KINETICS AND MECHANISM OF HYDROGENOLYSIS OF
A RUTHENIUM(II) ACYL COMPLEX

by

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ABSTRACT

This thesis describes the results of kinetic investigations into the hydrogenolysis of the ruthenium-acyl complex dicarbonylchloro-(norbornenoyl)bis(triphenylphosphine)ruthenium(II), $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$, **2**. N,N-Dimethylacetamide (DMA) and toluene solutions of **2** react with one mole equivalent of H_2 to give $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$, **3**, and the unsaturated aldehyde product $\text{C}_7\text{H}_9\text{CHO}$, **4**. The subsequent, relatively slow hydrogenation of **4** by a further mole of H_2 to give the saturated aldehyde $\text{C}_7\text{H}_{11}\text{CHO}$, **5**, was found to be catalyzed by **3**.

A detailed kinetic study on the hydrogenolysis of **2** in DMA solvent revealed a first-order rate dependence on $[\text{Ru}]_{\text{Total}}$, an inverse dependence on added $[\text{PPh}_3]$, and a first- to zero-order dependence on H_2 pressure. The following mechanism is proposed to account for these observations:

Values of k_1 and k_{-1}/k_2 have been evaluated at 65°C ($k_1 = 4.6 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$, $k_{-1}/k_2 = 1.7 \pm 0.2$) and the activation enthalpy and entropy for the k_1 step determined ($\Delta H^\ddagger = 69 \pm 7 \text{ kJ mole}^{-1}$, $\Delta S^\ddagger = -126 \pm 13 \text{ JK}^{-1} \text{ mole}^{-1}$).

New, and as yet incompletely characterized, ruthenium complexes of stoichiometry " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ ", 6, " $\text{RuCl}(\text{C}_6\text{H}_8)(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ -benzene solvate", 7, and $\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, 8, have been synthesized by the reactions of 1,4-cyclohexadiene (C_6H_8) with $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ (complexes 6 and 7), and $\text{RuCl}_2(\text{PPh}_3)_3$ (complex 8), respectively. Reactions of 6, 7, and 8 in DMA with H_2 and with CO were investigated, and the organic and inorganic products identified:

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LIST OF ABBREVIATIONS

The following list of abbreviations, most of which are commonly adopted in chemical literature, will be employed in this thesis:

$^{13}\text{C}\{^1\text{H}\}$	proton broad-band decoupled carbon n.m.r.
Cp	cyclopentadienyl, C_5H_5
CYHD	cyclohexadiene, C_6H_8
DMA	N,N-dimethylacetamide, $\text{CH}_3\text{CON}(\text{CH}_3)_2$
dppe	1,2-bis(diphenylphosphino)ethane $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$
Et	ethyl, C_2H_5
i.r.	infra-red
J	coupling constant, Hz
L, L'	ligands
ln	natural logarithm
M	molar concentration or metal atom
Me	methyl, CH_3
n.m.r.	nuclear magnetic resonance
P	phosphine ligands or pressure
$^{31}\text{P}\{^1\text{H}\}$	proton broad-band decoupled phosphorus n.m.r.
PPh_3	triphenylphosphine, $(\text{C}_6\text{H}_5)_3\text{P}$
Ptol_3	tri(p-tolyl)phosphine, $(\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{P}$
$[\text{Ru}]_{\text{T}}$	total initial concentration of $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$
UV	ultra-violet
X	halide ligands, Cl, Br or I

δ	chemical shift, ppm
ϵ	molar extinction coefficient
ν	frequency, cm^{-1}

Some of the compounds used during the course of this work have been referred to by numeral symbols in this thesis for the sake of brevity and simplicity. Following is the list of complexes corresponding to each such symbol:

<u>Symbol</u>	<u>Compound</u>
1	$\text{HRuCl}(\text{NBD})(\text{PPh}_3)_2$
2	$\text{RuCl}(\text{CO} \cdot \text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$
3	$\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$
4	$\text{C}_7\text{H}_9\text{CHO}$
5	$\text{C}_7\text{H}_{11}\text{CHO}$
6	" $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ "
7	" $\text{RuCl}(\text{C}_6\text{H}_9)(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ -benzene solvate"
8	$\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-R} \end{array}$$

$\text{CO} \cdot \text{R}$ denotes acyl substituent-

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Catalysis remains one of the most active fields of chemical research and has been highlighted in the Pimentel report¹ as one of key significance. The last three decades have witnessed an ever-increasing interest in the study of homogeneous catalysis resulting in tremendous advances and development in the area. A large number of coordination and organometallic compounds, particularly those of transition metals, have been tested for catalytic activity toward a wide range of chemical reactions; these include hydrogenation of unsaturated organic substrates, olefin isomerization, dehydration of tertiary alcohols, hydroformylation, and water-gas shift reaction, to name but a few.²

The relative merits and demerits of homogeneous and heterogeneous catalysts, especially from an industrial point of view, have been widely discussed.³⁻⁶ Homogeneous catalysis offers the following advantages over the industrially more prevalent heterogeneous catalysis:

- i) Higher activity of homogeneous catalysts allows use of milder reaction conditions.
- ii) Higher selectivity, specificity, and reproducibility of homogeneous catalysts are strongly desirable for industrial processes.
- iii) Catalytic properties of homogeneous catalysts may be varied systematically by changing the ligands.

iv) Ease of kinetic and mechanistic studies of homogeneous systems by conventional spectroscopic and kinetic techniques allows for more detailed mechanistic investigations.

Oxygen- and moisture-sensitivity can be a problem in homogeneous catalysis, but the principal drawback is the difficulty in separation of the reaction product(s) from the soluble catalyst. However, in recent years attempts have been made to overcome this problem by anchoring homogeneous catalysts on either insoluble inorganic supports such as silica, alumina and zeolites, or on organic polymer supports such as polystyrene cross-linked with divinylbenzene (DVB).^{6,7} A drawback of such cross-linked supports is the nonequivalence of active sites because of differences in accessibility and microenvironment with resulting differences in activity and stability.⁸ However, this problem may be solved by using noncross-linked polymer supports such as polyamides which also exhibit superior mechanical and thermal stabilities compared to the cross-linked styrene supports.⁸

A major thrust in research on metal cluster compounds is supposedly aimed at mimicking catalytic sites at a surface⁹⁻¹¹ and, to a lesser extent, development of "heterogenized" homogeneous catalysts.¹⁰⁻¹² In a related vein, a better knowledge of homogeneous catalysis particularly at a cluster site may lead to a better understanding of heterogeneous systems.⁹⁻¹⁴

The number of industrial processes currently using homogeneous catalysts is still relatively small. These processes include the Wacker process, the Oxo process, methanol carbonylation, oligomerization of

dienes, and some Ziegler-Natta systems.¹⁵

Use of homogeneous catalysts containing chiral ligands for syntheses of optically active amino acids is one of the most exciting, recent developments. A number of comprehensive reviews have been published.¹⁶⁻¹⁹ Currently, the Monsanto Chemical Company utilizes a Wilkinson-type rhodium(I) catalyst with chiral diphosphine ligands for large scale asymmetric synthesis of the amino acid drug L-Dopa which is used for treatment of Parkinson's disease. Homogeneous chiral catalyst systems are being deployed also for industrial scale asymmetric synthesis of L-aspartic acid and L-phenylalanine, which are used in the synthesis of a popular sugar substitute food additive, aspartame - a methyl ester of the dipeptide L-aspartyl-L-phenylalanine²⁰ - better known by its tradename "NutraSweet".

1.2 Homogeneous Hydrogenation

Although the first report on homogeneous hydrogenation dates back to the year 1938 when Calvin reported catalytic reduction of quinone to hydroquinone using a cuprous acetate - quinoline system,²¹ it was only in the early sixties that interest in this area received a boost. Some of the pioneering work was done by Halpern's group in this University between 1953-61.²²

Partly because of historical reasons and partly because of obvious potential commercial applications, a major portion of the vast literature on homogeneous catalysis accumulated to date deals with homogeneous hydrogenation of unsaturated organic substrates. A number of systems

have been studied in considerable detail and their mechanisms deduced. Literature on homogeneous hydrogenation, both catalytic as well as stoichiometric, is very well-documented. A number of excellent, comprehensive reviews^{3,23-26} and specialized texts, books and book sections are also available.²⁷⁻³¹

The four basic processes occurring during homogeneous hydrogenation of an unsaturated substrate by a transition metal complex are:

- i) activation of molecular hydrogen
- ii) substrate activation
- iii) hydrogen transfer to the substrate
- iv) release of the substrate and, in the case of a catalytic reaction, regeneration of the catalyst.

1.2.1 Hydrogen Activation

Catalytic properties of a metal complex are determined to a great extent by the coordination number and electron configuration of the metal.³² Activity and specificity of a hydrogenation catalyst are further influenced by the electronic properties, including π -effects, σ -effects, and also the steric properties of the surrounding ligands.³³ These factors supposedly provide the basis for catalyst design.

For a metal complex to be able to activate hydrogen or the substrate, coordinative unsaturation at the metal centre is usually

essential. Coordinatively saturated complexes, which generally are unreactive toward hydrogen for lack of a vacant active site, may become active in solution through dissociation of a labile ligand. Not surprisingly, complexes with d^8 electron configuration which are often coordinatively unsaturated, or the d^6 complexes which can easily become so by loss of a ligand, constitute the largest group of hydrogenation catalysts. However, complexes of Ti, Hf, Zr and Nb which have d^2 or d^3 electron configurations have also been investigated for possible catalytic activity with positive results.³⁴

The nature of interaction between molecular hydrogen and a metal complex is also dictated by the electronic and steric properties of the surrounding ligands;^{3,33} the principal types of such an interaction are i) end-on (Fig. 1.1a, 1.1b) and ii) sideways interaction (Fig. 1.1c).^{24,33a}

H_2 acts as an
electron donor

Fig. 1.1a

H_2 acts as an
electron acceptor

Fig. 1.1b

3-centre, 2-electron
transition state

Fig. 1.1c

Kubas and co-workers³⁵ have reported isolation of molybdenum and tungsten phosphine complexes with side-on bonded H_2 ligand, analogous to the transition state as in Fig. 1.1c. More recently, Morris et al.³⁶ have successfully isolated similar iron and ruthenium η^2 -dihydrogen complexes of the type $trans-[M(\eta^2-H_2)(H)(dppe)_2]BF_4$. The crystal structure of the iron complex clearly shows the symmetrically coordinated η^2-H_2 ligand. The energetics of hydrogen activation have important consequences on the catalytic activity of the metal complex; while too strong a metal-hydrogen (M-H) bond may retard or even prevent the transfer of hydride to the coordinated substrate, too weak an interaction between the metal and hydrogen may result in a concentration of the M-H species too small to achieve an appreciable reaction rate.

As noted by Halpern,³⁷ activation of hydrogen may involve a) homolytic cleavage, b) dihydride formation, or c) overall heterolytic splitting; these can be represented by the general equations 1.1-1.3.

Further, hydrogen activation may lead to hydrogenolysis of a metal-metalloid bond³⁸ such as M-Ge, M-Si, but most commonly a metal-carbon (M-C) bond (eq. 1.4).

These different processes of hydrogen activation have been discussed in detail in a number of review articles on hydrogenation.^{39,40} Of particular relevance to the topic of this thesis is the hydrogenolysis of metal-carbon bonds, which will be considered briefly in the following section.

1.2.2 Hydrogenolysis

Hydrogenolysis, which formally resembles a net heterolytic splitting, is exemplified by the reactions shown below (eqs. 1.5-1.7).³⁸

The importance of studies on hydrogenolysis can hardly be overemphasized, considering that a vast majority of stoichiometric as well as catalytic hydrogenation and hydroformylation reactions involve hydrogenolysis of metal-carbon bond as the final step.^{38,41} In addition, in a number of instances hydrogenolysis of metal alkyl or aryl derivatives provides a way of generating the catalytically active hydride species. Such is presumably the case with Ziegler hydrogenation catalyst systems (eqs. 1.8a - 1.8c). Alkene hydrogenation catalyzed by Ziegler-type catalysts probably involves hydrogenolysis of the metal alkyl formed after initial alkylation of the metal complex by an alkylating agent such as AlR_3 ; this leads to the catalytically active monohydride.⁴²

1.2.3 Substrate Activation

For hydrogenation to proceed, coordination of the unsaturated substrate to the metal is usually necessary at some stage during the catalytic cycle. Coordination of an unsaturated organic substrate, such as an alkene, to metal is visualized as overlap of the filled π -donor

orbitals of the alkene with the σ -acceptor orbitals of the metal (Fig. 1.2). The synergistic interaction - back donation of electron density from filled metal non-bonding orbitals to the empty antibonding orbitals of the alkene - further helps stabilize the metal-alkene bonding.

Fig. 1.2

Reduction of electron density on the coordinated alkene, as evidenced by a decrease in the double bond character, activates the alkene. The substrate must coordinate to the metal in a position cis to the hydride for a subsequent hydrogen transfer to occur. Electron withdrawing substituents on an olefin and lower oxidation state of the metal tend to favour coordination of the olefin.⁴³

Depending upon whether hydrogen activation precedes or follows substrate activation, reaction pathways of hydrogenation have been

classified as occurring via i) a hydride or saturate route and ii) an unsaturate route, respectively; the former is encountered more frequently. Alkene hydrogenation catalyzed by $\text{HRuCl}(\text{PPh}_3)_3$ provides an excellent example of the hydride route (eqs. 1.9a, 1.9b).⁴⁴

Hydrogenation of alkenes catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ is thought to proceed by either a saturate or an unsaturate route depending on the substrate, but sometimes via both the routes simultaneously.⁴⁵⁻⁴⁷ A simplified unsaturate route is shown in scheme 1.1.

Scheme 1.1

1.3 Hydroformylation

Discovered by Roelen in 1938,⁴⁸ hydroformylation, also known as the "Oxo" reaction, refers to the addition of carbon monoxide and hydrogen to an alkene to produce an aldehyde as represented by the general equation 1.10. Hydroformylation is industrially one of the most

important and widely utilized homogeneous catalytic processes, with the annual worldwide production of aldehydes from unsaturated hydrocarbons running into several millions of tons.^{49,50} The aldehydes themselves have little direct application. However, they serve as excellent intermediates for the production of commercially more important derivatives such as alcohols (eqs. 1.11a, 1.11b), acids (eq. 1.12), and amines (eq. 1.13), formed by hydrogenation, oxidation, and reductive amination, respectively.⁵⁰

R = alkyl, aryl

A large number of transition metal complexes catalyze the hydroformylation reaction,^{41,50,51} but cobalt and rhodium carbonyls as well as phosphine - containing derivatives are by far the most effective and efficient catalysts. Ruthenium catalysts, although not as efficient, are promising especially because of their relatively low cost, high stability, and high capacity for homologation reactions.⁵² Of late, platinum complexes have also received increasing attention.⁵³

Hydroformylation has been the subject of numerous exhaustive reviews,^{54,55} and while the majority of advanced inorganic chemistry texts⁵⁶ have sections dealing with this topic, a substantial amount of patent literature on hydroformylation continues to be published every year.

A number of review articles describe the kinetics and mechanisms of hydroformylation reactions. Many cobalt and rhodium systems have been investigated in considerable detail. The studies on the cobalt systems involve relatively high temperatures (80-200°C) and high CO/H₂ gas pressures (20-350 atm). The now generally accepted mechanism for hydroformylation of alkenes catalyzed by Co₂(CO)₈, the hydride HCo(CO)₄ being the active species, was first proposed by Heck and Breslow in 1961, and is outlined in equations 1.14-1.19.⁵⁷

In the late sixties, Wilkinson and co-workers suggested dissociative (D) as well as associative (A) mechanisms for alkene hydroformylation catalyzed by rhodium-triphenylphosphine systems under mild conditions (25°C, 1 atm CO/H₂ pressure);⁵⁸ the mechanisms are summarized in scheme 1.2. The complex $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$ was proposed as the key intermediate that reacted with the alkene. Later, a similar mechanism was proposed by Wilkinson et al. for ruthenium-phosphine systems.⁵⁹ The ruthenium(0) complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ was proposed as the key active intermediate.

Scheme 1.2

Based on these and other mechanistic studies, hydroformylation of alkenes catalyzed by a transition metal complex may be seen as consisting of:

- i) formation of a metal hydride complex, unless the precursor itself is a hydride,
- ii) formation of a metal-alkyl intermediate presumably via a π -olefinic complex,
- iii) CO insertion to give the corresponding acyl intermediate, and finally,
- iv) hydrogenolysis of the acyl complex by a) H_2 to afford the product aldehyde with regeneration of the metal hydride complex (eq. 1.18), or by b) the metal hydride to give the aldehyde and dinuclear metal precursor (eq. 1.19).

The various intermediates involved have been isolated and/or characterized spectroscopically for a number of systems including those of cobalt, rhodium, iridium, and ruthenium.

As described earlier (Section 1.2.1), the kinetics and mechanisms of the steps (i) and (ii) have been studied in much detail in relation to hydrogenation of alkenes. Similarly, voluminous work has been done on elucidation of the kinetic and mechanistic aspects of carbonyl insertion reactions using manganese alkyl carbonyls in particular.^{60,61} The review articles by Wojcicki,⁶¹ Calderazzo,⁶² and Kuhlmann et al.⁶³ among others provide excellent, detailed accounts of the progress in the understanding of carbonyl insertion reactions. Recent work from Halpern's group⁶⁴ on

nucleophilic catalysis of the CO migratory insertion reaction shows evidence for a dissociative trapping mechanism (Scheme 1.3).

Scheme 1.3

In contrast, very little is known about the important product-forming step involving hydrogenolysis of an acyl complex. A major problem concerns the general instability of acyl complexes. Metal-acyls, especially those of group VIII metals, are kinetically unstable and may undergo very facile carbonyl de-insertion as well as reductive elimination reactions, which is why of course, complexes of cobalt, rhodium, ruthenium, and palladium usually make good hydroformylation and decarbonylation⁶⁵ catalysts.

As noted above (see eqs. 1.14-1.19), hydrogenolysis of the acyl complex can be accomplished using either H_2 or a metal hydride. The latter allows for stoichiometric conversion of olefins to aldehydes⁶⁶ (eqs. 1.20, 1.21).

or alternatively,

Under hydroformylation conditions, however, hydrogenolysis by H_2 seems to prevail. The non-detection of $HCo(CO)_4$ by i.r. has been considered consistent with this,⁶⁷ while some recent work of Markó and coworkers⁶⁸⁻⁷⁰ reveals more substantial evidence. This recent work involves one of the very few kinetic investigations of hydrogenolysis of an acyl complex by H_2 . Rate measurements on the reactions of $(n-C_3H_7 \cdot CO)Co(CO)_4$ and $(i-C_3H_7 \cdot CO)Co(CO)_4$ with H_2 and with $HCo(CO)_4$ showed that H_2 is less reactive than the carbonyl hydride at lower temperatures but its relative reactivity increases with temperature so that under the high temperature and pressure conditions of hydroformylation hydrogenolysis by H_2 dominates.

The complex acetyldicarbonylbis(trimethylphosphite)cobalt(I) reacts with H_2 stoichiometrically to form a hydridocobalt species and acetaldehyde (eq. 1.22).⁷¹

Thomas,⁷¹ in a study of kinetics of this hydrogenolysis reaction, reported at a Chemical Society meeting:

- i) a first-order rate dependence on the acylcobalt complex concentration and,
- ii) a zero-order rate-dependence on the H_2 pressure. It was suggested that the rate controlling step involved loss of a coordinated phosphite ligand, this step being followed by a relatively fast reaction with H_2 .

1.4 AIM OF WORK

As pointed out above there are very few reports of kinetic studies of hydrogenolysis by H_2 of transition metal acyl complexes. While the recent work of Markó and coworkers⁶⁸⁻⁷⁰ and the report in 1971 by Thomas⁷¹ concern mainly acyl complexes of cobalt, and are probably the only such studies made so far, no kinetic studies on hydrogenolysis of ruthenium acyl complexes have been reported.

The ruthenium(II) acyl complex, dicarbonylchlorobis(triphenylphosphine)norbornenoylruthenium(II), $RuCl(CO \cdot C_7H_9)(CO)_2(PPh_3)_2$, was first synthesized and characterized in this laboratory.⁷² This air-stable, 6-coordinate, 18-electron ruthenium(II) complex was found in preliminary studies during the present work to react slowly with H_2 , and the system appeared to be an excellent candidate for conducting a detailed investigation into a hydrogenolysis reaction (products, stoichiometry and mechanistic aspects). The results of this investigation are described and discussed in Chapter III. Results of some experiments on related complexes, branching out from the main body of this work, are included in Chapter IV.

CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 Solvents

Spectral or analytical grade solvents were obtained from MCB, BDH, Mallinckrodt, Fisher, Eastman or Aldrich Chemical Co. Benzene, toluene and hexanes were refluxed with, and distilled from, sodium metal/benzophenone under a nitrogen atmosphere. N,N'-dimethylacetamide (DMA) was stirred with CaH_2 for at least 24 h, vacuum distilled at 35-40°C, and stored under argon in the dark. Methanol, ethanol, and dichloromethane were distilled after refluxing with the appropriate drying agents (Mg/I_2 for MeOH and EtOH, P_2O_5 for CH_2Cl_2). Diethyl ether and n-octane were used as supplied without further purification. All solvents were deoxygenated prior to use.

2.1.2 Gases

Purified argon (H.P.), nitrogen (U.S.P.), oxygen (U.S.P.), carbon monoxide (C.P.), hydrogen (U.S.P.) and ethylene (C.P.) were obtained from Union Carbide Canada Ltd.; all except hydrogen were used without further purification. Hydrogen was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove traces of oxygen.

2.1.3 Other Materials

Reagent grade triphenylphosphine (Strem Chemicals, Inc.) and

triethylamine (MCB) were used as supplied, without further purification, for synthetic purposes. Norbornadiene (Eastman) and 1,4-cyclohexadiene (Aldrich) were purified by passing through a column of activated alumina (Fisher, A-950 neutral chromatographic grade 80-200 mesh) prior to use. 5-Norbornene-2-carboxaldehyde was obtained from Aldrich and purified by vacuum distillation at 58-60°C, and stored under argon. Norbornane-2-carboxaldehyde was prepared by hydrogenation of a methanol (20 ml) solution of the norbornene precursor (5 ml) under a H_2 atmosphere (4 atm) using Pd/C as a catalyst; methanol was pumped off after 5 h and the product was purified by distillation.

2.1.4 Ruthenium Compounds

The ruthenium, supplied on loan by Johnson Matthey Ltd., was obtained as $RuCl_3 \cdot xH_2O$. Depending upon the batch, the ruthenium content varied from 35-40%.

All synthetic reactions, unless specified otherwise, were carried out under an atmosphere of argon, employing Schlenk techniques, as all the ruthenium(II) complexes prepared in the course of this work were susceptible to oxidation by air, at least in solution.

2.1.4.1 Dichlorotris(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$.⁷³

Hydrated ruthenium trichloride, $RuCl_3 \cdot xH_2O$ (2.0 g, 7 mmol) was refluxed in methanol (400 ml) for 15 minutes under a N_2 atmosphere. The solution was then cooled, PPh_3 (11.5 g, 43.4 mmol) added, and the solution refluxed for 3 h. The dark brown product which precipitated on cooling

was then filtered, washed with methanol and vacuum dried. Yield - 6.65 g (99%); calcd. for $C_{54}H_{45}Cl_2P_3Ru$ C: 67.61%, H: 4.69%, Cl: 7.41%; found C: 67.60%, H: 4.70%, Cl: 7.20%. The $^{31}P\{^1H\}$ n.m.r. data agree with those reported.^{73c}

2.1.4.2 Chlorohydridotris(triphenylphosphine)ruthenium(II) - benzene solvate, $HRuCl(PPh_3)_3 \cdot C_6H_6$.^{74,75}

A benzene (400 ml) suspension of $RuCl_2(PPh_3)_3$ (4.5 g, 4.7 mmol) was stirred with triethylamine, Et_3N (0.07 ml, 5.0 mmol) under a H_2 atmosphere for 18 h at room temperature. The violet product was filtered, washed first with ethanol (3 x 10 ml) to remove $Et_3N \cdot HCl$, then with diethyl ether, and vacuum dried. The complex is air-sensitive and blackens after a few hours exposure to air in the solid state. Its solutions are extremely air-sensitive and turn green within minutes of exposure to air. Yield - 4.1 g (87%); calcd. for $C_{60}H_{52}ClP_3Ru$ C: 71.86%, H: 5.19%, Cl: 3.54%; found C: 71.87%, H: 5.21%, Cl: 3.40%. ν_{Ru-H} : 2028 cm^{-1} . $\delta_{CDCl_3}^{20^\circ C}$: -17.75 ppm (Ru-H, q, 26 Hz). The spectroscopic data agree with those reported in the literature.⁷⁴

2.1.4.3 Bromohydridotris(triphenylphosphine)ruthenium(II) DMA solvate, $HRuBr(PPh_3)_3 \cdot DMA$.⁷⁶

A procedure similar to that used for preparation of the preceding compound (Section 2.1.4.2) was followed, but using $RuBr_2(PPh_3)_3$ as

precursor (1.0 g, 0.955 mmol) and DMA (10 ml) as the solvent. Addition of a base such as Et_3N was not necessary as the DMA solvent is basic enough to react with the HBr formed. The violet product was washed with DMA (2x2 ml) and vacuum dried. Similar to the preceding compound, this complex is air-sensitive both in solid state as well as in solution.

Yield - 0.52 g (51.6%); calcd. for $\text{C}_{58}\text{H}_{55}\text{NBrOP}_3\text{Ru}$, C: 65.95%, H: 5.25%, N: 1.33%; found C: 65.68%, H: 5.24%, N: 1.41%. $\nu_{\text{Ru-H}}$: 2035 cm^{-1} (literature - 2030).⁷⁶ The i.r. carbonyl stretch of DMA was observed at 1652 cm^{-1} (literature - 1650),⁷⁶ very close to the frequency for the uncoordinated solvent (1660 cm^{-1}) indicating that the DMA merely occupies a lattice site in the crystal, similar to the benzene molecule in

$\delta_{\text{C}_6\text{D}_6}^{20^\circ\text{C}}$: -16.46 ppm (Ru-H, q, 26 Hz).

The precursor $\text{RuBr}_2(\text{PPh}_3)_3$ complex was kindly made available by Dr. I. Thorburn of this laboratory.

2.1.4.4 Chlorohydrido(norbornadiene)bis(triphenylphosphine) ruthenium(II), $\text{HRuCl}(\text{NBD})(\text{PPh}_3)_2$.⁷⁵

This complex was prepared by adding norbornadiene (2 ml) to a benzene (50 ml) suspension of $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ (1.9 g, 1.9 mmol), and then stirring for 18h at room temperature. The resulting red-brown solution was filtered to remove any insoluble materials, and the filtrate reduced to $\approx 25\text{ ml}$ and added to hexane (100 ml). The pale brown solid which precipitated on stirring for 6-8 h was filtered, washed with hexane

(2x10 ml) and vacuum dried. Yield - 1.0 g (70%); $C_{43}H_{34}ClP_2Ru$ requires C: 68.47%, H: 5.21%, Cl: 4.71%; found C: 68.41%, H: 5.20%, Cl: 4.59%. ν_{Ru-H} : 2082 cm^{-1} . $\delta_{CD_2Cl_2}^{20^\circ C}$: -8.90 ppm (Ru-H, t, 24 Hz). $^{31}P\{^1H\}$ n.m.r. spectrum in CD_2Cl_2 showed a single peak at 40.4 ppm. The spectroscopic data agree with those reported in the literature.⁷²

2.1.4.5 Synthesis of bromohydrido(norbornadiene)bis(triphenylphosphine) ruthenium(II), $HRuBr(NBD)(PPh_3)_2$.

This compound was prepared by a procedure similar to that used for preparing the chlorohydrido counterpart (Section 2.1.4.4), but using $HRuBr(PPh_3)_3 \cdot DMA$ (0.45 g, 0.43 mmol) as precursor. The precipitated light brown solid was washed with diethylether (2x5 ml) in addition to hexane (2x5 ml) on filtration. Yield - 0.265 g (78%); $C_{43}H_{39}BrP_2Ru$ requires C: 64.66%, H: 4.93%, Br: 10.01%; found C: 64.61%, H: 5.04%, Br: 9.85%. ν_{Ru-H} : 2108 cm^{-1} . $\delta_{C_6D_6}^{20^\circ C}$: -8.43 ppm (Ru-H, t, 24.6 Hz). The $^{31}P\{^1H\}$ n.m.r. signal in C_6D_6 appeared at 39.4 ppm.

2.1.4.6 Dicarbonylchloro(norbornenoyl)bis(triphenylphosphine) ruthenium(II), $RuCl(CO \cdot C_7H_9)(CO)_2(PPh_3)_2$.⁷²

A benzene (15 ml) solution of $HRuCl(NBD)(PPh_3)_2$ (0.3 g, 3.6 mmol) was stirred under CO atmosphere for 18 h. The resulting yellow solution was filtered to remove any insoluble materials, and the filtrate reduced in volume to ~ 5 ml. The yellow product, which precipitated after addition of hexanes (20 ml) to the filtrate and stirring for 3 h, was then filtered, washed with hexane (2x5 ml) and dried in vacuo. Yield - 0.24 g

(73%). Calcd. for $C_{46}H_{39}O_3ClP_2Ru$, C: 65.91%, H: 4.66%, and Cl: 4.24%; found C: 65.75%, H: 4.61%, and Cl: 4.11%, ν_{CO} : 2024 s, 1940 vs, 1910 sh; $\nu_{C=O}$: 1610 w. The $^{31}P\{^1H\}$ n.m.r. singlet was observed at 30.4 ppm in DMA. The spectroscopic data are in agreement with those reported in the literature.⁷²

2.1.4.7 Dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II),
 $HRuCl(CO)_2(PPh_3)_2$.⁷⁸

A DMA (20 ml) suspension of $HRuCl(PPh_3)_3 \cdot C_6H_6$ (1.0 g, 1 mmol) was stirred under CO for 18 h. The purple suspension changed to a yellow solution. The solution was concentrated to ~10 ml by removing the DMA under reduced pressure at ~40°C. The white solid that precipitated out was filtered, washed first with ethanol (2x5 ml) to remove any traces of DMA, and then with acetone (5 ml), and dried under vacuum. Yield - 0.43 g (60%); calcd. for $C_{38}H_{31}ClO_2P_2Ru$, C: 63.55%, H: 4.32%, Cl: 4.95%; found C: 63.15%, H: 4.35%. $\delta_{CDCl_3}^{20^\circ C}$: -4.50 ppm (Ru-H, t, 19.4 Hz). The $^{31}P\{^1H\}$ n.m.r. spectrum in DMA showed a singlet at 39.5 ppm. The spectroscopic data agree with the literature data.⁷⁸

This complex was also prepared using benzene as solvent instead of DMA following a similar procedure. The white solid obtained was washed with hexane and dried under vacuum.

2.1.4.8 Carbonylchloro(propionyl)bis(triphenylphosphine)ruthenium(II),
 $RuCl(CO \cdot C_2H_5)(CO)(PPh_3)_2$.⁷⁹

A benzene (10 ml) suspension of $HRuCl(CO)_2(PPh_3)_2$ (0.3 g,

0.42 mmol) was heated at 80°C under an ethylene atmosphere (1.5 atm) for 5 h. Ethanol (10 ml) was added to the cooled solution, after venting the excess gas pressure. The solution was reduced to approximately half the volume, and the precipitated bright yellow solid filtered and washed with ethanol (2x5 ml), and dried under vacuum. Recrystallization from dichloromethane/ethanol produced bright yellow crystals of $\text{RuCl}(\text{CO} \cdot \text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$, which after prolonged drying (~3 days) under vacuum, afforded the propionyl complex $\text{RuCl}(\text{CO} \cdot \text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2$. Yield - 0.285 g (91%); calcd. for $\text{C}_{40}\text{H}_{35}\text{ClO}_2\text{P}_2\text{Ru}$, C: 64.38%, H: 4.73%; Cl: 4.76%; found C: 64.66%, H: 4.58%, Cl: 5.02%. ν_{CO} : 1950 vs, 1921 s, 1892 s cm^{-1} (literature - 1957 vs, 1926 s, 1900 s),⁷⁹ $\nu_{\text{C=O}}$: 1637 vs cm^{-1} (literature - 1643 vs).⁷⁹ In dichloromethane solution ν_{CO} and $\nu_{\text{C=O}}$ were observed at 1946, 1919 and 1640 cm^{-1} (literature - 1948, 1920, 1640),⁷⁹ respectively. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. in CH_2Cl_2 showed a single peak at 31.5 ppm.

2.2.1 Reaction of $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ with 1,4-cyclohexadiene

In an attempt to prepare a ruthenium(II) hydridodiene complex similar to $\text{HRuCl}(\text{NBD})(\text{PPh}_3)_2$, and possibly the corresponding acyl complex by subsequent reaction with CO, a benzene (20 ml) suspension of $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ (0.7 g, 0.7 mmol) was stirred with 1.3 ml (13.8 mmol) of 1,4-cyclohexadiene (C_6H_8) at ~ 55°C. The initially purple suspension, which changed into a dark red solution over ~ 48 h, was left stirring for another 12 h and then cooled to room temperature, reduced in volume to ~ 8 ml and filtered to remove the unreacted $\text{HRuCl}(\text{PPh}_3)_3$. Hexane (20 ml) was added to the filtrate and the solution stirred for 6 h. The brown

solid that precipitated was filtered off, washed with hexane (2x5 ml) and vacuum dried. The yellow filtrate was retained for further work-up.

Yield - 0.23 g (44%); calcd. for " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ ", $\text{C}_{42}\text{H}_{39}\text{ClP}_2\text{Ru}$,

C: 67.97%, H: 5.26%, Cl: 4.79%; found C: 68.28%, H: 5.21%,

Cl: 4.70%. The i.r. spectrum showed no Ru-H absorption, and also the ^1H n.m.r. spectrum, which has yet to be fully interpreted, showed no high-field hydride resonance(s). The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum showed just a singlet at 40.0 ppm, which is quite close to the norbornadiene analog (40.4 ppm). This brown complex was extremely air-sensitive in solution, and solid samples exposed to air slowly turned green within a few days. The nature of the brown solid is discussed further in Chapter IV.

The yellow filtrate (benzene:hexane) obtained along with the brown product was concentrated to give ~ 2 ml of a dark red oil. Addition of hexane (10 ml) precipitated a yellow solid, but much of it redissolved during washing with hexane. The relatively high solubility in a number of organic solvents (CH_2Cl_2 , MeOH, acetone, Et_2O) posed difficulties in isolation of this yellow complex. However, addition of about 5 ml n-octane to the red oil followed by refrigeration at 0°C for 2 days, precipitated the yellow complex that was quickly filtered and dried as such under vacuum for 2 days. Yield - 0.16 g. The i.r. spectrum showed no absorption in the hydride region. The ^1H n.m.r. spectrum in C_6D_6 at 20°C was again complicated, and has not yet been interpreted; there was, however, a complex pattern of weak high field signals in the -6 to -7 ppm region indicative of metal hydride(s) impurities. The $^{31}\text{P}\{^1\text{H}\}$ spectrum showed a broad singlet at 31.9 ppm, and also a few very low intensity signals which could not be assigned.

When the reaction between $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ and 1,4-cyclohexadiene was carried out for a longer period of time (~ 100 h instead of 60 h), only the yellow product was obtained, no brown complex could be isolated. Of interest, benzene solutions of the brown solid, henceforth represented as " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ ", when heated with excess 1,4-CYHD at $\sim 55^\circ\text{C}$ for 36 h, also yielded solutions of the yellow complex. Based on these results the chemistry in benzene can be summarized as:

brown product

yellow product

(2.2)

This yellow complex is tentatively formulated as " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ " (see Chapter IV) and is probably a benzene solvate (calcd. for $\text{C}_{54}\text{H}_{53}\text{ClP}_2\text{Ru}$, C: 72.35%, H: 5.89%; found C: 71.87%, H: 6.21%).

Reactions of both the brown and the yellow products with H_2 and with CO were investigated (Chapter IV). These investigations are incomplete but they do shed some light on the nature of the brown and the yellow species; further studies are necessary to establish the exact identity of the two products.

2.2.2 Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with 1,4-cyclohexadiene

A benzene (30 ml) suspension of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.5 g, 0.52 mmol) was stirred with 1,4-CYHD (0.75 ml, 9.4 mmol) at 60°C for 60 h, during which time the dark brown suspension changed to a reddish yellow solution containing a reddish orange precipitate. The mixture was reduced in volume to ~ 10 ml and the crystalline solid was filtered off, washed with hexane (2x5 ml), and dried in vacuo. Yield - 0.20 g (50% based on " $\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ " formulation); calcd. for $\text{C}_{42}\text{H}_{38}\text{Cl}_2\text{P}_2\text{Ru}$, C: 64.91%, H: 4.87%, Cl: 9.14%; found C: 64.95%, H: 4.64%, Cl: 9.61%. The UV-visible spectrum in DMA showed absorption maxima at 370 nm ($\epsilon = 1940 \text{ M}^{-1}\text{cm}^{-1}$) and ~ 475 nm (broad, $\epsilon = 480 \text{ M}^{-1}\text{cm}^{-1}$).

The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum in CD_2Cl_2 showed a single peak at 28.9 ppm, and a small amount of free PPh_3 (~ 3%) was also observed. The ^1H n.m.r. spectrum in CDCl_3 is shown in Fig. 2.1 The set of peaks in the $\delta = 7\text{-}8$ ppm region is assigned to the protons of the two PPh_3 ligands (30 H). The remaining signal at δ 5.40 ppm integrates to 8 H, which is assigned to the coordinated diene moiety.

Reactions of this complex with H_2 and with CO are discussed in Chapter IV.

2.3 Instrumentation

Infrared spectra were recorded on a Nicolet 5 DX FT-IR spectrophotometer as Nujol mulls between CsI plates, unless specified otherwise. UV-visible spectra were recorded on a Perkin Elmer 552A spectrophotometer with thermostatted cell compartments, using anaerobic spectral cells of path length 1.0 or 0.1 cm (Fig. 2.2).

Fig. 2.1: ^1H n.m.r. spectrum of $\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ in CDCl_3 .

Fig. 2.2: Anaerobic spectral cell used for UV-visible spectroscopy.

^1H and $^{31}\text{P}\{^1\text{H}\}$ -nuclear magnetic resonance spectra were recorded on a Bruker WP80 (80 MHz for ^1H , 32.44 MHz for $^{31}\text{P}\{^1\text{H}\}$), a Varian XL300 (300 MHz for ^1H , 121.4 MHz for $^{31}\text{P}\{^1\text{H}\}$ or a Bruker WH400 (400 MHz for ^1H) spectrometer, all operating in Fourier-transform mode, using tetramethylsilane (TMS) and PPh_3 (~ -6 ppm w.r.t. 85% H_3PO_4)⁸⁰ as standards. The spectrometers were equipped with variable temperature attachments which were used when necessary. All ^{31}P n.m.r shifts are reported relative to 85% H_3PO_4 , with downfield shifts taken as positive.

Gas chromatographic analyses were performed on a Carle AGC311 (constant temperature) gas chromatograph equipped with a thermal conductivity detector (TCD) as well as a flame ionization detector (FID), or a temperature programmable Hewlett Packard 5830A instrument equipped with a TCD. OV101 or 5% Carbowax capillary columns were used with helium as the carrier gas.

Gas uptakes for stoichiometric or kinetic studies were measured on the constant pressure apparatus as described in the following section.

Elemental analyses were performed by Mr. P. Borda of this department.

2.4 Gas-uptake Apparatus

2.4.1 The Apparatus

The constant pressure gas-uptake apparatus, used for stoichiometric determinations and kinetic studies of reactions with small gas molecules H_2 , CO and O_2 , is represented schematically in Fig. 2.3.

Fig. 2.3: The constant pressure gas uptake apparatus.

The apparatus consisted principally of three parts, viz. the reaction vessel, the measurement unit, and the gas-handling part.

The reaction vessel was a small, pyrex two-neck flask (A) of approximately 25 ml capacity, with a dimpled bottom, and equipped with a dropping side-arm bucket (B). The flask was connected to a capillary oil-manometer (F) containing n-butyl phthalate - a liquid of negligible vapour pressure, at tap E through a flexible glass spiral tube (C). When clipped to a piston-and-wheel mechanical shaker (G) driven by a Welch variable speed electric motor, the flask could be held immersed in a thermostatted oil-bath (H) - a four litre glass beaker filled with silicone oil in an insulated wooden box. The capillary manometer (F) was connected through tap I to a gas measuring burette, consisting of a precision bored tube (J) of known diameter, and a mercury reservoir (K). This measuring unit was thermostatted at 25°C in a water bath (M). The gas burette was connected via a Fischer and Porter teflon needle valve (O) to the gas-handling part of the apparatus, which included a gas inlet (P), a mercury manometer (Q) and a Welch Duo-Seal rotary vacuum pump (R). Stainless steel jacketed, electrically isolated heating coils were used to heat the two baths. Thermostating was achieved by using Juno thermo-regulators and Merc-to-Merc relay control circuits, along with mechanical stirring. Temperature of the two baths could be maintained within $\pm 0.05^{\circ}\text{C}$ of the set temperatures.

The gas uptake was measured with a vertically mounted cathetometer, and times were recorded from a Lab-Chron 1400 timer.

It was extremely important that the apparatus be maintained leak-free during a run. High vacuum Apiezon N grease was used for greasing all ground glass joints and taps in the apparatus.

2.4.2 Procedure for a Typical Experimental Run

In a typical experiment, 10 ml of DMA (or the appropriate solvent) were pipetted into the reaction flask. The complex was weighed on an analytical balance in the small sample bucket (B) and suspended in the flask on the side-arm hook. The flask was then attached to the gas-handling part of the apparatus at point S through the glass spiral tube. After a careful degassing of the solution by a freeze and thaw static vacuum procedure, repeated at least thrice, hydrogen was introduced into the flask till the gas pressure was slightly less than that desired. Taps D and T were closed, the spiral arm and the flask removed from the gas-handling part and attached to the capillary manometer (F) at joint E with the tap D still closed. The flask was placed in the oil bath preheated to the desired temperature, and clipped to the mechanical shaker which was then started. The rest of the apparatus upto tap D was evacuated keeping the taps E, I, L, N and O open. About 10 minutes (~25-30 minutes for gas pressures of 0.5 atm or less) were allowed for thermal equilibration between the reaction vessel and the oil-bath, and the shaker was then stopped. Meanwhile, hydrogen (or the appropriate gas) was admitted into the rest of the apparatus until the gas pressure was somewhat lower than that desired. Tap D was opened and the pressure adjusted to the desired value.

The needle-valve (O) and taps I and L were closed, and the initial reading of the mercury level in the gas measurement burette (J) taken. The gas pressure in the gas-handing part was raised over that in the reaction flask. The apparatus was now ready for a run.

The bucket containing the complex was dropped into the solution by turning the side-arm, and the shaker and the timer were started. For slow gas uptakes tap E was kept closed most of the time, but was opened ~ 2 minutes before taking a reading to allow for equilibration, and closed again.

The gas uptake indicated by the difference in the oil levels of the capillary manometer (F) was measured by carefully allowing the gas into the mercury reservoir via the needle valve (O) to balance the oil levels and noting the corresponding rise in the mercury level of the burette at appropriate time intervals.

From knowledge of the diameter of the gas burette, the volume of gas consumed could be calculated from the rise in the height of the mercury level and expressed as moles of gas uptake per litre of solution. The apparatus was precalibrated and a value of 1.98×10^{-5} moles of gas uptake per centimeter rise in the mercury level was calculated.

2.4.3 Measurement of Gas Solubilities

The gas-uptake apparatus described above was used for measurement of solubility of hydrogen in DMA at specific temperatures and pressures. Typically, DMA (10 ml) was degassed using the freeze-thaw

procedure, the taps D and T were then closed, and the flask along with the spiral arm transferred to the capillary manometer. After the system upto the tap D was evacuated, hydrogen was introduced, and its pressure adjusted approximately to that required. Tap D was opened and the exact pressure noted, the taps J, and L, and the needle valve (O) were closed, and the timer and the shaker started. The immediate gas-uptake was then measured.

CHAPTER III

RESULTS AND DISCUSSION

3.1 The Ruthenium-acyl Complex

The ruthenium(II) norbornadiene (NBD) complex $\text{HRuCl}(\text{NBD})(\text{PPh}_3)_2$, **1**, first reported by Wilkinson et al. in 1968,⁷⁵ exists in solution as a single isomer, with the metal, the hydride, and an alkene π -bond in a coplanar cis arrangement⁷² which is favourable for olefin insertion. Reaction of this hydridodiene complex with carbon monoxide, depicted in the equation 3.1, is irreversible and leads to the formation of the acyl complex dicarbonylchloro(norbornenoyl)bis(triphenylphosphine)-ruthenium(II), $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$, **2**, via consecutive olefin and carbonyl insertions into the metal-hydride and the metal-alkyl bonds, respectively.⁷²

Detailed ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. studies, including selective homonuclear decoupling experiments, by Dekleva from this laboratory showed that the acyl substituent occupies the thermodynamically less favourable endo position of the norbornene moiety, as represented by $\underline{2}$.⁷²

During preliminary studies in the present work, DMA and toluene solutions of $\underline{2}$ were found to absorb H_2 very slowly at 1 atm H_2 pressure and 40–60°C over a period of several hours. It was decided to investigate this reaction in more detail with regard to the products, the stoichiometry, and the kinetics of the reaction. The results and discussion of these studies are described in the following sections.

The bromo- complex $\text{HRuBr}(\text{NBD})(\text{PPh}_3)_2$ (Section 2.1.4.5) reacted with ~ 3 mole equivalents of CO in DMA solvent at 30°C to give presumably an acyl complex analogous to $\underline{2}$.

3.2 Hydrogenolysis of $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$, $\underline{2}$.

The DMA and the toluene solutions of $\underline{2}$ absorbed ~ one mole equivalent of hydrogen over about 20 hours at 65°C under 1 atm pressure of H_2 . The initial yellow colour of the solutions became more intense during the gas uptake. A typical plot of the H_2 -uptake against time in DMA is shown in Fig. 3.1. An extremely slow absorption of H_2 was then noted beyond the first mole equivalent uptake, until finally a total of ~ 1.9 mole equivalents of H_2 were consumed in ~ 130 hours. The 'extra' H_2 consumed arises from hydrogenation of the initially formed aldehyde product (see equation 3.3).

DMA solutions of the propionyl complex $\text{RuCl}(\text{CO}\cdot\text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2$ failed to react with 1 atm H_2 at 65°C.

Fig. 3.1: H_2 uptake by **2** in DMA at 65°C under 760 torr H_2 pressure.

3.2.1 Stoichiometry of the Reaction, and Product Identification

As seen from the Fig. 3.1, the DMA solutions of 2 finally absorb approximately two moles of H_2 per mole of the ruthenium complex. This observation is explained by (i) hydrogenolysis of 2 by the first mole of H_2 leading to a hydridoruthenium product (3) and the corresponding aldehyde (4):

and (ii) a relatively slow hydrogenation of 4 to the saturated aldehyde (5) by a second mole of H_2 :

Fig. 3.2: $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra in DMA at 20°C of (a) $\underline{2}$ (c) $\underline{2} + \text{H}_2$, after heating for 20 h at 65°C and
 (b) $\underline{2} + \text{H}_2$, after heating for 2 h at 65°C (d) the authentic sample of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$.

The hydrogenolysis of **2**, in DMA, was monitored by $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopy. The spectra are presented in Fig. 3.2 along with that of an authentic sample of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$, which was prepared by carbonylation of a DMA solution of $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ (see Section 2.1.4.7). A singlet appeared at 39.5 ppm and grew in intensity as the H_2 reaction proceeded; after ~ 1 mole equivalent H_2 -uptake the n.m.r. signal due to **2** (30.4 ppm) had disappeared.

Removal of DMA from the final solution yielded a pale yellow solid which showed strong i.r. absorption bands at 2042, 2036, 1994 and 1982 cm^{-1} , corresponding to those of the carbonyl absorption bands of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$ (2043, 2035, 1993 and 1981 cm^{-1}),⁷⁸ which however is a white solid. A weak absorption was also observed at $\sim 1886\text{ cm}^{-1}$, which is characteristic of an intense yellow photoisomerization product of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$.⁸¹ The yellow colour of the product isolated from the uptake solutions is presumably due to this photoisomerization product, which is of unknown geometry.⁸¹ Finally, a high field hydride resonance at $\delta_{\text{CDCl}_3}^{20^\circ\text{C}} = -4.49\text{ ppm}$ (t, 19.4 Hz) in the ^1H n.m.r. spectrum of **3** (Fig. 3.3) confirms the identity of the inorganic product.⁷⁸

The complex, $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$, was first prepared in this laboratory.⁷⁸ Although a number of geometrical isomers are possible, only one has been isolated in pure form (the white solid) and assigned the cis-cis-trans- structure shown for **3** in equation 3.2.

Fig. 3.3: High field ^1H n.m.r. spectrum of 3 in CDCl_3 .

The unsaturated aldehyde product 4 formed during the hydrogenolysis was detected and identified by gas chromatography by comparison with a commercially available sample of 5-norbornene-2-carboxaldehyde. Using a 3 m OV101 column at 100°C on a Carle AGC311 instrument equipped with a flame ionization detector (FID), a retention time of 14.8 min was measured for both 4 and the authentic sample of $\text{C}_7\text{H}_9\text{CHO}$ in toluene (Fig. 3.4). During hydrogenolysis of the CH_2Cl_2 solutions of 2, the disappearance of the acyl i.r. absorption band at 1610 cm^{-1} was accompanied by the appearance of a new i.r. absorption band at 1717 cm^{-1} , which is identical to the carbonyl stretch of the aldehyde $\text{C}_7\text{H}_9\text{CHO}$ in CH_2Cl_2 .

Fig. 3.4: Gas chromatograms of
(a) the reaction mixture after ~ 1 mole equivalent H_2 uptake by $\underline{2}$ in toluene,
(b) a standard solution of C_7H_9CHO in toluene.

The product of the hydrogenation reaction 3.3 was similarly detected and identified using gas chromatographic techniques, by comparison with $C_7H_{11}CHO$ (retention time 13.0 min under the conditions noted above), which was prepared by hydrogenation of the commercially available precursor (4).

The saturated aldehyde (5) could be detected by GC after approximately 0.9 mole equivalent of H_2 uptake; only ~ 5-10% of 5 was detected after 1 mole H_2 uptake (Fig. 3.4). An initial rate of about $3.5 \times 10^{-8} \text{ Ms}^{-1}$ was calculated for consumption of the second mole of H_2 at 65°C ($[Ru]_T = 4.56 \times 10^{-3} \text{ M}$, $P_{H_2} = 760 \text{ torr}$) in the range 0.95-1.30 mole equivalent H_2 -uptake (Fig. 3.5).

A very slow absorption of H_2 was observed by DMA solution of C_7H_9CHO in the presence of a stoichiometric amount of 3 at 65°C , with initial rates of the same order of magnitude ($\sim 10^{-8}$) as observed for the second mole of H_2 -uptake by solutions of 2. The hydrogenation of 4 was also found to be catalyzed by 3 at 65°C in DMA; with $[Ru] = 4.00 \times 10^{-3} \text{ M}$ and $[4] = 0.17 \text{ M}$, an initial linear rate of $1.35 \times 10^{-6} \text{ Ms}^{-1}$ was observed (Fig. 3.6). The data for this single experiment suggest the catalytic reaction is close to 1st order in unsaturated aldehyde concentration.

3.2.2 Rate Measurements

A constant pressure gas-uptake apparatus described earlier (Sections 2.4.1, 2.4.2) was used to monitor the reaction between the

Fig. 3.5: A typical rate plot for the consumption of the second mole of H₂ by DMA solutions of **2** at 65°C, [Ru]_T = 4.56x10⁻³ M

Fig. 3.6: Rate plot for the $\text{HRuCl}(\text{CO}_2)(\text{PPh}_3)_2$ -catalyzed hydrogenation of $\text{C}_7\text{H}_9\text{CHO}$ in DMA at 65°C

ruthenium acyl complex and H_2 . The H_2 gas-uptakes were measured at total ruthenium complex concentrations, $[Ru]_T$, ranging from 2.5×10^{-3} to 8.0×10^{-3} M, at different H_2 -pressures (190-760 torr), and at various temperatures (50-70°C), changing only one parameter at a time. Most measurements were made at 65°C, the rates becoming inconveniently slower at lower temperatures. Rates were measured for the initial uptakes of upto ~ 0.3 - 0.4 mole equivalents of H_2 . DMA was chosen as the solvent over toluene because of the convenient lower vapour pressure of the former (10-35 torr)⁸² compared to that of toluene (100-300 torr)⁸³ over the temperature range employed (50-70°C). Of interest, little difference was observed in the rates of the reaction using either DMA or toluene as solvent (see TABLE III-2). The rates of H_2 uptake by 2 remained close to linear over a longer range (upto ~ 0.4 mole equivalents uptake) than expected. This linearity of rates, even beyond ~ 0.2 mole equivalents (20%) initial uptake, is presumably due to additional contribution from the concurrent hydrogenation of the product aldehyde 4 (more discussion on p. 68) according to reaction 3.3. Rates calculated from the analyses of rate data for 1st order Ru-dependence within individual runs in the initial $\sim 20\%$ region were found to be almost identical to the initial rates measured directly from the respective H_2 uptake plots (see for example, Fig. 3.9 and TABLE III-2). Therefore, initial rates, which could be measured very conveniently, have been employed throughout this study.

The solubility of hydrogen in DMA at 65°C at various H_2 -pressures was determined using the procedure described in Section 2.4.3, and was found to obey Henry's law at least upto one atmosphere pressure of hydrogen (TABLE III-1, Fig. 3.7). The K value defined as the ratio of

the molar solubility of hydrogen $[H_2]$ to the hydrogen pressure $P(H_2)$ in torr, was calculated from the slope to be $2.86 \times 10^{-6} \text{ Mtorr}^{-1}$. Further H_2 -solubility data at different temperatures were taken from earlier measurements⁸⁴ from this laboratory ($K = 2.32$, 2.70 and $2.82 \times 10^{-6} \text{ Mtorr}^{-1}$ at 30 , 50 , and 60°C respectively).

TABLE III-1

Solubility of H_2 in DMA at 65°C .

P_{H_2} , torr	$[H_2] \times 10^3$, M
760	2.19
570	1.62
380	1.05
190	0.56

$$K = [H_2]/P_{H_2} = 2.86 \times 10^{-6} \text{ Mtorr}^{-1}$$

Fig. 3.7: H_2 solubility in DMA at 65°C .

TABLE III-2

Kinetic data for hydrogenolysis of $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$
in DMA at 65°C.

$[\text{Ru}]_{\text{T}}$ $\times 10^3$, M	P_{H_2} torr	$[\text{H}_2]$ $\times 10^3$ M	Initial rate $\times 10^7$, Ms^{-1}
2.50	760	2.17	1.11
3.13	760	2.17	1.42
3.88	760	2.17	1.75
4.56	760	2.17	1.95
4.81	760	2.17	2.09
6.03	760	2.17	2.69
7.58	760	2.17	3.40
4.56	660 ^a	1.89	1.96
4.56	660	1.89	1.93
4.56	570	1.63	1.99
4.56	380	1.09	1.91
4.56	190	0.54	2.01
4.56	760	2.17	1.22 ^b
4.56	570	1.63	1.09 ^b
4.56	300	0.86	0.73 ^b
4.56	760	2.17	0.73 ^c
4.56	760	2.17	0.53 ^d
4.56	760	2.17	0.46 ^e
4.56	760	2.17	0.00 ^f
4.80	760	2.05	0.67 ^g
4.80	760		0.62 ^h

(a) + $P_{\text{CO}} = 100$ torr, $P_{\text{Total}} = 760$ torr.

(b) - (f) At added $[\text{PPh}_3] \times 10^3 =$

(b) 0.966 M, (c) 2.42 M, (d) 3.87 M, (e) 4.83 M, and (f) 45.6 M

(g) Rate in DMA at 50°C

(h) Rate in toluene at 50°C.

Error in the rate values is estimated at ~5-10% from least squares analyses of the initial-rate plots.

The dependence of the initial rates on the total ruthenium concentration $[\text{Ru}]_{\text{T}}$, hydrogen pressure, and added triphenylphosphine were studied at 65°C. The reaction rates were also measured using H_2/CO mixtures in place of hydrogen to study any possible effect of external CO on the hydrogenolysis. The kinetic data are summarized in TABLE III-2. Finally, the temperature dependence of the initial rates was investigated at a single ruthenium concentration in the absence of added PPh_3 (TABLE III-3).

The rate plots for the hydrogenolysis at 65°C under one atmosphere hydrogen pressure for different total ruthenium concentrations ranging between $2.5\text{--}8.0 \times 10^{-3}$ M can be seen in Fig. 3.8. The individual rate plots analyzed well for a first-order dependence on $[\text{Ru}]$ (for example Fig. 3.9). The plot of the initial rate against the total ruthenium concentration is shown in Fig. 3.10 and is first order in $[\text{Ru}]_{\text{T}}$.

The effect of added PPh_3 was investigated at a total ruthenium concentration of 4.56×10^{-3} M, under 1 atm H_2 pressure. The rate of hydrogenolysis was found to decrease with added phosphine as seen in the Fig. 3.11, and at ~ 10 -fold excess of PPh_3 no H_2 uptake was observed over 24 hours.

The effect of varying the H_2 pressure was studied at $[\text{Ru}]_{\text{T}} = 4.56 \times 10^{-3}$ M without and with added PPh_3 (Fig. 3.12). Without PPh_3 , a zero-order dependence on H_2 pressure was observed from 760 to 190 torr, whilst at the added PPh_3 concentration of 9.66×10^{-4} M, a decrease in the rate of hydrogenolysis was observed on decreasing the H_2 pressure from 760 to 300 torr. For a reaction carried out under a mixture of H_2 and CO

Fig. 3.8: Rate plots for the hydrogenolysis of **2** in DMA, at 65°C, at various $[\text{Ru}]_{\text{T}}$.
 $[\text{Ru}]_{\text{T}} \times 10^3, \text{M}$ = (a) 7.58, (b) 6.03, (c) 4.81 and (d) 3.88.

Fig. 3.9: A rate plot analyzed for 1st-order Ru-dependence in DMA at 65°C
 $[\text{Ru}]_T = 7.58 \times 10^{-3} \text{ M}$

Fig. 3.10: Dependence of the hydrogenolysis rate on $[Ru]_T$ at 65°C.

Fig. 3.11: Dependence of the rate on added $[\text{PPh}_3]$, at constant $[\text{Ru}]_{\text{T}}$ and $[\text{H}_2]$ at 65°C $[\text{Ru}]_{\text{T}} = 4.56 \times 10^{-3}$ M, $P_{\text{H}_2} = 760$ torr

Fig. 3.12: Dependence of the rate on the H_2 pressure at constant $[Ru]_T$
 (a) added $[PPh_3] = 0$ (b) added $[PPh_3] = 9.66 \times 10^{-4} M$.
 $[Ru]_T = 4.56 \times 10^{-3} M$

($P_{H_2}=660$ torr and $P_{CO}=100$ torr), the initial rate was essentially the same as that measured under just 660 torr H_2 (TABLE III-2).

3.3 Analysis of the Kinetic Data

To explain the first-order dependence on $[Ru]_T$, the inverse dependence on added $[PPh_3]$, and the first- to zero-order dependence on H_2 pressure, the following mechanism is proposed:

where k_1 , k_{-1} , and k_2 are the rate constants of the individual steps, and K' represents the equilibrium constant for reaction 3.6.

Applying the steady-state treatment to the intermediate, $[RuCl(CO \cdot C_7H_9)(CO)_2(PPh_3)]$, the following rate law is obtained:

$$Rate = - \frac{d[Ru]_T}{dt} = \frac{d[H_2]}{dt} = - \frac{k_1 k_2 [Ru]_T [H_2]}{k_{-1} [PPh_3] + k_2 [H_2]} \quad (3.7)$$

3.3.1 Dependence of the Rate on Ruthenium Concentration, $[\text{Ru}]_T$

At constant $[\text{H}_2]$ and constant $[\text{PPh}_3]$, the rate equation 3.7 reduces to:

$$\text{Rate} = k_{\text{obs}} \cdot [\text{Ru}]_T \quad (3.8)$$

where

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{H}_2]}{k_{-1} [\text{PPh}_3] + k_2 [\text{H}_2]} \quad (3.9)$$

The Ru-dependence was measured in the absence of added PPh_3 . The first-order Ru dependence, evident from the straight-line plots shown in Figs. 3.9 and 3.10, requires that the $[\text{PPh}_3]$ term remains effectively constant and/or negligible. The independence of the reaction rate on H_2 under the conditions at which the Ru dependence was measured, requires that $k_2 [\text{H}_2] \gg k_{-1} [\text{PPh}_3]$, and this coupled with what must be a large value for K' (since the product is $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$ and $[\text{PPh}_3]$ cannot increase markedly during any single run), leads to the simple first-order in metal. The slope of the plot of $\log(\text{initial rate})$ vs. $\log([\text{Ru}]_T)$ also gives $n=1$ (Fig. 3.13), where n is the order of the reaction in Ru. A k_{obs} value of $4.4 \times 10^{-5} \text{ s}^{-1}$ is obtained from the slope of the plot of initial rate against $[\text{Ru}]_T$ (Fig. 3.9).

Fig. 3.13: Plot of $\log(\text{initial rate})$ against $\log([\text{Ru}]_T)$

3.3.2 Dependence of the Rate on Added PPh_3 Concentration

The rate equation 3.7 can be rearranged to give:

$$\frac{1}{\text{Rate}} = \frac{k_{-1}}{k_1 k_2 [\text{Ru}]_T [\text{H}_2]} \cdot [\text{PPh}_3] + \frac{1}{k_1 [\text{Ru}]_T} \quad (3.10)$$

At constant $[\text{Ru}]_T$ and $[\text{H}_2]$, therefore, the plot of $1/\text{rate}$ vs. added $[\text{PPh}_3]$ should be a straight line. The rate constant k_1 , and the relative magnitudes of k_{-1} and k_2 can then be calculated from the intercept, and the slope, respectively. Such a plot (Fig. 3.14) gives a straight line with slope = $3.59 \times 10^9 \text{ sM}^{-2}$, and intercept = $4.86 \times 10^6 \text{ sM}^{-1}$, from which a k_1 value of $4.5 \times 10^{-5} \text{ s}^{-1}$, and a k_{-1}/k_2 value of 1.6 are obtained for conditions when $[\text{Ru}]_T = 4.56 \times 10^{-3} \text{ M}$ and $[\text{H}_2] = 2.17 \times 10^{-3} \text{ M}$, at 65°C .

3.3.3 Dependence of the Rate on Hydrogen Concentration

Under the conditions that $k_{-1}[\text{PPh}_3] \ll k_2[\text{H}_2]$ in the absence of added PPh_3 , the rate equation 3.7 reduces to:

$$\text{Rate} = k_1 [\text{Ru}]_T \quad (3.11)$$

which is independent of $[\text{H}_2]$, as found experimentally. For $[\text{Ru}]_T = 4.56 \times 10^{-3} \text{ M}$, in the absence of added PPh_3 , the rates remained reasonably constant between the H_2 pressure range 190–760 torr (Table III-2, Fig. 3.12). However, the rate dependence on $[\text{H}_2]$ should eventually go from zero- to first-order as the hydrogen concentration is lowered, when

Fig. 3.14: Dependence of $1/\text{rate}$ on added PPh_3 concentration according to equation 3.10 $[\text{Ru}]_{\text{T}} = 4.56 \times 10^{-3} \text{ M}$, $P_{\text{H}_2} = 760 \text{ torr}$

$k_{-1}[\text{PPh}_3]$ becomes comparable to $k_2[\text{H}_2]$. Further, the rate should become strictly first-order in $[\text{H}_2]$ if and when $k_{-1}[\text{PPh}_3] \gg k_2[\text{H}_2]$. Alternatively, the $k_{-1}[\text{PPh}_3] \gg k_2[\text{H}_2]$ condition can be achieved by addition of PPh_3 , although such an addition would also result in an overall lowering of the rates due to the inverse dependence on $[\text{PPh}_3]$. The effect of $[\text{H}_2]$ on the rate, at an added $[\text{PPh}_3]$ of $9.66 \times 10^{-4} \text{M}$, is shown in Fig. 3.12. The added $[\text{PPh}_3]$ of $9.66 \times 10^{-4} \text{M}$ is apparently not large enough to obtain a strictly first-order H_2 dependence; nevertheless, the decrease in the rate with the lowering of H_2 pressure reveals the required zero- to first-order transition.

According to equation 3.10, the plot of $1/\text{rate}$ against $1/[\text{H}_2]$, at constant $[\text{Ru}]_{\text{T}}$ and added $[\text{PPh}_3]$, is expected to yield a straight line; k_1 and k_{-1}/k_2 can be obtained as before from the intercept and the slope, respectively. For $[\text{Ru}]_{\text{T}} = 4.56 \times 10^{-3} \text{M}$, at an added $[\text{PPh}_3] = 9.66 \times 10^{-4} \text{M}$, such a plot (Fig. 3.15) gives a straight line, and values of $k_1 = 5.0 \times 10^{-5} \text{s}^{-1}$ and $k_{-1}/k_2 = 1.9$ at 65°C are calculated from the intercept ($4.43 \times 10^6 \text{sM}^{-1}$) and the slope ($7.94 \times 10^3 \text{s}$) of this plot.

3.4 Dependence of the Rate-constant on Temperature

The dependence of k_{obs} on temperature was studied between the range $50\text{--}70^\circ\text{C}$; the data are summarized in Table III-3. The plot of $\ln(k_{\text{obs}}/T)$ vs. $1/T$ yields a reasonably good straight line (Fig. 3.16). Values of $\Delta H^\ddagger = 69 \pm 7 \text{ kJmole}^{-1}$ and $\Delta S^\ddagger = -126 \pm 13 \text{ JK}^{-1}\text{mole}^{-1}$ are calculated from the slope and the intercept, respectively.

Fig. 3.15: Dependence of the rate on $[\text{H}_2]$ according to equation 3.10,
 $[\text{Ru}]_{\text{T}} = 4.56 \times 10^{-3} \text{ M}$, added $[\text{PPh}_3] = 9.66 \times 10^{-4} \text{ M}$

TABLE III-3Dependence of k_{obs} on temperature

Temperature, K	$k_{\text{obs}} \times 10^5, \text{ s}^{-1}$
323	1.40
328	2.31
333	2.97
338	4.45
343	7.05

Fig. 3.16: Dependence of the rate-constant for hydrogenolysis of 2 on temperature

3.5 Discussion

The approximate 2 mole equivalent H_2 uptake by solutions of $RuCl(CO \cdot C_7H_9)(CO)_2(PPh_3)_2$, 2, is explained by the hydrogenolysis of the compound 2 (reaction 3.2), and the subsequent hydrogenation of the unsaturated aldehyde product 5-norbornene-2-carboxaldehyde, 4, to the saturated norbornane-2-carboxaldehyde, 5 (reaction 3.3). The inorganic product of the hydrogenolysis is identified as $HRuCl(CO)_2(PPh_3)_2$, 3.

Independent measurements of H_2 uptake by solutions of 4 in the presence of 3 show that the hydrogenation to 5 is catalytic in 3. The initial rate of hydrogenation measured in this catalytic reaction at $65^\circ C$, for a system with $[aldehyde]: [Ru] \approx 42$ was $1.35 \times 10^{-6} Ms^{-1}$ ($[Ru] = 4.00 \times 10^{-3} M$). The initial rate of hydrogenation measured for a system containing mole equivalents of Ru and aldehyde (at a metal concentration the same as in the catalytic system) was $\sim 3.8 \times 10^{-8} Ms^{-1}$. If the catalytic reaction were first order in aldehyde substrate, then the expected initial catalytic rate would be $(\sim 3.8 \times 10^{-8} \times 42)$ i.e. $1.6 \times 10^{-6} Ms^{-1}$. This is close to the experimentally noted $1.35 \times 10^{-6} Ms^{-1}$ value, and strongly indicates that the catalytic rate is 1st-order in unsaturated aldehyde. These data are also consistent with the rate of consumption of

the second mole equivalent of H_2 ($\approx 3.5 \times 10^{-8} \text{ Ms}^{-1}$; $[Ru]_T = 4.56 \times 10^{-3} \text{ M}$) measured during the H_2 uptake by 2 (Fig. 3.5).

The hydrogenation of the unsaturated aldehyde, which is ~ 7 times slower than the hydrogenolysis reaction, causes little interference in measurement of the initial rates of the hydrogenolysis reaction. However, the rate data analyses for a 1st-order ruthenium dependence within a single run (Fig. 3.9) clearly show a deviation from the straight-line log vs. time plot, towards a higher rate than expected, beyond about a 0.7 mole H_2 -uptake. The additional contribution to the rate of H_2 -uptake is attributed to the concurrent hydrogenation of 4.

The relatively slow rate of hydrogenation of the unsaturated aldehyde is consistent with previous findings. In earlier studies from this laboratory,^{78b} 3 was found to be quite inefficient as an olefin hydrogenation catalyst, under temperature and H_2 -pressure conditions similar to those used during the present work. Fahey⁸⁵ in 1973 reported on the $RuCl_2(CO)_2(PPh_3)_2$ - catalyzed selective hydrogenation of diene and triene substrates to monoenes, and these reactions were considered to involve 3 as the catalytically active species. Much more severe conditions were used ($130\text{--}160^\circ\text{C}$, $15\text{--}20 \text{ atm } P_{H_2}$), and the rates were slowest for the hydrogenation of internal alkenes. Catalytic activity of Ru complexes is commonly found to decrease with the introduction of π -acceptor carbonyl groups.⁸⁶

As mentioned in the Introduction (Section 1.2.1), the presence of a vacant coordination site on the metal is usually essential for H_2 activation to take place. The 6-coordinate ruthenium-acyl complex

$\text{RuCl}(\text{CO} \cdot \text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$ may become coordinatively unsaturated through loss of a coordinated ligand. The possibility of CO dissociation from 2 is ruled out because (a) the rate of hydrogenolysis remains unaffected by the presence of external CO and (b) the ruthenium product is still a dicarbonyl. Indeed, the kinetic data argue unambiguously for loss of coordinated phosphine in a slow (k_1) step (eq. 3.4).

The k_1 value of $4.5 \times 10^{-5} \text{ s}^{-1}$ obtained from the dependence of the hydrogenolysis rate on added $[\text{PPh}_3]$ is, within experimental error, the same as the k_{obs} value of $4.4 \times 10^{-5} \text{ s}^{-1}$ obtained from the $[\text{Ru}]_T$ -dependence, measured in the absence of added phosphine. Under the latter conditions, clearly $k_{-1}[\text{PPh}_3] \ll k_2[\text{H}_2]$ (eq. 3.7), with the rate being independent of H_2 from 190-760 torr (0.54 - $2.17 \times 10^{-3} \text{ M}$). The steady state concentration of PPh_3 must remain extremely low, and indeed the failure to detect any free PPh_3 by $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopy in solutions of 2 means that the equilibrium constant K for the dissociation of PPh_3 is immeasurably small. In any case, the hydrogenolysis of 2 does not result in a build-up of free PPh_3 as the reaction proceeds; the equilibrium constant K' for reaction 3.6 must presumably be very large,⁸⁵ and the originally dissociated PPh_3 quickly coordinates to the $[\text{HRuCl}(\text{CO})_2(\text{PPh}_3)]$ species to form 3.

The k_{-1}/k_2 ratio of 1.6, obtained from the inverse dependence of hydrogenolysis rate on added $[\text{PPh}_3]$ (Fig. 3.14), means that the rates of the phosphine association to, and hydrogenolysis of, $\text{RuCl}(\text{CO} \cdot \text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)$, (eqs. 3.4, 3.5) become comparable at relatively low added $[\text{PPh}_3]$. Consequently, in the presence of added phosphine, the H_2 -dependence is expected to go from zero- to first-order. Such a shift

in H_2 -dependence is evident from the data of Fig. 3.12b (Table III-2), even at the relatively small added $[PPh_3]$ of $9.66 \times 10^{-4} M$ ($[PPh_3]/[Ru] = 0.21$) and, since the $[H_2]$ is of the same order as the $[PPh_3]$, this immediately implies qualitatively that the k_{-1}/k_2 ratio is close to unity. Also, the k_1 value of $5.0 \times 10^{-5} s^{-1}$ and the k_1/k_2 ratio of 1.9 obtained from the H_2 -dependence data (Fig. 3.15) are in acceptable agreement with those determined experimentally from the inverse PPh_3 -dependence.

The measured $\Delta H^\ddagger$ value of $69 \pm 7 \text{ kJmole}^{-1}$ for the hydrogenolysis reaction refers to the k_1 step and is thus the enthalpy of activation for phosphine dissociation from 2 in DMA solvent. If the activated complex resembles closely the five-coordinate intermediate, then the 69 kJmole^{-1} could approximate to the bond dissociation energy of the Ru-P bond. However, the entropy of activation (see below) strongly suggests that solvation of the reaction intermediate is important, and solvation energies are thus likely contributing to the overall activation enthalpy value. The entropy of activation has a large negative value ($-126 \pm 13 \text{ JK}^{-1}\text{mole}^{-1}$), which initially might appear contrary to the expectation based on a dissociative mechanism. The only plausible explanation for a negative $\Delta S^\ddagger$ must lie in differences in solvation of the ground state reactant and activated state; the degree of solvation in the latter must be greater. For a transition state close to complete dissociation of the phosphine, solvation of the 5-coordinate intermediate and free phosphine could lead to an overall negative entropy of activation. A negative $\Delta S^\ddagger$ value for a rate determining ligand dissociation step is unusual; in solvents such as toluene the entropy of activation is invariably positive

for such a process.⁸⁷ The nature of the solvent (in this system, of coordinating and polar character) clearly plays a key role.

Hydrogenolysis reactions (cf. eq. 3.2) are known to proceed often via oxidative addition of H_2 , followed by fast reductive elimination of the products,^{58,59} and a 7-coordinate $Ru(IV)-H_2$ transition state or even a $Ru^{II}-(\eta^2-H_2)^{36}$ are both plausible (k_2 -step). Heterolytic activation of H_2 seems unlikely since the hydrogenolysis of 2 proceeds at about the same rates in both DMA and toluene solvents (Table III-2). It would be of considerable interest to measure the corresponding kinetics and activation parameters for the hydrogenolysis reaction in toluene.

The inability of the propionyl complex $RuCl(CO \cdot C_2H_5)(CO)(PPh_3)_2$, to react with H_2 is surprising in view of the availability of a vacant coordination site on this 5-coordinate, supposedly square-pyramidal⁷⁹ complex. Although blocking of the coordination site by a coordinating DMA solvent molecule is possible, the complex is known to react reversibly with CO very rapidly⁷⁹ and this was demonstrated for the complex in DMA solution:

CHAPTER IV

REACTIONS OF RUTHENIUM(II)-CYCLOHEXADIENE COMPLEXES

Reactions of new cyclohexadiene derivatives of ruthenium (Sections 2.2.1 and 2.2.2) with H_2 and with CO were investigated; preliminary results of these studies are described in the following sections.

4.1 Reactions of " $RuCl(C_6H_9)(PPh_3)_2$ ", 6

4.1.1 Reaction of " $RuCl(C_6H_9)(PPh_3)_2$ ", 6, with H_2

The brown product, 6, obtained from the reaction of $HRuCl(PPh_3)_3 \cdot C_6H_6$ with 1,4-CYHD, C_6H_8 , (Section 2.2.1), reacted with ~ 2.45 mole equivalents of H_2 per Ru in DMA, at 1 atm H_2 pressure. The H_2 uptake plot is shown in Fig. 4.1 and indicates a relatively rapid reaction with an initial 2 mole equivalents of H_2 , followed by a much slower uptake of the final ~ 0.5 mole equivalent of H_2 . The initially reddish brown solution of 6 turned deep red in colour as the uptake proceeded. The reaction was also followed by visible spectrophotometry, and a single absorption maximum was observed after completion of the reaction ($\lambda_{max} = 500$ nm, $\epsilon = 1425 \text{ M}^{-1}\text{cm}^{-1}$). The reaction also proceeded in CH_2Cl_2 and C_6H_6 solvents. The room temperature $^{31}P\{^1H\}$ n.m.r. spectrum of the product(s) in C_6D_6 showed peaks at 70.5 and 45.9 ppm.

These results are similar to those obtained by Dekleva in this laboratory during an investigation of the reaction of $HRuCl(NBD)(PPh_3)_2$, 7, with H_2 .^{72a,88} Dekleva found that 7 reacted with ~ 2.5 moles of H_2 per mole of Ru; the products were shown to be a dimeric ruthenium complex, $[H_2RuCl(PPh_3)_2]_2$ (λ_{max} at 500 nm, $\epsilon = 1410 \text{ M}^{-1}\text{cm}^{-1}$; $^{31}P\{^1H\}$ n.m.r.

Fig. 4.1: Rate plot for H_2 uptake in DMA by " $RuCl(C_6H_9)(PPh_3)_2$ " at $25^\circ C$
 $[Ru] = 2.72 \times 10^{-3}$ M. Inset - Initial portion of the rate plot expanded.

at 70.8 and 46.1 ppm in C_6D_6), and free norbornane (eq. 4.1).^{72a,88}

The inorganic product of the reaction of $\underset{\sim 6}{6}$ with H_2 must clearly be $[H_2RuCl(PPh_3)_2]_2$ by comparison of the spectroscopic data, while cyclohexane was detected qualitatively by gas chromatography. Therefore similar to reaction 4.1, the reaction between $\underset{\sim 6}{6}$ and H_2 can be written as:

Interestingly, the yellow complex, $\underset{\sim 7}{7}$, the second product obtained from the reaction of $HRuCl(PPh_3)_3 \cdot C_6H_6$ with 1,4-CYHD (Section 2.2.1, eq. 2.2), also reacted with H_2 (~ 4 mole equivalents of H_2 based on the " $RuCl(C_6H_9)(C_6H_8)(PPh_3)_2$ -benzene solvate" formulation; 4.5 mole equivalents would be expected for a reaction such as 4.2a) to give products which were found to be identical to those formed in reaction 4.2.

4.1.2 Reaction of "RuCl(C₆H₉)(PPh₃)₂" with CO

DMA solutions of **6** rapidly reacted with CO (1 atm) at 30°C. The brown solid turned yellowish, instantaneously, in the solid state on introduction of CO to the reaction-flask. This was then followed by CO uptakes of ~ 1.7 - 1.85 mole equivalents per mole of Ru (Fig. 4.2) by the solution which gradually turned from reddish brown to yellow in colour during the uptake. The inorganic product of this reaction was identified as HRuCl(CO)₂(PPh₃)₂, **3**, by ³¹P{¹H} n.m.r. (39.5 ppm, singlet) and also by i.r. spectroscopy (ν_{CO}: 2042, 2033, 1992 and 1982 cm⁻¹). The <2 mole equivalent uptakes are attributed to what appears to be a solid state reaction of **6** with CO. Thus, unlike the reaction between HRuCl(NBD)-(PPh₃)₂ and CO which leads to the formation of the acyl complex (Section 3.1), the reaction of **6** with CO presumably results in diene displacement with resulting formation of the dicarbonyl species, **3** (eq. 4.3):

Reaction of the yellow "RuCl(C₆H₉)(C₆H₈)(PPh₃)₂-benzene solvate", **7**, with CO in benzene also resulted in the formation of **3**.

4.2 Reactions of RuCl₂(C₆H₈)(PPh₃)₂, **8**

DMA solutions of **8** failed to react with 1 atm H₂ at 65°C. Previous work from this laboratory has shown that a norbornadiene analogue, RuCl₂(NBD)(Ptol₃)₂, is also unreactive towards H₂ under comparable conditions.⁸⁹

Fig. 4.2: Rate plot for CO uptake in DMA by " $RuCl(C_6H_9)(PPh_3)_2$ ", at 30°C
 $[Ru] = 2.32 \times 10^{-3} \text{ M}$

However, $\underline{8}$ was found to react with CO, and at 50°C under 1 atm CO DMA solutions of $\underline{8}$ absorbed ~ 1.9 mole equivalents of CO (Fig. 4.3). The initially orange solution changed to pale yellow during the uptake, while a new peak appeared at 16.9 ppm in the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum, accompanied by the simultaneous disappearance of the 28.9 ppm signal due to $\underline{8}$. The inorganic product was identified as cis-cis-trans $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ by comparison of the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. data with those reported in literature.⁹⁰ Thus, $\underline{8}$ almost certainly undergoes a diene displacement by CO as shown below:

4.3 Discussion

The brown complex $\underline{6}$ has the stoichiometry $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$, and consistent with this when reacted with H_2 , $\underline{6}$ takes up ~ 2.5 mole equivalents of H_2 and forms $[\text{H}_2\text{RuCl}(\text{PPh}_3)_2]_2$ and free cyclohexane (eq. 4.2). The expected formulation " $\text{HRuCl}(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ " has problems in that a Ru-H could not be detected for $\underline{6}$ by i.r. or ^1H n.m.r. spectroscopy; this seems to support the existence of a cyclohexenyl (or π -allyl) product rather than a 'hydridodiene' species (eq. 4.5). Alternatively, such non-detection of a hydride may result from a fast equilibrium conversion between the hydridodiene species and the species resulting from hydride transfer (eq. 4.5).

Fig. 4.3: Rate plot for CO uptake in DMA by $RuCl_2(C_6H_8)(PPh_3)_2$ at $50^\circ C$
 $[Ru] = 4.00 \times 10^{-3} M$

6a

6b

6c

etc.

Some support for such an equilibrium is provided by the reactivity of 6. The reaction of 6 with CO results in the formation of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$ by a net displacement of the diene, while 6 reacts with a further mole of 1,4-cyclohexadiene leading to the formation of the yellow complex, 7, which appears to contain both the C_6H_9 and the diene (C_6H_8) moieties:

That 7 takes up ~ 4 mole equivalents of H_2 , and yields the same products as those obtained during reaction 4.2, is consistent with the formulation shown.

The " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ " species is extremely reactive. For example, the species turns yellow in the solid state in the presence of CO. These reactivity observations can be rationalized if 6 existed at least partially as the coordinatively and/or electronically unsaturated

"hydride transferred" (6b, 6c) species, which must then react with CO almost instantaneously. Werner and Feser⁹¹ have reported on a rapid equilibrium conversion between a Rh(III) hydridoethylene complex and the corresponding ethyl-complex:

The hydridoethylene complex was found to undergo ethylene replacement by CO and not give an acyl insertion product, and yet yielded an ethyl-ethylene-complex on reaction with C_2H_4 :

Similarly, the chemistry of 6 would be consistent with a rapid equilibrium shown in eq. 4.5. Low temperature ^1H and ^{13}C n.m.r. studies are required to elucidate further the exact nature (geometry, configuration in solution) of 6 (and 7).

The investigation of the reaction between 1,4-cyclohexadiene and $\text{RuCl}_2(\text{PPh}_3)_3$ (Section 2.2.2) was prompted by the interest in the nature of 6 and 7. The orange product, 8, obtained during this reaction has the stoichiometry $\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, consistent with displacement of a phosphine by diene. Interestingly, low temperature ^1H n.m.r. studies of 8 in CDCl_3 show that all 8 protons of the diene are equivalent ($\delta_{\text{CDCl}_3} =$

5.40 ppm), at least down to -60°C . The ^1H n.m.r. chemical shift for the diene protons is close to that reported by Bennett and Smith⁹² for the coordinated arene protons of $\text{RuCl}_2(\text{C}_6\text{H}_6)(\text{PPh}_3)$ ($\delta_{\text{CDCl}_3} = 5.38$ ppm).

One possible explanation for the equivalence of the 8 diene protons is that the 1,4-cyclohexadiene may isomerise to 1,3-cyclohexadiene; rapid movement of the conjugated double-bonds in the latter, at least on the n.m.r. time-scale, could then result in the observed equivalence of the 8 protons. Such isomerization of 1,4- to 1,3-cyclohexadiene (before a subsequent dehydrogenation to an arene derivative) has been suggested previously;⁹² further studies are needed to explore this possibility.

CHAPTER V

GENERAL CONCLUSIONS AND SOME RECOMMENDATIONS FOR FUTURE WORK

5.1 General Conclusions

The analyses of the various kinetic data for the hydrogenolysis of the acyl bond in $\text{RuCl}(\text{CO}\cdot\text{C}_7\text{H}_9)(\text{CO})_2(\text{PPh}_3)_2$ are internally consistent and a mechanism has been proposed to account for the data (eqs. 3.4-3.6). Of interest, the first-order metal-dependence, and the zero-order H_2 -dependence in the absence of added phosphine, when the rate determining step becomes PPh_3 dissociation, are very similar to the results reported by Thomas⁷¹ on the cobalt(I)-phosphite system (Chapter I). While the similarity in the mechanism of hydrogenolysis of the Co(I) and the Ru(II) systems may be coincidental, the prospect of a general mechanism involving ligand dissociation as the primary slow step seems likely, at least for the hydrogenolysis of coordinatively and electronically saturated metal-acyl complexes. Obviously, more extensive kinetic studies on related systems, even for complexes of the same metal, are necessary before any conclusion regarding the generality of any mechanism can be reached. The kinetic instability of metal-acyl complexes³⁵ will be a major hurdle in attempting systematic kinetic studies on hydrogenolysis of such complexes.

A new ruthenium(II) complex of the stoichiometry " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{PPh}_3)_2$ ", **6**, a CYHD derivative formally analogous to $\text{HRuCl}(\text{NBD})(\text{PPh}_3)_2$, was prepared and its reactions with H_2 and CO investigated. While **6** reacted with H_2 in a manner identical to the NBD analogue, an attempt to prepare the corresponding acyl complex by

carbonylation was unsuccessful. Instead, the reaction of **6** with CO resulted in the formation of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$, presumably through a diene-displacement reaction (eq. 4.4). The product **7** from the reaction between **6** and 1,4-CYHD seems to have the stoichiometry " $\text{RuCl}(\text{C}_6\text{H}_9)(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ ". Another new complex $\text{RuCl}_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, **8**, was synthesized by reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ and 1,4-CYHD; the diene moiety exhibits fluxional behaviour, that makes all 8 protons equivalent even at -60°C . The characterization and study of these new Ru(II)-CYHD complexes is still in the preliminary stages.

5.2 Suggestions for Future Work

As well as further studies (particularly n.m.r.) to elucidate fully the nature of complexes **6**, **7** and **8**, other routes to Ru-CO.R species should be pursued. Ruthenium(0) complexes of the type $\text{Ru}(\text{CO})_2(\text{P})_3$, (P = phosphine) are known to undergo facile oxidative addition reactions,⁹³ and such reactions with acyl/aroyle halides may provide a convenient route to the syntheses of the required complexes, which could then be used for systematic kinetic studies on hydrogenolysis of the Ru-C bond.

REFERENCES

1. G.C. Pimentel in the NRC report "Opportunities in Chemistry", National Academy Press, Washington D.C., 1985; through executive summary from C&EN, Oct. 14, 13 (1985).
2. (a) J. Tsuji, "Organic Synthesis by means of Transition Metal Complexes", Springer-Verlag, New York, 1975.
(b) G.W. Parshall, "Homogeneous Catalysis", Wiley Interscience, New York, 1980.
(c) J.P. Collman and L.S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, Calif., 1980, Chs. 6 and 8.
3. G. Dolcetti and N.W. Hoffman, Inorg. Chim. Acta, 9, 269 (1974), and references therein.
4. E. Bayer and V. Shurig, CHEMTECH., 212 (1976).
5. K.J. Skinner, C & EN, Feb. 7, 18 (1977).
6. F.R. Hartley, "Supported Metal Complexes", Catalysis by Metal Complexes Ser., R. Ugo and B.R. James, Eds., D. Reidel Publishing Co., Boston (1985), Ch.1.
7. (a) J. Manassen, Plat. Met. Rev., 15, 142 (1971), and references therein.
(b) Ref. 3.
(c) F.R. Hartley and P.N. Vezey, Adv. Organomet. Chem., 15, 189 (1977).
(d) J. Haggin, C & EN, Nov. 15, 11 (1982).
8. Z.M. Michalska and B. Ostaszewski, J. Organomet. Chem., 299, 259 (1986).
9. E.L. Muettertides, T.N. Rhodin, E. Band, C.F. Brucker, and W.R. Pretzer, Chem. Rev., 79(2), 91(1979), and references therein.
10. B.F.G. Johnson, Ed., "Transition Metal Clusters", John Wiley and Sons, New York, 1980.
11. P.C. Ford, Acc. Chem. Res., 14(2), 31 (1981).
12. E.L. Muettertides, C & EN, Aug. 30, 28 (1982).
13. J. Evans, Chem. Soc. Rev., 159 (1981).
14. J. Haggin, C & EN, Feb. 8, 13 (1982).

15. (a) Ref. 2b.
(b) G.W. Parshall, J. Mol. Catal., 4, 243 (1978).
16. H.B. Kagan in "Comprehensive Organometallic Chemistry", G. Wilkinson, Ed., Pergamon Press, Oxford, Vol. 8, 1982, Ch. 53.
17. R.E. Merrill, CHEMTECH., 118 (1981).
18. B. Bosnich and M.D. Fryzuk in "Topics in Inorganic and Organometallic Stereochemistry", G. Geoffroy, Ed., Wiley, New York, 1981, p. 119.
19. (a) W.S. Knowles, Acc. Chem. Res., 16, 106 (1983).
(b) U. Matteoli, P. Fediani, M. Bianchi, C. Botteghi, and S. Gladiali, J. Mol. Catal., 12, 265 (1981).
(c) B.D. Vineyard, W.S. Knowles, and M.J. Sabacky, J. Mol. Catal., 19, 159 (1983).
20. M. Hatada, J. Jancarik, B. Graves, and S. Kim, J. Am. Chem. Soc., 107, 4279, (1985).
21. M. Calvin, Trans. Faraday Soc., 34, 1181 (1938).
22. J. Halpern, J. Organomet. Chem., 200, 133 (1980).
23. B.R. James in "Comprehensive Organometallic Chemistry" G. Wilkinson, Ed., Pergamon Press, Oxford, Vol. 8, 1982, Ch. 51.
24. P.J. Brothers, Prog. Inorg. Chem., 28, 1 (1981).
25. B.R. James, Adv. Organomet. Chem., 17, 319 (1979).
26. R.H. Crabtree, Acc. Chem. Res., 12, 331 (1979).
27. (a) Refs. 2a-c
(b) Ref. 18
28. P.N. Rylander, "Catalytic Hydrogenation in Organic Syntheses", Academic Press, New York (1979).
29. P. Pino and G. Consiglio, in "Fundamental Research in Homogeneous Catalysis", M. Tsutsui, Ed., Plenum, New York, Vol. 3, 1979, p. 519.
30. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, 4th edn., New York, 1980, Ch. 30.
31. B.R. James, "Homogeneous Hydrogenation", Wiley, New York (1973).
32. J. Halpern, Adv. Chem. Ser., Vol. 70, 1 (1968).

33. (a) R.E. Harmon, S.K. Gupta, and D.J. Brown, Chem. Rev., 73(1), 21 (1973).
(b) G. Henrici-Olivé and S. Olivé, Angew. Chem. Int. Ed., 10, 105 (1971).
34. (a) F.N. Tebbe, 2nd Joint CIC/ACS Conference, Inor 087 (1977).
(b) J.M. Mariguez, D.R. McAlister, R.D. Sanner, and J.E. Bercaw, J. Am. Chem. Soc., 98, 6733 (1976).
35. G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini, and H.J. Wasserman, J. Am. Chem. Soc., 106, 451 (1984).
36. R.H. Morris, J.F. Sawyer, M. Shiralian, and J.D. Zubkowski, J. Am. Chem. Soc., 107, 5581, (1985).
37. J. Halpern, Disc. Faraday Soc., 46, 7 (1968).
38. Ref. 23, p. 300.
39. Refs. 3, 23, 24, and 37.
40. B.R. James, Coord. Chem. Rev., 1, 505 (1966).
41. I. Tkatchenko in "Comprehensive Organometallic Chemistry", G. Wilkinson, Ed., Pergamon Press, Oxford, Vol. 8, 1981, Ch. 50.3.
42. M.F. Sloan, A.S. Matlock, and D.S. Breslow, J. Am. Chem. Soc., 85, 4014 (1963).
43. Ref. 33a.
44. Ref. 25, p. 324.
45. J.A. Osborn, F.H. Jardine, J.F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1711 (1966).
46. C.A. Tolman, P.Z. Meakin, D.L. Lindner, and J.P. Jesson, J. Am. Chem. Soc., 96, 2762 (1974).
47. J. Halpern, J. Mol. Catal., 2, 65 (1976).
48. (a) O. Roelen, German Patent 849,548 (1938).
(b) O. Roelen, U.S. Patent 2,317,066 (1943).
(c) O. Roelen, Angew Chem. A, 60, 62 (1948).
through ref. 41.
49. Ref. 41, p. 115.

50. R.L. Pruett, Adv. Organomet. Chem., 17, 1 (1979).
51. F.E. Paulik, Catalysis Reviews, 6(1), 49 (1972).
52. Ref. 50, p. 53.
53. "Asymmetric Catalysis", B. Bosnich, ed., Martinus Nijhoff Publishers, Boston (1986), p. 43-48.
54. Refs. 41, 50, and 51.
55. G. Henrici-Olivé and S. Olivé, Transition Met. Chem., 1, 77 (1976).
56. Refs. 2c, 30.
57. R.F. Heck and D.S. Breslow, J. Am. Chem. Soc., 83, 4023 (1961).
58. (a) D. Evans, J.A. Osborn, and G. Wilkinson, J. Chem. Soc. A 3133 (1968).
(b) C.K. Brown and G. Wilkinson, J. Chem. Soc. A, 1392 (1970).
(c) G. Yagupsky, C.K. Brown, and G. Wilkinson, J. Chem. Soc. A, 1392 (1970).
59. R.A. Sanchez-Delgado, J.S. Bradley, and G. Wilkinson, J. Chem. Soc. Dalton, 399 (1976).
60. for example - T.C. Flood, J.E. Jensen, and J.A. Statler, J. Am. Chem. Soc., 103, 4410 (1981).
61. A. Wojcicki, Adv. Organomet. Chem., 11, 88 (1972).
62. F. Calderazzo, Angew. Chem. Int. Ed. Engl., 16, 299 (1977).
63. E.J. Kuhlmann and J.J. Alexander, Coord. Chem. Rev., 33, 195 (1980).
64. (a) S.L. Webb, C.M. Giandomenico, and J. Halpern, J. Am. Chem. Soc., 108, 345 (1986).
(b) M.J. Nappa, R. Santi, and J. Halpern, Organometallics, 4(1), 34 (1985).
(c) M.J. Nappa, R. Santi, S.P. Diefenbach, and J. Halpern, J. Am. Chem. Soc., 104, 619 (1982).
65. J. Tsuji in "Organic Synthesis via Metal Carbonyls", I. Wender and P. Pino, eds., Wiley-Interscience, New York, Vol. II, 1977, p. 595.

66. M. Orchin and W. Rupilius, Catal. Rev., 6, 85 (1972).
67. M. Bianchi, F. Piacenti, P. Frediani, and U. Matteoli, J. Organomet. Chem., 135, 387 (1977).
68. F. Ungváry and L. Markó, Organometallics, 2, 1608 (1983).
69. F. Ungváry, I. Kovács, C.D. Hoff, and L. Markó, "XIIth International Conference on Organometallic Chemistry", Vienna, Austria, 1985, Abstr. #456.
70. C.D. Hoff, F. Ungváry, R.B. King, and L. Markó, J. Am. Chem. Soc., 107, 666 (1985).
71. J.A. Thomas, "The Chemical Society Autumn Meeting", University of York, York, England, 1971, Abstr. No. 324; through ref. 68.
72. (a) T.W. Dekleva, Ph.D. Dissertation, The University of British Columbia, Vancouver, B.C., 1983, Ch. 7.
(b) T.W. Dekleva and B.R. James, J. Chem. Soc., Chem. Commun., 1350 (1983).
73. (a) P.S. Hallman, T.A. Stephenson, and G. Wilkinson, Inorg. Syntheses, 12, 237 (1970).
(b) T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28, 945 (1966).
(c) P.R. Hoffman and K.G. Caulton, J. Am. Chem. Soc., 97, 4221 (1975).
74. R.A. Schunn, E.R. Wonchoba, and G. Wilkinson, Inorg. Syntheses, 13, 131 (1972).
75. P.S. Hallman, B.R. McGarvey, and G. Wilkinson, J. Chem. Soc., A, 3143 (1968).
76. L.D. Markham, Ph.D. Dissertation, The University of British Columbia, Vancouver, B.C., 1973, p. 47, 48.
77. A.C. Skapski and R. Troughton, J. Chem. Soc., Chem. Commun., 1230 (1968).
78. (a) B.R. James and L.D. Markham, Inorg. Nucl. Chem. Letters, 7, 373 (1971).
(b) B.R. James, L.D. Markham, B.C. Hui, and G.L. Rempel, J. Chem. Soc. Dalton Trans., 2247 (1973).
79. K.R. Grundy and J. Jenkins, J. Organomet. Chem., 265, 77 (1984).
80. G.M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds", 2nd edn., Wiley-Interscience, Toronto, Vol.1, 1972, p. 130.

81. G.L. Geoffroy and M.G. Bradley, Inorg. Chem., 16(4), 744 (1977).
82. DMA general information bulletin, Industrial and Biochemicals Department, E.I. Du Pont de Nemours and Co., Wilmington, Delaware (Publication year not stated).
83. Data from "Handbook of Chemistry and Physics", 56th edition, R.C. Weast, ed., CRC Press, Cleveland, Ohio, 1975-76, p. D-198.
84. H₂ solubility data in DMA:
 - (a) at 30°C, from I. Thorburn, M.Sc. Thesis, The University of British Columbia, Vancouver, B.C., 1980.
 - (b) at 50 and 60°C from S. Gamage Ph.D. Dissertation, The University of British Columbia, Vancouver, B.C., 1985.
85. (a) D.R. Fahey, J. Org. Chem., 38, 81 (1973).
(b) ibid., 38, 3343 (1973).
86. B.R. James, Inorg. Chim. Acta Rev., 4, 73 (1970).
87. B.R. James, K.J. Reimer, and T.C.T. Wong, J. Am. Chem. Soc., 99, 4815 (1977).
88. T.W. Dekleva, I.S. Thorburn, and B.R. James, Inorg. Chim. Acta, 100, 49 (1985).
89. Ref. 72a, p. 306.
90. Ref. 72a, p. 28,29.
91. H. Werner and R. Feser, Angew. Chem. Int. Ed. Engl., 18, 157 (1979).
92. M.A. Bennett and A.K. Smith, J. Chem. Soc. Dalton, 233 (1974).
93. (a) J.P. Collman and W.R. Roper, J. Am. Chem. Soc., 87, 4008 (1967).
(b) F. Porta, S. Cenini, S. Giordano, and M. Pizzotti, J. Organomet. Chem., 150, 261 (1978).