MECHANISM OF HYDROFORMYLATION OF ALKENES BY RHODIUM CATALYSTS

A Thesis submitted

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To my Parents and

my Wife

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ABBREVIATIONS

Me	methyl	Et	ethyl
Pr^i	iso-propyl	Bu^n	n-butyl
Ph	phenyl	acac.	acetylacetonate

Temperatures are given in degrees Centigrade.

Pressures are given in the following units

1 atm. = 76 cm Hg = 14.7 $lb.in^{-2}$.

g.l.c. gas-liquid chromatography

n.m.r. nuclear magnetic resonance

i.r. infra-red

i.r. spectra of solids were taken as nujol mulls.

ABSTRACT

The hydroformylation of alkenes using hydridocarbonyltris(triphenylphosphine)rhodium(I), $RhH(CO)(PPh_3)_3$, under mild conditions (ca 25° and 1 atm.) is described. The dependence of rate, substrate specificity and product distribution on catalyst concentration, partial pressures of carbon monoxide and hydrogen and temperature is discussed in terms of possible mechanisms.

The presence of excess triphenylphosphine is important in achieving high yields of straight-chain aldehydes from alk-1-enes and the use of molten PPh_3 as solvent allows high product specificity to be maintained at higher temperature and pressure (ca 100° and 300-700 $lb.in.^{-2}$).

Reactions of $RhH(CO)(PPh_3)_3$, $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ with alkenes and CO, H_2 or HCl to give alkyl and acyl species analogous to proposed intermediates in hydroformylation are described. The reactions of these species are shown to be consistent with the proposed hydroformylation mechanism. In particular the reversible carbonylation and CO-insertion reactions of the rhodium(I) and iridium(I) species and the inhibition of reactions of H_2 and HCl with $M(COR)(CO)_2(PPh_3)_2$, M = Rh, Ir, by CO are noted.

The preparation of π-allylic complexes $M(\pi\text{-A})(CO)(PPh_3)_2$, M = Rh, Ir; A = allylic group, by both diene insertion and Grignard reactions is described. N.m.r. spectra over the temperature range -80° to $+80^\circ$ show that the allylic groups are "dynamic". The reaction of $Ir(\pi\text{-A})(CO)(PPh_3)_2$ with CO in solution gives a mixture of σ- and π-allylic species and $Ir(\sigma\text{-A})(CO)_2(PPh_3)_2$ and $Ir(COA)(CO)_2(PPh_3)_2$ complexes have been isolated. Reactions of these allylic complexes with H_2 and HCl are also described. The mechanism of hydroformylation of butadiene is discussed in terms of these results.

INTRODUCTION

The "Oxo" or hydroformylation reaction is the conversion of an olefin into an aldehyde by interaction with carbon monoxide and hydrogen in the presence of a catalyst. The reaction was discovered[1] in 1938 by Roelen during studies on the Fischer-Tropsch process and has acquired considerable industrial importance. It is normally carried out[2] in an inert solvent (often a high-boiling phthalate ester which allows distillation of the reaction products) using a cobalt catalyst and CO + H_2 at pressures of 200-300 atm. and temperatures in the range 100-120°. At higher temperatures, 150-180°, reduction of the products to alcohols takes place. These "Oxo-alcohols" are widely used for the production of plasticisers for polyvinylchloride, for the preparation of detergents and as solvents. The annual world capacity[3] of Oxo-plant in 1968 was in excess of 1.5×10^6 ton.

Much of the early work on the process, recorded in the patent literature, was concerned with industrial and commercial aspects rather than with the reaction mechanism, but after it was realised[4] that homogeneous catalysis was involved mechanisms began to be postulated. The active catalyst was shown[5] to be $HCo(CO)_4$ formed *in situ* from metallic cobalt, cobalt salts or $Co_2(CO)_8$.

Alkyl- and acyl-tetracarbonylcobalt(I) complexes were then prepared[6] by reaction of alkyl- and acyl-halides with $Na[Co(CO)_4]$ and the equilibrium between $RCo(CO)_4$ and $RCOCo(CO)_3$, (R = alkyl group), demonstrated.[6b,7] The nature and reactions of these alkyl- and acyl-cobalt species has been reviewed.[8]

The evidence relating to the mechanism of hydroformylation, which is largely based on the reactions of $HCo(CO)_4$ with olefins at room temperature, has also been thoroughly reviewed[9] and a self-consistent scheme which seems to explain the known facts is as follows:

$$Co_2(CO)_8 + H_2 \rightleftarrows 2HCo(CO)_4 \quad (1)$$

$$HCo(CO)_4 \rightleftarrows HCo(CO)_3 + CO \quad (2)$$

$$RCH{=}CH_2 + HCo(CO)_3 \rightleftarrows \overset{RCH=CH_2}{\underset{HCo(CO)_3}{\downarrow}} \quad (3)$$

$$\begin{array}{ccccc} RCH{=}CH_2 & & RCH_2CH_2Co(CO)_3 & \overset{CO}{\rightleftarrows} & RCH_2CH_2Co(CO)_4 \\ \downarrow & \rightleftarrows & + & & + \\ HCo(CO)_3 & & RCHCo(CO)_3 & & RCHCo(CO)_4 \\ & & | & & | \\ & & CH_3 & & CH_3 \end{array} \quad (4)$$

$$R'Co(CO)_4 \rightleftarrows R'COCo(CO)_3 \quad (5)$$

$$R'COCo(CO)_3 \overset{CO}{\rightleftarrows} R'COCo(CO)_4 \quad (6)$$

$$R'COCo(CO)_3 \begin{cases} \xrightarrow{H_2} R'CHO + HCo(CO)_3 \\ \xrightarrow[HCo(CO)_4]{} R'CHO + Co_2(CO)_7 \end{cases} \quad (7)$$

$$R'COCo(CO)_4 \begin{cases} \xrightarrow{H_2} R'CHO + HCo(CO)_4 \\ \xrightarrow[HCo(CO)_4]{} R'CHO + Co_2(CO)_8 \end{cases} \quad (8)$$

From equation 5 R' = RCH_2CH_2 or $RCHCH_3$ and thus the products from hydroformylation of $RCH{=}CH_2$ are the isomeric aldehydes RCH_2CH_2CHO and $RCH(CH_3)CHO$. Clearly both 4- and 5-coordinate cobalt(I), d^8, species are important in the mechanism.

The straight-chain and branched-chain aldehyde products arising from hydroformylation of alk-1-ene are usually formed in a ratio of < 2:1 and alk-2-ene substrates yield a similar product distribution at low CO pressures[10] because rapid double-bond migration occurs and because terminal double bonds react more rapidly. Higher CO pressures inhibit the isomerisation. Commercial demand for straight-chain products has stimulated much research on modifying the catalytic system to increase the proportion of linear aldehyde and alcohol formed.

Thus in addition to the use of higher CO pressures it was shown[11] that lower reaction temperatures increase the product ratio. The use of polar solvents, e.g. methylethylketone in hydroformylation of propene, has been claimed[12] to greatly enhance the proportion of linear products.

The reaction of $HCo(CO)_4$ with alkenes at 1 atm. and ca room temperature[13] gives differing acyl products according to the temperature and composition of the gas phase. These acyls could be collected as stable triphenylphosphine adducts,[14] $RCOCo(CO)_3(PPh_3)$, and the configuration of the acyl group determined by g.l.c. analysis of the methyl esters formed after decomposition of the complexes with I_2 and MeOH. This reaction of alkene with $HCo(CO)_4$ under mild conditions was also shown to be affected[15] by the presence of nucleophiles such as benzonitrile. The interconversion of isomeric acyltetracarbonylcobalt(I) species was observed[16] at room temperature and, although CO does not alter the final isomer proportions, it slows the reaction which is also very sensitive to solvent. These results were interpreted in terms of the reversible equilibria represented by equations 3, 4 and 5 above and the effect of coordination of solvent or added nucleophile in stabilising tricarbonyl species.

It was thus a matter of importance to ascertain which of the factors revealed by these low pressure reactions is important in defining reaction products under hydroformylation conditions. These seem to be (i) specificity in direction of addition of Co-H to $RCH=CH_2$; (ii) selectivity of reaction of $HCo(CO)_3$ between alk-1-ene and alk-2-ene. The rate of alkene isomerisation is known to be dependent on CO pressure[10b] and isomerisation of intermediate acyls is thought[17] to be slow compared with the overall process, on the basis of results on the reaction of alkylorthoformates with CO and H_2 in the presence of $Co_2(CO)_8$ under hydroformylation conditions. This reaction is believed to involve alkyl- and acyl-cobalt intermediates and no isopropyl product was observed from n-propylorthoformate.[17]

$$HC(OR)_3 + HCo(CO)_4 \rightarrow HCOOR + ROH + RCo(CO)_4$$

$$RCo(CO)_4 + CO \rightarrow RCOCo(CO)_4$$

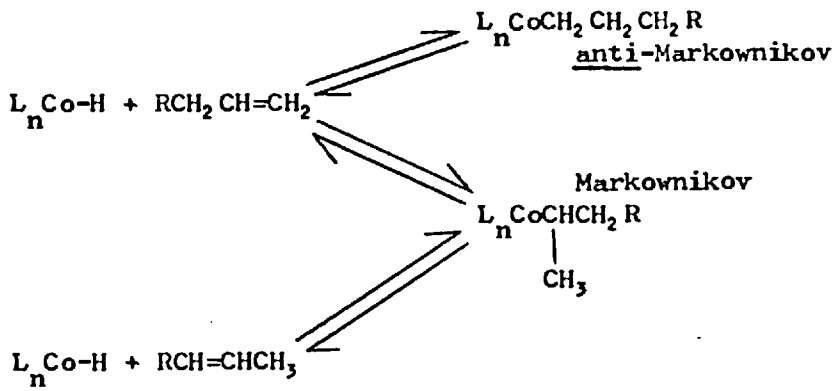
$$RCOCo(CO)_4 + H_2 \rightarrow RCHO + HCo(CO)_4$$

$$RCHO + HC(OR)_3 \rightarrow RCH(OR)_2 + HCOOR$$

A small fraction (5%) of n-butyraldehyde was, however, formed from isopropylorthoformate and it has been noted[16] that isomerisation reactions of the acyl species are very solvent dependent, so that it is unlikely that they can be completely excluded under catalytic conditions.

The addition of ligands which can compete with CO for coordination sites on the cobalt was also claimed[18] to alter significantly the characteristics of the hydroformylation system; important examples being tertiary phosphines, phosphites and amines. Thus the Shell process,[19] under which the preferred modifier is PBu^n_3, was claimed to allow the reaction to proceed at much lower pressures (ca 30 atm.) because of the stability of the catalytic hydride and, in spite of the low pressures, to give a high proportion of linear product. In addition this proportion could be maintained at higher temperatures, 180-200°, when rapid hydrogenation occurs giving high yields of linear alcohols in a single step reaction. The use of triphenylphosphite, on the other hand, was claimed[18a] to inhibit hydrogenation and allow preparation of alcohol-free aldehydes.

Recent work[20] on these processes has suggested that the increase in the proportion of straight-chain product is principally determined by increased specificity for anti-Markownikov addition of the Co-H to the terminal double-bond, caused by coordination of the phosphine to cobalt. Alkene isomerisation is also found to be slowed under these conditions and, since it probably occurs via reversible Markownikov addition, this may also be caused by the same enhanced specificity.



It has been suggested[20a,b] that the specificity for anti-Markownikov addition arises from the more hydridic nature of the modified cobalt hydride. Thus replacement of a CO group in $HCo(CO)_4$ by a tertiary phosphine which is a stronger σ-donor and a weaker π-acceptor has been

shown[21] to greatly reduce the acidity of the metal hydride to water. (When the phosphine is PPh_3 the acidity is reduced by ca 7 pK_a units). Steric factors have also been proposed[16] to account for the formation of linear products in the isomerisation of acyltetracarbonylcobalt(I) species because of interaction of the alkyl group on the alkene with the other ligands in the transition state leading to alkyl formation. Such effects may be expected to be greater when bulky phosphine groups are involved and may influence not only the direction of addition of Co-H to alk-1-ene but also the specificity of the interaction of the hydride between alk-1-ene and alk-2-ene (see rhodium system below).

The differing effectiveness of a variety of phosphine and phosphite modifiers has been discussed[20a,b,22] in terms of these effects and also in terms of the ease of displacement of such ligands by CO under "Oxo" conditions. The relative importance of electronic and steric factors in such systems is not clearly established but it is relevant to note that the extent of ligand replacement in $Ni(CO)_4$ and NiL_4 (L = tertiary phosphine) by different phosphines can be directly related[23] to the "angle of the cone swept out in space" by the particular ligand used.

Soluble complexes of metals other than cobalt have also been claimed in patents[18,24] to act as catalysts for hydroformylation. Only rhodium, however, appears to be useful under less drastic conditions than cobalt and it is assumed that the active species is $HRh(CO)_4$ formed *in situ* as in the cobalt case. Direct comparison using rhodium and cobalt carbonyls[25] has shown that hydroformylation rates are substantially higher ($\times 10^2$ - $\times 10^3$) when rhodium is used. Iridium, iron and nickel carbonyls failed to give significant conversion under similar conditions although at higher temperature (200°) iridium gave substantial hydrogenation. Reactions catalysed by rhodium carbonyls have been studied in detail[26] and found to give lower straight- to branched-chain product ratios than those with cobalt. This has been attributed[26a] to greater alkene isomerisation rates and faster relative hydroformylation of alk-2-ene compared to alk-1-ene.

Rhodium metal or rhodium sesquioxide have been used as starting materials for forming the catalyst *in situ* in a number of preparative studies[27] and the use of phosphine modifiers has also been found[28] to affect the product composition. Coordination complexes of rhodium

such as $RhCl_3(PPh_3)_3$, $RhCl_3(pyridine)_3$ and $Rh_2Cl_2(SrCl_2EtOH)_4$[29] have also been used. The complexes trans-$RhX(CO)(PR_3)_2$, (X = Cl, Br or I; R = alkyl or aryl) were found[30] to be particularly active. At 100 atm. and 70° such catalysts give a straight- to branched-chain product ratio of ca 2.7:1 from pent-1-ene and alk-2-enes were found to give only branched-chain products. Thus, although trans-$RhCl(CO)(PPh_3)_2$ catalyses alkene isomerisation in the presence of H_2 at 70°, such isomerisation is completely suppressed in hydroformylation, probably, as in the cobalt case, by the high CO pressure. More recently[31] a detailed study of the reaction with trans-$RhCl(CO)(PPh_3)_2$ at lower pressures (ca 34 atm.) and at temperatures of 100-150° has examined the effects of the various reaction parameters on the product distribution and shown that, with > 99% selectivity to aldehydes, the reaction can give a linear content of 75 to 80% from alk-1-enes if excess PPh_3 is added to prevent alkene isomerisation which otherwise occurs under these conditions.

An induction period observed in these reactions[30] could be removed by addition of a hydrogen-halide acceptor, e.g. Et_3N, when Et_3NHCl could be recovered after the reaction, which was found to proceed under milder conditions. This was interpreted as showing that the active species is $RhH(CO)(PPh_3)_2$ or another rhodium hydride formed by further carbonylation.

$$RhCl(CO)(PPh_3)_2 + H_2 \rightleftarrows RhH(CO)(PPh_3)_2 + HCl$$

$RhH(CO)(PPh_3)_2$, however, is very unstable and the pale-yellow solutions obtained after such amine-promoted hydroformylation reactions were extremely air sensitive. Addition of excess PPh_3 before these reactions allowed recovery of the stable yellow complex $RhH(CO)(PPh_3)_3$, previously prepared by Vaska.[32] This compound can thus be used as a convenient catalyst and no induction period was observed in such cases.

$RhH(CO)(PPh_3)_3$, which dissociates a PPh_3 ligand in solution,[33] is also an active catalyst at 25° and 1 atm. for hydrogenation,[34] isomerisation[35] and hydrogen atom exchange[30] reactions of alkenes. It reacts reversibly with CO at 1 atm. to form $RhH(CO)_2(PPh_3)_2$ and dimeric species;[33] the dicarbonyl hydride being much less active for isomerisation reactions. The properties of $RhH(CO)(PPh_3)_3$ are summarised in Table I.1.

Using $RhH(CO)(PPh_3)_3$ it was found[30] that hydroformylation can proceed at 1 atm. and 25° and that under certain conditions ratios of straight- to branched-chain aldehydes of ca 20:1 could be achieved. This was in an essentially stoicheiometric reaction in which a benzene solution of $RhH(CO)(PPh_3)_3$ was first treated with CO to give $RhH(CO)_2(PPh_3)_2$ and $[Rh(CO)_2(PPh_3)_2]_2$. Alkene was then added and H_2 bled into the system to give the aldehyde mixture (ca 100% based on Rh); the dimer $[Rh(CO)_2(PPh_3)_2]_2$ being cleaved by H_2 to regenerate the hydrido species under these conditions.

As a result of these investigations and in light of further information from the other catalytic reactions of $RhH(CO)(PPh_3)_3$ noted above, two mechanisms were proposed[30] for hydroformylation, which were based essentially on that of the cobalt system. They differ in the mode of attack of alkene on the catalyst.

(a) The associative pathway

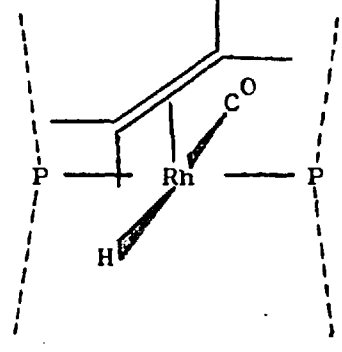
$$RhH(CO)_2(PPh_3)_2 \overset{\text{alkene}}{\rightleftharpoons} RhH(\text{alkene})(CO)_2(PPh_3)_2 \rightleftharpoons RhR(CO)_2(PPh_3)_2$$

(b) The dissociative pathway

$$RhH(CO)_2(PPh_3)_2 \overset{-PPh_3}{\rightleftharpoons} RhH(CO)_2(PPh_3) \overset{\text{alkene}}{\rightleftharpoons} RhH(\text{alkene})(CO)_2(PPh_3)$$

$$\overset{PPh_3}{\rightleftharpoons} RhR(CO)_2(PPh_3)_2$$

A third possibility is that attack of alkene on trans-$RhH(CO)(PPh_3)_2$, which is thought to be operative in hydrogenation reactions,[34] can lead to aldehyde products by carbonylation after or concurrently with the hydride transfer reaction. Such a pathway is expected to give a similarly high specificity in respect of alk-1-ene vs alk-2-ene substrates as observed in hydrogenation where it was attributed to the maximum steric interaction of the trans-PPh_3 groups, mutually cis to the hydride, with the approaching alkene.



In $RhH(CO)_2(PPh_3)_2$ the PPh_3 groups are probably *cis* and the molecule may also show fluxional behaviour like the iridium analogue, $IrH(CO)_2(PPh_3)_2$.[36]

The reaction was taken to proceed from $RhR(CO)_2(PPh_3)_2$ by alkyl transfer to coordinated CO giving a square acyl, $Rh(COR)(CO)(PPh_3)_2$; this then undergoes oxidative addition of H_2 to give a dihydridoacyl-rhodium(III) species, $Rh(COR)H_2(CO)(PPh_3)_2$, which rapidly eliminates aldehyde forming $RhH(CO)(PPh_3)_2$ which takes up CO to reform $RhH(CO)_2(PPh_3)_2$. It was also anticipated that addition of CO to the square acyl to give $Rh(COR)(CO)_2(PPh_3)_2$ would be likely and that such a reaction would block the oxidative addition of H_2, which is believed[30] to be the rate-determining step, and thus be inhibiting.

Hydroformylation using $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PBu^n_3)_2$ [24d] probably also proceeds by way of hydrido species and $IrH(CO)(PPh_3)_3$,[32] which has been shown[37] to act as an hydrogenation catalyst for ethylene and acetylene under mild conditions (*ca* 1 atm., 30°), has been used at 100 atm., 70° [30] but found to give considerably slower reaction than with the rhodium analogue. It is likely, however, that the reactions involved are broadly similar to those in cobalt and rhodium catalysis. These metals comprise the second subgroup of Group VIII in the Periodic Table (outer electron configuration d^7s^2) and can form compounds of similar stoicheiometry, albeit of vastly different stability. Although care must be exercised in comparing metals from different transition series studies of the compounds of one of these metals may give an insight into less readily studied reactions of another.

The object of this study was to investigate truly catalytic (i.e. high conversion : catalyst ratio) reactions using $RhH(CO)(PPh_3)_3$ under mild conditions with particular reference to the proposed mechanisms and to the factors influencing the product ratio in these circumstances.

The work is described in four chapters. The first is concerned with direct measurements on the $RhH(CO)(PPh_3)_3$ catalysed hydroformylation system at *ca* 1 atm. and 25°. In the second chapter hydroformylation at higher temperatures and pressures and control of reaction products by the use of large excesses of PPh_3 is described. Chapter III describes an approach to the mechanism of the catalytic reactions by isolation

and/or spectroscopic characterisation of postulated intermediates and study of the reactions of these species. Iridium complexes were of particular value, being considerably more stable than their rhodium analogues. This was also found to be true of the allylic complexes, formed by interaction of hydridocarbonyltriphenylphosphinerhodium(I) and iridium(I) compounds with conjugated dienes and allene and described in Chapter IV.

Table I.1. Properties of Hydridocarbonyltris(triphenylphosphine)rhodium(I)

Preparation[33]	trans-$RhCl(CO)(PPh_3)_2$ may be prepared[38] by interaction of $RhCl_3 \cdot 3H_2O$ with excess PPh_3 and aqueous formaldehyde in refluxing ethanol. (Yield ca 85%). Treatment of a suspension of trans-$RhCl(CO)(PPh_3)_2$ in refluxing ethanol with excess PPh_3 and $NaBH_4$ gives $RhH(CO)(PPh_3)_3$ in high yield (ca 90%).
Solid	Yellow crystals, stable to air; m.p. 117°.
Structure[39]	Trigonal bipyramidal with an axial H-Rh-CO group.
I.R. spectrum	Nujol mull. ν_{RhH} 2040 (m), ν_{CO} 1923 (s) cm^{-1}. Cyclohexane solution 2005 (s), 1935 (m).
N.M.R. spectrum (33,40)	Room temperature: single broad line τ 19.27 (C_6H_6) resulting from exchange broadening due to PPh_3 dissociation. -35° : 1:3:3:1 quartet of doublets τ 19.69 (CH_2Cl_2); J_{PH} 14Hz; J_{RhH} ca 1Hz.
Solubility[33]	Moderately soluble in $CHCl_3$, CH_2Cl_2 or C_6H_6 (ca 40 mg/ml). Sparingly soluble in cyclohexane (ca 1 mg/ml) and insoluble in light petroleum. The complex decomposes on standing in solution,[41] losing H_2 and forming a catalytically inactive dimer $[Rh(CO)(PPh_3)_2]_2$. With chlorinated solvents trans-$RhCl(CO)(PPh_3)_2$ is formed on refluxing.

CHAPTER I

Homogeneous Hydroformylation of Alkenes with Hydridocarbonyl-tris(triphenylphosphine)rhodium(I) as Catalyst : Low Pressure System

Introduction

As noted above the previous studies[30] using $RhH(CO)(PPh_3)_3$ as a catalyst for hydroformylation at 25° and 1 atm. involved reaction of solutions containing $RhH(CO)_2(PPh_3)_2$ and $[Rh(CO)_2(PPh_3)_2]_2$, formed[33] by passage of CO through benzene solutions of $RhH(CO)(PPh_3)_3$, with alkene and H_2.

$$RhH(CO)(PPh_3)_3 \rightleftarrows RhH(CO)(PPh_3)_2 + PPh_3$$

$$RhH(CO)(PPh_3)_2 \overset{CO}{\rightleftarrows} RhH(CO)_2(PPh_3)_2$$

$$2RhH(CO)_2(PPh_3)_2 \overset{-H_2}{\rightleftarrows} [Rh(CO)_2(PPh_3)_2]_2$$

In the absence of alkene a red, carbonyl-bridged dimer, $[Rh(CO)(PPh_3)_2S]_2$ (S = solvent) was shown[33] to be formed on sweeping solutions of the yellow $[Rh(CO)_2(PPh_3)_2]_2$ with an inert gas and may be collected as the EtOH or CH_2Cl_2 solvate.

$$[Rh(CO)_2(PPh_3)_2]_2 \overset{-CO}{\rightleftarrows} [Rh(CO)(PPh_3)_2S]_2$$

In the presence of even a 1 molar excess of PPh_3 [as when formed from $RhH(CO)(PPh_3)_3$] the red and yellow dimers are cleaved by H_2 at 1 atm. to reform the hydrido species. In the absence of excess PPh_3, however, an orange compound, $[Rh(CO)(PPh_3)_2]_2$, is formed.[41] This species is also formed by a slow decomposition of solutions of $RhH(CO)(PPh_3)_3$ and both reactions probably occur <u>via</u> $RhH(CO)(PPh_3)_2$.

$$2RhH(CO)(PPh_3)_2 \rightarrow [Rh(CO)(PPh_3)_2]_2 + H_2$$

This reaction is not reversed by H_2 at 1 atm. and is responsible for a marked loss of catalytic activity with time during hydrogenation[34] and isomerisation[35] reactions of alkenes using $RhH(CO)(PPh_3)_3$. Prolonged treatment of solutions of $[Rh(CO)(PPh_3)_2]_2$ containing

excess PPh_3 with CO at 1 atm. was, however, found[41] to give $[Rh(CO)_2(PPh_3)_2]_2$, from which the hydrido species can be formed. $RhH(CO)(PPh_3)_3$ can also be quantitatively regenerated by reaction of $[Rh(CO)(PPh_3)_2]_2$ with 80 atm. H_2 in the presence of a 2-fold excess of PPh_3 at 60°.

The use of $[Rh(CO)(PPh_3)_2S]_2$ as a catalyst for hydrogenation of hex-1-ene at ca 1 atm. and 25° was shown[41] to give rates initially faster by a factor of 1.4 than those found when $RhH(CO)(PPh_3)_3$ is used. This was attributed to the absence of the extra mole of PPh_3 which otherwise competes with the alkene for coordination to the rhodium and also to a greater proportion of a further dissociated species, $RhH(CO)(PPh_3)$, which was described[34] as a more active catalytic species present at low concentrations. The rate was however found to be slower after equilibration with H_2 for 20 min. when substantial conversion to $[Rh(CO)(PPh_3)_2]_2$ had occurred. Solutions of $[Rh(CO)(PPh_3)_2S]_2$ were also shown to decompose spontaneously, albeit slowly, to give the inactive, non-bridged, dimer.

The spectroscopic properties of these species in benzene solution are collected in Table 1.1, and Scheme I.1, reproduced from reference 41, is given as a convenient summary of the known chemistry of the system.

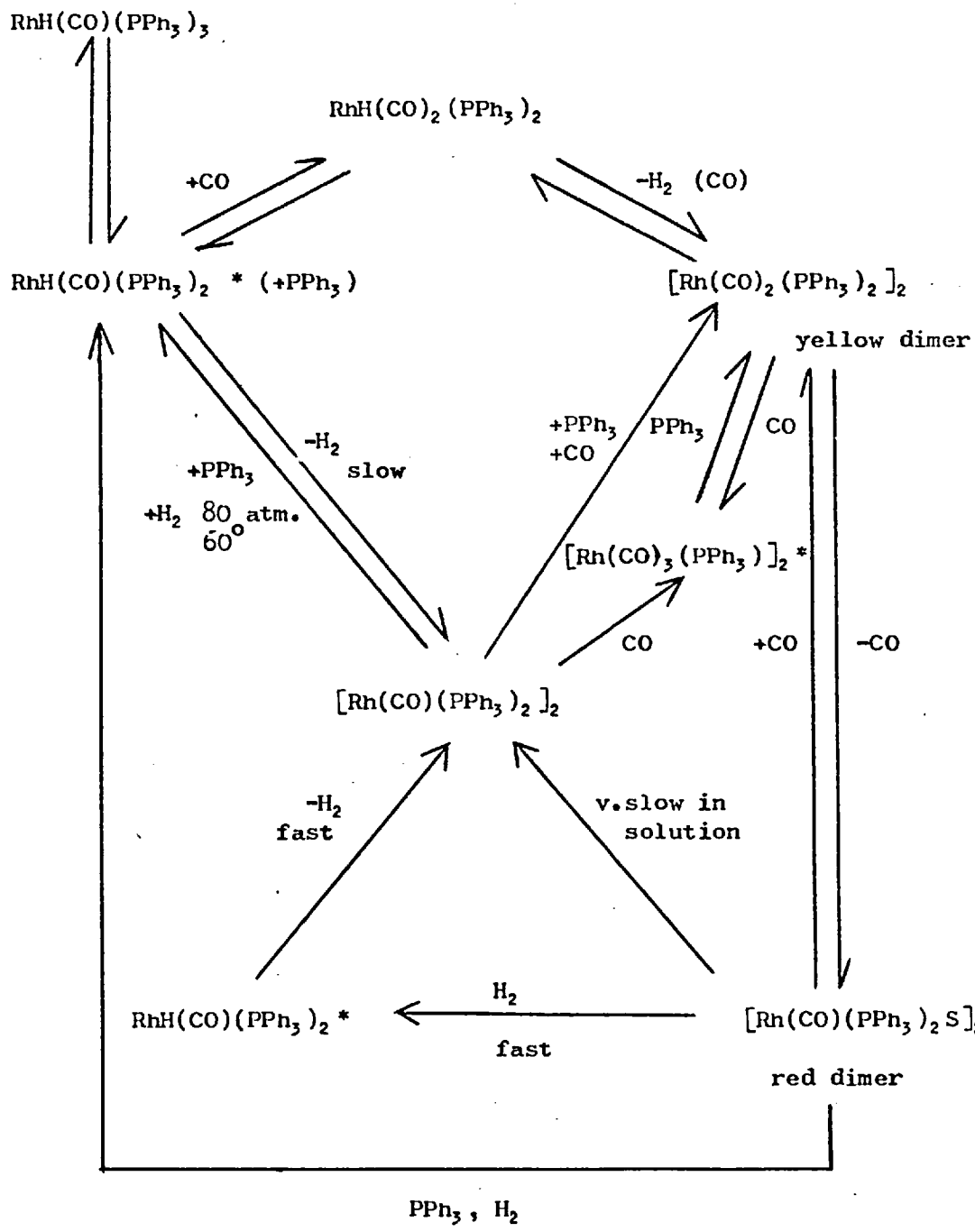
Table 1.1

Compound	I.r. spectrum (cm^{-1}) [a]		N.m.r. spectrum [b]
	ν_{RhH}	ν_{CO}	τ values
$RhH(CO)(PPh_3)_2$	2000 s	1920 m	19.27 (broad)
$RhH(CO)_2(PPh_3)_2$	2038	1980, 1939	19.10 (broad)
$[Rh(CO)_2(PPh_3)_2]_2$	-	2005 sh, 1985 s, 1790 sh, 1765 s	-
$[Rh(CO)(PPh_3)_2S]_2$	-	1740	-
$[Rh(CO)(PPh_3)_2]_2$	-	1965	-

a 0.1 mm solution cell with compensation, s = strong, m = medium, sh = shoulder

b 100 MHz, 35°.

Scheme 1.1



* compounds not isolable

A. Equilibria

The ready interconversion of the species other than $[Rh(CO)(PPh_3)_2]_2$ described in Table I.1 results in an equilibrium mixture being formed when $RhH(CO)(PPh_3)_3$ is dissolved in benzene under an atmosphere containing both CO and H_2. It is possible to make a rough estimate of the equilibrium proportions under an atmosphere of CO + H_2 (1:1) by measuring the high-field n.m.r. spectrum of 15 mM $RhH(CO)(PPh_3)_3$ in benzene before and after equilibration with this gas mixture and again after adding a drop of liquid alk-1-ene, whose sole effect is to cause disappearance of the high-field line due to $RhH(CO)_2(PPh_3)_2$. At 25° the approximate proportions are $RhH(CO)_2(PPh_3)_2$, 55%; $RhH(CO)(PPh_3)_2$, 25%; and $[Rh(CO)_2(PPh_3)_2]_2$, 20%. These measurements are of limited value and depend on the rate of the reaction of $RhH(CO)(PPh_3)_2$ with the products of the $RhH(CO)_2(PPh_3)_2$ + alk-1-ene reaction. The n.m.r. measurements show this to be slow under the conditions used.

Solution i.r. spectra confirm that at 1 atm. $RhH(CO)_2(PPh_3)_2$ is the major species for $CO:H_2 < 1:1$ but that at higher ratios $[Rh(CO)_2(PPh_3)_2]_2$ becomes more important. At 1 atm. $[Rh(CO)(PPh_3)_2S]_2$ is not an important contributor, even with $CO:H_2 = 1:6$, although at lower total pressures of CO + H_2 this species predominates. Quantitative estimation of the equilibrium proportions by i.r. is not possible because of overlap of bands.

The equilibria in the presence of excess alk-1-ene will clearly be very different and the more stable intermediates are probably present in appreciable concentrations. Spectroscopic study of the reaction mixture during hydroformylation by circulation of the solution through an i.r. cell was not found to be possible as the equilibria involved are critically dependent on the presence of CO and H_2 in solution, which must be continuously replenished otherwise the reaction uses CO and hydrogen from the complexes present to give aldehyde and $[Rh(CO)(PPh_3)_2S]_2$; this effect being faster the more concentrated the solution and the more H_2-rich the gas mixture. Thus sufficiently high circulation rates could not be achieved without formation of bubbles caused by pressure changes in the circuit.

B. Rates of Hydroformylation

1. Comparison of substrates

The rates were measured by uptake of CO + H_2 under standard conditions and are given in Table 1.2.

Table 1.2 Relative rates of hydroformylation of unsaturated substances [a] using $RhH(CO)(PPh_3)_3$ as catalyst.

Rate of uptake of H_2 + CO (1:1) in ml $min.^{-1}$ at 50 cm gas pressure; catalyst concentration 2.5 mM, substrate concentration 1.0 M in benzene; temperature 25°. (1 ml $min.^{-1}$ = 4.5 x 10^{-6} $mole.l^{-1}s^{-1}$).

Substrate	Rate	Substrate	Rate
Allyl alcohol	7.05	Hept-1-ene	3.50
Allylphenyl ether	5.78	Dodec-1-ene	3.18
Styrene	4.32	Vinyl acetate	0.75
Hexa-1,5-diene	4.26	Cyclo-octene	0.26
4-Vinyl-cyclohexene	4.21	Ethyl vinyl ether	0.20
o-Allyl-phenol	4.03	Pent-2-enes (cis and trans)	0.15
Pent-1-ene [b]	3.74	cis-Hept-2-ene	0.12
Allyl-cyanide	3.72	dl-Limonene	0.10
Allyl-benzene	3.56	2-Methylpent-1-ene	0.06
Hex-1-ene	3.52		

a 1:1:1 mixtures of alkene, H_2 and CO at 60 cm total gas pressure gave uptakes for ethylene and propylene of 4.55 and 1.60 ml $min.^{-1}$ respectively.

b In n-Hexaldehyde as solvent, rate = 2.20 ml $min.^{-1}$

These results are of more practical interest than quantitative significance as functional groups present may substantially alter the properties of the solvent medium and may also solvate the complex, so

inhibiting substrate coordination in intermediates. It appears that alk-1-enes, including non-conjugated, non-chelating dienes such as hexa-1,5-diene, react rapidly whereas alk-2-enes react more slowly by a factor of ca 25. Alkenes $R^1R^2C=CH_2$ react even more slowly. Electronic and steric factors in other substrates effect the rate and also the product distribution. No detectable uptake (< 0.05 ml $min.^{-1}$) was observed for cyclohexene, methylacrylate or α-pinene. Allyl-amine, hex-1-yne, penta-1,3-diene, cycloocta-1,3-diene, butadiene and allene react directly with the catalyst in the absence of CO and H_2 and show no uptake in their presence (cf Chapter IV). Allylchloride, methallylchloride and vinylchloride react to give trans-$RhCl(CO)(PPh_3)_2$ and alkene. (cf treatment of $RhH(CO)(PPh_3)_3$ with CH_3I gives CH_4).

2. Hydroformylation of hex-1-ene at low pressures

The rate of hydroformylation of hex-1-ene was measured with variance of catalyst concentration, alkene concentration, partial pressures of CO and H_2, and temperature. Analysis of the product solutions by g.l.c. showed that hydrogenation accounted for < 1% of the products and the gas uptake measured could clearly be taken as the rate of hydroformylation. Isomerisation of hex-1-ene to cis- and trans-hex-2-enes accounted for at most 2 - 3% of the products. Consumption of the substrate at the time of measurement was < 1% and overall reproducibility of the rate measurements was ca 4%.

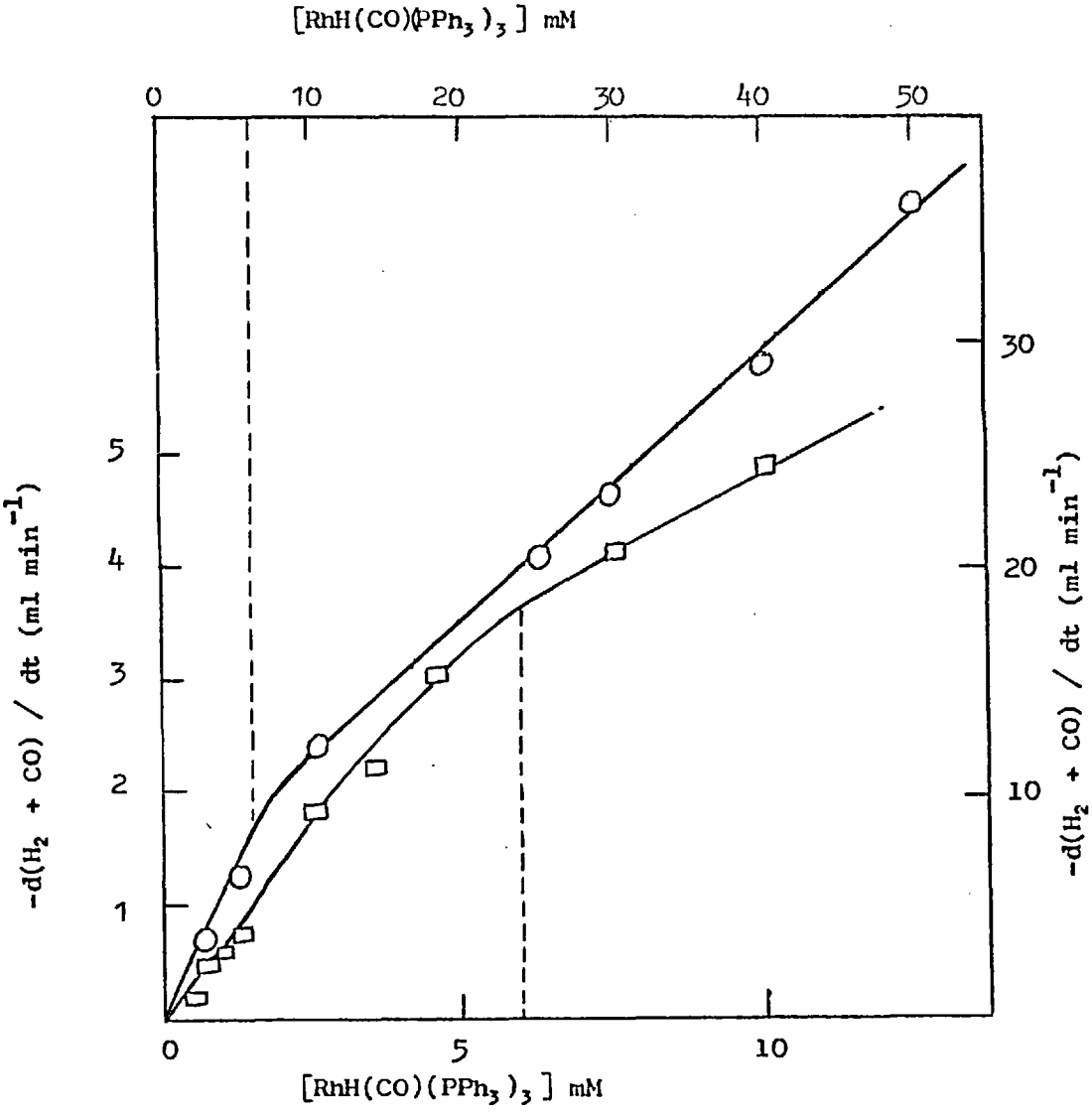
(a) Dependence on catalyst concentration. Results are shown in Figure 1.1. At catalyst concentrations above ca 6 mM the dependence is linear suggesting a pseudo-first-order behaviour. The apparent higher dependence at lower concentrations suggests a concentration-dependent change from one active species to another less-active one; i.e. a change of mechanism. A similar effect noted in hydrogenation with $RhH(CO)(PPh_3)_3$ [34] is attributed to further catalyst dissociation at concentrations below 1 mM.

$$RhH(CO)(PPh_3)_3 \overset{-PPh_3}{\rightleftharpoons} RhH(CO)(PPh_3)_2 \overset{-PPh_3}{\rightleftharpoons} RhH(CO)(PPh_3)$$

In hydroformylation the effect may similarly arise from dissociation of the type

$$RhH(CO)_2(PPh_3)_2 \overset{-PPh_3}{\rightleftharpoons} RhH(CO)_2(PPh_3)$$

Figure 1.1



Rate of hydroformylation of hex-1-ene as a function of catalyst concentration in benzene at 25° and 50 cm ($CO + H_2$) pressure (1:1);
○ hex-1-ene at 1.0 M, upper and right-hand scales;
□ hex-1-ene at 0.5 M, lower and left-hand scales.

which, essentially, amounts to a change from associative to dissociative mechanism as previously suggested (p. 13). That the effect occurs at higher concentration than in hydrogenation may be attributed to the coordination of an extra CO promoting further PPh_3 dissociation. If the initial addition of alkene to the Rh-H bond is the determining factor such loss of PPh_3 at low concentration should and indeed does result in lower specificity of the catalyst in respect of both substrate alkene and of straight- to branched-chain product formed from alk-1-ene (Table 1.3).

Table 1.3

Rate of uptake of CO + H_2 (1:1) for a 1.0 M solution of alkene at 25° and 50 cm gas pressure.

	Hex-1-ene		cis- and trans-Hex-2-enes
Catalyst conc. mM	Rate $ml\ min.^{-1}$	Straight-:branched-chain aldehyde	Rate $ml\ min.^{-1}$
2.5	3.52	ca 3:1	0.16
40.0	29.04	ca 10:1	0.34

It has already been noted (p.13) that $RhH(CO)_2(PPh_3)_2$ is not such a specific catalyst[30] as trans-$RhH(CO)(PPh_3)_2$ in hydrogenation and thus the importance of this effect of further dissociation may not be as important in hydroformylation.

At catalyst concentrations below 0.5 mM the reacting solutions, instead of being yellow, rapidly become colourless and gas uptake ceases. In order to produce such a colourless solution at this concentration of catalyst alkene and CO, but not H_2, are necessary. Further, the alkene must be added to the solvent under CO before the catalyst as otherwise a masking yellow colour, probably due to the yellow dimer, is formed. In Chapter III the ready reversible displacement of PPh_3 by CO in species of the type $MR(CO)_2(PPh_3)_2$ (M = Rh, R = C_2F_4H, EtCO, PhCO; M = Ir, R = EtCO, PhCO) to form $MR(CO)_3(PPh_3)$ is described. By analogy with this and in view of the impossibility of i.r. or n.m.r. measurements at such dilution this colourless solution may be assumed to result from formation of $Rh(COR)(CO)_3(PPh_3)$ species.

Since the equilibria in the system involve dimeric species the possibility of a concentration dependence of the rate arising from an equilibrium effect must be considered. It has been noted above that when the reaction is starved of CO and H_2 formation of the red dimer $[Rh(CO)(PPh_3)_2S]_2$ occurs, the rate depending on catalyst concentration. A similar effect is noted when the gas is pumped off after a kinetic run. The rate of hydroformylation however (Figure 1.1) does not show appreciable drop off in the high concentration range and it thus seems that, provided the gas pressures are maintained, the position of monomer-dimer equilibria is not important in determining the rate.

Measurements of the effects of other reaction variables were carried out at catalyst concentrations of 2.5 and 10.0 mM.

(b) Dependence on substrate concentration. As observed in hydrogenations with $RhCl(PPh_3)_3$ [42] and $RhH(CO)(PPh_3)_3$ [34] as catalysts, the rate approaches an asymptotic value with increasing alkene concentration (Figure 1.2). Plots of the reciprocal of the rate $1/R$ ($\ell.mol.^{-1}s$) against the reciprocal of the alkene concentration are linear with a positive intercept on the $1/R$ axis (Figure 1.3). The reciprocal of this intercept gives the maximum possible rate under the specified conditions.

Thus $1/R = C(1/[B]) + C'$, where B is substrate and C and C' are constants. This behaviour is consistent with sequences of the type 1 and 2, where A is catalyst

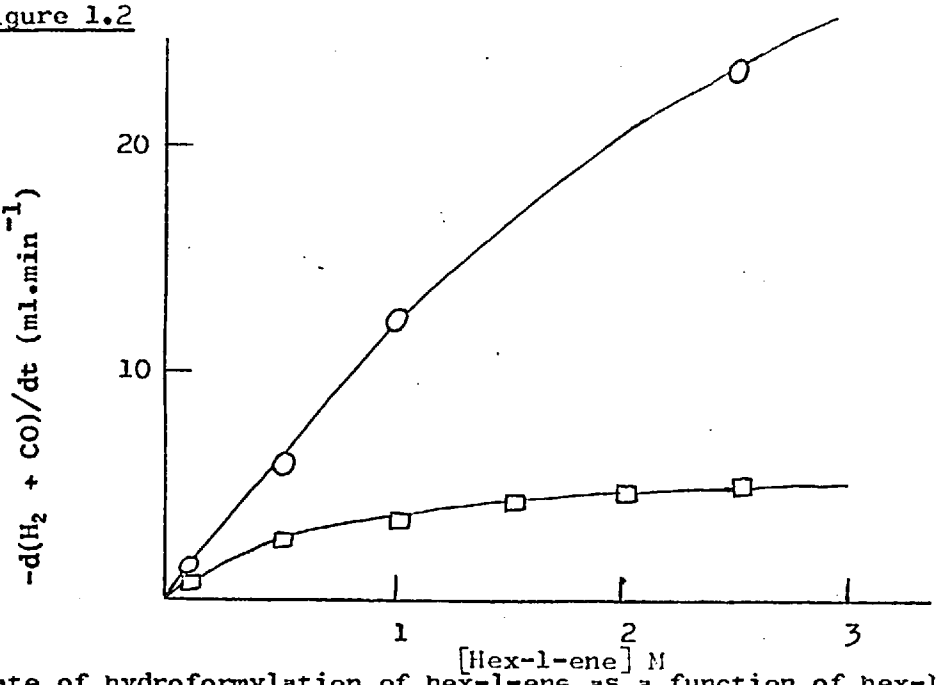
$$A + B \overset{K}{\rightleftarrows} AB \overset{\text{slow}}{\rightarrow} \text{products} \qquad 1$$

$$A + (\text{gases}) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A' \overset{k_2}{\rightarrow} \text{products} \qquad 2$$

and both k_2 and k_{-1} are fast and k_1 slow. A' would be either a Rh^{III} trihydrido-species or an active species formed by slow addition of CO to A. However, since there is no evidence at any stage in the reaction for a long-lived Rh^{III} species and the reactions of the catalyst with CO are fast, allowing very rapid hydroformylation at low CO pressures (see below) it is likely that sequence 1 represents the reaction pathway and that AB is probably an acyl species (see Chapter III).

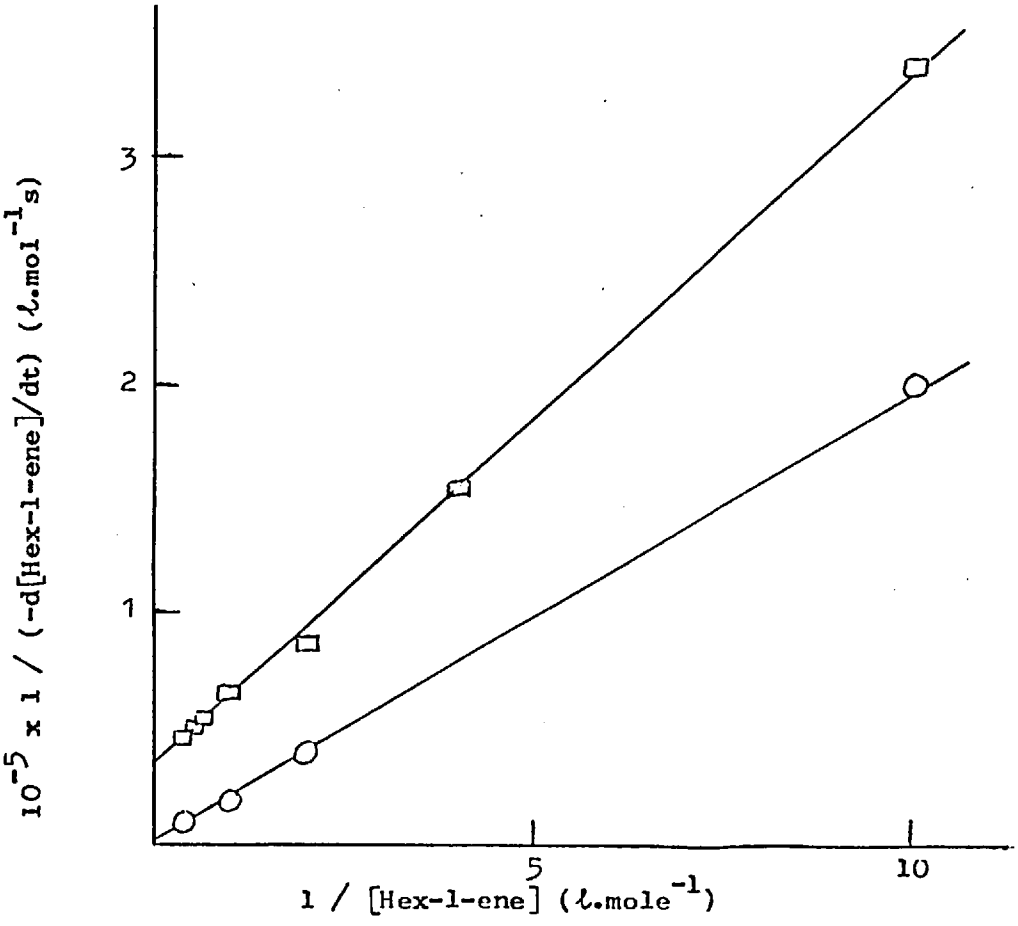
(c) Dependence on gas pressures. (i) Dependence on total pressure at $CO:H_2 = 1:1$. When a kinetic run is allowed to continue an uptake

Figure 1.2



Rate of hydroformylation of hex-1-ene as a function of hex-1-ene concentration in benzene at 25° and 50 cm ($CO + H_2$) pressure (1:1); O $[RhH(CO)(PPh_3)_3]$ at 10 mM; □ $[RhH(CO)(PPh_3)_3]$ at 2.5 mM.

Figure 1.3



Plot of reciprocal of rate of hydroformylation of hex-1-ene against the reciprocal of alkene concentration in benzene at 25° and 50 cm ($CO + H_2$) pressure (1:1); O $[RhH(CO)(PPh_3)_3]$ at 10 mM; □ $[RhH(CO)(PPh_3)_3]$ at 2.5 mM.

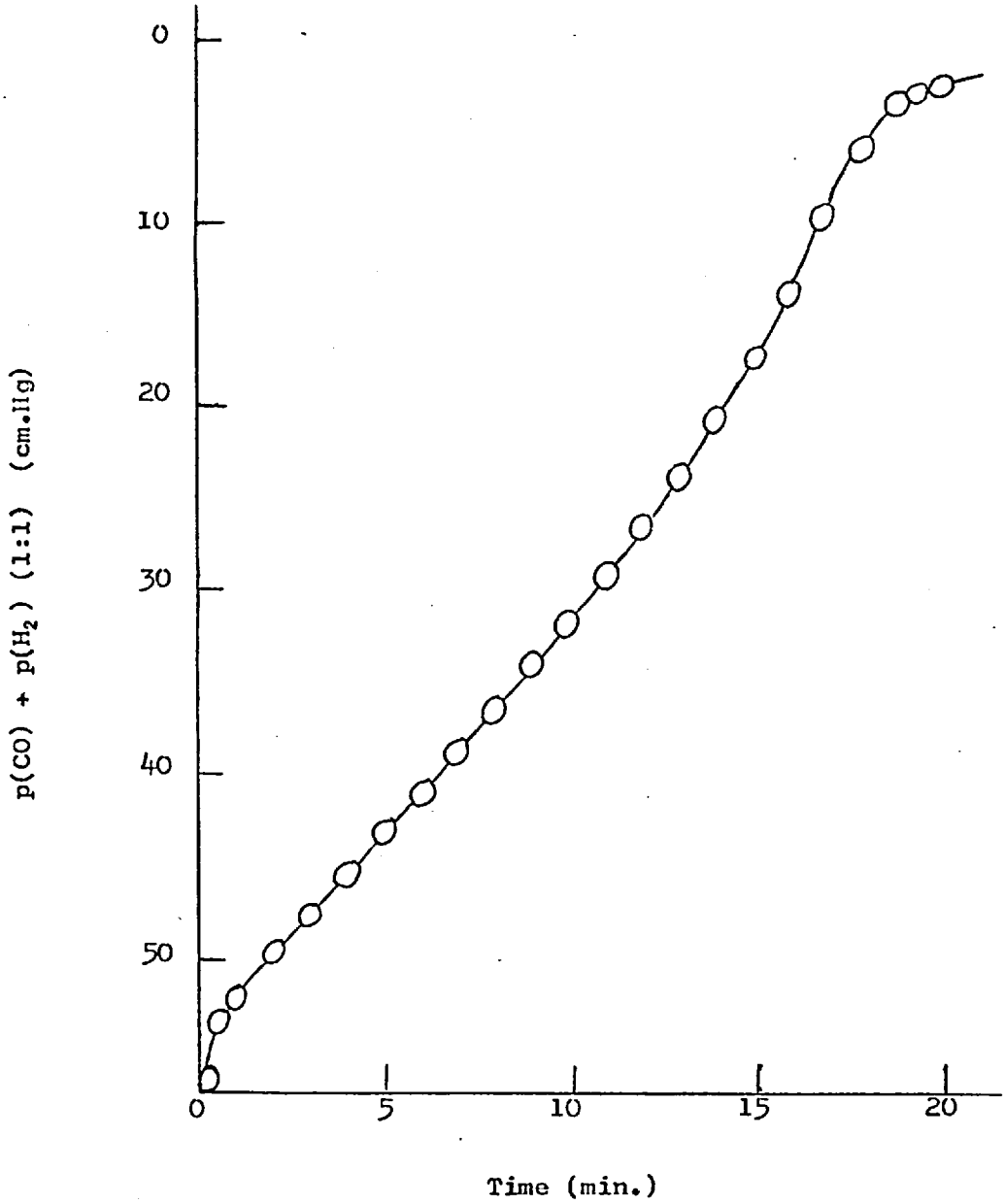
curve of the general form shown in Figure 1.4 is obtained for a wide variety of substrate, substrate concentration, catalyst concentration and temperature. During the fall in pressure measured ca 12% of the alkene is converted and in the absence of appreciable hydrogenation the gas available can be assumed to remain close to a 1:1 mixture. Thus it appears that the effect can be taken to be a significant increase in the rate at lower pressures. If the curve of Figure 1.4 is differentiated with respect to time a plot of rate against pressure is obtained (Figure 1.5, □).

(ii) Dependence on partial pressures of CO and H_2. Since the rates were not measured at constant pressure, these measurements are necessarily more qualitative. The rate was again taken at 50 cm total gas pressure, with the gas used consisting of the appropriate mixture of CO, H_2 and N_2 to give the partial pressure of 25 cm for one reaction gas at this point while variation of the other was studied. These results are also shown in Figure 1.5 from which it is seen that there is a strong CO inhibition factor which overshadows a lesser dependence on the partial pressure of H_2. For a 1:1 gas mixture at 50 cm total pressure the dependences are almost the same, accounting for the nearly linear uptake curves found in this region. The more rapid fall in rate as $p(H_2)$ is lowered below about 10 cm with $p(CO)$ = 25 cm for the 10 mM solution is probably associated with displacement of the monomer-dimer equilibria towards $[Rh(CO)_2(PPh_3)_2]_2$.

The possibility that the greater rates obtained at decreasing CO pressures [with $p(H_2)$ = 25 cm] are due to a steadily increasing contribution of hydrogenation to the uptake is excluded on the basis of g.l.c. analysis of the solutions. Further, such hydrogenation could not readily account for the very sudden fall in rate and subsequent uptake. It is most probable that the inhibition is due to formation of $Rh(COR)(CO)_2(PPh_3)_2$ and $Rh(COR)(CO)_3(PPh_3)$ which are unreactive to H_2 (see Chapter III).

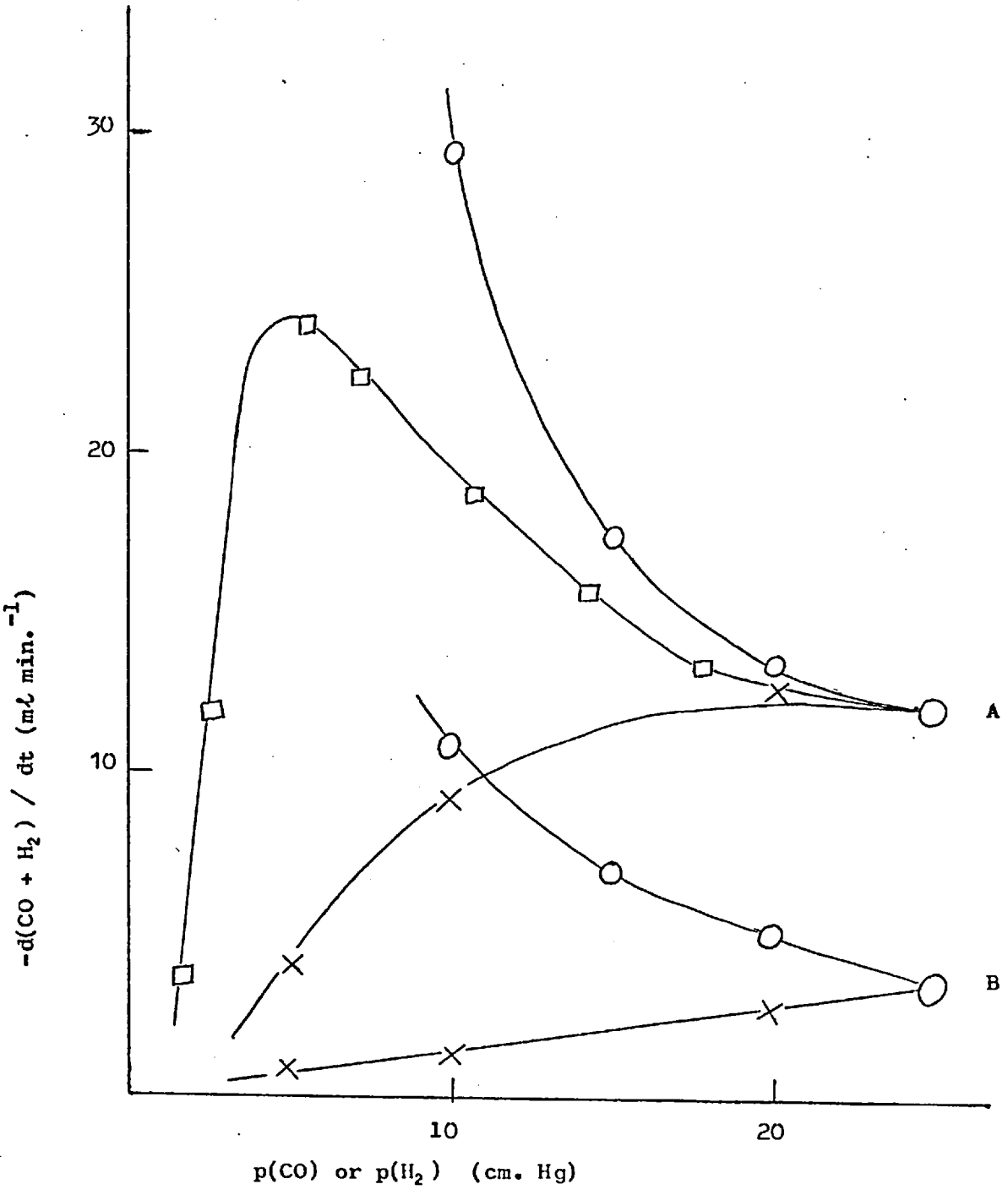
The colour of the hydroformylation solutions also changes from the initial yellow to reddish when the rate starts to accelerate noticeably at $p(CO)$ = ca 8 cm and becomes red by the time the rate suddenly slows again at $p(CO)$ = ca 2 cm. The red colour is formed by pumping on a reaction solution at any time as noted above. The

Figure 1.4



Plot of gas pressure against time for hydroformylation of hex-1-ene (1 M) in benzene at 25° with 10 mM-$RhH(CO)(PPh_3)_3$.

Figure 1.5



Plot of rate of hydroformylation of hex-1-ene (1 M) in benzene at 25° and 50 cm total gas pressure against partial pressure of CO (○) with $p(H_2)$ 25 cm, and against partial pressure of H_2 (X) with p(CO) 25 cm, the pressure being made up with N_2; A, $[RhH(CO)(PPh_3)_3]$ at 10 mM; B, $[RhH(CO)(PPh_3)_3]$ at 2.5 mM; □, gives rate as a function of total pressure (CO ; H_2 = 1:1) from differentiation of curve of Figure 1.4.

rate of formation of the red colour, as well as being slower at lower catalyst concentrations, is also slower with higher partial pressures of CO. These colour changes can be associated with the reactions.

$$\text{Acyl intermediates} \xrightarrow[-\text{CO}]{-\text{alkene}} RhH(CO)_2(PPh_3)_2 \xrightarrow{-H_2}$$

$$[Rh(CO)_2(PPh_3)_2]_2 \xrightarrow{-CO} [Rh(CO)(PPh_3)_2S]_2$$

yellow dimer red dimer

This was confirmed by i.r. study.

The reverse reaction occurs rapidly on adding H_2 and CO and clearly occurs stepwise. There is an immediate initial formation of the very bright yellow colour of $[Rh(CO)_2(PPh_3)_2]_2$ which then converts in about 1 min. to the more golden colour of the normal reaction mixture as the rate of uptake increases again. After such a gas consumption and refilling sequence there is a certain loss of activity (ca 20%). A smaller loss (< 10%) is also found when pressure is restored before it has fallen to the fast acceleration stage. These changes are probably greater than can be accounted for in terms of lowered alkene concentration but, as there are necessarily alterations in the solvent system owing to formation of aldehyde, no direct conclusion can be drawn except that the lability of the equilibria allows almost complete regeneration of catalytic activity from dimers very rapidly. Indeed the red dimer $[Rh(CO)(PPh_3)_2S]_2$, S = EtOH or CH_2Cl_2, may be used as a hydroformylation catalyst and under the standard conditions of Table 1.2 with 2.5 mM rhodium concentration the rate for hydroformylation of hex-1-ene was 3.70 ml $min.^{-1}$ compared with 3.52 ml $min.^{-1}$ with $RhH(CO)(PPh_3)_3$, probably as in the case of hydrogenation,[41] because of the absence of the extra mole of PPh_3. The solution became yellow on stirring the catalyst under CO and H_2 before adding the alkene, consistent with formation of $RhH(CO)_2(PPh_3)_2$ and $[Rh(CO)_2(PPh_3)_2]_2$, and did not show loss of catalytic activity after prolonged equilibration as found[41] in hydrogenation using $[Rh(CO)(PPh_3)_2S]_2$, when conversion to the inactive $[Rh(CO)(PPh_3)_2]_2$, which is not rapidly cleaved by H_2, occurs. The loss of activity observed after either the $RhH(CO)(PPh_3)_3$ or $[Rh(CO)(PPh_3)_2S]_2$

hydroformylation systems has been taken to very low pressures may be associated with some conversion to the inactive species *via* the red dimer which is the major rhodium species at these low pressures.

After a system with any gas mixture $p(H_2) > p(CO)$ has passed through the stages of rapid rise and fall of gas uptake rate the red solution continues to absorb gas at a rate which is faster the greater is the pressure of gas remaining [which depends on the initial $p(H_2)/p(CO)$]. This uptake is probably due to hydrogenation at the very low residual CO pressure.

(d) *Dependence on temperature.* Figure 1.6 shows values obtained in the range 15 - 30°. The dependence is quite regular but since rates in the system are determined by the complex equilibria as well as by kinetic considerations no attempt has been made to derive thermodynamic data or even a rate law.

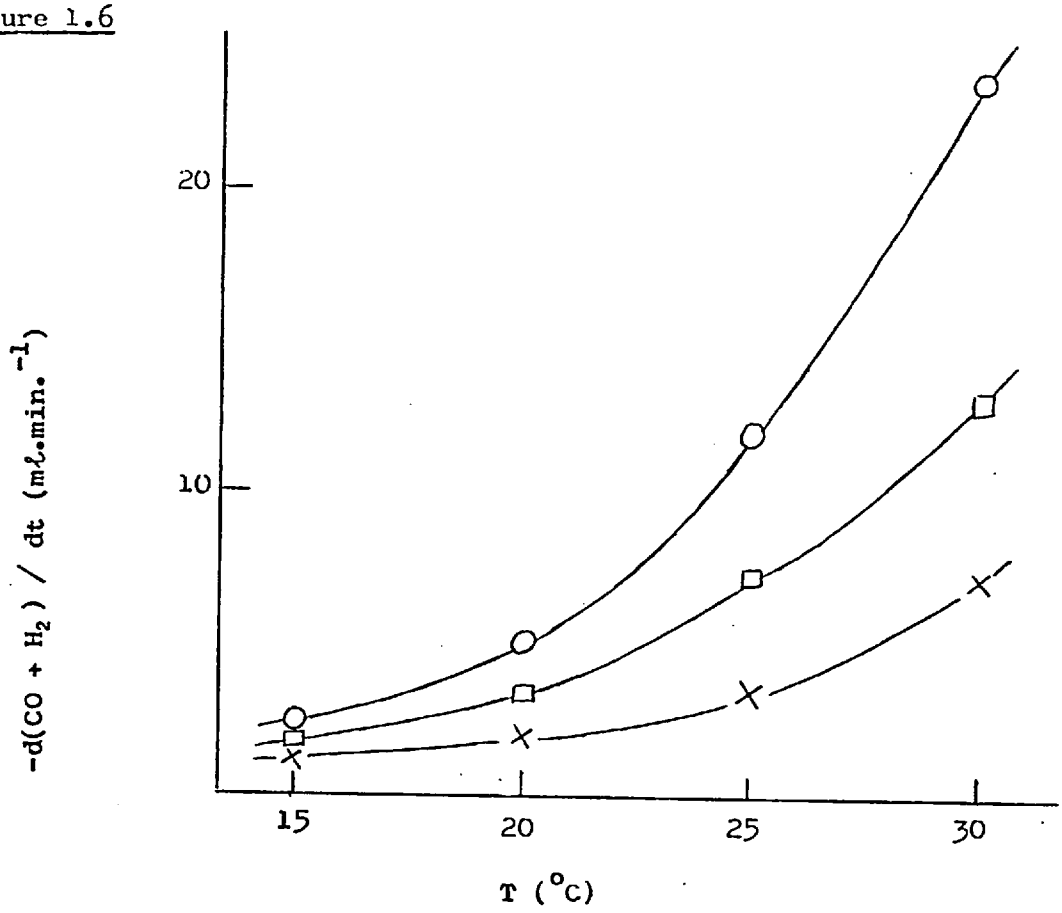
(e) *Effect of addition of excess PPh_3.* This suppresses dissociation of species in the system and for hydrogenation[34] a 2-fold molar excess was shown to decrease the rate by a factor of *ca* 18. The effect on the rate of hydroformylation is much less drastic (Figure 1.7) and this is of importance as the presence of excess PPh_3 has three marked and desirable effects: (i) it increases the ratio of straight- to branched-chain product (p.35), (ii) it effectively cuts down the amount of competing hydrogenation and alkene isomerisation at $CO:H_2$ ratios < 1:1 allowing use of such gas mixtures which are themselves associated with high rates and very high product ratios (pp.27,35), and (iii) it seems to inhibit dimerisation reactions in the system.

(f) *Hydroformylation in product aldehyde as solvent.* This was shown to be possible and for pent-1-ene in freshly purified *n*-hexaldehyde the rate of gas uptake was lower by a factor of 0.6 compared with the rate for reaction in benzene. In view of the large solvent effects observed in high-pressure hydroformylations using *trans*-$RhCl(CO)(PPh_3)_2$[31] a study of other solvent systems would be desirable. $RhH(CO)(PPh_3)_3$, however, has a very limited solubility in more polar solvents at 25°.

C. Products of Hydroformylation Reactions

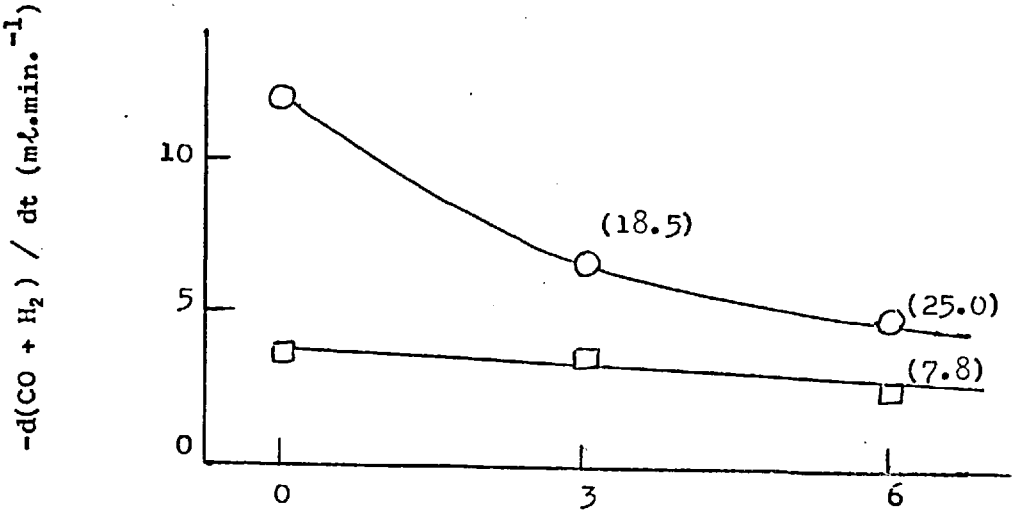
A series of experiments was carried out at 1 atm. total pressure to investigate the effect of conditions on the products of the hydroformylation of hex-1-ene. As found previously[30] no reduction to

Figure 1.6



Rate of hydroformylation of hex-1-ene (1 M) in benzene at 50 cm CO + H_2 pressure (1:1) as a function of temperature with $RhH(CO)(PPh_3)_3$ at O 10 mM, □ 5 mM, and X 2.5 mM.

Figure 1.7



Rate of hydroformylation of hex-1-ene (1 M) in benzene at 25° as a function of added excess of PPh_3 at p(CO) + p(H_2) (1:1) 50 cm. Figures in parentheses give ([n-heptaldehyde]/[2-methylhexaldehyde]) formed.

alcohol (or acetal) was observed. However in the catalytic reaction a certain proportion of n-hexane and cis- and trans-hex-2-enes is found in the products arising from hydrogenation and isomerisation reactions. This proportion is very sensitive to the ratio of $CO:H_2$ in the gas mixture used and becomes very important at ratios less than 1:1. The presence of PPh_3 reduces the importance of these competing reactions.

1. Aldehyde ratios

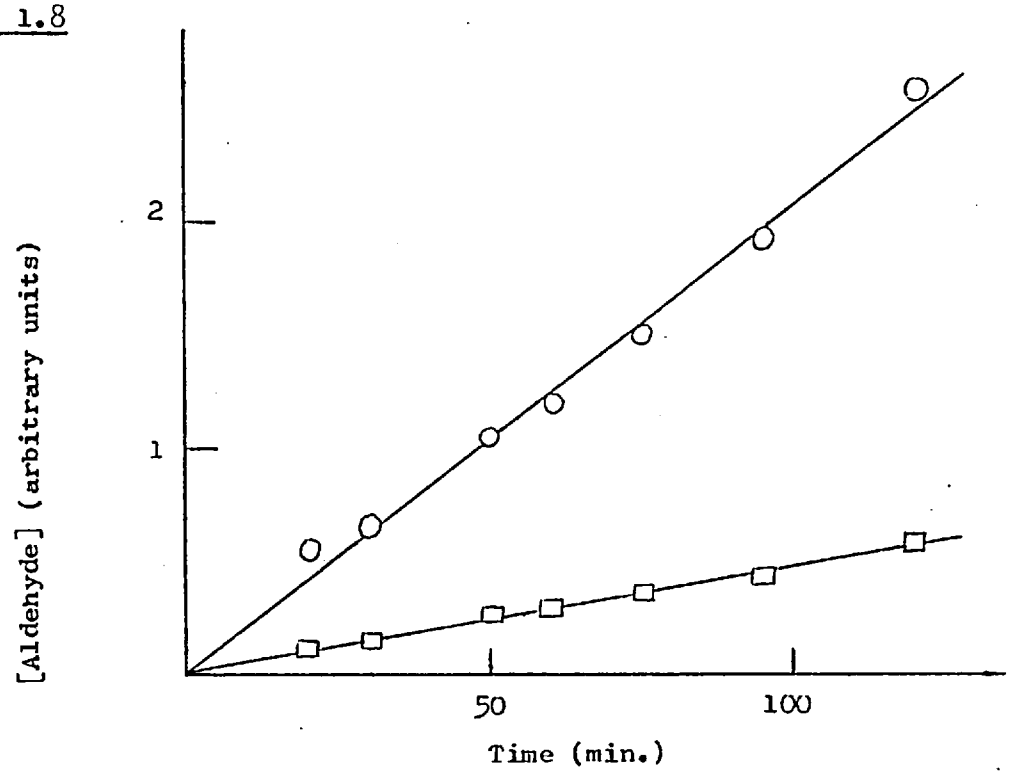
Hydroformylation of alk-1-ene, $RCH=CH_2$, leads to formation of the two isomeric aldehydes RCH_2CH_2CHO and $RCH(CH_3)CHO$ as described above (p. 8). Under the conditions studied the ratio of aldehydes formed in a given catalytic run is fairly insensitive to the percentage of alkene consumed. Figure 1.8 shows the amount of each aldehyde produced, relative to an internal standard, as a function of time under fairly typical conditions. It is also clear from this that the rate is maintained to a high percentage of conversion (> 80% in this case).

(a) Dependence on catalyst concentration. Under conditions at which the rate measurements were made, 2.5 mM catalyst concentration, the ratio of n-heptaldehyde to 2-methylhexaldehyde is ca 3:1 and is only slightly higher at 10 mM. The conditions of the stepwise reaction reported previously[30] to give ratios of ca 20:1 involve solutions 50 mM in catalyst. Under these conditions it was also noted that increasing reaction temperature from 25° to 50° caused a drop in ratio to ca 9:1.

For 1 M hex-1-ene in benzene and $CO + H_2$ (1:1) at a total pressure of 1 atm. the results are shown in Figure 1.9. This shows that increased ratios are to be obtained with higher catalyst concentration, which also means necessarily an increase in the concentration of free PPh_3. The effect is thus attributed to suppression of dissociation, an associative mechanism being expected to lead to preferred formation of the linear alkyl initially because of the larger steric interaction of the incoming alkene with two bulky PPh_3 groups.

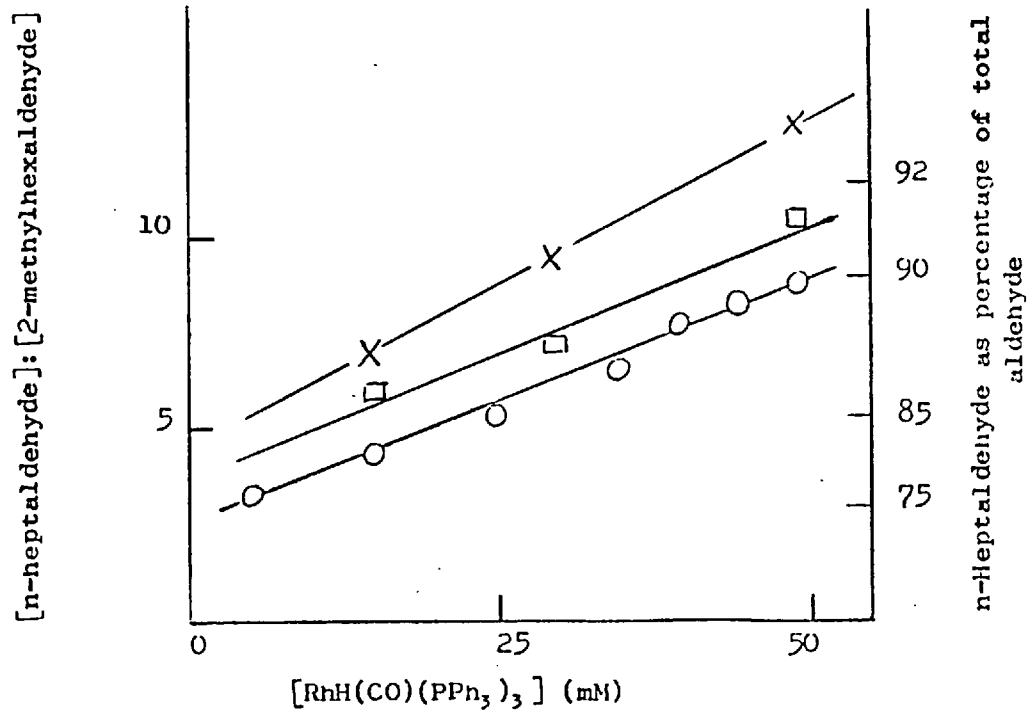
The observed temperature effect is small, but in the opposite sense to that noted previously. The same trend has, however, been found under a variety of conditions, e.g. in presence of a 3-fold excess of PPh_3 (at 30 mM catalyst, 1:1 gas mixture the ratio is 12.1:1 at 25°; 16.8:1 at 40°); with different gas mixtures (at 30 mM catalyst, $CO:H_2$ 0.8:1 the ratio is 10.5:1 at 25°; 19.5:1 at 40°).

Figure 1.8



Rate of formation of aldehydes from hex-1-ene (1 M) in benzene at 25° with $[RhH(CO)(PPh_3)_3]$ at 15 mM and CO + H_2 (1:1) at total pressure of 1 atm. Product ratio is 4.41:1 ○ n-heptaldehyde; □ 2-methylhexaldehyde.

Figure 1.9



Ratio([n-heptaldehyde]:[2-methylhexaldehyde]) formed from hydroformylation of hex-1-ene (1 M) in benzene under CO + H_2 (1:1) at a total pressure of 1 atm., as a function of $RhH(CO)(PPh_3)_3$ concentration: ○ 25°, □ 40°, X 50°.

At high catalyst concentrations precipitation of $[Rh(CO)_2(PPh_3)_2]_2$ occurs from the benzene-aldehyde mixtures rapidly formed, especially when CO-rich gas mixtures are used. For concentrations above 40 mM at 25° under a 1:1 gas mixture the yellow dimer begins to precipitate in ca 15 min. At higher temperatures, however, and with gas mixtures rich in H_2 there is no precipitation even with 50 mM solutions and complete conversion of alkene.

(b) Presence of excess PPh_3 This increases the product ratio at the expense of the rate as noted above. Thus at 1 atm., 25° for 30 mM catalyst and a 1:1 gas mixture, a 3-fold excess of PPh_3 increases the ratio from 6.4:1 to 9.0:1 and a 6-fold excess raises this to 10.5:1. It will be observed that these are not as high as found in solutions after measuring gas uptake for 10 mM catalyst solutions in the presence of PPh_3. (Figure 1.7). This is discussed below (p. 36).

The colour of solutions is bright lemon-yellow in presence of PPh_3 and shows no tendency to become red when agitation is stopped, even at high catalyst concentration.

(c) Dependence on partial pressures of CO and H_2. (i) The use of CO rich mixtures ($CO:H_2$ 2:1) causes reduction both in reaction rate and product ratio (Table 1.4). The colours of such solutions are very bright yellow and $[Rh(CO)_2(PPh_3)_2]_2$ is rapidly precipitated at higher concentrations. The solutions again show no tendency to become red when agitation is stopped. (ii) Use of 1:2 $CO:H_2$ gas mixtures give aldehyde ratios in excess of 26:1 even for 15 mM catalyst at 25°. The reaction is very fast but hydrogenation and isomerisation are serious competitors.

Table 1.4. Ratio of n-heptaldehyde to 2-methylhexaldehyde formed by hydroformylation of hex-1-ene (1.0 M) in benzene under different gas mixtures at 1 atm.

$[RhH(CO)(PPh_3)_3]$ m.mole. l^{-1}	Temperature	Product ratio under $CO:H_2$ ratios 2:1	1:1	0.5:1
15	25°	4.4:1	4.3:1	> 26:1
30	25°	5.6:1	6.5:1	
50	25°	6.4:1	8.6:1	
15	40°	4.4:1	6.0:1	
30	40°	5.6:1	7.1:1	
50	40°	7.0:1	10.5:1	

(iii) There is also an effect of total pressure on the ratios which accounts for the fact that product ratios in solutions hydroformylated on the gas uptake apparatus, where reaction occurs at pressures decreasing from ca 60 cm, are higher than those measured from 1 atm. reactions (cf. presence of excess PPh_3 (b) above, and Figure 1.7). In order to check this effect parallel experiments were carried out at 1 atm. using a 1:1 $CO:H_2$ gas mixture and a 1:1:1 $CO:H_2:N_2$ gas mixture. These showed that for 30 mM catalyst concentration, 1 M hex-1-ene at 25° there was a loss in rate of ca 12% caused by dilution with N_2 but a corresponding increase in aldehyde ratio from 6.5:1 (87% straight-chain) to 20.1:1 (95% straight-chain).

2. Products arising from competing reactions

Hydrogenation and isomerisation of the alkene compete with hydroformylation in the catalytic system. At 25° using 1:1 gas mixtures they account for 1 - 4% of the products and for lower $CO:H_2$ ratios they dominate the system. Cis- and trans-hex-2-enes are formed in approximately equal amounts under most conditions used. Addition of excess PPh_3 suppresses the rates of hydroformylation, hydrogenation and isomerisation but the last two are strongly suppressed as indicated by previous studies.[34,35] The results are summarised in Table 1.5.

Table 1.5 Reaction products from hydroformylation of hex-1-ene (1.0 M) in benzene by 30 mM- $RhH(CO)(PPh_3)_3$ under various conditions at 1 atm.

Mole excess PPh_3	Temp.	$CO:H_2$	n-Heptaldehyde as % of total aldehyde	% products of hydrogenation and isomerisation	Alk-2-enes / Alkane
-	25°	1.0:1	86	1 - 4	ca 10-20
-	40°	1.0:1	88	1 - 4	ca 10-20
3	25°	1.0:1	92	< 4	ca 20
3	40°	1.0:1	93	ca 4	ca 20
-	25°	0.8:1	91	10	ca 4
-	40°	0.8:1	95	22	ca 4
-	40°	0.5:1	97	60	ca 2
3	40°	0.5:1	98.5	31	ca 2

D. Hydroformylation of Styrene

To aid the study of the factors influencing product ratios hydroformylation of styrene was investigated as n.m.r. can be used to determine acyls and product aldehydes and the system is simplified in the absence of isomerisation.

When styrene is added to a benzene solution of $RhH(CO)(PPh_3)_3$ under N_2 there is no apparent reaction and alkyls cannot be detected by n.m.r. When CO is bubbled through the solution for a few seconds the colour becomes lighter and the high-field resonance of $RhH(CO)(PPh_3)_2$ disappears. If CO is then allowed to escape from the gas phase above the solution the colour becomes red and traces of aldehyde are observed. This is presumably due to disproportionation of acyls formed to give the red dimer, $[Rh(CO)(PPh_3)_2S]_2$ in a similar way to reactions noted above for hex-1-ene (p. 30). Thus addition of $RhH(CO)(PPh_3)_3$ to a solution of styrene in benzene under 1 atm. of CO showed rapid conversion to a mixture of $[Rh(CO)_2(PPh_3)_2]_2$ and acyl species (i.r. band at 1645 cm^{-1}; the terminal CO stretches overlap), to which can be assigned the formula $Rh(COR)(CO)_2(PPh_3)_2$ by comparison with the analogous rhodium and iridium propionyl derivatives described in Chapter III. N.m.r. showed that the species present contain the groupings $RhCOCH_2CH_2Ph$ [τ 6.75, 7.47 (triplets); J = 8.0 Hz] and small amounts of $RhCOCHPhCH_3$ [τ 8.94 (doublet); J = 7.5 Hz; the quartet is hidden at τ *ca* 6.7 by the low-field triplet of the more abundant linear acyl].

A series of catalytic runs were made at 1 atm. as for hex-1-ene using 1 M styrene in benzene with sampling for n.m.r. The product aldehydes give conveniently separated resonances.

$PhCH_2CH_2CHO$	τ 7.45, 7.94 (triplets), J = 8.0 Hz
$PhCHCHO$ $\quad\quad\vert$ $\quad CH_3$	τ 6.98 (quartet), 8.90 (doublet), J = 7.5 Hz

Relative amounts of each were estimated by averaging several runs to give the ratio of straight- to branched-chain aldehyde reproducible to within *ca* 20%. Estimation of the percentage conversion was achieved to similar accuracy by integration of the highest-field proton of styrene.

Estimations in the presence of ethylbenzene, which partially overlaps the β-proton resonance of the branched- and the α-proton resonance of the straight-chain aldehyde, are slightly less good. The results are shown in Table 1.6.

Table 1.6. Products from hydroformylation of styrene (1.0 M) in benzene at 1 atm. and 25°

$[RhH(CO)(PPh_3)_3]$ m.mole l^{-1}	Mole excess PPh_3	$CO:H_2$	% Conversion of styrene in 30 min.	Straight/branched chain aldehyde[a]	ethylbenzene/aldehyde[a]
15	-	1.0:1	15	0.11:1	b
50	-	1.0:1	25	0.13:1	b
50	20	1.0:1	< 5	0.27:1	b
15	-	0.5:1	43	0.50:1	0.48:1
50	-	0.5:1	65	0.58:1	0.50:1
15	3	0.5:1	15	0.24:1	b
50	6	0.5:1	12	0.45:1	b

a Average of samples taken over 2 hr reaction

b < 0.05:1

Under conditions relatively unspecific for hex-1-ene the ratio of straight- to branched-chain aldehydes was 0.11:1 and this is only slightly affected by changes of conditions. Only under conditions in which hex-1-ene gives very high ratios was a significant increase found. Addition of excess PPh_3 allows use of 1:2 $CO:H_2$ gas mixtures without hydrogenation but there is some indication that under these conditions the addition of PPh_3 does not continue to promote linear aldehyde formation. p-Fluorostyrene reacted faster than styrene to give similar product ratios but the maximum obtained was 0.44:1. p-Methoxystyrene reacted more slowly and gave even lower ratios.

Clearly formation of the branched aldehyde is preferred under these conditions although the addition of PPh_3 succeeds in increasing the proportion of linear product. The results, however, show that stoicheiometric reaction and catalytic hydroformylation give quite different products. Thus when styrene acyls are produced, as

described above, the straight-chain isomer is in great abundance (> 70%) and when H_2 is carefully bled into the n.m.r. tube conversion to straight-chain aldehyde occurs with the same predominance. Although the concentration of catalyst was approaching saturation in this case (but not greatly different from 50 mM) it is clear from comparison with Table 1.6 that the direction of initial addition cannot be the only factor determining the products.

The possibility of isomerisation of intermediates[16] occurring via the equilibria:

$$\text{acyl} \rightleftarrows \text{alkyl} \rightleftarrows \text{hydride} + \text{alkene}$$

was noted in the Introduction (p. 9) and such isomerisation at rates comparable with the catalytic reaction could explain the observed results. Thus styrene would be taken to give more rapid Markownikov addition to $RhH(CO)_2(PPh_3)_2$ initially with subsequent isomerisation allowing the acyls to reach their equilibrium proportions in the case of the step-wise reactions. Products in the catalytic hydroformylation would thus depend on the relative rates of isomerisation and oxidative-addition reactions.

Discussion

1. Mechanisms operating

The mechanisms proposed for the hydroformylation of alkenes catalysed by $RhH(CO)(PPh_3)_3$ are summarised on p.13 and have been used as a basis in the description of the new experimental evidence given above. The equilibria relating the species in solution and the rates of intermediate reactions, none of which are known quantitatively, will be sensitive functions of the reaction conditions and, in the absence of the possibility of direct measurements of these, information regarding the mechanism must be deduced from indirect evidence.

Three hydrido species seem to be present in solution under the catalytic conditions. These are expected[30] on the basis of steric interactions to show increasing selectivity with respect to substrate and specificity with respect to linear alkyl formation in the order $RhH(CO)_2(PPh_3) < RhH(CO)_2(PPh_3)_2 < RhH(CO)(PPh_3)_2$. It appears from

rate measurements (Figure 1.1) that $RhH(CO)_2(PPh_3)$ is probably the main active species at concentrations below ca 6 mM (dissociative mechanism), while above this concentration $RhH(CO)_2(PPh_3)_2$ dominates the reaction (associative mechanism). It has been found, however, that both the substrate and product specificity increase markedly with catalyst concentration and, although the ratio of rates of reaction for alk-1-ene and alk-2-ene at 40 mM (85:1) is still much smaller than that found in the hydrogenation reaction[34] at 0.5 mM (> 200:1), it seems likely that $RhH(CO)(PPh_3)_2$ cannot be excluded as a species contributing to the formation of aldehyde under these conditions. This is in agreement with the fact that it is present in substantial concentration in solutions of $RhH(CO)(PPh_3)_3$ under 1 atm. of $CO + H_2$ in the absence of alkene, and that high straight- to branched-chain aldehyde ratios are found with $CO:H_2 < 1:1$. Isomerisation and hydrogenation occurring simultaneously with hydroformylation probably also occur via this species.

2. Difference between stoicheiometric and catalytic hydroformylation

The results on hydroformylation of styrene show that when dicarbonyl acyls are formed and then treated in situ with H_2 the proportion of linear aldehyde formed is much greater than in the catalytic reaction under CO and H_2. Such a difference is not easily explained if the direction of initial addition of M-H to $RCH=CH_2$ is the only or prime factor determining the nature of the products. This is especially so as, in the step-wise reaction, acyls are formed under 1 atm. CO and thus the proportion of $RhH(CO)_2(PPh_3)_2$ should be greater compared with $RhH(CO)(PPh_3)_2$ than under a 1:1 gas mixture.

The different products could be explained if, following initial alkyl formation, there is an isomerisation of the intermediates at a slower rate than the catalytic reaction as noted above. In the $Co(COR)(CO)_4$ systems[16] steric effects were suggested to account for the resulting increase in the proportion of the less hindered linear acyl. The more bulky PPh_3 groups would doubtless make any such effects greater in the present system.

Such a scheme could also involve the two hydrido species present at higher concentrations, with trans-$RhH(CO)(PPh_3)_2$ providing a route for the formation of predominantly linear alkyls and acyls but at a slower rate than the less specific addition to $RhH(CO)_2(PPh_3)_2$. This

would be consistent with the fact that styrene is hydroformylated relatively rapidly whereas it reacts only slowly in hydrogenation[34] with this catalyst. The product distribution would thus depend on the relative rates of isomerisation and oxidative addition reactions, both probably occurring *via* the square acyl species as in Scheme 1.2.

The steric and electronic factors controlling such equilibria and rates are, of course, very different for hex-1-ene and styrene as exemplified by their relative rates of hydroformylation and hydrogenation[34] and the different product distribution in the former. The possibility of such intermediate isomerisation occurring at rates significant compared with the overall catalysis must, however, be considered. Thus the stepwise hydroformylation[30] by addition of hex-1-ene to $RhH(CO)_2(PPh_3)_2$ and $[Rh(CO)_2(PPh_3)_2]_2$ followed by treatment with H_2 yielded higher straight- to branched-chain ratios than catalytic hydroformylation under CO and H_2 in similar conditions.

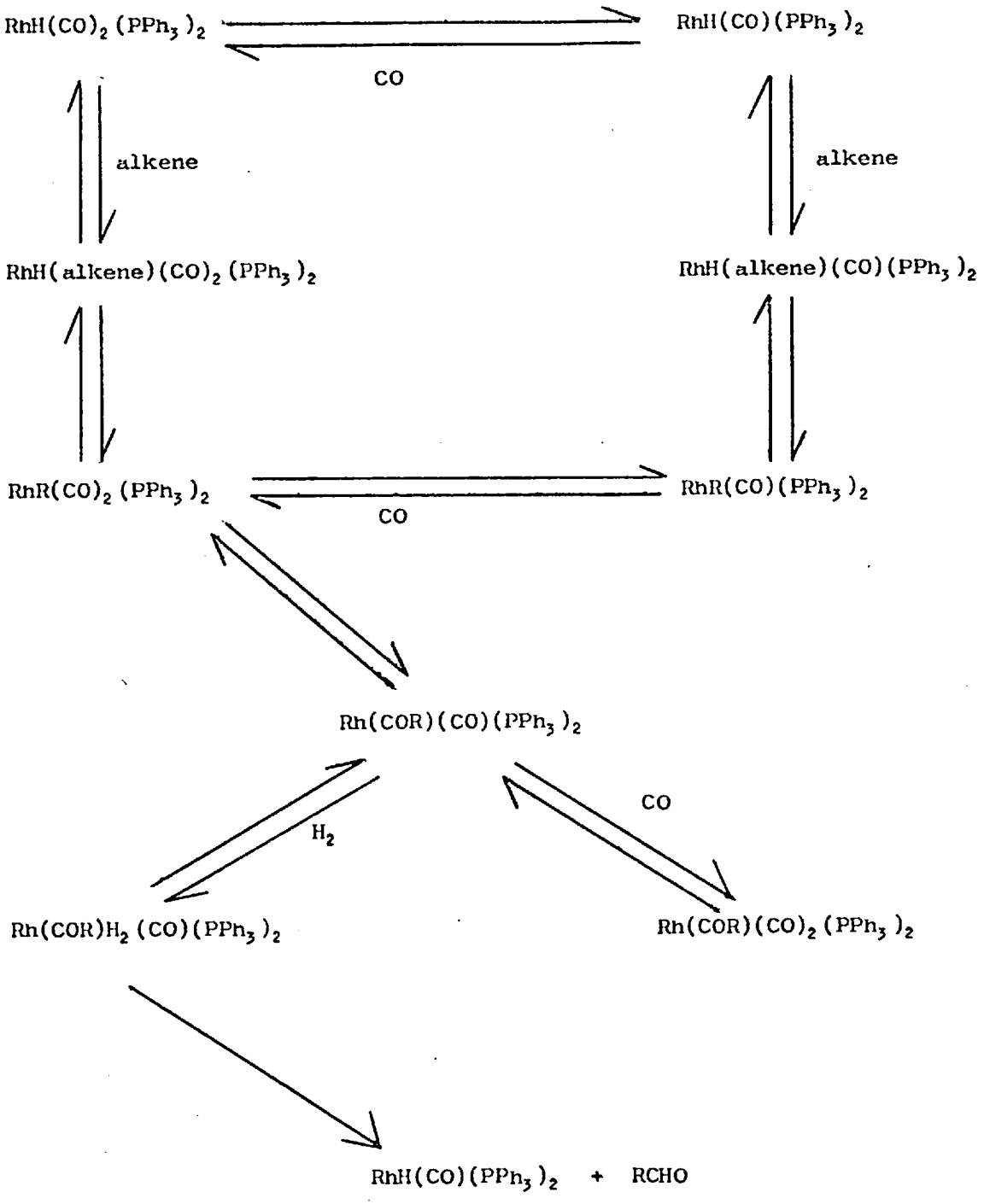
3. Effect of temperature

The formation of higher yields of linear aldehydes with increasing temperature has also been attributed to such isomerisation in cobalt systems[16] and the results found in the low-pressure hydroformylation of hex-1-ene (Figure 1.9) may be interpreted similarly. Hydroformylation of styrene at 50°, however, did not give a significant increase in the proportion of linear product. It is also possible that the trend observed in Figure 1.9 could be attributed to an increased proportion of alkene addition to *trans* $RhH(CO)(PPh_3)_2$ formed by dissociation of CO as the temperature is increased. The reverse dependence of product ratio on temperature is observed at higher pressures (see Chapter II).

4. Effect of gas ratios

The high straight- to branched-chain product ratios (> 26:1) found in rapid hydroformylation using 1:2 $CO:H_2$ mixture at 1 atm. may be similarly related to promotion of isomerisation by the effect of low CO pressure on the equilibria or to more initial addition of alkene to *trans* $RhH(CO)(PPh_3)_2$. Which of these is more important will depend on the proportions of $RhH(CO)(PPh_3)_2$ and $RhH(CO)_2(PPh_3)_2$ and their relative rates of alkene addition. It will also depend on the rate of CO addition to $RhR(CO)(PPh_3)_2$ to give acyls as compared with addition of H_2 or reversal of the addition causing hydrogenation

Scheme 1.2


RhH(CO)2(PPh3)2
RhH(CO)(PPh3)2
CO
alkene
alkene
RhH(alkene)(CO)2(PPh3)2
RhH(alkene)(CO)(PPh3)2
RhR(CO)2(PPh3)2
RhR(CO)(PPh3)2
CO
Rh(COR)(CO)(PPh3)2
H2
CO
Rh(COR)H2(CO)(PPh3)2
Rh(COR)(CO)2(PPh3)2
RhH(CO)(PPh3)2 + RCHO

or, potentially, isomerisation. Under such conditions a large proportion of the products arises from the latter reactions. In the absence of alkene, even under a 1:6 $CO:H_2$ atmosphere, the dicarbonyl hydride is found spectroscopically to be in high concentration.

5. Inhibition

The hydroformylation reaction is strongly inhibited by CO under the conditions studied, although CO is required to suppress hydrogenation and isomerisation. Such inhibition due to the formation of $Rh(COR)(CO)_2(PPh_3)_2$ species, which may be inactive towards oxidative addition of H_2, was anticipated[30] and will be discussed in Chapter III.

6. Effect of PPh_3

As noted in the Introduction much work has been devoted to improving yields of linear aldehydes and alcohols by addition of tertiary phosphine ligands to cobalt and rhodium catalysts.[20,22,28,30,31] The factors which can influence the proportion of linear products and which may be affected by the presence of such ligands are (i) Markownikov *vs* anti-Markownikov addition of M-H to $RCH=CH_2$; (ii) alkene isomerisation and subsequent hydroformylation of $RCH=CHR'$; and (iii) isomerisation of intermediates. These have been discussed on pp 9,10,11.

In the case of $RhH(CO)(PPh_3)_3$ the effect of PPh_3 dissociation on reaction specificity can be observed under mild conditions. Thus the change from the dissociative to the associative mechanism is reflected in both rate and product distribution while there is evidence at concentrations below 1 mM of tricarbonyl-mono-phosphine species and at high concentrations $RhH(CO)(PPh_3)_2$ is probably also involved in the reaction.

The much smaller inhibiting effect of excess PPh_3 on hydroformylation as compared with hydrogenation may be attributed to the ability of the 5-coordinate $RhH(CO)_2(PPh_3)_2$ to react with alkene more rapidly than the 5-coordinate $RhH(CO)(PPh_3)_3$ under mild conditions.

CHAPTER II

Hydroformylation at Higher Pressures

Introduction

The use of trans-$RhCl(CO)(PPh_3)_2$ as a catalyst for hydroformylation at ca 500 lb in^{-2} and 100 - 150° has been noted in the Introduction, and the report of this work[31] notes that the exceptional stability of this catalyst allowed product distillation and catalyst re-use without loss of activity. The addition of Et_3N to similar reactions[30] with trans-$RhCl(CO)(PPh_3)_2$, which confirmed that hydrogenolysis occurs to give HCl and an hydridorhodium species under hydroformylation conditions, also revealed that the removal of Cl^- from the system (as Et_3NHCl) destroyed this stability and resulted in an extremely air-sensitive solution, probably because trans-$RhH(CO)(PPh_3)_2$ is very reactive in the absence of excess stabilising ligand (cf ref.41). Thus addition of PPh_3 allowed the stable $RhH(CO)(PPh_3)_3$ to be collected after hydroformylation.

The use of $RhH(CO)(PPh_3)_3$ for hydroformylation of hex-1-ene in benzene at 70° and 1200 lb in^{-2} CO + H_2 (1:1) was found[30] to give rapid hydroformylation but low straight- to branched-chain product ratios (< 3:1).

In the present work it has been found that using 1:1 CO + H_2 at 400 lb in^{-2} and 25° the straight- to branched-chain product ratio from hydroformylation of hex-1-ene is 2.9:1 for a 15 mM solution of $RhH(CO)(PPh_3)_3$ in benzene compared with 4.3:1 at 1 atm, and at 45° the ratio is even lower at 2.4:1. Under a 1:2 CO + H_2 mixture at 400 lb in^{-2} and 25° the ratio is 4.0:1 but competing hydrogenation and isomerisation reactions are serious.

The use of excess PPh_3 to control the reaction selectivity has been described[31] for the trans-$RhCl(CO)(PPh_3)_2$ system, where up to 50-fold molar excesses were used to give 76% straight-chain aldehyde product in hydroformylation of hex-1-ene in benzene at 500 lb in^{-2} and 100°. The use of excess PPh_3 with a $RhH(CO)(PPh_3)_3$ system at 500 - 700 lb in^{-2} has also been reported[43] to give ca 70% of linear aldehyde from alk-1-enes and long continuous runs of up to 234 hr

have been carried out in a recycle-system with such specificity. In both cases the selectivity to aldehyde products was ca. 99%.

In view of the very marked effect of PPh_3 concentration on the product distribution in the low-pressure system described in Chapter I a series of experiments was carried out to ascertain the degree of control which might be achieved in the catalytic system at higher temperatures and pressures by the use of excess PPh_3.

A. High Concentration Phosphine Systems

At 65° and 400 lb in^{-2} of 1:1 gas mixture, with a 100-fold molar excess of PPh_3, a 10 mM $RhH(CO)(PPh_3)_3$ solution with 1.0 M hex-1-ene in benzene gave 77% conversion in 30 min. with a 4.3:1 product ratio (81% straight-chain) and less than 3% of products arising from hydrogenation and isomerisation reactions. With 1:2 and 1:5 CO + H_2 gas mixtures at constant p(CO), 133 lb in^{-2} product ratios of 5.6:1 (ca 85% straight chain) were achieved with 50-60% conversion in 30 min. at 65°, with hexane and hex-2-enes comprising 4 - 5% of the products. The increase in $p(H_2)$ did not increase the rate markedly. No reduction to alcohol was detected.

At 85 - 90° in molten PPh_3 (100 g) hydroformylation of hex-1-ene (20 ml, 0.16 mole) by $RhH(CO)(PPh_3)_3$ (10^{-3} mole) at 400 lb in^{-2} (1:1 gas mixture) gave 92% conversion in less than 20 min. The aldehyde ratio was 16.0:1 (94% straight-chain) and hex-2-enes and hexane in the ratio of 6:1 accounted for ca 7% of the products. At 110° conversion was complete in 6 - 8 min. with an aldehyde ratio of 6.5:1 (86.7% straight-chain) but ca 25% of the products were due to isomerisation and hydrogenation while traces of 2-ethylpentaldehyde, presumably from hydroformylation of hex-2-enes, were found. The high isomerisation may be caused by incomplete conversion of the catalyst to dicarbonyl species at this pressure of CO since at 110° and 700 lb in^{-2} side products were reduced to 7% with an aldehyde ratio of 10.1:1 (90.9% straight-chain) at complete conversion.

Hydroformylation of propene, in which isomerisation is not a competing reaction, can be achieved in molten PPh_3 to give aldehyde only. Using a 1:1:1 gas mixture of C_3H_6 + CO + H_2, $RhH(CO)(PPh_3)_3$ (10^{-3} mole) in PPh_3 (100 g) (with a small quantity of benzene as an

analytical reference), in the range 110 - 240 lb in^{-2} and 90 - 125°, n-butyraldehyde and iso-butyraldehyde are produced at rates which vary from 0.8 to 7.5 moles per mole catalyst per min. with 94 - 95% of linear product. Analysis of the gas phase by g.l.c. shows that loss of alkene by hydrogenation is only 0.3 - 0.4%. No butanol was detected.

At higher temperatures, 150° or above, with the same range of gas pressures, the product ratio falls to about 6:1 and the rates also decrease. This effect has also been reported[43] in other solvent systems and decomposition of the catalyst seems to be occurring at these temperatures. Thus the residual PPh_3 melt recovered from such reactions is brown rather than the bright-yellow found at lower temperatures.

Although hydroformylation of hex-1-yne and butadiene do not occur at 25° and 1 atm. with $RhH(CO)(PPh_3)_3$ these substrates react readily at higher temperatures and pressures and also in molten PPh_3. Thus at 100° and 700 lb in^{-2} CO + H_2 (1:1) in molten PPh_3 hex-1-yne (substrate:catalyst mole ratio 1400:1) reacted completely in less than 24 hr to give n-heptaldehyde and 2-methylhexaldehyde in the ratio 4.0:1. Together these comprised 96% of the products, some reduction to alcohols having occurred because of the extended reaction time.

Hydroformylation of butadiene with cobalt[44] and rhodium[45] catalysts normally gives only n-pentaldehyde and 2-methylbutyraldehyde and this has been attributed to rapid double-bond migration after the first hydroformylation step to give αβ-unsaturated aldehydes, the double-bonds of which are only hydrogenated.[46] It was suggested[47] that if such double-bond migration can be inhibited two hydroformylation steps should produce dialdehydes. Thus using[47] an 85-fold molar excess of PBu^n_3 as modifier and forming the catalyst *in situ* from Rh_2O_3 at 125° and *ca* 300 atm. in diethyl ether the products comprised 58% C_5-monoaldehydes (96% straight-chain) and 42% C_6-dialdehydes (2-methylpentan-1,5-dial, 2-ethylbutan-1,4-dial and hexan-1,6-dial in the ratio 6.4:3.2:1.0).

In molten PPh_3 (100 g) with $RhH(CO)(PPh_3)_3$ (10^{-3} mole) at 120° and 700 lb in^{-2} CO + H_2 (1:1) the mono-aldehyde fraction (91% straight-chain) was found to comprise 70% of the products, the remainder being

higher-boiling materials which were not individually identified. Thus, although isomerisation of hex-1-ene during hydroformylation is largely inhibited under these conditions, the selectivity to formation of dialdehydes from butadiene is not very greatly enhanced. The high proportion of linear product is, however, maintained. The hydroformylation of butadiene is discussed further in Chapter IV where a possible interpretation of these results in terms of π-allylic intermediates rather than double-bond migration is suggested.

It was not possible to study the reaction spectroscopically under the high-temperature and high-pressure conditions described above but the following observations are relevant:-

(i) N.m.r. spectra of $RhH(CO)(PPh_3)_3$ in molten PPh_3 at 90° show a single high-field line of half-width ca 2 Hz at τ 19.17, indicating rapid ligand exchange.

(ii) I.r. spectra in PPh_3 melts over the temperature range 80 - 160° show that $RhH(CO)(PPh_3)_3$ is stable up to ca 150°. Unfortunately the CO stretching region is substantially obscured by PPh_3 bands in the melt, but the Rh-H stretching frequency at 2010 cm^{-1} is lost at this temperature and a new band at 1965 cm^{-1}, as a shoulder on a PPh_3 band, is formed. This may possibly be associated with the decomposition product $[Rh(CO)(PPh_3)_2]_2$, which is formed[41] in solution (Scheme 1.1). No reaction was observed between $RhH(CO)(PPh_3)_3$ and CO at 1 atm. in such melts.

(iii) Under similar conditions to those described above for hydroformylation of hex-1-ene at 110°, but under N_2, 40% isomerisation to cis- and trans-hex-2-enes was found after 1 hr.

B. Relation to Other Catalyst Systems

Although $RhH(CO)(PPh_3)_3$ was used throughout this study as catalyst for hydroformylation and shows unique activity at low pressure, it has already been noted that at higher pressures the same catalytic system can be generated from trans-$RhCl(CO)(PPh_3)_2$ in the presence of a base and excess PPh_3.[30] The lower activity of $RhCl_3(CO)(PPh_3)_2$ has been attributed[29,30] to the effect of HCl, formed in reduction of the complex under hydroformylation conditions, on the equilibria relating

chloro- and hydrido-rhodium(I) species (see p. 12). In the use of rhodium(III) complexes of the type $RhHCl_2(CO)(PPh_3)_2$ [48] this inhibition should be relatively smaller.

Other rhodium(I) complexes which have been used as hydroformylation catalysts such as $[RhCl(CO)_2]_2$ [30,31,49], bridged carboxylates[24b,50], e.g. $[Rh(OCOCH_3)(CO)_2]_2$ or β-diketonates[51], e.g. $Rh(acac)(CO)_2$ may also be converted to hydrido species under hydroformylation conditions and in the presence of PPh_3 to a catalytic system essentially the same as that formed with $RhH(CO)(PPh_3)_3$. Thus $Rh(acac)(CO)_2$, when treated at 100 atm. with CO + H_2 (1:1) at 40° in benzene, gives free acetylacetone (detected by g.l.c. and i.r.) together with the binary carbonyls $Rh_3(CO)_{12}$ and $Rh_6(CO)_{16}$ [52]. In the presence of alk-1-ene or cyclohexene (alkene:catalyst 25:1) complete hydroformylation occurred in less than 12 hr but under these conditions the system is very unspecific and hex-1-ene gave n-heptaldehyde, 2-methylhexaldehyde and 2-ethylpentaldehyde in the ratio 2.1:1.8:1.0. In the presence of excess PPh_3, however, $Rh(acac)(CO)_2$ is converted quantitatively to $RhH(CO)(PPh_3)_3$ by CO + H_2 (1:1) at 700 lb in^{-2} and 60° and when used in molten PPh_3 as a catalyst for hydroformylation $Rh(acac)(CO)_2$ gave the same product distribution as found with $RhH(CO)(PPh_3)_3$. A lower conversion rate in hydroformylation of hex-1-ene [at 110° and 700 lb in^{-1}, 80% in *ca* 45 min. as compared with < 5 min. using $RhH(CO)(PPh_3)_3$] was found. This may be due to an induction period for conversion of the acetylacetonate to the hydride by analogy with the induction period found[30] when *trans*-$RhCl(CO)(PPh_3)_2$ is used.

Discussion

The lowered rates resulting from the use of very large excesses of PPh_3 can be offset by the use of increased temperature and gas pressures so that high straight- to branched-chain aldehyde ratios can be achieved in rapid catalysis. In the extreme of using molten PPh_3 as the reaction medium competing alkene isomerisation and hydrogenation can be minimised. The catalyst is fairly soluble (*ca* 0.08 g/g at 100°) in molten PPh_3 which has a long liquid range (79 - > 360°).

The rate of alk-1-ene isomerisation in PPh_3 by $RhH(CO)(PPh_3)_3$ under N_2 is much slower than hydroformylation at similar temperatures and the isomerisation occurring in competition is suppressed by increased CO pressure (cf refs. 30 and 31). It thus appears reasonable to suggest that under the conditions described above the main rhodium species which is attacked associatively by alkene is $RhH(CO)_2(PPh_3)_2$.

CHAPTER III

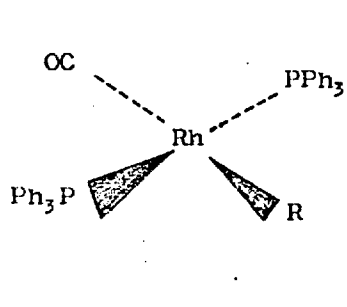
Intermediate Species in Hydroformylation; Rhodium and Iridium Analogues

Introduction

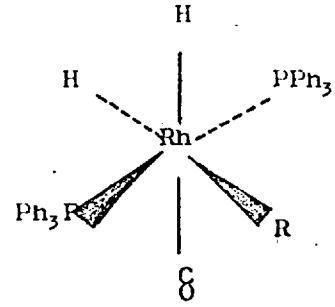
The mechanism proposed[30] for the hydroformylation of alkenes using $RhH(CO)(PPh_3)_3$ as homogeneous catalyst has been briefly summarised on p.13, and in Scheme 1.2. At the beginning of this study the only species directly involved in these mechanistic routes which had been characterised spectroscopically[33] was $RhH(CO)_2(PPh_3)_2$. The iridium analogues, $IrH(CO)(PPh_3)_3$ [32] and $IrH(CO)_2(PPh_3)_2$,[53] had also been prepared and $IrH(CO)_2(PPh_3)_2$ shown[36] to exist in at least two isomeric forms undergoing rapid fluxional transformations in solution.

The intermediate species which were quoted in the Introduction are summarised in Figure 3.1. The hydrogenation,[34] hydrogen atom exchange[30] and isomerisation[35] reactions are thus taken to proceed by way of alkene attack on the square hydride $RhH(CO)(PPh_3)_2$ to give the alkyl (I), the reverse reaction eliminating alkene and regenerating the hydride. At low concentrations, dissociation of PPh_3 to give a formally 3-coordinate species was proposed. If alkene addition to Rh-H is anti-Markownikov the elimination provides the path for only hydrogen atom exchange; Markownikov addition provides an additional pathway for isomerisation (see p.10). Oxidative addition of H_2 to (I) gives (II) from which alkane is eliminated with regeneration of the hydride. In hydroformylation the alkyl(III) is formed by either (a) coordination of alkene to $RhH(CO)_2(PPh_3)_2$ or $RhH(CO)_2(PPh_3)$ followed by hydride transfer (the associative or dissociative mechanisms), or (b) by coordination of CO to (I) (as discussed in Chapter I, p. 40). Alkyl transfer to coordinated CO in (III) leads to the square acyl (IV), or, if excess CO is present, probably also to (V). Oxidative addition of H_2 to (IV) gives (VI) from which aldehyde is eliminated to regenerate $RhH(CO)(PPh_3)_2$. The species (III) and (V) being 5-coordinate may be

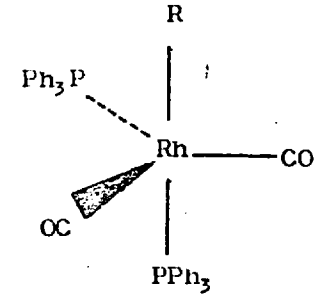
Figure 3.1



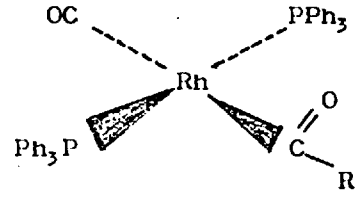
(I)



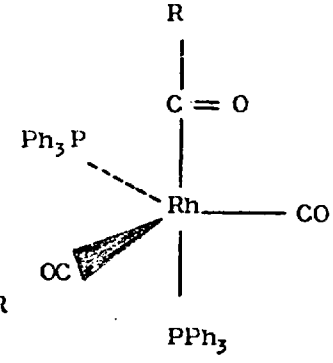
(II)



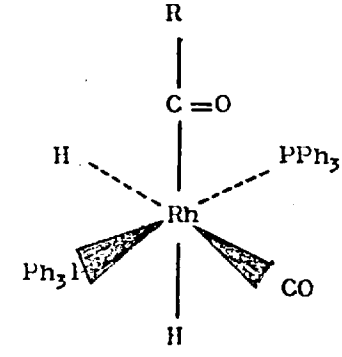
(III)



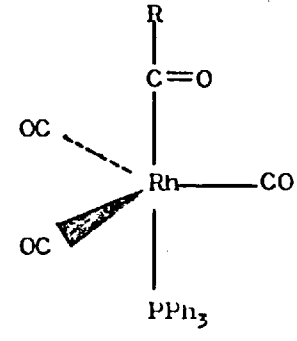
(IV)



(V)



(VI)



(VII)

fluxional and unique designation of the geometry cannot be made, but in the square species the PPh_3 groups are probably trans for reasons connected with the reaction specificity[30,34] (p.13). The possibility of formation of the tricarbonyl species (VII) from (V) by loss of PPh_3 at low concentration has been noted on p.24.

The species where R is a hydrocarbon alkyl are extremely labile with short lifetimes, necessarily so if the reactions are to be catalytic, and the possibility of detecting them in standing concentrations during the hydroformylation is remote. Even in absence of CO and H_2 treatment of $RhH(CO)(PPh_3)_2$ in solution with ethylene under pressure (ca 50 atm) and at low temperatures in an n.m.r. tube failed to reveal[30] a $Rh-C_2H_5$ group. The alkyl species (I) or (III) could, however, probably be stable for rhodium and/or iridium if R is e.g. fluoroalkyl, aryl, neopentyl or benzyl[54] since metal-fluorocarbon bonds are generally much stronger than metal-hydrocarbon bonds, as are metal-aryl bonds which, like neopentyl or benzyl, are further stabilised by their inability to undergo alkene elimination reactions by hydride abtraction from the β-carbon.[55] Benzyl compounds may in addition be stabilised by a π-allylic contribution to the bonding. The formation of relatively stable rhodium acyl species from styrene has been noted above (p. 37).

A. Fluoroalkyl Derivatives

1. Trans-1,1,2,2-tetrafluoroethylcarbonylbis(triphenylphosphine)rhodium(I)

When a solution of $RhH(CO)(PPh_3)_3$ in benzene is treated with tetrafluoroethylene (1 - 5 atm.) the yellow crystalline solid $Rh(C_2F_4H)(CO)(PPh_3)_2$ may be isolated (ν_{CO}, 1990 cm^{-1}). This frequency value, ca 30 cm^{-1} above that of trans-$RhCl(CO)(PPh_3)_2$, is consistent with replacement of Cl by C_2F_4H trans to CO,[56] therefore the compound can reasonably be formulated as trans. Molecular weight determinations indicate extensive dissociation in solution.

$$Rh(C_2F_4H)(CO)(PPh_3)_2 \rightleftarrows Rh(C_2F_4H)(CO)(PPh_3) + PPh_3$$

The ^{19}F and ^1H n.m.r. spectra are typical[56] for $Rh-C_2F_4H$ (Table 3.1), although the F_α resonance is broad and unresolved, probably due to PPh_3 exchange at intermediate rates in the n.m.r. time scale. (Multiplet splitting due to $F_\alpha - F_\beta$, $F_\alpha - H_\beta$, $F_\alpha - P$ and $F_\alpha - Rh$

is expected). On addition of excess PPh_3 both F_α and F_β signals move upfield by ca 20 Hz and the F_α signal is now a broad triplet (J 9.0 Hz). The splitting may be due to an equilibrium shift to the undissociated form with equivalent trans-PPh_3 ligands, or to an increase in the PPh_3 exchange rate to the fast exchange limit allowing a combination of the F_α - H and F_α - Rh couplings to be resolved.

The chemical properties of trans-$Rh(C_2F_4H)(CO)(PPh_3)_2$ are similar to those of trans-$MX(CO)(PPh_3)_2$, where M = Rh or Ir; X = halide,[38,57] except that the latter are not detectably dissociated in solution. Thus the complex undergoes several oxidative addition reactions as well as additions of neutral ligands to give 5-coordinate species. It acts as a moderately active catalyst for hydrogenation of alk-1-enes at 25° and 1 atm. in contrast to the inactivity of the halides under these conditions and this may be attributed to the formation of coordinatively unsaturated species by the dissociation of PPh_3 as noted above. No hydrogen adduct could be detected at 25° and 1 atm, however, in contrast to the extremely efficient catalyst $RhCl(PPh_3)_3$.[42]

Hydrogen chloride reacts instantaneously with the complex in toluene at -70° and a pink complex is formed, which turns pale yellow on standing at -60° for a few minutes. In CH_2Cl_2 the transformation from pink-red to yellow is very rapid even at -75°. The n.m.r. spectra of both pink and yellow solutions at -70° in toluene shows a broad unresolved hydride resonance at ca τ 22.6. Precipitation by chilled petroleum at -70° gives an unstable pale-yellow solid whose i.r. spectrum has bands at 2155 and 2090 cm^{-1}, assigned to ν_{RhH} and ν_{CO} for a Rh(III) species, and a weak band at 1990 cm^{-1} due to traces of starting material. At 25° the solid slowly loses HCl and reverts quantitatively to trans-$Rh(C_2F_4H)(CO)(PPh_3)_2$ as shown by changes in the i.r. spectrum. If the solutions of the Rh(III) - HCl adduct are allowed to warm to 25°, hydride transfer to the fluoroalkyl group to give fluoroalkane occurs rapidly. (Scheme 3.1); 1,1,2,2-tetrafluoroethane was readily identified by ^{19}F and ^1H n.m.r.

spectra[58] and trans-$RhCl(CO)(PPh_3)_2$ by isolation of the solid (ν_{CO} 1960; ν_{RhCl} 308 cm^{-1}).[38] The unstable pink and somewhat more stable pale-yellow species are probably two isomeric forms of $Rh(C_2F_4H)HCl(CO)(PPh_3)_2$ possibly arising from cis- and trans-addition of the HCl. Dissociation and exchange of a PPh_3 ligand to give a 5-coordinate species is also possible and this may account for the unexpected broadness of the n.m.r. resonances.

Direct hydrogenation of the fluoroalkyl complex can be achieved by hydrogen at 80 atm. pressure in presence of excess PPh_3 and $RhH(CO)(PPh_3)_3$ is regenerated; the presence of extra PPh_3 being required to prevent decomposition of the hydride to $[Rh(CO)(PPh_3)_2]_2$[41] (Scheme 1.1).

The fluoroalkyl reacts readily with SO_2 and the adduct is a yellow solid formulated as $Rh(C_2F_4H)(CO)(SO_2)(PPh_3)_2$. This loses SO_2 after standing in vacuum for ca 8 hr, while in solution SO_2 can be swept out by N_2.

2. Reaction of trans-$Rh(C_2F_4H)(CO)(PPh_3)_2$ with CO

Introduction of CO into a solution of the complex causes two consecutive reactions (Scheme 3.1) which can be followed by changes in i.r. and n.m.r. spectra. Small amounts of CO rapidly give complete conversion into a dicarbonyl species which has two strong CO stretches and which can be isolated as a stable white solid, $Rh(C_2F_4H)(CO)_2(PPh_3)_2$. The final product in cyclohexane solution has a weak band at 2075 cm^{-1} and a very strong one at 2020 cm^{-1}. This is consistent with $Rh(C_2F_4H)(CO)_3(PPh_3)$ of C_{3v} symmetry having three equatorial carbonyls, which would give a weak A_1 mode and a very strong E mode. Moreover, a weak ^{13}CO isotopic band is clearly observable ca 10 - 15 cm^{-1} below the 2075 cm^{-1} band as would be expected for isotopic substitution at the natural abundance level for a totally symmetric vibration involving three CO groups. (The intensity of the satellite should be ca 0.03 that of the main peak). This complex could not be isolated pure even under high pressures of CO and its identification is only spectroscopic. However, it may also be noted that the frequencies of the di- and tri-carbonyl species are very similar to those reported[53b] for the compounds

$Ir(SnMe_3)(CO)_2(PPh_3)_2$ (1930 and 1975 cm^{-1}) and

$Ir(SnMe_3)(CO)_3(PPh_3)$ (1950 vs and 2010 w cm^{-1}).

The carbonylation reactions are reversed on passing N_2 or H_2 through the solution; the latter appears to be much more effective suggesting the possible role of a transient hydride intermediate.

On treating $Rh(C_2F_4H)(CO)(PPh_3)_2$ with CO + H_2 (1:1) at 1 atm. an equilibrium mixture of di- and tri-carbonyl species is formed. The carbonylation in presence of excess PPh_3 is very much slower and the abundance of the tri-carbonyl species is greatly reduced by displacement of the equilibria towards bis-phosphine species.

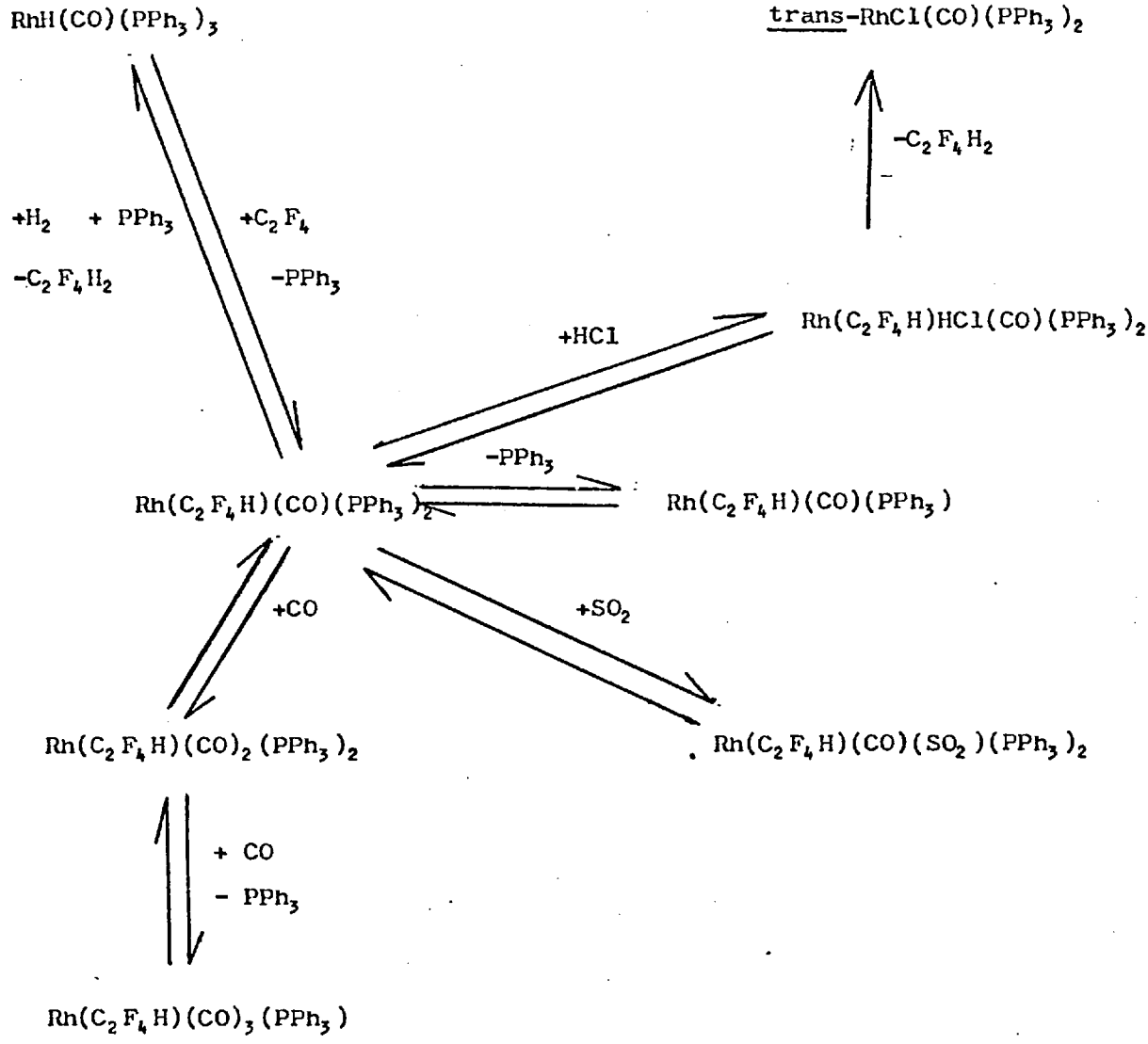
The n.m.r. spectra of the solutions during the addition of CO show a complete absence of ^{19}F signals at the dicarbonyl stage. This suggests that the spectrum is completely collapsed owing to an exchange mechanism taking place at an intermediate rate. The 5-coordinate dicarbonyl could be showing fluxional behaviour[36] or alternatively PPh_3 exchange could be occurring at a critical rate. The apparent molecular weight indicates that appreciable dissociation is occurring to give $Rh(C_2F_4H)(CO)_2(PPh_3)$. On conversion to the tricarbonyl the ^{19}F resonances reappear although at lower fields than the multiplets of $Rh(C_2F_4H)(CO)(PPh_3)_2$. When the conversion is only partial the signals are broader and are shifted to higher fields than in the final stage. It is probable that the resonances of the dicarbonyl intermediate are located between those of the mono- and tricarbonyls, and that intermolecular exchange is taking place between the species that are in equilibrium at each particular stage of this reaction.[59]

B. Reactions of $MH(CO)(PPh_3)_3$, M = Rh or Ir, with Ethylene and Carbon Monoxide

1. Rhodium System

The reaction of $RhH(CO)(PPh_3)_3$ with styrene in the presence of CO to give acyl species has been described above (p.37). An excess of liquid alk-1-ene, such as hex-1-ene, reacts in a similar way and in this case formation of the yellow dimer, $[Rh(CO)_2(PPh_3)_2]_2$ can be more easily avoided. The i.r. spectrum of a benzene solution shows

Scheme 3.1


RhH(CO)(PPh3)3
trans-RhCl(CO)(PPh3)2
-C2F4H2
+H2 + PPh3
-C2F4H2
+C2F4
-PPh3
+HCl
Rh(C2F4H)HCl(CO)(PPh3)2
-PPh3
Rh(C2F4H)(CO)(PPh3)2
Rh(C2F4H)(CO)(PPh3)
+CO
+SO2
Rh(C2F4H)(CO)2(PPh3)2
Rh(C2F4H)(CO)(SO2)(PPh3)2
+ CO
- PPh3
Rh(C2F4H)(CO)3(PPh3)

that a new species is rapidly formed which has two terminal carbonyl stretches at 1900 - 2000 cm^{-1} and an acyl band at 1620 - 1660 cm^{-1}. For more detailed study ethylene has been used as this simplifies the spectra for n.m.r. study. The acyl band in the solution i.r. spectra is generally broad and in some cases split into two separate peaks possibly due to rotational isomerism of the acyl group (in the case of the propionyl compound a shoulder is observed at 1650 cm^{-1} on the band at 1643 cm^{-1}). These peaks show a constant intensity ratio under a wide range of CO and C_2H_4 atmospheres and in the presence of excess PPh_3, and are therefore not due to different species.

The n.m.r. spectrum of a benzene solution of $RhH(CO)(PPh_3)_3$ under an equilibrium pressure of CO + C_2H_4 of ca 50 and 20 cm Hg respectively, shows a triplet and a quartet at τ 9.26 and 7.07 (ratio 3:2; J 7.5 Hz), characteristic of a propionyl group bound to rhodium(I) [cf $RhCOCH_2CH_2Ph$ and $RhCOCHPhCH_3$ groups, p.37]. The assignment of this compound as $Rh(COEt)(CO)_2(PPh_3)_2$ is confirmed by analogy with the stable iridium analogue described below.

The propionyl is stable in solution under an atmosphere of CO and C_2H_4 over a wide range of composition, but on evacuation or on sweeping with inert gas, C_2H_4 is readily eliminated and the yellow dimer, $[Rh(CO)_2(PPh_3)_2]_2$ is formed with loss of H_2; if the CO removal is carried too far $[Rh(CO)(PPh_3)_2S]_2$ is obtained. These reactions are similar to those described in Chapter I for the intermediates in hydroformylation reactions on evacuation of the gas phase or on cessation of stirring. At low CO pressures the propionyl can be stabilised by a high pressure (1 atm.) of C_2H_4 above the solution and, on addition of light petroleum to a toluene solution at - 10°, a very unstable solid is precipitated. This has an i.r. spectrum similar to that of the solution (Table 3.1). The solid decomposes rapidly on standing, losing C_2H_4 and CO to give a product with ν_{CO} 1960 cm^{-1}, presumably $[Rh(CO)(PPh_3)_2]_2$.[41] The dicarbonylpropionyl species may also be formed readily in solution even in presence of a 6-fold molar excess of PPh_3. It is readily shown that on addition of H_2 the propionyl reacts quantitatively to give propionaldehyde and $RhH(CO)(PPh_3)_2$; with gaseous HCl it reacts similarly to give aldehyde and trans-$RhCl(CO)(PPh_3)_2$ (Scheme 3.2).

This reaction of the propionyl with H_2 or HCl to give aldehyde is inhibited when the partial pressure of CO exceeds about 50 cm in the system at 1 atm. Thus under a CO + HCl (1:1) mixture there is no reaction even during 24 hr, but if the HCl pressure is increased to 1 atm the half-time for the aldehyde formation reaction is ca 5 min. With CO + H_2 (2:1) the propionyl is ca 50% converted in ca 1 hr whereas with CO + H_2 (1:2) the half-time is 5 min. This result is clearly of importance in understanding the inhibition of the catalytic hydroformylation reaction by CO. (p. 27).

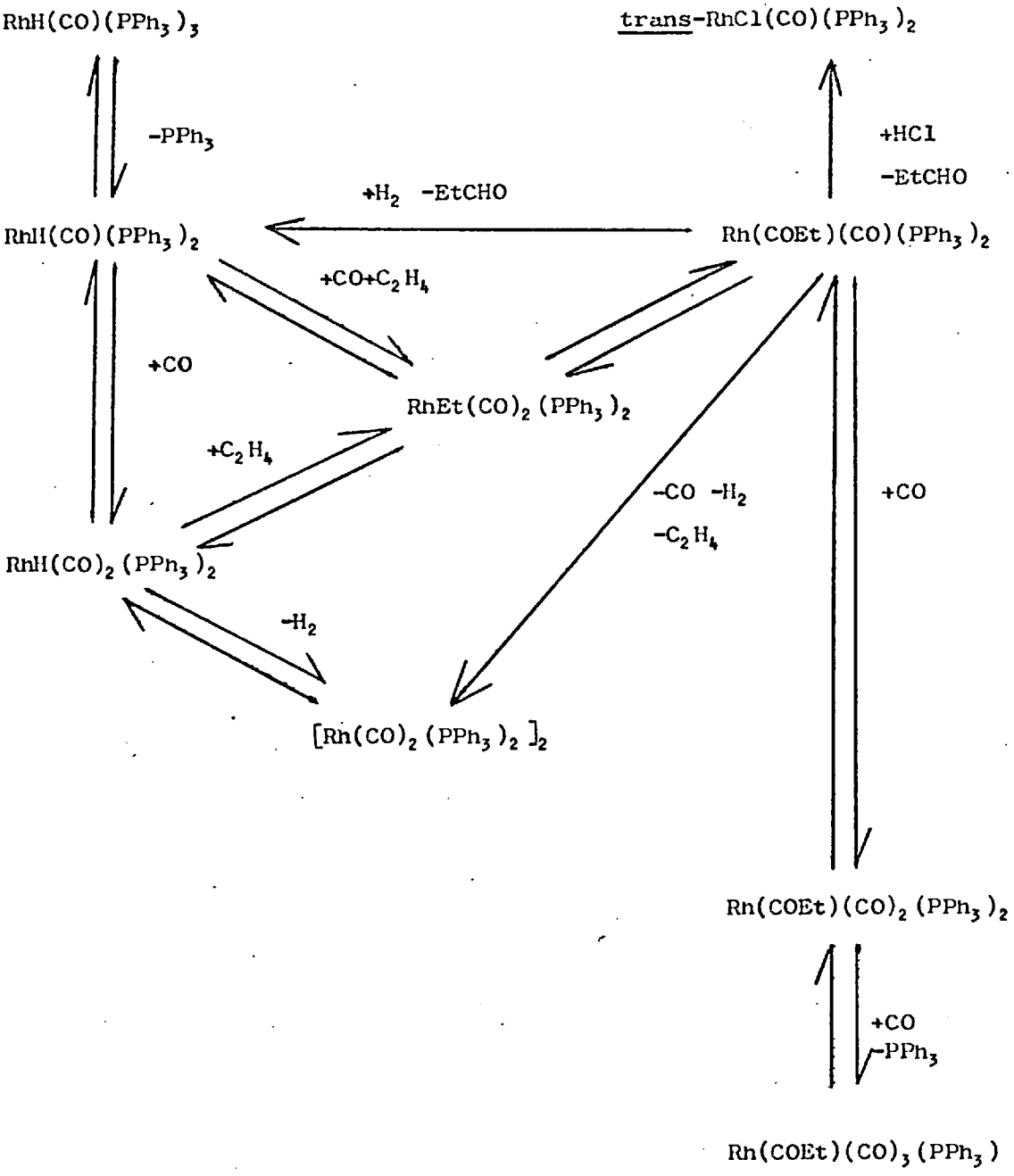
2. Iridium System

This was studied in order to obtain a more stable and less labile system.

$IrH(CO)_2(PPh_3)_2$ on treatment with CO + C_2H_4 (1:1, total 30 atm.) gave quantitative conversion into the stable crystalline acyl compound $Ir(COEt)(CO)_2(PPh_3)_2$ whose i.r. and n.m.r. spectra are virtually identical with the spectra assigned to the rhodium propionyl (Table 3.1) and provide conclusive evidence for the formulation of the latter as 5-coordinate. A similar iridium acetyl complex has been made[53b] by the interaction of $Na[Ir(CO)_3(PPh_3)]$ with PPh_3, MeI and CO, but this compound can also be obtained by interaction of trans-$IrCl(CO)(PPh_3)_2$ with MeLi followed by CO (20 atm.). This synthetic route should be a general procedure, as should the CO + alkene method if other alkenes are used. Thus reaction of $IrH(CO)_2(PPh_3)_2$ with CO + C_3H_6 (1:1) at 30 atm. gave $Ir(COC_3H_7)(CO)_2(PPh_3)_2$. The n.m.r. spectrum showed only the n-butyryl group [τ 7.11(triplet);8.69(multiplet);9.33(triplet)]. Small amounts of isobutyryl complex would not be easily detected, however, because of overlap in the methyl region and splitting of the unique proton. The preparation from the iridium dicarbonyl provides evidence for the original postulation[30] that in the rhodium hydroformylation system it is $RhH(CO)_2(PPh_3)_2$ which is attacked by alkene, whereas the preparation from $IrCl(CO)(PPh_3)_2$ is in part analogous to the route via $RhH(CO)(PPh_3)_2$ discussed in Chapter I (Schemes 1.2, 3.2).

The iridium propionyl reacts only slowly with H_2 or HCl to give propionaldehyde and $IrH(CO)_2(PPh_3)_2$ or $IrCl(CO)(PPh_3)_2$ respectively. (If excess HCl is used the adduct $IrHCl_2(CO)(PPh_3)_2$[60] is obtained).

Scheme 3.2


RhH(CO)(PPh3)3
trans-RhCl(CO)(PPh3)2
-PPh3
+HCl
-EtCHO
+H2 -EtCHO
RhH(CO)(PPh3)2
Rh(COEt)(CO)(PPh3)2
+CO+C2H4
+CO
RhEt(CO)2(PPh3)2
+C2H4
-CO -H2
-C2H4
+CO
RhH(CO)2(PPh3)2
-H2
[Rh(CO)2(PPh3)2]2
Rh(COEt)(CO)2(PPh3)2
+CO
-PPh3
Rh(COEt)(CO)3(PPh3)

An intermediate oxidative adduct with HCl, $Ir(COEt)HCl(CO)(PPh_3)_2$, can also be obtained as an unstable solid mixed with $IrCl(CO)(PPh_3)_2$ by precipitation from benzene with petroleum [ν_{CO} 2065; ν_{IrH} 2122; ν_{CO}(acyl) 1635 cm^{-1}] and can also be detected when the reaction is carried out in CH_2Cl_2 [ν_{CO} 2080; ν_{IrH} 2122; ν_{CO}(acyl) 1630 cm^{-1}].

The formation of aldehyde from the 5-coordinate acyls by action of either H_2 or HCl is inhibited by high concentrations of CO which illustrates the necessity for displacement of a CO ligand in order that two sites be available for oxidative addition without exceeding the coordination number of 6; the much faster reaction with rhodium doubtless reflects the greater dissociation of the 5-coordinate acyl in that case.

Further, the reaction of $Ir(COEt)(CO)_2(PPh_3)_2$ with H_2 in a closed system to give $IrH(CO)_2(PPh_3)_2$ and EtCHO can be assumed to involve either displacement of CO or of a PPh_3 ligand by H_2 giving either $Ir(COEt)H_2(CO)(PPh_3)_2$ or $Ir(COEt)H_2(CO)_2(PPh_3)$, these species then eliminating aldehyde and recombining with the stoicheiometric amount of CO or PPh_3 present to give $IrH(CO)_2(PPh_3)_2$. The isolation of a monocarbonyl iridium(III) intermediate suggests that the CO displacement route is probably operative. The path involving PPh_3 dissociation is probably unavailable in the rhodium system since the extra mole of free PPh_3 present in solution, owing to the use necessarily of $RhH(CO)(PPh_3)_3$, is likely to inhibit this dissociative step; moreover, any small amounts of the dissociated species formed would probably react immediately with the CO present in excess to give $Rh(COEt)(CO)_3(PPh_3)$, so blocking the coordination site (see below).

The dissociation of PPh_3 and its replacement by another ligand is readily demonstrated for $Ir(COEt)(CO)_2(PPh_3)_2$. Thus on treatment with CO (1 atm.) for 15 min., or for shorter periods at higher pressures, a new acyl species is partially formed as shown by i.r. and n.m.r. spectra. The latter shows a new triplet and quartet shifted to lower fields; in benzene the quartets of the two species partially overlap since the difference in τ values approximates to the coupling constants of both multiplets (7.5 Hz); in CH_2Cl_2, however, the two distinct quartets are clearly observed (Table 3.1).

The i.r. spectrum (cyclohexane solution) has three new bands plus those of unchanged starting material; a weak band at 2055 cm^{-1} (^{13}CO satellite at 2039 cm^{-1}), a strong band at 1972 cm^{-1}, and a new acyl peak at 1670 cm^{-1}. The new species is formulated as $Ir(COEt)(CO)_3(PPh_3)$ with C_{3v} symmetry since the weak A, and strong E, carbonyl modes have the proper relationship with those of the dicarbonyl acyl (Table 3.1) as found for other $-(CO)_3(PPh_3)$ and $-(CO)_2(PPh_3)_2$ species [cf $Rh(C_2F_4H)$ species above]. The acyl band is shifted 27 cm^{-1} to higher wavenumbers compared with the original compound owing to the stronger electron-withdrawing effect of the three CO groups. The tricarbonyl cannot be isolated pure owing to inhibition by the PPh_3 displaced:

$$Ir(COEt)(CO)_2(PPh_3)_2 + CO \rightleftarrows Ir(COEt)(CO)_3(PPh_3) + PPh_3$$

The formation in the rhodium system of small amounts of $Rh(COEt)(CO)_3(PPh_3)$ can be observed by increasing to ca 1 atm. the CO in equilibrium with $Rh(COEt)(CO)_2(PPh_3)_2$. In CH_2Cl_2 solution a weak triplet appears (at τ 9.01) below the strong triplet of the CH_3 group of $Rh(COEt)(CO)_2(PPh_3)_2$ (cf corresponding iridium values).

3. Decarbonylation of the propionyl compound

On treatment of $Ir(COEt)(CO)_2(PPh_3)_2$ at 120° in vacuo, slow liberation of C_2H_4 and CO occurs to leave a solid mixture in which $IrH(CO)_2(PPh_3)_2$ can be detected as the main product. No evidence of an alkyl intermediate was obtained. In solution, controlled stoicheiometric decarbonylation can be achieved by use of $RhCl(PPh_3)_3$.[42,61] On mixing equimolar CH_2Cl_2 solutions at 25° an immediate colour change occurs and trans-$RhCl(CO)(PPh_3)_2$ precipitates

$$Ir(COEt)(CO)_2(PPh_3)_2 + RhCl(PPh_3)_3 \rightarrow RhCl(CO)(PPh_3)_2 + IrH(CO)(PPh_3)_3 + CO + C_2H_4.$$

In benzene the reaction is slower and an unstable intermediate can be detected by its new strong band in the i.r. at 1912 cm^{-1}. Warming a benzene solution of the acyl alone under N_2 for ca 10 min. gives complete conversion to $IrH(CO)_2(PPh_3)_2$, CO and C_2H_4. The decomposition in cyclohexane is slower still and peaks of the intermediates can be observed, aided by the fact that their solubility is higher than that of the starting material. Thus when a suspension of $Ir(COEt)(CO)_2(PPh_3)_2$

is heated in cyclohexane for a few min. and then filtered, the i.r. spectrum of the solution shows the bands of the original compound at 1980 and 1938 cm^{-1} superimposed on those of the new species at 1975 and 1925 cm^{-1} (the difficulty of the partial overlap of the bands at 1980 - 1975 cm^{-1} can be overcome by observing the changes in the intensity of this band in several spectra at different stages of the decomposition). These two new strong bands can be assigned to the intermediate alkyl species $IrEt(CO)_2(PPh_3)_2$. Other weak peaks around 2025 and 1950 cm^{-1} may be due to isomers or to disproportionation products such as $IrEt(CO)(PPh_3)_2$ or $IrEt(CO)_3(PPh_3)$.

4. Interaction of $IrH(CO)_2(PPh_3)_2$ and C_2H_4

This reaction is complicated and the results depend on the temperature, solvent and pressure. In toluene at 25° with 10 atm. C_2H_4 with the proviso that the system is cooled to -70° before releasing the pressure, a white solid can be precipitated with chilled light petroleum (-70°). This product is the square acyl $Ir(COEt)(CO)(PPh_3)_2$ having a terminal ν_{CO} at 1955 cm^{-1} and an acyl band at 1635 cm^{-1}.

On working up the product at -50°a mixture of this and a second compound (ν_{CO} 1959, 1910 cm^{-1}), probably the ethyl, is obtained. The reaction

$$IrEt(CO)_2(PPh_3)_2 \rightleftharpoons Ir(COEt)(CO)(PPh_3)_2$$

appears to be displaced to the right at low temperatures or at high C_2H_4 concentrations. [The CO insertion could be promoted by co-ordination of C_2H_4 to give $Ir(COEt)(C_2H_4)(CO)(PPh_3)_2$, analogous to the adduct $IrI(C_2H_4)(CO)(PPh_3)_2$ [62]]. The two products are reasonably soluble in cyclohexane at 25° and both solutions have identical spectra with predominantly strong bands at 1975 and 1925 cm^{-1}, attributed, as before, to $IrEt(CO)_2(PPh_3)_2$. [The weak bands observed in the thermal decomposition of $Ir(COEt)(CO)_2(PPh_3)_2$ in cyclohexane and also a new band at 1940 cm^{-1}, probably obscured in that reaction by the bands of the starting material, are also observed]. On rapid evaporation the residue shows only the bands attributed to $IrEt(CO)_2(PPh_3)_2$.

The two compounds can be handled for only short periods (a few min.) as loss of C_2H_4 and regeneration of $IrH(CO)_2(PPh_3)_2$ occurs. If the cyclohexane solutions are treated with CO, the bands due to $Ir(COEt)(CO)_2(PPh_3)_2$ and $Ir(COEt)(CO)_3(PPh_3)$ appear rapidly with disappearance of the initial ones.

5. N.m.r. study of interaction of $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ with C_2H_4

The interaction of both $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ with C_2H_4 in CD_2Cl_2 solution can be studied by observation of the disappearance of the high-field lines and appearance of multiplets between τ 7 and 10.

(a) $IrH(CO)(PPh_3)_3$. The uptake of C_2H_4 by solutions of $IrH(CO)(PPh_3)_3$ at 70 cm and 20° has been reported[37] to give 28% conversion to species assigned as $IrH(C_2H_4)(CO)(PPh_3)_3$ or $IrEt(CO)(PPh_3)_3$ but no details were given to substantiate either compound.

At 10 atm., 35° only about 10 - 20% conversion was found. After 15 min. there is a broad triplet at τ 8.74 (J 8.0 Hz) and a broad unresolved signal at τ 8.22 attributable to an Ir-Et group. The fact that the reaction is also incomplete under these conditions suggests that PPh_3 dissociation is involved and there is an equilibrium:

$$IrH(CO)(PPh_3)_3 + C_2H_4 \rightleftharpoons IrEt(CO)(PPh_3)_2 + PPh_3.$$

The broadness of the signals could be due to coupling and/or to exchange.

After several hours the Et signals disappear and a sharp peak at τ 9.16 only is observed, which is due to C_2H_6. Since the hydrogen cannot come from the solvent the most likely source is the ortho-hydrogen of the phenyl group of one of the PPh_3 ligands as in the intramolecular reaction[63] of $RhMe(PPh_3)_3$ which liberates methane, i.e. the reaction may be:-

$$Ir(C_2H_5)(CO)(PPh_3)_2 \rightarrow C_2H_6 + Ir[(C_6H_4)PPh_2](CO)(PPh_3)$$

Such a reaction was not found to be the major pathway for the decomposition of $RhH(CO)(PPh_3)_2$ in solution,[41] where a dimerisation leads to $[Rh(CO)(PPh_3)_2]_2$ and H_2. Dimeric species, however, have

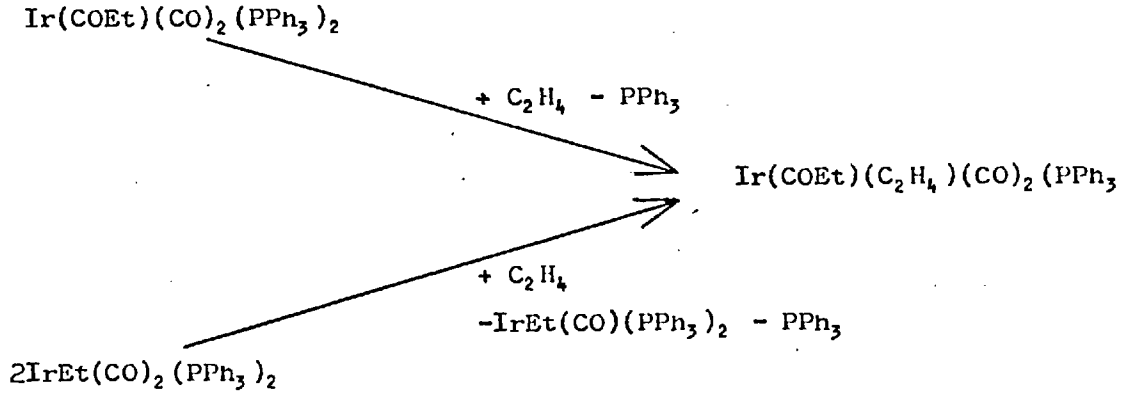
not been characterised in the related iridium system and dimerisation would also have been expected to give some C_4H_{10}.

(b) $IrH(CO)_2(PPh_3)_2$. This reacts completely with C_2H_4 at 35° and 10 - 15 atm. within 1 - 2 hr in two distinct stages (Figure 3.2). After the first 15 min. when ca 30% of the hydride is converted, the spectrum (CD_2Cl_2) consists of three triplets, τ 8.74 (J 8.0 Hz, broad), τ 9.17 (J 7.0 Hz), and τ 9.65 (J 7.5 Hz); two quartets, τ 7.48 and 7.24; and a broad multiplet at τ 8.22. The triplet at τ 8.74 and the multiplet are due to $IrEt(CO)(PPh_3)_2$ as observed in the reaction of $IrH(CO)(PPh_3)_3$. The triplet at τ 9.65 and quartet at τ 7.48 (ratio 3:2) can be assigned to $Ir(COEt)(CO)_2(PPh_3)_2$ by comparison with the spectrum of the isolated compound (Table 3.1). These two products, which are present in approximately equal concentration, may hence be formed by disproportionation:

$$IrH(CO)_2(PPh_3)_2 + C_2H_4 \rightleftharpoons IrEt(CO)_2(PPh_3)_2$$

$$2IrEt(CO)_2(PPh_3)_2 \rightleftharpoons IrEt(CO)(PPh_3)_2 + Ir(COEt)(CO)_2(PPh_3)_2$$

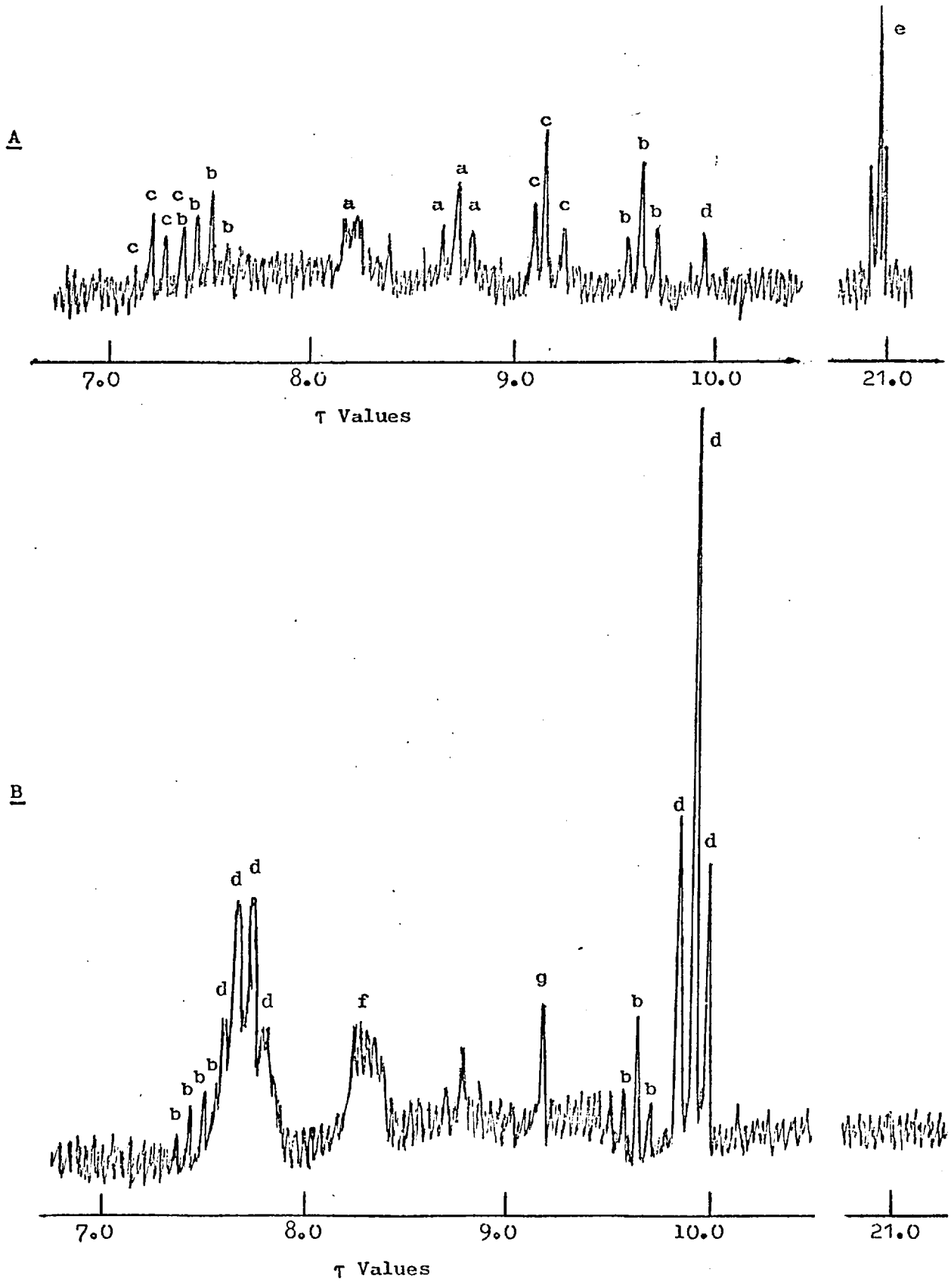
The triplet at τ 9.17 and the quartet at τ 7.24 could be due to $IrEt(CO)_2(PPh_3)_2$ but the chemical shift is more characteristic of a propionyl group (cf Table 3.1) and the spectrum may be attributed to a new propionyl species such as $Ir(COEt)(C_2H_4)(CO)_2(PPh_3)$ formed by one of the routes:



This interpretation is supported by the following observations:

(i) On treating pure $Ir(COEt)(CO)_2(PPh_3)_2$ in CH_2Cl_2 with C_2H_4 (10 - 15 atm) the triplet and quartet at τ 9.17 and 7.24 readily appear in small amounts.

Figure 3.2



N.m.r. spectra (100 MHz; 35°) of $IrH(CO)_2(PPh_3)_2$ in CD_2Cl_2 under C_2H_4 (ca 10 atm.) A. after 10 min.; B. after 2 hr. Assignments: a, $IrEt(CO)(PPh_3)_2$; b, $Ir(COEt)(CO)_2(PPh_3)_2$; c, $Ir(COEt)(C_2H_4)(CO)_2(PPh_3)$; d, $Ir(COEt)(CO)(PPh_3)_2$; e, $IrH(CO)_2(PPh_3)_2$; f, $IrEt(CO)_2(PPh_3)_2$; g, C_2H_6.

(ii) When $IrH(CO)_2(PPh_3)_2$ is treated with C_2H_4 in the presence of excess PPh_3 only the signals of $Ir(COEt)(CO)_2(PPh_3)_2$ are observed. (In presence of excess PPh_3 the reaction is slower and the first stage occurs in ca 1 hr).

During the second stage of the reaction new signals are observed with concomitant disappearance of the high-field line and of the signals due to $IrEt(CO)(PPh_3)_2$ and $Ir(COEt)(C_2H_4)(CO)_2(PPh_3)$: the species $Ir(COEt)(CO)_2(PPh_3)_2$ remains essentially unchanged until equilibrium is attained. The principal new features are a triplet at τ 9.95 and a quartet at τ 7.70 (J 7.25 Hz; ratio 3:2) which predominate at the end of the reaction. A broad multiplet at τ 8.30 is also observed and finally a sharp peak at τ 9.16 attributed to C_2H_6. The τ 9.95 and 7.70 bands can be assigned to the monocarbonyl $Ir(COEt)(CO)(PPh_3)_2$ (which was isolated at low temperatures as noted above) since:

(i) it has high abundance and a species containing three carbonyls $Ir(COEt)(CO)_2(PPh_3)_2$ is also present,

(ii) the chemical shifts correlate well with the other propionyls $Ir(COEt)(CO)_2(PPh_3)_2$, $Ir(COEt)(C_2H_4)(CO)_2(PPh_3)$ and $Ir(COEt)(CO)_3(PPh_3)$ (downfield shifts occur where PPh_3 is replaced by CO).

The multiplet at τ 8.30 is probably due to the alkyl species $IrEt(CO)_2(PPh_3)_2$, which may be fluxional, as on cooling this broad signal splits into several complex and superimposed multiplets at -35° (a complete analysis is not possible because of reduced solubility). The small amount of ethane probably arises as before.

In other solvents the spectra are also complicated but the behaviour is similar to that in CH_2Cl_2. It is important to note that in all final states the main species appears to be $Ir(COEt)(CO)(PPh_3)_2$ but the final equilibrium mixture depends on the temperature and the C_2H_4 pressure.

C. Aryl and Benzoyl Derivatives

The phenyl compound,[63] $RhPh(PPh_3)_3$, reacts very rapidly with CO in solution to give a mixture of benzoyl species, $Rh(COPh)(CO)_2(PPh_3)_2$ and $Rh(COPh)(CO)_3(PPh_3)$. The different steps, for which only spectroscopic evidence is available, can be readily interpreted on the basis of the following iridium chemistry.

When a suspension of trans-$IrCl(CO)(PPh_3)_2$ in diethyl ether is treated with PhMgBr, or better, PhLi, the crystalline complex $IrPh(CO)(PPh_3)_2$ (ν_{CO} 1940 cm^{-1}) can be readily obtained. This is moderately stable in diethyl ether although it decomposes rapidly in benzene or other hydrocarbons liberating benzene and forming a new species with ν_{CO} 1940 cm^{-1}. This decomposition is doubtless similar to that noted above for $IrEt(CO)(PPh_3)_2$ and described[63] for $RhMe(PPh_3)_3$ and $RhPh(PPh_3)_3$ which, on heating for several hr in solution give $Rh[(C_6H_4)PPh_2](PPh_3)_2$ and CH_4 or C_6H_6. The role of the ether in stabilising the square phenyl compound is probably a coordinative blocking of the free axial coordination site used to facilitate hydrogen transfer from the Ph group of coordinated PPh_3 and the formation of an intermediate iridium(III) compound, $IrHPh[(C_2H_4)PPh_2](CO)(PPh_3)_2$ which subsequently eliminates benzene. A band at 2045 cm^{-1} in the i.r. spectrum of the solid residue recovered after decomposition in benzene may be ν_{CO} of this iridium(III) species. $IrPh(CO)(PPh_3)_2$ also reacts rapidly with atmospheric O_2 to give the adduct, $Ir(Ph)O_2(CO)(PPh_3)_2$ (ν_{CO} 1980; ν_{OO} 835 cm^{-1}) analogous to $IrCl(O_2)(CO)(PPh_3)_2$[64].

A freshly prepared solution of $IrPh(CO)(PPh_3)_2$ in cyclohexane has ν_{CO} 1960 cm^{-1} although the compound is of low solubility. On treating a suspension with CO, the products are relatively soluble and a typical spectrum after ca 5 min. has two strong bands at 1980 and 1940 cm^{-1}, a weak band at 1960 cm^{-1} due to starting material, and an acyl band at 1620 cm^{-1}.

On concentration under CO, the complex $Ir(COPh)(CO)_2(PPh_3)_2$ precipitates pure (Table 3.1). The solution spectrum of this pure complex in cyclohexane has bands at 1980, 1940 and 1620 cm^{-1} but the relative intensities differ from those observed in the in situ preparation from $IrPh(CO)(PPh_3)_2$. This suggests overlapping of bands and the most obvious assumption is that a third species $IrPh(CO)_2(PPh_3)_2$ with accidentally coincident frequencies is present in equilibrium with $IrPh(CO)(PPh_3)_2$ and $Ir(COPh)(CO)_2(PPh_3)_2$. This is confirmed by displacement of CO on bubbling N_2 through the solution when complete disappearance of the 1620 cm^{-1} band occurs. The resulting spectrum is due to $IrPh(CO)(PPh_3)_2$ and $IrPh(CO)_2(PPh_3)_2$ and has ν_{CO} 1980, 1960

and 1940 cm^{-1}. [Some minor weak bands of uncertain assignment are also present, notably at 2025 cm^{-1}, as found in solutions of $IrEt(CO)_2(PPh_3)_2$].

On prolonged treatment of a solution of $Ir(COPh)(CO)_2(PPh_3)_2$ with CO substantial amounts of $Ir(COPh)(CO)_3(PPh_3)$ are formed [ν_{CO} 2059, 1998 cm^{-1}; ν_{CO} (acyl) 1637 cm^{-1}].

When the benzoyl mixture is treated with H_2 no benzaldehyde is obtained and all the Ph group appears as benzene. Similarly if CO + H_2 (1:1) is used only benzene appears but now more slowly. The difference from the propionyl is presumably due to the greater stability of the Ir - C bond in the phenyl relative to the benzoyl compound (cf also Ref. 56).

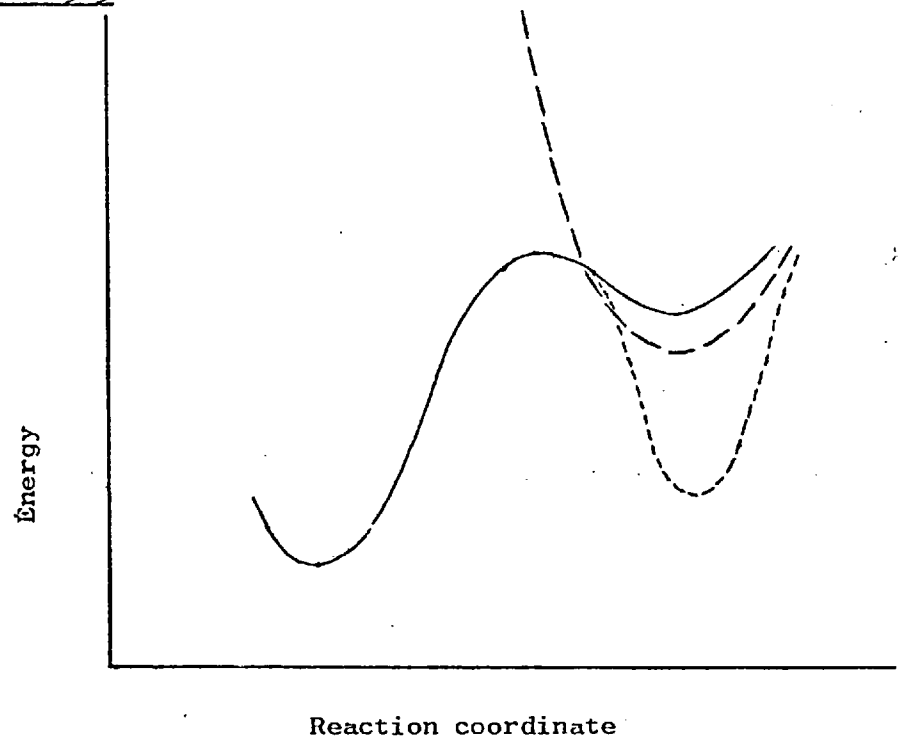
The reaction of $RhPh(PPh_3)_3$ can thus be seen to proceed rapidly to $Rh(COPh)(CO)_2(PPh_3)_2$ plus $Rh(COPh)(CO)_3(PPh_3)$. On sweeping the solution with N_2 for a few sec. the spectrum of pure $Rh(COPh)(CO)_2(PPh_3)_2$ is obtained and further sweeping gives a species with a single peak at 1978 cm^{-1}, presumably $RhPh(CO)(PPh_3)_2$, plus small amounts of $[Rh(CO)_2(PPh_3)_2]_2$. The reaction is reversed again by CO to give the benzoyl species. In contrast to the iridium system, on treatment with H_2 nearly quantitative conversion to benzaldehyde is observed.

Discussion

The above studies have enabled the isolation and/or spectroscopic characterisation of rhodium and iridium compounds which correspond closely to the rhodium complexes postulated to be involved in the catalytic hydroformylation of alkenes.

Simulating the square rhodium(I) alkyl (I) (Figure 3.1) are $Rh(C_2F_4H)(CO)(PPh_3)_2$ and $IrPh(CO)(PPh_3)_2$ with spectroscopic evidence for $RhPh(CO)(PPh_3)_2$ and $IrEt(CO)(PPh_3)_2$. The differences between these compounds and the actual alkyl intermediates in the catalytic reaction can be illustrated qualitatively as in Figure 3.3.

Figure 3.3



Qualitative form of energy diagram for $RhH(CO)(PPh_3)_3$ plus alkene to give $RhR(CO)(PPh_3)_2$ showing relative stabilities of product for R = Et ———— , C_2F_4H ------, and Ph — — —.

The catalytic alkyl intermediate is very short-lived and readily reverts to Rh-H + alkene since its stability towards elimination is small. The fluoroalkyl is more stable since the Rh - C bond is stronger owing to the electronegativity of the F atoms and a certain amount of ionic resonance $\overset{+}{M} - \overset{-}{C}$ or "double-bond character" in the metal to carbon bond. The Rh - C bond strength in the phenyl is probably slightly larger than in alkyls due to the same sort of bond strengthening[56] but the new stabilising feature is the unavailability of a direct pathway to regenerate the metal hydride by abstraction of hydrogen from the organic group.[55]

It is reasonable to assume, however, that some of the chemical properties of these related compounds which do not involve an elimination reaction will be very similar. Thus the behaviour of $Rh(C_2F_4H)(CO)(PPh_3)_2$ in readily dissociating suggests that

such dissociation may be expected in other square alkyls and may also reflect the loss of specificity to alk-1-ene in hydrogenation at low concentrations of $RhH(CO)(PPh_3)_3$, attributed[34] to a second PPh_3 dissociation.

Although it was not possible to obtain a stable example, even for iridium, of an oxidative addition product of the alkyl with H_2 such as (II), that such species are very short lived is suggested by the facile displacement by H_2 of CO in $Rh(C_2F_4H)(CO)_2(PPh_3)_2$. A tractable HCl adduct, $Rh(C_2F_4H)HCl(CO)(PPh_3)_2$, was, however, obtained. The slow uptake[37] of H_2 by $IrH(CO)(PPh_3)_3$ at 70 cm, 20° should also be noted in this connection. This reaction, which was reported for fairly dilute solutions (2.5 mM), probably gives the known[65] $IrH_3(CO)(PPh_3)_2$ rather than the 7-coordinate complex originally suggested.[37]

The driving force for hydride transfer to alkyl giving alkane is clearly large and several examples are noted, even with so stable a bond as the fluoroalkyl. Intramolecular transfer of an ortho-hydrogen from a phenyl ring of coordinated PPh_3 leading to elimination of alkane, probably also via an iridium(III) hydrido species, is noted. The steps of the hydrogenation reaction are thus clearly simulated.

Rapid reaction of the square fluoroalkyl and phenyl compounds with CO confirms the formation of 5-coordinate dicarbonyl alkyls species (III), $Rh(C_2F_4H)(CO)_2(PPh_3)_2$ and $IrPh(CO)_2(PPh_3)_2$, which may dissociate a PPh_3 ligand. The dicarbonyl alkyl species can also be formed by reaction of $MH(CO)_2(PPh_3)_2$ with alkene. As noted above these reactions to some extent parallel the alternative pathways discussed in Chapter I for the formation of such intermediates.

No evidence has been obtained to indicate whether an associative or dissociative mechanism is operative in the interaction of $IrH(CO)_2(PPh_3)_2$ with alk-1-enes, which causes their slow isomerisation to alk-2-enes at 25°[36] and from which the characterisation of a number of alkyl and acyl species has been described above. $IrH(CO)_2(PPh_3)_2$ does not dissociate appreciably in benzene solution at 25° although the presence of a kinetically significant concentration of a 4-coordinate species cannot be excluded. An associative pathway involving the intermediate $IrH(alkene)(CO)_2(PPh_3)_2$ is also possible. The objection

to such an intermediate on the basis that it formally breaks the "inert-gas rule" for a d^8 complex was discussed when the mechanisms were proposed for the rhodium system[30] and it was noted that there is evidence[36] for solvation of $IrH(CO)_2(PPh_3)_2$ by carbon disulphide. [In the related cobalt system it has been suggested[3] that a complex $CoH(alkene)(CO)_4$ may be formally regarded as $H^{\delta+}Co^{\delta-}(alkene)(CO)_4$.] It is clear, however, that a concerted mechanism involving coordination of alkene and simultaneous displacement of a PPh_3 ligand may also be considered under the heading of "associative pathway" but implying an extremely short-lived intermediate. Such a mechanism in no way contradicts the essential postulate that this route should be more substrate selective and more specific to linear alkyl formation than the dissociative route. The X-ray crystal structure[66] of $IrH(CO)_2(PPh_3)_2$ shows that a relatively large unhindered area exists for approach to the metal and although this does not necessarily mean that a similar situation exists in solution it may be taken as an indication. The three bulky PPh_3 groups in $IrH(CO)(PPh_3)_3$, on the other hand, will cause much greater steric hindrance to alkene approach to the metal. Thus, although $IrH(CO)(PPh_3)_3$ reacts initially with ethylene, the fact that the reaction then ceases suggests a dissociative pathway inhibited by excess PPh_3. Broadening and ultimate coalescence of the high field quartet of $IrH(CO)(PPh_3)_3$ on warming solutions from 35^o to 100^o confirms that rapid PPh_3 exchange occurs at these higher temperatures.[36]

Only one analogue of the proposed square acyl(IV) was obtained, namely $Ir(COEt)(CO)(PPh_3)_2$, and even this reverts easily to the dicarbonyl alkyl. The extraordinary ease with which decarbonylation and transfer reactions occur, not only with rhodium but also with iridium, shows that the activation energies for these elementary steps are very low. The difficulty in preparing the square acyls in presence of CO arises from the difficulty of preventing additional CO uptake to give $M(COR)(CO)_2(PPh_3)_2$, and even for the iridium acyl isolated the equilibrium

$$MR(CO)_2(PPh_3)_2 \rightleftharpoons M(COR)(CO)(PPh_3)_2$$

lies very much to the left. Since $Ir(COEt)(CO)(PPh_3)_2$ was obtained only in the reaction of $IrH(CO)_2(PPh_3)_2$ and C_2H_4 it is possible that coordination of C_2H_4 under pressure promotes the transfer.

The 5-coordinate dicarbonyl acyls (V) are easily obtained for both rhodium and iridium with either COEt or COPh and ready displacement of one of the PPh_3 groups by CO gives the tricarbonyl species VII. In the presence of excess CO it was shown that oxidative addition of H_2 or even HCl to the dicarbonyl acyls does not occur and that only when CO pressure is lowered does conversion to aldehyde proceed. Since at lower pressure the system should furnish some square acyl it seems likely that oxidative addition occurs only with the square species, only low concentrations of which may need to be present. Thus the CO inhibition in the catalytic hydroformylation reaction (p.27) is probably caused by formation of $Rh(COR)(CO)_2(PPh_3)_2$ and $Rh(COR)(CO)_3(PPh_3)$ and the latter may also be present in the colourless inactive solutions formed at catalyst concentrations below 0.5 mM (p.24). It will probably also be correct to expect that in the absence of substantial excesses of PPh_3 in catalytic reactions, intermediates having only one PPh_3 ligand are likely to be of importance. In principle a study of the reaction of $Rh(COR)(CO)_2(PPh_3)_2$ with CO and H_2 mixtures of varying composition under conditions directly comparable with the catalytic reaction would be instructive, but the rhodium dicarbonyl acyl species are so unstable that rapid alkene elimination or aldehyde formation in the absence of a stabilising gas phase precludes such an investigation.

The only example of the octahedral acyl intermediate (VI) detected was that in the reaction of HCl with $Ir(COEt)(CO)_2(PPh_3)_2$; however the formation of aldehyde establishes the principle of oxidative addition of H_2 and elimination of aldehyde. It is interesting to note that although when treated with CO + H_2 (1:1) the rhodium propionyl and benzoyl and the iridium propionyl gave aldehyde, the iridium benzoyl gave solely benzene; the analogy between the metals must hence always be treated with care.

Table 3.1. Infrared (1600-2200 cm^{-1} region) and nuclear magnetic resonance spectraldata for rhodium and iridium complexes[a]

Compound	I.r. (cm^{-1})[b]			n.m.r. (τ values)[c]
	Solid[e]	Solution	Solvent[f]	
$Rh(C_2F_4H)(CO)(PPh_3)_2$	1990s[g]	1995s	1	H 5.00tt; F_α - 74.83(broad); F_β-34.20d (J_{H-F_α} 9 Hz; J_{H-F_β} 56 Hz)
			2	H 4.91 tt; F_α-73.20(broad); F_β-34.55d
$Rh(C_2F_4H)(CO)_2(PPh_3)_2$	2003m, 1957s[g]	2020s, 1968s	1	No signals observed
		2005s, 1958s	3	
$Rh(C_2F_4H)(CO)_3(PPh_3)$[h]	-	2075w, 2015s	1	H 4.60tt; F_α-113.2(broad); F_β-40.90d (J_{H-F_α} 5 Hz; J_{H-F_β} 60 Hz)
		2075w, 2020s	3	
$Rh(C_2F_4H)(SO_2)(CO)(PPh_3)_2$	2060s[g,i]	2055s	1	H 4.38tt; F_α-83.9(broad); F_β-28.6d (J_{H-F_α} 8 Hz; J_{H-F_β} 55 Hz)
$Rh(COEt)(CO)_2(PPh_3)_2$	1975s, 1940s, 1628s	1990m, 1943s, 1643m 1650sh.	1	9.26t, 7.07q (J 7.5 Hz)
			4	9.55t, 7.34q
$Ir(COEt)(CO)_2(PPh_3)_2$	1978s, 1920s, 1628s	1975m, 1923s, 1634m	1	9.27t, 7.10q (J 7.5 Hz)
		1980m, 1928s, 1643m	3	
		1980m, 1930s, 1625m	4	9.65t, 7.48q
$Ir(COEt)(CO)_3(PPh_3)$[h]	-	2050w, 1980s, 1660m	1	8.97t, 7.03q (J 7.5 Hz)
		2055w, 1972s, 1670m	3	
			4	9.11t, 7.11q
$Ir(Et)(CO)_2(PPh_3)_2$	1959m, 1910s	?, 1912s	1	
		1975m, 1925s	3	
$Ir(COEt)(CO)(PPh_3)_2$	1955s, 1635m	-	4	9.95t, 7.70q (J 7.25 Hz)

Table 3.1 (continued)

$Rh(Ph)(CO)(PPh_3)_2$ [h]	-	1978s	3	
$Rh(COPh)(CO)_2(PPh_3)_2$ [h]	-	1980s, 1945s, 1620m 1985s, 1955s, 1630m	1 3	
$Rh(COPh)(CO)_3(PPh_3)$ [h]		2060w, 2005s, 1630m 2062w, 2010s, 1640m	1 3	
$Ir(Ph)(CO)(PPh_3)_2$	1940s	1948s 1960s	1 3	
$Ir(COPh)(CO)_2(PPh_3)_2$	1984m, 1930s, 1608m.	1980s, 1940s, 1620m	3	
$Ir(COPh)(CO)_3(PPh_3)$ [h]	-	2059w, 1998s, 1637m	3	-
$Ir(Ph)(CO)_2(PPh_3)_2$ [h]	-	1980s, 1940s	3	-

a) Data for the following compounds which were tentatively characterised spectroscopically are found in the text:
$Rh(C_2F_4H)HCl(CO)(PPh_3)_2$, $Ir(COEt)HCl(CO)(PPh_3)_2$, $Rh(COEt)(CO)_3(PPh_3)$

b) All compounds showed typical bands due to PPh_3; ν_{CO} values are given to $\pm$ 2 cm^{-1}; s = strong, m = medium, w = weak, sh = shoulder.

c) Proton resonances were measured at 100 MHz and are quoted as τ values. Fluorine resonances, measured at 94.1 MHz, are quoted as p.p.m. relative to C_6F_6 as internal standard. All spectra were taken at 35°; d = doublet of broad multiplets; t = triplet, tt = triplet of triplets, q = quartet.

e) Nujol mulls

f) Solvents:- 1, benzene; 2, toluene; 3, cyclohexane; 4, dichloromethane.

g) Compounds also showed bands typical of the fluoroalkyl group at ca 1140s, 1060s, and 915s cm^{-1}.

h) Compounds not isolated as pure solids.

i) Also bands due to coordinated SO_2 at 1190m, 1035s and 785s cm^{-1}.

CHAPTER IV

Interaction of Hydridocarbonyltriphenylphosphine Complexes of Rhodium and Iridium with Conjugated Dienes and Allene

Introduction

It has been noted in Chapter I that no uptake of CO + H_2 (1:1) at ca 1 atm. and 25° was detected in the attempted hydroformylation of conjugated dienes, such as penta-1,3-diene, or allene using $RhH(CO)(PPh_3)_3$ as catalyst and no hydrogenation of penta-1,3-diene was found[34] under similar conditions using this catalyst. It was clear that these substrates form relatively stable complexes with $RhH(CO)(PPh_3)_3$ in contrast to the intermediate species derived from alk-1-enes or ethylene described in Chapter III. These complexes, which are π-allylic, and their iridium analogues are described in this chapter.

Allylic complexes are usually more stable than simple alkyls[54] and by interaction with allylmagnesium chloride the complex $Rh(\pi\text{-allyl})(PPh_3)_2$ has been prepared[67] from $RhCl(PPh_3)_3$ and $Rh(\pi\text{-allyl})(CO)_2$ from $[RhCl(CO)_2]_2$.[68] Substituted allyl analogues of $Rh(\pi\text{-allyl})(PPh_3)_2$ have also been made[67] by addition of conjugated dienes to $RhH(PPh_3)_4$ and similar addition reactions of $CoH(CO)_4$ are well known.[69] Addition of PPh_3 to $Rh(\pi\text{-allyl})(CO)_2$ was reported[68] to give $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ but no details of this compound were given.

A. Preparation of the Complexes $M(\pi\text{-A})(CO)(PPh_3)_2$, M = Rh, Ir; A = Allylic Group

When allene or butadiene is bubbled through a benzene solution of $RhH(CO)(PPh_3)_3$ for 5 min. the yellow solids $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ or $Rh(\pi\text{-1-methylallyl})(CO)(PPh_3)_2$ (ν_{CO} 1938 cm^{-1}) may be crystallised by addition of ethanol.

$IrH(CO)_2(PPh_3)_2$ reacts similarly with allene to give $Ir(\pi\text{-allyl})(CO)(PPh_3)_2$ (ν_{CO} 1930 cm^{-1}) although the reaction takes ca 30 min. at room temperature.

Addition of butadiene requires interaction of the gas with a refluxing benzene solution of $IrH(CO)_2(PPh_3)_2$ for ca 2 hr while the addition of tetramethylallene and isoprene require refluxing of a benzene solution of the hydride with a 10-20 fold excess of alkene for ca 12 hr.

N.m.r. spectra of the products shows that tetramethylallene gives the allylic group CH_2 ═══ C(Me) ═══ CH ——— $CHMe_2$ probably by addition of the hydride to the more stable isomer CH_2 ═══ C(Me) ——— CH ═══ CMe_2 which is formed during the reaction. Isoprene gives the allylic group CH_2 ═══ C(Me) ═══ CHMe on addition to $IrH(CO)_2(PPh_3)_2$ whereas the addition to $CoH(CO)_4$ yielded only a product with the isomeric π - CH_2 ═══ CH ═══ CMe_2 group.[69]

Attempts to add cyclohexa-1,3-diene, cycloocta-1,3-diene and 2,5-dimethylhexa-2,4-diene to $IrH(CO)_2(PPh_3)_2$ under similar conditions gave only substantial amounts of $IrH(CO)(PPh_3)_3$ and an unidentified brown product.

The reactions of $RhH(CO)(PPh_3)_3$ in benzene solution with dienes other than allene and butadiene occur slowly at room temperature and are complicated by a competing reaction associated with the growth of a band in the i.r. spectrum at 1965 cm^{-1} similar to that attributed to $[Rh(CO)(PPh_3)_2]_2$ formed by the decomposition of $RhH(CO)(PPh_3)_3$ in solution.[41] Evidence for the formation of an allyl complex (ν_{CO} at ca 1940 cm^{-1}) in solution was observed in each case, but particularly with isoprene and tetramethylallene which react faster, however pure compounds could not be obtained. Excess tetramethylallene was isomerised to 2,4-dimethylpenta-1,3-diene. Preparations of the simple allyl and 1-methylallyl rhodium species are also subject to such competing reactions if carried out above ca 20°.

The complexes $Ir(\pi\text{-allyl})(CO)(PPh_3)_2$, $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$, $Ir(\pi\text{-2-methylallyl})(CO)(PPh_3)_2$ and $Ir(\pi\text{-2-methylallyl})(CO)(AsPh_3)_2$ were also prepared by reaction of the appropriate Grignard reagent with trans-$MCl(CO)(PPh_3)_2$ or trans-$IrCl(CO)(AsPh_3)_2$.

Stabilities of the complexes The iridium complexes are pale yellow crystalline materials stable in the solid state towards atmospheric oxidation. They are soluble in aromatic solvents and to a slight extent in cyclohexane. Although fairly stable in CH_2Cl_2 they react slowly with $CHCl_3$ and with CS_2.

The rhodium complexes are much less stable and decompose slowly in the solid state under N_2 or in vacuum to yield a yellow-orange material (ν_{CO} 1960 cm^{-1}). The decomposition in solution is quite fast and dominates the reactions of these species; it seems to occur more rapidly in cyclohexane and CH_2Cl_2 than in benzene and is accelerated when the solutions are treated with CO. The decomposition product can be precipitated with EtOH and analyses as $Rh(CO)(PPh_3)_2$.

Although decomposition via $RhH(CO)(PPh_3)_2$ to give $[Rh(CO)(PPh_3)_2]_2$ probably occurs during the slow preparative reactions, n.m.r. analysis of the gas formed by decomposition of preformed $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ (by condensation into an n.m.r. tube containing deuteriobenzene) showed no allene or methyl acetylene. Resonances due to propene were observed whether the decomposition occurred slowly at room temperature or rapidly at 60°. At room temperature the solution becomes slightly orange-red whereas on heating it becomes deep-red. Both solutions yield a yellow-orange solid (ν_{CO} 1960 cm^{-1}) on addition of EtOH. It is possible that under these conditions the decomposition is occurring by the reaction

$$Rh(\pi\text{-}C_3H_5)(CO)(PPh_3)_2 \rightarrow$$

$$RhH(\sigma\text{-}C_3H_5)[(C_6H_4)PPh_2](CO)(PPh_3) \rightarrow$$

$$Rh[(C_6H_4)PPh_2](CO)(PPh_3) + C_3H_6$$

involving activation of an ortho hydrogen of a phenyl ring of a PPh_3 ligand. A similar reaction is found[63] for the species $RhR(PPh_3)_3$ (R = alkyl) and has been noted in Chapter III as a possible explanation for the formation of ethane from iridium-ethyl compounds. Such a reaction was also discussed[41] as an alternative pathway for the decomposition of $RhH(CO)(PPh_3)_3$ in solution.

The complex $Ir(\pi\text{-2-methylallyl})(CO)(AsPh_3)_2$ is much less stable towards atmospheric oxidation than are the PPh_3 complexes of iridium and decomposes in solution even under N_2 as is shown by the replacement of the carbonyl band at 1940 cm^{-1} by another at 1975 cm^{-1} (in cyclohexane).

B. Nuclear Magnetic Resonance Spectra

The data for the various allyls is summarised in Table 4.1. All show typical dynamic allylic spectra. Thus the very broad spectrum

Table 4.1 Nuclear magnetic resonance spectra (100 MHz) of iridium and rhodium allylic complexes in benzene at 35°

Complex	Principal resonances (τ values)	Description
$Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$	5.60 m; 8.18 vb	Broad AX_4 spectrum
$Rh(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$	5.10 m	Other signals extremely broad
$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ *	5.77 m; 7.91 b (1-methyl)	Methyl unresolved, other signals broad
$Rh(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ *	5.12 m; 6.90 vb; 8.05 d (1-methyl, J = 6.0 Hz)	Higher field signals very broad
$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$ †	8.14 (2-methyl)	Other signals broadened between $A_3M_2X_2$ and A_3X_4 spectrum
$Ir(\pi\text{-}C_4H_7)(CO)(AsPh_3)_2$ †	7.32 b; 7.70 (2-methyl); 8.65	$A_3M_2X_2$ spectrum
$Ir(\pi\text{-}C_5H_9)(CO)(PPh_3)_2$	7.94 (2-methyl); 8.01 d (1-methyl, J = 6.0 Hz)	Other signals very broad
$Ir(\pi\text{-}C_7H_{13})(CO)(PPh_3)_2$	7.66 (2-methyl); 8.79 d (isopropyl, J = 7.0 Hz)	Other signals very broad

m = multiplet; b = broad, vb = very broad, d = doublet

* = 1-methylallyl derivative, † = 2-methylallyl derivative

of Rh(π-allyl)(CO)(PPh_3)$_2$ at 35° begins to sharpen on warming towards an AX_4 spectrum, although at 70° the X signal (τ 7.26) is still ca 18 Hz broad.

Ir(π-allyl)(CO)(PPh_3)$_2$, which shows a similar AX_4 pattern at 35° to that of the rhodium analogue at 55°, sharpens rapidly on warming and at 60° in CD_2Cl_2 the A proton shows a sharp 1:4:6:4:1 quintet (τ 6.06; J 6.0 Hz) and the X resonance is a single broad line (τ 8.74) which is not sharpened by irradiation of the quintet and is probably broadened by averaged ^{31}P coupling (see below). Irradiation at τ 8.74 collapses the quintet to a single line.

On cooling the CD_2Cl_2 solution of Ir(π-allyl)(CO)(PPh_3)$_2$ the spectrum first broadens and then becomes typical of an AM_2X_2 system at ca -20°. On further cooling the spectrum again broadens until at -80° there appears a new AGMPX spectrum showing five signals of equal intensities: three single lines (half-width ca 15 Hz) at τ 6.16, 7.04 and 8.75 and two doublets at τ 9.08 and 10.25 (J ca 22 and 20 Hz, respectively). Spectra at 100 MHz and 56.45 MHz confirmed that these doublets arise from couplings and not from separate conformers.

The 2-methylallyl complex, Ir(π-2-methylallyl)(CO)(PPh_3)$_2$, shows a similar spectrum at -80° in CD_2Cl_2 having two broad lines at τ 7.47 and 8.74, two doublets at τ 9.55 and 10.00 (J 22 and 24 Hz) and a strong doublet at τ 8.32 (J 6.5 Hz) associated with the methyl group. (Intensities 1:1:1:1.3). These splittings are also frequency independent. Resolution of the fine structure on these resonances was not achieved at -75 - -80°, even on irradiation of the A proton in the allyl case, probably because the averaging process is not completely quenched at these temperatures.

The arsine complex, Ir(π-2-methylallyl)(CO)($AsPh_3$)$_2$ shows only a simple A_3GMPX spectrum at -70° (in $CDCl_3$) with a sharp methyl at τ 8.01 and sharp single lines at τ 7.22, 8.48, 9.07 and 9.52 suggesting that the splittings observed in the complexes with PPh_3 are due to ^{31}P coupling.

The highest field resonances of these three compounds at low temperatures can be assigned as the anti protons, since these are generally found at higher field than corresponding syn protons[70] and are expected to be more strongly coupled with the ^{31}P of a PPh_3 ligand. Such ^{31}P coupling to anti protons has been observed in planar complexes[67] containing π-allyl groups and phosphine ligands, although the coupling constants for the formally 5-coordinate species described above are considerably larger. The magnitude of such couplings will doubtless depend on the geometry of the compound and the orbitals involved in the M-P and M-allyl bonding.

The splitting of the methyl resonance in Ir(π-2-methylallyl)(CO)$(PPh_3)_2$ at low temperatures may be associated with a long range spatial coupling with a ^{31}P nucleus (see Discussion, below).

On warming the solutions of Ir(π-2-methylallyl)(CO)$(PPh_3)_2$ from -80° the two high field doublets coalesce simultaneously as the two lower single proton resonances coalesce. An $A_3M_2X_2$ spectrum is observed at ca 10° and the doublet structure of the methyl signal collapses to a single line. At 60° an A_3X_4 spectrum is beginning to appear with a sharp methyl singlet but the X resonance is still very broad.

Ir(π-2-methylallyl)(CO)$(AsPh_3)_2$ shows a sharp $A_3M_2X_2$ spectrum at 35° which also collapses at higher temperatures but is even more broad than the PPh_3 complex at 60°.

The further substituted allyl complexes also give temperature-dependent n.m.r. spectra but show the sharp resonances of the substituent groups at 35° with the exception of Ir(π-1-methylallyl)(CO)$(PPh_3)_2$ in which the methyl is a broad signal not resolved into a sharp doublet as in the rhodium analogue at this temperature. The allylic protons of these complexes give broad and/or obscured signals at 35° but the observed resonances are given in Table 4.1.

C. Reactions with Carbon Monoxide

1. Infra-red spectra When a cyclohexane solution of any of the iridium complexes (ν_{CO} ca 1946 cm^{-1}) is treated with CO the solution becomes colourless and there is rapid growth of new i.r. absorptions at 2014 and 1958 cm^{-1} and others which are overlapped between 1960 and

1930 cm^{-1}. Prolonged treatment with CO changes the relative intensities of these bands, which are complicated by overlap, and slight growth of new bands including one at 1644 cm^{-1}, assigned to an acyl group, is observed. These changes are all reversible on passing N_2 through the solution. Reversible CO insertion reactions of allyl groups have also been observed with cobalt carbonyl complexes.[71]

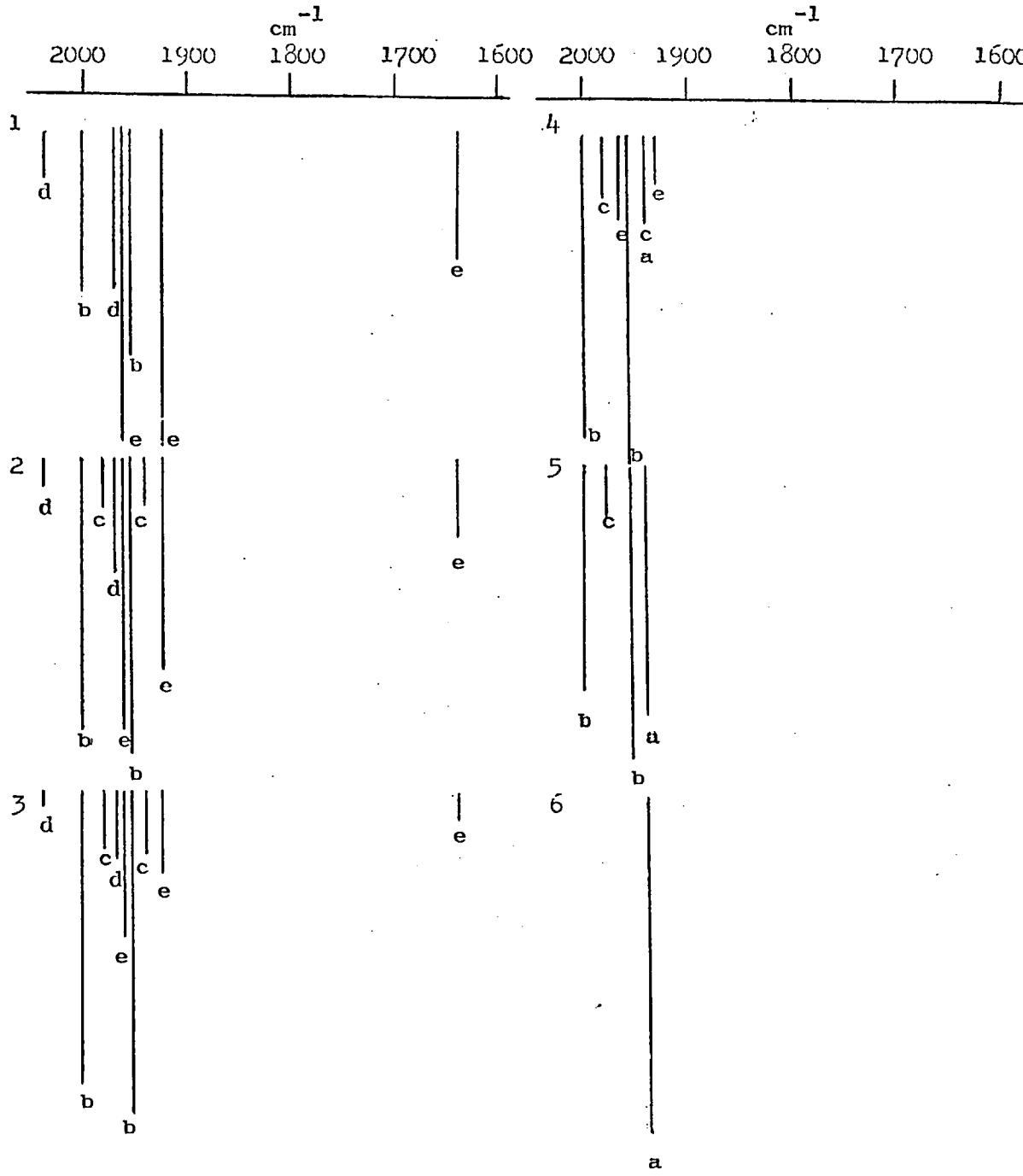
When suspensions of the allyl complexes in EtOH are stirred under an atmosphere of CO at room temperature for 6 - 8 hr the pure, white, crystalline complexes $Ir(COA)(CO)_2(PPh_3)_2$, A = allylic group, are obtained. [ν_{CO} 1973 s, 1925 s; ν_{CO}(acyl) 1638 m cm^{-1}]. On similar treatment at -5^{o} for 2 - 3 hr the allyl and 2-methylallyl complexes yielded pure, white crystals of $Ir(\sigma\text{-}C_3H_5)(CO)_2(PPh_3)_2$ and $Ir(\sigma\text{-}C_4H_7)(CO)_2(PPh_3)_2$ [ν_{CO} 1970 s, 1914 s; $\nu_{C=C}$(σ-allyl) 1617 w cm^{-1}]. Similar reactions of the other complexes, all of which have terminal substituents on the allyl group, yielded only mixtures of the starting complex and the corresponding acyl species.

The i.r. spectra of fresh cyclohexane solutions of $Ir(COA)(CO)_2(PPh_3)_2$ or $Ir(\sigma\text{-}A)(CO)_2(PPh_3)_2$ show the same complex pattern shown by the solutions formed by prolonged CO treatment of the monocarbonyl compounds, with only a very weak acyl absorption and dominated by bands at 2014 and 1958 cm^{-1}; these do not appear to correspond with any of the bands found in the mull spectra of the solids. Accordingly they are assigned to $Ir(\pi\text{-}A)(CO)_2(PPh_3)$, which is the principal dicarbonyl species present in solution. It is possible to follow the slow decomposition of the acyls $Ir(COA)(CO)_2(PPh_3)_2$ in CO-saturated cyclohexane solution (Figure 4.1). The assignment of the i.r. bands can be made on the basis of these results, n.m.r. data (see below) and by comparison with the spectra observed in the related alkyl and acyl systems described in Chapter III.

Table 4.2. Infrared spectra of species formed in the reaction of $Ir(\pi\text{-}2\text{-methylallyl})(CO)(PPh_3)_2$ with CO in cyclohexane solution

Compound	ν_{CO} cm^{-1}	Figure 4.1
$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$	1946 (s)	a
$Ir(\pi\text{-}C_4H_7)(CO)_2(PPh_3)$	2014 (s), 1958 (s)	b
$Ir(\sigma\text{-}C_4H_7)(CO)_2(PPh_3)$	1984, 1941	c
$Ir(\sigma\text{-}C_4H_7)(CO)_2(PPh_3)$	2044 (w), 1978 (s)	d
$Ir(COC_4H_7)(CO)_2(PPh_3)_2$	1968 (s), 1929 (s), 1644 (m)	e

Figure 4.1



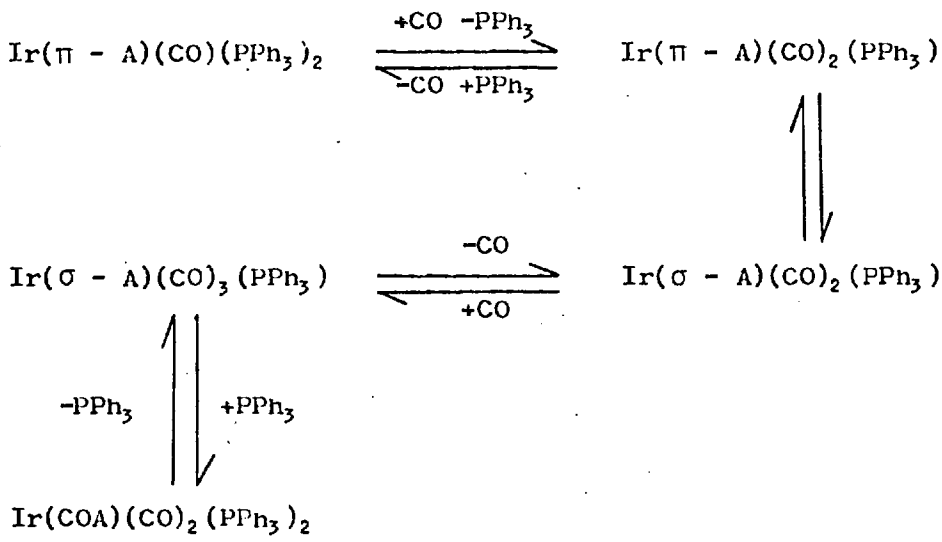
Infra-red spectra showing progressive changes on dissolution of $Ir(COC_4H_7)(CO)_2(PPh_3)_2$ in CO-saturated cyclohexane.

1. Immediately after dissolution.
2. After 1 min.
3. After 2 min.
4. After 15 min.
5. After then bubbling N_2 for 5 min.
6. After bubbling N_2 a further 15 min.

Assignments are given in Table 4.2.

Although $IrA(CO)_2(PPh_3)_2$ species decompose slowly in solution to the monocarbonyl, the i.r. spectra were studied between 25° and 60° in cyclohexane and 25° and -70° in CH_2Cl_2. The four bands at 2014 and 1958 cm^{-1} and 1984 and 1941 cm^{-1} were observed to change intensities reversibly in these pairs although the changes were relatively small. It is likely that the formal 5-coordination of iridium is not exceeded in the dominant π-form and that the σ-form exists in solution with only one PPh_3 group, particularly if σ - π exchange is important in averaging of the n.m.r. signals. This is further supported by the presence of tricarbonyl species in the system (Scheme 4.1).

Scheme 4.1.



Reactions of iridium allyl species in solution

The white acyl and dicarbonyl allyl species lose CO when heated in the solid state under N_2 at ca 80° to give the corresponding pale-yellow monocarbonyl complex.

In the preparations of the acyl $Ir(COC_7H_3)(CO)_2(PPh_3)_2$ white solids are often obtained which showed i.r. bands at 1988, 1966, 1923 and 1646 cm^{-1}. It is likely that the 1988 cm^{-1} band together with a weak absorption at 2045 cm^{-1} arise from contamination of the solid with $Ir(\sigma\text{-}C_7H_{13})(CO)_3(PPh_3)$, which is identified in solution

by its formation from the acyl, its n.m.r. spectrum and by comparison of its i.r. spectrum with other $IrR(CO)_3(PPh_3)$ species (see Chapter III).

$Ir(\pi\text{-2-methylallyl})(CO)(AsPh_3)_2$ reacts very rapidly with CO in cyclohexane to give a dicarbonyl, $Ir(\pi\text{-2-methylallyl})(CO)_2(AsPh_3)$ (ν_{CO} 2020; 1965 cm^{-1} in cyclohexane), which is unreactive both to further reaction with CO and to loss of CO on bubbling N_2 through the solution.

As noted above the reactions of the rhodium complexes in solution are complicated by decomposition which seems to be accelerated by interaction with CO. Thus treatment of a freshly prepared solution of $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ in cyclohexane (ν_{CO} 1955 cm^{-1}) with CO causes rapid replacement of the original spectrum by new bands at 2020, 2000 and 1965 cm^{-1}. Sweeping with N_2 then causes disappearance of the 2020 and 2000 cm^{-1} bands and growth of the 1965 cm^{-1} peak; only a small fraction of the starting material can be revived. The 1965 cm^{-1} band is that of the decomposition product while the other two bands may be assigned to $Rh(\pi\text{-allyl})(CO)_2(PPh_3)$ by comparison with the iridium system.

Prolonged treatment of $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ solutions with CO gives no new bands which can be related to allyl complexes but some absorption at 1785 and 1990 cm^{-1} (obscured) associated with the yellow dimer, $[Rh(CO)_2(PPh_3)_2]_2$. Subsequent treatment with N_2 leads to the replacement of these by the 1745 cm^{-1} band of the red, carbonyl-bridged dimer $[Rh(CO)(PPh_3)_2S]_2$ (see Scheme 1.1), concomitant with darkening of the colour to orange-red. The addition of PPh_3 to the CO treated solution followed by treatment with H_2 gives partial conversion to $RhH(CO)(PPh_3)_3$. These reactions are characteristic[41] of $[Rh(CO)(PPh_3)_2]_2$ which hence seems to be a major decomposition product of the allyls under these conditions.

2. N.m.r. Spectra When CO is passed through a deuteriobenzene solution of $Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$ for ca 5 min. a new broad AX_4 n.m.r. spectrum is observed at 35° with the A multiplet at τ 5.22 and the new X resonance, which is broader than in the starting material, centred at τ 8.12. After ca 2 hr treatment with CO this spectrum is substantially converted to another having a doublet

at τ 6.31 (J 6.0 Hz) and olefinic resonances at τ 4.50 to 5.10 which may be assigned to the acyl grouping Ir - CO - CH_2 - CH = CH_2. A weak broad resonance at τ 6.85 also grows with the acyl spectrum and may be assigned by comparison with other species to the methylene protons of a σ-C_3H_5 group. Thus the signal bears a similar chemical shift relation to the acyl methylene protons as found between $IrCH_2CH_3$ and $IrCOCH_2CH_3$ groups (Table 3.1), the difference being slightly smaller in this case because of the proximity of the double-bond. Its broadness may be ascribed to complex ^{31}P coupling and/or PPh_3 exchange and, in addition, the molecule being 5-coordinate may show fluxional behaviour (cf spectrum assigned to $Ir(C_2H_5)(CO)_2(PPh_3)_2$ in Chapter III).

As this signal appears with the acyl spectrum after prolonged CO treatment it is likely that it arises from $Ir(\sigma\text{-}C_3H_5)(CO)_3(PPh_3)$, which is expected to be an intermediate in forming the acyl and for which there is i.r. evidence. The species $Ir(\sigma\text{-}C_3H_5)(CO)_2(PPh_3)$, which is also present in the equilibria, was observed in the i.r. at an early stage in the reaction but may not be observed in the n.m.r. because of its low abundance, or if σ - π interconversion is an active mechanism for averaging of the $Ir(\pi\text{-}C_3H_5)(CO)_2(PPh_3)$ spectrum.

These spectra can all be interconverted by passage of CO or N_2 through the solution and are obtained whether $Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$, $Ir(\sigma\text{-}C_3H_5)(CO)_2(PPh_3)_2$ or $Ir(COC_3H_5)(CO)_2(PPh_3)_2$ are used as starting material, (Scheme 4.1). The substituted iridium allyl complexes behave similarly when treated with CO and the results are summarised below.

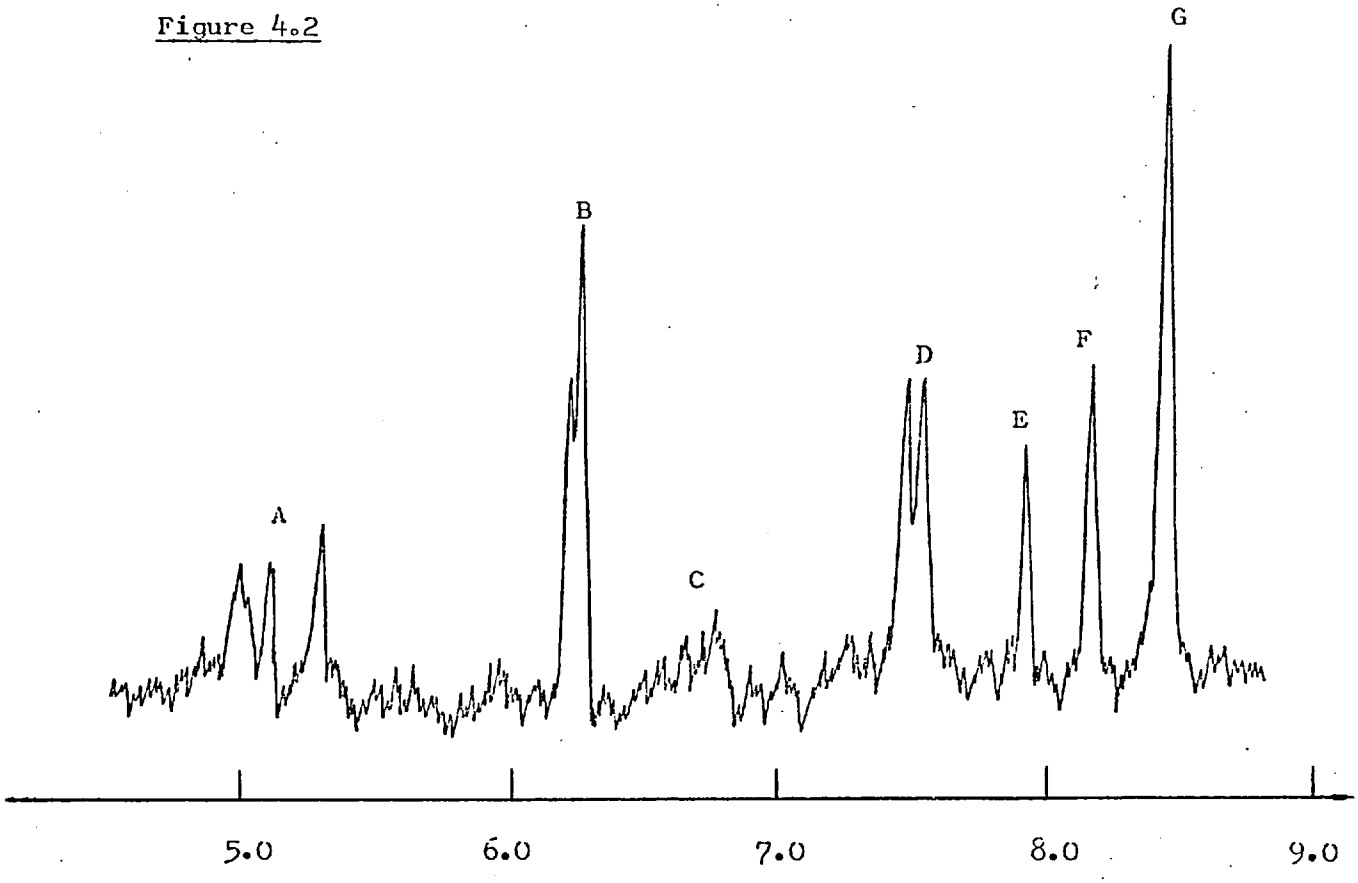
(a) Ir(π-1-methylallyl)(CO)$(PPh_3)_2$ gives rapidly a new multiplet at τ 5.28 and the methyl resonance is moved upfield to τ 8.29 while remaining broad. The rest of the signals are broadened as in the allyl case and the spectrum is associated with the dynamic allyl $Ir(\pi\text{-}C_4H_7)(CO)_2(PPh_3)$. Further treatment with CO slowly gives incomplete conversion to the acyl $Ir(COC_4H_7)(CO)_2(PPh_3)_2$ which has resonances at τ 4.3 to 4.75 (complex), 6.28 (four lines, apparently two doublets with $J_1 = J_2 = 6.0$ Hz) and 8.50 (methyl resonance, approximating to a triplet). This spectrum is readily explained

on the basis of an approximately 1:1 mixture of the isomers having cis- and trans-Ir-CO-CH_2-CH=CH-Me groups with separate methylene doublets at τ 6.22 and 6.33, and methyl doublets at τ ca 8.48 and 8.53 superimposed. There is no evidence for the Ir-CO-CH(Me)-$CH=CH_2$ grouping. A weak broad signal at τ 6.82 may be associated with a σ-C_4H_7 (but-2-enyl) species.

(b) Ir(π-2-methylallyl)(CO)$(PPh_3)_2$ gives a dynamic π-allylic dicarbonyl species with the methyl resonance as a doublet at τ 7.49 (J 6.0 Hz) and broad resonances at τ ca 7.50 and 8.75. This is similar to the spectrum of Ir(π-2-methylallyl)(CO)$(PPh_3)_2$ at 0° in CD_2Cl_2. The acyl next formed has olefinic signals at τ 4.75 to 5.35, a methylene signal at τ 6.21 and a methyl signal at τ 8.39. Splittings on the methyl signal were not resolved but the methylene appears as two peaks ca 3 Hz apart, with that to lower field being smaller. It is likely that these methylene protons are not equivalent and that rotational isomers together with allylic couplings give rise to the observed spectrum. A small broad signal at τ 6.74 and a singlet at τ 8.11 may be assigned to the σ-2-methylallyl group (see Figure 4.2).

(c) Ir(π-1,2-dimethylallyl)(CO)$(PPh_3)_2$. The dicarbonyl π-bonded species formed shows a doublet signal at τ 7.53 similar to that found in the 2-methylallyl complex and a slightly broad singlet at τ 8.33 as found for the 1-methylallyl complex. This group is clearly dynamic at 35° and some of the remaining protons are represented by a broad signal centred at τ ca 7.65, the others being obscured. The acyl species formed shows olefinic resonances (τ 4.25 - 4.90) and two peaks for the methylene protons - a singlet at τ 6.11 and a signal having two peaks at τ 6.20 and 6.24 similar to that found with the 2-methylallyl derivative. These can be assigned as in the case of the 1-methylallyl derivative [(a) above] as cis- and trans-Ir-CO-CH_2-C(Me)=CHMe, the methyl resonances all being superimposed in a broad signal at τ 8.44 to 8.55. The isomer having the more complex methylene signal accounts for ca 60% of the acyl in solution and is probably the trans one. Two small signals which grow at τ 8.10 and 8.22 and a broad resonance at τ 6.75 may be assigned as the two methyl and methylene resonances of Ir-CH_2-C(Me)=CHMe of Ir(σ-C_5H_9)$(CO)_3(PPh_3)$ as discussed above. No evidence is found for the Ir-CO-CH(Me)-C(Me)=CH_2 group.

Figure 4.2



τ Values

N.m.r. spectrum (100MHz) at 35° of deuteriobenzene solution of $Ir(\pi\text{-}2\text{-methylallyl})(CO)(PPh_3)_2$ after ca 2 hr treatment with CO

Signal	Assignment: Compound	Description
A	$\{ Ir(COC_4H_7)(CO)_2(PPh_3)_2 \}$ $\{ Ir(\sigma\text{-}C_4H_7)(CO)_3(PPh_3) \}$	olefinic
B	$Ir(COC_4H_7)(CO)_2(PPh_3)_2$	methylene
C	$Ir(\sigma\text{-}C_4H_7)(CO)_3(PPh_3)$	methylene
D	$Ir(\pi\text{-}C_4H_7)(CO)_2(PPh_3)$	methyl
E	solvent impurity	
F	$Ir(\sigma\text{-}C_4H_7)(CO)_3(PPh_3)$	methyl
G	$Ir(COC_4H_7)(CO)_2(PPh_3)_2$	methyl

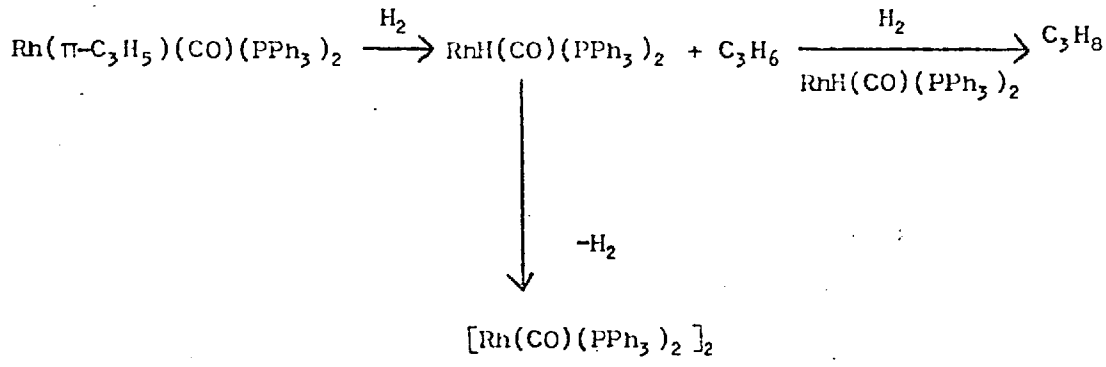
(d) Ir(π-1-isopropyl-,2-methylallyl)(CO)(PPh_3)$_2$. The π-bonded dicarbonyl shows a doubled methyl signal at τ 7.53 [cf (b) and (c) above], and a new isopropyl doublet at τ 8.96 (J 6.5 Hz). The acyl is associated with olefinic signals (τ 4.5 to 5.0), a singlet at τ 6.06, the complex τ 6.21 and 6.24 resonance [cf (b) and (c) above], a methyl singlet at τ 8.45 and two superimposed isopropyl doublets (J 6.5 Hz) at τ 9.06 and 9.07 which are also superimposed with that of the π-allylic dicarbonyl species. These signals are assigned to a mixture of cis- and trans- isomers of the Ir-CO-CH_2-C(Me)=CH-$CHMe_2$ group, as before, with ca 70% being that having the complex methylene signal (τ 6.23). As in the other reactions there is evidence for the presence of a small amount of σ-allyl species with signals at τ 6.75 (broad) and 8.18 (methyl) but there is no evidence for the acyl Ir-(CO)-$CH(Pr^i)$-C(Me)=CH_2.

(e) Ir(π-2-methylallyl)(CO)($AsPh_3$)$_2$ gave rapid replacement of the $A_3M_2X_2$ spectrum by another having equally sharp resonances at τ 7.14, 7.48 (methyl) and 8.72. No further significant signals were found after treatment with CO for 2 hr at 40°.

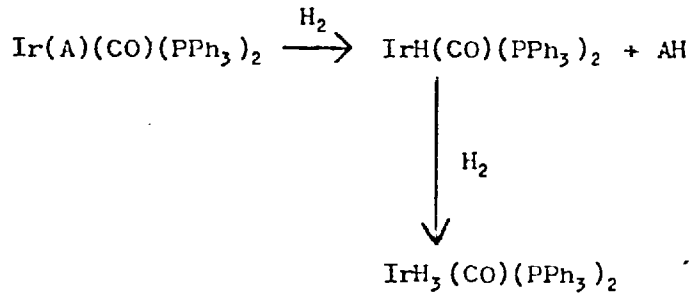
D. Reactions with Hydrogen and Hydrogen Chloride

The rhodium allyl species in benzene react very rapidly with H_2 at 1 atm. to give red solutions (ν_{CO} 1965 cm^{-1}) from which can be precipitated an orange solid (ν_{CO} 1960 cm^{-1}). If the reaction is carried out in a closed system and the gas condensed and sealed into an n.m.r. tube (containing deuteriobenzene) mixtures of propene and propane, whose ratio depends on the excess of H_2 used, are detected.

These reactions are readily explained by the ultimate formation of [Rh(CO)(PPh_3)$_2$]$_2$ through the decomposition of the intermediate RhH(CO)(PPh_3)$_2$ which acts as an hydrogenation catalyst.[41]



The iridium complexes $Ir(\pi - A)(CO)(PPh_3)_2$ also react with H_2 but the additionally carbonylated species do so only indirectly. Thus treatment of a solution of $Ir(COA)(CO)_2(PPh_3)_2$ and $Ir(A)(CO)_2(PPh_3)$ with H_2 first causes loss of CO to give $Ir(\pi - A)(CO)(PPh_3)_2$ before reaction with H_2 occurs. The species then formed is the known[65] $IrH_3(CO)(PPh_3)_2$ identified by analysis and i.r. (ν_{CO} 1965; ν_{IrH} 2080, 1785 cm^{-1}). This complex is presumably formed by oxidative addition of H_2 to $IrH(CO)(PPh_3)_2$.



$IrH_3(CO)(PPh_3)_2$ may also be prepared by addition of H_2 to $IrH(CO)_2(PPh_3)_2$ or by reaction of <u>trans</u>-$IrCl(CO)(PPh_3)_2$ with BH_4^- in ethanol in absence of excess PPh_3 or CO. It shows a very complex n.m.r. spectrum between τ 19.0 and 21.2.

The reaction of the iridium allyl complexes with HCl gives the very insoluble $IrHCl_2(CO)(PPh_3)_2$.[60] This prevents n.m.r. study to establish whether decarbonylation occurs before reaction with the acyl or dicarbonyl species; however, when HCl is passed into a cyclohexane solution of the carbonylated materials, $IrHCl_2(CO)(PPh_3)_2$ immediately precipitates and i.r. of the solution shows only bands of the dicarbonyl allyl species, which may indicate that, like H_2, HCl reacts rapidly only with $Ir(\pi\text{-}A)(CO)(PPh_3)_2$:

$$Ir(A)(CO)(PPh_3)_2 \xrightarrow{HCl} \text{trans-}IrCl(CO)(PPh_3)_2 + AH$$

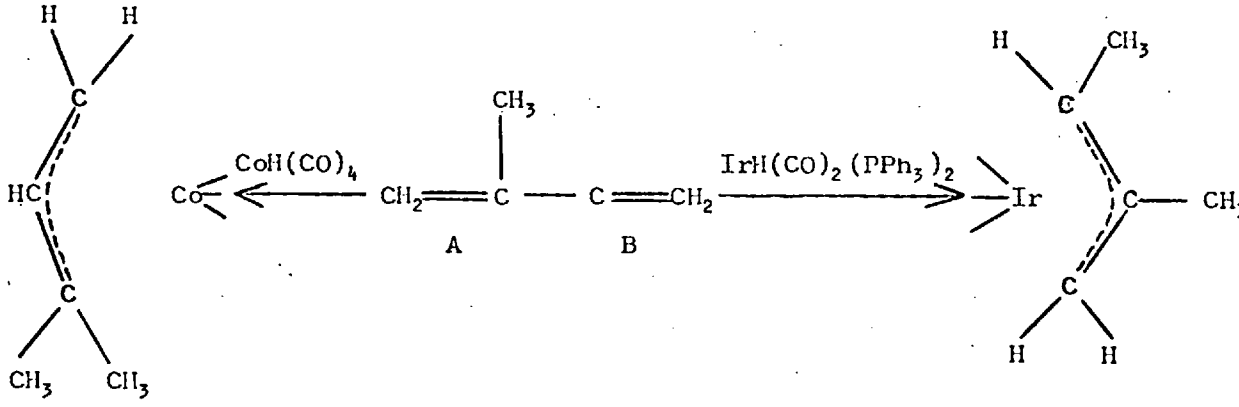
$$\text{trans-}IrCl(CO)(PPh_3)_2 \xrightarrow{HCl} IrHCl_2(CO)(PPh_3)_2$$

Discussion

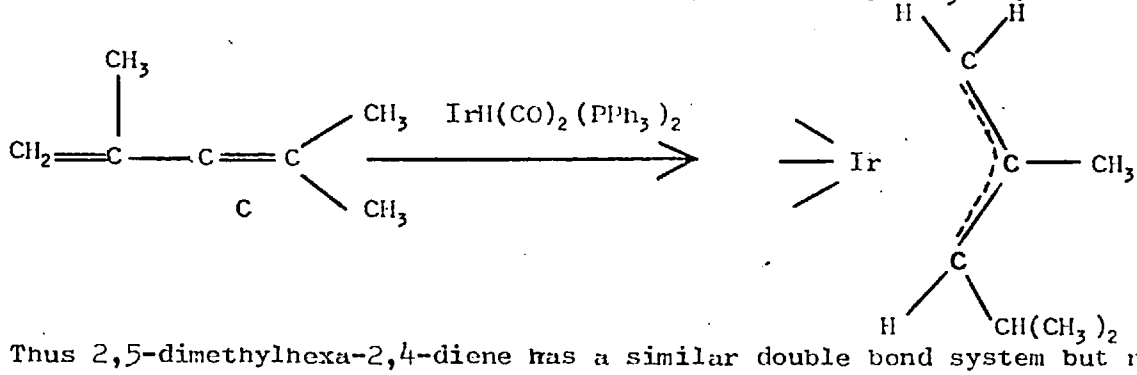
All of the stable solids described in this chapter contain π-allylic groups, with the exception of the two compounds $Ir(\sigma\text{-}A)(CO)_2(PPh_3)_2$, A = allyl or 2-methylallyl, which could be isolated presumably because of a fortuitous solubility effect. In all cases π-allylic species are dominant in solutions. The high stability compared with the simple alkyls described in Chapter III can be ascribed to the increased binding energy of the π-allylic system and also to the fact that hydride abstraction from the β-carbon of the alkyl chain to give the metal hydride is not favoured. This is so even in the σ-allyl form, because of the relatively high energy of the allene or acetylene which would thus be produced.

The fact that for the compounds with more than one CO group present decarbonylation occurs before reaction with H_2 at 1 atm., suggests that the relative strength of the $Ir\text{-}CH_2\text{-}$ and $Ir\text{-}CO\text{-}$ bonds in these complexes is more like $Ir\text{-}C_6H_5$ and $Ir\text{-}CO\text{-}C_6H_5$ than $Ir\text{-}CH_2\text{-}(CH_2)_nCH_3$ and $Ir\text{-}CO\text{-}(CH_2)_nCH_3$, since the benzoyl complex gives benzene on treatment with H_2 whereas aliphatic acyls give aldehydes. The complexes $Ir(COA)(CO)_2(PPh_3)_2$ are analogous to the stable acyl $Ir(COC_2H_5)(CO)_2(PPh_3)_2$, but on warming the solid the latter forms $IrH(CO)_2(PPh_3)_2 + C_2H_4 + CO$ (p.61) whereas the allylic derivatives only lose CO and retain the organic group as a π-allyl.

It was noted that the addition of $IrH(CO)_2(PPh_3)_2$ and $CoH(CO)_4$ to isoprene give different allyl products. If a simple 1,2-addition determines the nature of the products, then only Markownikov addition of a metal hydride to double bond A or B could lead to an allylic product. Thus the more acidic $CoH(CO)_4$ adds[69] to the more basic double bond (A) while $IrH(CO)_2(PPh_3)_2$ adds to double bond B.

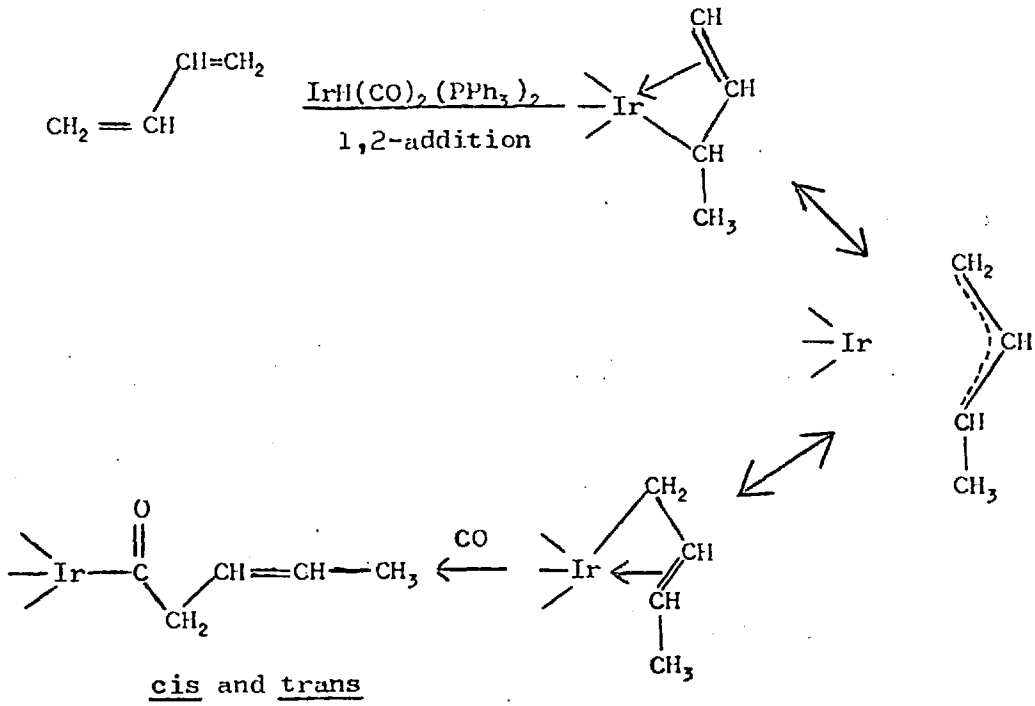


$IrH(CO)_2(PPh_3)_2$ adds to 2,4-dimethylpenta-1,3-diene (the isomer of tetramethylallene) at bond C but the reason is more likely to be steric than electronic as this addition gives the allyl group with fewer terminal substituents, which may interact sterically with bulky PPh_3 ligands.



Thus 2,5-dimethylhexa-2,4-diene has a similar double bond system but no addition was observed as a highly hindered allyl (1,1-dimethyl-, 3-isopropylallyl) would be formed.

The fact that CO insertion was found to occur only at the unsubstituted end of the allylic group further indicates that steric interactions are probably important. The final result in each case where an unsymmetrical allyl group is involved is thus a 1,4-addition, e.g.



cis and trans

The failure of cyclic conjugated dienes to add to the hydride also suggests that the formation of an allyl group with substituents on both terminal carbons is unfavourable.

Several structures can be proposed for the formally 5-coordinate complexes $Ir(\pi\text{-allyl})(CO)(PPh_3)_2$ involving square pyramidal or trigonal bipyramidal geometries and different ligand distributions. A reasonable proposal compatible with the experimental results is the idealised structure I (scheme 4.2). This has trans-PPh_3 ligands as postulated for the related 4-coordinate alkyl structures (Ref.30 and Chapter III), with the allylic group occupying a position trans to CO and the coordination site above the plane. In the alkyl species this vacant coordination site, if not blocked by a coordinating solvent, could activate an ortho proton of a phenyl group of one of the PPh_3 ligands providing a pathway for decomposition of the alkyl liberating alkane, or could activate a proton from the alkyl group leading to elimination of alkene. The structure I is only an extreme model and a whole range of distorted versions of this square-pyramid leading to the trigonal bipyramidal structure II are equally satisfactory.

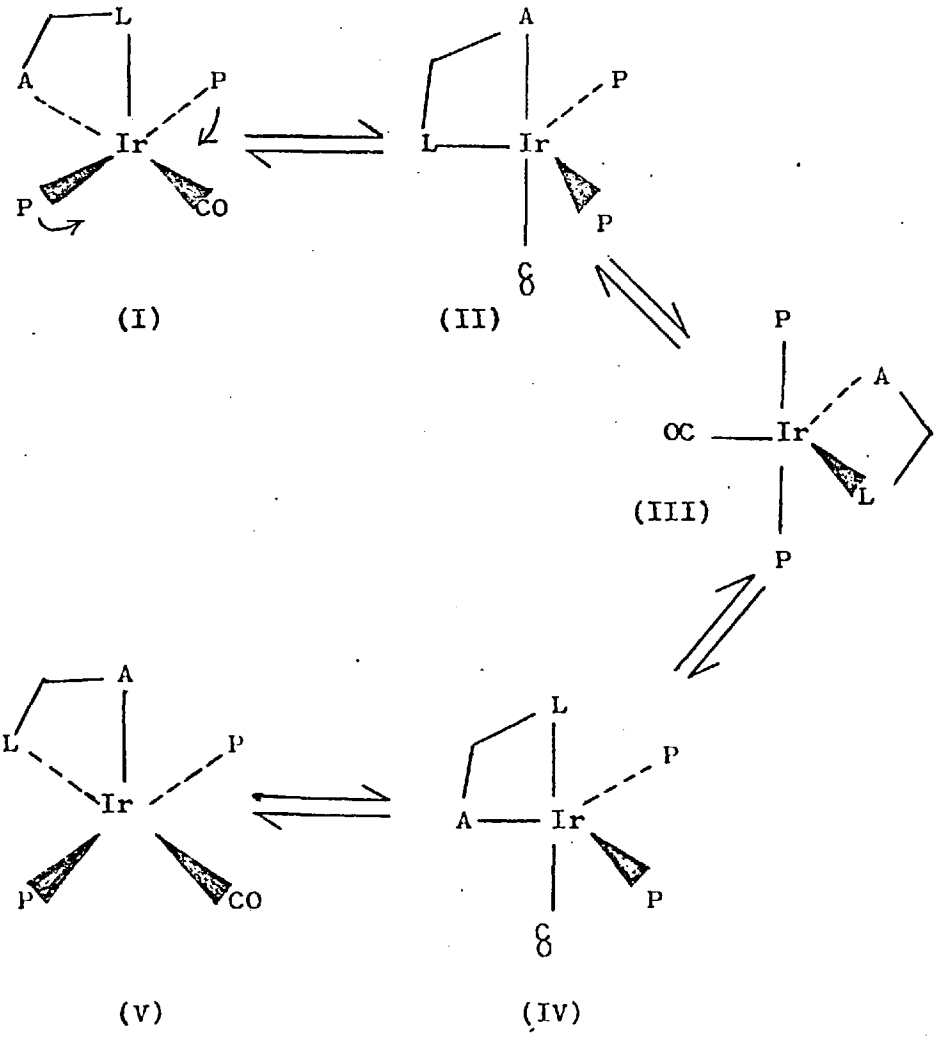
It can be noted that in any of these structures a close spatial relationship may exist between a 2-methyl substituent on the allyl group and a phosphorus atom of one of the ligands which could account

for the methyl doublet observed in the low temperature n.m.r. spectrum of Ir(π-2-methylallyl)(CO)(PPh_3)$_2$. Coupling was not observed[67] between ^{31}P and the 2-methyl group in Rh(π-2-methylallyl)(PPh_3)$_2$, but in a planar structure close approach would not be expected. The coupling should be destroyed by any relative motions of the ligands and is found to be lost at about the same temperature as the first averaging process for the terminal protons becomes rapid (see below) but is observed at 35° in the dicarbonyl 2-methylallyl species.

The proposed structure somewhere between I and II allows a simple mechanism to be envisaged which can explain the temperature dependence of the n.m.r. spectra which indicate, at first, syn-syn and anti-anti averaging which occur simultaneously. This can happen by rotation of the allyl group about an axis normal to the allyl plane and passing through the metal, or by a pseudo-rotation of the other ligands by a Berry-type mechanism[72] as in Scheme 4.2; such a mechanism providing a possible pathway for the fluxional behaviour of other formally 5-coordinate iridium(I) complexes, e.g. IrH(CO)$_2$(PPh_3)$_2$[36] and IrR(COD)($PPhMe_2$)$_2$, R = alkyl group; COD = cycloocta-1,5-diene.[73] A similar pseudo-rotation mechanism has been postulated[74] to account for averaging in the n.m.r. spectrum of Mo(π-C_5H_5)(π-C_4H_7)(CO)$_2$ which is formally 7-coordinate and in which fluxional behaviour may also be expected.

At higher temperatures syn-anti exchange becomes important. This can arise either from a σ - π mechanism or from a 'flip' mechanism[75] involving inversion of the allyl group about an axis through the terminal carbon atoms. The Ir(π-2-methylallyl)(CO)($AsPh_3$)$_2$ and Ir(π-allyl)(CO)(PPh_3)$_2$ species are at different stages of this averaging at 35° but neither the addition of a large excess of $AsPh_3$ or PPh_3 respectively, nor a change in basicity of solvent affected the line shapes appreciably. [Addition of excess PPh_3 to solutions of Ir(π-2-methylallyl)(CO)($AsPh_3$)$_2$ causes rapid exchange to give Ir(π-2-methylallyl)(CO)(PPh_3)$_2$]. This appears to rule out σ - π as the main mechanism for the averaging in the monocarbonyl species; however such a mechanism may operate in the dicarbonyl compounds as both σ- and π-allyl species are present in solution after treatment with CO.

Scheme 4.2



A L = allyl group.

Possible mechanism for syn-syn and anti-anti proton averaging by a pseudo-rotation mechanism.

The lability of the system $Ir(\pi - A)(CO)(PPh_3)_2 + CO$ in solution and the complex equilibria involved are such that no single species is ever present exclusively (Scheme 4.1). The complexes $Ir(\sigma - A)(CO)_2(PPh_3)$ may exist in solution with one or two PPh_3 ligands. No n.m.r. signal attributable to this σ-allyl group was observed but while this may indicate that the interconversion

$$Ir(\sigma - A)(CO)_2(PPh_3) \rightleftarrows Ir(\pi - A)(CO)_2(PPh_3)$$

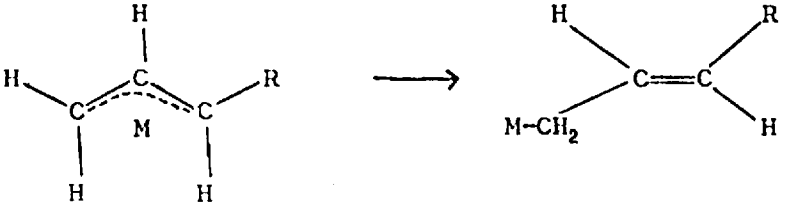
is occurring fast compared with the n.m.r. time scale, the low abundance of this σ-allyl species may equally be preventing observation of its spectrum.

CO insertion occurs exclusively at the unsubstituted end of the allyl group and cis and trans isomers about the double-bond are formed when a terminal substituent is present. The isomer which has the methylene resonance like that of the $Ir-CO-CH_2-C(Me) = CH_2$ group, and which becomes relatively more abundant with increasing substitution is assigned as that having the substituent trans to the acyl group.

Since syn - anti equilibration is occurring at 35° and the methyl resonance of the π-1-methylallyl is broadened it seems possible that there is an interchange of site between the terminal substituent and the allylic proton on the same carbon atom. At any given temperature the substituent group would be expected to populate the syn position increasingly in the order of increasing steric hindrance, i.e.

π-1-methylallyl < π-1,2-dimethylallyl < π-1-isopropyl-2-methylallyl,

the temperature for quenching of such averaging would indeed be expected to follow this order. It is consistent with this that the relative abundance of the trans isomer of the acyl increases from 50% to 70% in the same order if the syn position of the π-allyl becomes the trans position of the σ-allyl and thus the acyl, i.e.



syn trans

The hydroformylation of butadiene using $RhH(CO)(PPh_3)_3$ in molten PPh_3 under conditions in which double-bond migration during hydroformylation of alk-1-enes is largely inhibited has been described in Chapter II. Although a high ratio of straight- to branched-chain C_5-aldehydes (10:1) was found less than 30% of the products could be attributed to C_6-dialdehydes. It is thus possible that double-bond migration is not the principal factor responsible for the prevention of formation of dialdehydes.

If allylic rather than alkyl intermediates are favoured under hydroformylation conditions and since these can only arise from a Markownikov addition of the metal hydride to butadiene, the formation of a linear acyl must occur by CO insertion at the other, unsubstituted end of the allylic system, i.e. an overall 1,4-addition as described above for the iridium system. Such a pathway would thus account for the formation of predominantly linear aldehyde and also for the low conversion to dialdehyde as the remaining double-bond would be non-terminal in the $\beta\gamma$ position. Such an intermediate, $CH_3CH{=}CHCH_2CHO$, would also be consistent with the distribution reported for the dialdehyde fraction in a related system[47] (82% 2-methylpentan-1,5-dial + 2-ethylbutan-1,4-dial; ratio 2:1).

EXPERIMENTAL

A. General

Microanalyses were by the Microanalytical Laboratory, Imperial College, and are collected in Table E.1.

Molecular weights were determined using an Hitachi-Perkin Elmer Model 115 osmometer at 37° under N_2 and melting points (uncorrected) on a Köfler hot-stage microscope.

N.m.r. spectra at 35° were obtained using a Perkin Elmer R14 spectrometer at 100 MHz for protons and 94.1 MHz for fluorine. Measurements at other temperatures were obtained on Varian Associates HA 100 (100 MHz; by Mr P.N. Jenkins, Imperial College) and 43100 (56.45 MHz) spectrometers.

Infra-red spectra were taken on Perkin Elmer model 237 and 257 spectrophotometers; spectra of solids being measured as nujol mulls and solution spectra measured with compensation in 0.1, 0.5 and 1.0 mm liquid cells. A Research and Industrial Instrument Company variable temperature unit was employed in obtaining infra-red spectra in solution at other than room temperature.

G.l.c. measurements were made using Perkin Elmer model F11 chromatographs with flame ionisation detectors and peak areas obtained using a Kent Chromalogue electronic integrator.

Rhodium trichloride trihydrate was from Johnson Matthey Limited; the only transition metal impurity is believed to be possibly a trace of iridium;[76] triphenylphosphine (Albright and Wilson Limited) was recrystallised from benzene-ethanol before use. CO from Air Products was treated to remove pentacarbonyliron(0) impurity by passing the gas over asbestos wool at 500°. Hydrogen, from British Oxygen Company, was purified by passage through an Engelhard "Deoxo" catalyst tube. Premixed CO + H_2 and CO + C_3H_6 + H_2 (British Oxygen Company) were analysed mass spectroscopically and were within 2% of the nominal value.

All solvents were of reagent grade quality and were dried and degassed before use. All experiments were carried out under N_2.

$RhH(CO)(PPh_3)_3$ was prepared[33] by Mr H.J. Smith.

B. Chapter I

Sources and methods of purification of alkenes were as described previously[77] and sodium dried AnalaR benzene (Hopkins and Williams) was used throughout as a solvent.

1. Gas uptake measurements The method used was essentially that described previously[42,34] for hydrogenation reactions but with a different initiation procedure. Benzene was degassed by evacuation followed by saturation with CO + H_2 (1:1) six times in the thermostatically jacketed reaction flask attached to a vacuum line. The distilled alkene was added from a burette directly into the flask and, without further degassing, the pressure was adjusted so that the pressure at which the readings were required would be reached after 2-3 min. The reaction was started by adding the catalyst in a teflon bucket to the vigorously stirred solution. Complete dissolution was shown to occur very rapidly (< $^1/_4$ min.). This procedure was adopted in order to avoid pumping on the solution containing the catalyst since, after treatment with CO, rapid dimerisation occurs on lowering the pressure as discussed in Chapter I. On completion of each run the system was evacuated and the partial pressure of the solution determined to ± 0.2 cm.

For very high catalyst concentrations (25 to 50 mM) the bulk of catalyst required a different technique. The solid was weighed directly into the reaction flask and benzene was degassed and saturated with CO + H_2 in a pressure-equalised dropping funnel attached to the reaction flask. The benzene was then added to the catalyst, the solution stirred, the pressure adjusted to a suitable value and then alkene was added to initiate the run. The total volume of the solution was 50 ml.

As before[42,34] the rate of uptake of gases was taken at the standard gas pressure from the tangent of the plot of pressure vs time.

2. Reactions at 1 atmosphere A 25 ml flask with a side arm capped by a suba-seal, clamped to a shaker and immersed in a thermostat bath was attached by polythene tubing to a premixed gas cylinder. Catalyst was weighed directly into the flask which was then purged with reaction gas for 5 - 10 min. by allowing the gas to pass out of a thin steel tube inserted through the suba-seal. Benzene was then added by

syringe through the seal, followed by alkene; the steel tube was removed and the shaker started. The gas flow was maintained through a bubbler take-off placed near the neck of the flask to ensure that the correct gas mixture was constantly replenished during the reaction. Samples were removed by micro-syringe through the seal for g.l.c. analysis.

For separation of aldehydes a 2 m squalene column at 90° was used. Separation of alkene isomers and alkane was made using a 4 m silver nitrate-diethyleneglycol column at 40°. Convenient separation of hex-1-ene, hexane and hex-2-enes together, 2-methylhexaldehyde and n-heptaldehyde was achieved using a 2 m squalene column in conjunction with a linear temperature programmer between 40 and 130°. The ratio of straight- to branched-chain aldehyde was reproducible to within ca 3% and the proportion of hydrogenation and isomerisation products to within 10-15%.

Reactions with styrene were carried out similarly but samples were analysed by n.m.r. measurements.

The acyl species prepared from $RhH(CO)(PPh_3)_3$ and styrene were formed under an atmosphere of CO on dropping $RhH(CO)(PPh_3)_3$ in a teflon bucket into a benzene solution of styrene in a flask attached to a vacuum line. After stirring, the solution was passed by way of a steel tube inserted through a suba-seal on a side-arm of the flask directly into the i.r. cell or n.m.r. tube under the CO atmosphere.

C. Chapter II

Reactions at high pressures These reactions were carried out in a Parr series 4500 1 ℓ stainless steel autoclave fitted with a pressure gauge, stirrer and liquid and gas samplers.

The autoclave was charged with PPh_3 and dry benzene, if used. When liquid alkene was added the catalyst was suspended in a sealed thin-glass vial from an arm on the stirrer shaft and the autoclave sealed. (This precaution was taken in order to avoid alkene isomerisation before the desired reaction conditions had been attained and was not necessary in the case of propene, hex-1-yne or butadiene substrates). The interior of the autoclave was then purged with N_2, and brought to a temperature about 10° below that required. The premixed gases were

then admitted to the desired pressure and the stirrer started. The reaction began at once on pressure breakage of the glass vial. The hydroformylation reaction is appreciably exothermic and consequently, within a minute or so of initiation, temperature rises of up to 10°C were observed. The temperatures of the reactions quoted are hence those of the reacting system. The pressure was maintained to within 10 lb.in^{-2} during the reaction period, after which stirring was stopped and the autoclave rapidly cooled. Liquid samples were then withdrawn for analysis. For reactions without solvent crystallisation of PPh_3 occurred on cooling so that the supernatant liquid was decanted and filtered prior to analysis. For hydroformylation of butadiene the required amount was condensed into the autoclave at -80°. Propene was introduced with the gas mixture.

In hydroformylation of hex-1-ene with $CO:H_2$ different from 1:1 there is a slight enrichment of the more abundant gas during a reaction carried out in this way. Thus for $CO:H_2$ 1:2 at a total pressure of 400 lb.in^{-2} after complete conversion of 0.1 mole alkene the gas ratio would be ca 1:2.3.

D. Chapter III

Preparations

1,1,2,2-Tetrafluoroethylcarbonylbis(triphenylphosphine)rhodium(I)
$RhH(CO)(PPh_3)_3$ (0.8 g) was placed in a 50 ml Carius tube and toluene (20 ml) and C_2F_4 (equivalent to ca 5 atm. at 25°) were condensed in and the tube sealed. [The C_2F_4 was prepared by cracking P.T.F.E. (Fluon, Grade GI, I.C.I. Limited) at 600° and pressures below 5 mm]. After warming to room temperature the tube was shaken for 12 hr, during which time the colour of the solution changed to a brighter yellow. After opening the tube, petroleum (b.p. 60 - 80°) (10 ml) was added and the precipitated yellow complex filtered, washed with petroleum and dried in vacuum (0.66 g, 80%).

1,1,2,2-Tetrafluoroethyldicarbonylbis(triphenylphosphine)rhodium(I)
A suspension of $Rh(C_2F_4H)(CO)(PPh_3)_2$ (0.2 g) in EtOH (10 ml) was stirred for 45 min. under an atmosphere of CO and the precipitated white complex filtered under N_2, washed with EtOH and dried in vacuum (0.17 g, 82%).

1,1,2,2-Tetrafluoroethylcarbonyl(sulphurdioxide)bis(triphenylphosphine)-rhodium(I) Toluene (5 ml) was degassed in a flask provided with a magnetic stirrer and attached to a vacuum line. $Rh(C_2F_4H)(CO)(PPh_3)_2$ (0.1 g) was then dropped into the toluene from a bucket system under 1 atm. SO_2 and the solution stirred for 45 min. during which time the fine yellow complex precipitated. The system was flushed with N_2 and the solid collected, washed with petroleum (b.p. 40 - 60°) and dried in vacuum. (0.06 g, 55%).

Propionyldicarbonylbis(triphenylphosphine)iridium(I) $IrH(CO)_2(PPh_3)_2$ (1 g) was placed in a 100 ml autoclave and benzene (50 ml) added. The autoclave was pressurised with 15 atm. CO and 15 atm. C_2H_4 and rocked for 12 hr at 70°. After cooling to room temperature the pale yellow solution was siphoned into a flask together with a benzene washing of the autoclave and the volume taken to 10 ml under reduced pressure. EtOH (10 ml) was added to give the white complex which was filtered off, washed with EtOH and dried in vacuum. (1.0 g, 93%). The butyryl complex was obtained by the same procedure using C_3H_6 instead of C_2H_4.

Propionyldicarbonylbis(triphenylphosphine)rhodium(I) Benzene (5 ml) was degassed in a flask provided with a magnetic stirrer and attached to a vacuum line. $RhH(CO)(PPh_3)_3$ (0.1 g) was added from a bucket system under an atmosphere of CO + C_2H_4 (1:1). After being stirred for 10 min. the solution was a brighter yellow than the solution of the starting material. Samples for i.r. and n.m.r. were siphoned off under the CO + C_2H_4 atmosphere through steel tubing directly into the solution cell or n.m.r. tube and the compound characterised by comparison with the iridium analogue. An extremely unstable yellow solid was obtained by carrying out the reaction in toluene. After the solution had become bright yellow in ca 15 min. the atmosphere in the reaction flask was changed to nearly pure C_2H_4 without pumping on the solution, by equilibrating several times with a much larger volume of gas which was pumped each time and filled with pure C_2H_4. Light petroleum (b.p. 60 - 80°) (5 ml) saturated with C_2H_4 was then added and the mixture stirred for 30 min. at -10°, during which time the bright yellow complex precipitated. This was collected and shown to be the complex by i.r. (nujol mull); it could not however be pumped as in the absence of C_2H_4 it rapidly decomposed to give $[Rh(CO)(PPh_3)_2]_2$. Attempts to precipitate the compound in the presence of CO resulted in decomposition to $RhH(CO)(PPh_3)_3$ and $[Rh(CO)_2(PPh_3)_2]_2$.

Acetyldicarbonylbis(triphenylphosphine)iridium(I) $IrCl(CO)(PPh_3)_2$ (1 g) was dissolved in benzene (80 ml) and CO bubbled through the solution. 7 ml of a 10% solution of CH_3Li in diethyl ether was added dropwise and the colour changed to orange red. The volume was then taken to 50 ml at reduced pressure and the solution filtered. The filtrate was passed to a 100 ml autoclave and this was rocked for 12 hr at 60° under 40 atm. CO. After cooling to room temperature the clear yellow solution was extracted through steel tubing and when the volume had been reduced to 10 ml EtOH (10 ml) was added to give the yellow complex which was filtered off and dried in vacuum, (0.3 g, 29%). The compound was shown to be identical to that prepared by a different preparative route.[53b]

Phenylcarbonylbis(triphenylphosphine)iridium(I) To $IrCl(CO)(PPh_3)_2$ (0.5 g) in diethyl ether (25 ml) was added a slight excess of PhLi in diethyl ether solution prepared and standardised as described.[78] After being stirred for 12 hr the orange solution was filtered and the filtrate treated with an equal volume of EtOH to yield the orange complex which was filtered off, washed with EtOH, and dried in vacuum (0.2 g, 38%).

Benzoyldicarbonylbis(triphenylphosphine)iridium(I) Cyclohexane (15 ml) was saturated with CO and siphoned under CO into a flask containing $Ir(Ph)(CO)(PPh_3)_2$ (0.1 g). The solution was stirred and concentrated under a stream of CO to yield white crystals of the complex which were filtered off and dried in vacuum (0.1 g, 90%).

E. Chapter IV

Allene from the Matheson Company Limited, butadiene from British Hydrocarbon Chemicals Limited and tetramethylallene from Koch-Light Limited were used as supplied; isoprene; cyclohexa-1,3-diene and 2,5-dimethylhexa-2,4-diene from Koch-Light Limited, and cycloocta-1,3-diene from City Service Research and Development Company were purified by vacuum distillation before use.

1. Preparations, (a) Insertion reactions

π-Allylcarbonylbis(triphenylphosphine)rhodium(I) and π-1-Methylallylcarbonylbis(triphenylphosphine)rhodium(I) Allene or butadiene was bubbled through a solution of $RhH(CO)(PPh_3)_3$ (0.3 g) in toluene (10 ml)

for 5 min. The addition of EtOH (20 ml) with stirring of the solution under N_2 at 0^o precipitated yellow crystals of the complex which were filtered, washed with EtOH and dried in vacuum (ca 0.2 g, 87%).

π-Allylcarbonylbis(triphenylphosphine)iridium(I) and π-1-Methylallylcarbonylbis(triphenylphosphine)iridium(I) Allene or butadiene gas was bubbled through a solution of $IrH(CO)_2(PPh_3)_2$ (0.3 g) in benzene (10 ml). In the case of allene the solution was stirred for 1 hr at room temperature, while for butadiene the solution was refluxed for 2 hr. Addition of EtOH (20 ml) to the cold solution gave pale yellow crystals of the complex which were filtered, washed with EtOH and dried in vacuum (ca 0.25 g, 82%).

π-1,2-Dimethylallylcarbonylbis(triphenylphosphine)iridium(I) and π-1-Isopropyl-2-methylallylcarbonylbis(triphenylphosphine)iridium(I) Isoprene (0.8 ml) or tetramethylallene (1.0 ml) was added to a solution of $IrH(CO)_2(PPh_3)_2$ (0.3 g) in benzene (10 ml) and the solution refluxed for 12 hr. EtOH (20 ml) was added to the cold stirred solution to give pale-yellow crystals of the complex, which were filtered, washed with EtOH and dried in vacuum (ca 0.2 g, 62%).

Interactions of $IrH(CO)_2(PPh_3)_2$ with cycloocta-1,3-diene, cyclohexa-1,3-diene and 2,5-dimethylhexa-2,4-diene These were carried out as for the isoprene reaction. The i.r. spectrum of the solution was followed over a reflux period of 48 hr after which reaction seemed to be complete. EtOH was added to the stirred, brown solution at room temperature and a yellow solid precipitated which was identified by i.r. and n.m.r. as $IrH(CO)(PPh_3)_3$. The other product was not identified.

(b) Grignard reactions

π-2-Methylallylcarbonylbis(triphenylphosphine)iridium(I) and π-2-Methylallylcarbonylbis(triphenylarsine)iridium(I) To $IrCl(CO)(PPh_3)_2$ or $IrCl(CO)(AsPh_3)_2$ (0.5 g) in diethyl ether (25 ml) was added dropwise a slight excess of 2-methylallylmagnesium chloride in diethyl ether. After stirring for 4 hr the yellow solid was filtered and washed with EtOH. Recrystallisation from toluene-EtOH yielded the complex which was collected, washed with EtOH and dried in vacuum (ca 0.3 g, 60%).

π-Allylcarbonylbis(triphenylphosphine)iridium(I) and rhodium(I) identical with the products from the insertion reactions were also prepared by this method using allylmagnesium chloride.[79]

2. Reactions with carbon monoxide

(a) Dicarbonyl acyl species $Ir(COA)(CO)_2(PPh_3)_2$; A = C_3H_5, C_4H_7 (1-methylallyl and 2-methylallyl), C_5H_9 and C_7H_{13}

A suspension of $Ir(\pi\text{-}A)(CO)(PPh_3)_2$ (0.1 g) in EtOH (10 ml) was stirred under CO for 8 hr and the precipitated white crystalline complex filtered, washed with EtOH and dried in vacuum (ca 0.08 g, 75%).

(b) Dicarbonyl σ-allyl species $Ir(\sigma\text{-}A)(CO)_2(PPh_3)_2$; A = C_3H_5, C_4H_7 (2-methylallyl)

A suspension of $Ir(\pi\text{-}A)(CO)(PPh_3)_2$ (0.1 g) in EtOH (10 ml) was stirred under CO at -5° for 4 hr. The white precipitated complex was filtered cold, washed with cold EtOH and dried in vacuum (ca 0.08 g, 75%).

The dicarbonyl acyl and dicarbonyl σ-allyl species decompose on heating at ca 80° to give the compound $Ir(\pi\text{-}A)(CO)(PPh_3)_2$ from which they were formed.

3. Interactions with hydrogen

Trihydridocarbonylbis(triphenylphosphine)iridium(III)

(a) From $Ir(\pi\text{-}A)(CO)(PPh_3)_2$, A = C_3H_5, C_4H_7, C_5H_9, C_7H_{13}

Hydrogen was bubbled through a solution of $Ir(\pi\text{-}A)(CO)(PPh_3)_2$ (0.1 g) in benzene (5 ml) for 1 hr. Addition of EtOH yielded the yellow complex which was filtered, washed with EtOH and dried in vacuum (ca 0.075 g, 80%).

(b) From $IrH(CO)_2(PPh_3)_2$

Hydrogen was bubbled through a solution of $IrH(CO)_2(PPh_3)_2$ (0.2 g) in benzene (5 ml) under reflux for 2 hr. Addition of EtOH to the cold stirred solution yielded the yellow complex which was collected (0.15 g, 78%).

(c) From trans-$IrCl(CO)(PPh_3)_2$

A solution of $NaBH_4$ (0.05 g) in EtOH (5 ml) was added to a suspension of $IrCl(CO)(PPh_3)_2$ (0.1 g) in EtOH (15 ml) and the suspension stirred and heated for 1 hr. After cooling to 0° the yellow precipitate of the complex was collected (0.07 g, 73%). The product in each case was identified by analysis, i.r. and n.m.r. as that reported.[65]

Table E.1. Analytical Data

Compound	m.p.[a]	Found				Empirical Formula	Required			
		C(%)	H(%)	Other Elements (%)	M[b]		C (%)	H (%)	Other Elements (%)	M
$Rn(C_2F_4H)(CO)(PPh_3)_2$	116	62.0	3.9	P, 7.9	445	$C_{39}H_{31}OP_2Rh$	61.9	4.1	P, 8.2	756
$Rn(C_2F_4H)(CO)_2(PPh_3)_2$	[c]	61.8	4.2	F,9.9; P,7.8	[d]	$C_{40}H_{31}O_2P_2Rh$	61.2	4.0	F,9.7; P,7.9	784
$Rn(C_2F_4H)(CO)(SO_2)(PPh_3)_2$	[c]	56.8	3.7	P, 7.6	870	$C_{39}H_{31}O_3P_2RhS$	57.1	3.8	P, 7.6	820
$Ir(COC_2H_5)(CO)_2(PPh_3)_2$	116	58.8	4.3	O, 4.6	820	$C_{41}H_{35}IrO_3P_2$	59.3	4.2	O, 5.8	830
$Ir(Ph)(CO)(PPh_3)_2$	[c]	63.1	4.2	-	[d]	$C_{43}H_{35}IrOP_2$	62.8	4.3	-	822
$Ir(COPh)(CO)_2(PPh_3)_2$	[c]	61.6	4.3	-	[d]	$C_{45}H_{35}IrO_3P_2$	61.5	4.0	-	878
$Rn(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$	78	68.3	5.0	-	[d]	$C_{40}H_{35}OP_2Rh$	68.9	5.0	-	696
$Rn(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$[e]	76	69.2	5.2	-	[d]	$C_{41}H_{37}OP_2Rh$	69.3	5.3	-	710
$Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2$	145	59.8	4.3	-	751	$C_{40}H_{35}IrOP_2$	61.1	4.4	-	786
$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$[e]	142	61.6	4.7	-	805	$C_{41}H_{37}IrOP_2$	61.5	4.7	-	800
$Ir(\pi\text{-}C_5H_9)(CO)(PPh_3)_2$	133	62.2	4.9	-	781	$C_{42}H_{39}IrOP_2$	61.9	4.8	-	814
$Ir(\pi\text{-}C_7H_{13})(CO)(PPh_3)_2$	134	63.1	5.2	-	709	$C_{44}H_{43}IrOP_2$	62.7	5.1	-	842
$Ir(\pi\text{-}C_4H_7)(CO)(PPh_3)_2$[f]	143	61.7	4.7	-	778	$C_{41}H_{37}IrOP_2$	61.5	4.7	-	800
$Ir(\pi\text{-}C_4H_7)(CO)(AsPh_3)_2$[f]	125	54.5	4.4	-	[d]	$C_{41}H_{37}As_2IrO$	55.4	4.2	-	888
$Ir(COC_3H_5)(CO)_2(PPh_3)_2$	[c]	60.1	4.4	-	[d]	$C_{42}H_{35}IrO_3P_2$	59.9	4.2	-	842
$Ir(COC_4H_7)(CO)_2(PPh_3)_2$[e]	[c]	60.1	4.4	-	[d]	$C_{43}H_{37}IrO_3P_2$	60.3	4.3	-	856
$Ir(COC_4H_7)(CO)_2(PPh_3)_2$[f]	[c]	59.8	4.5	-	[d]	$C_{43}H_{37}IrO_3P_2$	60.3	4.3	-	856
$Ir(COC_5H_9)(CO)_2(PPh_3)_2$	[c]	60.8	4.7	-	[d]	$C_{44}H_{39}IrO_3P_2$	60.8	4.5	-	870

Table E.1. (continued)

Compound	m.p.[a]	Found				Empirical ormula	Required			
		C(%)	H(%)	Other Elements (%)	M[b]		C (%)	H (%)	Other Elements (%)	M
$Ir(COC_7H_{13})(CO)(PPh_3)_2$	c	61.4	5.0	-	d	$C_{46}H_{43}IrO_3P_2$	60.9	4.9	-	886
$Ir(\sigma\text{-}C_3H_5)(CO)_2(PPh_3)_2$	c	60.7	4.5	-	d	$C_{41}H_{35}IrO_2P_2$	60.4	4.3	-	814
$Ir(\sigma\text{-}C_4H_7)(CO)_2(PPh_3)_2$[f]	c	60.8	4.7	-	d	$C_{42}H_{37}IrO_2P_2$	60.9	4.5	-	828
$IrH_3(CO)(PPh_3)_2$		59.2	4.3	-		$C_{37}H_{33}IrOP_2$	59.4	4.4	-	748

(a) All compounds decompose on melting

(b) In benzene

(c) Compounds decompose in the solid state on warming

(d) Compound decomposes in solution

(e) 1-Methylallyl derivative

(f) 2-Methylallyl derivative

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