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by
Metal
Complexes**

***Homogeneous
Catalysis with
Compounds of
Rhodium and
Iridium***

by Ronald S. Dickson

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HOMOGENEOUS CATALYSIS WITH COMPOUNDS OF RHODIUM AND IRIDIUM



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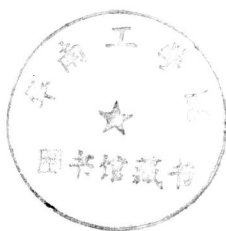
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HOMOGENEOUS CATALYSIS WITH COMPOUNDS OF RHODIUM
AND IRIIDIUM



CATALYSIS BY METAL COMPLEXES

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*To
two very different sources of inspiration –
my family (at home), and
my research group (in the lab.)*

PREFACE

Some years ago, I agreed to contribute a volume to the Academic Press 'Organometallic Chemistry' series — the metals to be covered were *rhodium* and *iridium*. Initially, my plan was to discuss both the fundamental organometallic chemistry and applications in organic synthesis. When the first draft of the manuscript was complete, it was apparent that I had exceeded my allowance of pages by a huge amount. It was then that I decided that the catalysis section warranted separate treatment. I am grateful to Reidel for agreeing to publish this volume on *Homogeneous Catalysis with Compounds of Rhodium and Iridium* as part of their 'Catalysis by Metal Complexes' series.

The material I had for the original Academic Press project covered the literature to the end of 1978. I decided to update this to the end of 1982 with a few key references from 1983. It is some measure of the rate of progress in this field that the number of references almost doubled during this revision.

Students often ask me what is special about rhodium and iridium — why are these particular metals so often used to catalyse organic reactions? An insight into the mechanism of the catalytic reactions, and in particular the role played by the metal, provides the answer. It is now well established that the reaction schemes for homogeneous catalysis are all based on the repetition of a limited set of reaction types. These are coordinative-addition, oxidative-addition plus its reverse, i.e. reductive-elimination, and *cis* migration. For a metal complex to be catalytically active, it must be capable of participating in all of these types of reaction and of exercising kinetic control over the total reaction. Rhodium, and to some extent iridium, fulfills these requirements better than most other metals. The high specificity that is often obtained with these metals offsets their relatively high cost.

The book has been written as a research monograph, and is intended to provide information useful to organic and organometallic chemists in industrial and research laboratories. The first chapter provides a general account of catalysis, contrasting homogeneous and heterogeneous systems, considering the problems associated with recovering soluble catalysts and pointing to the new challenges associated with changing feedstocks. The subsequent chapters deal individually with different classes of reaction — C—H bond activation, C—H

bond formation, carbonylation, C—O bond formation, functional group removal and C—C bond formation. Within this organization, the discussion is based predominantly on catalyst type.

In the writing of this book, I have been helped by a number of people. Peter Maitlis suggested the initial contact with Reidel. I am most grateful to Vicki who helped with the more recent literature search and with the organizing of reference material, and to Val who typed the final draft of the manuscript. The accuracy of the textual material and the diagrams are entirely my responsibility — if there are errors of fact or interpretation, I apologize. My research students again tolerated my preoccupation with book activities without complaint, and I appreciate their patience and cooperation. Finally, I promise my family that there are no plans to take on another project of this magnitude in the foreseeable future — thanks June, Mark, Paul, David, Gill and Ibi for your continuing love and friendship.

Ron S. Dickson

April, 1985

ABBREVIATIONS

Chemicals, ligands, radicals, etc.

Ac	acetyl, CH_3CO
acac	acetylacetonate anion
acacH	acetylacetone
Alk	alkyl
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bipy	2,2'-dipyridine, or bipyridine
BMPP	benzylmethylphenylphosphine
BPPFA	α [2,1'-bis(diphenylphosphinoferrocenyl) ethyldimethylamine
BPPM	<i>N</i> -(<i>t</i> -butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl] pyrrolidine
Bu	butyl (superscript i, s, or t refers to iso, secondary or tertiary butyl)
CAMP	cyclohexylisylmethylphosphine
CHAIRPHOS	1,3-bis(diphenylphosphino)butane
CHIRAPHOS	2,3-bis(diphenylphosphino)butane
COD	1,5-cyclooctadiene
Cy	cyclohexyl
DIOP	2,3- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane
DIOXOP	bis(diphenylphosphinomethyl)dioxolan
DIPAMP	1,2-bis(phenylisylphosphino)ethane
DMA	dimethylacetamide, MeCONMe_2
DMF	<i>N,N'</i> -dimethylformamide, HCONMe_2
DMG	dimethylglyoximate anion
DMGH ₂	dimethylglyoxime
DMSO	dimethyl sulfoxide, Me_2SO
Et	ethyl, CH_3CH_2
HMDB	hexamethyldewarbenzene
HMPT	hexamethylphosphoric triamide, $\text{OP}(\text{NMe}_2)_3$

L	ligand
Me	methyl, CH ₃
NBD	norbornadiene
NORPHOS	(-)-(R,R)-2- <i>exo</i> -3- <i>endo</i> -bis(diphenylphosphino)bicyclo[2.2.1]-heptene
NPTP	naphthylphenyltolylphosphine
OAc	acetate ion
Ⓢ	polymer support
PAMP	phenylanisylmethylphosphine
PDPE	1,2-bis(diphenylphosphino)-1-phenylethane
Ph	phenyl, C ₆ H ₅
phen	1,10-phenanthroline
PNNP	<i>N,N'</i> -bis(diphenylphosphino)-1,4-diphenyl-2,3-diaminobutane
PPFA	α-[2-diphenylphosphinoferrocenyl] ethyldimethylamine
PPPM	4-pivaloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)-methyl] pyrrolidine
Pr	propyl (superscript i refers to iso)
PROPHOS	1,2-bis(diphenylphosphino)propane
py	pyridine
pz	pyrazolyl
R	alkyl group
S	solvent
[Si]	silica support
SKEWPHOS	2,4-bis(diphenylphosphino)pentane
THF	tetrahydrofuran
X	halogen

Units, etc.

Å	Angstrom unit, 10 ⁻¹⁰ m
atm	atmospheres, 1 atm = 101 325 Pa
cm ⁻¹	wave number
ee	enantiomeric excess
EPR	electron paramagnetic resonance
ESCA	electron spectroscopy for chemical analysis
(g)	gaseous state
Hz	hertz, s ⁻¹
IR	infrared
kJ	kilojoule
MPa	megapascal
nm	nanometres, 10 ⁻⁹ m

NMR	nuclear magnetic resonance
Pa	pascal, $1 \text{ Pa} = 1 \text{ N m}^{-2}$
psi	pounds per square inch, $1 \text{ psi} = 6894.8 \text{ Pa}$
μm	micron, 10^{-6} m

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CHAPTER 1

SOME GENERAL COMMENTS ON TRANSITION METAL CATALYSTS

The making and breaking of metal-carbon bonds has become an important and versatile tool in synthetic organic chemistry [see, for example 50, 179, 339, 402, 766, 981, 1134, 1236, 1251, 1367]. Transition metal assisted reactions used for the manufacture of organic compounds on an industrial scale include the oxidation, hydrogenation, hydroformylation, isomerization and polymerization of alkenes, diene cyclooligomerization and alcohol carbonylation. Other reactions, such as the asymmetric hydrogenation of prochiral alkenes, the activation of C-H bonds for H/D exchange, the reduction of ketones by hydrosilation and the decarbonylation of aldehydes are also catalysed by complexes of transition metals. These reactions have wide application in laboratory-scale preparations, and some are also used in the manufacture of pharmaceuticals.

Reactions of the types just mentioned, and indeed, a majority of all organic reactions, are controlled by kinetic rather than thermodynamic factors. The addition of transition metal complexes that can become intimately involved in the reaction sequence is an effective way of increasing the reaction rates. The transition metal catalyst lowers the energy of activation for the reaction by changing the mechanism [981], and in some cases it relaxes restrictions imposed by orbital symmetry control [649, 1114, 1378].

1.1 Catalysts and Catalyst Recovery

During the last 30 years, industrial organic chemistry has been based largely on petroleum products, and most petrochemical processes use heterogeneous rather than homogeneous catalysts. This is principally because heterogeneous catalysts are generally more stable at higher temperatures and are less troublesome to separate from the substrate phase. However, there is a growing interest in homogeneous catalysts because they often show higher selectivity and greater catalytic activity, and they also provide greater control of temperature on the catalyst site. For some commercial processes it has been determined that these advantages of soluble catalysts outweigh the economic problems associated with catalyst recovery. Examples include the hydroformylation of alkenes specifically to straight-chain aldehydes which is catalysed by $\text{HRh}(\text{CO})(\text{PPh}_3)_2$,

and the carbonylation of methanol to acetic acid with $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ as the active catalyst; these processes are discussed in detail in later chapters. Some of the difficulties associated with separating homogeneous catalysts from the reaction products (and methods of overcoming them) are indicated in Table 1.1.

TABLE 1.1
Methods used for recovery and regeneration of rhodium catalysts
from carbonylation and hydroformylation processes

Process for separation from reaction mixture	Method [reference]
Reverse osmosis	Separation achieved with silicon latex membranes under pressure – catalyst and other species of molecular diameter $>10 \text{ \AA}$ are separated from organic material such as heptanal [608]; similarly with polyalkene membranes [607].
Adsorption	Adsorption on magnesium silicate, then desorption with THF containing Et_3N [509]; adsorption on refractory support, then volatilization and carbonization [547]; adsorption from acidic solution with activated carbon, and isolation by filtration [1196]; adsorption on 'Sirotherm TM ' (a thermally regenerable ion-exchange resin used for desalination) [936].
Precipitation	Treatment of the product mixture (alcohols) with anhydrous gaseous NH_3 to precipitate the rhodium complexes [1450].
Cation-exchange treatment	Oxidation with $\text{HNO}_3/\text{H}_2\text{O}_2$, followed by isolation of rhodium from aqueous phase with cation exchanger – desorption achieved with aqueous HCl [1017]; see also [1072, 1073].
Extraction: two-phase systems	Treatment of reaction residues with paraffins (e.g., hexane and polar organic solvent such as acetonitrile) – rhodium complexes found in polar phase [1194]; separation into aqueous phase by heating with 10% aqueous solution of organic acid such as HCO_2H or MeCO_2H [498]; amino group included in phosphine ligand, e.g., $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_3$ – catalyst then soluble in weakly acidic media without decomposition [64]; tarry residue treated with aqueous, alkaline NaCN – rhodium then found in aqueous phase [1329]; extraction with CO_2 , C_2 – C_4 hydrocarbon or $\text{HCl}(\text{g})$ under conditions above critical temperatures and pressures [1553]; other examples [204, 453, 472, 506, 750, 811, 1332].
<i>In situ</i> regeneration of catalyst	Soluble carbonyl–rhodium catalyst recovered by heating residue with H_2 at 100 – 180°C , 200 atm pressure in presence of carrier such as C/Pd , then treating with CO in methanol containing MeNH_2 , PPh_3 or other L at 120 – 160°C , 300–700 atm pressure [1877]; residue refluxed at high pressure, sediment isolated by decantation and solid residue dissolved in fresh catalyst solution under CO at elevated temperature and pressure [500]; treatment with aqueous acid, H_2O_2 , X^- ,