COORDINATION COMPOUNDS IN HOMOGENEOUS CATALYSIS

JACK HALPERN
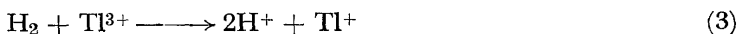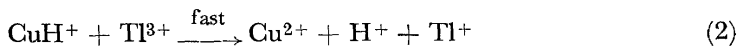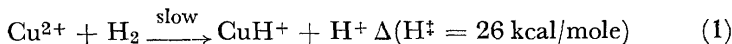
Department of Chemistry, The University of Chicago, Chicago, Illinois, U.S.A.
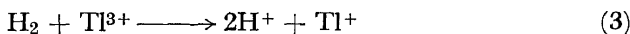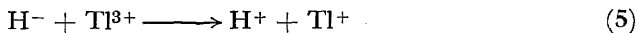
INTRODUCTION

Catalysts function by evoking new paths for chemical reactions, the contributions from which are reflected in increased reaction rates. Sometimes such catalytic paths are closely related to those which operate in the absence of the catalysts; more generally, the catalytic path is a distinctive one, into which the catalyst enters as a reactant, undergoes chemical transformation, but is ultimately regenerated, so that its concentration remains undiminished.

For any given catalytic path there can usually be constructed a corresponding uncatalyzed reaction path, which may or may not be an important contributing path for the actual uncatalyzed reaction. In this context, the role of the catalyst may be understood as that of stabilizing the intermediate states of the corresponding uncatalyzed reaction path, this stabilization necessarily being greater than that of the reactants.

An illustration of this theme is provided by the catalysis by Cu^{2+} and its complexes of the oxidation of molecular hydrogen by various oxidants, among them chromium(VI), iron(III), thallium(III) and iodate.[1, 2] This catalysis is effected through the mechanism, depicted by eqs. 1–3, in which the rate-determining step is the heterolytic splitting of H_2 by Cu^{2+}.

$$Cu^{2+} + H_2 \xrightarrow{\text{slow}} CuH^+ + H^+ \Delta(H^{\ddagger} = 26\,kcal/mole) \qquad (1)$$

$$CuH^+ + Tl^{3+} \xrightarrow{\text{fast}} Cu^{2+} + H^+ + Tl^+ \qquad (2)$$

$$H_2 + Tl^{3+} \longrightarrow 2H^+ + Tl^+ \qquad (3)$$

The corresponding uncatalyzed reaction path, depicted by eqs. 4 and 5,

$$H_2 \longrightarrow H^- + H^+ \qquad (4)$$

$$H^- + Tl^{3+} \longrightarrow H^+ + Tl^+ \qquad (5)$$

$$H_2 + Tl^{3+} \longrightarrow 2H^+ + Tl^+ \qquad (3)$$

is much less favourable, since the endothermicity of reaction 4 and, hence, its activation energy, can be estimated to exceed 35 kcal/mole,[3] as compared to $\Delta H^{\ddagger} = 26$ kcal/mole for the Cu^{2+}-catalyzed reaction. This lowering of the activation energy can be attributed to stabilization by the catalyst, Cu^{2+}, of the intermediate H^-. Other instances of catalysis may be similarly interpreted.

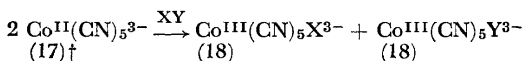# ORIGIN OF CATALYTIC ACTIVITY OF TRANSITION METAL COMPLEXES

Coordination compounds of transition metals play important catalytic roles in a variety of homogeneous, heterogeneous and biological reactions, including oxidation-reduction processes, hydrolytic reactions, substitution reactions, reactions of saturated molecules such as hydrogen, and a great variety of addition and isomerization reactions of unsaturated molecules such as olefins.[4] Contributing to this extraordinary catalytic versatility, the full scope of which has come to be appreciated only within the last few years, are a number of clearly recognizable factors. These include:

(1) The ability of transition metals to stabilize a great variety of ligands through coordination. Among these are σ-bonded ligands such as H^- and alkyl groups, as well as a variety of π-bonded ligands such as olefins, acetylenes, polyenes, allyl groups, etc.
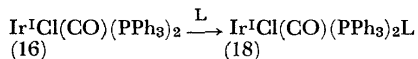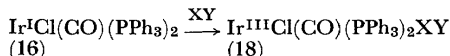
(2) The existence of relatively stable, but highly reactive, complexes of transition metals, notably low spin d^7 and d^8 complexes which, by virtue of their electronic and structural properties, exhibit high degrees of reactivity closely related to those of the "reactive intermediates" or organic chemistry, namely free radicals (five coordinate d^7 complexes), carbenes (four coordinate d^8 complexes) and carbanions (five coordinate d^8 complexes). *Table 1* illustrates these reactivity patterns.
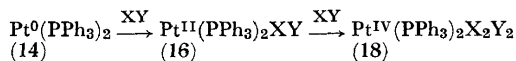
Table 1. Reactivity patterns of low-spin complexes

Five Coordinate d^7 Complexes:

$$2\ Co^{II}(CN)_5^{3-} \xrightarrow{XY} Co^{III}(CN)_5X^{3-} + Co^{III}(CN)_5Y^{3-}$$
$$(17)\dagger \qquad\qquad (18) \qquad\qquad (18)$$

Four-Coordinate d^8 Complexes:

$$Ir^ICl(CO)(PPh_3)_2 \xrightarrow{XY} Ir^{III}Cl(CO)(PPh_3)_2XY$$
$$(16) \qquad\qquad (18)$$

$$Ir^ICl(CO)(PPh_3)_2 \xrightarrow{L} Ir^ICl(CO)(PPh_3)_2L$$
$$(16) \qquad\qquad (18)$$

Two-Coordinate d^{10} Complexes:

$$Pt^0(PPh_3)_2 \xrightarrow{XY} Pt^{II}(PPh_3)_2XY \xrightarrow{XY} Pt^{IV}(PPh_3)_2X_2Y_2$$
$$(14) \qquad\quad (16) \qquad\qquad (18)$$

† (17) etc. = Number of Valence Electrons.
XY = HCl, Br$_2$, CH$_3$-I, H$_2$, etc.
L = CO, C$_2$H$_4$, etc.

The driving force responsible for the high reactivities of these complexes is provided, in part at least, by the increased stabilization of the closed shell 18-valence electron configuration which is achieved in these reactions, just as the reactivities of the corresponding open shell organic species (free radicals, carbenes, etc.) reflect the stabilization associated with the achievement of the four coordinate 8-valence electron configuration of carbon. As revealed by the examples cited, these reactivities, along with the abilities

of the transition metal atoms to stabilize the fragments of dissociation through coordination, are particularly significant for the activation and dissociation of inert saturated molecules such as molecular hydrogen and organic halides.

(3) The accessibility of different oxidation states and coordination numbers —a feature, not entirely restricted to, but most generally exhibited by, coordination compounds of transition metals.

ROLES OF TRANSITION METAL IONS AND COMPLEXES IN CATALYSIS

The characteristics cited above contribute to the catalytic activities of transition metal ions and complexes in a great variety of reactions, in which the catalyst may play one or more of a number of distinct roles. Some of these roles, the operations of which are not necessarily mutually exclusive, are described below.

I. Catalysis of nucleophilic reactions by electron withdrawal from reactants

Coordination to a positively charged metal ion is expected to increase the positive charge density on a substrate, thereby rendering it more susceptible to nucleophilic attack. The role of a metal ion catalyst in such cases is essentially that of a Lewis acid or "superacid" and the origin of such catalytic activity is closely related to that underlying many of the familiar catalytic effects of Bronsted acids.

Despite the higher positive charges which they can bear, metal ions are frequently not as effective, because of their more ionic bonding (particularly when coordinated to small electronegative atoms such as oxygen or nitrogen), in polarizing, or transferring positive charge to, coordinated substrates. This is reflected, for example, in the relative acidities of protonated and coordinated acids, some values of which are listed in *Table 2*.
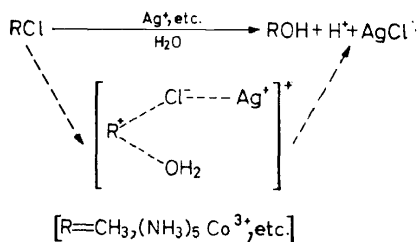
Table 2. Comparison of acidities of free (XH_n), protonated (XH_{n+1}) and coordinated (MXH_n) acids

Free Acid	pK_a	Protonated Acid	pK_a	Coordinated Acid	pK_a
H_2O	15·7	H_3O^+	−1·7	$Li(H_2O)_n^+$	14
				$Be(H_2O)_n^{2+}$	6
				$Ni(H_2O)_n^{2+}$	9
				$Fe(H_2O)_n^{3+}$	3
				$U(H_2O)_n^{4+}$	2
				$(NH_3)_5CoOH_2^{3+}$	6
$H_2PO_4^-$	7·2	H_3PO_4	1·1	$(NH_3)_5CoPO_4H_2^{2+}$	3·7
HPO_4^{2-}	12·7	$H_2PO_4^-$	7·2	$(NH_3)_5CoPO_4H^+$	8·5

There are, however, several circumstances in which metal ions may be more effective than protons in catalyzing nucleophilic reactions. Among these are:

(1) With species (*e.g.* "soft" or "class B" bases) such as halide ions, which exhibit low basicity toward protons, but high basicity toward certain

metal ions. Promotion by metal ions of halide ion displacement from both organic and inorganic halides (a class of reactions not generally susceptible to Bronsted acid catalysis) serves to illustrate this effect, *i.e.*

$$RCl \xrightarrow[\text{H}_2\text{O}]{\text{Ag}^+,\text{etc.}} ROH + H^+ + AgCl$$

$$\left[\begin{array}{c} Cl^- \cdots Ag^+ \\ R \\ OH_2 \end{array} \right]^+$$

$$[R = CH_3, (NH_3)_5 Co^{3+}, etc.]$$

(2) With species such as CO, olefins, acetylenes, etc. whose coordination to metal ions depends on π-bonding through donation of $d\pi$ electrons from the metal to the ligand. Catalysis by certain metal ions such as Ag^+ and Hg^{2+} of the oxidation of CO by MnO_4^- (eq. 7) is attributable to such interaction.[5]

$$3CO + 2MnO_4^- + 2H^+ \rightarrow 3CO_2 + 2MnO_2 + H_2O \tag{7}$$

The uncatalyzed reaction, which exhibits the rate-law, $k[CO][MnO_4^-]$ ($\Delta H^{\ddagger} = 13$ kcal/mole), has been interpreted in terms of a mechanism in which the rate-determining step involves nucleophilic attack of MnO_4^- on CO, *i.e.*

$$MnO_4^- + CO \rightarrow [O_3Mn-O-\overset{O}{\overset{\|}{C}}:]^- \xrightarrow{H_2O} MnO_4^{3-} + CO_2 + 2H^+ \tag{8}$$
$$I$$
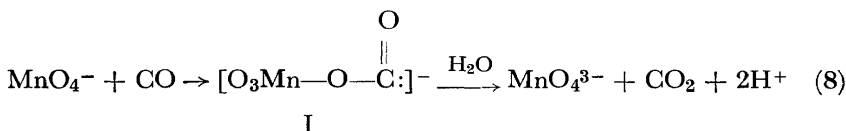
Ag^+ and Hg^{2+} are powerful catalysts for the reaction, the rate-law for the catalytic path in each case having the form, $k[CO][MnO_4^-][M^{n+}]$ ($\Delta H^{\ddagger} = 1$ kcal/mole for Ag^+ and 6 kcal/mole for Hg^{2+}). This catalysis can be understood in terms of stabilization of the intermediate I by coordination to Ag^+, *i.e.* in terms of the rate-determining step:

$$Ag^+ + CO + MnO_4^- \rightarrow [Ag-\overset{O}{\overset{\|}{C}}-OMnO_3] \rightarrow Ag^+ + \text{products} \tag{9}$$
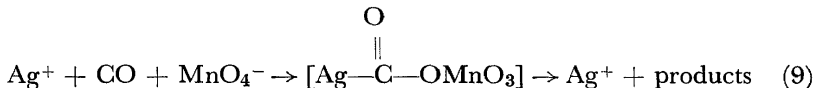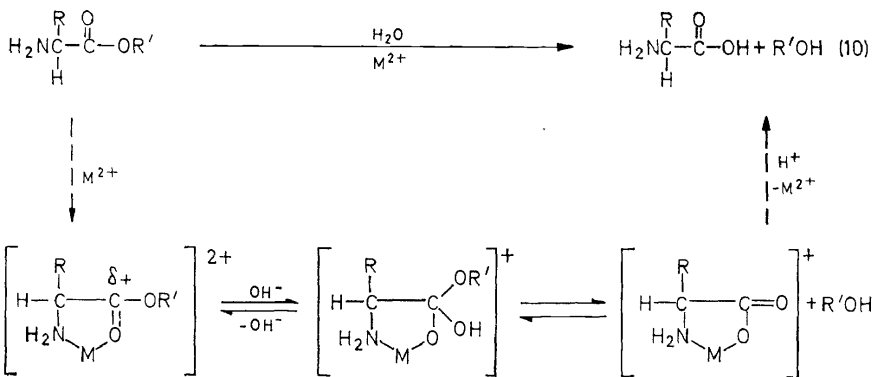
Other catalytic effects which may be interpreted in similar terms include the catalysis by mercury(II), ruthenium(III), etc. of the hydration of acetylenes,[6] the catalysis by palladium(II) of the oxidation of olefins,[7] and the catalysis by metal ions (and by acids) of the *cis-trans* isomerization of azobenzene.[8]

(3) When chelation contributes to the binding of the substrate to (and/or stabilization of the product by), the metal ion, as in the following examples:

(i) Catalysis by various metal ions of the hydrolysis of amino acid esters,[9] according to the mechanism:

$$H_2N\overset{R}{\underset{H}{C}}-\overset{O}{C}-OR' \xrightarrow[M^{2+}]{H_2O} H_2N\overset{R}{\underset{H}{C}}-\overset{O}{C}-OH + R'OH \quad (10)$$

The influence of coordination in activating amino acid esters for nucleophilic attack is also revealed by the facile N-terminal addition of amino acid or peptide esters to the coordinated glycine ester NH_2CH_2COR (where $R = OCH_3$) in the stable complex, $[Co(en)_2(NH_2CH_2OR)]^{3+}$, i.e.[10]

$R = OCH_3$

$\overset{\frown}{N \quad N} = en$
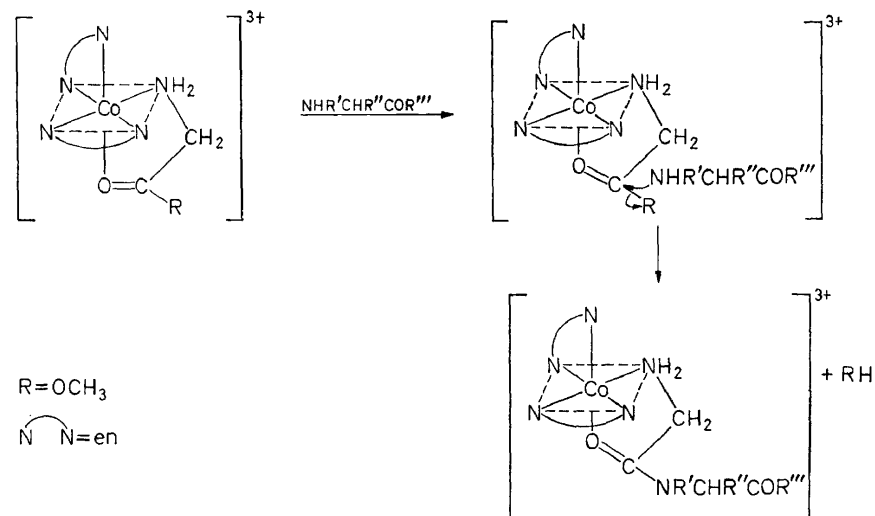
(ii) Catalysis by Ni^{2+}, Cu^{2+}, Zn^{2+} etc. of the hydration of phenanthroline nitrile.[11] Coordination of the phenanthroline nitrile to Ni^{2+} increases the rate of attack by OH^-, according to the following proposed mechanism, by a factor of about 10^7.

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(12)
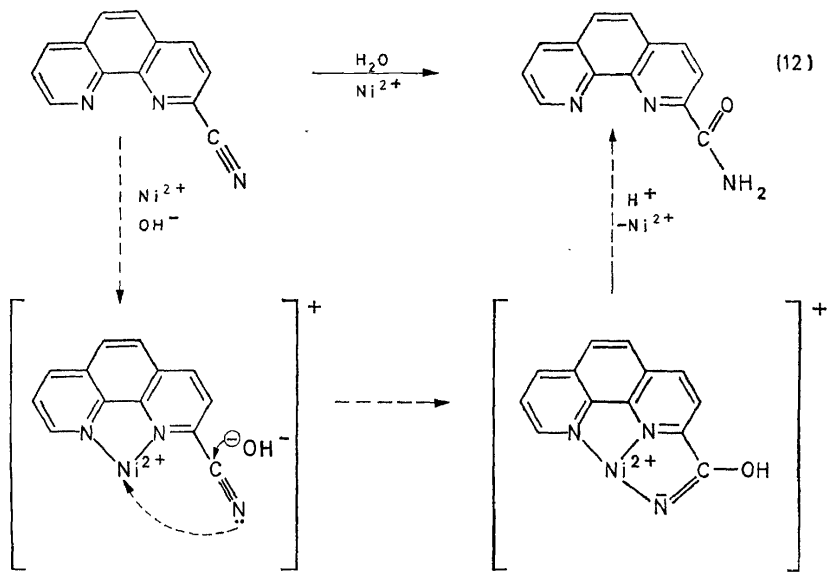
(iii) Catalysis by various metal ions (M = Cu, Zn, Co, Ni, Mn etc.) of the decarboxylation of oxaloacetic acids according to the following mechanism:[12]

$$\text{HOOCCCR}_2\text{COOH} \xrightarrow{M^{2+}} \text{HOOCCCR}_2\text{H} + \text{CO}_2 \quad (13)$$
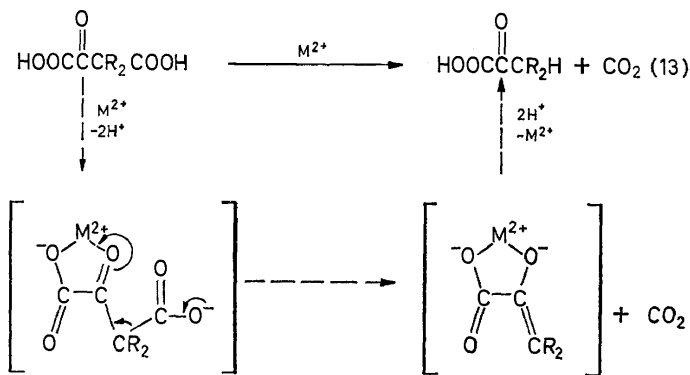
Not uncommonly, the products of such metal ion-catalyzed nucleophilic reactions form more stable complexes with the metal ions than do the reactants. In such case the additional driving force derived from the increase in stabilization through coordination, which accompanies reaction, undoubtedly contributes to the enhanced reactivity. Support for this is provided by the observation[12] (*Figure 1*) that the order of catalytic activities of various divalent metal ions for the last reaction ($Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+}$) parallels the order of stabilities of the complexes of these
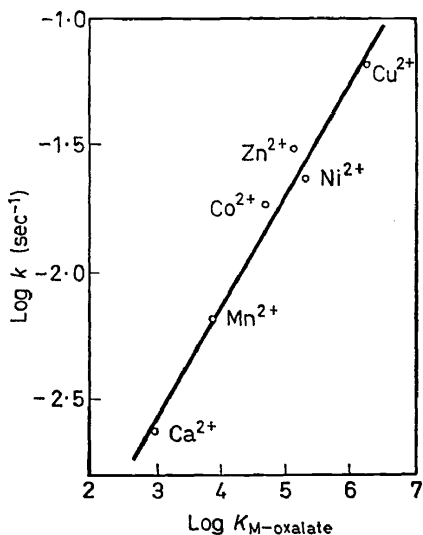
Figure 1. Dependence of the catalytic constant (k) for decarboxylation of oxaloacetic acid on the stability constant ($K_{\text{M-oxalate}}$) of the oxalate complex of the catalytic metal ion. (Based on data in Ref. [12])

metal ions with oxalate ($^-O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O^-$) which resembles the product ion

($^-O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle CR_2}{\|}}{C}\!-\!O^-$) rather than the reactant.

Catalysis of the hydrogenation of olefinic compounds by certain metal ions and complexes, such as ruthenium(II) chloride[13] (eq. 14) may also be considered as exemplifying this type of activation.


$$(14)$$
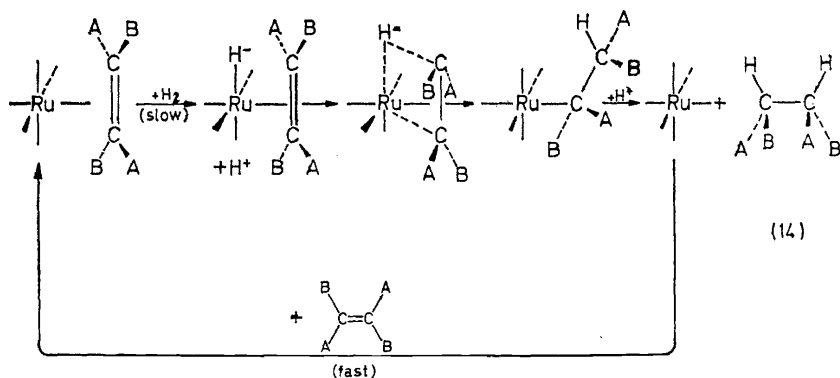
The insertion of the olefin into the metal-hydrogen bond, which is a step in this reaction, can be regarded as involving nucleophilic attack of the hydride ligand on the coordinated olefin, assisted by coordination of the latter to the metal ion as well as by the presence of electron withdrawing substituents, such as $-COOH$, which appear to be needed to activate the olefin for reaction.[13]
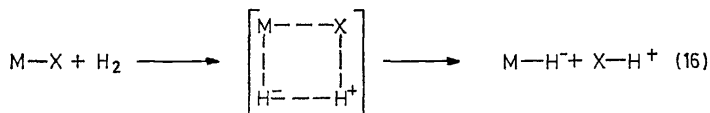
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II. Catalysis of electrophilic reactions by promotion of proton loss from a coordinated reactant

Paradoxically (in view of their positive charges), metal ions may also catalyze electrophilic attack by promoting the loss of a proton from a coordinated reactant, or by stabilizing a reactive (*e.g.* enol) form of the latter.

Catalysis by Cu^{2+} of the oxidation of molecular hydrogen (regarded as electrophilic attack on hydrogen) through a mechanism involving the heterolytic splitting of H_2 (eqs. 1–3) may be considered as an example of this effect. Other metal ions which catalyze the oxidation of H_2 by analogous mechanisms include Ag(I), Cu(I), Hg(II), Rh(III) and Ru(III). A complete description of the mechanisms of such reactions involves the recognition, (i) that coordination of the H^- ion to the metal ion involves the displacement of one of the original ligands of the catalyst, as in the reaction,[14]

$$RuCl_6{}^{3-} + H_2 \rightleftharpoons RuHCl_5{}^{3-} + H^+ + Cl^- \qquad (15)$$
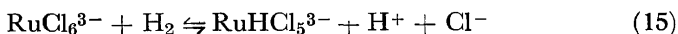
and, (ii) that, in addition to the metal ion, such catalyst systems must involve an appropriate base to stabilize the released proton. The role of this base may be assumed by a solvent molecule or, in certain cases, by the displaced ligand, the mechanism in such cases being of the form:

$$M{-}X + H_2 \longrightarrow \begin{bmatrix} M{-}{-}{-}X \\ \mid \quad\quad \mid \\ \mid \quad\quad \mid \\ H{=}{-}{-}H^+ \end{bmatrix} \longrightarrow M{-}H^- + X{-}H^+ \quad (16)$$

The variation of rate with the ligand X, in such cases, reflects the expected direct dependence on the basicity of X, and inverse dependence on the stability of the M—X bond.[15]
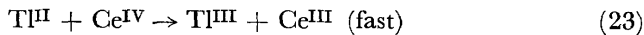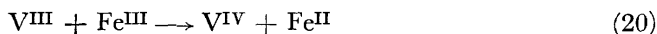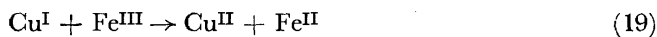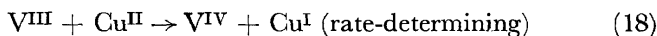
Other examples of electrophilic substitution reactions, catalyzed by metal ions through mechanisms involving the promotion of proton loss and stabilization of enol forms of reactants, include the bromination of β-diketones[16] (eq. 17) and of ketoesters.[17] The order of catalytic activities in the case of reaction (16) ($Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+}$) parallels the order of the stabilities of the acetonylacetonate complexes of the metal ions.
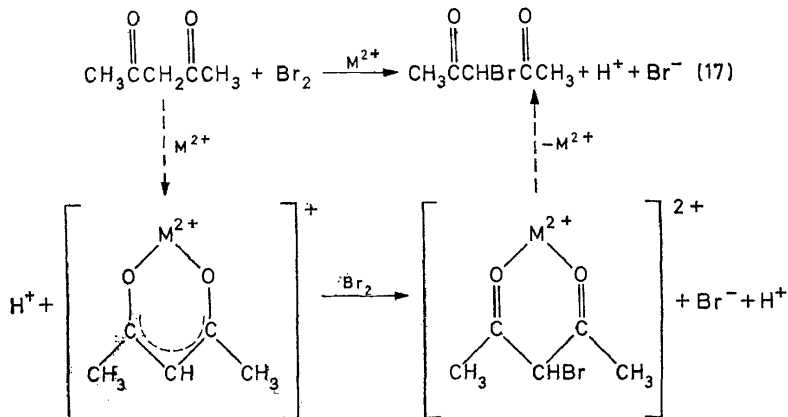
III. Catalysis of oxidation-reduction and of free radical reactions by electron transfer

The accessibility of different oxidation states for certain transition metal complexes (in some cases coupled with differences in coordination number) gives rise to catalysis of a variety of reactions, notably of the redox and free-radical types.

Among the simplest such examples are those reactions in which a metal ion or complex, having two accessible oxidation states, catalyzes electron transfer by acting as an electron carrier. Two such examples are the Cu^{II}-catalyzed oxidation of V^{III} by Fe^{III} (eqs. 18–20) according to the rate-law, $k[Cu^{II}][V^{III}]$, and the Ag^{I}-catalyzed oxidation of Tl^{I} by Ce^{IV} (eqs. 21–24)[18] according to the rate-law $k_1 k_2 [Tl^{I}] [Ce^{IV}] [Ag^{I}]/(k_{-1}[Ce^{III}] + k_2[Tl^{I}])$

$$V^{III} + Cu^{II} \rightarrow V^{IV} + Cu^{I} \text{ (rate-determining)} \qquad (18)$$

$$\underline{Cu^{I} + Fe^{III} \rightarrow Cu^{II} + Fe^{II}} \qquad (19)$$

$$V^{III} + Fe^{III} \longrightarrow V^{IV} + Fe^{II} \qquad (20)$$

$$Ag^{I} + Ce^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ag^{II} + Ce^{III} \qquad (21)$$

$$Tl^{I} + Ag^{II} \xrightarrow{k_2} Tl^{II} + Ag^{I} \qquad (22)$$

$$\underline{Tl^{II} + Ce^{IV} \rightarrow Tl^{III} + Ce^{III} \text{ (fast)}} \qquad (23)$$

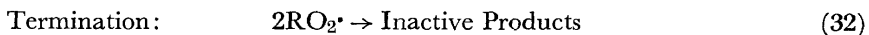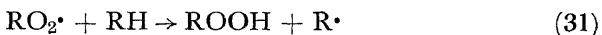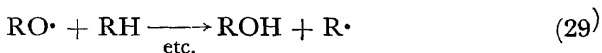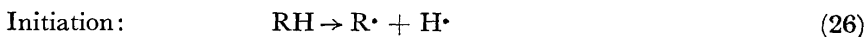$$Tl^{I} + 2Ce^{IV} \rightarrow Tl^{III} + 2Ce^{III} \qquad (24)$$

The basis for such catalysis (other examples of which include silver ion-catalyzed persulphate oxidations) is that electron transfer from the reductant to the catalyst, followed by electron transfer from the catalyst to the oxidant, is faster than direct electron transfer from the reductant to the oxidant. An obviously necessary, but insufficient, requirement for such catalysis is the accessibility of two oxidation states of the catalyst, neither of which must be too stable compared with the other. For reasons which are still not well understood, copper and silver ions are especially effective as catalysts of this type.

One-electron oxidation or reduction of saturated molecules frequently results in the generation of free radicals. The catalysis of certain free radical reactions, by ions or complexes of transition metals (such as Cu, Co and Mn) which exhibit variable oxidation states is a consequence of this. Among such reactions are autoxidation reactions of hydrocarbons (eq. 25), which proceed by free radical mechanisms, depicted in part by eqs. 26–34).
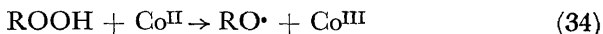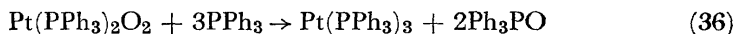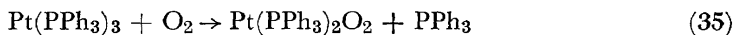
Overall Reaction: .

$$RH + O_2 \rightarrow ROOH \tag{25}$$

Uncatalyzed Mechanism:

Initiation: $\quad RH \rightarrow R\cdot + H\cdot \tag{26}$

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot \tag{27}$$

$$ROOH \rightarrow RO\cdot + OH\cdot \tag{28}$$

$$RO\cdot + RH \underset{etc.}{\longrightarrow} ROH + R\cdot \tag{29}$$

Propagation: $\quad R\cdot + O_2 \rightarrow RO_2\cdot \tag{30}$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \tag{31}$$

Termination: $\quad 2RO_2\cdot \rightarrow \text{Inactive Products} \tag{32}$

Mechanism of Catalyzed Initiation by Co^{III}, etc.:

$$ROOH + Co^{III} \rightarrow RO_2\cdot + Co^{II} \tag{33}$$

$$ROOH + Co^{II} \rightarrow RO\cdot + Co^{III} \tag{34}$$

The reactions responsible for the catalytic initiation, *i.e.* the oxidation and reduction of ROOH, probably involve coordination of ROOH to the metal ion catalysts. Deactivation of such catalysts by chelating agents such as ethylenediaminetetraacetic acid may result from the blocking of this coordination.[19]
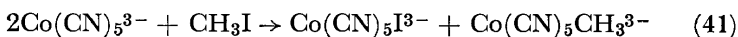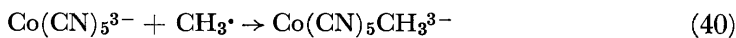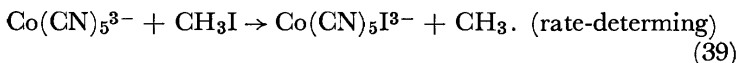
Not all cases of catalysis of oxidation reactions by metal complexes involve free-radical mechanisms: Catalysis of the oxidation of olefins by palladium(II) complexes, for example, probably involves a two-electron step in which the olefin is oxidized all the way to the aldehyde or ketone, and the palladium(II) reduced to palladium(0) or a palladium(II) hydride.[7] Another example of catalytic oxidation by a non-free radical mechanism is the catalysis of the oxidation of phosphines by platinum(0) complexes such as $Pt(PPh_3)_3$ depicted by eqs. 35–37.
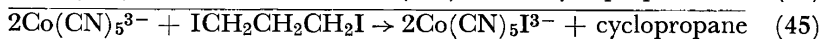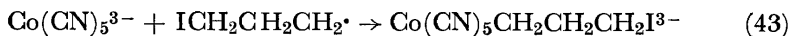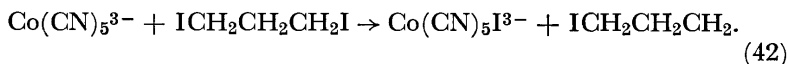
$$Pt(PPh_3)_3 + O_2 \rightarrow Pt(PPh_3)_2O_2 + PPh_3 \tag{35}$$

$$\underline{Pt(PPh_3)_2O_2 + 3PPh_3 \rightarrow Pt(PPh_3)_3 + 2Ph_3PO} \tag{36}$$

$$2PPh_3 + O_2 \rightarrow 2Ph_3PO \tag{37}$$

Certain one-electron reducing agents, such as hexaaquochromium(II),[21] pentacyanocobaltate(II)[22-25] and pyridinatobis(dimethylglyoximato)cobalt-(II),[26] are particularly effective in reducing saturated molecules, such reductions being accompanied by transfer of the fragments of reductive cleavage to the coordination shells of the metal ions, *e.g.*

$$2Co(CN)_5^{3-} + XY \rightarrow Co(CN)_5X^{3-} + Co(CN)_5Y^{3-} \qquad (38)$$
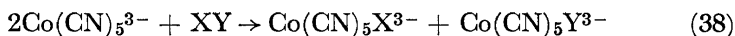
where X—Y = H_2, Br_2, HO—OH, HO—NH_2, I—CN, CH_3—I and other organic halides. Several such reactions have been shown[22-25] to proceed through free radical mechanisms of the type,

$$Co(CN)_5^{3-} + CH_3I \rightarrow Co(CN)_5I^{3-} + CH_3 \cdot \text{ (rate-determining)} \qquad (39)$$

$$\underline{Co(CN)_5^{3-} + CH_3 \cdot \rightarrow Co(CN)_5CH_3^{3-}} \qquad (40)$$

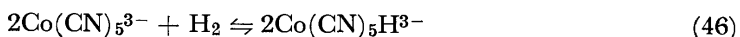$$2Co(CN)_5^{3-} + CH_3I \rightarrow Co(CN)_5I^{3-} + Co(CN)_5CH_3^{3-} \qquad (41)$$

The reactions of $Co(CN)_5^{3-}$ with certain other organic halides are characterized by further reactions of the organocobalt adducts. One example[25] of this is the reaction of $Co(CN)_3^{3-}$ with 1,3-diiodopropane which yields cyclopropane according to eqs. 42–45.

$$Co(CN)_5^{3-} + ICH_2CH_2CH_2I \rightarrow Co(CN)_5I^{3-} + ICH_2CH_2CH_2 \cdot \qquad (42)$$

$$Co(CN)_5^{3-} + ICH_2CH_2CH_2 \cdot \rightarrow Co(CN)_5CH_2CH_2CH_2I^{3-} \qquad (43)$$

$$\underline{Co(CN)_5CH_2CH_2CH_2I^{3-} \rightarrow Co(CN)_5I^{3-} + \text{cyclopropane}} \qquad (44)$$

$$2Co(CN)_5^{3-} + ICH_2CH_2CH_2I \rightarrow 2Co(CN)_5I^{3-} + \text{cyclopropane} \qquad (45)$$
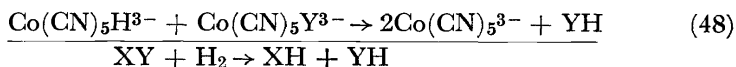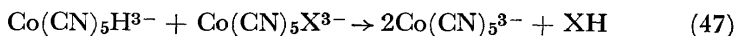
In contrast to the reactions with organic halides, H_2O_2, $HONH_2$ and ICN, all of which proceed by free radical mechanisms of the type depicted above, the reaction of $Co(CN)_5^{3-}$ with H_2, which obeys the rate law, $k[H_2][Co(CN)_5^{3-}]^2$ is apparently a concerted one-step process, *i.e.*

$$2Co(CN)_5^{3-} + H_2 \leftrightarrows 2Co(CN)_5H^{3-} \qquad (46)$$
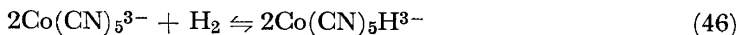
Reaction (46) is involved in a variety of hydrogenolysis and hydrogenation reactions catalyzed by $Co(CN)_5^{3-}$, *e.g.*

$$2Co(CN)_5^{3-} + H_2 \leftrightarrows 2Co(CN)_5H^{3-} \qquad (46)$$

$$2Co(CN)_5{}^{3-} + XY \rightarrow Co(CN)_5X^{3-} + Co(CN)_5Y^{3-} \qquad (38)$$

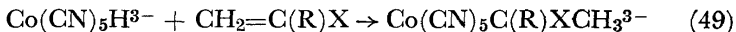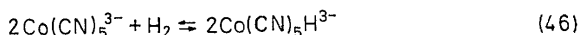$$Co(CN)_5H^{3-} + Co(CN)_5X^{3-} \rightarrow 2Co(CN)_5{}^{3-} + XH \qquad (47)$$

$$\underline{Co(CN)_5H^{3-} + Co(CN)_5Y^{3-} \rightarrow 2Co(CN)_5{}^{3-} + YH} \qquad (48)$$
$$XY + H_2 \rightarrow XH + YH$$
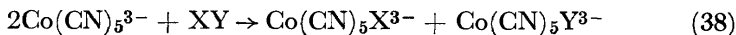
where $XY = H_2O_2$, Br_2 and certain organic halides.

$Co(CN)_5H^{3-}$ adds to a variety of olefinic and acetylenic compounds[27] to form organocobalt adducts in accord with eq. 49 (where $R = H$ or CH_3 and $X = COOH$, CN, C_6H_5, α—C_5H_4N, $CH=CH_2$, etc.).

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \rightarrow Co(CN)_5C(R)XCH_3{}^{3-} \qquad (49)$$

The $Co(CN)_5{}^{3-}$-catalyzed hydrogenation of unsaturated compounds such as butadiene[23,28] (eqs. 46, 50–52) and cinnamic acid[29] (eqs. 46, 53–55) involve such steps—

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2Co(CN)_5H^{3-} \qquad (46)$$

$$CH_2{=}CHCH{=}CH_2 + H_2 \longrightarrow 1{-}butene + trans{-}2{-}butene \qquad (52)$$

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2Co(CN)_5H^{3-} \qquad (46)$$

$$Co(CN)_5H^{3-} + PhCH{=}CHCOO^- \rightarrow [Co(CN)_5CH(Ph)CHOO]^{4-} \rightleftharpoons Co(CN)_5^{3-} + $$
$$Ph\dot{C}HCH_2COO^- \qquad (53)$$

$$Ph\dot{C}HCH_2COO^- + Co(CN)_5H^{3-} \rightarrow PhCH_2CH_2COO^- + Co(CN)_5^{3-} \qquad (54)$$

$$PhCH{=}CHCOO^- + H_2 \rightarrow PhCH_2CH_2COO^- \qquad (55)$$
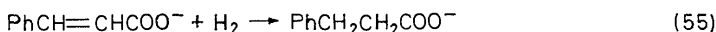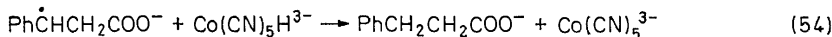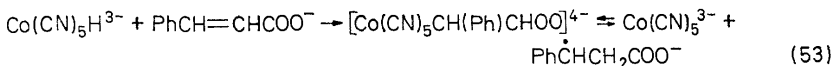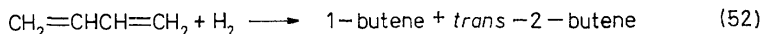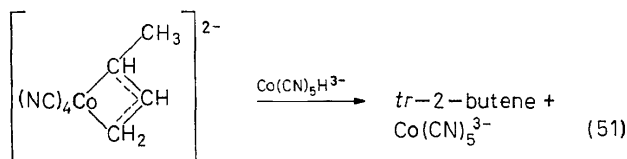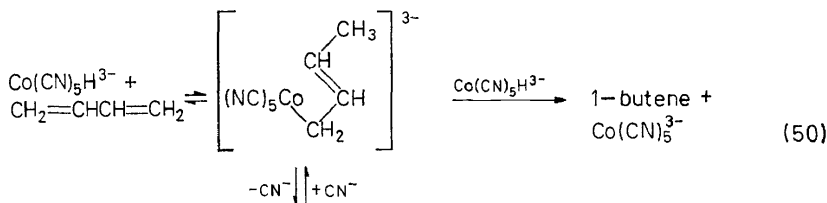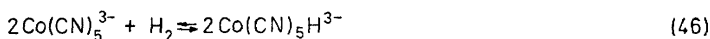
IV. Promotion of ligand synthesis by ligand stabilization and/or the template effect

The synthesis of species, which are stabilized by coordination to metal ions, is frequently promoted by the presence of such metal ions. Examples of such reactions include the oxidative dehydrogenation of bipipyridine[30] (eq. 56), the synthesis of Schiff's bases[31] (eq. 57) and, as an extreme case, the synthesis of a molecule, namely cyclobutadiene, which is stable only as a coordinated ligand[32] (eq. 58).

$$3 \quad + 3O_2 \quad \xrightarrow{Fe^{2+}} \quad \left[Fe \left(\right)_3 \right]^{2+} + 6H_2O \quad (56)$$

$$6NH_2CH_3 + 3 \quad \xrightarrow{Fe^{2+}} \quad \left[Fe \left(\right)_3 \right]^{2+} + 6H_2O \quad (57)$$

$$\xrightarrow{Fe_2(CO)_9} \quad Fe(CO)_3 \quad (58)$$
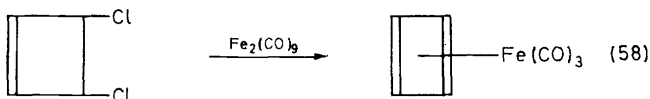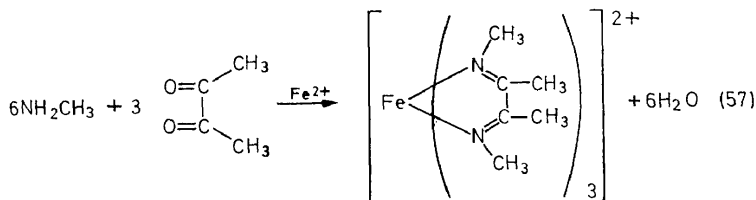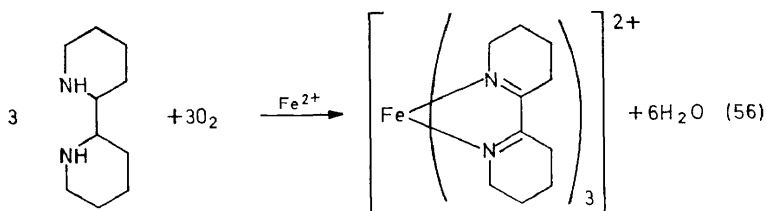
The products of such reactions frequently remain strongly coordinated to the metal, so that the reactions are promoted but not truly catalytic. The kinetic and mechanistic information available about these reactions is insufficient to determine whether kinetic or thermodynamic factors, or both, are responsible for the observed enhan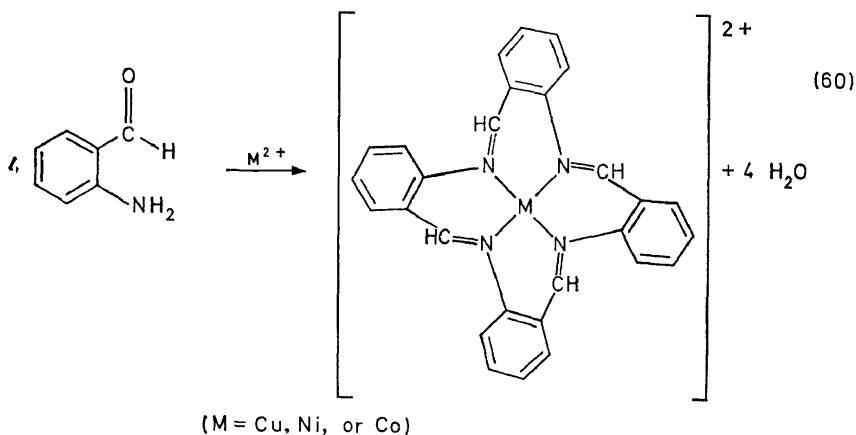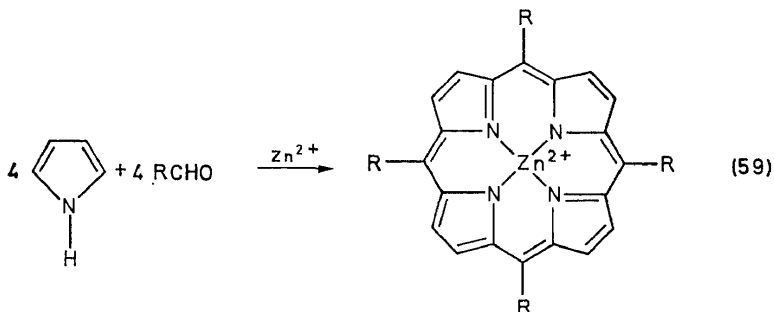cement of reactivity. This critical question also remains to be answered for a number of reactions in which it appears that catalysis or promotion of reaction results from the simultaneous coordination of two or more reactants to a metal ion in a manner which facilitates their mutual approach and favourable orientation for reaction. Examples in which such a "template effect" may be important include a number of reactions involving the synthesis of macrocylic ligands, such as the metal ion-promoted synthesis of porphyrins[33] (eq. 59), of corrins[34] and of phthalocyanines[35] and the cyclocondensation of *o*-aminobenzaldehyde[36] (eq. 60).

71

$$4 \quad \text{(pyrrole)} + 4 \text{ RCHO} \xrightarrow{Zn^{2+}} \text{(Zn porphyrin)} \qquad (59)$$

$$4 \quad \text{(2-aminobenzaldehyde)} \xrightarrow{M^{2+}} \text{(M complex)}^{2+} + 4 \text{ H}_2\text{O} \qquad (60)$$

$$(M = \text{Cu, Ni, or Co})$$

The cyclization of allylic dibromides by nickel carbonyl, recently described by Corey and West,[37] a possible mechanism of which is depicted in eq. 61, represents another interesting example of a "template" reaction.

$$\text{BrCH}_2\text{CH}=\text{CH (CH}_2)_6 \text{ CH}=\text{CHCH}_2\text{Br} \xrightarrow{2\text{Ni(CO)}_4} \text{(Ni complex)}^{II} \longrightarrow \text{(cyclic triene)} \qquad (61)$$

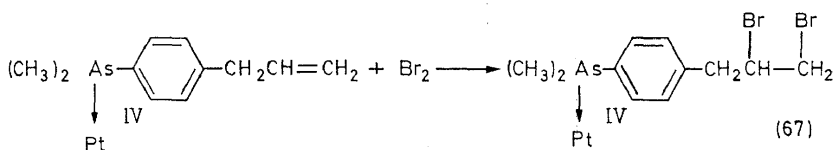$$+ \text{NiBr}_2 + 8\text{CO} \qquad\qquad + \text{Ni}^0$$
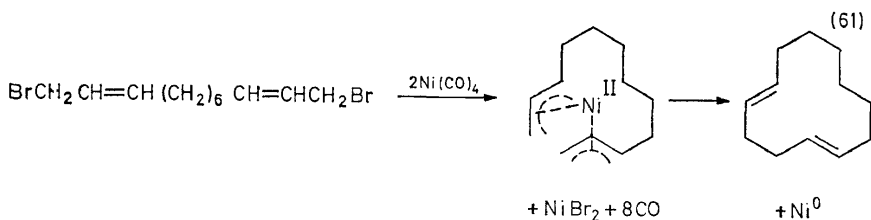
Clear cut indications of kinetic "template" effects are provided by a few reactions which, in contrast to those described above, are truly catalytic. Among these are the nickel(0)-catalyzed trimerization of butadiene to cyclododecetriene[38] (eq. 62) and the stereospecific dimerization of norbornadiene to "Binor-S"[39] (eq. 63).

$$3 \ CH_2{=}CHCH{=}CH_2 \xrightarrow{\ Ni(CDT)\ }$$

(62)

Cyclododecatriene (CDT)

+

Ni (CDT)
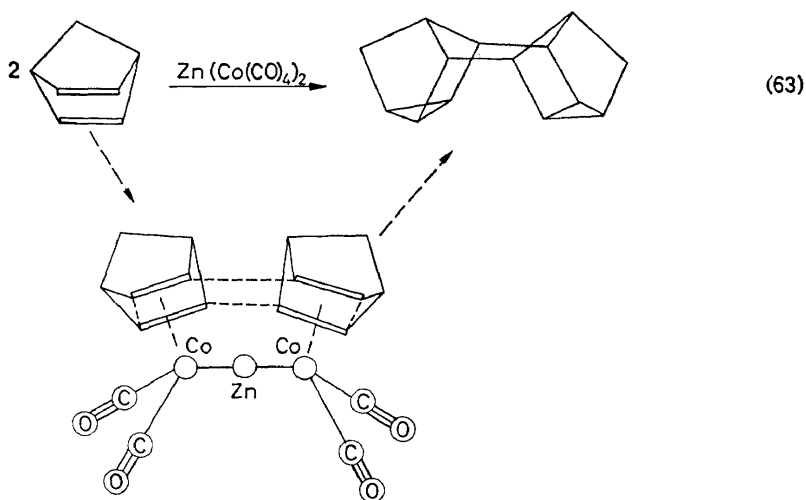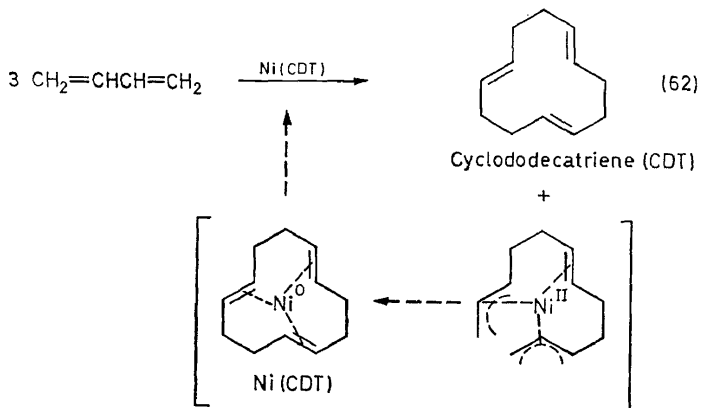
V. Modification of the course of reaction by blocking of a reactive site

The counterpart of the well known and widespread applications of "protective groups" in organic chemistry may be achieved through the blocking of reactive sites by coordination to a metal atom. While not catalytic in nature, this effect sometimes appears so because it results in the modification of the course of a reaction so that the formation of certain products is favoured over that of others. Two such examples are the modification of the course of alkylation of cyanide by coordination to silver(I) (eqs. 64 and 65) and the modification of the course of bromination of an unsaturated arsine by coordination to platinum(IV)[40] (eqs. 66 znd 67).

$$NaCN + RX \rightarrow RCN + NaX \qquad (64)$$

$$AgCN + RX \rightarrow RNC + AgX \qquad (65)$$

$$(CH_3)_2 \text{ As} - \langle \text{C}_6\text{H}_4 \rangle - CH_2CH=CH_2 + Br_2 \longrightarrow (CH_3)_2 \overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{As}} - \langle \text{C}_6\text{H}_4 \rangle - CH_2CH=CH_2 \quad (66)$$

$$(CH_3)_2 \overset{}{\underset{\overset{\displaystyle \downarrow IV}{Pt}}{As}} - \langle \text{C}_6\text{H}_4 \rangle - CH_2CH=CH_2 + Br_2 \longrightarrow (CH_3)_2 \overset{}{\underset{\overset{\displaystyle \downarrow IV}{Pt}}{As}} - \langle \text{C}_6\text{H}_4 \rangle - CH_2\overset{\overset{\displaystyle Br\ \ Br}{|\quad |}}{CH-CH_2} \quad (67)$$
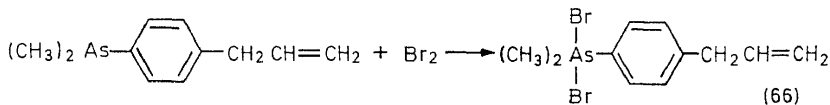
CONCLUDING REMARKS

The versatility of coordination compounds as catalysts is reflected in the number and variety of such compounds that exhibit catalytic activity, in the range of reactions which they catalyze, and in the great variety of mechanisms by which such catalysis is effected. This variety is striking even within a series of closely related reactions such as the hydrogenation of olefinic compounds under the catalytic influence of different metal complexes or under different conditions.

Only a few aspects of the subject encompassed by this symposium have been touched upon in this lecture, the main objective of which has been to convey some measure of overall perspective by classifying the reactions catalyzed by coordination compounds according to certain distinctly recognizable roles of such catalysts. The examples cited were selected principally with a view to illustrating these roles and are thus necessarily confined to some of the simpler reactions, in which the mechanistic features and the role of the catalyst are at least partially understoood. The reactions described are thus illustrative of the field of catalysis by coordination compounds but fall short, by a considerable margin, of conveying its full scope. Among the topics not touched upon in this lecture but covered in other recent reviews[4, 7] and monographs[41-44] are a great variety of addition and oligomerization reactions of olefins, dienes and acetylenes, carbonylation reactions, and recent work on the fixation of molecular nitrogen by coordination compounds of transition metals.

References

[1] E. Peters and J. Halpern. *J. Phys. Chem.* **59**, 793 (1955).
[2] J. Halpern, E. R. Macgregor and E. Peters. *J. Phys. Chem.* **60**, 1455 (1956).
[3] W. K. Wilmarth, J. C. Dayton and J. M. Fluornoy. *J. Am. Chem. Soc.* **75**, 4549 (1953).
[4] J. Halpern. *Advan. Chem. Ser.* **70**, 1 (1968).
[5] A. C. Harkness and J. Halpern. *J. Am. Chem. Soc.* **83**, 1258 (1961).
[6] J. Halpern, B. R. James and A. L. W. Kemp. *J. Am. Chem. Soc.* **83**, 4097 (1961).
[7] E. W. Stern. *Catalysis Rev.* **1**, 73 (1967).
[8] S. Ciccone and J. Halpern. *Can. J. Chem.* **37**, 1903 (1959).
[9] H. Kroll. *J. Am. Chem. Soc.* **74**, 2036 (1952).
[10] D. A. Buckingham, L. G. Marzilli and A. M. Sargeson. *J. Am. Chem. Soc.* **89**, 4540 (1967).
[11] R. Breslow, R. Fairweather and J. Keana. *J. Am. Chem. Soc.* **89**, 2135 (1967).
[12] E. Gelles and A. Salama. *J. Chem. Soc.* **1958**, 3689.
[13] J. Halpern, J. F. Harrod and B. R. James. *J. Am. Chem. Soc.* **88**, 5150 (1966).
[14] J. Halpern and B. R. James. *Can. J. Chem.* **44**, 671 (1966).
[15] J. Halpern and J. B. Milne. *Proc. 2nd Intern. Cong. Catalysis.* Ed. Technip, Paris, 1960. Vol. 1, p. 445.

16 K. Pederson. *Acta Chem. Scand.* **2**, 252 (1948).

17 W. J. Barry. *J. Chem. Soc.* **1960**, 670.

18 W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead and A. G. Sykes. *Disc. Faraday Soc.* **29**, 49 (1960).

19 A. J. Chalk and J. F. Smith. *Trans. Faraday Soc.* **53**, 1235 (1957).

20 J. P. Birk, J. Halpern and A. L. Pickard. *J. Am. Chem. Soc.* **90**. 4491 (1968), and references therein.

21 C. E. Castro and W. C. Kray, Jr. *J. Am. Chem. Soc.* **85**, 2768 (1963). J. K. Kochi and D. D. Davis. *J. Am. Chem. Soc.* **86**, 5264 (1964).

22 J. Halpern and J. P. Maher. *J. Am. Chem. Soc.* **86**, 2311 (1964). **87**, 5361 (1965).

23 J. K. Kwiatek and J. K. Seyler. *J. Organometal. Chem.* **3**, 421 (1965). *Advan. Chem. Ser.* **70**, 207 (1968).

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

25 P. B. Chock and J. Halpern. *J. Am. Chem. Soc.* **91**, 582 (1969).

26 P. W. Schneider, P. F. Phelan and J. Halpern. *J. Am. Chem. Soc.* **91**, 77 (1969).

27 J. Halpern and L. Y. Wong. *J. Am. Chem. Soc.* **90**, 6665 (1968).

28 J. Kwiatek. *Catalysis Rev.* **1**, 37 (1967).

29 L. Simandi and F. Nagy. *Acta Chim. Hungarica* **46**, 137 (1965).

30 P. Krumholz. *J. Am. Chem. Soc.* **75**, 2163 (1953).

31 P. E. Figgins and D. H. Busch. *J. Am. Chem. Soc.* **82**, 820 (1960).

32 G. F. Emerson, L. Watts and R. Pettit. *J. Am. Chem. Soc.* **87**, 132 (1965).

33 R. H. Ball, G. D. Dorough and M. Calvin. *J. Am. Chem. Soc.* **68**, 2278 (1946).

34 A. Eschenmoser. *Pure Appl. Chem.* **7**, 297 (1963).

35 T. J. Hurley, M. A. Robinson and S. I. Trotz. *Inorg. Chem.* **6**, 389 (1967).

36 G. A. Melson and D. H. Busch. *Proc. Chem. Soc.* **1963**, 223.

37 E. J. Corey and E. K. W. West. *J. Am. Chem. Soc.* **89**, 2757 (1967).

38 G. Wilke. *Angew. Chem. (Intern. Ed.)* **2**, 105 (1963).

39 G. N. Schrauzer, B. N. Bastian and G. A. Fosselius. *J. Am. Chem. Soc.* **88**, 4890 (1966).

40 M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long and R. S. Nyholm. *J. Chem. Soc. (A)* **1967**, 2301.

41 M. M. Jones. *Ligand Reactivity and Catalysis*, Academic Press, New York (1968).

42 J. P. Candlin, K. A. Taylor and D. T. Thompson. *Reactions of Transition–Metal Complexes*, Elsevier, Amsterdam (1968).

43 C. W. Bird. *Transition Metal Intermediates in Organic Synthesis*, Logos Press, London (1967).

44 *Organic Synthesis via Metal Carbonyls*, Ed. I. Wender and P. Pino. John Wiley, New York (1968).