

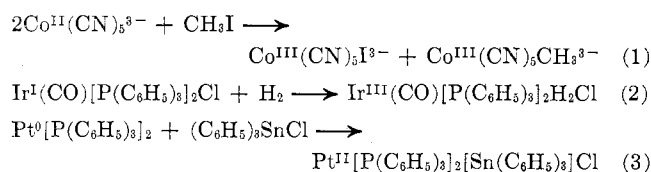
Oxidative-Addition Reactions of Transition Metal Complexes

JACK HALPERN

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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The term "oxidative addition" has come to be used to designate a rather widespread class of reactions, generally of low-spin transition metal complexes,¹ in which oxidation, *i.e.*, an increase in the oxidation number of the metal, is accompanied by an increase in the coordination number.² Illustrative of the reactions encompassed by this designation are the examples depicted by eq 1-3. This Account is concerned with the mechanisms and certain other features of such reactions.



The occurrence of oxidative-addition reactions is related to the pattern of characteristic coordination numbers of low-spin transition metal complexes depicted in Table I. Reflected in this pattern is an inverse dependence of the preferred coordination number on the d-electron population of the transition metal atom, a trend which becomes especially pronounced as the filling of the d subshell approaches completion. This trend reflects the constraints of the well-known "18-electron" (or "noble gas") rule, according to which stable configurations in such complexes are restricted to those in which the total number of valence electrons (comprising the d electrons of the metal and the σ -bonding electron pairs donated by each of the ligands) does not exceed 18.³ Closed-shell configurations corresponding to 18 valence electrons tend to be particularly stable and widespread (especially for complexes with good π -acceptor ligands, such as carbonyls), but

(1) The designation "low spin" (or "spin paired") refers to those transition metal complexes in which the ligand field splittings are sufficiently large that the d electrons first fill up (with pairing if necessary) all the available stable (bonding and nonbonding) orbitals before beginning to populate the antibonding orbitals. This class encompasses complexes of the first row (*i.e.*, 3d) transition elements with high-field ligands such as cyanide, carbon monoxide, phosphines, etc., as well as virtually all second and third row (*i.e.*, 4d and 5d) transition metal complexes.

(2) Our designation of oxidation numbers follows the generally accepted convention of "assigning" to the ligands in a complex the shared electron pairs which constitute the metal-ligand σ bonds. According to this convention the hydrogen ligand in hydride complexes is assigned the oxidation number 1-. Thus, the Co atom in the complex $\text{Co}(\text{CN})_5\text{H}^{3-}$ is assigned the oxidation number 3+, the Ir atom in $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}_2\text{Cl}$ the oxidation number 3+, etc. Reactions such as those depicted by eq 1-3, even when they involve addition of H_2 , thus correspond formally to "oxidation" of the metal, and the designation "oxidative addition" is considered appropriate for such reactions.

(3) This rule has a well-recognized origin in the familiar ligand field-molecular orbital description of transition metal compounds, according to which only nine stable (bonding and nonbonding) orbitals can be derived from the nine valence orbitals (*e.g.*, 3d, 4s, and 4p) of a transition metal atom.

configurations having fewer valence electrons, *e.g.*, square-planar d^8 complexes, also commonly occur.

One of the consequences of the trends described above is that the oxidations of certain classes of complexes (notably those with nearly filled d shells, *i.e.*, d^7 - d^{10}) are accompanied by increases in the preferred coordination numbers of the metal atoms and hence by the incorporation of additional ligands into their coordination shells. The ligands required to complete the coordination shells may in certain cases be derived from the oxidant itself and, indeed, such complexes are especially effective as reductants for molecular oxidants which undergo dissociative reduction to yield anionic ligands, *i.e.*, $\text{X-Y} + e^- \rightarrow \text{X}^- + \text{Y}^-$; $\text{X-Y} + 2e^- \rightarrow \text{X}^{2-} + \text{Y}^{2-}$.

Three such classes of reactions which have attracted particular attention in recent years are depicted in Chart I (encompassing the examples of eq 1-3), namely, the oxidative-addition reactions of five-coordinate d^7 , four-coordinate d^8 , and two-coordinate d^{10} complexes. In each of these cases the driving force for reaction is associated with the increase in stability in going from the initial open shell configuration (containing 17, 16, and 14 valence electrons, respectively) to the closed shell configuration of the product.⁴ The range of

Chart I
Oxidative-Addition Reactions

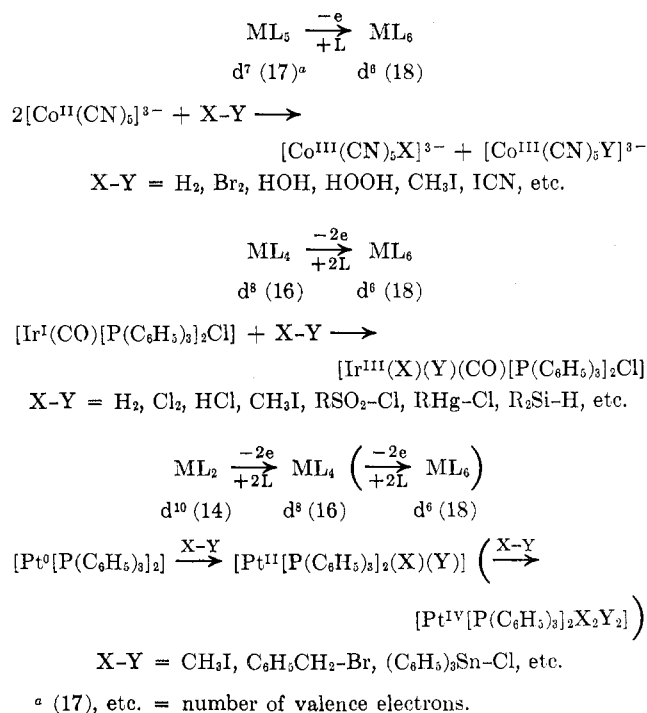
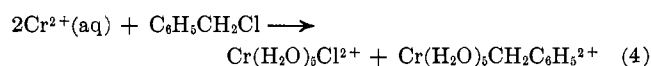


Table I
Characteristic Coordination Numbers of Low-Spin Complexes

Coordination no.	Examples	Electron configuration	Total no. of valence electrons
8	Mo(CN) ₈ ³⁻ , Mo(CN) ₈ ⁴⁻	d ¹ , d ²	17, 18
6	M(CN) ₆ ³⁻ (M = Cr, Mn, Fe, Co)	d ³ , d ⁴ , d ⁵ , d ⁶	15-18
5	Co(CN) ₅ ³⁻ , Ni(CN) ₅ ³⁻	d ⁷ , d ⁸	17, 18
4 (square planar)	Ni(CN) ₄ ²⁻	d ⁸	16
4 (tetrahedral)	Cu(CN) ₄ ³⁻ , Ni(CO) ₄ , Pt[P(C ₆ H ₅) ₃] ₄	d ¹⁰	18
3	Pt[P(C ₆ H ₅) ₃] ₃	d ¹⁰	16
2	Ag(CN) ₂ ⁻ , Pt[P(C ₆ H ₅) ₃] ₂	d ¹⁰	14

molecules which undergo oxidative addition to such complexes is very extensive and encompasses hydrogen, the halogens, hydrogen halides, water, and hydrogen peroxide, as well as various organic halides and metal halides which add through carbon-halogen and metal-halogen bonds, respectively. The oxidative addition of organic molecules through either carbon-carbon or carbon-hydrogen bonds is rare, although a few such cases are known and will be discussed later.

While, for the reasons discussed above, oxidative-addition reactions are especially characteristic of low-spin complexes with filled or nearly filled d subshells, certain high-spin complexes are known to undergo closely related reactions. A particularly striking example is chromium(II) (high-spin d⁴) whose reactions with halogens and organic halides (eq 4) closely resemble, in respect of both their stoichiometries and mechanisms, those of Co(CN)₅³⁻.⁶



The intensive study of oxidative-addition reactions in our own and other laboratories in recent years has encompassed the following themes. (1) The mechanisms of oxidative addition reactions, notably whether reactions such as (1) and (2) are concerted or stepwise processes. (2) The dependence of reactivity on electronic and structural factors, *e.g.*, comparisons of the reactivities toward oxidative addition (eq 2) of different square-planar d⁸ complexes such as Ir(CO)[P(C₆H₅)₃]₂Cl, Rh(CO)[P(C₆H₅)₃]₂Cl, and Rh[P(C₆H₅)₃]₃Cl. (3) Synthetic applications, notably in the synthesis of hydrido and organo transition metal compounds through the oxidative addition of hydrogen and of organic halides, respectively. (4) Catalytic applications, *e.g.*,

(4) The reactivity patterns of low-spin transition metal complexes are influenced by the great stability commonly associated with the (18 valence electron) six-coordinate d⁸ configuration (*e.g.*, Co(CN)₅³⁻, Co(CN)₅Cl³⁻, etc.) in much the same way that reactivity patterns in organic chemistry reflect the stability of the closed shell (four-coordinate, eight valence electron) configuration of saturated carbon. In each case the driving force for restoration of the pertinent closed-shell configuration dominates the reactivity patterns of species which depart from this configuration. Thus there are formal and quite far-reaching parallels between the reactivity patterns of five-coordinate d⁷ complexes (*e.g.*, Co(CN)₅³⁻) and organic free radicals; between four-coordinate d⁸ complexes and carbenes, etc. These parallels, which are quite pertinent to the reactivity patterns of oxidative-addition reactions, have been discussed elsewhere.⁵

(5) J. Halpern, *Advan. Chem. Ser.*, **No. 70**, 1 (1968).

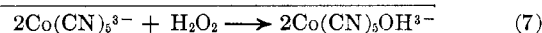
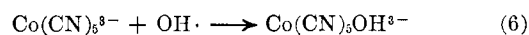
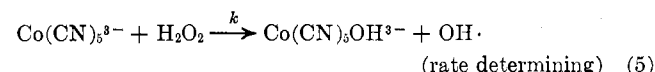
(6) F. A. L. Anet, *J. Amer. Chem. Soc.*, **79**, 2649 (1957); C. E. Castro and W. C. Kray, Jr., *ibid.*, **85**, 2768 (1963); J. K. Kochi and D. D. Davis, *ibid.*, **86**, 2649 (1964).

catalytic hydrogenation and certain other reactions involving the catalytic activation of covalent molecules through oxidative addition.

This Account touches upon all of these themes, with particular emphasis on the first and last. Although the distinction involved is somewhat arbitrary, consideration will be restricted to reactions involving *dissociative* oxidative addition such as those depicted by eq 1-3 and will not extend to the addition of ligands such as O₂, olefins, and acetylenes which occurs without dissociation. Attention is directed to several other recent reviews on related subjects including the Accounts by Collman,⁷ Cramer,⁸ Vaska,^{9a} and Parshall.^{9b}

Mechanisms

d⁷ Complexes. The principal studies on the mechanisms of oxidative-addition reactions of d⁷ complexes, exemplified by eq 1, have been concerned with Co(CN)₅³⁻. With the exception of the reaction with H₂ (and possibly with H₂O) which will be discussed later, these reactions have been shown to proceed through free-radical stepwise mechanisms illustrated by the reaction with H₂O₂ (eq 5-7). The evidence for this mechanism includes the second-order kinetic behavior (rate = k[Co(CN)₅³⁻][H₂O₂]) as well as "detection" of the intermediate OH· radical through its reaction with added I⁻.¹⁰



Other molecules which react with Co(CN)₅³⁻ by analogous free-radical mechanisms include NH₂-OH, I-CN, and various organic halides.^{10,11} The reactions with methyl (and benzyl) halides yield rather stable organocobalt derivatives in accord with eq 8 and 9. With ethyl and other alkyl halides, additional competing reactions, exemplified by eq 11b, which yield Co(CN)₅H³⁻ and olefins, are possible. In each case the

(7) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

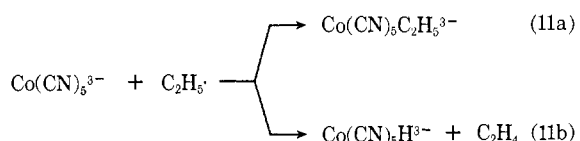
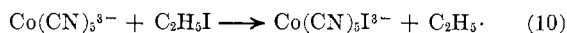
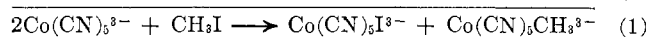
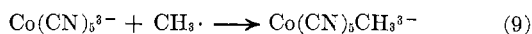
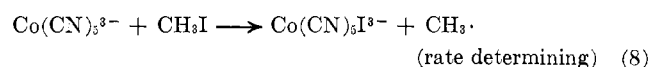
(8) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968), and references therein.

(9) (a) L. Vaska, *ibid.*, **1**, 335 (1968); G. W. Parshall, *ibid.*, **3**, 139 (1970).

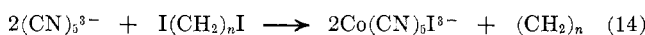
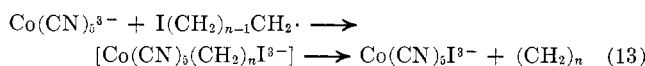
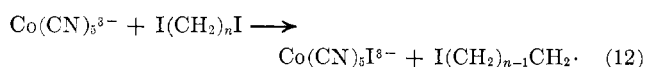
(10) P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *J. Amer. Chem. Soc.*, **91**, 82 (1969).

(11) J. Halpern and J. P. Maher, *ibid.*, **86**, 2311 (1964); **87**, 5361 (1965); P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

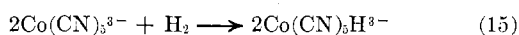
rate-determining step is halogen atom abstraction from the organic halide by $\text{Co}(\text{CN})_5^{3-}$, and the reactivity patterns are similar to those for halogen abstraction by other atom and free-radical reagents (*e.g.*, Na atoms and CH_3 radicals), *i.e.*: $\text{RCl} < \text{RBr} < \text{RI}$, and $\text{CH}_3\text{I} < \text{C}_2\text{H}_5\text{I} < (\text{CH}_3)_2\text{CHI} < (\text{CH}_3)_3\text{CI} < \text{C}_6\text{H}_5\text{CH}_2\text{I}$.¹¹



Other variants of these reactivity patterns are illustrated by eq 12–14, which depict the reactions of $\text{Co}(\text{CN})_5^{3-}$ with 1,2-diiodoethane ($n = 2$) and 1,3-diiodopropane ($n = 3$), in which formation of the organocobalt complex is followed by elimination of ethylene and cyclopropane, respectively.¹¹

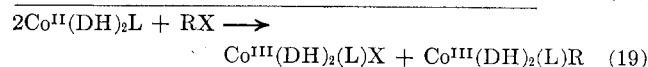
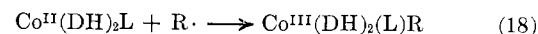
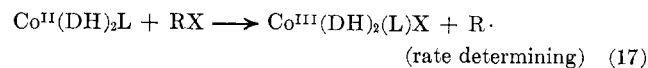


In contrast to the above reactions, the reaction of $\text{Co}(\text{CN})_5^{3-}$ with H_2 (eq 15) exhibits the third-order rate law, $k[\text{H}_2][\text{Co}(\text{CN})_5^{3-}]^2$, implying a "concerted" mechanism in which the driving force for dissociation of H_2 (104 kcal/mole) is provided by the simultaneous formation of two (58 kcal/mole) Co–H bonds.¹² In this case a stepwise mechanism, analogous to eq 5–7, involving an intermediate H atom, would be prohibitively endothermic. This also applies to the reaction with water (eq 16); the occurrence of which causes aqueous solutions of $\text{Co}(\text{CN})_5^{3-}$ to be somewhat unstable especially at high $\text{Co}(\text{CN})_5^{3-}$ concentrations.^{12,13}



We are currently extending these studies to other low-spin d^7 complexes with a view to obtaining a better understanding of the dependence of reactivity on electronic and structural factors. Some insight into these has already been provided through the study of reactions of bis(dimethylglyoximate)cobalt(II) complexes of the type $\text{Co}(\text{DH})_2\text{L}$ (where DH = dimethylglyoxime and L is an axial ligand such as pyridine, triphenylphosphine, etc.) with benzyl bromide and other organic halides (RX).¹⁴ These reactions proceed by free-

radical mechanisms (eq 17–19) analogous to those of $\text{Co}(\text{CN})_5^{3-}$.



These studies have revealed a marked dependence of the reactivity on the ligand L, reflected in values of the second-order rate constant for reaction 17 (for benzyl bromide in acetone at 25°) ranging from $4.3 \times 10^{-3} M^{-1} \text{sec}^{-1}$ for L = tricyclohexylphosphine through 1.7×10^{-1} for L = pyridine to $7 M^{-1} \text{sec}^{-1}$ for L = trimethylphosphine. For nitrogen bases the reactivity sequence [nicotinamide ($\text{p}K_a = 3.4$) < pyridine ($\text{p}K_a = 5.3$) < γ -picoline ($\text{p}K_a = 6.1$)] parallels the order of increasing basicity and, thus, the expected order of increasing stabilization of $\text{Co}(\text{III})$ relative to $\text{Co}(\text{II})$. For phosphine axial ligands (L = PR_3), however, the observed reactivity sequences are more complex (*e.g.*, R = *c*- C_6H_{11} < C_6H_5 < *n*- C_4H_9 < C_2H_5 < CH_3)¹⁴ and suggest that steric as well as electronic factors are important. Similar trends have been observed for the reactions of cobalt(II)–Schiff base complexes with organic halides.¹⁵

Interest in the study of the oxidative-addition reactions of low-spin cobalt complexes, notably reactions leading to organocobalt products, is enhanced by certain parallels with corresponding reactions of vitamin B₁₂ derivatives and consequently by their possible relevance as vitamin B₁₂ model systems.¹⁶

d^8 Complexes. The most extensive studies on the oxidative-addition reactions of d^8 complexes have been made on square-planar iridium(I) complexes of the type $\text{Ir}(\text{CO})\text{L}_2\text{Y}$ (Y = Cl, Br, I, etc.; L = $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$, $\text{PC}_6\text{H}_5(\text{CH}_3)_2$, etc.).^{7,9a} Such complexes oxidatively add a variety of molecules (eq 2), including H_2 and organic halides (RX = CH_3I , $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, etc.). The kinetic data, summarized in Table II, reveal marked differences between the two reactions, including systematically different activation parameters and different reactivity orders with respect to variation of the halide ligand Y. These results have been interpreted in terms of the two different limiting mechanisms depicted by eq 20a and 20b. The addition of H_2 (like the kinetically similar reaction with O_2 to form the adduct $\text{Ir}(\text{CO})\text{L}_2\text{Y}(\text{O}_2)$)¹⁷ appears to be a concerted process, involving a relatively nonpolar transition state and leading to a cis adduct. The oxidative addition of alkyl or benzyl halides, on the other hand, is believed to entail an $\text{S}_\text{N}2$ type attack, with at least partial halide displacement, through a highly unsymmetrical transi-

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(15) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

(16) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968), and references therein.

(17) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966); *Proc. Intern. Conf. Coord. Chem.*, 10th 135 (1967).

(12) B. DeVries, *J. Catal.*, **1**, 489 (1962); M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc. A*, 800 (1967); J. Halpern and M. Pribanić, *Inorg. Chem.*, **9**, 2616 (1970).

(13) C. S. Sokol and C. H. Brubaker, *J. Inorg. Nucl. Chem.*, **30**, 3267 (1968).

(14) P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer.*

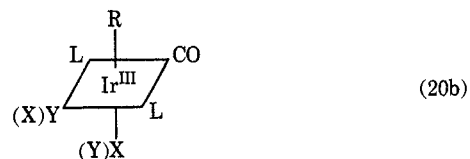
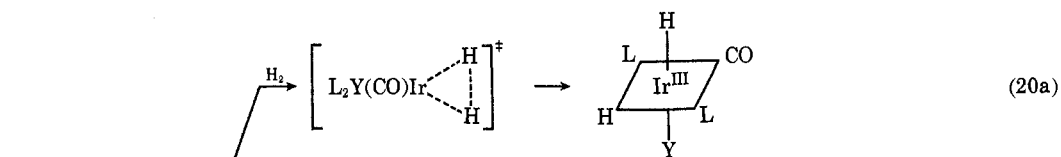
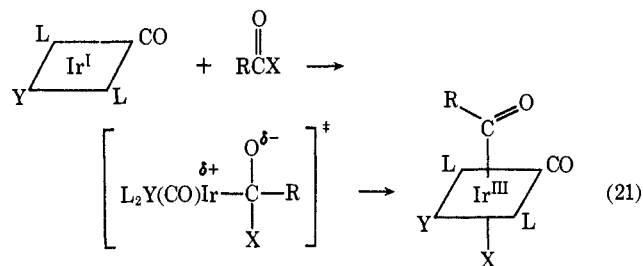


Table II
Kinetic Data for the Oxidative Addition of H_2 and CH_3I to Iridium(I) Complexes in Benzene at 25° (from Ref 17)

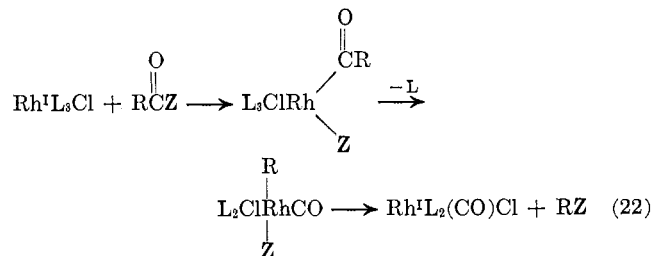
Reaction	$k, M^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal/mole}$	$\Delta S^\ddagger, \text{eu}$
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl} + \text{H}_2$	6.7×10^{-1}	10.8	-23
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Br} + \text{H}_2$	1.1×10	12.0	-14
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I} + \text{H}_2$	$>10^2$		
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl} + \text{CH}_3\text{I}$	3.5×10^{-3}	5.6	-51
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Br} + \text{CH}_3\text{I}$	1.6×10^{-3}	7.6	-46
$\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I} + \text{CH}_3\text{I}$	9.1×10^{-4}	8.8	-43

tion state. The latter mechanism is supported by various features of the kinetic behavior (activation parameters, solvent effects, substituent effects for substituted benzyl halides, etc.) which closely parallel those of other known $\text{S}_\text{N}2$ displacements such as the Menschutkin reactions (quaternary ammonium salt formation).¹⁷ The mechanism is also consistent with certain stereochemical features of the reactions, notably observations that at least under certain conditions the stereochemistry of oxidative addition of alkyl halides (unlike that of H_2) is trans,¹⁸ and (although the opposite behavior has also been reported)¹⁹ is accompanied by configurational inversion at the carbon center.²⁰ Some problems of interpretation, and of reconciliation of discordant observations, remain to be resolved. These are complicated by the fact that not all the pertinent kinetic and stereochemical data refer to the same reactions under the same conditions.

The oxidative additions of acyl halides (through the carbon-halogen bonds) to iridium(I) complexes have also been reported to yield trans adducts.¹⁸ The rates of reaction are higher than those of the corresponding alkyl halides,²¹ perhaps as a result of enhanced susceptibility to nucleophilic attack through a mechanism such as that depicted by eq 21.



The decarbonylation of acyl halides and aldehydes, RCOZ ($\text{Z} = \text{H}$ or halogen), by tris(triphenylphosphine)chlororhodium(I) ($=\text{Rh}^{\text{I}}\text{L}_3\text{Cl}$) has been interpreted in terms of an oxidative-addition mechanism such as that depicted by eq 22.²²⁻²⁴ Decarbonylation by palladium(II) compounds probably proceeds through analogous mechanisms.²⁵



The oxidative-addition reactions of halogen and hydrogen halide molecules to iridium(I) complexes have proved too fast for kinetic measurements, and the mechanisms of these reactions have not thus far been elucidated.¹⁷

The relative reactivities of different d^8 complexes toward oxidative addition are expected to reflect their tendencies to undergo oxidation to the corresponding d^6 configurations.²⁶ This tendency decreases in going from left to right across the periodic table (*i.e.*, with increasing initial oxidation number) and increases in going down a given group of the periodic table. The resultant reactivity toward oxidative addition (assum-

(18) J. P. Collman and C. T. Sears, Jr., *Inorg. Chem.*, **7**, 27 (1968); A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).

(19) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(20) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(21) J. Y. Chen and J. Halpern, unpublished results. Enhanced susceptibility of unsaturated carbon centers toward nucleophilic attack is probably also responsible for the apparently greater reactivity of acyl-hydrogen (and aryl-hydrogen) bonds, compared with alkyl-hydrogen bonds, toward oxidative addition.

(22) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).

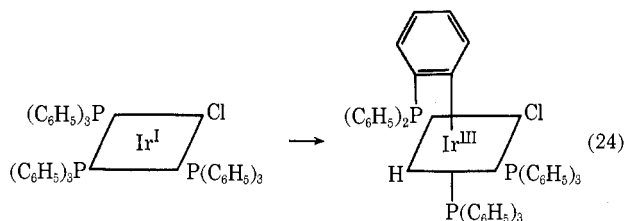
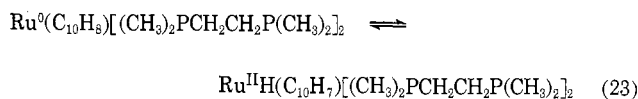
(23) K. Ohno and J. Tsuji, *ibid.*, **90**, 99 (1968).

(24) M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. A*, 348 (1968).

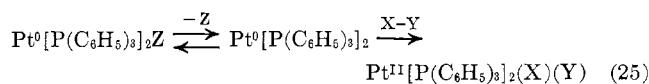
(25) J. Tsuji and K. Ohno, *J. Amer. Chem. Soc.*, **90**, 94 (1968).

(26) This theme has been discussed more fully by Collman.⁷

ing a constant ligand environment) is thus expected to decrease roughly in the following order: $\text{Os}^0 > \text{Ru}^0 > \text{Fe}^0, \text{Ir}^I > \text{Rh}^I > \text{Co}^I, \text{Pt}^{II} > \text{Pd}^{II} \gg \text{Ni}^{II}, \text{Au}^{III}$. For a given d^8 metal atom, the reactivity is expected to be enhanced by ligands which favor higher oxidation states (*e.g.*, $\text{P}(\text{C}_6\text{H}_5)_3 > \text{CO}$) and by ligands which favor the formation of four-coordinate d^8 complexes (rather than five-coordinate complexes such as $\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})_3$ and $\text{Os}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})_3$ which must lose a ligand in undergoing oxidative addition).^{27,28} The observed reactivity trends are generally in accord with these predictions, *e.g.*, $\text{Ir}^I[\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3]_2(\text{CO})\text{Cl} > \text{Ir}^I[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl} > \text{Rh}^I[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$;²⁹ $\text{Ir}^I[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl} > \text{Rh}^I[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl} > \text{Rh}^I[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$;³⁰ $\text{Ir}^I[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl} > \text{Pt}^{II}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}^+$; etc. The very high reactivities of certain d^8 complexes toward oxidative addition are reflected in the occurrence of intramolecular oxidative addition through carbon-hydrogen bonds of coordinated ligands, as in the following examples.^{9b,30,31}



d^{10} Complexes. The best characterized oxidative-addition reactions of d^{10} complexes are probably those of platinum(0), notably $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ and $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{C}_2\text{H}_4)$. These complexes react with a variety of molecules ($\text{X}-\text{Y} = \text{CH}_3-\text{I}, \text{C}_6\text{H}_5\text{CH}_2-\text{Br}, (\text{C}_6\text{H}_5)_3\text{Sn}-\text{Cl}$) to give adducts of the type $\text{Pt}^{II}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{X})(\text{Y})$.³² Several such reactions have been studied and shown to proceed through mechanisms of the type depicted in eq 25 in which oxidative addition actually occurs to $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ which is formed by dissociation of the parent complex ($\text{Z} = \text{P}(\text{C}_6\text{H}_5)_3$ or C_2H_4).³² The oxidative addition of acids, particularly those of nucleophilic anions ($\text{X}^- = \text{Cl}^-, \text{CH}_3\text{COO}^-$, etc.) follows a somewhat different course, depicted by eq 26, and in some cases the intermediate salt, $[\text{PtH}[\text{P}(\text{C}_6\text{H}_5)_3]_3]^+\text{X}^-$, can be isolated.³³



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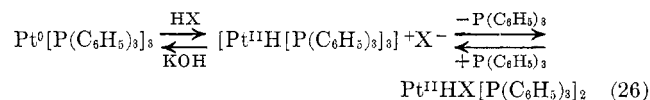
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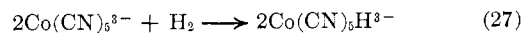


The tendency of (triphenylphosphine)platinum(0) complexes to undergo oxidative addition is limited to fairly reactive molecules such as acids, alkyl and acyl halides, and certain metal halides; unlike the d^7 and d^8 complexes discussed earlier, it does not extend to H_2 . Platinum(0) complexes of more basic phosphines (*e.g.*, tris-*p*-tolylphosphine) are somewhat more reactive but, correspondingly, less stable and more difficult to prepare. (The preparation of (trialkylphosphine)platinum(0) complexes does not appear to have been achieved.) Phosphine complexes of nickel(0) and palladium(0) are also known, but appear to be somewhat less stable than their platinum counterparts, and their oxidative-addition reactions have not been as extensively investigated. This general subject has recently been reviewed by Ugo.³⁴

Catalytic Applications

Hydrogenation and Related Reactions. The ability of certain transition metal complexes to dissociate molecular hydrogen through oxidative addition permits such complexes to function as catalysts for the hydrogenation of olefins and other substrates. Among the general requirements for such catalytic activity are the ability of the transition metal hydride, formed through oxidative addition of H_2 , to transfer the coordinated hydrogen ligands to the substrate and thereby regenerate the original complex to complete the catalytic cycle. The known homogeneous hydrogenation catalysts for which these conditions apparently are fulfilled (although the mechanisms in many cases are still incompletely understood) include several d^7 , d^8 , and d^{10} complexes, notably of $\text{Co}(\text{II})$, $\text{Co}(\text{I})$, $\text{Rh}(\text{I})$, $\text{Ir}(\text{I})$, $\text{Pt}(\text{II})$, $\text{Fe}(\text{0})$, etc.^{5,35}

Among d^7 complexes, the outstanding example of a hydrogenation catalyst is undoubtedly $\text{Co}(\text{CN})_5^{3-}$.^{36,37} This complex is catalytically active for the hydrogenation of a variety of organic substrates, including olefinic compounds containing conjugated (but not isolated) double bonds. Thus, butadiene, styrene, and cinnamic acid are selectively hydrogenated in aqueous (or aqueous-alcoholic) solutions, in the presence of $\text{Co}(\text{CN})_5^{3-}$, to butene, ethylbenzene, and phenylpropionic acid, respectively. A general mechanistic scheme which accommodates all these reactions is depicted by eq 27-28 (where X is a conjugating group such as $\text{CH}=\text{CH}_2$, C_6H_5 , CN , COOH , etc.). According to this scheme, the primary reaction in each case is the oxidative addition of H_2 to $\text{Co}(\text{CN})_5^{3-}$ to form $\text{Co}(\text{CN})_5\text{H}^{3-}$, followed by reaction of $\text{Co}(\text{CN})_5\text{H}^{3-}$ with the conjugated ole-

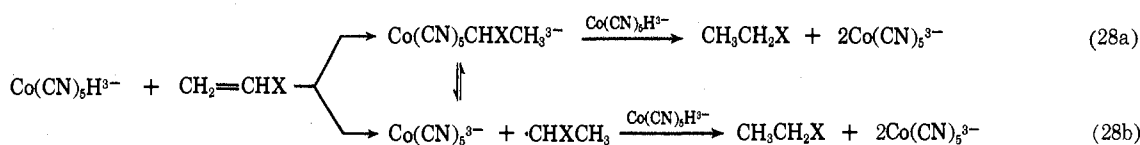


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fin.³⁸ The latter reaction leads either (through Co-H addition across the C=C bond) to an organocobalt adduct (eq 28a) or (through H-atom transfer) to a free radical (eq 28b), followed in each case by further reaction with $\text{Co(CN)}_5\text{H}^{3-}$ to complete the catalytic hydrogenation cycle and regenerate Co(CN)_5^{3-} . The former mechanism apparently applies to the hydrogenation of butadiene^{36,37} and the latter to cinnamic acid.³⁹

Recent reports indicate that mixed-ligand complexes of the type Co(dipy)(CN)_3^- (dipy = 2,2'-dipyridyl) are somewhat more active hydrogenation catalysts than Co(CN)_5^{3-} .^{40,41}

Oxidative addition of H_2 also appears to be a feature of the mechanisms of hydrogenation with catalysts of d^8 configuration. The mechanism of one such reaction which has been at least partially elucidated, namely that involving $\text{Ir(CO)[P(C}_6\text{H}_5)_3]_2\text{Cl}$ as a catalyst, is depicted in Figure 1.⁴² The versatile homogeneous hydrogenation catalyst, $\text{Rh[P(C}_6\text{H}_5)_3]_3\text{Cl}$, discovered and studied by Wilkinson, probably functions through a similar mechanism.⁴³

In addition to hydrogenation, there are several other reactions of olefins catalyzed by d^8 complexes that involve transition metal hydride intermediates, formed by oxidative addition either of H_2 or of hydrogen-containing molecules such as hydrogen halides or silanes. Such reactions include the hydroformylation of olefins catalyzed by cobalt(I) and rhodium(I) complexes,⁴⁴⁻⁴⁸ the hydrosilylation of olefins catalyzed by cobalt(I) and platinum(II) complexes,⁴⁹ and the isomerization of olefins, as well as various olefin-to-olefin addition reactions, catalyzed by complexes of rhodium(I).⁸

Cycloaddition and Other "Symmetry-Restricted" Reactions. This section is concerned with the catalysis by transition metal compounds of certain reactions

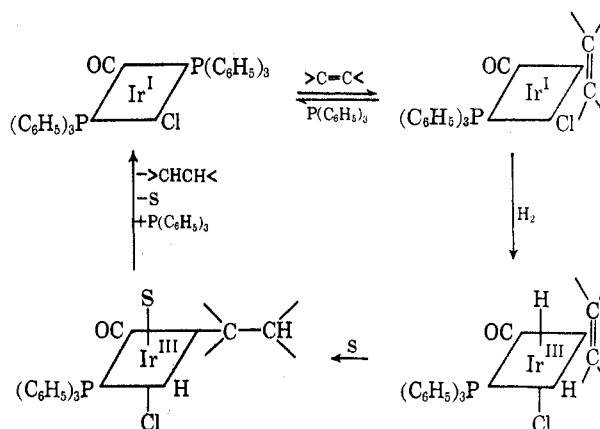


Figure 1. Proposed mechanism of the $\text{Ir(CO)[P(C}_6\text{H}_5)_3]_2\text{Cl}$ -catalyzed hydrogenation of maleic acid in dimethylacetamide (S = solvent) (after ref 42).

involving the formation or breaking of carbon-carbon bonds, the concerted pathways of which are "thermally forbidden" according to the Woodward-Hoffmann rules of orbital symmetry conservation.⁵⁰ Such reactions include the 1,2 cycloadditions of olefins to form cyclobutane rings and the reverse cycloreversion reactions. It has been found that certain such reactions, *e.g.*, the valence isomerizations of highly strained cyclobutane-containing compounds to the corresponding dienes (quadricyclene \rightarrow norbornadiene; hexamethylprismane \rightarrow hexamethyl(Dewar benzene)), are catalyzed by transition metal complexes, notably of rhodium(I).⁵¹ One suggested interpretation attributes this catalysis to relaxation of the symmetry constraints on the concerted pathways of the reactions in question, due to interaction with the *d* orbitals of the transition metal.^{52,53} However, a recent study of the catalysis of one such reaction, the valence isomerization of cubane to *syn*-tricyclooctadiene, by rhodium(I) complexes of the type $[\text{Rh}(\text{diene})\text{Cl}]_2$ (where diene = norbornadiene, *syn*-tricyclooctadiene, etc.) has demonstrated a non-concerted mechanism involving oxidative addition of the cubane through a carbon-carbon bond (eq 29).⁵⁴ The evidence for this includes the observed kinetic patterns and product distributions derived from substituted cubanes, as well as the direct demonstration of oxidative addition of cubane to the rhodium(I) com-

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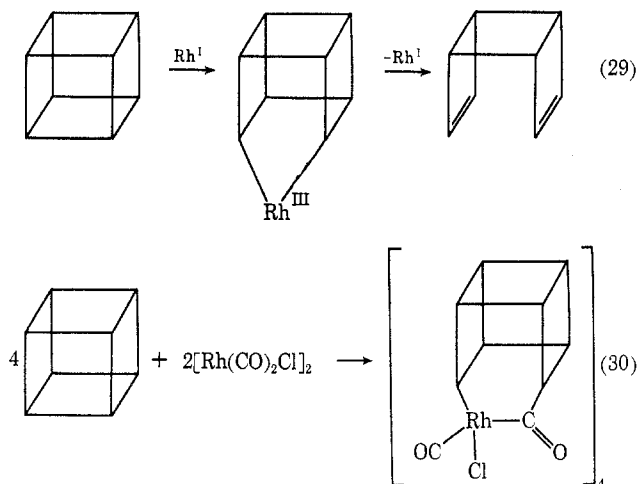
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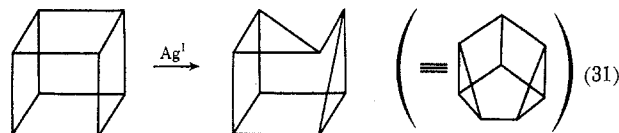
pound, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, to yield an isolable acyl-rhodium adduct, in accord with eq 30.



Analogous acyl-rhodium adducts have also been obtained from the reactions of cyclopropane⁵⁵ and of quadricyclene⁵⁶ with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. It thus seems highly likely that the rhodium(I)-catalyzed rearrangement of quadricyclene to norbornadiene, as well as other rhodium(I)-catalyzed symmetry-restricted reactions,⁵⁷ proceed through nonconcerted mechanisms involving oxidative-addition steps.

Silver salts catalyze a strikingly different rearrangement of cubane, depicted by eq 31,⁵⁸ as well as analogous rearrangements of the homocubane and 1,1'-bishomocubane systems^{59,60} and certain other symmetry-restricted reactions, such as the isomerization of tricyclooctadiene to cyclooctatetraene (interpreted as a se-

quence of disrotatory cyclobutene-butadiene transformations).⁵⁸ These reactions can also be interpreted in terms of nonconcerted mechanisms involving oxidative additions to the d^{10} silver(I) ion. However, the available evidence does not exclude alternative plausible interpretations.



The scope for catalysis of "symmetry-restricted" reactions by transition metal compounds and the implications of such catalysis for synthetic organic chemistry are very considerable. Other known reactions of this type include the cycloaddition reactions of norbornadiene (catalyzed by a variety of transition metal complexes)⁶¹ and various coupling and cyclooligomerization reactions catalyzed by nickel(0) complexes,^{62,63} as well as the recently discovered and highly novel olefin disproportionation (metathesis) reactions (induced both homogeneously and heterogeneously by various molybdenum and tungsten complex catalysts).⁶⁴⁻⁶⁶ The mechanisms of these reactions, some of which may well involve oxidative-addition steps, remain to be fully elucidated.

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