

Patterns of Organometallic Reactions Related to Homogeneous Catalysis

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Patterns of mechanistically similar transformations which are related to the function of homogeneous catalysts are evident when one considers the formal d^n electronic configuration and coordination number of the central metal atom. Applications of concepts such as coordinative unsaturation, oxidative addition, and intramolecular atom transfer redox reactions are illustrated. Catalytic acetylene cyclization, complexes of molecular nitrogen, and reactions of coordinated oxygen are discussed in the framework of these ideas.

The origin of modern organo transition metal chemistry can be traced to the discovery of ferrocene in 1951.¹ The following decade was necessarily dominated by considerations of bonding and structure. This period was illuminated by discoveries of hitherto unknown structural types such as cyclobutadiene² and carbene³ complexes. This profusion of novel structures shows no indication of abating.

Spurred by a growing interest in homogeneous catalysis, recent emphasis has been given to reactions of organo-transition metal complexes. Chemists have long found it useful to organize organic chemistry into patterns of mechanistically related transformations. It has become apparent that analogous patterns are also to be found among reactions of organo-transition metal compounds. This is particularly evident when the chemistry of these complexes is considered on the basis of the formal electronic configuration and coordination number of the central metal rather than in the context of a particular ligand or metal. Such correlations can serve as a framework for the development of homogeneous catalysis on a rational rather than an empirical basis. Presently organo-transition metal chemistry occupies a position similar to that of organic chemistry in the late 1940's when concepts of reaction mechanisms had developed to a point where new syntheses could be invented and put into experimental practice with some degree of confidence.

This essay is an attempt to describe some reaction patterns among organometallic complexes of the later transition elements and to indicate the relationships that these reaction types have to homogeneously catalyzed processes.

The working definition of oxidation state used herein is the charge left on the central metal after the ligands have been removed in their "normal" closed-shell configuration. Inasmuch as this definition is based on valence-bond formalism (*i.e.*, the drawing of line

bonds), instances of indeterminate oxidation state arise. Notions of localized bonds are also used to denote coordination number. For the purposes of computing d^n , the d electrons are considered to be in nonbonding levels directed away from the ligands. However imprecise, the concepts of oxidation state, d electron configuration, and coordination number are useful in providing a framework for organizing transition metal chemistry.

Coordinative Unsaturation

A vacant coordination site is perhaps the single most important property of a homogeneous catalyst.⁴ Latent coordination sites are not only necessary to activate a substrate molecule by bringing it into the coordination sphere, but coordinatively unsaturated complexes are especially reactive in migration^{5,6} and oxidative-addition⁷ reactions. The role of sulfur compounds, phosphines, and carbon monoxide as antagonists in both heterogeneously and homogeneously catalyzed reactions can be understood in terms of saturation of essential coordination sites. Induction periods and the requirement of thermal or photochemical stimulation are usually indications that the active catalyst is formed by expelling a ligand.

In a discussion of coordinative unsaturation, it is important to recognize the maximum coordination numbers for the different values of d^n . Considering only d^6 , d^8 , and d^{10} spin-paired configurations, six-, five-, and four-coordinate complexes are saturated and five-, four-, and three- (or two-) coordinate complexes are unsaturated. Coordinative unsaturation is often destroyed by forming bridged compounds, particularly with halide, hydroxide, and sulfur ligands. For this reason, the latter two ligands are seldom present in active homogeneous catalysts. Contributions from $(n + 1)p$ electrons have been ignored in this discussion.

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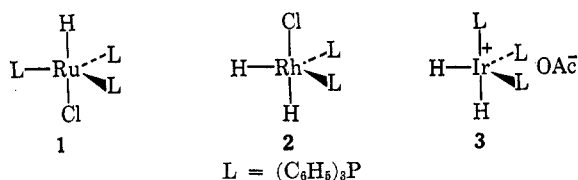
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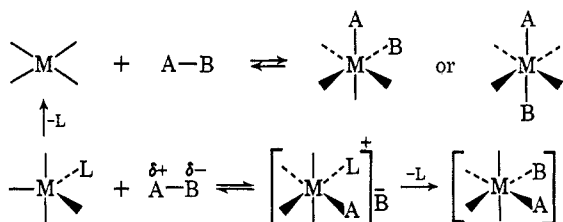
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The relationships between coordinative unsaturation, d^n , and catalytic activity may be illustrated by considering the catalysts **1–3**. Each is a five-coordinate (unsaturated) d^8 complex. Hydrogenations of terminal olefins⁸ (accompanied by isomerism and hydrogen scrambling), of unhindered olefins⁹ (stereospecific *cis* addition), and of aldehydes¹⁰ are catalyzed by **1**, **2**, and **3**, respectively. The Wilkinson hydrogenation catalyst $\text{RhCl}(\text{PPh}_3)_3$ (where L represents triphenylphosphine) loses a phosphine ligand and adds hydrogen to form the active form **2**. In the analogous iridium compound, $\text{IrCl}(\text{PPh}_3)_3$,^{11,12} the phosphines are bound more tightly, and the latter is not a hydrogenation catalyst¹³ even though it readily adds hydrogen. Further examples of the role of vacant coordination sites are described below.



Oxidative Addition to d^8 Complexes

Complexes of metals having a d^8 configuration are often converted into octahedral d^6 complexes by the addition of a covalent molecule to the coordination sphere.¹⁴ Coordinatively unsaturated d^8 complexes



reversibly add molecules such as protonic acids,^{15–17} alkyl halides,^{17–19} acyl halides,^{17,19} metal halides,^{20,21} halogens,²² pseudo-halogens,¹⁷ hydrogen,^{23–26} oxy-

gen,^{26,27} acetylenes,²⁸ and olefins.²⁸ Coordinatively saturated d^8 complexes (usually having a trigonal-bipyramidal configuration) react with polar or highly polarizable addenda such as protonic acids,²⁹ mercuric halides,³⁰ halogens,²⁹ and pseudo-halogens in a two-step mechanism, the second step being the irreversible loss of a neutral ligand such as carbon monoxide. Alternatively, five-coordinate d^8 complexes can react through dissociation of a ligand prior to oxidative addition.

Attention was drawn to these addition reactions by Vaska's²³ discovery of the planar iridium(I) carbonyl **4**. This complex undergoes a bewildering number of oxidative-addition reactions which may be conveniently followed by the shift in the infrared band of the CO group to a higher frequency as the degree of back-bonding is diminished through oxidation of iridium from I to III (Figure 1). These reversible additions

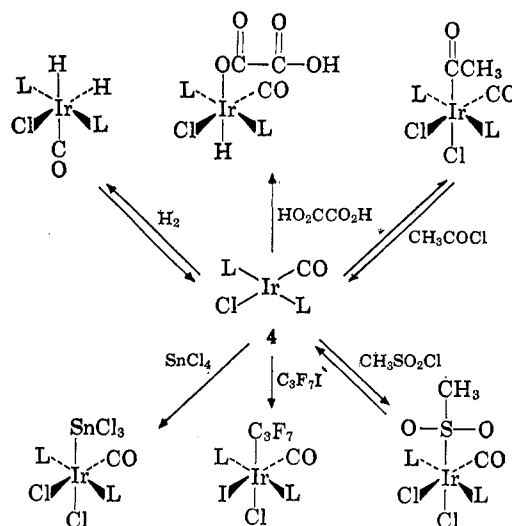


Figure 1.

often occur in a stereospecific manner; both *cis*^{26,31} and *trans*¹⁷ modes of addition have been observed depending on the reagent and the medium. The similarity between these addition reactions and chemisorption at a transition metal surface is apparent. Thus it is not surprising that such additions are often key steps in the mechanisms of homogeneously catalyzed reactions such as hydrogenation,^{25,32} hydroformylation,^{33,34} and olefin dimerization.^{35,36}

The tendencies for d^8 complexes to undergo oxidative addition depend markedly on the nature of the

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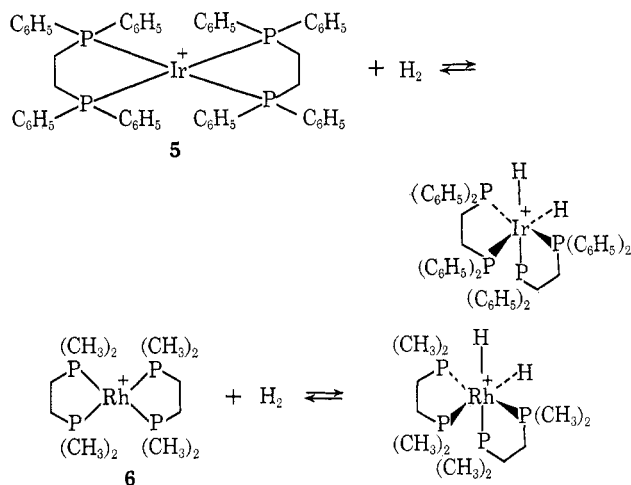
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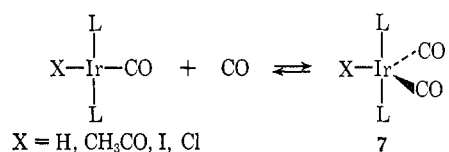
central metal ion and the ligands associated with it. Meaningful comparisons can only be made between complexes having the same coordination number and ancillary ligands. This is usually only possible for isostructural complexes within a given triad. The propensity of d^8 metals to undergo oxidative addition follows the familiar pattern of transition metal chemistry, increasing upon descending a triad or passing from right to left. Considering complexes in group VIII, it is easier to oxidize Pt(II) to Pt(IV) than Ni(II) to Ni(IV), but oxidation of Os(0) to Os(II) is more facile than Pt(II) to Pt(IV).

Ligands which increase electron density at the central metal enhance the tendency of a complex to undergo oxidative addition. These qualitative generalizations can be illustrated by considering the reaction of hydrogen, a reagent which adds to only the most active d^8 complexes. Whereas the iridium(I) carbonyl **4** readily forms an adduct with hydrogen, the isostructural rhodium carbonyl does not. The binding constant for the hydrogen adduct is greater for $X = I$ than for $X = Cl$.¹⁸ Bis(1,2-bis(diphenylphosphino)ethane)iridium cation (**5**) readily adds hydrogen,²⁶ but the rhodium analog does not; however, the similar bis(1,2-bis(dimethylphosphino)ethane)rhodium complex (**6**) does add hydrogen.³⁷ Similar effects can be found among other reactions of d^8 complexes with a variety of reagents.¹⁴



It is appropriate to consider here the factors influencing the tendency of coordinatively unsaturated d^8 complexes to achieve coordinative saturation by taking up a fifth ligand. Upon ascending a triad or passing from right to left within group VIII, the trend is for a d^8 complex to become coordinatively saturated.³⁸ Thus the stabilities of the pentacarbonyls ($M(\text{CO})_5$) toward CO dissociation are $\text{Fe} > \text{Ru} > \text{Os}$ and Pt(II) complexes have a pronounced inclination to be four-coordinate, whereas most Fe(0) complexes are five-coordinate. Planar d^8 complexes are capable of

forming three $d-\pi$ back-bonds, but trigonal-bipyramidal d^8 complexes can form four such π bonds. In the presence of effective π -acceptor ligands, an increase in electron density at the central metal stabilizes the five-coordinate form. That polarizable "soft" ligands promote the formation of the saturated complex is illustrated by the equilibria shown below where the stability of the five-coordinate form **7** follows the order $X = \text{H} \sim \text{CH}_3\text{CO} > \text{I} > \text{Cl}$.³⁹ Unfortunately quantitative equilibrium constants for such reactions have not yet been reported. The basis for the *trans* effect⁴⁰ of σ -bonding ligands such as hydride in nucleophilic displacement reactions of four-coordinate d^8 complexes probably lies in the stabilization of a five-coordinate intermediate.



The activation of hydrogen by oxidative addition to a metal complex—a key step in the function of homogeneous hydrogenation catalysts—can be used to illustrate the importance of equilibria between reactive unsaturated and relatively inert saturated d^8 complexes. Iron pentacarbonyl becomes a hydrogenation catalyst at temperatures above 160° .^{41,42} It is probable that this temperature is required to extrude CO and form $\text{Fe}(\text{CO})_4$ which can undergo oxidative addition with H_2 . On the other hand, $\text{Os}(\text{CO})_5$ reacts with H_2 at temperatures as low as 80° , forming a stable dihydride, $\text{OsH}_2(\text{CO})_4$, whose catalytic activity is unknown.⁴³ At temperatures below 150° the related ruthenium⁷ and osmium bis(triphenylphosphine)²⁹ complexes, *trans*- $M(\text{CO})_3\text{L}_2$, neither lose CO nor add H_2 , in spite of the increased activation toward oxidative addition expected when two CO ligands are replaced by phosphines. The stabilization of these complexes toward loss of CO can be explained by the synergistic effect of the phosphine ligands which increase back-bonding to the CO groups. These qualitative experiments suggest that five-coordinate d^8 complexes are incapable of adding H_2 . It is interesting that the ruthenium complex, $\text{Ru}(\text{CO})_3\text{L}_2$, when irradiated ($365 \text{ m}\mu$) does react with hydrogen, forming an unstable photoproduct which is capable of hydrogenating cyclohexene (dark reaction).⁴⁴

These ideas are useful in considering the remarkable reaction wherein a five-coordinate cobalt(I)-nitrogen

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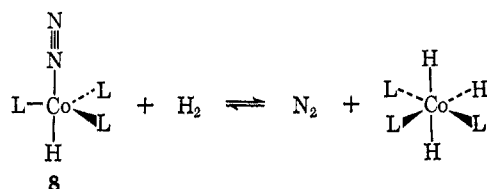
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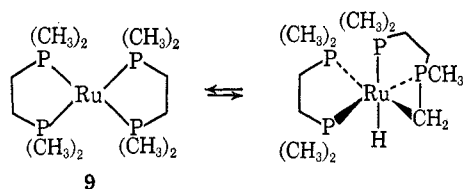
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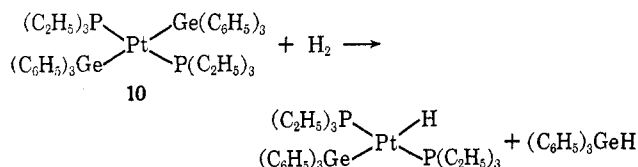
complex, **8**,⁴⁵ reversibly adds hydrogen and loses nitrogen. It seems likely that the nitrogen ligand is dissociated prior to reaction with hydrogen since the five-coordinate d^8 complex **8** is not likely to add hydrogen, and nitrogen is a deactivating ligand toward oxidative addition (*cf.* below). The other ligands on **8** tend to enhance the electron density at cobalt and promote back-bonding to nitrogen. Ibers has recently determined the structure of **8** by X-ray diffraction.⁴⁶



It is logical to wonder about the extreme limits of reactivity which d^8 complexes might exhibit. One would expect the most reactive d^8 compounds to be found in the lower left-hand corner of group VIII among four-coordinate complexes containing activating ligands. The tautomeric behavior of the ruthenium(0) complex **9**, which inserts into a C-H bond of a methyl group on one of its ligands,⁴⁷ illustrates the extreme in oxidative addition. The analogy to chemisorption of aliphatic C-H bonds on transition metal surfaces is notable.



The reversibility of oxidative-addition reactions provides a mechanism for the interchange of groups between the addendum and the d^8 complex. An example is the facile hydrogenolysis⁴⁸ of Pt-Ge bonds in **10**—a reaction which is thought to go through oxidative addition.



Another type of addition-elimination is encountered in the reaction of the iridium(I) carbonyl **4** with organic azides to form an isocyanate and a stable iridium-nitrogen complex, **11** (Figure 2).^{49,50} It is necessary to intercept the acyl isocyanates by trapping them with

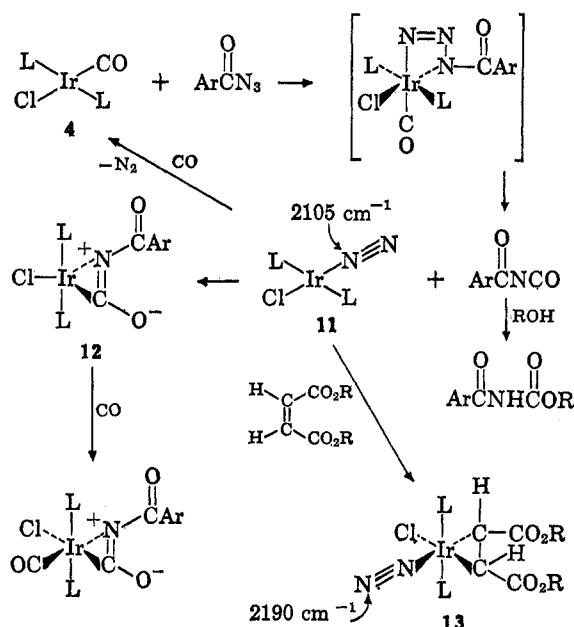


Figure 2.

an alcohol, otherwise these replace nitrogen, affording novel coordinatively unsaturated complexes provisionally formulated as **12**.⁵⁰ The analogous rhodium(I) carbonyl reacts similarly with azides, but the resulting nitrogen complex is extremely reactive and can only be isolated at low temperatures.⁵¹ The rate law for the azide reaction has the form

$$-\frac{d[\text{MCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]}{dt} = k[\text{RN}_3][\text{MCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$$

Activation parameters have been measured for the reaction between the iridium carbonyl chloride and α -furoyl azide in chloroform.⁵² The small enthalpy of activation, $\Delta H^\ddagger = 8$ kcal/mol, and large negative entropy of activation, $\Delta S^\ddagger = -37$ eu, are consistent with a transition state or intermediate which is an oxidative adduct. The effects on the reaction rate of changing the azide, the phosphine ligands, the halide ligand, and the metal have been studied. The influence of these variables on the rate follows the order $\text{C}_6\text{H}_5\text{CON}_3 > \text{C}_6\text{H}_5\text{N}_3 > \text{CH}_3\text{C}_6\text{H}_4\text{N}_3$; $\text{C}_6\text{H}_5\text{P}(\text{C}_2\text{H}_5)_2 > (\text{C}_6\text{H}_5)_2\text{PCH}_3 > (\text{C}_6\text{H}_5)_3\text{P}$; $\text{I} > \text{Br} > \text{Cl} > \text{N}_3$; and $\text{Ir} > \text{Rh}$.⁵² From these relative rates it is apparent that the central metal is acting as a base and the azide as an acid—behavior consistent with the idea that the reaction involves intermediate oxidative addition. Treatment of the nitrogen complex **11** with CO regenerates the starting carbonyl **4**.⁵³ Thus the iridium complex can serve as a catalyst for the atom transfer redox reaction between organic azides and carbon

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monoxide, a process which does not take place under these conditions in the absence of the catalyst. It is probable that many other types of atom transfer redox reactions can be catalyzed by incorporating oxidizing and reducing agents in *cis* positions of a coordination sphere.⁵³ This hypothesis is currently being investigated.

The quest for a substance which will catalyze the reduction (or oxidation) of molecular nitrogen under moderate conditions has long challenged chemists. This problem is made more intriguing by the existence of aerobic and anaerobic nitrogen-fixing microorganisms which function through the agency of metalloenzymes.⁵⁴ The magnitude of the modern commercial Haber process for ammonia production and the projected growth of ammonia consumption brought about by the world food crisis heighten interest in this problem.

A great deal of excitement has resulted from recent preparations of transition metal complexes containing molecular nitrogen as a ligand.^{45, 49, 55-60} These were followed by reports of transition metal complexes which reversibly bind gaseous nitrogen,^{45, 59} as well as an organic compound which captures nitrogen.⁶¹

Coordinated nitrogen has been shown to be susceptible to reduction by chemical reducing agents such as sodium borohydride.⁵⁵ Volpin⁶² has shown that various combinations of transition metal complexes and reagents such as aluminum alkyls or Grignard reagents effect the stoichiometric reduction of nitrogen to ammonia, the NH_3/metal ratio approaching but not exceeding unity. Similar systems have been reported by Olive.⁶³

Brintzinger⁶⁴ investigated the mechanism of the reaction between titanocene dichloride, ethyl Grignard reagent, and nitrogen. His experimental data support a mechanism involving the formation of a bridged nitrogen complex in which each metal center possesses a hydride. This picture is supported by recent kinetic studies.⁶⁵ Brintzinger has emphasized the apparent parallels between this system and enzymatic nitrogen fixation.⁵⁴ The nitrogen-fixing enzymes contain at least two metals (nonheme iron and occasionally molybdenum) at the active site. The ATP requirement of these enzymes and the formation of hydrogen in the absence of substrate are suggestive

of the presence of metal hydride groups. Sulfide ligands are thought to stabilize the hydride groups (and probably promote back-bonding to the coordinated nitrogen). Strong inhibition by CO but to a lesser degree by cyanide indicates the binding of nitrogen as a bridged ligand. Recently Taube⁶⁶ has discovered a binuclear nitrogen complex which may have the linear $\text{RuN}=\text{NRu}$ configuration. This complex should serve as a model for binding of nitrogen in the biological systems.

In spite of the recent intense interest in this problem, the development of nitrogen-fixation catalysts is in an embryonic stage. All of the discoveries of nitrogen complexes to date have been accidental or empirical. Neither catalytic chemical reductions nor even stoichiometric hydrogenation of coordinated nitrogen has been described. Nevertheless, the problems are now clearly formulated, and their eventual solution cannot be questioned. Even when an efficient homogeneous (or heterogeneous) nitrogen-fixation catalyst is developed, it will be some time before such a system could become competitive with the extremely efficient modern Haber process.

There would seem to be four critical steps which a catalyst must perform in the hydrogenation of nitrogen: (a) coordinate with gaseous nitrogen to form a bridged complex, (b) form metal hydrides by oxidative addition of hydrogen, (c) promote hydride migration to coordinated nitrogen, and (d) dissociate the coordinated ammonia. Only the first stage has been achieved.

It is significant the iridium-nitrogen complex **11** fails to add hydrogen even at elevated pressures. Apparently nitrogen is deactivating toward oxidative addition compared with carbon monoxide. This result suggests that nitrogen may be a stronger π acid than carbon monoxide. Comparison of the nitrogen infrared stretching frequencies in the four- and five-coordinate nitrogen complexes **11** and **13**⁶⁴ supports the role of nitrogen as a back-bonding ligand. The factors which stabilize bridged nitrogen complexes are less certain. It is probable that bridging is required to sufficiently activate coordinated nitrogen for a hydride migration. That biological systems seem to function through bridged nitrogen complexes appears to support this supposition.

When the nitrogen complex is treated with disubstituted acetylenes, nitrogen is displaced affording a mononuclear acetylene complex formulated as **14** in which the acetylene acts as a bidentate ligand.²⁸ This complex should be considered as a five-coordinate iridium(III) compound since it can acquire an additional CO group. Controversy has centered about the question of whether there are two limiting types of acetylene complexes:²⁸ one in which the acetylene behaves as a unidentate ligand similar to an olefin complex and the other wherein acetylene behaves as a bidentate ligand in a metallocyclopropene structure.

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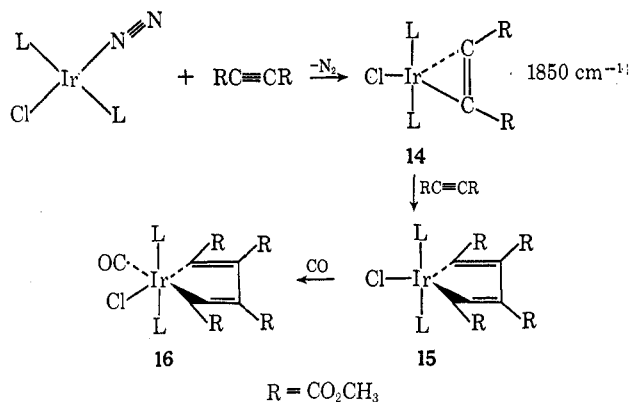
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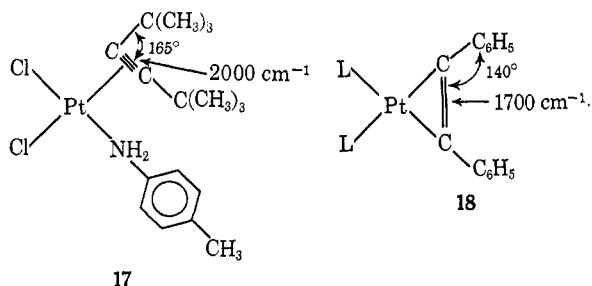
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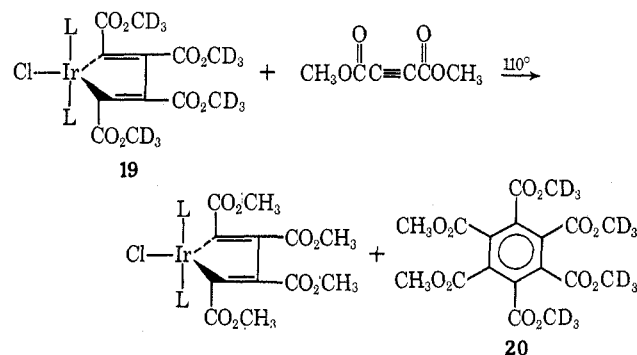


The first type is characterized by an acetylenic stretching bond at frequencies 150–200 cm⁻¹ lower than the uncoordinated acetylene, whereas the other exhibits a band lowered by 400–500 cm⁻¹. Recent independent X-ray diffraction studies have revealed structures **17** and **18** approximating each extreme.⁶⁷ Differences in the carbon-carbon bond angles characterize these limiting forms. Whether there are two discrete bond types (energy minima) or a gradual change from one limiting case to the other is an unsettled question, but the latter seems more likely. The near-trigonal angular disposition of acetylenic carbons in **18** leads one to anticipate the impending discovery of stable benzyne complexes. The first benzyne complex was reported⁶⁸ during the writing of this article.



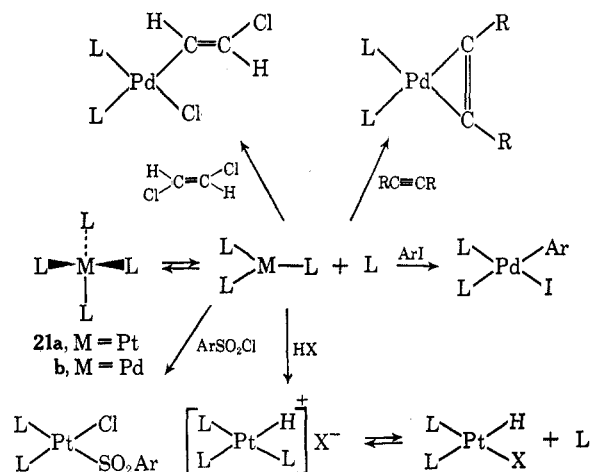
Mononuclear acetylene complexes **14** react with another mole of dimethyl acetylenedicarboxylate yielding a metalacyclopentadiene complex **15**.⁶⁹ That **15** is a coordinatively unsaturated complex of iridium(III) is revealed by its tendency to bind CO to form **16**. Above 100° the iridocycle **15** acts as a catalyst to cyclotrimerize excess acetylene. Using a perdeuterio-iridocycle¹⁹ it was shown that the iridocycle unit combines with another mole of acetylene to form dodeca-deuteriohexacarbomethoxybenzene,²⁰ generating a proto iridocycle. The vacant coordination site in **15** was found to be essential to the catalytic activity. Rhodium analogs behave similarly, but lower temperatures are required to catalyze trimerization. These

experiments confirm Meriwether's earlier hypothesis⁷⁰ that transition metal catalyzed trimerizations of di-substituted acetylenes go through metalacyclopentadiene intermediates. Metalacyclopentadiene complexes can be considered valence tautomers of cyclobutadiene complexes. Hagihara⁷¹ has reported a conversion of one of the former into the latter.



Oxidative Addition of d¹⁰ Complexes

Oxidative addition is not confined to d⁸ complexes but seems to be a general characteristic of basic transition metal compounds, especially coordinatively unsaturated complexes. Compounds having a formal d¹⁰ configuration have recently been found to undergo unusually facile oxidative-addition reactions.^{72–74} The most extensively studied d¹⁰ complex is PtL₄ (**21a**) which adds halogens, hydrogen halides, alkyl halides, acyl halides, sulfonyl halides, acetylenes, and oxygen.⁷² These additions appear to occur more rapidly and under milder conditions than the analogous reactions of d⁸ compounds. This is illustrated by the facile addition⁷⁴ of vinyl and aryl halides to PdL₄ (**21b**). The factors underlying oxidative-addition reactions of d¹⁰ complexes are not so well defined as those of d⁸ complexes. For example, little is known concerning the



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differences in reactivity between coordinatively saturated tetrahedral and unsaturated trigonal planar or dicoordinate linear d^{10} complexes. Undoubtedly the unsaturated d^{10} complexes will be found to be more reactive. The facile dissociation of platinum and palladium tetrakisphosphine complexes²¹ complicate the solution of this question.

The apparent failure of d^{10} complexes to add hydrogen lends support to the hypothesis⁷⁵ that reactions between transition metals and hydrogen take place by interaction of the bonding molecular orbital of the hydrogen molecule and an empty (antibonding) d orbital on the metal. Saturation of the d shell would preclude such an interaction.

Many of the organic reactions promoted by copper(I) complexes probably involve oxidative addition. An example is the elegant coupling reaction described by Corey.⁷⁶

Reactions of Oxygen Complexes

Molecular oxygen adds to several of the more reactive d^8 and d^{10} complexes to form diamagnetic compounds which retain an O—O bond.²⁷ Examples of such oxygen complexes are illustrated in Figure 3.

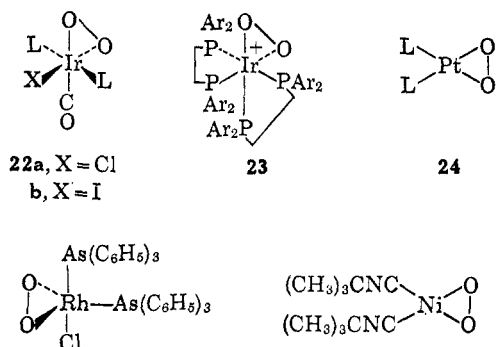
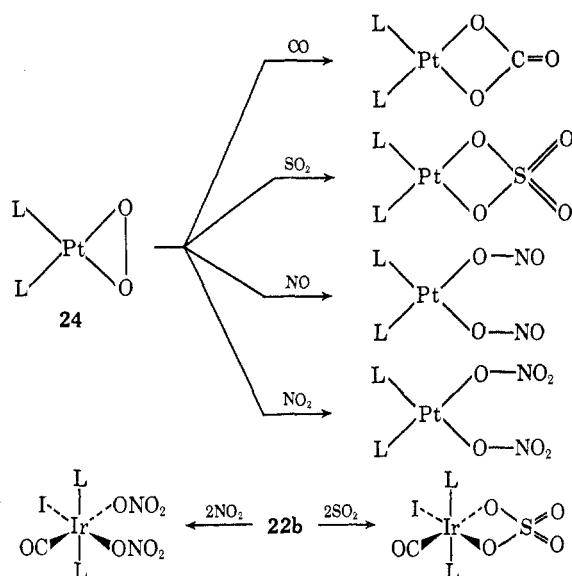


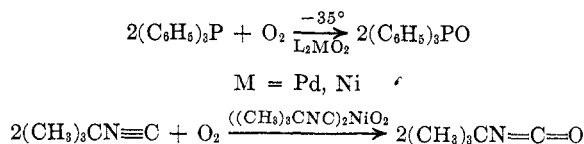
Figure 3.

By determining the structures of the oxygen complexes **22**^{27,77} and **23**,⁷⁸ Ibers discovered a remarkable trend in the O—O bond length. Both the O—O distance and the tendency to bind oxygen increase as the ancillary ligands become more electron releasing. For example, the O—O distances are 1.30 Å for the chloride complex **22a**, 1.51 Å for the analogous iodide **22b**, and 1.66 Å for the phosphine chelate **23**. The O—O bond length in **23** is 0.16 Å longer than that in organic peroxides.⁷⁸

The most significant property of these diamagnetic oxygen complexes is their ability to oxygenate sub-



strates under unusually mild conditions.⁵³ Both stoichiometric and catalytic oxidations have been described. For example, autoxidations of triphenylphosphine⁷⁹ and *t*-butyl isocyanide⁸⁰ are catalyzed by oxygen complexes of palladium and nickel.



Stoichiometric oxidations of gaseous nonmetal oxides are effected by oxygen complexes under very mild conditions. Reactions of the platinum oxygen complex **24** with CO,⁸¹ SO₂,^{72,82} NO,⁵³ and NO₂⁵³ and of the iridium complex **22b** with SO₂⁸² and NO₂⁸² are illustrated.

Reactions between singlet molecules and free (triplet) oxygen usually experience high activation energies⁸³ because of the problem of spin conservation.⁸⁴ Apparently this "symmetry barrier" may be overcome by forming singlet complexes between transition metals and oxygen. The long O—O bond length and diamagnetic character of these oxygen complexes suggest some similarity to singlet oxygen. However, one should remember that singlet oxygen is more energetic than the ground state by 23 kcal.⁸⁴

The mechanisms of these metal ion promoted autoxidations remain to be clarified. It seems likely that in many instances both the substrate and the oxygen molecule must be in the coordination sphere for oxygenation to take place. This supposition is

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supported by the facile oxidation of ligands such as CO, isocyanides, and phosphines by coordinatively unsaturated oxygen complexes. These reactions could then be considered as examples of metal ion promoted, atom transfer redox reactions discussed above.

The autoxidation of organic molecules is also catalyzed by these oxygen complexes.^{53,85} However, some of these reactions are inhibited by 2,4,6-tri-*t*-butylphenol, and it seems likely that these are chain radical processes. Nonradical autoxidative pathways may be found for organic substrates which can be incorporated in the coordination sphere adjacent to coordinated oxygen. The existence of numerous oxygenases,⁸⁶ metalloenzymes which catalyze the direct

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oxygenation of organic substrates (at least in some instances by nonradical pathways), sustains our expectation that nonradical, atom transfer oxidations of organic substrates by metal-oxygen complexes will be discovered.

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