	4-6
$^{13}\text{C}$	1.108	25.19	0.016	7
$^{15}\text{N}$	0.37	10.13	0.001	8
$^{19}\text{F}$	100.00	94.08	0.83	9
$^{29}\text{Si}$	4.67	19.86	0.08	10
$^{31}\text{P}$	100.00	40.48	0.07	11
$^{57}\text{Fe}$	2.24	3.24	0.000033	12
$^{77}\text{Se}$	7.50	19.10	0.007	13
$^{89}\text{Y}$	100.00	4.90	0.00012	14
$^{103}\text{Rh}$	100.00	3.15	0.000031	15
$^{107}\text{Ag}$	51.35	4.04	0.000067	16
$^{109}\text{Ag}$	48.65	4.65	0.0001	16
$^{111}\text{Cd}$	12.86	21.20	0.0095	17
$^{113}\text{Cd}$	12.34	22.18	0.011	17
$^{117}\text{Sn}$	7.67	35.62	0.045	18
$^{119}\text{Sn}$	8.68	37.27	0.052	18
$^{123}\text{Te}$	0.89	26.21	0.018	13
$^{125}\text{Te}$	7.03	31.59	0.032	13
$^{183}\text{W}$	14.58	4.11	0.00007	19
$^{195}\text{Pt}$	33.7	21.50	0.01	20
$^{199}\text{Hg}$	16.9	17.88	0.0057	20
$^{203}\text{Tl}$	29.5	57.22	0.19	21
$^{205}\text{Tl}$	70.5	57.79	0.19	21
$^{207}\text{Pb}$	21.1	20.86	0.01	22

<sup>a</sup> Relative sensitivity is scaled to  $^1\text{H} = 1$ .

TABLE 2: Magnetic Properties of Nuclei with  $I > 1/2^a$ 

Isotope	Natural Abundance	$I$	Frequency(MHz) for a 23.5 kG field	Relative Sensitivity <sup>b</sup>	Reference
$^2\text{H}$	0.015	1	15.35	0.0096	23
$^{10}\text{B}$	18.83	3	10.74	0.02	24
$^{11}\text{B}$	81.17	3/2	32.08	0.165	24
$^{14}\text{N}$	99.64	1	7.22	0.001	25
$^{17}\text{O}$	0.037	5/2	13.56	0.029	26
$^{27}\text{Al}$	100.00	5/2	26.06	0.207	27
$^{33}\text{S}$	0.74	3/2	7.67	0.0023	22
$^{45}\text{Sc}$	100.00	7/2	24.29	0.301	20
$^{47}\text{Ti}$	7.75	5/2	5.63	0.0021	20
$^{49}\text{Ti}$	5.51	7/2	5.64	0.0038	20
$^{51}\text{V}$	99.76	7/2	26.29	0.38	20
$^{53}\text{Cr}$	9.54	3/2	5.65	0.0001	19
$^{55}\text{Mn}$	100.00	5/2	24.78	0.18	20
$^{59}\text{Co}$	100.00	7/2	23.73	0.28	28
$^{61}\text{Ni}$	1.25	3/2	8.90	0.0035	29
$^{63}\text{Cu}$	69.09	3/2	26.50	0.094	30
$^{65}\text{Cu}$	30.91	3/2	28.40	0.12	30
$^{67}\text{Zn}$	4.12	5/2	6.25	0.0029	20
$^{69}\text{Ga}$	60.2	3/2	24.00	0.069	29
$^{71}\text{Ga}$	39.8	3/2	30.50	0.142	29
$^{73}\text{Ge}$	7.61	9/2	3.49	0.0014	29
$^{75}\text{As}$	100.00	3/2	17.13	0.025	29
$^{91}\text{Zr}$	11.23	5/2	9.30	0.0094	29
$^{93}\text{Nb}$	100.00	9/2	24.44	0.482	20

(Continued on following page)

TABLE 2. (cont.)

Isotope	Natural Abundance	I	Frequency(MHz) for a 23.5 kG field	Relative Sensitivity <sup>b</sup>	Reference
<sup>95</sup> Mo	15.78	5/2	6.51	0.0032	19
<sup>97</sup> Mo	9.60	5/2	6.65	0.0034	19
<sup>99</sup> Tc	100.00	9/2	4.61	0.4	29
<sup>99</sup> Ru	12.81	5/2	22.51	0.0011	22
<sup>101</sup> Ru	16.98	5/2	5.17	0.0014	22
<sup>105</sup> Pd	22.23	5/2	4.58	0.00078	29
<sup>113</sup> In	4.16	9/2	21.87	0.345	29
<sup>121</sup> Sb	57.25	5/2	23.93	0.16	29
<sup>123</sup> Sb	42.75	3/2	12.96	0.046	29
<sup>139</sup> La	99.91	7/2	14.12	0.059	20
<sup>177</sup> Hf	13.39	7/2	4.00	0.00064	29
<sup>179</sup> Hf	13.78	9/2	2.52	0.0022	29
<sup>181</sup> Ta	100.00	7/2	11.99	0.036	20
<sup>185</sup> Re	37.07	5/2	22.52	0.13	20
<sup>187</sup> Re	62.93	5/2	22.74	0.14	20
<sup>189</sup> Os	16.1	3/2	7.76	0.0022	29
<sup>191</sup> Ir	38.5	3/2	1.72	0.000035	29
<sup>193</sup> Ir	61.5	3/2	1.87	0.000042	29
<sup>197</sup> Au	100.00	3/2	1.72	0.000025	29
<sup>209</sup> Bi	100.00	9/2	16.07	0.14	29

<sup>a</sup>This table does not include data for Group I and II metals, the halogens, the noble gases, the lanthanides or the actinides.

<sup>b</sup> Relative sensitivity is scaled to <sup>1</sup>H = 1.

be encountered in the experiment. For most organometallic applications, dry, deoxygenated solvents are essential. When comparing the chemical shifts of an unknown complex to those of a literature compound, it is important to note the solvent used in both situations. Chemical shifts and coupling constants are quite solvent-dependent, and large changes in both are often observed, particularly between aromatic and non-aromatic solvents. Table 3 (courtesy of MSD Isotopes) lists commonly available deuterated solvents with their physical and spectral properties.

#### Sample Preparation

When preparing a sample, great care should be taken to insure that the solution is homogeneous and does not contain bits of paramagnetic material which will decrease magnetic relaxation times and therefore produce broad lines in the spectrum (soluble paramagnetic materials will also cause this problem). A method for removing insoluble paramagnetic impurities from the solution is to centrifuge the sample for a minute or two to force the undissolved solids to the bottom (or the top in a sealed sample) of the tube. When variable temperature work is to be done on a sample, the solvent should be degassed and the NMR tube should be flame sealed.

#### Potential Problems

Because organometallic complexes contain carbons and hydrogens in environments not encountered in purely organic compounds, the range of chemical shifts is somewhat larger for organometallic complexes. The result of this is that a proton or carbon resonance might easily be missed if a standard sweep width is used (0-12 ppm for protons, 0-220 ppm for carbons). For example, the chemical shift of a hydrogen directly bound to a transition metal may be found as far upfield as -40 ppm, or that of hydrogens bound to a transition metal carbene carbon may be found as far downfield as 20 ppm. In the carbon-13 NMR spectra of organometallic complexes, it is not unusual to find carbonyl carbons at 250 ppm, carbene carbons at 350 ppm, and carbons directly bound to the metal at -40 ppm. "Folded back" resonances are a good indication of protons or carbons that are not within the spectral range being observed. These "fold-back" resonances are observed only in FT-NMR spectra and usually appear as unphasable peaks that are (unfortunately) quite easy to dismiss as an instrumental "glitch". When this occurs or when a resonance is expected at an unusual location, it is necessary to widen the sweep width, i.e., increase the radio frequency "window" being observed.

Another problem that frequently arises is inaccuracy of the integrals obtained for the proton NMR of many organometallic complexes. Generally, this is due to long spin-lattice relaxation times ( $T_1$ 's) for protons in certain environments. In an FT experiment, insufficient relaxation of the nuclei between pulses results in saturation of the nuclei and excitation of fewer nuclei for each successive pulse. The result is that the nuclei with long  $T_1$ 's will produce a weaker signal relative to that observed for nuclei with short  $T_1$ 's, and the integrals will be inaccurate (See reference 3(c) or 4(a) for a brief explanation of  $T_1$ 's). Cyclopentadienyl hydrogens are particularly prone to this problem.

TABLE 3<sup>a</sup>

## DEUTERATED NMR SOLVENTS-HANDY REFERENCE DATA

P.O. BOX 2951 TERMINAL ANNEX  
LOS ANGELES, CA 90051  
213 723-9321

800 325-9034

MERCK & CO., Inc.  
4545 OLEATHA AVE.  
ST. LOUIS, MO 63116  
314 353-7000

P.O. BOX 899  
POINTE CLAIRE-DORVAL  
QUEBEC H9R 4P7  
514 697-2823

MERCK  
SHARP  
&  
CO.  
ISOTOPES

Compound  
Mol. Wt.

Compound Mol. Wt.	$\delta_4^{20}$	m.p.*	b.p.*	$\delta_{\text{H}}$ (mult)*	$J_{\text{HH}}$	$\delta_{\text{C}}$ (mult)*	$J_{\text{CH}}$ ( $J_{\text{CC}}$ )
Acetic Acid-d <sub>4</sub> 64.078	1.12	17	118	11.53(1) 2.03(5)	2	178.4(br) 200.0(7)	20
Acetone-d <sub>4</sub> 64.117	0.87	-94	57	2.04(5)	2.2	206.0(13) 29.8(7)	0.9 20
Acetonitrile-d <sub>4</sub> 44.071	0.84	-45	82	1.93(5)	2.5	118.2(br) 13(7)	21
Benzene-d <sub>6</sub> 84.152	0.95	5	80	7.15(br)		128.0(3)	24
Chloroform-d <sub>4</sub> 120.384	1.50	-64	62	7.24(1)		77.0(3)	32
Cyclohexane-d <sub>12</sub> 96.236	0.89	6	81	1.38(br)		26.4(5)	19
Deuterium Oxide 20.028	1.11	3.8	101.4	4.63(DSS) 4.67(TSP)			
1,2-Dichloroethane-d <sub>4</sub> 102.985	1.25	-40	84	3.72(br)		43.6(5)	23.5
Diethyl-d <sub>10</sub> Ether 84.185	0.82	-116	35	3.34(m) 1.07(m)		65.3(5) 14.5(7)	21 19
Diglyme-d <sub>10</sub> 148.263	0.95	-68	162	3.49(br) 3.40(br) 3.22(5)	1.5	70.7(5) 70.0(5) 57.7(7)	21
Dimethylformamide-d <sub>6</sub> 80.138	1.04	-61	153	8.01(br) 2.91(5) 2.74(5)	2	162.7(3) 35.2(7) 30.1(7)	30 21 21
Dimethyl-d <sub>6</sub> Sulphoxide 84.170	1.18	18	189	2.49(5)	1.7	39.5(7)	21
p-Dioxane-d <sub>8</sub> 96.156	1.13	12	101	3.53(m)		66.5(5)	22
Ethyl Alcohol-d <sub>6</sub> (anh) 52.106	0.91	<-130	79	5.19(1) 3.55(br) 1.11(m)		56.8(5) 17.2(7)	22 19
Glyme-d <sub>10</sub> 100.184	0.86	-58	83	3.40(m) 3.22(5)	1.6	71.7(5) 57.8(7)	21 21
Hexafluoroacetone Deuterate 198.067	1.71	21		5.26(1)		122.5(4) 92.9(7)	(287) (34.5)
HMPT-d <sub>10</sub> 197.314	1.14	7	106(11)	2.53(2 x 5)	2(9.5)	35.8(7)	21
Methyl Alcohol-d <sub>6</sub> 36.067	0.89	-98	65	4.78(1) 3.30(5)	1.7	49.0(7)	21.5
Methylene Chloride-d <sub>2</sub> 86.945	1.35	-95	40	5.32(3)	1	53.8(5)	27
Nitrobenzene-d <sub>6</sub> 128.143	1.25	6	211	8.11(br) 7.67(br) 7.50(br)		148.6(1) 134.8(3) 129.5(3) 123.5(3)	24.5(p) 25 26
Nitromethane-d <sub>5</sub> 64.059	1.20	-29	101	4.33(5)	2	62.8(7)	22
isoPropyl Alcohol-d <sub>9</sub> 68.146	0.90	-86	83	5.12(1) 3.89(br) 1.10(br)		62.9(3) 24.2(7)	21.5 19
Pyridine-d <sub>5</sub> 84.133	1.05	-42	116	8.71(br) 7.55(br) 7.19(br)		149.9(3) 135.5(3) 123.5(3)	27.5 24.5(y) 25
Tetrahydrofuran-d <sub>6</sub> 80.157	0.99	-109	66	3.58(br) 1.73(br)		67.4(5) 25.3(br)	22 20.5
Toluene-d <sub>6</sub> 100.191	0.94	-95	111	7.09(m) 7.00(br) 6.98(m) 2.09(5)	2.3	137.5(1) 128.9(3) 128.0(3) 125.2(3) 20.4(7)	23 24 24(p) 19
Trifluoroacetic Acid-d <sub>4</sub> 115.030	1.50	-15	72	11.50(1)		164.2(4) 116.6(4)	(44) (283)
2,2,2-Trifluoroethyl Alcohol-d <sub>7</sub> 103.059	1.45	-44	75	5.02(1) 3.88(4 x 3)	2(9)	126.3(4) 61.5(4 x 5)	(277) 22(36)

\*Melting and boiling points (in °C) are those of the corresponding light compound (except for D<sub>2</sub>O) and are intended only to indicate the useful liquid range of the materials.

<sup>a</sup>H (of the residual protons) and <sup>13</sup>C spectra were determined on HA-100 and XL-100-15 spectrometers, respectively, for the same sample of each solvent containing 5% TMS (v/v). The chemical shifts are in ppm relative to TMS; the coupling constants are in Hz. (Since deuterium has a spin of 1, triplets arising from coupling to deuterium have the intensity ratio of 1:1:1, etc.) The multiplicity br indicates a broad peak without resolvable fine structure, while m denotes one with fine structure. It should be noted that the chemical shifts, in particular, can be dependent on solute, concentration and temperature.

<sup>1</sup> $\delta_{\text{H}}(\text{CFCl}_3)$  82.6 (1)    <sup>1</sup> $\delta_{\text{H}}(\text{CFCl}_2)$  76.2 (1)    <sup>1</sup> $\delta_{\text{H}}(\text{CFCl}_2)$  77.8 (5),  $J_{\text{HH}}$  1.2    all determined on an HA-100 spectrometer.

<sup>a</sup>Reprinted with permission from MSD Isotopes

There are several solutions to this problem, one of which involves using a smaller pulse width so that fewer nuclei are excited to the upper spin state with each pulse. Alternatively, inserting a delay between pulses (5-20 seconds for protons, up to several minutes for carbons) will allow time for relaxation to occur. A combination of these two techniques is frequently the best compromise in terms of instrument time required to obtain a good spectrum.

#### Special Considerations for Carbon-13 NMR

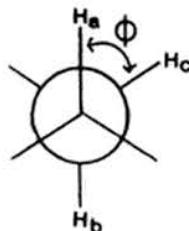
Long relaxation times present a special problem when obtaining carbon-13 NMR spectra of metal carbonyl compounds. Indeed, it is not uncommon for M-CO resonances to be completely invisible under normal spectral acquisition conditions. The tricks used above to obtain good integrals for proton NMR (using a smaller pulse width and inserting a pulse delay) are often not enough to facilitate obtaining a carbon spectrum within a reasonable period of time; however, there are other alternatives. Perhaps the most effective one is the use of "shiftless" relaxation reagents such as Cr(acac)<sub>3</sub>. These reagents are paramagnetic species that provide a pathway for rapid relaxation of excited nuclei and thus enhance the signal intensity without shifting the position of the resonances significantly. Because these reagents are paramagnetic, the carbons that are part of the reagent do not show up in the spectrum. Addition of 1% Cr(acac)<sub>3</sub> is sufficient to provide effective relaxation for the carbonyl carbons of an organometallic complex [31]. Obtaining the spectrum at low temperatures also serves to decrease the T<sub>1</sub>'s of the carbons of interest and therefore increase the signal intensity [32]. This method works because the ability of the molecule to relax increases as the molecular correlation time ( $\tau_c$ , the average time it takes for a molecule to reorient in solution) increases. At lower temperatures,  $\tau_c$  increases due to a decrease in energy available and to increased solvent viscosity, and thus T<sub>1</sub> decreases at lower temperatures; i.e.,  $T_1 \propto 1/\tau_c$ . (For more information on correlation times, see reference 4(a), pp. 116-117 and pp. 128-129).

#### **Coupling Constants**

The value of a proton-proton coupling constant gives information about the relative spatial orientation of the two protons. In aliphatic systems, the value of the coupling constant is proportional to the dihedral angle ( $\phi$ ) between the two C-H bonds. The mathematical relationship is given by the Karplus equation:

$$J = 10 \cos^2 \phi$$

For example, when the dihedral angle is 180° as for H<sub>a</sub> and H<sub>b</sub>, the value of the coupling constant will be ca. 10 Hz. When  $\phi=60^\circ$ , as for H<sub>a</sub> and H<sub>c</sub>, J should be ca. 2.5 Hz and when  $\phi=90^\circ$ , J should be zero.



For alkenes, the value of the coupling constant is indicative of the relative stereochemical orientation (i.e., cis, trans, or geminal) of the coupling protons. Cis couplings are usually small (3-18 Hz), trans couplings are larger (12-24 Hz) and geminal couplings are very small (-3 to 7 Hz) [4(a)].

Often there is more than one proton coupling to the proton in question and the result is a complex spectrum that may be difficult to interpret. In many cases, simplification of this type of spectrum is possible by a simple homonuclear decoupling experiment [4(a)] or if experimentally possible, by substitution of deuterium for one of the coupling hydrogens. For extremely complex systems, simplification of the spectrum can be achieved by computer simulation or through the use of two dimensional (2D) NMR techniques [33]. Some recent examples of 2D NMR applied to organometallic systems are cited in reference 34.

Carbon-carbon couplings are usually not observed in samples containing only natural abundance carbon-13, since the probability of having two carbon-13 atoms adjacent to one another is very small; however, carbon-hydrogen couplings are readily observable in the carbon spectrum acquired with off-resonance decoupling of the protons (see reference 4(a) for a description of off-resonance decoupling). The value of the coupling constant is proportional to the percent s character ( $\rho$ ) of the C-H bond as given by the equation below, and thus the hybridization of the carbon atoms in a molecule can readily be determined.

$$^1J_{CH} = 500 \rho$$

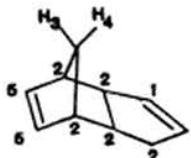
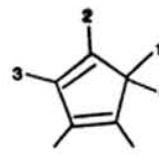
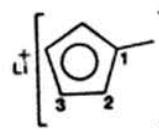
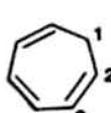
This relationship can only be strictly applied to simple hydrocarbons; however, an unexpected C-H coupling constant can be indicative of unusual bonding situations which can be further clarified by other means.

Coupling to other magnetically-active nuclei should also be anticipated. With nuclei having  $I = 1/2$  (see Table 1), proton-like splittings will be observed; however, the coupling constants may be quite large compared to C-H or H-H couplings. For carbons or hydrogens bound to nuclei with  $I > 1/2$  (see Table 2), quadrupolar broadening may be observed. If this interferes with resolution, acquisition of the spectrum at a lower temperature will often decrease quadrupolar broadening.

## IDENTIFICATION OF ORGANOMETALLIC COMPLEXES

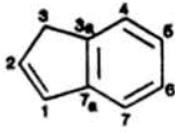
What follows is a number of tables of general information on typical proton and carbon-13 chemical shifts and IR stretching frequencies for commonly-encountered organometallic ligands. Where possible, the spectral data for the free ligands have also been included. These tables are meant to be a general guide. There certainly will be some situations in which the spectral characteristics of a complex will not fall in the range given. For Tables 6 and 7, the IR bands listed are for stretching frequencies only. Keep in mind that for NMR spectra, "low field" means larger  $\delta$  values and "high field" means smaller  $\delta$  values (in some cases, even negative).

TABLE 4. Spectral Data for Uncomplexed Unsaturated Organic Ligands

Ligand	$^1\text{H}$ NMR ( $\delta$ , ppm) <sup>a</sup>	$^{13}\text{C}$ NMR ( $\delta$ , ppm) <sup>a</sup>	Reference
$\text{C}_2\text{H}_4$	5.33(s)	123.3	7(f)
$\text{C}_2\text{H}_2$	1.80(s)	71.62 ( $\text{C}_6\text{D}_6$ )	35
	H1: 5.90(m) H2: 1.5-3.4(m) H3: 1.27(m) H4: 1.50(m) H5: 5.41(br, s)	c	36
	H1: 2.80(m) <sup>b,d</sup> H2: 6.28(m) H3: 6.42(m)	C1: 42.2 C2: 133.0 C3: 133.4	37
	$\text{CH}_3$ (1): 0.95(d, $J=8$ Hz) $\text{CH}_3$ (2,3): 1.75(br, s) H: 2.4(m)	C1: 52.08 <sup>g</sup> C2: 134.14 C3: 137.17 $\text{CH}_3$ (1): 14.56 $\text{CH}_3$ (2): 11.29 $\text{CH}_3$ (3): 11.78	38
$\text{MgCl}^+[\text{C}_5\text{H}_5]^-$	c	ring C: 108.51 <sup>g</sup> $\text{CH}_3$ : 11.42	38
$\text{Na}^+[\text{C}_5\text{H}_5]^-$	5.50(s) (THF) 5.25(s) (DMSO)	102.1 ( $\text{C}_6\text{D}_6$ )	37
$\text{Tl}^+[\text{C}_5\text{H}_5]^-$	6.08(s) (DMSO)	107.5 ( $\text{C}_6\text{D}_6$ )	37,7(f)
	c	C1: 113.1 C2: 103.1 C3: 101.7 $\text{CH}_3$ : 14.4	7(f)
$\text{C}_6\text{H}_6$	7.15(s) ( $\text{C}_6\text{D}_6$ )	128.0	Table 3
	H1: 2.20(m) H2: 5.28(m) H3: 6.12(m) H4: 6.55(m)	C1: 28.1 C2: 120.4 C3: 126.8 C4: 131.0	39

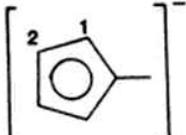
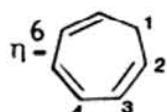
(Continued on the following page)

Table 4. (cont.)

Ligand	<sup>1</sup> H NMR (δ, ppm) <sup>a</sup>	<sup>13</sup> C NMR (δ, ppm) <sup>a</sup>	Reference
[C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup>	9.55 <sup>e</sup>	156.2 <sup>f</sup>	40
	H1: 6.67(d, 5.6 Hz) <sup>d</sup> H2: 6.14(dd) H3: 2.99(d, J=2 Hz) H4-7: 6.5-7.5(m)	C1: 133.6 C2: 131.8 C3: 38.7 C3a: 143.3 C4: 123.4 C5: 126.0 C6: 124.2 C7: 120.6 C7a: 144.6	37, 41

<sup>a</sup>Spectra were taken in CDCl<sub>3</sub> or CC<sub>l</sub><sub>4</sub> unless otherwise noted.<sup>b</sup>Cyclopentadiene exists as the dimer unless freshly distilled.<sup>c</sup>Not found.<sup>d</sup>Reference did not list solvent.<sup>e</sup>PF<sub>6</sub><sup>-</sup> salt in acetone-d<sub>6</sub>.<sup>f</sup>CIO<sub>4</sub><sup>-</sup> salt in CD<sub>3</sub>CN.<sup>g</sup>In THF-d<sub>8</sub>.

TABLE 5. Spectral Data for Unsaturated Organic Ligands Bound to Transition Metals

Ligand	$^1\text{H}$ NMR ( $\delta$ , ppm) <sup>a</sup>	$^{13}\text{C}$ NMR ( $\delta$ , ppm) <sup>a,b</sup>	Reference
$\eta^2-\text{C}_2\text{RR}'$	6-14 <sup>c</sup>	110-230 <sup>d,e</sup>	7(f),42
$\mu^2-(\text{C}_2\text{RR}')$	4-6 <sup>c</sup>	60-115	7(f),43
$\eta^2-\text{C}_2\text{H}_4$	0.5-5 <sup>f</sup>	7-110 <sup>a,f</sup>	7(f),44
$[\eta^3-\text{allyl}]^-$	terminal H: 2-4 <sup>g</sup> central H: 4-6	terminal C: 37-80 <sup>h,i</sup> central C: 88-125	7(f)
$\eta^4-\text{C}_4\text{R}_4$	1.5-6 <sup>c,f</sup>	60-110	7(f),45
$[\eta^5-\text{C}_5\text{H}_5]^-$	3.5-7	75-123 <sup>j</sup>	6,7(f)
$[\eta^5-\text{C}_5\text{Me}_5]^-$	1.5-2.0	ring C: 88-125 $\text{CH}_3$ : 0-20	6,7(f)
	$\text{CH}_3$ : 1.9-2.5 $\text{H}_1, \text{H}_2$ : 3.5-6.5	83-140 <sup>k</sup>	6,7(f)
$\eta^6-\text{C}_6\text{H}_6$	4-7.0	74-111	6,7(f)
	H1: 2.0-3.0 H2: 2.5-4 H3: 4-5 H4: 5-6	C1: 25-30 C2: 49-65 C3,C4: 90-106	7(f),46
$[\eta^7-\text{C}_7\text{H}_7]^+$	4.5-6.5 <sup>l</sup>	80-105 <sup>l</sup>	7(f),46
$\eta^5-\left[ \begin{array}{c} \text{3} \\   \\ \text{2} \end{array} \right. \text{C}_5\text{H}_5 \left. \begin{array}{c} \text{4} \\   \\ \text{5} \end{array} \right]$	H1,H3: 5-7 H2: 5-6.5 H4-7: 6-8	C1,C3: 60-115 C2: 65-110 C3a,C7a: 70-135 <sup>m</sup> C4,C7: 120-130 C5,C6: 110-125	7(f),41

<sup>a</sup>Strongly electron-donating or electron-withdrawing substituents may shift the observed resonances out of the given range.

<sup>b</sup>See reference 7(f) for an extensive collection of  $^{13}\text{C}$  NMR data for specific complexes.

(Notes continued on following page)

Notes for TABLE 5 (cont.)

<sup>c</sup>For R or R' = H.

<sup>d</sup>Acetylene can act as a two-, three-, or four-electron donor. The chemical shifts of the acetylenic carbons have been correlated with the number of electrons donated to the metal, with the lower field shifts observed for acetylenes donating four electrons and the higher field shifts observed for acetylenes donating two electrons. Intermediate values are observed for acetylenes acting as three-electron donors [42(b)].

<sup>e</sup>Platinum-acetylene complexes have chemical shifts for the acetylenic carbons over the range 70-115 ppm (see reference 7(f), p. 198).

<sup>f</sup>An extremely wide range of chemical shifts is observed for these types of complexes. See reference 7(f) for specific examples for comparison.

<sup>g</sup>Terminal allyl protons may resonate at unusually high field (0-1 ppm).

<sup>h</sup>Varies greatly with substituents.

<sup>i</sup>Sometimes observed out of range at lower field when substituents are present.

<sup>j</sup>Most Cp resonances seem to fall in this range, with the exception of some osmium complexes which have  $\delta_{Cp}$  around 65 ppm (see reference 7(f), p. 238).

<sup>k</sup>The ring carbon bound to the methyl group generally resonates at lower field than the other ring carbons.

<sup>l</sup>Most  $\eta^7-C_7H_7$  resonances (both  $^{13}C$  and  $^1H$ ) fall in the range given, with the exception of some bi- and trinuclear mixed-metal compounds (see reference 7(f), p. 258).

<sup>m</sup>The position of the chemical shifts of these carbons has been correlated to the hapticity of the indenyl ligand [41(b)]. For pentahapto indenyl complexes, carbons C3a and C7a fall at the low end of this range, and for trihapto complexes, carbons C3a and C7a fall at the high end of this range. A more quantitative evaluation of carbon-13 chemical shifts and hapticity of the indenyl ligand bound to d<sup>6</sup> and d<sup>8</sup> metals has also been made [41(a)].

# **Problems and Solutions in Organometallic Chemistry**

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Notes for TABLE 6 (cont.)

<sup>b</sup>For d<sup>0</sup> and d<sup>10</sup> metal hydrides [60].

<sup>c</sup>The chemical shift ranges for bridging and terminal CO's overlap; however, if both types of CO's are present in the same compound (a frequent occurrence), the  $\mu$ -CO will be observed at significantly lower field (20-70 ppm) than the terminal CO.

<sup>d</sup>Not stable.

<sup>e</sup>Isolated in a CS<sub>2</sub> matrix [47].

<sup>f</sup>For R=H.

<sup>g</sup>Nothing characteristic.

<sup>h</sup>Not found.

<sup>i</sup>For complexes with a M-M bond.

<sup>j</sup>For complexes without a M-M bond.

<sup>k</sup>Not found for R=H.

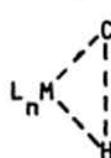
<sup>l</sup>Most -OH resonances of hydroxymethyl complexes occur in this range; however, one such complex, Cp\*Ru(CO)<sub>2</sub>CH<sub>2</sub>OH was reported to have a shift of 0.88 for this proton.

<sup>m</sup>Raman active.

<sup>n</sup>Depending on counterion.

<sup>o</sup>The nitrosyl group can be bound in two ways, linear or "bent". Generally, bent nitrosyl groups have IR stretching frequencies between 1525 and 1690 cm<sup>-1</sup>, i.e., they occur at the lower end of the range; however, some linear NO's also have NO stretching frequencies in the same range, so this cannot be used as a definitive criterion for identification of bent vs. linear NO.

TABLE 7.  $\eta^2$ -Ligands Bound to Transition Metals

Ligand	$^1\text{H}$ NMR ( $\delta$ , ppm)	$^{13}\text{C}$ NMR ( $\delta$ , ppm)	IR ( $\text{cm}^{-1}$ )	Reference
Free $\text{C}_2\text{H}_4$	5.33 <sup>a</sup>	123.3 <sup>a</sup>	1623 <sup>b</sup>	7(f), 53
$\eta^2\text{-C}_2\text{H}_4$	0.5-5 <sup>c</sup>	7-110 <sup>c</sup>	1500-1600 <sup>b</sup>	7(f), 44, 53
Free $\text{C}_2\text{RR}'$	1.8-3.5 <sup>d</sup>	60-90	2190-2260 <sup>e</sup>	35(a), 53
$\eta^2\text{-C}_2\text{RR}'$	6-14 <sup>d</sup>	110-230 <sup>f, g</sup>	1700-2000 <sup>e</sup>	7(f), 42
$\eta^2\text{-acyl}$	2-5	190-300	1465-1620	61
free $\text{H}_2$	4.62	—	4161	62, 53
$\eta^2\text{-H}_2$	-3 to -13 <sup>h</sup>	—	2690 <sup>i</sup>	63
	-16 to 5 <sup>j</sup>	j, k	2350-2700	64
$\eta^2\text{-O}_2$	—	—	800-900	53

<sup>a</sup> In  $\text{CDCl}_3$ .<sup>b</sup> C=C stretch.<sup>c</sup> An extremely wide range of chemical shifts is observed for these types of complexes. See reference 7(f) for specific examples for comparison.<sup>d</sup> For R or R' = H.<sup>e</sup> C≡C stretch.<sup>f</sup> Acetylene can act as a two-, three-, or four-electron donor. The chemical shifts of the acetylenic carbons have been correlated with the number of electrons donated to the metal, with the lower field shifts observed for acetylenes donating four electrons and the higher field shifts for acetylenes donating two electrons. Intermediate values are observed for acetylenes acting as three-electron donors [42(b)].<sup>g</sup> Platinum-acetylene complexes have chemical shifts for the acetylenic carbons over the range 70-115 ppm (see reference 7(f), p. 198).<sup>h</sup> These complexes are somewhat difficult to characterize definitively without X-ray or (preferably) neutron diffraction; however, Crabtree [63a-d] has recently discovered that the spin lattice relaxation time ( $T_1$ ) of the hydrogens in the  $\eta^2\text{-H}_2$  ligand are significantly shorter (15-40ms) than those of classical hydrides (390-800 ms) in the examples studied. The polyhydride examples of dihydrogen complexes often exhibit exchange between the M-H and M-H<sub>2</sub> units, which can lead to observation of short  $T_1$ 's for the classical hydrides. As a result, it may be necessary to cool the sample to slow down the fluxional process in order to get accurate  $T_1$  values.

(Notes continued on following page)

Notes for TABLE 7 (cont.)

<sup>i</sup>Generally weak or unobserved.

<sup>j</sup>At room temperature, these complexes are often fluxional between an alkyl-hydride complex and a 16-electron species with the (once-bridging) hydrogen bound only to the carbon. If this is so, the hydride resonance may be broad and will be located at a weighted average of the two possible static structures. The  ${}^1J_{C-H}$  is also an average of that observed for the two possible structures.

<sup>k</sup>In the same range as normal alkyl carbons; however, the  ${}^1J_{C-H}$  coupling constant for this type of complex is unusually low (75-100 Hz), due to the weakened C-H bond.

## DYNAMIC NUCLEAR MAGNETIC RESONANCE

The structures of many organometallic molecules in solution at room temperature are not static, and frequently this fluxional behavior can give important information about structure, reactivity, and reaction mechanisms. These dynamic processes can be studied by NMR spectroscopy. A great deal is presently known about the theory and practice of dynamic NMR (DNMR) as applied to organometallic systems [65], and the purpose of this section is to introduce the student to the types of information obtainable from a DNMR experiment.

Dynamic processes can be classified into two categories, intramolecular or intermolecular. Some examples of intramolecular processes include skeletal rearrangements of ligands around a metal, rotation around metal-metal or metal-ligand bonds (e.g., rotation around a metal-olefin bond), "ring-whizzing" [65(b)], hapticity changes for unsaturated organic ligands, and interconversion of bridging and terminal ligands such as CO, CH<sub>3</sub>, or NO. Intermolecular processes generally involve ligand dissociation/reassociation. If the exchanging nuclei are coupled to another magnetically active nucleus in the molecule, the couplings are retained if no bonds between the magnetically active nuclei are broken. In this situation, if rapid exchange is occurring, the value of the coupling constant is an average of the individual coupling constants for the nuclei in the different environments. If a bond between the magnetically active nuclei is broken during the exchange process, coupling to the other nucleus is lost.

Broad lines in the NMR spectrum of a molecule are one indication that a fluxional process is occurring. The lineshapes and positions will change with temperature in a way that is governed by the particular process that is exchanging the two sites and by the rate constants associated with this process. These first-order or pseudo-first-order rate constants give a measure of the lifetimes of species in equilibrium. Two different methods of obtaining these rate constants from NMR spectra will be discussed, line shape analysis and spin saturation transfer (SST). In general, line shape analysis of proton NMR spectra can be used to obtain rate constants for processes with rate constants between 10<sup>0</sup> to 10<sup>3</sup> s<sup>-1</sup>, while spin saturation transfer can be used to obtain rate constants for processes that are an order of magnitude slower, down to 10<sup>-1</sup> s<sup>-1</sup>.

### Line Shape Analysis

Figure 1-1 shows the broad-band-deuterium-decoupled, temperature-dependent proton NMR spectrum of cyclohexane-d<sub>11</sub> [66]. This is the simplest of exchanging systems, having only two sites (axial and equatorial), with no coupling present, and with equal populations of nuclei at the two sites.

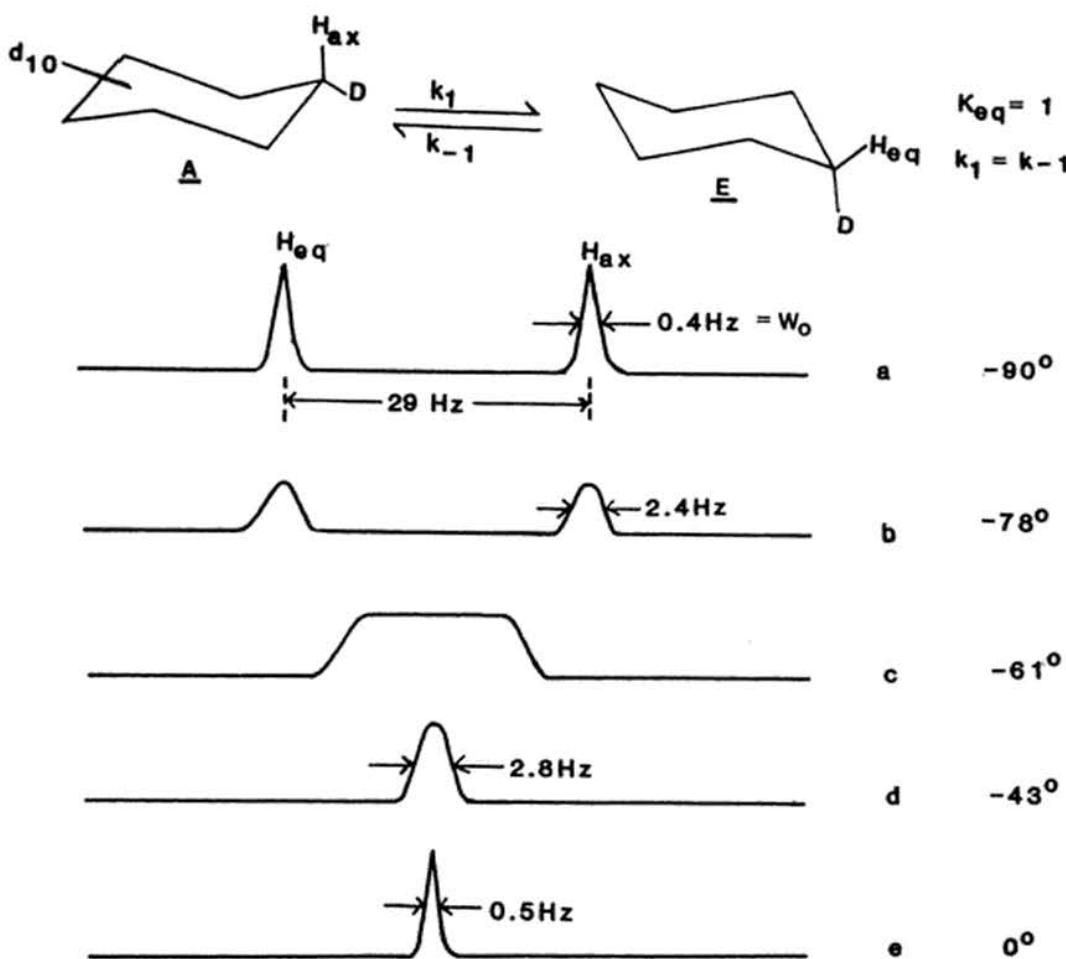


Figure 1-1

The spectrum at the slow exchange limit (a,  $T = -90^{\circ}\text{C}$  and below) demonstrates that the lifetime of both A and E is long relative to the timescale of the NMR experiment, i.e., the exchange between axial and equatorial positions is slow. Under these conditions, the linewidth of the peak is governed by the spin-spin relaxation time,  $T_2$ , and any viscosity broadening that might exist at low temperatures. This linewidth is denoted by  $W_o$  and is measured as the linewidth at half-height.

As the sample is warmed, the two distinct peaks for  $\text{H}_\text{ax}$  and  $\text{H}_\text{eq}$  begin to broaden and merge (b), and at the coalescence temperature,  $T_c = -61^{\circ}\text{C}$  (c), they coalesce into a single broad peak with a flat top. On further warming, the single peak sharpens (e). For this specific example, the system is said to be at the fast exchange limit at temperatures above  $0^{\circ}\text{C}$ , where the lifetimes of both species A and E are short relative to the timescale of the NMR experiment. The position of the peak at the fast exchange limit,  $\delta_f$ , is a weighted average of the positions of the two peaks visible for the static structure, as given by equation (1).

$$\delta_f = p_A \delta_A + p_E \delta_E \quad (1)$$

where  $p_A$  and  $p_E$  are the fractional populations of nuclei in sites A and E, and  $\delta_A$  and  $\delta_E$  are the chemical shifts of the axial and equatorial protons respectively. Since the two sites have equal populations,  $p_A$  and  $p_E$  are both 0.5, and the (now rapidly-exchanging) hydrogens will have a chemical shift exactly between the shifts observed for the two different hydrogens at the slow exchange limit.

There are several important mathematical relationships that apply at various temperatures. At the slow exchange limit (a),

$$k \ll \nu_A - \nu_E \quad (2)$$

where  $\nu_A$  is the chemical shift (in Hz) of the axial proton and  $\nu_E$  is the chemical shift of the equatorial proton. An approximation for obtaining rate constants at temperatures where slow exchange is taking place (b) involves using equation (3).

$$k = \pi (\Delta W) \quad (3)$$

where  $\Delta W = W - W_0$ , and  $W$  is the width at half-height of the broadened peak. For the cyclohexane example at  $-78^\circ\text{C}$

$$k(-78^\circ\text{C}) = \pi(2 \text{ s}^{-1}) = 6.28 \text{ s}^{-1} \quad (4)$$

At the coalescence temperature (c), the rate constant for exchange can be obtained from equation (5).

$$k = \frac{\pi(\nu_A - \nu_E)}{\sqrt{2}} \quad (5)$$

and for cyclohexane

$$k(-61^\circ\text{C}) = \frac{\pi(29 \text{ s}^{-1})}{\sqrt{2}} = 64 \text{ s}^{-1} \quad (6)$$

It is interesting to note that the greater the difference in Hz of the chemical shifts of the two exchanging protons, the faster the exchange rate required for coalescence to occur, and the higher  $T_c$ .

After coalescence (d), the rate constant can be calculated using the fast exchange approximation given by equation (7),

$$k = \frac{\pi(\nu_A - \nu_E)^2}{2(W - W_f)} \quad (7)$$

where  $W$  is again the width of the broadened peak at the temperature in question and  $W_f$  is the width at half height of the peak at the fast exchange limit. For cyclohexane,

$$k(-43^\circ\text{C}) = \frac{\pi (29 \text{ s}^{-1})^2}{2(2.3 \text{ s}^{-1})} = 566 \text{ s}^{-1} \quad (8)$$

At the fast exchange limit,  $e$ ,

$$k \gg v_A - v_E \quad (9)$$

The two-spin, equal population example is the simplest system and is the only one that will be discussed here. The analysis can become very complex if the two sites are not equally populated and/or if coupling to other nuclei exists. The reader is referred to other sources [65] for discussion of more involved systems.

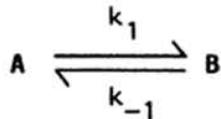
Several experimental aspects must also be taken into consideration when using or obtaining rate data from line shape analysis.

- 1) It is important to realize that the coalescence temperatures obtained in this manner are field-dependent, i.e., the  $\Delta v$  is given in Hz, not ppm; therefore, any report of a coalescence temperature must be accompanied by the field strength of the magnet used in the experiment.
- 2) It is important to be aware that the rate of a fluxional process is frequently solvent-dependent [67].
- 3) Precise temperature measurement and control of temperature fluctuations are essential for obtaining accurate rate data. There are a number of methods for accurately measuring temperature, as given in reference 65(a), pp. 71-76 or reference 5(b), pp. 331-339.

### Spin Saturation Transfer

The technique of spin saturation transfer (or magnetization transfer) was first developed by Forsén and Hoffman [68]. Many very detailed reviews on the subject are available [65], including some useful experimental tips [5(b), 65(a)]. This method allows the measurement of rates down to  $10^{-1} \text{ s}^{-1}$ , an order of magnitude slower than those obtainable from line shape analysis.

Consider a simple two-site exchange with equal populations and no coupling to other nuclei.



Experimentally, SST involves irradiating (saturating) the signal arising from nucleus B and observing a decrease in the signal arising

from nucleus A. Because irradiation of a nucleus equalizes the populations of the two spin states, i.e., that nucleus is "saturated", magnetization of the irradiated nucleus (B) goes to zero. If nucleus B is exchanging with nucleus A, some of the decrease in magnetization will be transferred to A if the longitudinal relaxation time ( $T_1$ ) of

nucleus A is of the same order of magnitude or slower than transfer of the saturation from B into that site. If nucleus A relaxes back to an equilibrium spin state faster than the magnetization can be transferred to A via the dynamic process, no change in the signal intensity of A is observed. If magnetization transfer occurs much faster than relaxation of the A nucleus, A will become rapidly saturated and no signal will be observed for nucleus A. SST is thus applicable to a system if the lifetimes of the exchanging nuclei in a particular site are on the same order of magnitude as the spin-lattice relaxation time ( $T_1$ ) of that nucleus.

Mathematically, rate constants can be extracted from the experimental data by consideration of the Bloch equation that applies to the system.

$$\frac{dM_{zA}}{dt} = \frac{M_{0A} - M_{zA}}{T_{1A}} - \frac{M_{zA}}{\tau_A} + \frac{M_{zB}}{\tau_B} \quad (10)$$

where  $M_{0A}$  = the equilibrium magnetization of the nuclei at site A before perturbation by radio frequency energy

$M_{zA}$  = magnetization of nucleus A at time t after perturbation by radio frequency energy

$M_{zB}$  = magnetization of nucleus B at time t after perturbation by radio frequency energy

$T_{1A}$  = longitudinal relaxation time of nucleus A

$\tau_A$  = the lifetime of nucleus A at site A

$\tau_B$  = the lifetime of nucleus B at site B

Irradiation of B causes the last term in equation (10) to go to zero, and the resulting equation (11) gives an expression for the change in magnetization of nucleus A with time.

$$\frac{dM_{zA}}{dt} = \frac{M_{0A}}{T_{1A}} - \frac{M_{zA}}{\tau_{1A}} \quad (11)$$

where  $\tau_{1A}$  is defined by equation (12).

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A} \quad (12)$$

Before perturbation of the system,  $M_{zA} = M_{0A}$  and  $t=0$ , and under these conditions equation (11) integrates to

$$M_{zA} = M_{0A} \left[ \frac{\tau_{1A}}{T_{1A}} + \frac{\tau_{1A}}{\tau_A} \exp(-t/\tau_{1A}) \right] \quad (13)$$

When the equilibrium magnetization is reached, the equation becomes

$$M_{zA} = M_{0A\infty} \left( \frac{\tau_{1A}}{T_{1A}} \right) \quad (14)$$

There are two methods for obtaining rate constants from these experiments. The first method involves measuring the decrease in magnetization of A ( $M_{zA}$ ) as this value approaches the equilibrium magnetization,  $M_{zA\infty}$ . A semilogarithmic plot of equation (13) as  $\ln(M_{zA} - M_{zA\infty})$  versus time gives a straight line, with the slope of the line being  $-1/\tau_{1A}$ . Since the area under the peak is proportional to the magnetization, the value of  $M_{zA}$  is simply the integral of the peak for nucleus A after irradiating nucleus B for time t. The value of  $M_{zA\infty}$  is the integral of the peak for nucleus A after equilibrium magnetization has been reached. The value of  $T_{1A}$  obtained from the plot and the value of  $T_{1A}$  (obtained from a separate  $T_1$  measurement (see references 65(a) and 5(b))) can be substituted into equation (12) to obtain a value for  $\tau_A$ , which is the inverse of the rate constant, k. Alternatively, nucleus B can be irradiated for long enough to ensure that the magnetization of A is at the equilibrium magnetization,  $M_{zA\infty}$ , and equations (14) and (12) can be combined to obtain the expression for the rate constant given in equation (15):

$$k = \frac{1}{T_{1A}} \left[ \frac{M_{0A}}{M_{zA\infty}} - 1 \right] \quad (15)$$

Some applications of SST to organometallic systems are given in reference 69, and Chapter 4 of this book provides some practice problems for both line shape analysis and spin saturation transfer.

### Calculating Activation Parameters

The rate constants obtained by the methods above can be used to calculate activation parameters for the fluxional process being studied. The Eyring equation (16) gives the relationship of the rate constant to the free energy of activation,  $\Delta G^\ddagger$ .

$$k = (kT/h) e^{-\Delta G^\ddagger/RT} \quad (16)$$

thus,  $\Delta G^\ddagger = -RT[\ln(k/T) + \ln(h/k)]$  (17)

where  $R = 1.987 \times 10^{-3}$  kcal/mol K

$k = \text{Boltzmann's constant} = 1.38054 \times 10^{-16}$  erg/K

$h = \text{Plank's constant} = 6.6256 \times 10^{-27}$  erg sec

T = temperature in K

The activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$  can be calculated from the temperature dependence of the rate constant according to equation (18).

$$k = (kT/h) e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (18)$$

The numbers for  $\Delta G^\ddagger$  obtained in this manner are fairly accurate; indeed, errors of 5°C in temperature and 15% in k will still give reasonably accurate values of  $\Delta G^\ddagger$ ; however, in order to obtain accurate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values, it is much more important to have very precise k versus T data over a wide temperature range.

#### MISCELLANEOUS ITEMS OF INTEREST

There are a number of NMR techniques that are beyond the scope of this book but may be applicable to certain systems. We thought it would be useful to have a leading reference to some of these techniques.

- 1) Solid state NMR can be applied to the study of polymer-bound organometallics and heterogeneous catalysts [70].
- 2) NMR spectra of paramagnetic molecules typically show broad lines that are spread out over a wide range (> 200 ppm for protons), or sharp lines that are shifted out of the usual range being observed. Paramagnetic NMR spectroscopy can give information about species that are difficult to characterize otherwise; however, special parameters for acquisition and processing of the spectrum are required [71].
- 3) Detection of radical pairs as intermediates in a reaction is often possible by the use of Chemically Induced Dynamic Nuclear Polarization (CIDNP) [72].
- 4) A wide variety of new pulse techniques are now available for obtaining information about couplings and exchange processes, including SEFT (spin echo fourier transform), SPI (selective population inversion), INEPT (insensitive nuclei enhanced by polarization transfer), DEPT (distortionless enhancement by polarization transfer), INADEQUATE (incredible natural abundance double quantum transfer experiment), and DANTE (delays alternating with nutation for tailored excitation). This information has been summarized through 1983 in reference 73, as well as descriptions of useful 2-D NMR techniques such as COSY (correlated spectroscopy), SECSY (spin echo correlated spectroscopy), 2-D INADEQUATE, and NOESY (nuclear Overhauser effect spectroscopy).

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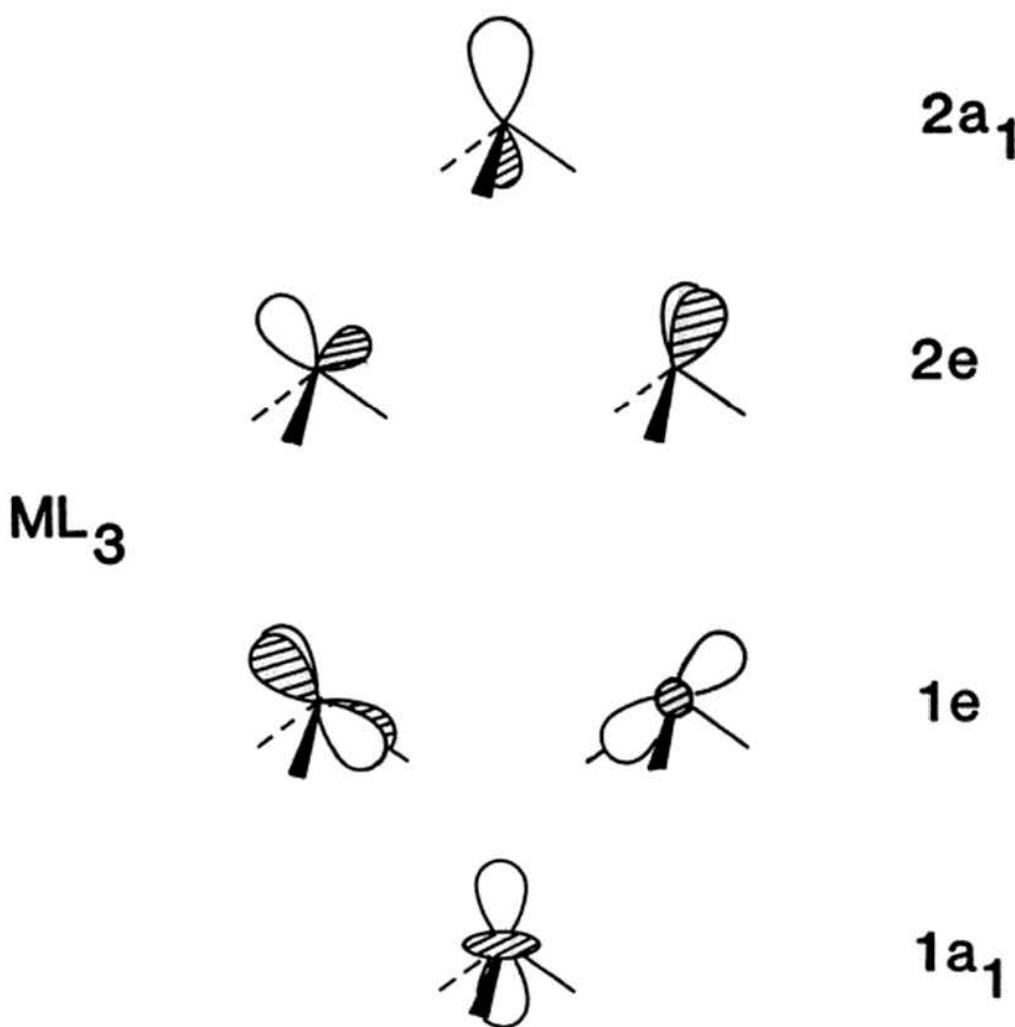
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# 2

## Structure and Bonding



## 2: STRUCTURE AND BONDING

### QUESTIONS

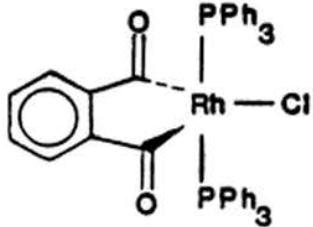
1. Give the formal oxidation state and d-electron count of the metal in the following complexes.

- a)  $(\eta^6-C_6H_6)_2Mo$
- b)  $Cp_2ZrCl(OMe)$
- c)  $[(PMe_3)_2Pd(\eta^3-C_3H_3)]^+$
- d)  $(CO)_5Re-Et$
- e)  $(diphos)Pt(OMe)_2$
- f)  $Cp^*(PMe_3)_2Ru-CI$
- g)  $(dtc)_2W(C_2H_4)(Ph-C\equiv C-Ph)$  (dtc = dithiocarbamate, see question 7.)
- h)  $[Cp(PMe_3)_3WH_2]^+$

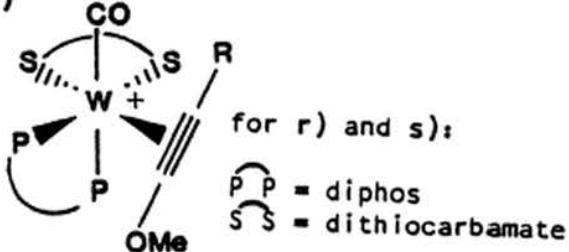
2. For each of the following species, indicate the number of electrons in the valence shell of the metal. Which of these complexes would you expect to be stable enough to be characterized?

- a)  $(\eta^6-C_6H_6)_2Fe$
- b)  $Ru(PPh_3)_2(CO)_2$
- c)  $Cp_2NbH(C_2H_4)$
- d)  $[HFe(CO)_4]^-$
- e)  $Re(CO)_5$
- f)  $Pt(PBu_3)_3$
- g)  $(RO)_3W\equiv CMe$
- h)  $[Cp(diphos)(CO)_2Mo]^+$
- i)  $(CO)_4(Br)W\equiv CPh$
- j)  $[Cp(CO)_2Fe(PhC\equiv CH)]^+$
- k)  $[PtCl_3(C_2H_4)]^-$
- l)  $[Cp(CO)(NO)Mo(\eta^3-C_3H_3)]^+$
- m)  $(\eta^6-C_6H_6)Mn(CO)_2(CH_3)$
- n)  $Cp(NO)_2W-H$
- o)  $[Ir(CO)(PPh_3)_2(Cl)(NO)]^+$
- p)  $Cp(CO)_2Re(CH_3)_2$

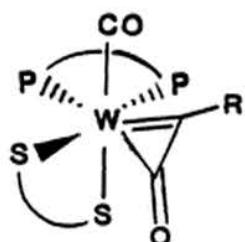
q)



r)



s)



3. For the following polynuclear complexes, indicate the total number of electrons, determine the number of M-M bonds present (assuming that all metals are coordinatively saturated), and predict a structure.

- a)  $\mu\text{-CO-}[(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})]_2$
- b)  $\mu\text{-CO-}\mu\text{-CRR'}-[Cp^*\text{Rh}]_2$
- c)  $\mu\text{-CRR'}-[Cp^*\text{Rh}(\text{CO})]_2$
- d)  $[\mu\text{-X-}\mu\text{-CH}_2\text{-}(\text{Os}_3(\text{CO})_{10})]^-$ , where X = halide
- e)  $[\mu\text{-Cl-Rh}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Ph}-\textcircled{P})]_2$ , where  $\textcircled{P}$  = polymer
- f)  $\mu\text{-PPh}_2[(\text{PPh}_3)(\text{CO})_3\text{FeIr}(\text{CO})_2(\text{PPh}_3)]$
- g)  $\mu^3\text{-CO-}[\text{Fe}_4(\text{CO})_{12}]^{-2}$
- h)  $[\mu\text{-Cl-PdCl}(\text{RC}\equiv\text{CR})]_2$
- i)  $(\mu\text{-CO})_2\text{-}[\text{CpRh}]_3(\text{CO})$
- j)  $(\mu\text{-Br})_2\text{-}[\text{Mn}(\text{CO})_4]_2$
- k)  $\text{Cp}_2(\text{t-BuO})\text{ZrRu}(\text{CO})_2\text{Cp}$
- l)  $(\mu\text{-CH}_2)_2\text{-}[\text{Cp}^*\text{Rh}(\text{CH}_3)]_2$
- m)  $[\text{Cp}(\text{CO})_2\text{Mo}]_2$
- n)  $[\mu\text{-H}]_2\text{-}[\text{Cp}(\text{NO})\text{W}(\text{H})]_2$

4. For each of the following metal and ligand combinations, formulate the simplest neutral compound that conforms to the 18-electron rule. Draw a reasonable structure for each compound.

- |               |                                    |
|---------------|------------------------------------|
| a) Ni, CO     | b) Fe, CO, COT = cyclooctatetraene |
| c) Co, Cp, CO | d) Fe, Cp, CO                      |
| e) Re, CO, H  | f) Mo, Cp, CO                      |
| g) Ni, Cp, NO | h) Cp, Co, NO                      |

5. Predict the structures of the complexes given.

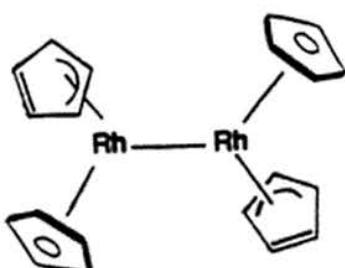
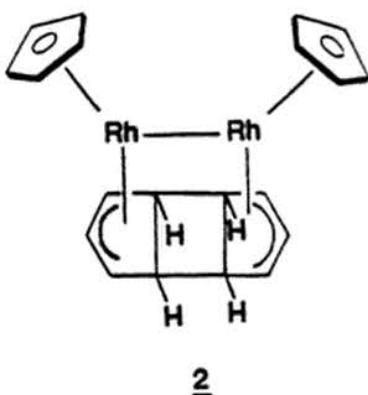
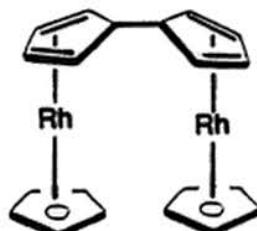
- |   |  |
|---|--|
| a) $\text{Ni}(\text{CO})_4$                       | b) $(\text{PET}_3)_2\text{Pd}(\text{CH}_3)_2$                |
| c) $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ | d) $\text{PdCl}_2(\text{CH}_3\text{CN})_2$                   |
| e) $\text{Rh}(\text{PPh}_3)_3\text{Cl}$           | f) $(\text{PPh}_3)_2\text{Pt}(\text{Ph-C}\equiv\text{C-Ph})$ |
| g) $[\text{Co}(\text{CO})_4]^-$                   | h) $[\text{Ir}(\text{diphos})_2]^+$                          |

## 5. (cont.)



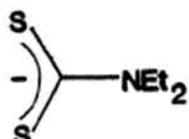
6. Although cobaltocene ( $\text{Cp}_2\text{Co}$ ) is stable (under  $\text{N}_2$ ) at room temperature, the rhodium and iridium analogs dimerize to give the compounds  $\text{M}_2\text{C}_{20}\text{H}_{20}$ . Three plausible structures are shown below. Are these 18-electron species? Use the following NMR data to determine the correct structure.

$^1\text{H}$  NMR:    5.2 (s, 10 H)  
                  5.0 (m, 4 H)  
                  3.3 (m, 4 H)  
                  2.2 (m, 2 H)

123

7. Determine the number of valence shell electrons in the metal-acetylene complexes below and indicate how many electrons the acetylene will donate to the metal.

- a)  $\text{W}(\text{CO})(\text{detc})_2(\text{HC}\equiv\text{CH})$  (detc = diethyldithiocarbamate, illustrated below)
- b)  $\text{CpW}(\text{CO})(\text{CH}_3)(\text{HC}\equiv\text{CH})$
- c)  $\text{Cp}_2\text{Mo}(\text{HC}\equiv\text{CH})$
- d)  $\text{Mo}(\text{detc})_2(\text{HC}\equiv\text{CPh})_2$



detc

8. For each pair of complexes, explain the relative values of  $\Delta G^\ddagger$  for rotation around the metal–carbon bond. In all cases, there is only one d-orbital hybrid available for pi interaction with the carbene ligand.

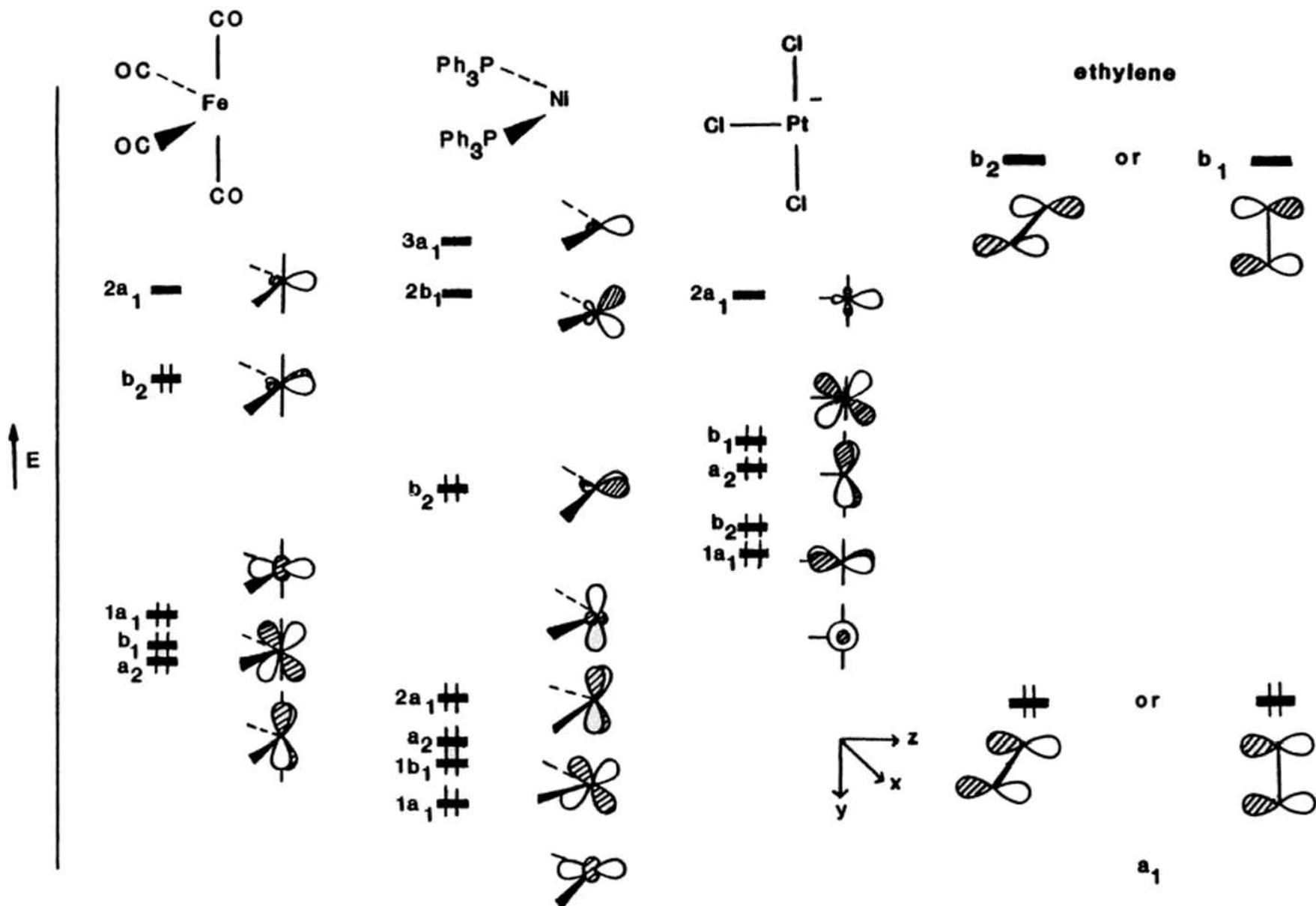
- a)  $[\text{Cp}(\text{CO})_2 \text{vs} (\text{PPh}_3) \text{Mo}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger < 6 \text{ kcal/mol}$   
 $[\text{Cp}(\text{CO})_2 (\text{PPh}_3) \text{W}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger = 8.3 \text{ kcal/mol}$
- b)  $[\text{Cp}(\text{CO})_2 \text{vs} (\text{PPh}_3) \text{W}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger = 8.3 \text{ kcal/mol}$   
 $[\text{Cp}(\text{CO})_2 (\text{PEt}_3) \text{W}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger = 9.0 \text{ kcal/mol}$
- c)  $[\text{Cp}(\text{diphos}) \text{Fe}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger = 10.4 \text{ kcal/mol}$   
 $[\text{Cp}(\text{NO})(\text{PPh}_3) \text{Re}=\text{CH}_2]^+$ ,  $\Delta G_{\text{rot}}^\ddagger > 15 \text{ kcal/mol}$

9. Which of the two complexes has the lower energy CO stretching frequency in the infrared spectrum? Rationalize your choice.

- a)  $[\text{W}(\text{CO})_5 \text{Cl}]^-$  or  $\text{Re}(\text{CO})_5 \text{Cl}$   
b)  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}(\text{CO})_4 \text{Br}_2$   
c)  $\text{Mo}(\text{CO})_6$  or  $\text{Mo}(\text{CO})_4 (\text{PPh}_3)_2$   
d)  $\text{Mo}(\text{CO})_4 (\text{PMe}_3)_2$  or  $\text{Mo}(\text{CO})_4 (\text{PPh}_3)_2$   
e)  $\text{Cp}(\text{CO})_2 \text{Fe-Br}$  or  $[\text{Cp}(\text{CO})_2 \text{Fe}]^-$

10. Using the Dewar-Chatt-Duncanson model of bonding, predict the orientation of the ethylene in each of the following complexes. The metal fragment orbitals and the pi orbitals of ethylene are shown on the following page. Explain your reasoning.

- a) (ethylene) $\text{Ni}(\text{PPh}_3)_2$   
b) (ethylene) $\text{Fe}(\text{CO})_4$   
c)  $[(\text{ethylene})\text{PtCl}_3]^-$



**11. Equilibrium constants for the reaction**



for various L are given below.

L	$K_d$	$\text{CO}(\text{cm}^{-1})$	cone angle (degrees)
$\text{PEt}_3$	(1)	1985	132
$\text{P(n-Pr)}_3$	1.1	1980	135
$\text{PEt}_2\text{Ph}$	2.5	1990	135
$\text{PEtPh}_2$	24.2	1990	140
$\text{PPh}_3$	750.0	1995	145

a) Is  $\text{CoBr}_2(\text{CO})\text{L}_2$  an 18-electron complex?

b) Rationalize the trends observed for  $K_d$ .

**12. Choose the appropriate molecular orbital diagram for the molecular orbitals of the following metal fragments and find the hydrocarbon isolobal analog for each one. Molecular orbital diagrams for the possible hydrocarbon fragments and the various metal fragments are given on the following pages.**

**HINTS**

- 1) The isolobal analogy allows one to compare systems that contain the same number of orbitals and electrons.
- 2) In using this analogy, it is necessary to decide which orbitals are important for bonding to an additional ligand or substituent i.e., the orbitals already involved in bond formation to other groups can be ignored, as well as any antibonding orbitals. The nonbonding orbitals of the metal fragment (those derived from the  $t_{2g}$  set) can also be ignored, since they are only involved in pi bonding and are therefore not available for sigma-type interactions with an incoming ligand.
- 3) If you are still stuck, see the answer to a) for an example.

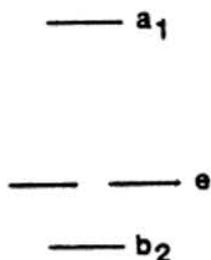
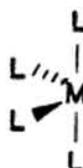
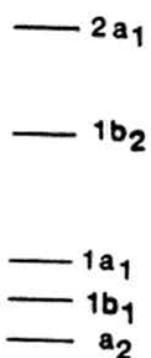
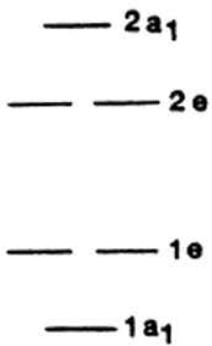
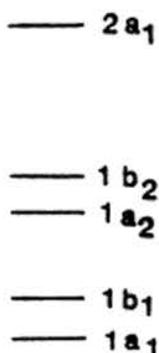
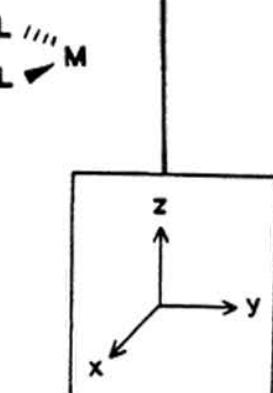
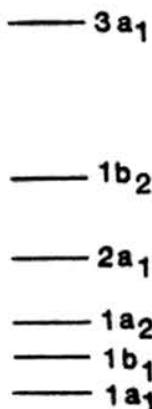
a)  $[\text{PtCl}_3]^-$

b)  $\text{Fe}(\text{CO})_3$

c)  $\text{Fe}(\text{CO})_4$

d)  $\text{Cp}(\text{CO})\text{Rh}$

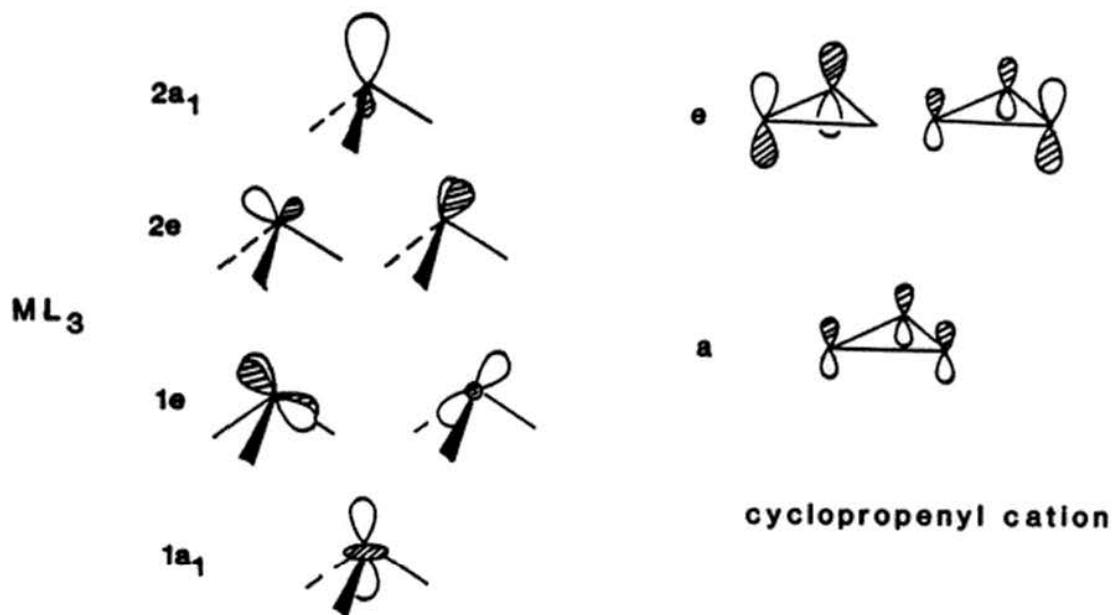
## 12. (cont.)

A.  $ML_5$  (Octahedral minus one ligand)B.  $ML_4$  (Octahedral minus two cis ligands)C.  $ML_3$  (Octahedral minus three facial ligands)D.  $ML_3$  ( $ML_5$  minus two trans ligands)E.  $ML_2$  ( $ML_4$  minus two axial ligands)

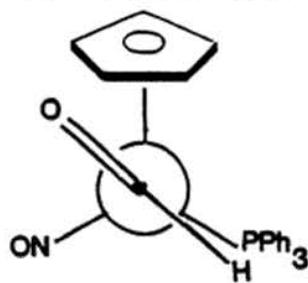
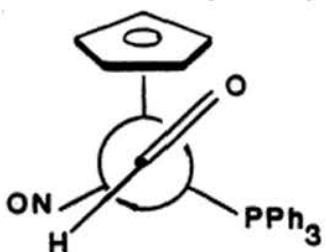
13. Using the orbitals of an  $ML_3$  fragment and the pi molecular orbitals of the cyclopropenyl cation given below, derive the molecular orbitals of  $[(\text{cyclopropenyl})\text{Ni}(\text{PPh}_3)_3]^+$ . Clearly explain:

a) which orbitals of each fragment interact to give the molecular orbitals of the final molecule

b) the proper relative orientation of the two C-3 rotors.



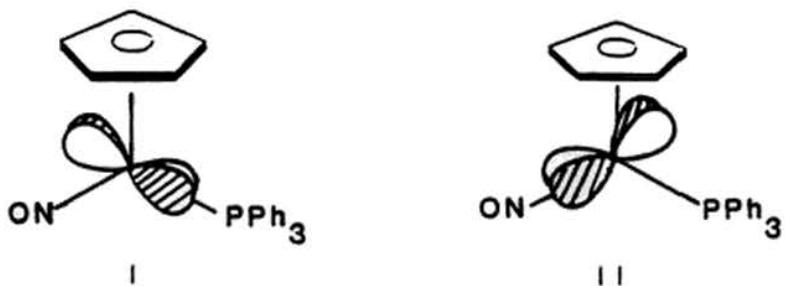
14. For the formyl complex  $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}-\text{CHO}$ , there are two possible orientations of the formyl ligand, A or B. Choose the correct orientation and explain your reasoning.



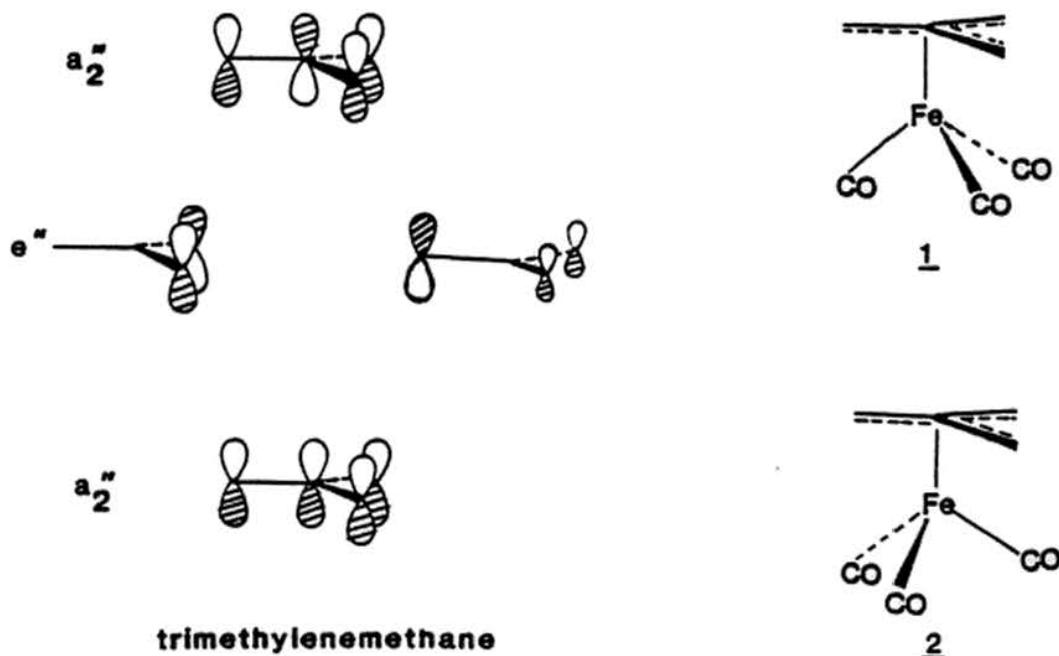
HINT

In an asymmetric  $\text{CpML}'$  system, there are two metal d-orbital hybrids (I and II, see following page) able to participate in M-L pi interactions.

14. (cont.)

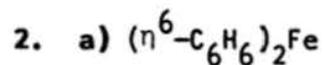


15. Using the orbitals of an  $ML_3$  fragment (see problem 13) and the pi molecular orbitals of trimethylenemethane (TMM) shown below, construct a qualitative molecular orbital interaction diagram for  $(\text{TMM})\text{Fe}(\text{CO})_3$ . Which is the proper relationship between the two 3-fold rotors of the molecule, 1 or 2?



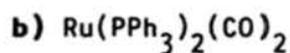
**ANSWERS**

1. a) Mo(0), d<sup>6</sup>. b) Zr(IV), d<sup>0</sup>. c) Pd(II), d<sup>8</sup>. d) Re(I), d<sup>6</sup>.  
 e) Pt(II), d<sup>8</sup>. f) Ru(II), d<sup>6</sup>. g) W(II), d<sup>4</sup>. h) W(IV), d<sup>2</sup>.



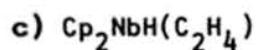
2	$(\eta^6\text{-C}_6\text{H}_6)$	12 electrons	neutral
	Fe(0)	<u>8 electrons</u>	neutral
	Total	20 electrons	

Unstable, a 20-electron complex; however, the 18-electron Fe(II) species  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Fe}]^{+2}$  is well known.



2	CO	4 electrons	neutral
2	PPh <sub>3</sub>	4 electrons	neutral
	Ru(0)	<u>8 electrons</u>	neutral
	Total	16 electrons	

Unstable, a 16-electron complex.



2	Cp <sup>-</sup>	12 electrons	- 2
	H <sup>-</sup>	2 electrons	- 1
	(C <sub>2</sub> H <sub>4</sub> )	2 electrons	neutral
	Nb(III)	<u>2 electrons</u>	+ 3
	Total	18 electrons	

Observable 18-electron complex.

2. d)  $[\text{HFe}(\text{CO})_4]^-$ 

4	CO	8 electrons	neutral
	$\text{H}^-$	2 electrons	- 1
	Fe(0)	<u>8 electrons</u>	neutral
	Total	18 electrons	

Observable 18-electron complex.

e)  $\text{Re}(\text{CO})_5$ 

5	CO	10 electrons	neutral
	Re(0)	<u>7 electrons</u>	neutral
	Total	17 electrons	

Unstable, a 17-electron species. Postulated as a radical intermediate in reactions which involve photolytic cleavage of the Re-Re bond of  $\text{Re}_2(\text{CO})_{10}$ .

f)  $\text{Pt}(\text{PBu}_3)_3$ 

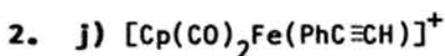
3	$\text{PBu}_3$	6 electrons	neutral
	Pt(0)	<u>10 electrons</u>	neutral
	Total	16 electrons	

A stable 16-electron species, not uncommon for Pt and Pd.

g)  $(\text{RO})_3\text{W}\equiv\text{CMe}$ 

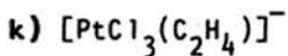
3	$\text{OR}^-$	10 electrons	- 3
	[carbyne] <sup>-</sup>	4 electrons	- 1
	W(IV)	<u>2 electrons</u>	+ 4
	Total	16 electrons	

At first glance, this complex may appear to be a 12-electron species; however, in many electron-deficient complexes that contain ligands with strong pi donating capabilities (e.g. halogens, oxygen, sulfur, nitrogen), the filled p-orbitals on the ligand can donate electrons into metal d-orbitals of the appropriate symmetry and increase the electron count around the metal. In this particular example, a 16-electron configuration is obtained by forming the triple bond to the carbyne and three sigma bonds, as well as two pi bonds resulting from the interaction of three filled oxygen pi orbitals with two



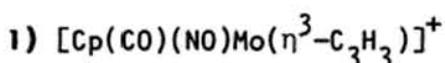
2	CO	4 electrons	neutral
	$\text{Cp}^-$	6 electrons	- 1
	$\text{PhC}\equiv\text{CH}$	2 electrons	neutral
	Fe(II)	<u>6 electrons</u>	+ 2
Total		18 electrons	

Observable 18-electron complex.



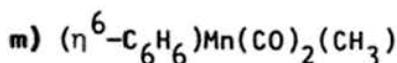
3	$\text{Cl}^-$	6 electrons	- 3
	$\text{C}_2\text{H}_4$	2 electrons	neutral
	Pt(II)	<u>8 electrons</u>	+ 2
Total		16 electrons	

A stable 16-electron species, not uncommon for Pt and Pd.



	CO	2 electrons	neutral
	$\text{NO}^+$	2 electrons	+ 1
	$\text{Cp}^-$	6 electrons	- 1
	$[(\eta^3-\text{C}_3\text{H}_3)]^-$	4 electrons	- 1
Total		18 electrons	

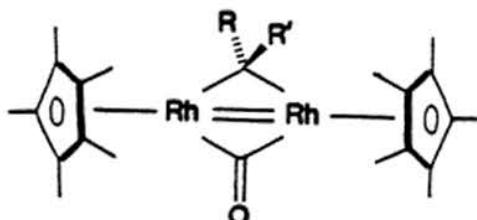
Observable 18-electron complex.



2	CO	4 electrons	neutral
	$\text{CH}_3^-$	2 electrons	- 1
	$(\eta^6-\text{C}_6\text{H}_6)$	6 electrons	neutral
	Mn(I)	<u>6 electrons</u>	+ 1
Total		18 electrons	

3. b) (cont.)  $[18(2)-32]/2 = 2$  Rh-Rh bonds predicted

Herrmann, W.A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M.L. Angew. Chem. Int. Ed. Engl. 1981, 20, 193.

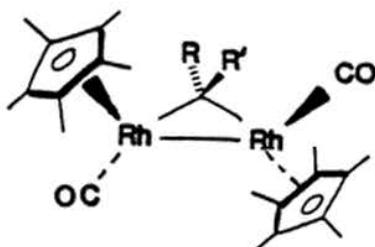


c)  $\mu\text{-CRR}'-\text{[Cp}^*\text{Rh(CO)}]_2$

$\mu\text{-CRR}'$	2 electrons	neutral
2 $\text{Cp}^*$	12 electrons	- 2
2 CO	4 electrons	neutral
2 Rh(I)	<u>16 electrons</u>	+ 2
Total	34 electrons	

$[18(2)-34]/2 = 1$  Rh-Rh bond predicted

Ibid., reference for 3b.



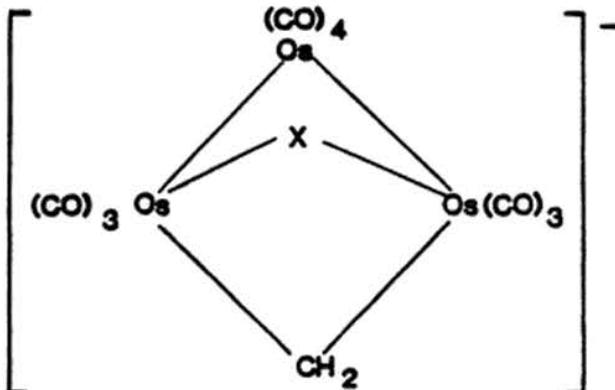
d)  $[\mu\text{-X}-\mu\text{-CH}_2-(\text{Os}_3(\text{CO})_{10})]^-$

$[\mu\text{-X}]^-$	4 electrons	- 1
$\mu\text{-CH}_2$	2 electrons	neutral
10 CO	20 electrons	neutral
3 Os(0)	<u>24 electrons</u>	neutral
Total	50 electrons	

3. d) (cont.)  $[18(3)-50]/2 = 2$  Os-Os bonds predicted

A halide can act as a terminal two-electron donor or a bridging four-electron donor.

Morrison, E.D.; Geoffroy, G.L.; Rheingold, A.L. *J. Am. Chem. Soc.* 1985, 107, 254.



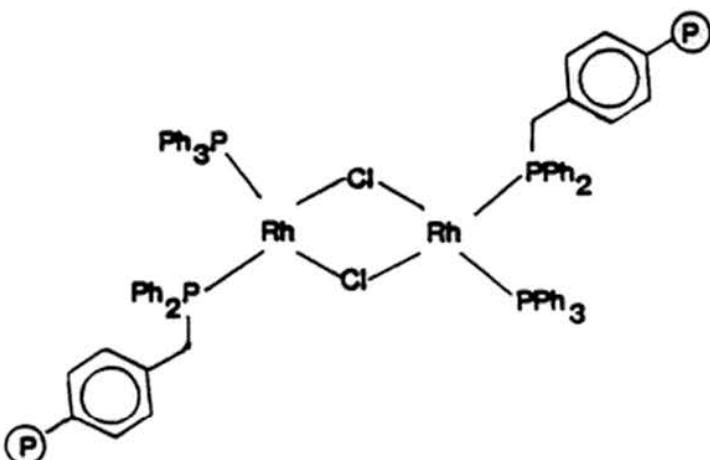
e)  $[\mu\text{-Cl-Rh}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Ph}-\text{P})]_2$ , where  $(\text{P})$  = polymer

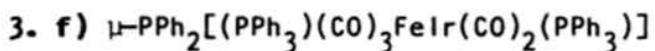
2	$[\mu\text{-Cl}]^-$	8 electrons	- 2
2	$\text{PPh}_3$	4 electrons	neutral
2	$\text{Ph}_2\text{P}(\text{CH}_2\text{Ph}-\text{P})$	4 electrons	neutral
2	Rh(I)	<u>16 electrons</u>	+ 2
	Total	32 electrons	

$[18(2)-32]/2 = 2$  Rh-Rh bonds predicted

Although 2 Rh-Rh bonds are predicted, the actual structure of the complex involves no M-M bonds. This is an example of a coordinatively unsaturated square planar rhodium dimer.

Collman, J.P.; Hegedus, L.S.; Cooke, M.P.; Norton, J.R.; Dolcetti, G.; Marquardt, D.N. *J. Am. Chem. Soc.* 1972, 94, 1789.

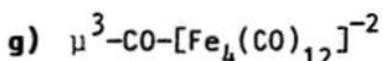
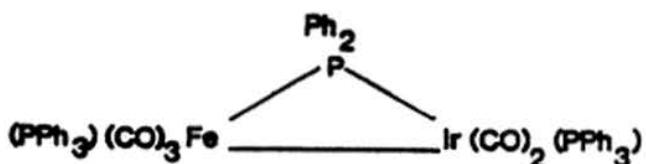




2	$\text{PPPh}_3$	4 electrons	neutral
5	CO	10 electrons	neutral
	$[\mu\text{-PPPh}_2]^-$	4 electrons	- 1
	Fe(1)	7 electrons	+ 1
	Ir(0)	<u>9 electrons</u>	neutral
Total		34 electrons	

$$[18(2)-34]/2 = 1 \text{ Fe-Ir bond predicted}$$

Mercer, W.C.; Whittle, R.R.; Burkhardt, E.W.; Geoffroy, G.L. Organomet. 1985, 4, 68.

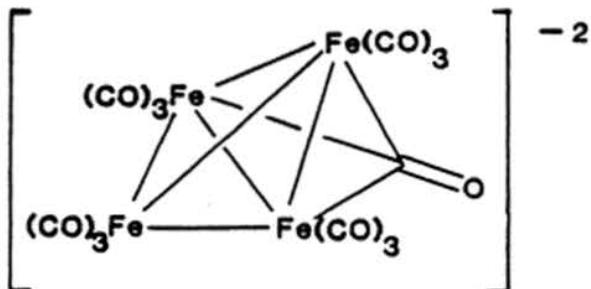


13	CO	26 electrons	neutral
2	Fe(-1)	18 electrons	- 2
2	Fe(0)	<u>16 electrons</u>	neutral
Total		60 electrons	

$$[18(4)-60]/2 = 6 \text{ Fe-Fe bonds predicted}$$

Van Buskirk, G.; Knobler, C.B.; Kaesz, H.D. Organomet. 1985, 4, 149.

The structure was originally determined by Doedens, R.J.; Dahl, L.F. J. Am. Chem. Soc. 1966, 88, 4847.



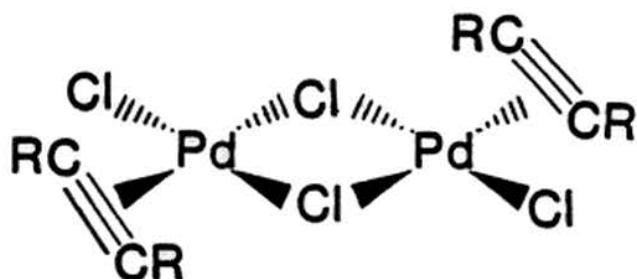
3. h)  $[\mu\text{-Cl-PdCl}(\text{RC}\equiv\text{CR})]_2$ 

2	$[\mu\text{-Cl}]^-$	8 electrons	- 2
2	$\text{Cl}^-$	4 electrons	- 2
2	$\text{RC}\equiv\text{CRR}$	4 electrons	neutral
2	Pd(II)	<u>16 electrons</u>	+ 4
	Total	32 electrons	

$$[18(2)-32]/2 = 2 \text{ Pd-Pd bonds predicted}$$

Although 2 Pd-Pd bonds are predicted based on the above calculation, the actual structure is a coordinatively unsaturated species with no metal-metal bonds. This is often the case with square-planar Pd or Pt dimers.

Collman, J.P.; Hegedus, L.S. "Principles and Applications of Organotransition Metal Chemistry", 1st ed., University Science Books (Mill Valley, CA, 1980), p. 639.

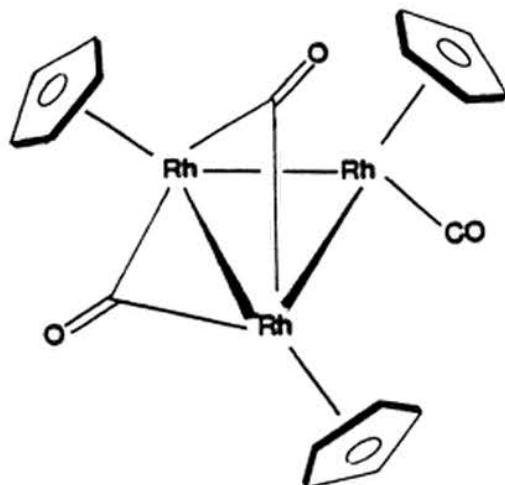
i)  $(\mu\text{-CO})_2\text{-}[\text{CpRh}]_3(\text{CO})$ 

2	$\mu\text{-CO}$	4 electrons	neutral
3	$\text{Cp}^-$	18 electrons	- 3
	CO	2 electrons	neutral
3	Rh(I)	<u>24 electrons</u>	+ 3
	Total	48 electrons	

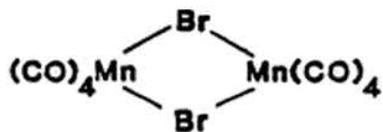
$$[18(3)-48]/2 = 3 \text{ Rh-Rh bonds predicted}$$

Lawson, R.J.; Shapley, J.R. Inorg. Chem. 1978, 17, 772.

i) (cont.)

j)  $(\mu\text{-Br})_2[\text{Mn}(\text{CO})_4]_2$ 

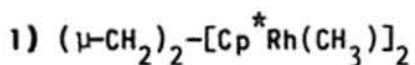
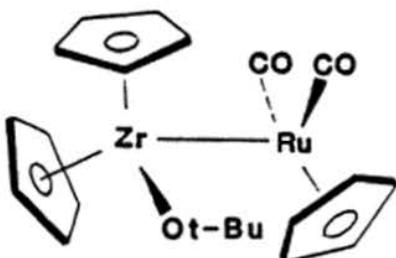
8	CO	16 electrons	neutral
2	$\mu\text{-Br}$	8 electrons	- 2
2	Mn(I)	<u>12 electrons</u>	+ 2
	Total	36 electrons	

 $[2(18)-36]/2 = 0$  Mn-Mn bonds predicted.k)  $\text{Cp}_2(0\text{-t-Bu})\text{ZrRu}(\text{CO})_2\text{Cp}$ 

3	$\text{Cp}^-$	18 electrons	- 3
	$\text{t-BuO}^-$	2 electrons	- 1
2	CO	4 electrons	neutral
	Zr(III)	1 electron	+ 3
	Ru(I)	<u>7 electrons</u>	+ 1
	Total	32 electrons	

 $[2(18)-32]/2 = 2$  Zr-Ru bonds predicted; however, only one is actually observed.

3. k) (cont.) Casey, C.P.; Jordan R.F. J. Am. Chem. Soc. 1983, 105, 665.

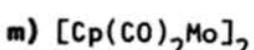
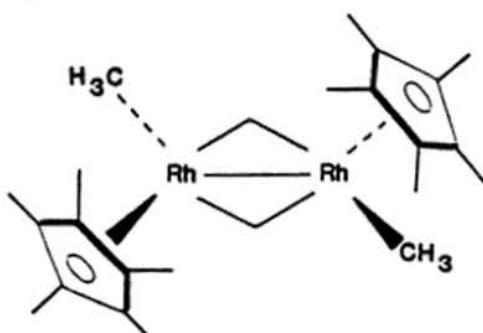


2	$\mu\text{-CH}_2^{-2}$	8 electrons	- 4
2	$[\text{Cp}^*]^-$	12 electrons	- 2
2	$\text{CH}_3^-$	4 electrons	- 2
2	Rh(IV)	<u>10 electrons</u>	+ 8
<b>Total</b>		<b>34 electrons</b>	

$[2(18)-34]/2 = 1$  Rh-Rh bond predicted.

Okeya, S.; Taylor, B.F.; Maitlis, P.M. J. Chem. Soc., Chem. Comm. 1983, 971.

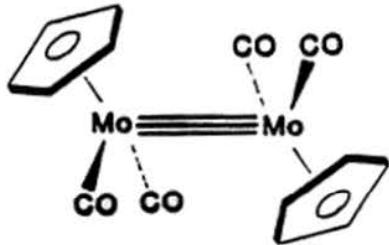
Mann, B.E.; Meanwell, N.J.; Spencer, C.M.; Taylor, B.F.; Maitlis, P.M. J. Chem. Soc., Dalton Trans. 1985, 1555.



2	$\text{Cp}^-$	12 electrons	- 2
4	CO	8 electrons	neutral
2	Mo(I)	<u>10 electrons</u>	+ 2
<b>Total</b>		<b>30 electrons</b>	

$[2(18)-30]/2 = 3$  Mo-Mo bonds predicted.

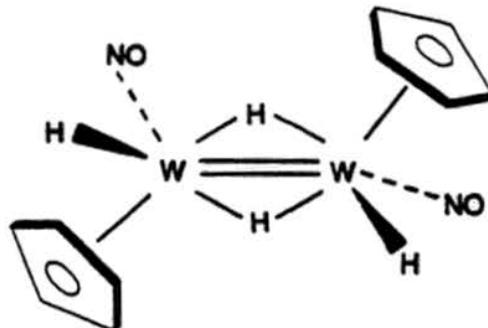
## 3. m) (cont.)



Klingler, R.J.; Butler, W.; Curtis, M.D. J. Am. Chem. Soc. 1975, 97, 3535.

n)  $[\mu\text{-H}]_2 - [\text{Cp}(\text{NO})\text{W}(\text{H})]_2$ 

2	$\text{Cp}^-$	12 electrons	- 2
2	$\text{H}^-$	4 electrons	- 2
2	$\text{NO}^+$	4 electrons	+ 2
2	$\mu\text{-H}^-$	4 electrons	- 2
2	$\text{W}(\text{II})$	<u>8 electrons</u>	+ 4
Total		32 electrons	



and other isomers

$$[2(18)-32]/2 = 2 \text{ W-W bonds predicted}$$

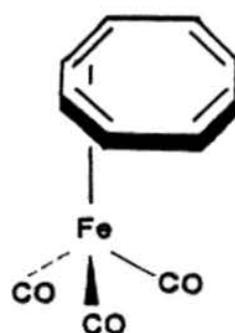
Legzdins, P.; Martin, J.T.; Oxley, J.C. Organomet. 1985, 4, 1263.

4. a)  $\text{Ni}(\text{CO})_4$ , tetrahedral

4	$\text{CO}$	8 electrons	neutral
	$\text{Ni}(0)$	<u>10 electrons</u>	neutral
Total		18 electrons	

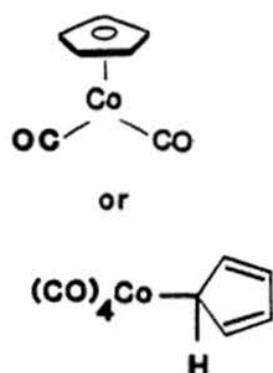
b)  $(\text{CO})_3\text{Fe}(\text{COT})$ 

3	$\text{CO}$	6 electrons	neutral
	$\text{Fe}(0)$	8 electrons	neutral
	COT	<u>4 electrons</u>	neutral
Total		18 electrons	

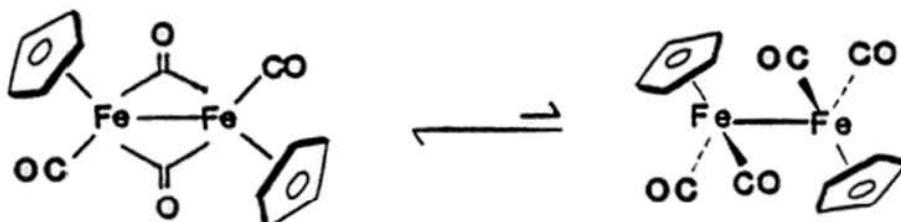


4. c)  $\text{CpCo}(\text{CO})_2$ 

2	CO	4 electrons	neutral
2	$\text{Cp}^-$	6 electrons	- 1
2	Co(I)	<u>8 electrons</u>	+ 1
Total		18 electrons	

d)  $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ 

4	CO	8 electrons	neutral
2	$\text{Cp}^-$	12 electrons	- 2
2	Fe(II)	<u>12 electrons</u>	+ 4
Total		34 electrons	plus 1 Fe-Fe bond

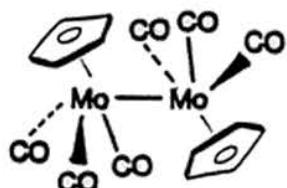
e)  $(\text{CO})_5\text{Re}-\text{H}$ , octahedral

5	CO	10 electrons	neutral
1	$\text{H}^-$	2 electrons	- 1
1	Re(I)	<u>6 electrons</u>	+ 1
Total		18 electrons	

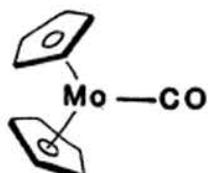
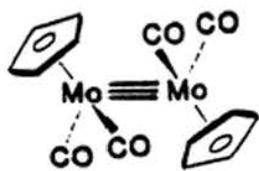
f)  $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ 

6	CO	12 electrons	neutral
2	$\text{Cp}^-$	12 electrons	- 2
2	Mo(II)	<u>8 electrons</u>	+ 4
Total		34 electrons	plus 1 Mo-Mo bond

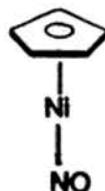
4. f) (cont.)



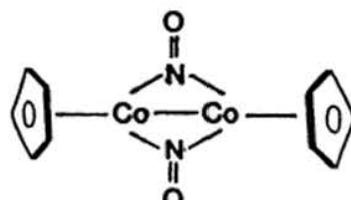
Other possibilities are  $[\text{Cp}(\text{CO})_2\text{Mo}]_2$  or  $\text{Cp}_2\text{Mo}(\text{CO})$

g)  $\text{CpNi}(\text{NO})$ 

$\text{Cp}^-$	6 electrons	- 1
$\text{NO}^+$	2 electrons	+ 1
$\text{Ni}(0)$	<u>10 electrons</u>	neutral
Total	18 electrons	

h)  $[\text{CpCo}(\text{NO})]_2$ 

2	$\text{Cp}^-$	12 electrons	- 2
2	$\text{NO}^+$	4 electrons	+ 2
2	$\text{Co}(I)$	<u>16 electrons</u>	+ 2
Total		34 electrons plus 1 Co-Co bond	



5. a) Tetrahedral b) Square planar c) Trigonal bipyramidal or octahedral if the complex is viewed as a metallacyclopropane d) Square planar e) Square planar f) Square planar g) Tetrahedral h) Square planar i) Square planar j) Distorted trigonal bipyramidal due to restrictions on the bond angles imposed by the chelating ligands.

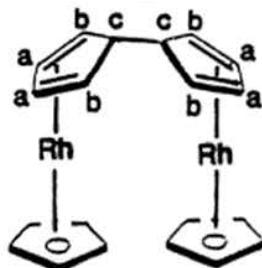
6. Both structures 1 and 2 contain two central allyl protons which should have a chemical shift in the NMR spectrum between 4 and 6 ppm, not at 2.2 ppm, so these two structures can be eliminated on this basis. The assignments of proton resonances for 3 are:

5.2 (s, 10 H, Cp)

5.0 (m, 4 H, H<sub>a</sub>)

3.3 (m, 4 H, H<sub>b</sub>)

2.2 (m, 2 H, H<sub>c</sub>)



Electron counts are as follows:

3

For 1 and 2, the electron count is the same:

2	Cp <sup>-</sup>	12 electrons	- 2
2	[n <sup>3</sup> -allyl] <sup>-</sup>	8 electrons	- 2
2	Rh(II)	14 electrons	+ 4
	Rh-Rh	<u>2 electrons</u>	neutral
Total		36 electrons	

For 3: 2 Cp<sup>-</sup> 12 electrons - 2

2	diene	8 electrons	neutral
2	Rh(I)	<u>16 electrons</u>	+ 2
Total		36 electrons	

Fischer, E.O.; Wawersik, H. J. Organomet. Chem. 1966, 5, 559.

7. a) W(CO)(detc)<sub>2</sub>(HC≡CH)

CO 2 e<sup>-</sup> neutral

2 detc 8 e<sup>-</sup> - 2

W(II) 4 e<sup>-</sup> + 2

HC≡CH 4 e<sup>-</sup> neutral

Total 18 electrons

Acetylene donates 4 electrons.

b) CpW(CO)(CH<sub>3</sub>)(HC≡CH)

CO 2 e<sup>-</sup> neutral

Cp<sup>-</sup> 6 e<sup>-</sup> - 1

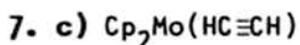
CH<sub>3</sub> 2 e<sup>-</sup> - 1

W(II) 4 e<sup>-</sup> + 2

HC≡CH 4 e<sup>-</sup> neutral

Total 18 electrons

Acetylene donates 4 electrons.



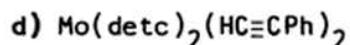
$2 \text{ Cp}^- \quad 12 \text{ e}^- - 2$

$\text{Mo(II)} \quad 4 \text{ e}^- + 2$

$\text{HC}\equiv\text{CH} \quad 2 \text{ e}^- \text{ neutral}$

Total 18 electrons

Acetylene donates 2 electrons.



$2 \text{ detc} \quad 8 \text{ e}^- - 2$

$\text{Mo(II)} \quad 4 \text{ e}^- + 2$

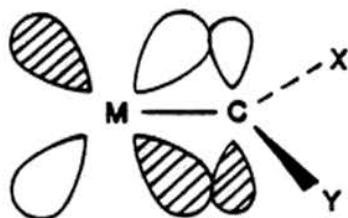
$2 \text{ HC}\equiv\text{CPh} \quad 6 \text{ e}^- \text{ neutral}$

Total 18 electrons

Each phenylacetylene donates 3 electrons.

Templeton, J.L.; Ward, B.C. J. Am. Chem. Soc. 1980, 102, 3288.

8. The bonding in a carbene complex is depicted below.



The pi bond between the metal and the carbon atoms arises as a result of a backbonding interaction between a filled metal d orbital of the appropriate symmetry and the empty carbene p orbital. Any factor that increases the electron density at the metal will increase the strength of the M-C pi bond, resulting in a higher activation energy for rotation around that bond. Aspects to consider include the d-electron count of the metal, the donor properties of the ligands, and in what row the metal is located.

a) In these two complexes, the only difference is the metal. The contrast between metals of different rows is apparent, with the rotational barrier increasing more than 2.3 kcal/mole on moving from second row molybdenum to third row tungsten. A possible explanation is that the electron density at a given metal atom increases down a column, thus the backbonding is increased and the metal-carbon pi bond is stronger.

b) In these two complexes, the only difference is the ligand. Because triethylphosphine is a better electron donor than triphenylphosphine, the complex with triethylphosphine as a ligand will have a stronger M-C pi bond.

c) Both Fe(II) and Re(I) are  $d^6$  metals, the iron with strong electron-donating ligands and the rhenium with one electron-donating ligand and one electron-withdrawing ligand. If the electronic properties of the ligand were the only operative factor, we would

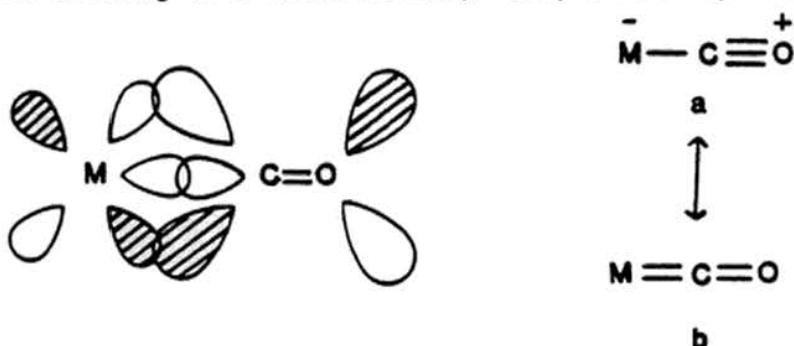
predict that the iron complex would have a higher  $\Delta G_{\text{rot}}^{\ddagger}$  than the rhenium complex. Since the observed trend is opposite, ligand effects must not be the major contributing factor. Thus, the increased electron density of a third row metal as compared to a first row metal explains the observed trends.

Brookhart, M.; Tucker, J.R.; Husk, G.R. J. Organomet. Chem. 1980, 193, C23.

Wong, W.K.; Tam, W.; Gladysz, J.A. J. Am. Chem. Soc. 1979, 101, 5440.

Kegley, S.E.; Brookhart, M.; Husk, G.R. Organomet. 1982, 1, 760.

**9. The bonding in a metal carbonyl complex is depicted below.**



The pi bond between the metal and the carbon atoms arises as a result of a backbonding interaction between a filled metal d orbital of the appropriate symmetry and the empty pi star orbital of the carbonyl. Any factor that increases the electron density at the metal will increase the strength of the M-C pi bond, and thus the contribution from resonance form b. The result is a decrease in the CO bond order and a resulting decrease in the CO stretching frequency in the infrared spectrum of the complex. Aspects to consider include the d-electron count of the metal, the donor properties of the ligands, and the charge on the complex.

a) Both metals are  $d^6$ , but since  $[\text{W}(\text{CO})_5\text{Cl}]^-$  is anionic, it will have a lower CO stretching frequency.

b) The  $d^8 \text{Fe}(\text{CO})_5$  has more electron density at the metal center than the  $d^6 \text{Fe}(\text{CO})_4\text{Br}_2$  because of the lower oxidation state of the metal, thus  $\text{Fe}(\text{CO})_5$  will have a lower CO stretching frequency.

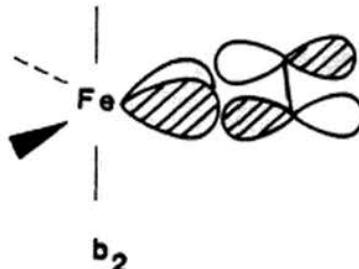
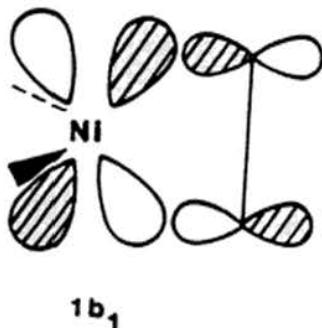
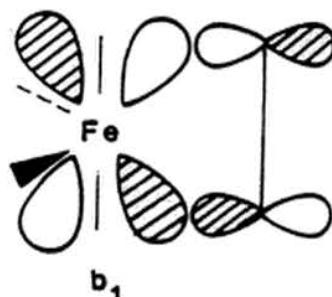
c) Both metals are  $d^6$ , but addition of phosphine ligands will increase the electron density at the metal. Thus, the CO stretch for  $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  will be at a lower frequency than that for  $\text{Mo}(\text{CO})_6$ .

d) The only difference between these two complexes is the nature of the ligands. Since trimethylphosphine is a better donor than

9. d) (cont.) triphenylphosphine,  $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$  will have a lower stretching frequency.

e) Both metals are  $d^8$ , but since  $[\text{Cp}(\text{CO})_2\text{Fe}]^-$  is anionic, it will have the lower CO stretching frequency.

10. For both a) and b), there are only two orbitals of the appropriate symmetry to interact with the olefin pi star orbitals, the  $b_2$  and the lowest energy  $b_1$ . The metal orbitals of a symmetry can only interact with the ethylene pi orbital and therefore have no preference for the orientation of the ethylene ligand.

 $b_2$  $b_2$  $1b_1$  $b_1$ 

In order to distinguish which orientation will give the lower overall energy, it is useful to draw interaction diagrams (See Figures 2-1 and 2-2 on the following page for the  $\text{NiL}_2$  case).

For both iron and nickel, the  $1b_1$  orbital on the metal is lower in energy than the  $b_2$  orbital, and thus interacts less with the relatively high-energy ethylene orbital of the same symmetry, since in general, the amount of bonding interaction between two orbitals is dependent on how close in energy they are. Thus, the lowest energy conformation will be that arising from interaction of the  $b_2$  orbital on the metal with the ethylene ligand. In addition, the  $b_2$  extends farther out in space and so has better overlap with the ethylene pi star orbitals, although this fact is not obvious from the information given.

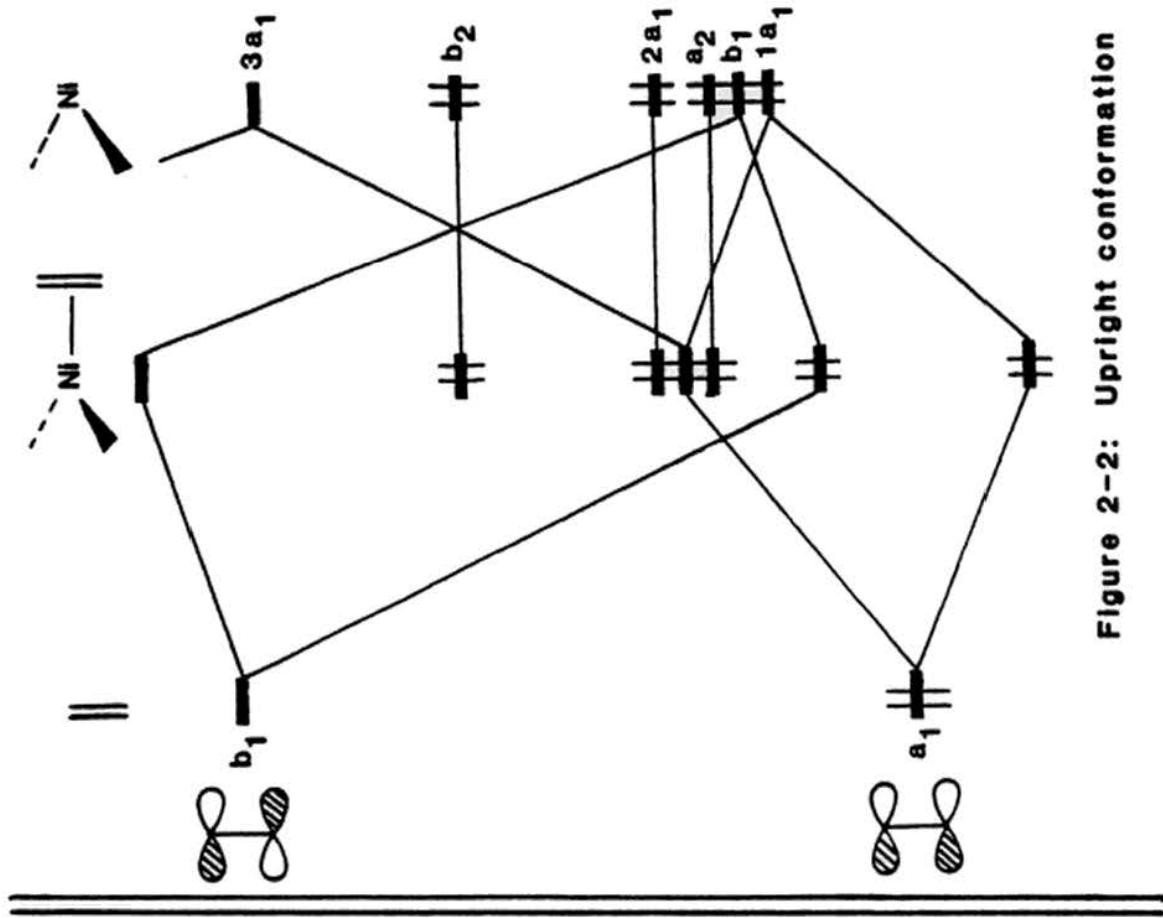


Figure 2-2: Upright conformation

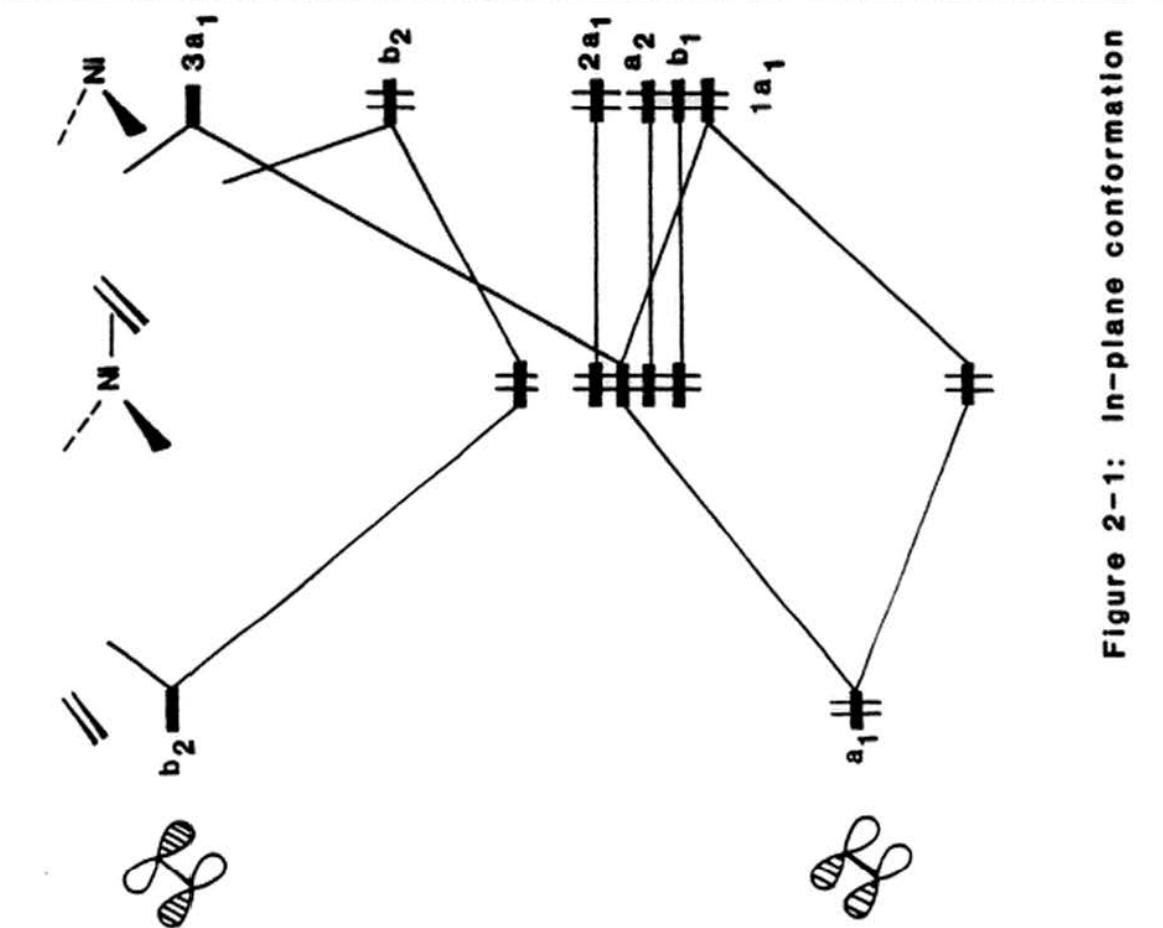
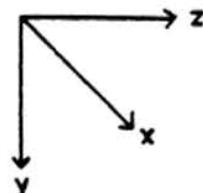
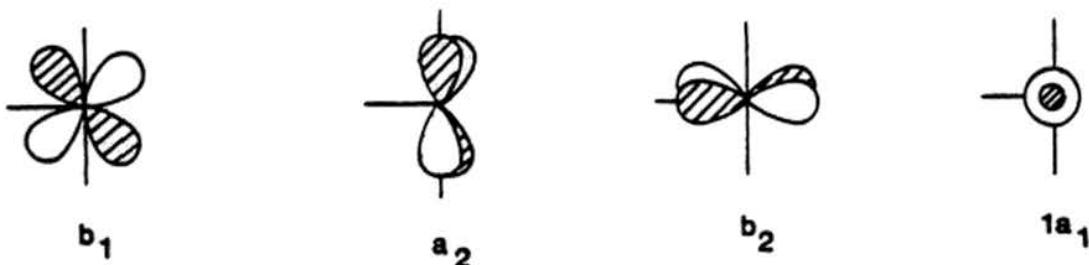


Figure 2-1: In-plane conformation

10. c) Electronically, either answer is correct. The barrier to rotation in Zeiss' salt is mainly steric and the observed orientation is perpendicular to the plane of the three chlorines, in order to minimize interactions between ethylene and the chlorines.



The  $a_1$  orbital does not have a rotational preference, the  $b_1$  orbital would prefer the in-plane geometry, and the  $b_2$  orbital would prefer the observed out-of-plane geometry. The  $b_1$  and  $b_2$  orbitals have similar energies and hybridizations, so both can bond equally well to the ethylene. With the in-plane geometry, there is a significant steric interaction between the chlorines and the ethylene; therefore the out-of-plane geometry is preferred.



Albright, T.A.; Hoffmann, R.; Thibeault, J.C.; Thorn, D.L. J. Am. Chem. Soc. 1979, 101 3801.

11. a)  $\text{CoBr}_2(\text{CO})\text{L}_2$  is a 17-electron species.

2	$\text{Br}^-$	4 electrons	- 2
	CO	2 electrons	neutral
2	L	4 electrons	neutral
	Co(II)	<u>7 electrons</u>	+ 2
	Total	17 electrons	

b) The CO stretching frequencies are indicative of the strength of the carbon-oxygen bond, and of the electron donating ability of the donor ligand. There are two resonance forms for the bonding of a metal-carbonyl:



A low CO stretching frequency is indicative of a significant amount of electron density between the metal and the carbonyl carbon and a significant amount of backbonding into the pi star orbital of the carbon monoxide (resonance structure I). This situation arises when the metal has electron-rich ligands. A metal with electron-deficient ligands would be more accurately represented by resonance structure II, for which a higher CO stretching frequency would be expected. For this reaction, electronic effects appear to be important if we compare complexes with ligands of identical steric requirements (cone angles). For example, for  $\text{P}(\text{n-Pr})_3$  and  $\text{PEt}_2\text{Ph}$ ,  $K_d$  increases with an increase in the CO stretching frequency.

Nevertheless, the dominant factor in these reactions appears to be the steric requirements of the phosphine ligands. The observed trend for the dissociation constants for these cobalt complexes correlates very well with cone angle, with a marked increase in  $K_d$  with an increase in the cone angle. Two causes of this effect are:

- 1) Release of strain energy upon loss of a ligand.
- 2) A secondary electronic effect which results from a longer M-P bond (and thus, less electron donation from the phosphine to the metal) because of the steric requirements of the groups on the phosphine ligand.

Tolman, C.A. Chem. Rev. 1977, 77, 313.

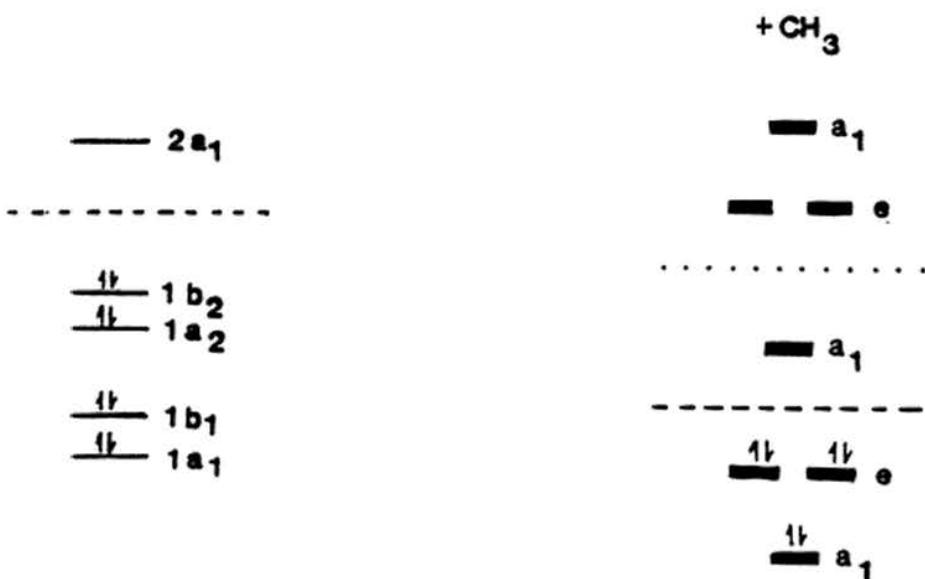
Tolman, C.A.; Seidel, W.C.; Gosser, L.W. J. Am. Chem. Soc. 1974, 96, 53.

Bressan, M.; Corain, B.; Rigo, P.; Turco, A. Inorg. Chem. 1970, 9, 1733.

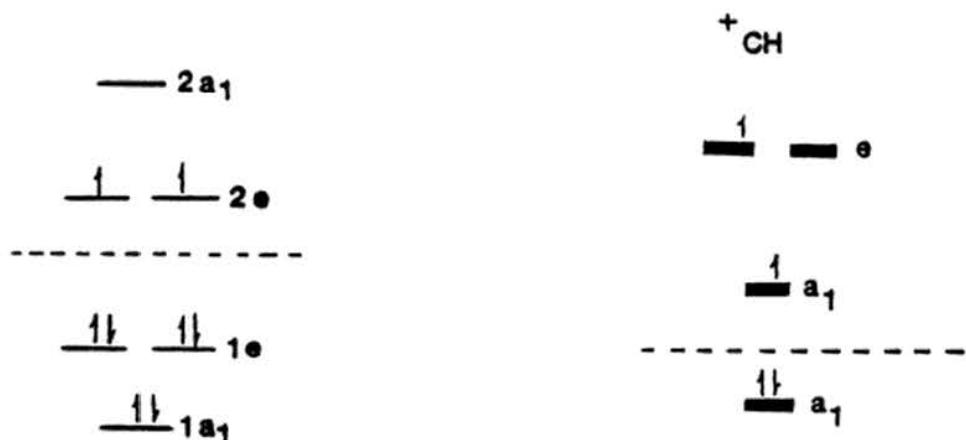
12. The proper approach for this problem is to:

- 1) Choose the correct molecular orbital diagram based on the geometry of the metal fragment.
- 2) Fill the metal orbitals with the appropriate number of d electrons.
- 3) Separate the relevant orbitals from the others, disregard the other orbitals, and compare the resulting MO diagram to the hydrocarbon fragment MO diagrams. (In the solutions that follow, the relevant orbitals are separated from the other orbitals by dotted lines.)
- 4) Choose the appropriate hydrocarbon fragment, supply enough electrons to match the d electron configuration of the metal, and assign a charge to the carbon fragment.
- 5) If all has gone well, get a beer.

a) The  $[\text{PtCl}_3]^-$  fragment is diagram D,  $d^8$ .  $\text{CH}_3^+$  is isolobal. With the  $\text{ML}_3$  (D) fragment, there is an additional nonbonding orbital,  $1a_1$  (similar to a  $dz^2$ ), that arises when this fragment is formed by removal of two axial (or trans) ligands from an  $\text{ML}_5$  system. Removal of these ligands decreases the energy of the  $a_1$  orbital and it becomes part of the nonbonding set. Thus for system D, there are four nonbonding orbitals that become unimportant in the isolobal analysis.

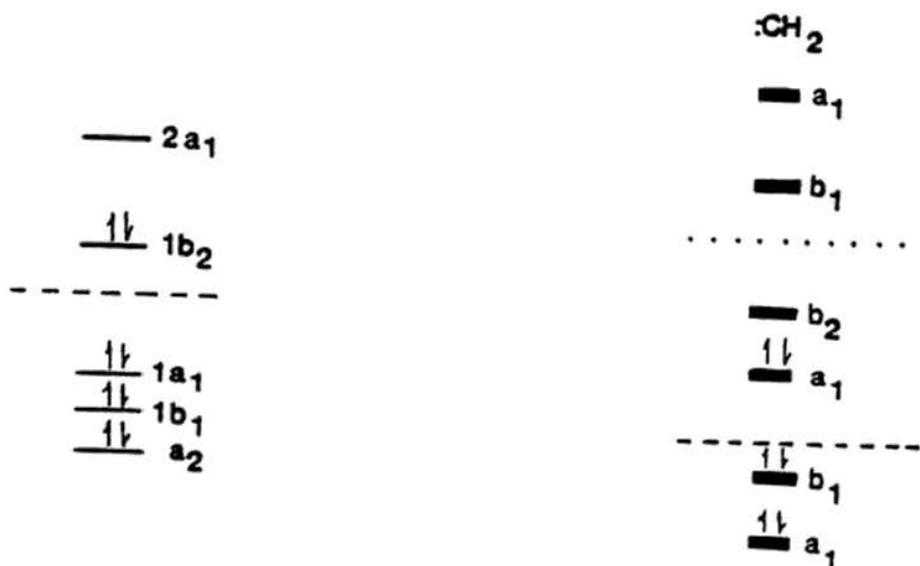


12. b) The  $\text{Fe}(\text{CO})_3$  fragment is diagram C,  $d^8$ .  ${}^+\text{CH}$  is isolobal.

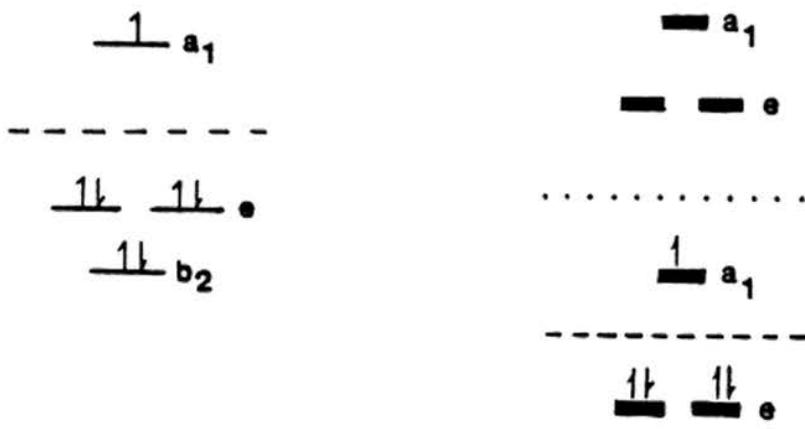


Note that the isolobal analogy does not imply that the ordering of the energy levels is the same for the metal fragment as for the carbon fragment; instead it tells us only that the number of available orbitals and electrons is the same. For both  $\text{Fe}(\text{CO})_3$  and  ${}^+\text{CH}$ , there are two electrons and three available orbitals.

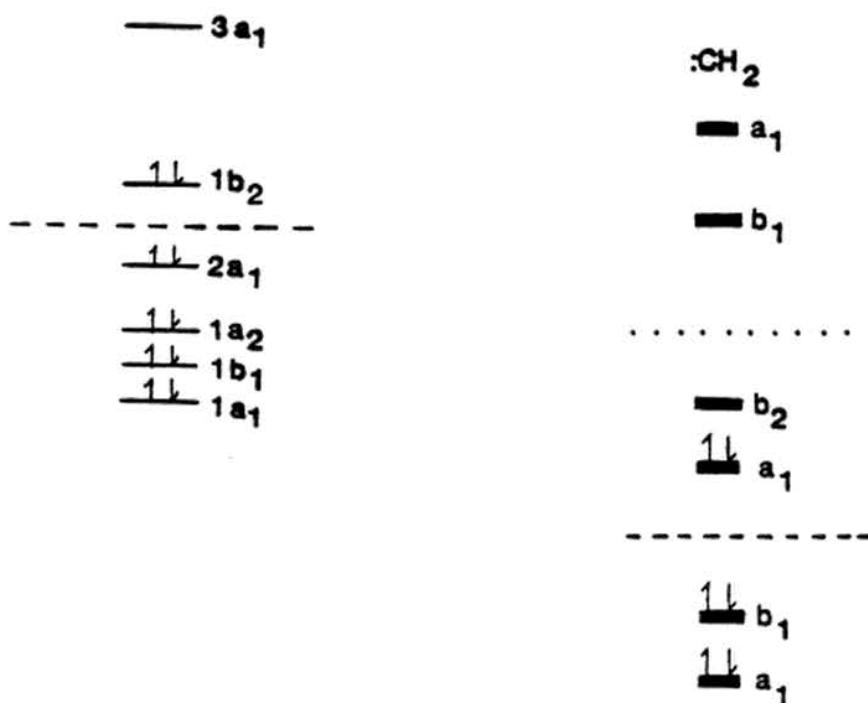
- c) The  $(\text{CO})_4\text{Fe}$  fragment is diagram B,  $d^8$ .  $:\text{CH}_2$  is isolobal.



12. h) The  $\text{Re}(\text{CO})_5$  fragment is diagram A,  $d^7$ .  $\cdot\text{CH}_3$  is isolobal.



i) The  $\text{Ni}(\text{CO})_2$  fragment is diagram E,  $d^{10}$ .  $\cdot\text{CH}_2$  is isolobal. With the  $\text{ML}_2$  (E) fragment, there is an additional nonbonding orbital,  $2\text{a}_1$  (similar to a  $\text{dz}^2$ ), that arises when this fragment is formed by removal of two axial (or trans) ligands from an  $\text{ML}_4$  system (Diagram B). Removal of these ligands decreases the energy of the  $2\text{a}_1$  orbital and it becomes part of the nonbonding set. Thus for system E, there are four nonbonding orbitals that become unimportant in the isolobal analysis.



12. (cont.) Note that most of these examples contain metals with a high d-electron count. These systems were chosen because the splitting between the bonding and nonbonding orbitals is large and thus electrons are necessarily added to the lower levels first. When the gap between nonbonding and bonding orbitals is relatively small, as for metals with a lower d-electron count, a number of possibilities exist for filling up the orbitals. For more information, see Hoffmann, R. Angew. Chem. Int. Ed. Engl., 1982, 21, 711.

Other useful references are:

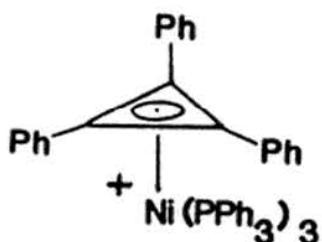
Elian, M.; Hoffmann, R. Inorg. Chem. 1975, 14, 1058.

Elian, M.; Chen, M.M.L.; Mingos, D.M.P.; Hoffmann, R. Inorg. Chem. 1976, 15, 1148.

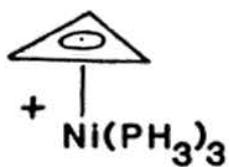
Hoffmann, R. Science 1981, 211, 995.

Pinhas, A.R.; Albright, T.; Hofmann, P.; Hoffmann, R. Helv. Chim. Acta. 1980, 63, 29.

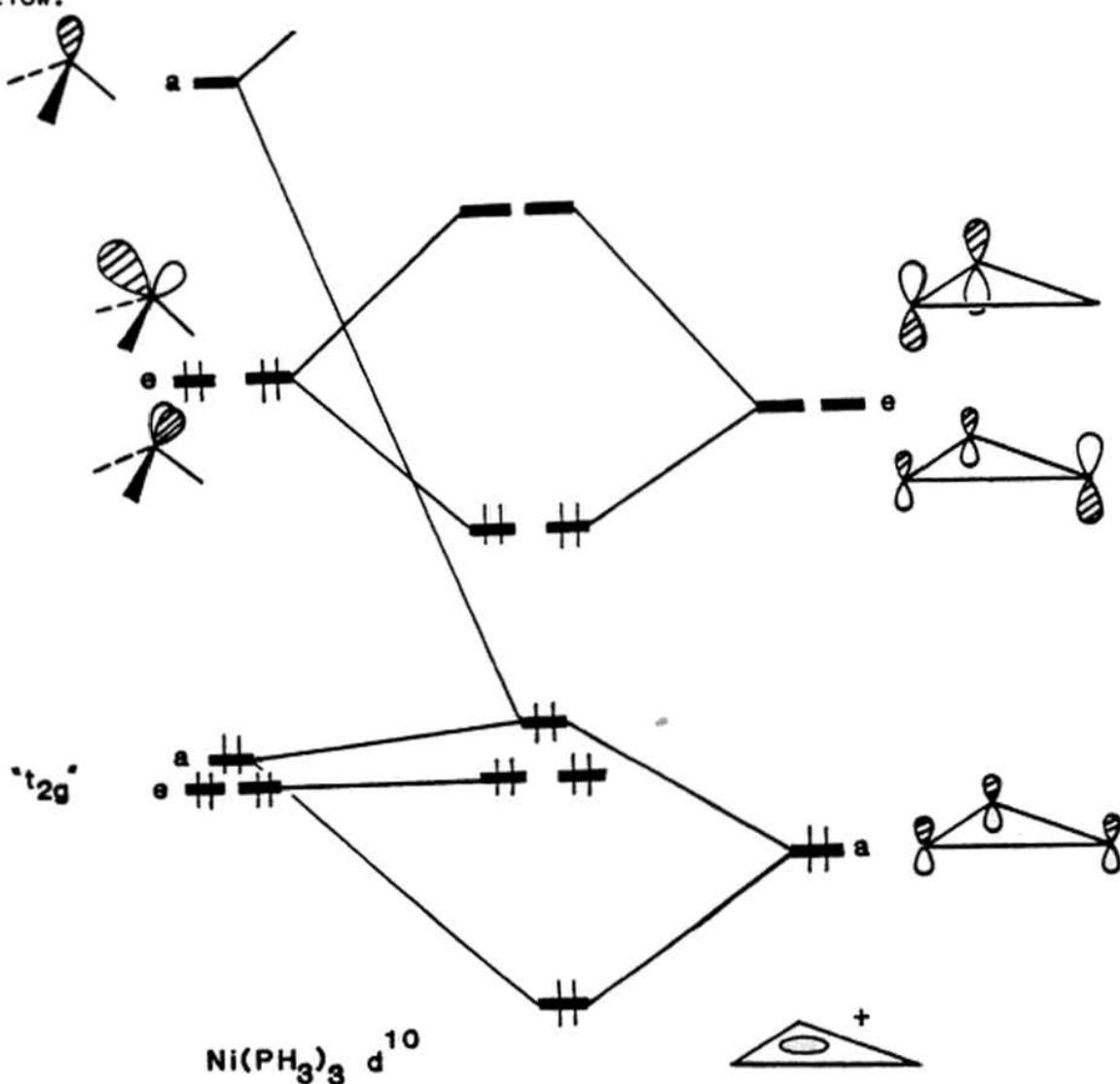
13. The complex that was actually studied experimentally was



and the one studied theoretically was



13. (cont.) The molecular orbital interaction diagram is shown below.



a) The major interaction is between the filled  $\text{ML}_3 \text{ e}$  set and the empty cyclopropenyl  $\text{e}$  set. These orbitals also determine the relative orientation.

b) Looking at the symmetric set of orbitals, it is clear that maximum overlap is obtained by conformation 2.



13. (cont.) The antisymmetric set of orbitals also prefers the same relative orientation of the two  $C_3$  rotors.



Thus the relative orientation (from a top view of the molecule) is shown below.



Mealli, C.; Midollini, S.; Moneti, S.; Sacconi, L.; Silvestre, J.; Albright, T.A. J. Am. Chem. Soc. 1982, 104, 95.

Jemmis, E.D.; Hoffmann, R. J. Am. Chem. Soc. 1980, 102, 2570.

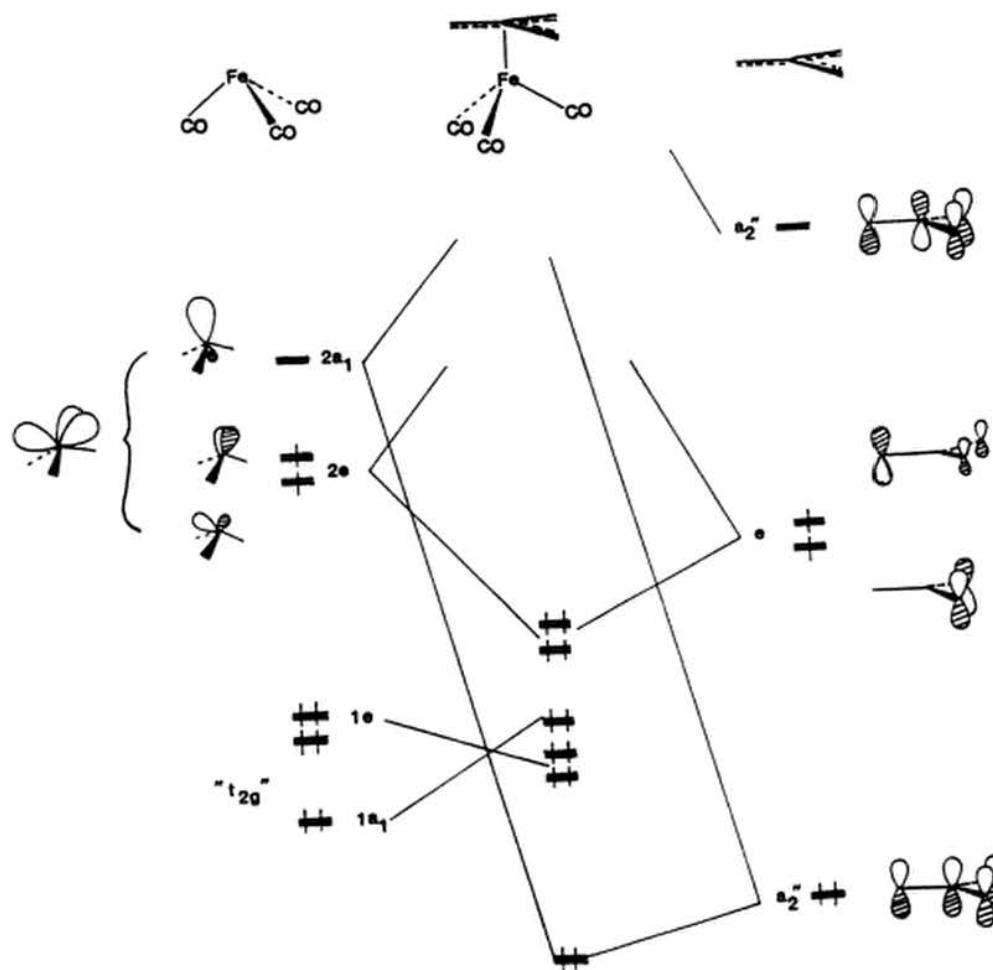
14. In the formyl complex, the best pi bonding between the p orbital of the formyl ligand and a metal d orbital will occur when the p orbital is aligned with the higher energy orbital, I, because of the better donor properties of triphenylphosphine compared to nitrosyl. Thus, the formyl ligand in this rhenium complex is oriented such that it is aligned with the nitrosyl group as shown below.



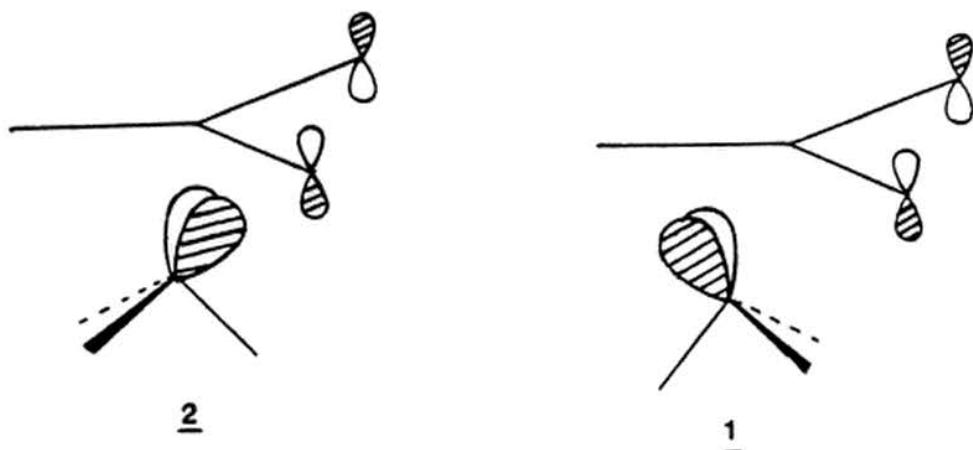
Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W.A.; Wong, V.K.; Gladysz, J.A. J. Am. Chem. Soc. 1982, 104, 141.

Schilling, B.E.R.; Hoffmann, R.; Faller, J.W. J. Am. Chem. Soc. 1979, 101, 592.

15. The molecular orbital interaction diagram for  $\text{Fe}(\text{CO})_3$  and trimethylenemethane is shown below.



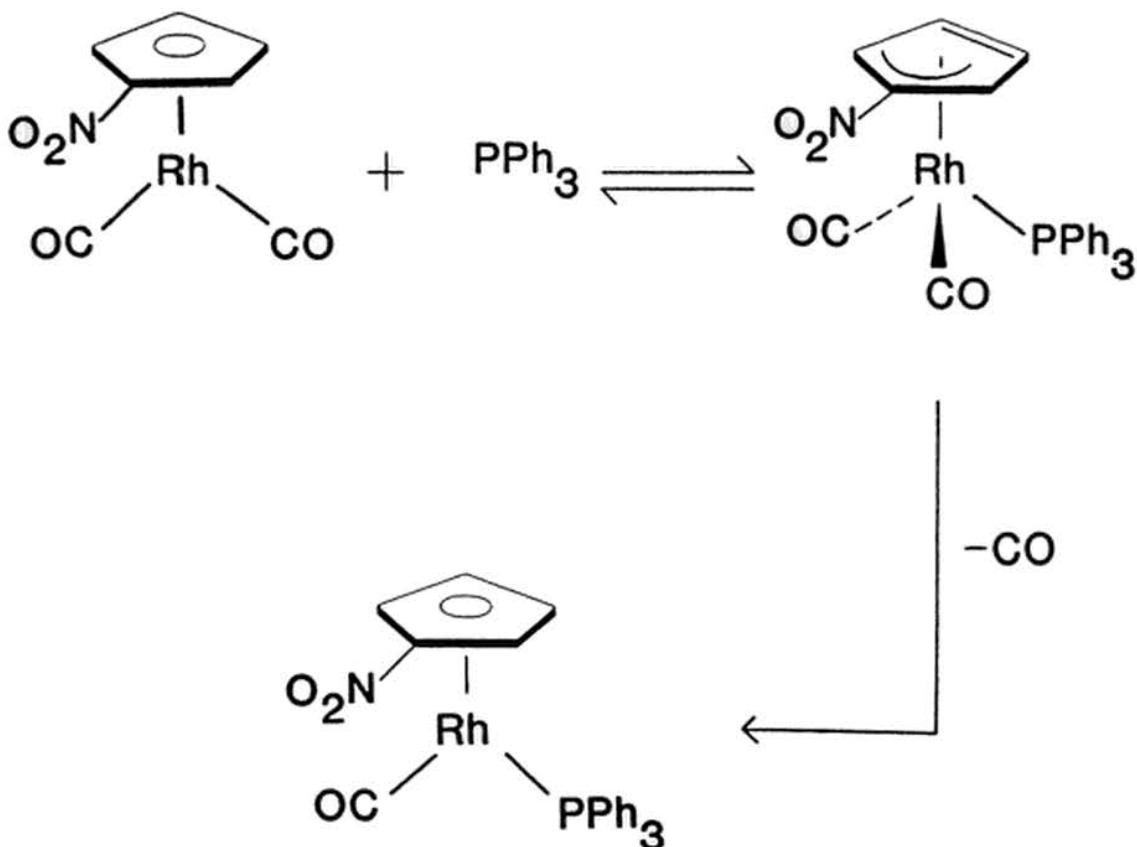
The preferred orientation is 2, since maximum orbital overlap is obtained in this conformation.



Albright, T.A.; Hofmann, P.; Hoffmann, R. J. Am. Chem. Soc. 1977, 99, 7546.

# 3

## Ligand Substitution Reactions

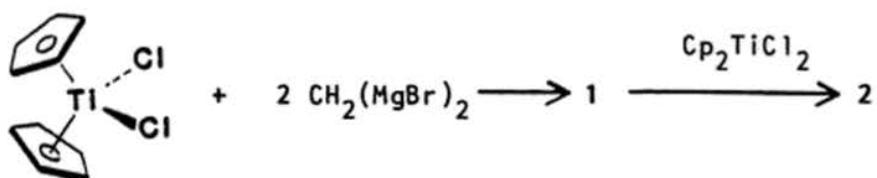


### 3: LIGAND SUBSTITUTION REACTIONS

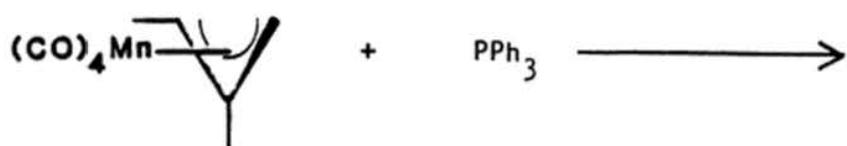
#### QUESTIONS

1. Predict reasonable products for the following reactions.

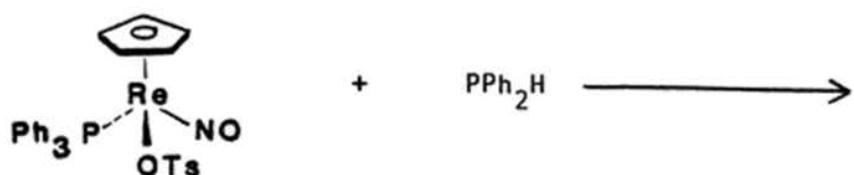
a)



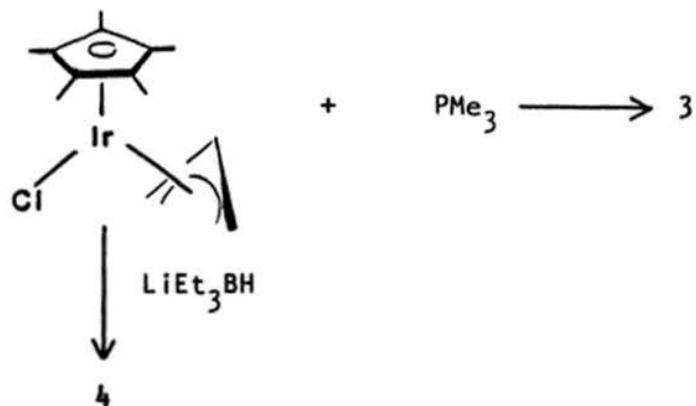
b)



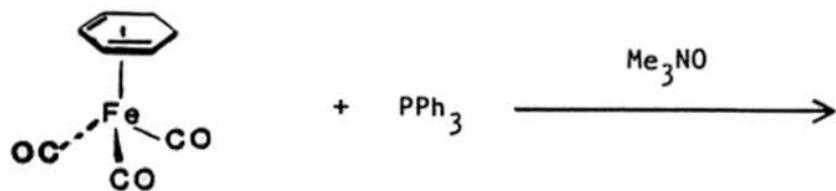
c)



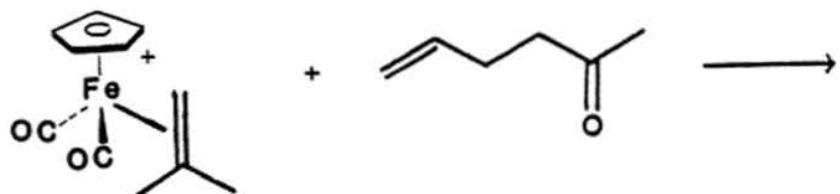
d)



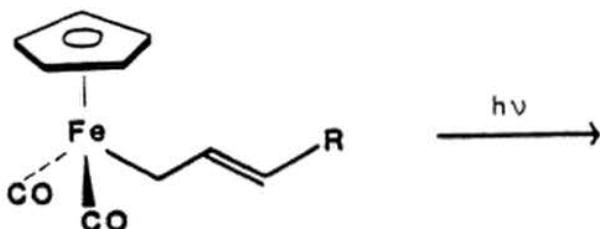
e)



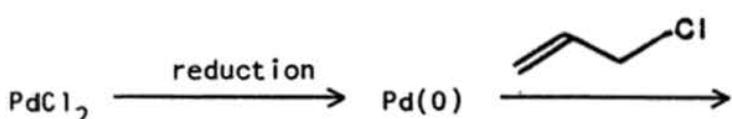
1. f)



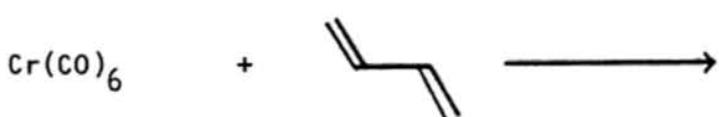
g)



h)



i)



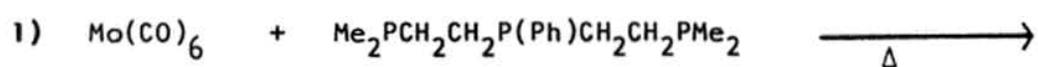
j)



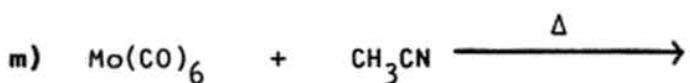
k)



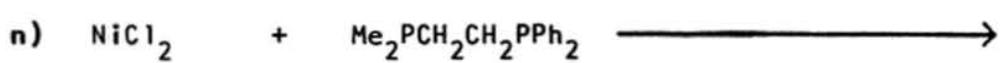
l)



m)

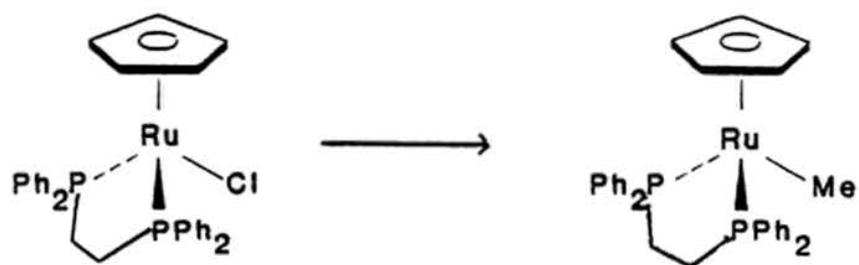


n)



2. Suggest reagents to carry out the following transformations.

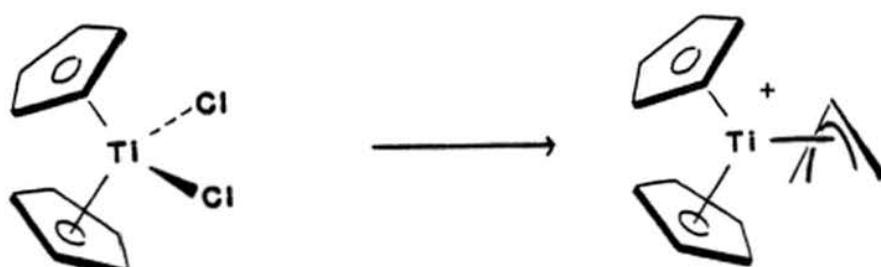
a)



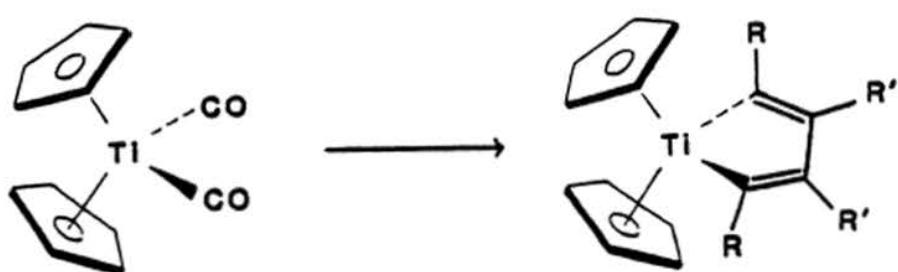
2. b)



c)



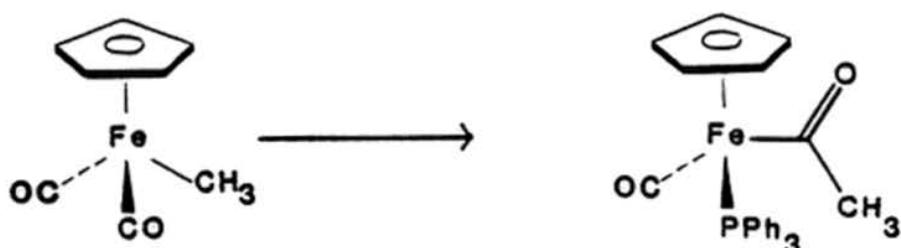
d)



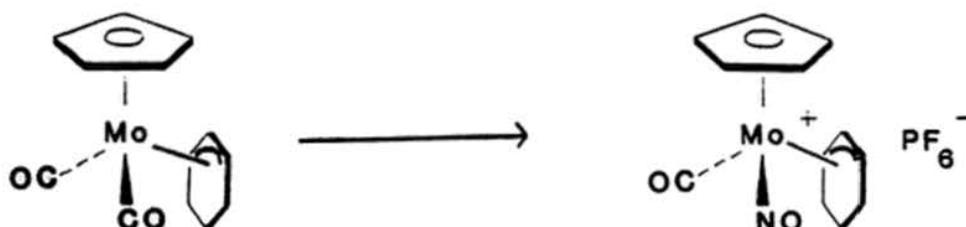
e)



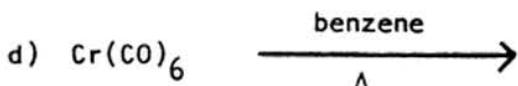
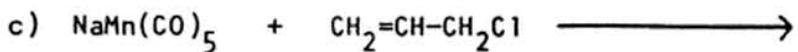
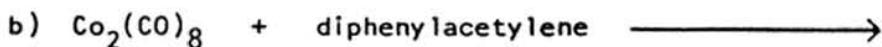
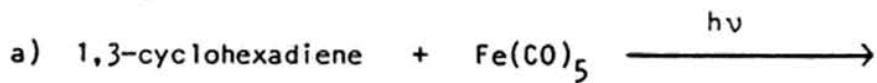
f)



g)



3. Provide metal-containing products for each of the following reactions:



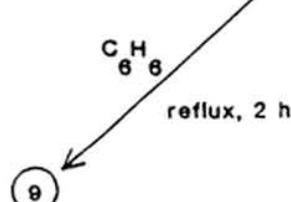
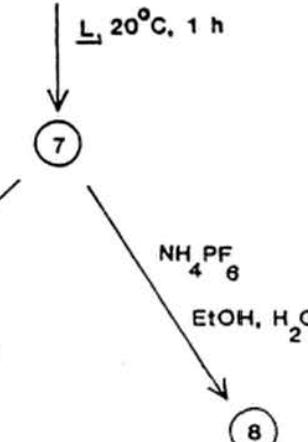
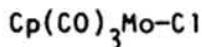
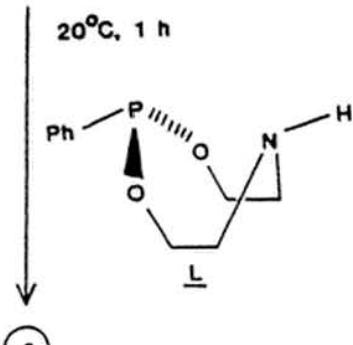
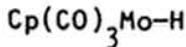
HINT

This is a dimeric product.

4. A mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$  dissolved in hexane was irradiated for 45 minutes with ultraviolet light from a mercury lamp. Volatile liquids were then removed under vacuum and the solid residue sublimed onto a cold finger as red crystals. This compound (5) was quite soluble in organic solvents; its IR spectrum showed bands at 2067, 2019, and  $1987\text{ cm}^{-1}$ . The mass spectrum of 5 showed a series of ions separated by 28 mass units starting at m/e 166 and proceeding to m/e 558. Significant amounts of other series of ions beginning at m/e 55, 56, and 111 were observed, but not from m/e 110. [Note:  $^{55}\text{Mn}$  and  $^{56}\text{Fe}$  are the dominant isotopes for manganese and iron, respectively.]

- Formulate a structure for 5 and relate it to the data given.
- Show that your structure conforms to the 18 electron rule.

5. The following reactions occur:



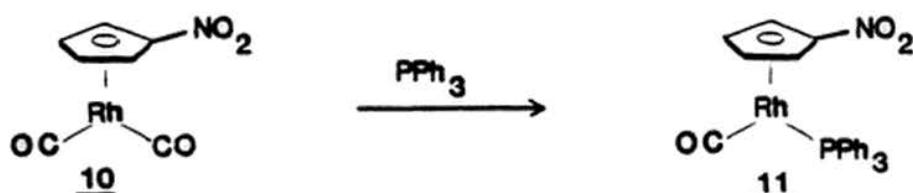
5. (cont.) Postulate structures for **6**, **7**, **8**, and **9** based on the data.

Complex	$^1\text{H}$ NMR	selected IR data ( $\text{cm}^{-1}$ )
<b>6</b>	3.44 (m, 4 H) 3.96 (m, 4 H) 5.26 (s, 5 H) 7.49 (m, 5 H) -6.41 (d, $J = 65 \text{ Hz}$ , 1 H)	3389 1945 1860
<b>7</b>	3.44 (m, 4 H) 4.01 (m, 4 H) 5.29 (s, 5 H) 7.50 (m, 5 H)	3355 1966 1880
<b>8</b>	3.21 (m, 4 H) 3.96 (m, 2 H) 4.64 (m, 2 H) 6.00 (s, 5 H) 7.42 (m, 1 H) 7.70 (m, 5 H)	3380-3400 1990 1900
<b>9</b>	3.38 (m, 4 H) 4.41 (m, 4 H) 5.06 (d, $J = 3 \text{ Hz}$ , 5 H) 5.72 (m, 1 H) 7.48 (m, 5 H)	3160 1800

## HINTS

- 1) Complex **8** is cationic.
- 2) Reaction of **6** with chloroform gives **7**.
- 3) N-H protons often appear as broad singlets which may be obscured by other proton resonances.
- 4) All complexes are 18-electron species.

## 6. Propose a mechanism for the following substitution reaction.



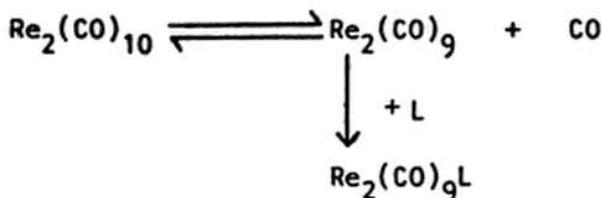
Your mechanism must be consistent with the following three observations:

- 1) Using excess  $\text{PPh}_3$ , the rate is first order in rhodium complex.
- 2) Plots of  $k_{\text{obs}}$  vs  $[\text{PPh}_3]$  are linear with a zero intercept.
- 3)  $\Delta S^\ddagger = -17.9 \text{ eu}$

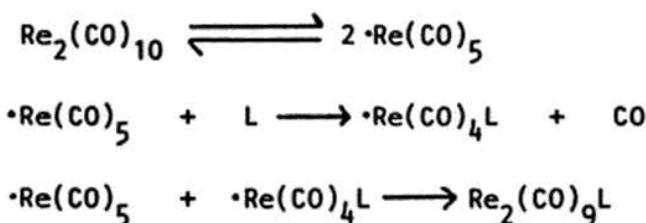
7. Two different mechanisms have been proposed to explain the following reaction.



Mechanism I



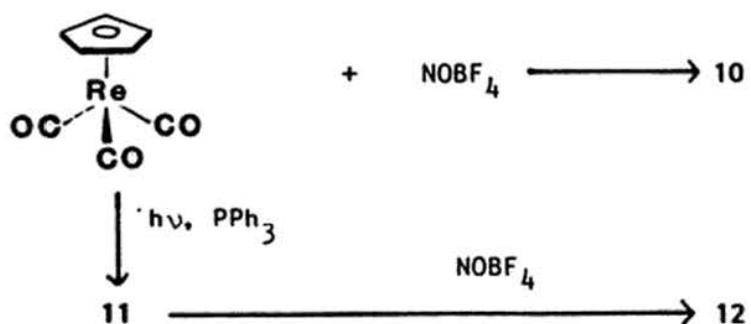
Mechanism II



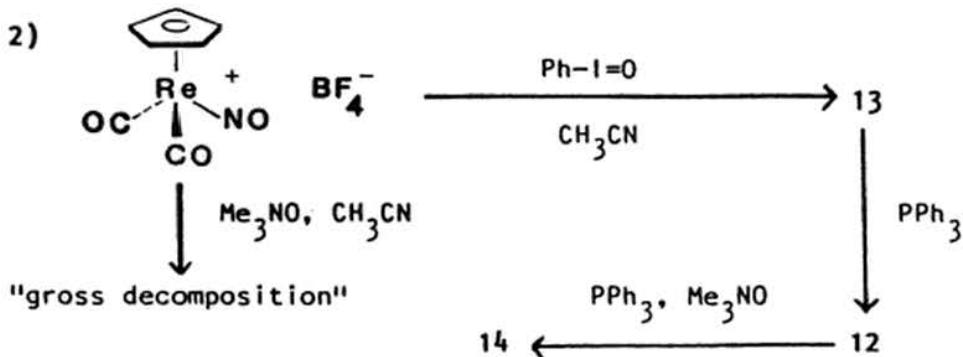
Using the fact that there are two isotopes of rhenium,  $^{185}\text{Re}$  and  $^{187}\text{Re}$ , how could you distinguish between these two mechanisms? What experimental technique(s) would be required?

8. Predict the products of the following reactions.

1)



2)

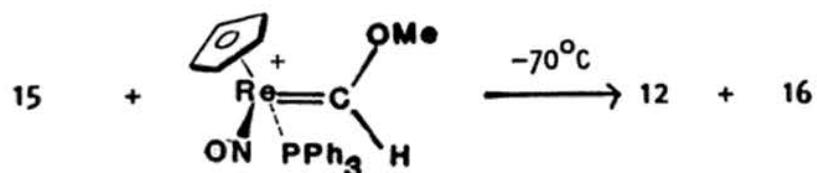


8. (cont.)

3)



4)

 $^1\text{H}$  NMR data for 15

7.50–7.36 (m, 15 H)  
5.25 (s, 5 H)  
16.48 (s, 1 H)

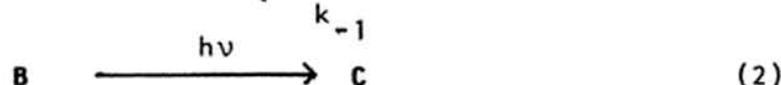
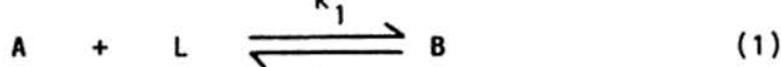
IR data for 15

$1560 \text{ cm}^{-1}$

 $^1\text{H}$  NMR data for 16

7.40–7.25 (m, 15 H)  
5.04 (d,  $J = 0.5 \text{ Hz}$ , 5 H)  
5.09 (d of d,  $J = 10.5, 5.6 \text{ Hz}$ , 1 H)  
5.45 (d of d,  $J = 10.5, 2.0 \text{ Hz}$ , 1 H)  
3.16 (s, 3 H)

9. Let  $A = [(\eta^6-\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$  and  $L = \text{PBu}_3$ .

Spectral DataIR( $\text{cm}^{-1}$ ) $^1\text{H}$  NMR( $\delta$ , acetone- $d_6$ )

A            2080, 2026            6.90

B            2028, 1950            6.30 (1 H), 5.50 (2 H),  
                                        4.40 (1 H), 3.40 (2 H),  
                                        plus  $\text{PBu}_3$  resonances

C            1997, 1950            6.42 plus  $\text{PBu}_3$  resonances

a) Identify B and C.

b) Kinetic data were obtained for the approach to equilibrium for reaction (1) with L in excess. The rate expression is shown in equation (3).

$$-\frac{d[A]}{dt} = (k_1[L] + k_{-1})([A] - [A]_\infty) \quad (3)$$

or in a simplified form,

## 9. (cont.)

$$-\frac{d[A]}{dt} = k_{\text{obs}}([A] - [A]_{\infty}) \quad (4)$$

where  $k_{\text{obs}} = k_1[L] + k_{-1}$

Plots of  $\ln([A] - [A]_{\infty})$  versus time were linear. Derive the rate expression in equation (3) and show the integrated form of this rate expression that was plotted to obtain the straight lines.

c) Calculate  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and  $K_{\text{eq}}$  at 25°C based on the data given below.

T (°C)	$k_1$ ( $s^{-1}M^{-1}$ )	$k_{-1}$ ( $s^{-1}$ )
10	480	0.55
20	770	1.8
33	1420	7.7

10. The following reaction is observed, with ligand substitution occurring before dimerization takes place.



The following observations have been made:

- 1) The pseudo-first-order rate constant is approximately proportional to  $[\text{CO}]$ .
- 2) Added L has no effect on the rate of the reaction.
- 3) The rate depends on the nature of L, with  $k_{\text{obs}} = 0.32 \text{ M}^{-1} \text{s}^{-1}$  for  $L = P(i\text{-Bu})_3$  and  $k_{\text{obs}} = 42 \text{ M}^{-1} \text{s}^{-1}$  for  $L = P(n\text{-Bu})_3$ .

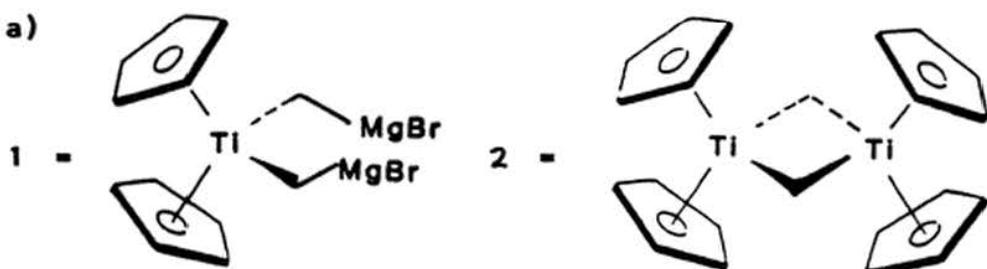
Propose a mechanism for the reaction, classify it as associative or dissociative, and derive the rate expression that is consistent with all observations. Clearly indicate which step is rate-determining.

11. In ten words or less, state why life exists.

## ANSWERS

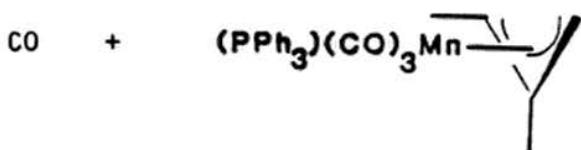
1. The answers here represent the actual products for the reactions as published in the literature; however, there may be other products that could reasonably be expected from the reactions given.

a)



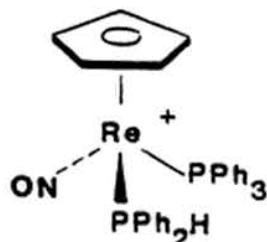
Van de Heisteeg, B.J.J.; Schat, G.; Akkerman, O.S.; Bickelhaupt, F.  
Organomet. 1985, 4, 1141.

b)



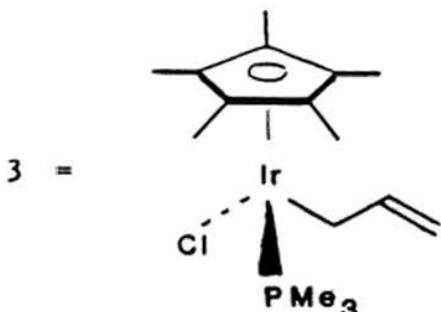
Palmer, G.T.; Basolo, F. J. Am. Chem. Soc. 1985, 107, 3122.

c)



Buhro, W.E.; Georgiou, S.; Hutchinson, J.P.; Gladysz, J.A. J. Am. Chem. Soc. 1985, 107, 3346.

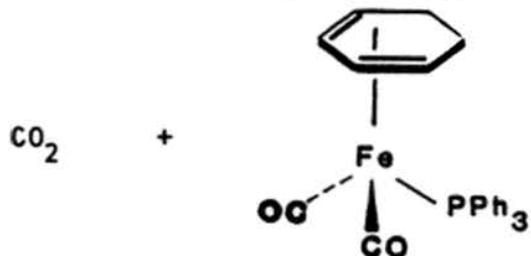
d)



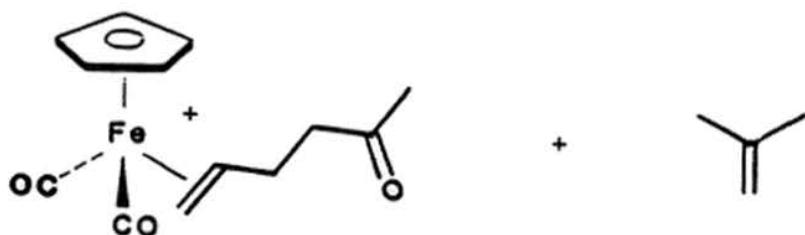
1. d) (cont.)

McGhee, W.D.; Bergman, R.G. *J. Am. Chem. Soc.* 1985, 107, 3388.

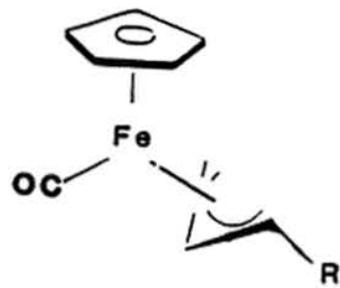
e)

Birch, A.J.; Kelly, L.F. *J. Organomet. Chem.* 1985, 286, C5.

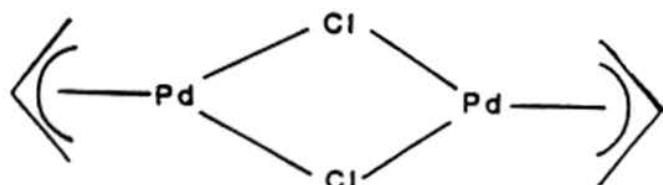
f)

Berryhill, S.R.; Rosenblum, M. *J. Org. Chem.* 1980, 45, 1984.

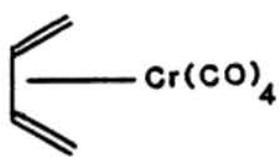
g)

Green, M.L.H.; Nagy, P.L.I. *J. Chem. Soc.* 1963, 189.

h)

Trost, B.M. *Tetrahedron* 1977, 33, 2615.

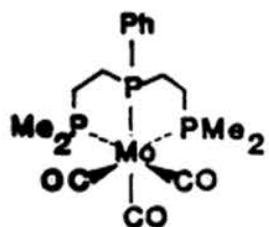
1. i)



Geoffroy, G.L.; Wrighton, M.S. "Organometallic Photochemistry" (Academic Press, 1979), p. 176.

j)  $\text{Co}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2$ Sabherwal, I.H.; Burg, A. Chem. Comm. 1969, 853.k)  $\text{MoCl}_3(\text{PMe}_3)_3$ Carmona, E.; Marin, J.M.; Poveda, M.L.; Atwood, J.L.; Rogers, R.D. J. Am. Chem. Soc. 1983, 105, 3014.

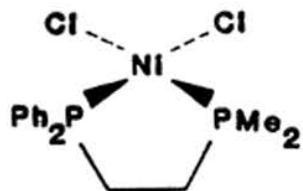
l)



King, R.B.; Zinich, J.A.; Cloyd, J.C., Jr. Inorg. Chem. 1975, 14, 1554.

m)  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ Tate, D.P.; Knipple, W.R.; Augl, J.M. Inorg. Chem. 1962, 1, 433.

n)



King, R.B.; Zinich, J.A.; Cloyd, J.C., Jr. Inorg. Chem. 1975, 14, 1554.

2. The answers here represent actual reagents used to carry out the transformations in a given literature reference. There may be other reagents that would effect the same transformations.

2. a) MeLi

Davies, S.G. "Organotransition Metal Chemistry: Applications to Organic Synthesis" (Pergamon Press, 1982), p. 25.

b) AlCl<sub>3</sub>, CO

Fischer, E.O.; Fichtel, K. Chem. Ber. 1961, 94, 1200.

c) Allyl-MgBr

Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed. (John Wiley and Sons, 1980), p. 705.

d) 2 R-C≡C-R'

Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed. (John Wiley and Sons, 1980), p. 706.

e) Zn, THF

Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed. (John Wiley and Sons, 1980), p. 864.

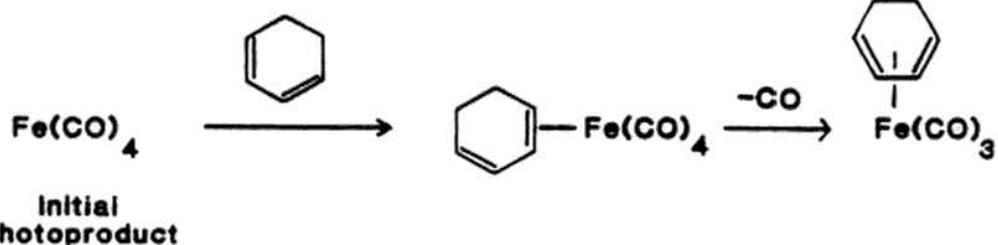
f) PPh<sub>3</sub>, Δ

Wojcicki, A. Adv. in Organomet. Chem. 1973, 11, 87.

g) NOPF<sub>6</sub>

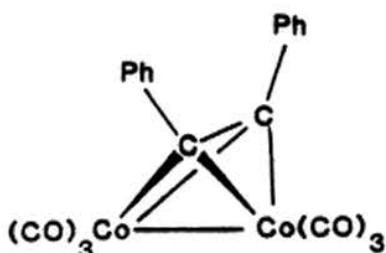
Faller, J.W.; Murray, H.H.; White, D.L.; Chao, K.H. Organomet. 1983, 2, 400.

3. a)



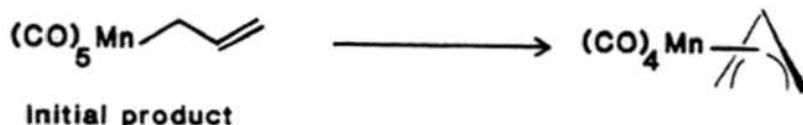
Hallam, B.F.; Pauson, P.L. J. Chem. Soc. 1958, 642.

b)



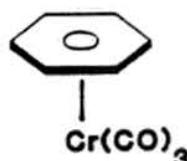
Sly, W.G. J. Am. Chem. Soc. 1959, 81, 18.

3. c)



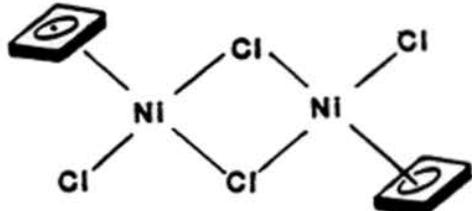
Collman, J.P.; Hegedus, L.S. "Principles and Applications of Organotransition Metal Chemistry" (University Science Books, 1980), p. 137.

d)



Lukehart, C.M. "Fundamental Transition Metal Organometallic Chemistry" (Brooks/Cole Publishing Co., 1985), p. 128.

e)

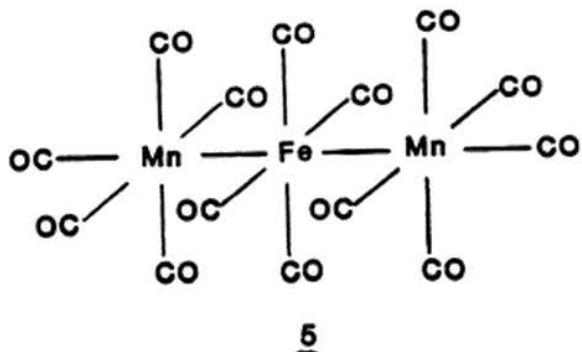


Efraty, A. Chem. Revs. 1977, 77, 691.

4. a) The infrared spectral data indicate that only terminal carbonyls are present, thus all structures involving bridging carbonyl groups can be eliminated. The mass spectral data shows a molecular ion at 558 m/e, which loses carbonyl groups (28 m/e) one at a time, down to a mass of 166, thus a total of 392 m/e or 14 carbonyl groups are lost. The fragment at 111 m/e corresponds to a  $\text{Mn}-\text{Fe}$  unit. Thus, the composition of the 166 peak is two Mn atoms and one Fe atom. From these data, an empirical formula of  $\text{Mn}_2\text{Fe}(\text{CO})_{14}$  can be obtained. The fact that no 110 m/e fragment was observed suggests that there is no Mn-Mn bond in the molecule.

The only reasonable structure is shown on the following page.

## 4. (cont.)



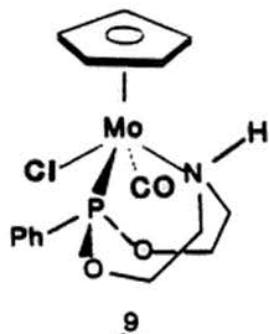
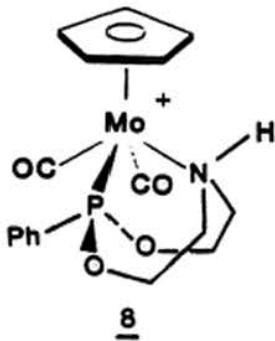
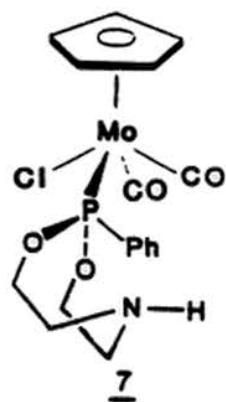
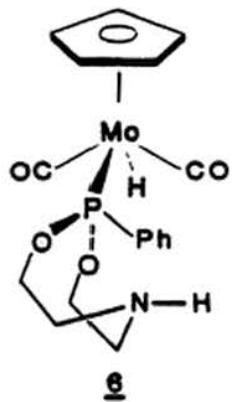
b) An X-ray structure of the compound proves this structure to be the correct one for 5.

Abel, E.W.; McLean, R.A.N.; Moorhouse, S. Inorg. Nucl. Chem. Lett. 1971, 7, 587.

Evans, G.O.; Sheline, R.K.; Inorg. Chem., 1971, 10, 1598.

Schubert, E.H.; Sheline, R.K. Z. Naturforsch. 1965, b20, 1306.

5. The structures of complexes 6-9 are shown below.



5. (cont.) The NMR and IR data are assigned as follows:

Complex	$^1\text{H}$ NMR	selected IR data ( $\text{cm}^{-1}$ )
6	3.44 (m, 4 H, $-\text{CH}_2\text{N}-$ ) 3.96 (m, 4 H, $-\text{CH}_2\text{O}-$ ) 5.26 (s, 5 H, Cp) 7.49 (m, 5 H, Ph) $-6.41$ (d, $J_{\text{p-H}} = 65$ Hz, 1 H, Mo-H)	3389 (N-H stretch) 1945 (CO stretch) 1860 (CO stretch)
7	3.44 (m, 4 H, $-\text{CH}_2\text{N}-$ ) 4.01 (m, 4 H, $-\text{CH}_2\text{O}-$ ) 5.29 (s, 5 H, Cp) 7.50 (m, 5 H, Ph)	3355 (N-H stretch) 1966 (CO stretch) 1880 (CO stretch)
8	3.21 (m, 4 H, $-\text{CH}_2\text{N}-$ ) 3.96 (m, 2 H, $-\text{CH}_2\text{O}-$ ) 4.64 (m, 2 H, $-\text{CH}_2\text{O}-$ ) 6.00 (s, 5 H, Cp) 7.42 (m, 1 H, -NH) 7.70 (m, 5 H, Ph)	3380-3400 (N-H stretch) 1990 (CO stretch) 1900 (CO stretch)
9	3.38 (m, 4 H, $-\text{CH}_2\text{N}-$ ) 4.41 (m, 4 H, $-\text{CH}_2\text{O}-$ ) $5.06$ (d, $J_{\text{p-H}} = 3$ Hz, 5 H, Cp) 5.72 (m, 1 H, -N-H) 7.48 (m, 5 H, Ph)	3160 (N-H stretch) 1800 (CO stretch)

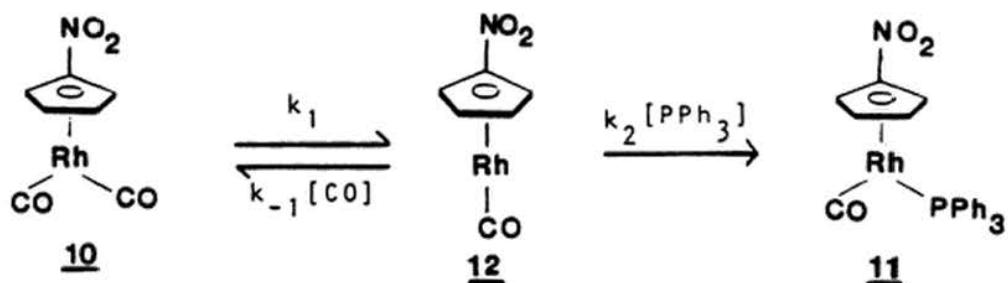
Points to note:

- Upon coordination of the nitrogen atom to the metal, the N-H stretching frequency decreases dramatically and the number of metal carbonyl stretches decreases to one, as it must. Additionally, the N-H proton becomes visible in the NMR spectrum.
- Upon formation of a cationic species, the Cp resonance shifts significantly downfield. In addition, the ethylene bridge hydrogens become nonequivalent, presumably because the structure is more rigid. The N-H proton is also visible in the NMR spectrum of this species. The CO stretches are shifted to higher energy, again because of the positive charge on the metal.

Wachter, J.; Jeanneaux, F.; Riess, J.G. Inorg. Chem. 1980, 19, 2169.

6. There are two possible mechanisms.

**1) Dissociative Mechanism**



Using a steady state approximation for the 16-electron intermediate 12, the rate expression derived is:

$$\text{rate} = k_{\text{obs}} [10], \text{ where}$$

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PPh}_3]}{k_{-1} [\text{CO}] + k_2 [\text{PPh}_3]}$$

If  $k_2 [\text{PPh}_3] \gg k_{-1} [\text{CO}]$ , then  $k_{\text{obs}} = k_1$ . This expression does not contain  $[\text{PPh}_3]$  so it cannot be correct.

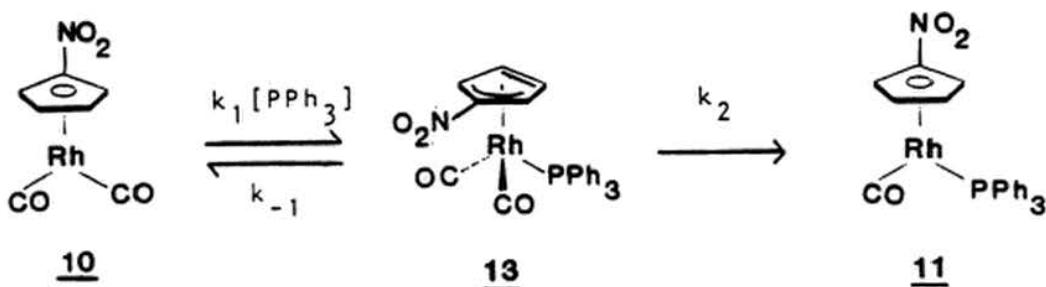
If  $k_2 [\text{PPh}_3] \ll k_{-1} [\text{CO}]$ , then

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PPh}_3]}{k_{-1} [\text{CO}]}$$

This expression shows a first order dependence on  $[\text{PPh}_3]$  but  $k_{\text{obs}}$  will not be a constant; instead, it will decrease as the reaction proceeds because  $[\text{CO}]$  is increasing (i.e. CO depresses the rate).

If an intermediate situation exists, the data suffer from both problems, i.e., an inverse dependence on  $[\text{CO}]$  and no direct dependence on  $[\text{PPh}_3]$ . In addition, a  $\Delta S^\ddagger$  value that is less than zero is inconsistent with a dissociative mechanism.

**2) Associative Mechanism**



6. (cont.) Slipping of the Cp ring from  $\eta^5$  to  $\eta^3$  occurs in order to prevent formation of a 20-electron complex. Using a steady state approximation for the intermediate 13, the rate expression derived is

$$\text{rate} = k_{\text{obs}} [10], \text{ where}$$

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PPh}_3]}{k_{-1} + k_2}$$

This expression gives a first-order dependence on 10 and  $[\text{PPh}_3]$ , with  $k_{\text{obs}}$  varying linearly with  $[\text{PPh}_3]$ . As for any associative mechanism,  $\Delta S^\ddagger$  should be less than zero. Therefore, the best mechanism appears to be the associative pathway.

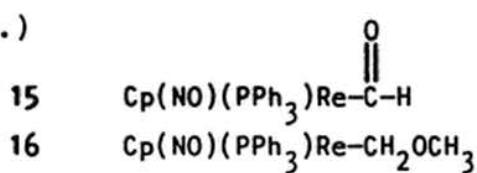
Rerek, M.E.; Basolo, F. J. Am. Chem. Soc. 1984, 106, 5908.

7. Mechanism I involves CO dissociation from the dimer, with the metal-metal bond remaining intact throughout the reaction. Mechanism II involves initial cleavage of the Re-Re bond, followed by ligand substitution on the 17-electron species  $\text{Re}(\text{CO})_5$  and recombination of the fragments to form the product dimer. The fact that there are two isotopes of rhenium suggests a double-labeling experiment to distinguish between the two mechanisms. The reaction can be carried out using a 1:1 mixture of  $^{185}\text{Re}_2(\text{CO})_{10}$  and  $^{187}\text{Re}_2(\text{CO})_{10}$ . If mechanism I were operative, the substitution product would contain only  $^{185}\text{Re}-^{185}\text{Re}$  and  $^{187}\text{Re}-^{187}\text{Re}$  metal-metal bonds in a 1:1 ratio. If mechanism II were operative, the product would contain  $^{185}\text{Re}-^{185}\text{Re}$ ,  $^{185}\text{Re}-^{187}\text{Re}$ , and  $^{187}\text{Re}-^{187}\text{Re}$  metal-metal bonds in a 1:2:1 ratio. These isotope ratios are easily detectable by mass spectroscopic analysis. Experimentally, the thermal reaction proceeds via mechanism I, and the photochemical reaction by mechanism II.

Stolzenberg, A.M.; Muetterties, E.L. J. Am. Chem. Soc. 1983, 105, 822.

8. 10  $[\text{CpRe}(\text{CO})_2(\text{NO})]^+ \text{BF}_4^-$
- 11  $\text{CpRe}(\text{CO})_2(\text{PPh}_3)$
- 12  $[\text{CpRe}(\text{CO})(\text{NO})(\text{PPh}_3)]^+ \text{BF}_4^-$
- 13  $[\text{CpRe}(\text{CO})(\text{NO})(\text{CH}_3\text{CN})]^+ \text{BF}_4^-$
- 14  $[\text{CpRe}(\text{PPh}_3)_2(\text{NO})]^+ \text{BF}_4^-$

8. (cont.)



Points to note about these syntheses:

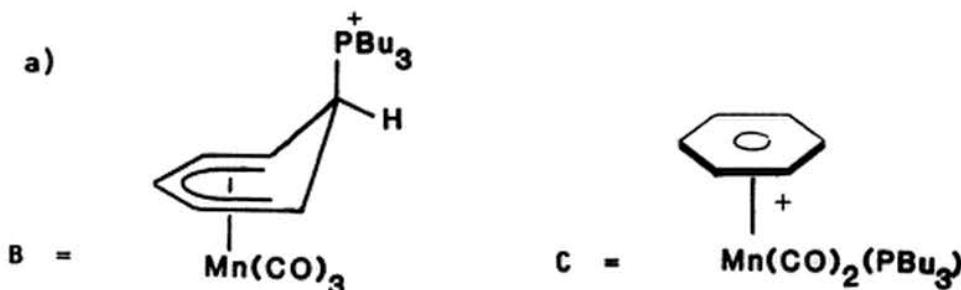
a) Both iodosobenzene and trimethylamine-N-oxide act as "CO-abtractors" by oxidizing CO to  $\text{CO}_2$ ; however, it is evident from this work that iodosobenzene is a more selective CO oxidant than  $\text{Me}_3\text{NO}$ .

b) Phosphine substitution will not occur on the nitrosyl complexes, so the phosphine ligand must be introduced before the nitrosyl group.

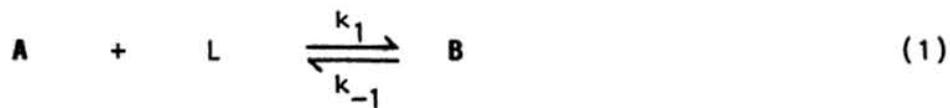
c)  $\text{Me}_3\text{NO}$  does not decompose the phosphine-substituted complexes.

Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W.A.; Wong, V.K.; Gladysz, J.A. J. Am. Chem. Soc. 1982, 104, 141.

9. a)



b)



The rate expression for this equation is

$$-\frac{d[\text{A}]}{dt} = k_1[\text{A}][\text{L}] - k_{-1}[\text{B}] \quad (2)$$

which under pseudo-first-order conditions (high [L]), becomes

$$-\frac{d[\text{A}]}{dt} = k_L[\text{A}] - k_{-1}[\text{B}] \quad (3)$$

where  $k_L$  is defined as  $k_1[\text{L}]$ .

In order to get this rate expression into an easily-integrable form, we must consider the following two equalities to find an expression for [B].

$$1. [\text{A}]_0 + [\text{B}]_0 = [\text{A}]_\infty + [\text{B}]_\infty = [\text{A}] + [\text{B}] \quad (4)$$

9. (cont.) and since the reaction is an equilibrium,

$$2. k_L [A]_\infty = k_{-1} [B]_\infty \quad (5)$$

From equation (4), we define [B].

$$[B] = [A]_\infty + [B]_\infty - [A] \quad (6)$$

and from equation (5), we can make an expression for  $[B]_\infty$  in terms of  $[A]_\infty$

$$[B]_\infty = (k_L/k_{-1})[A]_\infty \quad (7)$$

and substitute it into equation (6) to give equation (8).

$$[B] = [A]_\infty + (k_L/k_{-1})([A]_\infty) - [A] \quad (8)$$

Substituting this expression for [B] back into equation (3), we obtain equation (9),

$$-\frac{d[A]}{dt} = k_L[A] - k_{-1}\{[A]_\infty + (k_L/k_{-1})([A]_\infty) - [A]\} \quad (9)$$

which after simplification, yields the desired expression, equation (10).

$$-\frac{d[A]}{dt} = (k_1[L] + k_{-1})([A] - [A]_\infty) \quad (10)$$

To integrate, rearrangement is necessary.

$$\int_0^t \frac{d[A]}{[A] - [A]_\infty} = - \int_0^t (k_1[L] + k_{-1}) dt \quad (11)$$

Integration then yields:

$$\ln \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = -(k_1[L] + k_{-1})t \quad (12)$$

and the expression that was plotted is

$$\ln([A]_t - [A]_\infty) = -(k_1[L] + k_{-1})t + \ln([A]_0 - [A]_\infty) \quad (13)$$

c) We know that  $K_{eq} = k_1/k_{-1}$  and

$$\Delta G^\circ = -RT \ln K_{eq} \quad (15)$$

$$\ln K_{eq} = -\Delta G^\circ/RT \quad (16)$$

$$\ln K_{eq} = (-\Delta H^\circ/R)(1/T) + \Delta S^\circ R \quad (17)$$

so a plot of  $\ln K_{eq}$  versus  $1/T$  will give a straight line with slope equal to  $-\Delta H^\circ/R$  and y-intercept equal to  $\Delta S^\circ R$ . Thus:

## 9. (cont.)

$$-\Delta H^\circ_R = 5963 \text{ K}^{-1} \quad \text{and} \quad \Delta H^\circ = 11.8 \text{ kcal/mole}$$

$$\Delta S^\circ_R = -14.4 \quad \text{and} \quad \Delta S^\circ = -28.6 \text{ eu}$$

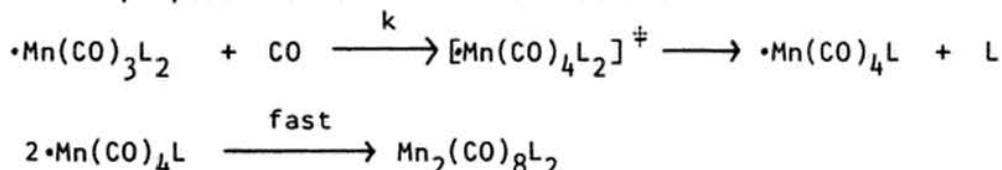
and at 25 °C,  $K_{eq} = 297$ .

Kane-Maguire, L.A.P.; Sweigart, D.A. Inorg. Chem. 1979, 18, 700.

For an analysis of the kinetics, see:

Espenson, J.H. "Chemical Kinetics and Reaction Mechanisms" (McGraw-Hill Book Company, 1981), p. 42.

## 10. The proposed mechanism is shown below.



The lack of inhibition of the reaction rate by excess L implies that ligand dissociation is not occurring prior to the rate-determining step. Because the presence of CO increases the rate of the reaction, the initial associative step must be rate-determining. The rate expression is:

$$-\frac{d[\cdot\text{Mn}(\text{CO})_3\text{L}_2]}{dt} = k[\cdot\text{Mn}(\text{CO})_3\text{L}_2][\text{CO}]$$

An associative mechanism also seems likely in view of the increase in reaction rate upon substitution of the less-bulky phosphine P(n-bu)<sub>3</sub> for P(i-bu)<sub>3</sub>.

The 19-electron complex  $[\cdot\text{Mn}(\text{CO})_4\text{L}_2]$  is proposed as the transition state, similar to the transition state for an S<sub>N</sub>2 organic substitution reaction.

McCullen, S.B.; Walker, H.W.; Brown, T.L. J. Am. Chem. Soc. 1982, 104, 4007.

Kidd, D.R.; Brown, T.L. J. Am. Chem. Soc. 1978, 100, 4095.

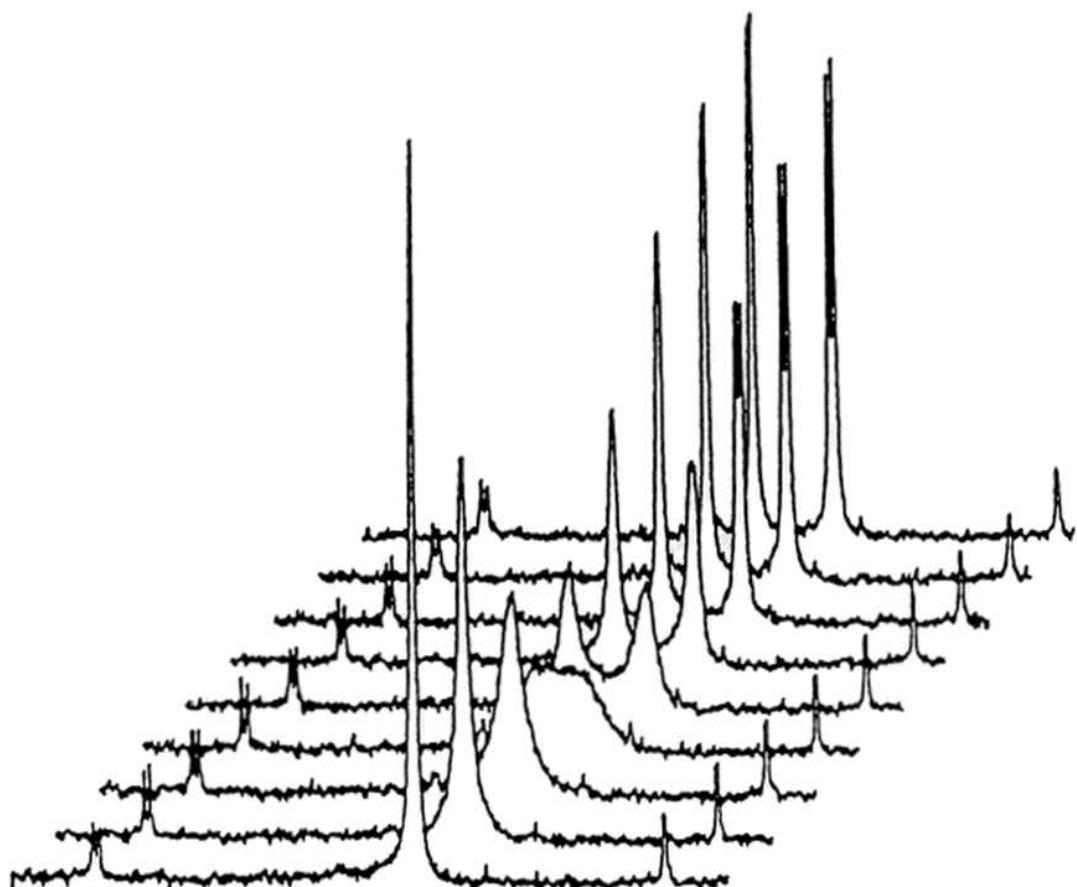
Fawcett, J.P.; Jackson, R.A.; Pöe, A.J. J. Chem. Soc., Dalton Trans. 1978, 789.

## 11. Because carbon is small.

Dewar, M.J.S.; Healy, E. Organomet. 1982, 1, 1705.

# 4

## Rearrangements and Fluxional Processes

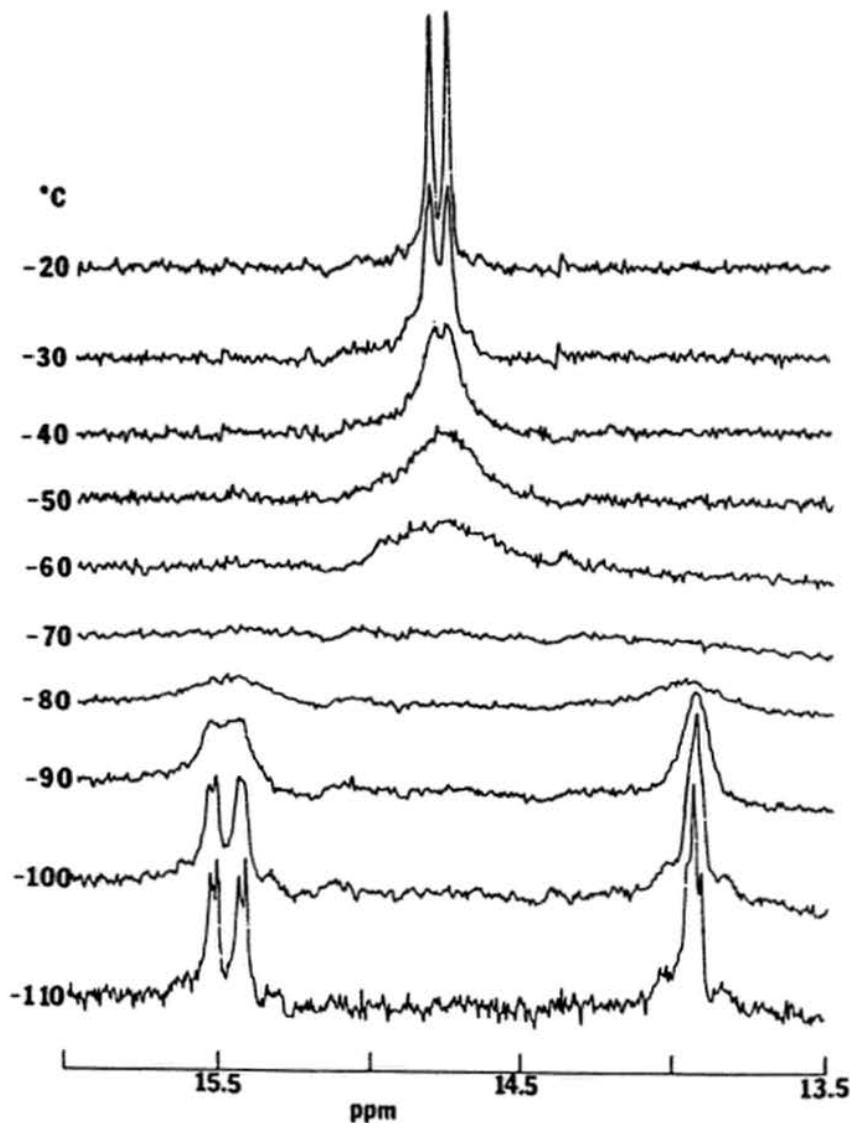


## 4: REARRANGEMENTS AND FLUXIONAL PROCESSES

### QUESTIONS

Reviewing the concepts covered in Chapter 1 will be helpful for solving some of the problems in this chapter.

1. In the 25 MHz  $^{13}\text{C}$  NMR spectrum of a metal complex at  $-97^\circ\text{C}$ , there are two signals, one at 182 ppm and one at 178 ppm. At  $-58^\circ\text{C}$  the signals have just coalesced into a broad signal at 180 ppm. What is the rate constant for exchange of the two carbon atoms that produce these signals.
2. Shown below is a section of the variable temperature 250 MHz proton NMR spectrum of  $[\text{Cp}(\text{CO})_2(\text{PEt}_3)\text{W}=\text{CH}_2]^+$ .



## 2. (cont.)

- a) Suggest a dynamic process that would cause the observed change in the spectrum with temperature.
- b) Explain why a doublet is observed at  $-20^{\circ}\text{C}$ .
- c) Explain why two different sets of peaks are observed at  $-110^{\circ}\text{C}$ .
- d) What is the coalescence temperature?
- e) What is the rate constant for the dynamic process at the coalescence temperature?
- f) What is the free energy of activation,  $\Delta G^{\ddagger}$ , for this dynamic process?

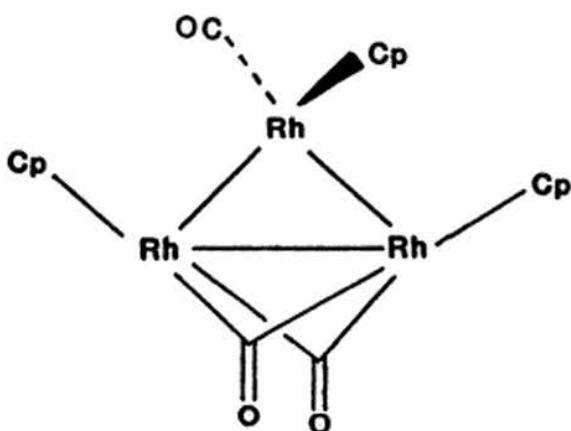
3. The proton NMR spectrum of  $\text{Cp}^*\text{Rh}(\text{C}_6(\text{COOCH}_3)_6)$  shows the following resonances at  $30^{\circ}\text{C}$ .

$\delta$  1.49 (s, 15 H)  
 $\delta$  3.40 (s, 6 H)  
 $\delta$  3.59 (s, 6 H)  
 $\delta$  3.61 (s, 6 H)

Upon heating the sample, the three closely-spaced peaks coalesce to one singlet while the high-field signal remains unchanged. The signal at  $\delta$  3.59 is observed to broaden much more rapidly than the signals at  $\delta$  3.40 and  $\delta$  3.61.

- a) What is the structure of the compound?
- b) Discuss the various processes which could cause the temperature-dependent behavior.
- c) What does the observation of selective broadening imply about the assignment of the  $\delta$  3.59 signal and about the actual dynamic process occurring?

4. An isomer of  $\text{Cp}_3\text{Rh}_3(\text{CO})_3$  is shown below.

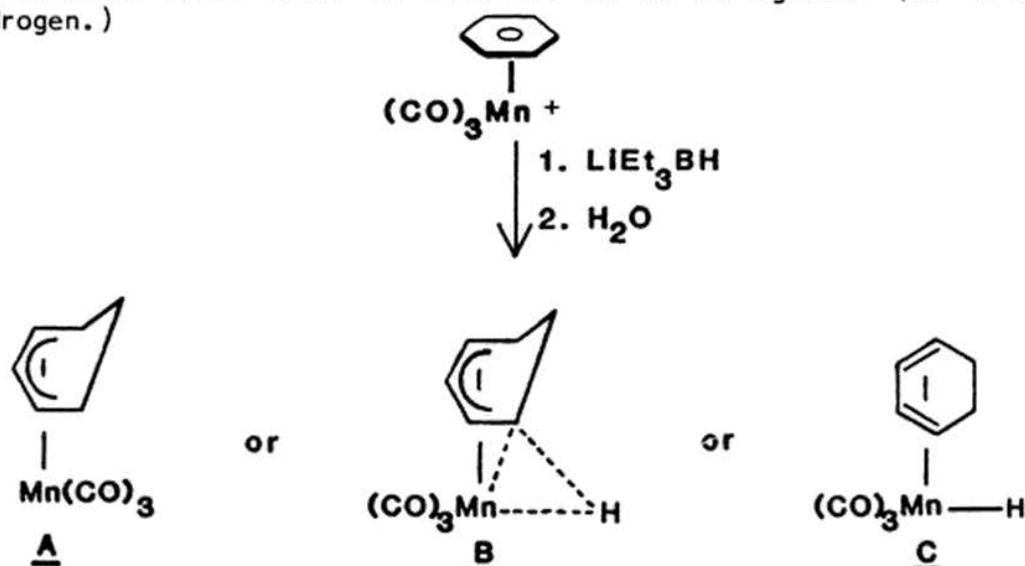


4. (cont.) This isomer is a fluxional molecule, i.e., the carbonyls scramble among the three rhodium atoms. Show the mechanism of the carbonyl scrambling process. In addition, sketch the rate-limiting  $^{13}\text{C}$  spectra, i.e., what does the carbonyl region of the NMR spectrum look like for both the low temperature static structure and the high temperature averaged structure. Be sure to indicate approximate chemical shifts for each spectrum.

Important information: Rh has  $I = 1/2$ . Approximate values for Rh-C coupling and chemical shifts of carbon bound to rhodium are shown below.

	terminal	$\mu^2$	$\mu^3$
$J_{\text{Rh}-\text{C}}$	80	40	30
$\delta_{\text{C}}$	180	200	230

5. The double reduction of benzenemanganese tricarbonyl cation by a powerful hydride source yields one of the three isomeric complexes shown below. (The dotted lines in B represent a three-center (Mn-C-H), two-electron bond which is referred to as an agostic (or bridging) hydrogen.)



The ground state molecule undergoes two dynamic processes and each of the other two isomers is proposed as an intermediate or transition state for these processes. From the variable temperature 100 MHz NMR spectra given on the following pages:

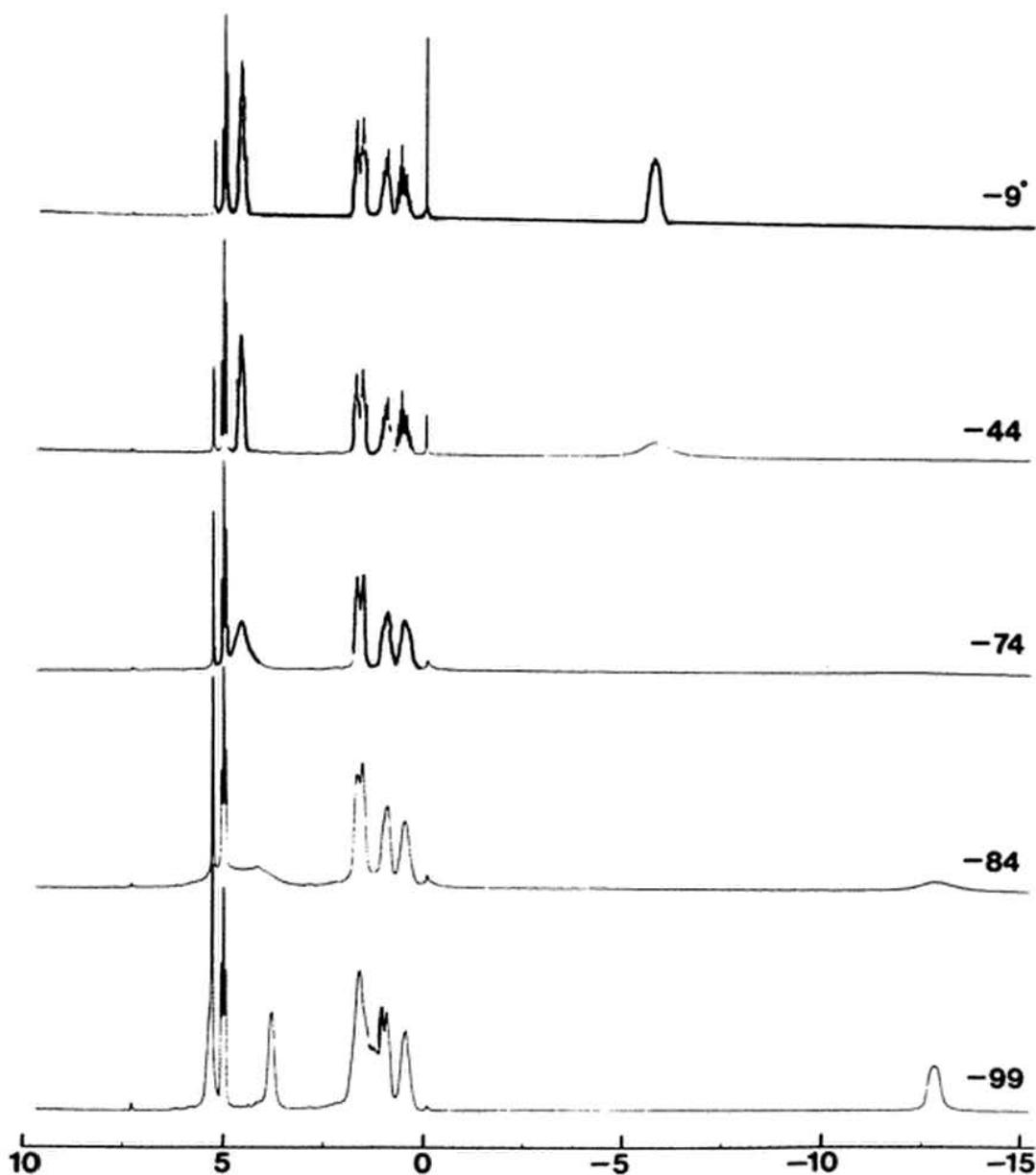
- Determine which of three structures is the lowest energy form and explain your reasoning.
- Propose a mechanism for each of the two dynamic processes.
- Determine  $\Delta G^\ddagger$  for these two dynamic processes.

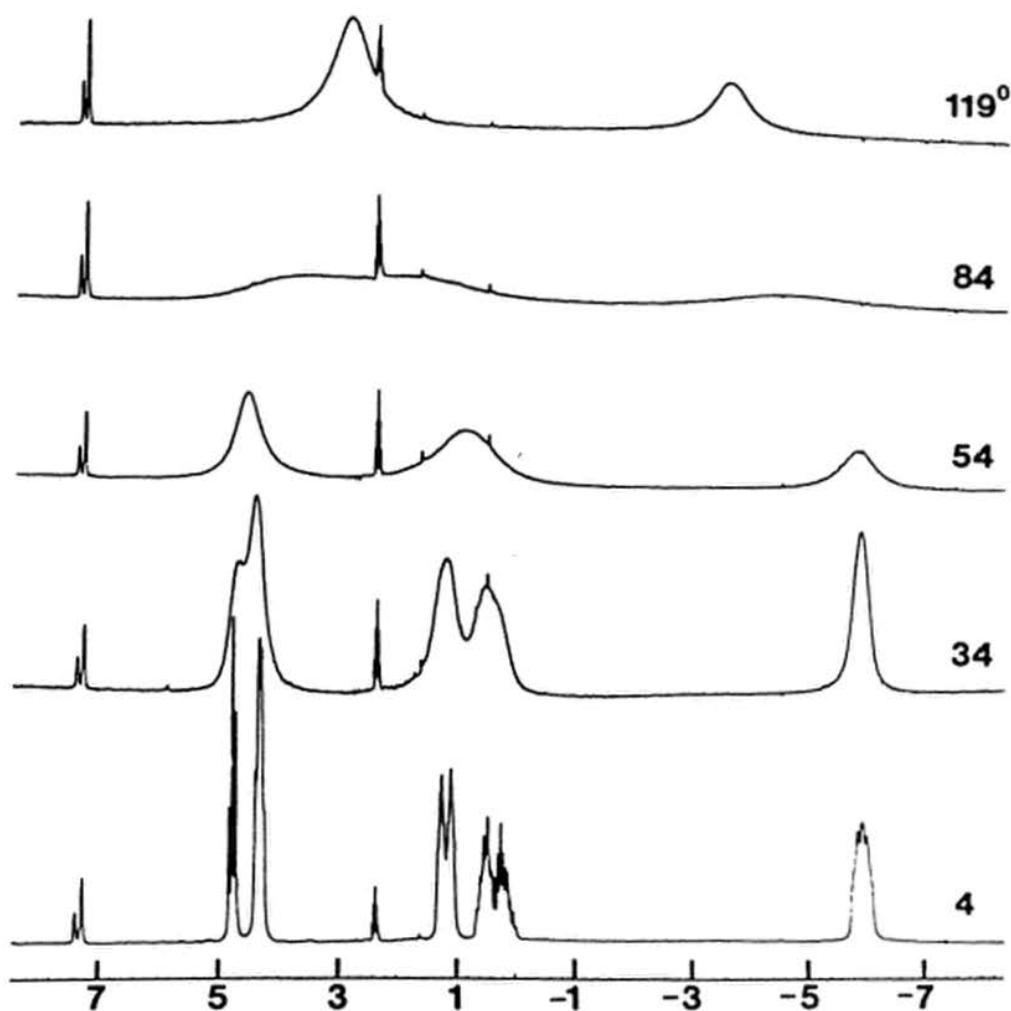
#### HINT

For the ground state molecule,  $J_{\text{C}-\text{H}}$  for the upfield hydrogen is 85 Hz.

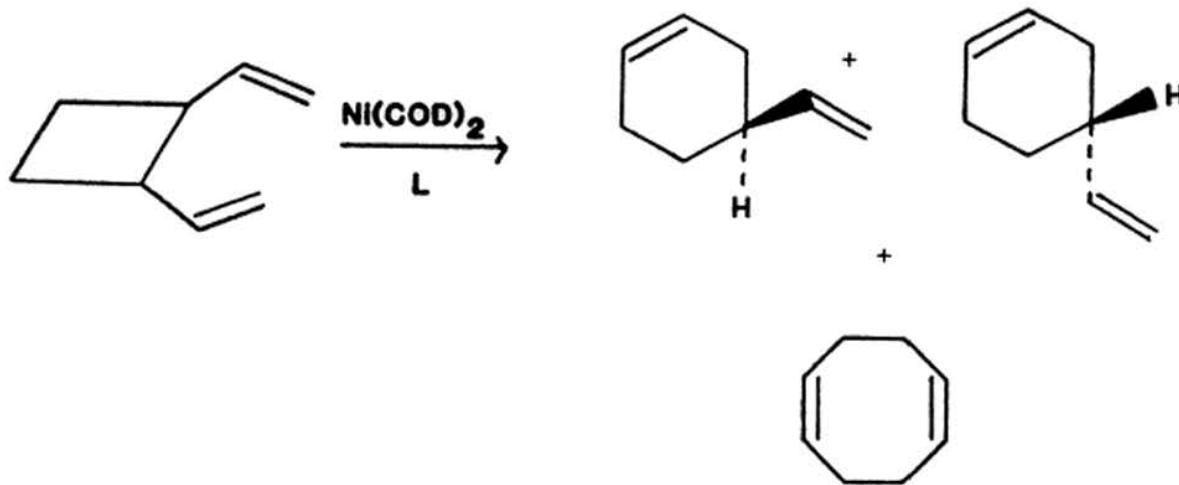
100 MHz  $^1\text{H}$  NMR spectra of  $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_3$

from  $-99^\circ$  to  $-9^\circ \text{ C}$  in  $\text{CD}_2\text{Cl}_2$



100 MHz  $^1\text{H}$  NMR spectra of  $\text{C}_6\text{H}_9\text{Mn}(\text{CO})_3$ from 4° to 119°C in toluene-d<sub>8</sub>

6. The following isomerization reaction ( $L$  is an optically-active phosphite) was found to give cyclooctatetraene and optically active vinyl cyclohexene with enantiomeric excesses ranging from 1–20%, depending on the specific phosphite used. Explain how each product is formed. Be sure to rationalize the observed optical activity.

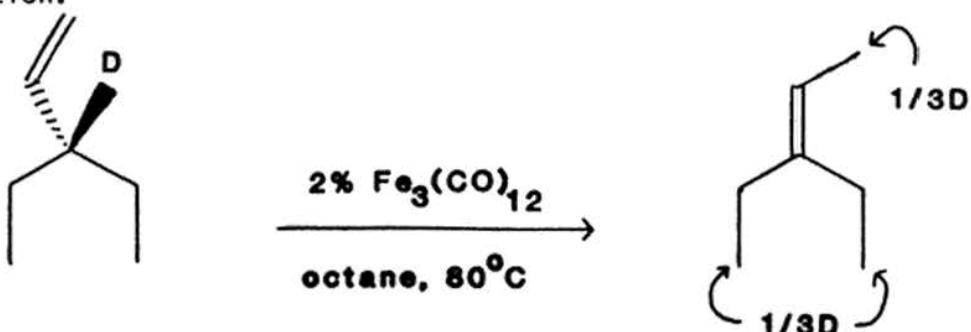


7. Propose a mechanism for the reaction shown below that is consistent with the following experimental observations:

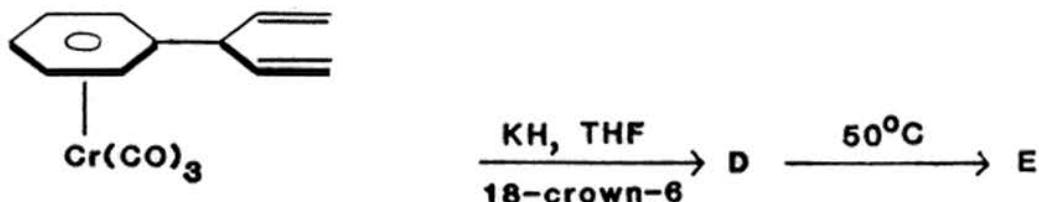
- The starting material shown (trans-diester) gives exclusively the Z-diene complex, as shown.
- The corresponding cis-diester gives exclusively the E-diene complex.
- The reaction as shown is very slow; however, if  $\text{Fe}_2(\text{CO})_9$  is added to the reaction mixture, the product is formed rapidly.



8. Provide a mechanism which explains the following experimental observation.



9. Give structures for compounds D and E and assign the peaks in the NMR spectra given below. Compound E is an isomer of D.



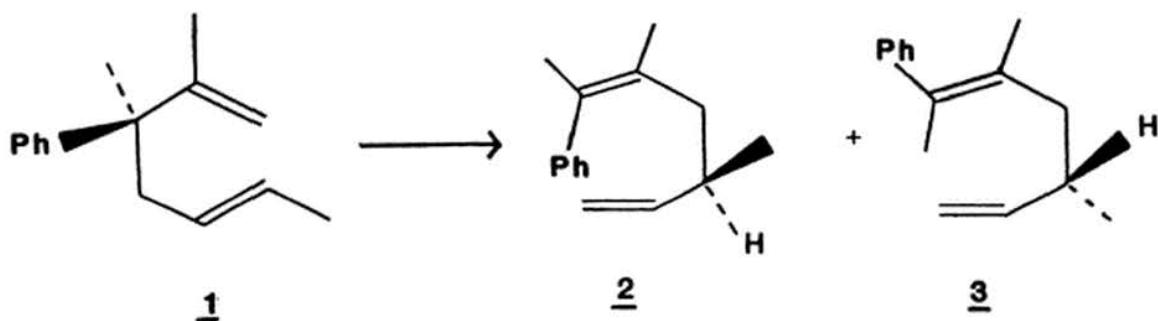
HINT

KH is a non-nucleophilic base.

$^1\text{H}$  NMR data ( $\delta$ ,  $\text{THF-d}_8$ )

D	4.32 (2 H, m) 4.46 (1 H, m) 4.60 (2 H, m) 4.65 (2 H, m) 5.06 (2 H, m) 6.35 (2 H, dd)	E	0.01 (2 H, d) 2.20 (2 H, d) 5.13 (2 H, t) 6.99 (1 H, m) 7.12 (2 H, m) 7.55 (2 H, m)
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10. Consider the following thermal and Pd(II)-catalyzed Cope rearrangements:

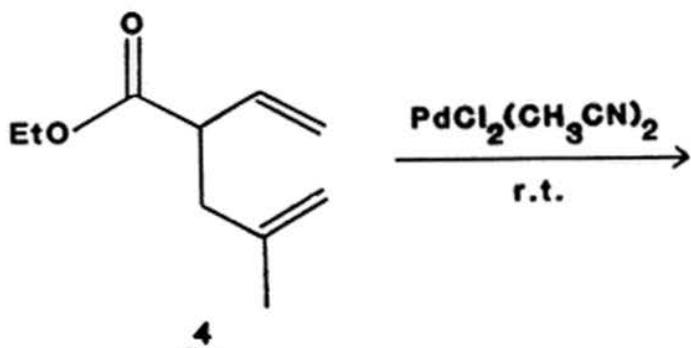


## 10. (cont.)

Conditions	Yield	Product Ratio (2/3)
240°C	50%	1:1
room temperature, $\text{PdCl}_2(\text{CH}_3\text{CN})_2$	86%	7:3

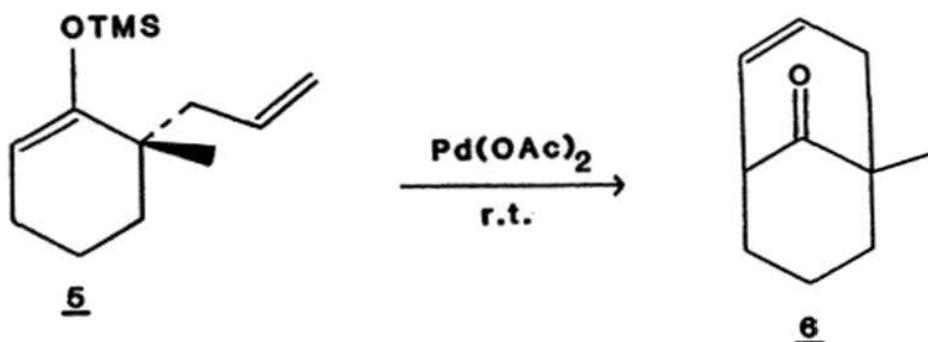
In strictly organic systems, the thermal Cope rearrangement proceeds through a "chair" transition state. Propose a mechanism for the Pd(II)-catalyzed reaction.

11. Remembering the "cyclization" mechanism of the Pd(II)-catalyzed Cope rearrangement (see preceding problem in this chapter), predict the product for the following reaction.



Be careful. The product shows only one vinylic resonance in the proton NMR spectrum and an unconjugated ester carbonyl stretch in the IR spectrum.

12. Again, remember the "cyclization" mechanism of the Pd(II)-catalyzed Cope rearrangement (Problem 10, this chapter) and propose a mechanism for the following reaction.



## ANSWERS

Reviewing the concepts covered in Chapter 1 will be helpful for solving the problems in this chapter.

1. At the coalescence temperature, the equation for the rate constant is

$$k = \frac{\pi(\Delta\nu)}{\sqrt{2}}$$

The difference in chemical shift of the two signals is 4 ppm, but the formula requires that this shift difference be in Hz. This value depends on the strength of the magnet used for the measurement and can be obtained by multiplying the operating frequency of the magnet (in MHz) and the difference in chemical shifts in ppm. Thus, for this example, we obtain a value of:

$$\Delta\nu = 4 \text{ ppm} (25 \text{ MHz}) = 100 \text{ Hz}$$

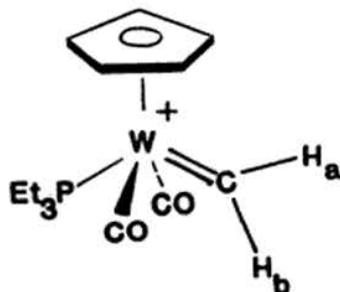
and the value of the rate constant at  $-58^{\circ}\text{C}$  is calculated to be

$$k = (\pi/\sqrt{2})(100 \text{ s}^{-1})$$

$$k = 2.2 \times 10^2 \text{ s}^{-1}$$

If a magnet of different field strength were used for this same measurement, the coalescence temperature would also be different.

2. a) The dynamic process that averages  $\text{H}_a$  and  $\text{H}_b$  is rotation around the  $\text{W}=\text{C}$  bond. Since the two protons are nonequivalent in the static structure, the preferred orientation of the carbene ligand must be the upright position. It is interesting to note that the value of  $J_{\text{P}-\text{H}_a}$  is smaller than  $J_{\text{P}-\text{H}_b}$ .



- b) At  $-20^{\circ}\text{C}$ , rotation around the  $\text{W}=\text{C}$  bond is rapid on the NMR timescale and the observed chemical shift is the average of the chemical shifts of  $\text{H}_a$  and  $\text{H}_b$  in the static structure. The doublet is due to phosphorus coupling, with the value of the coupling constant equal to  $1/2(J_{\text{P}-\text{H}_a} + J_{\text{P}-\text{H}_b})$ .

2. c) At  $-110^{\circ}\text{C}$ , the rotation around the W=C bond is slow on the NMR timescale and  $\text{H}_a$  and  $\text{H}_b$  appear as non-equivalent hydrogens. In addition,  $\text{H}_a$  and  $\text{H}_b$  are coupled to each other and are coupled to phosphorus with  $J_{\text{P}-\text{H}_a} \neq J_{\text{P}-\text{H}_b}$ . The result is two sets of doublet of doublets.

d)  $T_c = -70^{\circ}\text{C}$

e) The rate constant for exchange at the coalescence temperature is given by the equation:

$$k = \frac{\pi(\Delta v)}{\sqrt{2}}$$

The two resonances are separated by 1.6 ppm and at 250 MHz

$$\Delta v = 1.6 \text{ ppm (250 MHz)} = 400 \text{ Hz}$$

and thus, at the coalescence temperature ( $-70^{\circ}\text{C}$ )

$$k = (\pi/\sqrt{2})(400 \text{ s}^{-1}) = 888 \text{ s}^{-1}$$

f) The Eyring equation gives the relationship of the rate constant to  $\Delta G^{\ddagger}$

$$k = (kT/h) e^{-\Delta G^{\ddagger}/RT}$$

thus,  $\Delta G^{\ddagger} = -RT[\ln(k/T) + \ln(h/k)]$

where  $R = 1.987 \times 10^{-3} \text{ kcal/mol}\cdot\text{K}$

$k = \text{Boltzmann's constant} = 1.38054 \times 10^{-16} \text{ erg/K}$

$h = \text{Plank's constant} = 6.6256 \times 10^{-27} \text{ erg}\cdot\text{sec}$

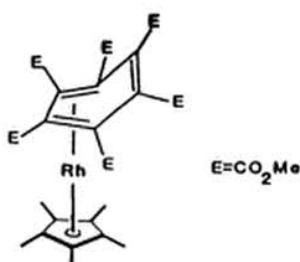
$T = \text{temperature in K}$

thus, for this example

$$\Delta G^{\ddagger} = 9.0 \text{ kcal/mol}$$

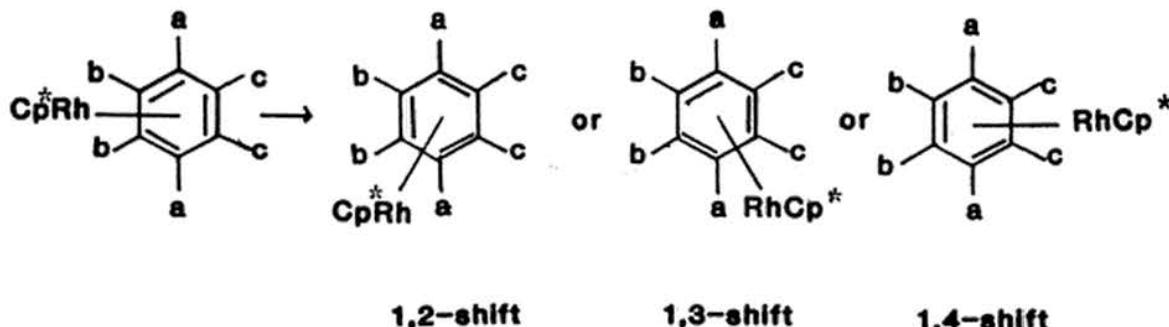
Kegley, S.E.; Brookhart, M.; Husk, G.R. Organomet. 1982, 1, 760.

3. a) One type of methyl on the Cp ring and three types of carbomethoxy groups on the benzene ring are most easily accounted for by the 18-electron species shown below.



3. (cont.) This compound is isoelectronic with  $\eta^6, \eta^4-(C_6H_6)_2Ru$ . (Darensbourg, M.Y.; Muettterties, E.L. *J. Am. Chem. Soc.* 1978, 100, 7425)

b) The methyl groups on the  $Cp^*$  ring remain equivalent at all temperatures, while the carbomethoxy groups exchange. This observation can be explained by the  $Cp^*Rh$  unit moving around the benzene ring, which can be accomplished in a number of ways: 1) The  $Cp^*Rh$  can shift one bond at a time around the ring (a 1,2-shift), 2) two bonds at a time (a 1,3-shift), 3) three bonds at a time (a 1,4-shift), or 4) randomly. If the three resonances are assigned a, b, and c as shown below, the results of three of the above processes can be depicted as follows:



Redefining each resonance of the products in terms of the type of proton it was in the starting material gives the following information:

1,2-shift	1,3-shift	1,4-shift
a → c	a → c	a → a
b → a	b → c	b → c
b → b	b → a	b → c
a → b	a → b	a → a
c → a	c → b	c → b
c → c	c → a	c → b

c) If the scrambling were occurring via a random process, each signal must broaden equally. Since this is not observed, the random process can be eliminated.

If a 1,4-shift were occurring, the "a" methyl signals can not broaden since they are not exchanging. This is also not observed and the 1,4-shift can be eliminated.

If a 1,3-shift were occurring, all methyls must exchange at an equal rate, thus the rate of broadening must be the same for methyls a, b, and c. This is not observed.

If a 1,2-shift were occurring, the "a" methyl group exchanges twice as fast as "b" and "c"; as a result, the signal due to "a" should broaden twice as fast as the others. This is in fact what is observed and allows assignment of the signal at  $\delta 3.59$  to the carbomethoxy groups at position "a". The other two resonances cannot be assigned absolutely.

## 3. c) (cont.) Additional point to note:

When the fluxional process is very fast on the NMR timescale, a single carbomethoxy signal will appear at a chemical shift that is the average of the three contributing signals, e.g.

$$\delta = \frac{3.40 + 3.59 + 3.61}{3} = 3.53 \text{ ppm}$$

Kang, J.W.; Childs, R.F.; Maitlis, P.M. *J. Am. Chem. Soc.* 1970, **92**, 720.

4. The NMR spectrum of the static structure (Figure 1) should show three types of carbonyls, one terminal and two bridging. Note that the two  $\mu^2$ -carbonyls are not equivalent—one is cis to a Cp and the other is cis to a CO. The terminal CO should appear as a doublet since it is coupled to one rhodium. The bridging CO's should appear as a triplet since they are coupled to two rhodium atoms.

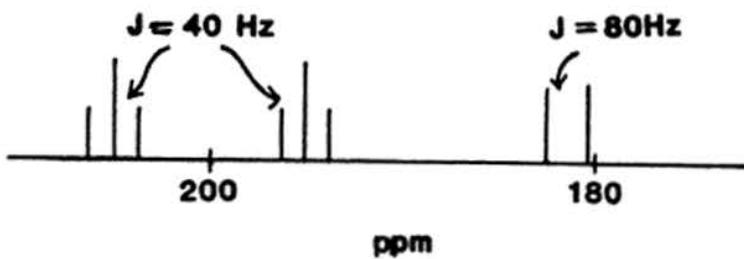
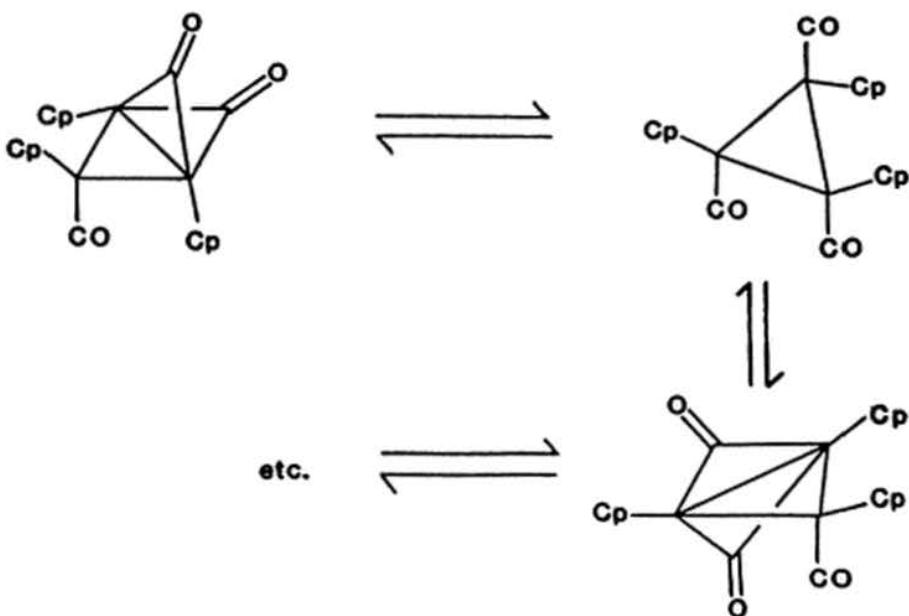


Figure 1: Carbon-13 NMR spectrum of the static structure

The fluxional process is outlined below.



4. (cont.) Notice that by this mechanism, each CO can bond to each Rh atom; however, one CO is unique since it is always on the top face of the Rh-Rh-Rh plane while the other two are on the bottom face (and are equivalent). Thus in a static structure, the CO on top is always bridging, and of the other two, one is bridging and one is terminal.

The NMR spectrum of the fluxional molecule (Figure 2, next page) should show the following:

- 1) Two sets of peaks in a ratio of 1:2.
- 2) The unique CO will be at approximately 200 ppm, since it is always  $\mu^2$ .
- 3) Each of the two other CO's bridges half of the time and is terminal half of the time; thus the other set of peaks will appear at

$$\delta = \frac{200 \text{ ppm} + 180 \text{ ppm}}{2} = 190 \text{ ppm}$$

- 4) Each CO is coupled to all three Rh atoms, thus each peak will appear as a 1:2:2:1 quartet.
- 5) Coupling constants: For both types of CO, we must average all  $J_{\text{Rh}-\text{C}}$ .

For the unique CO:

$$\begin{array}{rcl} J_{\text{Rh}(1)-\text{C}} & = & 40 \text{ Hz} \\ J_{\text{Rh}(2)-\text{C}} & = & 40 \text{ Hz} \\ J_{\text{Rh}(3)-\text{C}} & = & 0 \text{ Hz} \\ \hline J_{\text{Rh}(\text{avg.})-\text{C}} & = & 27 \text{ Hz} \end{array}$$

For the equivalent CO's:

$$J_{\text{avg.}} = 1/2(\text{bridging } J_{\text{Rh}-\text{C}} + \text{terminal } J_{\text{Rh}-\text{C}})$$

Bridging	Terminal
$J_{\text{Rh}(1)-\text{C}} = 40 \text{ Hz}$	$J_{\text{Rh}(1)-\text{C}} = 0 \text{ Hz}$
$J_{\text{Rh}(2)-\text{C}} = 40 \text{ Hz}$	$J_{\text{Rh}(2)-\text{C}} = 0 \text{ Hz}$
$J_{\text{Rh}(3)-\text{C}} = 0 \text{ Hz}$	$J_{\text{Rh}(3)-\text{C}} = 80 \text{ Hz}$
<hr/>	<hr/>
$J_{\text{Rh}(\text{avg.})-\text{C}} = 27 \text{ Hz}$	$J_{\text{Rh}(\text{avg.})-\text{C}} = 27 \text{ Hz}$

Thus, the overall  $J_{\text{avg.}} = 27 \text{ Hz}$ .

## 4. (cont.)

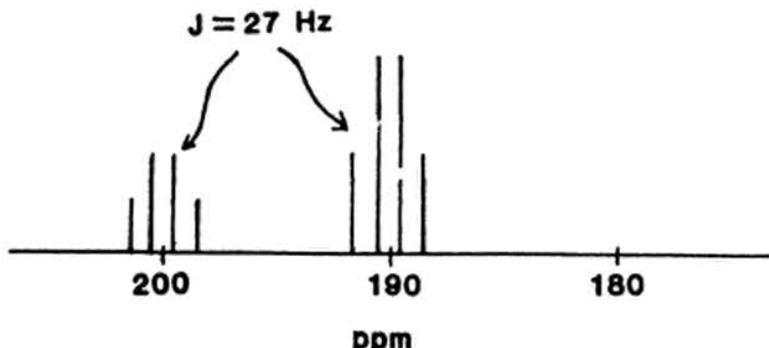
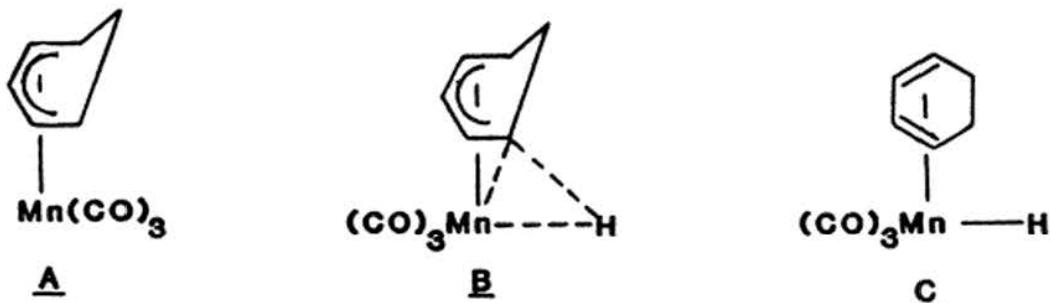


Figure 2: Carbon-13 NMR spectrum of the fluxional molecule

Lawson, R.J.; Shapley, J.R. Inorg. Chem. 1978, 17, 772.

Lawson, R.J.; Shapley, J.R. J. Am. Chem. Soc. 1976, 98, 7433.

5. a) The lowest energy form will be that observed as the static structure at the low temperature limit.



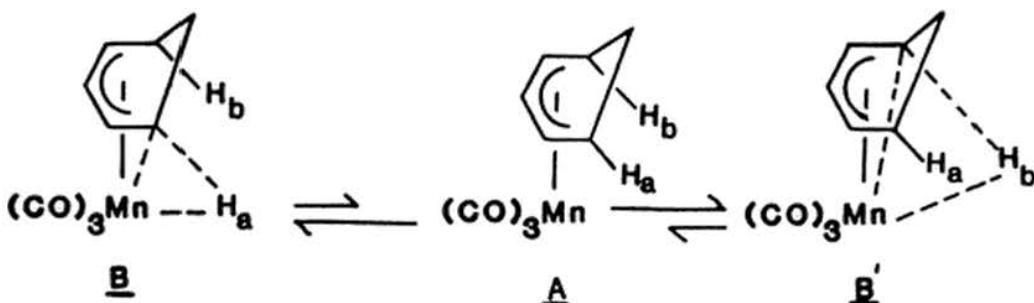
The spectrum obtained at  $-99^{\circ}\text{C}$  rules out structure A. Structure A would be expected to have only alkyl and allylic protons and no resonances at -12.8 ppm. Both structures B and C would be expected to have an upfield resonance. Structure C has a mirror plane and thus five different types of protons. On the other hand, B has no mirror plane, and all nine protons are inequivalent. The low temperature spectrum is thus more consistent with B than with C. The observed  $J_{\text{C}-\text{H}}$  of 85 Hz is also indicative of a significant amount of C-H interaction. An approximate value of  $J_{\text{C}-\text{H}}$  can be obtained by the equation

$$J = 500(\rho)$$

where  $\rho$  is the percent s-character of the orbitals involved. For structure C, no C-H interaction is involved. For structure B, where the amount of C-H interaction is less than that in a pure  $\text{sp}^3$ -hybridized system, we would expect a value of  $J_{\text{C}-\text{H}}$  that is somewhat less than 125 Hz.

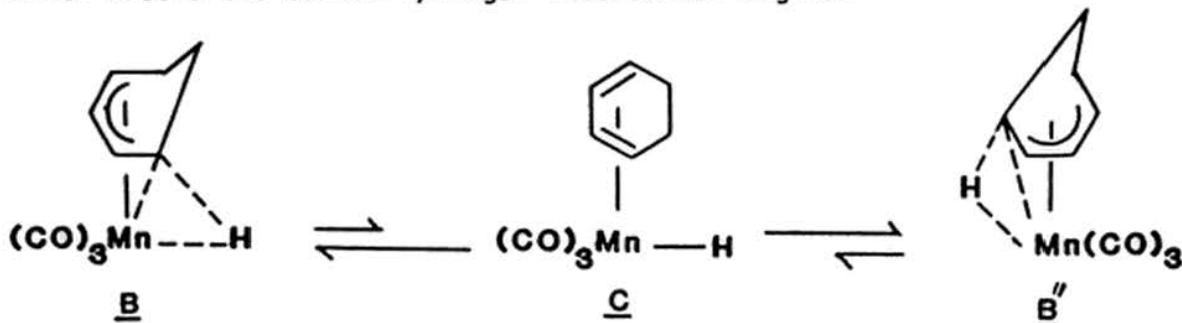
b) Both dynamic processes disrupt the three-center, two-electron bond. The lower temperature process breaks the metal-hydrogen interaction.

## 5. b) (cont.)



When the bridge is reformed, either of two endo hydrogens can bond to the metal. Thus, at  $-9^{\circ}\text{C}$ , the upfield peak is shifted to  $-5.7$  ppm which is the average of the shifts for the two endo hydrogens ( $1.4$  and  $-12.8$  ppm) in the static structure observed at  $-99^{\circ}\text{C}$ . This dynamic process introduces a mirror plane and thus the spectrum simplifies to only six peaks.

As the temperature continues to increase, a second dynamic process which breaks the carbon-hydrogen interaction begins.



When the bridging hydrogen is reformed, the hydrogen can go to either side of the diene. This process, in conjunction with the lower-temperature process (which is quite rapid since the temperature is well above  $-9^{\circ}\text{C}$ ), will make all three endo hydrogens equivalent. The result is that at  $119^{\circ}\text{C}$ , only two peaks are observed.

c) Spin saturation transfer experiments (SST) were used to accurately determine the values of  $\Delta G^{\ddagger}$  for these two processes; however, approximate values can be obtained using line broadening.

For the low-temperature process:

$$T_c = -74^{\circ}\text{C}$$

and the rate constant for exchange at the coalescence temperature can be calculated by the following formula.

$$k = \frac{\pi(v_a - v_x)}{\sqrt{2}} = \frac{\pi[140 - (-1280)\text{Hz}]}{\sqrt{2}} = 3154 \text{ s}^{-1}$$

5. c) (cont.) The Eyring equation gives the relationship of the rate constant to  $\Delta G^\ddagger$

$$k = (\kappa T/h) e^{-\Delta G^\ddagger/RT}$$

thus,  $\Delta G^\ddagger = -RT[\ln(k/T) + \ln(h/\kappa)]$

where  $R = 1.987 \times 10^{-3} \text{ kcal/mol}\cdot\text{K}$

$$\kappa = \text{Boltzmann's constant} = 1.38054 \times 10^{-16} \text{ erg/K}$$

$$h = \text{Plank's constant} = 6.6256 \times 10^{-27} \text{ erg}\cdot\text{sec}$$

T = temperature in K

and for the low temperature process,  $\Delta G^\ddagger = 8.3 \text{ kcal/mol}$ .

For the high-temperature process, the calculation is repeated, considering the two-proton resonance at -5.7 and the one-proton resonance at 0.5 ppm.

$$T_c = 84^\circ\text{C}$$

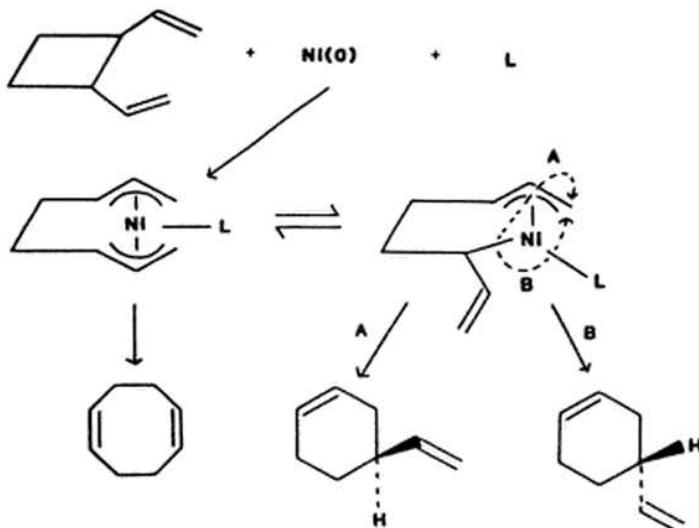
$$k = \frac{\pi(v_a - 2v_x)}{\sqrt{2}} = \frac{\pi[50 - 2(-570 \text{ Hz})]}{\sqrt{2}} = 2644 \text{ s}^{-1}$$

$$\Delta G^\ddagger = 15.5 \text{ kcal/mol}$$

These values agree fairly well with the more accurate values determined by SST:  $\Delta G^\ddagger$  (low-temperature process) = 8.3 kcal/mol and  $\Delta G^\ddagger$  (high-temperature process) = 15.4 kcal/mol.

Brookhart, M.; Lamanna, W.; Humphrey, M.B. J. Am. Chem. Soc. 1982, 104, 2117.

6. The reaction proceeds via an insertion of Ni(0) into the C-C bond of cyclobutane.

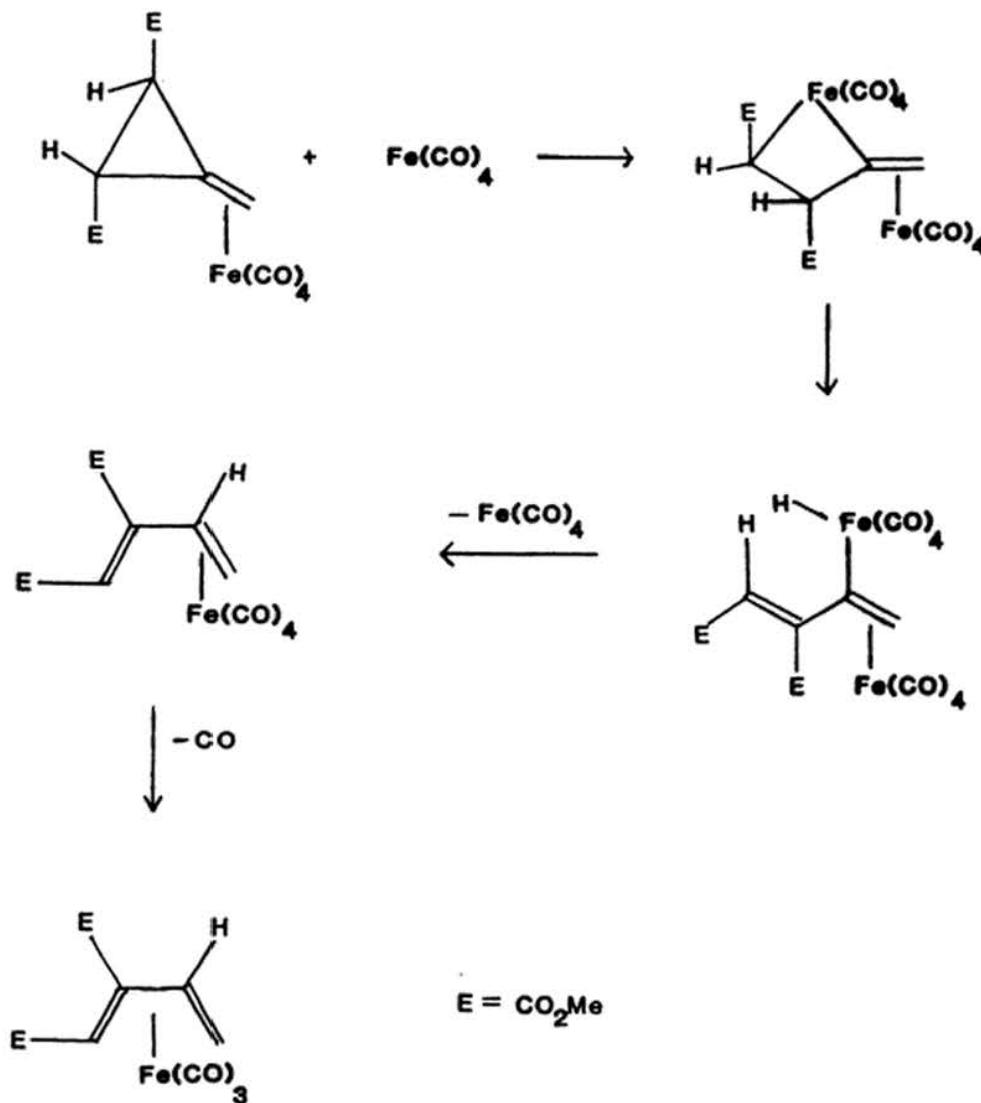


6. (cont.) Because L is optically active, the transition state for ring closure to cyclohexene via pathway A is different in energy than the transition state for ring closure via pathway B. Thus, closure to the cyclohexene products via the different pathways will produce compounds of opposite chirality. Because cyclooctadiene contains a plane of symmetry, no optical activity is observed for this product

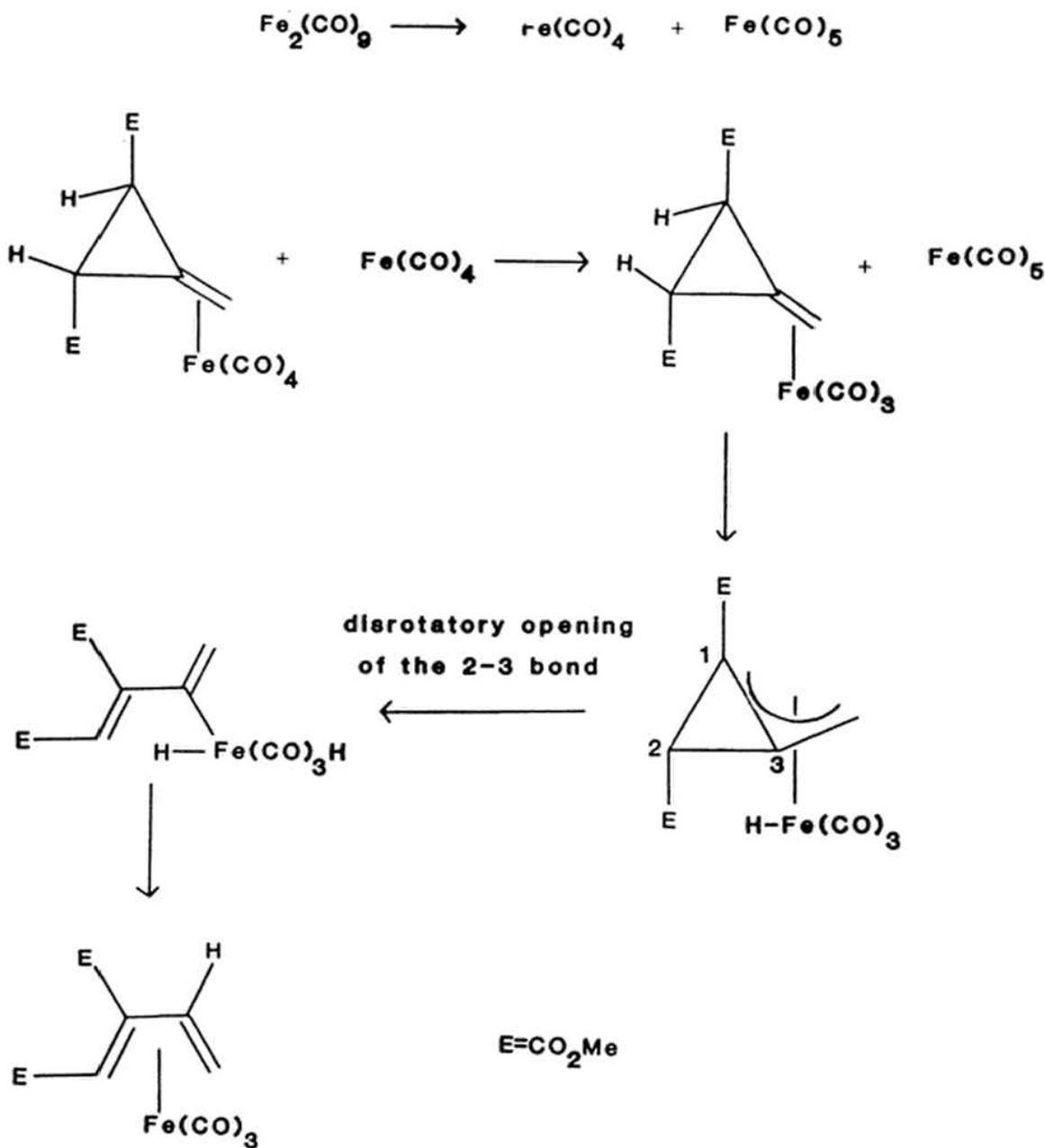
Richter, W.J. *J. Mol. Cat.* 1983, 18, 145.

7. Two different mechanisms for this reaction have been proposed in the literature.

Mechanism I



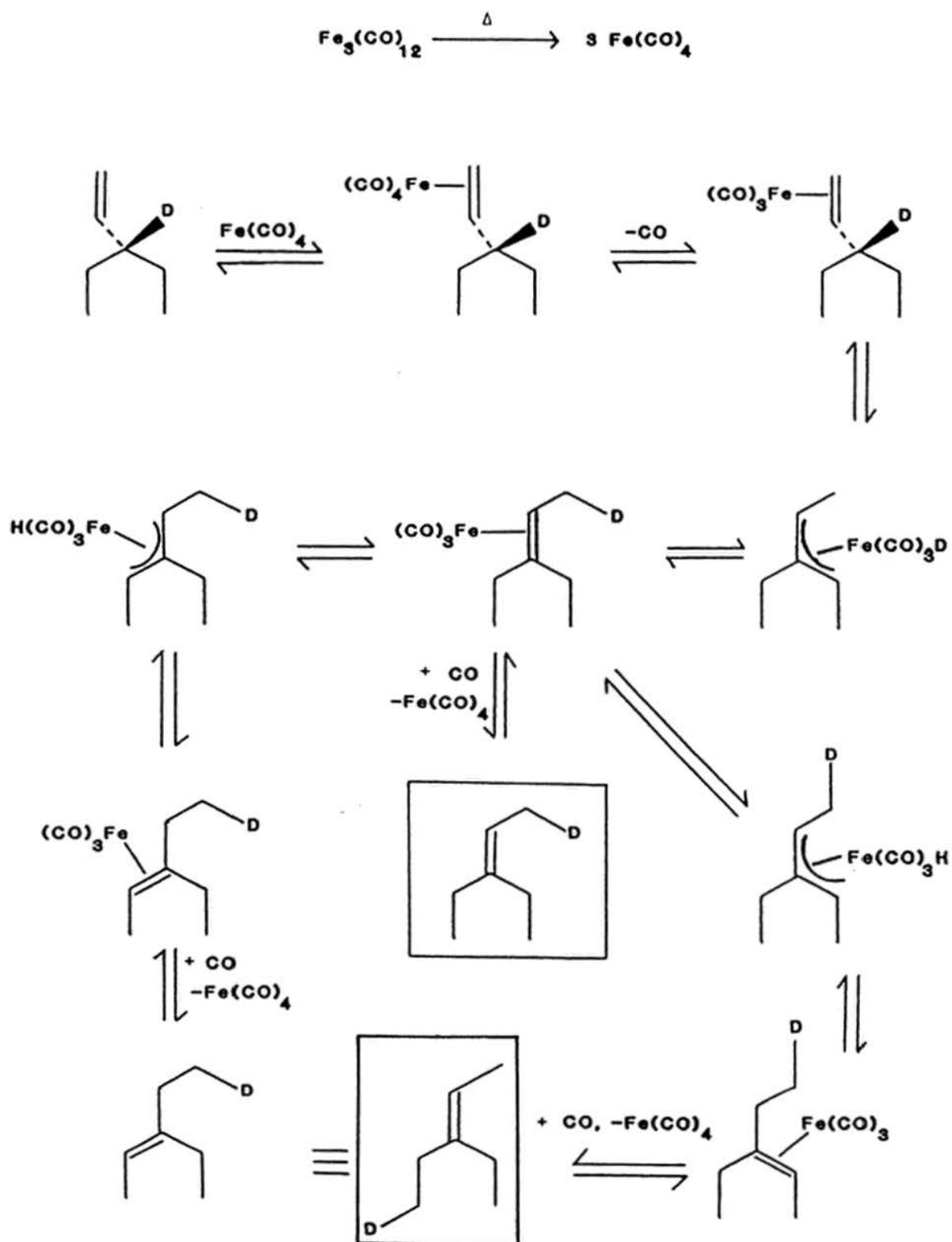
Whitesides, T.H.; Slaven, R.W. *J. Organomet. Chem.* 1974, 67, 99.

7. (cont.) Mechanism II

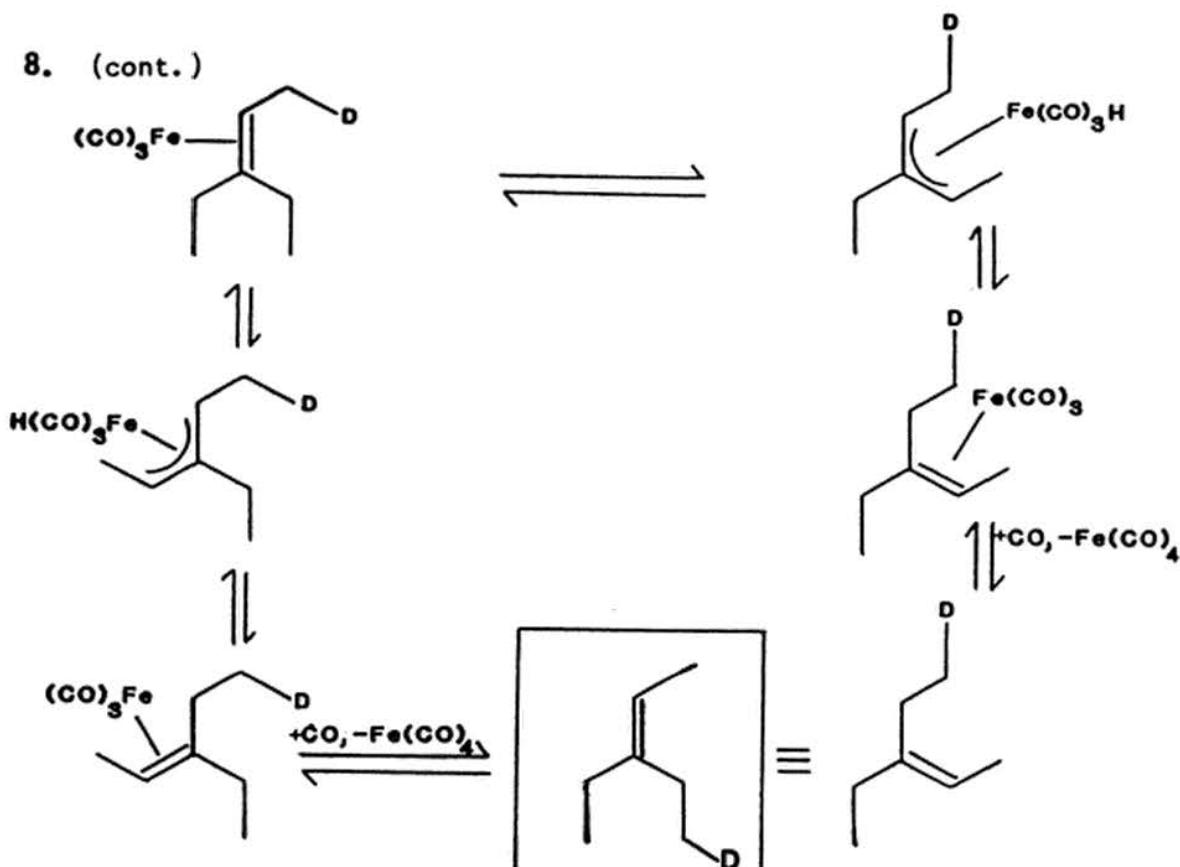
Pinhas, A.R.; Samuelson, A.G.; Risemberg, R.; Arnold, E.V.; Clardy, J.; Carpenter, B.K. J. Am. Chem. Soc. 1981, 103, 1668.

For both of these mechanisms, addition of  $\text{Fe}_2(\text{CO})_9$  should increase the rate of the reaction by providing a source of  $\text{Fe}(\text{CO})_4$ . In the absence of added  $\text{Fe}_2(\text{CO})_9$ , the starting olefin- $\text{Fe}(\text{CO})_4$  complex is the source of  $\text{Fe}(\text{CO})_4$ .

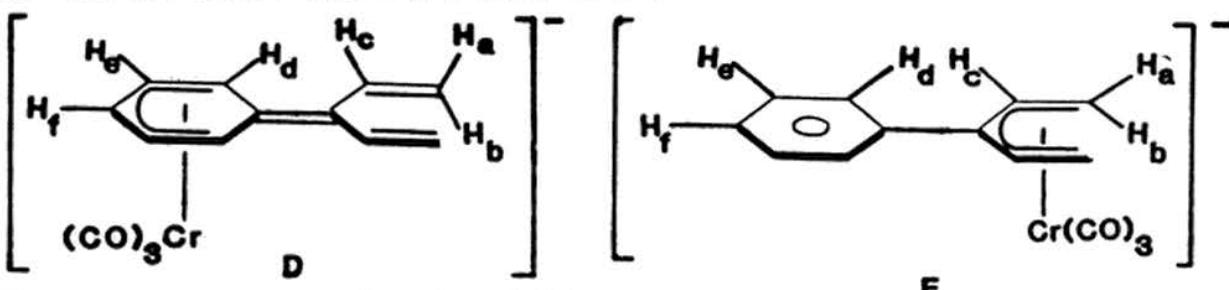
8. The postulated mechanism is shown below.



8. (cont.)

Casey, C.P.; Cyr, C.R. J. Am. Chem. Soc. 1973, 95, 2248.

9. The products D and E are shown below.



The resonances are assigned as follows.

D	$\delta$ 4.32 (2 H, m, a)
	$\delta$ 4.46 (1 H, m, f)
	$\delta$ 4.60 (2 H, m, d)
	$\delta$ 4.65 (2 H, m, b)
	$\delta$ 5.06 (2 H, m, e)
	$\delta$ 6.35 (2 H, dd, c)

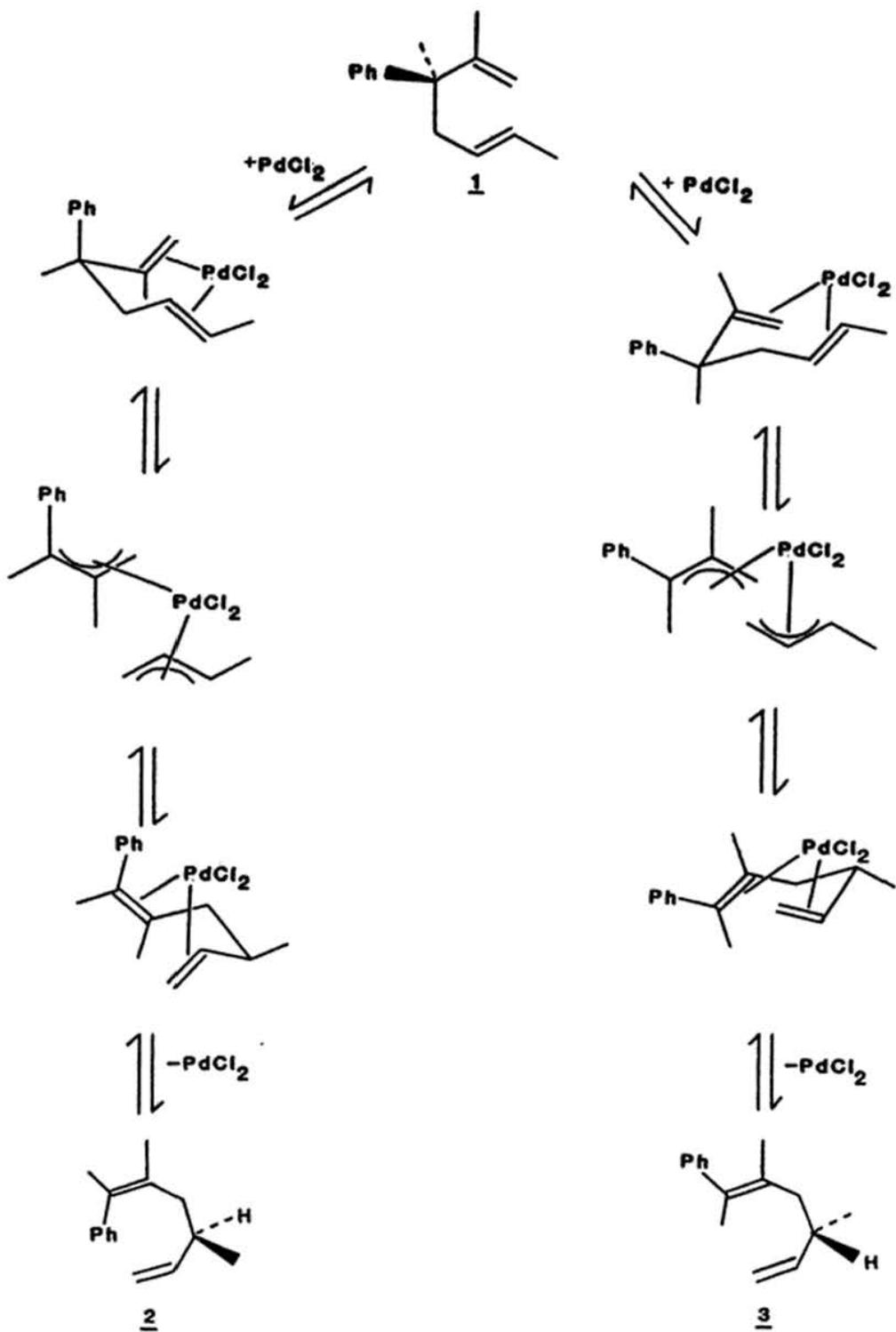
E	$\delta$ 0.01 (2 H, d, b)
	$\delta$ 2.20 (2 H, d, a)
	$\delta$ 5.13 (2 H, t, c)
	$\delta$ 6.99 (1 H, m, f)
	$\delta$ 7.12 (2 H, m, e)
	$\delta$ 7.55 (2 H, m, d)

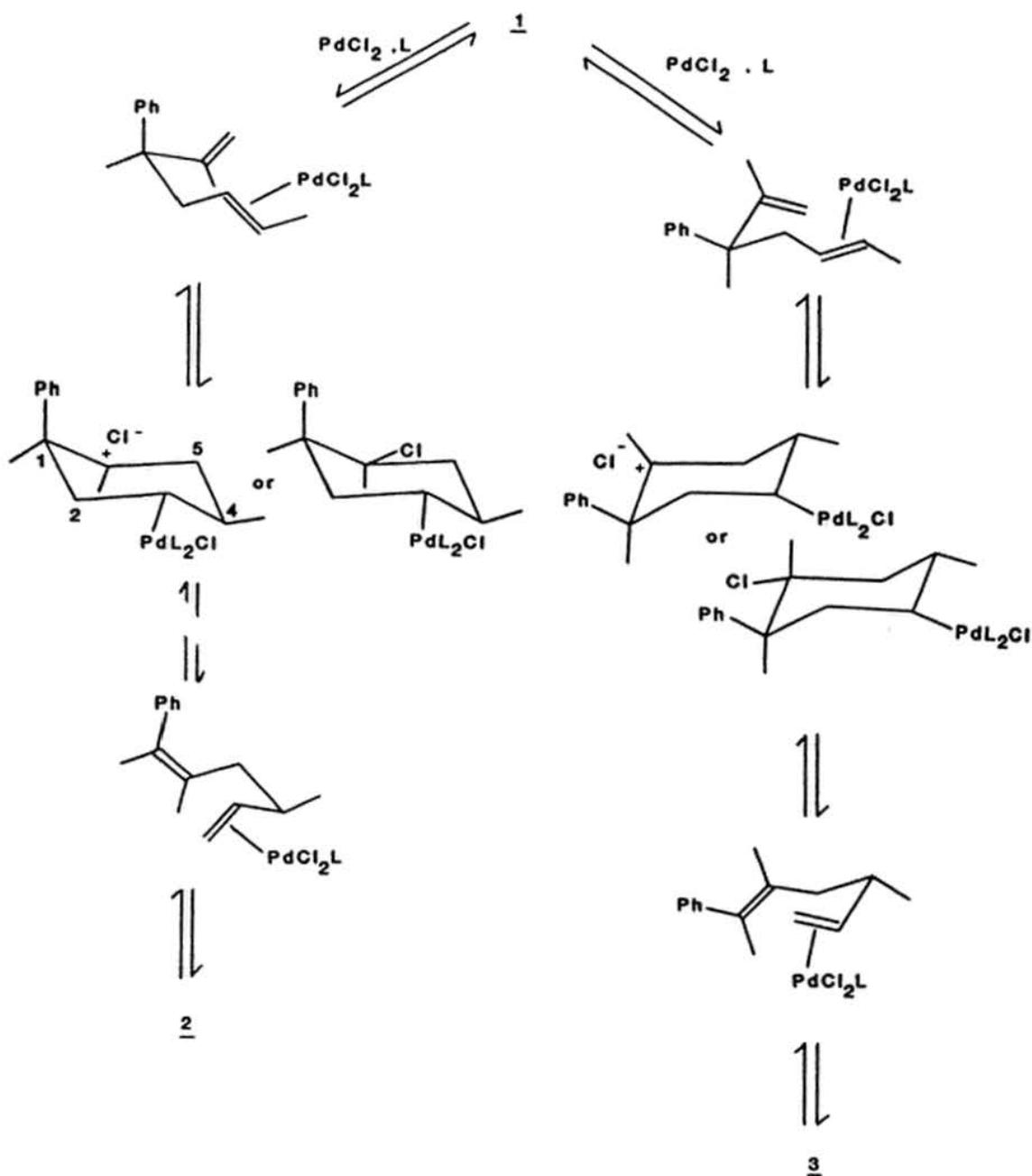
The peak at  $\delta$  5.13 in the spectrum of E should be a doublet of doublets; however, since the two coupling constants are equivalent, the resonance appears as a triplet.

Ceccon, A.; Gambaro, A.; Venzo, A. J. Chem. Soc., Chem. Comm. 1985, 540.

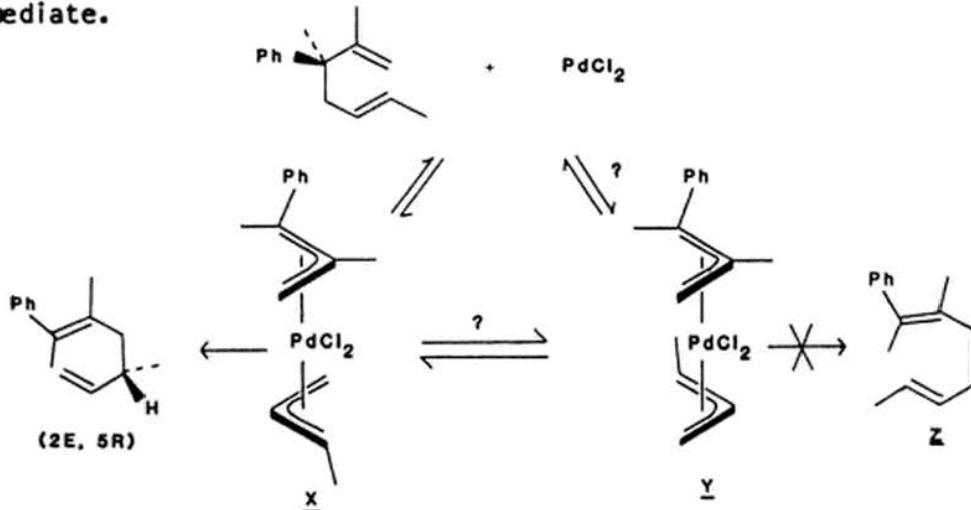
10. Since the Pd(II)-catalyzed reaction gives the same products as the thermal rearrangement (although in a different ratio), it is reasonable to assume that this reaction also proceeds via an intermediate with a chair conformation. Two different mechanisms have been proposed.

Mechanism I



10. (cont.) Mechanism II

10. (cont.) In mechanism I, a bis- $\pi$ -allyl Pd(IV) complex is formed. Intermediate X has the "chair-like" conformation required to give the observed product, i.e. the open sides of the allyl moieties are pointing in opposite directions. Intermediate Y has a "boat-like" conformation, and since product Z is not observed, we can assume either that Y is not present or that no product formation occurs via this intermediate.



In mechanism II, a cyclohexyl-palladium intermediate is formed. Due to the large number of substituents on the ring, the chair conformation is highly favored over the boat. In this mechanism, the cyclization step is a nucleophilic attack on a Pd(II)-coordinated double bond in which the nucleophile is also an olefin. The intermediate can proceed to the product by breaking the C<sub>1</sub>-C<sub>2</sub> bond or back to the starting material by breaking the C<sub>4</sub>-C<sub>5</sub> bond.

At the present time, neither mechanism has been disproven and each is favored by a different research group.

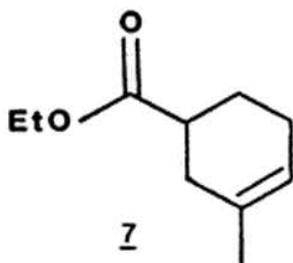
Henry, P.M. *J. Am. Chem. Soc.* 1972, **94**, 5200.

Hamilton, R.; Mitchell, T.R.B.; Rooney, J.J. *J. Chem. Soc., Chem. Comm.* 1981, 456.

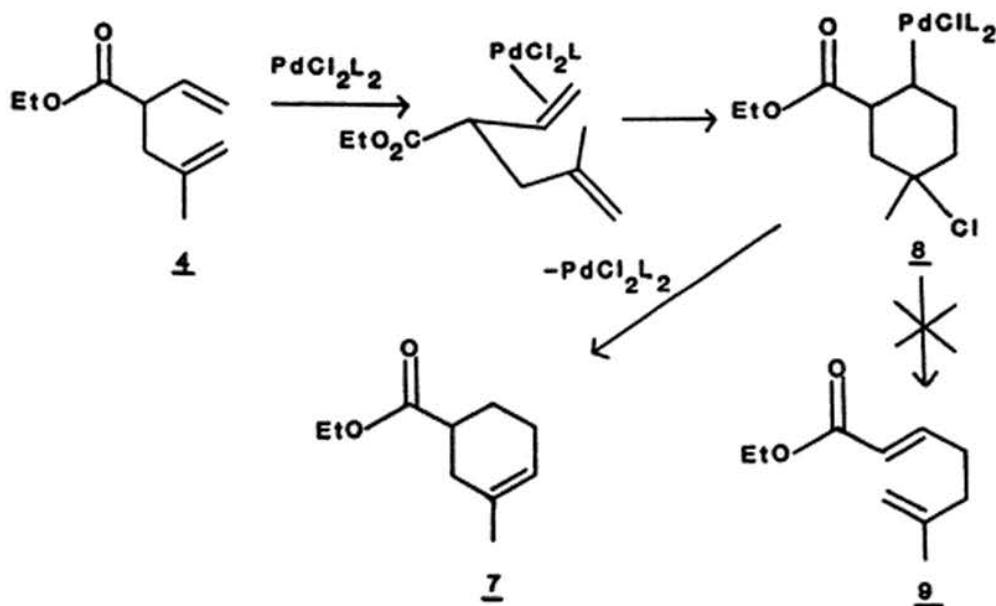
Overman, L.E.; Jacobsen, E.J. *J. Am. Chem. Soc.* 1982, **104**, 7225.

Overman, L.E. *Angew. Chem. Int. Ed. Engl.* 1984, **23**, 579.

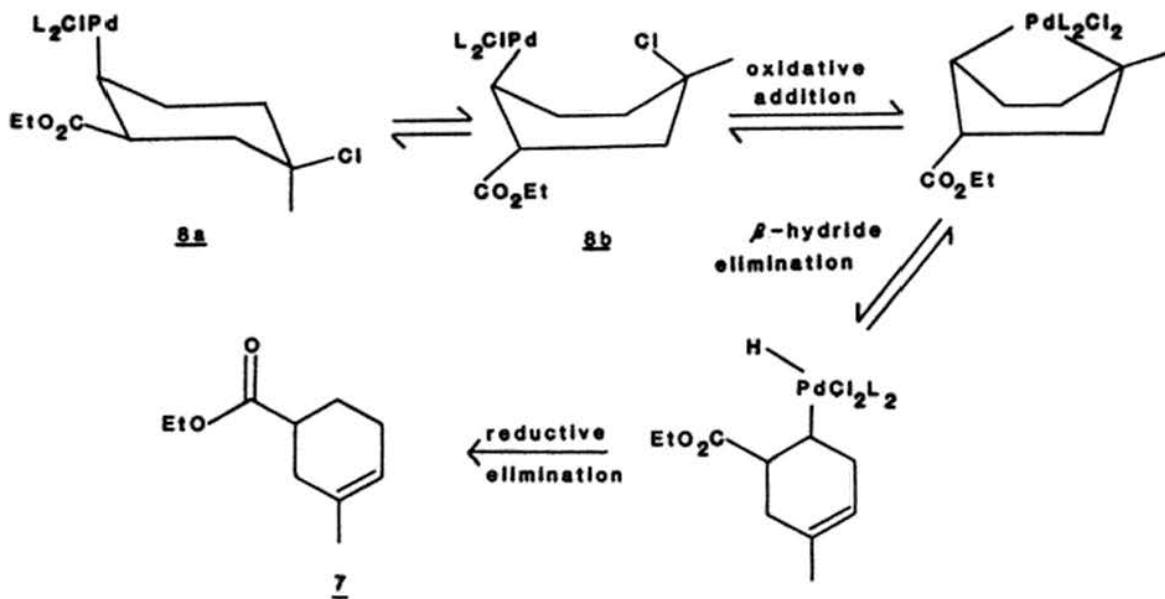
11. The observed product is shown below.



11. (cont.) The proposed mechanism is:

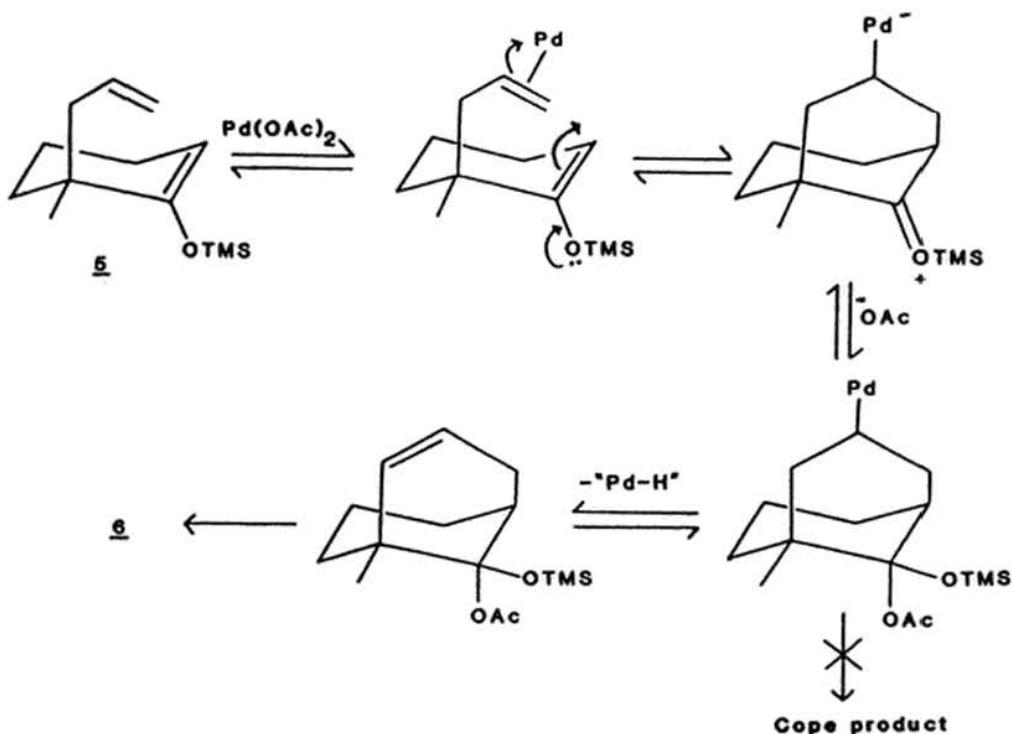


The cyclic intermediate 8 (formed in the same manner as in Mechanism 11, problem 10) does not give the Cope product due to the instability of the palladium-olefin complex 9 formed from an electron-deficient olefin. Instead, 8 gives the cyclic product 7 by an unknown mechanism. A possible (but unproven) mechanism is shown below.



Overman, L.E.; Renaldo, A.F. Tet. Lett. 1983, 24, 2235.

12. As in problem 10; the first step is a nucleophilic attack by one olefin on the coordinated olefin.



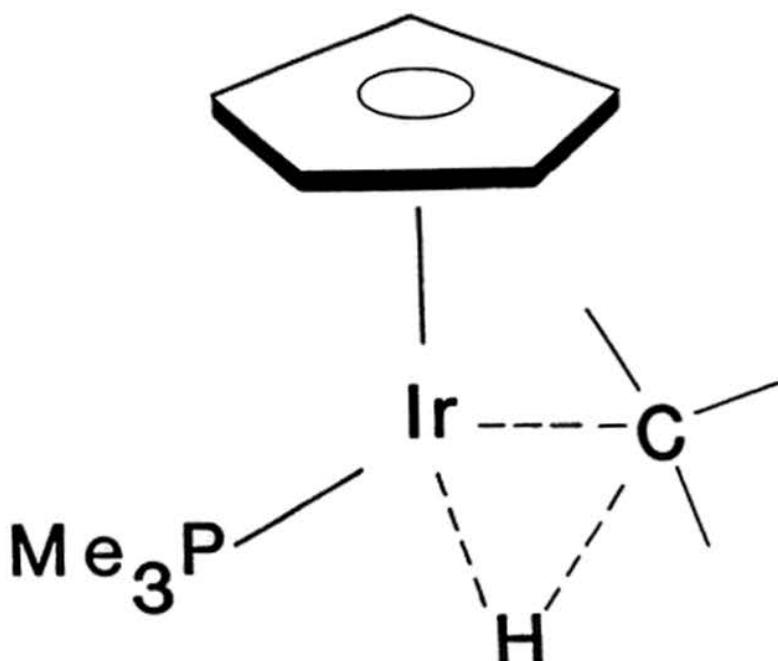
It is not clear why this reaction does not give the Cope rearrangement product.

Kende, A.S.; Roth, B.; Sanfilippo, P.J. J. Am. Chem. Soc., 1982, 104, 1784.

Kende, A.S.; Roth, B.; Sanfilippo, P.J.; Blacklock, T.J. ibid, 5808.

# 5

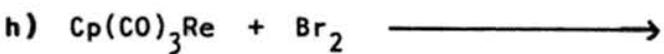
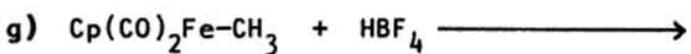
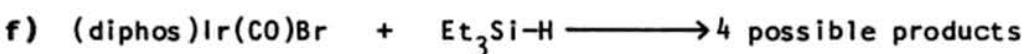
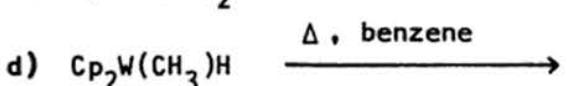
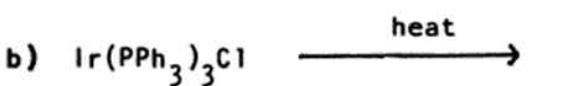
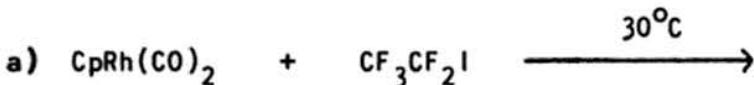
## Oxidative-Addition and Reductive-Elimination Reactions



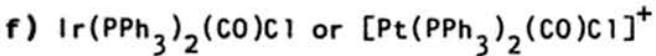
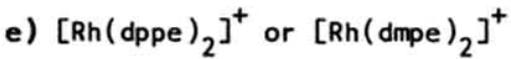
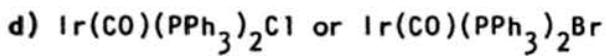
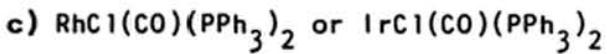
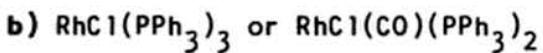
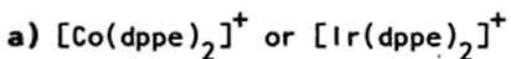
## 5: OXIDATIVE-ADDITION AND REDUCTIVE-ELIMINATION REACTIONS

### QUESTIONS

1. Predict the products of the following reactions and classify them as either oxidative-addition or reductive-elimination. Indicate the change that occurs in the formal oxidation state of the metal.

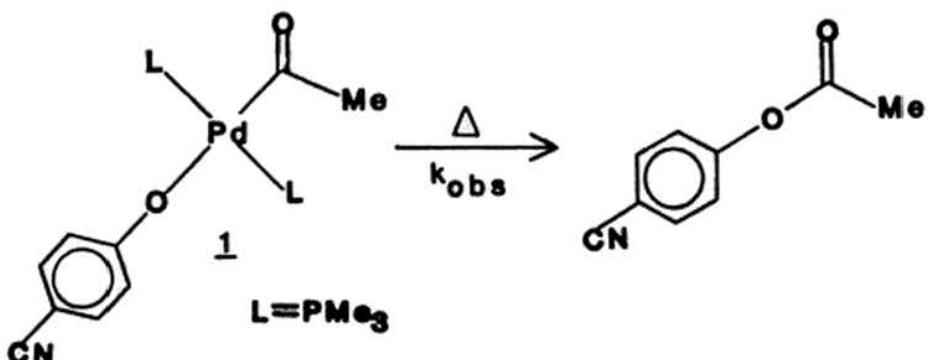


2. For each pair of complexes given below, predict which one will be more reactive towards oxidative-addition of  $\text{H}_2$ .



3. The complex  $(\text{Ph}_3\text{P})_3\text{Rh}-\text{CH}_3$  is cleaved by  $\text{D}_2$  into  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{H})(\text{PPh}_2(\text{C}_6\text{H}_4\text{D}))$  and  $\text{CH}_4$ . Suggest a mechanism for this reaction.

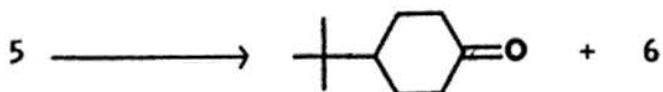
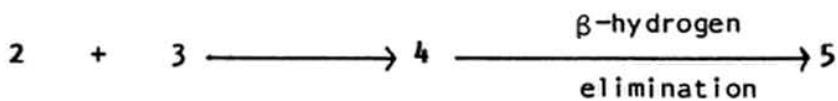
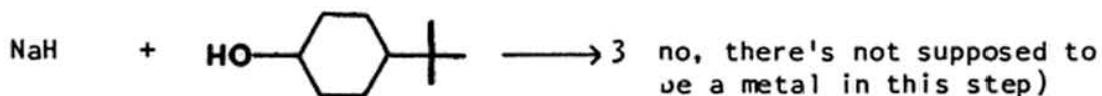
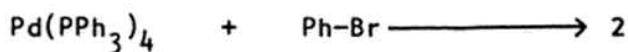
4. The following reaction is observed:



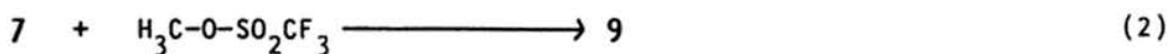
OBSERVATIONS

- 1) The rate law is of the form  $-d[1]/dt = k_{\text{obs}} [1]$ .
  - 2) Addition of excess  $\text{PMe}_3$  decreases the rate of the reaction up to a concentration of 0.4 M. At higher concentrations, no further depression of the rate is noted.
  - 3) In contrast, addition of dimethylphosphinoethane (dmpe) increases the rate of this reaction.
- a) Suggest a mechanism for this reductive-elimination reaction.
- b) In the context of your proposed mechanism, explain the observed changes in rate with a change in the type of phosphine added.

5. Identify the intermediates 2, 3, 4, 5, and 6 in the following catalytic reaction. Clearly indicate which steps involve oxidative-addition or reductive-elimination.



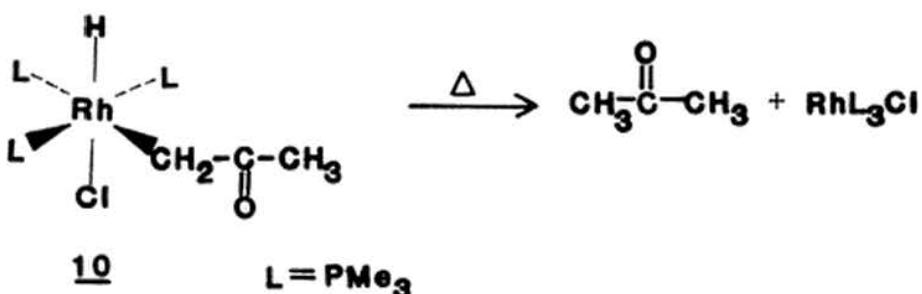
6. The following two reactions have been shown to proceed via different mechanisms:



a) Predict the products, including stereochemistry, and present a reasonable mechanism for each reaction.

b) Speculate as to why different mechanisms prevail for the different reactions.

7. The following reaction is observed:



#### OBSERVATIONS

- 1) When the reaction is carried out with equimolar amounts of  $^{10-d_0}$  and  $^{10-d_6}$ , only  $d_0$ -acetone and  $d_6$ -acetone were obtained.
- 2) The rate of disappearance of **10** follows first order kinetics and is not affected by variations in the initial concentration of **10**.
- 3) The rate decreases when  $PMe_3$  is added, although first order kinetics are still observed. Additionally, the value of  $1/k_{obs}$  varies linearly with the amount of  $PMe_3$  added.
- 4) The rate increases when "phosphine sponge"  $(Rh(acac)(ethylene))_2$  is added.
- 5) A kinetic isotope effect of  $k_{obs}^H/k_{obs}^D = 1.3$  is observed for the reaction.

7. (cont.) Your mission, should you choose to accept, is to:

- postulate a mechanism consistent with the observations given above;
- derive the rate expression for your mechanism.

This page will self-destruct in 10 seconds. Good luck.

8. Oxidation potentials for several ruthenium compounds are shown in the table below.

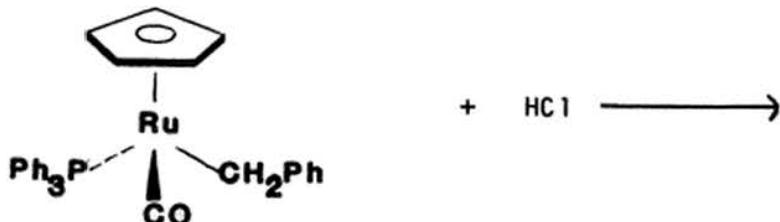
Compound	$(E_p)_a/V^*$
CpRu(CO) <sub>2</sub> Me	1.55
CpRu(CO)(PPh <sub>3</sub> )Me	1.02
CpRu(CO)(PPh <sub>3</sub> )CH <sub>2</sub> Ph	1.03
CpRu(PPh <sub>3</sub> ) <sub>2</sub> Me	0.39
CpRu(PPh <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Ph	0.40

\* $(E_p)_a$  = anodic peak potential vs Ag/AgCl/aqueous KCl/reference, 0.1 V/s, CH<sub>2</sub>Cl<sub>2</sub> solvent, 0.05 M Bu<sub>4</sub>NBF<sub>4</sub> supporting electrolyte.

a) Predict the relative reactivities of the compounds in the table towards electrophilic attack by HgX<sub>2</sub>, CuX<sub>2</sub> (X = Cl, Br), and HCl. Explain your reasoning.

b) Predict the products of the following reactions and propose reasonable intermediates.

1)

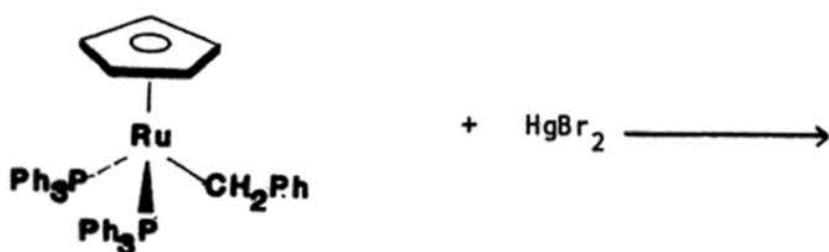


8. (cont.)

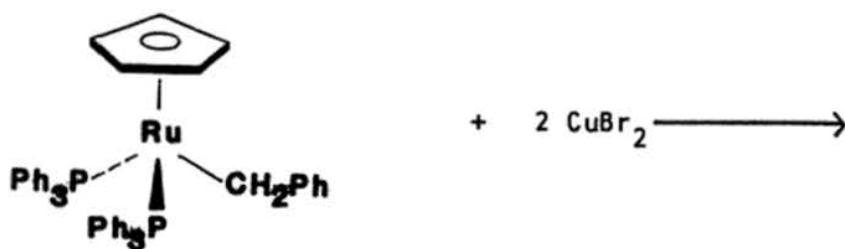
2)



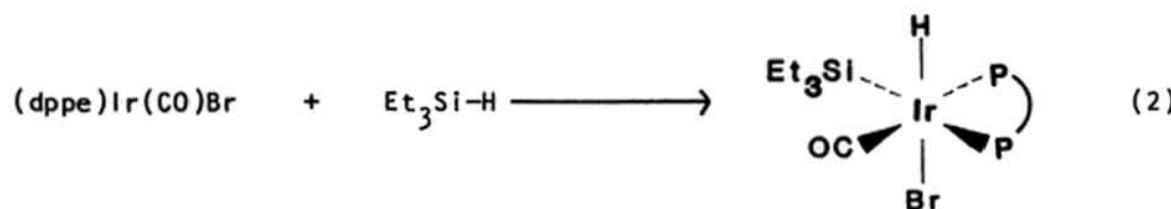
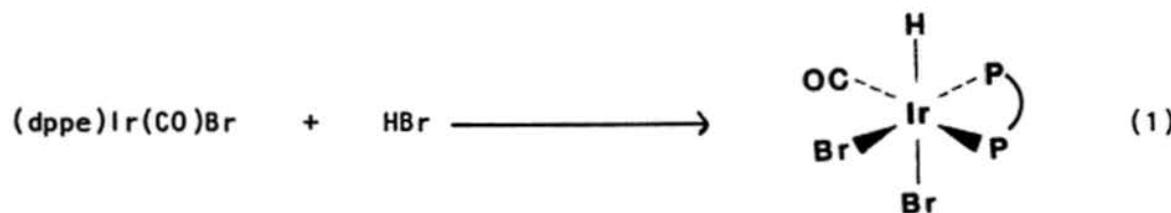
3)



4)

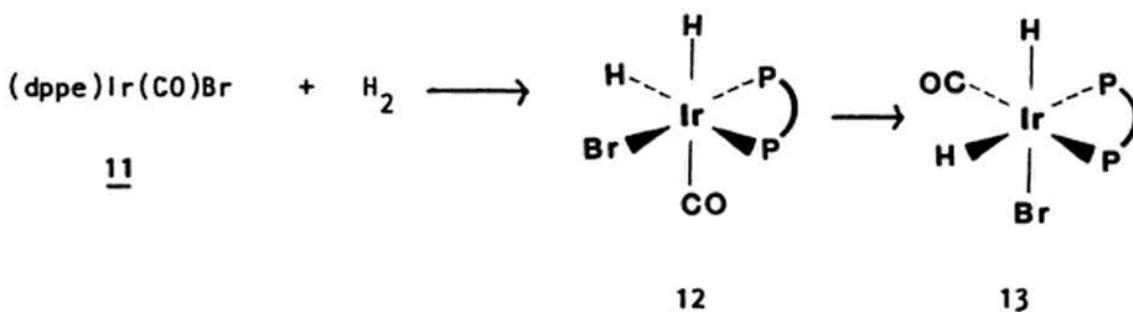


9. The following oxidative-addition reactions have been shown to occur:



9. (cont.) When reaction (2) is carried out, the final products are  $\text{Et}_3\text{Si-SiEt}_3$ ,  $(\text{dppe})\text{Ir}(\text{CO})(\text{Br})\text{H}_2$ , and  $(\text{dppe})\text{Ir}(\text{CO})(\text{SiEt}_3)\text{H}_2$ . Propose a mechanism that accounts for all products.

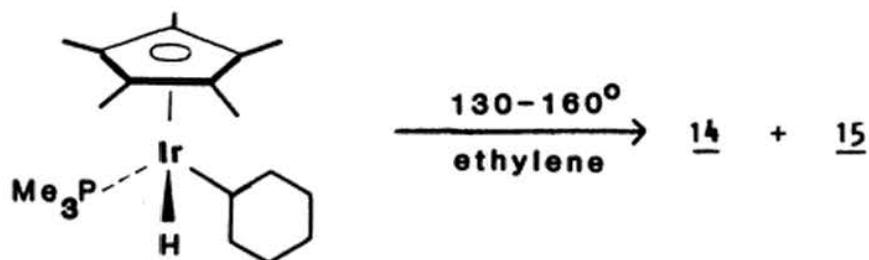
10. The reaction of  $\text{H}_2$  with  $(\text{dppe})\text{Ir}(\text{CO})\text{Br}$ , 11, in acetone initially gives the kinetic product 12 which isomerizes to the thermodynamic product 13 with  $t_{1/2} = 35 \text{ h}$  at  $25^\circ\text{C}$ . Additionally, mixing 12 with  $\text{D}_2$  gives 12-d<sub>2</sub> with  $t_{1/2} = 10 \text{ min.}$  at  $25^\circ\text{C}$ .



Two mechanisms proposed for the interconversion of 12 and 13 are:

- 1) an intramolecular rearrangement of 12, or
  - 2) reductive-elimination of hydrogen to reform 11, followed by oxidative addition of hydrogen with a different stereochemistry.
- a) Derive a rate expression for mechanism 2), assuming that 11 and 12 are in equilibrium.
  - b) Derive a rate expression for the intramolecular rearrangement. Are there any differences in the observables between this expression and the one derived for the two-step mechanism?
  - c) Experimentally, how could the rate of deuterium incorporation be monitored?

11. Products 14 and 15 are obtained from the following reaction.



11. (cont.) At higher temperatures, 14 is converted to 15; however, 15 can not be converted to 14.

Spectral data for 14:

$^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )

-16.88 (d,  $J=36$  Hz, 1 H)  
 1.86 (dd,  $J=1.8$ , 0.8 Hz, 15 H)  
 1.24 (d,  $J=10.1$  Hz, 9 H)  
 5.75, 6.95 (m, 2 H)  
 8.12 (ddd,  $J=3.3$ , 10.2, 17.5 Hz, 1 H)

$^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ , broad-band decoupled)

10.27 (s)  
 18.82 (d,  $J=38.6$  Hz)  
 92.50 (d,  $J=2.6$  Hz)  
 123.78 (d,  $J=3.0$  Hz)  
 129.18 (d,  $J=13.4$  Hz)

IR (KBr,  $\text{cm}^{-1}$ )

2903, 2105, 1553, 953, 940

Spectral data for 15:

$^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )

1.86 (d,  $J=1.5$  Hz, 15 H)  
 1.01 (d,  $J=9.0$  Hz, 9 H)  
 1.13, 1.27 (m, 4 H)

$^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ , gated decoupled)

10.29 (q,  $J=126.1$ )  
 10.55 (dd,  $J=150.6$ , 150.6 Hz)  
 16.93 (dq,  $J=33.9$ , 126.6 Hz)  
 90.19 (s)

IR ( $\text{C}_6\text{H}_6$ ,  $\text{cm}^{-1}$ )

2960, 2900, 1360, 940

a) From the data given, identify 14 and 15. Assign all resonances in the NMR spectra.

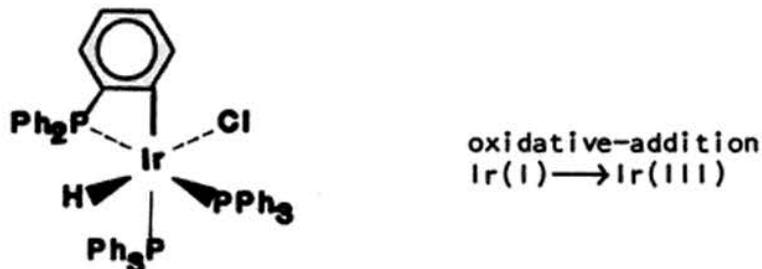
b) Postulate a mechanism for the reaction.

## ANSWERS

1. a)  $\text{CpRh}(\text{CO})(\text{CF}_2\text{CF}_3)\text{I} + \text{CO}$ , oxidative-addition,  $\text{Rh(I)} \rightarrow \text{Rh(III)}$

Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 81.

b)



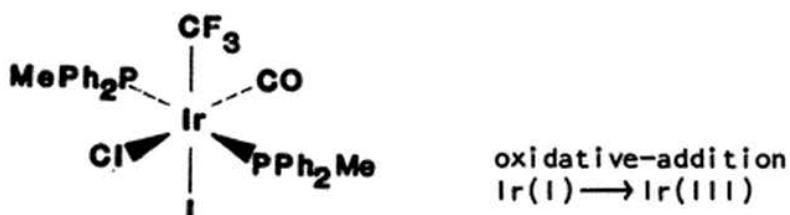
c) The initial product of this reaction is  $\text{Cp}^*\text{IrCO}$ , formed by photolytically-induced loss of CO. The sixteen-electron intermediate then undergoes an oxidative-addition reaction with neopentane to form  $\text{Cp}^*\text{Ir}(\text{CO})(\text{CH}_2\text{C}(\text{CH}_3)_3)\text{H}$ , with a formal oxidation state change from Ir(I) to Ir(III).

Hoyano, J.K.; Graham, W.A.G. J. Am. Chem. Soc. 1982, 104, 3723.

d) The initial product of this reaction is  $\text{Cp}_2\text{W}$ , formed by reductive-elimination of methane. The formal oxidation state change for this process is W(IV) to W(II). The sixteen-electron intermediate then undergoes an oxidative-addition reaction with the solvent benzene to form  $\text{Cp}_2\text{W}(\text{Ph})\text{H}$ , with a formal oxidation state change from W(II) to W(IV).

Cooper, N.J.; Green, M.L.H.; Mahtab, R. J. Chem. Soc., Dalton Trans. 1979, 1557.

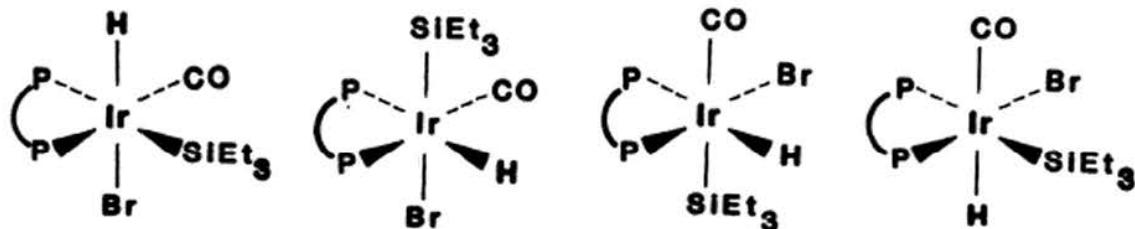
e)



Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 81.

f) The four possible products resulting from oxidative-addition of the silane are shown on the following page. All oxidation state changes are Ir(I) to Ir(III).

## 1. f) (cont.)



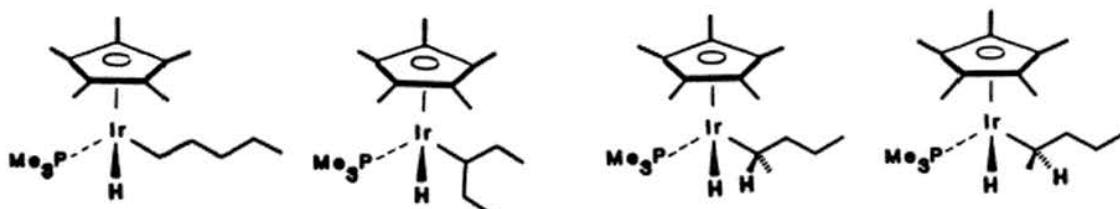
Johnson, C.E.; Eisenberg, R. J. Am. Chem. Soc. 1985, 107, 6531.

g) The initial product of this reaction is the protonated complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3)\text{H}]^+$  with a formal oxidation state change of Fe(II) to Fe(IV). The next step is reductive-elimination of  $\text{CH}_4$ , leaving  $[\text{Cp}(\text{CO})_2\text{Fe}]^+ [\text{BF}_4]^-$ . The formal oxidation state change for this step is Fe(IV) to Fe(II).

h)  $\text{Cp}(\text{CO})_2\text{ReBr}_2 + \text{CO}$ , oxidative-addition, Re(I)  $\longrightarrow$  Re(III).

Einstein, F.W.B.; Klahn-Oliva, A.H.; Sutton, D.; Tyers, K.G. Organomet. 1986, 5, 53.

i) The initial product of this reaction is  $\text{Cp}^*\text{Ir}(\text{PMe}_3)$ , formed by reductive-elimination of  $\text{H}_2$ . The formal oxidation state change for this process is Ir(III) to Ir(I). The four different products shown below result from oxidative-addition [Ir(I) to Ir(III)] to the different types of C-H bonds in n-pentane. Because the metal center is chiral, addition at the 2-position of n-pentane gives rise to two products that are diastereomeric.



Janowicz, A.H.; Bergman, R.G. J. Am. Chem. Soc. 1983, 105, 3929.

2. In general, the tendency of a complex to undergo oxidative-addition reactions is governed by the amount of electron density at the metal, i.e. by the ease with which the metal can be oxidized. Thus, several general trends have been observed:

- 1) The presence of electron-rich ligands in the coordination sphere of the metal increases the rate of oxidative-addition.

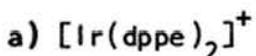
## 2. (cont.)

2) A low initial oxidation state of the metal is more favorable for oxidative-addition reactions to occur; e.g., all other factors being equal, Fe(0) is easier to oxidize than Co(I), which is easier to oxidize than Ni(II), even though the d-electron configuration is the same for these metals.

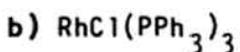
3) The tendency for oxidative-addition to occur increases down a given group, e.g. Ir(II) is easier to oxidize than Rh(II), which is easier to oxidize than Co(II).

4) Oxidative-addition occurs more readily in coordinatively unsaturated systems.

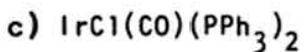
Steric effects have also been shown to be important. In general, valid predictions of relative reactivities can only be made between compounds of very similar structure.



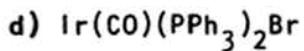
Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 53.



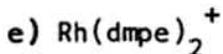
Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 53.



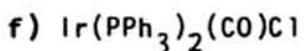
Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 53.



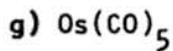
Halpern, J. Accts. Chem. Res. 1970, 3, 386.



Collman, J.P. Accts. Chem. Res. 1968, 1, 136.

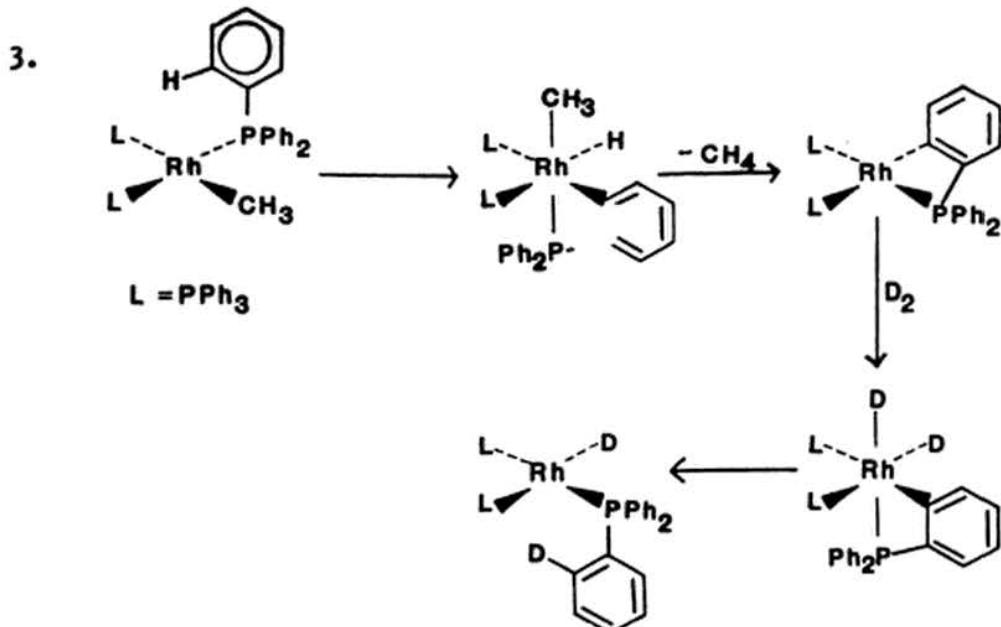


Halpern, J. Accts. Chem. Res. 1970, 3, 386.



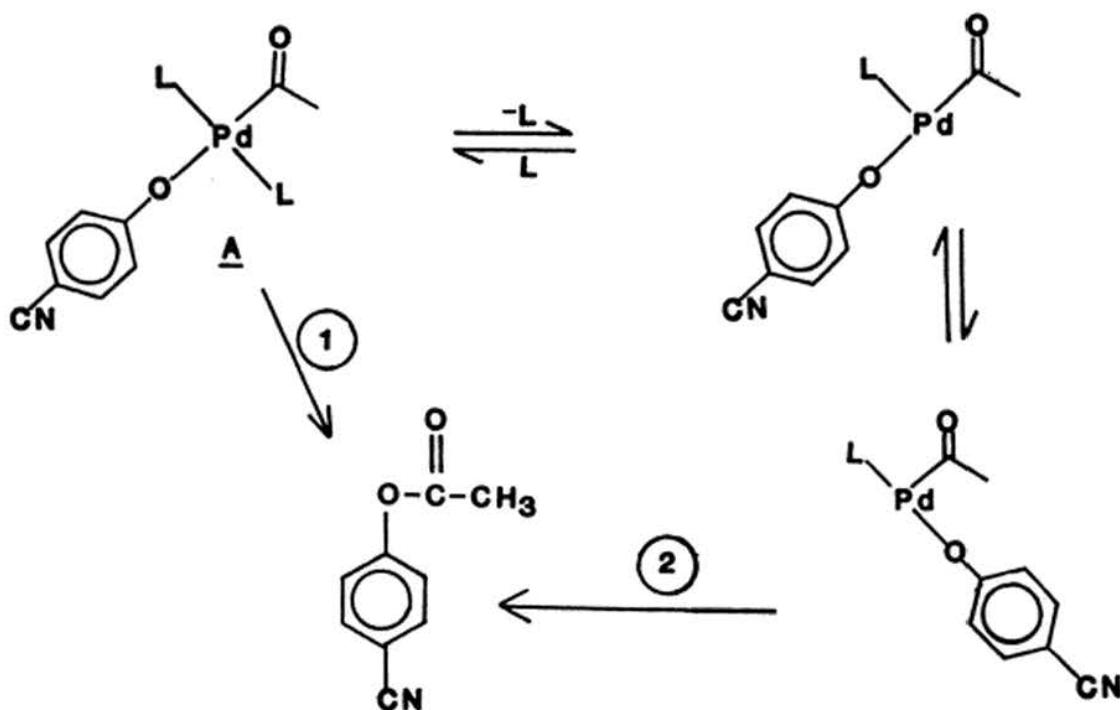
Although addition of electron-donating groups enhances reactivity towards oxidative-addition, CO must dissociate first in this reaction. The presence of the phosphine ligands strengthens the Os-CO bond, thus preventing the dissociation necessary for the oxidative addition reaction to occur.

Collman, J.P.; Roper, W.R. Adv. Organomet. Chem. 1968, 7, 53.



Keim, W. J. Organomet. Chem. 1969, 19, 161.

4. a) The independence of  $k_{obs}$  on  $[PMe_3]$  above a certain concentration suggests that there may be two possible reaction pathways.



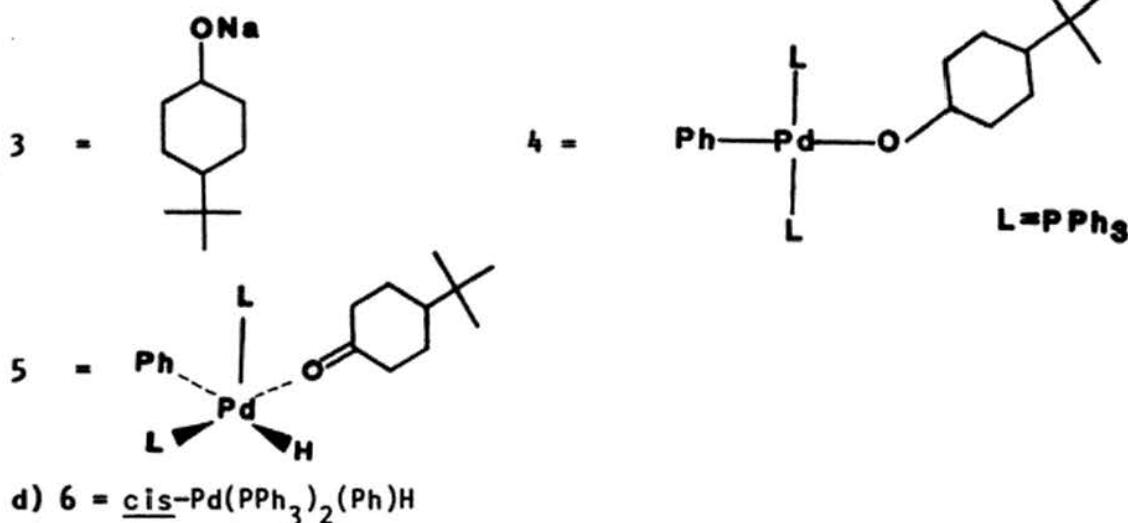
Pathway 2, involving initial dissociation of L and isomerization to a *cis*-acyloxy compound will be shut off with the addition of excess L, while pathway 1 will be operative at all concentrations of L. Direct reductive-elimination from the trans-acyloxy compound, A, (Pathway 1)

4. a) (cont.) seems unlikely, since reductive-elimination reactions do not occur readily from trans compounds; however, it fits the observed kinetic data. Another possibility is isomerization of the four-coordinate trans isomer to the cis isomer followed by reductive-elimination. Kinetically, this is indistinguishable from the reductive-elimination from the four-coordinate trans isomer.

b) The increase in  $k_{\text{obs}}$  when dmpe is added to the reaction mixture is thought to be due to displacement of both  $\text{PEt}_3$  ligands by the chelating ligand, with a corresponding change in geometry to a cis-acyloxy complex, from which reductive-elimination is more facile.

Komiya, A.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. Organomet. 1985, 4, 1130.

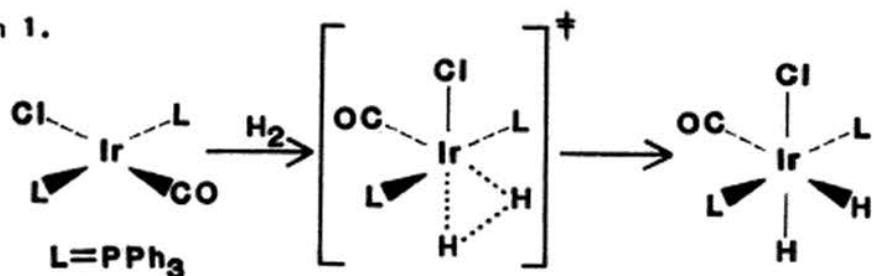
5. 2 = trans- $\text{Pd}(\text{PPh}_3)_2(\text{Ph})\text{Br}$ , oxidative-addition



The last step is a reductive-elimination.

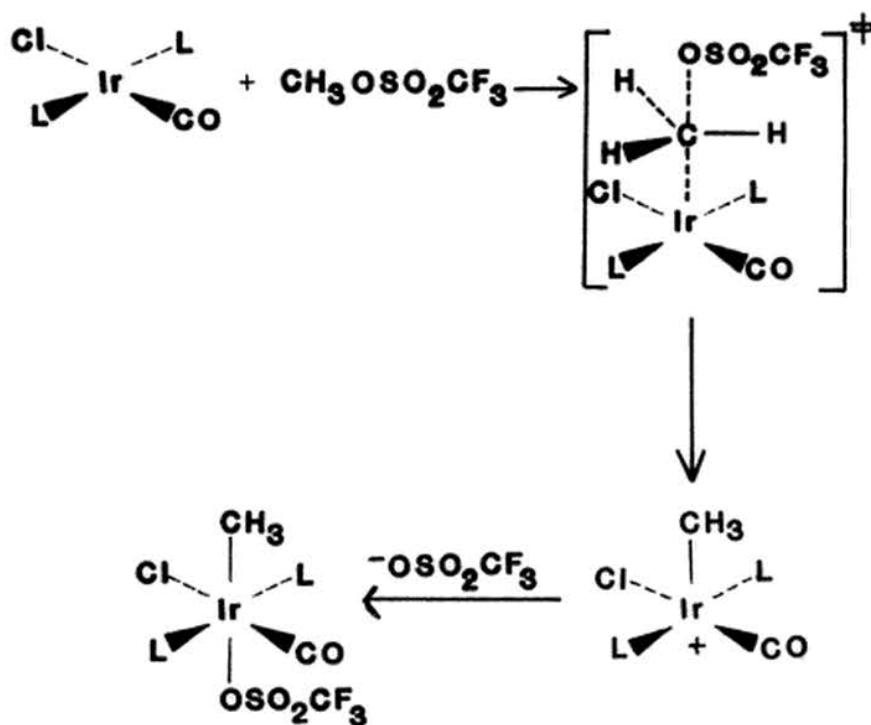
Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. J. Org. Chem. 1983, 48, 1286.

6. a) The mechanism involves a concerted addition of  $\text{H}_2$  for reaction 1.



Longato, B.; Morandini, F.; Bresadola, S. Inorg. Chem. 1976, 15, 650.

6. a) (cont.) For reaction 2, the mechanism involves an  $S_N^2$ -type attack of the metal on methyltriflate.



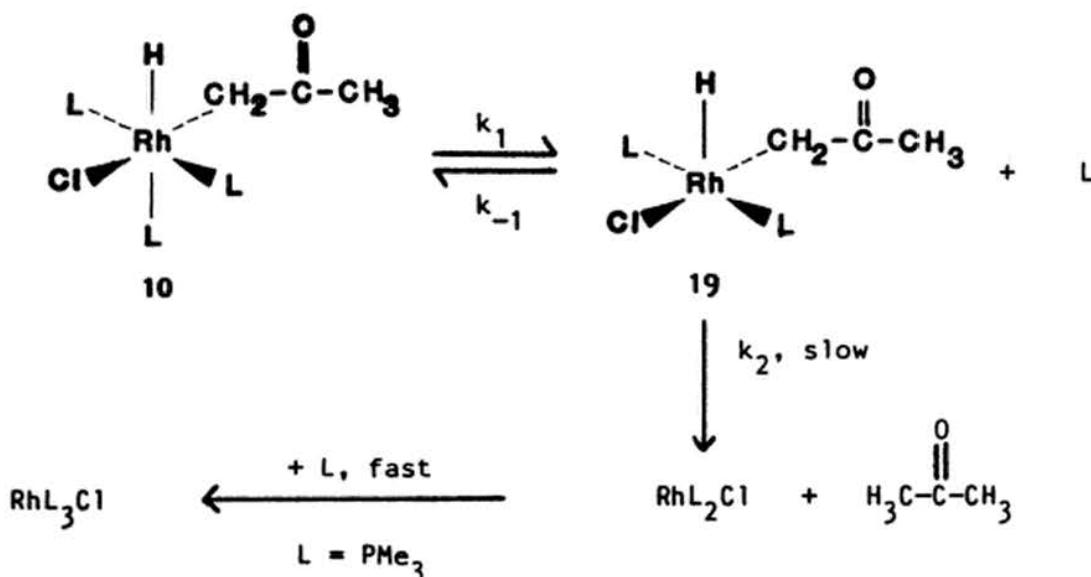
b) Oxidative-addition to polar molecules with good leaving groups tend to favor  $S_N^2$ -type reactions.  $H^-$  is a terrible leaving group compared to  $[OSO_2CF_3]^-$ .

A radical mechanism is also a possibility. To determine whether or not this is the case, one must:

- 1) check for inhibition by radical scavengers such as galvinoxyl or duroquinone and initiation by radical initiators such as benzoyl peroxide or 2, 2'-azobisisobutyronitrile (AIBN);
- 2) carry out the reaction using chiral substrates (alkyl halides or tosylates) and look for racemization of the products; and
- 3) determine the effect of the polarity of the solvent on the rate of the reaction. This effect should be minimal for a radical reaction.

Stang, P.J.; Schiavelli, M.D.; Chenault, H.K.; Breidegam, J.L. *Organomet.* 1984, 3, 1133 and references therein.

7. a) The mechanism of the reaction is shown below:



Because no crossover products are obtained when the reaction is carried out with  $10-d_0$  and  $10-d_6$ , the reductive-elimination must be intramolecular. This conclusion is also supported by observation 2). The existence of an isotope effect indicates that reductive-elimination must occur at or before the rate-determining step. A dissociative first step is supported by observations 3) and 4), where addition of excess ligand decreases the rate and "phosphine sponge" increases the rate of the reaction. The linear variation in  $1/k_{\text{obs}}$  versus  $[PMe_3]$  is indicative of a rate law with  $[PMe_3]$  in the denominator.

b) The rate expression can be derived as follows:

$$\frac{d[\text{acetone}]}{dt} = k_2[19]$$

Using a steady state approximation for the intermediate 19,

$$\frac{d[19]}{dt} = 0 = k_1[10] - k_{-1}[19][PMe_3] - k_2[19]$$

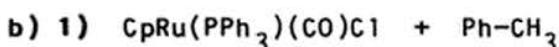
$$\text{therefore, } k_1[10] = (k_{-1}[PMe_3] + k_2)[19]$$

$$[19] = \frac{k_1[10]}{k_{-1}[PMe_3] + k_2}$$

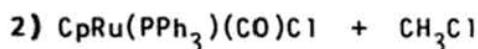
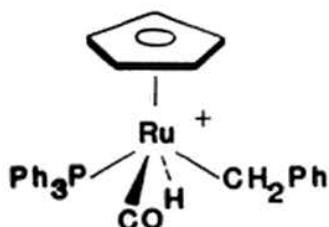
$$\frac{d[\text{acetone}]}{dt} = \frac{k_2 k_1 [10]}{k_{-1}[PMe_3] + k_2} = k_{\text{obs}}[10], \text{ at constant } [PMe_3]$$

Milstein, D. Accts. Chem. Res. 1984, 17, 221.

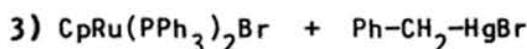
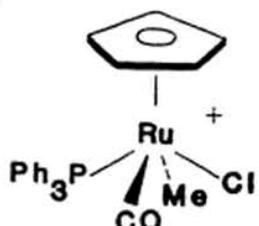
8. a) Electrophilic cleavage reactions of this type are thought to occur via one or two electron oxidation steps involving formally Ru(III) or Ru(IV) intermediates. The ease with which these reactions occur is a function of the oxidation potential of the complex; thus, the lower the oxidation potential, the more facile the reaction. The compounds in the table can be placed in order of increasing reactivity based on their oxidation potentials:  $\text{CpRu}(\text{PPh}_3)_2\text{Me} \sim \text{CpRu}(\text{PPh}_3)_2\text{CH}_2\text{Ph} > \text{CpRu}(\text{PPh}_3)(\text{CO})\text{Me} \sim \text{CpRu}(\text{PPh}_3)(\text{CO})\text{CH}_2\text{Ph} > \text{CpRu}(\text{CO})_2\text{Me}$ . This trend in oxidation potentials is directly related to electron density at the metal. The addition of electron-rich phosphine ligands increases the electron density on the metal, thereby making the complex more susceptible to oxidation.



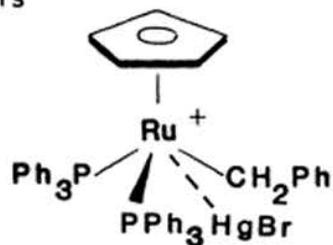
The proposed intermediate is



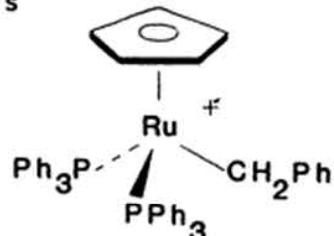
The proposed intermediate is



The proposed intermediate is



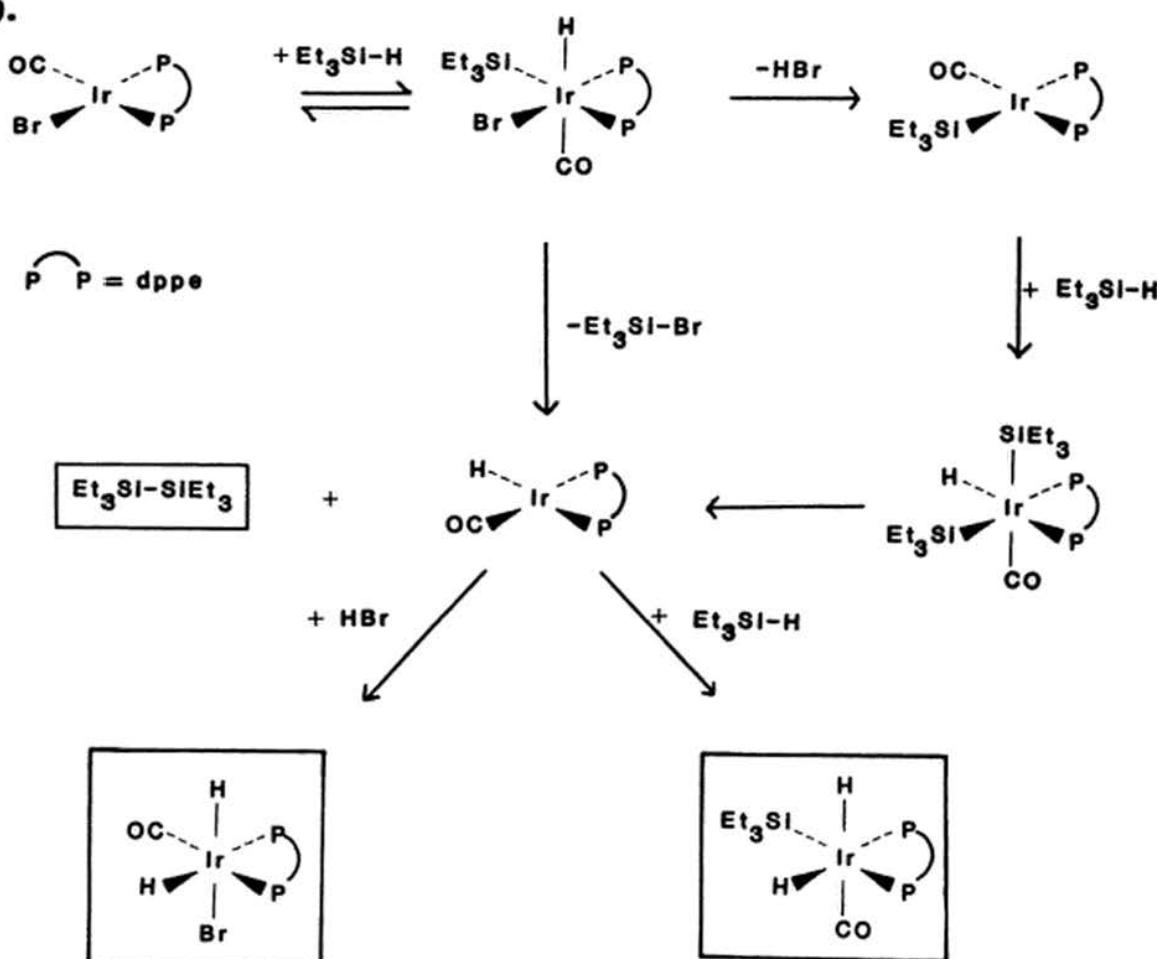
The proposed intermediate is



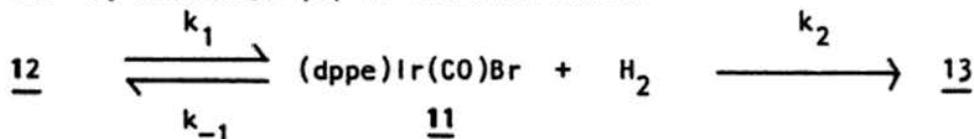
8. b) (cont.) In the first three cases, electrophilic cleavage is proposed to occur via a two-electron oxidative-addition to give an 18-electron Ru(IV) intermediate. Reductive-elimination of R-X (R =  $\text{CH}_2\text{Ph}$ ,  $\text{CH}_3$ ; X =  $\text{HgBr}$ , Cl, H) to give a 16-electron  $[\text{CpRu}(\text{L})(\text{L}')]^+$  species, followed by coordination of  $\text{Cl}^-$  or  $\text{Br}^-$ , gives the observed products. In the oxidation involving copper halides, electrophilic cleavage is proposed to occur via an initial one-electron oxidation to give a 17-electron intermediate. The organic product  $\text{PhCH}_2\text{Br}$  is then formed by nucleophilic attack by  $\text{Br}^-$  on the benzyl carbon atom. The resulting radical species  $[\text{CpRu}(\text{PPh}_3)_2]^*$  abstracts a halogen atom from  $\text{CuBr}_2$  to give the observed organometallic product  $\text{CpRu}(\text{PPh}_3)_2\text{Br}$ .

Joseph, M.F.; Page, J.A.; Baird, M.C. Organomet. 1984, 3, 1749.

9.



10. a) Mechanism (2) is detailed below.



The rate expression is:

$$\frac{d[13]}{dt} = k_2[11][\text{H}_2]$$

Because  $t_{1/2}$  for deuterium incorporation is fast relative to  $t_{1/2}$  for isomerization, it is clear that 11 and 12 are in a rapid pre-equilibrium, and thus

$$K_{\text{eq}} = \frac{k_1}{k_{-1}} = \frac{[11][\text{H}_2]}{[\text{12}]}$$

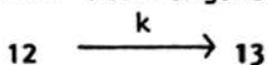
Solving the equilibrium expression for [11] gives

$$[11] = \frac{k_1[\text{12}]}{k_{-1}[\text{H}_2]}$$

and substituting into the initial rate expression gives

$$\frac{d[13]}{dt} = k_2[\text{H}_2] \left( \frac{k_1[\text{12}]}{k_{-1}[\text{H}_2]} \right) = \frac{k_1 k_2 [\text{12}]}{k_{-1}} = k_{\text{obs}}[\text{12}]$$

b) For the intramolecular rearrangement, the equation is:



and the rate is given by  $\frac{d[13]}{dt} = k[\text{12}]$ . This expression has the same form as that derived for the two step mechanism in part a).

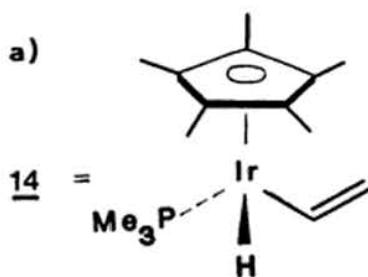
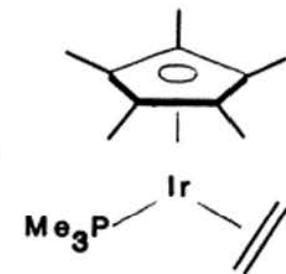
#### NOTE

The fact that deuterium incorporation is rapid relative to the isomerization process indicates that the coordinatively unsaturated intermediate 11 is a plausible intermediate in the mechanistic scheme; however, this is not sufficient evidence to eliminate an intramolecular pathway. There is literature precedent for both types of reactions (see reference). Thus, neither mechanism can be excluded by the data given.

c) The rate of deuterium incorporation could be monitored by either  $^1\text{H}$  or  $^2\text{H}$  NMR of the hydride region of the spectrum. The method actually used was  $^1\text{H}$  NMR. Another possibility is to monitor the Ir-H(D) stretches in the infrared spectrum, although this may be difficult experimentally.

Johnson, C.E.; Eisenberg, R. J. Am. Chem. Soc. 1985, 107, 3148.

11. a)

 $\underline{15} =$ 

Assignments for NMR data:

Complex 14

 $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )

- 16.88 (d,  $J_{\text{P}-\text{H}}=36$  Hz, 1 H, Ir-H)
- 1.86 (dd,  $J_{\text{P}-\text{H}}=1.8$ ,  $J_{\text{H}-\text{H}}=0.8$  Hz, 15 H,  $\text{C}_5\text{Me}_5$ )
- 1.24 (d,  $J_{\text{P}-\text{H}}=10.1$  Hz, 9 H,  $\text{PMMe}_3$ )
- 5.75, 6.95 (m, 2 H,  $-\text{CH}=\text{CH}_2$ )
- 8.12 (ddd,  $J_{\text{P}-\text{H}}=3.3$ ,  $J_{\text{H}-\text{H}(\text{cis})}=10.2$ ,  $J_{\text{H}-\text{H}(\text{trans})}=17.5$  Hz,  $-\text{CH}=\text{CH}_2$ )

 $^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ , broad-band decoupled)

- 10.27 (s,  $\text{C}_5\text{Me}_5$ )
- 18.82 (d,  $J_{\text{P}-\text{C}}=38.6$  Hz,  $\text{PMMe}_3$ )
- 92.50 (d,  $J_{\text{P}-\text{C}}=2.6$  Hz,  $\text{C}_5\text{Me}_5$ )
- 123.78 (d,  $J_{\text{P}-\text{C}}=3.0$  Hz,  $-\text{CH}=\text{CH}_2$ )
- 129.18 (d,  $J_{\text{P}-\text{C}}=13.4$  Hz,  $-\text{CH}=\text{CH}_2$ )

Complex 15

 $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )

- 1.86 (d,  $J_{\text{P}-\text{H}}=1.5$  Hz, 15 H,  $\text{C}_5\text{Me}_5$ )
- 1.01 (d,  $J_{\text{P}-\text{H}}=9.0$  Hz, 9 H,  $\text{PMMe}_3$ )
- 1.13, 1.27 (m, 4 H,  $\text{CH}_2=\text{CH}_2$ )

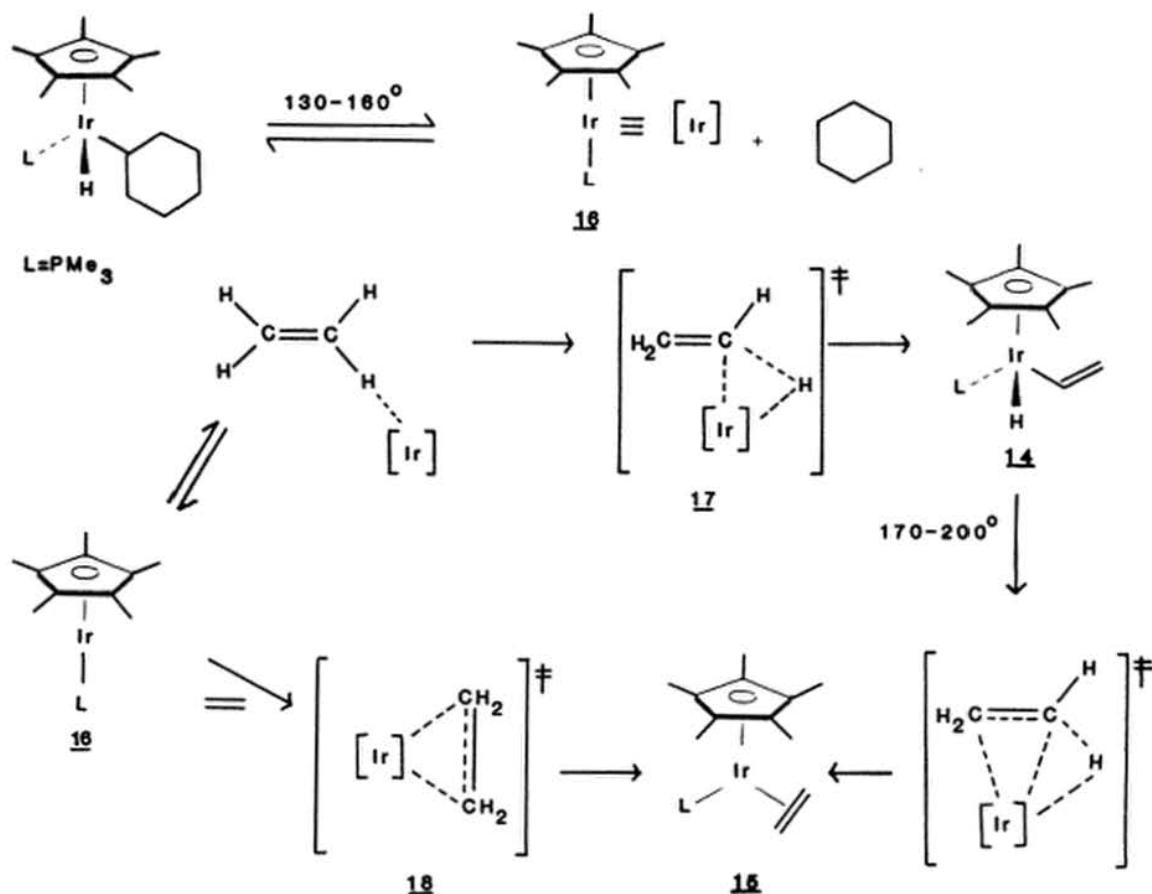
 $^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ , gated decoupled)

- 10.29 (q,  $J_{\text{C}-\text{H}}=126.1$ ,  $\text{C}_5\text{Me}_5$ )
- 10.55 (dd,  $J_{\text{C}-\text{H}1}=J_{\text{C}-\text{H}2}=150.6$  Hz,  $\text{CH}_2=\text{CH}_2$ )
- 16.93 (dq,  $J_{\text{P}-\text{H}}=33.9$ ,  $J_{\text{C}-\text{H}}=126.6$  Hz,  $\text{PMMe}_3$ )
- 90.19 (s,  $\text{C}_5\text{Me}_5$ )

b) The mechanism of this reaction is not fully known; however, certain conclusions can be drawn about possible mechanisms from the knowledge of other systems. The first step is a reductive-elimination of cyclohexane to give the sixteen-electron intermediate  $\text{Cp}^*\text{Ir}(\text{PMMe}_3)$ , 16.

A logical second step would then be coordination of ethylene to 16 to give the ethylene complex 15. Oxidative-addition of a C-H bond of the bound ethylene could be envisioned as the next step, leading to the vinyl hydride 14; however, the fact that 15 can not be independently converted to 14 makes this step unlikely. The authors propose the following mechanism involving two independent transition states, 17 and 18, leading to the two different products 14 and 15.

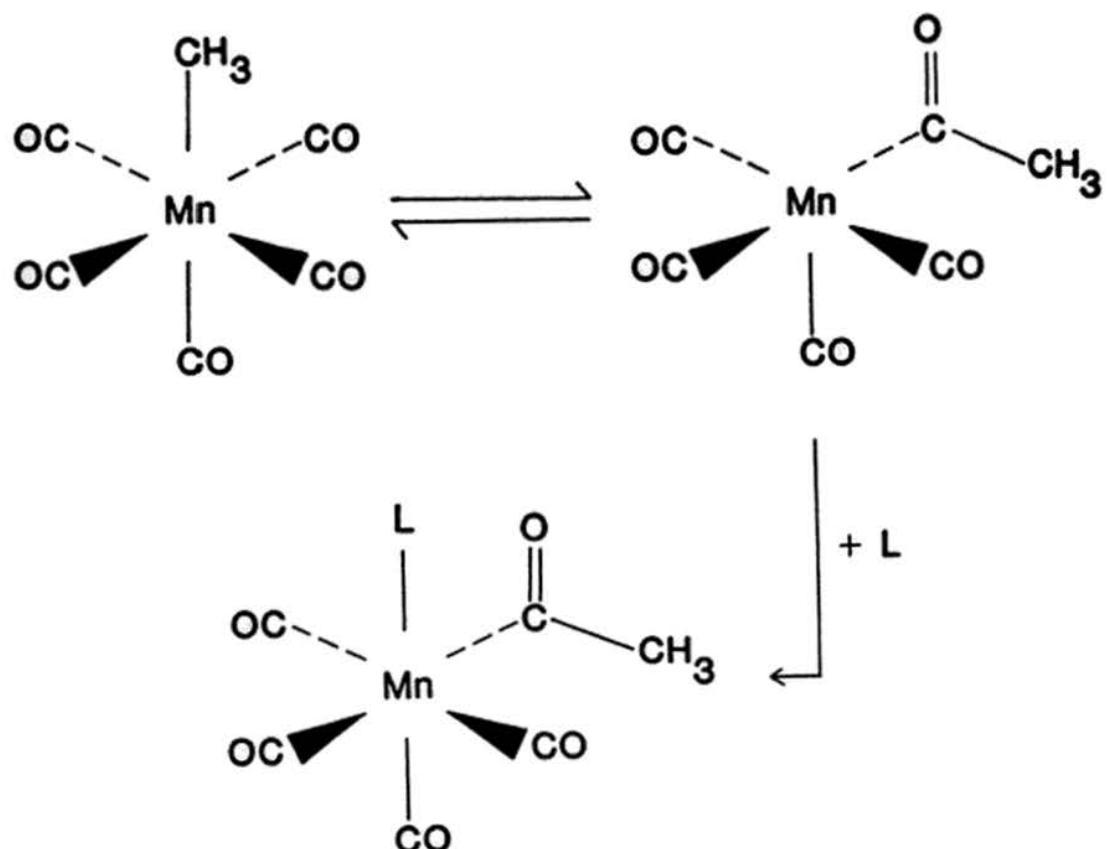
## 11. (cont.)



Stoutland, P.O.; Bergman, R.G. J. Am. Chem. Soc. 1985, 107, 4581.

# 6

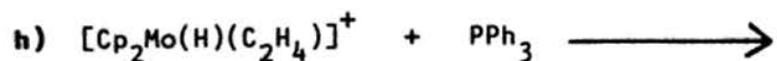
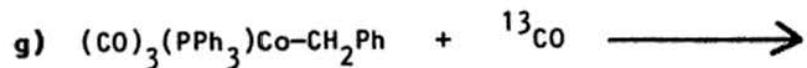
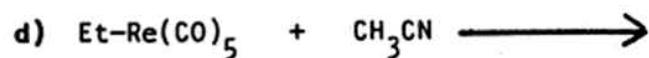
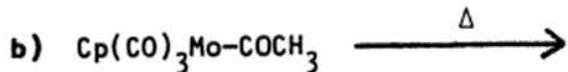
## Insertion Reactions



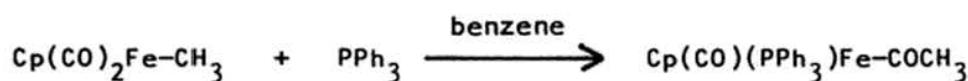
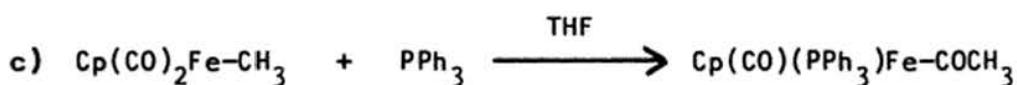
## 6: INSERTION REACTIONS

### QUESTIONS

1. Predict the products of the following reactions.



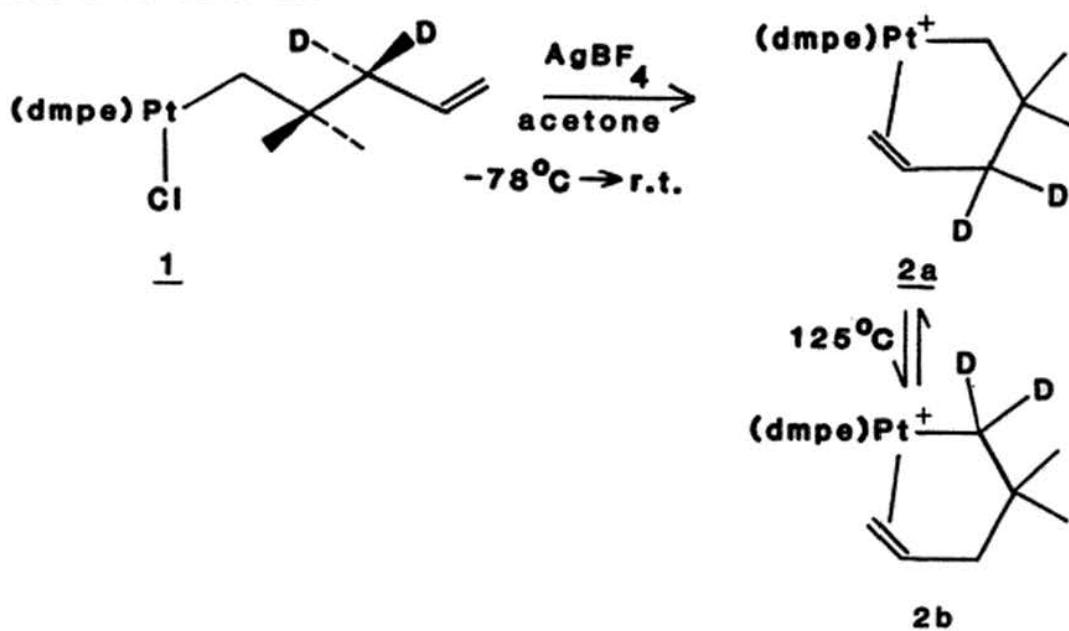
2. For each group of insertion reactions given, predict which reaction will occur most rapidly. Explain your reasoning.



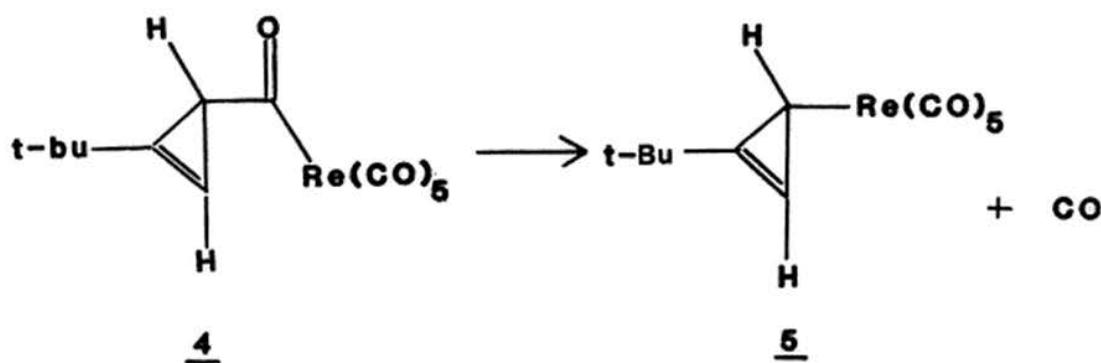
2. (cont.)



3. When 1 is treated with  $Ag^+$ , 2a is formed. If 2a is heated, a 50/50 mixture of 2a and 2b is generated. Propose a mechanism for the conversion of 2a to 2b.



4. Upon standing at room temperature, compound 4 will decarbonylate to give 5.



$^1H$  NMR ( $\delta$ ,  $CDCl_3$ )

For 4:

- 1.15 (s, 9 H)
- 2.92 (d, 1 H,  $J = 1.2$  Hz)
- 6.18 (d, 1 H,  $J = 1.2$  Hz)

For 5:

- 1.20 (s, 9 H)
- 2.20 (d, 1 H,  $J = 1.2$  Hz)
- 6.20 (d, 1 H,  $J = 1.2$  Hz)

## 8. (cont.)

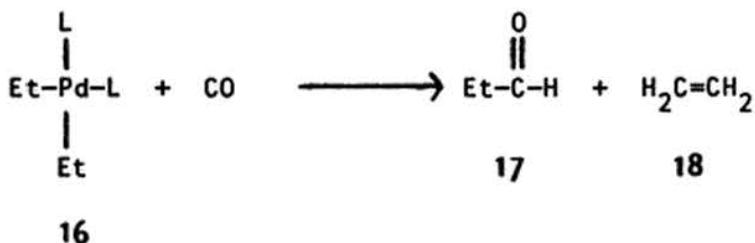
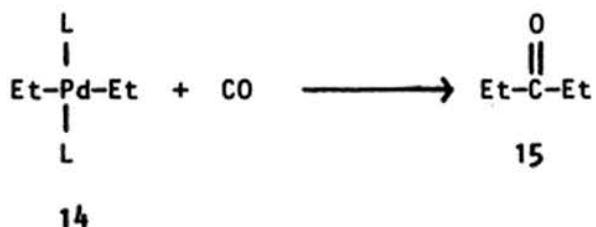
In addition, the following two observations have been made.

1) Addition of 0.5 eq of L decreases the rate by a factor of 50.

2) Without added phosphine, a plot of  $-\ln(A-A_\infty)$  vs time shows upward curvature at short reaction times.

Propose a mechanism for this reaction. Be sure to show all intermediates. In addition, state which steps are fast, which are slow, and which are equilibria.

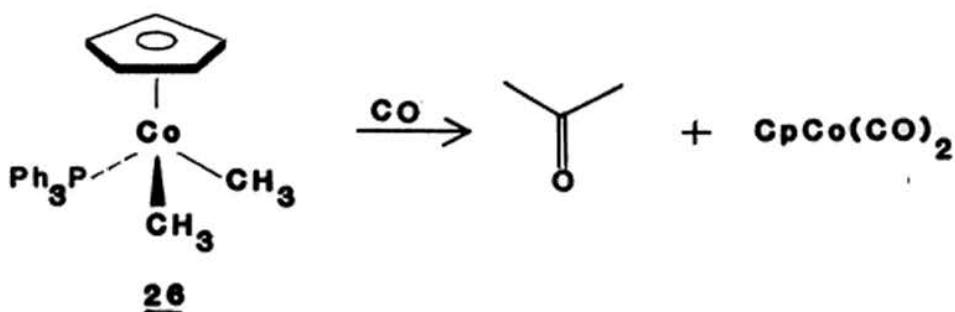
## 9. The following reactions are observed



Propose a mechanism(s) to account for the different behavior of the cis and trans isomers.

## 10. Supply plausible mechanisms for the following reactions:

a)



**12. (cont.)**

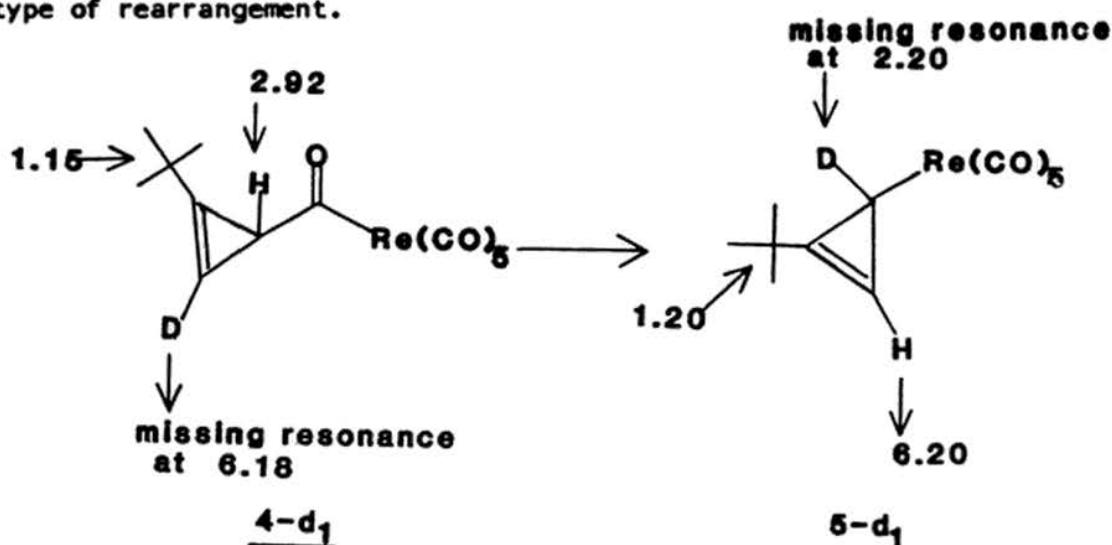
<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 5.57 (s, 5 H)  
4.60 (t, J = 7 Hz, 2 H)  
3.60 (t, J = 7 Hz, 2 H)  
1.92 (quint., J = 7 Hz, 2 H)

<sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>, broad-band decoupled): 316.6  
223.4  
96.9  
82.0  
58.8  
22.5

a) Identify **28** and **29** based on the spectral data given.

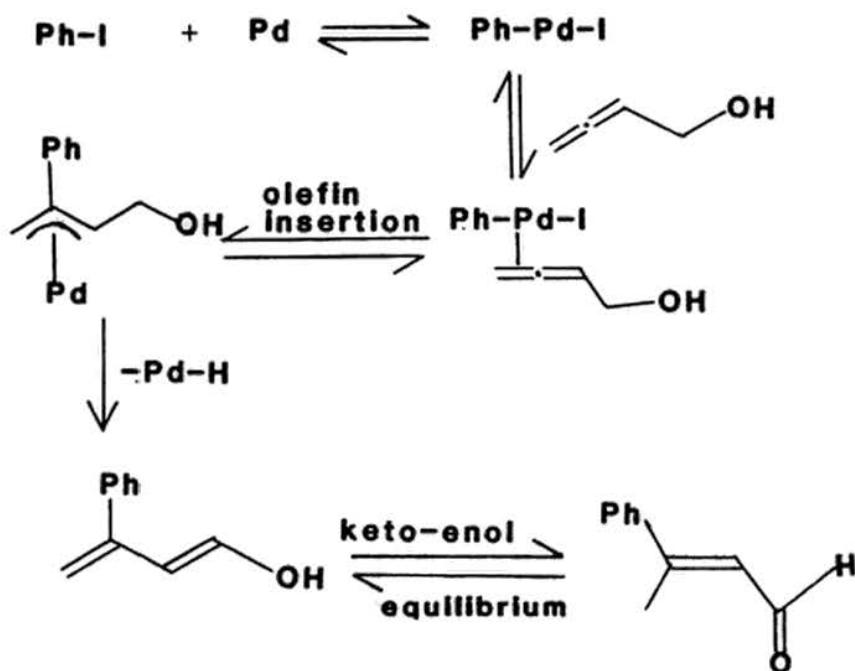
b) Postulate a mechanism for the conversion of **28** to **29**.

4. For this compound, the decarbonylation occurs with an allylic rearrangement. This reaction represents the first known case of this type of rearrangement.



DeSimone, D.M.; Desrosiers, P.J.; Hughes, R.P. *J. Am. Chem. Soc.* 1982, 104, 4842.

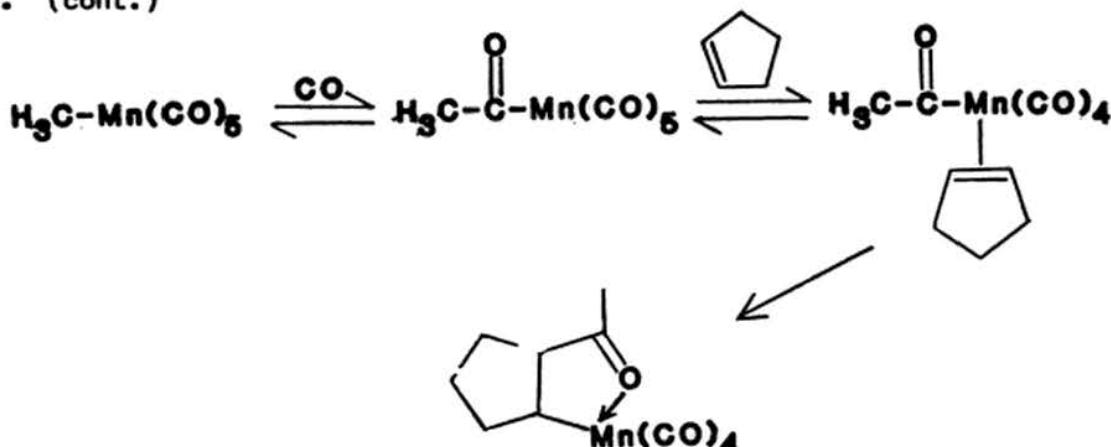
5. In the mechanistic scheme shown below, "Pd" represents the metal and an unknown number of ancillary ligands.



Shimizu, I.; Sugiura, T.; Tsuji, J. *J. Org. Chem.* 1985, 50, 537.

6. This reaction involves two insertion reactions. The first is a CO insertion and the second an olefin insertion.

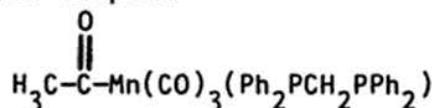
6. (cont.)



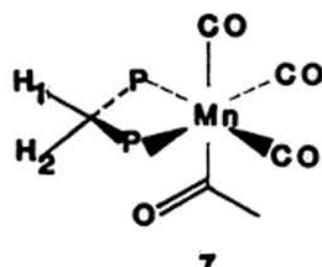
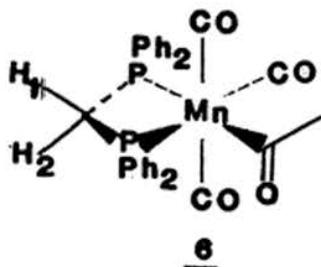
The product shows no tendency toward further CO or olefin insertions.

DeShong, P.; Slough, G.A. Organometal. 1984, 3, 636.

7. The IR spectrum shows terminal carbonyls and an acyl, implying that a CO insertion has taken place. Thus, the product is the six-coordinate octahedral complex



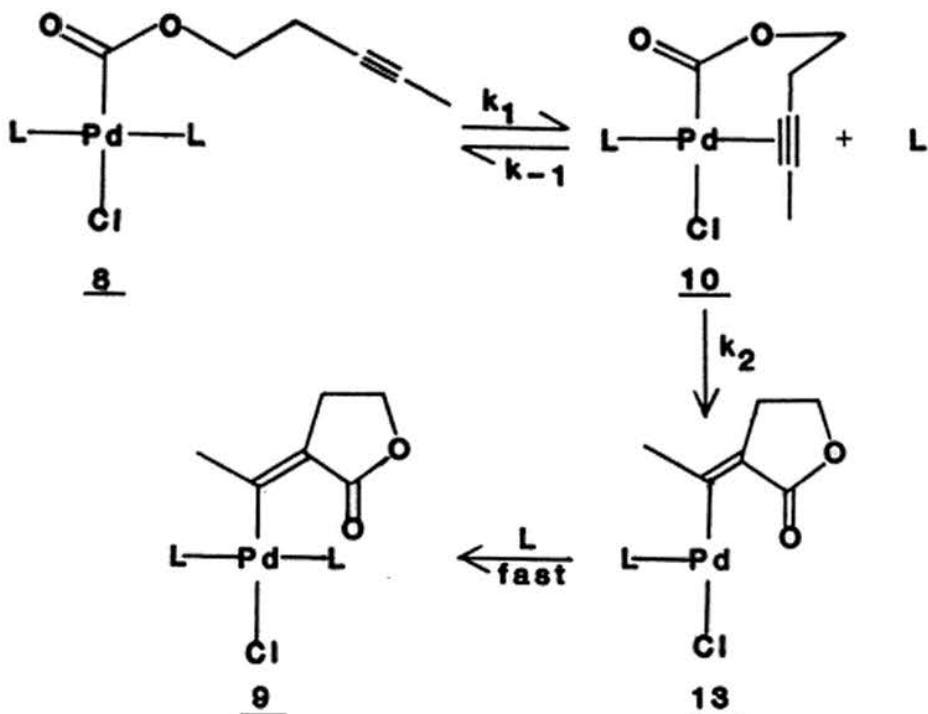
The two phosphorus atoms of the chelating phosphine must be cis, so the question is whether the acyl ligand is trans to a CO (6) or trans to a phosphine (7).



Each molecule has only one mirror plane. In 6, H<sub>1</sub> and H<sub>2</sub> are equivalent because the mirror plane passes between them. On the other hand, the phosphorous atoms are not equivalent, so each should split the proton signal into a doublet thus giving a doublet of doublets or 4 peaks total.

In 7, H<sub>1</sub> and H<sub>2</sub> are not equivalent since they lie in the mirror plane. Each will split the other into a doublet. Here the two phosphorus atoms are equivalent and will split each proton signal into a triplet (this is for the same reason that in e.g. CH<sub>2</sub>CH<sub>3</sub>, the methyl is split into a triplet by the two equivalent hydrogens on the methylene). For

8. (cont.)



We must now ask if **10** is a steady state intermediate. In other words, is  $k_1 \ll k_{-1} + k_2$  or is  $k_2 \ll k_1$  and  $k_{-1}$ ?

The upward curvature in the plot of  $-\ln(A - A_\infty)$  vs time indicates that the initial rate is slower than the final rate. We know that phosphine will decrease the rate of the reaction. If **10** were a steady-state intermediate, then the amount of free **L** generated in the reaction is negligible. On the other hand, if  $k_1/k_{-1}$  were a rapid equilibrium with  $k_2$  as the slow step, a significant quantity of free **L** will be generated to slow down the reaction. As the reaction proceeds, the amount of free **L** will decline as it becomes coordinated to the product and the rate of reaction will increase. Thus, there must be a fast equilibrium followed by a rate determining insertion reaction.

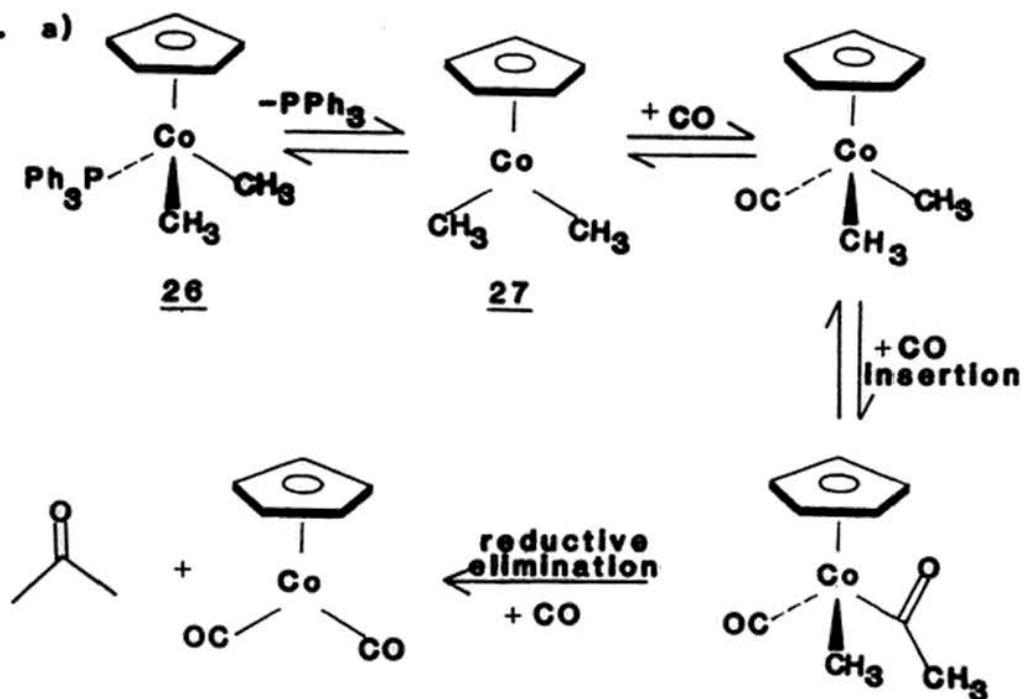
Samsel, E.G.; Norton, J.R. J. Am. Chem. Soc. 1984, **106**, 5505.

9. The authors propose that all reactions have configurationally stable three-coordinate intermediates. However, they say that other possibilities involving five-coordinate intermediates cannot be excluded.

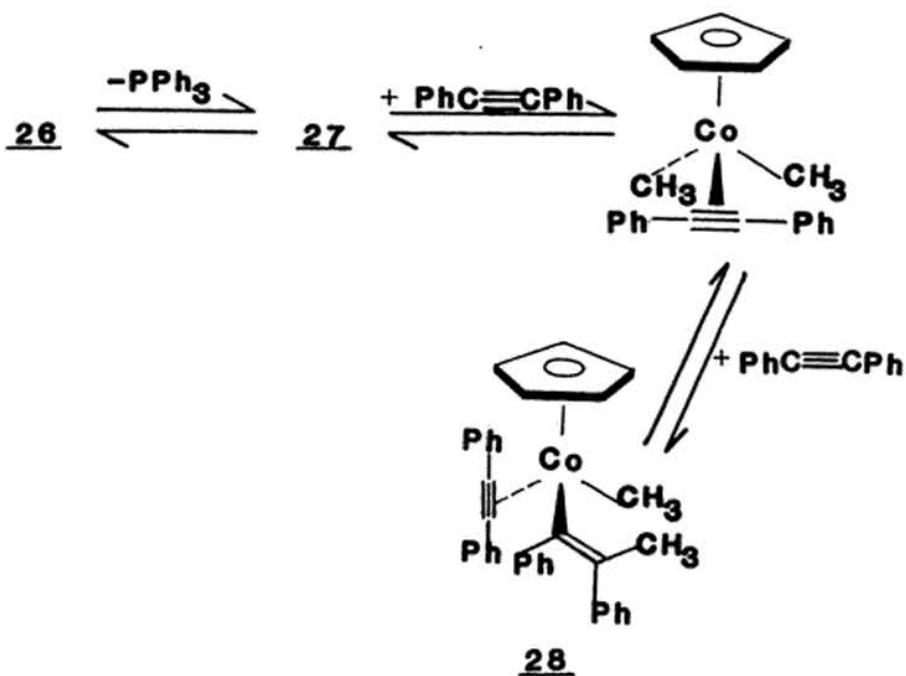
9. (cont.) Ozawa, F.; Yamamoto, A. Chem. Lett. 1981, 289.

For further information regarding three-coordinate group 10 metal complexes, see: Thorn, D.L.; Hoffmann, R. J. Am. Chem. Soc. 1978, 100, 2079.

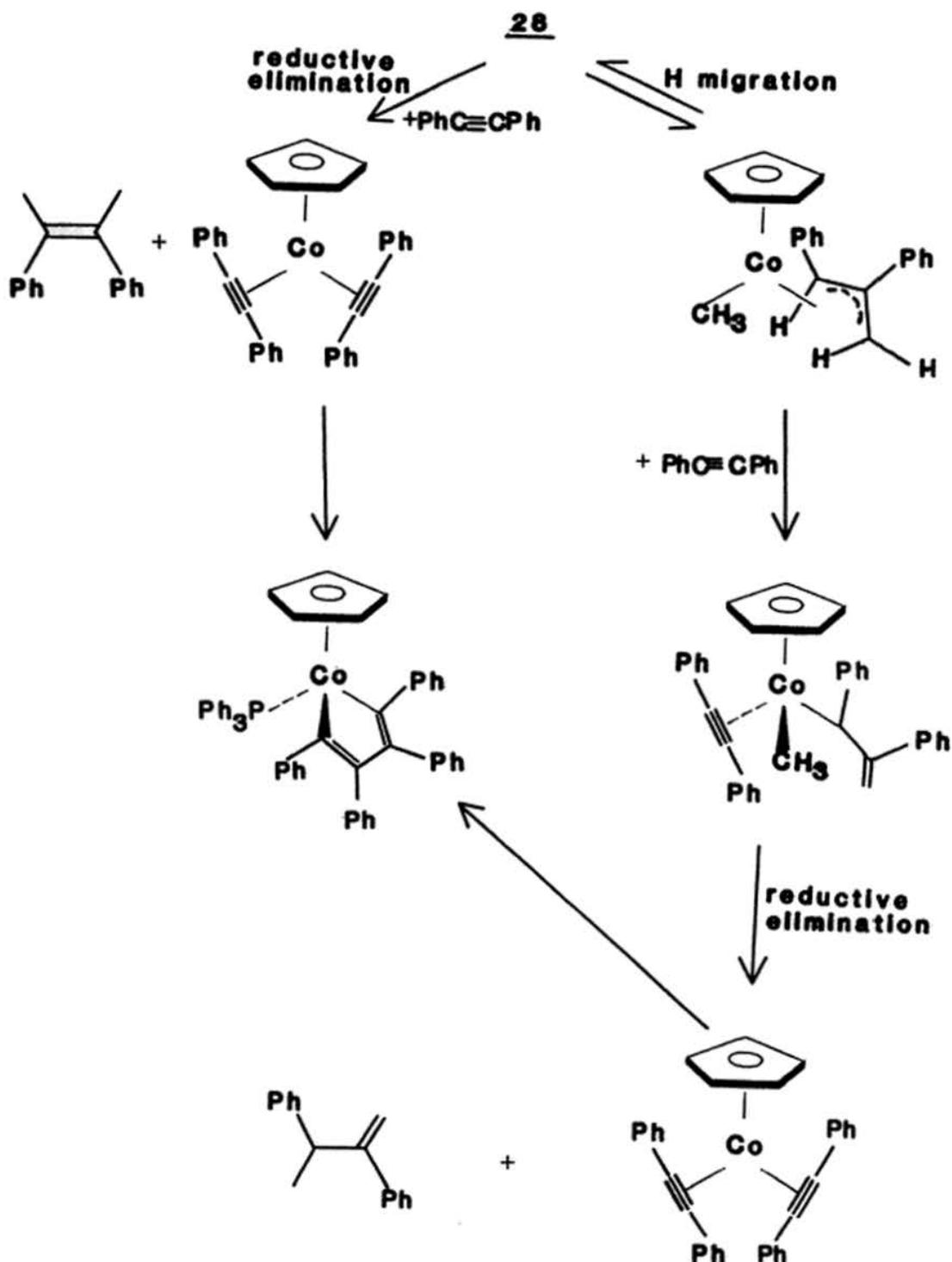
10. a)



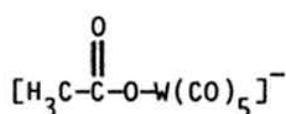
b)



10. b) (cont.)



11. The product is the result of  $\text{CO}_2$  insertion into a tungsten-methyl bond.



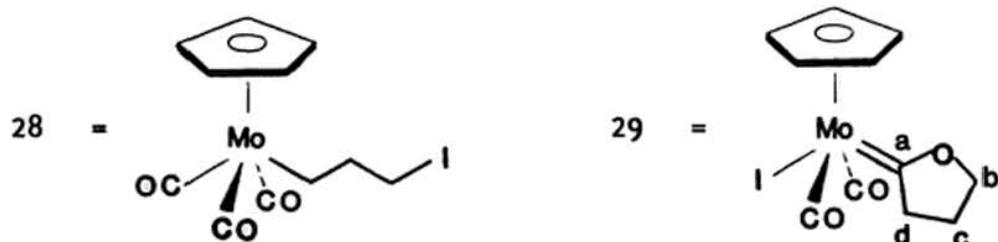
The  $^{13}\text{C}$  NMR data are assigned as follows:

$\delta$	22.1	$-\text{CH}_3$
		$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{W} \end{array}$
$\delta$	175.7	axial CO
$\delta$	200.3	equatorial CO

The  $\delta$  175.7 resonance is a typical value for the carbonyl of a carboxylic acid. The peaks in the infrared spectrum are assigned to the terminal carbonyls in the anionic product.

Darensbourg, D.J.; Kudaroski, R.A. Adv. Organomet. Chem. 1983, 22, 129.

12. a)



Assignments for NMR data for 29:

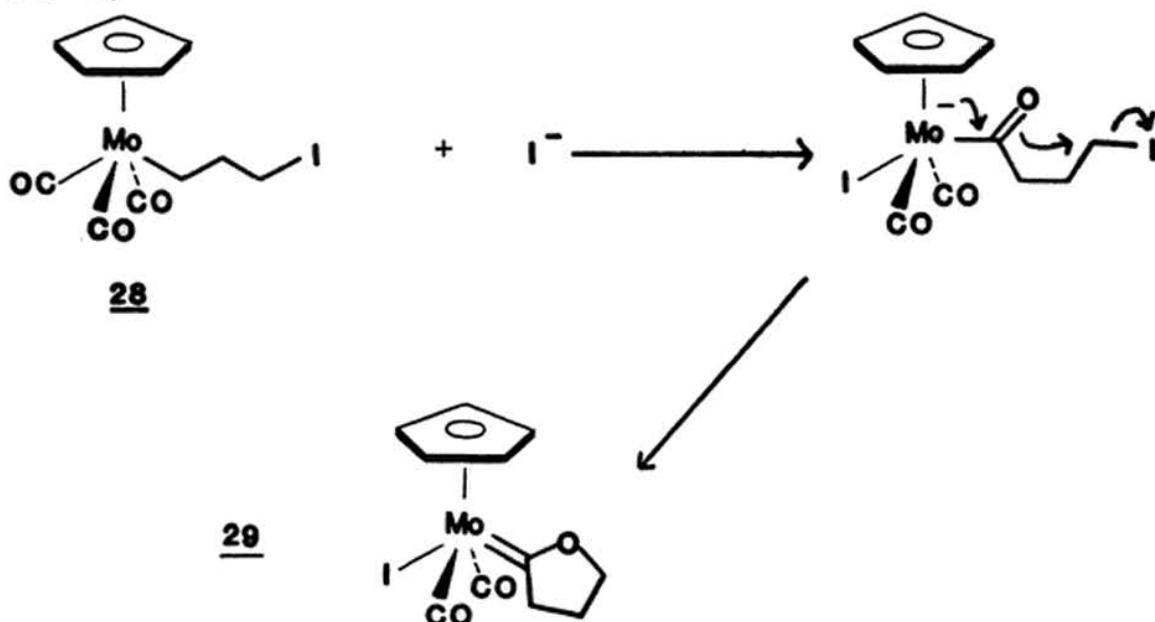
$^1\text{H}$  NMR

- 5.57 (s, 5 H, Cp)
- 4.60 (t,  $J = 7$  Hz, 2 H,  $\text{H}_b$ )
- 3.60 (t,  $J = 7$  Hz, 2 H,  $\text{H}_d$ )
- 1.92 (quint.,  $J = 7$  Hz, 2 H,  $\text{H}_c$ )

$^{13}\text{C}$  NMR

- 316.6 ( $\text{C}_a$ )
- 223.4 (CO carbons)
- 96.9 (Cp carbons)
- 82.0 ( $\text{C}_b$ )
- 58.8 ( $\text{C}_d$ )
- 22.5 ( $\text{C}_c$ )

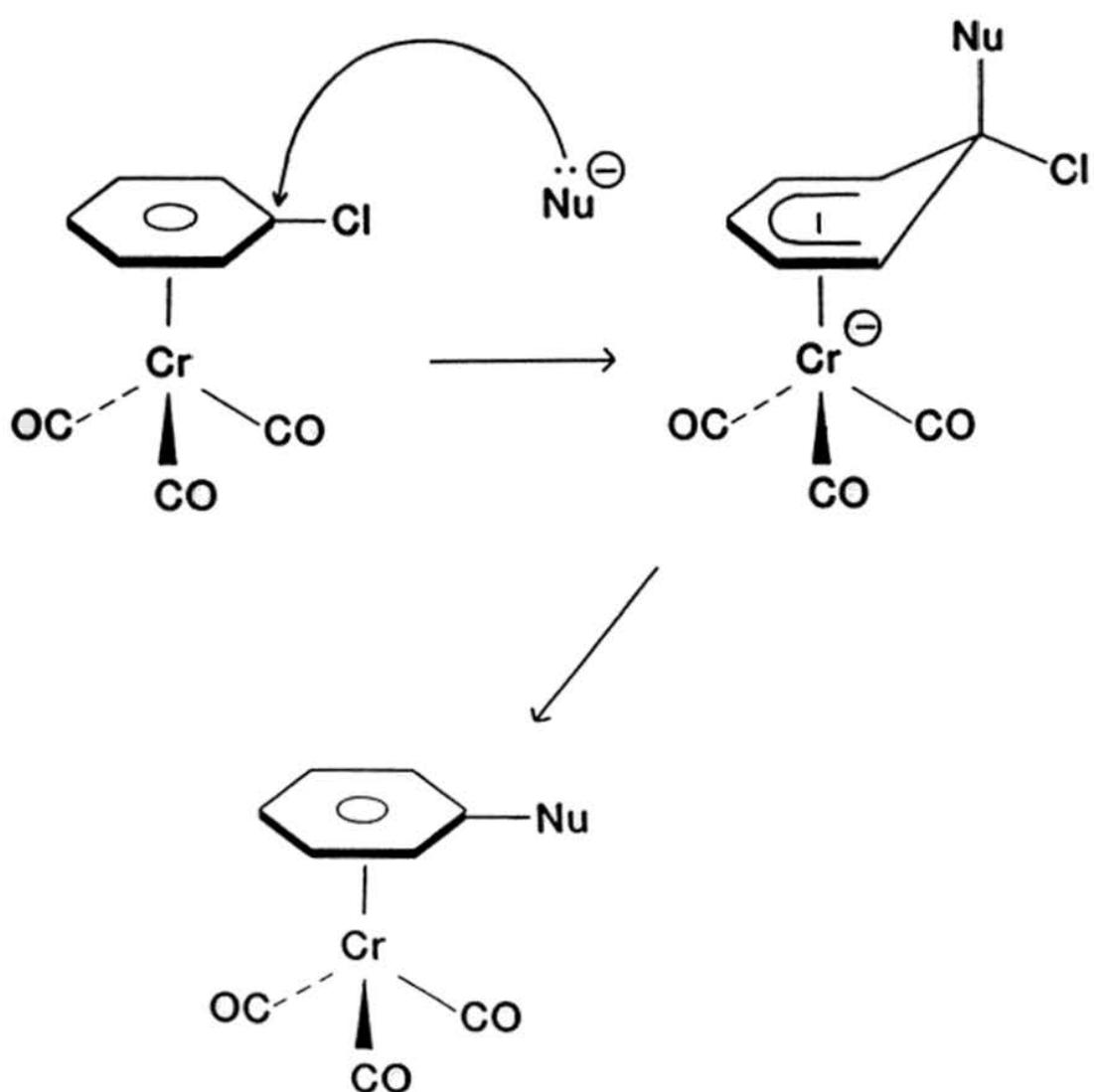
12. b)



Bailey, N.A.; Chell, P.L.; Mukhopadhyay, A.; Tabron, H.E.; Winter, M.J. J. Chem. Soc., Chem. Comm. 1982, 215.

# 7

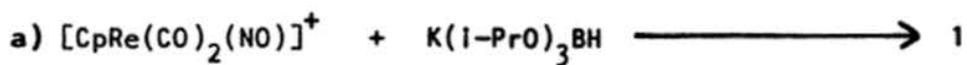
## Nucleophilic Attack on Coordinated Ligands



## 7: NUCLEOPHILIC ATTACK ON COORDINATED LIGANDS

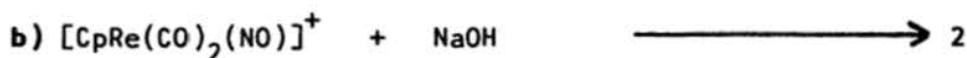
### QUESTIONS

1. Predict the products of the following reactions.



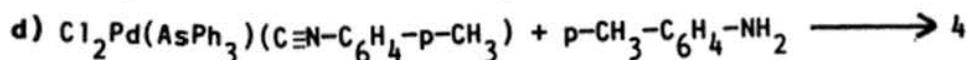
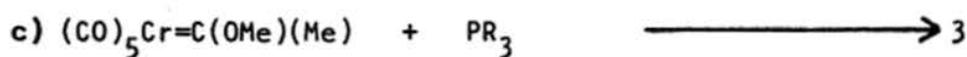
$^1\text{H}$  NMR of 1 ( $\delta$ , THF-d<sub>8</sub>): 16.29 (s, 1 H), 5.87 (s, 5 H)

IR (THF): 1991, 1723, 1619  $\text{cm}^{-1}$

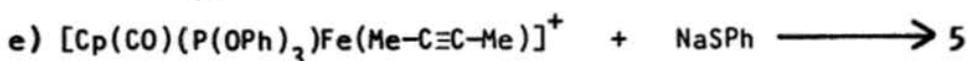


$^1\text{H}$  NMR of 2 ( $\delta$ , CD<sub>3</sub>CN): 8.6 (br, 1 H), 5.84 (s, 5 H)

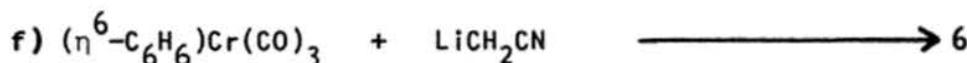
IR (Nujo1): 2960, 2860, 2705, 2690, 1985, 1715, 1585  $\text{cm}^{-1}$



IR of 4:  $\nu_{\text{CN}}$  1536  $\text{cm}^{-1}$

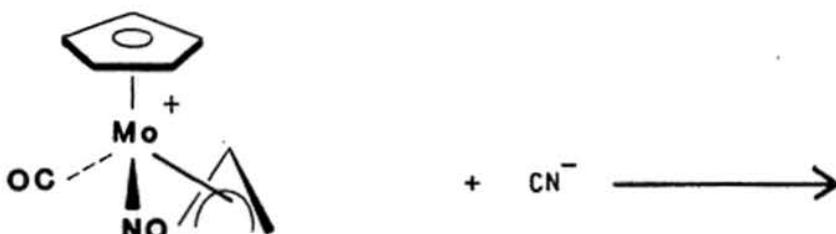


$^1\text{H}$  NMR of 5 ( $\delta$ , CDCl<sub>3</sub>): 7.20 (m, 20 H), 4.37 (s, 5 H), 2.5 (br s, 3 H), 2.28 (s, 3 H)

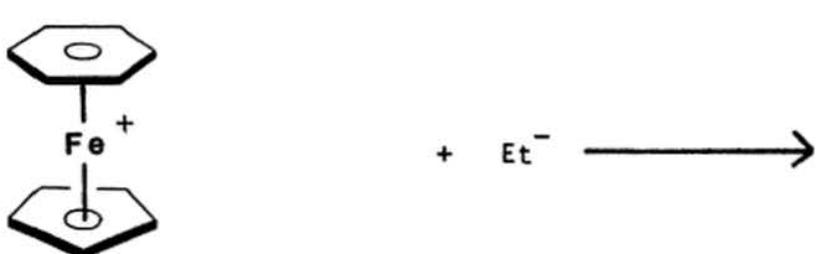


2. Using the rules of Davies, Green, and Mingos (*Tetrahedron* 1978, 34, 3047), predict the kinetically-controlled product of nucleophilic attack on the unsaturated ligands of the following complexes.

a)



b)

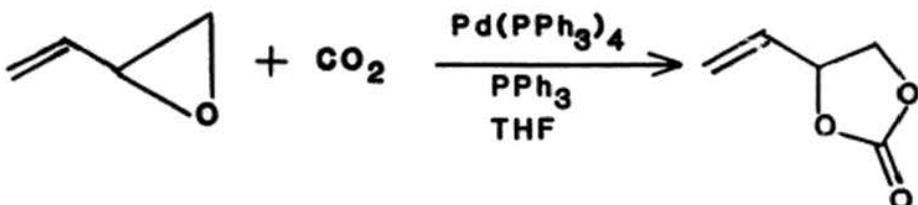


## 3. (cont.)

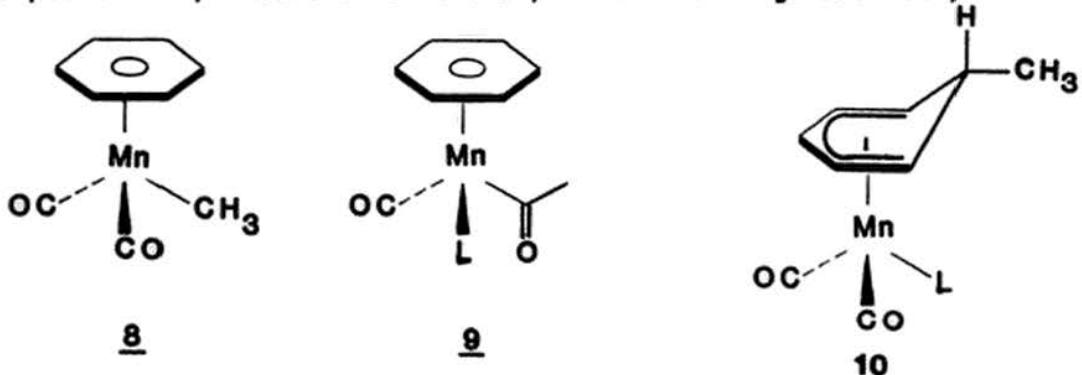
$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 217.5 (s)  
61.4 (q,  $J = 137$  Hz)

Identify **7** and propose a mechanism for its formation.

## 4. Propose a mechanism for the following catalytic conversion.



5. When heated in the presence of an added ligand, L (usually a phosphine), complex **8** reacts to give compound **9** by  $\text{CO}$ -insertion or compound **10** by insertion of the aryl into the manganese-methyl bond.

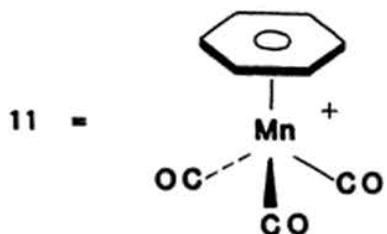


a) Propose a mechanistic scheme which accounts for the formation of these two products.

b) Derive a kinetic rate expression for formation of each of these products.

c) Experimentally, it is found that at high  $[L]$ , **9** is formed exclusively, and at low  $[L]$ , **10** is formed exclusively. How do you have to change your kinetic expression to fit these experimental results? In other words, what do these results imply about the relative rates of reactions?

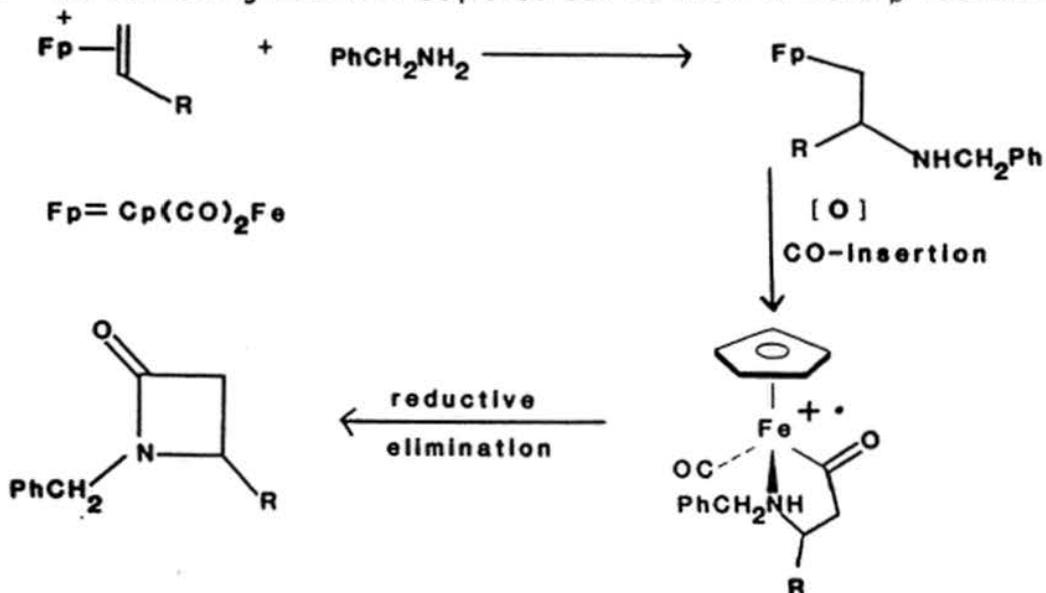
## 6. Based on the spectral data, determine the product of each of the following reactions.



## 6. (cont.)

- a) 11  $\xrightarrow[2) \text{H}_2\text{O work-up}]{1) \text{MeLi, THF, } -30^\circ\text{C}}$  12  
 IR( $\text{cm}^{-1}$ ): 2023, 1950, 1940  
 $^1\text{H NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ):  
 0.4 (d, 3 H)  
 2.5 (m, 1 H)  
 3.1 (t, 2 H)  
 4.6 (t, 2 H)  
 5.6 (tt, 1 H)
- b) 11  $\xrightarrow[2) \text{H}_2\text{O work-up}]{1) \text{LiMe}_2\text{Cu, } -78^\circ\text{C, ether}}$  13  
 IR( $\text{cm}^{-1}$ ): 1965, 1915, 1630  
 $^1\text{H NMR}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ):  
 2.60 (br s, 3 H)  
 4.52 (s, 6 H)
- c) 11  $\xrightarrow[2) \text{H}_2\text{O work-up}]{1) \text{LiMe}_2\text{Cu, } 0^\circ\text{C, ether}}$  14  
 IR( $\text{cm}^{-1}$ ): 1975, 1930  
 $^1\text{H NMR}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ):  
 0.17 (s, 3 H)  
 4.40 (s, 6 H)

7. The following reaction sequence can be used to make  $\beta$ -lactams.



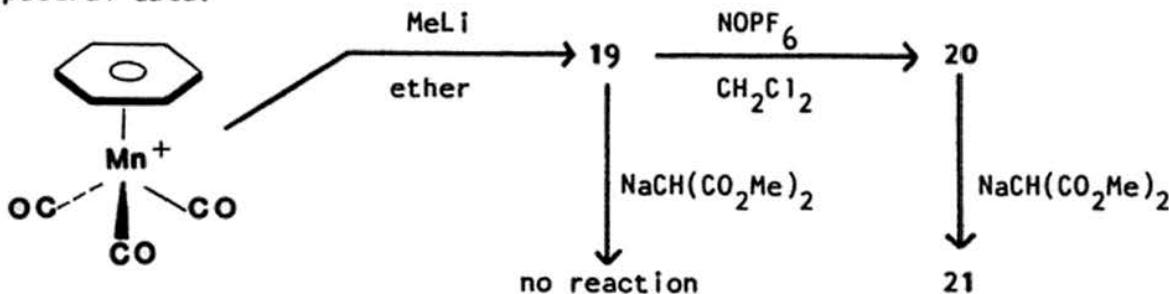
## 8. (cont.) Spectral Data for 18:

IR ( $\text{CCl}_4$ ): 1945, 1870, 1740  $\text{cm}^{-1}$  (major peaks)

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 0.65 (d,  $J = 14.5$  Hz, 1 H)  
 0.85 (dm,  $J = 14.5$  Hz, 1 H)  
 1.22 (d,  $J = 7.2$  Hz, 3 H)  
 1.90 (m, 1 H)  
 2.30 (m, 1 H)  
 2.55 (d,  $J = 6.8$  Hz, 2 H)  
 3.5–3.75 (m, 2 H)  
 3.69 (s, 3 H)  
 4.17 (t,  $J = 7.0$  Hz, 1 H)  
 5.29 (s, 5 H)

Assign all peaks in the IR and NMR spectra.

## 9. Give structures for compounds 19, 20, 21 and rationalize all spectral data.



19:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 0.4 (d, 3 H)  
 2.5 (m, 1 H)  
 3.1 (t, 2 H)  
 4.6 (t, 2 H)  
 5.6 (tt, 1 H)

partial IR ( $\text{cm}^{-1}$ ): 2023, 1950, 1940

20:  $^1\text{H}$  NMR ( $\delta$ , toluene- $d_8$ ): 0.78 (d, 3 H)  
 2.94 (m, 1 H)  
 4.81 (t, 2 H)  
 6.02 (t, 2 H)  
 6.98 (t, 1 H)

partial IR ( $\text{cm}^{-1}$ ): 2109, 2073, 1840

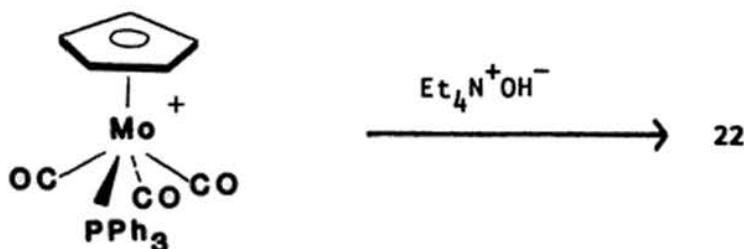
21:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 0.55 (d, 3 H)  
 2.24 (m, 1 H)  
 2.43 (ddd,  $J = 6.5, 3, 1.5$  Hz, 1 H)  
 2.98 (ddd,  $J = 6.5, 2, 1.5$  Hz, 1 H)  
 3.22 (s, 3 H)  
 3.24 (s, 3 H)  
 3.29 (m, 2 H)  
 4.72 (dd,  $J = 6.5, 5$  Hz, 1 H)  
 4.91 (dd,  $J = 6.5, 5$  Hz, 1 H)

## 9. (cont.)

21: partial IR ( $\text{cm}^{-1}$ ): 2041, 1993, 1752

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 21.8  
33.6  
40.0  
52.0  
57.5  
66.7  
73.6  
86.5  
89.4  
168.8  
168.9  
223.0

10. Determine the structure of the product of the following reaction.



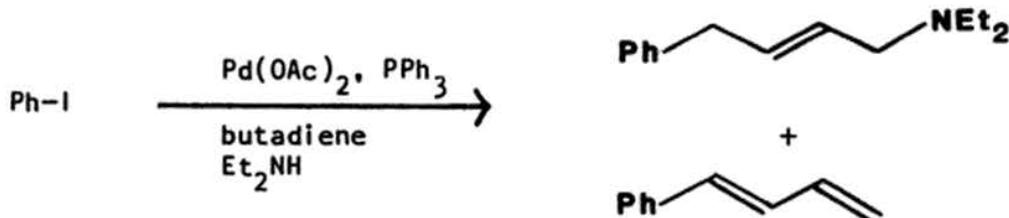
Spectral data for 22:

IR (Nujol,  $\text{cm}^{-1}$ ): 1955, 1862, 1616

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ): 5.08 (d,  $J = 1.3$  Hz, 5 H)  
7.42 (m, 16 H)

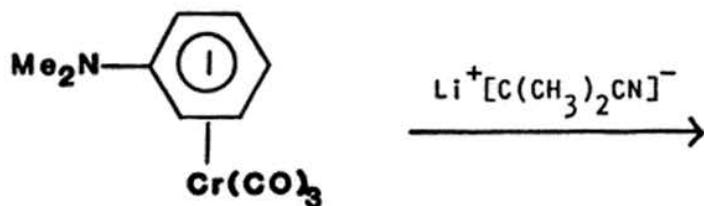
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ): 95.5 (s)  
128.9 (s)  
129.0 (s)  
130.9 (s)  
133.2 (s)  
209.5 (d,  $J = 11$  Hz)  
238.5 (d,  $J = 26$  Hz)

11. The following reaction sequence has recently been observed:

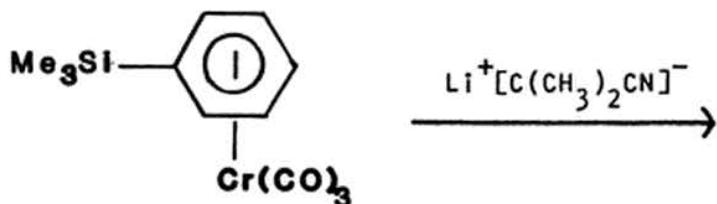


Propose a mechanism for the formation of the two products.

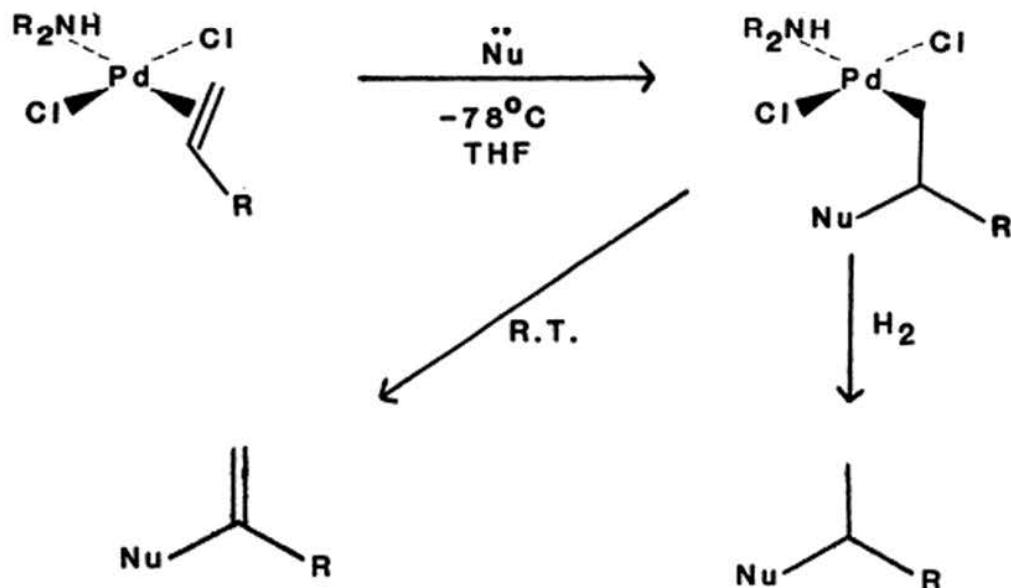
12. a) The following reaction gives exclusively one product. What product is formed and why are no others formed?



b) The reaction shown below also gives exclusively one product; however, here the regiochemistry is different from that observed above. What is the product formed and why is a different regiochemistry observed?

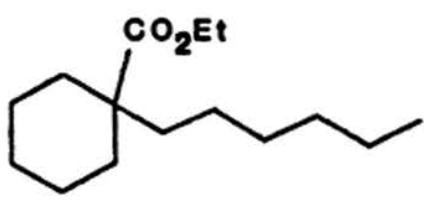


13. A variety of organic products can be obtained from the reaction of a palladium-olefin complex with nucleophilic reagents, as shown below. Note that addition of hydrogen to the reaction mixture gives the saturated alkyl product, and simple warming to room temperature gives the substituted olefin. Another interesting aspect of the reaction is that stabilized carbanions ( $\text{pK}_a < 15$ ) usually attack at the more-substituted end of the olefin, whereas non-stabilized carbanions ( $\text{pK}_a > 15$ ) are less selective and often give products that result from attack at the less-substituted end of the olefin.

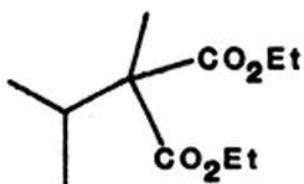


13. (cont.) Using this reaction sequence, design syntheses for the following organic molecules.

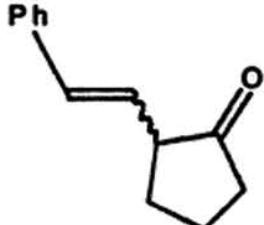
a)



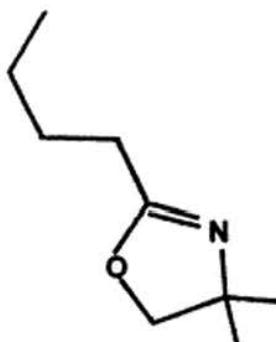
b)



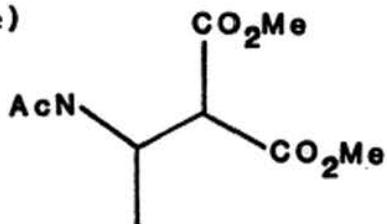
c)



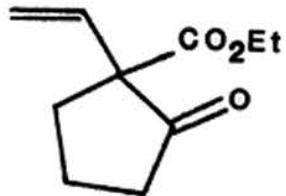
d)



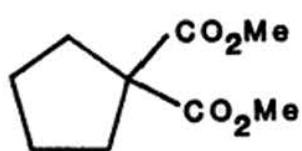
e)



f)



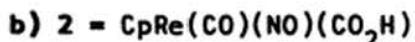
g)



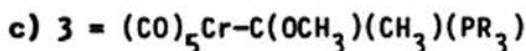
## ANSWERS



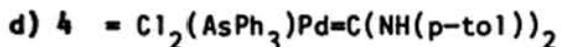
Casey, C.P.; Andrews, M.A.; Rinz, J.E. J. Am. Chem. Soc. 1979, 101, 741.



Casey, C.P.; Andrews, M.A.; Rinz, J.E. J. Am. Chem. Soc. 1979, 101, 741.

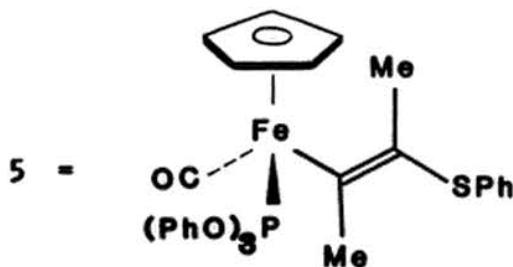


Fischer, E.O. Adv. Organomet. Chem. 1976, 14, 1.



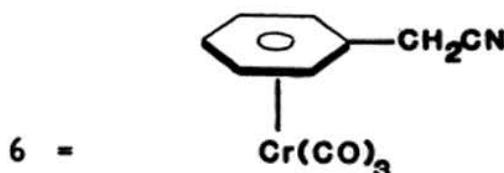
Crociani, B.; Boschi, T.; Nicolini, M.; Bellucco, U. Inorg. Chem. 1972, 11, 1292.

e)



Reger, D.L.; Belmore, K.A.; Mintz, E.; McElligott, P.J. Organomet. 1984, 3, 134.

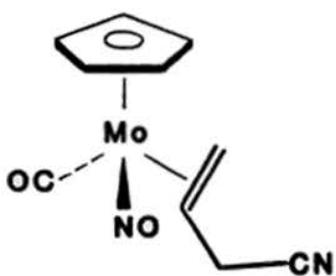
f)



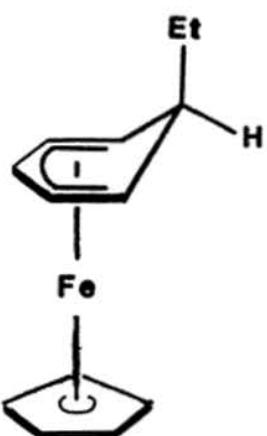
Semmelhack, M.F.; Hall, H.T.; Yoshifuji, M.; Clark, G. J. Am. Chem. Soc. 1975, 97, 1247.

2. Briefly, the rules state that unsaturated hydrocarbon ligands can be classified as **even** or **odd** (depending on their *hapto* ( $\eta$ ) number), and **open** for acyclic (or nonconjugated cyclic) ligands or **closed** for cyclic conjugated systems. Under kinetically controlled conditions and for 18-electron systems, nucleophilic attack will occur preferentially at an **even** ligand before an **odd** one, and on an **open** system before a **closed** one. The preferential site of nucleophilic attack for **even open** polyenes will be at a terminal carbon atom (unless sterically hindered), and for **odd open** polyenes, no attack at the terminal positions is seen unless the metal is very electron-deficient.

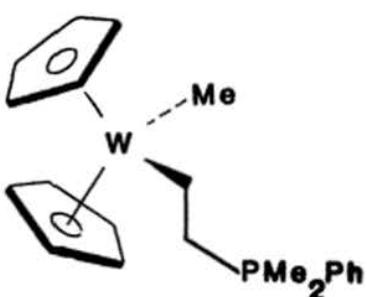
2. a)



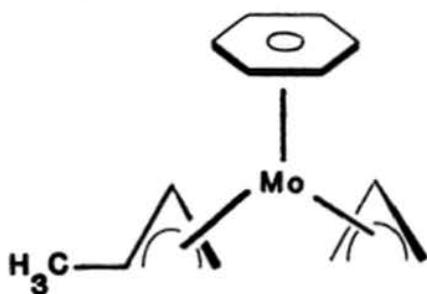
b)



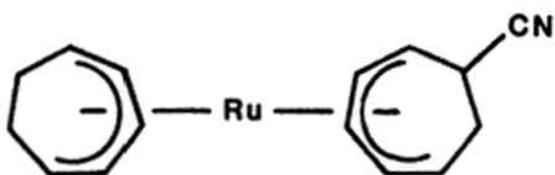
c)



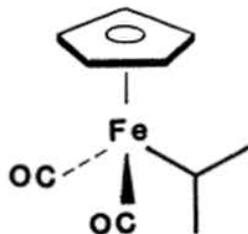
d)



e)

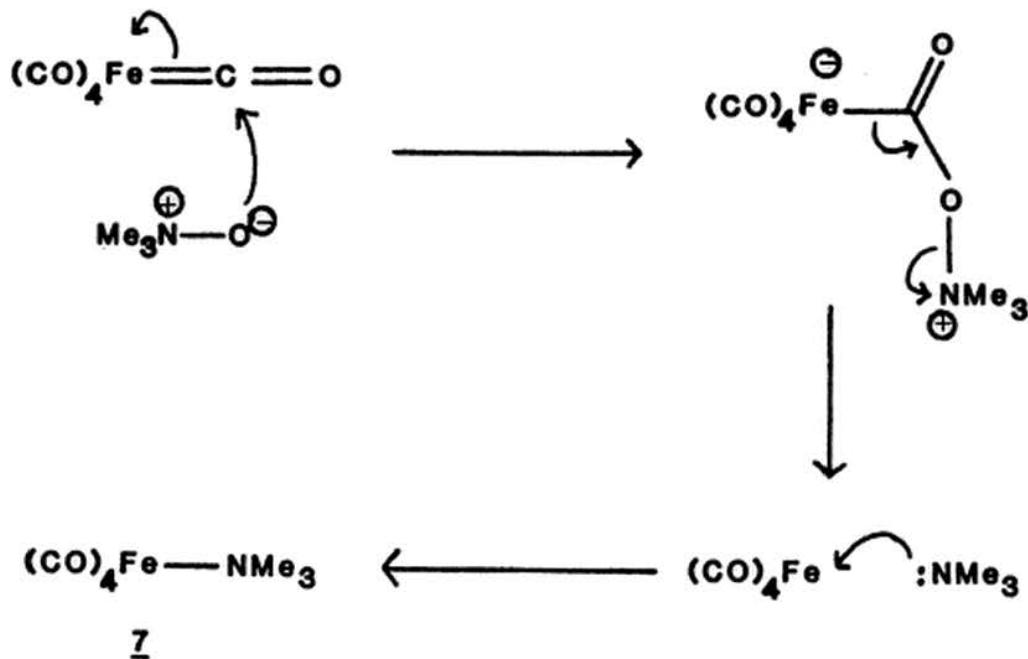


f)



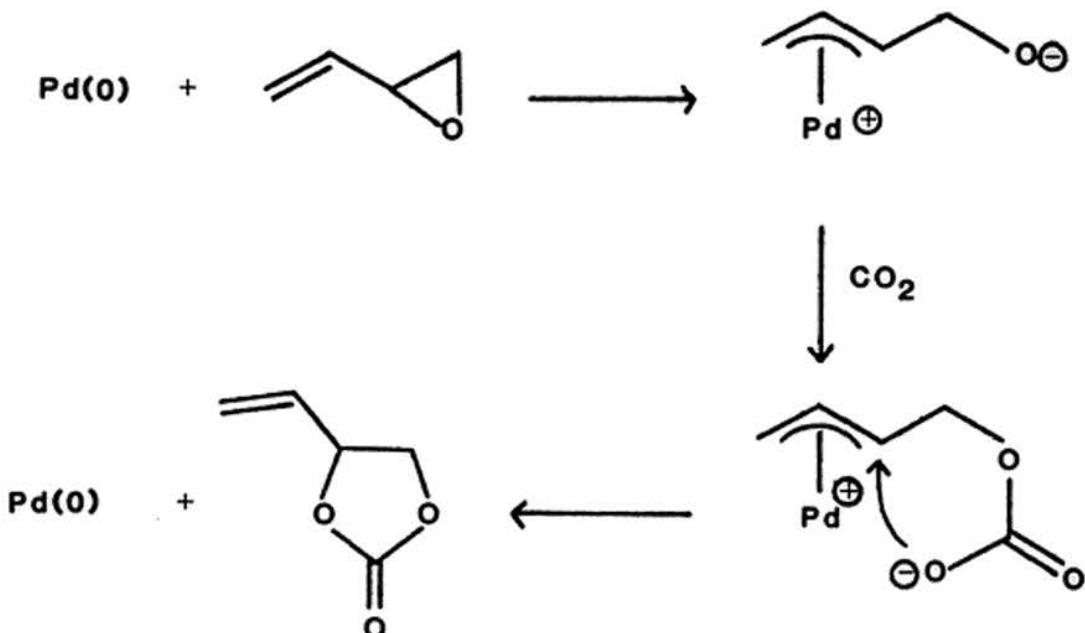
Davies, S.G.; Green, M.L.H.; Mingos, D.M.P. Tetrahedron, 1978, 34, 3047.

3.



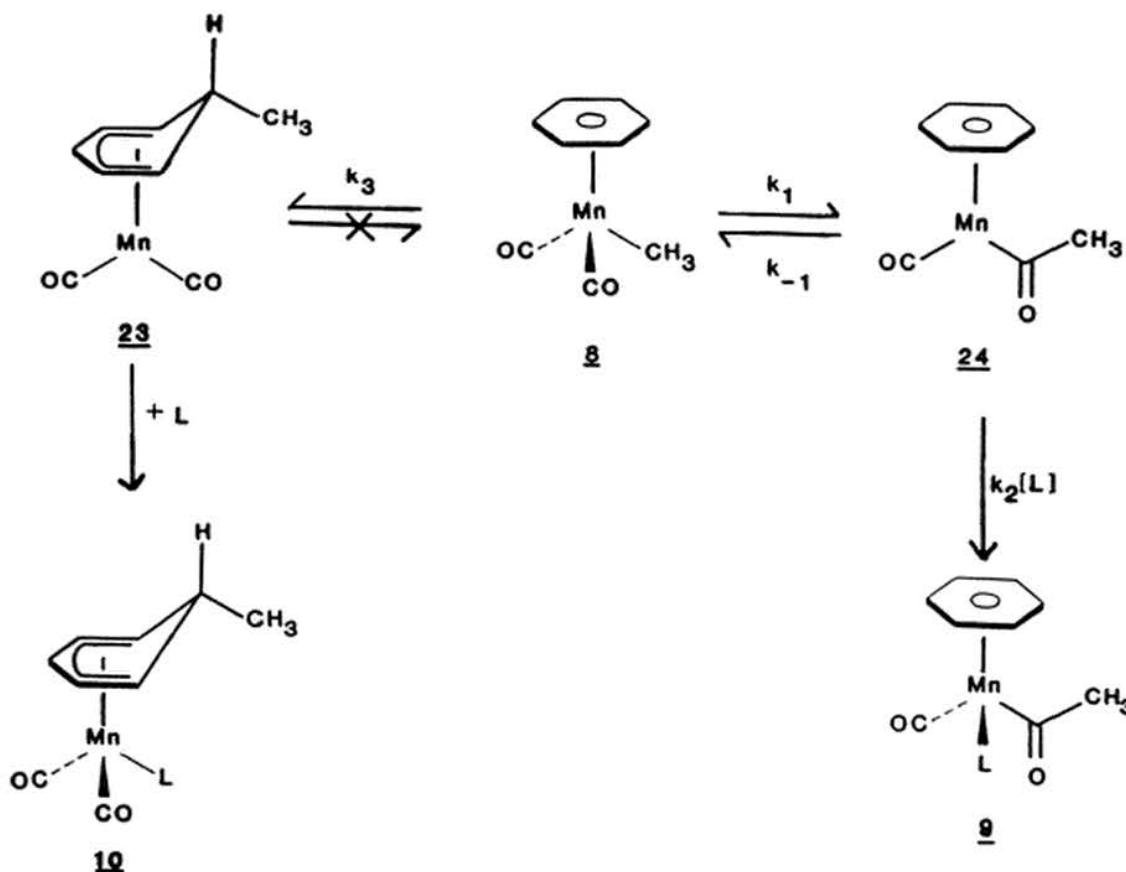
Elzinga, J.; Hogeveen, H. J. Chem. Soc. Chem. Comm., 1977, 705.

4. In the scheme below, Pd(0) represents the transition metal and an unknown number of associated ligands.



Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. Chem. Lett., 1985, 199.

5. a) The proposed mechanism is shown below.



b) Since a carbon-carbon bond is very difficult to break, it is unlikely that the conversion of **8** to **23** is a reversible reaction. Assuming that **23** and **24** are steady-state intermediates, the following kinetic expressions can be obtained:

$$\frac{d[9]}{dt} = \frac{k_1 k_2 [8][L]}{k_{-1} + k_2[L]} \quad \text{and} \quad \frac{d[10]}{dt} = k_3[8]$$

c) At high concentrations of external ligand, the kinetic expression for formation of **9** reduces to :

$$\frac{d[9]}{dt} = k_1[8]$$

Since **9** is the observed product,  $k_1$  must be larger than  $k_3$ , a very reasonable assumption. At low ligand concentrations, the kinetic expression for the formation of **9** becomes:

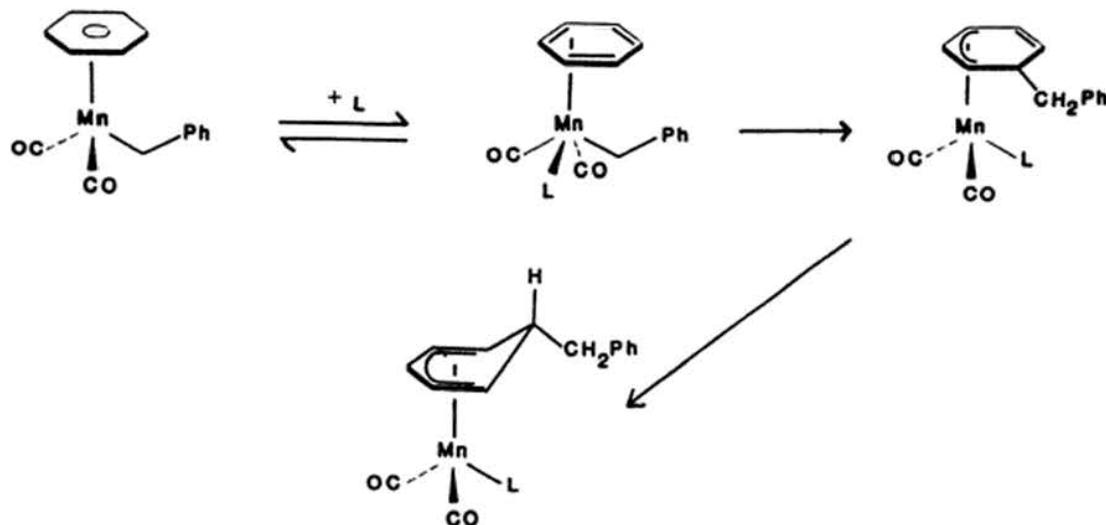
$$\frac{d[9]}{dt} = \frac{k_1 k_2 [8][L]}{k_{-1}}$$

The second-order reaction at small  $[L]$  is slow; therefore, the first-order formation of **10** predominates.

## 5. (cont.)

## NOTE

The mechanism for the formation of 10 may be more complex than is indicated here. For the benzyl analog, the following mechanism has recently been proposed for migration of the benzyl group to the ring.

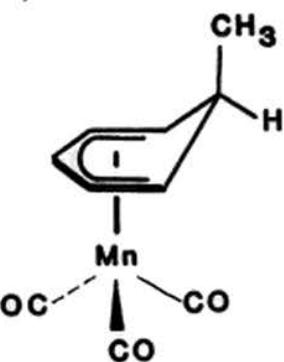


Brookhart, M.; Pinhas, A.R.; Lukacs, A. *Organometal.* 1982, 1, 1730.

Brookhart, M., personal communication.

6. a)

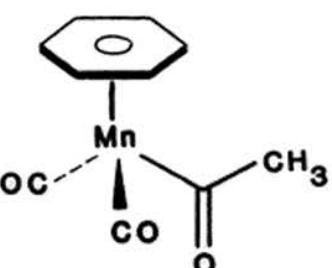
12 =



This product is formed by a direct nucleophilic attack on the coordinated benzene ring.

b)

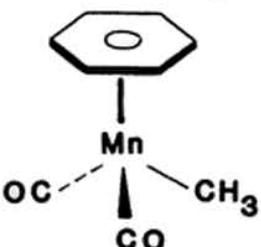
13 =



This product is formed by a nucleophilic attack on the carbonyl.

c)

14 =



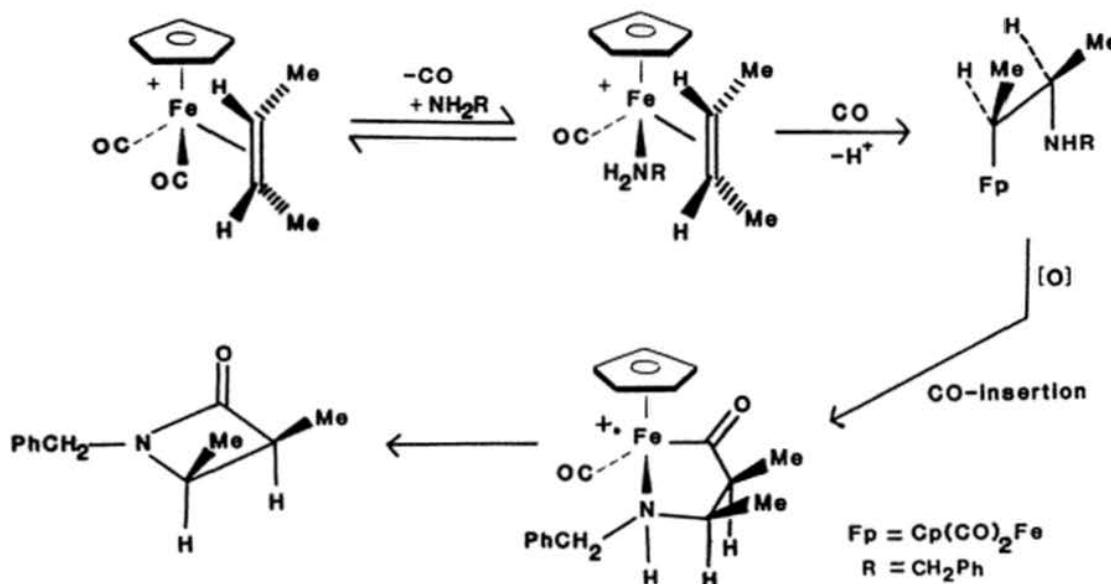
This product arises from 13, but the manner in which decarbonylation occurs is not known.

6. (cont.) The reason for the different reactivities of  $\text{MeLi}$  and  $\text{LiMe}_2\text{Cu}$  with  $[(\text{benzene})\text{Mn}(\text{CO})_3]^+$  is not known.

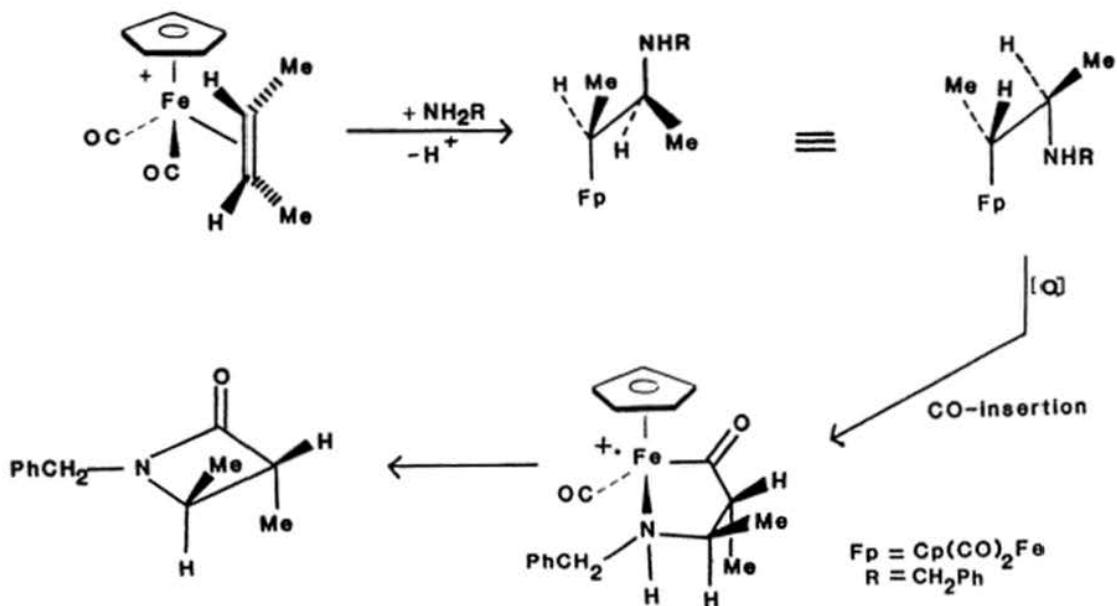
Reference for a): Munro, G.A.M.; Pauson, P.L. *Isr. J. Chem.*, 1976-7, 15, 258.

Reference for b) and c): Brookhart, M.; Pinhas, A.R.; Lukacs, A. *Organomet.*, 1982, 1, 1730.

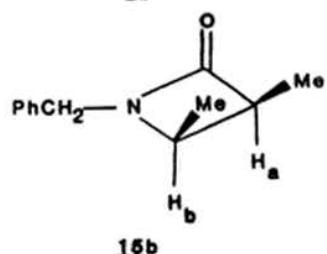
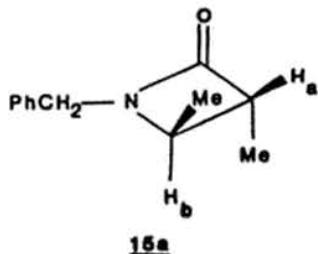
7. a) For cis (internal) nucleophilic attack, the product will have the methyl groups cis to one another.



b) For trans (external) nucleophilic attack, the product will have the methyl groups trans to one another.



7. c) The value of the coupling constant  $J_{ab}$  is indicative of the dihedral angle  $\phi$  between  $H_a$  and  $H_b$ , with  $J_{ab} = 10\cos^2\phi$ .



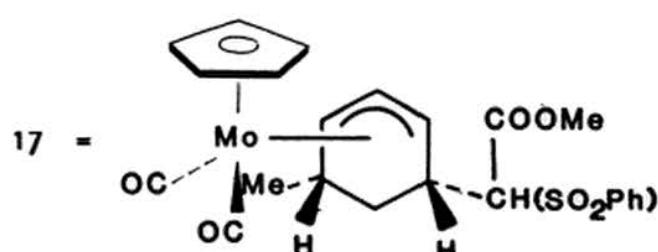
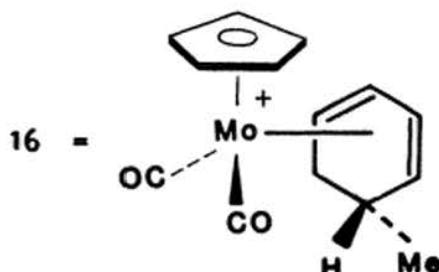
The relative magnitudes of the coupling constants  $J_{ab}$  for the products expected from the reaction of the amine with both cis- and trans-2-butene by the different modes of attack are listed in the table below.

Olefin	Expected $J_{ab}$		Observed $J_{ab}$
	Internal attack	External attack	
<u>cis</u> -2-butene	large	small	2 Hz
<u>trans</u> -2-butene	small	large	6 Hz

The NMR data agree with the external or trans mode of nucleophilic attack, thus the product of the reaction of cis-2-butene with benzylamine is 15a and the product of the reaction of trans-2-butene with benzylamine is 15b.

Wong, P.K.; Madhavarao, M.; Marten, D.F.; Rosenblum, M. J. Am. Chem. Soc. 1977, 99, 2823.

8.



## 9. (cont.) Spectral data for 21:

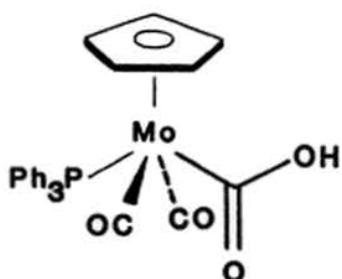
$^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 0.55 (d, 3 H,  $\text{CH}_3$ (g))  
 2.24 (m, 1 H,  $\text{H}_e$ )  
 2.43 (ddd,  $J = 6.5, 3, 1.5$  Hz, 1 H,  $\text{H}_f$ )  
 2.98 (ddd,  $J = 6.5, 2, 1.5$  Hz, 1 H,  $\text{H}_c$ )  
 3.22 (s, 3 H,  $-\text{CO}_2\text{CH}_3$ )  
 3.24 (s, 3 H,  $-\text{CO}_2\text{CH}_3$ )  
 3.29 (m, 2 H,  $\text{H}_d, \text{H}_h$ )  
 4.72 (dd,  $J = 6.5, 5$  Hz, 1 H,  $\text{H}_a$ )  
 4.91 (dd,  $J = 6.5, 5$  Hz, 1 H,  $\text{H}_b$ )

$^{13}\text{C}\{\text{H}\}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 21.8 ( $\text{C}_g$ )  
 33.6 ( $\text{C}_e$ )  
 40.0 ( $\text{C}_d$ )  
 52.0 ( $\text{CO}_2\text{CH}_3$ )  
 57.5 ( $\text{C}_h$ )  
 66.7 ( $\text{C}_f$ )  
 73.6 ( $\text{C}_c$ )  
 86.5 ( $\text{C}_a$ )  
 89.4 ( $\text{C}_b$ )  
 168.8 ( $\text{CO}_2\text{CH}_3$ )  
 168.9 ( $\text{CO}_2\text{CH}_3$ )  
 223.0 (Mn-CO)

Chung, Y.K.; Sweigart, D.A.; Connelly, N.G.; Sheridan, J.B. J. Am. Chem. Soc. 1985, 107, 2388.

Spectra of 19: Munro, G.A.M.; Pauson, P.L. Isr. J. Chem. 1976-7, 15, 258.

## 10.



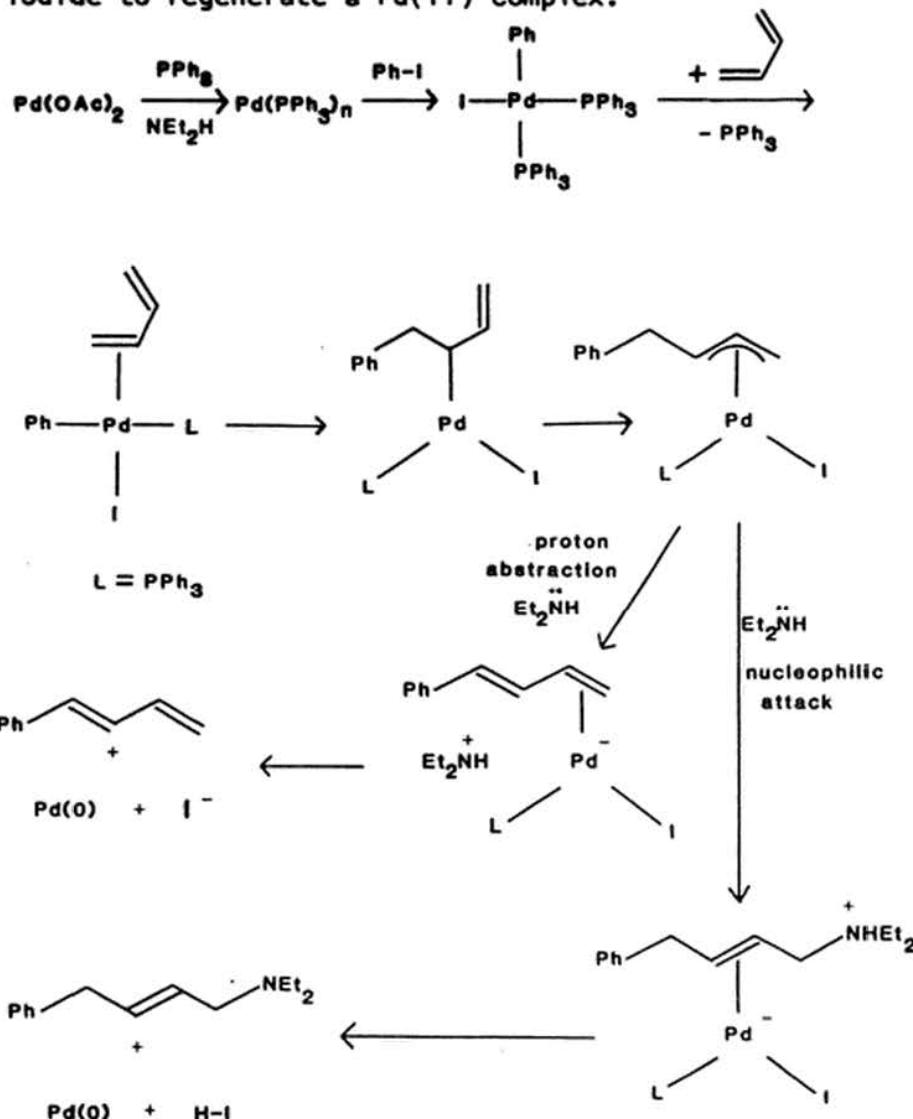
## 10. (cont.)

<u>IR (cm<sup>-1</sup>)</u>	<u><sup>13</sup>C NMR</u>	<u><sup>1</sup>H NMR</u>
1616 acyl C=O stretch 1955 and 1862 M-CO stretches	95.5 (Cp) 128-134 (Ph carbons) 209.5 (COOH) 238.5 (M-CO)	5.08 (Cp) 7.42 (Ph and COOH)

The  $\text{PPh}_3$  and  $\text{COOH}$  ligands must be trans for the carbonyls to be equivalent in the  $^{13}\text{C}$  NMR spectrum.

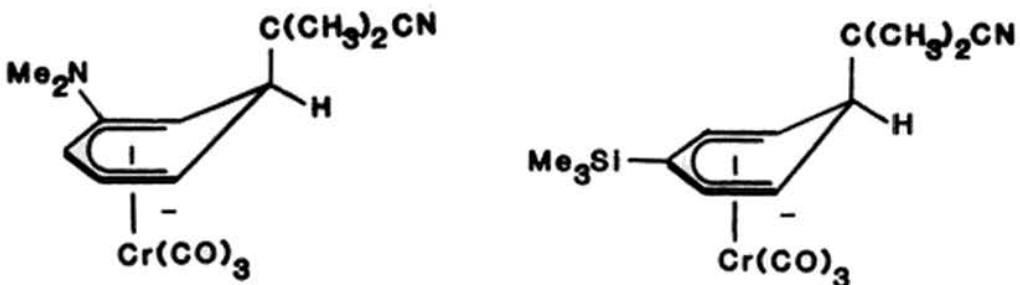
Gibson, D.H.; Owens, K.; Ong, T.-S. J. Am. Chem. Soc., 1984, 106, 1125.

11. Under the reaction conditions, the  $\text{Pd(II)}$  is reduced to  $\text{Pd(0)}$  by the amine. The  $\text{Pd(0)}$  species then undergoes an oxidative-addition with phenyl iodide to regenerate a  $\text{Pd(II)}$  complex.



O'Connor, J.M.; Stallman, B.J.; Clark, W.G.; Shu A.Y.L.; Spada, R.E.; Stevenson, T.M.; Dieck, H.A. J. Org. Chem., 1983, 48, 807.

12. a) and b) The two products are:



It has been found that these reactions are subject to both orbital control and to charge control. The following conclusions about the position of nucleophilic attack have been drawn.

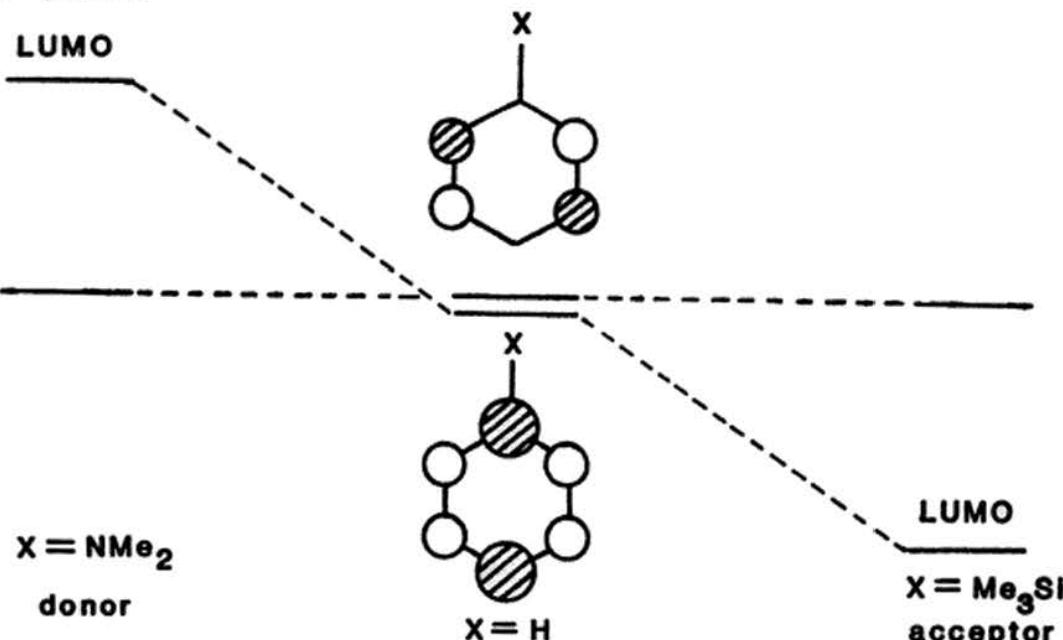
- (1) Steric effects are important in comparing primary, secondary, and tertiary carbanion nucleophiles, with ortho substitution nearly completely inhibited with tertiary carbanions.
- (2) When there are no steric effects present, the amount of ortho substitution becomes comparable to the amount of meta substitution, with the ratio reaching one to one with reactive anions. Usually, there is more meta substitution than ortho.
- (3) Para substitution is only important when large alkyl substituents are present on the arene ring.
- (4) With more stable nucleophiles, more para substitution is observed.

Since the nucleophile is tertiary, no ortho substitution is expected or observed; thus, it must be either meta or para substitution. According to the rules, the anion should attack the aniline complex at the meta position, which is what is observed. This is due to orbital control.

Since the two reactions have different regiochemistries and since ortho attack has been ruled out, the trimethylsilyl complex must be attacked at the para position. A possible explanation is that large substituents direct the attack to the para position, as predicted by rule (3).

Another explanation for the different regiochemistry observed for the two reactions is based on the effect the donor amine and the acceptor silyl group have on the lowest unoccupied orbital (LUMO) of the arenechromium tricarbonyl complex, a top view of which is shown on the next page. In benzenechromium tricarbonyl, the LUMO is a degenerate set of two orbitals; however, upon substitution, this degeneracy is broken, as shown on the following page.

## 12. (cont.)



The LUMO of the aniline complex has non-zero coefficients at the ortho and meta positions, and for reasons stated above, meta attack is preferred. On the other hand, the silyl-substituted complex has its largest coefficient in the LUMO at the para position, and thus, para substitution is observed.

Semmelhack, M.F.; Hall, H.T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* 1979, 101, 3535.

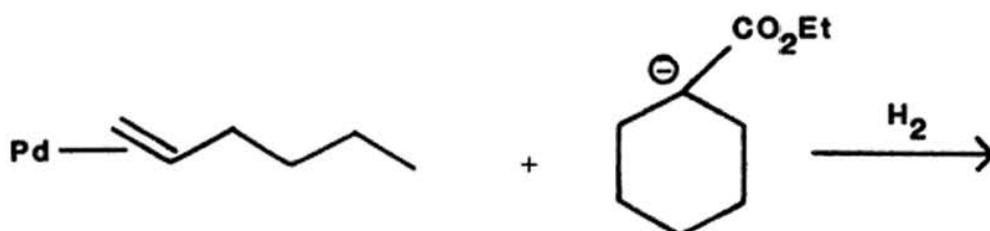
Semmelhack, M.F.; Clark, G.R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.*, 1979, 101, 217.

Albright, T.A.; Carpenter, B.K. *Inorg. Chem.* 1980, 19, 3092.

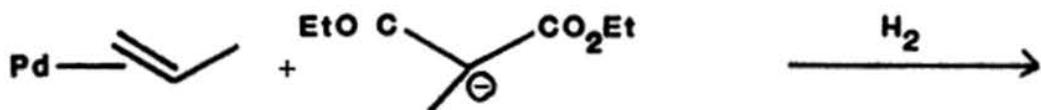
Semmelhack, M.F.; Garcia, J.L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B.K. *Organomet.* 1983, 2, 467.

13. In all cases,  $\text{Pd} = (\text{R}_2\text{NH})\text{PdCl}_2$ 

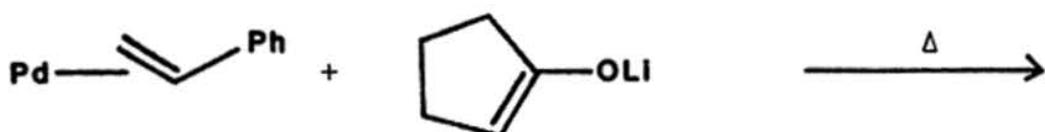
a)



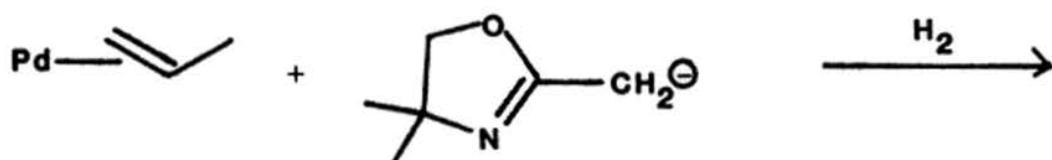
13. b)



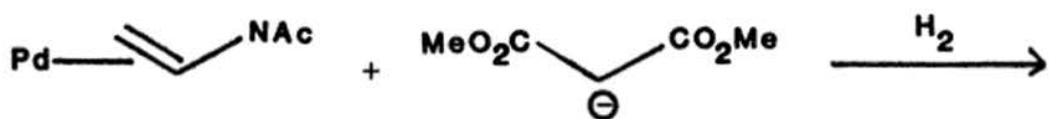
c)



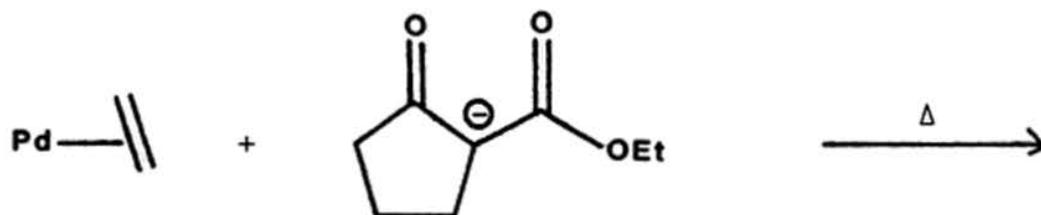
d)



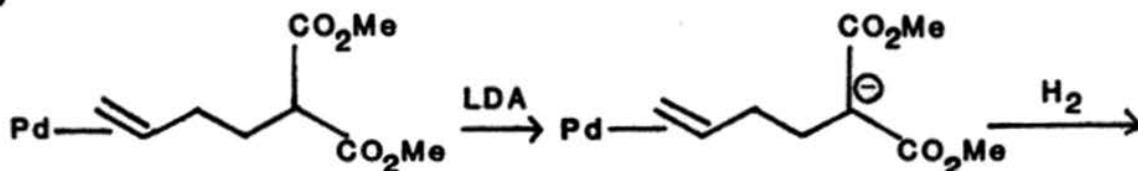
e)



f)



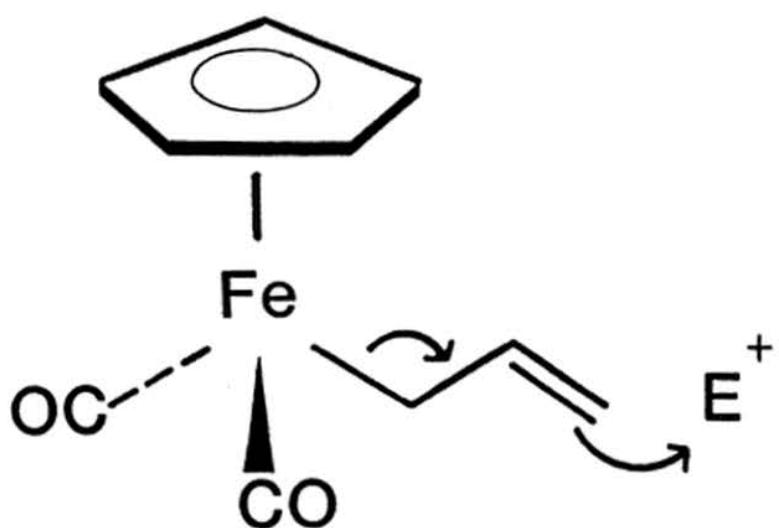
g)



Hegedus, L.S.; Williams, R.E.; McGuire, M.A.; Hayashi, T. J. Am. Chem. Soc. 1980, 102, 4973.

# 8

## Electrophilic Attack on Coordinated Ligands

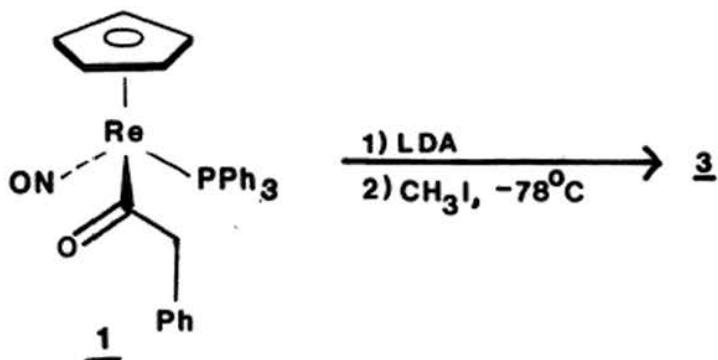


## 8: ELECTROPHILIC ATTACK ON COORDINATED LIGANDS

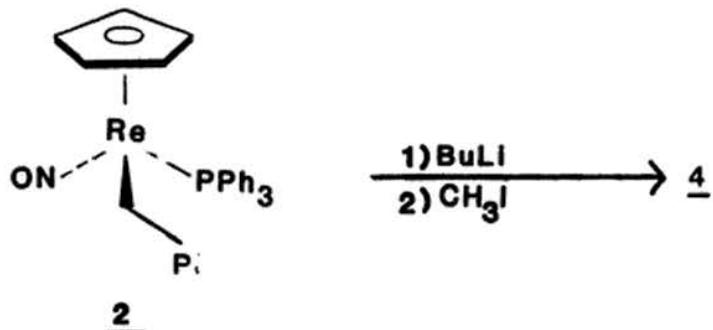
### QUESTIONS

1. Propose a structure for the product of each of the following reactions. Give a mechanism for the formation of each product.

a)



b)



Spectral data:

For 3

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )

7.47–7.21 (m, 20 H)  
5.48–4.12 (br m, 4 H)  
3.78 (s, 2 H)  
0.82 (d,  $J=5.5$  Hz, 3 H)

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )

(broad-band decoupled)

194.1 (s)

135.9 (s)

135.4 (d,  $J=53.2$  Hz)

134.2 (d,  $J=10.5$  Hz)

131.1 (s)

130.2 (s)

129.1 (d,  $J=11.3$  Hz)

129.0 (s)

( $^{13}\text{C}$  data continued on the following page)

For 4

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )

8.03–7.37 (m, 20 H)  
5.84–4.79 (m, br, 4 H)  
4.11 (dd,  $J=11.5, 8.5$  Hz, 1 H)  
3.26 (dd,  $J=11.5, 2.0$  Hz, 1 H)  
2.36 (s, 3 H)

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )

(broad-band decoupled)

159.9 (d,  $J=3.5$  Hz)

137.0 (d,  $J=50.8$  Hz)

134.3 (d,  $J=15.1$  Hz)

130.6 (s)

129.0 (d,  $J=10.8$  Hz)

128.0 (s)

127.7 (s)

122.3 (s)

1. (cont.)

Spectral data (cont.):

For 3

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )  
(broad-band decoupled)

127.3 (s)  
103.0 (s)  
96.1 (s)  
95.0 (d,  $J=5.7$  Hz)  
86.3 (s)  
85.1 (s)  
53.8 (s)  
-30.0 (d,  $J=6.9$  Hz)

IR (cm<sup>-1</sup>,  $\text{CH}_2\text{Cl}_2$ )

1660(m), 1640(s)

For 4

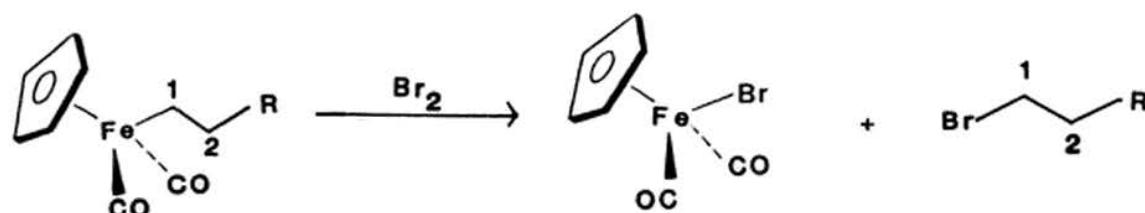
$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )  
(broad-band decoupled)

105.3 (s)  
95.5 (d,  $J=4.0$  Hz)  
92.3 (s)  
89.6 (s)  
86.3 (s)  
13.4 (s)  
-2.0 (d,  $J=4.2$  Hz)

IR (cm<sup>-1</sup>, thin film)

1628(s)

2. The iron compounds **5a** and **5b** suffer Fe-C bond cleavage by bromine, as shown.



**5a:** R = t-Bu

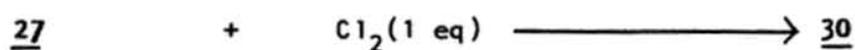
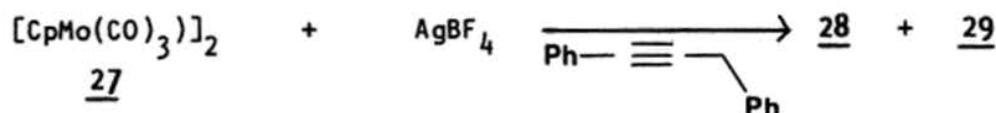
**5b:** R = Ph

a) What experiment can be done to determine the stereochemistry of this reaction at carbon 1?

b) The results of such an experiment are that compound **5a** undergoes cleavage with inversion of configuration at carbon 1, whereas compound **5b** undergoes cleavage with retention of configuration at carbon 1. Suggest an explanation for these results.

c) Design an experiment to test your hypothesis for part b).

8. Identify the products of the following reactions:



HINT

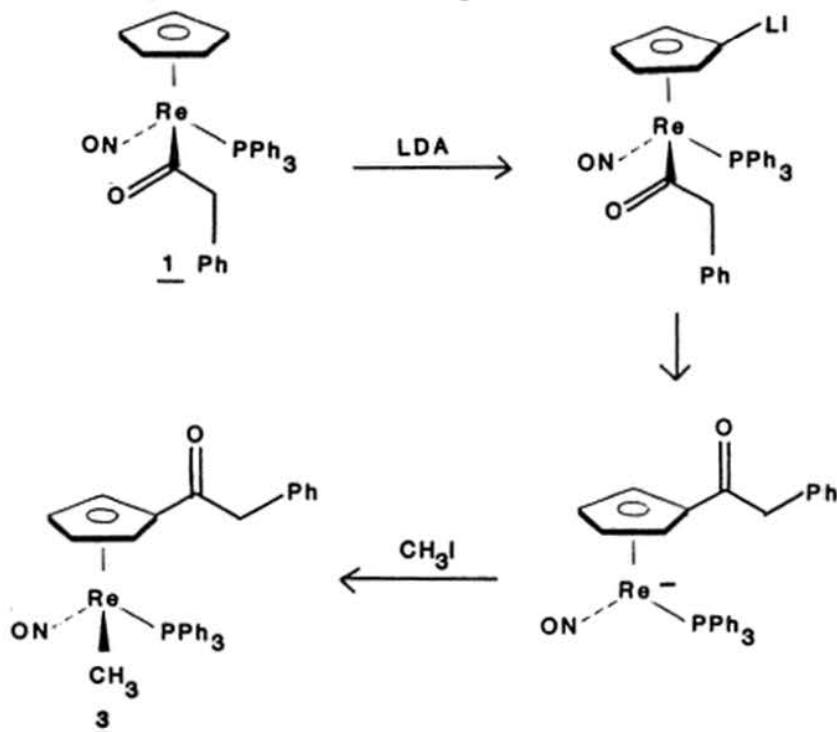
Compounds **28** and **29** are isomers.

Spectral data:

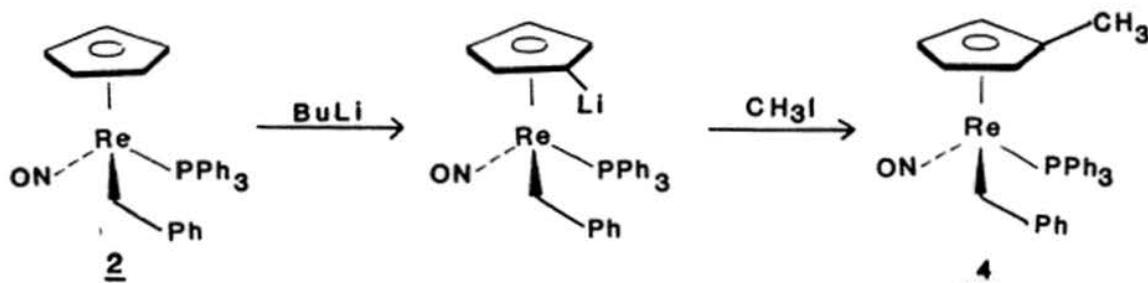
Compound	$^1\text{H}$ NMR ( $\delta$ , $\text{CDCl}_3$ )	IR ( $\text{cm}^{-1}$ )
<b>27</b>	5.29 (s)	2010, 1945, 1910
<b>28</b>	7.6–6.6 (m, 20 H) 5.90 (s, 5 H) 5.10 (d, $J=16.6$ Hz, 1 H) 5.09 (d, $J=17.5$ Hz, 1 H) 4.72 (d, $J=16.6$ Hz, 1 H) 4.71 (d, $J=17.5$ Hz, 1 H)	2050
<b>29</b>	7.6–6.6 (m, 20 H) 6.03 (s, 5 H) 4.79 (d, $J=17.1$ Hz, 2 H) 4.32 (d, $J=17.1$ Hz, 2 H)	2050
<b>30</b>	4.25 (s)	2055, 1983, 1960
<b>31</b>	6.51 (s, acetone- $d_6$ )	2105, 2063

## ANSWERS

1. a) Initial deprotonation of the Cp ring of 1 is followed by migration of the acyl group to the ring. Reaction with methyl iodide then serves to alkylate the metal to give 3.



b) Because the alkyl group of **2** does not migrate to the ring, alkylation by methyl iodide occurs at the ring to give product **4**.



Assignments for spectral data:

For 3

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>)  
 7.47–7.21 (m, 20 H, Ph's)  
 5.48–4.12 (br m, 4 H, C<sub>5</sub>H<sub>4</sub>)  
 3.78 (s, 2 H, CH<sub>2</sub>Ph)  
 0.82 (d, J=5.5 Hz, 3 H, -CH<sub>3</sub>)

For 4

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>)  
 8.03–7.37 (m, 20 H, Ph's)  
 5.84–4.79 (m, br, 4 H, C<sub>5</sub>H<sub>4</sub>)  
 4.11 (dd, J=11.5, 8.5 Hz, 1 H,  
 -CHH'Ph)  
 3.26 (dd, J=11.5, 2.0 Hz, 1 H,  
 -CHH'Ph)  
 2.36 (s, 3 H, -CH<sub>3</sub>)

## 1. (cont.) Assignments for spectral data:

For 3

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )  
(broad-band decoupled)

194.1 (s, C=O)  
135.9 (s, ipso-C of acyl Ph)  
135.4 (d,  $J=53.2$  Hz, ipso-C of  $\text{PPh}_3$ )  
134.2 (d,  $J=10.5$  Hz, C of  $\text{PPh}_3$ )  
131.1 (s, p-C of  $\text{PPh}_3$ )  
130.2 (s, C of acyl Ph)  
129.1 (d,  $J=11.3$  Hz, C of  $\text{PPh}_3$ )  
129.0 (s, C of acyl Ph)  
127.3 (s, C of acyl Ph)  
103.0 (s,  $\text{C}_5\text{H}_4$ , ipso-C of  $\text{C}_5\text{H}_4$ )  
96.1 (s,  $\text{C}_5\text{H}_4$ )  
95.0 (d,  $J=5.7$  Hz,  $\text{C}_5\text{H}_4$ )  
86.3 (s,  $\text{C}_5\text{H}_4$ )  
85.1 (s,  $\text{C}_5\text{H}_4$ )  
53.8 (s,  $\text{CH}_2\text{Ph}$ )  
-30.0 (d,  $J=6.9$  Hz,  $\text{CH}_3$ )

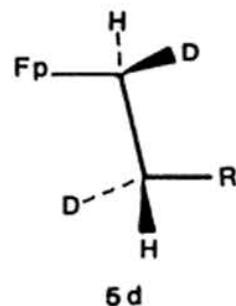
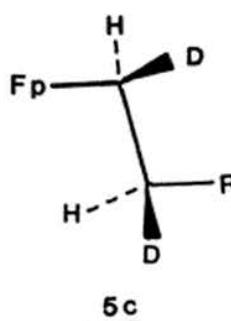
For 4

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ )  
(broad-band decoupled)

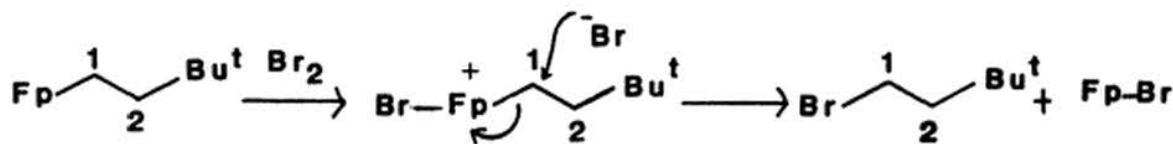
159.9 (d,  $J=3.5$  Hz, ipso-C of benzyl group)  
137.0 (d,  $J=50.8$  Hz, ipso-C of  $\text{PPh}_3$ )  
134.3 (d,  $J=15.1$  Hz, C of  $\text{PPh}_3$ )  
130.6 (s, p-C of  $\text{PPh}_3$ )  
129.0 (d,  $J=10.8$  Hz, C of  $\text{PPh}_3$ )  
128.0 (s, C of benzyl group)  
127.7 (s, C of benzyl group)  
122.3 (s, C of benzyl group)  
105.3 (s, ipso-C of  $\text{C}_5\text{H}_4$ )  
95.5 (d,  $J=4.0$  Hz,  $\text{C}_5\text{H}_4$ )  
92.3 (s,  $\text{C}_5\text{H}_4$ )  
89.6 (s,  $\text{C}_5\text{H}_4$ )  
86.3 (s,  $\text{C}_5\text{H}_4$ )  
13.4 (s,  $\text{CH}_3$ )  
-2.0 (d,  $J=4.2$  Hz, Re- $\underline{\text{CH}_2\text{Ph}}$ )

Heah, P.C.; Gladysz, J.A. J. Am. Chem. Soc. 1984, 106, 7636.

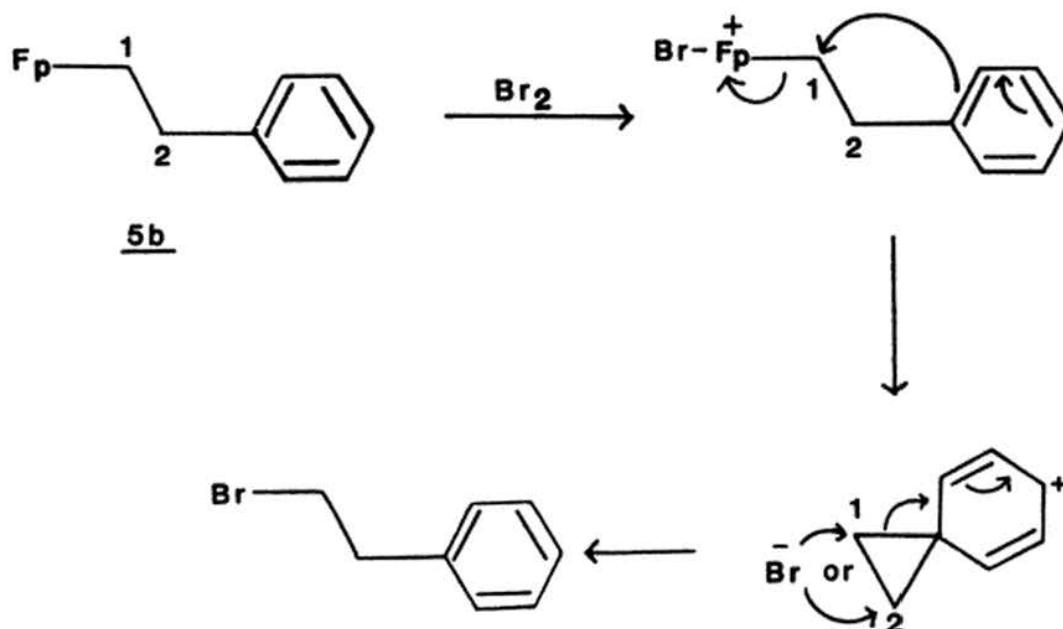
2. a) In order to determine the stereochemistry of the reaction, the experiment should be carried out with the labeled compounds **5c** and **5d**. If threo/erythro interchange occurs, the reaction occurs with inversion of configuration; otherwise, the reaction occurs with retention of configuration. Experimentally, this is verifiable by NMR. See answer to problem 2, Chapter 14 for details of this analysis.



2. b) For R = t-Bu, 5a, a normal S<sub>N</sub><sup>2</sup> attack by bromide occurs with inversion at carbon 1.

5a

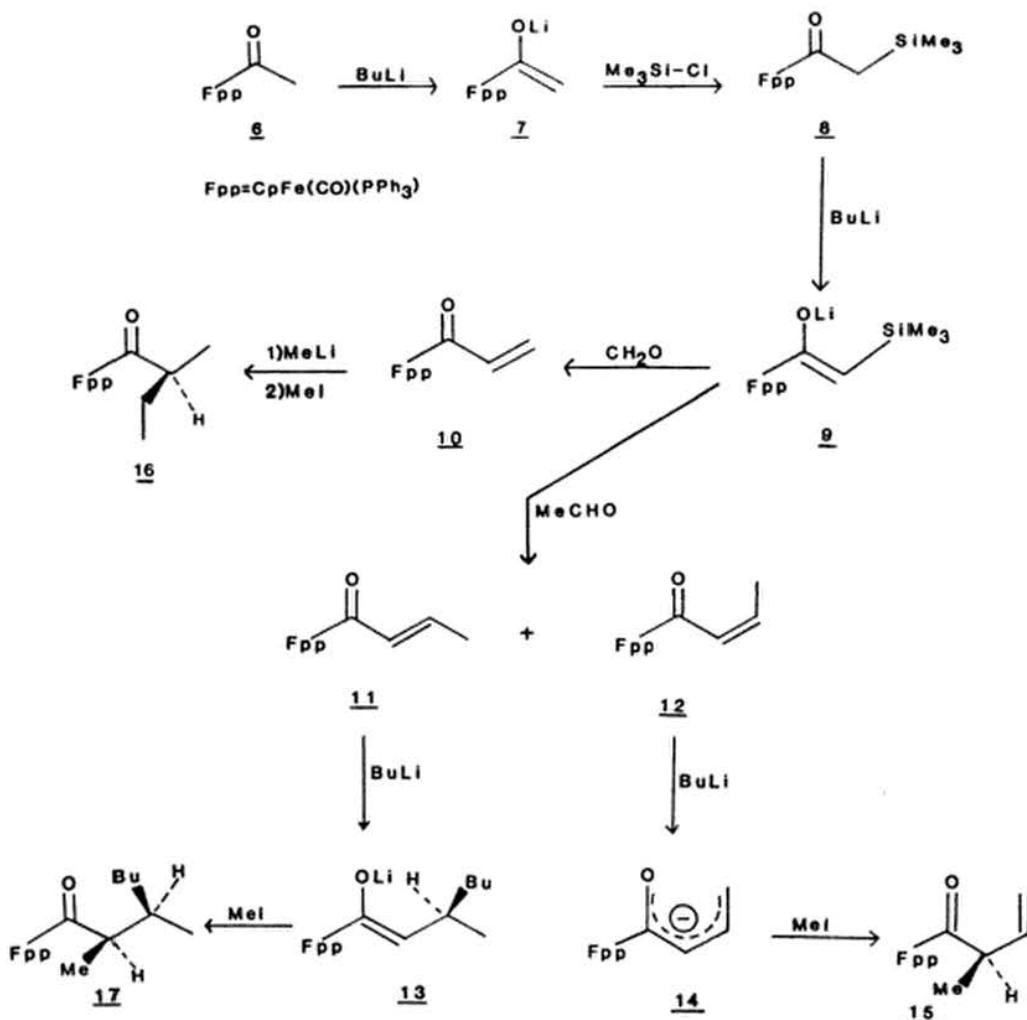
For R = Ph, 5b, a carbocation is formed and stabilized by neighboring phenyl participation. Attack by bromide on this carbocation results in a net retention of configuration at carbon 1.



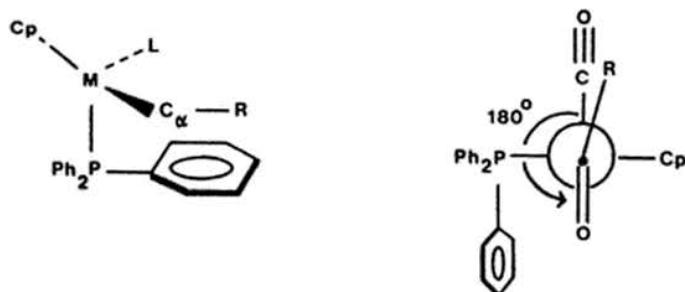
c) To verify this experimental hypothesis, the experiment can be carried out using 1,1-dideutero-5a and 5b. The t-butyl compound, 5a, should give exclusively 1,1-dideuteroiodobromoalkane and the phenyl compound, 5b, should give a 50:50 mixture of 1,1-dideutero- and 2,2-dideuteroiodobromoalkanes (excluding any isotope effect).

Whitesides, G.M.; Boschetto, D.J. J. Am. Chem. Soc. 1971, **93**, 1529.

2. The reactions and products are detailed below.



Note that these alkylation reactions are diastereoselective, with the products arising from attack on only one face of the enolate or acyl compounds. Davies and Seeman have postulated a set of rules that govern the stereochemistry of the formation of chiral centers at the organic ligand in complexes of the type CpM(PPh<sub>3</sub>)(L)R, where M = Fe, Co, Mn, Re; L = CO, NO; R = prochiral fragment. The basis for these rules is that one phenyl ring of the PPh<sub>3</sub> seems to prefer to be in a plane parallel to that of the L-M-C<sub>α</sub> entity, and any conformations of the R group that result in positioning of an alkyl or aryl substituent in between the C<sub>α</sub>-M-L plane and the PPh<sub>3</sub> plane are energetically unfavorable.

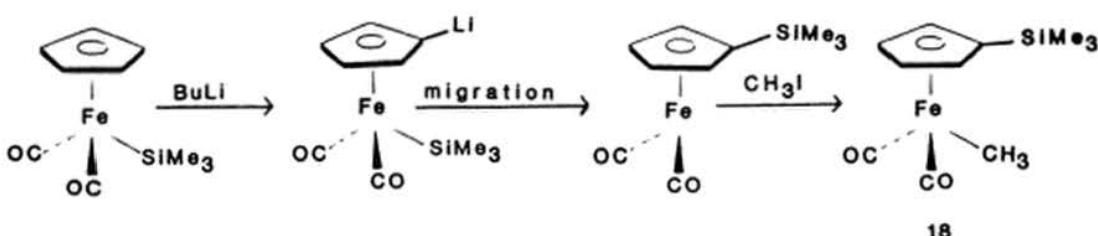


Additionally, the acyl oxygen prefers to be anti to the CO, i.e., the  $O-C_\alpha-M-CO$  dihedral angle is  $180^\circ$ . Thus 12 is simply deprotonated by Bu-Li to give 14, while 11 undergoes a nucleophilic attack by Bu-Li to give 13.

Davies, S.G.; Walker, J.C. J. Chem. Soc., Chem. Comm. 1985, 209.

Davies, S.G.; Seeman, J.I. Tetrahedron Lett. 1984, 1845.

4.



Assignments for NMR data for 18:

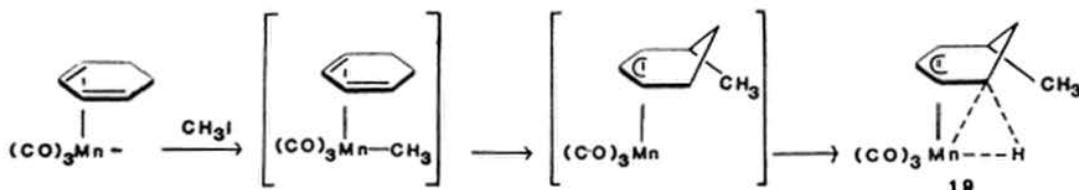
$^1H$  NMR ( $\delta$ ,  $CS_2$ ):

4.67-4.90 (m, 4 H, Cp)  
0.31 (s, 9 H,  $Me_3Si-$ )  
0.18 (s, 3 H,  $CH_3$ )

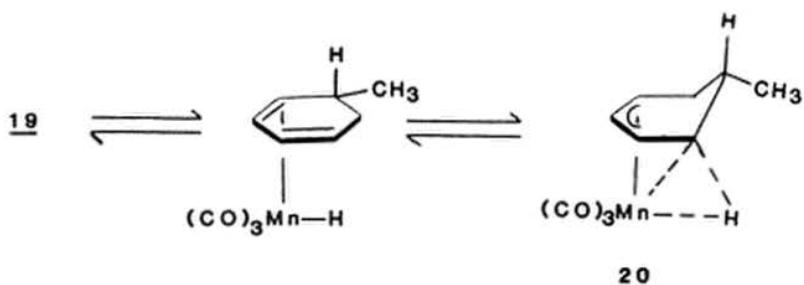
Berryhill, S.R.; Sharenow, B. J. Organomet. Chem., 1981, 221, 143.

5. a) The product ratio is probably due to steric reasons. The major isomer has the methyl group farther away from the  $Mn(CO)_3$ .

b) A mechanism for the formation of product 19 is shown below:

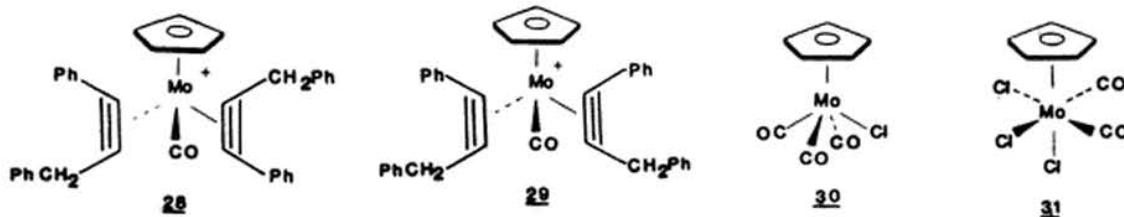


A mechanism for the formation of product 20 is shown below:



Brookhart, M.; Lamanna W.; Pinhas, A.R. Organomet., 1983, 2, 638.

8. Compounds 28-31 are shown below:



The NMR data are assigned as follows:

Compound  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )

<u>28</u>	7.6-6.6 (m, 20 H, Ph's) 5.90 (s, 5 H, Cp) 5.10 (d, $J=16.6$ Hz, 1 H, $\text{CHH}'\text{Ph}$ ) 5.09 (d, $J=17.5$ Hz, 1 H, $\text{CHH}'\text{Ph}$ ) 4.72 (d, $J=16.6$ Hz, 1 H, $\text{CHH}'\text{Ph}$ ) 4.71 (d, $J=17.5$ Hz, 1 H, $\text{CHH}'\text{Ph}$ )
<u>29</u>	7.6-6.6 (m, 20 H, Ph's) 6.03 (s, 5 H, Cp) 4.79 (d, $J=17.1$ Hz, 2 H, $\text{CHH}'\text{Ph}$ ) 4.32 (d, $J=17.1$ Hz, 2 H, $\text{CHH}'\text{Ph}$ )
<u>30</u>	4.25 (s, Cp)
<u>31</u>	6.51 (s, acetone- $d_6$ , Cp)

#### NOTE

In these systems, low field Cp resonances and high energy CO stretches are characteristic of electron deficient or cationic species.

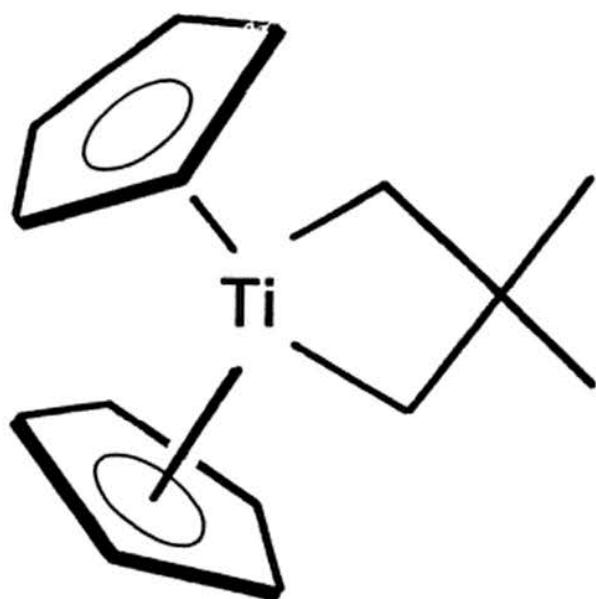
For 28 and 29: Allen, S.R.; Beevor, R.G.; Green, M.; Norman, N.C.; Orpen, A.G.; Williams, I.D. *J. Chem. Soc., Dalt. Trans.* 1985, 435.

For 30 and 31: Burkett-St. Laurent, J.C.T.R.; Field, J.S.; Haines, R.J.; McMahon, M. *J. Organomet. Chem.* 1979, 181, 117.

Haines, R.J.; Nyholm, R.S.; Stiddard, M.H.B. *J. Chem. Soc. (A)* 1966, 1606.

# 9

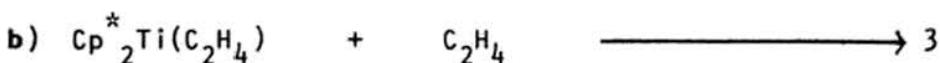
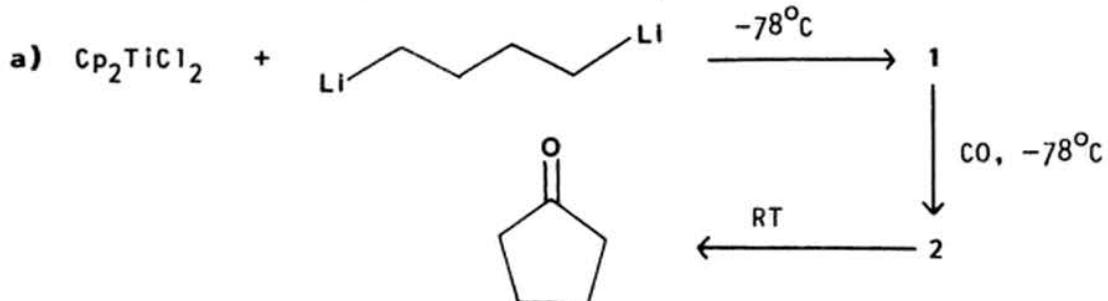
## Metallacycles



## 9: METALLACYCLES

### QUESTIONS

1. Predict the products of the following reactions:



$^1\text{H}$  NMR data for 3 ( $\delta$ , toluene-d<sub>8</sub>):

1.80 (s, 15 H)

1.72 (m, 4 H)

0.60 (m, 4 H)

c)



HINT

See problem 6 in this chapter (DMAP = 4-dimethylaminopyridine).

d)



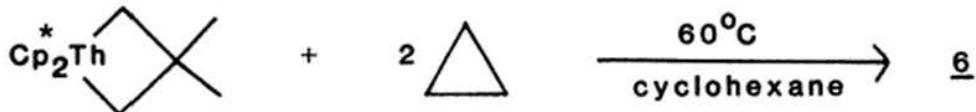
$^1\text{H}$  NMR data for 5 ( $\delta$ , C<sub>6</sub>D<sub>6</sub>):

4.19 (s, 10 H)

3.55 (q, J=8 Hz, 2 H)

0.69 (t, J=8 Hz, 4 H)

e)



1. e) (cont.)

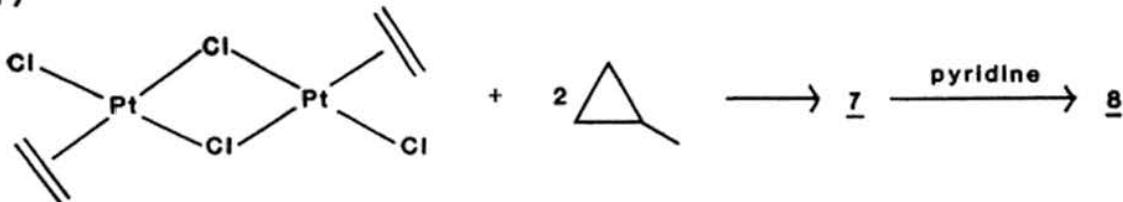
 $^1\text{H}$  NMR data for 6 ( $\delta$ , ppm):

0.78 (d, 4 H)  
 -0.03 (d, 4 H)  
 -0.72 (m, 2 H)

 $^{13}\text{C}$  NMR data for 6 ( $\delta$ , ppm):

123.47  
 70.33  
 11.54  
 8.59

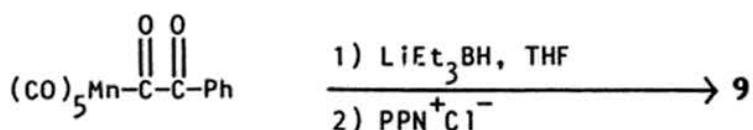
f)



## HINTS

- 1) Complex 7 is oligomeric and very insoluble in non-donor solvents.  
 2) Complex 8 exists as a mixture of two isomers.

2. The following reaction occurs to produce the novel metallacycle 9.



## Spectral data for 9:

 $^1\text{H}$  NMR ( $\delta$ , acetone- $d_6$ )

7.60, 7.23 (m, 35 H)  
 4.57 (s, 1 H)

IR ( $\text{cm}^{-1}$ , THF)

2043, 1959, 1940,  
 1664, 1636

 $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )  
 (broad-band decoupled)

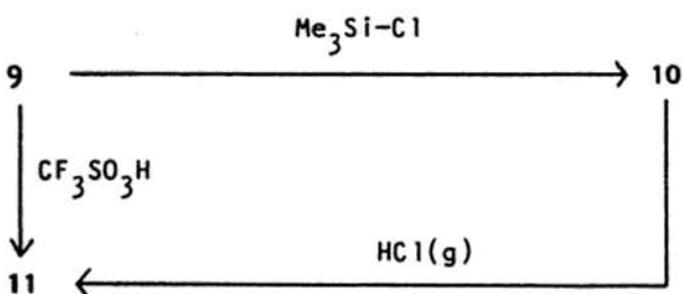
288.1 (s)  
 229.0 (s)  
 218.9 (s)  
 215.4 (s)  
 138.4 (s)  
 134.2 (s)  
 132.4 (t,  $J=6$  Hz)  
 129.9 (t,  $J=7$  Hz)  
 127.8 (s)  
 127.0 (d,  $J=108$  Hz)  
 126.7 (s)  
 126.1 (s)  
 94.2 (s)

a) Provide a structure for 9 and propose a mechanism for its formation.

## HINT

When the reaction is monitored by  $^1\text{H}$  NMR, no low field resonances (below 8 ppm) are observed.

2. b) Complex **9** undergoes the transformations shown below.



Spectral data:

For **10**

<sup>1</sup>H NMR ( $\delta$ , CC<sub>l</sub><sub>4</sub>)

7.33 (m, 5 H)  
4.68 (s, 1 H)  
0.20 (s, 9 H)

IR (cm<sup>-1</sup>, CHCl<sub>3</sub>)

2119, 2048, 2020, 1638

For **11**

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>)

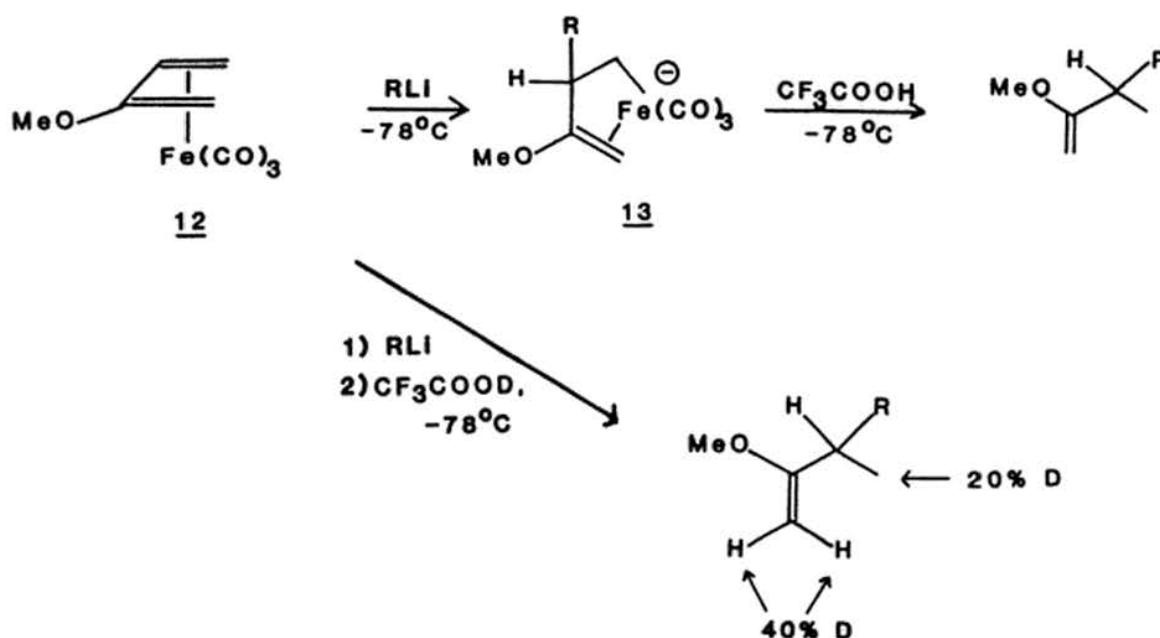
7.2 (m, 5 H)  
6.2 (s, 1 H)  
5.0 (s, 1 H)

IR (cm<sup>-1</sup>, CHCl<sub>3</sub>)

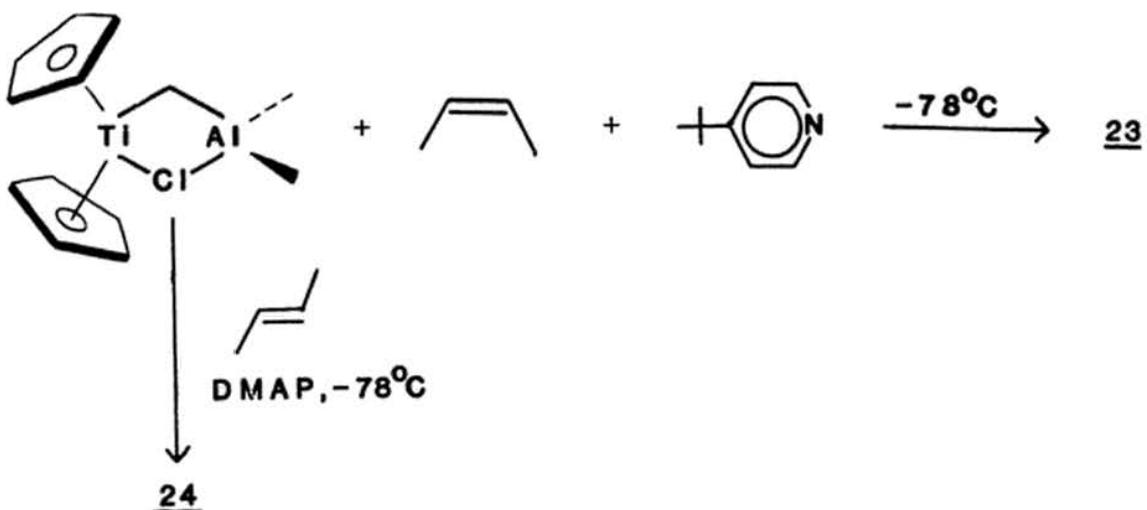
3610-3260, 2116, 2052, 2016, 1639

Analytical data for **10**: 47.59% C, 3.91% H, 13.49% Mn

3. The following reactions have been observed.



6. The following reactions are observed (DMAP = 4-dimethylamino-pyridine).



<sup>1</sup>H NMR data ( $\delta$ , toluene-d<sub>8</sub>, -30°C):

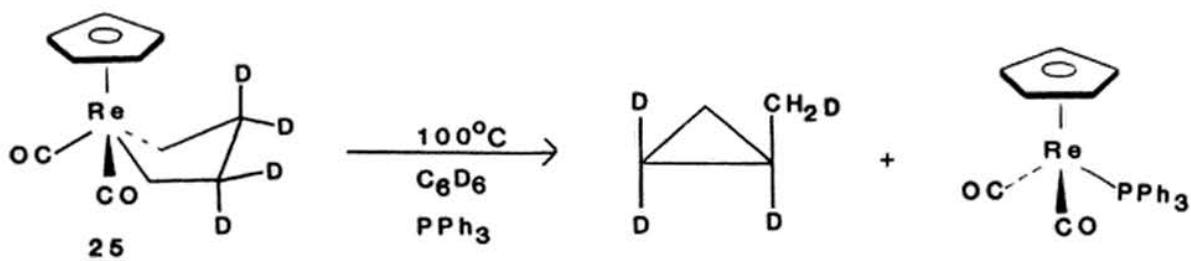
For 23                          For 24

0.03 (m, 1 H)	-0.80 (m, 1 H)
1.02 (d, 3 H)	1.04 (d, 3 H)
1.58 (d, 3 H)	1.68 (d, 3 H)
2.31 (t, 1 H)	2.33 (dd, 1 H)
3.51 (m, 2 H)	2.81 (dd, 1 H)
5.23 (s, 5 H)	3.05 (dd, 1 H)
5.32 (s, 5 H)	5.27 (s, 5 H)
	5.36 (s, 5 H)

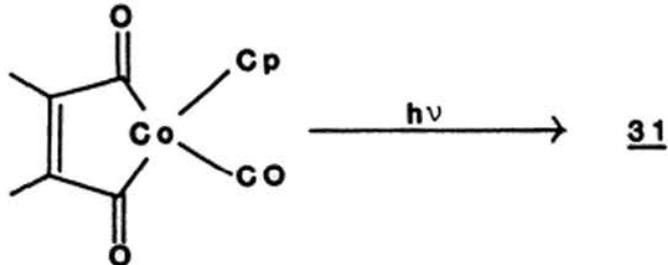
a) Propose structures for compounds 23 and 24.

b) What is the purpose of the amine in the reactions?

7. The following conversion has been shown to occur.



9. Propose a structure for product 31 and assign all spectroscopic data.



Spectral data for 31:

$^1\text{H}$  NMR (  $\delta$ , ppm)

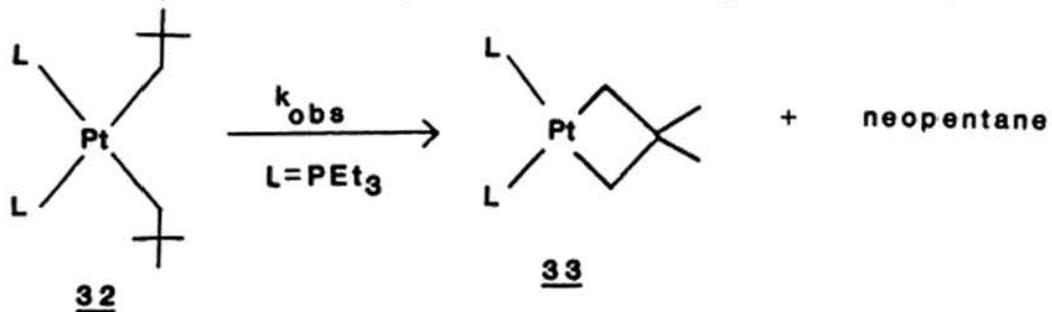
1.91 (s, 6 H)  
5.02 (s, 5 H)

$^{13}\text{C}$  NMR (  $\delta$ , ppm)

10.8  
51.3  
86.8  
225.9

partial IR ( $\text{cm}^{-1}$ ): 1810, 1760

10. Thermolysis of 32 in cyclohexane at  $150^\circ\text{C}$  gives metallacycle 33.



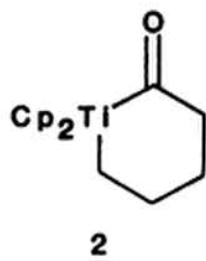
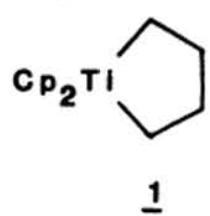
#### OBSERVATIONS

- 1) When excess  $\text{PEt}_3$  is added,  $k_{\text{obs}}$  decreases.
- 2) Thermolysis of 32 in cyclohexane- $d_{12}$  gives neopentane,  $\text{C}(\text{Me})_4$ , that is 97%  $d_0$  and 3%  $d_1$ .
- 3) Thermolysis of  $\text{L}_2\text{Pt}(\text{CD}_2-\text{CMe}_3)_2$  in cyclohexane- $d_{12}$  gives neopentane that is 93%  $d_2$  and 7%  $d_3$ .

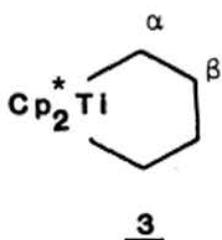
Propose a mechanism for metallacycle formation that is consistent with the above observations.

**ANSWERS**

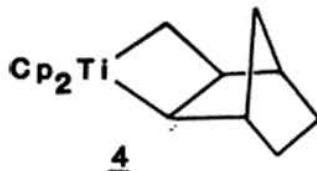
1. a)



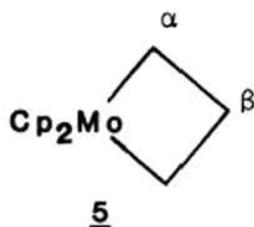
b)

Assignments for  $^1\text{H}$  NMR data for 3:1.80 (s, 15 H,  $\text{Cp}^*$ )1.72 (m, 4 H,  $\alpha$ -hydrogens of metallacycle)0.60 (m, 4 H,  $\beta$ -hydrogens of metallacycle)

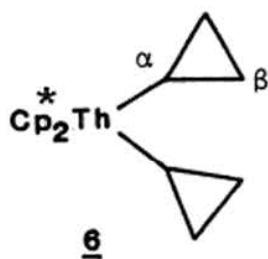
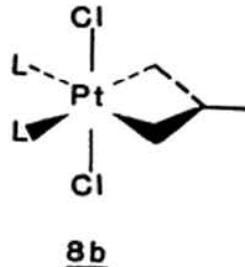
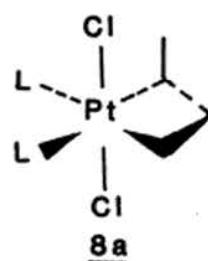
c)



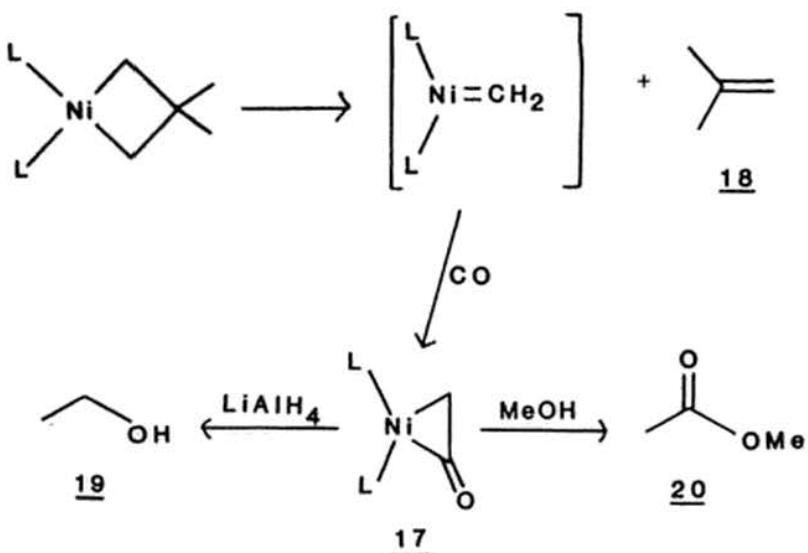
d)

Assignments for  $^1\text{H}$  NMR data for 5:4.19 (s, 10 H,  $\text{Cp}$ )3.55 (q,  $J=8$  Hz, 2 H,  $\beta$ -hydrogens of metallacycle)0.69 (t,  $J=8$  Hz, 4 H,  $\alpha$ -hydrogens of metallacycle)

e)

f)  $\text{7} = [\text{PtCl}_2(\text{C}_5\text{H}_5\text{Me})]_n$ Assignments for spectral data for 6: $^1\text{H}$  NMR ( $\delta$ , ppm)0.78 (d, 4 H,  $\beta$ -H's)  
-0.03 (d, 4 H,  $\beta$ -H's)  
-0.72 (m, 2 H,  $\alpha$ -H's) $^{13}\text{C}$  NMR ( $\delta$ , ppm)123.47 ( $\text{C}_5\text{Me}_5$ )  
70.33 ( $\alpha$ -C's)  
11.54 ( $\text{C}_5\text{Me}_5$ )  
8.59 ( $\beta$ -C's)

4. The authors believe that elimination of isobutylene (18) occurs from the metallacycle to give a nickel carbene complex as the reactive intermediate. Carbonylation of this carbene produces the ketene complex 17, which can react with  $\text{LiAlH}_4$  and methanol to give ethanol (19) and methyl acetate (20) respectively. In the scheme below,  $L = \text{PPh}_3$ .



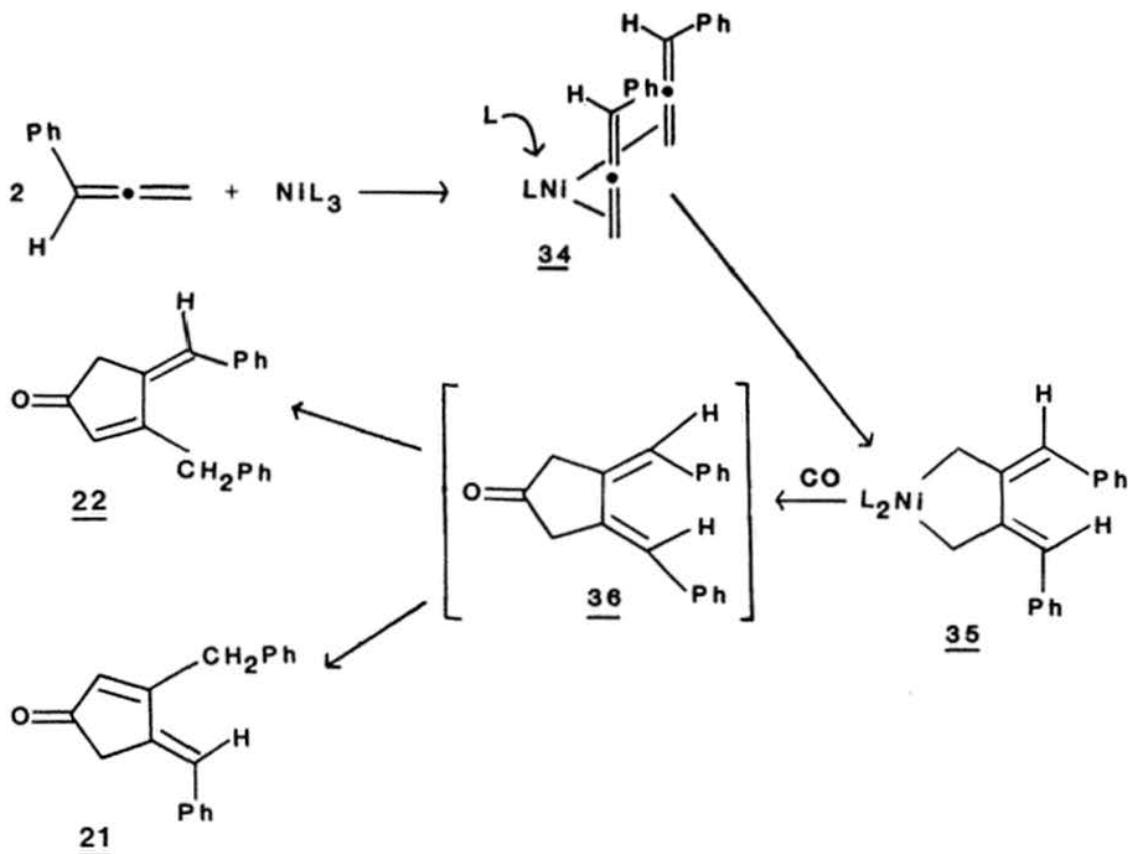
Miyashita, A.; Shitara, H.; Nohira, H. J. Chem. Soc., Chem. Comm. 1985, 850.

5. The proposed mechanism is shown on the following page. In all cases,  $L = \text{PPh}_3$ . Pi-coordination of two phenylallenes by the unsubstituted double bond occurs initially to give 34. Stereospecific and regiospecific coupling then occurs to give metallacycle 35. The stereochemistry and regiochemistry of this coupling is thought to be controlled by steric effects, i.e., the benzylidene rotates away from the approaching  $\text{PPh}_3$  ligand. Carbonylation of 35 gives the undetected intermediate 36 which isomerizes to give either 21 or 22.

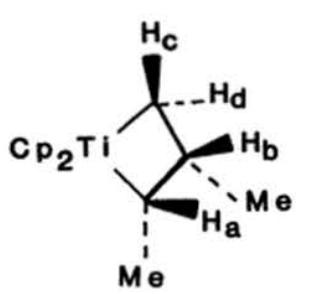
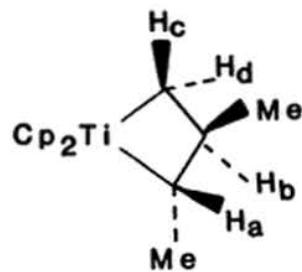
#### NOTE

Although mono- and trans bis-pi-complexes must be present during this reaction, they do not lead to the products shown.

## 5. (cont.)



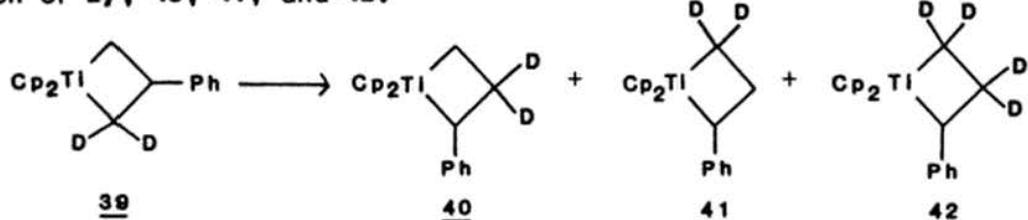
Pasto, D.J.; Huang, N.-Z.; Eigenbrot, C.W. J. Am. Chem. Soc. **1985**, 107, 3160.

6. a) Complexes 23 and 24 are shown below:2324

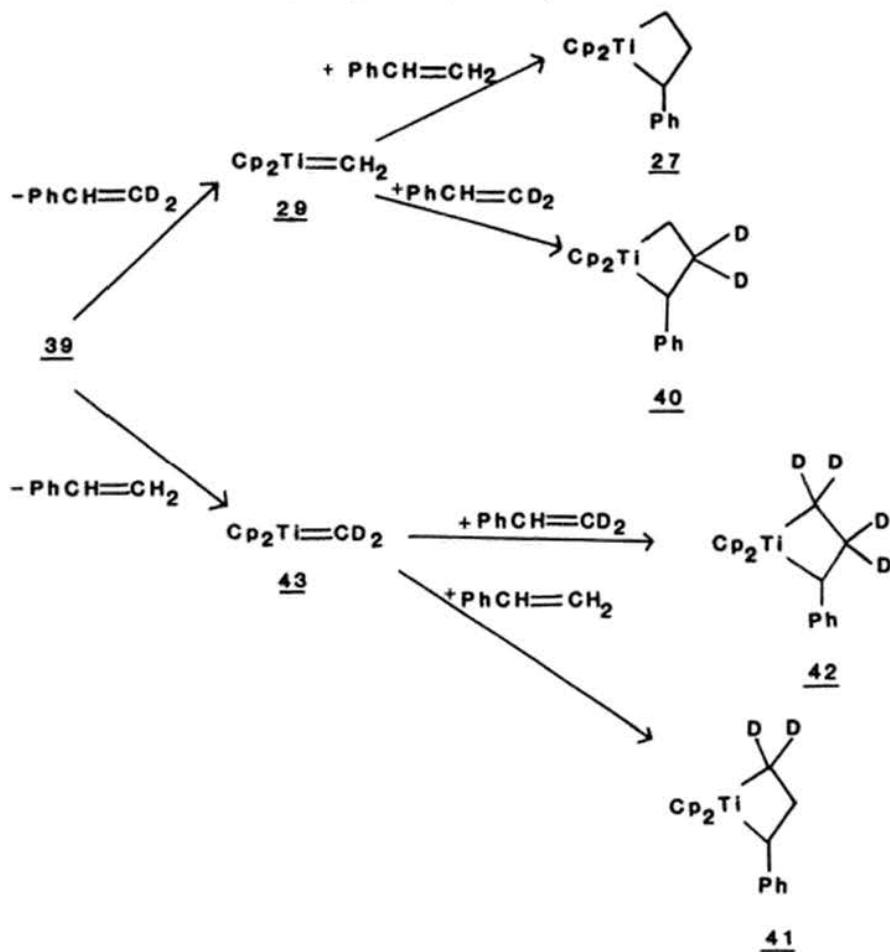
## 8. (cont.)

2) Add labeled styrene,  $\text{PhCH=CD}_2$ , to a solution of 26 and look for exchange into the isomerized metallacycle, 27, and into the starting complex.

3) Use a labeled titanacyclobutane, such as 39, and look for the formation of 27, 40, 41, and 42.



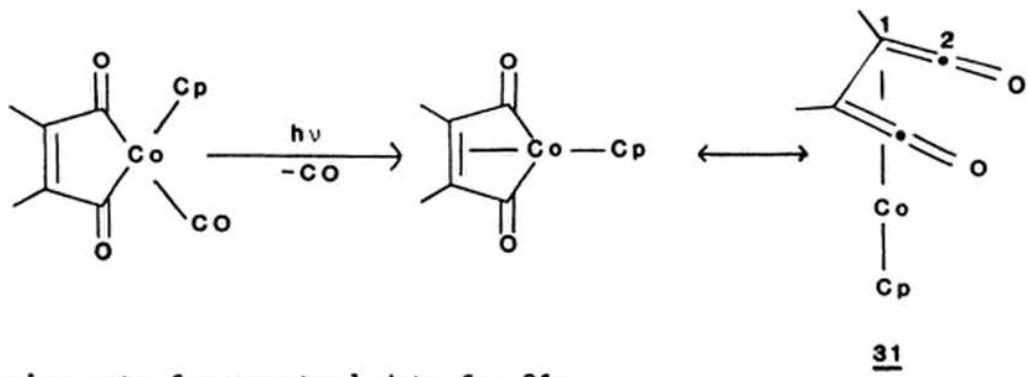
These products can be formed by the pathways shown below.



The use of  $^2\text{H}$  NMR spectroscopy would greatly simplify the analysis of the products from this reaction. The signals are well separated and the spectrum will show only the deuterated products.

Ikariya, T.; Ho, S.C.H.; Grubbs, R.H. Organomet. 1985, 4, 199.

9. The reaction to give complex 31 is shown below:



Assignments for spectral data for 31:

$^1\text{H}$  NMR ( $\delta$ , ppm)

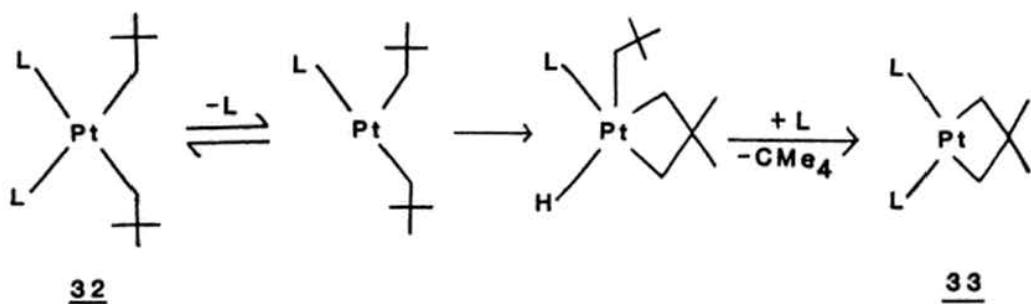
1.91 (s, 6 H,  $-\text{CH}_3$ )  
5.02 (s, 5 H, Cp)

$^{13}\text{C}$  NMR ( $\delta$ , ppm)

10.8 ( $-\text{CH}_3$ )  
51.3 ( $\text{C}_1$ )  
86.8 (Cp)  
225.9 ( $\text{C}_2$ )

Jewell, C.F.; Liebeskind, L.S.; Williamson, M. J. Am. Chem. Soc. 1985, 107, 6715.

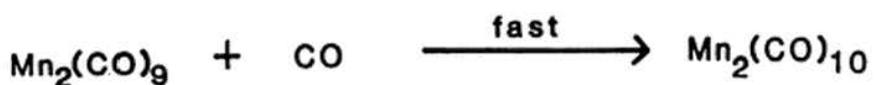
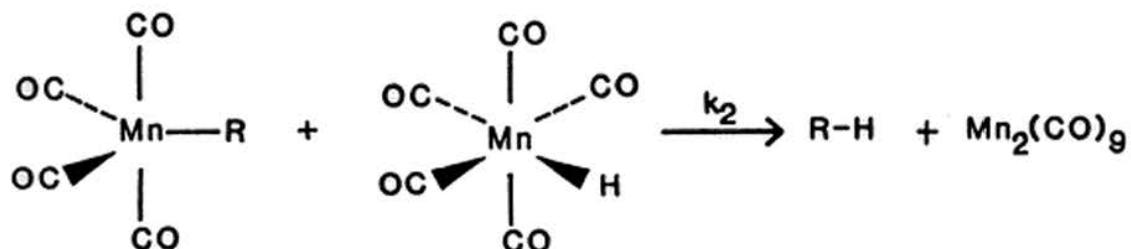
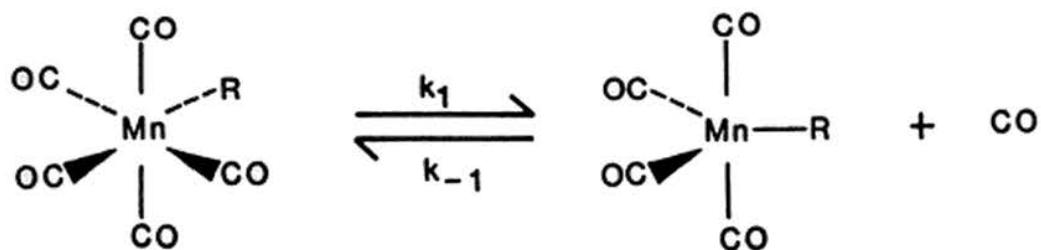
10. The proposed mechanism involves initial dissociation of  $\text{PET}_3$ , followed by oxidative-addition of a C-H bond of one of the neopentyl ligands. Reductive-elimination of neopentane and reassociation of  $\text{PET}_3$  gives metallacycle 33.



Foley, P.; Whitesides, G.M. J. Am. Chem. Soc. 1979, 101, 273.

# 10

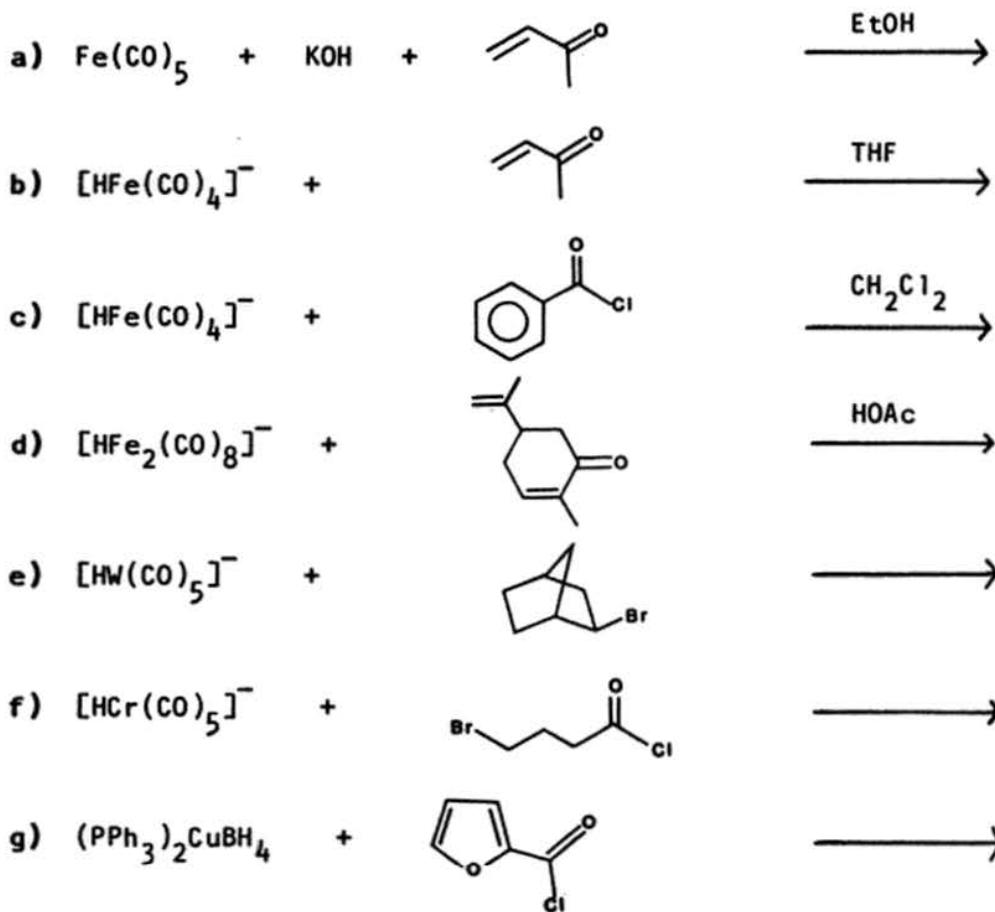
## Reactions of Transition Metal Alkyl and Hydride Complexes



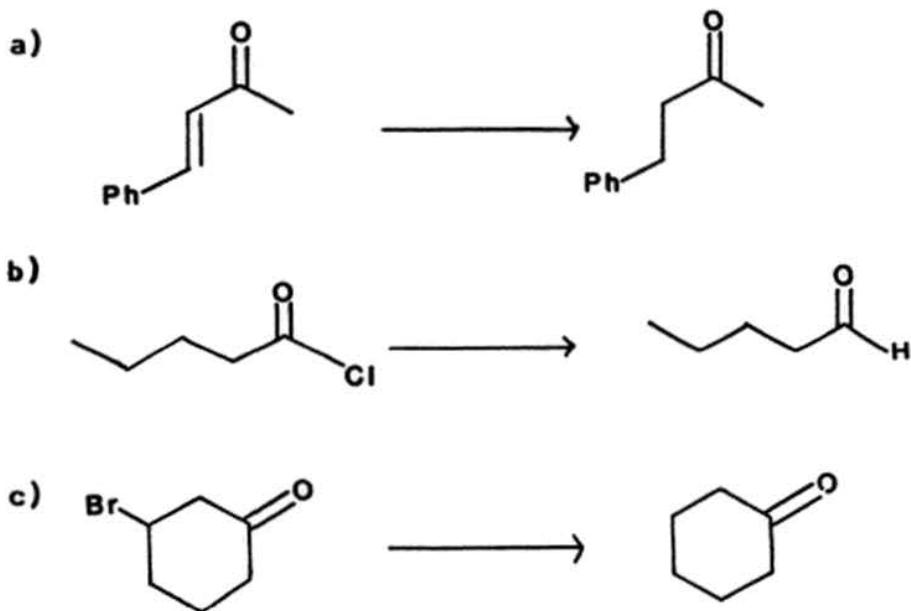
## 10: REACTIONS OF TRANSITION METAL ALKYL AND HYDRIDE COMPLEXES

### QUESTIONS

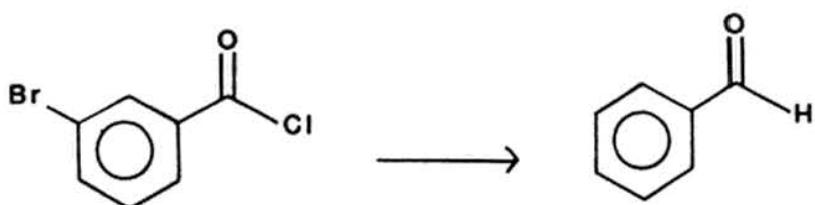
1. Predict the organic products of the following reactions:



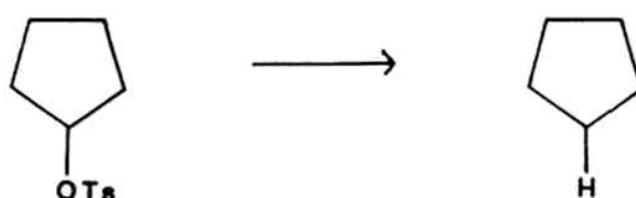
2. Suggest an organometallic reagent to carry out the following transformations.



2. d)



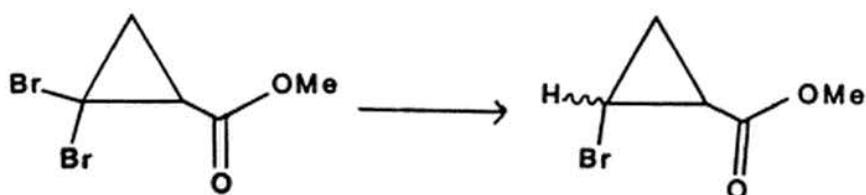
e)



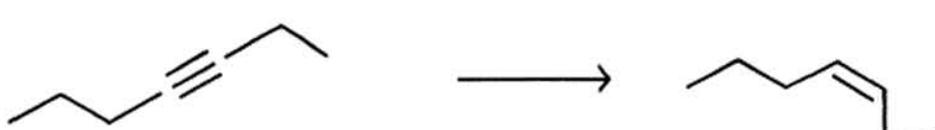
f)



g)



h)



3. Predict the products of the reaction (if any) of  $[\text{CpV}(\text{CO})_3\text{H}]^-$  with the following substrates.

a)

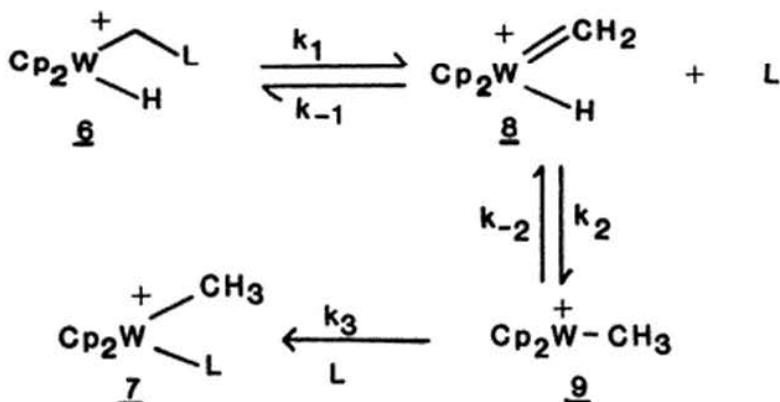


b)

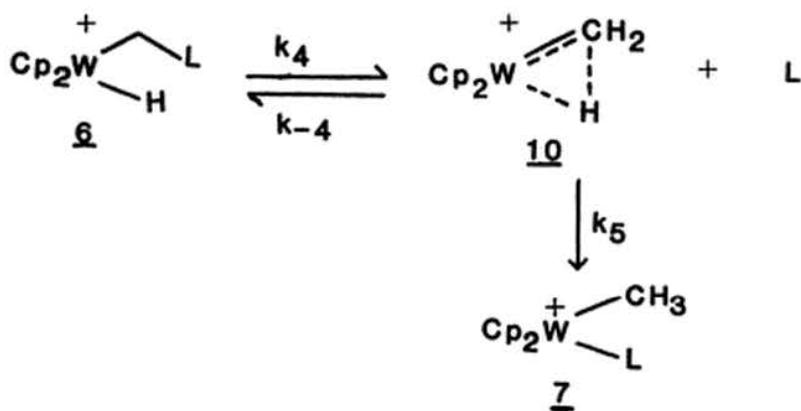


7. (cont.) The authors propose the two different mechanisms, outlined below:

**Mechanism I**



**Mechanism II**



a) For each mechanism, write a kinetic expression for the disappearance of 6 in terms of the rate constants given. Assume all intermediates are at a steady-state concentration.

b) Can these two mechanisms be kinetically distinguished by the fact that there is no inverse dependence of the rate on the phosphine concentration? Why or why not?

8. The following reaction occurs:



**OBSERVATIONS**

1) Second order kinetics are observed, i.e.,

$$-\frac{d[12]}{dt} = k_{\text{obs}} [11][12]$$

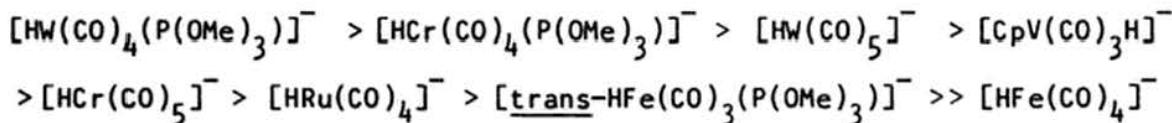
## 8. (cont.)

2) The rate is not affected by 1 atmosphere of CO.

3) An inverse isotope effect is observed, i.e.  $\text{Cp}(\text{CO})_3\text{M-D}$  reacts faster than  $\text{Cp}(\text{CO})_3\text{M-H}$ . No D-incorporation into the methyl group of unreacted 12 is observed.

Postulate a mechanism consistent with all observations.

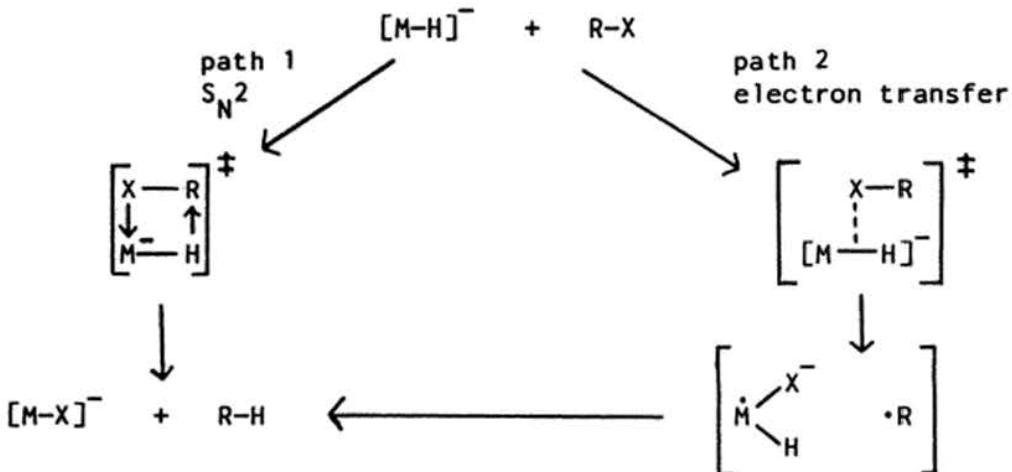
9. Below is a series of hydride reducing agents listed in order of decreasing reactivity towards primary alkyl halides:



Two mechanistic pathways are possible:

1) Ionic ( $S_N^2$ -like) hydride transfer, or

2) single electron transfer, followed by hydrogen atom abstraction.

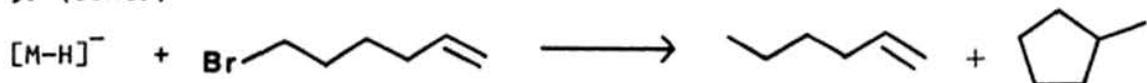


Based on the following observations, decide which pathway is favored for each of the two complexes,  $[\text{HW}(\text{CO})_4\text{P}]^-$  ( $\text{P}=\text{P}(\text{OMe})_3$ ) and  $[\text{HW}(\text{CO})_5]^-$ . Explain all observations in light of your conclusions.

## OBSERVATIONS

1) Reaction of  $[\text{HW}(\text{CO})_4\text{P}]^-$  and  $[\text{HW}(\text{CO})_5]^-$  with 6-bromo-1-hexene gives the mixtures of products shown.

9. (cont.)



$[\text{M}-\text{H}]^-$       Product Ratio, 1-hexene:methylcyclopentane

$[\text{HW}(\text{CO})_4\text{P}]^-$       1 : 0

$[\text{HW}(\text{CO})_5]^-$       1 : 0.67

2) Reaction of  $[\text{HW}(\text{CO})_4\text{P}]^-$  and  $[\text{HW}(\text{CO})_5]^-$  with cyclopropylcarbinyl bromide gives the mixtures of products shown.



$[\text{M}-\text{H}]^-$       Product Ratio, methylcyclopropane:1-butene

$[\text{HW}(\text{CO})_4\text{P}]^-$       1 : 0.1

$[\text{HW}(\text{CO})_5]^-$       1 : 3.5

$(n\text{-Bu})_3\text{Sn-H}$       1 : 200

3) The half-lives for displacement of tosylate from n-butyltosylate are:

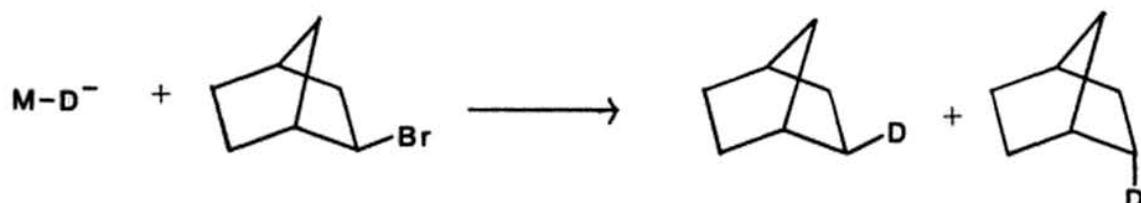
$[\text{M}-\text{H}]^-$        $t_{1/2}$

$[\text{HW}(\text{CO})_4\text{P}]^-$       22 min.

$[\text{HW}(\text{CO})_5]^-$       > 8 h

$[\text{HCr}(\text{CO})_5]^-$       33 h

4) Reaction of  $[\text{DW}(\text{CO})_4\text{P}]^-$  and  $[\text{DW}(\text{CO})_5]^-$  with exo-2-bromonorbornane gives the products shown.



$[\text{M}-\text{H}]^-$       Product ratio, exo/endo-2-deuterionorbornane

$[\text{DW}(\text{CO})_4\text{P}]^-$       1 : 0.43

$[\text{DW}(\text{CO})_5]^-$       1 : 0

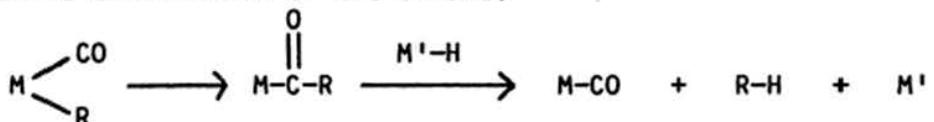
$[\text{Et}_3\text{BD}]^-$       0 : 1

10. There are a number of possible reaction mechanisms that have been postulated for binuclear reductive-elimination reactions between transition metal alkyl and transition metal hydride complexes.

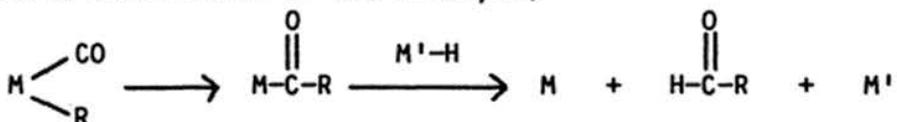


These mechanisms are:

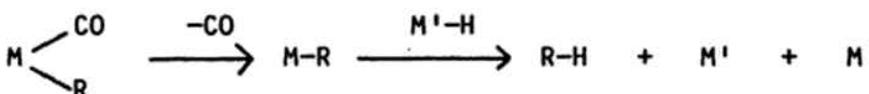
- 1) Migration of the alkyl moiety to coordinated CO, followed by reductive-elimination of the alkane;



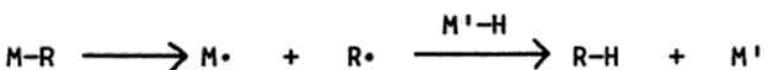
- 2) migration of the alkyl moiety to coordinated CO, followed by reductive-elimination of the aldehyde;



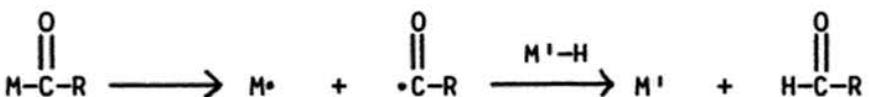
- 3) dissociation of CO, followed by elimination of the alkane;



- 4) homolytic cleavage of the M-R bond, followed by H-atom abstraction;



- 5) insertion of CO into the metal-alkyl bond, followed by homolytic cleavage of the metal-acyl bond and H-atom abstraction.

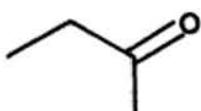


Reactions of  $\text{HMn}(\text{CO})_5$  with manganese alkyls have been studied in order to determine the mechanism(s) for binuclear reductive-elimination in these systems. From the data given for the following two reactions, classify each one into one of the given categories.

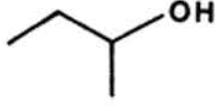
## ANSWERS

1. The organic products are shown below:

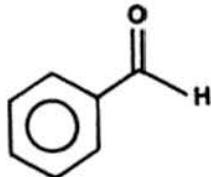
a)



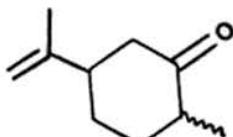
b)



c)



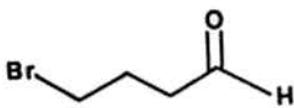
d)



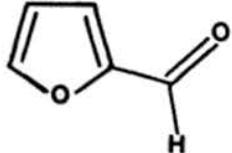
e)



f)



g)



Collman, J.P.; Hegedus, L.S.; Norton, J.R.; Finke, R.G. "Principles and Applications of Organotransition Metal Chemistry", 2nd ed., University Science Books (Mill Valley, CA), Chapter 13.

2. The reagents given are only those discussed in Chapter 13 of Collman, Hegedus, Norton, and Finke's "Principles and Applications of Organotransition Metal Chemistry", 2nd edition, University Science Books (Mill Valley, CA). There may also be other reagents that effect the same transformations.

a) Possible reagents are  $[\text{HFe}(\text{CO})_4]^-$  in a protic solvent,  $[\text{HFe}_2(\text{CO})_8]^-$ ,  $[\text{HCr}_2(\text{CO})_{10}]^-$ ,  $[\text{n-Pr-C}\equiv\text{C-Cu-H}]^-$ , and  $\text{Bu}_3\text{Sn-H/Pd(0)}$ .

b) Possible reagents are  $[\text{HFe}(\text{CO})_4]^-$  in an aprotic solvent,  $[\text{HCr}(\text{CO})_5]^-$ ,  $[\text{CpV}(\text{CO})_3\text{H}]^-$ , and  $\text{Bu}_3\text{Sn-H/Pd(0)}$ .

c) Possible reagents are  $[\text{HCr}(\text{CO})_5]^-$ ,  $[\text{HW}(\text{CO})_5]^-$ , and  $[\text{CpV}(\text{CO})_3\text{H}]^-$ .

d) Possible reagents are  $[\text{HCr}(\text{CO})_5]^-$  and  $[\text{HW}(\text{CO})_5]^-$ .

e) Possible reagents are  $[\text{n-BuCuH}]^-$  and  $\text{LiAlH}_4/\text{NiCl}_2$ .

*image  
not  
available*

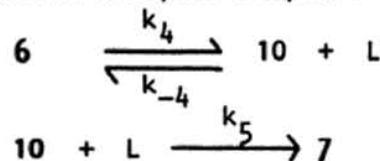
7. (cont.)

$$\text{and } [8] = \frac{k_1[6] + k_{-2}[9]}{k_{-1}[L] + k_2} \quad (5)$$

Combination of these two equations (a somewhat involved, but straightforward algebraic manipulation) will give an expression for 9 that can be substituted into equation (1) to give the rate expression

$$\frac{-d[6]}{dt} = \frac{k_1 k_2 k_3 [6]}{k_{-1} k_{-2} + k_2 k_3 + k_{-1} k_3 [L]} \quad (6)$$

For Mechanism II, there is only one steady-state intermediate, 10, which makes the kinetic analysis simpler.



The rate of the reaction is given by equation (7)

$$-d[6]/dt = k_5[10][L] = d[7]/dt \quad (7)$$

A steady-state approximation for 10 gives:

$$d[10]/dt = k_4[6] - k_{-4}[10][L] - k_5[10][L] \quad (8)$$

$$\text{and } [10] = \frac{k_4[6]}{[L](k_{-4} + k_5)} \quad (9)$$

Substituting this expression for [10] back into equation (7) gives the rate expression

$$\frac{-d[6]}{dt} = \frac{k_4 k_5 [6]}{k_{-4} + k_5} \quad (10)$$

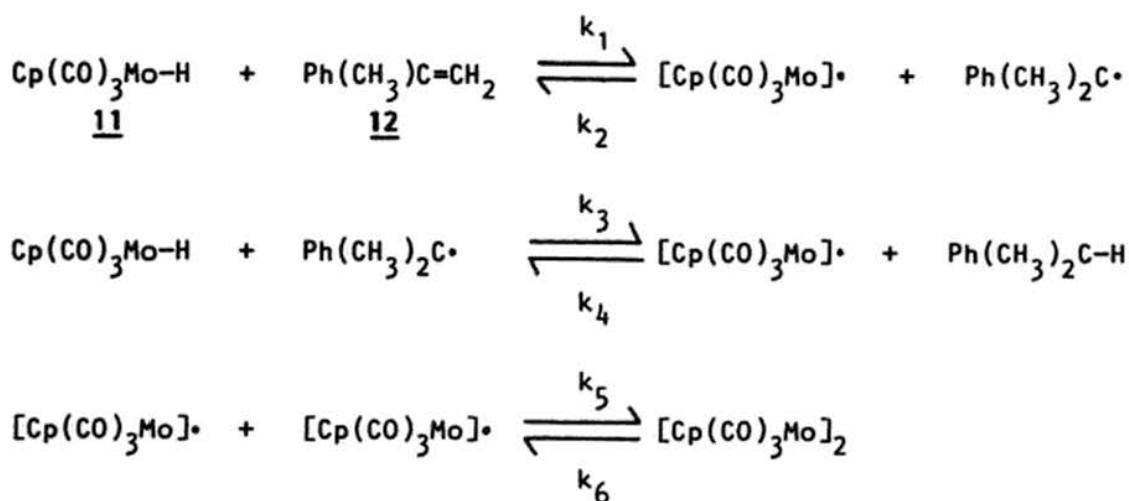
b) Initially it might be thought that a lack of an inverse dependence on L rules out Mechanism I; however, if the equilibrium between 8 and 9 is established very quickly (i.e.,  $k_2$  and  $k_{-2}$  are large), then  $k_{-1}k_{-2} + k_2k_3 \gg k_{-1}k_3[L]$ , and the rate expression for Mechanism I reduces to

$$\frac{-d[6]}{dt} = \frac{k_1 k_2 k_3 [6]}{k_{-1} k_{-2} + k_2 k_3}$$

As a result, the fact that the rate does not depend on phosphine concentration does not enable one to distinguish between these two mechanisms.

Green, J.C.; Green, M.L.H.; Morley, C.P. Organomet. 1985, 4, 1302.

8. The postulated mechanism is shown below:



The rate constants  $k_4$  and  $k_6$  must be negligible because of the endothermicity of these processes. The absence of deuterium exchange between  $\text{Cp(CO)}_3\text{Mo-D}$  and the olefin, 12, implies that the  $k_2$  step is slow relative to the  $k_3$  step. Thus, the rate-determining step must be the  $k_1$  step.

The inverse isotope effect can be explained as follows: The zero point energy of the M-H bond is greater than that of the C-H bond, and therefore the transition state is unsymmetrical, as shown in A, below. When D is substituted for H, the zero point energies of both M-D and C-D are less than the corresponding M-H and C-H bond energies; however, because of the lighter mass of C relative to M, the difference is greater for C-D than for M-D. Thus the transition state becomes more unsymmetrical and is further along the reaction coordinate for M-D bond-breaking, as shown in B. Thus, the zero point energy difference between the transition states is greater than between the reactants, producing an inverse isotope effect.



A



B

Sweany, R.L.; Comberrel, D.S.; Dombourian, M.F.; Peters, N.A. J. Organomet. Chem. 1981, 216, 57.

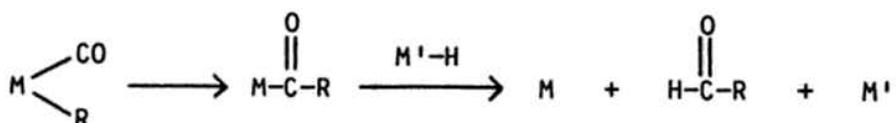
9. The phosphite-substituted hydride  $\text{HW(CO)}_4[\text{P(OMe)}_3]^-$  appears to reduce alkyl halides by more of an ionic mechanism, while reductions using  $[\text{HW(CO)}_5]^-$  have more radical character. The observations support this hypothesis:

- 1) The fact that methylcyclopentane is observed as a product in the

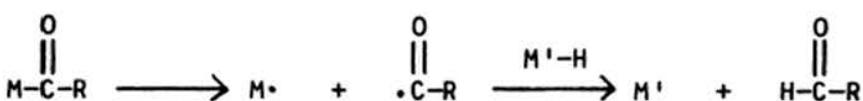
## 10. Reaction 1

The possible reaction pathways that yield aldehydes as products are 2) and 5).

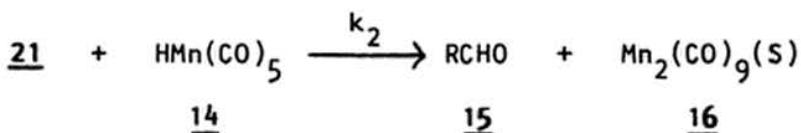
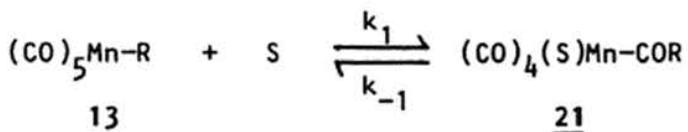
2)



5)



Because  $\Delta S^\ddagger$  is negative, Mechanism 5 seems unlikely, since it involves a dissociative rate-determining step. The observation of completely different products in benzene indicates that the donor nature of the solvent is quite important, probably in the stabilization of a coordinatively unsaturated intermediate. The postulated mechanism, involving solvent-assisted CO-insertion, is shown below ( $\text{R} = -\text{CH}_2\text{C}_6\text{H}_4-\text{p-OMe}; \text{S} = \text{CH}_3\text{CN}$ ):



Using a steady-state approximation, the rate law shown in equation (11) can be derived.

$$\frac{-d[13]}{dt} = \frac{k_1 k_2 [13][14][\text{S}]}{k_{-1} + k_2 [14]} \quad (11)$$

Since the solvent concentration is large, and therefore essentially constant, equation (11) simplifies to equation (12).

$$\frac{-d[13]}{dt} = \frac{k_1 k_2 [13][14]}{k_{-1} + k_2 [14]} \quad (12)$$

This equation can be simplified further by dividing both sides by [13] to give

$$\frac{-d[13]}{[13]dt} = \frac{k_1 k_2 [14]}{k_{-1} + k_2 [14]} \quad (13)$$

10. (cont.) and since  $-d[\text{13}]/[\text{13}] = -d\ln[\text{13}]$ , equation (13) can now be written as

$$\frac{-d\ln[\text{13}]}{dt} = \frac{k_1 k_2 [\text{14}]}{k_{-1} + k_2 [\text{14}]} \quad (14)$$

The physical significance of this equation is that  $-d\ln[\text{13}]/dt$  is simply  $k_{\text{obs}}$  and is equal to the slope of the line arising from a plot of  $\ln[\text{13}]$  vs time. A plot of  $1/k_{\text{obs}}$  vs  $1/[\text{14}]$  should be linear with a slope of  $k_{-1}/k_1 k_2$ , as given by equation (15).

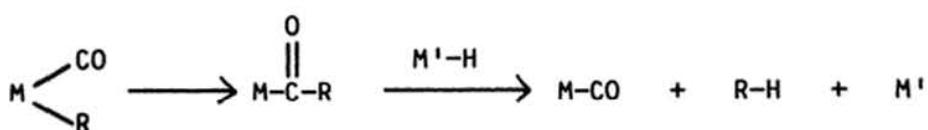
$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}}{k_1 k_2 [\text{14}]} + \frac{1}{k_1} \quad (15)$$

The fact that completely different products are observed when benzene was used as a solvent is a result of the fact that CO loss followed by alkane elimination (Mechanism 3) is faster than alkyl migration in non-stabilizing solvents.

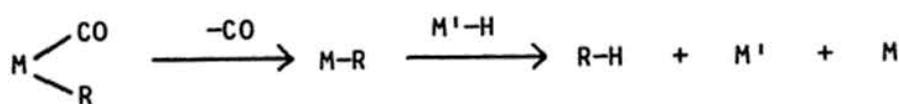
### Reaction 2

The possible reaction pathways that yield alkanes as products are 1), 3), and 4).

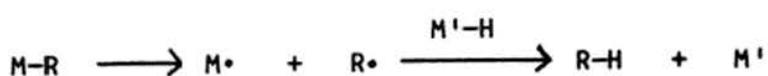
1)



3)

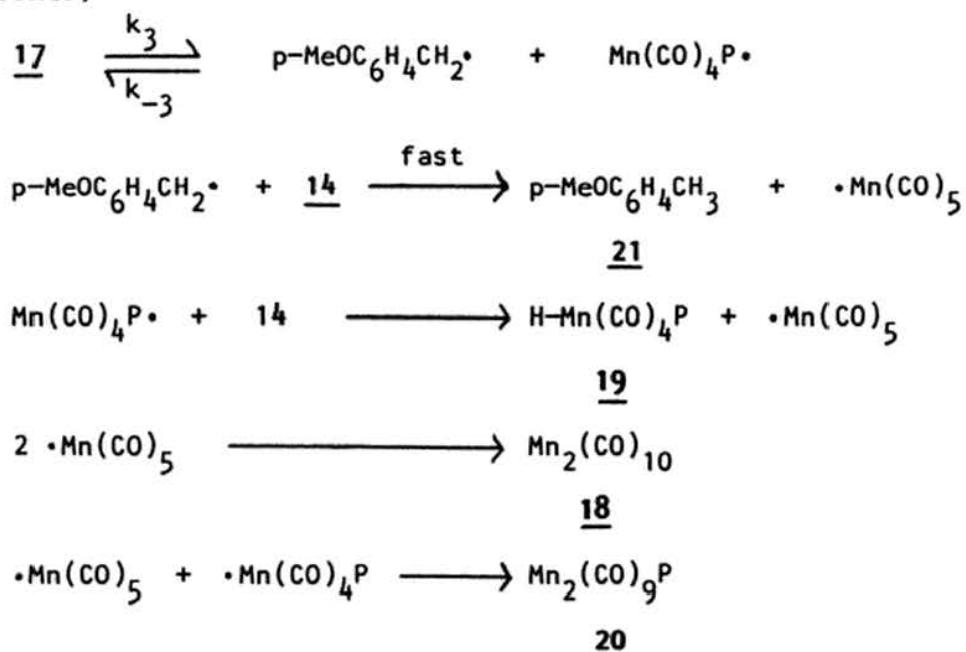


4)



The fact that crossover products are observed for the reaction of 17 with  $\text{Mn}_2(\text{CO})_8(\text{PMePh}_2)_2$  implies the presence of a radical species. This is also supported by observation 2), which suggests that  $\cdot\text{Mn}(\text{CO})_4\text{P}$  is present and reacts rapidly with 14 to give  $\text{H}-\text{Mn}(\text{CO})_4\text{P}$ . The postulated mechanism is shown on the following page:

10. (cont.)

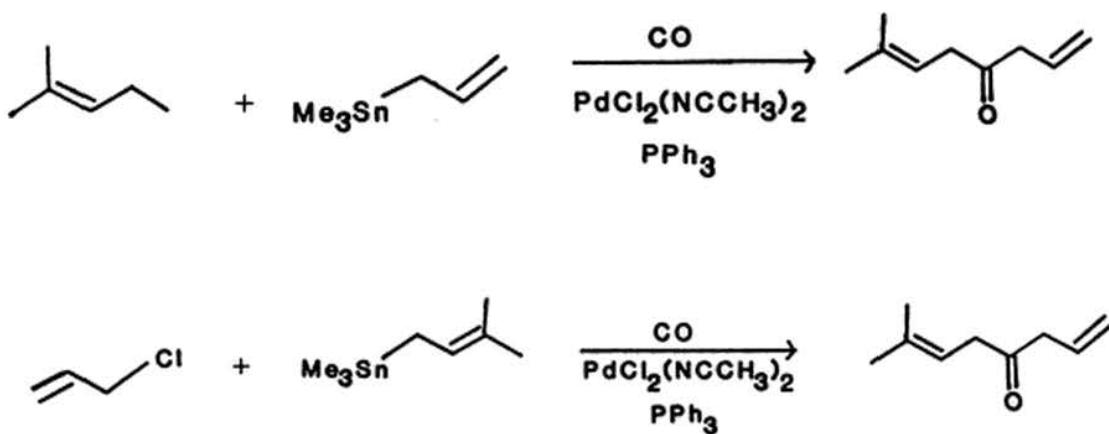


The fact that **17** does not lose CO at the reaction temperature suggests that mechanism 3) is not important for this system. This observation is consistent with a stronger M-CO bond expected for a complex with better backbonding capabilities such as **17**.

Nappa, M.J.; Santi, R.; Halpern, J. *Organomet.* 1985, **4**, 34.

11. The allyl moieties in the following products can be introduced into the molecule either from the allyl chloride or from the allyl tin reagent; however, since the allyl tin reagents are made via a Grignard reaction, it is typically easier to have more of the functionality on the allyl chloride.

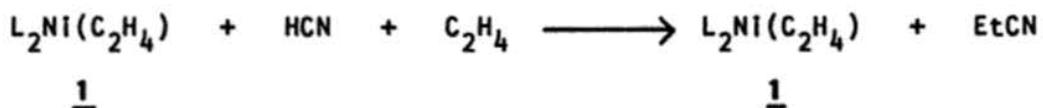
a) This compound can be made from either route.



## 11: CATALYTIC REACTIONS

### QUESTIONS

1. The following catalytic reaction is observed ( $L = P(0\text{-}o\text{-tolyl})_3$ ):



#### OBSERVATIONS

1)  $\Delta H^\ddagger = 8.9 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -34 \text{ eu}$

2) During the reaction, intermediate isomeric species 2a-c can be detected by phosphorous, proton, and carbon NMR spectroscopies. The observed data for the reaction mixture are given below.

#### $^{31}\text{P}$ NMR ( $\delta$ , ppm):

116.9  
117.7  
118.1  
129.8 (free  $P(0\text{-}o\text{-tolyl})_3$ )

#### $^1\text{H}$ NMR ( $\delta$ , ppm):

0.61 (m)  
2.03 (s)  
2.09 (br, s)

#### $^{13}\text{C}$ NMR using $^{13}\text{C}$ -labeled $\text{C}_2\text{H}_4$ ( $\delta$ , ppm):

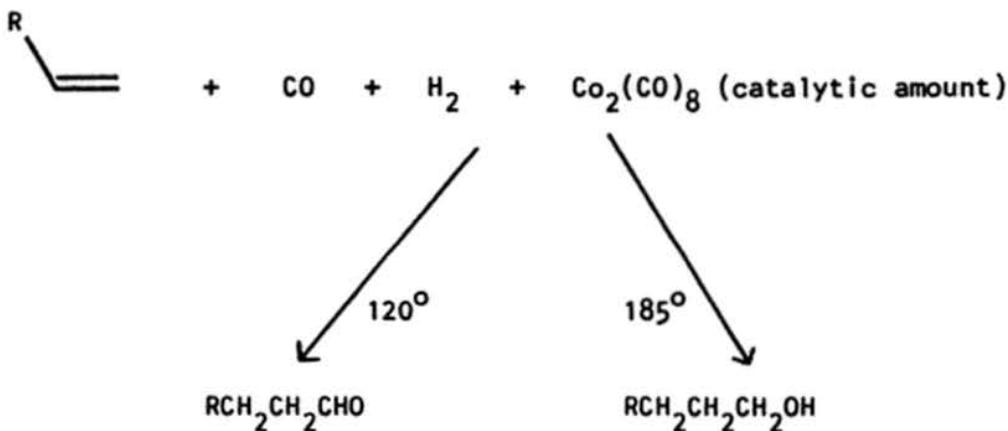
11.7  
14.1  
58.9

3) The rate law is of the form  $d[\text{EtCN}]/dt = k[2][L]$ .

a) Identify 2a-c.

b) Propose a stepwise mechanism for the reaction and verify that your mechanism agrees with the observed rate law.

2. Propose a mechanism(s) for the following reactions.



3. The complex  $(\eta^5-C_5H_5)Ni(\eta^3-C_5H_7)$ , 4, catalyzes the conversion of ethylene to 1-butene. Propose a catalytic cycle for the conversion of ethylene to 1-butene which is consistent with the following observations:

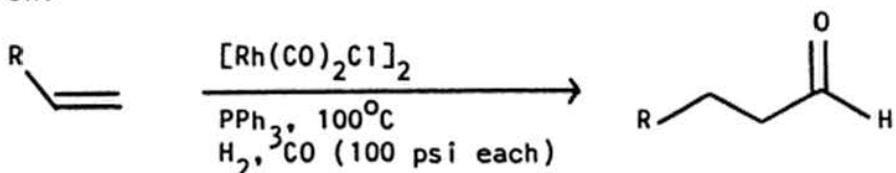
**OBSERVATIONS**

- 1) Introduction of a solution of 4 into a gas chromatography column at  $150^\circ C$  indicates the presence of both cyclopentadiene and cyclopentadiene dimer.
- 2) If the reaction is carried out in the presence of one equivalent of triphenylphosphine, 1-butene still accounts for most of the product; however, the percentage conversion of ethylene to 1-butene is greatly decreased, even if the reaction is allowed to proceed for longer times. Complex 5,  $CpNi(PPh_3)(n-C_4H_9)$ , is isolated from this reaction mixture.

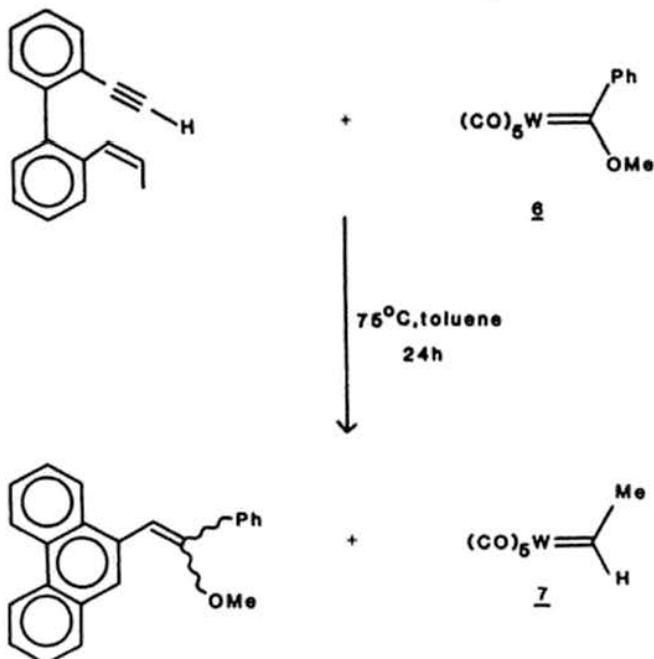
**HINT**

Consider a Ni-H species as an intermediate.

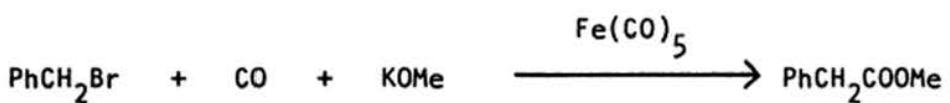
4. Propose a mechanism for the following conversion. Be sure your mechanism accounts for an induction period which is observed for this reaction.



5. Propose a mechanism for the following metathesis reaction.

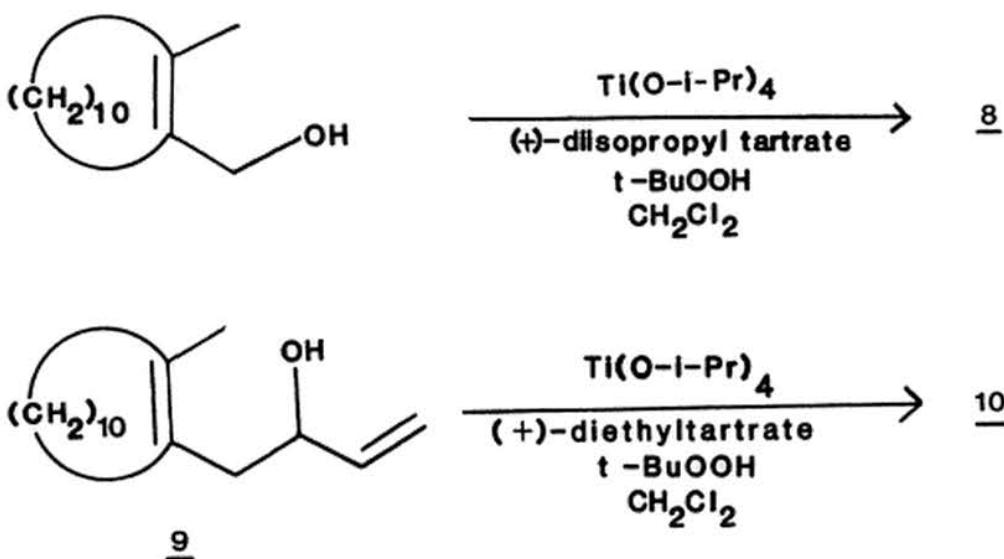


6. Benzyl bromide can be converted to methylphenylacetate in one pot, as shown below.



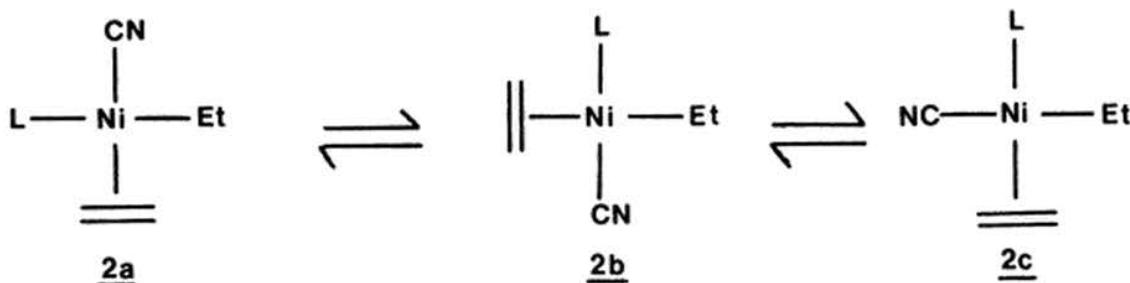
Propose a mechanism for this reaction which is catalytic in  $\text{Fe(CO)}_5$  and stoichiometric in the other reagents.

7. Propose structures for compounds 8 and 10.



## ANSWERS

1. a) Intermediates  $2a-c$  are shown below.

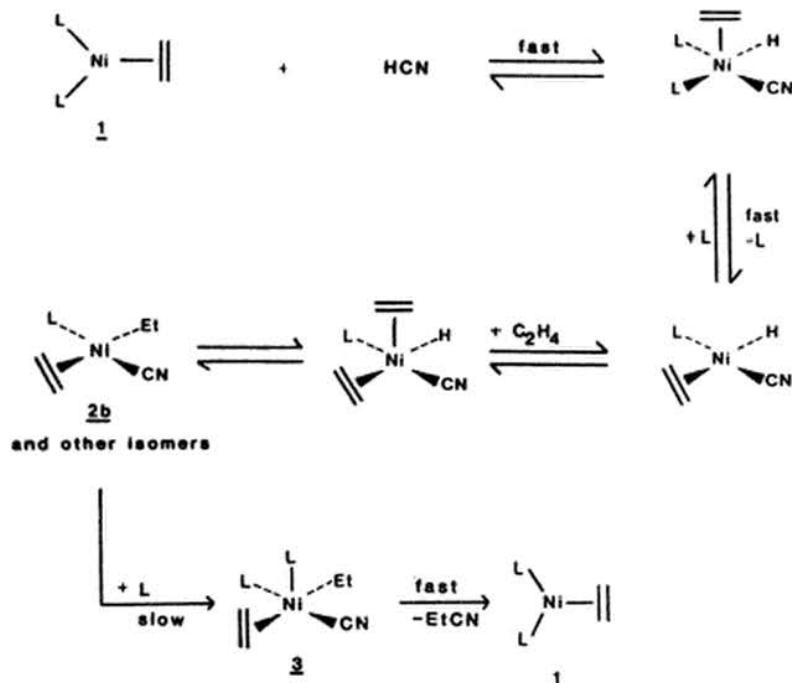


Complex  $2a$  is the predominant isomer, but not necessarily the most reactive.

b) In the scheme below,  $L = P(0\text{-}o\text{-toly1})_3$ . Three pieces of information suggest that the formation of  $3$  from  $2$  is the slow step in the reaction:

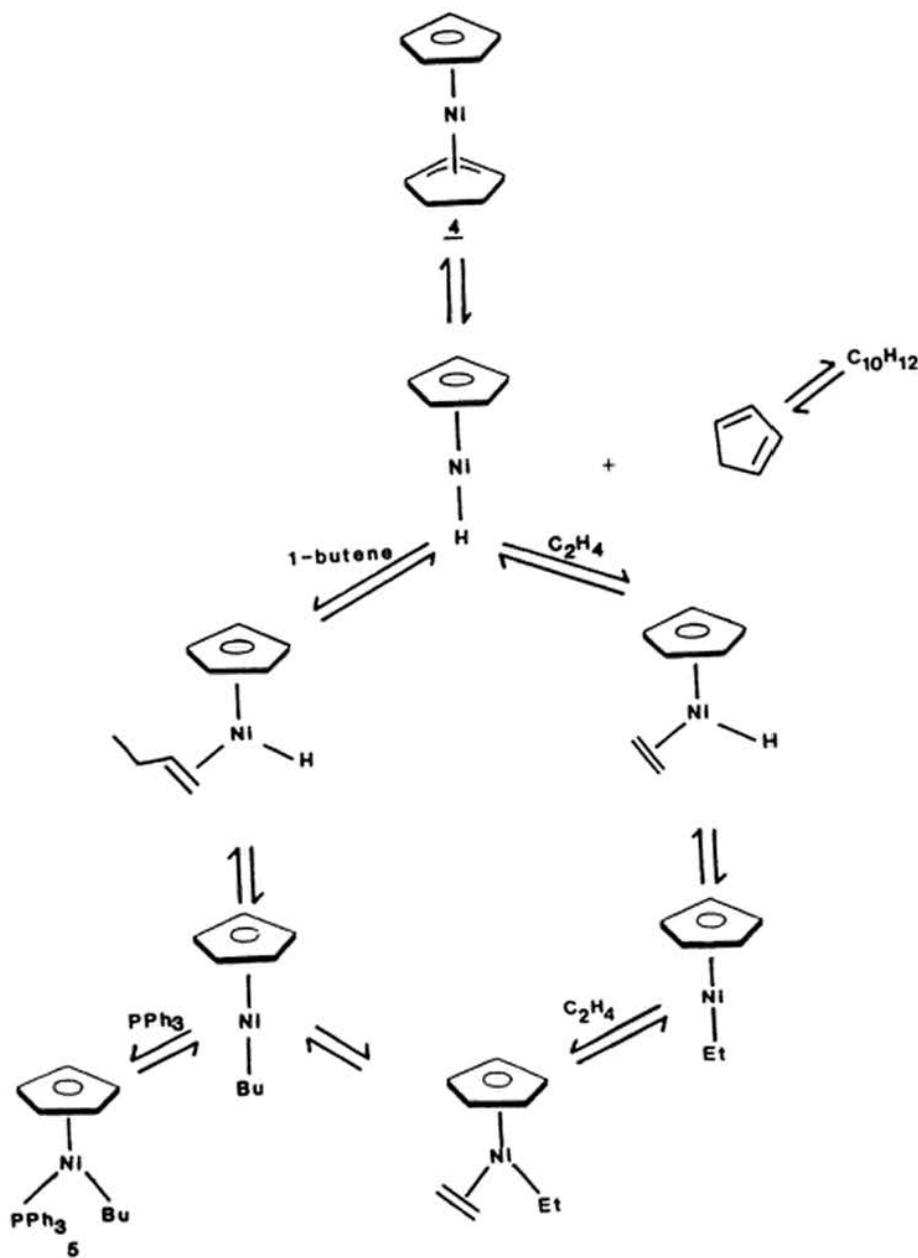
- 1) The observation of the stable intermediates  $2a-c$ ,
- 2) the dependence of the rate on both  $[2]$  and  $L$ , and
- 3) the large negative entropy of activation, which supports an associative transition state.

The stability of the nickel complex,  $L_2Ni(C_2H_4)$ ,  $1$ , produced upon reductive-elimination of  $Et\text{-}CN$  is certainly a driving force for reductive-elimination to occur from the 5-coordinate nickel species  $3$ , as opposed to reductive-elimination occurring directly from the 4-coordinate species  $2$ .



McKinney, R.J.; Roe, D.C. *J. Am. Chem. Soc.* 1985, 107, 261.

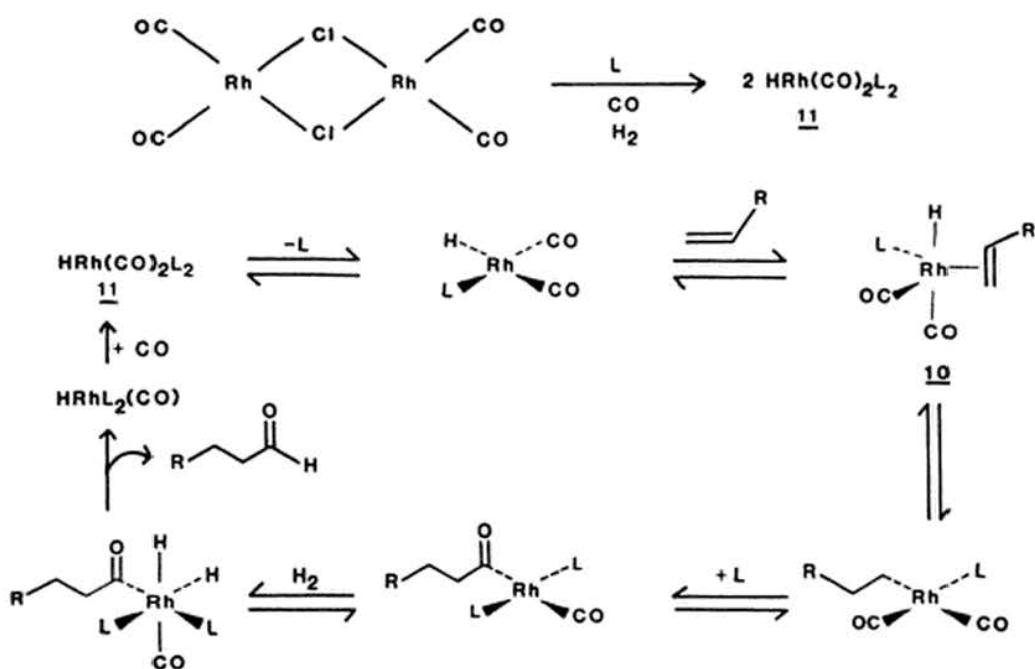
3. The proposed mechanism is shown below:



An initial beta-hydrogen abstraction from the  $\eta^3\text{-C}_5\text{H}_7$  ring gives free cyclopentadiene (which rapidly dimerizes when heated) and a  $\text{CpNi-H}$  species that adds a molecule of ethylene. Olefin insertion to give  $\text{CpNi-Et}$  followed by addition of another molecule of ethylene and another insertion reaction gives the butyl complex,  $\text{CpNi-Bu}$ . Beta-hydrogen abstraction, followed by ligand dissociation gives the observed 1-butene and regenerates the catalyst  $\text{CpNi-H}$ . Addition of  $\text{PPh}_3$  to the reaction decreases the amount of catalyst in solution by forming complex 5.

McClure, J.D.; Barnett, K.W. J. Organomet. Chem. 1974, 80, 385.

4. In the scheme below, L =  $\text{PPh}_3$ .

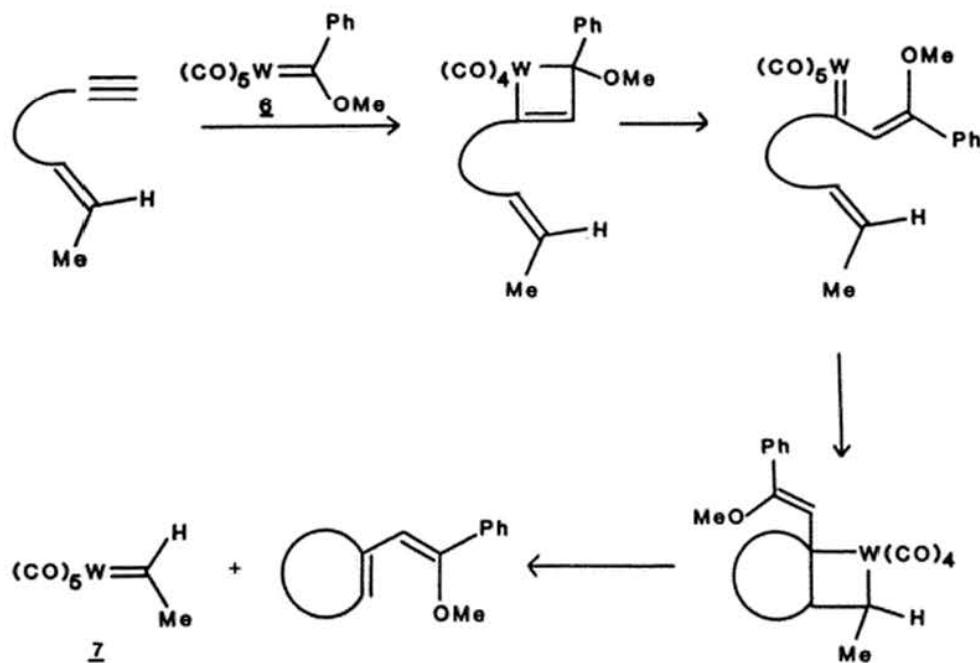


The active catalyst is complex 11. The induction period is the time necessary to form this complex.

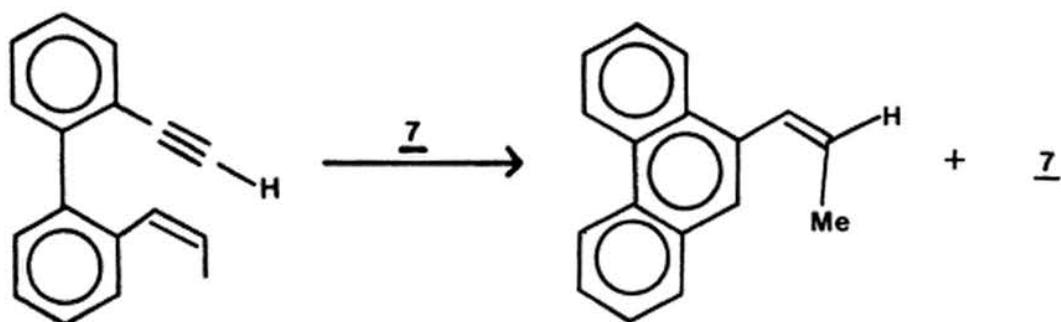
Pruett, R.L. Adv. Organomet. Chem. 1979, 17, 1.

Evans, D.; Osborn, J.A.; Wilkinson, G. J. Chem. Soc. A 1968, 3133.

5. This is not a simple olefin metathesis reaction, since a third ring has been formed. Schematically, the proposed mechanism is:

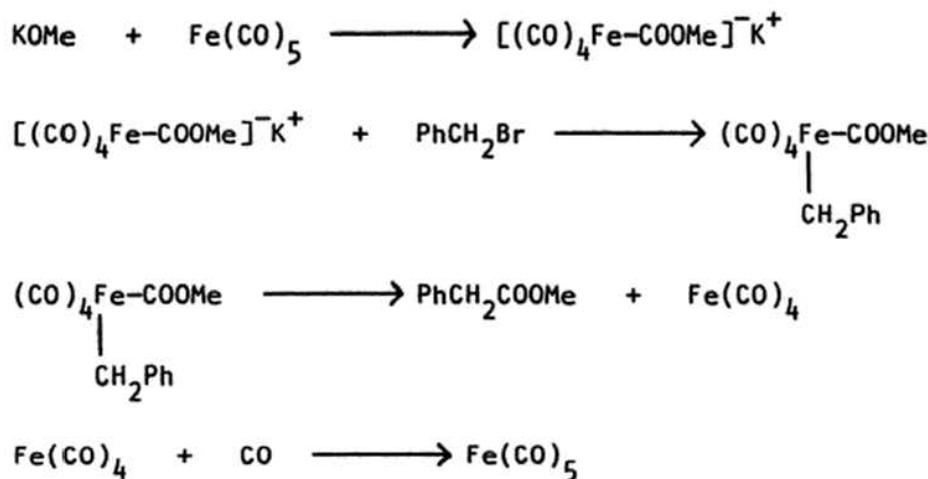


5. (cont.) Since a carbene is one of the products, this type of reaction can be performed catalytically using the heteroatomcarbene, 6, as an initiator. The propagation step for the catalytic reaction is:



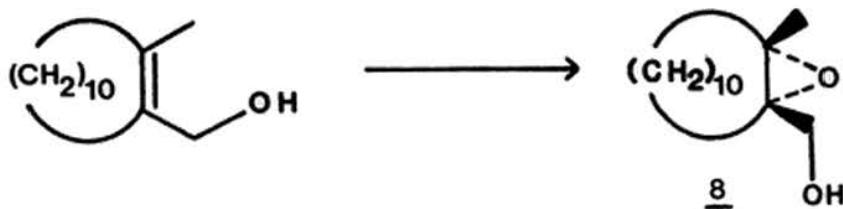
Katz, T.J.; Sivavec, T.M. J. Am. Chem. Soc. 1985, 107, 737.

#### **6. The proposed mechanism is:**



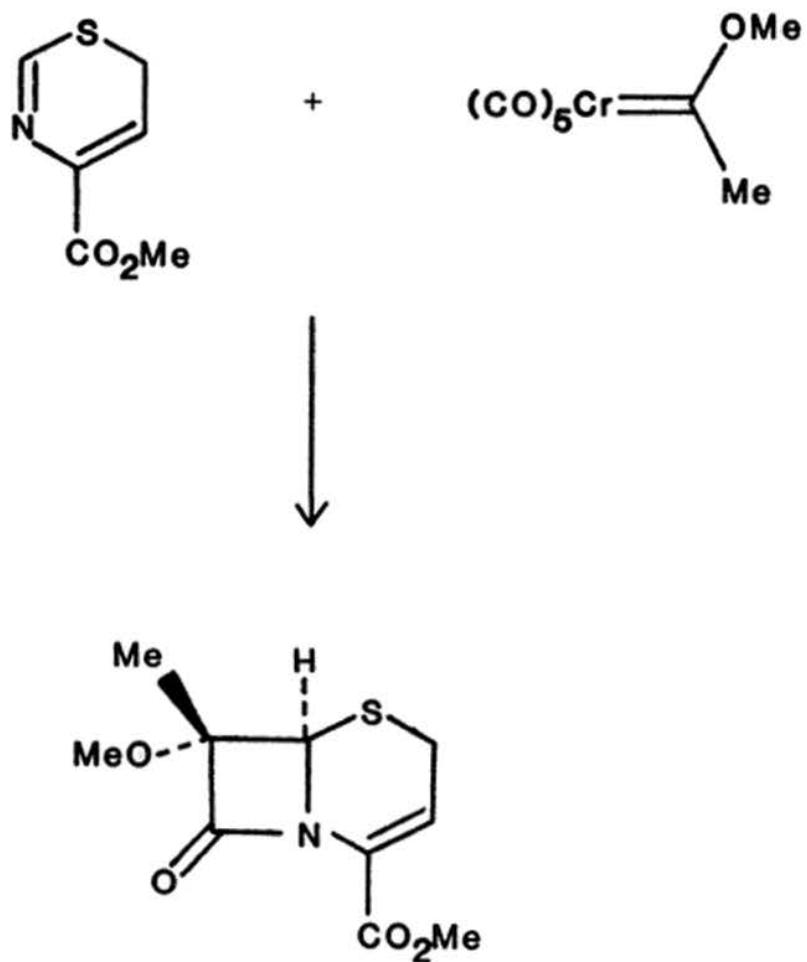
Tustin, G.C.; Hembre, R.T. *J. Org. Chem.* 1984, 49, 1761.

7. The first reaction is a variation on a scheme developed by K.B. Sharpless for the conversion of allyl alcohols to epoxy-alcohols. In this particular example, the (-)-epoxy-alcohol (8) is obtained in 94% enantiomeric excess. The catalyst contains the optically-active tartrate ligand and is the source of the stereospecificity of the reaction.



# 12

## Organometallic Complexes in Organic Synthesis

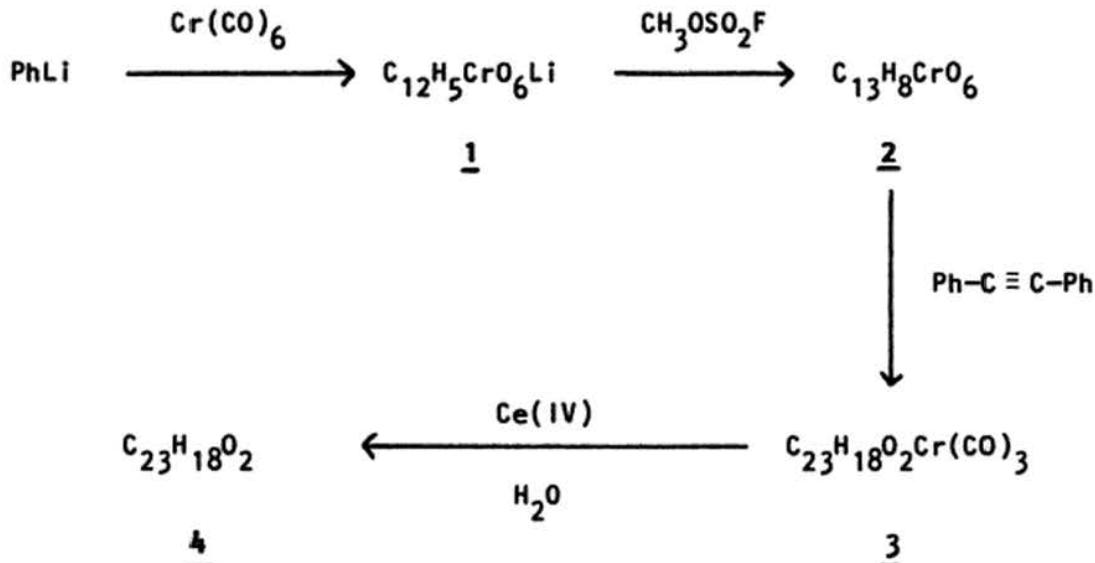


## 12: ORGANOMETALLIC COMPLEXES IN ORGANIC SYNTHESIS

### QUESTIONS

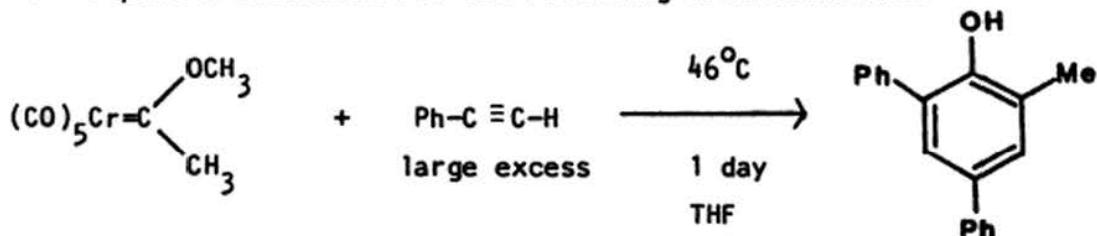
Issue number 24 of Tetrahedron for 1985 contains a large number of papers dealing with applications of transition metal organometallic chemistry to organic synthesis.

1. Provide a structure for compounds 1, 2, 3, and 4.

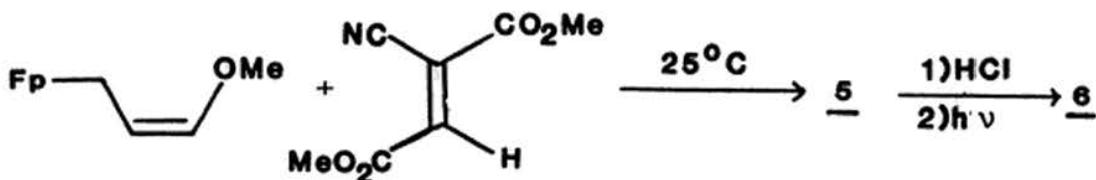


Compound 4 is soluble in NaOH. Its NMR spectrum consists of a singlet at 3.2 ppm and aromatic resonances, and its IR spectrum has a peak at  $3550\text{ cm}^{-1}$ .

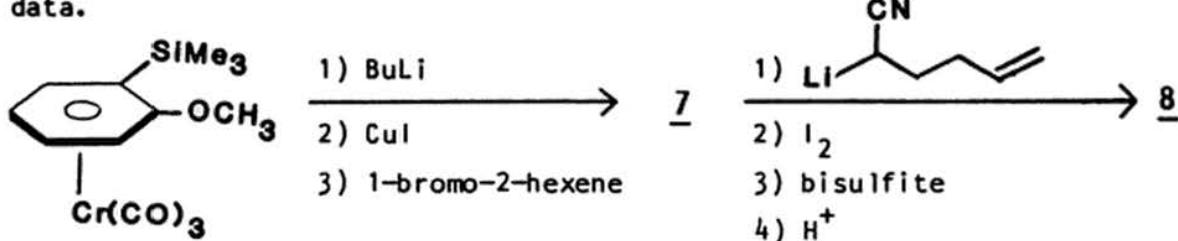
2. Propose a mechanism for the following transformation:



3. Predict the products and propose a mechanism for the following reaction.



4. Propose structures for compounds 7 and 8 and assign all spectral data.



Spectral data for 7

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )

0.17 (s, 9H)  
0.71 (t,  $J=7$  Hz, 3 H)  
0.92-1.44 (m, 2 H)  
1.64-1.98 (m, 2 H)  
2.99 (br d,  $J=4.7$  Hz, 2 H)  
3.53 (s, 3 H)  
4.65 (dd,  $J=6.2, 6.2$  Hz, 1 H)  
5.08-5.26 (m, 4 H)

IR (neat,  $\text{cm}^{-1}$ )

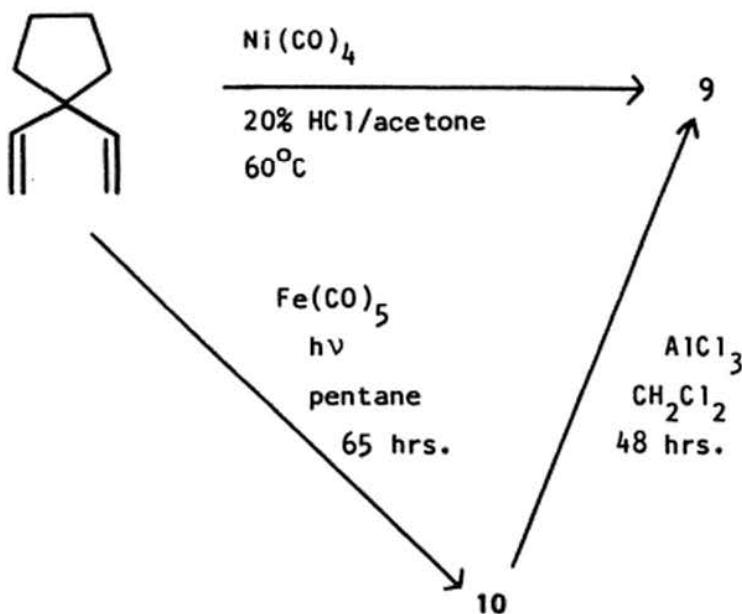
1960 (s), 1886 (s)

Spectral data for 8

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )

0.85 (t, 3 H)  
1.12-1.56 (m, 2 H)  
1.71-2.24 (m, 6 H)  
3.20 (dd,  $J=14.4, 3.8$  Hz, 1 H)  
3.48 (dd,  $J=14.4, 4.3$  Hz, 1 H)  
3.80 (s, 3 H)  
4.03 (dd,  $J=8.6, 5.6$  Hz, 1 H)  
4.96-6.02 (m, 5 H)  
6.74-7.36 (m, 3 H)

5. Give structures for compounds 9 and 10 and assign all spectral data.



## 5. (cont.)

## Spectral data for 9

IR (cm<sup>-1</sup>)

1740

<sup>1</sup>H NMR (δ, CC<sub>14</sub>)0.93 (d, J=7 Hz, 3 H)  
1.23-2.30 (m, 13 H)Mass Spectrum (m/e)

152 (38%)

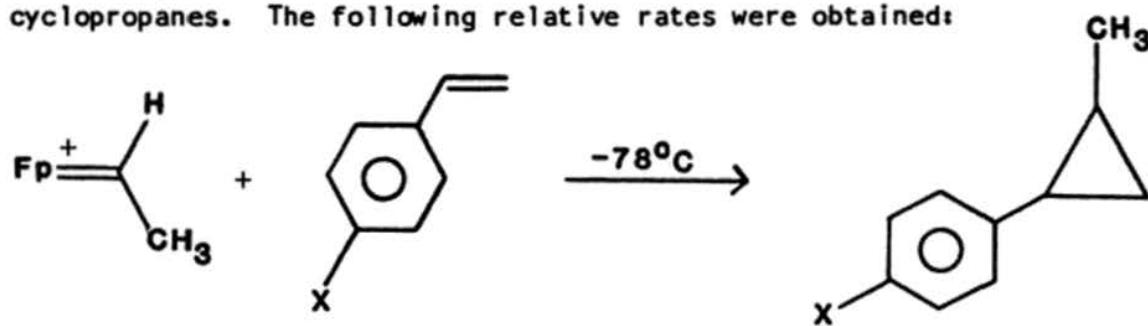
## Spectral data for 10

IR (cm<sup>-1</sup>)

2035, 1970-1950

<sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>)0.33(dd, J=12, 2 Hz, 2 H)  
0.50-0.70 (m, 8 H)  
1.07 (dd, J=7, 2 Hz, 2 H)  
2.68 (dd, J=12, 7 Hz, 2H)Mass Spectrum (m/e)262 (7%), 234 (17%),  
206 (23%), 178 (100%)

6. As shown below, the reaction of the cationic carbene complex  $\text{Fp}=\text{C}(\text{H})\text{CH}_3^+$  with para-substituted styrenes generates aryl methyl cyclopropanes. The following relative rates were obtained:

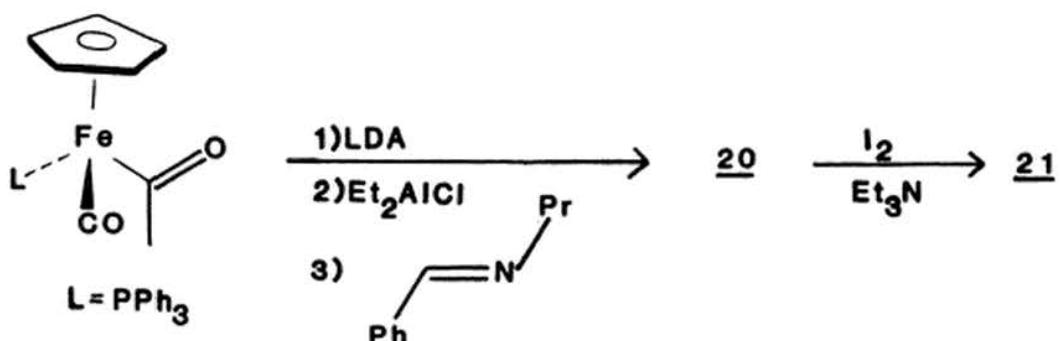


cis and trans

X	$k_{\text{rel}}$	$\sigma_p^+$
OMe	74	-0.78
Me	5.9	-0.31
H	1.0	0.00
F	0.9	-0.07
Cl	0.3	0.11

a) Using a Hammett plot of the equation,  $\log k_{\text{rel}} = \sigma_p^+ \rho$ , find the rho ( $\rho$ ) value for this reaction.

10. Propose structures for compounds 20 and 21.



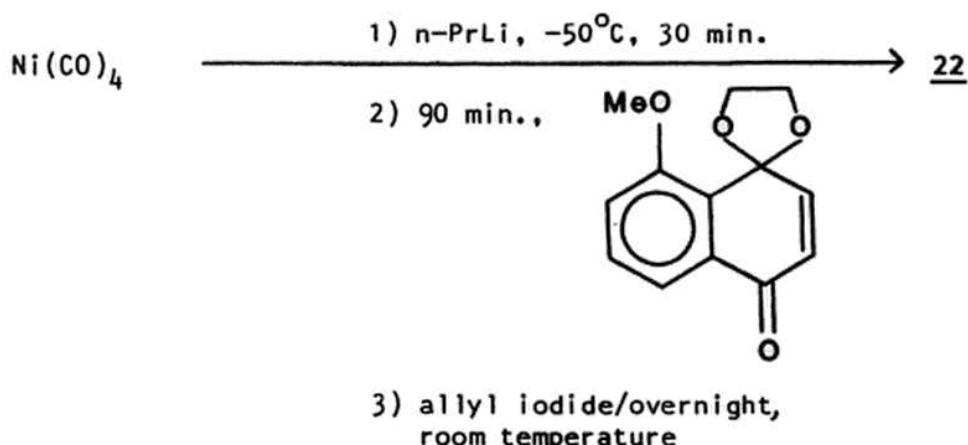
HINT

Compound 21 is related to compound 19 of the previous problem.

Spectral data for 20

IR ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR ( $\delta$ , $\text{CDCl}_3$ )
1918	0.79 (t, $J=7$ Hz, 3 H)
1591	1.36 (m, 2 H)
	2.16 (m, 2 H)
	2.84 (dd, $J=18, 2$ Hz, 1 H)
	3.26 (dd, $J=18, 10$ Hz, 1 H)
	3.47 (dd, $J=10, 2$ Hz, 1 H)
	4.41 (d, $J=1$ Hz, 5 H)
	7.07-7.73 (m, 15 H)

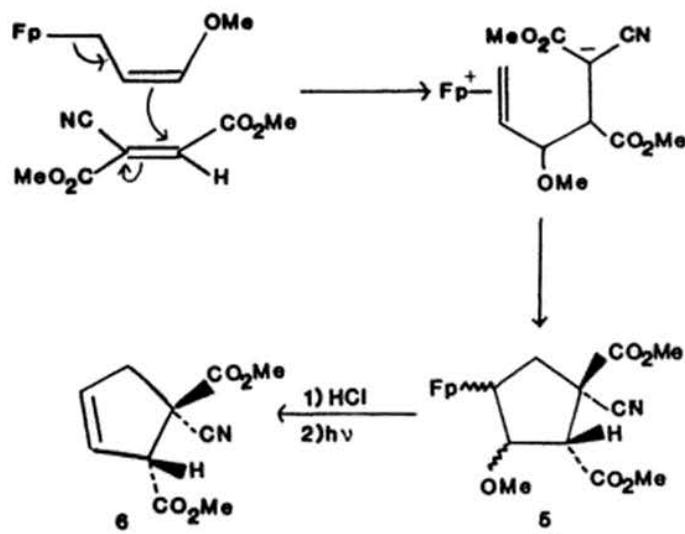
11. Propose a structure for compound 22 and a mechanism for its formation.



**11. (cont.)****Spectral data for 22**

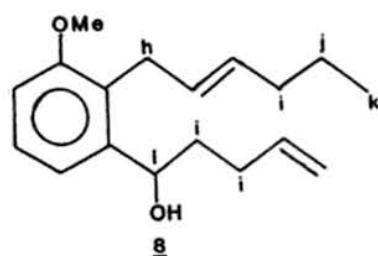
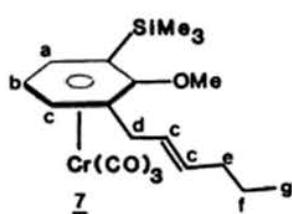
<u>IR (CHCl<sub>3</sub>, cm<sup>-1</sup>)</u>	<u><sup>1</sup>H NMR ( δ, CDCl<sub>3</sub>)</u>
3080 (w)	0.90 (t, J=7.0 Hz, 3 H)
3000 (m)	1.4–1.7 (m, 2 H)
2970 (s)	2.2–3.2 (m, 5 H)
2840 (w)	3.65 (d, J=6.5 Hz, 1 H)
1710 (s)	3.88 (s, 3 H)
1690 (s)	4.0–4.5 (m, 4 H)
1640 (w)	4.9–5.2 (m, 2 H)
1590 (s)	5.6–6.0 (m, 1 H)
1480 (s)	7.13 (dd, J=8.0, 1.5 Hz, 1 H)
1270 (s)	7.40 (t, J=7.0 Hz, 1 H) 7.70 (dd, J=7.0, 2.0 Hz, 1 H)

3. The proposed mechanism is shown below:



Baker, R.; Keen, R.B.; Morris, M.D.; Turner, R.W. J. Chem. Soc., Chem. Comm. 1984, 987.

4. Both steps involve a nucleophilic attack on the coordinated benzene ring. I<sub>2</sub> serves to oxidatively cleave the product from the metal. Complexes 7 and 8 are:



The NMR data are assigned as follows:

Spectral data for 7

<sup>1</sup> H NMR ( $\delta$ , CDCl <sub>3</sub> )
0.17 (s, 9H, SiMe <sub>3</sub> )
0.71 (t, J=7 Hz, 3 H, H <sub>g</sub> )
0.92–1.44 (m, 2 H, H <sub>f</sub> )
1.64–1.98 (m, 2 H, H <sub>e</sub> )
2.99 (br d, J=4.7 Hz, 2 H, H <sub>d</sub> )
3.53 (s, 3 H, OMe)
4.65 (dd, J=6.2, 6.2 Hz, 1 H, H <sub>b</sub> )
5.08–5.26 (m, 4 H, H <sub>a</sub> , H <sub>c</sub> )

Spectral data for 8

<sup>1</sup> H NMR ( $\delta$ , CDCl <sub>3</sub> )
0.85 (t, 3 H, H <sub>k</sub> )
1.12–1.56 (m, 2 H, H <sub>j</sub> )
1.71–2.24 (m, 6 H, H <sub>i</sub> )
3.20 (dd, J=14.4, 3.8 Hz, 1 H, H <sub>h</sub> )
3.48 (dd, J=14.4, 4.3 Hz, 1 H, H <sub>h</sub> )
3.80 (s, 3 H, OMe)
4.03 (dd, J=8.6, 5.6 Hz, 1 H, H <sub>1</sub> )
4.96–6.02 (m, 5 H, vinyls)
6.74–7.36 (m, 3 H, aromatics)

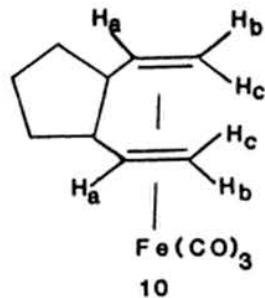
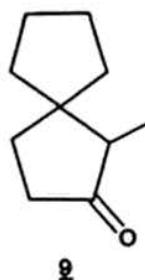
## 4. (cont.)

IR for 7 (neat, cm<sup>-1</sup>)

1960 (s), 1886 (s): Terminal metal carbonyl stretches.

Semmelhack, M.F.; Zask, A. J. Am. Chem. Soc. 1983, 105, 2034.

## 5. Complexes 9 and 10 are shown below:



The spectral data are assigned as follows:

Spectral data for 9IR (cm<sup>-1</sup>)

1740 (C=O of 5-membered ring)

<sup>1</sup>H NMR ( $\delta$ , CCl<sub>4</sub>)

0.93 (d, J=7 Hz, 3 H, Me)

1.23–2.30 (m, 13 H, methylenes)

Mass Spectrum (m/e)

152 (38%), M<sup>+</sup>

Spectral data for 10IR (cm<sup>-1</sup>)

2035, 1970–1950 (terminal M–C≡O's)

<sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>)

0.33 (dd, J=12, 2 Hz, 2 H, H<sub>c</sub>)

0.50–0.70 (m, 8 H, methylenes)

1.07 (dd, J=7, 2 Hz, 2 H, H<sub>b</sub>)

2.68 (dd, J=12, 7 Hz, 2H, H<sub>a</sub>)

Mass Spectrum (m/e)

262 (7%), M<sup>+</sup>

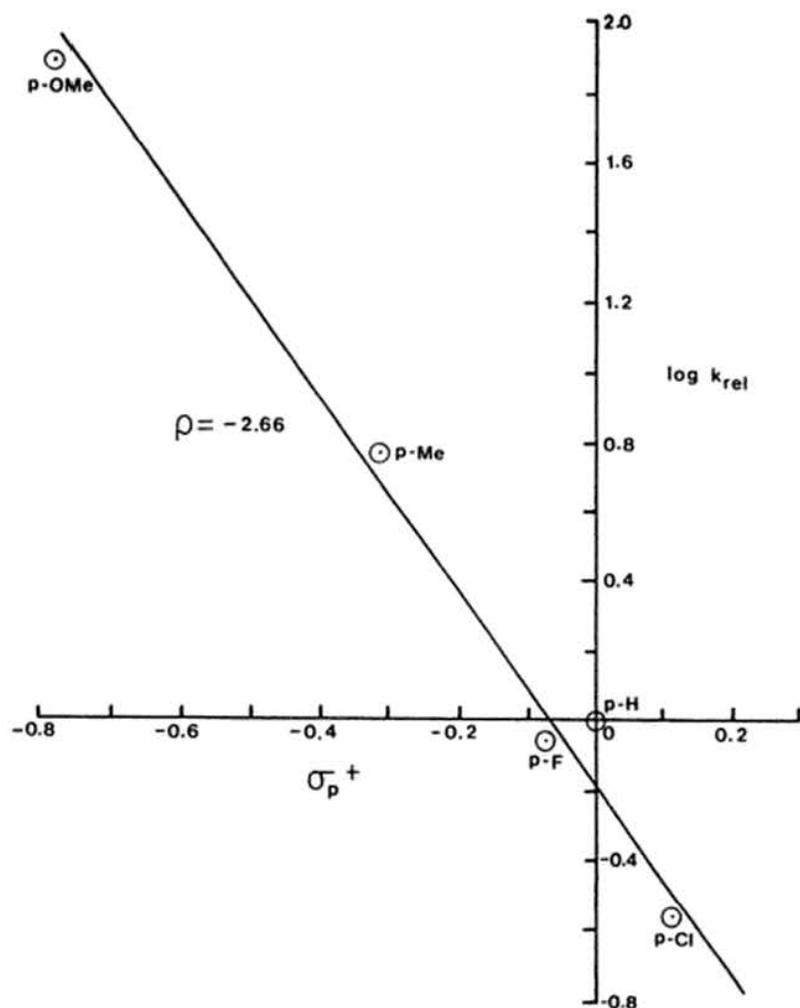
234 (17%), M<sup>+</sup>–CO

206 (23%), M<sup>+</sup>–2 CO

178 (100%), M<sup>+</sup>–3 CO

Eilbracht, P.; Acker, M.; Totzauer, W. Chem. Ber. 1983, 116, 238.

6. a) The Hammett plot is shown below:

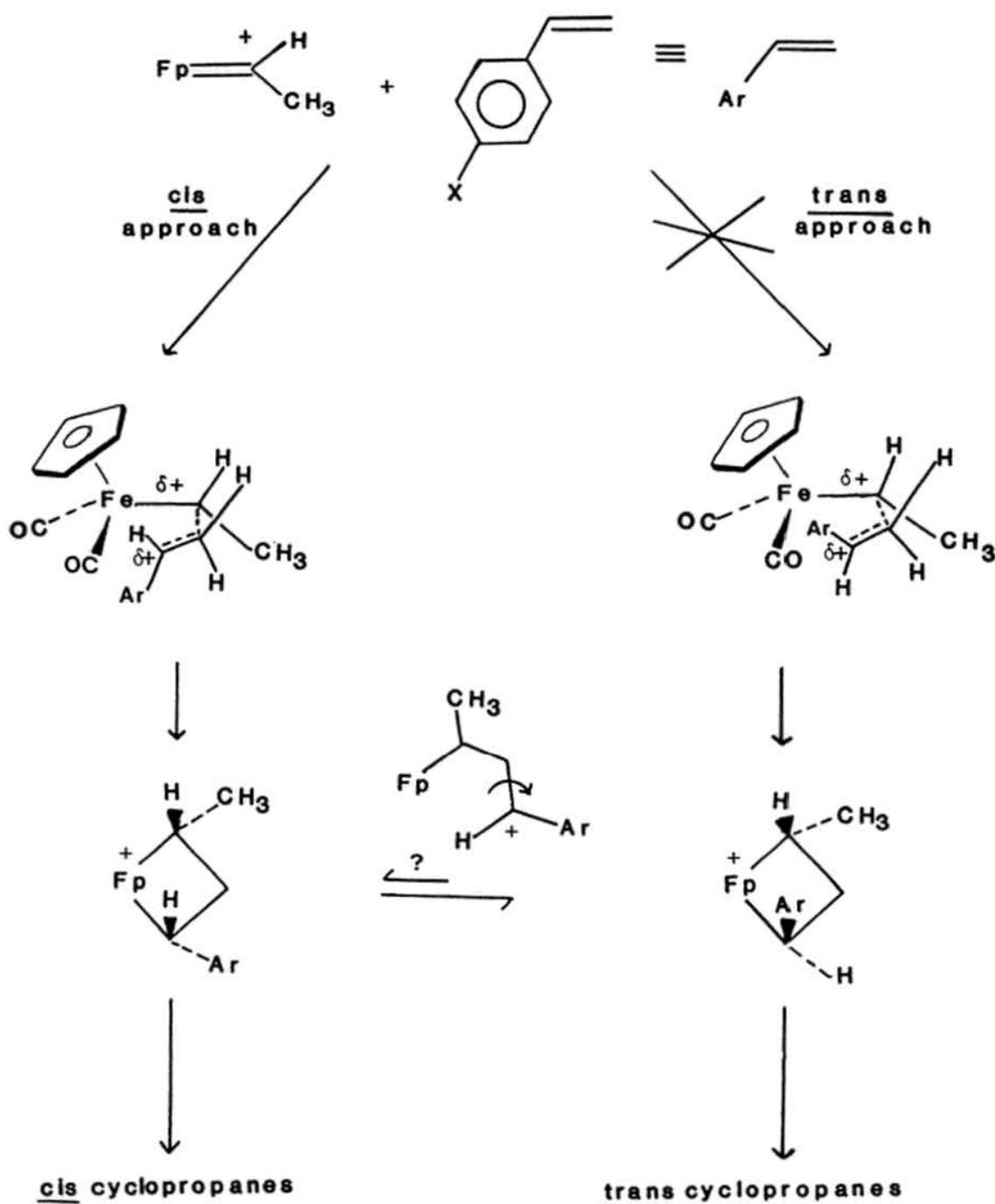


Sigma plus substituent constants generally give a better correlation than sigma constants for reactions in which the substituent can enter into direct resonance interaction with an electron-deficient reaction site in the transition state. The reaction constant rho is the slope of the line and is equal to -2.66 for this reaction.

b) The rho value for a reaction gives a measure of the amount of charge development at the carbon alpha to the aromatic ring in the transition state. A negative rho value indicates that the reaction is accelerated by electron-donating substituents and is supportive of a highly polarized cationic transition state, but not one with sufficient charge development at the alpha carbon such that it could be considered a free carbonium ion. (For comparison, consider the rho value of -4.48 obtained for the solvolysis of cumyl chloride ( $C_6H_5CMe_2Cl$ ), in which the transition state closely resembles a free carbonium ion.) The linearity of these points indicates that no change in mechanism is occurring with a change in the electron-donating ability of the substituent.

c) The proposed mechanism is shown on the following page:

## 6. (cont.)

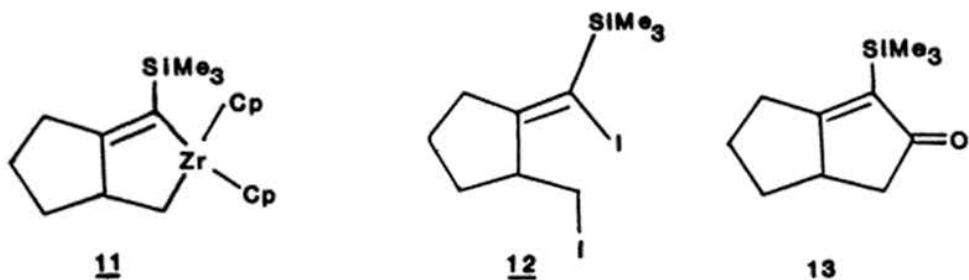


Brookhart, M.; Kegley, S.E.; Husk, G.R. *Organomet.* 1984, 3, 650.

Kegley, S., Ph.D. Thesis, University of North Carolina, 1982.

For more information on Hammett relationships, see March, J. "Advanced Organic Chemistry, Reactions, Mechanisms, and Structure", 3rd ed., John Wiley and Sons (New York, 1985), p. 242.

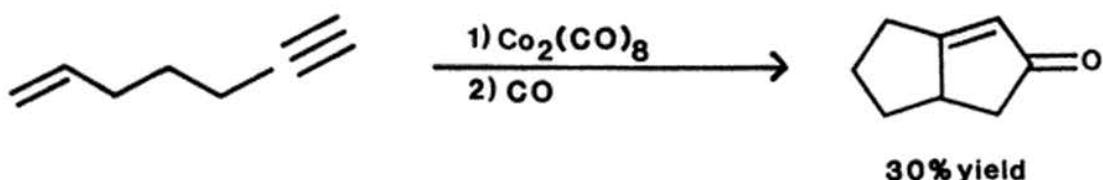
7. The structures of 11, 12, and 13 are shown below:



Negishi, E.; Holmes, S.J.; Tour, J.M.; Miller, J.A. J. Am. Chem. Soc. 1985, 107, 2568.

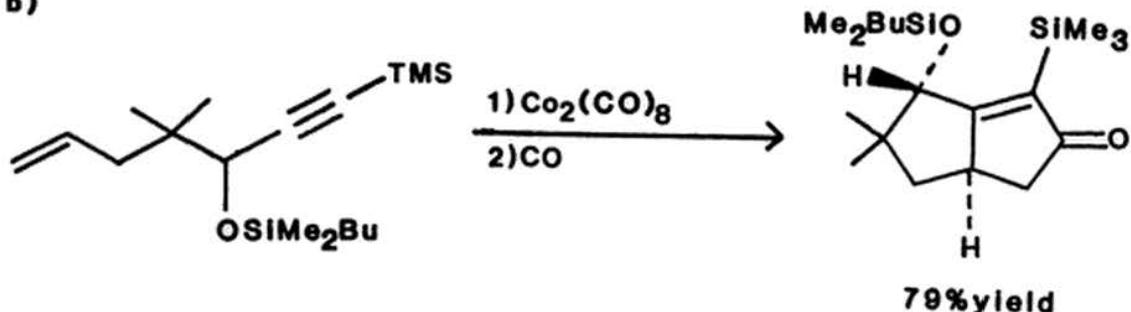
8. At room temperature, the cobalt-acetylene complex is formed. Upon heating, this complex reacts with the olefin and CO to give the cyclopentenone derivative.

a)



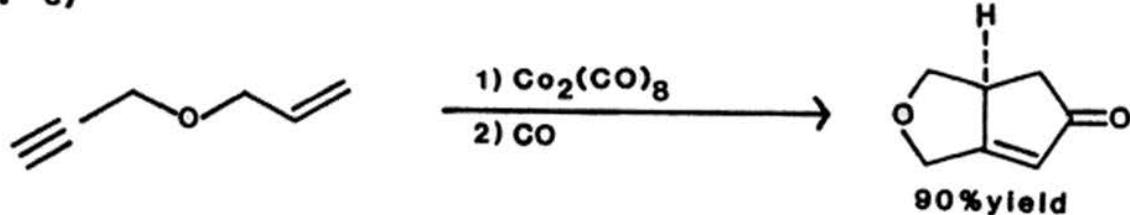
Schore, N.E.; Croudace, M.C. J. Org. Chem. 1981, 46, 5436.

b)



Exon, C.; Magnus, P. J. Am. Chem. Soc. 1983, 105, 2477.

8. c)



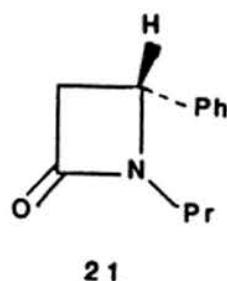
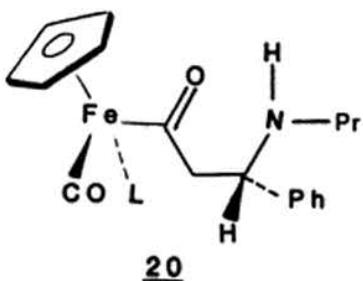
Billington, D.C.; Willison, D. Tetrahedron Lett. 1984, 25, 4041.

*image  
not  
available*

9. (cont.) This reaction is significant because it readily affords  $\beta$ -lactams, which are structurally related to penicillin and penicillin derivatives.

McGuire, M.A.; Hegedus, L.S. J. Am. Chem. Soc. 1982, 104, 5538.

10. Structures for 20 and 21 are shown below:



The spectral data for 20 are assigned as follows:

Spectral data for 20

IR (cm<sup>-1</sup>)

1918 (Fe-C≡O)

1591 (C=O)

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>)

0.79 (t, J=7 Hz, 3 H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)

1.36 (m, 2 H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)

2.16 (m, 2 H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)

2.84 (dd, J=18, 2 Hz, 1 H, -COCHH'CHPh-)

3.26 (dd, J=18, 10 Hz, 1 H, -COCHH'CHPh-)

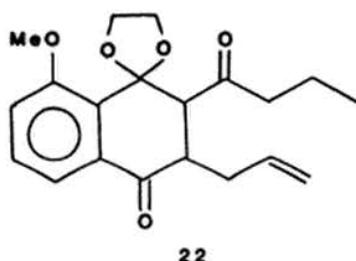
3.47 (dd, J=10, 2 Hz, 1 H, -COCHH'CHPh-)

4.41 (d, J=1 Hz, 5 H, Cp)

7.07-7.73 (m, 15 H, PPh<sub>3</sub>)

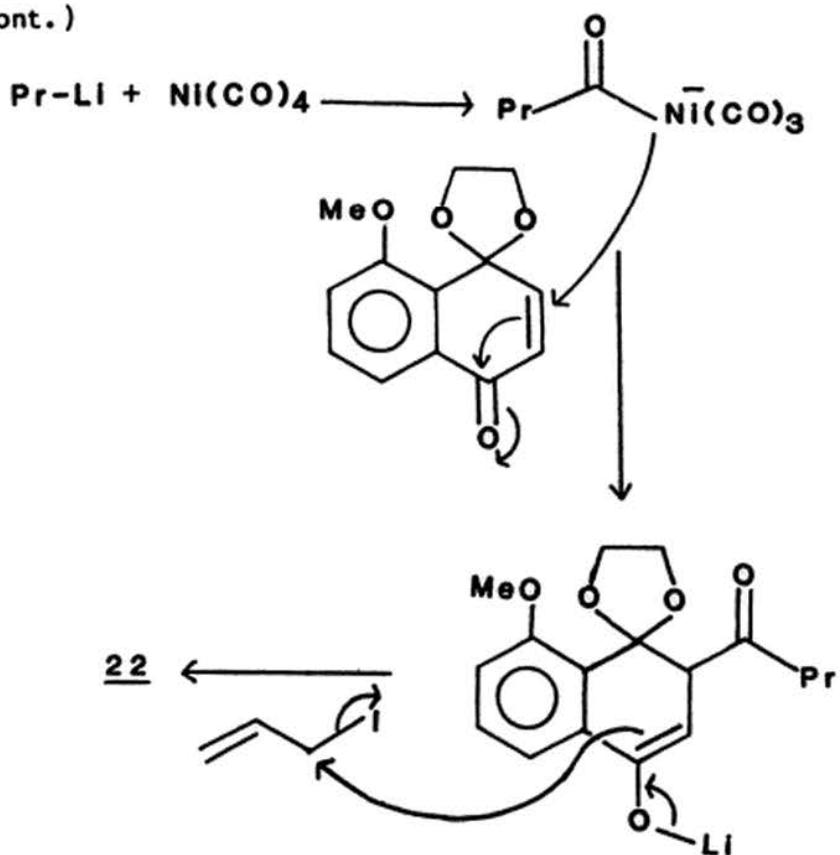
Liebeskind, L.S.; Welker, M.E.; Goedken, V. J. Am. Chem. Soc. 1984, 106, 441.

11. Compound 22 is shown below:



The proposed mechanism for the formation of 22 is shown on the following page.

11. (cont.)



Semmelhack, M.F.; Keller, L.; Sato, T.; Spiess, E. J. Org. Chem.  
1982, 47, 4382.

13

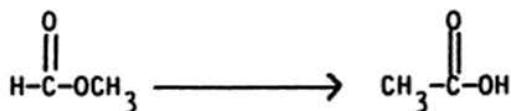
## Additional Problems



## 13: ADDITIONAL PROBLEMS

## QUESTIONS

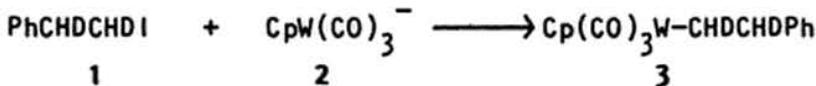
1. Propose a mechanism for the catalytic reaction shown below, which is consistent with the following observations.



## OBSERVATIONS

- 1) The catalyst is  $[\text{Ir}(\text{COD})\text{Cl}]_2$ .
- 2) A carboxylic acid must be used as the solvent.
- 3) Methyl iodide must be added to the reaction or be generated by the reaction before the "isomerization" will occur.

2. A 50/50 mixture of threo- and erythro-PhCHDCHDI was allowed to react with  $\text{CpW}(\text{CO})_3^-$  to give two isomeric compounds, 3a and 3b.



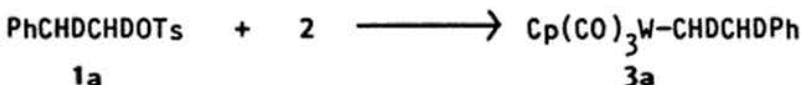
$^1\text{H}\{^2\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) of 1

3.08 (2 d,  $J=9.4, 6.0$  Hz)  
 3.32 (2 d,  $J=9.4, 6.0$  Hz)  
 plus phenyl resonances

$^1\text{H}\{^2\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) of 3

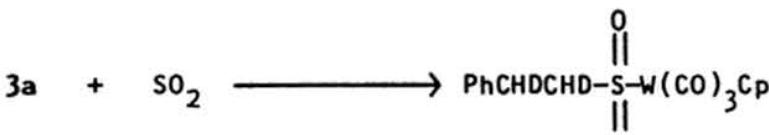
1.71 (2 d,  $J=13.1, 4.6$  Hz)  
 2.77 (2 d,  $J=13.1, 4.6$  Hz)  
 plus phenyl resonances

On the other hand, reaction of 2 with 100% erythro-PhCHDCHDOTs generates only one product, 3a.

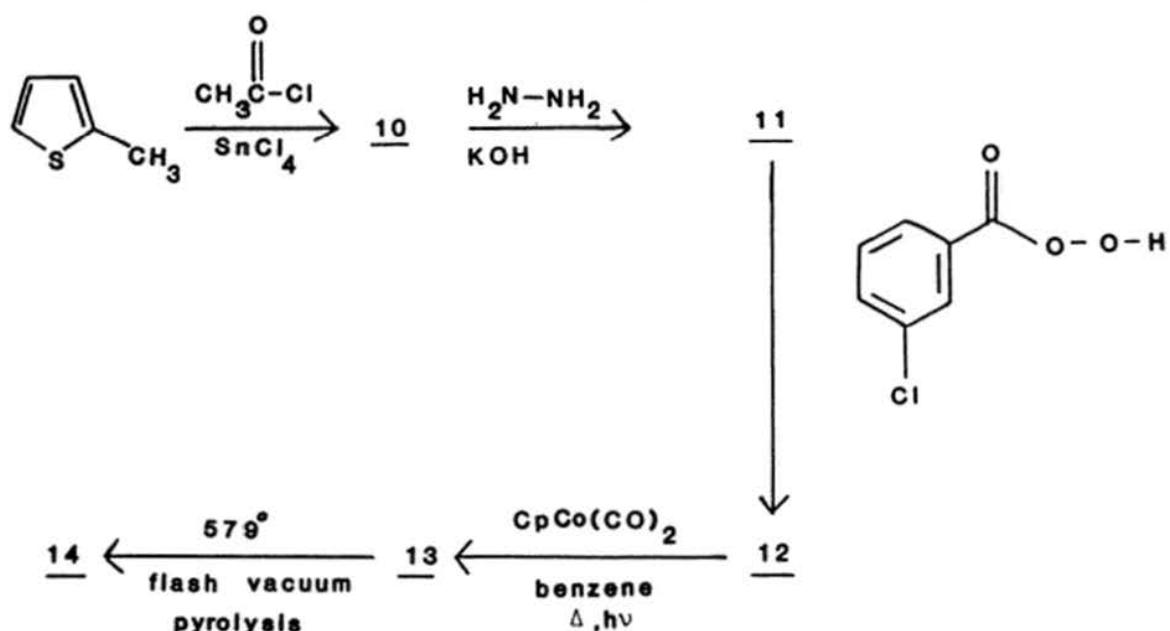
 $^1\text{H}\{^2\text{H}\}$  NMR of 3a

1.71 (d,  $J=4.6$  Hz)  
 2.77 (d,  $J=4.6$  Hz)  
 plus phenyl resonances

The reactions of 3a with  $\text{SO}_2$  and  $\text{I}_2$  proceed as follows:



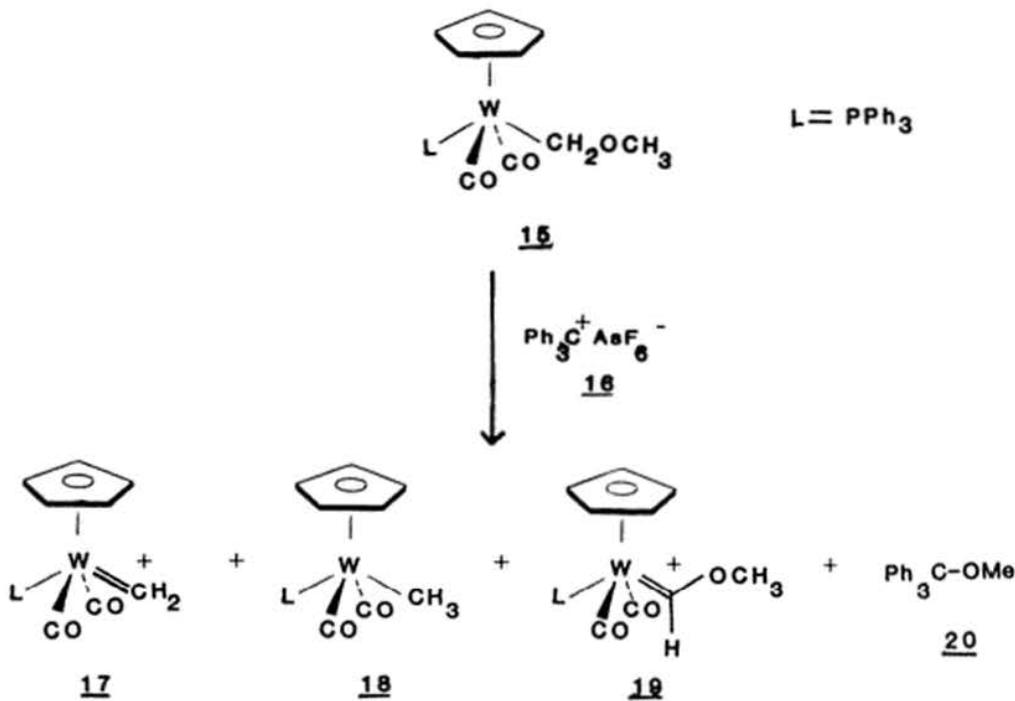
5. Give structures for compounds 10, 11, 12, 13, and 14, and propose a mechanism for the formation of 14 from 13.



<sup>1</sup>H NMR data for 14 ( $\delta$ , CDCl<sub>3</sub>)

1.01 (t, J=7 Hz, 3 H)  
1.54 (s, 3 H)  
1.89 (q, J=7 Hz, 2 H)  
3.65 (s, 1 H)  
3.72 (s, 1 H)  
4.77 (s, 5 H)

6. When complex 15 is allowed to react with a source of triphenylmethyl cation (16), the following products result:



## 6. (cont.)

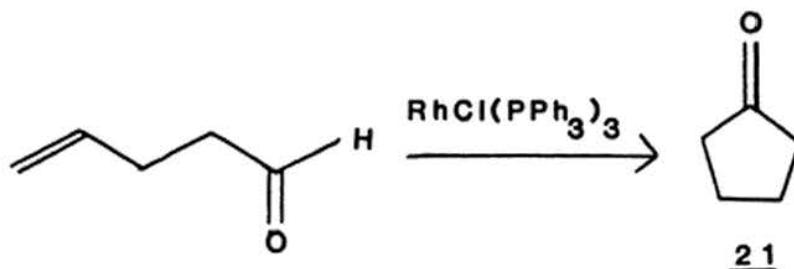
HINT

18 and 19 are formed in a 1:1 ratio.

a) Explain the formation of compounds 17, 18, 19, and 20.

b) Design an experimental procedure that will cleanly generate 17, i.e., a procedure that will not form any 18 or 19.

7. Propose a mechanism for the following cyclization. In addition, predict the major side product from this reaction.

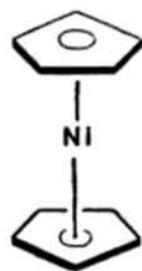
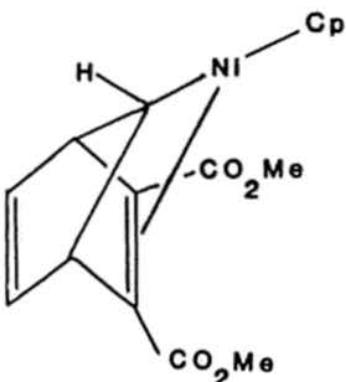
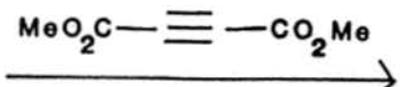
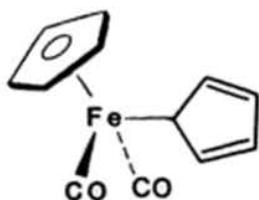
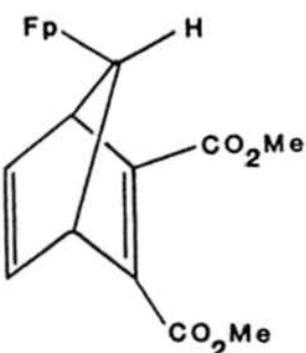
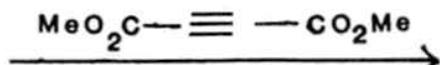


Your mechanism must be consistent with the following experimental observations:

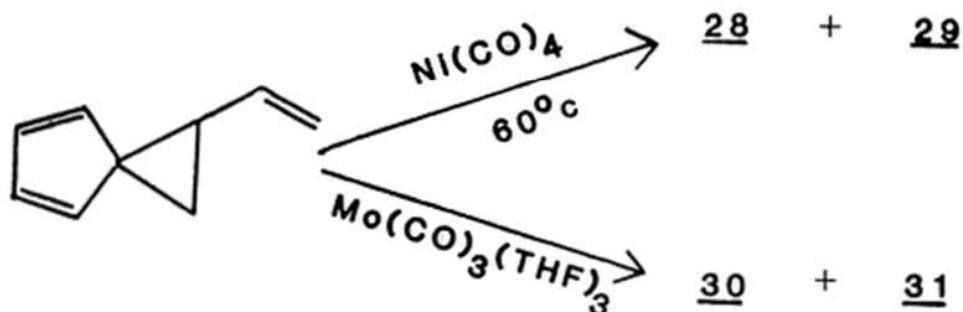
- 1) Radical scavengers have no effect on this reaction.
- 2) It is intramolecular.
- 3) If the aldehydic proton is replaced by deuterium, then cyclopentanone-3-d<sub>1</sub> is formed.

8. Nickelocene ( $Cp_2Ni$ ) reacts in a Diels-Alder fashion with dimethyl acetylenedicarboxylate to give the syn isomer 25. It has been found that  $CpFe(CO)_2$ (cyclopentadienyl), 26, also undergoes a Diels-Alder reaction, with the major product being the anti isomer, 27. Suggest a mechanism(s) which explains the difference in the product stereochemistry for these two seemingly related reactions.

8. (cont.)

24252627

9. Propose structures for compounds 28, 29, 30, and 31.



## 10. (cont.)

 $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) for 33

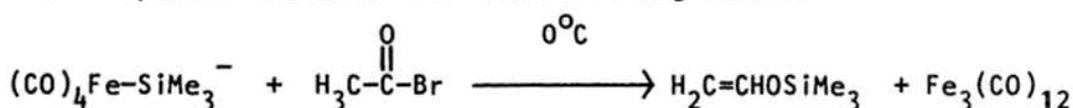
1.58–1.68 (ddd, 1 H)  
 2.11–2.20 (ddd, 1 H)  
 2.20–2.40 (m, 2 H)  
 2.46–2.65 (dddd, 1 H)  
 3.40–3.60 (m, 1 H)  
 3.67 (s, 3 H)  
 5.70–6.00 (m, 2 H)  
 7.15–7.35 (s, 5 H)

 $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) for 34

1.87–1.97 (ddd, 1 H)  
 2.00–2.07 (ddd, 1 H)  
 2.25–2.45 (m, 2 H)  
 2.92–2.98 (dddd, 1 H)  
 3.70 (s, 3 H)  
 4.15–4.25 (m, 1 H)  
 5.70–5.95 (m, 2 H)  
 7.40–7.60 (m, 3 H)  
 7.90–8.00 (m, 2 H)

b) Given the fact that  $\text{PhCH}_2\text{Pd}(\text{PPh}_3)_2\text{Cl}$  is present in catalytic amounts and that in solution it will generate a Pd(0) species, propose a mechanism for the formation of 33 and 34.

## 11. Propose a mechanism for the following reaction.

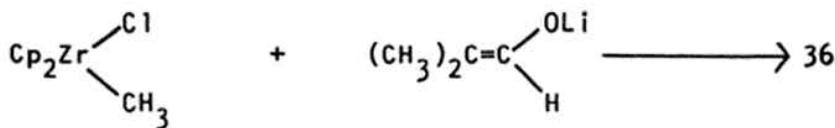
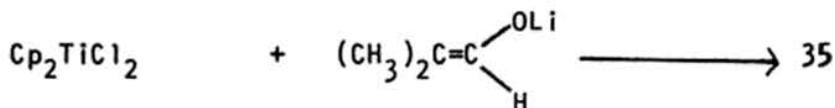


## HINT

If the reaction is carried out at  $-50^\circ\text{C}$ , an intermediate with the following spectral data is observed.

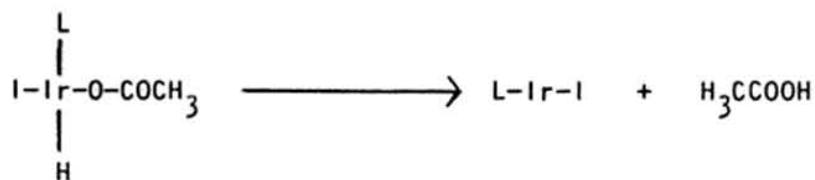
IR ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR ( $\delta$ , $\text{CD}_2\text{Cl}_2$ )	$^{13}\text{C}$ NMR ( $\delta$ , $\text{CD}_2\text{Cl}_2$ )
2058 (m)	0.45 (s, 9 H)	0.2
1988 (m)	2.98 (s, 3 H)	51.0
1963 (s)		215.2
1954 (s)		341.3
1944 (sh)		

## 12. Propose structures for compounds 35 and 36.



1. (cont.)

6) The product-forming step is a reductive elimination.

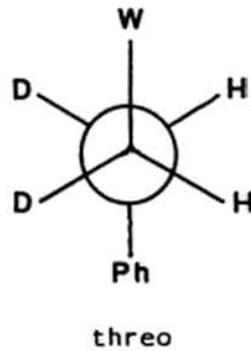
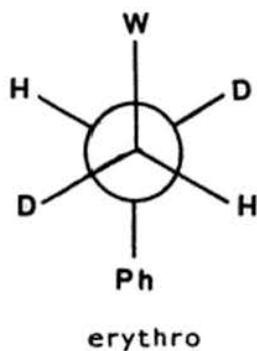


7) The final step is the regeneration of methyl iodide from the ester of the solvent and the HI generated in step 3.



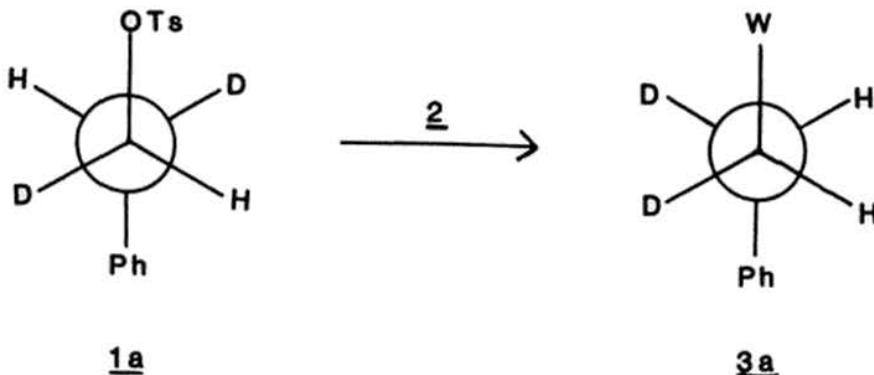
Pruett, R.L.; Kacmarcik, R.T. Organomet. 1982, 1, 1693.

2. The reaction of 1 and 2 must give a 50/50 mixture of the erythro and threo products. (In the drawing below, W represents  $\text{CpW}(\text{CO})_3$ .)

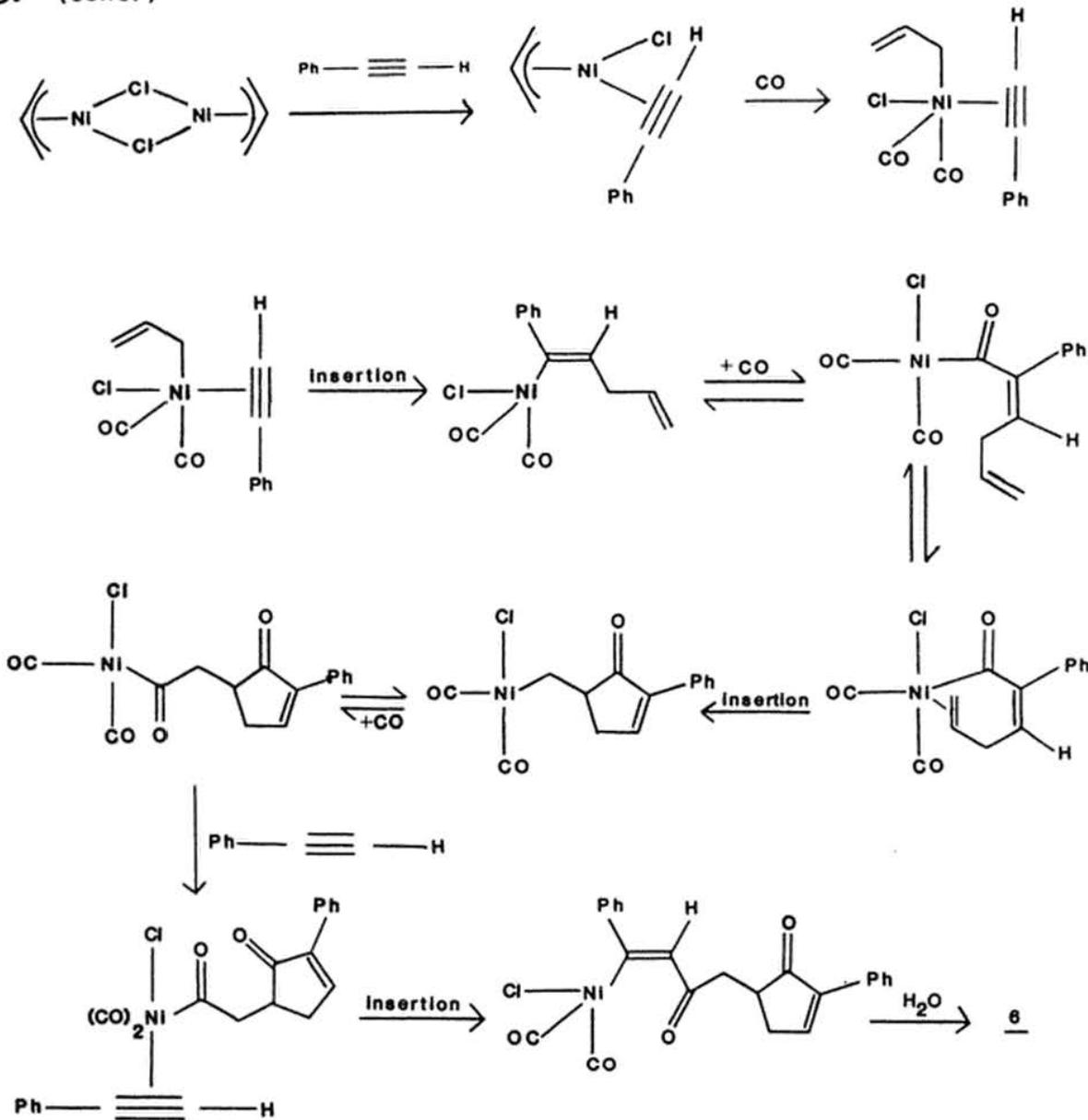


The two H-H coupling constants are 4.6 and 13.1 Hz. The dihedral angle between the hydrogens in the erythro isomer is  $180^\circ$ , while in the threo isomer it is  $60^\circ$ . Thus, by the Karplus relationship, the threo isomer must have the smaller J value, and the erythro isomer, the larger value. Therefore,  $J_{\text{erythro}} = 13.1 \text{ Hz}$  and  $J_{\text{threo}} = 4.6 \text{ Hz}$ .

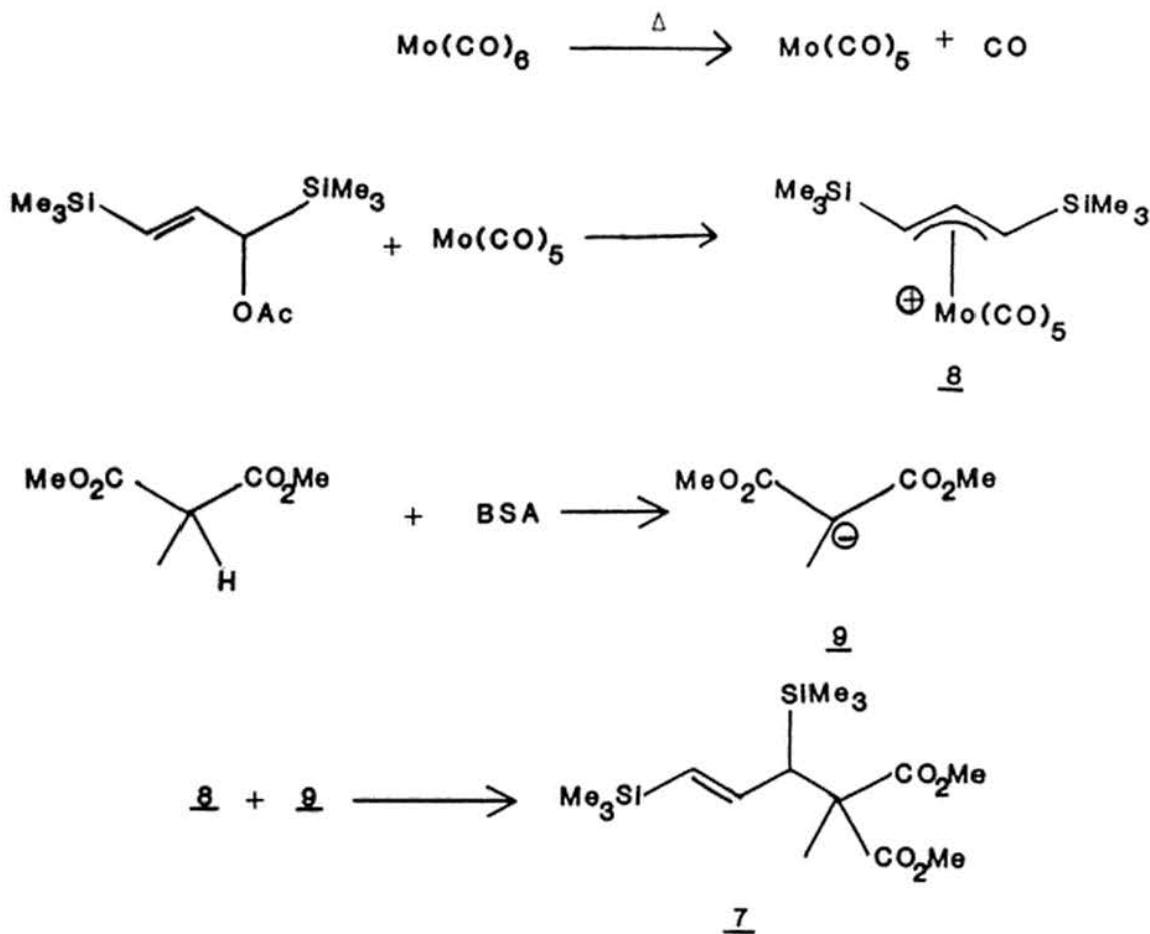
From these values, it may be concluded that the reaction of 1a and 2 gives only the threo product, i.e., complete inversion takes place in this reaction.



3. (cont.)

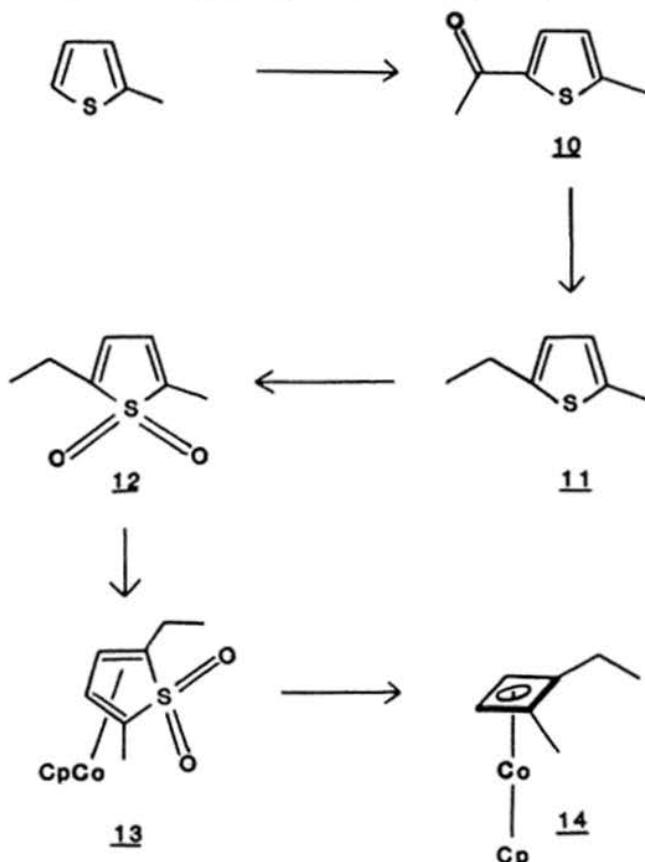
Heck, R.F. Accts. Chem. Res. 1969, 2, 10.

4. The product and proposed mechanism are shown below.

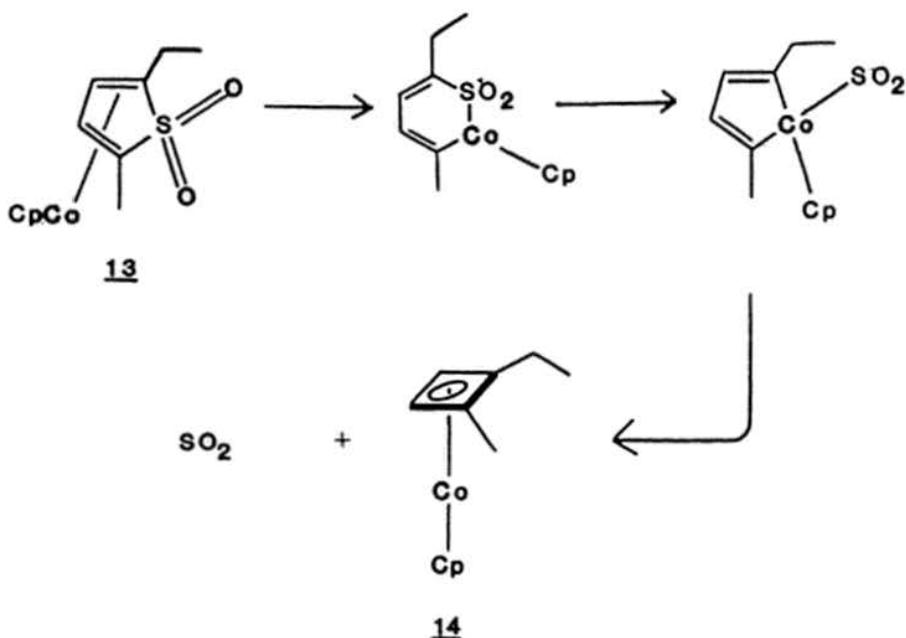


Trost, B.M.; Brandi, A. J. Org. Chem. 1984, 49, 4811.

5. The structures of compounds **10**, **11**, **12**, **13**, and **14** are:

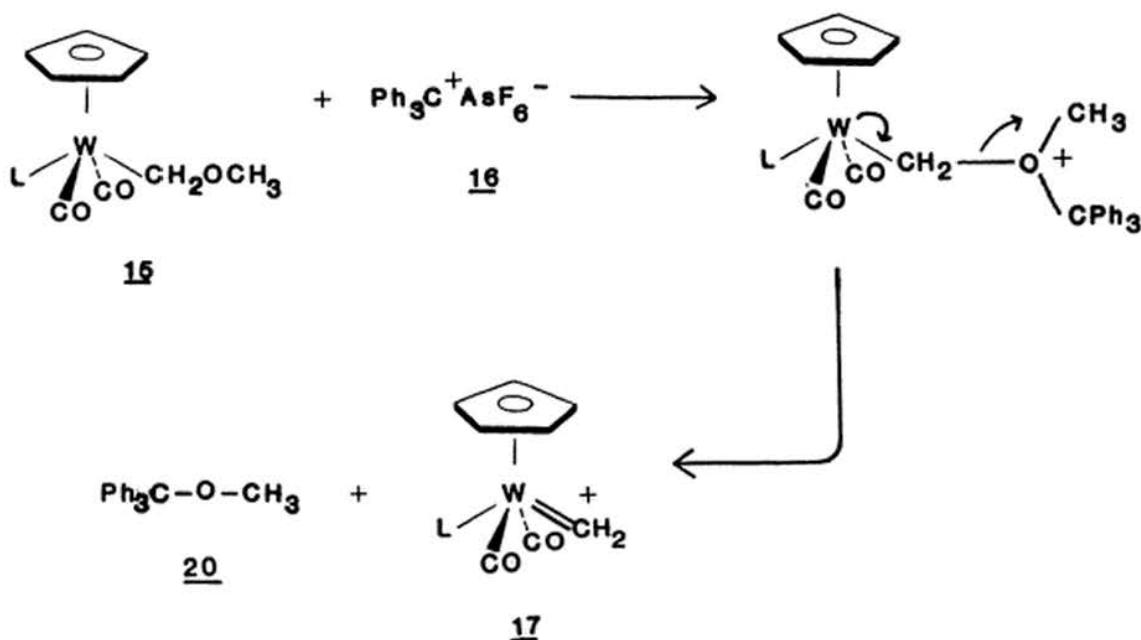


The authors propose four different mechanisms for this reaction. Based upon other work, they prefer the following mechanism:

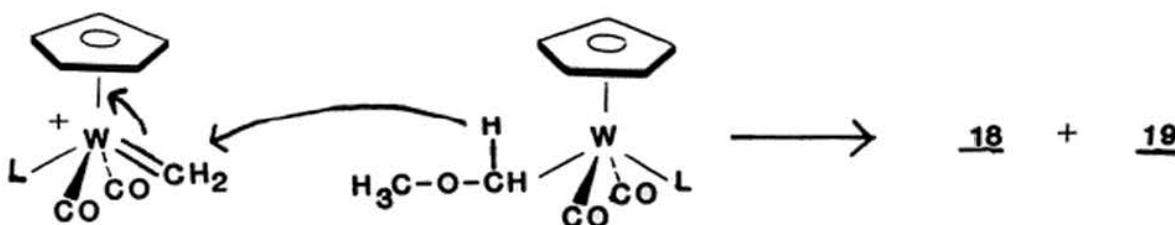


Drage, J.S.; Vollhardt, K.P.C. *Organomet.* 1985, 4, 389.

6. Compound **17** is formed in the following manner:



However, **17** is a highly reactive hydride abstractor and can react with **15** to give **18** and **19** in a 1:1 ratio.

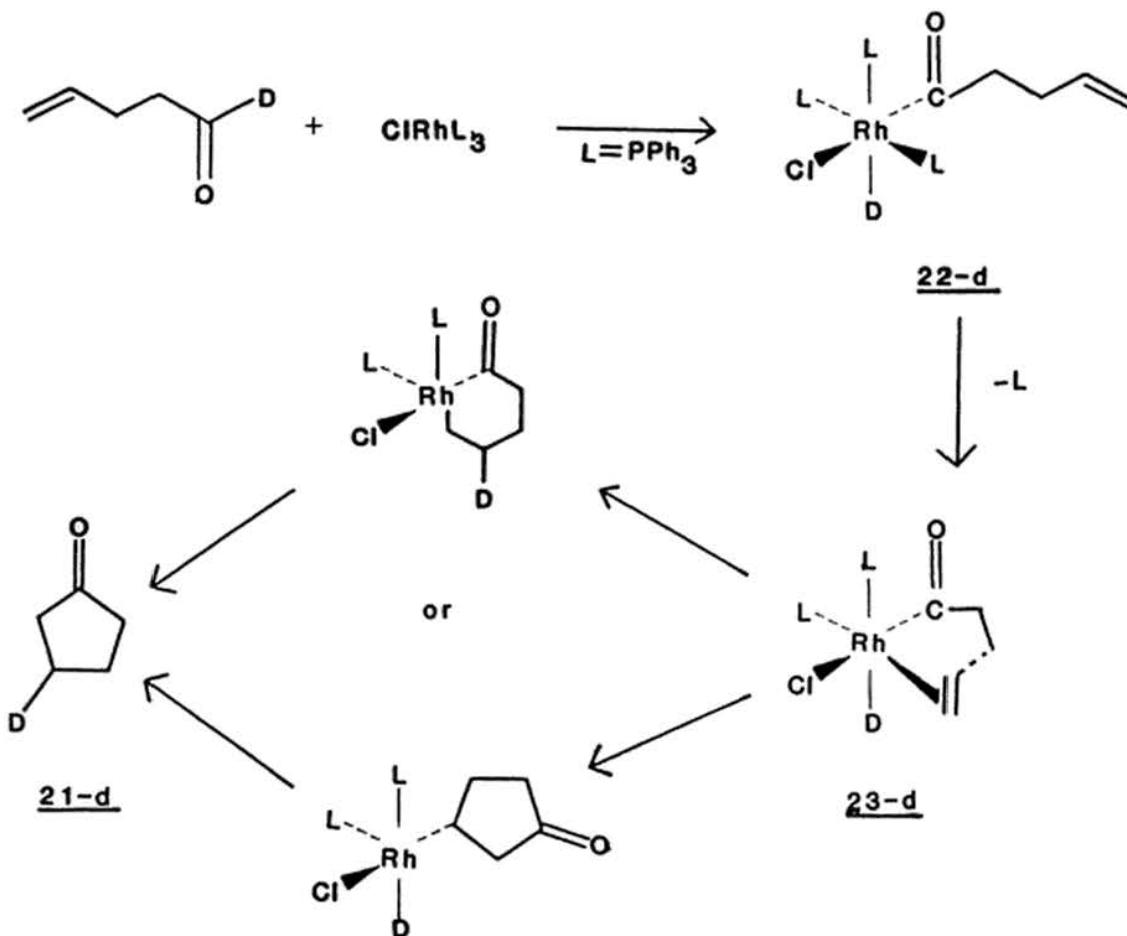


Generation of **17** without contamination by **18** and **19** can be achieved by the slow addition of **15** to a solution of **16** or by reaction of **15** with a more reactive alkoxide abstractor such as  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ . The ultimate goal is to generate **17** with little **15** present to react with it.

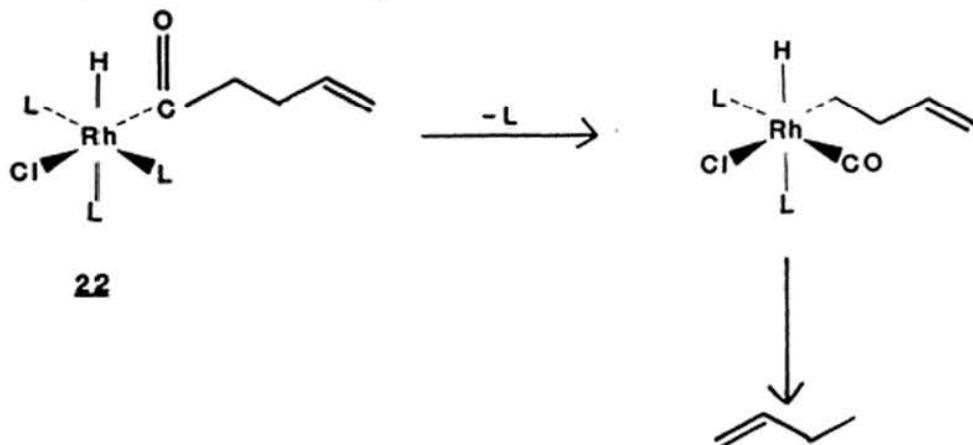
Kegley, S.E.; Brookhart, M.; Husk, G.R. *Organomet.* 1982, **1**, 760.

Davies, S.G.; Maberly, T.R. *J. Organomet. Chem.* 1985, **296**, C37.

7. The three steps of this mechanism are an oxidative-addition, an olefin insertion, and a reductive-elimination.



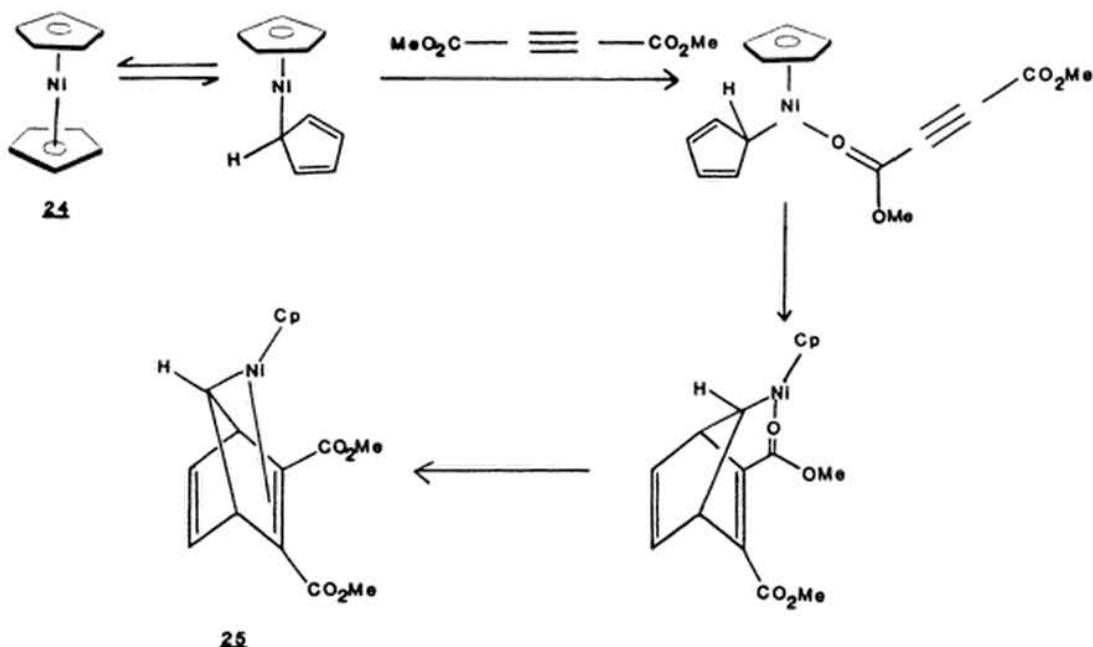
The major side product arises from a decarbonylation of the organic molecule by a reverse carbonyl insertion reaction.



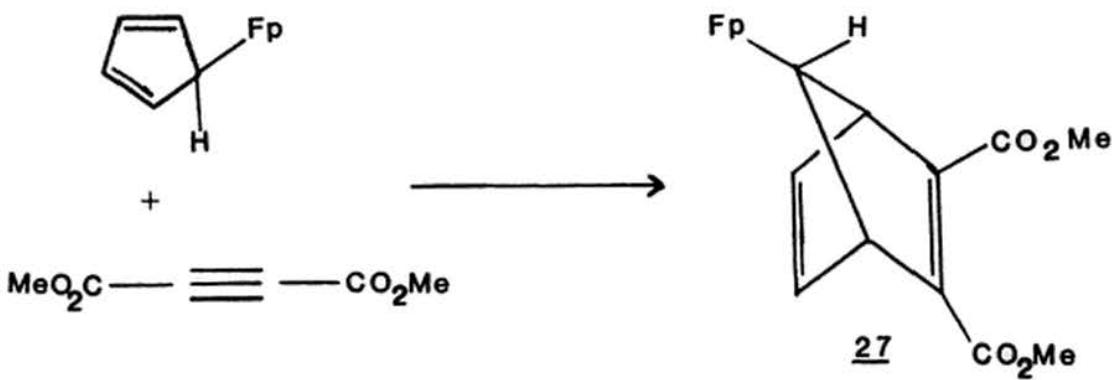
Campbell, R.E.; Lochow, C.F.; Vora, K.P.; Miller, R.G. J. Am. Chem. Soc. 1980, 102, 5824.

Milstein, D. J. Chem. Soc., Chem. Comm. 1982, 1357.

8. In the nickel example, the dienophile coordinates with the sixteen-electron nickel complex prior to the Diels-Alder reaction. This forces the syn addition as shown:



On the other hand, complex 26 has eighteen electrons around the metal, and therefore, prior coordination of the dienophile is not possible. This results in attack of the dienophile on the olefin from the less sterically crowded side of the diene, i.e., anti to the metal.

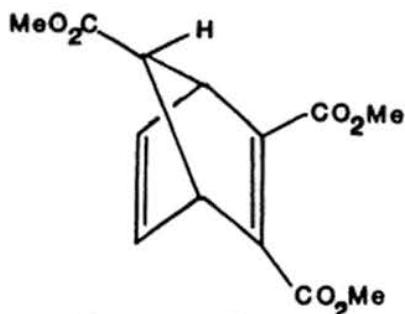


#### NOTE

Compound 26 also reacts with maleic anhydride, dimethyl fumarate, and chloroacrylonitrile, but not with methyl acrylate or dimethyl maleate.

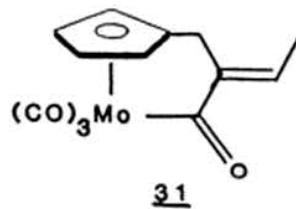
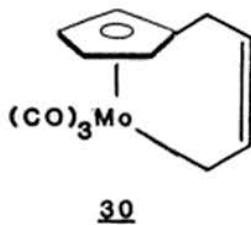
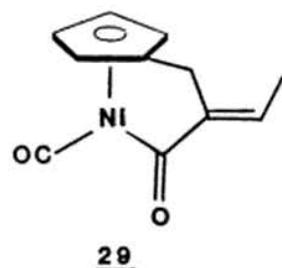
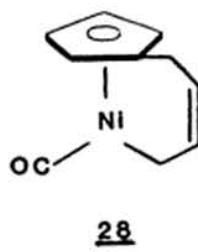
## 8. (cont.)

In addition, the iron may be oxidatively removed from the product with Ce(IV) in methyl alcohol to generate a carboxylic derivative.



Wright, M.E. Organomet. 1983, 2, 558.

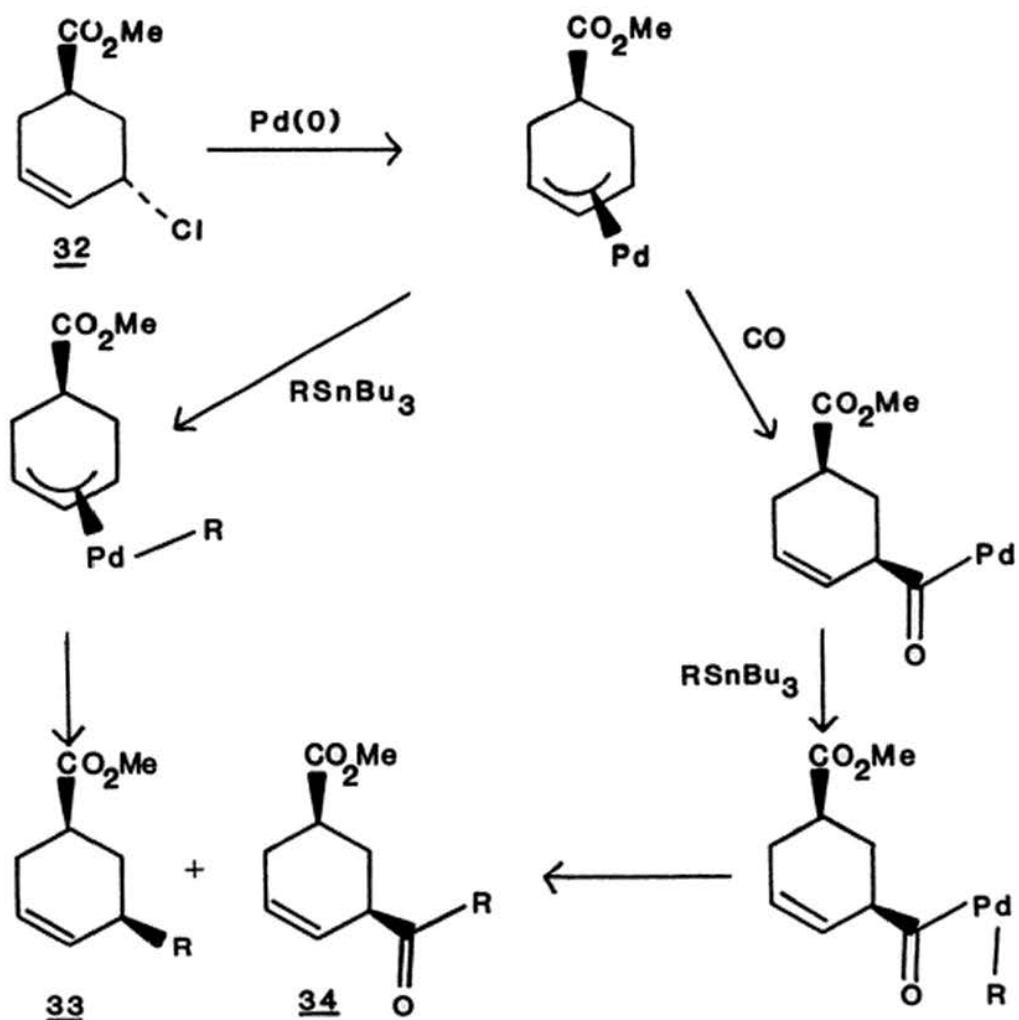
9. In all cases, it is the 1-3 bond of the starting material which is broken by the transition metal.



Eilbracht, P. J. Organomet. Chem. 1976, 120, C37; Chem. Ber. 1976, 109, 1429.

Eilbracht, P.; Mayser, U.; Tiedtke, G. Chem. Ber. 1980, 113, 1420.

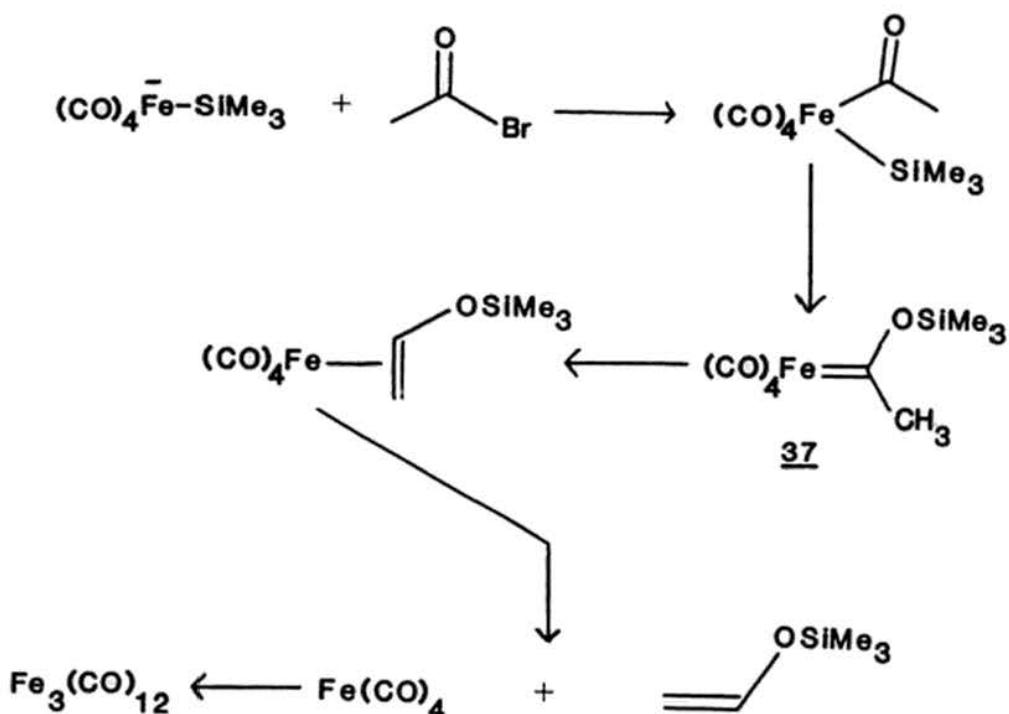
10. a) and b) The tin complex is the nucleophile and the allyl-palladium complex is the electrophile.



Sheffy, F.K.; Godschalk, J.P.; Stille, J.K. J. Am. Chem. Soc. 1984, 106, 4833.

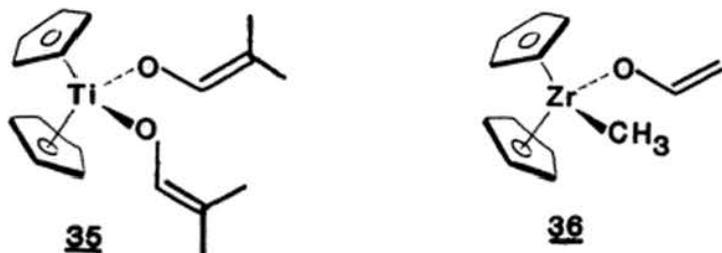
11. The proposed mechanism is shown on the following page. The first step is a nucleophilic attack to give an acyl silyl iron complex which rapidly rearranges to the heterocarbene complex, 37. It is 37 which is detected at low temperature. At room temperature, this carbene complex rearranges to the olefin complex, followed by dissociation of the free olefin.

11. (cont.)



Brinkman, K.C.; Blakeney, A.J.; Krone-Schmidt, W.; Gladysz, J.A.  
Organomet. 1984, 3, 1325.

12. The enolate is a strong nucleophile and attacks the electrophilic metal complex with subsequent loss of chloride.



Curtis, M.D.; Thanedar, S.; Butler, W.M. Organomet. 1984, 3, 1855.

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