LIGAND REACTIVITY AND CATALYSIS

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PREFACE

This is a book which has several purposes. The first and most obvious is that of collecting information bearing on the problems of coordination and ligand reactivity. But the mere collection of such data is not really a final goal, so a second purpose has been to attempt to provide an organizational framework into which much of this information could be placed in a logical manner. The principal testing ground for such a framework, however, lies not in the ease with which it can accommodate known information, but its fruitfulness in assisting the application of general principles to completely new situations. This kind of test can only be applied over a period of years. At this point it is necessary to confess that some shortcomings must inevitably be found as new *types* of reactions in this area are being discovered almost continuously.

As the manuscript of this book has grown it has become increasingly obvious that the literature bearing on this subject is not only extensive, but also widely dispersed. Work in this area has been carried out by investigators who have had little interest in many of the broader problems of the field. As a result, some areas have been intensively studied, and other areas with an equivalent intrinsic interest have been largely ignored. A third purpose of this book is then to encourage further work in this field with the goal of making the book itself obsolete.

The enormous extent of the literature has necessitated decisions as to what topics should be covered in great detail, what ones are to be glossed over, and what ones are to be largely omitted. My criterion for these decisions has been a very personal one, namely, my own interest in that particular aspect of the subject. This has had the result that the work on classic types of complexes has been emphasized at the expense of the metallocenes, the metal aromatic complexes, and the organometallic complexes. Since these are covered already in existing treatises the duplication that would have been involved seemed unjustified. The citations given will allow the interested reader to obtain information on these areas from other sources.

I wish to thank the University Research Council of Vanderbilt University for financial assistance in the preparation of the manuscript, and to acknowledge the assistance of my collaborators, with whom investigations in this area have been carried out, especially Drs. W. A. Connor, K. D. Maguire, C. H. Oestreich, and D. G. Lambert. I must also acknowledge a considerable debt to some of my colleagues in the chemistry department at Vanderbilt who have provided me with an enormous amount of very fruitful criticism. Those to whom I have such an obligation include Drs. Thomas M. Harris, John C. D. Brand, and K. Keith Innes. Naturally they cannot be held responsible for any of the mistakes or errors that I have persisted in. I also wish to thank Dr. John H. Craddock of the Monsanto Co. for his careful reading of the manuscript and the many improvements which resulted from his suggestions. I must offer my sincerest thanks to participants in a course based on these notes. Members of the class have given suggestions on many details and points of presentation of the notes. For such help I wish to thank Dr. J. W. Hosking and Messrs. A. E. Gebala, K. P. Lannert, D. T. Livak, R. S. McDow, K. A. Morgan, M. F. Prysak, F. G. Schroeder, C. E. Skinner, II, and M. V. Stevens. Finally, I wish to acknowledge my obligation to my wife, Shirley, who has patiently typed and retyped the various sections of the manuscript.

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Nashville, Tennessee
April, 1968

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Chapter I INTRODUCTION

1.1. Scope

Metal ions are involved in a very large number of reactions by virtue of their ability to coordinate to simple or polyatomic donor species. In most of these cases, the involvement of the metal results in a modification of either the mechanism of the reaction or its rate, or both. At present, the various types of chemists (organic, inorganic, biochemical, and physical) who study aspects of this have quite different ways of looking at the general problem. It is obvious that it would be very desirable to have some way of predicting the effect of metal ions on the course of *any* ligand reaction. It would be even more desirable to be able to predict when coordination will allow an otherwise impossible reaction to proceed to give reasonable amounts of products. Although this is not yet possible, the mere collection of the work done to date suggests many general patterns and also shows further fruitful lines of investigation. The goal *here* is to present *some* of the physical and chemical evidence that is available on ligand reactivity and to show what meaningful patterns have been revealed. The author's prejudices are inescapable, unfortunately, but the most important one, which may be subject to revision in the light of new facts, is a simple one. It is merely the belief that this field must develop in a manner compatible with its character as a border area between inorganic and organic chemistry. It must ultimately form a smooth bridge from one to the other, and violate the spirit of neither.

1.2. Historical Introduction

The study of the reactivity of ligands in complexes may be traced back over one hundred years. Much of this earlier work was cursory and more was incidental to studies of other aspects of coordination chemistry. The chief reasons for surveying it in any detail are that it shows clearly how some

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important ideas have been developed and that it presents some problems which have not yet received a satisfactory solution.

The dependence of the ligand reactivity on the nature of the central ion can be seen in data on the reactivity of complex oxalates collected prior to 1860. The corresponding variations in the behavior of cyanide were noted even earlier, as were aspects such as the loss of basicity of coordinated ammonia. The systematic study of this field dates from a much later period, however, and much of this earlier work has not yet been satisfactorily incorporated into later theories.

Over one hundred years ago, Gibbs and Genth[1] noted that the coordination of the oxalate group to cobalt(III) resulted in some striking changes in its reactivity towards oxidizing agents. Such oxalate groups were found to be *less* susceptible to attack by oxidizing agents than free oxalate ions. They also attempted to reduce the nitro group in $[Co(NH_3)_5(NO_2)]Cl_2$ by boiling it with a mixture of acetic acid and iron filings in a conscious effort to see if the reaction were analogous to that found with nitrobenzene. The experiments were not successful.

Since that time an enormous number of observations of this kind have been recorded and it has been established that the pattern of reactivity changes is very complicated. Coordination may result in masking that makes one reaction of a ligand no longer possible, and, at the same time, may allow another reaction to proceed more easily, even one that is otherwise sterically almost impossible. It is obvious that a highly charged metal ion will always polarize a ligand brought into its vicinity, but this may either facilitate a reaction, slow it down, or have no obvious effect depending upon the kind of reorganization required to reach the transition state and the proximity of the cation to the reaction site.

An early example of the appreciation of the differences between free and complexed ligands may be seen in studies of the toxicity of various cyanide complexes. In general, those cyanides that give hydrocyanic acid in the presence of dilute acid (such as is found in the stomach) are poisonous in the same manner as hydrocyanic acid itself.[2] Inert cyanide complexes such as those derived from Fe(II), Au(I), Cr(III), Co(III), and Pt(IV) are either non-poisonous, or much less so than normal cyanides. Much information of this sort was obtained by Pelikan prior to 1860.[2]

The inability of simple complexed anions to undergo their typical precipitation tests was noted very early and formed one of the most convincing chemical proofs for the formation of a new compound. Thus treatment of platinum(II) sulfite complexes with dilute sulfuric or hydrochloric acid results in a solution

1. W. Gibbs and F. A. Genth, *Am. J. Sci.* (2) **23**, 241 (1857); (2) **24**, 89 (1857).
2. A. Heffter, "Handbuch der Experimentallen Pharmakologie," Bd. 1, pp. 776–778. Springer, Berlin, 1923.

from which only a portion of the SO_2 is expelled by gentle heat,[3] and treatment of chloroplatinic acid with silver nitrate solution results in the precipitation of $Ag_2[PtCl_6]$, not $AgCl$.[4] The inability of barium ion to precipitate more than a fraction of the sulfate in various forms of chromium(III) sulfate[5] was also noted years ago. As a general rule, coordinated anions in inert complexes do not undergo typical precipitation reactions and also their participation in *their* characteristic redox reactions is restricted to a greater or lesser extent. With a *polyatomic* ligand such as thiocyanate, tying up one end in a coordinate bond does not necessarily destroy the ability of the other end to undergo reaction. Thiocyanate coordinated to chromium(III) through the nitrogen, Cr—NCS, can form a coordinate bond with silver through the sulfur to give CrNCSAg.[6] Since this is a characteristic reaction of the sulfur in thiocyanate, it would appear that the changes in reactivity of the ligand atoms become more pronounced as one approaches the coordinate bond.

Examples of more detailed studies of the reactions of coordinated ligands began to appear in the chemical literature before 1900. In 1872, Schutzenberger[7] showed that the alcoholysis of phosphorus trichloride, which is a well-established reaction for the free ligand, also occurs in the complexes $(PtCl_2 \cdot PCl_3)_2$ and $PtCl_2 \cdot 2PCl_3$. These reactions are

$$PCl_3 + 3CH_3OH = P(OCH_3)_3 + 3HCl$$
$$(PtCl_2 \cdot PCl_3)_2 + 6CH_3OH = [PtCl_2 \cdot P(OCH_3)_3]_2 + 6HCl$$
$$PtCl_2 \cdot 2PCl_3 + 6CH_3OH = PtCl_2 \cdot 2P(OCH_3)_3 + 6HCl$$
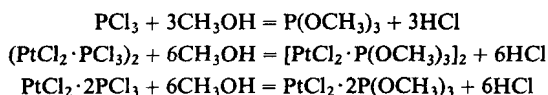
The alcoholysis reaction follows the same general course in both cases, though differences in the kinetic behavior would be expected. The same kind of reaction is of some generality for complexes of phosphorus trichloride and has been studied by other workers.[8-11]

A very significant advance in studies of ligand reactivity was brought about by the pioneering work of Meerwein. The polarization that the ligand undergoes when brought near a charged ion, or when it donates a share in one of its electron pairs to a cation, leads to a number of changes which Meerwein
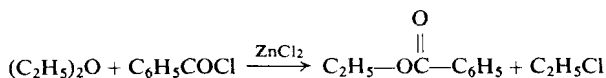
3. A. Litton and G. Schnederman, *Ann. Chem. Liebigs* **42**, 319 (1842).
4. C. Claus, "Beitrage zur Chemie der Platinmetalle." Festschrift Universität Kazan, Dorpat, Russia, 1854.
5. A. Recoura, *Ann. Chim. Phys.* **4** (7), 494 (1895). The literature on this topic is collected by I. Koppel, *in* "Handbuch der Anorganischen Chemie" (R. Abegg, ed.), Bd. 4, Abt. 1, Hefte 2, pp. 132–168. Hirzel, Leipzig, 1921.
6. W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Am. Chem. Soc.* **84**, 2958 (1959).
7. P. Schutzenberger, *Bull. Soc. Chim. France* **17**, 482 (1872); **18**, 101 (1872).
8. M. Risler, *Bull. Soc. Chim. France* **18**, 151 (1872).
9. E. M. Pomey, *Jahresberichte* p. 612 (1887).
10. M. L. Lindel, *Ann. Chim. Paris* **11** (6), 190 (1887).
11. A. E. Arbusov and V. M. Zoroastrova, *Bull. Acad. Sci. USSR Div. Chem. Sci.* (*English Transl.*) p. 809, 818 (1952).

showed to be general phenomena. The most important of these is the weakening of the other bonds formed by the donor atom. The example of water is typical; coordination results in a polarization of electrons in the oxygen–hydrogen bond toward the donor atom and as a result the hydrogen atoms of coordinated water molecules are considerably more acidic than water itself. Meerwein showed that the same increase in acidity occurred with coordinated alcohols.[12,13]

$$B(OC_2H_5)_3 + C_2H_5OH \rightarrow H[B(OC_2H_5)_4] \rightleftarrows H^+ + [B(OC_2H_5)_4]^-$$
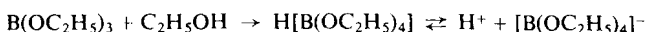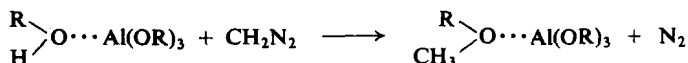
Shortly afterward, Meerwein considered the more general problem of the effect of complex formation on ligand properties. In an unusual, but almost completely neglected paper,[14] Meerwein proposed that the effect of coordination of an —OH, —NH$_2$, or —OR group in an organic compound could be estimated from the behavior of the corresponding compound in which a carbonyl group was attached to the particular functional group. This was intended to cover adducts with species such as BF$_3$ and SbCl$_5$ and it is a reasonable procedure. Meerwein ascribed the increased reactivity of coordinated species to the considerably greater dipole moments possessed by the adducts.[15] This presumably provides a path of lower activation energy in a large number of reactions in which a charged or highly polar attacking species is involved *if the orientation of the attacking species* favored by the large dipole moment is the proper one for the given reaction. Meerwein also reasoned that coordination of an unsaturated linkage, such as —C=C—, should increase the ease with which it undergoes addition reactions. This statement was based on the behavior of α,β-unsaturated ketones.

Meerwein studied a number of reactions in which coordination was involved, including the splitting of coordinated ethers,[16]

$$(C_2H_5)_2O + C_6H_5COCl \xrightarrow{ZnCl_2} C_2H_5-O\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + C_2H_5Cl$$

the methylation of alcohols,[17]

$$C_4H_9OH + CH_2N_2 \xrightarrow{FeCl_3} C_4H_9OCH_3 + N_2$$

$$\underset{H}{\overset{R}{>}}O\cdots Al(OR)_3 + CH_2N_2 \longrightarrow \underset{CH_3}{\overset{R}{>}}O\cdots Al(OR)_3 + N_2$$

12. H. Meerwein, *Schriften Konigsberger Gelehrten Ges. Naturw. Kl.* **3**, 129–166 (1927).
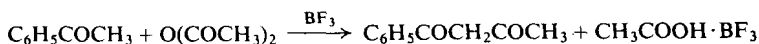13. H. Meerwein, *Ann. Chem. Liebigs* **455**, 227–253 (1927).
14. H. Meerwein, *Marburger Sitzber.* **65**, 119–135 (1930).
15. See for example: H. Ulich and W. Nespital, *Angew. Chem.* **44**, 750 (1931).
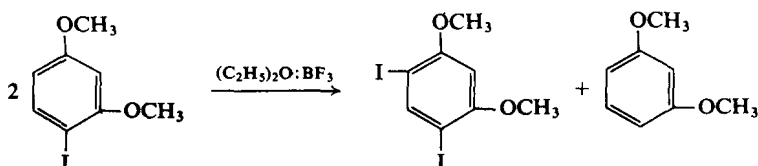16. H. Meerwein and H. Maier-Hüser, *J. Prakt. Chem.* **134**, 51–81 (1932).
17. H. Meerwein and G. Hinz, *Ann. Chem. Liebigs* **484**, 1–25 (1931).

the use of boron trifluoride for syntheses,[18]

$$C_6H_5COCH_3 + O(COCH_3)_2 \xrightarrow{BF_3} C_6H_5COCH_2COCH_3 + CH_3COOH \cdot BF_3$$

the migration of aromatic iodo groups in the presence of BF_3 complexes,[19]

and the addition of diazomethane to anhydrous acetone, which is catalyzed by lithium chloride, presumably via the formation of a complex.[20]
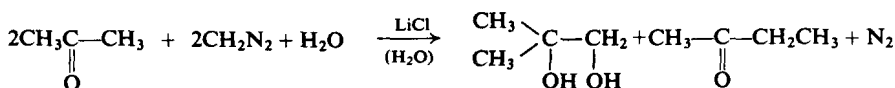
Meerwein also showed that the general principles he had proposed could serve as a valuable guide to the development of new synthetic procedures.

In the years between the First and the Second World Wars, there are to be found a number of studies of ligand reactions of a different type than those examined by Meerwein. Among these, the work of Pfeiffer and of Hölzl are of special interest. Pfeiffer studied several reactions in which the coordination of an ester or an ether to a metallic chloride (such as $SbCl_5$ or $SnCl_4$) gives a product that splits off an alkyl halide when heated. These included complexes formed by oxalic acid esters[21]
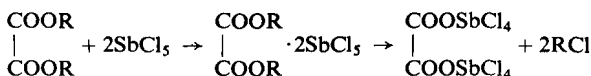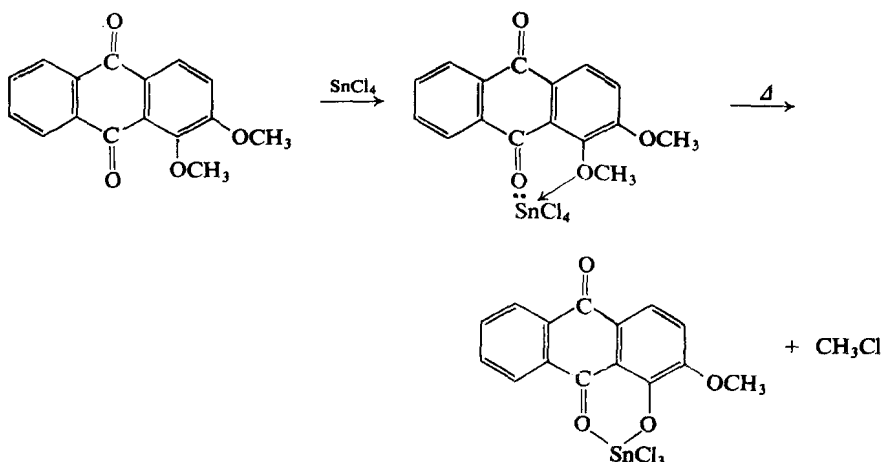
18. H. Meerwein, *Ber. Deut. Chem. Ges.* **66B**, 411–414 (1933).
19. H. Meerwein, P. Hoffman, and F. Schill, *J. Prakt. Chem.* **154**, 266–283 (1940).
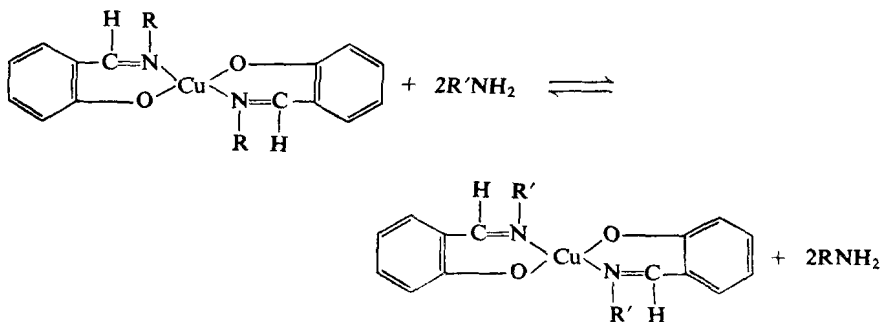20. H. Meerwein and W. Burneleit, *Ber. Deut. Chem. Ges.* **61**, 1840 (1928).
21. P. Pfeiffer, *Z. Anorg. Allgem. Chem.* **133**, 101–106 (1924).

and ethers cf alizarin[22]:

Later work included studies of the complexes formed with ketones by Grignard reagents,[23] and the exchange of amine moieties in inner complex salts of Schiff bases.[24] This last reaction is of the type

Shortly afterward, Pfeiffer reported that the use of optically active amino acid esters (to furnish the amine) in Schiff base chelates with copper, resulted in the racemization of the asymmetric center.[25] When the attempt was made to prepare the corresponding nickel chelates an oxidative reaction occurred and the nickel chelate of salicylaldimine was obtained.
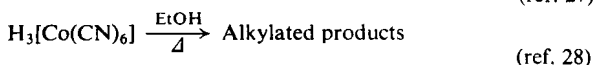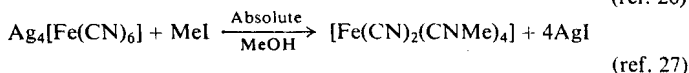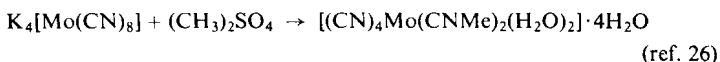
22. P. Pfeiffer, P. Fischer, J. Kuntner, P. Monti, and Z. Pros, *Ann. Chem. Liebigs* **398**, 137–196 (1913).
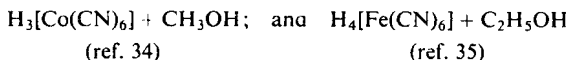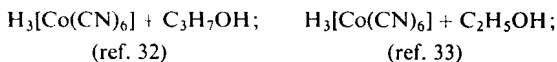23. P. Pfeiffer and H. Blank, *J. Prakt. Chem.* **153**, 242–256 (1939).
24. P. Pfeiffer and H. Glaser, *J. Prakt. Chem.* **153**, 265–284 (1939).
25. P. Pfeiffer, W. Offermann, and H. Werner, *J. Prakt. Chem.* **159**, 313 (1942).

The work of several other investigators, such as that of Hölzl and Baudisch, is roughly contemporaneous with that of Pfeiffer. Hölzl's studies were concerned with the reactions of cyanide complexes. He and his co-workers examined the alkylation of these compounds by the use of a variety of alkylating agents: $(CH_3)_2SO_4$, CH_3I, and alcohols. Examples of these reactions include

$$K_4[Mo(CN)_8] + (CH_3)_2SO_4 \rightarrow [(CN)_4Mo(CNMe)_2(H_2O)_2] \cdot 4H_2O$$

(ref. 26)

$$Ag_4[Fe(CN)_6] + MeI \xrightarrow[\text{MeOH}]{\text{Absolute}} [Fe(CN)_2(CNMe)_4] + 4AgI$$

(ref. 27)

$$H_3[Co(CN)_6] \xrightarrow[\Delta]{\text{EtOH}} \text{Alkylated products}$$

(ref. 28)

Hölzl also carried out similar reactions with $H_4[W(CN)_8]$,[29] cadmium cyanides,[30] and $K_3Cr(CN)_6$.[31] Studies of the reactions of the parent acids of complex cyanides and alcohols showed that the products were often complex and that the degree of alkylation was generally slight. Some related systems examined were

$$H_3[Co(CN)_6] + C_3H_7OH; \qquad H_3[Co(CN)_6] + C_2H_5OH;$$

(ref. 32) (ref. 33)

$$H_3[Co(CN)_6] + CH_3OH; \quad \text{and} \quad H_4[Fe(CN)_6] + C_2H_5OH$$

(ref. 34) (ref. 35)

Hölzl's work revealed that reactions carried out on complexes with a number of identical functional groups result in a mixture of products and that such systems are often difficult to characterize thoroughly.

O. Baudisch and his co-workers emphasized the viewpoint that organic ligands that are coordinated to a metal ion become activated and more easily available for oxidative cleavage or chemical replacement.[36-41] Baudisch used

26. F. Hölzl and G. I. Xenakis, *Monatsh. Chem.* **48**, 689–709 (1924).
27. F. Hölzl, *Monatsh. Chem.* **48**, 71–86 (1927).
28. F. Hölzl, T. Meier-Mohar, and F. Viditz, *Monatsh. Chem.* **53/54**, 237–245 (1929).
29. F. Hölzl, *Monatsh. Chem.* **51**, 1–22 (1929).
30. F. Hölzl and S. Kirschmayr, *Monatsh. Chem.* **51**, 397–419 (1929).
31. F. Hölzl and F. Viditz, *Monatsh. Chem.* **49**, 241–264 (1928).
32. F. Hölzl, W. Brell, and G. Schinko, *Monatsh. Chem.* **62**, 349 (1933).
33. F. Hölzl and G. Schinko, *Monatsh. Chem.* **58**, 249 (1931).
34. F. Hölzl and S. Sallmann, *Monatsh. Chem.* **58**, 29–46 (1931).
35. F. Hölzl and J. Krakora, *Monatsh. Chem.* **64**, 97–105 (1934).
36. O. Baudisch, *Biochem. Z.* **232**, 35 (1931).
37. O. Baudisch, *Ber. Deut. Chem. Ges.* **62**, 2699 (1929).
38. O. Baudisch and D. Davidson, *J. Biol. Chem.* **71**, 501 (1927).
39. M. H. Pfaltz, *J. Am. Chem. Soc.* **45**, 2980 (1923).
40. M. H. Pfaltz and O. Baudisch, *J. Am. Chem. Soc.* **45**, 2972 (1923).
41. O. Baudisch, *Ber. Deut. Chem. Ges.* **54**, 406 (1921).

pentacyanoaquoferrate(II) as a catalyst; here the water can be displaced as a ligand by a large variety of organic molecules such as pyridine, nitrosobenzene, p-nitrosodimethylaniline, and pyrimidines. Baudisch also postulated that when this complex functioned as a catalyst for oxidation reactions, it did so by activating molecular oxygen by coordination in the complex $[Fe(CN)_5(O_2)]^{3-}$. Earlier work of Manchot[42] showed that pentacyanoammineferrate(II) absorbed carbon monoxide, nitric oxide, and oxygen from the air but the oxygen oxidizes the iron(II) to iron(III). (Manchot had previously shown that hemoglobin and ethylene form a weak complex.[43]) Baudisch found that the pentacyanoammineferrate catalyzed oxidations by molecular oxygen by a redox process that involved the iron in two different oxidation states, either of which could be added to obtain the catalyst.

Though not concerned directly with the reactions of coordinated ligands, Pfeiffer and Wizinger's paper on the mechanism of aromatic substitution[44] is worthy of note as being the first paper in which the action of halogen carriers, such as $FeCl_3$, was ascribed to the ability of these substances to form co-ordinate bonds with the halogen and to assist the reaction by this process.

A number of other studies of the reactions of coordinated ligands may be found in the literature prior to 1940. Some of those that approach this from the viewpoint of coordination chemistry are listed in Table I.

In addition to these studies there are a very large number that were carried out on systems in which the complex was not characterized at the time. These include many studies of reactions such as the Friedel-Crafts, the Fries, and halogenation reactions carried out with halogen carriers derived from metallic halides. Although the complexes in such systems are often less thoroughly characterized, they are among the most interesting because of their direct involvement in important metal-catalyzed reactions. Many of these will be cited later when the behavior they exemplify is discussed in more detail. It should be noted that the complexes most used in *organic chemistry* are labile ones that rapidly reach equilibrium with their environment as it is altered. This makes their characterization *in the reaction media* often a task of very considerable difficulty. In many cases the exact composition of the complexes present in the multicomponent reaction mixtures is still uncertain and the reactive forms of the complexes are not agreed upon in several *important* reactions.

1.3. Classification Schemes

It is usually found convenient to set up some kind of a classification scheme if one wishes to consider a large number of different reactions in some

42. W. Manchot, *Ber. Deut. Chem. Ges.* **45**, 2869 (1912).
43. W. Manchot, *Ann. Chem. Liebigs* **370**, 241 (1909).
44. P. Pfeiffer and R. Wizinger, *Ann. Chem. Liebigs* **461**, 138–139 (1928).

TABLE I

SOME STUDIES OF THE REACTIONS OF LIGANDS PRIOR TO 1940

Reaction	Reference
Reaction of nickel dimethylglyoxime with acetic anhydride	45
Acetylation of the lead salts of aminothiophenols	46
Esterification of the zinc iodide–ether complex with benzoyl chloride	47
Amination of 3-bromopyridine in the presence of a copper salt	48
Stabilization of aliphatic diazo compounds as CuCl adducts	49
Nonreactivity of carbonyl group of metal acetylacetonates with phenyl-hydrazine	50
Oxygen absorption of manganous acetylacetonate	51
Methyl iodide and the silver salt of o-aminobenzoic acid	52
Reactions of copper enolates	53
Reactions of various complexes	54
Halogenation of cupric ethylacetoacetate	55
Failure of nickel dimethylglyoxime to react with phenyl isocyanide	56
Reaction of copper acetylacetonate and S_2Cl_2	57

systematic fashion. The reactions of coordinated species form such a hetero-geneous group that some such classification scheme is necessary if any order is to be discerned at all. The type of classification scheme may be expected to vary with the viewpoint of its originators and inorganic, organic, or biological chemists may be expected to favor radically different schemes. Another point of choice is whether the classification is primarily to assist in the application of such reactions to new situations or whether the goal is a much deeper theoretical understanding of the basic processes at work.

45. M. F. Barker, *Chem. News* 130, 99 (1925).
46. H. Bauer and K. Bursshkies, *Ber. Deut. Chem. Ges.* 66, 1041 (1933).
47. E. Blaise, *Compt. Rend.* 140, 661 (1905).
48. H. J. Den Hertog and J. P. Wibaut, *Rec. Trav. Chim.* 55, 122 (1936).
49. O. Diels and W. Kohl, *Ann. Chem. Liebigs* 443, 262 (1925).
50. R. Emmert and O. Schneider, *Ber. Deut. Chem. Ges.* 69, 1316 (1936).
51. R. Emmert, H. Gsottschneider, and H. Stanger, *Ber. Deut. Chem. Ges.* 69, 1319 (1936).
52. P. Karrer, C. Nageli, H. Weidmann, and L. Wilbuschewich, *Helv. Chim. Acta* 2, 242 (1919).
53. A. Michael and G. H. Carlson, *J. Am. Chem. Soc.* 58, 353 (1936).
54. H. Reihlen, R. Illig, and R. Wittig, *Ber. Deut. Chem. Ges.* 58, 12 (1925).
55. B. Schonbrodt, *Ann. Chem. Liebigs* 253, 171 (1889).
56. L. Chugaev, *J. Chem. Soc.* 105, 2192 (1914).
57. M. Vaillant, *Compt. Rend.* 119, 647 (1894).

The first classification scheme was that of Martell and Calvin[58] who restricted their attention to *chelate* catalyst systems. The three kinds of reactions they listed are

(1) Reactions in which the chelate underwent no permanent chemical change (e.g., reversible redox systems such as those found with oxygen-carrying chelates).

(2) Reactions in which the donor group underwent a chemical reaction such as oxidation, halogenation, or rearrangement. An example of this is the catalytic oxidation of oxalates by Mn(III).

(3) Negative catalysis resulting from the removal of catalytically active metals by the chelating agent, for example, the inhibition of hemoglobin by carbon monoxide.

Chaberek and Martell[59] used a similar scheme but modified the second class to include reactions in which either the donor group or the metal ion suffered some permanent chemical change.

A rather different scheme was presented by Beck.[60] He divided the catalytic reactions of coordination chemistry into

(1) Catalysis of the formation of complex compounds, including
    (a) coordination catalysis by either the ligand or the cation;
    (b) catalysis of redox reactions;
    (c) heterogeneous catalysis.
(2) Catalysis by complex compounds.

Another classification scheme, oriented toward a phenomenological classification, was given by Jones and Connor.[61] The classes given by this scheme are

(1) Reactions in which coordination allows the ligand and another reactant to come together more easily for reaction in a mixed complex.

(2) Reactions in which the polarization of the ligand by the positive charge on the central metal ion is the principal source of any change in reactivity.

(3) Instances in which coordination stabilizes a ligand in a form especially suitable for certain reactions.

(4) Reactions in which coordination masks one or more of the reactive

58. A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," p. 336 ff. Prentice-Hall, Englewood Cliffs, New Jersey, 1952.
59. S. Chaberek and A. E. Martell, "Organic Sequestering Agents," p. 378 ff. Wiley, New York, 1959.
60. M. T. Beck, *J. Inorg. Nucl. Chem.* **15**, 250 (1960). A more detailed scheme is presented by this same author in *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **27**, 37 (1966).
61. M. M. Jones and W. A. Connor, *Ind. Eng. Chem.* **55** (9), 14 (1963).