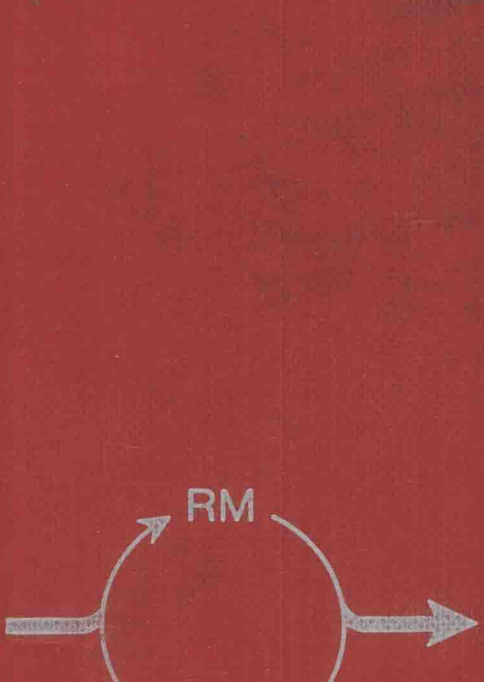
ORGANOMETALLIC MECHANISMS AND CATALYSIS

Jay K. Kochi



Organometallic Mechanisms and Catalysis

The Role of Reactive Intermediates in Organic Processes

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Preface

The renascence in inorganic chemistry over the past two decades has spurred a corresponding activity in the interdisciplinary field of organometallic chemistry. Coupled with the importance of catalysis to most industrial chemical processes, the twin fields of organometallic chemistry and catalysis of organic reactions are now burgeoning in many directions. A number of important reviews and books on this subject have become available, as listed in the bibliography to Chapter 1. The usual treatment of organometallic chemistry and catalysis emphasizes either the metal, the organic functional group, or the reaction type. However, no attempt has been made heretofore to cover the field from a unifying, mechanistic point of view underlying the basic chemical transformations. The absence of such a treatment is understandable since the details of many processes, let alone individual reactions, are not completely understood to a degree commonly held in wholly organic or inorganic systems. Nonetheless, it is now opportune for such an undertaking—certainly with an eye to delineating what is known from what has been intuited. The proper mechanistic delineations will also provide additional insights in the further development of this important area of chemical research.

The organization of this book is designed to cope with the pitfalls inherent in any mechanistic treatment of organometallic chemistry and catalysis. By its nature, a mechanism is an interpretation of a reaction or process, and as such it depends largely on the eyes of the beholder. Like the characters in Kurosawa's classic, *Rashomon*, each sees truth and reality from a different view and at a different level. By considering oxidation-reduction, organometals, and charge transfer interactions separately in Parts One, Two, and Three of this book, I have attempted to minimize the mechanistic bias. As a result, a number of the topics are described in several parts of the book. For example, organic halides are considered as oxidants in various pathways for oxidative additions in Part One, as reagents for effecting the catalytic formation of carbon–carbon bonds in Part Two, and as electron acceptors in Part Three. Similarly, carbon monoxide and metal carbonyls are considered in the three parts, each time from a slightly different, but supportive, perspective. The net result should increase our understanding of organometals, both as reagents and as intermediates. An extensive Index is provided in order to encourage the reader to interconnect these parts and to facilitate the cross referencing.

Two important consequences follow the organization of the subject according to mechanism. First, a number of usually disparate subjects, such as catalytic hydrogenation and polymerization of olefins, become juxtaposed. Second, no rigorous distinction can be made between the behavior of the organometals of the main group elements and that of their transition metal counterparts. Indeed, there are numerous examples in which their chemistries show striking similarities. Taken further, the basic mechanistic considerations in traditional organic chemistry parallel those in purely inorganic systems—beyond the usual comparison often made between S_N1–S_N2 mechanisms of organic derivatives with dissociative-associative mechanisms in metal complexes—and include the area of oxidation–reduction usually considered only in inorganic chemistry.

This book assumes a level of chemical understanding beyond the first year courses in both organic and inorganic chemistry, including a general knowledge of the kinetics and mechanisms of organic and inorganic reactions. It is directed primarily to chemists engaged in the fields of organometallic or inorganic chemistry and catalysis, and to those interested in applying inorganic and organometallic reagents to organic syntheses. In keeping with my concern for excessive mechanistic bias, I have refrained from overinterpreting the data. In many instances I have deliberately presented only the experimental evidence—the reader is encouraged to develop the principal mechanistic conclusions for himself, and to consult the original literature where more speculative interpretations may have been included. As a result, the book may be slow reading; but I hope this less restrictive approach to organometallic mechanisms is worth the added effort, and that it will stimulate further research.

An extensive bibliography of additional material is included at the end of each chapter to provide for further reading. The literature is covered through the end of 1977. Since it is not possible for this book to be free of oversights and errors, either misprints or more serious ones, I will appreciate corrections and criticisms.

The writing of this book has been a labor of love and joy—aided immeasurably by the able and keen assistance of Joy Daniels and the unflagging support of my family.

January, 1978 *Jay K. Kochi*

Glossary

Autoxidation: Oxidations with dioxygen.

Cage effect: Self-reactions of geminate pairs (e.g., derived by the cleavage of an organometal) as a result of constraints imposed by the solvent "wall." See T. Koenig and H. Fischer *in* "Free Radicals," J. K. Kochi, ed., Vol. I, Wiley, New York, 1973.

Chemically induced dynamic nuclear polarization: CIDNP is detected in the nmr spectra of products arising from homolytic reactions performed in a magnetic field. The nuclear polarizations can be observed as *net* effects [i.e., emission (E) or enhanced absorption (A)] or *multiplet* effects [simultaneous emission and absorption (EA or AE)], which arise according to Closs, Kaptein and Oosterhoff from radical pairs either in singlet states from $|S\rangle$ precursors, in triplet states from $|T\rangle$ precursors or with uncorrelated spins from $|F\rangle$ diffusional encounters. See R. Kaptein, *Adv. Free Radical Chem.*, **5**, 319 (1975).

Electron transfer: Addition or removal of an electron from a metal complex or a chemical species leading to its reduction or oxidation, respectively. Reference to *electron transfer* may be made either in the context of the stoichiometry of a redox process or with reference to the mechanism of a particular step (usually outer-sphere). See Chapters 15 and 16 for the comparison with *charge transfer.*

Hammett equation: A linear free energy relationship in which *meta* and *para* substituents on phenyl derivatives are used to measure the sensitivity of the rate of reaction to polar effects. Typically, electrophilic processes have $\rho < 0$ and nucleophilic ones have $\rho > 0$. Also applies to equilibria.

Homolysis: Fragmentation of a diamagnetic molecule into two paramagnetic species, e.g.,

$$CH_3HgCH_3 \longrightarrow CH_3Hg + CH_3\cdot$$

or cleavage of a paramagnetic molecule to produce a radical, e.g.,

$$CH_3CuCH_3 \longrightarrow CH_3Cu + CH_3\cdot$$

Homolyses of organometals can also be considered as one-equivalent reductive eliminations. Furthermore, *homolysis* is implicit in oxidation-reduction reactions in which radicals are produced as a result of one-equivalent changes, e.g.

$$CH_3OOCH_3 + Cu^{I} \longrightarrow CH_3O\cdot + CH_3OCu^{II}$$

Homolytic substitution: Inner-sphere reactions of metal complexes with radicals involving either a *displacement* (S_H2) as in

$$CH_3\cdot + R_3B^{III} \longrightarrow CH_3B^{III}R_2 + R\cdot$$

or *atom transfer* as in

$$CH_3\cdot + Cu^{II}Cl_2 \longrightarrow CH_3Cl + Cu^{I}Cl$$

The distinction between S_H2 and atom transfer is largely made on whether attack occurs on the metal or on the ligand, respectively. Atom transfer involves a one-equivalent change in the formal oxidation state of the metal whereas S_H2 does not.

Inhibition: Prevention of the propagation cycle in a radical chain or catalytic process by destruction of the reactive intermediates or potential initiators. The processes of inhibition and initiation are opposed.

Insertion: The interposition of a molecule into a ligand-metal bond, e.g.,

$$CpFe(CO)_2Me + SO_2 \longrightarrow CpFe(CO)_2OSOMe$$

The term is usually synonymous with *addition*—focus being primarily placed on the addend in insertion.

Kinetic chain length or ***turnover number:*** In a chain or catalytic process, the number of reaction cycles carried out per initiating or catalytic species. The kinetic chain length is equal to the rate of one of the propagation steps divided by the rate of termination.

Oxidation number: The formal oxidation state of the metal in a complex determined as:

$$\text{metal charge} = \text{charge on complex ion} - \Sigma \text{ ligand charges}$$

Some examples are: $Fe(0)(CO)_5$, $HFe(II)(CO)_5^+$, $H_2Ir(III)Cl(CO)L_2$. The designation is completely arbitrary. It is useful as a bookkeeping device to keep track of electron changes in oxidation-reduction processes.

Oxidative addition: Reaction in which the oxidation of a metal complex by an electrophile is accompanied by an increase in its coordination number, e.g.,

$$Fe(CO)_5 + H^+ \longrightarrow HFe(CO)_5^+$$

$$IrCl(CO)L_2 + H_2 \longrightarrow H_2IrCl(CO)L_2$$

usually applied to two-equivalent changes of the metal center without regard to the mechanism. When oxidative addition involves an overall one-equivalent change, a radical is implicated, e.g.

$$CH_3\cdot + Co^{II}(DMG)_2 \longrightarrow CH_3Co^{III}(DMG)_2$$

Reductive elimination: The reverse of oxidative addition, e.g.,

$$(CH_3)_3AuL \longrightarrow CH_3CH_3 + CH_3AuL$$

$$(C_4H_9)_2PtL_2 \longrightarrow C_4H_8 + C_4H_{10} + PtL_2$$

See also *homolysis*.

Retardation: The slowing up of a chain or catalytic process, usually due to inefficient inhibition.

Selectivity: The relative rates of two or more simultaneous processes occurring on the same substrate. Commonly measured by product distributions.

Abbreviations

A	electron acceptor
A	olefin
acac	acetylacetonate
AIBN	azo-bisisobutyronitrile
aq	aquated species
Ar	aryl
bipy	bipyridyl
Bu	butyl
CG	cyclohexanedionedioximate
chel	chelating ligand
Cp	η^5-cyclopentadienyl
CT	charge transfer
D	electron donor
D_n or $\overline{D}$	bond dissociation energy
depe	bisdiethylphosphinoethane ($Et_2PCH_2CH_2PEt_2$)
DME	dimethoxyethane
DMF	dimethylformamide
DMG	dimethylglyoximate
dmpe	bisdimethylphosphinoethane ($Me_2PCH_2CH_2PMe_2$)
DMSO	dimethylsulfoxide
dppe	bisdiphenylphosphinoethane ($Ph_2PCH_2CH_2PPh_2$)
DPPH	diphenylpicrylhydrazyl
dppm	bisdiphenylphosphinomethane
DTBP	di-*t*-butyl peroxide
E or E^+	electrophile
E_A	electron affinity
ee	enantiomeric excess
en	ethylenediamine
ESCA	electron spectroscopy for chemical analysis
ET	electron transfer
Et	ethyl
g	g-value (esr)
hfs	hyperfine splitting
HMPA	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
I_D	ionization potential
L	neutral ligand (usually phosphine)
LUMO	lowest unoccupied molecular orbital
M or m	metal
Me	methyl
MO	molecular orbital
Nuc or Nuc^-	nucleophile
OAc	acetate
OTf	trifluoromethanesulfonate
OTs	*p*-toluenesulfonate
pes	photoelectron spectroscopy
Ph	phenyl
Pr	propyl
py	pyridine
pz	pyrazyl
R	alkyl
S	solvent
SCE	standard calomel electrode
TCNE	tetracyanoethylene
TCNQ	tetracyanoquinodimethane
THF	tetrahydrofuran
X	anionic group, usually halide

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Chapter 1

Metal Catalysis in Organic Chemistry

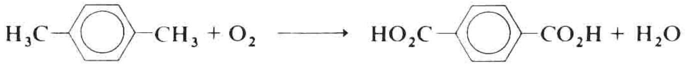
Inorganic complexes are finding increasing use in organic chemistry, both as reagents and as catalysts for carrying out a variety of syntheses.[1–4] In a number of cases, metal catalysis is uniquely suited for effecting reactions which are not otherwise possible, including such conceptually simple transformations as:

$$\mathrm{CH_2{=}CH_2 + HOAc + O_2 \longrightarrow CH_2{=}CH{-}OAc + H_2O}$$

(1)[5–7]

$$\mathrm{CH_3OH + CO \longrightarrow CH_3CO_2H}$$

(2)[8, 9]



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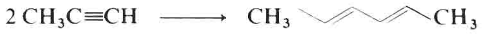
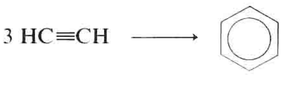


(4)[11, 12]

$$\mathrm{CH_2{=}CHCH_3 + NH_3 + O_2 \longrightarrow CH_2{=}CHCN + H_2O}$$

(5)[13, 14]



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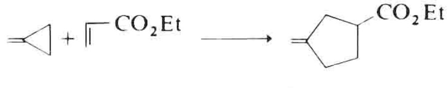
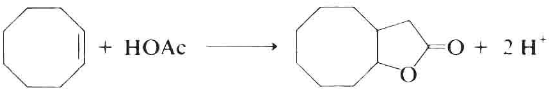


(7)[17]

$$\mathrm{2\,CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_3CH{=}CHCH_3}$$

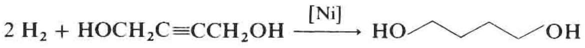
(8)[18a, b]



(9)[19]

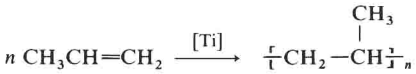
Metal catalysis is important in industrial chemistry[20] since it allows for high selectivity and economic efficiency in such processes as:

Hydrogenation



(10)[21–23]

Polymerization



$$n\ CH_3CH{=}CH_2 \xrightarrow{[Ti]} \left[CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}H\right]_n$$

(11)[24, 25]

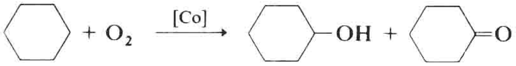
Oxychlorination

$$CH_2{=}CH_2 + HCl + O_2 \xrightarrow{[Cu]} CH_2{=}CHCl + H_2O \qquad (12)^{26}$$

Hydroformylation

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{[Rh]} CH_3CH_2CH_2CHO \qquad (13)^{27,28}$$

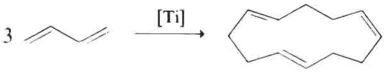
Oxidation



(14)[29]

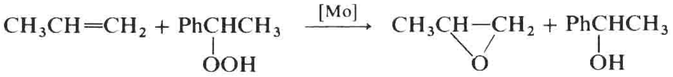
$$CH_2{=}CH_2 + O_2 \xrightarrow{[Pd]} CH_3CHO \qquad (15)^{30}$$

Oligomerization



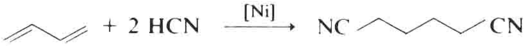
(16)[31]

Epoxidation



(17)[32, 33]

Hydrocyanation



(18)[34a, b]

Despite the large number and variety of important catalytic processes extant, many of the major processes are understood only in general outline, and others are hardly understood at all. This situation is a natural consequence of the difficulty of studying catalytic reactions in which the steady state concentrations of the reactive intermediates are perforce low. To promote further developments in this field, a mechanistic understanding of the chemical interactions between the metal complex and the organic substrate