

PART ONE
PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE
BETWEEN BIS (CYCLOPENTADIENYL) ZIRCONIUM
DICHLORIDE AND ITS ANALOG SYSTEM

PART TWO
PHOTOCHEMICAL REACTIONS OF
BIS (CYCLOPENTADIENYL) DIPHENYL TITANIUM (IV)

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
MIEN HSIAO PENG

1976

ABSTRACT

PART ONE

PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE BETWEEN
BIS(CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDE AND ITS ANALOG SYSTEMS

PART TWO

PHOTOCHEMICAL REACTIONS OF
BIS(CYCLOPENTADIENYL)DIPHENYL TITANIUM(IV)

By

Mien Hsiao Peng

PART ONE

Irradiation of the mixture of zirconocene dichloride and (D-10)-zirconocene dichloride in benzene solution leads to the exchange of cyclopentadienyl ligands under conditions of constant incident light intensity. A 450 watt medium pressure mercury-vapor lamp, Hanovia #679 A 0360, was used as the light source which emitted 313 nm light by through the filter solution cells. The lamp and filter cells were mounted inside a merry-go-round rotator. The photolytic formation of (D-5)-zirconocene dichloride was detected by mass spectrometry. A quantum yield for the ligand exchange of 0.021 mol/Ei was calculated by using the McKay analysis based on mass spectrographic data within suitable irradiation time. The equilibrium constant was 2.8.

Zirconocene dichloride was found to exchange cyclopentadienyl ligand photolytically with bis(methylcyclopentadienyl)zirconium dichloride with the constant for approach to equilibrium 2.3.

PART TWO

Photolysis of diphenyl titanocene, resulting in loss of phenyl ligands, is a generally useful approach to the generation of coordinatively unsaturated complex species. The low temperature nuclear magnetic resonance method was employed to investigate the transient titanocene. The course of photoreaction was followed by using the electron paramagnetic resonance method at low temperature and room temperature.

Isolation and characterization of electron deficient intermediate were attempted. The species of green $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}]_x$ polymer was obtained in solid state, which was converted to the dark green transient $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}$ species in solvents at low temperature. Formation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}]_x$ as a distinct isolated species was supported by its ir spectrum and titanium analysis.

Some stable titanocene adducts were prepared from the reduction of diphenyl titanocene by photolysis in the presence of various substrates such as carbon monoxide and diphenylacetylene. They all formed in quantitative yield. Presumably, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(II)}$ is involved as the intermediate in these reactions, therefore, this photolysis is a convenient method for synthesis of novel titanocene derivatives.

PART ONE

PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE BETWEEN
BIS(CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDE AND ITS ANALOG SYSTEMS

PART TWO

PHOTOCHEMICAL REACTIONS OF
BIS(CYCLOPENTADIENYL)DIPHENYL TITANIUM(IV)

By

Mien Hsiao Peng

A THESIS

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

MASTER OF SCIENCE

Department of Chemistry

1976

DEDICATION

To My Parents and My Husband

ACKNOWLEDGMENT

The author wishes to express her sincere appreciation to Professor Carl H. Brubaker for his guidance and encouragement throughout the course of this study.

She would like to express her gratitude to Michigan State University for granting her teaching and research assistantships.

TABLE OF CONTENTS

PART ONE

PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE BETWEEN BIS(CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDE AND ITS ANALOG SYSTEMS

	Page
INTRODUCTION	2
EXPERIMENTAL	4
A. General Technique	4
B. Preparation of Compounds	4
C. Exchange Experiments	5
Photolytic Cyclopentadienyl Ligand Exchange between Zirconocene Dichloride and (D-10)-zirconocene Dichlo- ride	5
Photolytic Cyclopentadienyl Ligand Exchange between Zirconocene Dichloride and Bis(methylcyclopentadienyl)- zirconium Dichloride	8
D. Chemical Actinometry	8
Photolysis of Actinometer Solution	8
Light Intensity Determination	9
Quantum Yield Determination	10
RESULTS AND DISCUSSION	14
A. General Observation	14
B. Light Intensity Determination	14
C. Calculation of Exchange Results	17
D. Possible Mechanism	21

TABLE OF CONTENTS (Cont.)

PART TWO

PHOTOCHEMICAL REACTIONS OF BIS(CYCLOPENTADIENYL)DIPHENYL TITANIUM(IV)

	Page
INTRODUCTION	24
EXPERIMENTAL	28
A. Materials and General Technique	28
B. Photolysis of Cp_2TiPh_2 in Various Organic Solvents .	29
1. Photolysis in Benzene	29
2. Photolysis in Benzene- d_6	29
3. Photolysis in Diethyl Ether	29
4. Photolysis in Carbon Tetrachloride	29
C. Low Temperature Photolysis of Cp_2TiPh_2 in the absence of Substrates	30
D. Low Temperature Photolysis of Cp_2TiPh_2 in the presence of Substrates	30
1. Photolysis in the presence of Carbon Monoxide . .	30
2. Photolysis in the presence of Diphenylacetylene .	31
3. Photolysis in the presence of Carbon Dioxide . .	31
RESULTS AND DISCUSSION	33
General Theorey	33
The Esr Spectrum Detection	35
The Photoreaction of Cp_2TiPh_2	48
Possible Mechanism	49
BIBLIORGRAPHY	52

LIST OF TABLES

TABLE	Page
1. Light Intensity Determination	16
2. Mass Spectrographic Data for the Zirconocene Dichloride /(D-10)-zirconocene Dichloride Ligand Exchange	17

LIST OF FIGURES

FIGURE	Page
1. Infrared Spectra (a) (D-10)Cp ₂ ZrCl ₂ and (b) Cp ₂ ZrCl ₂ . . .	6
2. Proton nmr Spectra of (a) Cp ₂ ZrCl ₂ and (b) (D-10)Cp ₂ ZrCl ₂ . . .	7
3. Mass Spectrum of Cp ₂ ZrCl ₂	11
4. Mass Spectrum of (D-10)Cp ₂ ZrCl ₂	12
5. UV and Visible Spectra of (a) Cp ₂ ZrCl ₂ /(D-10)Cp ₂ ZrCl ₂ and (b) Cp ₂ ZrCl ₂ /(MeCp) ₂ ZrCl ₂ in Benzene Solution	15
6. Photoconversion of Valerophenone in Benzene	16
7. Mass Spectra of Exchange Mixtures	18
8. McKay Plot for Cp ₂ ZrCl ₂ /(D-10)Cp ₂ ZrCl ₂ Exchange	20
9. Infrared Spectrum of [Cp ₂ TiH] _x	34
10. Esr Spectrum of Cp ₂ TiPh ₂ for 18 min Irradiation in THF at -60°	36
11. Esr Spectrum of Cp ₂ TiPh ₂ for 55 min Irradiation in THF at -60°	37
12. Esr Spectrum of Cp ₂ TiPh ₂ for 55 min Irradiation in THF at -60° and 3 min at -40°	38
13. Esr Spectrum of Cp ₂ TiPh ₂ for 55 min Irradiation in THF at -60° and 5 min at -20°	39
14. Esr Spectrum of Cp ₂ TiPh ₂ for 55 min Irradiation in THF at -60° and 2 min at 0°	40
15. Esr Spectrum of Cp ₂ TiPh ₂ for 55 min Irradiation in THF at -60° then allowed to warm to room temperature	41

LIST OF FIGURES (Cont.)

FIGURE	Page
16. Esr Spectrum of Cp_2TiPh_2 for 10 min Irradiation in THF at room temperature and then 30 min at -60°	43
17. Esr Spectrum of Cp_2TiPh_2 for 8 min Irradiation in THF at room temperature	44
18. Esr Spectrum of Cp_2TiPh_2 for 18 min Irradiation in THF at room temperature	45
19. Esr Spectrum of Cp_2TiPh_2 for 27 min Irradiation in THF at room temperature	46
20. Esr Spectrum of Cp_2TiPh_2 for 50 min Irradiation in THF at room temperature	47
21. Photoreactions of Cp_2TiPh_2	49

PART ONE

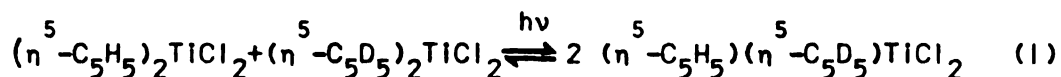
**PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE
BETWEEN BIS(CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDE
AND ITS ANALOG SYSTEM**

PART ONE

INTRODUCTION

The photochemistry of titanocene derivatives has recently received considerable attention. Harrigan, et al.¹ found that the irradiation of cyclopentadienyl derivatives of titanium(IV) in solvents containing halogen atoms leads to photolysis and abstraction of halogen. The photochemical reactions of dimethyl derivatives of titanocene, zirconocene, hafnocene were studied by Ald and Rausch.²

Vitz and Brubaker³ reported the first exchange of π -bonded cyclopentadienyl ligands between identical titanium metal complexes. Irradiation of benzene solutions in both (D-10)-titanocene dichloride and titanocene dichloride (d^0 system) with 313, 360, 400, and 520 nm light produce the exchange of the cyclopentadienyl ligand according to the following reaction :



with quantum yields of 0.02, 0.005, 0.01, and 0.007 mol/Ei, respectively. The equilibrium constant of equation (1) is calculated as 4.^{3,4} Photodecomposition of titanocene dichloride is negligible even at longer photolysis times.

The more remarkable findings on the ligand exchange systems with d^1 metal ions involve bis(methylcyclopentadienyl)vanadium dichloride/bis(cyclopentadienyl)vanadium dichloride and titanocene monochloride/

titanocene- d_{10} monochloride.⁵ These systems demonstrate : (1) the effect of the single d electron (absent in titanocene dichloride) and (2) the effect of involving the halogen ligands in bridging (in titanocene monochloride dimer). The low exchange rates reflect the importance of photodecomposition. The presence of the methyl group decreases the rate of ligand exchange.

Since the initial studies in the photoexchange of $C_5H_5^-$ ligands have been undertaken with titanium compounds, it should be extended to the zirconium system. Therefore, this system was selected as my research problem for part one. The purpose of the preceeding section was to present a survey of the photolytic cyclopentadienyl ligand exchange between zirconium systems.

EXPERIMENTAL

A. General Technique

All preparations were carried out under dry argon or in a vacuum and all solvents were refluxed continuously with the appropriate drying agent under argon and distilled prior to use.⁶ It was found that benzene with no impurities detectable by flame ionization glc was obtained by irradiating reagent grade benzene thirty minutes in the presence of chlorine. The solution was washed with distilled water and sodium carbonate solution. The by-products of the process were easily removed by distillation. This procedure offers a very economical source of benzene that is free of toluene, aliphatic, and olefinic impurities.

Infrared spectra were measured by means of a Perkin Elmer 457 and 237B grating spectrophotometer in nujol; visible and ultraviolet light absorption spectra were obtained on benzene solutions in a 10 mm cell by use of a Unicam SP-800 spectrophotometer. Mass spectra were recorded on a Hitachi Perkin Elmer RMU-6 mass spectrometer. Proton nmr spectra were measured at 60 MHz and 100 MHz in deuteriochloroform with Varian A56/60D and HA-100 spectrometers.

B. Preparation of Compounds

Bis(η^5 -cyclopentadienyl)zirconium dichloride was purchased from Arapahoe Chemical Company and sublimed at 150-180⁰. This material was stored in the dark.

Bis(η^5 -methylcyclopentadienyl)zirconium dichloride was prepared

according to Reynolds and Wilkinson⁷ with a modification. After crystallization from hot toluene (saturated with hydrogen chloride), the colorless material was purified by sublimation at 110-130⁰.

Cyclopentadiene-d₆ : Monomer C₅H₆, KOH, and D₂O-dioxane co-solvent were vigorously stirred for 3 hours. There were always two layers.⁸ The C₅H_xD_{6-x} was then distilled directly through a 10 cm Vigreux column. The procedure was repeated five times. The percent deuteration was obtained by integrating the proton nmr spectrum of C₅H_xD_{6-x} relative to that of pure C₅H₆. The C₅D₆ was dried with Linde 3A and 4A molecular sieves.

(D-10)-zirconocene dichloride was prepared from zirconium tetrachloride and sodium cyclopentadienide-d₅ in tetrahydrofuran. The yield was about 40% on zirconium tetrachloride, m.p. 246-248⁰. The deuterium content of the product obtained was evaluated by proton nmr measurement, Figure 1, and from the intensity decrease of C-H vibrations in ir spectrum, Figure 2.

C. Exchange Experiments

Photolytic Cyclopentadienyl Ligand Exchange between Zirconocene Dichloride and (D-10)-zirconocene dichloride

Weighed amounts of zirconocene dichloride and (D-10)-zirconocene dichloride were stirred with benzene in 50 ml volumetric flasks in the glove box under argon. Then the solutions were mixed thoroughly and diluted to 200 ml which gave 7.46×10^{-3} M in zirconocene dichloride and 8.46×10^{-3} M in (D-10)-zirconocene dichloride. After mixing, the sighting area was covered with Al-foil. Four-milliliter aliquots were added into the 13 x 100 mm pyrex culture tubes by a syringe to make

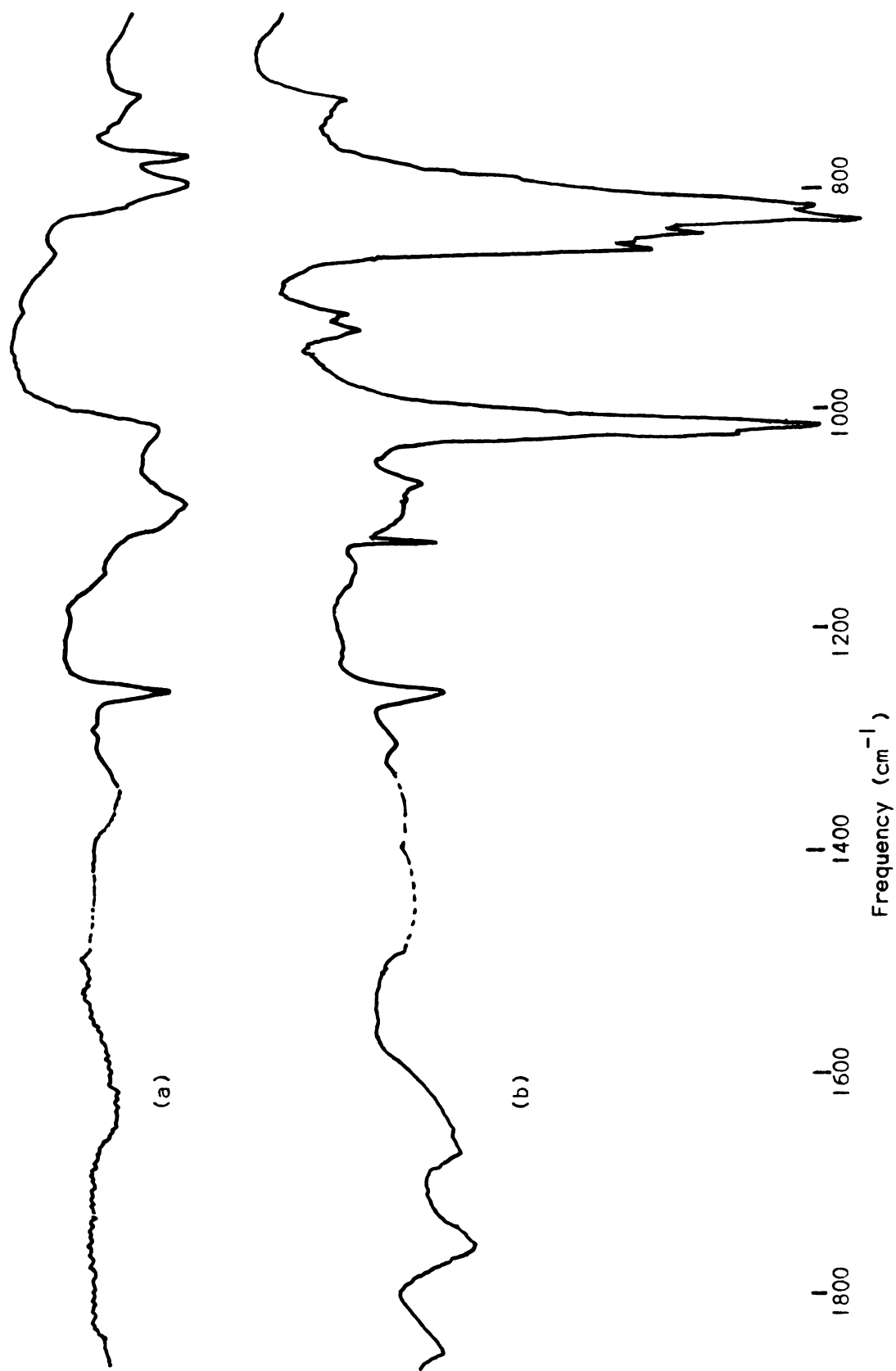


Figure 1. IR Spectra of (a) (D-10) Cp_2ZrCl_2 and (b) Cp_2ZrCl_2

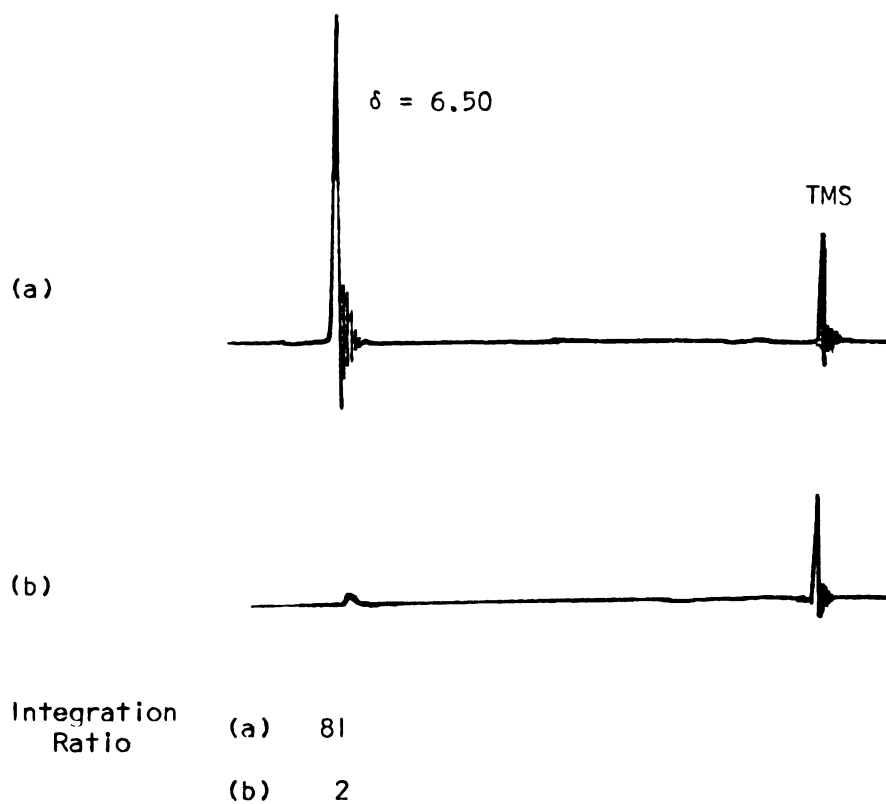


Figure 2. Proton nmr Spectra of (a) Cp_2ZrCl_2
and (b) $(\text{D-10})\text{Cp}_2\text{ZrCl}_2$

about 45 samples. The tubes were securely stopped under argon and sealed with an oxypropane torch. Twenty-four exchange samples and six actinometers were mounted in the merry-go-round photolysis apparatus in which a medium-pressure mercury lamp centered with 313 nm light filter solution. The temperature of photolysis was kept at 23⁰. The equipment has been described previously.^{9,10} After measured periods of irradiation, four samples and one actinometer were withdrawn. The samples were pooled, evaporated to dryness, and sublimed at 110-120⁰ before analyzing by mass and uv spectrometry. The actinometer was analyzed by gas chromatography.

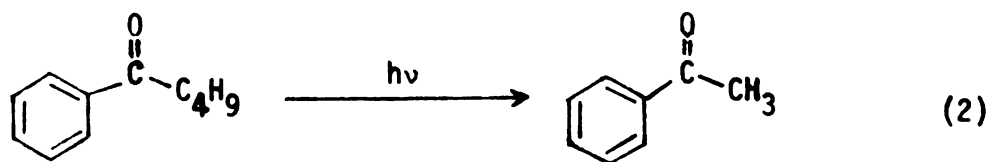
Photolytic Cyclopentadienyl Ligand Exchange between Zirconocene Dichloride and Bis(methylcyclopentadienyl)zirconium dichloride

The procedure was the same as described as above. It was given a mixture of 7.40×10^{-3} M in zirconocene dichloride and 7.43×10^{-3} M in bis(methylcyclopentadienyl)zirconium dichloride.

D. Chemical Actinometry

Photolysis of Actinometer Solution

The valerophenone actinometer¹¹ was used to determine the lamp intensity because it absorbs strongly at 313 nm ($\epsilon = 50$ l/mol-cm). A 0.225 M solution of valerophenone was prepared with 0.011 M tetradecane in benzene. The quantum yield for the conversion :



is 0.33 mol/Ei. Actinometer solutions were photolyzed under essentially the same conditions as the exchange solutions. In order to prevent excessive photoreaction, one can either dilute the solution or shorten the irradiation time. The total conversion of valerophenone was kept to less than 25%.

Light Intensity Determination

The actual light intensity from a source is usually measured by means of actinometry. It is more convenient, efficient and reproducible. After photolysis, the actinometer solution (0.2 μ l) was injected into the column of a Varian Aerograph Series 1200 gas chromatograph with a flame detector. The column material was 10% QF 1, 1% carbowax 20 M on chromosorb G 60/80, 3.2 ft x 0.1 in, and maintained at 130⁰. An inf- ortronic CRS 208 Automatic Digital Integrator was used to determine the peak area ratio of the acetophenone to the tetradecane peaks. The number moles of photons absorbed can be calculated by the following equation :

$$\frac{I_{\text{acetophenone}}}{I_{\text{tetradecane}}} \times 2.0 \times [\text{tetradecane}] \times V = 0.33 n \text{ (Ei)} \quad (3)$$

where $I_{\text{acetophenone}}$ = the peak area integral for the acetophenone peak

$I_{\text{tetradecane}}$ = the peak area integral for the tetradecane peak

2.0 = an empirical correction factor depending on the column material

$[\text{tetradecane}]$ = the concentration of tetradecane in the actinometer

V = the actinometer sample volume (0.2 μ l)

and 0.33 = the quantum yield for the formation of acetophenone

The light intensity was expressed in einstein/liter-hour.

Quantum Yield Determination

The quantum yield for ligand exchange process was determined by applying the approach of McKay analysis¹² on the mass spectrographic data. It was calculated from the exchange rate and the light intensity.

The mass spectrum of zirconocene dichloride has been measured^{13,14} with a parent ion peak at $m/e = 290$, Figure 3. The breakdown pattern proceeds via the preferential removal and fragmentation of the cyclopentadienyl ligands. This was thought to be indicative of the probable greater bond strength and higher ionic character of the chlorine-zirconium bond. The perdeutero-compound exhibits analogous trends in the mass spectrum, Figure 4, with parent ion peak at $m/e = 300$.

Zirconium has four major isotopes, ^{90}Zr (51%), ^{91}Zr (11%), ^{92}Zr (17%), ^{94}Zr (17%), while chlorine has two isotopes, ^{35}Cl (75%) and ^{37}Cl (25%). Consequently the mass peaks for a given chemical structure occur in groups characteristic of the isotope distribution of Zr and Cl atoms which they contain the variations in C, H, and D isotopes being negligible when compared to those of Zr and Cl. This enables the proposed structures to be confirmed both by observed mass and isotopic pattern. The peak at $m/e = 295$ is non-zero but small (generally about 8 % of the peak at $m/e = 290$). Photolyzed samples show increased intensity of the peak at $m/e = 295$, which corresponds to $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{D}_5)\text{ZrCl}_2^+$. The ratio of the peaks at $m/e = 295$ and 290 for various periods irradiation reflects the extent of exchange.

The logarithmic form of the McKay equation¹⁵, as applied to the exchange system, is as follows :

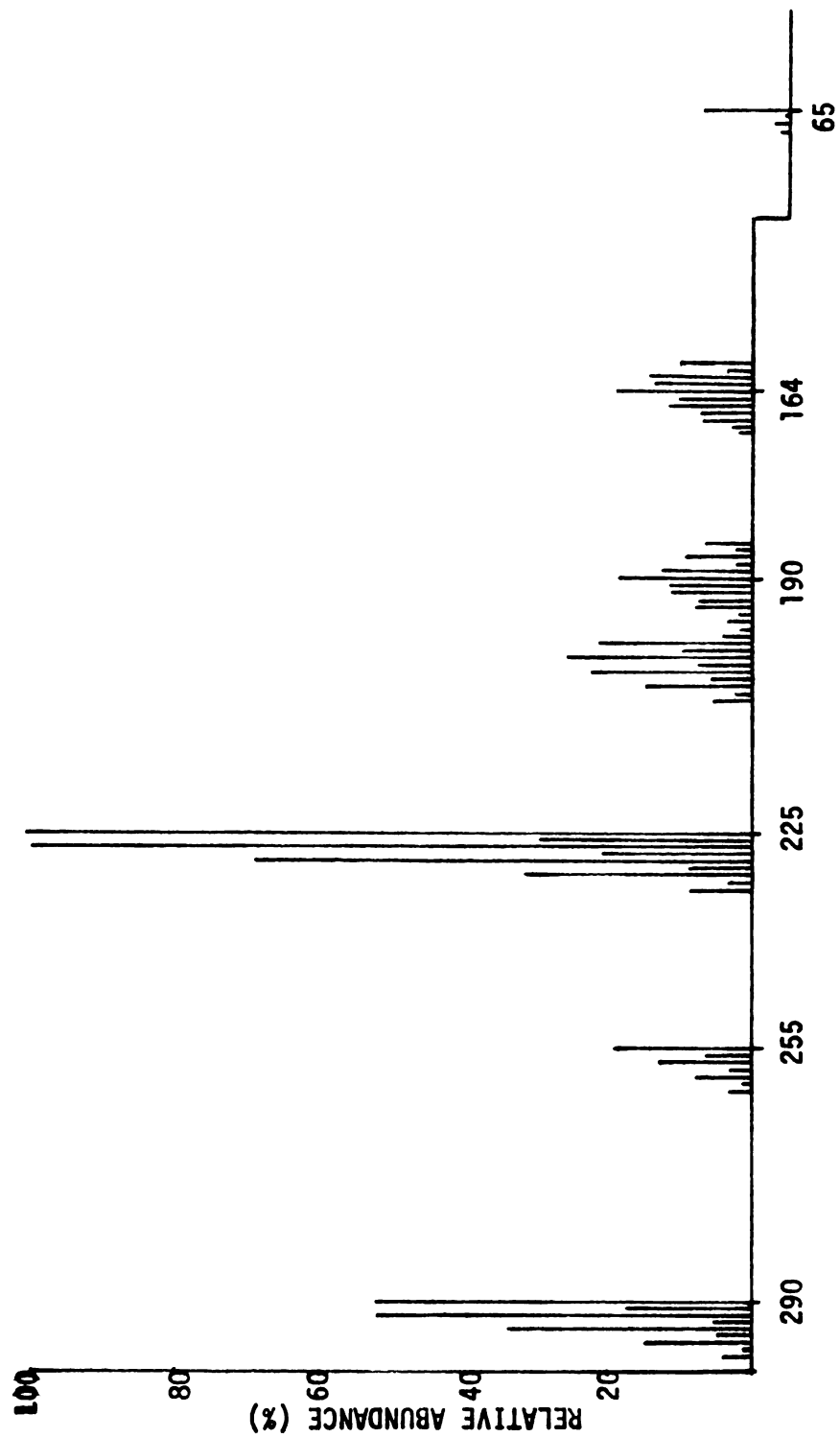


Figure 3. Mass Spectrum of Zirconocene Dichloride

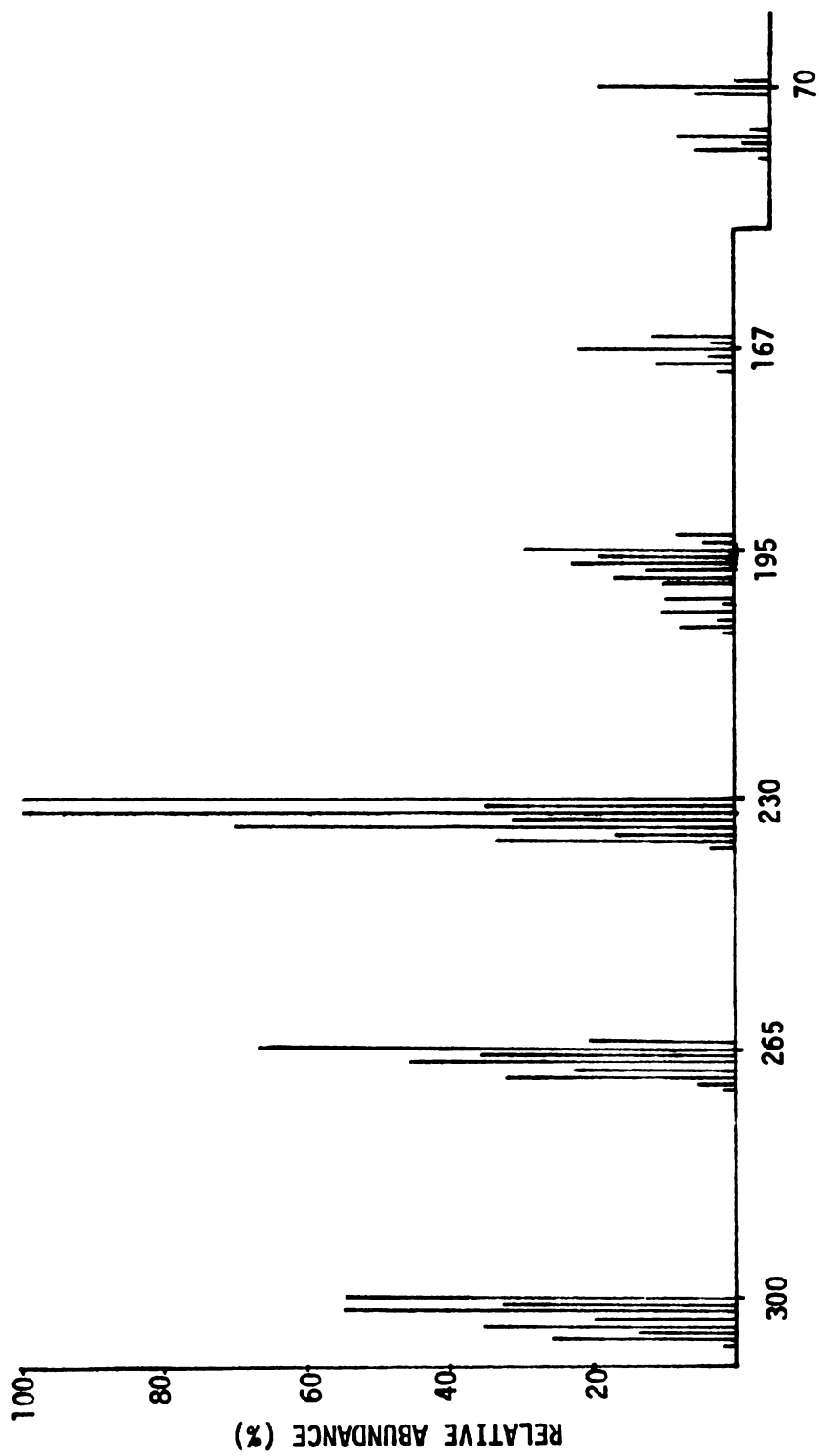


Figure 4. Mass Spectrum of (D-10)Zirconocene Dichloride

$$\ln(1-F) = - R \frac{[\text{reactant A}] + [\text{reactant B}]}{[\text{reactant A}][\text{reactant B}]} t \quad (4)$$

where R is the exchange rate and the bracketed quantities are the concentrations of A and B species. F represents the fraction of exchange in time t to exchange at equilibrium ($t = \infty$) :

$$F = \frac{(I_{295/290})_t}{(I_{295/290})_{\infty}} \quad (5)$$

where $I_{295/290}$ is the ratio of the peaks at $m/e = 295$ and 290.

The quantum yield, computed directly from the experimentally observed exchange rate R and corresponding absorbed intensity I, can be generally expressed as¹⁶ :

$$\phi = \frac{R \text{ (mol/l-hr)}}{I \text{ (Ei/l-hr)}} \quad (6)$$

This analysis requires the intensity of the lamp to be constant with time. The most probable slope and intercept of $\ln(1-F)$ vs time can be calculated by a standard least squares method.¹⁷

RESULTS AND DISCUSSION

A. General Observation

The ultraviolet and visible absorption spectrum of the mixture of zirconocene dichloride and (D-10)-zirconocene dichloride (or methyl-derivative) in benzene solution showed only one strong absorption band at $\lambda = 295$ nm with a shoulder at 335 nm, Figure 5, which had the characteristic of compounds containing π -bonded cyclopentadienyl rings. No electronic transition bands due to the metal atoms were observed. The exchange reaction photochemically induced by visible light was inherently slow since there were no absorption bands above 370 nm. The monochromic light 313 nm was chosen in the overall irradiation process. The molar absorptivity for zirconocene dichloride mixture at 313 nm was $5 \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ for the solution of 10^{-4} M . The sample (10^{-2} M) absorbance at 313 nm, by using a 1 cm cell path length and all incident light absorbed, was about 50 which was similar to that of valerophenone actinometer solution.

B. Light Intensity Determination

$I_{\text{acetophenone}} / I_{\text{tetradecane}}$ vs photolysis time was a straight line, Figure 6, which established that the light intensity was constant over the photolysis period, Table 1. The light intensity as well as the number moles of photons was computed from the actinometric data in accordance with equation (3). The concentration of tetradecane was 0.0109 M and the photoconversion was kept under 25%. The average light intensity, calculated from the different degree of conversion of

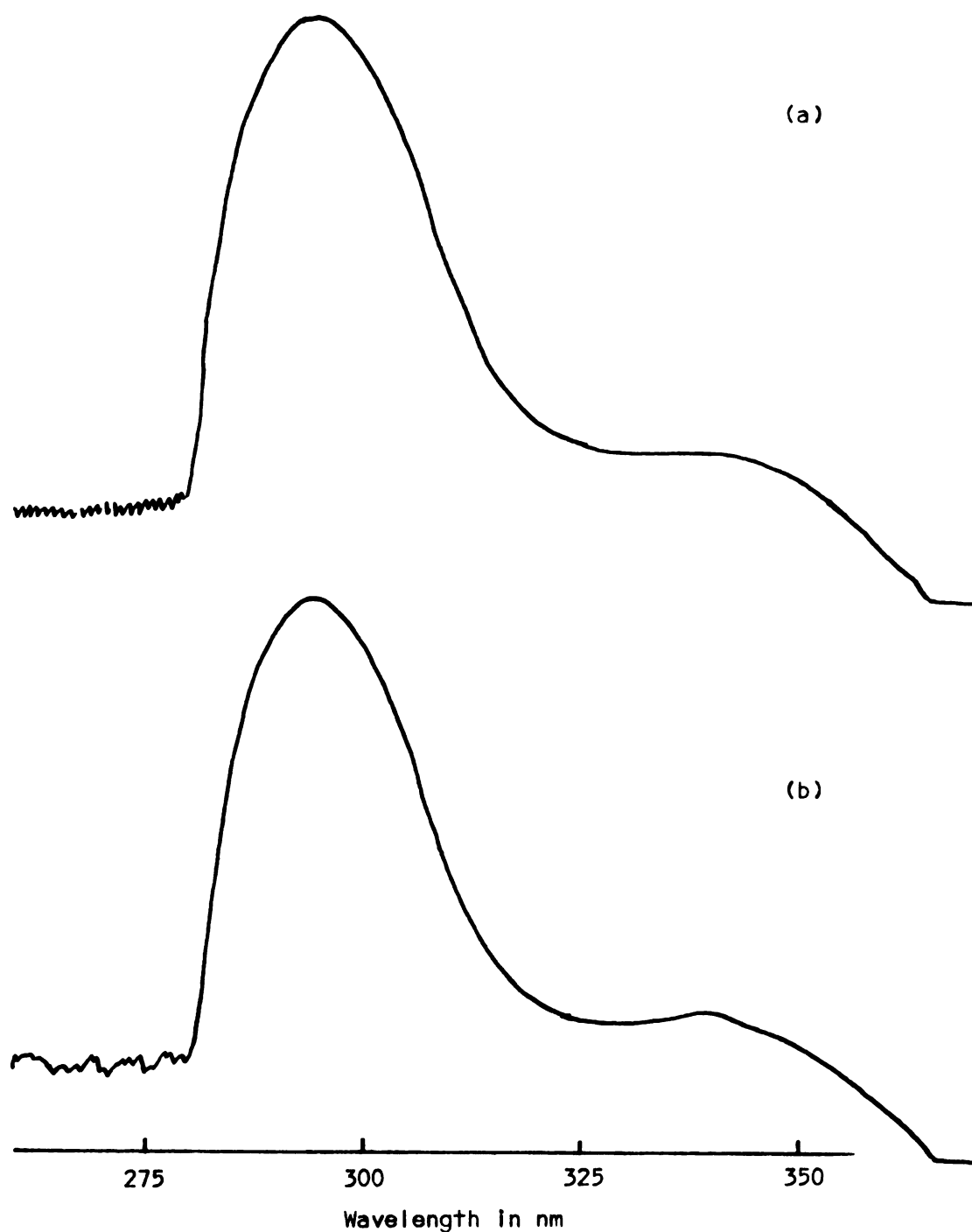


Figure 5. UV Spectra of (a) $\text{Cp}_2\text{ZrCl}_2/(\text{D-10})\text{Cp}_2\text{ZrCl}_2$ and
(b) $\text{Cp}_2\text{ZrCl}_2/(\text{MeCp})_2\text{ZrCl}_2$ in benzene solution.

Table 1. Light Intensity Determination

Time (hr)	$\frac{I_{\text{acetophenone}}}{I_{\text{tetradecane}}}$	$n \times 10^9$ (Ei)	Light Intensity $(Ei/l\text{-hr}) \times 10^3$
0	0	0	0
4	0.1393	1.845	2.31
8	0.2785	3.812	2.38
14	0.4257	5.624	

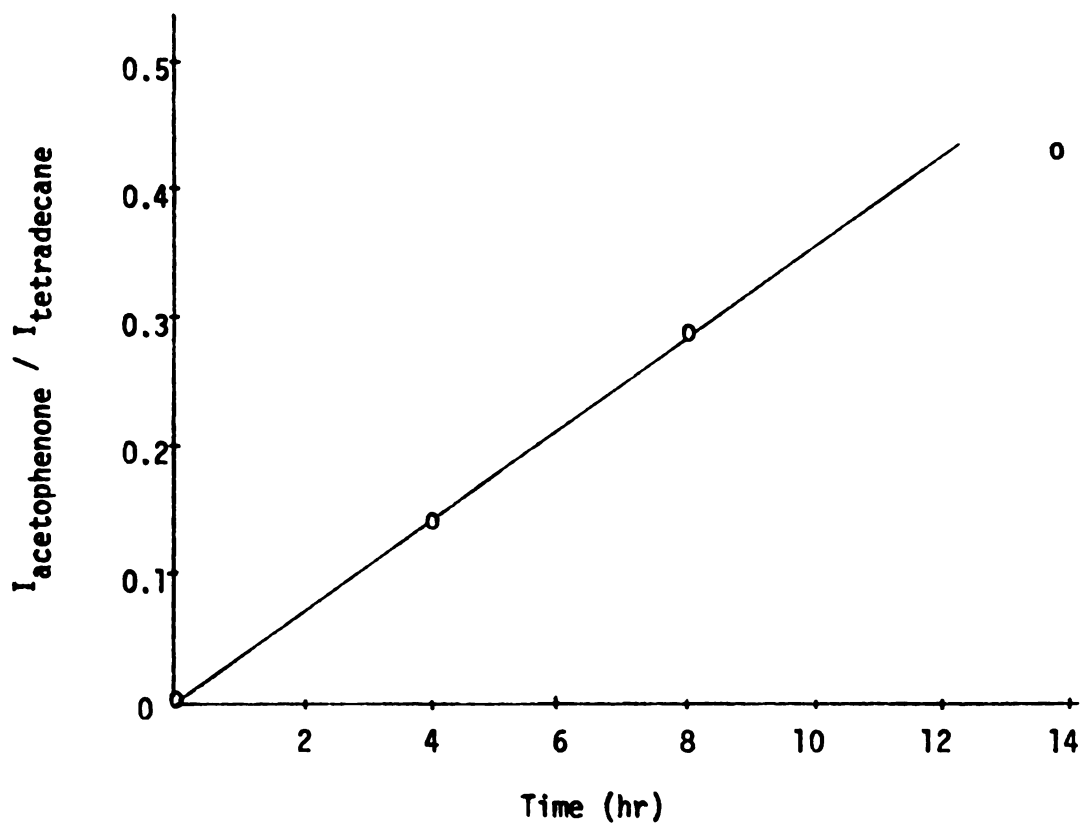


Figure 6. Photoconversion of Valerophenone in benzene

several actinometer samples, was 0.00235 Ei/ μ -hr.

C. Calculation of Exchange Results

A study of Table 2 indicated that zirconocene dichloride and (D-10)-zirconocene dichloride ligand exchange resulted in the increase of the peak at $m/e = 295$ (Figure 7) relative to those at 290 and 300.

Table 2. Mass Spectrographic Data for the Zirconocene Dichloride/(D-10)-zirconocene Dichloride Ligand Exchange

Time (hr)	$m/e=290$	Normalized Intensities						$I_{295/290}$	F
		295	300	65	66	70	71		
0	100	8	95	100	62	84	50	0.08	0.044
1	100	13	98	100	40	88	30	0.13	0.070
2	100	24	110	100	52	90	30	0.24	0.13
4	100	15	99	100	76	86	52	0.15	0.08
8	100	21	100	100	47	86	43	0.21	0.11
16	100	31	102	100	44	86	29	0.31	0.17
24	100	40	95	100	51	86	46	0.40	0.22
36	100	74	108	100	55	84	42	0.74	0.40
48	100	96	112	100	50	84	30	0.96	0.52
60	100	136	122	100	65	87	51	1.36	0.73
71	100	186	125	100	68	85	40	1.86	1.0
83	100	185	123	100	55	85	30	1.85	1.0

The peaks between $m/e = 60$ and 71 were included to demonstrate that

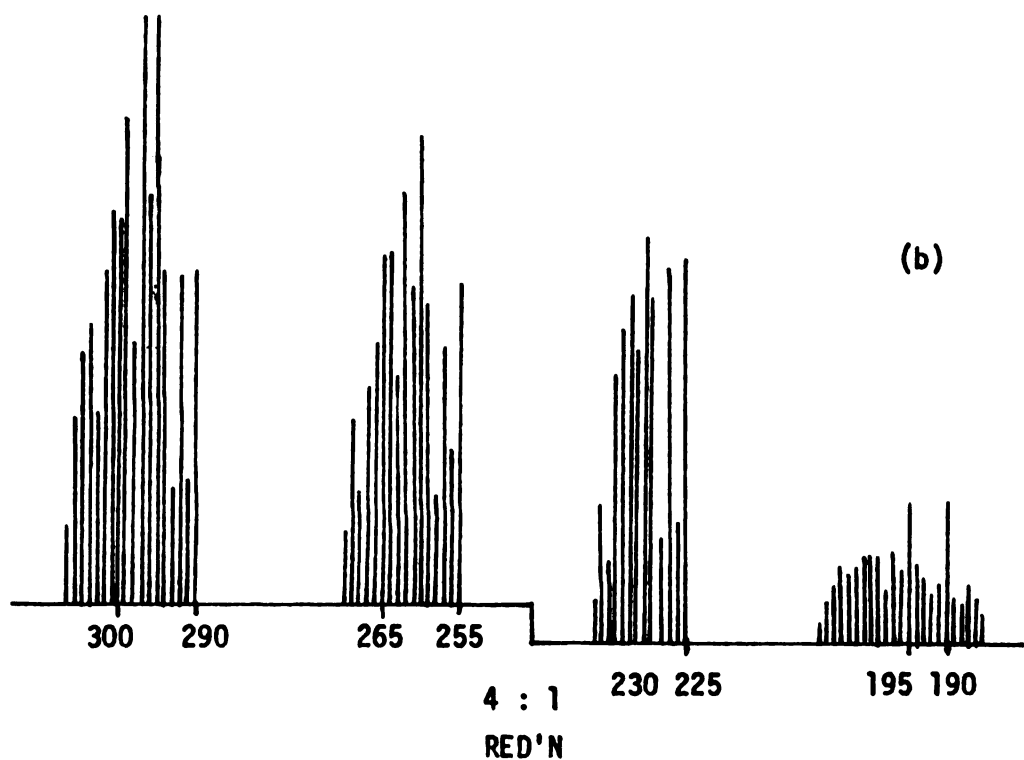
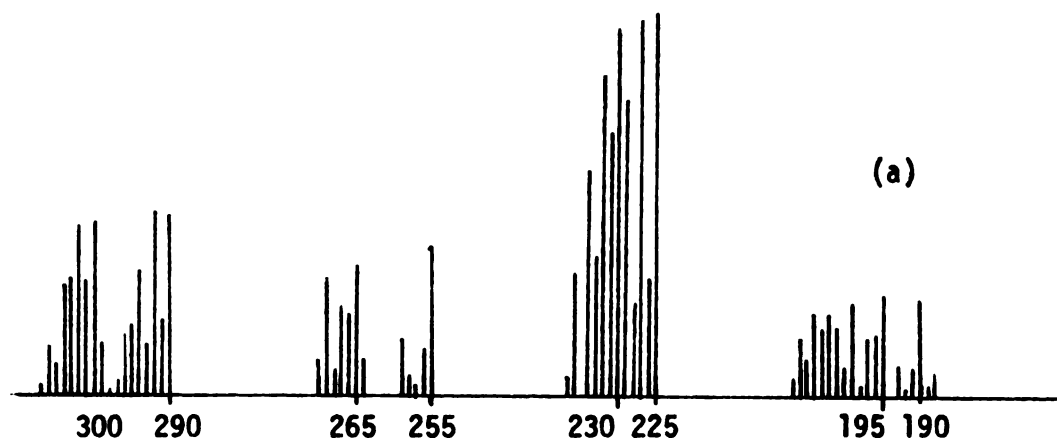
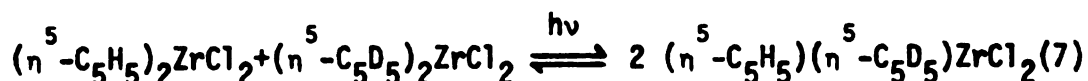


Figure 7. Mass Spectra of Exchange Mixtures
(a) at t_0 and (b) at t

ligand exchange, and not hydrogen exchange on the ligand, is the main process in the photolysis. The absence of thermal exchange was demonstrated by allowing a sample solution to reflux for 72 hours in the dark, and obtaining the mass spectrum of the zirconocene dichloride species. No peak corresponding to the (D-5) species appeared in the mass spectrum. The ratio of the intensities of the $m/e = 295$ and 290 peaks, $I_{295/290}$, was computed for each irradiation time.

The fractions of exchange, F , were calculated on the basis of equilibrium value of 1.86 for the ratio of the peaks at $m/e = 295$ and 290. The equilibrium value was determined by irradiating samples for up to 83 hours, a period that required to reach a constant peak intensity ratio. The plot of $\ln(1-F)$ vs photolysis time, Figure 8, had a slope of -0.013 and the intercept of $(1-F) = 1.04$, which were determined by a linear least squares treatment of the data. Writing the McKay equation in the term of (4), the slope would be equal to $-R\{[\text{reactant A}] + [\text{reactant B}]/[\text{reactant A}][\text{reactant B}]\}$ and the exchange rate, R , was computed as 5.2×10^{-5} M/hr. The quantum yield calculated by using equation (6), dividing the exchange rate by the light intensity, was 0.021 mol/Ei.

The equilibrium constant for the reaction :



calculated from the intensities of the exchange peaks in the mass spectrum at t_{∞} was $K = (I_{295})^2 / (I_{290})(I_{300}) = 2.8$.

The photolytic cyclopentadienyl ligand exchange between zirconocene dichloride and bis(methylcyclopentadienyl)zirconium dichloride

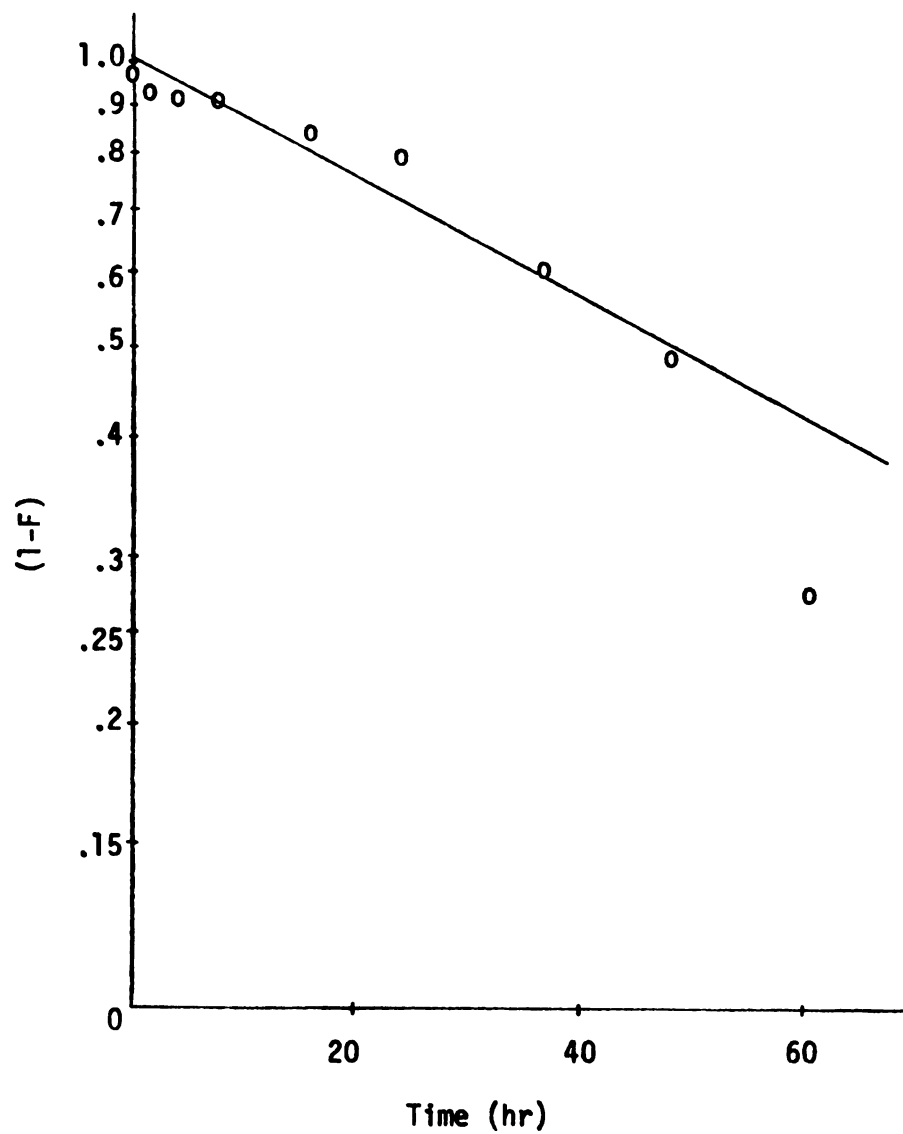
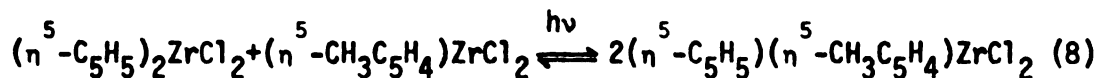


Figure 8. McKay Plot for $\text{Cp}_2\text{ZrCl}_2/(\text{D-10})\text{Cp}_2\text{ZrCl}_2$ Exchange

was observed by the increasing intensity of the peak at $m/e = 304$ which corresponds to $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{ZrCl}_2^{+\cdot}$:



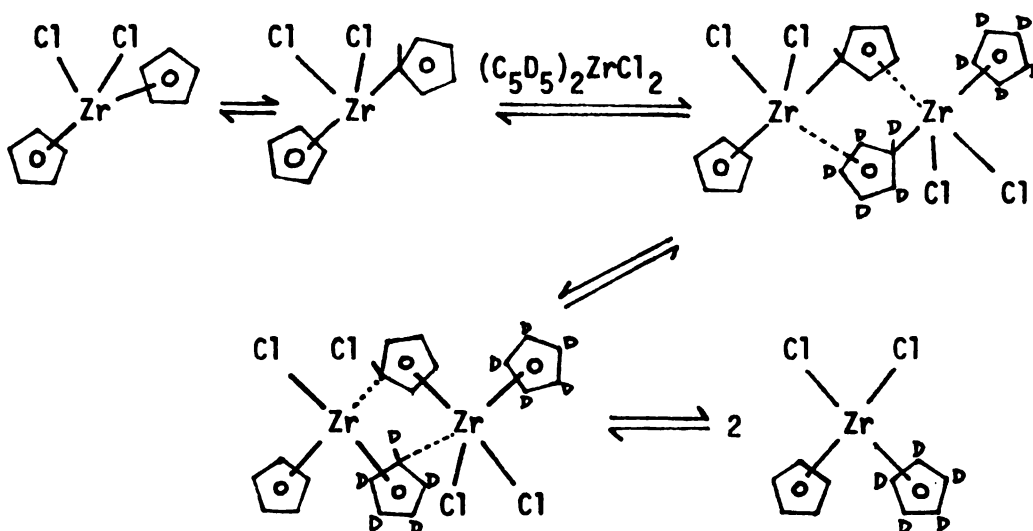
The constant for approach to equilibrium for the reaction (8) was measured as 2.3. These low figures for both systems might reflect the side reaction with impurities or the simple photodecomposition at the longer photolysis times. The exchange rate for equation (8) was estimated as 4×10^{-5} M/hr. The presence of methyl group might decrease the rate of ligand exchange as compared with the zirconocene dichloride/(D-10)-zirconocene dichloride system.

An attempt was made to investigate the photoexchange mechanism by following the proton nmr spectra for each irradiation sample. Only slight broadening of the signal of the ten equivalent hydrogen in zirconium system was observed.

D. Possible Mechanism

A possible mechanism is proposed for the photoexchange of the cyclopentadienyl ligand on titanocene dichloride on the basis of fundamental group theoretical and chemical considerations.⁹

It is reasonable to propose that the reduction in bond order from π -bonded to a lower coordination number as the first step in the zirconocene dichloride/(D-10)-zirconocene dichloride ligand exchange reaction :



The attack of the entering group is thus allowed, following by the possible rearrangement of σ -ligand to π -bonded to give the exchanged species. These are known for the thermal processes on some titanocene species.^{18,19}

It must be noted that this sort of mechanism is uncertain in the photolysis experiments. Further work is required for this mechanism study.

PART TWO

**PHOTOCHEMICAL REACTIONS OF
BIS(CYCLOPENTADIENYL)DIPHENYL TITANIUM(IV)**

PART TWO

INTRODUCTION

The origin of organo-transition metal chemistry can be traced to the discovery of ferrocene in 1951.²⁰ Similar "sandwich" compounds have been obtained for some of the metals in the d-transition block of the periodic table. Bis- η^5 -cyclopentadienyl complexes of vanadium, chromium, manganese, iron, cobalt, and nickel are fairly stable and can be easily prepared by standard methods of organometallic synthesis.^{21,22} However, bis(η^5 -cyclopentadienyl)titanium(II) appeared to have eluded all attempts of its isolation. The initial preparation of titanocene was done by Fischer and Wilkinson²³ in 1955. Magnesium²⁴ or sodium²⁵ had been reported to reduce titanium(IV) to titanium(II). Electrochemical reduction of titanocene dichloride destroyed the titanium to chloride bonds, leaving the titanium to cyclopentadienyl bonds intact.²⁶⁻⁸ Thermal degradation of alkyl²⁹ or aryl^{30,31} derivatives or, in some cases, their reaction with hydrogen³²⁻³⁴ will often give titanium(II) compounds.

The nature of titanocene varies with the methods of preparation; thus, the parent titanocene (η^5 -C₅H₅)₂Ti, the dimer, its rearrangement product [$(\eta^5$ -C₅H₅)(μ -C₅H₄)TiH]_x, the hydride [$(\eta^5$ -C₅H₅)₂TiH]_x (x ≥ 2), can all be formed. Several authors³⁵⁻³⁷ have assumed a ferrocene-type structure for titanocene and have attempted to calculate the electronic energy states for titanocene (and zirconocene) in order to account for their diamagnetism. It has been contended that the high reactivity

and, hence, instability of the monomeric $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}$ species lies in its carbenoid-type behavior.^{38,39} A number of characteristic reactions of the highly reactive titanocene species have been observed by which these reaction intermediates can be identified even in those reaction systems in which their actual isolation is not feasible. Many reaction with $[\text{Cp}_2\text{TiH}]_x$, for instance, exhibit virtually all the characteristics of titanocene, which are summarized in Figure 9 :^{40,41}

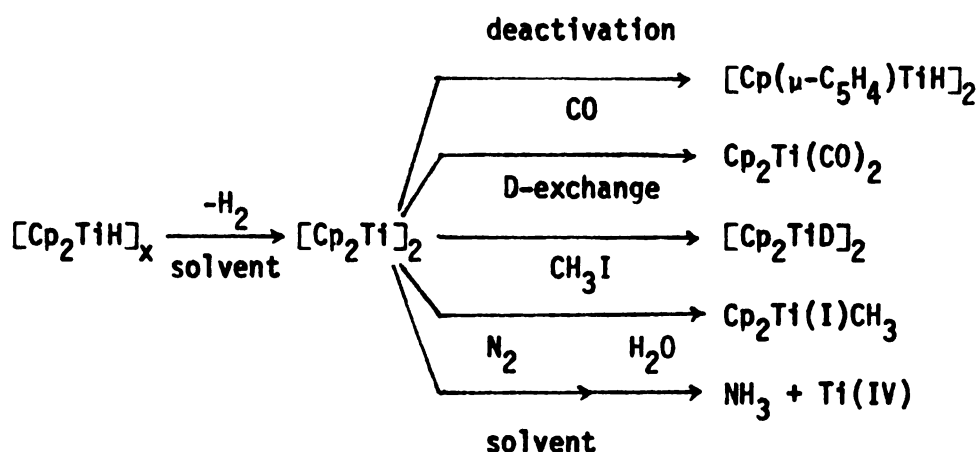


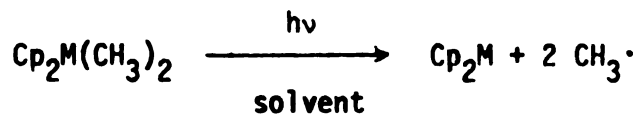
Figure 9. Reactions of $[\text{Cp}_2\text{TiH}]_x$ in which titanocene appeared to occur as an intermediate

presumably, titanocene $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(II)}$ is an intermediate in these reactions.

As early as 1915 Benrath⁴² observed the photoreduction of alcoholic solutions of titanium tetrachloride. Hunt and Winter⁴³ found that titanium halo alkoxides were eminently suitable for photoreduction to provide a very simple route to titanium(III) complexes.

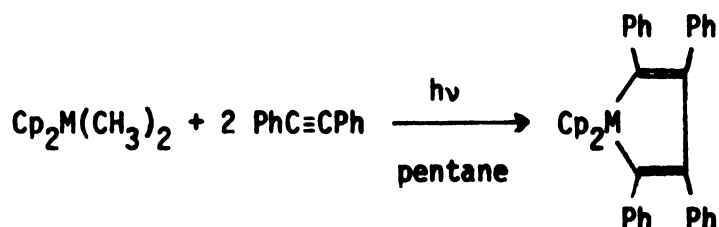
The dimethyl derivatives of titanocene, zirconocene, hafnocene decomposed readily on photolysis with homolytic cleavage of the methyl-

metal bond :²



where M = Ti, Zr, Hf

In pentane the methyl radicals appeared as CH_4 . All spectroscopic evidences indicated the presence of only π -bonded cyclopentadienyl rings in the diamagnetic pyrophoric residues. In the presence of diphenylacetylene, the metallocycles shown below were produced :



while carbon monoxide formed $\text{Cp}_2\text{Ti}(\text{CO})_2$ with the titanium residue. It is also able to form stable adducts with various substrates such as hydrogen, nitrogen, nitric oxide, hydrochloric acid, and olefins as well as acetylenes.

A photolysis of dialkyltitanocene compounds Cp_2TiR_2 ($\text{R} = \text{CH}_3, -\text{CH}_2\text{C}_6\text{H}_5$) in the presence of elemental sulfur produced titanocene pentasulfide Cp_2TiS_5 along with other organic polysulfides.⁴⁴

The photolysis of bis(fluorenyl)dimethyl zirconium in solution⁴⁵ leads to cleavage of the methyl groups, with formation of methane and a bis(fluorenyl)zirconium-type compound of possible polynuclear nature.

A similar investigation of the chemical behavior of titanocene was apply to bis(cyclopentadienyl)diphenyl titanium system. Convenient

ways to generate and isolate titanocene were sought from this complex as well as by means at low temperature. These reactions may have proved to be an elegant way to prepare new organometallic compounds of titanium.

EXPERIMENTAL

A. Materials and General Technique

Standard Schlenck-tube and high-vacuum techniques used for handling of the highly air-sensitive compounds involved in this work have been presented in detail elsewhere.^{46,47}

All spectra were recorded under similar conditions to those described in part one. The esr spectra were recorded by use of a Varian E-4 esr spectrometer and the instrument was calibrated with a pitch sample (diphenylpicrylhydrazyl in potassium chloride and peroxyamine disulfonate). A Hanovia 100 watt high pressure mercury arc lamp with focus and power supplies was used to provide a point source of uv light.

Reagent grade diethyl ether, tetrahydrofuran (THF), petroleum ether (b.p. 30-60°), benzene, toluene and hexane were refluxed continuously over appropriate drying agents and distilled immediately before use. Prepurified argon was further purified by passing it through an activated copper catalyst (BTS catalyst) and subsequently through Aquasorb (containing phosphorous pentoxide). Carbon monoxide was Matheson Prepurified grade. Diphenylacetylene was recrystallized from alcohol. Bis(cyclopentadienyl)diphenyl titanium was prepared by a modification of the published method.⁴⁸ After reaction of titanocene dichloride with two equivalents of phenyl lithium, the solvent was removed by vacuum; the residue was extracted with methylene dichloride and then diethyl ether and then recrystallized from diethyl ether. A yellow-orange crystal was obtained with 70% in yield.

B. Photolysis of Bis(cyclopentadienyl)diphenyl Titanium(IV) in various Organic Solvents at Room Temperature.

1. Photolysis in benzene

A solution of 165 mg (0.5 mmol) of Cp_2TiPh_2 in 50 ml of benzene was irradiated through pyrex glass filter under argon with a 450 watt Hanovia lamp at room temperature for 3 hr. The color of the solution was changed from yellow-orange to dark green. After the evaporation of solvent, biphenyl was sublimed for 24 hr. under vacuum at room temperature to give about 70% in yield. The dark green residue was identified to be the polymeric $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}]_x$ by comparison of its ir to that given by Brintzinger.⁴⁰

2. Photolysis in benzene-d₆

Dissolved 10 mg of Cp_2TiPh_2 in 1 ml of benzene-d₆. After 2 hr irradiation, the dark green mixture was passed through a silicar gel (60-200 mesh) column and eluted with hexane. The colorless crystal which recrystallized from ethanol was analyzed by mass spectrometry as biphenyl and biphenyl-d₅ in a ratio of 8 to 1.

3. Photolysis in diethyl ether or hexane

The reactions were carried out in the same manner as described as above. The biphenyl and polymeric $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}]_x$ were produced in major amounts.

4. Photolysis in carbon tetrachloride

About 90 mg of Cp_2TiPh_2 was dissolved in 10 ml carbon tetrachloride and irradiated for 2 hr. A dark red mixture was obtained. After removal the solvent, the dark red residue was sublimed at room temperature to give biphenyl and continuously at 130° to give titanocene dichloride which was identified by its color, m.p., and proton nmr spectrum.

C. Low Temperature Photolysis of Bis(cyclopentadienyl)diphenyl titanium in the absence of Substrates

About 600 mg (1.8 mmol) of freshly powdered Cp_2TiPh_2 was dissolved in 90 ml toluene or 180 ml diethyl ether under argon. The yellow-orange solution was immersed into an acetone-dry ice bath for cooling at least half hour before irradiation. After 2 hr of irradiation at -78° , a dark green solution was obtained. The volume of the solution was reduced to ca 20 ml by removing solvent in vacuo at $-70 \sim -30^\circ$. Twenty-five milliliters of hexane was added slowly into the slurry by a syringe at -78° . A grayish precipitate was filtered and washed twice with fresh cold hexane, then dried under vacuum. Yield ca 80%. Titanium analysis was performed by ignition to titanium oxide as : 26.62%, 28.08%, and 23.98%. Calculated Ti-% is 26.77% for $[\text{Cp}_2\text{TiH}]_x$.

D. Low Temperature Photolysis of Bis(cyclopentadienyl)diphenyl Titanium(IV) in the presence of Substrates

1. Photolysis in the presence of carbon monoxide

Cp_2TiPh_2 (600 mg, 1.8 mmol) was dissolved in 90 ml toluene at -78° . One atmosphere of carbon monoxide was introduced at this temp-

for at least half hour before irradiation. The solution was still kept as no color change. After 2 hr irradiation with carbon monoxide bubbling through, the solution was readily changed to dark green. Upon slowly warming the mixture to room temperature, the color changed to red-brown. The toluene was removed in vacuum leaving a dark red solid. The red residue was sublimed at 50-80° (0.1 mm Hg) to give a red crystal which was confirmed as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ by comparison of its ir spectrum to that given by Calderazzo et al..⁴⁹ Yield in 70%.

2. Photolysis in the presence of diphenylacetylene

About 1.1 g (6.2 mmol) of diphenylacetylene was added to the toluene solution of Cp_2TiPh_2 (3 mmol) under argon. The solution was cooled for at least half hour and irradiated at -78° for 2 hr.. A dark green solution was obtained. Upon removal of solvent, excess diphenylacetylene and biphenyl were removed by sublimation at 40° for 24 hr. The dark green residue was washed by 30 ml petroleum ether and recrystallized from n-hexane. Yield 1.2 g (ca. 75%) of green crystal which was confirmed to be $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$ by comparison of its nmr (in CCl_4), ir (in Nujol), uv (in THF), and mass spectra to those given by Sonogashira.⁵⁰

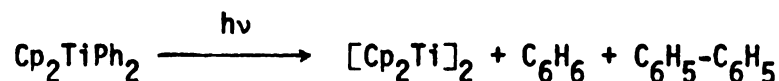
3. Photolysis in the presence of carbon dioxide

About 10^{-2} M solution of Cp_2TiPh_2 in toluene was irradiated with carbon dioxide bubbling through for 2 hr at -78°. A dark green solution was obtained. After dryness, the green residue was confirmed as $[\text{Cp}_2\text{TiH}]_x$ polymer by comparison of its ir spectrum to that given by Marvich.⁵¹ The carboxylation of the phenyl ring and to metallocyclo

formation was found at very low concentration.

RESULTS AND DISCUSSION

The photolysis of bis(cyclopentadienyl)diphenyl titanium in benzene solution produced the products such as biphenyl, benzene, and titanocene :



A free radical mechanism is likely since the radical coupling product biphenyl is formed in detectable amounts and the radical termination reactions like the abstraction of hydrogen from solvents of the other phenyl group to give the quantitative formation of benzene is detected. The presence of benzene is established by photolysis of Cp_2TiPh_2 in benzene- d_6 solution for different periods and the intensity of the peak of benzene protons in nmr spectrum is increased gradually and reaches a limiting value in 2 to 3 hr. The formation of biphenyl suggests that the reduction of Cp_2TiPh_2 might lead directly to $\text{Cp}_2\text{Ti(II)}$ or its dimer as a reaction intermediate. It is also likely that the photo-reduction follows some more complicated reaction pathways.

The isolation of $[\text{Cp}_2\text{TiH}]_x$ from the photoreduction of Cp_2TiPh_2 in various organic solvents is identified by its ir spectrum and titanium analysis.⁵¹ The ir spectrum, Figure 9, shows the lack of any observable splitting in the out-of-plane C-H bending mode at 800 cm^{-1} and the presence of an absorption at 1260 cm^{-1} instead of 1230 cm^{-1} , which has been attributed to the anti-symmetric vibration of TiH_2Ti ring in the so called "titanocene".⁵² Absorption characteristic for π -bonded cyclopentadienyl groups are found at about 3100 w, 1440 m, 1360 w,

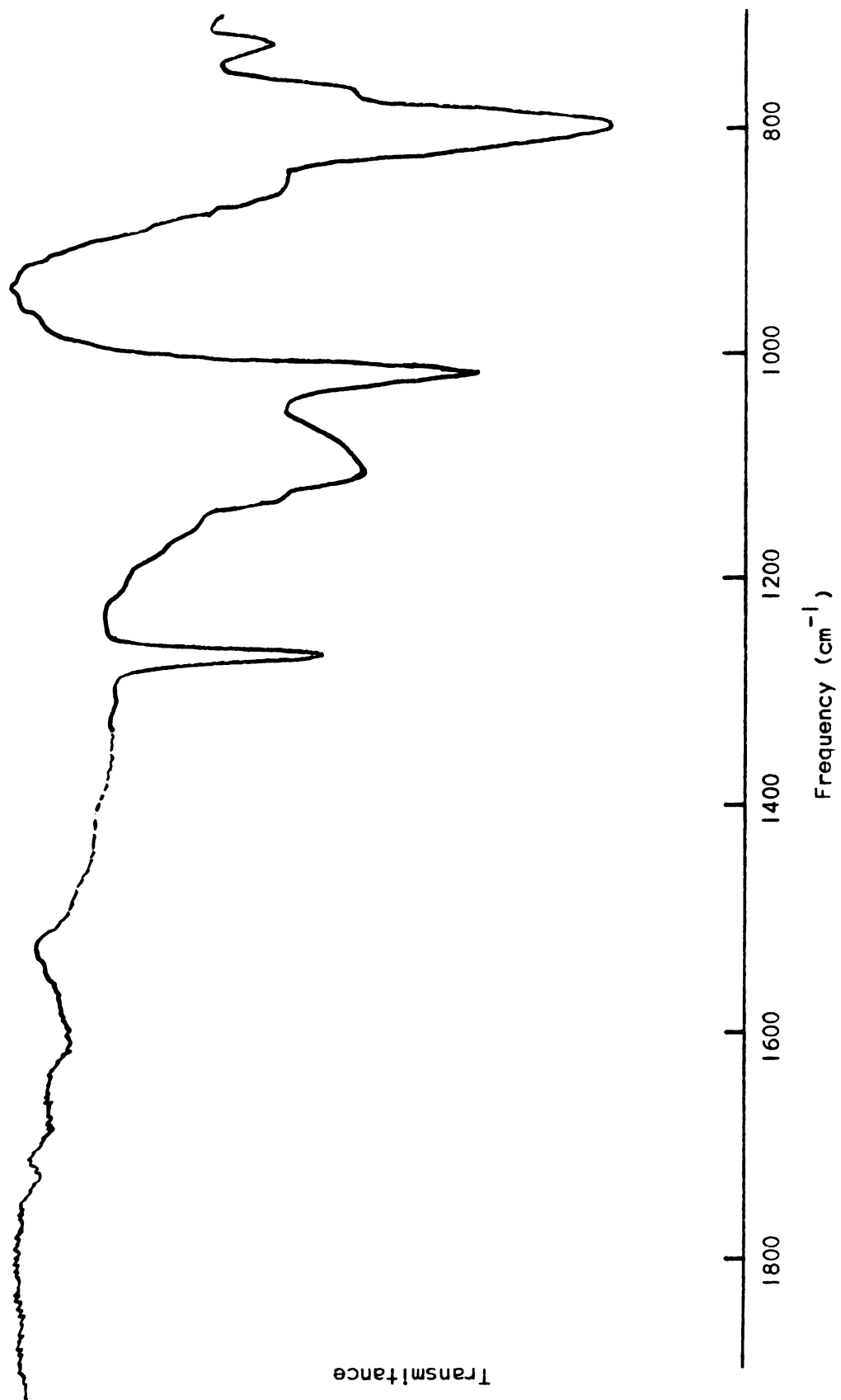


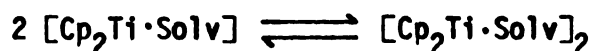
Figure 9. The IR Spectrum of $[\text{Cp}_2\text{TiH}]_x$ Polymer

1120 vw, 1010 s and 800 vs cm^{-1} .⁵³

Irradiation of Cp_2TiPh_2 in THF-d_8 at -78° leads to the broadening of the the proton nmr signal of the ten equivalent hydrogens in bis-(cyclopentadienyl)diphenyl titanium, indicating the generation of a diamagnetic species.

The esr method is applied to trace the course of the photoreduction of Cp_2TiPh_2 in THF solution at low temperature. A complex signal is observed at the field of about 3320 gauss for an initial period of 30 minutes irradiation at -60° , Figure 10. Through the intermediary stages, the esr spectrum of the solution consists of two signals,⁵⁴ the number of particles $[\text{Cp}_2\text{Ti}\cdot\text{Solv}]$ or $[\text{Cp}_2\text{Ti} \xrightarrow{\text{II}} \text{Cp}^-\text{Ti}^+\text{Cp}]$ are responsible for the appearance of the singlet at $g = 1.979$ changing with temperature. The singlet 2 with $g = 1.985$ probably relates to particles of the type $[\text{Cp}_2\text{Ti}\cdot\text{Solv}]_2$, which were described previously.⁵⁵ At temperature above -60° , the intensity of the one signal at high field is increased gradually as prolonged irradiation time, see Figures 12-14.

The similar appearance, Figure 15, is shown in the esr spectrum as that of Figure 11, which is allowed to warm to room temperature with the interruption of irradiation. The dependence of the intensity of the signal 1 on temperature shows that the disappearance of this signal is related to the process of dimerizing this complex :⁵⁴



Therefore, when the solution temperature is lowered, there is a dimerization of titanium reduction products.

When the sample solution irradiated at room temperature for 10



Figure 10. ESR Spectrum of Cp_2TiPh_2 for 18 min
Irradiation in THF at -60°

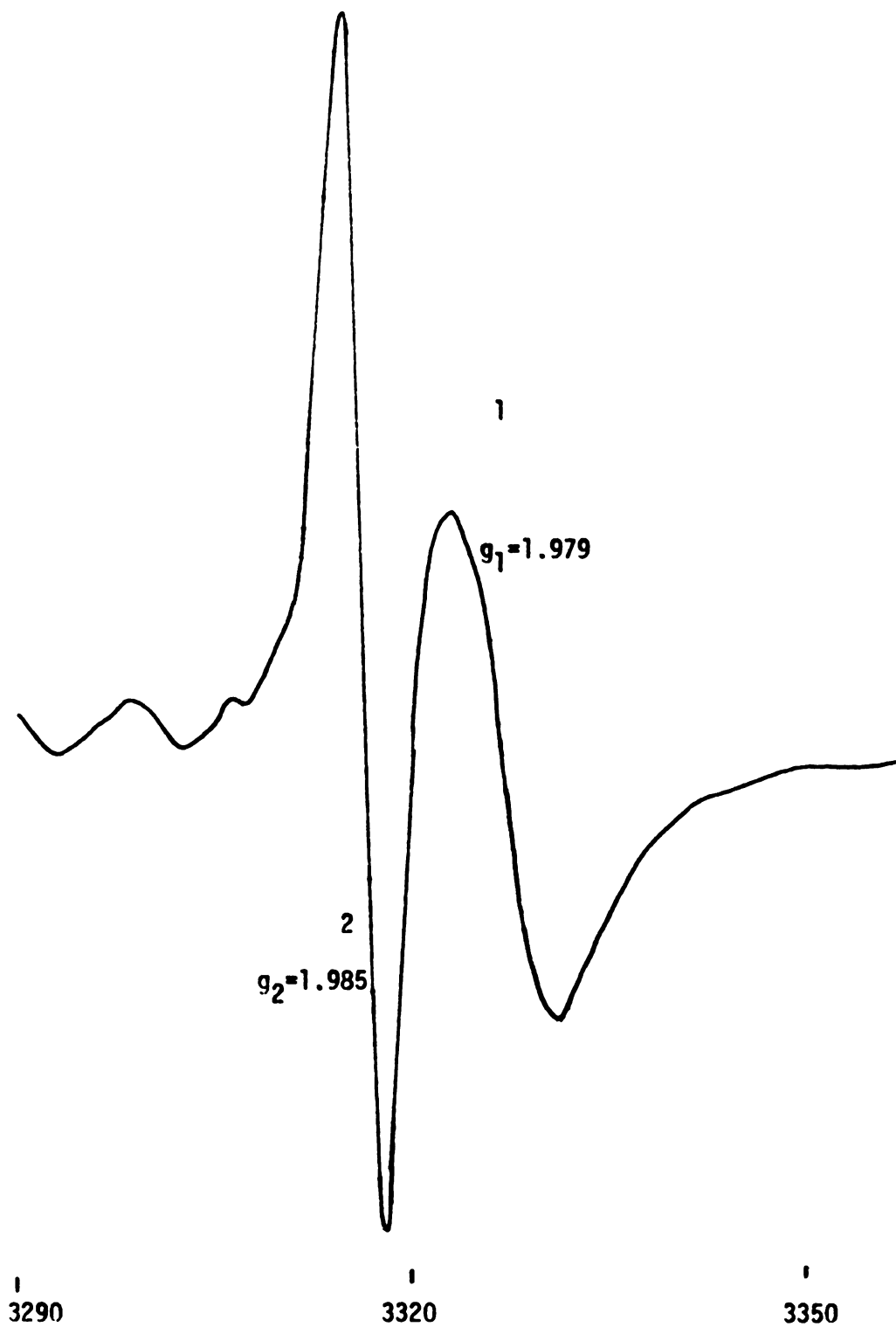


Figure 11. ESR Spectrum of Cp_2TiPh_2 for 55 min
Irradiation in THF at -60°



Figure 12. ESR Spectrum of Cp_2TiPh_2 for 55 min Irradiation in THF at -60° and 3 min at -40°

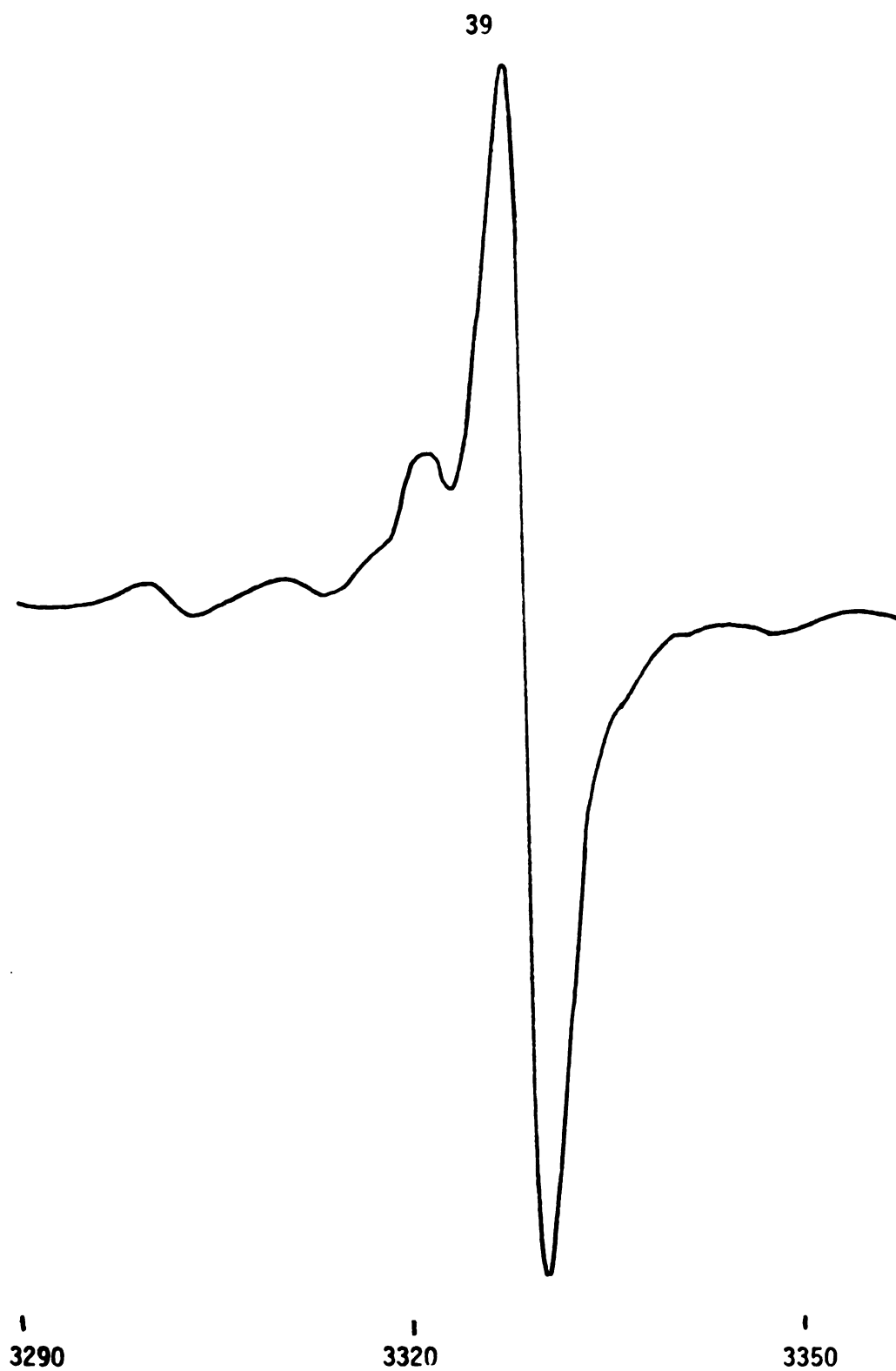


Figure 13. ESR Spectrum of Cp_2TiPh_2 for 55 min Irradiation in THF at -60° and 5 min at -20°



Figure 14. ESR Spectrum of Cp_2TiPh_2 for 55 min Irradiation in THF at -60° and 2 min at 0°

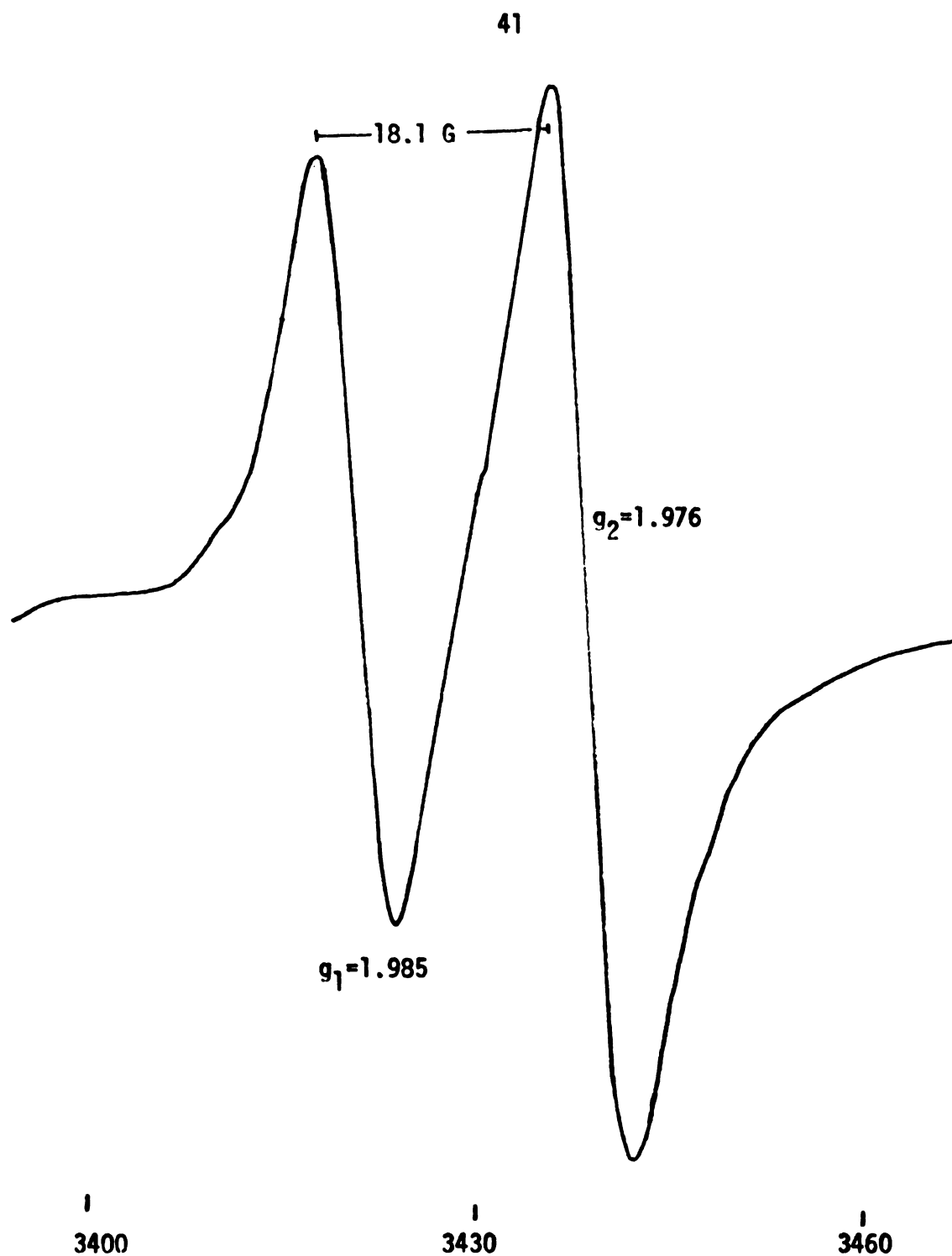


Figure 15. ESR Spectrum of Cp_2TiPh_2 for 55 min Irradiation in THF at -60° then allowed to warm to room temp.

minutes, a singlet at $g = 1.986$ is observed. When cooled to -60° , a similar esr spectrum as that of Figure 10 is appeared. As irradiation time continued 30 minutes in THF at -60° , the esr spectrum consists sort of triplet, Figure 16, the dihydride titanium complexes responsible for the appearance of this triplet at $g = 1.986$ with one of the triplet superimposed with the siglet at $g = 1.979$ which probably results to the particles $[\text{Cp}_2\text{Ti}\cdot\text{Solv}]$ or $[\text{Cp}_2\text{Ti}^{\text{II}}\text{H}(\text{C}_6\text{H}_5)]$.

The esr spectra recorded in the course of photoreduction of bis-(cyclopentadienyl)diphenyl titanium in THF at room temperature are shown in Figures 17-20. The sample solution shows a singlet at $g = 1.980$ as irradiated for 27 min., Figure 18. By continuously irradiating at room temperature, a species of $[\text{Cp}_2\text{TiH THF}]$ is observed in Figure 20. The signal is split by an interaction with two non-equivalent hydrogen atoms. A main doublet splitting of 4.8 gauss is in turn split by a second hydrogen atom with 1.5 gauss. Both signals are existable for less than 10 minutes at room temperature.

On the basis of the analysis of these esr spectra, it indicates that the photochemical reaction of Cp_2TiPh_2 in solutions produces the solvated monohydride titanium species as the first step or the phenylene titanium complexes, $[\text{Cp}_2\text{Ti}^{\text{II}}\text{H}(\text{C}_6\text{H}_5)]$, which one of the originally σ -bonded phenyl ligands might be promoted to π -allylic transition state by interaction of π -electron system of the phenyl group with a vacant metal orbital. This type of σ - π rearrangement has been reported for other transition-metal phenyl derivatives.⁵⁶ The second step of this photoreduction results in the titanium(II), Cp_2Ti moiety, as the reaction intermediate.

The isolated $[\text{Cp}_2\text{TiH}]_x$ is a convenient source of a highly reactive

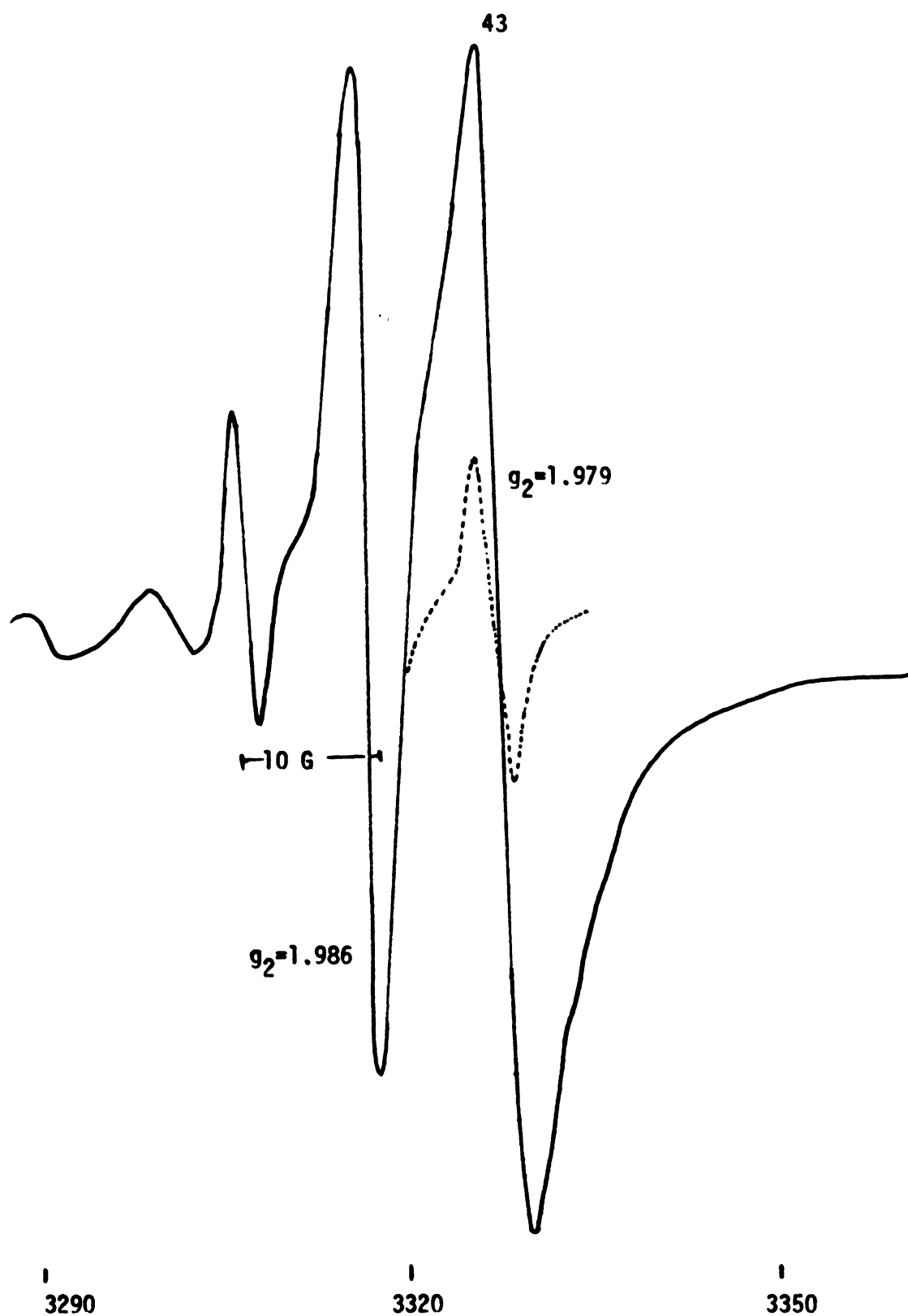


Figure 16. ESR Spectrum of Cp_2TiPh_2 for 10 min Irradiation in THF at room temp. and then 30 min at -60°

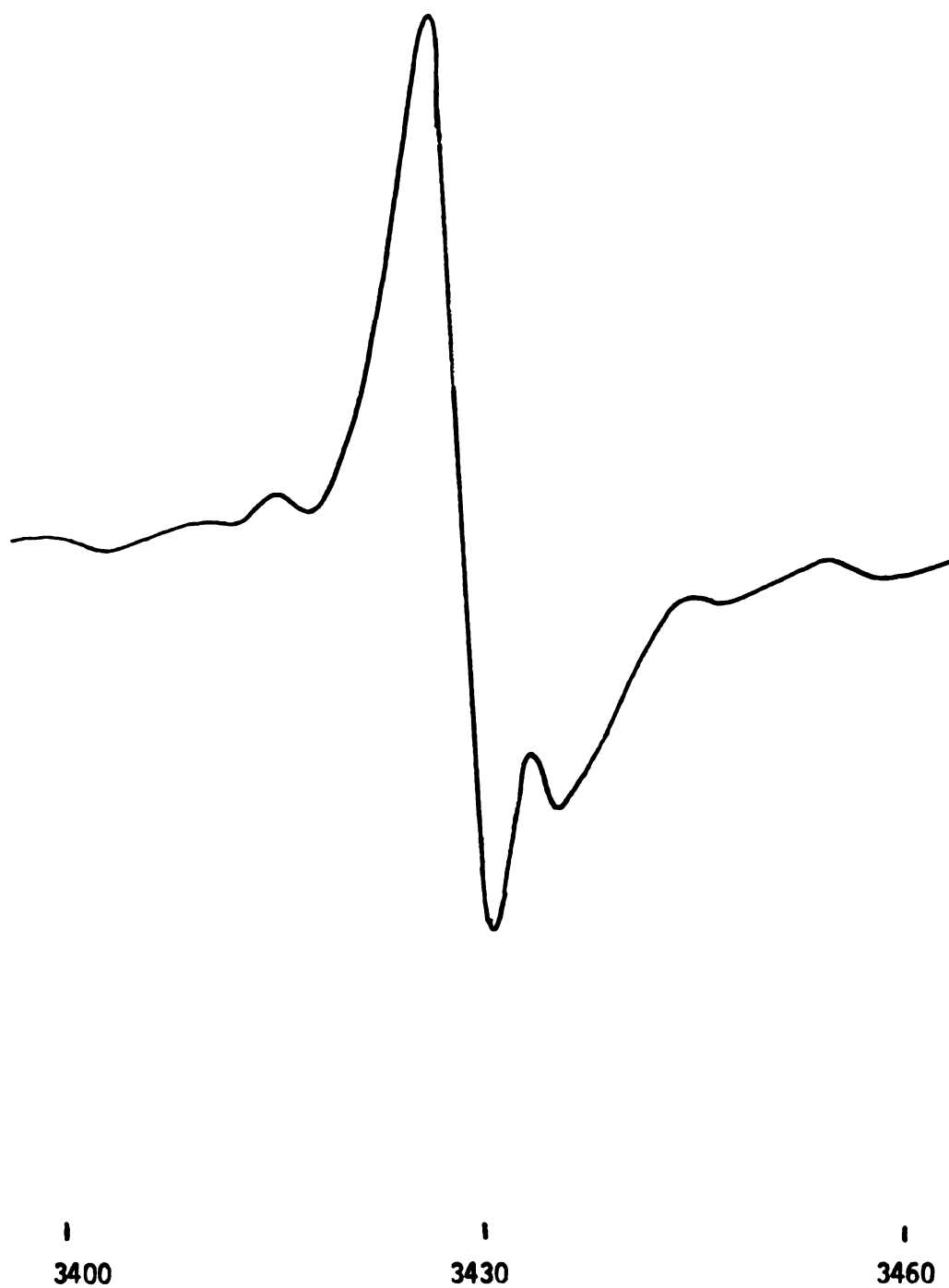


Figure 17. ESR Spectrum of Cp_2TiPh_2 for 8 min Irradiation in THF at room Temp.

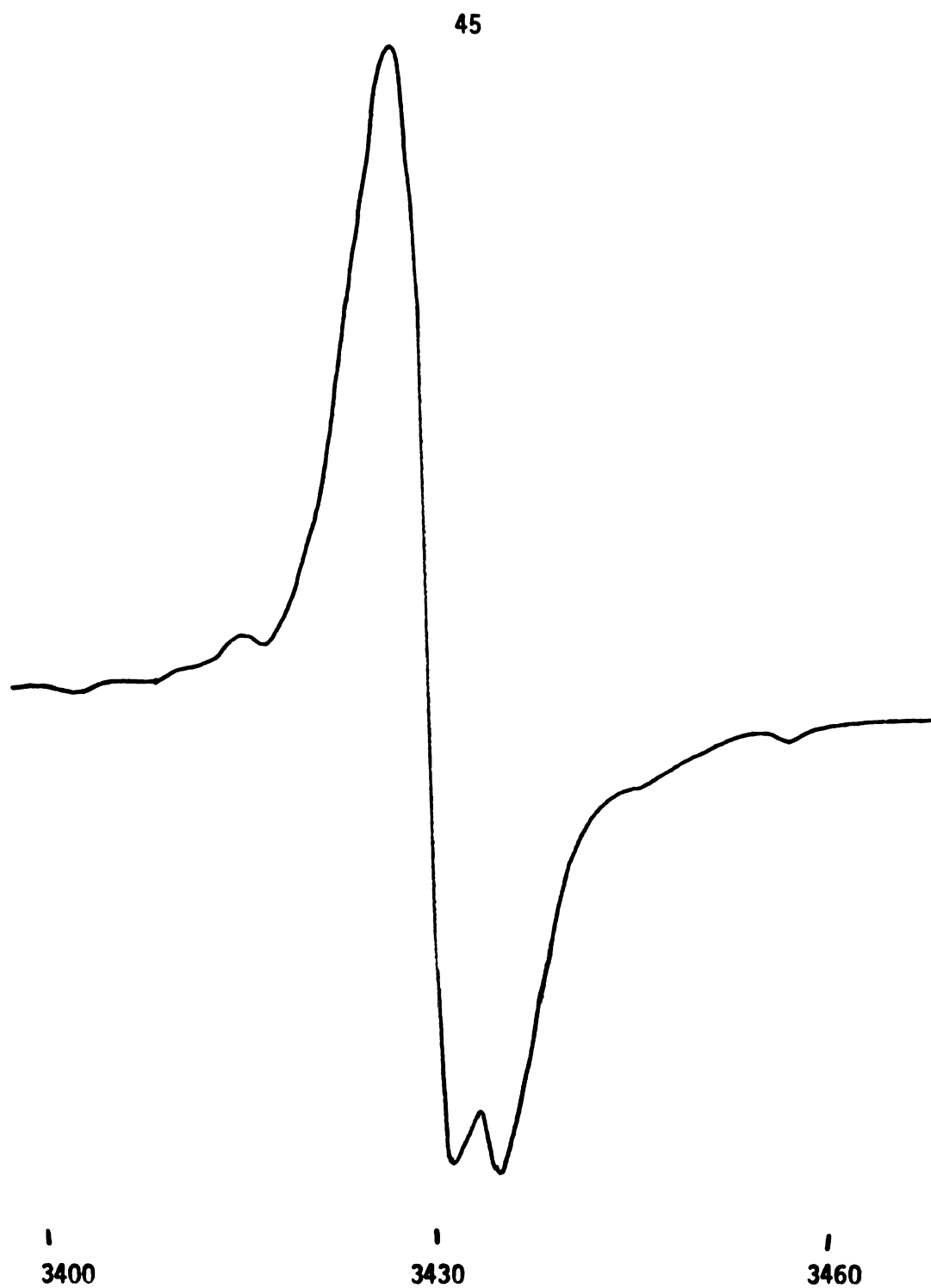


Figure 18. ESR Spectrum of Cp_2TiPh_2 for 18 min Irradiation in THF at room temp.

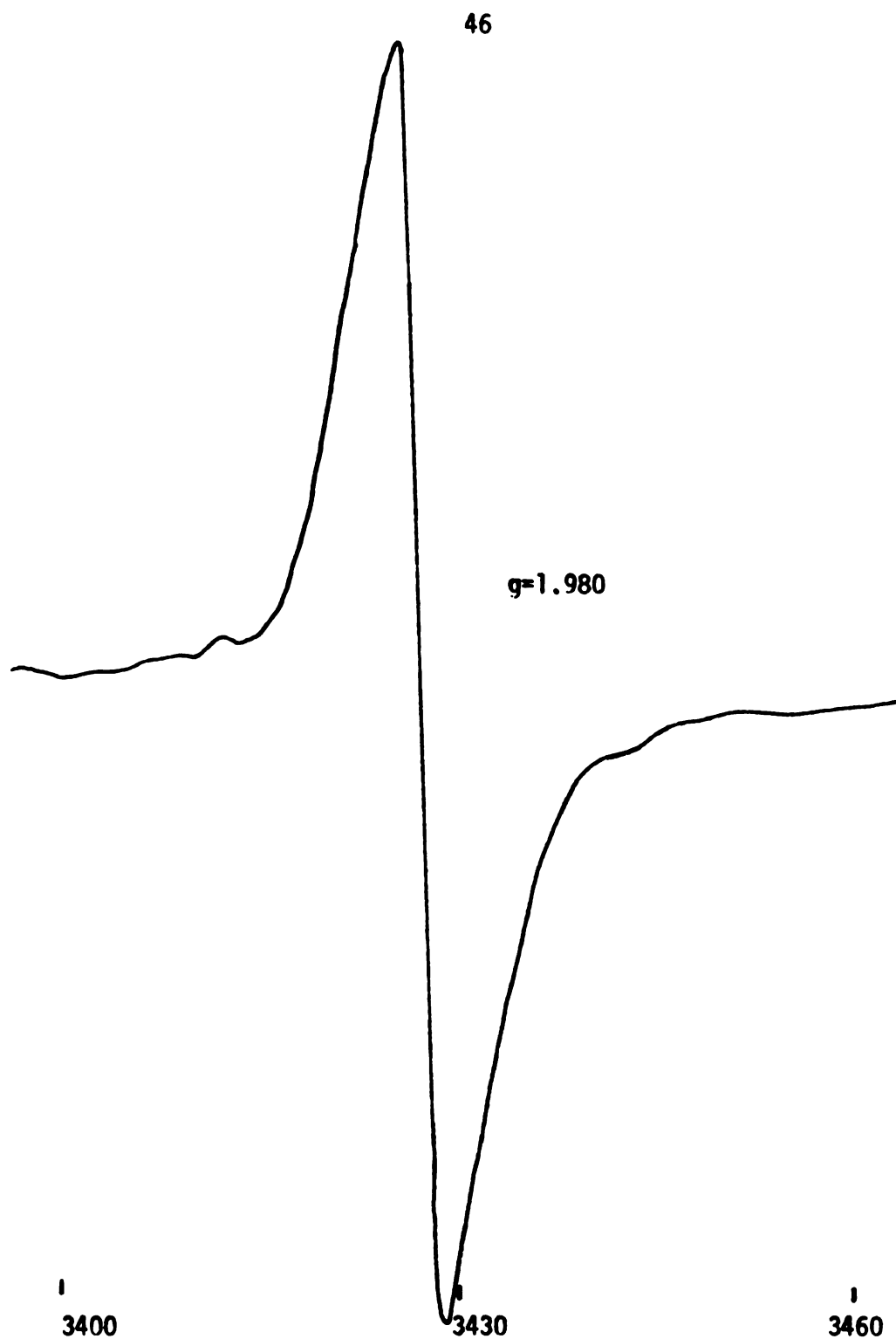


Figure 19. ESR Spectrum of Cp_2TiPh_2 for 27 min
Irradiation in THF at room temp.

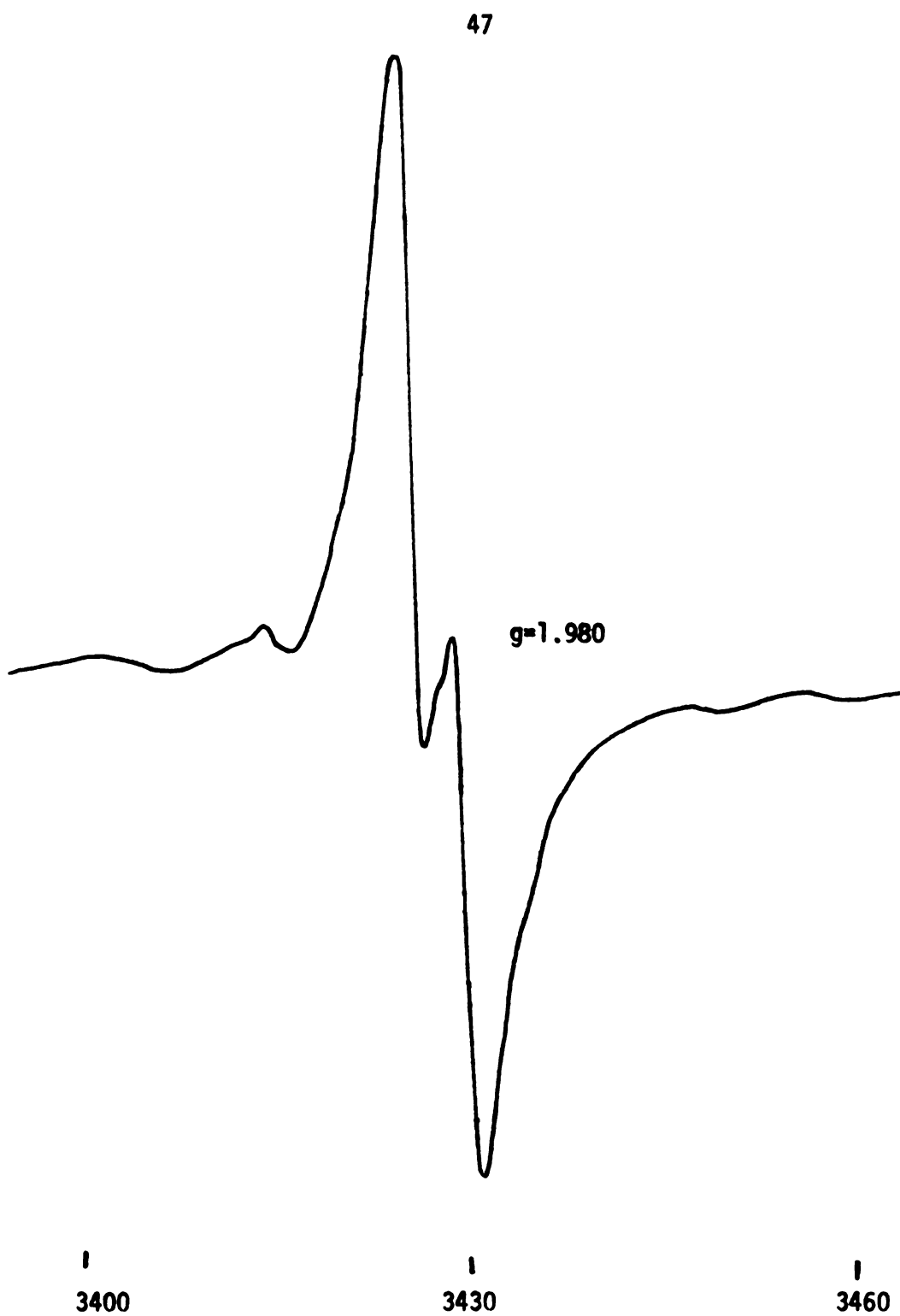


Figure 20. ESR Spectrum of Cp_2TiPh_2 for 50 min
Irradiation in THF at room temp.

form of titanocene. When the hydride is suspended and stirred in solvents, a species of composition of $[\text{Cp}_2\text{Ti}]_2$ results :⁴⁰



The postulated intermediate $[\text{Cp}_2\text{Ti}]_2$ exhibits a striking analogy of its reaction patterns to those of a carbene. Stable titanocene adducts can be formed from the reactions of $[\text{Cp}_2\text{TiH}]_x$ with various substrates.

An oxidation-reduction reaction has been reported³⁹ in which an interaction of titanocene with diphenylacetylene leads to the formation of an adduct, $\text{Cp}_2\text{Ti} [\text{C}_2(\text{C}_6\text{H}_5)_2]_2$, heterocyclo-1,1-dicyclopentadienyl-2,3,4,5,-tetraphenyl-1-titanacyclopentadiene, which is quite air stable at room temperature.

The ir spectrum of red adduct $\text{Cp}_2\text{Ti}(\text{CO})_2$ shows two very strong bands at 1975 cm^{-1} and 1897 cm^{-1} in Nujol, which indicate the characteristic of C-O stretching region. The photolysis reaction provides a simpler synthesis of $\text{Cp}_2\text{Ti}(\text{CO})_2$ with a higher yield than that in the literature,⁵⁷ which requires the use of high pressure and temperature. Our results are to be compared with those reported⁵⁸ for the carbonylation of Cp_2TiPh_2 in good yields of benzophenone, but no carbonyltitanium was obtained.

The photoreactions of bis(cyclopentadienyl)diphenyl titanium in various substrates were summarized in Figure 21. In the absence of other substrates, the irradiation of Cp_2TiPh_2 in solvents only gave titanocene monohydride polymer. Many stable titanocene adducts are obtained in the presence of substrates :

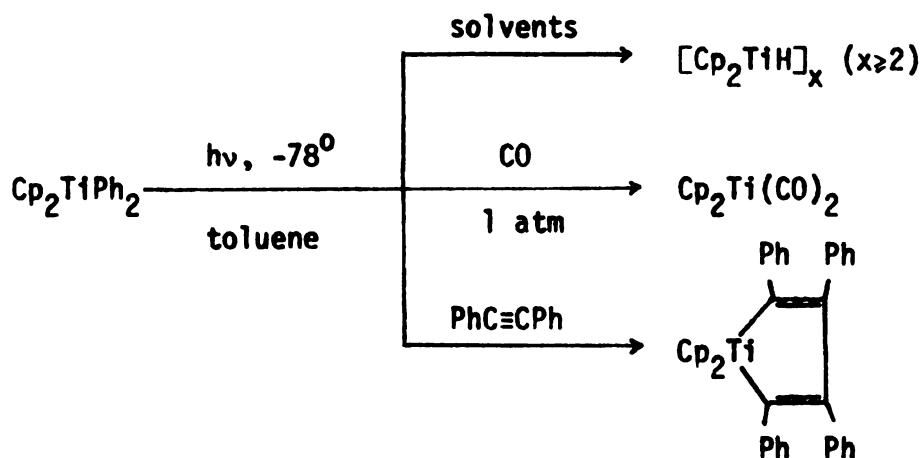
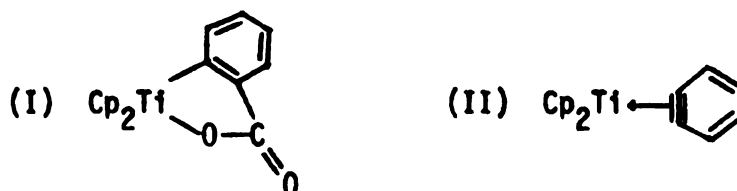


Figure 21. Photoreactions of Cp_2TiPh_2

The photoreaction of Cp_2TiPh_2 with carbon dioxide would not lead to carboxylation of the phenyl ring to form metallocycle (I) as re-

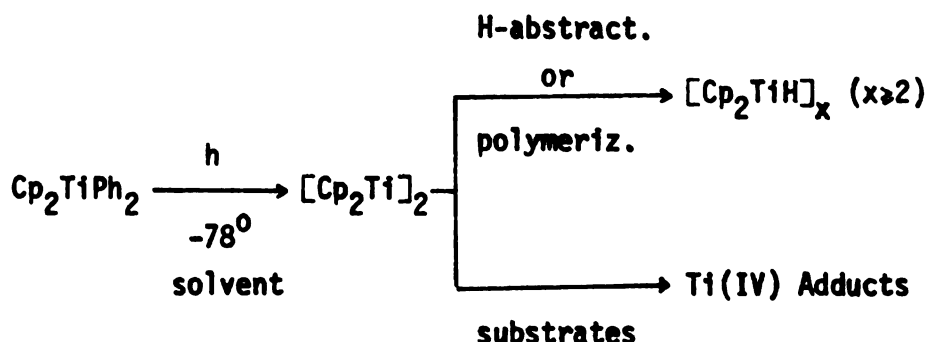


ported.⁵⁹ This probably suggests that either the intermediate phenylene titanium complex (II) would not exist or the concentration is too low to catch up to form the adduct (I).

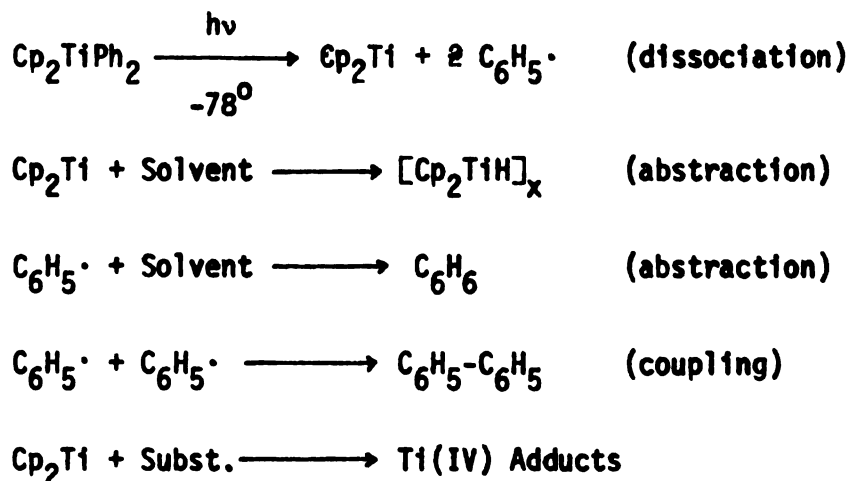
Possible Mechanism

The above experimental results seem to be best explained by the intermediary formation of a reactive metallocene via photodissociation of the phenyl ligands. The reactive intermediate might then react

either by attacking the available substrates to form a stable adduct, or else, via dimerization or polymerization to form titanocene mono-hydride :



A conceivable reaction route is radical coupling (or abstraction) followed by recombination steps :



All of the previous photolysis products were characterized by comparing their proton nmr and ir or mass spectra with the reported data. They were obtained virtually without side reactions. However, the photolysis pathways can be utilized as a convenient new route to synthesize the titanocene derivatives. Since a variety of titanium compounds has shown to catalytically hydrogenate alkenes and alkynes,

and the ability of fixation and reduction of molecular nitrogen.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. R. W. Harrigan, G. S. Hammond, and H. B. Gray, J. Amer. Chem. Soc., 81, 79 (1974).
2. H. Ald and M. D. Rausch, J. Amer. Chem. Soc., 96, 5936 (1974).
3. E. W. Vitz and C. H. Brubaker, J. Organometal. Chem., 86, C16(1974).
4. E. W. Vitz and C. H. Brubaker, J. Organometal. Chem., 104, C33 (1976).
5. E. W. Vitz, P. J. Wagner, and C. H. Brubaker, J. Organometal. Chem., 107, 301 (1976).
6. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", 1st ed., Pergamon Press, Oxford, New York, 1966.
7. L. T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 9, 86(1965)
8. M. E. Switzer and M. F. Rettig, Inorg. Chem., 13, 1975 (1974).
9. E. W. Vitz, Ph. D. Thesis, Michigan State University, 1974.
10. F. G. Moses, R. S. H. Liu, and B. M. Monroe, Mol. Photochem., 1, 245 (1969).
11. P. J. Wagner, J. Amer. Chem. Soc., 89, 5898 (1967).
12. H. A. C. McKay, Nature, 148, 997 (1938).
13. A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailles, Aust. J. Chem., 18, 173 (1965).
14. J. Dillard and R. W. Kiser, J. Organometal. Chem., 16, 265 (1969).
15. G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radio-chemistry", 2nd ed., Wiley, New York, 1955, p.197.
16. J. D. Hosechele, Ph. D. Thesis, Michigan State University, 1969.
17. W. J. Youden, "Statistical Methods for Chemist", Wiley, New York, 1951, pp. 40-45.

18. A. Z. Rubezhov and S. P. Gubin, "Advanced in Organometallic Chemistry", F. G. A. Stone and R. West, Eds., Academic Press, New York, 1972, vol. 10, p. 347.
19. H. H. Brintzinger and L. S. Bartell, J. Amer. Chem. Soc., 92, 1105 (1970).
20. T. J. Kealy and P. L. Pauson, Nature, 168, 1039 (1951).
21. R. B. King, "Organometallic Syntheses : Volume 1, Transition Metal Compounds", Academic Press, New York, 1965.
22. G. Wilkinson, Org. Syn., 36, 31 (1956).
23. A. K. Fischer and G. Wilkinson, J. Inorg. Nucl. Chem., 2, 149 (1956).
24. E. E. van Tamelen and H. Rudler, J. Amer. Chem. Soc., 92, 5253(1970).
25. J. J. Salzmänn and P. Mosimann, Helv. Chem. Acta., 50, 1831 (1967).
26. H. Hsiung and G. H. Brown, J. Electrochem. Soc., 110, 1035 (1963).
27. R. E. Dessey and R. B. King, J. Amer. Chem. Soc., 88, 5112 (1966).
28. S. P. Gubin and S. A. Smirnova, J. Organometal. Chem., 20, 229(1969).
29. G. A. Razuaev, V. N. Latyaeva, and L. I. Vyshinskaya, Dokl. Akad. Nauk SSSR, 159, 383 (1964).
30. J. Dvorak, R. J. O'Brien, and W. Santo, Chem. Commun., p.411 (1970).
31. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, J. Organometal. Chem., 102, 161 (1975).
32. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, J. Organometal. Chem., 102, 317 (1975).
33. K. Clauss and C. Beermann, Justus Liebigs. Ann. Chem., 654, 8 (1962).
34. J. E. Bercaw and H. H. Brintzinger, J. Amer. Chem. Soc., 91, 7301 (1969).
35. R. H. Marvich and H. H. Brintzinger, J. Amer. Chem. Soc., 93, 2046 (1971).
36. W. Moffitt, J. Amer. Chem. Soc., 76, 3386 (1954).
37. E. M. Shustorovich and M. E. Dyatkina, Russ. J. Inorg. Chem., 4,

251 (1959).

38. D. A. Bochvar and A. L. Chistyakov, Zh. Strukt. Kim., 9, 267(1968).
39. M. E. Vol'pin, V. A. Duboritskii, O. V. Nogina, and D. N. Kursanov, Dokl. Akad. Nauk SSSR, 151, 1100 (1963).
40. L. S. Bartell and H. H. Brintzinger, J. Amer. Chem. Soc., 92, 1105 (1970).
41. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Amer. Chem. Soc., 94, 1219 (1972).
42. A. Benrath and A. Obladen, Z. wiss. Photogr., 22, 65 (1922).
43. M. R. Hunt and G. Winter, Inorg. Nucl. Chem. Lett., 6, 529 (1970).
44. E. Samuel and C. Ginanotti, J. Organometal. Chem., 113, C17 (1976).
45. E. Samuel, H. G. Alt, D. C. Hrnclir, and M. D. Rausch, J. Organometal. Chem., 113, 331 (1976).
46. D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw Hill, New York, 1969.
47. A. D. Broadbent, J. Chem. Educ., 44, 145 (1967).
48. L. Summers, R. Uloth, and A. Holmes, J. Amer. Chem. Soc., 77, 3605 (1955).
49. F. Calderazzo, J. J. Szilzmann, and P. Mosimann, Inorg. Chem. Acta., 1, 65 (1967).
50. K. Sonogashira and N. Hagihara, Bull. Chem. Soc. Jap., 39, 1178 (1966).
51. R. H. Marvich, Ph. D. Thesis, University of Michigan, 1970.
52. J. E. Bercaw and H. H. Brintzinger, J. Amer. Chem. Soc., 93, 2045 (1971).
53. F. A. Cotton and T. J. Marks, J. Amer. Chem. Soc., 91, 7281 (1969).
54. V. B. Panov, Yu. M. Shul'ga, E. F. Kvashina, and Yu. G. Borod'ko, Kinetika i Kataliz, 15, 518 (1974).
55. H. H. Brintzinger, J. Amer. Chem. Soc., 89, 6871 (1967).

56. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, J. Organometal. Chem., **81**, 371 (1974).
57. J. G. Murray, J. Amer. Chem. Soc., **83**, 1287 (1961).
58. H. Masai, K. Sonogashira, and N. Hagihara, Bull. Chem. Soc. Jap., **41**, 750 (1968).
59. I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbachevskaya, G. G. Aleksandrov, Yu. T. Struckhov, and M. E. Vol'pin, Chem. Commun., p.972 (1971).

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03142 8620