

ORGANOMETALLIC CHEMISTRY OF RHODIUM AND IRIDIUM

Ronald S. Dickson

ORGANOMETALLIC CHEMISTRY

A Series of Monographs

Organometallic Chemistry of Rhodium and Iridium

Ronald S. Dickson

Department of Chemistry
Monash University
Clayton, Victoria
Australia

1983



Academic Press

A Subsidiary of Harcourt Brace Jovanovich, Publishers

London New York

Paris San Diego San Francisco

São Paulo Sydney Tokyo Toronto

ACADEMIC PRESS INC. (LONDON) LTD.
24/28 Oval Road
London NW1

United States Edition published by
ACADEMIC PRESS INC.
111 Fifth Avenue
New York, New York 10003

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British Library Cataloguing in Publication Data

Dickson, R. S.
Organometallic chemistry of Rhodium and Iridium
1. Rhodium
I. Title
547'.05634 QD181.R5

ISBN 0-12-215480-0
LCCCN 83-70441

Typeset by Bath Typesetting Ltd., Bath
and printed in Great Britain by
St. Edmundsbury Press, Bury St. Edmunds, Suffolk

*Organometallic
Chemistry of
Rhodium and Iridium*

ORGANOMETALLIC CHEMISTRY

A Series of Monographs

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Preface

I accepted an invitation to write this book when I was on study leave in 1971. During the next several years, there were many half-hearted attempts to get started, but finally the detailed writing was delayed until I could again take study leave in 1978. My collection of reference cards expanded incredibly during the interval of six years, and at many times during the writing period I despaired that the job could ever be finished. At last the volume is complete; the literature has been covered (fairly) comprehensively to the end of 1978 and some key references from 1979 have been included. (An addendum to the key references from the recent literature has also been included.) I have greatly expanded my own knowledge of the *Organometallic Chemistry of Rhodium and Iridium*, and so it has been a worthwhile task for me. If others who refer to the book from time to time find that it provides useful information, or better that it stimulates new research, then I will be doubly rewarded.

I have presented and discussed results, developments and applications obtained by thousands of investigators from research and industrial laboratories around the world. If anyone feels offended by my presentation and/or interpretation of their results, I apologize. With so much to cover, I may have missed the point occasionally, and I imagine that some worthwhile contributions have been missed entirely.

My warm thanks are extended to several friends and colleagues who found time to help me with the book. In the United Kingdom, Gordon Stone and Peter Maitlis set me going initially and then provided support and encouragement when the going got tough. My many friends in the Department of Inorganic and Analytical Chemistry at LaTrobe University provided an ideal environment for book writing during 1978. During 1979–1982, my research students at Monash tolerated my preoccupation with manuscript preparation when I should have been writing research papers. In Canberra, Martin Bennett offered many useful comments on the first draft, and I took heed of most of them. Vicki helped with the organization of references, and with checking proofs. My greatest thanks are reserved for a very special friend—my wife June. She suffered my many moods, provided constant encouragement, and uncomplainingly transformed my scribbles into

readable typescript which became the first draft. Sharon, Val and Anne typed the final version of the manuscript, and they did it wonderfully well.

Clayton, Victoria
May 1983

Ronald S. Dickson

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Chapter I

The General Chemistry of Rhodium and Iridium—A Brief Survey

The chemical usefulness of rhodium and iridium stems from two quite different characteristics. First, the metals are especially inert—they are classified as *noble metals*. Secondly, the complexes of the metals display a particularly *rich chemistry* which has led to many *catalytic applications*.

A. Noble metals (231)*

In the massive state, both rhodium and iridium are highly resistant to oxidation and corrosion. They are unaffected by all acids, including aqua regia. Attack by oxygen and the halogens does occur at red heat, but it is rather slow, particularly for rhodium. Some applications of the metals are based on this inertness. Thus, rhodium is used in furnace windings, thermocouples, and for plating jewellery. The metals can be used as adsorption catalysts for reactions which require high temperatures and oxidizing conditions. This is well illustrated by the use of platinum-rhodium gauzes to catalyse the oxidation at 850°C of ammonia to nitric acid. The metals are also important catalysts at lower temperatures and under reducing conditions. For instance, a particularly effective catalyst for the reforming of crude oils is obtained by supporting iridium with platinum on alumina. Other applications of rhodium and iridium in heterogeneous catalysis are numerous, but they are outside the scope of this book.

* Numbers in parentheses refer to numbered references at the end of the book.

B. Rich chemistry (506)

The metals can be converted by direct reaction to halides such as RhCl_3 and IrCl_3 . These anhydrous halides are insoluble in water, and they are rather inert. The hydrated chloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, can be obtained by dissolving Rh_2O_3 in aqueous hydrochloric acid, and by electrolytic dissolution of the metal in hydrochloric acid. It dissolves readily in a variety of organic solvents and in water, and it is the usual starting material for preparing complexes of rhodium. Hydrated iridium(III) halides are obtained in similar manner by dissolving $\text{Ir}_2\text{O}_3(\text{aq})$ in the appropriate acid; salts of the type $\text{M}_3[\text{IrX}_6]$ can be isolated from the solutions by the addition of MX (M = alkali metal or NH_4^+ , X = halide). Solutions containing $[\text{IrCl}_6]^{3-}$ are often used to prepare other complexes of iridium(III). Treatment of a suspension of hydrous IrO_2 in aqueous hydrochloric acid with an alkali metal chloride yields Na_2IrCl_6 , and this water soluble salt is the usual starting material for the preparation of other iridium(IV) complexes.

Some reactions of the metal halides result in reduction of the metal. For instance, treatment of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with excess triphenylphosphine in ethanol yields the rhodium(I) compound $\text{RhCl}(\text{PPh}_3)_3$, and $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ is obtained by reacting Na_2IrCl_6 with triphenylphosphine in refluxing 2-methoxyethanol under an atmosphere of CO . Further reduction gives complexes in which zero or negative formal oxidation states are stabilized by π -acceptor ligands. The binary carbonyl $\text{Rh}_4(\text{CO})_{12}$ and the carbonylate anion $[\text{Rh}(\text{CO})_4]^-$ are examples of complexes with the metal in the oxidation state 0 and -1 respectively.

The chemical behaviour of 4-coordinate complexes of rhodium(I) and iridium(I) is extensive and significant. These compounds are coordinatively unsaturated species, and they undergo an important series of reactions that provide the basis for our understanding of homogeneous catalysis (466). The main reaction types are termed coordinative-addition, oxidative-addition, reductive-elimination, and *cis*-migration.

Complexes of metals with a d^8 (Rh^{I} , Ir^{I}) or d^6 (Rh^{III} , Ir^{III}) electron configuration are coordinatively-saturated when the coordination number is 5 or 6 respectively. Consequently, species such as $\text{RhCl}(\text{PPh}_3)_3$ and $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ (d^8 , 4-coordinate), or $\text{H}_2\text{RhCl}(\text{PPh}_3)_2$ and $[\text{H}_2\text{Ir}(\text{PPh}_3)_3]^+$ (d^6 , 5-coordinate), are classified as coordinatively-unsaturated complexes (1808). The existence of vacant coordination sites is an essential property of homogeneous catalysts because it permits substrate molecules to enter the coordination sphere of the metal. The binding of two or more substrate molecules in a well defined geometric relation can then lead to specificity of reaction. The iridium(I) complex $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ is often taken as a model for illustrating the behaviour of coordinatively-unsaturated complexes. As shown in Fig. I.1,

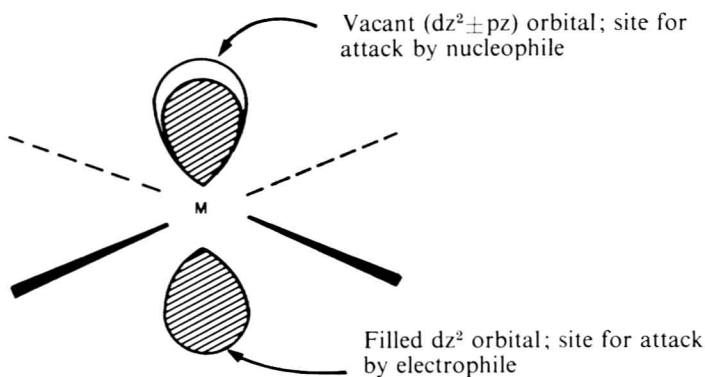


FIG. I.1.

the planar configuration permits, at least in principle, attack by both nucleophilic and electrophilic reagents on an orbital of σ -symmetry. In some cases, it is possible to generate a vacant site in a metal complex by expulsion of a ligand. For example, ligand dissociation from $\text{HIr(CO)(PPh}_3)_3$ (d^8 , 5-coordinate) can be induced either thermally or photochemically, and this procedure transforms a catalytically inactive system into an active one:



The addition of substrate molecules to coordinatively-unsaturated metal complexes can occur by coordinative-addition (i.e. there is increase in the coordination number but not in the oxidation state of the metal). This is illustrated by treatment of $\text{Ir(CO)Cl(PPh}_3)_2$ (Fig. I.2) with Lewis acids such as BF_3 or Lewis bases including CO to form the adducts $\text{Ir(CO)Cl(PPh}_3)_2 \cdot \text{Y}$ (Fig. I.3; $\text{Y} = \text{BF}_3$ or CO): An important consequence of this type of addition reaction is that the coordinated ligand is often kinetically more reactive than the free ligand. Coordinated ethylene, for example, is susceptible to electrophilic attack by HCl whereas free ethylene is relatively inert to such reagents. To explain this change in reactivity, it is conceptually useful to relate the coordination of small molecules to the process of electronic excitation (416).

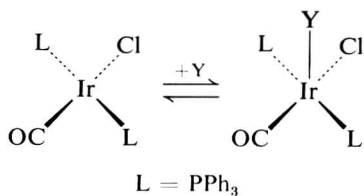


FIG. I.2

FIG. I.3

The addition of some substrates to coordinatively-unsaturated complexes occurs in a different manner. Thus, there is dissociation of the coordinating molecule with concomitant oxidation of the metal. Conversion of the 4-coordinate, iridium(I) complex (Fig. I.4) to the 6-coordinate iridium(III) species (Fig. I.5) illustrates this process which is known as oxidative-addition

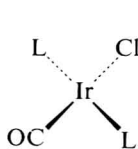


FIG. I.4

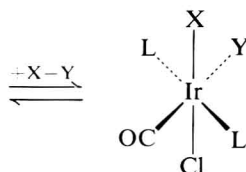


FIG. I.5

(1761). The reverse process is termed reductive-elimination. Oxidative-addition occurs when some 4-coordinate, d^8 metal complexes are treated with substrates such as H_2 , HCl , Br_2 , RX and $RCOX$.

When various substrates are bound to the same metal, interaction between neighbouring groups sometimes occurs. The conversion of an alkyl-carbonyl-metal species (Fig. I.6) to an acyl-metal complex (Fig. I.7) provides one



FIG. I.6

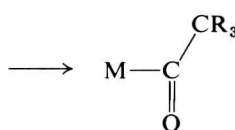
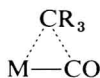


FIG. I.7

example of this type of behaviour. Another important example involves the inter-conversion between alkene-hydrido-metal complexes (Fig. I.8) and the alkyl-metal systems (Fig. I.9). Reactions of these types are termed *cis*-migration or insertion reactions.

A great deal of the recent development of rhodium and iridium chemistry has been concerned with reactions involving organic species that lead to complexes containing $M-C$ bonds. The range of such complexes is incredibly large; the ethylene complex $[Rh(C_2H_4)_2Cl]_2$, the tris-allyl complex

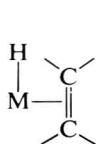


FIG. I.8

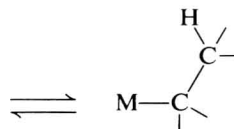
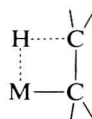


FIG. I.9

$\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$, the species $\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3)$ in which 1,5-cyclooctadiene is bound to the metal in *tetrahapto*-manner, the bis-cyclopentadienyl cations $[(\eta\text{-C}_5\text{H}_5)_2\text{M}]^+$ ($\text{M} = \text{Rh}, \text{Ir}$), the alkyne complex $\text{Rh}_2(\text{PF}_3)_6(\text{MeC}_2\text{Me})$, and the σ -bonded species $\text{Ir}(\text{CO})(\text{Pr})(\text{PPh}_3)_2$ and $\text{Rh}(\text{COMe})\text{Cl}_2(\text{PPh}_3)_2$ are just a few representative examples. There has been considerable interest in the molecular structures of many of these complexes, and in relating bonding models to the observed geometries. In many cases, spectroscopic results are consistent with the existence of dynamic structures in solution.

Many of these organometallic complexes exhibit interesting and synthetically useful chemical behaviour. The lability and volatility of cyclooctene in $[\text{Ir}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$, for example, provides a convenient route to a large range of complexes of iridium(I). The enhanced reactivity of coordinated ligands has been mentioned already, and this can lead to the formation of interesting substitution derivatives of unsaturated hydrocarbons. In other cases, two or more unsaturated molecules which are coordinated to the metal undergo intramolecular condensation reactions. An interesting example of this behaviour is the cyclization of two alkynes to form a coordinated cyclobutadiene.

C. Catalytic applications

The making and breaking of metal-carbon bonds has become an important and versatile tool in synthetic organic chemistry (66, 209, 977, 1157), and compounds of rhodium and iridium have played a particularly important role in the recent development of this area. Indeed, there are now several major industrial processes, as well as a number of selective reaction steps used in the synthesis of pharmaceuticals and other fine chemicals, that are based on the catalytic activity of these metals. In a book of this size, it is not possible to cover this area in any detail. However, the following selected examples will give some idea of the range of reactions and catalysts that have been discussed in the recent literature.

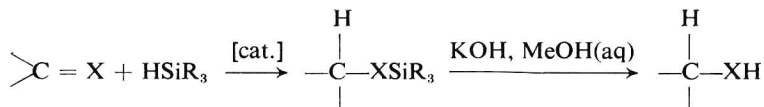
Many different compounds of rhodium and iridium are effective hydrogenation catalysts (1020). Perhaps the best known is "Wilkinson's catalyst", $\text{RhCl}(\text{PPh}_3)_3$; others include $\text{HM}(\text{CO})(\text{PPh}_3)_a$ ($\text{M} = \text{Rh}$ and Ir), RhCl_3py_3 in the presence of NaBH_4 , and the solvated, cationic complexes $[\text{H}_2\text{Rh}(\text{PR}_3)_2\text{S}_2]^+$. In general, compounds of rhodium are more reactive than analogous compounds of iridium (1763). Related complexes with chiral ligands have been used for the asymmetric hydrogenation of prochiral substrates (1070, 1394), and many of the catalytic systems have been attached to polymer or other insoluble supports (890, 958).

Although hydrogenation is generally achieved with H_2 (or mixtures of CO and H_2), other sources of $[\text{H}]$ are sometimes used. The reduction of

alkenes and alkynes by means of formic acid in the presence of complexes such as $\text{RhCl}(\text{PPh}_3)_3$ has been described (1933). Another example is provided by the reduction of some ketones by H-transfer from alcoholic solvents; catalysts formed from $[\text{IrCl}_6]^{3-}$ and $\text{P}(\text{OEt})_3$ in Pr^iOH are particularly effective (911).

Two modes of reaction are possible in metal catalysed hydrogenation reactions. Formation of a hydride can be followed by coordination of an alkene, or alternatively, formation of the alkene complex can precede the reaction with H_2 . It has been established (1501) that the former pathway is followed when $\text{RhCl}(\text{PPh}_3)_3$ is the catalyst. However, there is some uncertainty about other aspects of the overall reaction pathway despite detailed kinetic investigations (see, e.g. 576, 875, 1644). With some other catalysts (e.g. $\text{HRh}(\text{CO})(\text{PPh}_3)_a$ (1477, 1768)), alkene coordination precedes the oxidative addition of H_2 .

Many systems that will catalyse the homogeneous hydrogenation of C—C multiple bonds lack activity towards the reduction of other unsaturated bonds such as C=O. Hydrosilation of the C=X group followed by hydrolysis provides a means of overcoming these problems (1119, 1257, 1487).



Some of the more effective hydrosilation catalysts are RhClL_3 compounds (L = tertiary phosphine), $\text{HRh}(\text{PPh}_3)_a$, $\text{M}(\text{CO})\text{ClL}_2$ (M = Rh and Ir), and $\text{HRh}(\text{CO})(\text{PPh}_3)_a$. The mechanism of the hydrosilation reaction is probably closely related to that of hydrogenation.

Some complexes of rhodium and iridium are effective catalysts for reactions that require the activation of C—H bonds (1520). These include dehydrogenation reactions, H—D exchange, and double bond migrations. Some related reactions which involve C—C bond rupture include alkene metathesis (1095, 1386) and ring opening (208, 1305); some compounds of rhodium and iridium are able to promote these reactions.

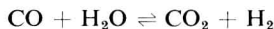
Many rhodium compounds catalyse the addition of CO to organic substrates, and these reactions are useful for the formation of oxygenated compounds such as carboxylic acids, acid halides, ketones and isocyanates. The best known carbonylation reactions are those that involve the formation of aldehydes and alcohols by the simultaneous addition of CO and H_2 to an alkene:



Rhodium carbonyl compounds are effective catalysts for this type of hydroformylation reaction, particularly when used with excess tertiary phosphine—this system is now used in the commercial production of linear aldehydes. Several recent reviews (497, 745, 1316, 1580) discuss the essential chemistry of the rhodium catalysed hydroformylation reaction.

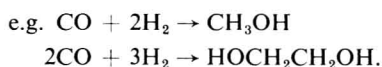
A range of rhodium compounds (e.g. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$) in the presence of promoters such as iodomethane, are highly active and selective for the carbonylation of methanol to acetic acid. This process has been developed by Monsanto for the commercial production of acetic acid (1387), and the detail of the system is described in several reviews (1642, 1707).

The carbonylation of a number of organic substrates has been achieved in the presence of water or secondary alcohols. Reactions involving $\{\text{CO} + \text{H}_2\}$ are of particular interest because this mixture is recognized (734) as a valuable source of hydrogen:



This system, known as the “water–gas shift reaction”, is catalysed by several transition metal complexes including $[\text{Rh}(\text{CO})_2\text{I}]_2$ in aqueous acetic acid (379). With appropriate adjustment of the $\text{CO}:\text{H}_2\text{O}$ ratio, it is possible to generate a useful reaction mixture containing CO and H_2 plus the relatively inert CO_2 .

Renewed interest in the water–gas shift reaction has been coupled with attempts to find new catalysts for the formation of oxygenated products from direct reaction between CO and H_2 :



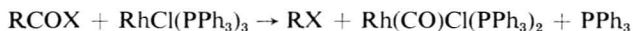
These reactions proceed under high pressures in the presence of various rhodium carbonyl compounds, and the product distribution is consistent with a hydroxymethylene growth reaction (1580).

The oxygenation of organic substrates is promoted by various complexes of rhodium and iridium (1260), and the formation of methyl ketones, $\text{RC}(\text{:O})\text{CH}_3$, from terminal alkenes, $\text{RCH}:\text{CH}_2$, is a good example. Compounds such as $\text{RhCl}(\text{PPh}_3)_3$, $\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ ($\text{M} = \text{Rh}$ and Ir), and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ are effective catalysts for the reactions with particular alkenes. Several other reactions that involve the formation of new $\text{C}—\text{O}$ bonds have H_2O or ROH as the source of $[\text{O}]$. A simple example is the hydration of acetylene to acetaldehyde which is catalysed by $[\text{RhCl}_a(\text{H}_2\text{O})_{6-a}]^{(a-3)-}$ (1026).

There are some catalytic cycles that convert nitric oxide and carbon monoxide to nitrous oxide and carbon dioxide. An understanding of the mechanism of this reaction may be of value in relation to car exhaust emission

controls. Amongst the transition metal compounds that effectively catalyse this reaction in solution are the dinitrosyl cations $[M(NO)_2(PPh_3)_2]^+$ ($M = Rh$ and Ir) (901) and the dicarbonyl anion $[Rh(CO)_2Cl_2]^-$ (913, 1369).

The removal of particular functional groups from organic molecules is achieved in reactions with some rhodium compounds. A well studied example is the stoichiometric decarbonylation of acid halides by treatment with $RhCl(PPh_3)_3$ (1760, 1818):



Some reactions of unsaturated organic substrates lead to the formation of new C—C bonds. Examples are the dimerization of ethylene to 1-butene, the formation of 1,4-hexadiene by the co-dimerization of ethylene and 1,4-butadiene, the polymerization of norbornene, and the alkylation of ketones. These and many related reactions are catalysed by various compounds of rhodium and iridium. The insertion of an alkene into a M—C bond plays a key role in many of the reaction pathways, and this topic has been reviewed recently (914).

D. Analytical procedures

Elemental analysis plays an important role in the characterization of organo-rhodium and -iridium compounds. Classical procedures for the determination of carbon and hydrogen can be used. One account (787) describes the combustion of samples in a quartz container under a stream of O_2 and determination of C and H in the usual way by absorption of CO_2 and H_2O , followed by determination of the metal in the ash. Iridium is determined in metallic form by combusting the sample at $800^\circ C$ followed by reduction of the oxide in a stream of H_2 . Rhodium is determined as Rh_2O_3 by weighing the ash from the initial combustion at $800^\circ C$. An alternative procedure for the microanalytical determination of rhodium in organometallic compounds is based on polarographic studies of rhodium(III) in thiocyanate media (1541). Numerous other techniques for the quantitative determination of rhodium and iridium are described in a reference book by Ginsburg *et al.* (808).

Infra-red, n.m.r. and mass spectroscopy are powerful tools for the characterization of organometallic compounds (376). A host of applications of these techniques to organo-derivatives of rhodium and iridium are described in the following chapters. The characterization of carbonyl compounds is especially dependent on assignment of the $\nu(CO)$ frequencies in the infra-red spectra, and mass spectroscopy is a powerful analytical tool for cluster compounds. The nuclear spin of rhodium ($S = \frac{1}{2}$, 100% natural abundance)