PART ONE
THE PREPARATION AND CHARACTERIZATION OF A SERIES OF CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) AND DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) COMPOUNDS

PART TWO
NITROGEN FIXATION UNDER MILD CONDITIONS BY USING SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION ELEMENTS AS THE ACTIVATING AGENTS

Thesis for the Degree of Ph.D.
MICHIGAN STATE UNIVERSITY
DONALD R. GRAY
1970

This is to certify that the

thesis entitled

PART ONE: THE PREPARATION AND CHARACTERIZATION OF A SERIES OF
CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM (IV) AND
DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM (IV) COMPOUNDS
PART TWO: NITROGEN FIXATION UNDER MILD CONDITIONS BY USING
SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION
ELEMENTS AS THE ACTIVATING AGENTS

presented by

DONALD R. GRAY

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker, Jr.
Major professor

Date December 8, 1970

O-7639

ABSTRACT

PART ONE

THE PREPARATION AND CHARACTERIZATION OF A SERIES OF CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) AND DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) COMPOUNDS

PART TWO

NITROGEN FIXATION UNDER MILD CONDITIONS BY USING SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION ELEMENTS AS THE ACTIVATING AGENTS

By

Donald R. Gray

PART ONE

A new series of zirconium(IV) compounds of the type $(C_5H_5)_2Zr(OR)_nCl_{2-n}$ (n = 1 and 2; R = CH_3, C_2H_5, i-C_3H_7) were prepared and characterized. The compounds were prepared by allowing the appropriate alcohol to react with $(C_5H_5)_2ZrCl_2$ and triethylamine in tetrahydrofuran solvent. All the compounds were purified by sublimation under vacuum.

The nuclear magnetic resonance spectra of the compounds were used to show unequivocally the presence of the cyclopentadienyl and alkoxide groups. The integrated areas of the resonance peaks were used to determine 'n'. The change in chemical shifts of $(C_5H_5)_2Zr(OR)_nCl_{2-n}$ as 'n' increased showed the opposite trend from what has been observed in similar series of titanium(IV) compounds.

The infrared spectra were studied to prove further the existence of the cyclopentadienyl and alkoxide ligands and to speculate on the electron density change about the zirconium as 'n' increased. The far-infrared spectra gave clear indication of the presence of the Zr-OR and Zr-ring bonds. The shifts in all infrared and far-infrared frequencies were consistent with basicity arguments.

The hydrolysis reactions were studied. For n = 1, the hydrolysis product was of the form $(Cp_2ClZr)_2O$ with a zirconoxane (Zr— O — Zr) linkage. For n = 2, the hydrolysis product was of a more complicated form, probably $-[O-Zr(OH)_2]_n-$. The infrared spectra, weight changes, and melting point changes were consistent with these conclusions.

Polarograms of the compounds in THF were attempted but were unsuccessful in yielding the desired reduction potential.

PART TWO

A survey of several early second-row transition metal organometallic compounds was made to determine their efficacy as nitrogen-fixation agents under mild conditions. Most of the compounds used were of the form $(C_5H_5)_2MCl_{x-2}$, where x is the oxidation state of M. Some of the compounds prepared in Part One were also used.

The experiment was similar in all cases. Nitrogen was continually passed through a solution of the complex in tetrahydrofuran. A two-electron reduction of the compound was attempted by using sodium naphthalenide. If the reduction was effected, the compound conceivably attached a molecule of nitrogen. Hydrolysis at this point produced ammonia.

The experiment gave measurable quantities of ammonia when $(C_5H_5)_2NbCl_3$, $(C_5H_5)_2ZrCl_2$, and $(C_5H_5)_2Zr(OC_3H_7)Cl$ were used. Several other compounds were effective in producing very small amounts of ammonia.

PART ONE

THE PREPARATION AND CHARACTERIZATION OF A SERIES OF CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) AND DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) COMPOUNDS

PART TWO

NITROGEN FIXATION UNDER MILD CONDITIONS BY USING SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION ELEMENTS AS THE ACTIVATING AGENTS

By

Donald R.ichard Gray

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1970

DEDICATION

This work is dedicated to the following:

Joan, my wife, whose constant love and encouragement made these years very good years;

Rick and Cindy, my children, whose existence makes everything worthwhile;

Mr. and Mrs. W. Russell Gray, my parents, whose understanding and assistance have made rough times smooth and whose general attitude has created a close and wonderful family;

Vera Elliott, my mother-in-law, whose self-sacrifice for her family has been inspirational.

ACKNOWLEDGMENT

The author wishes to express his appreciation for the guidance and leadership of Professor Carl H. Brubaker, Jr.

Financial support from the National Institute of Health (Predoctoral Fellowship) was profoundly appreciated.

TABLE OF CONTENTS

PART ONE

THE PREPARATION AND CHARACTERIZATION OF A SERIES OF CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) AND DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) COMPOUNDS

TABLE OF CONTENTS (Cont.)

PART TWO

NITROGEN FIXATION UNDER MILD CONDITIONS BY USING SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION ELEMENTS AS THE ACTIVATING AGENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont.)

PART I

THE PREPARATION AND CHARACTERIZATION OF A SERIES OF CHLOROALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) AND DIALKOXOBISCYCLOPENTADIENYLZIRCONIUM(IV) COMPOUNDS

PART I

INTRODUCTION

Little research has been undertaken to synthesize systematically and characterize mixed cyclopentadienyl-alkoxide compounds [$(C_5H_5)_nM(OR)_{4-n}$] and cyclopentadienyl-alkoxide-chloride compounds [$(C_5H_5)_mM(OR)_{3-m}Cl$] of the metals Ti and Zr. This void in organometallic chemistry is noteworthy because of the increasingly widespread use of organometallic complexes in homogeneous catalysis.

More work has probably been done with titanium alkoxide-cyclopentadienide systems than with any other metal. The complexes $(C_5H_5)Ti(OC_2H_5)_3$ and $(C_5H_5)Ti(OC_3H_7)_3$ were synthesized by Nesmeyanov[1] in 1960. The preparation of $(C_5H_5)_2Ti(OC_2H_5)Cl$ was reported in the same article, but attempts to prepare the biscyclopentadienyldialkoxide complexes were evidently unsuccessful. Complete nuclear magnetic resonance[2] and infrared spectra[3] have been measured for the series $(C_5H_5)Ti(OR)_{3-n}Cl_n$. The biscyclopentadienyldialkoxide complexes have been conspicuously neglected.

The analogous zirconium complexes have also received little attention. The complexes $(C_5H_5)_2Zr(OC_2H_5)Cl$ and $(C_5H_5)_2Zr(OC_3H_7)Cl$ were reported but not convincingly characterized by Brainina[4]. This work was mainly concerned with the study of zirconoxane (-Zr - O - Zr -) likages and not the study of the $(C_5H_5)_2Zr(OR)Cl$ complexes. The only other mixed cyclopentadienyl-alkoxide zirconium complex reported is $(C_5H_5)_2Zr(OC_3H_7)_2$,[5] but the complex has not been obtained completely pure.

Part One of this research deals with the preparation and characterization of the series $(C_5H_5)_2Zr(OR)Cl$ and $(C_5H_5)_2Zr(OR)_2$, ($R = CH_3$, C_2H_5, $\underline{i}$-C_3H_7). These complexes should not only be interesting from a synthetic standpoint but may also be interesting as possible nitrogen-fixation agents. Their role in the latter is discussed in Part Two.

EXPERIMENTAL SECTION

A. Materials

Bis(π-cyclopentadienyl)dichlorozirconium(IV) was obtained from Arapahoe Chemical Company and used without further purification.

Analysis Calcd for $C_{10}H_{10}ZrCl_2$: Zr, 31.22; Cl, 24.26.

Found: Zr, 31.09; Cl, 24.13.

Triethylamine was dried over barium oxide and pipetted as needed.

Tetrabutylammonium iodide was obtained from Eastman Organic Chemicals. The commercial product was further purified by standard procedures.[6]

Solvents. All solvents were refluxed with the appropriate drying agent under a nitrogen atmosphere unless indicated otherwise.

Tetrahydrofuran (THF) was refluxed continuously with lithium aluminum hydride and distilled immediately before use.

Benzene was refluxed continuously with calcium hydride and distilled immediately before use.

Hexane was continuously refluxed in the presence of sodium metal and distilled immediately before use.

Methyl alcohol was dried by distillation in the presence of magnesium. The magnesium was activated with iodine according to the method of Lund and Bjerrum.[7]

Absolute ethyl alcohol was dried by distillation in the presence of sodium ethoxide and diethylphthalate.

Isopropyl alochol was dried by distillation in the presence of sodium isopropoxide.

Gases. Prepurified nitrogen from Liquid Carbonics was passed through an activated copper catalyst (BTS catalyst - BASF R-3-11 from Badische Anilin-Soda-Fabrik AG) to remove oxygen. It was then passed through two drying towers filled with calcium sulfate and barium oxide to remove any water present.

B. Analytical Methods

Carbon and Hydrogen Analysis. These analyses were performed by Spang Microanalytical Laboratories and by the microanalytical laboratory of the Institute of Water Resources at Michigan State University. The latter laboratory was not equipped to handle the moisture-sensitive zirconium complexes properly. Spang reported that the complexes were very difficult to handle and that the analyses reported were a result of experimenting with several handling techniques. Identical samples gave divergent results, and the reported analyses may not be totally reliable.

Chloride Analysis. About 100 mg of the sample of the zirconium compound was destroyed by being heated in dilute nitric acid. This solution was made basic with dilute aqueous ammonia. The hydrous oxide of zirconium thus formed was removed by filtration, and the filtrate was collected in a 100 ml volumetric flask. The precipitate was washed with several portions of dilute ammonia. The filtrate was diluted with distilled water to 100.00 ml. Twenty-five ml aliquots were made acidic with dilute sulfuric acid. Chloride was then determined by a differential potentiometric titration with a standard silver nitrate solution.[8] Duplicate samples showed reproducible results.

Zirconium Analysis. Zirconium was initially analyzed by igniting the hydrous oxide to zirconium oxide. This method failed to give reproducible data. A modified version of the cupferron method was finally employed, and this method gave results of high precision. One-hundred mg samples of the compound were decomposed by being heated in 10% sulfuric acid. This solution was cooled to 10°. An excess of cupferron (the ammonium salt of nitrosophenylhydroxylamine) solution (6 g in 100 ml water and filtered) was added. The white, curdy precipitate was filtered and washed with several portions of 1:10 hydrochloric acid. The filtered precipitate was then ignited at 1000° for six hours, and the zirconium content was determined by weighing ZrO_2.

C. Experimental Apparatus and Technique

Practically all the compounds dealt with in this research were extremely sensitive to oxygen and/or water vapor. All reactions and manipulations were thus performed in an atmosphere of dry nitrogen. Schlenk vessel techniques, similar to those reported by Herzog,[9] were used extensively. The compounds were stored in closed vials in an inert-atmosphere box. These manipulations included preparation of Nujol mulls for infrared measurements, filling of nuclear magnetic resonance tubes, and scraping sublimation products from cold-finger condensers.

The use of a vacuum manifold in conjunction with the nitrogen line allowed facile Schlenk manipulations which precluded the presence of air in the reaction vessels. Glassware was dried for several hours at 180°. It was then evacuated and filled with nitrogen several times while it cooled. Dry nitrogen gas was forced into the vessels through a sidearm stopcock whenever a glassware connection was made or broken.

D. Preparation of Compounds

Chloromethoxobis(π-cyclopentadienyl)zirconium(IV). A mixture of methyl alcohol (32.2 mmol) and triethylamine (32.2 mmmol) in 20 ml THF was added dropwise to a stirred solution of zirconocene dichloride (16.1 mmol) in 80 ml THF. This reaction mixture was allowed to reflux for three hours.

The dense white precipitate, $(C_2H_5)_3N \cdot HCl$, was filtered. The filtrate, an orange-brown solution, was treated by removing the solvent under vacuum. Seventy ml of hexane was added to the remaining amorphous reddish-brown mass. This mixture was vigorously stirred for six hours and crystals formed. These beige crystals were filtered and dried. Sublimation under vacuum (10^{-1} mm) at 103° caused pure white crystals to condense on the cold-finger condenser. Yield 1.4 g. Melting Point = 111-114.5°.

Analysis Calcd for $ZrClC_{11}H_{13}O$: Zr, 31.69; Cl, 12.32; C, 45.89; H, 4.52.

Found: Zr, 31.51; Cl, 12.06; C, 45.35; H, 4.15.

Dimethoxobis(π-cyclopentadienyl)zirconium(IV). A solution of methyl alcohol (83.6 mmol) and triethylamine (41.8 mmol) in 10 ml THF was added dropwise to a solution of zirconocene dichloride (20.9 mmol) in 80 ml THF. The $(C_2H_5)_3N \cdot HCl$ was removed by filtration. A brown oil remained after the solvent was removed from the filtrate. Thirty ml of hexane was added to this oil, and beige crystals formed. These crystals were removed by filtration. The filtrate was evaporated and the remaining solid was dried. The resulting brown solid was sublimed under vacuum (10^{-1} mm) at 85°. Pale yellow crystals of product formed on the cold-finger condenser. Yield $\approxeq$ 1.4 g. Melting point = 63-68°.

Analysis Calcd for $ZrC_{12}H_{16}O_2$: Zr, 32.19; C, 50.86;

H, 5.65.

Found: Zr, 32.20; C, 48.91; H, 5.11.

Chloroethoxobis(π-cyclopentadienyl)zirconium(IV). A solution of ethyl alcohol (40.2 mmol) in 10 ml THF was added to a solution of zirconocene dichloride (20.1 mmol) in 80 ml THF. This reaction mixture was allowed to reflux for two hours. A solution of triethylamine (40.2 mmol) in 10 ml THF was then added, and the refluxing was allowed to continue for two more hours. The white precipitate, $(C_2H_5)_3N \cdot HCl$, was removed by filtration. The filtrate was clear yellow. A small amount of solid formed after the bulk of the THF had been removed. These crystals were removed by filtration. Removal of the remaining THF by evaporation left a dark brown oil. About 30 ml hexane was added, and beige crystals formed. The crystals were filtered and dried. This product was purified by sublimation under vacuum (10^{-1} mm) at 92°. White crystals of product were obtained. Yield $\approx$ 3 g. Melting Point = 72-77°.

Analysis Calcd for $ZrClC_{12}H_{15}O$: Zr, 30.24; Cl, 11.75; C, 47.77; H, 4.97.

Found: Zr, 30.09; Cl, 11.87; C, 47.48; H, 4.78.

Diethoxobis(π-cyclopentadienyl)zirconium(IV). A solution of ethyl alcohol (65.9 mmol) in 10 ml THF was added to a solution of zirconocene dichloride (18.8 mmol) in 75 ml THF. This mixture was allowed to reflux for one hour. A solution of triethylamine (37.6 mmol) in 10 ml THF was added, and refluxing was continued for an additional two hours. The precipitate, $(C_2H_5)_3N{\cdot}HCl$, was separated by filtration. Additional solid formed after most of the THF had been removed from the filtrate. This solid was removed by filtration, and the remaining THF was removed from the filtrate by evaporation. The resulting oil was sublimed under vacuum (10^{-1} mm) at 92°. Proton magnetic resonance spectroscopy showed the sublimation product was a mixture of $(C_5H_5)_2Zr(OC_2H_5)_2$, $(C_5H_5)_2Zr(OC_2H_5)Cl$, and $Zr(OC_2H_5)_4$. The desired product $(C_5H_5)_2Zr(OC_2H_5)_2$ was isolated by resubliming it from this mixture at 55°. The crystalline product was pale yellow. Yield $\approx$ 0.5 g. Melting point = 52-57°.

Analysis Calcd for $ZrC_{14}H_{20}O_2$: Zr, 29.30; C, 54.00; H, 6.42.

Found: Zr, 29.01; C, 52.06; H, 6.01.

Chloroisopropoxobis(π-cyclopentadienyl)zirconium(IV). A solution of isopropyl alcohol (13.8 mmol) and triethylamine (20.7 mmol) in 10 ml THF was added to a solution of zirconocene dichloride (13.8 mmol) in 60 ml THF. This reaction mixture was allowed to reflux for two hours. The insoluble $(C_2H_5)_3N{\cdot}HCl$ precipitate was removed by filtration. The THF was then removed from the filtrate and a dark brown liquid remained. Thirty ml of hexane was added to this liquid, and a very small quantity of crystals formed. These were removed by filtration and the filtrate was treated by removing the hexane by evaporation. The resulting dark brown oil was sublimed under vacuum (10^{-1} mm) at 86^0. A large quantity of white crystals formed on the cold-finger condenser. Yield ≈ 3 g. Melting Point = $81\text{-}82.5^0$.

Analysis Calcd for $ZrClC_{13}H_{17}O$: Zr, 28.88; Cl, 11.23; C, 49.44; H, 5.38.

Found: Zr, 29.21; Cl, 11.21; C, 48.90; H, 5.07.

Diisopropoxobis(π-cyclopentadienyl)zirconium(IV). A solution of isopropyl alcohol (45.1 mmol) and triethylamine (33.9 mmol) in 10 ml THF was added to a solution of zirconocene dichloride (11.3 mmol) in 50 ml THF. This mixture was allowed to reflux for two hours. The white precipitate, $(C_2H_5)_3N\cdot HCl$, was removed by filtration. The bulk THF was removed from the filtrate by evaporation. Twenty-five ml of hexane was added, and the small quantity of resulting crystals was separated by filtration. The hexane was removed by evaporation and a yellow-brown solid remained. Vacuum sublimation at 68^0 produced white crystals on the cold-finger condenser. Yield ≈ 1.5 g. Melting Point = $110\text{-}116.5^0$.

Analysis Calcd for $ZrC_{16}H_{24}O_2$: Zr, 26.88; C, 56.62; H, 7.07.

Found: Zr, 26.92; C, 56.29; H, 7.36.

Tetraethoxozirconium(IV). A solution of ethyl alcohol (73.8 mmol) and triethylamine (37.0 mmol) in THF was added to a solution of zirconocene dichloride (18.5 mmol) in THF.

This mixture was allowed to reflux for two hours. The precipitate, $(C_2H_5)_3N\cdot HCl$, was separated by filtration. Sublimation under vacuum (10^{-1} mm) at 165° produced white crystals of product on the cold-finger condenser. Yield $\approx$ 1 g. Melting Point = 172-180°. The physical data agreed with those given by Bradley and Wardlaw [10] for $Zr(OC_2H_5)_4$ prepared by a different method.

Analysis Calcd for $ZrC_8H_{20}O_4$: Zr, 33.62.
Found: Zr, 34.14.

Tetraisopropoxozirconium(IV). This compound was prepared in somewhat questionable purity by continued sublimation of the residue from the $(C_5H_5)_2Zr(OC_3H_7)_2$ preparation (see above). All of the $(C_5H_5)_2Zr(OC_3H_7)_2$ had sublimed at 90°. Further sublimation produced white crystals of product $Zr(OC_3H_7)_4$. Yield $\approx$ 0.5 g. Melting Point = 180-200° with decomposition. The infrared spectrum agreed closely with that reported by Bradley[11] and Lynch.[12]

E. Hydrolysis Reactions

These reactions were simply performed by exposing the compounds to air. This treatment was generally sufficient to cause almost total hydrolysis to occur in about thirty minutes. A more efficient method, ensuring that complete hydrolysis had taken place, was to place the samples in air saturated with water vapor. This was accomplished by filling the bottom section of a desiccator with water, placing the samples (in open vials) on the plate, and closing the desiccator lid. The sample vials were periodically removed, evacuated several times in a vacuum desiccator, and weighed until further hydrolysis caused no further weight loss.

F. Spectroscopic Measurements

Infrared Spectra. The infrared spectra were determined by means of Nujol mulls on cesium iodide plates with a Perkin-Elmer 457 grating spectrophotometer. All mulls of the moisture-sensitive compounds were prepared in an inert-atmosphere box.

Nuclear Magnetic Resonance Spectra. Nuclear magnetic resonance spectra were recorded with a Varian A56/60D Analytical NMR Spectrometer. The nmr tubes were filled with sample in an inert-atmosphere box. All work was done in deuterated benzene as the solvent.

G. Polarography

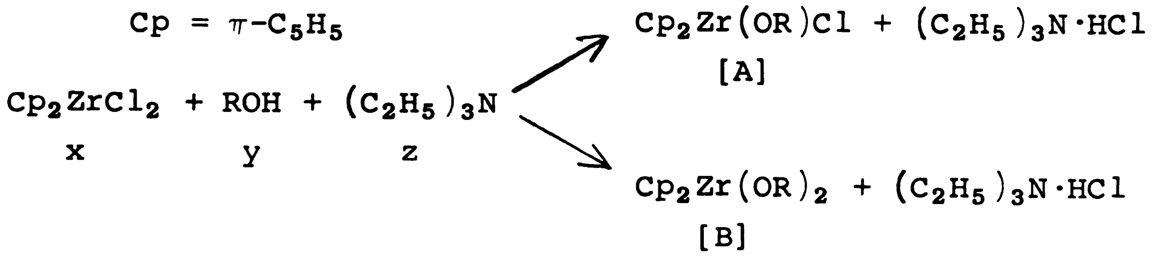
Attempts to obtain polarograms were made with a Sargent Model XV Polarograph. Tetrahydrofuran was used as the solvent, and tetrabutylammonium iodide (TBAI) was the supporting electrolyte. To obtain a 0.1N solution of TBAI in THF it was necessary to maintain a temperature of 55^0. A dropping mercury electrode was used as the indicating electrode. The reference electrode was a saturated calomel electrode. A three-compartment cell was used to ensure that no aqueous solution would diffuse into the sample.

RESULTS AND DISCUSSION

Part One of this research is concerned with the preparation and characterization of compounds of the forms $(\pi\text{-}C_5H_5)_2Zr(OR)Cl$ and $(\pi\text{-}C_5H_5)_2Zr(OR)_2$ (R = CH_3, C_2H_5, $\underline{i}\text{-}C_3H_7$). The results and discussion of this work are conveniently presented under the following headings: A. Preparations, B. Nuclear Magnetic Resonance Spectra, C. Infrared Spectra, D. Hydrolysis Reactions, and E. Miscellaneous Observations.

A. Preparations

The preparation of all these compounds was accomplished by allowing zirconocene dichloride (Cp_2ZrCl_2) to react with the appropriate alcohol in the presence of triethylamine [$(C_2H_5)_3N$]. Tetrahydrofuran (THF) was used as the solvent. If the alcohol was used as the solvent, the $Zr(OR)_4$ compound resulted. The ratio of Cp_2ZrCl_2:ROH:$(C_2H_5)_3N$ was of utmost importance if reasonable yields of product were to be obtained. The presence of $(C_2H_5)_3N$ was necessary to produce alkoxide ions and allow the reactions to proceed. The reactions were as follows:



$Cp = \pi\text{-}C_5H_5$

$$\begin{array}{lll} & & Cp_2Zr(OR)Cl + (C_2H_5)_3N\cdot HCl \\ & & \quad [A] \\ \underset{x}{Cp_2ZrCl_2} + \underset{y}{ROH} + \underset{z}{(C_2H_5)_3N} & \begin{array}{l}\nearrow \\ \searrow\end{array} & \\ & & Cp_2Zr(OR)_2 + (C_2H_5)_3N\cdot HCl \\ & & \quad [B] \end{array}$$

The $(C_2H_5)_3N\cdot HCl$ is insoluble in THF whereas the products [A] and [B] are appreciably soluble. The extent of the reaction could thus be easily monitored by weighing the filtered $(C_2H_5)_3N\cdot HCl$.

All of the compounds were isolated and purified by sublimation under vacuum (10^{-1} mm) at a given temperature. This temperature was critical. Too high a sublimation temperature often caused cosublimation of undesirable product. Table I shows the correct x : y : z ratios and the proper sublimation temperature for each compound.

The absence of any indication of $CpZr(OR)_3$ should be noted. The titanium analogs exist and have been the subject of extensive infrared[3] and nuclear magnetic resonance[2] studies. When the Cp_2ZrCl_2 - C_2H_5OH reaction (x : y : z = 1 : 4 : 2) is studied, the final product (sublimed at 165^0) shows the presence of three species. The species present can be shown by NMR to be $Cp_2Zr(OC_2H_5)Cl$, $Cp_2Zr(OC_2H_5)_2$, and $Zr(OC_2H_5)_4$. It appears that the two chloride ligands are successively replaced by ethoxide ligands, but that the cyclopentadienyl rings are displaced either simultaneously or not at all.

Table I. Reactant Ratios and Sublimation Temperatures for the Compounds $Cp_2Zr(OR)Cl$, $Cp_2Zr(OR)_2$, and $Zr(OR)_4$ according to the reaction:

$$\underset{x}{Cp_2ZrCl_2} + \underset{y}{ROH} + \underset{z}{(C_2H_5)_3N} = \underset{\text{Compound}}{\text{Product}}$$

Compound	x	y	z	Subl Temp (at 10^{-1} mm)
Class: $Cp_2Zr(OR)Cl$				
R = CH_3	1	2	2	103^0
R = C_2H_5	1	2	2	92
R = $\underline{i}$-C_3H_7	1	1	1.5	86
Class: $Cp_2Zr(OR)_2$				
R = CH_3	1	4	2.5	105
R = C_2H_5	1	3.5	2	55
R = $\underline{i}$-C_3H_7	1	4	3.5	68
Class: $Zr(OR)_4$				
R = C_2H_5	1	>4	4	120
R = $\underline{i}$-C_3H_7	1	>4	4	120

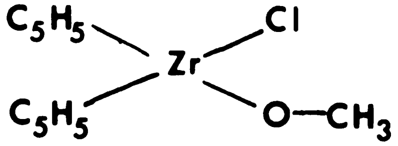
B. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance provided a convenient method of characterizing the compounds and of checking for the presence of impurities. The spectra were recorded in C_6D_6, and the resonance peaks were sharp and well-defined. The nmr spectra, along with important analytical results and melting points, are shown in Figures 1-6. A summary of the chemical shift data is shown in Table II.

The chemical shift results are especially noteworthy. Nesmeyanov has studied the nmr of the series of compounds $CpTi(OC_2H_5)_nCl_{3-n}$ $(n = 0 - 3)$.[2] His results show that the chemical shifts of the ring, methyl, and methylene groups shift to higher frequencies as 'n' increases. This trend is explained by invoking electronegativity arguments. As the ethoxide groups are replaced by the more electronegative chloride ligands, the electron density is decreased about the Cp ring and the methylene and methyl groups of the ethoxide ligand. The result is a shift toward lower frequencies in the nmr spectrum.

Nesmeyanov's results are significant because the exact opposite effect is seen with the zirconium compounds (see Table II). As the number of alkoxide groups is decreased, the chemical shifts of the ring and alkoxide resonances increase. The electronegativity argument cannot be used to explain this apparently anomalous behavior. The primary differences between the Nesmeyanov work and the present

COMPLEX



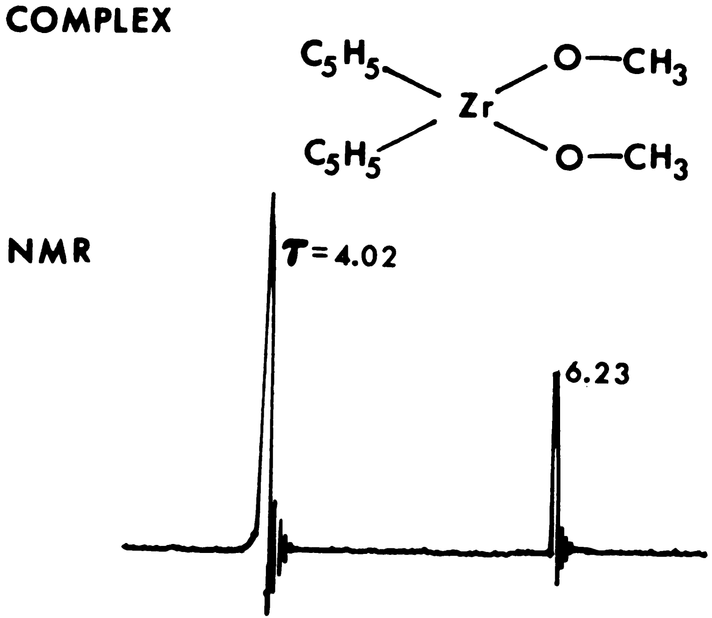
NMR

intensity	10	2.7
theor	10	3.0

el. anal.		Zr	Cl	C	H
	calcd	31.69	12.32	45.89	4.52
	found	31.5_1	12.0_6	45.3_5	4.15

m.p. 111 – 114.5

Figure 1. Proton nmr of $Cp_2Zr(OCH_3)Cl$. Chemical shifts in ppm.



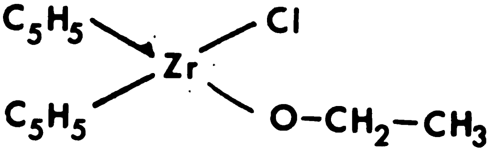
intensity	10	5.7
theor	10	6.0

el. anal.	**Zr**	**C**	**H**
calcd	32.19	50.86	5.65
found	32.20	48.91	5.02

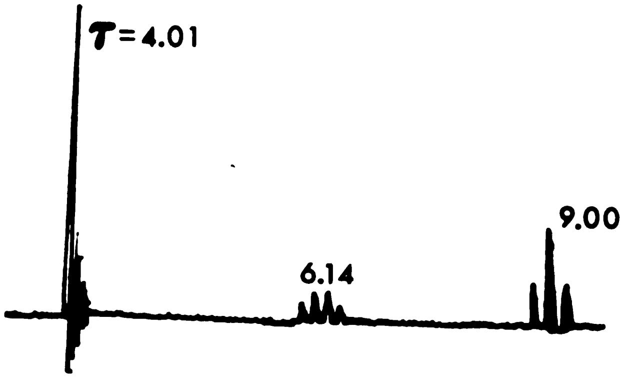
m.p. 63-68°

Figure 2. Proton nmr of $Cp_2Zr(OCH_3)_2$. Chemical shifts in ppm.

COMPLEX



NMR



intensity···	10	1.9	2.8
theor···	10	2.0	3.0

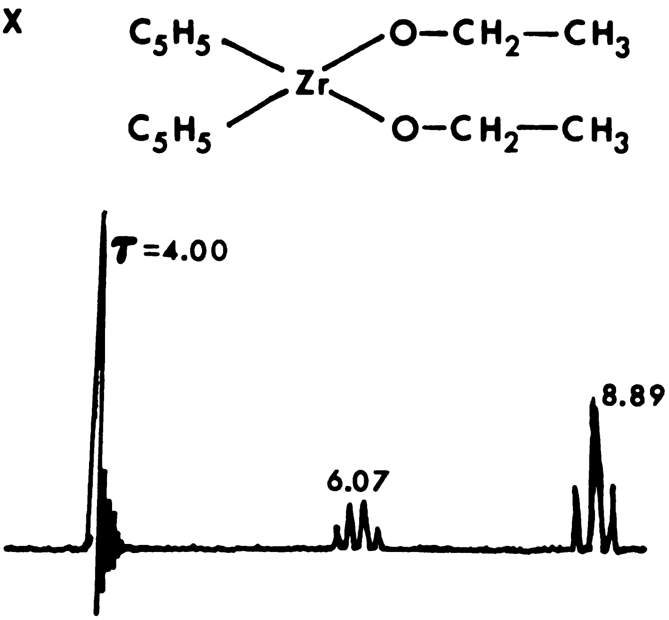
el. anal.		Zr	Cl	C	H
	calcd	30.24	11.75	47.77	4.97
	found	30.09	11.87	47.48	4.78

m.p. 72-77°

Figure 3. Proton nmr of $Cp_2Zr(OC_2H_5)Cl$. Chemical shifts in ppm.

COMPLEX

NMR

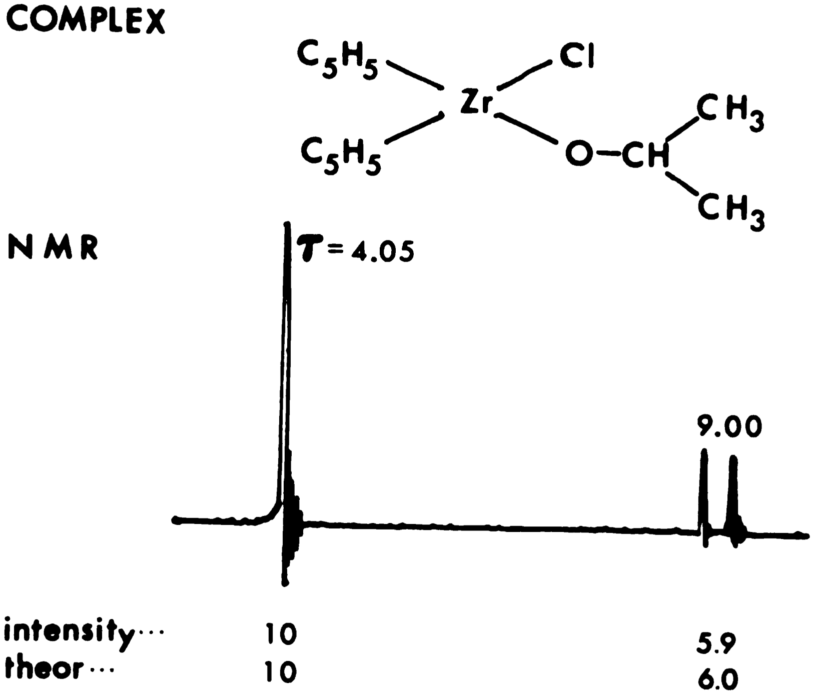


intensity···	10	3.8	6.4
theor···	10	4.0	6.0

el. anal.		Zr	C	H
	calcd	29.30	54.00	6.42
	found	29.01	52.03	6.01

m.p. 52–54°

Figure 4. Proton nmr of $Cp_2Zr(OC_2H_5)_2$. Chemical shifts in ppm.

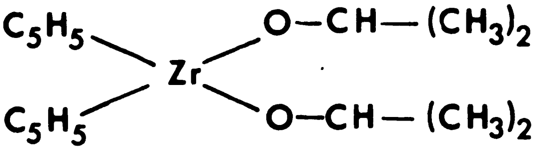


el. anal.		Zr	Cl	C	H
	calcd	28.88	11.23	49.44	5.38
	found	29.21	11.21	48.90	5.07

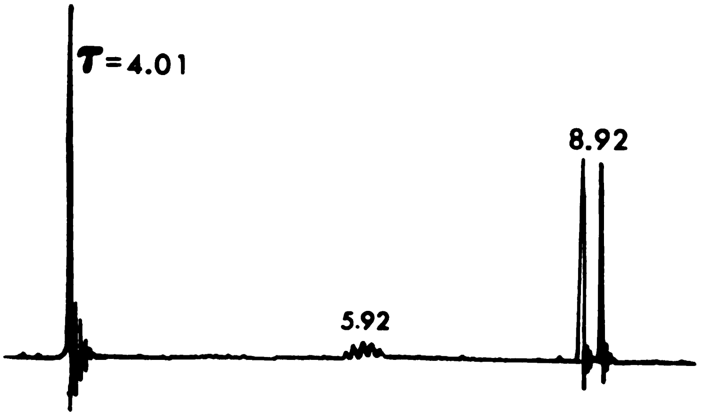
m.p. 81 – 82.5°

Figure 5. Proton nmr of $Cp_2Zr(OC_3H_7)Cl$. Chemical shifts in ppm.

COMPLEX



NMR



intensity···	10	12
theor···	10	12

el. anal.		Zr	C	H
	calcd	26.88	56.62	7.07
	found	26.92	56.29	7.36

m.p. 110.5–115°

Figure 6. Proton nmr of $Cp_2Zr(OC_3H_7)_2$. Chemical shifts in ppm.

Table II. Proton NMR Chemical Shifts for $Cp_2Zr(OR)_nCl_{2-n}$ and $Zr(OR)_4$ (solvent = C_6D_6; τ-scale; internal standard = TMS).

	Chemical Shifts (ppm)		
Compound	Ring	Methyl	Methylene
Cp_2ZrCl_2	4.09	-	
$Cp_2Zr(OCH_3)Cl$	4.05	6.35	
$Cp_2Zr(OCH_3)_2$	4.02	6.23	
$Cp_2Zr(OC_2H_5)Cl$	4.01	9.00	6.14
$Cp_2Zr(OC_2H_5)_2$	4.00	8.89	6.07
$Zr(OC_2H_5)_4$	-	8.64	5.73
$Cp_2Zr(OC_3H_7)Cl$	4.05	9.00	
$Cp_2Zr(OC_3H_7)_2$	4.01	8.92	
$Zr(OC_3H_7)_4$	-	8.65	

zirconium work are (1) the central metal, and (2) the number of cyclopentadienyl rings bonded to the central metal.

Wales[13] has published the nmr work of the only other relevant series, $Cp_2Ti(SR)_nCl_{2-n}$ (n = 0,1,2). Because this series contains two Cp rings, the analogy to the zirconium series may be more valid than the Nesmeyanov series. However, Wales' results show the same trends in chemical shifts as the Nesmeyanov compounds show. The presence of thio-alkoxide groups rather than alkoxide groups makes this comparison questionable.

Until additional work is done with the zirconium series, it is futile to attempt an explanation of the anomalous chemical shift observations. The reason could perhaps be the result of using zirconium rather than titanium. The series of compounds $Cp_2Ti(OR)_nCl_{2-n}$ and $CpZr(OR)_nCl_{3-n}$, neither of which has been characterized, should clarify this matter. The anomaly could also be a solvent effect. The Nesmeyanov compounds were studied in THF, the Wales compounds in $CDCl_3$, and the zirconium compounds in C_6D_6.

C. Infrared Spectra

The infrared spectra of these compounds also provide an important characterization technique. Coordinated cyclopentadienyl rings and the alkoxide groups give characteristic infrared absorption bands in the 3500 - 700 cm^{-1} region. In addition, valuable information about the

Zr - ring and Zr - OR bonds can be obtained by a study of the far infrared (700 - 250 cm^{-1}) region.

The infrared spectra of the 3500 - 700 cm^{-1} region for the compounds studied are presented in Figures 7 - 15. The bands characteristic of the vibrations of the cyclopentadienyl rings (3100, 1020-1010, 850-840-815) are all present in the series of compounds $Cp_2Zr(OR)_nCl_{2-n}$. There is a slight shift towards lower frequencies of the 1020-1010 and 850-840-815 bands as 'n' increases. This may well reflect the increased electron density on the ring as the alkoxide groups replace the chlorides.

The bands characteristic of the OR groups become much more intense (relative to the Cp bands) as "n" increases. The band assignments, based on standard spectra for the pure alcohol, are presented in Table III. The CH_3-bending modes which are not shown are overlapped by the Nujol bands in the 1400 - 1500 cm^{-1} region.

A study of Table III shows that insignificant shifts occur in the OR bands as 'n' goes from 1 to 2. The unassigned bands in the 730 - 770 cm^{-1} region, however, undergo significant shifts to lower frequencies as 'n' goes from 1 to 2. These bands are absent in the spectra of the pure alcohols and the Cp_2ZrCl_2. It is reasonable, therefore, to assume that they arise from the Zr - O bond. The presence of a chloride ligand should decrease the electron density about the central metal, thus allowing a stronger Zr - O bond to be formed. This is consistent with the

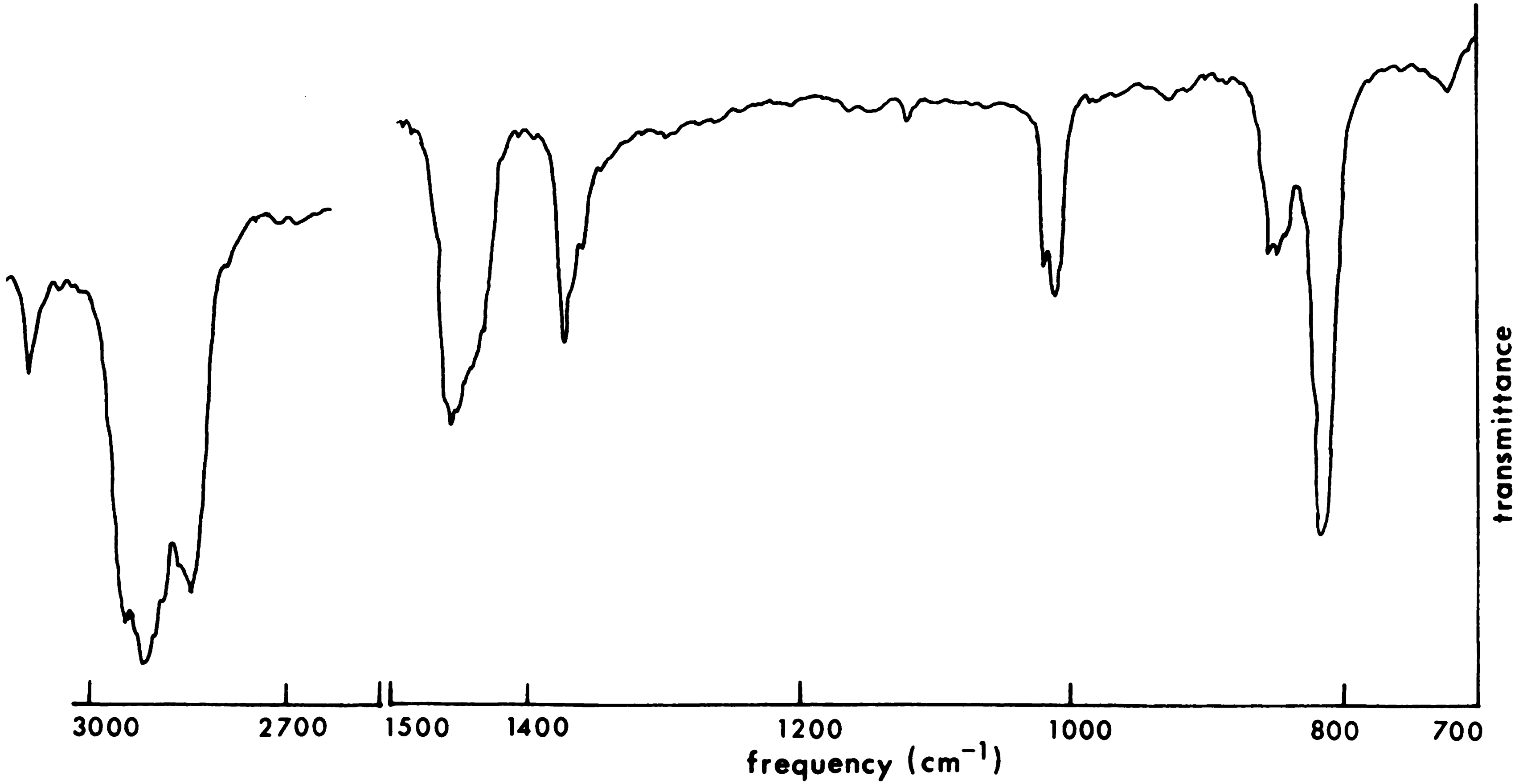


Figure 7. Infrared spectrum of Cp_2ZrCl_2.

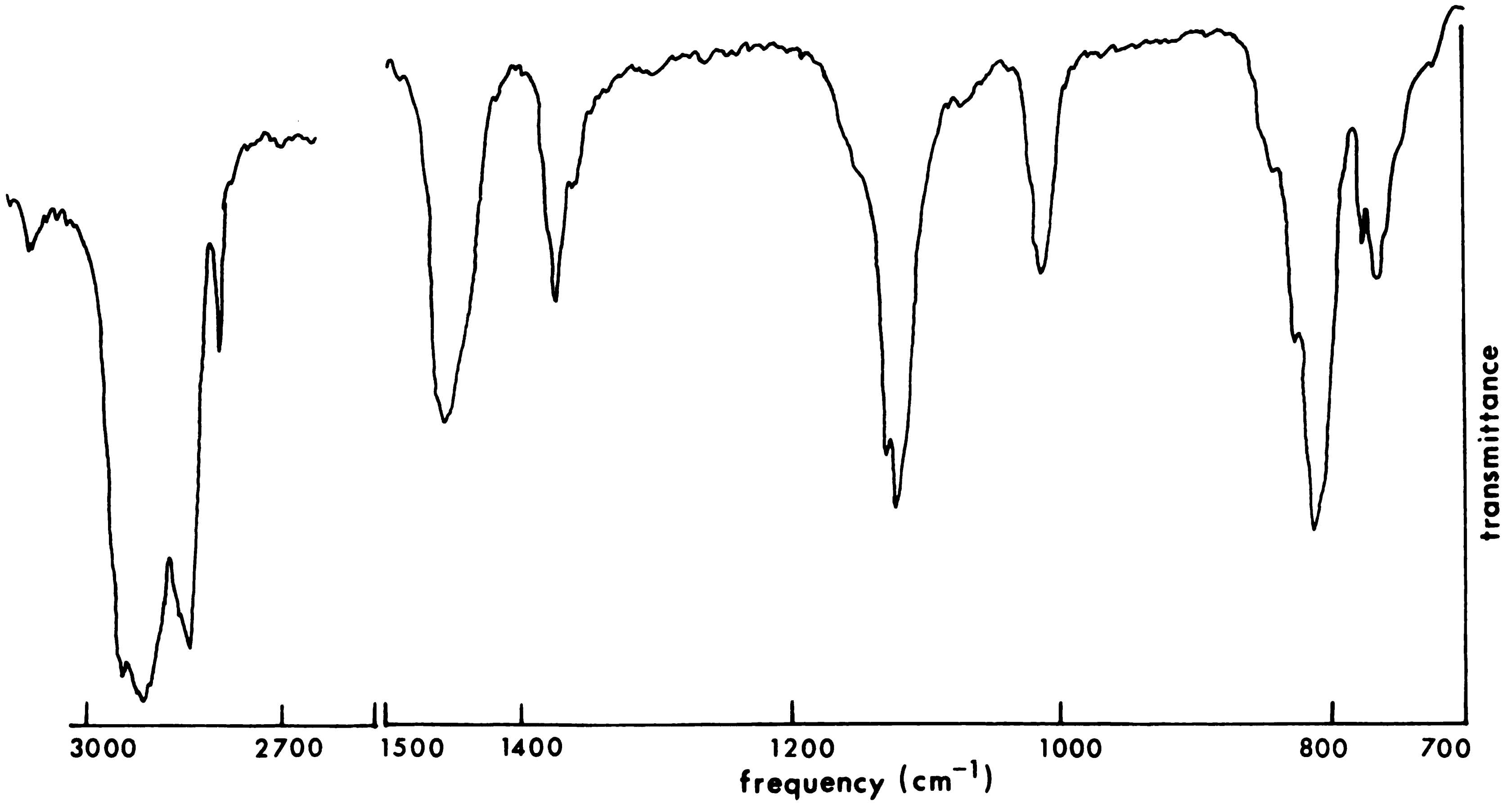


Figure 8. Infrared spectrum of $Cp_2Zr(OCH_3)Cl$.

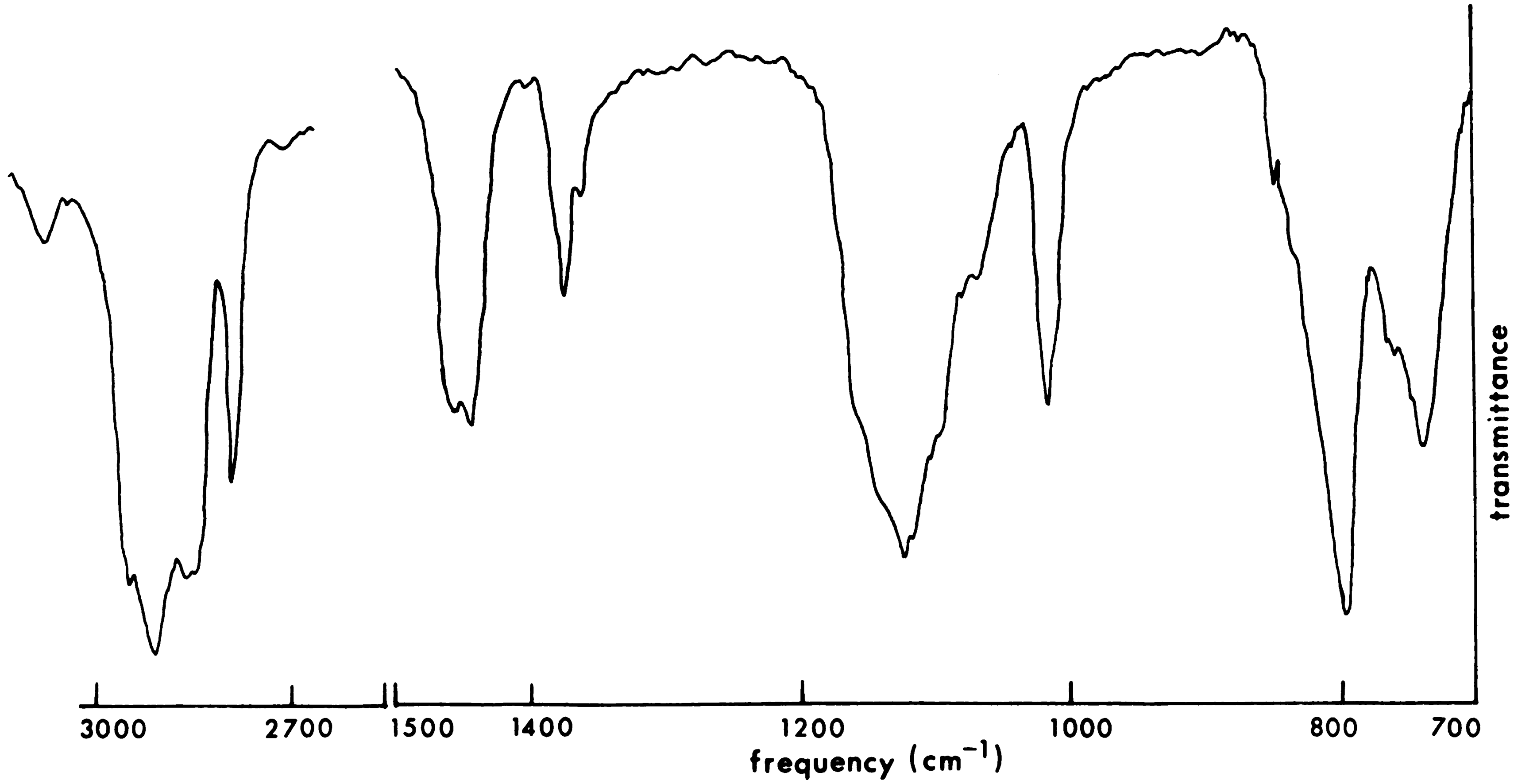


Figure 9. Infrared spectrum of $Cp_2Zr(OCH_3)_2$.

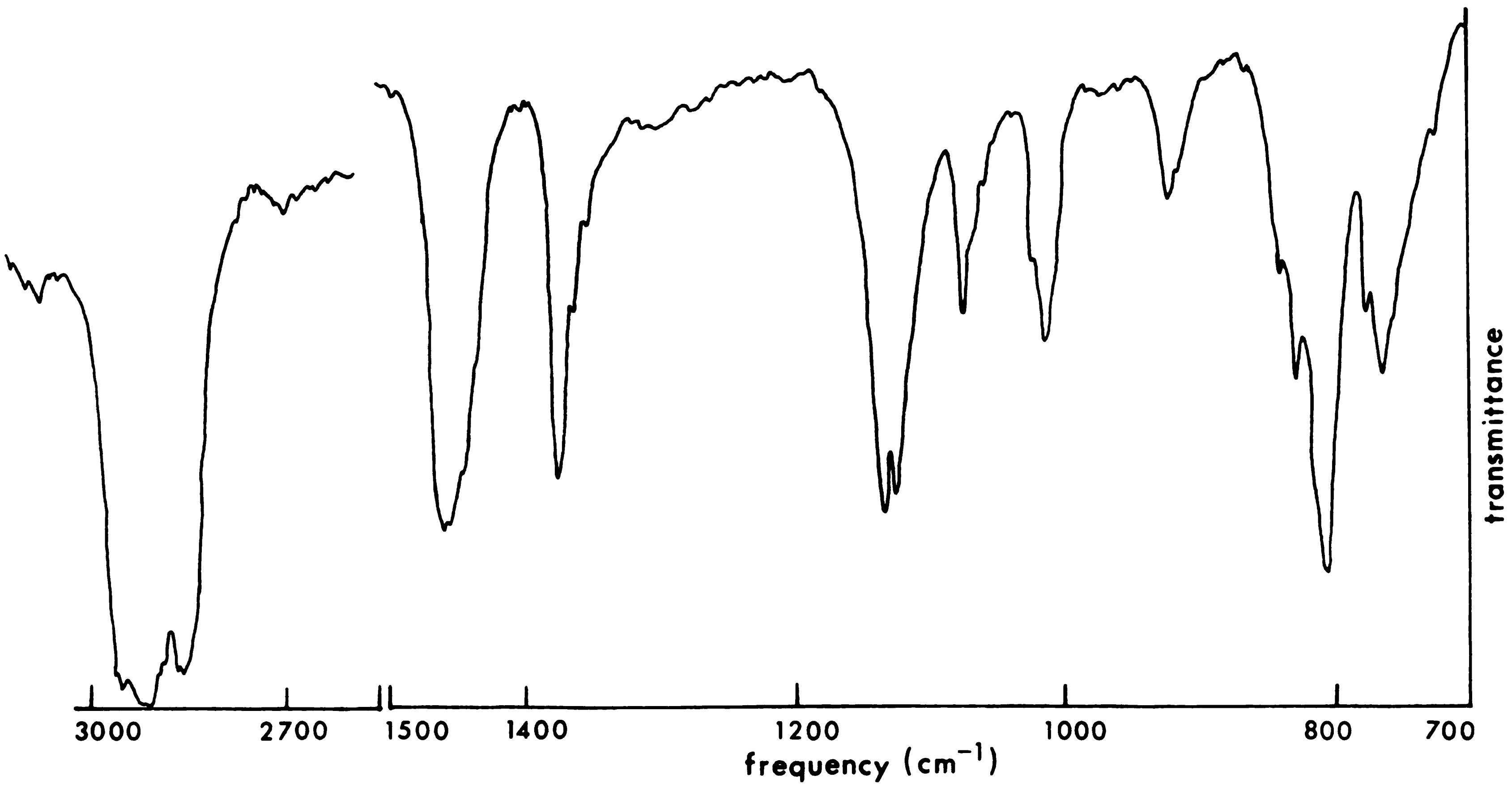


Figure 10. Infrared spectrum of $Cp_2Zr(OC_2H_5)Cl$.

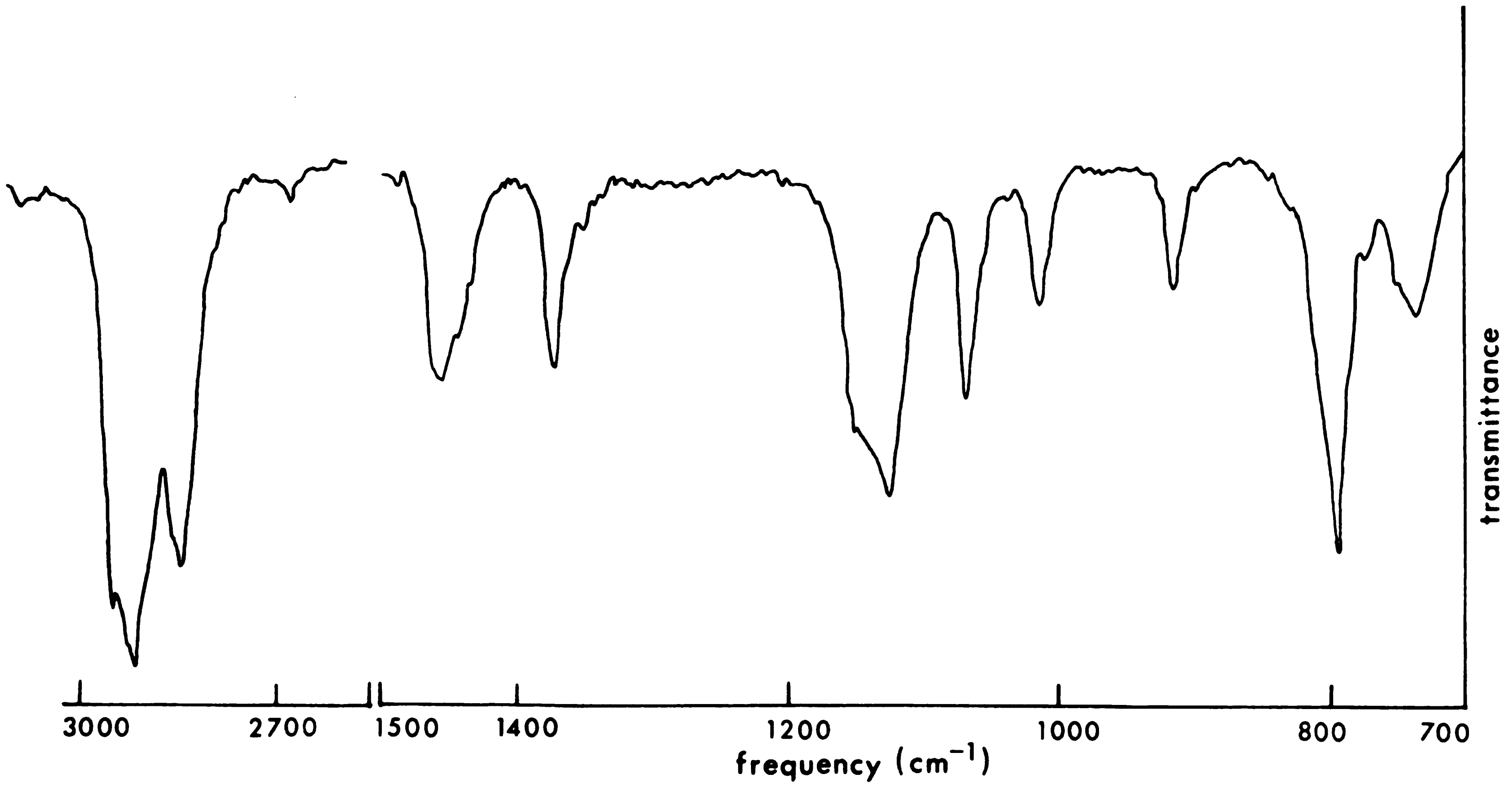


Figure 11. Infrared spectrum of $Cp_2Zr(OC_2H_5)_2$.

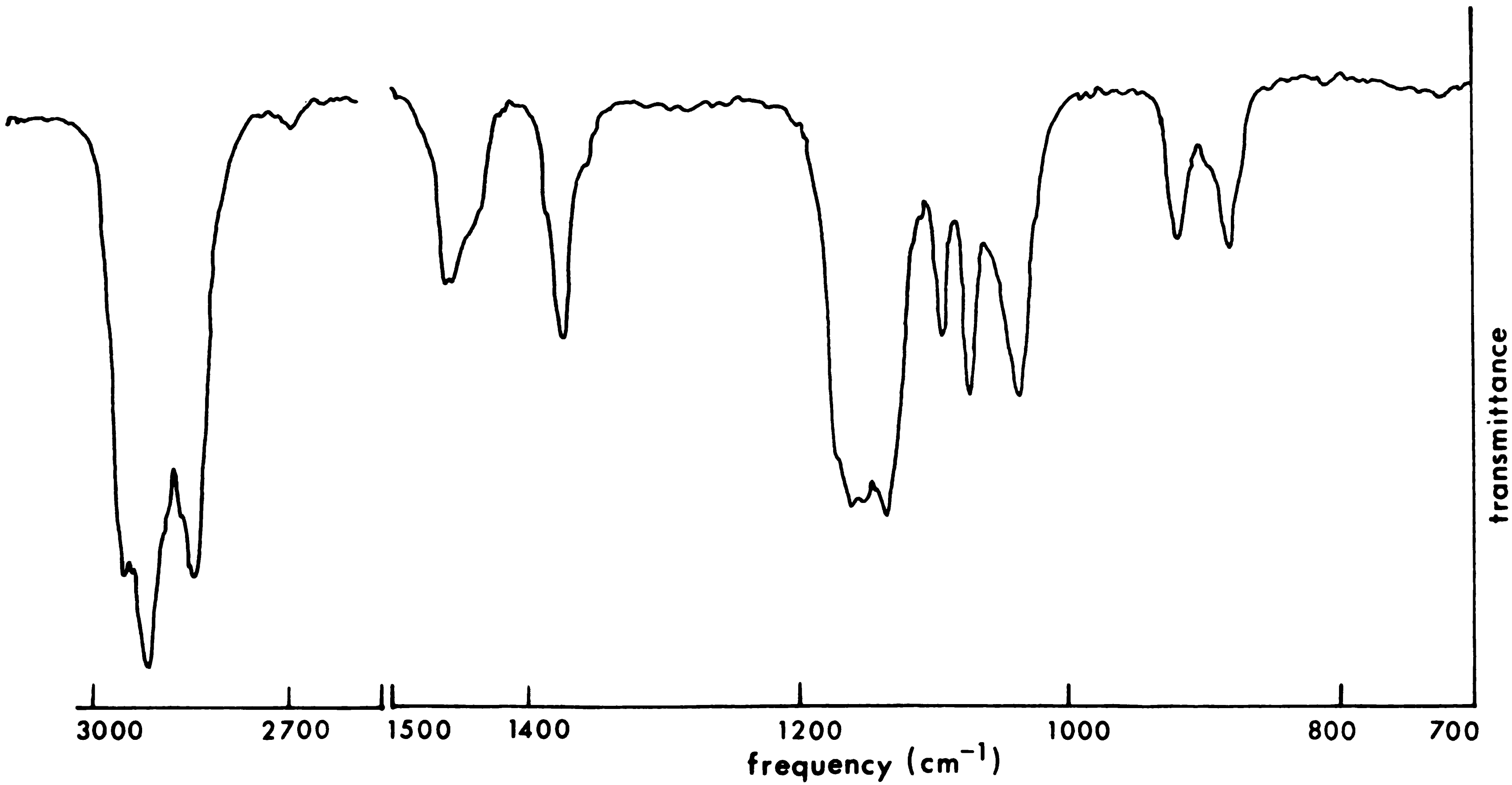


Figure 12. Infrared spectrum of $Zr(OC_2H_5)_4$.

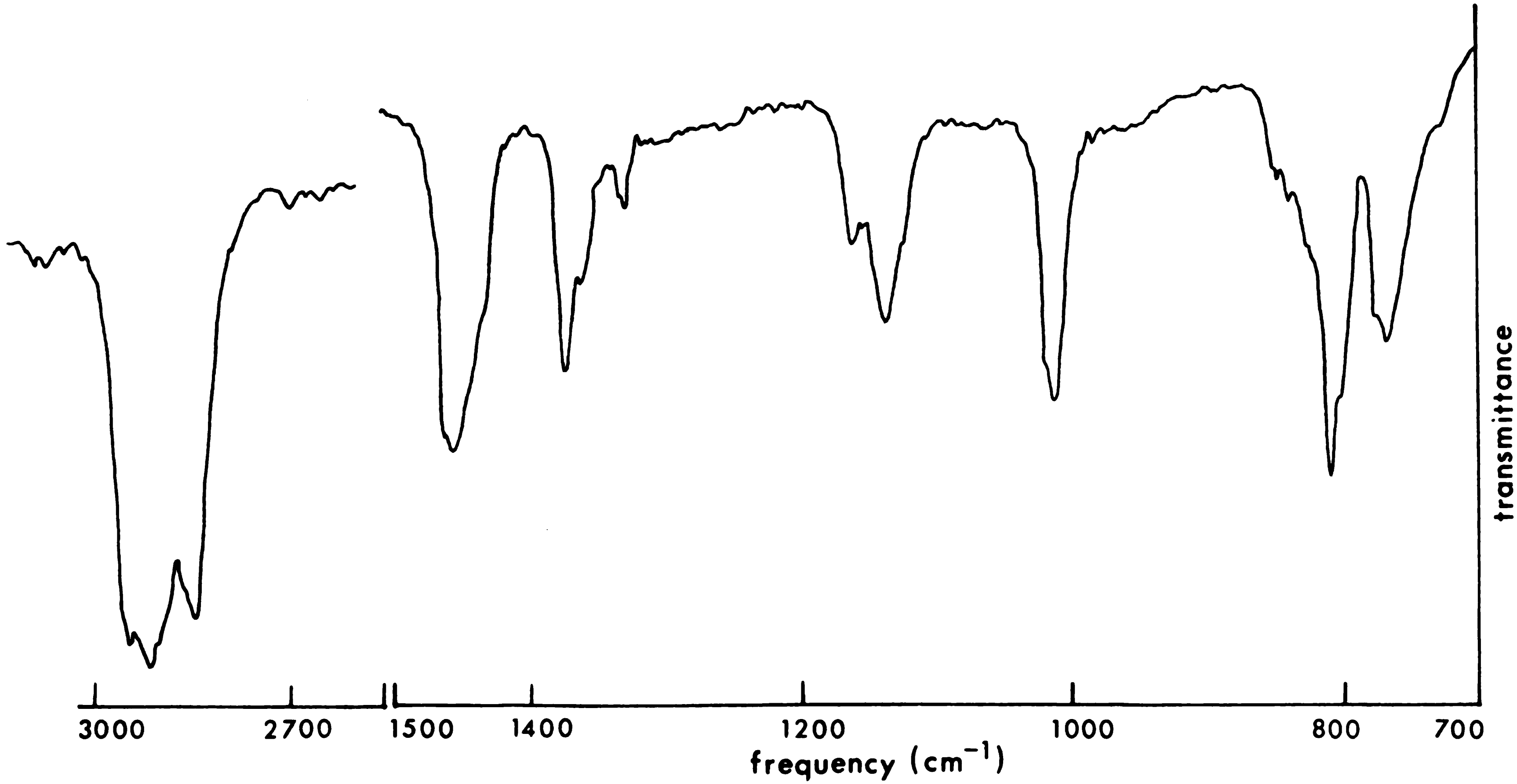


Figure 13. Infrared spectrum of $Cp_2Zr(OC_3H_7)Cl$.

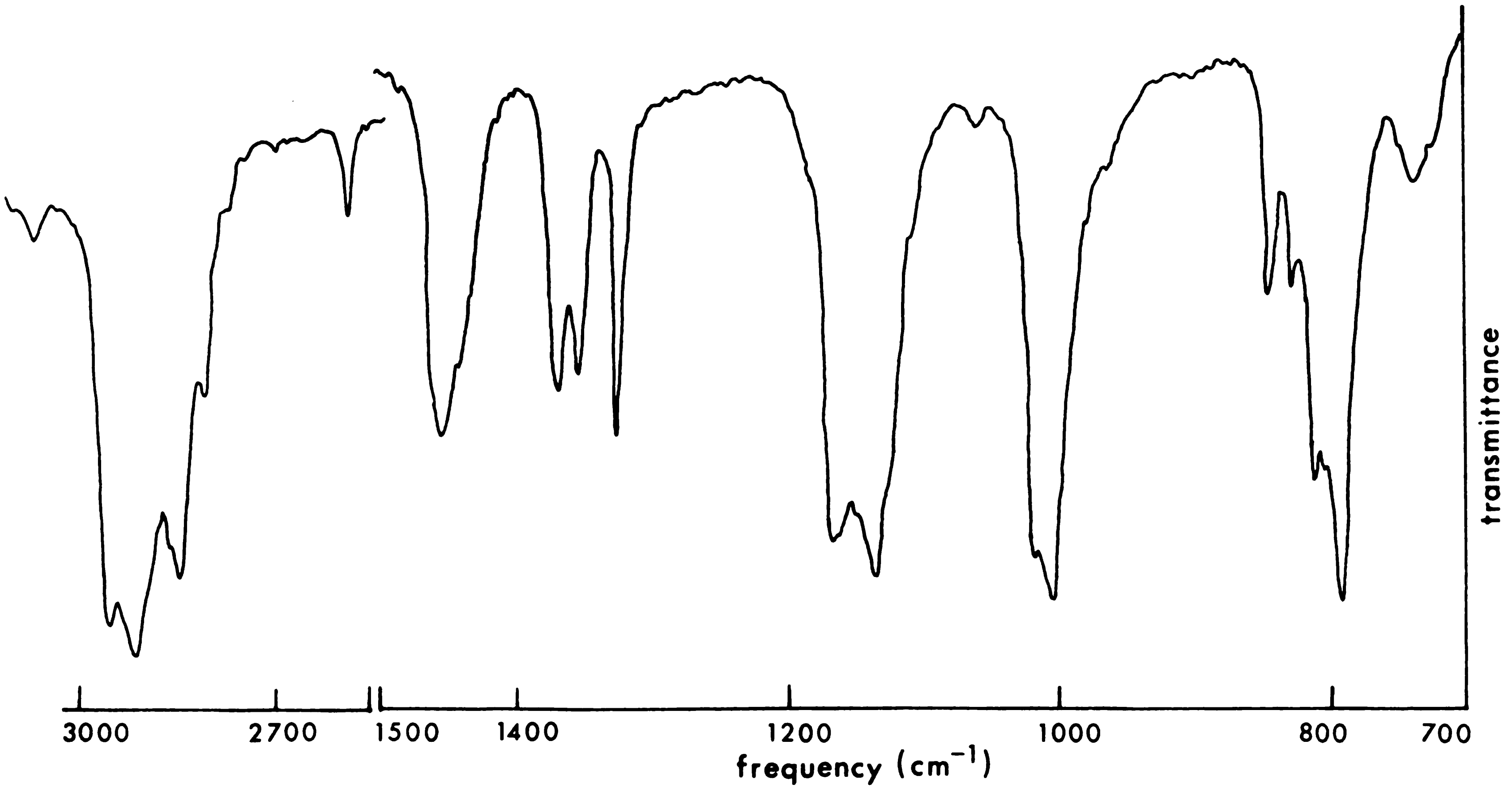


Figure 14. Infrared spectrum of $Cp_2Zr(OC_3H_7)_2$.

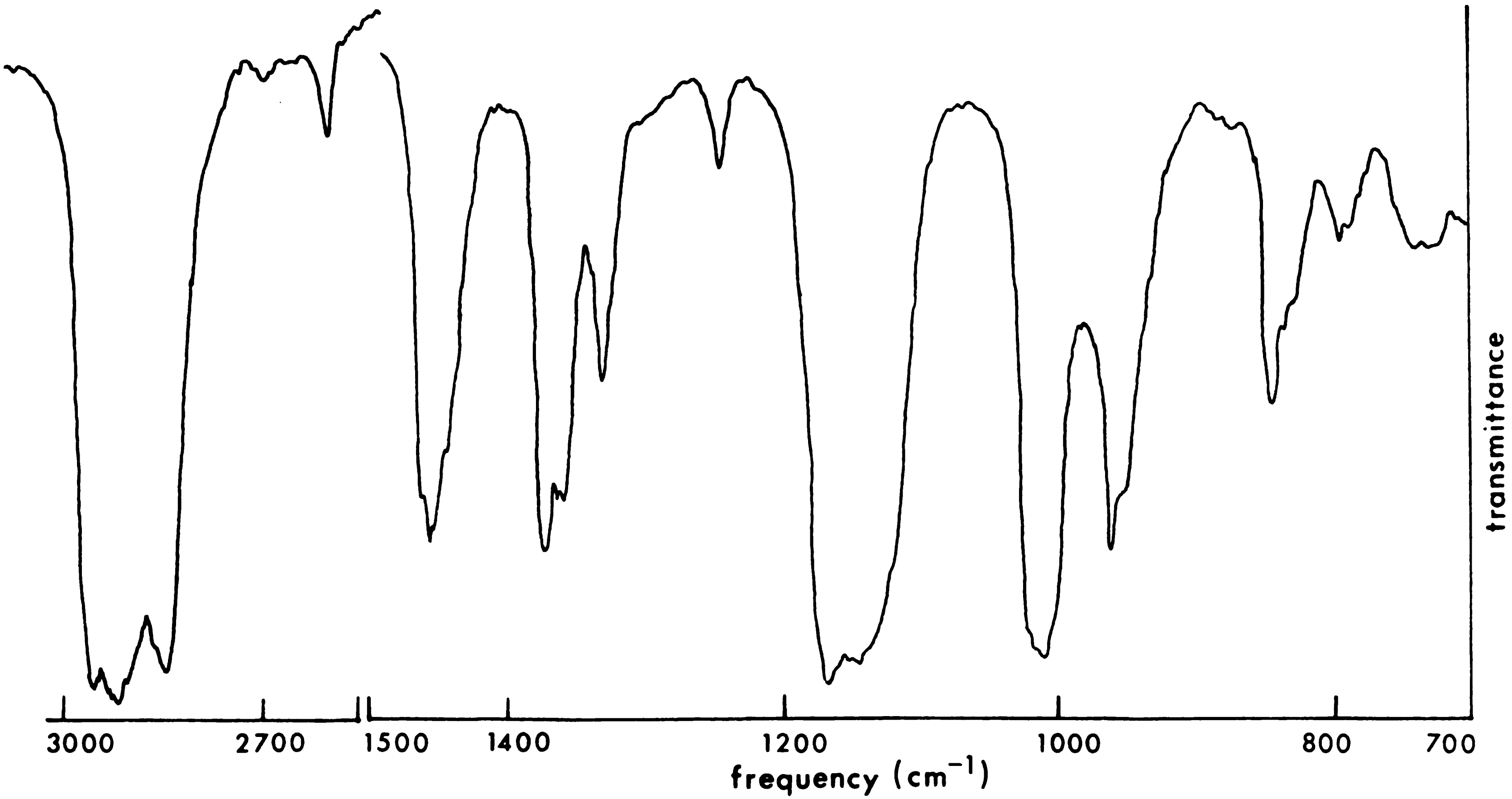


Figure 15. Infrared spectrum of $Zr(OC_3H_7)_4$.

Table III. Characteristic Frequencies (cm^{-1}) of Alkoxide Groups in $Cp_2Zr(OR)_nCl_{2-n}$.

Compound	C-H Stretch	C-H Bend	C-O Stretch	C-O Bend	C-C Stretch	Unassigned (Zr-O)(?)
$Cp_2Zr(OCH_3)Cl$	2805		1120			762
$Cp_2Zr(OCH_3)_2$	2800		1120			730
$Cp_2Zr(OC_2H_5)Cl$		1072	1130-1122		920	763
$Cp_2Zr(OC_2H_5)_2$		1070	1140-1122		913	732
$Cp_2Zr(OC_3H_7)Cl$	2600	1330		1161-1137		765
$Cp_2Zr(OC_3H_7)_2$	2600	1329		1163-1136		740

observed shift to higher frequency of the Zr - O bond assignment as chloride replaces alkoxide in each case. Since the Zr - O stretching frequencies are found at much lower frequencies, the frequency in the 730 - 770 cm^{-1} region is possibly a bending mode.

The far-infrared spectra (700 - 250 cm^{-1}) of the compounds of interest are shown in Figures 16-18. The important features of these spectra are the assignments and observed shifts in the Zr - O and the Zr - ring stretching frequencies. These frequencies are summarized in Table IV. The assignments were made by comparing the spectra of $Cp_2Zr(OR)_nCl_{2-n}$ with the spectrum of Cp_2ZrCl_2.

From Table IV it is seen that the Zr - O and the Zr - ring frequencies are shifted to lower frequencies as the chlorides are successively replaced by alkoxides. This is once again consistent with the electron density argument expressed above. The Zr - O and Zr - ring bonds are equally affected by the presence or absence of chloride ligands.

Figure 16. Far-infared spectra of $Cp_2Zr(OCH_3)_nCl_{2-n}$ (n = 0-2).

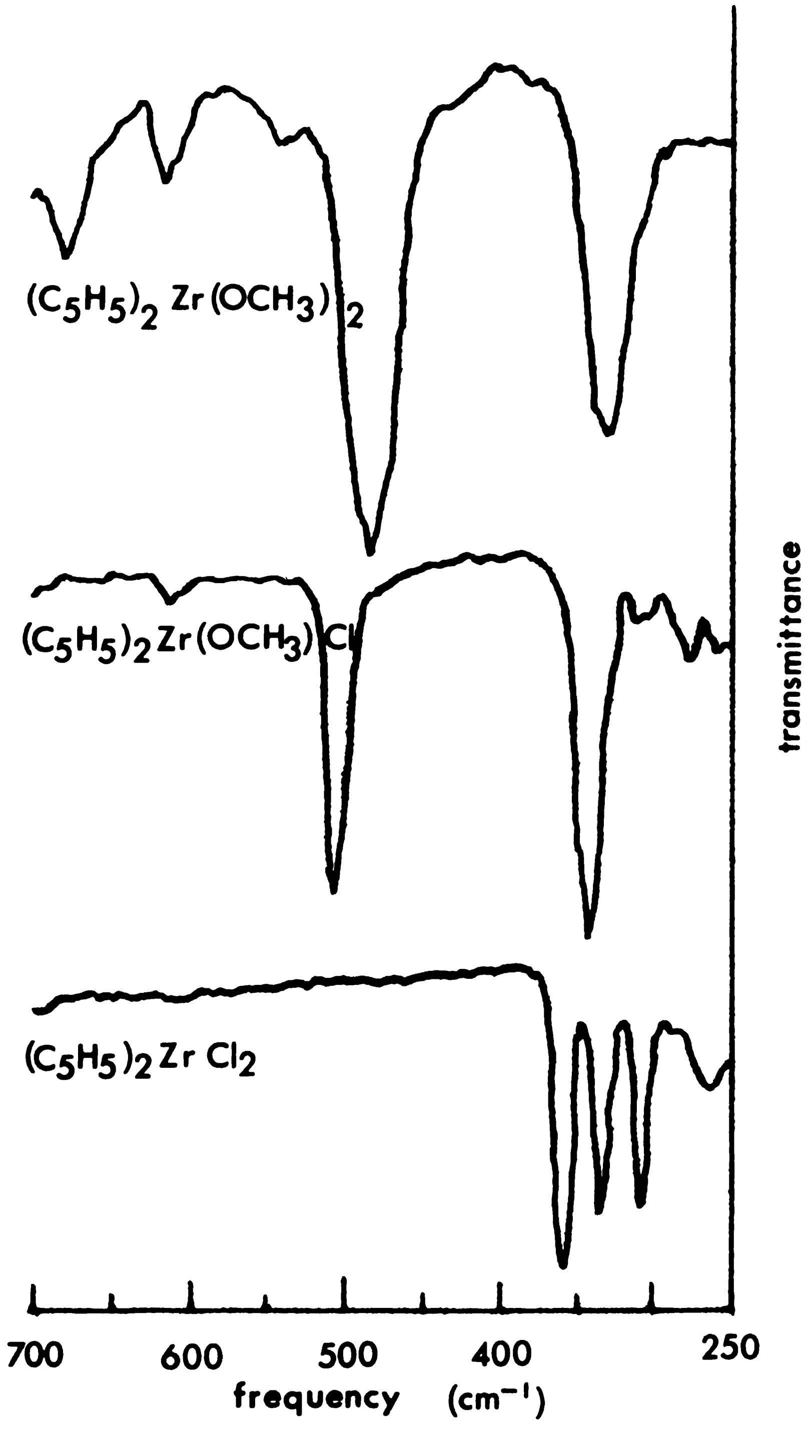


Figure 17. Far-infrared spectra of $Cp_2Zr(OC_2H_5)_nCl_{2-n}$ (n = 0-2) and $Zr(OC_2H_5)_4$.

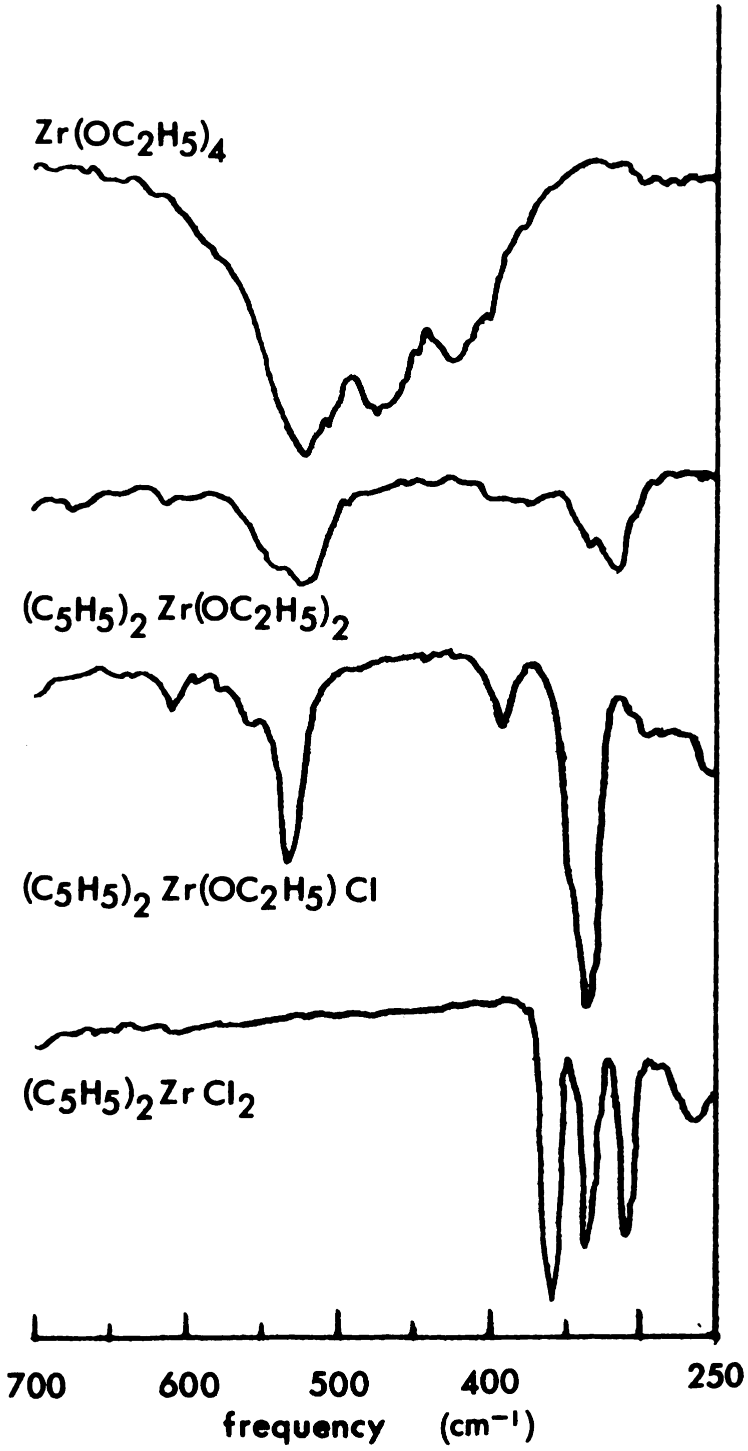


Figure 18. Far-infrared spectra of $Cp_2Zr(OC_3H_7)_nCl_{2-n}$ (n = 0-2) and $Zr(OC_3H_7)_4$.

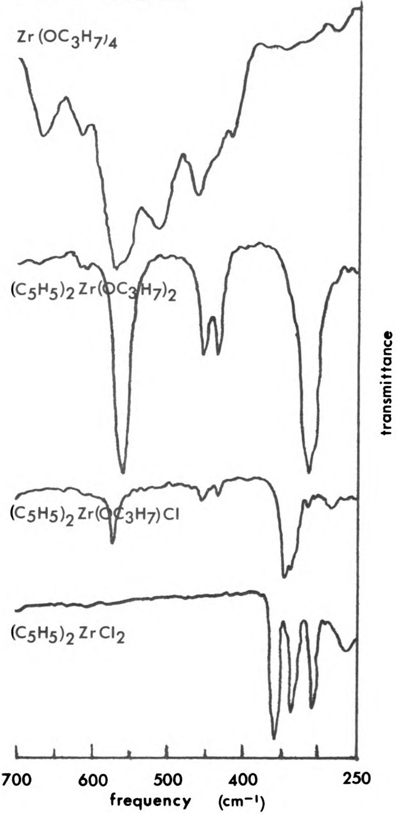


Table IV. Far-infared Frequencies (cm^{-1}) of Zr-O and Zr-ring Bonds.

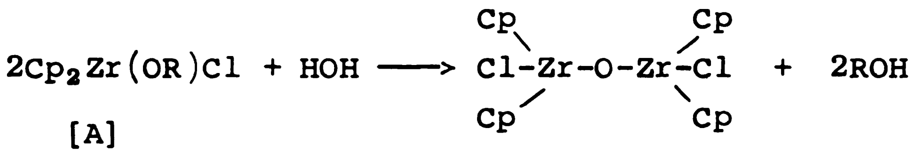
Compound	Zr-O Stretch	Zr-ring Stretch
Cp_2ZrCl_2	-	359
$Cp_2Zr(OCH_3)Cl$	507	342
$Cp_2Zr(OCH_3)_2$	482	329
$Cp_2Zr(OC_2H_5)Cl$	532	338
$Cp_2Zr(OC_2H_5)_2$	521	318
$Zr(OC_2H_5)_4$	(520,472,421)	-
$Cp_2Zr(OC_3H_7)Cl$	572	344
$Cp_2Zr(OC_3H_7)_2$	560 (453,435)	315
$Zr(OC_3H_7)_4$	(570,516,463)	-

D. Hydrolysis Reactions

It has been previously noted that the compounds $Cp_2Zr(OR)Cl$ and $Cp_2Zr(OR)_2$ are extremely sensitive to moisture. If water vapor is allowed to come in contact with the compounds, the compounds are quickly destroyed. This section will deal with the products of these hydrolysis reactions.

If the compounds are exposed to air saturated with water vapor, they lose weight rapidly. No physical change can be visibly observed, but the melting points change from the relatively low values reported earlier to values in the range of 300^0 or greater. The infrared spectra undergo marked changes.

The infrared spectra and melting points indicate that the end hydrolysis product for each of the three compounds $Cp_2Zr(OR)Cl$ ($R = CH_3$, C_2H_5, $\underline{i}\text{-}C_3H_7$) is the same. Furthermore, the weight loss corresponds to the hydrolysis reaction



$$2Cp_2Zr(OR)Cl + HOH \longrightarrow Cl\text{-}\underset{Cp}{\overset{Cp}{Zr}}\text{-}O\text{-}\underset{Cp}{\overset{Cp}{Zr}}\text{-}Cl + 2ROH$$

[A]

This is the same noted by Brainina[4] when he performed an elaborate hydrolysis reaction with $Cp_2Zr(OC_2H_5)Cl$.

The infrared spectrum of the hydrolysis products of $Cp_2Zr(OR)Cl$ is shown in Figure 19. The spectrum (the same regardless of 'R') is consistent with the above reaction. The absorption bands characteristic of the cyclopentadienyl

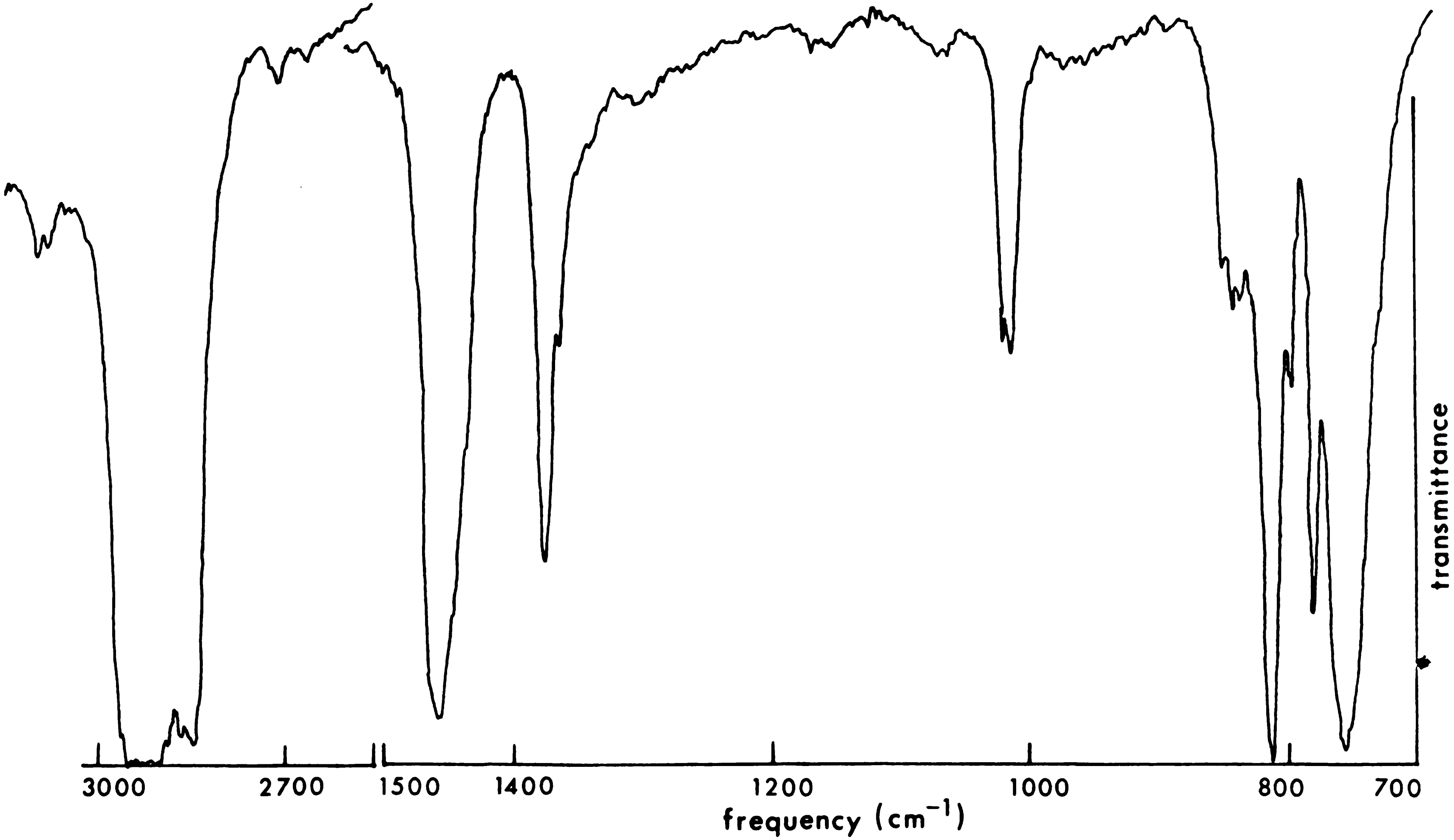
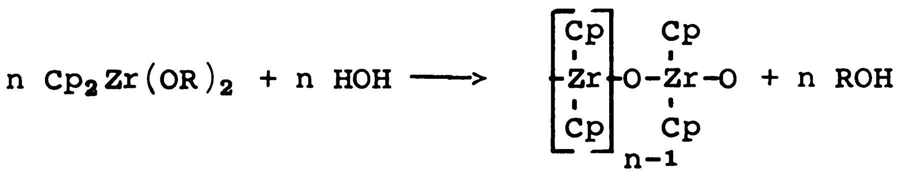


Figure 19. Infrared spectrum of hydrolysis product of $Cp_2Zr(OR)Cl$.

rings (3100, 1030-1020, 840-810 cm^{-1}) are still present. All bands characteristic of the R-groups are absent. There are additional strong bands at 779 and 752 cm^{-1} which may be additional cyclopentadienyl bands. The far-infrared region (see Figure 20) shows the Zr-ring stretching band at 349 cm^{-1} and the lower frequency broader bands characteristic of a Zr-Cl bond.

The hydrolysis of the compounds $Cp_2Zr(OR)_2$ [B] is much different from and less straightforward than the hydrolysis of $Cp_2Zr(OR)Cl$ [A]. The weight loss (relative to weight of original product) attending the hydrolysis of [B] is much greater than the weight loss for [A]. The hydrolysis of [B] seems to proceed in two rather ill-defined steps. On the basis of infrared spectral evidence and weight loss calculations, the two steps can be expressed as follows:

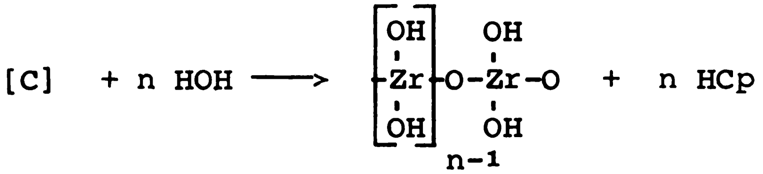
(1)



$$n\,Cp_2Zr(OR)_2 + n\,HOH \longrightarrow \left[\begin{array}{c} Cp \\ | \\ -Zr- \\ | \\ Cp \end{array}\right]_{n-1}\!\!O-\begin{array}{c} Cp \\ | \\ Zr \\ | \\ Cp \end{array}-O + n\,ROH$$

[C]

(2)



$$[C] + n\,HOH \longrightarrow \left[\begin{array}{c} OH \\ | \\ -Zr- \\ | \\ OH \end{array}\right]_{n-1}\!\!O-\begin{array}{c} OH \\ | \\ Zr \\ | \\ OH \end{array}-O + n\,HCp$$

[D]

The above steps are undoubtedly an oversimplification. If the hydrolysis is allowed to proceed for about 30 minutes,

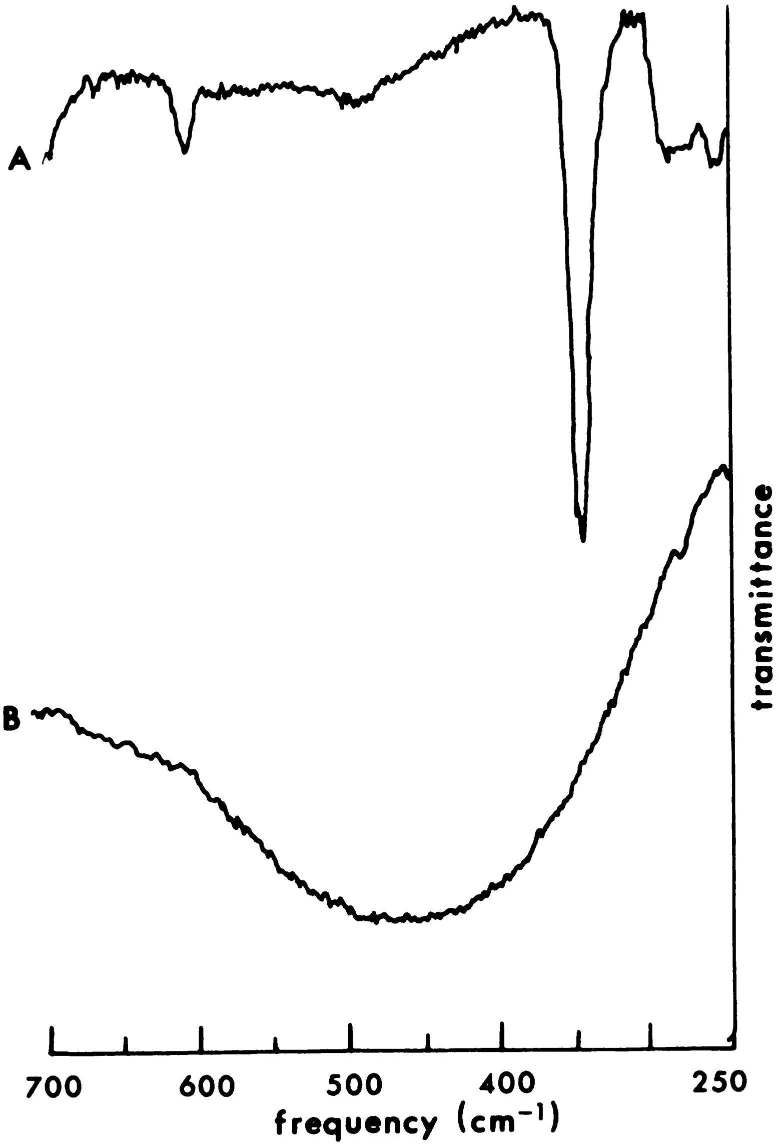


Figure 20. Far-infared spectra of hydrolysis products of (A) $Cp_2Zr(OR)Cl$; (B) $Cp_2Zr(OR)_2$.

the weight loss corresponds roughly to the weight lost by elimination of alkoxide groups in step (1). The infrared spectrum shows that all bands characteristic of the R-groups are absent. The spectrum shows, however, that the cyclopentadienyl absorption bands are superimposed on the broad band characteristic of the Zr-OH band (very broad centering at 480 cm^{-1}). See Figure 20. This would indicate that step (2) has already begun. Further hydrolysis results in a slower weight loss until a constant weight is finally observed. This weight loss corresponds roughly to the elimination of HCp as in step (2). The distinctive odor of cyclopentadiene is observed during the latter stage of hydrolysis. The infrared spectrum of [D] shows no indication of the presence of Cp. Broad bands are observed at 3300, 1480, and 480 cm^{-1}. The former two are indicative of bound OH while the latter is probably due to the Zr-OH bond.

E. Miscellaneous Observations

Reduction Potentials. It was hoped that reduction potentials for each of the compounds could be determined. This information would be particularly useful in relation to Part Two of this work. The polarograms were attempted in THF solution. The resistance of THF, however, could not be sufficiently overcome by the presence of supporting electrolyte (TBAI) to obtain valid polarograms. This work is being continued.

<u>Melting Points</u>. Each of the compounds gave clear melts with no apparent decomposition. Brainina[4] reported that his preparation of $Cp_2Zr(OC_2H_5)Cl$ melted with decomposition. It is possible that his compound was not sufficiently purified. Small quantities of hydrolysis product cause the melt to become brown. This gives the appearance of decomposition.

PART TWO

NITROGEN FIXATION UNDER MILD CONDITIONS BY USING SOME ORGANOMETALLIC COMPOUNDS OF THE SECOND-ROW TRANSITION ELEMENTS AS THE ACTIVATING AGENTS

INTRODUCTION

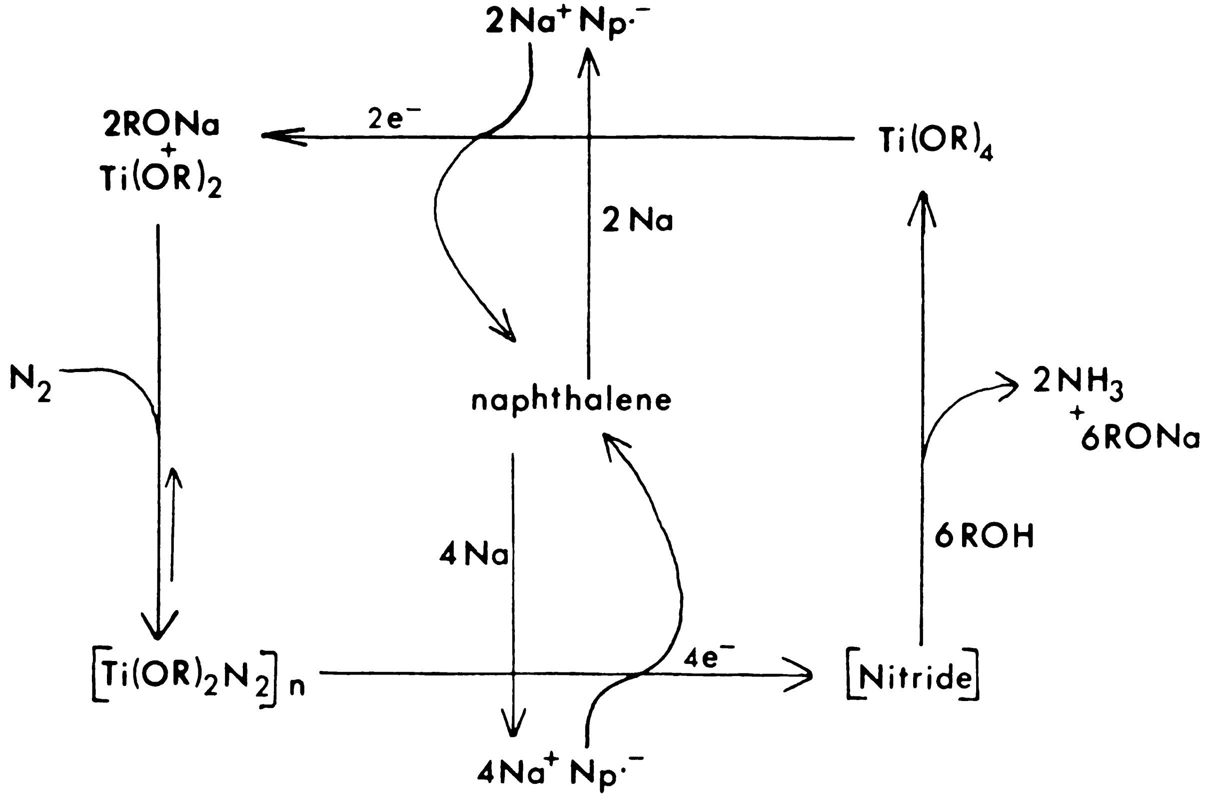
The process by which nature converts molecular nitrogen to ammonia and other more useful compounds has long been a fascinating puzzle to the chemist and the biologist. Nitrogen can be industrially converted to ammonia only under severe conditions of temperature and pressure.[14] Micro-organisms, however, have the ability to "fix" molecular nitrogen under the mild conditions of ambient temperature and pressure. These natural systems inevitably contain iron and molybdenum components, and for this reason inorganic chemists have long tried to duplicate the nitrogen-fixing process.

The first major breakthrough in molecular nitrogen activation under mild conditions by a transition metal was made by Vol'pin in 1966.[15] By allowing one of several Ti(IV) compounds to react with an alkyl magnesium halide in the presence of molecular nitrogen, Vol'pin found that subsequent hydrolysis produced detectable quantities of ammonia. Since then this system has acted as the model for most attempts to "fix" molecular nitrogen by inorganic or organometallic complexes.

The mechanistic concept by which Vol'pin's system "fixes" molecular nitrogen remains to be elucidated. Brintzinger has suggested that the monomeric dihydride anion $[(\pi\text{-}C_5H_5)_2TiH_2]^-$ may be an intermediate.[16,17] The focus of this topic has shifted away from Vol'pin's system, however, and little mechanistic work seems to be in process.

Much work in the last two years has been done by van Tamelen and co-workers.[18-24] Van Tamelen has worked with a variety of titanium(IV) systems and has achieved a significant amount of success. He asserts that a Ti(II) species is the activating intermediate in practically all of his systems. A strong reducing agent, either chemical or electrical, is employed to give the two-electron reduction. In this reduced state, the Ti(II) species perhaps "complexes" a molecule of molecular nitrogen. Van Tamelen suggests that the N-N bond is cleaved by further reduction at this stage, and the result is a nitride-type structure. Subsequent hydrolysis of this species liberates ammonia and possibly regenerates the initial Ti(IV) species. If van Tamelen's suggested mechanism is correct (see Figure 21), a true catalytic process is possible. Yields of greater than 100% (based on moles of ammonia produced per mole of initial titanium compound) have been realized by van Tamelen's procedure, but a true catalytic process is yet to be shown.

An alternative mechanism for the van Tamelen-type process has been proposed by Henrici-Olivé and Olivé.[25] The



Overall net process: $N_2 + 6e^- + 6ROH \longrightarrow 2NH_3 + 6OR^-$

Figure 21. Van Tamelen's proposed mechanism for nitrogen fixation.

Olivés' mechanism, unlike van Tamelen's, involves a hydrogen-bridged Ti(III) dimer as the activating intermediate. Van Tamelen has recently shown that this is highly unlikely.[24]

Regardless of which mechanism one chooses to believe, it is nevertheless clear that somehow the molecular nitrogen has been chemically activated. No actual molecular nitrogen complex of the early transition metals has been isolated. The nature of the metal-dinitrogen bond is thus not known. It is quite probable, however, that an olefinic-type of π-complex is formed. This type of complexation is a common phenomenon in complex catalysis. The usual result of such a π-complex formation is the activation of the multiple bond. The activation is a result of the donation of the π-electrons of the multiple bond to the empty d-orbitals of the transition metal, which causes a partial rupture of the multiple bond and imparts a slight positive charge to the atoms comprising the multiple bond. These effects produce a weakening of the multiple bond and permit further reaction to occur. It is quite probable that bonding of this type is somehow involved in the nitrogen fixation-reduction cycle.

A large number of stable molecular nitrogen complexes have been prepared and characterized, but these complexes invariably involve a transition metal containing six to eight d-electrons. The most interesting from both a historical and theoretical perspective are $[Ru(NH_3)_5N_2]Cl_2$,[26] $IrCl(Ph_3P)_2N_2$,[27] $HCo(Ph_3P)_3N_2$[28], and $[Ru(NH_3)_5]_2N_2$.[29] The important feature of all these complexes is that all attempts at further activation of the bound molecular nitrogen have proven futile. In each case the metal-dinitrogen bond is nearly linear. The bonding is analogous to the metal-carbonyl bond. Back π-bonding from the filled d-electrons of the transition metal to the empty antibonding p-orbitals of the molecular nitrogen is thought to be the stabilizing factor. Because the electrons involved in the multiple N≡N bond are not significantly affected, it is not difficult to understand why further activation is improbable. This is quite different from what would be expected if the bonding were of the olefinic type as described previously. The stable molecular nitrogen complexes are further hindered as possible intermediates in the nitrogen-fixing cycle if one accepts van Tamelen's suggestion that a two-electron reduction is a necessary first step. In each case this would mean forcing electrons into the next higher molecular orbital, but the next higher molecular orbital in these molecules is an antibonding orbital of high energy.

Because the titanocene dichloride system works well in the van Tamelen experiments, perhaps the biscyclopentadienyl-halide and the mixed cyclopentadienyl-alkoxide compounds of the second-row transition metals also have the ability to fix nitrogen. Part Two of this research project deals with a survey of these organometallic compounds and their efficacy in the fixation-reduction cycle.

EXPERIMENTAL

A. Materials

Bis(π-cyclopentadienyl)dichlorozirconium(IV) was obtained from Arapahoe Chemical Company and used without further purification.

Anal. Calcd for $C_{10}H_{10}ZrCl_2$: Zr, 31.22; Cl, 24.26.
Found: Zr, 31.09; Cl, 24.13.

Niobium pentachloride was obtained from Research Inorganic Chemicals and used without further purification.

Molybdenum pentachloride was obtained from Climax Molybdenum Company. The commercial product was further purified by vacuum sublimation. The green oxychloride impurities were removed by gradually increasing the temperature until no more green substance sublimed. The shiny black crystals of pure $MoCl_5$ were then sublimed and stored under dry nitrogen. This process was accomplished by the use of a three-component Pyrex tube and a tube furnace.

Ruthenium trichloride was purchased from Alfa Inorganics and used without further purification.

Sodium was used in the form of finely dispersed sodium prepared according to the method of T. P. Whaley.[30] The sodium was stored under sodium-dried xylene in a dry nitrogen atmosphere. Transfers of sodium were effected by use of a pipet. The xylene was removed under vacuum before the sodium was weighed and used.

Cyclopentadiene was freshly prepared by depolymerization of dicyclopentadiene by heating the dicyclopentadiene until the depolymerization occurred. The cyclopentadiene was fractionally distilled into a flask and stored until used at -78°.

$[W(OCH_3)_2Cl_3]_2$ and $[W(OC_2H_5)_2Cl_2(C_2H_5OH)]_2$ were obtained from D. Paul Rillema.[31]

Solvents. All solvents were refluxed with the appropriate drying agent under a nitrogen atmosphere unless indicated otherwise.

Tetrahydrofuran (THF) was refluxed continuously with lithium aluminum hydride and distilled immediately before use.

Benzene was refluxed continuously with calcium hydride and distilled immediately before use.

Hexane was continuously refluxed in the presence of sodium metal and distilled immediately before use.

Chloroform was washed with water and dried over calcium chloride. The chloroform was then refluxed in the presence of phosphorus pentoxide and distilled. The distilled chloroform was stored in the absence of light.

Gases. Prepurified nitrogen from Liquid Carbonics was passed through an activated copper catalyst (BTS catalyst - BASF R-3-11 from Badische Anilin - Soda-Fabrik AG) to remove oxygen. It was then passed through two drying towers filled with calcium sulfate and barium oxide to remove any water present.

Argon was obtained from Liquid Carbonics and used without further purification.

B. Analytical Methods

Niobium Analysis. The solid sample was decomposed by dissolution in very dilute nitric acid and digesting the solution over a steam bath for about an hour. This solution was made basic by addition of aqueous ammonia, and the digestion was continued for an additional two hours. Dilute nitric acid was added until the solution was acidic. The precipitate was removed by filtration and washed three times with dilute nitric acid. This precipitate was ignited for several hours at 700^0, and the niobium was weighed as Nb_2O_5. The filtrate was saved and used for determination of chloride content.

Molybdenum Analysis. The samples were decomposed by dissolution in $3\underline{N}$ aqueous ammonia. This solution was acidified with $3\underline{N}$ nitric acid and heated to the boiling point.

The solution was then diluted to 100.00 ml. Twenty-five-ml aliquots were analyzed for molybdenum according to the method of Pribil and Malat.[32]

Ammonia Analysis. Ammonia was detected qualitatively by the use of Nessler's Reagent. Nessler's Reagent was prepared as follows: (1) Fifty grams of potassium iodide were dissolved in 50 ml cold water; (2) A saturated solution of mercuric chloride (about 22 g in 350 ml of water) was added until an excess was indicated by the formation of a precipitate; (3) Two-hundred ml of 5N sodium hydroxide was added, and the solution was diluted to one liter.

Ammonia was quantitatively determined by being passed through standard hydrochloric acid. The remaining hydrochloric acid was then titrated with standard sodium hydroxide solution, and the ammonia was determined from the amount of acid which had been neutralized. Phenolphthalein was used as the indicator.

C. Experimental Apparatus and Technique

Most of the materials dealt with in this research were sensitive to oxidation and/or hydrolysis. Similar techniques to those explained in Part One were used.

D. The Nitrogen-Fixation Experiment

The general procedure followed in the nitrogen-fixation experiments was essentially the same for each compound studied. The apparatus used and a simplified procedure are illustrated in Figure 22. A more detailed experimental description follows:

1. The reducing solution of sodium naphthalenide was prepared by allowing stoichiometric (1:1) quantities of finely dispersed sodium to react with reagent naphthalene in THF. A deep emerald-green solution resulted.
2. The appropriate transition-metal complex was dissolved in THF. The quantity of complex was stoichiometrically one-sixth that of the sodium naphthalenide. This solution of complex in THF was added dropwise to the reducing solution. A constant stream of nitrogen was bubbled through the reaction mixture and directed through Nessler's Reagent, which was used for qualitative detection of ammonia in the escaping gas.
3. A slight excess of ethanol, diluted with THF, was added dropwise to the mixture of complex and reducing agent. If fixation-reduction occurred, the mixture remained dark; ammonia was very quickly observed in the Nessler's Reagent. If no fixation-reduction occurred, the alcohol reacted with the sodium naphthalenide, the solution became clear, and no ammonia was detected in the Nessler's Reagent.

PROCEDURE:

1 Prepare reducing soln of $Na^+C_{10}H_8^-$ in THF.

2 Add appropriate complex, also in THF.

3 Test for evolution of NH_3.

4 Add ethanol slowly and with stirring.

5 Test for NH_3 via N.R. and collect evolved NH_3 in HCl for later analysis.

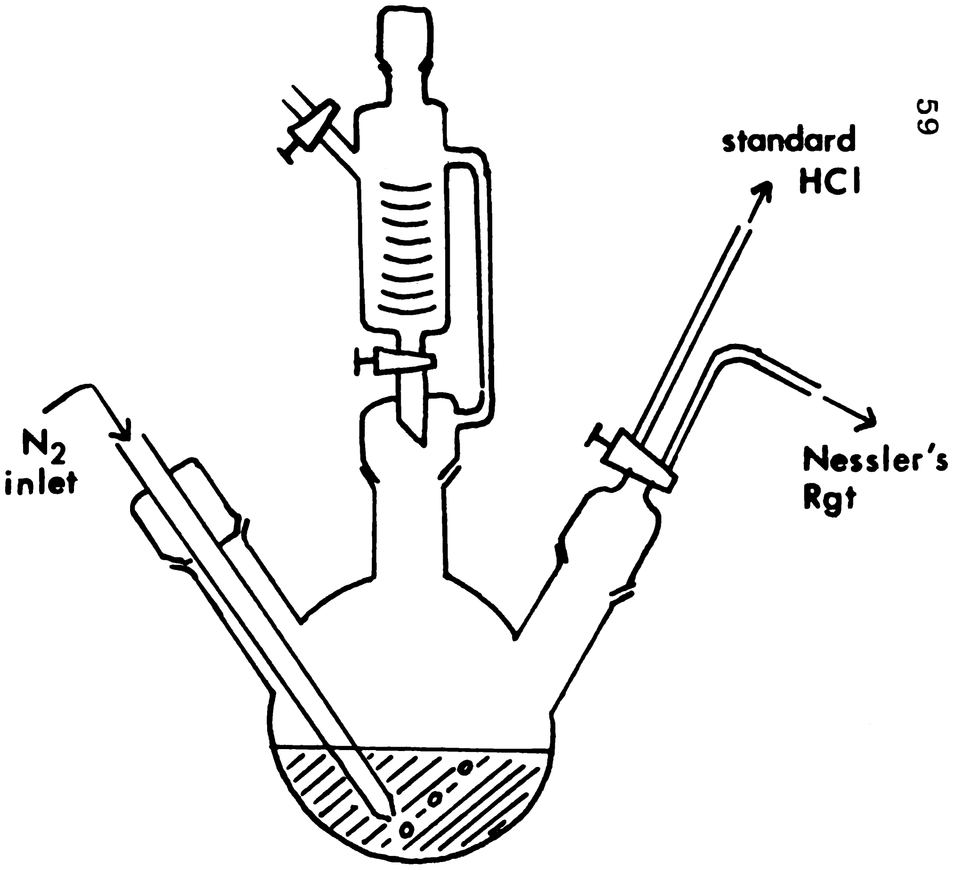


Figure 22. Experimental apparatus and procedure for the nitrogen-fixation experiment.

4. If fixation-reduction occurred, the escaping nitrogen stream was passed through standard hydrochloric acid solution for 24 hours. Ammonia was determined as previously described under Analytical Methods.

E. Preparation of Compounds

Trichlorobis(π-cyclopentadienyl)niobium(V). A combination and modification of the methods of Birmingham[33] and Brantley[34] were used. A solution of sodium cyclopentadienide in THF was prepared by adding 8.1 ml freshly distilled cyclopentadiene to 2.54 g of finely dispersed sodium. This solution was added dropwise to a suspension of 10 g $NbCl_5$ in 50 ml dry benzene. Vigorous mechanical stirring and strict exclusion of air were required. The reaction contents were vigorously stirred for several hours. The solvents were removed under vacuum. A brownish-black dry solid resulted. This solid was ground to a powder. The powder was placed in a continuous extraction apparatus and extracted with benzene. The extracted product was recrystallized from benzene. The product crystals were deep purple. Yield = 4.3 g. The infrared spectrum agreed closely with that reported by Birmingham.[33]

Analysis Calcd for $NbCl_3C_{10}H_{10}$: Nb, 28.21; Cl, 32.29.
Found: Nb, 28.05; Cl, 33.16.

Dichlorobis(π-cyclopentadienyl)molybdenum(IV).[35,36,37] Freshly sublimed molybdenum pentachloride (0.05 mol) was added very slowly to an ice-cooled solution of sodium cyclopentadienide (0.25 mol) and sodium borohydride (0.13 mol) in 125 ml THF. This mixture was stirred and allowed to reflux for several hours. The solvent was removed by evaporation, and the residue was sublimed under vacuum (about 10^{-1} mm) at 120°. Bright yellow crystals of $(C_5H_5)MoH_2$ were obtained. These crystals were extremely sensitive to air, and extreme precautions had to be taken. Exposure to air caused the crystals to turn brown immediately. The $(C_5H_5)_2MoH_2$ product was added to 50 ml anhydrous chloroform, and a dark green solution resulted. Green crystals of $(C_5H_5)_2MoCl_2$ crystallized from this solution. The physical properties of the product agreed with those given by Cotton and Wilkinson.[35]

Biscyclopentadienylruthenium(II).[35] Ruthenium trichloride (0.01 mol) was added gradually to a solution of sodium cyclopentadienide (0.06 mol) in THF at -80°. The contents of the flask were warmed to room temperature. As the temperature was raised the contents became purple. This reaction mixture was allowed to reflux for two hours. The solvent was removed by evaporation and the remaining solid material was dried. This violet-purple solid was ground to a fine powder and sublimed under vacuum (10^{-1} mm) at 120°. The resulting product crystals of $(C_5H_5)_2Ru$ were light-yellow.

RESULTS AND DISCUSSION

Part Two of this research is concerned with a general survey of the possible nitrogen-fixing ability of some early transition metal organometallic compounds. It is not an in-depth study, but is rather an overview with the purpose of pointing out some of the possibilities for future study. The emphasis is on the biscyclopentadienyl compounds of the second-row transition metals. This work will be discussed by each group metal. The discussion will thus be divided into the following headings: A. General Observations, B. Compounds of Zirconium, C. Compounds of Niobium, D. Compounds of Molybdenum and Tungsten, and E. Ruthenocene.

A. General Observations

Except as otherwise noted, the nitrogen-fixation experiment was performed according to the directions prescribed in the Experimental section (see Figure 22). The important aspect of this experiment is to see whether a given transition metal compound is capable of activating molecular nitrogen. The proposed mechanism for the activation has already been reviewed in the Introduction (see Figure 21). The results are summarized in Table V.

Table V. A Summary of the Results Obtained by Using Various Transition Metal Compounds in the Nitrogen-Fixation Experiment.

$$\text{'Compound'} + Na^{+}C_{10}H_{8}^{\cdot -} + N_2 \xrightarrow{hyd} NH_3$$

Compound	$\%NH_3$[a]	Comments
Cp_2ZrCl_2	0	$NaBH_4$ used rather than $Na^{+}C_{10}H_{8}^{\cdot -}$
Cp_2ZrCl_2	2.7,4.1	
$Cp_2Zr(OC_3H_7)Cl$	1.3	
$Cp_2Zr(OC_3H_7)_2$	0	
Cp_2NbCl_3	2.6	
$NbCl_5$	0	$NbCl_5$ reacts with THF at 25°
Cp_2MoCl_2	?	Solubility problems not overcome
Cp_2MoH_2	P[b]	
$W(OCH_3)_2Cl_3$	0.3	
$W(OC_2H_5)_2Cl_2(C_2H_5OH)$	P	
Cp_2Ru	0	

[a] Based on moles NH_3 : moles of compound.

[b] Positive qualitative test but not measurable quantitatively.

It was necessary to test the validity of the experiment. Spurious conclusions could be drawn if ammonia were already present in the gaseous nitrogen or if some substance present in the compound or reducing agent were to react with Nessler's Reagent. The following tests show that the experiment is indeed valid: (1) If nitorgen gas was bubbled through the reducing agent and the escaping gas was directed through Nessler's Reagent, no ammonia was detected. There is no ammonia in the nitrogen. (2) If the experiment was conducted as outlined but without the addition of transition metal complex, no ammonia was detected. The transition metal complex is a necessary constituent in the experiment. (3) If a transition metal compound was found to have the ability to fix nitrogen, the experiment was repeated but argon was substituted for nitrogen. No ammonia was detected when the argon was used. Molecular nitrogen was the source of the nitrogen in the ammonia. (4) If no reducing agent was used, no ammonia was detected. Reduction of the transition metal complex is an important step in the mechanism. (5) No ammonia was detected until the final hydrolysis and thus the source of the NH_3 protons is probably the alcohol used for the hydrolysis.

B. Compounds of Zirconium

Only for zirconium was a systematic study of related compounds possible. The compounds which were used were those synthesized and characterized according to Part One of this research. The only compounds available in large enough quantities to permit a valid study were Cp_2ZrCl_2, $Cp_2Zr(OC_3H_7)Cl$, and $Cp_2Zr(OC_3H_7)_2$. The results of the nitrogen-fixation experiment for these three compounds are shown below:

Compound	%NH_3
Cp_2ZrCl_2	2.7, 4.1
$Cp_2Zr(OC_3H_7)Cl$	1.3
$Cp_2Zr(OC_3H_7)_2$	0.0

The yields of ammonia produced are disappointingly small, and any conclusions must be drawn with considerable uncertainty. However, it does appear that the nitrogen-fixing ability of the series decreases as the chloride ligands are replaced by isopropoxide groups. One can only speculate about the effect being related to the ease of the two-electron reduction of Zr(IV)-Zr(II). Watt and Drummond[38] have shown that sodium naphthalenide is capable of reducing Cp_2ZrCl_2 to Cp_2Zr. Unfortunately the actual reduction potentials are not known. Attempts to obtain these reduction potentials polarographically (see Part One, Results and Discussion, Section E) were unsuccessful.

The speculated "ease-of-reduction" series $Cp_2ZrCl_2 > Cp_2Zr(OR)Cl > Cp_2Zr(OR)_2$ may be a result of the relative electron density about the zirconium. As the chlorides are replaced by the more basic alkoxide groups, the electron density about the zirconium should increase and may have the effect of raising the energy of the lowest-lying d-orbital slightly. Such an effect would make reduction more difficult. This would be consistent with the trend seen in the relative nitrogen-fixing abilities of the compounds.

C. Compounds of Niobium

No niobium series similar to that discussed with zirconium was available. The two compounds studied were Cp_2NbCl_3 and $NbCl_5$. When Cp_2NbCl_3 was used in the experiment, yields of 2.6% NH_3 were realized. The $NbCl_5$ gave no indication that NH_3 had been produced. The yield of NH_3 produced by Cp_2NbCl_3 was too close to the yield given by Cp_2ZrCl_2 to allow a significant comparison.[39]

During the course of the Cp_2NbCl_3 experiment, several of the possible variables were investigated for their effect on the nitrogen-fixation process. After the ammonia-producing process had been proceeding for several hours, the nitrogen flow was replaced by an argon flow. Ammonia production ceased immediately. When the nitrogen flow was once again begun, more ammonia was detected. The addition of more sodium after the reaction had proceeded for a day caused slightly more ammonia to be produced. Adding more Cp_2NbCl_3 had no effect.

D. Compounds of Molybdenum and Tungsten

The compounds of molybdenum used were Cp_2MoCl_2 and Cp_2MoH_2. The Cp_2MoCl_2 was difficult to study because of its insolubility in THF and most other organic solvents. This insolubility necessitated a vigorously-stirred solid-(Cp_2MoCl_2)-liquid(NaNp)-gas(N_2) reaction, and the reported results are probably not a valid indication of the ability of Cp_2MoCl_2 to fix nitrogen.

The tungsten compounds used were the dimers $[W(OCH_3)_2Cl_3]_2$ and $[W(OC_2H_5)_2Cl(C_2H_5OH)]_2$. Each produced small quantities of NH_3.

E. Ruthenocene (Cp_2Ru)

It was thought that Cp_2Ru would be most significant if it could fix molecular nitrogen. Isolated molecular nitrogen complexes of ruthenium have been isolated,[26] and it would be significant to show that other compounds of the same metal could work in the nitrogen-fixation experiment. It was also hoped that Cp_2Ru would be an ideal compound to try since the ruthenium is already in a reduced state, but Cp_2Ru gave only negative results in the nitrogen-fixation experiment.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. A. N. Nesmeyanov, O. V. Nogina, and A. M. Berlin, *Dokl. Akad. Nauk. SSSR*, **134**, 607 (1960).

2. A. N. Nesmeyanov, E. I. Fedin, P. V. Petrovskii, V. A. Dubovitskii, O. V. Nogina, and N. A. Lazareva, *Dokl. Akad. Nauk. SSSR*, **163** (3), 659 (1965).

3. G. G. Dvoryantseva, Y. N. Sheinker, A. N. Nesmeyanov, O. V. Nogina and V. A. Dubovitskii, *Dokl. Akad. Nauk. SSSR*, **161** (3), 603 (1965).

4. E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk. SSSR*, **154**, 1113 (1964).

5. P. C. Wales and H. Weigold, *J. Organometal. Chem.*, **24**, 413 (1970).

6. C. K. Mann in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1969, p. 132.

7. H. Lund and J. Bjerrum, *Ber. Deut. Chem. Gesell.*, **64**, 210 (1931).

8. H. F. Walton, "Principles and Methods of Chemical Analysis," Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1964, p. 236.

9. S. Herzog, J. Dehnert, and K. Luhder in "Techniques of Inorganic Chemistry," Vol. III, H. B. Jonassen and A. Weissberger, Eds., Interscience Publishers, New York, N.Y., 1968.

10. D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 1951, 280.

11. D. C. Bradley, C. G. Barraclough, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 1961, 2601.

12. C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, *Anal. Chem.*, **36** (12), 2332 (1964).

13. R. S. P. Coutts, J. R. Surtees, J. M. Swan, and P. C. Wales, *Aust. J. Chem.*, **19**, 1377 (1966).

14. B. Timm, *Chem. Ind.* (London), 1960, 274.

15. M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966).

16. H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4307 (1966).

17. H. Brintzinger, *J. Am. Chem. Soc.*, **89**, 6871 (1967).

18. E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).

19. E. E. van Tamelen, G. Boche, and R. Greeley, *J. Am. Chem. Soc.*, **90**, 1677 (1968).

20. E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967).

21. E. E. van Tamelen and B. Akermark, *J. Am. Chem. Soc.*, **90**, 4492 (1968).

22. E. E. van Tamelen and D. Seeley, *J. Am. Chem. Soc.*, **91**, 5194 (1969).

23. E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *J. Am. Chem. Soc.*, **91**, 1551 (1969).

24. E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Am. Chem. Soc.*, **92**, 5251 (1970).

25. G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **81**, 679 (1969).

26. A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

27. J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Am. Chem. Soc.*, **90**, 5430 (1968).

28. A. Sacco and M. Rossi, *Inorganica Chimica Acta*, **2**, 127 (1968).

29. H. Scheidegger, J. N. Armor, and H. Taube, *J. Am. Chem. Soc.*, **90**, 3263 (1968).

30. T. P. Whaley in "Inorganic Syntheses," Vol. V, T. Moeller, Ed., McGraw-Hill Book Company, New York, N.Y., 1957, pp 6-10.

31. D. Paul Rillema, Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1969.

32. R. Pribil and M. Malat in "Gravimetric Analysis," Part II, L. Erdey, Ed., Pergamon Press, New York, N.Y., 1965, p 540.

33. G. Wilkinson and J. M. Birmingham, J. Am. Chem. Soc., **76**, 4281 (1954).

34. J. C. Brantley, U. S. Patent 2,921,948 (1960); Chem. Abstr., **54**, 11048i.

35. F. A. Cotton and G. Wilkinson, Z. Naturforsch, **9b**, 417 (1954).

36. M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 280 (1951).

37. M. H. Green, University of Oxford, private communication, 1969.

38. R. S. P. Coutts, J. R. Surtees, J. M. Swan, and P. C. Wales, Aust. J. Chem., **19**, 1377 (1966).

39. D. R. Gray and C. H. Brubaker, Jr., Chem. Commun., 1239 (1969).