A STUDY OF THE INTERACTION

OF

SOME CATIONIC TRANSITION-METAL COMPOUNDS

WITH CARBON MONOXIDE AND NUCLEOPHILES

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ABSTRACT

A number of novel cationic carbonyl complexes of ruthenium and rhodium have been synthesised and characterised. The work also investigates the attack of nucleophiles on such species and examines the feasibility of these reactions as a possible first step in the catalytic production of organic esters. Mono and dipositive species of ruthenium have been effectively prepared by the reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$. The cationic species $[RuCl(CO)_2(PPh_3)_2][BF_4] . 1/2(CH_2Cl_2)$ and $[Ru(CO)_2(PPh_3)_2][BF_4]_2 . CH_2Cl_2$ have been prepared under nitrogen. The compound $[Ru(CO)_3(PPh_3)_2][BF_4]_2$ has been synthesised in the presence of CO. The compound, $[RuCl(CO)_2(PPh_3)_2][BF_4] . 1/2(CH_2Cl_2)$ reacts with CH_3O^- under CO to give $[RuCl(COOCH_3)(CO)_2(PPh_3)_2$. The compounds $[Ru(CO)_2(PPh_3)_2][BF_4]_2 . CH_2Cl_2$ and $[Ru(CO)_3(PPh_3)_2][BF_4]_2$ effectively form cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ by the reaction of CH_3ONa in the presence of CO at room temperature. This dialkoxycarbonyl compound preparation from the dipositive species are energetically more favourable than the cis-$[RuCl_2(CO)_2(PPh_3)_2]$, where the reaction takes place at CO high pressure. The compound $[Ru(CO)_2(PPh_3)_2][BF_4]_2 . CH_2Cl_2$ reacts with $NaBH_4$, NaI, conc. HCl and CH_3COONa to give the dihydrido, diiodo, dichloro and bisethanoato compounds respectively.

Cationic complexes of rhodium have been synthesised by the reaction of trans-$[RhCl(CO)(L)_2]$, (L = PPh_3, $AsPh_3$, PCy_3) with $AgBF_4$ in the absence and presence of CO to give $[Rh(CO)(L)_2][BF_4] . n\ CH_2Cl_2$ [where n = 1/2 or 3/2] and trans- $[Rh(CO)_2(L)_2][BF_4]$ respectively. These cations react with RONa (R = CH_3, C_2H_5) to give $[Rh(OR)(CO)(L)_2]$ and $[Rh(COOR)(CO)(L)_2]$, (R = CH_3, L = PPh_3, PCy_3). The alkoxycarbonyl compound, $[Rh(COOR)(CO)_2(L)_2]$ is formed by the reaction of sodium alkoxide in the presence of CO, (when R = CH_3, C_2H_5, C_3H_7, then L = PPh_3 and when R = CH_3 then L = $AsPh_3$). The alkoxo compound, $Rh(OCH_3)(CO)(L)_2$, (L = PPh_3) oxidatively adds CH_3I to give $[Rh(OCH_3)(CH_3)I(CO)(L)_2]$.

The cation $[Rh(CO)(L)_2]^+$, reacts with RCOONa to give the carboxylato compounds, trans-$[Rh(OOCR)(CO)(L)_2]$, when L = PPh_3 then R = CH_3, C_2H_5, when L = $AsPh_3$ then R = H, CH_3, C_2H_5 and when L = PCy_3 then R = CH_3. The compound $[Rh(CO)_2(SbPh_3)_3][BF_4] . CH_2Cl_2$ has been formed from $[RhCl(CO)(SbPh_3)_2]$ with $AgBF_4$ in the presence of CO. The cation $[Ru(CO)_2(PPh_3)_2]^{2+}$ reacts with CH_3O^- in the presence of CO (10 atmospheres) to give $[Ru(CO)_3(PPh_3)_2]$ and a trace amount of dimethylcarbonate. The same compound is obtained by using triethylamine in methanol under CO (10 atmospheres) at 65-70°C. Dimethylcarbonate rapidly reacts with CH_3ONa in contact with air to form a white precipitate, suggested to be Na_2CO_3. Homogeneous solutions of $[RuCl_2(CO)_2(PPh_3)_2]$, $[Ru(CO)_2(PPh_3)_2]^{2+}$ and $[Rh(CO)(PPh_3)_2]^+$ in dichloromethane produce benzene in the presence of CH_3ONa in air. The cationic complexes of rhodium $[Rh(CO)(L)_2]^+$, where L = PPh_3, $AsPh_3$, PCy_3 and ruthenium complex $[RuCl(CO)_2(PPh_3)_2]^+$ are effective catalysts for the hydrogenation of alkenes under hydrogen at atmospheric pressure and ambient temperature.

The compounds have been characterised by analysis, infrared, ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR spectroscopy and the organic products have been characterised by gas chromatography and in one case, GC/MS.

CONTENTS

ABBREVIATIONS

α	alpha
Å	angstrom unit (10^{-10} metre)
Ar	Aryl
ν_{asy}	asymmetric stretch
atm	atmosphere
β	beta
ca	approximately
cm^3	centimetre cubed
Cy	cyclohexyl, C_6H_{11}
dm^3	decimetre cubed
^oC	degree centigrade
^oK	degree Kelvin
DMA	dimethylacetamide
DMF	N, N' -dimethylformamide
DMSO	dimethyl sulphoxide
dien	diethylenetriamine $[H_2N(CH_2CH_2NH)_2H]$
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Eq	equation
e/au^3	electron per atomic unit cubed
η	eta
ft	feet
Fig	figure
e.g.	for example
ν	frequency (or Hertz)

GC/MS gas chromatography / mass spectrum (spectrometry)

GLC gas liquid chromatography

g gramme

Hz hertz, (S^{-1})

IR infrared (for infrared spectra, b = broad, m = medium and s = strong)

IUPAC International Union of Pure and Applied Chemistry

KNM^{-2} killonewton per metre squared

m metre

mm millimetre

mmol millimole

m/z mass to charge ratio

μ mu

mV millivolts

NMR Nuclear Magnetic Resonance (for NMR s = singlet, d = doublet, t = triplet, q = quartet amd m = multiplet)

S_N1 Nucleophilic Substitution reaction where reaction rate depends upon the concentration of only one reactant

S_N2 Nucleophilic Substitution reaction where reaction rate depends upon the concentration of both reactants

OC Octahedral

Oxid-Add Oxidative Addition

ppm parts per million

Ph phenyl, C_6H_5

Π pi

Py pyridine

Red-Elim Reductive Elimination

Ref.	references
Sec.	section
σ	sigma
σ^*	sigma star (sigma antibonding orbital)
SP	square planar
STP	Standard Temperature and Pressure
ν_{sy}	symmetric stretch
THF	tetrahydrofuran
TMP	tetramethylphosphate
TMS	tetramethylsilane
TBPY	trigonal bipyramidal
vs	versus
vol	volume
cm^{-1}	wave number (per centimetre)

CHAPTER-1

GENERAL INTRODUCTION

1.1 AIMS AND OBJECTIVES.

Many important industrial processes involve the interaction of carbon monoxide (CO) with other species on transition metal centres, e.g. the Fischer-Tropsch synthesis[1] and hydroformylation reactions[2]. Carbon monoxide, either alone or in conjunction with one of its simple derivatives (e.g. formaldehyde), can serve as the unique source of carbon in the synthesis of oxygenated compounds (e.g. oxalates, glycolic acid, glycol aldehyde, ethylene glycol and glycerine). Many of these syntheses have been carried out on a laboratory scale, though some have been taken to the pilot plant stage and others exploited industrially[3].

The interaction of bonded CO with strong nucleophiles gives alkoxycarbonyl and carbamoyl compounds and such species have been implicated in many CO based syntheses of organic compounds[3] e.g.

(i) alkoxycarbonyl compounds undergo many reactions characteristic of organic esters,

(ii) alkoxycarbonyls are probable intermediates in the oxidative alkoxycarbonylation of alkenes,

(iii) alkoxycarbonyls have been implicated as possible intermediates in the formation of formates, carbonates and oxalates.

The aim of this work is to investigate the attack of nucleophiles on carbonyl groups attached to transition metal centres as a possible first step in the catalytic production of the industrially important class of organic compounds known as glycol esters. The glycol esters are produced from oxalic acid esters by hydrogenation. Oxalic acid esters are key

organic compounds used in a wide variety of different processes. They are possible precursors to ethylene glycol (widely used as an anti-freeze), are important in the production of some classes of polymers, are used as solvents in industrial extraction processes and are used in a wide variety of other industrial processes. At present the main route to this class of compounds is via oxidation of scarce organic feedstocks[4]. In the literature it is reported that the interaction of neutral metal species with nucleophiles in the presence of CO has been examined to investigate the synthesis of glycol esters. The product is usually a species which contains both carbon monoxide and alkoxycarbonyl bonded to the metal and no catalysis is exhibited[5-7].

(1) In order to faciliate the attack of the nucleophile on the second CO, the first phase of the present project was to synthesise some cationic complexes, by the reaction of silver tetrafluoroborate ($AgBF_4$) with ruthenium and rhodium chloro species at ambient temperature in the presence and absence of carbon monoxide.

(2) The second phase of the project was to examine the interaction of these cationic compounds with nucleophiles (e.g. CH_3O^-, $C_2H_5O^-$, CH_3COO^-) in the presence and absence of carbon monoxide at ambient and elevated temperature.

(3) The third phase of this work was to investigate by gas chromatography (in one case by GC/MS) the presence of any organic product produced from the reaction of cationic complexes with the nucleophile (CH_3O^-) under carbon monoxide at normal and elevated pressures (up to 10 atmospheres) and at various temperatures. This work also investigated any catalytic effect of the cationic complexes with

respect to hydrogenation of alkenes with hydrogen at atmospheric pressure. The organic products were analysed by gas chromatography.

1.2 METAL CARBONYLS AND RELATED BACKGROUND.

(I) Bonding in Metal Carbonyls.

An understanding of the bonding in metal carbonyls is useful, not only for the study of reactions and structures of metal carbonyls, but also for that of the organo derivatives. Infrared spectroscopy can be used to provide a great amount of information about the molecular structure and bonding of metal carbonyl complexes as well as their organo derivatives[8]. The bonding in metal carbonyls is best described by molecular orbital theory[2].

(1) There is first, a dative overlap of a filled carbon σ orbital with an empty metal σ orbital as in Fig. 1a. Electron flow C→ M in such a dative overlap, would lead to an unacceptable concentration of electron density on the metal atom when the latter is not a +2 or more highly charged ion. The metal therefore attempts to reduce this charge (Pauling's Electroneutrality Principle) by pushing electrons back to the ligand. This, of course, is possible only if the ligand has suitable acceptor orbitals.

(2) A second, dative overlap of a filled dΠ or hybrid dpΠ metal orbital with an empty antibonding pΠ orbital of carbon monoxide can reduce electron density on the metal as in Fig. 1b.

This bonding mechanism is synergic, since the drift of metal electrons into CO orbitals, referred to as "back bonding", will tend to make the CO as a whole negative. Hence its basicity is increased via the σ orbital of carbon. Also the drift of electrons to the metal in the

σ bond tends to make the CO positive, thus enhancing the acceptor strength of the orbitals. Thus, the effects of σ-bond formation strengthen the Π bonding and vice versa. As the extent of back donation from M to CO increases, the M—C bond becomes stronger and the C≡O bond becomes weaker. Thus, the multiple bonding should be evidenced by shorter M—C and longer C—O bonds as compared with M—C single bonds and C≡O triple bonds, respectively.

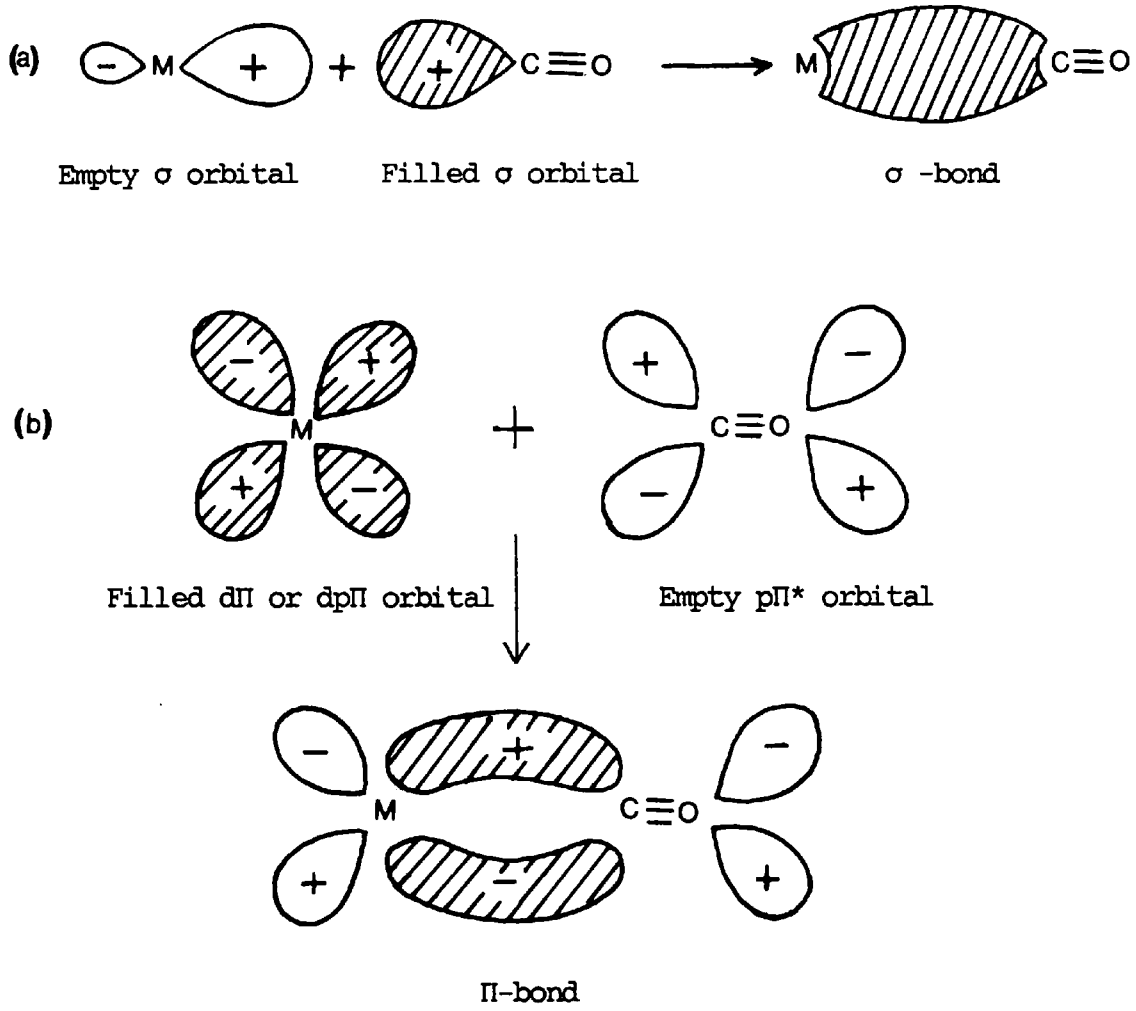


Fig. 1 : (a) The formation of the metal ⟵ carbonyl σ bond using an unshared pair on the C atom. (b) The formation of the metal⟶ carbon Π bond. The other orbitals on the CO are omitted for clarity.

Evidence for the back bonding model in the metal carbonyl described in Fig. 1 could be obtained from infrared spectroscopy which shows a reduction in stretching frequency of the carbonyl bond upon coordination with a metal, as well as a variation in stretching frequency with metal oxidation state[8], as in Table 1. The stretching frequency of free CO is at 2140 cm^{-1}, whereas it is only 2000 cm^{-1} in $Cr(CO)_6$. Back bonding populates the antibonding CO orbital, for this reason the CO stretching frequency increases in the isoelectronic series $[V(CO)_6]^-$ < $Cr(CO)_6$ < $[Mn(CO)_6]^+$, while the M—C stretching frequency decreases. This is due to the fact that a positive charge inhibits the shift of electron from metal to CO antibonding orbitals. A negative charge, in contrast, enhances the back donation.

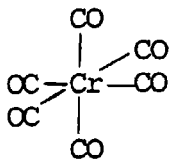
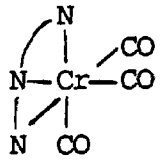
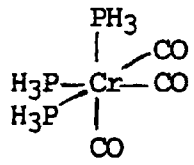
Table 1 : Infrared Results for the Isoelectronic Series[8] $[V(CO)_6]^-$, $[Cr(CO)_6]$, $[Mn(CO)_6]^+$.

Bond	Stretching frequencies in cm^{-1}		
	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$
M—C	460	441	416
C—O	1859	1981	2101

The bond length in CO itself is 1.13 Å, while the bond lengths in metal carbonyl molecules are around 1.15 Å, a shift in the expected direction but of little quantitative significance owing to its small magnitude and the uncertainties (± 0.02 Å) in the individual distances. The shortening of M—C distances as in Table 2 due to the Π-back bonding can be demonstrated by replacing the three or four CO groups from $Cr(CO)_6$ by

ligands such as aliphatic amines, which have no capacity to compete with CO trans to them for Π bonding, or the PH_3 ligand, which has very little capacity to do so. It is seen that in such cases that the remaining CO groups have shorter Cr—C bonds because of even more extensive development of Cr—C Π-back bonding.

Table 2 :

Compound	M—C	Ref.
	1.91 Å	9
	1.82 Å	10
	1.84 Å	9

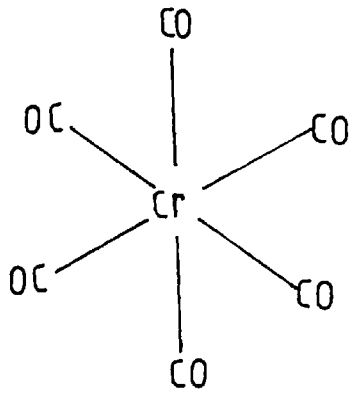
Where N-N-N = $[H_2N(CH_2)_2NH(CH_2)NH_2]$.

(II) Metal Carbonyls and Structural Diagnosis by Infrared Spectroscopy[2, 11, 12].

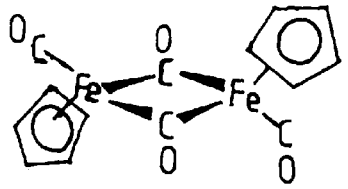
The infrared spectra of metal carbonyls have therefore proved to be a rich and convenient source of information concerning both structure and bonding. Indeed, it is such a powerful tool that it deserves more detailed comment for those wishing to do more extensive work in complex compounds and organometallic chemistry. Perhaps the most day to day use of infrared spectra in the inorganic research laboratory is in deducing the structures of molecules containing carbonyl groups. This may be done in a number of ways.

(i) Detection of Terminal and Bridging Carbonyl Groups.

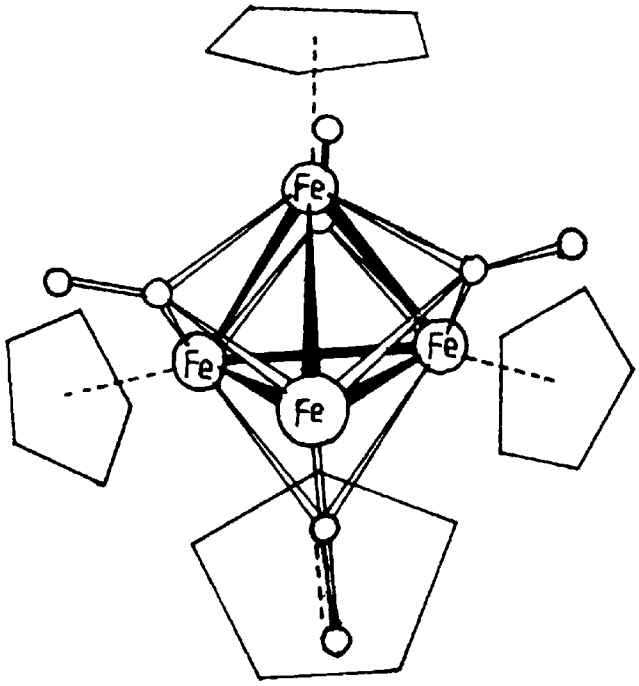
The stretching frequencies of terminal carbonyls generally lie in the region from 2140 to 1800 cm^{-1}, while bridging carbonyl ligands have lower frequencies. For a carbonyl group bridging two metals, the stretching frequencies[13] have been found in the region from 1700 to 1850 cm^{-1}, whereas a carbonyl bridging three metal atoms may have a frequency[14] as low as about 1620 cm^{-1}. Examples[8] are shown in Fig. 2. In using the positions of CO stretching bands to infer the presence of bridging CO groups, it is necessary to keep certain conditions in mind. The frequencies of terminal CO stretching can be quite low if (a) there are a number of ligands present that are good donors but poor Π-acceptors, or (b) there is a net negative charge on the molecule[2]. In either case, back donation to the CO groups becomes very extensive, thus increasing the M—C bond orders, decreasing the C═O bond order, and



ν(CO)=2000 cm^{-1}



ν(CO) bridge=1781 cm^{-1}



ν(CO)=1620 cm^{-1} in $[Fe_4(\eta^5-C_5H_5)_4(CO)_4]$

Fig. 2

driving the CO stretching frequencies down. Thus in the $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ ion one of the ν(CO) is as low as 1739 cm^{-1}.

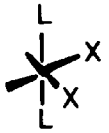
(ii) **Determination of Molecular Symmetry from the Number of Carbonyl Bands**[2,8].

It is often possible to infer the symmetry of the arrangement of the carbonyl groups from the number of carbonyl stretching bands that are found in the infrared spectrum. The number and intensity of the bands depend largely on the local symmetry about the metal to which the carbonyls are attached. The symmetry of the other ligands and their influence on the true molecular symmetry is usually not important. For example, group theory predicts that a complex such as cis-$[MX_2L_2(CO)_2]$ (which has C_{2v} symmetry if the ligands are treated as point groups) will have two (a_1+b_2) infrared active carbonyl stretching vibrations. Another consequence of group theory is that the more symmetric the molecule, the fewer the number of distinct bands expected. Therefore, trans-$[MX_2L_2(CO)_2]$, which has D_{2h} symmetry (more symmetry elements are present in this point group than in C_{2v}) has only one (b_{1u}) infrared active band compared with two for the cis compound. The numbers of bands expected for some common geometries are summarised in Table 3.

(III) Bonding in Π-Acid Ligands : Trivalent Phosphorus Compounds[2].

Phosphorus compounds of the type PX_3 (as well as AsX_3, SbX_3) especially when X is relatively electronegative, such as Ph, OR, Cl or F are important Π-bonding ligands. Thus PF_3 forms many compounds[16] comparable

Table 3 : Number and Type of Infrared Stretching Frequencies Expected from Common Metal Carbonyl Compounds[8].

Molecule		Point Group	Number of ν(CO) Expected	Symmetry of ν(CO) Bands
$[M(CO)_5L]$		C_{4v}	3	$2a_1 + e$
	cis-$[M(CO)_4L_2]$	C_{2v}	4	$2a_1 + b_1 + b_2$
trans-$[M(CO)_4L_2]$		D_{4h}	1	e_u
	cis-$[M(CO)_3L_3]$	C_{3v}	2	$a_1 + e$
trans-$[M(CO)_3L_3]$		C_{2v}	3	$2a_1 + b_2$
	cis-$[M(CO)_2L_2X_2]$	C_{2v}	2	$a_1 + b_2$
trans-$[M(CO)_2L_2X_2]$		D_{2h}	1	b_{1u}
	$[M(CO)_4L]$	C_{3v}	3	$2a_1 + e$
$[M((CO)_4L]$		C_{2v}	4	$2a_1 + b_1 + b_2$
	$[M(CO)_3L_2]$	D_{3h}	1	e'
$[M(CO)_3L_2]$		C_s	3	$2a' + a''$

with those of CO, for example, $[Ni(PF_3)_4]$ and $[Cr(PF_3)_6]$. Tertiary phosphines are also much better Lewis bases than CO and can form many compounds where Π acidity plays little or no role. This is observed with the phosphine compounds of the early transition metals and with metal atoms in their higher oxidation states. In the compound $[PtCl_4\{P(CH_3)Ph_2\}_2]$ the M—P bonds show no evidence of significant Π bonding[17]. The M to P dative bonding is a generally acknowledged fact, the explanation for it entails controversy. The classical and still widely credited picture is that shown in Fig. 3, in which phosphorus specifically employs a pair of its d orbitals to accept metal electrons.

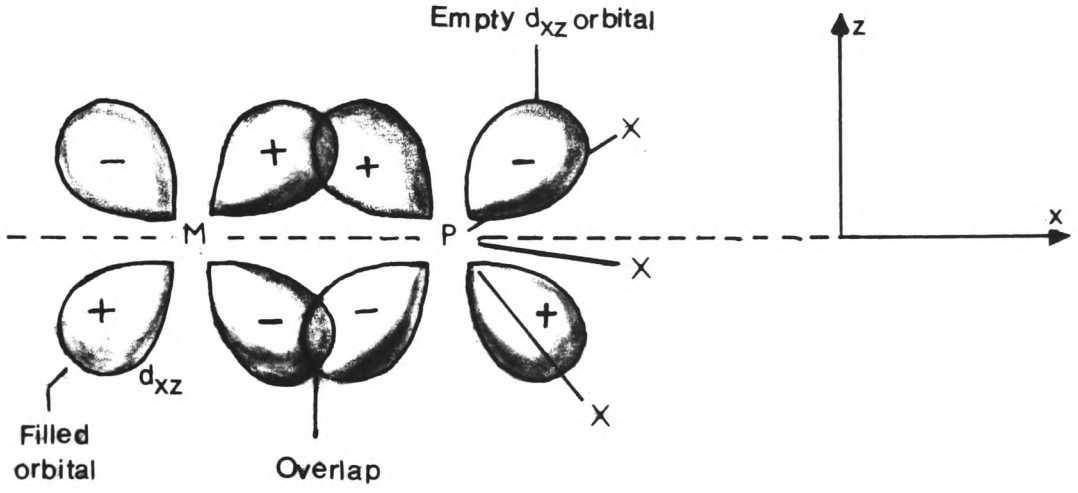


Fig. 3 : The back-bonding from a filled metal d orbital to an empty phosphorus 3d orbital in the PX_3 ligand taking the internuclear axis as the x axis. An exactly similar overlap occurs in the xy plane using the d_{xy} orbitals[2].

Recently, it has been proposed[18,19] on the basis of quantum mechanical calculations that phosphorus p orbitals and the P—X σ^* orbitals may play a major role in accepting metal dΠ electrons, the phosphorus dΠ orbitals are not necessary as seen in Fig. 4.

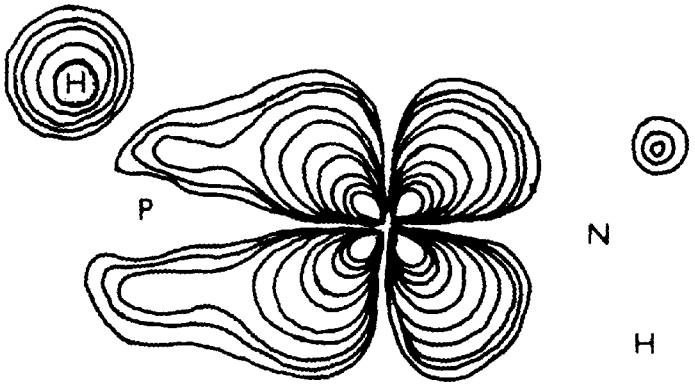


Fig. 4 : Electron density plot of one of the two Π-donating d orbitals in $[Cr(NH_3)_5(PH_3)]$ without using d orbitals on phosphorus. The contour[18] levels on the metal are 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.0035, and 0.002 e/au^3.

The extent of donation both from the lone pair on the P atom and back donation depends on the nature of the groups attached to P. For PH_3 and $P(alkyl)_3$, Π-acceptor ability is very low, but it becomes important with more electronegative groups. Analogous PX_3, AsX_3, SbX_3 compounds differ very little, but ligands having a nitrogen atom, which lacks Π orbitals, cause significantly lower frequencies for the CO vibrations, as indicated by the CO stretching frequencies in cm^{-1} in a series of compounds in Table 4.

Table 4 :

Compound	ν(CO) cm^{-1}
$[(PCl_3)_3Mo(CO)_3]$	2040, 1991
$[(AsCl_3)_3Mo(CO)_3]$	2031, 1992
$[(SbCl_3)_3Mo(CO)_3]$	2045, 1991
$[(dien)Mo(CO)_3]$	1898, 1758

The more electronegative group attached to the phosphorus the higher the ν(CO) frequencies in cm^{-1}. This can be seen from the series in Table 5. The more electronegative group will reduce the σ-donor character, so that there will be less P to M electron transfer and MdΠ to PdΠ transfer should be aided. Therefore, PX_3 and CO are quite comparable in their Π-bonding capacity.

Table 5 :

Compound	ν(CO) cm^{-1}
$[\{P(C_2H_5)_3\}_3Mo(CO)_3]$	1937, 1841
$[\{P(OPh)_3\}_3Mo(CO)_3]$	1994, 1922
$[\{PCl_2(OC_2H_5)\}_3Mo(CO)_3]$	2027, 1969
$[(PCl_3)_3Mo(CO)_3]$	2040, 1991
$[(PF_3)_3Mo(CO)_3]$	2090, 2055

The Π-accepting capacities of the phosphorus ligands are in the following order (As and Sb ligands come very close to their corresponding P ligands) :

$PF_3 > PCl_3 > P(OAr)_3 > P(OR)_3 > P(Ar)_3 > PR(Ar)_2 > PR_2(Ar) > PR_3$.

Generally the σ-donor ability decreases as P > As > Sb. The steric effects due to the donor atoms itself will increase in the order P < As < Sb, while steric effects[2] of the substituents on the ligand atom will be in the order P > As > Sb.

(IV) NMR Spectroscopy of Complex Compounds.

Characterisation of complex compounds relies heavily on NMR spectroscopy[20]. It is important to bear in mind that metal complexes can be paramagnetic, leading to large shifts and broadening in the NMR resonance. However, ^{1}H-NMR spectroscopy is an important technique for characterisation of complex compounds and organometallic compounds.

^{1}H-NMR spectroscopy is useful to distinguish between coordinated organic ligands and non-coordinated organic ligands. When an organic ligand is coordinated its electron environment changes, i.e. its electron density changes and a different chemical shift is obtained. For example, the methyl protons[21] of CH_3COOCH_3 show a signal at 3.70 ppm but the methyl protons of the complexes[6,22] $[Pt(COOCH_3)_2(dppe)]$ and $[Pt(COOCH_3)_2(PPh_3)_2]$ show shifts at 3.21 ppm and 2.50 ppm respectively. Similarly, the methyl protons of ethanoic acid shows a singlet at 2.10 ppm but on coordination[23] to metal as in $[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$, the methyl protons shows a signal at 1.11 ppm. Thus ^{1}H-NMR is useful to distinguish between coordinated and uncoordinated organic ligands.

In addition, ^{31}P-NMR spectroscopy[24,25] is very useful in the study of phosphine complexes. Like ^{1}H, ^{31}P is a NMR active nucleus, with a spin quantum number I = 1/2. Normally all the ligand protons are decoupled so as to simplify the ^{31}P-NMR spectra (an exception is made, when there is a need to determine the number of hydrides present in a phosphine hydride compound). It is a useful method to distinguish free phosphine from coordinated phosphine. Due to the coordination of the ligand, the difference between the chemical shift of coordinated and free phosphine is very large. For example, the ^{31}P-NMR shift for free PPh_3 is -6.00 ppm and when it is coordinated as in the compound[26] $[RuCl_2(CO)_2(PPh_3)_2]$, the shift is at +17.40 ppm (where phosphorus are trans, carbonyls and chlorides are cis in position) or in the compound[27] $[RuCl_2(PPh_3)_3]$ the shift is at +40.90 ppm at room temperature. The ^{31}P-NMR shifts for the compound[28,29] $[RhCl(PPh_3)_3]$ are at +31.50 and +48.00 ppm and for the compound[28] trans-$[RhCl(CO)(PPh_3)_2]$ the shift is at +29.10 ppm. Generally coordination to a transition metal results in a shift to lower field[30]

but some exceptions are observed, e.g. in PCl_3 compounds of nickel carbonyls the ^{31}P-NMR shifts are upfield[30]. In the proton decoupling technique, sometimes the phosphorus nuclei are coupled to the central metal atom, e.g. phosphine compounds of ^{103}Rh (100% natural abundance) and ^{195}Pt metals are coupled by the metals, because their spin is 1/2. However, ^{101}Ru metal is non-coupled and has a spin of 5/2, it has a much larger quadrupole moment[31] than its less abundant isotope ^{99}Ru.

1.3 REACTIVITY OF METAL CARBONYLS[2,20].

The reactivity of metal carbonyls depends upon the polarisation of the CO on bonding, and so changes as the coligands and net charge change. The reactions of the metal carbonyls are promoted by the electrophilicity of the CO carbon (nucleophilic attack on carbon) and the nucleophilicity at CO oxygen (electrophilic attack at oxygen).

(I) Nucleophilic Attack on Carbonyl Carbon.

Nucleophiles are neutral or negative species (e.g. NH_3, CH_3^-, OH^-, F^-, Cl^-, Br^-), they are attacked by a positive centre. Nucleophilicity is roughly in order of basicity, though basicity is thermodynamically controlled and nucleophilicity is kinetically controlled. Simple nucleophilic substitution reactions in organic chemistry follow two mechanisms, S_N1 and S_N2. A carbonyl carbon is more likely to be attacked by a nucleophile than a saturated carbon, because carbonyl carbon is a much harder acid than a saturated carbon. The following nucleophilicity

order for these substrates has been reported[32]. $(CH_3)_2C{=}NO^-$ > $C_2H_5O^-$ > CH_3O^- > OH^- > PhO^- > N_3^- > F^- > H_2O > Br^- > I^-.

Nucleophilic attack on the carbonyl carbon in transition metal carbonyl complexes is rather common[33]. The carbonyl carbon acquires an electrophilic character upon coordination to transition metals. The cationic metal carbonyl complexes, $[M{-}CO]^+$ faciliate the nucleophilic attack on carbonyl carbon.

(i) **Hydride Attack (H^-)** : The interaction of H_2 and CO to give organic products is of very great importance, and catalytic reactions probably involve attack of H^- on coordinated[2] CO as in Eq. 1.

$$Fe(CO)_5 + H^- \longrightarrow \left[(CO)_4Fe{-}C(=O)H\right]^- \qquad \text{[Eq. 1]}$$

The attack of the hydride ion (from $NaBH_4$ in THF) on carbonyls can give formyls, hydroxymethyls or finally methyls[2] as in Eq. 2.

$$M{-}CO \longrightarrow M{-}CHO \longrightarrow M{-}CH_2OH \longrightarrow M{-}CH_3 \qquad \text{[Eq. 2]}$$

(ii) **Hydroxide Ion (OH^-)** : The attack of OH^- on metal carbonyl complexes gives hydroxycarbonyl species[34], e.g. $[IrCl_2(COOH)(CO)\{P(CH_3)_2Ph\}_2]$, which have been shown to decompose giving CO_2 and the metal hydride. These hydroxycarbonyl adducts are, in general, readily attacked by acids to regenerate the M—CO compound[35], but some of these species can also react with base with proton loss[35] to give $M{-}CO_2^-$. $[Fe(COOH)(CO)(PPh_3)(\eta^5{-}C_5H_5)]$ reacts[35] with acid and with the base KOH

to give $[Fe(CO)_2(PPh_3)(\eta^5\text{—}C_5H_5)]^+$ and $K^+[Fe(CO_2)(CO)(PPh_3)(\eta^5\text{—}C_5H_5)]^-$ respectively.

(iii) **Ammonia, Amines** : Attack of ammonia or amines on cationic carbonyls leads to carbamoyl or carboxamido complexes[36] as in Eq. 3.

$$[L_nM\text{—}CO]^+ + 2NHRR' \rightleftharpoons L_nM\text{—}C(=O)(NRR') + [NH_2RR']^+ \qquad \text{[Eq. 3]}$$

The detailed discussion of carbamoyl complexes is given in [Sec. 1.3(IV)].

(iv) **Lithium Alkyls** : Metal carbonyls interact with lithium alkyls to give anionic complexes. The acyl tetracarbonyl ferrates obtained from reacting $[Fe(CO)_5]$ with lithium alkyl as in Eq. 4 are particularly useful as reagents in organic synthesis[37].

$$[Fe(CO)_5] + LiR = Li^+\left[(CO)_4Fe\text{—}C(=O)(R)\right]^- \qquad \text{[Eq. 4]}$$

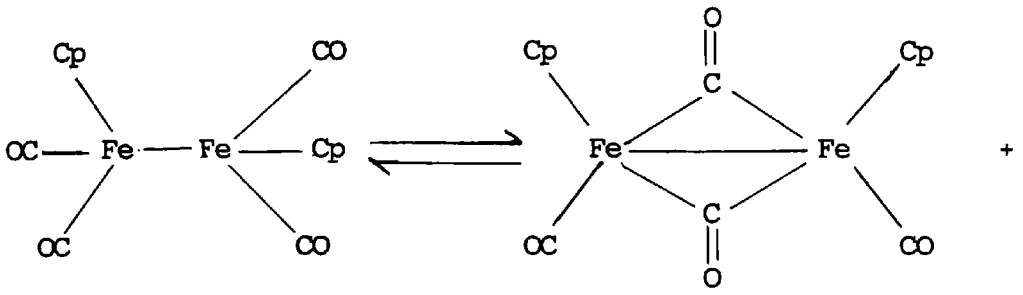
where R = alkyl group.

(v) **Alkoxide Ions (RO^-)** : Alkoxide ions attack coordinated CO to form alkoxycarbonyl complexes. The metal pentacarbonyl reacts with the methoxide ion[2] as in Eq. 5. Alkoxycarbonyl compounds have been discussed in detail in Sec. 1.3(IV).

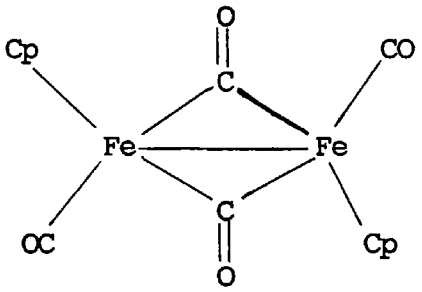
$$[M(CO)_5] + CH_3O^- = [M(CO)_4(COOCH_3)]^- \qquad \text{[Eq. 5]}$$

where M = Fe, Ru and Os.

(vi) A Second Metal can Effect Attack at the CO Carbon : A second metal can attack at the carbonyl carbon as a nucleophile [20] as in Eq. 6.



cis



trans

[Eq. 6]

where Cp = η^5–C_5H_5

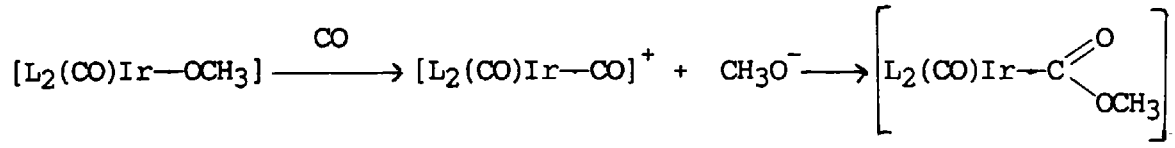
(vii) Nucleophilic Substitution Reactions : A weak nucleophile is substituted by a strong nucleophile and the attack is directly at the metal atom as seen in Eq. 7.

$$[PtCl_2(dppe)] \xrightarrow[C_6H_6,\ CH_3OH]{CH_3ONa} [Pt(OCH_3)_2(dppe)] \qquad \text{[Eq. 7]}$$

$$[Pt(OCH_3)_2(dppe)] \xrightarrow{CO} [Pt(COOCH_3)_2(dppe)] \qquad \text{[Eq. 8]}$$

Here, in Eq. 8, the CO insertion take place between the Pt—OCH_3 bond[6]

in the presence of CO. Sometimes the insertion can go by an entirely different route[20] as seen in Eq. 9. The transition metal alkoxide is unstable (CH_3O being a good Π donor) and the CH_3O group dissociates as CH_3O^- to leave a vacant site at the cationic metal. The CO present, then binds to this site, and is strongly activated by the positive charge on the metal towards nucleophilic attack at the CO carbon. The product is the metal-ester[38] compound as shown in Eq. 9.

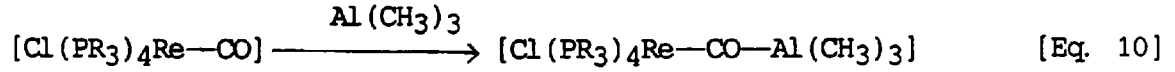


[Eq. 9]

where L = PPh_3.

(II) Electrophilic Attack at Oxygen of the Metal Carbonyls.

The bridging CO in metal carbonyls and substituted carbonyls can also be attacked by electrophiles[39] and strong Lewis acids. For example, BX_3 or AlX_3 (where X = alkyl group) may give adducts[20] that have a C—O—AlX_3 group as in Eq. 10.



[Eq. 10]

(III) : Π-Acidity of Nucleophiles and ν(CO) Frequencies of Complex Compounds.

Depending upon the Π-interaction ability of the anionic ligands in complex compounds, Singh and Goswami[40] have divided the ligands into three groups which show three distinct sets of ν(CO) values for the complexes trans-[$RhX(CO)L_2$], where X is an anion or nucleophile and L is $AsPh_3$ or $SbPh_3$.

(i) Hard bases (e.g. $X = OH^-$, F^-) having no Π-donor-acceptor ability[41], may be considered as σ-donors and show low ν(CO) frequencies.

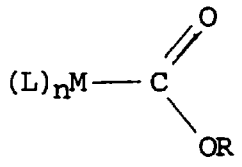
(ii) Soft bases which can exhibit Π-acceptor ability, withdraw electrons from the metal dΠ orbitals into empty dΠ orbitals of the ligand. ($X = Cl^-$, Br^-, I^-).

(iii) The pseudo halogeno ligands ($X = CN^-$, SCN^-) or other ligands which are soft bases, can function as both Π-acids as well as Π-bases and show high ν(CO) frequencies in the complex. This type of ligand donates electrons from filled Π-bonded orbitals to empty p_z orbitals of the metal and accepts metal electrons from filled dΠ orbitals to empty antibonding orbitals.

Therefore, the ν(CO) frequencies for the complex increase as type i < ii < iii bases or nucleophiles. For halogen ligands the nucleophilicity varies as $I^- > Br^- > Cl^- >> F^-$ and the ν(CO) values increase in the sequences $F^- < Cl^- < Br^- < I^-$ in these rhodium complexes[40] and as well as iridium complexes[41].

(IV) Alkoxo, Alkoxycarbonyl and Carbamoyl Compounds.

Although alkoxycarbonyl and carbamoyl functional groups have been known in organic chemistry for over a century, only in the past thirty years have inorganic analogs been reported[36]. The interaction of a strong nucleophile (e.g. methoxide, ethoxide) with bonded CO in neutral or cationic transition metal complexes gives alkoxycarbonyl compounds (in Fig. 5). The replacement of a weak nucleophile by a strong nucleophile followed by CO insertion can take place to give an alkoxycarbonyl compound.



[where L is the ligand, M is a metal, R is an alkyl group and n is the number of L]

Fig. 5 : Typical example of an alkoxycarbonyl compound.

(1) The complex[42] $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]^+$ reacts with CH_3O^- and CH_3NH_2 to give $[(\eta^5\text{-}C_5H_5)Ru(COOCH_3)(CO)_2]$ and $[(\eta^5\text{-}C_5H_5)Ru(CONHCH_3)(CO)_2]$.

$$[(L)_nMC\text{—}O]^+ \quad + \quad RO^- \longrightarrow [(L)_nMCOOR] \qquad \text{[Eq. 11]}$$

where R = alkyl group.

Some cationic complexes[43-45] which are known to react as in Eq. 11 are $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]^+$, $[OsCl(CO)_3(PPh_3)_2]^+$, $[Mn(CO)_4(PPh_3)_2]^+$ and $[RuI(CO)_3(PPh_3)_2]^+$.

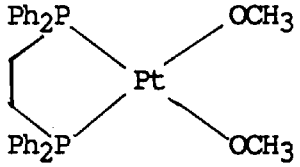
(2) Reactions of $[PtCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$ with alkoxide in the presence of CO give the alkoxycarbonyl compounds as in Eq. 12.

$$[MCl_2(PPh_3)_2] + RO^- + CO \longrightarrow [M(COOR)_2(PPh_3)_2] \qquad [Eq. 12]$$

where M = Pt, Pd. The reaction is believed to proceed through the cationic carbonyl intermediate[36], $[MCl(CO)(PPh_3)_2]^+$.

(3) The cation complex[22] $[Pt(COOCH_3)(CO)(PPh_3)_2]^+$ reacts with CH_3O^- to give the alkoxycarbonyl compound, $[Pt(COOCH_3)_2(PPh_3)_2]$.

(4) $[PtCl_2(dppe)]$ reacts[46] with excess CH_3ONa in benzene-methanol to give $[Pt(OCH_3)_2(dppe)]$. This compound decomposes rapidly at room temperature in a non-donor solvent such as CD_2Cl_2 to generate a formaldehyde oligomer as in Eq. 13.



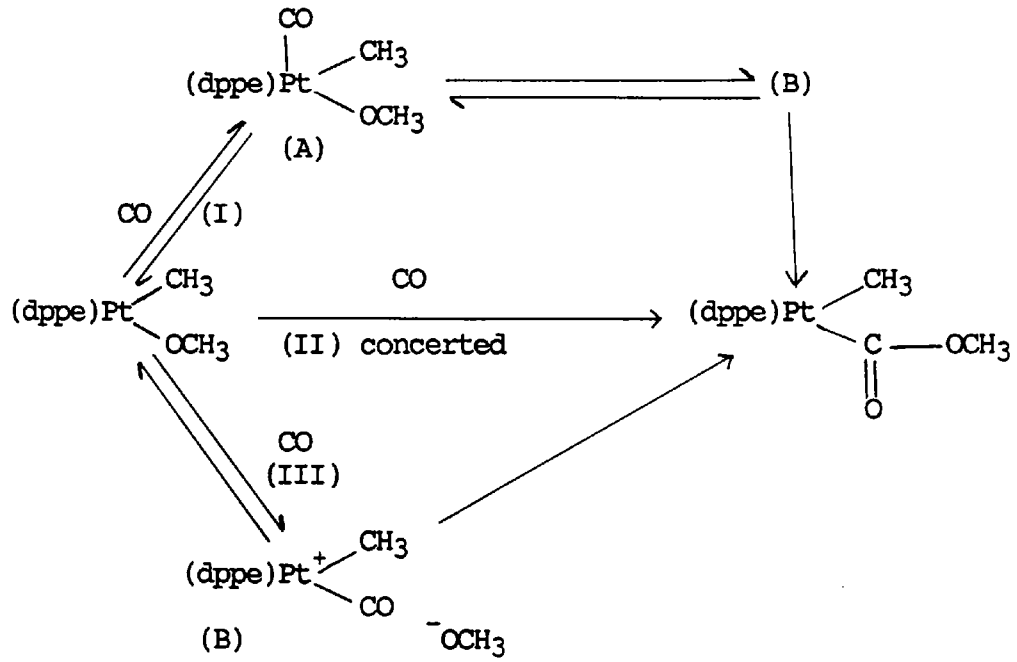
$$\xrightarrow{25^oC} CH_3OH + (CH_2O)_x + CO \qquad [Eq. 13]$$

Reaction of $[Pt(OCH_3)_2(dppe)]$ with CO gives[6] $[Pt(COOCH_3)_2(dppe)]$. This compound is probably formed by CO insertion between the metal-oxygen bond[47]. The compound is stable at 25°C but decomposes slowly at temperatures 80°C to generate CO, methanol and a formaldehyde oligomer. The compound under 12 atmospheres of CO decomposes above 160°C and the observed products are methanol, a formaldehyde oligomer, CO_2 and dimethylcarbonate. Oxidation of this compound using stoichiometric or catalytic amounts of $NOPF_6$, $AgBF_4$ or $AgPF_6$ forms a complex mixture of dimethyloxalate, dimethylcarbonate, CO, CO_2, methanol and formaldehyde oligomers[6].

(5) The cation $[Pd(COOCH_3)(CO)(PPh_3)_2]^+$ reacts with methanol to give dimethylcarbonate[22].

(6) Bryndza reported that the carbonylation[47] of $[Pt(CH_3)(OCH_3)(dppe)]$ to yield $[Pt(CH_3)(COOCH_3)(dppe)]$ is a first order reaction. Low temperature ^{13}C-NMR suggests the formation of a five coordinated carbonyl intermediate (A) in Scheme 1 and crossover experiments rule out the involvement of the dissociated species (B) in Scheme 1 during this reaction. The same type of reaction mechanisms is proposed for the carbonylation[47] of $[Pt(OCH_3)_2(dppe)]$ to $[Pt(COOCH_3)_2(dppe)]$.

Scheme 1 :



(7) $PdCl_2$ reacts with ethanol, CO and base to gives diethylcarbonate through the $Pd(COOC_2H_5)_2$, palladium ethoxycarbonyl intermediate[48]. The overall reaction is as in Eq. 14.

$$2C_2H_5OH + CO + PdCl_2 + 2Na_2CO_3 \longrightarrow (C_2H_5O)_2CO + Pd + 2NaCl + 2NaHCO_3$$ [Eq. 14]

Under more vigorous conditions, $PdCl_2$ together with a cocatalyst such as $CuCl_2$ or $FeCl_3$ and a dehydrating agent catalyses the reaction of ethanol, CO and O_2 to give diethyloxalate as in Eq. 15 and smaller amounts of diethylcarbonate[48].

$$2C_2H_5OH + 2CO + 1/2\ O_2 \longrightarrow C_2H_5OOC—COOC_2H_5 + H_2O$$ [Eq. 15]

This reaction is also postulated to involve the formation of an ethoxycarbonyl complex ($PdCOOC_2H_5$), which is then converted to the oxalate ester. At high CO pressures, this latter step could proceed via CO insertion into the Pd—C bond to give an $PdCOCOC_2H_5$ complex as in Eq. 16,

$$PdCOOC_2H_5 + CO \longrightarrow Pd—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—OC_2H_5$$ [Eq. 16]

which would undergo attack by $C_2H_5O^-$ giving the product.

(8) $[Pd(OOCCH_3)_2(PPh_3)_2]$ reacts with CO and methanol to give $[Pd(COOCH_3)_2(PPh_3)_2]$ as in Eq. 17, which decomposes in chlorinated solvent and dimethyloxalate may be detected by GLC of the liquid solution[49].

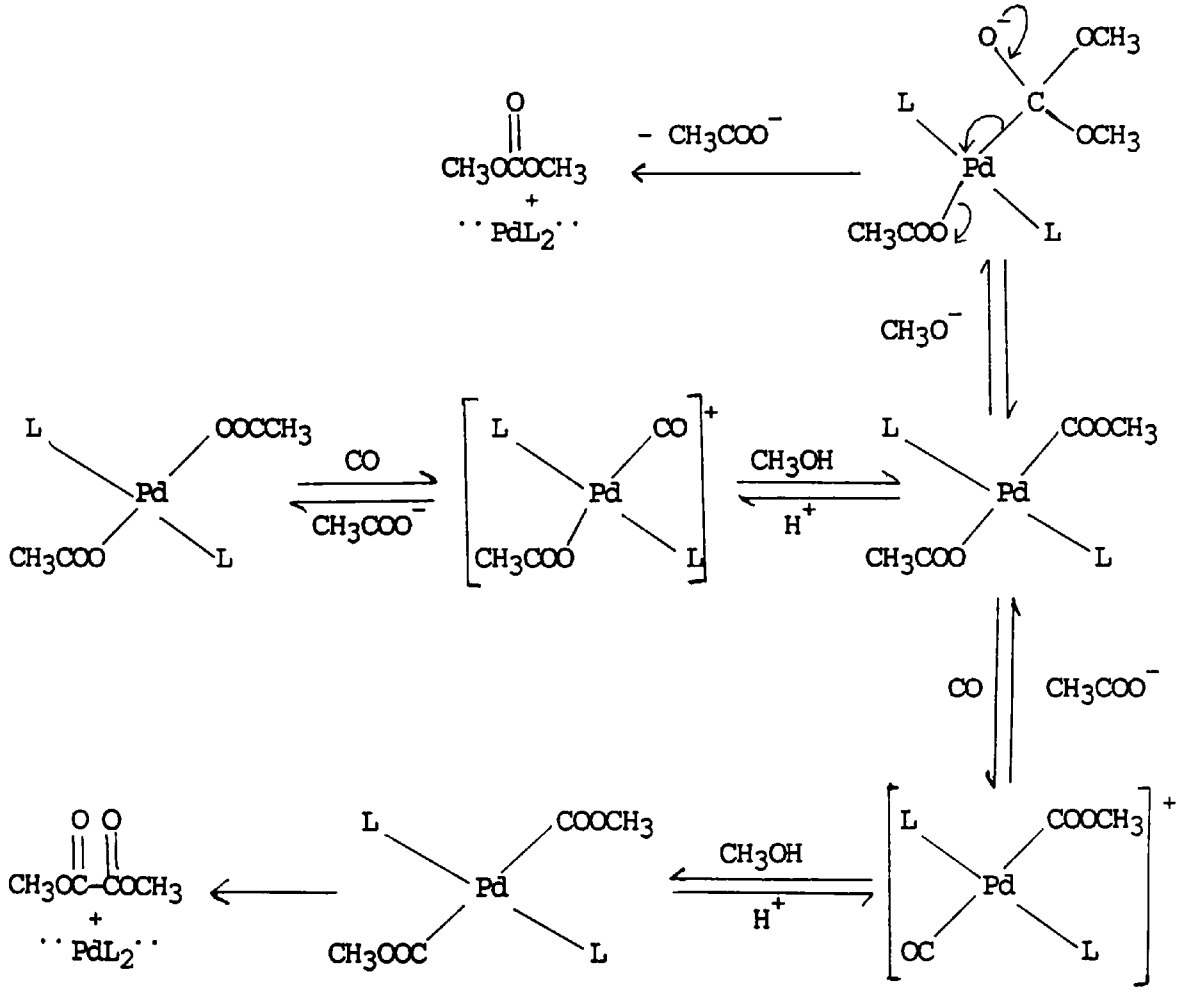
$$[Pd(OOCCH_3)_2(PPh_3)_2] \xrightarrow[-CH_3COOH]{CO,\ CH_3OH} [Pd(COOCH_3)(OOCCH_3)(PPh_3)_2]$$

$$[Pd(COOCH_3)(OOCCH_3)(PPh_3)_2] \xrightarrow[-CH_3COOH]{CO,\ CH_3OH} [Pd(COOCH_3)_2(PPh_3)_2]$$

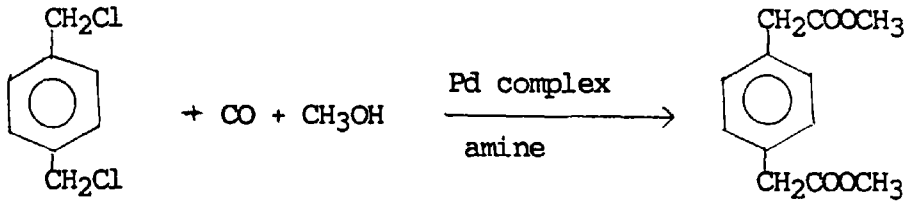
$$[Pd(COOCH_3)_2(PPh_3)_2] \longrightarrow [Pd^o] + (COOCH_3)_2$$ [Eq. 17]

(9) The carbonylation of methanol to dimethyloxalate and dimethylcarbonate in the presence of palladium(II) ethanoate is influenced by the ligand, CO pressure and added base[50]. The phosphine's influence appears to be related mainly to their electronic properties. Alkylphosphines inhibit carbonylation almost completely. The mechanisms for the formation of dimethylcarbonate and dimethyloxalate[50] are shown in Scheme 2.

Scheme 2 :

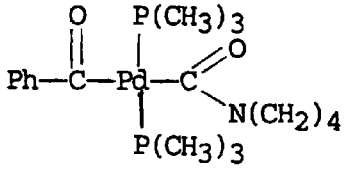


(10) $[PdCl_2(PPh_3)_2]$ reacts with 1,4-bis(chloromethyl)benzene in the presence of CO, CH_3OH and an amine (e.g. triethylamine) to give bis(alkoxycarbonylmethyl)benzene as in Eq. 18, which is almost quantitatively obtained under optimum conditions without side reactions[51], such as quaternization of amine and alcoholysis of the benzylic chloride.



[Eq. 18]

(11) The cationic complex[52] $[Pd(PhOC)(CO)\{P(CH_3)_3\}_2]^+[BF_4]^-$ reacts with pyrrolidine, $HN(CH_2)_4$ to give the benzoylcarbamoylpalladium compound,



(12) The cationic complex[53], $[Ir(CO)_2(SbPh_3)_3]^+$ reacts with alcoholic KOH solution to give $[Ir(COOR)(CO)(SbPh_3)_3]$, where R = CH_3, C_2H_5.

(13) The cationic complex[54], $[IrI_2(CO)_2(PPh_3)_2]^+$ reacts directly with alcohol to give an alkoxycarbonyl compound.

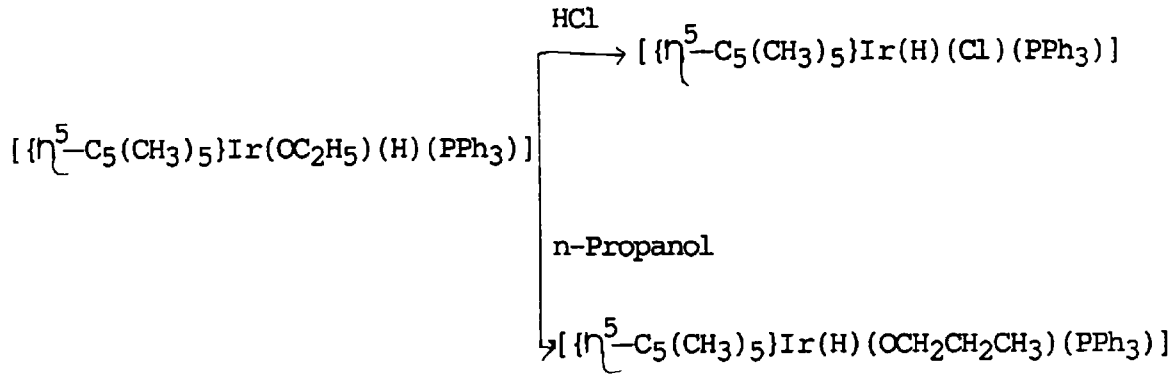
(14) Reaction of trans-$[IrCl(CO)(PPh_3)_2]$ with sodium methoxide in THF gives trans-$[Ir(OCH_3)(CO)(PPh_3)_2]$, if any trace of water is present then the hydroxo complex $[Ir(OH)(CO)(PPh_3)_2]$ is formed. Carbonylation of $[Ir(OR)(CO)(PPh_3)_2]$ compounds, where R = CH_3, $CH_2CH_2CH_3$ leads to the formation of alkoxycarbonyl compounds[38] $[Ir(COOR)(CO)_2(PPh_3)_2]$.

(15) Treatment of $[Ir(CO)_3(PPh_3)_2]^+[ClO_4]^-$ with CH_3ONa gives the compound[38] $[Ir(COOCH_3)(CO)_2(PPh_3)_2]$.

(16) $[\{\eta^5\text{—}C_5(CH_3)_5\}IrCl_2(PPh_3)]$ reacts with sodium ethoxide to give the ethoxo compound[55], $[\{\eta^5\text{—}C_5(CH_3)_5\}Ir(OC_2H_5)(H)(PPh_3)]$ as in Eq. 19 and this compound undergoes reaction with a wide range of substrates under mild conditions as in Scheme 3.

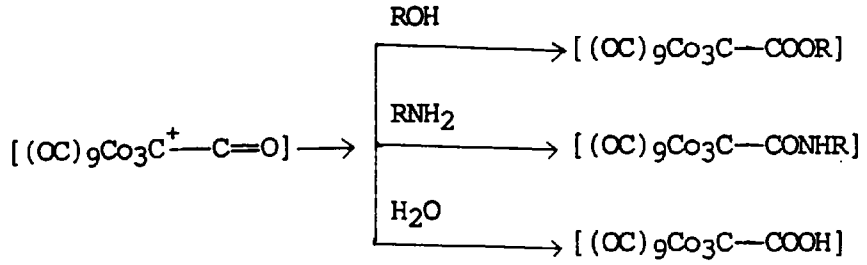
$$[\{\eta^5\text{—}C_5(CH_3)_5\}IrCl_2(PPh_3)] + C_2H_5ONa \longrightarrow [\{\eta^5\text{—}C_5(CH_3)_5\}Ir(OC_2H_5)(H)(PPh_3)] \quad \text{[Eq. 19]}$$

Scheme 3:



(17) The cobalt cluster compound $[(OC)_9Co_3C\text{—}Cl]$ reacts[56] with $AlCl_3$ and carbonylated to form the acylium ion $[(OC)_9Co_3C^+\text{—}C{=}O]$ via an inter or intramolecular CO transfer. This acylium ion then reacts with different nucleophiles[8], e.g. ROH, RNH_2 and H_2O to give alkoxycarbonyl, carbamoyl compounds and oxalic acid as in Scheme 4.

Scheme 4 :



where R = alkyl group.

(18) The cationic complexes of $[M(\eta^5\text{-}C_5H_5)(CO)_4]^+[PF_6]^-$ (where M = Mo or W) react with secondary alkylamines [$NH(CH_3)_2$, piperidine] to form the carboxamido compounds[15] $[(\eta^5\text{-}C_5H_5)M(CO)_3\{CON(CH_3)_2\}]$. These cationic complexes are formed by the reaction of $[(\eta^5\text{-}C_5H_5)MCl(CO)_3]$ with $AlCl_3$ in dry benzene under CO pressure and subsequent treatment with NH_4PF_6 in acetone or ether[57].

(19) Neutral metal carbonyls, such as, $Fe(CO)_5]$ react with alkoxide ions to produce $[Fe(COOR)(CO)_4]^-$, [where R = CH_3, $C(CH_3)_3$], with which $BrCH_2COOCH_3$ produces stable alkoxycarbonyl compounds[58] $[Fe(COOR)(CO)_4(CH_2COOCH_3)]$. This compound thermally decomposes to yield $[Fe(CO)_5]$ and malonic esters, $ROOCCH_2COOCH_3$ under a CO atmosphere[58].

(20) Alkoxycarbonyl compounds react with acid to give the carbonyl compounds[35], e.g. $[IrCl_2(COOCH_3)(CO)\{P(CH_3)_2Ph\}_2]$ reacts with HCl to give $[IrCl_2(CO)_2\{P(CH_3)_2Ph\}_2]^+[Cl]^-$.

1.4 CATALYSIS (HOMOGENEOUS AND HETEROGENEOUS).

(I) Homogeneous Catalysis.

In homogeneous catalysis, the metal atoms or ions of a complex as the catalyst are potentially available as catalytic centres. The reactions usually occur in solution.

(i) Advantages of Homogeneous Catalysis

(1) **Efficiency** : Homogeneous catalytic processes are potentially more efficient in terms of the amount of catalyst needed to catalyse a given amount of reaction, i.e. all metal atoms are active, whereas in heterogeneous catalysis only the surface sites are active.

(2) **Reproducibility** : Homogeneous catalysts have the advantage over heterogeneous catalysts of being totally reproducible, because they have a definite stoichiometry and structure.

(3) **Specificity** : Homogeneous catalysts have only one type of active site and therefore are more specific than a heterogeneous catalyst, which can have several types of active sites. If required the specificity of a homogeneous catalyst can be modified.

(4) **Controllability** : A homogeneous catalyst has a definite structure, it is much easier to modify in order to control the reaction.

(5) **Temperature and Pressure** : Homogeneous catalysts generally operate under much milder conditions of temperature and pressure than

heterogeneous catalysts.

(6) In homogeneous catalysis, transition metals form stable complexes where the metal atoms are very often in positive oxidation states and with different coordination numbers, although a number of zerovalent catalysts are known[2,59]. This variable oxidation state property of the metal can facilitate the coordination of unsaturated molecules, nucleophiles or negative species to the metal centres. The molecules then combine with each other or with other reagents (also coordinated to a metal centre) in specific ways. The organic product is then eliminated from the complex. Because separation is expensive in homogeneous catalysis practical application has been limited.

(ii) Homogeneous Catalytic Cycles Involved in Transition Metal Complexes.

A transition metal catalyst provides a site where the rate-determining step of a reaction can take place more easily than it can in the absence of the catalyst. The energy of activation is less for a catalysed reaction than the uncatalysed reaction. Therefore, the catalysed reaction is more rapid than the uncatalysed reaction. Some of the steps in a homogeneous catalytic cycle are shown below[60].

(1) **Addition and Dissociation** : Many transition metal compounds have only 16 electrons {or even 14 electrons, e.g. $[RhF(PCy_3)_2]$} in the valence shell of the metal atom. These 16-electron compounds, found with d^8 metal ions, such as Co(I), Rh(I), Ni(II) and Pd(II), are coordinatively unsaturated. Unsaturated compounds can add ligands to

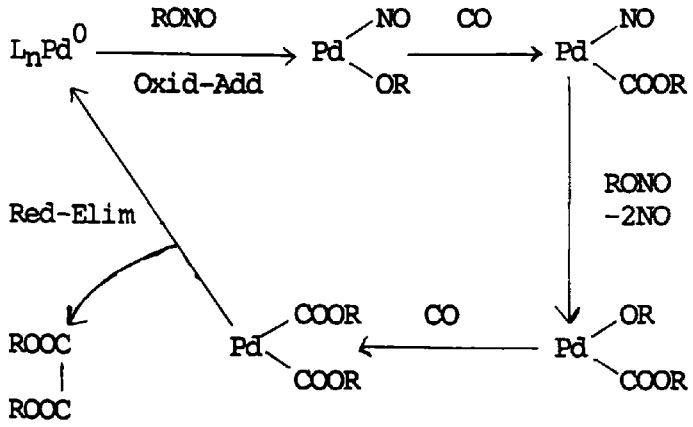
form coordinatively saturated 18-electron compounds, and conversely the 18-electron compounds can undergo dissociation to form coordinatively unsaturated compounds. Compounds of both kinds are commonly involved in the catalytic process. Metal compounds of d^8 configuration, by gain of a ligand can form 5-coordinated species as in Eq. 20.

$$L_4M + :Y \rightleftharpoons L_4MY \qquad \text{[Eq. 20]}$$

where Y is a species such as CO, an alkene or a halide ion and the coordination number changes from 4 to 5.

(2) **Oxidative-Addition and Reductive-Elimination** : Oxidative-addition and reductive-elimination reactions are often important steps in the catalytic cycle, e.g. a reaction cycle in homogeneous solution which involves oxidative-addition of RONO, then CO insertion with a final reductive-elimination of dialkyloxalate is shown [2,59] in Scheme 5.

Scheme 5.



where R = alkyl group.

(3) **Insertion Reactions**: A third important type of reaction involved in catalysis amounts to the insertion of a group between the metal atom and a ligand. The coordination number of the metal atom decreases by one. One example of migratory insertion (i.e. intramolecular insertion) is shown in Fig. 6.

Fig. 6 .

Intermolecular insertion reactions involve the direct attack of nucleophilic reagents on unsaturated ligands without prior coordination of the nucleophile to the metal, e.g. alkyl and aryllithium reagents react directly with iron pentacarbonyl to form anionic acyl derivatives as in Eq. 21.

$$RLi + Fe(CO)_5 \longrightarrow Li^+[Fe(CO)_4(C(=O)R)]^- \qquad [Eq.\ 21]$$

(iii) Some Examples of Homogeneous Catalysis in which Dialkylcarbonates, Dialkyloxalates and Ethylene Glycols are Formed.

(1) Dimethylcarbonate and dimethyloxalate are formed when a methanolic solution of $PdCl_2$-$CuCl_2$ and an organic base, $N(C_2H_5)_3$ react with CO in the presence of oxygen[59].

(2) The literature[51] shows that the complex, $Pd(PPh_3)_4$ catalyses carbonylation of 1,4-bis(chloromethyl)benzene in methanol to

bis(methoxycarbonylmethyl)benzene in the presence of CO and the bases N,N-dicyclohexylmethylamine or N,N-diisopropylethyleneamine.

(3) Another economically practical industrial application is Union Carbide's rhodium carbonyl catalysed ethylene glycol synthesis, using synthesis gas[61] as in Eq. 22.

$$2CO + 3H_2 \rightleftharpoons HOCH_2CH_2OH \qquad \text{[Eq. 22]}$$

The reaction in Eq. 22 requires high pressures to bias the equilibrium towards ethylene glycol. The product selectivity in this process is up to 70% ethylene glycol.

(II) Heterogeneous Catalysis.

In heterogeneous catalysis, the catalyst is present in the solid state, reactions are usually in the gaseous state and the catalysed reaction takes place at the surface of the catalyst.

(i) Advantages of Heterogeneous Catalysis

(1) **Separation of Catalyst** : The major disadvantage of homogeneous catalysis is the separation of the catalyst after the reaction, a very efficient distillation is usually required. In heterogeneous catalysis separation is easier, i.e. some kind of coarse filtration is required.

(2) **Thermal Stability** : The thermal stability of heterogeneous catalysts is often higher than that of homogeneous catalysts.

(3) **Solvent** : The range of suitable solvents for a homogeneous catalyst is often limited, but generally this is not a problem for a heterogeneous catalyst.

(4) In heterogeneous catalysts, transition metals are often in zero oxidation state, one exception to this is the Ziegler-Natta catalyst[2].

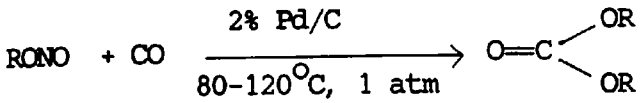
(ii) Some Examples of Heterogeneous Catalysis Reactions which form Dialkylcarbonates, Dialkyloxalates or Ethylene Glycols.

(1) In a recent practical application by the UBE chemical company[59], a new CO coupling process has been developed to produce alkyl oxalates and the company has used the process industrially since 1978. In the process, dibutyloxalate is produced from CO and $CH_3(CH_2)_3ONO$ in the presence of a palladium catalyst as seen in Eq. 23.

$$CH_3(CH_2)_3ONO + CO \xrightarrow{\text{Pd catalyst}} \begin{matrix} CH_3(CH_2)_3O{-}C{=}O \\ | \\ CH_3(CH_2)_3O{-}C{=}O \end{matrix} \qquad \text{[Eq. 23]}$$

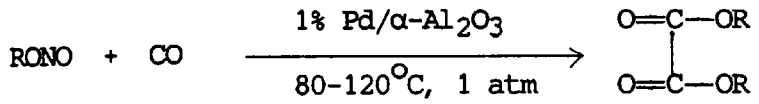
(2) Dialkyloxalates are obtained directly[59] from a reaction involving CO, ROH and O_2 in the presence of a palladium catalyst ($PdCl_2$) and the bases K_2CO_3 or Na_2CO_3 under high pressure. In this process no dehydrating agent is needed and a KCl or NaCl precipitate is formed.

(3) Dialkyloxalates and dialkylcarbonates are formed by the reaction of RONO (R = CH_3, C_2H_5) and CO on palladium support catalysts at atmospheric pressure in the vapour phase[62] and the reaction products are dependent on the nature of the support material as seen from Eq. 24 and Eq. 25.



[Eq. 24]

Dialkylcarbonate



[Eq. 25]

Dialkyloxalate

CHAPTER - 2

METHODS AND MATERIALS.

The complex compounds prepared in this work were generally unstable in oxygen. The sensitivity to oxygen was usually greater in solution than in the solid state. Therefore, the absence of oxygen was essential while carrying out reactions to prepare many complexes. For this reason, all the reactions were carried out under a nitrogen atmosphere (Fig. 7). The solvents were deoxygenated by bubbling nitrogen through the solvent for about 5 minutes or strictly deoxygenated by using Schlenk apparatus (Fig. 7). Air sensitive filtration was carried out under a nitrogen atmosphere (Fig. 8).

(I) Use of Schlenk Apparatus for Deoxygenation of Solvents.

The Schlenk apparatus used to deoxygenate solvents contains two parallel tubes as shown in Fig. 7. One is for the vacuum line, which has four taps (V_1, V_2, V_3 and V_4) and the other tube is for the nitrogen line, which also has four taps (A, B, C and D). Nitrogen from the cylinder is passed through tubes, which contain KOH and P_2O_5 respectively. Then it passes through the tube which has four taps (A, B, C and D), bubbles through the paraffin oil jar J and is finally vented out by G. The efficiency of the vacuum line can be checked by the vacustat gauge. The pressure inside the apparatus for experiments in the present work was around 0.1 mm of Hg.

The solvent was placed in the Schlenk tube S and its open head E was stopped by a rubber Subaseal (Fig. 7). Then the Schlenk tube was connected by the side arm F to the vacuum line through K by opening the tape V_2 (all other vacuum taps V_1, V_3 and V_4 were closed). When bubbles of the solvent appeared, then the tap V_2 was closed and the tap B was

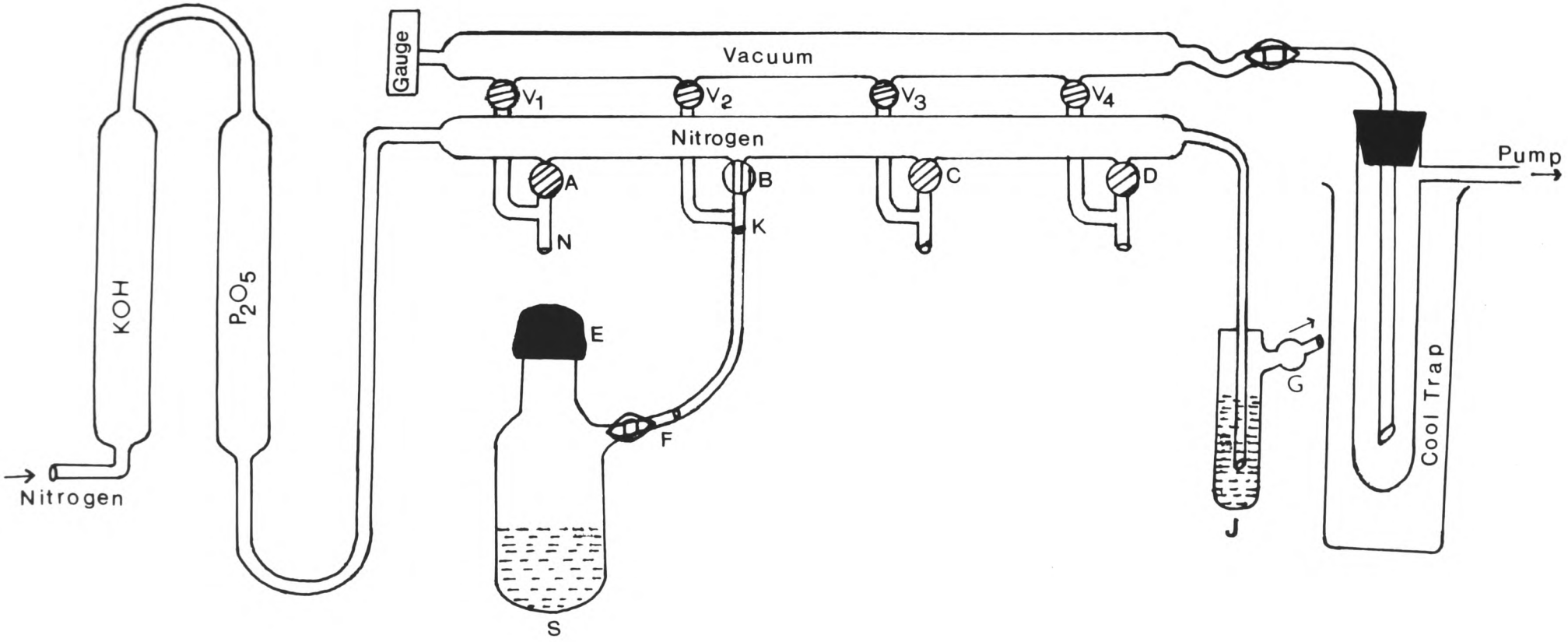


Fig. 7 : Schlenk apparatus

opened to flush through nitrogen (all other nitrogen taps A, C, and D were closed). This operation of evacuating and flushing of nitrogen was carried out three times. The sample was added to the solvent in the Schlenk tube by opening the rubber Subaseal E under a positive stream of nitrogen. After addition of the sample, the rubber Subaseal E was replaced. The sample was stirred for the required time under nitrogen.

(II) Filtration under Nitrogen.

A filtration apparatus W was placed on a empty Schlenk tube P as in Fig. 8. A small amount of kieselguhr was put on the sinterglass Z of the filtration apparatus to remove fine, unwanted precipitates. The top head Q of the filtration apparatus was closed by a rubber Subaseal. The side arm (tap M) of the Schlenk tube P was connected to N of Fig. 7, but taps M, V_1 and A were closed. The Schlenk tube S which contained the reaction product under nitrogen (which had been already connected to the nitrogen line B of Fig. 7) was connected to the filtration apparatus by a transfer tube T. Initially, the end T_1 of the transfer tube was not put into the solution. For ten minutes nitrogen was passed through the transfer tube to ensure the whole system was under a nitrogen atmosphere and nitrogen was vented out through the open tap O. After that, T_1 of the transfer tube was dipped into the solution. The solution was transferred from Schlenk tube S to the Schlenk tube P under nitrogen pressure by siphoning. The taps M and A were opened, the nitrogen flow reduced and taps F and B closed. Nitrogen was now passing through M and vented out through O. The filtration apparatus W was dismantled. The head R of the Schlenk tube P was sealed under nitrogen by a rubber

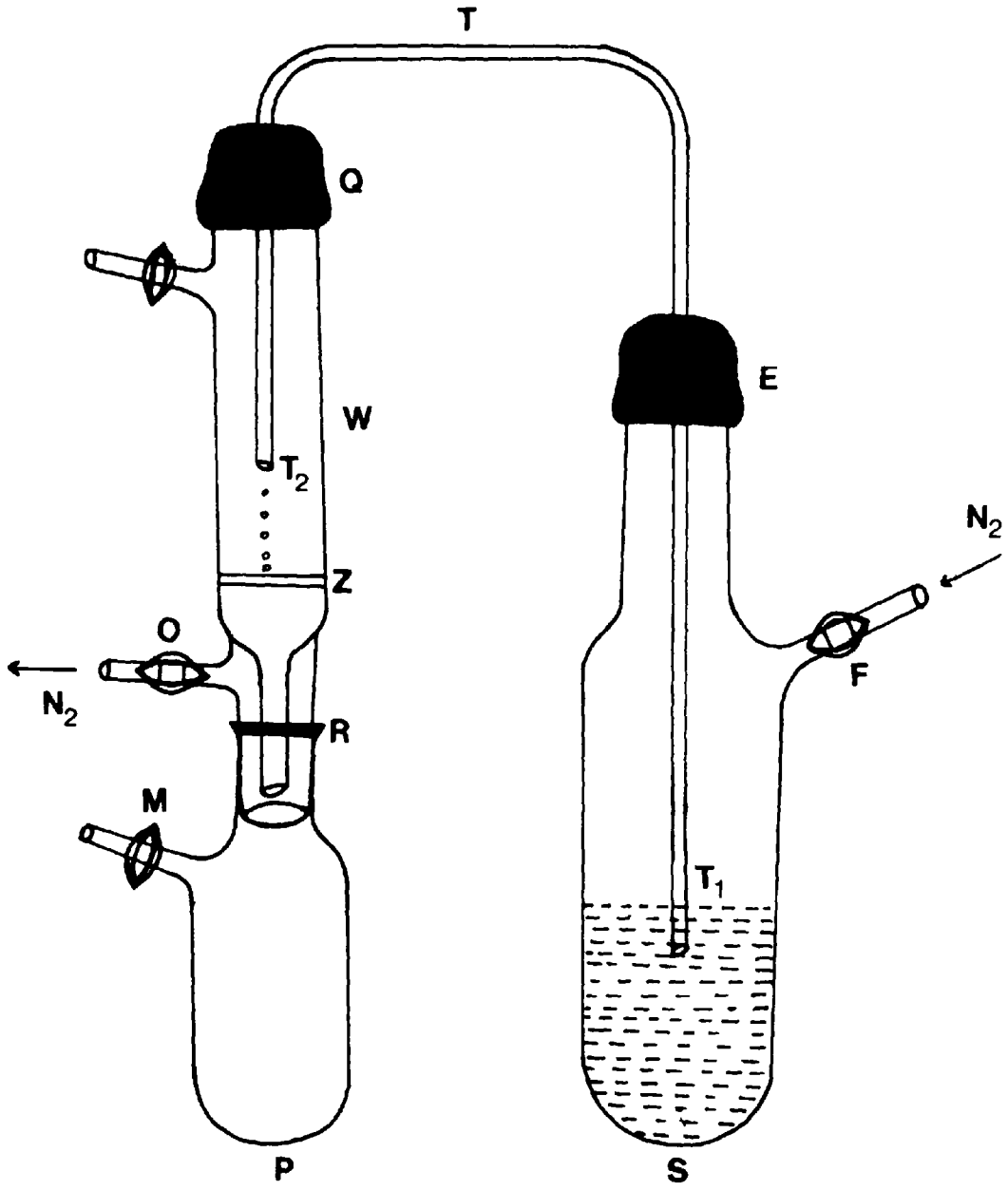


Fig. 8 : Filtration under nitrogen

Subaseal. Tap A was closed and tap V_1 of the vacuum line opened in order to evaporate the solvent. After that the tap V_1 was closed and tap A opened. Finally, tap M was closed and the product was stored under nitrogen in the Schlenk tube P.

(III) The Carbon Monoxide Pressure Reaction.

The arrangement of the apparatus is shown in Fig. 9. First the reactants were charged in the pressure bomb and the bomb head was placed on the bomb and secured. The pressure head was connected to the bomb head and the bomb flushed with nitrogen several times to remove air by using taps A and C. Finally, carbon monoxide pressure was applied [maximum pressure 10 atmospheres as checked by pressure gauge G] by opening the tap B and stopping tap C. For the reaction at elevated temperature the bomb was heated by immersing into a paraffin oil bath. At the end of the reaction tap C was opened and all the carbon monoxide pressure was vented out. The product was collected in a small volumetric flask. If the products which formed were solid and liquid, then simple filtration was performed to collect both.

(IV) Preparation of Sample for NMR Studies under Nitrogen.

The solvent was placed in a small Schlenk tube and deoxygenated by using Schlenk apparatus [as described in Fig. 7]. The sample was placed in a NMR tube and sealed with a rubber Subaseal, then deoxygenated by passing nitrogen for 5 minutes through needles, one needle as outlet and one as inlet. Then the deoxygenated solvent was added by a syringe to the

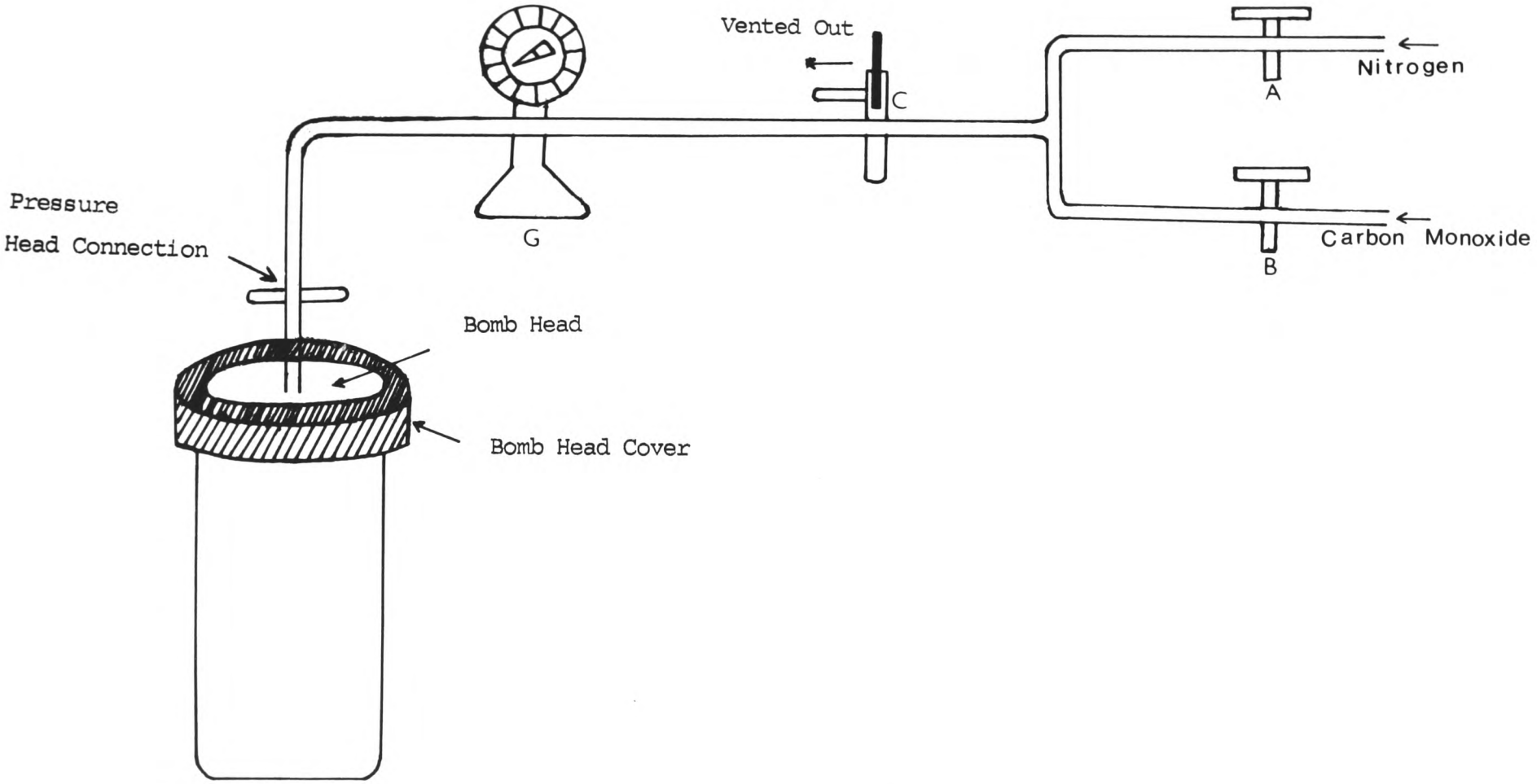


Fig. 9 : Arrangement of carbon monoxide pressure reaction.

sample in the NMR tube and the needles were disconnected. All the ^{31}P-NMR and ^{13}C-NMR spectra were proton-decoupled. The chemical shifts were expressed in ppm relative to TMS as internal standard in the ^{1}H-NMR. Also, 85% H_3PO_4 and trimethylphosphate (TMP) were used as (internal and external) standards in the ^{31}P-NMR. The solvents used were $CDCl_3$, Acetone-d^6, C_6D_6 and D_2O.

(V) Catalytic Hydrogenation Apparatus.

This is shown in Fig. 10. The solvent (e.g. 10 cm^3) was placed in the flask S and connected to the vacuum pump by opening taps A and E, whilst keeping taps B, C, D, F and G closed. Agitation of the solvent was achieved by operating the magnetic stirrer in the flask at S. When bubbles appeared in the solvent, tap E was closed and hydrogen introduced by opening tap F until the apparatus was pressurised i.e. bubbles of hydrogen appeared at I. Tap F was then closed and the operation repeated three times until the apparatus was flushed out with hydrogen. Tap D was used to check the efficiency of the vacuum system. The samples (a known amount of catalyst and oct-1-ene) were introduced through the glass stopper at Q into the flask at S under a positive stream of hydrogen i.e. taps F and A open, the rest closed. The stopper at Q was then replaced. The graduated glass tubes and reservoirs at M and N had been previously filled with water. The reservoirs could be clamped at various heights and initially were kept at a higher level than the graduated glass tubes, so that the tubes were full of water up to taps B and C. The stoppers in reservoirs M and N had ridges cut in them so that the contents of M and N were open to atmospheric pressure.

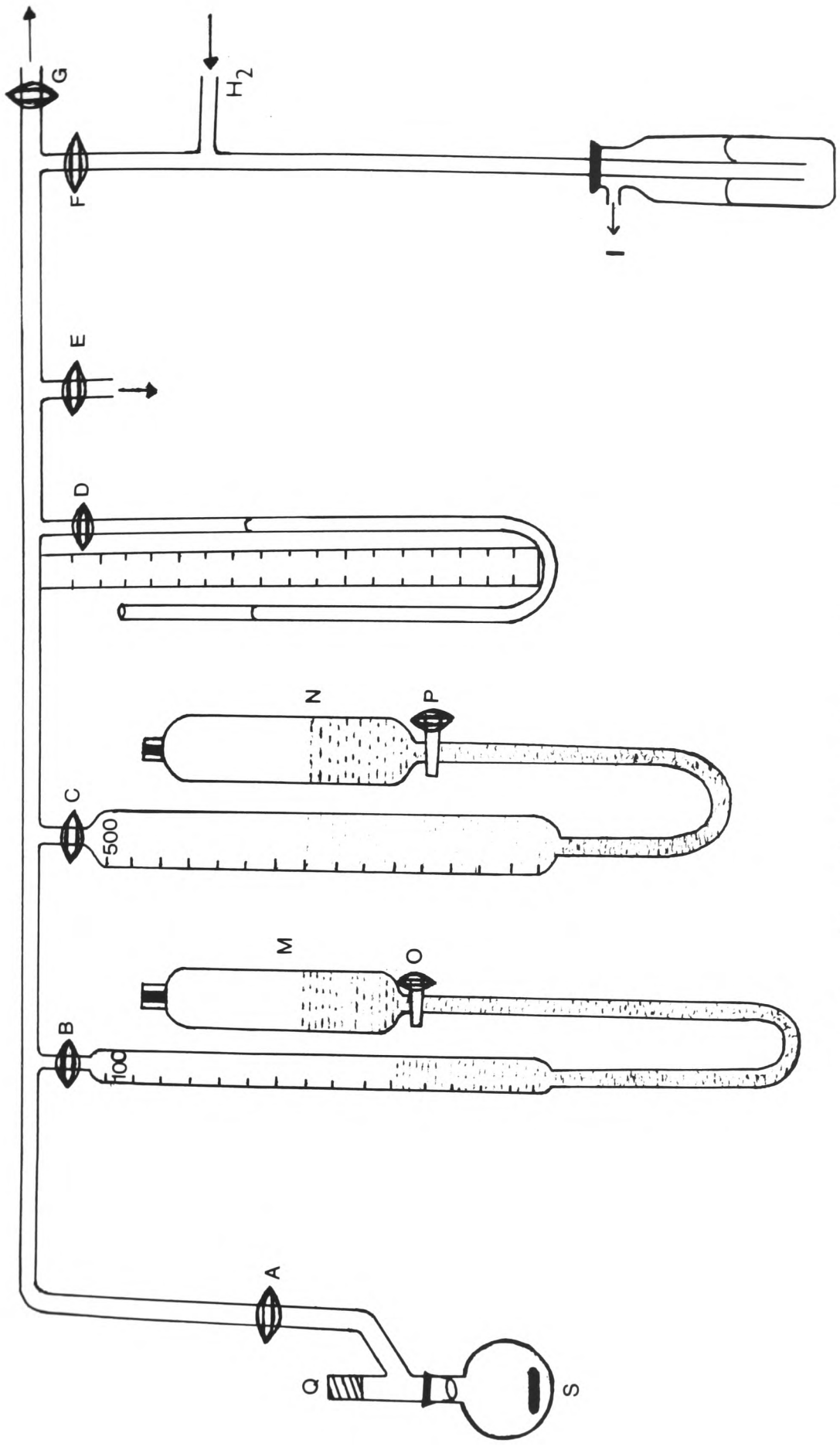


Fig. 10 : Catalytic hydrogenation apparatus

After introduction of the samples, the line was again flushed out with hydrogen as previously described, then taps F, C, A and P were opened. A volume of hydrogen (ca. 250 cm^3) was introduced into the graduated glass tube associated with reservoir N (reservoir M could be used if a smaller volume of hydrogen was needed). When bubbles of hydrogen appeared at I, tap F was closed. An initial reading of the volume of water in the graduated tube was taken, whilst simultaneously adjusting the height of the reservoir at N. This was done by keeping the level of water in N the same as that in the graduated tube associated with it. After the initial reading had been taken, the timer was started and the agitated mixture of sample and solvent left under hydrogen for twenty four hours. Then a final reading of water was taken in the manner previously described.

In this way, the volume of hydrogen that had been used to convert oct-1-ene to octane could be determined and by correcting the reading to standard temperature and pressure, the number of moles of hydrogen that had reacted could be found. The mixture at S was collected and analysed using gas chromatography and infrared spectroscopy.

(VI) Instrumentation.

Analysis : C and H analyses were measured by MEDAC Ltd., Brunel University.

Infrared Spectra : Infrared spectra (4000-600 cm^{-1}) were measured on a Perkin Elmer 881 Spectrometer and far-infrared spectra (600-250 cm^{-1}) on a Perkin Elmer 457 Spectrometer.

NMR Spectra : NMR spectra were measured by using a JOEL FX90Q 90MHz Fourier Transform Spectrophotometer.

Gas Chromatography : Gas chromatographs were obtained using a Perkin Elmer F17 Gas Chromatography Apparatus with Flame Ionization Detector and Perkin Elmer Data Station 3600.

Columns Used : For the analysis of dimethylcarbonate, dimethyloxalate and benzene 10% SP2330 column (10% Biscyanopropylphenylpolysiloxane is coated on Supelcoport)) was used. For the analysis of octane a 15% Apiezon L column (15% methylchlorosilane is coated on acid wash Chromosorb W) was used.

GC Mass Spectra : GC mass spectra were obtained from Lancashire Polytechnic, using GC Perkin Elmer 8500 and MS Perkin Elmer ITD (Ion Trap Detector).

(VII) Purification of Solvents[63].

(i) **Dichloromethane** : The commercial grade of dichloromethane was purified by washing with 5% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride and then distilled. The fraction, boiling point. 40-41^{o}C was collected and stored over type 4A molecular sieves.

(ii) **Ethanol** : A dry round bottom flask (1.5-2.0 dm^3) was fitted with a double surface condenser and a calcium chloride guard-tube. Clean dry magnesium turnings (5.0 g) and iodine (0.5 g) were placed in the flask, followed by 75 cm^3 of commercial absolute ethanol. The mixture was

warmed until the iodine had disappeared. Heating was continued until all the magnesium was converted into ethoxide, then 900 cm^3 of absolute ethanol was added and the mixture refluxed for 30 minutes. After cooling the ethanol was distilled off directly into a vessel in which it was stored, by reassembling the condenser for downward distillation via a splash head adapter. Then the ethanol was stored over type 4A molecular sieves.

(iii) **Methanol** : Anhydrous methanol was obtained by distillation of methanol with magnesium turnings in exactly the same procedure for ethanol and stored over 4A type molecular sieves.

(iv) **Acetone** : The acetone was heated under reflux with successive quantities of potassium permanganate until the violet colour persisted. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Precaution was taken to exclude moisture, i.e. a calcium chloride guard-tube was used.

(v) **Benzene** : The analytical reagent grade benzene was first treated with anhydrous calcium chloride, filtered and then placed over sodium wire.

(vi) **Hexane** : Analytical grade hexane was stored over type 4A molecular sieves.

(vii) **Tetrahydrofuran** : Sodium wire and benzophenone were added in to the THF until a blue colour persisted. Then the blue coloured solution was distilled under nitrogen and the fraction (boiling point 65-66^{o}C) was collected and stored over type 4A molecular sieves, under nitrogen.

(viii) **Diethyl ether** : Diethyl ether was dried by sodium wire.

(VIII) Chemicals.

Triphenylphosphine (PPh_3), triphenylantimony ($SbPh_3$), tricyclohexylphosphine (PCy_3), rhodium trichloride trihydrate ($RhCl_3.3H_2O$), silver tetrafluoroborate ($AgBF_4$), dimethylcarbonate, dimethyloxalate, trioxane, octane, nonane, oct-1-ene were obtained from Aldrich Chemical Company, Inc. Ruthenium trichloride trihydrate ($RuCl_3.3H_2O$) was obtain from Lancaster Synthesis Ltd. and Johnson Matthey Materials Technology. Triphenylarsine ($AsPh_3$) was obtained from Lancaster Synthesis Ltd. Sodium methanoate, Sodium ethanoate and sodium propanoate were obtained from BDH Chemicals Ltd. Carbon monoxide and Hydrogen were obtained from British Oxygen Ltd.

The above chemicals were reagent grade, they were used without further purification.

CHAPTER-3

RUTHENIUM CHEMISTRY.

3.1 INTRODUCTION.

Transition metal carbonyl or cationic transition metal carbonyl compounds react with nucleophiles to give alkoxycarbonyl or alkoxo compounds. Sometimes these alkoxycarbonyl compounds give organic products. Ruthenium compounds generally undergo the sort of reactions mentioned in Sec. 1.4 [I(ii)], e.g. $[RuCl_2(PPh_3)_3]$ is a good catalyst for the hydrogenation of alkenes. Ruthenium carbonyl phosphine cationic complexes have not been widely explored as catalysts. Therefore, in order to study their catalytic properties, some ruthenium carbonyl phosphine cationic complexes were synthesised in the present work. The reactivity of these cationic complexes towards nucleophiles in the presence and absence of carbon monoxide, enabled some alkoxycarbonyl compounds to be synthesised. The cationic carbonyl phosphine and alkoxycarbonyl phosphine compounds of ruthenium have been synthesised from cis and trans-dicarbonyldichlorobis(triphenylphosphine)-ruthenium(II). The starting materials cis and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ have been prepared from dichlorotris(triphenylphosphine)ruthenium(II), $[RuCl_2(PPh_3)_3]$ and carbon monoxide. $[RuCl_2(PPh_3)_3]$ is prepared from hydrated ruthenium trichloride and triphenylphosphine.

(I) Preparation of Dichlorotris(triphenylphosphine)ruthenium(II), $[RuCl_2(PPh_3)_3]$ and its Properties.

(i) Preparation of $[RuCl_2(PPh_3)_3]$.

Dichlorotris(triphenylphosphine)ruthenium(II) was first synthesised in 1965 from hydrated ruthenium trichloride and triphenylphosphine[64]. The reaction between this compound, and the products isolated depend upon the molar ratios of the reactants, reaction time, temperature and solvent. Some of the possible products[65] are shown in scheme 6. $[RuCl_2(PPh_3)_3]$ has proved to be an important precursor of many ruthenium(II) compounds. This tris(triphenylphosphine) compound is coordinatively unsaturated. It can function as an important homogeneous catalyst and is the forerunner of important catalytic species[65]. In homogeneous hydrogenation the catalytic activity of the ruthenium system is very selective under mild conditions, but of surprisingly wide application at high temperatures. It is one of the most active transfer hydrogenation catalysts yet discovered. In many ways it is complementary[65] to $[RhCl(PPh_3)_3]$ and $[RhH(CO)(PPh_3)_3]$.

(ii) Physical Properties of $[RuCl_2(PPh_3)_3]$.

The melting temperature of $[RuCl_2(PPh_3)_3]$ is reported to be 132-134^{o}C in air[64]. Thermogravimetric analysis[66] reveals that it begins to react with oxygen at 115^{o}C. This reaction is rapid at 140^{o}C and the black triphenylphosphine oxide compound, $[RuCl_2(OPPh_3)_3]$ is formed.

Scheme 6 : Reaction between Hydrated Ruthenium Trichloride and Triphenylphosphine[65].

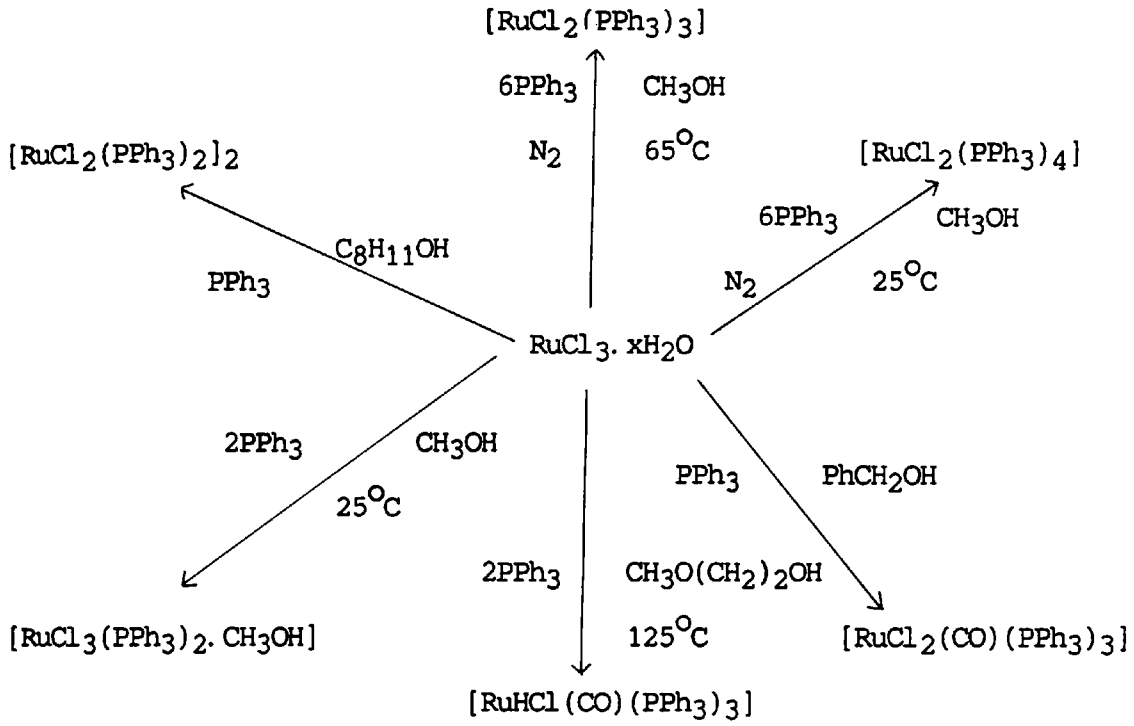


Table 6 : Far-Infrared and ^{31}P-NMR Data of [$RuCl_2(PPh_3)_3$].

		Ref.
Infrared	v(Ru—Cl) 315 cm^{-1}	67
Temperature	^{31}P-NMR	
30°C	+40. 90 ppm	27
-97°C	+75. 70 (t), +24. 10 (d) ppm (with J_{p-p} = 30. 5 Hz)	

(iii) **Chemical Properties of** $[RuCl_2(PPh_3)_3]$.

(1) Dichlorotris(triphenylphosphine)ruthenium(II) can abstract hydrogen from primary alcohols as seen in Eq. 26.

$$[RuCl_2(PPh_3)_3] + CH_3CH_2OH \longrightarrow [RuHCl(PPh_3)_3] + CH_3CHO + HCl \qquad \text{[Eq. 26]}$$

Deuterium labelling shows that the hydrogen transferred to ruthenium is that from the alpha (α) carbon atom. The hydroxy proton forms hydrogen chloride[68].

(2) Proton donor alcohols form alkoxo compounds with ruthenium[69], then the alkoxo group eliminates as aldehyde as shown in Eq. 27.

$$[RuCl_2(PPh_3)_3] + PhCH_2OH \longrightarrow [RuCl(OCH_2Ph)(PPh_3)_3] + HCl$$

$$\downarrow$$

$$[RuHCl(PPh_3)_3] + PhCHO \qquad \text{[Eq. 27]}$$

(3) When methanolic $[RuCl_2(PPh_3)_3]$ is allowed to react with silver(I) tetraphenylborate it forms a red solution, supposedly containing the cationic species[70], $[Ru(PPh_3)_3]^{2+}$ as seen in Eq. 28. The reaction is reversed by the addition of the chloride ion[70].

$$[RuCl_2(PPh_3)_3] \underset{Cl^-}{\overset{AgBPh_4}{\rightleftharpoons}} [Ru(PPh_3)_3]^{2+} \qquad \text{[Eq. 28]}$$

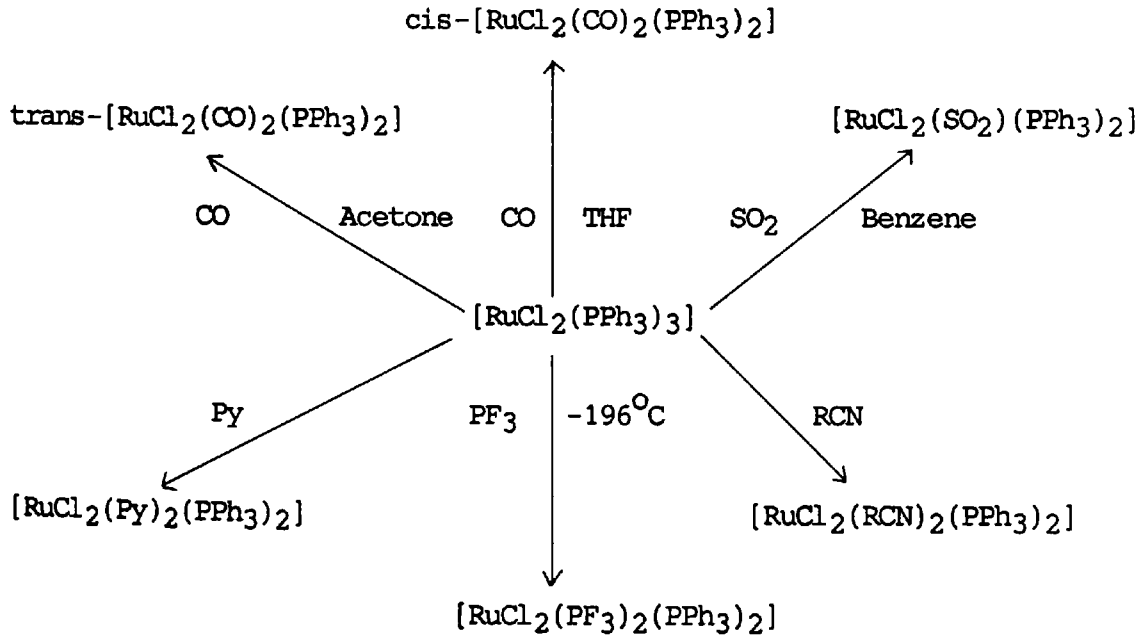
(4) It has also been claimed that $[RuCl_2(PPh_3)_3]$ catalysed exchange with tritiated water brings about incorporation of tritium still further into the alkyl group of the primary alcohol[71] as in Eq. 29. Alkoxo compounds are the most probable intermediates in the process.

$$RCH_2CH_2OH + T_2O \xrightarrow{[RuCl_2(PPh_3)_3]} RCH_2CHTOH \xrightarrow[T_2O]{[RuCl_2(PPh_3)_3]} RCHTCHTOH$$

[Eq. 29]

(5) One or more triphenylphosphine ligands are commonly displaced when $[RuCl_2(PPh_3)_3]$ is reacted with other potential ligands. Some reactions of this type are illustrated in scheme 7. $[RuCl_2(PPh_3)_3]$ is a coordinatively unsaturated, 16-electron compound. The usual reaction of this penta-coordinated compound is that one bulky PPh_3 ligand is displaced, allowing two additional smaller ligands to coordinate.

Scheme 7 : Some PPh_3 Substitution Reactions of $[RuCl_2(PPh_3)_3]$[65].

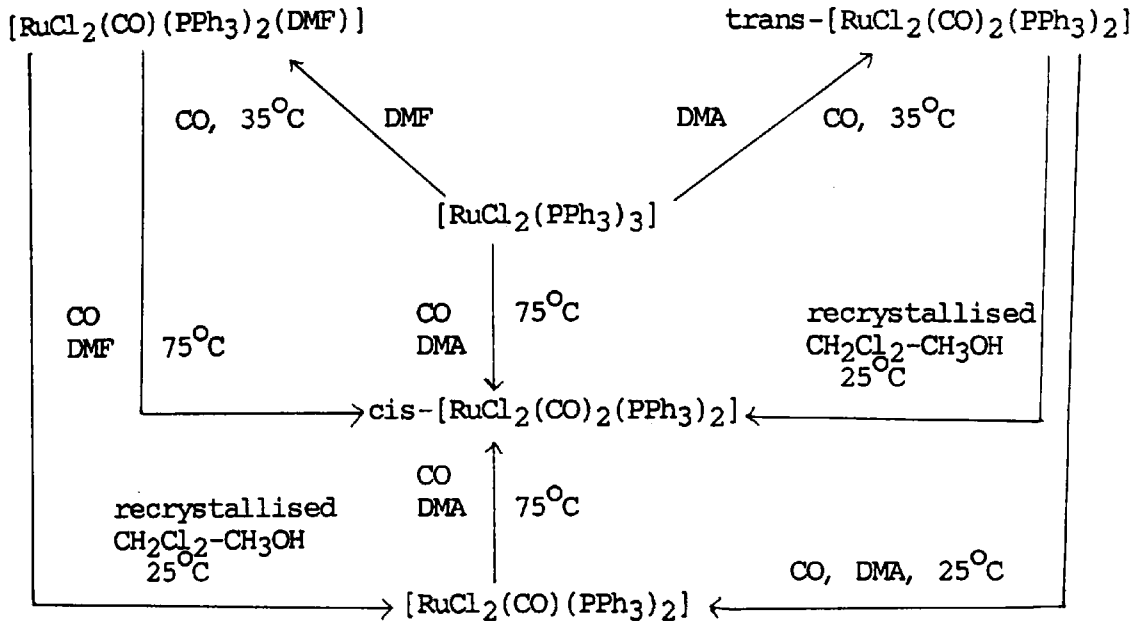


In the literature dibromotris(triphenylphosphine)ruthenium(II), $[RuBr_2(PPh_3)_3]$ has been prepared as dark-brown crystals by shaking $RuCl_3.xH_2O$ with a large excess of lithium bromide, followed by the addition of excess triphenylphosphine, then refluxing the resulting mixture[64].

(II) Preparation of Dicarbonyldichlorobis(triphenylphosphine)-ruthenium(II), $[RuCl_2(CO)_2(PPh_3)_2]$.

$[RuCl_2(CO)_2(PPh_3)_2]$ can be prepared by the reaction of $[RuCl_2(PPh_3)_3]$ with CO. In tetrahydrofuran (THF) white cis-$[RuCl_2(CO)_2(PPh_3)_2]$ is obtained[72]. In acetone yellow trans-$[RuCl_2(CO)_2(PPh_3)_2]$ is isolated[72]. The cis- form is more stable at higher temperatures. In N,N-dimethylacetamide the trans-isomer can be obtained at 35°C, although at 75°C the cis-isomer is formed[73]. When the reaction between $[RuCl_2(PPh_3)_3]$ and CO is carried out in N,N-dimethylformamide, intermediate monocarbonyl compounds can be obtained at 35°C as shown in Scheme. 8. Initially, a six-coordinated compound of dimethylformamide is isolated but this easily loses dimethylformamide to give the penta-coordinated monocarbonyl compound $[RuCl_2(CO)(PPh_3)_2]$. The latter can react with more CO to form the two dicarbonyl compounds[73]. At 25°C this reaction gives trans-$[RuCl_2(CO)_2(PPh_3)_2]$ and at 75°C the product is cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

Scheme 8 :



In dichloromethane the reactions between $[RuCl_2(PPh_3)_3]$ and ^{13}CO or $C^{18}O$ follow similar sequences[74] as in Eq. 30.

$$[RuCl_2(PPh_3)_3] + {}^{13}CO \xrightarrow{CH_2Cl_2} \text{trans-}[RuCl_2({}^{13}CO)_2(PPh_3)_2] \xrightarrow[CH_2Cl_2]{\text{Heat}} \text{cis-}[RuCl_2({}^{13}CO)_2(PPh_3)_2] \qquad \text{[Eq. 30]}$$

The corresponding bromo-analog[64], cis-$[RuBr_2(CO)_2(PPh_3)_2]$ is formed when carbon monoxide is passed through boiling $RuCl_3.xH_2O$ and excess lithium bromide (1:6) in ethanol. Addition of excess triphenylphosphine gives white crystals. The trans-compound is formed when carbon monoxide is passed through the concentrated solution of $[RuBr_2(PPh_3)_3]$ or $[RuBr_2(PPh_3)_4]$ in acetone. The iodo compound, cis-$[RuI_2(CO)_2(PPh_3)_2]$ is prepared from $[Ru(CO)_3(PPh_3)_2]$ by oxidative addition of iodine[75] or from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ by heating[76,77] with KI.

Table 7 : Literature Value of the Carbonyl Stretching Frequencies of Some Compounds of Ruthenium.

Compound	ν(CO) cm^{-1},	Ref.
trans-$[RuCl_2(CO)_2(PPh_3)_2]$	2000[a]	73
	1997[b]	73
	2000[a]	72
cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (white)	2064, 2001[a]	64, 73
cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (yellow)	2065, 1990[a]	78
cis-$[RuBr_2(CO)_2(PPh_3)_2]$	2061, 1980[a]	78
trans-$[RuBr_2(CO)_2(PPh_3)_2]$	2004	78
cis-$[RuI_2(CO)_2(PPh_3)_2]$	2055, 1994[c]	77
cis-$[RuI_2(CO)_2\{PPh(CH_3)_2\}_2]$	2037, 1968[a]	76
$[RuCl_2(CO)(PPh_3)_2]$	1931, 1921[a]	73
	1940[b]	73
$[RuBr_2(CO)(PPh_3)_2]$	1938[b]	73
$[RuHCl(CO)_2(PPh_3)_2]$	2042, 1983[b]	73
$[RuH_2(CO)(PPh_3)_3]$	1940	79
$[RuH_2(CO)_2(PPh_3)_2]$	2015, 1970	78
	2011, 1974	80
	2018, 1979[d]	81
$[Ru(CO)_3(PPh_3)_2]$	1895[b]	75
$[Ru(CO)_2(PPh_3)_3]$	1905	82

[Where a = Nujol mull, b = CH_2Cl_2, c = $CHCl_3$, d = CS_2].

Table 8 : Far-Infrared and ^{31}P-NMR Data of $[RuCl_2(CO)_2(PPh_3)_2]$.

Compound	ν(Ru-Cl) cm^{-1}	^{31}P-NMR (ppm)	Ref.
trans-$[RuCl_2(CO)_2(PPh_3)_2]$	328[a]		67, 72, 83
cis-$[RuCl_2(CO)_2(PPh_3)_2]$	300, 275[a]	+17.40(s)[b]	26, 67, 72, 83

[Where a = Nujol mull, b = CD_2Cl_2 and s = Singlet].

(III) Cationic Complexes of Ruthenium.

Transition metal cationic complexes containing carbonyl groups undergo nucleophilic reactions with alkoxides and amines (primary and secondary) to give alkoxycarbonyl and carbamoyl compounds[15, 22, 42]. Some of these alkoxycarbonyl compounds can go on to give organic products[7]. So the importance of transition metal cationic complexes is well recognised.

(1) $[Ru(CO)_3(L)_2]$, [where L = PPh_3, $P(4\text{-}CH_3C_6H_4)Ph_2$] reacts[78] with an equimolar quantity of a diazonium salt in dry benzene to give a series of cationic arylazo derivatives of ruthenium as in Eq. 31.

$$[Ru(CO)_3(L)_2] + ArN_2^+X \longrightarrow [Ru(N_2Ar)(CO)_2L_2]^+X^- \qquad \text{[Eq. 31]}$$

where, L = PPh_3, $P(4\text{-}CH_3C_6H_4)Ph_2$ and Ar = $4\text{-}RC_6H_4$, $2,6\text{-}R_2C_6H_3$, X = BF_4, BPh_4 and R = alkyl group.

(2) $[RuCl(CO)_2(N_2Ph)(PPh_3)_2]$ reacts with perchloric acid in ethanol to give the cationic salt[84] as in Eq. 32.

$$[RuCl(CO)_2(N_2Ph)(PPh_3)_2] + HClO_4 \xrightarrow{C_2H_5OH} [RuCl(CO)_2(HN_2Ph)_2]^+[ClO_4]^- \quad \text{[Eq. 32]}$$

(3) Aryldiazo compounds[85] of the type $[Ru(CO)_2(N_2Ph)(PPh_3)_2]^+[PF_6]^-$, have been prepared by allowing diazonium salts to react with $[Ru(CO)_3(PPh_3)_2]$.

(4) A benzene suspension of $[RuX_2(CO)_2L_2]$ reacts with the halogen acceptor $AlCl_3$ in the presence of CO to give monocationic salts of the type[44] $[RuX(CO)_3L_2]^+[AlCl_3X]^-$, where X = Cl, I, and L = PPh_3 or $P(C_6H_{11})_3$.

(5) $[\{\eta^5\text{-}C_5(CH_3)_5\}Ru(CO)_2]_2$ reacts with HBF_4 in CH_2Cl_2 at room temperature to yield the hydrido-bridge dinuclear compound, $[\{\eta^5\text{-}C_5(CH_3)_5\}_2Ru_2(H)(CO)_4]^+[BF_4]^-$ and after refluxing in propionic anhydride, $[\{\eta^5\text{-}C_5(CH_3)_5\}Ru(CO)_3]^+[BF_4]^-$ is obtained[86].

(6) When CO is bubbled through a mixture of $[(\eta^5\text{-}C_5H_5)RuCl(CO)_2]$ and $AlCl_3$ in benzene at an elevated temperature (40-50°C), it gives[42] $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]^+[AlCl_4]^-$. Reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-$ with $ClCOOCH_3$ in THF gives[42] $[(\eta^5\text{-}C_5H_5)Ru(COOCH_3)(CO)_2]$. When this is treated with gaseous HCl and $NaBPh_4$, $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]^+[BPh_4]^-$ is formed.

(7) Treatment of $[RuCl(CO)(NO)(PPh_3)_2]$ with $AgPF_6$ in a mixture of dichloromethane and acetone produces a highly reactive yellow system tentatively formulated as $[Ru(CO)(NO)(PPh_3)_2.Acetone]^+[PF_6]^-$ which readily reacts with additional ligands to produce trisubstituted derivatives[87] as in Scheme 9.

Scheme 9 :

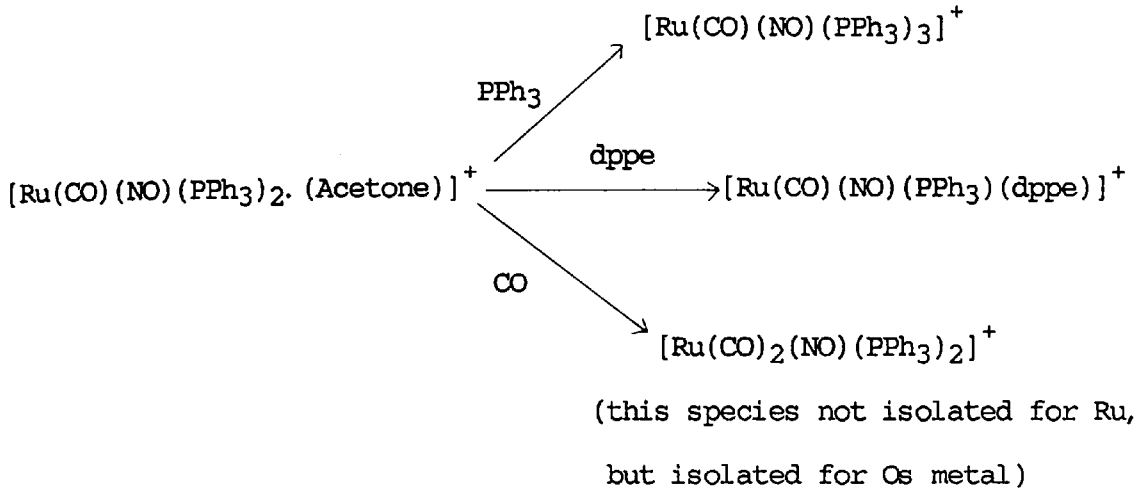


Table 9 : Literature Value of the Carbonyl Stretching Frequencies of Some Ruthenium Cationic Complexes.

Compound	ν(CO) cm^{-1}	Ref.
$[Ru(CO)_3(PPh_3)_2Cl]^+[AlCl_4]^-$	2148(w), 2082(s), 2059(sh)[a]	44
$[Ru(CO)_3(PPh_3)_2I]^+[AlCl_3I]^-$	2136(w), 2077(s), 2057(s)[b]	44
$[Ru(CO)_3\{P(C_2H_5)Ph_2\}_2]^+[AlCl_3I]^-$	2128(w), 2078(s), 2055(sh)[c]	44
$[(\eta^5\text{-}C_5H_5)Ru(CO)_3]^+[BPh_4]^-$	2125(s), 2075(s), 2066(s)[d]	42
$[Ru(4\text{-}N_2C_6H_4NO_2)(CO)_2(PPh_3)_2]^+[BF_4]^-$	2080-1980[d]	78
$[Ru(N_2C_6H_5)(CO)_2(PPh_3)_2]^+[BF_4]^-$	2060-1970[d]	78
$[Ru(4\text{-}N_2HC_6H_4NO_2)(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.H_2O$	2100-2050[d]	78
$[Ru(N_2HC_6H_5)(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.H_2O$	2090-2040[d]	78

[Where s = Strong, sh = Shoulder, w = Weak, a = KBr disc, b = THF, c = CH_2Cl_2, d = Nujol mull].

(IV) Reactions of Ruthenium Compounds in the Presence of the Nucleophiles, RONa (R = CH_3, C_2H_5, C_3H_7) and CO.

Nucleophilic attack at the carbonyl carbon of transition metal-carbon compounds is rather common. The carbon acquires an electrophilic character upon coordination to transition metals[33]. Thus the reactions of RO^- [R = CH_3, C_2H_5, iso-C_3H_7] with cationic complexes give alkoxycarbonyl compounds but, in the presence of the nucleophiles reduction can take place depending upon the temperature and the nature of the solvents used[88]. In some cases strong nucleophiles replace weak ones[6].

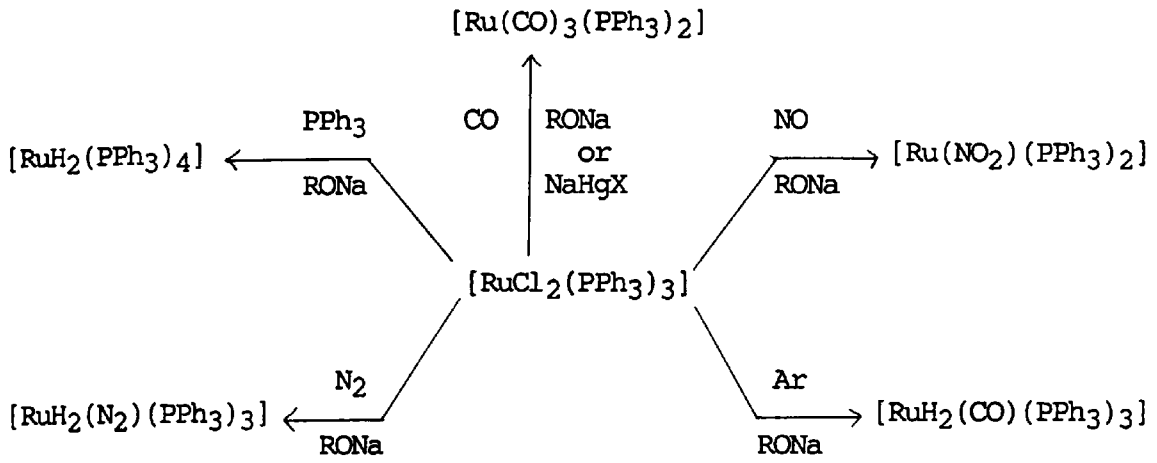
(1) Cenini et al. investigated the reaction of $[RuCl_2(PPh_3)_3]$ with sodium ethoxide and carbon monoxide in ethanol and the results are shown in Scheme 10. Within an hour of reaction the reduction product $[Ru(CO)_3(PPh_3)_2]$ is formed[88] as in Eq. 33. When the reaction is continued for a longer time then an unidentified product is formed, which is difficult to separate by crystallisation.

$$[RuCl_2(PPh_3)_3] + C_2H_5ONa + CO \xrightarrow{C_2H_5OH} [Ru(CO)_3(PPh_3)_2] \qquad \text{[Eq. 33]}$$

The reaction of $[RuCl_2(PPh_3)_3]$ in the presence of excess PPh_3 with RONa (R = C_2H_5, iso-C_3H_7) under a nitrogen atmosphere gives the yellow compound $[RuH_2(PPh_3)_4]$. Sodium alkoxides have been used as reducing agents for the synthesis of low oxidation states compounds[88].

(2) When $[RuH(CO)_2(PPh_3)_3]^+$, reacts[82] with the methoxide ion, then deprotonation of the salt takes place to give $[Ru(CO)_2(PPh_3)_3]$.

Scheme 10 : Reactions[88] of $[RuCl_2(PPh_3)_3]$ with RONa.



[Where R = C_2H_5, iso-C_3H_7 and Ar = argon]

(3) Reaction of $RuCl_3.xH_2O$ with PPh_3 and aqueous HCHO in alcoholic KOH gives the reduction product[79,89], $[Ru(CO)_3(PPh_3)_2]$.

(4) The compound $[Ru(CO)_3(PPh_3)_2]$ is formed when cis-$[RuCl_2(CO)_2(PPh_3)_2]$ reacts with CO in hot DMF in the presence of reducing agents (e.g. zinc dust)[75].

(5) Reaction of $[Ru(4\text{-}N_2C_6H_4OCH_3)(CO)_2(PPh_3)_2]^+[BF_4]^-$ with PPh_3 in the presence of C_2H_5OLi in ethanol also gives a reduction product[78], $[Ru(CO)_2(PPh_3)_3]$.

(6) When $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]^+[PF_6]^-$ is treated[42] with CH_3ONa in methanol it gives $[(\eta^5\text{-}C_5H_5)Ru(COOCH_3)(CO)_2]$.

(7) Reaction of $[Ru(CO)_3(PPh_3)_2I]^+$ with methanolic KOH solution gives the alkoxycarbonyl compound[44], $[RuI(COOCH_3)(CO)_2(PPh_3)_2]$.

(8) $[\{\eta^5\text{—}C_5(CH_3)_5\}RuX(CO)_2]$, (where X = Cl, I) reacts with sodium methoxide in benzene at room temperature to give an alkoxo compound[86], $[\{\eta^5\text{—}C_5(CH_3)_5\}Ru(OCH_3)(CO)_2]$.

(9) Reaction[90] of $[\{\eta^5\text{—}C_5(CH_3)_5\}RuCl_2]_2$ with two molar equivalents of sodium methoxide in methanol gives the ruthenium methoxo dimer, $[\{\eta^5\text{—}C_5(CH_3)_5\}Ru(\mu\text{-}OCH_3)]_2$. This reaction probably involves reduction of Ru(III) to Ru(II) via elimination of formaldehyde and hydrogen from the metal as in Eq. 34.

$$Ru(III)\text{—}OCH_3 \xrightarrow{-\ H_2C=O} Ru(III)\text{—}H \xrightarrow{-(1/2)H_2} Ru(II) \qquad \text{[Eq. 34]}$$

An attempt has been made to prepare ruthenium alkoxo compound by the reaction of $[RuHCl(PPh_3)_3]$ with sodium methoxide but investigations have shown that methoxo compounds in this system are thermally unstable and they decompose to formaldehyde, formyl and carbonyl derivatives[91].

Table 10 : Infrared Data of Some Alkoxo, Alkoxycarbonyl Compounds of Ruthenium.

Compound	ν(CO) cm^{-1}	ν(CO) cm^{-1} (alkoxycarbonyl)	Ref.
$[RuI(COOCH_3)(CO)_2(PPh_3)_2]$	2042, 1987	1651[a]	44
$[RuI(COOCH_3)(CO)_2[P(C_6H_{11})_3]_2]$	2017, 1950	1657[a]	44
$[(\eta^5\text{—}C_5H_5)Ru(CO)_2(COOCH_3)]$	2047, 1988	1660[b]	42
$[\{\eta^5\text{—}C_5(CH_3)_5\}Ru(OCH_3)(CO)_2]$	2001, 1941[c]		86

[Where a = KBr disc, b = Cyclohexane and c = C_6H_6].

(V) Carboxylato Compounds of Ruthenium.

A large number of carboxylato compounds of ruthenium have been reported [23,75,92-95], some of these have good catalytic properties.

(1) When $[Ru(CO)_3(PPh_3)_2]$ in benzene or 2-methoxyethanol is treated with an excess of ethanoic acid and the mixture refluxed, it gives cis-$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$. The compounds, $[Ru(OOCR)_2(CO)_2(PPh_3)_2]$ (where R = H, C_2H_5) are prepared from $[Ru(CO)_3(PPh_3)_2]$ and the appropriate acid in a similar way[23,92].

(2) When H_2 is bubbled through a suspension of $[RuCl_2(PPh_3)_3]$ in methanol containing two molar equivalents of a carboxylic acid salt (RCOONa), light yellow crystals of $[RuH(OOCR)(PPh_3)_3]$ are formed[94].

(3) The compound, $[RuH(OOCCH_3)(CO)(PPh_3)_2]$ is formed when ethanoic acid is added to a boiling suspension of $[RuH_2(CO)(PPh_3)_3]$ in 2-methoxyethanol[92].

Table 11 : Literature Value of the Carbonyl Stretching Frequency of Some Carboxylato Compounds of Ruthenium.

Compound	ν(CO) cm^{-1}	ν_{asy}(OCO) cm^{-1}	ν_{sy}(OCO) cm^{-1}	Ref.
cis-$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$[a]	2044, 1973	1613, 1596	1315	92
$[Ru(OOCH)_2(CO)_2(PPh_3)_2]$[b]	2055, 1994 1962	1615	1298	23
$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$[b]	2051, 2011 1991, 1964	1606, 1597	1321	23
$[Ru(OOCC_2H_5)_2(CO)_2(PPh_3)_2]$[b]	2049, 1899	1606	1267	23
$[RuCl(OOCCH_3)(CO)(PPh_3)_2]$[a]	1941	1507	1465	92
$[Ru(OOCCH_3)_2(CO)(PPh_3)_2]$[a]	1960	1630, 1517		93
$[RuH(OOCCH_3)(CO)(PPh_3)_2]$[a]	1928	1528		93

[Where a = Nujol mull and b = CCl_4].

Table 12 : ^{1}H-NMR Data of Some Carboxylato Compounds of Ruthenium[23].

Compound	$RCOO^-$ (ppm)	PPh_3 (ppm)
$[Ru(OOCH)_2(CO)_2(PPh_3)_2]$	2.34 (s)	7.46 (m), 7.72 (m)
		(18H) (12H)
$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$	1.11 (s)	7.43 (m), 7.63 (m)
		(18H) (12H)
$[Ru(OOCC_2H_5)_2(CO)_2(PPh_3)_2]$]	0.45 (t)	7.43 (m), 7.71 (m)
	1.36 (q)	(18H) (12H)

[Where s = Singlet, m = Multiplet, t = Triplet and q = Quartet and solvent = $CDCl_3$].

3.2 EXPERIMENTAL.

(i) Preparation[64] of Dichlorotris(triphenylphosphine)ruthenium(II), $[RuCl_2(PPh_3)_3]$.

Methanol (80 cm^3) was placed in a clean, dry Schlenk tube and the solvent was deoxygenated by passing nitrogen through the solvent for 5 minutes. Then, under a positive nitrogen flow, hydrated ruthenium trichloride, ($RuCl_3.3H_2O$), (1.00 g, 4.17 mmol), was added and the mixture was refluxed for 5 minutes with stirring. The solution was then allowed to cool and triphenylphosphine, (PPh_3), (6.50 g, 25.00 mmol) added. The mixture was then refluxed for 1 hour under nitrogen. The resulting reddish-brown precipitate was filtered off and washed with cold methanol, followed by diethyl ether then dried by suction. Yield = 2.80 g, (70%).

(ii) Preparation[72] of trans-Dicarbonyldichlorobis(triphenylphosphine-ruthenium(II), trans-$[RuCl_2(CO)_2(PPh_3)_2]$.

Acetone (60 cm^3) was taken in a 100 cm^3 three-necked round bottom flask and degassed by passing nitrogen through the solvent for 5 minutes. Then $[RuCl_2(PPh_3)_3]$, (2.00 g, 2.08 mmol), was added to the acetone under nitrogen. The nitrogen flow was stopped and CO passed through the solution with stirring. Within 15 minutes the reddish-brown colour disappeared and a canary-yellow precipitate was formed. The product was filtered off and washed with dry acetone, followed by diethyl ether and suction dried on the filter paper.

Yield = 1.25 g, (80%).

IR : ν(CO) at 2000 cm^{-1} (s) (KBr disc).

The literature value gives ν(CO) at 2000 cm^{-1} (Nujol mull) (Table 7).

(iii) Preparation of cis-Dicarbonyldichlorobis(triphenylphosphine)-ruthenium(II), cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

Acetone (60 cm^3) was placed in a three necked round bottom flask and degassed by bubbling nitrogen through the solvent for about 5 minutes. Then $[RuCl_2(PPh_3)_3]$, (2.00 g, 2.02 mmol), was added to the solvent under a positive nitrogen flow. The nitrogen flow was stopped and CO was passed through the solution. Within 15 minutes a canary-yellow product was formed. This was refluxed for 30 minutes to give a white precipitate. The white product was filtered off and washed with dry acetone, followed by diethyl ether. The compound was recrystallised from dichloromethane-methanol solution. Yield = 1.20 g, (77%). The melting temperature of the compound was 257-60^{o}C (decomposed). The white compound was soluble in dichloromethane, chloroform and insoluble in methanol. In the literature the solvents THF[72] and DMA[73] were used instead of acetone.

IR : ν(CO) at 2062 (s), 2000 cm^{-1} (s) (KBr disc) and ν(Ru—Cl) at 300, 275 cm^{-1} (m) (Nujol mull). The literature value gives ν(CO) at 2064, 2001 cm^{-1} (Nujol mull) (Table 7) and ν(Ru—Cl) at 300, 275 cm^{-1} (Nujol mull) (Table 8).

^{31}P-NMR : +17.40 ppm (s) (in $CDCl_3$). The literature value is +17.40 ppm (Table 8).

(iv) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$ (1:2 molar ratio) : Synthesis of cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$, Compound (I).

In a Schlenk tube dry dichloromethane (40 cm^3) was taken and degassed as described in Sec. 2. Then, under a positive nitrogen flow, cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.60 g, 0.80 mmol) was added. To this solution $AgBF_4$, (0.31 g, 1.59 mmol) was added. The Schlenk tube was covered with aluminium foil and the resulting solution stirred for 10 hours under nitrogen at room temperature. The white precipitate formed was filtered through kieselguhr under nitrogen and the solvent removed from the filtrate on a vacuum line to give a white solid. Yield = 0.45 g, (60%). The melting temperature of the compound was 200°C (decomposed). The solid was soluble in dichloromethane, acetone, chloroform and methanol. This reaction could also be carried out in acetone. The compound could also be prepared from trans-$[RuCl_2(CO)_2(PPh_3)_2]$ in dichloromethane and the reaction time was only 2-3 hours.

IR : ν(CO) at 2081 (s), 2024 cm^{-1} (s) and $\nu(BF_4^-)$ at 1091 cm^{-1} (b) (KBr disc).

^{1}H-NMR : (7.40-7.80) ppm (m, 30H) and 5.23 ppm (s, 2H) (in $CDCl_3$).

^{31}P-NMR : +25.50 ppm (s) (in $CDCl_3$).

When the reaction is carried out in acetone then the spectrum of the product was :

IR : ν(CO) at 2090 (s), 2030 cm^{-1} (s) and 1660 cm^{-1} (m) for coordinated acetone and $\nu(BF_4^-)$ at 1091 cm^{-1} (b) (KBr disc).

Analysis for $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ = $C_{39}H_{32}B_2Cl_2F_8O_2P_2Ru$

	C%	H%
Found	50.1	4.0
Calculated	49.8	3.4

(v) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$ (1:2 molar ratio) in the Presence of CO : Synthesis of $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$, Compound (II).

Dichloromethane (25 cm^3) was placed in a Schlenk tube and degassed by passing nitrogen through it. Then cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.40 g, 0.53 mmol) was added under a positive nitrogen flow and to this solution $AgBF_4$ (0.21 g, 1.06 mmol) was added. The Schlenk tube was then covered with aluminium foil and the nitrogen replaced with CO, which was then bubbled through the solution for 6 hours at room temperature. Some white precipitate formed, which was filtered off through kieselguhr under CO. The solvent was evaporated from the filtrate on a vacuum line leaving a white solid. Recrystallisation of this product from dichloromethane and hexane under CO, afforded a white solid. Yield = 0.28 g, (60%). The compound was soluble in dichloromethane, chloroform, methanol and acetone.

IR : ν(CO) at 2151 (w), 2086 (s), 2025 cm^{-1} (s) and $\nu(BF_4^-)$ at 1091 cm^{-1} (b) (KBr disc).

^{31}P-NMR : +22.50 ppm (s) (in $CDCl_3$).

(vi) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$ (1:1 molar ratio) : Synthesis of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Compound (III).

Cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.40 g, 0.53 mmol) was dissolved in degassed dichloromethane (30 cm^3) under a nitrogen atmosphere. To this solution, $AgBF_4$ (0.11 g, 0.56 mmol) was added and the Schlenk tube covered with aluminium foil. The resultant suspension was stirred for 7 hours at room temperature. This was filtered through kieselguhr under nitrogen and the solvent was removed on a vacuum line whereupon a pale yellow solid was obtained. The solid was recrystallised from dichloromethane and hexane under nitrogen to yield white crystals. Yield = 0.28 g (62%). The melting temperature of the compound was 208-210^oC (decomposed). The compound was soluble in methanol, acetone, dichloromethane. The compound could also be prepared from the trans-compound by same method.

IR : ν(CO) at 2070 (s), 2006 cm^{-1} (s) and $\nu(BF_4^-)$ at 1090 cm^{-1} (b) (KBr disc).

^{1}H-NMR : (7.30-7.80) ppm (m, 30H) and 5.28 ppm (s, 1H) (in $CDCl_3$).

^{31}P-NMR : +24.50 ppm (s) (in $CDCl_3$)

Analysis for $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2) = C_{38.5}H_{31}BCl_2F_4O_2P_2Ru$

	C%	H%
Found	54.0	3.9
Calculated	54.6	3.7

(vii) Reaction of Compound (I) with CH_3ONa in the Presence of CO : Synthesis of cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, Compound (IV).

The solid, cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.40 g, 0.42 mmol) was dissolved in dry methanol (15 cm^3) under nitrogen. To this solution freshly prepared sodium methoxide solution (excess, ca. 2.20 mmol in 10 cm^3 of methanol) was added by a syringe under nitrogen. The nitrogen was replaced by CO, which was bubbled through the solution. Within 15 minutes a white precipitate started to form, the mixture was stirred for 1 hour. The product was filtered off, washed with dry methanol, then recrystallised from benzene and hexane under nitrogen to give a white solid. Yield = 0.20 g, (60%). The product was soluble in dichloromethane, chloroform, acetone, benzene and insoluble in methanol. The solid compound was stable in air, but in solution in air decomposed. The melting temperature of the compound was 135-140^oC.

IR : ν(CO) at 2033 (s), 1978 cm^{-1} (s) and 1654 (m), 1637 cm^{-1} (sh) for the methoxycarbonyl bands and $\nu(C—OCH_3)$ at 1009 cm^{-1} (m) (KBr disc). ν(CO) at 2032 (s), 1977 cm^{-1} (s) and 1653 (m), 1637 cm^{-1} (sh) for the methoxycarbonyl bands and $\nu(C—OCH_3)$ at 1008 cm^{-1} (m) (Nujol mull).
^{1}H-NMR : 2.80 ppm (s, 6H) and (7.30-7.80) ppm (m, 30H) (in $CDCl_3$).
^{31}P-NMR : +30.50 ppm (s) (in $CDCl_3$).

Analysis for $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2] = C_{42}H_{36}O_6P_2Ru$

	C%	H%
Found	63.0	4.5
Calculated	63.0	4.5

(viii) Reaction of Compound (II) with CH_3ONa in the Presence of CO : Synthesis of cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, Compound (IV).

The compound (II), $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$ (0.15 g, 0.17 mmol) was dissolved in dry methanol (7 cm^3) under a nitrogen atmosphere. To this solution freshly prepared excess sodium methoxide (ca. 1.10 mmol in 5 cm^3 of methanol) solution was added. Then nitrogen was removed and CO passed through the solution. Within 15 minutes a white precipitate was formed. The precipitate was filtered off and washed with methanol. Recrystallisation from benzene and hexane under nitrogen gave a white solid. Yield = 0.09 g, (65%). The infrared and NMR spectra were as described for compound (IV).

(ix) Reaction of Compound (I) with CO and Methanol in the Presence of Organic Base [e.g. $N(C_2H_5)_3$] : Synthesis of cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, Compound (IV).

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.40 g, 0.42 mmol) was dissolved in methanol (20 cm^3) under a nitrogen atmosphere and to this solution excess $N(C_2H_5)_3$ (ca. 0.50 g) was added. Carbon monoxide was then bubbled through the solution. Within 15 minutes a white precipitate formed. The product was filtered off and washed with excess methanol. Recrystallisation from benzene and hexane under nitrogen gave a white solid. Yield = 0.20 g (60%). Infrared and NMR spectra were as for compound (IV).

(x) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with CH_3ONa under CO high Pressure : Synthesis of cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, Compound (IV).

In a pressure apparatus (as in Fig. 9) cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.25 g, 0.33 mmol) and freshly prepared excess sodium methoxide (ca. 2.20 mmol, in 10 cm^3 of methanol) solution was added. The apparatus was flushed with nitrogen and finally charged with 10 atmospheres of CO for 64 hours. The CO pressure was then released. The resulting solid product was filtered off and washed with excess dry methanol and recrystallised from benzene and hexane. This gave white crystals. Yield = 0.18 g, (70%). The infrared and NMR spectra were as described for compound (IV).

(xi) Reaction of Compound (III) with CH_3ONa in the Presence of CO : Synthesis of $[RuCl(COOCH_3)(CO)_2(PPh_3)_2]$, Compound (V).

Compound (III), $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, (0.40 g, 0.47 mmol) was dissolved in dry degassed methanol (20 cm^3) under nitrogen and the solution cooled to -10^oC. Freshly prepared sodium methoxide solution (ca. 0.47 mmol in 1 cm^3 of methanol) was added and CO passed through the solution. Within 15 minutes a white precipitate formed, this was filtered off and washed with excess methanol. Yield = 0.18 g, (50%). The melting temperature of the product was $160-162^oC$ (decomposed).

IR : ν(CO) at 2042 (s), 1986 cm^{-1} (s) and 1655 cm^{-1} (m) for the methoxycarbonyl band (Nujol mull).

^{1}H-NMR : 2.88 ppm (s, 3H) and (7.40-7.80) ppm (m, 30H) (in $CDCl_3$).

Analysis for $[RuCl(COOCH_3)(CO)_2(PPh_3)_2] = C_{40}H_{33}ClO_4P_2Ru$

	C%	H%
Found	61.8	4.4
Calculated	61.8	4.3

When the reaction was carried out at room temperature with excess sodium methoxide then compound (IV) was obtained instead of compound (V).

(xii) Preparation[44] of $[RuCl(CO)_3(PPh_3)_2]^+[AlCl_4]^-$.

To sodium dried benzene (50 cm^3), cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.75 g, 1.00 mmol) and a halogen acceptor, $AlCl_3$ (0.66 g, 5.00 mmol), were added under a CO atmosphere. The suspension was stirred under CO until a clear solution resulted. The clear solution was partially evaporated, and CO saturated diethyl ether added. A white precipitate formed. Excess $AlCl_3$ was removed by rapidly washing with diethyl ether. The white solid was filtered off and dried.

IR : v(CO) at 2147 (w), 2083 (s) and 2055 cm^{-1} (sh) (KBr disc).
The literature value[44] of v(CO) at 2148, 2082 and 2059 cm^{-1} (KBr disc) (Table 9).

(xiii) Reaction of $[RuCl(CO)_3(PPh_3)_2]^+[AlCl_4]^-$ with CH_3ONa : Synthesis of $[RuCl(COOCH_3)(CO)_2(PPh_3)_2]$, Compound (V).

$[RuCl(CO)_3(PPh_3)_2]^+[AlCl_4]^-$, (0.25 g, 0.27 mmol) was dissolved in dry methanol (15 cm^3) at -10°C under nitrogen and to this solution freshly prepared sodium methoxide solution (1 cm^3, ca. 0.45 mmol) was added

quickly at -10°C. Within 15 minutes white crystals were formed. The product was filtered off and washed with excess methanol. Yield = 0.15 g, (70%).

The infrared spectrum was similar to that of compound (V). The compound (V) prepared in this process contained a trace amount of $[RuCl_2(CO)_2(PPh_3)_2]$ as identified by infrared spectroscopy.

(xiv) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with $NaBH_4$.

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.20 g, 0.21 mmol) was dissolved in dry ethanol (10 cm^3) under nitrogen. Then $NaBH_4$ solution (0.10 g, 2.60 mmol in 10 cm^3 dry ethanol) was added. A fast reaction occurred giving brown crystals. The mixture was stirred for 30 minutes and the crystals were filtered off and washed with excess ethanol followed by hexane. Yield = 0.09 g, (65%). The melting temperature of the compound was 166-167°C.

IR : ν(CO) at 2015 (s), 1970 cm^{-1} (s) and ν(Ru-H) at 1870 (m) and 1820 cm^{-1} (m) (Nujol mull).

^{1}H-NMR : -4.50 ppm (t, J_{P-H} = 19.8 Hz) and (7.20—7.90) ppm (m) (in $CDCl_3$).

(xv) An Attempt to Prepare cis-$[RuH_2(CO)_2(PPh_3)_2]$ from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ and $NaBH_4$ in Ethanol.

To a suspension of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.10 g, 0.13 mmol) in 10 cm^3 of ethanol, $NaBH_4$ solution (0.05 g, 1.30 mmol, in 5 cm^3 of ethanol) was

added and the mixture stirred for 6 hours at room temperature. The suspension was filtered off and washed with excess ethanol. The infrared spectrum indicated only the presence of the starting material, i.e. cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

(xvi) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with conc. HCl.

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.10 g, 0.11 mmol) was dissolved in methanol (5 cm^3) under nitrogen and to this solution conc. HCl (ca. 0.20 g) was added dropwise. Within 10 minutes a white precipitate was formed. This was filtered off and washed with excess methanol, then dried on the filter paper. The melting temperature of the product was 257°C.

IR : ν(CO) at 2062 (s), 2000 cm^{-1} (s) and no band for $\nu(BF_4^-)$ (KBr disc).
^{31}P-NMR : +17.40 ppm (s) (in $CDCl_3$).

(xvii) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with KI.

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.20 g, 0.21 mmol) was dissolved in methanol (10 cm^3) under nitrogen and to this a KI solution (0.10 g, 0.60 mmol, in 5 cm^3 of methanol) was added and the resulting mixture stirred. Within 15 minutes the white colour changed and yellow crystals were formed. Then the crystals were filtered off and washed with excess methanol. Recrystallisation from dichloromethane

and hexane gave yellow crystals. The melting temperature of the yellow crystals was 320°C.

IR : ν(CO) at 2045 (s), 1990 cm^{-1} (s) and no band for $\nu(BF_4^-)$ (KBr disc) and ν(CO) at 2055 (s), 1994 cm^{-1} (s) (in $CHCl_3$).

Test for I^- : A test for iodide was performed by adding a solution of $AgNO_3$ to the sodium fusion solution of the compound. It gave a yellow coloured precipitate of AgI, which was insoluble in NH_3 solution.

(xviii) An Attempt to Prepare cis-$[RuI_2(CO)_2(PPh_3)_2]$ from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with KI.

The compound, cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.10 g, 0.13 mmol) was stirred in methanol (5 cm^3) and to this suspension a KI solution (0.10 g, 0.60 mmol in 5 cm^3 of methanol) was added. The mixture was stirred for 6 hours. Then the suspension was filtered and washed with methanol. The infrared spectrum indicated only the starting material, i.e. cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

(xix) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CH_3COONa.

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.20 g, 0.21 mmol) was dissolved in methanol (10 cm^3) and to this sodium ethanoate solution (0.10 g, 1.20 mmol, in 5 cm^3 of methanol) was added and stirred under CO for 1 hour. White crystals were formed. These were filtered off and

washed with methanol. The melting temperature of the compound was 214-216^{o}C.

IR : ν(CO) at 2042 (s), 1980 cm^{-1} (s) and ν_{asy}(OCO) 1613 (m), 1596 cm^{-1} (m) and ν_{sy}(OCO) 1316 cm^{-1} (m) (KBr disc).

^{1}H-NMR : 1.10 ppm (s, 6H) and (7.30-7.80) ppm (m, 30H) (in $CDCl_3$).

If the reaction was performed in the absence of CO, then the product showed infrared bands as follows ,

IR : ν(CO) at 2042 (m), 1941 cm^{-1} (b) (KBr disc).

(xx) An Attempt to Prepare cis-$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$ from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ and CH_3COONa.

Excess CH_3COONa solution (0.10 g, 1.20 mmol) in methanol (5 cm^3) was added to a suspension of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.20 g, 0.26 mmol) in methanol (15 cm^3). The mixture was refluxed for 6 hours. No colour change occurred. The mixture was filtered off and washed with methanol. The infrared spectrum indicated only the starting complex, cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

(xxi) Reaction of Compound (IV), cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ with conc. HCl.

To the suspension of compound (IV), $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ (0.10 g, 0.13 mmol) in methanol (5 cm^3), conc. HCl (0.20 g) was added. Immediately the suspension disappeared and within 10 minutes white crystals formed. The crystals were filtered off and washed with methanol

and finally with petroleum ether (60-80°C). Yield = 0.07 g, (75%).

IR : ν(CO) at 2062 (s), 2000 cm^{-1} (s) and no methoxycarbonyl band (KBr disc).

^{31}P-NMR : +17.40 ppm (s) (in $CDCl_3$).

(xxii) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa under Reflux in Methanol in the Presence of CO.

To the suspension of cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.20 g, 0.26 mmol) in methanol (10 cm^3), freshly prepared excess sodium methoxide solution (ca. 2.20 mmol in 10 cm^3 of methanol) was added under nitrogen. The nitrogen flow was stopped and CO was then passed through the mixture, which was refluxed for 1 hour. Yellow crystals were formed. The product was filtered off and washed with excess methanol followed by petroleum ether (60-80°C). Yield = 0.15 g. The compound could also be prepared from trans-$[RuCl_2(CO)_2(PPh_3)_2]$ under exactly the same conditions.

IR : ν(CO) at 1897 cm^{-1} (s) (KBr disc).

^{31}P-NMR : +55.35 ppm (s) (in $CDCl_3$).

(xxiii) Reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa under Reflux in Methanol.

To the suspension of cis-$[RuCl_2(CO)_2(PPh_3)_2]$, (0.20 g, 0.26 mmol) in methanol (10 cm^3) freshly prepared excess sodium methoxide solution (ca. 2.20 mmol in 10 cm^3 of methanol) was added under nitrogen. The resulting suspension was refluxed. Within 30 minutes an orange-yellow coloured

precipitate formed. This was filtered off and washed with excess methanol followed by petroleum ether. Yield = 0.15 g.

IR : ν(CO) at 1971 (s), 1941 (w), 1900 (s) and 1878 cm^{-1} (w) (KBr disc).

(xxiv) Reaction of trans-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa in Methanol under Reflux.

To the suspension of trans-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.20 g, 0.26 mmol) in methanol (10 cm^3) freshly prepared excess sodium methoxide solution (ca. 2.20 mmol in 10 cm^3 of methanol) was added under nitrogen. The mixture was refluxed for 2 hours. The yellow crystals which were formed, were filtered off and washed with excess methanol. Yield = 0.16 g.

IR : ν(CO) 1941 (s), 1897 cm^{-1} (s) (KBr disc).

3.3 RESULTS AND DISCUSSION OF RUTHENIUM COMPOUNDS.

The starting materials $[RuCl_2(PPh_3)_3]$, trans-$[RuCl_2(CO)_2(PPh_3)_2]$ and cis-$[RuCl_2(CO)_2(PPh_3)_2]$ have been prepared [Sec. 3.2(i, ii, iii) respectively] by literature procedures[64, 72, 73]. However, in the present work cis-$[RuCl_2(CO)_2(PPh_3)_2]$ has been prepared in acetone instead of THF[72] or DMA[73]. The cis-compound in the present work shows ν(CO) at 2062, 2000 cm^{-1} (KBr disc, the spectrum is in Appendix-1) and the ν(Ru-Cl) at 300, 275 cm^{-1} (Nujol mull). The ^{31}P-NMR shows a singlet at +17.40 ppm in $CDCl_3$ (Appendix-2). All the spectral values are consistent with the literature values [Table 7 and 8]. The configurations of cis- and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ are shown in Fig. 11. The prefix refers to the configuration of carbonyl groups. In the present work only relevant bands in the infrared spectra of the compounds have been discussed, i.e. carbonyls, alkoxycarbonyls and (BF_4^-) bands. The bands for (P-aryl) or (P-alkyl) are approximately in the same region for the starting materials and for the prepared compounds, the ν(P-aryl) band is in the region 1430-1435 cm^{-1} (KBr disc)[96]. Throughout the text known compounds are named, as they are named in the literature for easier reference. Only the novel compounds prepared have been given systematic IUPAC names which refer to the suggested structures of the compounds.

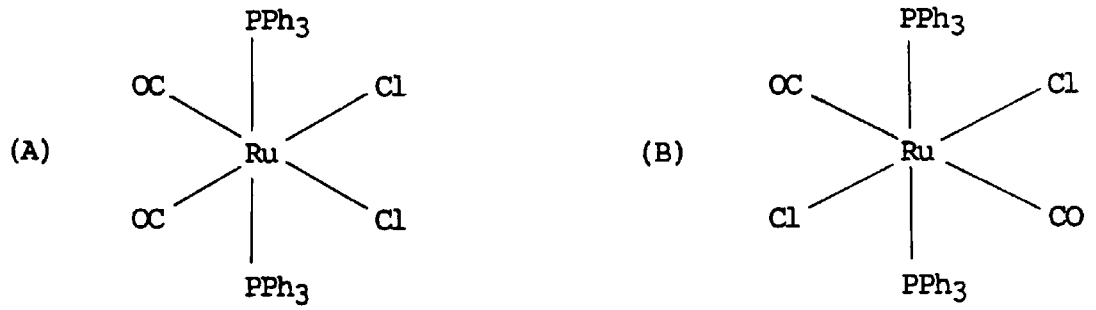


Fig. 11 : (A) Structure of cis- and (B) structure of trans-$[RuCl_2(CO)_2(PPh_3)_2]$.

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the $\nu(BF_4^-)$ value suggests that the (BF_4^-) anion is free in the compound, not coordinated[98].

The ^{1}H-NMR spectrum of the compound (I), (Fig. 13) shows a multiplet at (7.40-7.80) ppm, (30H) representing the aromatic protons of the coordinated PPh_3 and a singlet at 5.23 ppm, (2H) for protons of dichloromethane. The ^{31}P-NMR spectrum (Fig. 14) shows a singlet at +25.50 ppm.

The compound (I) is an unsaturated 14-electron species. Therefore, coordination or solvation of CH_2Cl_2 is needed to stabilise the compound as a whole. In the literature this type of 14-electron species of ruthenium, such as $[RuCl_2(CO)_2(solvent)]$ has been proposed as an intermediate[99,100]. A large number of catalytic reactions[94,101] postulate such four coordinated ruthenium(II) species as intermediates; i.e. the catalysis proceeds through 14-electron species. Also, a 12-electron species of ruthenium has been proposed as the red solution of $[Ru(PPh_3)_3]^{2+}[BF_4]^-_2$, which is prepared from the reaction of $[RuCl_2(PPh_3)_3]$ with $AgBF_4$ in alcohol[70]. When the present reaction was carried out in a polar solvent like acetone, it gave a product which shows two strong carbonyl bands at 2090 (s), 2030 cm^{-1} (s) and a medium band at 1660 cm^{-1} (m). The band at 1660 cm^{-1} is attributed to the coordination of acetone[102,103]. A broad band at 1091 cm^{-1} is attributed[97, 98] to $\nu(BF_4^-)$. When this is treated with a non-oxygen containing solvent like dichloromethane it gave the compound (I). In the literature[87] a solvent coordinated ruthenium compound, tentatively formulated as $[Ru(CO)(NO)(PPh_3)_2.(Acetone)]^+[PF_6]^-$ has been reported. Its preparation is described in Sec. 3.1(III). Additionally, solvent coordinated 14-electron cationic complexes of rhodium are also well

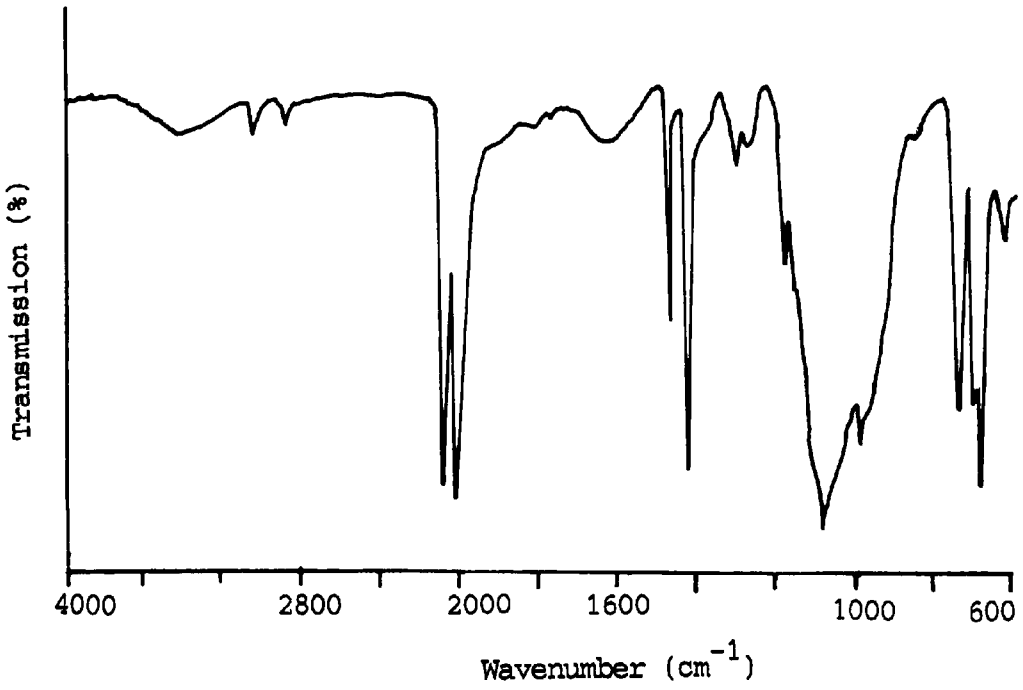

Fig. 12 : Infrared spectrum of cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (KBr disc)

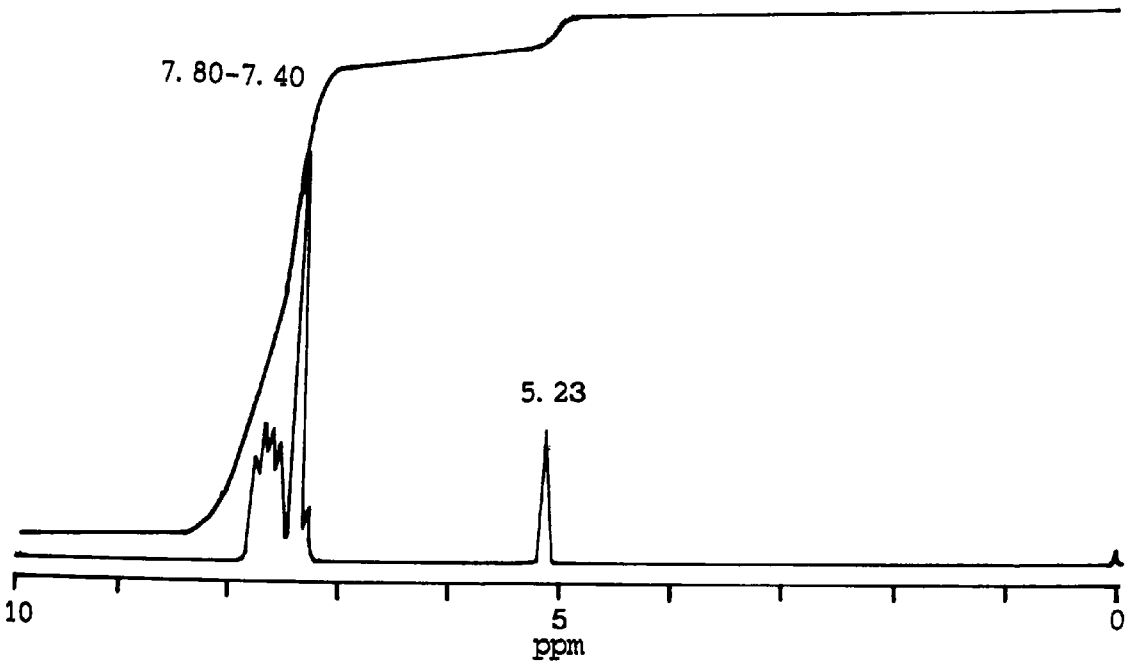

Fig. 13 : ^{1}H-NMR spectrum of cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (in $CDCl_3$, TMS).

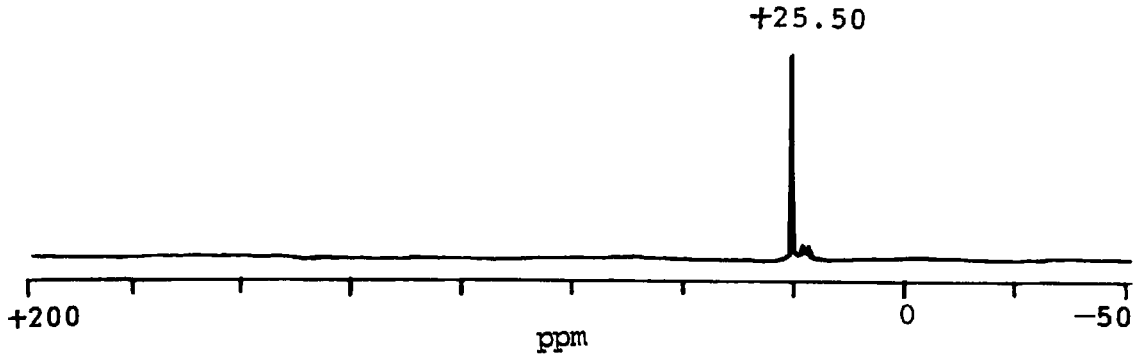

Fig. 14 : ^{31}P-NMR spectrum of cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (in $CDCl_3$).

known[102, 104] e.g. $[Rh(PPh_3)_3 .S]^+$, where S = acetone. When $[Rh(PPh_3)_3.S]^+[ClO_4]^-$ is recrystallised in a non-oxygen containing solvent like CH_2Cl_2 it gives the lattice solvated species[102], $[Rh(PPh_3)_3]^+[ClO_4]^-.CH_2Cl_2$. The literature also shows that when cationic complexes are prepared in dichloromethane solvent, sometimes dichloromethane coordinate compound forms[105, 106]. Sunkel et al.[106] reported that coordination may have a small ^{1}H-NMR chemical shift from the signal for free dichloromethane, but no values were mentioned. At -60°C they observed a single resonance for the coordinated and free dichloromethane, where two signals might have been expected. They concluded that the signals overlapped to form one broad resonance.

The spectral data and analysis of the compound (I) are consistent with the formula cis-$[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$.

O)(NO)$(PPh_3)_3]^+[PF_6]^-$ where M = Ru and Os. These compounds were ared from the yellow system tentatively formulated as O)(NO)$(PPh_3)_2$.(Acetone)$]^+[PF_6]^-$, described in Sec. 3.1(III).

(ii ound (I) when treated with CO gave compound (II). If nitrogen is pho led through the solution of compound (II), it does not form compound (as shown by no change in the infrared spectrum). The suggested The on is because it forms a more stable 16-electron species from the rat able 14-electron species. Many 16-electron species of ruthenium are The le[107], e.g. $[RuCl_2(PPh_3)_3]$.

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Synthesis of $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$, Tricarbonylbis(triphenylphine)ruthenium(II) tetrafluoroborate, Compound (II).

reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$ in a (1:2) molar o in the presence of CO [Sec. 3.2(v)] gave the white compound (II).

infrared spectrum (Fig. 15) of the compound (II) gives three bands 2151 (w), 2086 (s) and 2025 cm^{-1} (s) for the carbonyl groups and a d band[97,98] at 1091 cm^{-1} for $\nu(BF_4^-)$. There are no bands[67,72,83] een 400-250 cm^{-1} indicating no (Ru-Cl) bond. Three carbonyl groups dinated to ruthenium[44] shows three carbonyl stretching frequencies

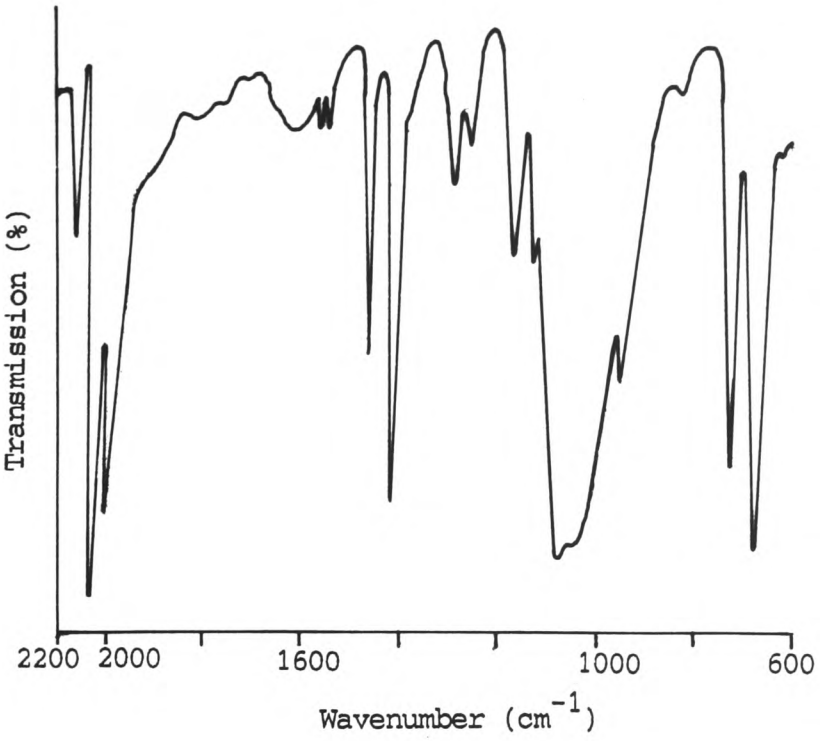

Fig. 15 : Infrared spectrum of $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$ (KBr disc).

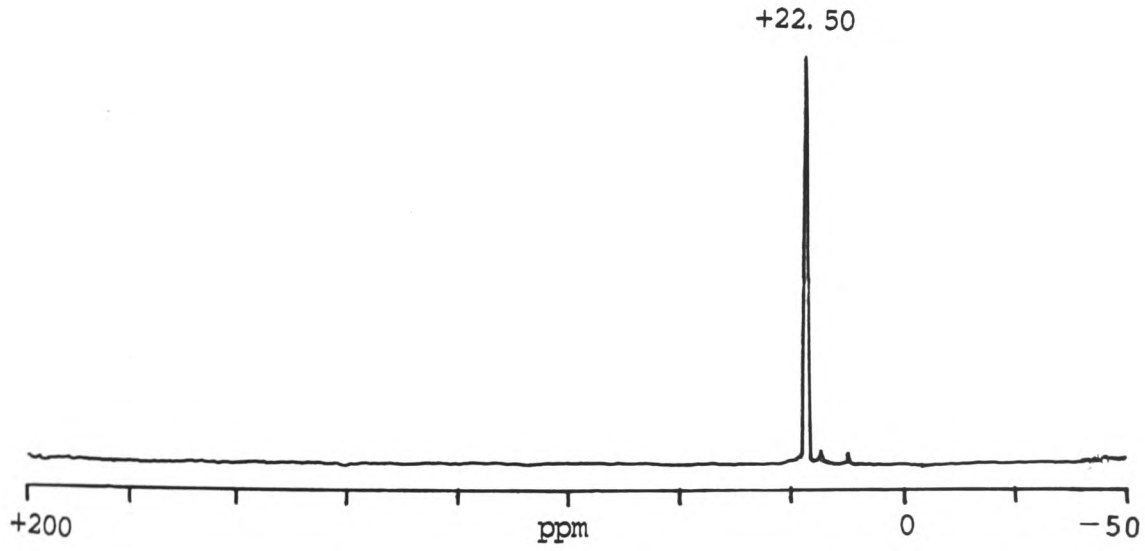

Fig. 16 : ^{31}P-NMR spectrum of $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$ (in $CDCl_3$)

The structure of the complex may be either square-pyramidal [Fig. 17(A)] or trigonal bipyramidal [Fig. 17(B)]. Both structures have C_s symmetry. The unoccupied octahedral site of a square-pyramidal configuration may be blocked by some bigger group, e.g. in $[RuCl_2(CO)(PCy_3)_2]$, it is occupied by a cyclohexyl group[108]. In the present case such blocking by a smaller phenyl group may be less probable. The structure could be confirmed by X-ray crystallography.

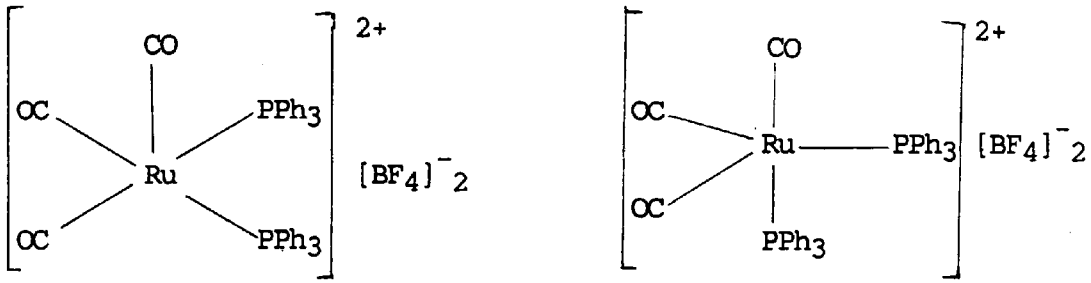

Fig. 17 : Structure of $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$, (A) Square-pyramidal and (B) Trigonal-bipyramidal.

(iii) Synthesis of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Dicarbonylchlorobis(triphenylphosphine)ruthenium(II) tetrafluoroborate dichloromethane solvate, Compound (III).

The compound (III), $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ has been prepared by the reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with $AgBF_4$ in a 1:1 molar ratio [Sec. 3.2(vi)]. The compound is characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 18) of the compound (III) shows two strong carbonyl stretching frequencies at 2070 and 2006 cm^{-1} and a broad

band[97,98] at 1090 cm^{-1} for $v(BF_4^-)$. The carbonyl stretching frequencies are at higher frequencies compared with the starting material, again, indicating a cationic complex has been formed [42,44,78,85]. Compound (III) shows v(CO) at a lower frequency region as compared to the compound (I), [Sec. 3.2(iv)] where the reaction has been carried out in 1:2 molar ratio. From here it is assumed that a monopositive complex has been formed. This compound shows two carbonyl bands indicating they are cis to each other[87,109]. All the reported five coordinated ruthenium monopositive compounds[78,85] (Table 9) have v(CO) in the range of 1980-2080 cm^{-1} and the compound (III) has a reasonable agreement with these values. The far-infrared spectrum shows a band at 310 cm^{-1} for v(Ru-Cl) (CsI disc).

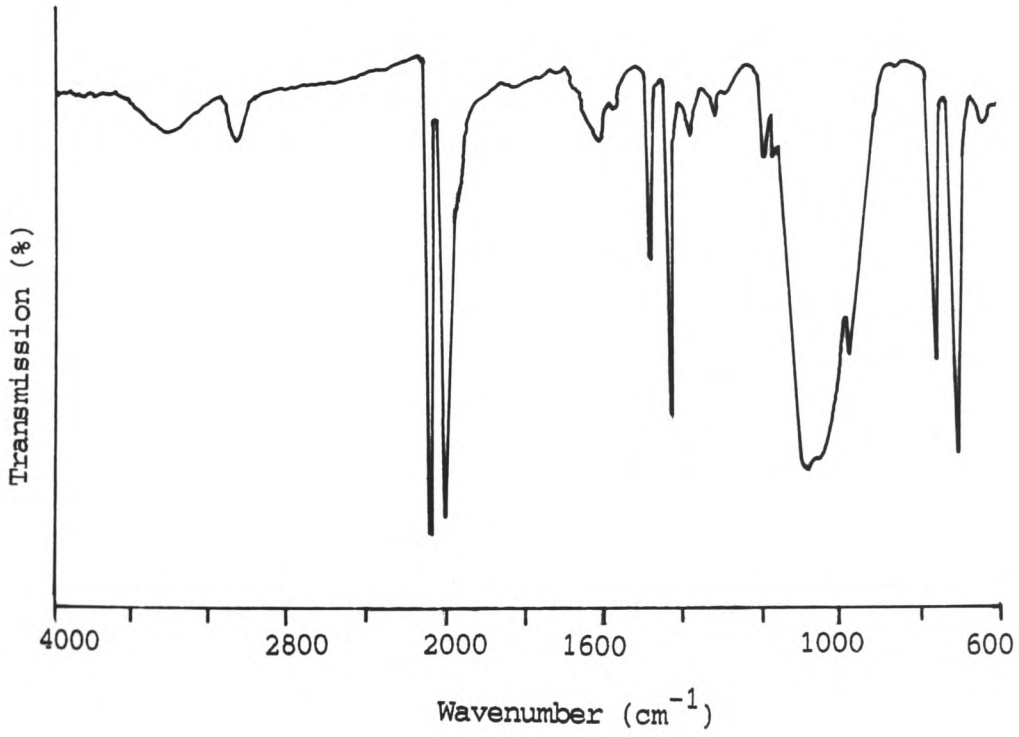

Fig. 18 : Infrared spectrum of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (KBr disc).

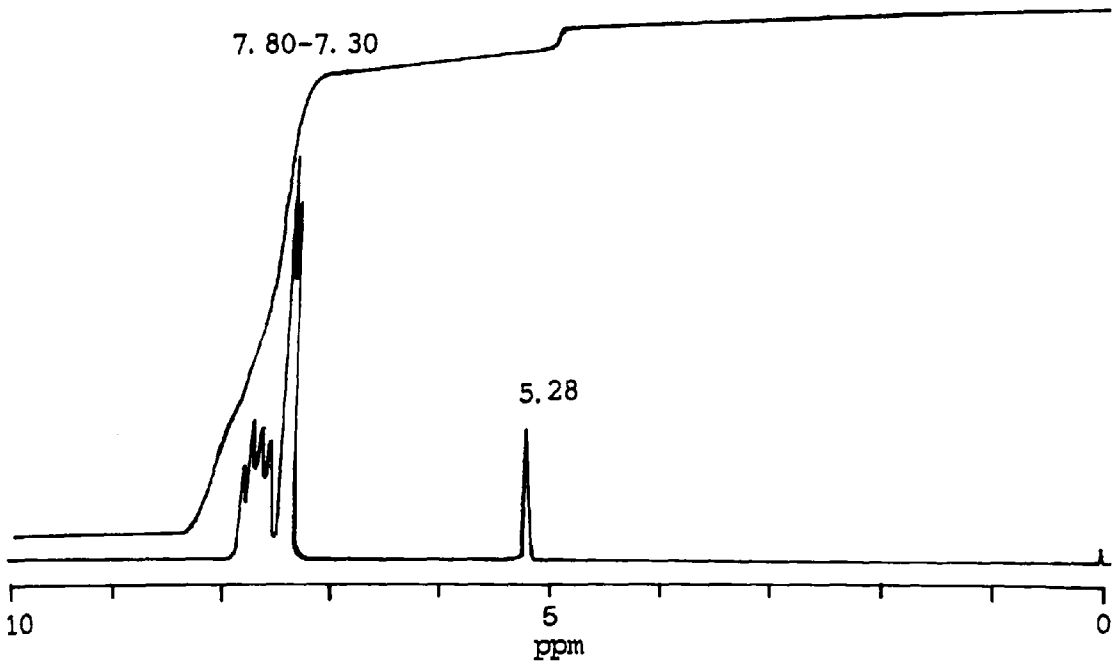

Fig. 19 : ^{1}H-NMR spectrum of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (in $CDCl_3$, TMS).

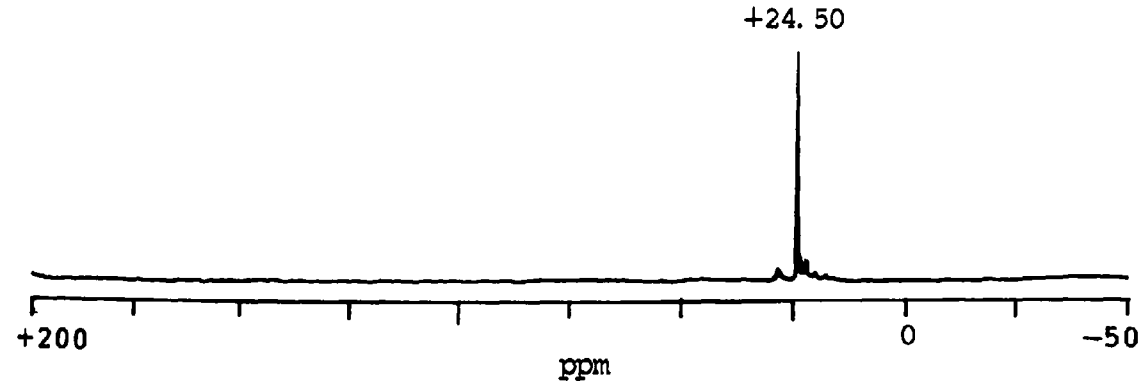

Fig. 20 : ^{31}P-NMR spectrum of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (in $CDCl_3$).

The ^{1}H-NMR spectrum (Fig. 19) of the compound shows a multiplet at (7.30-7.80) ppm (30H) for the aromatic protons and a singlet at 5.28 ppm (1H) for protons of the weakly coordinated or solvated dichloromethane[105, 106], which may stabilise the compound as a whole. The ^{31}P-NMR spectrum (Fig. 20) shows a singlet at +24.50 ppm.

From infrared, ^{1}H-NMR and ^{31}P-NMR spectroscopy and analysis, the five coordinated compound (III) may be formulated as $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ and the structure of the compound may be either square pyramidal (C_s symmetry) as in Fig. 21(A) or trigonal bipyramidal (C_{2v} symmetry) as in Fig. 21(B).

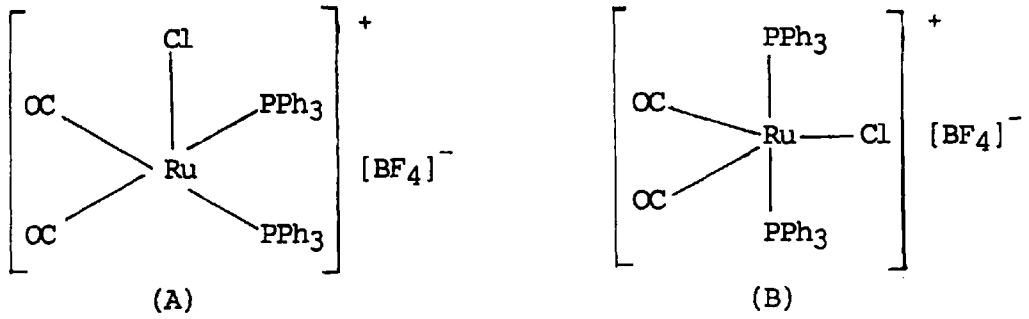

Fig. 21 : Structure of $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, (A) Square pyramidal and (B) Trigonal bipyramidal.

Johnson and Segal reported[87] that a five coordinate ruthenium compound, $[Ru(CO)_2(NO)(PPh_3)_2]^+[PF_6]^-$ shows two strong carbonyl bands at 2065 and 2014 cm^{-1}. The proposed structure of this compound is trigonal bipyramidal and the nitrosyl group (NO) is linearly bonded and located in the plane of the trigonal bipyramid as compared with the compound $[Os(CO)_2(NO)(PPh_3)_2]^+[ClO_4]^-.CH_2Cl_2$, whose structure has been characterised[109] by X-ray crystallography. Pierpont et al.[110] reported that the crystal structure of acetone coordinated

$[Ru(NO)(dppe)_2]^+[BPh_4]^-$ possess a trigonal bipyramidal structure and the nitrosyl group (NO) is linearly bonded and located in the plane of the trigonal bipyramid. The structure of these compounds and the present compound (III) may be similar. However, the structure of compound (III) could only be confirmed by X-ray crystallography.

(iv) Synthesis of cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, Dicarbonyldi(methoxycarbonyl)bis(triphenylphosphine)ruthenium(II), Compound (IV).

The compound (IV), cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ has been formed by the reaction of compound (I) and compound (II) with sodium methoxide in the presence of CO [Sec. 3.2{(vii), (viii)} respectively]. Compound (IV) is also formed from the reaction of compound (I) with CO and methanol in the presence of organic bases [e.g. $N(C_2H_5)_3$] [Sec. 3.2(ix)]. The same compound (IV) has also been formed by the reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with sodium methoxide under CO at high pressure [Sec. 3.2(x)]. The compound has been characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 22) of the compound (IV) shows two strong bands at 2033, 1978 cm^{-1} in the carbonyl region. The bands at 1654 (m) and 1637 cm^{-1} (sh) are attributed to the methoxycarbonyl groups [42,44]. Also, a band at 1009 cm^{-1} (m) is due[22] to $\nu(C—OCH_3)$. The band at 2932 cm^{-1} (m) represents the $\nu(C—H)$, stretching frequency of the methoxycarbonyl group. The frequencies of the carbonyl and methoxycarbonyl bands of the compound are in good agreement with a large number of alkoxycarbonyl compounds[6,22,42,44] (Table 10).

The ^{1}H-NMR spectrum of the compound (Fig. 23) shows a singlet at 2.80 ppm, this is assigned to the methyl protons (6H) of the methoxycarbonyl group and a multiplet at (7.30-7.80) ppm assigned to the aromatic protons (30H) of the PPh_3. The signal for methyl protons at 2.80 ppm is in good agreement with the literature values of the methoxycarbonyl compounds[42,87]. The ^{31}P-NMR spectrum of the compound (Fig. 24) shows a singlet at +30.50 ppm, this is assigned to the phosphorus atoms in a trans-position[26].

The spectral data and analysis of the compound (IV) are consistent with the formula cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$. The compound (I) gives compound (IV) in the presence of organic bases [e.g. $N(C_2H_5)_3$] and CO in methanol [Sec. 3.2(ix)]. Here, the base abstracts a proton from methanol to generate the nucleophile, CH_3O^-, which produces the alkoxycarbonyl compound[7] in the presence of CO as in Eq. 35 and 36.

$$CH_3OH + N(C_2H_5)_3 \longrightarrow CH_3O^- + [NH(C_2H_5)_3]^+ \qquad \text{[Eq. 35]}$$

$$[Ru(CO)_2(PPh_3)_2]^{2+} + 2CH_3O^- \xrightarrow{CO} Ru(COOCH_3)_2(CO)_2(PPh_3)_2 \qquad \text{[Eq. 36]}$$

In the formation of compound (IV), the possible mechanism is that the nucleophile (CH_3O^-) attacks the coordinatively unsaturated (14-electron species) metal atom and forms an intermediate 18-electron species, $[Ru(OCH_3)_2(CO)_2(PPh_3)_2]$. This could not be isolated and no direct evidence for it was found. It seems that immediate CO insertion[6] takes place between the (Ru—OCH_3) bond, which then forms

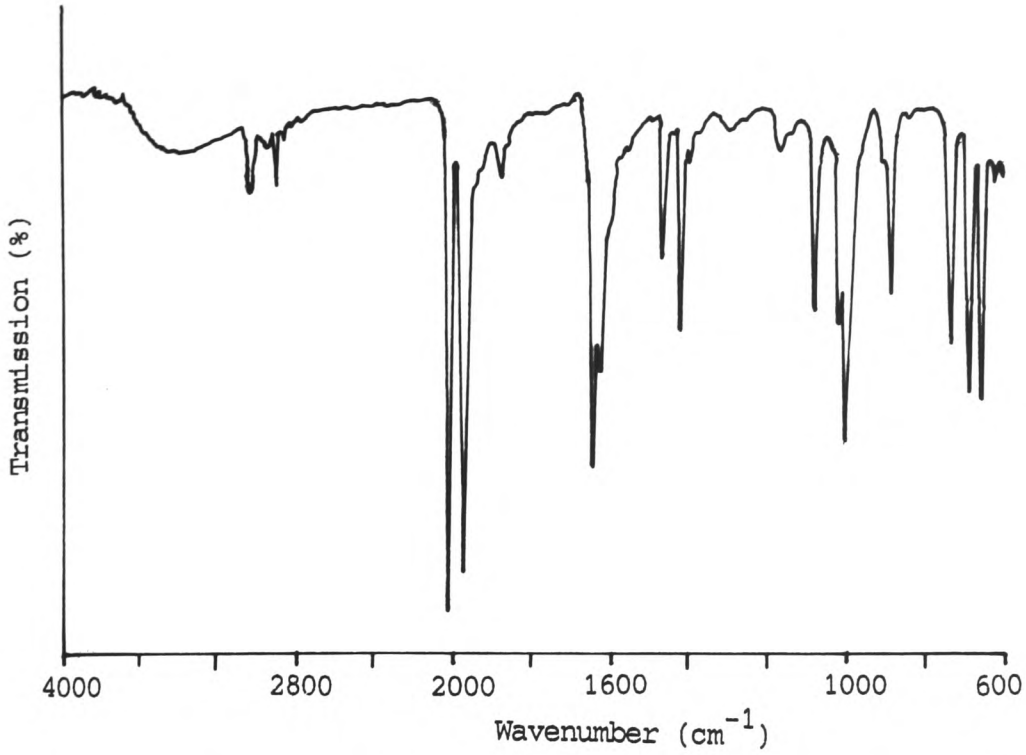

Fig. 22 : Infrared spectrum of cis-[$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$] (KBr disc).

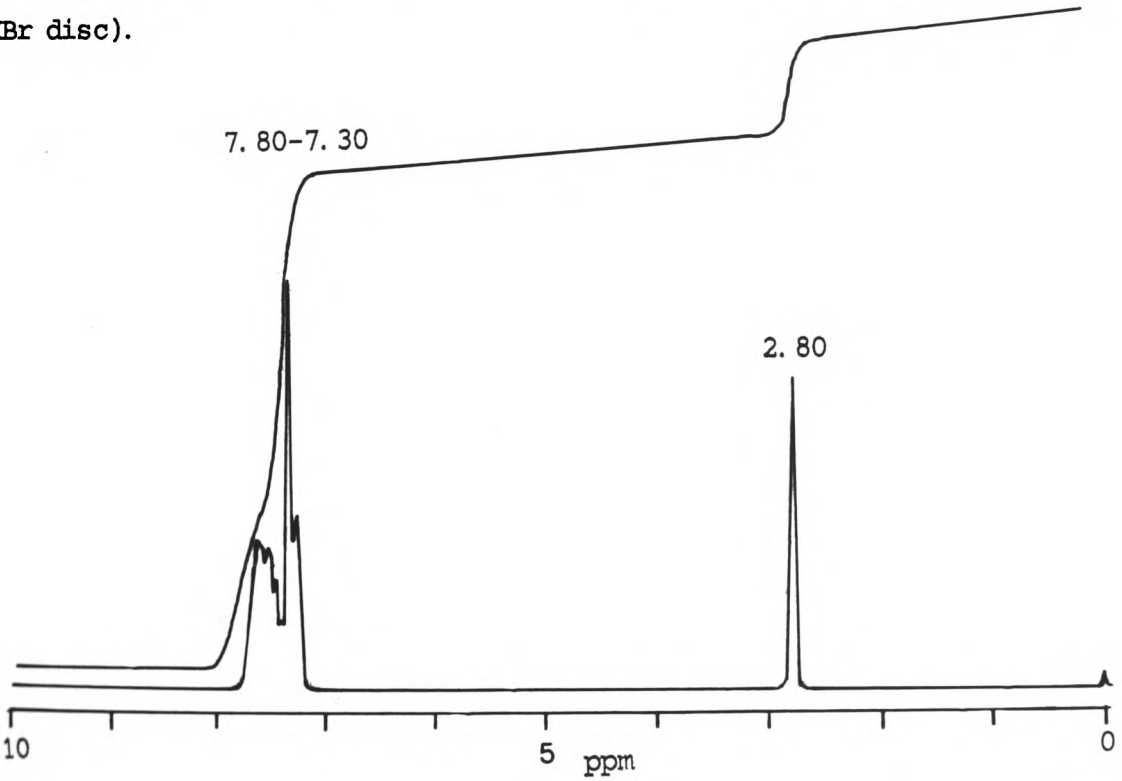

Fig. 23 : ^{1}H-NMR spectrum of cis-[$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$] (in $CDCl_3$, TMS).

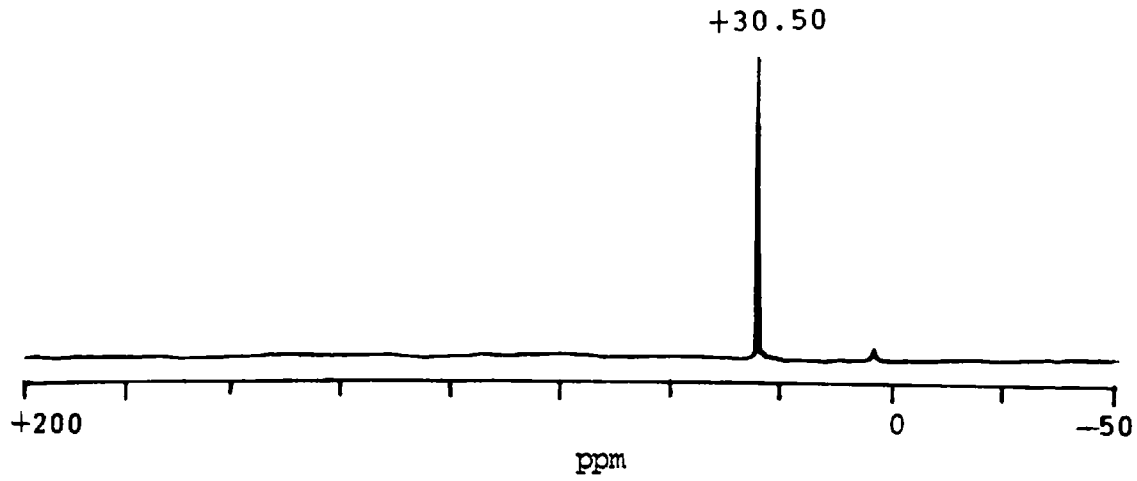

Fig. 24 : ^{31}P-NMR spectrum of cis-[$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$] (in $CDCl_3$).

[$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$]. The compound (IV) is also formed when the reaction of cis-[$RuCl_2(CO)_2(PPh_3)_2$] is carried out with CH_3O^- at a high CO pressure. At 1 atmosphere pressure the reaction does not occur. From here it is assumed that first a chloride ion is replaced by the CH_3O^- group[6] and then CO insertion[6,47] takes place between the (Ru—OCH_3) bond to form [$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$].

The compound (IV), shows two carbonyl stretching frequencies, therefore the carbonyl groups are cis in position[73]. The ^{31}P-NMR shows only a singlet. Therefore the compound is suggested as octahedral structure (C_{2v} symmetry) as in Fig. 25.

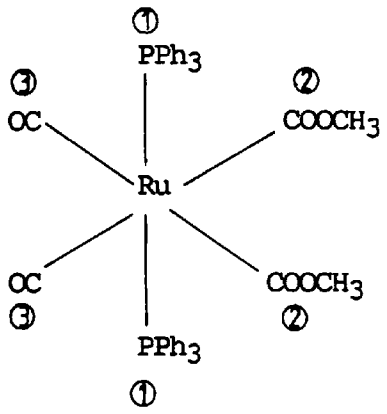

Fig. 25 : Structure of cis-[$Ru(COOCH_3)_2(CO)_2(PPh_3)_2$]. [IUPAC name, (OC-6-13)-dicarbonyldi(methoxycarbonyl)bis(triphenylphosphine)-ruthenium(II)].

(v) Reaction of Compound (III) with Nucleophile (CH_3O^-) : Synthesis of [$RuCl(COOCH_3)(CO)_2(PPh_3)_2$], Dicarbonylchloro(methoxycarbonyl)bis-(triphenylphosphine)ruthenium(II), Compound (V).

The compound (III), $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ reacts with sodium methoxide in the presence of carbon monoxide at -10^oC to give the compound (V), $[RuCl(COOCH_3)(CO)_2(PPh_3)_2]$ [Sec. 3.2(xi)]. The compound has also been prepared from the reaction of $[RuCl(CO)_3(PPh_3)_2]^+[AlCl_4]^-$ with sodium methoxide [Sec. 3.2(xiii)]. The compound has been characterised by infrared, ^1H-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 26) of the compound (V) shows two strong carbonyl bands at 2042 and 1986 cm^{-1}, which suggest that the carbonyl groups are cis in position. A medium band at 1655 cm^{-1} is due to the methoxycarbonyl group[42,44]. No band is present[97,98] for $\nu(BF_4^-)$. The carbonyl and methoxycarbonyl stretching frequencies are in reasonable

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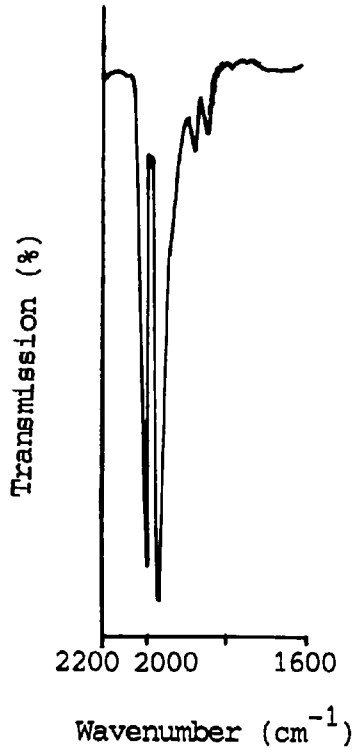


Fig. 28 : Infrared spectrum of cis-$[RuH_2(CO)_2(PPh_3)_2]$ (Nujol mull).

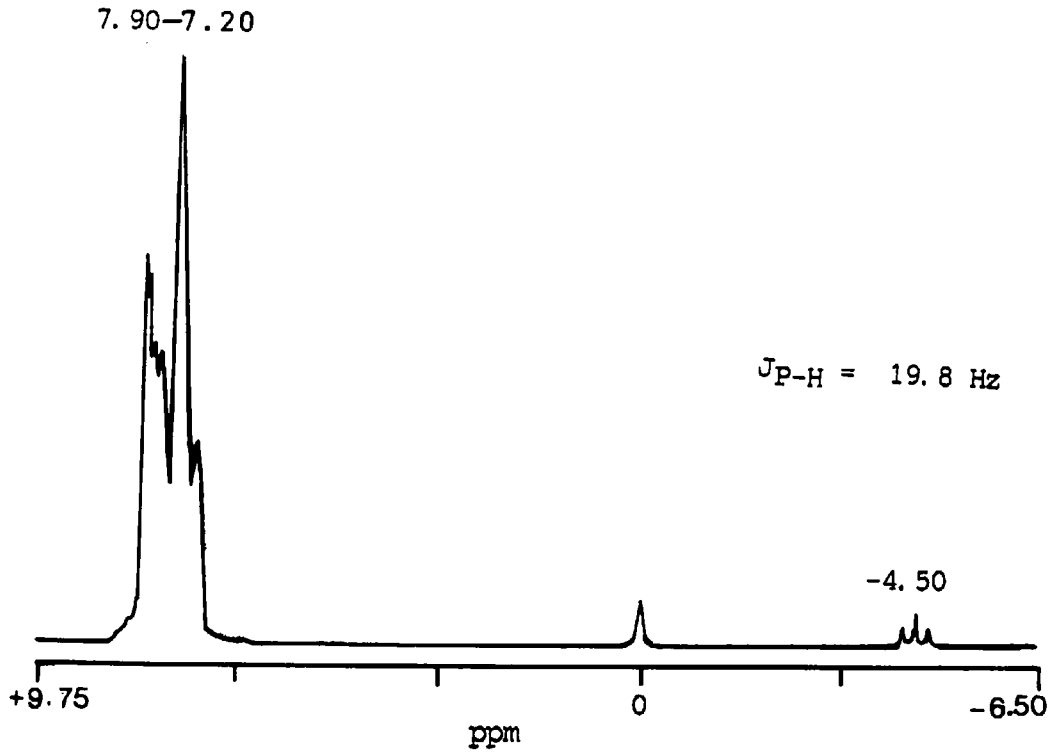


Fig. 29 : ^1H-NMR spectrum of cis-$[RuH_2(CO)_2(PPh_3)_2]$ (in $CDCl_3$, TMS).

reported values[78]. In the literature the compound cis-$[RuH_2(CO)_2(PPh_3)_2]$ was prepared from the reaction of $[Ru(N_2Ar)(CO)_2(PPh_3)_2]^+[BF_4]^-$ and $NaBH_4$ in ethanol[78], and the reaction of $[Ru(CO)_3(PPh_3)_2]$ with hydrogen at high temperature and pressure in tetrahydrofuran[80]. Compound (I), gives cis-$[RuH_2(CO)_2(PPh_3)_2]$ on reaction with $NaBH_4$, but cis-$[RuCl_2(CO)_2(PPh_3)_2]$ does not react with $NaBH_4$ in ethanol under these conditions. The cationic complex more readily forms the hydride compound than the chloro precursor. Both the carbonyls and hydrides have cis configuration as in Fig. 11(A), where Cl = H.

(vii) Reaction of Compound (I) $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with conc. HCl : Formation of cis-$[RuCl_2(CO)_2(PPh_3)_2]$, Dicarbonyldichloro-bis(triphenylphosphine)ruthenium(II).

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ reacts with conc. HCl [Sec. 3.2(xvi)] to give the known white compound, cis-$[RuCl_2(CO)_2(PPh_3)_2]$. The infrared spectrum of the white product shows two strong carbonyl bands[64,73] at 2062 and 2000 cm^{-1}. There is no band[97,98] for $\nu(BF_4^-)$. The far-infrared spectrum shows two bands at 300, 275 cm^{-1} representing[67,72,83] ν(Ru-Cl) and the chlorides are cis in position.

The ^{31}P-NMR spectrum shows a singlet at +17.40 ppm, which suggest that the phosphorus are trans in position[26]. All these spectral data are consistent with the literature[26,64,67,73,83] values of the compound cis-$[RuCl_2(CO)_2(PPh_3)_2]$ as in Fig. 11(A).

(viii) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with KI : Formation of cis-$[RuI_2(CO)_2(PPh_3)_2]$, Dicarbonyldichlorobis-(triphenylphosphine)ruthenium(II).

The reaction of compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-.CH_2Cl_2$ [Sec. 3.2(xvii)] with KI gives yellow crystals. The infrared spectrum of the yellow compound shows two strong carbonyl bands at 2055, 1994 cm^{-1} (in $CHCl_3$). These values suggest that the carbonyl groups are cis to each other[77]. There is no band[97,98] for $\nu(BF_4^-)$. A sodium fusion solution of the compound also gives a yellow precipitate of AgI by the addition of $AgNO_3$, which is insoluble in ammonia solution. This indicates the presence of iodide in the compound. Therefore, the infrared spectrum and physical properties suggest that the complex[77] may be cis-$[RuI_2(CO)_2(PPh_3)_2]$ as in Fig. 11(A), where Cl = I.

Here the nucleophile, I^- has been coordinated with the cationic metal complex to form cis-$[RuI_2(CO)_2(PPh_3)_2]$. This product could not be prepared from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ by reaction with KI under exactly the same conditions [Sec. 3.2(xviii)]. It is possible that cis-$[RuCl_2(CO)_2(PPh_3)_2]$ may react with KI by heating[76,77]. In the compound (I) vacant sites are available, so the steric effects are less. There is another factor also, the metal atom in the compound (I) is positively charged, and open to nucleophilic attack which may aid formation of cis-$[RuI_2(CO)_2(PPh_3)_2]$ at room temperature.

(ix) Reaction of Compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CH_3COONa : Formation of $[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$, Dicarbonylbis-(ethanoato)bis(triphenylphosphine)ruthenium(II).

The compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ reacted with sodium ethanoate under CO to give cis-$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$ [Sec. 3.2(xix)].

The infrared spectrum of this compound shows two strong bands at 2042 and 1980 cm^{-1} which are attributed to the carbonyl groups. The medium bands at 1613 and 1596 cm^{-1} represent $\nu_{asy}(OCO)$, and there is a band at 1316 cm^{-1} for $\nu_{sy}(OCO)$. These values[111] are different from the free CH_3COONa values, $\nu_{asy}(OCO)$ at 1578 cm^{-1} and $\nu_{sy}(OCO)$ at 1414 cm^{-1} and are consistent with the reported values[92] (Table 11). The ^1H-NMR spectrum shows a singlet at 1.10 ppm (6H), for methyl protons and a multiplet at (7.30-7.80) ppm (30H), for aromatic protons and is in good agreement with the published value[23] (Table 12).

If the reaction is carried under nitrogen instead of CO, the product shows ν(CO) at 2042 (m) and 1941 cm^{-1} (b). This could be a mixture of $[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$ and $[Ru(OOCCH_3)_2(CO)(PPh_3)_2]$. These could result from the loss of CO in solution during compound formation. The medium band at 2042 cm^{-1} may be one of the ν(CO) bands of $[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$ and the other medium band may be hidden by the broad and strong band at 1941 cm^{-1}. The bis(ethanoato) compound, $[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$ was not formed from cis-$[RuCl_2(CO)_2(PPh_3)_2]$ and sodium ethanoate in room temperature [Sec. 3.2(xx)]. Even under reflux, the chloride was not replaced by the ethanoate groups. Energetically the cis-$[RuCl_2(CO)_2(PPh_3)_2]$ is stable and the CH_3COO^-

group is not a strong enough nucleophile to replace the two chloride groups from the stable cis-$[RuCl_2(CO)_2(PPh_3)_2]$. But in the present case the ethanoate group coordinated to the cationic salt to give the neutral compound cis-$[Ru(OOCCH_3)_2(CO)_2(PPh_3)_2]$. In the literature[23, 92] the bis(ethanoato) compound was prepared from $[Ru(CO)_3(PPh_3)_2]$ [Sec. 3.1(V). The preparation of the ethanoato compound may be effected in an easier manner from the compound (I).

(x) Reaction of Compound (IV), $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ with conc. HCl : Formation of cis-$[Ru(Cl_2(CO)_2(PPh_3)_2]$.

Compound (IV), cis-$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ when reacted with conc. HCl in methanol [Sec. 3.2(xxi)] gave white crystals of cis-$[RuCl_2(CO)_2(PPh_3)_2]$.

The infrared spectrum of the white crystals shows two strong bands in the carbonyl region at 2062 and 2000 cm^{-1}. The carbonyl stretching frequencies suggested that they are cis to each other[64, 73]. There is no band for the methoxycarbonyl group. The far-infrared spectrum shows two bands at 300, 275 cm^{-1}. These bands are assigned to ν(Ru—Cl) and they are cis to each other[67, 72, 83].

The ^{31}P-NMR spectrum shows a singlet at +17.40 ppm. This suggests that the phosphorus atoms are trans in position[26]. The spectral data suggest that the compound is $[RuCl_2(CO)_2(PPh_3)_2]$ as in Fig. 11(A). Alkoxycarbonyl and carbamoyl compounds react with strong acids to generate metal carbonyl compounds[36, 112]. Also, $[RuCl(CS_2CH_3)(CO)(PPh_3)_2]$ reacts with hydrochloric acid (HCl) in ethanol to give

$[RuCl_2(CO)(CS)(PPh_3)_2]$ and CH_3SH[112]. A chloroform solution of $[IrCl_2(COOCH_3)(CO)\{P(CH_3)_2Ph\}_2]$ reacts with dry HCl to give a metal carbonyl compound[35] $[IrCl_2(CO)_2\{P(CH_3)_2Ph\}_2]^+[Cl]^-$. The present reaction may form a dichloro compound by loosing CO and CH_3OH, as in Eq. 37.

$$[Ru(COOCH_3)_2(CO)_2(PPh_3)_2] + 2HCl \longrightarrow [Ru(CO)_4(PPh_3)_2]^{2+}[Cl]^-_2 + 2CH_3OH$$

$$\downarrow \text{unstable}$$

$$\downarrow -2CO$$

$$[RuCl_2(CO)_2(PPh_3)_2] \qquad \text{[Eq. 37]}$$

(xi) Reaction of cis and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa under Reflux in Methanol in the Presence of CO : Formation of $[Ru(CO)_3(PPh_3)_2]$, Tricarbonylbis(triphenylphosphine)ruthenium(0).

The compounds cis- and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ gave the reduction product, $[Ru(CO)_3(PPh_3)_2]$ when treated with excess CH_3ONa and in the presence of CO [Sec. 3.2(xxii)]. The infrared spectrum (Fig. 30) of $[Ru(CO)_3(PPh_3)_2]$ shows a strong ν(CO) at 1897 cm^{-1}. This carbonyl value is identical to the reported value[75,88], where the carbonyl groups are in the equatorial position. ^{31}P-NMR of the product (Fig. 31) shows a singlet at +55.35 ppm. This suggests that the phosphorus atoms are trans in position.

In the literature this reduction product was prepared from the reaction of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ with CO in the presence of Zn dust[75] or the reaction of $[RuCl_2(PPh_3)_3]$ with CO in sodium ethoxide solution[88].

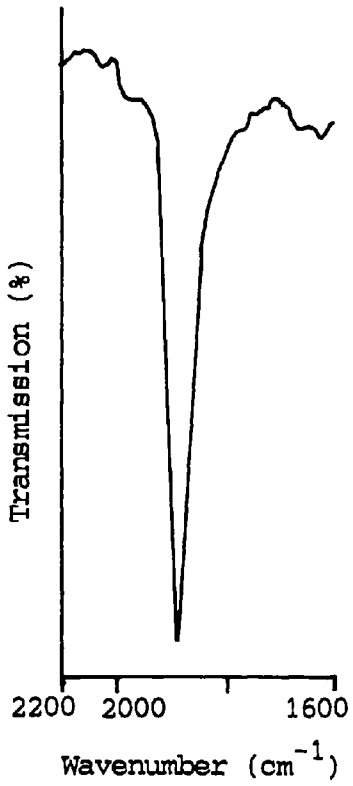


Fig. 30 : Infrared spectrum of $[Ru(CO)_3(PPh_3)_2]$ (KBr disc).

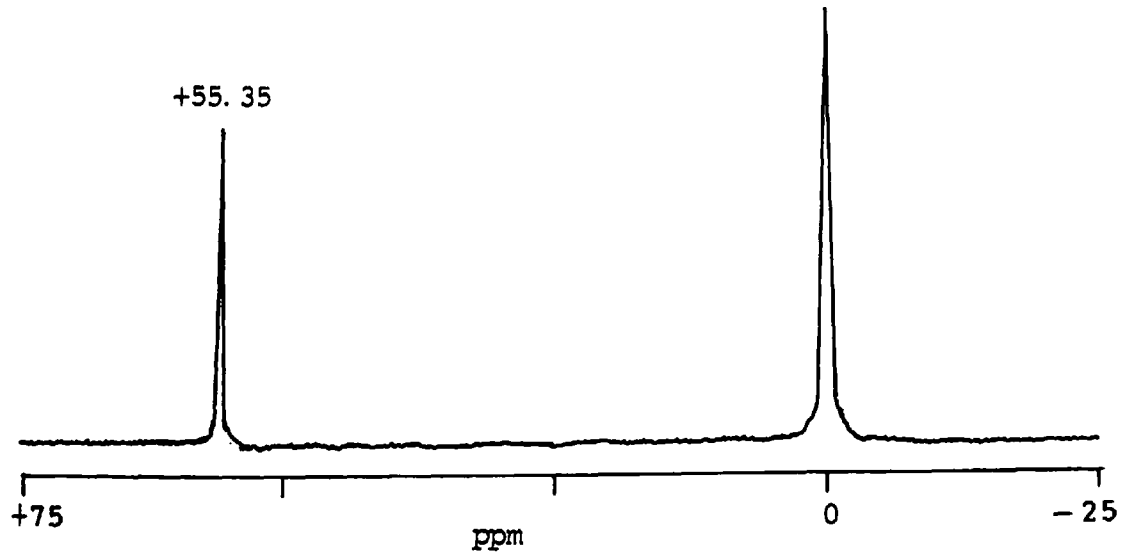


Fig. 31 : ^{31}P-NMR spectrum of $[Ru(CO)_3(PPh_3)_2]$ (in $CDCl_3$, 85% H_3PO_4).

Therefore, from the infrared and NMR spectroscopy the compound is suggested as $[Ru(CO)_3(PPh_3)_2]$ and the structure is trigonal bipyramidal (D_{3h} symmetry) as in Fig. 32.

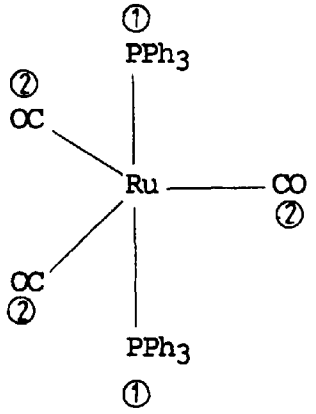


Fig. 32 : Structure of $[Ru(CO)_3(PPh_3)_2]$.
[IUPAC name, (TBPY-5-11)-tricarbonylbis(triphenylphosphine)ruthenium(0)].

(xii) Reaction of cis- and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa under Reflux in Methanol.

The reaction of cis- and trans-$[RuCl_2(CO)_2(PPh_3)_2]$ with excess CH_3ONa under reflux in methanol [Sec. 3.2{(xxiii) and (xxiv))] may have given a mixture of $[RuCl_2(CO)(PPh_3)_2]$ and $[Ru(CO)_3(PPh_3)_2]$ as indicated by the infrared spectrum of the product. The infrared spectrum of the product obtained by the reaction of trans-$[RuCl_2(CO)_2(PPh_3)_2]$ and CH_3ONa, shows two strong carbonyl bands at 1941 and 1897 cm^{-1}. These bands suggest that the product is a mixture of two compounds. The band at 1941 cm^{-1} suggests the compound[73] $[RuCl_2(CO)(PPh_3)_2]$. The band at 1897 cm^{-1} suggests the reduction[75] product, $[Ru(CO)_3(PPh_3)_2]$.

However, the reaction of CH_3ONa with cis-$[RuCl_2(CO)_2(PPh_3)_2]$ gave a orange-yellow compound, which shows four bands in the carbonyl region at

1971 (s), 1941 (w), 1900 (s) and 1887 (w) cm^{-1}. Probably, this is also a mixture. The band at 1941 cm^{-1} may suggest[73] $[RuCl_2(CO)(PPh_3)_2]$ and the band at 1900 cm^{-1} suggests[75] $[Ru(CO)_3(PPh_3)_2]$. The remaining two bands at 1971 and 1887 cm^{-1} cannot be identified.

A summary of the spectral data of the novel compounds of ruthenium prepared follows on the next page.

Table 13 : Infrared Data of Novel Cationic Complexes of Ruthenium.

Compound	ν(CO) cm^{-1}	$\nu(BF_4^-)$ cm^{-1}
(I) $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$	2081(s), 2024(s)	1091(b)
(II) $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$	2151(w), 2086(s), 2025(s)	1091(b)
(III) $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-$ $.1/2(CH_2Cl_2)$	2070(s), 2006(s)	1090(b)

[Where s = Strong and w = Weak and b = Broad. All the spectra in KBr disc].

Table 14 : NMR Data of Novel Cationic Complexes of Ruthenium.

Complex	^{1}H-NMR (ppm)	^{31}P-NMR (ppm)
(I) $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$	7.40-7.80 (m) 5.23 (s)	+25.50 (s)
(II) $[Ru(CO)_3(PPh_3)_2]^{2+}[BF_4]^-_2$		+22.50 (s)
(III) $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-$ $.1/2(CH_2Cl_2)$	7.30-7.80 (m) 5.28 (s)	+24.50 (s)

[Where s = Singlet and m = Multiplet. Solvent $CDCl_3$. TMS as internal standard in ^{1}H-NMR and 85% H_3PO_4 value as a reference in ^{31}P-NMR and the samples were prepared under nitrogen].

Table 15 : Infrared Data of Novel Alkoxycarbonyl Compounds of Ruthenium.

Compound	ν(CO) cm^{-1}	ν(CO) cm^{-1} (alkoxy carbonyl)	ν(O-CH_3) cm^{-1}
(IV) $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$	2033 (s) 1978 (s)	1654 (m) 1637 (sh)	1009 (m)[a]
	2032 (s) 1977 (s)	1653 (m) 1637 (sh)	1008 (m)[b]
(V) $[RuCl(COOCH_3)(CO)_2(PPh_3)_2]$	2042 (s) 1986 (s)	1655 (m)[b]	

[Where s = Strong, sh = Shoulder, m = Medium, a = KBr disc and b = Nujol mull].

Table 16 : NMR Data of Novel Alkoxycarbonyl Compounds of Ruthenium.

Compound	^{1}H-NMR (ppm)	^{31}P-NMR (ppm)
(IV) $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$	(7.30-7.80) (m, 30H) 2.80 (s, 6H)	+30.50 (s)
(V) $[RuCl(COOCH_3)(CO)_2(PPh_3)_2]$	(7.40-7.80) (m, 30H) 2.88 (s, 3H)	

[Where s = Singlet and m = Multiplet. Solvent $CDCl_3$. TMS as internal standard in ^{1}H-NMR and 85% H_3PO_4 value as a reference in ^{31}P-NMR and the samples were prepared under nitrogen].

CHAPTER-4

RHODIUM CHEMISTRY.

4.1 INTRODUCTION.

The aim of the present work is to synthesise some cationic metal carbonyl compounds and study their interaction with nucleophiles in the presence and absence of CO. Rhodium compounds can generally undergo the sort of reactions mentioned in Sec. 1.4{I(ii)}. Therefore, rhodium compounds have great practical importance in synthetic chemistry and are good catalysts, e.g. Wilkinson's catalyst [$RhCl(PPh_3)_3$] is widely used for hydrogenation and hydroformylation of alkenes[2]. Rhodium cationic complexes containing carbonyls and other ligands like PPh_3, $AsPh_3$, $SbPh_3$, PCy_3 have not been widely explored as catalysts for ester synthesis, hydrogenation or hydroformylation. Therefore, they were synthesised in order to investigate their possible catalytic potential in the area.

The stronger the σ donor property of the ligands, the more stable the cationic complexes should be. Therefore, in order to examine the effect of changing the σ donating properties of the phosphine type ligands on the stability of the cationic complexes, species containing the ligands PPh_3, $AsPh_3$, $SbPh_3$ and PCy_3 were synthesised. These ligands also differ in bulk, thus providing an opportunity to observe the effect of changing the size of ligands on the stability and reactivity of the complexes. These species were then reacted with nucleophiles in the presence and absence of CO in order to investigate the feasibility of preparing the corresponding alkoxycarbonyl compounds.

Trans-[$RhCl(CO)(L)_2$], (where L = PPh_3, $AsPh_3$, $SbPh_3$, PCy_3) was the main starting material. The starting material was prepared from hydrated

rhodium trichloride with the corresponding triphenylphosphine, arsine, stibine or tricyclohexylphosphine under carbon monoxide[40,113,114]. It could also be prepared from the reaction of $[RhCl(CO)_2]_2$ with the corresponding ligands[115]. Trans-$[RhCl(CO)(PPh_3)_2]$ could also be prepared from $[RhCl(PPh_3)_3]$ and carbon monoxide[116].

(I) Preparation of Chlorotris(triphenylphosphine)rhodium(I), $[RhCl(PPh_3)_3]$ and its Properties.

(i) Preparation[116] of $[RhCl(PPh_3)_3]$.

The burgundy-red[116] crystalline compound $[RhCl(PPh_3)_3]$ is formed by the reaction of rhodium(III) chloride hydrate with an excess (ca. 6 fold) of triphenylphosphine in boiling ethanol under a nitrogen atmosphere. A large excess of triphenylphosphine is essential to prevent the formation of a bridged dimer and to further the reduction of the rhodium(III) species formed initially. Reduction does not occur in ethanol heated under reflux unless an excess of triphenylphosphine is used. Acetone-water mixtures can be used in place of ethanol as a solvent. If insufficient ethanol is used as a solvent, an orange crystalline material is at first precipitated, which gives the red complex on continuous heating under reflux. The orange complex is a second crystalline form[117].

The corresponding bromo analog, $[RhBr(PPh_3)_3]$ can be prepared by the addition of excess lithium bromide to the hydrated rhodium trichloride and triphenylphosphine. The iodo compound, $[RhI(PPh_3)_3]$ can be prepared

by the addition of lithium iodide to the hydrated rhodium trichloride and triphenylphosphine.

(ii) Physical Properties of $[RhCl(PPh_3)_3]$.

The melting temperature of $[RhCl(PPh_3)_3]$ is 157-158^{o}C. The compound is moderately soluble in dichloromethane or chloroform (20 g/dm^3), slightly soluble in benzene or toluene (4 g/dm^3) and considerably less soluble in ethanoic acid, ketones and alcohols. It is virtually insoluble in light petroleum and cyclohexane. The complex gives $[RhCl(PPh_3)_2.S]$, in donor solvents [S = pyridine, DMSO, acetonitrile][116]. The compound $[RhCl(PPh_3)_3]$, dissociates in solution[116] according to Eq. 38 and the solution species may dimerise as shown in Eq 39.

$$[RhCl(PPh_3)_3] \underset{PPh_3}{\overset{\text{solvent}}{\rightleftharpoons}} [RhCl(PPh_3)_2] + PPh_3 \qquad \text{[Eq. 38]}$$

$$2[RhCl(PPh_3)_2] \longrightarrow [RhCl(PPh_3)_2]_2 \qquad \text{[Eq. 39]}$$

(iii) Chemical Properties of $[RhCl(PPh_3)_3]$.

The coordinatively unsaturated nature of the compound is demonstrated by its reaction with donor molecules, (DMSO, pyridine) to form adducts.

The compound reacts with carbon monoxide or aldehyde to give trans-$[RhCl(CO)(PPh_3)_2]$ quantitatively and the reaction is not reversible as shown in Eq. 40 and Eq. 41.

$$[RhCl(PPh_3)_3] \xrightarrow[CO]{\text{Benzene/Chloroform}} \text{trans-}[RhCl(CO)(PPh_3)_2] \qquad \text{[Eq. 40]}$$

$$[RhCl(PPh_3)_3] + C_7H_{14}O \text{ (aldehyde)} \xrightarrow{\text{Benzene}} \text{trans-}[RhCl(CO)(PPh_3)_2] \qquad \text{[Eq. 41]}$$

The reaction of $[RhCl(PPh_3)_3]$ with $TlClO_4$ in acetone gives the acetone coordinated cationic complex[102] as in Eq. 42.

$$[RhCl(PPh_3)_3] + TlClO_4 \xrightarrow{\text{Acetone}} [Rh(PPh_3)_3.S]^+[ClO_4]^- \qquad \text{[Eq. 42]}$$

where S = acetone.

(iv) ^{31}P-NMR of $[RhCl(PPh_3)_3]$.

After proton decoupling the ^{31}P-NMR spectrum of $[RhCl(PPh_3)_3]$, in dichloromethane consists of a doublet of doublets and a doublet of triplets. The trans-phosphorus atoms (P_1) as in Fig. 33 couple with the cis-phosphorus atom (P_2). Large Rh-P coupling is superimposed upon the smaller P_1-P_2 coupling.

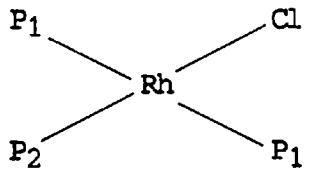


Fig. 33. Structure of $[RhCl(PPh_3)_3]$, where P_1 and P_2 = PPh_3

The negative chemical shift[18] for phosphorus atoms as in Table 13 indicates that the phosphorus resonance occurs at a high frequencies and therefore the nuclei are less shielded than their reference (85% H_3PO_4).

Table 17 : ^{31}P-NMR Data[28,29] of [RhCl(PPh$_3$)$_3$] at 32°C.

P_1 (ppm)	P_2 (ppm)	$J(Rh-P_1)$ Hz	$J(Rh-P_2)$ Hz	$J(P_1-P_2)$ Hz
+31.50	+48.00	142.0	189.0	38.0

(II) Preparation of trans-Carbonylchlorobis(triphenylphosphine)-rhodium(I), [RhCl(CO)(PPh$_3$)$_2$] and its Properties.

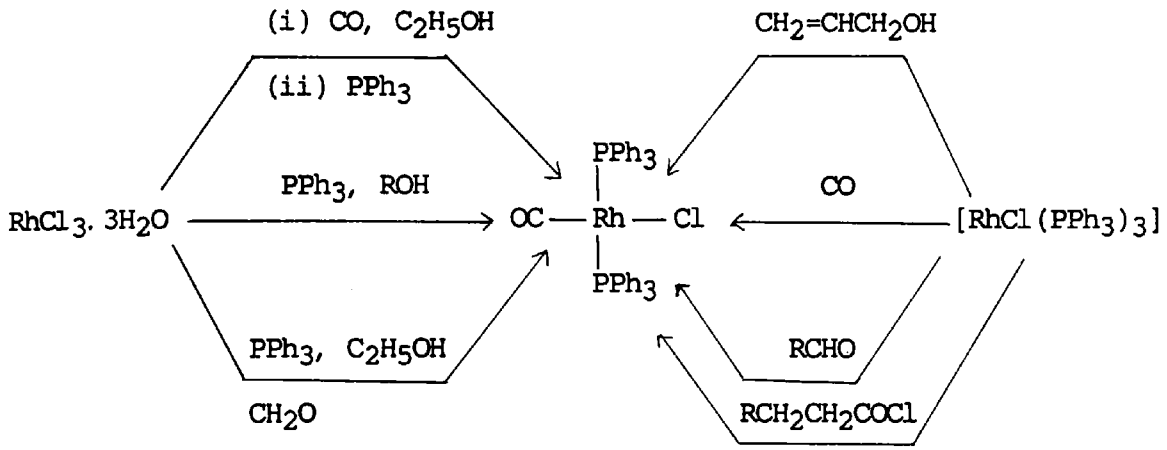
(i) Preparation of trans-[RhCl(CO)(PPh$_3$)$_2$].

(1) The compound trans-[RhCl(CO)(PPh$_3$)$_2$] can be prepared from $RhCl_3.3H_2O$, or [RhCl(PPh$_3$)$_3$] or [RhCl(CO)$_2$]$_2$ (Schemes 11 and 12). In some cases gaseous carbon monoxide is used and in other cases the solvents used are the source of CO.

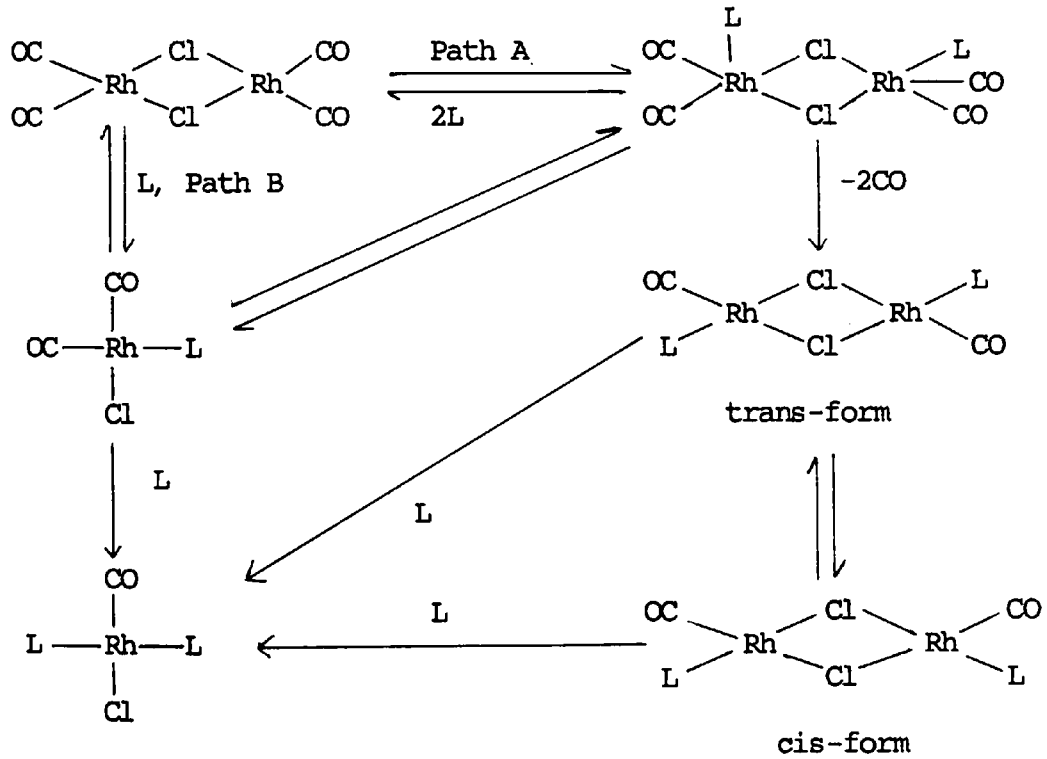
(2) When HCHO solution[118] is added to ethanolic solution of $RhCl_3.3H_2O$ and PPh_3, yellow trans-[RhCl(CO)(PPh$_3$)$_2$] is produced rapidly.

(3) [RhCl(PPh$_3$)$_3$] reacts[116] with CO in benzene or chloroform to give trans-[RhCl(CO)(PPh$_3$)$_2$].

Scheme 11 : Preparation[119] of trans-[RhCl(CO)(PPh$_3$)$_2$].



Scheme 12 : Reaction[119] of [RhCl(CO)$_2$]$_2$ to form trans-[RhCl(CO)(PPh$_3$)$_2$].



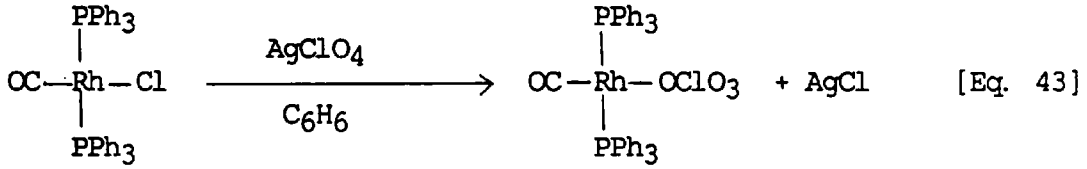
(L = tertiary phosphine)

(ii) **Physical Properties of trans-[RhCl(CO)(PPh_3)$_2$].**

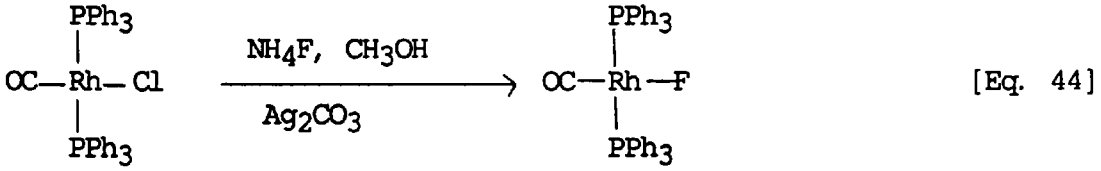
The compound trans-[RhCl(CO)(PPh_3)$_2$] is yellow with melting[115] temperature 195-200^{o}C. It is soluble in chloroform or benzene and insoluble in methanol or ethanol. The infrared spectrum of the compound[120] shows ν(CO) at 1960 cm^{-1} (KBr disc). After proton decoupling the ^{31}P-NMR spectrum[28,29] shows a doublet at +29.10 ppm, split by $J_{(Rh-P)}$ = 124.0 Hz.

(iii) **Chemical Properties of trans-[RhCl(CO)(PPh_3)$_2$].**

(1) The chloride ion of [RhCl(CO)(PPh_3)$_2$] is abstracted[119,121] by Ag^+ ion as in Eq. 43 and in Eq. 44.

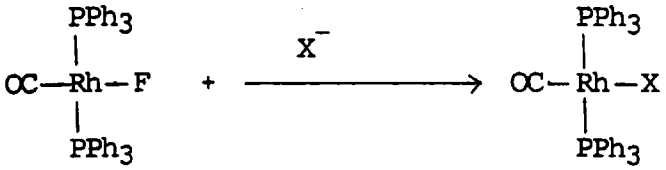


[Eq. 43]



[Eq. 44]

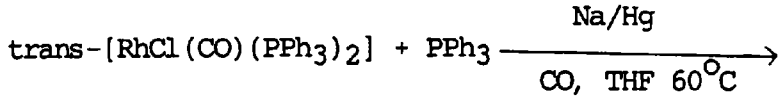
This fluoride compound is air stable. The fluoride ligand is very labile and can be displaced by a wide variety of anionic species[121,122] in Eq. 45.

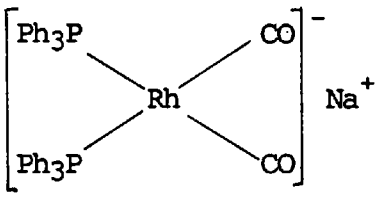


[Eq. 45]

where X^- is the anionic species (X = Cl, Br, I, NCO, NCS, NCSe, CN, NO_2, NO_3, $OClO_3$, OH, OPh, SePh, OOCH, $OOCCH_3$, OOCPh).

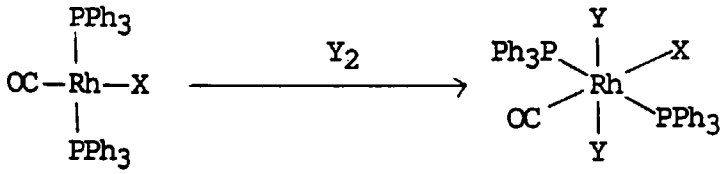
(2) The trans-compound reacts with CO in the presence of Na/Hg to give the anionic complex[119] in Eq. 46.





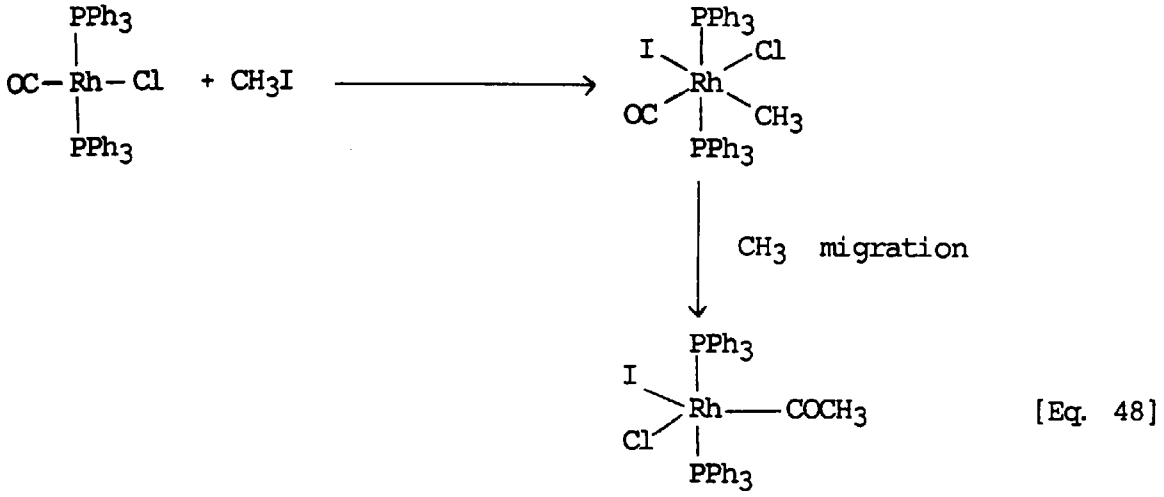
[Eq. 46]

(3) The trans-compound reversibly forms adducts[123,124] with small molecules like O_2 and SO_2 and also undergoes oxidative addition reactions with halogens[125], Eq. 47 and with alkylhalides as shown Eq. 48 to give octahedral Rh(III) compounds[126], which then migrate the alkyl group to give a five coordinate acyl compound.



[Eq. 47]

[Where X = Y = Cl].



[Eq. 48]

(III) Preparation of trans-Carbonylchlorobis(triphenylarsine)rhodium(I), trans-[RhCl(CO)($AsPh_3$)$_2$] and its Properties.

The compound trans-[RhCl(CO)($AsPh_3$)$_2$] can be prepared[40, 113, 115] from $RhCl_3 . 3H_2O$ or from [RhCl(CO)$_2$]$_2$.

(1) When an alcoholic solution of $AsPh_3$ is added to the lemon yellow solution of $RhCl_3 . 3H_2O$ and CO in alcohol[40, 113], trans-[RhCl(CO)($AsPh_3$)$_2$] is formed.

(2) Trans-[RhCl(CO)($AsPh_3$)$_2$] can also be prepared by the reaction of $AsPh_3$ with [RhCl(CO)$_2$]$_2$ in benzene solution[115].

The compound, trans-[RhCl(CO)($AsPh_3$)$_2$] gives the same type of reactions[40] as trans-[RhCl(CO)(PPh_3)$_2$] as seen in Eq. 49.

$$[RhCl(CO)(AsPh_3)_2] + MX \longrightarrow [RhX(CO)(AsPh_3)_2] + MCl \qquad \text{[Eq. 49]}$$

when M = K, X = NO_2, SCN, ClO_4 and M = Na, X = I, CN, SeCN and M = Ag, X = F.

(IV) Preparation of trans-Carbonylchlorobis(tricyclohexylphosphine)-rhodium(I), trans-[RhCl(CO)(PCy_3)$_2$] and its Properties.

The reaction of cyclohexylphosphine (PCy_3) with the lemon yellow[114] solution of $RhCl_3.3H_2O$ and CO in alcohol gives trans-[RhCl(CO)(PCy_3)$_2$]. The carbonyl stretching frequency of the compound is 1941 cm^{-1} (KBr disc). The ^{31}P-NMR spectrum of the compound shows a doublet at +11.90 ppm (with J_{Rh-P} = 119.9 Hz) in benzene with respect to trimethylphosphate as internal standard[127].

Also a few stable, three coordinated (14-electron) compounds of rhodium are known[127], e.g. [RhX(PCy_3)$_2$], where X = F, Cl, Br, I. These three-coordinate compounds react with CO to give trans-[RhCl(CO)(PCy_3)$_2$].

(V) Preparation of trans-Carbonylchlorobis(triphenylstibine)rhodium(I), trans-[RhCl(CO)($SbPh_3$)$_2$] and its Properties.

The preparation of trans-[RhCl(CO)($SbPh_3$)$_2$] is the same as for the $AsPh_3$ analog[40]. The compound is formed when $SbPh_3$ solution is added to the lemon-yellow solution[40] of $RhCl_3.3H_2O$ and CO.

The reactions of trans-[RhCl(CO)($SbPh_3$)$_2$] are similar to those of the PPh_3 or $AsPh_3$ compounds, as shown in Eq. 50.

[RhCl(CO)($SbPh_3$)$_2$] + MX ⟶ trans-[RhX(CO)($SbPh_3$)$_2$] [Eq. 50]

[where X = F, I, CN, SCN].

Table 18 : Infrared Data of trans-[RhX(CO)L_2]

L	X	ν(CO) cm^{-1}	Ref.
PPh_3	Cl	1960[a]	120, 128
	Br	1966[a] 1980[c]	41 41
	I	1981[c] 1970[b]	41 129
	F	1971[c] 1956[b]	41 121
	OH	1950, 1940(sh)	130
	ClO_4	1992[d]	41
	CN	2003[c]	41
$AsPh_3$	Cl	1963[a] 1964[b]	120 40
	Br	1966[b]	40
	I	1980[b]	40
$SbPh_3$	Cl	1960[b] 1975[c]	40 40
	Br	1965[b] 1978[c]	40 40
	I	1980[b]	40
	F	1966[b]	40
PCy_3	Cl	1941[a]	114

[Where a = KBr disc, b = Nujol mull, c = $CHCl_3$, d = C_6H_6 and sh = Shoulder].

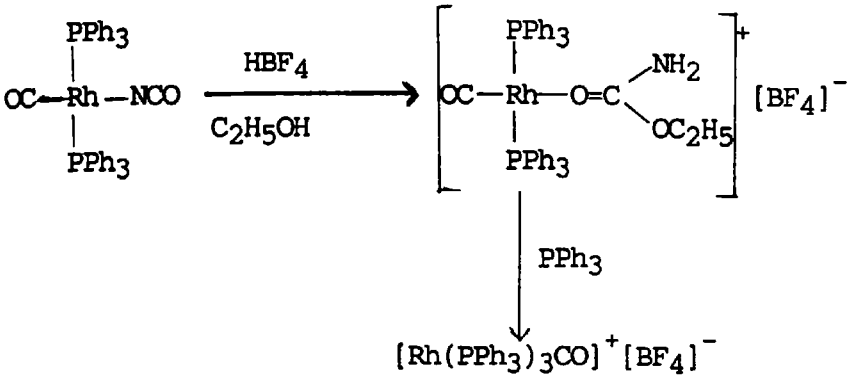
(VI) Cationic Complexes of Rhodium

Cationic rhodium complexes are effective catalysts for many organic syntheses[131,132], such as alkene isomerisation, hydroformylation, dehydrogenation and C-H activation processes. Some of these cationic complexes serve as useful intermediates for the syntheses of many other cationic complexes of rhodium(I) and rhodium(III) species[103]. Also, some of these cationic complexes give alkoxycarbonyl compounds[53].

(1) Treatment of $[RhCl(PPh_3)_3]$ with $TlClO_4$ in donor solvents such as acetone, ethers, or alcohols precipitates the halide as TlCl, allowing isolation of the orange crystalline complexes $[Rh(PPh_3)_3.(solvent)]^+[ClO_4]^-$. Recrystallisation[102] of this species in CH_2Cl_2 gives $[Rh(PPh_3)_3]^+[ClO_4]^-.CH_2Cl_2$.

A green solution of Rh_2^{4+} is prepared by treating a suspension of a methanolic adduct of Rh(II) ethanoato, $Rh_2(OOCCH_3)_2.2CH_3OH$ in methanol with fluoroboric acid (40% aqueous solution) at 60°C for 16 hours or overnight. When a methanolic solution of triphenylphosphine is added to this green solution, the compound $[Rh(PPh_3)_3(BF_4)]$ is formed[133]. Bubbling carbon monoxide through the above green methanolic solution, causes no visible colour change, the addition of excess triphenylphosphine to this solution followed by cooling gives orange crystals[133] of $[Rh(CO)(PPh_3)_3]^+[BF_4]^-$.

(2) The isocyanato compounds $[Rh(NCO)(CO)(PPh_3)_2]$ react with HBF_4 and ethanol to give carbamic ester compounds[22]. These react with PPh_3 to give the tris(triphenylphosphine) compound as in Eq. 51.

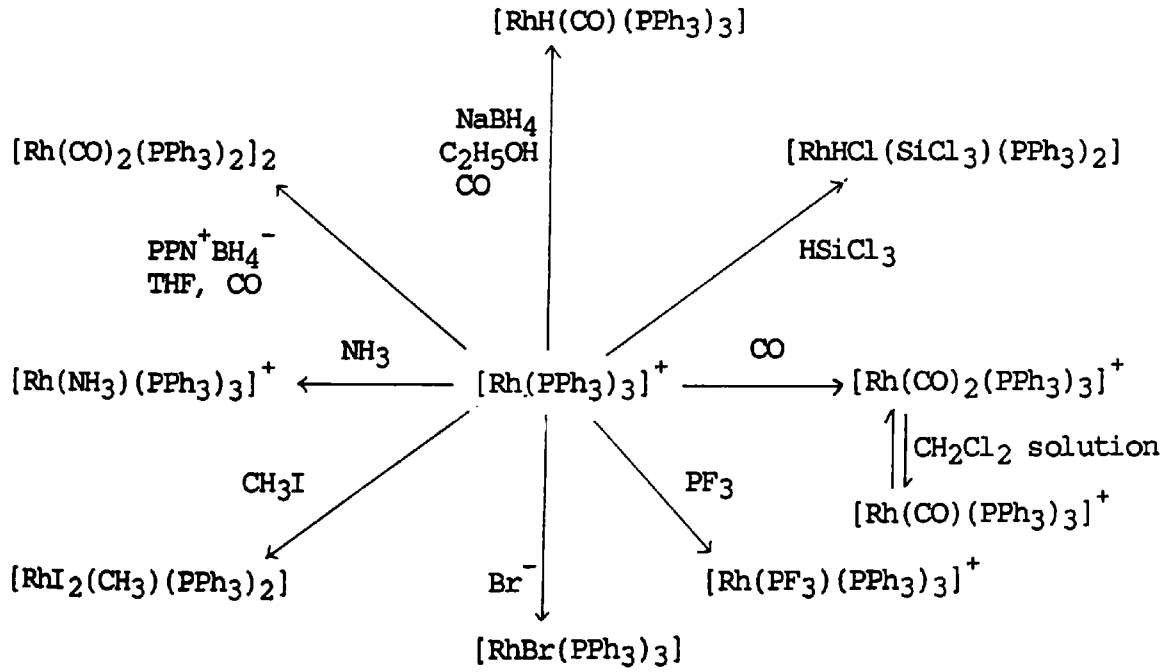


[Eq. 51]

(3) The covalent compound $[Rh(dppe)(\eta^1\text{-}BPh_4)]$ reacts with CO in polar solvents to give the cationic dicarbonyl compound[134] cis-$[Rh(dppe)(CO)_2]^+[BPh_4]^-$.

(4) Protonation of $[RhH(PPh_3)_4]$ with $H_2C(SO_2CF_3)_2$ gives the cationic species $[Rh(PPh_3)_3]^+[HC(SO_2CF_3)_2]^-$. This cation then undergoes a series of reactions[135], shown in the scheme, 13.

Scheme 13 : Reactions[135] of the Cation Complex $[Rh(PPh_3)_3]^+$.



Where PPN^+ = bis(triphenylphosphine)nitrogen(1+).

(5) The species $[Rh(COD)Cl]_2$ [COD = 1,5-cyclooctadiene] reacts[103] with PPh_3 in CH_2Cl_2 in the presence of $KPF_6/NaClO_4$ to give $[Rh(COD)(PPh_3)_2]^+$. When a solution of this salt is treated with carbon monoxide (1 atmosphere 25°C), rapid displacement of COD occurs to give $[Rh(CO)_3(PPh_3)_2]^+$. This tricarbonyl species is not stable, it loses CO slowly in the solid state but very rapidly in solution. When it is dissolved in polar solvents such as acetone, DMA, DMF or acetonitrile, $[Rh(CO)(PPh_3)_2.(solvent)]^+$ is formed.

Table 19 : Infrared Data of Some Cationic Complexes of Rhodium.

Compound	ν(CO) cm^{-1}	ν(CO) cm^{-1} (others)	Ref.
$[Rh(CO)(PPh_3)_2.(Acetone)]^+[ClO_4]^-$	1998	1664[a]	103
$[Rh(CO)(PPh_3)_2.DMF]^+[ClO_4]^-$	1994	1652[a]	103
$[Rh(CO)_3(PPh_3)_2]^+[BPh_4]^-$	2037, 2023[a]		103
$[Rh(PPh_3)_3.(Acetone)]^+[ClO_4]^-$		1665	102
$[Rh(CO)_2\{P(2\text{-}CH_3C_6H_4)_3\}_2]^+[ClO_4]^-$	2040[a]		97
$[Rh(CO)_2(SbPh_3)_3]^+[ClO_4]^-$	2006[a]		97
$[Rh(CO)_2(SbPh_3)_3]^+[AlCl_4]^-$	2009[b]		53
$[Rh(CO)_2(PCy_3)_2]^+[AlCl_4]^-$	1997[a]		53

[Where a = Nujol mull, b = KBr disc].

(6) $[RhCl(CO)(SbPh_3)_3]$ reacts[53] with $AlCl_3$ in the presence of CO to give $[Rh(CO)_2(SbPh_3)_3]^+[AlCl_4]^-$.

(7) The compound, $[Rh(CO)_2\{P(2\text{-}CH_3C_6H_4)_3\}_2]^+[ClO_4]^-$ is formed by the reaction of a calculated amount (2 : 1 molar) of $P(2\text{-}CH_3C_6H_4)_3$ and rhodium perchlorate and carbon monoxide[97].

(8) The compound, trans-$[Rh(CO)_2(PCy_3)_2]^+[AlCl_4]^-$ is formed when trans-$[RhCl(CO)(PCy_3)_2]$ is treated with $AlCl_3$ in benzene in the presence of carbon monoxide[53].

(VII) Reactions of Rhodium Compounds with Nucleophiles, RONa (R = CH_3, C_2H_5).

A large number of nucleophilic reactions of Pd, Pt and Ru have been reported[6, 22, 36, 42, 44, 79, 82, 89] as seen in Sec. 1.3{(I) and (IV)} and they formed alkoxo and alkoxycarbonyl compounds. However there are only a limited number of nucleophilic reactions with rhodium compounds, which produce the alkoxo and alkoxycarbonyl compounds[7, 22], some of these reactions are discussed below.

(1) Treatment of a alcohol suspension[7] of $[\{\eta^5\text{-}C_5(CH_3)_5\}RhCl_2]_2$ with bubbling CO and excess of triethylamine at room temperature gives $[\{\eta^5\text{-}C_5(CH_3)_5\}Rh(CO)(COOR)_2]$, in Eq. 52, where R = CH_3, C_2H_5.

$$[\{\eta^5\text{-}C_5(CH_3)_5\}RhCl_2]_2 + N(C_2H_5)_3 + CO \xrightarrow{ROH} [\{\eta^5\text{-}C_5(CH_3)_5\}Rh(CO)(COOR)_2] + 2(C_2H_5)_3N.HCl \qquad [Eq.\ 52]$$

Coupling of this alkoxycarbonyl compound's ligands is induced to produce a dialkyloxalate and dialkylcarbonate. This occurs when $[\{\eta^5\text{-}C_5(CH_3)_5\}Rh(CO)(COOC_2H_5)_2]$ is dissolved in dichloromethane under

nitrogen and a solution of iodine in dichloromethane added dropwise. After stirring for 30 minutes the reaction is quenched with aqueous bisulphite and upon subjecting the product mixture to GLC/mass spectral analysis diethyloxalate and diethylcarbonate are identified as seen in Eq. 53.

$$[\{\eta^5\text{-}C_5(CH_3)_5\}Rh(CO)(COOC_2H_5)_2] \xrightarrow[CH_2Cl_2]{I_2} (COOC_2H_5)_2 + \{C_5(CH_3)_5COOC_2H_5\} + O{=}C(OC_2H_5)_2 \qquad \text{[Eq. 53]}$$

(2) The compound $[Rh(CO)(PPh_3)_2(NHCOOC_2H_5)]$ is converted to alkoxycarbonyl compounds, $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$ by carbonylation in methanol[22].

(3) $[Rh(CO)_2(SbPh_3)_3]^+$ reacts with a methanolic KOH solution[53], to give $[Rh(COOCH_3)(CO)(SbPh_3)_3]$.

Table 20 : Infrared and ^{1}H-NMR Data of Some Alkoxycarbonyl Compounds of Rhodium.

Compound	IR in cm^{-1}			^{1}H-NMR in ppm	
	v(CO)	v(CO) (alkoxy carbonyl)	v(C-OR)	CH_3/C_2H_5	Ref.
$[Rh(COOCH_3)(CO)_2(PPh_3)_2]$	2000 1954	1637	1032[a]	2.81[c]	22
$[Rh(COOCH_3)_2(CO)\{C_5(CH_3)_5\}]$[d]	2056	1668, 1645[a]			7
$[Rh(COOCH_3)(CO)(SbPh_3)_3]$	1981	1621[b]			53

[Where a = Nujol mull, b = Tetrahydrofuran and c = $CDCl_3$ and d = $\{\eta^5\text{-}C_5(CH_3)_5\}$].

(VIII) Preparation of Some Carboxylato Compounds of Rhodium.

(1) When ethanoic acid is added to a boiling suspension of carbonyl(hydrido)tris(triphenylphosphine)rhodium(I) in ethanol it gives the carbonyl(ethanoato)bis(triphenylphosphine)rhodium(I) compound[92], $[Rh(OOCCH_3)(CO)(PPh_3)_2]$. The following compounds are prepared in a similar way, $[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$ and $[Rh(4\text{-}CH_3C_6H_4COO)(CO)(PPh_3)_2]$.

(2) Carboxylatotris(triphenylphosphine)rhodium(I) compounds of the type $[Rh(OOCR)(PPh_3)_3]$, [where R = CH_3, C_2H_5, C_3H_7] are prepared as follows[136]. To the green methanolic solution of Rh_2^{4+}, [see Sec. 4.1(vi)] a solution of triphenylphosphine in methanol is added, followed by an excess of a methanolic solution of lithium carboxylate. The resultant red mixture is refluxed for 20 minutes to give the crystalline product.

(3) Carbonyl(carboxylato)bis(triphenylphosphine)rhodium(I), Compounds of the type $[Rh(OOCR)(CO)(PPh_3)_2]$ [where R = CH_3, C_2H_5, C_3H_7] are prepared[136] by passing carbon monoxide through a suspension of carboxylato compound $[Rh(OOCR)(PPh_3)_3]$ in benzene to give a bright yellow solution. Concentration and addition of diethyl ether gives the product.

Table 21 : Infrared and ^{1}H-NMR Data of Carboxylato Compounds of Rhodium.

Compound	ν(CO) (cm^{-1})	ν_{asy}(OCO) (cm^{-1})	ν_{sy}(OCO) (cm^{-1})	CH_3/ C_2H_5 (ppm)	Ref.
$[Rh(OOCCH_3)(CO)(PPh_3)_2]$	1970	1604	1376	0.76	92
$[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$	1976	1601	1382		92
$[Rh(4\text{-}CH_3C_6H_4COO)(CO)(PPh_3)_2]$	1963	1615	1354		92

[Infrared spectra in Nujol mull and ^{1}H-NMR in $CDCl_3$].

4.2 EXPERIMENTAL.

(A) RHODIUM-PHOSPHINE COMPOUNDS.

(i) Preparation[116] of Chlorotris(triphenylphosphine)rhodium(I), [RhCl(PPh$_3$)$_3$].

To a solution of excess triphenylphosphine (PPh_3), (12.00 g, 45.68 mmol) in hot ethanol (350 cm^3) was added a solution of hydrated rhodium trichloride, ($RhCl_3.xH_2O$), (2.00 g, 8.08 mmol) in hot ethanol (70 cm^3) and the solution was heated under reflux for 30 minutes under nitrogen. The hot solution was filtered and the burgundy-red crystals of the compound were washed with diethyl ether (50 cm^3) and dried in vacuo. Yield = 6.25 g, (81%).

(ii) Preparation[116] of trans-Carbonylchlorobis(triphenylphosphine)-rhodium(I), trans-[RhCl(CO)(PPh$_3$)$_2$].

When carbon monoxide was passed through a solution of [RhCl(PPh$_3$)$_3$] (1.50 g, 1.62 mmol) in benzene (60 cm^3) the burgundy-red solution rapidly turned yellow. After evaporation of the solvent the crude product was recrystallised from chloroform and hexane mixture and gave yellow crystals. Yield = 0.90 g, (80%). The compound was also easily prepared by passing CO through the solution of [RhCl(PPh$_3$)$_3$] in dichloromethane. The resulting pale yellow crystals were washed with excess dichloromethane.

IR : ν(CO) at 1960 cm^{-1} (s) (KBr disc). Literature value 1960 cm^{-1} (Table 18).

^{31}P-NMR : +29.08 ppm (d, with J_{Rh-P} = 130.6 Hz) (in $CDCl_3$).
Literature[28,29] value +29.10ppm (d, with J_{Rh-P} = 124.0 Hz).

(iii) Reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with $AgBF_4$ in Dichloromethane : Synthesis of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Complex (VI).

Dry dichloromethane (50 cm^3) was placed in a Schlenk tube and carbonylchlorobis(triphenylphosphine)rhodium(I), (0.60 g, 0.87 mmol) and silver tetrafluoroborate, $AgBF_4$ (0.17 g, 0.87 mmol) were added under nitrogen. The Schlenk tube was covered with aluminium foil and the mixture was stirred for 1 hour at room temperature. Some white precipitate was formed. The mixture was then filtered through kieselguhr under nitrogen. Evaporation of the solvent from the filtrate on the vacuum line afforded yellow crystals. The product was recrystallised from a dichloromethane-hexane mixture under nitrogen. Yellow crystals were produced. Yield = 0.46 g, (67%). The melting temperature of the complex was 120-125^oC (decomposed) and was soluble in chloroform, methanol and acetone. The reaction could also be carried out in acetone.

IR : ν(CO) at 1994 cm^{-1} (s) and $\nu(BF_4^-)$ at 1090 cm^{-1} (b) (Nujol mull).
^{1}H-NMR : 7.50 ppm (m, 30H) and 5.28 ppm (s, 1H) (in $CDCl_3$).
^{31}P-NMR : +30.70 ppm (d, with J_{Rh-P} = 123.0 Hz) (in $CDCl_3$).

Analysis for $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ = $C_{37.5}H_{31}BClF_4OP_2Rh$

	C%	H%
Found	57.0	4.0
Calculated	57.3	4.0

When the reaction was carried out in acetone then the acetone

coordinated compound was found.

IR : ν(CO) at 1999 cm^{-1} (s) and 1651 cm^{-1} (m) and $\nu(BF_4^-)$ at 1095 cm^{-1} (b) (KBr disc).

^{1}H-NMR : 1.35 ppm (s, 6H) and 7.50 ppm (m, 30H) (in $CDCl_3$).

^{31}P-NMR : +31.60 ppm (d, with J_{Rh-P} = 126 Hz) (in $CDCl_3$).

(iv) Reaction of Compound (VI) with CO : Synthesis of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$, Compound (VII).

Compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in dichloromethane (15 cm^3) and CO bubbled through the solution for 1 hour. Then the solvent was evaporated to give an orange-yellow solid. This was recrystallised from a dichloromethane-hexane mixture in the presence of CO to give orange-yellow crystals. Yield = 0.13 g, (65%). The complex was soluble in dichloromethane, chloroform and methanol. It was insoluble in pentane and hexane. The melting temperature of the crystals was 150^{o}C (decomposed). The reaction could also be carried out in benzene.

IR : ν(CO) at 2046 cm^{-1} (s) and $\nu(BF_4^-)$ at 1057 cm^{-1} (b)(Nujol mull).
ν(CO) at 2047 cm^{-1} (s) and $\nu(BF_4^-)$ at 1065 cm^{-1} (b) (KBr disc).

^{1}H-NMR : 7.58 ppm (m) (in $CDCl_3$).

^{31}P-NMR : +26.90 ppm (d, with J_{Rh-P} = 108.7 Hz) (in $CDCl_3$).

Analysis for $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ = $C_{38}H_{30}BF_4O_2P_2Rh$

	C%	H%
Found	59.6	3.7
Calculated	59.2	3.9

(v) Reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with $AgBF_4$ in the Presence of CO : Synthesis of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$, Compound (VII).

Trans-$[RhCl(CO)(PPh_3)_2]$, (0.80 g, 1.16 mmol) was suspended in dry, degassed dichloromethane (60 cm^3) in a Schlenk tube. To this mixture silver tetrafluoroborate, $AgBF_4$, (0.23 g, 1.18 mmol) was added under nitrogen. The Schlenk tube was covered with aluminium foil. Then the nitrogen was stopped and CO bubbled through the mixture with stirring. Within 1 hour the initial yellow suspension changed colour and a white precipitate formed. The mixture was filtered through kieselguhr under nitrogen. The solvent was evaporated off on a vacuum line to give an orange-yellow solid. This was recrystallised from a dichloromethane-hexane mixture under CO to give orange-yellow crystals. Yield = 0.60 g, (67%). All physical and chemical properties were identical as described for the compound (VII) in Sec. 4.2A(iv).

(vi) Reaction of Compound (VI) with CH_3ONa in the Presence of CO : Synthesis of $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$, Compound (VIII).

Compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in methanol (10 cm^3) under CO and to this freshly prepared sodium methoxide solution (ca. 1.10 mmol in 5 cm^3 of methanol) was added and CO was bubbled through the mixture. Within 15 minutes yellow crystals were formed and the product was filtered off and washed with excess degassed methanol. Yield = 0.12 g, (65%). The melting temperature of the compound was 129°C.

IR : ν(CO) at 2004 (s), 1957 (s) cm^{-1} and 1637 cm^{-1} (m) for the methoxycarbonyl band and ν(C-OCH_3) at 1040 cm^{-1} (m) (KBr disc). ν(CO) at 2005 (s), 1956 cm^{-1} (s) and 1636 cm^{-1} (m) for the methoxycarbonyl band (Nujol mull).

^{1}H-NMR : 2.81 ppm (s, 3H) and (7.40-7.80) ppm (m, 30 H) (in Acetone-d^6).

^{31}P-NMR : +26.40 ppm (d, with J_{Rh-P} = 130.5 Hz) (in $CDCl_3$).

(vii) Reaction of Compound (VI) with C_2H_5ONa in the Presence of CO : Synthesis of $[Rh(COOC_2H_5)(CO)_2(PPh_3)_2]$, Compound (IX).

Compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in ethanol (10 cm^3) under CO and to this solution freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 5 cm^3 of ethanol) was added and CO passed through the solution. Within 20 minutes yellow crystals were formed. The crystals were filtered off and washed with excess ethanol. Yield = 0.11 g, (60%). The product was soluble in dichloromethane and chloroform.

IR : ν(CO) at 2003 (s), 1954 cm^{-1} (s) and 1629 cm^{-1} (m) for the ethoxycarbonyl band and ν(C-OC_2H_5) at 1046 cm^{-1} (m) (KBr disc).

(viii) Reaction of Compound (VI) with C_3H_7ONa in the Presence of CO : Synthesis of $[Rh(COOC_3H_7)(CO)_2(PPh_3)_2]$, Compound (X).

The compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in n-propanol (10 cm^3) under CO and to this solution freshly prepared sodium propoxide solution (ca. 1.10 mmol in 5 cm^3 of n-propanol) was added and CO was bubbled through the solution

for 30 minutes. Yellow crystals were formed. These were filtered off and washed with excess propanol. Yield = 0.07 g, (40%).

IR : ν(CO) at 2000 (s), 1953 cm^{-1} (s) and 1627 cm^{-1} (m) for the propoxycarbonyl band and $\nu(C\text{-}OC_3H_7)$ at 1048 cm^{-1} (m) (KBr disc).

(ix) Reaction of Compound (VI) with CH_3ONa under Nitrogen : Synthesis of trans-$[Rh(OCH_3)(CO)(PPh_3)_2]$, Compound (XI).

Compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in methanol (10 cm^3) under nitrogen and to this solution freshly prepared sodium methoxide solution (ca. 1.10 mmol in 5 cm^3 of methanol) was added and the mixture stirred at room temperature. Within 30 minutes some yellow crystals were formed. The product was filtered off and washed with excess methanol and dried. The product was recrystallised from benzene and hexane. The melting temperature of the compound was 120°C (decomposed). Yield = 0.10 g, (60%).

IR : ν(CO) at 1946 (s) cm^{-1} and no $\nu(BF_4^-)$ band (KBr disc).

^{1}H-NMR : 3.05 ppm (s), 7.00 ppm (m) and 7.80 ppm (m) (in C_6D_6).

^{31}P-NMR : +24.60 ppm (d, with J_{Rh-P} = 139.1 Hz) (in C_6D_6).

Analysis for $[Rh(OCH_3)(CO)(PPh_3)_2] = C_{38}H_{33}O_2P_2Rh$

	C%	H%
Found	66.0	4.7
Calculated	66.4	4.8

(x) Reaction of Compound (VI) with C_2H_5ONa under Nitrogen : Synthesis of trans-$[Rh(OC_2H_5)(CO)(PPh_3)_2]$, Compound (XII).

Compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in ethanol (10 cm^3) under nitrogen and to this solution freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 5 cm^3 of ethanol) was added and stirred for 30 minutes. The volume of the mixture was reduced to one half under vacuum and yellow crystals were appeared. The product was filtered off and washed with ethanol. Yield = 0.07 g, (40%).

IR : ν(CO) at 1944 cm^{-1} (s) and no $\nu(BF_4^-)$ band (KBr disc).

(xi) Reaction of Compound (VII) with CH_3ONa : Synthesis of trans-$[Rh(COOCH_3)(CO)(PPh_3)_2].CH_3OH$, Compound (XIII).

Compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (0.40 g, 0.52 mmol) was added to freshly prepared sodium methoxide solution (ca. 0.80 mmol in 20 cm^3 of methanol) and the mixture was stirred for 30 minutes. The initial orange-yellow colour changed to yellow. The product was filtered off and washed with excess methanol. Yield = 0.26 g, (65%). The melting temperature of the compound was 85-90°C. The compound was soluble in dichloromethane and chloroform.

IR : ν(CO) at 1971 (s) and 1618 cm^{-1} (m) for the methoxycarbonyl band and $\nu(C\text{-}OCH_3)$ at 1019 cm^{-1} (m) and no $\nu(BF_4^-)$ band (KBr disc).
^{1}H-NMR : 2.62 ppm (s, 3H), 3.45 ppm (s, 3H) and (7.20-7.80) ppm (m, 30H) (in $CDCl_3$).

^{31}p-NMR : +28.75 ppm (d, with J_{Rh-P} = 126.8 Hz) (in $CDCl_3$).

Analysis for $[Rh(COOCH_3)(CO)(PPh_3)_2].CH_3OH = C_{40}H_{37}O_4P_2Rh$

	C%	H%
Found	64.3	4.5
Calculated	64.3	4.9

When the compound was left for a longer time ca. 3 to 4 hours in the reaction system the band at 1618 cm^{-1} gradually decreased and a new band at 1735 cm^{-1} appeared, possibly due to a bridging carbonyl moiety. This species could not be isolated.

(xii) Reaction of Compound (VII) with C_2H_5ONa under Nitrogen : Synthesis of $[Rh(COOC_2H_5)(CO)(PPh_3)_2]$, Compound (XIV).

Compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (0.20 g, 0.26 mmol) was added to freshly prepared sodium ethoxide solution (ca. 0.40 mmol in 10 cm^3 of ethanol) and the mixture was stirred for 15 minutes under nitrogen. Then the volume of the yellow solution was reduced to half on a vacuum line, resulting in the formation of some yellow crystals. The product was filtered off and washed with ethanol.

IR : ν(CO) at 1969 (s) and 1609 cm^{-1} (m) for the ethoxycarbonyl band (KBr disc).

(xiii) Reaction of Compound (VII) with CH_3ONa in Presence of CO : Synthesis of $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$, Compound (VIII).

Compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (0.20 g, 0.26 mmol) was dissolved in methanol (10 cm^3) under CO and to this solution freshly prepared sodium methoxide solution (ca. 1.10 mmol in 5 cm^3 of methanol) was added and CO bubbled through the solution for 15 minutes. The yellow crystals that formed were filtered off and washed with methanol. Yield = 0.13 g, (70%). The melting temperature of the compound was 129°C. Spectral data are identical to the compound (VIII) [Sec. 4.2A(vi)].

(xiv) Reaction of Compound (VII) with C_2H_5ONa in the Presence of CO : Synthesis of $[Rh(COOC_2H_5)(CO)_2(PPh_3)_2]$, Compound (IX).

Compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (0.20 g, 0.26 mmol) was dissolved in ethanol (10 cm^3) under CO and to this solution freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 5 cm^3 of ethanol) added and CO was bubbled through the resultant solution. Within 20 minutes yellow crystals appeared. The product was filtered off and washed with excess ethanol. Yield = 0.12 g, (60%). Spectral data are identical to the compound (IX) [Sec. 4.2A(vii)].

(xv) Reaction of Compound (VII) with C_3H_7ONa in the Presence of CO : Synthesis of $[Rh(COOC_3H_7)(CO)_2(PPh_3)_2]$, Compound (X).

Compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (0.20 g, 0.26 mmol) was dissolved in n-propanol (10 cm^3) under CO and to this solution freshly prepared sodium propoxide solution (ca. 1.10 mmol in 5 cm^3 of n-propanol) was added and CO was passed through the resultant solution. Within 30 minutes a yellow precipitate was formed. The product was filtered off and washed with excess propanol. Yield = 0.10 g, (50%). Spectral data are identical to the compound (X) [Sec. 4.2A(viii)].

(xvi) Reaction of Compound (VI) with CH_3COONa : Synthesis of trans-$[Rh(OOCCH_3)(CO)(PPh_3)_2]$, Compound (XV).

The cationic compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20g, 0.25 mmol) was dissolved in 10 cm^3 of dichloromethane and cooled to 0^oC under nitrogen. To this sodium ethanoate solution (0.05 g, 0.60 mmol in 10 cm^3 of methanol) was added and the mixture stirred at room temperature for 30 minutes. Then the volume was reduced to ca. one half. The resulting yellow precipitate was filtered off and washed with methanol. Yield = 0.12 g, (65%).

IR : ν(CO) at 1972 cm^{-1} (s), ν_{asy}(OCO) at 1605 cm^{-1} (m) and ν_{sy}(OCO) at 1374 cm^{-1} (m) (Nujol mull). ν(CO) at 1965 cm^{-1} (s), ν_{asy}(OCO) at 1608 cm^{-1} (m) and ν_{sy}(OCO) at 1370 cm^{-1} (m) (KBr disc).

^{1}H-NMR : 0.76 ppm (s, 3H) and 7.40 ppm (m, 18H) and 7.80 ppm (m, 12H) (in $CDCl_3$).

^{31}P-NMR : +32.48 ppm (d, with J_{Rh-P} = 132.2 Hz) (in $CDCl_3$).

(xvii) Reaction of Compound (VI) with CH_3CH_2COONa : Synthesis of trans-$[Rh(OOCCH_2CH_3)(CO)(PPh_3)_2]$, Compound (XVI).

The cationic compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was dissolved in methanol (5 cm^3) and sodium propanoate solution (0.05 g, 0.52 mmol in 5 cm^3 of methanol) was added under a nitrogen atmosphere and stirred for 15 minutes at ambient temperature. The resulting yellow precipitate was filtered off and washed with methanol. The precipitate was recrystallised from dichloromethane and methanol. Yield = 0.11 g, (60%).

IR : ν(CO) at 1975 cm^{-1} (s), ν_{asy}(OCO) at 1599 cm^{-1} (m) and ν_{sy}(OCO) at 1379 cm^{-1} (m) (Nujol mull). ν(CO) at 1973 cm^{-1} (s), ν_{asy}(OCO) at 1602 cm^{-1} (m) and ν_{sy}(OCO) at 1377 cm^{-1} (m) (KBr disc).

^{1}H-NMR : 0.20 ppm (t, 3H), 0.98 ppm (q, 2H) and 7.40 ppm (m, 18H) and 7.70 ppm (m, 12H) (in $CDCl_3$).

^{31}P-NMR : +31.55 ppm (d, with J_{Rh-P} = 134.6 Hz) (in $CDCl_3$).

^{13}C-NMR : 10.00 ppm (s, CH_3), 29.50 ppm (s, CH_2), (129.00-136.00) ppm (m, C_6H_5), 179.50 ppm (s, COO^-) and 190.50 ppm (d, with J_{Rh-C} = 67.5 Hz, Rh-CO) (in $CDCl_3$).

(xviii) Reaction of Compound (XI) with CH_3I : Formation of $[RhI(OCH_3)(CH_3)(CO)(PPh_3)_2]$, Compound (XVII).

To a solution of compound (XI), $[Rh(OCH_3)(CO)(PPh_3)_2]$ (0.20 g, 0.29 mmol) in 10 cm^3 of benzene, CH_3I (0.05 cm^3) was added under nitrogen. The resulting mixture was stirred for 15 minutes. The solvent

was removed on a vacuum line. The remaining yellow solid was washed twice with hexane. Yield = 0.14 g, (60%). Test for I^-: When $AgNO_3$ solution was added to the sodium fusion solution of the compound, a yellow precipitate of AgI formed, which was insoluble in ammonia solution.

IR : v(CO) at 1980 cm^{-1} (s) (KBr disc).

(B) RHODIUM-ARSINE COMPOUNDS.

(xix) Preparation of trans-Carbonylchlorobis(triphenylphosphine)-rhodium(I), trans-[RhCl(CO)($AsPh_3$)$_2$].

The compound trans-[RhCl(CO)($AsPh_3$)$_2$] can be prepared from (a) hydrated rhodium trichloride[40,113], $RhCl_3.xH_2O$ and from (b) tetracarbonyldichlorodirhodium(I)[115], [RhCl(CO)$_2$]$_2$.

Preparation[40] of trans-[RhCl(CO)($AsPh_3$)$_2$] from $RhCl_3.xH_2O$.

$RhCl_3.xH_2O$ (1.00 g, 4.04 mmol) was dissolved in 125 cm^3 of dimethylformamide (DMF) and refluxed for 3 hours whilst bubbling CO through the solution. Then to this lemon yellow solution[113], a solution of $AsPh_3$ (2.48 g, 8.10 mmol in 75 cm^3 of DMF) was added. The mixture was stirred for 1 hour and the solvent was evaporated. The product was recrystallised from a dichloromethane and hexane mixture. Yield = 2.20 g, (70%). The melting temperature of the compound was 242-244^{o}C.

IR : ν(CO) at 1963 cm^{-1} (s) (KBr disc), literature value 1963 cm^{-1} (Table 18).

Preparation[137] of [RhCl(CO)$_2$]$_2$.

Carbon monoxide was passed over the crystals of rhodium(III) chloride (1.00 g, 4.04 mmol) at 100^{o}C for 3 hours and the orange-red sublimate of [RhCl(CO)$_2$]$_2$ formed. The product was purified[115] by extracting with

boiling hexane. The filtered hot resultant solution was by cooled to -20°C to give orange-red crystals. Yield = 0.50 g, (65%).

Preparation[115] of trans-$[RhCl(CO)(AsPh_3)_2]$ from $[RhCl(CO)_2]_2$.

A solution of $[RhCl(CO)_2]_2$, (0.50 g, 1.29 mmol) in benzene (60 cm^3) and a solution of $AsPh_3$, (2.00 g, 6.53 mmol) in benzene (40 cm^3) were mixed together and stirred for 1 hour under nitrogen at room temperature. Then the volume of the solution was reduced to 10 cm^3 on a vacuum line and ethanol added. The resulting yellow crystals were filtered off and washed with ethanol and diethyl ether respectively. The product was recrystallised from chloroform and ethanol mixture. Yield = 1.60 g, (80%). The melting temperature of the compound was 242-244°C.

(xx) Reaction of trans-$[RhCl(CO)(AsPh_3)_2]$ with $AgBF_4$ in Dichloromethane : Synthesis of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Compound (XVIII).

Dichloromethane (25 cm^3) was placed in a dry Schlenk tube, and this was degassed as in Fig. 7. Trans-$[RhCl(CO)(AsPh_3)_2]$ (0.20 g, 0.26 mmol) was then added. To this solution $AgBF_4$ (0.05 g, 0.26 mmol) was added, the Schlenk tube covered with aluminium foil and the mixture stirred for 15 minutes. A white precipitate was formed. The mixture was filtered through kieselguhr under nitrogen and the solvent evaporated on a vacuum line to give a yellow solid. This was recrystallised from a dichloromethane and hexane mixture under nitrogen. Yellow crystals formed. Yield = 0.16 g, (70%). The melting temperature of the compound was 215-220°C. The compound was soluble in dichloromethane, chloroform,

and methanol. The reaction could also be carried out in acetone.

IR : ν(CO) at 1989 cm^{-1} (s) and $\nu(BF_4^-)$ at 1078 cm^{-1} (b) (KBr disc).

^{1}H-NMR : (7.30-7.50) ppm (m, 30H) and 5.28 ppm (s, 1H) (in $CDCl_3$).

Analysis for $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2) = C_{37.5}H_{31}BClF_4OAs_2Rh$

	C%	H%
Found	51.7	3.7
Calculated	51.6	3.6

When the reaction was carried out in acetone, then an acetone coordinated compound was formed.

IR : ν(CO) at 1991 cm^{-1} (s), 1649 cm^{-1} (m) for coordinated acetone and $\nu(BF_4^-)$ at 1078 cm^{-1} (b) (KBr disc).

(xxi) Reaction of Compound (XVIII) with CO : Synthesis of trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$, Compound (XIX).

Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.10 g, 0.11 mmol) was taken in dichloromethane (10 cm^3) and CO was bubbled through the solution for 10 minutes. The solvent was evaporated from the solution on a vacuum line and orange-yellow crystals were obtained. The reaction could also be carried out in benzene.

IR : ν(CO) at 2037 cm^{-1} (s) and $\nu(BF_4^-)$ at 1054 cm^{-1} (b) (KBr disc).

(xxii) Reaction of trans-$[RhCl(CO)(AsPh_3)_2]$ with $AgBF_4$ in the Presence of CO : Synthesis of trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$, Compound (XIX).

Dichloromethane (25 cm^3) was placed in a Schlenk tube and degassed as in Fig. 7. Trans-$[RhCl(CO)(AsPh_3)_2]$, (0.20 g, 0.26 mmol) was dissolved in the solvent under nitrogen. The Schlenk tube was covered with aluminium foil and $AgBF_4$ (0.05 g, 0.26 mmol) was added. The flow of nitrogen was stopped and CO was bubbled through the solution for 30 minutes with stirring. The product was filtered through kieselguhr under CO and evaporation of the solvent on a vacuum line afforded orange-yellow crystals. Yield = 0.16 g, (70%).

IR : ν(CO) at 2037 cm^{-1} (s) and $\nu(BF_4^-)$ at 1054 cm^{-1} (b) (KBr disc).

(xxiii) Reaction of Compound (XVIII) with CH_3ONa in the Presence of CO : Synthesis of $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$, Compound (XX).

To freshly prepared sodium methoxide solution (ca. 1.10 mmol in 10 cm^3 of methanol) the compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.15 g, 0.17 mmol), was added under CO. Then CO was bubbled through the suspension for 5 minutes. The product was filtered off and washed with excess methanol. Yield = 0.08 g, (60%). The melting temperature of the compound was 90°C.

IR : ν(CO) at 2005 (s), 1954 cm^{-1} (s) and 1636 cm^{-1} (m) for the methoxycarbonyl band and $\nu(C\text{-}OCH_3)$ at 1039 cm^{-1} (m) (KBr disc). ν(CO) at 2004 (s), 1954 cm^{-1} (s) and 1630 cm^{-1} (m) for the methoxycarbonyl band and $\nu(C\text{-}OCH_3)$ at 1039 cm^{-1} (m) (Nujol mull).

^{1}H-NMR : 2.80 ppm (s, 3H) and 7.20 ppm (m, 30H) (in $CDCl_3$).

(xxiv) An Attempt to Prepare $[Rh(COOC_2H_5)(CO)_2(AsPh_3)_2]$ from Compound (XVIII) under CO.

To freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 10 cm^3 of ethanol) the compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.15 g, 0.17 mmol), was added under CO. Then CO was bubbled through the solution for 5 minutes. The compound may have been formed, but it decomposed in solution. Even at low temperature (-10°C) isolation was not possible.

(xxv) Reaction of Compound (XVIII), with CH_3ONa under Nitrogen : Synthesis of trans-$[Rh(OCH_3)(CO)(AsPh_3)_2]$, Compound (XXI).

To a freshly prepared sodium methoxide solution (ca. 1.10 mmol in 10 cm^3 of methanol) the compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.15 g, 0.17 mmol), was added under nitrogen. The yellow compound (XVIII) gradually dissolved and the solution was stirred for 30 minutes. The volume of the solution was reduced to one half on a vacuum line to give yellow crystals. The crystals were filtered off and washed with excess methanol, then recrystallised from benzene and hexane.
Yield = 0.09 g, (65%). The melting temperature of the compound was 114-115°C.

IR : ν(CO) at 1935 cm^{-1} (s) and no $\nu(BF_4^-)$ band (KBr disc).
^{1}H-NMR : 3.00 ppm (s, 3H) and (7.40-7.60) ppm (m, 30H) (in C_6D_6).

Analysis for $[Rh(OCH_3)(CO)(AsPh_3)_2] = C_{38}H_{33}O_2As_2Rh$

	C%	H%
Found	60.7	4.2
Calculated	58.9	4.3

The compound was not so air stable. Therefore, the analysis is not adequate.

(xxvi) Reaction of Compound (XVIII) with C_2H_5ONa : Synthesis of trans-$[Rh(OC_2H_5)(CO)(AsPh_3)_2]$, Compound (XXII).

To a freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 10 cm^3 of ethanol) the compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20 g, 0.23 mmol), was added under nitrogen. The mixture was stirred for 10 minutes. The solvent was evaporated on a vacuum line, extracted with benzene and filtered through a fine sintered crucible under nitrogen. The solvent was evaporated to give a yellow solid.
Yield = 0.08 g, (45%).

IR : $\nu(CO)$ at 1940 cm^{-1} (s) (KBr disc).
NMR : The NMR spectrum gave no signal for $C_2H_5O^-$ protons, the yellowish solution was changed to brownish yellow, probably the compound decomposed in the solution.

(xxvii) Reaction of Compound (XVIII) with HCOONa : Synthesis of trans-[Rh(OOCH)(CO)($AsPh_3$)$_2$], Compound (XXIII).

To a solution of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, (0.50 g, 0.57 mmol in 10 cm^3 of methanol), sodium methanoate solution (0.10 g, 1.28 mmol in 10 cm^3 of methanol) was added under nitrogen and the mixture stirred for 1 hour. The yellow crystals were filtered off and washed with water and methanol. The product was recrystallised form dichloromethane and methanol. Yield = 0.27 g, (60%). The melting temperature of the compound was 120-121^oC. The compound was soluble in chloroform, dichloromethane and acetone.

IR : ν(CO) at 1980 cm^{-1} (s), ν_{asy}(OCO) at 1602 (m) and ν_{sy} at 1382 cm^{-1} (m) (Nujol mull)

^{1}H-NMR : 7.00 ppm (m, 18H), 7.84 ppm (m, 12H) and 3.14 ppm (s, 1H) (in C_6D_6). Also 7.35 ppm (m, 18H), 7.65 ppm (m, 12H) and 3.40 ppm (s, 1H) (in $CDCl_3$).

(xxviii) Reaction of Compound (XVIII) with CH_3COONa : Synthesis of trans-[Rh($OOCCH_3$)(CO)($AsPh_3$)$_2$], Compound (XXIV).

Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.5 g, 0.57 mmol) was dissolved in methanol (10 cm^3) under nitrogen. To this sodium ethanoate solution (0.10 g, 1.20 mmol in 10 cm^3 of methanol) was added and the mixture stirred for 1 hour. The resulting yellow crystals were filtered off and washed with water and methanol. The product was recrystallised from dichloromethane and methanol. Yield = 0.37 g, (80%). The product was soluble in chloroform, dichloromethane and acetone and

insoluble in methanol, water and petroleum ether. The melting temperature of the yellow crystals was 188°C.

IR : ν(CO) at 1970 cm^{-1} (s), ν_{asy}(OCO) at 1610 cm^{-1} (m) and ν_{sy}(OCO) at 1375 cm^{-1} (m) (Nujol mull).

^{1}H-NMR : 0.84 ppm (s, 3H), 7.40 ppm (m, 18H) and 7.64 ppm (m, 12H) (in $CDCl_3$).

^{13}C-NMR : 23.00 ppm (s, CH_3), (129.50, 130.00, 134.50 and 135.00) ppm for (C_6H_5) and 176.30 ppm (s, COO^-) and 187.50 ppm (d, CO, with J_{Rh-C} = 60.0 Hz) (in $CDCl_3$).

Analysis for $[Rh(OOCCH_3)(CO)(AsPh_3)_2] = C_{39}H_{33}O_3As_2Rh$

	C%	H%
Found	58.4	4.1
Calculated	58.3	4.1

(xxix) Reaction of Compound (XVIII) with C_2H_5COONa : Synthesis of trans-$[Rh(OOCC_2H_5)(CO)(AsPh_3)_2]$, Compound (XXV).

Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.50 g, 0.57 mmol) was dissolved in methanol (10 cm^3) and to this sodium propanoate solution (0.12 g, 1.20 mmol in 10 cm^3 of methanol) was added under nitrogen and the mixture stirred for 30 minutes. The yellow crystals were filtered off and washed with water and methanol. They were recrystallised from dichloromethane and methanol mixture. Yield = 0.35 g, (75%). The melting temperature of the compound was 190°C. The compound was soluble in chloroform, dichloromethane, acetone and insoluble in methanol. The compound was less soluble than the

ethanoato compound.

IR : ν(CO) at 1975 cm^{-1} (s), ν_{asy}(OCO) at 1605 cm^{-1} (m) and ν_{sy}(OCO) at 1378 cm^{-1} (m) (Nujol mull). ν(CO) at 1975 cm^{-1} (s), ν_{asy}(OCO) at 1596 cm^{-1} (m) and ν_{sy}(OCO) at 1382 cm^{-1} (m) (KBr disc).

^{1}H-NMR : 0.20 ppm (t, 3H), 1.06 ppm (q, 2H) and 7.40 ppm (m, 18H) and 7.64 ppm (m, 12H) (in $CDCl_3$).

^{13}C-NMR : 9.90 ppm (s, CH_3), 29.70 ppm (s, CH_2), (128.70, 129.80, 134.00 and 134.60) ppm for (C_6H_5), 179.20 ppm (s, COO^-) and 189.20 ppm (d, with J_{Rh-C} = 61.8 Hz, Rh-CO) (in $CDCl_3$).

Analysis for $[Rh(OOCCH_2CH_3)(CO)(AsPh_3)_2] = C_{40}H_{35}O_3As_2Rh$

	C%	H%
Found	58.3	4.2
Calculated	58.8	4.3

(xxx) Reaction of Compound (XVIII) with KI : Formation[40] of trans-$[RhI(CO)(AsPh_3)_2]$.

Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.20g, 0.23 mmol) was dissolved in 10 cm^3 of methanol. To this solution, KI solution (0.1 g, 0.06 mmol in 10 cm^3 of methanol) was added and the mixture stirred under nitrogen. Within 30 minutes yellow microcrystals were formed. The product was filtered off and washed with methanol. The product was recrystallised from benzene and hexane mixture. Yield = 0.14 g, (70%).

Test for I^- : To the sodium fusion solution of the compound, $AgNO_3$

solution was added to give a yellow precipitate of AgI, which was insoluble in ammonia solution.

IR : ν(CO) at 1980 cm^{-1} (s) (KBr disc).

(C) RHODIUM-CYCLOHEXYLPHOSPHINE COMPOUNDS.

(xxxi) Preparation[114] of trans-Carbonylchlorobis(tricyclohexylphosphine) ruthenium(I), trans-[RhCl(CO)(PCy_3)$_2$].

Carbon monoxide was passed through a boiling solution of $RhCl_3.xH_2O$ (0.50 g, 2.02 mmol) in ethanol (60 cm^3) for about 30 minutes. Then an ethanolic solution of tricyclohexylphosphine, PCy_3 (1.13 g, 4.04 mmol) was added. The mixture was refluxed whilst stirring for about 15 minutes, then the yellow precipitate filtered off. Recrystallisation of the yellow precipitate was performed from a chloroform and methanol mixture. Yield = 0.91 g, (62%).

IR : ν(CO) at 1941 cm^{-1} (s) (KBr disc). Literature value 1941 cm^{-1} (Table 18).

(xxxii) Reaction of trans-[RhCl(CO)(PCy_3)$_2$] with $AgBF_4$ in Dichloromethane : Synthesis of [Rh(CO)(PCy_3)$_2$]$^+$[BF_4]$^-$.3/2(CH_2Cl_2), Compound (XXVI).

Dry dichloromethane (40 cm^3) was placed in a Schlenk tube and deoxygenated as described in Sec. 2 and trans-[RhCl(CO)(PCy_3)$_2$] (0.40 g, 0.55 mmol) added under a positive nitrogen flow. To this solution $AgBF_4$ (0.11 g, 0.55 mmol) was added and the Schlenk tube covered with aluminium foil. Then the mixture was stirred for 1 hour. The mixture was filtered through kieselguhr under nitrogen and the solvent was reduced to approximately 5 cm^3 on a vacuum line. Deoxygenated hexane was added and the yellow crystals were filtered and dried. Yield = 0.33 g, (66%).

The melting temperature of the compound was 150°C.

IR : ν(CO) at 1965 cm^{-1} (s) and $\nu(BF_4^-)$ at 1083 cm^{-1} (b) (KBr disc).

^{1}H-NMR : 1.22, 1.88 ppm (m, 66H) and 5.28 ppm (s, 3H) (in C_6D_6).

^{31}P-NMR : +35.25 ppm (d, with J_{Rh-P} = 117.2 Hz) (in C_6D_6).

Analysis for $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ = $C_{38.5}H_{69}BCl_3F_4OP_2Rh$

	C%	H%
Found	51.2	7.8
Calculated	51.0	7.6

(xxxiii) Reaction of Compound (XXVI) with CO : Synthesis of trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$, Compound (XXVII).

Carbon monoxide was passed through the solution of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (0.21 g, 0.23 mmol in 15 cm^3 of dichloromethane) for 30 minutes. The solvent was reduced to approximately 5 cm^3 on a vacuum line and hexane added to give a orange-yellow crystals. Yield = 0.11 g, (60%). The melting temperature of the compound was 160°C (decomposed). If benzene is used as a solvent the same product was obtained as identified by infrared spectroscopy.

IR : ν(CO) at 2005 cm^{-1} (s) and $\nu(BF_4^-)$ at 1050 cm^{-1} (b) (Nujol mull).

^{31}P-NMR : +42.14 ppm (d, with J_{Rh-P} = 97.7 Hz) (in C_6D_6).

(xxxiv) Reaction of Compound (XXVI) with CH_3ONa in the Presence of CO : Synthesis of trans-$[Rh(COOCH_3)(CO)(PCy_3)_2]$, Compound (XXVIII).

To a freshly prepared sodium methoxide solution (ca. 1.00 mmol in 15 cm^3 of methanol) compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (0.21 g, 0.23 mmol) was added under CO. Then CO was passed through the solution and within 10 minutes a yellow precipitate was formed. The precipitate was filtered off and washed with excess methanol. The compound also formed when sodium methoxide solution was added to the compound (II), $[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$ under CO.

IR : ν(CO) at 1950 cm^{-1} (s) and alkoxycarbonyl band at 1620 cm^{-1} (m) (KBr disc).

^{1}H-NMR : 1.20, 1.75 ppm (m), 3.22 ppm (s) and 3.42 ppm (s) (in $CDCl_3$).

^{31}P-NMR : +36.70 ppm (with J_{Rh-P} = 112.0 Hz) (in $CDCl_3$).

(xxxv) Reaction of Compound (XXVI) with CH_3ONa : Synthesis of trans-$[Rh(OCH_3)(CO)(PCy_3)_2]$, Compound (XXIX).

To the compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (0.21 g, 0.23 mmol) freshly prepared sodium methoxide solution (ca. 1.00 mmol in 15 cm^3 of methanol) was added and the mixture stirred for 2 hours. The volume of the clear yellow solution was reduced to one half and the yellow precipitate was filtered off and washed with excess methanol. Yield = 0.11g, (65%).

IR : ν(CO) at 1921 cm^{-1} (s) (KBr disc).

(xxxvi) Reaction of Compound (XXVI) with CH_3COONa : Synthesis of trans-$[Rh(OOCCH_3)(CO)(PCy_3)_2]$, Compound (XXX).

To the solution of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (0.21 g, 0.23 mmol in 10 cm^3 of methanol) sodium ethanoate solution (0.10 g, 1.20 mmol in 10 cm^3 of methanol) was added. A yellow precipitate rapidly formed. The mixture was stirred for 15 minutes. The yellow precipitate was filtered off and washed with methanol, followed by water and methanol. The solid was recrystallised using dichloromethane and methanol.

IR : ν(CO) at 1943 cm^{-1} (s), ν_{asy}(OCO) at 1622 cm^{-1} (m) and ν_{sy}(OCO) at 1367 cm^{-1} (m) (KBr disc).

(D) RHODIUM-STIBINE COMPOUNDS.

(xxxvii) Preparation of $[RhCl(SbPh_3)_3]$.

The compound $[RhCl(SbPh_3)_3]$ was prepared with the same procedure as for the preparation[116] of $[RhCl(PPh_3)_3]$ described in Sec. 4.2A(i).

(xxxviii) An Attempt to Prepare $[RhCl(CO)(SbPh_3)_2]$ from $[RhCl(SbPh_3)_3]$.

$[RhCl(SbPh_3)_3]$ (0.20 g, 0.16 mmol) was dissolved in dichloromethane (20 cm^3). Through this red solution, CO was passed for 3 hours. Then the solvent was evaporated off. The infrared spectrum of the product did not show any carbonyl band.

(xxxix) Preparation[40] of trans-$[RhCl(CO)(SbPh_3)_2]$.

A lemon-yellow solution was obtained by passing CO through a hot solution of $RhCl_3.xH_2O$ (0.60 g, 2.43 mmol) in 75 cm^3 of dimethylformamide (DMF). To this lemon-yellow solution $SbPh_3$ solution (1.72 g, 4.87 mmol in 50 cm^3 of DMF) was added. The bright red crystals obtained were recrystallised from chloroform and ethanol.

Yield = 1.70 g, (80%).

IR : ν(CO) at 1962 cm^{-1} (s) (KBr disc). Literature value 1960 cm^{-1} (Nujol mull)[40] (Table 18).

(xL) An Attempt to Prepare $[Rh(CO)(SbPh_3)_2]^+[BF_4]^-$ from trans-$[RhCl(CO)(SbPh_3)_2]$.

To the solution of trans-$[RhCl(CO)(SbPh_3)_2]$ (0.20 g, 0.22 mmol in 20 cm^3 of dichloromethane) $AgBF_4$ (0.05 g, 0.25 mmol) was added under nitrogen. The mixture was stirred for 30 minutes and filtered through kieselguhr under nitrogen. After evaporation of the solvent, a reddish-yellow gummy mass was obtained. The infrared spectrum of the product indicated the decomposition of the compound (KBr disc). The preparation was repeated at low temperatures (-10°C).

(xLi) Reaction of trans-$[RhCl(CO)(SbPh_3)_2$ with $AgBF_4$ in the Presence of CO : Formation of $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$, Compound (XXXI).

To degassed dichloromethane (40 cm^3), trans-$[RhCl(CO)(SbPh_3)_2]$ (0.4 g, 0.45 mmol) was added. To this solution $AgBF_4$ (0.09 g, 0.46 mmol) was added and stirred for 30 minutes, passing CO through the solution. Along with the white precipitate, some dark reddish solid material formed. Then the mixture was filtered off under nitrogen through a small amount of kieselguhr. The volume of the yellow filtrate was reduced to ca. 10 cm^3 on a vacuum line and by the addition of hexane, yellow crystals were formed. Yield = 0.27 g, (42%). The melting temperature of the compound was 170°C. The compound was soluble in dichloromethane, chloroform and benzene.

IR : ν(CO) at 2006 cm^{-1} (s), $\nu(BF_4^-)$ at 1061 cm^{-1} (b) (KBr disc) and ν(CO) at 2004 cm^{-1} (s) (Nujol mull).

Analysis for $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2 = C_{57}H_{47}Cl_2BF_4O_2Sb_3Rh$

	C%	H%	
Found	49.3	3.4	(Separate preparations).
	49.2	3.4	
Calculated	49.3	3.4	

(x,ii) Reaction of $[RhCl(SbPh_3)_3$ with $AgBF_4$ in the Presence of CO in Dichloromethane : Formation of $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$, Compound (XXXI).

To degassed dichloromethane (40 cm^3) $[RhCl(SbPh_3)_3]$ (0.40 g, 0.33 mmol) was added under nitrogen. To this red solution $AgBF_4$ (0.07 g, 34 mmol) was added. Nitrogen was replaced by CO. The mixture was stirred for 1 hour, passing CO through the solution. The yellow solution was filtered through kieselguhr under nitrogen. The volume of the solution was reduced to ca. 10 cm^3 on a vacuum line. To this hexane was added to give yellow crystals. Yield = 0.32 g, (70%).

IR : ν(CO) at 2006 cm^{-1} (s) and $\nu(BF_4^-)$ at 1061 cm^{-1} (b) (KBr disc).

(x,iii) Reaction of Compound (XXXI), $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ with CH_3ONa : Synthesis of $[Rh(COOCH_3)(CO)(SbPh_3)_3]$, Compound (XXXII).

To a freshly prepared sodium methoxide solution (ca. 1.10 mmol in 10 cm^3 of methanol) $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ (0.30 g, 0.22 mmol) was added under nitrogen and stirred for 3 hours. The suspension changed from bright yellow to pale yellow. The solid was filtered off and washed

with methanol. Yield = 0.16 g, (60%). The melting temperature of the compound was 140°C. The compound was soluble in dichloromethane, chloroform and benzene.

IR : ν(CO) at 1979 (s) and 1603 cm^{-1} (m) for the methoxycarbonyl band (KBr disc). ν(CO) at 1981 (s), 1603 cm^{-1} (m) for the methoxycarbonyl band (Nujol mull).

^{1}H-NMR : 2.41 ppm (s, 3H) and (7.10-7.50) ppm (m, 45H) (in $CDCl_3$).

(xliv) Reaction of Compound (XXXI), $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ with C_2H_5ONa : Synthesis of $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$, Compound (XXXIII).

To a freshly prepared sodium ethoxide solution (ca. 1.10 mmol in 10 cm^3 of ethanol), $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ (0.30 g, 0.22 mmol) was added under nitrogen and stirred for 2 hours. The pale yellow solid was filtered off and washed with ethanol. Yield = 0.18 g, (55%).

IR : ν(CO) at 1982 cm^{-1} (s) and 1601 cm^{-1} (m) for the ethoxycarbonyl band (Nujol mull).

^{1}H-NMR : 1.22 ppm (t, 3H), 2.95 ppm (q, 2H) and (7.10-7.50) ppm (m, 45H) (in $CDCl_3$).

4.3 RESULTS AND DISCUSSION.

(A) RHODIUM-PHOSPHINE COMPOUNDS.

(i) Synthesis of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Carbonylbis-(triphenylphosphine)rhodium(I) tetrafluoroborate dichloromethane solvate, Compound (VI).

The compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ has been prepared [Sec. 4.2A(iii)] by the reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with silver tetrafluoroborate, ($AgBF_4$) and the compound is characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 34) of the compound shows only one carbonyl band at 1994 cm^{-1} and a broad band at 1090 cm^{-1} represents[97,98] $\nu(BF_4^-)$. The carbonyl band is at higher frequency than the precursor compound[116], trans-$[RhCl(CO)(PPh_3)_2]$ in which the ν(CO) band appears at 1960 cm^{-1} (infrared spectrum Appendix-3). This higher frequency is due to the formation of a salt. The formation of the cation results in an overall decrease of the electron density on the metal. The back donation from metal to carbonyl moiety decreases and as a result the antibonding electron density on the carbonyl group decreases, i.e. the bond order increases, the bond length decreases and the carbonyl stretching frequency goes to a higher frequency [detailed explanation in Sec. 3.3(i)]. Wilkinson[133] reported that (BF_4^-) also forms a coordination compound, $[Rh(PPh_3)_3(BF_4)]$. When the (BF_4^-) group is coordinated[98], it shows a broad band at 1110-1170 cm^{-1} and for the free (BF_4^-) group it shows a broad band at 1050-1080 cm^{-1}. From the $\nu(BF_4^-)$ value of the

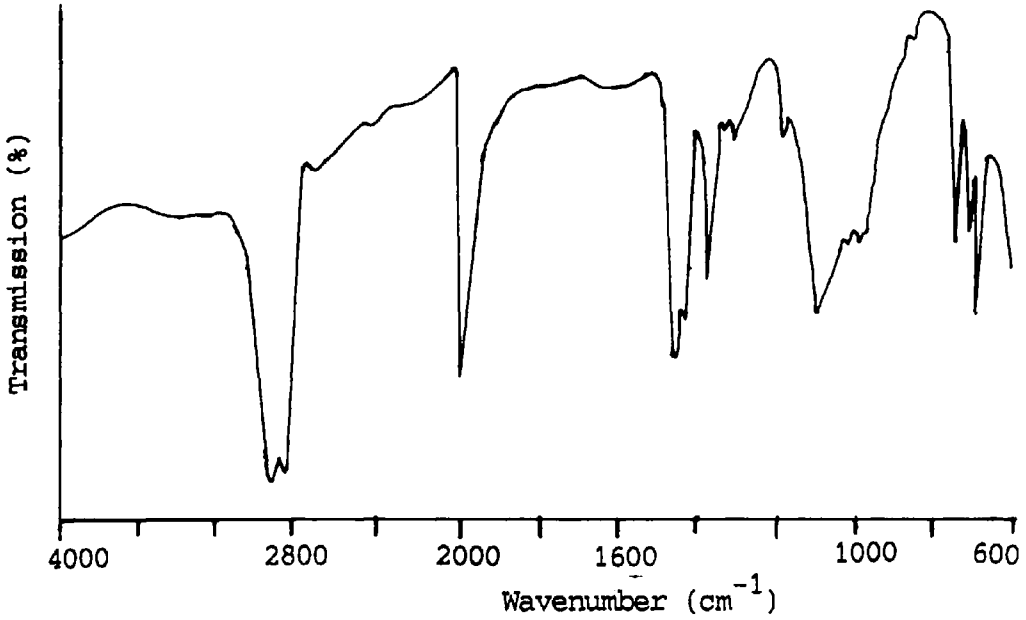


Fig. 34 : Infrared spectrum of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (Nujol mull).

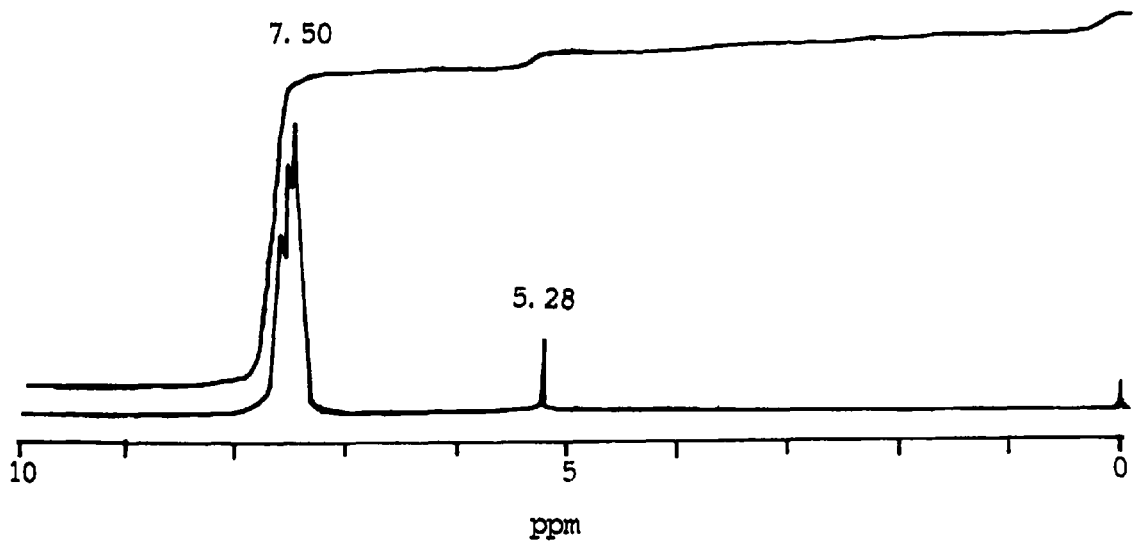


Fig. 35 : ^{1}H-NMR spectrum of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (in $CDCl_3$, TMS).

present compound, it seems that the (BF_4^-) anion is not coordinated[97,98] to the metal but remains free forming a salt.

The ^{1}H-NMR spectrum (Fig. 35) of the compound shows a multiplet at 7.50 ppm is assigned to the aromatic protons of PPh_3 and a singlet at 5.28 ppm, attributed to the methylene protons of dichloromethane. The integration ratio of aromatic and methylene protons is 30:1, i.e. half of a molecule of dichloromethane is present in the compound.

The ^{31}P-NMR spectrum of the compound (Fig. 36) shows a doublet at +30.70 ppm (with J_{Rh-P} = 123.0 Hz) at room temperature. The coupling constant of the cationic complex (VI) is smaller than the non-cationic precursor $[RhCl(CO)(PPh_3)_2]$. In the literature[138] the same trend of coupling constant was observed for the cationic complex $[Rh(CO)(ttp)]^+$ as compared with its non-cationic precursor [RhCl(CO)(ttp)], where ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$. This change of coupling constant is very small[138]. The same trend of coupling constant has been observed for the complex $[Rh(CO)(PCy_3)_2]^+$ [Sec. 4.3C(xiv)]. The chemical shift of the present cationic complex is downfield from the non-cationic precursor, due to less back donation from the metal to phosphorus. So the electron density on the phosphine is less in the cationic complex than the non-cationic precursor. In the literature[139] this deshielding pattern is also observed for the cationic complexes as compared with their precursors. For example, the ^{31}P-NMR of the cationic complex $[Ir(CO)(PPh_3)_2.(Acetone)]^+[B_{11}CH_{12}]^-$ is +52.35 ppm, but for the precursor $[IrCl(CO)(PPh_3)_2]$ the value is +47.64 ppm.

When the reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with $AgBF_4$ is carried out in acetone, then the acetone coordinated compound,

$[Rh(CO)(PPh_3)_2.(Acetone)]^+[BF_4]^-$ is formed. The infrared spectrum (Fig. 37) shows a strong carbonyl band at 1999 cm^{-1} and a medium band at 1651 cm^{-1} due to the coordinated acetone and a broad band at 1095 cm^{-1} for the $\nu(BF_4^-)$. The $\nu(BF_4^-)$ value suggests that it is free state[97,98] in the compound. The free acetone shows a band at 1705 cm^{-1}. The ^{1}H-NMR spectrum (Fig. 38) also shows a singlet at 1.35 ppm (6H) and a multiplet at 7.50 ppm (30H). The signal at 1.35 ppm is assigned to the coordinated acetone[103,140]. The signal for free acetone is 2.06 ppm. The ^{31}P-NMR of acetone coordinated compound is at +31.60 ppm (with J_{Rh-P} = 126.0 Hz). When acetone is added to the compound (VI), then the acetone

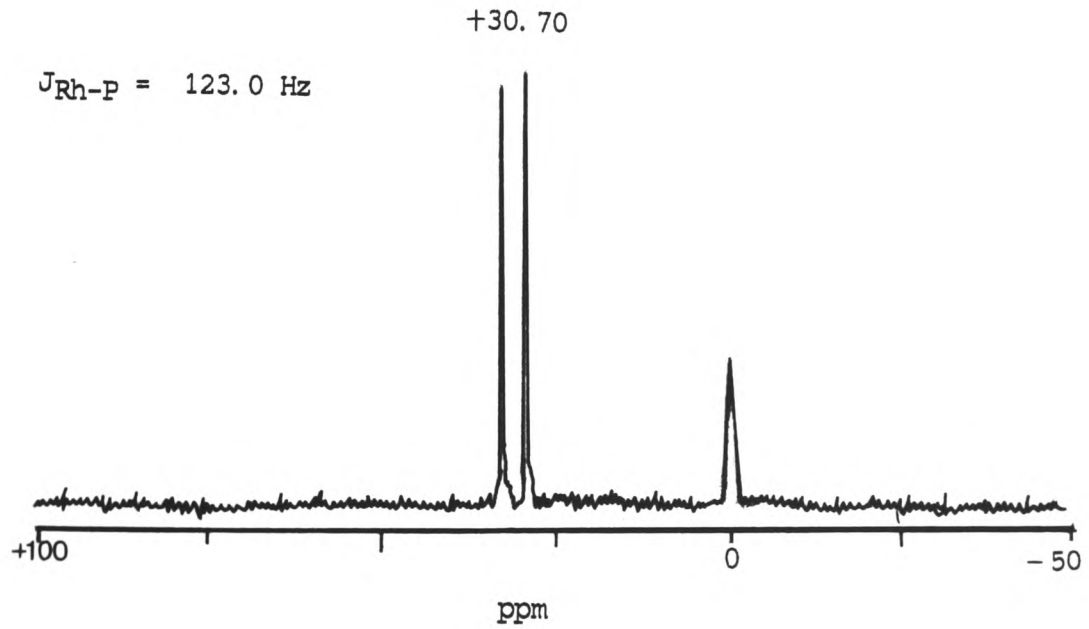


Fig. 36 : ^{31}P-NMR spectrum of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (in $CDCl_3$, 85% H_3PO_4).

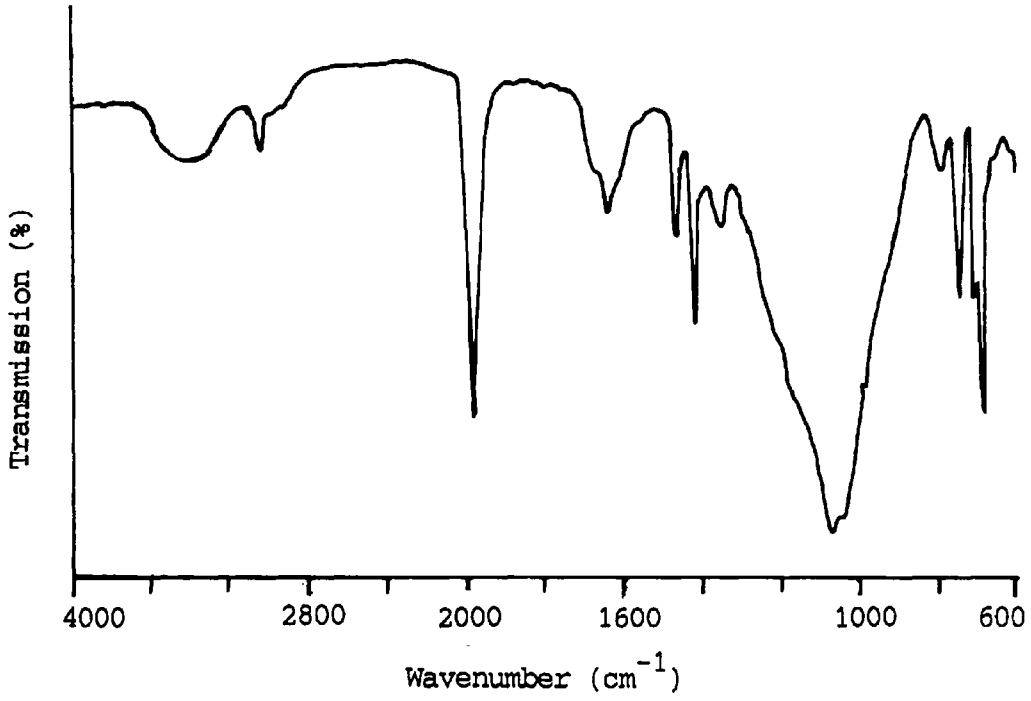


Fig. 37 : Infrared spectrum of $[Rh(CO)(PPh_3)_2.(Acetone)]^+[BF_4]^-$ (KBr disc).

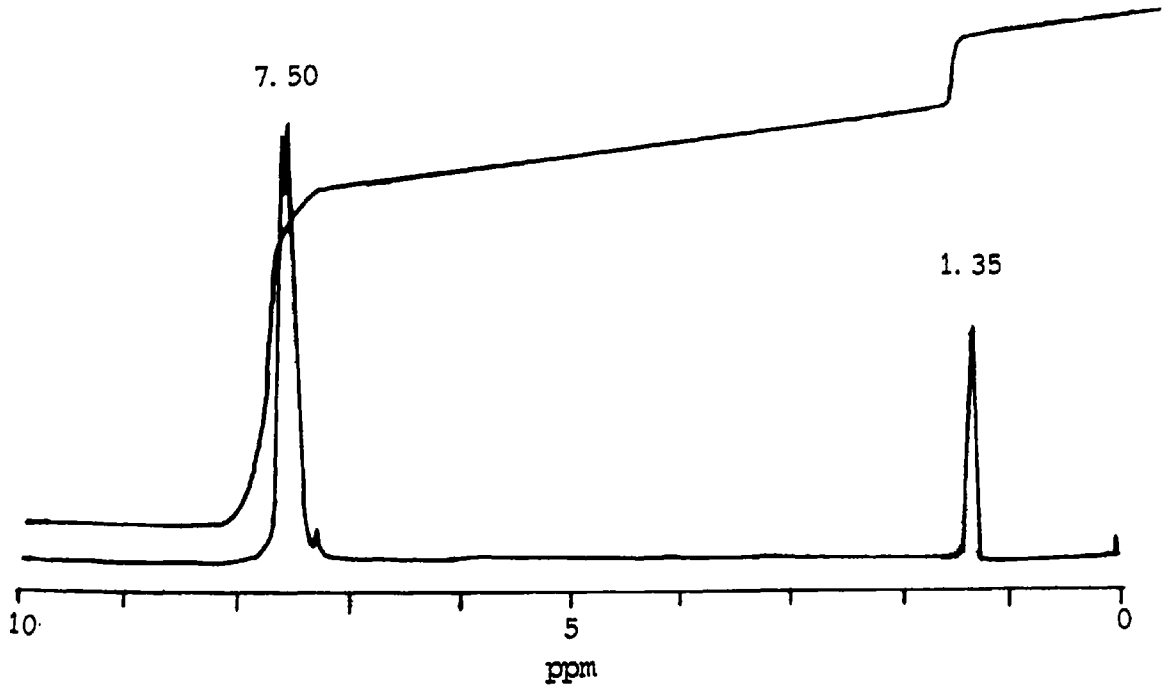


Fig. 38 : ^{1}H-NMR spectrum of $[Rh(CO)(PPh_3)_2.(Acetone)]^+[BF_4]^-$ (in $CDCl_3$, TMS).

coordinated compound is formed, because acetone is more coordinating than dichloromethane[102]. For example, it has been shown in the literature[102] that the complex $[Rh(PPh_3)_3]^+$, when prepared in acetone, forms the acetone coordinated compound. However, when this acetone coordinated compound is recrystallised from dichloromethane then the lattice solvated species $[Rh(PPh_3)_3]^+[ClO_4]^-.CH_2Cl_2$ is formed[102].

Rhodium compounds with coordinated acetone or methanol are known[102,103]. The acetone coordinated compound, $[Rh(CO)(PPh_3)_2.(Acetone)]^+[ClO_4]^-$ has been prepared from the unstable $[Rh(CO)_3(PPh_3)_2]^+[ClO_4]^-$ by decarbonylation in acetone[103]. The literature has also reported that rhodium(I) derivatives of the type $[RhCl(CO)L_2]$, [where L = PPh_3, $AsPh_3$, $SbPh_3$] have no tendency to oxidise spontaneously or to reduce silver nitrate or mercuric chloride[115]. Therefore, it can be assumed that Cl^- has been replaced by (BF_4^-) and due to the cation formation the ν(CO) moves to higher frequency than the precursor. From infrared, NMR spectroscopy and analysis it has been found that half a molecule of dichloromethane is contained in the compound (VI) and it is assumed that the 14-electron complex is stabilised by the solvent molecule[132] either by solvation or coordination. In the present case in compound (VI) dichloromethane may be weakly coordinated, because the ^{1}H-NMR shows only a small shift from the free dichloromethane. The chemical shift of free dichloromethane is at 5.35 ppm and in the compound the value is at 5.28 ppm. In the literature[106] it is also reported that the chemical shifts of coordinated dichloromethane and free dichloromethane are in the same region that was discussed in Sec. 3.3(i).

Although the haloalkane has very weak ligating properties[141], species containing coordinated dichloromethane are known[106, 141-144]. Additionally, cationic species containing dichloromethane as a ligand have been reported in the literature when halide abstractions have been carried out in the same as solvent[105, 145]. Beck and Schloter[141] observed small shifts for the symmetric and asymmetric values of v(C-Cl) in the infrared spectrum of weakly coordinated, as opposed to free, dichloromethane. This region is obscured by broad-based phosphine bands and therefore provides no evidence to support coordination of solvent. A Lassaigne fusion test shows the presence of chlorine in the compound.

Stable 14-electron compounds of rhodium of type $[RhX(PCy_3)_2]$, (where X = F, Cl, Br, I) have already been reported[127]. The structure of the compound $[RhX(PCy_3)_2]$ has been proposed as trigonal with the two PCy_3 ligands equivalent. In the literature another three-coordinated stable compound with a different anion $[Rh(CO)(PPh_3)_2]_4SiW_{12}O_{40}$ is reported[146], which shows v(CO) at 1990 cm^{-1} and the ^{31}P-NMR shows a broad singlet at +29.00 ppm (unresolved coupling with Rh) with only 2.00 ppm deshielded from the precursor $[Rh(CH_3CN)(CO)(PPh_3)_2]_4SiW_{12}O_{40}$. The compound $[Rh(PPh_3)_3]^+[ClO_4]^-.CH_2Cl_2$ exhibits diamagnetism, which for a three-coordinate d^8 system necessitates distortion from ideal trigonal planar geometry[102]. The diamagnetism of compound (VI) would therefore indicate departure from trigonal planar geometry - possibly by solvent interaction.

Therefore, from infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis, the compound (VI) is formulated as $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$.

A recent publication[147] has described a species formulated as $[Rh(CO)(PPh_3)_2.H_2O]^+[BF_4]^-.1/2(H_2O).1/4(C_6H_{12})$, prepared from the reaction of $[RhCl(CO)(PPh_3)_2]$ and $AgBF_4$ in benzene and characterised by X-ray crystallography only. The compound was prepared and crystallised in undried reagent grade solvents and the workup process was not under nitrogen. Therefore, it appears that the moisture (H_2O) in the compound was taken from the solvents or from the air.

In the present work, all the solvents were distilled and dried and the experiments were carried out under dry nitrogen. Moreover the analysis of the compound is consistent with dichloromethane, not with water. The Nujol mull spectrum of the compound does not indicate the presence of any water in the compound. Although the infrared spectrum in KBr disc shows a trace of water, it is suggested that it is present in the KBr. Similar spectra for blank KBr discs all showed equivalent traces of water. In the present case, if water was not rigorously excluded, the reactions of the cation with nucleophiles, RO^-(alkoxides) to form alkoxycarbonyl or alkoxo compounds would not work as in Sec. [4.3A{(iii), (iv), (v)} and 4.3B(x), (xi)}] instead hydroxo or hydroxycarbonyl compounds would form[35,38]. Their infrared and NMR spectra together with analyses suggest the alkoxycarbonyl or alkoxo compounds, not the hydroxycarbonyl or hydroxo compounds.

Analysis and the nature of the preparation, together with the nature of the rhodium compounds suggest the formulation of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$. However, only by X-ray crystallography could this structure be confirmed.

(ii) Synthesis of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$, Dicarbonylbis-(triphenylphosphine)rhodium(I) tetrafluoroborate, Compound (VII).

The orange-yellow crystalline compound (VII), trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ has been prepared [Sec. 4.2A(iv)] by the reaction of compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with CO. The compound (VII) has also been prepared by the reaction of trans-$[RhCl(CO)(PPh_3)_2]$ with $AgBF_4$ in the presence of CO [Sec. 4.2A(v)]. The compound (VII) is characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 39) of the compound shows a strong band at 2046 cm^{-1} in the carbonyl region and a broad band[97,98] at 1057 cm^{-1} for $\nu(BF_4^-)$. The carbonyl frequency of compound (VII) moves to higher frequency than the precursor compound (VI) due to the coordination of another Π-acid ligand. The back donation from M to C is shared by two CO moieties. As a result the antibonding electron density of the CO decreases, the bond order increases and the bond length decreases. The infrared spectrum of the present compound is in reasonable agreement with a similar compound[96] $[Rh(CO)_2\{P(2\text{-}CH_3C_6H_4)_3\}_2]^+[ClO_4]^-$, which shows ν(CO) at 2040 cm^{-1} (Table 19). In the literature[53] a similar compound, $[Rh(CO)_2(PPh_3)_2]^+[AlCl_4]^-$ was prepared from the reaction of $[RhCl(CO)(PPh_3)_2]$ with $AlCl_3$ in the presence of CO. Due to the instability of the compound, it was not possible to obtain carbon and hydrogen analyses only rhodium and chloride values[53]. The ν(CO) value of this compound was 2017 cm^{-1} (KBr disc)[53].

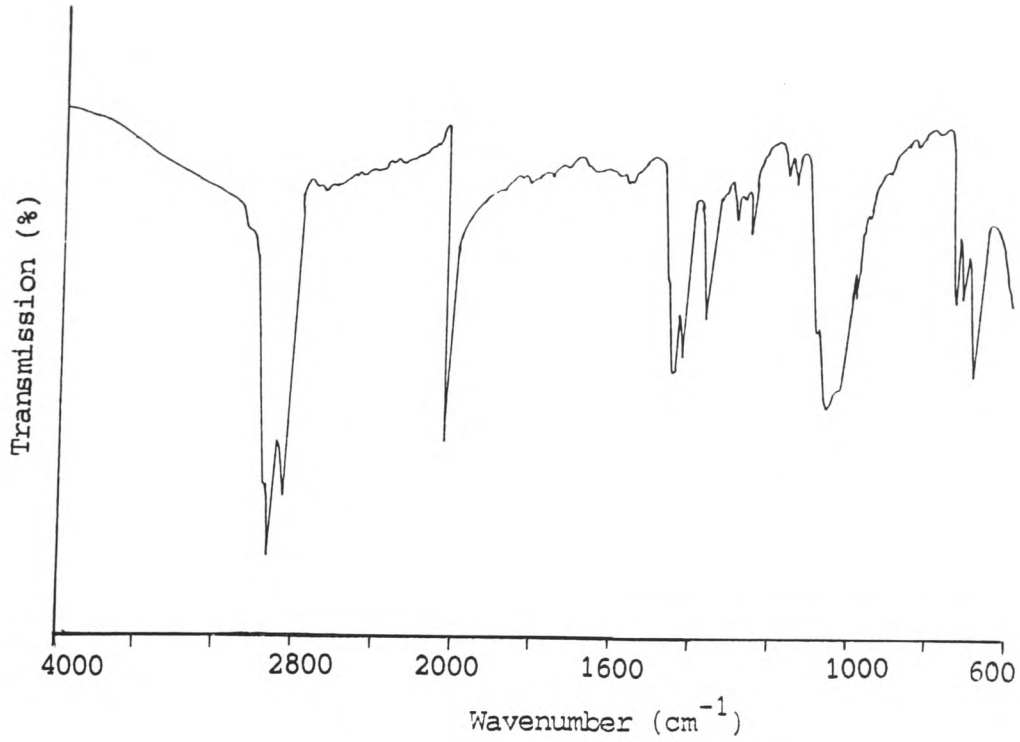


Fig. 39 : Infrared spectrum of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (Nujol mull).

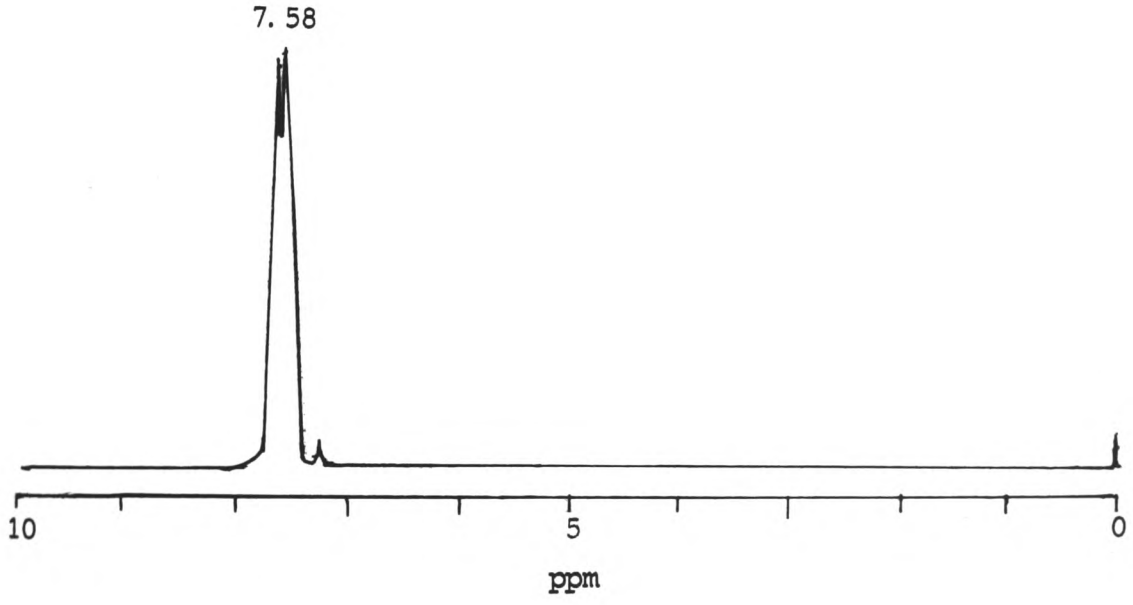


Fig. 40 : ^{1}H-NMR spectrum of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (in $CDCl_3$, TMS).

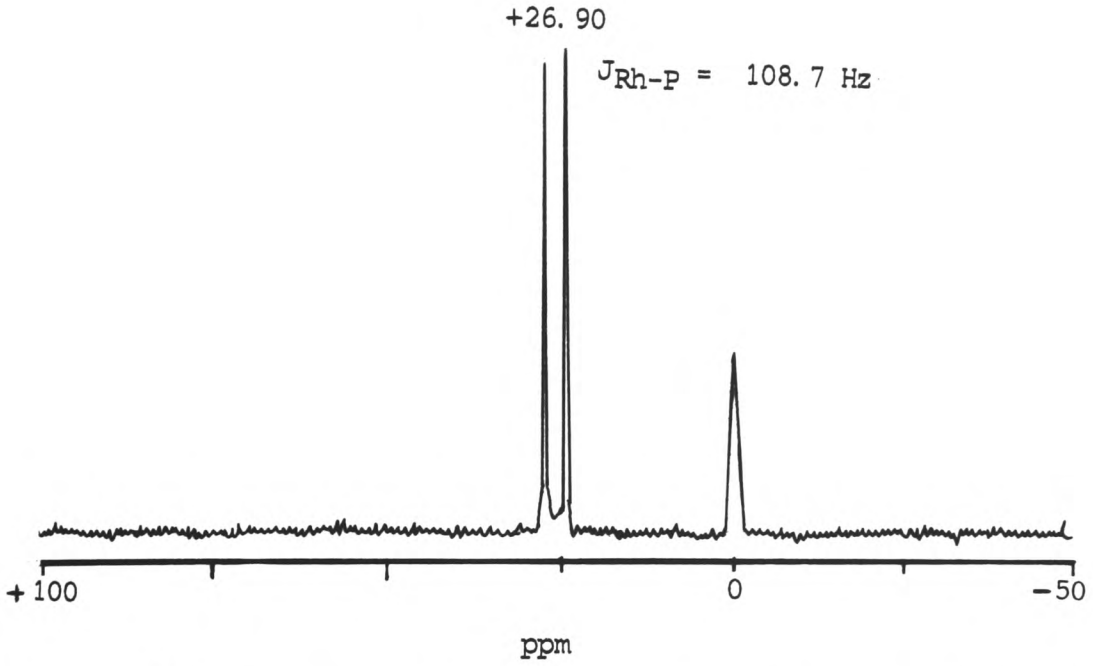


Fig. 41 : ^{31}P-NMR spectrum of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ (in $CDCl_3$, 85% H_3PO_4).

The ^{1}H-NMR spectrum (Fig. 40) of the compound (VII) shows a multiplet at 7.58 ppm for the aromatic protons of PPh_3. The ^{31}P-NMR spectrum (Fig. 41) of the compound shows a doublet at +26.90 ppm (with J_{Rh-P} = 108.7 Hz). The value is consistent with a similar type of compound[135] $[Rh(CO)_2(PPh_3)_2]^+[HC(SO_2CF_3)_2]^-$, which shows chemical shift at +26.60 ppm (with J_{Rh-P} = 106.0 Hz).

The spectral data and analysis of compound (VII) are consistent with the formula $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$. By analogy with the four-coordinated compound of rhodium(I), $[RhCl(CO)(L)_2]$ (where L = PPh_3, $AsPh_3$, $SbPh_3$) the complex $[Rh(CO)_2(PPh_3)_2]^+$ should have a square planar configuration and the rhodium atom have dsp^2 hybridisation[115], since the compound has

only one carbonyl band. Therefore, the carbonyl groups should be trans in position, rather than cis carbonyl groups, which should have two carbonyl bands. Therefore, the proposed structure of the compound is square planar (D_{2h} symmetry) as in Fig. 42.

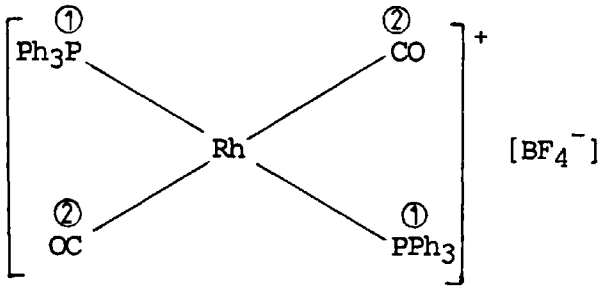


Fig. 42 : Structure of trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$. [IUPAC name, (SP-4-1)-dicarbonylbis(triphenylphosphine)rhodium(I) tetrafluoroborate.

The present compound is comparatively more stable in dichloromethane and benzene than in acetone. In acetone the compound rapidly loses one CO and gives the acetone coordinated compound, $[Rh(CO)(PPh_3)_2.(Acetone)]^+[BF_4]^-$ as identified from its infrared spectrum. The infrared spectrum of the compound (VII) sometimes gave a weak broad band at 1985 cm^{-1} along with the band at 2047 cm^{-1} (KBr disc). This may be due to the decomposition of compound in the KBr disc. It was observed that when the same KBr disc was left for two hours in air, the intensity of the band 2047 cm^{-1} decreased. The band at 1985 cm^{-1} is not due to the formation of bromo compound by bromide coordination (Table 18). It is probably due to decomposition of the compound, because the band is not sharp, rather weak and broad.

There seems to be some confusion as to whether $[Rh(CO)(PPh_3)_2.H_2O]^+$ reacts with CO to give $[Rh(CO)_3(PPh_3)_2]^+$ or cis-$[Rh(CO)_2(PPh_3)_2]^+$ which

shows[147] ν(CO) at 2037, 2023 cm^{-1}. The present compound is not consistent with the formula $[Rh(CO)_3(PPh_3)_2]^+[BF_4]^-$. Therefore the analysis, infrared and ^{31}P-NMR evidence suggest that the compound (VII) is trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$.

(iii) Synthesis of $[Rh(COOR)(CO)_2(PPh_3)_2]$, Alkoxycarbonyl(dicarbonyl)-bis(triphenylphosphine)rhodium(I), where R = CH_3, C_2H_5 and C_3H_7-Compounds (VIII), (IX) and (X) respectively.

The alkoxycarbonyl compounds, $[Rh(COOR)(CO)_2(PPh_3)_2]$ have been prepared from the reaction of compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with sodium alkoxide (RONa, where R = CH_3, C_2H_5, C_3H_7) in the presence of CO [Sec. 4.2A{(vi), (vii), (viii)}] to give the compounds [(VIII), (IX) and (X)] respectively. The compounds could also be prepared from the reaction of compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ with sodium alkoxide in the presence of CO [Sec. 4.2A{(xiii), (xiv), (xv)}]. The compounds are characterised by infrared, ^{1}H-NMR and ^{31}P-NMR spectroscopy.

The infrared spectrum (Fig. 43) of the compound (VIII) shows two strong carbonyl bands at 2004 and 1957 cm^{-1}. These carbonyl bands suggest that there may be two distinct carbonyl moieties in the compound[22]. The band at 1637 cm^{-1} is assigned to the methoxycarbonyl group[22, 42, 44, 49] and a band at 1040 cm^{-1} is assigned[22, 49] to the ν(C-OCH_3).

The ^{1}H-NMR spectrum (Fig. 44) of the compound shows a singlet at 2.81 ppm, (3H) is assigned to the methyl protons of the ($COOCH_3$) group. A multiplet at (7.40-7.80) ppm, (30H) is assigned to the

aromatic protons of the PPh_3. The spectral data are consistent[22] with the reported compound, $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$. In the literature this compound was prepared from $[Rh(CO)(NHCOOC_2H_5)(PPh_3)_2]$ by carbonylation in methanol, where the compound was characterised by infrared, ^{1}H-NMR spectroscopy and analysis. The ^{31}P-NMR spectrum (Fig. 45) of the compound (VIII) shows a doublet at +26.40 ppm (with J_{Rh-P} = 130.5 Hz).

Five-coordinated rhodium(I) compounds generally prefer the trigonal bipyramidal configuration[2]. The spectral data of the present rhodium compound has a similarity with the corresponding iridium compound[22,38] $[Ir(COOCH_3)(CO)_2(PPh_3)_2]$, where the structure was proposed as trigonal bipyramidal with cis carbonyl groups.

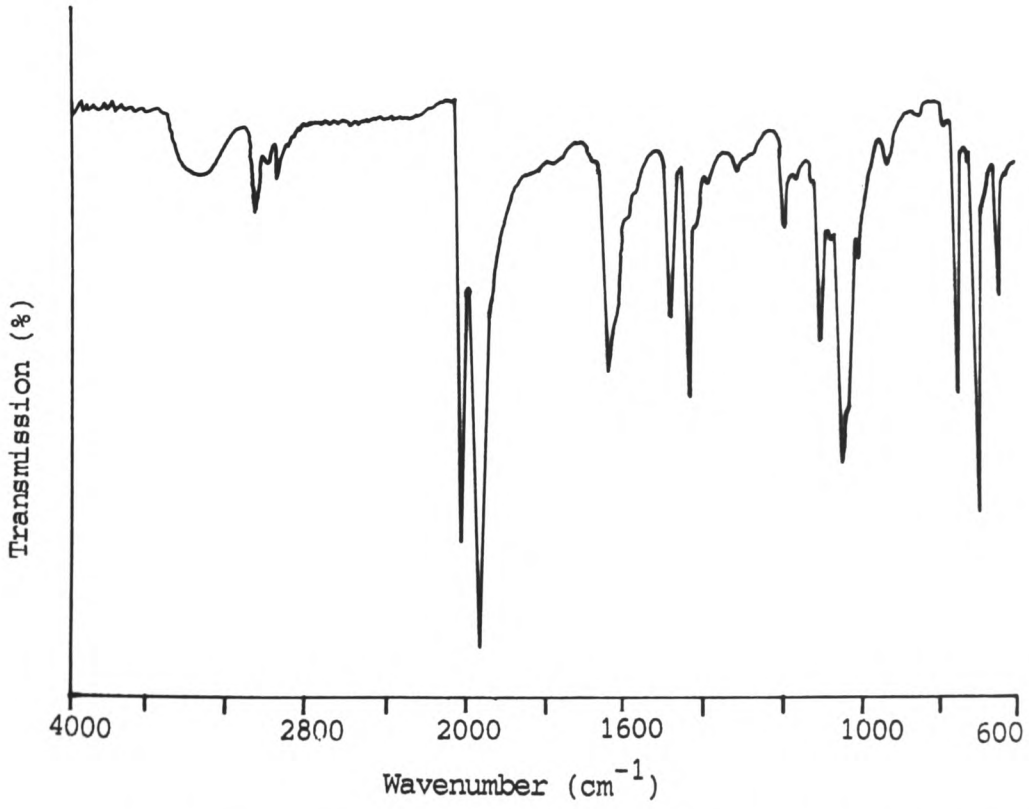


Fig. 43 : Infrared spectrum of $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$ (KBr disc).

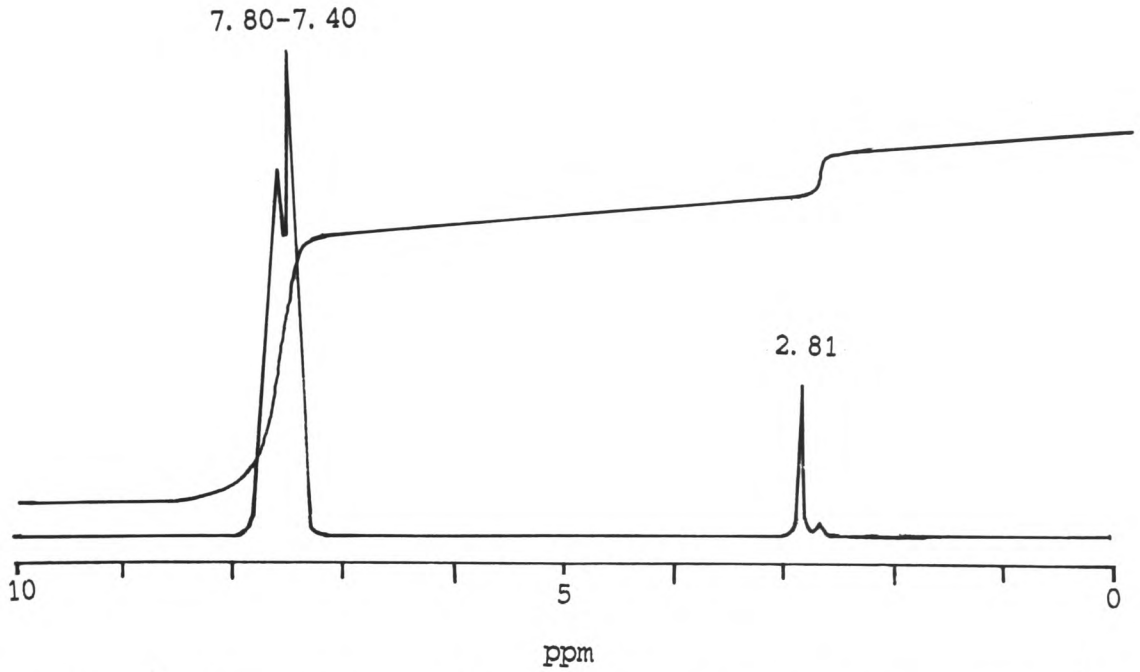


Fig. 44 : ^{1}H-NMR spectrum of [Rh(COOCH$_3$)(CO)$_2$(PPh$_3$)$_2$] (in Acetone-d^6).

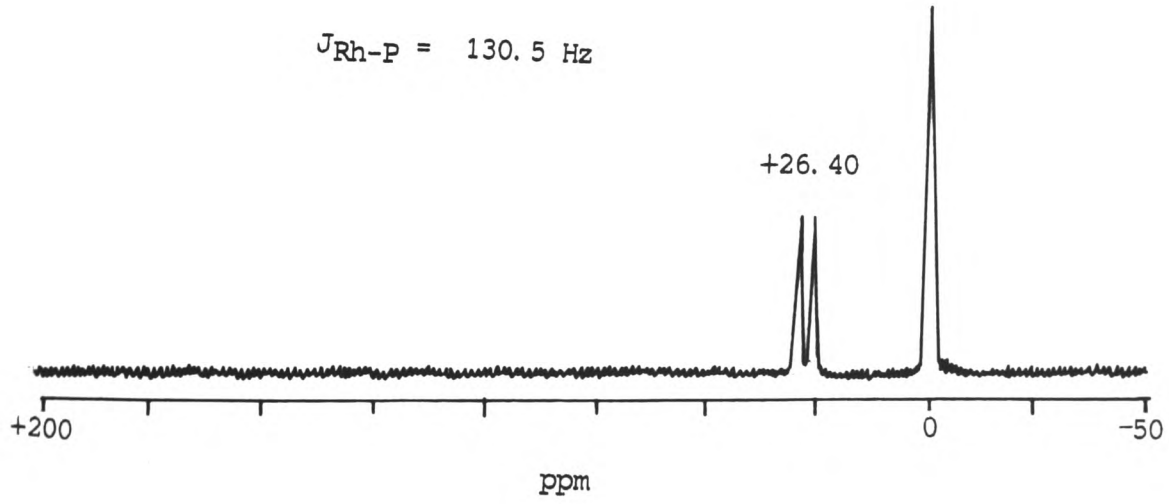


Fig. 45 : ^{31}P-NMR spectrum of [Rh(COOCH$_3$)(CO)$_2$(PPh$_3$)$_2$] (in CDCl$_3$, 85% H$_3$PO$_4$).

Therefore, from infrared, ^{1}H-NMR and ^{31}P-NMR spectra the structure of the five coordinated $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$ is proposed to be trigonal bipyramidal (C_{2v} symmetry) as in Fig. 46, [where R = CH_3], drawing an analogy with the reported iridium compound[22, 38].

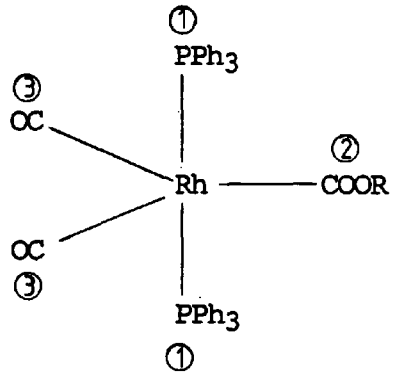


Fig. 46 : Structure of $[Rh(COOR)(CO)_2(PPh_3)_2]$. [IUPAC name, where R = CH_3, (TBPY-5-11)-dicarbonyl(methoxycarbonyl)bis(triphenylphosphine)-rhodium(I)].

The compound (VIII) gradually decomposed in solution, even in the solid state it decomposed slowly in air. The solid changed colour from yellow to brown-yellow over a period of days. This decomposition was also seen from the infrared spectrum (Fig. 47). The original two strong carbonyl bands at 2004 and 1957 cm^{-1} disappeared and a very weak band at 2042 cm^{-1} and a medium band at 1962 cm^{-1} appeared. Also the band at 1637 cm^{-1} for the alkoxycarbonyl group disappeared and two new bands were found at 1495 and 1195 cm^{-1}. The band at 1195 cm^{-1} suggested the compound decomposed and the phosphine was converted to phosphine oxide[148, 149]. The band at 2042 cm^{-1} could have been a hydride band[79], but the ^{1}H-NMR of the same product did not indicate any hydride resonance up to -30 ppm.

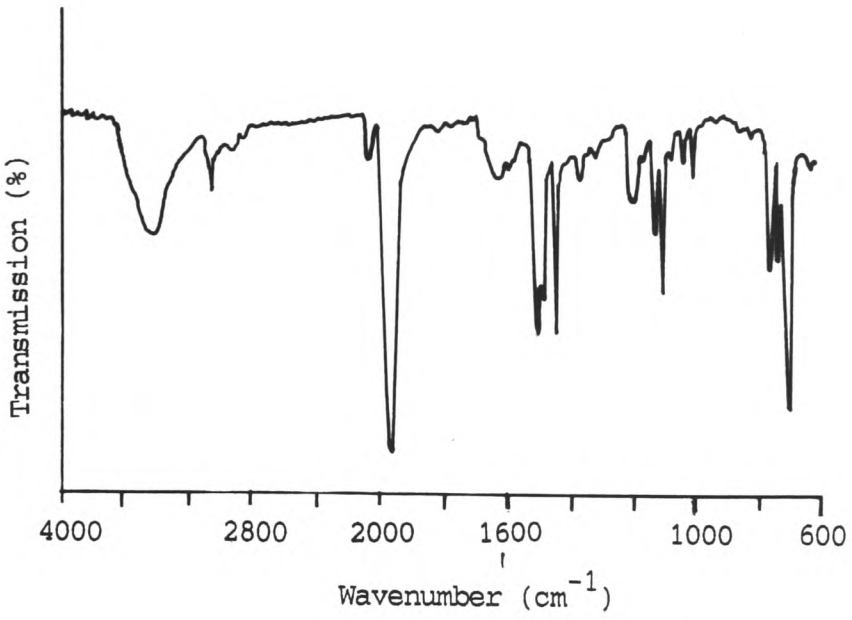


Fig. 47 : Infrared spectrum of decomposed [$Rh(COOCH_3)(CO)_2(PPh_3)_2$] (KBr disc).

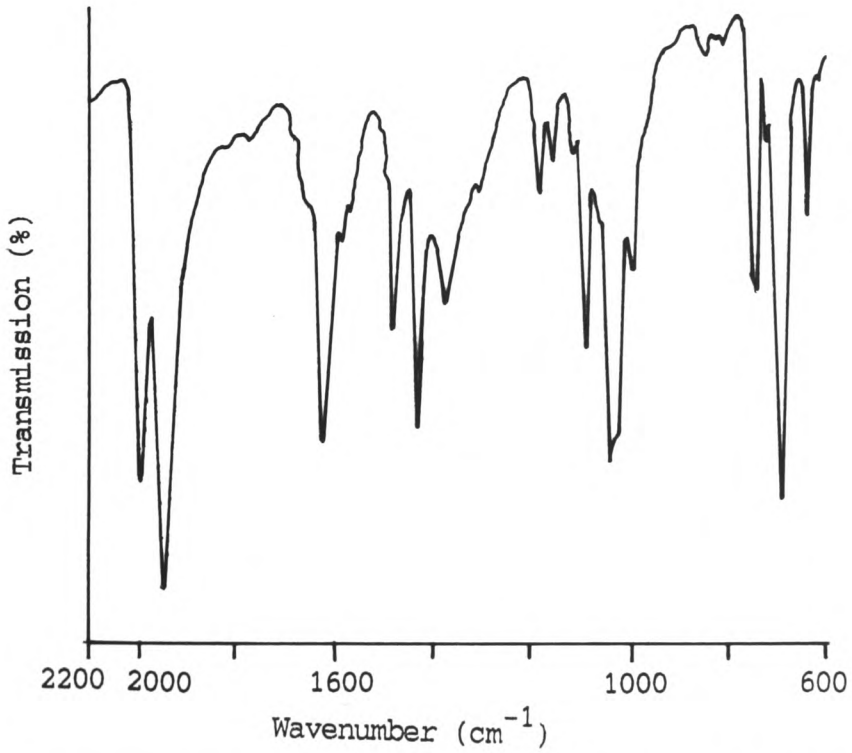


Fig. 48 : Infrared spectrum of [$Rh(COOC_2H_5)(CO)_2(PPh_3)_2$] (KBr disc).

The infrared spectrum (Fig. 48) of the compound (IX), $[Rh(COOC_2H_5)(CO)_2(PPh_3)_2]$ shows two strong carbonyl bands at 2003, 1954 cm^{-1}. A medium band at 1629 cm^{-1} is assigned to the ethoxycarbonyl band[22, 42, 44, 49] and a band at 1046 cm^{-1} is due to the $\nu(C\text{-}OC_2H_5)$ group[22, 49]. The infrared spectrum pattern suggests that there may be two carbonyl groups in the compound[22]. The infrared data suggest that the compound (IX), is analogous to compound (VIII). Therefore the structure of the compound is proposed as in Fig. 46, where R = C_2H_5.

The infrared spectrum of the compound (X), $[Rh(COOC_3H_7)(CO)_2(PPh_3)_2]$ shows two strong bands at 2000, 1953 cm^{-1}. A medium band at 1627 cm^{-1} is assigned to the propoxycarbonyl band [22, 42, 44, 49] and a band at 1048 cm^{-1} is due to the $\nu(C\text{-}OC_3H_7)$ group [22, 49]. Again the infrared spectrum suggests that there may be two carbonyl groups in the compound[22]. Therefore, the infrared spectrum of the compound (X) suggests that it is analogous to the compound (VIII), i.e. the structure is suggested as in Fig. 46, where R = C_3H_7.

The compounds (IX) and (X) are unstable in solution. So ^{1}H-NMR of the compounds (IX) and (X) were not possible. They are even less stable in solid state than the compound (VIII).

(iv) Reaction of Compound (VI) with RONa under Nitrogen : Synthesis of trans-[Rh(OR)(CO)(PPh_3)$_2$], Alkoxo(carbonyl)bis(triphenylphosphine)-rhodium(I), where R = CH_3, C_2H_5, Compounds (XI) and (XII) respectively.

The compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ reacts with sodium alkoxide [Sec. 4.2A{(ix), (x)}] to give $[Rh(OR)(CO)(PPh_3)_2]$ where R = CH_3, C_2H_5 - compounds [(XI) and (XII)] respectively. The compounds are characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 49) of the yellow compound (XI), $[Rh(OCH_3)(CO)(PPh_3)_2]$ shows one strong carbonyl band at 1946 cm^{-1}. The ^{1}H-NMR spectrum (Fig. 50) of the compound shows a singlet at 3.05 ppm, (3H). This is assigned to the methyl protons of (OCH_3) group and multiplets at 7.00 ppm and 7.80 ppm are assigned to the aromatic protons of the PPh_3 groups. The ^{31}P-NMR spectrum (Fig. 51) of the compound shows a doublet at +24.60 ppm (with J_{Rh-P} = 139.1 Hz).

The carbonyl band of the compound moves to lower frequency than the starting compound (VI). This is also lower frequency than the original chloro compound, i.e. $[RhCl(CO)(PPh_3)_2]$. Here the CH_3O^- is a stronger nucleophile, than Cl^-. The CH_3O^- group donates more electron density to the metal than Cl^-. When the donor group CH_3O^- is bonded to the metal, the electron density of the metal increases. As a result more electron density goes to the antibonding orbital of CO and its bond order decreases, bond length increases and v(CO) moves to lower frequency compared with v(CO) in the chloro compounds of the metal.

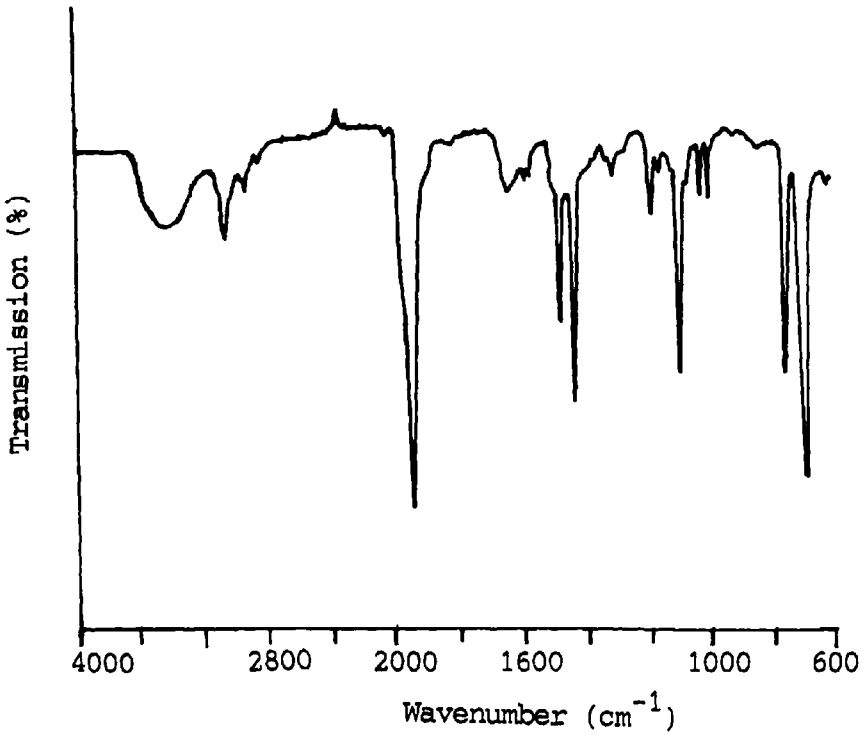


Fig. 49 : Infrared spectrum of trans-[Rh(OCH_3)(CO)(PPh_3)$_2$] (KBr disc).

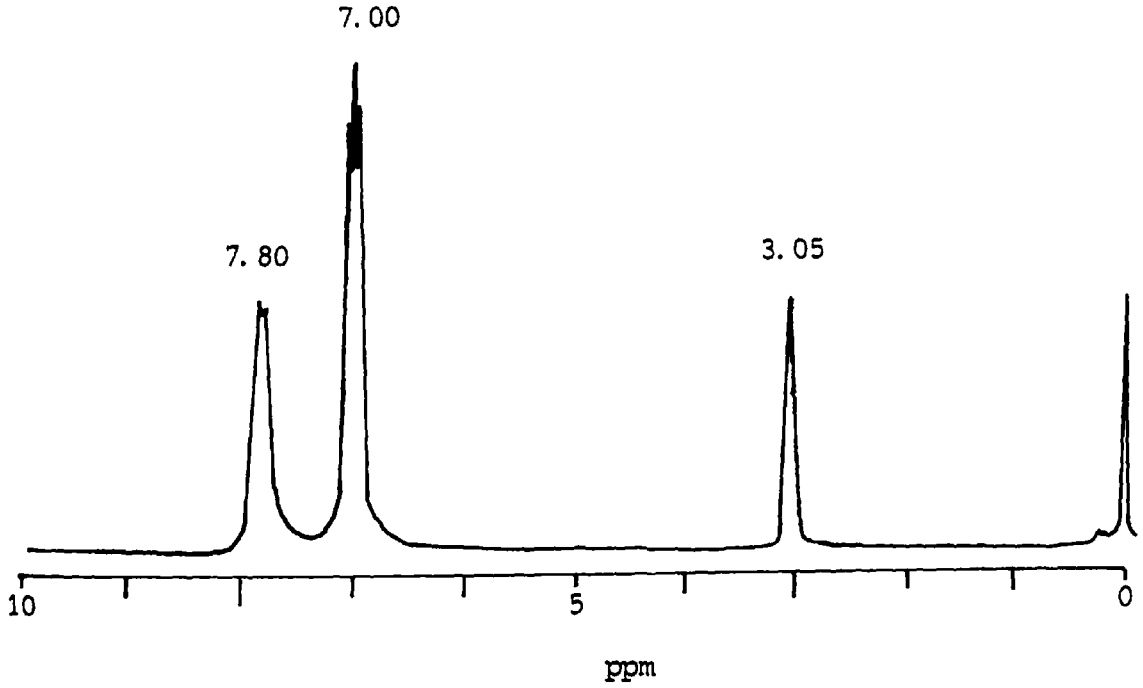


Fig. 50 : ^{1}H-NMR spectrum of trans-[Rh(OCH_3)(CO)(PPh_3)$_2$] (in C_6D_6, TMS).

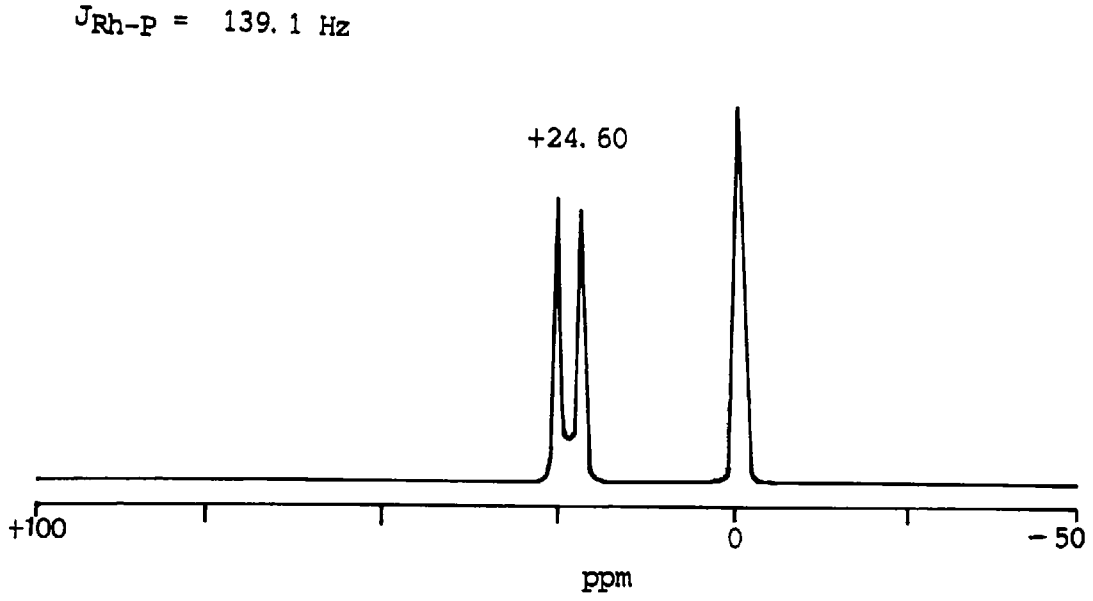


Fig. 51 : ^{31}P-NMR spectrum of trans-$[Rh(OCH_3)(CO)(PPh_3)_2]$ (in C_6D_6, 85% H_3PO_4).

Thus the v(CO) frequency of $[Rh(OCH_3)(CO)(PPh_3)_2]$ is lower than the corresponding trans-$[RhCl(CO)(PPh_3)_2]$. The infrared value is consistent with an iridium compound[38], i.e. trans-$[Ir(OCH_3)(CO)(PPh_3)_2]$ in which the v(CO) band is at 1936 cm^{-1}. The v(CO) of the iridium compound, $[IrCl(CO)(PPh_3)_2]$ is at 1945 cm^{-1} (KBr disc)[109].

Four-coordinated methoxo compound of rhodium also reported[150], e.g. $[Rh(OCH_3)(CO)\{P(iso\text{-}C_3H_7)_3\}_2]$. From the infrared, NMR spectroscopy and analysis the formula of the compound (XI) is suggested as trans-$[Rh(OCH_3)(CO)(PPh_3)_2]$. Therefore, the proposed structure of the compound is square planar (C_{2v} symmetry) as in Fig. 52, where R = CH_3.

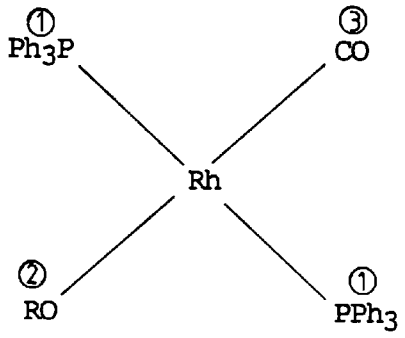


Fig. 52 : Structure of trans-[Rh(OR)(CO)(PPh_3)$_2$]. [IUPAC name, where R = CH_3, (SP-4-1)-carbonyl(methoxo)bis(triphenylphosphine)rhodium(I)].

The infrared spectrum of the yellow compound (XII), trans-[Rh(OC_2H_5)(CO)(PPh_3)$_2$] shows a strong carbonyl band at 1944 cm^{-1}. Again the ν(CO) moves to lower frequency than the precursor chloro compound as described for the analogous compound (XI), trans-[Rh(OCH_3)(CO)(PPh_3)$_2$]. The infrared spectrum, preparation procedure and starting material suggest that the compound is trans-[Rh(OC_2H_5)(CO)(PPh_3)$_2$] and the structure is likely to be as in Fig. 52, where R = C_2H_5. It is unstable, so no meaningful NMR spectrum could be obtained. It decomposed in solution.

(v) Reaction of Compound (VII) with RONa under Nitrogen : Synthesis of trans-[Rh(COOR)(CO)(PPh_3)$_2$], Alkoxycarbonyl(carbonyl)bis(triphenylphosphine)rhodium(I), where R = CH_3, C_2H_5, Compounds (XIII) and (XIV) respectively.

The compound (VII), $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ reacts with sodium alkoxide under nitrogen [Sec. 4.2A{(xi), (xii)}] to give trans-$[Rh(COOR)(CO)(PPh_3)_2]$ compounds {(XIII), (XIV)} where R = CH_3 and C_2H_5 respectively.

The infrared spectrum (Fig. 53) of the methoxycarbonyl compound (XIII), $[Rh(COOCH_3)(CO)(PPh_3)_2].CH_3OH$ shows a strong carbonyl band at 1971 cm^{-1} and a medium band at 1618 cm^{-1} is assigned to the methoxycarbonyl moiety[22, 42, 44, 49]. A band at 1019 cm^{-1} is attributed to $\nu(C\text{-}OCH_3)$[22, 49] and there is no $\nu(BF_4^-)$ band. The ^{1}H-NMR spectrum of the compound (Fig. 54) shows a multiplet at (7.20-7.80) ppm, (30H) for the aromatic protons of PPh_3 and a singlet at 2.62 ppm, (3H) due to the methyl protons of the methoxycarbonyl group[22]. A signal at 3.45 ppm (3H) is assigned to trapped or associated methanol. Free methanol also shows a resonance at 3.45 ppm. The ^{31}P-NMR spectrum (Fig. 55) of the compound shows a doublet at +28.75 ppm (with J_{Rh-P} = 126.8 Hz). The spectroscopic data and analysis are consistent with the formula $[Rh(COOCH_3)(CO)(PPh_3)_2].CH_3OH$.

Yoshida et al. reported[150] a similar four-coordinated alkoxycarbonyl compound trans-$[Rh(COOCH_3)(CO)\{P(iso\text{-}C_3H_7)_3\}_2]$, whose methoxycarbonyl band is at 1613 cm^{-1}. This value is consistent with the present compound.

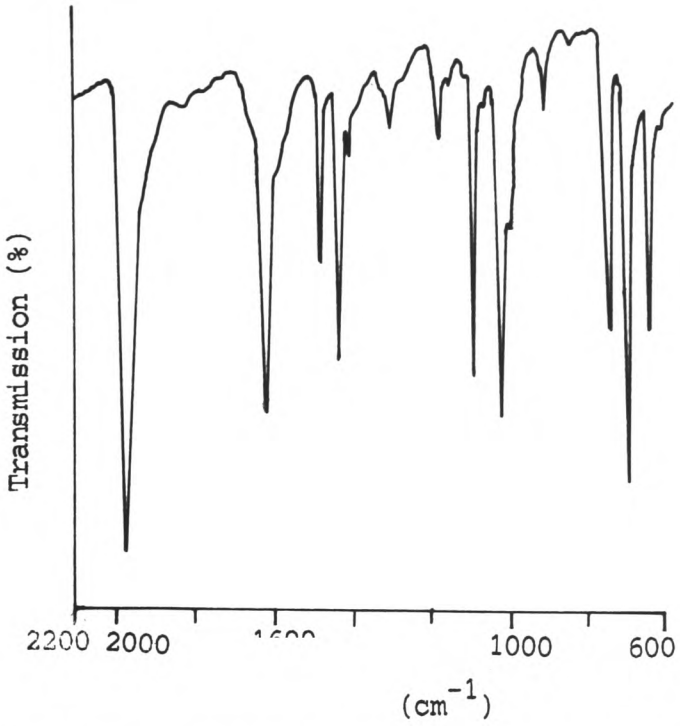


Fig. 53 : Infrared spectrum of trans-[Rh($COOCH_3$)(CO)(PPh_3)$_2$].CH_3OH (KBr disc).

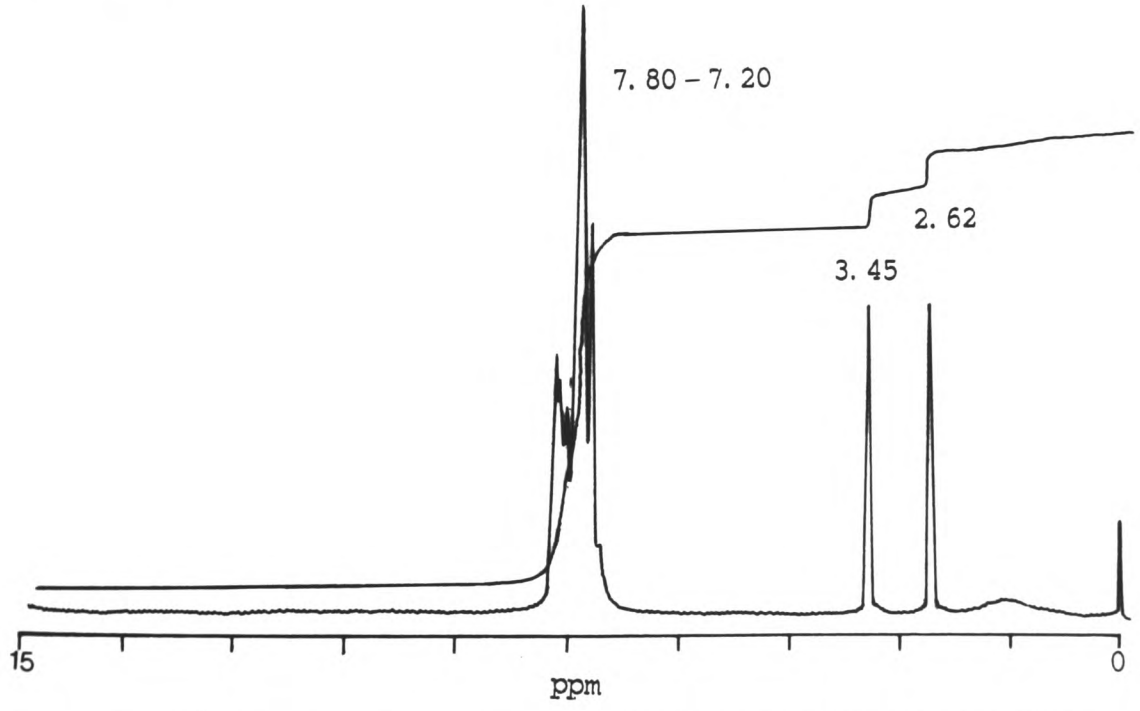


Fig. 54 : ^{1}H-NMR spectrum of trans-[Rh($COOCH_3$)(CO)(PPh_3)$_2$].CH_3OH (in $CDCl_3$, TMS).

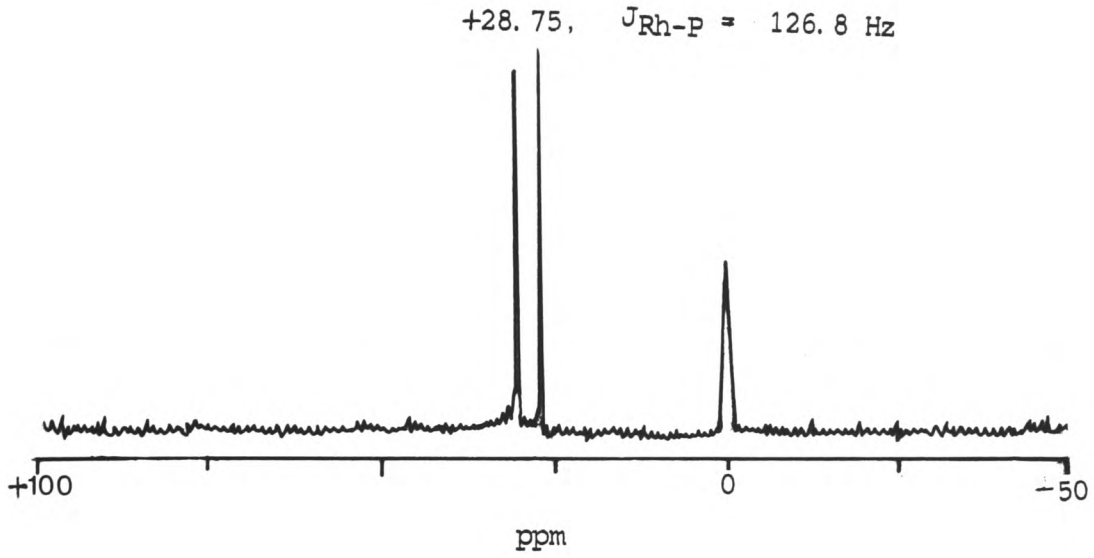


Fig. 55. ^{31}P-NMR spectrum of trans-[Rh($COOCH_3$)(CO)(PPh_3)$_2$].CH_3OH (in $CDCl_3$, 85% H_3PO_4).

Therefore, the four-coordinated compound of rhodium(I) should have a dsp^2 hybridisation and a square planar structure. By analogy with previous compounds, the structure of the compound (XIII) is proposed to be as square planar (C_{2v} symmetry) as in Fig. 56, where R = CH_3.

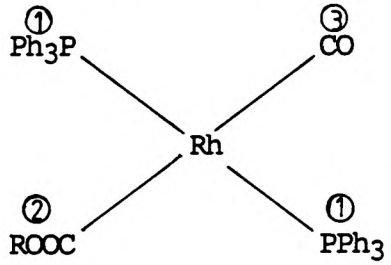


Fig. 56 : Structure of trans-[Rh(COOR)(CO)(PPh_3)$_2$]. [IUPAC name, where R = CH_3, (SP-4-1)-carbonyl(methoxycarbonyl)bis(triphenylphosphine)-rhodium(I)].

The compound is moderately stable in the solid state at room temperature and fairly stable at low temperature. When the reaction is carried out over a longer time (3 to 4 hours) the band at 1618 cm^{-1} gradually disappears and a new band at 1735 cm^{-1} appears. It may be that the compound decomposes and a bridged carbonyl species is formed[132], a rhodium(0)/phosphine entity. A similar species has been formed as a side product[150] in the related synthesis of $[Rh(COOCH_3)(CO)\{P(iso\text{-}C_3H_7)_3\}_2]$.

The infrared spectrum of the compound (XIV), trans-$[Rh(COOC_2H_5)(CO)(PPh_3)_2]$ shows a strong carbonyl band at 1969 cm^{-1} and also a medium band at 1609 cm^{-1}. The band at 1609 cm^{-1} is assigned to the ethoxycarbonyl group[22, 42, 44, 49]. These values are consistent with the corresponding methoxycarbonyl compound (XIII). Therefore, the suggested structure is as in Fig. 56, where R = C_2H_5.

(vi) Reaction of Compound (VI) with (RCOONa) : Synthesis of trans-$[Rh(OOCR)(CO)(PPh_3)_2]$, Carbonyl(carboxylato)bis(triphenylphosphine)rhodium(I), where R = CH_3, C_2H_5- Compounds (XV) and (XVI) respectively.

The compound (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ reacts with sodium carboxylate [Sec. 4.2A{(xvi), (xvii)}] to give trans-$[Rh(OOCR)(CO)(PPh_3)_2]$ where R = CH_3, C_2H_5 compounds {(XV), (XVI)} respectively. The compounds have been characterised by infrared, ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR spectroscopy. In the literature the carboxylato compound $[Rh(OOCR)(CO)(PPh_3)_2]$ has been prepared from different starting materials[92, 136]. It has been prepared by the reaction of $[RhH(CO)(PPh_3)_3]$[92] with ethanoic acid and also from the reaction of

$[Rh(OOCR)(PPh_3)_3]$ with carbon monoxide (where R = CH_3, C_2H_5, C_3H_7)[136].

The infrared spectrum (Fig. 57) of the compound (XV), $[Rh(OOCCH_3)(CO)(PPh_3)_2]$ shows a strong band at 1972 cm^{-1}, assigned to the carbonyl stretching frequency. Two medium bands at 1605 and 1374 cm^{-1} are assigned to the v(OCO) asymmetric and symmetric stretching frequencies respectively[92]. These values suggest that the carboxylato group is monodentate. These infrared data are consistent with literature values[92] (Table 21). The ^{1}H-NMR spectrum (Fig. 58) of the compound shows a singlet at 0.76 ppm (3H). This is attributed to the methyl protons of the carboxylato group as compared with a literature value[92]. The multiplets at 7.40 ppm (18H) and 7.80 ppm (12H) are assigned to the aromatic protons of the PPh_3. The ^{31}P-NMR spectrum (Fig. 59) of the compound shows a doublet at +32.48 ppm (with J_{Rh-P} = 132.2 Hz).

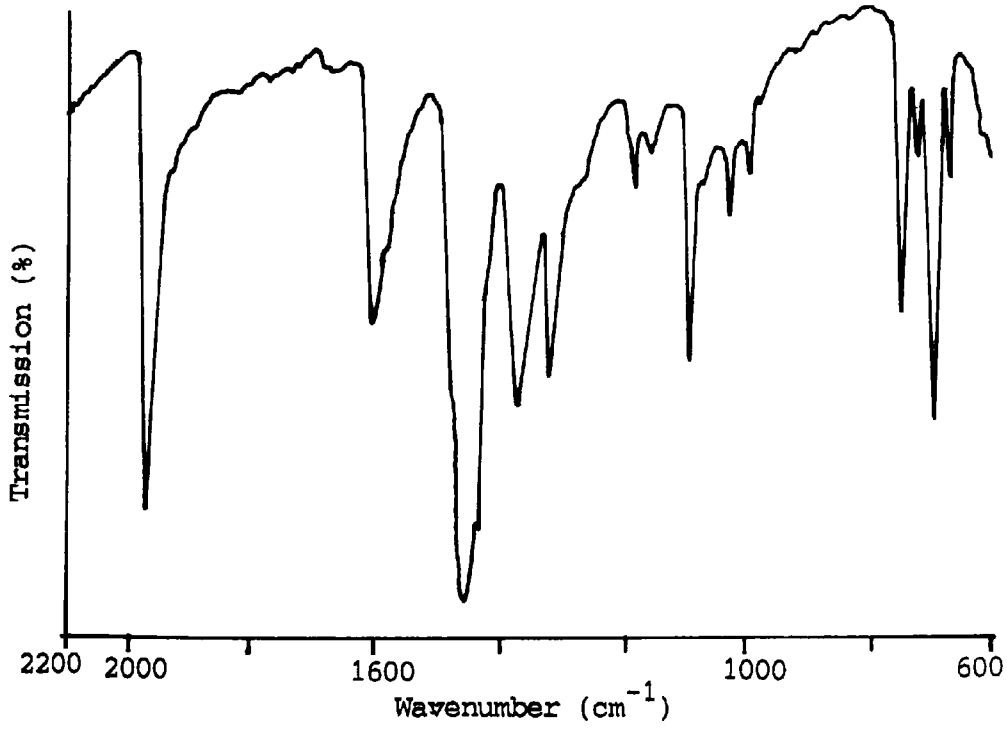


Fig. 57. Infrared spectrum of trans-$[Rh(OOCCH_3)(CO)(PPh_3)_2]$ (Nujol mull).

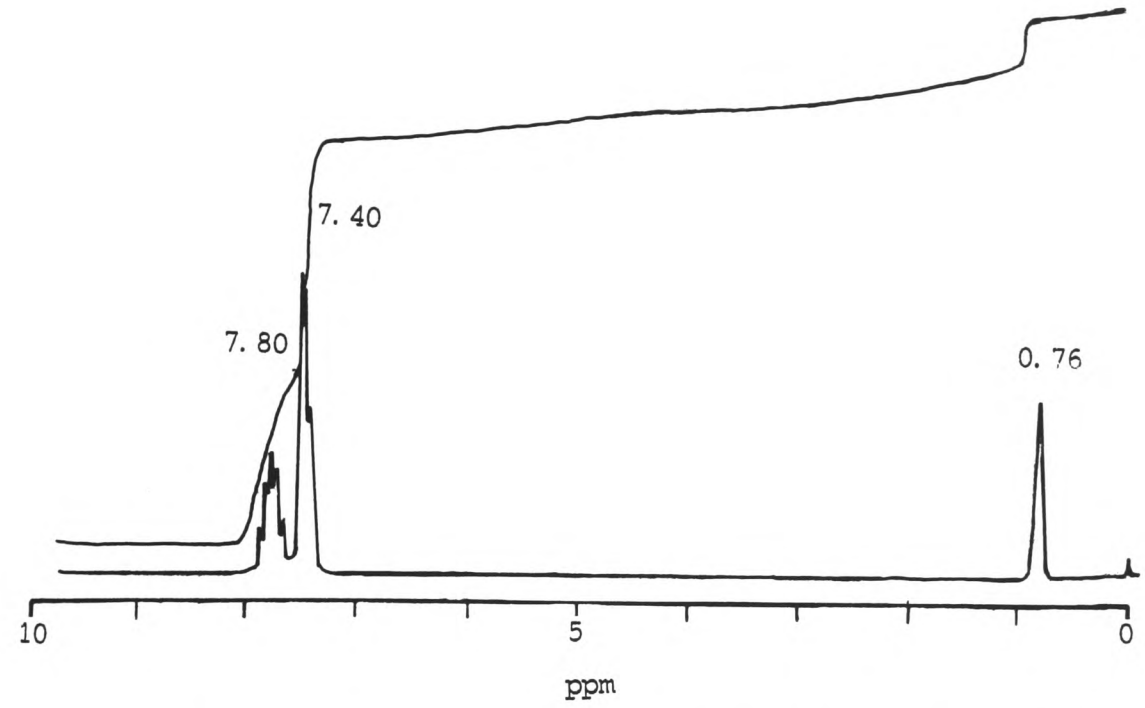


Fig. 58 : ^{1}H-NMR spectrum of trans-[Rh(OOCCH$_3$)(CO)(PPh$_3$)$_2$] (in CDCl$_3$, TMS).

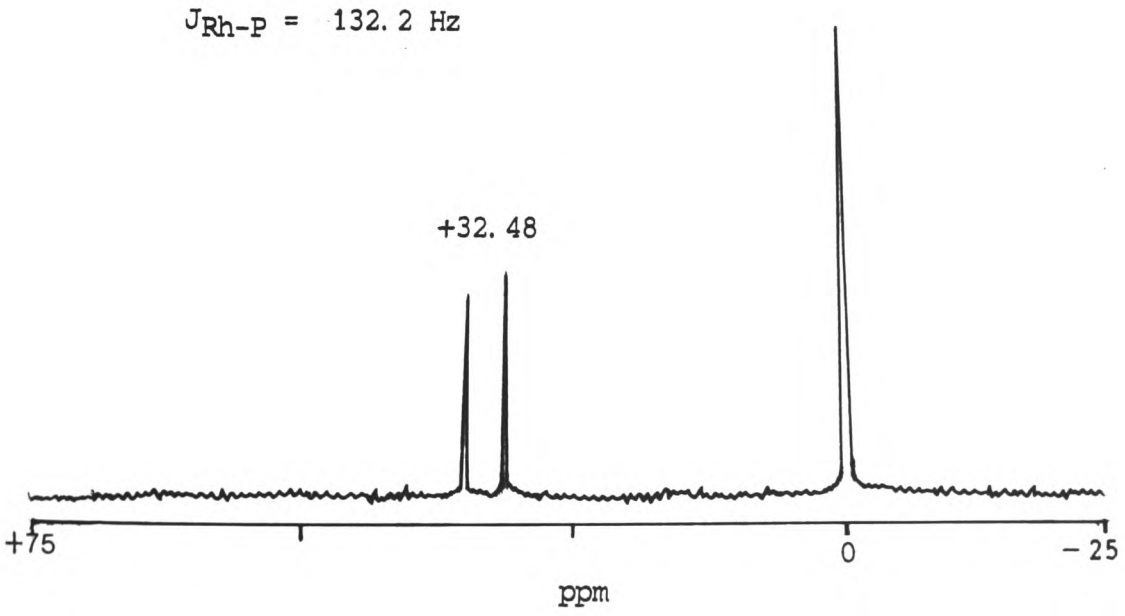


Fig. 59 : ^{31}P-NMR spectrum of trans-[Rh(OOCCH$_3$)(CO)(PPh$_3$)$_2$] (in CDCl$_3$, 85% H$_3$PO$_4$).

Therefore, from spectral data it is suggested that the compound (XV) is a square planar structure (C_{2v} symmetry) as shown in Fig. 60, where R = CH_3.

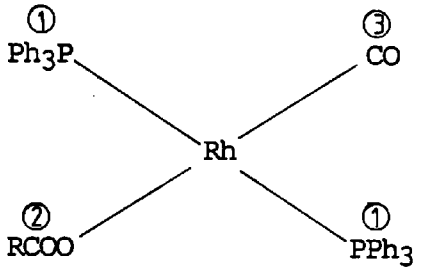


Fig. 60 : Structure of trans-[Rh(OOCR)(CO)(PPh_3)$_2$]. [IUPAC name where R = CH_3, (SP-4-1)-carbonyl(ethanoato)bis(triphenylphosphine)rhodium(I)].

Van Vliet et al.[151] reported a ethanoato compound [Rh($OOCCH_3$)(CO)(L)$_2$] [L = PPh_3, $AsPh_3$] prepared by the reaction of [RhCl(CO)(L)$_2$] with Tl($OOCCH_3$)$_3$. Their spectral data are not consistent with the other published data[92] (Table 21) and also with the present compound (XV) [Sec. 4.3A(vi)] and compound (XXIV) [Sec. 4.3B(xii)]. For example, for the compound [Rh($OOCCH_3$)(CO)(PPh_3)$_2$], the reported[151] value for the ν(CO) is at 1989 cm^{-1} and the signal for methyl protons is at 1.43 ppm with a signal in the ^{31}P-NMR at +31.22 ppm (with J_{Rh-P} = 132.0 Hz).

The infrared spectrum (Fig. 61) of the yellow crystalline compound (XVI), trans-[Rh($OOCC_2H_5$)(CO)(PPh_3)$_2$] shows a strong band at 1975 cm^{-1}, assigned to the carbonyl stretching frequency. Two medium bands at 1599 and 1379 cm^{-1} are assigned to the ν(OCO) asymmetric and symmetric stretching frequencies respectively. These infrared bands are in good agreement with the literature values[92] (Table 21).

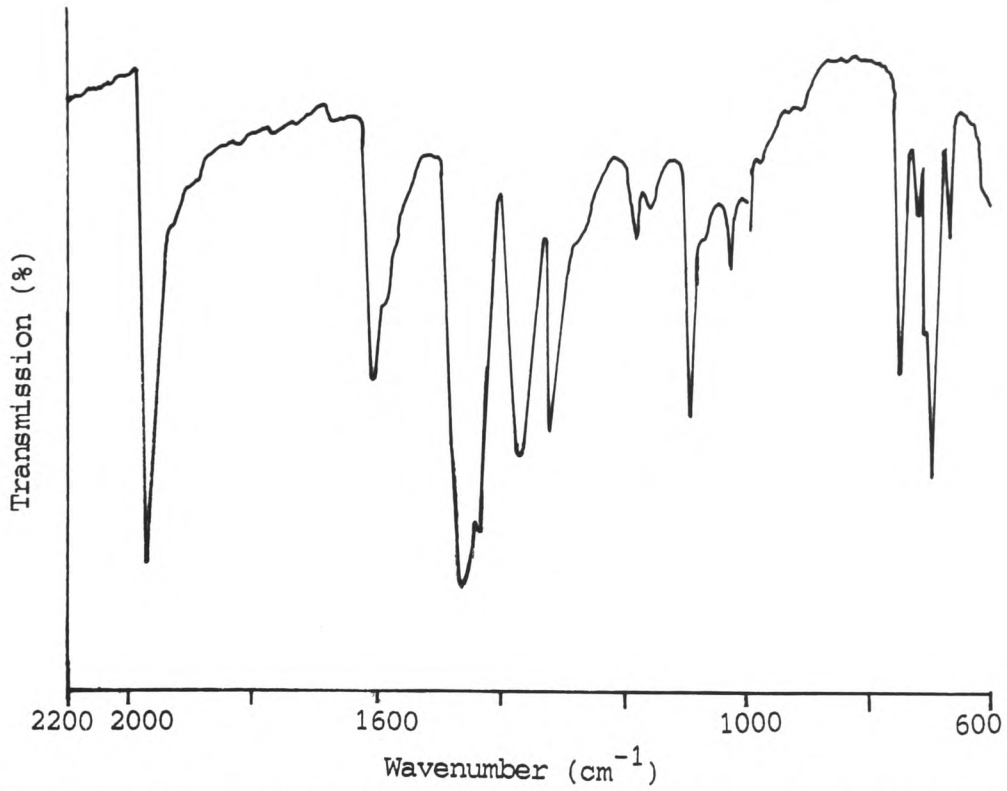


Fig. 61 : Infrared spectrum of trans-$[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$

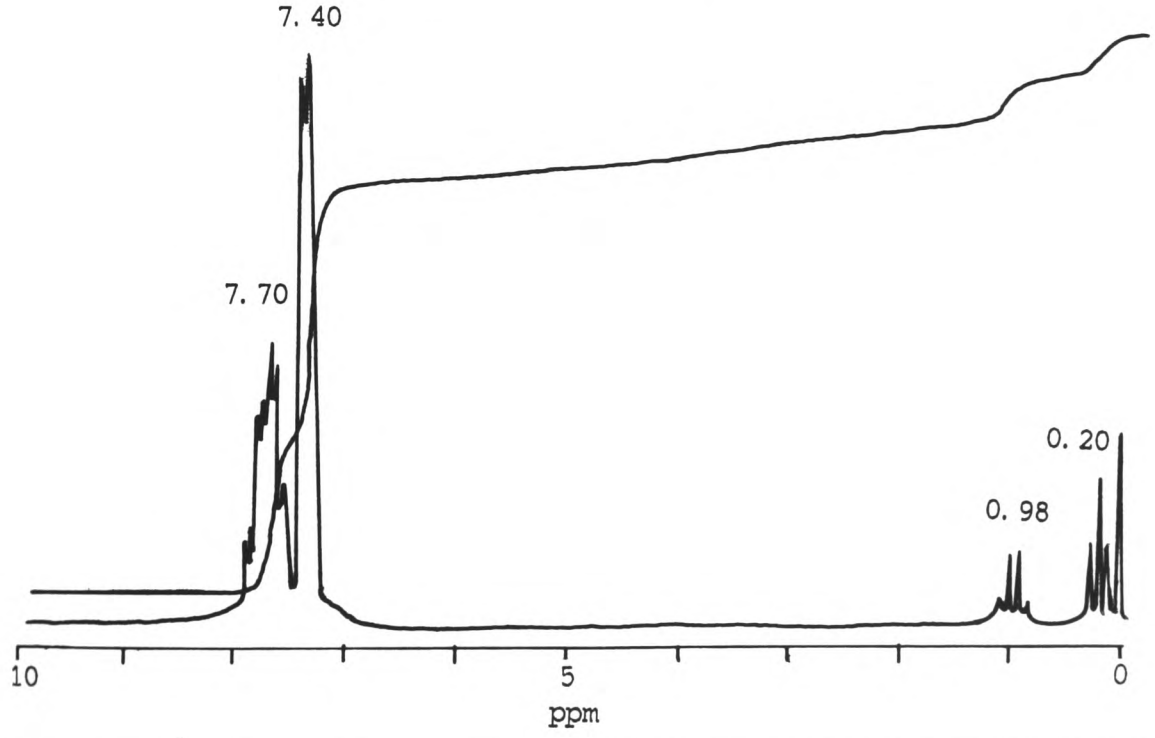


Fig. 62 : ^{1}H-NMR spectrum of trans-$[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$ (in $CDCl_3$, TMS).

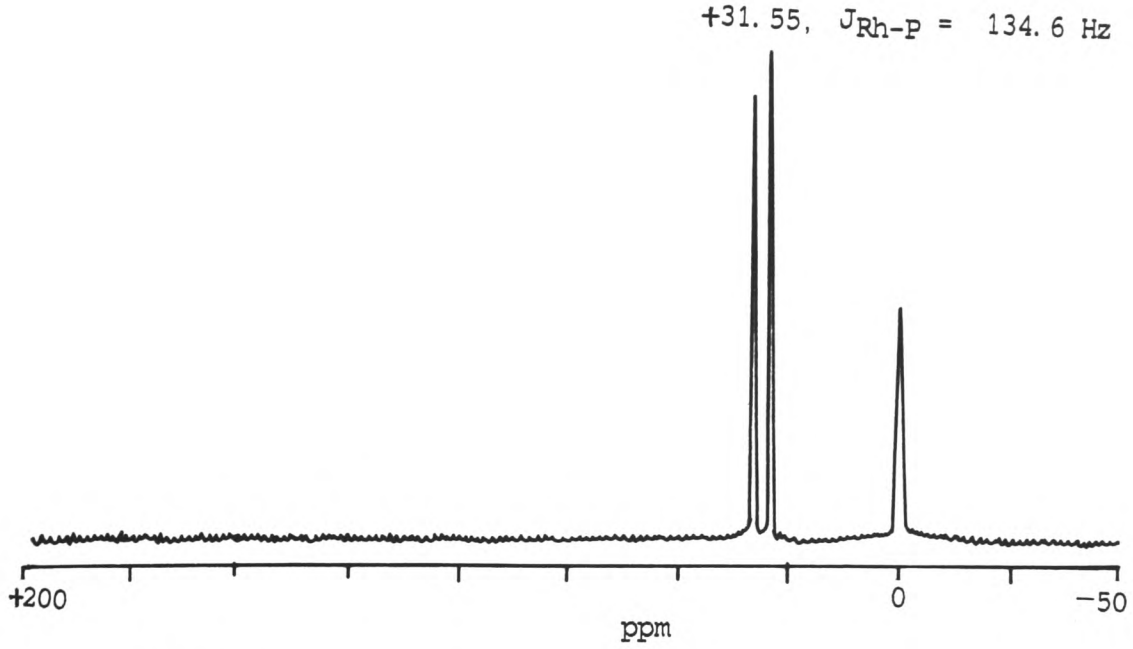


Fig. 63 : ^{31}P-NMR spectrum of trans-[Rh($OOCC_2H_5$)(CO)(PPh_3)$_2$] (in $CDCl_3$, 85% H_3PO_4).

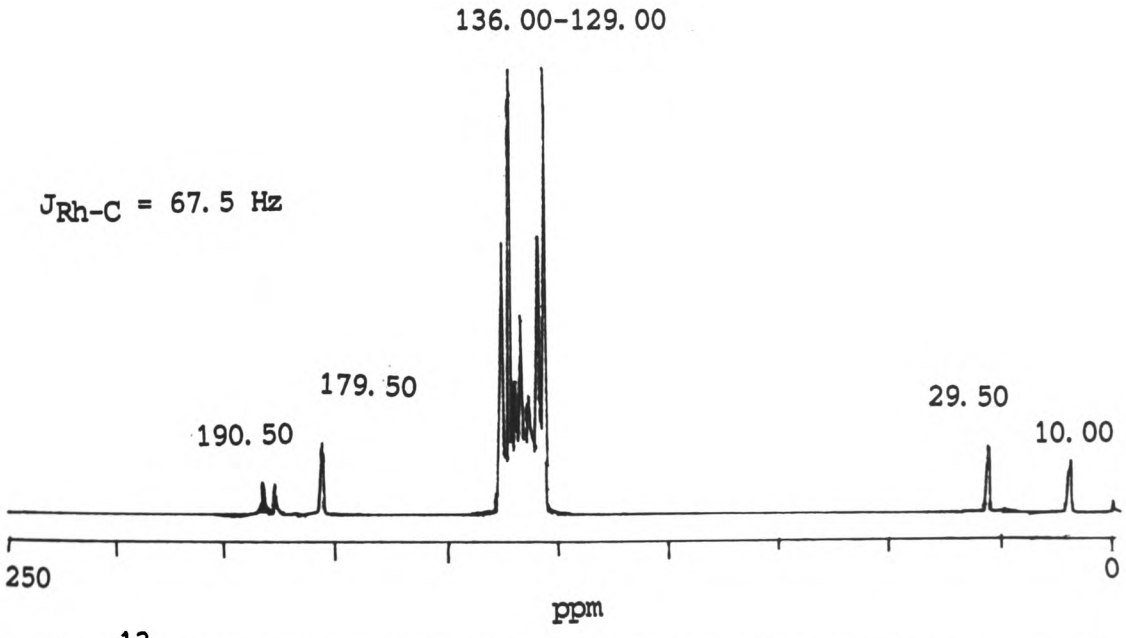


Fig. 64 : ^{13}C-NMR spectrum of trans-[Rh($OOCC_2H_5$)(CO)(PPh_3)$_2$] (in $CDCl_3$, TMS).

The ^{1}H-NMR spectrum (Fig. 62) shows a triplet at 0.20 ppm (3H, J = 7.0 Hz) and a quartet at 0.98 ppm (2H, J = 7.0 Hz). These are assigned to the methyl and methylene protons of the $CH_3CH_2COO^-$ group respectively. The multiplets at 7.40 ppm (18H) and 7.70 ppm (12H), are assigned to the aromatic protons of PPh_3. The ^{1}H-NMR data are consistent with a similar compound $[Rh\{OOCCH(CH_3)_2\}(CO)(PPh_3)_2]$, which shows chemical shift at 0.20 ppm for the (CH_3) protons and 1.27 ppm for the (CH) proton[152].

The ^{31}P-NMR spectrum (Fig. 63) of the compound shows a doublet at +31.55 ppm (with J_{Rh-P} = 134.6 Hz). The ^{13}C-NMR spectrum (Fig. 64) of the compound shows signals at 10.00 and 29.50 ppm, which represents the methyl and methylene carbons of the $CH_3CH_2COO^-$ group. A multiplet at (129.00-136.00) ppm is assigned to the aromatic carbons of the PPh_3 (multiplicity due to C-P coupling). A singlet at 179.50 ppm represents the (COO^-) carbon[153]. A doublet at 190.50 ppm (with J_{Rh-C} = 67.5 Hz) represents the (Rh-CO) carbon[7]. Therefore, from infrared, ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR spectra the structure of the compound (XVI) is suggested as in Fig 60, where R = C_2H_5.

(vii) Oxidative Addition of CH_3I to Compound (XI), $[Rh(OCH_3)(CO)(PPh_3)_2]$: Formation of $[RhI(OCH_3)(CH_3)(CO)(PPh_3)_2$, Carbonyliodo(methoxo)-(methyl)bis(triphenylphosphine)rhodium(III), Compound (XVII).

The possible preparation of the oxidative addition product, $[RhI(OCH_3)(CH_3)(CO)(PPh_3)_2]$ has been described in [Sec. 4.2A(xviii)] and the compound only characterised by infrared spectroscopy and the iodide test. The infrared spectrum (Fig. 65) shows a strong carbonyl band at 1980 cm^{-1}. The $\nu(CO)$ cm^{-1} is at a higher frequency than in the starting material, compound (XI). This is also higher than the Rh(I) compound, i.e. $[RhCl(CO)(PPh_3)_2]$. In the oxidative addition product, the oxidation state of rhodium changes from (+1) to (+3) state. As a result the

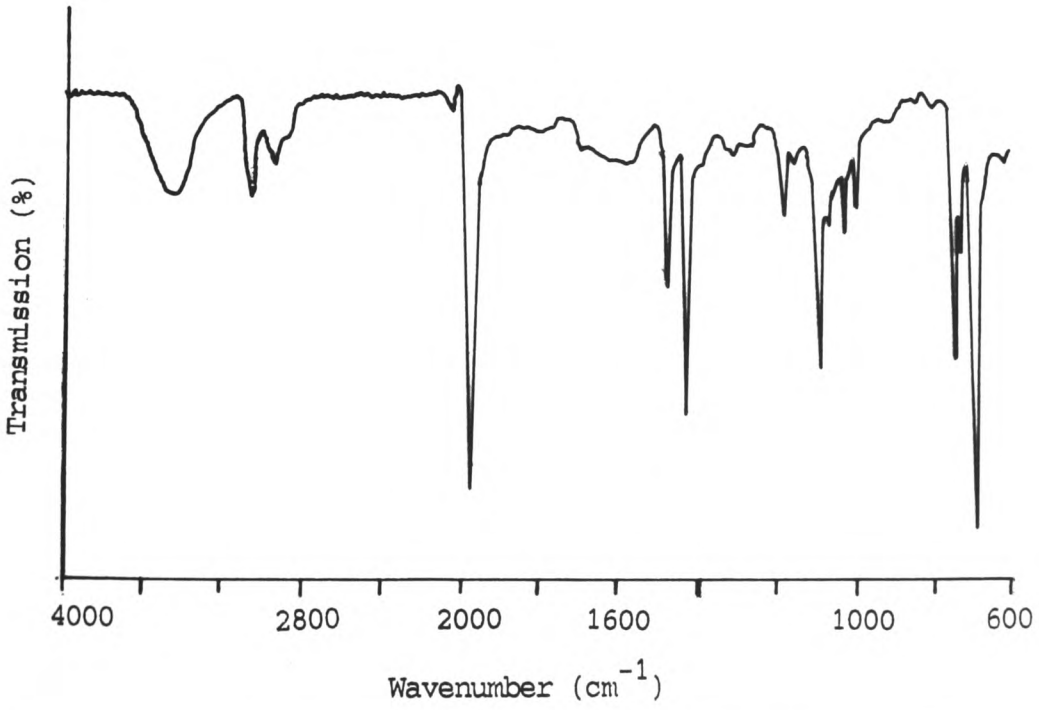


Fig. 65 : Infrared spectrum of $[RhI(OCH_3)(CH_3)(CO)(PPh_3)_2]$ (KBr disc).

electron density of rhodium decreases and back donation from Rh to CO moiety decreases. Therefore, v(CO) moves to higher frequency than the starting compound. The v(CO) is similar to that in the iridium compound[154], $[IrI(OCH_3)(CH_3)(CO)(PPh_3)_2]$. The compound gave a positive Lassaigne fusion test for iodine. It was impossible to obtain ^{1}H-NMR and ^{31}P-NMR, because the compound decomposed in solution.

A summary of the spectral data of rhodium-phosphine compounds follows on the next page.

Table 22 : Infrared Data of Rhodium-Phosphine Cationic, Alkoxo and Alkoxycarbonyl Compounds.

Compound	ν(CO)	ν(CO) (alkoxy-carbonyl)	ν(C-OR)	$\nu(BF_4^-)$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
(VI) $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.$ $1/2(CH_2Cl_2)$*	1994(s)			1090(b)[a]
(VII) $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$*	2046(s) 2047(s)			1057(b)[a] 1065(b)
(VIII) $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$	2004(s) 1957(s)	1637(m)	1040(m)	
	2004(s) 1956(s)	1634(m)[a]		
(IX) $[Rh(COOC_2H_5)(CO)_2(PPh_3)_2]$*	2003(s) 1954(s)	1629(m)	1046(m)	
	2003(s) 1953(s)	1629(m)	1048(m)[a]	
(X) $[Rh(COOC_3H_7)(CO)_2(PPh_3)_2]$*	2000(s), 1953(s)	1627(m)	1048(m)	
(XI) $[Rh(OCH_3)(CO)(PPh_3)_2]$*	1946(s)			
(XII) $[Rh(OC_2H_5)(CO)(PPh_3)_2]$*	1944(s)			
(XIII) $[Rh(COOCH_3)(CO)(PPh_3)_2].$ CH_3OH*	1971(s)	1618(m)	1019(m)	
	1969(s)	1617(m)[a]		
(XIV) $[Rh(COOC_2H_5)(CO)(PPh_3)_2]$*	1969(s)	1609(m)		

[Where s = Strong, b = Broad, m = Medium, a = Nujol mull and all other spectra KBr disc and * indicates novel compound].

Table 23 : NMR Data of Rhodium-Phosphine Cationic, Alkoxo and Alkoxycarbonyl Compounds.

Compound	^{1}H-NMR (ppm)	^{31}P-NMR (ppm)	J_{Rh-P} (Hz)
(VI) $[Rh(CO)(PPh_3)_2]^+[BF_4]^-$. $1/2(CH_2Cl_2)$	7.50(m, 30H) 5.28(s, 1H)	+30.70(d)	123.0
(VII) $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$	7.58 (m)	+26.90(d)	108.7
(VIII) $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$	(7.40-7.80)(m, 30H) 2.81(s, 3H)	+26.40(d)	130.5
(XI) $[Rh(OCH_3)(CO)(PPh_3)_2]$	(7.40-7.80)(m, 30H) 3.05(s, 3H)	+24.60(d)	139.1[a]
	(7.40-7.80)(m, 30H)[b] 2.81(s, 3H)		
(XIII) $[Rh(COOCH_3)(CO)(PPh_3)_2]$. CH_3OH	(7.20-7.80)(m, 30H) 2.62(s, 3H) 3.45(s, 3H)	+28.75(d)	126.8

[Where m = Multiplet, s = Singlet, d = Doublet, a = C_6D_6 and b = Acetone-d^6 and all other spectra in CDCl3 (TMS as internal standard in ^{1}H-NMR and 85% H_3PO_4 as external standard in ^{31}P-NMR)].

Table 24 : Infrared Data of Rhodium-Phosphine Carboxylato Compounds.

Compound	ν(CO) cm^{-1}	ν_{asy}(OCO) cm^{-1}	ν_{sy}(OCO) cm^{-1}
(XV) $[Rh(OOCCH_3)(CO)(PPh_3)_2]$	1972(s)	1605(m)	1374(m)[a]
	1965(s)	1608(m)	1370(m)[b]
(XVI) $[Rh(OOCCH_2CH_3)(CO)(PPh_3)_2]$	1975(s)	1599(m)	1379(m)[a]
	1973(s)	1602(m)	1377(m)[b]

[Where s = Strong, m = Medium, a = Nujol mull and b = KBr disc]

Table 25 : NMR Data of Rhodium-Phosphine Carboxylato Compounds.

Compound	^{1}H-NMR (ppm)	^{31}P-NMR (ppm)	J_{Rh-P} (Hz)
(XV) $[Rh(OOCCH_3)(CO)(PPh_3)_2]$	7.40(m, 18H) 7.80(m, 12H) 0.76(s, 3H)	+32.48(d)	132.2
(XVI) $[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$	7.40(m, 18H) 7.70(m, 12H) 0.40(t, 3H) 1.26(q, 2H)	+31.55(d)	134.6

[Where m = Multiplet, s = Singlet, d = Doublet, t = Triplet and q = Quartet. All spectra in $CDCl_3$ (TMS in ^{1}H-NMR and 85% H_3PO_4 in ^{31}P-NMR as internal standards)].

(B) RHODIUM-ARSINE COMPOUNDS.

(viii) Synthesis of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$, Carbonylbis-(triphenylarsine)rhodium(I) tetrafluoroborate dichloromethane solvate, Compound (XVIII).

The compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ has been prepared by the reaction of trans-$[RhCl(CO)(AsPh_3)_2]$ with $AgBF_4$ [Sec. 4.2B(xx)] and characterised by infrared, ^{1}H-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 66) of the compound shows only one strong carbonyl band at 1989 cm^{-1} and a broad band at 1078 cm^{-1} for $\nu(BF_4^-)$. The value at 1078 cm^{-1} indicates that the (BF_4^-) group in the compound is not coordinated to the metal but remains free forming a salt[97,98]. The carbonyl band is at a higher frequency than the precursor compound[103]. The carbonyl stretching frequency moves to higher frequency due to the formation of a salt and for the same reason as described for $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ [Sec. 4.3A(i)].

The ^{1}H-NMR spectrum of the compound (Fig. 67) shows a multiplet at (7.30-7.50) ppm, which is assigned to the aromatic protons of the $AsPh_3$. A singlet at 5.28 ppm is assigned to the methylene protons of solvated or weakly coordinated dichloromethane[105,106], which may be stabilised the compound. The coordination of dichloromethane[105-6,141-5] was described in Sec. [3.3(i) and 4.3A(i)]. The ratio of the aromatic and methylene protons is 30:1.

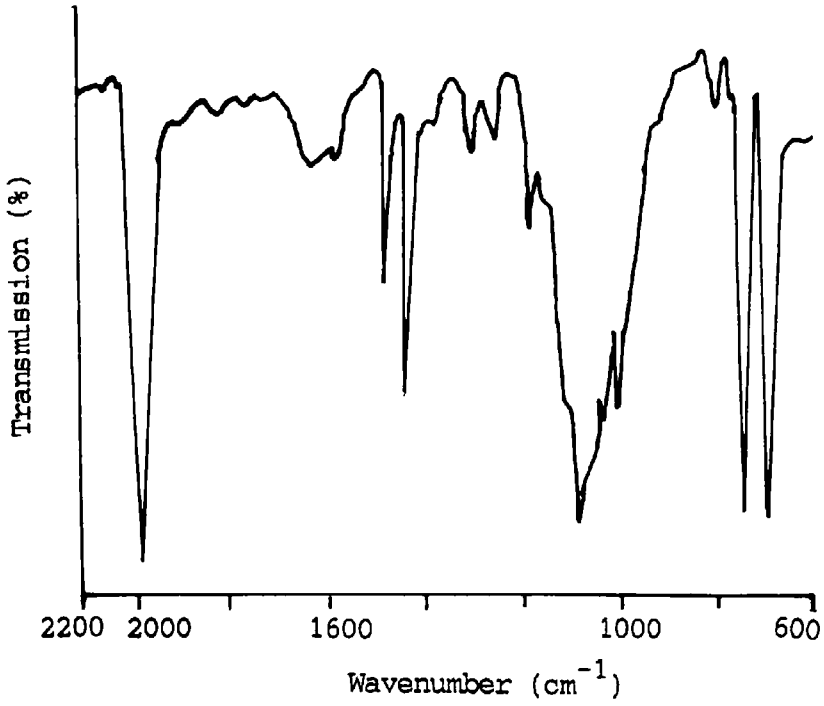


Fig. 66 : Infrared spectrum of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (KBr disc).

Rhodium compounds of 14-electron species are known[102,103,127], as described in Sec. 4.3A(i), for example $[Rh(PPh_3)_3]^+$ and $[RhX(PCy_3)_2]$ (where X = F, Cl, Br, I). In the present reaction when acetone is used then the acetone coordinated compound, $[Rh(CO)(AsPh_3)_2.(Acetone)]^+[BF_4]^-$ is formed. This is ascertained[103] from the band at 1649 cm^{-1}. It is assumed that the oxygen atom containing solvent is coordinated to the electron deficient compound (XVIII) through the oxygen atom and stabilises the compound as a whole. The ν(CO) of the acetone coordinated compound is 1991 cm^{-1}. When to the compound (VIII) acetone is added, then acetone coordinated compound is formed, because acetone is more coordinating than dichloromethane.

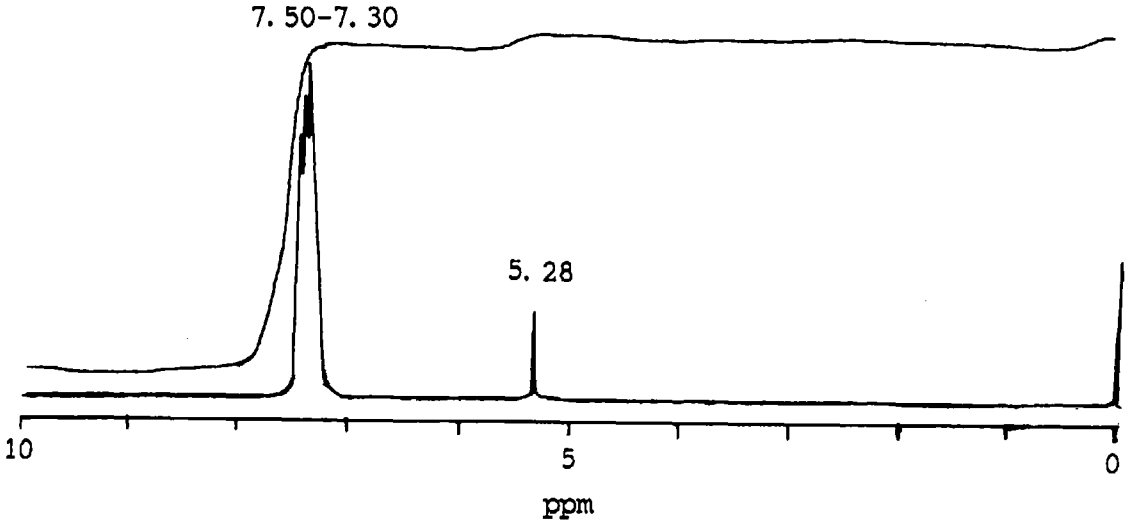


Fig. 67 : ^{1}H-NMR spectrum of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (in $CDCl_3$, TMS).

Analysis of the compound (XVIII) suggested that it contained half a molecule of dichloromethane. Therefore, infrared, ^{1}H-NMR spectroscopy and analysis of the compound are consistent with the formula $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$.

(ix) Synthesis of trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$, Dicarbonylbis-(triphenylarsine)rhodium(I) tetrafluoroborate, Compound (XIX).

The orange-yellow crystalline compound (XIX), trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$ has been synthesised by the reaction [Sec. 4.2B(xxi)] of compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with CO. The compound is also formed when trans-$[RhCl(CO)(AsPh_3)_2]$ was reacted [Sec. 4.2B(xxii)] with $AgBF_4$ in the presence of CO.

The infrared spectrum (Fig. 68) of the compound shows a strong carbonyl band at 2037 cm^{-1} and a broad $\nu(BF_4^-)$ band at 1054 cm^{-1}. The ν(CO) band is at a higher frequency than the precursor compound (XVIII) and for the

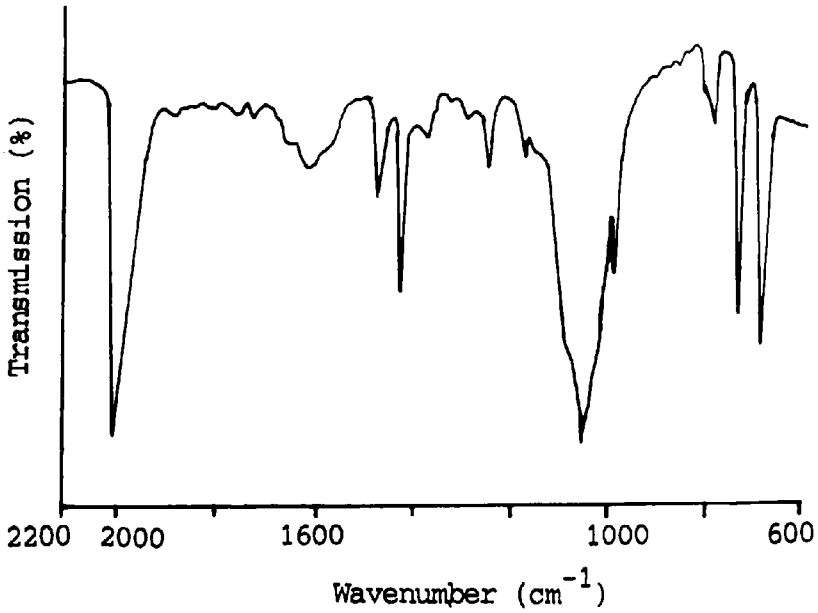


Fig. 68 : Infrared spectrum of trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$ (KBr disc).

same reason as described for $[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$ [Sec 4.3A(ii)]. The v(CO) is analogous to trans-$[Rh(CO)_2(PPh_3)_2]^+[BF_4]^-$, in which the v(CO) is at 2046 cm^{-1} and trans-$[Rh(CO)_2\{P(2\text{-}CH_3C_6H_4)_3\}_2]^+[ClO_4]^-$, in which the v(CO) is at 2040 cm^{-1} (Table 19). Again the $v(BF_4^-)$ value suggests that it is not coordinated, rather remains free in the compound[97,98].

Therefore, the infrared value suggests that the compound (XIX) may have two carbonyl groups and they may be trans to each other[97]. By analogy with the four-coordinated rhodium(I) phosphine compound (VII) [Sec. 4.3A(ii)], the structure of the compound (XIX) may be a square planar (D_{2h} symmetry) as in Fig. 69.

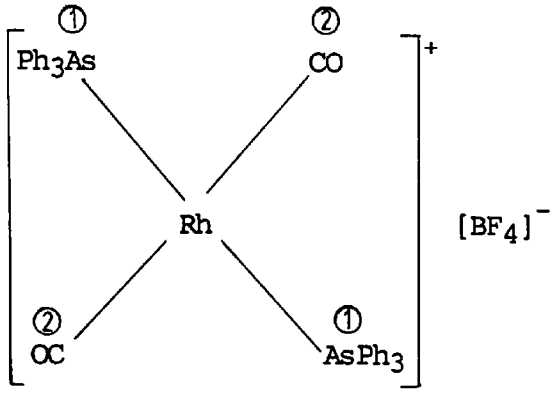


Fig. 69 : Structure of trans-$[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$. [IUPAC name, (SP-4-1)-dicarbonylbis(triphenylarsine)rhodium(I) tetrafluoroborate].

<u>(x) Reaction of Compound (XVIII) with CH_3ONa in the Presence of CO : Synthesis of $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$, Dicarbonyl(methoxycarbonyl)bis-(triphenylarsine)rhodium(I), Compound (XX).</u>

The methoxycarbonyl compound (XX), $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$ has been synthesised by the reaction of $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with CH_3ONa in the presence of CO [Sec. 4.2B(xxiii)].

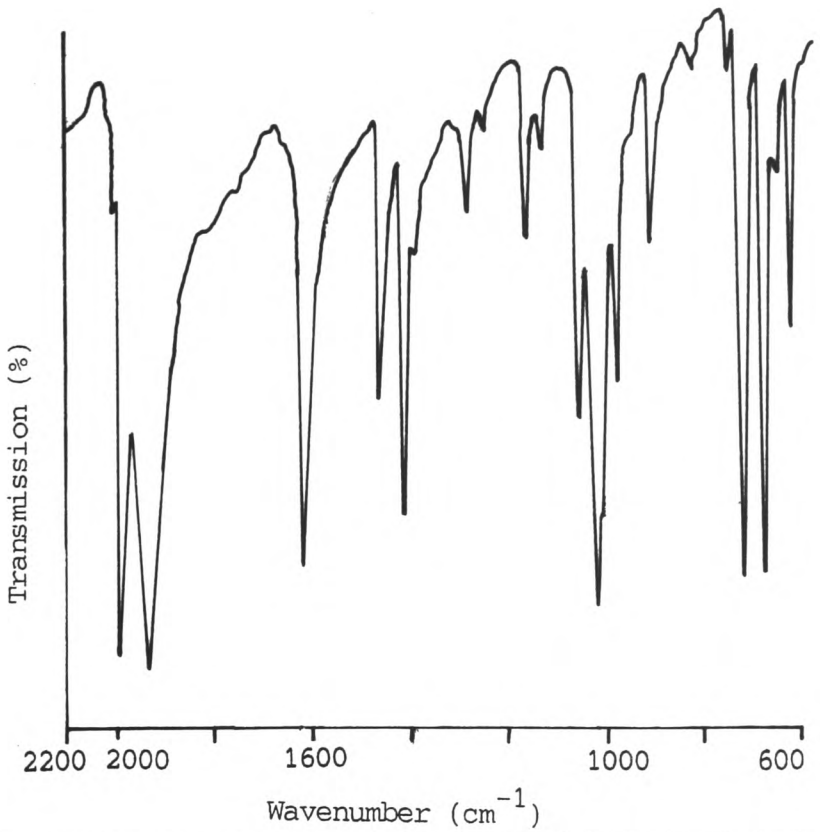


Fig. 70 : Infrared spectrum of $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$ (KBr disc).

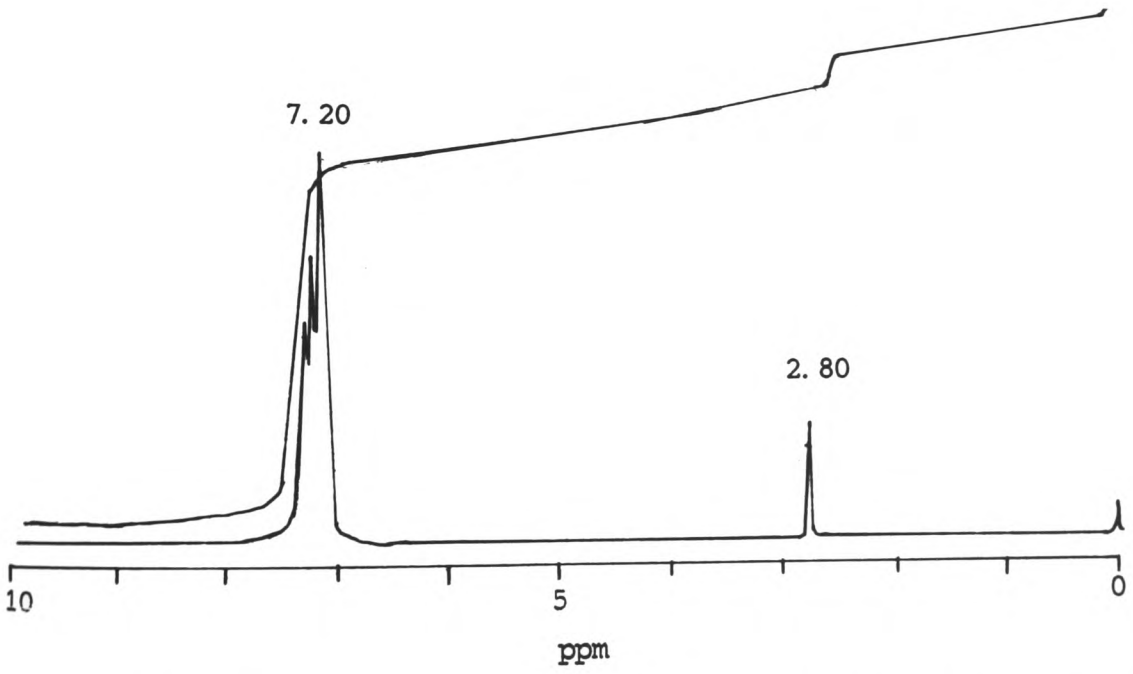


Fig. 71 : ^{1}H-NMR spectrum of $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$ (in $CDCl_3$, TMS).

The infrared spectrum (Fig. 70) of the compound shows two strong carbonyl bands at 2005, 1954 cm^{-1} and a medium band at 1636 cm^{-1}. The band at 1636 cm^{-1} is assigned to the methoxycarbonyl band[22, 42, 44, 49]. The band at 1039 cm^{-1} represents the $\nu(C-OCH_3)$ stretching[22, 49]. The two carbonyl groups may be in the equatorial position of a trigonal bipyramid.

The ^1H-NMR spectrum (Fig. 71) of the compound shows a singlet at 2.80 ppm (3H) which is assigned to the methyl protons[44] of the ($COOCH_3$) group and a multiplet at 7.20 ppm (30H) which represents the aromatic protons of the $AsPh_3$ group. The spectral data suggested that the compound (XX) is similar to the compound[22] $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$ [Sec. 4.3A(iii)]. Therefore, by analogy with $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$, the proposed compound (XX) is $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$ and the suggested structure is as in Fig. 72.

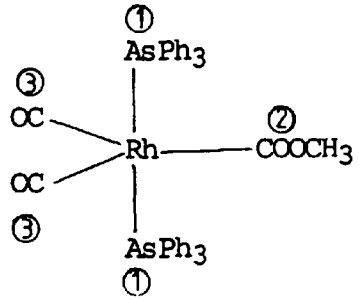


Fig. 72 : Structure of $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$. [IUPAC name, (TBPY-5-11)-dicarbonyl(methoxycarbonyl)bis(triphenylarsine)rhodium(I)].

An attempt was made to prepare the analogous compound $[Rh(COOC_2H_5)(CO)_2(AsPh_3)_2]$ [sec. 4.2B(xxiv)]. The ethoxycarbonyl compound could not isolated. It appeared to decompose during the experiment even at low (-10^oC) temperatures (the low temperature was maintained by using an ice and sodium chloride mixture).

(xi) Reaction of Compound (XVIII) with RONa under Nitrogen : Synthesis of trans-[Rh(OR)(CO)($AsPh_3$)$_2$], Alkoxo(carbonyl)bis(triphenylarsine)rhodium(I), where R = CH_3, C_2H_5, Compounds (XXI) and (XXII) respectively.

Reaction of compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with CH_3ONa gave the compound (XXI), trans-$[Rh(OCH_3)(CO)(AsPh_3)_2]$ [Sec. 4.2B(xxv)].

The infrared spectrum (Fig. 73) of the yellow compound shows a strong carbonyl band at 1935 cm^{-1} and does not indicate the presence of the $\nu(BF_4^-)$ band[98]. The lower frequency of the carbonyl band suggested that the compound has a coordinated methoxo group. The carbonyl stretching is lower than the precursor compound (XVIII), or from the

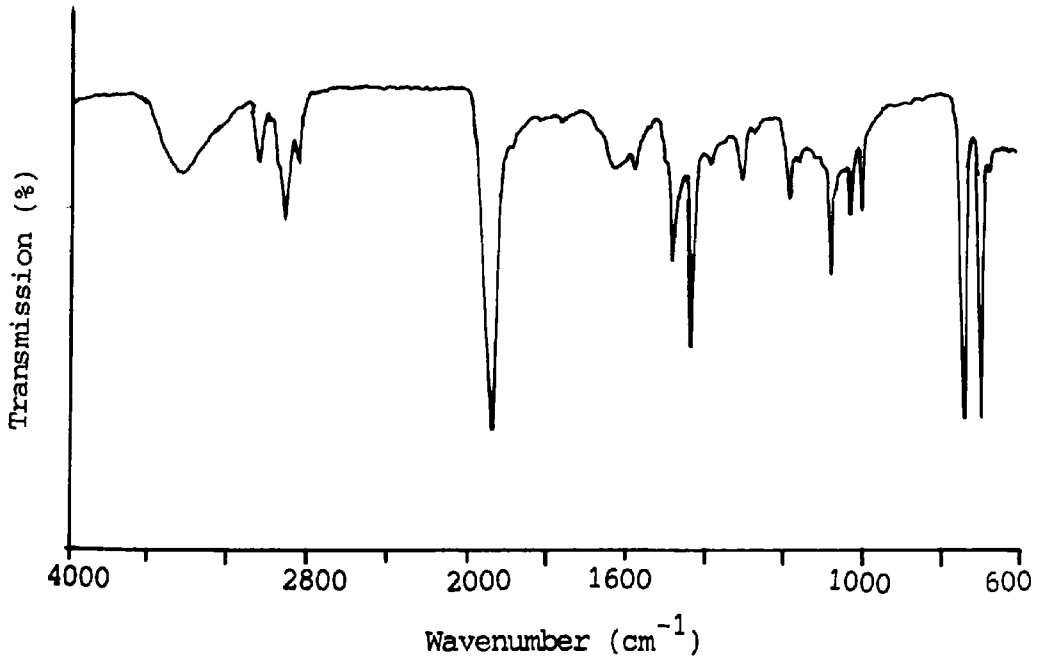


Fig. 73 : Infrared spectrum of trans-$[Rh(OCH_3)(CO)(AsPh_3)_2]$ (KBR disc).

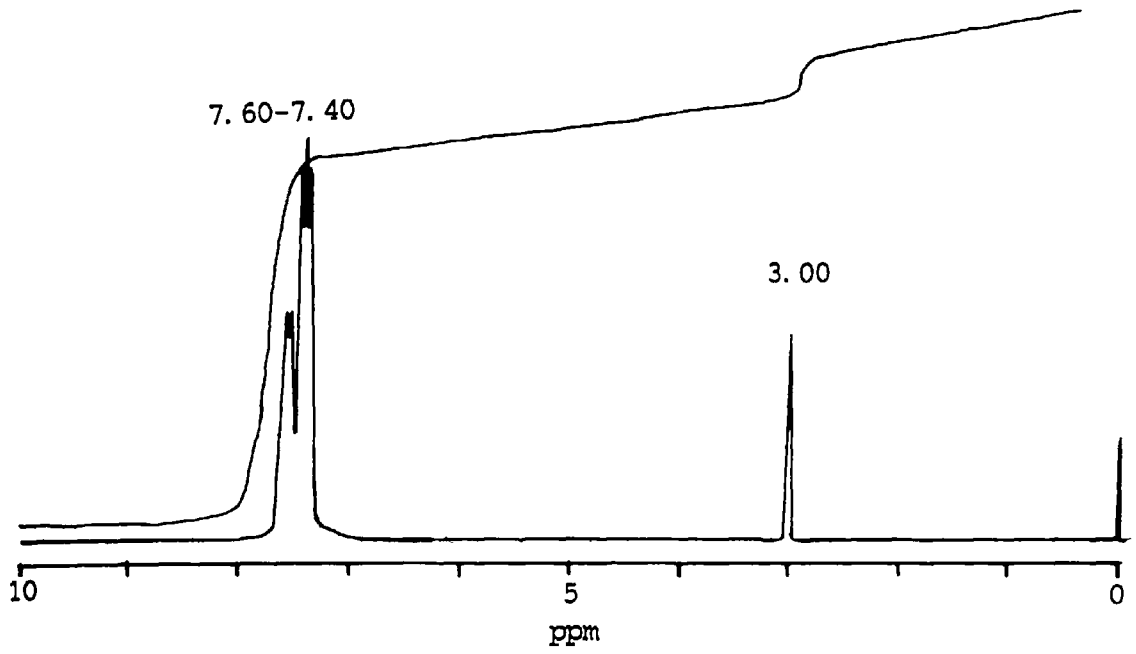


Fig. 74 : ^{1}H-NMR spectrum of trans-[Rh(OCH_3)(CO)($AsPh_3$)$_2$] (in C_6D_6, TMS).

trans-[RhCl(CO)($AsPh_3$)$_2$] for the same reason that has been described in the case of trans-[Rh(OCH_3)(CO)(PPh_3)$_2$] [Sec. 4.3A(iv)]. The v(CO) value of the present compound is consistent with the compound [Rh(OCH_3)(CO)(PPh_3)$_2$] and also consistent with the iridium compound[38], i.e. [Ir(OCH_3)(CO)(PPh_3)$_2$], which shows v(CO) at 1936 cm^{-1}. The ^{1}H-NMR spectrum (Fig. 74) of the compound shows a singlet at 3.00 ppm (3H) for the methyl protons of the methoxo group and a multiplet at (7.40-7.60) ppm (30H) is assigned to the aromatic protons of the $AsPh_3$ group.

The infrared, ^{1}H-NMR and analysis are consistent with the formula [Rh(OCH_3)(CO)($AsPh_3$)$_2$]. By analogy with trans-[Rh(OCH_3)(CO)(PPh_3)$_2$], the proposed structure of the compound (XXI) is as in Fig. 75, where R = CH_3.

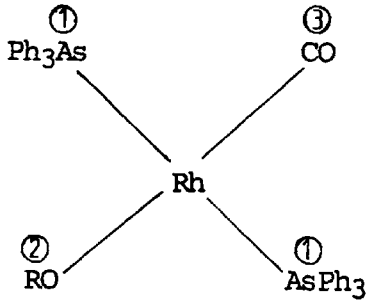


Fig. 75 : Structure of trans-$[Rh(OR)(CO)(AsPh_3)_2]$. [IUPAC name where R = CH_3, (SP-4-1)-carbonyl(methoxo)bis(triphenylarsine)rhodium(I)].

The analogous compound (XXII), trans-$[Rh(OC_2H_5)(CO)(AsPh_3)_2]$ has been prepared [Sec. 4.2B(xxvi)]. The infrared spectrum of the compound shows a strong carbonyl band at 1940 cm^{-1}. This value is consistent with the reported alkoxo compound[38] and with the present work [Sec. 4.3A(iv)]. Therefore, the proposed structure of the compound is as in Fig. 75, where R = C_2H_5.

(xii) Reaction of Compound (XVIII) with RCOONa : Synthesis of trans-$[Rh(OOCR)(CO)(AsPh_3)_2]$, Carbonyl(carboxylato)bis(triphenylarsine)-rhodium(I), where R = H, CH_3, C_2H_5 - Compounds (XXIII), (XXIV) and (XXV) respectively.

The reaction of compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with sodium carboxylate [Sec. 4.2B{(xxvii), (xxviii), (xxix)}] gives trans-$[Rh(OOCR)(CO)(AsPh_3)_2]$ where R = H, CH_3, C_2H_5 - compounds (XXIII), (XXIV) and (XXV) respectively. The compounds have been characterised by infrared, ^{1}H-NMR, ^{13}C-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 76) of compound (XXIII), trans-[Rh(OOCH)(CO)($AsPh_3$)$_2$], shows a strong carbonyl band at 1980 cm^{-1}. Two medium bands at 1602 and 1382 cm^{-1} are assigned to the v(OCO) stretching frequencies for the asymmetric and symmetric modes respectively[92]. The present v(OCO) values are different from the HCOONa values[111], v_{asy}(OCO) at 1567 cm^{-1} and v_{sy}(OCO) at 1366 cm^{-1}. The infrared data are in good agreement[92] with the carboxylato compounds.

The ^{1}H-NMR spectrum (Fig. 77) of the compound shows multiplets at 7.00 ppm (18H) and 7.84 ppm (12H) which are assigned to the aromatic protons of $AsPh_3$ and a singlet at 3.14 ppm (1H) for the methanoate proton (in C_6D_6). In $CDCl_3$ the same compound shows multiplets at 7.35 ppm and 7.65 ppm for the aromatic protons of $AsPh_3$ and a singlet at 3.40 ppm for the methanoate proton[23].

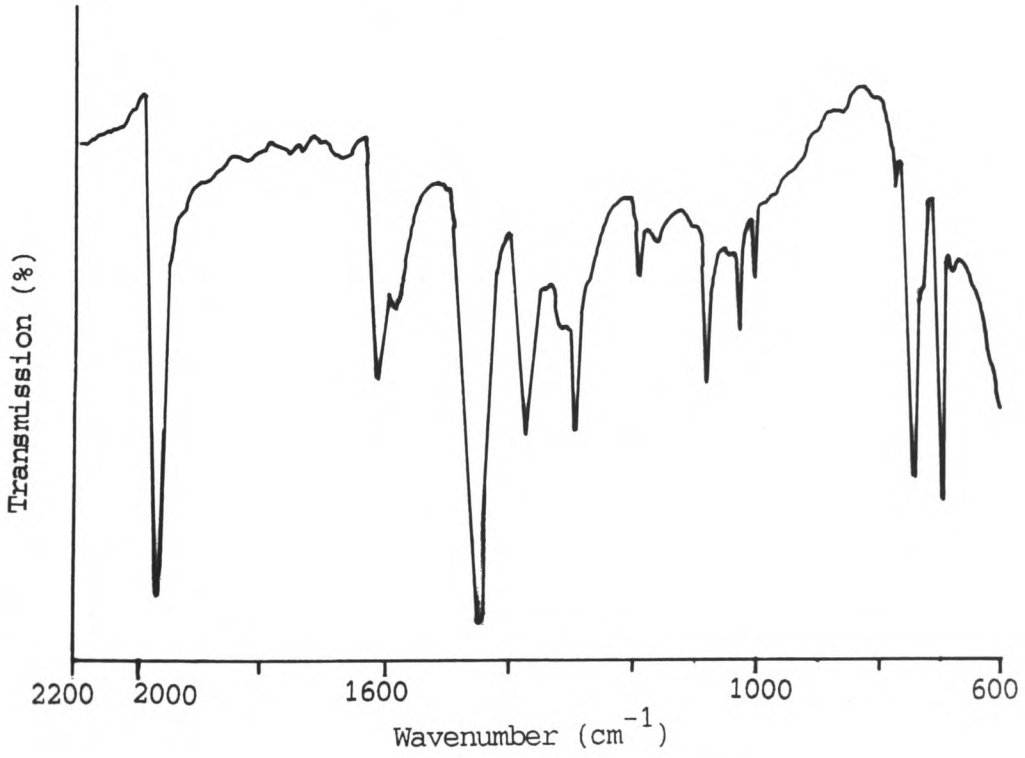


Fig. 76 : Infrared spectrum of trans-[Rh(OOCH)(CO)($AsPh_3$)$_2$] (Nujol mull).

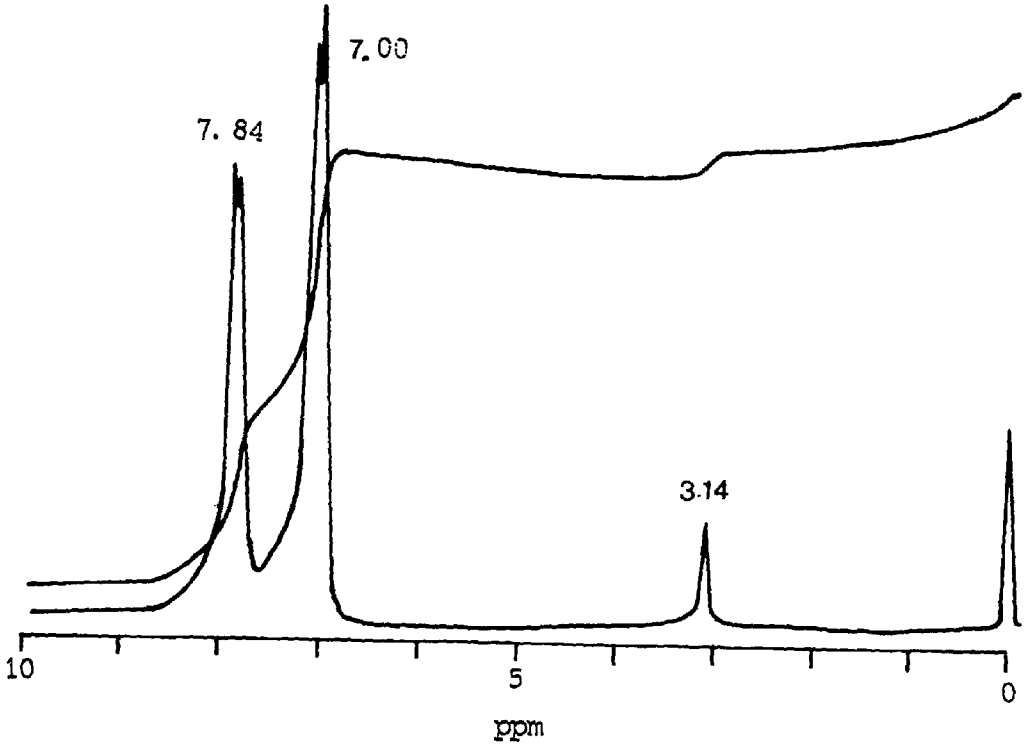


Fig. 77 : ^{1}H-NMR spectrum of trans-[Rh(OOCH)(CO)($AsPh_3$)$_2$] (in C_6D_6, TMS)

The infrared spectrum (Fig. 78) of the yellow crystalline compound (XXIV), trans-[Rh($OOCCH_3$)(CO)($AsPh_3$)$_2$] shows a strong carbonyl band at 1970 cm^{-1}. The bands at 1610 and 1375 cm^{-1} are assigned to the asymmetric and symmetric stretching of ν(OCO) respectively[92,136]. The ν(OCO) bands of CH_3COONa are 1578 and 1414 cm^{-1} for the asymmetric and symmetric stretching modes respectively[111]. The ν(OCO) bands of the present compound are different from those of the CH_3COONa bands. For monodentate compounds the asymmetric ν(OCO) stretching frequencies increase and the symmetric ν(OCO) stretching frequencies decrease as the M—O bond becomes stronger[111]. In the compound (XXIV) the ν(OCO) asymmetric and symmetric stretching values are increased and decreased respectively from the ν(OCO) values of CH_3COONa. This is due to Rh—$OOCCH_3$ bond formation in the compound (XXIV) as compared with the

negatively charged CH_3COO^-. The infrared bands of the compound (XXIV) are consistent[92, 136] with those of trans-$[Rh(OOCCH_3)(CO)(PPh_3)_2]$ [Sec. 4.3A(vi)]. The infrared spectrum also suggests that the ethanoato group is monodentate[92]. When the ethanoato is monodentate, one of the C—O bonds should have enhanced double-bond character and should give rise to a higher frequency for $\nu_{asy}(OCO)$ band[2] than the free ethanoato group. Generally a monodentate carboxylato compound[92] shows $\nu_{asy}(OCO)$ at 1580-1620 cm^{-1} and $\nu_{sy}(OCO)$ at 1350-1415 cm^{-1}.

The ^1H-NMR spectrum (Fig. 79) of the compound shows a singlet at 0.84 ppm (3H) which is assigned to the methyl protons of the coordinated ethanoate group[49]. The multiplets at 7.40 ppm (18H) and 7.64 ppm (12H) are assigned to the aromatic protons[49] of the $AsPh_3$ group. The data are consistent with the same type of compound, trans-$[Rh(OOCCH_3)(CO)(PPh_3)_2]$ in the present work [Sec. 4.3A(vi)].

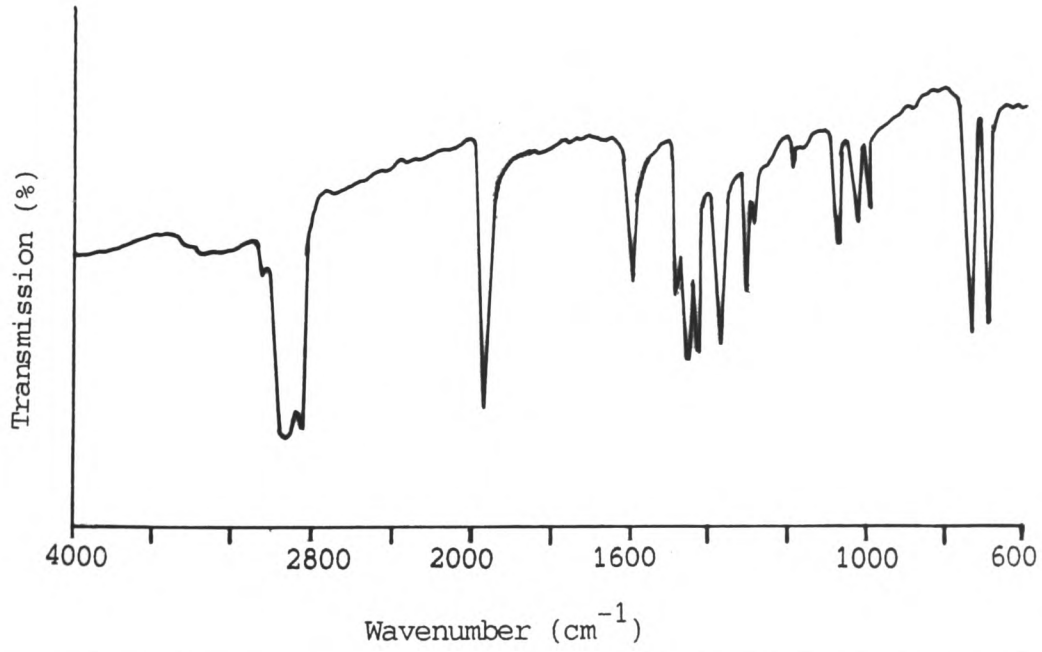


Fig. 78 : Infrared spectrum of trans-$[Rh(OOCCH_3)(CO)(AsPh_3)_2]$ (Nujol mull).

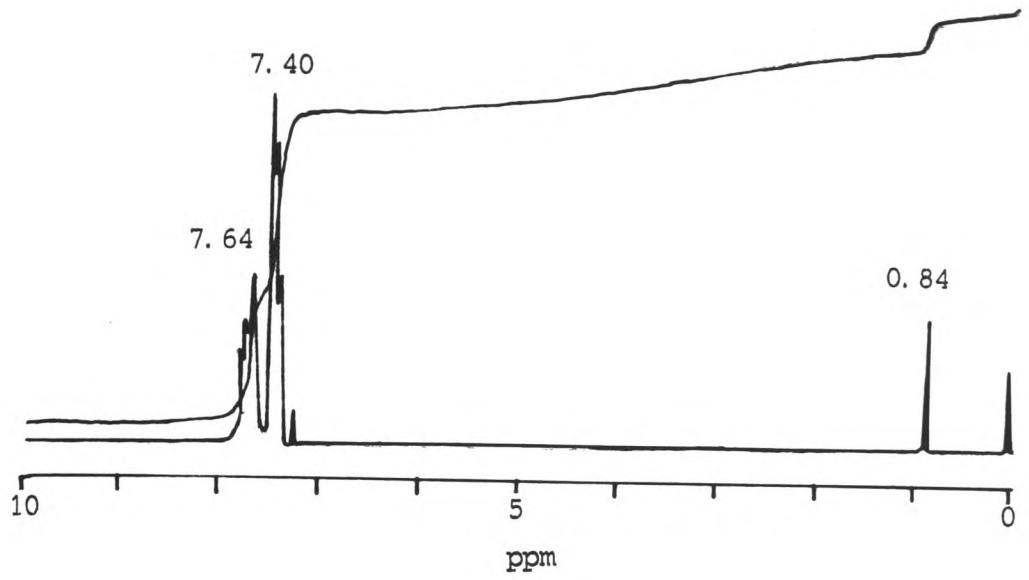


Fig. 79 : ^{1}H-NMR spectrum of trans-[Rh(OOCCH$_3$)(CO)(AsPh$_3$)$_2$] (in CDCl$_3$, TMS).

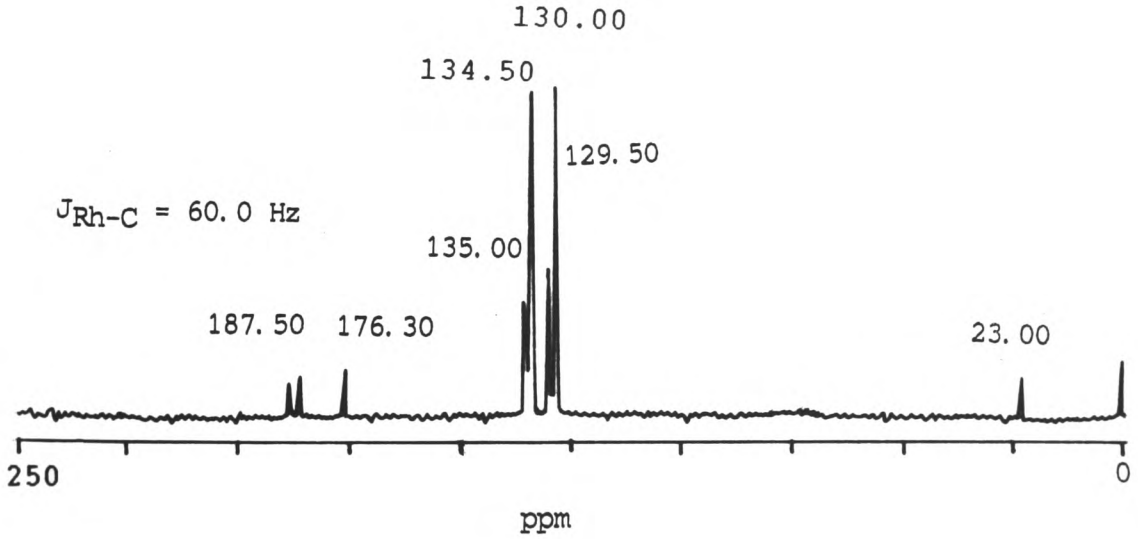


Fig. 80 : ^{13}C-NMR spectrum of trans-[Rh(OOCCH$_3$)(CO)(AsPh$_3$)$_2$] (in CDCl$_3$, TMS).

The ^{13}C-NMR spectrum (Fig. 80) shows a singlet at 23.00 ppm which is assigned to the methyl carbon of the ethanoate group. The signals at 129.50, 130.00, 134.50 and 135.00 ppm are assigned to the aromatic carbons of the $AsPh_3$ group. A singlet at 176.30 ppm is attributed to the carboxylato carbon[153] and a doublet at 187.50 ppm (with J_{Rh-C} = 60.0 Hz) is assigned to the carbonyl carbon[7]. The preparation of the compound (XXIV) is similar to that of trans-$[Rh(OOCCH_3)(CO)(PPh_3)_2]$ and in both cases the precursor materials are of same type i.e. three coordinate cations. The spectroscopic data and analysis are consistent with the formula $[Rh(OOCCH_3)(CO)(AsPh_3)_2]$. Therefore, by analogy with the four-coordinate compound[92,136] of rhodium(I), $[Rh(OOCCH_3)(CO)(PPh_3)_2]$ the proposed structure of the compound (XXIV) is square planar (C_{2v} symmetry) as in Fig. 81, where R = CH_3.

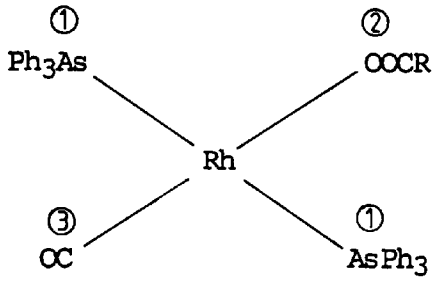


Fig. 81 : Structure of trans-$[Rh(OOCR)(CO)(AsPh_3)_2]$. [IUPAC name where R = CH_3, (SP-4-1)-carbonyl(ethanoato)bis(triphenylarsine)rhodium(I)].

The infrared spectrum (Fig. 82) of the compound (XXV), trans-$[Rh(OOCC_2H_5)(CO)(AsPh_3)_2]$ shows a strong carbonyl band at 1975 cm^{-1}. The spectrum shows bands at 1605 and 1378 cm^{-1} for the asymmetric and symmetric ν(OCO) stretching frequencies. These values for CH_3CH_2COONa are 1560 and 1414 cm^{-1} respectively. The spectral data for the ν(OCO) of

the present compound are different from the ν(OCO) of CH_3CH_2COONa for the same reason as described for the rhodium-ethanoato compound (XXIV). These carbonyl and carboxylato data are consistent with the similar type of propanoato compound[92, 136], trans-$[Rh(OOCC_2H_5)(CO)(PPh_3)_2]$ (Table 21).

The ^{1}H-NMR spectrum (Fig. 83) of the compound (XXV) shows a triplet at 0.20 ppm (3H, J = 7.0 Hz) which is assigned to the methyl protons and a quartet at 1.06 ppm (2H, J = 7.0 Hz) is attributed to the methylene protons of the coordinated $CH_3CH_2COO^-$ group. The multiplets at 7.40 ppm (18H) and 7.64 ppm (12H) represent the aromatic protons of the $AsPh_3$. The ^{1}H-NMR data are in good agreement with the same type of compound, $[Rh(OOCCH_2CH_3)(CO)(PPh_3)_2]$ [Sec. 4.3A(vi)].

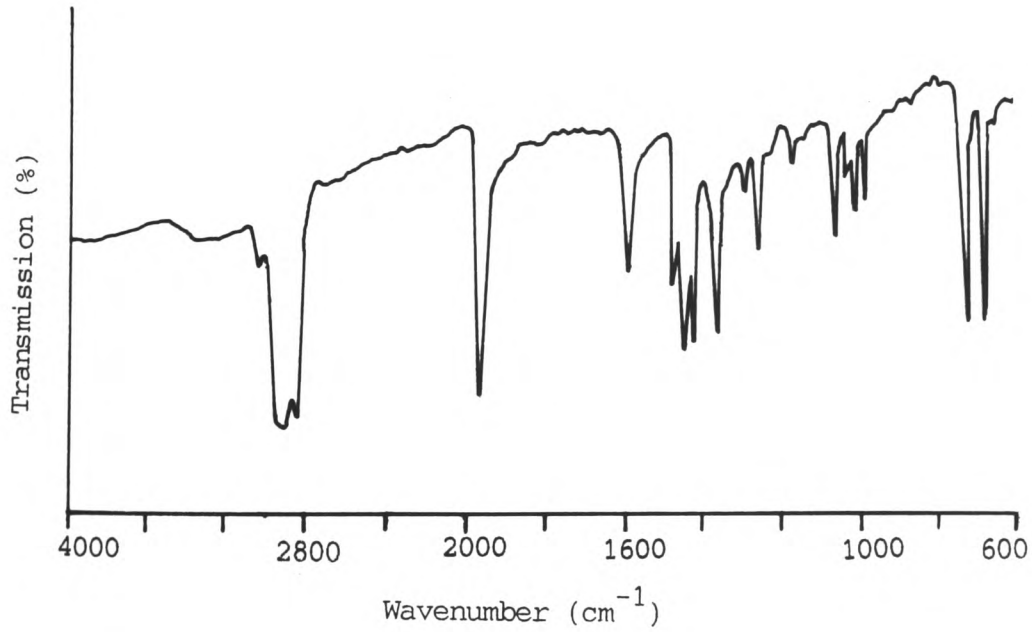


Fig. 82 : Infrared spectrum of trans-$[Rh(OOCCH_2CH_3)(CO)(AsPh_3)_2]$ (Nujol mull).

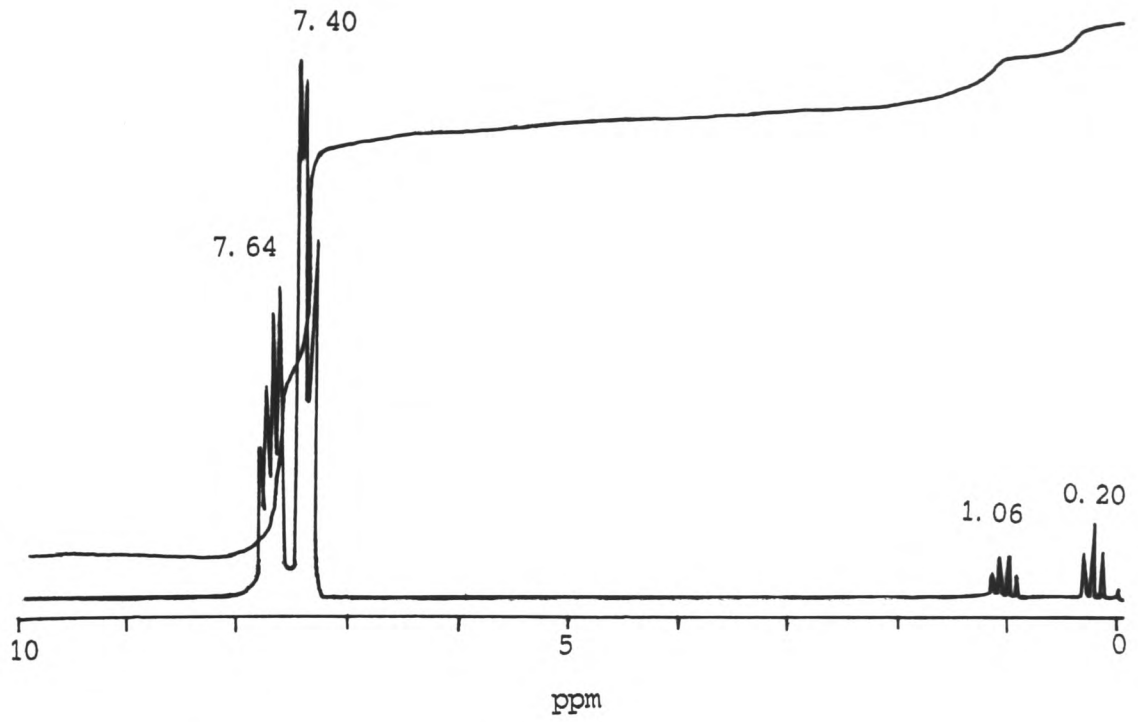


Fig. 83 : ^{1}H-NMR spectrum of trans-[Rh($OOCCH_2CH_3$)(CO)($AsPh_3$)$_2$] (in $CDCl_3$, TMS).

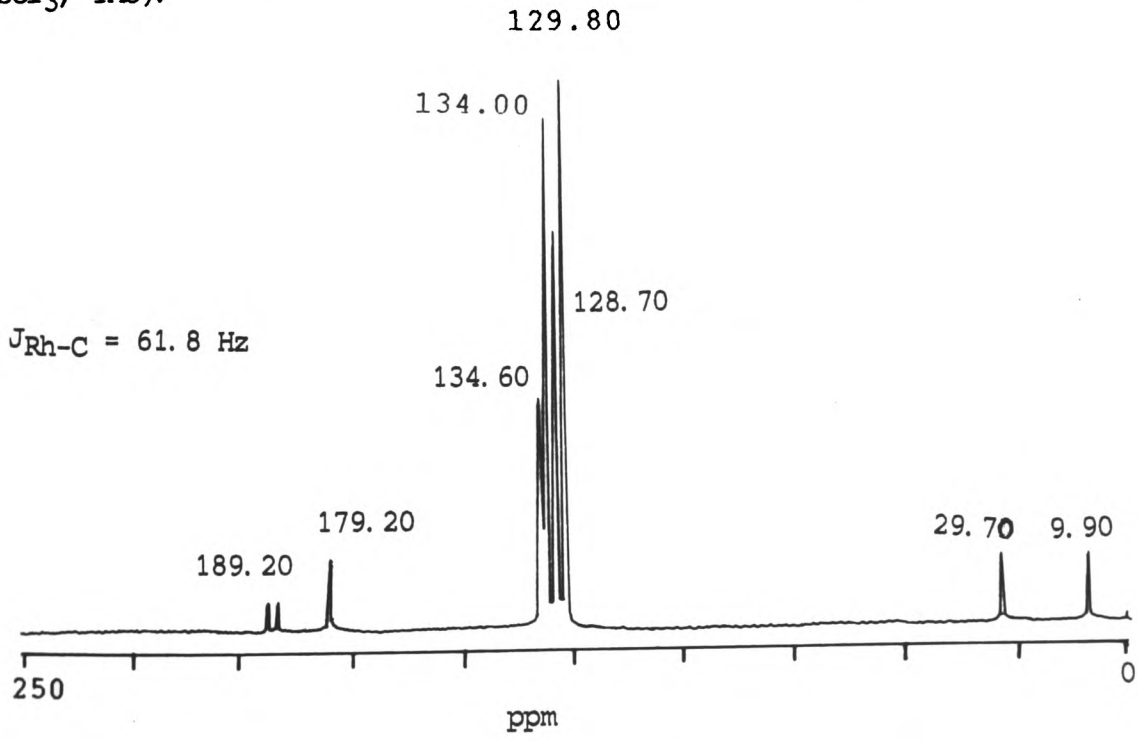


Fig. 84 : ^{13}C-NMR spectrum of trans-[Rh($OOCCH_2CH_3$)(CO)($AsPh_3$)$_2$] (in $CDCl_3$, TMS).

The ^{13}C-NMR spectrum (Fig. 84) of the compound shows a singlet at 9.90 and 29.70 ppm which are attributed to the methyl and methylene carbons of the $CH_3CH_2COO^-$ group respectively. The signals at 128.70, 129.80, 134.00 and 134.60 ppm are assigned to the aromatic carbons of the $AsPh_3$. A singlet at 179.20 ppm represents the carboxylate carbon[153]. A doublet at 189.20 ppm (with J_{Rh-C} = 61.8 Hz) is assigned to the carbonyl carbon[7]. The ^{13}C-NMR data are consistent with the similar compound trans-$[Rh(OOCCH_2CH_3)(CO)(PPh_3)_2]$ [Sec. 4.3A(vi)].

The infrared, ^1H-NMR, ^{13}C-NMR spectra and analysis of the compound are consistent with the formula trans-$[Rh(OOCCH_2CH_3)(CO)(AsPh_3)_2]$. Therefore, by analogy with the similar compound (XVI), the proposed structure of the compound (XXV) is as in Fig. 81, where R = CH_2CH_3.

(xiii) Reaction of Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with KI : Formation of trans-$[RhI(CO)(AsPh_3)_2]$.

Compound (XVIII), $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ reacts with KI [Sec. 4.2B(xxx)] to give yellow crystals. The product is proposed to be $[RhI(CO)(AsPh_3)_2]$. The compound shows a strong carbonyl band at 1980 cm^{-1}. The $\nu(CO)$ band is consistent with the literature value[40]. There is no $\nu(BF_4^-)$ band[98]. The compound shows a positive Lassaigne fusion test for iodine. Therefore, these results suggest that the compound may be trans-$[RhI(CO)(AsPh_3)_2]$.

A summary of the spectral data of rhodium-arsine compounds follows on the next page.

Table 26 : Infrared Data of Rhodium-Arsine Cationic, Alkoxo and Alkoxycarbonyl Compounds.

Compound	ν(CO) cm^{-1}	ν(CO) cm^{-1} (alkoxy-carbonyl)	$\nu(BF_4^-)$ cm^{-1}
(XVIII) $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-$. $1/2(CH_2Cl_2)$*	1989 (s)		1078 (b)
(XIX) $[Rh(CO)_2(AsPh_3)_2]^+[BF_4]^-$*	2037 (s)		1054 (b)
(XX) $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$*	2005 (s) 1954 (s)	1636 (m)	
	2004 (s) 1954 (s)	1630 (m)[a]	
(XXI) $[Rh(OCH_3)(CO)(AsPh_3)_2]$*	1935 (s)		
(XXII) $[Rh(OC_2H_5)(CO)(AsPh_3)_2]$*	1940 (s)		

[Where s = Strong, b = Broad, m = Medium, a = Nujol mull and all other spectra are KBr disc and * indicates novel compound].

Table 27 : ^{1}H-NMR Spectrum of Rhodium-Arsine Cationic, Alkoxo and Alkoxycarbonyl Compounds.

Compound	(CH_3/C_2H_5) ppm or others	(Ph) ppm
(XVIII) $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-$. $1/2(CH_2Cl_2)$	5.28 (s, 1H)	7.30-7.50 (m, 30H)[a]
(XX) $[Rh(COOCH_3)(CO)_2(AsPh_3)_2]$	2.80 (s, 3H)	7.20 (m, 30H)[a]
(XXI) $[Rh(OCH_3)(CO)(AsPh_3)_2]$	3.00 (s, 3H)	7.40-7.80 (m, 30H)[b]

[Where s = Singlet, m = Multiplet, a = $CDCl_3$, b = C_6D_6 and TMS as internal standard].

Table 28 : infrared Data of Rhodium-Arsine Carboxylato Compounds.

Compound	ν(CO) cm^{-1}	ν_{asy}(OCO) cm^{-1}	ν_{sy}(OCO) cm^{-1}
(XXIII) $[Rh(OOCH)(CO)(AsPh_3)_2]$*	1980(s)	1602(m)	1382(m)
(XXIV) $[Rh(OOCCH_3)(CO)(Ash_3)_2]$	1970(s)	1610(m)	1375(m)
(XXV) $[Rh(OOCC_2H_5)(CO)(AsPh_3)_2]$*	1975(s)	1605(m)	1378(m)
	1975(s)	1596(m)	1382(m)[a]

[Where s = Strong and m = Medium, a = KBr disc and all other spectra in Nujol mull and * indicates novel compound].

Table 29 : ^{1}H-NMR Data of Rhodium-Arsine Carboxylato Compounds.

Compound	^{1}H-NMR (CH/CH_3/C_2H_5) ppm	(Ph) ppm
(XXIII) $[Rh(OOCH)(CO)(AsPh_3)_2]$	3.14(s, 1H)	7.00(m, 18H)[a] 7.84(m, 12H)
	3.40(s, 1H)	7.35(m, 18H) 7.65(m, 12H)
(XXIV) $[Rh(OOCCH_3)(CO)(AsPh_3)_2]$	0.84(s, 3H)	7.40(m, 18H) 7.64(m, 12H)
(XXV) $[Rh(OOCC_2H_5)(CO)(AsPh_3)_2]$	0.20(t, 3H) 1.06(q, 2H)	7.40(m, 18H) 7.64(m, 12H)

[Where s = Singlet, m = Multiplet, t = Triplet, q = Quartet, a = C_6D_6 and all other spectra in $CDCl_3$, TMS as internal standard].

Table 30 : ^{13}C-NMR Data of Rhodium-Arsine Carboxylato Compounds.

Compound	CH_3	CH_2	Ph	COO^-	CO
(XXVI) $[Rh(OOCCH_3)(CO)(AsPh_3)_2]$	23.00 (s)		129.50 130.00 134.50 135.00	176.30 (s)	187.50 (d)
(XXV) $[Rh(OOCCH_2CH_3)(CO)(AsPh_3)_2]$	9.90 (s)	29.70 (s)	128.70 129.80 134.00 134.60	179.20 (s)	189.20 (d)

[Where s = Singlet, d= Doublet and all spectra in $CDCl_3$ and the values are in ppm. Compound (XXIV) J_{Rh-C} = 60.0 Hz and compound (XXV) J_{Rh-C} = 61.8 Hz].

(C) RHODIUM-CYCLOHEXYLPHOSPHINE COMPOUNDS.

(xiv) Synthesis of $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$, Carbonylbis-(tricyclohexylphosphine)rhodium(I) tetrafluoroborate dichloromethane solvate, Compound (XXVI).

The compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ has been prepared from trans-$[RhCl(CO)(PCy_3)_2]$ with $AgBF_4$ [Sec. 4.2C(xxxii)] and characterised by infrared, ^{1}H-NMR, ^{31}P-NMR spectroscopy and analysis.

The infrared spectrum (Fig. 85) of the compound (XXVI) shows a strong carbonyl band at 1965 cm^{-1} and a broad band at 1083 cm^{-1} for $\nu(BF_4^-)$. The $\nu(BF_4^-)$ band suggests that it is free[97,98] in the compound. The carbonyl stretching frequency of the compound is higher than the precursor[114,127], due to the salt formation as described in Sec. 4.3A(i). In the literature, 14-electron compounds[127] or cationic 14-electron complexes[102,103,146] of rhodium are known. Similar cationic complexes of rhodium have been described in Sec. [4.3A(i) and 4.3B(viii)], where the ligands are PPh_3 and $AsPh_3$ respectively. The electron unsaturated compound may be stabilised by the solvent, dichloromethane.

The ^{1}H-NMR spectrum (Fig. 86) of the compound shows a multiplet at 1.22 and 1.88 ppm. These signals are assigned to the methylene protons of the cyclohexylphosphine and a singlet at 5.28 ppm is assigned to the methylene protons of dichloromethane. More detailed descriptions about coordinated dichloromethane have been given in Sec. [3.3(i) and 4.3A(i)].

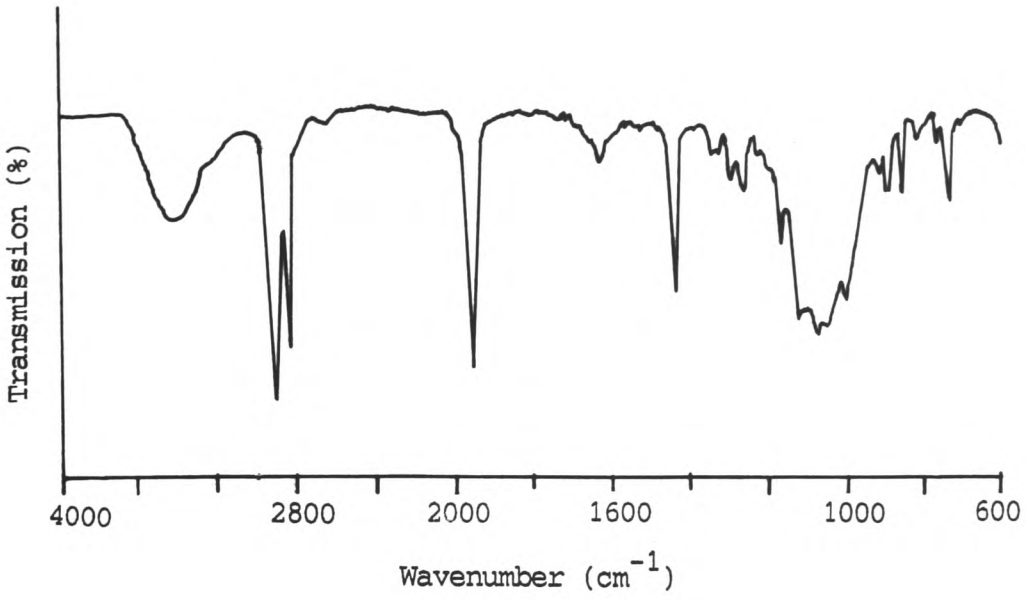


Fig. 85 : Infrared spectrum of $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2CH_2)$ (KBr disc).

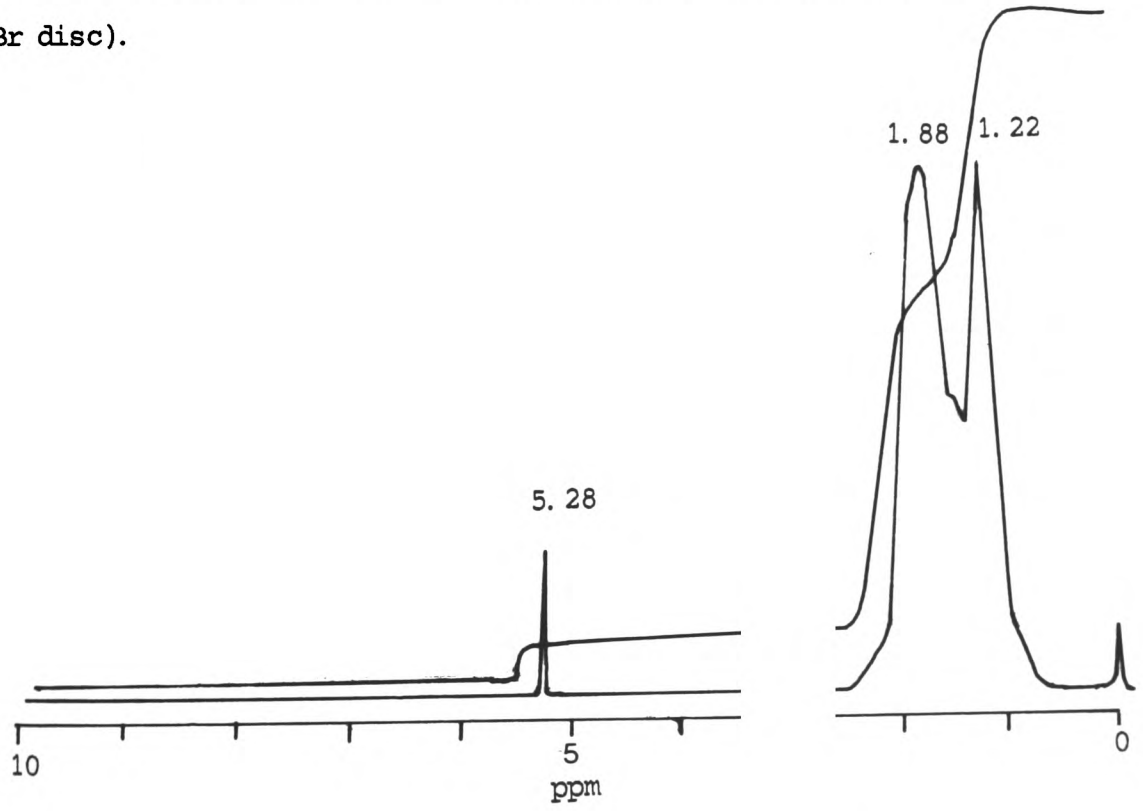


Fig. 86 : ^{1}H-NMR spectrum of $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (in C_6D_6, TMS).

J_{Rh-P} = 117.2 Hz

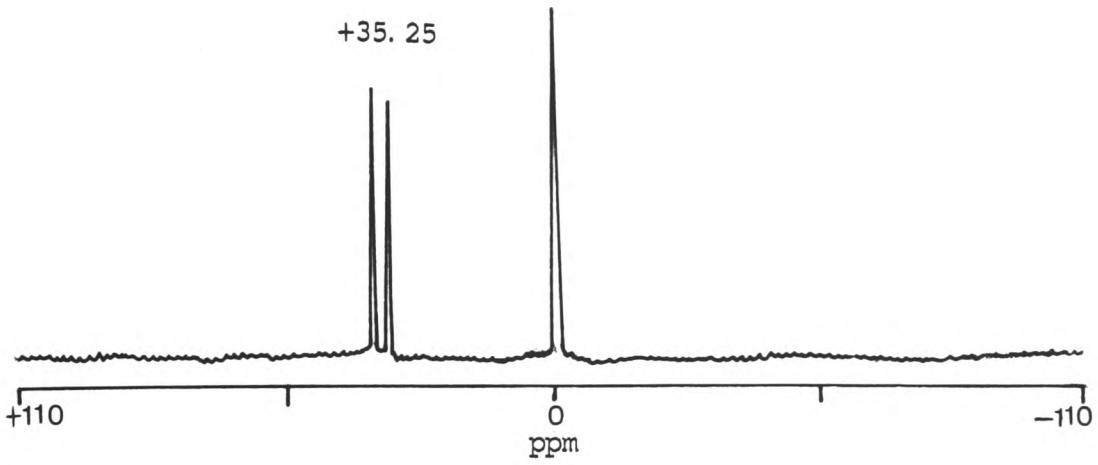


Fig. 87 : ^{31}P-NMR spectrum of $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (in C_6D_6, TMP).

The ^{31}P-NMR spectrum (Fig. 87) of the compound shows a doublet at +35.25 ppm (with J_{Rh-P} = 117.2 Hz) with respect to trimethylphosphate (TMP) as internal standard. This ^{31}P-NMR value is different (i.e. downfield) from the precursor[127] compound. The reported value of the precursor is +11.90 ppm (with J_{Rh-P} = 119.9 Hz) with respect to TMP[127]. Due to cation formation, the back donation from Rh to P decreases, as a result electron density on phosphorus decreases, i.e. phosphorus is deshielded as compared with phosphorus in the precursor. More detail descriptions were given in Sec. 4.3A(i).

The infrared and NMR spectra and analysis of the compound are consistent with the formula $[Rh(CO)(PCy_3)_2]^+[BF_4^-].3/2(CH_2Cl_2)$. Three-coordinate rhodium(I) compounds of the type $[RhX(PCy_3)_2]$ (where X = F, Cl, Br and

I) are known and their phosphines are equivalent[127]. The ^{31}P-NMR of the compound (XXVI) shows a doublet, suggesting that the phosphines are equivalent and coupled to the rhodium. The smaller coupling constant again indicates the solvent interaction, i.e. the ideal trigional geometry of the compound was distorted by solvent, dichloromethane [more detailed descriptions were given in Sec. 4.3A(i)].

(xv) Synthesis of trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$, Dicarbonylbis-(tricyclohexylphosphine)rhodium(I) tetrafluoroborate, Compound (XXVII).

Compound (XXVII), trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$ is formed when carbon monoxide is bubbled through the solution [Sec. 4.2C(xxxiii)] of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ and is characterised by infrared and ^{31}P-NMR spectroscopy.

The infrared spectrum (Fig. 88) of the compound shows a strong carbonyl band at 2005 cm^{-1}, which suggests a cationic complex with trans-carbonyl groups[53]. This band is at higher frequency than the cationic precursor, $[Rh(CO)(PCy_3)_2]^+$ and non-cationic precursor trans-$[RhCl(CO)(PCy_3)_2]$. The explanation for this is the same as in Sec. 4.3A(ii). The $\nu(BF_4^-)$ value of the anion is at 1050 cm^{-1}, indicates that it is free in the compound[97,98].

The ^{31}P-NMR spectrum (Fig. 89) of the compound shows a doublet at +42.14 ppm (with J_{Rh-P} = 97.7 Hz) with respect to trimethylphosphate as an internal standard. This value is lower field than the cationic precursor compound (XXVI) and also lower field than the non-cationic precursor trans-$[RhCl(CO)(PCy_3)_2]$.

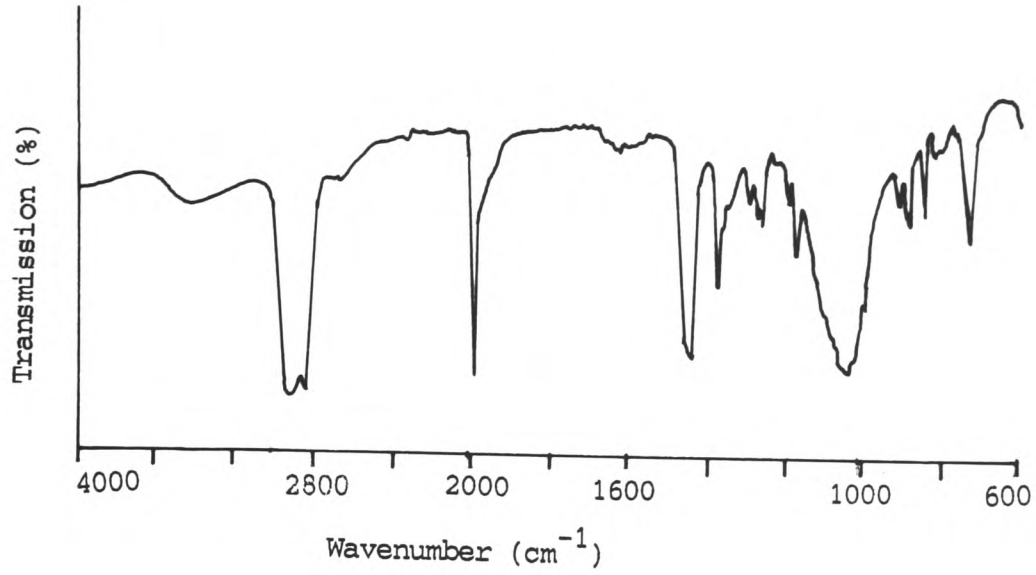


Fig. 88 : Infrared spectrum of trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$ (Nujol mull).

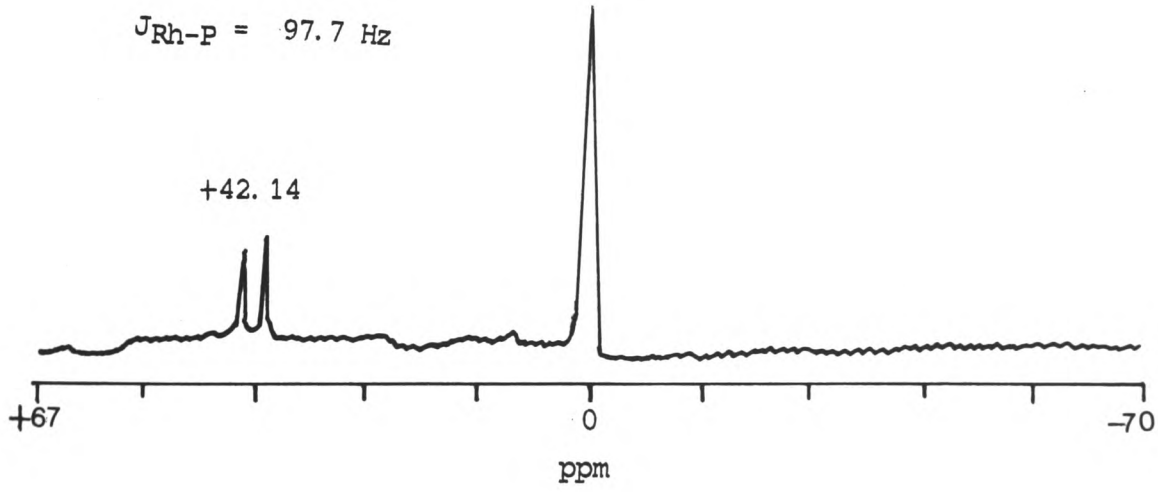


Fig. 89 : ^{31}P-NMR spectrum of trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$ (in C_6D_6, TMP).

The infrared spectrum is consistent with the same type of cationic complex[53], trans-$[Rh(CO)_2(PCy_3)_2]^+[AlCl_4]^-$ in which the ν(CO) is at 1997 cm^{-1}. Therefore, by analogy with trans-$[Rh(CO)_2(PCy_3)_2]^+[AlCl_4]^-$, the structure of the compound (XXVII) is suggested as square planar as in Fig. 90.

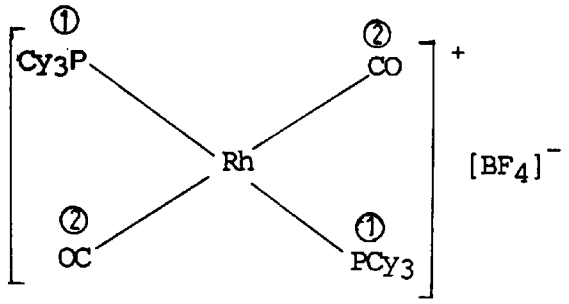


Fig. 90 : Structure of trans-$[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$.
[IUPAC name, (SP-4-1)-dicarbonylbis(tricyclohexylphosphine)rhodium(I)-tetrafluoroborate].

(xvi) Reaction of Compound (XXVI) with CH_3ONa : Synthesis of trans-$[Rh(COOCH_3)(CO)(PCy_3)_2]$, carbonyl(methoxycarbonyl)bis(tricyclohexylphosphine)rhodium(I), Compound (XXVIII).

The compound (XXVIII), $[Rh(COOCH_3)(CO)(PCy_3)_2]$ has been prepared by the reaction of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ with sodium methoxide in the presence of CO [Sec. 4.2C(xxxiv)]. The compound can also be prepared by reacting compound (XXVII) with sodium methoxide under CO.

The infrared spectrum (Fig. 91) of the compound shows a strong carbonyl band at 1950 cm^{-1}. The band at 1620 cm^{-1} represents[22,42] the alkoxycarbonyl band. The infrared spectrum of the compound is consistent

with the similar compound, trans-[Rh(COOCH$_3$)(CO)(PPh$_3$)$_2$] [Sec. 4. 3A(v)]. A similar reported compound[150] is trans-[Rh(COOCH$_3$)(CO){P(iso-C$_3$H$_7$)$_3$}$_2$], which shows v(CO) at 1949 cm^{-1} and methoxycarbonyl band at 1613 cm^{-1}.

The ^{1}H-NMR spectrum (Fig. 92) of the present compound shows a singlet at 3. 22 ppm, (3H) which is assigned to the methyl protons of the methoxycarbonyl group. The multiplets at 1. 20 and 1. 75 ppm (66H) are assigned to the methylene protons of the cyclohexylphosphine group. The signal at 3. 42 ppm (3H) is assigned to trapped or associated methanol. Free methanol also shows a resonance at 3. 45 ppm. The methyl protons shift is consistent with similar methoxycarbonyl compounds of the literature[150] and also with similar compound in the present work Sec. 4. 3A(v). The ^{31}P-NMR spectrum (Fig. 93) of the compound shows a doublet at +36. 70 ppm (with J_{Rh-P} = 112. 0 Hz).

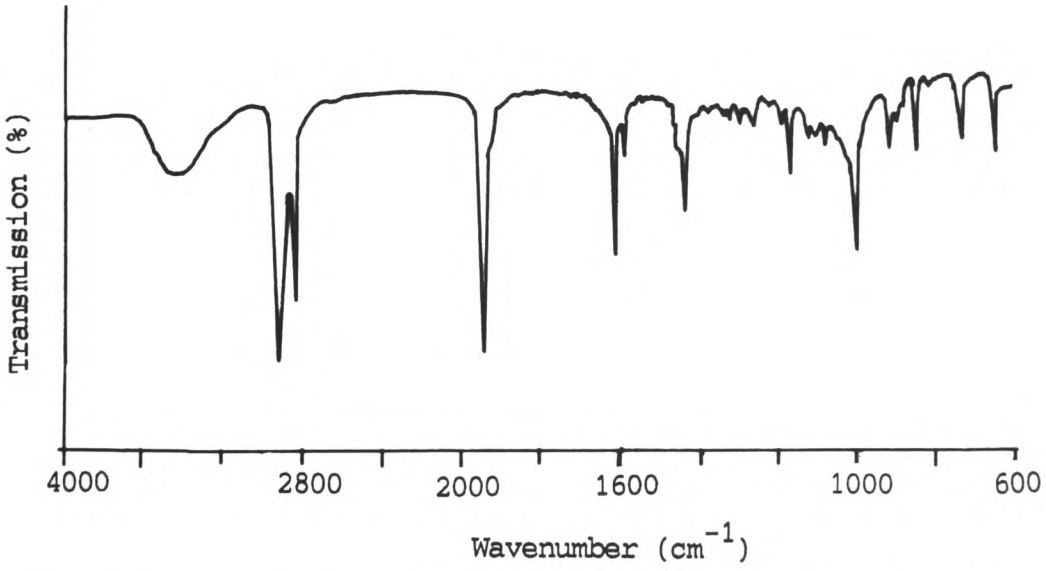


Fig. 91 : Infrared spectrum of trans-[Rh(COOCH$_3$)(CO)(PCy$_3$)$_2$] (KBr disc).

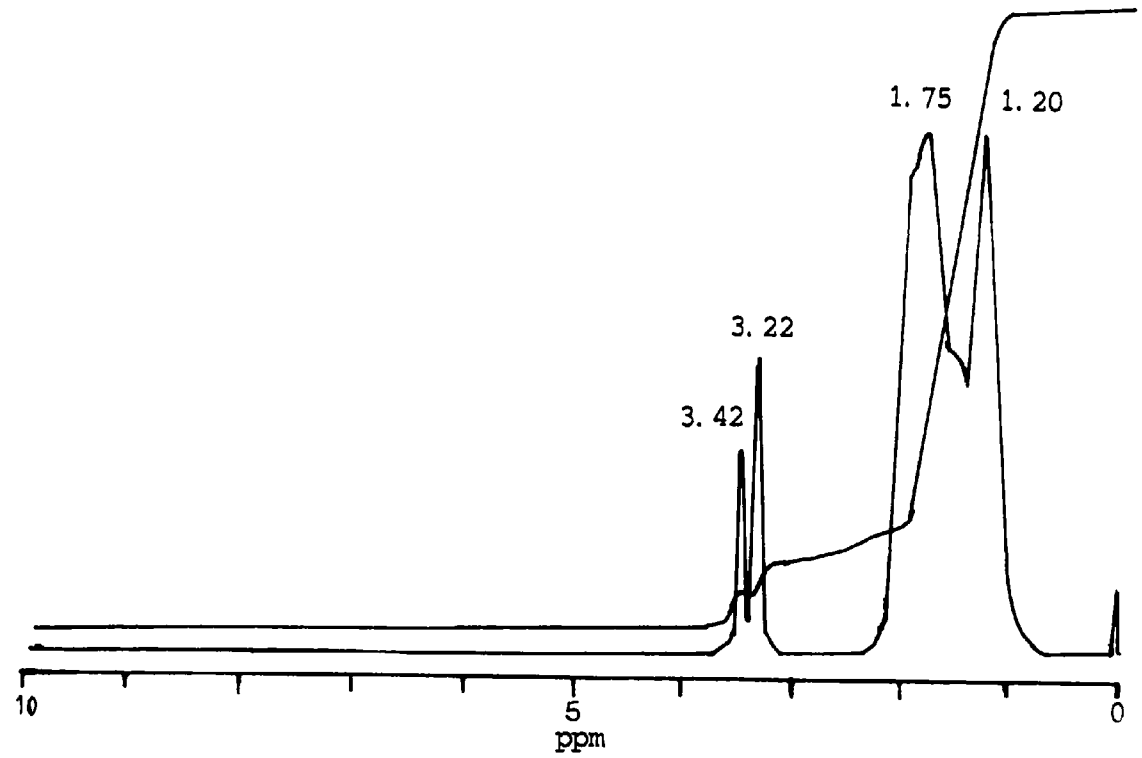


Fig. 92 : ^{1}H-NMR spectrum of trans-[Rh($COOCH_3$)(CO)(PCy_3)$_2$] (in $CDCl_3$, TMS).

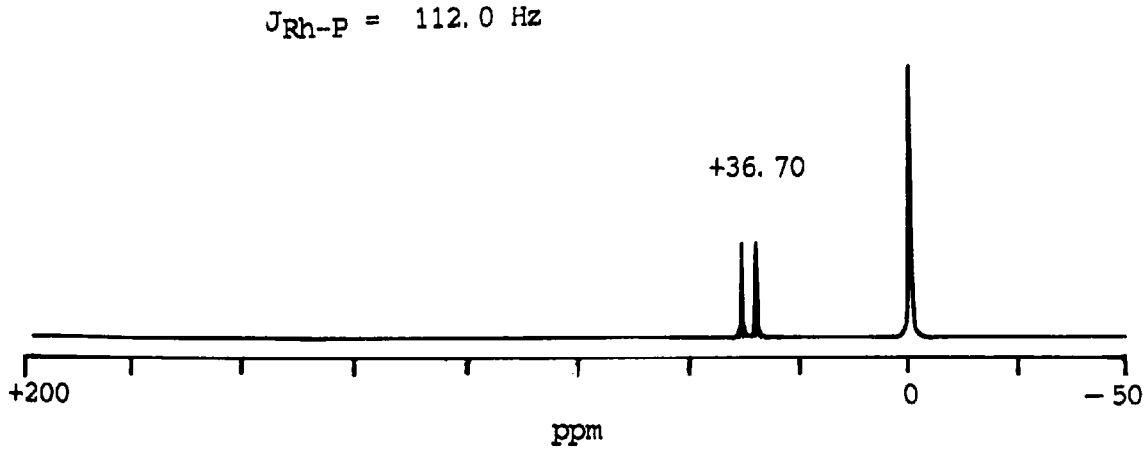


Fig. 93 : ^{31}P-NMR spectrum of trans-[Rh($COOCH_3$)(CO)(PCy_3)$_2$] (in $CDCl_3$, 85% H_3PO_4).

By analogy with the compound (XIII) [Sec. 4.3A(v)], the structure of the proposed compound is trans-$[Rh(COOCH_3)(CO)(PCy_3)_2]$.

(xvii) Synthesis of trans-$[Rh(OCH_3)(CO)(PCy_3)_2]$, carbonyl(methoxo)bis-(tricyclohexylphosphine)rhodium(I), Compound (XXIX).

The compound (XXIX), trans-$[Rh(OCH_3)(CO)PCy_3)_2]$ is prepared by the reaction of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ with sodium methoxide [Sec. 4.2C(xxxv)].

The infrared spectrum (Fig. 94) of the compound shows a strong carbonyl band at 1921 cm^{-1}. The carbonyl stretching frequency suggests that the compound may have a coordinated methoxo group[150].

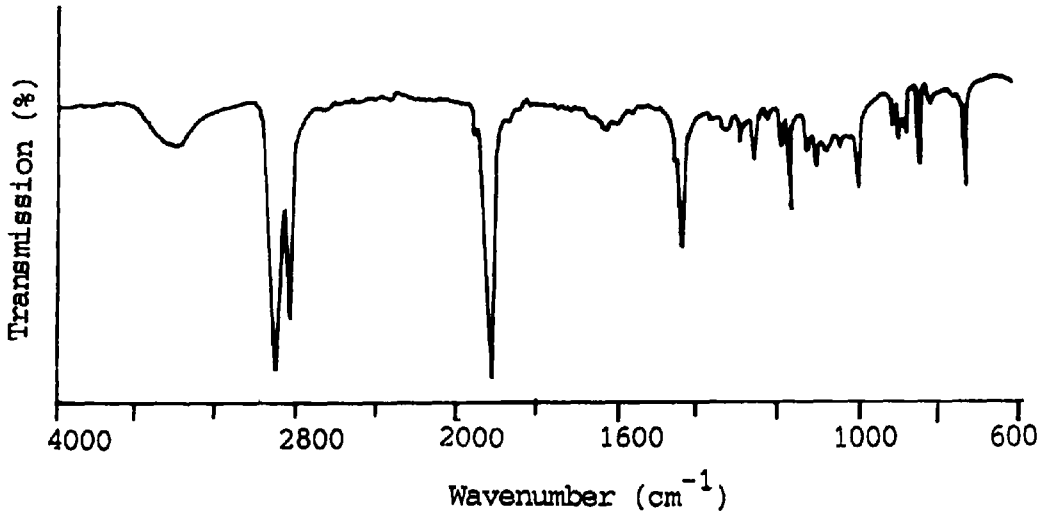


Fig. 94 : Infrared spectrum of trans-$[Rh(OCH_3)(CO)(PCy_3)_2]$ (KBr disc).

A similar methoxo compound[150] $[Rh(OCH_3)(CO)\{P(iso\text{-}C_3H_7)_3\}_2]$, which shows v(CO) at 1925 cm^{-1}. The carbonyl band moves to lower frequency than the cationic precursor, compound (XXVI) and also from the non-cationic precursor trans-$[RhCl(CO)(PCy_3)_2]$ due to the same reason as described in Sec. 4.3A(iv). By analogy with the same type of compounds of PPh_3 and $AsPh_3$ [Sec. 4.3A(iv) and 4.3B(xi)] and with the reported compound[150] of $P(iso\text{-}C_3H_7)_3$ the suggested structure of the compound is trans-$[Rh(OCH_3)(CO)(PCy_3)_2]$. No meaningful NMR spectrum of the compound could be obtained due to the instability of the compound.

(xviii) Synthesis of trans-$[Rh(OOCCH_3)(CO)(PCy_3)_2]$, Carbonyl(ethanoato)-bis(tricyclohexylphosphine)rhodium(I), Compound (XXX).

The compound (XXX), trans-$[Rh(OOCCH_3)(CO)(PCy_3)_2]$ has been prepared by the reaction of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ with sodium ethanoate [Sec. 4.2C(xxxvi)].

The infrared spectrum (Fig. 95) of the compound shows a strong carbonyl band at 1943 cm^{-1} and the bands at 1622 and 1367 cm^{-1} are assigned to the v(OCO) asymmetric and symmetric stretching frequencies respectively[127]. This infrared value is consistent with the reported value[127], where the compound was prepared from the 14-electron species $[RhF(PCy_3)_2]$. The ^{1}H-NMR spectrum of the compound shows a broad band at (1.00-2.10) ppm for the cyclohexyl protons of the PCy_3 group. The methyl protons of the coordinated ethanoate group[92] generally appeared in this region. Therefore, it is assumed that the methyl protons of the ethanoato group in the compound is overlapped by the broad band of the cyclohexyl protons of the PCy_3.

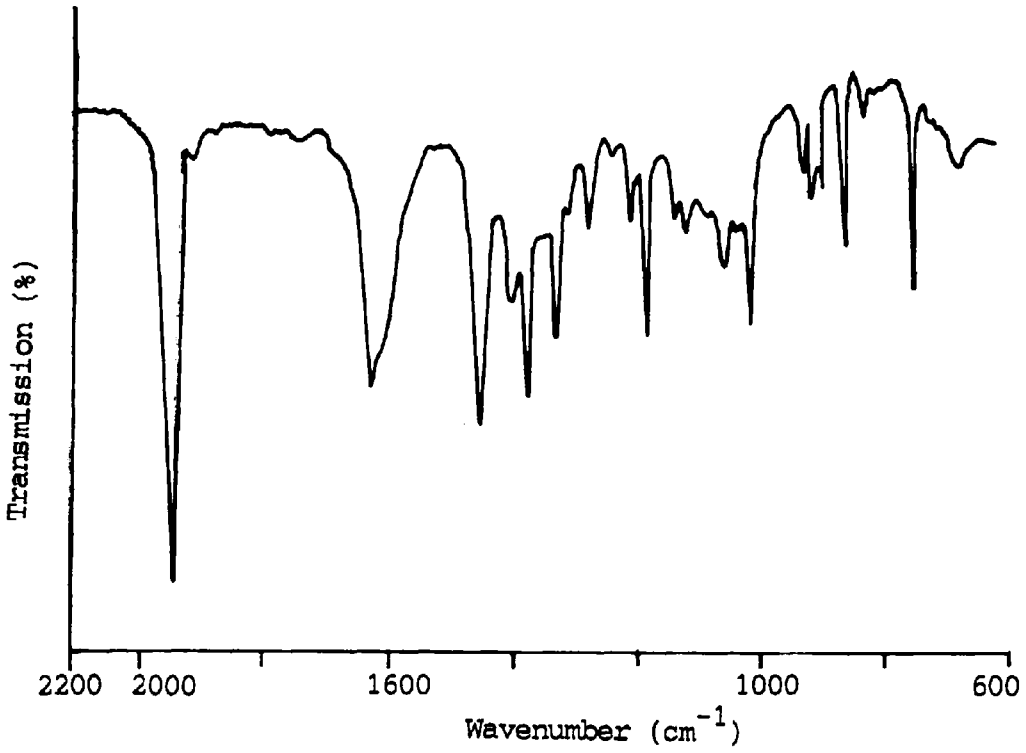


Fig. 95 : Infrared spectrum of trans-[Rh($OOCCH_3$)(CO)(PCy_3)$_2$] (KBr disc).

A summary of the spectral data of the rhodium-cyclohexylphosphine compounds follows on the next page.

Table 31 : Infrared Data of Rhodium-Cyclohexylphosphine Compounds.

Compound	ν(CO)	ν(CO) (alkoxy-carbonyl)	ν(OCO)	$\nu(BF_4^-)$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
(XXVI) $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.$ $3/2(CH_2Cl_2)$*	1965(s)			1083(b)
(XXVII) $[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$*	2005(s)			1050(b)[a]
(XXVIII) $[Rh(COOCH_3)(CO)(PCy_3)_2]$*	1950(s)	1620(m)		
(XXIX) $[Rh(OCH_3)(CO)(PCy_3)_2]$*	1921(s)			
(XXX) $[Rh(OOCCH_3)(CO)(PCy_3)_2]$	1943(s)		1622(m), 1367(m)	

[Where s = Strong, b = Broad, m = medium, a = Nujol mull and all other spectra in KBr disc and * indicates novel compound].

Table 32 : ^{1}H-NMR and ^{31}P-NMR Data of Rhodium-Cyclohexylphosphine Compounds.

Compound	^{1}H-NMR (ppm)	^{31}P-NMR (ppm)	J_{Rh-P} (Hz)
(XXVI) $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.$ $3/2(CH_2Cl_2)$	1.22 (m, 66H) 1.88 5.28 (s, 2H)	+35.25 (d)	117.2[a]
(XXVII) $[Rh(CO)_2(PCy_3)_2]^+[BF_4]^-$		+42.14 (d)	97.7[a]
(XXVIII) $[Rh(COOCH_3)(CO)(PCy_3)_2]$	1.20 (m, 66H) 1.75 3.22 (s, 3H) 3.42 (s, 3H)	+36.70 (d)	112.0[b]

[Where m = Multiplet, d = Doublet, s = Singlet, a = C_6D_6, b = $CDCl_3$. TMS in ^{1}H-NMR and TMP in ^{31}P-NMR as internal standards and 85% H_3PO_4 as external standard for compound (XXVIII)].

(D) RHODIUM-STIBINE COMPOUNDS.

(xix) Synthesis of $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$, Dicarbonyltris(triphenylstibine)rhodium(I) tetrafluoroborate dichloromethane solvate, Compound (XXXI).

Reaction of trans-$[RhCl(CO)(SbPh_3)_2]$ with $AgBF_4$ in the presence of CO [Sec. 4.2D(xli)] gave $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$, compound (XXXI). The same compound also formed, with the reaction of $[RhCl(SbPh_3)_3]$ to $AgBF_4$ in the presence of CO [Sec. 4.2D(xlii)]. The compound was characterised by infrared spectroscopy and analysis.

The infrared spectrum (Fig. 96) of the compound shows a strong carbonyl band at 2006 cm^{-1}. A broad band at 1061 cm^{-1}, which represents[97,98] the $\nu(BF_4^-)$ anion free in the compound. The carbonyl stretching frequency is consistent with other compounds[53] of the type $[Rh(CO)_2(SbPh_3)_3]^+[AlCl_4]^-$, in which the $\nu(CO)$ band appears at 2009 cm^{-1}, where the compound was prepared from the reaction of $[RhCl(CO)(SbPh_3)_3]$ with $AlCl_3$ in the presence of CO. Also a similar compound[97], $[Rh(CO)_2(SbPh_3)_3]^+[ClO_4]^-$, is reported in which the $\nu(CO)$ band is at 2006 cm^{-1}, where the compound was prepared from the reaction of rhodium perchlorate, CO and a calculated amount of $SbPh_3$. The reaction of trans-$[RhCl(CO)(SbPh_3)_2]$ with $AgBF_4$ in the presence of CO would be expected to give either $[Rh(CO)_2(SbPh_3)_2]^+$ or perhaps $[Rh(CO)_3(SbPh_3)_2]^+$ to maintain the metal to $SbPh_3$ ratio consistent in the compound. However, the analysis and infrared spectrum suggest that the compound is $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$.

This is an unusual result that the precursor has only two $SbPh_3$ groups but in the product are three $SbPh_3$ groups. It may be that the longer metal-stibine bond distance allows less steric hindrance, so that more $SbPh_3$ ligands can be accommodated around the central metal atom. Examples of similar five-coordinated species of $SbPh_3$ have been found in the literature[40].

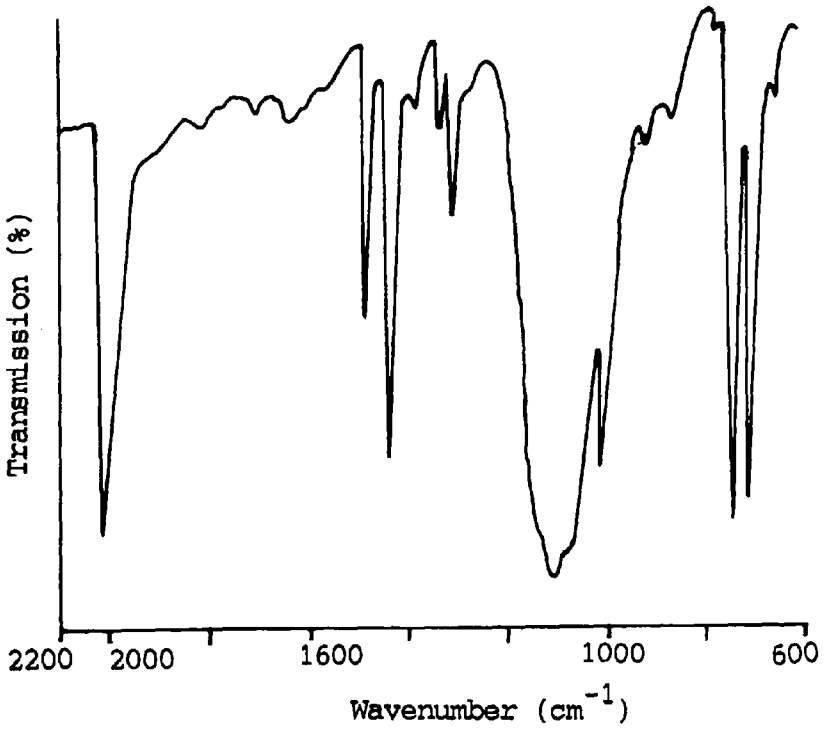


Fig. 96 : Infrared spectrum of $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ (KBr disc).

However, the literature[40,155] shows that the carbonyl stretching frequencies of $[RhCl(CO)(SbPh_3)_2]$ and $[RhCl(CO)(SbPh_3)_3]$ are at 1960 and 1980 cm^{-1} (Nujol mull). This report also showed that when $[RhCl(CO)(SbPh_3)_3]$ was recrystallised from chloroform and ethanol it

gave $[RhCl(CO)(SbPh_3)_2]$. In the present work the compound $[RhCl(CO)(SbPh_3)_2]$ was recrystallised from chloroform and ethanol twice and $\nu(CO)$ of the product was at 1960 cm^{-1}. There was no evidence of any trace of $[RhCl(CO)(SbPh_3)_3]$ with a band at 1980 cm^{-1}.

An attempt was made to prepare the compound $[Rh(CO)(SbPh_3)_2]^+[BF_4]^-$ from $[RhCl(CO)(SbPh_3)_2]$ and $AgBF_4$ [Sec. 4.2D(xL)], as for the PPh_3, $AsPh_3$ and PCy_3 analogues Sec. [4.2A, 4.2B and 4.2C] respectively. The infrared spectrum of the product of the attempted reaction shows weak and broad bands, inconsistent with $[Rh(CO)(SbPh_3)_2]^+$ and indicates decomposition.

By analogy with a number of similar five-coordinate cationic complexes of rhodium and iridium[97] and from spectroscopic evidence, the compound $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ may have a trigonal bipyramidal stereochemistry (D_{3h} symmetry) with the carbonyl groups occupying axial positions as shown in Fig. 97.

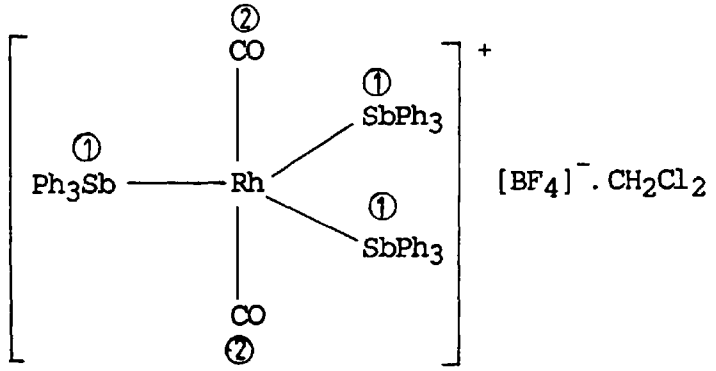


Fig. 97 : Structure of $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$. [IUPAC name, (TBPY-5-22)-Dicarbonyltris(triphenylstibine)rhodium(I) tetrafluoroborate dichloromethane solvate].

The compound $[RhCl(SbPh_3)_3]$ does not react with CO to give $[RhCl(CO)(SbPh_3)_2]$ [Sec. 4.2D(xxxviii)]. But $[RhCl(PPh_3)_3]$ when treated with CO [Sec. 4.2A(ii)] gives the compound $[RhCl(CO)(PPh_3)_2]$. Thus it is

assumed that $SbPh_3$ is less labile in the compound $[RhCl(SbPh_3)_3]$ than PPh_3 in the compound $[RhCl(PPh_3)_3]$. This, again may be due to the fact that the longer rhodium—$SbPh_3$ bond results in a compound with less steric crowding and hence greater stability[40].

(xx) Reaction of Compound (XXXI), $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ with RONa to form $[Rh(COOR)(CO)(SbPh_3)_3]$, Alkoxycarbonyl(carbonyl)tris-(triphenylstibine)rhodium(I), where R = CH_3 and C_2H_5 Compound (XXXII) and (XXXIII) respectively.

The compound $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$ reacts with RONa to form $[Rh(COOR)(CO)(SbPh_3)_3]$, where R = CH_3, C_2H_5, compounds (XXXII) and (XXXIII) [Sec. 4.2D{(xliii) and (xliv)}] respectively. These compounds have been characterised by infrared and ^{1}H-NMR spectroscopy.

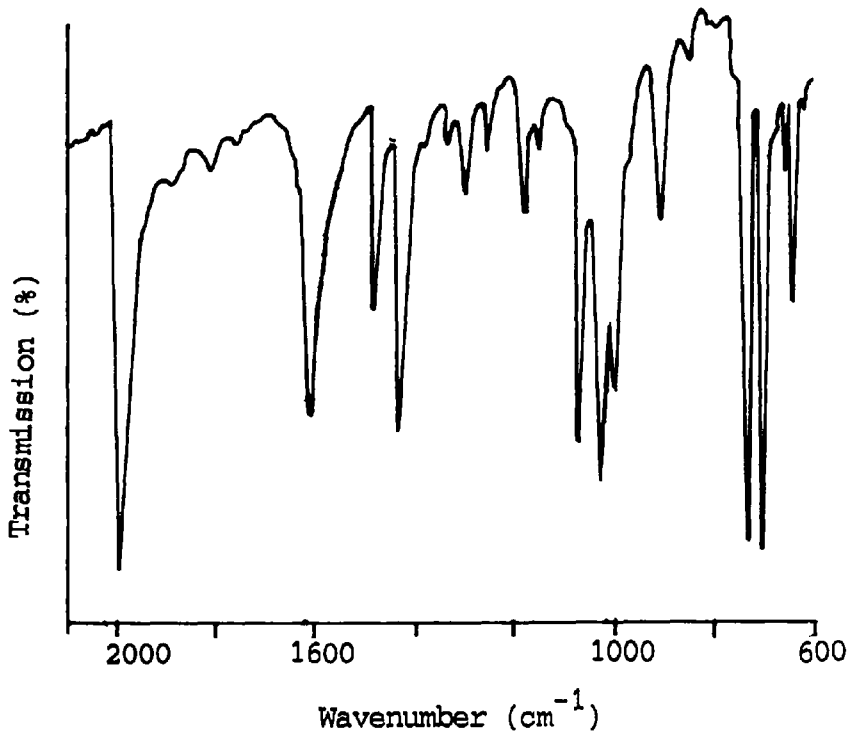


Fig. 98 : Infrared spectrum of $[Rh(COOCH_3)(CO)(SbPh_3)_3]$ (KBr disc).

The infrared spectrum (Fig. 98) of the compound (XXXII) shows a strong carbonyl band at 1979 cm^{-1}. A medium intensity band at 1603 cm^{-1} is assigned to the methoxycarbonyl band. The carbonyl and methoxycarbonyl bands are consistent with the literature[53] value of the compound $[Rh(COOCH_3)(CO)(SbPh_3)_3]$. The ^{1}H-NMR spectrum (Fig. 99) of the compound (XXXII) shows a singlet at 2.41 ppm (3H) which represents the methyl protons of methoxycarbonyl group[22,48]. A multiplet at (7.10-7.50) ppm (45H) is assigned to the aromatic protons of the coordinated $SbPh_3$. By analogy with the precursor compound (XXXI), the three $SbPh_3$ may be in the equatorial positions, the suggested structure of the complex (XXXII) is as in Fig. 100, where R = CH_3. It could be another isomer, but this isomer may be more stable than the others, because three bulky groups are in equatorial positions. The actual structure could be confirmed by X-ray crystallography.

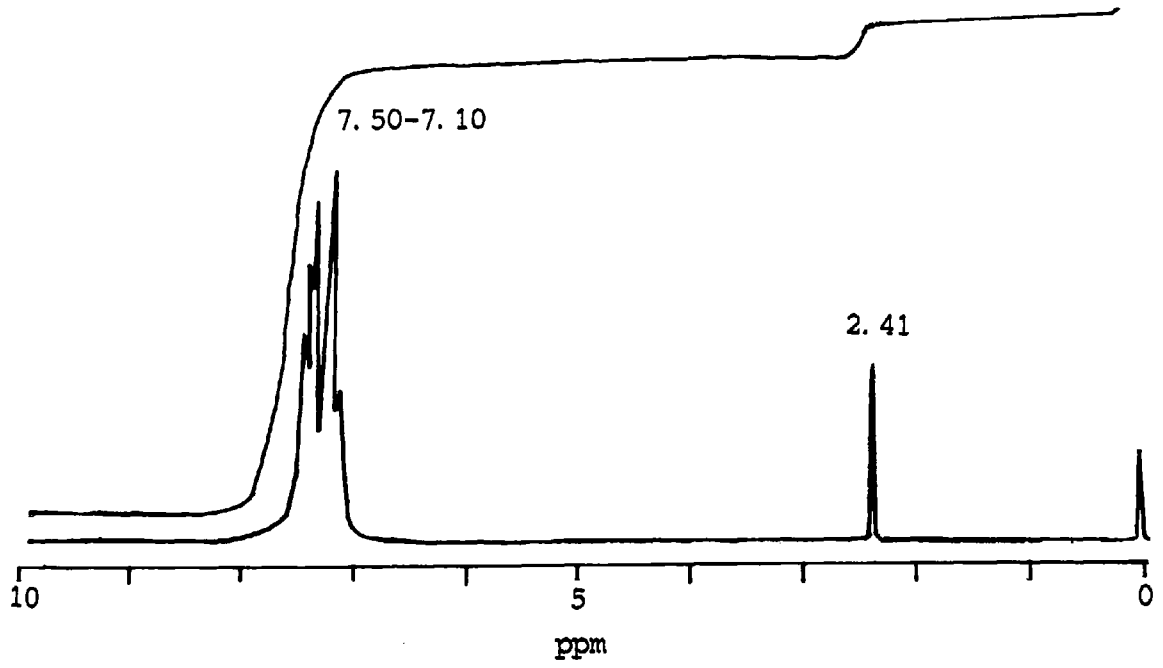


Fig. 99 : ^{1}H-NMR spectrum of $[Rh(COOCH_3)(CO)(SbPh_3)_3]$ (in $CDCl_3$, TMS).

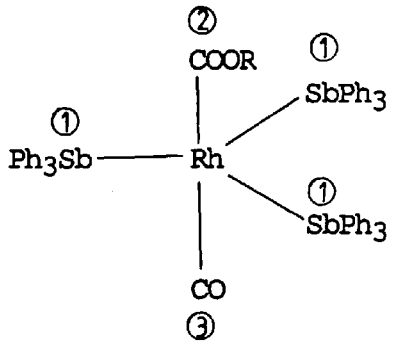


Fig. 100 : Structure of $[Rh(COOR)(CO)(SbPh_3)_3]$. [IUPAC name, where R = CH_3, (TBPY-5-23)-carbonyl(methoxycarbonyl)tris(triphenylstibine)-rhodium(I)].

The infrared spectrum (Fig. 101) of the compound (XXXIII) shows a strong band at 1982 cm^{-1} taken to represent the carbonyl stretch. A medium intensity band at 1601 cm^{-1} is assigned to the ethoxycarbonyl band.

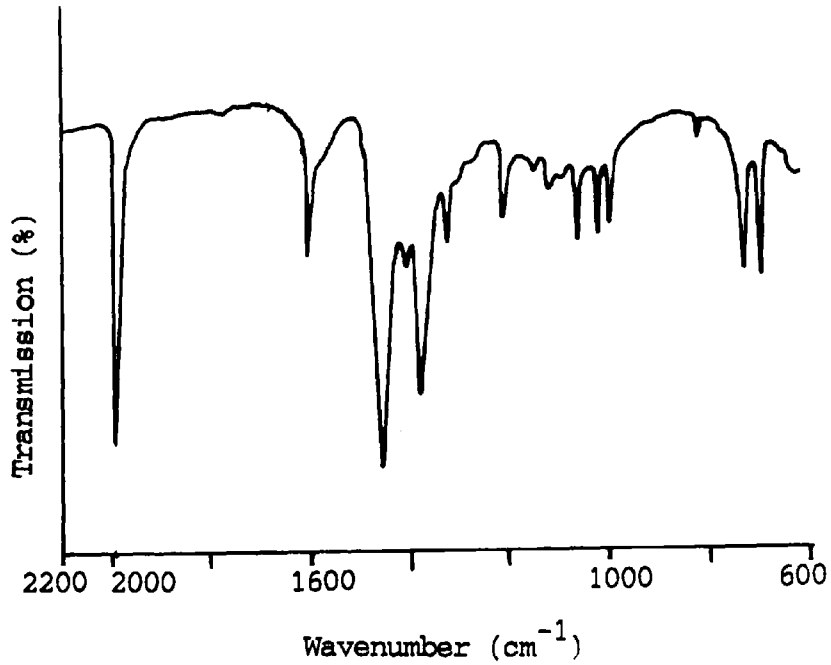


Fig. 101 : Infrared spectrum of $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$ (Nujol mull).

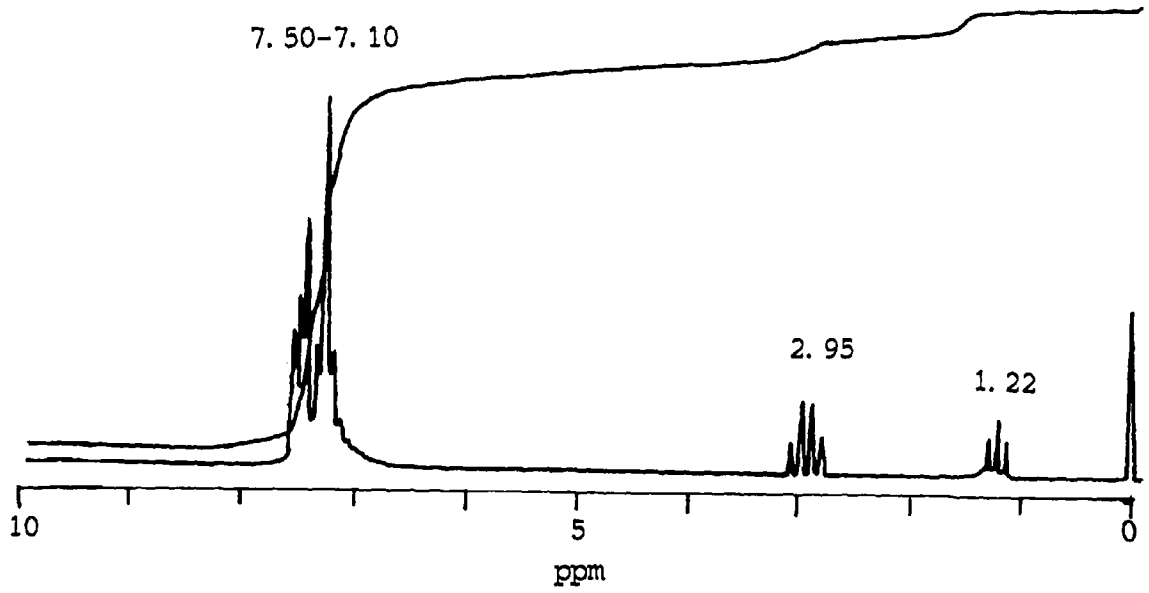


Fig. 102 : ^{1}H-NMR spectrum of $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$ (in $CDCl_3$, TMS).

The carbonyl and ethoxycarbonyl bands are consistent with a similar type of iridium compound[53] $[Ir(COOC_2H_5)(CO)(SbPh_3)_3]$.

The ^{1}H-NMR spectrum (Fig. 102) of the compound shows a triplet at 1. 22 ppm (3H, J = 7. 0 Hz) and a quartet at 2. 95 ppm (2H, J = 7. 0 Hz), which are assigned to the methyl and methylene protons of ethoxycarbonyl group. A multiplet at (7. 10-7. 50) ppm (45H) is attributed to the aromatic protons of the coordinated $SbPh_3$. By analogy with the compound (XXXII), it is suggested that the compound (XXXIII) is $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$ and the structure is as in Fig. 100 where R = C_2H_5.

A summary of the spectral data of the rhodium-stibine compounds follows on the next page.

Table 33 : Infrared Data of Rhodium-Stibine Compounds.

Compound	ν(CO) cm^{-1}	ν(CO) (alkoxy-carbonyl) cm^{-1}	$\nu(BF_4^-)$ cm^{-1}
(XXXI) $[Rh(CO)_2(SbPh_3)_3]^+[BF_4]^-.CH_2Cl_2$*	2006 (s)		1061 (b)[a]
(XXXII) $[Rh(COOCH_3)(CO)(SbPh_3)_3]$	1979 (s)	1603 (m)[a]	
(XXXIII) $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$*	1982 (s)	1601 (m)	

[Where s = Strong, m = Medium, b = broad, a = KBr and other spectra in Nujol mull and * indicates novel compound].

Table 34 : ^{1}H-NMR Data of Rhodium-Stibine Compounds.

Compound	^{1}H-NMR (ppm)
(XXXII) $[Rh(COOCH_3)(CO)(SbPh_3)_3]$	2.41 (s, 3H) (7.10-7.50) (m, 45H)
(XXXIII) $[Rh(COOC_2H_5)(CO)(SbPh_3)_3]$	1.22 (t, 3H) 2.95 (q, 2H) (7.10-7.50) (m, 45H)

[Where s = Singlet, M = Multiplet, t = Triplet, q = Quartet. All the spectra in $CDCl_3$ and TMS as internal standard].

CHAPTER-5

CATALYSIS REACTIONS.

5.1 CARBONYLATION REACTIONS IN THE PRESENCE OF NUCLEOPHILES.

(A) INTRODUCTION

Alcohol and carbon monoxide are sources for the synthesis of many oxygen containing organic compounds[4] e.g. methanol on oxidative carbonylation gives dimethylcarbonate and dimethyloxalate, on oxidative dehydrogenation gives formaldehyde. Dimethyloxalate produces ethylene glycol on hydrogenation. Ethylene glycol is widely used as an anti-freeze. Industrially, the conversion of methanol to dimethylcarbonate or dimethyloxalate and then to ethylene glycol are all economically expensive, because they require high temperature and pressures.

Ethanol may give diethylcarbonate and diethyloxalate by a metal catalysed reaction, e.g. $PdCl_2$ promots the catalytic reaction[50] of ethanol with CO in the presence of the base, Na_2CO_3 as seen in Eq. 54, where the reaction has been postulated to proceed through a palladium ethoxycarbonyl intermediate.

$$2C_2H_5OH + CO + PdCl_2 + 2Na_2CO_3 \longrightarrow (C_2H_5)_2CO + Pd + 2NaCl + 2NaHCO_3 \qquad \text{[Eq. 54]}$$

Dialkyloxalates can also be prepared in good yield by oxidative carbonylation[156] of alcohols in the presence of a dehydrating agent using a palladium redox system according to Eq. 55 and Eq. 56.

$$2CO + 2ROH + 1/2\ (O_2) \xrightarrow{[Pd]} ROOCCOOR + H_2O \qquad \text{[Eq. 55]}$$

$$H_2O + (RO)_3CH \longrightarrow 2ROH + HCOOR \qquad \text{[Eq. 56]}$$

The dehydrating agent is necessary, otherwise large amounts of carbon dioxide are produced and no oxalates are found.

Uchiumi and Yamashita[59] reported that $PdCl_2$-$CuCl_2$ catalytically convert methanol and CO to dimethylcarbonate and dimethyloxalate in the presence of an organic base (e.g. triethylamine), where no dehydrating agent is required [detailed description in Sec. 1.4{I(iii)}].

Cupric dimethoxide reacts with CO in pyridine solution at 35-70°C to produce dimethylcarbonate[157] in yield as high as 84% as seen in Eq. 57.

$$Cu(OCH_3)_2 + CO \longrightarrow O{=}C(OCH_3)_2 \qquad \text{[Eq. 57]}$$

Alkoxycarbonyl compounds may decompose to dialkylcarbonate, dialkyloxalate, and formaldehyde oligomers, e.g. $[Pd(COOCH_3)_2(dppe)]$ decomposes[6] to methanol, a formaldehyde oligomer, CO_2 and dimethylcarbonate at 12 atmospheres of CO and a temperature of 160°C. The organic products were identified by GC/MS. A more detailed description of the formation of dialkylcarbonate and dialkyloxalate is given in Sec. [1.3(IV), 3.1(IV) and 4.1(VII)].

In the present work, methoxycarbonyl compounds have been synthesised from cationic complexes. If the same reactions could be carried out under CO pressure, dimethylcarbonate, dimethyloxalate or formaldehyde oligomers may be formed, catalytically or stoichiometrically. Some preliminary work is reported here.

(B) EXPERIMENTAL

(i) Reactions of Dimethyloxalate and Dimethylcarbonate with Sodium Methoxide.

Dimethyloxalate (0.70 g, 5.92 mmol) solution in dry methanol (15 cm^3) was added to sodium methoxide solution (ca. 11.86 mmol) in dry methanol 10 cm^3 under nitrogen and no precipitate formed. However, when the mixture came in contact with air a white precipitate started to appear and after ca. 4 hours a white precipitate (0.60 g) was isolated. The white solid was insoluble in chloroform, dichloromethane and acetone. The infrared spectrum of the precipitate showed two broad bands at 1637 and 1325 cm^{-1} (KBr disc). The ^{13}C-NMR of the white precipitate showed a singlet at 178.00 ppm and the ^{1}H-NMR did not show any signal in D_2O.

Similarly, when dimethylcarbonate solution was added to sodium methoxide solution under nitrogen no precipitate was formed, but when it came in contact with air it gave a white precipitate. The white precipitate showed broad bands at 1630, 1470, 1377 cm^{-1} (KBr disc) and the ^{13}C-NMR it showed a singlet at 171.00 ppm in D_2O.

For example, when dimethylcarbonate (0.21 g, 0.23 mmol) and sodium methoxide solution in methanol (ca. 1.1 mmol in 10 cm^3) were left for ca. 12 hours in air, then gas chromatography of the filtrate did not show the presence of dimethylcarbonate. This concentration range was approximately the concentration expected to form as a product from the present reactions using the metal complexes.

The operation conditions for gas chromatography of dimethylcarbonate, dimethyloxalate, trioxane and benzene were as follows :

Column = (10% SP2330, packed column), 10% biscyanopropylphenylpoly-siloxane is coated on supelcoport.

Column length = 6 ft x (1/8) inch

N_2 flow = 100 KN/m^2

H_2 flow = 150 KN/m^2

Air flow = 150 KN/m^2

Oven Temperature :

Initial = 80^oC (for 4 minutes)

Rate 7.5^oC/minute

Final = 200^oC (for 4 minutes)

Detection Threshold = 5.00

Minimum Peak Width = 5.00

Area Rejected = 100

Retention time of compounds are follows and the chromatogram in Appendix-4.

Benzene = 2.60 minutes

Dimethylcarbonate = 3.40 minutes

Hexadecane (internal standard) = 11.30 minutes

Dimethyloxalate = 11.90 minutes

Under this condition, detection limit = signal to noise ratio (3:1).

Detection limit of dimethylcarbonate = 4 $mmol/dm^3$.

Detection limit of dimethyloxalate = 2 $mmol/dm^3$.

Detection limit of trioxane = 7 $mmol/dm^3$.

Detection limit of benzene = 2 $mmol/dm^3$.

(ii) Reaction of CH_3ONa with CO at 10 atmospheres pressure in Methanol at 65-70°C.

Freshly prepared sodium methoxide (ca. 1.10 mmol) in 10 cm^3 of methanol was stirred under 10 atmospheres of CO at 65-70°C for 5 hours. Then the solvent was evaporated on a vacuum line. The solid product showed bands at 1600 (b), 1462 (b) and 1362 cm^{-1} (b) in (KBr disc).

(iii) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with the Nucleophile CH_3O^- under CO.

A mixture of compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.20 g, 0.21 mmol) and sodium methoxide solution (ca. 1.10 mmol in 10 cm^3 of methanol) was stirred under carbon monoxide (10 atmospheres) for 5 hours at ambient temperature as described in Sec. 2(III). The filtrate and the solid product both were collected. The infrared and NMR of the solid product indicated the compound (IV), $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$. The filtrate was checked by gas chromatography for dimethylcarbonate and dimethyloxalate, but did not indicate the presence of either. When the same reaction was carried out for more than five hours, a mixture of compound (IV) and $[Ru(CO)_3(PPh_3)_2]$ was formed[75,88], as seen from the infrared spectrum. When this reaction was carried out for more than 10 hours, the solution immediately after opening the reaction apparatus showed the presence of a trace amount of dimethylcarbonate. After the time taken for filtration and the addition of internal standard it could not be detected. The solid was identified as $[Ru(CO)_3(PPh_3)_2]$. If the same reaction was heated to a temperature of 65-70°C the reduction

product $[Ru(CO)_3(PPh_3)_2]$ was formed within fifteen minutes.

(iv) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 \cdot CH_2Cl_2$ with CO in the Presence of an Organic Base Triethylamine in Methanol at ambient Temperature.

A mixture of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 \cdot CH_2Cl_2$ (0.20 g, 0.21 mmol) and triethylamine (0.20 g, 1.97 mmol) in methanol (10 cm^3) was stirred under 10 atmospheres of CO at ambient temperature for 5 hours. A white precipitate was formed, which showed similar spectral data as compound (IV), $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$. Gas chromatography did not show any organic products in the filtrate.

(v) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 \cdot CH_2Cl_2$ with CO in the Presence of an Organic Base Triethylamine in Methanol at 65-70°C.

A mixture of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 \cdot CH_2Cl_2$ (0.20 g, 0.21 mmol), triethylamine (0.20 g, 1.97 mmol) and 10 cm^3 of methanol were charged in the pressure apparatus at 10 atmospheres of CO as described in Sec. 2(III). Then the apparatus was heated to 65-70°C for 4 hours by immersing in a paraffin oil bath. The filtrate and a trace of residue were collected. The residue showed ν(CO) at 1895 cm^{-1} (KBr disc). The filtrate was analysed by gas chromatography and showed the presence of 10 mmol/dm^3 of dimethylcarbonate and trace amount of unidentified compounds.

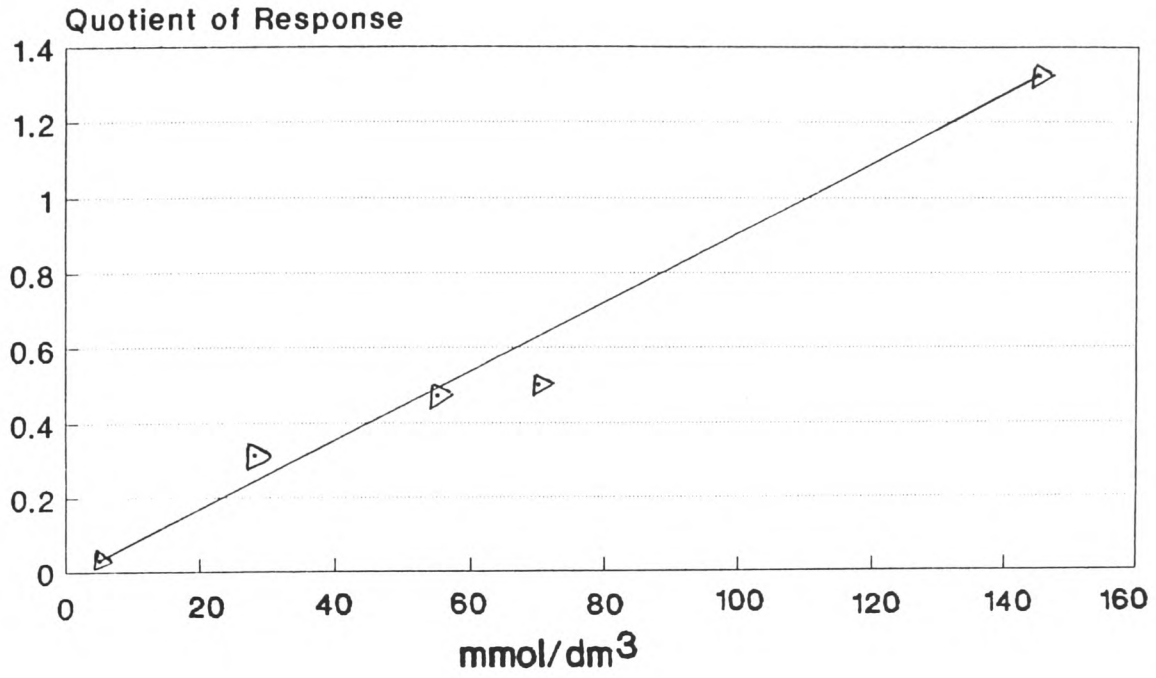


Fig. 103 : Calibration curve for determination of dimethylcarbonate. Data and calculations are in the Appendix-5.

(vi) Reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ solution in Dichloromethane with CH_3ONa solution in Methanol in the Presence of CO under Reflux.

A solution of $[RuCl_2(CO)_2(PPh_3)_2]$ (0.20 g, 0.26 mmol) in 15 cm^3 of dichloromethane was added to sodium methoxide solution (ca. 1.10 mmol in 5 cm^3 of methanol). The mixture was refluxed for 1 hour whilst passing CO through the solution. The yellowish solution changed to greenish-brown when the reaction apparatus was opened to collect the homogeneous solution. This colour became deeper with time as the reaction was exposed to air. The GC/MS of this solution showed benzene, a trace amount of biphenyl and PPh_3.

(vii) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 . CH_2Cl_2$ with CH_3ONa solution in Methanol in the Presence of CO in Dichloromethane.

A solution of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 . CH_2Cl_2$ (0.20 g, 0.21 mmol) in 8 cm^3 of dichloromethane and sodium methoxide (ca. 1.10 mmol) solution in 2 cm^3 of methanol were stirred under carbon monoxide (10 atmospheres) for 10 hours at room temperature. When the apparatus was opened the yellow solution turned greenish-yellow. Gas chromatographic analysis indicated the presence of benzene, approximately 10 $mmol/dm^3$.

(viii) ^{1}H-NMR Spectrum of the Decomposed solution of $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$.

The ^{1}H-NMR of the compound $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ in $CDCl_3$ solution initially did not show any signal at 5.25-5.15 ppm. When this solution (sealed under nitrogen) was left for a few days in an NMR tube, the signal for the methyl protons of the methoxycarbonyl group at 2.80 ppm disappeared and a new signal appeared at 5.20 ppm (d).

(ix) Reaction of $[Rh(CO)(PPh_3)_2]^+[BF_4]^- . 1/2(CH_2Cl_2)$ with CH_3ONa.

The cationic complex (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4^-] . 1/2(CH_2Cl_2)$ (0.20 g, 0.25 mmol) was reacted with sodium methoxide (ca. 1.10 mmol) in 10 cm^3 of methanol in the presence of CO. The spectral data of the solid product indicated $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$. The same reaction was carried out with a methanol solution of sodium methoxide, in dichloromethane (10 cm^3) under CO pressure (10 atmospheres) for 4 hours

at ambient temperature. When the homogeneous solution came in contact with air the colour of the solution changed from yellowish to greenish-yellow. This solution only showed the presence of benzene as analysed by gas chromatography. When this reaction was carried out in the presence of triethylamine in methanol, no alkoxycarbonyl compound was isolated. The filtrate did not indicate any dimethylcarbonate, dimethyloxalate, formaldehyde oligomer or benzene from gas chromatography.

(C) DISCUSSION.

(i) Reactions of Dimethyloxalate and Dimethylcarbonate with Sodium Methoxide.

When dimethyloxalate solution in dry methanol is added to sodium methoxide solution in dry methanol under nitrogen no precipitate is formed. However, when the mixture comes in contact with air a white precipitate is formed. The precipitate may be sodium oxalate, $(COONa)_2$ as seen from infrared spectroscopy. The infrared spectrum of the precipitate shows $\nu_{asy}(OCO)$ at 1637 cm^{-1} and $\nu_{sy}(OCO)$ at 1325 cm^{-1} (KBr disc). These bands are not exactly consistent with the infrared spectrum of authentic $(COONa)_2$, with $\nu_{asy}(OCO)$ at 1630 cm^{-1} and $\nu_{sy}(OCO)$ at 1319 cm^{-1} (KBr disc). The literature value[158] of $(COONa)_2$ is $\nu_{asy}(OCO)$ at 1630 cm^{-1} and $\nu_{sy}(OCO)$ at 1335, 1316 cm^{-1}. All the bands of the white precipitate are broad. The broad band at 1325 cm^{-1} may be the the overlapped result of the two expected bands at 1335 and 1316 cm^{-1}. Anyway, they are roughly consistent with the authentic $(COONa)_2$. The infrared spectrum of dimethyloxalate shows $\nu_{asy}(OCO)$ at 1739 cm^{-1} and $\nu_{sy}(OCO)$ at 1440 cm^{-1} (KBr disc).

Sodium methoxide shows bands at 1630, 1446, 1381, 1100 cm^{-1} (KBr disc). According to the literature[111] metal alkoxides [M(OR) where R = alkyl group] generally exhibit a ν(C—O) stretch at about 1000 cm^{-1} and a ν(M—O) stretch at 650 cm^{-1}. The band at 1630 cm^{-1} in sodium methoxide may be due to moisture, because it is moisture sensitive and water[111] shows a band at 1627 cm^{-1}. When CH_3O^- in methanol under CO pressure is heated at 65-70^oC [Sec. 5.1B(ii)] after evaporation of the solvent,

some white solid remains and shows broad bands at 1600, 1462 and 1362 cm^{-1} (KBr disc).

Therefore, from infrared no decision as to the nature of the white precipitate could be achieved, because all the bands are broad. More information could be found from NMR spectroscopy. The white precipitate obtained form the reaction of dimethyloxalate and CH_3ONa, does not show any signal in the ^{1}H-NMR but in the ^{13}C-NMR of the white precipitate shows a singlet at 178.00 ppm, which is consistent with the authentic $(COONa)_2$, at 178.00 ppm. The authentic dimethyloxalate shows two singlets at 58.50 and 162.50 ppm for the methyl and carboxylate carbons respectively.

Similarly when dimethylcarbonate solution is added to sodium methoxide solution under nitrogen no precipitate formed. When it comes in contact with air it gives a white precipitate. The white precipitate shows bands at 1630, 1470, 1377 cm^{-1}. The bands at 1630 and 1377 cm^{-1} also exist in the sodium methoxide solution. The band at 1630 cm^{-1} may be due to moisture. The band at 1470 cm^{-1} is roughly consistent with Na_2CO_3. The literature[111] shows that the carbonate ion shows a band at 1429-1492 cm^{-1}. An authentic sample of Na_2CO_3 shows a broad band at 1459 cm^{-1}. The ^{13}C-NMR of the white precipitate shows a singlet at 171.00 ppm and the authentic Na_2CO_3 shows a singlet at 172.00 ppm. The ^{13}C-NMR of the white precipitate and the authentic Na_2CO_3 are roughly consistent. The authentic dimethylcarbonate shows two singlets at 59.50 and 161.50 ppm for the methyl and carbonyl carbons respectively.

Therefore, the reaction of sodium methoxide with dimethylcarbonate or dimethyloxalate may produce Na_2CO_3 or $(COONa)_2$. When the mixture of

dimethylcarbonate solution [approximately within the same concentration range as might be expected as a product in the reactions Sec. 5.1B(iii)] and sodium methoxide solution in methanol is left, ca. 12 hours in air, then the mixture does not show the presence of any dimethylcarbonate. The precipitation rate increased if a trace of water is added to this solution.

For the reaction of dimethylcarbonate and sodium methoxide in air, the white precipitate formed is suspected as Na_2CO_3. An exact decision is difficult, because all the bands in the region 1630-1362 cm^{-1} are broad. But the ^{13}C-NMR are roughly consistent. The main fact is that in the presence of sodium methoxide, dimethylcarbonate or dimethyloxalate disappear, if the solution comes in contact with air.

(ii) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 . CH_2Cl_2$ with the Nucleophile CH_3O^- under CO.

The reaction of a mixture of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 . CH_2Cl_2$ with sodium methoxide solution under carbon monoxide at ambient temperature has been described in Sec. 5.1B(iii). The infrared and NMR spectra of the solid product indicate $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$, compound (IV). The gas chromatography analysis of the filtrate does not indicate any organic products, e.g. dimethylcarbonate and dimethyloxalate. When the same reaction was carried out for more than five hours, a mixture of compound (IV) and $[Ru(CO)_3(PPh_3)_2]$ was formed[75,88], as seen from the infrared spectrum. When this reaction was carried out for more than 10 hours, then only the reduction product was found and the filtrate

contained a trace amount of dimethylcarbonate. If the same reaction was heated to a temperature of 65-70°C the reduction product $[Ru(CO)_3(PPh_3)_2]$ was formed within fifteen minutes.

Cenini et al. have reported[88] that the ruthenium compound, $[RuCl_2(PPh_3)_3]$ in the presence of a sodium alkoxide (e.g. sodium ethoxide) and carbon monoxide gives the reduction product, $[Ru(CO)_3(PPh_3)_2]$. There is no suggested mechanism for this reaction. In the present work [Sec. 3.2(xxii)], the reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with sodium methoxide in the presence of carbon monoxide under reflux forms the reduction product $[Ru(CO)_3(PPh_3)_2]$. However, the reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with sodium methoxide under carbon monoxide pressure (10 atmospheres) at ambient temperature [Sec. 3.2(x)] gives the alkoxycarbonyl compound, $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$.

In the reaction Sec. 5.1B(iii), where the reaction was carried out for more than 10 hours, the solution immediately after opening the reaction apparatus showed the presence of a trace amount of dimethylcarbonate. After the time taken for filtration and the addition of internal standard it could not be detected. The solid product was characterised as $[Ru(CO)_3(PPh_3)_2]$. This may be due to the fact that the dimethylcarbonate formed gradually converted to the white precipitate as the authentic dimethylcarbonate showed with sodium methoxide in Sec. 5.1B(i). The same thing happened when the reduction product was formed by heating. After filtration and addition of internal standard no dimethylcarbonate could be detected. After evaporation of the solvent a solid product was formed which showed broad bands at 1600, 1468 and 1361 cm^{-1}. The band at 1468 cm^{-1} was roughly consistent with the band at

1470 cm^{-1}. This band was shown by the white precipitate formed from the reaction of dimethylcarbonate and sodium methoxide [Sec. 5.1B(i)].

Therefore, dimethylcarbonate or dimethyloxalate identification is difficult in these experiments. Dimethylcarbonate may be formed but these experiments suggest that it is converted into another product under the conditions described.

(iii) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CO in the Presence of an Organic Base Triethylamine in Methanol at ambient Temperature.

The reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CO in the presence of an organic base triethylamine in methanol at ambient temperature has been described in Sec. 5.1B(iv). A white precipitate of compound (IV), $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ was formed and no evidence was found to suggest the presence of dimethylcarbonate or dimethyloxalate in the filtrate.

(iv) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CO in the Presence of an Organic Base Triethylamine in Methanol at 65-70°C.

The reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CO in the presence of an organic base triethylamine in methanol has been described in Sec. 5.1B(v). The infrared spectra of the residue shows v(CO) at 1895 cm^{-1} (KBr disc) which suggests[75,88] the presence of $[Ru(CO)_3(PPh_3)_2]$. The filtrate shows 10 $mmol/dm^3$ of dimethylcarbonate and trace amounts of unidentified compounds as seen in Fig. 104. This calculation has been

done with respect to hexadecane as internal standard from the calibration curve in Fig. 103. Triethylamine may not absorb moisture (H_2O) as sodium methoxide does and this may prevent the conversion of dimethylcarbonate to the white precipitate suspected to be sodium carbonate. Reaction of sodium methoxide with moisture in the air may be the initial step in the conversion of dimethylcarbonate to white precipitate.

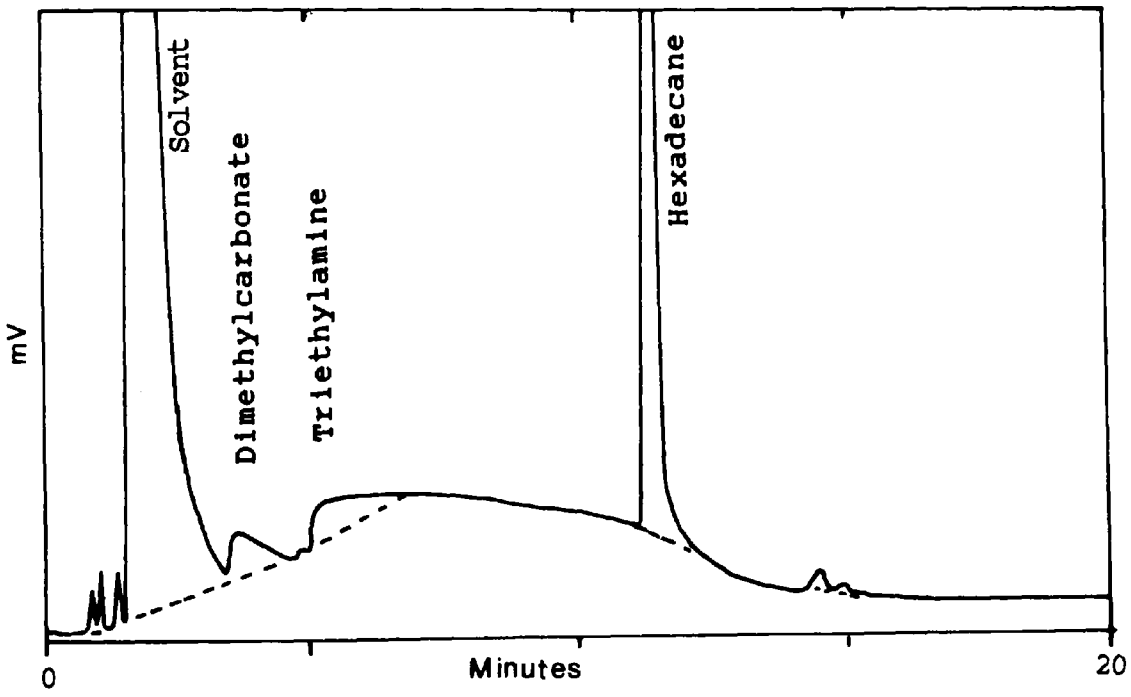


Fig. 104 : Chromatogram of dimethylcarbonate formed by the reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2 . CH_2Cl_2$ with CO in the presence of an organic base triethylamine in methanol.

(v) Reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ solution in Dichloromethane with CH_3ONa solution in Methanol in the Presence of CO under Reflux.

The reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with sodium methoxide solution in dichloromethane has been described in Sec. 5.1B(vi). Gas chromatography of the resultant solution does not show dimethylcarbonate or dimethyloxalate, but some benzene has been formed. The yellow solution changes to greenish-brown when the solution comes in contact with air. The colour becomes deeper with time as the reaction is exposed to air and may indicate oxidation of Ru(II) to Ru(III). The colour of Ru(III) species is often green[2]. Another possibility is that a Ru-O=PPh_3 complex is formed[88]. The GC/MS of this solution shows benzene, a trace amount of biphenyl and PPh_3 (Fig. 105, 106, 107 and 108).

Buss and Warren[159] reported that NaOH converted $[RPPh_3]^+X^-$ to $OP(R)Ph_2$ and benzene. They also reported that the base $(CH_3)_3CO^-K^+$ breaks[159] the P—(CH_2R) bond of $OP(CH_2R)Ph_2$, where R = alkyl group. In the present work, dissociated PPh_3 from $[RuCl_2(CO)_2(PPh_3)_2]$ in the homogeneous solution may be oxidised to $OPPh_3$ and then react with the base CH_3O^-, forming benzene by the same mechanism as in the literature[159]. The base NaOH would be expected to form when sodium methoxide solution was exposed to absorbed moisture from air as seen in Eq. 58.

$$CH_3ONa + H_2O \longrightarrow NaOH + CH_3OH \qquad \text{[Eq. 58]}$$

The PPh_3 present in Fig. 105 may be dissociated from the ruthenium compound in the solution. This PPh_3 may be oxidised to $OPPh_3$ which is

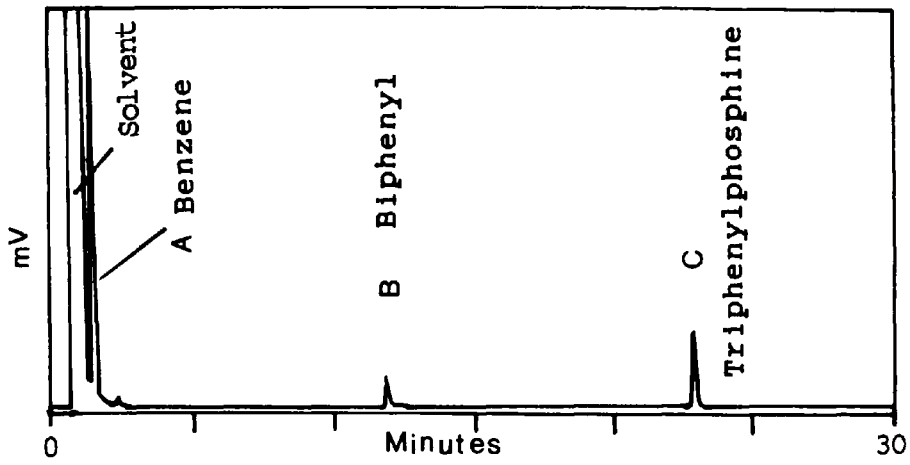


Fig. 105 : GC/MS chromatogram of compounds A (benzene), B (biphenyl) and C (triphenylphosphine) formed by the reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with CO in the presence of CH_3ONa in dichloromethane.

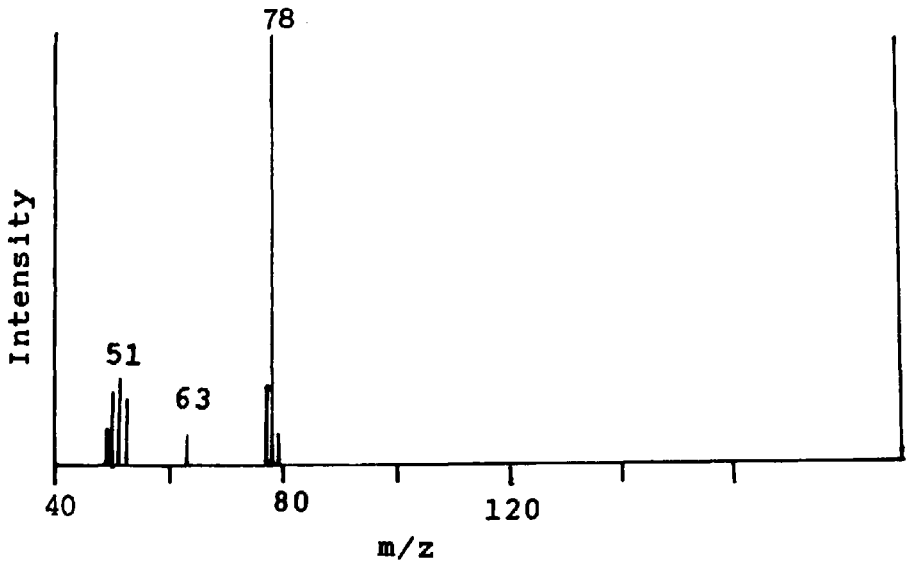


Fig. 106 : Mass spectrum of compound A of Fig. 105 which shows a molecular ion peak of 78 (benzene).

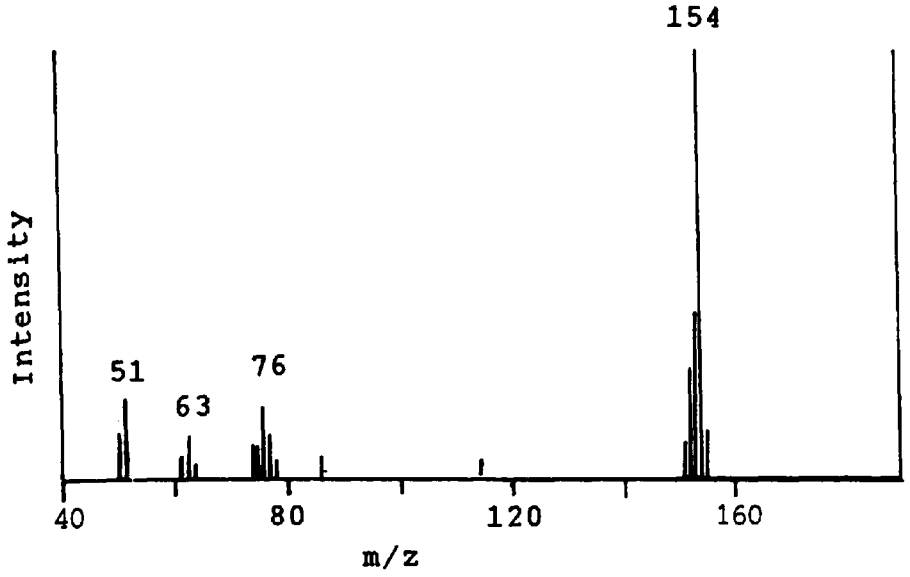


Fig. 107 : Mass spectrum of compound B of Fig. 105 which shows a molecular ion peak of 154 (biphenyl).

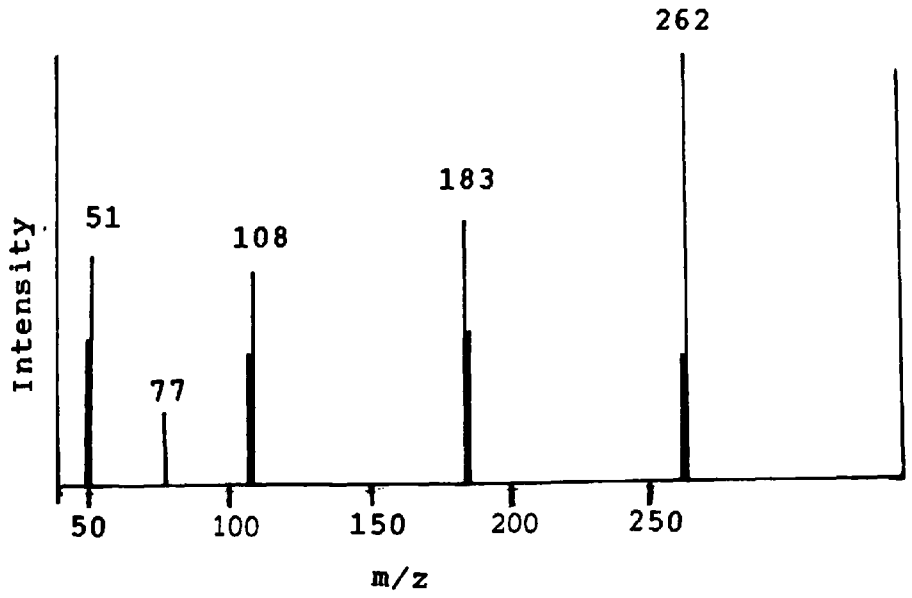


Fig. 108 : Mass spectrum of compound C of Fig. 105 which shows a molecular ion peak of 262 (triphenylphosphine).

converted to benzene by CH_3O^- and moisture. When a $OPPh_3$ solution in dichloromethane was added to sodium methoxide solution in air, the resultant solution showed the presence of benzene as seen by gas chromatography. Similarly, when PPh_3 solution in dichloromethane was added to sodium methoxide solution, immediately the mixture showed no chromatogram for benzene, but after 2/3 days a trace amount of benzene was identified.

(vi) Reaction of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ with CH_3ONa solution in Methanol in the Presence of CO in Dichloromethane.

When $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ was reacted with sodium methoxide solution in the presence of carbon monoxide in dichloromethane, the homogeneous solution did not contain any dimethylcarbonate or dimethyloxalate. Instead a trace amount of benzene was formed in the solution as seen from gas chromatography as in Fig. 105. As the reaction product was exposed to air, the concentration of benzene increased. As time progressed, it is possible more PPh_3 dissociated from the ruthenium precursor and was converted to benzene by the same mechanism as described in Sec. 5.1C(v).

(vii) ^{1}H-NMR Spectrum of the Decomposed solution of $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$.

The ^{1}H-NMR of the compound $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ in $CDCl_3$ solution initially did not show any signal at 5.25-5.15 ppm. When this solution (sealed under nitrogen) was left for a few days in the NMR tube, the

signal for the methoxy group at 2.80 ppm disappeared and a signal at 5.20 ppm (d) appeared (Fig. 109). The signal may be a formaldehyde oligomer. Trioxane has a reported chemical shift in the same region[21], i.e. 5.15 ppm. An authentic sample of trioxane showed a doublet at 5.17 ppm. Therefore, the signal at 5.20 ppm may be a trace amount of trioxane but gas chromatography of the same solution did not show any trioxane, the concentration may have been below its detection limit.

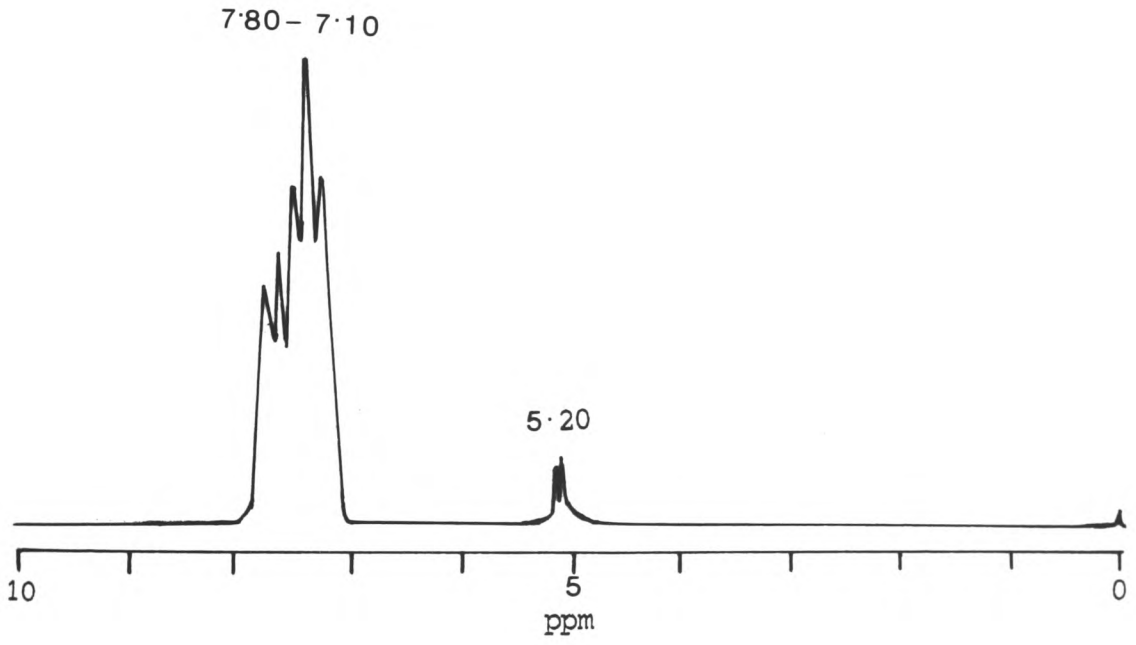


Fig. 109 : ^{1}H-NMR spectrum of decomposed $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2]$ (in $CDCl_3$, TMS).

(viii) Reaction of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ with CH_3ONa.

The cationic complex (VI), $[Rh(CO)(PPh_3)_2]^+[BF_4^-].1/2(CH_2Cl_2)$ reacted with sodium methoxide in the presence of CO as described in Sec. 5.1B(ix). The infrared spectrum of the solid product indicated the presence of $[Rh(COOCH_3)(CO)_2(PPh_3)_2]$. This compound slowly decomposed even in the solid state in air [as seen from the infrared spectrum, described in Sec. 4.3A(iii) to give $OPPh_3$ and an unidentified carbonyl compound]. When this reaction of complex (VI) was carried out with a methanol solution of sodium methoxide, in dichloromethane under CO pressure for 4 hours, it was noticed that when the homogeneous solution came in contact with air the colour of the solution changed from yellowish to greenish-yellow. This solution only showed the presence of benzene as analysed by gas chromatography as in Fig. 105. When this reaction was carried out in the presence of triethylamine, no alkoxycarbonyl compound was isolated. The filtrate did not indicate any dimethylcarbonate, dimethyloxalate, formaldehyde oligomer or benzene.

5.2 HYDROGENATION REACTIONS.

(A) INTRODUCTION

Siedle et al. reported that the cationic complex $[Rh(CO)(PPh_3)_2]_4SiW_{12}O_{40}$ is an effective heterogeneous catalyst for hydrogenation and hydroformylation of alkenes[131, 132]. Also, homogeneous non-cationic rhodium catalysts are well known for the hydrogenation of alkenes e. g. $[RhCl(PPh_3)_3]$. In the literature it is well documented[160] that $[RhCl(PPh_3)_3]$ dissociates in solution into PPh_3 and the 14-electron species, $[RhCl(PPh_3)_2]$ (which may be solvated) to generate a vacant site for the hydrogenation reaction as seen in Fig. 110.

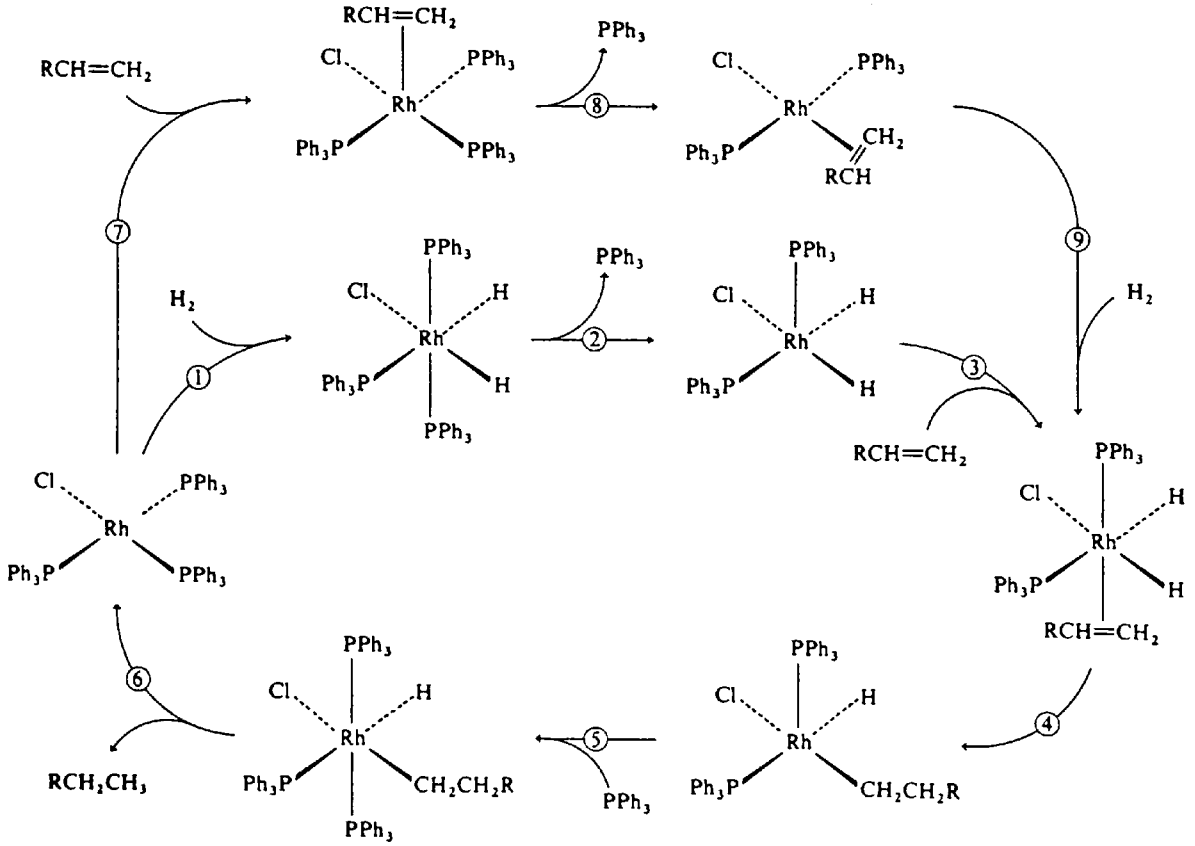


Fig. 110 : Mechanism for the hydrogenation of alkenes[160] by $[RhCl(PPh_3)_3]$.

(B) EXPERIMENTAL

(i) Hydrogenation of Oct-1-ene, $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

A solution of $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.06 g, 0.08 mmol) and oct-1-ene (0.60 g, 5.35 mmol) in 10 cm^3 of benzene was stirred under hydrogen at atmospheric pressure at ambient temperature, for 24 hours as described in Fig. 10, Sec. 2. The amount of hydrogen absorbed after conversion to STP was ca. 115 cm^3. After the reaction, the mixture contained a trace amount of solid, whose infrared spectrum gave ν(CO) at 1992 and 1979 cm^{-1} and $\nu(BF_4^-)$ at 1065 cm^{-1} (KBr disc). The filtrate was analysed by gas chromatography, using a 15% Apiezon L column. The concentration of octane was calculated with respect to nonane as internal standard and was found to be 510 mmol/dm^3.

(ii) Hydrogenation of Oct-1-ene, $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

A solution of compound (XVI) $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.08 g, 0.08 mmol) and oct-1-ene (0.60 g, 5.35 mmol) in 10 cm^3 of benzene was stirred under hydrogen at atmospheric pressure for 24 hours at ambient temperature. The amount of hydrogen absorbed after conversion to STP was ca. 77 cm^3. This reaction also formed a trace amount of solid after the reaction. The solid shows the same pattern of two carbonyl bands at 1989 and 1979 cm^{-1}. The solution was checked by gas chromatography and the concentration of octane was 340 mmol/dm^3.

(iii) Hydrogenation of Oct-1-ene, $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ as Catalyst.

A solution of compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ (0.07 g, 0.08 mmol) and oct-1-ene (0.6 g, 5.35 mmol) in 10 cm^3 of benzene was stirred under hydrogen at atmospheric pressure for 24 hours at ambient temperature. The amount of hydrogen absorbed after conversion to STP was ca. 18 cm^3. The homogeneous solution was checked by gas chromatography and the concentration of octane was 80 $mmol/dm^3$.

The volume of hydrogen absorbed was an approximate measurement, because the fluctuation of water level within the apparatus made exact measurement of hydrogen difficult. The gas chromatogram operation conditions for checking octane for all hydrogenation reactions were the same and they were as;

Column = (15% Apiezon L, packed column), 15% Methylchlorosilane is coated on acid wash Chromosorb W .

Column length = 6 ft x (1/8) inch

N_2 flow = 65 KN/m^2

H_2 flow = 150 KN/m^2

Air flow = 110 KN/m^2

Oven Temperatures :

Initial = 80^oC

Rate 1^oC/minute

Final = 130^oC

Detection Threshold = 20

Minimum Peak Width = 20

Retention time of the components are

Oct-1-ene = 10.8 minutes

Octane = 12.1 minutes

Nonane = 20.5 minutes (internal standard)

Area Rejected = 500

Detection limit of the octane under this condition was 3 mmol/dm^3.

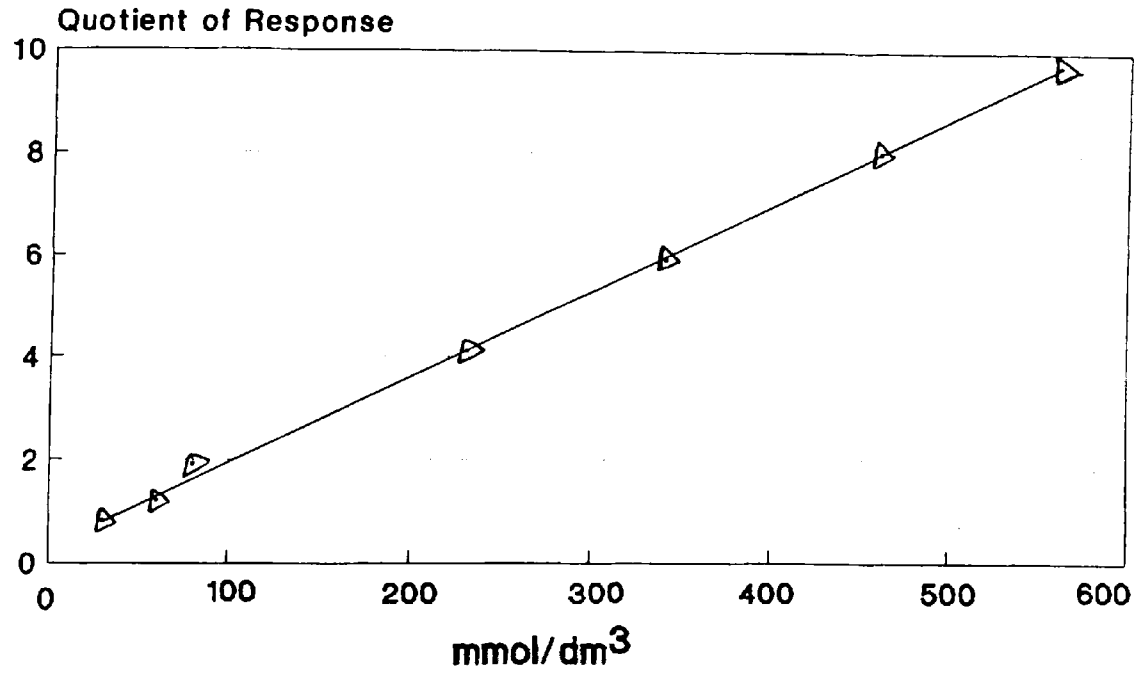


Fig. 111 : Calibration curve for determination of octane. Data and calculations are in Appendix-6.

(iv) Hydrogenation of Oct-1-ene, $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

The cationic complex, $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ (0.10 g, 0.12 mmol) and oct-1-ene (0.20 g, 1.78 mmol) in 10 cm^3 of benzene were stirred under hydrogen at atmospheric pressure at ambient temperature for 24 hours. The amount of hydrogen absorbed after conversion to STP was 22 cm^3. The solution was checked by gas chromatography and the concentration of octane was 95 $mmol/dm^3$.

(v) An Attempt to Hydrogenate of Oct-1-ene by the Compound (I), $[RuCO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ in Benzene.

A suspension of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.11g, 0.12 mmol) and oct-1-ene (0.20g, 1.78 mmol) in 10 cm3 of benzene were stirred for 24 hours under atmospheric hydrogen at ambient temperature. The infrared of the solid indicated decomposition of the compound. The filtrate was checked by gas chromatography, but no octane was found.

(vi) An Attempt to Hydrogenate of Oct-1-ene by compound (I), $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ in Dichloromethane.

The homogeneous solution of $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ (0.11 g, 0.12 mmol) and oct-1-ene (0.20 g, 0.1.78 mmol) in dichloromethane was stirred atmospheric hydrogen for 24 hours at ambient temperature. The homogeneous solution in gas chromatography did not indicate any octane.

(C) DISCUSSION.

(i) Hydrogenation of Oct-1-ene, $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

The catalytic hydrogenation of oct-1-ene by the cationic complex, $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ at atmospheric pressure of hydrogen at ambient temperature has been described in Sec. 5.2B(i). The reaction product shows a trace amount of solid, whose infrared spectrum shows two carbonyl bands at 1992 and 1979 cm^{-1} and $\nu(BF_4^-)$ at 1065 cm^{-1} (KBr disc). Here, it is assumed that the band at 1992 cm^{-1} is from the cation $[Rh(CO)(PPh_3)_2]^+[BF_4]^-$ and the band at 1979 cm^{-1} may be from a species formed on decomposition of $[Rh(CO)(PPh_3)_2]^+$. The analysis of the filtrate by gas chromatography shows octane of concentration 510 $mmol/dm^3$, which is calculated from the calibration curve Fig. 111. The chromatogram of the product is shown in Fig. 112. The actual hydrogen pressure, temperature and volume absorbed at STP are in the Appendix-7, together with other hydrogenation reactions using rhodium catalysts.

(ii) Hydrogenation of Oct-1-ene, $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

The catalytic hydrogenation of oct-1-ene to octane, by using the compound (XVI) $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ and oct-1-ene in benzene, under hydrogen at atmospheric pressure at ambient temperature has been described in Sec. 5.2B(ii). This reaction also formed a trace amount of solid after the reaction. The solid shows two carbonyl bands

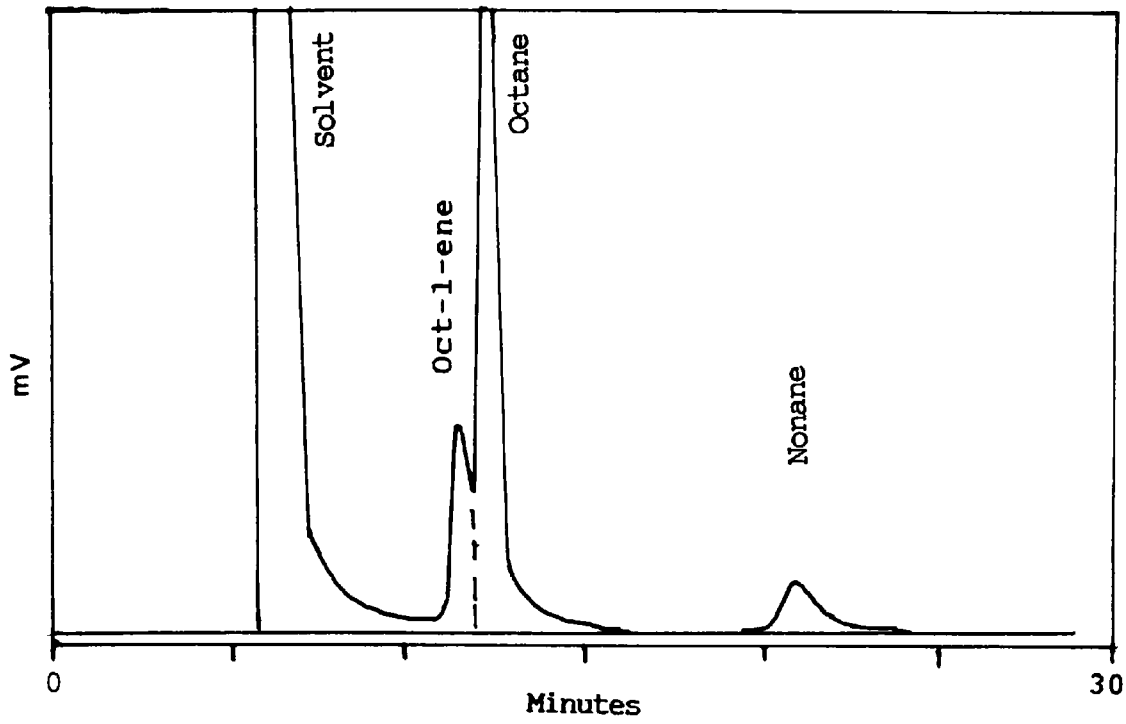


Fig. 112 : Chromatogram of the hydrogenation of oct-1-ene and catalyst $[Rh(CO)(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$.

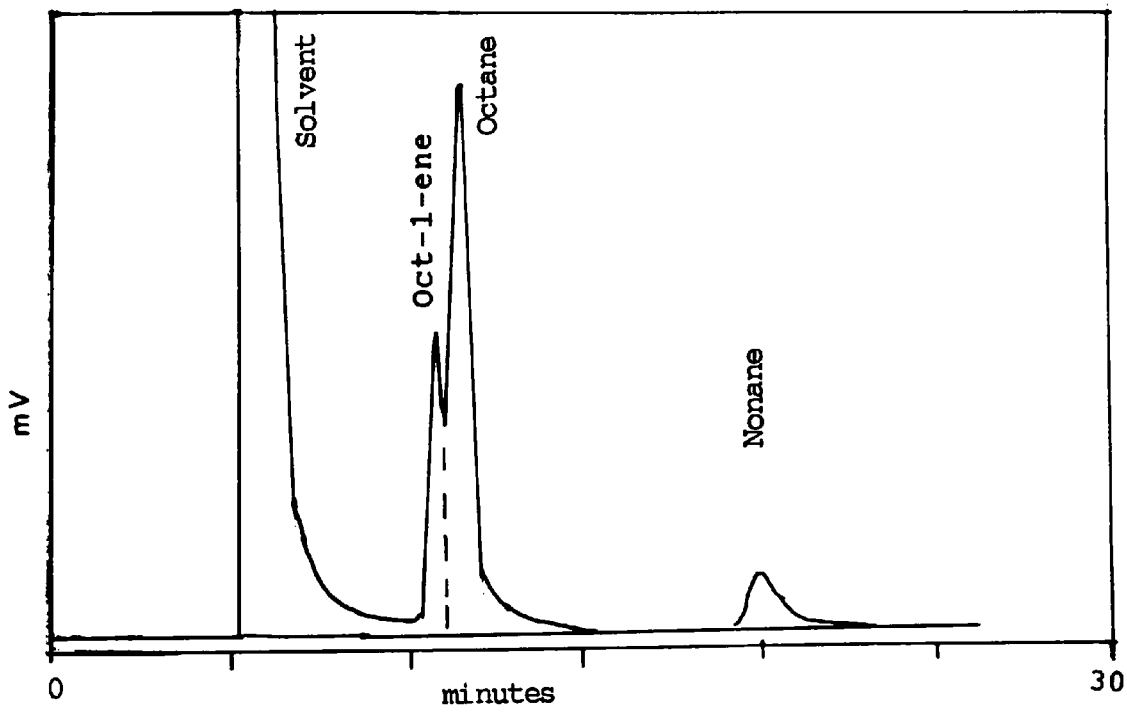


Fig. 113 : Chromatogram of hydrogenation of oct-1-ene and catalyst $[Rh(CO)(AsPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$.

at 1989 and 1979 cm^{-1}. Again the carbonyl band at 1989 cm^{-1} is assigned to the starting catalyst and the band at 1979 cm^{-1} may be due to decomposition of the complex. The gas chromatography analysis shows that the concentration of octane 340 $mmol/dm^3$. and the chromatogram is seen in Fig. 113.

(iii) Hydrogenation of Oct-1-ene, $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ as Catalyst.

The hydrogenation of oct-1-ene by the compound (XXVI), $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$ in benzene under hydrogen at atmospheric pressure at ambient temperature has been described in Sec. 5.2B(iii). The gas chromatographic analysis of the homogeneous solution shows the concentration of octane is 80 $mmol/dm^3$. This smaller

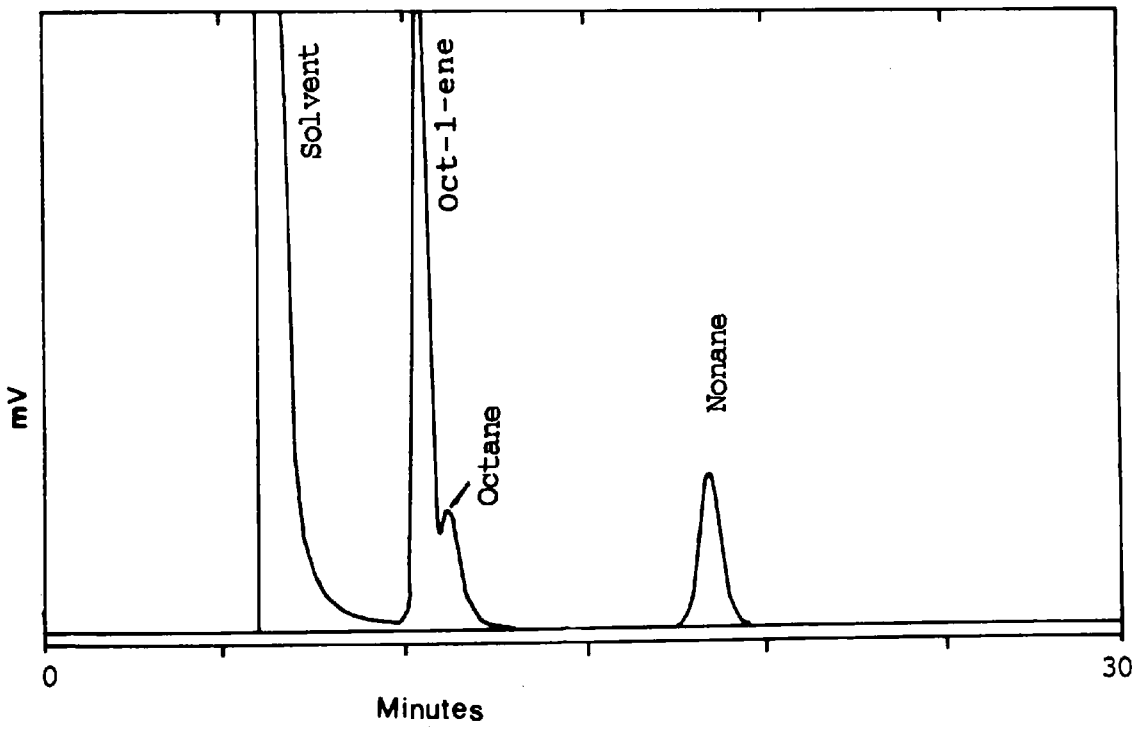


Fig. 114 : Chromatogram of hydrogenation of oct-1-ene and catalyst $[Rh(CO)(PCy_3)_2]^+[BF_4]^-.3/2(CH_2Cl_2)$.

conversion by the Rh--PCy_3 compound may be due to the fact that PCy_3 is a much bulkier ligand, inhibiting coordination of the alkene. The chromatogram is seen in Fig. 114.

For the compounds, $[Rh(CO)(L)_2]^+[BF_4]^-$, where L = PPh_3, $AsPh_3$ and PCy_3 the uptake of hydrogen measurement conversion to STP shows that the initial absorption is rapid for the reactions Sec. 5.2B[(i), (ii) and (iii)]. Only 5 hours measurement is plotted in Fig. 115. The reaction rate is slower for the ligands in the order PPh_3 > $AsPh_3$ > PCy_3. For the bulkier ligand the absorption rate is slow.

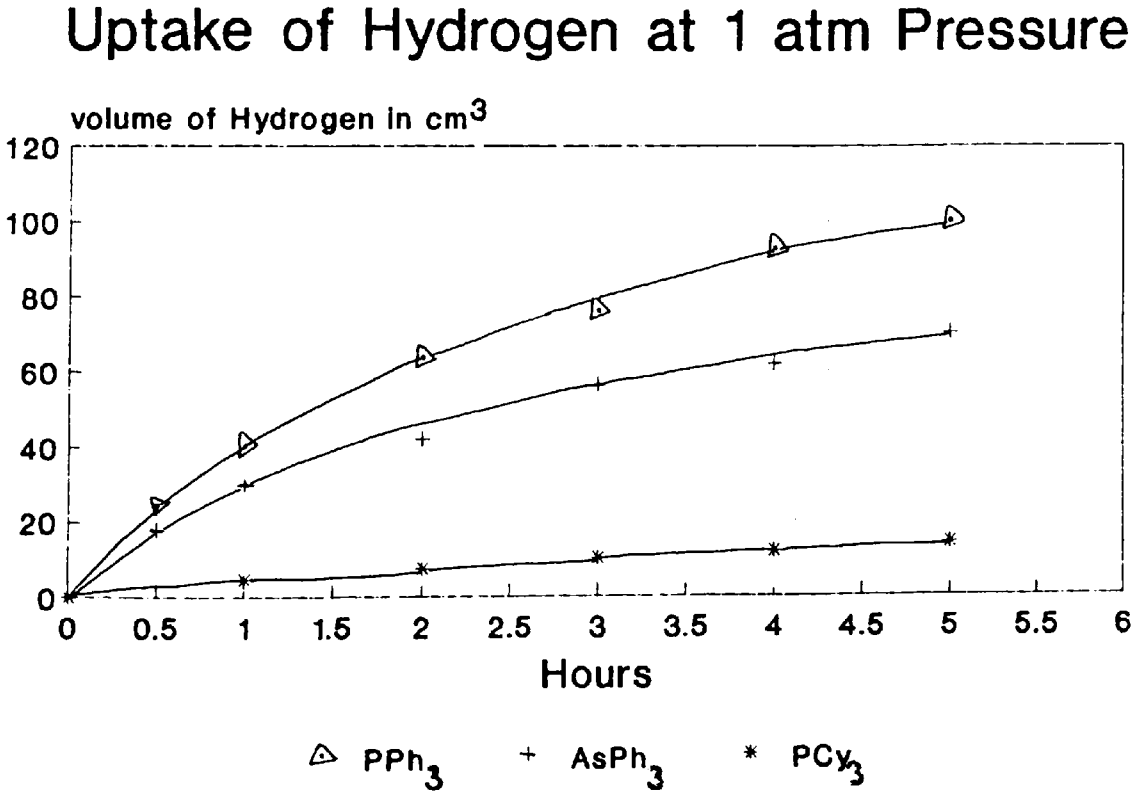


Fig. 115 : Catalytic absorption of hydrogen, volume vs. time by $[Rh(CO)(L)_2]^+[BF_4]^-$, where L = PPh_3, $AsPh_3$ and PCy_3 ligands and the volume of hydrogen absorbed after conversion to STP. Amount of catalyst 0.08 mmol in 10 cm^3 solution. Data are in appendix-7.

Therefore, the cationic complexes [(VI), (XVIII) and (XXVI)] are effective homogeneous catalysts for the hydrogenation of oct-1-ene to octane at atmospheric hydrogen at ambient temperature.

(iv) Hydrogenation of Oct-1-ene, $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ as Catalyst.

The hydrogenation of oct-1-ene to octane has been also effected by the ruthenium cationic complex, $[RuCl(CO)_2(PPh_3)_2]^+[BF_4]^-.1/2(CH_2Cl_2)$ in benzene under hydrogen at atmospheric pressure at ambient temperature as described in Sec. 5.2B(iv). The concentration of octane is 95 mmol/dm^3. The experimental temperature, pressure and volume of hydrogen is corrected to STP in Appendix-8. The chromatogram is seen in Fig. 116.

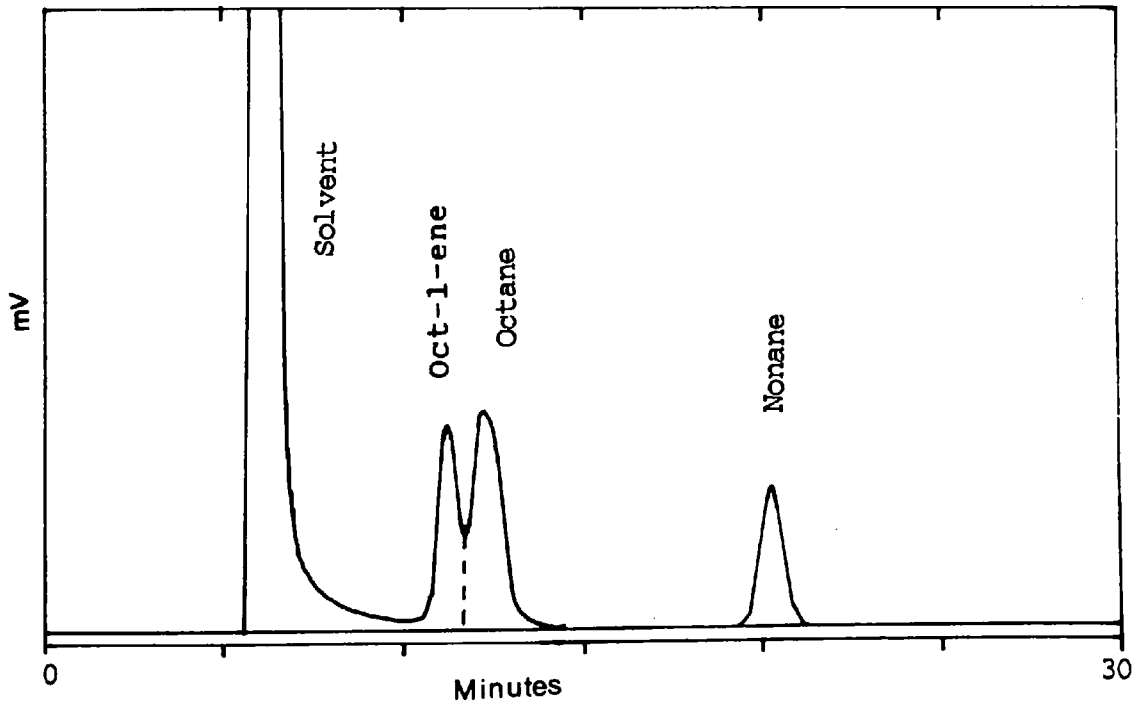


Fig. 116 : Chromatogram of hydrogenation of oct-1-ene and catalyst $[RuCl(CO)_2(PPh_3)_2][BF_4]^-.1/2(CH_2Cl_2)$.

(v) An Attempt to Hydrogenation of Oct-1-ene by compound (I) $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$.

The hydrogenation reactions of oct-1-ene by the compound, $[Ru(CO)_2(PPh_3)_2]^{2+}[BF_4]^-_2.CH_2Cl_2$ in benzene and in dichloromethane have been described in Sec. 5.2B(v) and (vi) respectively. Hydrogenation by this compound does not take place, because the compound is not soluble in benzene and it decomposed as seen from the infrared spectra. The compound is soluble in dichloromethane, but hydrogenation in chlorinated solvents like dichloromethane does not occur[161]. The polarity of the solvent may stabilise the compound so that hydrogenation does not take place.

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK.

In the present work the cationic complexes of the type $[RuCl(CO)_2(L)_2]^+$, $[Ru(CO)_2(L)_2]^{2+}$, $[Ru(CO)_3(L)_2]^{2+}$, where L = PPh_3 have been synthesised, in the absence and presence of CO, from $[RuCl_2(CO)_2(PPh_3)_2]$ by abstraction of Cl^-. These type of cationic complexes could be prepared for the ligands L = $AsPh_3$, PCy_3 and $SbPh_3$. From these cationic complex compounds the alkoxycarbonyl compounds should be able to be prepared by their reaction with nucleophiles in the presence of CO. Their reactivity and catalytic potential could then be assessed.

The present work also describes the synthesis of the electron unsaturated cationic complexes $[Rh(CO)(L)_2]^+$ where L = PPh_3, $AsPh_3$, PCy_3. As the size of the P, As, Sb atoms increases the stability of the cationic complexes decreases. The present work did not isolate the $SbPh_3$ species containing a three coordinate cationic complex. Changing the Ph or Cy group in the ligands to smaller σ donating groups e. g. C_2H_5, C_2H_5O, or changing the ligands to dppe, dppm, for example would provide a further opportunity to investigate how different ligands influence the stability of the cationic species. The behaviour of these cationic complexes with respect to preparing the alkoxo, alkoxycarbonyl and carboxylato compounds could also be investigated.

These cationic complexes could give organic products (e. g. dialkylcarbonate, dialkyloxalate or a formaldehyde oligomer) catalytically or stoichiometrically when they react with nucleophiles (RO^-) and CO at atmospheric pressure or CO at high pressure. In the present work when the catalytic reaction is carried out with CO and sodium methoxide, then dimethylcarbonate or dimethyloxalate identification is difficult, because sodium methoxide is moisture

sensitive. A trace amount of dimethylcarbonate is formed in the reaction mixture that is possibly converted to an unidentified compound, suspected to be the sodium carbonate as described in Sec. 5.1C(ii). The white precipitate formed by the reaction of sodium methoxide and dimethylcarbonate in air, is suspected to be sodium carbonate by infrared and ^{13}C-NMR; that could be confirmed by elemental analysis. The reactions involving a cationic complex and CO could be carried out using an organic base e.g. triethylamine, which is not moisture sensitive unlike sodium methoxide. Fenton and Steinwand[156] reported that in using a palladium redox catalyst, when moisture was formed in the reaction system, then no oxalates were formed. Therefore, to get dimethylcarbonate or dimethyloxalate it seems a non-moisture sensitive reactant is required.

In the present work the compounds contain a (BF_4^-) group proposed to be free, not coordinated as seen by infrared spectroscopy. This could be more fully investigated by ^{19}F-NMR and conductance measurements. Similar types of cationic compounds could be prepared for other anions, e.g. PF_6^-, BPh_4^-, ClO_4^-.

In the present work the reaction mechanism for the formation of the dimethyoxycarbonyl compound, $[Ru(COOCH_3)_2(CO)_2(PPh_3)_2$ from the dipositive complex $[Ru(CO)_2(PPh_3)_2]^{2+}$ or from $[RuCl_2(CO)_2(PPh_3)_2]$ was suggested to proceed through the intermediate $[Ru(OCH_3)_2(CO)_2(PPh_3)_2]$ state then rapid CO insertion took place, but the intermediate stage was not isolated. Alternatively, first free CO coordinates and then the nucleophile (CH_3O^-) attacks the coordinated CO. The mechanism could be confirmed by using isotopic labelled CO. The complex $[Ru(CO)_2(PPh_3)_2]^{2+}$

reacts with CO in the presence of CH_3O^- or with CO in the presence of triethylamine in methanol to give dimethylcarbonate and $[Ru(CO)_3(PPh_3)_2]$. This reaction may proceed through the $Ru(COOCH_3)$ complex, because the ruthenium methoxycarbonyl compound has been isolated and characterised. Therefore, in the reactions which gave the alkoxycarbonyl compounds, there is a probability that organic esters from that type of reaction may be obtained by breaking the metal-alkoxycarbonyl bonds. The catalytic carbonylation reactions could be carried out at high CO pressure and temperature, to find out whether the amount or nature of the organic product changes.

Reaction of $[RhCl(CO)(L)_2]$ or $[Rh(CO)(L)_2]^+$ with CO gave the complex $[Rh(CO)_2(L)_2]^+$, where L = PPh_3, $AsPh_3$, PCy_3. In the present work, when $[Rh(CO)(L)_2]^+$ or $[Rh(CO)_2(L)_2]^+$ reacted with the nucleophile (RO^-) in the presence of CO, they gave the alkoxycarbonyl compound $[Rh(COOR)(CO)_2(L)_2]$, (L = PPh_3, $AsPh_3$ and R = alkyl). In the literature it is reported[38] that carbonylation of $[Ir(OCH_3)(CO)(PPh_3)_2]$ to give $[Ir(COOCH_3)(CO)_2(PPh_3)_2]$ proceed through the intermediate five coordinated $[Ir(CO)_3(PPh_3)_2]^+OR^-$ state. Therefore, the present alkoxycarbonyl compound, $[Rh(COOR)(CO)_2(L)_2]$ may proceed through the intermediate $[Rh(CO)_3(L)_2]^+OR^-$ state. It could be possible to detect the intermediate five coordinated state, if the reaction is carried out at low temperature, by checking the infrared spectra of the solution at regular intervals. On the other hand, reaction of $[Rh(CO)(L)_2]^+$ or $[Rh(CO)_2(L)_2]^+$ (where L = PCy_3) with the nucleophile (RO^-) in the presence of CO, did not form $[Rh(COOR)(CO)_2(L)_2]$ instead the four coordinated alkoxycarbonyl compound $[Rh(COOR)(CO)(L)_2]$ was formed. The bulkier PCy_3 ligand may inhibit the formation of intermediate

five-coordinated $[Rh(CO)_3(L)_2]^+$ species or coordination of another CO. Therefore, the steric effect or size effect of the ligands may have an importance in the formation of compounds. Substitution of the PCy_3 ligand by other bulky ligands, e.g. $P(C_6H_4CH_3)_3$, $P(C_6H_4OCH_3)_3$ would allow investigation as to whether bulky ligands affect the formation of five coordinated alkoxycarbonyl compounds, $[Rh(COOR)(CO)_2(L)_2]$, where R = alkyl group.

The cationic complexes of ruthenium and rhodium have been synthesised in the present work are effective catalysts for the hydrogenation of oct-1-ene at atmospheric pressure at ambient temperature. The electron deficient cationic complexes of rhodium e.g. $[Rh(CO)(PPh_3)_2]_4SiW_{12}O_{40}$ are effective catalysts for the hydroformylation of alkenes[131,132]. Therefore, the cationic complexes that have been synthesised in the present could be investigated with the object of producing hydroformylation reactions of alkenes with CO and H_2.

REFERENCES

1. C. Masters, "Advances in Organometallic Chemistry", 17, 61, (1979), Academic Press, Inc.
2. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry" John Wiley and Sons, 1988 (5th Edn.).
3. R. P. A. Sneeden, "Comprehensive Organometallic Chemistry" 8, 79 (1982), Pergamon press Ltd.
4. D. L. King and J. H. Grate, Chemtech. April, 244 (1985).
5. H. S. Kesling Jr., Am. Symp. Seris No. 328, 77 (1987).
6. H. E. Bryndza, S. A. Kretchmar and T. H. Tulip, J. Chem. Soc. Chem. Commun. 977 (1985).
7. P. L. Burk, D. V. Engen and K. S. Campo, Organometallics 3, 493 (1984).
8. K. F. Purcell and J. C. Kotz, "Inorganic Chemistry" W. B. Saunders Company, 1977.
9. G. Huttner and S. Schelle, J. Crystallogr. Mol. Struct. 1, 69 (1971).
10. F. A. Cotton and D. C. Richardson, Inorg. Chem. 5, 1851 (1966).
11. D. M. Adams, "Metal-Ligand and Related Vibrations" St. Martin's Press, New York, 1968.
12. L. M. Haines and M. H. B. Stiddard, Adv. Inorg. Chem. Radiochem. 12, 53 (1969).
13. J. G. Bullitt, F. A. Cotton and T. J. Marks, Inorg. Chem. 11, 671 (1972).
14. R. B. King, Inorg. Chem. 5, 2227 (1966).
15. W. Jetz and R. J. Angelici, J. Am. Chem. Soc. 94, 3799 (1972).
16. J. F. Nixon, Adv. Inorg. Chem. Radiochem. 29, 42 (1985).

17. A. Pidcock, R. E. Richards and L. M. Venanzi, J. Chem. Soc. (A) 1707 (1966).

18. D. S. Marynick, J. Am. Chem. Soc. 106, 4064 (1984).

19. S. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkovitch-Yellion, J. Am. Chem. Soc. 105, 7033 (1983).

20. R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals" John Wiley and Sons, 1988.

21. C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR" 1974, Aldrich Chemical Company.

22. K. V. Werner and W. Beck, Chem. Ber. 105, 3947 (1972).

23. B. F. G. Johnson, R. D. Johnston, J. Lewis and I. G. Williams, J. Chem. Soc. (A) 689 (1971).

24. P. S. Pregosin and R. W. Kunz, "^{31}P and ^{13}C-NMR Spectroscopy of Transition Metal Complexes" Springer-Verlay, Heidelberg, 1979.

25. D. G. Gorenstein, Prog. NMR Spectroscopy 16, 1 (1983).

26. D. F. Gill, B. E. Mann and B. L. Shaw, J. Chem. Soc. Dalton Trans. 311 (1973).

27. P. R. Hoffman and K. G. Caulton , J. Am. Chem. Soc. 97, 4221 (1975).

28. T. H. Brown and P. J. Green, J. Am. Chem. Soc. 91, 3378 (1969).

29. T. H. Brown and P. J. Green, J. Am. Chem. Soc. 92, 2359 (1970).

30. C. A. McAuliffe and W. Levason, "Studies in Inorganic Chemistry 1, Phosphine, Arsine and Stibine Complexes of the Transition Elements" Elsevier Scientific Publishing Company, 1979, p-55.

31. J. J. Dechter, "Progress in Inorganic Chemistry" 33, 438 (1985), John Wiley and Sons.

32. J. March, "Advanced Organic Chemistry, Reactions Mechanism and Structure" John Wiley and Sons, 1985, Ch-10 (3rd Edn.).

33. L. Busetto, M. Graziani and U. Belluco, Inorg. Chem. 10, 78 (1971).

34. D. J. Darensbourg, M. Y. Darensbourg, N. Walker, J. A. Froelich and H. L. C. Barros, Inorg. Chem. 18, 1401 (1979).

35. K. Bowman, A. J. Deeming and G. P. Proud, J. Chem. Soc. Dalton Trans. 857 (1985).

36. R. J. Angelici, Account Chem. Res. 5, 335 (1972).

37. C.P. Casey and C.A. Bunnell, J. Am. Chem. Soc. 98, 436 (1976).

38. W. M. Rees and J. D. Atwood, Organometallics 4, 402 (1985).

39. H. A. Hodoli and D.E. Shriver, Inorg. Chem. 18, 1236 (1979).

40. K. Goswami and M. M. Singh, J. Indian. Chem. Soc. LVI, 477 (1979).

41. L. Vaska and J. P. Jun, J. Chem. Soc. Chem. Commun. 418 (1971).

42. A. E. Kruse and R. J. Angelici, J. Organometal. Chem. 24, 231 (1970).

43. L. Busetto and R. J. Angelici, Inorg. Chim. Acta. 2, 391 (1968).

44. W. Hieber, V. Frey and P. John, Chem. Ber. 100, 1961 (1967).

45. T. Kruch and M. Noack, Chem. Ber. 97, 1693 (1964).

46. H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam and J. E. Bercaw, J. Am. Chem. Soc. 108, 4805 (1986).

47. H. E. Bryndza, Organometallics 4, 1686 (1985).

48. E. D. Dobrzynski and R. J. Angelici, Inorg. Chem. 14, 59 (1975).

49. F. Rivetti and U. Romano, J. Organometal. Chem. 154, 323 (1978).

50. F. Rivetti and U. Romano, J. Organometal. Chem. 174, 221 (1979).

51. T. Kobayashi, F. Abe and M. Tanaka, J. Mol. Catal. 45, 91 (1988).

52. L. Huang, F. Ozawa, K. Osakada and A. Yamamoto, Organometallics 8, 2065 (1989).

53. W. Hieber and V. Frey, Chem. Ber. 99, 2614 (1966).

54. L. Malatesta, M. Angoletta and G. Caglio, J. Chem. Soc. (A) 1836 (1970).

55. L. J. Newman and R. G. Bergman, J. Am. Chem. Soc. 107, 5314 (1985).

56. D. Seyferth and G. A. Williams, J. Organometal. Chem. 38, C11 (1972).

57. E. O. Fischer, K. Fichlet and K. Öfele, Chem. Ber. 95, 249 (1962).

58. P. Laurent, S. Sabo-Etienne, A. Larsonneur and H. Abbayes, J. Chem. Soc. Chem. Commun. 929 (1988).

59. S. Uchiumi and M. Yamashita, J. Japan Petrol. Inst. 25, 197 (1982).

60. W. L. Jolly, "Modern Inorganic Chemistry" McGraw-Hill International Edition, 1985, Ch-20.

61. R. L. Pruett, W. E. Walker, US. Patent 3,833,634 (1974).

62. X. Z. Jiang, "Platinum Metal Review" 34(4), 178 (1990), Johnson Matthey Public Ltd. Company.

63. B. S. Furniss, A. J. HannaFord, P. W. G. Smith and A. R. Tatchell, "Vogel's Practical Organic Chemistry" Longman Scientific and Technical and John Wiley and Sons, 1989 (5th Edn.).

64. T. A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem. 28, 945 (1966).

65. F. H. Jardine, "Progress in Inorganic Chemistry" 31, 269 (1984) John Wiley and Sons.

66. Y. N. KuKushkin, E. I. Maslov and T. P. Ryabkova, Russ. J. Inorg. Chem. 26, 1334 (1981).

67. S. Cenini, A. Fusi and G. Capparella, Inorg. Nucl. Chem. Lett. 8, 127 (1972).

68. Y. Sasson and G. L. Rempel, Tetrahedron Lett. 3221 (1974).

69. G. Speier and L. Markó, J. Organometal. Chem. 210, 253 (1981).

70. R. W. Mitchell, A. Spencer and G. Wilkinson, J. Chem. Soc. Dalton Trans. 846 (1973).

71. J. M. A. Al-Rawi, J. A. Elvidge, J. R. Jones, R. B. Mane and M. Saieed, J. Chem. Res. Synop. 298 (1980).

72. S. Cenini, A. Fusi and F. Porta, Gazz. Chim. Ital. 108, 109 (1978).

73. B. R. James, L. D. Markham, B. C. Hui and G. L. Rempel, J. Chem. Soc. Dalton Trans. 2247 (1973).

74. D. T. Doughty, R. P. Stewart Jr. and G. Gordon, J. Am. Chem. Soc. 103, 3388 (1981).

75. J. P. Collman and W. R. Roper, J. Am. Chem. Soc. 87, 4008 (1965).

76. J. M. Jenkins, M. S. Lupin and B. L. Shaw, J. Chem. Soc. (A) 1787 (1966).

77. C. F. J. Barnard, J. A. Daniels, J. Jeffery and R. J. Mawby, J. Chem. Soc. Dalton Trans. 953 (1976).

78. S. Cenini, F. Porta and M. Pizzotti, Inorg. Chim. Acta. 20, 119 (1976).

79. N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, Inorg. Synth. 15, 45 (1974).

80. F. L' eplattenier and F. Calderazzo, Inorg. Chem. 7, 1290 (1968).

81. J. D. Cotton, M. I. Bruce and F. G. A. Stone, J. Chem. Soc. (A) 2162 (1968).

82. B. E. Cavit, K. R. Grundy and W. R. Roper, J. Chem. Soc. Chem. Commun. 60 (1972).

83. S. Cenini, A. Fusi and G. Capparella, J. Inorg. Nucl. Chem. 33, 3576 (1971).

84. B. L. Haymore and J. A. Ibers, J. Am. Chem. Soc. 97, 5369 (1975).

85. B. L. Haymore and J. A. Ibers, Inorg. Chem. 14, 2784 (1975).

86. A. Stasunik and W. Malisch, J. Organometal. Chem. 270, C56 (1984).

87. B. F. G. Johnson and J. A. Segal, J. Chem. Soc. Dalton Trans. 478 (1973).

88. S. Cenini, A. Mantovani, A. Fusi and M. Keubler, Gazz. Chim. Ital. 105, 255 (1975).

89. N. Ahmad, S. D. Robinson and M. F. Uttley, J. Chem. Soc. Dalton Trans. 843 (1972).

90. S. D. Loren, B. K. Campion, R. H. Heyn, T. D. Tilley, B. E. Bursten and K. W. Luth. J. Am. Chem. Soc. 111, 4712 (1989).

91. B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr and G. Wilkinson, J. Chem. Soc. Dalton Trans. 1546 (1977).

92. S. D. Robinson and M. F. Uttley, J. Chem. Soc. Dalton Trans. 1912 (1973).

93. A. Dobson and S. D. Robinson, Inorg. Chem. 16, 1321 (1977).

94. D. Rose, J. D. Gilbert, R. P. Richardson and G. Wilkinson, J. Chem. Soc. (A) 2610 (1969).

95. A. Dobson, S. D. Robinson and M. F. Uttley, J. Chem. Soc. Dalton Trans. 370 (1975).

96. D. E. C. Corbridge, J. Appl. Chem. 6, 456 (1956).

97. G. K. N. Reddy and B. R. Ramesh, J. Organometal. Chem. 67, 443 (1974).

98. W. Beck and K. Sünkel, Chem. Rev. 88, 1405 (1988).

99. I. Pri-Bar and O. Buchman, J. Org. Chem. 45, 4418 (1980).

100. D. Evans, J. A. Osborn, F. H. Jardine and G. Wilkinson, Nature 208, 1203 (1965).

101. D. R. Fahey, J. Org. Chem. 38, 3343 (1973).

102. Y. W. Yared, S. L. Miles, R. Bau and C. A. Reed, J. Am. Chem. Soc. 99, 7076 (1977).

103. R. R. Schrock and J. A. Osborn, J. Am. Chem. Soc. 93, 2397 (1971).

104. P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick and G. Wilkinson, J. Chem. Soc. (A) 3322 (1970).

105. B. M. Mattson and W. A. G. Graham, Inorg. Chem. 20, 3186 (1981).

106. K. Sünkel, G. Urban and W. Beck, J. Organomet. Chem. 252, 187 (1983).

107. S. J. Laplaca and J. A. Ibers, Inorg. Chem. 4, 778 (1965).

108. F. G. Moers, R. W. M. Ten Hoedt and J. P. Langhout, J. Organometal. Chem. 65, 93 (1974).

109. G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters and K. R. Whittle, J. Chem. Soc. Chem. Commun. 119 (1972).

110. C. G. Pierpont, A. Pucci, R. Eisenberg, J. Am. Chem. Soc. 93, 3050 (1971).

111. K. Nakamoto, "Infrared Spectra of Inorganic Chemistry" 1970, John Wiley and Sons, 2nd Edn.

112. K. R. Grundy, R. O. Harris and W. R. Roper, J. Organometal. Chem. 90, C34 (1975).

113. A. Rusina and A. A. Vlček, Nature 206, 295 (1965).

114. F. G. Moers, J. A. M. De Jong and P. M. H. Beaumont, J. Inorg. Nucl. Chem. 35, 1915 (1973).

115. L. Vallarino, J. Chem. Soc. 2287 (1957).

116. J. A. Osbone, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. (A) 1711 (1966).

117. M. J. Bennett and P. B. Donaldson, Inorg. Chem. 16, 655 (1977).

118. D. Evans, J. A. Osborn and G. Wilkinson, Inorg. Synth. 11, 99 (1968).

119. R. P. Hughes, Comprehensive Organometallic Chemistry, Pergamon Press Ltd. Vol- 5, 1982 and their reference.

120. W. Hieber, H. Heusinger and O. Vohler, Chem. Ber. 90, 2425 (1957).

121. L. Vaska and J. Peone Jr, Inorg. Synth. 15 64 (1974).

122. L. Vaska and J. Peone Jr., J. Chem. Soc. Chem. Commun. 418 (1971).

123. K. W. Muir and J. A. Ibers, Inorg. Chem. 8, 1921 (1969).

124. C. T. Mortimer and S. J. Ashcroft, Inorg. Chem. 10, 1326 (1971).

125. R. F. Heck, J. Am. Chem. Soc. 86, 2796 (1964).

126. I. C. Douek and G. Wilkinson, J. Chem. Soc. (A) 2604 (1969).

127. H. L. M. Van Gaal and F. L. A. Van Den Bekerom, J. Organometal. Chem. 134, 237 (1977).

128. J. A. McCleverty and G. Wilkinson, Inorg. Synth. 8, 214 (1966).

129. D. N. Lawson, J. A. Osborn and G. Wilkinson, J. Chem. Soc. (A) 1733 (1966).

130. R. A. Jewsbury, Inorg. Chim. Acta. 49, 141 (1981).

131. A. R. Siedle, C. G. Markell, P. A. Lyon, K. O. Hodgson and A. L. Roe, Inorg. Chem. 26, 219 (1987).

132. A. R. Siedle, R. A. Newmark, W. B. Gleason, R. P. Skarjune, K. O. Hodgson, A. L. Roe and V. W. Day, Solid State Ionics 26, 109 (1988).

133. G. Wilkinson, US. Patent 3,794,671 (1974).

134. P. Albano and M. Aresta, J. Organometal. Chem. 190, 243 (1980).

135. A. R. Siedle, R. A. Newmark and R. D. Howells, Inorg. Chem. 27, 2473 (1988).

136. R. W. Mitchell, J. D. Ruddick and G. Wilkinson, J. Chem. Soc. (A) 3224 (1971).

137. J. A. McCleverty and G. Wilkinson, Inorg. Synth. 8, 211 (1966).

138. J. A. Tiethof, J. L. Peterson and D. W. Meek, Inorg. Chem. 15, 1365 (1976).

139. D. J. Liston, Y. J. Lee, W. R. Scheidt and C. A. Reed, J. Am. Chem. Soc. 111, 6643 (1989).

140. E. W. Evans, "The Synthesis and Properties of Selected Transition Metal-Pyrazole Complexes and Their Application toward Homogeneous Catalysis" PhD. Thesis, The Polytechnic of Wales, 1991.

141. W. Beck and K. Schloter, Z. Naturforsch. 33b, 1214 (1978).

142. E. K. G. Schmidt and C. H. Thiel, J. Organomet. Chem. 220, 87 (1981).

143. J. M. Fernández and J. A. Gladysz, Inorg. Chem. 25, 2672 (1986).

144. S. K. Agbossou, J. M. Fernández and J. A. Gladysz, Inorg. Chem. 29, 476 (1990).

145. E. Horn and M. R. Snow, Aust. J. Chem. 33, 2369 (1980).

146. A. R. Siedle, W. B. Gleason, R. A. Newmark, R. P. Skarjune, P. A. Lyon, C. G. Markell, K. O. Hodgson and A. L. Roe, Inorg. Chem. 29, 1667 (1990).

147. D. M. Branan, N. W. Hoffman, E. A. McElroy, N. ProKopuk, A. B. Salazar, M. J. Robbins, W. E. Hill and T. R. Webb, Inorg. Chem. 30, 1200 (1991).

148. F. A. Cotton, R. D. Barnes and E. Bannister, J. Chem. Soc. 2199 (1960).

149. J. C. Sheldon and S. Y. Tyree, J. Am. Chem. Soc. 80, 4775 (1958).

150. T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, J. Am. Chem. Soc. 103, 3411 (1981).

151. P. I. Van Vliet and K. Vrieze, J. Organometal. Chem. 139, 337 (1977).

152. J. Kuyper and K. Vrieze, J. Organometal. Chem. 107, 129 (1976).

153. J. A. Miller and J. A. Nelson, Organometallics 10, 2958 (1991).

154. K. A. Bernard and J. D. Atwood, Organometallics 6, 1133 (1987).

155. R. Ugo, F. Bonati and S. Cenini, Inorg. Chim. Acta. 3, 220 (1969).

156. D. M. Fenton and P. J. Steinwand, J. Org. Chem. 39, 701 (1974).

157. M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis" Vol- 4, 1974, John Wiley and Sons.

158. J. Fujita, K. Nakamoto and M. Kobayashi, J. Phys. Chem. 61, 1014 (1957).

159. A. D. Buss and S. Warren, J. Chem. Soc. Perkin Trans. 1, 2307 (1985).

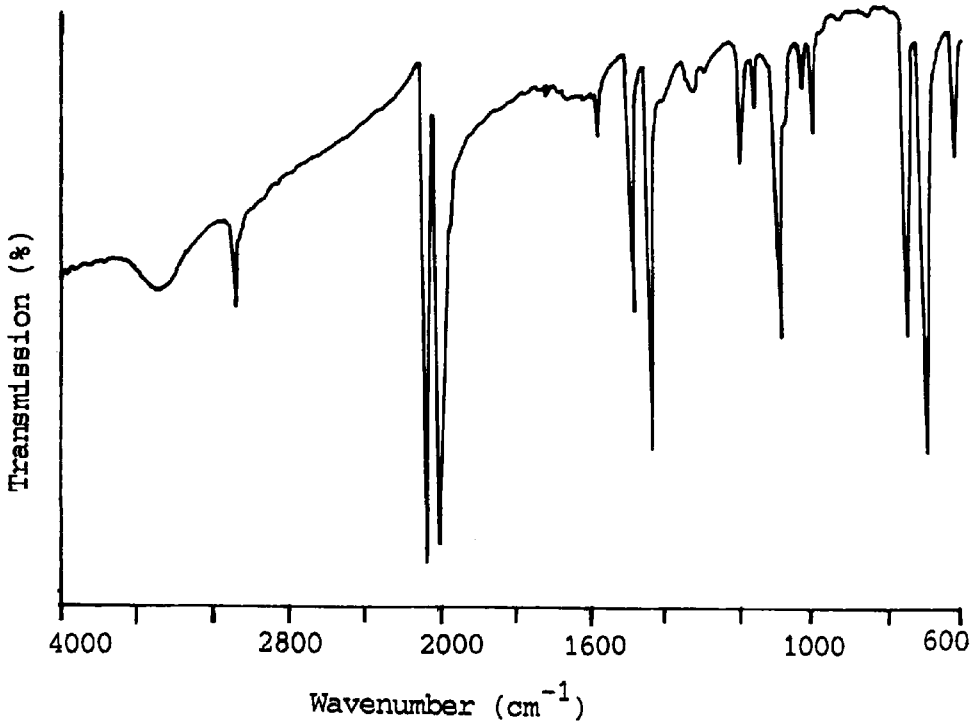
160. F. H. Jardine, "Progress in Inorganic Chemistry" 28, 124 (1981), John Wiley and Sons.

161. P. S. Hallman, B. R. McGarvey and G. Wilkinson, J. Chem. Soc. (A) 3143 (1968).

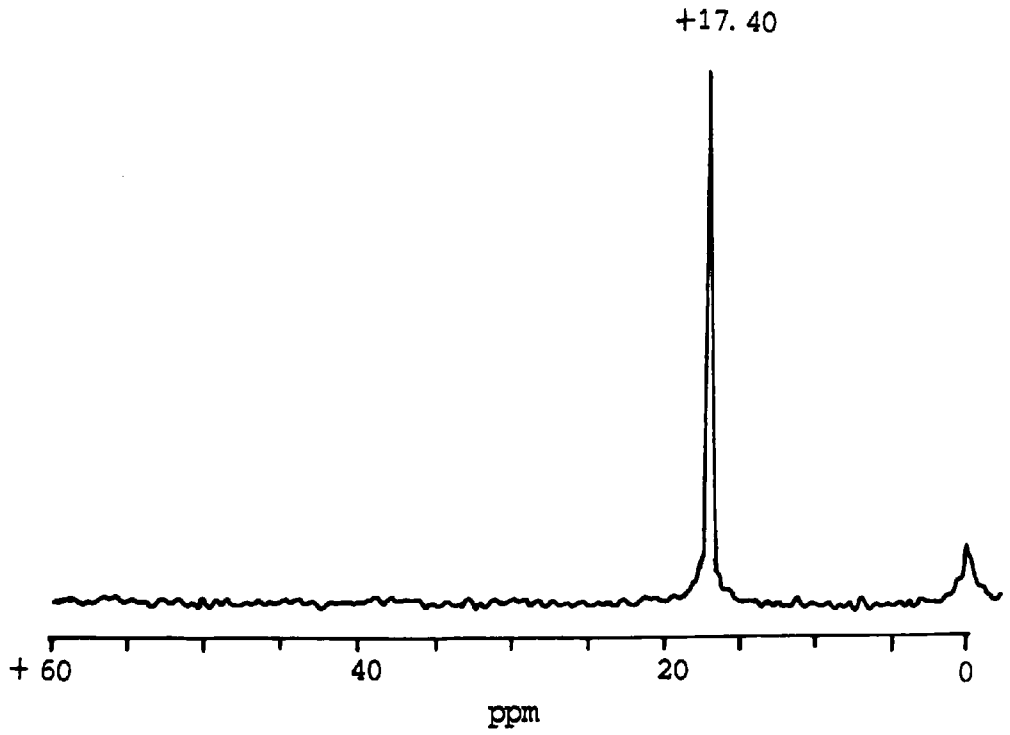
APPENDICES.

REFERENCE SPECTRA AND CHROMATOGRAM

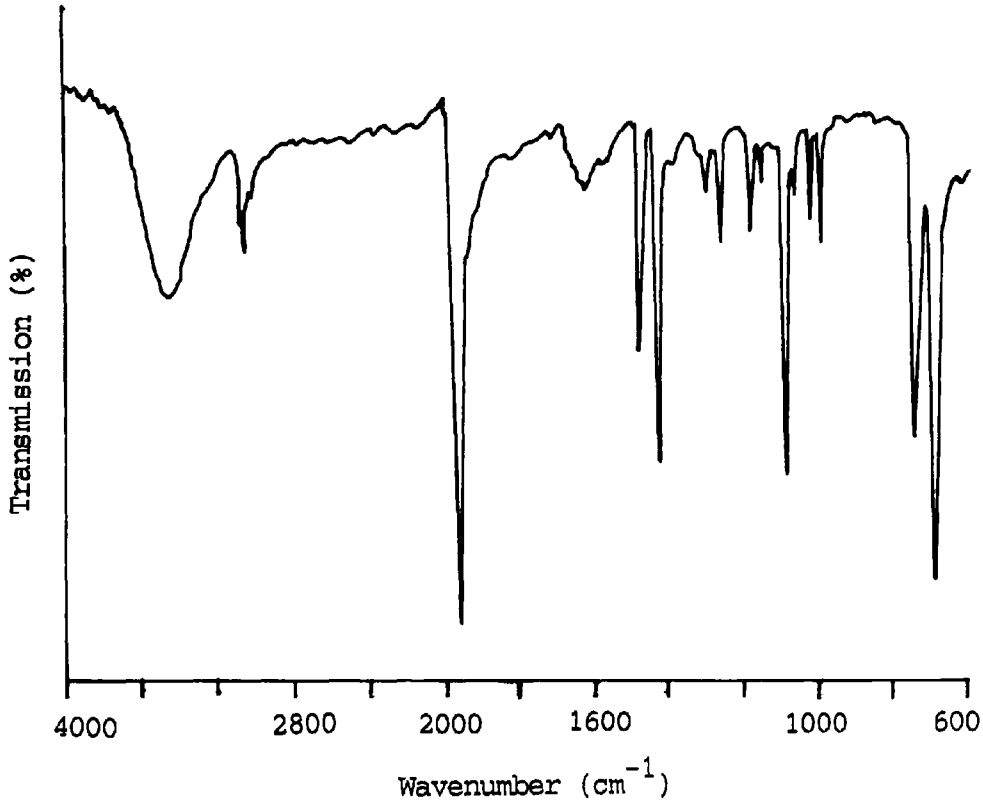
(1) Infrared Spectrum of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (KBr disc).



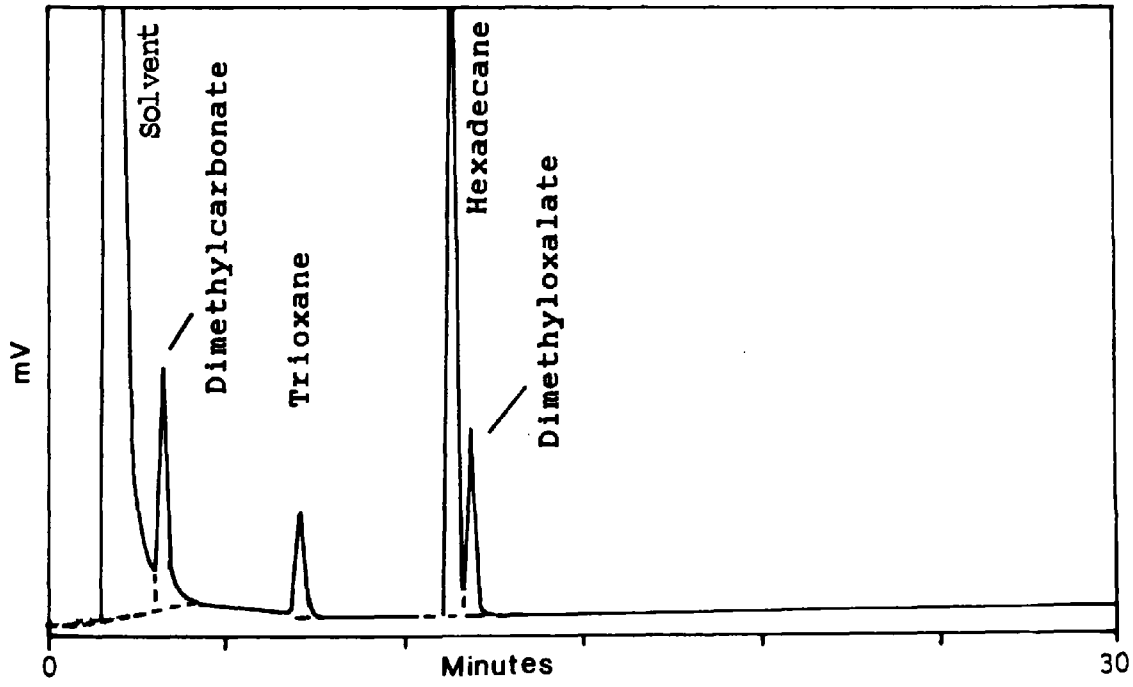
(2) ^{31}P-NMR Spectrum of cis-$[RuCl_2(CO)_2(PPh_3)_2]$ (in $CDCl_3$, 85% H_3PO_4).



(3) Infrared Spectrum of trans-[RhCl(CO)(PPh_3)$_2$] (KBr disc).



(4) Chromatogram of Standard Dimethylcarbonate, Dimethyloxalate, Trioxane and Internal Standard Hexadecane.



GRAPHICAL DATA AND CALCULATIONS.

(5) Data for Calibration Curve of Dimethylcarbonate and their Calculations as in Fig. 103.

Quotient of response is the ratio of area of target compound against the area of internal standard.

For example the calculation for one sample was done below. An equal amount internal standard was added in every case to varying quantities of target compound and the total volume of the solution was same.

$$\text{Quotient of response} = \frac{\text{area of dimethylcarbonate}}{\text{area of hexadecane}}$$

$$= \frac{0.6930}{2.245} = 0.31$$

For the quotient of response of 0.31, the concentration of solution was 28 mmol/dm^3.

Quotient of response	Amount in mmol/dm^3
0.03	5
0.31	28
0.47	55
0.50	70
1.32	145

(6) **Data for Calibration Curve of Octane and their Calculations as in Fig. 111.**

$$\text{Quotient of response} = \frac{\text{area of octane}}{\text{area of Nonane}}$$

$$= \frac{5.445}{1.333} = 4.10$$

For the quotent of response of 4.10 the concentration of solution was 230 mmol/dm^3. Similar calculations were done for other samples. An equal amount of internal standard was added in every case to varying quantities of the target compound and the total volume of the solution was same.

Quotient of response	Amount in mmol/dm^3
0.80	30
1.20	60
1.90	80
4.10	230
5.90	340
8.00	460
9.70	560

(7) **Uptake of Hydrogen by $[Rh(CO)(L)_2]^+$, where L = PPh_3, $AsPh_3$ and PCy_3 at Atmospheric Pressure at ambient Temperature.**

Experimental temperature was 18^oC (291^oK) and Pressure was 759 mm of Hg.

L =	PPh_3		$AsPh_3$		PCy_3	
Hour	Vol. Exp.	Vol. STP	Vol. Exp.	Vol. STP	Vol. Exp.	Vol. STP
0.5	26	24.4	19	17.8		
1	43	40.3	32	30	5	4.7
2	68	63.7	45	42.2	8	7.5
3	81	76	60	56.2	11	10.3
4	99	92.8	66	61.8	13	12.1
5	107	100	75	70	15	14.1
24	123	115	82	76.8	19	18

Where Vol. Exp. = Volume at experimental condition, Vol. STP = Volume at STP.

(8) **Uptake of Hydrogen by $[RuCl(CO)_2(PPh_3)_2]^+$, as described in Sec. 5.2B(iv).**

Here experimental temperature was 20.5^oC (293.5^oK) and Pressure was 781.6 mm of Hg. The volume of Hydrogen absorbed at experimental temperature and pressure was 23 cm^3 and at STP the volume was 22 cm^3.