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# Syntheses and Electrochemistry of Monosubstituted Carbonyl Complexes of Low Valent Ruthenium

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# Syntheses and Electrochemistry of Monosubstituted Carbonyl Complexes of Low Valent Ruthenium

(TITLE)

BY

Nor Azowa Ibrahim

**THESIS**

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1986
YEAR

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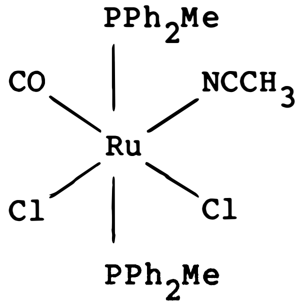
# Syntheses and Electrochemistry of Monosubstituted Carbonyl Complexes of Low Valent Ruthenium

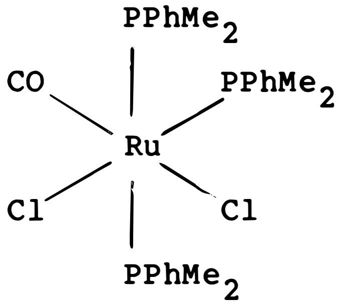
Thesis Approved

| | |
|---|---|
| Dr. R. L. Keiter | date |
| Dr. D. W. Ebdon | date |
| Dr. D. H. Buchanan | date |
| Dr. J. W. Ellis | date |

# Abstract

The reactions of $Ph_2MeP$ and $PhMe_2P$ with $(PPh_3)_4RuCl_2$ yield $(PPh_2Me)_4RuCl_2$ and $(PPhMe_2)_4RuCl_2$, respectively. These complexes have been shown by conductivity studies to be dissociated in acetonitrile and exist as $[(PPh_2Me)_4RuCl(CH_3CN)]Cl$ and $[(PPhMe_2)_4RuCl(CH_3CN)]Cl$. When carbon monoxide was bubbled into these solutions, monocarbonyl complexes were obtained. Elemental analyses, $^1H$ NMR, $^{31}P$ NMR, infrared spectroscopy, conductivity measurements, and polarography were used to analyse the products, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$. The structures of the complexes were elucidated and in each case two phosphine ligands were trans and two chloride ligands were cis.





Conductivity measurements established that the chloride ligands remain coordinated in acetonitrile.

The redox properties of $(PPh_2Me)_4RuCl_2$, $(PPhMe_2)_4RuCl_2$, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$ in acetonitrile indicated that these compounds were reduced irreversibly with the uptake of two electrons. Phosphine ligand exchange with the solvent led to the presence of at

least two electroactive species in solution. The exchange of phosphine ligands decreased the ease of the reduction of the complexes by 300- 350 mV. The half-wave potentials in solution indicate that the electron density around the metal was not changed appreciably by substituting $PPh_2Me$ and $PPhMe_2$.

Attempts to reduce $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$ with 1 % Na-Hg amalagam yielded mixtures of compounds that appeared as a brown powder and an intractable oil, respectively. Characterization of these zerovalent products was not accomplished.

The electrochemical synthesis of $(PPh_3)_4Ru(\eta^2$ $CH_3CN).CH_3CN$ was carried out electrochemically. When the complex was heated under reflux in hexane, an air-sensitive unsaturated compound, identified as $(PPh_3)_4Ru$ was obtained. The exact nature of the complex was not established.

## Acknowledgements

I would like to extend my deepest gratitute to the late Dr. E. O. Sherman, for his knowledgeable assistance and direction. His patience and guidance were very much appreciated.

I would sincerely like to thank Dr. R.L. Keiter for his assistance and advice, especially during the writing of this thesis.

Special thanks must go to Robert Turner for his helpful discussions and suggestions, and for his patience and support.

I also would like to extend my gratitude to Kenneth Osborne for all his help to make this project possible.

I also wish to acknowledge Dr. E.A. Keiter who obtained all the $^{31}P$ NMR spectra for this thesis.

Much appreciation is also given to the rest of the faculty and staff in this Chemistry Department for all their help.

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# INTRODUCTION

Reactions of hydrocarbons derived from petroleum with small molecules (e.g. water, cabon dioxide, chlorine) yield chemical intermediates whose further reactions provide the basic chemical items of commerce. Interaction of the hydrocarbon with small molecules usually requires a catalyst to enhance the rate of reaction and ensure adequate production levels. The classical method for hydrocarbon substitution requires a highly reactive reagent and catalysts have been used to generate the reagent.

Recently, some evidence indicates that soluble transition-metal complexes can activate the C-H bonds of a hydrocarbon. Bergman discovered that iridium[1], rhodium[2] and rhenium[3] complexes add oxidatively to C-H bonds in alkanes to give hydridoalkyl metal complexes (eq 1).

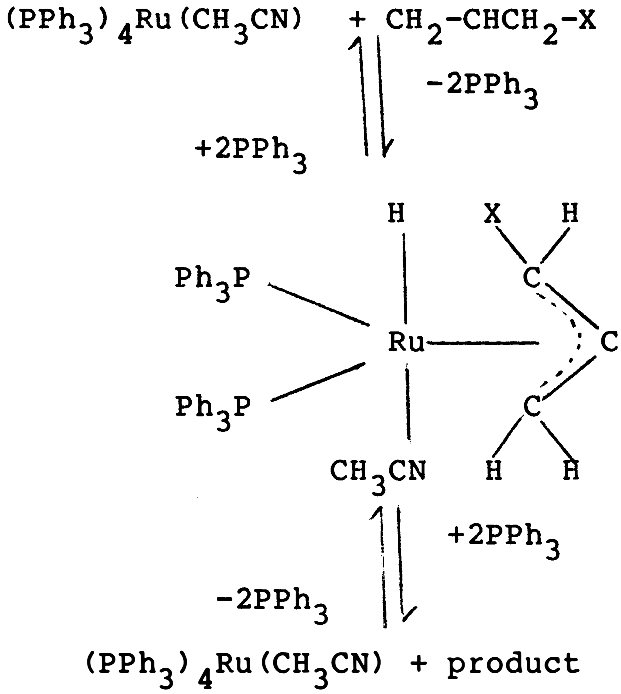
$$\mathrm{M} + \mathrm{R{-}H} \longrightarrow \mathrm{R{-}M{-}H} \qquad (1)$$

However, the chemical factors which determine the effectiveness of the catalyst are poorly understood.

Several ruthenium compounds which exhibit novel catalytic activity in hydrocarbon reactions have been made in these laboratories. The ruthenium center, where the catalysis occurs, is uncharged in these unusual materials. The complex, $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN).CH_3CN$ synthesized by electrochemical reduction of $(PPh_3)_4RuCl_2$ in $CH_3CN$[4], adds oxidatively to an allylic carbon-hydrogen bond of propylene to produce an isolable hydrido-$\eta^{2}$-allylruthenium (II) compound (Eq 2).

$$(PPh_3)_4Ru(CH_3CN) + C_3H_6 \xrightarrow{CH_3CN} (PPh_3)_4RuH(\eta^{3}\text{-}C_3H_5)CH_3CN + 2PPh3 \qquad (2)$$

It also isomerizes allyl benzene to cis and tran--methylstyrene, a reaction presumably initiated by oxidative-addition of Ru(0) by an allylic C-H bond. The isomerization proceeds via an intramolecular 1,3-hydrogen shift$^5$. The general mechanism for the isomerization of these allyl complexes can be presented as:



Reactions with other substituted allylic olefins such as allyl halides, allyl methyl ether and allyl cyanide support the proposed mechanism. Additional information was obtained by Olson$^6$ about the catalysis mechanism from studies of $(PPh_3)_3RuCO(CH_3CN)$. This monocarbonyl complex was synthesized by potentiostatic reduction of

$[(PPh_3)_2RuCOCl_2]_2$ in excess $PPh_3$ at a potential of $-2.30V$ vs $Ag/0.1\ AgNO_3$ (eq 3-5).

$$[(PPh_3)_2RuCOCl_2]_2 + CH_3CN \quad (PPh_3)_2RuCO(CH_3CN)Cl_2 \qquad (3)$$

$$(PPh2)2RuCO(CH3CN)Cl2 + 2e \xrightarrow{CH3CN} (PPh3)2RuCO(CH3CN) + 2Cl^- \qquad (4)$$

$$(PPh2)2RuCO(CH3CN) + PPh3 \longrightarrow (PPh3)3RuCO(CH3CN) \qquad (5)$$

Unlike $(PPh3)4Ru(\eta^2\text{-}CH3CN)$, the monocarbonyl complex does not insert into the allylic carbon hydrogen bond of propylene to form a hydrido π-allyl complex. The study suggests that the electron density at the metal center is critical for the oxidative-addition reaction. In the complex, $(PPh_3)_3RuCO(CH_3CN)$, the carbonyl ligand reduces the Lewis basicity of the ruthenium atom by accepting electron density from its filled d-orbital. The above hypothesis was supported by comparing $(PPh_2Me)_4Ru(CH_3CN)$, a complex which contains phosphines which are more basic than $PPh_3$, with $(PPh_3)_3RuCO(CH_3CN)$. The complex $(PPh_2Me)_4Ru(\eta^2\text{-}CH_3CN)$ readily inserts into the allylic carbon-hydrogen bond of propylene and isobutylene.

Unlike propylene, allyl benzene and allyl cyanide isomerise to β-methyl styrene and crotonitrile, respectively, in the presence of $(PPh_3)_3RuCO(CH_3CN)$. Olson suggested that the isomerization occurs via a 1,3-hydrogen shift mechanism. It seems that phenyl and cyano groups can increase the stabilization of the π-allyl ligand complex, and this offsets the increased promotional energy required by $(PPh_3)_3RuCO(CH_3CN)$. Although isomerization occurs, the rate of the reaction is much slower than for $(PPh_3)_4Ru(CH_3CN)$. These results show that the electron density around the ruthenium center is an important factor.

From the above observations, a potential method for studying the basis for different reactivities is to synthesize a series of complexes in which there is a systematic change in the R group of the phosphine ligand, $R_3P$, attached to the ruthenium center. Variation of the molecules attached to the ruthenium center will lead to systematic changes in the electronic enviroment of the metal, hence permitting assessment of the role of this key parameter in the observed reactivity of such systems.

A metathesis of $(PPh_3)_3RuCO(CH_3CN)$ with $R_3P$ ligand was attempted by Bady[7] (Eq 6).

$$(PPh_3)_3RuCO(CH_3CN) + 6R_3P \xrightarrow{CH_3CN} (R_3P)_3RuCO(CH_3CN) \quad (6)$$

Although uncharged ruthenium products were obtained, each compound was contaminated with impurities which subsequently led to ambiguity in the interpretation of its catalytic activity and its relationship to the induced charge in the environment of ruthenium. Attempts to purify the complexes were unsuccessful and the yields were very low.

Another route to the preparation of zerovalent ruthenium compounds utilizes potentiostatic electrolysis of divalent ruthenium complexes in acetonitrile (eq 7) at a mercury pool cathode (similar to the method used for the synthesis of $(PPh_3)_3RuCO(CH_3CN)$.

$(R_3P)_3RuCOCl_2 + 2\bar{e} \xrightarrow{CH_3CN} (R_3P)_3RuCO(CH_3CN + 2Cl^-$ (7)

Few general methods have been reported for the synthesis of monocarbonyl ruthenium (II) complexes with tertiary phosphine ligands, $R_3P$, where $R_3P$ is dimethylphenylphosphine and diphenylmethylphosphine. Although all the methods gave the desired precursor, $(R_3P)_3RuCOCl_2$, with one or more isomers, the yield or the purity of the precursor was unsatisfactory.

Jenkin, Lupin and Shaw[8] made the complexes by carbonylation of $RuCl_3$ followed by addition of ligand.

$RuCl_3 + CO \xrightarrow{C_2H_5OH}$ product $\xrightarrow{R_3P} (R_3P)_3RuCOCl_2$

Although they isolated a high purity product, the yield for this one-step process was low (46%).

Mawby, et al[9] made the complex by ligand substitution of neutral halides, $(R_3P)_2Ru(CO)_2Cl_2$

$(R_3P)_2Ru(CO)_2Cl_2 + R_3P \xrightarrow{C_6H_6} (R_3P)_3RuCOCl_2$

The product was obtained in one isomeric form and the yield was 50%.

The third method for the preparation of the monocarbonyl ruthenium(II) complex, was reported by Chatt, Shaw and Field[10]. The reaction scheme can be represented as a two-step process.

$[(R_3P)_6Ru_2Cl_2]Cl + 2KOH + 2C_2H_5OH \longrightarrow 2(R_3P)_3RuH(CO)Cl$

(R3P)3RuH(CO)Cl2 + HCl $\longrightarrow$ (R3P)3RuCOCl2

The product isolated by this method exhibited two carbonyl bands which indicated two different species were present. When dimethylphenylphosphine was used as ligand, only the starting material and unidentified products were obtained[7]. The yield for the two-step synthesis of the diphenylmethyl derivative was 90%.

A procedure from the work of Armit and Stephenson[11] which utilizes ligand exchange in noncarbonyl containing ruthenium(II) complexes was adapted by Bady[7] to synthesize the monocarbonyl complex. The yield of the isolated product for each complex was satisfactory but each complex contained impurities. Attempts to recrystallize the isolated products were unsuccessful.

Although the methods for the synthesis of the precursor, $(R_3P)_3RuCOCl_2$, did not give pure product, an attempt to electrolyse the impure $(PPh_2Me)_3RuCOCl_2$ was made by Mooney[12]. Results similar to that for the reduction of $(PPh_3)_3RuCO(CH_3CN)$ were obtained; however the reduction product remained soluble in the catholyte in contrast to the production of $(PPh_3)_3RuCO(CH_3CN)$ where precipitation occurred during the reduction. Although these divalent compounds can be selectively reduced electrochemically to the zero state, the isolation of the product was difficult. The reduction product was separated from the supporting electrolyte by extracting it into benzene. Evaporation of benzene gave product contaminated with impurities from the starting material. Recrystallization from benzene led to decomposition of the product. A color change of red to yellow was observed. Both infrared and proton nuclear magnetic resonance spectroscopy indicated the presence of a hydrido ligand.

The principal object of this research was to synthesize divalent ruthenium complexes in high purity and yield. These precursors were characterized electrochemically to determine the experimental conditions for their conversion to the uncharged form. Polarography was used to determine the optimum reduction conditions for the charged ruthenium compounds. This method was used to identify the number of electrons added in reduction, the required strength of the reducing agent and any side reactions in the reduction process which might lead to impurities in the final product. Based on the electroanalytical data, the divalent ruthenium complex was shown to be both reducible chemically and electrochemically. Chemical reduction with alkali metal amalgam was explored since the electrochemical method requires isolation of the product from the supporting electrolyte and also has to be carried out in a non-coordinating solvent, which leads to orthometallated products. In addition, the reaction of $(PPh_3)_4Ru(CH_3CN).(CH_3CN)$ with aliphatic hydrocarbons was carried out to study the ability of the Ru(0) center to activate the C-H bond. Success in these endeavors would permit evalution of the role of the electronic factor at the catalytic center, and the catalytic efficiency and possibly suggest necessary changes for catalyst improvement.

# EXPERIMENTAL

## 1. General Methods

All operations were carried out under a nitrogen atmosphere whether on the bench or in a Vacuum Atmospheres Dri-lab glove box, Model HE 43/243, equipped with a model HE493 Dri-train. Nitrogen used was supplied by Gano Welding of Charleston, Illinois. A 25 W% solution of diethyl zinc in toluene was used in the glove box to check for oxygen contamination. If no fumes were observed when the bottle was opened, the amount of oxygen present was assumed to be less than 5 ppm.

Infrared spectra were recorded in the range of 4000-400 $cm^{-1}$ with a Perkin-Elmer grating Model 337 spectrometer. Spectra of solids were obtained from Nujol mulls between KBr plates. All spectra were calibrated with a polystrene film.

$^{1}H$ NMR spectra were recorded with a Varian T-60 spectrometer at 60 Mhz. Tetramethylsilane was used as an internal or external reference as required. $^{31}P$ NMR spectra were obtained from a homebuilt 250 Mhz spectrometer at the University of Illinois operating at 101.265 Mhz. An 85% phosphoric acid external reference was used.

Conductivity data were obtained from a YSI Model 31 conductivity bridge equipped with matching conductivity cell. The cell constant was determined from a 0.0200 M potassium chloride solution. All measurements were made in a constant temperature bath (Forma-Temp Jr. Bath and Circulator).

Four basic electrochemical units were used to do polarography. These were: a programmer (EG and G Parc model 175 universal programmer), the potentiostat (EG and G Parc 173), the coulometer (EG and G Parc model 179 digital Coulometer) and an X-Y recorder.

Uncorrected melting points were obtained under nitrogen in 1.5 X 90 mm sealed capillary tubes with a Thomas-Hoover capillary melting point apparatus. Analyses were performed by Galbraith laboratories Inc, Knoxville, Tennessee. Only single analyses were obtained for each compound.

### 2. Preparation and purification of the starting materials.

### A. Phosphine ligands.

Three different types of phosphine ligands were used in this research. Triphenylphosphine ($PPh_3$), Aldrich Chem. Co, Inc. was recrystallized from hot absolute ethanol. The $PPh_3$ was dried at room temperature under wacuum for 24 hrs. The purity of the ligand was established by both infrared spectroscopy and melting point determination (m.p= 80.0-80.5$^{o}$C). Diphenylmethylphosphine ($PPh_2Me$) and dimethylphenylphosphine ($PPhMe_2$) were obtained from Pressure Chemical Company and used as received. All the phosphine ligands were stored in the dry box.

### B. Solvent

Two different qualities of acetonitrile were used throughout the research. Reagent grade acetonitrile from Eastman was used in the preparation of the compounds and HPLC grade $CH_3CN$ from Baker Chemical Co. was used in the conductivity and electrochemical measurements. Both types of $CH_3CN$ were dried over $CaH_2$ for 24 hrs, distilled through a glass bead column under nitrogen, and stored in the dry box until needed.

Reagent grade hexanes from Fisher Scientific Company were dried over $CaH_2$ overnight and distilled in a dry solvent still. The hexanes were degassed with $N_2$ prior to use. Pentane from Aldrich was purified in the same manner and stored in the dry box.

### C. Supporting electrolyte

Tetraethylammonium perchlorate (TEAP) was obtained from Eastman (white label grade) and recrystallized three times from deionized water. The salt was dried at 65 $^oC$ under vacuum and stored over Drierite in a desiccator.

### D. Miscellaneous chemicals

Ruthenium trichloride trihydrate was obtained from the Alfa division of Ventron Corporation. The triply distilled mercury was received from Bethlehem Apparatus and pinholed twice prior to use in the dropping mercury electrode and in the preparation of the Na-Hg amalgam. Reagent grade $AgNO_3$, received from Fisher Scientific, was dried at 110 $^{o}$C prior to use.

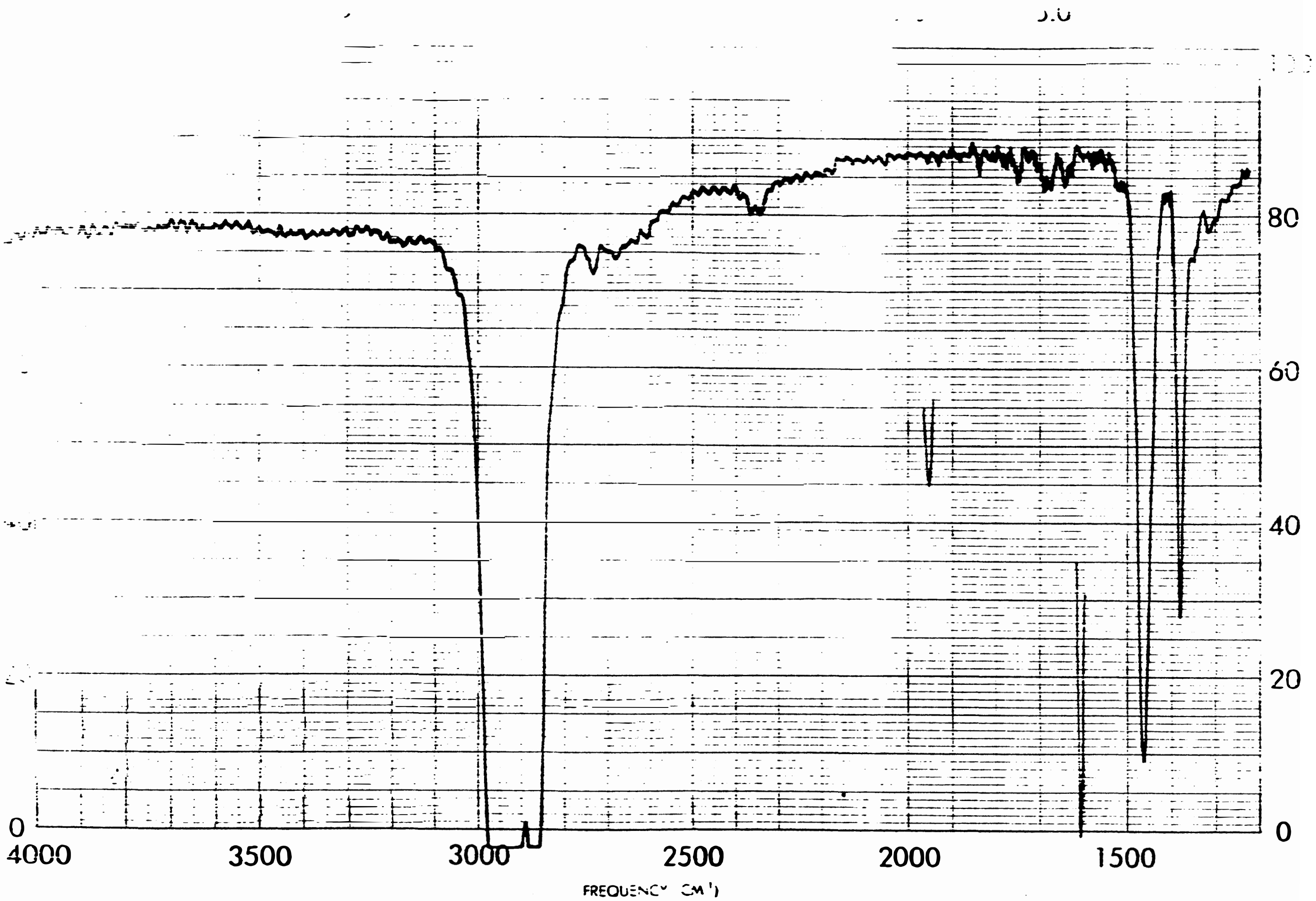
### 3. Preparation of ruthenium tertiary phosphine complexes.

### A. Preparation of $(PPh_3)_4RuCl_2$

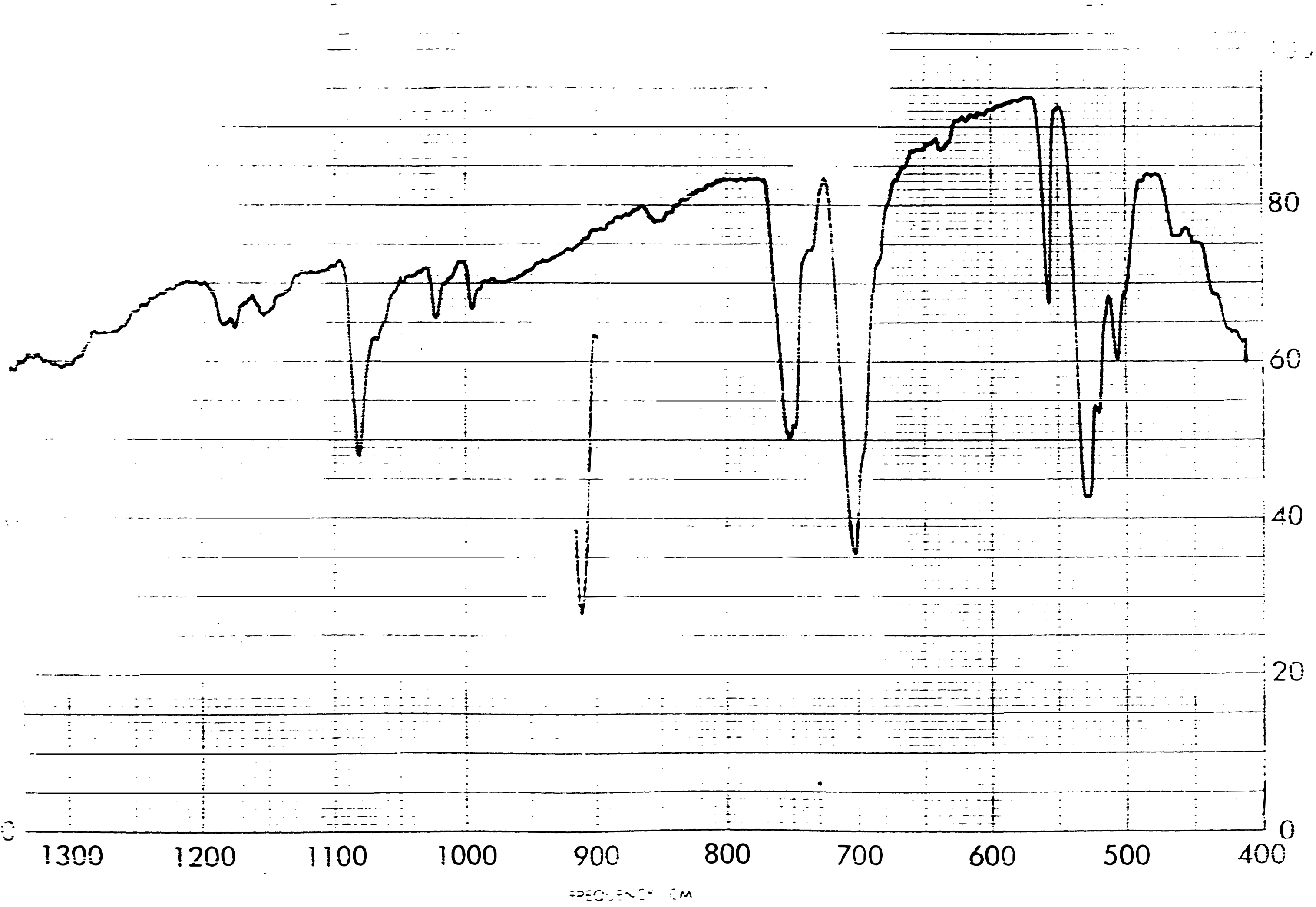
The procedure for the preparation of $(PPh_3)_4RuCl_2$ was first reported by Stephenson and Wilkinson[13]. A modification of the procedure, leading to an improved yield, was employed[6].

Reagent grade, degassed, anhydrous methanol (900 mL) was placed in the round bottom flask. Ruthenium trichloride trihydrate (3.000g, 11.70mmol) was added to the methanol and stirred. When all of the solid had dissolved, 18.000g (66.66 mmol) of recrystallized triphenylphosphine was added. The solution was stirred until all of the triphenylphosphine dissolved and was filtered by suction in the hood to remove the unreacted polymeric ruthenium complex. The filtrate was placed in a 1000 mL round bottom flask and stirred under nitrogen for 4 days. The red brown solid which precipitated was collected by suction filteration in the hood and dried under vacuum for 24 hrs. The yield of $(PPh_3)_4RuCl_2$ was 9.408g (66%). The solid decomposed at 135-136 $^{o}$C under nitrogen (Lit 132-134$^{o}$C). The purity of this complex was checked by comparing the infrared spectrum (Fig. 1) and

Figure 1 : Infrared spectrum of $(PPh_3)_4RuCl_2$



| | | |
|---|---|---|
| SAMPLE ~~$Cl_2Ru(PPh_3)_4$~~<br>$(PPh_3)_4RuCl_2$ | CURVE NO. | SCAN SPEED fast |
| | CONC. | SLIT normal |
| ORIGIN | CELL PATH KBr press plates | OPERATOR hsr |
| SOLVENT Nujol | REFERENCE Air | DATE 4/23/85 |
| | | REMARKS 1944 cm⁻¹, 1601 cm⁻¹ |



| | | | |
|---|---|---|---|
| SAMPLE $Cl_2Ru(PPh_3)_4$ | CURVE NO | SCAN SPEED fast | OPERATOR Dor |
| | CONC. | SLIT | DATE [illegible] |
| ORIGIN | CELL PATH KBr press plates | REMARKS 907 cm | |
| SOLVENT Nujol | REFERENCE air | | |

the melting point with those previously reported.[14]

The filtrate was refluxed for 48 hrs under nitrogen to recover the remaining ruthenium. The brown solid, $(PPh_3)_3RuCl_2$, was collected by suction filteration and dried under vacuum. The yield was was 2.192g (20% based on Ru).

### B. Preparation of $(PPh_2Me)_4RuCl_2$ and $(PPhMe_2)_4RuCl_2$.

These complexes were prepared by direct replacement of $PPh_3$ from $(PPh_3)_4RuCl_2$ as described by Armit and Stephenson[15].

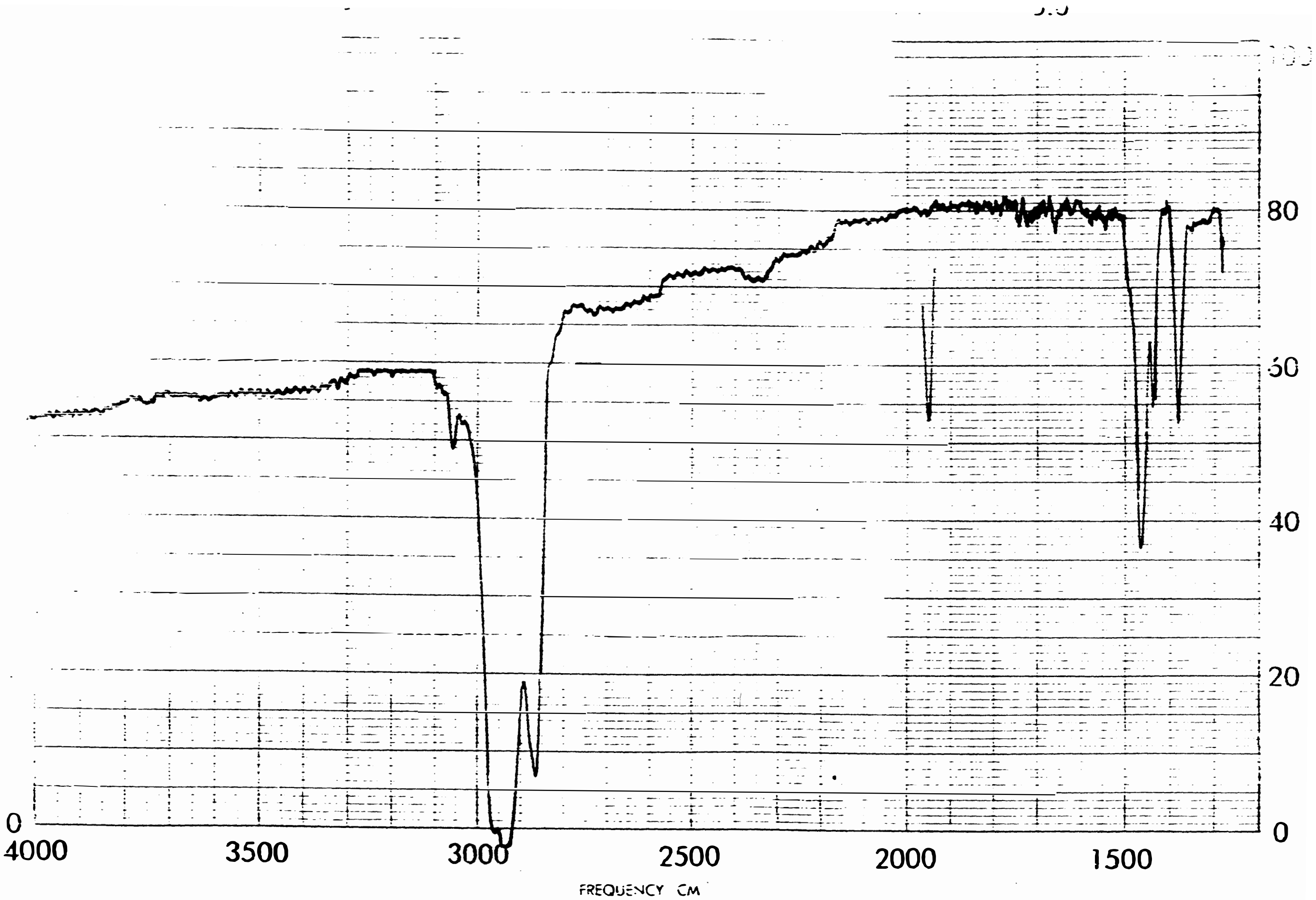
Into a 250 mL round bottom flask was placed $(PPh_3)_4RuCl_2$ (2.000g, 1.640 mmol). Hexane (100 mL) and a six fold excess of $PPh_2Me$ (2.16 mL,9.84 mmol) were added. The brown suspension of $(PPh_3)_4RuCl_2$ was taken out of the box and refluxed for 15 hrs under a nitrogen atmosphere. The brown suspension turned orange after 4 hrs. The precipitate, $(PPh_2Me)_4RuCl_2$, was filtered under vacuum. The yield was 1.524g (88% based on Ru). This compound decomposed at 138-139 °C under nitrogen[14,16].

The complex, $(PPhMe_2)_4RuCl_2$, was prepared by the same method. The yield was 93%. The complex decomposed at 190-195 °C (lit 165-170°C). The infrared spectrum for both complexes (Fig 2-3) were identical with those previously reported[14,16].

### C. Preparation of $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN).(CH_3CN)$

The complex, $(PPh_3)_4Ru(\ CH_3CN).(CH_3CN)$, was

Figure 2 : Infrared spectrum of $(PPh_2Me)_4RuCl_2$



SAMPLE Ru (PPh$_2$Me)$_4$ Cl$_2$

ORIGIN

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH KBr

REFERENCE Air

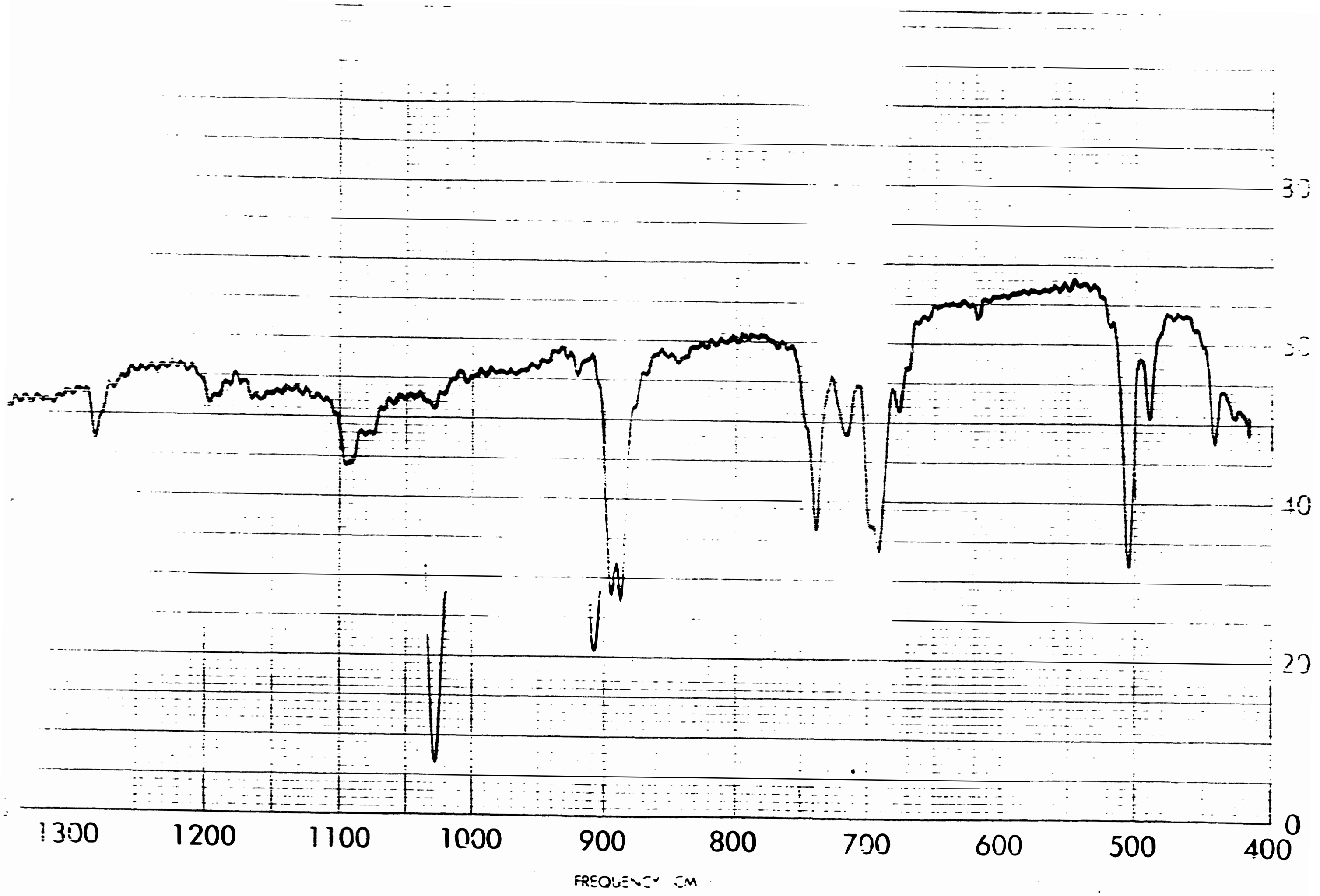
SCAN SPEED fast

SLIT Normal

OPERATOR NAI

DATE [illegible]

REMARKS Substance obtained from [illegible] on Jun /25.



SAMPLE (PPh₂ Me)₄ RuCl₂

ORIGIN Sept/21st/55

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH CBR

REFERENCE

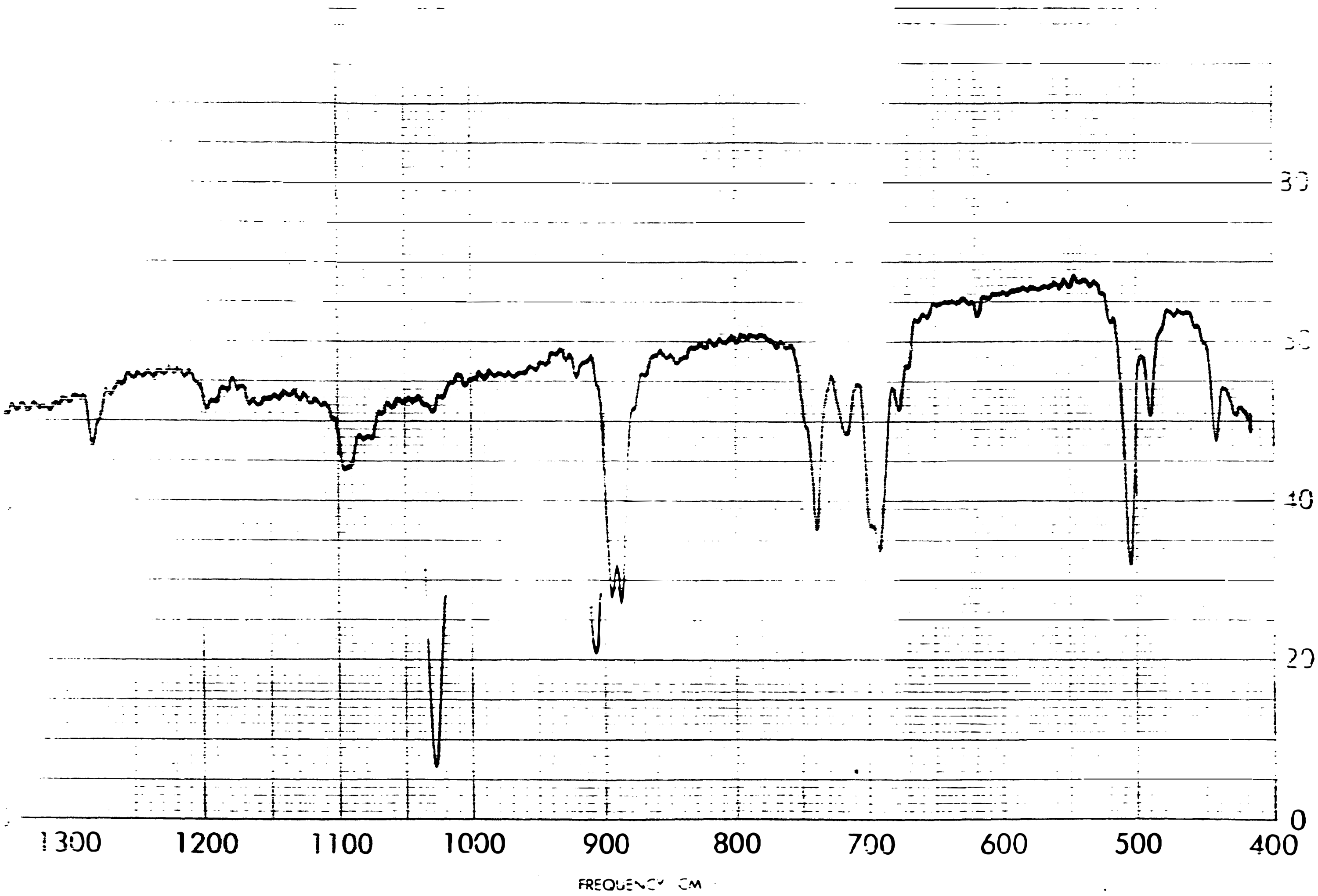
SCAN SPEED Fast

SL N

REMARKS

OPERATOR NAI

DATE Oct/2/55



SAMPLE $(PPh_2Me)_4RuCl_2$

ORIGIN Sept/21st/55

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH CBR

REFERENCE

SCAN SPEED Fast

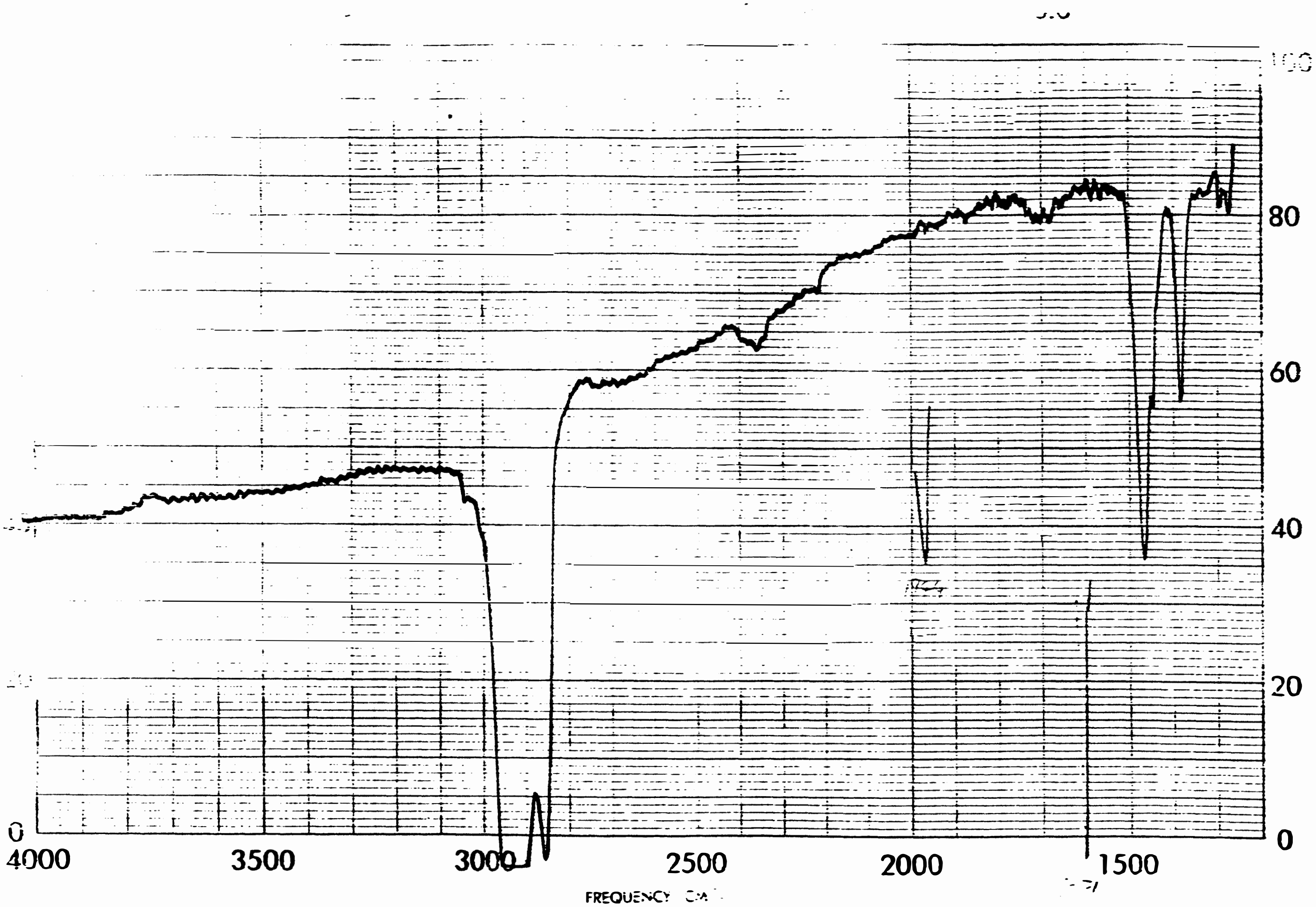
SLIT N

REMARKS

OPERATOR NAI

DATE Oct/2/55

Figure 3 : Infrared spectrum of $(PPhMe_2)_4RuCl_2$



SAMPLE (PPhMe$_2$)$_4$RuCl$_2$

ORIGIN Aug 5 ri.

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED fast

SLIT N

OPERATOR NAi

DATE AUG 6 81

REMARKS

PR 1122 (337-1203)

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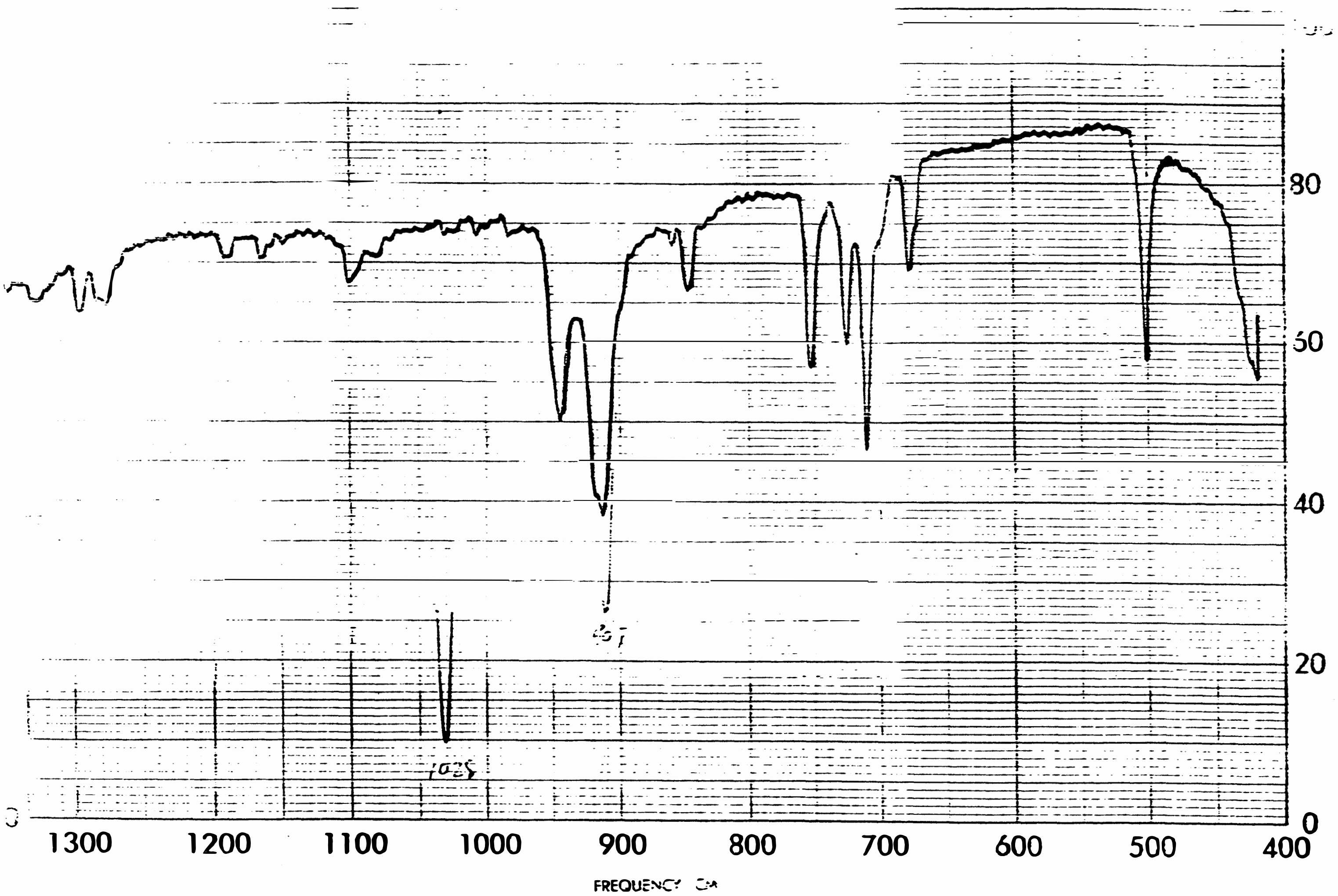

SAMPLE $(PPhMe_2)_4RuCl_2$

ORIGIN Aug 3rd 1985

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED fast

SLIT N

REMARKS

OPERATOR N.v

DATE Aug 6th

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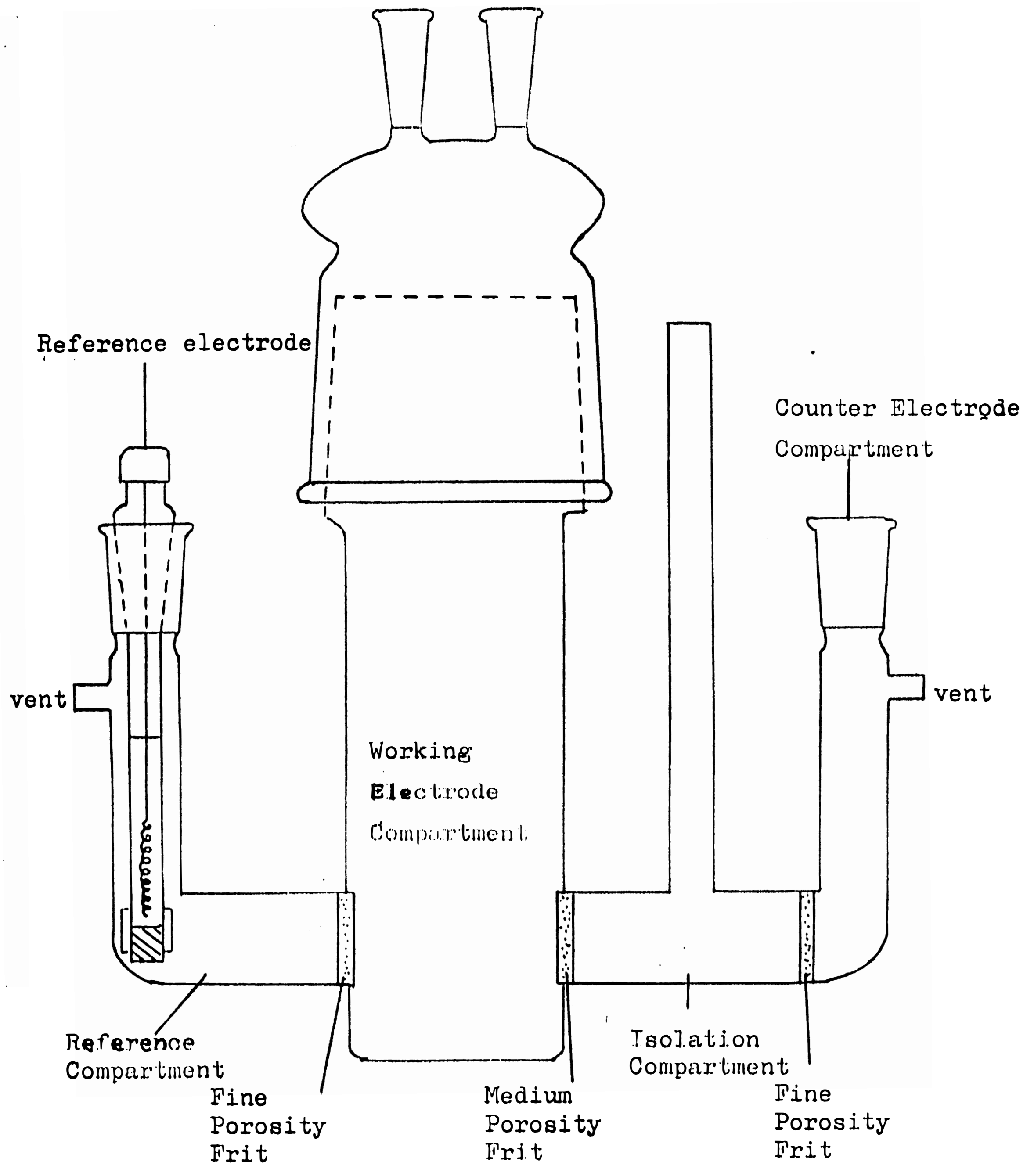
prepared according to the method of Sherman and Schreiner[4]. The electrolysis of the ruthenium (II) complex, $(PPh_3)_4RuCl_2$ (5.000g, 200 mL $CH_3CN$) was carried out in the dry box with a pyrex electrolysis cell consisting of four compartments separated by glass frits as shown in Fig. 4. The reaction was carried out in the large central compartment. The working electrode and the counter electrode were isolated to prevent diffusion of the products formed at the counter electrode into the compartment containing the working electrode. A large platium foil electrode was used as the working electrode and it funtioned as a cathode since a reduction process was carried out. The anode was also composed of platinum foil. A 0.100 M silver/silver nitrate electrode was used as the reference.

The compartments of the cell were filled with 0.100M tetraethylammonium perchlorate in $CH_3CN$ in a specific order. The reference and the counter electrode compartments were filled and sealed with the serum caps to prevent leakage of TEAP solution into the central compartment. After removal of any traces of the solution, the central compartment was filled with a 0.021M solution of $(PPh_3)_4RuCl_2$ in 0.100M TEAP in $CH_3CN$. The cathode was placed in the compartment and the solution levels in the anode, intermediate and cathode compartments were adjusted so that no hydrostatic head existed between the chambers.

FIGURE 4: ELECTROLYTIC CELL



The potential was set at -2.25 V with a current of 90 mA and the catholyte was stirred vigorously with a magnetic stirring bar during electrolysis. The green solution became yellow and then intense red-brown within several minutes.

The electrolysis was carried out until the current dropped to 6 mA (4hrs). The dark red brown solution was poured into a beaker and then transferred to a 250 mL round bottom flask. As the volume was reduced under vacuum , a yellow solid was observed to form. The suspension was stirred overnight and a yellow powder was collected by vacuum filteration and dried under vacuum at room temperature for 24 hrs to give 1.799g (58%).

The yellow product was identified as $(PPh_3)_4Ru(\eta^2-CH_3CN)\cdot CH_3CN$ by comparing its infrared spectrum and melting point to that reported by Sherman and Shreiner[4]. The solid melted at 125-130 °C under nitrogen (lit 124-131 °C). Characteristic infrared vibrations were observed at 2254 $cm^{-1}$ and 1910 $cm^{-1}$ corresponding to uncoordinated and $\eta^2$-coordinated acetonitrile respectively. The spectrum is shown in fig 5.

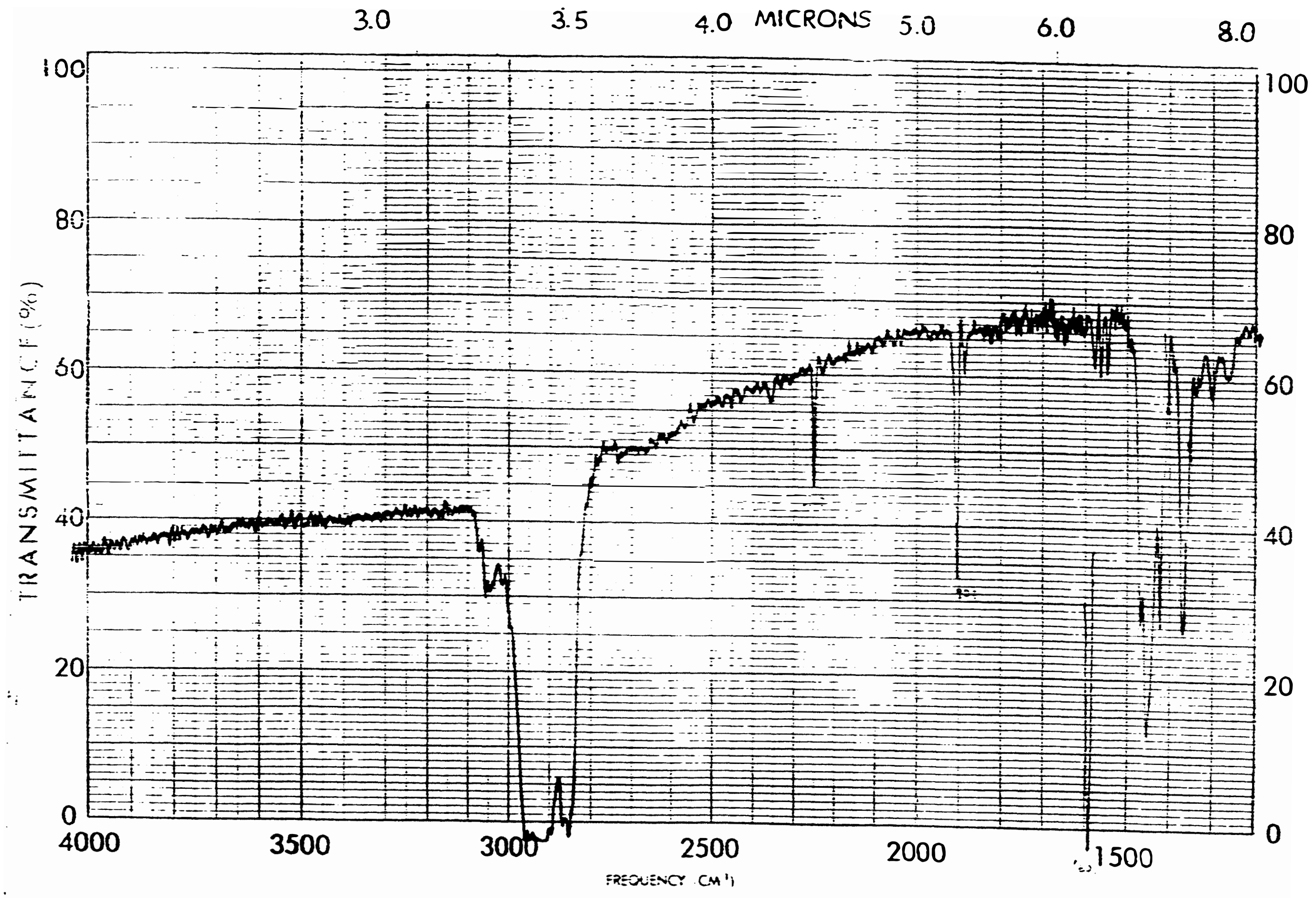
### 4. Synthesis of Ruthenium (II) carbonyl tertiary Phosphine complexes.

#### A. Synthesis of $(PPhMe_2)_3RuCOCl_2$.

Two different procedures for the preparation of this complex have been employed, but the product obtained in each

Figure 5: Infrared spectrum of

$(PPh_3)_4Ru(\eta^2 CH_3CN) \cdot CH_3CN$



SAMPLE Ru (0) complex

Expt March 4th

333-130

CURVE NO.

CONC.

CELL PATH KBr

REFERENCE Nujol

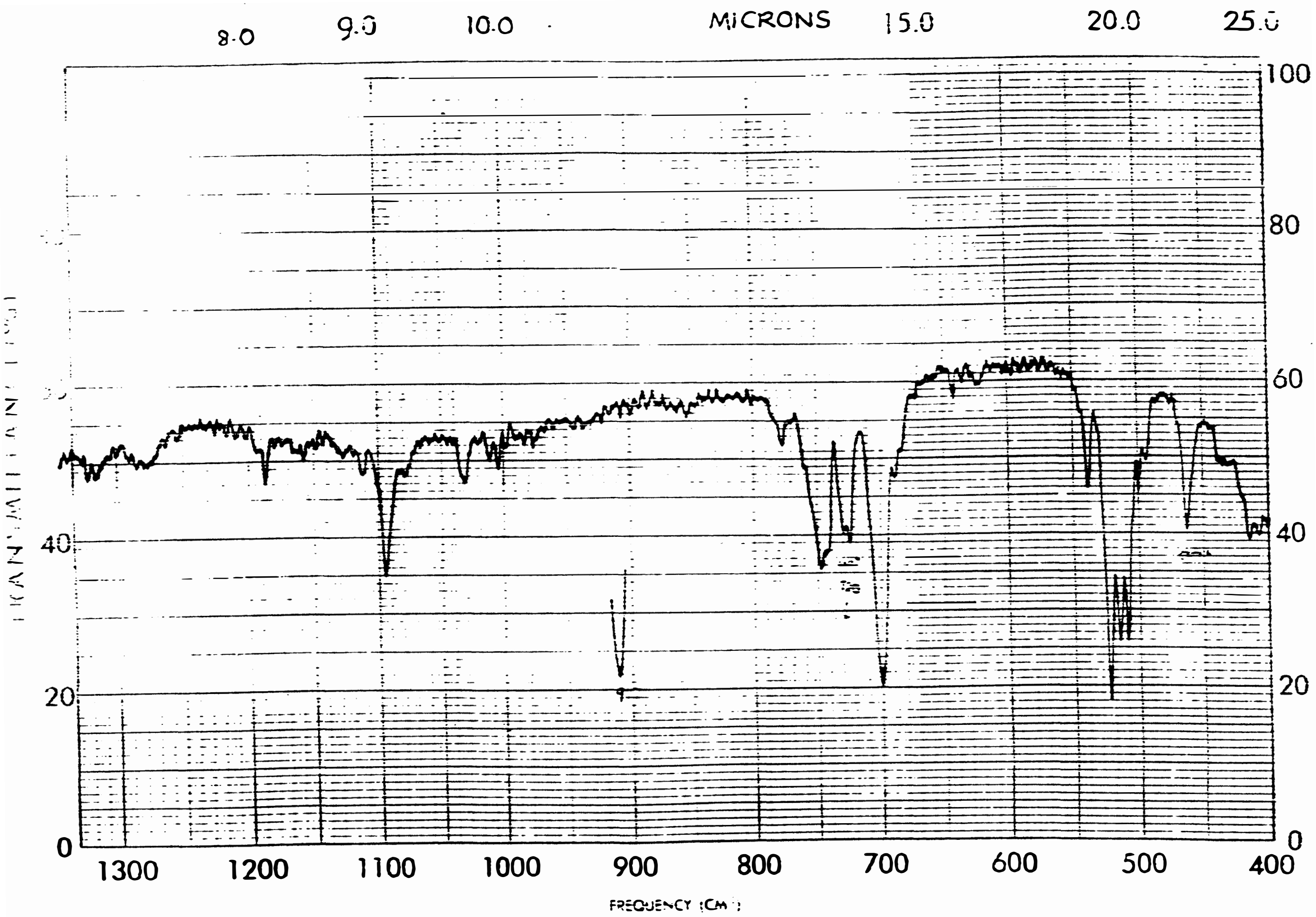
SCAN SPEED Fast

SLIT Normal

REMARKS

OPERATOR NAI

DATE March 6th.



SAMPLE Ru (0) complex.

ORIGIN Expt March 4th

SOLVENT

CURVE NO.

CONC.

CELL PATH KBr

REFERENCE Nujol

SCAN SPEED Fast

SLIT Normal

OPERATOR NAS

DATE March 6th

REMARKS

case was contaminated with impurities[7]. Therefore, a new approach for the preparation of pure product was sought. Insertion of CO as shown in eq. (8) was accomplished.

$$(PPhMe_2)_4RuCl_2 + xsCO \xrightarrow{CH_3CN} (PPhMe_2)_3RuCOCl_2 \quad (8)$$

Into a 250 mL round bottom flask, equipped with a z-neck was placed, $(PPhMe_2)_4RuCl_2$ (2.438g, 3.365 mmol). To this solid in the dry box was added 120 mL of dry degassed $CH_3CN$. The yellow slurry, under $N_2$, was removed from the box, and CO was bubbled with stirring through it for 4 hrs. Most of the solid dissolved, and a yellow solution resulted. The solution was filtered in the box and the solvent was pumped off under vacuum . As the volume was reduced, a bright oily yellow liquid was obtained. The yellow oil was triturated with hexane. A light yellow powder was formed after the mixture was stirred overnight. The powder was collected by filtration in the box and dried under vacuum for 15 hrs at room temperature. The yield was 90% based on Ru. This complex melted at 179-181 $^{o}C$ to give a yellow liquid (lit. 179-181 $^{o}C$)[17]. The carbonyl band was observed at 1952 $cm^{-1}$.

### B. Synthesis of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$

This complex was prepared by insertion of CO.

$$\begin{array}{c} (PPh_2Me)_4RuCl_2 \quad + \quad xsCO \\ \downarrow CH_3CN \\ (PPh_2Me)_2RuCO(CH_3CN)Cl_2 \end{array}$$

Into a 100 mL z-neck round bottom flask inside the dry box was placed $(PPh_2Me)_4RuCl_2$ (1.000g, 1.027 mmol) and $CH_3CN$ (60 mL). The orange suspension was taken out of the box and CO was bubbled through it. The orange suspension dissolved, and a lemon yellow solution was obtained after one hour. The yellow solution was purged with CO for another 3 hrs, taken into the box, and filtered. The solvent was removed by stirring the solution under vacuum . As the volume was reduced, a mixture of a milky yellow precipitate and an oil was observed. The mixture was triturated with hexane and stirred overnight. A pale yellow powder was collected by filtration and dried under vacuum for 24 hrs at room temperature.

The product, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ (0.657g) was obtained in 99% yield. The solid melted at 163-165 $^{o}C$ to give an orange liquid. The carbonyl band of the solid was observed at 1940 $cm^{-1}$.

### 5. Conductivity Measurement

### A. Cell constant

The conductivity cell constant was determined from a standard 0.0200M potassium chloride solution. This solution was made by dissolving 0.1491g (2.0000 mmol) of potassium chloride in 100 mL of deionised water. The conductivity cell was mounted in a 25.0 $^{o}C$ thermostat bath. The resistance of the solution was measured with a conductivity bridge.

The mean resistance of the 0.0200 M KCl was found to be 188.1 ± .4 ohms. The specific conductance of 0.0200 M KCl[18] at 25.0 °C is 0.002768 $ohm^{-1}$ $cm^{-1}$. The cell constant was calculated and a value of 0.327 ± 0.001 was obtained.

## B. Standard solutions

The complexes, $[(CH_3CH_2)_4N]ClO_4$ and $[(CH_3CN)_6Ni](BF_4)_2$, prepared by Sherman, were used as the standards in determining the number of ions present in the solution. The former dissociated in $CH_3CN$ to give 2 ions and the latter gives 3 ions. In addition, a table for general values of molar conductivities for the number of ions present in the solution was used[19].

## C. Conductivity of Ru (II) complexes.

The Ru (II) complexes used were $(PPh_3)_4RuCl_2$, $(PPh_2Me)_4RuCl_2$, $(PPMe_2)_4RuCl_2$, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$.

The resistance of dry, degassed $CH_3CN$ and the resistance of the circuit were measured in the same conductivity cell. The resistance measured were used to calculate the background conductance. All the measurements were done in the dry box at 29.0 °C.

The solution of Ru (II) complexes were made by dissolving a weighed amount of the complex in 50 mL of

$CH_3CN$ in a volumetric flask. The cell was rinsed with the prepared solution three times and then filled with the test solution. The resistance measurements were made and tabulated as shown in Table 1.

Excess ligand was also added to the test solution to study the effect of the ligand on the dissociation of the Ru (II) complexes. The resistance of the solution remained the same.

Table 1: Mean Resistance of Ru (II) complexes in $CH_3CN$

| Compound | Concentration (mM) | Mean Resistance x10$^{-2}$ (ohm$^{-1}$) |
|---|---|---|
| $CH_3CN$ | --- | 13.5 ± 0.1 |
| $[(C_2H_5)_4N]ClO_4$ | 5.00 | 3.91 ± 0.02 |
| $[(CH_3CN)_6Ni](BF_4)_2$ | 8.62 | 1.51 ± 0.01 |
| $(PPh_3)_4RuCl_2$ | 5.00 | 5.64 ± 0.01 |
| $(PPh_2Me)_4RuCl_2$ | 7.47 | 4.32 ± 0.02 |
| $(PPhMe_2)_4RuCl_2$ | 4.29 | 4.86 ± 0.04 |
| $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ | 3.36 | 13.4 ± 0.1 |
| $(PPhMe_2)_3RuCOCl_2$ | 5.36 | 13.5 ± 0.1 |

## 6. Polarography

### A. Apparatus

The electrochemical cell employed in all polarographic measurement was manufactured by IBM Instruments Inc. The 100 mL pyrex cell had a teflon cap with five ports, each fitted with Teflon sleeves. The ports contained the working electrode, auxiliary electrode, reference electrode and gas dispersion inlets both in and over the solution. The cell was airtight and the temperature was controlled by fitting a plastic jacket around the cell which was connected to a constant temperature water bath.

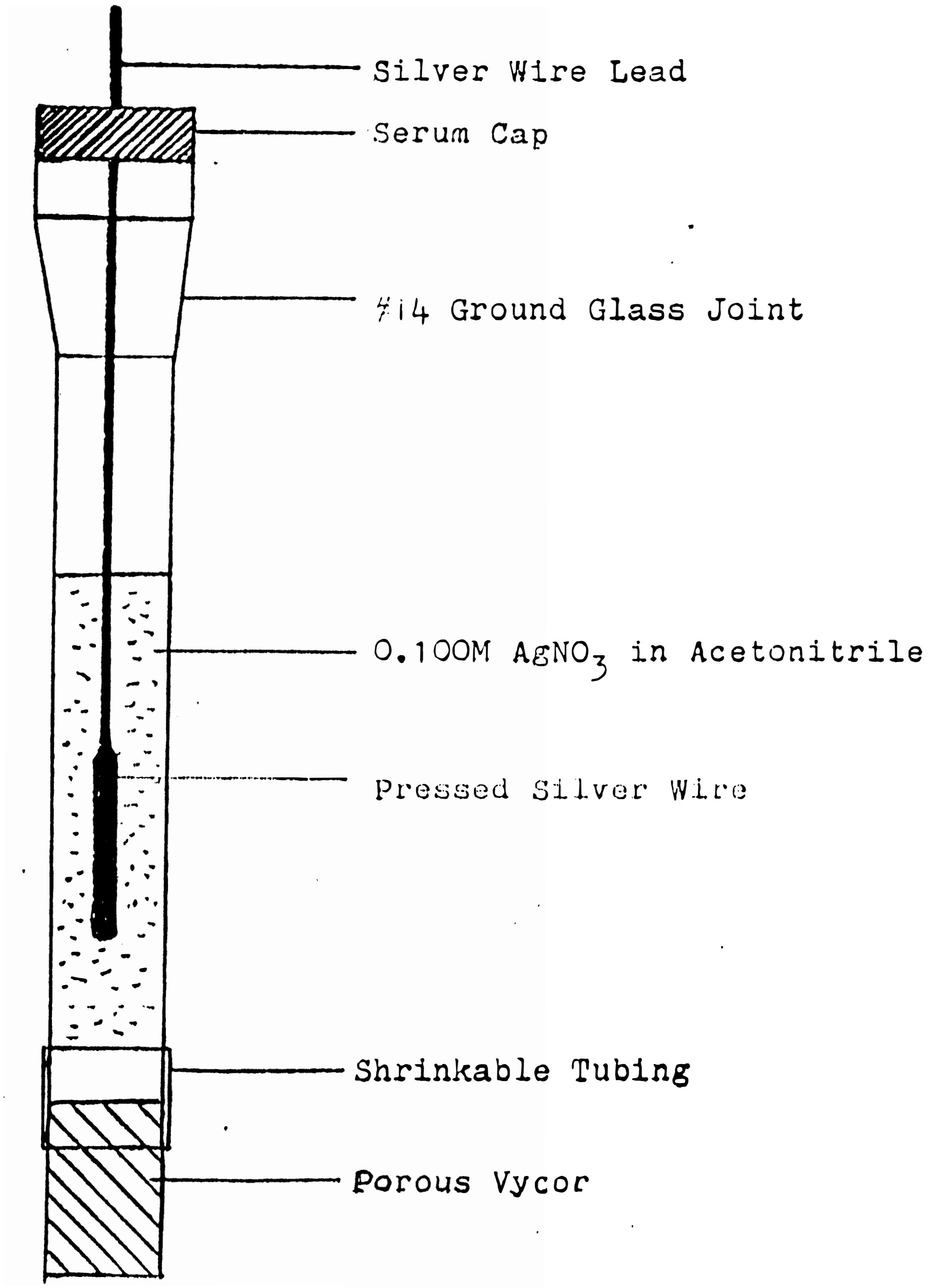
The working electrode was a conventional dropping mercury electrode. The Hg column included a 14.1 cm length of Capillary (Sargent Welch) attached to a 75.0 cm length of 6 mm pyrex tubing by short tygon tubing. Upon varying the height of a mercury reservoir connected to the column, the mercury pressure could be controlled.

The reference electrode chosen for these studies was a 0.100 M Ag/$AgNO_3$ (Fig. 6). The electrode was made from a tapered-end glass tube with 14/23 ground glass joint. An 8 mm porous Vycor plug was attached with shrinkable teflon to the tapered end. The electrode was soaked in 0.100 M TEAP solution of $CH_3CN$ for one day prior to addition of 0.100M silver nitrate. A silver wire and 0.100 M $AgNO_3$ solution in $CH_3CN$ were placed inside the tube. The tube was then sealed with rubber septum cap. The reference electrode was isolated from the test solution by a glass tube containing a fine porous glass frit.

The auxiliary electrode consisted of a coil of platinum wire sealed in soft glass tubing, 7 mm in diameter. The inside contact to the platium wire was made by partially filling the tube with mercury in contact with

FIGURE 6

Ag/0.10M $AgNO_3$ in Acetonitrile Reference Electrode



copper wire which extended outside the glass tube. A serum cap was used to seal the end.

The nitrogen introduced for deaeration was saturated with $CH_3CN$ by passing it through a presaturater containing HPLC grade $CH_3CN$, emersed in a temperature bath. The saturated nitrogen was transported to the cell via pyrex lines with two teflon spindle stopcocks to allow either purging or maintaining the $N_2$ pressure within the cell.

### B. Solutions

Each polarographic solution consisted of a 1 x $10^{-1}$M concentration of the electroactive species of interest along with the supporting electrolyte present as 0.100 M TEAP in $CH_3CN$. The solution of each complex was prepared in the dry box by adding the appropriate amount of the electroactive species to 0.10 M TEAP in a 25 mL volummetric flask. The empty electrochemical cell was first purged with nitrogen for at least 15 mins. The solution was then transferred into the cell via a 50 mL syringe or by direct addition from the volummetric flask through the reference electrode port. Deaeration was achieved by degassing with $N_2$ for another 15 mins prior to the polarographic measurements. A nitrogen atmosphere was maintained above the test solution during the measurements.

### C. Polarographic measurements.

Polarographic data were observed by measuring the current as a function of the applied potential displayed on the Varian X-Y recorder. For each polarographic wave observed the diffusion current was measured as a function of the mercury pressure (height).

The measurements of the half-wave potential ($E_{1/2}$) and limiting current ($i_L$), were obtained in the following manner. The limiting current was obtained by drawing a line parallel to the residual current, obtained by extrapolation of the linear flat portion of the curve preceeding the wave, and measuring the difference between the lines. The $E_{1/2}$ is the potential at which 1/2 of the measured diffusion current crosses the rising portion of the wave.

The constant mt (where m is the mass flow rate in mg/sec and t is the drop time ) was measured in $CH_3CN$ at different potentials. This constant is needed in the correction of the pressure of the mercury due to the surface tension of the solution. The measurement was made by collecting 25 drops of mercury, washing with $CH_3CN$, drying with kimwipes and finally weighing the mercury. The time for collecting 25 drops was obtained with a stopwatch (±.1 sec). From the mass per drop and the drop time, the capillary constant was thus determined.

### 7. Attempted preparation of Ru(0) complexes

#### A. Preparation of 1 % sodium amalgam[20]

The triple-distilled mercury was pinholed twice to remove oxide and kept in the box prior to use. The sodium was cut, washed with hexane and weighed in the box.

Sodium (1.074g, 0.04700 mol) was placed in a wide neck Erlermeyer flask and 3.9 mL of mercury was added to it. Another 4.0 mL of the mercury was added slowly to keep the reaction going. The amalgam was cooled and kept in an airtight vial.

#### B. Reaction of $CH_3CN$ with 1% Na-Hg

Since $CH_3CN$ was used as the solvent, its reactivity towards 1 % Na-Hg was studied.

In a 50 mL round bottom flask, 20 mL of $CH_3CN$ was placed and 1 mL of 1% Na-Hg was added and stirred for 10 hrs. The solution was decanted into the beaker and filtered. A grey solid was obtained. The infrared spectrum of this product did not show any absorption.

#### C. Reaction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 1% Na-Hg

In an attempt to prepare $(PPh_2Me)_2RuCO(CH_3CN)_2$, the reaction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 1% Na-Hg was carried out.

Into a 100 mL round bottom flask was added $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ (0.737g, 1.15mmol) to 50 mL

$CH_3CN$. The amalgam, Na-Hg, (1%, 2 mL) was added to the slurry and stirred. All of the solid dissolved, and an orange solution resulted. After 10 mins the solution turned dark green and after 20 mins it changed to a dark brown color. After 15 hrs the dark brown solution was decanted into a beaker, and the amalgam was rinsed with $CH_3CN$. The solution was filtered, and a grey solid was obtained. The infrared spectrum of the grey solid indicated that it was the same product as in reduction of $CH_3CN$. The dark brown solution was pumped off under vacuum, and a dark brown solid was obtained.

About 40 mL of dry, degassed HPLC hexane was added to the dark brown solid and stirred. The dark brown powder was collected by filtration and dried at room temperature under vacuum. An Orange-brown solid (0.616g) was obtained. The solid melted at 124-126 $^{o}C$ and decomposed at 135 $^{o}C$. The solid was studied with infrared, $^{1}H$ and $^{31}P$ NMR spectroscopy.

The infrared spectrum gave two characteristic peaks due to the CN stretching at 2150 and 2180 $cm^{-1}$, A broad peak with a shoulder due to CO was observed at 1910 $cm^{-1}$. The observed shoulder might be due to Ru-H stretching (1905 $cm^{-1}$). Signals at 1550 and 1410 $cm^{-1}$ were observed and assigned to orthometallated species.

The $^{1}H$ and $^{31}P$ NMR spectra from $C_6D_6$ could not be interpreted since the signals were poorly resolved as a result of low solubility. The elemental analysis did not agree with the expected formula, $(PPhC_6H_4)HRuCO(CH_3CN)PPh_2Me$. The calculated values for the expected product were 61.05 %C, 5.12 %H, 10.85 %P and 2.45 %N, but the elemental analysis values were 66.68 %C, 5.64 %H, 8.65 %P and 0.99 %N.

D. Reaction of $(PPhMe_2)_3RuCOCl_2$ with 1 % Na-Hg

The procedure for the attempted synthesis of the complex, $(PPhMe_2)_3RuCO(CH_3CN)$ was based on the work of Wilkinson[21].

A solution of $(PPhMe_2)_3RuCOCl_2$ (1.11g, 1.80 mmol) in 50 mL of HPLC $CH_3CN$ was prepared. To the slightly yellow solution was added Na-Hg (1 %, 2 mL). The mixture was stirred, and its color changed from orange to dark brown within 3 mins.

The solution was stirred for 15 hrs, and a greyish blue solid was formed. The amalgam was decanted into a beaker and the solid was collected under vacuum. The solid obtained appeared to be the same as that from the reaction of $CH_3CN$ with 1% Na-Hg.

The filtrate was transferred to a 100 mL round bottom flask and the volume was reduced under vacuum. As the volume decreased, a dark brown oil was obtained. The oil was triturated with 40 mL HPLC grade hexane and stirred overnight. Some of the oil dissolved and gave a dark brown solution. The volume of hexane was reduced by half under vacuum and 20 mL of benzene was added. All of the oil dissolved.

The dark brown solution was divided into two halves. The first half was pumped to dryness. The oil obtained was studied by infrared, $^1H$ and $^{31}P$ NMR spectroscopy. The ligand, $PPhMe_2$, was added to the other half of the solution and stirred. The volume of the solution was reduced and a thick oil was obtained. Benzene, toluene, ethanol and a mixture of pentane/acetonitrile were used in an attempt to crystallize the oil, but none of the solvents gave a successful result.

### 8. Reaction of $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN)\cdot CH_3CN$ with hexane

A suspension of 0.468g (0.380mmol) of $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN)\cdot CH_3CN$ in 35 mL of hexane was stirred and refluxed in the dry box. The yellow suspension turned brown after 10 mins. The brown suspension was heated under reflux for 16 hrs. The dark brown slurry was cooled and filtered under vacuum. The brown powder collected was dried under vacuum for 24 hrs. The yield of the product was 0.16g. The product decomposed at 127 $^oC$. The product was studied by infrared and $^{31}P$ NMR spectroscopy.

The volume of the filtrate was reduced under vacuum and a dark brown oil was obtained. Pentane (10 mL) was added and stirred until all the oil dissolved. The sealed flask was taken out of the box and cooled in a dry ice and acetone mixture ($-10^oC$). The solution become colorless and a dark green suspension was obtained. The product was insoluble in acetonitrile, hexane, benzene, methylene chloride and toluene.

# RESULTS AND DISCUSSION

## 1. Synthesis of Ruthenium (II) complexes

### A. Synthesis of $(PPhMe_2)_3RuCOCl_2$

The compound, $(PPhMe_2)_3RuCOCl_2$ was synthesized by the following reactions (Eq 9-11).

$RuCl_3\ 3H_2O + 6PPh_3 \xrightarrow{CH_3OH} (PPh_3)_4RuCl_2$ (9)

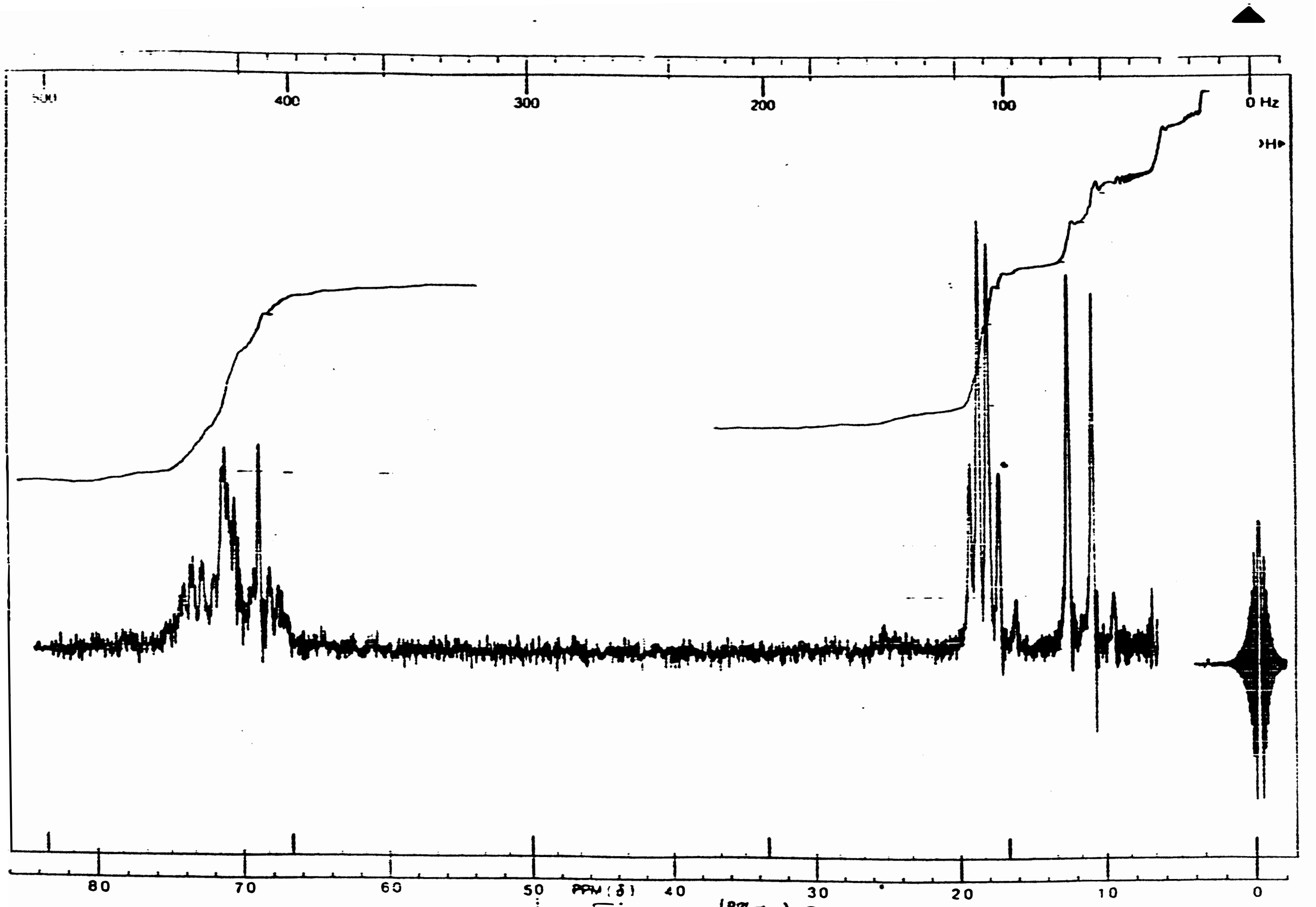
$(PPh_3)_4RuCl_2 + 6PPhMe_2 \xrightarrow{C_6H_{14}} (PPhMe_2)_4RuCl_2$ (10)

$(PPhMe_2)_4RuCl_2 + xsCO \xrightarrow{CH_3CN} (PPhMe_2)_3RuCOCl_2$ (11)

The isolated complexes obtained from reactions 9 and 10 were identified by comparing their melting points and infrared spectra with literature values. The complex isolated from reaction 10 was identified as $(PPhMe_2)_3RuCOCl_2$. Elemental analysis (48.78% C, 5.35% H and 15.66% P) agreed with that expected (48.87% C, 5.41% H and 15.12% P). This compound melted under nitrogen at 179-181 $^oC$, in agreement with the literature value, to give a yellow liquid[17].

Infrared, $^1H$ and $^{31}P$ NMR spectroscopy were used to determine the structure of the complex made by CO insertion . The $^1H$ NMR spectrum (Fig 7) of the complex in $CD_3Cl$ exhibited a doublet ($\delta$=1.38ppm, $J_{PH}$=10.4 Hz), a quartet, 1:3:3:1, caused by two overlapping triplets ($\delta$=1.93ppm and $\delta$=2.02ppm, $J_{PH}$=4.4 Hz) and a multiplet at 7.16 ppm. The doublet indicated a methyl group coupled to a single phosphorus nucleus. The two overlapping triplets suggested that the methyl groups on the phosphorus atoms

Figure 7: $^1H$ NMR spectrum of $(PPhMe_2)_3RuCOCl_2$ in $CD_3Cl$



MANUAL

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INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 | 100 | 250 | 500 | 1000
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500
FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: 0.03

AUTO ☐
(250)
(500)
( 2)
( 05)

SAMPLE: (PPhme$_2$)$_3$ RuCoCl$_2$
SOLVENT: CDCl$_3$
DEC. LEVEL:

REMARKS: lock on Tms

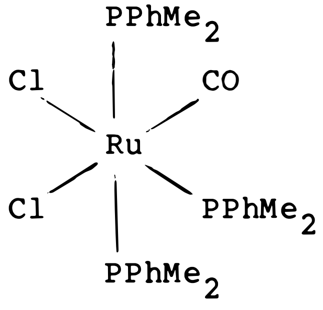
**NORELL, INC.**
LANDISVILLE, N.J. 08326
T60 Phone: (609) 697-0020

DATE:

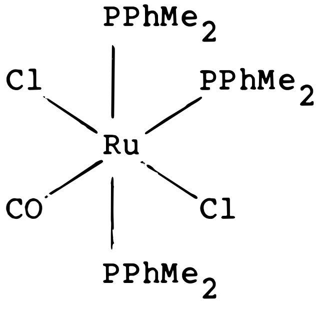
OPERATOR: NAI.

SPECTRUM NO:

were not equivalent or that there were two isomers present. The two possible isomers can be presented as in structure I and II

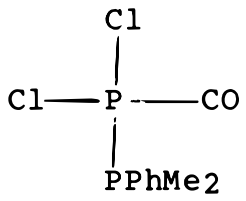


(I)



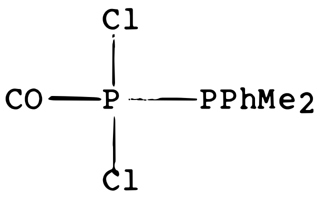
(II)

It is unlikely that phosphorous-proton coupling for the cis phosphine would the same for isomer (I) and (II), and thus the appearance of the single doublet argues against the existance of both isomers. The methyl groups on the phosphorus atoms trans to one another should be equivalent unless there is no plane of symmetry through them. Such is the case for isomer (I) as shown below, but is not the case for isomer (II). Thus isomer (I) is most consistent with the presence of overlapping triplets. A complex multiplet at 7.16 ppm arises from the phenyl groups of the ligands.



$\mathrm{Cl{-}\overset{Cl}{\underset{PPhMe_2}{P}}{-}CO}$

top view (I)



$\mathrm{CO{-}\overset{Cl}{\underset{Cl}{P}}{-}PPhMe_2}$

top view (II)

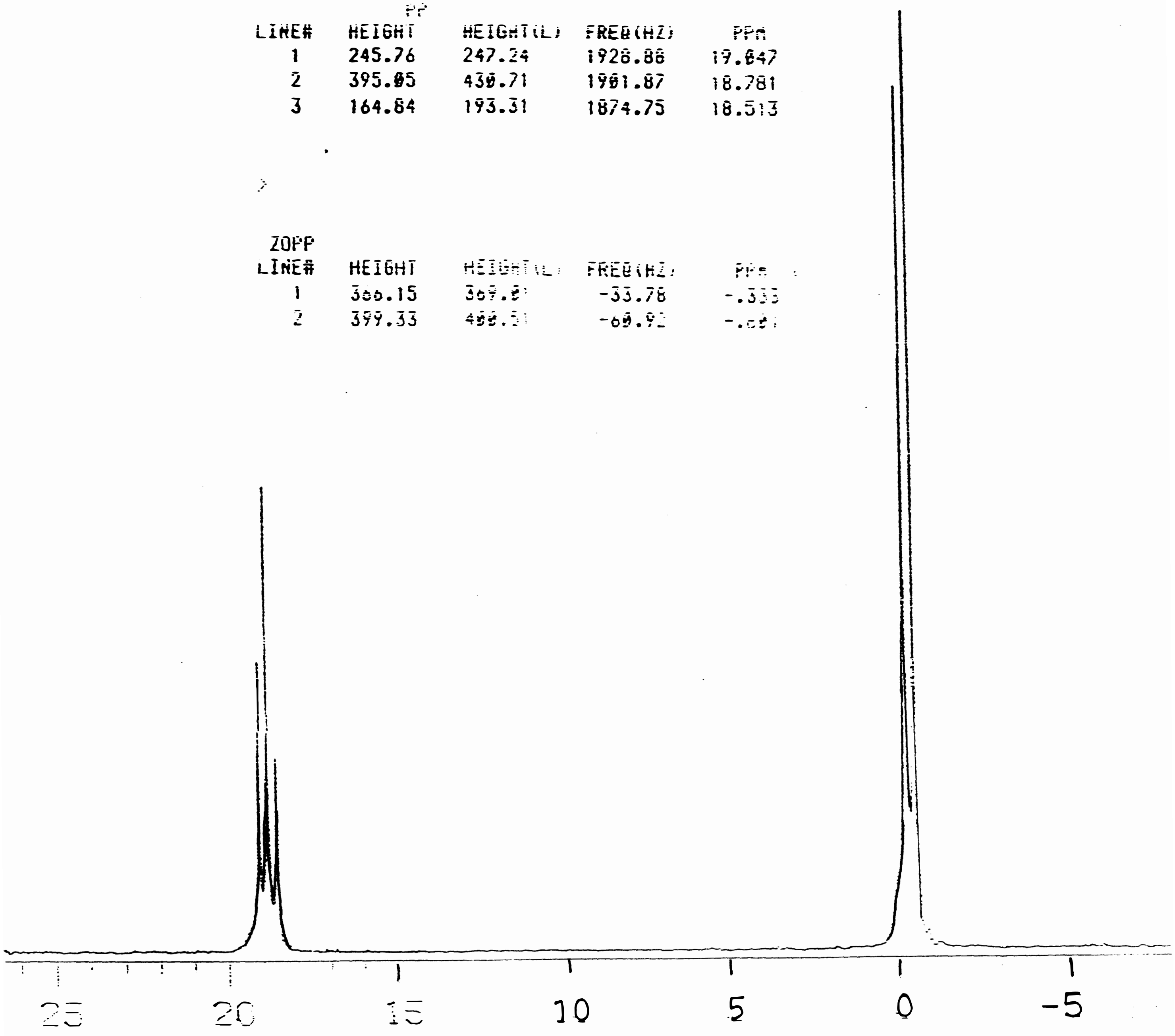
The $^{31}P$ NMR spectrum (Fig 8) exhibits a doublet at -1.42 ppm ($J_{PP}$ = 27.1 Hz) and a triplet at 17.74 ppm ($J_{PP}$ = 27.5 Hz). The spectrum shows the expected $A_2X$

Figure 8: $^{31}P$ NMR spectrum of $(PPhMe_2)_3RuCOCl_2$ in $CD_3Cl$

```
                PP
LINE#   HEIGHT     HEIGHT(L)  FREQ(HZ)     PPM
   1    245.76     247.24     1928.86    19.047
   2    395.05     430.71     1901.87    18.781
   3    164.64     193.31     1874.75    18.513


>


 ZOPP
LINE#   HEIGHT     HEIGHT(L)  FREQ(HZ)     PPM
   1    366.15     369.0[illegible]      -33.78     -.333
   2    399.33     400.5[illegible]      -60.92     -.601
```



pattern and is consistent with either isomer (I) or isomer (II). The doublet arises from two phosphorus ligand atoms in a trans configuration coupled to one cis phosphorus atom. The triplet can be explained by one phosphine ligand split by the two equivalent phosphorus atoms of the remaining ligands. No evidence for the presence of the two isomers could be obtained from the $^{31}P$ NMR spectrum.

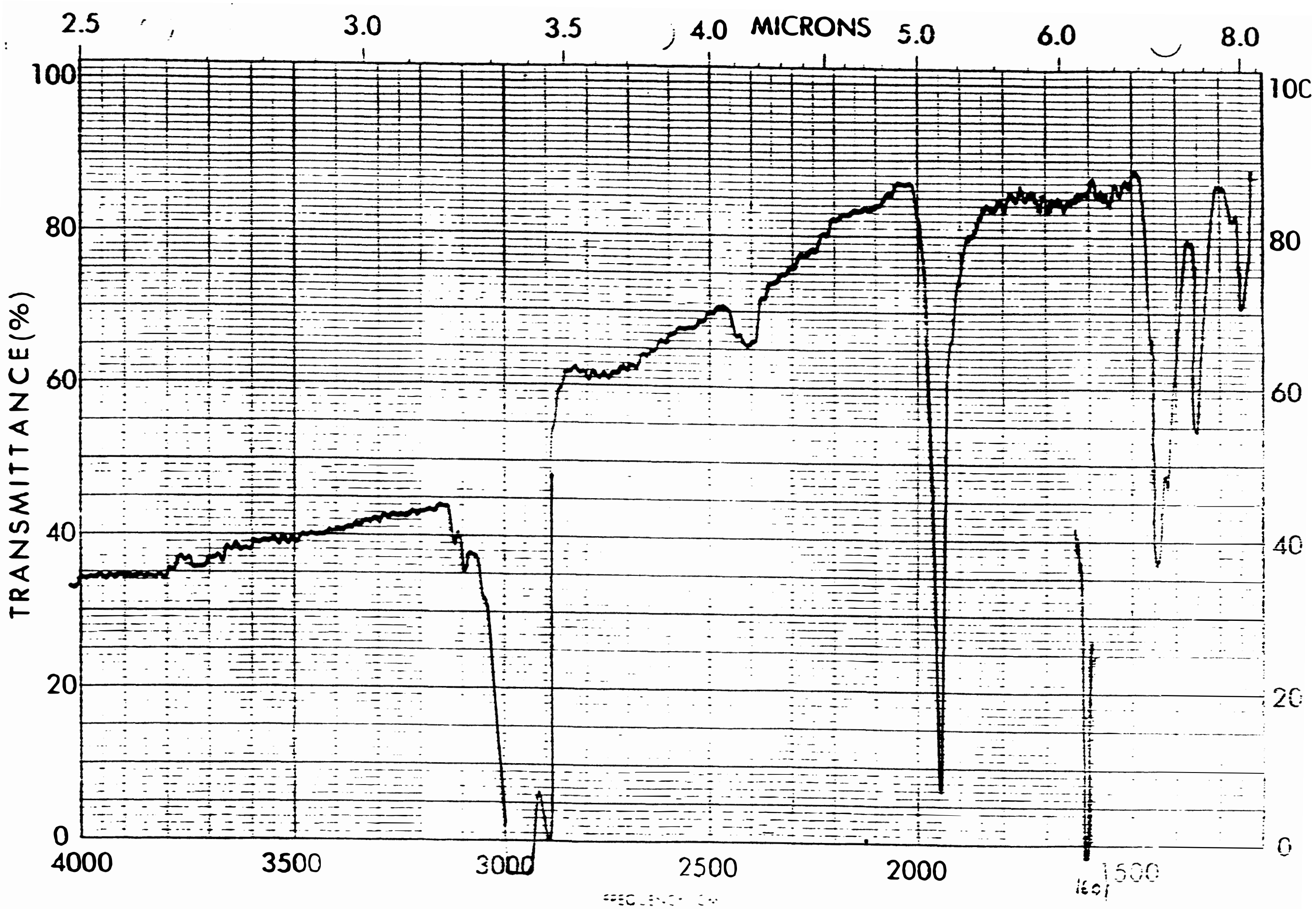
Isomer (I) can be distinguished from (II) by looking at the C=O stretching mode in the infrared spectrum. Most carbonyl ruthenium complexes show strong infrared absorptions in the range 1900-2050 $cm^{-1}$ due to carbonyl stretching modes. Mawby[9] observed the CO stretching for CO trans to Cl at 1952 $cm^{-1}$ and CO trans to $PPhMe_2$ at 1980 $cm^{-1}$. From our observed CO stretching frequency, 1950 $cm^{-1}$ (Fig 9), one can conclude that only one isomer was made by our method of synthesis (isomer I). This also agrees with the $^1H$ NMR data, which exhibited two overlap triplets indicating the methyl groups on the trans phosphorus atom in this complex were not equivalent.

## B. Synthesis of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$

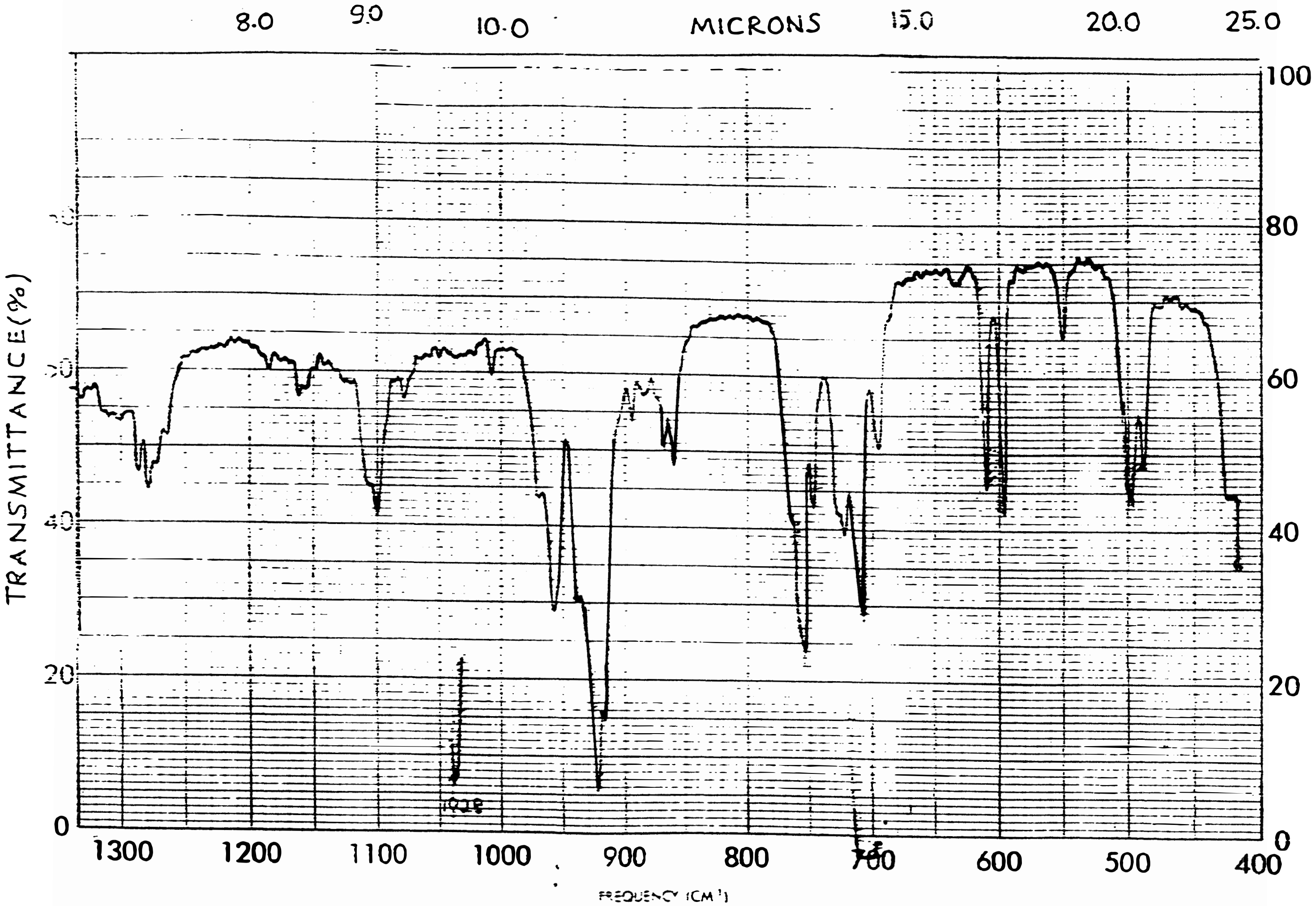
The attempted synthesis of $(PPh_2Me)_3RuCOCl_2$, by the reactions shown in equations 9-11 gave $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$. The calculated values for C, H, P and N for the complex are 54.30%, 4.56%, 9.66%, and 2.18%, respectively. Elemental analysis gave 54.38% C, 4.18% H, 10.15% P and 2.15% N.

Figure 9: Infrared spectrum of

$(PPhMe_2)_3RuCOCl_2$



SAMPLE (PPhMe$_2$)$_3$ Ru(CO)H$_2$
CURVE NO
ORIGIN Aug 74
CELL PATH KBR
SOLVENT Nujol
SCAN SPEED Fast
SLIT N
OPERATOR NAI



SAMPLE (PPhMe₂)₃ Ru CO Cl₂

ORIGIN Aug 7th 1985 .

SOLVENT Nujol

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED fast

SLIT N

OPERATOR ND)

DATE

REMARKS

DP 1123 (3373204)

The unexpected composition of the product of reaction 11 when $PPh_2Me$ is used, instead of $PPhMe_2$, suggests that the precursor to $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ is different from the precursor to $(PPhMe_2)_3RuCOCl_2$. Earlier work by Olson provides some insight into the nature of the complexes $(PPh_3)_4RuCl_2$ and $(PPh_2Me)_4RuCl_2$ and indicates that the phosphorus ligands exchange with the coordinating solvent.

$$(PPh_3)_4RuCl_2 \xrightarrow{CH_3CN} [(PPh_3)_2Ru(CH_3CN)_3Cl]Cl + 2PPh_3 \quad (12)$$

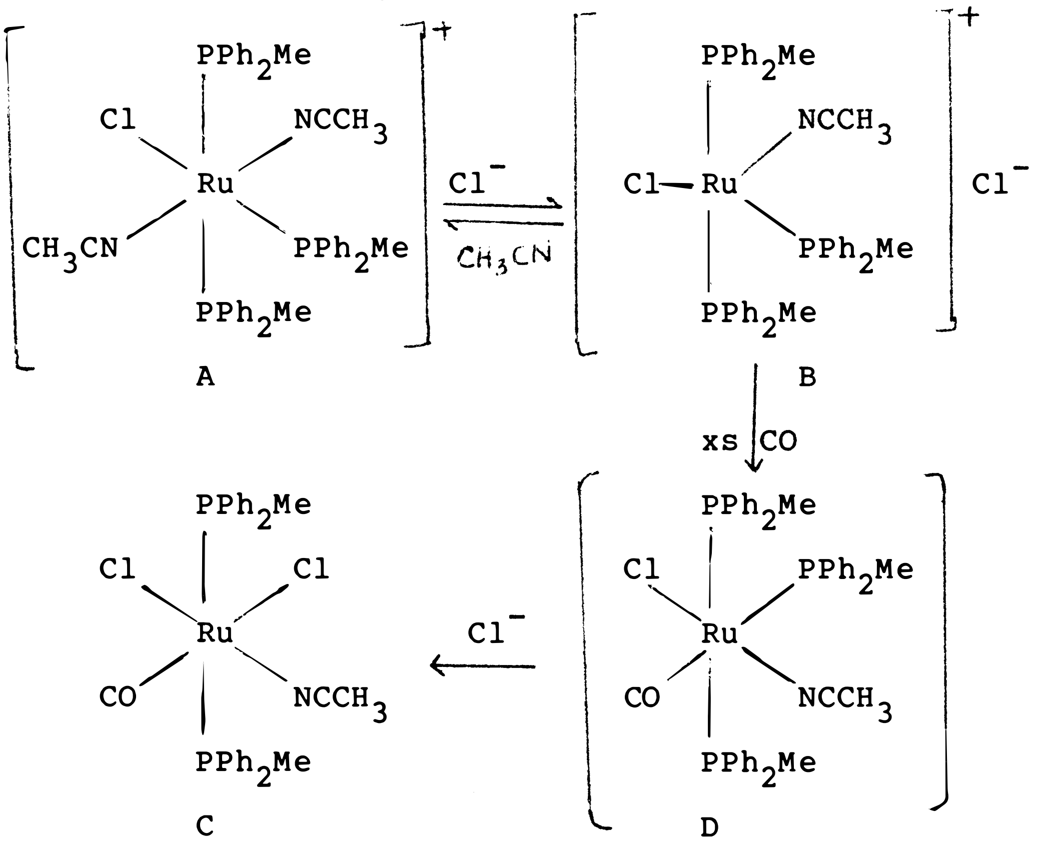
$$(PPh_2Me)_4RuCl_2 \xrightarrow{CH_3CN} [(PPh_2Me)_3Ru(CH_3CN)_2Cl]Cl + PPh_2Me \quad (13)$$

In constrast, exchange was not observed for $(PPhMe_2)_4RuCl_2$ possibly because of reduced the steric requirement of the phosphine.

As in most Ru(II) complexes, $[(PPh_2Me)_3Ru(CH_3CN)_2Cl]Cl$ dissociates to form a 5-coordinate complex. The coordination of carbon monoxide is then possible since there is a vacant coordination site. The suggested scheme for the formation of the monocarbonyl complex can be shown as scheme 1. The insertion of carbon monoxide in cation B could lead to CO trans to $CH_3CN$ or $PPh_2Me$ but CO trans to $PPh_2Me$ is more often observed in ruthenium (II) complexes. According to Chatt[22], a strong $\pi$-bonding ligand such as CO could remove electron density from the metal through back-bonding. As a result, the metal center becomes more positive, which weakens the Ru-$PPh_2Me$ bond. This facilitates the replacement of $PPh_2Me$ by

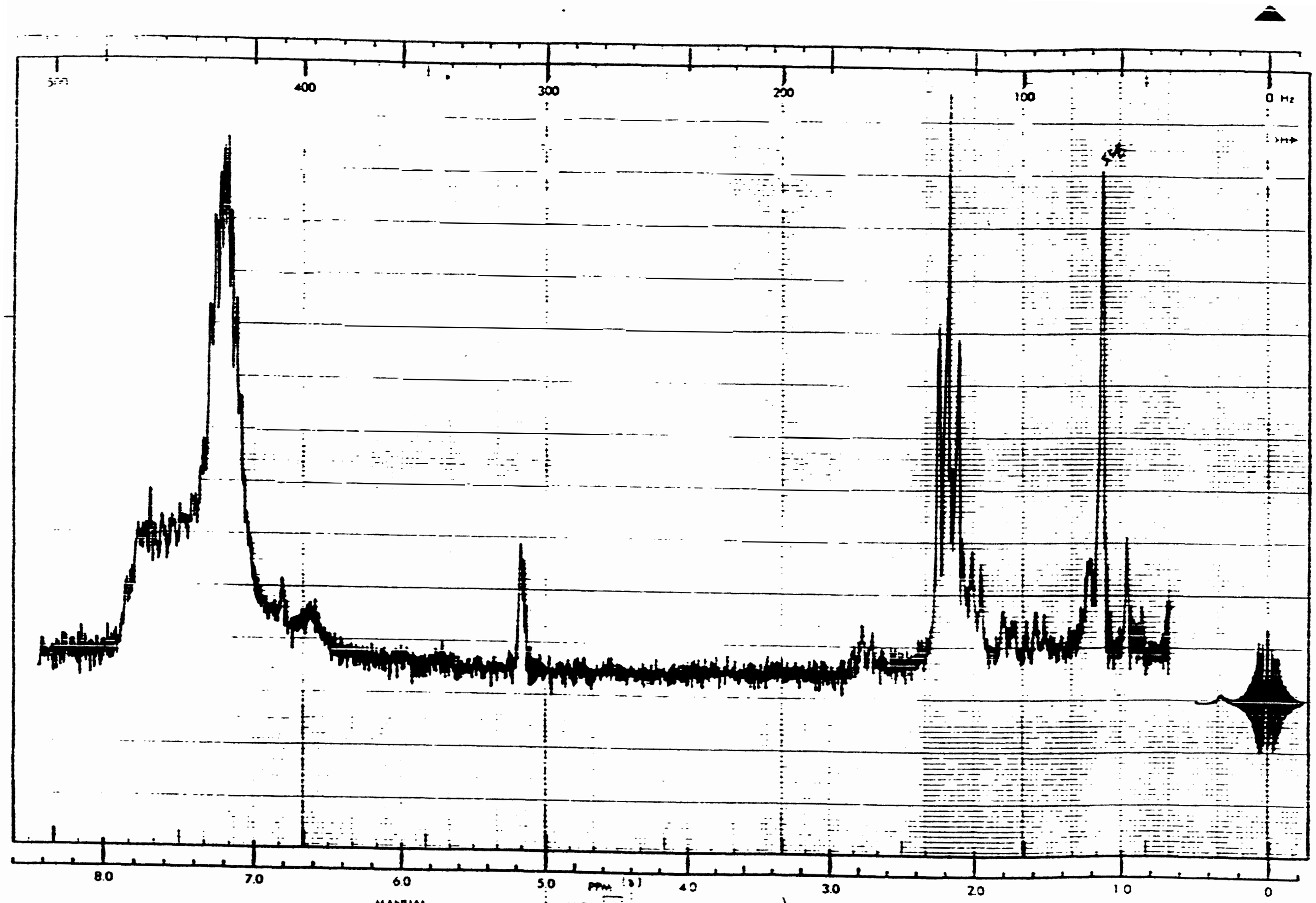
$Cl^-$. This mechanism agrees with the structure of the isolated product.

SCHEME 1



The structure of the $(PPh_2Me)_2Ru(CH_3CN)COCl_2$ was determined by infrared, $^1H$ and $^{31}P$ NMR spectroscopy. The $^1H$ NMR spectrum from $CD_2Cl_2$ (Fig 10) gives a singlet at 1.2 ppm, a triplet at 2.2 ppm and a multiplet at 7.4 ppm. A singlet at 1.2 ppm is due to the methyl group from the coordinated acetonitrile. A triplet ($J_{PH}$ = 3.5 Hz) indicates that the two diphenylmethylphosphine are mutually trans, with the methyl group on the phosphorus atoms virtually coupling with both phosphorus nuclei. The phenyl groups on the ligand give rise to the multiplet at

Figure 10: $^1H$ NMR spectrum of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ in $CD_2Cl_2$



SWEEP OFFSET (Hz): 500
SPECTRUM AMPLITUDE: 63
INTEGRAL AMPLITUDE:
SPINNING RATE (RPS): 40

MANUAL
SWEEP TIME (SEC): 30 | 120
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500
FILTER: ☑ 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: 0.05

AUTO ☐
(250)
(500)
( 2)
(.05)

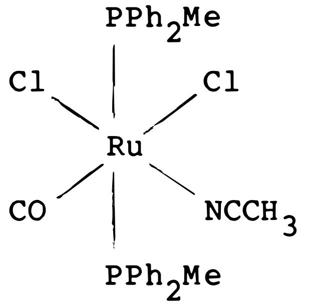
SAMPLE: ($\Phi_2$PMe)$_2$ RuCOCl$_2$ REMARKS: Lock on TMS.
obtained from Oct 2nd.
SOLVENT: $CD_2Cl_2$

DATE: Jan 15th 86
OPERATOR: NH
60 MHz NMR
SPECTRUM NO.

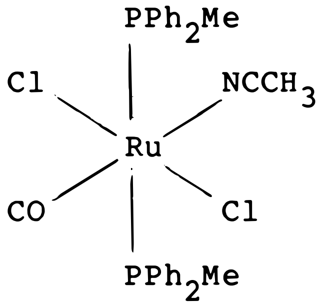
7.4 ppm. A small triplet at 2.00 ppm and a singlet at 0.9 ppm might be due to the other isomer of the compound. The peak at 5.2 ppm arises from $CH_2Cl_2$ presence in the solvent.

A singlet occurring at 17.6 ppm in the $^{31}P$ NMR spectrum of $(PPh_2Me)_2(CH_3CN)COCl_2$ (Fig 11) indicates that the phosphorus nuclei in the complex are equivalent. The $^{31}P$ and $^1H$ NMR data suggests that the two phosphorus atoms are trans to one another. A tiny triplet and a doublet caused by the impurity, $(PPh_2Me)_3RuCOCl_2$, is also present in the spectrum[7].

Since Ru(II) is a $d^6$ complex, an octahedral geometry was expected. Two diferrent isomers (structure III and IV) which are consistent with the $^1H$ and $^{31}P$ NMR results can be drawn.



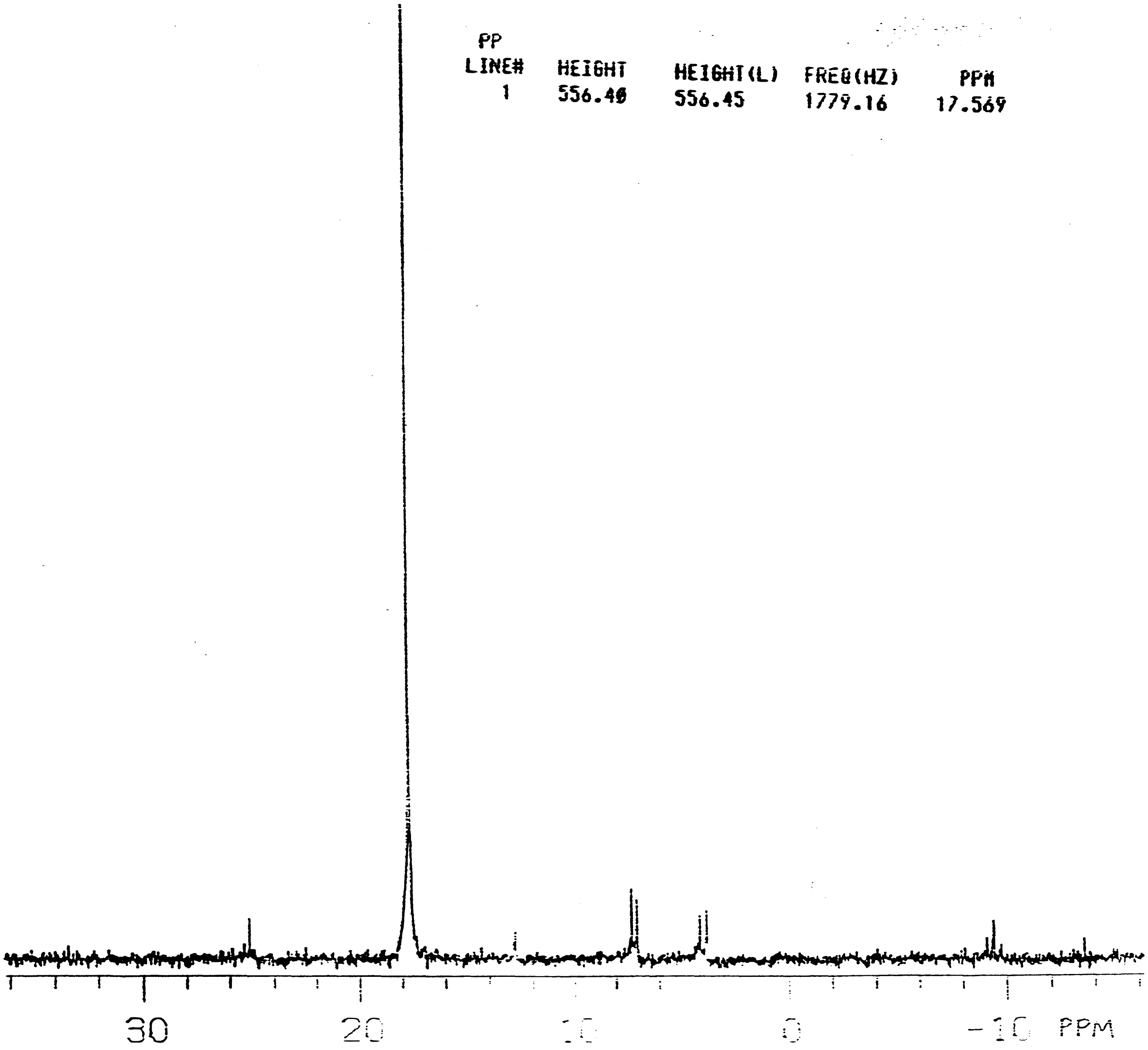
(III)



(IV)

As for the complex $(PPhMe_2)_3RuCOCl_2$, CO stretching modes in the infrared spectrum could be used to distinguish between structures (III) and (IV). Mawby[9] found out that a CO trans to an electron withdrawing group has a lower stretching frequency (1930-1950 $cm^{-1}$) than a CO trans to a donor ligand (1960-1990 $cm^{-1}$). Based on the carbonyl band

Figure 11: $^{31}P$ NMR spectrum of $(PPh_2Me)RuCO(CH_3CN)Cl_2$ in $CD_2Cl_2$



PP

| LINE# | HEIGHT | HEIGHT(L) | FREQ(HZ) | PPM |
|---|---|---|---|---|
| 1 | 556.40 | 556.45 | 1779.16 | 17.569 |

at 1938 $cm^{-1}$ (Fig 12), $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$, made by the insertion of carbon monoxide, was assigned structure (III).

Since electrochemical measurements were made in $CH_3CN$, $^1H$ NMR spectra of the complex in $CD_3CN$ were obtained. The slow exchange of coordinated $CH_3CN$ with $CD_3CN$ (solvent) was shown to occur. This exchange was indicated by a diminishing absorption with time (Fig 13 & 14) due to coordinated $CH_3CN$ (1.20 ppm) and an increasing absorption due to uncoordinated $CH_3CN$ (2.23 ppm). The multiplet centered at 1.8 ppm was due to $CD_2HCN$ and $CH_2DCN$ present in $CD_3CN$ (Fig 15). The triplet centered at 2.14 ppm and the multiplet at 7.30 ppm arise from the methyl and the phenyl group on the $PPh_2Me$ ligand. One could suggest, based on this exchange, that in solution, the observed Ru(II) complex dissociates into a 5-coordinate complex .

$$(PPh_2Me)_2RuCO(CH_3CN)Cl_2 \xrightleftharpoons{CD_3CN} (PPh_2Me)_2RuCOCl_2 + CH_3CN$$

The $^1H$ NMR spectrum of the complex in the presence of excess ligand,$PPh_2Me$, does not change as a function of time. This suggests that the complex remains intact in $CD_3CN$ in the presence of excess ligand.

## 2. Conductivity measurement of Ru(II) complexes.

### A. Theory of conductivity.

The most direct evidence for the existance of ions in the solution is the observation that the solution can conduct an electric current. Electrolytic solutions obey

Figure 12: Infrared spectrum of

$(PPh_2Me)RuCO(CH_3CN)Cl_2$

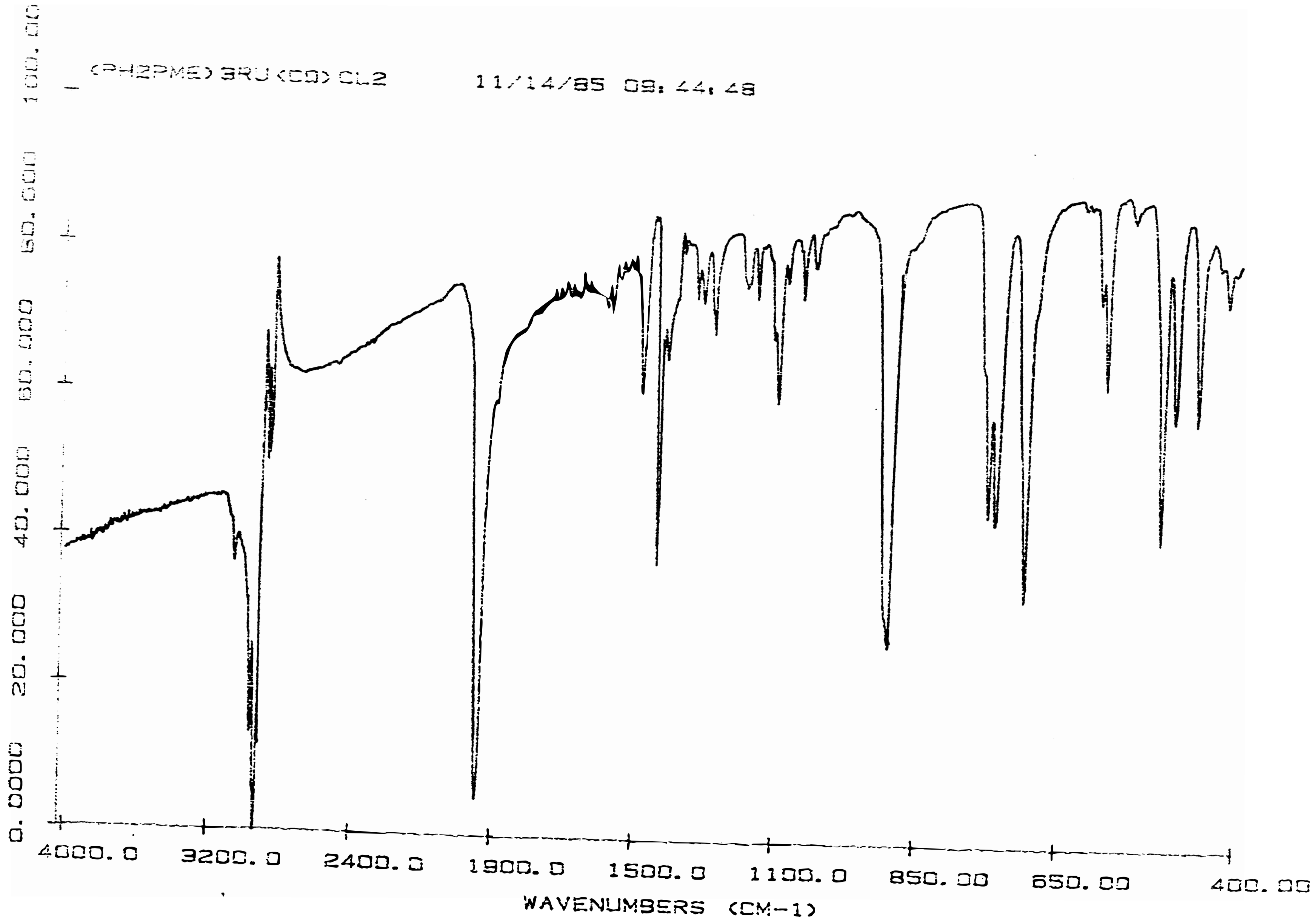
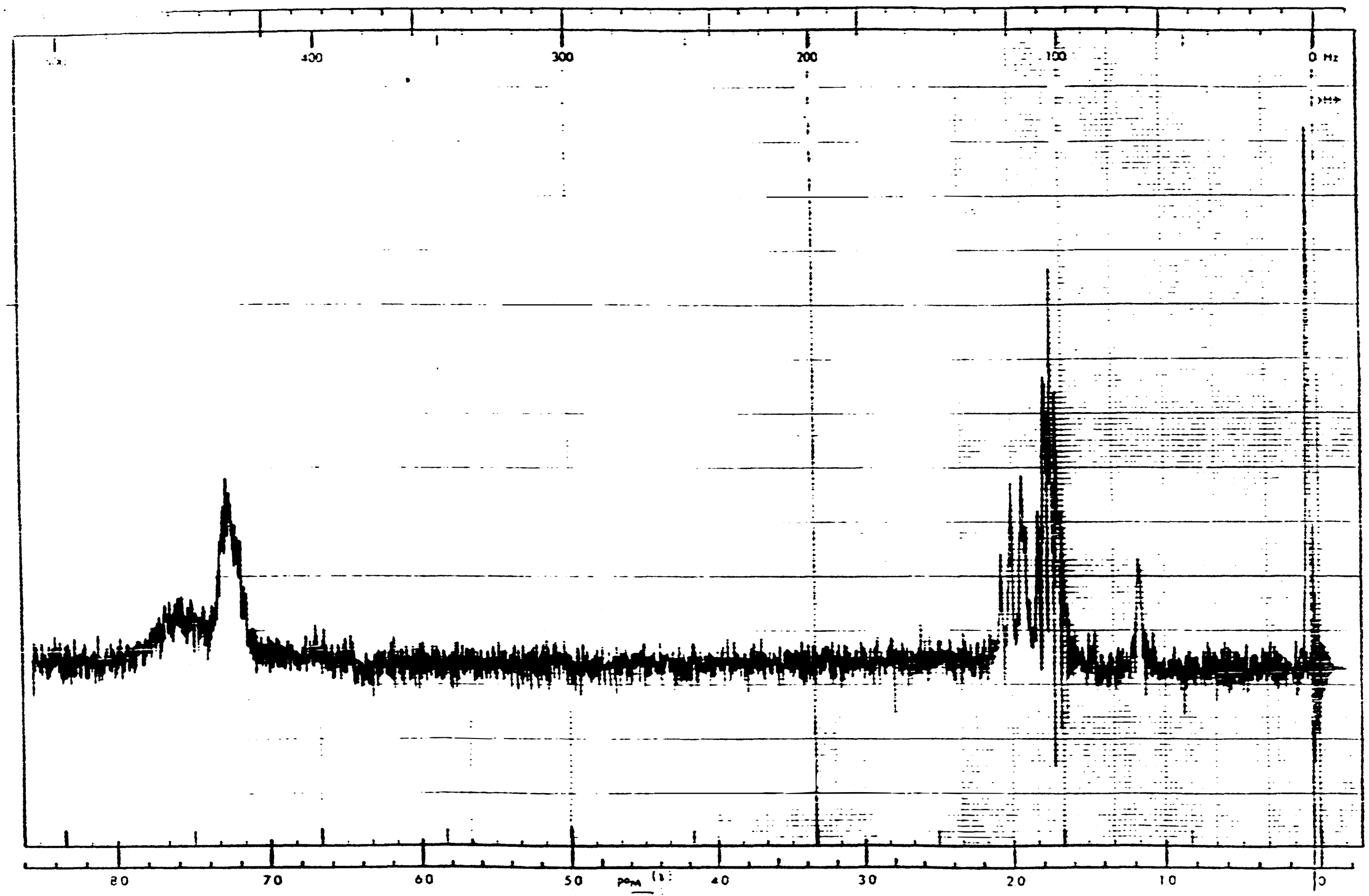

(PH2PME)3RU(CO)CL2
11/14/85 08:44:48
100.00
80.000
60.000
40.000
20.000
0.0000
4000.0
3200.0
2400.0
1900.0
1500.0
1100.0
850.00
650.00
400.00
WAVENUMBERS (CM-1)

Figure 13: $^{1}H$ NMR spectrum of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ in $CD_3CN$ at time = 0



MANUAL

SWEEP OFFSET (Hz): 0

SPECTRUM AMPLITUDE: 1.0

INTEGRAL AMPLITUDE:

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 [✓ 250]

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]

FILTER: [✓ 1] 2 3 4 5 6 7 8

RF POWER LEVEL: 0.05

AUTO ☐

(250)

(500)

( 2)

(.05)

SAMPLE: $\{PPh_2Me\}_2$ Ru $(CH_3CN)Cl_2$

REMARKS: Time = 8 hrs

SOLVENT: $CD_3CN$

DATE: June 8th

OPERATOR:

60 MHz NMR

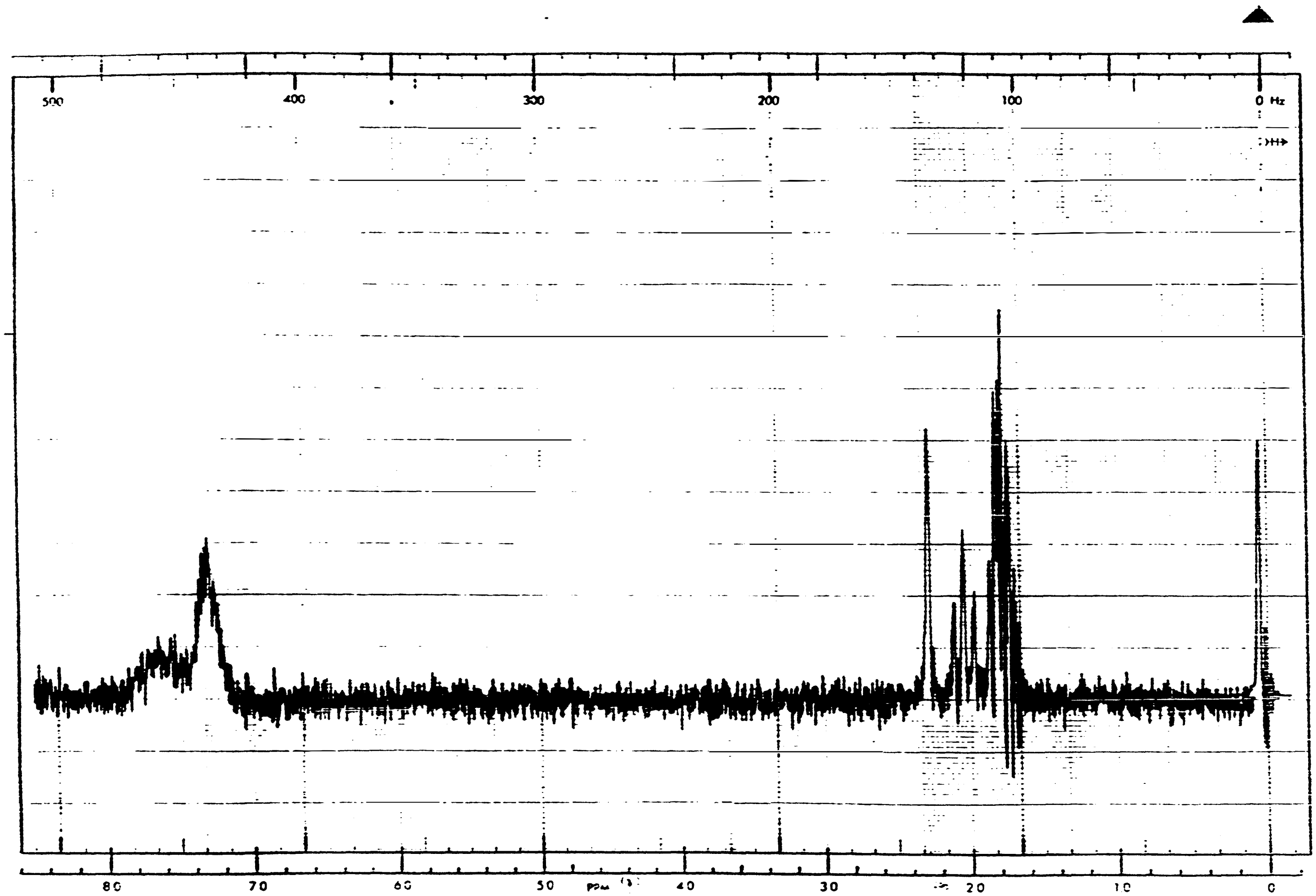
SPECTRUM NO

RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK
PRINTED IN U.S.A.

NO. VN 1009 (S-60T)

Figure 14: $^1$H NMR spectrum of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ in $CD_3CN$ at time = 3 hrs.



MANUAL

SWEEP OFFSET (Hz): 0

SPECTRUM AMPLITUDE: 160

INTEGRAL AMPLITUDE:

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 [✓ 250]

SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]

FILTER: [✓ 1] 2 3 4 5 6 7 8

RF POWER LEVEL: 0.05

AUTO ☐

(250)

(500)

( 2)

(.05)

SAMPLE: $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$

REMARKS: Time = 3 hrs

SOLVENT: $CD_3CN$

DATE: June 8th

OPERATOR: NPI

60 MHz NMR

SPECTRUM NO.

RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION
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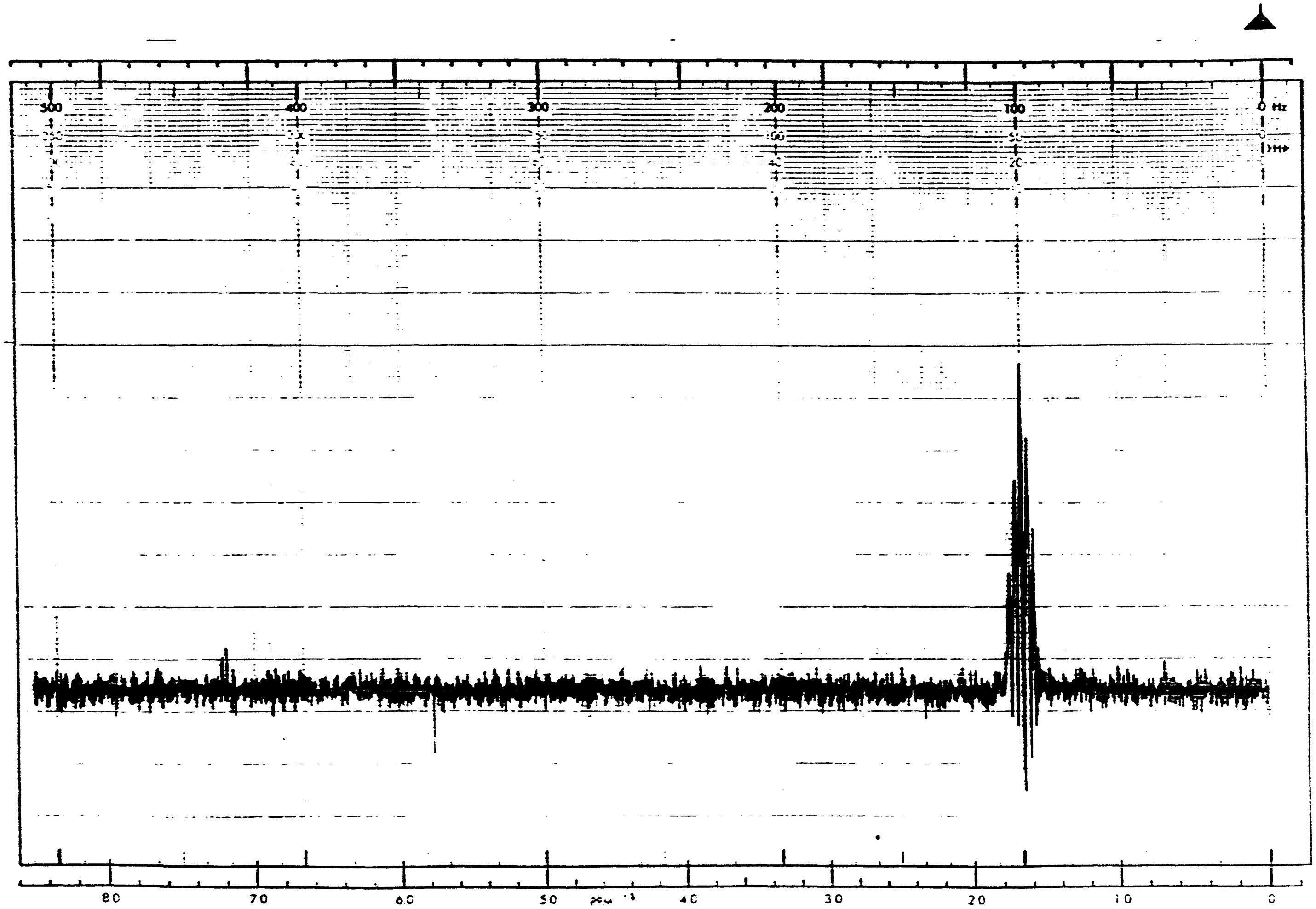
NO. VN 1009 (S-60T)

Figure 15: $^{1}H$ NMR spectrum of 99 % $CD_3CN$



MANUAL

SWEEP OFFSET (Hz) 600

SPECTRUM AMPLITUDE 80

INTEGRAL AMPLITUDE

SPINNING RATE (RPS) 30

SWEEP TIME (SEC) 50 | 250

SWEEP WIDTH (Hz) 25 | 50 | 100 | 250 | 500

FILTER 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8

RF POWER LEVEL

AUTO ___ SAMPLE CD₃CN

SOLVENT

REMARKS

DATE

OPERATOR

60 MHz NMR
SPECTRUM NO.

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK
PRINTED IN U.S.A.

NO VN 1009 (S-60T)

Ohm's law just as metallic conductors do. Therefore, the conductivity of the solution can be determined by measuring the resistance of the solution.

The resistance of the material increases with its length ($\ell$), but decreases with its cross-sectional area A. To standardize the resistance, one uses specific resistance ($\rho$). This is defined as the resistance in ohms of the solution in a cell which has 1 $cm^2$ electrodes that are separated from each other by a distance of 1 cm. This relation between resistance and specific resistance is as shown in equation 14. Therefore a cell constant,k ($\ell$/A) is needed to change resistance to specific resistance.

$$R = (\ell/A) = \rho k \qquad (14)$$

A cell constant k, can be determined by measuring the resistance of the standard solution with a known specific conductance $\bar{L}$, since $\bar{L}$ is inversely proportional to $\rho$.

$$\bar{L} = 1/\rho = k/R \qquad (15)$$

Since the conductivity depends on the number of charged carriers (ions) present, it is usually expressed as a molar quantity. Molar conductance $\Lambda m$, is defined as the conductance 1000/M $cm^3$ of solution which contains one mole of solute (eq 16).

$$m = 1000L/M \quad \text{where } M = \text{molarity} \quad (16).$$

The degree of dissociation can be determined by comparing the molar conductance with that of known ionic substances. The general values of the number of ions present in water solution are tabulated below[19]:

Table 2: Range of molar conductance

| No of ions | Molar conductance |
|---|---|
| 2 | 118-131 |
| 3 | 235-273 |
| 4 | 408-435 |
| 5 | 560 |

Values slightly less are obtained when $CH_3CN$ is used as the solvent.

B. Conductivity of $(R_3P)_4RuCl_2$, $(PPhMe_2)_3RuCOCl_2$ and $(PPh_2Me)RuCO(CH_3CN)Cl_2$.

The resistance measurements were made on HPLC grade $CH_3CN$ solutions and specific conductance values were calculated with equation 14. The conductance values were corrected by subtracting the conductance value of the solvent. The molar conductance was then calculated with eq. 16. The calculated values are tabulated in in Table 3.

Two ionic complexes, $[(C_2H_5)_4N]ClO_4$ and $[(CH_3CN)_6Ni](BF)_4$ which are known to dissociate in acetonitrile to give two and three ions, respectively, were used as standards. The values obtained in these experiments agreed with those in Table 2. The molar conductance values suggest that $(R_3P)_4RuCl_2$ complexes ($R_3P$ = $PPh_3$, $PPh_2Me$ and $PPhMe_2$) partially dissociate in $CH_3CN$. The degree of dissociation of the ions depends on the ligands attached to Ru(II). As expected, the degree of dissociation increases as the donor strength

Table 3 : Conductance, specific conductance and molar conductance for standard solution and Ru (II) complex in acetonitrile.

| Compound | $\bar{L} \times 10^4$ | $\bar{L}_{corr} \times 10^4$ | $\Lambda m$ |
|---|---|---|---|
| $CH_3CN$ | 2.4 ± 0.2 | 0.0 | - |
| $[(C_2H_5)_4N]ClO_4$ | 8.4 | 5.9± 0.2 | 118.8 ± 0.2 |
| $[(CH_3CN)_6Ni](BF)_4$ | 21.6 | 19.2 | 222.7 |
| $(PPh)_4RuCl_2$ | 5.8 | 3.4 | 68.2 |
| $(PPh_2Me)_4RuCl_2$ | 7.6 | 5.2 | 68.7 |
| $(PPhMe_2)_4RuCl_2$ | 6.7 | 4.3 | 100.5 |
| $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ | 2.4 | 0.0 | - |
| $(PPhMe_2)_3RuCOCl_2$ | 2.4 | 0.0 | - |

increases, $PPhMe_2 > PPh_2Me > PPh_3$. One can also suggest that the dissociation is enhanced by a strong electron drift along the $\overrightarrow{\text{P-Ru-Cl}}$ vector which weakens the Ru-Cl bond.

The complexes, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$, behaved as expected, i.e. both chlorides remained coordinated to Ru. The result agrees with the postulated structure and is consistent with CO trans to Cl. Carbon monoxide is a much poorer $\sigma$-donor but a better $\pi$-acceptor than a tertiary phosphine. This makes the Ru-Cl bond trans to CO much stronger than those trans to a tertiary phosphine.

The dissociation of the phosphine ligands cannot be studied by the conductivity method since the ligands are neutral. A conductivity study in excess ligand was carried out to observe the effect of excess ligand on the degree of the dissociation of the ions. The result indicated that excess ligand does not play any role in the dissociation of the ions.

## 3. Polarography of Ru (II) complexes

### A. Introduction

Once the composition and structure of the Ruthenium complexes $(PPh_2Me)_4RuCl_2$, $(PPhMe_2)_4RuCl_2$, $(PPh_2Me)_2Ru(CH_3CN)COCl_2$ and $(PPhMe_2)_3RuCOCl_2$ were determined, the redox properties could then be studied through electroanalytical techniques. The proposed electrochemical method, polarography, can supply information about the ease, reversibility, and number of steps in the overall reduction of the ruthenium metal complexes to their lower oxidation states. The polarogram itself (current/ potential curves) reveals qualitative information about the overall reduction by the number of cathodic waves that are present. More than one wave can indicate that the complex of interest is undergoing a series of electron transfers (steps) to achieve its lowest oxidation state. The positions of waves in the polarogram can indicate what possible species are present in solution and the number of overall steps in the reduction. In addition, quantitative values of the half-wave potentials ($E_{1/2}$), and limiting currents are obtained for each wave of a polarogram. Reversibility of each wave can be determined both in a qualitative and quantitative way. One major disadvantage of polarography is that on the electrochemical time scale polarography is slow.

Polarography with a Dropping Mercury Electrode (DME) is one of many electroanalytical methods applied to the study of redox behavior of transition metal complexes. Past experience proves that very negative potentials are required to reduce similar ruthenium complexes[6]. With the appropriate solvent and supporting electrolyte, the DME can achieve the required potentials before discharge, while platinum electrodes under the same conditions cannot. In addition, most ruthenium complexes are known to be both irreversible and to form films on the metal surface of the electrodes. Upon consideration, it follows that the DME with a new surface every 2-3 sec is favored over electrodes that have surfaces dependent on past experiments. Thus, the motivation to employ polarography rather than voltammetry in the study of the ruthenium metal systems is clear.

The solution in the cell for all experiments consisted of tetraethylammonium perchlorate as the supporting electrolyte, acetonitrile as the solvent, and the electroactive species under study. The ruthenium complexes were sensitive to both oxygen and water. Thus, aqueous electrochemical cells cannot be used. Past experience has shown acetonitrile as a useful non aqueous electrochemical solvent. All electroactive ruthenium complexes were readily soluble and considered non reactive in acetonitrile; hence all polarographic experiments were run in this solvent. Due to the sufficiently negative discharge potential of the tetraethylammonium ion, the obvious choice of supporting electrolyte was the tetraethylammonium perchlorate salt (TEAP). TEAP was present in 100 fold excess over the electroactive species to ensure diffusion control rather than coulombic or convection as the mode of the mass transport.

Each wave that appears in the polarogram had a current plateau. The currents at this point were limited by the mode of transport of the electroactive species to the electrode surface. The possible currents for mass transport other than convection or coulombic (eliminated by supporting electrolyte and experimental design) were diffusion, kinetic, or adsorption as described in equations (17), (18) and (19)[23].

$$i_d = 708nD^{1/2}Cm^{2/3}t^{1/6} \qquad (17)$$

$$i_k = 493nD^{1/2}Cm^{2/3}t^{2/3} \qquad (18)$$

$$i_a = 13.66nm^{2/3}t^{-1/3}/a \qquad (19)$$

Where $i_d$, $i_k$ and $i_a$ are diffusion, kinetic and adsorption currents respectively, D is the diffusion coefficient, C is the concentration of the electroactive species, and a is the area the mercury drop covered by adsorbed electroactive complexes.

Recalling that the mass flow rate (m) is proportional to and that the drop time ($t_{max}$) is inversely proportional to the mercury pressure, substitution into equations (17), (18) and (19) provides a generalized equation for dependence of limiting current on the height of the mercury column (20).

$$i_L = kh^x_{corr} \qquad (20)$$

Where $i_L$ is limiting current, $h_{corr}$ is a corrected height of the mercury column, x is a constant which depends on the process that controls mass transport to the electrode, and k is a collection of constants.

Variation in height of the mercury column thus reveals the form of mass transport, and the type of plateau current, of the electroactive species to the electrode through information obtained in a plot of ln $i_L$ vs ln $h_{corr}$. This plot will give a straight line with a slope from 0 to 1. A slope of zero indicates kinetic control, slope of 0.5 indicates diffusion, and a slope of 1 indicates adsorption on the electrode surface.

The shape of the polarogram provides qualitative information about the reversibility of the electron transfer. A sharp rising curve indicates a reversible process whereas the more "drawn out" curve indicates an irreversible one.

If the mass transport is solely by diffusion, a quantitative description of reversibility can be established. All the points along the wave must follow equation (21) if the electon transfer is truly reversible.

$$E_{DME} = E_{1/2} - RT/nF \ln (i/i_d - i) \qquad (21)$$

$$E_{DME} = E_{1/2} - 0.0582/n \log (i/i_d - i) \qquad (22)$$

For a ideally reversible one electron transfer at 20.0$^{o}$c, a plot of the potential versus log (i/id-i) for the wave in question must give a slope of 58.2 mV. The half wave potential of this plot, the intercept, should show agreement with the potential found from the wave by a independent method. Thus it is clear that a simple reversible one electron transfer is easy to analyze. However, with a polarogram that produces a number of irreversible waves, the interpretation of the electochemistry occurring in the system can become complex. The exprimental values of half-wave potentials coupled with the limiting currents and spectral data for the ruthenium complexes can provide possible information that can be used in such a way as to determine the number of electrons involved in each step and the probable species that are responsible for that reduction. For example, the diffusion current for a ruthenium complex can be compared to the current in a reversible one electon transfer of ferrocene or with a similar ruthenium complex that undergoes electron transfer in the same manner as the species under study.

From the above discussion it can be seen that various types of information can be extracted from one or more polarographic waves. The number of waves can indicate either different types of electrospecies being reduced or a number of "electron steps" involved in the overall reduction. The half-wave potentials will indicate the ease of reduction compared to other ruthenium complexes which is a essential parameter in order to later synthesize the zerovalent complexes.

### B. Polarogram of Ferrocene

The oxidation of ferrocene is a known reversible one electron diffusion controlled electrochemical process in acetonitrile. The iron complex can be used to test both the experimental system design and the validity of equations introduced for reversiblity and diffusion control. Ferrocene could be employed as an internal standard to determine the number of electrons needed in each wave when diffusion control is obeyed.

Experimental restrictions to the design of the system involve attention from proper alignment of the DME in the cell to vibrations in the hood. From the values obtained for the limiting currents and mercury drop times it can be verified that the system design will eliminate all experimental and theoretical variables considered above that could complicate the polarographic measurment. For example, when the slope of the reversibility plot, E vs ln $(i/i_d-i)$, is significantly smaller than 58.2 mV for ferrocene, the currents and potentials are not well behaved along the wave due to incorrect geometry of the electrodes in the cell. Qualitative observations of the wave shape and the currents for each drop reveals important information concerning vibrations and functional design of the DME.

The verification of equations derived for diffusion control and reversibility is obtained in the following manner. From values of limiting current at various corrected mercury column heights (Table 4), a current control plot is constructed(Figure 16). The value of the slope, 0.48 ± 0.02, is certainly an acceptable value within the precision of that predicted for an "ideal" diffusion current, 0.50. The reversibility plot (Figure 17) of potential versus log $(i/i_d-i)$ (Table 5) for the wave at the corrected height of 67.44 cm produces a slope

Table 4 : Dependence of limiting current on corrected height for 1.07 mM Ferrocene

| Height (cm) | $h_{corr}$ (cm) | $i_L$ (uA) |
|---|---|---|
| 74.9 ± .1 | 73.1 ± .1 | 8.88 ± .01 |
| 69.2 | 67.4 | 8.46 |
| 65.3 | 63.5 | 8.25 |
| 56.9 | 55.1 | 7.75 |
| 47.8 | 46.0 | 7.10 |

Table 5 : The potential and current for reversibility plot of ferrocene at height = 67.44 cm

| Edme (V) | i (uA) | log (i/id-i) |
|---|---|---|
| -0.030 | 0.67 | -1.065 |
| -0.019 | 1.01 | -0.868 |
| -0.007 | 1.55 | -0.649 |
| 0.006 | 2.21 | -0.451 |
| 0.018 | 3.06 | -0.247 |
| 0.029 | 4.05 | -0.037 |
| 0.040 | 5.06 | 0.173 |
| 0.050 | 5.95 | 0.375 |
| 0.061 | 6.72 | 0.587 |
| 0.072 | 7.28 | 0.790 |
| 0.086 | 7.68 | 0.991 |
| 0.99 | 7.89 | 1.144 |

Figure 16 : Current control plot for ferrocene

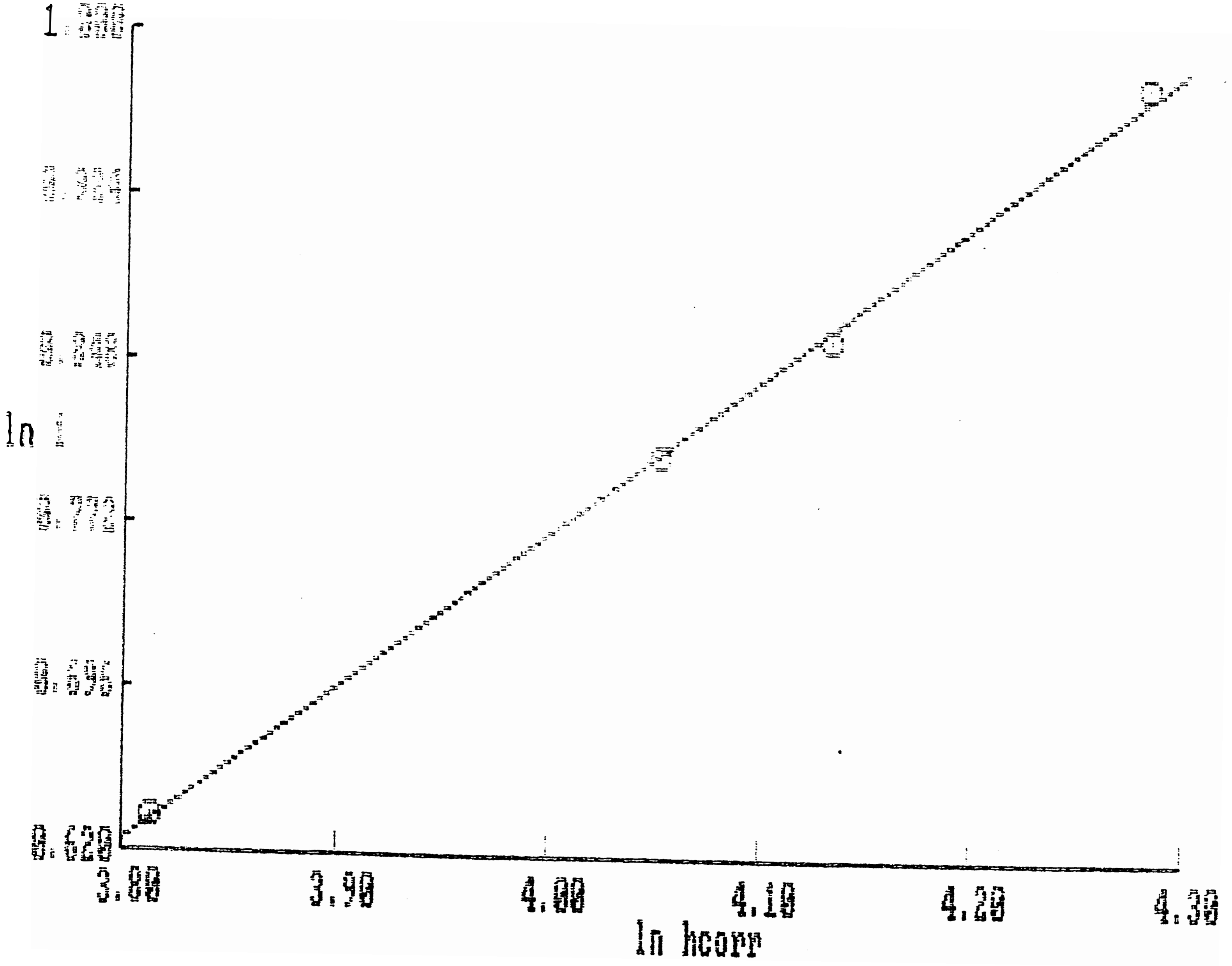
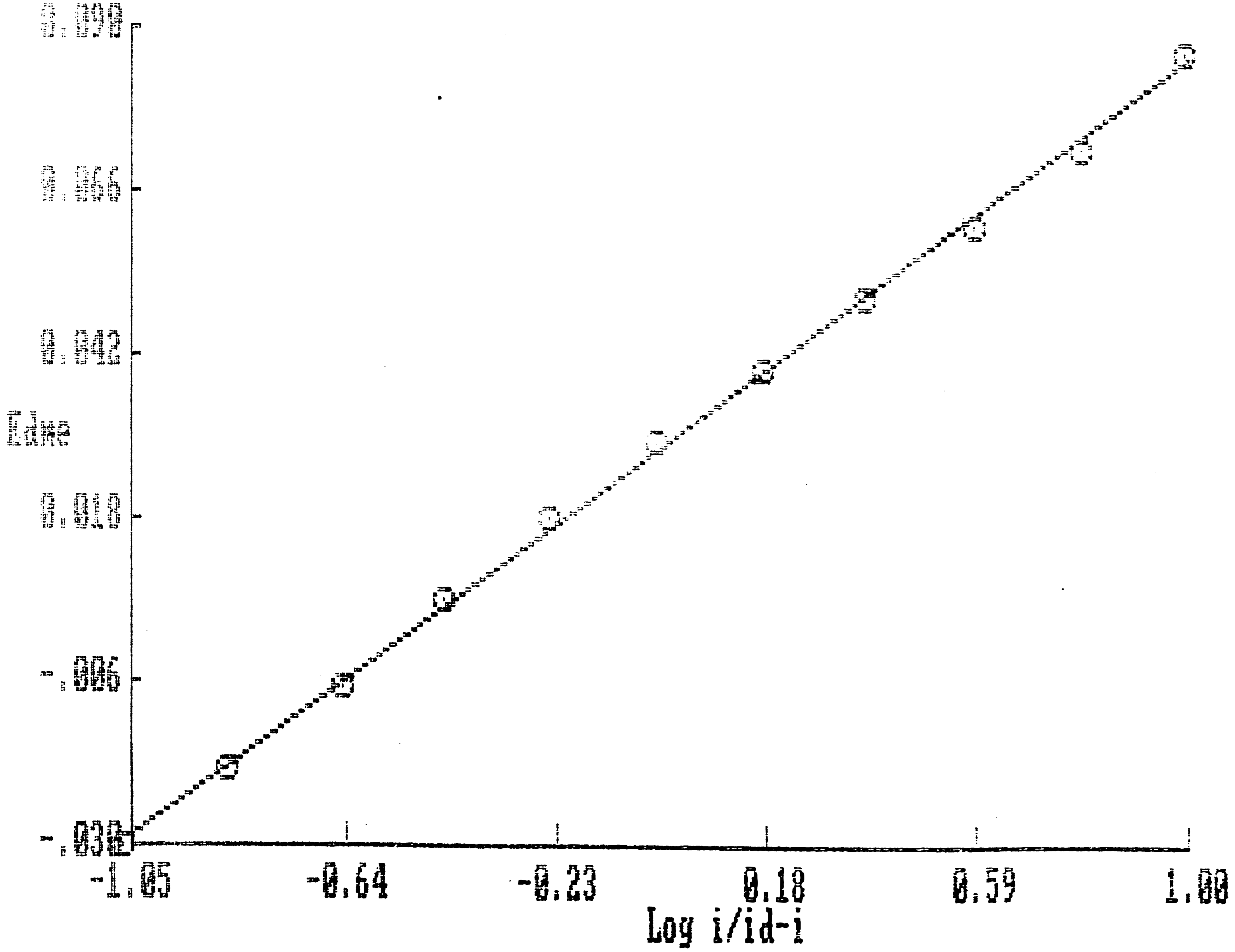

1.000
0.924
0.848
0.772
0.696
0.620
ln i
3.80
3.90
4.00
4.10
4.20
4.30
ln hcorr

Figure 17 : Reversibility plot for ferrocene


0.090
0.066
0.042
0.018
-.006
-.030
Edme
-1.05
-0.64
-0.23
0.18
0.59
1.00
Log i/id-i

of 57 ± 3 mV. The reversibility test also holds within experimental precision. Similar slopes were obtained for plots at other heights (Table 6).

The polarogram of 1.00 mM Ferrocene (Fig 18) shows a reversible wave with half-wave potential of +0.03 ± 0.01 V. The half wave potentials from the waves at all heights are in agreement with the half wave potentials found in the reversibility plots (Table 6).

In conclusion, any ruthenium wave obtained under the same experimental conditions present for ferrocene will be considered reversible and/or a diffusion controlled process when having similar values to the ferrocene "reference".

## C. Polarography of $(PPh_2Me)_4RuCl_2$ and $(PPhMe_2)_4RuCl_2$

A typical polarogram of $(PPh_2Me)_4RuCl_2$ is shown in Fig 19. From values in table 7, the current control plot of ln $i_L$ vs ln $h_{corr}$, yields a slope of 0.42 ± 0.02 for the first wave at a half wave potential of -2.25 ± 0.03 V. This indicates essentially a diffusion control current with some kinetics involved in the electron transfer. The second wave, occurring at -2.53 ± 0.03 V, has a slope of 0.72 ± 0.02 which indicated adsorption on the electrode surface.

If both waves of the overall reduction are considered as a two step process,

Table 6 : Data obtained from reversibility plot at various height for ferrocene

| $h_{corr}$ (cm) | Slope | E (calculated) | E (measure) |
|---|---|---|---|
| 73.2 ± .05 | 57 ± 3 | .031 | .030 |
| 67.4 | 57 | .030 | .030 |
| 63.5 | 55 | .025 | .028 |
| 55.1 | 56 | .032 | .032 |
| 46.0 | 56 | .027 | .028 |

Table 7 : Dependence of limiting current on corrected height for 1.00 mM $(PPh_2Me)_4RuCl_2$

| $h_{corr1}$ ±.1(cm) | $i_{L1}$ ± .01(uA) | $h_{corr2}$ ± .1(cm) | $i_{L2}$ ± .01(uA) | $i_L$ total ± .01(uA) |
|---|---|---|---|---|
| 72.5 | 8.26 | 72.4 | 2.66 | 10.92 |
| 62.5 | 7.74 | 62.4 | 2.36 | 10.10 |
| 57.7 | 7.57 | 57.5 | 2.24 | 9.81 |
| 52.0 | 7.17 | 51.9 | 1.92 | 9.09 |
| 45.5 | 6.77 | 45.3 | 1.89 | 8.66 |

Figure 18 : Polarogram of 1.00 mM Ferrocene
in acetonitrile

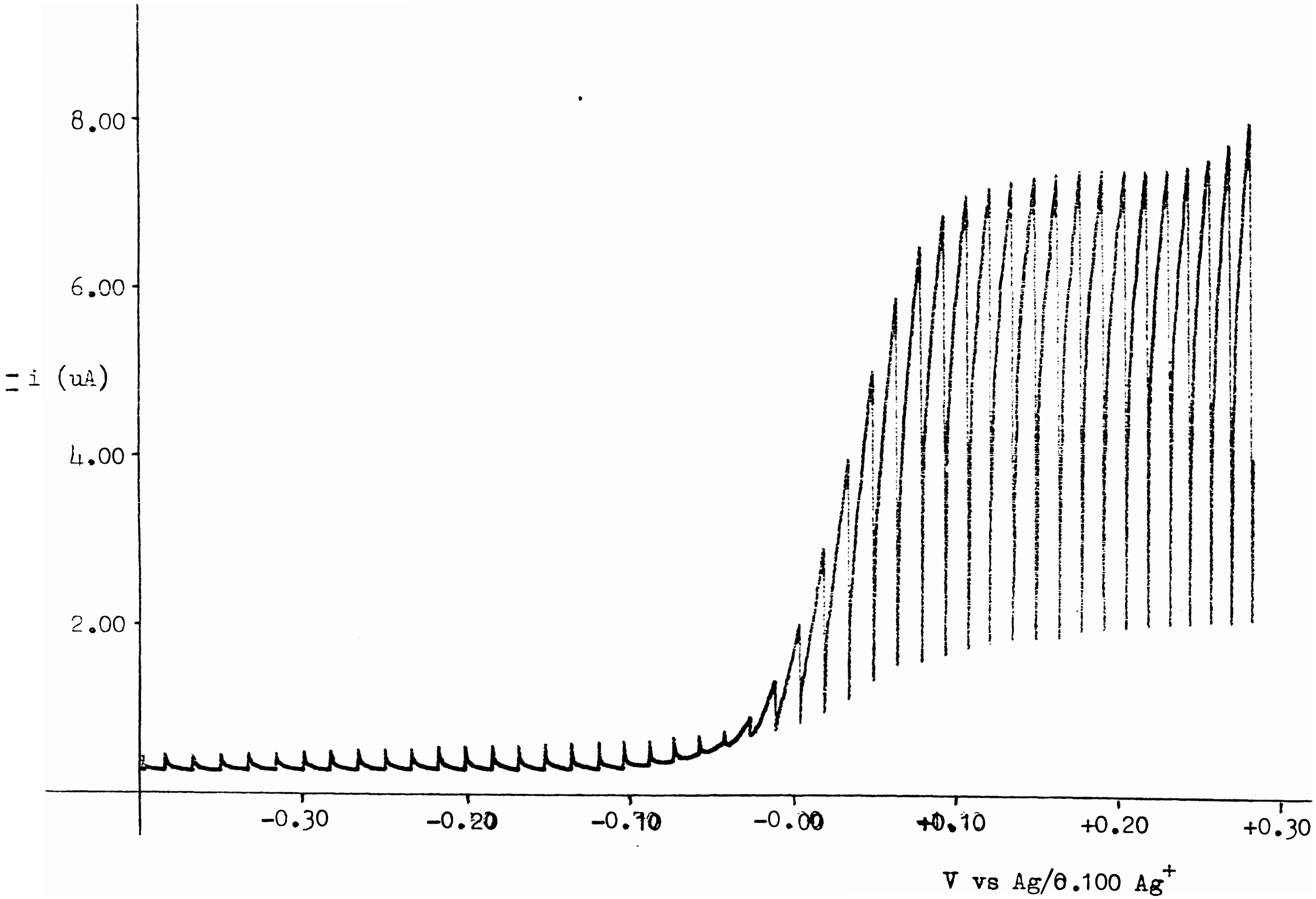
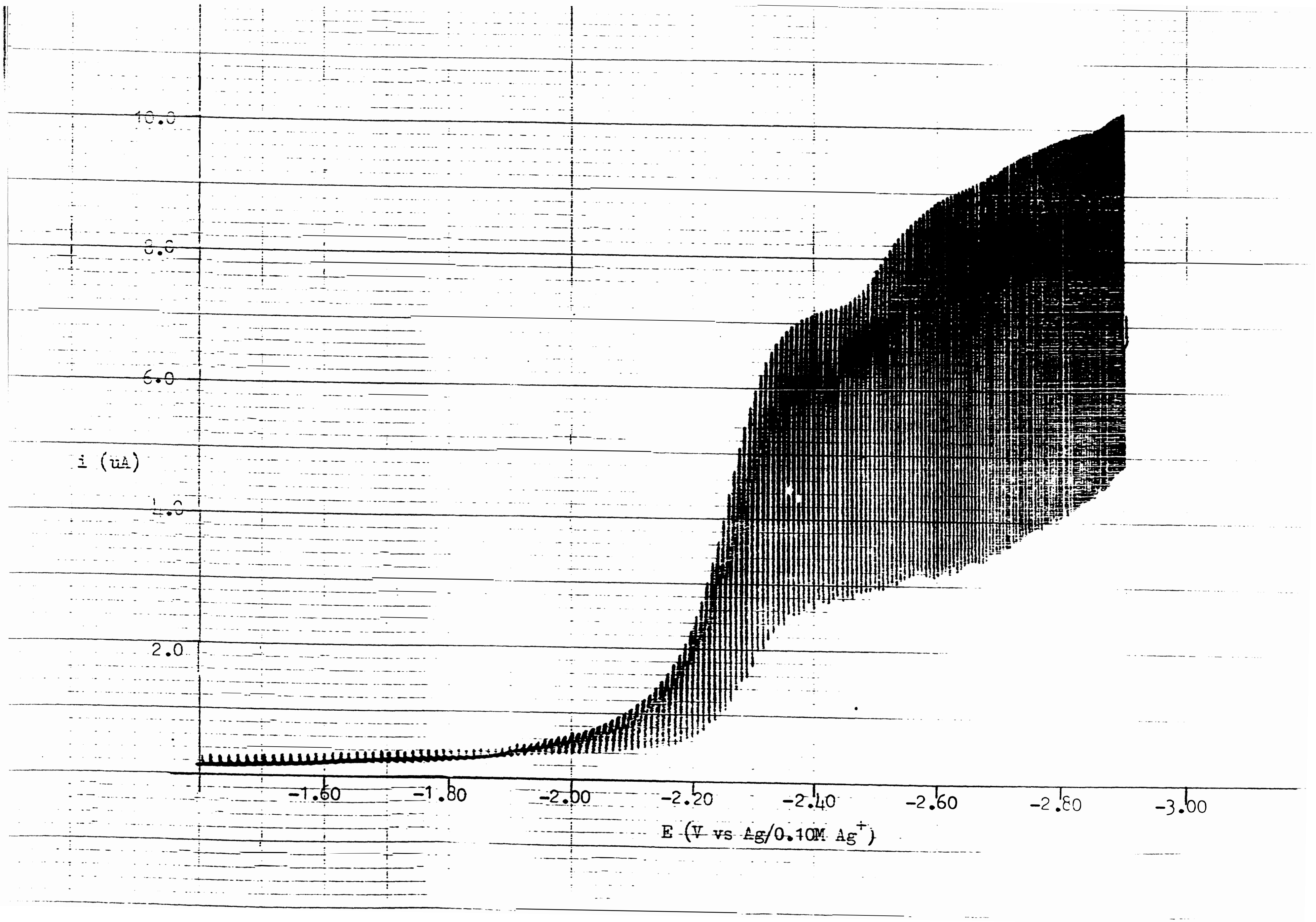

8.00
6.00
± i (uA)
4.00
2.00
-0.30
-0.20
-0.10
-0.00
+0.10
+0.20
+0.30
V vs Ag/0.100 Ag+

Figure 19 : Polarogram of 1.00 mM $(PPh_2Me)_4RuCl_2$
in acetonitrile


10.0
8.0
6.0
i (uA)
4.0
2.0
-1.60
-1.80
-2.00
-2.20
-2.40
-2.60
-2.80
-3.00
E (V vs Ag/0.10M Ag$^+$)

$$Ru(II) + e \longrightarrow Ru(I)$$

$$Ru(I) + e \longrightarrow Ru(0)$$

the limiting currents should be 1:1. However, the ratio of 3.4:1.0 suggests that two electroactive species may be present. Conductivity and $^{31}P$ NMR spectroscopy[6] studies support this idea by indicating that both species, $[RuCl(CH_3CN)(PPh_2Me)_4]Cl$ and $[RuCl(CH_3CN)_2(PPh_2Me)_3]Cl$, are present in solution. From $^{31}P$ NMR spectroscopy the predominant species in solution was shown to be the $[RuCl(CH_3CN)PPh_2Me)_4]^+$ ion. A greater amount of current then be would expected for this ion than for the $[RuCl(CH_3CN)_2(PPh_2Me_3]^+$ ion.

The number of electrons involved in each wave was difficult to determine. Ferrocene could not be used as an internal standard because of the interference of kinetic and adsorption currents on the limiting wave current. Thus, a different method was employed. The ruthenium (II) complex $(PPh_3)_4RuCl_2$ was known to undergo an overall two electron transfer[6]. At identical concentrations, the total limiting current for the ruthenium complex under study, the sum of both waves, should be equal to the total limiting current of $(PPh_3)_4RuCl_2$ if a two electron transfer process takes place. If only a one electron transfer process takes place, then the total limiting current should be half that of the $(PPh_3)_4RuCl_2$ complex. The comparison of the total limiting currents does indicate that a two electron transfer takes place for the combination of both waves.

Due to the "drawn out" shape of each wave, qualitative examination predicts non-reversible behavior. After electron transfer takes place, the complex loses a chloride ligand. By definition this constitutes irreversible behavior. Thus, none of the complexes were expected to undergo reversible reduction. The reversibility plot of the first wave of $(PPh_2Me)_4RuCl_2$ had a slope of 134 mV. A reversible wave has 29 mV. This indicates a totally irreversible process. Since the current in the second wave is governed by adsorption, a quantitative evaluation as above was not done.

Consider the following equilibrium present in

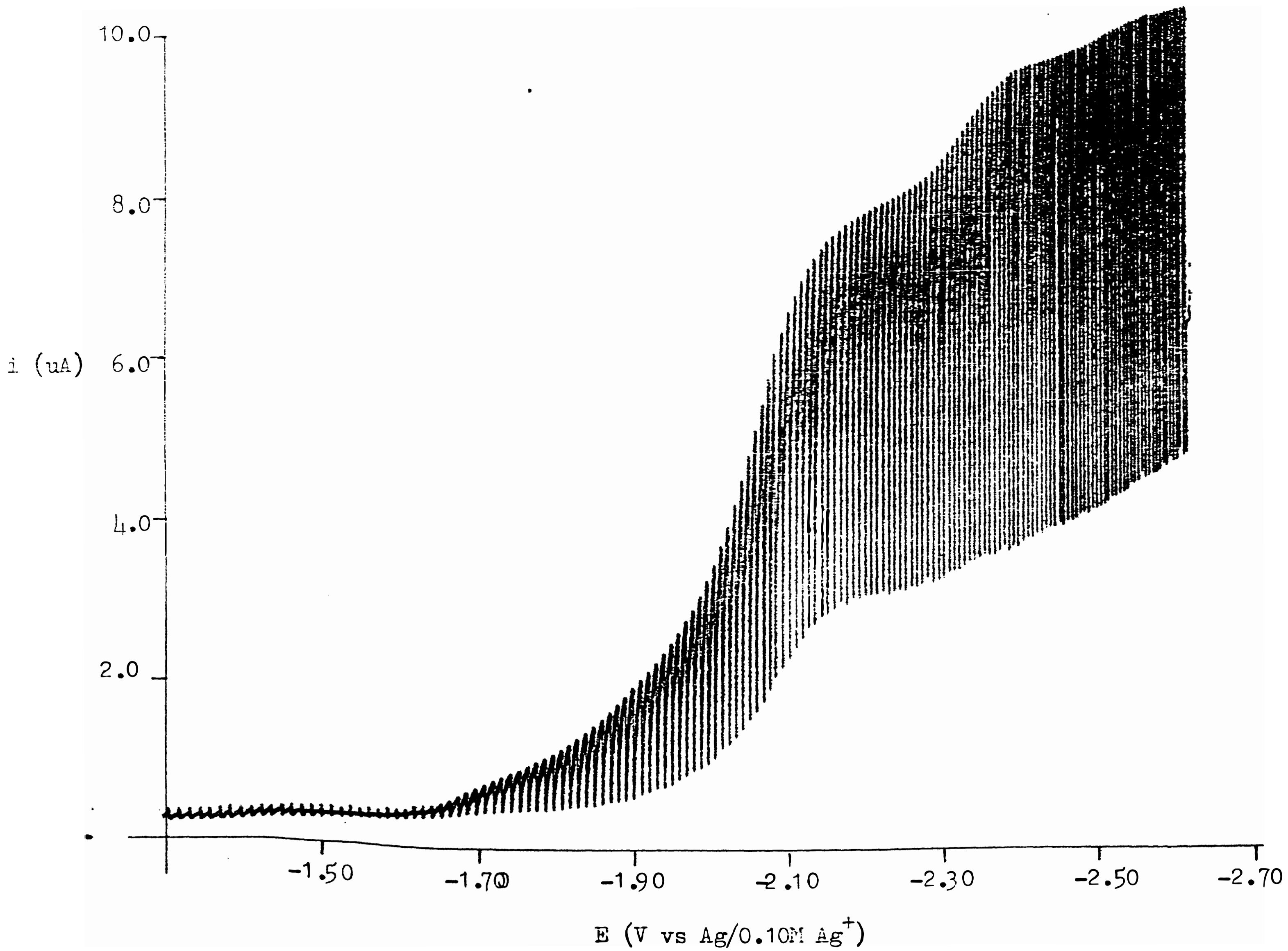
$$[RuCl(CH_3CN)(PPh_2Me)_4]^+ + CH_3CN$$

$$\uparrow\downarrow$$

$$[RuCl(CH_3CN)_2(PPh_2Me)_3]^+ + PPh_2Me$$

acetonitrile. As shown by $^{31}P$ studies done by Olson, the addition of excess $PPh_2Me$ ligand decreases the concentration of the $[RuCl(CH_3CN)_2(PPh_2Me)_3]^+$ ion in solution. This in turn should decrease the current for the reduction wave due to this complex ion. The ratio of the first wave to the second wave should increase. When a 10-fold excess of $PPh_2Me$ was added, a typical polarogram as in Fig 20 was obtained. The current ratio changed to 4.6 : 1.0. The current control slopes, $0.42 \pm 0.02$ and $0.82 \pm 0.02$ for the first and second waves respectively, remained essentially the same as in those

Figure 20 : Polarogram of 1.00 mM $(PPh_2Me)_4RuCl_2$ with 10-fold excess of $PPh_2Me$ ligand

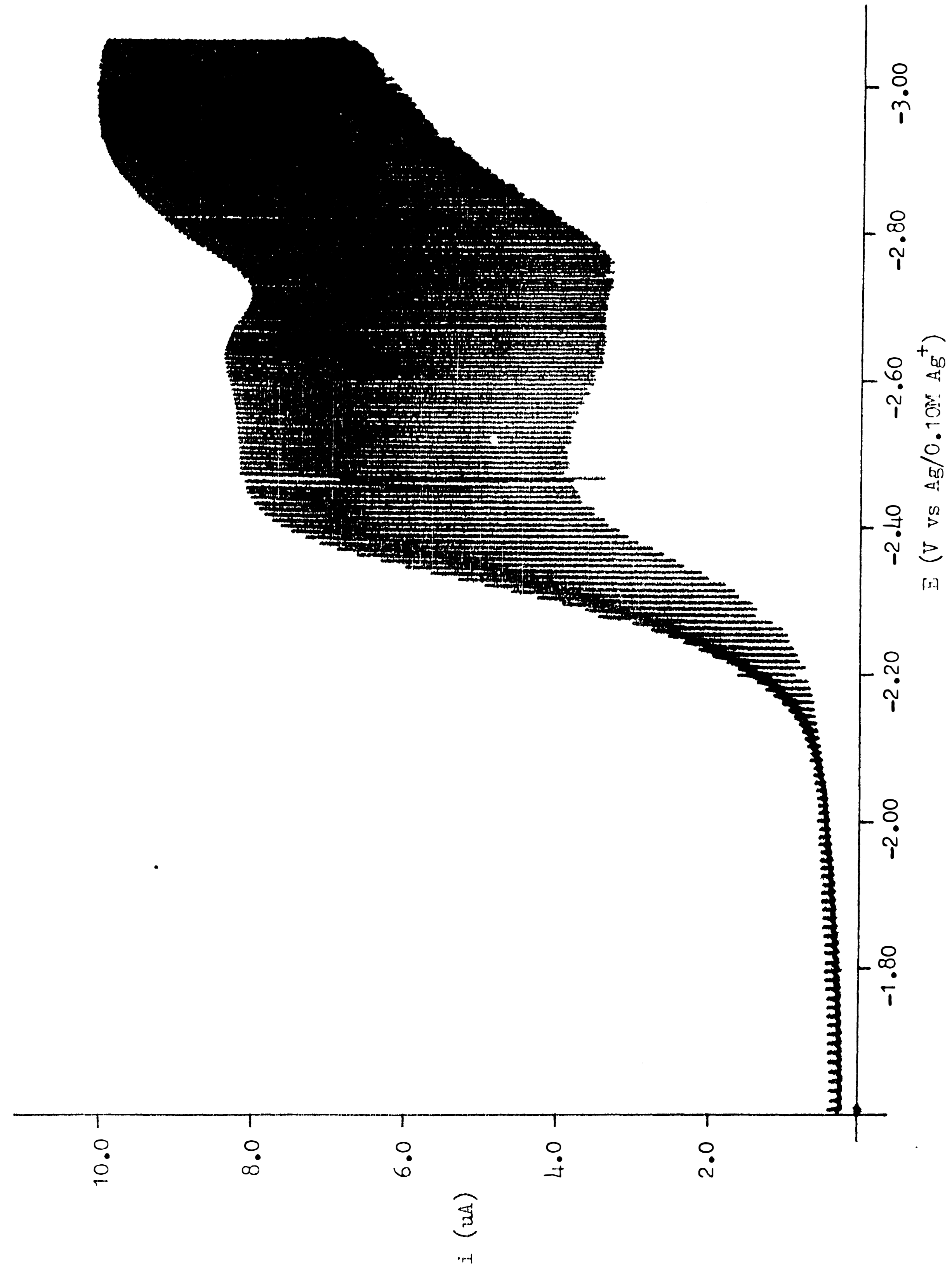

i (uA)
10.0
8.0
6.0
4.0
2.0
-1.50
-1.70
-1.90
-2.10
-2.30
-2.50
-2.70
E (V vs Ag/0.10M Ag+)

waves obtained from solution without excess ligand. Both half wave potentials shift the same degree in a positive direction, -2.22 ± .03 and -2.52 ± 0.03 V. However within experimental error the position of the wave and the type of current control and the reversiblity characteristics have not changed. This suggests that both waves observed in the presence of a 10-fold excess of $PPh_2Me$ ligand are from the same species that produced both waves of the polarograms in the absence of excess ligand. Armed with these results, the first wave can now be assigned to a 2e reduction of the $[RuCl(CH_3CN)(PPh_2Me)_4]^+$ ion and the second wave a 2e reduction of the $[RuCl(CH_3CN)_2(PPh_2Me)_3]^+$ ion. This indicates greater electron density on the ruthenium metal center in the $[RuCl(CH_3CN)_2(PPh_2Me)_3]^+$ ion than on the $[RuCl(CH_3CN)(PPh_2Me)_4]^+$ ion.

Another phosphine ligand of interest was dimethylphenyl phosphine. The increase in Lewis basicity of this ligand will increase the electron density around the metal compared to a similar complex with methyldiphenyl phosphine. A more negetive potential was then expected to be required to reduce $(PPhMe_2)_4RuCl_2$ than to reduce $(PPh_2Me)_4RuCl_2$.

A polarogram obtained from a 1.00 mM $(PPhMe_2)_4RuCl_2$ solution shows three waves at -2.28 ± 0.03V (first wave), -2.59 ± 0.03V (second wave) and -2.80 ± 0.03V (third wave), figure 21. Values of the current as a function of height are recorded in table 8 for both waves one and

Figure 21 : Polarogram of 1.00 mM $(PPhMe_2)_4RuCl_2$
in acetonitrile



i (uA)
10.0
8.0
6.0
4.0
2.0
-1.80
-2.00
-2.20
-2.40
-2.60
-2.80
-3.00
E (V vs Ag/0.10M Ag+)

three. The second wave was ill-defined in wave shape and magnitude of current, thus precluding an accurate measurement of the limiting current. The current control plots yielded slopes of 0.41 ± 0.02 and 0.38 ± 0.02 for the first and the third wave, respectively. These slopes suggested that the current was governed by a mixture of diffusion and kinetic control. The value for the slope of the first wave of $(PPhMe_2)_4RuCl_2$ was identical to the first wave slope of $(PPh_2Me)_4RuCl_2$.

The current ratio of the first, second, and third waves was 3.9 : 0.1: 1.0. Once again, three species were responsible for the waves rather than three steps of one species. A two electron transfer was comfirmed for all the waves with the same method as that done with $(PPh_2Me)_4RuCl_2$. Conductivity measurements confirmed the presence of a 1:1 electrolyte. However, the $^{31}P$ NMR spectrum was complicated and difficult to interpret. Olson offered the existence of an equilibrium between the tris and tetrakis dimethylphenylphosphine complexes as an explanation for his findings. Adopting this idea, the following ligand exchange equilibria were proposed:

$$\begin{array}{ccc}
 & [RuCl(CH_3CN)(PPhMe_2)_4]^+ + CH_3CN & \\
[O]_1 & \upharpoonleft\downharpoonright & \\
 & [RuCl(CH_3CN)_2(PPhMe_2)_3]^+ + PPhMe_2 & \\
[O]_2 & \upharpoonleft\upharpoonright & CH_3CN \\
 & [RuCl(CH_3CN)_3(PPhMe_2)_2]^+ + PPhMe_2 & \\
[O]_3 & &
\end{array}$$

TABLE 8 : Values of limiting current as a function of corrected height for $(PPhMe_2)_4RuCl_2$

| Height<br>cm ± .1 | $h_{corr1}$<br>cm ± .1 | $i_{L1}$<br>uA ± .05 | $h_{corr2}$<br>cm ± .1 | $i_{L2}$<br>uA ± .05 |
|---|---|---|---|---|
| 74.5 | 72.3 | 8.81 | 71.7 | 2.24 |
| 66.2 | 64.0 | 8.39 | 63.4 | ---- |
| 61.0 | 58.8 | 8.10 | 58.2 | 2.08 |
| 53.6 | 51.5 | 7.64 | 50.8 | 1.95 |
| 44.5 | 42.4 | 7.10 | 41.7 | 1.83 |

The presence of rapidly exchanging ligands for all three of these intermediates would indeed produce a complicated $^{31}P$ NMR spectrum. Since it was confirmed earlier that substitution of phosphine ligands with acetonitrile makes the complex more difficult to reduce, the first wave was assigned to $[O]_1$, the second to $[O]_2$ and the third to $[O]_3$.

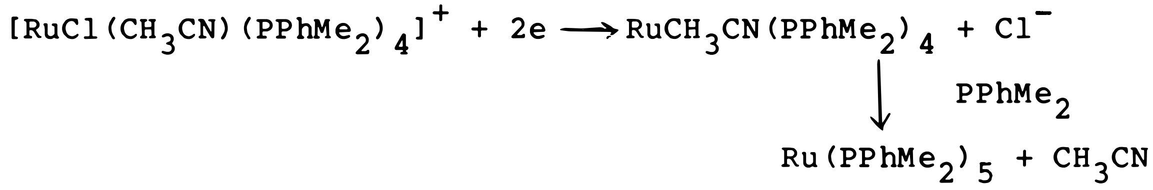
From the size of the reduction current, the two predominant species in solution were $[RuCl(CH_3CN)(PPhMe_2)_4]^+$ and $[RuCl(CH_3CN)_3(PPhMe_2)]^+$.

Qualitative examination of the slopes of all waves in the polarograms for $(PPhMe_2)_4RuCl_2$ showed irreversible behavior.

With the presence of a 10-fold excess of $PPhMe_2$ ligand the polarogram produced three waves at -2.19 ± 0.03 V (first), -2.56 ± 0.03 V (second), and -2.83 ± 0.03 V (third), Figure 22. The values of the current at each height for waves one, two, and three, Table 9, gave slopes of 0.44 ± 0.03, 1.3 ± 0.1, and 0.20 ± 0.02 respectively in the current control plots. The second wave was obviously the result of current due to absorption in the electron transfer.

From the values of the potentials, reversibility, and wave characteristics, the second and third waves were considered as unchanged in the presence of excess ligand. The current ratios of the first wave, to the second wave, and to the third wave, 3.8: 0.2: 1.0, also remain unchanged and supported this statement. Thus, the ratios or concentrations of the species present which gave rise to each wave remained unchanged in the presence of excess ligand. This result also supported Olson's interpretation of his $^{31}P$ NMR spectroscopy experiments[6].However, the shift in potential of the first wave remains to be understood.

The positive shift of the wave indicated a following fast chemical reaction coupled to the electron transfer of the $[\mathrm{RuCl(CH_3CN)(PPhMe_2)_4}]^+$ complex. The shift was a positive 0.09 ± 0.03 V. The species that resulted after the electron transfer takes place and its possible subsequent reaction is shown below.



$$\begin{array}{l} [\mathrm{RuCl(CH_3CN)(PPhMe_2)_4}]^+ + 2e \longrightarrow \mathrm{RuCH_3CN(PPhMe_2)_4} + \mathrm{Cl}^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \big\downarrow \; \mathrm{PPhMe_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{Ru(PPhMe_2)_5} + \mathrm{CH_3CN} \end{array}$$

The position of the wave suggests that a rapid ligand exchange occurs in the zerovalent ruthenium complex.

The above information was used to assign the first wave as a two electron, irreversible, slightly kinetic controlled reduction of $[\mathrm{RuClCH_3CN(PPhMe_2)_4}]^+$. The second wave represented an adsorption controlled, two electron, irreversible reduction of $[\mathrm{RuCl(CH_3CN)_2(PPhMe_2)_3}]^+$. The third wave arose from a kinetically controlled two electron irreversible reduction of $[\mathrm{RuCl(CH_3CN)_3(PPhMe_2)_2}]^+$.

A comparison of the reduction potentials for

Figure 22 : Polarogram of 1.00 mM $(PPhMe_2)_4RuCl_2$ with 10-fold excess of $PPhMe_2$ ligand.

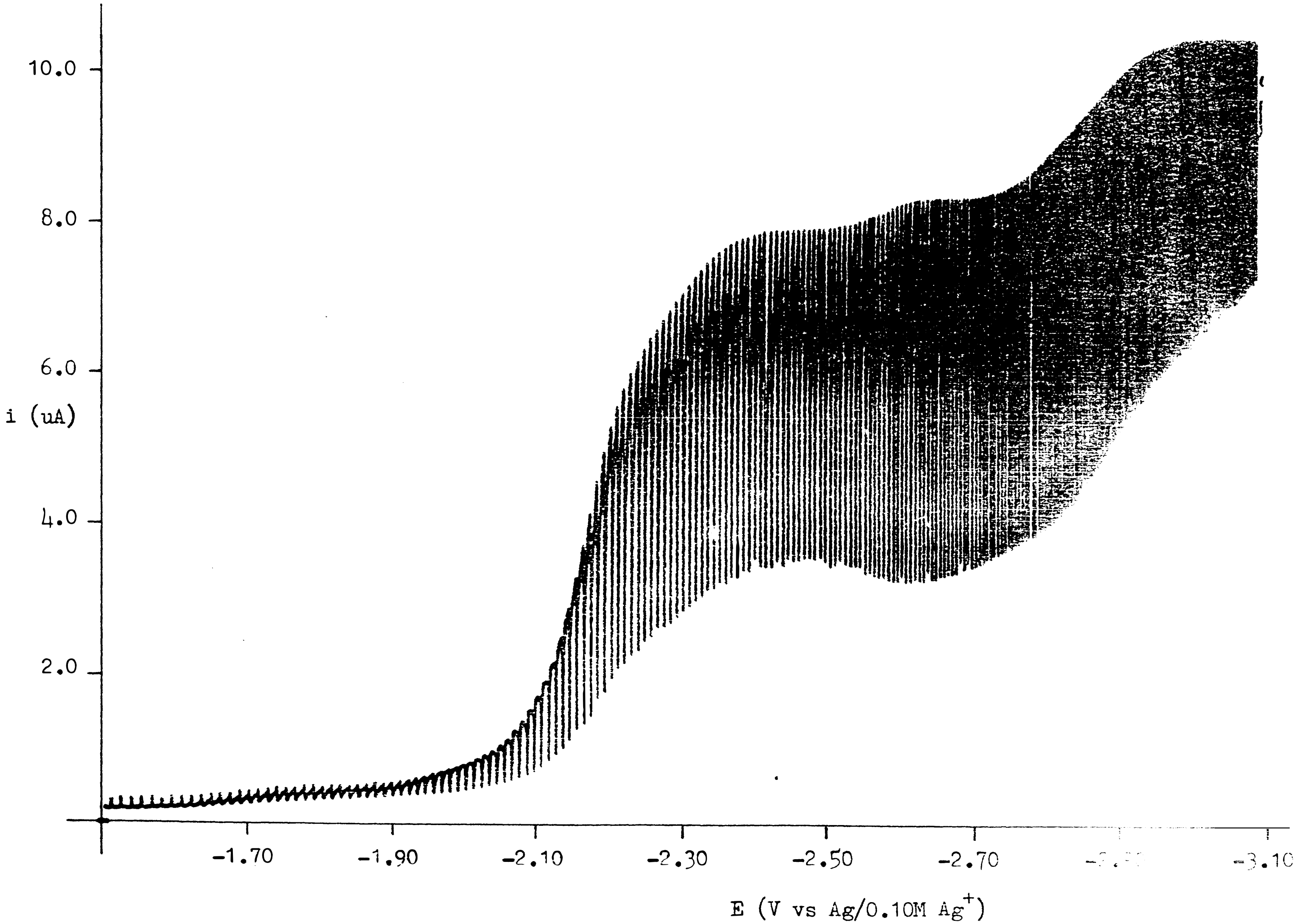

10.0
8.0
6.0
i (uA)
4.0
2.0
-1.70
-1.90
-2.10
-2.30
-2.50
-2.70
-3.10
E (V vs Ag/0.10M Ag+)

TABLE 9 : Value of limiting current as a function of corrected height for $(PPhMe_2)_4RuCl_2$ with 10-fold excess of $PPhMe_2$ ligand

| Height<br>± 0.1 cm | $i_{L1}$<br>± .05 uA | $h_{corr1}$<br>± 0.1 cm | $i_{L2}$<br>± .05 uA | $h_{corr2}$<br>± 0.1 cm | $i_{L3}$<br>± .05 uA | $h_{corr3}$<br>± 0.1 cm |
|---|---|---|---|---|---|---|
| 72.4 | 8.71 | 70.4 | 0.61 | 70.1 | 2.20 | 69.5 |
| 64.3 | 8.31 | 62.3 | 0.43 | 62.0 | 2.10 | 61.4 |
| 59.0 | 7.99 | 57.0 | 0.43 | 56.7 | 2.12 | 56.0 |
| 54.0 | 7.50 | 52.0 | 0.41 | 51.7 | 2.05 | 51.1 |
| 45.1 | 7.08 | 43.1 | 0.31 | 42.8 | 1.96 | 42.1 |

$(PPh_2Me)_4RuCl_2$ (-2.25 V) and $(PPhMe_2)_4RuCl_2$ (-2.28) showed that there was no significant difference in the electron density around the metal centers for the two complexes. It was predicted that the complex with the $PPhMe_2$ ligand would have a more negative potential than the complex with the $PPh_2Me$. Such cathodic shifts with increasing donor strength have been observed by Mazzocchin et. al[24].

### 3. Polarography of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$

The polarogram of the complex $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ shows three poorly defined reduction waves (fig 23) with half wave potentials at -2.28 ± 0.03, -2.42 ± 0.03, and -2.65 ± 0.03 V.

The current control plots gave slopes of 0.81 ± 0.03, 0.38 ± 0.02 and 0.58 ± 0.02 for the first ,second, and third waves, respectively, from the data summarized in table 10. The slope for the first wave suggested that the electroactive species or the product of the electrode reaction was adsorbed on the surface of the drop. A study done on height dependence of the total limiting current of waves one and two provided information about possible adsorption of the reduced product. A plot of ln $(i_{L1}+i_{L2})$ vs ln $h_{corr}$ gave a diffusion controlled slope of 0.46 ± 0.02. This suggested that only one electroactive species was responsible for the combination wave, and this species was under diffusion control at the more negative

Figure 23 : Polarogram of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ in acetonitrile

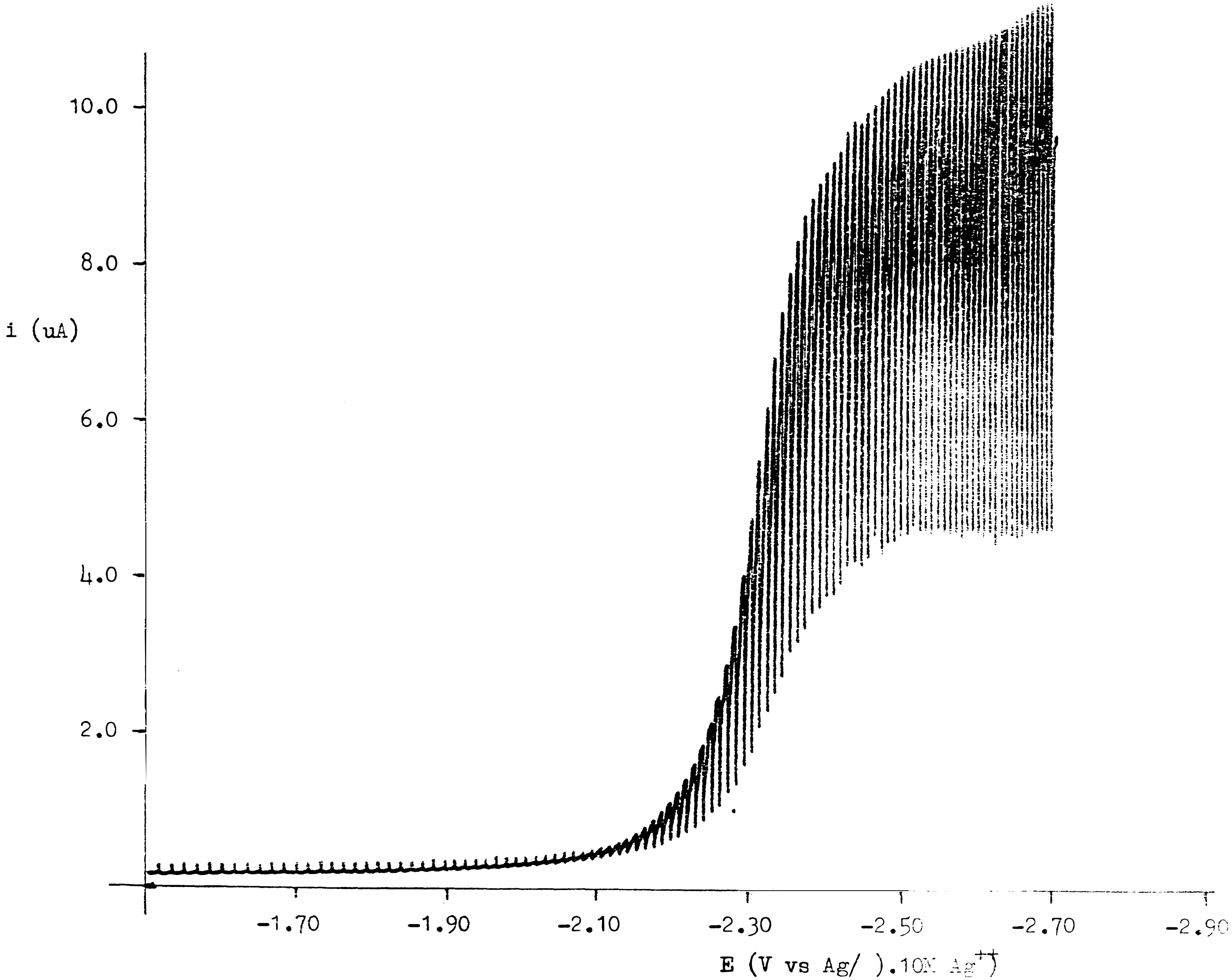

10.0
8.0
i (uA)
6.0
4.0
2.0
-1.70
-1.90
-2.10
-2.30
-2.50
-2.70
-2.90
E (V vs Ag/ ).10M Ag++)

TABLE 10: Dependence of limiting current on corrected height for $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$

| Height<br>cm ± .1 | $h_{corr1}$<br>cm ± .1 | $i_{L1}$<br>uA ± .05 | $h_{corr2}$<br>cm ± .1 | $i_{L2}$<br>uA ± .05 |
|---|---|---|---|---|
| 73.6 | 71.4 | 13.18 | 71.2 | 1.39 |
| 64.2 | 62.0 | 12.35 | 61.8 | 1.26 |
| 59.0 | 56.7 | 11.95 | 56.5 | 1.19 |
| 53.6 | 51.3 | 11.35 | 51.1 | 1.13 |
| 44.5 | 42.3 | 10.37 | 42.1 | 1.03 |

TABLE 11 : Dependence of limiting current on corrected height for $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 10-fold excess of $PPh_2Me$ ligand

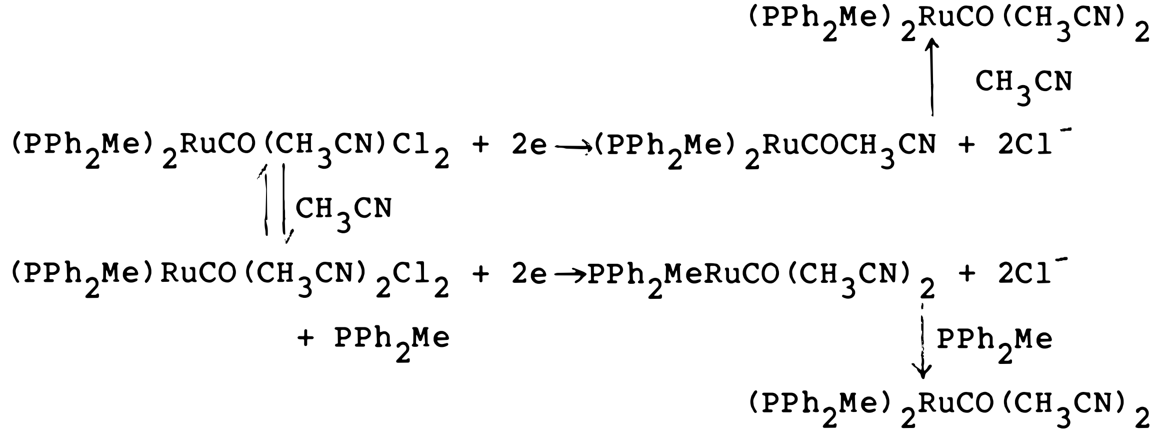
| Height<br>cm ± .1 | $h_{corr1}$<br>cm ± .1 | $i_{L1}$<br>uA ± .05 |
|---|---|---|
| 71.3 | 69.3 | 10.58 |
| 64.5 | 62.4 | 10.26 |
| 58.8 | 56.7 | 9.59 |
| 54.2 | 52.2 | 9.28 |
| 46.7 | 44.6 | 8.58 |

potential. The adsorption of the reduced species was reflected in the rising portion of the combination wave. Since the complex was more difficult to reduce and solvate than to reduce and adsorb, the upper part of the wave represents reduction followed by dissolution[25].

The ratio of limiting current of both waves 1 and 2 to the third wave was 8.0 : 1.0. The presence of the third wave thus suggested that another electroactive species was present. The current ratios also indicated that the formation of the electroactive species was not favorable. Conductivity measurements made on the complex showed no dissociation of chloride ligands in acetonitrile. The observed waves would suggest that the following $PPh_2Me$ ligand exchange equilibrium was taking place:

$$\begin{array}{c} (PPh_2Me)_2RuCO(CH_3CN)Cl_2 + CH_3CN \\ \big\uparrow\big\downarrow \\ PPhMeRuCO(CH_3CN)_2Cl_2 + PPh_2Me \end{array}$$

As has been seen above, the complex with two $CH_3CN$ ligands would be expected to reduce at a more negative potential than the complex with one $CH_3CN$ ligand, and both the current and concentration were expected to be sensitive to the presence of excess ligand. The exchange with carbon monoxide is also a distinct possibility. In constrast, excess ligand should not affect the current of the polarogram or the concentration of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ in the carbonyl/acetonitrile equilibrium. All reduction waves were found to be two electron transfers by comparison with the established current of the $(PPh_3)_4RuCl_2$ complex. The reduction in the absence of excess ligand follow the proposed mechanism:



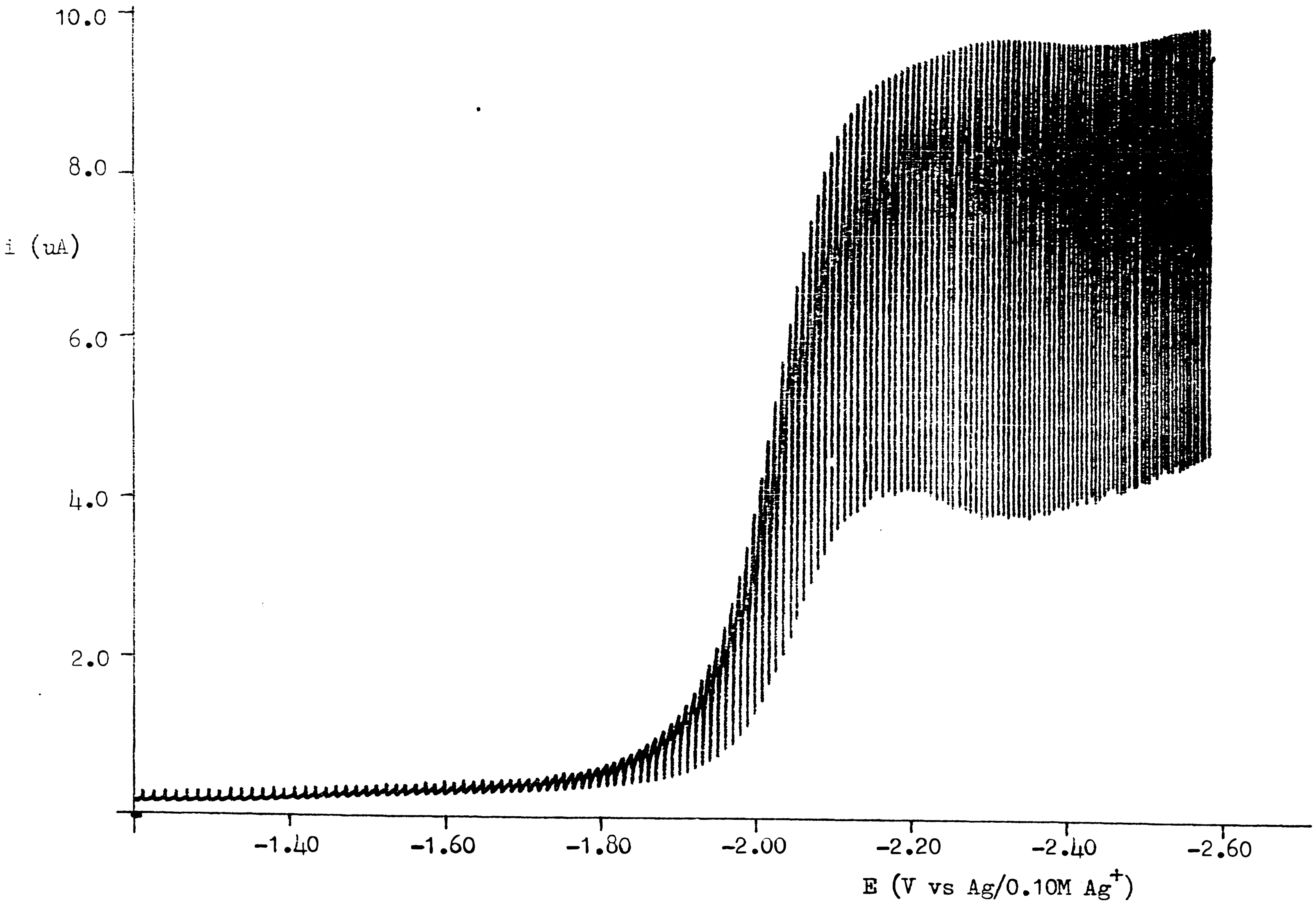
$$\begin{tikzcd}
 & \mathrm{(PPh_2Me)_2RuCO(CH_3CN)_2} \\
\mathrm{(PPh_2Me)_2RuCO(CH_3CN)Cl_2} + 2e \arrow[r] \arrow[d, shift left, "\mathrm{CH_3CN}"] & \mathrm{(PPh_2Me)_2RuCOCH_3CN} + 2\mathrm{Cl}^- \arrow[u, "\mathrm{CH_3CN}"'] \\
\mathrm{(PPh_2Me)RuCO(CH_3CN)_2Cl_2} + 2e \arrow[r] \arrow[u, shift left] & \mathrm{PPh_2MeRuCO(CH_3CN)_2} + 2\mathrm{Cl}^- \arrow[d, "\mathrm{PPh_2Me}"] \\
+ \mathrm{PPh_2Me} & \mathrm{(PPh_2Me)_2RuCO(CH_3CN)_2}
\end{tikzcd}$$

All waves for these complexes revealed irreversible reduction.

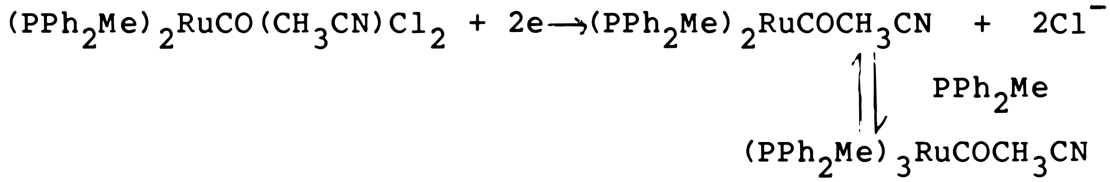
Addition of a 10-fold excess of $PPh_2Me$ ligand resulted in a combination wave as shown in figure 24. It was clear that the first part of the wave was dominant and behaved as the combination wave discussed above. The half wave potentials for both waves have shifted more anodic (-2.21,-2.40 V). The third wave was absent indicating that addition of excess $PPh_2Me$ ligand did indeed confirm the presence of a phosphine/acetonitrile ligand exchange and shifted this equilibrium totally in favor of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$.

The total current for both waves as a function of height (Table 11) indicated that mass transport of the electrospecies was a mixture of diffusion and kinetic control (slope = 0.40 ± 0.02). The positive shift of the

Figure 24 : Polarogram of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 10-fold of $PPh_2Me$ excess ligand


10.0
8.0
6.0
4.0
2.0
i (uA)
-1.40
-1.60
-1.80
-2.00
-2.20
-2.40
-2.60
E (V vs Ag/0.10M Ag+)

potential of the total wave was explained by the following fast chemical reaction which occurred during electron transfer:



$$\begin{tikzcd}(PPh_2Me)_2RuCO(CH_3CN)Cl_2 + 2e \arrow[r] & (PPh_2Me)_2RuCOCH_3CN + 2Cl^- \arrow[d, shift left, "PPh_2Me"] \\ & (PPh_2Me)_3RuCOCH_3CN \arrow[u, shift left]\end{tikzcd}$$

Mass transport effects could also have been held responsible for the shift in the potential.

For the efficient electrosynthesis of the zerovalent oxidation state of the ruthenium atom of this complex, a potential of -2.40V must be applied. Addition of excess ligand was also necessary to make the reduction more favorable.

### 5. Polarogram of $(PPhMe_2)_3RuCOCl$

Two poorly defined reduction waves at -1.93 V ± 0.03 (first) and -2.25 ± 0.03 V (second) were present in the polarogram of $(PPhMe_2)_3RuCOCl_2$, Figure 25. Data in Table 12 was used to find the slopes of the current control plots. The first wave was found to be totally kinetically controlled. The current was independent of the height or the drop time. The second wave had a slope of 0.67 ± 0.02 which was indicative of absorption current.

The ratio of the first to the second wave, 0.35:1.0, again indicated two species giving rise to two waves. The species that produced the first wave had a current which shows that it is not favorable under those conditions.

Figure 25 : Polarogram of $(PPhMe_2)_3RuCOCl_2$
in acetonitrile

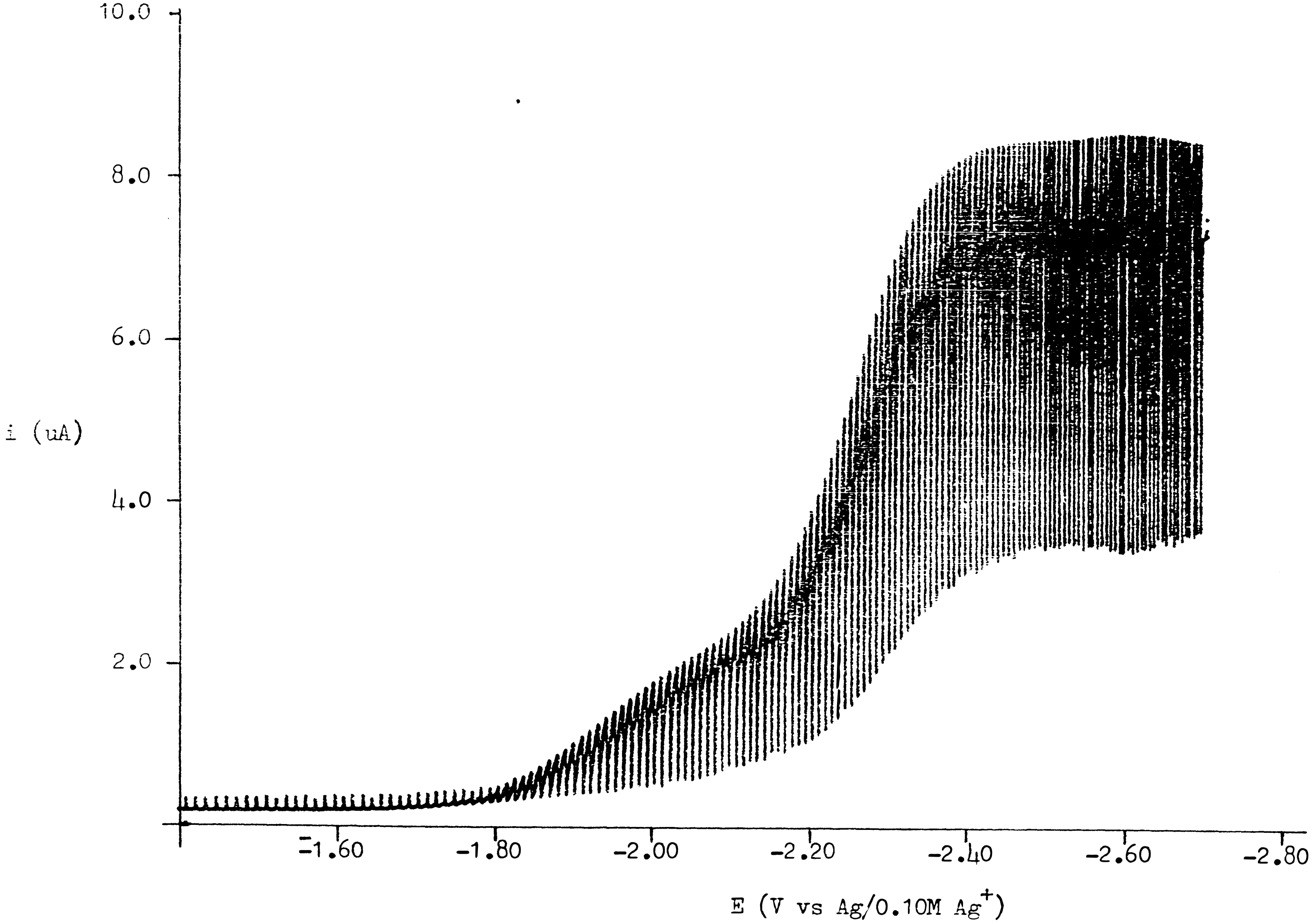

10.0
8.0
6.0
i (uA)
4.0
2.0
-1.60
-1.80
-2.00
-2.20
-2.40
-2.60
-2.80
E (V vs Ag/0.10M Ag+)

TABLE 12: Dependence of limiting current on the corrected height for $(PPhMe_2)_3RuCOCl_2$

| Height<br>cm ± .1 | $h_{corr1}$<br>cm ± .1 | $i_{L1}$<br>uA ± .05 | $h_{corr2}$<br>cm ± .1 | $i_{12}$<br>uA ± .05 |
|---|---|---|---|---|
| 73.9 | 72.0 | 2.11 | 71.8 | 6.84 |
| 64.4 | 62.4 | 2.13 | 62.3 | 6.22 |
| 59.7 | 57.7 | 2.17 | 57.5 | 6.05 |
| 52.8 | 50.8 | 2.20 | 50.7 | 5.45 |
| 43.7 | 41.7 | 2.20 | 41.5 | 4.74 |

Conductivity measurements exclude the loss of the chloride in the coordination sphere. Ligand exchange with either carbonyl or phosphine ligands in acetonitrile accounted for the observed waves on the polarogram. Literature sources suggested that carbonyl/acetonitrile ligand exchange is much less favored than phosphine/acetonitrile exchange.

$$\begin{array}{l} (PPhMe_2)_3RuCOCl_2 \quad + \quad CH_3CN \\ \qquad\qquad\quad \upharpoonleft\!\downharpoonright \\ (PPhMe_2)_2RuCOCl_2CH_3CN \quad + \quad PPhMe_2 \end{array}$$

From the reactions above, the complex $(PPhMe_2)_2RuCO(CH_3CN)$ was assigned to the wave at -2.25 V while $(PPhMe_2)_3RuCOCl_2$ was assigned to the wave at -1.93 V. Excess phosphine ligand should shift the equilibrium in the direction of the trisubstituted phosphine complex if there is a phosphine/ acetonitrile exchange, while no change in the concentration of $(PPhMe_2)_3RuCOCl_2$ should occur if a carbonyl/ acetonitrile exchange was present. However, since the mass transport of the electroactive species is under kinetic control, the current of the first wave did not represent the concentration of the electroactive species in the bulk solution. Thus, the change in equilibrium was not observed.

All waves were again found to be two electron irreversible reductions by the method already discussed above. It is believed that the reduction in the absence of excess ligand follows the proposed mechanism:

$$\begin{tikzcd}
 & \mathrm{(PPhMe_2)_3RuCOCH_3CN} & \\
\mathrm{(PPhMe_2)_3RuCOCl_2 + 2e} \arrow[r] \arrow[d, shift left, "\mathrm{CH_3CN}"] & \mathrm{(PPhMe_2)_3RuCO} \arrow[u, "\mathrm{CH_3CN}"'] & \mathrm{+\ 2Cl^-} \\
\mathrm{(PPhMe_2)_2RuCO(CH_3CN)Cl_2 + 2e} \arrow[u, shift left] \arrow[r] & \mathrm{(PPhMe_2)_2RuCOCH_3CN} \arrow[d, "\mathrm{PPhMe_2}"] & \mathrm{+\ 2Cl^-} \\
\mathrm{+PPhMe_2} & \mathrm{(PPhMe_2)_3RuCOCH_3CN} &
\end{tikzcd}$$

Addition of a 10-fold excess of $PPhMe_2$ ligand essentially did not change the features of the polarogram, Fig 26. The two waves were at -1.91 ± 0.03 and -2.25 ± 0.03 V with slopes of zero and 0.84 ± 0.02 in the current control plots for the first and second waves, respectively. These results added no additional information.

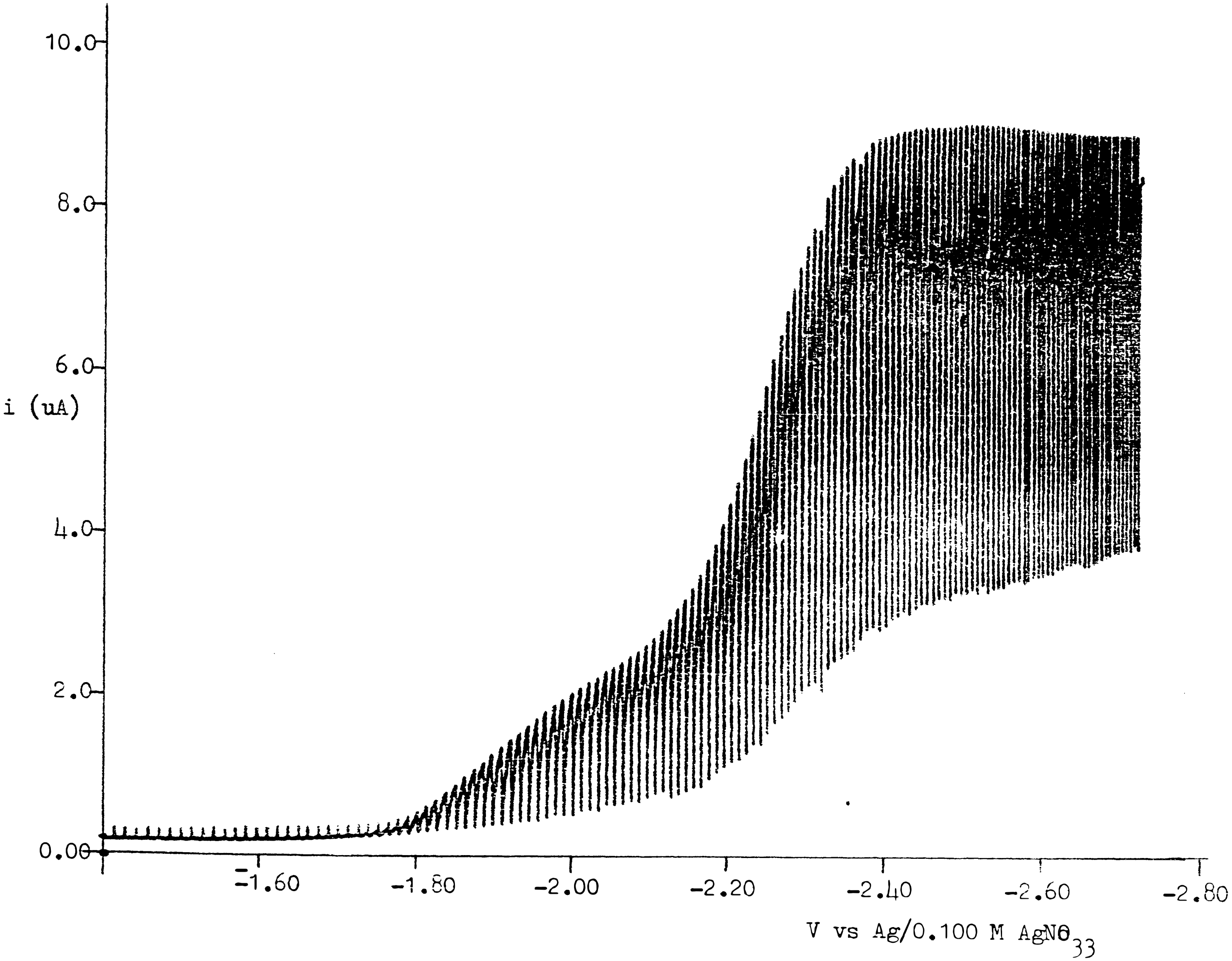
From the above discussion, the first wave was assigned as an irreversible, totally kinetic controlled, two electron transfer to $(PPhMe_2)_3RuCOCl_2$ and the second as an irreversible, adsorption controlled, two electron transfer to $(PPhMe_2)_2RuCOCl_2CH_3CN$. The electrosynthesis of this complex in the absence of excess phosphine ligand required an applied potential of -2.40 V to achieve optimun reduction to the Ru (0) complex.

D. Attempted synthesis of Ru (0) complexes.

1. Synthesis of $(PPhMe_2)_3RuCO(CH_3CN)$

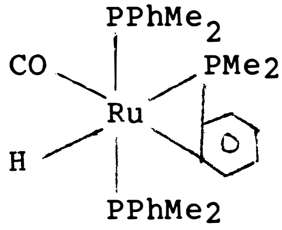
Attempts to reduce $(PPhMe_2)_3RuCOCl_2$ with sodium

Figure 26 : Polarogram of $(PPhMe_2)_3RuCOCl_2$
with 10-fold excess of $PPhMe_2$ ligand

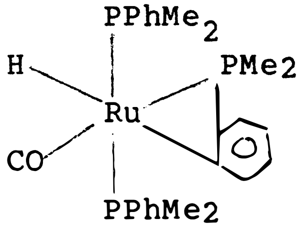

10.0
8.0
6.0
i (uA)
4.0
2.0
0.00
-1.60
-1.80
-2.00
-2.20
-2.40
-2.60
-2.80
V vs Ag/0.100 M AgNO33

amalgam in acetonitrile give an intractable oil. The oil obtained after removal of all solvent was characterized with infrared, $^{31}P$ and $^{1}H$ NMR spectroscopy.

The infrared spectrum (Fig 27) of the oil showed two bands (2150 and 2180 $cm^{-1}$), one broad band (1940 $cm^{-1}$) for C=O strectching and one band (1850 $cm^{-1}$) for Ru-H stretching. The source of the hydride in the complex was most probably the $PPhMe_2$ ligand. Either the protons of the methyl group[26] or the ortho-hydrogens on the phenyl rings[27] could supply the necessary hydride by the insertion of the metal into the appropriate carbon-hydrogen bond. Characteristic bands for orthometallated phenyl rings[28] show signals at 1560 and 1420 $cm^{-1}$, and such bands are seen in Fig. 27. Thus, the predominant source of the hydride ligand appears to be the phenyl rings (structures V and VI). Additional confirmation of the assignment was obtained by examination of the region where C-H out of plane deformation for ortho-disubstituted aromatics occurs[28]. A band at 737 $cm^{-1}$, consistent with this assignment was observed. Structure V is more likely since orthometallation generally occurs so that the hydride is located cis to the phenyl ring[29].

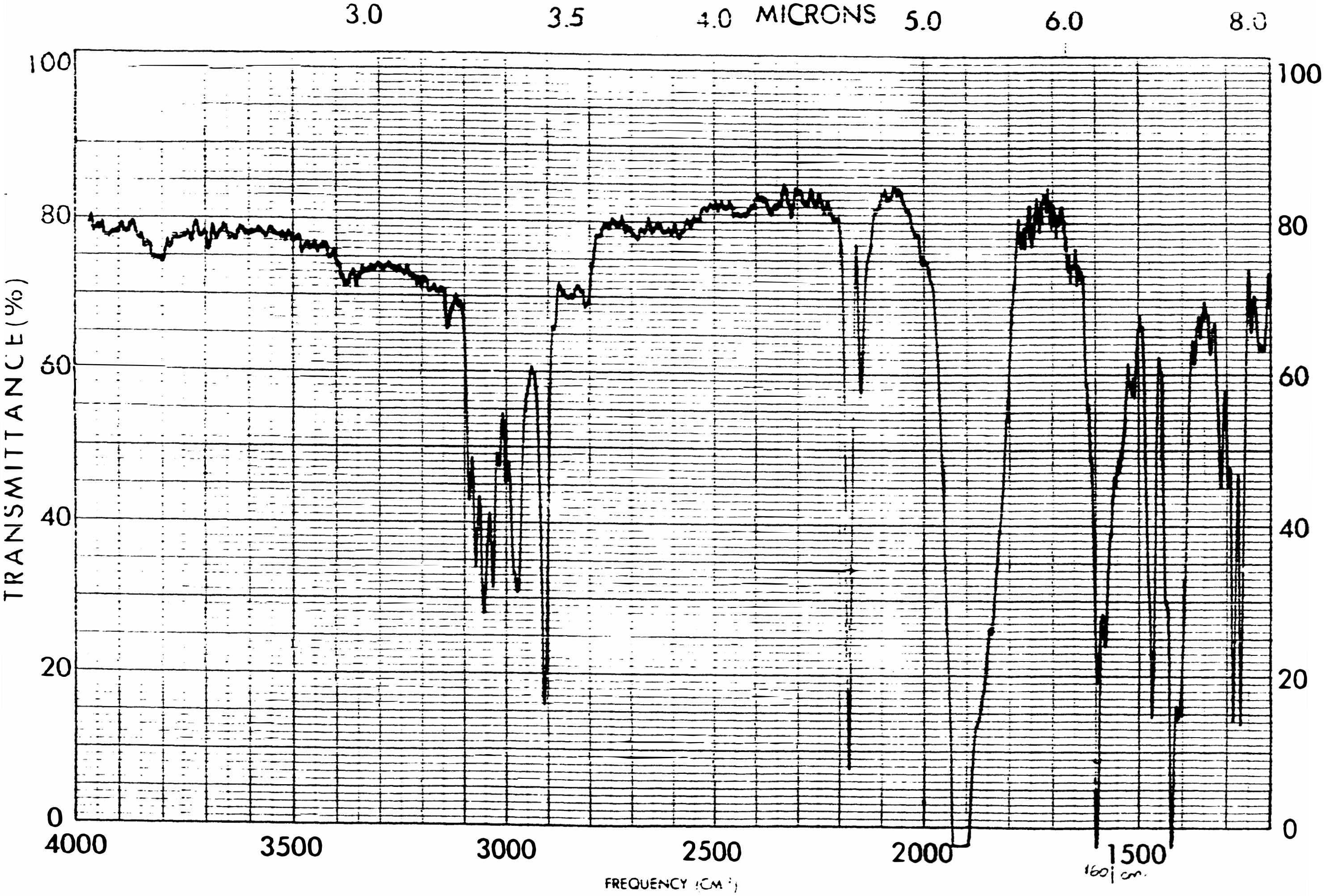


(V)



(VI)

Figure 27: Infrared spectrum of the oil obtained from reduction of $(PPhMe_2)_3RuCOCl_2$ with Na-Hg amalgam



SAMPLE Oil (A)

ORIGIN Page 94

SOLVENT

CURVE NO.

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REFERENCE

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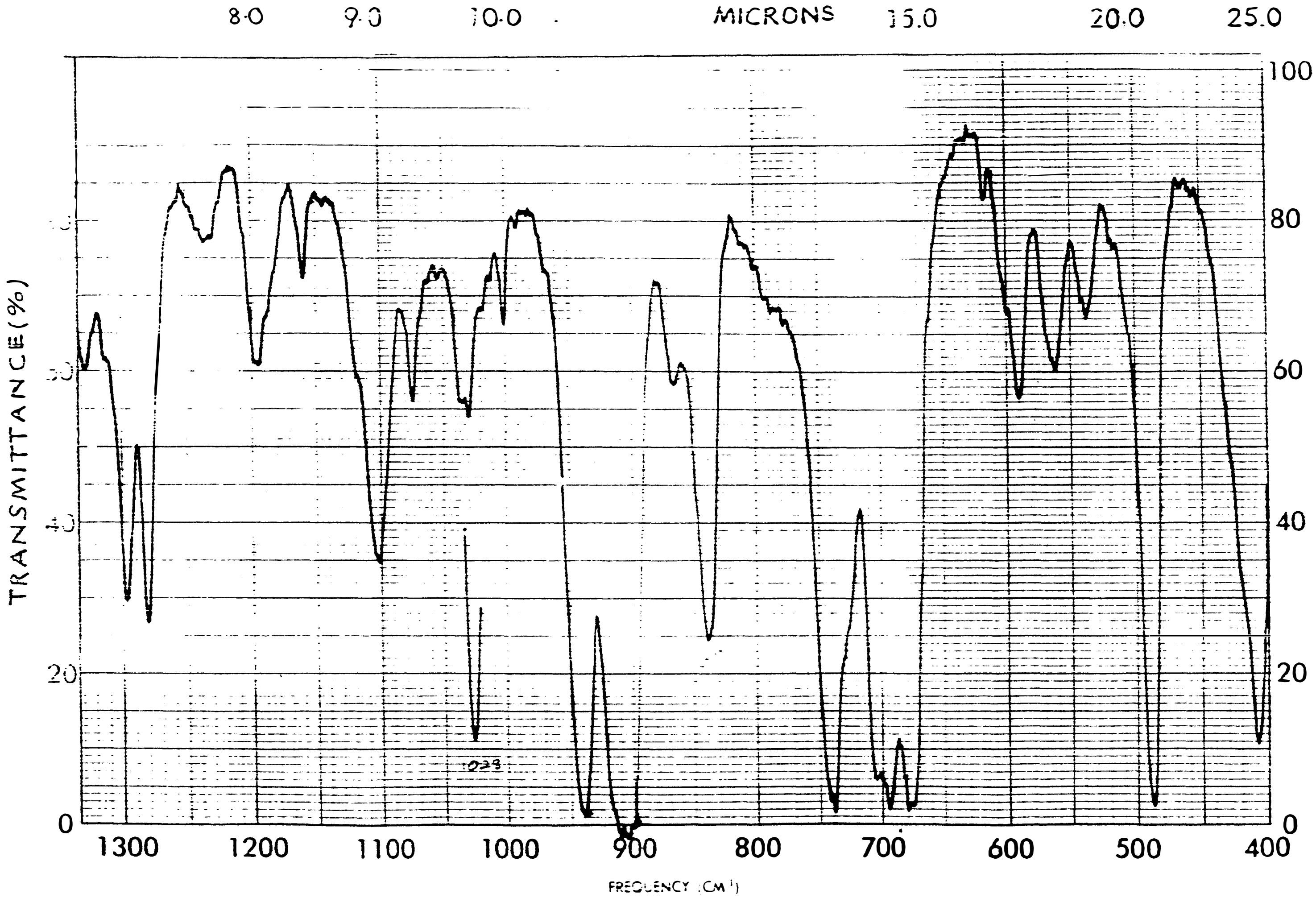
SLIT N

OPERATOR N M

DATE 6/23/56

REMARKS

PR 1122 337-120



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| SAMPLE Oil (*) | CURVE NO. | SCAN SPEED F | OPERATOR NM |
| | CONC. | SLIT N | DATE 6/23/86 |
| ORIGIN Page 94 | CELL PATH KBr | REMARKS | |
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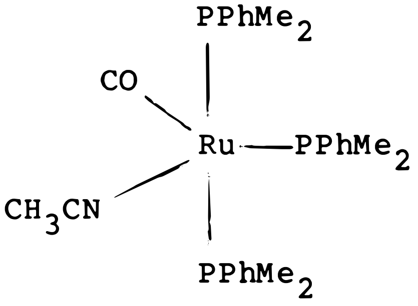
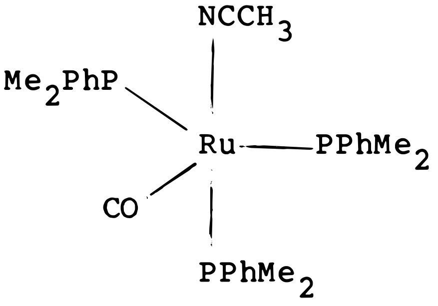
1123/2371204

The infrared spectrum (Fig 27) also revealed that a complex containing acetonitrile coordinated to ruthenium was present as an impurity.

The $^{31}P$ NMR spectrum of the oil, obtained from acetonitrile solution (Fig 28) exhibited two major doublets (9.07 and 7.70 ppm) and a broad triplet (-6.38 ppm). The spectrum indicates that the major complexes present in solution are unorthometallated since $^{31}P$ chemical shifts are upfield from the chemical shift range for orthometallated species[30]. The doublet arises from two phosphorus ligand atoms in a trans configuration coupled to one cis phosphorus atom. The two separate doublets indicate the presence of two isomers. The broad triplet, which suggests the overlapping of signals, arises from the cis phosphorus ligand coupled to the two trans phosphorus atoms of the two different isomers.



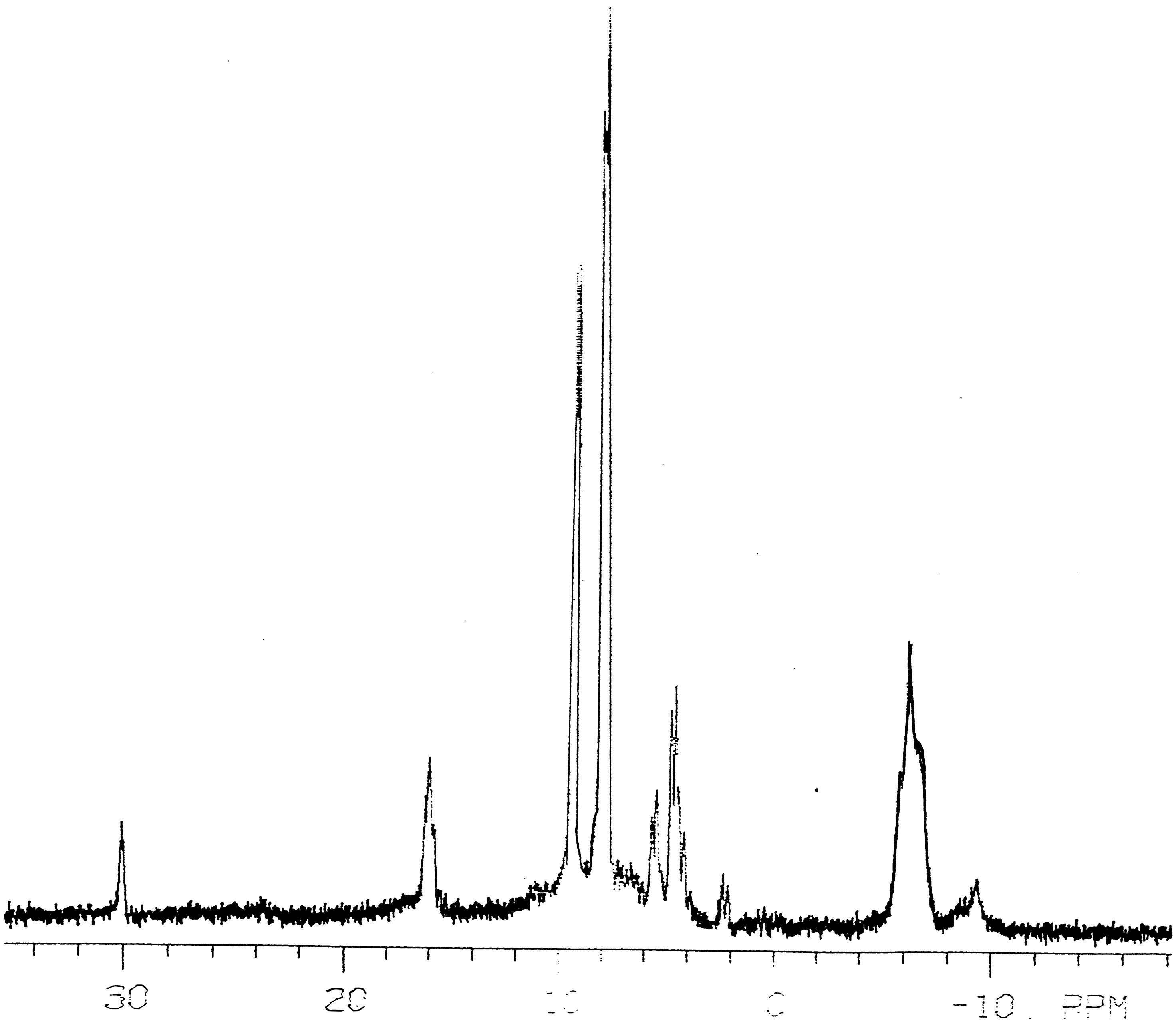
(VII)



(VIII)

The $^{31}P$ NMR spectrum suggests that the complex dissociates in the coordinating solvent to give unmetallated product[31]. In this way the result obtained from the infrared studies of the oil without solvent are consistent with the result obtained from the $^{31}P$ studies

Figure 28: $^{31}P$ NMR spectrum of the oil obtained from reduction of $(PPhMe_2)_3RuCOCL_2$ with Na-Hg amalgam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20
10
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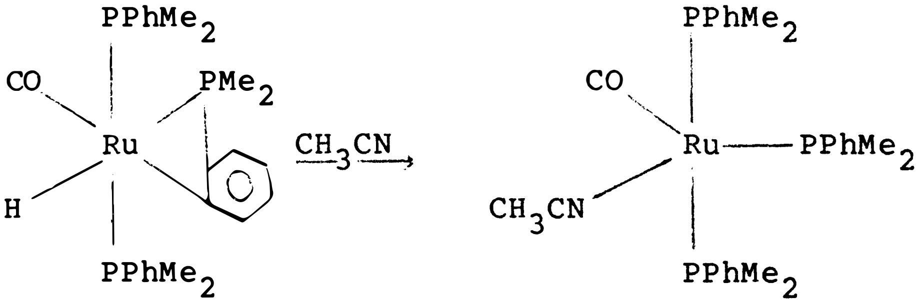
-10 . PPM

on the oil dissolved in a coordinating solvent.



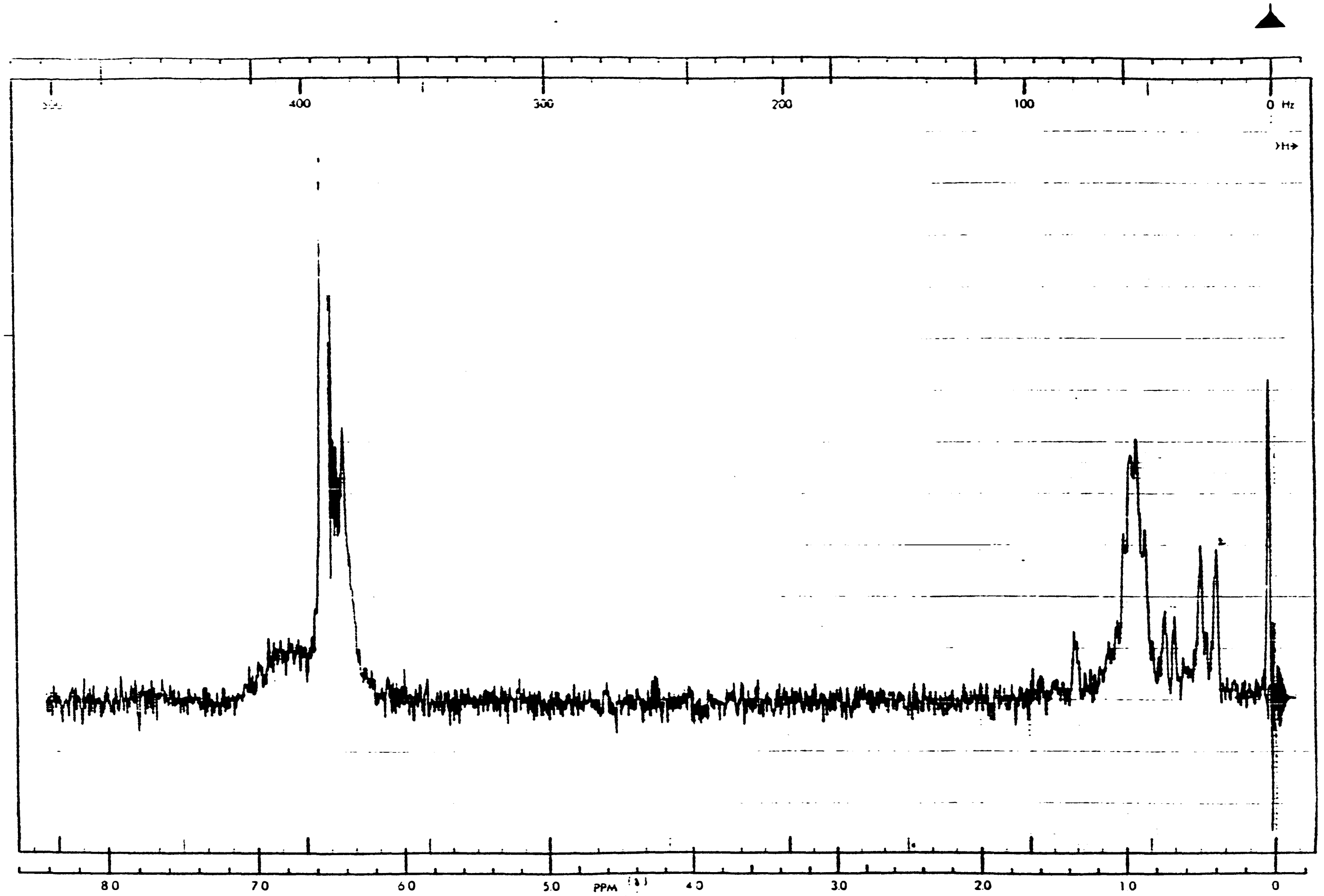
Minor peaks at 30.0 and 15.9 ppm indicate complexes as in structure V and VI are also present in solution. The $^1H$ NMR spectrum in benzene (Fig 29) reveals complicated splittings in the methyl region suggesting that several complexes are present in solution. Attempts to isolate solid products from a variety of solvents were unsuccessful.

B. Synthesis of $(PPh_2Me)_2RuCO(CH_3CN)_2$

Reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 1% Na-Hg in $CH_3CN$ gave a dark brown oil from which came a reddish brown powder when the oil was treated with hexane. This brown powder was found to be a mixture of orthometallated compounds and unidentified, incompletely reduced species. Attempts to recrystallize the brown powder with a variety of solvents were unsuccessful.

The infrared spectrum of the brown powder (Fig 30) shows characteristic peaks for C=N and C=O stretching. The characteristic peaks for orthometallated phenyl rings occur at approximately 1550 $cm^{-1}$. From the broad peak centered at 2150 $cm^{-1}$, it appears that several different complexes containing acetonitrile were present. The

Figure 29: $^1H$ NMR spectrum of the oil obtained from reduction of $(PPhMe_2)_3RuCOCl_2$ with Na-Hg amalgam



MANUAL

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INTEGRAL AMPLITUDE:
SPINNING RATE (RPS): 32

SWEEP TIME (SEC): 50 [✓ 250]
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]
FILTER: [✓ 1] 2 3 4 5 6 7 8
RF POWER LEVEL: 0.09

AUTO ☐
(250)
(500)
( 2)
(.05)

SAMPLE: Oil (A)
page 94.

SOLVENT: $C_6D_6$

REMARKS: external ref TMS.

**RECORDING CHARTS**
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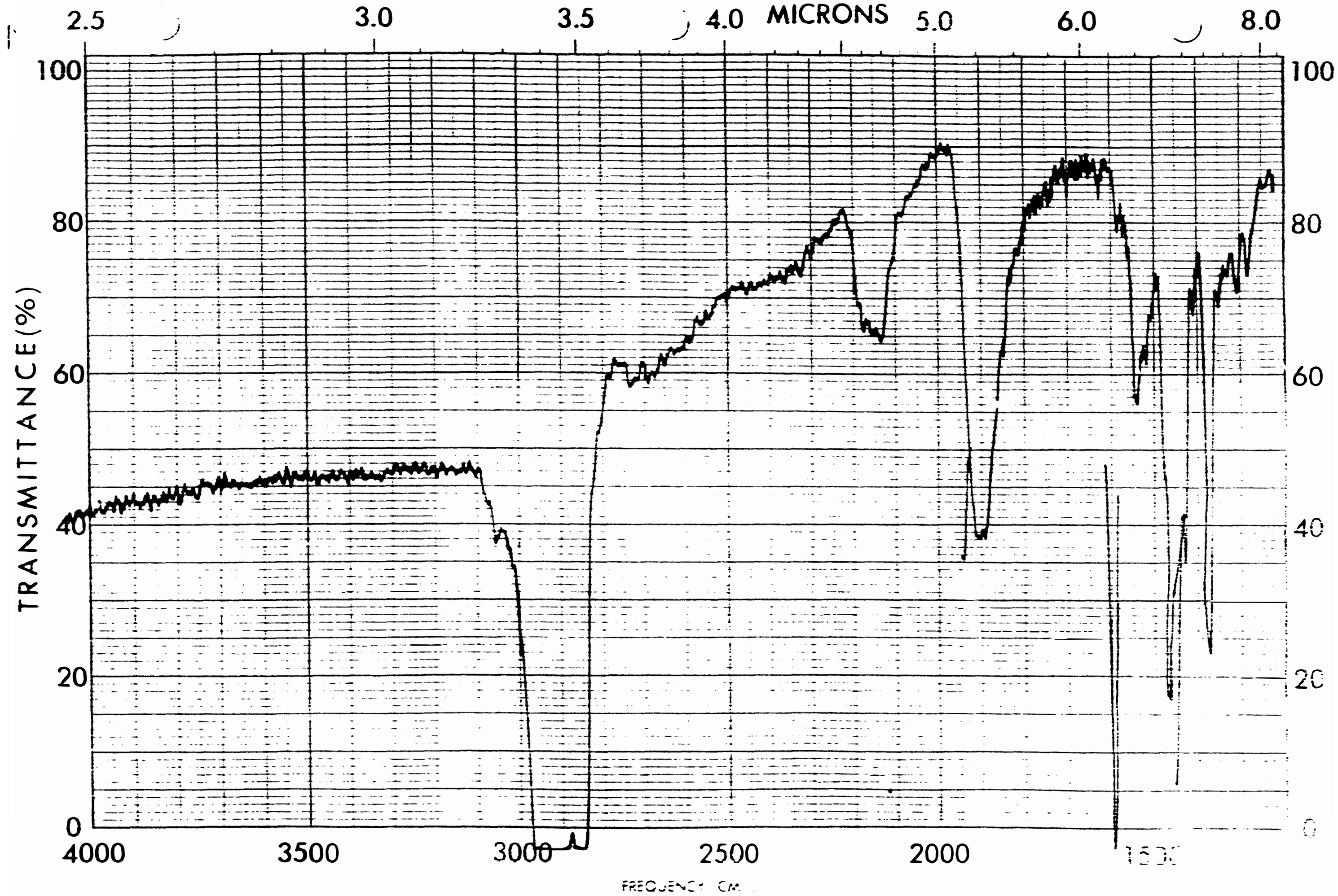
DATE: July 4th 86

OPERATOR: NAI

60 MHz NMR
SPECTRUM NO

Figure 30: Infrared spectrum of the brown solid obtained from reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with Na-Hg amalgam



SAMPLE Ru° - PPh$_2$me) CO

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ORIGIN page 1 (7/7/86)

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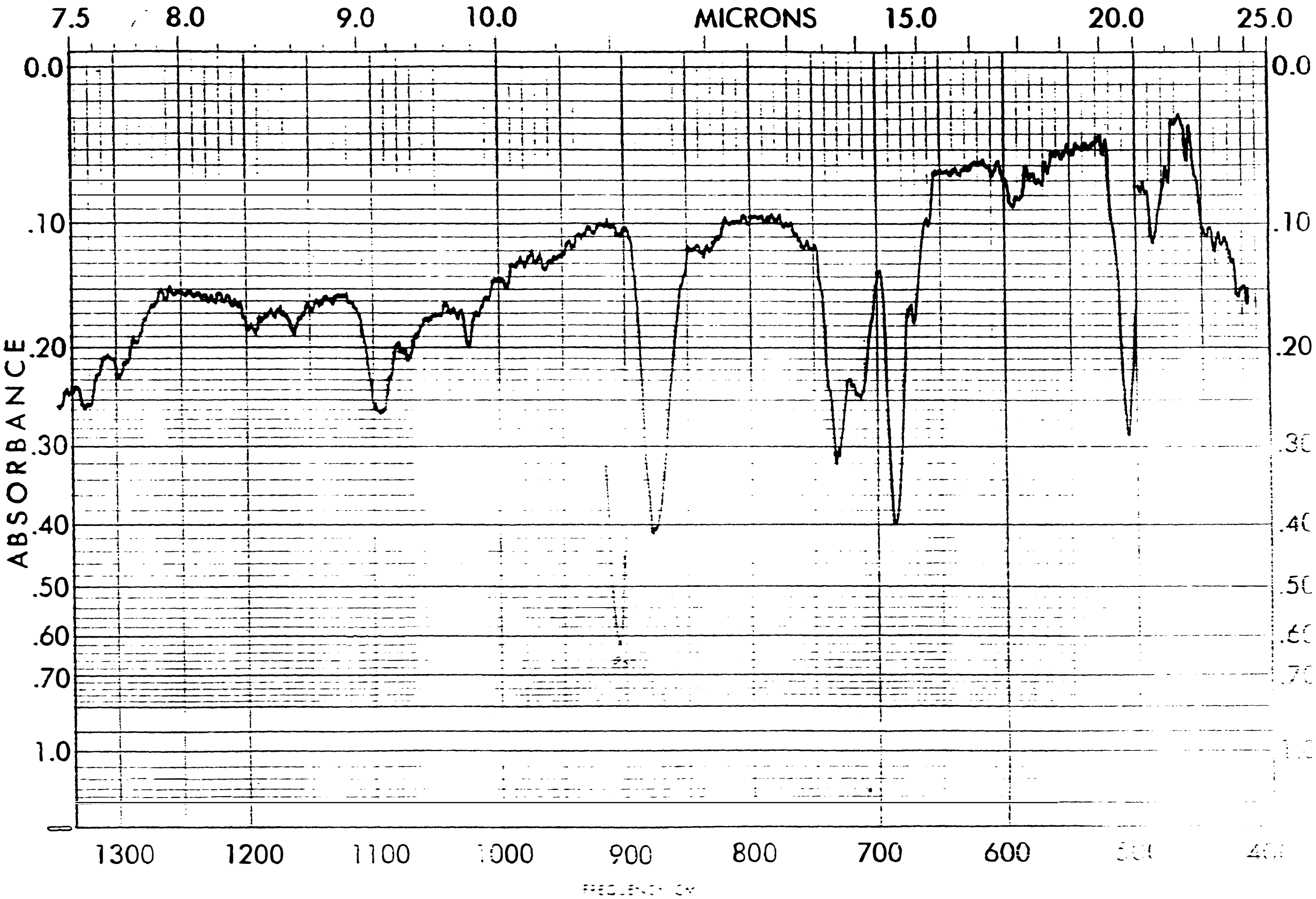

SAMPLE Ru$^{0}$(PPh$_2$me) Co

ORIGIN page 1 (7/7/86)

SOLVENT NUJOL

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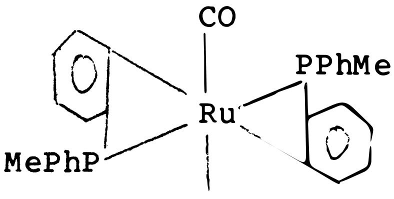
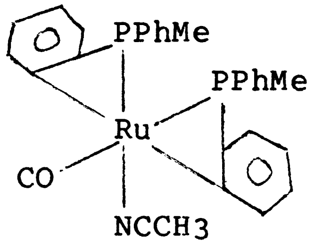
decrease in $C\equiv N$ frequency indicates that the d-electrons of ruthenium back-bond to the nitrile $\pi^*$ orbitals to reduce the $C\equiv N$ bond order[32]. The presence of a $C=O$ stretching band with shoulders centered at 1900 $cm^{-1}$ supports this hypothesis.

The $^{31}P$ NMR spectrum (Fig 31) indicates that the major product obtained was orthometallated since the major signal was shifted significantly downfield from the signal of the starting material[30], characteristic of non-orthometallated complexes. The two different isomers for the major product can be presented as structures (IX and X)

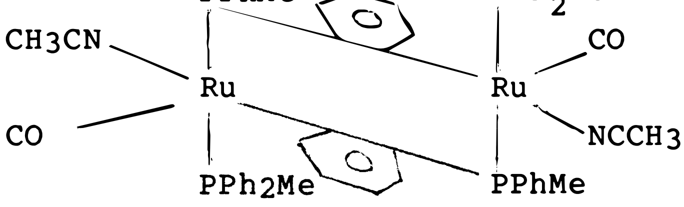


(IX)



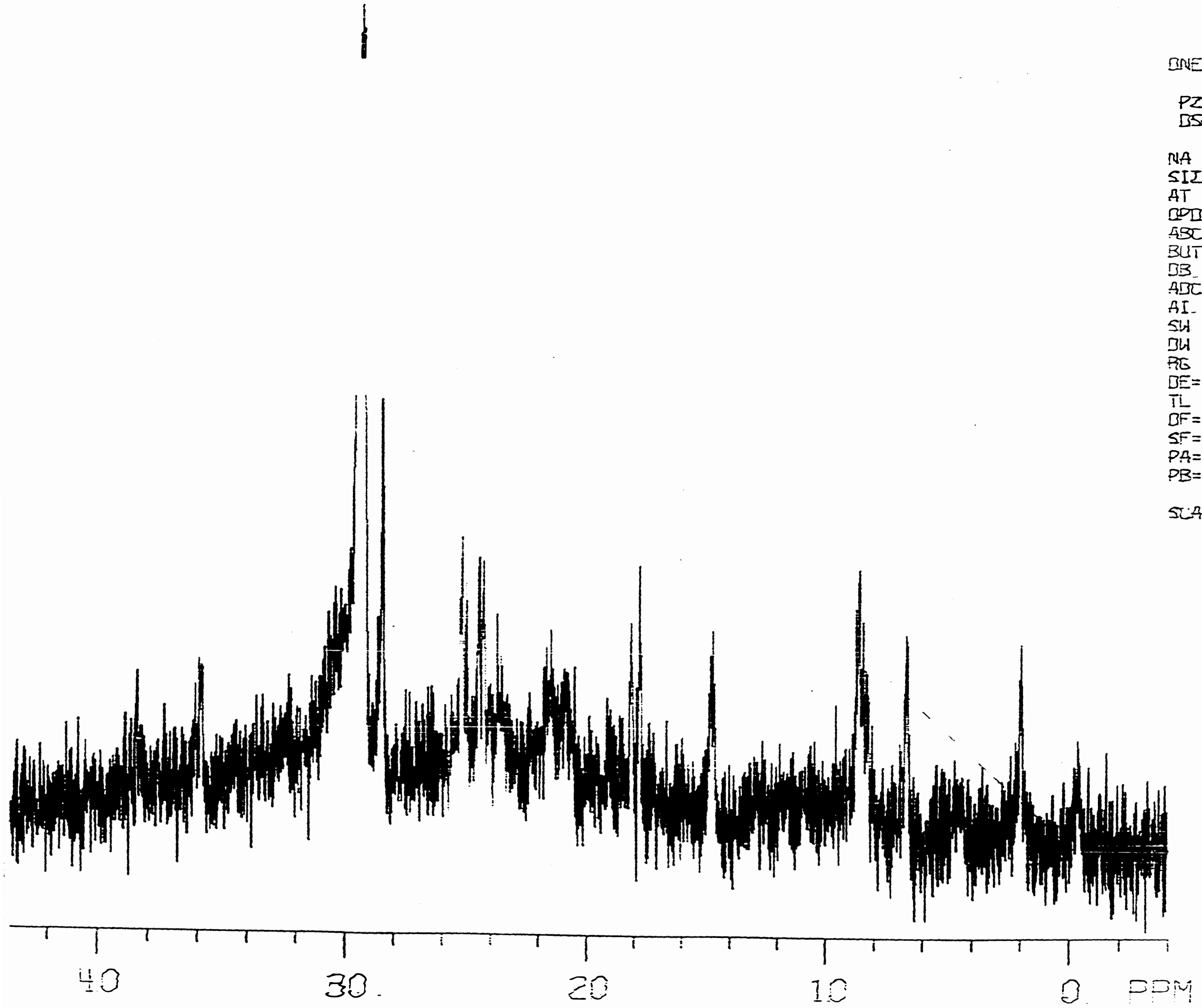
(X)

The structure determination of other components shown to be present by $^{31}P$ and $^{1}H$ NMR spectroscopy was impossible due to their low solubility. The insolubility suggests that a dimeric structure XI similar to that observed for $\{RuH(dmpe)[CH_2PMe]CH_2CH_2PMe_2\}_2$ is reasonable[33].



(XI)

Figure 31: $^{31}P$ NMR spectrum of the brown powder obtained from reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with Na-Hg amalgam



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AT =        655.36 MSEC
OPD ON. =         0
ABC ON
BUTTERWORTH FILTER ON
DB_ATT.=          3
ADC =    8 BITS
AI. =        8
SW = +/- 25000.0
DW =        20
RG =        25 USEC
DE=       30 USEC
TL HIGH POWER OFF
OF=    -744.46
SF=      101.265000
PA=     299.9
PB=     636.0

SCALE      240.24 HZ/CM
       =       2.3724 PPM
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Elemental analysis values of the material fit no simple formulation. From the collected information it was concluded that $(PPh_2Me)_2RuCO(CH_3CN)_2$ was not made by reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with 1% Na-Hg in $CH_3CN$.

Reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ with Na-Hg in THF, rather than $CH_3CN$, might give the desired product. Since THF is less polar than $CH_3CN$, the reduction product might be isolable without using a non-coordinating solvent. It has been proven[6] that Ru (0) complexes react with tertiary phosphines to undergo orthometallation in non-coordinating solvents. A mixture of 10% $CH_3CN$ with THF might be the best choice of solvent since the desired product will have $CH_3CN$ coordinated instead of THF[34]. In addition the isolation of the product from benzene or hexane could be avoided.

An electrochemical route would most likely give the desired product since close control of the strength of the reducing agent would be possible. This could eliminate side-reactions which occur in the reduction process.

### 3. Reaction of $(PPh_3)_4Ru(\eta^2CH_3CN)\cdot CH_3CN$ with Hexane

In the determination of the melting point of $(PPh_3)_4Ru(\eta^1\text{-}CH_3CN)\cdot CH_3CN$ under vacuum, it was noted that the complex, underwent a change from a yellow solid to a red-brown liquid without apparent decomposition. During the heating process, a small amount of $CH_3CN$

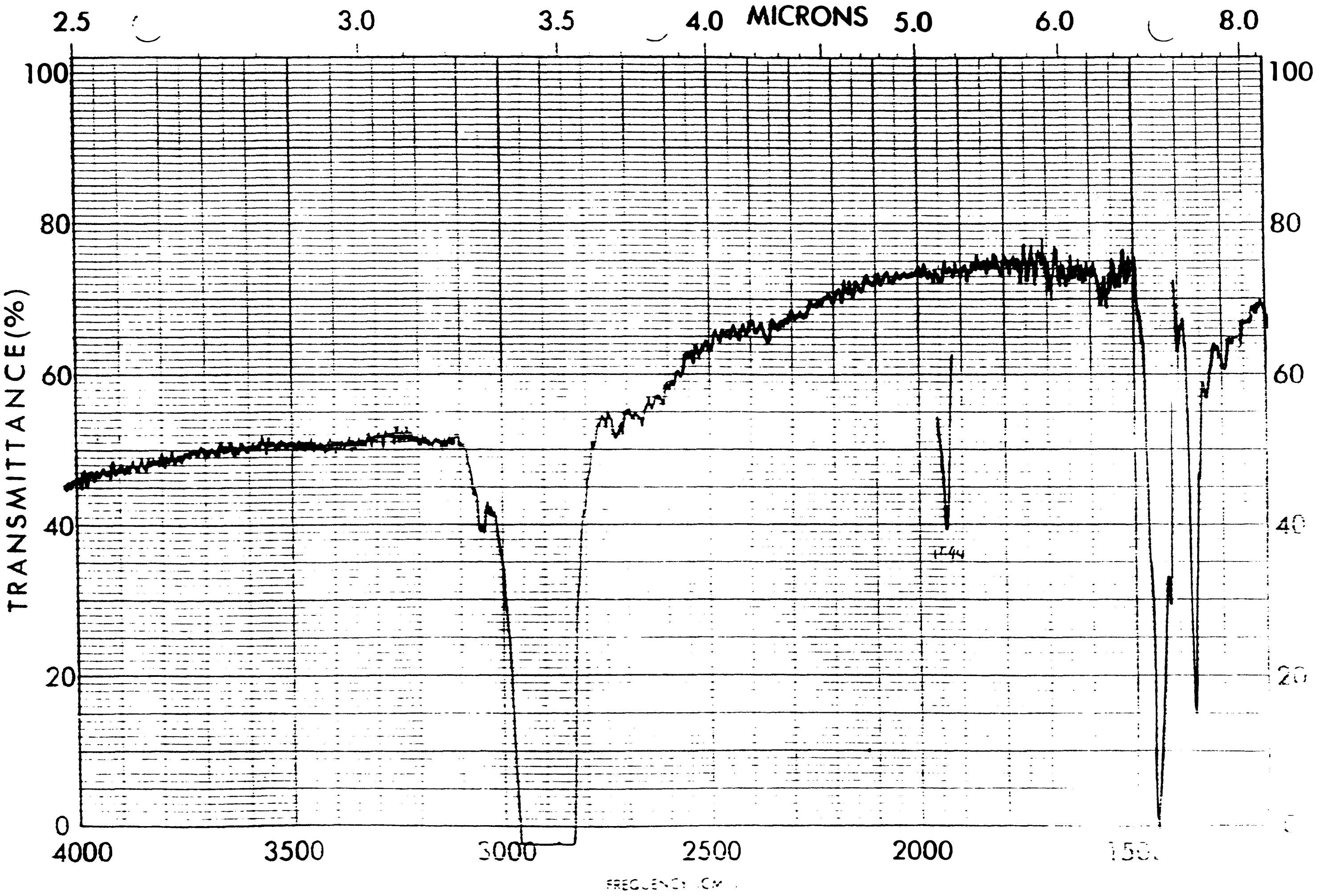
liquid condensed in the cool upper section of the melting point capillary. These observations suggest that the acetonitrile in the complex can be removed without the decomposition of the complex.

Sherman[31] used a controlled pyrolysis under vacumn to remove the $CH_3CN$ from the complex, $(PPh_3)_4Ru(\eta^1\text{-}CH_3CN)\cdot CH_3CN$. The isolated product, after 24 hrs of heating was $(PPh_3)_4Ru$ with traces of impurities. Based on Sherman's results and the melting point observations $(PPh_3)_4Ru(\eta^1CH_3CN)\cdot CH_3CN$ was heated under reflux in hexane in hopes of obtaining a reaction between $(PPh_3)_4Ru$ and the solvent.

Hexane was choosen as the solvent because Bergman[35] et al discovered that some transition metal complexes are capable of undergoing oxidative addition to C-H bonds of alkane and also because hexane has a boiling point appropriate for refluxing purposes in a dry box (without a water condensor). As expected, when the yellow slurry of the complex was heated under reflux for 24 hrs in the dry box, a dark brown powder in a dark brown solution was obtained. The dark brown powder decomposes at 124-127°C and turned black when exposed to air.

The infrared spectrum (Fig 32) of the isolated product exhibited only a triphenyl phosphine band. There are no bands which can be associated with Ru-H or orthometallated phenyl rings. A comparison of the infrared spectrum and the melting point of the dark brown

Figure 32: Infrared spectrum of the product obtained from the reaction of $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN)\cdot CH_3CN$ with hexane.



SAMPLE Reaction of (PPh3 & [illegible]

in [illegible]

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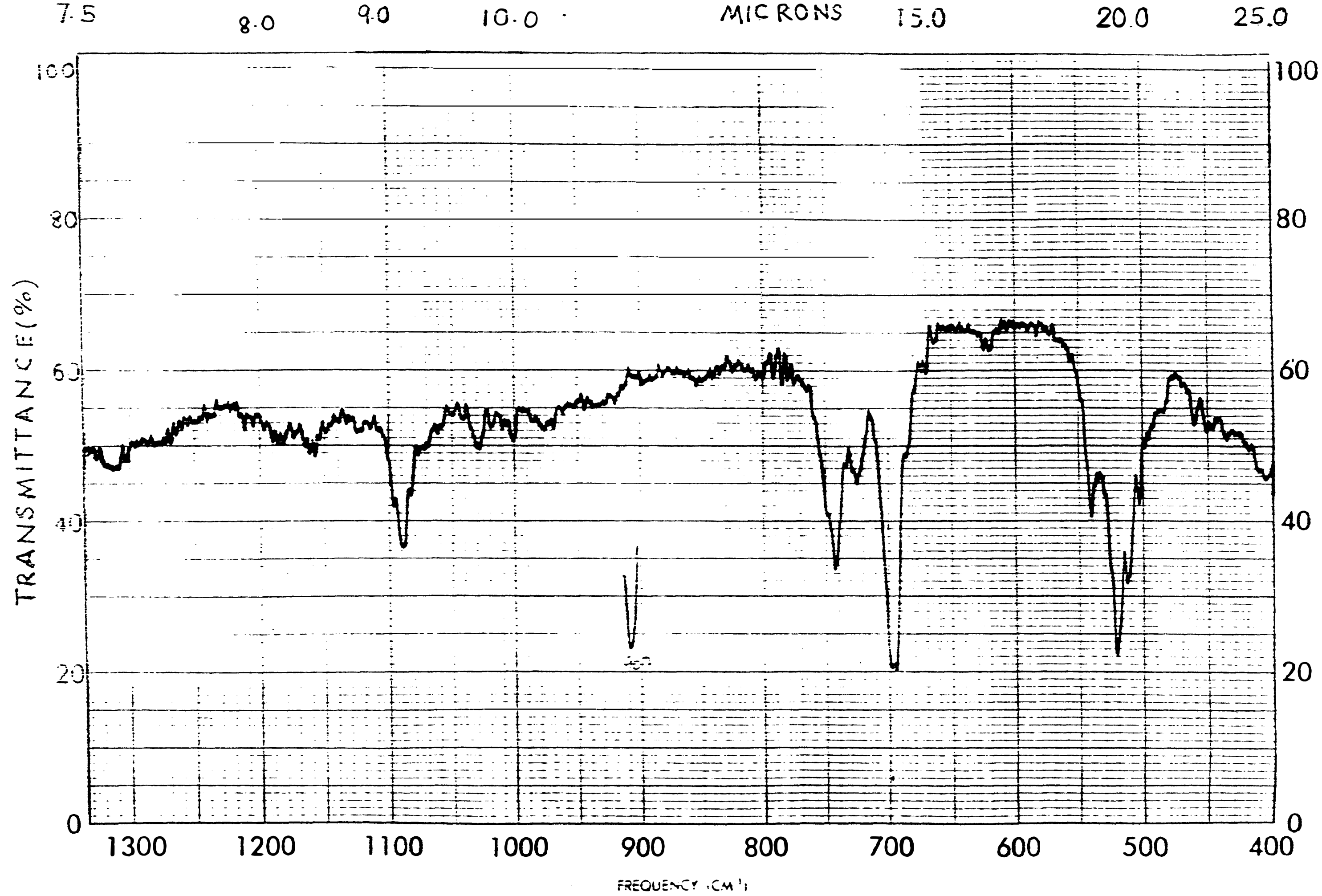
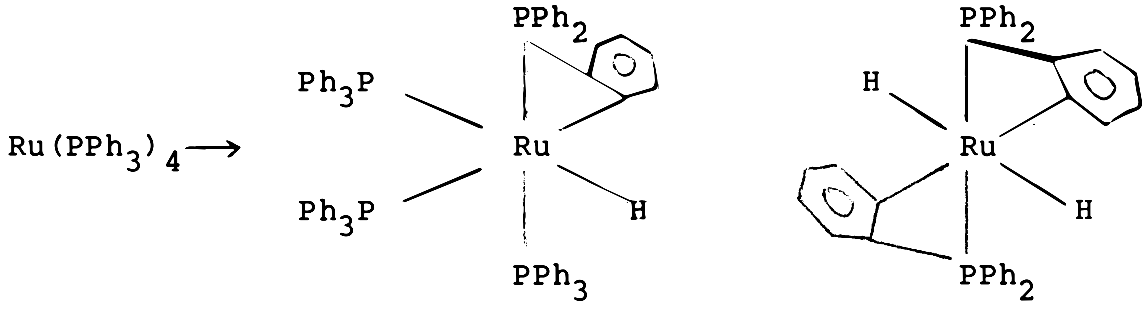


| | | | |
|---|---|---|---|
| SAMPLE Reaction of $(PPh_3)_4 Ru\ CH_3CN\}$ $CH_3CN$<br>in Hexane . | CURVE NO. | SCAN SPEED F | OPERATOR NAI |
| | CONC. | SLIT N | DATE 2/20/86 |
| ORIGIN | CELL PATH KBR | REMARKS | |
| SOLVENT | REFERENCE Nujol | | |

powder with the reported complex, $(PPh_3)_4Ru^{31}$, indicates that $(PPh_3)_4Ru$ can be made by refluxing $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN)\cdot CH_3CN$ in hexane.

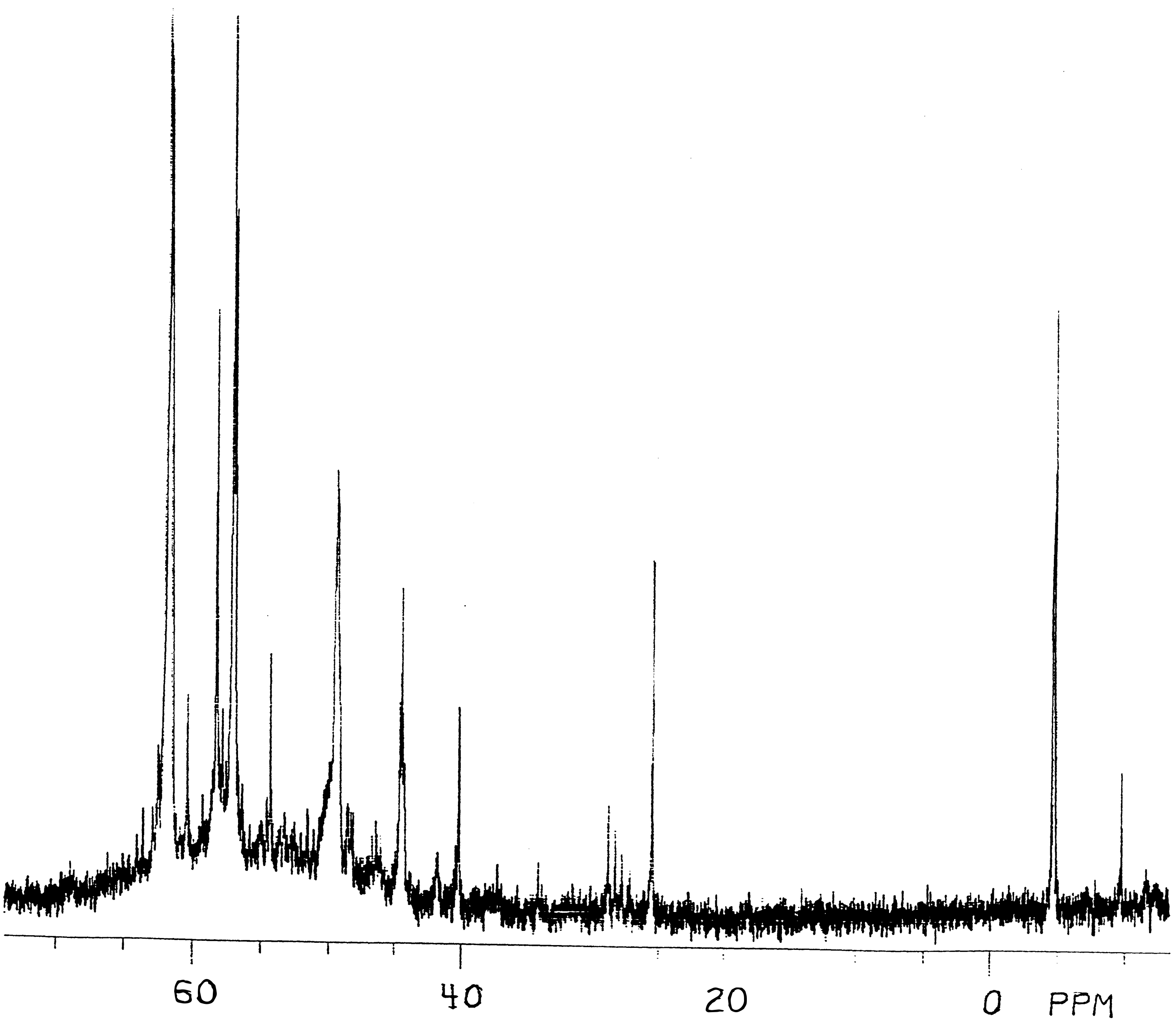
The $^{31}P$ NMR spectrum of this complex in benzene gave a complicated spectrum (Fig.33). The spectrum suggests that the complex dissociates in solution. The existence of a peak due to free triphenyl phoshines (-4.91ppm) suggests that the complex loses $PPh_3$ in solution. A triplet at 61.74 ppm indicates coupling to two phosphines as shown in structure XII. Peaks centered at 49.36 ppm may be due to orthometallated phosphines. A singlet at 57.00 ppm suggests that all of the phoshines are equivalent and was assigned to the undissociated complex, $(PPh_3)_4Ru$. Other signals are difficult to assign but probably result from various orthometallations. Structures with two ruthenium centers may also result if XIII dimerizes.



(XII) (XIII)

These very reactive and labile complexes are difficult to study. Probably, low temperature $^{31}P$ studies would have furnished more information since exchange processes would be slower and the great

Figure 33: $^{31}P$ NMR spectrum of the product obtained from reaction of $(PPh_3)_4Ru(\eta^2\text{-}CH_3CN)\cdot CH_3CN$ with hexane in $C_6H_6$


60
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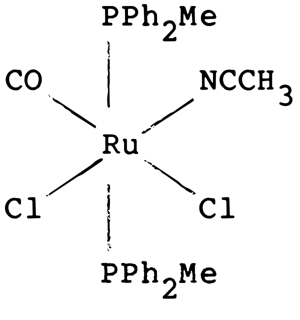
PPM

reactivity of the complexes would be reduced.

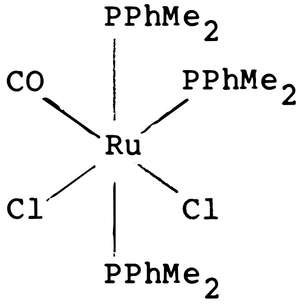
It is clear that these ruthenium complexes are sufficiently active to initiate and possibly catalyze many reactions. Lability is required for catalytic activity and it remains to be seen whether these ruthenium zero valent complexes can be put to practical use.

## Summary and Conclusion

Ruthenium (II) monocarbonyl complexes were synthesized by reaction of CO with $(R_3P)_4RuCl_2$, where $R_3P$ was $PPh_2Me$ or $PPhMe_2$. Both complexes, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$ were characterized by elemental analysis, infrared, $^1H$ NMR, and $^{31}P$ NMR spectroscopy. The structures of these complexes have been determined as (1) and (2).



(1)



(2)

Conductivity studies in acetonitrile indicate the dissociation of one chloride ion in the complexes of the type $(R_3P)_4RuCl_2$. No dissociation of chloride ion was observed in the monocarbonyl complexes.

The redox properties of $(PPh_2Me)_4RuCl_2$, $(PPhMe_2)_4RuCl_2$, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ and $(PPhMe_2)_3RuCOCl_2$ were determined from a 0.100 M tetraethylammonium perchlorate acetonitrile solution. Polarographic data indicate that two different electroactive species were present in solution and that both undergo an irreversible two electron reduction. The exchange of coordinated phosphine and chloride with the donor solvent was responsible for the two electroactive species of the $(R_3P)_4RuCl_2$ complexes. Only exchange of phosphine with solvent caused the formation of the two electroactive species in $(PPhMe_2)_3RuCOCl_2$ and $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ complexes. Exchange of the phosphine ligands decreases in the presence of excess ligand.

The half-wave potentials indicate that the presence of $PPh_2Me$ or $PPhMe_2$ ligands appears to have no significant effect upon the electron density around the metal center. Exchange of phosphine ligand with the solvent, however, appears to increase the electron density around the metal center (Table 13).

According to the polarographic data, all of the ruthenium (II) complexes under study were reduced electrochemically to ruthenium (0) species. The potentials of -2.40, -2.25, -2.60, and -3.00 V versus $Ag/Ag^+$ for $(PPhMe_2)_3RuCOCl_2$, $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$, $(PPh_2Me)_4RuCl_2$ and $(PPhMe_2)_4RuCl_2$, respectively, were required for electrolysis at the mercury cathode.

Chemical reduction with 1 % Na-Hg amalgam failed to yield ruthenium (0) complexes of the type $(R_3P)_3RuCO(CH_3CN)_2$. The chemical reduction of $(PPhMe_2)_3RuCOCl_2$ yielded an intractable oil, whereas the chemical reduction of $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ gave a mixture of products.

The reaction of $(PPh_3)_4Ru(CH_3CN).CH_3CN$ with

TABLE 13: The half-wave potential of Ruthenium (II) complexes

| Electroactive species | $E_{1/2}$ ± .03 V |
|---|---|
| $[RuCl(CH_3CN)(PPh_2Me)_4]^+$ | -2.25 |
| $[RuCl(CH_3CN)_2(PPh_2Me)_3]^+$ | -2.53 |
| $[RuCl(CH_3CN)(PPhMe_2)_4]^+$ | -2.28 |
| $[RuCl(CH_3CN)_2(PPhMe_2)_3]^+$ | -2.56 |
| $[RuCl(CH_3CN)_3(PPhMe_2)_2]^+$ | -2.80 |
| $(PPh_2Me)_2RuCO(CH_3CN)Cl_2$ | -2.28 |
| $(PPh_2Me)RuCO(CH_3CN)_2Cl_2$ | -2.65 |
| $(PPhMe_3)_3RuCOCl_2$ | -1.93 |
| $(PPhMe_2)_2RuCO(CH_3CN)Cl_2$ | -2.25 |

hexane led to removal of both acetonitrile molecules. The complex, $(PPh_3)_4Ru$, obtained from this reaction was air sensitive.

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