

THE CHEMISTRY OF SOME
RUTHENIUM TRIPHENYLPHOSPHINE COMPLEXES

A Thesis submitted by

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ABSTRACT

Reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with alkali hydroxides under various conditions produce $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_n$ ($\text{S} = \text{H}_2\text{O}, \text{THF}; n = 1; \text{S} = \text{H}_2\text{O}, \text{Me}_2\text{CO}, t\text{-BuOH}, \text{THF}, n = 2$). In acetone another compound believed to be the tetramer of formulation $\text{Ru}_4\text{H}_4(\text{OH})_2(\text{PPh}_2)_2(\text{Me}_2\text{CO})_2(\text{CO})_2(\text{PPh}_3)_6$ is obtained. From $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuCl}(\text{OH})(\text{PPh}_3)_2\text{S}_2$ ($\text{S} = \text{H}_2\text{O}, \text{THF}$) and $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$ were isolated, some reactions of the monomeric chloro hydroxo complex were also undertaken.

Reactions to prepare alkoxo complexes were attempted by both direct and indirect methods but unsuccessfully. From the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with NaOMe two compounds postulated as containing a formyl group and coordinated formaldehyde ligand were obtained.

$[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3](\text{PF}_6)_2 \cdot 2\text{MeCN}$ was obtained through the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with AgPF_6 in MeCN and addition of NaOH to the dication produced $[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]\text{PF}_6 \cdot 2\text{MeOH}$.

$\text{RuH}_2(\text{PPh}_3)_4$ reacts with styrene (St) to afford the tetra-coordinate ruthenium(0) complex $\text{Ru}(\text{St})_2(\text{PPh}_3)_2$. This compound reacts with hydrocarbons in the presence of excess PPh_3 to yield $\text{RuH}_2(\text{PPh}_3)_4$. In the absence of added PPh_3 green compounds analysing for $[\text{Ru}(\text{PPh}_3)_2\text{St}] \cdot 0.5\text{RH}$ are obtained at room temperature whilst an unidentified orange material is obtained under reflux. $\text{Ru}(\text{St})_2(\text{PPh}_3)_2$ oxidatively adds hydrogen in petrol and water in THF to give $\text{RuH}_4(\text{PPh}_3)_2$ and $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$ respectively.

Finally the reactions of the bis styrene complex with a number of olefins were investigated. With ethylene, but-1-ene butadiene and hex-2-ene, new ruthenium(0) complexes were obtained namely $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, $\text{Ru}(\eta\text{-1-4-C}_4\text{H}_6)(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, $\text{Ru}(\eta\text{-1-2-C}_4\text{H}_6)(\eta\text{-1-4-C}_4\text{H}_6)(\text{PPh}_3)_2$ and $\text{Ru}(\eta\text{-1-4-C}_6\text{H}_{10})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$. The known

$\text{Ru}(\text{C}_3\text{H}_5)_2(\text{PPh}_3)_2$ and $\text{RuH}(\eta\text{-1-5-C}_5\text{H}_5)(\text{PPh}_3)_2$ were obtained from propylene and cyclopentadiene and the new ruthenium(II) complexes, $\text{RuH}(\eta\text{-1-3-C}_6\text{H}_{11})(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$, $\text{RuH}(\eta\text{-1-5-C}_6\text{H}_7)(\text{PPh}_3)_2$, $\text{Ru}(\text{C}_6\text{H}_{11})(\eta\text{-1-5-C}_6\text{H}_7)(\text{PPh}_3)_2$ and $\text{RuH}(\eta\text{-1-2-C}_6\text{H}_{10})(\eta\text{-1-3-C}_6\text{H}_7)(\text{PPh}_3)_2$ the first from hex-1-ene and the rest from cyclohexene, were synthesized. The last three compounds have been shown to be interconvertible and this system is active for the transfer hydrogenation of cyclohexene to cyclohexane producing cyclohexane and benzene in a two to one ratio.

$\text{RuH}_2(\text{PPh}_3)_4$ reacts with diphenylacetylene, phenylacetylene and dimethylacetylene in toluene to give $\text{Ru}(\text{PhC}=\text{CPhCPh}=\text{CPh})(\text{PhHC}=\text{CHPh})(\text{PPh}_3)$ $[\text{Ru}(\text{-CH}=\text{CPhC}\equiv\text{CPh})(\text{-C}\equiv\text{CPh})(\text{PPh}_3)_2]_2$ and $\text{Ru}(\eta\text{-1-4-C}_4\text{H}_6)(\text{PPh}_3)_3$ (C_4H_6 = butadiene). $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ reacts with dimethylacetylene to give the orthometallated complex $[\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{H}_2\text{O})]_2 \cdot \text{H}_2\text{O}$

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ABBREVIATIONS

bipy	:	$C_{10}H_8N_2$	2,2'-bipyridyl
t_{Bu}	:	$-C(CH_3)_3$	t-butyl
Cp	:	$(\eta-1-5-C_5H_5)$	cyclopentadienyl
COD	:	C_8H_{12}	cyclooctadiene
DMF	:	C_3H_7NO	dimethylformamide
DMSO	:	C_2H_6OS	dimethylsulphoxide
Et	:	$-C_2H_5$	ethyl
Me	:	$-CH_3$	methyl
Ph	:	$-C_6H_5$	phenyl
phen	:	$C_{12}H_8N_2$	1,10-phenanthroline
py	:	C_5H_5N	pyridine
St	:	C_8H_8	styrene
THF	:	C_4H_8O	tetrahydrofuran
TMS	:	$C_4H_{12}Si$	tetramethylsilane

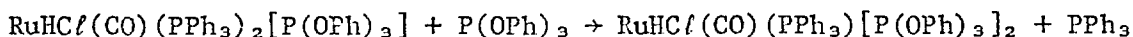
CHAPTER I

SURVEY OF THE KNOWN CHEMISTRY OF RUTHENIUM HYDRIDO COMPLEXES CONTAINING TRIPHENYLPHOSPHINE

The introductory chapter to this thesis contains a brief survey of the known chemistry of hydrido triphenylphosphine ruthenium(II) complexes. A general review on metal hydrides appeared in 1971,¹ and the introductory chapter of a recent thesis contained a review on ruthenium hydrides up to 1975.² This review concentrates on the literature published since then.

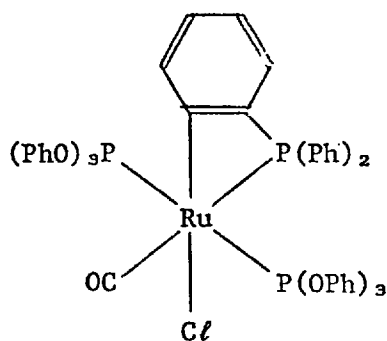
In 1961 Vaska and Diluzio reported the first hydrido triphenylphosphine complex of ruthenium,³ $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, prepared by the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with triphenylphosphine in 2-methoxyethanol. The photolysis of this complex⁴ has recently been shown to give $\text{RuHCl}(\text{PPh}_3)_3$, and $\text{RuHCl}(\text{CO})_2(\text{PPh}_3)_2$ produced by the reaction of free CO generated in situ with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. Although the authors could not isolate $\text{RuHCl}(\text{PPh}_3)_3$ free from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{CO})_2(\text{PPh}_3)_2$, they detected it by its colour and its spectroscopic and catalytic properties.

Addition of triphenylphosphite to $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ initially gives simple substitution products⁵:



and on further reaction, the orthometallated complex (I).

$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (vide infra) react with diazenium salts in acetone⁶ to yield the aryldiimine complexes $\text{RuCl}(\text{NH}=\text{NAr})(\text{CO})(\text{PPh}_3)_2(\text{BF}_4)$ and $[\text{RuH}(\text{NH}=\text{NAr})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$ respectively.



(I)

The former product is a salt in polar solvents, such as acetonitrile, but BF_4 may be coordinated in the solid state. If the reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $(\text{ArN}_2)\text{PF}_6$ is carried in acetonitrile,⁷ $[\text{RuCl}(\text{CO})(\text{NCMe})(\text{HN=NAr})(\text{PPh}_3)_2]\text{PF}_6$ ($\text{Ar} = \text{o-}, \text{m-}$ or $\text{p-MeOC}_6\text{H}_4$) is obtained. These salts react in acetone with CO ⁶ to give the dicarbonyl complexes $[\text{RuCl}(\text{NH=NAr})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$ and $[\text{RuH}(\text{NH=NAr})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$, and with lithium chloride to afford the neutral compounds $\text{RuCl}_2(\text{NH=NAr})(\text{CO})(\text{PPh}_3)_2$ and $\text{RuHCl}(\text{NH=NAr})(\text{CO})_2(\text{PPh}_3)_2$.

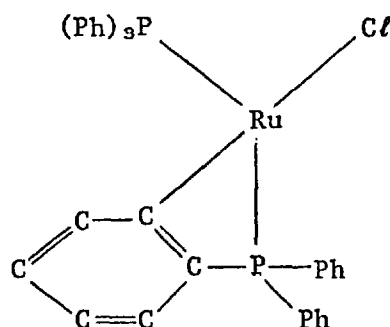
Ibers et al. prepared the first aryldiazohydrido complexes of ruthenium⁸ $\text{RuH}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2$ and $\text{RuH}(\text{CO})(\text{NNPh})(\text{PPh}_3)_2$ by deprotonation of the respective phenyldiazene complexes using sodium hydroxide in methanol at -20°C .

$\text{RuHCl}(\text{CO})_2(\text{PPh}_3)_2$ ⁹ was obtained in 1973 from the reaction of CO with $\text{RuHCl}(\text{PPh}_3)_3$ in $\text{N,N'$ -dimethylacetamide.

$\text{RuHCl}(\text{PPh}_3)_3$ ¹⁰ was first obtained from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with hydrogen in the presence of a base (triethylamine or sodium phenoxide) in benzene. It was shown to be the most effective catalyst known for the hydrogenation of terminal olefins. The hydrogenation of 1-hexene and ethyl acrylate by $\text{RuHCl}(\text{PPh}_3)_3$ prepared in situ from $\text{RuCl}_2(\text{PPh}_3)_3$ in ethanol or benzene/ethanol has been studied,¹¹ and turnover numbers up to 3300 were reported.

$\text{RuHCl}(\text{PPh}_3)_3$ reacts with stoichiometric amounts of maleic acid¹²

to afford the hydrogenated organic product and the orthometallated complex (II).



(II)

This compound reacts with hydrogen to give a red complex which, although not isolated, is thought to be $\text{RuHCl}(\text{PPh}_3)_2$, and which reacts further with one mole of triphenylphosphine to yield $\text{RuHCl}(\text{PPh}_3)_3$.

$\text{RuHCl}(\text{PPh}_3)_3$ has been shown to catalyse the deuteration of the ortho positions of the phenyl rings of triphenylphosphine,¹³ the recovered catalyst itself having ortho deuterated triphenylphosphine rings. More recently it was shown to catalyse the deuteration of carboranes and metallocarboranes¹⁴ and the H_2/D_2 exchange to afford HD.¹⁵

The oxidative additions of carboranes ($7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ and $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$) to $\text{RuHCl}(\text{PPh}_3)_3$ have yielded novel dihydrido complexes of ruthenium: 3,1,2- and 2,1,7- $\text{RuH}_2(\text{PPh}_3)_2(\text{C}_2\text{B}_9\text{H}_{11})$.¹⁶ The latter complex, the structure of which has been confirmed by X-ray crystallography has been found to eliminate reversibly its hydride ligands as H_2 upon heating in vacuo.

$\text{RuHCl}(\text{PPh}_3)_3$ reacts with the diphenyl triazenido anion¹⁷ to yield the hydrido complex: $\text{RuH}(\text{N}_3\text{Ph}_2)(\text{PPh}_3)_3$ and with $(\text{ArN}_2)\text{X}$ in methanol⁷ ($\text{Ar} = \text{pMeC}_6\text{H}_4$, o-, m- or p- MeOC_6H_4 ; $\text{X} = \text{BF}_4$ or PF_6) to afford $[\text{RuCl}(\text{N}_2\text{Ar})_2(\text{PPh}_3)_2]\text{X}$.

Similarly, $\text{RuHCl}(\text{PPh}_3)_3$ was shown to react with 1,3-di-p-tolyl-triazene¹⁸ to afford $\text{Ru}(\text{N}_3\text{Ar}_2)(\text{PPh}_3)_2$ which is also obtained from $\text{RuH}_2(\text{PPh}_3)_4$ and diphenyltriazene ($\text{Ar} = \text{Ph}$).

$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ react with Ph_2N_3 , in benzene/ethanol and benzene respectively,¹⁸ to yield $\text{Ru}(\text{PhNNNPh})(\text{CO})-(\text{PPh}_3)_2$. The entire ruthenium triazenido system of this species has been shown to be essentially planar by X-ray crystallography.¹⁹

Cenini *et al.* have found that the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with SO_2 in hexane affords $\text{RuHCl}(\text{SO}_2)(\text{PPh}_3)_2$, one of the very few known hydrido sulphurdioxide complexes.

Several reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with alkylating agents have been investigated.²¹ The hydrido alkyl complexes $\text{RuH}(\text{Me})(\text{PPh}_3)_2(\text{Et}_2\text{O})_2$ and $\text{RuH}(\text{Me})(\text{PPh}_3)_2(\text{MeLiS}_2)_2$ ($\text{S} = \text{Et}_2\text{O}$) were isolated from the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with MeLi (small and large excesses respectively) at 0°C . These compounds are very reactive and decompose at room temperature to yield methyl or hydrido orthometallated complexes depending upon the reaction conditions. If the reaction is carried out at room temperature with different alkylating agents orthometallated complexes invariably result: $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{THF}, \text{Et}_2\text{O}$) or $\text{RuMe}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{Et}_2\text{O})$ from $\text{Me}_3\text{SiCH}_2\text{Li}$ or MeLi , $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{Zn}_2\text{Me}_3\text{Cl})$ from ZnMe_2 and $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2[\text{Mg}_2\text{Me}_3-\text{Cl}(\text{OEt})_2]$ from MgMe_2 .

Finally, the related compounds $\text{RuHBr}(\text{PPh}_3)_3$,¹⁰ $\text{RuHI}(\text{PPh}_3)_3$,²² $\text{RuHCl}(\text{bipy})(\text{PPh}_3)_2$ ¹⁰ and $\text{RuHCl}(\text{C}_7\text{H}_8)(\text{PPh}_3)_2$ ¹⁰ are also known.

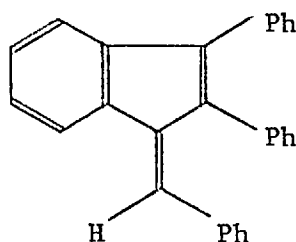
$\text{RuHCp}(\text{PPh}_3)_2$,²³ which was first prepared in 1971 by the reaction of $\text{RuClCp}(\text{PPh}_3)_2$ with LiAlH_4 in diethyl ether, was shown to react with acetylenes $\text{RC}\equiv\text{CR}$ ²⁴ ($\text{R} = \text{CF}_3, \text{CO}_2\text{Me}$) to give $\text{Ru}(\text{Cp})(\text{PPh}_3)_2(-\text{RC}=\text{C}(\text{R})\text{H})$ with the R groups mutually cis for $\text{R} = \text{CF}_3$ or trans ($\text{R} = \text{CO}_2\text{Me}$) and $(\text{Cp})(\text{PPh}_3)\text{RuC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)=\text{CH}(\text{CF}_3)$. A new reaction between

$\text{Ru}(-\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me}))(\text{Cp})(\text{PPh}_3)_2$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ yielding:

$\text{Ru}[\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}](\text{PPh}_3)(\text{Cp})$ was observed and the structure of the compound confirmed by X-ray crystallography.²⁵

The hydrido nitrosyl complex $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ was first obtained from the reaction of ethanolic potassium hydroxide with trichloronitrosyl bis(triphenylphosphine)ruthenium,²⁶ but can be prepared in one operation from ruthenium trichloride trihydrate.²⁷ The solid state structure of this compound has been shown by X-ray crystallography to be a slightly distorted trigonal bipyramid.²⁸

This complex has recently been shown to dimerise diphenylacetylene²⁹ to the unusual dimer (III)



(III)

It trimerises phenylacetylene at room temperature and yields higher polymers if the temperature is raised. Hex-1-yne, prop-2-ynyl alcohol, propiolic acid and hexafluorobut-2-yne are also polymerised by $\text{RuH}(\text{NO})(\text{PPh}_3)_3$.

$\text{RuH}(\text{NO})(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$ react with $\text{Co}(\text{NO})\text{D}_2$ in THF³⁰ (D = monoanion of dimethylglyoxime) to afford $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ obtained originally from $\text{RuH}_4(\text{PPh}_3)_3$ and NO (vide infra).

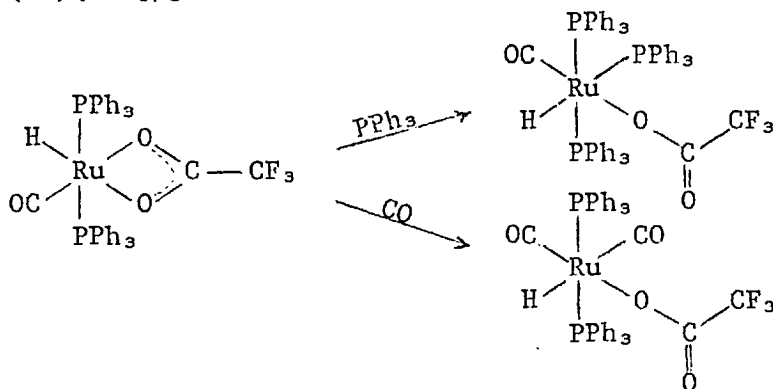
$\text{RuH}(\text{RCO}_2)(\text{PPh}_3)_3$ (R = Me, CH_2Cl , CF_3 , Et, ^nPr , ^iPr , Me_3C , Ph, $o\text{-(OH)-C}_6\text{H}_4$)³¹ were prepared in 1969 by Wilkinson et al.. These compounds have been found to be very efficient hydrogenation catalysts.³² The crystal structure of the acetato complex shows it to be octahedral, possessing meridionally arranged phosphines with the hydride mutually

cis to them and a bidentate acetate group.³³ At 100 MHz the ^1H n.m.r. spectra of the hydrido carboxylato complexes show quartet resonances for the hydride ligand.³¹ This was interpreted as indicative of the hydride coupling to three equivalent cis phosphorus nuclei, which in turn required a rearrangement of the complex in solution.

These spectra have been reexamined at 220 MHz^{34,35} and found to consist of a doublet of triplets with the two coupling constants being almost identical, this interpretation fitting the crystal structure. This and the proton decoupled ^{31}P n.m.r. spectrum show that the hydrido acetate is stereochemically rigid in solution at room temperature and that no dissociation of a ligand occurs. From the catalytic point of view this implies that the active species is spectroscopically unidentifiable,³⁵ a vacant site being necessary for the catalysis to occur. $\text{RuHCl}(\text{PPh}_3)_3$ was also found not to dissociate in solution.

$\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ first prepared by Wilkinson et al.³¹ has also been obtained from the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with trifluoroacetic acid.³⁶

$\text{RuH}(\text{OCORF})(\text{CO})(\text{PPh}_3)_2$ ($\text{RF} = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_6\text{F}_5$) is formed during the catalytic reaction of $\text{Ru}(\text{OCORF})_2(\text{CO})(\text{PPh}_3)_2$ with primary and secondary alcohols to afford aldehydes and ketones,³⁷ it was shown to be itself a catalyst for these reactions in the presence of the corresponding perfluorocarboxylic acid. $\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$ reacts with CO or PPh_3 in ethanol to give respectively $\text{RuH}(\text{OCOCF}_3)(\text{CO})_2(\text{PPh}_3)_2$ and $\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_3$



Solutions obtained by protonation of carboxylato complexes with strong acids in methanol have been shown to hydrogenate alkenes.^{32,39} For $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$ the acid dependent selectivity for hydrogenation of olefins has also been studied.⁴⁰

The isolation of the catalytically active species from this system has been attempted,⁴¹ and it was shown that the protonation of $\text{RuH}(\text{OCOMe})(\text{PPh}_3)_3$ in methanol with fluoroboric acid yields first a red compound shown to be $[\text{RuH}(\text{PPh}_3)_3\text{L}]\text{BF}_4$ ($\text{L} = \text{solvent}$) and that this ages to the yellow $[\text{RuH}(\text{PPh}_3)_2(\text{H}_2\text{O})_2(\text{MeOH})]\text{BF}_4$. In the presence of excess triphenylphosphine the finally isolated complex is $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2]\text{-BF}_4$. An intermediate in this reaction is $[\text{RuH}(\text{PPh}_3)_4]^+$ prepared by reaction of $\text{RuH}_2(\text{PPh}_3)_4$ and tritylhexafluorophosphate in dichloromethane which reacts with other phosphines or nitriles to give a range of six coordinate cations $(\text{RuHP}_5)^+$ ($\text{P} = \text{P}(\text{OEt})_2\text{Ph}$, $\text{P}(\text{OMe})_2\text{Ph}$, PPh_2H and $[\text{RuH}(\text{PPh}_3)_2(\text{RCN})_3]^+$ ($\text{R} = \text{Me}$, ^nPr , ^iPr , Ph , MeC_6H_4 , MeOC_6H_4 , ClC_6H_4) respectively.⁴² $[\text{RuH}(\text{PPh}_3)_3]\text{BF}_4$ has been postulated as having a phosphine ligand coordinated through one of its phenyl rings.^{41,42} This structure has been confirmed by X-ray crystallography.⁴³

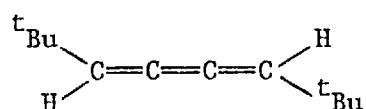
The dimeric $[\text{RuHX}(\text{PPh}_3)_2]_2$ were obtained from the reaction of hydrogen with ruthenium(III) complexes $\text{RuX}_3(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}$, Br) in N,N -dimethylacetamide or toluene.⁴⁴ Using AsPh_3 as a ligand instead of PPh_3 the first hydrido ruthenium(III) complex $\text{RuH}(\text{Br})_2(\text{AsPh}_3)_2$ was obtained.

$\text{RuH}(\text{BH}_4)(\text{PPh}_3)_3$ and $\text{RuH}(\text{BH}_4)(\text{CO})(\text{PPh}_3)_2$ were prepared from the reaction of ruthenium trichloridetrihydrate in ethanol with sodium borohydride in the presence of triphenylphosphine, and from the red carbonyl ruthenium solution in ethanol with sodium borohydride and triphenylphosphine respectively.⁴⁵

The interaction of $\text{RuCl}_2(\text{PPh}_3)_3$ and sodium borohydride in refluxing

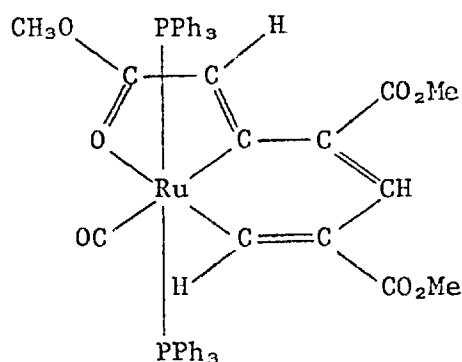
mixtures of benzene and methanol or ethanol has been shown by Wilkinson *et al.* to yield $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$.¹⁰ This reaction has more recently been shown to produce $\text{RuH}_4(\text{PPh}_3)_3$, if carried out at room temperature or $\text{RuH}_2(\text{PPh}_3)_4$,⁴⁶ if excess PPh_3 is added. The photolysis of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ produces hydrogen and a compound which is apparently $\text{Ru}(\text{CO})(\text{PPh}_3)_3$ but which is probably an hydrido orthometallated complex, although it has not been fully characterized.^{4b}

$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ catalyses the dimerisation of *t*-butyl acetylene at 100°C in benzene.⁴⁷ The main product of the reaction is (IV).



(IV)

It also reacts with methyl propiolate to yield the metallocycle (V).⁴⁸



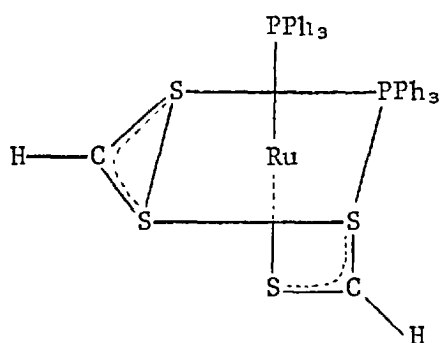
(V)

Wilkinson and co-workers have studied the homogeneous hydroformylation of alkenes by use of ruthenium complex catalysts.⁴⁹ Starting from a number of different ruthenium complexes including the hydrido species $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$, $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}(\text{NO})(\text{PPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_4$, $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuHCp}(\text{PPh}_3)_2$, they found that the ruthenium complex recovered from the reaction is invariably $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and they

proposed a mechanism involving $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ as the principal catalytic species.

Dihydridotetrakis(triphenylphosphine)ruthenium was first obtained in 1970 by Yamamoto et al. from the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Ru}(\text{acac})_3$ with triphenylphosphine and triethylaluminium in tetrahydrofuran.²² It was shown to dissociate in benzene and undergo reversible combination with molecular hydrogen and nitrogen to give respectively $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2\text{N}_2(\text{PPh}_3)_3$. When dissolved in benzene in the presence of a large excess of deuterium, $\text{RuH}_2(\text{PPh}_3)_4$ was found to exchange approximately 24-25 hydrogen atoms per mole of complex, indicating the reversible exchange of all the ortho hydrogen atoms of the phenyl rings.

$\text{RuH}_4(\text{PPh}_3)_3$, which can be prepared more directly from $\text{RuCl}_2(\text{PPh}_3)_3$ and sodium borohydride in benzene/methanol⁴⁶ (see above), reacts with N_2 , CO , NO , SO_2 , NOCl , MeCN and PhCN to give $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$, $\text{Ru}(\text{SO}_2)_2(\text{PPh}_3)_2$, $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_3$, $\text{RuH}_2(\text{MeCN})(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PhCN})(\text{PPh}_3)_3$. $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ react with CS_2 ,⁴⁶ the former liberating 0.9 moles of hydrogen per mole of complex, to give the red crystalline complex $\text{Ru}(\text{HCS}_2)_2(\text{PPh}_3)_2$ which has structure (VI).



(VI)

This reaction was also reported by Robinson and co-workers⁵⁰ who investigated the reaction of CS_2 with a number of hydrido ruthenium complexes, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, $\text{RuHBr}(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$

and $\text{RuH}_2(\text{PPh}_3)_4$ react to give: $\text{Ru}(\text{S}_2\text{CH})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, $\text{Ru}(\text{S}_2\text{CH})\text{Br}(\text{CO})(\text{PPh}_3)_2$, $\text{Ru}(\text{S}_2\text{CH})(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{S}_2\text{CH})_2(\text{PPh}_3)_2$. $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ react to give sulphur containing compounds which could not be isolated.

Vol'pin et al. have reported the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuH}_2\text{N}_2(\text{PPh}_3)_3$ with CO_2 which lead in benzene to a compound of stoichiometry $\text{RuH}_2(\text{CO}_2)(\text{PPh}_3)_3$.⁵¹ Although the addition of CO_2 is reversible, the properties of this complex are best explained in terms of the equilibrium:



If the reaction is carried out in methanol or ethanol, $\text{RuH}(\text{O}_2\text{COR})(\text{PPh}_3)_3$ ($\text{R} = \text{Me}$ or Et respectively) is obtained.⁵²

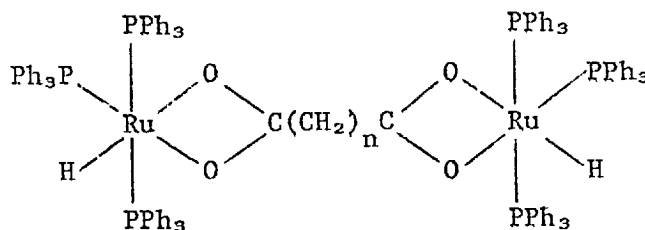
Similarly in an ethanol-dimethylamine mixture, $\text{RuH}(\text{O}_2\text{CNMe}_2)(\text{PPh}_3)_3$ is obtained.⁵³

$\text{RuH}_2(\text{PPh}_3)_4$, in the presence of trialkylamines has been shown to catalyse the reactions of CO_2 with alcohols and hydrogen⁵⁴:
 $\text{ROH} + \text{CO}_2 + \text{H}_2 \rightarrow \text{HCO}_2\text{R} + \text{H}_2\text{O}$ and of CO_2 with hydrogen⁵⁵: $\text{CO}_2 + \text{H}_2 \rightarrow \text{HCO}_2\text{H}$.

Yamamoto et al. have reinvestigated the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with CS_2 , CO_2 and SO_2 ,⁵⁶ and have essentially found the same compounds as had previously been described.

$\text{RuH}_2(\text{PPh}_3)_4$ has been shown to react with vinyl acetate and vinyl propiolate to yield $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$ and $\text{RuH}(\text{CO}_2\text{Et})(\text{PPh}_3)_3$,⁵⁷ and $\text{RuH}_2\text{CO}(\text{PPh}_3)_3$ reacts with weak carboxylic acids in 2-methoxyethanol to form hydrido carboxylato derivatives.⁵⁸

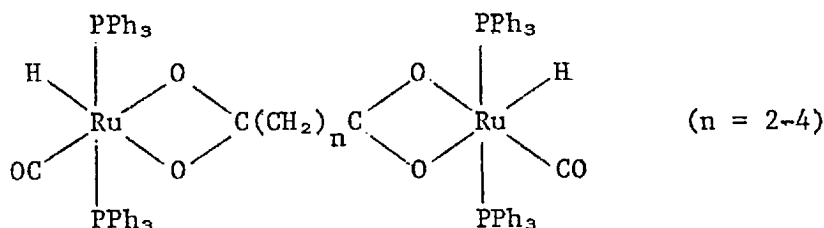
Recently the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with dicarboxylic acids and α -hydroxy acids have been reported⁵⁹ and compounds of type (VII) are obtained for $n = 2-4$.



(VII)

With $\text{CH}_2(\text{COOH})_2$, $\text{RuH}(\text{O}_2\text{CCH}_2\text{COOH})(\text{PPh}_3)_3$ is obtained and α -hydroxy acids afford $\text{RuH}(\text{PPh}_3)_3(\text{O}_2\text{CCH}(\text{OH})\text{R})$ ($\text{R} = \text{Me}$ or Ph).

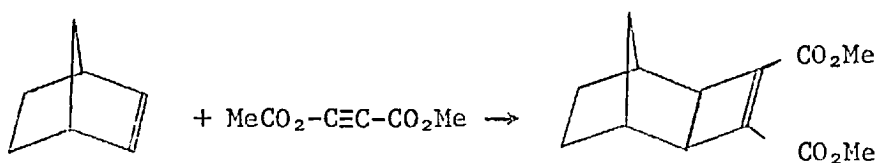
Similar reactions occur with $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ yielding the compounds $\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{CCH}_2\text{OH})$ and (VIII)



(VIII)

These hydrido carboxylato compounds have been found to be effective catalysts for the hydrogenation and isomerisation of alkenes.⁵⁹

The addition of dimethylacetylene dicarboxylate to norbornene derivatives has been shown to be catalysed by $\text{RuH}_2(\text{PPh}_3)_4$ in benzene at 80°C ,⁶⁰ the exo compound always being obtained.



The reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with silicon hydrides (R_3SiH) in benzene has been shown to give $\text{RuHCl}(\text{PPh}_3)_3$ when $\text{R} = \text{Et}$, $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_3$ ($\text{R} = \text{OEt}$, Cl) and $\text{Ru}(\text{SiR}_3)_2(\text{PPh}_3)_3$ ($\text{R} = \text{Cl}$).⁶¹

These results have been confirmed by Kono and co-workers⁶² but they also found that in the absence of solvent $\text{RuCl}_2(\text{PPh}_3)_3$ reacted with R_3SiH ($\text{R}_3 = \text{Cl}_3, \text{Cl}_2\text{Me}, \text{ClMe}_2, \text{Ph}(\text{MeO})_2, (\text{EtO})_3$) to give the four coordinate $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_2$.

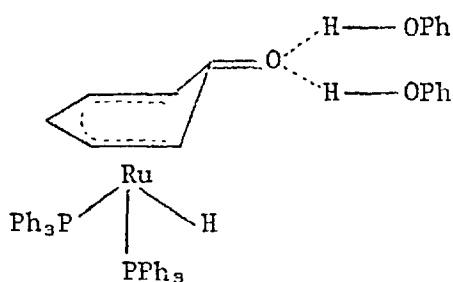
Finally they found that the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with organo-silicon hydrides gave the seven coordinate ruthenium(IV) complexes of general formula $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ ⁶² ($\text{R}_3 = \text{Et}_3, \text{EtMe}_2, \text{PhMe}_2, \text{Ph}_3, \dots$).

$[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2]\text{X}$ ($\text{X} = \text{BF}_4, \text{PF}_6$) is obtained from the reactions of $[\text{RuH}(\text{PPh}_3)_4]\text{PF}_6$ in dichloromethane⁴² and $\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3$ with fluoroboric acid and excess phosphine in methanol⁴¹ (see above).

The same compound is obtained if $\text{RuH}_2(\text{PPh}_3)_4$ is used instead of $\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3$.⁶³ Furthermore, it has been shown that if

protonation of $\text{RuH}_2(\text{PPh}_3)_4$ is carried out in the presence of benzene or toluene, hydrido compounds containing π -bonded rings are obtained:

$[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{PPh}_3)_2]\text{BF}_4$ ($\text{R} = \text{H}$ or Me respectively). Similarly the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with excess phenol in toluene produces a yellow neutral complex analysing for $\text{RuH}(\text{OC}_6\text{H}_5)(\text{PPh}_3)_2 \cdot 2\text{PhOH}$, which has structure (IX).⁶³



(IX)

If stoichiometric amounts of phenol are employed in the reaction $\text{RuH}(\eta^5\text{-OPh})(\text{PPh}_3)_2$ is obtained.

$\text{RuH}_2(\text{PPh}_3)_4$ has been shown to be an active catalyst for the hydrogenation of ethylene and styrene⁶⁴ and $\text{RuH}_4(\text{PPh}_3)_3$ for the

hydrogenation of 1-pentene.⁶⁵

$\text{RuH}_2\text{N}_2(\text{PPh}_3)_3$ has been shown to isomerize 1-pentene in toluene at 25°C ,⁶⁶ and the inhibiting influence of molecular nitrogen on this reaction studied. During these reactions some ruthenium olefin complexes were isolated or postulated; they will be discussed later.

Imai and co-workers have shown that $\text{RuH}_2(\text{PPh}_3)_4$ catalyses the hydrogen transfer reactions, from isopropanol to cyclohexene giving acetone and cyclohexane,⁶⁷ from ethylbenzene or indane to aldehydes giving the corresponding olefins and alcohols⁶⁸ and from 2,5-dihydrofuran, tri-n-propylamine benzyl alcohol, to aldehydes and ketones.^{69,70} At least some of this work has been doubted recently by Wilkinson *et al.*^{71,72} since for example, Imai reports that $\text{RuH}_2(\text{PPh}_3)_4$ and n-hexaldehyde react in chloroform to form $\text{Ru}(\text{PPh}_3)_3$ whereas $\text{RuH}_2(\text{PPh}_3)_4$ reacts immediately with chloroform to give $\text{RuHCl}(\text{PPh}_3)_3$ which with n-hexaldehyde under similar conditions gives either $\text{RuCl}(\text{CO})(\text{COR})(\text{PPh}_3)_2$ or $\text{RuCl}(\text{COR})(\text{PPh}_3)_3$.

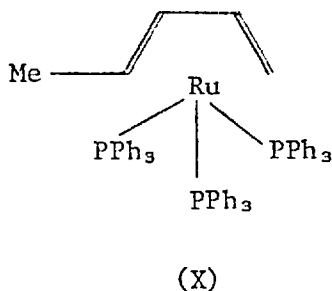
This anomalous behaviour may be explained by the fact that Imai uses Robinson's method for the preparation of $\text{RuH}_2(\text{PPh}_3)_4$ and this has been found unsatisfactory by Wilkinson *et al.*⁷²

$\text{RuH}_2(\text{PPh}_3)_4$ was shown to initiate the polymerisation of substituted olefins of high e values, for example, acrylonitrile, methacrylonitrile, acrolein and methyl acrylate, and to form unstable complexes with olefins of low e values. Tetracyanoethylene (TCNE) maleic anhydride (MANh), methyl and ethyl methacrylate (MMA and EMA) styrene (St) and ethylene (E) afforded respectively the complexes $\text{Ru}(\text{TCNE})_3(\text{PPh}_3)_2$, $\text{Ru}(\text{MANh})_n(\text{PPh}_3)_{5-n}$, $\text{Ru}(\text{MMA})(\text{PPh}_3)_3$, $\text{Ru}(\text{EMA})(\text{PPh}_3)_3$, $\text{RuSt}(\text{PPh}_3)_3$ and $\text{Ru}(\text{E})(\text{PPh}_3)_3$. The full characterisation and in some cases re-investigation of the new complexes has been reported recently and will be discussed later in this chapter.

The kinetics of the polymerisation of olefins of high e value by $\text{RuH}_2(\text{PPh}_3)_4$ were studied and a mechanism involving a slow initiation step followed by rapid propagation and termination was proposed.⁷³

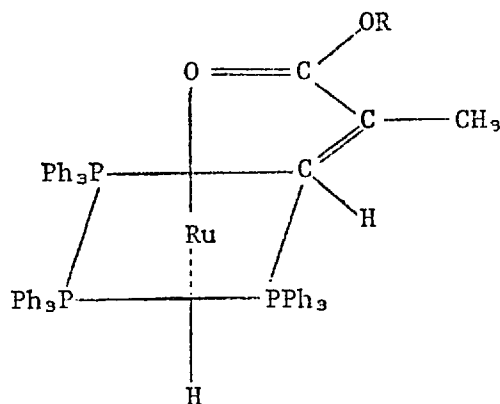
During studies on hydrogenation and isomerisation of 1-pentene using $\text{RuH}_2\text{N}_2(\text{PPh}_3)_3$ and $\text{RuH}_4(\text{PPh}_3)_3$,^{62,74} Penella proposed a mechanism involving a dihydrido complex $\text{RuH}_2(\text{PPh}_3)_3(\text{C}_5\text{H}_{10})$ which could be prepared by the reaction of $\text{RuH}_2\text{N}_2(\text{PPh}_3)_3$ or $\text{RuH}_4(\text{PPh}_3)_3$ with 2-pentene or a small excess of 1-pentene and a ruthenium(0) complex $\text{Ru}(\text{PPh}_3)_3(\text{C}_5\text{H}_{10})$ prepared from the same ruthenium complexes and a large excess of 1-pentene.

This has been shown to be incorrect⁷² since the first reaction leads in fact to $\text{RuH}_2(\text{PPh}_3)_4$ and the second one to a 1,3-pentadiene ruthenium(0) complex $\text{Ru}(\text{C}_5\text{H}_8)(\text{PPh}_3)_3$ which has structure X.



Following the observation that complexes are formed by the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ and various olefins⁷³ (see above), Yamamoto and co-workers have studied these reactions in detail.

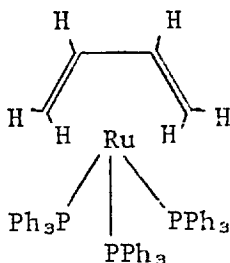
With alkyl methacrylate,⁷⁵ they found that the complex analysing for $\text{Ru}(\text{alkylmethacrylate})(\text{PPh}_3)_3$ is in fact an hydrido vinylic compound formed through cleavage of a C-H bond. X-ray crystallography has confirmed the structure to be (XI).



(XI)

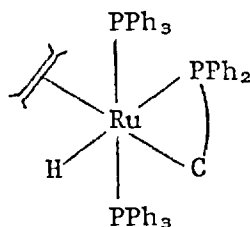
They investigated the reactions of ethylene, propylene, styrene and butadiene with $\text{RuH}_2(\text{PPh}_3)_4$ ⁷⁶ and found that invariably an equimolar amount of the hydrogenated product of the olefin and of a ruthenium(0) complex $\text{Ru}(\text{olefin})(\text{PPh}_3)_3$ was obtained. They found that with styrene a purple compound analysing as $\text{Ru}(\text{St})(\text{PPh}_3)_3$ is obtained and that in toluene it reacts to give back $\text{RuH}_2(\text{PPh}_3)_4$. We have re-investigated this reaction and found this compound to be in fact $\text{Ru}(\text{St})_2(\text{PPh}_3)_2$, the preparation and reactions of $\text{RuSt}_2(\text{PPh}_3)_2$, mainly with hydrocarbons, are the subject of the third chapter of this thesis.

Wilkinson and co-workers re-investigated the reactions of other olefins with $\text{RuH}_2(\text{PPh}_3)_4$ or $\text{RuH}_4(\text{PPh}_3)_3$ ⁷² and found that the reactions of butadiene, 1-butene and 1-pentene with the di- and the tetra-hydrido complexes of ruthenium led to ruthenium(0) diene complexes $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$ (XII) and $\text{Ru}(\text{C}_5\text{H}_8)(\text{PPh}_3)_3$ (X) [see above].



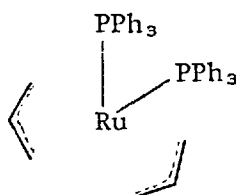
(XII)

The reaction with ethylene afforded a compound which analyses for $\text{Ru}(\text{C}_2\text{H}_4)(\text{PPh}_3)_3$ but which is correctly written as the hydridoorthometallated complex (XIII)



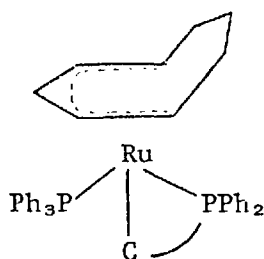
(XIII)

The reaction with propylene gave a bis allyl complex (XIV), probably through an hydrido allyl intermediate which could not be isolated, $\text{Ru}(\text{C}_3\text{H}_5)_2(\text{PPh}_3)_2$. This compound was found to possess a cis stereochemistry.



(XIV)

Finally the product of the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with cyclooctadiene was found to be the orthometallated compound (XV)

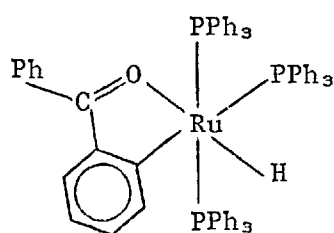


(XV)

The reactions of $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuH}_4(\text{PPh}_3)_3$ with aldehydes and ketones were also investigated ⁷² and it was shown that with enolisable

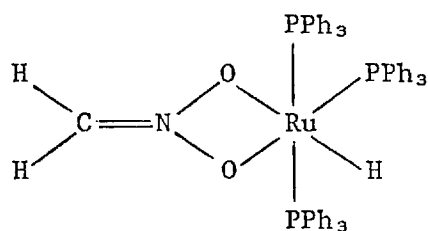
ketones $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ is obtained through hydrogenation of the carbon oxygen double bond to the corresponding alcohols and subsequent decarbonylation.

In acetone, if traces of water are present a red air-sensitive compound is obtained which was found to be $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$. The preparation of this compound through a more direct route, its chemistry and the preparation of related compounds are the subjects of Chapter II of this thesis. With benzophenone, the compound obtained has one of the ortho positions of the phenyl rings of benzophenone metallated (XVI).



(XVI)

Finally the reactions of $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{Et}_2\text{O})$ with weak acids have been investigated, with water $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ is obtained, whereas with nitromethane the complex $\text{RuH}(\text{CH}_2\text{NO}_2)(\text{PPh}_3)_3$ (XVII) which contains an unusual bidentate nitromethanato ion is produced.



(XVII)

This is also obtained from $\text{RuH}_2(\text{PPh}_3)_4$ and nitromethane.

CHAPTER II

REACTIONS OF $\text{RuHCl}(\text{PPh}_3)_3$ AND $\text{RuCl}_2(\text{PPh}_3)_3$ WITH ALKALI HYDROXIDES AND ALKOXIDES AND RELATED REACTIONS

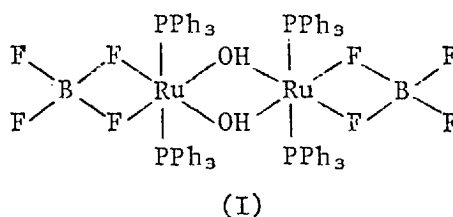
Introduction

Ruthenium hydroxo complexes have been known since 1889 when A. Joly reported $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]\text{X}_2$ ($\text{X} = \text{Cl}$ or I),⁷⁷ but apart from the purely inorganic complexes⁷⁸ little work has been done on these compounds and no systematic attempts to prepare them have been reported.

The known hydroxo complexes of ruthenium can be divided into five classes.

Hydroxynitrosyl Complexes of Ruthenium $\text{RuI}_2(\text{OH})(\text{NO})(\text{py})_2$ was reported in 1931 by R. Charronnat.⁷⁹ More recently W.R. Roper reported the preparation of some new hydroxo nitrosyl complexes which were obtained as follows: $\text{Ru}(\text{OH})(\text{NO})(\text{CO})(\text{PPh}_3)_2$ by chromatography of $\text{RuCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2$ on deactivated alumina;⁸⁰ $[\text{Ru}(\text{OH})(\text{NO})_2(\text{PPh}_3)_2]^+$ by prolonged reaction of $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ with sodium nitrite in dimethylformamide in the presence of oxygen⁸¹ and $\text{Ru}(\text{O}_2)(\text{OH})(\text{NO})(\text{PPh}_3)_2$ by the reaction of $\text{Ru}(\text{OH})(\text{CO})(\text{NO})(\text{PPh}_3)_2$ with O_2 in a dichloromethane/ethanol mixture.⁸²

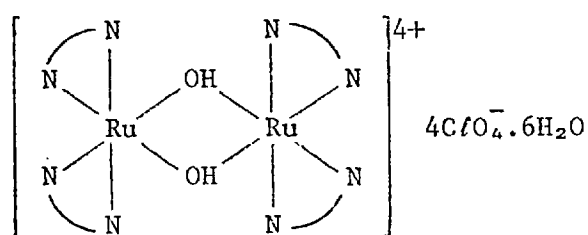
Carboxylatohydroxo Complexes of Ruthenium In 1966 Wilkinson reported the preparation of $[\text{Ru}_2(\text{OCOR})_3(\text{OH})(\text{H}_2\text{O})](\text{BPh}_4)$ obtained by addition of tetraphenylborate ion to an aqueous solution of $\text{Ru}_2(\text{OCOR})_4\text{Cl}$ ⁸³ and both $\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{OH})$ and $[\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})(\text{OH})_2]^-$ obtained by titration of $[\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]^+$ with sodium hydroxide.⁸⁴ The compound initially thought to have a μ -dihydroxo bridged structure (I),³²



isolated from the reaction between $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$ and aqueous fluoroboric acid in methanol has recently been reformulated as $[\text{Ru}(\text{H})(\text{H}_2\text{O})_2(\text{MeOH})(\text{PPh}_3)_2]\text{BF}_4$.⁴¹ Finally Ishinory has reported $(\text{Ru}_3\text{O}(\text{CH}_2\text{C}(\text{O})_2)_6(\text{OH})(\text{H}_2\text{O})_2)$ ⁸⁵ similar to the acetato complex quoted above.

Hydroxo Complexes Containing Nitrogen Donor Ligands

$[\text{RuCl}(\text{OH})(\text{py})_4]\text{Cl}$ ⁸⁶ and $\text{Ru}(\text{phen})_2(\text{OH})(\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})_3$ believed to have the hydroxo bridged structure⁸⁷ (II) have been known for some years



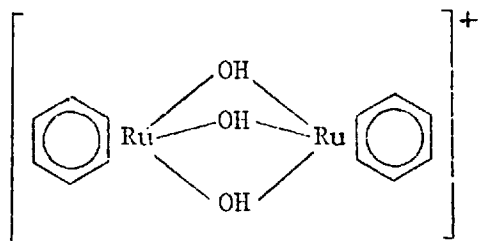
(II)

but more recently Ishimaya has synthesized a series of hydroxo (nitrogen heterocycle) complexes of ruthenium: $[\text{Ru}(\text{OH})_3(\text{phen})]_2\text{O}$,⁸⁸ $\text{Ru}(\text{O}_2)(\text{OH})_2(\text{bipy})$,⁸⁸ $\text{Ru}(\text{OH})_2(\text{py})_2(\text{N-N})$ ⁸⁹ ($\text{N-N} = \text{bipy}$ or phen), $\text{Ru}(\text{OH})_3(\text{H}_2\text{O})(\text{phen})$,⁹⁰ and $\text{Ru}(\text{OH})_2(\text{bipy})_2$.⁹⁰

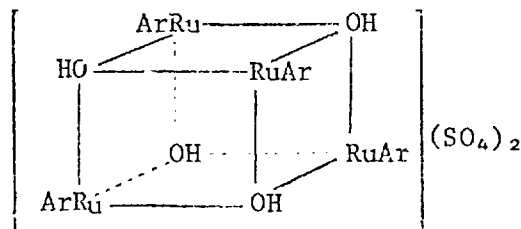
Hydroxodiene and arene Complexes

During attempts to prepare

$\text{Ru}_3(\text{CO})_{12}$ under mild conditions by reduction of $(\text{Ru}(\text{NBD})\text{Cl}_2)_n$ with hydrazine under a CO atmosphere, the dihydroxo compound $\text{Ru}(\text{OH})_2(\text{CO})_2(\text{NBD})$ was obtained in high yield.⁹¹ More recently the reactions of $[\eta^6(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ with sodium hydroxide and sodium carbonate were attempted by Stephenson *et al.*, the triply hydroxo bridged dimer⁹² (III)



(III)



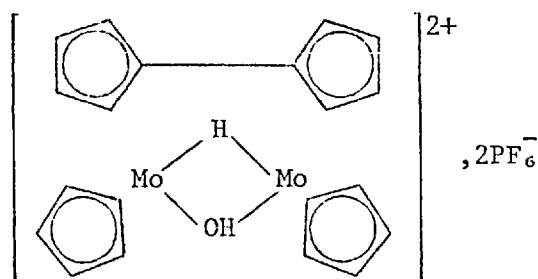
(Ar = Ph)

(IV)

and the tetramer (IV) ⁹³ (in the presence of magnesium sulphate) were obtained.

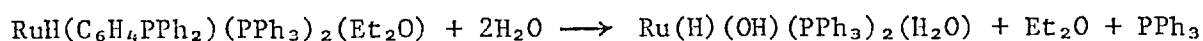
Hydroxocarbonyl Complexes of Ruthenium Finally a number of hydroxo carbonyl clusters have been reported in 1977 by J. Lewis. ⁹⁴ They were obtained as by-products from the carbonylation of hydrated ruthenium trichloride in the presence of zinc shavings. They are: $\text{Ru}_4(\text{CO})_{10}\text{Cl}_2(\text{OH})_2$, $\text{Ru}_4(\text{CO})_{10}\text{Cl}_2(\text{OMe})(\text{OH})$, and $\text{Ru}_4(\text{CO})_{10}\text{Cl}(\text{OMe})_2(\text{OH})$. The last two complexes are, together with $\text{Ru}_4(\text{CO})_{10}\text{Cl}_2(\text{OMe})_2$ and $\text{Ru}_4(\text{CO})_{10}\text{Cl}(\text{OMe})_3$, the only known alkoxo complexes of ruthenium.

No hydrido hydroxo complexes of ruthenium were known prior to this work and only three such complexes have been reported for other metals: two molybdenum complexes, $\text{Mo}_2(\text{CO})_6(\text{OH})_3(\text{H})_3$ ⁹⁵ and $\{[\eta^5(\text{C}_5\text{H}_5)\text{Mo}]_2(\mu\text{-OH})(\mu\text{-H})[\mu(\eta^5\text{C}_5\text{H}_4-\eta^5\text{C}_5\text{H}_4)]\}2\text{PF}_6$ which has the structure (V), ⁹⁶ and one osmium cluster $\text{Os}_3(\text{CO})_{10}(\text{H})(\text{OH})$ obtained by



(V)

the reaction of $\text{Os}_3(\text{CO})_{12}$ with water. ⁹⁷ Following the observation that orthometallated triphenylphosphine complexes of ruthenium will react with water ⁷²:



we attempted to prepare hydridohydroxo complexes of this kind by the more direct route of reacting $\text{RuHCl}(\text{PPh}_3)_3$ with NaOH or KOH.

Since very little is known about hydroxo complexes of ruthenium,

this study was extended to the preparation and reactions of chloro-hydroxo and hydroxo cationic complexes of ruthenium.

Finally we have also investigated the reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with alkali metal alkoxides since no monomeric ruthenium(II) alkoxo complexes have been reported although it has been proposed on the basis of i.r. evidence that alkoxo intermediates of this kind are important in the well-known decarbonylation of alcohols by low valent ruthenium phosphine complexes.^{98,99}

Results and Discussion

1) Reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with Hydroxide Ion

The reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with excess aqueous carbonate-free NaOH or KOH in tetrahydrofuran (THF) yield red solutions from which a red crystalline compound of stoichiometry $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$ may be isolated. If, however, the reaction is carried out in acetone, the nature of the products is critically dependent upon the reaction conditions. Thus, if the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with NaOH or KOH in acetone at room temperature is carried out in the presence of > 10% by volume of water, a red solid analysing as $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ is precipitated. The yellow filtrate contains only triphenylphosphine and Na or KCl. The complex $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ is also formed from $\text{RuHCl}(\text{PPh}_3)_3$ and KOH in toluene-water mixtures.

On reducing the percentage of water in acetone, the yield of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ decreases and more ruthenium now remains in solution. If only one drop (ca. 0.1 cc) of water is added to 50 cc of acetone, an orange-red solution is formed. From this solution, red and yellow crystalline complexes may be isolated, together with small amounts of

$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$.¹⁰ The red complex is considered, on the basis of i.r., ^1H n.m.r. and ^{31}P data, as well as its crystallographic molecular weight (ca. 2500) to be a polynuclear* species probably of stoichiometry $\text{Ru}_4\text{H}_4(\text{OH})_2(\text{PPh}_2)_2(\text{CO})_2(\text{PPh}_3)_6(\text{acetone})_2$ and is discussed in detail later.

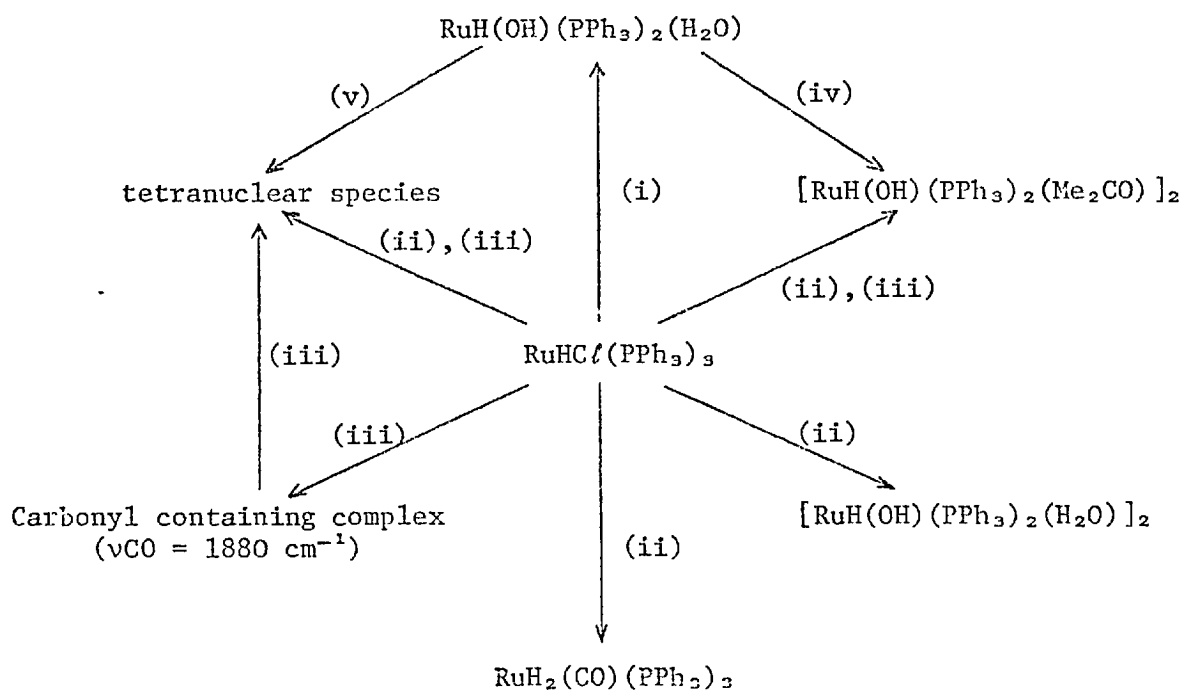
The two yellow complexes which are obtained analyse as $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_2$ ($\text{S} = \text{H}_2\text{O}$ or acetone), the complex with coordinated water being less soluble and obtained in higher yield after longer reaction times.

In the absence of added water, $\text{RuHCl}(\text{PPh}_3)_3$ will not react with KOH pellets in acetone, presumably on account of the insolubility of KOH in acetone.

From the prolonged reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH in refluxing acetone in the presence of traces (< 1%) of water, the tetranuclear species and $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{acetone}]_2$ are the only products, but if the reaction is stopped after a short time (ca. 1 hr), spectroscopic evidence indicates the presence of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$ and a small amount of another CO-containing compound ($\nu_{\text{C-O}} = 1880 \text{ cm}^{-1}$).

The tetranuclear species may also be prepared by reaction of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ with KOH in acetone in the presence of less than 1% water, whilst refluxing $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ in dry acetone for several days produces $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$, indicating that $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ is intermediate in the formation of both $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$ and the tetranuclear species. These reactions are outlined in Scheme 1 and the mechanism of formation of the tetranuclear species is discussed later.

* Hereinafter referred to as 'The tetranuclear species'.

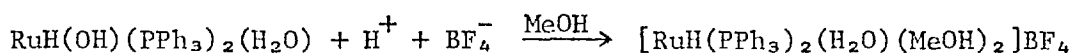


- (i) NaOH , 10% H_2O , 25° (iii) KOH , < 1% H_2O , reflux
(ii) KOH , < 1% H_2O , 25° (iv) Reflux dry acetone
(v) KOH , dry acetone, 25°

Scheme 1 Reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH or NaOH in acetone

The reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH pellets in *t*-butanol yields $\text{RuH}_2(\text{PPh}_3)_4$ together with yellow crystals of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{}^t\text{BuOH})]_2$. The latter complex is also formed on reacting $\text{RuHCl}(\text{PPh}_3)_3$ with potassium *t*-butoxide in *t*-butanol (see later).

All these hydridohydroxo complexes have been fully characterised by elemental analysis, as well as by i.r., ^1H , and ^{31}P n.m.r. spectroscopy. Chemical evidence for the presence of hydroxide ion in $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ is also afforded by its reaction with aqueous fluoroboric acid in methanol to yield the known ⁴¹ complex ion, $[\text{RuH}(\text{PPh}_3)_2(\text{H}_2\text{O})(\text{MeOH})_2]^+$, presumably by protonation of the coordinated hydroxo group:



Evidence that $\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{H}_2\text{O}$, THF) contain only one coordinated solvent molecule per ruthenium atom comes from analytical data and from integration of solvent resonances in the ^1H n.m.r. spectrum against those of the phenyl groups of PPh_3 .

It has not proved possible to measure molecular weights of these complexes on account of their insolubility (dimeric species) and air-sensitivity (monomers), but $\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{H}_2\text{O}$, THF) are considered to be monomeric on the basis of their solubility, and scarlet colour which appears to be characteristic of five coordinate sixteen electron complexes of ruthenium(II) ^{35,42} [but see below for $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{ROH})$]. The yellow colour and relative insolubility, together with infrared evidence (two $\nu\text{O-H}$), on the other hand, suggest dimeric formulations for $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{L}]$ [$\text{L} = \text{H}_2\text{O}$, Me_2CO , $\text{}^t\text{BuOH}$ or THF (see below)]. Finally $\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{THF}$ or H_2O) does not react with 2,2-dimethoxypropane or with sodium amalgam in THF but reacts with P_2O_5 in toluene. The ruthenium complex is fixed on P_2O_5

and cannot be extracted by organic solvents. Destruction of P_2O_5 by water in THF liberates the complex as a brown powder soluble in DMSO which analyses for $Ru(PO_4H_2)_2(PPh_3)_2$. $RuH(OH)(PPh_3)_2S$ ($S = THF, H_2O$) also reacts with CO in THF to give $Ru(CO)_3(PPh_3)_2$. We have followed the reaction of $RuH(OH)(PPh_3)_2(THF)$ with CO by infrared and it is clear that water (broad peaks at 3300 and 1620 cm^{-1}) not formic acid is formed, presumably by reductive elimination. However, the reaction is very complex giving several different species as intermediates which we have been unable to isolate or characterise, but a transient peak at 1700 cm^{-1} may suggest the formation of a coordinated formyl or $HO(O)C$ -group by insertion of CO into the Ru-H or Ru-OH bond. This kind of reaction has not previously been reported but is considered to be a crucial step in the reduction of CO by hydrogen.¹⁰⁰ However since formic acid is not detected as a product, it is perhaps more likely that the absorption near 1700 cm^{-1} arises from a transient complex which contains a bridging CO group.

2) Reactions of $RuCl_2(PPh_3)_3$ with Hydroxide Ion

$RuCl_2(PPh_3)_3$ does not react with KOH or NaOH in dry tetrahydrofuran at room temperature but if 10% by volume of water is added, a reaction does occur despite there being no apparent change in the orange brown colour of the solution.

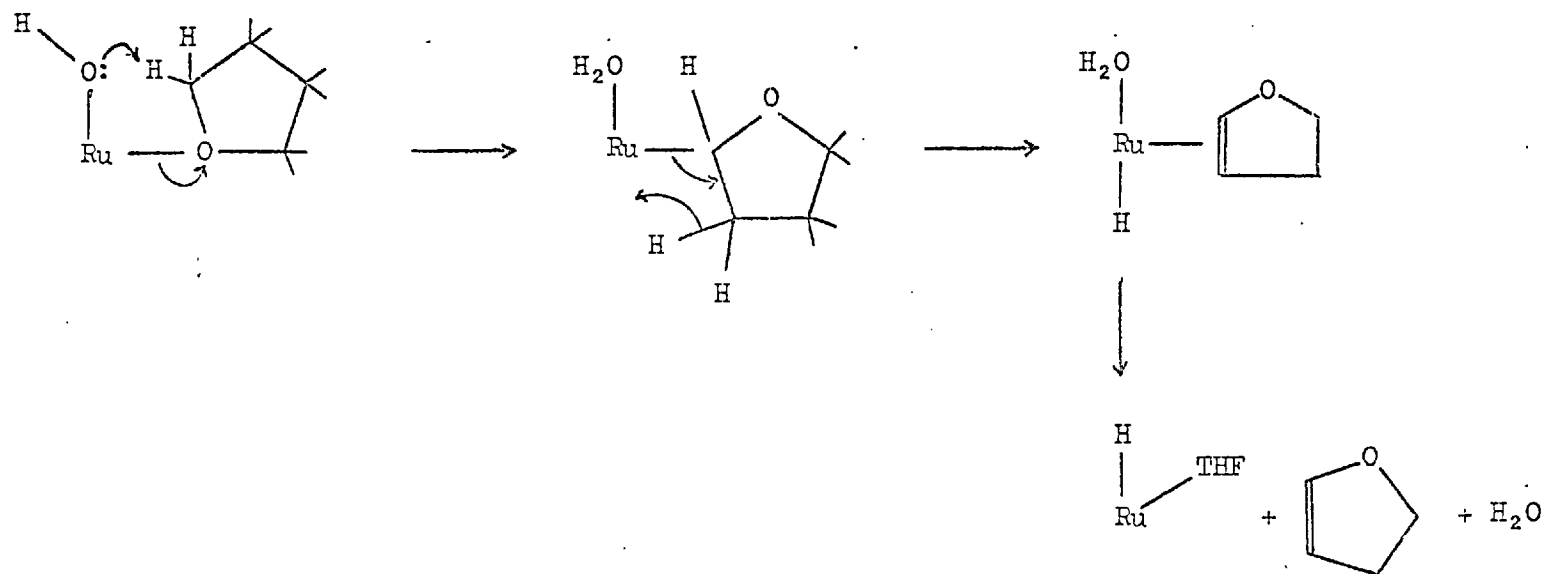
The first complex that may be isolated from the tetrahydrofuran solution is $RuCl(OH)(PPh_3)_2(H_2O)_2$ which may be recrystallised unchanged from toluene but which converts into $RuCl(OH)(PPh_3)_2(THF)_2$ on a recrystallisation from tetrahydrofuran-petroleum. Longer reaction times lead to the isolation of yellow-brown microcrystals of stoichiometry $[RuCl(OH)(PPh_3)_2(H_2O)]_2$ which may also be obtained by recrystallisation of $RuCl(OH)(PPh_3)_2(H_2O)_2$ from warm toluene-petroleum mixtures.

In refluxing tetrahydrofuran containing 10% water, $\text{RuCl}_2(\text{PPh}_3)_3$ and NaOH give a mixture of $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$ and, more surprisingly, $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_2$, which is the sole product if refluxing is prolonged for several hours. The origin of the hydride in this complex is not clear but it is possible that it occurs by preliminary formation of a dihydroxo species followed by elimination of water from the hydroxide and an α -hydrogen atom of a cis-coordinated tetrahydrofuran moiety then β -elimination of dihydrofuran from the alkyl, as in Scheme 2. A similar mechanism is thought to account for the reaction of $\text{RuMe}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_n\text{L}_{3-n}$ ($n = 2$, $\text{L} = \text{Et}_2\text{O}$; $n = 1$, $\text{L} = \text{MeLi} \cdot \text{Et}_2\text{O}$) with tetrahydrofuran to give $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_n(\text{THF})_{3-n}$ and methane.²¹ * If this mechanism does account for the formation of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_2$ it is probable that it occurs in a dimeric species $[\text{Ru}(\text{OH})_2(\text{PPh}_3)_2(\text{THF})]_2$ since there is no evidence for formation of the dimeric hydridohydroxo compound from $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$ even on prolonged reflux in tetrahydrofuran, the monomer being recovered unchanged. In refluxing toluene containing aqueous sodium hydroxide a complicated mixture of compounds was obtained but no dihydroxo species.

Although $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$ does not react with sodium borohydride in tetrahydrofuran, in toluene-water mixtures both $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ are formed in the presence of excess triphenylphosphine, suggesting that, although both the OH and Cl groups are reducible, the OH group is reduced preferentially. This may reflect the higher six-coordinate trans-effect of the Cl^- group, or may simply be due to the greater intrinsic strength of the Ru-Cl bond over the Ru-OH bond, or to the different lattice energies of NaCl and NaOH.

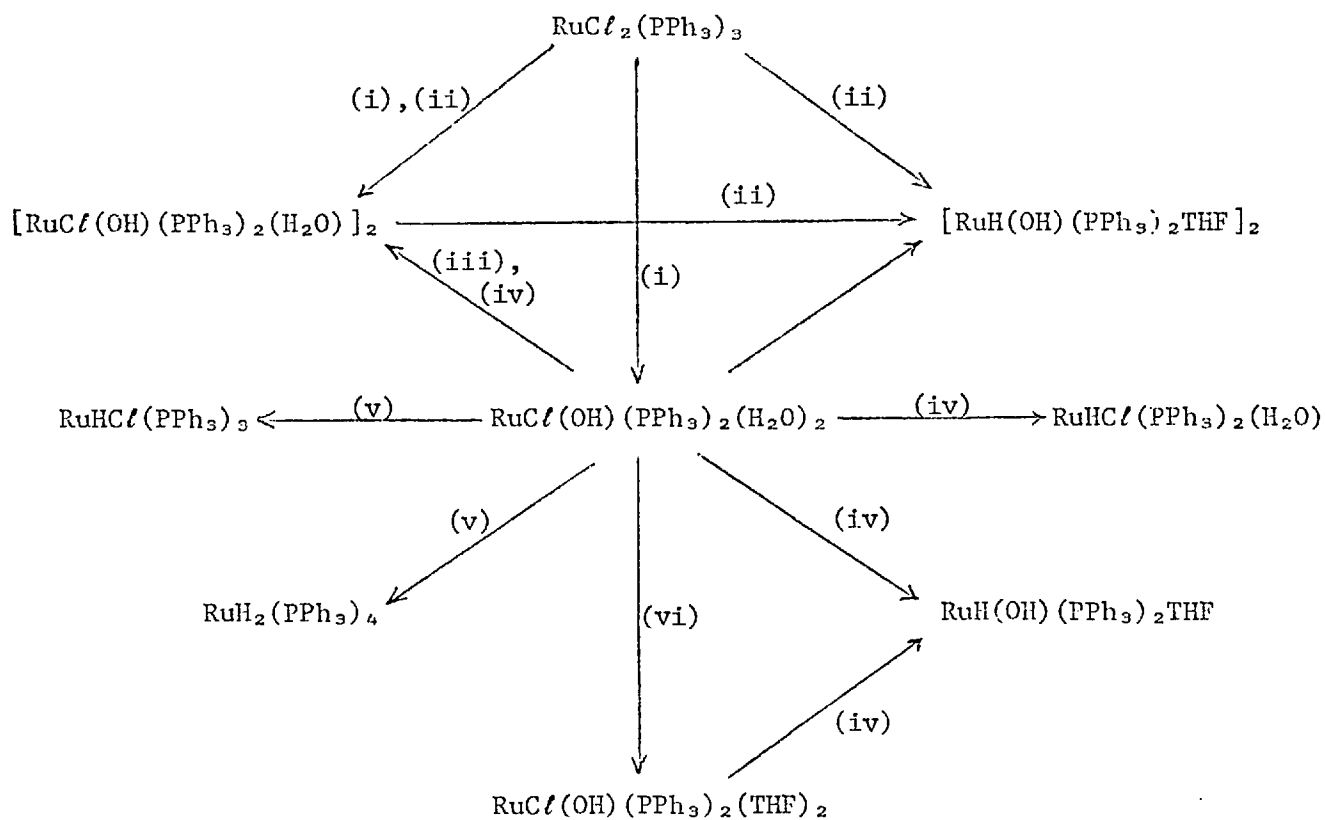
Using the milder reducing agent, hydrogen in the presence of base

* A similar mechanism may also operate in transfer hydrogen reactions catalysed by low valent ruthenium compounds.^{101,70}



Scheme 2

Formation of hydride from coordinated hydroxide ion and tetrahydrofuran



- (i) NaOH , 10% H_2O , THF, 25°C
- (ii) NaOH , 10% H_2O , THF, under reflux
- (iii) Recrystallised from toluene-petroleum, 60°C
- (iv) H_2 , excess KOH , THF, under reflux
- (v) NaBH_4 , PPh_3 , toluene, water, 25°C
- (vi) Recrystallised from THF-petroleum

Scheme 3

Preparation and reactions of $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$

(KOH) in tetrahydrofuran, a mixture of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_n$ ($n = 1$ or 2) is formed. Although this appears to indicate that the chloride group is preferentially reduced under these conditions, this is in fact not the case, since, if less KOH is employed in the reaction, the main product is the red-purple complex $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$, which is presumably analogous to the previously reported,¹² though not isolated " $\text{RuHCl}(\text{PPh}_3)_2$ ". The hydridohydroxo-complexes are then presumably formed by attack of OH^- on this complex.

As in previous studies,¹⁰² a qualitative order of the trans effects of the anionic ligands ($\text{H}^- > \text{Cl}^- > \text{OH}^-$) in five- and six-coordinate complexes of ruthenium(II) is indicated by the much slower reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with OH^- than of $\text{RuHCl}(\text{PPh}_3)_3$, and the observation that only one chloride ion of $\text{RuCl}_2(\text{PPh}_3)_3$ is replaced by hydroxide ion under mild conditions.

In a further attempt to prepare a dihydroxo species, the previously unknown dication $[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3]^{2+}$ was prepared by reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with AgPF_6 in acetonitrile. With one mole of NaOH in a thf-water mixture the monohydroxo cation $[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]^+$ was obtained but no dihydroxo species could be isolated even employing a large excess of NaOH.

3) Reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with Alkoxide Ions

The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with NaOR ($\text{R} = \text{Et}$ or $i\text{Pr}$) has previously been studied²⁰ under various conditions and dihydrido-ruthenium complexes; $\text{RuH}_2(\text{PPh}_3)_3\text{X}$ ($\text{X} = \text{N}_2, \text{H}_2, \text{CO}, \text{PPh}_3$) invariably result.

The prolonged reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with NaOMe in diethyl ether or tetrahydrofuran in the presence of ca. 2% methanol also leads to the formation of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$. However, the reaction in tetrahydrofuran

in addition gives a yellow crystalline complex, $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$ * in about 20% yield. If this reaction in tetrahydrofuran is stopped as soon as the purple colour of $\text{RuHCl}(\text{PPh}_3)_3$ has disappeared, $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$ is obtained in higher yield (ca. 50%), indicating that $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$ is probably an intermediate in the formation of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ but that not all of it is carbonylated in the long term.

Since the isolation of other intermediates from this reaction should shed some light on the mechanism of decarbonylation of alcohols in basic media by low-valent ruthenium phosphine complexes (which has been postulated from i.r. evidence but never proved), we have investigated the reactions of $\text{RuHCl}(\text{PPh}_3)_3$ with NaOMe in the presence of methanol under different conditions.

Thus, if the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with solid NaOMe is carried out in ether in the presence of ca. 1% methanol at low temperature (0°) a yellow microcrystalline solid is deposited after several hours.

This solid (A) has absorptions in its i.r. spectrum arising from $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$,¹⁰ as well as extra peaks at 2010w, 1632vsbr and 825m cm^{-1} .[†] On some occasions another yellow compound (B), with extra peaks in its i.r. spectrum at 2720w, 2030w, 1600vs, 875m and 780s is isolated under ostensibly the same reaction conditions. The strong peaks near 1600 cm^{-1} for both of these complexes are presumably indicative of aldehydic C=O linkages. Complex B which has an extra peak at 2720 cm^{-1} ($\nu\text{C-H}$) probably contains a coordinated formyl group since $\nu\text{C=O}$ of the other known formyl complexes^{104,105,106} are at

* This compound is also the sole product from the reaction in tetrahydrofuran of $\text{RuHCl}(\text{PPh}_3)_3$ with $\text{Me}_3\text{SiCH}_2\text{Li}$ which has been allowed to stand in air for several days and hence formed $\text{Me}_3\text{SiCH}_2\text{OLi}$.¹⁰³

† It is unlikely that all the absorptions (see Experimental section) arise from one compound since the relative intensities of the peaks at 1940 and 1632 cm^{-1} are variable.

1580-1610 cm^{-1} , and since these compounds as well as other aliphatic aldehydes, although not formaldehyde, have $\nu\text{C-H}$ of the aldehydic moiety near 2700 cm^{-1} .¹⁰⁷ Further, alkyl aldehydes, e.g., acetaldehyde, have C-H deformations at 875 and 780 cm^{-1} ,¹⁰⁷ exactly the positions of the other two extra peaks in the i.r. spectrum of B. We therefore suggest that this compound is $\text{RuH}(\text{CHO})(\text{PPh}_3)_3\text{S}$ with the acyl group bound through the carbon atom rather than through the C=O bond as is found for the related $\text{RuCl}(\text{C}(\text{O})\text{R})(\text{CO})(\text{PPh}_3)_2$,¹⁰⁸ since in these complexes C=O is at much lower frequency - 1505-1510 cm^{-1} .

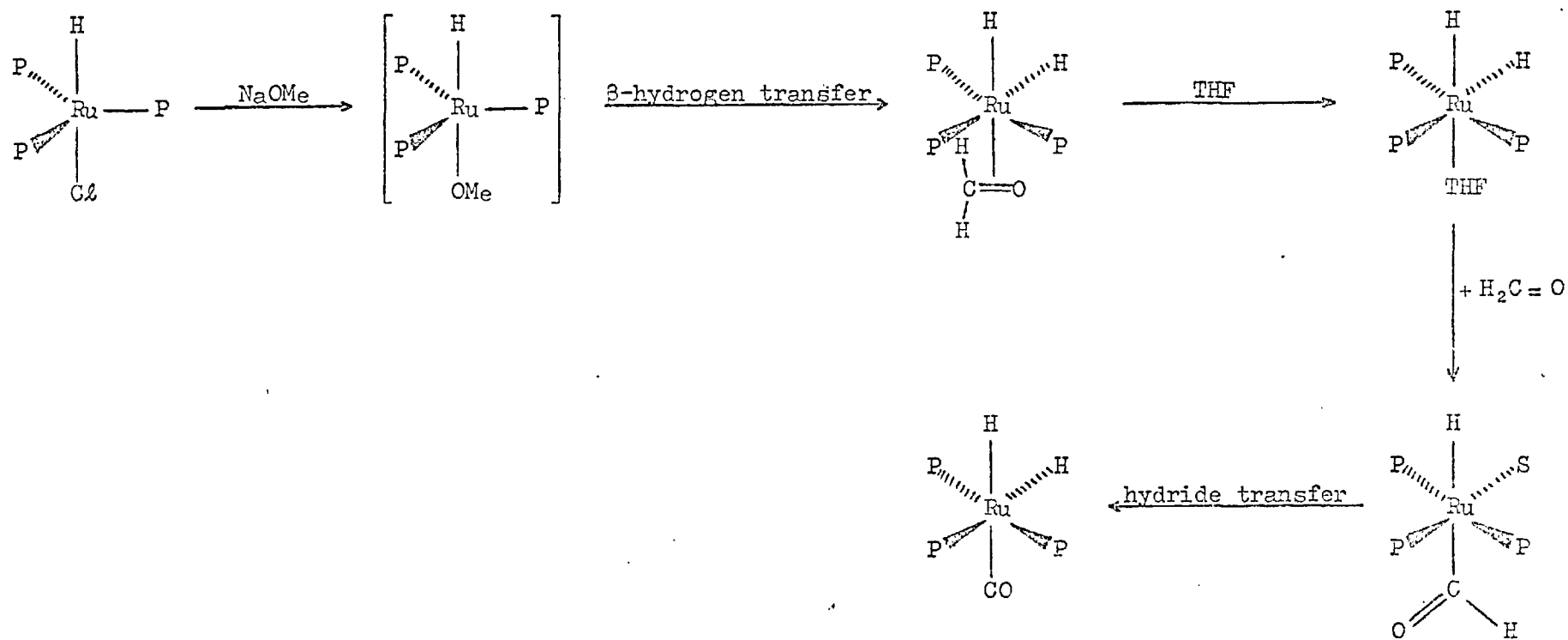
Compound A, on the other hand, like formaldehyde itself,¹⁰⁷ does not have $\nu\text{C-H}$ below 2800 cm^{-1} and we formulate the compound as $\text{RuH}_2(\text{OCH}_2)(\text{PPh}_3)_3$. Since $\nu\text{C=O}$ in this complex is 113 cm^{-1} below that of the free ligand (1745 cm^{-1}) it is probable that the formaldehyde group is bound to the metal via the C=O double bond, rather than through a lone pair on oxygen.

Unfortunately, it has not proved possible to purify these compounds since recrystallisation leads only to $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, which is also obtained from the filtered reaction solutions.

It is not clear what the difference is between the preparations of complexes A and B but it may be that small changes in the percentage of methanol in the system tip the balance one way or the other, since $\text{RuHCl}(\text{PPh}_3)_3$ will not react with NaOMe in diethyl ether in the absence of methanol, whilst if 5% methanol is employed, spectroscopic evidence indicates that a mixture of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuH}_4(\text{PPh}_3)_3$ ^{22,46} is formed.

Finally, the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with gaseous formaldehyde gives $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ in high yield.

These reactions are summarised in Scheme 4 and suggest a similar mechanism for alcohol decarbonylation to those which have previously



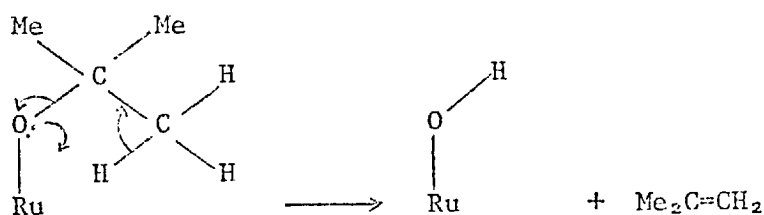
Scheme 4 Mechanism of formation of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ from $\text{RuHCl}(\text{PPh}_3)_3$ and NaOMe [compound in brackets not isolated]

been postulated; ^{98,99} the only difference being that formaldehyde, having left the coordination sphere of the ruthenium atom oxidatively adds a C-H bond to form an hydridoformyl derivative which, on hydride transfer, leads directly to a C bound CO group and precludes the necessity of postulating an O bound CO group.⁹⁸

Since it appears that the β -hydrogen transfer reaction is important in the decarbonylation of alkoxo complexes of ruthenium, those which do not contain β -hydrogen atoms on the alkoxide moiety (OPh, OBu^t) should be elimination stabilized and should be isolable.

The reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with sodium phenoxide, which leads to $\text{RuH(OPh)}(\text{PPh}_3)_2$, in which the phenoxo group is coordinated to the ruthenium atom via its ring system rather than the oxygen atom has been described.⁶³ However, all attempts to prepare a t-butoxo complex have been fruitless giving only $[\text{RuH(OH)}(\text{PPh}_3)_2(\text{tBuOH})]_2$ and small amounts of $\text{RuH}_2(\text{PPh}_3)_4$, despite numerous attempts to remove any water from t-butanol, by drying over sieves, distillation from magnesium or both. Using sublimed KOBU^t in THF the reaction is not clean and a mixture of a hydroxo compound and $\text{RuH}_2(\text{PPh}_3)_4$ is formed.

The isolation of hydroxo complexes from these reactions with tBuO^- suggests that water may be present and KOH formed in situ. However, this does not appear to be the case, as reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH in tBuOH under similar conditions is much slower (3 days as against 3 hours) and produces higher yields of $\text{RuH}_2(\text{PPh}_3)_4$. It may be that the t-butoxide forms but decomposes as shown in Scheme 5 to give a coordinated hydroxo group and isobutylene. On heating to 500°C t-butanol undergoes dehydration via a similar four-centred transition state to give isobutylene.¹⁰⁹



Scheme 5 Mechanism of decomposition of coordinated t-butoxide ligand

4) Further Attempts to Isolate Alkoxo Complexes

In a further attempt to prepare alkoxo complexes, the reactions of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ with alcohols, ROH ($\text{R} = \text{Me}, \text{Et}$ or ^tBu) were attempted. Although no reaction was observed with t-butanol, methanol and ethanol gave red solids, $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2.\text{ROH}$, together with small amounts of $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ ¹¹⁰ and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ¹¹¹ (i.r. evidence) on prolonged reflux.

The bright red colours of these complexes suggest five-coordinate formulations^{35,42} with one molecule of alcohol of crystallisation. The proton n.m.r. spectrum of the methanol complex, however, indicates a non-fluxional cis dihydride with one of the phosphines trans to a hydride, so it seems likely that the complex is six-coordinate with structure I (Figure 1). We cannot, however, rule out the possibility that the complex has structure II and is rearranging slowly at room temperature. The observations that the methanol is retained on recrystallisation of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2.\text{MeOH}$ from benzene-petroleum mixtures and that $\nu_{\text{C-O}}$ of the alcohol is at 1050 cm^{-1} (cf. 1030 cm^{-1} for free methanol¹¹²) strongly support the contention that methanol is coordinated.

These complexes are presumably formed by trans-esterification of the coordinated hydroxo group with alkoxide followed by decarbonylation via a pathway similar to that shown in Scheme 4.

The failure to prepare alkoxides of low valent ruthenium-phosphine complexes is perhaps not surprising since to our knowledge the only phosphine containing alkoxo complex of a metal in the iron triad is fac-Os(OEt)(S₂CNMe₂)(PMe₂Ph)₃.¹¹³

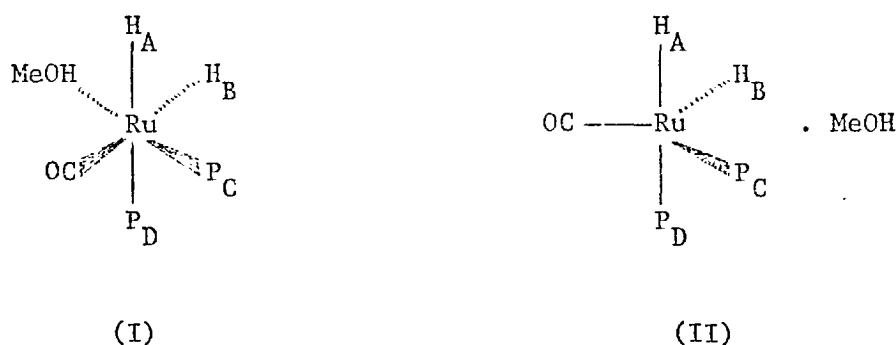


Figure 1

Possible structures of RuH₂(CO)(PPh₃)₂(MeOH)

5) Spectroscopic Properties

a) Infrared Spectra (Table 1)

All of the complexes show absorptions in their i.r. spectra characteristic of coordinated triphenylphosphine groups, together with other peaks which give some structural information.

For RuH(OH)(PPh₃)₂S, RuCl(OH)(PPh₃)₂S₂ and [Ru(OH)(PPh₃)₃(MeCN)(H₂O)]PF₆ (S = H₂O or THF) a single peak near 3600 cm⁻¹ is indicative of coordinated hydroxide ion,¹¹⁴⁻¹¹⁹ whilst two peaks in this region for [RuH(OH)(PPh₃)₂L]₂ (L = H₂O, Me₂CO or ^tBuOH) and [RuCl(OH)(PPh₃)₂(H₂O)]₂ indicate either terminal hydroxo groups which are mutually cis or, more likely, bridging hydroxo groups. For [RuH(OH)(PPh₃)₂(THF)]₂ only

TABLE 1

Infrared Spectra of Ruthenium Complexes^a

Compound	$\nu_{\text{Ru-H}}$ cm^{-1}	$\nu_{\text{O-H}}$ cm^{-1}	Other Bands
$\text{RuH(OH)(PPh}_3)_2(\text{H}_2\text{O})$	2100w	3600m	
$\text{RuH(OH)(PPh}_3)_2(\text{THF})$	2080w	3590m	
$[\text{RuH(OH)(PPh}_3)_2(\text{H}_2\text{O})]_2$	1980w	3570m, 3590m	
$[\text{RuH(OH)(PPh}_3)_2(\text{Me}_2\text{CO})]_2$	1980w	3580m, 3600m	1715 ^b _m
$[\text{RuH(OH)(PPh}_3)_2(\text{THF})]_2$	2110m	3570mbr	
$[\text{RuH(OH)(PPh}_3)_2(\text{}^t\text{BuOH})]_2$	1890m	3590m, 3610m	
$\text{RuCl(OH)(PPh}_3)_2(\text{H}_2\text{O})_2$		3600m	300 ^c _w
$\text{RuCl(OH)(PPh}_3)_2(\text{THF})_2$		3580m	300 ^c _w
$[\text{RuCl(OH)(PPh}_3)_2(\text{H}_2\text{O})]_2$		3580m, 3605m	280 ^c _w
$\text{RuHCl(PPh}_3)_2(\text{H}_2\text{O})$	2020m		265 ^c _w
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})$			1935 ^d _s , 1050 ^e _{mbr}
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{EtOH})$			1940 ^d _s , 1050 ^e _{mbr}
$\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$	1985w, 2045w	-	
Tetranuclear species	2005w	3585m	1910 ^d _s , 1715 ^b _m
$\text{Ru(PPh}_3)_2(\text{PO}_4\text{H}_2)_2$		3300br	1260 ^f , 1000 ^f , 870 ^g
$[\text{Ru(PPh}_3)_3(\text{MeCN})_3](\text{PF}_6)_2 \cdot 2\text{MeCN}$			2310 ^h _w , 2290 ^h _w , 835 ⁱ _s
$[\text{Ru(OH)(PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]\text{PF}_6 \cdot 2\text{MeOH}$		3580m	2250 ^h _w , 835 ⁱ _s

^a In Nujol mulls^b $\nu_{\text{C=O}}$ of coordinated acetone^c $\nu_{\text{Ru-Cl}}$ ^d $\nu_{\text{C}\equiv\text{O}}$ ^e $\nu_{\text{C-O}}$ of coordinated alcohol^f ν_{As} and ν_{S} of PO_2^- group^g $\nu_{\text{P-O}}$ ^h Free and coordinated MeCNⁱ $\nu_{\text{P-F}}$

one $\nu\text{O-H}$ is seen but since this is significantly broader than the single $\nu\text{O-H}$ of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$, it is probable that two absorptions of very similar energies are in fact present.

A single absorption near 2000 cm^{-1} for $\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{H}_2\text{O}$ or THF), $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{L}]_2$ ($\text{L} = \text{H}_2\text{O}$, Me_2CO , THF or $^t\text{BuOH}$) and $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$ indicates the presence of an Ru-H bond. For $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$, the presence of two $\nu\text{Ru-H}$ at 1985 and 2045 cm^{-1} confirms it as a cis-dihydride and, although $\nu\text{Ru-H}$ in the other dihydrido complexes, $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2.\text{ROH}$ ($\text{R} = \text{Me}$ or Et), are not immediately apparent, slight asymmetry of $\nu\text{C=O}$ indicates that they are probably near 1950 cm^{-1} .

The metal-chlorine stretches of $\text{RuCl}(\text{OH})(\text{PPh}_3)_2\text{S}_2$ ($\text{S} = \text{H}_2\text{O}$ or THF) and $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$ being near 300 cm^{-1} are indicative of terminal chlorine atoms.¹²⁰ $\nu\text{Ru-Cl}$ at 265 cm^{-1} for $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$ is close to the value found¹⁰ in the monomeric $\text{RuHCl}(\text{PPh}_3)_3$ in which the chloride is trans to the hydride¹²¹ and since $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$ is deeply coloured, it seems likely that it is a five-coordinate monomer with the chloride trans to hydride.

$\text{RuH}_2(\text{CO})(\text{PPh}_3)_2.\text{ROH}$ ($\text{R} = \text{Me}$ or Et) show absorptions near 1950 cm^{-1} indicative of terminal CO groups trans to hydrides (cf. 1940 cm^{-1} for νCO of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$).¹⁰ Absorptions near 1050 cm^{-1} are in the region accepted for coordinated alcohol moieties.¹²² The O-H absorptions of $\text{Ru}(\text{PPh}_3)_2(\text{PO}_4\text{H}_2)_2$ are seen at 3300 cm^{-1} whereas the asymmetric and symmetric $\nu\text{P=O}$ of the PO_2^- moiety are at 1260 and 1000 cm^{-1} respectively, $\nu\text{P-OH}$ is at 860 cm^{-1} .

Although absorptions arising from coordinated solvent molecules do not appear to be present in the case of THF , H_2O and $^t\text{BuOH}$ (some may be hidden under phosphine absorptions) a peak near 1715 cm^{-1} in the i.r. spectrum of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$ is assigned to $\nu\text{C=O}$ of

coordinated acetone, and peaks around 2300 cm^{-1} in $[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3]-(\text{PF}_6)_2$ and $[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]\text{PF}_6$ are assigned to coordinated acetonitrile.

b) ^1H and ^{31}P N.M.R. Spectra (Table 2)

Peaks between τ 2.4 and 3.5 for all the complexes herein reported indicate the presence of coordinated triphenylphosphine groups, although little stereochemical information is available from the broad resonances.

The presence of coordinated water in $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_n$ ($n = 1$ or 2), $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$, $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$, $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$ and $[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})](\text{PF}_6)$ is confirmed by peaks near τ 9, whilst the characteristic second order resonances for coordinated tetrahydrofuran are observed near τ 6.2 and 8.5 for $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_n$ ($n = 1$ or 2), $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{THF})_2$ and $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$. In $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$ coordinated acetone resonates near τ 8.3 whilst the tertiary butanol moieties in $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(^t\text{BuOH})]_2$ resonate at τ 7.9 (OH) and 8.9 (^tBu). Finally the presence of coordinated acetonitrile in $[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3](\text{PF}_6)_2$ and $[\text{Ru}(\text{OH})(\text{PPh}_3)_3-(\text{MeCN})(\text{H}_2\text{O})](\text{PF}_6)$ is detected by resonances near τ 8.0, and the hydroxo protons of $\text{Ru}(\text{PPh}_3)_2(\text{PO}_4\text{H}_2)_2$ resonate at τ 6.7. More structural information is available from analysis of the high field region in ^1H n.m.r. spectrum since many of the complexes show well resolved hydride resonances.

For $\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}$ ($\text{S} = \text{THF}$ or H_2O), as well as for $\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})$, a triplet near τ 30 indicates coupling of the hydride to two equivalent phosphorus atoms as would be expected for the presumably fluxional five coordinate species. The proton noise decoupled ^{31}P n.m.r. spectrum of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$ in benzene, which shows a single line, split into a doublet ($J_{\text{PH}} = 39\text{ Hz}$) when only the

TABLE 2
¹H n.m.r. Spectra of Ruthenium Complexes^a

Compound	Hydride τ (J_{PH})	Hydroxide τ	Coordinated Solvent τ ($J_{\text{H-H}}$)	
RuH(OH)(PPh ₃) ₂ (H ₂ O)	34.1 (39)t	9.95s	8.5s	
RuH(OH)(PPh ₃) ₂ (THF)	34.0 (39)t	10.00s	6.30s ^b	8.45 ^b
[RuH(OH)(PPh ₃) ₂ (Me ₂ CO)] ₂	27.7 (29)t	11.30s	8.3s	
[RuH(OH)(PPh ₃) ₂ (THF)] ₂	27.9 (32)t	11.65s	6.33 ^b	8.48 ^b
[RuH(OH)(PPh ₃) ₂ (^t BuOH)] ₂	27.95(29)t	11.75s	7.9s	8.9s
RuCl(OH)(PPh ₃) ₂ (H ₂ O) ₂	-	10.00s	9.4s	
RuCl(OH)(PPh ₃) ₂ (THF) ₂		10.00s	6.05 ^b	8.25 ^b
[RuCl(OH)(PPh ₃) ₂ (H ₂ O)] ₂		14.85	9.6s	
RuHCl(PPh ₃) ₂ (H ₂ O)	30.10(34)t	-	9.0s	
RuH ₂ (PPh ₃) ₃ (THF)	20.30(36)q	-	6.54 ^b	8.68 ^b
RuH ₂ (CO)(PPh ₃) ₂ (EtOH)		-	6.2(7)q ^c	8.7(7)t ^c
RuH ₂ (CO)(PPh ₃) ₂ (MeOH)	H _A 21.1 ^e (6, H _A H _B) ^d H _B 30.0 (16, H _A P _C) (76, H _A P _D) (33, H _B P _C) (42, H _B P _D)	-	6.7s ^c	
Ru(PO ₄ H ₂) ₂ (PPh ₃) ₂			6.67	
[Ru(PPh ₃) ₃ (MeCN) ₃](PF ₆) ₂ ·2MeCN			7.9	7.95
[Ru(OH)(PPh ₃) ₃ (MeCN)(H ₂ O)]PF ₆ ·2MeOH		9.95	8.4	7.7

s = singlet; d = doublet; t = triplet; q = quartet.

^a In C₆D₆ at 36° at 60 MHz, J in Hz;

^b Second order pattern for coordinated THF;

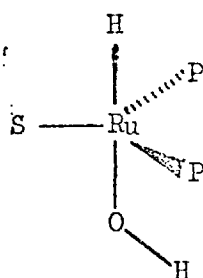
^c Coordinated alcohol; ^d For assignments see Figure 1;

^e Broad.

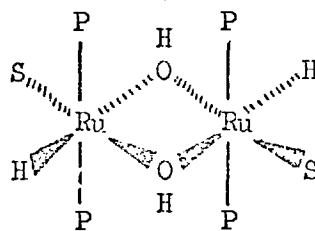
phenyl region of the proton spectrum is decoupled, is in total agreement with this structure; whilst its chemical shift (76.2 ppm)^{*} is close to that found for the unique phosphorus atom of $\text{RuH}(\text{OAc})(\text{PPh}_3)_3$ and of $\text{RuCl}_2(\text{PPh}_3)_3$ at low temperatures,³⁵ indicating that the phosphines are probably trans to ligands of low trans-influence (Structure III, Figure 2), since for P trans to P typical chemical shifts are closer to 40 ppm³⁵ and for P trans to H negative chemical shifts are often observed.^{21,72}

Once isolated, the dimeric species, $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_2$ ($\text{S} = \text{H}_2\text{O}$, Me_2CO , THF), as well as $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2 \cdot \text{EtOH}$, are all too insoluble for observation of their hydride resonances in the proton n.m.r. spectra, but the presence of a resonance (τ 4.8) corresponding to CHDCl_2 when they are dissolved in CDCl_3 strongly indicates that the hydride is indeed present. For $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_2$ ($\text{S} = \text{Me}_2\text{CO}$ or THF) it has also proved possible to observe the hydride resonances in super-saturated reaction solutions prior to isolation of the complexes. Thus, both these complexes, as well as the more soluble $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{tBuOH})]_2$ show triplet resonances near τ 28 ($J_{\text{PH}} \approx 30$ Hz). This suggests that the hydride is cis to the two phosphines and that the phosphines are equivalent, as in IV or V (Figure 2), although it is possible that the phosphines are non-equivalent but are fortuitously equally coupled to the hydride, as in $\text{RuH}(\text{OAc})(\text{PPh}_3)_3$.³⁵ For $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{tBuOH})]_2$ the observation of a singlet in the proton noise decoupled ^{31}P n.m.r. spectrum at 75.5 ppm which splits into a doublet ($J_{\text{PH}} = 36$ Hz) when only the phenyl region is decoupled confirms that the phosphorus atoms are equivalent and are in the thermodynamically more favourable ^{123,124} cis configuration, as in structure V.

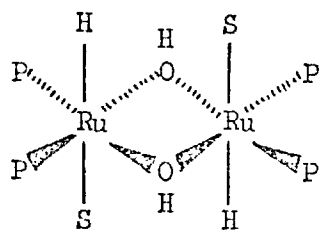
* Chemical shifts are to high frequency of external 85% H_3PO_4 .



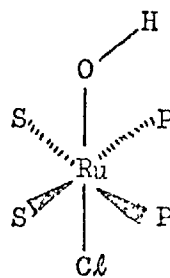
III



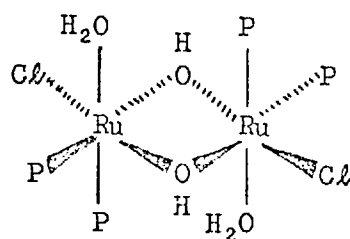
IV



V



VI



VII

Figure 2 Structures of some hydroxoruthenium complexes.

P = PPh_3

The observation of a quartet at τ 20.3 ($J_{\text{PH}} = 36$ Hz) for $\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$ indicates that unlike $\text{RuH}_2(\text{PPh}_3)_3\text{L}$ ($\text{L} = \text{CO}$,¹⁰ or DMF ⁷³), this is a fluxional dihydrido complex. Eight line resonances for each of the hydrides of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})$ on the other hand indicate a non-fluxional cis dihydrido stereochemistry.

Finally, the resonances of the protons of the coordinated hydroxo moieties are of interest since they provide unequivocal correlations of chemical shift with mode of coordination. Thus, in $\text{RuH}(\text{OH})(\text{PPh}_3)_3\text{S}$, $\text{RuCl}(\text{OH})(\text{PPh}_3)_2\text{S}_2$ ($\text{S} = \text{H}_2\text{O}$ or THF), and $[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})](\text{PF}_6)$ where terminal hydroxo groups are indicated by their i.r. spectra and stoichiometries, the resonance is near τ 10 whilst for the bridging hydroxides of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_2$ ($\text{S} = \text{H}_2\text{O}$, Me_2CO , THF or $t\text{-BuOH}$) and $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$, the resonances are to higher field (τ 12-15).

At first sight these resonances appear to be to somewhat higher field than is usual for transition metal hydroxo compounds (τ 6-8)¹¹⁵,^{119,125} however, for the bridging hydroxo groups in $\text{Fe}_2(\text{CO})_6(\text{OH})[\text{P}(\text{p-C}_6\text{H}_4\text{Me})_2]$,¹¹⁸ and $[\text{Ni}(\text{CCl}=\text{CCl}_2)(\text{OH})(\text{PPh}_3)]_2$ ¹²⁶ the chemical shifts are τ 12.86 and 13.62 respectively whilst for trans- $\text{PtR}(\text{OH})(\text{PPh}_3)_2$,¹²⁶ the terminal OH proton resonates between τ 9 and 12.5.

The fact that the bridging O-H protons in all the dimeric hydridohydroxo complexes appear as a single line suggests that the two O-H groups are equivalent, as in structure V (Fig. 2). We do not observe coupling of the O-H protons to the phosphorus atoms in these complexes, as is sometimes reported,¹²⁶ for any of the complexes apart from the tetranuclear species (see below) but since the resonances are slightly broad, it is possible that this broadening is produced by small P-H couplings.

The solvent groups in $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2.\text{KOH}$ resonate at τ 6.7 (OMe)

and τ 6.2 and 8.7 (OEt) which are typical chemical shifts for coordinated alcohol moieties.

It is not possible to ascertain unequivocally the structures of the chlorohydroxo complexes but, on the basis of their preparations (from trans- $\text{RuCl}_2(\text{PPh}_3)_3$ under mild conditions) and the non-lability of the second chloride ligand we propose that the hydroxide moiety is trans to chloride and that the phosphines are mutually cis, as in VI and VII (Fig. 2). This structure (VII) for the dimeric species is in part supported by the very different chemical shift of the bridging O-H protons, compared with those in $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{S}]_2$ ($\text{S} = \text{H}_2\text{O}$, THF, Me_2CO or $^t\text{BuOH}$) and the observation of only one O-H resonance, indicating that the O-H groups are chemically equivalent but that the structure is different from those of the hydridohydroxo dimers.

6) Nature and Mechanism of Formation of the Tetranuclear Complex

As noted above, the prolonged reaction between $\text{RuHCl}(\text{PPh}_3)_3$ and NaOH in acetone in the presence of < 1% water gives a red crystalline complex which, on the basis of its crystallographic molecular weight (ca. 2500) and complex spectra is evidently a polynuclear, probably tetranuclear species.

The i.r. spectrum of this complex shows absorptions attributable to coordinated triphenylphosphine and acetone (1715 cm^{-1}), as well as peaks at 3585 , 2005 and 1910 cm^{-1} indicating the presence of coordinated OH^- , H^- and CO respectively. The presence of only one νCO indicates that no more than two CO groups are present in the molecule.

The ^1H and ^{31}P n.m.r. spectra are collected in Table 3. Integration of the resonances arising from the OH, H_1 and H_2 protons indicates that there is an equal number of each of these three

TABLE 3

 ^1H and ^{31}P n.m.r. Data for Tetranuclear Species ^a

Chemical Shifts		Coupling Constants, Hz ^d					
τ ^b	δ ^c						
Me_2CO 8.3	P_1 75.3	H_1P_1 8.0	H_2P_1 26.4	P_1P_2 35.0	P_2P_4 44.8		
OH_3 12.08	P_2 71.5	H_1P_2 22.3	H_2P_2 36.0	P_1P_3 0	P_3P_4 13.6		
OH_4 12.25	P_3 55.4	H_1P_3 16.5	H_2P_3 0	P_1P_4 0	H_1H_2 0		
H_1 19.4	P_4 26.6	H_1P_4 88.0	H_2P_4 0	P_2P_3 3.6	H_3P_3 3.0		
H_2 27.8							

a In C_6D_6 at 36° , for assignments see text.

b Me_4Si at τ 10.

c In ppm to high frequency of external 85% H_3PO_4 .

d Assignments based on heteronuclear double resonance and partial decoupling studies.

different types of hydrogen atom. Further, since the region for bridging hydroxo groups contains two resonances of equal intensity, one a doublet ($J_{\text{P}_3\text{H}_3} = 3 \text{ Hz}$) (OH_3) and the other a singlet (OH_4)*, it seems probable that there are two of each kind of hydride atom, H_1 and H_2 , and two non-equivalent hydroxo moieties.

The proton noise decoupled ^{31}P n.m.r. spectrum shows that there are four different types of phosphorus atom in the intensity ratio 1 : 1 : 1 : 1, numbered in order of decreasing chemical shift. Of these, P_2 is coupled to all the other phosphorus atoms whilst P_1 is only coupled to P_2 . P_3 and P_4 couple to one another as well as to P_2 .

The only possible explanation of these coupling phenomena which does not invoke zero coupling between phosphorus atoms on the same ruthenium atom, is that P_2 bridges two ruthenium atoms one of which (Ru_1) has P_1 bonded to it and the other (Ru_2) accommodates P_3 and P_4 . Since bridging triphenylphosphine groups are unknown and unlikely, it is probable that P_2 is the phosphorus atom of a bridging diphenylphosphido group.

Since H_2 is coupled only to P_1 and P_2 it seems probable that it is a terminal hydride on Ru_1 . H_1 , on the other hand, being coupled to all four phosphorus atoms probably bridges the two ruthenium atoms. The chemical shifts of the two hydrides are somewhat unusual since, in general, bridging hydrides resonate at higher fields than do terminal ones.^{1,127} However, in the recently isolated ¹²⁸ $[\text{Ir}_2\text{H}_5(\text{PPh}_3)_4]\text{PF}_6$ the bridging hydrides resonate at lower fields (τ 16.9, 18.4) than do the

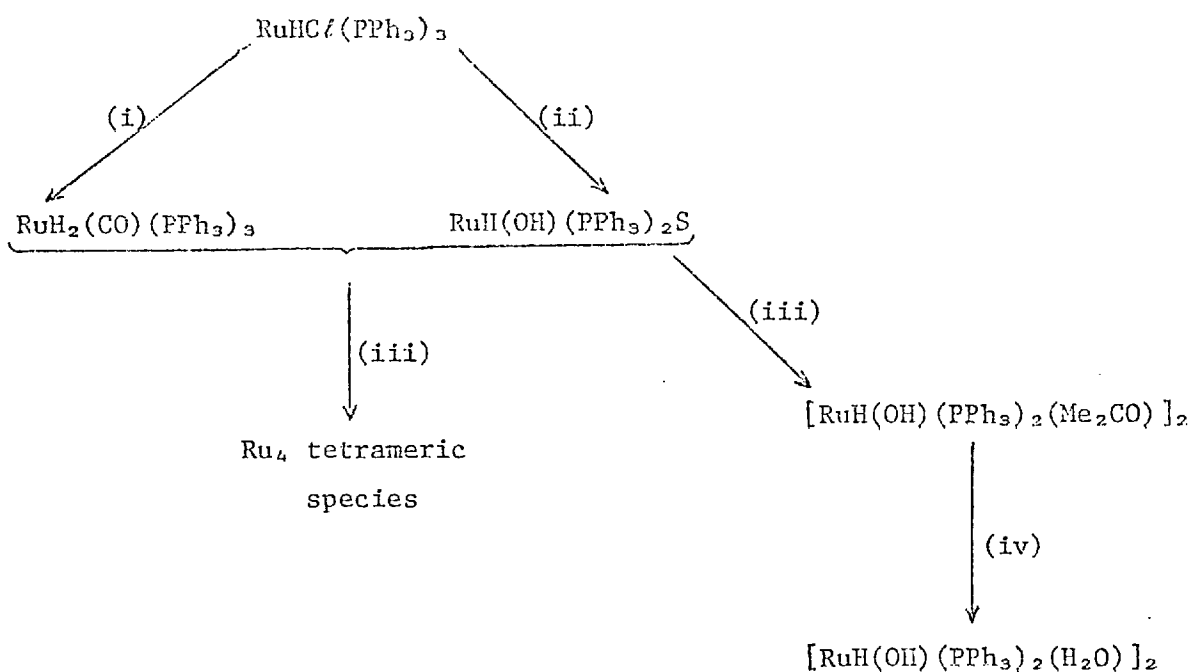
* This singlet resonance moves to higher field (τ 12.4) on addition of water to the n.m.r. tube and we suggest that this is probably due to the replacement of coordinated acetone by coordinated water. Support for this contention comes from the observation that recrystallisation of the tetranuclear complex from wet benzene gives a less soluble red solid which has an identical n.m.r. spectrum to that of the starting compound except that there is no resonance at τ 8.3, indicating loss of coordinated acetone.

terminal ones (τ 33.9); also, with different trans ligands and different chemical environments, shielding effects of the phenyl rings may be sufficiently different to render assignments based on chemical shift data alone relatively meaningless.

Since $J_{P_4H_1}$ is so large (80 Hz), P_4 and H_1 are likely to be mutually trans. The chemical shift of P_4 (26.6 ppm) being of much lower frequency than those of the other phosphorus atoms is also consistent with its being trans to a hydride, although since the resonance is not to such low field as is sometimes observed.^{21,72} For phosphorus trans to hydride, it suggests that the bridging hydride does not have such a marked effect on the chemical shift of the phosphorus atom trans to it as do terminal hydride ligands.

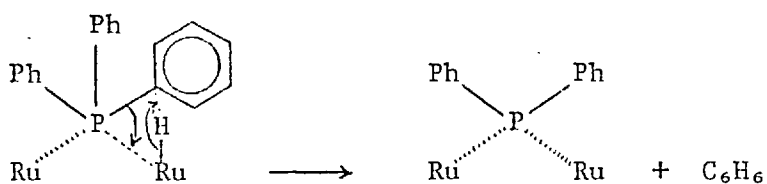
Unfortunately, little information is available on the chemical shifts and coupling constants of bridging phosphido groups so it is not possible to deduce structural information from the coupling constants of P_2 to the other magnetic nuclei but the values of $J_{P_1H_1}$, $J_{P_1H_2}$, $J_{P_2H_1}$ and $J_{P_2H_2}$ strongly suggest that both H_1 and H_2 are cis to both P_1 and P_2 , as well as to one another, which is only possible if P_1 and P_2 are mutually trans. The very low value of $J_{P_2P_3}$ suggests that these two phosphorus atoms are not mutually trans.

We are not able, on the basis of spectroscopic studies alone, unequivocally to assign a structure to this complex but we suggest that it is similar to one of those shown in Figure 3. Both of these structures fit about 90% of the data but in VIII, although the OH protons are non-equivalent, as required, it is expected that if the OH proton on Ru_2 couples to one P_3 it should also be coupled to the other one and a triplet rather than a doublet should be observed. In IX, on the other hand, the two O-H protons are equivalent, and coupling to P_3 should give a single doublet. A similar type of skeleton containing single

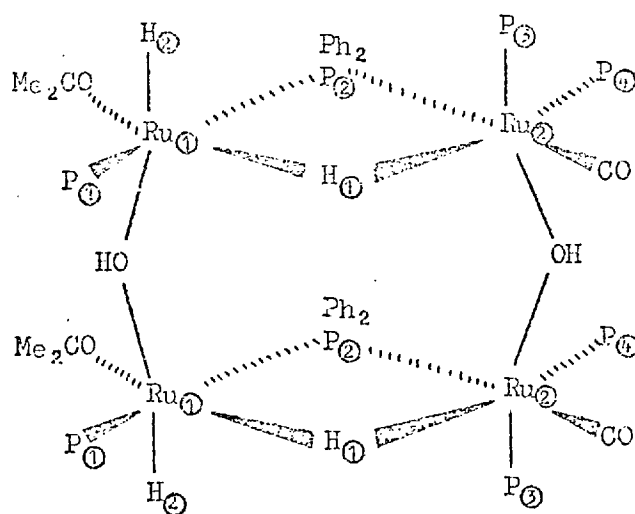


- (i) Base catalysed decarbonylation of acetone
 (ii) KOH
 (iii) Dimerisation
 (iv) Solvent exchange

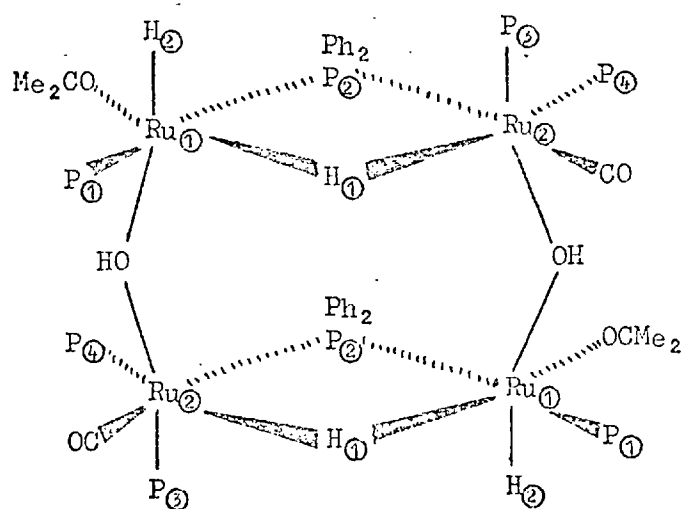
Scheme 6 Mechanism of reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH in acetone containing < 1% water



Scheme 7 Formation of a bridging phosphido group from coordinated PPh_3 and hydride



VIII



IX

Figure 3 Two possible structures of the tetranuclear species. P = Triphenylphosphine. CO and acetone may be interchanged in a dimeric unit.

and double bridges has recently been reported¹²⁹ for $\text{Na}_4[\text{Mo}_4\text{O}_4(\text{OH})_2(\text{edta})_2] \cdot 12\text{H}_2\text{O}$.

If the structure is similar to one of those illustrated in Figure 3, it is clear that the dinuclear species which constitutes half of the molecule could be formed from reaction of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, with loss of benzene and a triphenylphosphine group. Indeed, the reaction between these two complexes in acetone under reflux or at room temperature does give the tetranuclear species and benzene is detected in the reaction solution by g.l.c.. Benzene is also present in the reaction mixture when the tetranuclear species is prepared from $\text{RuHCl}(\text{PPh}_3)_3$ and KOH .

Cleavage of a P-C bond of a triphenylphosphine group is not unusual and a similar reaction¹³⁰ to the one postulated here is the thermolysis of $\text{RuHNO}(\text{PPh})_3$ in decalin which leads to $\mu, \mu'(\text{PPh}_2)_2\text{Ru}_2(\text{NO})_2(\text{PPh}_3)_2$. These reactions presumably occur via a transition state such as that shown in Scheme 7.

Finally, the carbonyl containing compound, which is obtained in low yield if the reaction between $\text{RuHCl}(\text{PPh}_3)_3$ and KOH in refluxing acetone containing less than 1% water is stopped after a short reaction time, could either be a dimer of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ or the dimeric unit from which the tetranuclear species is formed. We prefer the latter explanation, firstly on account of the fact that the complex is not present after longer reaction times and secondly because treating $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ under identical conditions gives an orange compound whose resonances in the ^{31}P n.m.r. spectrum are not present in that of the reaction mixture from which the carbonyl species is obtained.

The mechanism of the reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with NaOH in acetone is outlined in Scheme 6.

Experimental

Microanalyses are by Butterworth Microanalytical Consultancy Limited. Infrared spectra were obtained using a Perkin-Elmer PE457 grating diffractometer, n.m.r. spectra using Perkin-Elmer R12 (60 MHz) and Varian Associates XL-100-12 spectrometer (^{31}P), the latter in the Fourier transform mode with noise proton decoupling. Melting points were determined in closed capillaries under argon on an Electrothermal melting-point apparatus and are uncorrected.

All solvents were thoroughly degassed before use and all operations were carried out in an argon atmosphere, using standard suba-seal and catheter tubing techniques. The petroleum used had boiling range 40-60°C.

MeONa and $^t\text{BuOK}$ were made from the alcohol (purified by distillation from magnesium) and the metal followed by evaporation to dryness and sublimation (KO^tBu).

$\text{RuHCl}(\text{PPh}_3)_3$, $^{131}\text{RuCl}_2(\text{PPh}_3)_3$, ^{132} and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ ^{10} were prepared by published procedures.

Microanalytical data for the new complexes are given in Table 4.

1. Hydridohydroxo(tetrahydrofuran)bis(triphenylphosphine)ruthenium(II)

a) $\text{RuHCl}(\text{PPh}_3)_3$ (1 g, 1.08 mmole) was stirred in tetrahydrofuran (100 cc) containing carbonate-free NaOH (10 cc, 0.5 M in water, 5 mmole) for 16 hrs. On evaporation to small volume and addition of excess water the very air-sensitive scarlet complex was precipitated. This was collected and recrystallised from tetrahydrofuran-petroleum. Yield ca. 90%.

b) As above but using KOH pellets and 10 cc water.

2. Hydridohydroxo(aquo)bis(triphenylphosphine)ruthenium(II)

a) As for 1(a) or (b) but using acetone (100 cc) as solvent.

After 3 hrs stirring or 0.5 hrs refluxing the complex precipitated from the solution as very air-sensitive scarlet micro-crystals. It was washed several times with water. Yield ca. 100%. Evaporation of the residual pale yellow solution left only a white solid identified as triphenylphosphine from its i.r. spectrum.

b) $\text{RuHCl}(\text{PPh}_3)_3$ (0.5 g, 0.54 mmole) and KOH (0.2 g, 3.6 mmole) were stirred overnight in a 1 : 1 mixture of toluene and water (50 cc). The scarlet solid that collected at the interface was filtered off, washed several times with water and dried in vacuo. Yield ca. 80%; m.p. 172° decomp.

3. Reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH in acetone containing < 1% water

a) $\text{RuHCl}(\text{PPh}_3)_3$ (1 g, 1.08 mmole) and KOH (0.57 g, 10 mmole) were stirred in acetone (100 cc) containing 2 drops (ca. 0.1 cc) water for two days. The yellow solid that precipitated (ca. 20%) was filtered off and, after washing with water, dried in vacuo. It was identified as μ, μ' -dihydroxodihydridodiaquotetrakis(triphenylphosphine)diruthenium(II). On evaporation to 20 cc and addition of petroleum to the orange filtered solution, orange crystals of the tetranuclear species (40%) were isolated. These were sometimes contaminated with a yellow powder, $[\text{RuH}(\text{OH})(\text{PPh}_3)_2\text{Me}_2\text{CO}]_2$ (ca. 20%) but these two compounds were separated by extraction of the orange crystals with acetone followed by addition of petroleum. After crystallisation of the orange and yellow solids the filtrate was further reduced in volume (to ca. 2 cc) and addition of petroleum caused precipitation of a white solid identified as $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (i.r. evidence) (ca. 10%). The yield of $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$ from this reaction was increased after longer reaction times (7 days) and it may also be prepared by washing $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{t}^\text{BuOH})]_2$ with water.

4. The tetranuclear complex

a) $\text{RuHCl}(\text{PPh}_3)_3$ (1 g, 1.08 mmole) and KOH (0.57 g, 10 mmole) were refluxed in acetone (100 cc) containing ca. 0.1 cc water for three hours. A small amount of red $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ precipitated and was filtered off. The red solution which was shown to contain benzene (g.l.c. evidence), was evaporated to 20 cc and petroleum added until the solution just became turbid. The yellow solid that formed (ca. 10%) was identified as $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$ and after filtration, addition of more petroleum and cooling the orange crystals of the complex were collected, washed with petroleum and dried in vacuo. Yield, ca. 50%; m.p. 118° . When shorter reaction times (ca. 0.5 hrs) were employed and the solution evaporated to dryness, there was i.r. evidence of another CO containing compound - $\nu\text{CO} - 1880 \text{ cm}^{-1}$.

b) $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.5 g, 0.76 mmole) and KOH 0.28 g, 5 mmole) were stirred, in acetone (100 cc) containing ca. 0.1 cc water for 16 hrs. Filtration of the solution followed by evaporation to 20 cc and addition of petroleum (100 cc) caused red needles of the complex to be precipitated. Yield ca. 50%.

c) $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.17 g, 0.26 mmole) and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (0.24 g, 0.26 mmole) were refluxed in acetone (10 cc) for 3 hrs. The orange solution, which was shown to contain benzene (g.l.c. evidence) was filtered to remove excess $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ and evaporated to dryness. I.r. and ^1H n.m.r. evidence confirmed the presence of the complex as the only acetone soluble product. Yield ca. 50%.

5. μ, μ' -dihydroxodihydridobis(acetone)tetrakis(triphenylphosphine)-diruthenium(II)

$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.5 g, 0.76 mmole) was stirred in dry

acetone for several days, after which the yellow complex which had precipitated was collected, washed with acetone and dried in vacuo. Yield ca. 50%.

6. μ, μ' -dihydroxodihydridobis(t-butanol)tetrakis(triphenylphosphine)-diruthenium(II)

a) Potassium metal (0.5 g, 25 mmole) was dissolved in dry t-butanol (40 cc) and the resulting solution filtered onto $\text{RuHCl}(\text{PPh}_3)_3$ (0.5 g, 0.54 mmole). After stirring for several hours the yellow precipitate was collected. It was recrystallized from toluene-petroleum as yellow-orange crystals. Yield ca. 60%. Addition of petroleum to the t-butanol filtrate produced $\text{RuH}_2(\text{PPh}_3)_4$ in low yield.

b) $\text{RuHCl}(\text{PPh}_3)_3$ (0.5 g, 0.54 mmole) and KOH (0.57 g, 10 mmole) were stirred in t-butanol (50 cc) for several days. The yellow solid that precipitated was identified by i.r. spectroscopy as a mixture of $\text{RuH}_2(\text{PPh}_3)_4$ and the complex. Recrystallisation from toluene-petroleum yielded $\text{RuH}_2(\text{PPh}_3)_4$ as yellow crystals.

7. Reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KO^tBu in tetrahydrofuran

$\text{RuHCl}(\text{PPh}_3)_3$ (0.6 g, 0.65 mmole) and KO^tBu (0.15 g, 1.34 mmole) were stirred in tetrahydrofuran (50 cc) for 16 hrs. The resulting brown solution was evaporated to dryness and extracted with toluene (10 cc). After filtration and addition of petroleum (20 cc) a small amount of a brown amorphous solid, which was not identified but contained coordinated - OH (n.m.r. evidence) separated. On standing, the filtrate deposited yellow crystals identified as $\text{RuH}_2(\text{PPh}_3)_4$ from their infrared spectrum.

8. Dihydridocarbonylbis(triphenylphosphine)methanolruthenium(II)

$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.5 g, 0.76 mmole) was stirred under methanol

(100 cc) for sixteen hours during which time the colour changed from scarlet to crimson. The complex was collected and dried in vacuo. Yield ca. 80%. Evaporation of the yellow filtrate to dryness produced a small amount of yellow solid which contained $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (i.r. evidence).

9. Dihydridocarbonylbis(triphenylphosphine)ethanolruthenium(II)

As in 8, by refluxing in ethanol for 4 days to give crimson microcrystals. Yield ca. 80%, m.p. 160° decomp.

10. Bis(dihydrogenphosphato)bis(triphenylphosphine)ruthenium(II)

P_2O_5 (1 g, excess) was added to $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.5 g, 0.76 mmole) in 50 ml of toluene. The solution was stirred under reflux for 5 hours during which it became colourless and the insoluble powder, P_2O_5 , became brown. The solution was filtered and attempts to extract the powder with THF were unsuccessful. Finally, water (50 ml) was added to a suspension of this powder in THF, P_2O_5 reacted to give H_3PO_4 and a brown powder remained. It was washed several times with water and gave the pure complex.

This compound was found to be soluble only in DMSO. Yield ca. 95%.

11. Chlorohydroxobis(aquo)bis(triphenylphosphine)ruthenium(II)

$\text{RuCl}_2(\text{PPh}_3)_3$ (1 g, 1.04 mmole) and carbonate-free NaOH (5 cc, 0.5 M aqueous, 2.5 mmole) were stirred in tetrahydrofuran for 16 hours. On evaporation to 10 cc and addition of 50 cc water, an orange tar was formed. Recrystallisation from toluene by concentrating a solution in a stream of argon at room temperature gave the complex as orange microcrystals. Yield ca. 20%; m.p. 160° . Warming the solution during recrystallisation from toluene-petroleum caused some dimerisation to $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$. Recrystallisation from tetrahydrofuran-petroleum

gave yellow-brown needles of chlorohydroxobis(tetrahydrofuran)bis-(triphenylphosphine)ruthenium(II) in high yield.

12. μ, μ' -dihydroxodichlorobis(aquo)tetrakis(triphenylphosphine)-diruthenium(II)

a) As in 9 but with a reaction time of five days. Yield ca. 60%, m.p. 144°C.

13. [Tris(acetonitrile)tris(triphenylphosphine)ruthenium(II)]bis-hexafluorophosphate.bisacetonitrile

$\text{RuCl}_2(\text{PPh}_3)_3$ (1 g, 1.04 mmole) was added to a suspension of AgPF_6 (0.15 g, 2.0 mmole) in degassed acetonitrile (50 ml). The mixture became rapidly green, the solution was evaporated to a small volume, extracted with 30 ml methanol and left at room temperature affording yellow crystals of the complex. Yield ca. 60%.

The carbon analysis of this compound is consistently low (2%) although the hydrogen, nitrogen and phosphorus analyses are very good. This problem has also been shown to arise in the case of the similar complex $[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_2(\text{H}_2\text{O})](\text{BF}_4)_2$.⁴¹

14. Hydroxo(aquo)acetonitriletris(triphenylphosphine)ruthenium(II)-hexafluorophosphate.bismethanol

$[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3]^{2+}(\text{PF}_6)_2 \cdot 2\text{MeCN}$ (0.7 g, 0.5 mmole) was added to a mixture of 1 ml aqueous sodium hydroxide 0.5 M (0.5 mmole) in 50 ml THF. The colour went from yellow-green to gold yellow. After 3 hours the solution was evaporated to dryness and recrystallised from 40 ml methanol giving yellow crystals of the complex. Yield ca. 30%.

15. μ, μ' -dihydroxodihydridobis(tetrahydrofuran)tetrakis(triphenylphosphine)diruthenium(II)

$\text{RuCl}_2(\text{PPh}_3)_3$ (1 g, 1.04 mmole) and NaOH (6 cc, 0.5 M aqueous;

3 mmole) were refluxed in tetrahydrofuran (50 cc) for 2 days. The yellow-brown solution was evaporated to 5 cc and 20 cc water added. The resulting oil was recrystallised from tetrahydrofuran-petroleum as a yellow microcrystalline powder. Yield ca. 30%. Using a reaction time of 16 hours, and a similar work-up procedure, but recrystallisation from toluene-petroleum, $[\text{RuCl}(\text{OH})(\text{PPh}_3)_2\text{H}_2\text{O}]_2$ and the complex were obtained successively in approximately equal yield (ca. 20%).

16. Hydridochloro(aquo)bis(triphenylphosphine)ruthenium(II)

$\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$ (0.6 g, 0.85 mmole) and KOH (0.16 g, 2.85 mmole) were refluxed in tetrahydrofuran with hydrogen passing for six hours. On evaporation to 20 cc and addition of water (50 cc) a dark oil separated. This was collected and recrystallised from toluene-petrol as red-purple microcrystals. Yield ca. 70%.

An n.m.r. spectrum of the reaction solution obtained from the same reaction but with 0.2 g $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$ showed only $[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_n$ ($n = 1$ or 2) to be present.

17. Reaction of $\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$ with NaBH_4 in the presence of excess PPh_3

$\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2$ (0.5 g, 0.7 mmole), PPh_3 (0.3 g, 1.14 mmole) and NaBH_4 (0.1 g, 2.5 mmole) were stirred in toluene (60 cc) containing water (10 cc) for 16 hours. Separation of the toluene followed by evaporation to 30 cc and addition of petroleum (50 cc) gave $\text{RuH}_2(\text{PPh}_3)_4$ (ca. 60%) and $\text{RuHCl}(\text{PPh}_3)_3$ (ca. 30%), identified by their infrared spectra.

18. Dihydridotris(triphenylphosphine)tetrahydrofuranruthenium(II)

$\text{RuHCl}(\text{PPh}_3)_3$ (0.7 g, 0.75 mmole) and MeONa (0.08 g, 1.5 mmole) were stirred in tetrahydrofuran (30 cc) containing methanol (1 cc) for 0.5 h.

The orange solution was filtered and evaporated to half-volume. On addition of petroleum (20 cc) and cooling, the complex separated as yellow crystals that were collected and dried in vacuo. Yield ca. 50%, m.p. 170-200° decomp. On standing the orange filtrate deposited white needles of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (i.r. evidence). Longer reaction times (16 hr) led to reduced yields (ca. 20%) of the complex, and increased yields of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$.

19. Reaction of $\text{RuHCl}(\text{PPh}_3)_3$ with sodium methoxide in diethyl ether at low temperature

$\text{RuHCl}(\text{PPh}_3)_3$ (0.5 g, 0.54 mmole) and MeONa (0.05 g, 0.9 mmole) were stirred in diethyl ether (20 cc) and methanol which had not been pre-dried (0.25 cc) at 0°C. After three hours the yellow precipitate was collected and dried in vacuo. I.r. - 2010w, 1960w, 1940vs, 1900vsbr, 825m. Recrystallisation from toluene-petroleum afforded white crystals of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (i.r. comparison with an authentic sample). On some occasions a different yellow complex (i.r. 2720w, 2030w, 1600vs, 875m, 780s) was isolated from an ostensibly identical reaction.

20. Reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with formaldehyde

Formaldehyde, prepared by heating paraformaldehyde to 180° in a slow stream of argon was passed through a solution of $\text{RuH}_2(\text{PPh}_3)_4$ (0.5 g, 0.43 mmole) in tetrahydrofuran (25 cc). After 5 min. the white solid formed was collected and identified as paraformaldehyde. On standing the pale filtrate deposited white needles of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$.

TABLE 4
Analytical Data for New Ruthenium Complexes

COMPOUND	COLOUR	FOUND				REQUIRED			
		C	H	P	Other	C	H	P	Other
$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$	Scarlet	64.7	5.1	8.8		65.4	5.1	9.4	
$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})$	Scarlet	65.9	5.3	8.7		67.1	5.6	8.7	
$[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]_2$	Yellow	66.6	4.9	8.7		66.8	5.4	8.8	
$[\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{THF})]_2$	Yellow	67.3	5.2	8.6		67.1	5.6	8.7	
$[\text{RuH}(\text{OH})(\text{PPh}_3)_2^t\text{BuOH}]_2$	Yellow	65.9	5.0	8.8		66.9	5.9	8.7	
$\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})_2^a$	Yellow-Brown	61.5	4.4	8.4	Cl, 5.0	60.5	4.9	8.7	Cl, 7.1
$\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{THF})_2$	Yellow-Brown	65.6	5.5	6.9	Cl, 6.2	64.3	5.7	7.6	Cl, 4.3
$[\text{RuCl}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})]_2$	Yellow-Brown	61.3	5.1	8.5	Cl, 5.4	62.1	4.7	8.9	Cl, 5.1
$\text{RuHCl}(\text{PPh}_3)_2(\text{H}_2\text{O})^b$	Red-Purple	63.6	4.8	9.8		63.6	4.9	9.1	
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})$	Crimson	64.4	5.0	9.0		63.8	4.8	8.7	
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_2(\text{EtOH})^c$	Crimson	65.0	5.3	8.6		64.2	4.9	8.5	
$\text{RuH}_2(\text{PPh}_3)_3(\text{THF})$	Yellow	72.9	5.6	10.0		72.4	5.7	9.7	
Tetranuclear species ^d	Red-Orange	65.5	6.2	8.2	O, 5.2	65.7	5.0	9.7	O, 3.8
$\text{Ru}(\text{PO}_4\text{H}_2)_2(\text{PPh}_3)_2$	Brown	52.8	4.8	14.6		52.9	3.9	15.2	
$[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3](\text{PF}_6)_2 \cdot 2\text{MeCN}$	Yellow	50.1	4.2	11.1	N, 5.1	52.1	4.3	11.2	N, 5.1
$[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]\text{PF}_6 \cdot 2\text{MeOH}$	Yellow	58.3	5.1	11.1	N, 1.3	59.3	5.0	10.6	N, 1.2

^a M.W. 750(713.5) cryoscopically in benzene; ^b Chlorine analysis for this complex is consistently low (ca. 1%);
^c M.W. 672(701) osmometrically, in benzene; ^d M.W. 2500(2556) crystallographically.

TABLE 5

Molar Conductance (Λ m) and Electrolyte Types
of Ruthenium Complexes

Measured at 26°C in degassed nitromethane (10^{-3} solutions)

Complex	(Λ m) $\text{ohm}^{-1} \times \text{cm} \times \text{mole}^{-1}$	Electrolyte Type
$[\text{Ru}(\text{PPh}_3)_3(\text{MeCN})_3](\text{PF}_6)_2 \cdot 2\text{MeCN}$	190	2 : 1
$[\text{Ru}(\text{OH})(\text{PPh}_3)_3(\text{MeCN})(\text{H}_2\text{O})]\text{PF}_6 \cdot 2\text{MeOH}$	70	1 : 1

CHAPTER III

PREPARATION OF BIS(STYRENE)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(0)

ITS REACTIONS WITH SATURATED HYDROCARBONS AND OLEFINS

AND SOME OXIDATIVE ADDITION REACTIONS OF

THIS COMPOUND

Introduction

Complexes of ruthenium in the formal oxidation state zero have been postulated in many reactions such as transfer hydrogenation using $\text{RuH}_2(\text{PPh}_3)_4$ as the catalyst⁶⁷ or hydrogenation of olefins.^{64, 133} These compounds are thought to be extremely active towards oxidative addition²¹ and may even be capable of activating alkyl C-H bonds. Apart from the compounds containing CO or PF_3 ¹³⁴ only a few compounds of ruthenium in oxidation state zero are known.

Ruthenium(0) cyclodiene and arene complexes $\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_8)$ and $\text{Ru}(\text{C}_8\text{H}_{10})(\text{C}_8\text{H}_{12})$ have been prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and zinc dust in ethanol in the presence of cyclohexadiene and cyclo-octadiene respectively.¹³⁵ The latter has recently been shown to be a valuable starting material for the synthesis of a number of other ruthenium zero cyclo olefin and arene complexes.¹³⁶ $\text{Ru}(\text{C}_7\text{H}_8)(\text{C}_8\text{H}_{12})$, $\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_8\text{H}_{12})$, $\text{Ru}(\text{C}_6\text{H}_5\text{CH}_3)(\text{C}_8\text{H}_{12})$, $\text{Ru}(\text{p-C}_6\text{H}_4(\text{CH}_3)_2)(\text{C}_8\text{H}_{12})$ and $\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_8)$ were obtained respectively from the reactions of $\text{Ru}(\text{C}_8\text{H}_{10})(\text{C}_8\text{H}_{12})$ with cycloheptatriene, benzene, toluene, para-xylene and cyclohexadiene.

The compound analysing for $\text{Ru}(\text{PPh}_3)_4(\text{MeCN})_2$ obtained by electro-chemical reduction of $\text{RuCl}_2(\text{PPh}_3)_4$ in acetonitrile has been postulated to have a π bonded acetonitrile ligand and to be best formulated as the ruthenium zero complex $\text{Ru}(\text{PPh}_3)_4(\pi\text{-MeCN})\cdot\text{MeCN}$.¹³⁷

$\text{Ru}[\text{P}(\text{OCH}_3)_3]_5$ has recently been prepared by reduction of $\text{RuCl}_2(\text{P}(\text{OCH}_3)_3)_4$ using sodium amalgam in the presence of trimethylphosphite.¹³⁸

Some ruthenium zero olefin complexes $\text{Ru}(\text{C}_2\text{H}_4)(\text{PPh}_3)_3$,⁷⁶ $\text{Ru}(\text{St})(\text{PPh}_3)_3$,⁷⁶ (St = styrene), and $\text{Ru}(\eta\text{-1-2-C}_5\text{H}_{10})(\text{PPh}_3)_3$,^{62,74,133} have been reported. The first and the third complexes have recently been reformulated as $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and $\text{Ru}(\eta\text{-1-4-C}_5\text{H}_9)(\text{PPh}_3)_3$.⁷² We find that the second complex is in fact $\text{Ru}(\text{St})_2(\text{PPh}_3)_2$; its structure and chemistry are discussed in this Chapter.

Two ruthenium zero butadiene complexes $\text{Ru}(\eta\text{-1-4-C}_4\text{H}_6)(\text{PPh}_3)_3$,^{72,76} and $\text{Ru}(\eta\text{-1-4-C}_4\text{H}_6)_2(\text{PPh}_3)$,⁷² have also been isolated.

Finally $\text{RuN}_2(\text{PPh}_3)_3$ has been reported, solely on the basis of infrared evidence, to be the product of the reaction of $\text{Ru}(\text{C}_5\text{H}_{10})(\text{PPh}_3)_3$ with N_2 .¹³³

The activation of C-H bonds by means of transition metals is one of the subjects in organometallic chemistry for which great interest has been shown in recent years.

Insertion into an activated aliphatic C-H bond has been achieved in the following ways.

- 1) $\text{MH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ (dmpe = bis(dimethylphosphino)ethane, C_{10}H_7 = naphthyl, M = Fe, Ru)¹³⁹ and $[\text{Ir}(\text{depe})_2]\text{Cl}$ (depe = bis(diethylphosphino)ethane)¹⁴⁰ react with acetonitrile to afford $\text{MH}(\text{CH}_2\text{CN})(\text{dmpe})_2$ and $[\text{IrH}(\text{CH}_2\text{CN})(\text{depe})_2]\text{Cl}$ respectively.
- 2) Under U.V. irradiation toluene oxidatively adds to $\text{W}(\text{Cp})_2\text{H}_2$ giving $\text{W}(\text{Cp})_2\text{H}(\text{CH}_2\text{Ph})$.¹⁴¹

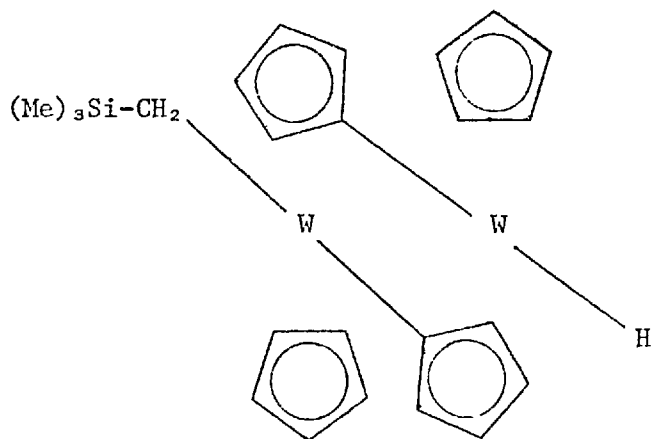
Activation of aromatic C-H bands has also been obtained:

$\text{MH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ reacts with ArH ($\text{ArH} = \text{C}_6\text{H}_5\text{CH}_3$, C_6H_6 , $\text{C}_6\text{H}_5\text{CN}$, $\text{C}_6\text{H}_5\text{NH}_2$) to give $\text{MH}(\text{Ar})(\text{dmpe})_2 + \text{C}_{10}\text{H}_8$,¹³⁹ and $\text{W}(\text{Cp})_2\text{H}_2$ reacts with benzene and substituted benzenes to give $\text{W}(\text{Cp})_2\text{H}(\text{Ar})$ and $\text{W}(\text{Cp})\text{ArAr}'$ (Ar' = substituted

aryl).¹⁴¹ As noted above toluene gives first $W(Cp)_2H(CH_2Ph)$ but on further reaction $W(Cp)_2(CH_2Ph)(C_6H_4CH_3)$ can be obtained.

Finally a few cases of activation of alkanes are known.

$WH_2(Cp)_2$ under U.V. irradiation conditions reacts with tetramethylsilane to afford the compound of Structure I.¹⁴¹



I

Cyclohexane is dehydrogenated to cyclohexene through U.V. irradiation of solutions containing benzophenone and copper(II).¹⁴²

Finally an exchange between hydrogen and deuterium in aromatic and aliphatic hydrocarbons has been achieved by a number of catalytic systems.¹⁴³ The following systems are active:

- 1) $(PtCl_4)^{2-}$ salts in acetic acid for exchange of hydrogen atoms of hydrocarbons with D_2O .^{144,145}
- 2) Polyhydrides such as $NbH_3(C_5H_5)_2$,¹⁴⁶ $TaH_5(dmpe)_2$ ¹⁴⁷ and $ReH_5(PPh_3)_3$ ¹⁴⁸ for exchange of hydrogen atoms of aromatic hydrocarbons with deuterium.
- 3) Finally $Nb(Cp)_2(C_2H_5)(C_2H_4)$ ¹⁴³ and $RhCp(C_2H_4)_2$ ¹⁴⁹ exchange hydrogen atoms of their ligands with hexadeuterobenzene.

In the reaction of triruthenium dodecacarbonyl with n-nonane

under reflux affording $\alpha\text{-Ru}_4(\text{CO})_{13}\text{H}_2$ and $\alpha\text{-Ru}_4(\text{CO})_{12}\text{H}_2$ which had been thought to proceed via activation of nonane, it has recently been shown that traces of water are in fact the hydride source.⁹⁷

In this Chapter we report the preparation and isolation of the tetracoordinate ruthenium zero complex $\text{Ru}(\text{St})_2(\text{PPh}_3)_2$, the first ruthenium zero sixteen electron complex isolated. We also report its reactions with saturated hydrocarbons and its use as starting material for a number of ruthenium zero and ruthenium two olefin complexes. Finally oxidative addition reactions of this compound with H_2 and H_2O are also described.

Results and Discussion

1) Preparation and Characterisation of $\text{Ru}(\text{styrene})_2(\text{PPh}_3)_2$

As reported by Yamamoto,⁷⁶ $\text{RuH}_2(\text{PPh}_3)_4$ reacts rapidly in styrene to give very deep purple solutions from which diamagnetic purple crystals may be obtained in addition of petroleum and cooling. Yamamoto assigned the complex the composition $\text{Ru}(\text{C}_8\text{H}_8)(\text{PPh}_3)_3$ on the basis of analytical (C and H only), i.r. and ^1H n.m.r. data. We find that the complex analyses (C, H and P) better for $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$. The i.r. spectrum of the complex does not show peaks assignable to $\nu\text{M-H}$ or to the presence of an orthometallated phenyl ring, and $\nu\text{C=C}$ of coordinated styrene is observed at 1589 cm^{-1} . An X-ray diffraction study confirms the bis phosphine formulation (see Appendix) and it is thus the first sixteen electron complex of ruthenium(0), the molecule adopts a distorted tetrahedral configuration. The instability of this complex in common organic solvents other than styrene has precluded a full n.m.r. characterisation of the complex. However, broad peaks at δ 2.7 and 4.3 in the ratio 2 : 1 in the ^1H n.m.r. spectrum measured quickly in C_6D_6 or in styrene are tentatively assigned to the methylene

and methyne protons of coordinated styrene, respectively, by analogy with the relative chemical shifts of the protons in $K[PtCl_3(C_6H_5)]$,¹⁵⁰ although in our complexes the resonances are both to higher field.

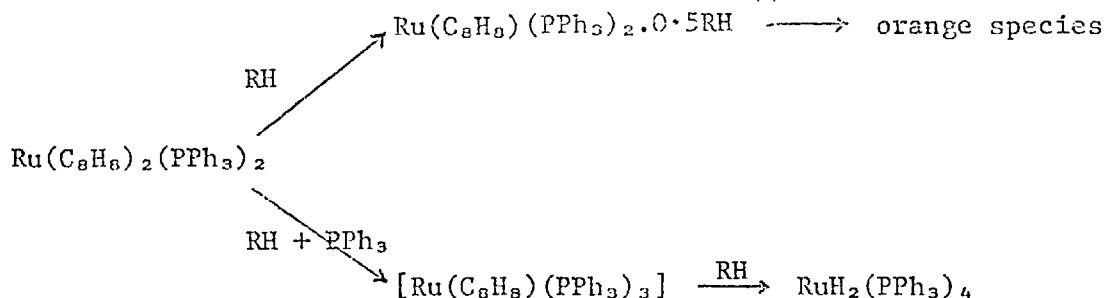
A few other complexes of ruthenium(0) are known (see Introduction) but the fact that, in contrast⁷² to other triphenylphosphine containing olefin complexes of ruthenium, ortho-metallation of a phenyl group on phosphorus or styrene does not occur is presumably a reflection of the steric congestion around the metal. This steric congestion presumably also explains the relative insensitivity of $Ru(C_6H_6)_2(PPh_3)_2$ to air - the solid may be handled in air for several minutes before it starts to deteriorate although it reacts with water in tetrahydrofuran to give $RuH(OH)(PPh_3)_2(THF)$ - one of the few cases in which water is oxidatively added to a complex.⁹⁷

2) Reactions of $Ru(C_6H_6)_2(PPh_3)_2$ with Saturated Hydrocarbons (Scheme 1)

a) In the absence of added triphenylphosphine

During our initial attempts to isolate $Ru(C_6H_6)_2(PPh_3)_2$ by evaporation of reaction solutions in styrene to dryness and trituration under petroleum we observed essentially quantitative conversion to $RuH_2(PPh_3)_4$. It appeared that the hydrogen source might be the saturated hydrocarbon. This, coupled with Yamamoto's observation⁷⁶ that $Ru(C_6H_6)_2(PPh_3)_2$ also gives $RuH_2(PPh_3)_4$ on interaction with excess toluene, prompted us to investigate the reactions of $Ru(C_6H_6)_2(PPh_3)_2$ with saturated hydrocarbons.

Thus, stirring crystalline samples of $Ru(C_6H_6)_2(PPh_3)_2$ as suspensions in hydrocarbons (RH, R = hexyl, isopentyl, trimethylsilylmethyl) for several hours at room temperature invariably produced green solids which analyse closely for $Ru(C_6H_6)(PPh_3)_2 \cdot 0.5RH$. Mass spectral studies of the gases above the green complexes show no evidence for



Scheme 1

alkane or alkene but on decomposition of the complex, R = hexyl, with air, water, H_2SO_4 , $\text{LiOH}/\text{H}_2\text{O}$, benzene or MeI, alkane is released and no deuterium incorporation is observed if the decomposition is carried out using D_2O , D_2SO_4 or $\text{LiOD}/\text{D}_2\text{O}$. Thus it is clear that the alkane moiety is either trapped in the lattice or is present in the form of an alkyl hydrido complex.

The infrared spectra of all the green complexes have a weak peak of variable intensity at 2080 cm^{-1} and are all very similar except that for $\text{R} = \text{Me}_3\text{SiCH}_2^-$, absorptions at 1248 and 860 cm^{-1} are observed. The close proximity of the positions of these bands to those of free tetramethylsilane, together with the lack of observable splitting,¹⁵¹ strongly suggests that the tetramethylsilane is clathrated in the molecule, and that activation of a C-H bond has not occurred. The ^1H n.m.r. spectrum of the complex obtained from TMS, apart from phenyl resonances, only shows one resonance from free TMS, at $\delta\ 0.0$.

Further confirmation that C-H activation has not occurred is afforded by the reaction of $\text{Ru}(\text{styrene})_2(\text{PPh}_3)_2$ with hexafluorobenzene which again yields a green complex of formula $\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_3)_2 \cdot 0.5\text{C}_6\text{F}_6$ with an i.r. spectrum identical to those obtained from hexane and

iso-pentane, except that the peak in the i.r. spectrum at 2080 cm^{-1} is totally absent and there are strong sharp peaks at 1570 and 1010 cm^{-1} which are assigned to a clathrated C_6F_6 moiety. That activation of a C-F bond has not occurred is confirmed by the absence of any absorption assignable to $\nu\text{Ru-F}$ and the fact that there is only one $\nu\text{C-F}$.

The peak at 2080 cm^{-1} in the i.r. spectrum of the green complexes obtained from hydrocarbons probably arises from small amounts of $\text{RuH}_2(\text{PPh}_3)_4$ whose presence is confirmed by ^{31}P n.m.r. spectra of the green complexes. The hydride is formed in high yield when $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ is reacted with hydrocarbons in the presence of excess PPh_3 (see below).

The exact nature of the green complexes has proved elusive since they all decompose in solution to give an orange-brown species (hereinafter referred to as the "orange species") which we have been unable to obtain in a crystalline state, but which ^{31}P n.m.r. studies suggest is a complex mixture of several compounds. Solutions of $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ in benzene, toluene or tetrahydrofuran rapidly become green and then brown, the "orange species" being isolated from the brown solutions. In contrast to Yamamoto's report⁷⁶ we find that $\text{RuH}_2(\text{PPh}_3)_4$ can be isolated only if $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ is recrystallised from toluene in the presence of excess PPh_3 (see later).

Finally, if the reaction of $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ with hydrocarbons are carried out under reflux, the "orange species" is obtained with very little contamination by $\text{RuH}_2(\text{PPh}_3)_4$, presumably, because the rate of formation of the "orange species" is increased more than the rate of formation of $\text{RuH}_2(\text{PPh}_3)_4$.

b) In the presence of excess PPh_3

Reaction of $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ with hexane and excess PPh_3 at room

temperature produces a yellow solid in high yield which is identified as $\text{RuH}_2(\text{PPh}_3)_4$ by its i.r. and ^{31}P n.m.r. spectra. The orange solution contains small amounts of other phosphine containing ruthenium complexes including the "orange species". Under reflux, a mixture of $\text{RuH}_2(\text{PPh}_3)_4$ and the "orange species" is obtained. In order to test whether the hydride source in this reaction was triphenylphosphine or hexane, $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ was treated with triphenylphosphine in hexafluorobenzene both in the absence and presence of added hexane. The reactions are very slow at room temperature but on warming, in the absence of added hexane, no $\text{RuH}_2(\text{PPh}_3)_4$ is formed and only the "orange species" is recovered whereas when the reaction is carried out in the presence of alkane, a mixture of $\text{RuH}_2(\text{PPh}_3)_4$ and the "orange species" is recovered.*

These experiments show unequivocally that the hydride source in the formation of $\text{RuH}_2(\text{PPh}_3)_4$ from $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ and hexane in the presence of PPh_3 is the hexane and that the system represents a rare example of activation of alkanes by a discrete transition metal atom. The necessity for the presence of excess PPh_3 for this reaction to occur suggests that the active metal species is not $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ but rather a transient species, probably $\text{Ru}(\text{C}_6\text{H}_5)(\text{PPh}_3)_3$. This is probably formed by initial dissociation of styrene followed by attack of PPh_3 since this would account for the stability of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ in the presence of excess styrene. Furthermore, PPh_3 being a less

* It is essential that all reagents used in these reactions be scrupulously dried since if wet solvents are used, hydrido species are always obtained but these also appear to contain coordinated OH - $\nu_{\text{O-H}}$ ca. 3600 cm^{-1} so that some hydrido hydroxy complex is present.

good π -acceptor than styrene, the electron density on the metal atom of $\text{Ru}(\text{C}_6\text{H}_5)(\text{PPh}_3)_3$ would be higher than on that of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$, thus rendering the metal atom more susceptible to oxidative addition reactions. These reactions are outlined in Scheme 1.

The fate of the hydrocarbon in this reaction is not clear although it is unlikely that hex-1-ene or hex-2-ene is formed as a by-product since these react instantaneously with $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (see below) and resonances from the products of these reactions are not observed in the ^{31}P n.m.r. spectrum of the products of reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with hexane in the presence of excess PPh_3 after evaporation to dryness and redissolving in C_6H_6 . Attempts to identify the fate of the hydrocarbon by carrying out the reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with a small excess of hexane in hexafluorobenzene in the presence of excess PPh_3 show that some modification of the hydrocarbon occurs since the two broad ^1H n.m.r. resonances of hexane which are of relative intensity ca. 2 : 1 are found to be equally intense at the end of the reaction. A new peak is also present in the alkane region of the gas chromatograph but we have been unable to identify it unequivocally.

In an attempt to provide unequivocal rather than circumstantial proof that activation of hydrocarbons is occurring in these systems, we have carried out the reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with d^{14} -hexane in an attempt to show that deuterium incorporation into the product occurs. Unfortunately, $\nu_{\text{Ru-D}}$ in $\text{RuD}_2(\text{PPh}_3)_4$ is obscured by ligand vibrations and attempts to detect the presence of deuterium by direct ^2D n.m.r. proved fruitless. This is perhaps not surprising since the facile exchange of hydride hydrogen atoms with the ortho hydrogen atoms of the phenyl rings on coordinated triphenylphosphine in $\text{RuH}_2(\text{PPh}_3)_4$ is well documented.²² Furthermore, since the reaction was carried out in the presence of excess PPh_3 , with which the coordinated PPh_3 groups of

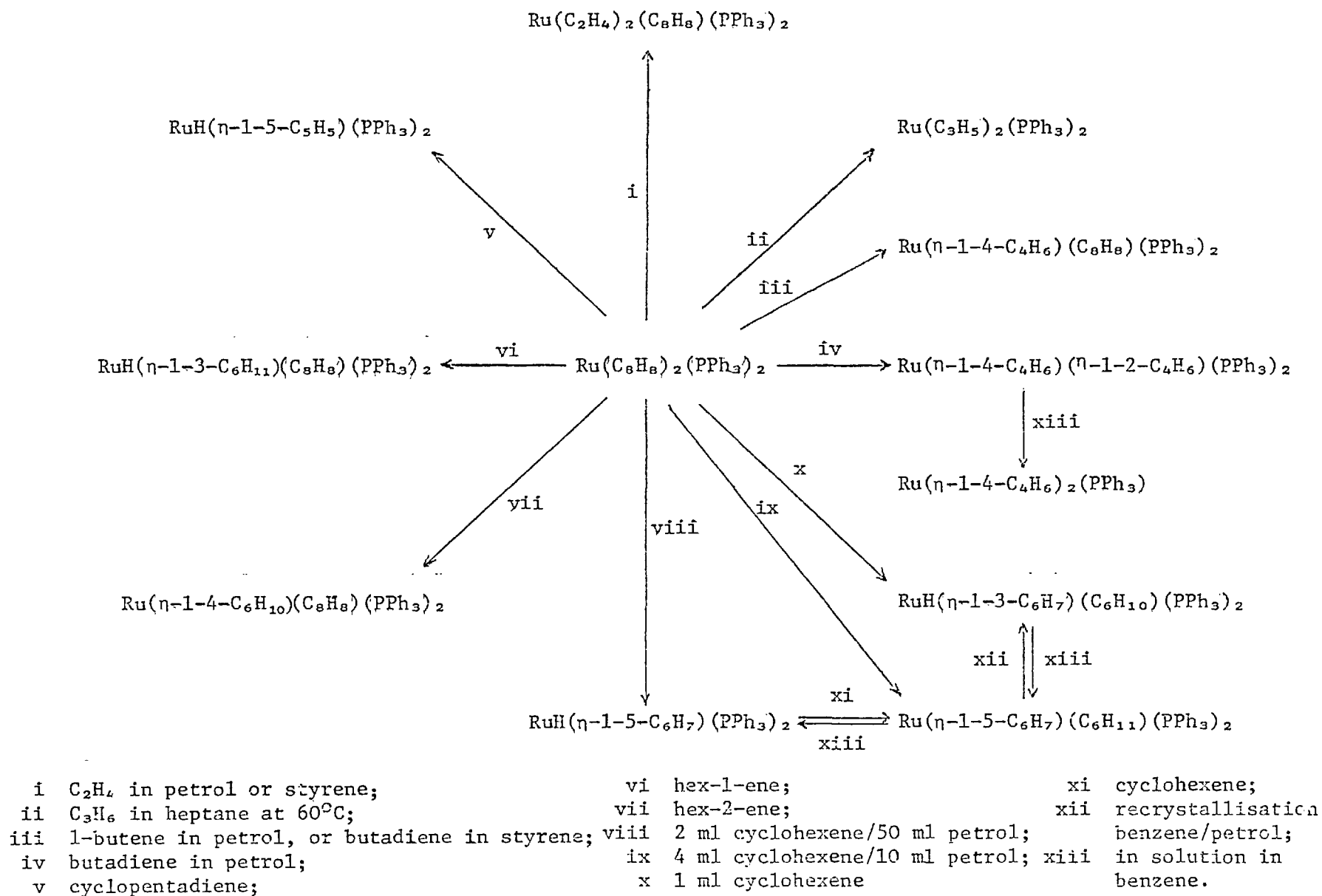
$\text{RuH}_2(\text{PPh}_3)_4$ readily exchange, the deuterium incorporation could be such that the two deuterium atoms which should be incorporated into the molecule if hydrocarbon activation is occurring may be spread over many sites and much of it may be removed from the $\text{RuH}_2(\text{PPh}_3)_4$ formed. This together with the splitting of the signals from the deuterium atoms by phosphorus, the dissociation and exchange of free and bound PPh_3 at room temperature and the low solubility and high molecular weight of $\text{RuH}_2(\text{PPh}_3)_4$ render it very unlikely that the enrichment would give ^2D resonances which are greater in intensity than those arising from the natural abundance of deuterium in the solvent benzene. Since the resonance from the deuterium of the solvent was not observed we do not think that the lack of observation of deuterium incorporation into $\text{RuH}_2(\text{PPh}_3)_4$ in this reaction negates our theories that the hydride ligands arise, initially at least, from the hydrocarbon.

Finally it is of interest that aromatic hydrocarbons (benzene, toluene and even PPh_3 in large excess) produce $\text{RuH}_2(\text{PPh}_3)_4$ on interaction with $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ in the presence of excess PPh_3 , although for PPh_3 the yield is very low, the major product being the "orange species".

3) Reactions of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ with alkenes and dienes (see Scheme 2)

a) Ethylene

Ethylene reacts slowly at room temperature with petroleum suspensions of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ to give an orange powder, $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$. The same compound is obtained more rapidly if the reaction is carried out in styrene, suggesting that it proceeds via an associative mechanism to give the transient species $\text{Ru}(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ which has not been isolated. This reaction in styrene is evidently reversible since passing nitrogen through the solution of the ethylene complex in styrene



Scheme 2 Reactions of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ with olefins and dienes

regenerates the purple colour of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$.

Infrared and ^1H n.m.r. studies on $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$ give no indication of the presence of a metal-hydride or an ortho-metallated ring system but the presence of coordinated styrene is confirmed by $\nu\text{C}=\text{C}$ at 1595 cm^{-1} . $\nu\text{C}=\text{C}$ for coordinated ethylene is either too weak to be observed or is masked by some other absorptions.

The ^1H n.m.r. spectrum of the complex shows a series of broad resonances at δ 5.3, 1.9, 1.2 and 0.9 which presumably arise from the olefinic protons but which we do not attempt to assign. The ^{31}P n.m.r. spectrum which consists of two doublets at δ 67.1 and 51.2 ($J_{\text{PP}} = 9.5\text{ Hz}$) indicates that the complex has a rigid five coordinate stereochemistry and the low value of J_{PP} appears not to be unusual for five coordinate complexes of ruthenium(0) (cf. for $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$, $J_{\text{PP}} = 4.9\text{ Hz}$).^{72,76}

Like $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$, $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$ is unstable in solvents other than styrene, giving an orange decomposition product and $\text{RuH}_2(\text{PPh}_3)_4$ in the presence of excess PPh_3 . However, the compound can be crystallised from styrene-petroleum mixtures at low temperature.

b) Propene

Propene reacts only very slowly with petroleum suspensions of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ so that after 15 hours, mostly the green $\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_3)_2 \cdot 0.5\text{RH}$ is obtained. However, at 60° in n-heptane reaction proceeds smoothly to give the previously characterised⁷² bis- π -allyl complex, cis- $\text{Ru}(\text{C}_3\text{H}_5)_2(\text{PPh}_3)_2$ as an off-white powder which may be recrystallised from benzene as orange crystals.

c) But-1-ene and 1,3-butadiene

Interaction of but-1-ene with a petroleum suspension of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ gives a yellow powder which can be recrystallised from

toluene or deuterobenzene as yellow crystalline solvates, $\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_6\text{H}_5)(\text{PPh}_3)_2 \cdot \text{S}$ ($\text{S} = \text{PhMe}$ or C_6D_6). This compound is also obtained from $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ and butadiene in styrene in the presence of excess PPh_3 . The formation of butadiene from but-1-ene has previously been observed in the reaction of $\text{RuCl}_2(\text{PPh}_3)_4$ with but-1-ene to give $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$ and presumably proceeds via a similar mechanism.⁷²

The presence of coordinated styrene in this complex is confirmed by a peak at 1592 cm^{-1} and broad resonances at δ 5.7 (CH) and 3.2 (CH_2) in the ^1H n.m.r. spectrum whilst broad resonances from coordinated butadiene are observed at δ 4.3, 1.6 and -0.5.

In solution, $\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$ apparently exists as an equilibrium mixture of two isomeric forms in each of which the phosphines are equivalent since the ^{31}P n.m.r. spectrum invariably shows two singlet resonances of relative intensity, ca. 1 : 1.2 at 60.9 and 40.5 ppm. On slow crystallisation, however, only one isomer is isolated, presumably on account of its lower solubility but this again gives two resonances in the ^{31}P n.m.r. spectrum on redissolving. A small amount of $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$ ^{72,76} appears also to be present in solution (^{31}P n.m.r. data). The chemical shifts of the two resonances suggest that cis (60.9) and trans (40.5) phosphine containing complexes are present and we tentatively assign them structures A and B ($\text{R} = \text{H}$), (see Figure 1) based on a square pyramidal geometry, although the complexes probably have structures which are severely distorted from any idealised stereochemistry.

In contrast to the reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with butadiene in styrene, the reaction in petroleum produces a white powder, $\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)_2$, which rapidly forms the known $\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)$ ⁷² on dissolving in aromatic solvents.

The i.r. spectrum of $\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)_2$ contains strong sharp

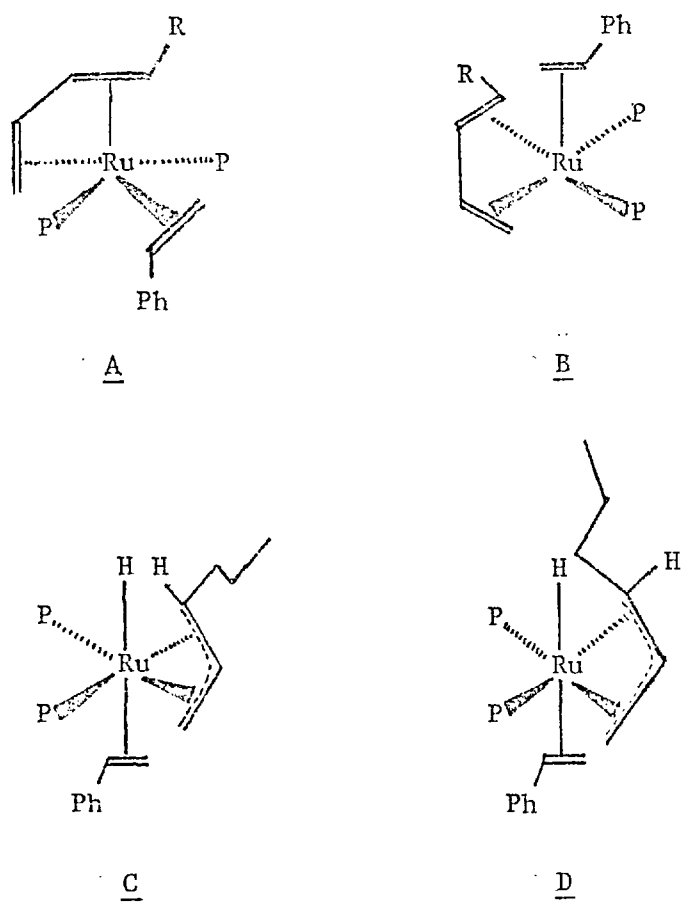


Figure 1

Structure of some Ruthenium Olefin Complexes

absorptions at 1610 ($\nu_{C=C}$) and 1209 (δ_{CH_2}) cm^{-1} , the former of which is close to the position of $\nu_{C=C}$ for the free double bonds in $[\text{Fe}(\eta^3\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_4\text{H}_6)]^+\text{PF}_6^-$ ¹⁵³ and $\text{Fe}(\text{CO})_4(\text{C}_4\text{H}_6)$ ¹⁵⁴ indicating that the butadiene moiety coordinates through only one double bond and that the complex has a structure similar to the other complexes of general formula $\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_2\text{L}$ ($\text{L} = \text{PPh}_3$ or C_6H_5) that we have isolated.

Solution studies on the complex are rendered very difficult on account of its ready decomposition to $\text{Ru}(\text{C}_4\text{H}_6)_2\text{PPh}_3$,⁷² but an ^1H n.m.r. spectrum of a freshly prepared solution in C_6D_6 shows a series of broad resonances stretching from δ -0.5 to 6.4 (see Table II) indicating that the two butadiene groups are not equivalent.

d) Hex-1-ene

$\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ reacts with neat hex-1-ene or with hex-1-ene in petroleum to give a yellow powder analysing for $\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ which may be recrystallised from toluene as the yellow crystalline toluene solvate. No ν_{M-H} is visible in the i.r. spectrum of this complex but the presence of the hydride is established by the observation of two triplets to high field in the ^1H n.m.r. spectrum. The presence of styrene is confirmed by an absorption at 1592 cm^{-1} in the i.r. spectrum.

The fully decoupled ^{31}P n.m.r. spectrum of the main species present in solution consists of three doublets at δ 64.9, 64.8 and 51.3 ppm, all with $J_{\text{PP}} = 18$ Hz and in the relative ratio 1 : 1 : 2. On allowing coupling to the hydride, each of these doublets splits into a further doublet ($J_{\text{PH}} = 27$ Hz). This together with the observation of two triplets of equal intensity in the high field region of the ^1H n.m.r. spectrum can only be explained by there being two metal centres each of which accommodates one hydride and two phosphine groups in a facial

configuration and with the resonances from one of the phosphorus atoms on each centre having identical chemical shifts whilst the chemical shift of the other two phosphorus atoms differs by 0.1 ppm.

Since the low field ^1H n.m.r. spectrum of this compound is very similar to that of the mixture exo and endo (n -1-3-pentenyl) in HCoL_4 ($\text{L} = \text{Co}^{155}$ or PF_3^{156}), we attribute the structures C and D (see Figure 1) to the two isomers of $\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$. The presence of other resonances in the ^{31}P n.m.r. spectrum together with a high field signal at $\delta -0.35$ in the ^1H n.m.r. spectrum even of crystalline samples of $\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ indicates that in solution a rearrangement occurs giving a hexadiene complex which was not identified. This lends support to the mechanism proposed ⁷² for the formation of a butadiene complex from 1-butene through an hydrido allyl intermediate.

e) cis-trans-hex-2-ene (87:13)

Interaction of $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ with a cis-trans mixture of hex-2-ene either neat or in petroleum gives a complex of formula $\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$. Although the infrared spectrum of this complex is very similar to that of $\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$, its n.m.r. spectra indicate that it is a hexadiene complex of ruthenium(0). As with the analogous butadiene complex, $\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ exists in solution in two isomeric forms and gives rise to two singlets of equal intensity in the ^{31}P n.m.r. spectrum. Once again, only one isomer crystallises from solution.

The presence of complex resonances in the ^1H n.m.r. spectrum at $\delta 2.7$ (vbr multiplet) and $\delta 1.0$ (triplet with increased intensity on high frequency side) clearly indicates the presence of an ethyl group and hence that 1-3-hexadiene, rather than 2-4-hexadiene is coordinated

to the metal whilst broad resonances at δ -0.2 and -0.9 suggest that the ethyl group is exo with respect to the metal as in A and B, R = Et (see Figure 1).

It is worth noting that in the presence of excess triphenylphosphine both hex-1-ene and cis-trans-hex-2-ene give a mixture of $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$. The reaction is noticeably slower in the case of hex-1-ene which suggests that isomerisation to hex-2-ene occurs as the first step of this reaction. Such isomerisations are well known to be catalysed by hydrido ruthenium phosphine complexes.¹³³

f) Cyclohexene

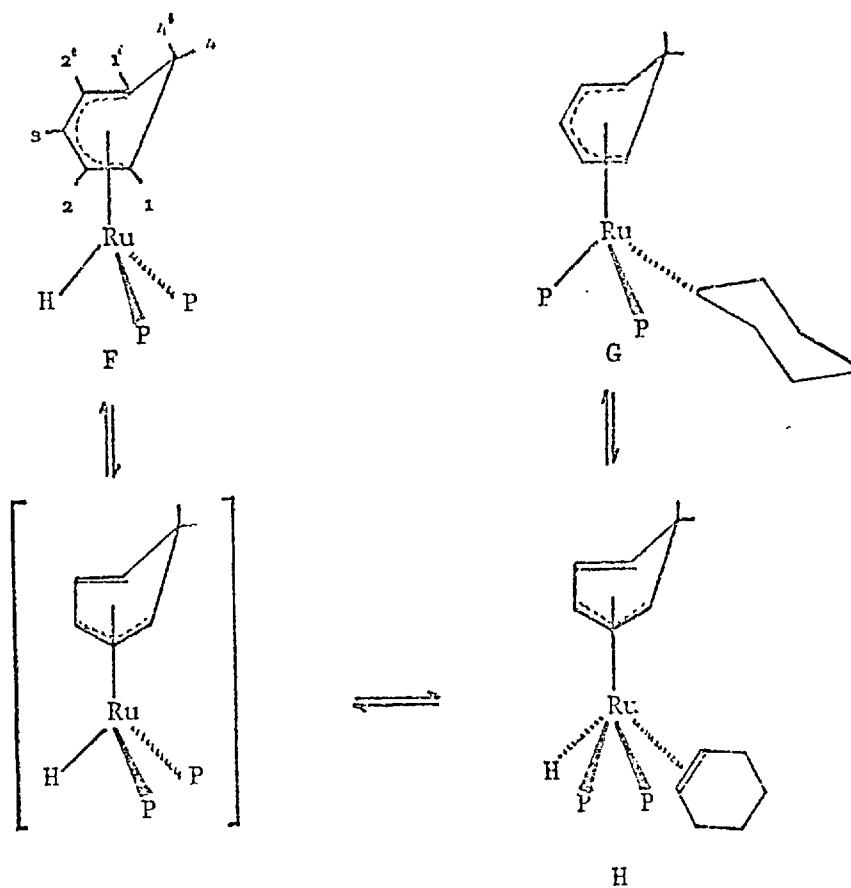
From the reaction of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ with cyclohexene, three different products may be obtained, depending upon the reaction conditions. Thus, reaction of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ with neat cyclohexene affords an off white complex of stoichiometry $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ whilst another complex, which is darker yellow but has the same empirical formula is obtained if the reaction is carried out in petroleum containing a large excess of cyclohexene. This complex is $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$. From $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ and a small excess of cyclohexene in petroleum a third complex, $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ is obtained. Recrystallisation of $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ from toluene/petroleum at -20° gives $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ whilst the slow reaction of $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ with excess cyclohexene in benzene gives $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ (n.m.r. evidence - see later).

The infrared spectra of all the complexes show absorptions between 2700 and 2800 cm^{-1} attributable to $\nu\text{C-H}$ of the methylene group of a coordinated cyclo hexadienyl moiety¹⁵⁷: $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ and $\text{RuH}(\text{PPh}_3)_2(\text{C}_6\text{H}_7)$ also show peaks attributable to $\nu\text{M-H}$.

This strongly suggests that $\text{RuH}(\text{PPh}_3)_2(\text{C}_6\text{H}_7)$ is the hydrido cyclohexadienyl complex (E in Scheme 3) isoelectronic with

$\text{RuH}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)$ ²³ and $\text{RuH}(\text{PPh}_3)_2(\text{PhO})$. ⁶³ In agreement with this, a sharp triplet from the metal hydride is observed at $\delta -12.4$ ($J_{\text{PH}} = 27$ Hz) in the ^1H n.m.r. spectrum and poorly resolved resonances at $\delta 5.0(1)$, $4.85(2)$, $2.7(3)$, $1.6(1)$ are assigned to the proton 3; 2 and 2'; 1, 1' and 4; and 4' (for assignments see Scheme 2), the exo proton of the methylene group being to high field of the endo.¹⁵⁸ The ^{31}P n.m.r. spectrum shows a sharp singlet in the region expected for mutually cis phosphines which splits into a doublet $J_{\text{PH}} = 27$ Hz when coupling to the hydride is introduced.

When either $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ or $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ is dissolved in benzene at room temperature, all the resonances from $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ together with those from free cyclohexene are observed. In addition, a poorly resolved triplet ($J_{\text{PH}} = 5$ Hz) at $\delta -5.6$ and a singlet at $\delta 2.7$ are observed. The triplet at $\delta -5.6$ which is sharper at higher temperatures, could arise from a metal hydride but the coupling constant to phosphorus suggests that the hydrogen atom is two bonds removed from the metal atom and that the resonance arises from the α hydrogen atom of a coordinated cyclohexyl group as in F (Scheme 3). The peak at $\delta 2.7$ is assigned to the various protons of the cyclohexyl group. J_{PH} is then similar to that observed²¹ for the hydrogen atom on the unique methyl group of $\text{RuHMe}(\text{PPh}_3)_2(\text{MeLiOEt}_2)$ in thf (4 Hz). The very high-field shift of this hydrogen atom is unusual but may be caused partly by shielding by the metal atom but also by shielding from the ring currents of the phenyl groups on phosphorus or of the cyclohexadienyl ligand. Since this complex contains no hydride we suggest that it is the compound isolated as $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$. The ^{31}P n.m.r. spectrum of this compound only shows a single line at $\delta 59.65$ which does not change if coupling with hydride is introduced.



Scheme 3

Mechanism of insertion of cyclohexene into an Ru-H bond. Compound in brackets not isolated.

Even if solutions of $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ are made up at -30° and the ^1H n.m.r. spectrum run at this temperature, only peaks assignable to $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ and free cyclohexene are observable. On warming, these peaks increase in intensity (owing to the greater solubility of the complex) and those from $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ appear (these may also be present at -30°C but the low solubility of the complex at this temperature would preclude their observation. Thus, we have no direct ^1H n.m.r. data on $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ but in view of its decomposition to give $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$, cyclohexene and $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$, the presence of a $\nu\text{M-H}$ in the i.r. spectrum and analytical data we propose that the complex contains an $\eta(1-3)$ -cyclohexadienyl moiety and a coordinated cyclohexene ligand as in G (Scheme 3). The free double bond in this complex should show $\nu\text{C=C}$ near 1655 cm^{-1} ,^{159, 160} and although there is a weak broad peak in this region it is also present in the i.r. spectra of the $\eta(1-5)$ cyclohexadienyl complexes so probably does not arise from the free double bond. $\nu\text{C=C}$ in this kind of complex is sometimes weak.¹⁶⁰

If these structures are in fact correct, we believe this to be a very rare example of a system in which all the steps of the insertion of a free alkene into an M-H bond are directly observable and for which all the intermediates are isolable.[†] Thus, the cyclohexadienyl ring of the coordinatively saturated $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ dissociates a double bond of the ring system to give a transient 16e complex containing an $\eta(1-3)$ cyclohexadienyl ring. The vacant site on the metal is

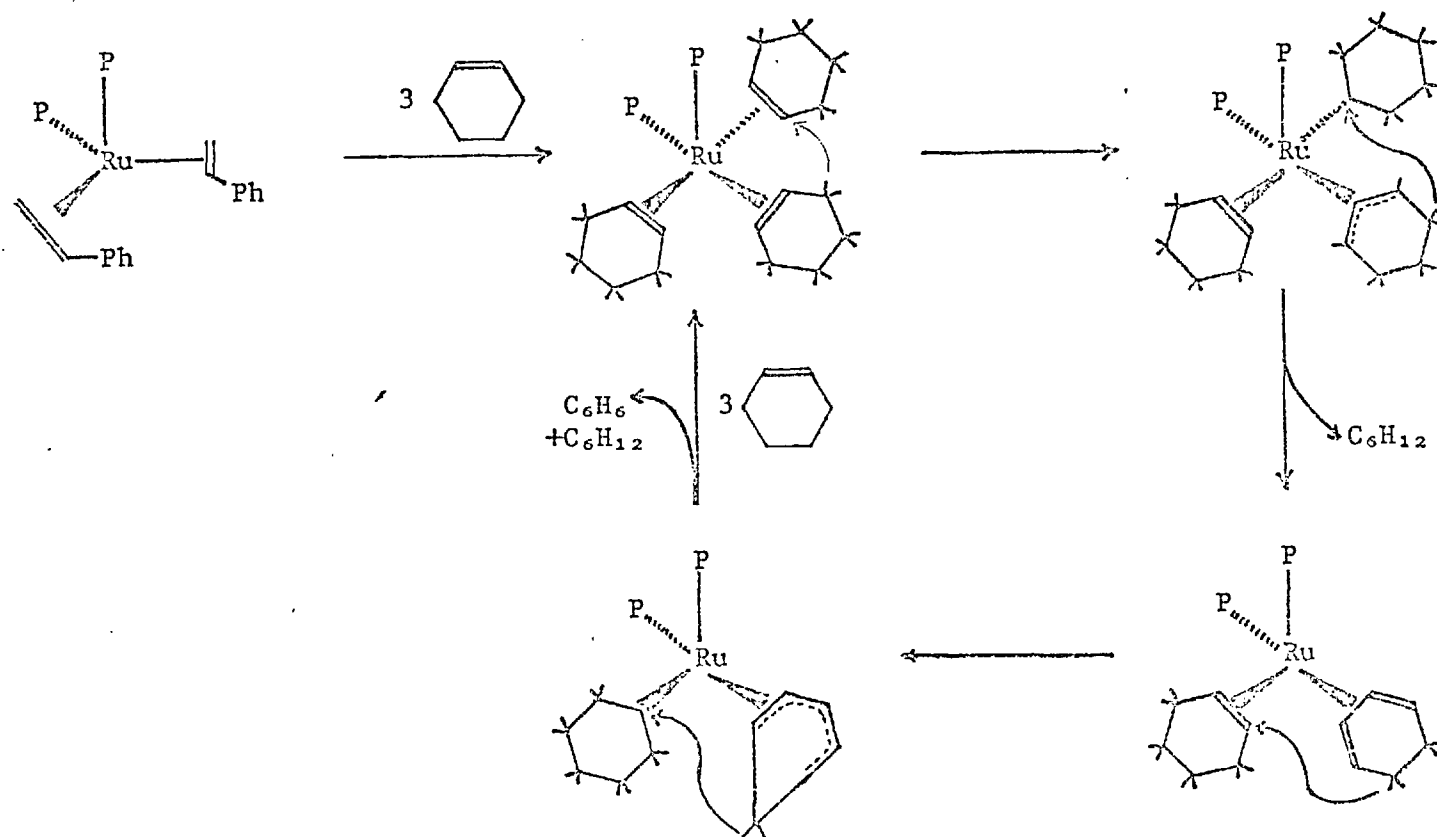
[†] $\text{FeH}_2(\text{N}_2)(\text{PPh}_3)_3$ is said¹⁶¹ to give $\text{FeH}(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ (solvent) on interaction with cyclohexene but the evidence is not compelling. Osborn has observed¹⁶² a dynamic reversible insertion of C_2H_4 into an Mo-H bond.

then occupied by an incoming cyclohexene ligand which then inserts into the M-H bond with concomitant recoordination of the free double bond of the cyclohexadiene molecule (see Scheme 3).

Finally, if solutions of $\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$ or $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})-(\text{PPh}_3)_2$ are heated to 60° in deuterio toluene the resonances from free cyclohexene and from the coordinated cyclohexadienyl group disappear and sharp peaks attributable to benzene and cyclohexane appear in the ^1H n.m.r. spectrum (G.L.C. evidence shows that benzene and cyclohexene are formed in approximately 1 : 1 ratios). The most rational explanation of this observation is that transfer of hydrogen from the methylene group of the cyclohexadienyl moiety to the cyclohexyl group occurs, thus giving direct evidence for the type of mechanisms that has been postulated for the removal of hydrogen from the ortho-position on a triphenylphosphine, ²¹ propene, but-1-ene, pent-1-ene and cyclooctadiene ⁷² in related ruthenium systems. We cannot rule out the possibility that this reaction proceeds by initial formation of an hydrido alkyl intermediate followed by loss of alkane and benzene but we think it more likely that direct inter-ligand hydrogen transfer occurs.

This disproportionation of cyclohexene to cyclohexane and benzene is evidently catalytic since if 0.2 g $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ is refluxed in cyclohexene (5 ml) for 16 hours, glc data show that 9.8% of cyclohexane and 4.5% benzene are formed. After a further 20 hours, 23.7% cyclohexane and 10% benzene are present, which represents about 25 catalytic cycles. A mechanism for this reaction is proposed in Scheme 4.

This catalytic reaction slowly poisons as a black solid, assumed to be ruthenium metal, slowly precipitates. This problem can be circumvented since the reaction also proceeds slowly at room temperature (catalysed by $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$) and n.m.r. evidence suggests that both $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ and $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ are present at



Scheme 4. Proposed mechanism for the catalytic disproportionation of cyclohexene to benzene and cyclohexane. P = PPh₃. Arrows within structures represent shifts of hydrogen atoms.

all times in the solution.

g) Cyclopentadiene

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ reacts rapidly with neat cyclopentadiene to give a yellow complex identified as $\text{RuH}(\eta\text{-1-5-C}_5\text{H}_5)(\text{PPh}_3)_2$ ²³ by its i.r. and ¹H n.m.r. spectrum.

4. Other Reactions of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$

a) Carbon Monoxide

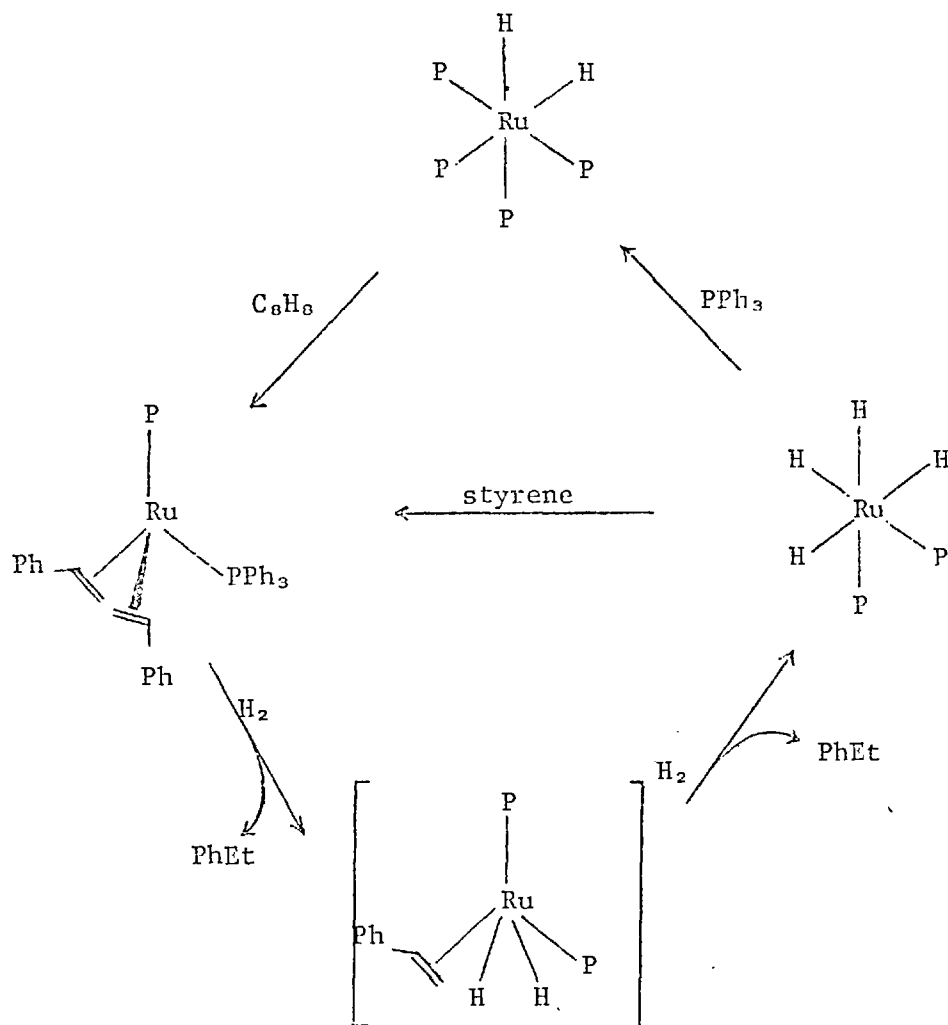
$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ reacts rapidly with CO in styrene in the presence of excess PPh_3 to give a pale yellow solution from which $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ¹¹¹ may be isolated on addition of petroleum. $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ is also obtained on reaction of green $\text{Ru}(\text{C}_6\text{H}_5)(\text{PPh}_3)_2 \cdot 0.5$ hexane with CO in hexane.

b) Hydrogen

Yamamoto has reported⁷⁶ that $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ reacts with hydrogen in styrene to give ethyl benzene and $\text{RuH}_2(\text{PPh}_3)_4$.

In petroleum we find that $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ reacts with hydrogen at room temperature to give a chocolate brown complex, $\text{RuH}_4(\text{PPh}_3)_2$. The i.r. spectrum of this complex is similar to that of $\text{RuH}_4(\text{PPh}_3)_3$ ⁴⁶ and $\nu\text{Ru-H}$ appears as a broad peak at 1945 cm^{-1} (1950 for $\text{RuH}_4(\text{PPh}_3)_3$). The proton n.m.r. spectrum shows only one broad peak in the hydride region at δ -10.25 (-7.05 for $\text{RuH}_4(\text{PPh}_3)_3$) which sharpens slightly on warming to 50°C and broadens considerably on cooling to 0°C . The ³¹P n.m.r. spectrum at 28 or 100°C consists of two slightly broad singlets of equal intensity at δ 75.5 and 56.1 both of which broaden considerably when coupling to the hydride is introduced (the higher field signal appears as a broad doublet, $J_{\text{PH}} \approx 40\text{ Hz}$). This suggests that the two phosphines are non-equivalent even at 100°C , but that some

kind of exchange process (perhaps dissociation of just one of the phosphines) removes the coupling. This compound is probably an intermediate in the hydrogenation of styrene by $\text{RuH}_2(\text{PPh}_3)_4$ (see Scheme 5).



Scheme 5

Hydrogenation of Styrene Using $\text{RuH}_2(\text{PPh}_3)_4$ as
the Catalyst

[Compound in bracket not isolated]

Experimental

As in Chapter II except for Microanalyses by F. and E. Pascher (Bonn), Butterworth Microanalytical Consultancy (Teddington), and Imperial College Microanalytical laboratories.

All solvents were thoroughly degassed and dried over sodium-benzophenone ketyl (toluene, diethyl ether, tetrahydrofuran) or sodium (petroleum, boiling range 40-60°C and n-heptane) n-hexane was shaken with concentrated sulphuric acid (99%), washed with water and distilled from lithium.

Gaseous olefins were used without further purification.

Styrene was distilled under reduced pressure and stored under argon (this was found not to be necessary for the preparation of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$). Hex-1-ene, hex-2-ene and cyclo-hexene were purified by shaking with acidified solutions of ferrous ammonium sulphate and passing through an alumina column.

Hexafluorobenzene was dried over molecular sieves.

Cyclopentadiene was obtained through cracking of dicyclopentadiene.

1) Bis(styrene)bis(triphenylphosphine)ruthenium(0)

$\text{RuH}_2(\text{PPh}_3)_4$ (1.15 g, 1 mmole) was dissolved in styrene (12 ml). The colour changed immediately from yellow to purple. After one hour petroleum (40 ml) was added, the solution was filtered and cooled to -15°C affording deep red-purple crystals of the complex. Yield ca. 65%. The crystallisation time was found to be variable (3 days - 4 weeks). However, by seeding the solution with previously obtained crystals of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ crystallisation is complete within 16 hours.

2) Reactions of $\text{Ru}(\text{C}_6\text{H}_6)_2(\text{PPh}_3)_2$ with saturated hydrocarbons

$\text{Ru}(\text{St})_2(\text{PPh}_3)_2$ (0.4 g, 0.48 mmoles) was stirred in alkane (40 ml)

(TMS, isopentane, n-hexane) for 24 hours, (72 hours in the case of tetramethylsilane). The green powder which separated was collected, washed with alkane (10 mls) and dried in vacuo. Yield ca. 90%. The complex was identified as mainly $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2 \cdot 0.5\text{RH}$ contaminated with a small amount of $\text{RuH}_2(\text{PPh}_3)_4$ ($\nu_{\text{Ru-H}} = 2080 \text{ cm}^{-1}$).

When the above reaction was carried out under reflux an orange-brown material which ^{31}P n.m.r. spectroscopy suggested was a complex mixture of compounds was obtained. It did not contain $\text{RuH}_2(\text{PPh}_3)_4$ and is hereafter referred to as the "orange-species".

3) Reaction of $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ with alkanes in the presence of PPh_3

$\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ (0.4 g, 0.48 mmole) was added to n-hexane (50 ml) containing triphenylphosphine (0.15 g, 0.57 mmoles). After stirring for 15 hours the yellow-brown solid was collected, washed with n-hexane and dried in vacuo. It was identified as a mixture of $\text{RuH}_2(\text{PPh}_3)_4$ and the "orange species" by its ^1H and ^{31}P n.m.r. spectra.

Under reflux the same mixture was obtained but with a higher proportion of the "orange species".

4) Reaction of $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ with C_6F_6

As in (2) above but using hexafluorobenzene (10 ml) in place of alkane. The green product which was collected and dried in vacuo was identified as $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2 \cdot 0.5\text{C}_6\text{F}_6$ and contained no $\text{RuH}_2(\text{PPh}_3)_4$. Yield, ca. 90%.

Under reflux the "orange species" was again obtained in high yield.

5) Reaction of $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ with C_6F_6 in the presence of excess PPh_3

As (4) above but adding PPh_3 (0.15 g, 0.57 moles) and carrying out the reaction at 60° . The orange-brown powder which precipitated was collected and dried in vacuo, it was identified as the "orange-species"

by its infrared spectrum. It contained no $\text{RuH}_2(\text{PPh}_3)_4$.

At room temperature the reaction is very slow, no change being observed after 1 week in C_6F_6 (1.5 ml).

6) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with n-hexane in hexafluorobenzene in the presence of excess PPh_3 .

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.3 g, 0.36 mmole) was added to C_6F_6 (1.5 ml) containing n-hexane (100 μl , 0.9 mmole) and triphenylphosphine (0.15 g, 0.57 mmole) and the resulting suspension stirred for a week. Reaction was not complete but an i.r. spectrum of the brown solid obtained on filtration contained a peak at 2080 cm^{-1} attributable to $\nu\text{M-H}$ of $\text{RuH}_2(\text{PPh}_3)_4$.

7) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with triphenylphosphine

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.4 g, 0.48 mmole) was added to PPh_3 (1 g) and the mixture heated until the PPh_3 was molten. The resulting orange-brown solution was stirred for one hour after which excess PPh_3 was sublimed at 120° in vacuo. The resulting orange tar consisted mainly of the "orange species" but contained a small amount of $\text{RuH}_2(\text{PPh}_3)_4$ (i.r. evidence).

8) Styrenebis(ethylene)bis(triphenylphosphine)ruthenium(0)

a) Ethylene was passed through a stirred suspension of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.4 g, 0.48 mmole) in petroleum (50 ml) for 5 hr at room temperature. The complex separated as an orange powder which was collected and dried in vacuo. Yield, ca. 80%.

b) $\text{RuH}_2(\text{PPh}_3)_4$ (0.5 g, 0.435 mmole) was stirred in styrene (10 ml) at room temperature for 30 min. Ethylene was then bubbled through the purple solution for 30 min to give an orange solution from which the complex was obtained as orange crystals on addition of petroleum (40 ml)

and cooling to -20°C . Yield, ca. 30%.

The following compounds were prepared as in 8(a).

Styrenebutadienebis(triphenylphosphine)ruthenium(0) from but-1-ene. Yield, ca. 90%; it was also prepared from butadiene as in 8(b). Yield, ca. 60%; recrystallisation from toluene (2 ml) or C_6D_6 (1 ml) gave the complex as the 1 : 1 solvates.

$\eta(1-2)$ butadiene- $\eta(1-4)$ butadienebis(triphenylphosphine)ruthenium(0) from butadiene as an off-white powder. Yield ca. 80%. Recrystallisation from C_6D_6 -petroleum gave $\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)$ (identified by its i.r. and ^1H n.m.r. spectra) as pale yellow crystals; and Tetrahydridobis(triphenylphosphine)ruthenium(IV) from hydrogen as a chocolate brown powder. Yield, ca. 80%.

9) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with propene

Propene was passed through a suspension of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ in n-heptane at 60° for five hours. The off-white powder obtained was collected and recrystallised from benzene (2 ml) to give orange crystals of cis- $\text{Ru}(\text{C}_3\text{H}_5)_2(\text{PPh}_3)_2$ identified by its i.r. and ^1H n.m.r. spectra.

10) Hydrido $\eta(1-3)$ hexenylstyrenebis(triphenylphosphine)ruthenium(II).0.5-toluene

a) $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.4 g, 0.48 mmole) was stirred with hex-1-ene (3 ml) for 15 hr at room temperature during which time a yellow solid precipitated. This was collected and recrystallised from toluene-petroleum as yellow crystals. Yield after recrystallisation ca. 20%.

b) as 10(a) above but the reaction was carried out with hex-1-ene (2 ml) in petroleum (15 ml).

Prepared as in 10(a) but without recrystallisation were:

Styrenhexadienebis(triphenylphosphine)ruthenium(0) from cis-trans-hex-2-ene as a yellow powder. Yield, ca. 80%. This compound is also obtained along with $\text{RuH}_2(\text{PPh}_3)_4$ from the reaction between $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ and hex-1-ene or hex-2-ene in petroleum in the presence of excess PPh_3 (^{31}P n.m.r. evidence)

and Hydrido- η (1-3)cyclohexadienylcyclohexenebis(triphenylphosphine)-ruthenium(II) from cyclohexene as off white microcrystals. Yield ca. 60%. This compound was also obtained on recrystallisation of $\text{Ru}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$ from toluene (2 ml).

Prepared as in 10(b) above was:

Cyclohexyl- η (1-5)cyclohexadienylbis(triphenylphosphine)ruthenium(0) from cyclohexene as yellow microcrystals.

11) Hydridocyclohexadienylbis(triphenylphosphine)ruthenium(II)

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.15 g, 0.18 mmole) was stirred in petroleum (50 ml) containing cyclohexene (3 ml) for 18 hrs. The yellow solid that precipitated was collected and dried in vacuo. Yield, ca. 80%.

12) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with cyclopentadiene

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.3 g, 0.36 mmole) was dissolved in freshly distilled cyclopentadiene (5 ml). Addition of petroleum (30 ml) to the yellow solution obtained after 15 min afforded a yellow powder identified as $\text{RuH}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2$ from its i.r. and ^1H n.m.r. spectra.

13) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with CO

$\text{RuH}_2(\text{PPh}_3)_2$ (0.3 g, 0.36 mmole) was stirred in styrene (4 ml) for 30 mins at room temperature. CO was then passed through the purple solution for 30 mins, during which time the colour changed to pale yellow. On addition of petroleum (40 ml), $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$, identified

by its i.r. spectrum, separated as pale yellow microcrystals.

14) Reaction of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ with water

$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ (0.2 g, 0.24 mmole) was stirred with tetrahydrofuran (4 ml) containing water (1.5 ml) for 10 hours at room temperature during which time the colour of the suspension changed from purple to red. The red solid was collected, dried in vacuo and identified as $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{thf})$ by its i.r. spectrum.

TABLE I

INFRARED SPECTROSCOPY (cm^{-1}) DATA FOR RUTHENIUM COMPLEXES
(Assigned absorptions)

Compound	Styrene		$\nu\text{M-H}$	Other
	$\nu\text{C=C}$	$\delta = \text{C-H}$ in plane		
$\text{Ru}(\text{St})_2(\text{PPh}_3)_2$	1589m	1220m		
$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_3)_2] \cdot 0.5\text{RH}$ $\text{R} = \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_{13}$	1591m	1215m,s	2080w	
$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_3)_2] \cdot 0.5\text{SiMe}_4$	1591m	1215m,s	2080w	1245m, ^b 860s, ^b
$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_3)_2] \cdot 0.5\text{C}_6\text{F}_6$	1591m	1215m,s		1525s, ^c 1010s, ^c
$\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	1595m			
$\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	1592m	1230m		
$\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_6\text{H}_6)(\text{PPh}_3)_2\text{C}_6\text{D}_6$	1595m	1235m		2280w, ^a
$\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)_2$				1610s, ^d 860s, ^d
$\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	1592m	1230m	not seen	
$\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	1592m	1230m		
$\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$			2015msh	2790w, ^e 2760w, ^e
$\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$				2770w, ^e
$\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$			1960m	2780w, ^e 2740w, ^e
$\text{RuH}_4(\text{PPh}_3)_2$			1945m	

^a $\nu\text{C-D}$;^d vibrations of free double bond;^b bands from TMS;^e $\nu\text{C-H}$ of the methylene protons of C_6H_7 ;^c bands from C_6F_6 .

TABLE II

¹H N.M.R. DATA FOR RUTHENIUM COMPLEXES^a

Compound	styrene δ		η ⁴ coordinated dienes δ			Coordinated olefins	Hydride (J _{PH}) δ	Other δ
			H _{AA'}	H _{BB'}	H _{CC'}			
Ru(C ₈ H ₈) ₂ (PPh ₃) ₂ b	2.7	4.35						
	2.5	4.2						
Ru(C ₈ H ₈)(PPh ₃) ₂ ·0.5RH	3.7	4.9						0.0 ^c
Ru(C ₂ H ₄) ₂ (C ₈ H ₈)(PPh ₃) ₂								0.95, 1.3, 1.95, 5.3 ^d
Ru(C ₄ H ₆)(C ₈ H ₈)(PPh ₃) ₂ ·C ₇ H ₈	3.2	5.7	-0.45	1.55	4.3			2.3 ^e
Ru(C ₄ H ₆) ₂ (PPh ₃) ₂			-0.5	2.1	4.7	1.5, 2.5		5.2, 5.4
RuH(C ₆ H ₁₁)(C ₈ H ₈)(PPh ₃) ₂ (C)		5.55				4.35, 4.9	-10.5t(29.3 Hz)	-0.35, ^f 0.85, 1.6
RuH(C ₆ H ₁₁)(C ₈ H ₈)(PPh ₃) ₂ (D)		5.55				4.35, 4.9	-12.3t(29.3 Hz)	-0.35, ^f 0.85, 1.6
Ru(C ₆ H ₁₀)(C ₈ H ₈)(PPh ₃) ₂		5.5	-0.2, -1.0		5.1			1.7, ^g 1.0 ^g
RuH(C ₆ H ₇)(PPh ₃) ₂							-12.4t(27.0 Hz)	5.0, 4.85, 2.7, 1.6 ^h
Ru(C ₆ H ₁₁)(C ₆ H ₇)(PPh ₃) ₂								-5.6, 2.7, 1.3, 1.0 ^h
RuH ₄ (PPh ₃) ₂							20.25br	

a = in C₆D₆ unless otherwise stated; b = in styrene; c = SiMe₄ for RH = SiMe₄; d = not assigned; e = toluene of crystallisation; f = contaminated with an unidentified hexadiene complex (see text); g = aliphatic proton; h = for assignment see text.

TABLE III

 ^{31}P N.M.R. DATA

Compounds	Chemical Shifts* and Coupling Constants
$\text{Ru}(\eta\text{-1-4-C}_4\text{H}_6)(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	60.91(s) (B), 40.50(s) (A)
$\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$ (C)	64.87(d) and 51.35(d) $J_{\text{P}_1\text{P}_2}$ (40 Hz) J_{PH} 29 Hz
$\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$ (D)	64.77(d) and 51.35(d) $J_{\text{P}_1\text{P}_2}$ (40 Hz) J_{PH} 29 Hz
$\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	54.37(s) (B), 43.62(s) (A)
$\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_6)(\text{PPh}_3)_2$	67.15(d) 51.20(d) $J_{\text{P}_1\text{P}_2}$ 9.6 Hz
$\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$	61.46(s) J_{PH} 27 Hz
$\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$	59.65(s)
$\text{RuH}_4(\text{PPh}_3)_2$	75.5(brs) 56.1(brs)

* In ppm to high frequency of external 85% H_3PO_4 .

TABLE IV

COMPLETE LIST OF BANDS

- 1) $\text{Ru}(\text{C}_9\text{H}_8)_2(\text{PPh}_3)_2$
 3140vw, 3050m, 3010w, 1590ms, 1580m, 1570w, 1430s, 1310w, 1300w,
 1285w, 1220m, 1200m, 1180m, 1165m, 1155w, 1080ms, 1025m, 995m,
 935w, 900w, 850vw, 770wsh, 760wsh, 750s, 740s, 720w, 700s, 690vs,
 620m, 590w, 540s, 530s, 515vs, 500ms, 480m, 450m, 435m, 410w.
- 2) $\text{Ru}(\text{C}_6\text{H}_8)(\text{PPh}_3)_2 \cdot 0.5\text{RH}$ (R = hexyl or isopentyl)
 3130vw, 3050m, 2080w, 1590m, 1580m, 1570m, 1430s, 1305w, 1210m,
 1180m, 1150w, 1080ms, 1020m, 995w, 910w, 850w, 800m, 780vw, 740vs,
 720w, 690vs, 615w, 515s, 505vs, 440m, 410m.
- 3) $\text{Ru}(\text{C}_9\text{H}_8)(\text{PPh}_3)_2 \cdot 0.5\text{SiMe}_4$
 as (2) plus: 1245m, 860s.
- 4) $\text{Ru}(\text{C}_6\text{H}_8)(\text{PPh}_3)_2 \cdot 0.5\text{C}_6\text{F}_6$
 as (2) but no absorption at 2080 cm^{-1}
 and plus 1525s, 1010s.
- 5) Orange species
 3140vw, 3050m, 1590m, 1580m, 1570m, 1500w, 1430s, 1305w, 1330vw,
 1215m, 1180m, 1150w, 1110w, 1080m, 1065w, 1020m, 995m, 980w, 800m,
 750s, 740w, 720w, 695vs, 680w, 615w, 530vs, 505s, 490m, 455w,
 420m.
- 6) $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$
 3140vw, 3050m, 1595msh, 1580msh, 1570m, 1430s, 1355w, 1310w, 1290w,
 1260w, 1195m, 1180m, 1160mw, 1155mw, 1115w, 1080ms, 1025m, 1015w,
 995m, 975w, 930w, 915w, 905w, 880w, 850m, 835w, 750s, 740s, 720w,
 695vs, 620w, 600w, 530s, 510vs, 475m, 455m, 440w, 430m, 400m, 375w.

7) $\text{Ru}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)(\text{PPh}_3)_2 \cdot \text{C}_6\text{D}_6$

3050m, 2280w, 1595m, 1585m, 1570m, 1495m, 1480w, 1475w, 1430s,
 1330w, 1310w, 1290vw, 1235m, 1200m, 1188m, 1182m, 1160m, 1115w,
 1080m, 1070w, 1040w, 1025m, 1000m, 950w, 900w, 880w, 850w, 810mw,
 790w, 750s, 740s, 730w, 720w, 700vs, 680w, 620w, 550w, 550w,
 540w, 528b, 515s, 508s, 490m, 450m, 410m.

8) $\text{Ru}(\eta\text{-}1\text{-}4\text{-}\text{C}_6\text{H}_5)(\eta\text{-}1\text{-}2\text{-}\text{C}_6\text{H}_5)(\text{PPh}_3)_2$

3140vw, 3060vw, 3040m, 3020w, 1610s, 1580m, 1510m, 1430s, 1330w,
 1310w, 1285w, 1210msh, 1200m, 1185m, 1175w, 1105w, 1080m, 1040w,
 1025w, 1015w, 1000m, 950w, 920w, 910w, 890w, 870w, 860s, 850w,
 845w, 780vw, 750m, 740s, 720w, 695vs, 675w, 615w, 550w, 525s,
 515s, 495s, 450ms, 430m, 420m, 405m.

9) $\text{RuH}(\eta^3\text{-}\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$

3050m, 1590m, 1580m, 1570m, 1490m, 1430s, 1310w, 1250vw, 1230m,
 1220w, 1185m, 1180w, 1155w, 1075ms, 1025m, 995m, 975w, 945m,
 920w, 880w, 860m, 850w, 840w, 750s, 740s, 720w, 700vs, 678w, 660w,
 620w, 560m, 550m, 535m, 525s, 515s, 500s, 490m, 450m, 430w, 410w,
 405m.

10) $\text{Ru}(\eta\text{-}1\text{-}4\text{-}\text{C}_6\text{H}_2\text{O})(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$

3050m, 1590m, 1580m, 1570m, 1490m, 1430s, 1305w, 1230m, 1220w,
 1195w, 1185m, 1150w, 1115w, 1075ms, 1020w, 995w, 940w, 900w,
 850m, 745s, 740s, 720w, 690vs, 620vw, 558w, 550m, 535m, 525m, 510s,
 500s, 490m, 450m, 430w, 405m.

11) $\text{RuH}(\eta\text{-}1\text{-}3\text{-}\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{13})(\text{PPh}_3)_2$

3130vw, 3040ms, 3000vw, 2790w, 2760wsh, 2010m, 1580m, 1570w, 1430s,
 1305w, 1295w, 1180m, 1175w, 1150w, 1080ms, 1040w, 1025w, 995w,
 960w, 930w, 900w, 870vw, 850w, 830w, 790w, 745s, 735s, 720w, 690s,
 650m, 615w, 590m, 530s, 515s, 505s, 490s, 455m, 425m, 420m.

12) $\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$

3140vw, 3050m, 3010w, 2770w, 1585m, 1570m, 1350w, 1340w, 1315w,
 1305w, 1300w, 1200w, 1180m, 1170vw, 1160w, 1115w, 1080ms, 1165w,
 1140w, 1025m, 995m, 965w, 930w, 915w, 900w, 850m, 835w, 775w,
 745s, 740s, 720m, 695vs, 680w, 650w, 620w, 595m, 335s, 515s, 505s,
 490s, 455m, 435w, 420m.

13) $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$

3040m, 2780w, 2740w, 1580m, 1570w, 1430s, 1305w, 1295m, 1180m,
 1150w, 1080ms, 1070w, 1040w, 1025m, 995w, 970w, 930w, 900w, 850w,
 830w, 780m, 735s, 720w, 690vs, 650m, 645m, 620m, 595m, 530m, 515s,
 505s, 490s, 455m, 435m, 420m.

14) $\text{RuH}_4(\text{PPh}_3)_2$

3040w, 1945m, 1580w, 1565w, 1430s, 1305w, 1185m, 1155w, 1115w,
 1080m, 1065w, 1020m, 995s, 750w, 745m, 740m, 730m, 720m, 695s,
 680w, 630w, 615w, 545w, 540w, 520s, 450w, 415w, 400w.

Compound	Colour	m.p.	Found				Required			
			C	H	P	Others	C	H	P	Others
$\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$	Purple	86d	75.3	5.6	6.7		74.9	5.6	7.4	
$\text{Ru}(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{SiMe}_4$	Green-grey		72.9	6.4	7.2	Si: 1.9	71.4	5.7	8.0	Si: 1.8
$\text{Ru}(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{C}_5\text{H}_{12}$	Green		72.4	5.5	8.4		72.9	5.7	8.1	
$\text{Ru}(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$	Green		72.9	5.5	8.5		73.1	5.8	8.0	
$\text{Ru}(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{C}_6\text{F}_6$	Green	60d	67.25	4.7	7.4		68.6	4.6	7.5	
$\text{Ru}(\text{C}_2\text{H}_4)_2(\text{C}_8\text{H}_8)(\text{PPh}_3)_2$	Orange	121	73.0	6.5	7.6		73.4	5.9	7.9	
$\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \text{C}_7\text{H}_8$	Pale yellow	147	74.75	6.4	7.4		75.4	6.0	7.1	
$\text{Ru}(\text{C}_4\text{H}_6)(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot \text{C}_6\text{D}_6$	Pale yellow	—	74.4	6.3	7.1		74.7	5.8	7.2	
$\text{Ru}(\text{C}_4\text{H}_6)_2(\text{PPh}_3)_2$	Creamy-white	106d	72.0	5.8	8.6		72.0	5.7	8.5	
$\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_8\text{H}_8)(\text{PPh}_3)_2$	Yellow	119	74.2	6.3	7.4		73.8	6.15	7.6	
$\text{RuH}(\text{C}_6\text{H}_{11})(\text{C}_8\text{H}_8)(\text{PPh}_3)_2 \cdot 0.5\text{C}_7\text{H}_8$	Yellow	—	74.7	6.2			74.7	6.3		
$\text{Ru}(\text{C}_6\text{H}_{10})(\text{C}_8\text{H}_8)(\text{PPh}_3)_2$	Yellow	122	73.6	6.0	7.8		74.0	5.9	7.6	
$\text{RuH}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{10})(\text{PPh}_3)_2$	Creamy-white	109	72.8	6.0	8.0		73.2	6.1	7.9	
$\text{Ru}(\text{C}_6\text{H}_7)(\text{C}_6\text{H}_{11})(\text{PPh}_3)_2$	Yellow	115	72.8	6.15	7.7		73.2	6.1	7.9	
$\text{RuH}_4(\text{PPh}_3)_2$	Chocolate-brown	118-122	67.4	5.4	9.1		68.7	5.4	9.9	
$\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$	Pale yellow		71.1	5.5	9.0		71.5	5.4	8.8	

TABLE V

ANALYTICAL DATA

CHAPTER IV

SOME REACTIONS OF RUTHENIUM HYDRIDO COMPLEXES

WITH ACETYLENIC COMPOUNDS

Introduction

The reactions of transition metal complexes with acetylenic compounds have received much attention during the past twenty years.¹⁶⁵ Although the chemistry of ruthenium has developed considerably during this period, little work has been done on the reactions of ruthenium complexes with acetylenes. In particular, the reactions of ruthenium hydrido complexes with acetylenes have been limited to compounds containing cyclopentadienyl, carbonyl or nitrosyl ligands.^{24,25,29,47,48,163,164}

After the investigation of the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with olefins,⁷² and the work described in the third chapter of this thesis, it was of interest to study the reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with acetylenes. We have also investigated the reaction of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ with but-2-yne.

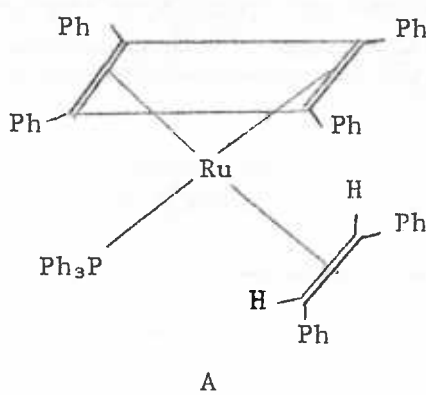
Results and Discussion

1) Reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with diphenylacetylene

$\text{RuH}_2(\text{PPh}_3)_4$ reacts rapidly in toluene with 3 or more equivalents of diphenylacetylene to give a deep red solution from which yellow crystals can be isolated. Analytical and mass spectroscopic studies on this complex are consistent with the composition $\text{Ru}(\text{H}_2)(\text{PhC}\equiv\text{CPh})_3(\text{PPh}_3)$. Infrared and ^1H n.m.r. spectroscopy clearly demonstrate the absence of hydride and $-\text{C}\equiv\text{C}-$ containing species. A broad band at δ 3.8 in the ^1H n.m.r. spectrum indicates the presence of olefinic protons. In the mass spectrum diphenylethylene and a diphenylacetylene dimer are found,

together with a diphenylacetylene dimer . triphenylphosphine adduct, diphenylacetylene and a small peak at m/e corresponding to $C_4Ph_4H_2$. This last peak could be, for example, 1,2,3,4-tetraphenylbutadiene but since the intensity of this peak is much lower than that of the diphenylacetylene dimer it is more likely that this peak comes from reactions in the mass spectrometer.

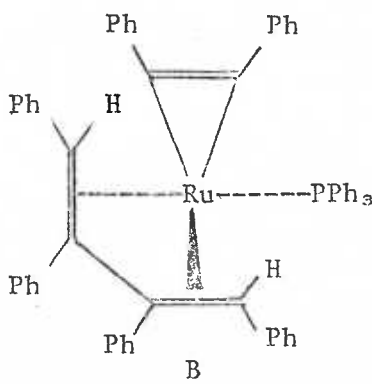
These data suggest the presence in the molecule of 1,2-diphenyl-ethylene and of 1,2,3,4-tetraphenylcyclobutadiene (Structure A).



The dimerisation of diphenylacetylene to give 1,2,3,4-tetraphenylcyclobutadiene coordinated to a metal atom is not unusual.¹⁶⁶

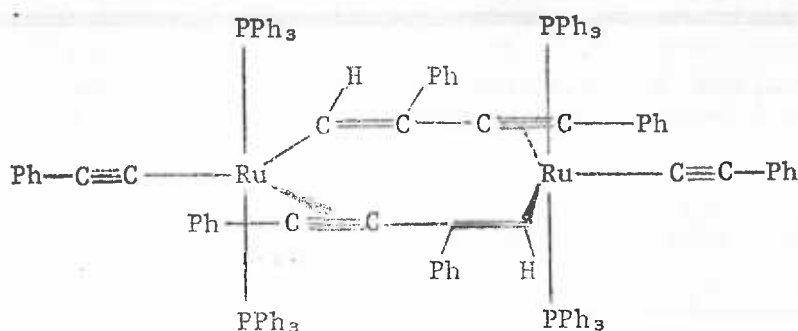
This compound would be a four coordinate sixteen electron ruthenium(0) complex in agreement with its very deep colouration in solution (see preceding chapter).

Another possibility is a five coordinate ruthenium(II) complex (Structure B).



2) Reactions of $\text{RuH}_2(\text{PPh}_3)_4$ with phenylacetylene

$\text{RuH}_2(\text{PPh}_3)_4$ reacts rapidly in toluene with 3 moles of phenylacetylene to give a deep green solution, from which green dichroic crystals can be isolated. Analytical and spectroscopic data are consistent with structure C. Evidence for a dimeric structure comes from mass spectroscopy. The monomer can be detected together with peaks at higher m/e which were identified as decomposition products of C.



C

The deep green colour of this complex is again in agreement with a sixteen electron system. A mechanism for the formation of this complex is proposed in Scheme 2. It is noteworthy that phenyl and diphenylacetylene react very differently, particularly that phenyl acetylene reacts as a weak acid, the first step of this reaction probably being similar to the formation of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ from $\text{RuH}_2(\text{PPh}_3)_4$ and H_2O .⁷²

If excess phenylacetylene is added and the mixture is allowed to react for longer periods of time or if the reaction is carried out under reflux, the solution turns brown and a brown powder can be isolated. This solid was shown to be a mixture of several species (mass spectrometry), but attempts to separate them by recrystallisation or chromatography were unsuccessful.

3) Reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with dimethylacetylene (but-2-yne)

$\text{RuH}_2(\text{PPh}_3)_4$ reacts with an excess of dimethylacetylene in toluene, the colour of the solution changing from yellow to pale yellow. Recrystallisation affords pale yellow crystals identified by infrared, ^1H n.m.r. and ^{31}P n.m.r. spectroscopy, and elemental analysis as $\text{Ru}(\text{butadiene})(\text{PPh}_3)_3$. This isomerisation of a triple bond to two double bonds is a rather unusual reaction. A plausible mechanism is proposed in Scheme 3; it is similar to the formation of this butadiene complex from 1-butene and $\text{RuH}_2(\text{PPh}_3)_4$.⁷²

4) Reaction of $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ with dimethylacetylene

$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ reacts with an excess of dimethylacetylene in diethyl ether to give an orange microcrystalline compound analysing for $[\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{H}_2\text{O})]_2 \cdot \text{H}_2\text{O}$, together with an unidentified yellow brown solution. The presence of an extra molecule of water of crystallisation comes probably from a side reaction in which $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ yields the yellow brown solution and liberates H_2O .

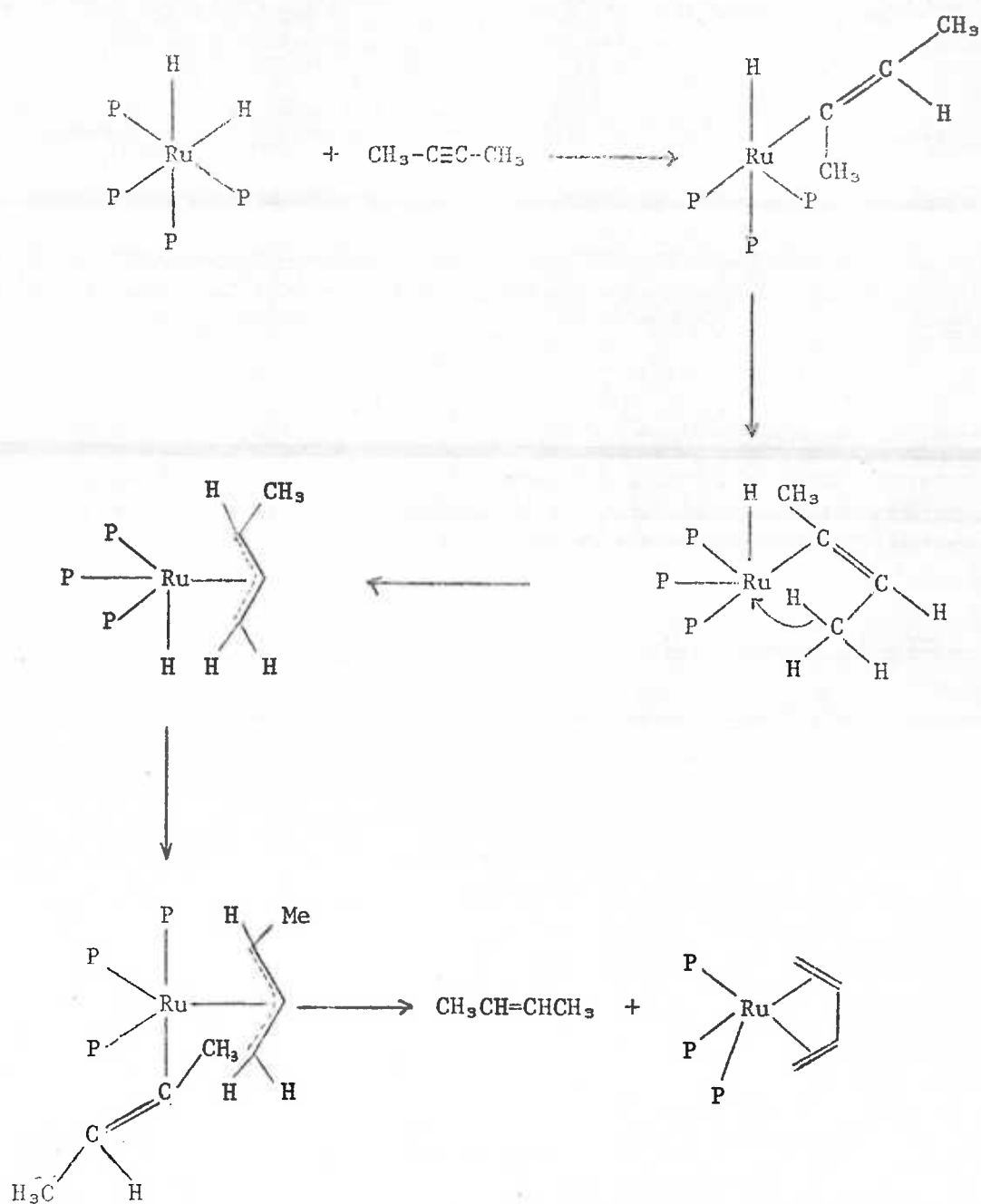
The hydroxo ortho-metallated complex was identified by spectroscopic methods (see later). A mechanism for its formation is proposed in Scheme 4. This reaction is similar to that of $\text{RuHCl}(\text{PPh}_3)_3$ and activated olefins in the absence of hydrogen in which hydrogenation of the olefin occurs with formation of a chloro ortho-metallated complex.

This compound can exist in four isomeric forms of which three were detected in the high field region (hydroxo resonances) of the ^1H n.m.r. spectrum.

5) Infrared spectroscopy (see Table)

All the compounds prepared show the characteristic absorptions of triphenylphosphine at ca. 500, 700, 750, 1080, 1570 and 1580 cm^{-1} .

In $\text{Ru}(\overbrace{\text{PhC}=\text{CPhCPh}=\text{CPh}})(\text{PhHC}=\text{CHPh})(\text{PPh}_3)$ no coordinated $\text{PhC}\equiv\text{CPh}$ was

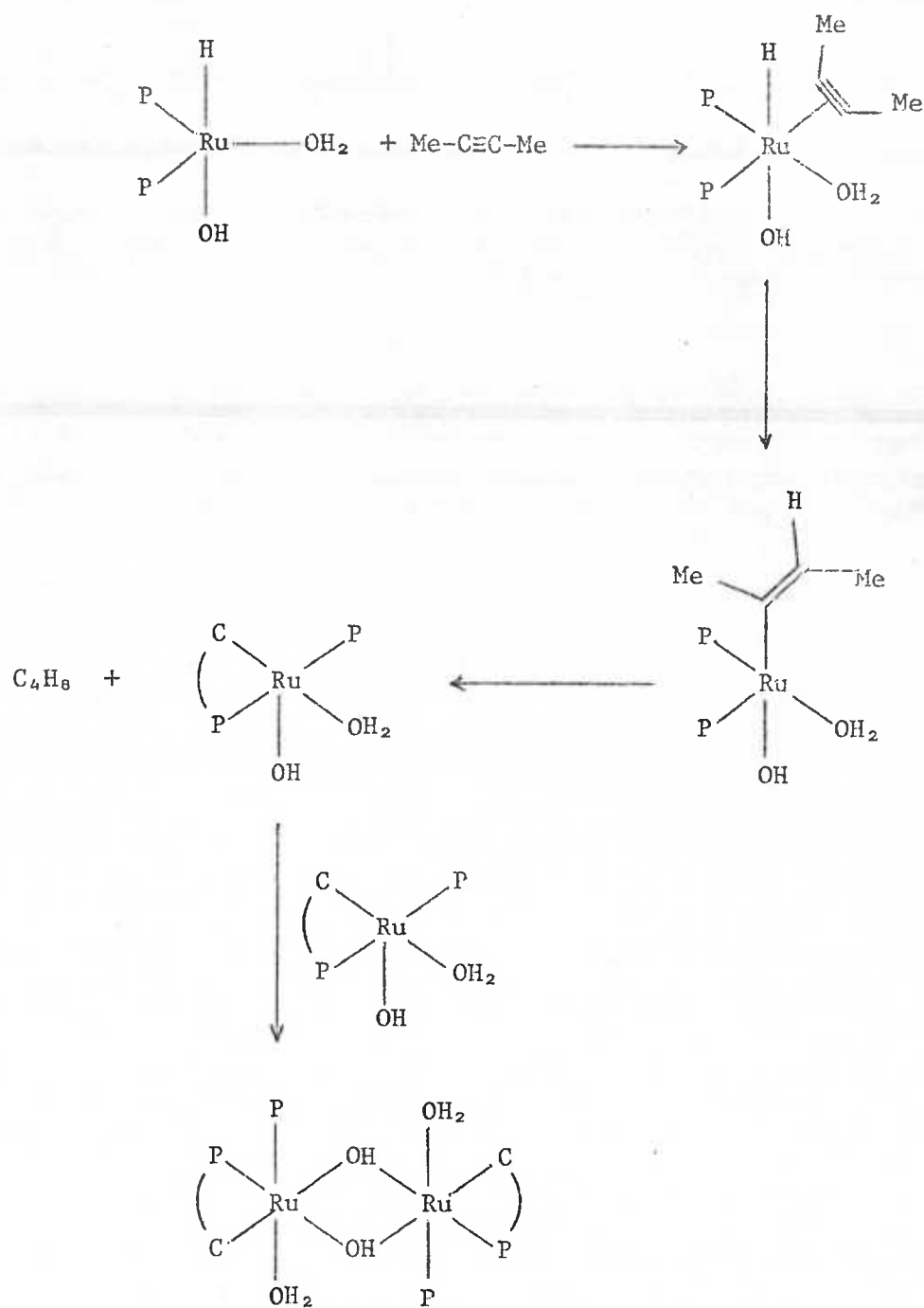


Scheme 3

Mechanism of formation of

$\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_2$ from $\text{RuH}_2(\text{PPh}_3)_4$ and

$\text{CH}_3\text{-C}\equiv\text{C-CH}_3$



Scheme 4

Formation of $(\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{H}_2\text{O}))_2$

from but-2-yne and $\text{RuH}_2(\text{PPh}_3)_4$

observed, in agreement with the proposed structure, $\text{C}\equiv\text{C}$ for coordinated Ph_2C_2 was expected near 1800 cm^{-1} (1776 cm^{-1} for $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})$).¹⁶³ All the ($-\text{C}\equiv\text{C}-$) stretching frequencies in $[\text{Ru}\{\text{(-CH=CPhC}\equiv\text{CPh)}\text{(-C}\equiv\text{CPh)}\text{-(PPh}_3)_2\}]_2$ were found at the same position (2045 cm^{-1}), whereas the carbon-carbon double bond stretching frequencies in the two complexes were at 1590 cm^{-1} .

Finally $[\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{H}_2\text{O})]_2\cdot\text{H}_2\text{O}$ shows ν_{OH} at 3600 cm^{-1} (like $\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$, see Chapter II of this thesis), and the characteristic absorptions of an ortho-disubstituted phenyl ring at 1550 and 1410 cm^{-1} (similar to other ortho-metallated ruthenium complexes).^{21,72}

6) N.M.R. Spectroscopy

All the compounds prepared show broad peaks between $\delta\ 6.5$ and $\delta\ 8$ due to the phenyl ring protons. $\text{Ru}(\text{PhC}=\text{CPhCPh}=\text{CPh})(\text{PhHC}=\text{CHPh})$ shows a broad peak at $\delta\ 3.8$ attributed to the two protons of the diphenyl-ethylene moiety.

$[\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{H}_2\text{O})]_2\cdot\text{H}_2\text{O}$ shows a peak attributed to the protons on the bridging hydroxo groups at $\delta\ -0.75$, and coordinated water at $\delta\ 1.8$. Two other small peaks are detected at $\delta\ -1.15$ and $\delta\ -1.7$ which are probably due to the presence of different isomers in solution.

Finally, the ^{31}P n.m.r. spectrum of $[\text{Ru}\{\text{(-CH=CPhC}\equiv\text{CPh)}\text{(-C}\equiv\text{CPh)}\text{(PPh}_3)_2\}]_2$ exhibits a singlet at 47.6 ppm , indicating two equivalent phosphorus atoms probably trans to one another because of the low chemical shift.³⁵

7) Mass Spectroscopy

The mass spectrum of $\text{Ru}(\text{PhC}=\text{CPhCPh}=\text{CPh})(\text{PhHC}=\text{CHPh})(\text{PPh}_3)_2$ shows the parent ion at $m/e\ 899$ ($\text{Ru}\ 102$), expected $m/e\ 900$ ($\text{Ru}\ 102$) and organic decomposition products at $m/e\ 440$: $\text{Ph}_3\text{P}-\text{CPh}=\text{CPhCPh}=\text{CPh}^+$; 356 : $\text{PhC}=\text{CPhCPh}=\text{CPh}^+$; 180 , $\text{PhHC}=\text{CHPh}^+$; 179 , $\text{PhHC}=\text{CPh}^+$;

178, $\text{PhC}\equiv\text{CPh}^+$ (these three peaks having approximately the same intensity) and a small peak at m/e 358 which could be $\text{PhHC}=\text{CPhCPh}=\text{CHPh}^+$.

The parent ion of $[\text{Ru}\mu(-\text{CH}=\text{CPhC}\equiv\text{CPh})(-\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]_2$ is not seen but the monomer is observed at m/e 929 (Ru 102), expected m/e 930 (Ru 102) and loss of $(-\text{C}\equiv\text{CPh})$ at m/e 828 (Ru 102) expects 829 (Ru 102). Peaks of higher m/e corresponding to compounds possessing two ruthenium atoms are also detected at m/e 1008, 1037 and 1136 (Ru 102).

Experimental

[See Chapters II and III for general conditions]

1) 1,2,3,4-tetraphenylcyclobutadiene diphenylethylene(triphenylphosphine)-ruthenium(0)

$\text{RuH}_2(\text{PPh}_3)_4$ (0.45 g, 0.39 mmole) was added to a solution of diphenyl acetylene (0.30 g, 1.68 mmole) in toluene (40 ml). The solution colour changed immediately to deep red, no other change in colour being observed with further stirring. After 2 hours the solution was evaporated to about 10 ml and petroleum was added. Filtering and cooling at -15°C afforded yellow crystals of the complex. Yield, ca. 75%. Significant infrared bands: 1500s, 1200w, 1180w, 810w, 790w, 765w, 760w, 750m, 730w, 720w, 705s, 695s, 610m, 592m, 565m, 550m, 530s, 510s, 500m, 450m.

2) bis{[μ (2,4-bisphenylbut-3-yne-1-enyl)](phenyl ethynyl)bis(triphenylphosphine)ruthenium(II)}

$\text{RuH}_2(\text{PPh}_3)_4$ (0.5 g, 0.43 mmole) was added to a solution of phenyl acetylene (0.279 g, 2.73 mmole) in toluene (45 ml). The colour changed immediately to deep green. After one hour the solution was evaporated to 10 ml, petroleum was added and the mixture cooled to -15°C . Deep

green crystals of the complex were obtained. Yield, ca. 50%.

Significant infrared bands: 2045m, 1590s, 1205w, 1185w, 1155w, 535s, 515s, 490w.

3) Reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with but-2-yne, new preparation of butadiene tris(triphenylphosphine)ruthenium(0)

$\text{RuH}_2(\text{PPh}_3)_4$ (0.5 g, 0.43 mmole) was added to a solution of but-2-yne (0.2 ml, 2.5 mmole) in toluene (40 ml). The solution was stirred for 15 hours during which time the colour became very pale yellow. After evaporation to 10 ml, petroleum was added. Cooling to -15°C gave pale yellow crystals of butadiene tris(triphenylphosphine)-ruthenium(0). Yield, ca. 40%.

4) μ, μ' -dihydroxobis(η^3 -2, diphenylphosphinophenyl)di(aquo)bis-(triphenylphosphine)diruthenium(II) water.

$\text{RuH}(\text{OH})(\text{PPh}_3)_2(\text{H}_2\text{O})$ (0.5 g, 0.76 mmole) was added to a solution of but-2-yne (0.2 g, 2.5 mmole) in diethyl ether (50 ml). The solution was stirred for 15 hours after which time the complex separated as orange microcrystals from a yellow brown solution. Yield, ca. 40%.

TABLE

Analytical and Infrared (cm^{-1}) Data for Some Ruthenium Complexes

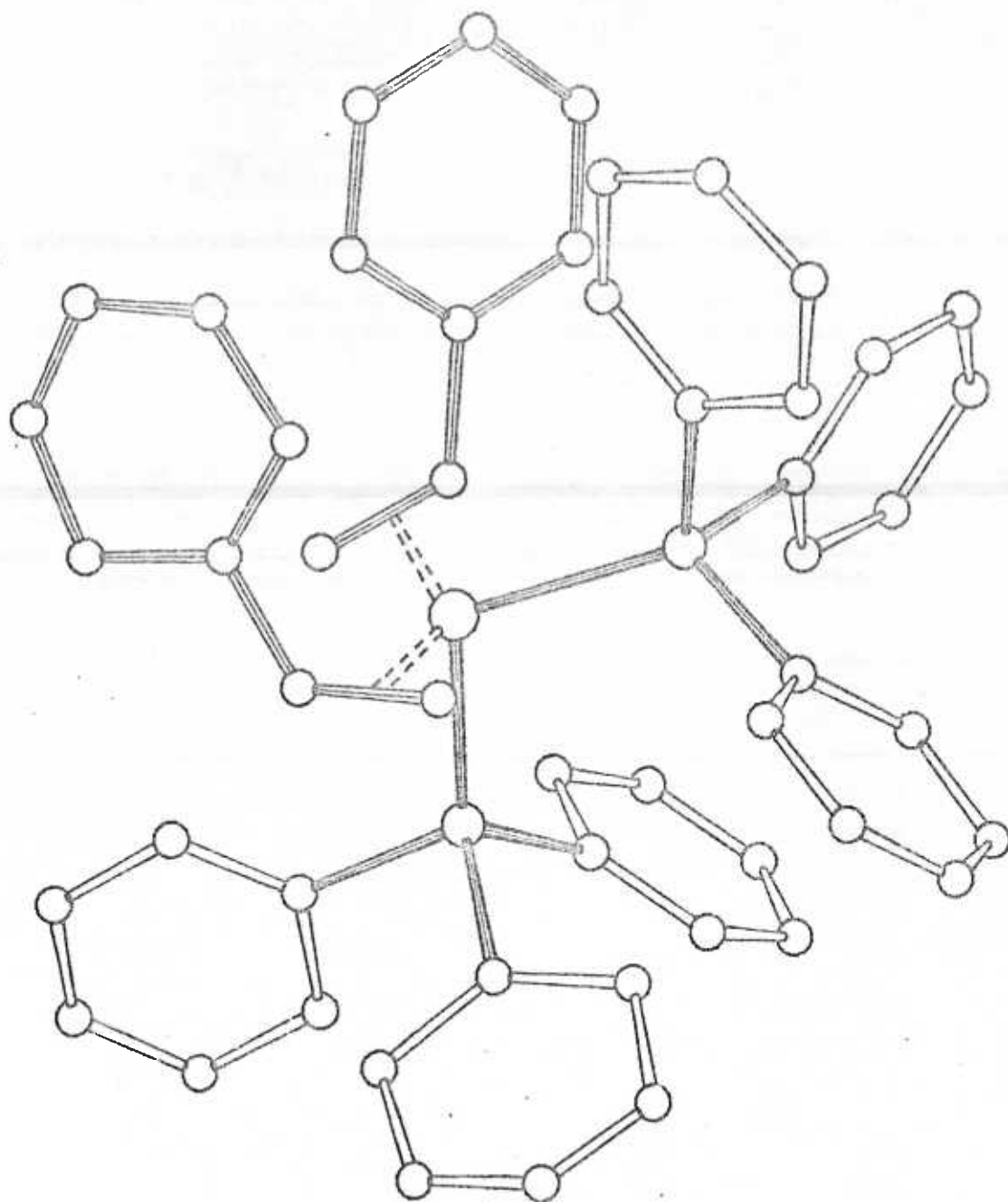
COMPLEX	COLOUR	ANALYTICAL						INFRARED			
		Found (%)			Required (%)			$\nu\text{C}\equiv\text{C}$	$\nu\text{C}=\text{C}$	νOH	Other
$\text{Ru}(\text{PhC}=\text{CPhCPH}=\text{CPh})(\text{PhHC}=\text{CHPh})(\text{PPh}_3)$	Yellow	80.3	5.3	4.2	80.1	5.2	3.5		1590s		
$[\text{Ru}\mu(-\text{CH}=\text{CPhC}\equiv\text{CPh})(-\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]_2$	Green	77.2	5.9	6.8	77.3	5.2	6.7	2045m	1590s		
$\text{Ru}(\text{C}_4\text{H}_6)(\text{PPh}_3)_3$	Yellow	74.2	6.1	8.9	74.0	5.4	9.9				
$[\text{Ru}(\text{OH})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{H}_2\text{O})]_2 \cdot \text{H}_2\text{O}$	Orange	64.1	5.0	8.5	64.7	4.9	9.3			3600m, sh	1550m, 1410m

APPENDIXTHE CRYSTAL STRUCTURE OF $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$

The crystal structure of $\text{Ru}(\text{C}_6\text{H}_5)_2(\text{PPh}_3)_2$ has been determined by Dr. M.A.A.F. De C.T. Carrondo and Dr. A.C. Skapski. The compound crystallises in the triclinic group. The space group is $\text{P}\bar{1}$, $Z = 4$. The molecule is a distorted tetrahedron with two molecules of styrene, coordinated through their olefinic carbon-carbon double bonds, and one molecule of triphenylphosphine being almost coplanar and the other molecule of triphenylphosphine being perpendicular to this plane (see diagram on following page).

Most important bond lengths and angles:

Ru-P (in plane of styrene C=C)	:	2.40 Å
Ru-P (perpendicular to plane of styrene C=C)	:	2.23 Å
P-Ru-P	:	107.9 Å
Mean of Ru-C	:	2.20 Å
Mean of C=C (olefinic double bond of coordinated styrene)	:	1.47 Å



Structure of $\text{Ru}(\text{C}_3\text{H}_5)_2(\text{PPh}_3)_2$

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