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# TRANSITION METAL CHEMISTRY

*A Series of Advances*

EDITED BY  
RICHARD L. CARLIN

DEPARTMENT OF CHEMISTRY  
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**TRANSITION METAL  
CHEMISTRY**

*Volume 2*

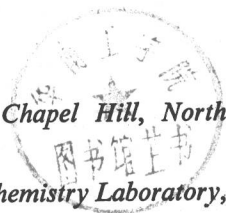
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# Contents of Other Volumes

## VOLUME 1

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## OTHER VOLUMES

To be announced

# Contents of Volume 2

CONTRIBUTORS TO VOLUME 2 . . . . .	v
CONTENTS OF OTHER VOLUMES . . . . .	xi

## Reactions of Ligands Coordinated with Transition Metals

*James P. Collman*

I. Introduction . . . . .	2
II. Reactions of $\sigma$ -Bonded Donor Atoms . . . . .	4
III. Quasi-Aromatic Metal Complexes . . . . .	24
IV. Reactions of $\pi$ -Bonded Ligands . . . . .	58
V. References . . . . .	104

## Transition Metal Ions as Reagents in Metallo-enzymes

*A. E. Dennard and R. J. P. Williams*

I. Introduction . . . . .	116
II. Hydrolysis in Model Systems . . . . .	122
III. Hydrolysis Mechanisms and Metallo-enzymes . . . . .	127
IV. Some Metallo-enzymes . . . . .	130
V. Transition Metal Ions of Later Periods . . . . .	158
VI. Concluding Remarks . . . . .	162
VII. Notes Added in Proof . . . . .	162
VIII. References . . . . .	163

## Optical Activity in Inorganic and Organic Compounds

*Andrew D. Liehr*

I. Trigonal Dihedral Compounds . . . . .	166
II. Digonal Dihedral Compounds and Compounds of Lower Symmetry . . . . .	190
III. References . . . . .	255

AUTHOR INDEX . . . . .	341
SUBJECT INDEX . . . . .	349

## Chapter 1

# Reactions of Ligands Coordinated with Transition Metals

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I. Introduction . . . . .	2
II. Reactions of $\sigma$ -Bonded Donor Atoms . . . . .	4
A. Reactions of Coordinated Nitrogen . . . . .	4
B. Nucleophilic Reactions of Coordinated Sulfur . . . . .	6
C. Substitution Reactions on Coordinated Phosphorus . . . . .	8
D. Reactions of Uncoordinated Carbonyl Groups in Metal Complexes . . . . .	9
E. Reactions of Coordinated Carbonyl and Related Groups . . . . .	12
III. Quasi-Aromatic Metal Complexes . . . . .	24
A. Ferrocene and Cyclobutadieneiron Tricarbonyl . . . . .	25
B. Ruthenocene and Osmocene . . . . .	30
C. $\pi$ -Cyclopentadienyl Metal Carbonyl Derivatives . . . . .	30
D. Neutral Arene $\pi$ Complexes . . . . .	31
E. Metal Acetylacetonates . . . . .	35
F. $\alpha$ -Diimine Chelates . . . . .	45
G. Outer Ligand Reactions, Role of Metal as Protective or Activating Group . . . . .	47
IV. Reactions of $\pi$ -Bonded Ligands . . . . .	58
A. Introduction . . . . .	58
B. $\sigma$ to $\pi$ Ligand Rearrangements . . . . .	59
C. Ligand Reactions of Non-Aromatic Metallocenes . . . . .	61
D. Electrophilic Attack of $\pi$ -Bonded Olefin Complexes . . . . .	66
E. Nucleophilic Addition to $\pi$ -Bonded Ligands . . . . .	71



F. Homogeneous Hydrogenation of Organic Substrates . . . . .	79
G. Hydroformylation . . . . .	86
H. Transition Metal Catalyzed Polymerization of Olefins . . . . .	87
I. Cyclooligomerization . . . . .	89
V. References . . . . .	104

## I. INTRODUCTION

The binding of an organic substrate by a metal to form a coordination or organometallic compound often has a powerful influence on the chemical reactivity of the ligand group. Although dramatic alterations of chemical properties of coordinated groups were recognized many years ago, only recently have reactions of coordinated ligands been actively investigated. The limited development of this field resulted from lack of mutual interests and understanding between organic and inorganic chemists.

The chemical reactions of coordinated ligands is now recognized as a field of great potential with tremendous technological implications. The Ziegler-Natta olefin polymerization, the hydroformylation process, and the Wacker olefin oxidation illustrate the already substantial commercial applications of this concept. Furthermore, the role of metal ions at the active sites of many enzyme systems has attracted a great deal of interest in biochemistry. Basic chemical applications include the preparation of new complexes and organic syntheses using metal catalysts or chelate protective groups. It might be said that this area gives a new dimension to inorganic chemistry.

In the present chapter an attempt is made to discuss reactions of ligands co-ordinated to transition metals. Complexes of nontransition metals also undergo many similar transformations. The major differences between these two classes of complexes lie in the greater stability of the transition metal complexes and the existence of  $\pi$ -bonded organometallic compounds of the transition metals.

During the past few years, Busch,<sup>6</sup> Dwyer,<sup>26</sup> Heck,<sup>171</sup> and Jones<sup>145</sup> (among others) have reviewed various aspects of ligand reactions. The scope and organization of each of these surveys have differed from the present one. However, the author has made liberal use of these reviews in compiling examples of ligand reactions. Because of the enormous scope of this subject, the present effort is far from exhaustive. In many instances, pertinent literature is cited through May 1965. Electron transfer processes and reactions of carbon-metal  $\sigma$ -bonded species have been omitted and will doubtless appear elsewhere in the near future. Apologies are offered

in advance to those authors whose work has been omitted or overlooked in the following discussion.

The arbitrary organization used in this chapter is based partially on the substrates undergoing reactions and partially on the type of reactions. With time, this type of outline will undoubtedly crumble under the weight of such a rapidly advancing subject. Reactions of coordinated ligands can be further divided into two general categories: (a) reactions in which the ligand is bound to the metal during the entire process; and (b) reactions in which the metal functions as a catalytic labile intermediate. Since these two processes differ only in the relative stabilities of the coordination compounds participating in the reaction, they will not be segregated in the following account.

Before proceeding with detailed examples of ligand reactions, it may be profitable to discuss briefly the ways in which a metal might be expected to influence ligand reactions.

Metal ions in cationic complexes can have the effect of a "super acid" polarizing the ligand and depleting the basic property of the donor atoms. Various reactions depending upon nucleophilic attack on the ligand can be enhanced by this effect. Electrophiles which might be expected to attack the donor atoms in the free ligand may seek another point of reaction on a coordinated ligand. The metal can then function as a protective group towards an otherwise sensitive part of the ligand.

The overall charge on the complex is often important. Nucleophilic attack is usually facilitated and electrophilic attack retarded by the charge on cationic complexes. One should be reminded that the charge on an ionic complex is distributed to the ligands rather than localized at the metal ion.

Another major distinction between neutral and charged complexes is the reaction medium. Experiments with charged complexes are often limited to aqueous solutions which impose rather narrow boundary conditions on the acid-base strength and oxidation-reduction potential of attacking reagents. Furthermore, the nucleophilicity of water is enormous compared with non-polar organic solvents.

Perhaps the most dramatic effect which can be exerted by the metal is stereochemical. The metal places strict requirements on ligand substrates which participate in catalytic processes. More important, a metal can greatly reduce the entropy of reaction by positioning reacting groups on adjacent places in the coordination sphere. This phenomenon is of critical importance in metal enzyme reactions, chelate forming "template" condensations, organometallic insertion reactions, and cyclooligomerization of alkynes and alkenes.

The metal may accelerate a reaction by providing an unusually stable transition state. In many instances the metal may also favorably influence

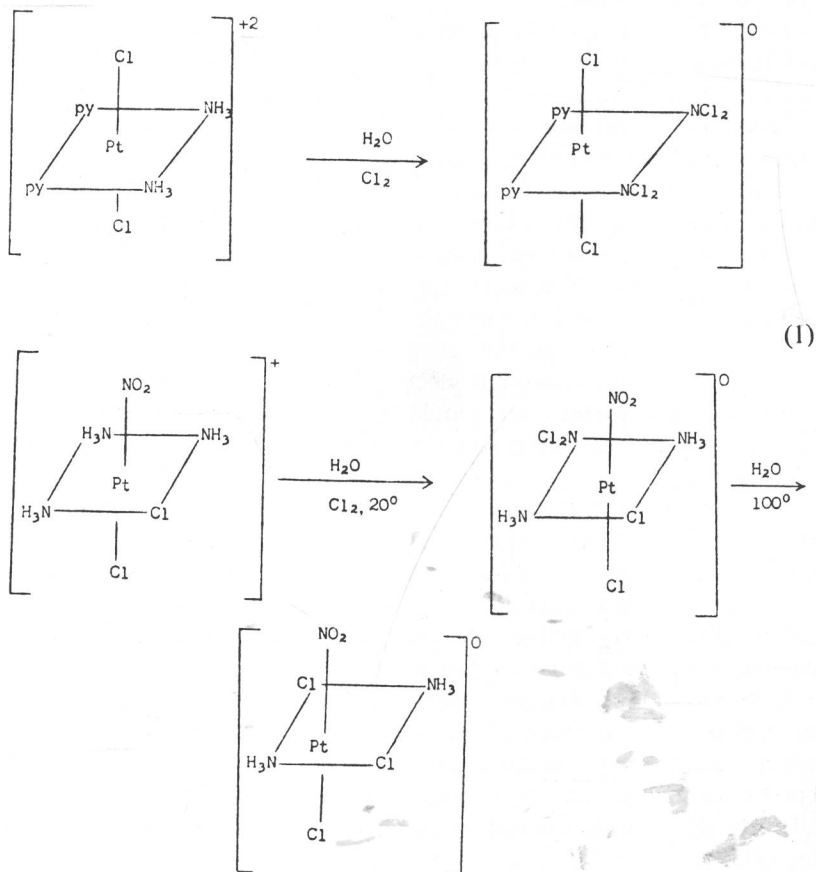
the thermodynamics of a reaction by stabilizing the product through coordination. Numerous examples of these principles are to be found in the following examples of ligand reactions.

## II. REACTIONS OF $\sigma$ -BONDED DONOR ATOMS

### A. Reactions of Coordinated Nitrogen

Although coordinated nitrogen fails to exhibit nucleophilic properties, two reactions of nitrogen donor atoms have been characterized.

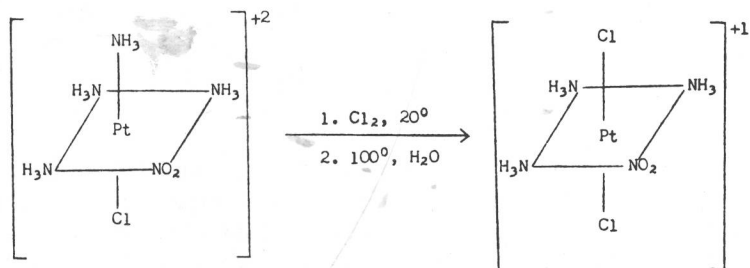
Aqueous solutions of complex ions containing ammonia or amines



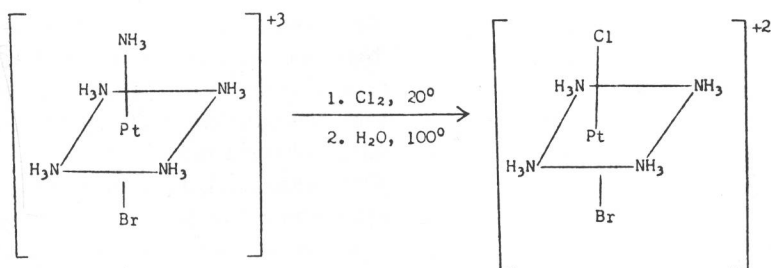
undergo rapid hydrogen exchange with water, apparently without breaking the nitrogen to metal coordinate bond. Such interchange processes are conveniently studied by observing the proton magnetic resonance spectra

of diamagnetic amine complexes in  $D_2O$  as a solvent.<sup>1</sup> The exchange rate is dependent on the pH of the solution. For example *bis*-(ethylenediamine)-cobalt(III) complexes undergo very rapid hydrogen exchange at pH ranges above 4, but at pH 1 and below the proton spectra of these complexes in  $D_2O$  show distinct  $NH_2$  signals which are invariant with time (no exchange observed). *Tris*-(ethylenediamine)cobalt(III) ions exhibit a similar effect. Spectra of this type can be useful in determining the stereoisomerism of nitrogen complexes.<sup>2</sup>

In certain instances coordinated amines can be directly converted into chloramine complexes by treatment with chlorine. Kukushkin<sup>3</sup> has studied



(2)

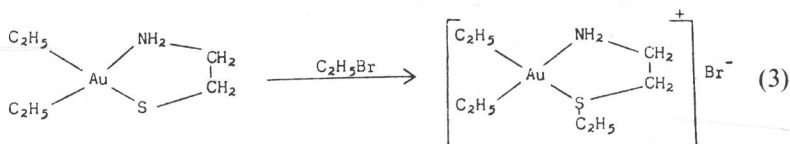


the chlorination of platinum(IV) complexes of ammonia and amines. He has found that  $NH_3$  groups are converted into dichloroamido ( $NCl_2^-$ ) groups and that the *trans* effect is operative in activating specific  $NH_3$  groups to oxidation. When aqueous solutions of the chloramine complexes are heated to  $100^\circ\text{C}$ , the complexed dichloroamido groups are smoothly converted to chloride groups with retention of geometrical configuration. The overall process of converting platinum amines to chloro complexes by oxidation with chlorine is over 100 years old but was not understood until Kukushkin's work. Complexes containing two dichloroamido groups are dangerously explosive, whereas compounds containing one such group are usually more stable. Ethylenediamine and methylamine groups are also attacked by chlorine, but pyridine groups are not (1).

The selectivity of chlorination has been used to prepare specific geometrical isomers (2).<sup>3</sup>

### B. Nucleophilic Reactions of Coordinated Sulfur

Ewens and Gibson<sup>4</sup> first demonstrated the nucleophilic character of coordinated mercaptide ions. A molecular gold(III) chelate was found to react rapidly with ethyl bromide to form a cationic sulfide complex which was isolated as a picrate (3). The analogous reaction with methyl iodide occurred with explosive violence.



More recently, Busch and his students have extensively investigated the alkylation of  $\beta$ -mercaptoamine complexes.<sup>5</sup> Their experiments indicate that coordinated mercaptide ions can be transformed into thioether chelates without breaking the metal-sulfur bond. The nucleophilicity of coordinated mercaptide ion is often greater than the corresponding free mercaptan. Bridging sulfur, coordinated thioethers, and coordinated amines were not attacked by the alkylating agents employed.

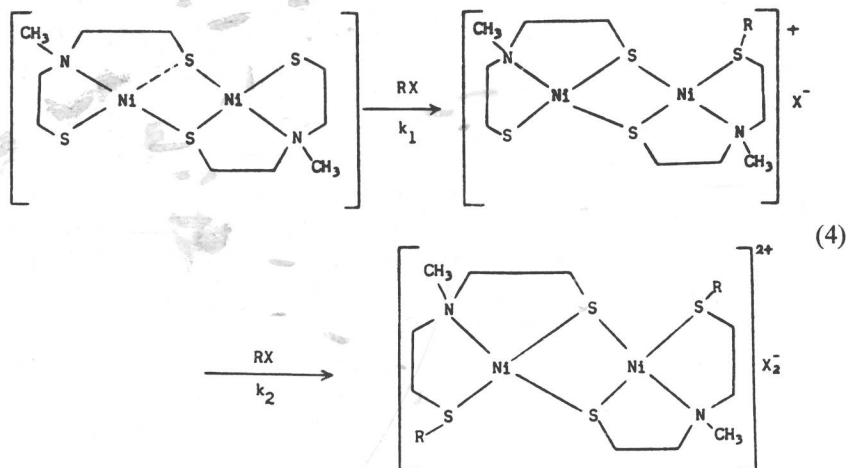
Kinetic measurements were made on several of these alkylations;<sup>5</sup> however, these data were complicated by consecutive reactions, dissociative equilibria, ligand interchange, polynuclear complex formation through bridging sulfur, and solvent competition. Nevertheless some significant conclusions were drawn from interpretation of these rate data.

The most definitive kinetic measurements were carried out on the reactions of *bis*-(methyl-2,2'-dimercaptodiethylamine)dinickel(II) with alkyl halides. Reactions with methyl iodide, benzyl bromide, and substituted benzyl chlorides in chloroform were second order. Isolation of the dialkylated product chelates indicated that the reaction took place in two steps, the second much faster than the first ( $k_2 > k_1$ ). Bridged sulfur atoms were not affected. These kinetic results seem to rule out prior dissociative equilibria (4).

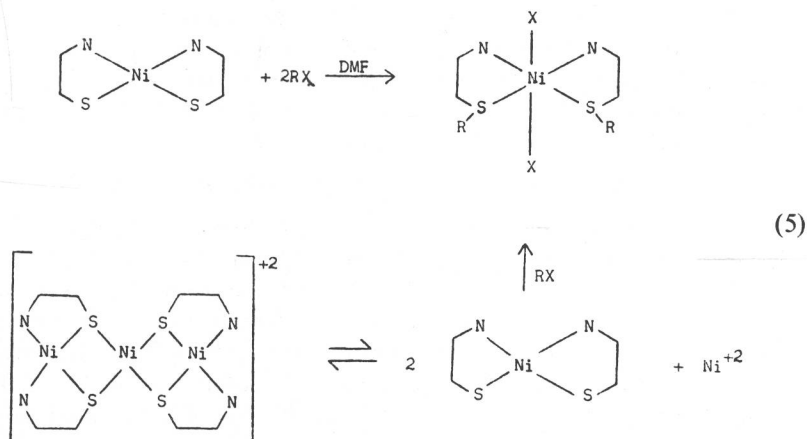
The relative rates of the different alkylating agents are compatible with an  $S_N2$  attack at a saturated carbon atom. The activation energies were found to be around 10 kcal. mole<sup>-1</sup>. It was suggested that these small activation energies might be accounted for by a pre-equilibrium in which the metal acts as an electrophile polarizing the halogen atom.

Alkylation of the simple mononuclear nickel(II) chelate of  $\beta$ -mercaptoethylamine afforded octahedral sulfide complexes. However, these reactions proved to be deceptively complex. Trinuclear nickel chelates were

shown to be intermediates in stepwise alkylations. The same types of alkylation products were obtained by treating the trinuclear complexes with alkyl halides. Because of the complexity of these reactions, kinetic

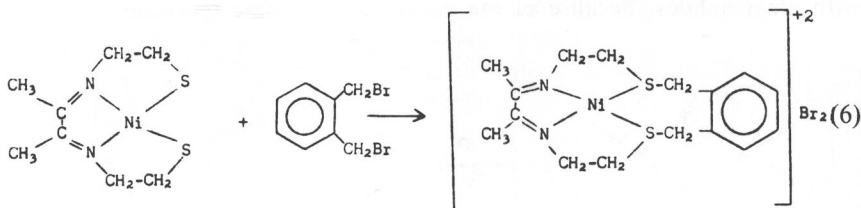


studies were less definitive. However, the results of rate measurements were compatible with the conclusions reached in the dinuclear system. The mononuclear complex was considered to be the active nucleophilic species (5).



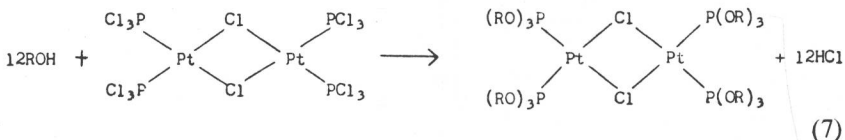
Busch developed an elegant synthetic application of these ligand reactions by constructing macrocycle chelates through difunctional alkylation

of *cis*-coordinated mercaptide groups. This synthesis of a polycyclic chelate is an excellent illustration of a metal ion acting as a template (6).<sup>6</sup>



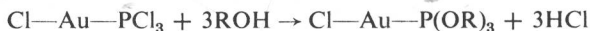
### C. Substitution Reactions of Coordinated Phosphorus

Coordinated phosphorous halides often undergo facile solvolyses during which the phosphorus-metal bond remains intact. Platinum(II)<sup>7-9</sup> and palladium(II)<sup>10</sup> complexes of phosphorus trichloride solvolyze in water and alcohols to form phosphorous acid or orthophosphite complexes (7).



Palladium(II) complexes of phenyldichlorophosphine react with excess ethylene glycol, pyrocatechol, and diphenylphosphinic acid to afford complexes of the corresponding phosphorus esters (8).<sup>11</sup> Attempts to use these reactions for cyclization to multidentate complexes have been unsuccessful. Trace amounts of base, excess water, or excess methanol lead to immediate reductive decomposition of the palladium complexes.

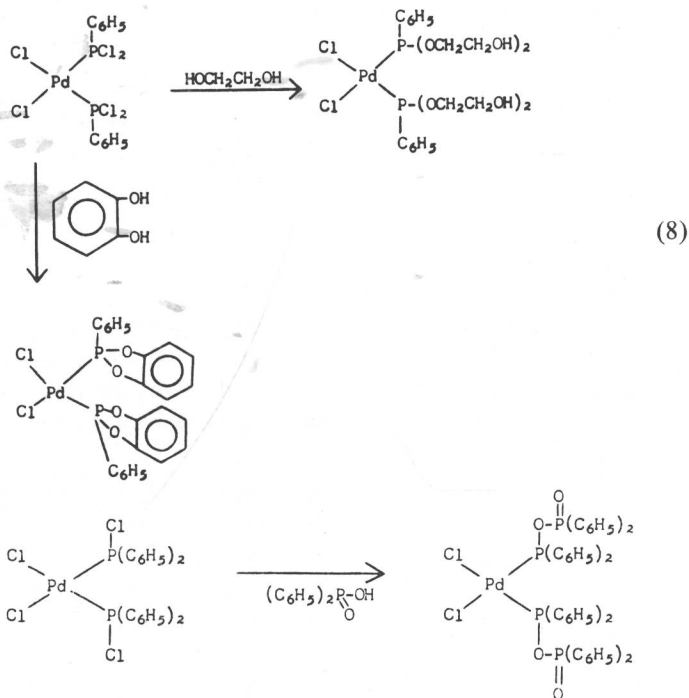
The related gold(I) phosphorus trichloride complex forms stable solvolysis products from alcohols but is reduced by water.<sup>12,13</sup> On the other hand, the iridium(III) compound  $\text{IrCl}_3(\text{PCl}_3)_3$  does not react with cold ethanol, cold sulfuric acid, or organic bases.<sup>14,15</sup>



Fluorination of nickel(0) *tetrakis*-chlorophosphine complexes is the only practical method of preparing fluorophosphine-nickel(0) derivatives.<sup>16,17</sup> The reaction is best carried out with potassium fluorosulfate,  $\text{KSO}_2\text{F}$ , in boiling *o*-dichlorobenzene. The fluorophosphine complexes exhibit markedly greater chemical and thermal stability than the corresponding chlorophosphine complexes. The remarkable hydrolytic stability of these complexes is illustrated by steam distillation of *tetrakis*-(trifluorophosphine)nickel(0).<sup>18</sup>



Fluorination of the free chlorophosphine ligands afforded phosphonic fluorides rather than fluorophosphines.<sup>17</sup> The metal thus acts to protect the phosphine from oxidation by the fluorinating agent.



#### D. Reactions of Uncoordinated Carbonyl Groups in Metal Complexes

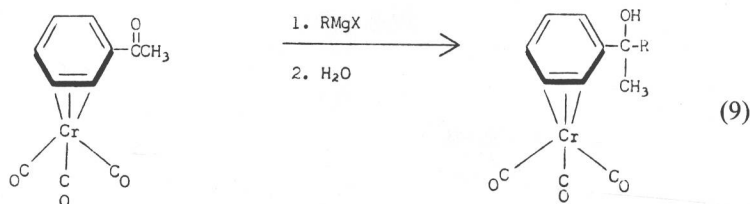
Carbonyl groups which are not directly involved in the coordination sphere of a metal ion usually undergo their normal organic reactions. However, this generalization may be altered by the lability of the complex to certain reaction conditions, by steric shielding of the carbonyl group, or by the overall charge on the coordination compound. Reactions of peripheral carbonyl groups in charged chelates do not appear to have been examined.

The ketone in acetophenone chromium tricarbonyl is reported to react normally with Grignard reagents to form carbinols (9).<sup>19</sup> Similar results have been reported with ferrocenyl ketones<sup>20</sup> and derivatives of cyclopentadienylidene manganese tricarbonyl.

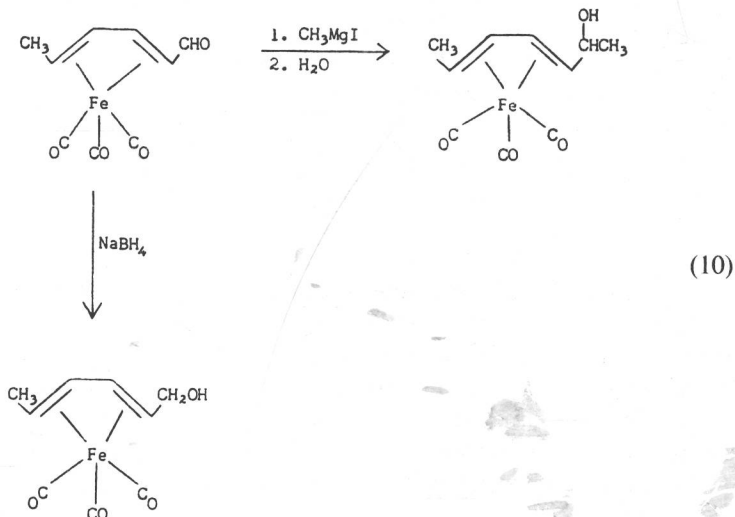
Coordinated carbon monoxide is usually not affected by strongly basic (reducing) conditions, but mild oxidizing agents degrade such complexes by oxidation of the metal. Sodium borohydride reduction of an aldehyde



group in a diene iron tricarbonyl was recently described (10).<sup>21-23</sup> The aldehyde was also treated with a Grignard reagent to form a diastereoisomeric mixture of alcohols. In each instance the diene iron tricarbonyl group remained intact during the reaction. However, Fischer has recently reported reaction of metal carbonyls with phenyllithium. This will be discussed later.



The uncoordinated aldehyde and ketone groups on certain 3-substituted *tris*-acetylacetonates have thus far proven inert to carbonyl reactions—probably because of steric shielding by the flanking methyl groups as well as a high electron density at the adjacent carbon in the chelate ring. A



dramatic illustration of this is the failure of the uncoordinated aldehyde in monoformyl chromium acetylacetonate to react with excess methyl Grignard reagent (11).<sup>24</sup> The starting material was recovered unchanged.

The amide group in *bis*-(asparagine)platinum(II) undergoes alkaline hydrolysis at twice the rate of the free ligand, asparagine (12).<sup>25</sup> The difference in reaction rates has been attributed to neutralization of the