To My Parents and
my Sister Maryam

THE REACTIONS OF CARBON DIOXIDE WITH COMPLEXES

BY

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S. Ashuri.

SUMMARY

THE UNIVERSITY OF ASTON IN BIRMINGHAM
THE REACTION OF CARBON DIOXIDE WITH COMPLEXES

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The studies described in this thesis are concerned with the reaction of carbon dioxide and transition metal complexes of Co, Ir, Rh, Ru. Due to the important role of group VIII transition metals in homogeneous catalytic reactions, the work is mainly concerned with complexes of ruthenium.

The reactions of carbon dioxide with pentaamminehydrateruthenium(II) and its analogous pentaamminedinitrogen complex (monomeric and dimeric) in solution and in the solid form result in the formation of new compounds. The infra-red spectra of these compounds mainly show the appearance of two new infra-red bands around 2340^{-1} and $660cm^{-1}$, comparable with the vibrational frequencies ν_3 and ν_2 of the gaseous CO_2.(4)

The complex $RuCl_2(PPh_3)_3$ has been chosen as a base compound for the preparation of other phosphine complexes such as $Ru(salen)(PPh_3)_2$, $Ru(DH)_2(PPh_3)_2$ and $RuCl_2(DH)(PPh_3)_2$. These complexes react with CO_2 and produce products with several new infra-red bands compared with the starting materials. The IR studies suggest that the nature of the products obtained from the reaction of phosphine complexes of ruthenium with CO_2 in solution is similar.

The kinetics of carbon dioxide uptake could only be studied for reaction with complex $RuCl_2(PPh_3)_3$ in toluene solution. Finally, infra-red spectroscopy has been chosen as one of the most important techniques for the investigation of the reactions of carbon dioxide with complexes.

Key Words

Carbon dioxide
Ruthenium
Rhodium

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CHAPTER I

INTRODUCTION.

Unless the current estimates of fuel reserves are wrong by orders of magnitude, we must accept that much more carbon is available to us in the form of carbonate rocks than as coal or oil. In consequence it is easy to envisage a time when carbon dioxide from the atmosphere or from carbonate rocks must replace oil as the major carbon containing chemical feed stock. The recognition of this eventuality has provided a major spur to the study of complexes containing carbon dioxide as a ligand, and into the reactivity of this coordinated ligand. A second drive may be detected in the development of this research interest namely, curiosity about naturally occuring processes. In the past photo-synthesis has given us coal, oil and gas, fuel wood, food, fibre and chemicals. The relative use of these fixed carbon sources has varied over the years and will undoubtedly do so in future. Each year plant photo-synthesis fixes about 2 x 10^{11} tonnes of carbon with an energy content of 3 x 10^{21} J. This is about 10 x the world's annual(1) energy use and 200 x our food energy consumption. Even though the photo-synthetic process is operating at only a 0.1 percent efficiency (total in coming radiation on earth, surface over whole year). All the atmospheric CO_2 is cycled through plants every 300 yr, all the O_2 every 2000 yr and all the H_2O every 2 million year. The magnitude and role of photo-synthesis is largely unrecognized principally because we utilize such a small fraction of the fixed carbon and because we do not realize the important recycling phenomena - any interference in this later role from pollution could have serious consequences. Fortunately for us plants are very adaptable and exist in great diversity.

They could thus continue indefinitely to supply us with renewable quantities of food, fuel, and chemicals.

1.1.1 SOURCES OF CO_2

Carbon dioxide is present in the atmosphere at a concentration of 300 ppm, it issues(2) from the earth in volcanic regions, and from super saturated solution in some mineral springs. As a product of human respiration it occurs to the extent of about 4% in exhaled air, exhaust gases from petrol engines contain up to 13% carbon dioxide and it is also present in appreciable concentration in water gas, producer gas and blast furnace gas. The main source is however, carbonate rocks, (especially the carbonates of calcium and magnesium) which constitute whole mountain ranges.

Most carbon dioxide, and especially that used in the manufacture of sodium carbonate,is obtained from lime stone heated by burning producer gas. The carbon dioxide (about 30%) is removed by absorption in potassium carbonate from which it is liberated on warming.

Solid carbon dioxide (dry ice) is made either by rapid expansion of carbon dioxide under pressure or by slower expansion, cooled by rapidly evaporating liquid ammonia at - 60°C . Its use as a cooling agent and as a source of carbon dioxide is now familiar. Sublimation of solid carbon dioxide produces gas which is sufficiently pure for most purposes.

1.1.2 PHYSICAL PROPERTIES AND STRUCTURE OF CO_2

Carbon dioxide is a linear triatomic molecule of AB_2 type in which the carbon atom forms two equivalent bonds with the oxygen atoms via the σ and π bonds, the planes of overlapping π orbitals of oxygen and carbon being mutually perpendicular. The C = O distance in carbon dioxide is equal to 1.16Å.

According to Mulliken(3) the C —— O bond in carbon dioxide is 75% heteropolar, while Moffitt has shown that each atom has practically zero charge. Malligan and Long and Walsh reported 10% hetero-polarity of the bond, which is in better agreement with Moffitt's results. There is information that carbon dioxide molecule has non-zero dipole-moment (0.06×10^{-18}), however in newer investigation the results could be consistent with $\mu = 0^{(3)}$.

A resonance hybrid model, to which it structures contribute signif-icnatly, may be postulated

$$O = C = O \qquad \overset{-}{O} - C \equiv \overset{+}{O} \quad \text{and} \quad \overset{+}{O} \equiv C - \overset{-}{O}$$

The two latter forms are identical and contribute equally, presumably to a much lesser extent than the first.

The infra-red spectrum of carbon dioxide shows two bands in the region of 2349 cm^{-1} and 667 cm^{-1} due to C - O stretching and C - O bending respectively.(4) In figure 1.1 vibrational modes designated ν_3 and ν_2 are accompanied by dipole moment changes and are therefore infra-red active, vibration ν_1 shows no change in dipole moment and is therefore infra-red inactive.

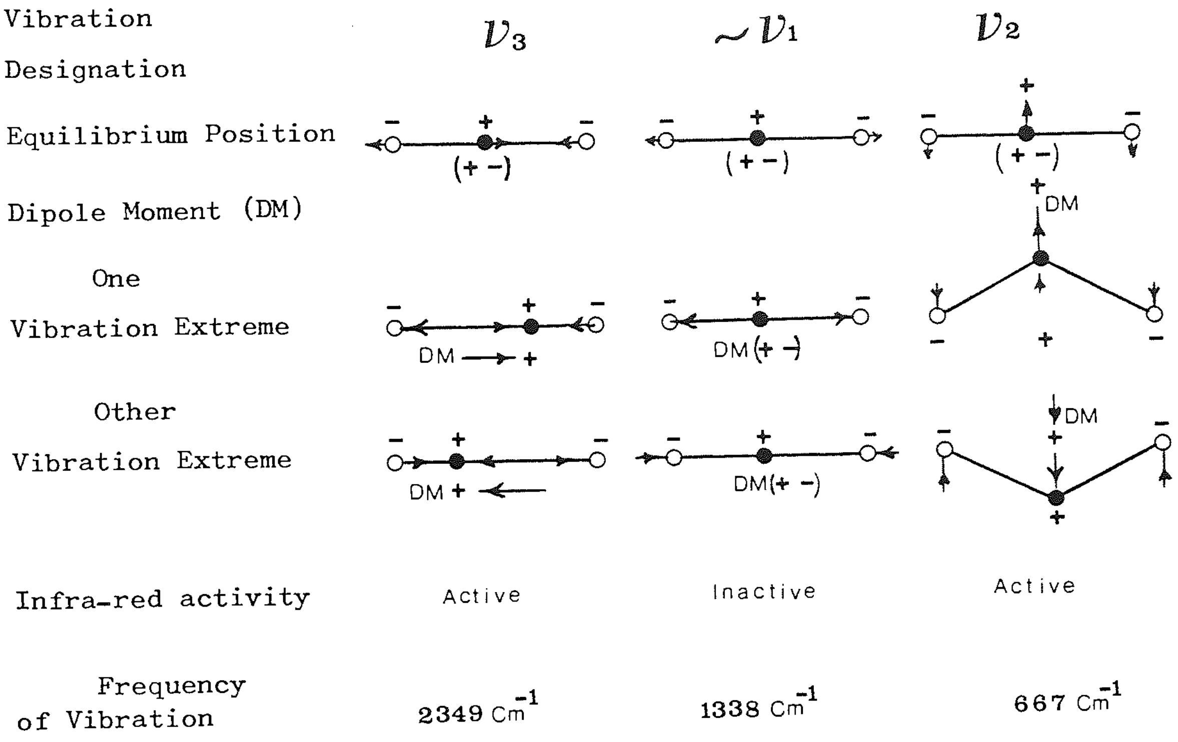


Fig 1.1. Fundamental vibrations of CO_2 and dipole moment changes.

Comparison of the energy level diagram of carbon dioxide with the isoelectronic carbon disulphide molecule shows that the highest occupied πg and πu orbitals of CO_2 are essentially below the corresponding species CS_2 molecule$^{(5)}$. In this view the first ionization potential of CO_2 (13.7 ev) is considerably greater than that of CS_2 (10.1 ev) thus CO_2 is the weaker donor of electrons with respect to CS_2. On the other hand carbon dioxide is specified by the lower energy of vacant orbital and therefore by the high electron affinity (about 3.8 ev). Thus one may expect that CO_2 in its reactions should be a comparatively poor donor and good electron acceptor. It should also be expected that upon excitation of the CO_2 molecule to the lowest excited state, or upon electron attraction, its configuration would change from a linear to non linear one.

The physical properties of carbon dioxide are given in table 1.1.

Melting point 56.6^{o} (5.2 atm)
Boiling point -78.5^{o} sublimes
Critical temperature 31.00^{o} $\pm$ .001
Critical pressure 75.282 $\pm$ 1 atm
Density 1.977 g l^{-1} gas
1.101 g cm^{-3} liq (-37^{o})
1.56 g cm^{-3} solid (-79^{o})
Solubility (100 cm^{3}) water, 0.385 g at 0^{o}
0.097 g at 40^{o}
0.058 g at 60^{o}
C = O bond length, 1.1632 A.
Bond dissociation energy, 127 kcal $mole^{-1}$
$\Delta H^{o}f$, 94.0518 kcal $mole^{-1}$
$\Delta G^{o}f$, 94.2598 kcal $mole^{-1}$
S^{o}, 1.061 cal deg^{-1} $mole^{-1}$
Ionization potentials, 13.79, 17.59, 18.07 and 19.38 eV
Dielectric constant, 10^{4} (ϵ - 1) = 9.88 at 0^{o}
Vapour point equation (liq), $p = a\left(\frac{T}{100} - b\right)^{n}$
p ($kg\ cm^{-2}$): $a = 7.856$, $b = 1.261$, $n = 3.917$

Table 1.1

As can be seen from table 1.1 carbon dioxide is very stable thermodynamically. Also critical temperature and pressure of carbon dioxide indicate that thermal reactions with the gas at positive pressure are possible but very high pressure of carbon dioxide are not available. Finally CO_2 is cheaply and readily available as a solid, therefore a wide range of experimental conditions are available for studies its reaction.

1.1.3 CHEMICAL REACTIONS OF CARBON DIOXIDE

The reaction of CO_2 with transition metal complexes and non transition metal compounds have been studied, and discussed in this chapter. Russian workers have made a large contribution to the current knowledge of complexes containing CO_2 and to the related ligand reactivity.(3,5,36) One important aspect of carbon dioxide reactions is homogenous catalytic processes with CO_2 participation. These reactions can be divided into two groups, one group includes the processes where carbon dioxide is the source for the synthesis of various organic compounds, the other group comprises reactions in which CO_2 is the ligand modifying the catalyst. Thus, the first group includes the synthesis of formic acid derivates via the hydrogenation of carbon dioxide with molecular hydrogen. The reaction of:

$$CO_2 \quad + \quad H_2 \rightleftharpoons HCOOH$$

is thermodynamically disadvantageous. For shifting the reaction to the right,one should bind the generating formate fragment or form a derivative, for example by its transformation to form amide or alkyl formate.(6)

Some examples of such a desirable transformation are given below:

$$CO_2 + H_2 + ROH \longrightarrow \left[HCOOR \quad \text{or} \quad RCO_2H \right] + H_2O$$

$$CO_2 + H_2 + R_2NH \longrightarrow HCO\ NR_2 + H_2O$$

$$CO_2 + H_2 + R_2C = CH_2 \longrightarrow R_2CH\ CH_2\ COOH$$

Some formates can be synthesized from alcohols, CO_2 gas and H_2 gas by a new catalytic combination of group VIII low valent complexes and tertiary amines. It has been shown that low valent or hydrido complexes especially those of Ru, Rh and Ir are more effective. Actually, Haynes, Slaugh and Kohnle have shown that a large number of the transition metal phosphine complexes are the catalyst for dimethyl formamide formation in the reduction of carbon dioxide with molecular hydrogen in the presence of dimethylamine (Table 1.2) (3,7).

Other secondary amine such as di-n-propylamine, pyrrolidine and piperidine, also are readily converted to the corresponding form-amide in the presence of e.g. $(Ph_3P)_3$ RhCl.$^{(7)}$

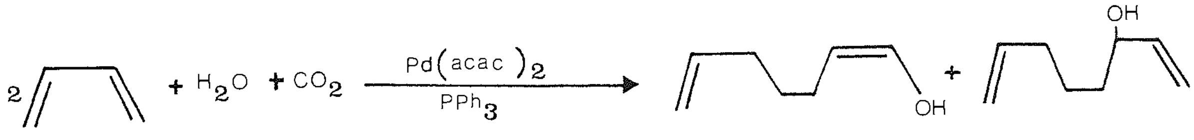
Results with primary amines varied. In some instances quaternery ammonium carbamates were formed while in other cases the anticipated N-alkyl formamides were produced. N-Ethyl formamide was obtained from ethylenamine at 125° in the presence of $(Ph_3P)_2CO_3Pt$. The author failed to extend this reaction to the synthesis of N, N´ - dimethyl thioformamide using carbon disulphide or carbon oxysulphide.

TABLE 1.2.

N, N-Dimethylamide Formation from Carbon Dioxide.

Catalyst	Amount of Catalyst, mmoles	$(CH_3)_2NH$, mmoles	Temperature °C	mmoles DMF/mmole of Catalyst
$(Ph_2PCH_2CH_2PPh_2)_2CoH$	1.08	138	100	5
$(Ph_2PCH_2CH_2PPh_2)_2$ CoH	0.05	131	125	1,000
$(Ph_3P)_3RhCl$	0.30	122	100	43
$(Ph_3P)_3RhCl$	0.02	138	125	>170
$(Ph_3P)_2(CO)RhCl$	0.38	144	100	1
$(Ph_3P)_2(CO)IrCl$	0.35	133	100	28
$(Ph_3P)_2(CO)IrCl$	0.2^c	138	125	1,200
$(Ph_3P)_2(CO_3)Pd$	0.79	159	100	120
$(Ph_3P)_2(CO_3)Pt$	0.70	155	125	104
$(Ph_3P)_3Pt$	0.56	155	125	19
$(Ph_3P)_3RuCl_2$	0.39	132	125	8
$(Ph_3P)_3CuCl$	0.63	133	100	8
$(Ph_3P)_3CuCl$	0.03	142	125	>900
$H_2PtCl_4 \cdot 6H_2O$	0.56	124	125	11

The following example can describe the modifying action(3) of carbon dioxide in the formation of octadienol from butadiene in the presence of water. The reaction of butadiene with water in the presence of $Pd(acac)_2$ - triphenyl-phosphine complex under argon gives octatriene as the main product. In the presence of carbon dioxide however, octadienols are the main products while octatriene is a by-product.



+ octadiene ethers

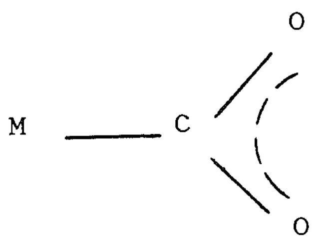
It can be noted that catalytically small amounts of carbon dioxide are sufficient for this reaction.

1.1.4 REACTION OF TRANSITION METAL COMPLEXES WITH CO_2

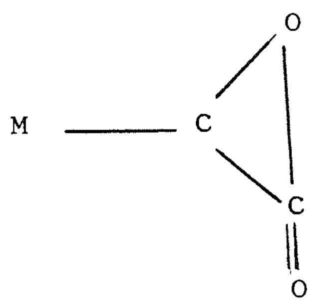
During the last few years there has been a considerable growth of interest in the reactions of carbon dioxide with transition metal compounds, primarily owing to the considerable advances made recently in the field of metal complex catalysis and in the first place in the activation of inert molecules (hydrogen, nitrogen, etc) which leads to the expectation that catalytic processes involving carbon dioxide will also be carried out successfully.(36)

Some complexes formed from CO_2 in reaction with low valent transition metals have been investigated(8-16) and CO_2 insertion into transition metal hydrogen,(17-21) Nitrogen(24,25) and Carbon(22,23) bonds has been observed.

Carbon dioxide displays several alternate modes of coordination with transition metal compounds- via oxygen by donation of the oxygen lone P electron pair to the vacant orbital of the metal, by electron donation from metal to the carbon orbital which results in type A or B(26) complexes or finally by way of π complex formation via C═O double bond.



Type A



Type B

The reactions mainly were studied in benzene, toluene, and tetrahydrofuran solution. Complexes containing CO_2 as ligand release CO_2 when heated or treated with acids.(26,27) It should be noted that in the majority of cases CO_2 reacts with other ligands to give products such as phosphine oxide, formate, carbonate, and carboxylate.

Two X-ray structural studies of CO_2 coordination complexes

$Ni(CO_2)(P(C_6H_{11})_3)_2 \cdot 0.75\ C_6H_5CH_3$ (28) (I) and

$\left\{ IrCl(C_2O_4)\left[P(CH_3)_3 \right]_3 \right\}$ (29) (II)

have been reported. It is note-worthy that both reports stressed the basicity of the metal centres in its reaction with CO_2. The IR spectrum of both complexes altogether with structural information and chemical reactions were studied and features of carbon dioxide acting as bidentate (type B) and mono-dentate (type A) ligand were assigned for complex (I) and (II) respectively. Unlike many other small molecules, carbon dioxide very rarely forms adducts with transition metals. Formation of elusive CO_2 complexes is normally followed by ready metal - promoted elementary transformations, which include dimerization, disproportionation, and deoxygenation of carbon dioxide.

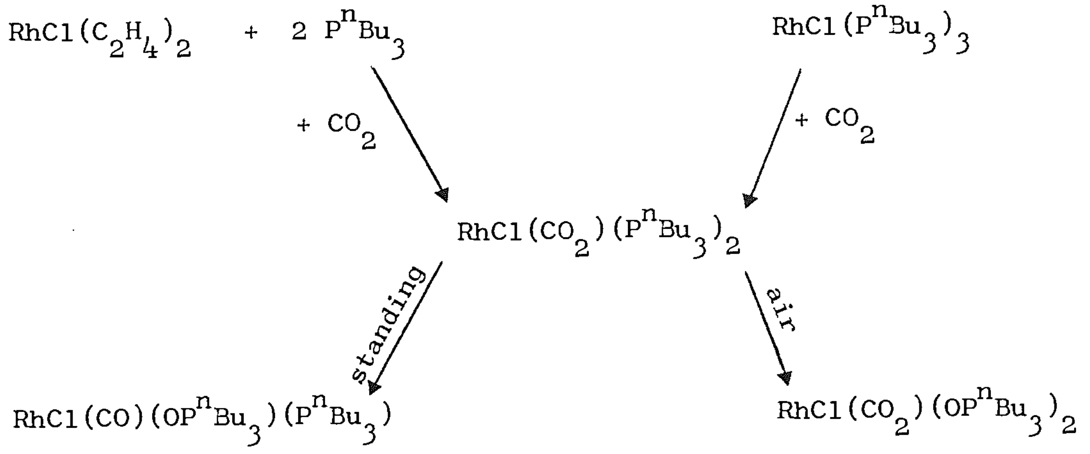
The infra-red data of some of the carbon dioxide adduct complexes with respect to their mode of bonding are classified in table (1.3). An inspection of these data shows that the assignment of a bonding mode is not straight forward and more structural analysis and information about their chemical reactivity and stability is needed. Aresta and Nobile have prepared the complex of $RhCl(CO_2)(PR_3)_2$ (III) and $RhCl(CO_2)(PR_3)_3$ (IV).

Table 1.3.

Assignment of infra-red bands (cm $^{-1}$)

Compound	ν(C=O)	ν_{asym}(CO)	ν_{sym}(CO)	π	
Class A					
$\{(Co[(Pr\text{-}Salen)])_2K_2(THF)_2(CO_2)_2\}_n$	1650 (s)	1280 (m-s)	1215 (s)	745 (s)	(30)
$Na[Co(Salen)CO_2]$	1680	1278	1213		(31)
$Na[Co(Salen)(CO_2)\cdot py]$	1700	1273	1208		(31)
$RhCl(CO_2)(PEt_2Ph)_3$	1670(vs) 1635(sh)	1255(m)	963(m)	780(m)	(26)
Class B					
$Ni(CO_2)(P^chex_3)_2\cdot 0.75C_7H_8$	1740(vs) 1698(w)	1150	1094	845	(32)
$Ni(CO_2)(PEt_3)_2$	1660(vs) 1635(vs)	1203(vs)	1009(s)	828	(32)
$Ni(CO_2)(P^nBu_3)_2$	1660(vs) 1632(vs)	1200(vs)	1008(s)	825	(32)
$RhCl(CO_2)(P^nBu_3)_2$	1668(s) 1630	1165(m)	1120(m)		(26)

On standing these compounds decompose yielding coordinated carbon monoxide and trialkyl phosphine oxide. The reaction can be represented as:



It has been found that these complexes with two phosphine ligands per rhodium are the more stable with respect to loss of carbon dioxide on evacuation. The instability of complex (IV) with respect to complex (III) may be due to steric effect produced by phosphine ligands.

The reaction of CO_2 with transition metal complexes may produce dimeric species. Although some of these complexes are known, no structural information on them is available. The following dimeric formulae for rhodium complexes have been reported:

$(PPh_3)_3\ RhCl(CO_2)(PPh_3)_2RhCl$, $Rh_2(CO)_2(CO_2)(PPh_3)_3 \cdot C_6H_6$ (33)

$Rh_2H_2(CO_2)(PPh_3)_6 \cdot C_7H_8$ (19), $(PPh_3)_3Rh_2\ (CO_2)_2(CO)_2 \cdot C_6H_6$ (12)

and $(PPh_3)_3\ Rh_2(CO_2)(CO)_2 \cdot C_6H_6$. (12)

The carbon dioxide in these complexes can be replaced by the action of heat, acid, better ligand or nitrogen stream.

The carbon dioxide adduct can be converted to other species. For instance treatment of $Ni(CO_2)(PCy_3)_2$ with O_2 at less than one atmosphere pressure, yields a peroxocarbonate complex of $Ni(C_2O_4)(PCy_3)_2$ or heating an iridium complex $Ir(dmpe)_2Cl.CO_2$ in closed system produces a new carboxylate complex. The more detailed information about this transformation is as follows.(27)

The IR spectrum of complex $Ir(dmpe)_2Cl.CO_2$ displays two strong bands due to the bound CO_2 at 1550 cm^{-1} and 1230 cm^{-1} as confirmed by isotope labelling. Heating a solution or suspension of this adduct at 120°C in a closed system transforms it to a solid with the same C, H, O analysis but with IR bands at 2180 and 1640 cm^{-1} replacing those mentioned above. The 2180 cm^{-1} band is assigned to ν Ir-H consistent with various other iridium(III) hydrides. The IR band at 1640 cm^{-1}, shown to be due to the bound CO_2 is assigned to ν C = O of mono-dentate carboxylate. Thus the above data suggest that a coordinated dmpe has been metalated and carboxylated. The simplest representation of this transformation is:

$$Ir(dmpe)_2Cl\ .CO_2 \xrightarrow{\Delta} \left[Ir(H)\ (Me(CH_2CO_2)\ (PC_2H_4PMe_2)(dmpe)\right]Cl$$

The structure of the product is not yet known.

The following examples consider the disproportionation reactions of carbon dioxide in which C-O bond cleavage is involved.

When the solid $Ni(CO_2)(P^{c}hex_3)_2 \cdot 0.75C_7H_8$ is heated at 83°C under argon, a mixture of products is obtained. This mixture includes $Ni(CO)_2(P^{c}hex_3)_2, CO_3^{=}$ and oxidation products of toluene, but no phosphine oxide. Similar cleavages with the transfer of oxygen to another component of the reaction system, seen when solutions are allowed to age, can be summarized in the following lines.(26,48,16)

$$RhCl(CO_2)(P^nBu_3)_2 \longrightarrow RhCl(CO)(OP^nBu_3)(P^nBu_3)$$

$$Fe(CO_2)(PMe_3)_4 \longrightarrow Fe(CO)_2(PMe_3)_3 \text{ , } Fe(CO)(PMe_3)_4 \text{ and } Me_3PO$$

$$Mo(CO_2)_2(PMe_2Ph)_4 \longrightarrow (PMe_2Ph)_3(CO)Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3$$

In the case of the rhodium complex cited above, reaction in the presence of air yields $Rh(CO_2)(OP^nBu_3)_2$. This product could either arise as a result of the reoxidation of the carbonyl or from the formation of a peroxo-carbonate intermediate.

Herskovitz and Guggenberger(29) report the preparation and structure of an iridium complex containing a C_2O_4 chelating ligand Fig (1.2) resulting from CO_2 uptake in benzene solution.

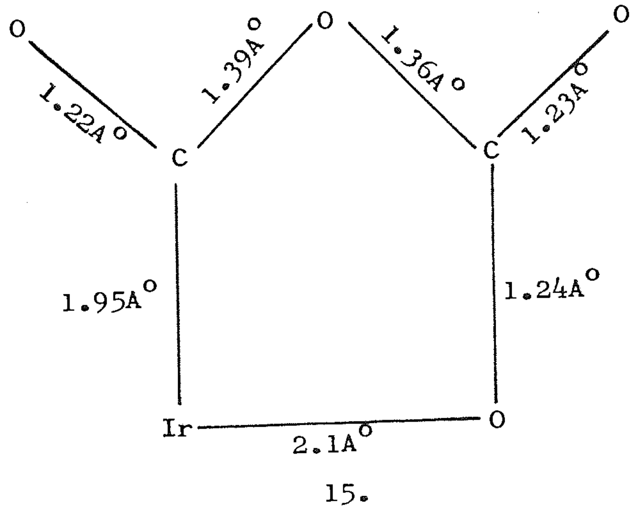


Fig 1.2.

$$\mathrm{Ir\ Cl(C_8H_{14})\ (PMe_3)_3 \xrightarrow{CO_2} Ir\ Cl(C_2O_4)\ (PMe_3)_3 \cdot 0.5C_6H_6}$$

on heating to 150° C this solid decomposes giving a mixture which includes a carbonyl and 1:1 Ir:CO_2 adduct. Thus the coupling of two carbon dioxide units can be reversed or can lead to what is presumably a disproportionation reaction.

Fachinetti, Floriani and co-workers$^{(43)}$ cite another reaction in which the C_2O_4 ligand is probably involved:

$$\mathrm{4\ Cp_2Ti(CO)_2 \ + \ 4\ CO_2 \longrightarrow \left[(Cp_2Ti)_2\ (CO_3)\right]_2 \ + \ 10\ \ CO.}$$

Where Cp represents the cyclopentadienyl ligand. When this reaction is carried out using $^{13}CO_2$ it is found that the carbonato ligands, and 20% of the liberated CO are labelled with ^{13}C. All the carbonate has been found by the disproportionation of carbon dioxide. An intermediate dimer of the type found by Herskovitz would explain such a result.

The following examples show the reaction of carbon dioxide with early transition metal complexes in toluene solution leading to deoxygenation or disproportionation and reduction.$^{(43)}$ The three reactions are shown as (a, b, c)

$$\mathrm{\left[Cp_2TiCl\right]_2 \ + \ CO_2 \ \xrightarrow[10\ atm]{90^{\circ}\ ,\ \ 18\ h} \left[Cp_2TiCl\right]_2O \ + \ CO} \qquad \text{(a)}$$

$$\mathrm{4\ Cp_2Ti\ (CO)_2 \ + \ 4\ \ {*}CO_2 \ \xrightarrow{52^{\circ},\ \ 2\,d} \left[(Cp_2Ti)_2\ ({*}CO_3)\right]_2 + 2{*}CO + 8CO} \qquad \text{(b)}$$

$$\mathrm{3\ Cp_2Zr\ (CO)_2 \ + \ 3\ CO_2 \ \xrightarrow{74^{\circ},\ \ 4d} (Cp_2ZrO)_3 \ + \ 9CO} \qquad \text{(c)}$$

The disproportionation of the CO_2 in (b) to CO and $CO_3^{=}$ has been verified by isotope labeling as shown, and the structures of the metal - containing products in (b) and (c) have also been determined.

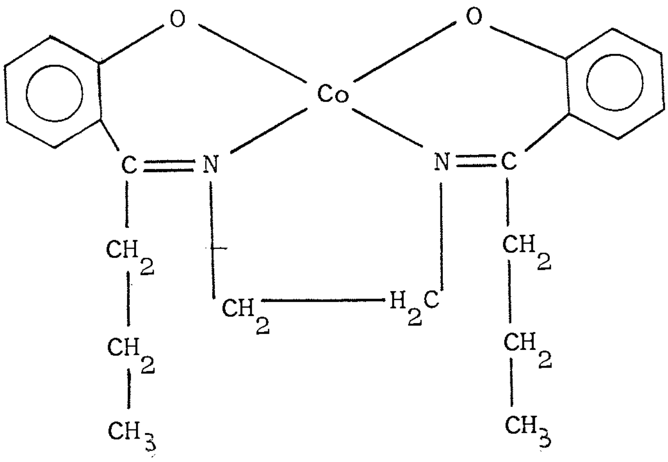
A report of the disproportionation and reduction of CO_2 by reaction with a variety of metal carbonyl anions has also appeared.$^{(49)}$ In particular, the reaction with CpFe $(CO)_2^-$ was studied, which proceeds as in (d).

$$2\,\overset{+}{Na}\left[CpFe(CO)_2\right]^{-} + 2\,CO_2 \xrightarrow{THF} \left[CpFe(CO)_2\right]_2 + Na_2CO_3 + CO. \quad (d)$$

A proposed mechanistic sequence involved stepwise coordination of two molecules of CO_2 to $CpFe(CO)_2^-$, followed by formation of Na_2CO_3 and transient formation of $CpFe(CO)_3^+$ which quickly reacts with more of the anion to form the dimer. Support for this mechanism comes from the observation that reaction with labeled CO_2 results in extensive and rapid incorporation of labeled CO in the product dimer.

The bifunctional nature of some metal complexes which contain transition metals in low oxidation state, along with alkali cation, could be taken into account as playing an unexpected role in carbon dioxide fixation. This hypothesis comes from the fact that in many simple reactions carbon dioxide seems to require for its activation, in addition to a basic centre, the assistance of an acidic partner. Many of these bifunctional complexes have been found to react with carbon dioxide e.g. the isolation of 1:1 Co (Salen) $NaCO_2$$^{(31)}$ adduct reported many years ago. Another example of this type ofreaction is as follows:

A deep green THF solution of Co(Pr-Salen)K (1) reacts with CO_2 (30) at room temperature and produces deep red crystals of Co(Pr-Salen)–KCO_2 (2) which releases carbon dioxide in vacuo giving back the starting deep green solution.



Co (Pr-salen)

$$\underset{(1)}{\left[\mathrm{Co\ (Pr\text{-}Salen)K}\right]} + \mathrm{CO_2} \overset{\mathrm{THF}}{\rightleftharpoons} \underset{(2)}{\left[\mathrm{Co\ (Pr\text{-}Salen)KCO_2 \cdot THF}\right]}$$

The structural analysis of complex (2) indicates the presence of intact carbon dioxide and the special bonding mode of carbon dioxide interaction with three metal centers (Fig 1.3), (34) which can be taken in support of the hypothesis that carbon dioxide fixation by complexes like Co (Salen) M involves concerted attack of the nucleophilic cobalt (I) on the electrophilic carbon of carbon dioxide while the acid partner M^+ interacts with the basic oxygen.

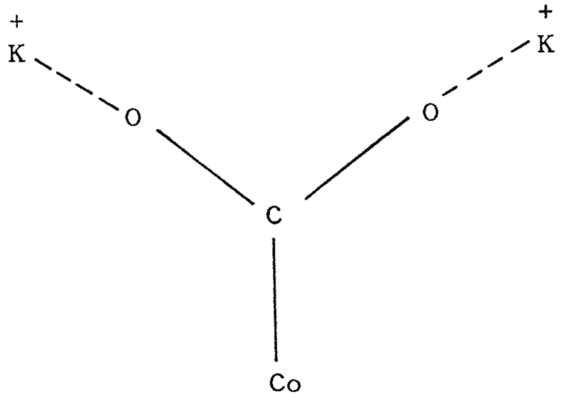


Fig (1.3)

The bonding of the carbon dioxide (CO_2 is C bonded to cobalt and O bonded to the two different K^+ ions) is bent as expected from an approximately SP^2 geometry around carbon. C - O bond lengths (1.24 and 1.22A^o are comparable with free CO_2 (1.16A^o) and with CO_2 η^2 C,O - bonded in $(Cy_3P)_2Ni(CO_2)$ (1.17 and 1.22A^o)

The interaction between metal d orbitals and carbon dioxide π bonding system may play an important role in CO_2 bond order reduction. Aresta and Nobile reported that the noticeable difference of $\bar{\nu}$(CO) between the penta-coordinate $Ir^{(I)}$ (1550 cm^{-1}) and Rh^I (about 1670 cm^{-1}) complexes can be explained taking into account that the lower energy of the $Ir^{(I)}$ d orbitals (with respect to Rh^I) can allow a greater π - bond back donation from the metal d orbitals to antibonding $2\pi_u$ CO_2. The important role played by the d orbitals energy is also demonstrated by the slight tendency of the $\left[Rh(L_2)_2\right]^+$ moiety to bind CO_2 under the same conditions as $\left[Ir(L_2)_2\right]^+$ in which L = $Et_2PC_2H_4PEt_2$.

Finally infra-red spectroscopy can be employed as one of the useful techniques to follow the reaction of carbon dioxide with the complexes of transition metals, because in most cases the IR spectrum of the product (reacted with CO_2) shows several new bands due to carbon dioxide coordination or insertion reaction compared with starting materials.

1.1.5 INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL - HYDROGEN BONDS

Depending on the polarity of the transition metal hydrogen bonds, carbon dioxide can be inserted either with formation of formate complexes (normal insertion) or of metal - carboxylic acids (anomalous insertion): (35,36)

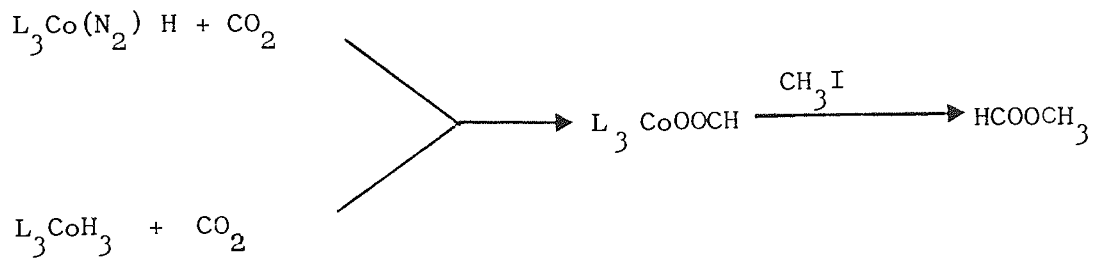
$$O = \overset{\delta+}{C^{+}} = \overset{\delta-}{O^{-}} + \overset{\delta+}{M^{+}} - \overset{\delta-}{H^{-}} \longrightarrow M - OO\,CH$$

$$O = \overset{\delta+}{C^{+}} = \overset{\delta-}{O^{-}} + \overset{\delta-}{M^{-}} - \overset{\delta+}{H^{+}} \longrightarrow M - COOH$$

The first reaction can serve as the basis of the catalytic reduction of CO_2 by molecular hydrogen with formation of formic acid derivatives, methanol, and other products. The reaction involving the formation of a metal-carboxylic acid can be of interest both for the synthesis of complexes of a new type and for the study of their properties, on the one hand and on the other hand for catalytic reactions involving the transfer of the carboxy group to olefines and acetylenes.

It is noteworthy that, when CO_2 is inserted in transition metal - hydrogen bonds with formation of both a formate complex and a metal carboxylic acid, the complex hydride may form a complex with a CO_2 molecule in the first stage, this being followed by insertion in the M - H bond. Thus, in a study of the kinetics of analogous insertion of carbon disulphide in the transition metal-hydrogen bond in the complex $(Et_3P)_2$ Pt (H) Cl, the authors showed that the complex $(Et_3P)_2$ Pt(H)Cl CS_2 is formed in the first stage.

The first carbon dioxide insertion into M - H bond giving formates was observed by Minso and Yamamoto(17,18) for the reaction of carbon dioxide with cobalt dinitrogen hydride complexes (L = PPh_3).



Recently Italian authors(23) have carried out a similar reaction for the corresponding iron compounds and a reaction of the same type of hydride complexes of osmium, iridium, and platinum, has also been observed. Such carbon dioxide insertion reactions into transition metal-hydrogen bond disclose possibilities for developing different catalytic processes and first of all homogenous hydrogenation of carbon dioxide in the presence of complex catalyst which has been discussed previously.

Low oxidation state and unsaturated coordination of the metal, high σ donor capacity and small bulk of the ligands, all are factors which condition the simple coordination or the insertion of carbon dioxide. In this latter case, the hydrogen atom bonded to the metal plays a fundamental role. In order to establish the influence of the nature and basicity of the ligands on the behaviour of hydrido complexes of transition metals toward carbon dioxide, some complexes of iron were considered with unchanging oxidation state and coordination number of the metal.

The following six-coordinate complexes of iron (II) were examined.

FeH_2L_4 (I) (L = $PMePh_2$, PMe_2Ph, PEt_2, $P(OEt)_2Ph$, $P(OEt)_3$; FeH_2L_2 (II) (L = $Ph_2-PCH_2CH_2-PPh_2$); $FeH_2(N_2)L_3$ (III) (L = $PEtPh_2$, $PBuPh_2$)

Complex I and II did not react with carbon dioxide either in solution or in the solid state. Where as complex (III) reacted with carbon dioxide giving rise to insertion products. The unsuccessful reaction of complex (I) and (II) seems to be ascribed more to the bulk of the ligands and to absence of easily accessible reaction site than to the basicity of phosphines. In solution, owing to solute-solvent interaction, the approach of carbon dioxide to the metal may occur. From this point of view, it is possible to hypothetize the following mechanism reaction scheme:

$$FeH_2\ (N_2)\ L_3 + L' \longrightarrow FeH_2\ (N_2)\ L_2\ L' + L \quad (L' = \text{solvent}) \qquad (1)$$

$$FeH_2\ (N_2)\ L_2\ L' + CO_2 \longrightarrow FeH_2\ (CO_2)\ L_2\ L' + N_2 \qquad (2)$$

$$FeH_2\ (CO_2)\ L_2\ L' \longrightarrow FeH\ (OCOH)\ L_2\ L' \qquad (3)$$

$$FeH\ (OCOH)\ L_2\ L' + CO_2 \longrightarrow FeH\ (OCOH)\ (CO_2)\ L_2 + L' \qquad (4)$$

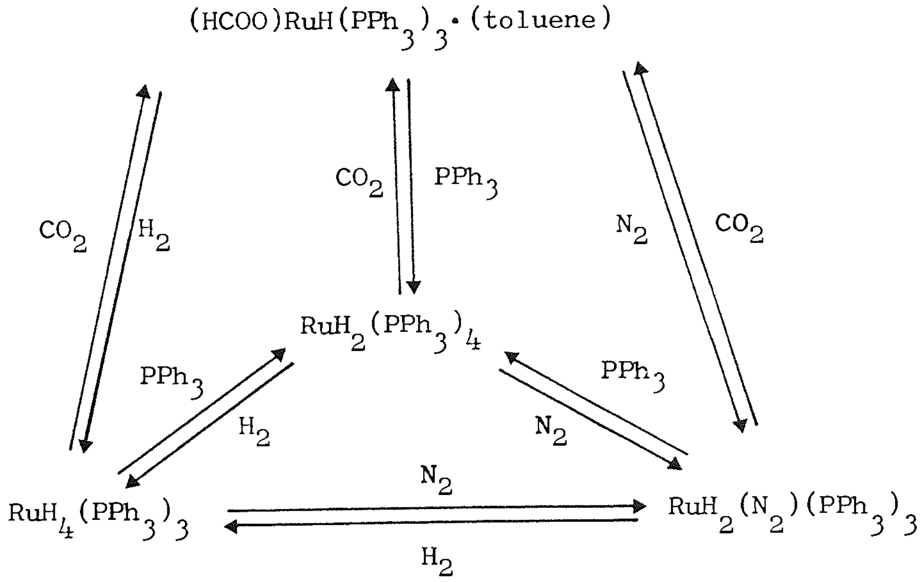
$$FeH\ (OCOH)\ (CO_2)\ L_2 \longrightarrow Fe\ (OCOH)_2\ L_2 \qquad (5)$$

This involves, at first, the loss of the phosphine and the coordination of the solvent. Then nitrogen is released and CO_2 merely coordinated to the metal. Finally, the real insertion of carbon dioxide takes place, successively into both Fe-H bonds, giving rise to diformate complex.

The reaction of carbon dioxide with complexes $RuH_2(PPh_3)_4$ (19) and $RhH(PPh_3)_4$ (42) may produce two different type of products. Volpin reported that $RuH_2(PPh_3)_4$ (I) gave $HRu(CO_2)(OMe)(PPh_3)_3$ on reaction with CO_2. (21,37) Another research group characterized the product as a formate complex of $(HCOO)RuH(PPh_3)_3$. (toluene) (II). The complex (II) was found to release carbon dioxide when treated with alkyl halide (eq 1) or heated at 140°C.

$$(HCOO)RuH(PPh_3)_3 \cdot \text{toluene} + RX \longrightarrow HRuX(PPh_3)_3 + RH + CO_2 + \text{toluene} \quad \text{(eq 1).}$$

The complex $RuH_2(PPh_3)_4$ reacts with nitrogen and hydrogen reversibily yielding $RuH_4(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$ which are ~~labile~~ towards CO_2 reaction according to the scheme given below:

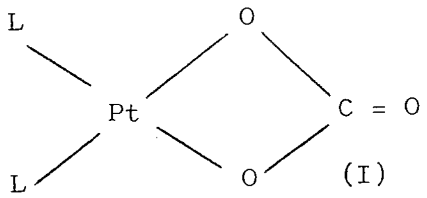


Tetrahydrido(triphenylphosphine)ruthenium (IV), (RuH_4 (PPh_3)$_4$,)was obtained as white or tan needles from (II) in benzene by contact with hydrogen in a sealed system at room temperature. Bubbling CO_2 into the toluene solution of the resulted tetra-hydro complex of ruthenium again gave (II), in which the presence of the formate was confirmed by IR spectroscopy.

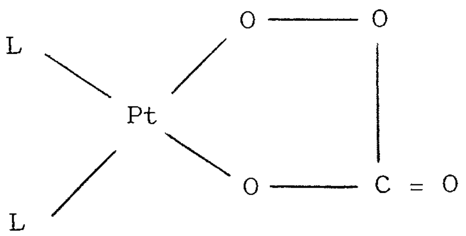
1.1.6 CARBONATE AND BICARBONATE COMPLEXES:

Although literally hundreds of carbonate - transition metal complexes are known isolable and well defined , analogous compounds containing bicarbonate as a ligand are at best scarce.

The reaction of carbon dioxide with (Ph_3P)$_3$ Pt or (Ph_3P)$_4$Pt in presence of oxygen yields carbonate(I), and peroxy carbonate (II) platinum complexes.(38) These compounds are also formed by the action of carbon dioxide on (Ph_3P)$_2$ PtO_2. The carbonate platinum complex may also be obtained from Ag_2 CO_3 and cis (Ph_3P)$_2$ $PtCl_2$ or by oxidation of carbon monoxide with oxygen coordinated at platinum.(3)



(I)



(II)

When L =PPh_3. Wilkinson etal have assigned the band in the IR spectrum of two compounds.(17)

Compound	νC = O	ν^{as}C-O	ν^{s}C-O	$\nu^{s}\pi$	νO-O	νM-O	νM-P
L_2PtCO_3	1685(VS)	1185	980	815	-	363	409
L_2PtOCO_3	1678(VS)	1243	978	836	780	305	429

The structure of the platinum carbonate complex was confirmed by x-ray analysis. The formation of the platinum carbonate complex from CO_2, O_2 and the zero valent platinum complex depends essentially on the nature of the coordinated ligand. Thus if the carbonate complex forms more easily in the case of the (Ph_3P) ligand than with $(P\text{-tolyl})_3P$ the formation of the complex occurs in a low yield and the complex does not form with $(p\text{-chloro phenyl})_3P$ as ligand. One of the uses of these carbonate complexes of platinum is as catalysts for the synthesis of dimethyl formamide from CO_2, H_2 and Me_2NH and in dimerization of 1, 3 butadiene to 1, 3, 7 cyclo octatriene.

Nakamoto et.al have studied in detail the IR spectra of cobalt carbonate complexes and found that C - O stretching modes of the monodentate complexes are observed at 1360 - 1380 cm^{-1} and 1450 - 1500 cm^{-1}, while the corresponding modes of bidentate complexes are at 1260 - 1290 and 1590 - 1640 cm^{-1}.

It is known that generally in the carbonates of small cations the three C - O distances are equal at 1.294Å. Distortion of the carbonate ion by hydrogen bonding is found in, for example, sodium bicarbonate (with C - O distances, 1.346, 1.263, 1.264Å), in basic carbonates the effect of the hydroxylion may be observed as producing either abnormal C - O distances (e.g. in basic lead carbonate $Pb_3(CO_3)_2(OH)_2$, all C - O distances 1.45Å) or in distortion (e.g. azurite $Cu_3(OH)_2(CO_3)_2$ with C - O distances 1.30, 1.27 and 1.24Å).(2)

The reaction of carbon dioxide with complexes of Iridium^{I} and Rhodium^{I} in ethanolic solution producing bicarbonate complexes has been reported(39) (eq.1) and the chemistry

$$(PPh_3)_2(CO)M(OH) + CO_2 \xrightarrow{C_2H_5OH} (PPh_3)_2(CO)M(OCO_2H) \qquad (1)$$

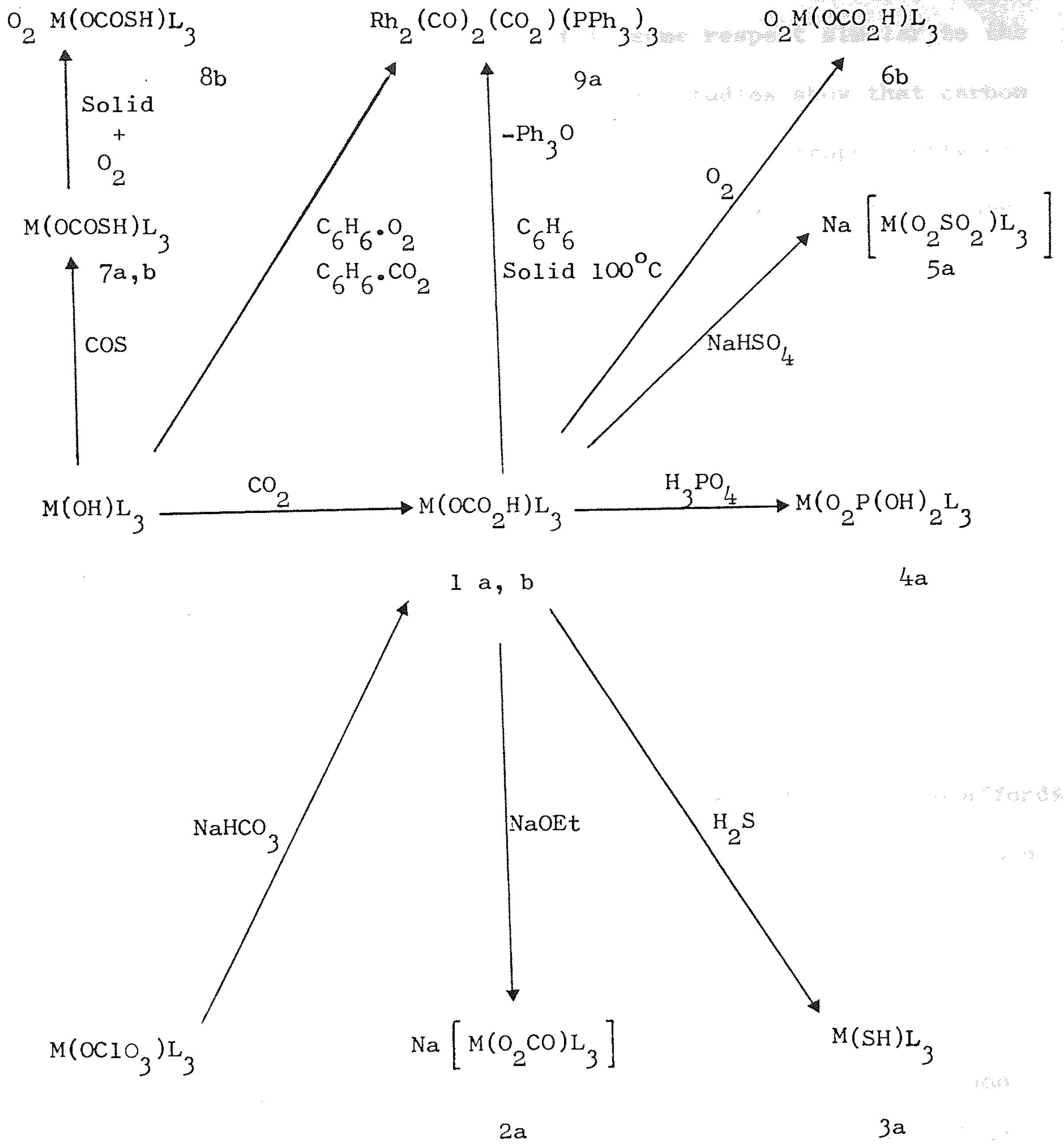
of the novel $MOCO_2H$ complexes together with the infra-red spectral data for the bicarbonate species and related complexes are given in scheme 1.1 and table 1.4 respectively. The constancy of the OCO_2H vibrations upon oxygenation of the Ir complex may be taken in support of monodentate OCO_2H in these present compounds.

No[b]	Complex[c]	ν(CO)(metal)[d]	ν(CO)(Carboxylate)[e]
2a	$Na[Rh(O_2CO)(CO)L_2]$	1940	1620(s), 1350(m), 1053(m)
1a	$Rh(OCO_2H)(CO)L_2$	1977	1655(s), 1368(s), 1290(s)br 1083(m)
1b	$Ir(OCO_2H)(CO)L_2$	1965	1655(s), 1368(s), 1285(s)br 1088(m)
6b	$O_2Ir(OCO_2H)(CO)L_2$[f]	2016	1655(s), 1368(s), 1285(s)br 1088(m)
7a	$Rh(OCOSH)(CO)(L_2)$	1973	1626(s), 1169(w), 1159(w), 1115(s)
7b	$Ir(OCOSH)(CO)L_2$	1959	19637(s), 1169(w), 1159(w), 1116(s)

Table 1.4 Principle IR spectral data (cm^{-1}) for selected complexes[a].

a. Measured in Nujol. b. See Scheme 1.1, [c] L = PPh_3 d. All very strong. e. several lower frequency spectral bands have been omitted

f. νIrO_2, 858m.



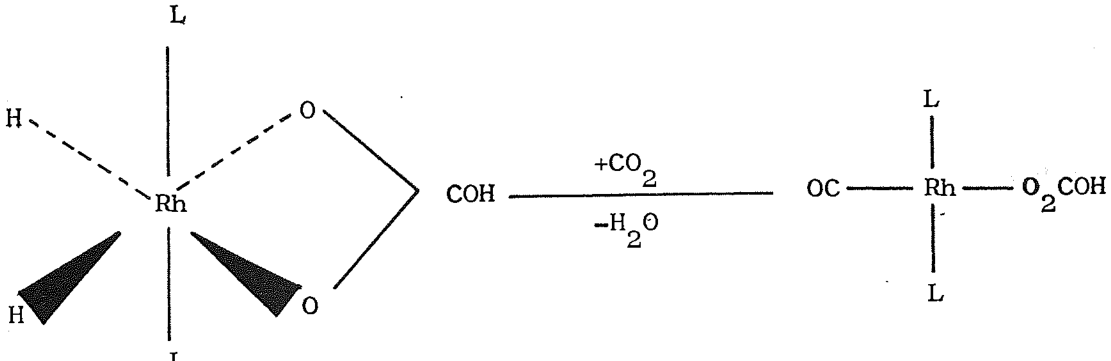
Scheme 1.1. $L_3 = (CO)(PPh_3)_2$. $M = Rh(a), Ir(b)$

Reaction medium is ethanol unless indicated otherwise.

The data for the OCO_2H complexes are sufficiently different from those of all known metal CO_3 associations but in some respect similar to the spectra of bicarbonate ion. While the cobalt studies show that carbon dioxide can only add to an hydroxy ligand and that nucleophilicity of this ligand determines the rate of gas uptake, it is hoped that planned mechanistic studies with labeled reactants will solve the problem for the four coordinated M (I) d^8 complexes.

The dihydrido bicarbonato complexes $RhH_2(O_2COH)L_2$(1-L=$P(i\text{-}Pr)_3$ 2-L=$PPh(t\text{-}Bu)_2$ 3-L=$P(c\text{-}C_6H_{11})_3$) can be obtained from the reaction of Rh^I hydride complexes $RhH(P(i\text{-}Pr)_3)_3$, $[RhH(N_2)(PPh(t\text{-}Bu)_2)_2]$ and $Rh_2H_2(N_2)(P(c\text{-}C_6H_{11})_3)_4$ with carbon dioxide. These dihydrido bicarbonato complexes 1 - 3 are the first η^2- bicarbonato compound reported from the reaction of CO_2, H_2O and low valent transition metal complexes. A similar reaction of $PdMe_2(PMe_3)_2$ with CO_2 and H_2O affords the η^1- bicarbonato compound trans $PdMe(O_2COH)(PMe_3)_2$. (Presence of H_2O may have an important role in the formation of carbonato complexes in non aqueous system).

The dihydrido bicarbonate complexes 1, 3 were found to reduce carbon dioxide to give the carbonyl bicarbonato complex and water according to the following equation:



The similar reaction with $RhCl(PPh_3)_3$, H_2 and CO_2 at high pressure and 100°C to give $RhCl(CO)(PPh_3)_2$ has also been observed.

1.1.7 INSERTION OF CO_2 INTO METAL-NITROGEN BOND:

The insertion of carbon dioxide into the metal - nitrogen $M - NR_2$ bond has been the subject of general investigation for many years. These reactions were found to proceed as shown in equation (1) and (2).(47) First the carbon dioxide molecule is fixed by the nitrogen electron pair and then the $M\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NMe_2$ bond is formed.

$$W(NMe_2)_n + nCO_2 \longrightarrow M(O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NMe_2)_n \qquad (1)$$

$M = Ti, Zr, V, Mo \qquad n = 4$

$M = Nb, Ta \qquad n = 5$

$M = Bi \qquad n = 3$

$$W(NMe_2)_6 + 3CO_2 \longrightarrow W(NMe)_3(O_2CNMe_2)_3 \qquad (2)$$

Early transition metal N, N - dimethyl carbonato compounds show strong IR absorption in the region 1690 - 1550 cm^{-1} attributed to a stretching mode of the NCO_2 moiety. From infra-red studying of these compounds two different forms of bidentate and monodentate Me_2NCO_2 can be distinguished. For instance a comparison of the infra-red spectra of $Nb(O_2CNMe_2)_5$ with those of the presumed eight coordinated $Zr(O_2CNMe_2)_4$ and the known six coordinate $W(NMe_2)_3(O_2CNMe_2)_3$ suggests that

$Nb(O_2CNMe_2)_5$ has both mono-dentate and bidentate $Me_2N\overline{CO_2}$ ligand. See table 1.5.

Table 1.5. Infra-red absorption maxima in the 1690 - 1550 cm^{-1} region characteristic of ν str (NCO_2).

Compound	$\nu str N^{12}C^{16}O_2$	$\Delta^{13}C^a$	$\Delta^{18}O_b$
$Zr(O_2CNMe_2)_4$	1594	29	4
$W(NMe_2)_3(O_2CNMe_2)_3$	1640	43	23
$Nb(O_2CNMe_2)_5$	1616 1685	24 40	0 25

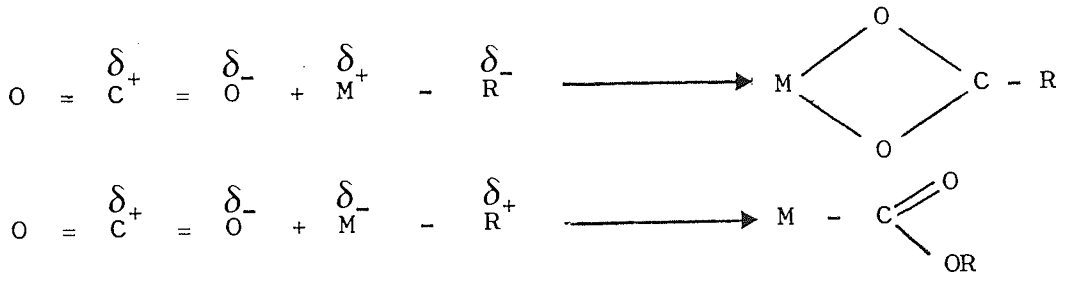
a $\Delta^{13}C = \nu$ str $(N^{12}C^{16}O_2) - \nu$ str $(N^{13}C^{16}O_2)$. b $\Delta^{18}O = \nu$ str $(N^{12}C^{16}O_2) - \nu$ str $(N^{12}C^{18}O_2)$.

To confirm the infra-red data other techniques of structural determination such as X-ray have also been employed. Most of the carbamato products are known to be labile with respect to carbon dioxide exchange$^{(25)}$. Thus when reaction of CO_2 with $Nb(O_2CNMe_2)_5$ was studied by nmr in toluene-d_8 significant concentration of $Nb(O_2CNMe_2)_4(NMe_2)$ were observed unless a positive pressure of CO_2 was used. The kinetic studies of these reactions are in progress.

1.1.8 INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL - CARBON BOND:

The insertion of CO_2 in a M - C bond is well known and has been used$^{(36)}$ successfully in the chemistry of non-transition metals. However, reports of the insertion of gaseous CO_2 in a transition metal - carbon bond have appeared only very recently. Furthermore, such reactions are of great interest because they lead to the possibility of introducing CO_2 into catalytic and synthetic processes.

As in the reaction where CO_2 is inserted in a transition metal - hydrogen bond, when it is inserted in a transition metal - carbon bond, two pathways may obtain - the normal pathway with formation of carboxylate complexes and the anomalous pathway with formation of metal - carboxylate esters.



The normal insertion of CO_2 in transition metal - carbon σ bonds has been described for titanium, zirconium, zinc, cobalt, rhodium and copper compounds.

Insertion of carbon dioxide into the methyl - copper bond of methyl bis(triphenylphosphine)copperetherate, (I) to give acetobis(triphenylphosphine)copper, $(CH_3COO)Cu\ (PPh_3)_2$ (II) and its carbon dioxide adduct, aceto(carbondioxide)bis(triphenylphosphine)copper, $(CH_3COO)Cu(CO_2)(PPh_3)_2$ (III) has been reported.

The acetate complex (II) can also be prepared by treatment of I(9) with, acetic acid.

$$\left.\begin{array}{l} CH_3Cu\ (PPh_3)_2 \cdot (ether)_{\frac{1}{2}} + CO_2 \\ \\ CH_3Cu\ (PPh_3)_2 \cdot (ether)_{\frac{1}{2}} + CH_3COOH \end{array}\right] \longrightarrow (CH_3COO)\ Cu\ (PPh_3)_2$$

On prolonged bubbling of carbon dioxide into the tetrahydrofuran solution of (I) at room temperature the complex (II) which first formed dissolved again and another copper complex, (III) precipitated as heavy white crystals.

The carboxylate copper (I) complexes without coordinated CO_2 can be generally prepared by the reaction of CO_2 with alkyl copper complexes(10) at 0°C in THF according to the scheme given below.

$$R\ Cu\ Ln + CO_2 \xrightarrow[-20^{\circ}C \quad to \quad 0^{\circ}C]{} (RCOO)\ Cu\ (PPh_3)_2 \qquad (3)$$

(3a) Ln = $(PPh_3)_3$, $(PPh_3)_2 \cdot 0.5\ Et_2O$; R = Me

(3b) Ln = $(PPh_3)_2$; R = Et

(3c) Ln = $(PPh_3)_2$; R = n - Pr

(3d) Ln = $(PPh_3)_2$; R = i - Bu

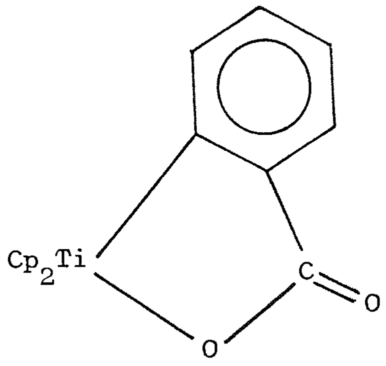
Insertion of carbon dioxide into rhodium-carbon bonds has also been investigated. Carbon dioxide reacts with $(PPh_3)_3RhPh$ at room temperature under pressure to form red crystals of $(Ph_3P)_3RhOOC\ Ph$.(44)

The same complex can be obtained from the reaction of benzoic acid and $(PPh_3)_3RhOH$. The IR spectrum of $(Ph_3P)_3Rh$ OOCPh shows the absorption bands characteristic of transition metal carboxylate complex:

ν(OCO) as 1608s and 1570s and ν(OCO)s 1360vs (cm^{-1})

It should be noted that the insertion of carbon dioxide into the rhodium carbon σ bond occurs easily only for monovalent rhodium compounds. An attempt to obtain rhodium carboxylate complexes by action of carbon dioxide (pressure 30 at, temperature 20 - 100°C) on the complexes $L_3\overset{(III)}{Rh}(C_2H_5)Cl_2$, $L_3\overset{(III)}{Rh}Cl(I)CH_3$ and $L_3\overset{(III)}{Rh}Cl(I)C_2H_5$ (where L = PPh_3) was unsuccessful.

Insertion of carbon dioxide into a metal carbon bond of a phenylene titanium species is believed to occur in the reaction of CO_2 with $(Cp_2TiPh_2)^{(23)}$ yielding $(Cp_2TiPhCO_2)$.



Carbon dioxide insertion into the metal carbon bond forming an ester species M-C(O)OR is also known to occur, although less commonly.

1.1.9 REACTION OF CO_2 WITH NON TRANSITION METAL COMPOUND:

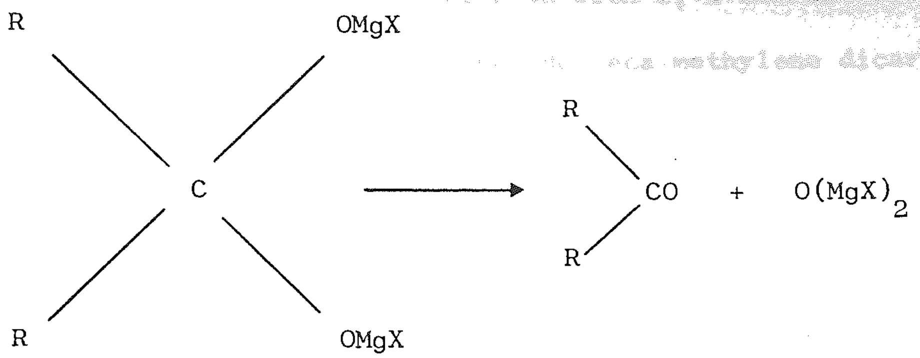
a) REACTION WITH GRIGNARD REAGENTS:

The reaction between carbon dioxide and alkylmagnesium halides is an important laboratory method for synthesizing carboxylic acids. Grignard reagents react very readily with carbon dioxide.(45)

$$RMgX + CO_2 \longrightarrow RCOOMgX$$

These mixed magnesium salts are readily hydrolyzed by treatment with dilute mineral acids to liberate the carboxylic acid. While this reaction is widely used, the yields of acids are theoretical only in special cases and that only under very favourable conditions. This is because the carbon dioxide is quite insolu ble in the ether solution of the Grignard (especially before saturation). Thus the Grignard is always present in excess, and side processes are thus very frequent. In particular, the nascent mixed magnesium salt of the carboxylic acid can react with another molecule of Grignard reagent:

Now, the resulting dimagnesium compound can be decomposed with water or acid to obtain a ketone,tertiary alcohols are also occasionally found in the products. Their presence is explained by the fact that the dimagnesium compound decomposes spontaneously to a ketone and a magnesium oxyhalide:

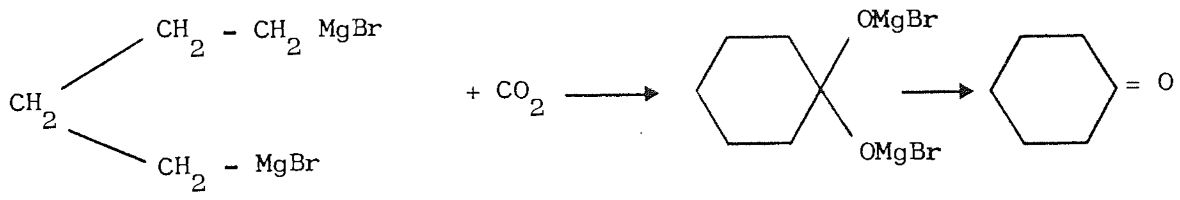


The ketone then reacts with a third Grignard molecule:

$$R\ MgX + R_2CO \longrightarrow (R)_2C\begin{matrix} OMgX \\ R \end{matrix}$$

Thus Gilman and John (45) obtained a 46% yield of triphenyl carbinol by passing carbon dioxide through a hot solution of phenylmagnesium bromide (in benzene; 9 hours). Under special conditions; it was also possible to obtain benzophenone (20% yield).

Dicarboxylic acids can be obtained by CO_2 treatment of dimagnesium compounds obtained from dihalo paraffins. It should be noted that magnesium derivatives of 1, 4 dibromobutane and 1,5 dibromopentane show a tendency to form five and six membered rings, i.e.:



Moreover, the condensation induced by magnesium (Wurtz reaction) produces dicarboxylic acids with a larger number of carbons.

Thus Braun and Sobecki,(45) who started with 1, 4 dibromo butane, reported the formation of sebacic and even do-deca-methylene dicarboxylic acids.

b) REDUCTION WITH LITHIUM ALUMINUM HYDRIDE:

An extensive study has been made of the reaction of carbon dioxide with lithium aluminum hydride forming methanol. Side reactions have been reported to give formic acid, formaldehyde and methyl formate. It has been suggested that the reduction of carbon dioxide may proceed first to a formate, then to the methylene glycol salt, and finally to the alcoholate. Thus at least three reactions seem possible, each of which represents a definite degree of reduction.(46)

$$4\ CO_2 + LiAlH_4 \longrightarrow LiAl(OCH_3)_4 \qquad (1)$$

$$2\ CO_2 + LiAlH_4 \longrightarrow LiAl(OCH_2)_2 \qquad (2)$$

$$4\ CO_2 + 3\ LiAlH_4 \longrightarrow LiAl(OCH_3)_4 + 2\ LiAlO_2 \qquad (3)$$

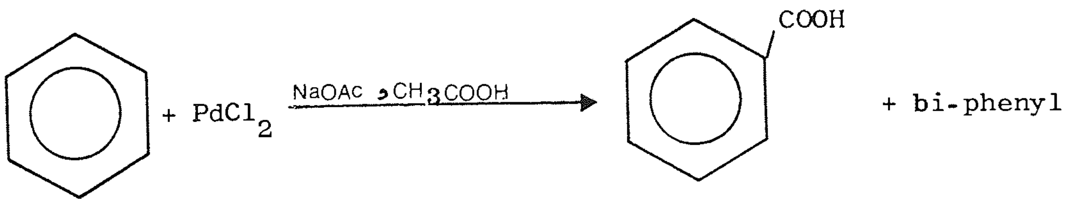
Hydrolysis or alcoholysis of the salts would give formic acid, formaldehyde or methanol. The plausibility of the suggested mechanism has been strengthened in this work by the proportion of formic acid in good yield according to equation (1). A similar reduction of carbon dioxide to formate in yields of 69 - 88% has been accomplished with lithium borohydride although the reaction takes a different course with the formation of diborane as a by product.

1.1.10 REACTION OF THE ORGANIC MOLECULES WITH TRANSITION METAL COMPLEXES VIA CO_2 ELIMINATION:

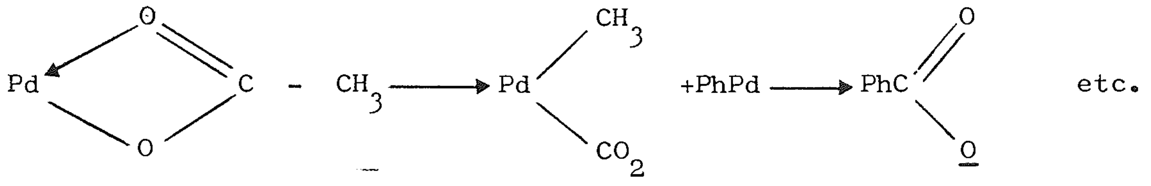
Here we discuss briefly a rather wide number of reactions involving CO_2 elimination$^{(3)}$ and consider only two groups of them: 1) - decarboxylation of acids and 2) - oxidation of the carbonyl group in organic molecules to CO_2 with transition metal oxo complexes or oxidation of a CO ligand at the transition metal atom to CO_2 by organic molecules containing active oxygen. One may assume that the occurrence of such reactions is caused by intermediate formation of a transition metal complex with CO_2 that could be more or less tightly bound to the metal. In a number of cases, the study of such reactions may provide convenient routes to the synthesis of transition metal - carbon dioxide complexes.

Carboxylic acids may undergo decarboxylation under mild conditions in the presence of transition metal complexes. Thus, Coffey$^{(3)}$ has demonstrated the decarboxylation of acetic acid in the presence of transition metal complexes. This was confirmed by means of decomposition of the carbon labeled acetic acid.

Such carbon - carbon bond cleavage may take place also in carboxylation of an aromatic system in the presence of palladium salts:



It is most probable that the benzene C - H bond cleavage occurs at the palladium atom and the rupture of the C - C bond of acetic acid follows with formation of a Pd - COO fragment and subsequent transfer of the - COO - group to a phenyl radical.



Decarboxylation has been employed widely in the synthesis of organo metallic compounds. Recently this reaction has been extended to the synthesis of the organometallic compounds of copper, gold, silver and nickel.

It has been reported that the intermediates produced in the decarboxylation of copper compounds and in the Ullmann reaction are of the same nature. In the case of decarboxylation of copper pentafluoro benzoate, copper pentafluorophenylis formed, which may be isolated in the form of brown powder:

$$C_6F_5\ COO\ Cu \xrightarrow{60^{o}C} C_6F_5Cu\ \ \text{quinoline}\ \ + CO_2$$

Basic solvents and the electron donor subsitutents facilate the decarboxylation. The organo copper compound may also act as selective catalysts for decarboxylation. The decarboxylation of CF_3 COO Ag gives CF_3 Ag, while that of Ph_3P Au $OOCC_6F_5$ at 120° produces $Ph_3PAuC_6F_5$. In boiling toluene the compounds $L_2Ni\ (OOCR)_2$ are decarboxylated to

L_2NiR_2, L = bipyridyl, phenanthroline and R = C_6F_5, p-Me OC_6F_4, etc. It has been shown that CO readily oxidizes to CO_2 with dimethyl sulfoxide in the presence of univalent copper. Later it was shown that $Fe(CO)_5$ reduces sulfoxides to the respective sulphides with evolution of carbon dioxide. Finally, there are a large number of other reactions with participation of transition metal compound that result in carbon dioxide elimination. They may be regarded as reactions somewhat the reverse of CO_2 insertion at a transition metal - element bond.

CHAPTER II

INTRODUCTION

2.1.1 DINITROGEN COMPLEXES OF COBALT

There is probably more confusion in the literature concerning cobalt dinitrogen complexes than those of any other element, and it is doubtful whether the situation is yet completely clarified.(50,51)

The discovery of cobalt dinitrogen complexes seems to have been made independently in three laboratories. The first paper to appear on this system was by Yamamoto who described the synthesis of $Co(N_2)(PPh_3)_3$ by way of the reduction of cobalt (III) acetylacetonate with diethyl aluminum ethoxide in the presence of triphenylphosphine in ether or toluene under dinitrogen. The infra-red spectrum exhibited a strong band at 2088 cm^{-1}, and liberated the calculated amount of dinitrogen on warming to $80^{o}C$.(50,52) There is no mention of infra-red bands assignable to ν (Co-H) or of dihydrogen produced on thermal decomposition.(50) Subsequently, Yamamoto etal(53) reported on some exchange reactions of this complex and were able to establish reversible equilibria with hydrogen, ethylene, etc.(54)

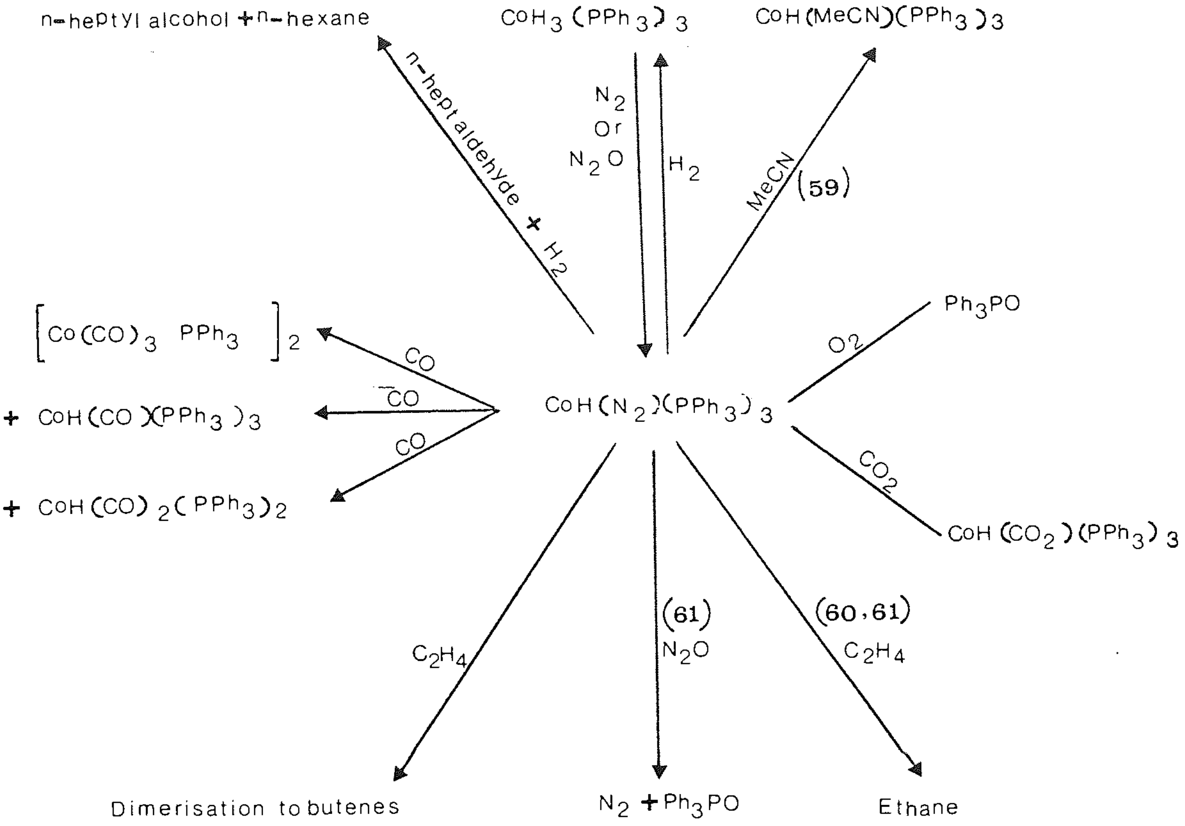
Minso et.al(54,55) were working simultaneously on an identical system except that triisobutyl aluminium was used as the alkylating agent. Thermal decomposition of their product yielded hydrogen as well as nitrogen and they concluded that two products $(Ph_3P)_3\ CoN_2$ and $(Ph_3P)Co(N_2)(H)$ were formed. Replacing hydrogen by nitrogen atmosphere the compound $(Ph_3P)_3CoH_2$ has been isolated. Thermal decomposition of this product at 77^{o} in vacuo yielded hydrogen and benzene.(56)

The diamagnetic property of this complex suggests a dimeric structure, however this structure could not be confirmed by molecular weight determination. Also the infra-red spectrum showed three bands at 1755 cm^{-1}, 1900 cm^{-1} and 1935 cm^{-1}, where-as the symmetrical dimeric structure requires only one infra-red active band.

The above details are more consistent with a cobalt (III) trihydride structure such as $(Ph_3P)_3\ CoH_3$. The high field quartet in the ^1H NMR spectrum of this tri-hydride complex is comparable with the NMR spectrum of $(Et_2PhP)_3\ IrH_3$ which was found to show a high field quartet.(54) Finally a third group of workers (Sacco and Rossi) described the preparation of cobalt (III) tri-hydride by the reduction of $(Ph_3P)_2CoX_2$ (X = Cl, Br or I) with borohydride in ethanol in the presence of free triphenylphosphine in an atmosphere of hydrogen or argon.(57,50,54) However the infra-red spectrum exibited only two bands in the metal-hydrogen stretch region, at 1745 cm^{-1} and 1933 cm^{-1}. This complex readily and reversibly reacts with nitrogen to form a nitrogen hydrido complex with elimination of hydrogen.

$$CoH_3\ (PPh_3)_3 + N_2 \rightleftharpoons CoH(N_2)(PPh_3)_3 + H_2$$

In the following scheme some reactions of trihydridotris(triphenylphosphine)cobalt(III) and its related dinitrogen complex are summarized.(58)

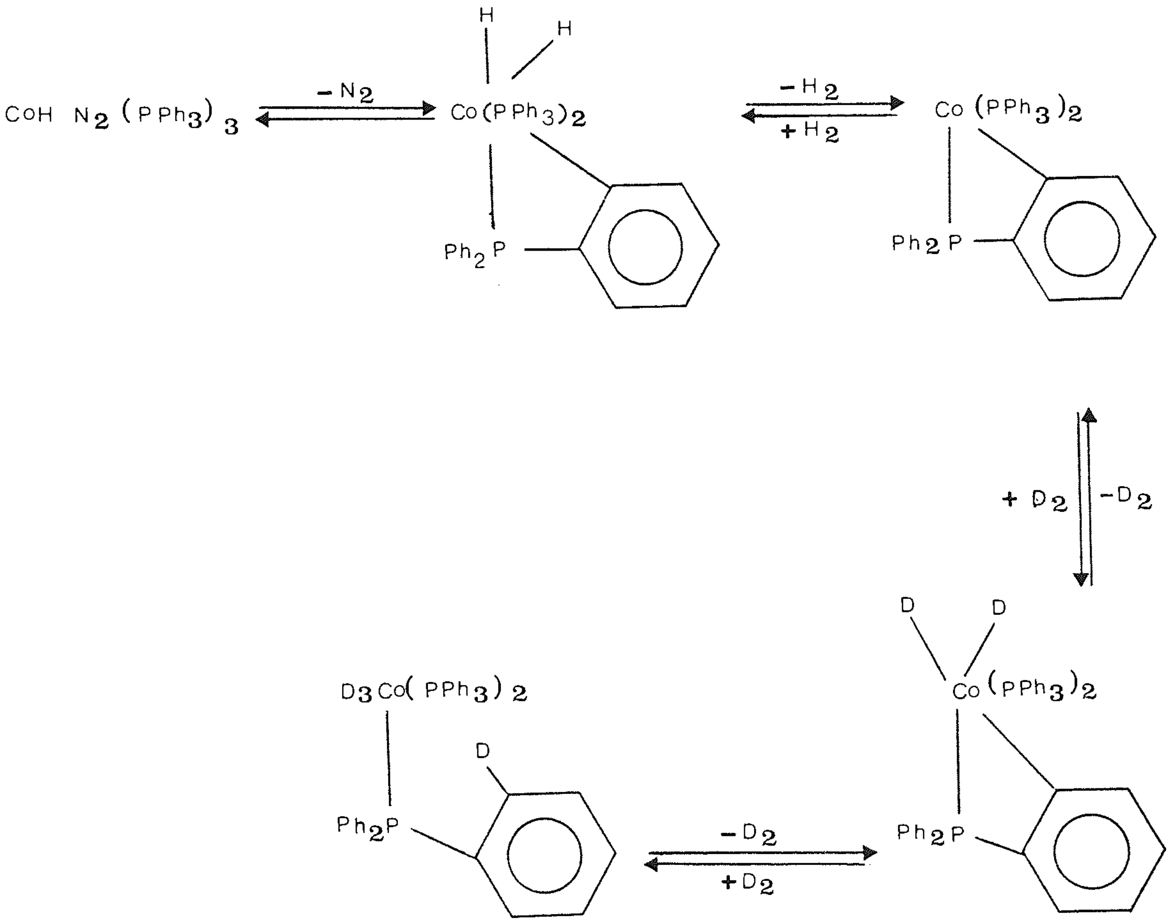


The complex $CoH(N_2)(PPh_3)_3$ is not very stable in air. Even in the solid the coordinated dinitrogen can be displaced reversibly by H_2, NH_3, C_2H_4, MeCN and EtCN.(50) The compound reduces aldehydes to alcohols and catalyses the dimerization of ethylene and propylene at 0°C. The compound reacts with nitrous oxide in the presence of PPh_3 to form $OPPh_3$ catalytically. On the other hand the trihydride $CoH_3(PPh_3)_3$ reacts with nitrous oxide to form the dinitrogen complex. Carbon monoxide reacts irreversibly with the dinitrogen complex, depending on conditions producing $[Co(CO)_3(PPh_3)]_2$, $CoH(CO)(PPh_3)_3$ and $[CoH(CO)_2(PPh_3)_2]$. Carbon dioxide in toluene at 0°C yields an uncharacterized cobalt formate and $Co(CO)(PPh_3)_3$. The dinitrogen complex reacts with hydrogen chloride to give first green $CoCl(PPh_3)_3$

and then blue $CoCl_2(PPh_3)_2$. Ammonia reacts reversibly with the dinitrogen complex and releases nitrogen.(13)

$$CoH(N_2)(PPh_3)_3 + NH_3 \rightleftarrows CoH(NH_3)(PPh_3)_3 + N_2$$

The facile H/D exchange reactions of $CoH(N_2)(PPh_3)_3$ were described by Parshall according to the following route.(50)



Using Yamamoto's method of $CoH(N_2)(PPh_3)_3$ preparation Ibers. et. al were once able to obtain crystals which were suitable for an X-ray study. The complex crystallized as $(Ph_3P)_3\ CoN_2(H)\cdot Et_2O$ and showed infra-red bands at 2085 and 2105 cm^{-1}, which may be due to resolution of the metal hydride band from the N ≡ N stretch.(54) Unfortunately the complex decomposed before sufficient data could be obtained for a very refined structure. However there seems no doubt that nitrogen is coordinated in an approximately linear manner and that there is sufficient space, trans to the nitrogen for a hydride ligand to reside without any steric interference.

A drawing of the coordination about the cobalt atom appears in figure (2.1.1) together with selected bond distances and angles.[67] The coordination about cobalt is best described as trigonal-bi-pyramidal, with the cobalt atom 0.3Å above the equatorial plane of the phosphorus atoms, and with one apical site apparently vacant.

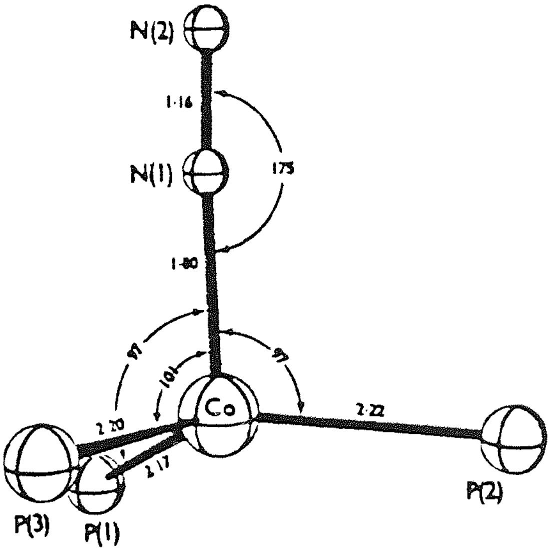


Fig (2.1.1) Coordination about the Co atom.

The P-Co-P angles are:

P(1)-Co-P(2)=115.5°, P(1)-Co-P(3)=114.6° ,

and P(2)-Co-P(3)=123.3°, all ± 0.6°.

2.1.2 OXYGEN CARRIER COMPLEXES

Certain metal complexes provide the delicate balance required to form adducts with dioxygen without the metal (M) or the ligands (L) being irreversibly oxidized. Such systems are known as oxygen carriers. The equation for adduct formation is written as an equilibrium process.(63)

$$nM\ (L) + O_2 \rightleftarrows \left[M\ (L) \right]_n \cdot (O_2)$$

$n = 1$ or 2

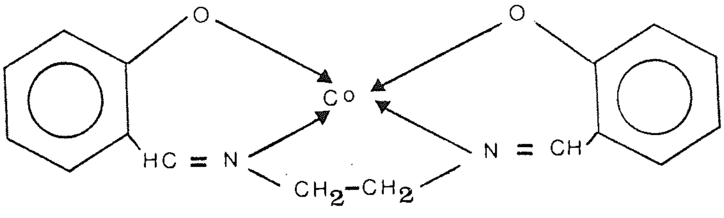
To be classified as an oxygen carrier, it is necessary that the reverse reaction i.e. the dissociation of the dioxygen complex to give M (L) and O_2 be observable. In practice this process can be observed by lowering the partial pressure of O_2, by heating the complex, or by the addition of a ligand capable of replacing the bound oxygen.

Synthetic reversible oxygen carring chelates have been of interest as model compounds in the study of the reversible oxygenation mechanisms involved in the very complex natural oxygen carriers such as hemoglobins, and as a means of separating molecular oxygen from the air.(64) The first example of a synthetic reversible oxygen carring chelate was prepared in 1933 by Pfeiffer, Breith, Lubbe and Tsumaki,(65) who observed that the red brown crystals of bis(salicylaldehyde)ethylenediimine cobalt(II) darkened on exposure to air. However, it was not until five years later that Tsumaki proved that the colour change was due to reversible absorption of molecular oxygen. Since then a large number of bis(salicylaldehyde)iminecobalt(II) derivative have been prepared and examined for oxygen carring properties.

The red complex of cobalt-di-(salicylal)-ethylene-diimine obtained from aqueous alcohol was recrystallized from benzene and from chloroform by Tsumaki.(65) From benzene he obtained red brown needles which were slowly oxygenated in air and would, when heated to 100°, return to their original colour and weight. From chloroform he obtained shining dark-red prisms which contained one solvated chloroform molecule. By heating the dark-red prisms to 100° they changed to a red brown powder which would absorb oxygen much more rapidly than the needle-like crystals. They would become black after a day and reach a constant weight. The black powder would lose its oxygen easily when heated in stream of carbon dioxide and return to its original colour and weight. The black compound contained one mole of oxygen to three molesof cobalt.

Carbon dioxide reacts with Co(salen) Na, obtained by controlled reduction of the corresponding cobalt (II) compound Co(salen), with sodium.

The green solution of Co(salen)Na in tetrahydrofuran absorbed one mole of(66) carbon dioxide per cobalt atom in a few minutes at room temperature giving a brown solid insoluble in THF.



Co(salen)

$$\text{Co (salen) Na} + CO_2 \overset{\text{THF}}{\rightleftharpoons} \text{Co (salen) } CO_2 \text{ Na} \qquad (1)$$

(A) (B)

The suspension so obtained lost carbon dioxide in vacuo at room temperature in a few minutes, reverting to the green solution of (A), this absorption - desorption cycle can also be observed in the solid state. The infra-red spectrum of the complex (B) compared with that of Co(salen) or Co(salen) Na shows three additional strong bands at 1680, 1278 and 1213 cm^{-1} due to coordinated carbon dioxide. Treatment of complex (B) with dilute sulfuric acid releases one mole of carbon dioxide.

A similar reaction to (1) between carbon dioxide and the complex (A) in pyridine has been reported (eq. 2).

$$\underset{(A)}{\text{Co (salen) Na}} + CO_2 \xrightleftharpoons{Py} \underset{(G)}{(Py)\cdot\text{Co (salen) } CO_2 \text{ Na}} \qquad (2)$$

The infra-red spectrum of (G) compared with that of Co(salen)·Py shows three additional strong bands at 1700, 1273 and 1208 cm^{-1}. It can be dried in vacuo without significant loss of carbon dioxide. The infra-red spectrum of (B) and (G) suggests that carbon dioxide has been reduced and should have the bent form in both complexes.

The equations (1) and (2) do not indicate the molecular arrangement in complexes B and G, which may be determined principally by the coordination sphere of the sodium cation, to which the CO_2 and salen oxygen atom can contribute. Generally the reaction between Co(salen)M complexes and CO_2 does not afford suitable crystals for X-ray analysis. However the structural analysis of the similar complex to B and G, obtained from the reaction of Co (Pre-salen)K and CO_2 in THF solution was found to have a polymeric structure

$$\left\{ \left[Co(Pre\text{-}salen) \right]_2 K_2 THF_2 (CO_2)_2 \right\}_n$$

The reaction of carbon dioxide with Co(salen) in ethanolic solution using sodium borohydride as the reducing agent has been a subject of our investigations and is discussed in the subsequent part of this chapter.

2.2. EXPERIMENTAL

2.2.1 INFRA-RED

The infra-red spectra in the range of 4000 - 600 cm^{-1} in Nujol were recorded. The mulls were prepared under an inert atmosphere (H_2, N_2, CO_2) in dark.

2.2.2 CONDUCTIVITY

The conductivity of the compound was measured in the range 10^{-3} - 10^{-4}M in methanol using a Grayshaw conductivity bridge L.t.D.

2.2.3 X-Ray

The X-ray fluorescence spectrum of the compound was obtained using stereo scan 5150 + Kevex E.D.X. Analyser. 6000.

Deoxygenation of the solvents

The solvents were deoxygenated according to literature methods.(68)

2.3 EXPERIMENTAL

2.3.1 PREPARATION OF HYDRIDODINITROGENTRIS(TRIPHENYLPHOSPHINE) COBALT(III)

Sodium tetra-hydrido-borate (0.45g) in 15ml of absolute ethanol is(68) transferred to container A (fig 2.3.1) which is charged in the counter current of the nitrogen gas. Cobalt chloride hexahydrate (0.42g) is dissolved in 20ml of boiling ethanol and added to a solution made by dissolving triphenylphosphine (1.5g) in 40ml of hot ethanol. After cooling to about 50° this solution is added in a container A containing the sodium borohydride solution. Bubbling of the nitrogen through this solution for 2 hrs at 0°C gives a green product. The vacuum filtration apparatus (B, C) (Fig 2.3.1) previously filled with nitrogen is connected to container A and the apparatus is rotated, so that the reaction mixture flows onto the filter paper. After filtration is finished, the precipitate is washed with ethanol and n-heptane. After drying a product under an atmosphere of nitrogen a uniform green product is obtained.

Analytical data:

Found:	%C	58.3	%H	5.1 - 5.4	%P	4.2
the $CoHN_2(PPh_3)_3$ requires:	%C	74.2	%H	5.1	%P	10.64

(See also discussion part)

The green product is soluble in chloroform and tetrahydrofurn. The infra-red spectrum of a Nujol Mull shows two N≡N stretch bands at 2100 and 2080 cm^{-1}.

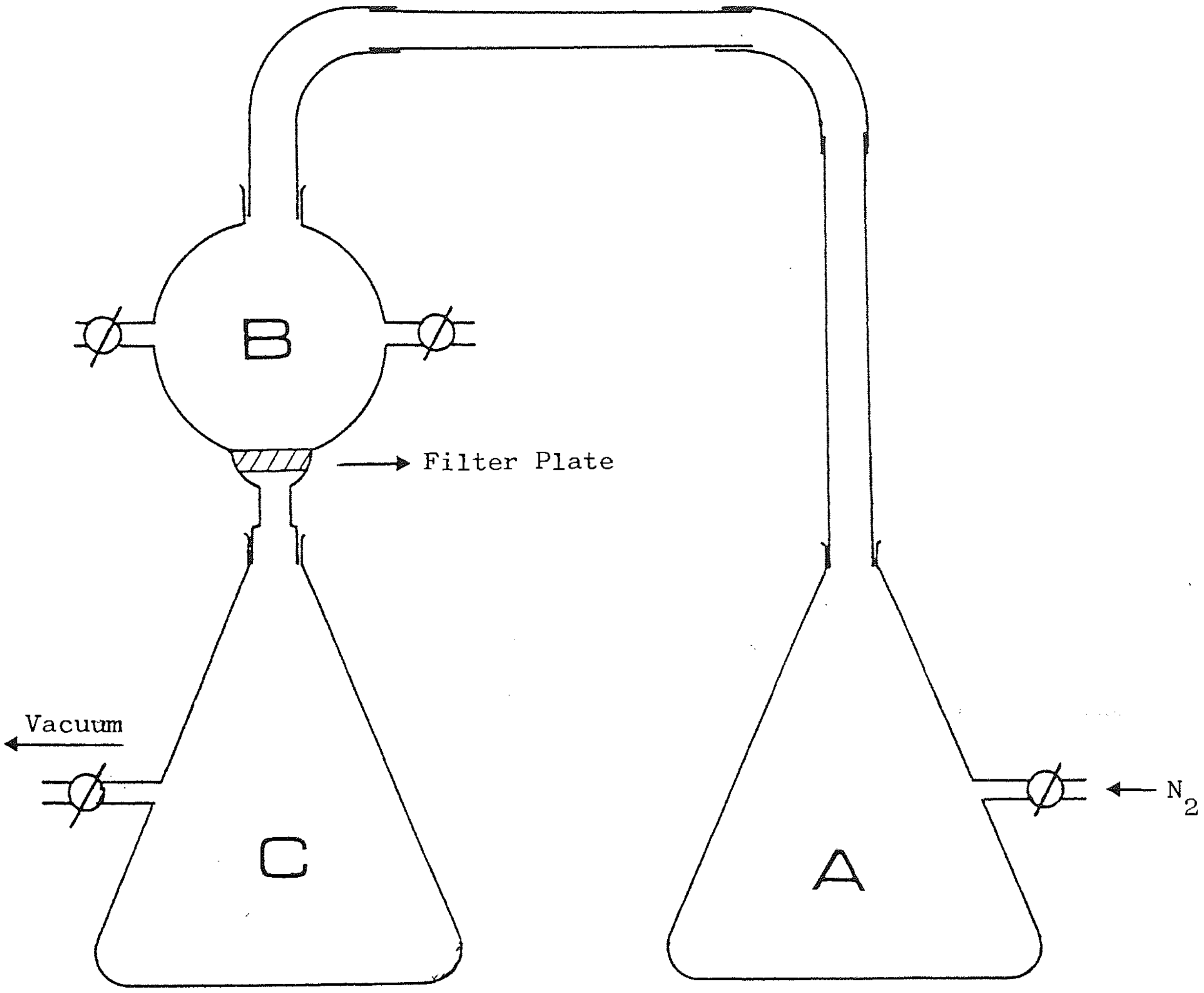


Fig. 2.3.1

The vacuum filtration apparatus

2.3.2 PREPARATION OF TRI-HYDRIDOTRIS(TRIPHENYLPHOSPHINE)COBALT(III)

Replacing nitrogen in procedure (2.3.1) by hydrogen gives a yellow-green product with the following analytical data:

Found:	%C	61.1	%H	4.8	%P	8.8
The $CoH_3\ (PPh_3)_3$ requires:	%C	76.4	%H	5.6	%P	10.9

2.3.3 EFFECT OF LIGHT ON PRODUCT OBTAINED FROM THE PROCEDURE (3.2.1)

Doing the experiment (2.3.1) in absence of the light produce the yellow-green product. The infra-red spectrum of this product does not show any band due to dinitrogen but it shows two infra-red bands in the region of 1620 and 1735 cm^{-1} assignable to Co-H.

2.3.4 REACTION OF CARBON DIOXIDE WITH PRODUCT OBTAINED FROM PROCEDURE (2.3.1) IN THE SOLID FORM

The crude product obtained from the procedure (2.3.1) (approximately 0.5g) was transferred into a three neck flask and kept under an atmosphere of carbon dioxide. After 24 hrs the product was washed with ethanol saturated with carbon dioxide and dried under a stream of carbon dioxide.

Analytical data:

Found:	%C	54.8	%H	5.1	%P	7
$Co(BH_4)(PPh_3)_2CO_2$ requires:	%C	69.3	%H	5	%P	9.68

2.3.5 REACTION OF CARBON DIOXIDE WITH THE PRODUCT OBTAINED FROM THE PROCEDURE 2.3.2 IN THE SOLID FORM

Treatment of the product obtained from procedure (2.3.2) with carbon dioxide in the solid form gave the purple product with the same infra red spectrum as the product obtained in reaction (2.3.4)

2.3.6 REACTION OF CARBON DIOXIDE WITH THE PRODUCT OBTAINED FROM THE PROCEDURE 2.3.1 IN SOLUTION

Carbon dioxide was brought into contact with the tetrahydrofuran solution of the dinitrogen product obtained from the reaction (2.3.1) for a day (Solution A). The solvent was evaporated and the product was dried under a stream of carbon dioxide.

The infra-red spectrum of the product does not show any band due to coordinated carbon dioxide.

The infra-red spectrum of the solution A shows a strong band at 2350 cm^{-1}, but no band in the region of Co-H vibrational frequency was observed.

2.3.7 PREPARATION OF HYDRIDO-TRIS(TRIPHENYLPHOSPHINE)COBALT(III) UNDER AN ATMOSPHERE OF CARBON DIOXIDE

Replacing the nitrogen in reaction (2.3.1) by carbon dioxide and following the same procedure gives a product which does not show any infra red band due to coordinated carbon dioxide.

2.3.8 PREPARATION OF (COBALT-DI(SALICYLAL)ETHYLENEDIIMINE)UNDER AN ATMOSPHERE OF NITROGEN

11.5g of salicyl-aldehyde and 4g of ethylene-diamine were(65) dissolved in 130ml of ethanol placed in a flask with stopcock. They react together to give the schiff base which will disolve above 60°C.

11.5g of cobaltous acetate tetrahydrate was dissolved in 60ml of water and heated to 60°C. The cobaltous acetate solution was then poured with shaking into the alcoholic solution of the schiff base under the atmosphere of nitrogen. The flask is then heated for about 1 hour. After cooling, crystals were filtered, washed with water and ether. Red brown crystals were obtained.

Analytical data:

Found:	%C	54.8	%H	3.83	%N	8.2
Co(salen) requires:	%C	59.1	%H	4.3	%N	8.6

Analytical data for schiff base:

Found:	%C	71.5	%H	5.8	%N	10.4
Sal en: requires:	%C	72.1	%H	5.2	%N	10.5

Purification of the crude Co(salen) with acetone or nitromethane after drying in the air produces red and green crystals respectively. Also treatment of the red brown products with boiling ethanol for half an hour produces the same red crystals which is obtained by purification with acetone.

2.3.9 PREPARATION OF COBALT-DI(SALICYLAL)ETHYLENEDIIMINE UNDER NORMAL ATMOSPHERE

Replacing ethanol by methanol in procedure (2.3.8) and doing the reaction under the normal atmosphere produces a brown product which is purified with water and ether. The yield is (3.8g).

Analytical data for this product:

Found:	%C 55.3	%H 4.7	%N 8.5
Co(salen) requires:	%C 59.1	%H 4.3	%N 8.6

The magnetic measurement using Goug method proved that the compound is diamagnetic and the conductivity measurement in methanol solution shows that the compound does not conduct an electric current.

2.3.10 REDUCTION OF COBALT-DI(SALICYLAL)ETHYLENEDIIMINE

1.5g of Co(salen) which is prepared according to procedure (2.3.8) in 30ml of tetrahydrofurn is transferred into a flask and 0.7g of sodium borohydride is gently added. The solution was stirred for 10 minutes under an atmosphere of nitrogen until a green solution was obtained.

2.3.11 REACTION OF CARBON DIOXIDE WITH THE GREEN SOLUTION OBTAINED IN REACTION 2.3.10

The carbon dioxide was bubbled through the THF solution of reduced Co(salen) complex and a green product was recovered within a day. The compound is stable in the air and the infra-red spectrum does not show any evidence due to presence of carbon dioxide in the molecule.

2.3.12 REACTION OF CARBON DIOXIDE WITH SODIUM (NN′— ETHYLEN-BIS-SALICYLIDENEIMINATO)-COBALTATE (I)

0.1g of Co(salen) in 20ml of ethanol was transferred into a 3 neck flask and 0.2g sodium borohydride in 20ml of ethanol added. The solution was stirred for 15 minutes under an atmosphere of nitrogen until a green solution was obtained. Carbon dioxide was bubbled through the green solution (1 hr), the yellow precipitate was obtained, which was collected, washed with ethanol saturated with carbon dioxide and dried understream of CO_2.

IR: 1620, 1340, 1070 cm^{-1}.

MASS spectra: m/e: 44, 279, 280, 281.

Bubbling nitrogen through a green solution , and drying off the solvent produces a green solid. When this green product is exposed to carbon dioxide a white solid was obtained which was washed with ethanol saturated with carbon dioxide and dried under a stream of carbon dioxide.

The infra-red spectrum of this product shows several new bands in the same region as that of the yellow product.

2.3.13 PREPARATION OF μ-DICHLOROTETRAKIS-(CYCLOOCTENE)-DI-IRIDIUM(I)

$IrCl_3$ $3H_2O$ (1g) was dissolved in a solution of isopropanol$^{(69)}$ (11 ml) and water (4 ml). An excess of cylooctene (2 ml) was then added and the solution stirred for a few minutes at room temperature. The solution was then heated at 78°C for 3 hours and changed from dark red to yellow in colour, during which time $\left[IrCl(C_8H_4)_2\right]_2$ precipitated from the solution. The complex was collected by filtration, washed with ice cold methanol and dried in vacuo. The yield is 0.6g .

2.3.14 PREPARATION OF CHLORO-BIS(DIMETHYLPHOSPHIN ETHANE)IRIDIUM(I)

0.6g $IrCl(C_8H_{14})_2$ in 20 ml of benzene is transferred into a flask and 1.2g 1,2-dimethylphosphine-ethane is added. The mixture is heated under reflux for 2 hours and allowed to cool. The product is filtered, washed with benzene and dried in vacuo. The yield is 1.2g.

Analytical data:

Found:	%C	60.4	%H	4.8	%P	11.8
Ir(dmpe)$_2$Cl requires:	%C	60.96	%H	4.7	%P	12.1

2.3.15 THE REACTION OF CHLORO-BIS(DIMETHYLPHOSPHINEETHANE)IRIDIUM(I) WITH CARBON DIOXIDE IN SOLUTION

Carbon dioxide was bubbled through the alcoholic solution of $\left[\mathrm{Ir(dmpe)_2\ Cl}\right]$ (0.1g in 20 ml of methanol) and a pale green product was collected within 2 days. The infra-red spectrum of the product does not show any new bands compared with that of starting material. Also no reaction between carbon dioxide and $\left[\mathrm{Ir(dmpe)_2\ Cl}\right]$ in benzene, methanol, acetone solution was observed.

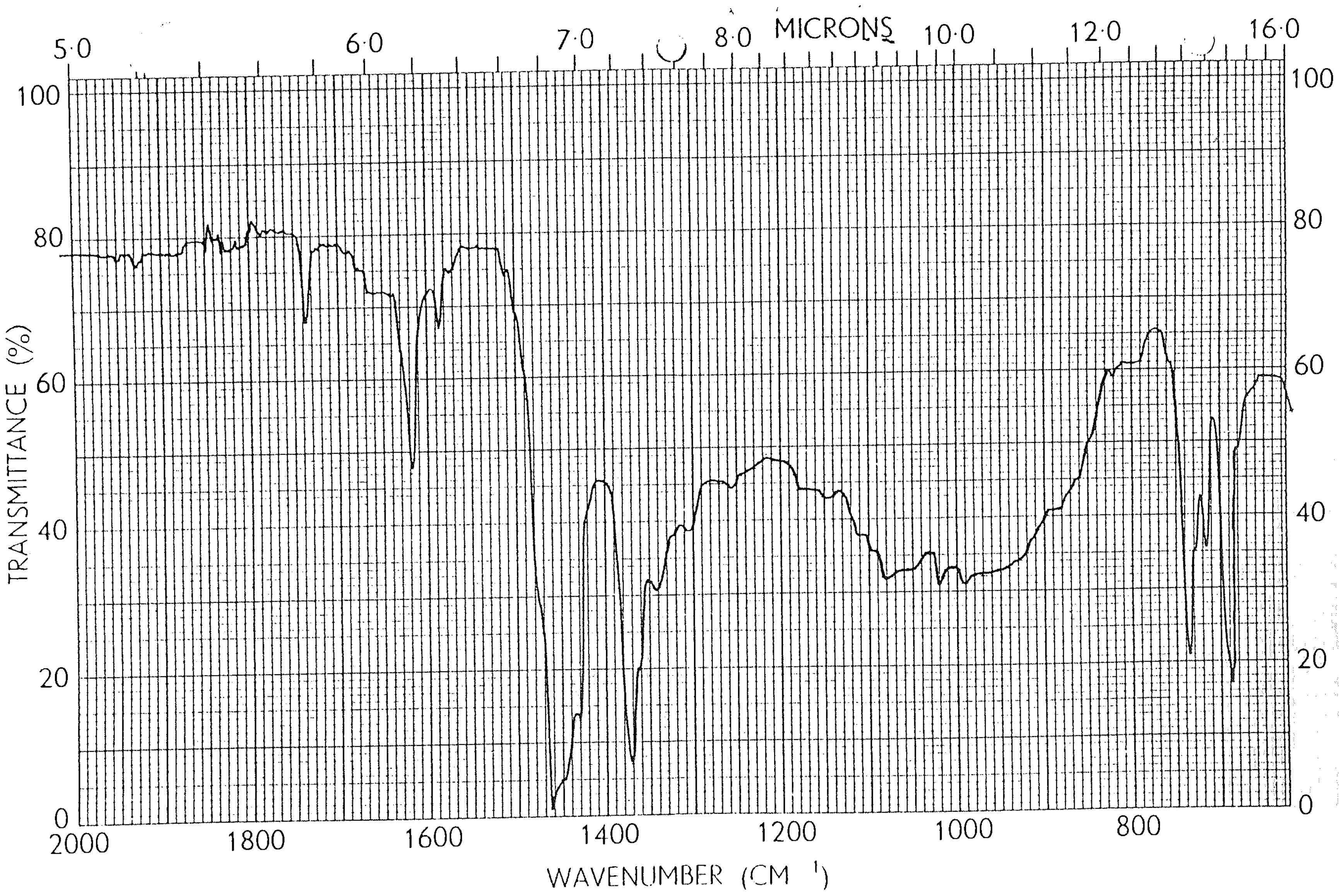
2.4.1 RESULTS AND DISCUSSION

The controversy about preparation and structural analysis of the cobalt dinitrogen complexes, particularly where the question of the number of hydride ligands is concerned, shows the complication of studying these systems. The details about chemistry of hydridodinitrogen-tris(triphenylphosphine)cobalt(III) and the relevant complexes are given in the introductory part of this chapter and therefore only further necessary information about these complexes will be given in this section. The compound $CoHN_2(PPh_3)_3$ can be prepared by different routes, and that by the reaction between trihydridotris(triphenylphosphine)cobalt (III) and elementry nitrogen has been subject of our study. The preparation of $CoH_3(PPh_3)_3$ from the reaction between cobaltchloridehexahydrate, triphenylphosphine and sodium borohydride in ethanolic solution has been reported to produce a yellow product. The infra-red spectrum of this yellow complex shows two Co-H stretching bands at 1933(m) and at 1745(s) cm^{-1}. The workers who checked the reaction(68) noted that a brown precipitate formed at initial stage of the preparation, which slowly turned to yellow green. Their attempts at recrystallization were unsuccessful and therefore the crude $CoH_3(PPh_3)_3$ was used for synthesis of $CoHN_2(PPh_3)_3$.

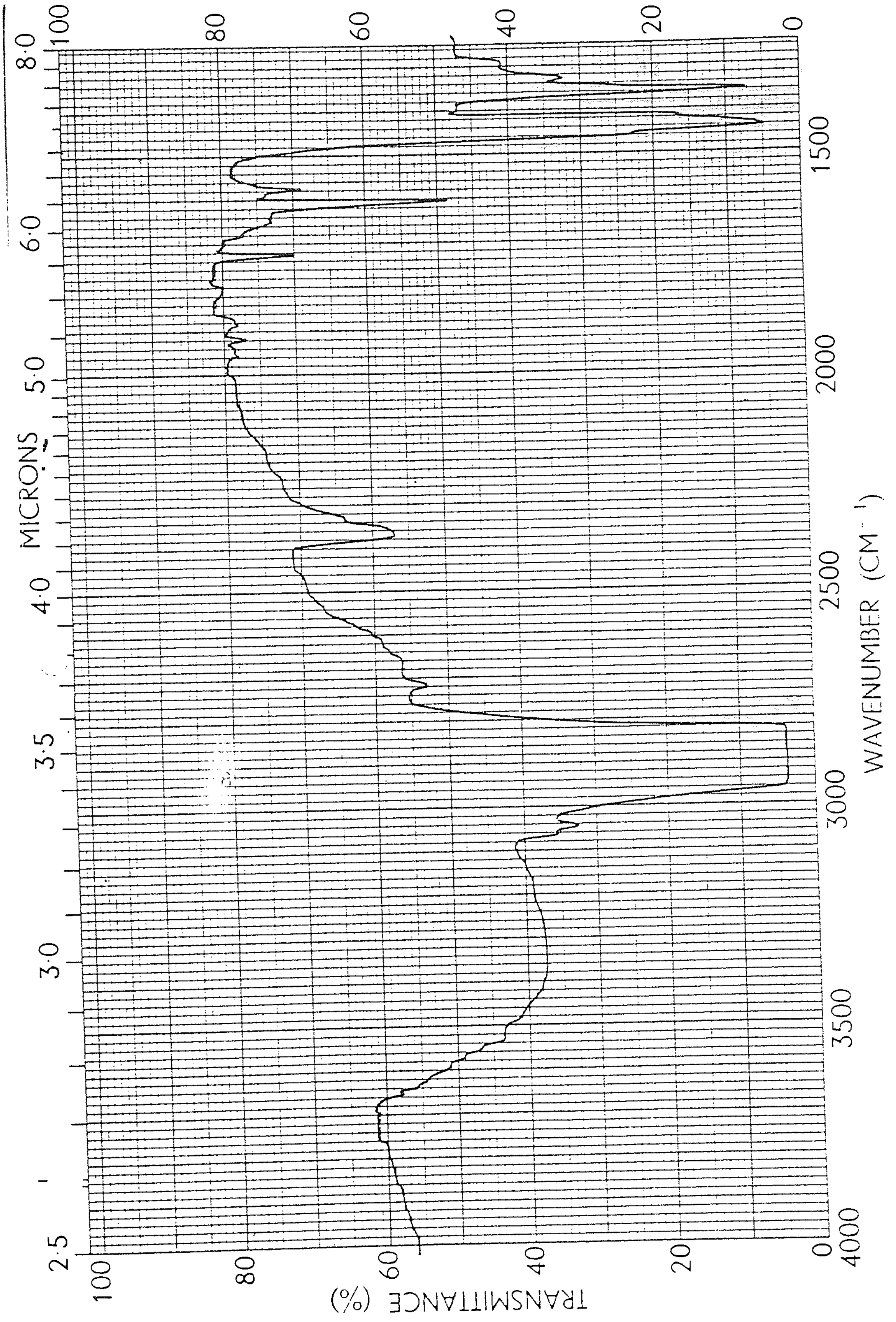
The reaction of carbon dioxide with $CoH_3(PPh_3)_3$ in benzene or tetrahydrofuran solution has been reported to give $HCOO.Co(PPh_3)_3$. The infra-red spectrum of this formate shows two strong bands at 1620 and 1300 cm^{-1} due to antisymmetric and symmetric stretching vibrations of the HCOO group attached to cobalt. We have tried to reproduce the complexes $CoH_3(PPh_3)_3$ and $CoHN_2(PPh_3)_3$ and study their reactions with carbon dioxide.

Although our investigation of these systems provided some new results and some part of the observations confirmed the literature findings, the problems concerning the structural analysis and purification of the compounds could not be totally resolved. The preparation of trihydridotris(triphenylphosphine)cobalt(III) according to procedure (2.3.2) resulted in the formation of a yellow green product(C). The infra-red spectrum of this compound does not show any band due to Co-H. When the same procedure was followed in the absence of light the greenish compound was obtained (Complex D).The infra-red spectrum of this compound (spectrum 2.4.1) shows two infra-red bands in the region of 1620 and 1735 cm^{-1} assignable to Co-H. The elemental analysis of the product after purification was found to be inconsistent and no reaction between complex (D) and molecular nitrogen either in the solid form or in solution was observed. To prepare the dinitrogen complex the procedure for preparation of $CoH_3 (PPh_3)_3$ was followed under an atmosphere of nitrogen and a green product was collected. (Complex E) The infra-red spectrum of this product (spectrum 2.4.2) shows two bands at 2080, 2100 cm^{-1} assignable to M-N_2.

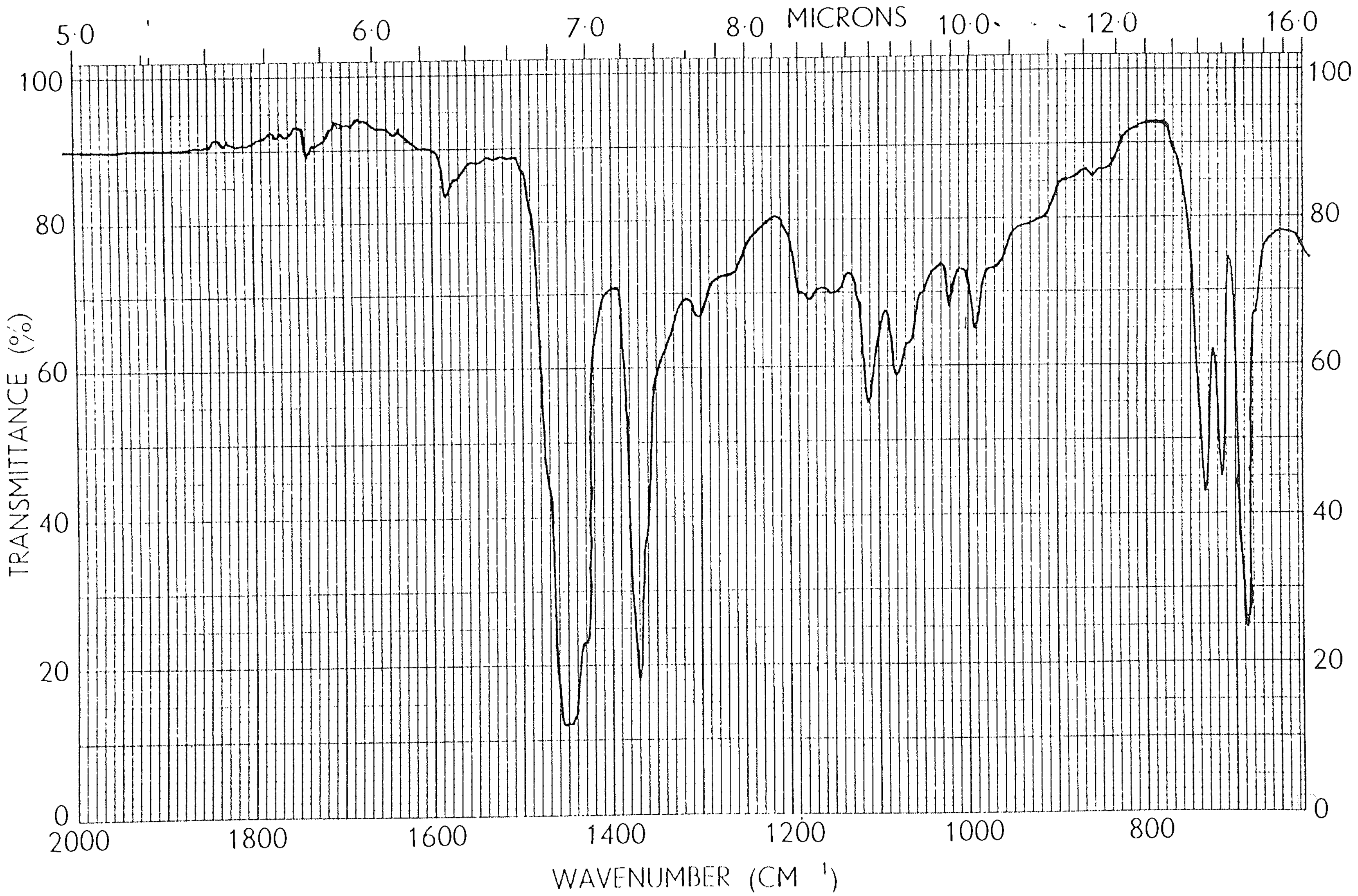
The reaction of crude products (D) and (E) with carbon dioxide in the solid form gave purple products with identical analytical data (both complexes (D) and (E) failed to react with carbon dioxide after purification. Also no reaction between the complex (D) and (E) with carbon dioxide in presence of light or oxygen was observed). The infra-red spectrum of this purple complex (spectrum 2.4.3) shows several new infra red bands in the region of 1620, 1090, 830 cm^{-1} compared with that of starting materials, however the spectrum does not show any bands due to coordinated nitrogen or metal hydride.



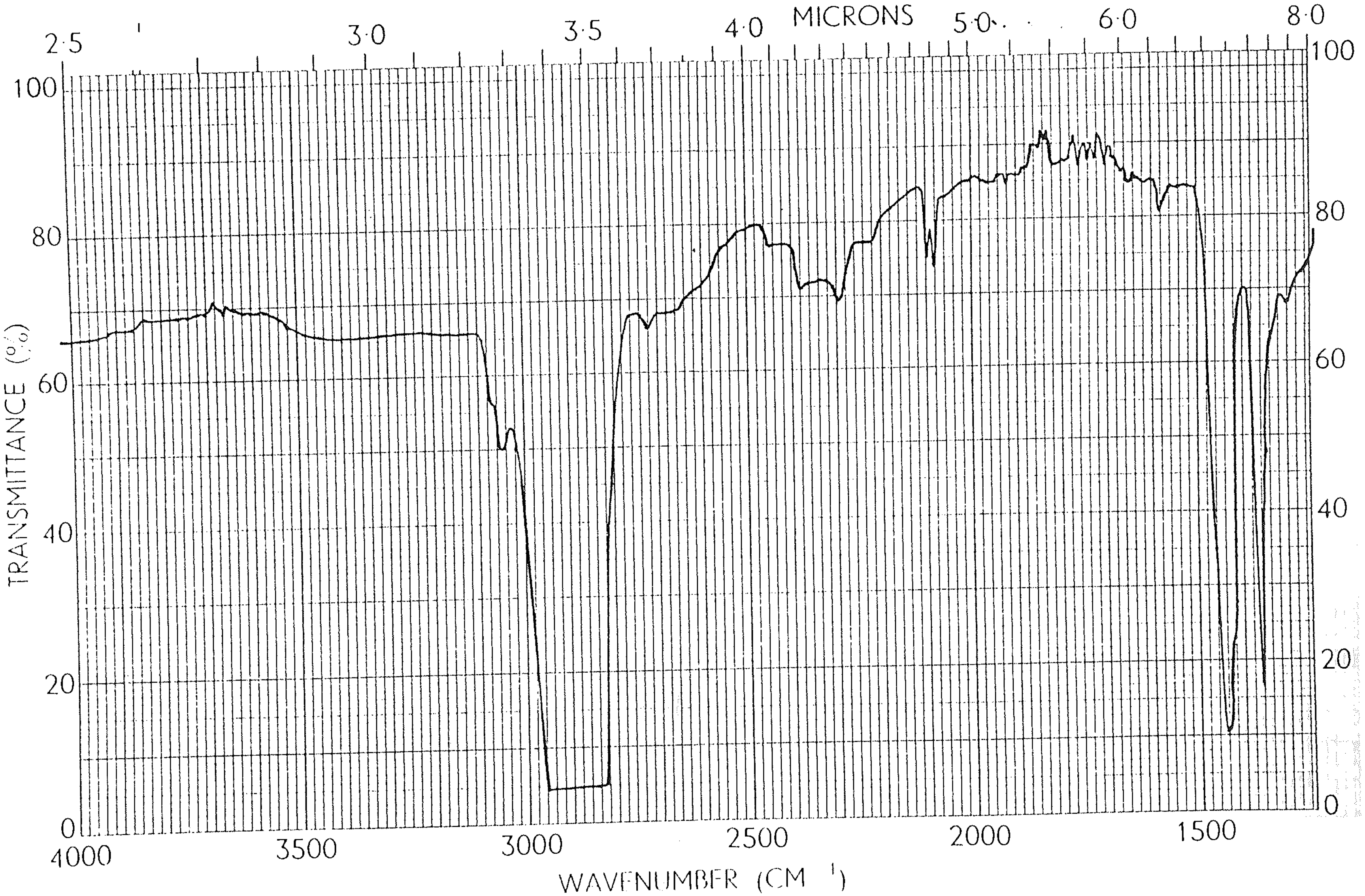
Spectrum (2.4.1) Infra-red spectrum of compound D.



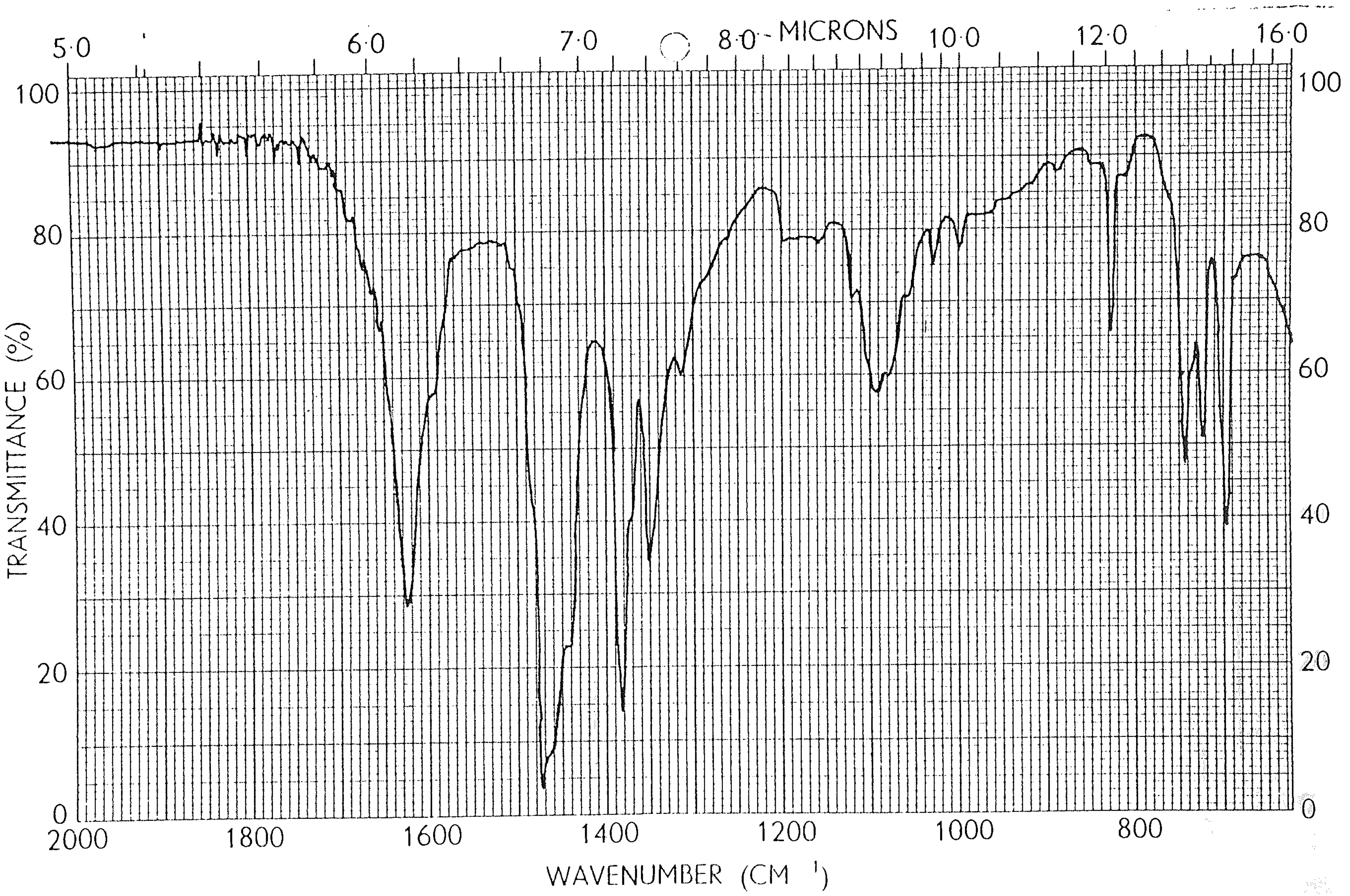
Spectrum (2.4.1) Infra-red spectrum of compound D.



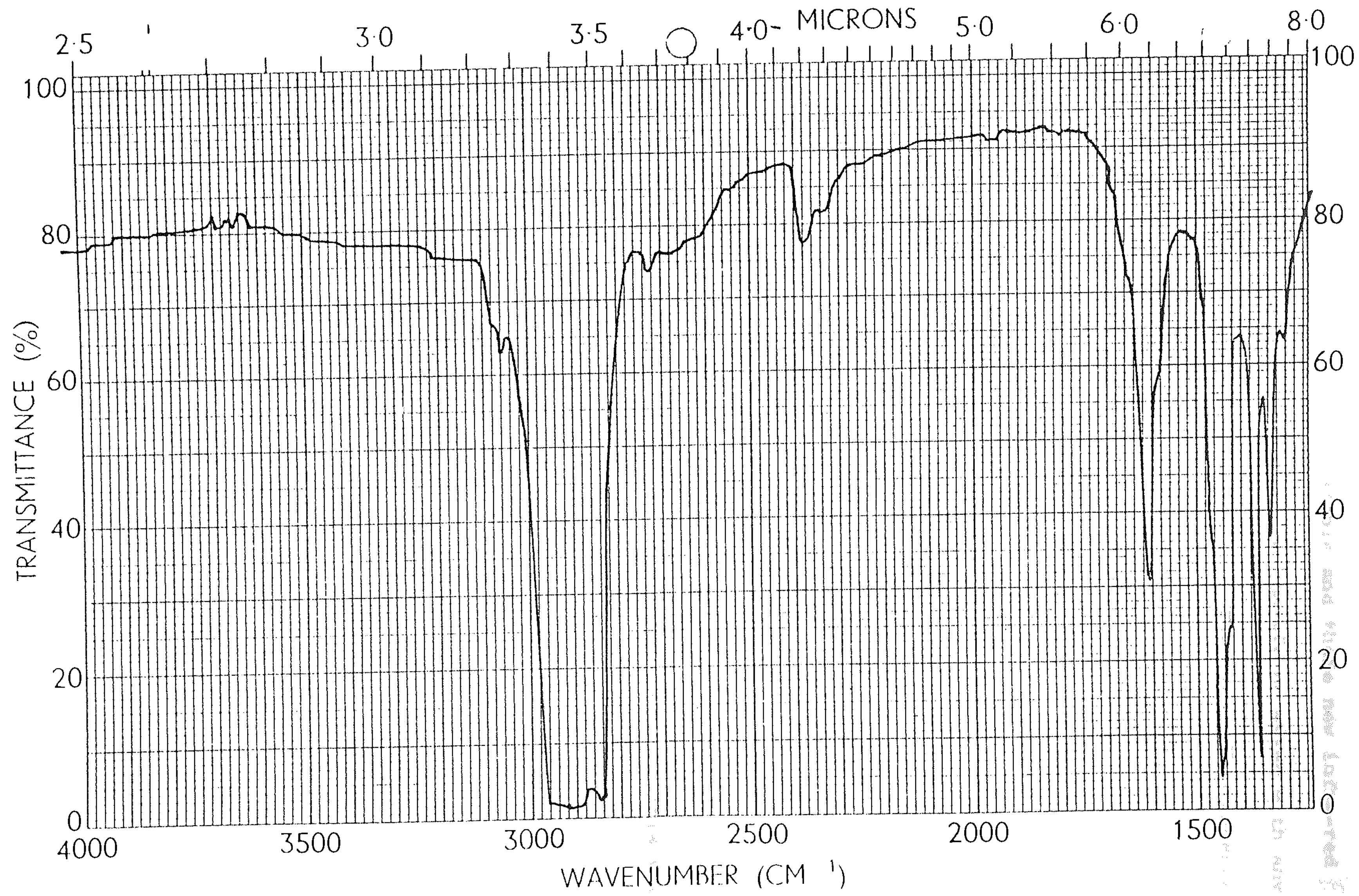
Spectrum (2.4.2) Infra-red spectrum of compound E.



Spectrum (2.4.2.) Infra-red spectrum of compound E.



Spectrum (2.4.3) Infra-red spectrum of the purple complex, obtained from the reaction of complex D or E with CO_2.



Spectrum (2.4.3) Infra-red spectrum of the purple complex, obtained from the reaction of complex D or E with CO_2.

The product was found to be very unstable and those new infra-red bands disappear if the compound is exposed to air or mixed with any solvents not saturated with carbon dioxide. The X-ray fluorescence spectrum of the compound (spectrum 2.4.4) after purification with ethanol saturated carbon dioxide and decomposition shows ratio of

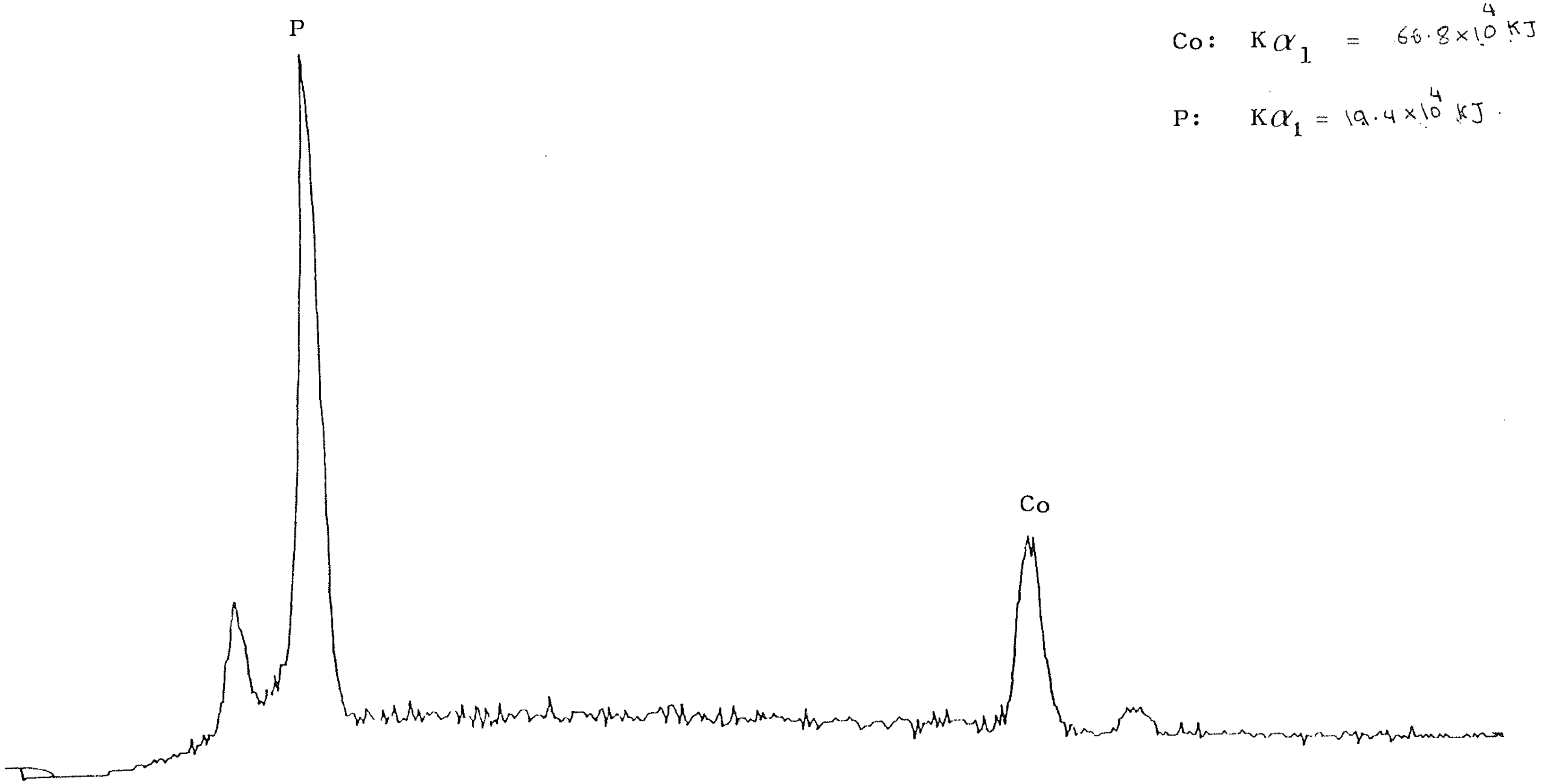
$$\frac{1}{3} \quad \text{for} \quad \frac{\text{Cobalt}}{\text{Phosphorus}}$$

The sample for X-ray analysis was ground to a fine powder and five spectra were taken at different areas of the surface and the average value of $\frac{Co}{P}$ is reported.

The elemental analyses of the compounds C, D, E and the purple complex were not satisfactory. This is because during the time of this work, due to technical difficulties the analytical services could not provide reasonable results. This does not affect the interpretation of data to a great extent since the techniques of X-ray fluorescence and infra-red were available and with other information reported in literature the structural analysis could be achieved.

The following article is important for interpretation of the results and should be noted:

Hola has reported(70) that the reaction of cobaltchloridehexahydrate with triphenylphosphine in ethanolic solution, in the presence of excess sodium borohydride yields the compound $Co(BH_4)(PPh_3)_3$ which shows two infra-red bands at 2340 and 2390 cm^{-1} related to coordinated borohydride. Treatment of $Co(BH_4)(PPh_3)_3$ with nitrogen saturated



Co: $K\alpha_1 = 66.8 \times 10^4$ KJ

P: $K\alpha_1 = 19.4 \times 10^4$ KJ.

S1 Spectrum (2.4.4) X-ray fluorescence spectrum of the purple product after purification with ethanol saturated CO_2.

benzene or n-hexane produces a yellow brown complex of formulation $CoN_2(BH_4)(PPh_3)_3$. The analytical data have been reported to be insufficient to clarify the bonding in this molecule.

On the basis of the information given so far it appears that the preparation of $CoH_3(PPh_3)_3$ and $CoN_2H\ (PPh_3)_3$ has not produced the same complex which was reported in reference (68), but it confirms the Hola work. With reference to the infra-red spectra of complex (D) and (E) the structure $CoH_2(BH_4)(PPh_3)_3$ and $CoN_2(BH_4)(PPh_3)_3$ can be inferred respectively. The infra-red bands in the region of 2340 and 2380 cm^{-1} in both compounds related to coordinate borohydride. (To avoid formation of the metal - borohydride, the procedure (2.3.1) was followed except no sodium borohydride was used. Attempts were then made to reduce the resulting product with various quantities of sodium borohydride. However these attempts were not successful and in all instances the green product was obtained which contained coordinated borohydride. Using amalgamated zinc in place of sodium borohydride as a reducing agent resulted in a product which does not react with carbon dioxide).

The instability and insolubility of the purple product obtained from the reaction of complex (D) or (E) with carbon dioxide made molecular weight determination impossible. However on the basis of the X-ray analysis and the infra-red spectrum the structure $Co(BH_4)(PPh_3)_3\ CO_2$ is suggested. The colour change of the complex D and E after reaction with carbon dioxide from the green to purple can also be taken in support of the metal centre interaction with CO_2.

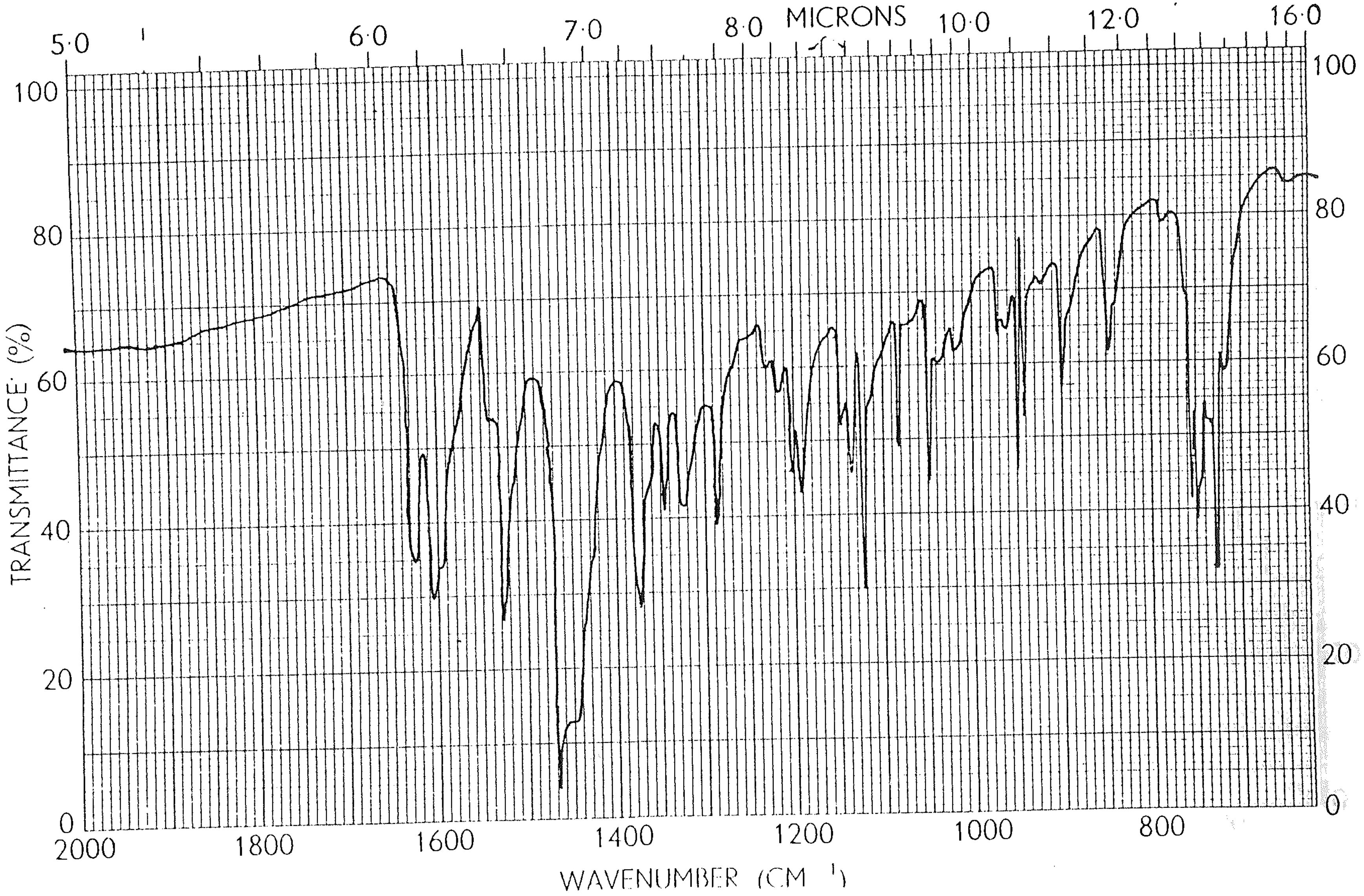
Both complex (D) and (E) can easily be affected by light and loose nitrogen or hydrogen which was proved by the infra-red spectrum.

The compounds do not react with carbon dioxide any further at this stage. Therefore it is not possible to propose that the nitrogen and the hydrogen from compounds $CoN_2(BH_4)(PPh_3)_3$ and $CoH_2(BH_4)(PPh_3)_3$ are replaced by carbon dioxide.

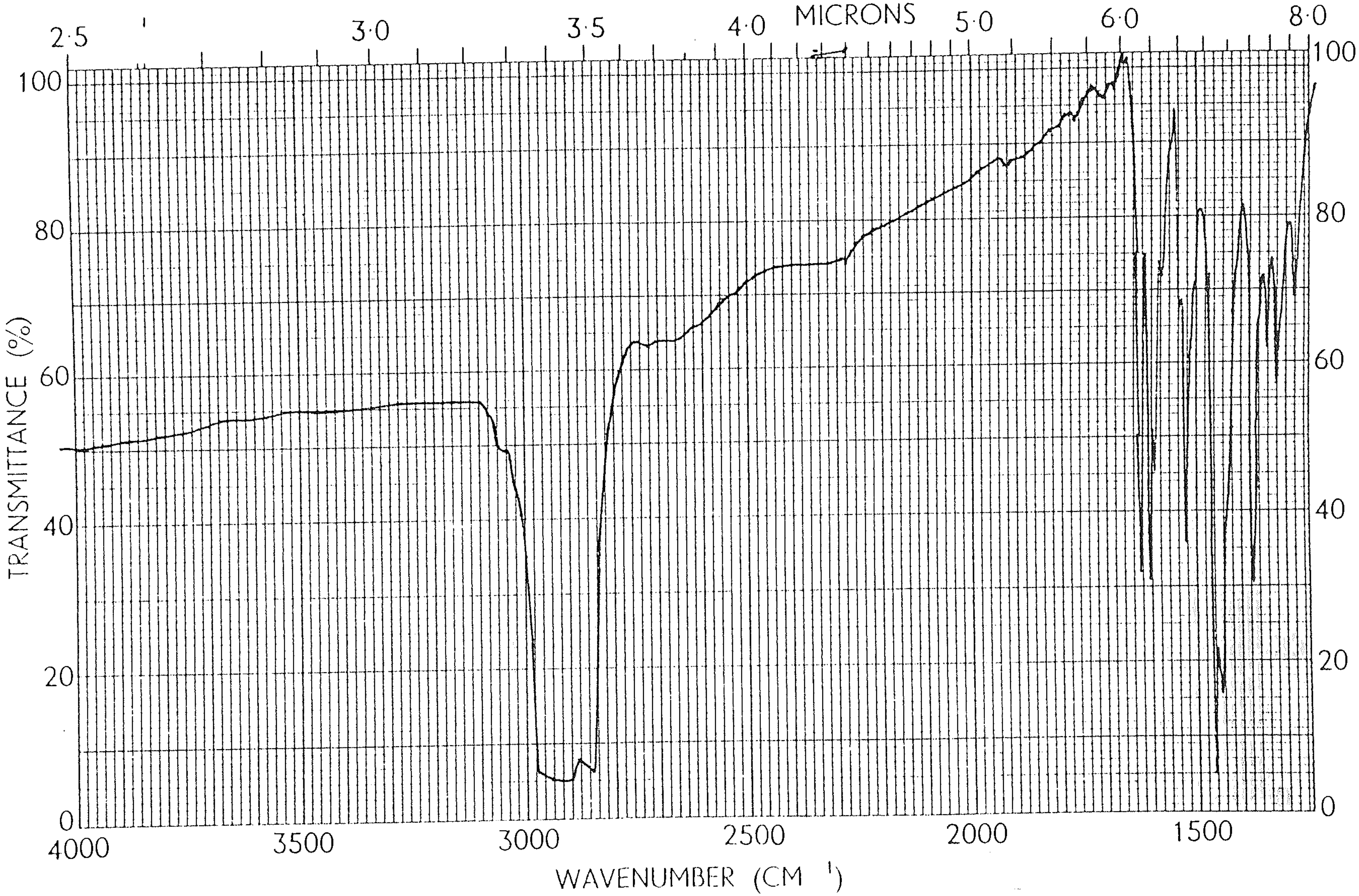
2.4.2 THE REACTION OF COBALTDI(SALICYLAL)ETHYLENEDIIMINE AND CHLORO-BIS-(1,2 DIMETHYLPHOSPHINOETHANE)IRIDIUM(I) WITH CARBON DIOXIDE

The preparation of Co(salen) complex was tried under atmospheric conditions, and under an atmosphere of the nitrogen. These products were found to be very similar and show a similar behaviour in reactions. To study the reaction of reduced Co(salen) with carbon dioxide the brown product obtained from the procedure (2.3.9) was mainly used.

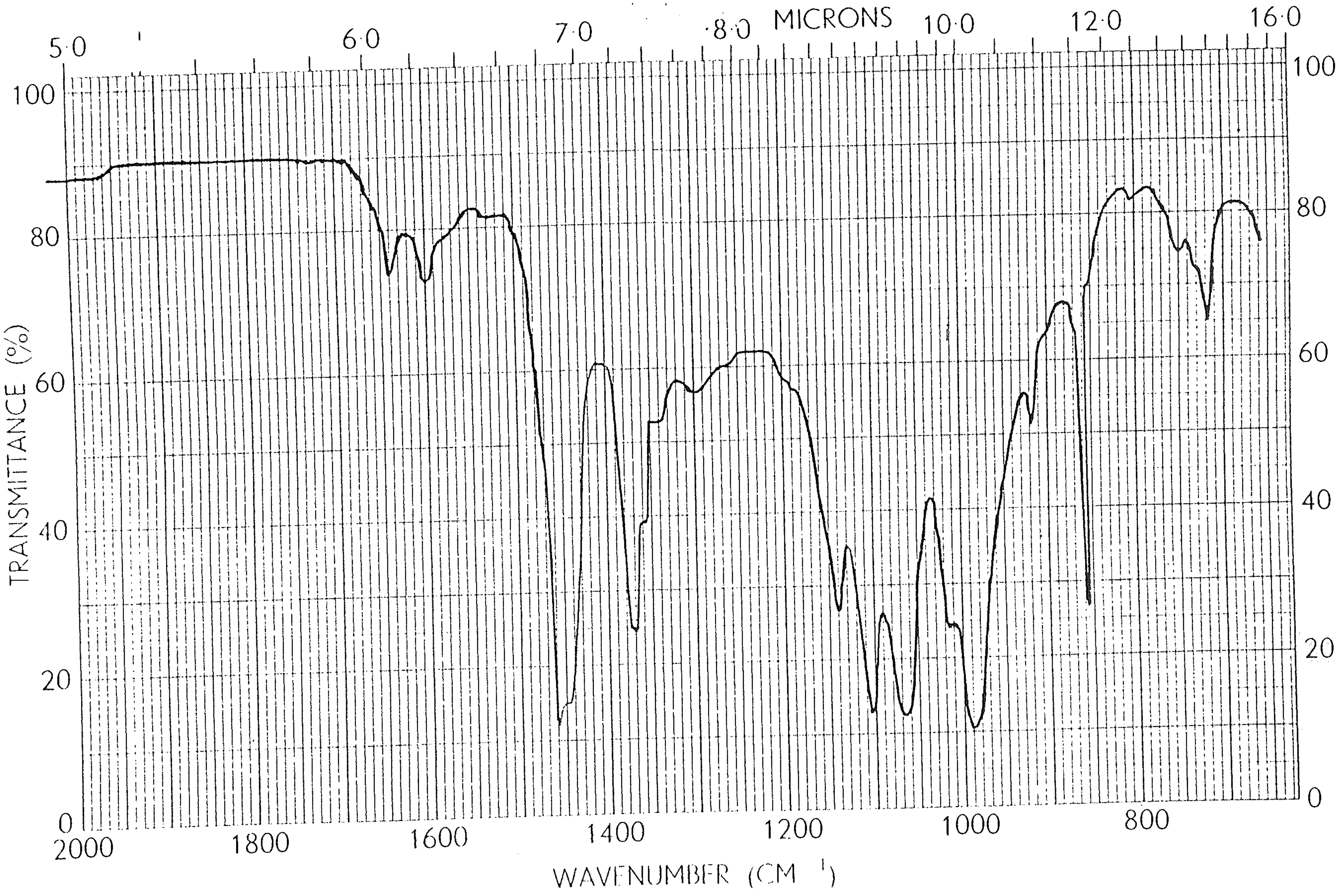
The reduction of Co(salen) using sodium in tetrahydrofuran produces(31) a green solution which has been reported to react with carbon dioxide to give Co(salen) CO_2Na (I). In our investigation the alcoholic solution of sodium borohydride was used to reduce the Co(salen) complex. The reduction was successful and produced a green solution. The reaction of carbon dioxide with this solution gave a yellow product which was purified by washing the product with alcohol saturated with carbon dioxide. The infra-red spectrum of this compound (spectrum 2.4.7) shows several new bands in the region of 1620, 1340, 1070 cm^{-1} compared with the infra-red spectrum of $\overset{I}{\mathrm{Co}}$(salen) Na (spectrum 2.4.6) or Co(salen) (spectrum 2.4.5). When this yellow product is heated up to $100^{\circ}C$ a certain amount of gas was evolved which was analysed by mass



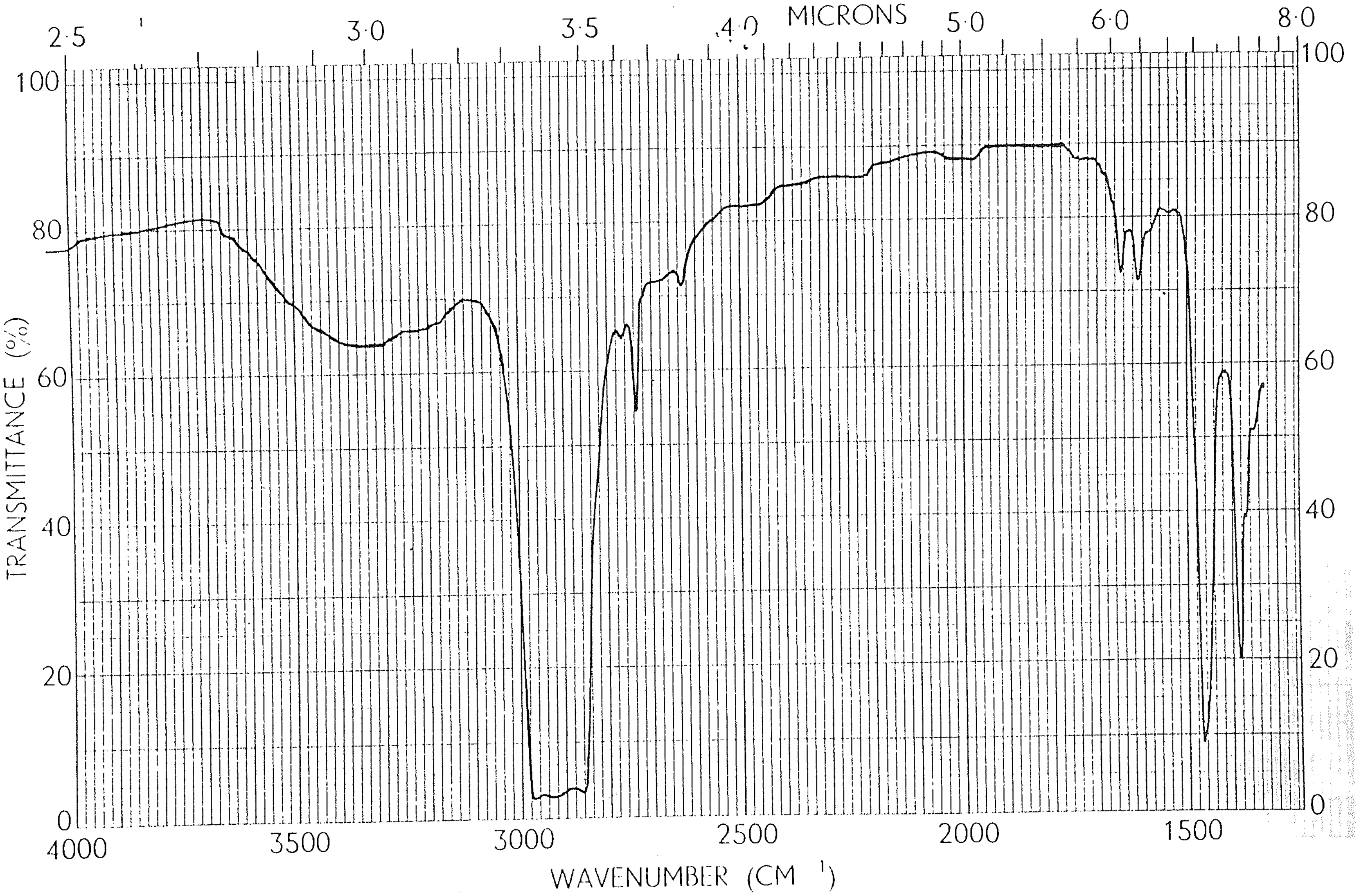
Spectrum (2.4.5) Infra-red spectrum of cobalt-di(salicylal)ethylenediimine



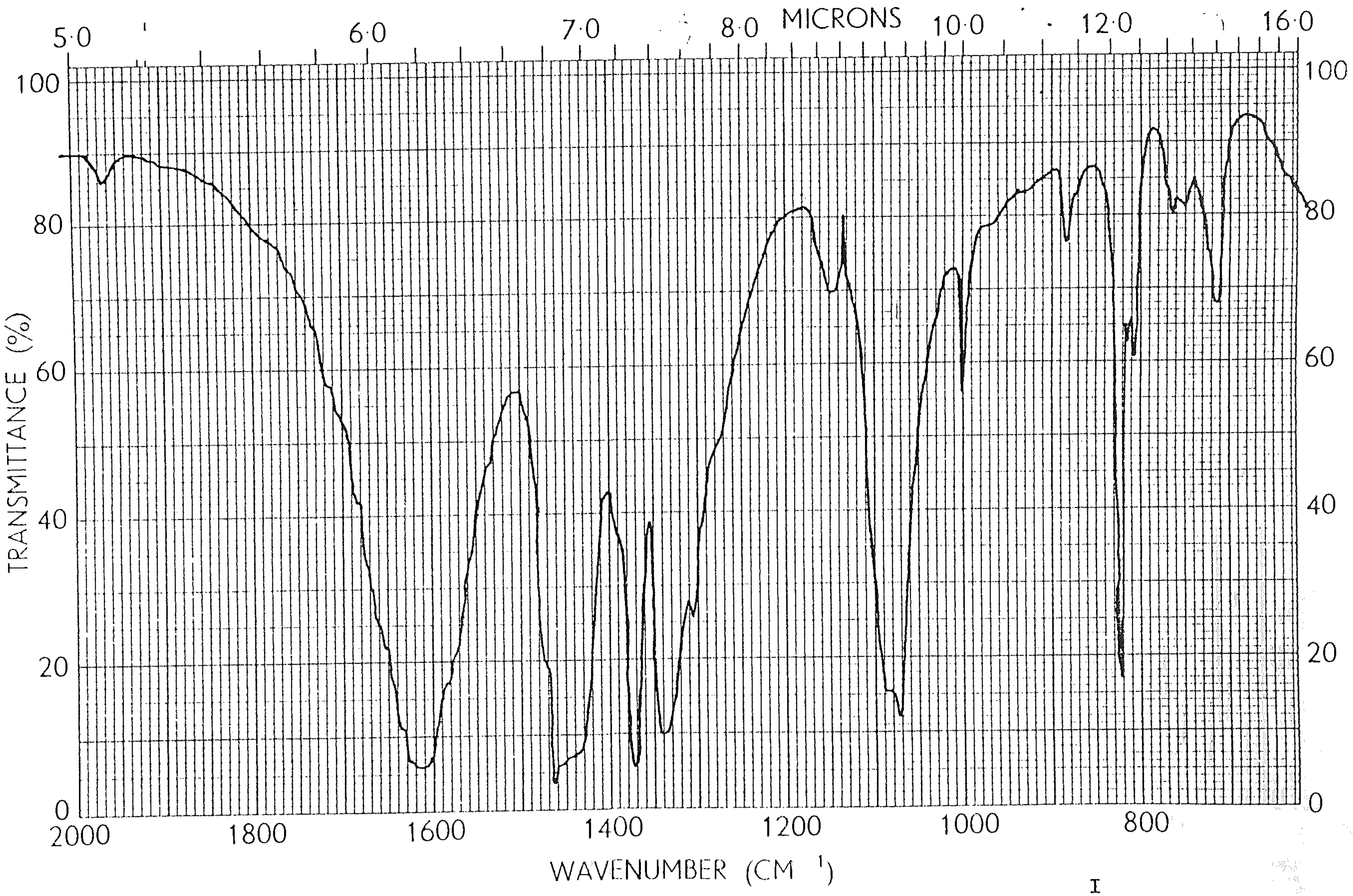
Spectrum (2.4.5.) Infra-red spectrum of cobalt-di(salicylal)ethylenediimine.



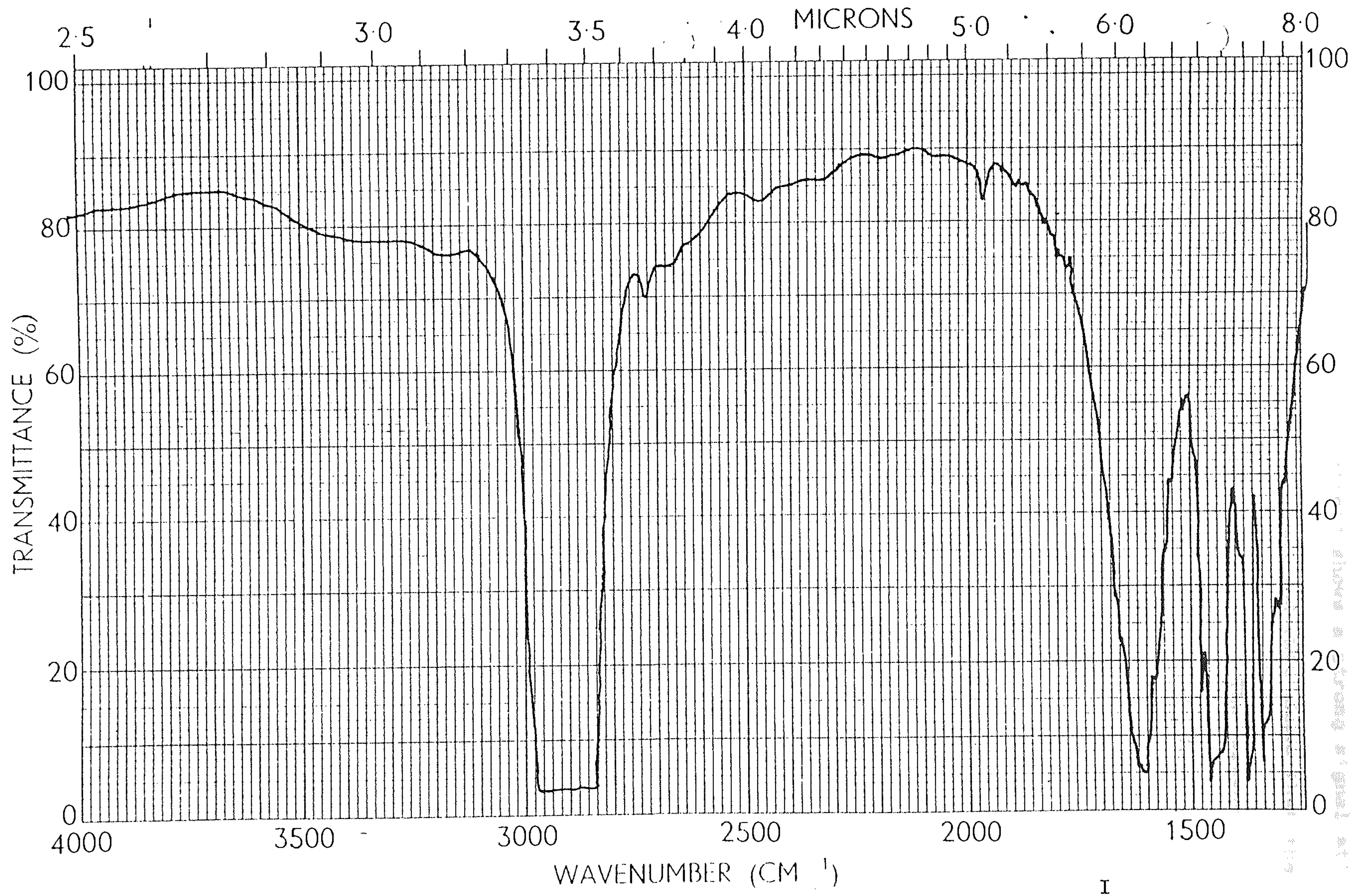
Spectrum (2.4.6) Infra-red spectrum of $\overset{I}{\text{Co}}$(salen)Na.



Spectrum (2.4.6) Infra-red spectrum of $\overset{I}{\mathrm{Co}}$(salen)Na.



Spectrum (2.4.7) Infra-red spectrum of the product obtained from reaction of $\overset{I}{\mathrm{Co}}$(salen)Na and CO_2 in ethanolic solution.



Spectrum (2.4.7) Infra-red spectrum of the product obtained from reaction of Co^{I}(salen)Na and CO_2 in ethanolic solution.

spectrometer. The fragmentation pattern shows a strong signal at m/e 44 and those related to ligand (salen) and this shows that the ligand has not decomposed to any organic species. The compound decomposes on exposure to air and those new infra-red bands disappear. Ratio of $\frac{Co}{Na}$ in the yellow compound using atomic absorption technique was found to be $\frac{1}{1}$.

The comparison of this yellow product with the complex Co(salen)CO_2Na(I) is given in the following table.

Table 2.4.1

The yellow complex	Co(salen)CO_2Na (31)
IR: 1620, 1340, 1070 cm^{-1}	1680, 1278, 1213

The data obtained from this yellow complex suggest the structure Co(salen)CO_2Na. The colour and the shift of those new infra-red bands (table 2.4.1) compared with those found for complex (I) in literature suggest a different type of bonding for carbon dioxide in this product.

The compound Ir (dmpe)$_2$Cl has been reported to react with carbon dioxide (27) in benzene solution to give Ir (dmpe)$_2$Cl.CO_2. The infra-red spectrum of this product shows two bands at 1550 and 1230 cm^{-1} due to coordinated carbon dioxide. In our investigation it was tried to reproduce the same reaction in benzene solution, however no reaction was observed. Using other solvents such as alcohol, chloroform, acetone were not also successful, and no new product was obtained.

CHAPTER III

INTRODUCTION

3.1.1 DINITROGEN COMPLEXES:

The dinitrogen molecule has a very high dissociation energy (943.8 kJ mole^{-1}) which is reflected in a Raman - active vibrational frequency at 2330.7 cm^{-1}. On mixing the 2S and 2P orbitals on nitrogen because of their relatively low energy separation, we have the configuration:

$$(\sigma s)^2 \quad (\sigma^*_s)^2 \quad (\pi y,z)^4 \quad (\sigma x)^2$$

The highest occupied orbital is thus a σ orbital, and not the degenerate π orbital and the first empty orbitals are the degenerate anti bonding orbitals $\pi^*_{2Py,Pz}$.

Infra-red studies of dinitrogen chemisorbed on nickel, palladium and platinum show absorption at around 2200 - 2000 cm^{-1}.(71) This suggests an electronic interaction with the absorbed nitrogen, and coordination to the bulk metal. The bonding of dinitrogen in metal complexes(72) is often compared with that of carbonyls, and it is deduced that dinitrogen is a weaker σ and π bonder than carbon monoxide.

The dinitrogen molecule has been considered as a potential ligand(73) for many years, but dinitrogen complexes were first prepared only in 1965. Orgel had suggested that a simultaneous transfer of electrons(89) from the σ orbital of the ligand to the metal, and from the metal to a π orbital of the ligand, should correspond to bring the molecule, whether carbon monoxide or dinitrogen in an excited state in which a $n \longrightarrow \pi$ transition has taken place, the energy of $n \longrightarrow \pi$ upper state of CO being of about 6 ev in comparison with 7.3 ev for N_2. This suggestion was used for explaining the inability of nitrogen to act as ligand analogously to carbon monoxide. The recent isolation of dinitrogen complexes demonstrated that this hypothesis is not valid. However, dinitrogen complexes are generally less stable than the corresponding carbonyl derivatives, and up to now a pure metal dinitrogen complex such as $M(N_2)_x$ has not been isolated.

3.1.2 PREPARATION OF DINITROGEN COMPLEXES:

The preparation of any dinitrogen complex may be(74) categorized under at least one of the following general preparative route.

a) - Direct reaction with nitrogen:

1 - Reduction of a metal complex under nitrogen.

2 - Addition of nitrogen to a coordinatively unsaturated complex.

3 - Displacement of a coordinated ligand by nitrogen.(81)

4 - Interaction of nitrogen with metal atoms and surfaces.

b) - Conversion of N-N or N species into the nitrogen ligand.

c) - Reaction of a nitrogen complex with retention of N_2.

The boundaries between these routes are not clearly defined and, the preparation of dinitrogen complexes by reduction of a metal species appears to proceed also via displacement of a coordinated ligand by nitrogen or by addition of nitrogen to a coordinatively unsaturated species. More-over the same di-nitrogen complex may be prepared in some cases by quite different routes. The more detailed information about these processes has been reviewed in reference (74).

Allen and Senoff reported the preparation of the first dinitrogen$^{(75,93)}$ complexes from aqueous solutions of ruthenium trichloride and hydrazine hydrate at 25°C. The isolated complexes appear to be of the type $[Ru(NH_3)_5N_2]X_2$ where $X = Br^-, I^-, BF_4^-$, and PF_6^-. The complexes are only moderately stable towards air and decompose fairly rapidly in water. The infra-red spectra of these compounds contain a strong sharp band between 2170 - 2115 cm^{-1} (table 3.1.1) which is assigned to the N_2 stretch.

X	Br^-	I^-	BF_4^-	PF_6^-
νN_2	2118(s)	2129(s)	2154(s)	2167(s)

Table 3.1.1.

As can be seen from table3.1.1 the ν(NN) stretching frequency increases with counteranion in $[Ru(NH_3)_5N_2]X_2$ in the order:
$X = Br^- < I^- < BF_4^- < PF_6^-$. A similar effect occurs for isocyanide complexes $[Ru(NH_3)_5CNR]X_2$. In this case, direct anion$^{(72)}$..... C≡N interaction is ruled out because of the protection provided by the R

groups. Hence direct anion ... $N\equiv N$ interaction in the dinitrogen complexes is said to be unlikely also. The ν(NN) stretch is independent of the anion in solution, hence the anion must have some influence in the solid state. It is suggested that the anion polarises the hydrogens of the ammonia ligands, which increases the strength of the $H_2N \rightarrow Ru$ σ bond, which in turn leads to an increase in the strength of the $Ru \rightarrow N_2$ π bond. The smallest anions have the greatest influence. For the dimeric complex ion $\left[(NH_3)_5 Ru - N_2 - Ru (NH_3)_5\right]^{+4}$, the ν(NN) stretch shifts in the opposite way with counterion. The reason suggested is that, for the dimer, electron release from ruthenium is into π bonding orbitals of N_2, whereas for the monomer the release is into π^* orbitals. Reduction in the ν(NN) stretching frequency occurs in solid solution of $\left[Ru(NH_3)_5N_2\right] Cl_2$ and $\left[Ru(NH_3)_5Cl\right] Cl_2$ as the concentration of the dinitrogen complex decreases. This may be explained in terms of a reduction in the space occupied by the $Ru - N_2$ group, as the lattic parameters are more and more dominated by the smaller Ru - Cl group. In effect the dinitrogen is pushed closer to the metal, increasing the π overlap and reducing the ν(NN) stretching frequency.

And finally because of the lability of the dinitrogen ligand(75) these complexes are ideal starting materials for the preparation of ruthenium (II) and ruthenium (III) complexes.

3.1.3 REACTIVITY OF NITROGEN COMPLEXES:

The di-nitrogen molecule exhibits a high ionization(76) potential (1504.8kJ mole^{-1}) and a large negative electron affinity (estimated as

$- 351.1$ kJ mol^{-1}). Hence it is difficult to oxidize or reduce. Moreover, the N - N bond is hard to weaken due to the high stablization energy between the double and the triple bond (522.5 KJ mole^{-1}) compared to 271.7 for CO and 221.5 for C_2H_2 , which has been rationalized by considering the lower repulsion energy of the electron lone pair of $N \equiv N$.

Generally the activation the N_2 molecule attains upon coordination is not enough to induce further attack upon it and most of the reactions involving dinitrogen complexes lead to the rupture of the M - N bond with N_2 liberation. Reactions which do not proceed through attack at the N_2 ligand can be classified as follows:

a) - Oxidation and reduction.

Electron - rich dinitrogen complexes are generally easily oxidized and reagents such as hydrogen or iodine may oxidize them readily. Halogenated species are also effective and, for example, the complexes $MoX_2(dppe)_2$ (X = I, Cl) may be formed from reaction of trans - $Mo(N_2)_2(dppe)_2$ (I) with ICN and the imidoyl halide $\left[HC(Cl){=}NMe_2 \right] Cl$ respectively. In reactions with acids or other hydrogen sources, facile protonation at the metal often occurs thus substantiating the electron rich metal character. Dinitrogen evolution may result from oxidation or reduction, or photochemical excitation of the metal in complex (I) but in some cases N_2 displacement is believed to precede the metal oxidation.

b) - Displacements

The M - N bond of a dinitrogen complex may be sufficiently stable for displacement of co-ligands to occur without splitting of that bond, thus allowing the preparation of some dinitrogen complexes with sulphur - bonded ligands, such as trans-$\left[\mathrm{Mo(N_2)_2(PMe_2Ph)_2(dpte)}\right]$ and mer - $\left[\mathrm{Re(S_2CNR_2)(N_2)(PMe_2Ph)_3}\right]$ to be carried out by this route. However in most of the reactions the M - N_2 grouping is not retained and N_2 is evolved. Some of these displacing agents (mainly isonitriles) which are isoelectronic with N_2, are activated upon co-ordination to the dinitrogen fixation site in such a way that they undergo reactions which may be related to those observed for N_2 when ligating the same metal centers.

c) - N_2 Complexes in catalysis

Dinitrogen fixation site have been shown to catalyse various reaction types. It has been shown that the coordinatively unsaturated complex $\mathrm{RhCl(PR_3)_2}$ which can bind dinitrogen for certain phosphines, is an important reactive intermediate in the hydrogenation of olefins by Wilkinson catalyst $\mathrm{RhCl(PR_3)_3}$ from which it is derived by loss of one phosphine ligand in solution. The presence of N_2 may modify the reaction pathway and the product distribution. This must be taken into account particularly when the reactions are carried out under N_2. The catalytic activity of $\mathrm{CoH(N_2)(PPh_3)_3}$, $\mathrm{CoH_3(PPh_3)_3}$ and of $\mathrm{CoN_2(PPh_3)_3}$ in olefin isomerization is prompted by the presence of N_2, whereas the double bond migration catalysed by $\mathrm{RuH_2N_2(PPh_3)_3}$ and by $\mathrm{RuH_4(PPh_3)_3}$ is inhibited by the presence of N_2. It is believed that in the Co species the rate determining step is the displacement of product olefin by the reactant olefin which is promoted by N_2. The inhibiting effect of N_2 in Ru system is explained by the competition of N_2 for the active metal site $RuH_2(PPh_3)_3$ and $Ru(PPh_3)_3$.

d) - Addition reactions

Olefins may add to unsaturated dinitrogen complexes. For example the four coordinate Ir (I) complex trans — $\left[IrCl(N_2)(PPh_3)_2\right]$ undergoes addition reactions with diethylmaleate (DEM) yielding the higher co-ordinate $IrCl(N_2)(L)(PPh_3)_2$ (L = DEM)

e) - Reactions of coligands

These reactions may proceed with either retention or loss of N_2. Examples of displacing reactions of co - ligands have been given in section b.

3.1.4 NITROUS OXIDE COMPLEXES:

Nitrous oxide (N_2O) is isoelectronic with carbon dioxide and appears to be an extremely inert molecule at room (77) temperature and atmospheric pressure, comparable even with N_2 in its inertness, which is surprising in view of its positive free energy of formation (ΔG^o = 104 kJ $mole^{-1}$) and potential oxidizing power.

With the discovery of dinitrogen complexes of transition metals (78) came the possibility of preparing analogous complexes of nitrous oxide.

Pratt and co-workers showed that nitrous oxide could be reduced by a variety of transition metals.

The complex $\left[Ru(NH_3)_5.N_2O \right] (BF_4)_2.H_2O$ has been obtained from the reaction of $\left[Ru(NH_3)_5 H_2O \right]^{+2}$ with N_2O at high pressure (30 - 40 atm) in absence of oxygen and in presence of sodium fluoroborate.(79) The infra-red spectrum of the solid shows a medium absorption band at 2275 cm^{-1} and a very strong absorption band at 1210 cm^{-1}. These two bands have been assigned to the ν_3 and ν_1 stretching vibrations of N_2O with a shift of +51 cm^{-1} for ν_3 and -76 cm^{-1} for ν_1 compared to the spectrum of gaseous N_2O. There are also two ill defined bands in the region 500 - 250 cm^{-1}. It is not as yet possible to decide whether these bands are due to the bending mode of the N_2O molecule (ν_2 in N_2O (g) = 589 cm^{-1}) or due to metal ligand vibrations. The spectrum also shows the fluoroborate, and the ammine vibrations expected for a Ru^{II} ammine complex, bands at 3615, 3525 and a shoulder at 1700 cm^{-1} were assigned to lattice water. In some preparations a weak band at 2144 cm^{-1} was observed. This was assigned to the ν N-N of $\left[Ru(NH_3)_5N_2 \right] (BF_4)_2$ present as an impurity.

A binuclear nitrous oxide complex $\left[(Ru(NH_3)_5)_2\ N2O \right] (BF_4)_4$ from the reaction of aqua-penta-ammine-ruthenium (II) and N_2O at 1 atm has also been reported.(80)

Dinitrogen oxide and penta-ammine-aqua-ruthenium (II) are(84) known to react according to these following equations:

$$\left[Ru(NH_3)_5(OH_2)\right]^{+2} + N_2O \longrightarrow \left[Ru(NH_3)_5N_2O\right]^{+2} + H_2O$$

and

$$\left[Ru(NH_3)_5.N_2O\right]^{+2} + 2\bar{e} + 2\overset{+}{H} \longrightarrow \left[Ru(NH_3)_5N_2\right]^{+2} + H_2O$$

At a pressure of one atmosphere of dinitrogen oxide and at low concentrations of ruthenium (II) about 10% of the ruthenium (II) is present as the dinitrogen oxide complex; at higher concentrations $\left[Ru(NH_3)_5OH_2\right]^{+2}$ acts as a reducer, forming the dinitrogen complex $Ru(NH_3)_5N_2^{+2}$ and $\left[(Ru(NH_3)_5)_2N_2\right]^{+4}$. In the presence of an external reducerthe dinitrogen complexes are formed in high yield.

Recent reports that nitrous oxide is reduced to molecular nitrogen(85) by transition metals prompted the investigation of the gas above the reaction mixture. Analysis by mass spectrometry showed that it contained nitrous oxide, hydrogen and insignificant amounts of molecular nitrogen. The products and yields of the dinitrogen species produced from reaction of $\left[Ru(NH_3)_5Cl\right]^{+2}$ with amalgamated zinc as reducing agent under nitrous oxide are given in table 3.1.2. Data from table (3.1.2) show that the formation of the nitrogen complexes is faster under nitrous oxide than under nitrogen at the same pressure and high ratios of mononuclear to binuclear nitrogen complex are formed with nitrous oxide.

REACTION	TIME(hr)	% YIELD OF $\left[Ru(NH_3)_5N_2\right]^{+2}$	% YIELD OF $\left[Ru(NH_3)_5)_2N_2\right]^{+4}$
N_2 (1 atm)	3	16.5	20.6
	6	21.1	31.1
N_2O (0.065 atm)	3	21.5	19
	18	35	35.5
N_2O (1 atm)	1	81.4	7.4
	3	82.7	9.1

Table 3.1.2. Formation of molecular nitrogen complexes from nitrous oxide at room temperature.

Coordination of dinitrogen oxide has a major effect on the intensity(84) of its absorptions. The relative intensities in gaseous dinitrogen oxide are altered in the complexes and are also dependent on the anion. In the hexafluorophosphate salt ν_3 and ν_1 are of approximately equal intensity. The intensity of ν_3, however decreases in the order, $PF_6 > BF_4 > I > Br$ in such a way that in the bromide salt it is very weak and could only be assigned by comparison with the spectra of the ^{15}N isotopmers. The stability of the nitrous oxide complexes was also dependent(86) on anion $(\bar{I} > \bar{Br} > \bar{Cl})$. The iodide salt was found to be stable for several weeks in dry air, but the chloride salt decomposed in a few days. The rate of decomposition may be an inverse function of the sample purity, since the very soluble chloride salt was found to be difficult to obtain pure.

3.1.5 PENTA-AMMINE-AQUA-RUTHENIUM II:

This cation can be prepared from reaction of $Ru(NH_3)_5Cl_3$ by(82) amalgamated zinc in dilute sulphuric acid. It reacts with dinitrogen molecule at one atmosphere pressure and ambient temperature yielding $\left[Ru(NH_3)_5N_2\right]^{+2}$. Allen and Bottomley have shown that the solution of this penta-ammine-aqua-hydrate-ruthenium II compound fixes even atmospheric nitrogen.(83) The interesting aspect of this reaction appears to be an effective nucleophilicity of dinitrogen molecule for ruthenium II in presence of oxygen. This opens up new possibilities for the direct utilization of atmospheric nitrogen and is an important step towards our understanding of biological nitrogen fixation. Further investigation has revealed that during the preparation of $Ru(NH_3)_5N_2^{+2}$ from

$Ru(NH_3)_5H_2O^{+2}$, the nitrogen complex reacts in solution with the hydrate complex forming a binuclear ion $\left[(NH_3)_5RuN_2Ru(NH_3)_5\right]^{+4}$ and water.(84)

$$\left[Ru(NH_3)_5\ N_2\right]^{+2} + \left[Ru(NH_3)_5OH_2\right]^{+2} \longrightarrow \left[(Ru(NH_3)_5)_2\ N_2\right]^{+4} + H_2O$$

The process is reversed on dilution and the $\left[Ru(NH_3)_5.N_2\right]^{+2}$ ion forming again. The infra-red spectrum of the binulclear ion indicates that nitrogen is symmetrically bonded. A competition reaction of penta-ammine-aqua-hydrate-ruthenium (II) with both oxygen and nitrogen occurs yielding simultaneously an oxidized compound, probably a penta-amine-hydroxy-ruthenium(II) ($Ru(NH_3)_5OH^{+2}$) cation and a mixture of nitrogen complexes, $Ru(NH_3)_5N_2^{+2}$ and $(NH_3)_5RuN_2Ru(NH_3)_5^{+4}$. The crystal structure of this dinitrogen complex is given below (fig 3.1.1), which indicates a linear bonding for metal - N=N system.(94)

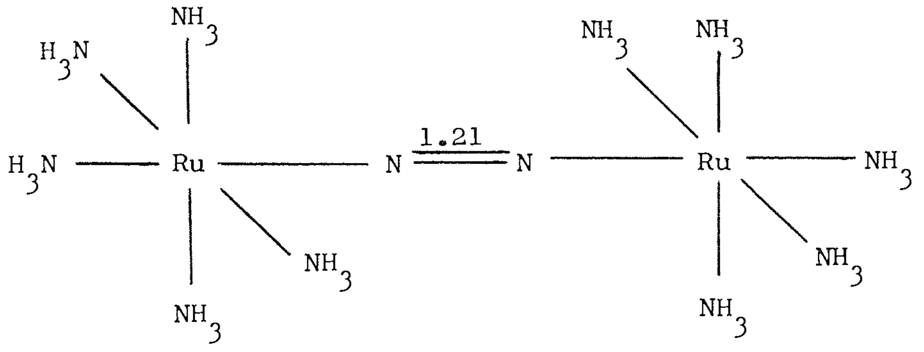


Fig (3.1.1)

Since the complex $\left[Ru(NH_3)_5)_2N_2\right]^{+4}$ is the only binuclear dinitrogen complex which concerns the work in this chapter, no further detail about other dinitrogen complexes of transition metals with this type of bonding or the other μ-dinitrogen complexes with hetero nuclear structure will be given.

3.1.6 CARBON DIOXIDE AND COORDINATION AT NITROGEN BINDING SITE:

The importance of the activation of carbon dioxide by transition(88) metal elements and its reactions have been discussed in the first chapter. Carbon dioxide is neither isoelectronic with nitrogen nor a substrate of nitrogenous. However, activation by nitrogen fixation site, or related one, has been reported and its importance justifies this chapter. Many of the dinitrogen complexes have metal atoms in low oxidation states and the co-ligands are generally good electron donors such as tertiary phosphines, ammonia, hydride, and halide and this is comparable with some of the characteristic behaviour of carbon dioxide complexes. Some of the examples of carbon dioxide activation via coordination at nitrogen binding sites are as follows:

The complex $\left\{ \left[(C_6H_{11})_3P \right]_2 Ni \right\}_2 N_2$ (I) which is obtained from reaction of nickel acetylacetonate with trimethyl aluminum(87) in the presence of tricyclohexylphosphine and nitrogen reacts with carbon dioxide in toluene at room temperature yielding red orange crystal of $\left[Ni(PCy_3)_2 \cdot CO_2 \right]$ 0.75 toluene (II) which is air stable for a few hours. The infra-red spectrum of II shows band at 1740(vs), 1698(vw) and (1150)s cm^{-1}. These bands are assigned to coordinated carbon dioxide.(15) The complex (I) was found to have a linear Ni-N-N-Ni system in which the nitrogen molecule is enclosed in a cage formed by four of the cyclohexyl rings. The N - N bond distance is 1.12Å and the N_2 can easily be displaced to give $\left[(C_6H_{11})_3P \right]_2$ Ni.

The complex $\left[Mo(N_2)_2(PMe_2Ph)_4 \right]$ also reacts with carbon dioxide(16) in toluene at room temperature yielding $\left[Mo(CO_2)_2(PMe_2Ph)_4 \right]$ (III).

The infra-red spectrum of III shows bands at 1760, 1510 and 1335 cm^{-1} which are assigned to the coordinated group or groups derived from the carbon dioxide. It was found that complex III changes spontaneously in solution into a carbonato bridge complex $\left[(PMe_2Ph)_3(CO)Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3\right]$.

3.2 EXPERIMENTAL

3.2.1 MODE OF OPERATION:

Most compounds prepared in this chapter were found to be sensitive to air. Consequently, after precipitating the product, by using a saturated solution of a suitable anion, the solution was filtered under a suitable atmosphere (N_2O or CO_2 or Ar). The product was then washed with solvents saturated with this same gas and dried under a stream of the gas. Samples were then submitted for elemental analysis before they could react with oxygen. The excess product was either stored under a suitable atmosphere or checked by infra-red and used for the subsequent reaction immediately.

3.2.2 THE REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) AND ITS ANALOGOUS COMPLEXES WITH CARBON DIOXIDE AT PRESSURES ABOVE ATMOSPHERIC

A known volume of the solution (15 - 18) ml (or known weight of solid) (30 - 100) mg was transferred into a test tube and put in the auto clave which had previously been filled with a known amount of solid carbon dioxide. The system was then allowed to reach equilibrium, at the temperature of laboratory. The pressure in the autoclave was calculated to be 12 - 18 atmosphere. The product was then removed from the autoclave and submitted for analysis.

3.3 EXPERIMENTAL

3.3.1 PREPARATION OF 2 PERCENT ZINC AMALGAM (121)

Shake 3g of pure zinc for a short time with normal HCl to which a trace of copper sulphate has been added. When the surface of the metal has been throughly freed from oxide, add an aqueous solution of mercuric chloride and shake until the zinc is well covered with a deposit of mercury. Wash the metal by decantation, add 10ml of clean mercury, and cover the mixture with fresh dilute acid. After a few hours the zinc has dissolved completely and the amalgam is ready for use. It should be preserved under dilute acid in a loosely stoppered bottle.

3.3.2 PREPARATION OF DINITROGENPENTAAMMINERUTHENIUM(II)

Ruthenium trichloride (1.0g) was dissolved in water (12 ml) and (122) hydrazine hydrate (10 ml) was added carefully over a period of 5 minutes. The initial vigorous, exothermic reaction was allowed to subside: the mixture was stirred over-night and filtered by gravity. Saturated solution of sodium perchlorate (20 ml) was added to the filtrate. The product was collected by filtration,washed with water, alcohol, and then air dried. The yield is 0.47 g.

Analytical data

Found: %H 4.2 %N 20.7

$[Ru(NH_3)_5N_2](ClO_4)_2$

requires: %H 3.6 %N 23.7

IR: 2140 cm^{-1}

using the saturated solution of ammonium hexa-fluorophosphate (20 ml) or sodium iodide (20 ml) the following data were obtained:

Found for attempted

$[Ru(NH_3)_5 N_2](PF_6)_2$ product:

%H 3.4 %N 22.7

$[Ru(NH_3)_5N_2](PF_6)_2$

requires: %H 3 %N 19.4

IR: 2160 cm^{-1}

Found for attempted

$[Ru(NH_3)_5N_2] I_2$

%H 3.5 %N 17.8

$[Ru(NH_3)_5N_2] I_2$

requires: %H 3.2 %N 20.9

3.3.3 PREPARATION OF PENTAAMMINECHLORORUTHENIUM(III)CHLORIDE

To the filtered solution, prepared as in (3.3.2) is carefully added (93) concentrated hydrochloric acid until the pH is 2.

Vigorous gas evolution takes place. The solution is boiled with stirring, and becomes yellow, slowly precipitating the yellow product. When no further precipitation is observed, the mixture is cooled to room temperature and the crude pentaamminechlororuthenium(III)—chloride is collected by filtration, washed once with 6M hydrochloric acid, alcohol, and acetone and then air dried. The yield of crude product is (0.65g).

The product is purified by heating an aqueous slurry (0.65g in 10 ml of water) to 60°C and adding concentrated ammonia drop wise, until the yellow complex dissolves to give a yellow solution. The solution is filtered hot and then cooled in an ice bath. To the cold solution concentrated hydrochloric acid is added dropwise to re-precipitate the yellow pentaamminechlororuthenium (III)chloride. The product is collected by filtration, washed with 6M hydrochloric acid, and then washed with water, alcohol, and acetone and dried over P_2O_5. The yield is (0.58g).

<u>Analytical data:</u>

Found	%H	5.4	%Cl	33.3	%N	24.2
$Ru(NH_3)_5Cl_3$ Requires:	%H	5.19	%Cl	36.3	%N	24

3.3.4 REACTION OF DINITROGENPENTAAMMINERUTHENIUM(II)PERCHLORATE WITH CARBON DIOXIDE IN SOLUTION

Dinitrogenpentaammineruthenium(II)perchlorate (0.1g) was transferred into a 3 neck flask. Carbon dioxide was bubbled through 10 ml aliquots of solutions made up using the following solvents alcohol, water, aqueous alkali, tetrahydrofuran, benzene. Infra-red spectra of the products were recorded.

3.3.5 REACTION OF DINITROGENPENTAAMMINERUTHENIUM(II) SALTS WITH CARBON DIOXIDE AT PRESSURES ABOVE ATMOSPHERIC

Solid samples of (perchlorate, hexafluorophosphate and iodide) salts of dinitrogenpentaammineruthenium(II) obtained from procedure (3.3.2) were separately kept for 1-2 days under pressure in a carbon dioxide atmosphere. Analytical data of the products after removing the resulting solids from the autoclave for perchlorate salt:

Found: %C 0.7 %H 4.2 %N 19.7

IR: 2330 cm^{-1}

Hexafluorophosphate salt:

Found: %C 2.3 %H 3.3. %N 14

IR: 2330 cm^{-1}(s)

3.3.6 PREPARATION OF PENTAAMMINEHYDRATERUTHENIUM(II)

The modified version of the procedure outlined given in reference (91) was followed.

Pentaamminechlororuthenium(III)chloride (0.3g) in sulphuric acid 0.1M (30 ml) was transferred into a three neck flask and 5 ml of amalgamated zinc, prepared as in (3.3.1), was added. Argon was bubbled through the mixture (1 hr) until all solid material dissolved. The yellow solution above the amalgamated zinc (solution A) was then withdrawn by syringe and added to a saturated solution of ammonium hexafluorophosphate(20 ml). (The ammonium hexafluorophosphate solution had also been previously saturated with argon). The yellow precipitate was collected by filtration, washed with argon saturated water and alcohol and dried.

The yield was 0.11g.

Analytical data:

Found:	%H	3.7	%N	14.9
$\left[Ru(NH_3)_5 \cdot H_2O\right](PF_6)_2$				
Requires:	%H	3.4	%N	14.1

3.3.7 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) WITH NITROUS OXIDE IN PRESENCE OF AMALGAMATED ZINC

Nitrous oxide was bubbled through a solution (A) in the presence of amalgamated zinc (5 ml) (procedure 3.3.6) (1 hr). The solution was then kept under an atmosphere of nitrous oxide.

After 3 hours, the solution above the amalgamated zinc was transferred to a three neck flask (previously filled with nitrous oxide at atmospheric pressure) (solution B). On addition of c. 20 ml saturated solution of ammonium hexafluorophosphate (also saturated with nitrous oxide) a yellow precipitate was obtained which was then filtered, washed with water, and alcohol saturated with nitrous oxide and dried.

Analytical data:

Found:	%H	3.2	%N	16.2	%P	12.8
$[Ru(NH_3)_5)_2N_2](PF_6)_4$						
Requires:	%H	3.1	%N	17.1	%P	12.6

IR: 2150(w)cm^{-1}, 2220(w)cm^{-1}

3.3.8 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) WITH NITROUS OXIDE IN THE ABSENCE OF AMALGAMATED ZINC

Treatment of solution (A) (procedure 3.3.6) with nitrous oxide in the absence of amalgamated zinc produces a small quantity of yellow precipitate which could not be collected.

3.3.9 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) WITH CARBON DIOXIDE IN THE PRESENCE OF REDUCING AGENT AND PRESSURE

Solution (A) (using 0.2g $Ru(NH_3)_5Cl_3$ in 20 ml H_2SO_4 0.1M and 3 ml of Zn/Hg) from the reaction (3.3.6) was kept for 48 hrs under pressure in a carbon dioxide atmosphere in the presence of fresh zinc amalgam (1 ml). The solution was then transferred into a saturated solution of sodium tetrafluoroborate (15 ml) saturated with carbon dioxide. The yellow precipitate obtained was then filtered, washed with a few drops of water, and alcohol saturated with carbon dioxide and dried. IR: 1980 (m) cm^{-1}.

3.3.10 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) WITH CARBON DIOXIDE IN THE ABSENCE OF REDUCING AGENT

Following procedure (3.3.8) in the absence of amalgamated zinc and precipitating the solution using saturated solution of ammonium hexafluorophosphate resulted in a yellow complex with an IR band at 2340 (w) cm^{-1}.

3.3.11 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) WITH CARBON DIOXIDE IN PRESENCE OF AMALGAMATED ZINC UNDER ATMOSPHERIC PRESSURE

Carbon dioxide was bubbled through solution A in the presence of zinc amalgam (5 ml) (3.3.6) for 1 hr. The solution was then kept under an atmosphere of carbon dioxide for 24 hours.

The solution above the Zinc amalgam was withdrawn by syringe and added to a saturated solution of ammonium hexafluorophosphate(20 ml) saturated with carbon dioxide. No precipitate was obtained.

3.3.12 UV STUDY OF THE REACTION (3.3.10)

Carbon dioxide was bubbled through a solution of pentaamminehydrateruthenium(II) (3.4×10^{-6}M) for 1 hour in the presence of amalgamated zinc. After keeping the solution under an atmosphere of carbon dioxide for 20 hours, the solution was transferred to a UV cell (under CO_2 atmosphere) and the spectrum recorded. The UV spectrum of the solution after treatment with carbon dioxide shows two maximum at $\lambda_1 = 255$nm ($\epsilon_1 = 4.5 \times 10^4$) and $\lambda_2 = 325$ nm ($\epsilon_2 = 3.6 \times 10^4$) The UV spectrum of pentaamminehydrateruthenium(II) (3.4×10^{-6}M) in 0.1M sulphuric acid shows one maximum at $\lambda = 310$ nm with $\epsilon = 2.3 \times 10^4$.

3.3.13 REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II)HEXAFLUOROPHOSPHATE WITH CARBON DIOXIDE IN AUTOCLAVE

Pentaamminehydrateruthenium(II)hexafluorophosphate was kept for 24 hours under pressure in a carbon dioxide atmosphere. The product was then removed from autoclave and submitted for analysis.

Analytical data:

Found: %C 0.6 %H 3.2 %N 15.8

$\left[Ru(NH_3)_5)_2CO_2\right](PF_6)_4$

Requires: %C 1.2 %H 3.0 %N 14.0

IR: 2340(w) cm^{-1}.

3.3.14 REACTION OF CARBON DIOXIDE WITH PRODUCT OF THE REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) AND NITROUS OXIDE IN AUTOCLAVE

Solution B obtained from procedure (3.3.7) was kept for 30 hrs under pressure in a carbon dioxide atmosphere in the presence of fresh zinc amalgam (1 ml). The solution was then added to a 15 ml saturated solution of sodium tetrafluoroborate (saturated with carbon dioxide). The yellow product was then filtered, washed with water and alcohol saturated with carbon dioxide and dried under a stream of carbon dioxide.

Analytical data:

Found: %C 1.3 %H 3.8 %N 20.4

$\left[Ru(NH_3)_5)_2CO_2\right]\cdot(BF_4)_4$

Requires: %C 1.5 %H 3.9 %N 18.3

IR: 2340(s)cm^{-1}, 660(s)cm^{-1}.

3.3.15 THERMAL STABILITY OF THE PRODUCT OBTAINED IN REACTION (3.3.14)

The product of the reaction (3.3.14) (30 mg) was transferred to a test tube and heated for 4 hrs in a water bath at 80°C and its infra-red spectrum then recorded.

IR: 2340(m)cm^{-1}, 660(m)cm^{-1}.

3.3.16 REACTION OF CARBON DIOXIDE WITH THE PRODUCT OF THE REACTION OF PENTAAMMINEHYDRATERUTHENIUM(II) AND NITROUS OXIDE IN ABSENCE OF AMALGAMATED ZINC UNDER PRESSURE

Following procedure (3.3.14) in the absence of amalgamated zinc and precipitating the product using saturated solution of ammonium hexafluorophosphate resulted in a yellow product.

IR: 2340 cm^{-1}(m), 660 cm^{-1}(w)

3.3.17 REACTION OF CARBON DIOXIDE WITH PRODUCT OF THE REACTION (3.3.7) IN THE SOLID FORM:

The product of the reaction (3.3.7) was kept for (24 hours) under pressure in a carbon dioxide atmosphere. The product was then removed from the autoclave and submitted for analysis.

Analytical data:

Found: %C 1.3 %H 3.5 %N 15.3

$\left[(Ru(NH_3)_5)_2CO_2\right](PF_6)_4$

Requires: %C 1.2 %H 3.0 %N 14.0

IR: 2340(vs)cm^{-1}, 660(s)cm^{-1}.

3.3.18 REACTION OF CHLOROPENTAAMMINERUTHENIUM(III)CHLORIDE WITH CARBON DIOXIDE UNDER PRESSURE

Chloropentaammineruthenium(III)chloride was kept for 48 hours under pressure in a carbon dioxide atmosphere. The infra-red spectrum of the product after removing from the autoclave was found to be the same as the infra-red spectrum of the starting material.

3.3.19 PREPARATION OF HEXAKIS(METHYLAMINE)RUTHENIUM(II) (128)

Ruthenium trichloride (0.1g) in distilled water (25 ml) was added to methylamine solution (10 ml), followed by the introduction of zinc dust (0.1g). The solution was then refluxed under an atmosphere of argon for 1 hr, and filtered. Upon addition of saturated potassium bromide solution (25 ml), 0.08 g of a light green product was obtained.

Analytical data:

Found: %C 15.7 %H 6.6 %Br 36.4 %N 17.9

$[Ru(CH_3NH_2)_6]Br_2$

Requires: %C 16.1 %H 6.7 %Br 35.6 %N 18.8

3.3.20 PREPARATION OF HEXAKIS(N-BUTYLAMINE)RUTHENIUM(II) (129)

Ruthenium trichloride (0.1g) in distilled water (25 ml) was mixed with n-butylamine (10 ml) under an atmosphere of Argon. The mixture was treated with zinc dust (0.1g) and refluxed under argon until the solution assumed a pale green colour (1 hour). The warm solution was filtered into a clean flask and treated with a saturated solution of potassium bromide (25 ml) which was then filtered, washed with distilled water and dried in vacuo.

Analytical data:

Found: %C 40.0 %H 9.0 %Br 26.7 %N 11.0

$[Ru(n\text{-}Bu\ NH_2)_6]Br_2$

Requires: %C 41.1 %H 8.7 %Br 23 %N 12

3.3.21 REACTION OF HEXAKIS(METHYLAMINE AND N-BUTYLAMINE) RUTHENIUM(II) WITH CARBON DIOXIDE IN AUTOCLAVE

Treatment of the dibromide salts of the Hexakis(methylamine and n-butylamine)ruthenium(II) obtained from the reaction (3.3.19) and (3.3.20) with carbon dioxide in an autoclave resulted in materials with the same infra-red spectra as those of the starting materials.

3.3.22 THE REACTION OF CARBON DIOXIDE WITH HEXAKIS-N-BUTYLAMINE RUTHENIUM(II) IN SOLUTION

Carbon dioxide was bubbled (1 hr) through the filtrate solution obtained from procedure (3.3.19), the solution was kept under an atmosphere of carbon dioxide for 1 day and was then precipitated by adding 25 ml of saturated solution of potassium bromide (saturated with carbon dioxide). The tarry product was collected, washed with water and dried in a desiccator.

Analytical data:

Found: %C 25.9 %H 6 %Br 26.7 %N 7.8

IR: 2100 cm^{-1} (m-s) 2220 cm^{-1} (w-m)

3.3.23 REACTION OF CARBON DIOXIDE WITH HEXAKIS(METHYLAMINE) RUTHENIUM(II) IN SOLUTION

By following the procedure (3.3.22) and replacing the hexakis-(n-butylamine)ruthenium(II) with hexakis(methylamine)ruthenium(II) no precipitate was obtained.

3.4.1 RESULTS AND DISCUSSION:

The reaction of nitrous oxide with the complex pentaamminehydrateruthenium(II) has been investigated and the formation of mono-nuclear and binuclear nitrous oxide pentaammineruthenium(II) complexes has been reported.(79,80) Pentaamminehydrateruthenium(II) can be used as a starting material for the preparation of the analogous dinitrogen complex which can yield the binuclear dinitrogen complex in the presence of water. Since nitrous oxide is an isoelectronic molecule with carbon dioxide, a reaction of pentaammine-hydrateruthenium(II) with carbon dioxide, analogous to that with nitrous oxide may be expected.

The low oxidation state of the ruthenium in these compounds may also favour the reaction for the fixation of carbon dioxide. With reference to the idea given above, we have tried to study the reaction of pentaamminehydrateruthenium(II) and its analogous complexes with carbon dioxide in solution and in the solid form. A reducing agent (amalgamated zinc) and pressure were found to affect the reaction greatly.

The poor solubility of pentaamminehydrateruthenium(II) and its analogous complexes in some common laboratory solvents together with their sensitivity to oxygen, low yield and limited analytical facilities restricted our choice of techniques to elemental analysis and infrared spectroscopy as the main sources of information. Although the preparation of pentaamminehydrateruthenium(II) and its analogous complexes were taken from literature (or modified versions were used) optimum conditions were found with difficulty, and in many instances no precipitate was obtained.

Much time was also put into the preparation of excess starting material and checking the reproducibility of the reactions. An interesting point about those pentaammine complexes chosen for our study of carbon dioxide fixation is that ruthenium was in oxidation state II with the exception of chloropentaammineruthenium(III)chloride.

To avoid confusion the results of the reactions of carbon dioxide with pentaamminehydrateruthenium(II) and its analogous complexes are discussed separately, and a general discussion of all the reactions is given afterwards.

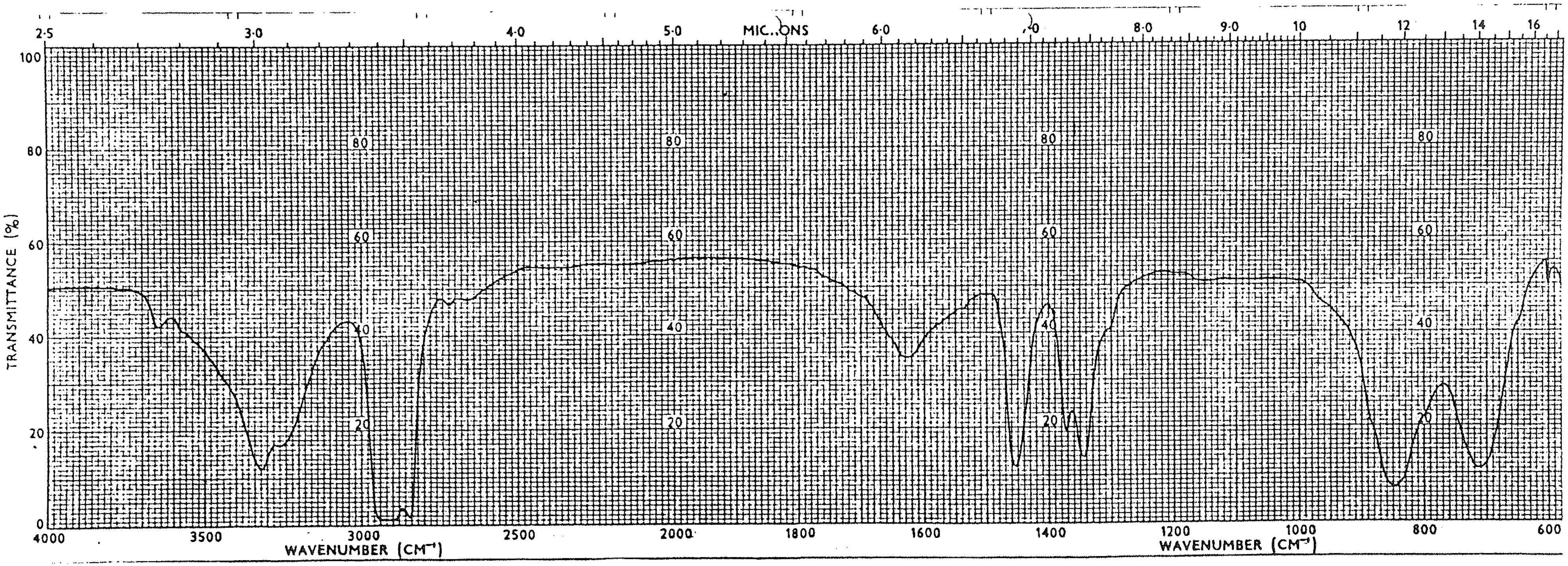
3.4.2 REACTION OF CARBON DIOXIDE WITH PENTAAMMINEHYDRATERUTHENIUM(II)

The preparation of pentaamminehydrateruthenium(II) has been$^{(92)}$ reported and the hexafluorophosphate salt formulated as $\left[Ru(NH_3)_5.H_2O\right](PF_6)_2$ (A). The preparation of a similar complex to (A) containing one molecule of water in its crystal lattice has also been reported and formulated as $\left[Ru(NH_3)_5\ H_2O\right](PF_6)_2.H_2O$, but isolation of tetrafluoroborate salt resulted in a yellow complex with no consistent analytical data$^{(84)}$. The infra-red spectrum of complex (A) in Nujol was reported to be more complicated in the 3200-3600 cm^{-1} region than are the spectra of other pentaammineruthenium(II)-fluorophosphates and a strong broad band was observed at 1630 cm^{-1}, which is more intense than the N-H bending bands observed in the other salts, providing some evidence for the presence of aqua ligand.

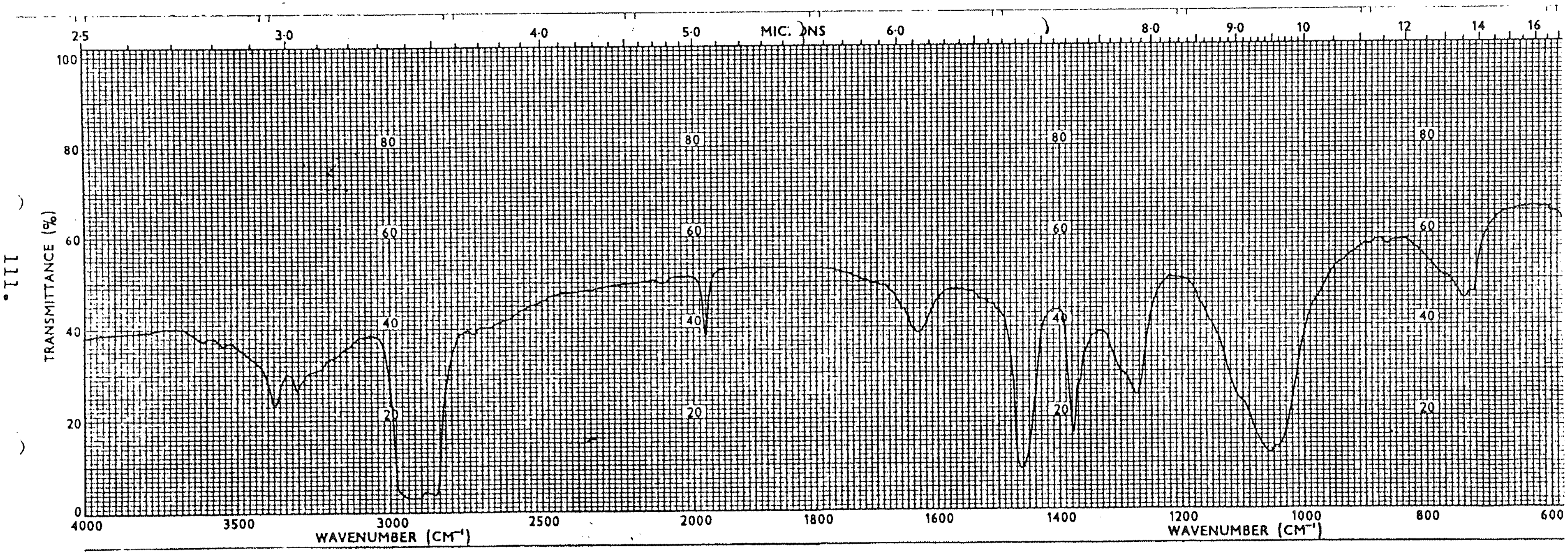
The pentaamminehydrateruthenium(II) complex whose preparation was given in the experimental part of this chapter shows a weak infra-red band at 3650 cm^{-1} and 3320 cm^{-1} (spectrum 3.4.1). Broadening of a band in the region of 3200 - 3600 cm^{-1} can be due to interference of vibrational frequencies.

With reference to the elemental analysis, this complex may be formulated to be similar to complex (A). To avoid confusion this complex is called (B). Precipitation of complex (B) using a saturated solution of sodium iodide or sodium perchlorate in place of ammonium hexafluorophosphate was not successful. Treatment of complex (B) with carbon dioxide in the autoclave and in the presence of amalgamated zinc according to procedure (3.3.9), before precipitation by ammonium hexafluorophosphate solution, resulted in a yellow-green product which was soluble in acetone. Due to the insufficient quantity of the sample, elemental analysis could not be done. The infra-red spectrum of this compound (spectrum 3.4.2) shows a new band at 1980 cm^{-1} which can be assigned to a carbonyl species of formula $\left[Ru(NH_3)_5CO\right](BF_4)_2$ (C) which may have been produced from the disproportionation reaction of carbon dioxide. The compound $\left[Ru(NH_3)_5.CO\right](BF_4)_2$ is known. The infra-red spectrum of this compound has been reported to show a band at 1972 cm^{-1} in Nujol due to νCO. (92)

There are examples of carbon dioxide disproportionation reactions in the literature which have been studied in detail using isotope labelling and spectroscopic techniques.(26,43) In general the disproportionation reaction of carbon dioxide involves C-O bond cleavage and also C-O bond making. The latter can be promoted when a good alternative



Spectrum (3.4.1) Infra-red spectrum of $\left[Ru(NH_3)_5 \cdot H_2O\right](PF_6)_2$ obtained from procedure (3.3.6.) (Nujol Mull)



Spectrum (3.4.2) Infra-red spectrum of compound C. (Nujol Mull) source of oxygen is available.

In our case considering the presence of the reducing agent and metal ion the following routes for the formation of complex (C) may be postulated. The first possibility can be explained by the following equations:

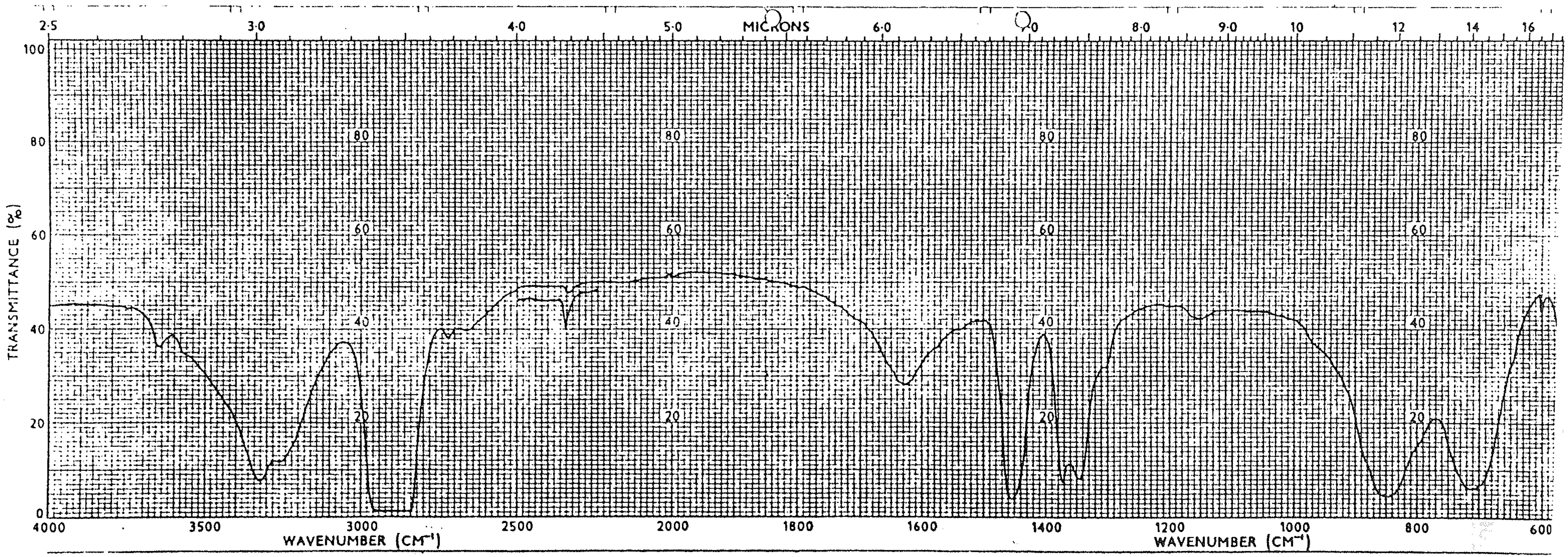
$$2CO_2 \quad + \quad 2\bar{e} \longrightarrow CO_3^{=} \quad + \quad CO$$

$$\left[Ru(NH_3)_5.H_2O\right]^{+2} \quad + \quad CO \longrightarrow \left[Ru(NH_3)_5CO\right]^{+2} \quad + \quad H_2O$$

The source of electrons in the above equation is presumably the amalgamated zinc. Such a route is similar to what is postulated by Chatt et.al$^{(16)}$ in the formation of bis - μ (carbonato) - molybdenum from $\left[Mo(CO_2)_2(PMe_2Ph)_4\right]$. The other possibility is that the carbon dioxide has formed an adduct complex such as $\left[Ru(NH_3)_5CO_2\right]^{+2}$, the adduct then being transformed into a carbonyl species $\left[Ru(NH_3)_5CO\right]^{+2}$, by the transfer of one oxygen from the carbon-oxygen cleavage to another molecule. The formation of carbonato species may also suggested but there is no evidence to prove it. This is because after recovery of the complex (C) according to procedure (3.3.9) no more solid substance could be recovered from the filtrate by any other ion.

The reaction of pentaamminehydrateruthenium(II) with carbon dioxide in the absence of a reducing agent in an autoclave and precipitation by ammonium hexafluorophosphate or treatment of the hydrate complex (B) in the solid form with carbon dioxide under pressure resulted in a compound which gave a similar infra-red spectrum with a new infra-red band at 2340 cm^{-1} compared with complex (B) (Spectrum 3.4.3.) From the low but non-zero percentage of the carbon and the observation of a band at 2340 cm^{-1} the uptake of the carbon dioxide by this hydrate complex may be inferred. The compound releases carbon dioxide on exposure to air and the band at 2340 cm^{-1} disappears. Carbon dioxide can be regained if the complex is kept under pressure in an atmosphere of carbon dioxide. Keeping the sample for a longer period of time under an atmosphere of carbon dioxide slightly increases the intensity of the band at 2340 cm^{-1}.

The reaction of pentaamminehydrateruthenium(II) with carbon dioxide under one atmosphere pressure of carbon dioxide in aqueous solution was also investigated. The UV spectrum of this hydrate complex before treatment with carbon dioxide shows a maximum at $\lambda = 310$ nm. When carbon dioxide is bubbled through this solution as explained in procedure (3.2.12) the band at $\lambda = 310$ nm disappears and new bands with λ max = 255 nm and $\lambda = 325$ nm appear. Although the change in the UV spectrum of the solution before and after treatment with carbon dioxide may suggest a reaction between pentaamminehydrateruthenium(II) and carbon dioxide, it does not prove it. Attempts at the precipitation of the complex $\left[Ru(NH_3)_5.H_2O\right]^{+2}$ treated in solution with carbon dioxide at atmospheric pressure, failed to yield any solid product after the addition of the saturated solution of ammonium hexafluorophosphate.



Spectrum (3.4.3) Infra-red spectrum of the compound obtained from reaction of $\left[\mathrm{Ru(NH_3)_5 \cdot H_2O}\right](\mathrm{PF_6})_2$ with CO_2 in autoclave. (Nujol Mull).

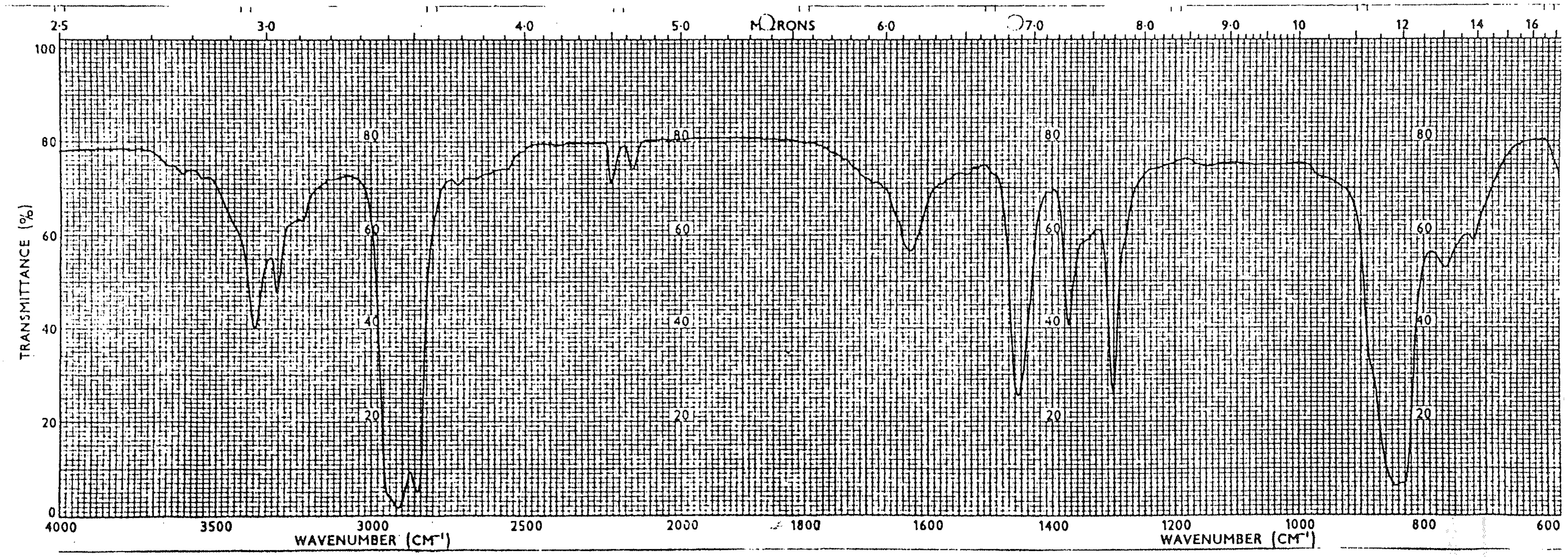
3.4.3 REACTION OF NITROUS OXIDE WITH PENTAAMMINEHYDRATERUTHENIUM(II):

The reaction between dinitrogen oxide and pentaamminehydrateruthenium (II) to form (dinitrogen oxide) pentaammineruthenium(II) has been investigated.(79,84) At a high pressure of nitrous oxide the Br^-, I^-, BF_4^-, and PF_6^- salts of $\left[Ru(NH_3)_5.N_2O\right]^{+2}$ were isolated. The above reaction under atmospheric pressure was investigated by Armor and (80) Taube who formulated their product as a binuclear nitrous oxide complex $\left[Ru(NH_3)_5)N_2O\right]^{+4}$ (D). The infra-red spectrum of compound D obtained from Nujol mulls revealed new bands at 2110(w-m) and 2105 cm^{-1} and new strong bands at 1160 and 1155 cm^{-1} for the bromide and tetrafluoroborate salts respectively, in addition to bands at 3450 (sh), 3290, 1625, 1290 (sh), 1275, 790 cm^{-1} due to ammonia and water on ruthenium.

The reaction of pentaamminehydrateruthenium(II) with nitrous oxide in the presence of a reducing agent was reported to give analogous monomeric and dimeric nitrogen complexes (84).

In the present work the complex prepared according to the procedure (3.3.7) from the reaction of $\left[Ru(NH_3)_5H_2O\right]^{+2}$ and N_2O in presence of reducing agent shows two weak bands at 2150 and 2220 cm^{-1} (spectrum 3.4.4) but shows no band in the region of 1160 cm^{-1}. The bands due to ammonia are also present. The elemental analysis of this compound can be fitted to either of the following structures (table 3.4.1):

$\left[(Ru(NH_3)_5)_2N_2O\right](PF_6)_4$ and $\left[(Ru(NH_3)_5)_2N_2\right](PF_6)_4$.



Spectrum (3.4.4) Infra-red spectrum of $\left[(Ru(NH_3)_5)_2 N_2\right](PF_6)_4$ obtained from procedure (3.3.7) (Nujol Mull)

Compound	Elemental analysis required %H	%N	%P
$\left[(Ru(NH_3)_5)_2N_2O\right](PF_6)_4$	3.01	16.8	12.4
$\left[(Ru(NH_3)_5)_2N_2\right](PF_6)_4$	3.1	17.1	12.6

Analytical data found for the compound obtained from the reaction of pentaamminehydrateruthenium(II)and nitrous oxide in presence of amalgamated zinc.

%H	3.2	%N	16.2	%P	12.8

Table 3.4.1.

A comparison of the infra-red data reported for complex $\left[(Ru(NH_3)_5)_2N_2O\right] X_4$ in which (X = Br^-, BF_4^-) with that observed here favours the assignment of the product as the dinitrogen complex $\left[(Ru(NH_3)_5)_2.N_2\right] (PF_6)_4$ (E).

The bands at 2150 and 2200 cm^{-1} (spectrum 3.4.4.) are presumably due to monomeric dinitrogenpentaammineruthenium(II) impurities. The two different dinitrogen frequencies may be due to two different types of dinitrogen bonding to the metal ion. Another possibility is that the complex contains two dinitrogen ligands whose position within the molecule are not the same.

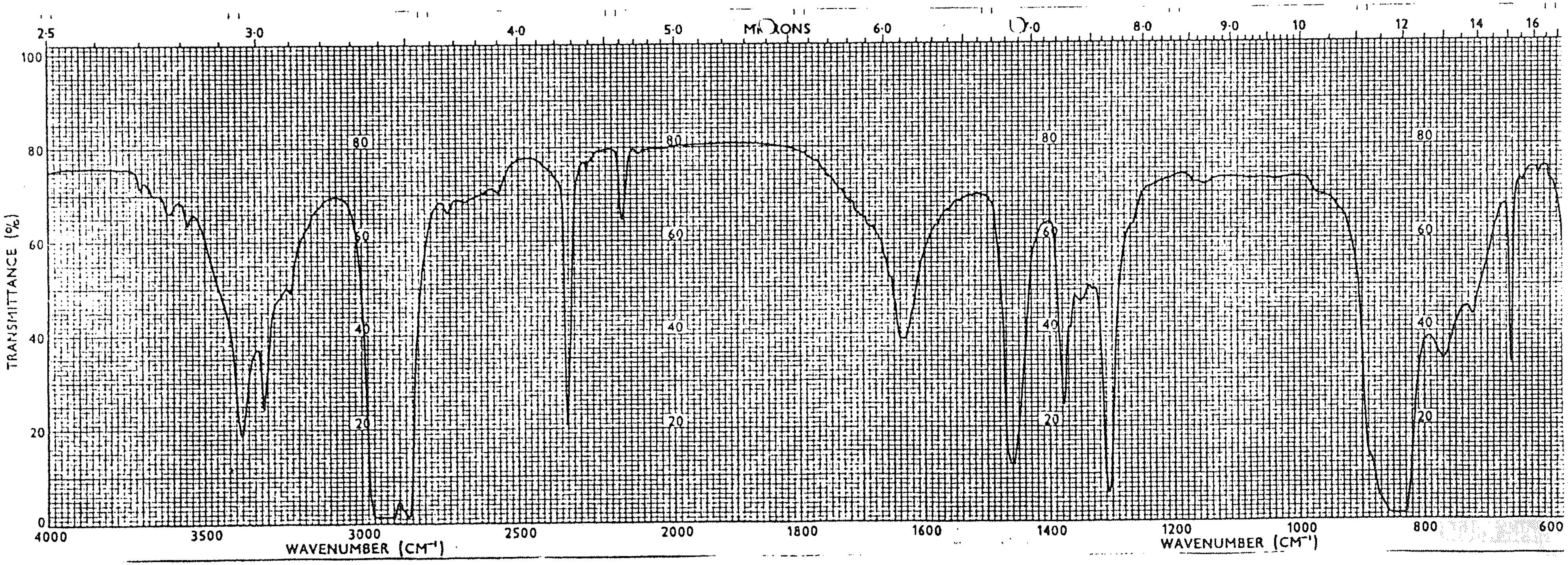
The result is also in agreement with information given in reference (84) which discusses the formation of monomeric and dimeric dinitrogenpentaammineruthenium(II) complexes from the reaction of pentaamminehydrateruthenium(II) and nitrous oxide which was discussed previously.

The reaction of complex $\left[(Ru(NH_3)_5)_2N_2\right](PF_6)_4$ (E) with CO_2 in the autoclave resulted in a product which shows two strong infra-red bands at 2340 cm^{-1} and 660 cm^{-1} (spectrum 3.4.5) attributed to uptaken carbon dioxide, since no other bands in this region are expected. With reference to the elemental analysis (procedure 3.3.17) the dimeric structure, $\left[(Ru(NH_3)_5)_2CO_2\right](PF_6)_4$ (F) can be inferred.

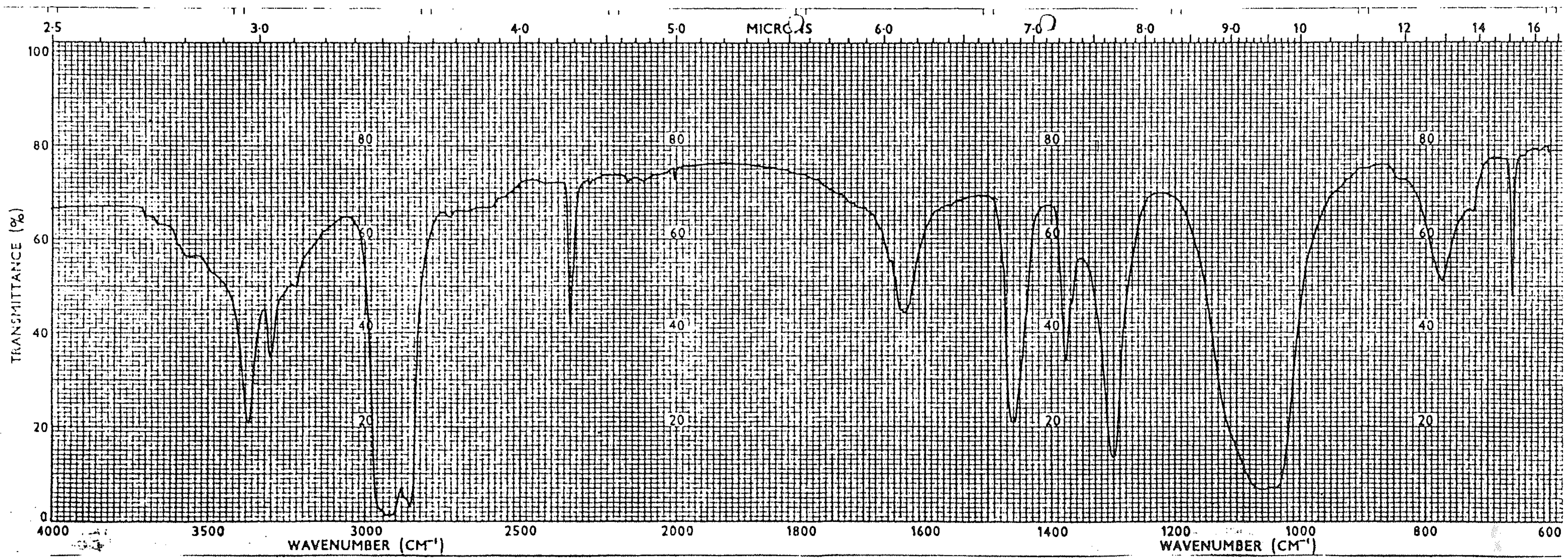
The reaction of pentaamminehydrateruthenium(II) with nitrous oxide in the absence of amalgamated zinc followed by the precipitation of the solution using a saturated solution of ammonium hexafluorophosphate resulted in a yellow complex which could not be studied due to insufficient quantity of the sample. Because of the limited facilities the reaction at a higher pressure of nitrous oxide could not be investigated.

The reaction of $\left[(Ru(NH_3)_5)_2N_2\right]^{+4}$ with CO_2 in an autoclave and in the presence of amalgamated zinc according to the procedure (3.3.14) gives a yellow complex which shows two strong infrared bands in the region of 2340 and 660 cm^{-1} (spectrum 3.4.6) attributable to carbon dioxide. Bands at 2150 and 2220 cm^{-1} due to monomeric dinitrogenpentaammineruthenium(II) impurities were not observed. The intensity of the bands at 2340 and 660 cm^{-1} decreases when the complex is heated up to 80°C for 4 hours. From the elemental analysis and the infra-red data this product was formulated as $\left[(Ru(NH_3)_5)_2CO_2\right](BF_4)_4$.

As discussed above the reaction of $\left[(Ru(NH_3)_5)_2N_2\right]^{+4}$ in solution in the presence of Zn/Hg and of $\left[(Ru(NH_3)_5)_2N_2\right](PF_6)_4$ in the solid form in autoclave with CO_2 produce similar products.



Spectrum (3.4.5) Infra-red spectrum of $(Ru(NH_3)_5)_2CO_2(PF_6)_4$ (Nujol Mull)



Spectrum (3.4.6) Infra-red spectrum of $\left[(Ru(NH_3)_5)_2\ CO_2\right](BF_4)_4$ (Nujol Mull)

They show two new strong infra-red bands in the region of 2340(s) and 660(s)cm^{-1}. These infra-red bands are characteristic of carbon dioxide and were assigned with reference to (130).

3.4.4 REACTION OF DINITROGENPENTAAMMINERUTHENIUM(II) WITH CARBON DIOXIDE

The details concerning dinitrogen complexes and the activation of carbon dioxide via the nitrogen site have been discussed in the introduction of this chapter. The preparation of dinitrogenpentaammineruthenium(II) was given in procedure (3.3.2) and the salts of PF_6^-, I^- and ClO_4^- were isolated. The vibrational frequency of dinitrogen in these salts is given in table (3.4.2)

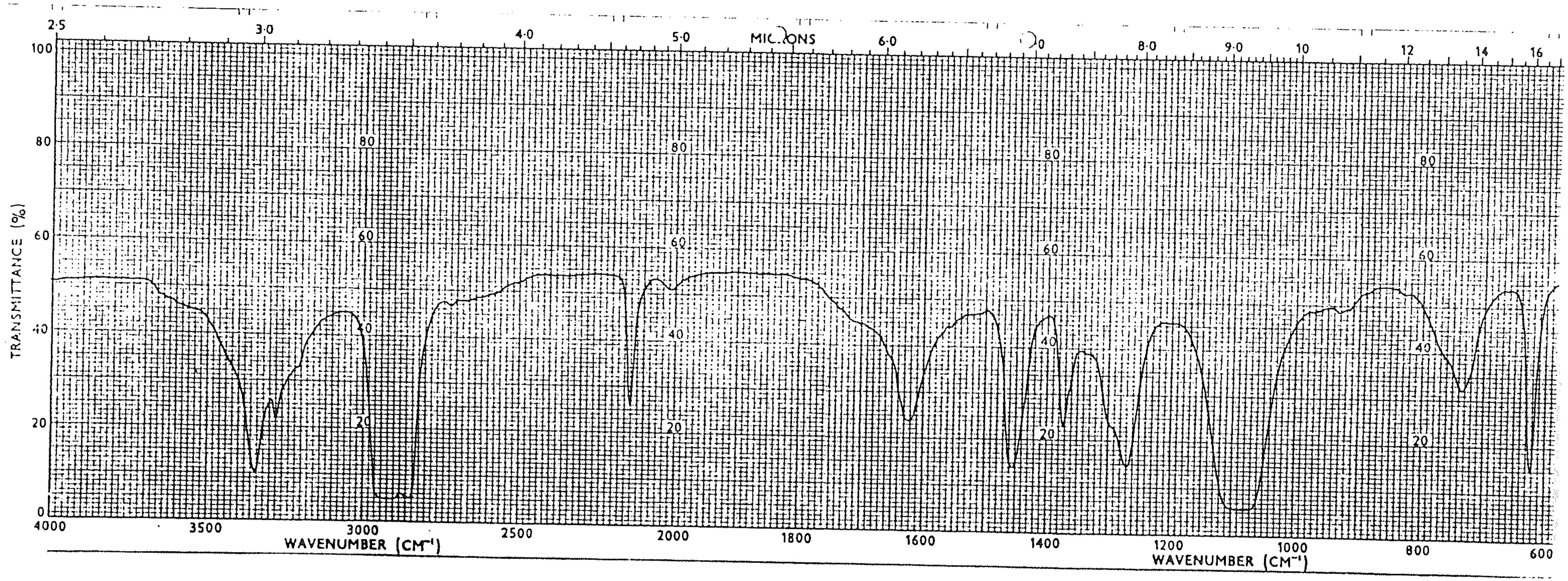
Compound	$\nu(N_2)$
$[Ru(NH_3)_5N_2](PF_6)_2$	2160 cm^{-1}
$[Ru(NH_3)_5N_2](ClO_4)_2$	2140 cm^{-1}
$[Ru(NH_3)_5N_2]I_2$	2120 cm^{-1}

Table 3.4.2.

and found to increase according to the following order $P\bar{F}_6 > Cl\bar{O}_4 >$ $\bar{I}$. The iodide salt was found to release dinitrogen more easily than the perchlorate salt. The hexafluorophosphate was quite stable compared with the other two salts. The reaction of dinitrogenpentaammineruthenium(II) perchlorate with carbon dioxide in the autoclave produced a product with a new infra-red band at 2330 cm^{-1} attributed to carbon dioxide taken up (spectrum 3.4.7 and 3.4.8)

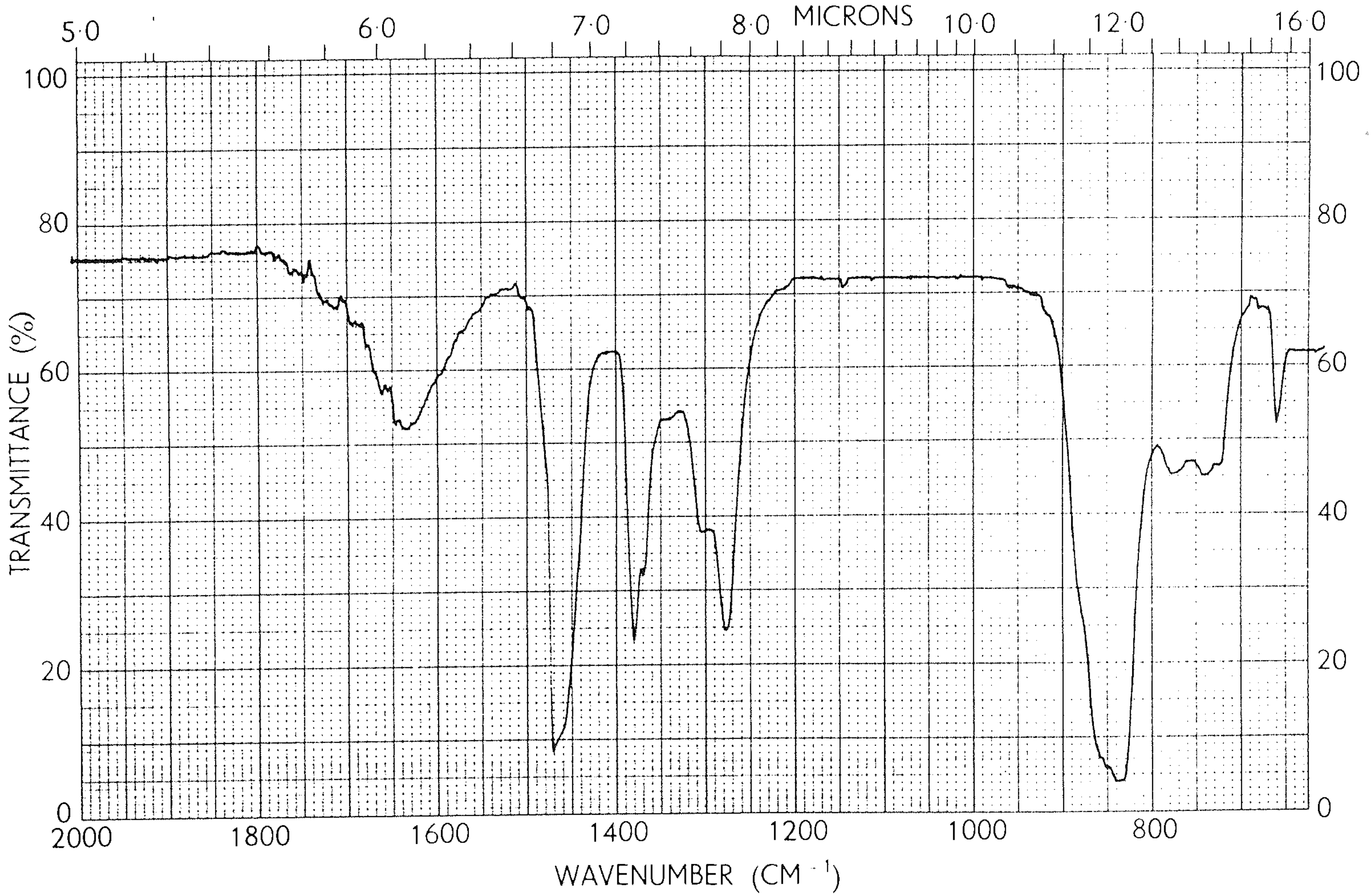
A similar infra-red band at 2330 cm^{-1} was also obtained when dinitrogenpentaammineruthenium(II) hexafluorophosphate salt was treated with carbon dioxide in the autoclave (spectrum 3.4.9) but no reaction between the iodide salt and carbon dioxide in the solid form was observed. The infra-red band at 2330 cm^{-1} for the hexafluorophosphate salt slightly decreases when the compound is exposed to air or put under vacuum. In the case of perchlorate salt the band at 2330 cm^{-1} completely disappears.

In one experiment, not fully reproduced later, the reaction of dinitrogenpentaammineruthenium(II) perchlorate with carbon dioxide in the presence of a small amount of alcohol in the autoclave gave a purple product, soluble in alcohol and water. The infra-red spectrum of this compound (spectrum 3.4.10) showed a band at 2310 cm^{-1} and 1860 cm^{-1} which can be attributed to carbon dioxide and carbonyl or nitrosyl ligand respectively. Attempts to reproduce the same reaction resulted in a yellow complex which showed only a new band at 2330 cm^{-1} attributed to carbon dioxide the infra-red spectrum (3.4.10) suggests that purple product might have one of the following structures:

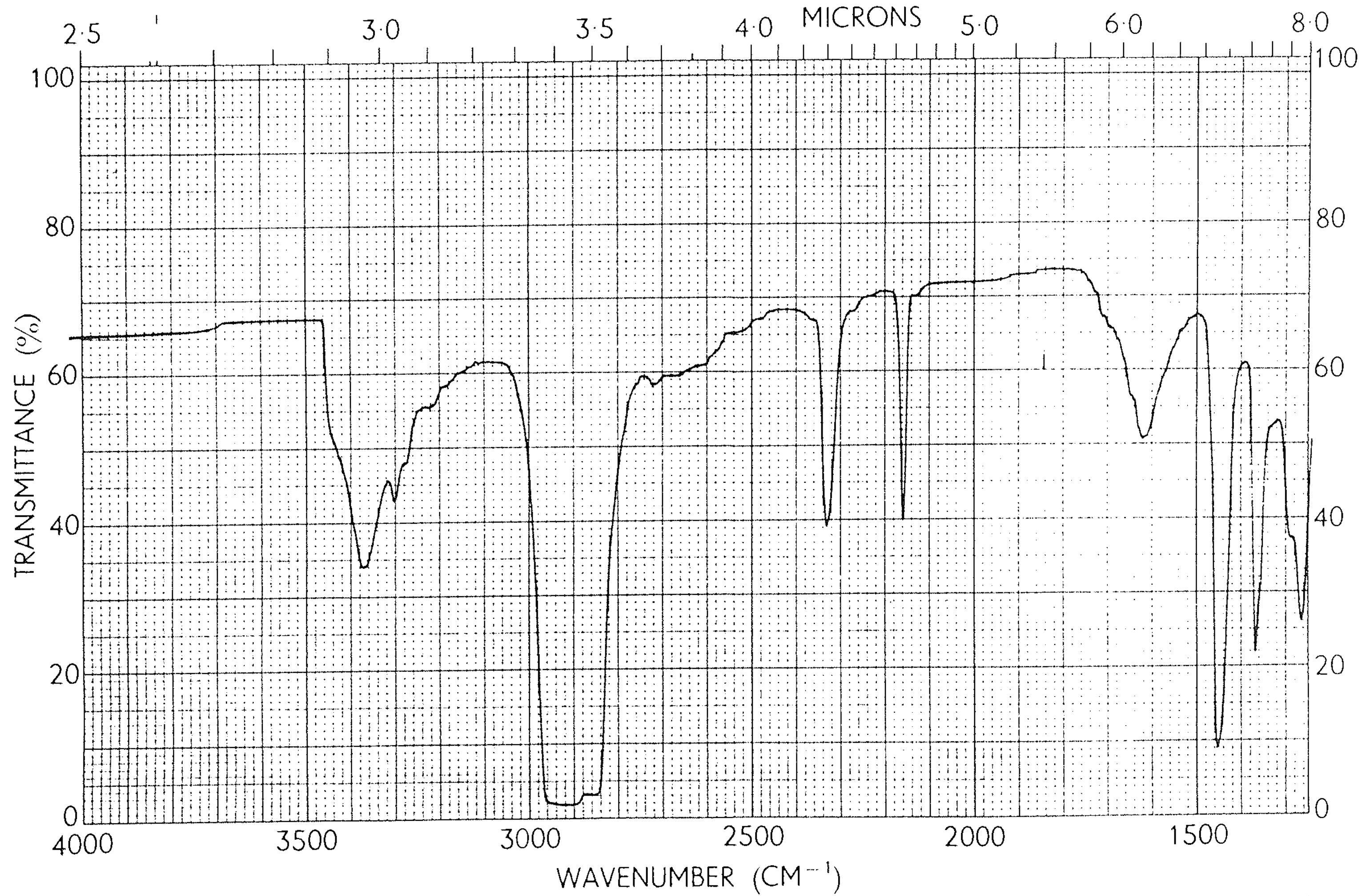


Spectrum (3.4.7) Infra-red spectrum of $\left[\mathrm{Ru(NH_3)_5N_2}\right](\mathrm{ClO_4})_2$ (Nujol Mull)

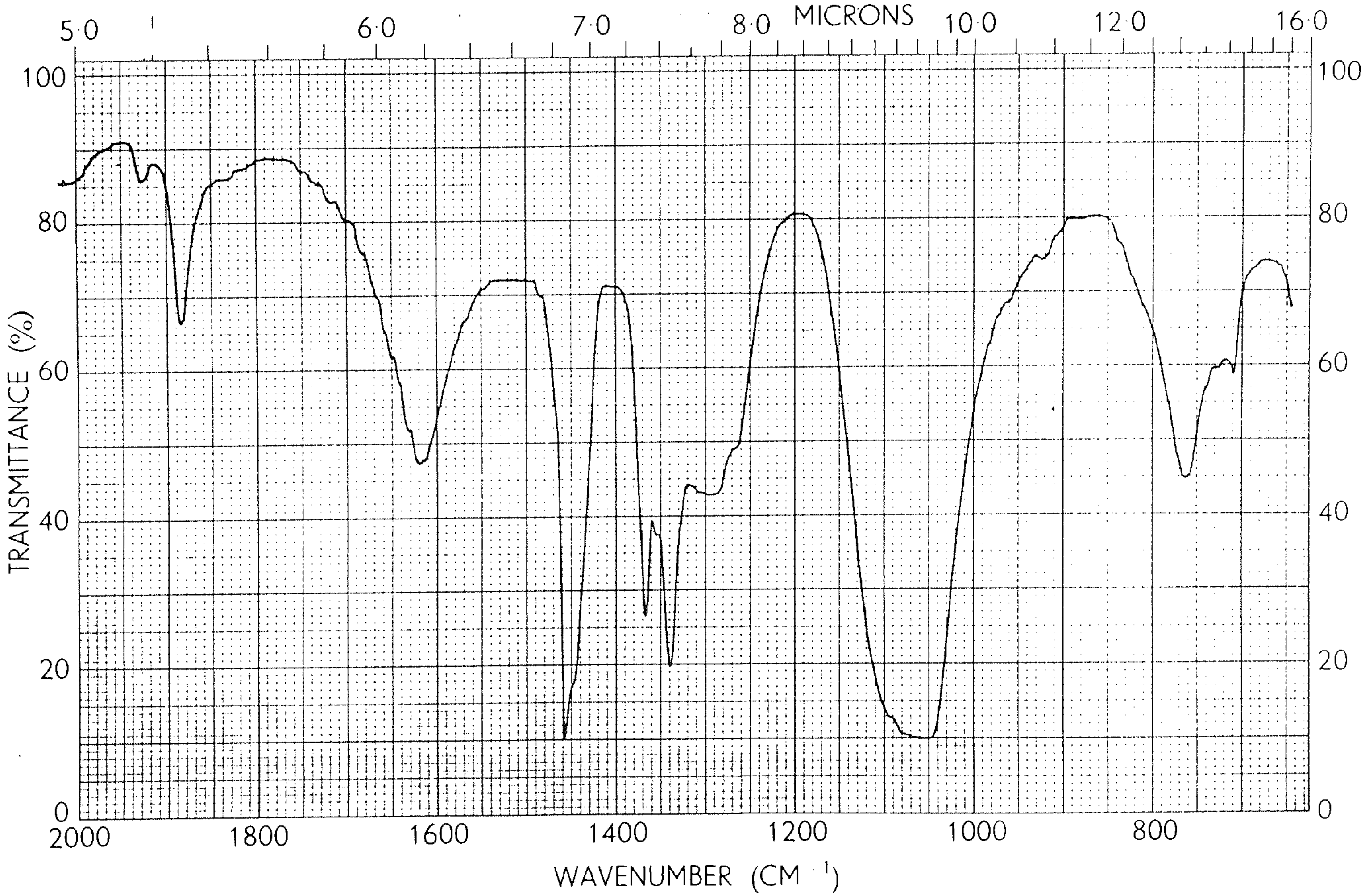
Spectrum (3.4.8) Infra-red spectrum of the compound obtained from the reaction of $\left[Ru(NH_3)_5 \cdot N_2 \right](ClO_4)_2$ and CO_2. (Nujol Mull)



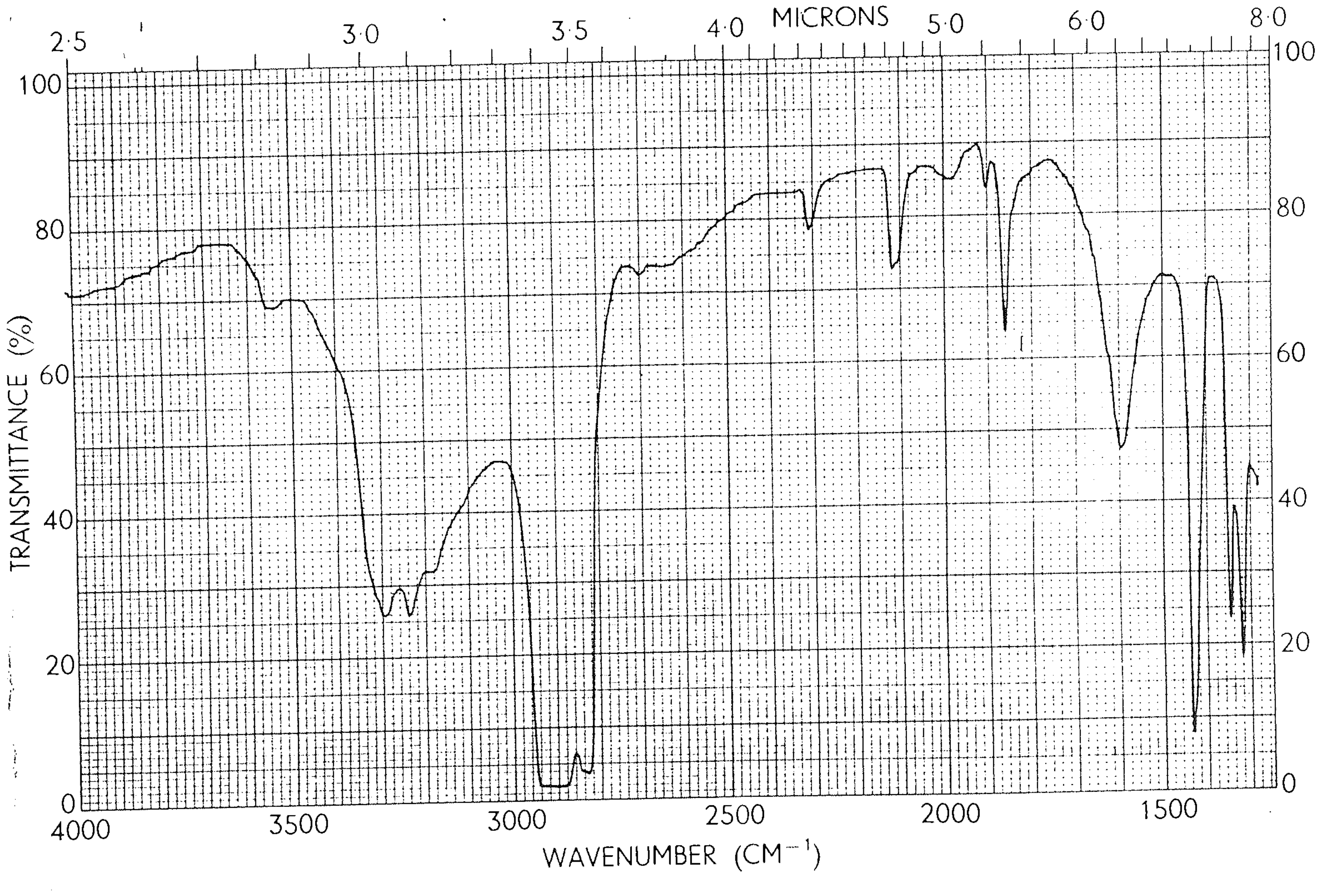
Spectrum (3.4.9) Infra-red spectrum of the compound obtained from reaction of $\left[Ru(NH_3)_5N_2\right](PF_6)_2$ and CO_2 in autoclave. (Nujol Mull)



Spectrum (3.4.9) Infra-red spectrum of the compound obtained from reaction of $\left[Ru(NH_3)_5N_2\right](PF_6)_2$ and CO_2 in autoclave. (Nujol Mull)



Spectrum (3.4.10) Infra-red spectrum of the perchlorate salt compound obtained from procedure (3.3.5) (Nujol Mull)



Spectrum (3.4.10) Infra-red spectrum of the perchlorate salt compound obtained from procedure (3.3.5) (Nujol Mull)

$[Ru(NH_3)_5NO](ClO_4)_2$ or $[Ru(NH_3)_5CO](ClO_4)_2$

The results of the reactions of dinitrogenpentaammineruthenium(II) salts with carbon dioxide under pressure suggests that the anions used for precipitating the products can have an important effect on the solid chemistry of these salts, since some of the salts uptake and stabilize carbon dioxide better than others.

The reaction of dinitrogenpentaammineruthenium(II) perchlorate with carbon dioxide has also been investigated in water, alcohol, aqueous alkali ,tetrahydrofuran and benzene. The infra-red spectrum after treatment does not show any change compared with starting material except for THF in which a side reaction takes place.

From the study of the reaction of carbon dioxide with pentaammine-hydrateruthenium(II) and its analogous dinitrogen complexes (monomeric and dimeric species) the following conclusions may be drawn.

1 - An examination of the infra-red spectra of the species before and after treatment with carbon dioxide and a comparison of the new infra-red bands with the infra-red data given for gaseous carbon dioxide, suggests that carbon dioxide has weakly interacted with these species in such a way that the linear structure of carbon dioxide has not changed, since no additional bands due to a symmetry change of the molecule was observed.

2 - The results from elemental analysis and infra-red data suggest that carbon dioxide can replace dinitrogen in binuclear dinitrogen pentaammineruthenium(II) while it can be partially taken up by monomeric species.

3 - The presence of amalgamated zinc may promote the carbon dioxide disproportionation reaction.

Finally the position of the band at approximately 2340 cm^{-1} due to the uptake of carbon dioxide in the species is comparable with that due to the uptake of carbon dioxide by some of the copper (II) complexes with chelating ephedrine ligands in benzene solution. (These complexes exhibit bands at 2350 and 2380 cm^{-1} assigned to ν_3 CO_2). This is the only reported example of carbon dioxide uptake in a chemical system which shows end-on attachment. $(M\cdots\cdots O = C = O)$ (12)

3.4.5 REACTION OF HEXAKISAMINE COMPLEXES WITH CARBON DIOXIDE

Since the reaction of 6 co-ordinate pentaammineruthenium(II) complexes with carbon dioxide in solution and in the solid form sometimes resulted in successful reactions, the reaction of carbon dioxide with some other complexes of ruthenium(II) has been tried. (hexakis(methylamine) ruthenium(II) (G) and hexakis(n-butylamine) ruthenium(II) (H)). The preparation of complex (G) and (H) was according to the procedure given in reference (128,129) .The procedure relevant to the preparation of complex (G) has been slightly varied since in the absence of heat no precipitate was obtained. Both complexes (G) and (H) show consistent analytical data. The reaction of the dibromide salts of complexes (G) and (H) with carbon dioxide have been investigated in the autoclave. The infra-red spectra of the salts before and after treatment with carbon dioxide are identical, indicating that no reaction between the dibromo salts of complex (G) and (H) with carbon dioxide has taken place.

The reaction of complex (H) with carbon dioxide in solution gave a tarryproduct which shows two new infra-red bands at 2100 (m-s)cm^{-1} and 2220cm^{-1}(w-m).

The results of thin layer chromatography obtained from this tar show that the product is a mixture. (The thin layer chromatography was done in the following solvents: ether, benzene, hexane, chloroform. The mixture was not separated by benzene or hexane. In ether two different points were observed and in chloroform the thin layer chromatography shows the presence of three components in the mixture).

According to the following information the reaction of complex (H) with carbon dioxide is probably an oxidative reaction which gives nitrile species as a major product.

The complex of hexakis(amine)ruthenium(II) has been reported to react with oxygen to yield a tarry product with infra-red bands above 2000 cm^{-1}. These are consistent with the presence of coordinated nitrile. Also evidence from the infra-red spectrum of the product of the reaction of dichlorohexakis(n-butylamine)ruthenium(II) with oxygen and propyl cyanide suggests a similar reaction (in both reactions the product shows a band at 2205 cm^{-1}). Comparing the product of the reaction of complex (H) with carbon dioxide, with those of hexakis (n-butylamine)ruthenium(II) and oxygen or propylcyanide it is possible to formulate one of the tar species as $Ru(CH_3CH_2CH_2CN)(CH_3CH_2CH_2CH_2NH_2)_5$ The peak at 2100 and 2220 cm^{-1} arises from the butyl nitrile (these two peaks are also comparable with the two infra-red bands observed for organonitriles).

CHAPTER IV

4.1.1 INTRODUCTION

Since work in this chapter is concerned with complexes of ruthenium and rhodium so the introduction in this chapter will be concerned with the relevant chemistry of both metals.

Ruthenium is a silver-white metal, with a brilliant lustre, hard and rather brittle.(108) It is a little heavier than lead, the specific gravity being 12.2. The melting point is extremely high (1950°C); the metal can only just be melted in the oxy-hydrogen flame. Ruthenium resembles osmium far more than it does iron, and also shows certain similarities to iridium and rhodium in the trivalent state.(109) The greatest similarities between ruthenium and osmium are found in the oxides and fluorides and in the chemistry of the lower oxidation states (II to 0), and the greatest differences between the two arise in the trivalent state. Amongst the platinum metals ruthenium has two outstanding features. One is its tendency, particularly when in the tetravalent state, to form polynuclear complexes with oxide, nitride, or hydroxybridges; this is shared by osmium, but to a more limited extent. Secondly, ruthenium forms more nitrosyl complexes than any other metal.

Various compounds of ruthenium are known in which the metal appears to exercise(108) valencies of II to VIII. The low oxidation states (-II to II) are obtained in combination with ligands which have stronger π acceptor properties.

Most of the ruthenium complexes are in II or III oxidation states. The + II state is particularly versatile because being d^6, it obeys the eighteen-electron rule when octahedrally coordinated and is stablized by π - bonding ligands, while also it is a high enough oxidation state to bond with amines or other ligands that rely on σ electron donation only.(111) Ruthenium trichloride is the(109) commonest compound of ruthenium. Like many trichlorides it exists in both water - insoluble and water soluble forms. The water insoluble ruthenium trichlorides are two modifications. The dark brown β form is obtained by heating ruthenium sponge at 330° in a 1:3 mixture of carbon monoxide and chlorine, and the black α form by heating the β form in a current of chlorine to 700°. The $\beta - \alpha$ transition occurs at 450° and is irreversible. The water soluble hydrate of ruthenium trichloride can be got by the prolonged action of hydrochloric acid on ruthenium tetroxide. The aqueous solution is red and at first contains no ionized chloride, but aquation of the complex slowly occurs, and the resulting solution is fairly easily hydrolysed. The monomeric species is present in aqueous solutions of the trichloride but polymeric complexes are undoubtedly present in the solutions. A brown, anhydrous water-soluble form is also known.(112)

Commercial ruthenium trichloride frequently contains polynuclear Ru(IV) oxy and hydroxy chloro species and may often contain the nitrosyl chloride $\left[Ru(NO)Cl_3\right]_n$. The chemical reactions of ruthenium trichloride are summerized in fig 4.1.1. Reaction of $RuCl_3.xH_2O$ with triphenylphosphine leads to a number of complexes, dependent on the conditions.(113) Excess phosphine causes reduction to the divalent state.

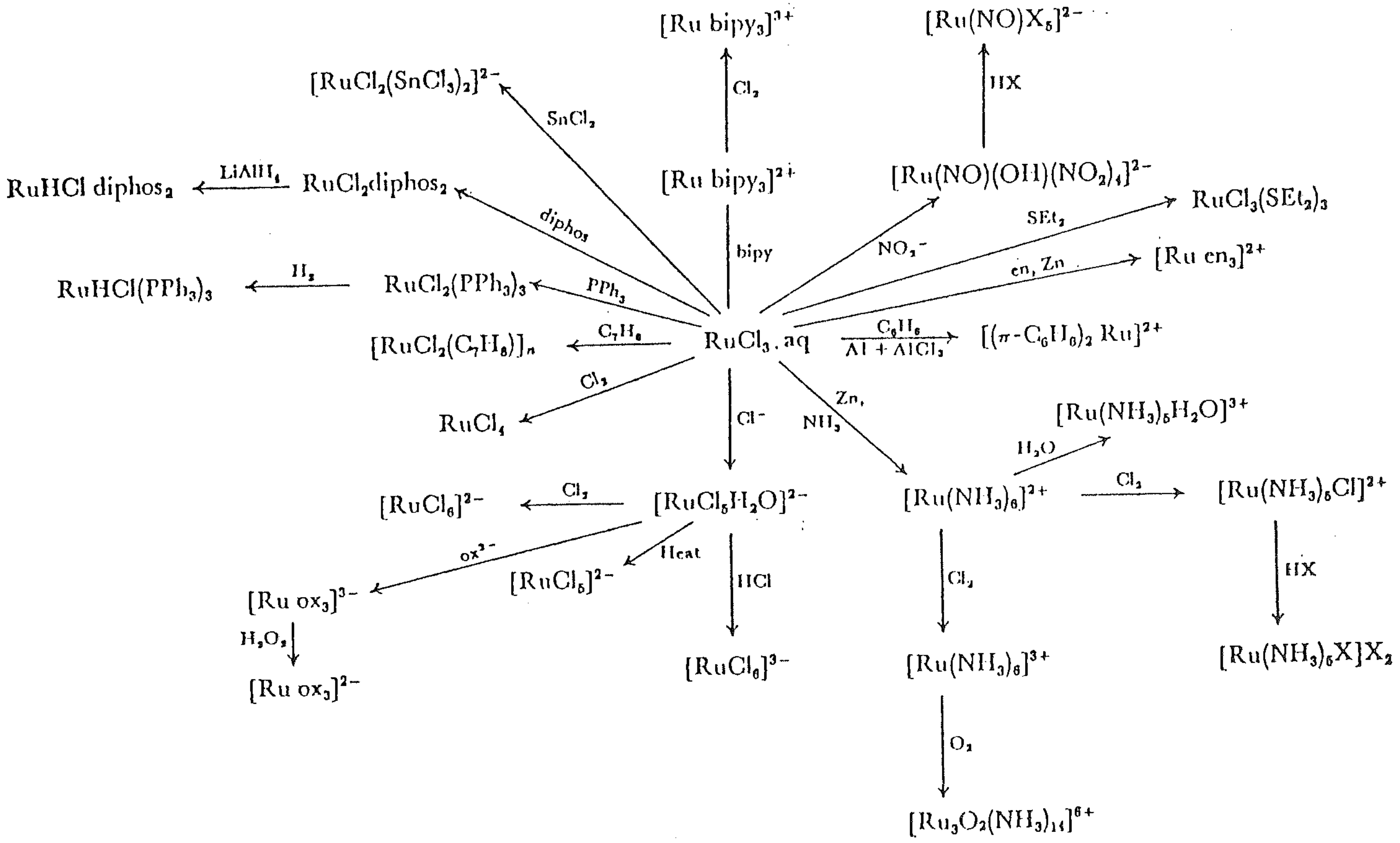
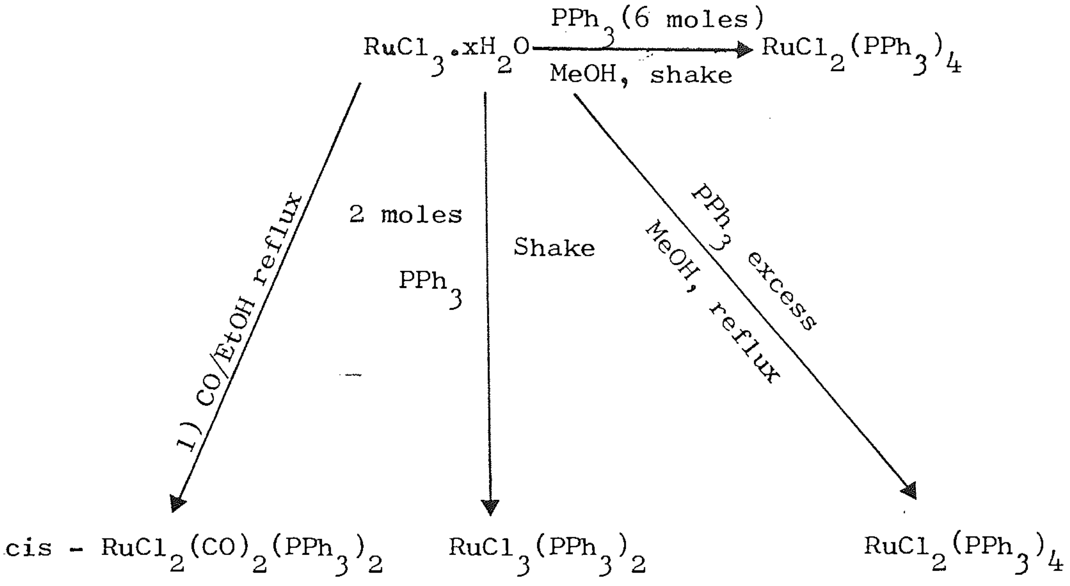


Fig. 4.1.1 Reaction of ruthenium trichloride.

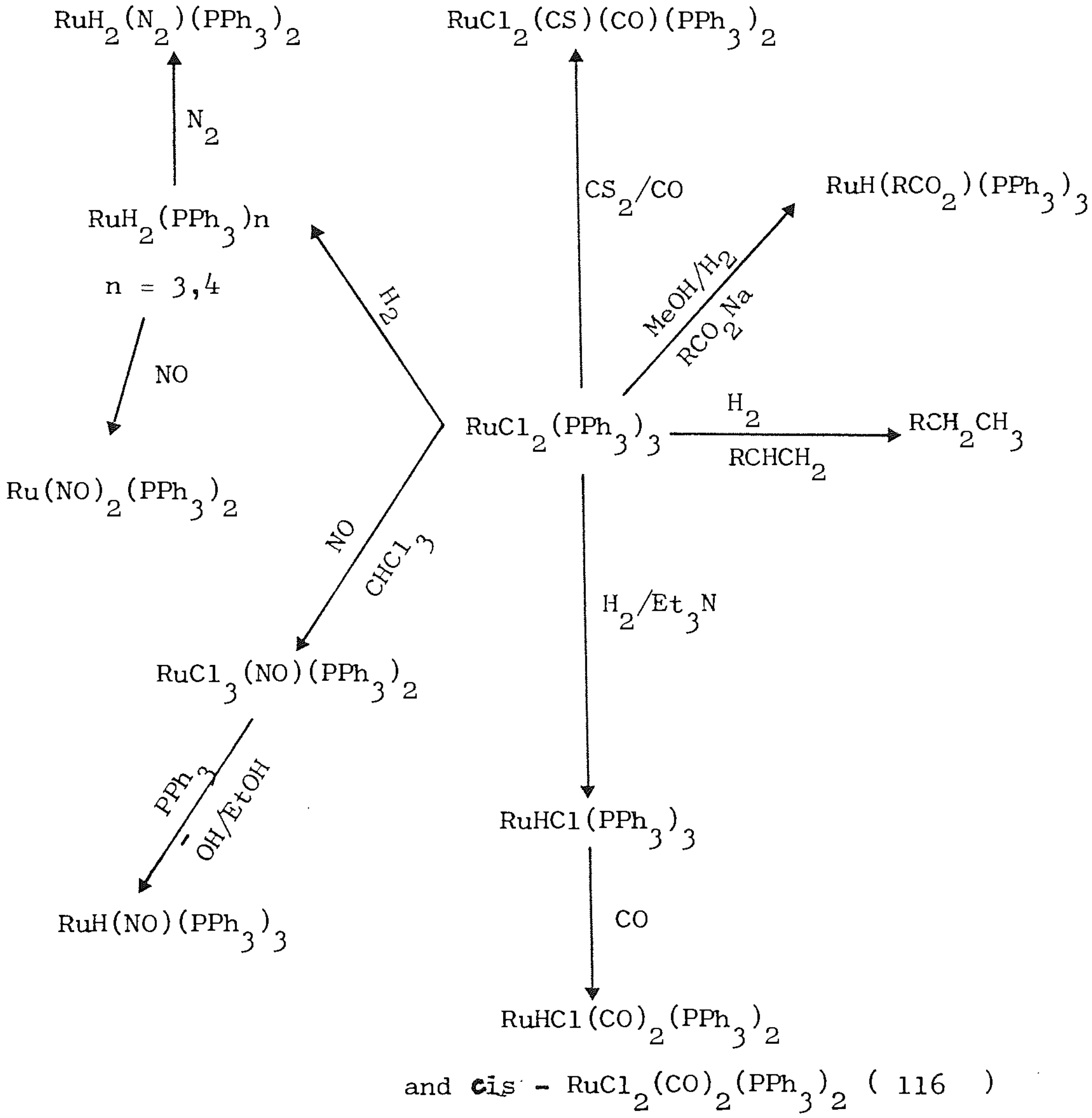


(Figure 4.1.2)

As can be seen from figure 4.1.2 the dichlorotris(triphenylphosphine) ruthenium(II) can be prepared by the action of an excess of triphenylphosphine on ruthenium trichloride. The X-ray crystal structure analysis of this complex shows that it is penta coordinated,(109) the metal atom lying close to the center of a distorted square based pyramid. The two trans chlorine atoms in the basal plane are each 2.387 ± 0.007 Å from the metal and the two metal phosphrous distances in this plane are 2.38 Å, while the apical metal-phosphrous bond length is only 2.23 Å. The base is not quite flat, the phosphorus atom being a little above and the chlorine atoms a little below the hypothetical plane. The next closest approach to the ruthenium, in the position trans to the apical phosphorus atom, is made by a hydrogen atom on a β carbon of a phenyl ring; the metal-hydrogen distance is approximately 2.59Å, but there is no evidence for a metal-hydrogen interaction.

The (109) conclusion drawn from this X-ray study was that the complex is a true penta coordinated species, and that its stability arises from intermolecular blocking of the unused actahedral site by the phenyl ring.

Dichlorotris(triphenylphosphine)ruthenium(II), is one of the most important (111) ruthenium (II) compounds, and it is readily converted into $RuHCl(PPh_3)_3$. Some reactions of $RuCl_2(PPh_3)_3$ are as follows:



(Figure 4.1.3.)

The reaction chemistry of both (tris and tetrakis) phosphine ruthenium(II) complexes appears to be the same, but the structure of the latter is unknown. Both are dark solids which form solutions with similar colours.(113) It has been shown that tetrakis(triphenylphosphine)ruthenium(II) completely dissociates one phosphine ligand in solution(113); indeed it has been suggested that this complex exists in the solid state as $\left[Ru(PPh_3)_3Cl_2\right].PPh_3$ in which the fourth PPh_3 molecule is trapped in the lattice, and this would explain the essentially identical chemistry of the tris and tetrakis complexes. The dichlorotris(triphenylphosphine)ruthenium(II) also dissociates phosphine partially in solution in non polar solvents as shown by molecular weight determination.(115) In polar solvents partial ionization of the chloride ligands also occurs.

Dissociation of complexes $RuCl_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ in benzene - ethanol solutions and loss of one molecule of phosphine can be summarized according to the following scheme:(109,119)

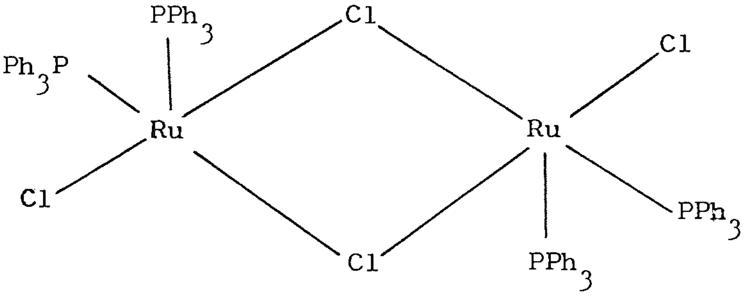
$$RuCl_2(PPh_3)_4 \underset{-s}{\overset{s}{\rightleftarrows}} RuCl_2(PPh_3)_3(s) + PPh_3$$

$$RuCl_2(PPh_3)_3 \underset{-s}{\overset{s}{\rightleftarrows}} RuCl_2(PPh_3)_2(s)_2 + PPh_3$$

in which s = solvent molecule.

Both of the solution species above will catalyse the homogeneous reduction by molecular hydrogen of alkenes and alkynes under ambient conditions. In the absence of olefines the solutions will catalyse the molecular hydrogen - deuterium exchange.

The 31p NMR spectrum of dichlorotris(triphenylphosphine)ruthenium (II)(95,96) in chloroform has been reported and the dissociative behaviour of the complex results in chloride-bridged dimeric structure $(RuCl_2(PPh_3)_2)_2$ where ruthenium has square pyramidal geometry indicated. The nature of the solid $\left[Ru(PPh_3)_2Cl_2\right]_n$ is unclear, although its insolubility suggests a polymeric structure.(97)



The reactivity of $Ru(PPh_3)_3Cl_2$ towards small molecules was confirmed by the easy isolation of an adduct with SO_2. By bubbling sulfur dioxide into a warm acetone solution of the ruthenium complex, a red insoluble compound of formula - $Ru(PPh_3)_2(SO_2)Cl_2.CH_3COCH_3$ can be obtained.(116) Reaction of dichlorotris(triphenylphosphine)ruthenium (II) with some other small molecule such as (CO, NO, O_2) to give, $Ru(PPh_3)_2(CO)_2Cl_2$ (117,98), $Ru(PPh_3)_2$ $NOCl_3$ (118), and $Ru(O_2)(PPh_3)_2Cl_2$ (116) respectively have also been reported. Some of these reactions were summarized in figure 4.1.3. previously.

$RuCl_2(PPh_3)_3$ can be used as a starting material for the preparation of some divalent and trivalent chelate ruthenium compounds.

The complex $RuCl_2(PPh_3)_3$ reacts with N,N´ - ethelyenbis(salicylaldimine) under(100) reflux condition in benzene in the presence of NEt_3 to yield the complex Ru(Salen)$(PPh_3)_2$. The compound is diamagnetic and stable to air in the solid state. In solution however it is readily oxidized by air to a green ruthenium (III) complex.

The reaction of $RuCl_2(PPh_3)_3$ with the free ligand in methanol in contact with air results in the formation of Ru(Salen)(PPh_3)Cl which can be converted into the bromo derivative by reaction with NEt_4Br.

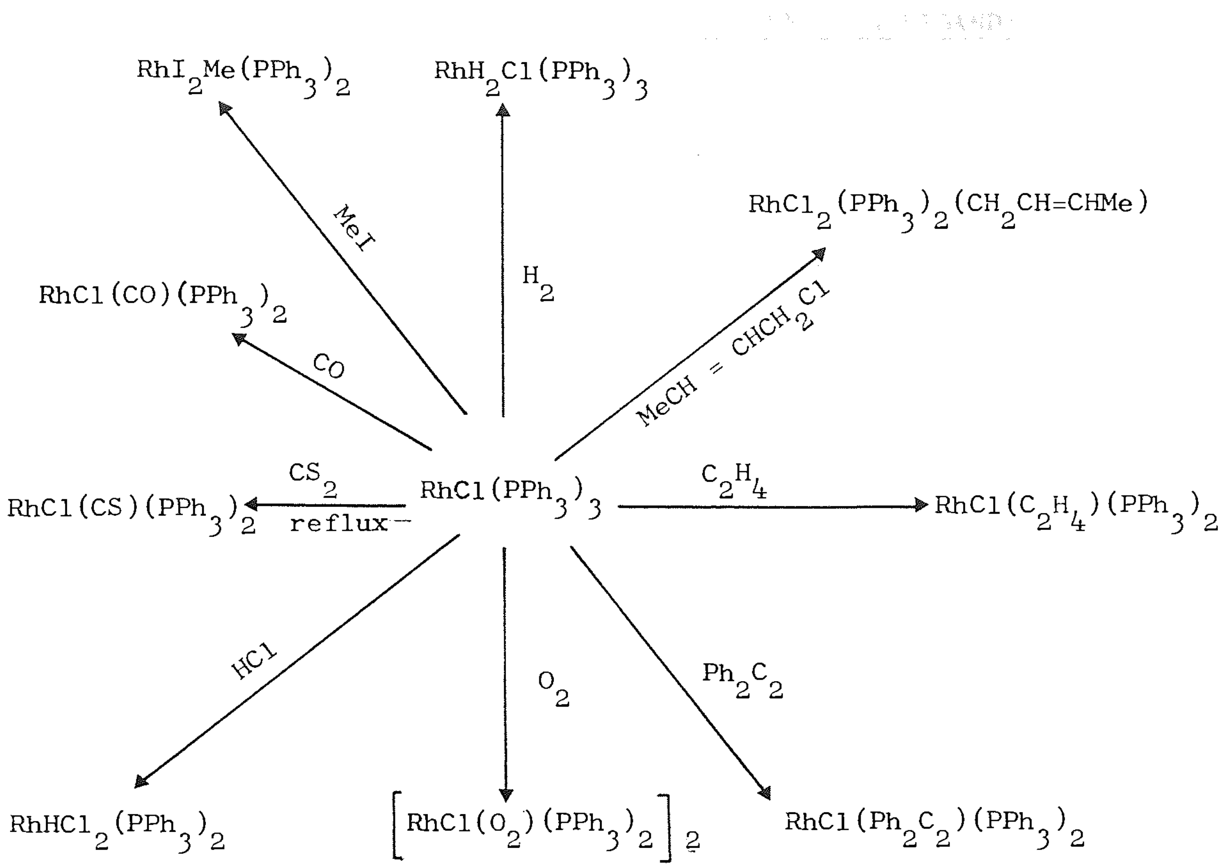
Since the chemistry of the ruthenium compounds of interest has been discussed I do not propose to discuss this chemistry further and the rest of this introductory chapter will be concerned with the chemistry of rhodium. However a great deal of information about chemistry of ruthenium has been given in references (123, 124).

Rhodium like ruthenium is the member of group VIII and it is a white(103) metal melting at 1,966°. At a red heat it is slowly oxidized by air or oxygen to the sesquioxide Rh_2O_3, which at a much higher temperature breaks up again into its elements. Chlorine at a red heat converts it into the trichloride, but it is extremely resistant to fluorine. Rhodium shows a variable valencies from (-I to VI) in which the trivalent is the commonest oxidation state for the metal and almost all rhodium (III) species are octahedral.

Rhodium trichloride is the most common compound of the metal. This compound has a peculiar behaviour, which indicates it can occur(103) in several forms some of them certainly complex. A hydrate $RhCl_3$, 4 or 3 H_2O is very soluble in water. This hydrate loses its water of crystallization in a stream of hydrogen chloride gas at 180°C, but the anhydrous product so formed is still very soluble in water. If this soluble anhydrous chloride is heated to a higher temperature it becomes insoluble. This however, is not all. It has been shown that the dark-red hydrated chloride $RhCl_3$, $3H_2O$ when dissolved in water gives a brown solution which is quite stable in the cold, and gives with silver nitrate only a slight turbidity. But if this brown solution is heated nearly to boiling it suddenly becomes yellow and now silver-nitrate will precipitate the whole of the chlorine. This loss of colour does not occur with concentrated solutions, and there may be an equilibrium between the two forms, the (brown) form which gives no chloride ions being favoured by a higher concentration, and so presumably more condensed . Attempts to isolate the yellow form have failed,(103) if the yellow solution is evaporated down it is the original brown-red modification which separates, probably because the equilibrium goes over to this side as the concentration increases.

Rhodium trichloride can be used as a starting material for preparation(104) of phosphines complexes of rhodium and this can be done by refluxing $RhCl_3$ with excess of phosphine in ethanolic solution. The best known example is the square planar $RhCl(PPh_3)_3$, one of the most interesting complexes known.

Some reactions of $RhCl(PPh_3)_3$ are as follows:



The main types of reaction of $RhCl(PPh_3)_3$ are a) the ready replacement of PPh_3 ligand and b) addition reactions giving a Rh(III) complex, both (a) and (b) may or may not be reversible, depending on the added ligand. The reversible reaction with hydrogen is of some importance, since it leads to the catalytic cis hydrogenation of olefines.

Chlorotris(triphenylphosphine)rhodium(I) is very air sensitive, both in the solid state and solution.(105) It can partially dissociate phosphine in benzene solution according to the following equation:(106)

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3$$

and in favourable conditions the chloride bridged dimer $[Rh(PPh_3)_2Cl]_2$ can be obtained.(107,120)

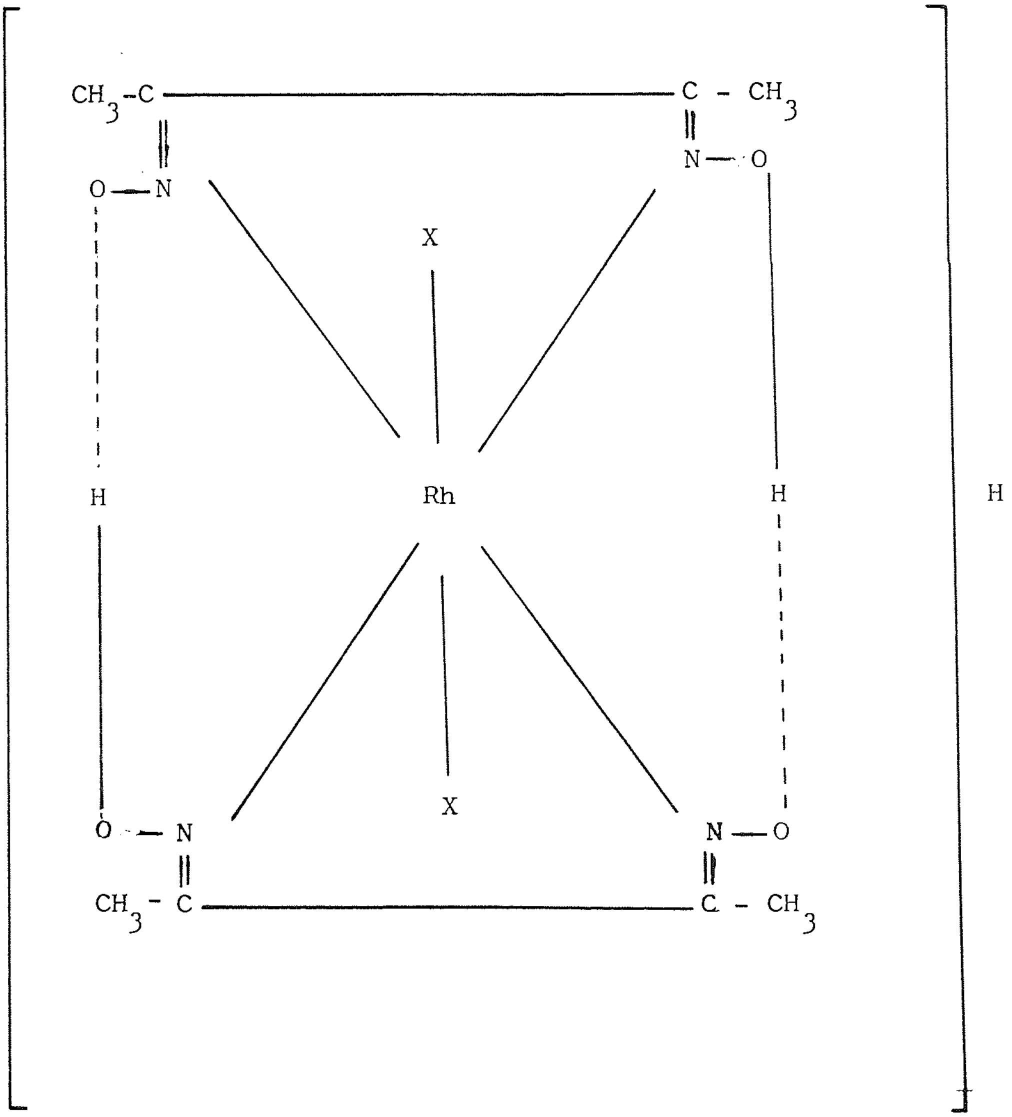
4.1.2 RHODIUM COMPLEXES WITH DIMETHYLGLYOXIME AS A LIGAND:

Several complexes of rhodium (III) with dimethylglyoxime have been reported.(101) The dichlorobis(dimethylglyoximato)rhodium(III) is readily formed from aqueous alcoholic solutions of the reactants. However, if acetone - water is used to dissolve the reactants little reaction is noted even after boiling for sometime. However, on addition of a few drops of alcohol, the reaction goes quickly to completion. The alcohol serves both as solvent and catalyst in this reaction acting as a reducing agent forming catalyst quantities of Rh(I). It should be noted that the synthesis of the dichlorobiscyclo-(102) hexanedionedioximatorhodium(III) anion can also not be achieved by boiling aqueous solutions of the ligand and rhodium trichloride, but on addition of alcohol the required product is quickly formed in solution.

The best known complex of rhodium(III) with dimethylglyoxime is that formulated as hydrogen-dichlorobis(dimethylglyoximato)rhodium(III). This formulation is undoubtedly correct in aqueous solution as it has been shown by the ultra-violet spectra of the monobasic acid and its salts.(102) However, the formulation is incorrect for the solid state of the acid since an O - H stretching mode is apparent at 3400 cm^{-1}. The compound in the solid form has formulated as $Rh(DMGH_2)(DMGH)X_2$. The compounds $H\left[RhX_2(DH)_2\right]$ function as(101) strong monobasic acids, giving stable insoluble silver salts, and stable water soluble alkali metal, barium and ammonium salts. The halogen could not be precipitated by boiling with silver nitrate, which merely yielded the silver salt - itself easily soluble in dilute nitric acid.

The halogen atoms are thus bonded covalently.

The rhodium(III) compound $Rh(DH)_3$ was ultimately prepared in small yield from rhodium (III) sulphate as a brown, highly insoluble powder. It is insoluble in alkalis, but dissolves in dilute hydrochloric acid to a reddish solution, containing probably the cis-dihalide- bis glyoxime compound. The reddish lightens gradually and deposits the usual yellow trans compound of the following structure.



(I)

The structure (I) has been suggested on the basis of the information obtained from a similar nickel complex and the compound $H\left[Rh(DH)_2Cl_2\right]$. The reaction of the nickel complex with two hydrogen atoms with methylmagnesium iodide failed to produce any methane. This lack of reactivity has been suggested to be due to hydrogen bonding and a similar explanation seems feasible for the pronounced monobasic character of the rhodium compound (I).

The compounds $Rh(DH_2)(DH)X_2$ (X = Cl, Br) have been the subject of our studies which will be discussed on the following part of this chapter.

4.2 EXPERIMENTAL

4.2.1 ANALYSIS OF GASES BY MASS SPECTROMETER

A suitable quantity of the sample was transferred into a flask and connected to the inlet of the mass spectrometer. The system was evacuated and heated up to the appropriate temperature until evolution of the gas was observed. When the gas above the sample reached to a suitable pressure it was let into a spectrometer and the spectrum recorded.

4.2.2 ELEMENTAL ANALYSIS

Micro analysis for, carbon, hydrogen, nitrogen and halide was obtained from the analytical services of the chemistry department of Aston University.

4.2.3 SOLVENTS

Solvents were obtained from commercial sources, and were dried and further purified, where necessary.

4.2.4 INFRA-RED SPECTRA

The infra-red spectra of the compound were studied in the range of 4000-650cm^{-1}. The samples were examined as Nujol mulls or as solid discs by pressing a mixture of sample and powdered KBr.

4.2.5 NUCLEAR MAGNETIC RESONANCE

The ^{31}P and ^{13}C NMR spectra of the compound recorded on a JNM - FX90Q FT NMR spectrometer, in chloroform before and after treatment with carbon dioxide. Ortho-phosphoric acid and deuterated chloroform are respectively chosen as reference for ^{31}P and ^{13}C spectrum.

4.2.6 THERMOGRAVIMETRIC ANALYSIS DATA

T.G.A. data were obtained on a Stanton thermobalance (T.R. Decimilligram model), ambient to 1000°C with static air.

4.2.7 VAPOUR PRESSURE OSMOMETER

All molecular weight measurement were carried out in appropriate solvents using a Knauer vapour pressure osmometer.

4.3.1 PREPARATION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE) RUTHENIUM(II)(110)

Trihydrate ruthenium trichloride (0.265g) in hot ethanol (10 ml) was added rapidly to a vigorously stirred solution of triphenylphosphine (1.57g) in boiling ethanol (60 ml). Subsequent rapid portion wise addition of sodium borohydride (0.19g) in hot ethanol (10 ml) under an atmosphere of hydrogen gave a yellow precipitate which was filtered off, washed with ethanol, water, ethanol, and dried in vacuo.
The yield was 2.1g.

Analytical data:

Found:	%C	72.9	%H	5.4	%P	11.6
$RuH_2(PPh_3)_4$						
Requires:	%C	75	%H	5.4	%P	10.8

The NMR spectrum of the product in toluene does not show any peak in the region of 20-30τ.

4.3.2 PREPARATION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE) RUTHENIUM(II) UNDER ATMOSPHERE OF ARGON

Following the procedure (4.3.1) and replacing the hydrogen atmosphere with argon results in a yellow-greenish product (0.9g).

Analytical data:

Found:	%C	67.5	%H	4.6	%P	7.9
$Ru(PPh_3)_4$						
Requires:	%C	75	%H	5.2	%P	10.7

4.3.3 REACTION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE) RUTHENIUM(II) WITH CARBON DIOXIDE IN TOLUENE SOLUTION

Dihydrido-tetrakis(triphenylphosphine)ruthenium(II) (0.33g) was added to 30 ml of toluene (saturated with carbon dioxide), carbon dioxide was bubbled through the solution for 1 hr. The system was then kept under an atmosphere of carbon dioxide for 24 hrs. The solution above the orange crystalline complex was removed. The product was then washed with toluene (saturated with carbon dioxide) and dried in a stream of carbon dioxide.

Analytical data:

Found:	%C 72	%H 5.5	%P 7
$(HCOO)RuH(PPh_3)_3$.(toluene)			
Requires:	%C 72.6	%H 5.4	%P 9.1

IR: 1555(s)cm^{-1}, 1310(m-s)cm^{-1}, 2000(w)cm^{-1}

Bubbling of carbon dioxide through the mixture of orange complex and toluene and drying off the solvent gives a green product which does not show any new infra-red bands due to presence of carbon dioxide or formate within the molecule.

4.3.4 REACTION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE IN PRESENCE OF REDUCING AGENT

$RuH_2(PPh_3)_4$ (0.1g) in 10 ml toluene was transferred into a three neck flask and 2ml of 2% Zinc amalgam added.

The solution was stirred for 5 minutes, and left over-night. Carbon dioxide was bubbled through the solution until the whole solvent dried off and a dark green tarry product was obtained. The infra-red spectrum of the product shows two bands in the region of 1260 cm^{-1} and 800 cm^{-1}. The product is soluble in toluene, acetone, alcohol, chloroform and could not be purified.

4.3.5 PREPARATION OF HYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE) RHODIUM(I)(125)

Hot solutions of 0.26g (1.0m mole) of rhodium trichloride 3 - hydrate in 20 ml of ethanol and 0.4g of potassium hydroxide in 20 ml of ethanol are added rapidly and successively to a vigorously stirred boiling solution of 2.62 g (10m moles) of triphenylphosphine in 80 ml of ethanol. The mixture is heated under reflux for 10 minutes and allowed to cool to 30°C. The precipitated product is filtered, washed with ethanol, water, ethanol, and n-hexane, and dried in vacuo.

Analytical data:

Found:	%C	68.7	%H	5	%P	8.1
$RhH(PPh_3)_4$ Requires:	%C	75	%H	5.3	%P	10.7

IR: 2150(w-m)cm^{-1} MP = 145°C.

4.3.6 REACTION OF HYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RHODIUM(I) WITH CARBON DIOXIDE IN SOLUTION

Hydrido-tetrakis(triphenylphosphine)rhodium(I) (0.2g) was transferred into a three neck flask, and 40 ml of toluene saturated with carbon dioxide was added (under CO_2 atmosphere). Carbon dioxide was bubbled through the solution for 1 hr. The solution was then kept under an atmosphere of carbon dioxide for 24 hours until an orange solution was obtained (solution A). The solution A was refluxed under an atmosphere of argon for 3 hours until a brown solution was obtained. Carbon dioxide was bubbled through this brown solution and the solvent was dried off. The brown product was then washed with toluene and alcohol saturated with carbon dioxide and dried under a stream of carbon dioxide.

Analytical data:

Found: %C 63.3 %H 5.6

IR: $1260cm^{-1}$, $1120cm^{-1}$, $800cm^{-1}$.

Refluxing solution A under an atmosphere of carbon dioxide in place of argon and following the same procedure gives a red-brown product with the same infra-red spectrum as brown product.

The brown product is soluble in acetone, ether, alcohol. The compound decomposes at 170°C. Analysis of the gas released at 170°C using the mass spectrometer shows the presence of carbon dioxide (m/e.44). The molecular weight determination using osmometery technique shows an apparent molecular weight of 526.

4.3.7 RECOVERY OF THE PRODUCT FROM SOLUTION (A) OBTAINED IN REACTION (4.3.6) IN THE ABSENCE OF THE HEAT

Carbon dioxide was bubbled through the solution (A) obtained in procedure (4.3.6) and the solvent was dried off. The red product was washed with toluene saturated with carbon dioxide and dried under a stream of CO_2.

Analytical data:

Found:	%C	72.6	%H	5.4
$Rh_2H_2(CO_2)(PPh_3)_6$(toluene)				
Requires:	%C	72.6	%H	5.5

4.3.8 REACTION OF HYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RHODIUM(I) WITH CARBON DIOXIDE AND OXYGEN IN SOLUTION

Hydrido-tetrakis(triphenylphosphine)rhodium(I)(0.2g) was transferred into a three neck flask, and 40 ml of toluene added. The solution was exposed to air for about 3 minutes and carbon dioxide was bubbled through the solution for 1 hour. The solution was then kept under an atmosphere of carbon dioxide (24 hrs). Refluxing the solution under an atmosphere of carbon dioxide for 1 hr. and bubbling the carbon dioxide through the solution and drying off the solvent, gives a yellow-greenish product. The infra-red spectrum of this product is similar to the infra-red spectrum of the starting material in which the band due to (Rh-H) at 2150cm^{-1} disappeared.

4.3.9 REACTION OF SOLUTION (A) (PROCEDURE 4.3.6) WITH OXYGEN AND CARBON DIOXIDE

Oxygen was bubbled through the solution (A) obtained from the reaction (4.3.6) for 10 minutes. The yellow precipitate which was obtained was filtered and washed with alcohol and toluene. This yellow compound does not react with carbon dioxide in solution. The infra-red spectrum of the product is similar to the infra-red spectrum of $RhH(PPh_3)_4$ except that the band due to (Rh-H) at 2150 cm^{-1} disappeared.

4.3.10 PREPARATION OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

Ruthenium trichloride trihydrate (0.5g) is dissolved in methanol (125 ml)(126) and the solution refluxed under nitrogen for 5 minutes. After cooling, triphenylphosphine (3.0g) is added in the ratio of 6 moles of $(C_6H_5)_3P$. Per mole of $RuCl_3.3H_2O$, and the solution is again refluxed under nitrogen for 3 hours. The complex precipitates from the hot solution as shiny black crystals; on cooling, they are filtered under nitrogen, washed several times with degassed ether, and dried under vacuum. The yield is 1.6g.

MP = 132°C.

IR: 1000(m-w), 1030(m-w), 1090(s), 1160(w), 1190(m-w)

4.3.11 PREPARATION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO) BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

This compound was prepared according to the method described in reference(100). Dichlorotris(triphenylphosphine)ruthenium(II) (4.79g) was dissolved in dry benzene (80 ml) under nitrogen. A mixture of N,N'-ethylenebis(salicylaldimine) (1.44g) and triethylamine (1.5g) was added and the reaction mixture was refluxed under nitrogen for 5 hours. The solution was filtered to remove triethylamine hydrochloride. Deareated methanol (150 ml) was added to the filtrate and refluxed for a further 4 hours. On cooling, purple crystals were filtered under nitrogen and washed with methanol and ether saturated with carbon dioxide and dried in vacuo.

Analytical data:

Found:	%C	69.5	%H	5	%N	3.4	%P	7.3
Ru(salen)($PPh_3)_2$								
Requires:	%C	70.1	%H	4.9	%N	3.1	%P	6.9

4.3.12 REACTION OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE IN SOLUTION

$RuCl_2(PPh_3)_3$ (0.2g) in 30 ml of toluene was transferred into a three neck flask. Carbon dioxide was bubbled through the solution for 1 hr and the system was kept under an atmosphere of carbon dioxide for 48 hrs. The solvent was then dried off under an atmosphere of carbon dioxide.

The brown product is washed with toluene saturated with carbon dioxide and dried under a stream of carbon dioxide.

Analytical data:

Found:	%C	53.2	%H	4.6	%Cl	10.5	%P	8.3

IR: 1260cm^{-1}(m-s)cm^{-1} 800cm^{-1}(m-s)

The brown product is soluble in chloroform, acetone and partially soluble in toluene. The molecular weight determination using osmometry technique shows apparent molecular weight of 547.3 in acetone. Thermal gravimetry analysis shows decomposition at 180°C and analysis of the gas at this temperature using mass spectrometer gives (m/e = 44). The compound is diamagnetic.

4.3.13 REACTION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE IN SOLUTION

Ru(salen)$(PPh_3)_2$ (0.2g) in 30 ml of toluene was transferred into a flask and carbon dioxide was bubbled through the solution (1 hr). (The colour of the solution is greenish at this stage). The system was kept under an atmosphere of carbon dioxide for 48 hrs. Carbon dioxide was bubbled through the solution and the solvent dried off. (Before the solvent was dried off completely, the colour of the solution had turned to deep brown). The brown product was then washed with ether saturated with carbon dioxide, (using methanol in place of ether gives a tar), and dried under a stream of carbon dioxide.

Analytical data:

Found:	%C	64.4	%H	5.5	%N	2.4	%P	11

IR: 1265cm^{-1}, 800cm^{-1}.

The molecular weight determination using osmometry technique shows an apparent molecular weight at 675.3 in chloroform, thermal gravimetry analysis shows decomposition at 190°C and analysis of the gas at this temperature using mass spectrometer gives (m/e = 44).

4.3.14 REACTION OF TRANS-N,N'ETHYLENEBIS(SALICYLALDIMINATO)BIS TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH OXYGEN IN SOLUTION

Ru(salen)(PPh$_3$)$_2$ (0.2g) was transferred into a flask and oxygen was bubbled through the solution for (1 hr). The system was then kept under an atmosphere of oxygen (48 hrs) and the solvent was dried off. The infra-red spectrum of the product is similar to the infra-red spectrum of the starting material.

4.3.15 REACTION OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) AND N,N'-ETHYLENBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE IN AUTOCLAVE

RuCl$_2$(PPh$_3$)$_3$ (0.1g) and Ru(salen)(PPh$_3$)$_2$ (0.1g) was transferred into a test-tube and placed into an autoclave which had been previously filled with solid carbon dioxide. The system was then kept under an atmosphere of carbon dioxide (48 hrs). (The pressure in the autoclave was calculated to be 12-18 atmosphere). The sample was then removed and the infra-red spectrum recorded. The infra-red spectra of the products were found to be identical to those of the starting material.

4.3.16 PREPARATION OF N,N'-ETHELENEBIS(SALICYLDIMINATO)TRIPHENYLPHOSPHINECHLORORUTHENIUM(III)

The stoichiometric quantity of dichlorotris(triphenylphosphine)ruthenium (II) and N,N'-ethelenebis(salicylaldimine) in methanol was stirred for (12 hrs), the solution was then filtered and the solvent dried off. The tarry product was washed with toluene and dried in the air.

Analytical data:

Found:	%C	68.8	%H	5.4	%Cl	5.6.	%N	4.6	%P	6.3
Ru(salen)(PPh$_3$)Cl										
Requires:	%C	61.4	%H	4.4	%Cl	5.3	%N	4.2	%P	4.7

4.3.17 REACTION OF N,N'-ETHELENE-BIS(SALICYLDIMINATO)TRIPHENYLPHOSPHINECHLORORUTHENIUM(III) WITH CARBON DIOXIDE

To a tarry product obtained from the reaction (4.3.16) was added 20 ml of toluene and carbon dioxide was bubbled through the solution for 1 hr. The system was kept under an atmosphere of carbon dioxide (48 hrs) and the solvent dried off. The product was washed with toluene saturated with carbon dioxide and dried under a stream of carbon dioxide.

Analytical Data:

Found:	%C	71·6	%H	5.6	%Cl	5.1	%N	3.1	%P	4.6
Ru(salen)(PPh_3)Cl										
Requires:	%C	61.4	%H	4.4	%Cl	5.3	%N	4.2	%P	4.7

The infra-red spectrum of the product does not show any new bands due to the presence of carbon dioxide within the molecule.

4.3.18 PREPARATION OF DICHLORO(DIMETHYLGLYOXIME)BIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

Dichlorotris(triphenylphosphine)ruthenium(II) (1g) was added(121) to a suspension of dimethylglyoxime (0.2g) in methanol (30 ml) and the suspension refluxed (2 hrs). The resulting red precipitate was washed with methanol, thf, and ether, and dried in vacuo. The yield is 0.38g.

Analytical Data:

Found:	%C	59.8	%H	5	%Cl	8.7	%N	5.7	%P	8.8
$RuCl_2(DH)(PPh_3)_2$										
Requires:	%C	59.1	%H	4.7	%Cl	8.7	%N	3.4	%P	7.6

4.3.19 PREPARATION OF BIS(DIMETHYLGLYOXIMATO) BIS (TRIPHENYLPHOSPHINE) RUTHENIUM(II)

To a solution of H_2dmg (0.24g) and NaOH (0.08g) in methanol (30 ml)(121) was added $RuCl_2(PPh_3)_3$ (1.0g) and the mixture refluxed (10 hrs). The solid was collected, washed with water and methanol, and recrystallized from hot thf (300 ml) to give yellow micro crystals. The yield is 0.14g.

Analytical Data:

Found:	%C	61.9	%H	5.7	%N	6.1	%P	12
$Ru(DH)_2(PPh_3)_2$								
Requires:	%C	61.6	%H	5.3	%N	6.5	%P	7.2

4.3.20 REACTION OF BIS(DIMETHYLGLYOXIMATO) BIS (TRIPHENYLPHOSPHINE) RUTHENIUM(II) WITH CARBON DIOXIDE IN SOLUTION

$Ru(DH)_2(PPh_3)_2$ (0.07g) was transferred into a three neck flask and (15 ml) of toluene added. Carbon dioxide was bubbled through the solution for 1 hr, and the system was kept under an atmosphere of carbon dioxide for 24 hrs. The solvent was then dried off. The yellow product was obtained which was washed with toluene and methanol saturated with carbon dioxide and dried under a stream of CO_2.

Analytical Data:

Found: %C 47.4 %H 4.7 %N 8.5 %P 14.1

$H(Ru(DH)_2(PPh_3)CO_3$

Requires: %C 49.4 %H 4.7 %N 8.5 %P 4.7

IR: 1260(s)cm^{-1} 800(s)cm^{-1}

For further purification the product was transferred into a thimble and placed into a Soxhlet. The system was then fixed on a suitable flask which contained thf saturated with carbon dioxide. The solvent was refluxed for 4 hours under an atmosphere of CO_2. The product was then removed from the thimble and dried under a stream of carbon dioxide.

4.3.21 REACTION OF DICHLORO(DIMETHYLGLYOXIME)BIS(TRIPHENYLPHOSPHINE) RUTHENIUM(II) WITH CARBON DIOXIDE IN SOLUTION

$RuCl_2(DH)(PPh_3)_2$ (0.28g) was transferred into a flask and 30 ml of toluene was added, followed with bubbling of carbon dioxide through the solution (1 hr) and the system was kept under an atmosphere of carbon dioxide for 48 hrs. The solution was then heated under an atmosphere of carbon dioxide until a mixture of two crystalline substances (red and yellow crystals) were obtained. The yellow crystals were isolated using toluene saturated with carbon dioxide while the red crystals were insoluble in toluene. The infra-red spectrum of the red crystals is similar to the infra-red spectrum of the starting material, but the infra red spectrum of the yellow product shows two new bands at 1260cm^{-1} and 800cm^{-1}. Using higher quantity of starting material and following the same procedure did not increase the quantity of yellow product.

4.3.22 PREPARATION OF DIBROMO(DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME) RHODIUM(III)

$RhCl_3$ (0.26g) in aqueous solution (10 ml) was treated with excess of KBr (1g), the solution was boiled for 2 minutes, then dimethylglyoxime (0.2g) in hot ethanol (4 ml) was added. The mixture was heated until the colour of the solution gradually faded, at this stage heating was stopped and crystals of the desired compound began to appear on cooling. The solution was filtered and the product washed with ethanol and water and dried in a desiccator.

Analytical Data:

Found:	%C	19.9	%H	3.1	%Br	31.8	%N	9.4
$Rh(DH_2)(DH)Br_2$								
Requires:	%C	19.8	%H	3	%Br	32.3	%N	11.3

4.3.23 PREPARATION OF DICHLORO(DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME) RHODIUM(III)

A slightly acid solution of rhodium trichloride containing 0.19g of rhodium was treated with dimethylglyoxime (0.8g) in alcohol (15 ml) and refluxed for ten minutes. On cooling yellow crystals were precipitated. The product was filtered and washed with alcohol and ice water and dried.

Analytical Data:

Found:	%C	24.8	%H	4.1	%Cl	15.5	%N	13.7
Rh $(DH_2)(DH)Cl_2$								
Requires:	%C	23.7	%H	3.75	%Cl	19.8	%N	13.8

4.3.24 PREPARATION OF (DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME) RHODIUM(I)TRIHYDRATE

(a) Trans-dichloro(dimethylglyoximato)(dimethylglyoxime)rhodium(III) (0.432g) dissolved in aqueous ethanol (50% 180cm^3) was added to 0.0119M, sodium hydroxide solution (180cm^3), in a nitrogen atmosphere. The solution was stirred and heated up to boiling point until the colour of the solution turned to blue. The solution was then cooled in an ice bath and filtered under an atmosphere of nitrogen. A small quantity of the blue product was obtained which could not be separated from the filter paper.

(b) Reduction of dichloro(dimethylglyoximato)(dimethylglyoxime) rhodium(III) using sodium borohydride in methanolic solution also did not give any precipitate.

4.3.25 REDUCTION OF DIBROMO(DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME)-RHODIUM(III)

Following the procedure (4.3.24) and using $Rh(DH)_2Br_2$ in place of $Rh(DH)_2Cl_2$ produced a blue product which was filtered, washed with ethanol and dried under a stream of nitrogen. The yield is 80 mg.

4.3.26 THE REACTION OF BLUE PRODUCT OBTAINED IN PREPARATION (4.3.25) WITH CARBON DIOXIDE IN SOLUTION AND IN THE SOLID FORM

(a) The blue product obtained from procedure (4.3.25) (60 mg) was transferred into a three neck flask and 15 ml of toluene saturated with carbon dioxide added. Carbon dioxide was bubbled through the solution for 1 hr and the system was then kept under an atmosphere of carbon dioxide for 24 hrs. The solvent was dried off and the product washed with a few drops of alcohol saturated with carbon dioxide and dried under a stream of carbon dioxide.
IR: 1260(w)cm^{-1}, 800(w)cm^{-1}.

(b) The blue product obtained from procedure (4.3.25) (20 mg) was kept in autoclave under an atmosphere of carbon dioxide at 12 - 18 atmospheres pressure for 8 weeks. The sample was then removed from the autoclave and the infra-red spectrum recorded.

Analytical Data:

Found:	%C	27.9	%H	4.7	%N	17.6
$(Rh(DH)_2)CO_2$						
Requires:	%C	28.5	%H	4.2	%N	14.7

IR: $1600cm^{-1}$, $1010cm^{-1}$, $770cm^{-1}$.

4.3.27 REACTION OF CARBON DIOXIDE WITH (DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME)RHODIUM(I) IN ETHANOLIC SOLUTION

Reduction of $Rh(DH)_2Br_2$ in ethanolic solution was followed according to procedure (4.3.25), when the solution turned to blue, carbon dioxide was bubbled through a solution (1 hr) and the system was kept under an atmosphere of carbon dioxide (24 hrs). The solution was then filtered. The product was washed with ethanol saturated with carbon dioxide and dried in a stream of carbon dioxide. The infra-red spectrum of this product was found to be similar to that of the blue product obtained in reaction (4.3.25).

4.3.28 REDUCTION OF DIBROMO(DIMETHYLGLYOXIMATO)(DIMETHYLGLYOXIME) RHODIUM(III) USING SODIUM BOROHYDRIDE

Dibromo(dimethylglyoximato)(dimethylglyoxime)rhodium(III) (0.6g) in 30 ml of methanol saturated with nitrogen was transferred into a three neck flask and 0.05g of sodium borohydride added under an atmosphere of nitrogen. The solution was stirred for 15 minutes and a purple-blue precipitate was filtered under an atmosphere of nitrogen, washed with methanol saturated with N_2 and dried over a stream of N_2. The product changed its colour to yellow in exposure to air.

4.3.29 REACTION OF THE BLUE PRODUCT OBTAINED FROM PROCEDURE (4.3.28) WITH CARBON DIOXIDE IN SOLUTION AND IN THE SOLID FORM

No reaction between carbon dioxide and the blue product was obtained in reaction (4.3.28) either in solution or in the solid form

4.4.1 RESULTS AND DISCUSSION

The catalytic properties of transition metal complexes, especially those containing group VB donors as ligands and metals in low oxidation states, and their reactivity towards small molecules such as (N_2O,CS_2,O_2,....) have encouraged us to study the reaction of carbon dioxide with some of the phosphine complexes of ruthenium such as $RuCl_2(PPh_3)_3$, Ru(salen)$(PPh_3)_2$, $Ru(DH)_2(PPh_3)_2$, $RuCl_2(DH)(PPh_3)_2$, $RuH_2(PPh_3)_4$ in solution and in the solid form. This chapter describes the results thus obtained and also deals with the reactions of the phosphine and dimethylglyoxime complexes of rhodium such as $Rh(DH)_2Br_2$, $Rh(DH)_2Cl_2$, $RhH(PPh_3)_4$ with carbon dioxide.

The preparations of all starting materials are given in the experimental part of this chapter, and were found to give satisfactory analytical data.

Although the preparation of some of these complexes (i.e. $RuCl_2(PPh_3)_3$ and $Ru(DH)_2(PPh_3)_2$) was straight-forward, the preparation of others such as $RhH(PPh_3)_4$ and Ru(salen)$(PPh_3)_2$ was found to be extremely sensitive to manipulation and reaction conditions. A variety of analytical techniques was employed for our investigation, however poor solubility and low yield, together with technical difficulties with some of the complexes (i.e: $Ru(DH)_2(PPh_3)_2$) restricted our interpretation of data mainly to infra-red and elemental analysis.

The ^{13}C and ^{31}P NMR spectra could only be obtained for $RuCl_2(PPh_3)_3$.

The reactions of carbon dioxide with the phosphine complexes, mentioned previously, were mainly studied in toluene solution. The reactions of carbon dioxide with complexes in the solid form were studied in autoclave at 12 - 18 atmosphere pressure.

Although investigation of the reaction of carbon dioxide with the ruthenium and rhodium complexes in solution and in the solid form resulted in the formation of new compounds, interpretation and characterization of these products should be treated carefully. This is because in most cases either all structural information about products could not be obtained or the nature and quantity of the compounds restricted our choice to a few techniques. Factors such as concentration of the starting material, oxygen, ligand impurity, temperature, pressure, were often found to affect reactions in such a way that an incomplete reaction occurred, or even no reaction took place at all. While a great deal of time was spent in finding optimum conditions and a large number of experiments were tried, only those few reactions which were found to be more satisfactory are reported in the experimental section.

The reactions of the complexes dihydridotetrakis(triphenylphosphine) ruthenium(II) and hydrido-tetrakis(triphenylphosphine)rhodium(I) with carbon dioxide in solution have been investigated and the formation of different types of products for both complexes reported(19). To find optimum conditions in systems under our investigation and to obtain further information about reaction of carbon dioxide with complexes $RuH_2(PPh_3)_4$, and $RhH(PPh_3)_4$ we have tried to reproduce these results from the literature.(19) The observations and some of the analytical data obtained from these systems confirm the literature.

Further investigation resulted in the formation of new products.

The reaction of carbon dioxide with most complexes in solution results in the appearance of new infra-red bands in the region of 1260, 1080, 800cm^{-1}. (A band or bands around 1080cm^{-1} could not be distinguished reliably because of the presence of other infra-red bands in this region) regardless of metal ion (Rh or Ru). Comparison of the infra-red spectra of these products suggests that the nature of the co-ordinated carbon dioxide (or it's derivatives) should be similar or the same in all these compounds. However the stability of these compounds differs from one to another, for instance the complex obtained from the reaction of $Ru(DH)_2(PPh_3)_2$ with carbon dioxide in toluene is very sensitive to air in solution in such a way that infra-red bands at 1260, 1080, 800cm^{-1} became weaker while the product obtained from the reaction of $RuCl_2(PPh_3)_3$ and CO_2 in toluene was found to be quite stable to air in solution compared with previous system. Similarly if the product obtained from reaction of $RhH(PPh_3)_4$ and CO_2 in toluene under reflux is exposed to air in solution those infra-red bands (1260, 1080, 800cm^{-1}) disappear completely.

4.4.2 THE REACTION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RUTHENIUM (II) WITH CARBON DIOXIDE

The preparation of dihydrido-tetrakis(triphenylphosphine)ruthenium(II) under two different atmospheres (hydrogen and argon) has been carried out as given in procedures (4.3.1 and 4.3.2). The compound obtained under an atmosphere of hydrogen shows an infra-red band in the region of

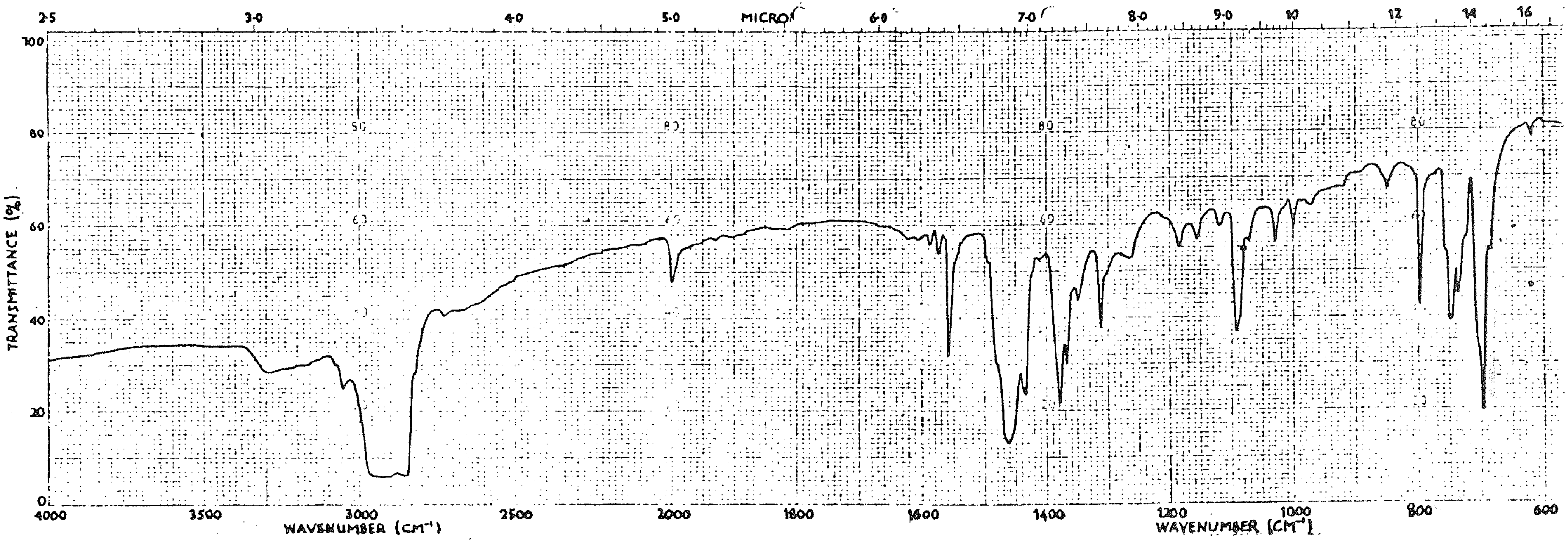
2080cm^{-1} due to Ru-H while the compound obtained under an atmosphere of argon does not show any band in this region. The ^1H nmr spectrum of the hydride complex was also studied in toluene saturated with hydrogen but no evidence due to the presence of hydride was observed.

When carbon dioxide was bubbled into the toluene solution of $RuH_2(PPh_3)_4$ an orange precipitate was formed in about 1 day. (The preparative work was given in procedure (4.3.3.). The infra-red spectrum of this orange complex (spectrum 4.4.1) shows several new bands compared with the infra-red spectrum of the starting material (spectrum 4.4.2). The thermal analysis of this product along with elemental analysis also is in a good agreement with the literature (19) and helps to confirm the structure $(HCOO)RuH(PPh_3)_3$.(toluene).

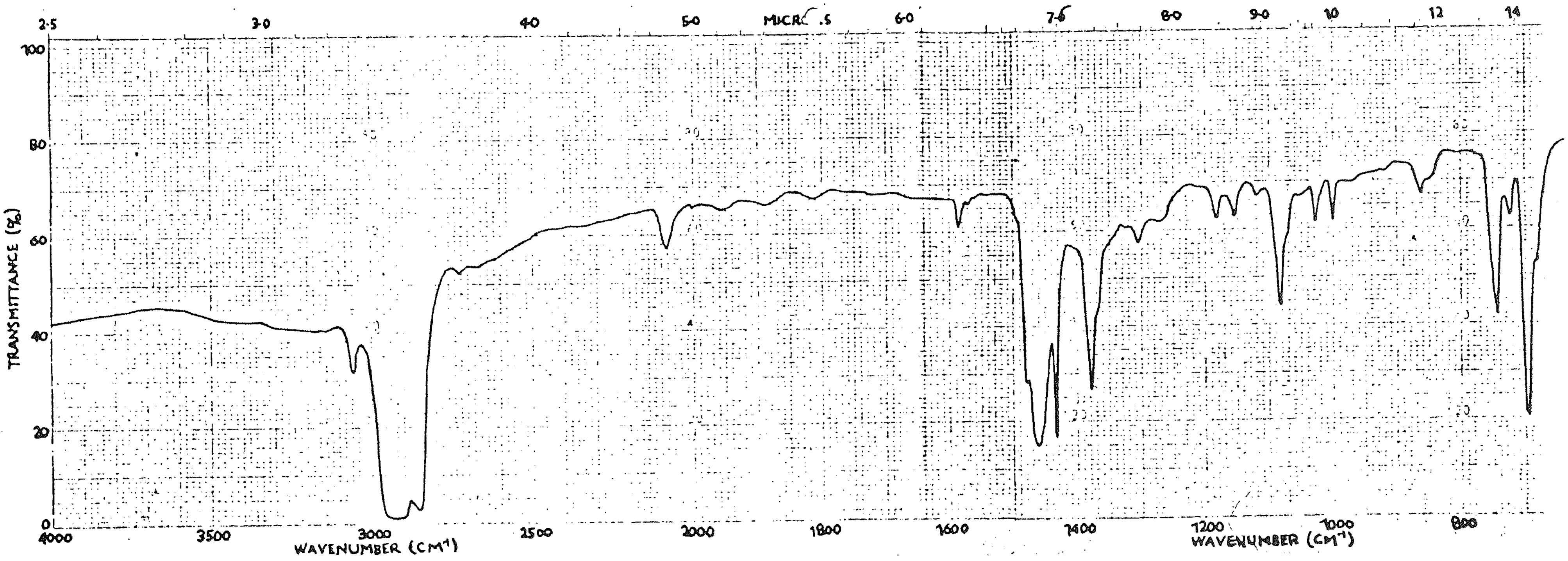
The comparison of data for this orange product and the yellow product reported in the literature are given in table (4.4.1) and the infra-red spectra of $RuH_2(PPh_3)_4$ and $(HCOO)RuH(PPh_3)_3$.(toluene) are presented.

Table 4.4.1

Orange $(HCOO)RuH(PPh_3)_3$.(toluene)	Yellow $(HCOO)RuH(PPh_3)_3$(toluene) reported in literature (19)
Elemental analysis	
Found: %C 72 %H 5.5	Found: %C 72.7 %H 5.3
$(HCOO)RuH(PPh_3)_3$(toluene) requires: %C 72.6 %H 5.4	
T.G.A. release of gas at 140°C	T.G.A. release of CO_2 at 140°C.
IR: 1555cm^{-1}, 1310cm^{-1}, 2000cm^{-1}	IR: 1553cm^{-1}, 1310cm^{-1}, 1996cm^{-1}.



Spectrum (4.4.1) Infra-red spectrum of (HCOO)RuH$(PPh_3)_3$.(toluene) (Nujol Mull)



Spectrum (4.4.2) Infra-red spectrum of $RuH_2(PPh_3)_4$ (Nujol Mull)

The concentration of $RuH_2(PPh_3)_4$ and excess triphenylphosphine were found to be important and either resulted in an incomplete reaction or no reaction was observed at all. The following points should also be noted:

(a) - The reaction of $RuH_2(PPh_3)_4$ with carbon dioxide in toluene solution and in the presence of oxygen results in the formation of a green product which does not show any infra-red band due to formate structure or coordinated carbon dioxide. Therefore it is important to saturate the toluene with carbon dioxide before $RuH_2(PPh_3)_4$ is introduced in to the system.

(b) - No reaction between the product obtained from the procedure (4.3.2) and carbon dioxide in toluene (either saturated with carbon dioxide or in the presence of oxygen) was observed.

The results and observations along with the nmr spectrum of $RuH_2(PPh_3)_4$ in toluene saturated with hydrogen suggests that the ruthenium-hydride bond is very sensitive to oxygen and can easily be lost in solution even under an atmosphere of argon or hydrogen. The orange product $HCOORuH(PPh_3)_3$.(toluene) was found to be reasonably stable in the solid form and it can be stored in a sample bottle for a long period of time. (2 weeks in these studies) However, in solution, especially in the presence of oxygen the compound decomposes and the bands at 1555, 1310, 2000 cm^{-1} disappear. This can be taken in support of the following equilibrium:

$$\underset{(I)}{(HCOO)RuH(PPh_3)_3} \rightleftharpoons \underset{(II)}{H_2Ru(CO_2)(PPh_3)_3}$$

Since the adduct complex (II) may be expected to be more reactive towards oxygen compared with (I). A similar equilibrium has been studied for the complex $\left[Ru(O_2CH)(PMe_2Ph)_4\right]^+$ by other workers and was reported in literature.(131) The detailed infra-red study of (20) complex (I) confirms the formate structure, therefore it must be assumed that structure (II) is favoured in solution, but (I) in the solid. The product obtained from the decomposition of the orange complex ($HCOORuH(PPh_3)_3$·toluene) is greenish and was found to be unreactive towards carbon dioxide in toluene. This evidence shows the importance of Ru-H as an active site in the molecule.

4.4.3 REACTION OF DIHYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE IN SOLUTION AND IN THE PRESENCE OF REDUCING AGENT

The reaction of $RuH_2(PPh_3)_4$ with carbon dioxide in toluene and in the presence of the zinc amalgam according to procedure (4.3.4) resulted in a green tarry product which shows two new infra-red bands in the region of 1260, 800cm^{-1}. Due to similar solubility of the ligand and product in solvents (toluene, chloroform, alcohol, acetone) this compound could not be purified. Therefore the infra-red spectrum reported above was taken with difficulty from the crude sample, since the compound was tarry and the Nujol mull could not easily be prepared. By relying on the infra-red spectrum only and with reference to table (4.4.2) this product may be suggested to have the structure $H\left[Ru(PPh_3)_3CO_3\right]$ The low intensity of those new infra-red bands may suggest an incomplete reaction.

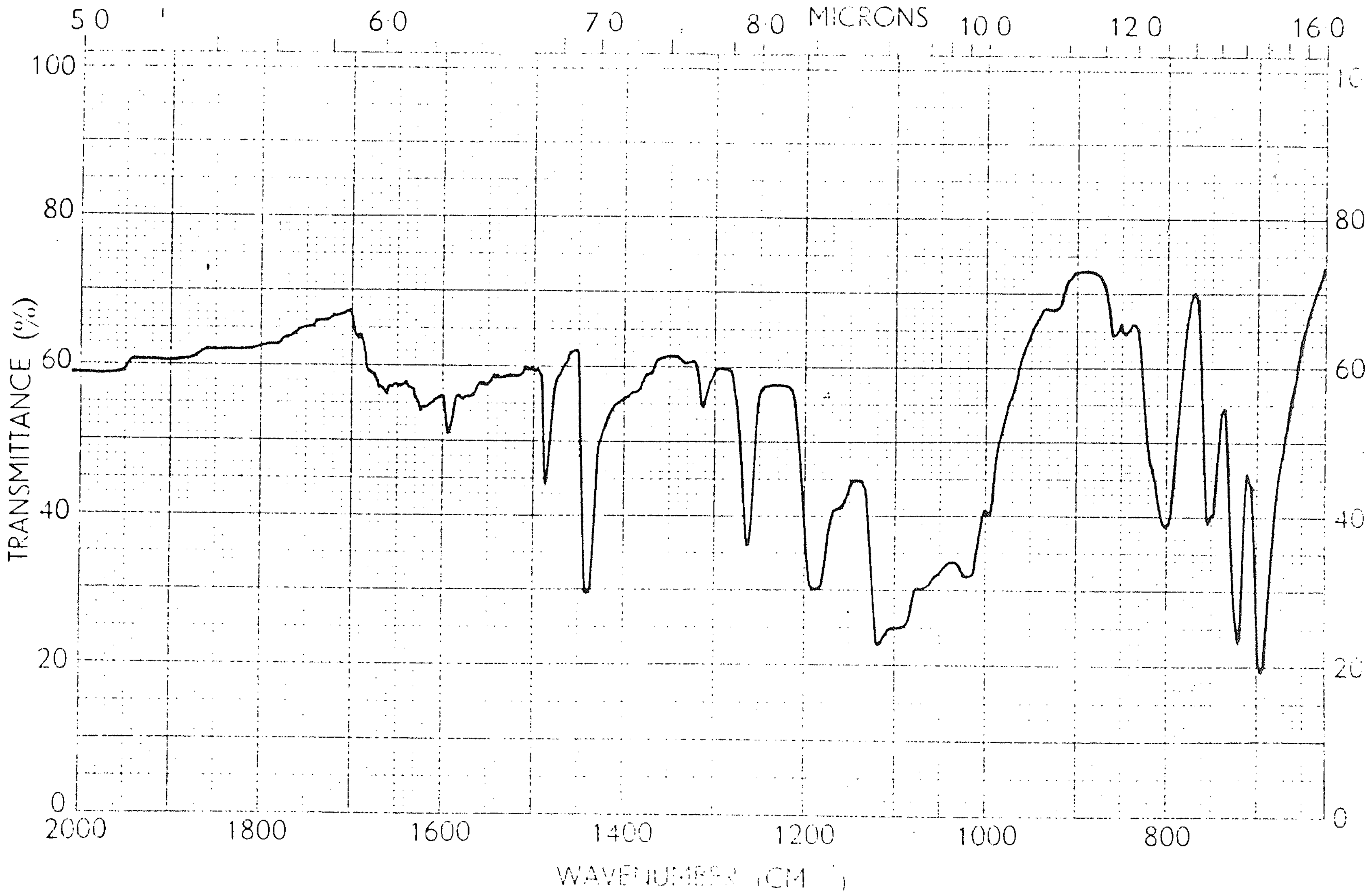
4.4.4 REACTION OF HYDRIDO-TETRAKIS(TRIPHENYLPHOSPHINE)RHODIUM(I) WITH CARBON DIOXIDE

The reaction of $RhH(PPh_3)_4$ with carbon dioxide in solution has been investigated and formation of the products $Rh_2H_2(CO_2)(PPh_3)_6$(toluene)(I) and $Rh_2(CO_3)(PPh_3)_5$ (II) reported.(19,114) Complex (I) has been reported to show an infra-red band at 1460 cm^{-1} and a Raman band at 1300 cm^{-1} due to ν(OCO) assymmetric and symmetric respectively. The molecular weight measurement could not be done and the infra-red spectrum does not show any band due to Rh-H. The hydride structure is favoured on the basis of chemical reactions. Thermal analysis of the compound has shown that only CO_2 is released up to 220°C.(19) The complex (II) has been characterized as a carbonate. The infra-red spectrum of this carbonate shows several new infra-red bands in the regions of 1485, 1460, 1360, 1350 and 820 cm^{-1} and the Raman spectrum shows two bands at 1300 and 1660 cm^{-1}.(114)

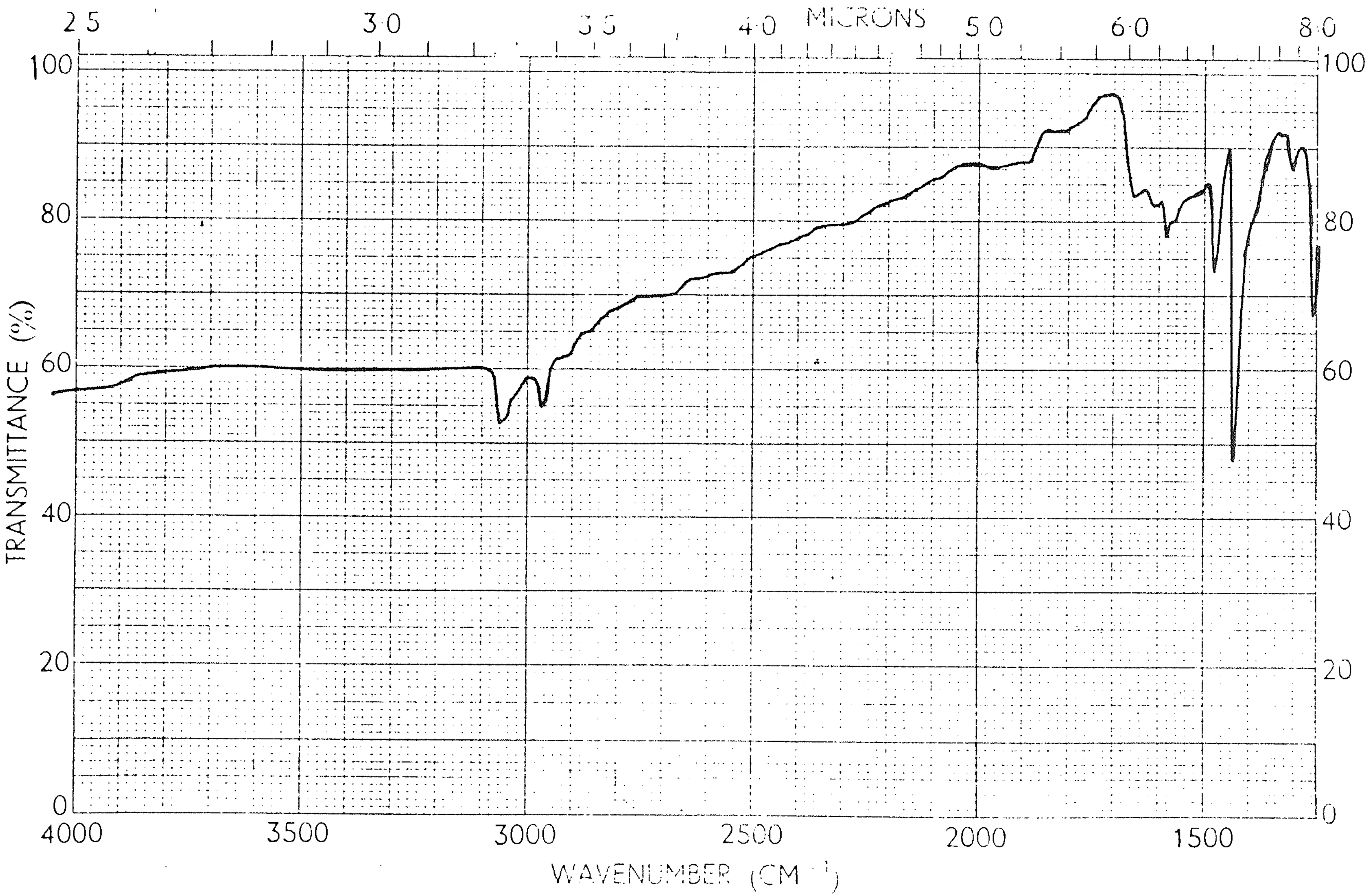
Our observations and results from studying the reaction of carbon dioxide and hydrido-tetrakis(triphenylphosphine)rhodium(I) in toluene solution are as follows:

Passing gaseous carbon dioxide through a yellow solution of $RhH(PPh_3)_4$ in toluene saturated with carbon dioxide at room temperature yielded an orange complex in about 1 day. After the solvent had been evaporated off, the orange red complex was washed with toluene and alcohol saturated with carbon dioxide and dried under a stream of CO_2. The infra-red spectrum does not show any band due to carbonato species, but it shows a strong band at 1480cm^{-1}. While our observations show the formation of an orange complex as reported in the literature, the compound cannot be fully characterized on the basis of one infra-red band since the bands due to ligand are also present in this region. Presence of the other band at 1300 cm^{-1} due to ν(OCO sym) could not be observed because the technique of Raman spectroscopy was not available. The elemental analysis of this orange complex is in a good agreement with the structure $Rh_2H_2(CO_2)(PPh_3)_6$.(toluene). (Analytical data: calculated %C 72.6 %H 5.5 Found: %C 72.6 %H 5.4) It should also be noted that keeping the orange solution obtained from reaction of $RhH(PPh_3)_4$ and CO_2 (solution A) from procedure (4.3.6) for a longer period of time (7 - 10 days) under an atmosphere of carbon dioxide failed to give any precipitate and in all instances only the orange solution was obtained. This solution is extremely sensitive to air. Exposure to air results in the precipitation of the yellow complex in a few seconds and the colour of the solution changes from orange to yellow (these two colours are quite distinguishable). The infra-red spectrum of this yellow complex was found to be identical with that of $RhH(PPh_3)_4$ except that no band due to Rh-H was observed. Reaction of this yellow complex with toluene saturated with carbon dioxide neither produced any orange complex nor any other products.

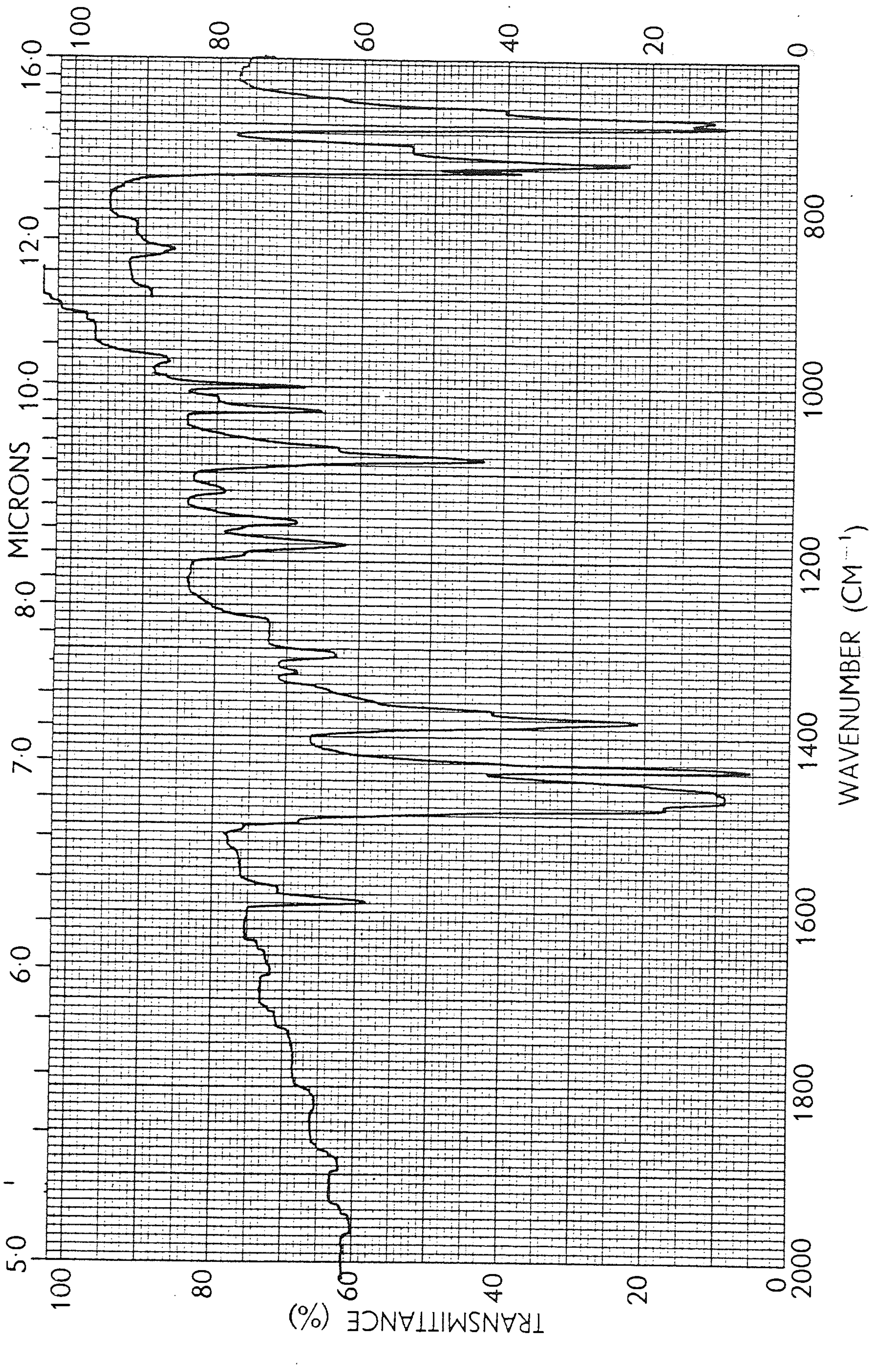
Refluxing the orange solution made by reaction of $RhH(PPh_3)_4$ and toluene saturated with CO_2 under an atmosphere of argon or carbon dioxide according to procedure (4.3.6) results in brown and red-brown products respectively. The infra-red spectra of both products were found to be identical (spectrum 4.4.3) and show several new bands in the region of 1260, 1080, 800cm^{-1} compared with that of the $RhH(PPh_3)_4$. spectrum (4.4.4.). These products are sensitive to air in solution



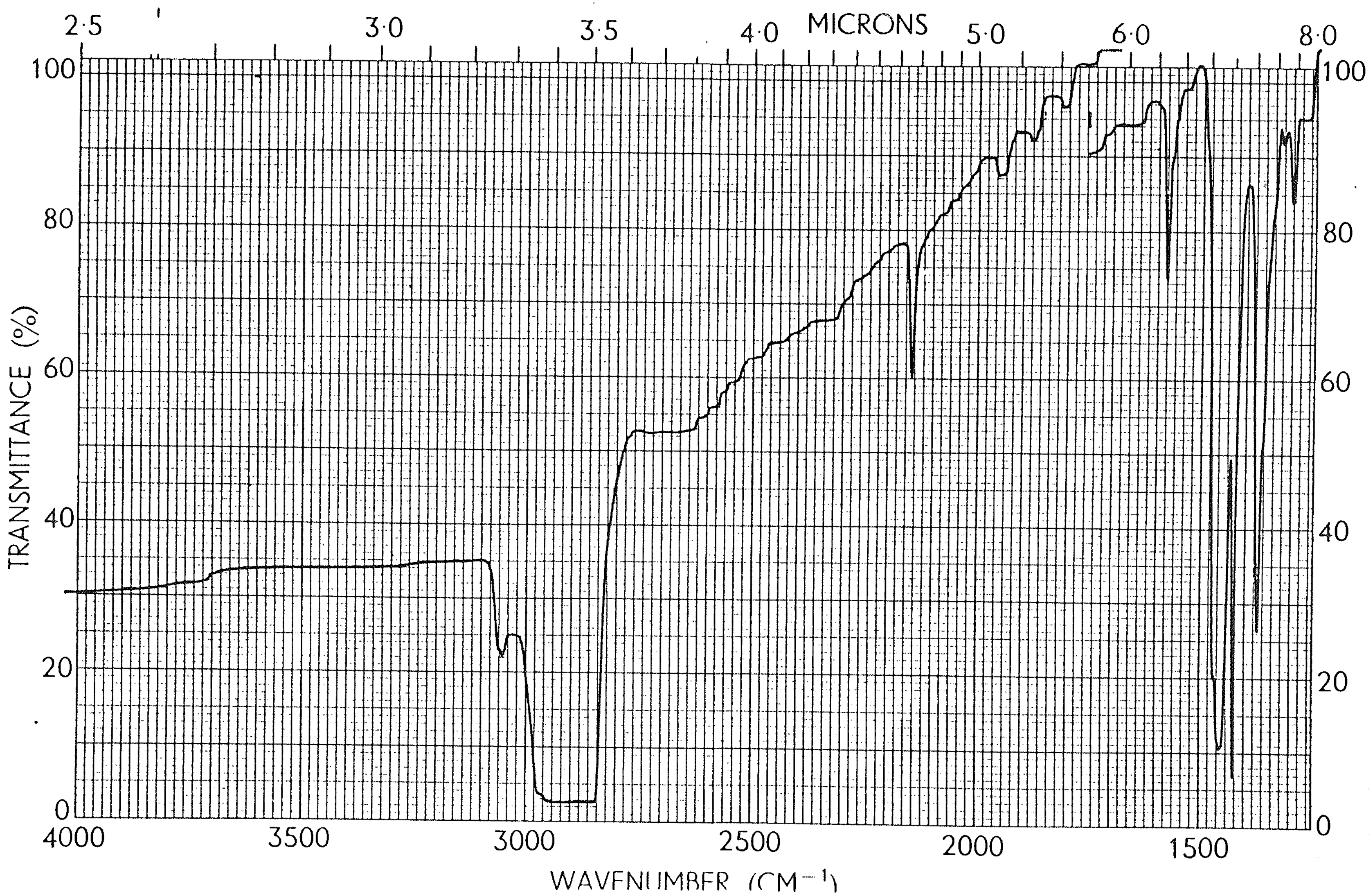
Spectrum (4.4.3) Infra-red spectrum of the compound recovered after refluxing the solution of $RhH(PPh_3)_4$ in toluene saturated with CO_2 (KBr disc)



Spectrum (4.4.3) Infra-red spectrum of the compound recovered after refluxing the solution of $RhH(PPh_3)_4$ in toluene saturated with CO_2 (KBr disc)



Spectrum (4.4.4) Infra-red spectrum of RhH(PPh$_3$)$_4$ (Nujol Mull)



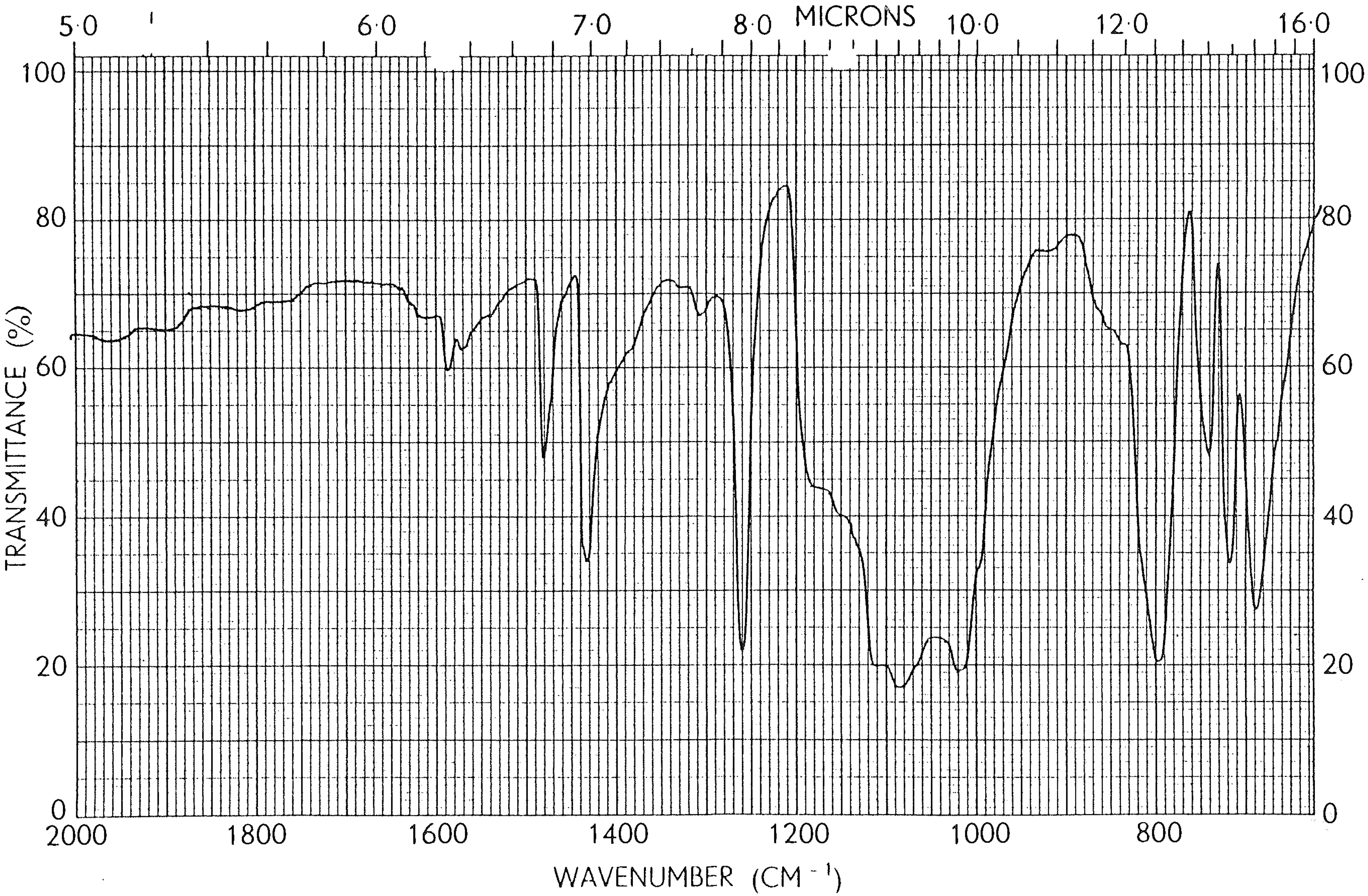
Spectrum (4.4.4) Infra-red spectrum of $RhH(PPh_3)_4$ (Nujol Mull) and bands at 1260, 1080, 800cm^{-1} disappear on exposure to air. The T.G.A. analysis of the brown product shows release of a gas at 170°C and analysis of the gas using mass spectrometer shows m/e at 44 due to carbon dioxide. The molecular weight measurement using osmometry technique shows an apparent molecular weight of 52 6. Elemental analysis of the brown product was found to be inconsistent, consequently on the basis of infra-red spectrum, mass spectrum and with reference to table (4.4.2) this brown product may be characterized as $(Rh(PPh_3)_3)_2CO_3$ or mono-dentate carbonato $H\left[Rh(PPh_3)_3.CO_3\right]$.

4.4.5 THE REACTION OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) WITH CARBON DIOXIDE

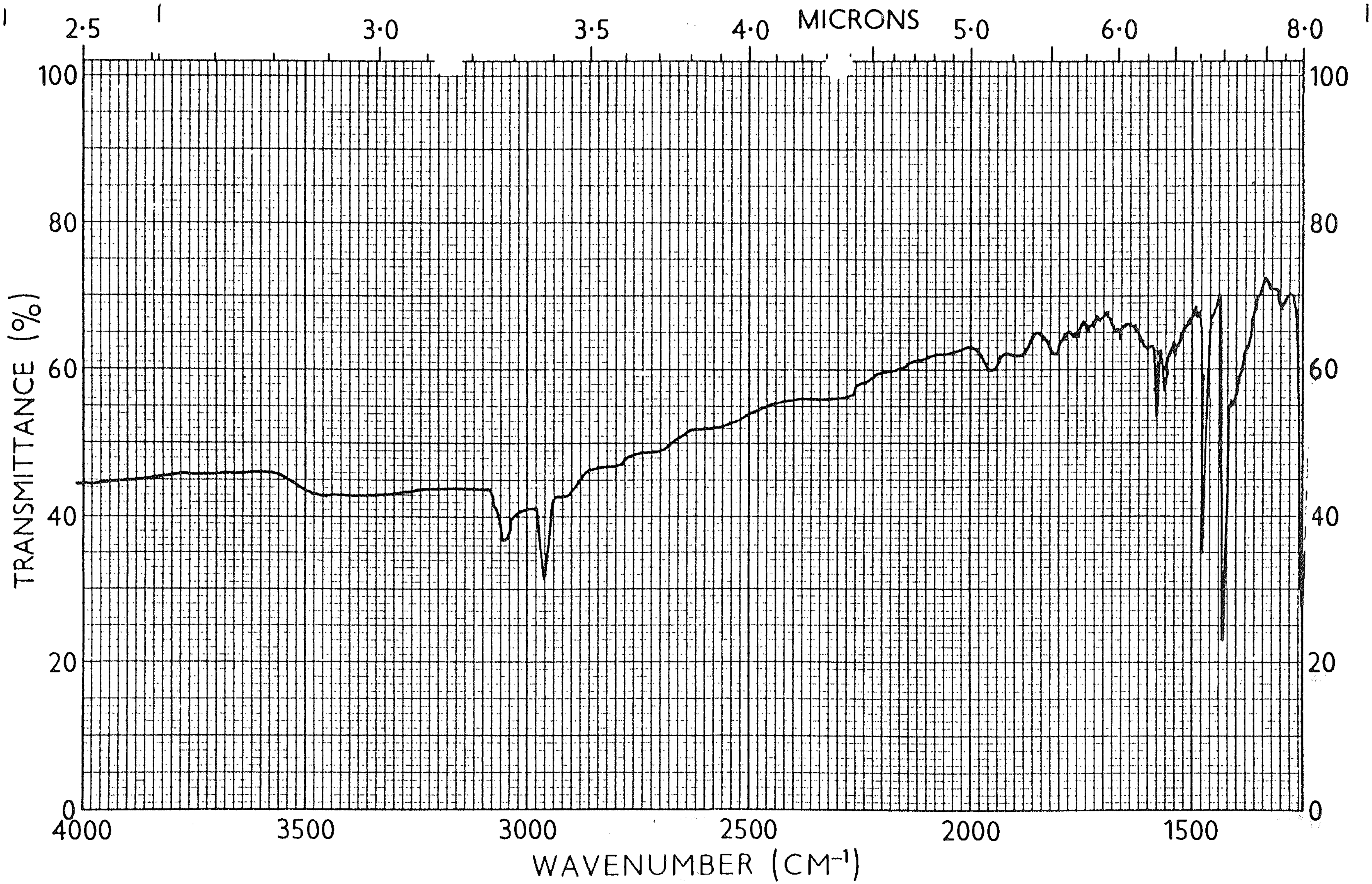
Details of the chemistry of $RuCl_2(PPh_3)_3$ are given in the introductory section. This compound was used as a base compound for the preparation of the other phosphine complexes of ruthenium in this chapter. The preparation of $RuCl_2(PPh_3)_3$ was found to be easy and resulted in a product of the same characteristics as reported in the literature.(126) The compound was also found to be stable in the solid form. It gives a brown solution when dissolved in solvents such as benzene or toluene saturated with nitrogen. These solutions absorb oxygen and produce a green solution. From the information given in the literature, the presence of two species $Ru(O_2)Cl_2(PPh_3)_2$ and $O = P(PPh_3)_3$ may be found in this green solution, in addition to the other components of the reactions.(116,113) Considering the reaction of the oxygen adduct complex $O_2Pt(PPh_3)_2$ with molecules such as (SO_2, CO_2, CS_2) and formation of the products ——

$Pt(PPh_3)_2SO_4$, $Pt(PPh_3)_2OCO_3$ or $Pt(PPh_3)_2CO_3$, $Pt(PPh_3)_2(OCS_2)_2$(130) together with the reactivity of $RuCl_2(PPh_3)_3$ and some of the oxygen adduct complexes of ruthenium towards small molecules such as CS_2 (isoelectronic with CO_2) and SO_2 we may have enough evidence to be able to predict a reaction between carbon dioxide and the complex $RuCl_2(PPh_3)_3$ in solution. When carbon dioxide is brought into contact with a toluene (or benzene) solution of $RuCl_2(PPh_3)_3$ a dark brown solution is obtained within 2-3 days, from which a brown solid product could be recovered. The infra-red spectrum of this brown product (spectrum 4.4.5) shows several new bands in the region of 1260, 1080, 800cm^{-1} compared with the infra-red spectrum of the starting material (spectrum 4.4.6).

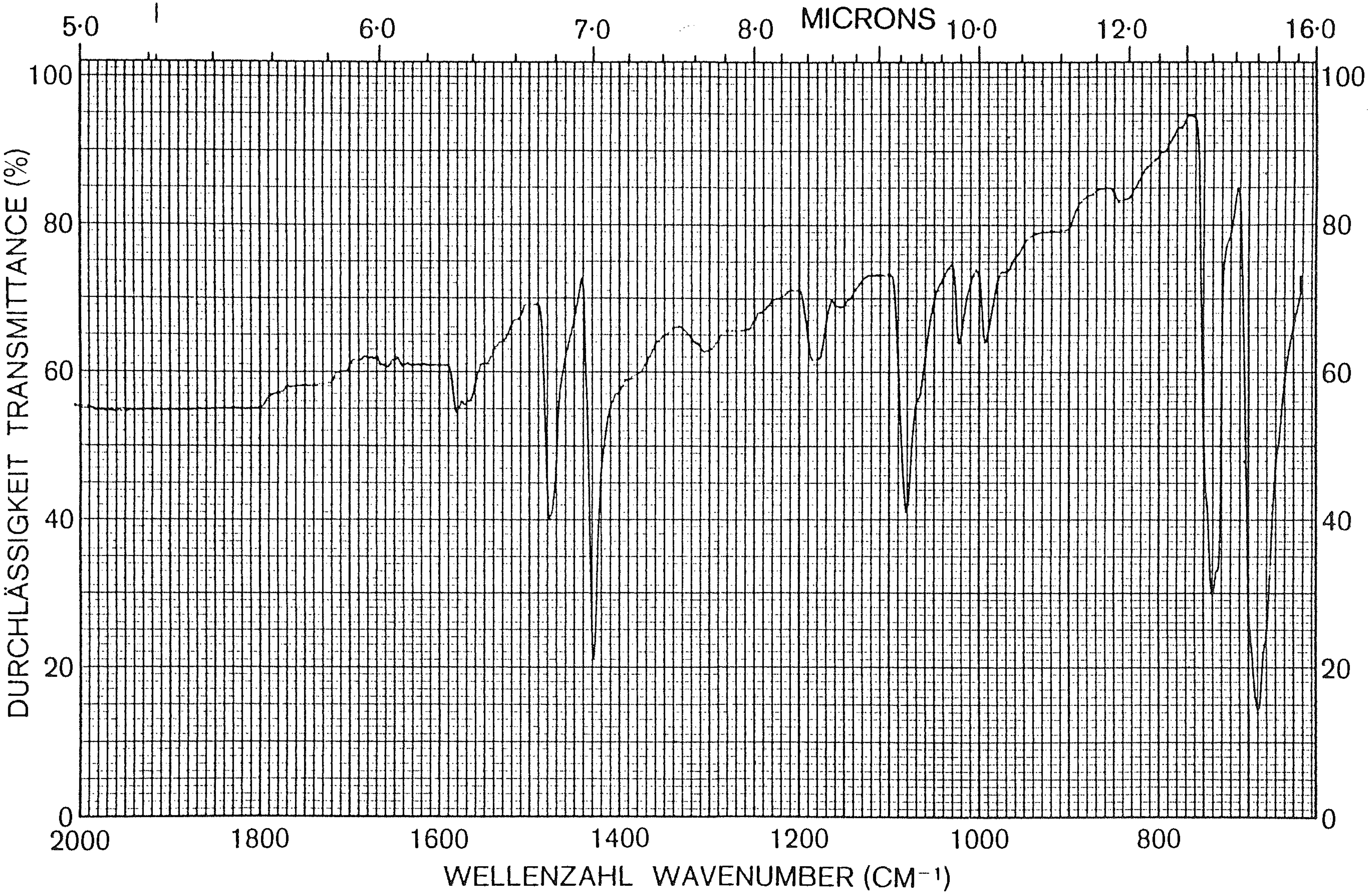
To study the effect of oxygen on the reaction, the same procedure was followed but carbon dioxide was replaced by oxygen and a green product was recovered. The infra-red spectrum of this product was found to be similar to that of $RuCl_2(PPh_3)_3$ and no new infra-red bands were observed. The temperature was also found to be important. For instance heating the reaction vessel up to 30°C resulted in formation of the brown product in a shorter period of time. The thermal analysis of this brown product shows that the compound decomposes at 180°C and analysis of the gas at this temperature shows the evolution of carbon dioxide. To obtain more structural information (i.e. to show whether the intact CO_2 unit is present in the molecule) the reaction of this brown product with a Grignard reagent (phenylmagnesium bromide) was carried out. The product was found to be a mixture from which no predictable species such as benzoic acid could be isolated.



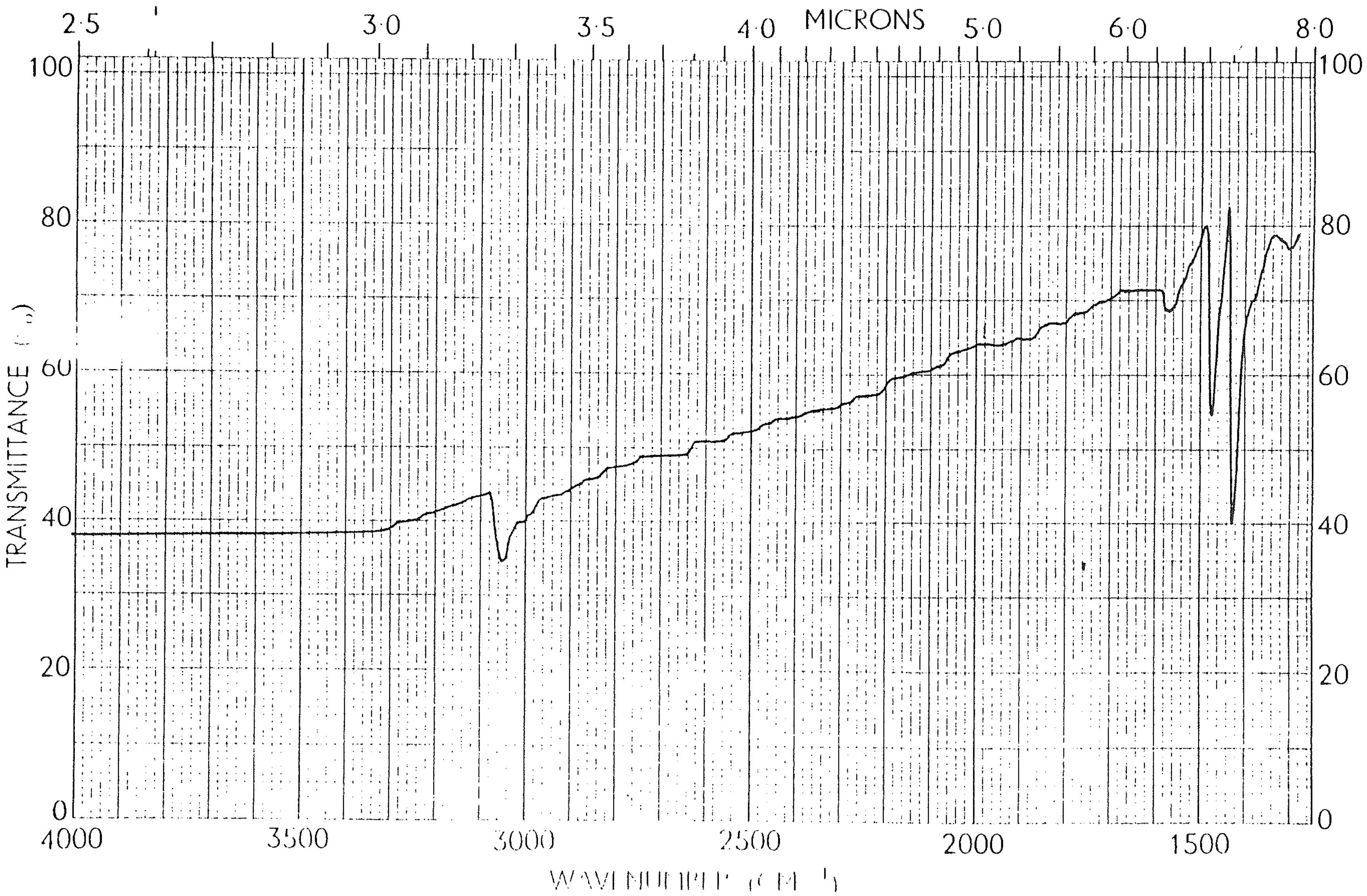
Spectrum (4.4.5) Infra-red spectrum of the compound obtained from the reaction of $RuCl_2(PPh_3)_3$ and CO_2 in toluene solution (KBr disc)



Spectrum (4.4.5) Infra-red spectrum of the compound obtained from the reaction of $RuCl_2(PPh_3)_3$ and CO_2 in toluene solution (KBr disc)



Spectrum (4.4.6) Infra-red spectrum of $RuCl_2(PPh_3)_3$ (KBr disc)



Spectrum (4.4.6) Infra-red spectrum of $RuCl_2(PPh_3)_3$ (KBr disc)

The ^{31}P and ^{13}C nmr spectra of $RuCl_2(PPh_3)_3$ and its products in chloroform saturated with CO_2 have also been studied. Although the information obtained from these studies suggest a reaction between CO_2 and the $RuCl_2(PPh_3)_3$, the data are not sufficiently clear to provide useful structural information (see also 4.4.6). This ambiguity is not the only example in our case since the nmr spectrum of $PtH_2(P^chex_3)_2$ under a CO_2 atmosphere in toluene-d_8 has been reported to show the dominant spectrum of starting material(99). (The reaction of $PtH_2(P^chex_3)_2$ with CO_2 in benzene solution is known to give trans-$PtH(O_2CH)(P^chex_3)_2 \cdot 2C_6H_6$).

The fact that no new infra-red bands were observed from the green product obtained from the reaction of $RuCl_2(PPh_3)_3$ with oxygen in toluene solution suggests that the brown product obtained from the reaction of $RuCl_2(PPh_3)_3$ and CO_2 in toluene solution does not contain a co-ordinated triphenylphosphine oxide ligand, since the formation of triphenylphosphine oxide is more favourable under an atmosphere of oxygen then carbon dioxide. The absence of ir bands in the region of Ru - CO may also reject the formation of $OPPh_3$ as a major product.

However, triphenylphosphine oxide may be present in the product as an impurity. So far our observations and data about this brown product confirm the presence of carbon dioxide or its derivatives in this complex, therefore the main questions remaining at this stage are what is the major product of the reaction of $RuCl_2(PPh_3)_3$ and CO_2 and can a plausible route be suggested for formation of this product?

Due to the presence of water and oxygen in the reaction between $RuCl_2(PPh_3)_3$ and CO_2 the formation of species such as carbonate, peroxycarbonate, bicarbonate may be expected. The adduct $RuCl_2(PPh_3)_3CO_2$ may also be produced (see also discussion in chapter V) at the initial stage of the reaction. However chemical reaction and the stability of the brown product in the solid form and solution favour the other species mentioned above. Table (4.4.2) shows the infra-red active bands for some of the known carbonates, bicarbonates, and peroxycarbonates and may help to characterize the brown product. As can be seen, the infra-red active bands of the brown product obtained from the reaction of $RuCl_2(PPh_3)_3$ and CO_2 (1260, 1080, 800cm^{-1}) are comparable with some of the infra-red bands of the compound reported in table (4.4.2). The band above 1450cm^{-1} in the brown product could not be identified due to the presence of the ligand vibrations in this region. The following information may limit our choice and lead us to characterize the brown product correctly.

The study of the visible spectrum of the compound $RuCl_2(PPh_3)_3$ under an atmosphere of CO_2 and O_2 shows competition between these molecules for reaction with $RuCl_2(PPh_3)_3$ and therefore the formation of the peroxy carbonate is unlikely as the major product.

The fact that the infra-red spectrum of the brown product does not show any band in the region of OH vibrational frequency may suggest that this product does not have the bicarbonate structure, especially since the absence of the OCO_2H group is suggested by the ^1H nmr spectrum of the brown product in $CHCl_3$. Obviously bicarbonate species could be present as an impurity in the final product.

Table (4.4.2)

Compound	Infra-red active bands/cm^{-1}	Ref
$(Ph_3P)_2PtCO_3$	1685(vs), 1185(s), 980(s), 815cm^{-1}	(38)
$(Ph_3P)_2PdCO_3$	1655(vs) 1630(vs), 1200(vs), 989, 817cm^{-1}	(38)
$(Ph_3P)_2PtOCO_3$	1678(vs), 1243(vs), 978(s) 836cm^{-1}	(38)
$(Ph_3P)_2PdOCO_3$	1661(vs) 1604(m), 1256(vs), 978(vs), 833(sh)cm^{-1}	(38)
Monodentate $\left[Co(NH_3)_5CO_3\right]Br$	1453, 1373, 1070, 850 cm^{-1}	(131)
Bidentate $\left[Co(NH_3)_4CO_3\right]Cl$	1593, 1265, 1030, 834 cm^{-1}	(131)
Bridge $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$	1485(s), 1460(vs), 1360(m), 1350(m) 820(w)	(114)
Bicarbonato $RhH_2(O_2COH)\ P(i\text{-}Pr)_{3\,2}$	2650(m), 1587(s), 1338(s), 792(m)	(40)
$(O_2COH)_2^{-2}$	2620(w), 1618(s), 1405, 1367(s), 830(m)	(40)

With reference to information given so far the product of the reaction of CO_2 with $RuCl_2(PPh_3)_3$ in toluene solution may be characterized as monodentate carbonato $\left[RuCl_2(PPh_3)_2CO_3\right]_2(H)_2$ or a bridged carbonato $\left[RuCl_2(PPh_3)_2\right]_2CO_3$.

4.4.6 THE ^{31}P AND ^{13}C NMR STUDIES OF THE $RuCl_2(PPh_3)_3$ IN CHLOROFORM SATURATED WITH CO_2

The ^{31}P nmr spectrum of my preparation of $RuCl_2(PPh_3)_3$ in chloroform shows a singlet at 41.1 ppm related to three equivalent phosphine ligands, indicating a trigonal bipyramidal structure. The position of this peak is in good agreement with that been reported in the literature and given in table (4.4.3).

Bubbling carbon dioxide through the chloroform solution of $RuCl_2(PPh_3)_3$ and keeping the solution under an atmosphere of the gas gives a red-brown solution within 2 days. The ^{31}P nmr spectrum of this red-brown solution (spectrum 4.4.7) shows three singlets at 41.1, 29.2, -5.16 ppm relative to the singlet observed for an external standard of 85% orthophosphoric acid (spectrum 4.4.8) (relative intensities 1:1.1:1.8). The results obtained from the ^{31}P nmr spectrum of the $RuCl_2(PPh_3)_3$ in chloroform saturated with CO_2 are comparable with the chemical shifts for free triphenylphosphine oxide, triphenylphosphine and dichloro-tris(triphenylphosphine)ruthenium(II) in table (4.4.3) and may suggest the presence of these species in the red-brown solution.

Table (4.4.3)

Compound	Observed ^{31}P(ppm)	^{31}P reported in literature
$RuCl_2(PPh_3)_3$	41.1	40.9 (113)
$OPPh_3$	29.2	27.7
PPh_3	-5.16	-5.5

Spectrum (4.4.7) 31p nmr spectrum of $RuCl_2(PPh_3)_3$ in chloroform saturated with CO_2.

Singlet 1	41.1 ppm
Singlet 2	29.2 ppm
Singlet 3	-5.16 ppm

Spectrum (4.4.8) 31p nmr spectrum of ortho-phosphoric acid

To interpret the result the following plausible schemes may be considered:

(a) - Supposing the reactions of CO_2 with $RuCl_2(PPh_3)_3$ both in chloroform and toluene solutions are similar and that the ^{31}P resonance frequency of $RuCl_2(PPh_3)_2CO_3$ is at 29.2, it is possible to propose the following scheme for the reaction of $RuCl_2(PPh_3)_3$ with CO_2 in chloroform solution.

$$RuCl_2(PPh_3)_3 + CO_2 \rightleftharpoons RuCl_2(PPh_3)_3.CO_2 \longrightarrow RuCl_2(PPh_3)_2.CO_2 + PPh_3$$

$$\longrightarrow RuCl_2(PPh_3)_2CO_3 + 2PPh_3$$

$$PPh_3 \xrightarrow{O_2} OPPh_3$$

This scheme is similar to the one given to explain the kinetic results obtained for the reaction in toluene solution.

(b) - If oxygen and water impurities are present and important during the reaction of CO_2 with $RuCl_2(PPh_3)_3$ in chloroform solution the following reactions may have occurred.

$$RuCl_2(PPh_3)_3 \rightleftharpoons RuCl_2(PPh_3)_2 + PPh_3$$

$$RuCl_2(PPh_3)_3 + CO_2 \rightleftharpoons RuCl_2(PPh_3)_3.CO_2 \longrightarrow RuCl_2(PPh_3)_2(O_2) + PPh_3$$

$$PPh_3 \xrightarrow{O_2} OPPh_3$$

Considering the possibilities (a) and (b), and the information obtained from the kinetic study of the reaction of $RuCl_2(PPh_3)_3$ in toluene saturated with CO_2 I suggest that the reaction in chloroform solution may be considered as a mixture of scheme (a) and (b). The peaks 1, 2, 3 in spectrum (4.4.7) are then interpreted as $RuCl_2(PPh_3)_3$, ($OPPh_3$ or $RuCl_2(PPh_3)_2CO_3$), PPh_3.The permeation of oxygen into the experimental solution during the time a spectrum was taken is very likely due to the unavailability of a suitable nmr tube. This is one of the most important reasons for favouring scheme (b). This is strongly supported by the results obtained from the visible study of the $RuCl_2(PPh_3)_3$ in toluene saturated with CO_2 and O_2, which suggests a competition between these molecules for reaction with $RuCl_2(PPh_3)_3$.

The absence of any peak due to $RuCl_2(PPh_3)_2(O_2)$ in spectrum (4.4.7) is in agreement with the literature since this species has not been detected (116) spectroscopically in the reactions. The difference between the observed ^{31}P chemical shifts of the species produced in the reaction and the one quoted from the literature for $RuCl_2(PPh_3)_3$, $OPPh_3$, and PPh_3 (table 4.4.3) may be due to different experimental conditions since the chemical shifts quoted in table (4.4.3) from the literature have been obtained from CH_2Cl_2 solution at 30°C while the observed chemical shift was obtained from chloroform solution at 20°C.

The polarity of the solvent may promote the disproportionation reaction of carbon dioxide in metal - CO_2 adduct complexes. One example of such a reaction is the conversion of the complex $RhCl(CO_2)(P^nBu_3)_2$ on standing in CH_2Cl_2 solution to $RhCl(CO)(OP^nBu_3)(P^nBu_3)$. (26) This may suggest the following side reaction between CO_2 and $RuCl_2(PPh_3)_3$ in chloroform solution:

$$RuCl_2(PPh_3)_3 + CO_2 \rightleftharpoons RuCl_2(PPh_3)_3.CO_2 \longrightarrow RuCl_2(PPh_3)_2(OPPh_3)CO$$

The above possibility is highly unlikely since the change in resonance frequency of the phosphine ligands after $RuCl_2(PPh_3)_3$ has been converted to $RuCl_2(PPh_3)_2(OPPh_3)(CO)$ could not be detected from spectrum (4.4.7).

The ^{13}C nmr spectrum of $RuCl_2(PPh_3)_3$ in chloroform saturated with CO_2 did not provide any useful information since the presence of new peaks from the background noise could not be distinguished and interpreted.

4.4.7 THE REACTION OF CARBON DIOXIDE WITH BIS(DIGLYOXIMATO)RHODIUM(I)

The reaction of nitrous oxide with the complex $\overset{I}{Co}(DH)_2$ has been reported to be feasible.(123) Since nitrous oxide is an isoelectronic molecule with carbon dioxide, a similar reaction between carbon dioxide and the complex $\overset{I}{M}(DH)_2$ in which M = Co or Rh may be expected. This information encouraged us to study the reaction of bis(diglyoximato)rhodium(I) with carbon dioxide in solution and in the solid form. The dichloro and dibromo complexes with bis(diglyoximato)rhodium(III) have been chosen as starting materials and alcoholic solutions of sodium hydroxide were used to reduce these salts to rhodium(I) species. The preparations of $Rh(DH)_2Br_2$ and $Rh(DH)_2Cl_2$ were straight forward and resulted in a compounds of desired analytical data. While the reduction of $Rh(DH)_2Cl_2$ failed to produce sufficient samples for further studies, the reduction of $Rh(DH)_2Br_2$ was successful and gave a collectable quantity of the blue product.

An attempt by increasing the quantities involved, to increase the quantity of the blue product obtained from the reduction of these salts in alcoholic solution of sodium hydroxide was not successful.

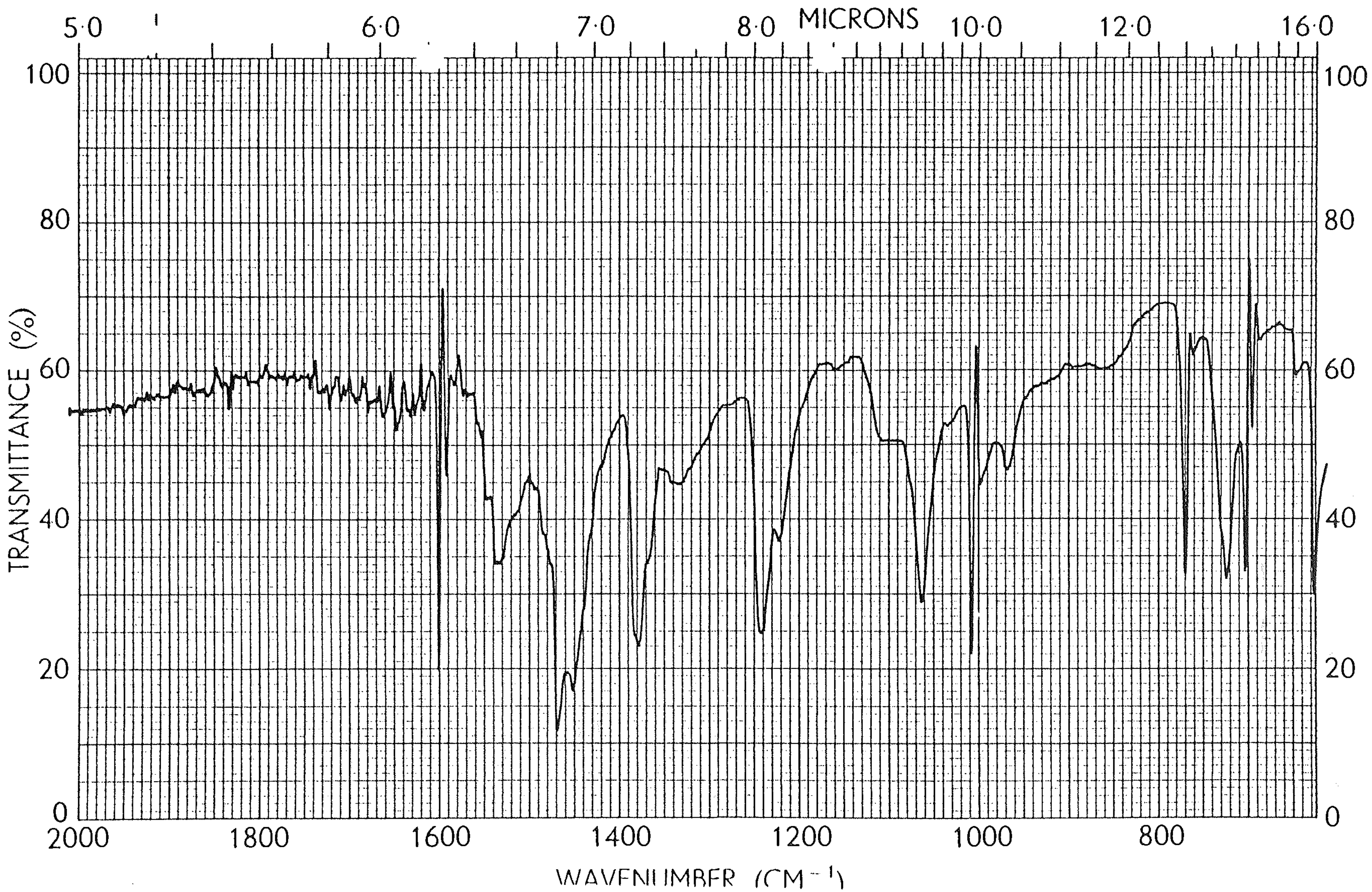
When carbon dioxide was bubbled through a toluene solution of $\overset{I}{Rh}(DH)_2$ (procedure 4.3.26a) obtained from the reaction of $Rh(DH)_2Br_2$ and NaOH in ethanolic solution a brown solution was obtained within a day from which a small quantity of brown product was recovered. The infra-red spectrum of this compound shows two weak bands in the region of 1260 and 800cm^{-1} and a weak band at 1070cm^{-1}. The position of the former band is not clear and cannot distinctively be distinguished. Due to loss of some product during the purification process and consequently having insufficient quantity of the sample for sufficient analysis, the information about this compound was restricted only to an infra-red spectrum which could only be obtained with difficulty.

Considering the presence of O_2 and H_2O impurity in the reaction between $\overset{I}{Rh}(DH)_2$ and CO_2 in toluene solution and by relying only on the infra-red spectrum it may be suggested that the brown product obtained from the above reaction may be characterized as the carbonato complex $Rh(DH)_2CO_3$. The weak infra-red bands in the region of 1260, 1070 and 800cm^{-1} may suggest an incomplete reaction. While not a great deal of information could be obtained in solution, the reaction of solid $\overset{I}{Rh}(DH)_2$ with carbon dioxide in an autoclave could provide a better result.

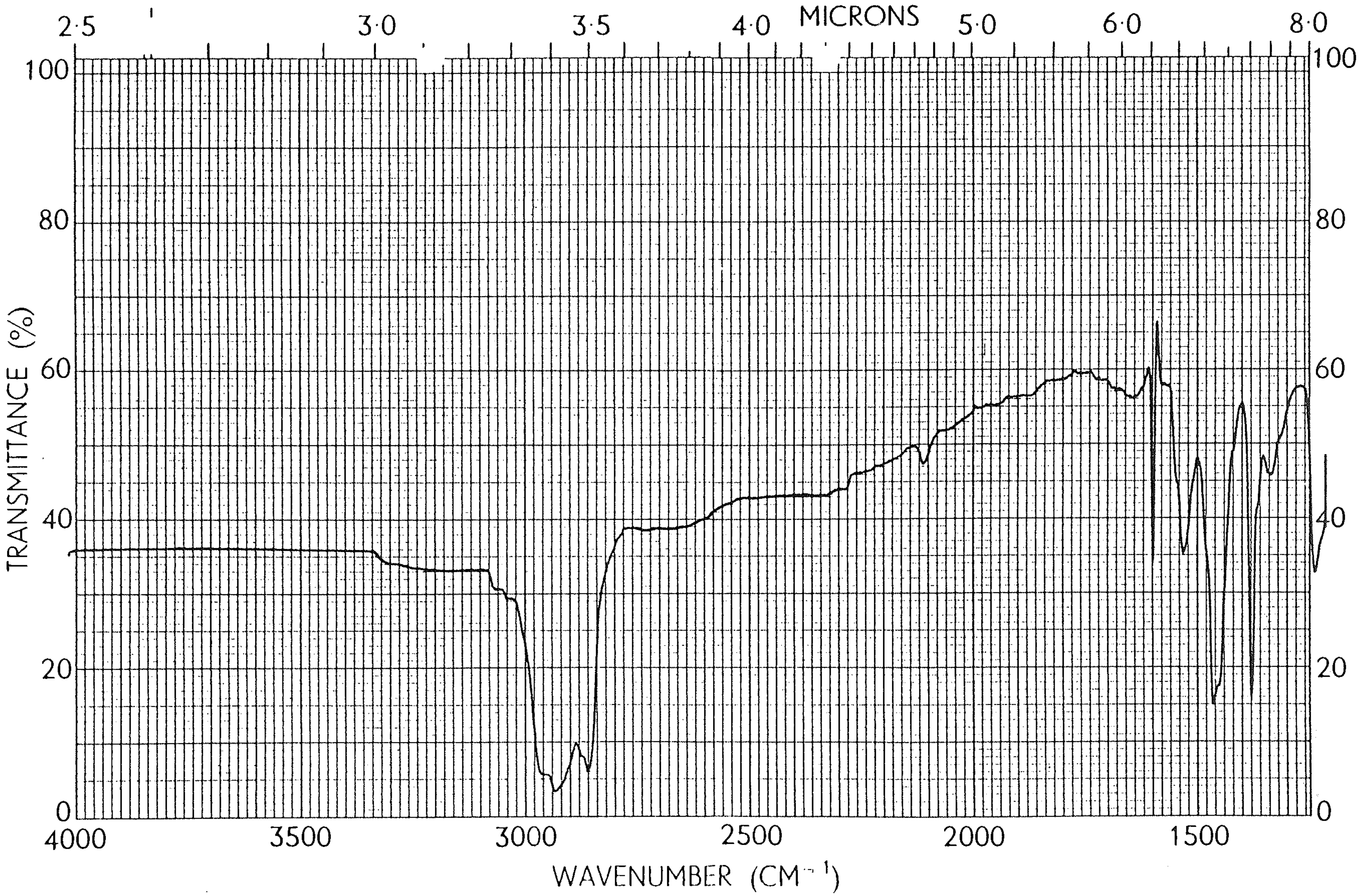
According to procedure (4.3.26b) the solid $\overset{I}{Rh}(DH)_2$ reacts with carbon dioxide at 12-18 atmosphere in 8 weeks and produces a yellow product.

The infra-red spectrum of this yellow complex (spectrum 4.4.9) shows three new strong bands in the region of 1600, 1010, 770 cm^{-1} compared with that of $Rh(DH)_2Br_2$ (spectrum 4.4.10). The elemental analysis of this complex may suggest a structure $[Rh(DH)_2CO_2]$. However Halogen analysis shows that this compound cannot be obtained free from bromine impurity. This yellow complex is air sensitive and those new infra-red bands become weaker when the compound is exposed to air (these bands may disappear completely if the compound is exposed to air for a longer period of time).

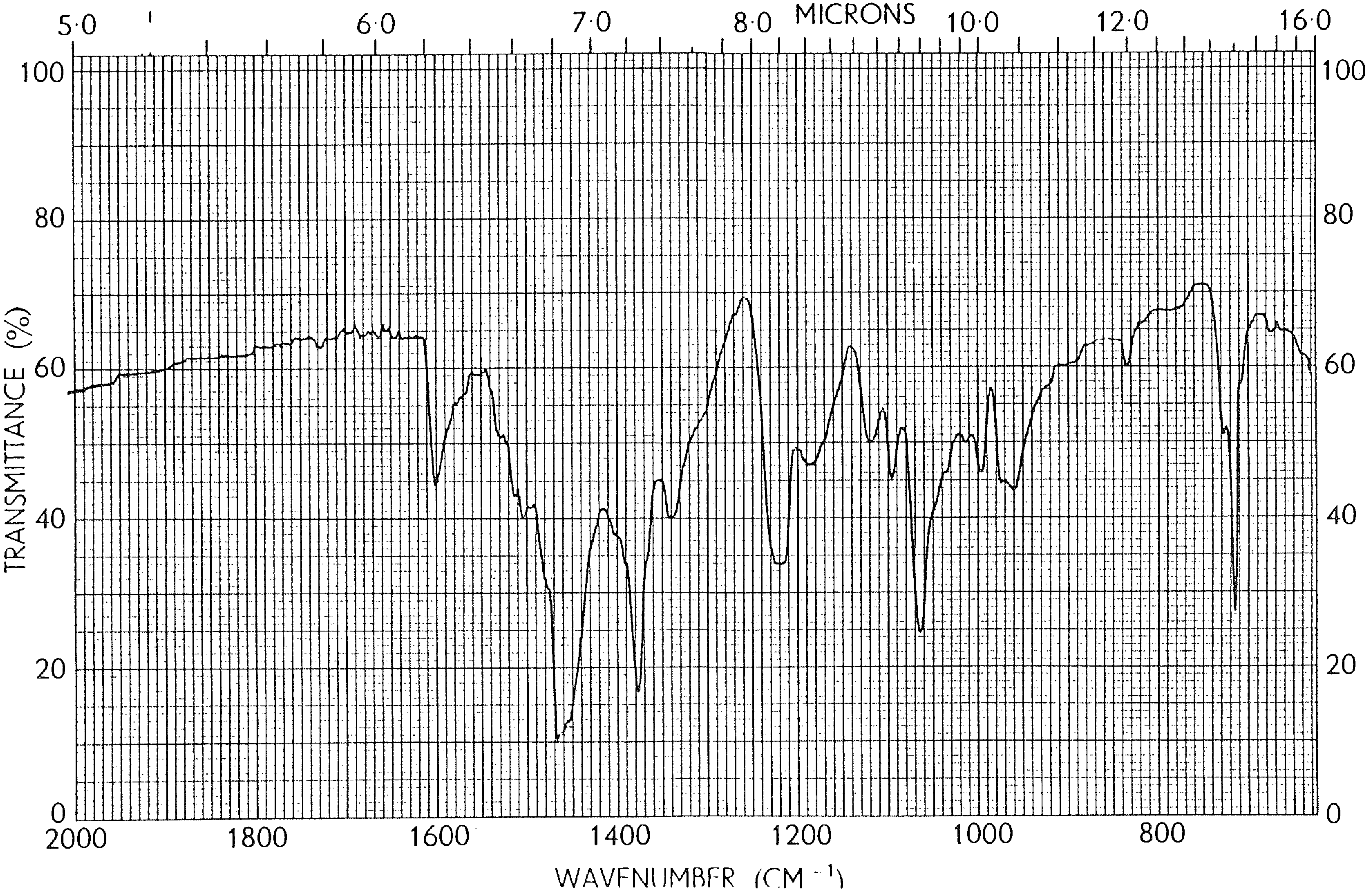
The reaction time was found to be important. When solid $\overset{I}{Rh}(DH)_2$ was kept under an atmosphere of carbon dioxide in the autoclave for a shorter period of time (four weeks) the yellow brown product was obtained, in which the intensities of the new infra-red bands were weaker. This evidence may suggest an incomplete reaction especially that the colour change of the product from blue-brown to yellow was not completed. The significant change in the colour of solid $\overset{I}{Rh}(DH)_2$ after the reaction with carbon dioxide suggests an interaction between the metal centres and carbon dioxide, rather than any reaction between carbon dioxide and the ligand. The sharp infra-red bands in the region of 1600, 1010, 770 (spectrum 4.4.9) and decrease in intensity of these bands when the compound is exposed to air and the colour change from yellow to brown suggests that these infra-red bands are attributable to coordinated carbon dioxide, therefore this yellow complex may be characterized as an adduct $[Rh(DH)_2CO_2]$. The survey of the literature shows carbon dioxide has got a bent structure in almost all adduct complexes. Therefore it is conceivable to suggest a bent structure for CO_2 in adduct $Rh(DH)_2CO_2$.



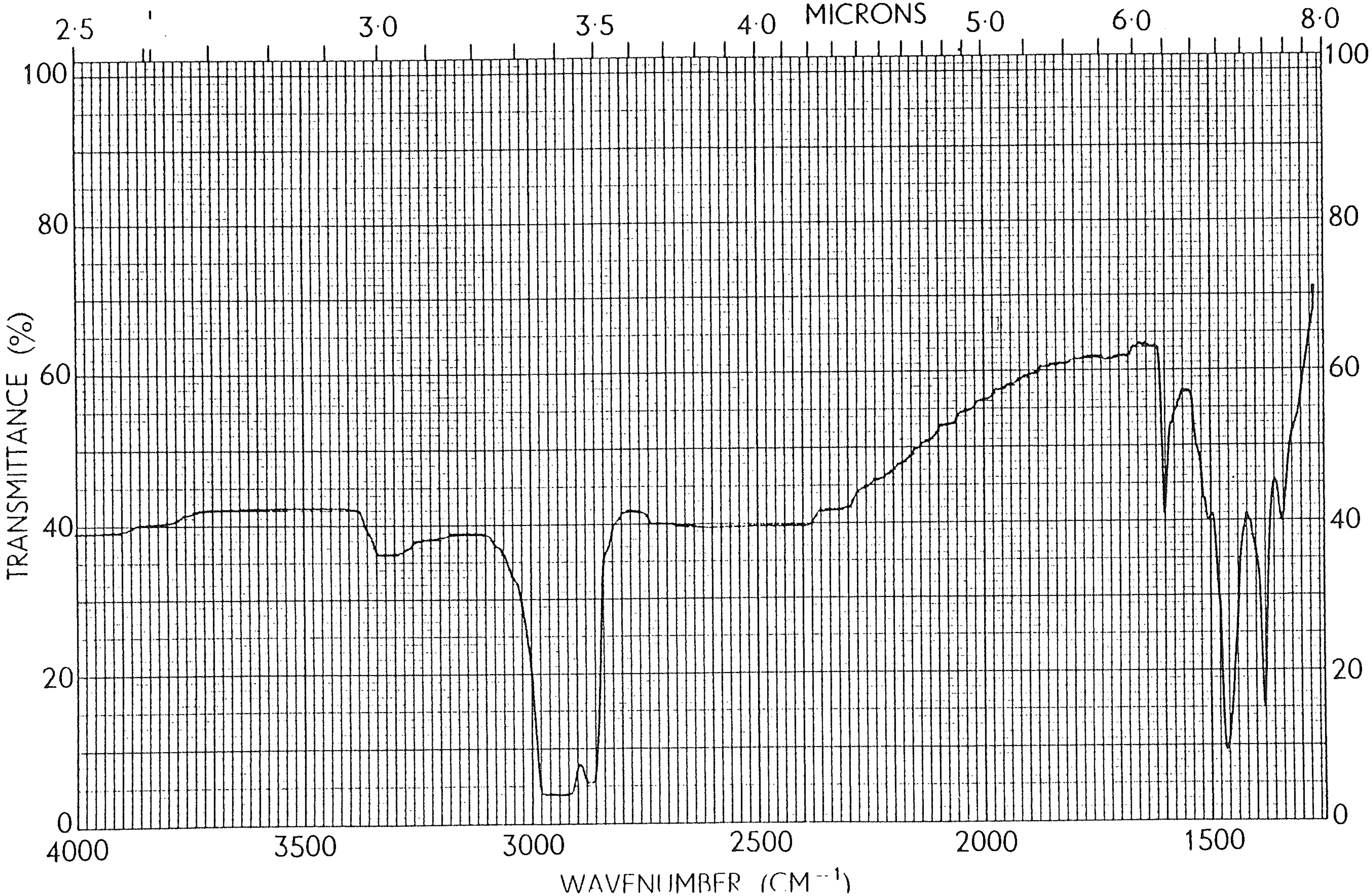
Spectrum (4.4.9) Infra-red spectrum of the compound obtained from the reaction of $Rh^{I}(DH)_2$ with CO_2 in autoclave (Nujol Mull)



Spectrum (4.4.9) Infra-red spectrum of the compound obtained from the reaction of $Rh^{I}(DH)_2$ with CO_2 in autoclave (Nujol Mull)



Spectrum (4.4.10) Infra-red spectrum of $Rh(DH)_2Br_2$ (Nujol Mull)



Spectrum (4.4.10) Infra-red spectrum of $Rh(DH)_2Br_2$ (Nujol Mull)

The interactions of $\overset{(III)}{Rh}(DH)_2Br_2$ and $\overset{(III)}{Rh}(DH)_2Cl_2$ with carbon dioxide have also been investigated, but no reaction either in solution or in the solid form was observed. This is quite predictable since crowding of the ligands around the central atom and the high oxidation state of the rhodium makes conditions unfavourable towards the reaction with carbon dioxide.

4.4.8 THE REACTION OF CO_2 WITH COMPLEXES $Ru(DH)_2(PPh_3)_2$, $RuCl_2(DH)(PPh_3)_2$ AND $Ru(salen)(PPh_3)_2$

Since the appearance of the new infra-red bands in the region of 1260, 1080 and 800 cm^{-1} was found to be similar for complexes obtained by reaction of $Ru(DH)_2(PPh_3)_2$, $RuCl_2(DH)(PPh_3)_2$, and $Ru(salen)(PPh_3)_2$ with CO_2 in toluene solution, and can be compared with the product obtained by reaction of $RuCl_2(PPh_3)_3$ with CO_2 in toluene solution, a similar explanation of the results for these complexes is suggested, namely the formation of carbonato species, further relevant information to each of the complexes is given below.

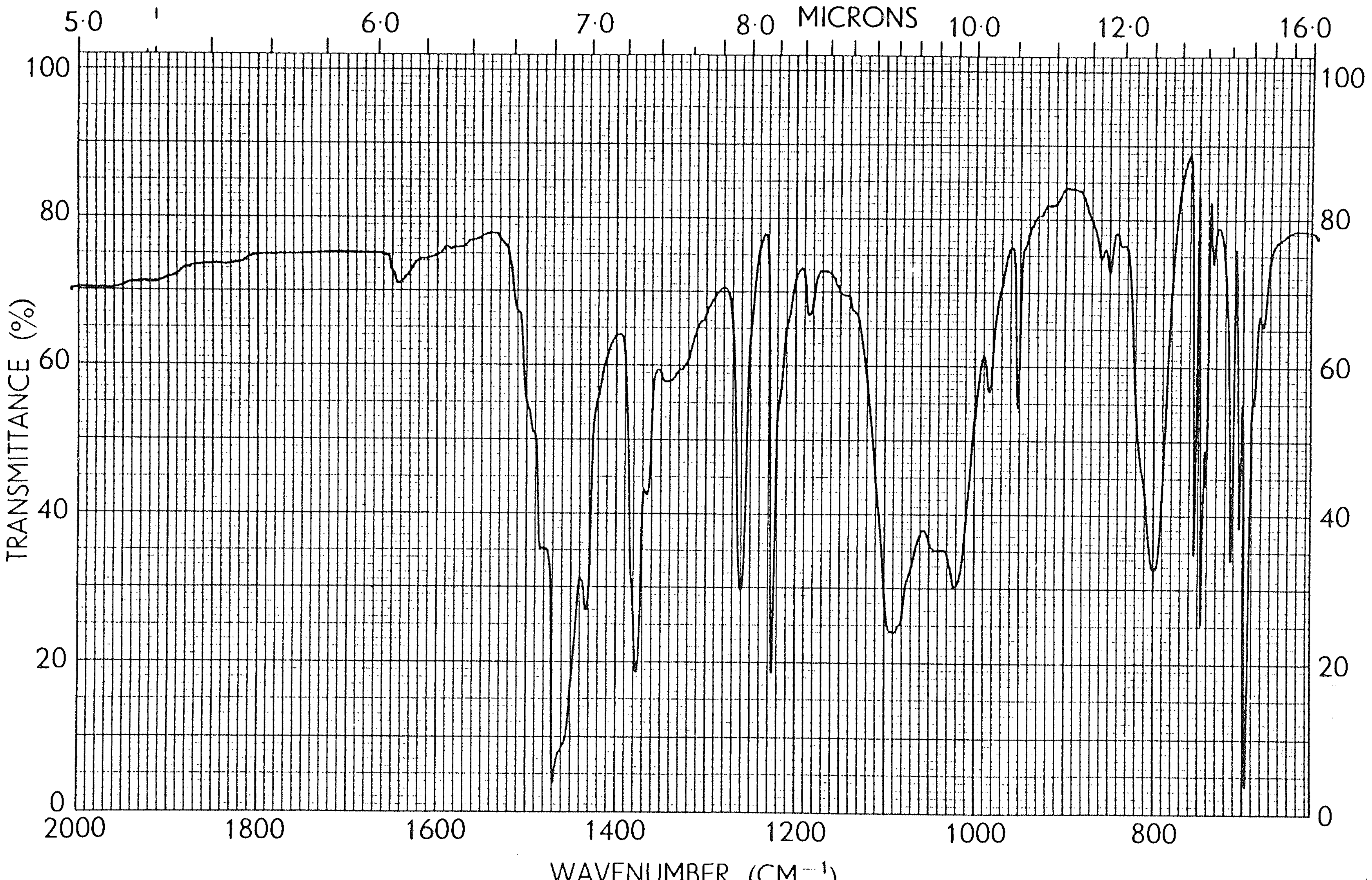
4.4.9 THE REACTION OF CARBON DIOXIDE WITH BIS(DIGLYMOXIMATO)BIS (TRIPHENYLPHOSPHINE)RUTHENIUM(II) AND CHLORO-DIGLYMOXIMATOBIS(TRIPHENYL PHOSPHINE)RUTHENIUM(II)

When carbon dioxide was brought into contact with the mixture of solid and toluene solution of $Ru(DH)_2(PPh_3)_2$ a yellow complex was obtained within 2 days.The infra-red spectrum of this product (spectrum 4.4.11) shows several new bands in the region of 1260, 1080, 800 cm^{-1} compared with that of $Ru(DH)_2(PPh_3)_2$ (spectrum 4.4.12). The product is stable in the solid form but decomposes in tetrahydrofuran solution and those new infra-red bands 1260, 1080, $800cm^{-1}$ become weaker. The molecular weight measurement could not be done due to insolubility of the product in common laboratory solvents. The elemental analysis of the product is close to monomeric carbonato species and suggests the structure $H\left[Ru(DH)_2(PPh_3)CO_3\right]$.

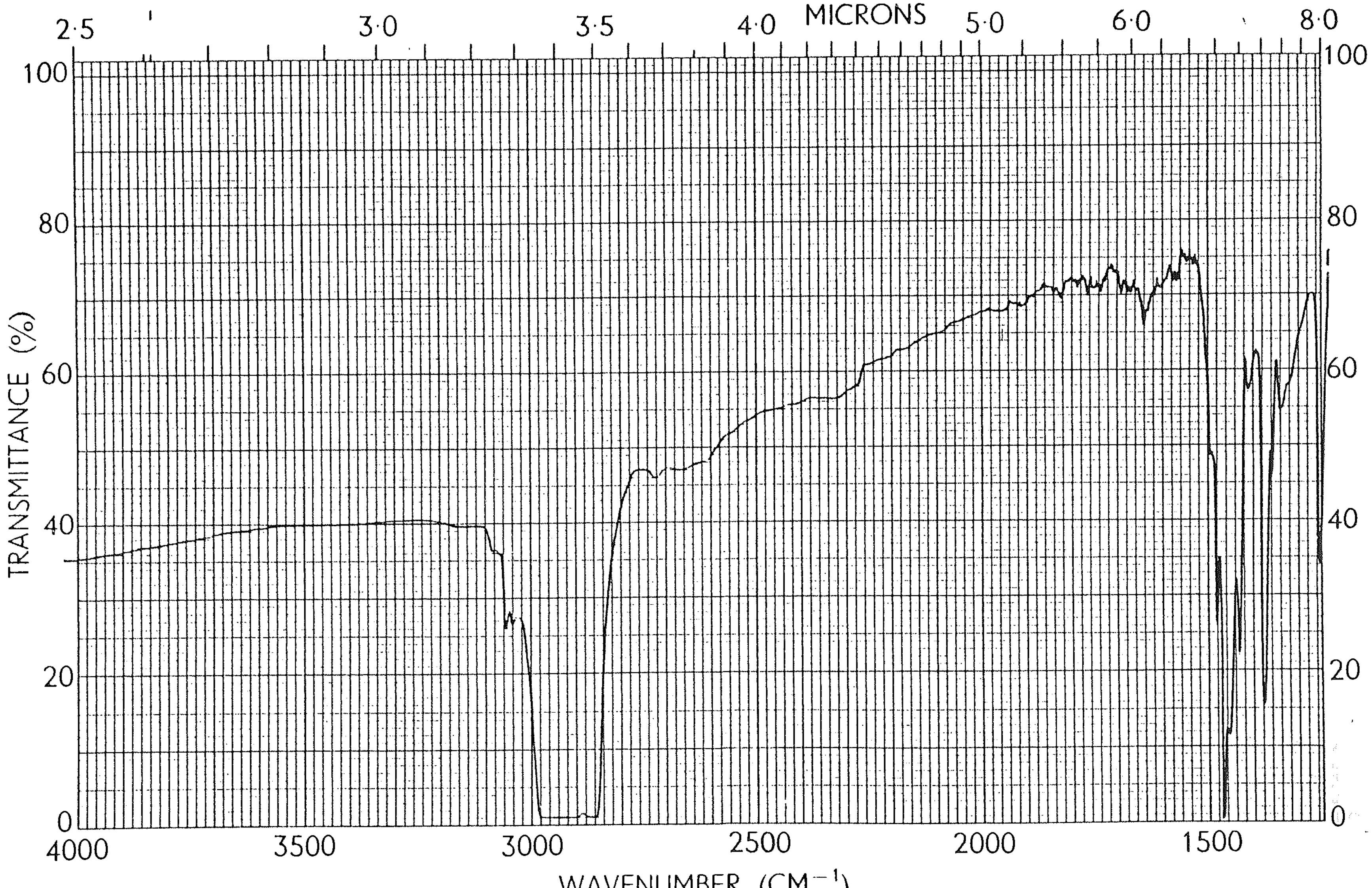
The reaction of carbon dioxide with the complex $RuCl_2(DH)(PPh_3)_2$ gave a mixture of yellow and red products. The infra-red spectrum of the yellow complex shows two new infra-red bands in the region of 1260 and $800cm^{-1}$ (spectrum 4.4.13) compared with that of $RuCl_2(DH)(PPh_3)_2$. (Spectrum 4.4.14). No further information could be obtained about this yellow complex because of the difficulties with purification and the low yield. The reaction of $RuCl_2(DH)(PPh_3)_2$ with carbon dioxide in the presence of oxygen did not give any positive results, also when the toluene solution of $RuCl_2(DH)(PPh_3)_2$ was kept under an atmosphere of oxygen or exposed to air a large quantity of metallicruthenium was obtained and the compound decomposed.

With reference to the infra-red spectrum (4.4.13) and the fact that the appearance of those new infra-red bands is attributed to the presence of carbon dioxide within the molecule, the carbonato structure such as $H\left[RuCl_2(DH)(PPh_3)CO_3\right]$ may be suggested for this yellow complex.

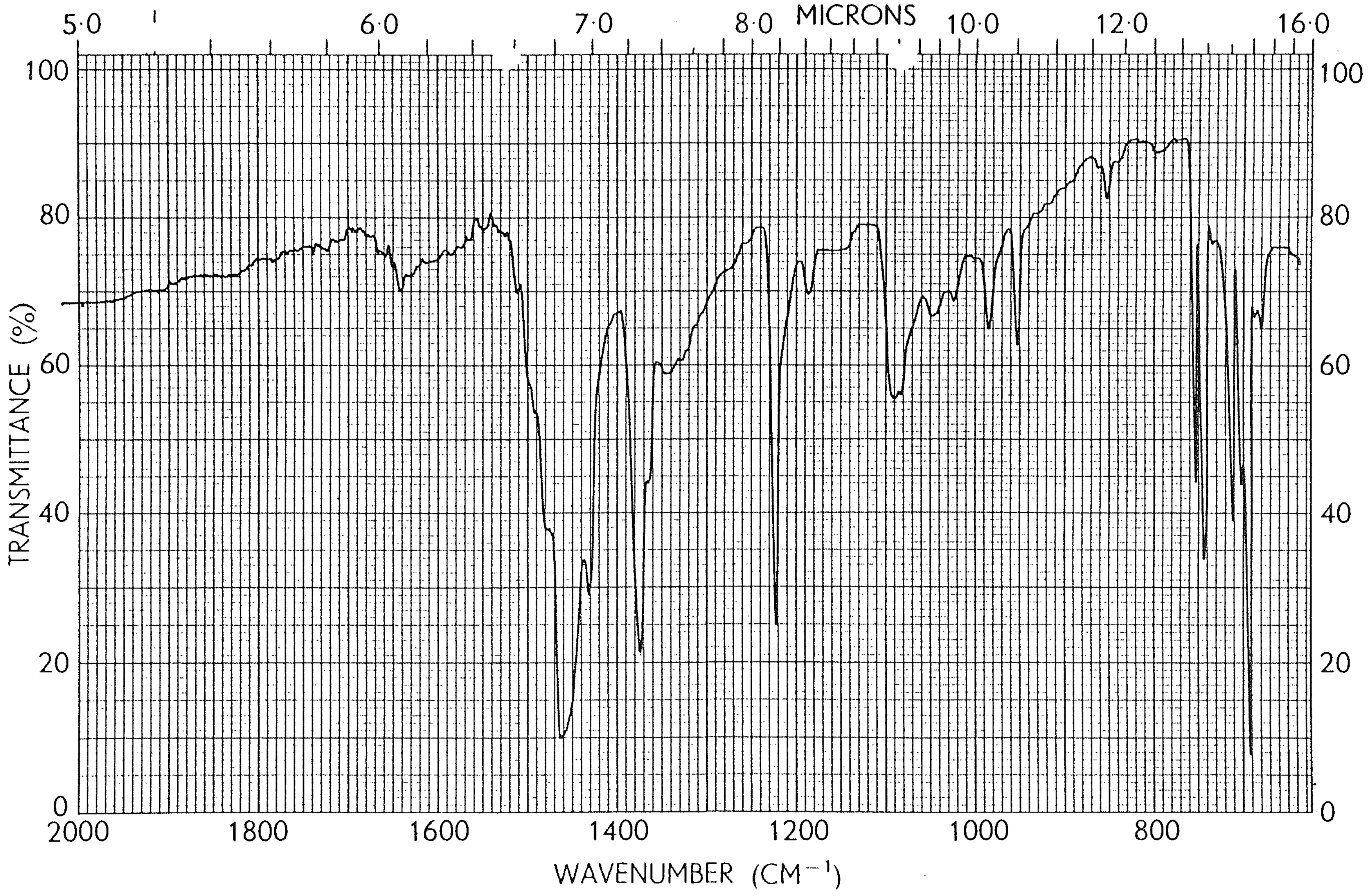
The red product obtained from the reaction of $RuCl_2(DH)(PPh_3)_2$ and CO_2 in toluene was found to be insoluble in common laboratory solvents.



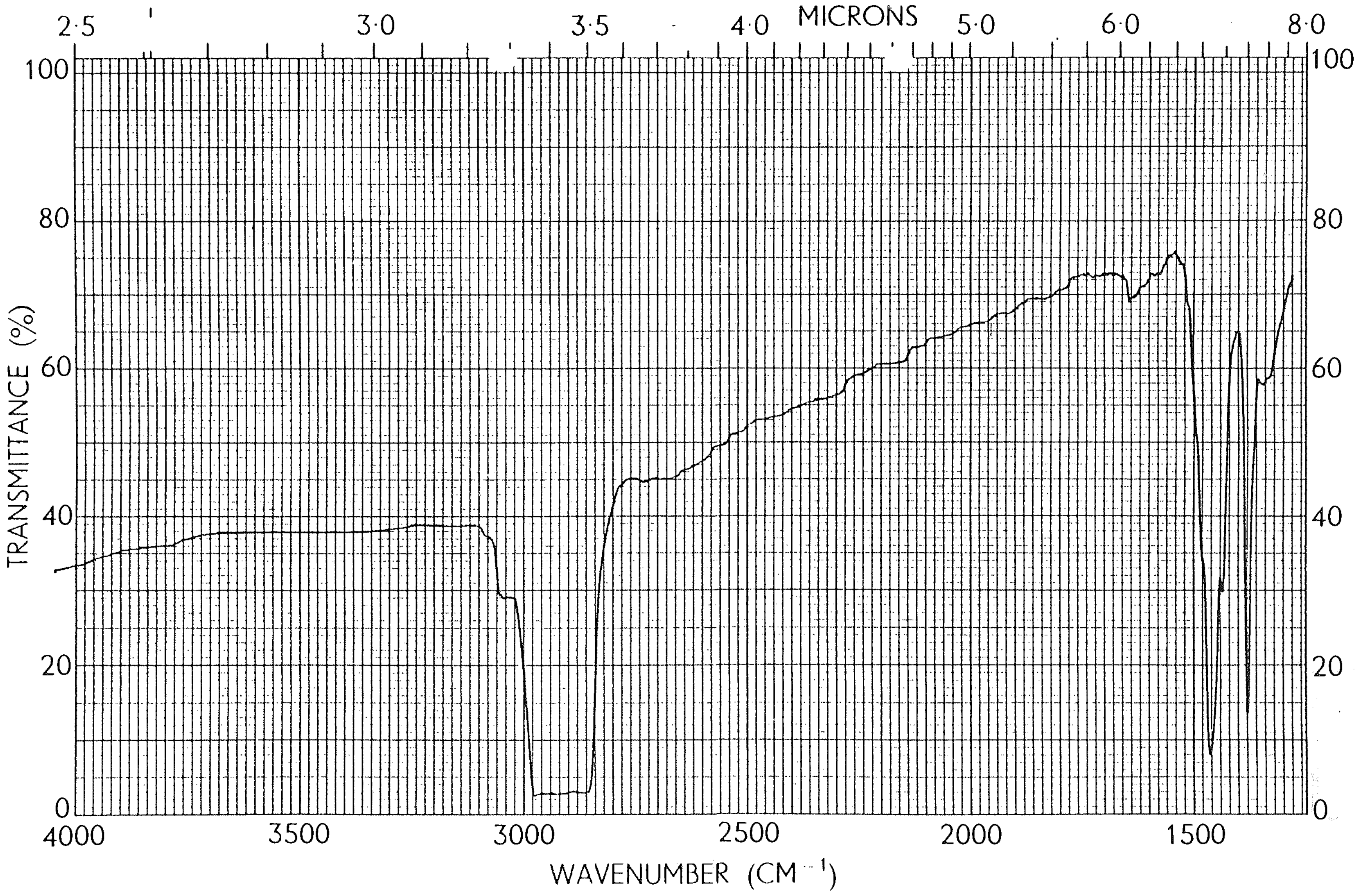
Spectrum (4.4.11) Infra-red spectrum of the compound obtained from the reaction of $Ru(DH)_2(PPh_3)_2$ with CO_2 in toluene solution. (Nujol Mull)



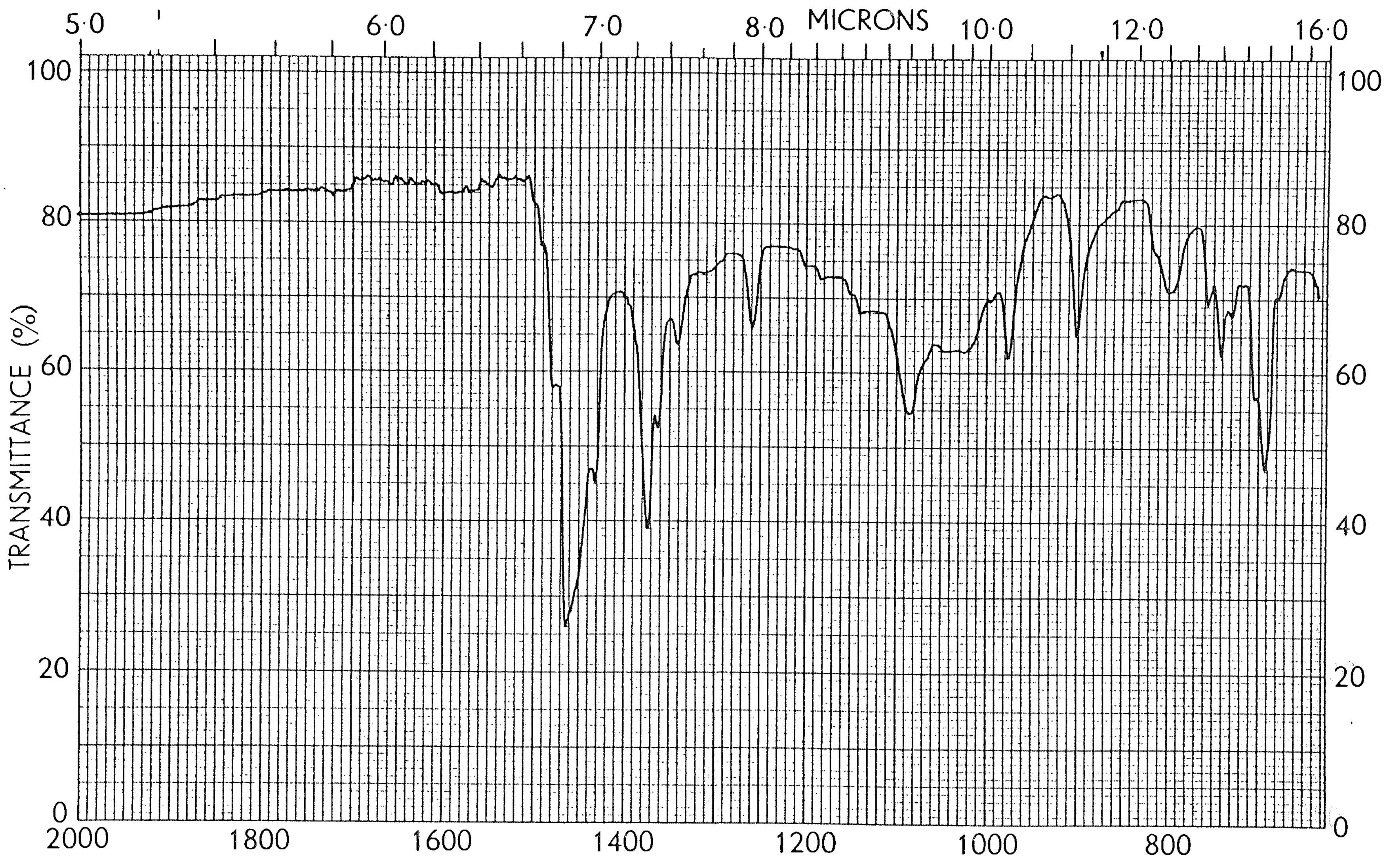
Spectrum (4.4.11) Infra-red spectrum of the compound obtained from the reaction of $Ru(DH)_2\,(PPh_3)_2$ with CO_2 in toluene solution (Nujol Mull)



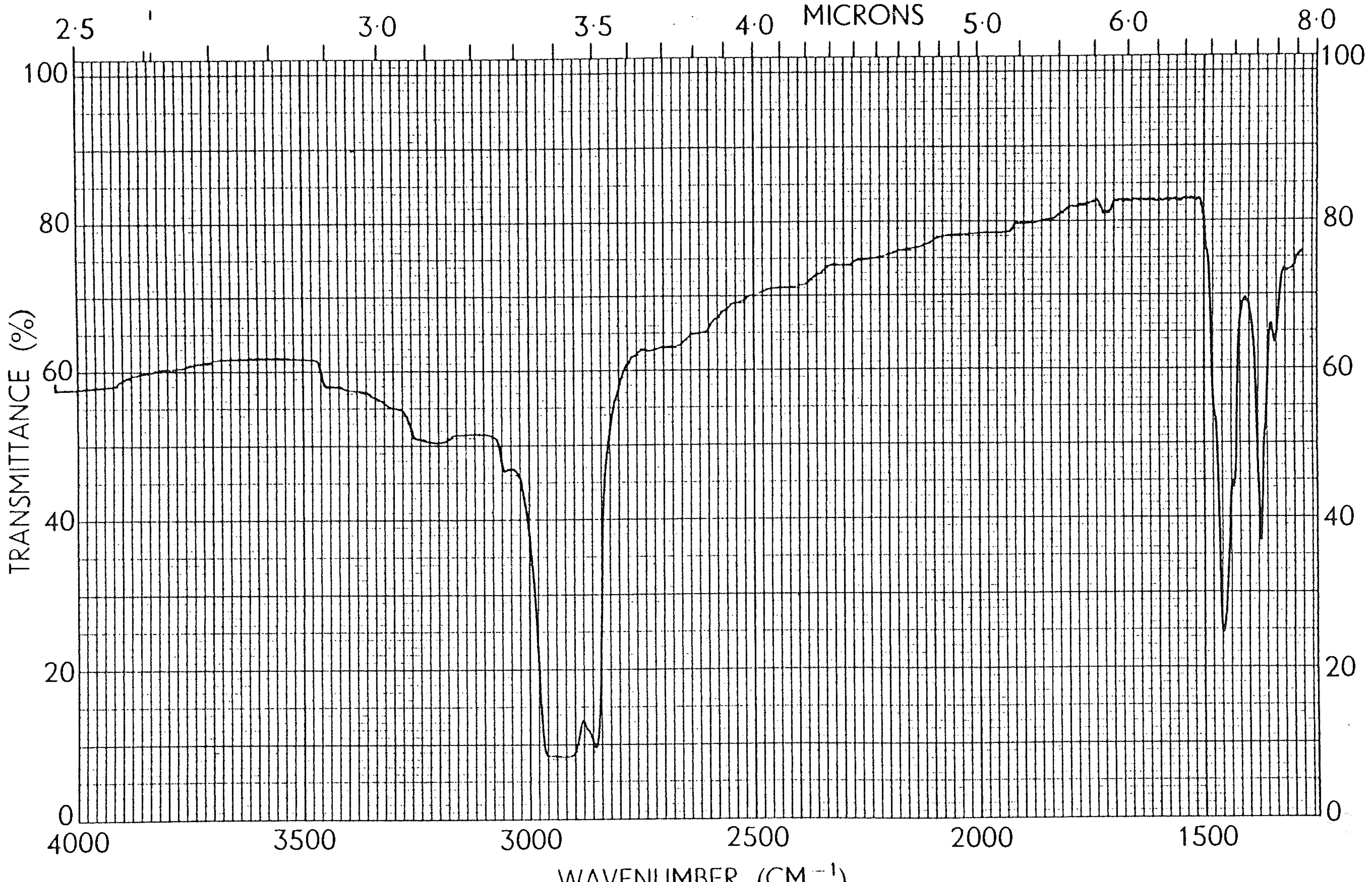
Spectrum (4.4.12) Infra-red spectrum of $Ru(DH)_2(PPh_3)_2$ (Nujol Mull)



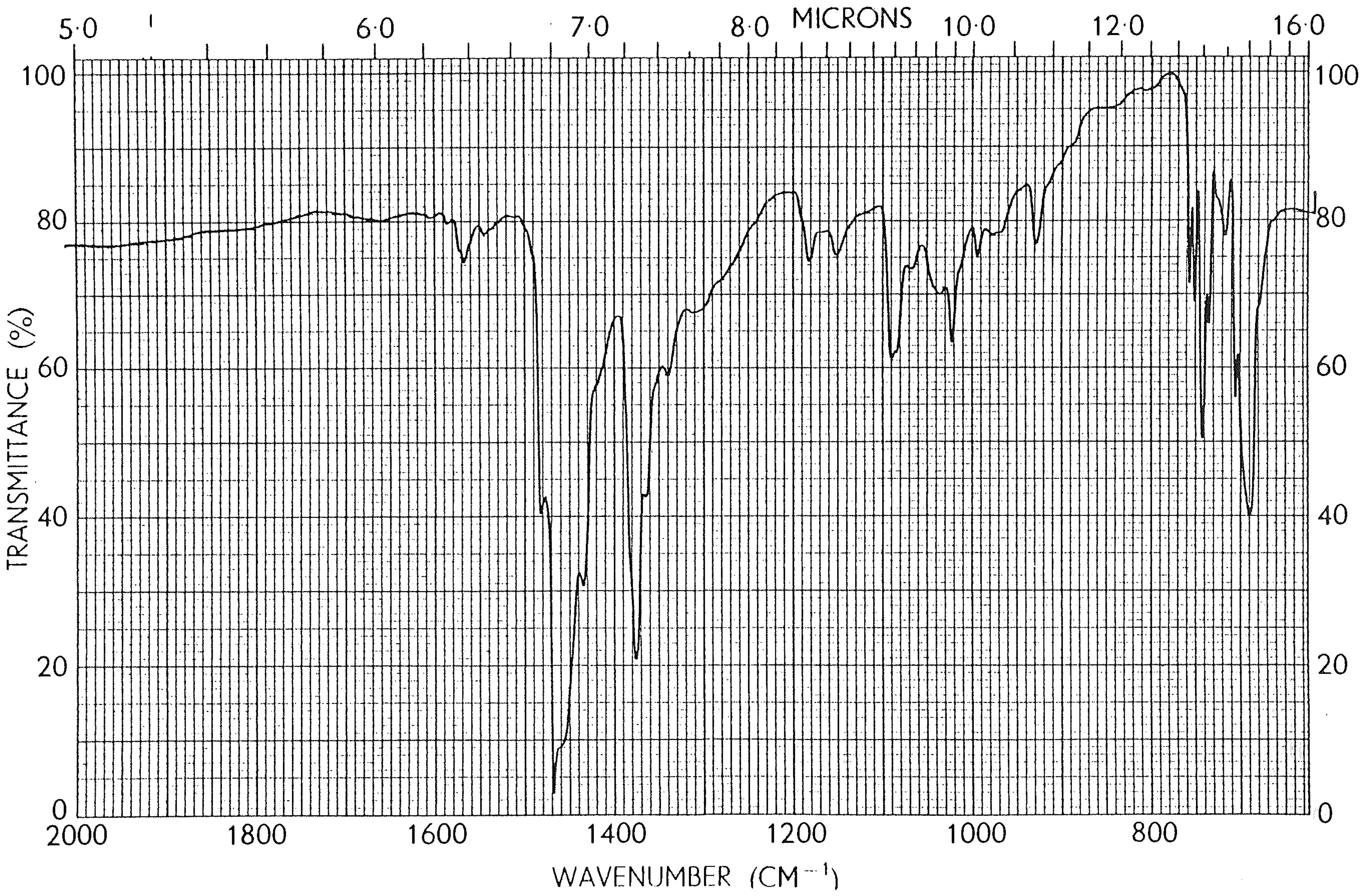
Spectrum (4.4.12) Infra-red spectrum of $Ru(DH)_2(PPh_3)_2$ (Nujol Mull)



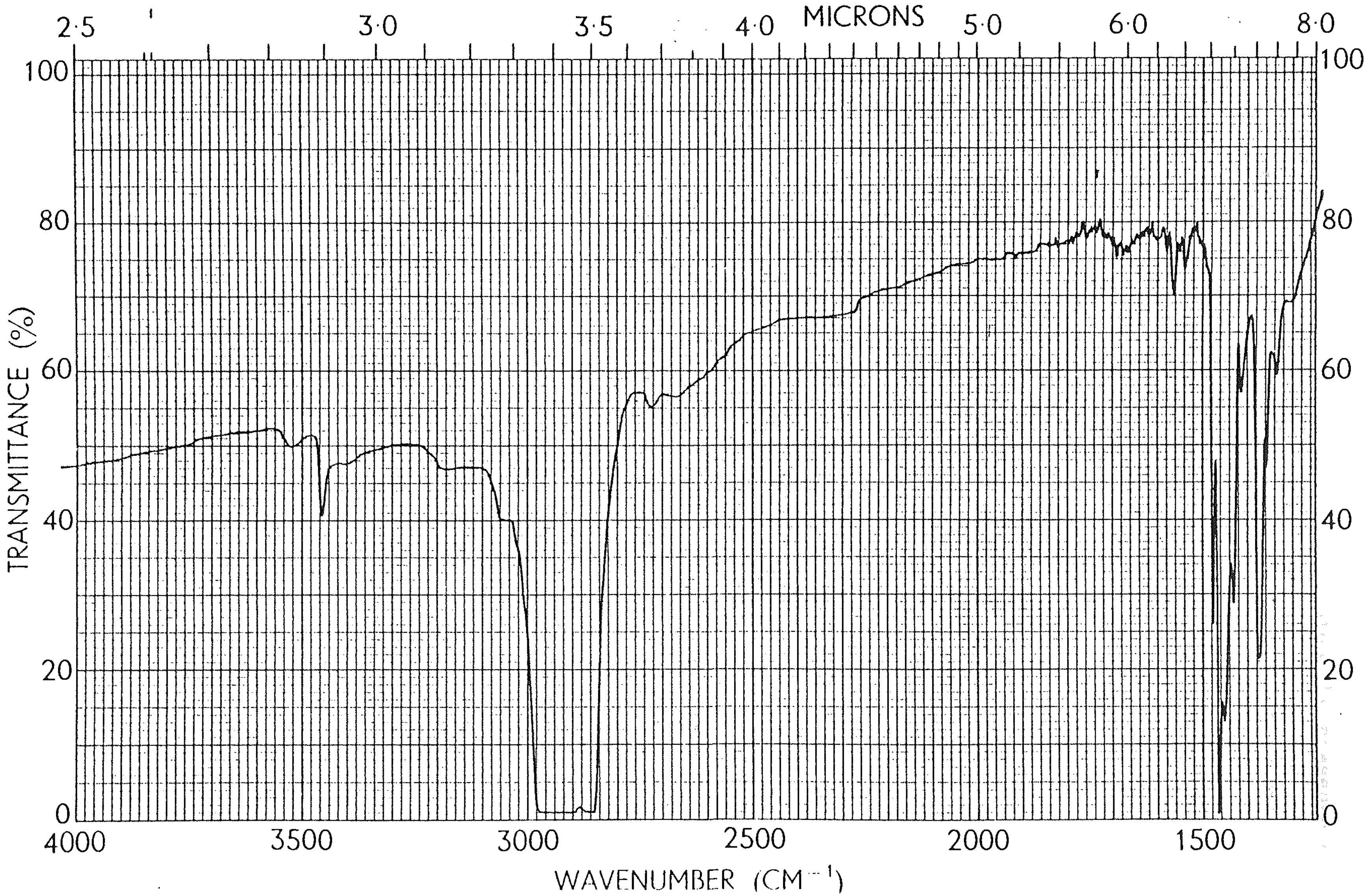
Spectrum (4.4.13) Infra-red spectrum of the yellow complex, obtained from the reaction of $RuCl_2(DH)(PPh_3)_2$ with CO_2 in toluene solution (Nujol Mull)



Spectrum (4.4.13) Infra-red spectrum of the yellow complex, obtained from the reaction of $RuCl_2(DH)(PPh_3)_2$ with CO_2 in toluene solution (Nujol Mull)



Spectrum (4.4.14) Infra-red spectrum of the $RuCl_2(DH)(PPh_3)_2$ (Nujol Mull)



Spectrum (4.4.14) Infra-red spectrum of the $RuCl_2(DH)(PPh_3)_2$ (Nujol Mull)

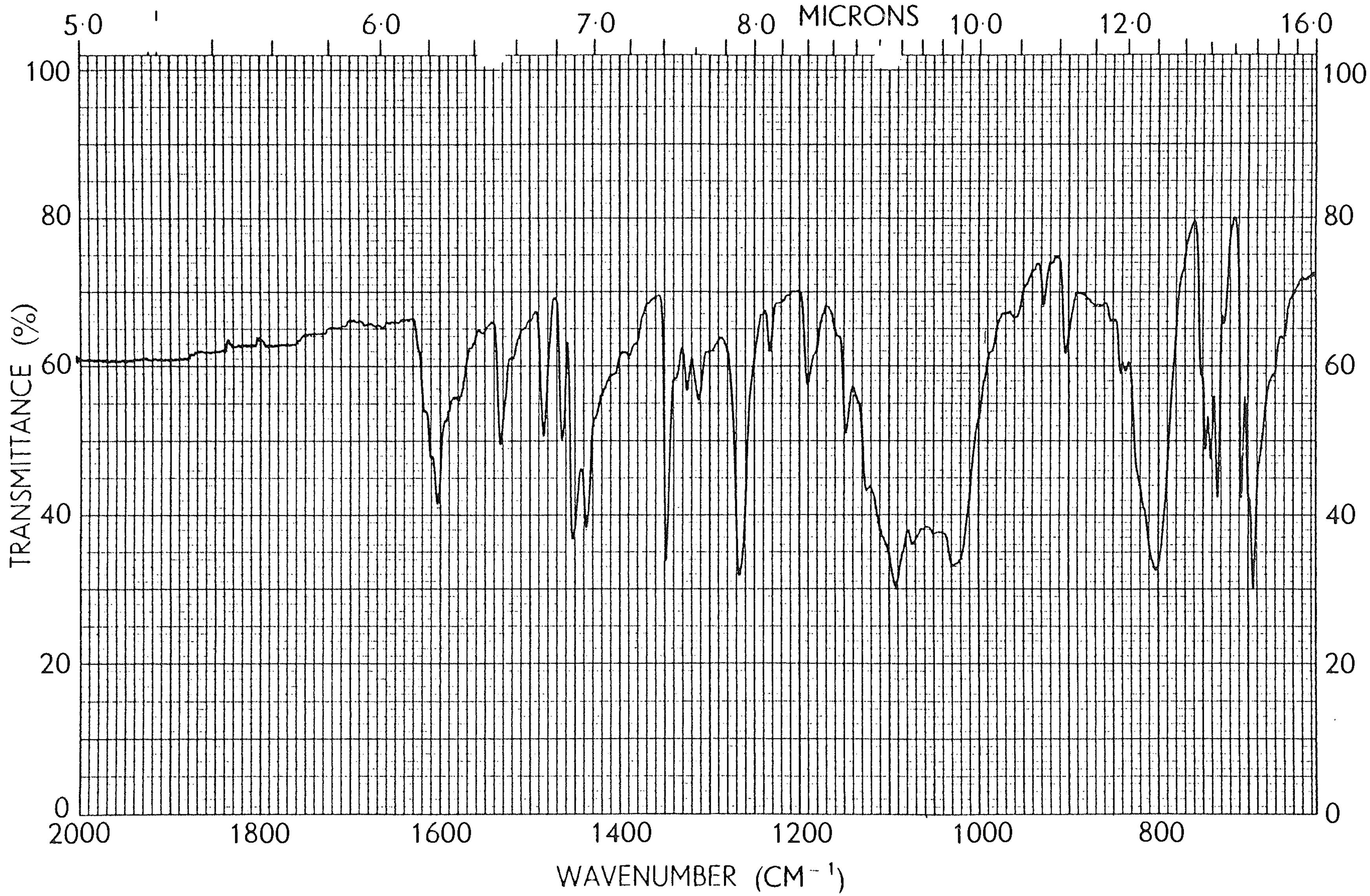
The infra-red spectrum of this product is similar to that of $RuCl_2(DH)(PPh_3)_2$. Since no evidence concerning the presence of carbon dioxide in this molecule was observed, further investigation stopped.

4.4.10 REACTION OF CARBON DIOXIDE WITH N.N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

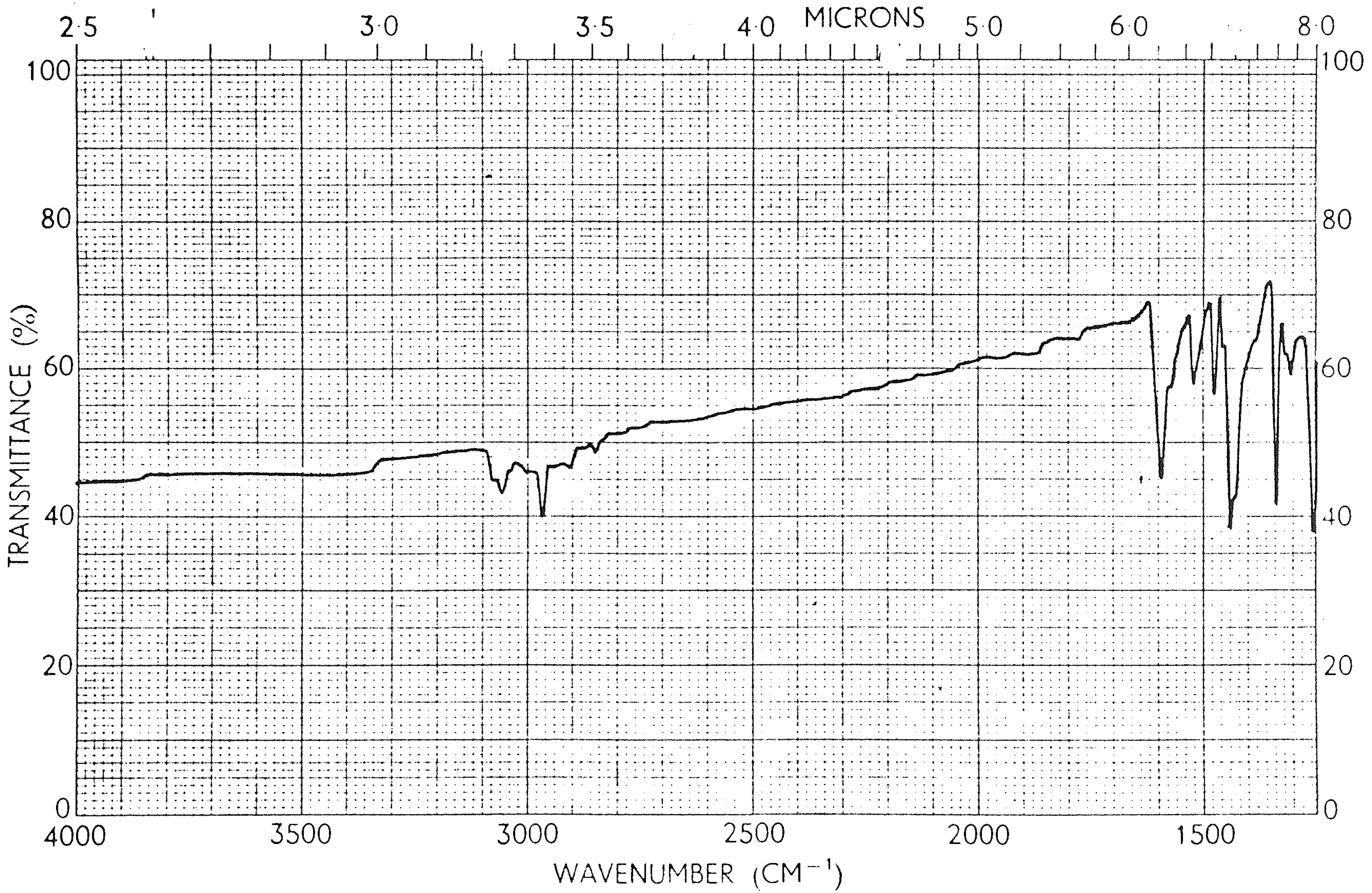
The reaction of carbon dioxide with the complex $Ru(salen)(PPh_3)_2$ in toluene or benzene solution resulted in formation of a dark brown solution from which a brown product was recovered. The infra-red spectrum of the product shows three new infra-red bands in the region of 1260, 1080, 800cm^{-1} (spectrum 4.4.15) compared with that of starting material (spectrum 4.4.16). The elemental analysis of the compound was found to be inconsistent with all formulas considered likely and the molecular weight determination was not helpful due to dissociative nature of the product.

The analysis of the gas above the sample at 190°C using mass spectrometer shows a signal at 44 m/e, however due to the fragmentation pattern of the ligands, the presence of carbon dioxide cannot be confirmed. The following experiment and artical can indirectly be taken in support of the presence of the carbon dioxide in this product:

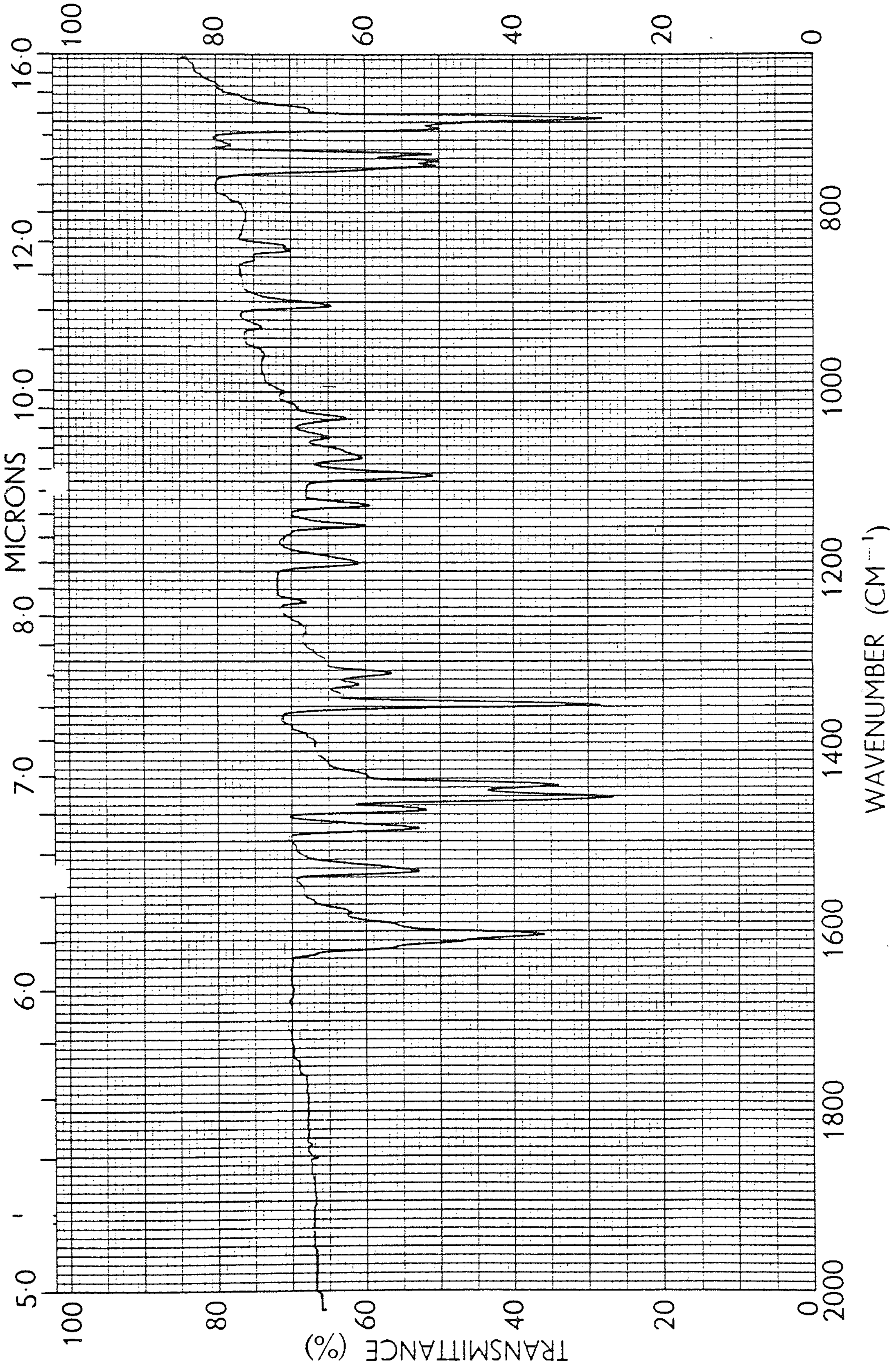
When oxygen was brought into contact with the toluene solution of the $Ru(salen)(PPh_3)_2$ a green solution was obtained within 2 days from which a green product was recovered. The infra-red spectrum of this product



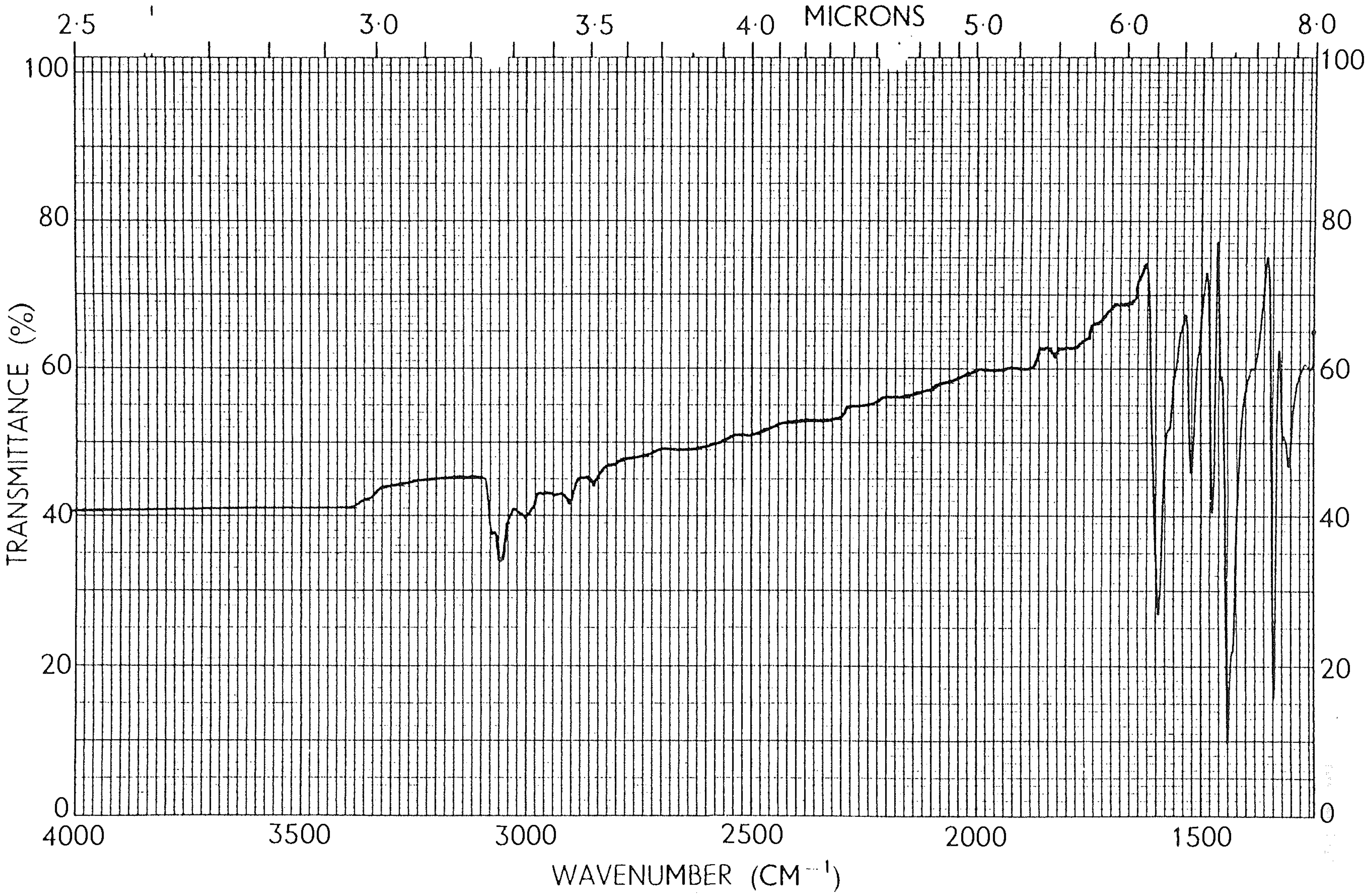
Spectrum (4.4.15) Infra-red spectrum of the brown product obtained from the reaction of Ru(salen)$(PPh_3)_2$ with CO_2 in toluene solution (KBr disc)



Spectrum (4.4.15) Infra-red spectrum of the brown product obtained from the reaction of Ru(salen)$(PPh_3)_2$ with CO_2 in toluene solution (KBr disc)



Spectrum (4.4.16) Infra-red spectrum of the Ru(salen)$(PPh_3)_2$ (KBr disc)



Spectrum (4.4.16) Infra-red spectrum of the Ru(salen)$(PPh_3)_2$ (KBr disc) was found to be similar with that of the starting material. This product also did not react with carbon dioxide in toluene solution any further.

M. Hekmat(127) has studied the reaction of triphenylphosphine oxide and the complex Ru(salen)$(PPh_3)_2$ in ethanol and obtained a green product. The infra-red spectrum of this product was found to be similar to that of Ru(salen)$(PPh_3)_2$ and no obvious change was observed. Refluxing Ru(salen)$(PPh_3)_2$ in ethanol, in the presence of air has also been reported to give a green product with a similar infra-red spectrum to that of Ru(salen)$(PPh_3)_2$.

The above evidence along with the fact that the infra-red spectrum of the brown product obtained from the reaction of Ru(salen)$(PPh_3)_2$ with carbon dioxide in toluene or benzene solution does not show any band due to carbonyl species, may indirectly confirm the presence of the carbon dioxide in this molecule. Considering the solubility properties, the structure (Ru(salen)(PPh_3))$_2CO_3$ or $\left[\text{Ru(salen)(PPh}_3\text{)CO}_3\right]_2$ may be suggested for this product.

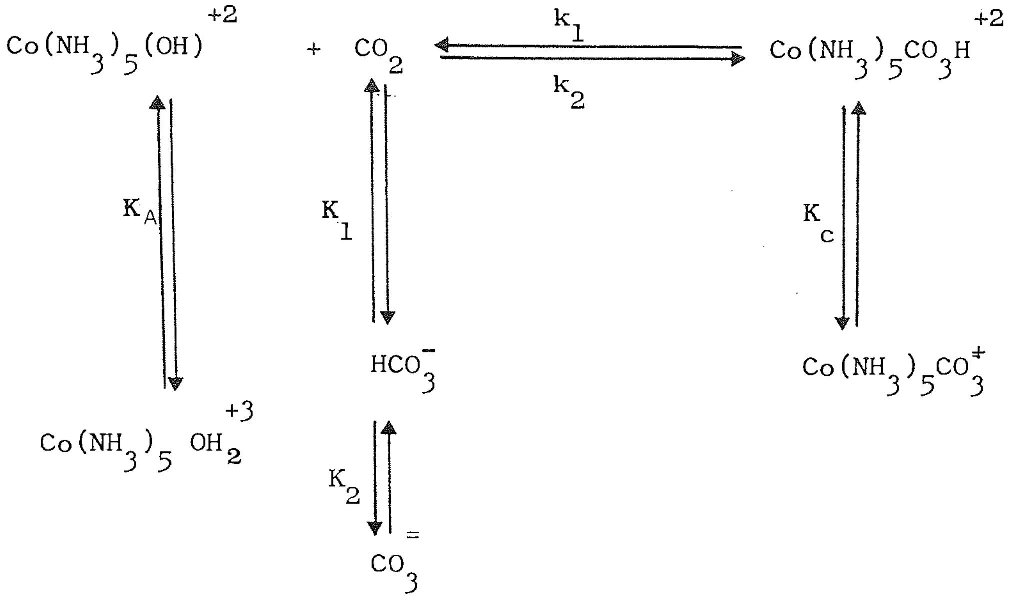
CHAPTER V

5.1.1 INTRODUCTION

The activation of carbon dioxide through coordination to transition metal complexes has received considerable attention in the last few years and the reactions of carbon dioxide with various transition metal complexes have been studied. But there is still only limited information available about the kinetics and in consequence the mechanisms of these reactions.

The kinetics of CO_2 uptake and release have been investigated for some of the cobalt (II) complexes in aqueous solution and the mechanism of these reactions seems to be well understood now. There are also some kinetic data available for the (carbonato)pentaamine complexes of rhodium (III) and iridium (III) and for the ring closed species cis - (carbonato) bis(oxalato)chromate(III) ion. These results generally do agree with the accepted behavioural patterns of cobalt (III) compounds.

The kinetics of the formation of the complex $Co(NH_3)_5CO_3^+$ (132) formed by reaction of carbonate with the ion $Co(NH_3)_5(OH)_2^{+3}$ havebeen studied as a function of acidity in the range $7 < pH < 9$ and of carbonate concentration. These data, combined with the findings of an earlier study of the acid - catalysed elimination of CO_2 from the pentaamine carbonato species, suggests a direct CO_2 uptake process according to the following scheme.



In this k_1 and k_2 are the rate constants for CO_2 elimination and uptake, respectively and the K_s are the acid dissociation constant of the various specious identified.

There are also some kinetic studies in progress involving the CO_2 exchange reactions with early transition metal complexes of $M(O_2CN\ Me_2)_n$

In the case of our study, we have tried to investigate the kinetics of the reaction of carbon dioxide with the complex dichlorotris-(triphenylphosphine)ruthenium (II) in toluene to find a suitable mechanism of carbon dioxide uptake by this complex which is discussed in the subsequent part of this chapter.

5.2. EXPERIMENTAL

5.2.1 PREPARATION OF THE SOLUTIONS:

All the sample solutions were prepared by dissolving a suitable quantity of the compound in toluene under an atmosphere of nitrogen. Toluene used in these experiments was distilled and deoxygenated by refluxing under a nitrogen or carbon dioxide atmosphere.

5.2.2. VISIBLE SPECTRA:

Variation of optical density was measured on a pye-unicam SP6-400 spectrophotometer at a fixed wave-length (475nm). The cell compartment of this spectrophotometer was equipped with jackets so that temperature control could be achieved simply by circulating water at the desired temperature through the cell holder.

5.2.3 MODE OF THE OPERATION:

The solutions were prepared by transferring a suitable quantity of compound into a 3 neck flask (which comprise an gas inlet and outlet with stoppered middle neck) (Fig 5.2.1) under an atmosphere of nitrogen and adding a suitable volume of toluene saturated with carbon dioxide by a syringe through the rubber stopper. The solution was stirred and allowed to reach a constant temperature by using the same water bath as the one used for circulating water through the cell holder of the spectrophotometer. The solutions were transferred consecutively into a 4 cm cell under a nitrogen atmosphere. The changes in optical density were read at suitable intervals of time manually.

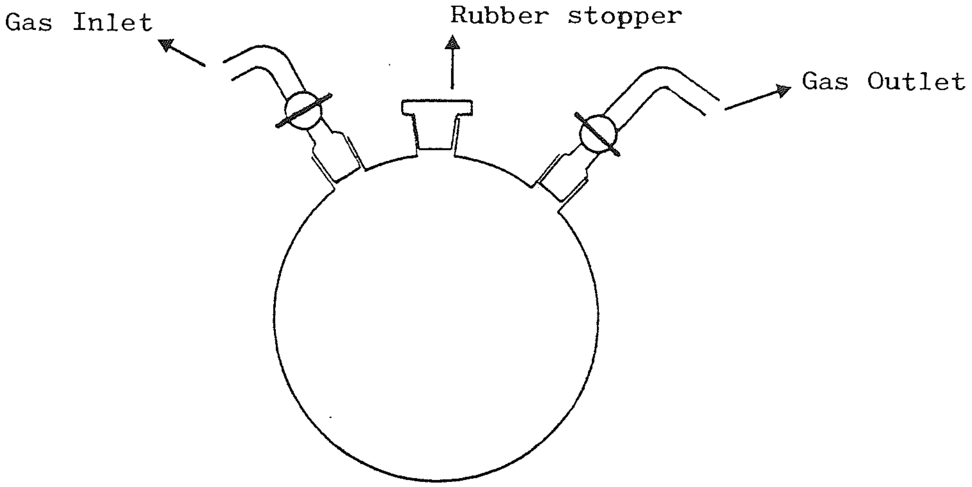


Figure 5.2.1

5.3 EXPERIMENTAL

5.3.1 EXPERIMENT NO 1:

Dichlorotris(triphenylphosphine)ruthenium(II) (30 mg) dissolved in deoxygenated toluene (30 ml) and stirred under an atmosphere of nitrogen at a constant temperature (25°C). Solution A.

Solution B was prepared by refluxing the toluene under an atmosphere of carbon dioxide and allowing to cool in a water bath to the same temperature as that of A. The reaction between the dichlorotris(triphenylphosphine)ruthenium (II) and carbon dioxide was started by mixing a known volume of each of these reagent solutions and monitoring the change in optical density at 475 nm of the reaction solutions.

5.3.2 EXPERIMENT NO 2:

Solutions of triphenylphosphine (1,5,7 and 10 mg) in deoxygenated toluene (30 ml) were prepared under a nitrogen atmosphere. The known volume of solution (A) in Experiment (1) was added to the known volume of these solutions and changes in optical density were measured at λ max = 475 nm.

5.3.3 EXPERIMENT NO 3:

Effect of temperature:

An equal volume of solutions A and B were mixed and changes in optical density as a function of time at 20,25,30,35 and 40°C were measured.

5.4.1 THE SOLUBILITY OF CARBON DIOXIDE IN TOLUENE:

The solubility of carbon dioxide in toluene was determined using the apparatus shown in figure 5.4.1. It consists of a gas burette A and levelling tube B, containing mercury. Solution of the carbon dioxide in toluene takes place in the absorption vessel C. A and C are connected via three-way taps D and E by means of thick walled rubber tubing.

PROCEDURE:

Determine the volume of the absorption vessel C between two taps E and F by filling with water and then running this out into a flask and weighing, prepare a quantity of air free toluene by boiling out. This can be conveniently done by using a flask N. (Fig 5.4.2) Fill the flask with toluene and boil for about 15 minutes and close the tap G under vacuo and allow the toluene to cool.

Invert the flask and connect via tap G with the lower tube of the absorption vessel (tap F). Evacuate the absorption vessel by connecting the tap E to the water pump, then open tap G and immediately after wards open tap F. Air free toluene will then be drawn up into the absorption vessel C without coming into contact with air. When C has been filled with toluene place it in a 25°C thermostatted bath. Raise the mercury in the gas burette A until it completely fills the burette to the tap D. Pass a stream of carbon dioxide through tap D and along the rubber tube, allowing the gas to escape to the atmosphere at tap E.

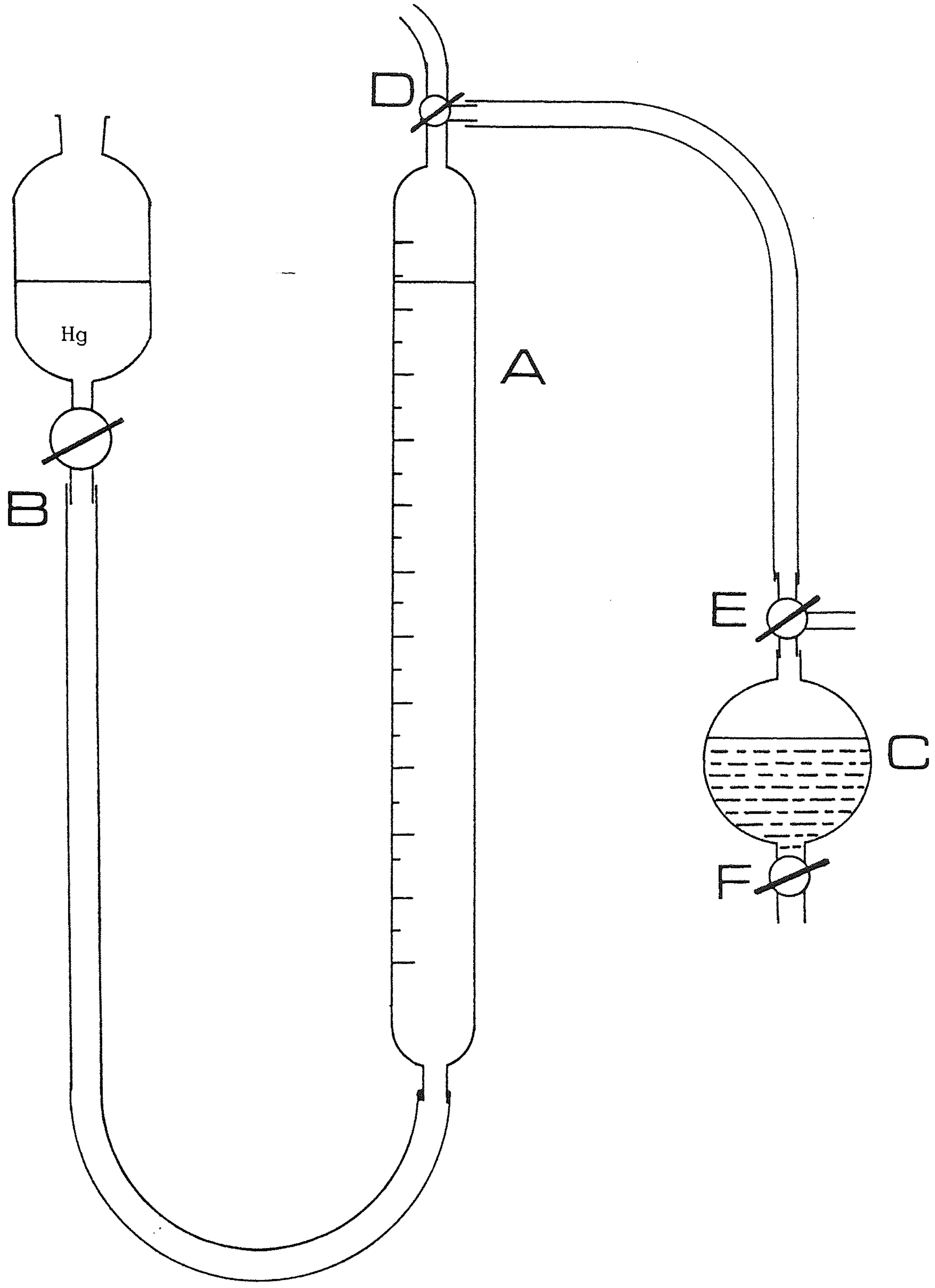


Figure 5.4.1.

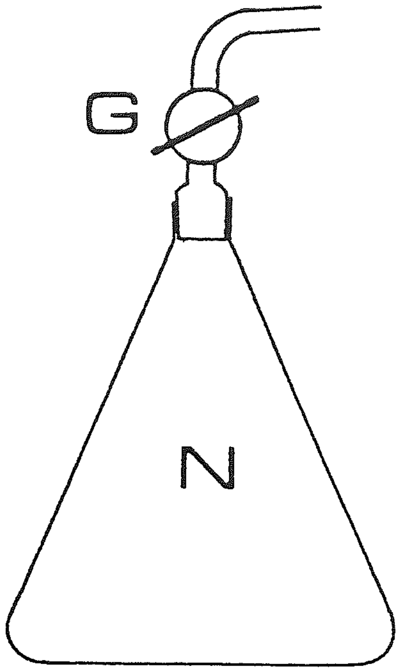


Figure 5.4.2.

When the tube is filled with gas, turn tap D and E and almost fill the gas burette A. Equalize the levels of mercury in A and B and then read off the volume of gas. Now raise B a little so that a slight excess of pressure is established in A. Turn tap D so that connection is made to the rubber tube. Open tap F and then tap E and allow few ml of toluene to run out of the absorption vessel into a weighed flask. The weight of water is determined. From this, the volume of toluene remaining in the absorption vessel and the free space can be calculated, the total volume of the vessel being known.

Replace the absorption vessel in the thermostatted bath and shake carefully from time to time. As carbon dioxide dissolves in the toluene adjust the levelling tube B so that pressure is maintained at one atmosphere. When absorption is complete read off the burette volume. Read the barometer to obtain the atmospheric pressure.

CALCULATIONS:

If the solubility S of the carbon dioxide is defined as the volume of carbon dioxide dissolved in unit volume of toluene then it can readily be shown, assuming no change in atmospheric pressure that:

$$S = \frac{1}{V_t}\left[\frac{v_1 T_2 P}{T_1 (P-P_2)} - v_2 \frac{(P-P_1)}{(P-P_2)} \cdot \frac{T_2}{T_1} + V_2\left\{\frac{P_1}{P_1-P_2} \cdot \frac{T_2}{T_1}\right\} - V_1\right] \quad (1)$$

Where v_1 and v_2 are the initial and final volume of the gas in the burette, P is the barometric pressure, P_1 is the partial vapour pressure of toluene at the temperature of the gas burette (i.e. room temperature) and P_2 is the partial vapour pressure of toluene at the temperature of the thermostatted bath (P_1 and P_2 may be obtained from tables), T_1 is the absolute temperature of the gas burette and T_2 the absolute temperature of the bath, V_1 is the free volume in the flask C and V_2 is the volume of tubing between burette and flask C and V_t is the volume of toluene in the flask C.

The term $\frac{P_1}{P_1-P_2} \cdot \frac{T_2}{T_1}$ in equation (1) will disappear if V_2 is very small or if V_2 is added to the reading taken and used as v_1 and v_2. Solubility of CO_2 obtained from this method at 25°C is equal to 2.031 $\frac{\text{ml}CO_2}{\text{volume}}$

5.5.1 RESULTS AND DISCUSSION:

The visible spectra of the compound dichlorotris(triphenylphosphine)-ruthenium (II) in toluene saturated with nitrogen, oxygen, or carbon dioxide have been studied and three different peaks with maximum wave lengths (λmax), 710 nm, 650 nm, and 475 nm, respectively, have been observed. The results of these experiments provide a method of studying the kinetics of the reaction of dichlorotris(triphenylphosphine)—ruthenium (II) with carbon dioxide in toluene and, in consequence, of determining the mechanism of the reaction.

During the kinetic investigation of this reaction two major problems have been considered. Firstly: not knowing the nature of the species being produced at different stages and not having sufficient and accurate information about the final product of the reaction of carbon dioxide with dichlorotris(triphenylphosphine)ruthenium (II). Secondly: finding a suitable technique for kinetic studies. To overcome this problem we have tried using a peristaltic pump for circulation and keeping the whole system under an atmosphere of CO_2. (This technique could have the advantage of proper mixing of the solutions during the course of the reaction). The system was not suitable because of the permeation of oxygen through the rubber tubing and also the loss of a significant amount of toluene by evaporation causing a change in concentration of the reactants. Finally we have tried a technique which is described in the experimental part of this chapter. Although we tried to minimize the amount of oxygen in this system we could not keep all traces out and experiments sometimes suffer from leakage towards the end of a reaction.

Our suitable range of temperature was found to be between 20-40^{o}C, beyond this limit data are ambiguous and can not be interpreted.

Using this technique the solution is withdrawn by syringe under an atmosphere of nitrogen or carbon dioxide through a rubber septum and mixed in the spectrophotometer cell (the temperature of solutions and cell were allowed to reach a constant value). Using a flow of nitrogen above the cell and having the whole system under a nitrogen atmosphere afterwards.

Most experiments were repeated several times and found to be reproducible within experimental error over most of the range of reaction. To find the most suitable concentrations of the reactants and the largest convenient range of optical density change several conditions have been tried. Most conditions tried above result in ambiguous changes of optical density. The optimum conditions and concentrations of reactants were found with difficulty and are given in table 5.5.3.along with experimental procedure.

An optical density versus time curve shows an induction period at the beginning of the reaction (fig 5.5.1)and sometimes a larger than expected change in optical density occurs near the end of the curve. The existance of an induction period is related either to the nature of the reaction or has arisen from some physical phenomenon, such as improper mixing of the solutions.

The increase of the optical density towards the end of the curve is probably due to absorption of oxygen from the air by the sample in

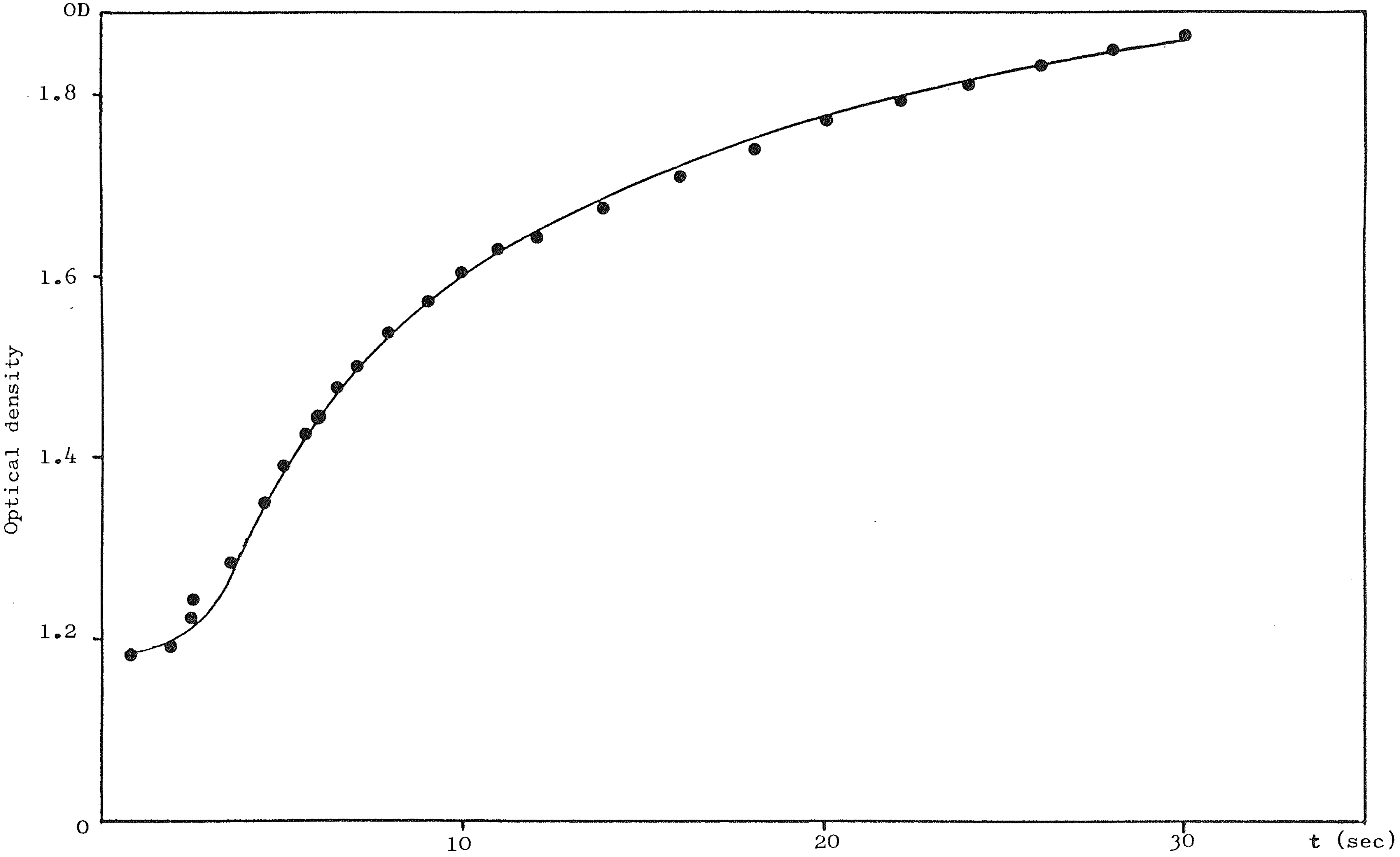


Figure (5.5.1) A typical variation of optical density with time for the $RuCl_2(PPh_3)_3$ in toluene saturated with CO_2.

spite of the fact that reactions were carried out under an atmosphere of nitrogen.

To interpret the data and fit into a plausible rate equation three general forms of reaction sequence have been considered, and calculations of rate constants (k) for each form are presented in table 5.5.1, 5.5.2 and 5.5.3 respectively. These three general forms may be classified as shown below.

1. $$A \xrightarrow{k_1} P$$

2. $$A \underset{k_3}{\overset{k_2}{\rightleftharpoons}} B + L$$

$$B \xrightarrow{k_4} P$$

3. $$A \xrightarrow{k_5} B \xrightarrow{k_6} C$$

As can be seen from tables 5.5.1, 5.5.2, 5.5.3, adding excess triphenylphosphine changes the rate of the reaction. Using data from table 5.5.1 and table 5.5.2 and plotting the concentration of carbon dioxide or triphenylphosphine versus k did not produce a consistent smooth curve to be fitted with the schemes $\underline{1}$ and $\underline{2}$. When the data from table 5.5.3 were used to plot carbon dioxide concentration versus rate constant k_1 and the concentration of triphenylphosphine versus reciprocal of rate constant $\frac{1}{k_1}$, both gave straight lines. (Graph 5.5.1 and 5.5.2)

By referring to the evidence, given above, the reaction of dichlorotris(triphenylphosphine)ruthenium (II) with carbon dioxide in toluene may be interpreted as two consecutive pseudo first order reactions, with a slower stage with rate constant (k_5) and a fast one with rate constant k_6. Both rate constants were calculated by using the general form given below. (See also appendix 1)

$$y = a \left(1 + \frac{k_c}{k_d - k_c} e^{-k_d t} - \frac{k_d}{k_d - k_c} e^{-k_c t}\right) \qquad \text{eq. (1)}$$

The following tables are relevant to schemes 1, 2 and 3 respectively. The data from table 5.5.3 are used to interpret the result.

mole lit^{-1} $[RuCl_2(PPh_3)_3]$	k/min^{-1}
2.6×10^{-4}	0.291
3.64×10^{-4}	0.145
3.9×10^{-4}	0.109
4.16×10^{-4}	0.112
4.69×10^{-4}	0.0596
4.95×10^{-4}	0.0613

mole lit^{-1} $[CO_2]$	k/min^{-1}
4.7×10^{-3}	0.0613
9.4×10^{-3}	0.0596
18.8×10^{-3}	0.112
28.2×10^{-3}	0.145
47×10^{-3}	0.291

T°K	k/min^{-1}
293	0.115
298	0.291
303	0.345
308	0.125
313	0.132

mole lit^{-1} $[PPh_3]$	k/min^{-1}
6.3×10^{-5}	0.0966
1.27×10^{-4}	0.126
3.16×10^{-4}	0.0809
4.4×10^{-4}	0.048

Table 5.5.1

mole lit^{-1} $[RuCl_2(PPh_3)_3]$	k/min^{-1}
2.6×10^{-4}	0.066
3.64×10^{-4}	0.146
3.9×10^{-4}	0.111
4.16×10^{-4}	0.110
4.69×10^{-4}	0.0693
4.95×10^{-4}	0.0734

mole lit^{-1} $[CO_2]$	k/min^{-1}
4.7×10^{-3}	0.0734
9.4×10^{-3}	0.0693
18.8×10^{-3}	0.110
28.2×10^{-3}	0.146
47×10^{-3}	0.066

T°K	k/min^{-1}
293	0.0892
298	0.066
303	0.110
308	0.125
313	0.132

mole lit^{-1} $[PPh_3]$	k/min^{-1}
6.3×10^{-5}	0.105
3.16×10^{-4}	0.0955
6.3×10^{-4}	0.0356
4.4×10^{-4}	0.048

Table 5.5.2

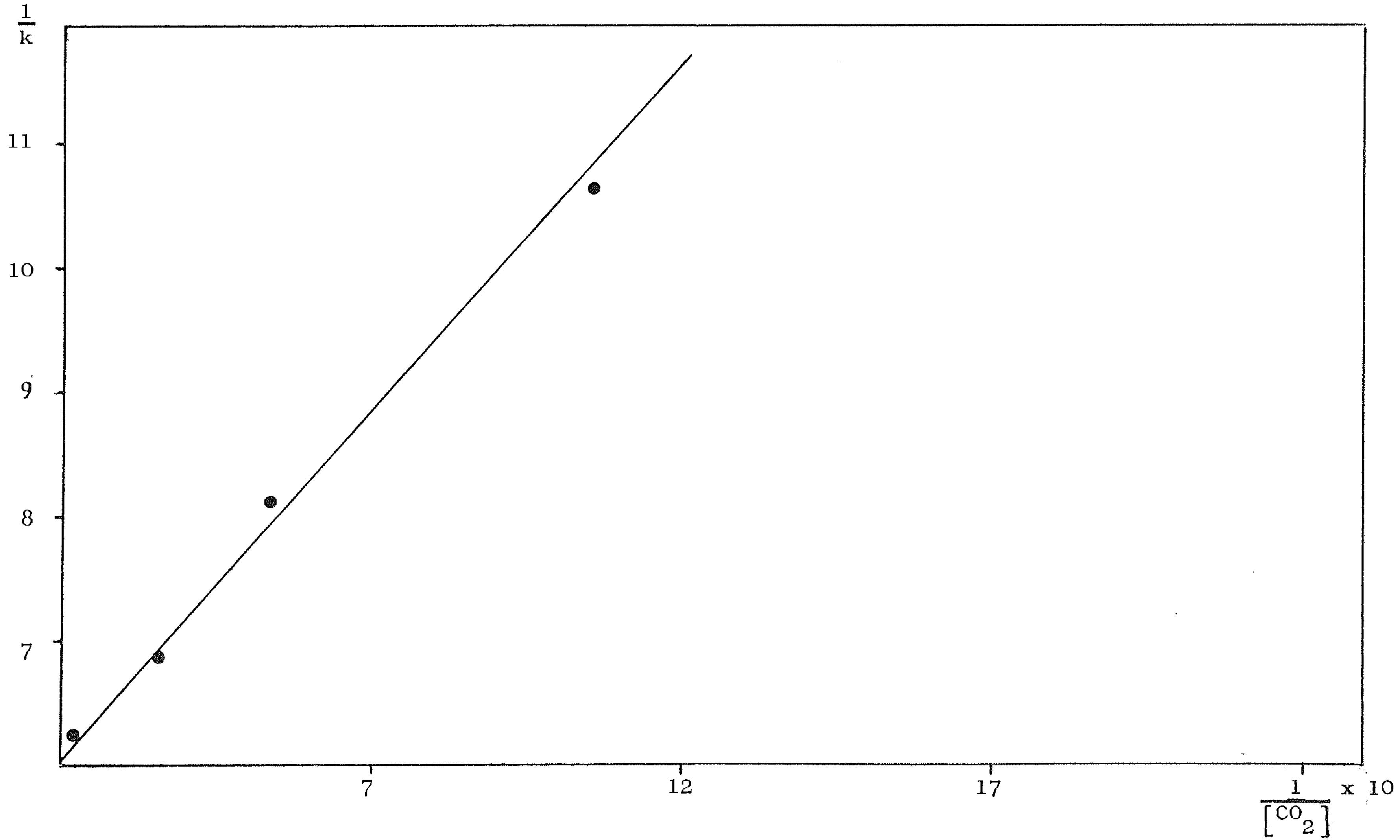
mole lit^{-1} $[RuCl_2(PPh_3)_3]$	k_1/min^{-1}	k_2/min^{-1}
2.6×10^{-4}	0.160	2.304
3.9×10^{-4}	0.146	1.17
3.64×10^{-4}	0.145	0.449
4.16×10^{-4}	0.123	0.738
4.69×10^{-4}	0.0935	3.93
4.95×10^{-4}	0.089	1.80

mole lit^{-1} $[CO_2]$	k_1/min^{-1}	k_2/min^{-1}
4.7×10^{-3}	0.089	1.80
9.4×10^{-3}	0.0935	3.93
18.8×10^{-3}	0.123	0.738
28.2×10^{-3}	0.145	0.449
47×10^{-3}	0.160	2.304

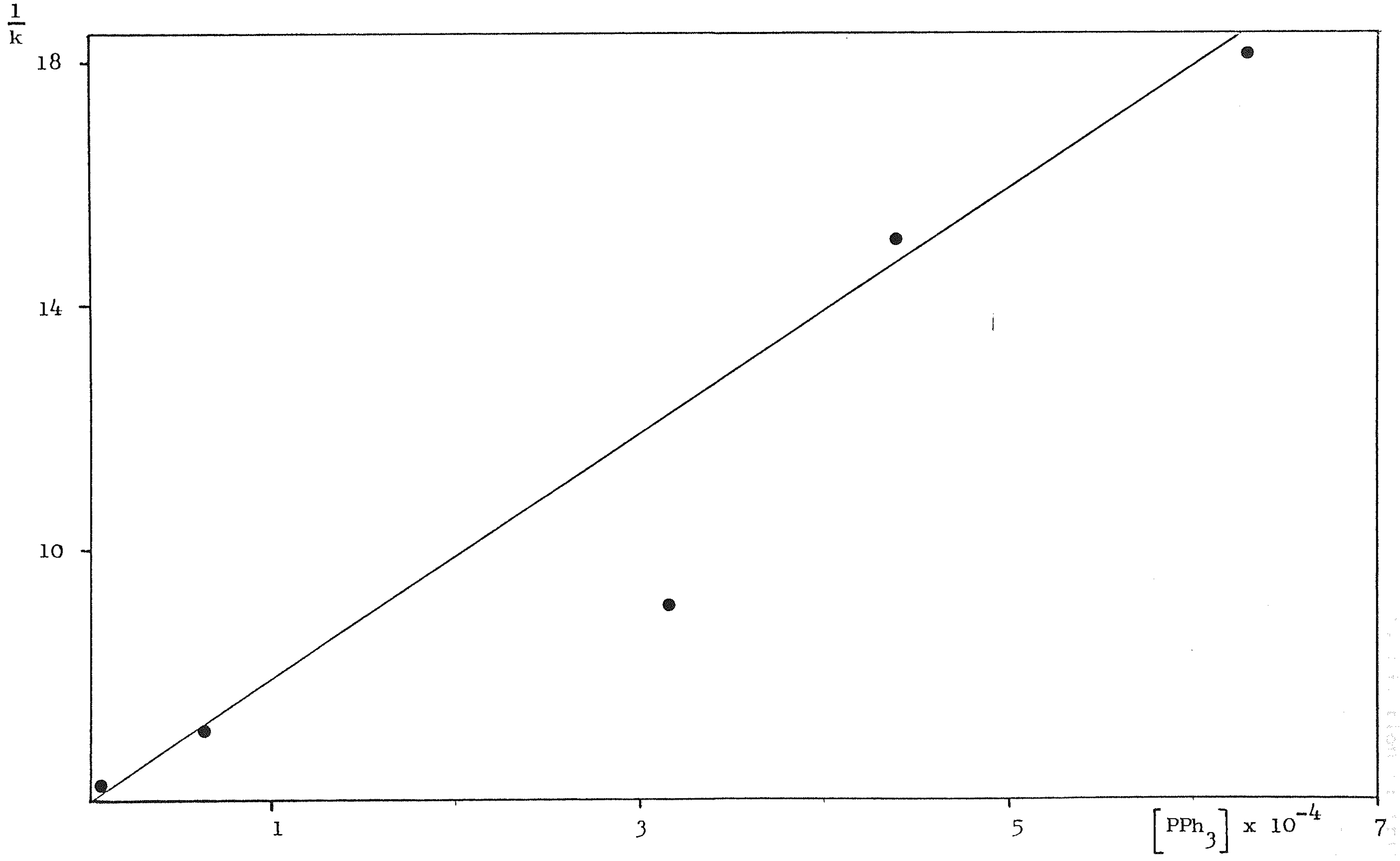
T°K	k_1/min^{-1}	k_2/min^{-1}
293	0.106	1.63
298	0.160	2.304
303	0.125	5
308	0.147	2.65
313	0.199	21.9

mole lit^{-1} $[PPh_3]$	k_1/min^{-1}	k_2/min^{-1}
0	0.160	2.304
6.3×10^{-5}	0.141	8.65
3.16×10^{-4}	0.108	0.5
4.4×10^{-4}	0.066	0.595
6.3×10^{-4}	0.055	0.22

Table 5.5.3.



Graph (5.5.1) A variation of $\frac{1}{k}$ against $\frac{1}{[CO_2]}$ for the kinetic profile studies in chapter V.



Graph (5.5.2.) A variation of $\frac{1}{k}$ against $\left[PPh_3\right]$ for the kinetic profile studies in chapter V

As can be seen the rate constant is affected by addition of triphenylphosphine. It will be shown in the mathematical part of the mechanism that this variation matches the scheme suggested for the mechanism of the reaction of dichlorotris(triphenylphosphine)ruthenium(II) with carbon dioxide in toluene.

To avoid confusion the rate constants k_c and k_d used for theoretical justification of two consecutive pseudo first order reactions and numerical subscripts are used with the rate constants in the scheme relevant to the mechanism of the reactions. The rate constant (k_1), calculated in table 5.5.3 and used to draw up graphs 5.5.1, 5.5.2 is k_{obs}.

The value of k_c was estimated from a single first order scheme at the beginning. By assuming an approximate value of k_c and by using a least squares computer programme the real values of k_c and k_d (given in table 5.5.3), were obtained from equation (1). It should be noted that optical density was replaced by concentration in equation (1).

Referring to the kinetic information available about the reaction of dichlorotris(triphenylphosphine)ruthenium(II) with carbon dioxide in toluene the mechanism given below is suggested. (Scheme 5.5.1)

$$RuCl_2(PPh_3)_3 \quad + \quad PPh_3 \;\overset{K_1}{\rightleftharpoons}\; RuCl_2(PPh_3)_4$$

$$RuCl_2(PPh_3)_3 \quad + \quad CO_2 \;\overset{K_2}{\rightleftharpoons}\; RuCl_2(PPh_3)_3 \cdot CO_2$$

$$RuCl_2(PPh_3)_3 \cdot CO_2 \;\xrightarrow{k_3}\; F$$

$$F \xrightarrow{k_4} G$$

Scheme 5.5.1.

Here K_1 and K_2 are equilibrium constants and k_3 and k_4 are rate constants.

The real value of k_d (k_2 from table 5.5.3) is large compared with k_c (k_1 from table 5.5.3) because of the active species produced when F is converted to G. Thus this part of the reaction is not very informative. Because of the lack of available information about the species formed at stages F and G the nature of their products can not be well interpreted. Due to the presence of impurities of water and oxygen, carbonate species might have been formed at stage F which could then decompose or be oxidized to other ruthenium species with higher oxidation states. The green colour of the solution produced in the end of the reaction may support this assumption. The mathematical expression of the mechanism suggested in scheme 5.5.1 is as follows:

The rate of formation of F is:

$$\frac{d\left[F\right]}{dt} = k_3 \cdot \left[RuCl_2(PPh_3)_3.CO_2\right]$$

The relationship between equilibrium constants (K_1 and K_2) and the concentrations of the relevant components are:

$$\left[RuCl_2(PPh_3)_4\right] = K_1 \left[RuCl_2(PPh_3)_3\right]\left[PPh_3\right] \qquad (2)$$

$$\left[RuCl_2(PPh_3)_3.CO_2\right] = K_2 \left[RuCl_2(PPh_3)_3\right]\left[CO_2\right] \qquad (3)$$

Assuming the concentrations of carbon dioxide and triphenylphosphine can be treated as constant, the total concentration of the components (T) at time t is:

$$T = \left[RuCl_2(PPh_3)_3\right] + \left[RuCl_2(PPh_3)_4\right] + \left[RuCl_2(PPh_3)_3.CO_2\right] \qquad (4)$$

Substituting the value of $\left[RuCl_2(PPh_3)_3\right]$ and $\left[RuCl_2(PPh_3)_4\right]$ from equations (2) and (3) into equation 4 gives:

$$T = \frac{\left[RuCl_2(PPh_3)_3.CO_2\right] \cdot \left(1 + K_1\left[PPh_3\right] + K_2\left[CO_2\right]\right)}{K_2\left[CO_2\right]} \qquad (5)$$

Mathematically this scheme is of the same form as:

$$X \xrightarrow{k_5} y$$

except, that we must use equation (6) as the composite rate constant.

$$k_{obs} = \frac{K_2k_3\left[CO_2\right]}{1+K_1\left[PPh_3\right] + K_2\left[CO_2\right]} \qquad (6)$$

If the concentration of triphenylphosphine is zero then equation (6) becomes:

$$\frac{1}{k_{obs}} = \frac{1}{K_2 \cdot k_3} \cdot \frac{1}{\left[CO_2\right]} + \frac{1}{k_3} \qquad (7)$$

The following equation is obtained when the concentration of triphenyl phosphine is not zero.

$$\frac{1}{k_{obs}} = \frac{K_1}{K_2k_3\left[CO_2\right]} \cdot \left[PPh_3\right] + \frac{1 + K_2\left[CO_2\right]}{K_2k_3\left[CO_2\right]}$$

According to equation (7) and (8), plotting $\frac{1}{k_{obs}}$ Vs $\frac{1}{\left[CO_2\right]}$ and $\frac{1}{k_{obs}}$ Vs $\left[PPh_3\right]$ should produce straight line. In the case of our study these conditions have been satisfied and have been discussed previously.

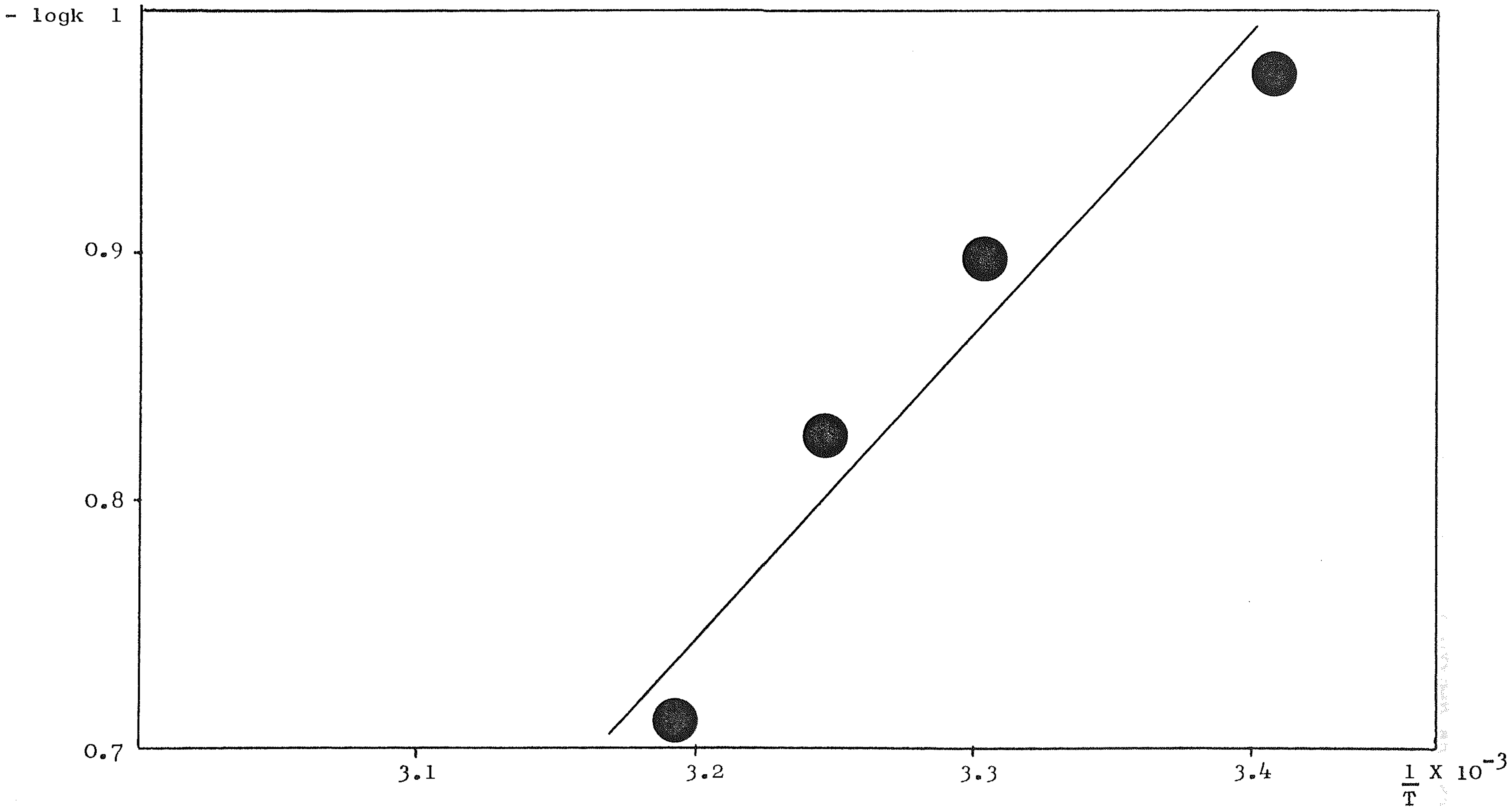
By plotting $-\log k_1$ against $\frac{1}{T}$ a straight line graph was obtained which demonstrates that this first consecutive reaction obeys the Arrhenius equation (graph 5.5.3)

$$\log k_a = \text{constant} \cdot \frac{-Ea}{RT} \quad x \quad 2.303$$

Determining the gradient for the graph a value for Ea the activation energy was calculated at 3.3 ± 0.01 kJ/mole.

The nature of species up to stage F are clear, however more details about the products obtained at stage F and G are required and will be given in the following paragraph.

Considering the rate constants at stage F and G it may be suggested that the adduct complex $RuCl_2(PPh_3)_3CO_2$ is converted to $RuCl_2(PPh_3)_2.CO_2$ by loss of one triphenylphosphine at stage F, this product is then



Graph (5.5.3) Graph of - logk against $\frac{1}{T}$ for the kinetic profile studied in chapter V.

converted to the other species in the presence of oxygen and water impurities.

Due to presence of traces of oxygen and metal ions, oxidation of triphenylphosphine to triphenylphospine oxide can be prompted and therefore it may be suggested that triphenylphosphine oxide either free or coordinated to the ruthenium is one of the species at stage G. Such a suggestion is strongly supported by ^{31}P nmr evidence obtained from the chloroform saturated carbon dioxide solution of dichlorotris(triphenylphosphine)ruthenium(II). (See page 190).

When the toluene saturated carbon dioxide solution of $RuCl_2(PPh_3)_3$ was exposed to oxygen the band at 475 nm (visible spectrum) disappears and no further reaction with carbon dioxide was observed. This study shows that the carbon dioxide and oxygen are in competition in reaction with $RuCl_2(PPh_3)_3$. The other aspect of such a study is that the adduct complex $RuCl_2(PPh_3)_3.CO_2$ can easily lose carbon dioxide or converted to other products in the presence of an oxygen.

From the above experiments the presence of $RuCl_2(PPh_3)_2O_2$ as one of the species may be proposed for stage G. The main products at stage G may be the bicarbonate complex $RuCl_2(PPh_3)_2CO_3H$ or the carbonato complex $\left[RuCl_2(PPh_3)_2.CO_3\right]$ which are obtained from the reaction of adduct $RuCl_2(PPh_3)_2CO_2$ and water or oxygen impurity. The detailed discussions about these products were given previously, therefore the reader should refer to the discussion part of chapter four.

With reference to the information given above the scheme (5.5.1) can be presented as follows:

$$\mathrm{RuCl_2(PPh_3)_3 + PPh_3 \xrightleftharpoons{K_1} RuCl_2(PPh_3)_4}$$

$$\mathrm{RuCl_2(PPh_3)_3 + CO_2 \xrightleftharpoons{K_2} RuCl_2(PPh_3)_3 \cdot CO_2}$$

$$\mathrm{RuCl_2(PPh_3)_3CO_2 \xrightarrow{k_3} RuCl_2(PPh_3)_2\ CO_2 + PPh_3}$$

$$\mathrm{RuCl_2(PPh_3)_2CO_2 \xrightarrow{\text{traces of } O_2 \text{ of } H_2O} RuCl_2(PPh_3)_2CO_3H}$$

APPENDIX 1

$(A \xrightarrow{k_c} B \xrightarrow{k_d} C)$ At the start of the reaction $(t = 0)$ the concentration of A is a, the substances B and C being absent. By time t the concentrations are: $a - x$ for substance A; $x - y$ for the substance B; and y for the substance C. Applying the basic law of kinetics and the principle of independancy:

$$\frac{dx}{dt} = k_c \cdot (a - x) \qquad (1)$$

$$\frac{dy}{dt} = k_d \cdot (x - y) \qquad (2)$$

The solution of the first equation, i.e, the simplest first order equation, is represented in the form:

$$x = a \left(1 - e^{-k_c t}\right) \qquad (3)$$

Substituting the values of x from eq. (3) into eq. (2) yields an equation for the rate of change of y:

$$\frac{dy}{dt} = -k_d y + k_d a \left(1 - e^{-k_c t}\right) \qquad (4)$$

This equation of the Leibnitz equation type is solved by equating provisionally the second term on the right hand size of eq. (4) to zero:

$$\frac{dy}{dt} = -k_d y$$

or

$$\text{Ln } y = -k_d t + \text{Ln } Z \qquad (5)$$

Where Ln Z is the integration constant. Presenting eq. (5) as:

$$y = Z \cdot e^{-k_d t} \qquad (6)$$

We take into account that Z is not a true constant it must be a function of time because of eq. (4) being simplified. Further, to obtain the form of this function, we differentiate eq. (6) with respect to time. We have:

$$\frac{dy}{dt} = \frac{dZ}{dt} e^{-k_d t} - Zk_d e^{-k_d t}$$

or taking cognizance of eq. (6),

$$\frac{dy}{dt} = -k_d y + \frac{dZ}{dt} e^{-k_d t} \qquad (7)$$

Now, comparing eq. (7) and (4), we find that

$$dZ = k_d a \left[e^{k_d t} - e^{(k_d - k_c)t} \right] dt$$

on integration this leads to:

$$Z = k_d a \left[\frac{1}{k_d} e^{k_d t} + \frac{1}{k_d - k_c} e^{(k_d - k_c)t} \right] + \text{constant} \qquad (8)$$

substituting the value of Z into the expression for y, eq. (6) gives:

$$y = k_d a \cdot \left[\frac{1}{k_d} - \frac{1}{k_d - k_c} e^{-k_c t} \right] + \text{const.}\ e^{-k_d t} \qquad (9)$$

The integration constant is found, as always, from the initial condition t = o, y = o.

$$\text{Const} = a \frac{k_c}{k_d - k_c}$$

Thus we obtain the following expression for the dependence of the product concentration on time.

$$y = a \left(1 + \frac{k_c}{k_d - k_c} e^{-k_d t} - \frac{k_d}{k_d - k_c} e^{-k_c t}\right)$$

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