PHOTOCHEMICAL REACTIONS OF
BIS(η^{5} -CYCLOPENTADIENYL)
TITANIUM DICHLORIDE

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
EDWARD WALTER VITZ
1974

This is to certify that the

thesis entitled

Photochemical Reactions

of Bis(η^5-cyclopentadienyl)titanium Dichloride

presented by

Edward W. Vitz

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker
Major professor

Date December 12, 1974

O-7639

Ca248e

ABSTRACT

PHOTOCHEMICAL REACTIONS OF BIS(η^5-CYCLOPENTADIENYL)TITANIUM DICHLORIDE

By

Edward Walter Vitz

The exchange of cyclopentadienyl ligands between molecules of bis(η^5-cyclopentadienyl)titanium dichloride (titanocene dichloride) is exclusively photolytic. The increase in the (D-5)titanocene dichloride concentration in benzene solutions which initially contained only titanocene dichloride and (D-10)titanocene dichloride was detected by mass spectrometry. A quantum yield of 0.23 moles/einstein was calculated, and the equilibrium constant for the reaction was 4.0. Cyclopentadienyl ligand exchange between titanocene dichloride and titanocene monochloride dimer also proved to be photolytic, and had a higher quantum yield than the above photoexchange.

The alcoholysis of titanocene dichloride in benzene-methanol solutions was also shown to be exclusively photolytic at room temperature. The quantum yield was 0.44 moles/einstein for solutions 8.1×10^{-3} $\underline{M}$ in titanocene dichloride and 1.0 $\underline{M}$ in methanol, and the product was η^5-cyclopentadienyl(methoxo)titanium dichloride by mass spectrometry.

Studies of several nonphotolytic reactions are appended. These reactions included the halide exchange between titanocene dichloride and titanocene dibromide (which was complete, with an equilibrium

constant of 0.5, in the time of mixing and quenching in the dark) and two electron exchange reactions. First, the electron exchange between titanocene dichloride and titanocene monochloride in tetrahydrofuran was complete in the time of mixing and separating (*ca*. 30 seconds) in the dark. Second, a minimum rate constant of 4×10^3 was established for the electron exchange between bis(benzene)chromium and its cation.

PHOTOCHEMICAL REACTIONS OF BIS(η^5-CYCLOPENTADIENYL)TITANIUM DICHLORIDE

By

Edward Walter Vitz

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1974

To Mimi, Yossarian and

The Greenville Granfalloon

ACKNOWLEDGEMENT

I would like to acknowledge the contributions of Professor Carl H. Brubaker, whose professional assistance was most helpful and whose personal inspiration was indispensable.

The financial support of the National Science Foundation and the Dow Chemical Company has been greatly appreciated.

TABLE OF CONTENTS

INTRODUCTION 1

EXPERIMENTAL 7

- A. General 7
- B. Purification of Materials 7
- C. Preparations 8
- D. Photolysis Apparatus 9
- E. Chemical Actinometer Solutions 10
- F. Determination of Lamp Intensity 12
- G. Photolytic Cyclopentadienyl Ligand Exchange Between Titanocene Dichloride and Perdeuterotitanocene Dichloride 13
- H. Photolytic Cyclopentadienyl Ligand Exchange Between Perdeuterotitanocene Dichloride and Titanocene Monochloride Dimer 13
- I. McKay Analysis of Mass Spectrographic Data for Ligand Exchange Processes 14
- J. Photolytic Methanolysis of Titanocene Dichloride . . 19

RESULTS AND DISCUSSION 21

- A. Photolytic Cyclopentadienyl Ligand Exchange Between Titanocene Dichloride and Perdeuterotitanocene Dichloride 21
- B. Photolytic Cyclopentadienyl Ligand Exchange Between Perdeuterotitanocene Dichloride and Titanocene Monochloride Dimer 25
- C. Photolytic Methanolysis of Titanocene Dichloride . . 30
- D. Reaction Mechanisms 36

SUMMARY 42

APPENDIX A. The Halide Exchange Between Titanocene Dichloride and Titanocene Dibromide 43

- Experimental 43
- Discussion 44

APPENDIX B. The Electron Exchange Between Bis(arene)chromium Complexes and Their Cations 46

- I. Introduction 46
- II. Quenched-Flow Study of the Electron Exchange Between Bis(benzene)chromium(0) and Bis(benzene)chromium(I). 49

Experimental 49
A. Preparation of Materials 49
B. Gamma Counting Procedures 50
C. Quantitative Analysis of Chromium . . . 51
D. The Szilard-Chalmers Reaction of Bis(benzene)chromium Iodide 51
E. Quenched-Flow Experiments 52
Discussion 54
III. Study of the Electron Exchange Between Bis(arene)chromium Complexes and Their Cations by ESR Techniques 56

Experimental 58
A. Preparation and Purification of Materials 58
B. Exchange Experiments 59
C. Photochemistry of Bis(biphenyl)chromium Iodide 59
Results and Discussion 60
IV. Study of the Electron Exchange Between Bis(arene)chromium Complexes and Their Cations by NMR Techniques 67
Experimental 67
Results and Discussion 68

APPENDIX C. The Electron Exchange Between Titanocene Dichloride and Titanocene Monochloride 70

Experimental 70
Discussion 72

BIBLIOGRAPHY 76

LIST OF TABLES

Table Page

1. Mass spectrographic data for the perdeuterotitanocene dichloride - titanocene dichloride ligand exchange . . . 22

2. Mass spectrographic data for the perdeuterotitanocene dichloride - titanocene monochloride exchange 28

3. Mass spectrographic data for the perdeuterotitanocene dichloride - titanocene monochloride equilibrium mixture 29

4. Photomethanolysis data for titanocene dichloride 33

5. Quenched-flow exchange experimental data 55

6. NMR linewidths for exchange solutions 69

LIST OF FIGURES

Figure Page

1. Photolysis apparatus 1

2. Mass spectrum of titanocene dichloride 15

3. Mass spectrum of (D-10)titanocene dichloride 16

4. Mass spectra of exchange solutions 18

5. McKay plot for perdeuterotitanocene dichloride - titanocene dichloride exchange 23

6. Direct mechanism for ligand exchange between titanocene dichloride and titanocene monochloride 26

7. Oxidation state interchange mechanism for ligand exchange between titanocene dichloride and titanocene monochloride 27

8. The mass spectrum of the photomethanolysis product . . . 35

9. Coordinate axes chosen for titanocene dichloride 37

10. Titanocene dichloride molecular orbitals 37

11. Ultraviolet-visible spectrum of titanocene dichloride . . 38

12. Proposed mechanism for photolytic reactions of titanocene dichloride. 41

13. Mass spectrum of the halide exchange products 45

14. Quenched-flow apparatus 53

15. Exchange broadened esr spectrum of bis(biphenyl)chromium iodide 61

16. Weissman plot for electron exchange between bis(biphenyl)-chromium(0) and its univalent cation 62

17. Exchange broadened esr spectra of bis(benzene)chromium(I) 63

18. Exchange broadened esr spectra of bis(benzene)chromium(I) 64

19. Apparatus for electron exchange experiment 71

20. Mass spectrum of titanocene dichloride from electron exchange solution 73

INTRODUCTION

This is the first report of exchange of π-bonded ligands between identical transition metal complexes, and the first report of photosubstitution reactions of the cyclopentadienyl ligands in titanocene derivatives. Studies of some electron exchange reactions in bis(arene)-chromium systems and between selected titanocene derivatives, and halide exchange reactions of titanocene dihalides, which are not photochemical and for which rate constants were not determined exactly, are appended.

Ligand exchange processes involve isotopic equilibration between two chemically identical reactant complexes, only one of which initially contains the tracer ligand. The present study concerns the equilibration of deuterocyclopentadienyl ligands between $(\eta^5\text{-}C_5D_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)_2TiCl_2$. The system is always at chemical equilibrium, and there is no free energy change except that which arises as the entropy of isotopic mixing. Studies of these processes and their kinetics yields fundamental information about molecular properties and reaction mechanisms which may in turn be useful in explaining more complex chemical behavior.

Ligand substitution or transfer reactions, which involve chemically different reactants and generally have a large free energy of reaction, are important synthetic routes to many transition metal complexes, and consequently have been studied extensively. This report concerns the photosubstitution of methoxide for cyclopentadienyl ligands in $(\eta^5\text{-}C_5H_5)_2TiCl_2$. Because of the inertness of the titanium to cyclopentadienyl bond in titanocene dichloride few thermal substitution reactions have been reported, and the only photosubstitution reaction of titanocene derivatives that has been reported involves the sigma bonded methyl groups in dimethyltitanocene, $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$.[1] The generalization that has been applied to ligand substitution processes is that thermal substitution in arene metal tricarbonyl complexes usually involves the arene ligand, while photosubstitution usually involves the carbonyl ligands, and in mixed cyclopentadienyl-(arene)-metal complexes, substitution involves the arene moiety.[2]

Substitution of π-bonded ligands in general has received much attention, and serves well as an historical introduction to the present photosubstitution and photoexchange studies. In 1956, Wilkinson, Cotton and Birmingham reported the first π-ligand transfer reaction, in which ferrocene was prepared from chromocene and ferrous chloride.[3] Processes of this type were first termed π-ligand transfers by Maitlis.[4] Two comprehensive reviews have recently been published by Avi Efraty[5] and A. Z. Rubezhov and S. P. Gubin.[6] The general field of ligand substitution has been reviewed by several writers.[7,8]

Following the paradigm of Wilkinson, et al., most π-ligand transfer reactions have been studied for their synthetic utility, not for mechanistic detail. However, kinetics of the ethyleneplatinum chloride exchange with deuteroethylene has been studied, and was found to be complete in 15 minutes.[9] The rate of exchange of ethylene with Zeise's salt is greater than 70 sec^{-1},[10] and ethylene exchange can proceed rapidly enough to be studied by nmr line-broadening methods.[11] Also, the kinetics of π-ligand transfer between π-tetraphenylbutadienyl paladium dihalides and π-cyclopentadienyliron dicarbonyl bromide has been studied as well as the transfer of the allyl ligand between (π-allyl)palladium chloride and iron carbonyl.[12,13]

A mechanism that is consistant with the kinetics data for these systems involves three steps that do not necessarily occur in the order given:

1. Coordination of the attacking reagent on the substrate.
2. Rearrangement of π-ligands on the substrate to a lower coordination number, with formation of σ bonds as the extreme case.
3. Ligand removal, possibly concerted with rearrangement of the entering group bonding from σ to π bonds.

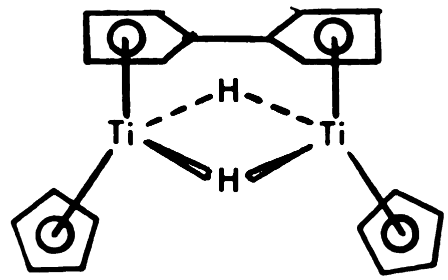
This sort of mechanism is suggested by Rubezhov and Gubin[6] and is now supported by independent information. For example, the bonding in tris(cyclopentadienyl)titanium, where one cyclopentadienyl ligand is considered to have only a 3 electron bond with titanium, might be suggested as evidence for step 2[14] and known σ to π rearrangements[15] increase the acceptability of steps 2 and 3.

There are only two qualitative reports of π-ligand exchange which are related to the present work. First, Strohmeier[16] reported that on untraviolet irradiation of arene tricarbonyls in the presence of the corresponding ^{14}C arenes, labelled arene metal carbonyls result. Second, King and Bisnette[17] reported the potent thermal cyclopentadienylating agent, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ yields $[(CF_3)_2C_2S_2]_2Fe$ on ultraviolet irradiation in the presence of the ligand.

The kinetics of π-ligand substitution or exchange has presumably been ignored for the titanocene derivatives for several reasons. First, the cyclopentadienyl ligand is unstable in the uncoordinated state, and complicated reactions might be expected. Mixtures of organic products are found, for instance, in the study of photosubstitution reactions of ferrocene. Second, the π-bond between the cyclopentadienyl ligand and titanium is very stable, expecially in titanocene dichloride and its analogs. For instance, titanocene dichloride is not subject to thermal alcoholysis and other substitution reactions that occur readily in bis(alkoxo)titanocene derivatives.[19] Titanocene dichloride will not yield ferrocene on reaction with ferrous chloride[20] even after 8 hours in a sealed tube at 150°. Similarly, no nickelocene results from the reaction of titanocene dichloride and nickel carbonyl.[21]

Electrochemical reduction of titanocene dichloride destroys the titanium to chlorine bonds, leaving the titanium to cyclopentadienyl bonds intact.[22-24] Chemical reduction of titanocene dichloride with aluminum in tetrahydrofuran yields titanocene monochloride dimer.[25] Similar reactions occur in water with zinc, and in nonaqueous solvents with aluminum alkyls. The reactions of titanium π-complexes are systemmatically presented in reviews by R. S. P. Coutts and P. C. Wailes[26] and by J. M. Birmingham.[27]

Reduction of titanocene dichloride to lower oxidation states can also be effected with metallic sodium[28] or sodium naphthalene[29] and a green compound results, which was originally thought to be titanocene, bis(η^5-cyclopentadienyl)titanium(II) or its dimer.[30] Recently, however, Brintzinger and his coworkers have shown that the compound must be a hydrogen bridged dimer,[31] and Davison and Wreford have demonstrated that the structure contains a μ-(η^5,η^5-fulvalene) ligand:[32]



The elusive "true" titanocene can be prepared only by stirring the polymer $[(\eta^5\text{-}C_5H_5)_2TiH]_x$ in ether[33] or by irradiating dimethyl titanocene.[1] This compound is important in the present work because the ring hydrogen atoms exchange with gas phase deuterium to give the necessary tracer compounds.

There are two notable exceptions to the rule of the inertness of the bond between cyclopentadienyl ligands and titanium in titanocene dichloride. First, it is cleaved by ammonia and amines.[34] Second, the important synthetic route to $(\eta^5\text{-}C_5H_5)TiCl_3$ involves a ligand transfer in boiling xylene:[35]

$$TiCl_4 + (\eta^5\text{-}C_5H_5)_2TiCl_2 \rightarrow 2\ (\eta^5\text{-}C_5H_5)TiCl_3$$

The possibility of photochemical pathways for this reaction should of course be explored.

The photochemistry of transition metal complexes is rapidly becoming a well-developed field, whereas only five years ago authors were lamenting its neglect. Balzani and Carassiti have authored a book[36] devoted exclusively to that subject, which contains references to sources of background information as well as current research. Several review articles have appeared in recent years, including those by A. W. Adamson[37,38] A. W. Adamson et al.,[39] P. D. Fleischauer et al.,[40,41] E. L. Wehry,[42] J. F. Endicott,[43] W. Strohmeier,[15] and P. C. Ford.[44] Photochemistry of the metallocenes in particular has been reviewed recently by R. E. Bozak.[45]

The only work on titanocene systems even remotely related to those in the present study was the (previously mentioned) recent discovery of the photodecomposition of dimethyltitanocene.[1]

While photosubstitution reactions are the main subject of transition metal photochemistry, only a few photosubstitution reactions[1,17] involve π-bonded ligands. Most attempted photochemistry of π-complexes leads to decomposition, sometimes with intractable products, as in the case of $(C_4H_4)Fe(CO)_3$[46] and Zeise's salt.[47] Many attempted photochemical reactions of ferrocene gave only cyclopentadiene (or organic mixtures) and iron metal.[48] Likewise, the photolysis of bis(benzene)-chromium(I) yields Cr(III) and benzene.[45]

The present study therefore makes inroads into a little known type of reaction (π-ligand photoexchange and photosubstitution) and involves a system (titanocene dichloride and its analogs) which deserves further photochemical study. Complexes related to titanocene dichloride are, of course, extremely important in the areas of catalysis and nitrogen fixation.

EXPERIMENTAL

A. General

All materials were manipulated under argon or vacuum in Schlenk type apparatus.[49] Argon was purified by passage through, first, a 70 x 5 cm column of Aquasorb ,[50] then a 70 x 6 cm column of BTS catalyst[51] in its reduced form, heated to 180°, and finally, through a second 70 x 6 cm column of Aquasorb. When necessary, manipulations were executed in an argon filled glove box. The argon was continually recirculated through a column of Dow Q-1 "oxygen grabber" and Linde 4A molecular sieves. The inert atmosphere was typically pure enough so that a 25 watt tungsten lamp with an exposed filament would burn for 300 hours.

B. Purification of Materials

Titanocene Dichloride: The impure titanocene dichloride obtained from Alfa Products was recrystallized in a Soxhlet apparatus from chloroform saturated with HCl, under HCl and argon. Finally, the titanocene dichloride was sublimed at 0.1 mm pressure and 100-140°, and stored in the dark.

Benzene: Benzene was purified by shaking with concentrated sulfuric acid several times, washing with aqueous sodium hydroxide, drying over calcium hydride, then distilling from sodium metal and benzophenone.

Valerophenone: Valerophenone was obtained from the J. T. Baker Chemical Company. The impure liquid was passed through an alumina column, then vacuum distilled.

Methanol: Methanol was stirred over calcium hydride overnight and distilled through a 30 cm Vigreaux column under argon. Residual air was removed by the vacuum freeze-thaw technique.

Deuterium: C. P. deuterium gas was obtained from Matheson Gas Products and used without further purification.

C. Preparations

Perdeuterotitanocene dichloride: The exchange of the ring hydrogen atoms on titanocene with deuterium, discovered by Marvich,[52] was utilized to prepare the perdeuterotitanocene dichloride tracer. Titanocene hydride polymer, $[(\eta^5\text{-}C_5H_5)_2TiH]_x$, (0.3 g) was added to 20 ml of distilled toluene in a 250 ml rould bottom flask containing a Teflon coated magnetic stirrer. The suspension was stirred for several minutes, which was usually adequate for the formation of $(\eta^5\text{-}C_5H_5)_2Ti$ solutions. The flask was then partially evacuated and deuterium gas was added at one atmosphere pressure. The solution was then stirred overnight, and the flask was evacuated and refilled with deuterium several times to ensure complete deuteration. Finally, the solution was cooled in a dry ice/acetone bath, the flask was partially evacuated, and hydrogen chloride was added gradually while stirring was continued. Hydrogen chloride was added until the pressure in the flask reached one atmosphere and no gas evolution was evident. The reaction mixture was then allowed to warm to room temperature, and was stirred for ca. one hour. The toluene was then evaporated, and the product extracted with air saturated chloroform which was subsequently evaporated to leave reddish crystals. These were sublimed to give pure $(\eta^5\text{-}C_5D_5)_2TiCl_2$ as indicated by the melting point and mass spectrum.

Titanocene hydride polymer: The gray polymer $[(\eta^5\text{-}C_5H_5)_2TiH]_x$ was prepared from $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ which in turn was prepared according to the method of Clauss and Bestian.[53] This method involves treating titanocene dichloride with methyllithium (in this case a 2 *M* solution in ether) at -70°. The dimethyltitanocene thus obtained as a *ca.* 0.1 *M* solution in hexane is stirred under hydrogen gas at 0° to give the polymer as reported by Brintzinger *et al.*[54]

Titanocene monochloride (bis(η^5-cyclopentadienyl)titanium chloride: A solution of about 5 g of titanocene dichloride in 50 ml of tetrahydrofuran was treated with aluminum foil (activated by treatment with mercurous nitrate solution) after the method of Coutts, Wailes, and Martin.[55] The excess aluminum was removed by filtration, and the filtrate was evaporated. The residue was extracted with ether to remove the aluminum halide, then vacuum sublimed to give the pure, greenish brown $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$.

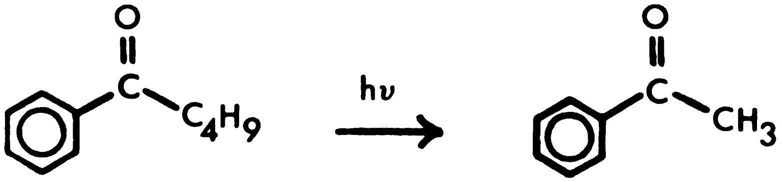
D. Photolysis Apparatus

Photolyses were effected with a 450 watt medium pressure mercury lamp, Hanovia #679 A 0360, which was mounted in a quartz cooling jacket through which tap water circulated. This assemply was mounted inside a 70 mm quartz filter solution cell which contained 0.002 *M* potassium chromate in 1% aqueous potassium carbonate. The path length of the filter solution was 1.0 cm so that the 313 nm line of the lamp was effectively isolated.[56] The lamp assembly was mounted at the center of a merry-go-round apparatus[57] to assure the uniform illumination of all samples and actinometer solutions (see Figure 1). The distance from the center of the lamp to the sample cell front surface was 8 cm, and the merry-go-round window size was 7 x 19 mm. The entire apparatus was mounted in an alcohol-water bath to moderate temperature fluctuations, and the temperature stayed in the range 25±2°C. The bath was 20% by volume alcohol to retard the growth of microorganisms.

Samples and actinometer solutions of a precisely known volume (typically 3.0 ml) were added to 13 mm o.d. pyrex culture tubes by use of a syringe in the glove box. The necks of the tubes were constricted to facilitate sealing with an oxypropane torch. The tubes were stoppered in the glove box, then removed so that they could be frozen with liquid nitrogen and sealed.

E. Chemical Actinometer Solutions

The valerophenone actinometer[56] was chosen because it absorbs strongly (ε = 50 l/mole cm) at 313 nm and the quantum yield is 0.33 mole/einstein, similar to that of the experimental samples. The conversion



was kept to less than 25% of the total valerophenone to prevent product interference.

Actinometer solutions were typically prepared by weighing valerophenone (1.80 g) and tetradecane (0.1000 g) into a 50 ml volumetric

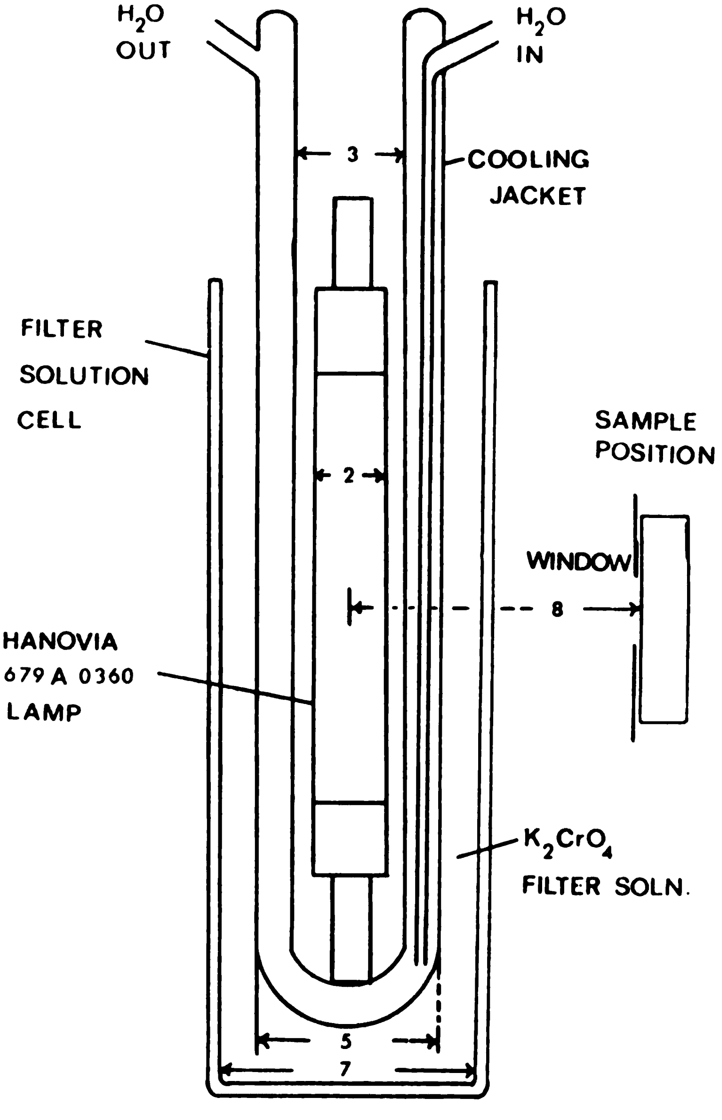


Figure 1. Photolysis apparatus.

flask and diluting with purified and deoxygenated benzene. The actinometer solution was sealed in 13 mm pyrex culture tubes so that all dimensions were identical to the experimental samples.

F. Determination of Lamp Intensity

After photolysis, the actinometer solution (ca. 1 μl) was injected onto the column of a Varian Aerograph Series 1200 gas chromatograph with a flame detector. The column material was 4% QF1, 1.2% carbowax 20 M on Chromasorb G 60/80, and it was maintained at 100°C.

An Infotronics CRS 208 Automatic Digital Integrator was used to facilitate the determination of the peak area ratio of the acetophenone to the tetradecane peaks. The number of moles of photons, n, in einsteins can then be calculated from the following equation:

$$\frac{I_{\text{acetophenone}}}{I_{\text{tetradecane}}} \times 2.0 \times [\text{tetradecane}] \times V = 0.33\ n$$

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

[tetradecane] = the concentration of tetradecane in the actinometer solution

V = the actinometer sample volume

and 0.33 = the quantum yield for the formation of acetophenone.

G. Photolytic Cyclopentadienyl Ligand Exchange Between Titanocene Dichloride and Perdeuterotitanocene Dichloride

Weighed amounts of titanocene dichloride and perdeuterotitanocene dichloride were stirred with benzene in 50 ml volumetric flasks in the glove box until the crystals were totally dissolved (this sometimes required several hours). The solutions were diluted to the mark with benzene to give the desired 10^{-2} to 10^{-3} $\underline{M}$ solutions, which were then mixed in dim light and added in 3.0 ml aliquots to the 13 mm culture tubes to make about 30 samples. One sample was retained to determine the initial optical absorbance at 520 nm. The tubes were sealed with an oxypropane torch and mounted, along with 6 actinometer cells, in the merry-go-round apparatus. Generally, the lamp was turned on and allowed to warm up for at least an hour before the samples were introduced. After measured periods of illumination, 4 or 5 sample tubes and one actinometer tube were withdrawn from the merry-go-round. The actinometer was analyzed as described previously. The samples were pooled, evaporated to dryness, and sublimed (the sublimation step was used mainly as a collection device, as very little impurity remained unsublimed. The mass spectrum was then obtained on a Hitachi Perkin Elmer RMU-6 mass spectrometer. The absence of side reactions was established by measuring the optical absorbance at 520 nm of a sample which had been photolyzed the maximum time.

H. Photolytic Cyclopentadienyl Ligand Exchange Between Perdeuterotitanocene Dichloride and Titanocene Monochloride Dimer

Weighed amounts of perdeuterotitanocene dichloride and titanocene monochloride were dissolved separately in benzene to give 50 ml of each solution. The samples were then treated as above, except that after photolysis, the titanocene monochloride was separated from the exchange mixture by precipitation with 2,2'-bipyridine.[58] The blue precipitate coagulated in about a minute to yield a mixture which was easily separated by filtration through a fine frit. The filtrate was then evaporated and the residue sublimed as above. The bipyridine adduct was converted to titanocene dichloride by dissolving it in a minimum of oxygen free, deionized water to give a blue solution. The solution was treated with excess hydrogen chloride at 0°, then stirred at room temperature for several hours under HCl until it turned orange. The water was then evaporated and the bipyridine sublimed from the product at 95° and 0.1 mm pressure. Finally the product was sublimed and the mass spectrum was obtained.

As in the previous experiment, the absorbance of the exchange solution at 520 nm was measured before and after photolysis to demonstrate that no decomposition had occured.

I. McKay Analysis of Mass Spectrographic Data for Ligand Exchange Processes

Titanocene dichloride has a well characterized mass spectrum[59-61] with a parent ion peak at m/e = 248. The mass spectrum of the perdeutero compound is, of course, identical except that the peaks corresponding to fragments with one or two cyclopentadienyl moieties appear 5 or 10 units higher, respectively. Figures 2 and 3 show the mass spectra of the two derivatives. In the mass spectrum of an unphotolyzed mixture of titanocene dichloride and its perdeutero analog there are peaks at 248 and 258 with associated manifolds due to the isotopes ^{37}Cl, ^{35}Cl, ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, ^{50}Ti, ^{12}C and ^{13}C. The peak at m/e = 253 is nonzero but small (typically less than 5% of the 248 peak). Photolyzed

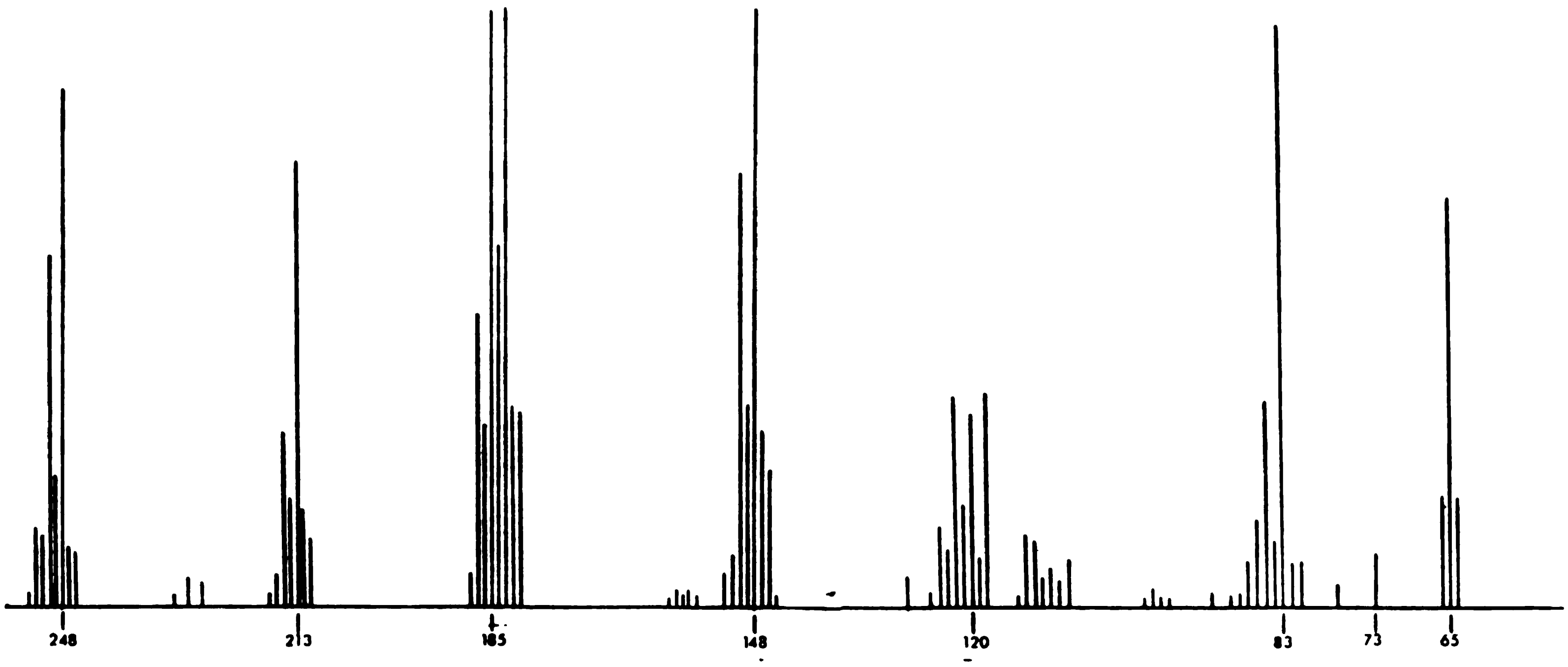


Figure 2. Mass spectrum of titanocene dichloride

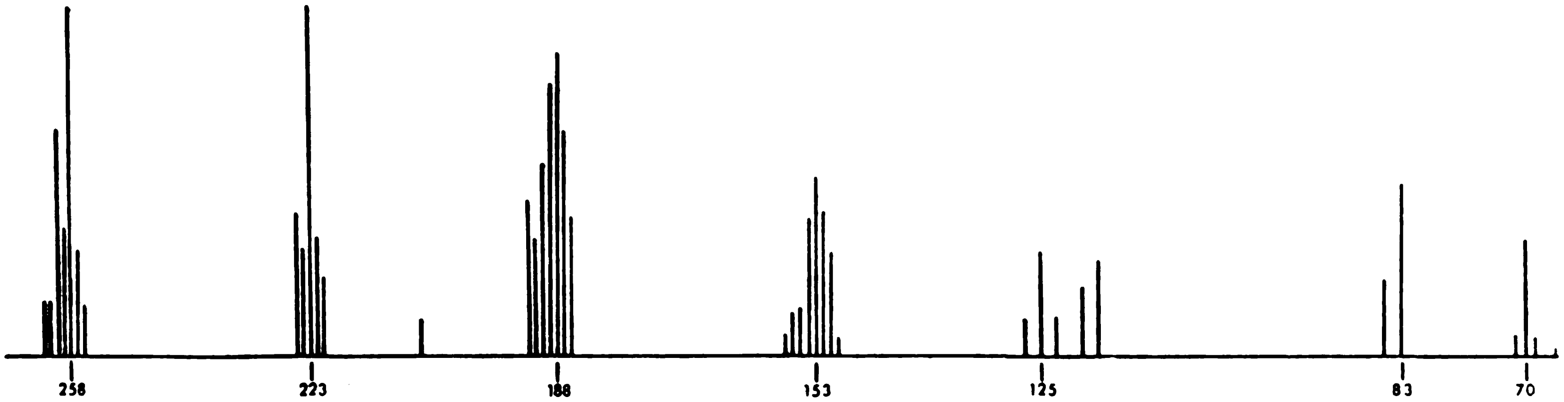


Figure 3. Mass spectrum of (D-10)titanocene dichloride

samples show increased intensity of the 253 peak (Figure 4), which corresponds to $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5D_5)TiCl_2^+$. Samples photolyzed for extended periods of time, typically ten times longer than the time required to reach equilibrium, show no change in the ratio of the m/e = 253, 258 and 248 peaks, and this ratio consequently can be used to indicate the relative concentrations of the corresponding species at $t = \infty$. Furthermore, the ratio of the m/e = 253 and 248 peaks for various periods of illumination reflects the extent of the reaction which has been completed. The fraction, F, of the exchange process which is complete after a particular time is the ratio of the m/e = 253 and 248 peaks for a sample withdrawn at that time divided by the same ratio for a sample which has reached equilibrium:

$$F = \frac{(I_{253/248})_t}{(I_{253/248})_\infty}$$

If ln(1-F) is plotted vs. time (the McKay[62] plot) a straight line will result. The most probable slope of the line was calculated by a standard least squares treatment of the data, and the rate was calculated by using the equation:[63]

$$\text{slope} = -R \left[\frac{[\text{reactant A}] + [\text{reactant B}]}{[\text{reactant A}]\ [\text{reactant B}]} \right]$$

where the bracketed quantities represent the concentrations of the indicated species.

The quantum yield was calculated by using the equation:[64]

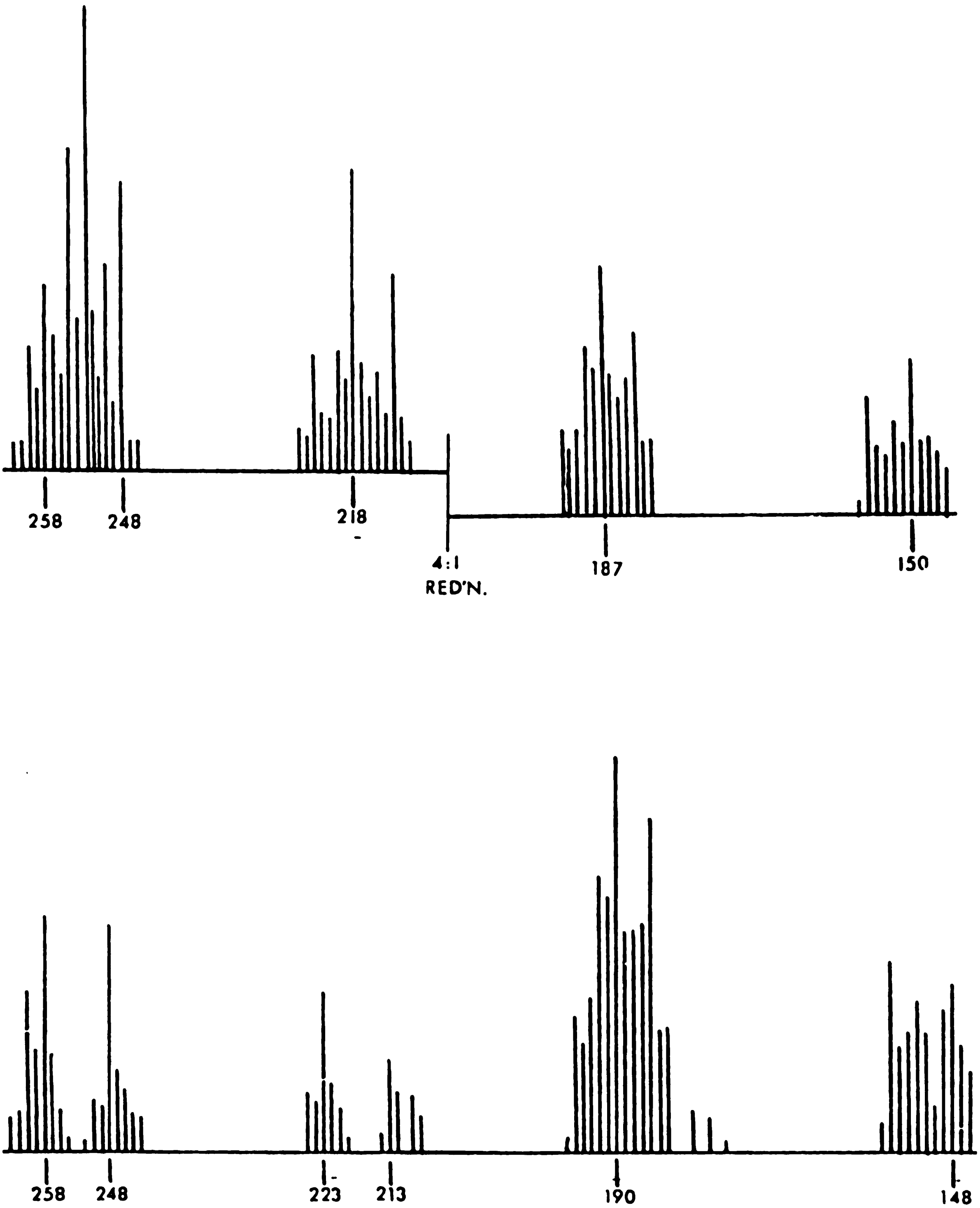


Figure 4. Mass spectra of exchange mixtures.

A. At t_∞. B. At t_0.

$$\Phi = \frac{\text{Rate (moles/liter hour)}}{\text{Intensity (einsteins/liter hour)}}$$

It should be noted that this analysis requires the intensity of the lamp to be constant with time.

The most probable intercept of the ln(1-F) axis was calculated by standard linear least squares methods, and the standard deviation of residuals was calculated by using the equation,

$$S_{\ln(1-F)} = \left[\frac{d^2}{N-1}\right]^{\frac{1}{2}}$$

J. Photolytic Methanolysis of Titanocene Dichloride

Weighed amounts of titanocene dichloride were added to about 60 ml of benzene in 100 ml volumetric flasks in the glove box and stirred until dissolution was complete. Purified methanol was then added by use of a syringe and the solution was diluted to the mark with benzene. The solutions were exposed only to very dim light after the addition of the methanol. As before, the solutions were added in 3.0 ml aliquots to pyrex culture tubes and sealed with an oxypropane torch. One sample was retained for a determination of the optical absorbance at 520 nm before photolysis, and constancy of this absorbance in the dark for up to one week. Other samples were mounted in the merry-go-round apparatus with actinometers, after the lamp had stabilized. The samples were withdrawn at about 10 minute intervals and the absorbance at 520 nm was measured to determine the extent of methanolysis. A Unicam SP 800 recording spectrophotometer and matched quartz 1 cm cells were used for all measurements. The actinometer tubes were withdrawn after longer periods of illumination to allow more conversion and thus more accurate integration of the gas chromatogram. Some sample tubes were stored in the dark for varying periods of time and the optical absorbance at 520 nm was redetermined to check for secondary thermal reactions of the photolysis products.

RESULTS AND DISCUSSION

A. Photolytic Cyclopentadienyl Ligand Exchange Between Titanocene Dichloride and Perdeuterotitanocene Dichloride

A new type of reaction, the exchange of π-bonded cyclopentadienyl ligands between identical transition metal complexes, is evidenced by the increasing concentration of (D-5)titanocene dichloride in irradiated benzene solutions originally containing (D-10)titanocene dichloride and titanocene dichloride.

Table 1 shows the pertinent peaks in the mass spectrum of the exchange mixture after selected periods of irradiation. The peaks between m/e = 60 and 72 are included to demonstrate that ligand exchange, and not hydrogen exchange on the ligands, is the process which results in the increase of the peak at m/e = 253 relative to those at 248 and 258. The small fragment and large fragment peaks are normalized separately in the table.

The calculated values for F, the fraction of exchange after selected periods of illumination, are also displayed in the table. They are calculated on the basis of the equilibrium value of 2.4 for the ratio of the m/e = 253 and 258 peaks as outlined in the experimental section. The ratio of the m/e = 253 and 248 peaks, of course, gives similar results with comparable scatter. The initial concentrations of titanocene dichloride and perdeuterotitanocene dichloride were 4.4×10^{-3} and 3.9×10^{-3} $\underline{M}$ respectively. The plot of $\ln(1-F)$ *vs.* time shown in Figure 5 indicates that the half life for the exchange was 0.83 hour,

Table 1. Mass spectrographic data for the perdeuterotitanocene dichloride-titanocene dichloride ligand exchange.

	Normalized intensities												
Time (hr) m/e =	248	253	258	65	66	67	68	69	70	71	72	I_{253}/I_{258}	F
0.0	71	4	100	100	37	9	6	17	71	21	4	0.055	0.023
0.5	71	48	100	100	39	8	5	17	73	22	4	0.68	0.28
1.0	67	84	100	100	34	7	6	17	73	18	4	1.2	0.49
1.5	68	115	100	100	34	6	5	17	72	17	5	1.7	0.70
2.0	69	135	100	100	39	7	5	17	70	21	4	1.97	0.81
2.5	67	145	100	100	41	8	6	19	71	22	5	2.17	0.89
3.0	67	151	100	100	37	8	5	17	72	20	4	2.24	0.92
4.0	65	155	100	100	49	8	6	20	68	30	5	2.39	0.98
18.0	67	163	100	100	38	6	4	17	75	15	4	2.44	1.0

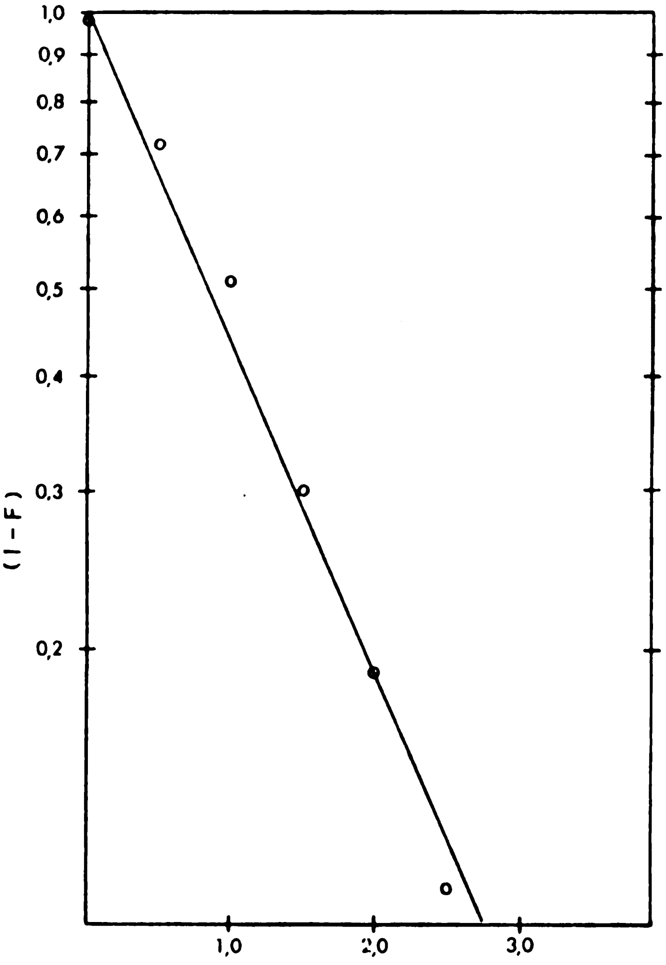


Figure 5. McKay plot for perdeuterotitanocene dichloride-titanocene dichloride exchange.

and the corresponding rate, calculated by the method outlined in the experimental section, is 1.8 x 10^{-3} $\underline{M}$ hr^{-1}. The best intercept, calculated by standard linear least squares methods, is ln(1-F) = 1.1, and the standard deviation in ln(1-F) is 0.08. The intensity of the incident radiation was 0.0078 einsteins/hr liter. The quantum yield, which is the ratio of the rate to the intensity, is 0.23 moles/einstein.

In a typical experiment, the total concentration of titanocene dichloride was 10^{-2} $\underline{M}$ (and about half of this was the deuterated species). The molar absorptivity for titanocene dichloride at 313 nm is 6 x 10^3 $\underline{M}^{-1}$ cm^{-1}, so the sample absorbance at this wavelength, assuming a 1 cm cell path length, was about 60, and all incident light was absorbed.

The actinometers were 0.107 $\underline{M}$ in valerophenone, which has a molar absorptivity of 50 $\underline{M}^{-1}$ cm^{-1}. Again assuming a path length of 1 cm, the absorbance at 313 nm was 5, so all incident light was absorbed within the limits of experimental error. Conversion of valerophenone to acetophenone was never allowed to exceed 25%.

The average intensity of the lamp, calculated from the degree of conversion of several actinometer samples, was 0.0078 einsteins/liter hr. The actinometers were exposed over different periods of time before, during, and after the sample photolysis, and established that the intensity was constant over the photolysis period.

The equilibrium constant for the reaction,

$$(\eta^5\text{-}C_5D_5)_2TiCl_2 + (\eta^5\text{-}C_5H_5)_2TiCl_2 \rightarrow 2\ (\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5D_5)TiCl_2$$

can be calculated from the intensities of the indicated peaks in the mass spectrum of the equilibrated mixture by using the equation,

$$K = \frac{(I_{253})^2}{(I_{248})(I_{258})} = 4.0$$

The empirical value of 4.0 agrees with that calculated[65] by assigning symmetry numbers to the products and reactants and calculating the entropy of mixing. Since there is little or no enthalpy change for the exchange reaction, the free energy change is due to the entropy change, and the equilibrium constant can be calculated from it by simple arguments involving only classical thermodynamics.[65]

B. Photolytic Cyclopentadienyl Ligand Exchange Between Perdeuterotitanocene Dichloride and Titanocene Monochloride Dimer

The ligand exchange between titanocene dichloride and titanocene monochloride may proceed by two mechanisms. The first is direct ligand exchange, as shown in Figure 6. The rapid oxidation state interchange illustrated in Figure 7 creates a second pathway, the ligand exchange between titanocene dichloride and itself. The mechanism illustrated in Figure 7 can be expected to contribute after a maximum induction time of less than a minute (see Appendix C).

The kinetics of the overall ligand exchange reaction (via both mechanisms) was studied only briefly because it does not add significant novel information to that obtained from the titanocene dichloride - perdeuterotitanocene dichloride system, and it is much more complicated. The data in Table 2 for the exchange in a solution initially 4.3 x 10^{-3} $\underline{M}$ in perdeuterotitanocene dichloride and 2.6 x 10^{-3} $\underline{M}$ in titanocene

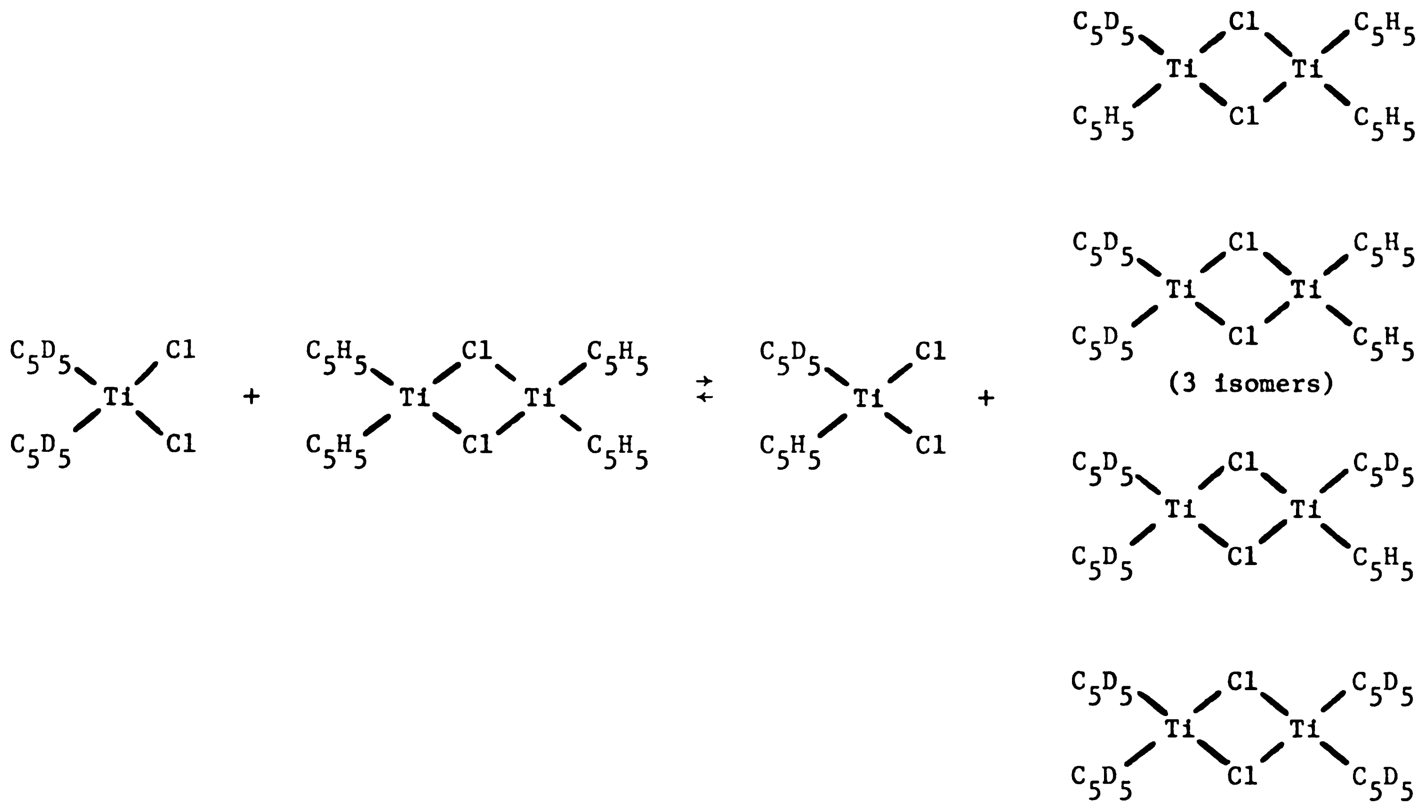


Figure 6. Direct mechanism for ligand exchange between titanocene dichloride and titanocene monochloride

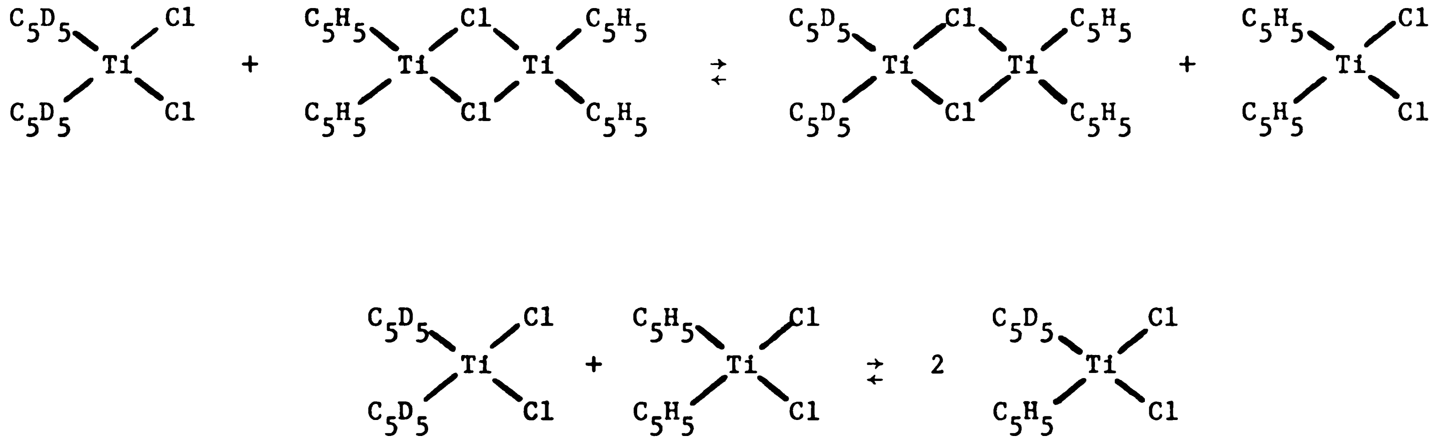


Figure 7. Oxidation state interchange mechanism for ligand exchange between titanocene dichloride and titanocene monochloride

Table 2. Mass spectrographic data for the perdeuterotitanocene dichloride-titanocene monochloride ligand exchange

Irradiation time (min)	**Normalized peak intensities** m/e = 248	253	258	**Lamp intensity*** (ei/l x1000)	**F**
10	1.1	0.31	1.0	1.2	0.17
	1.3	0.37	1.0		
20	1.5	2.3	1.0	2.4	1.0
	1.3	2.2	1.0		
30	1.3	2.1	1.0	3.6	1.0
70	1.7	2.3	1.0	8.4	1.0

*Estimated from the calculated average intensity of 7.2×10^{-3} einstein/liter hr over 100 minutes of actinometer photolysis time which spanned the sample irradiation period.

monochloride dimer clearly indicate that a simple second order treatment is not appropriate.

The equilibrium constant was not calculated because most of the species present at equilibrium were indistinguishable by mass spectrometry. The ligand exchange between titanocene dichloride and titanocene monochloride has a larger entropy change than the ligand exchange between titanocene dichloride and itself because a mixture of several isotopes is produced. The equilibrium constant for the former reaction would be larger than that for the latter because it increases as the magnitude of the entropy change increases.

The data in Table 3 were obtained for a solution which was initially 4.0×10^{-3} M in perdeuterotitanocene dichloride and 2.3×10^{-3} M in titanocene monochloride dimer. The solution was photolyzed for 27 hours, but no variation in the peak ratios occured in samples taken at 0.75, 1.5, 2.3, 3.0, 4.0, and 27 hours. The incident intensity was approximately 4×10^{-3} einsteins/liter hr. No decrease in the absorbance at 520 nm was observed for the photolyzed samples.

Table 3. Mass spectrographic data for the perdeuterotitanocene dichloride - titanocene monochloride equilibrium mixture.

Sample	Normalized peak intensities m/e = 248	253	258
Titanocene dichloride separated from the exchange solution	1.7	2.5	1.0
Titanocene monochloride separated from the exchange solution and converted to titanocene dichloride	2.0	2.5	1.0

The air sensitivity of the titanocene monochloride bipyridyl adduct precluded a direct measurement of the extent of substitution by deuterated ligands by mass spectrometry. To confirm the exchange process, the titanocene monochloride bipyridyl adduct separated from the exchange mixtures was converted to titanocene dichloride, for which the mass spectrum could easily be obtained. Information was thus necessarily lost on the total number of deuterated ligands on the dimer.

C. Photolytic Methanolysis of Titanocene Dichloride

Extensive work has been done on the substitution reactions of titanocene dichloride by A. N. Nesmeyanov and his coworkers.[66-75] It was found that the reactivity toward ferrous chloride (exchange of the η^5-cyclopentadienyl ligand to give ferrocene), toward water (hydrolysis of the η^5-cyclopentadienyl to titanium bond), and toward alcohols (alcoholysis of the η^5-cyclopentadienyl to titanium bond) increases as the electron withdrawing tendencies of other substituents on the titanocene derivative decrease. Consequently, titanocene dichloride reacted with ethanol only to a small extent, even after eight hours at reflux temperature,[68] while titanocene bis-acyl complexes react smoothly to produce cyclopentadiene and (η^5-cyclopentadienyl)(dichloro)(ethoxo)titanium(IV).[72]

Because of the inertness of the cyclopentadienyl to titanium bond in titanocene dichloride, the synthetic route to compounds such as (η^5-cyclopentadienyl)(dichloro)(alkoxo)titanium(IV) has been either the reaction of (η^5-cyclopentadienyl)titanium trichloride with hot methanol,[76] the reaction of (η^5-cyclopentadienyl)tris(alkoxo)titanium complexes with acetyl chloride,[67,69]

$$(\eta^5\text{-}C_5H_5)Ti(OR)_3 + 2\ CH_3COCl \rightarrow (\eta^5\text{-}C_5H_5)Ti(OR)Cl_2 + 2\ CH_3COOR$$

$$(\eta^5\text{-}C_5H_5)Ti(OEt)_3 + CH_3COCl \rightarrow (\eta^5\text{-}C_5H_5)Ti(OEt)_2Cl + CH_3COOEt$$

$$(\eta^5\text{-}C_5H_5)Ti(OR)_3 + 3\ CH_3COCl \rightarrow (\eta^5\text{-}C_5H_5)TiCl_3 + 3\ CH_3COOR$$

or by the redistribution reaction between cyclopentadienyltitanium trichloride and cyclopentadienyltitanium triethoxide in a 2:1 ratio,[73,74]

$$2\ (\eta^5\text{-}C_5H_5)TiCl_3 + (\eta^5\text{-}C_5H_5)Ti(OEt)_3 \rightarrow 3\ (\eta^5\text{-}C_5H_5)Ti(OEt)Cl_2$$

Alcoholysis of the titanium to chlorine bond in titanocene dichloride can be induced by the presence of a tertiary amine,[68]

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + ROH + (C_2H_5)_3N \rightarrow (\eta^5\text{-}C_5H_5)_2Ti(OR)Cl + (C_2H_5)_3N\cdot HCl$$

The bis(cyclopentadienyl)(alkoxo)(chloro)titanium complexes are usually prepared by the action of sodium cyclopentadienide on alkoxotitanium halides,[67]

$$Ti(OEt)Cl_3 + Na(C_5H_5) \rightarrow (\eta^5\text{-}C_5H_5)_2Ti(OEt)Cl$$

$$Ti(OEt)_2Cl_2 + Na(C_5H_5) \rightarrow (\eta^5\text{-}C_5H_5)Ti(OEt)_3 + (\eta^5\text{-}C_5H_5)_2Ti(OEt)Cl$$

The reaction between (η^5-cyclopentadienyl)(dichloro)(methoxo)titanium(IV) and sodium cyclopentadienide, however, does not yield the desired bis(η^5-cyclopentadienyl)(chloro)(methoxo)titanium(IV).[76]

The present work thus, provides a much-needed facile route to the (η^5-cyclopentadienyl)(dihalo)(alkoxo)titanium(IV) complexes. The quantum yield is large, especially for solutions with high concentrations of both alcohol and titanocene dichloride, and gram quantities of product can be prepared in about an hour in a suitable preparative cell. This is also a convenient route to the (η^5-cyclopentadienyl)titanium trihalides, which can be prepared from the (η^5-cyclopentadienyl)(dichloro)(alkoxo)titanium(IV) complexes:

$$(\eta^5\text{-}C_5H_5)Ti(OR)Cl_2 + HCl \rightarrow (\eta^5\text{-}C_5H_5)TiCl_3 + HOR$$

In the photolysis experiment, the lamp was allowed to stabilize for one day before the actinometer tubes were mounted in the merry-go-round (at time = 0). Methanolysis samples with concentrations of reactants as shown in Table 4 were mounted at 1800 seconds, then removed at 4200 and 6100 seconds. The actinometers were removed after 7500 and 10,400 seconds, so that they were exposed long enough to give an accurately measurable conversion. Table 4 shows the initial absorbance at 520 nm, and the absorbance of the solutions after each photolysis period. Control samples which were stored in the dark for 36 hours showed no change in absorbance at 520 nm, and photolyzed samples which were stored in the dark for 36 hours showed no change in absorbance from that measured immediately after photolysis. Thus no thermal reaction occurred at room temperature, and no secondary thermal reaction of the photolysis product occurred.

Since the molar absorptivity of titanocene dichloride is 6×10^3 and the initial concentration of titanocene dichloride was always greater than 4×10^{-3} $\underline{M}$, the initial absorbance was greater than 24, and all incident light was absorbed. Even after 4300 second photolysis periods, the titanocene dichloride concentration was at least 7.7×10^{-4} $\underline{M}$, so that the absorbance was 4.8 at 313 nm, and again all light was absorbed, within experimental error. Neither benzene nor methanol absorb at 313 nm although they both absorb strongly below 280 nm. The product does absorb at 313 nm, and since it is produced in concentrations greater than 2×10^{-3} $\underline{M}$ it might be expected to reduce quantum efficiency. The fact that the decrease in absorbance of the photolyzed samples was

Table 4. Photomethanolysis data for titanocene dichloride

Sample	$[(\eta^5\text{-}C_5H_5)_2TiCl_2]$, $\underline{M} \times 10^3$	[Methanol], $\underline{M}$	A_o	A_{2400}	A_{4300}	A^*_o	A^*_{2400}	Φ**
A	8.1	0.25	1.80	1.34	1.02	1.80	1.32	0.28
B	8.1	0.50	1.80	1.23	0.84	1.80	0.84	0.35
C	8.1	1.00	1.80	1.08	0.54	1.80	0.55	0.44
D	4.05	0.25	0.95	0.52	0.34	0.95	0.34	0.25
E	4.05	0.50	0.95	0.46	0.24	0.96	0.25	0.29
F	4.05	1.00	0.95	0.38	0.18	0.95	0.16	0.33

*After 36 hours in the dark

**Based on the 2400 second reaction period proportional to photolysis time up to 4300 seconds indicates, however, that there was little product interference.

The actinometers were 0.204 M in valerophenone, and thus absorbed all incident light. The light intensity was 4.6×10^{-3} einsteins/liter-hr. The quantum yield, Φ, was calculated by using the equation,

$$\Phi = \left[\frac{A_o - A_t}{(2.2 \times 10^2)(L)}\right] \times \left[\frac{1}{4.6 \times 10^{-3}}\right] .$$

where A_o = the initial absorbance at 520 nm

A_t = the absorbance at 520 nm after photolysis for t hours

2.2×10^2 = the molar absorptivity for titanocene dichloride at 520 nm

L = the cell path length in cm.

The product obtained from the photolysis melts at approximately 100°. This can be compared to the previously reported melting point of 93-96°.[76] The mass spectrum of the methanolysis product (Figure 8) shows a parent ion peak manifold centered at m/e = 214, which corresponds to $(\eta^5\text{-}C_5H_5)Ti(OCH_3)Cl_2^+$. The relative peak intensities are close to those expected for a species containing two chlorine atoms.[77] The spectrum is otherwise predictable[72, 59-61] except for the absence of a peak at m/e = 183 and the presence of several impurity peaks. The most intense of the large fragment peaks is at m/e = 148, and the surrounding manifold reflects a high abundance of both $(\eta^5\text{-}C_5H_5)TiCl^+$ (m/e = 148) and $Ti(OCH_3)Cl_2^+$ (m/e = 149).

Extended photolyses, and photolyses conducted with unfiltered light gave mixtures of products.

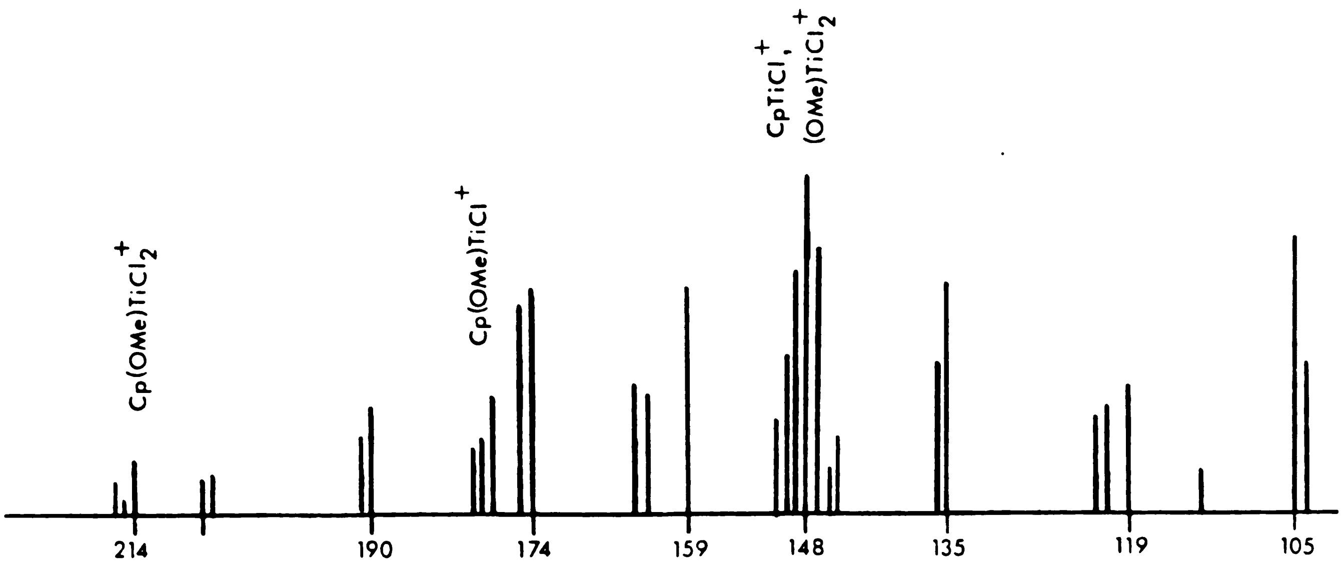


Figure 8. The mass spectrum of the photomethanolysis product.

D. Reaction Mechanisms

A mechanism can be proposed for the photosubstitution and photoexchange reactions of the cyclopentadienyl ligand on titanocene dichloride on the basis of fundamental group theoretical and chemical considerations. The symmetry of titanocene dichloride is C_{2v}. Titanium is in the +4 oxidation state in titanocene dichloride, and therefore has a d^0 electronic configuration. If coordinate axes are chosen as in Figure 9, the nonbonding titanium d_{z^2} and d_{xy} orbitals will be the lowest unoccupied molecular orbitals.[78] As Figure 10 shows, the molecular orbitals of interest in titanocene dichloride might arise from either a distortion of the ferrocene (D_{5d}) configuration or a distortion of the tetrahedral (T_d) configuration. A representation of titanocene monochloride dimer analogous to Figure 9 would show that it has D_{2h} symmetry, with d_{z^2} and d_{xy} orbitals available for metal-metal bonding.[79]

The visible spectrum of titanocene dichloride, shown in Figure 11, is explained by three charge transfer transitions. The weak, narrow band at 520 nm and the stronger, narrow band at 390 nm ($\varepsilon = 2000$) probably arise from ligand to a_1 and ligand to b_1 transitions. Both the a_1 (d_{z^2}) and b_1 (d_{xy}) orbitals are nonbonding, so little or no vibrational excitation would accompany the electron transfer and narrow bands would be expected. The broad, intense band centered at 280 nm ($\varepsilon_{max} = 13{,}000$) probably arises from a ligand to a_1 ($d_{x^2-y^2}$) antibonding orbital. It is this transition which results from irradiation with the 313 nm light used in the photolysis experiments.

In substituted ferrocene systems, and in the bis(benzene)chromium system, a common photolytic pathway is scission of the metal to ring

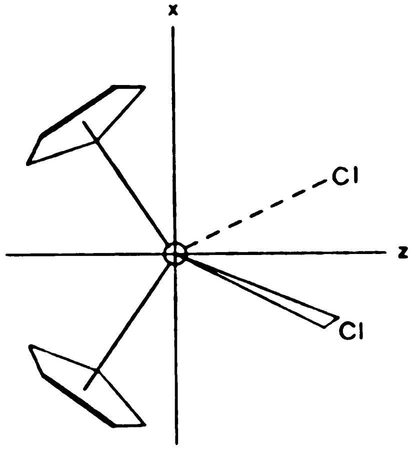


Figure 9. Coordinate axes chosen for titanocene dichloride

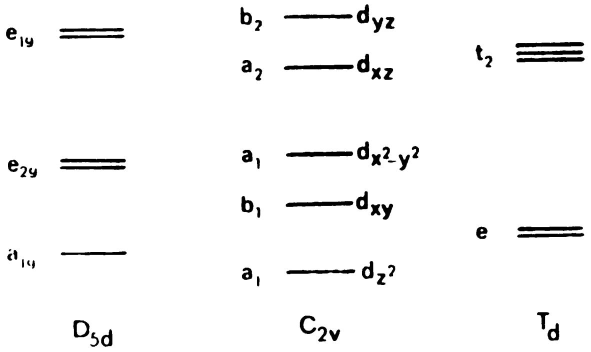


Figure 10. Titanocene dichloride molecular orbitals.

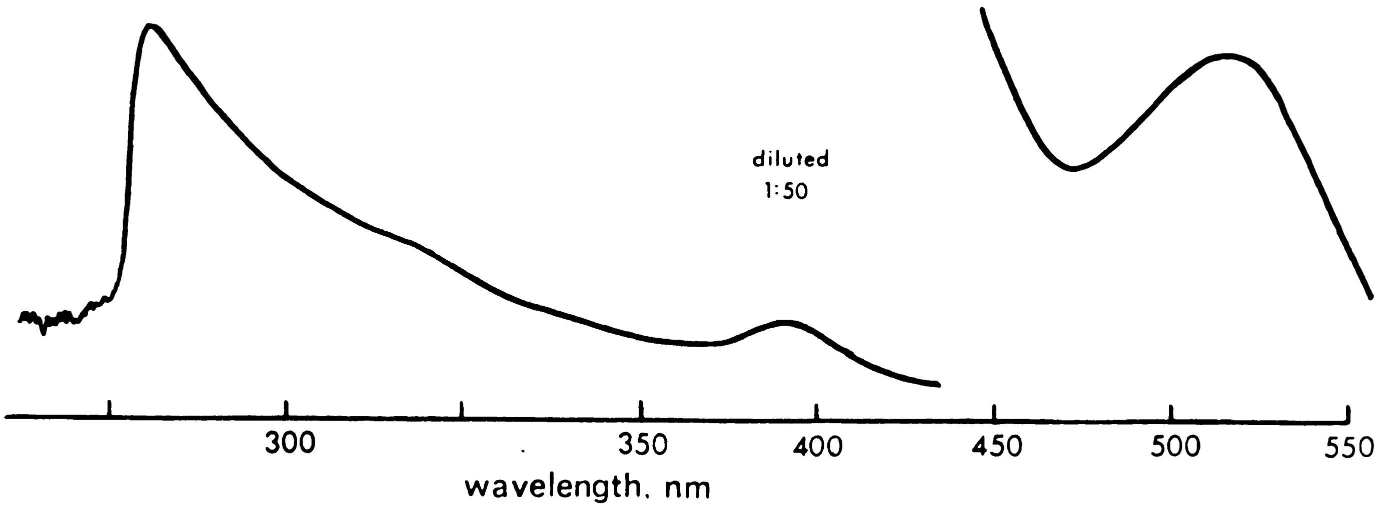


Figure 11. Ultraviolet-visible sbsorption spectrum of titanocene dichloride

bond.[45] The titanium to cyclopentadienyl bond may, of course, be broken in the present system, but this is unlikely for several reasons: First, this would probably lead to decomposition and intractible photolysis products. In ligand exchange experiments, however, decomposition was negligible compared to the primary process. Furthermore, a bound cyclopentadienyl radical would tend to abstract a proton from a methanol molecule attacking adjacent to it, while a dissociated cyclopentadienyl radical would tend to react with other dissociated radicals. Second, the titanium to cyclopentadienyl bond is a multiple bond and it is particularly inert to substitution in titanocene dichloride. Reduction of bond order, rather than total bond scission, would be a more reasonable hypothesis with regard to reaction energetics. Third, thermal processes in which the η^5-cyclopentadienyl ligand probably undergoes a conversion to a σ-bonded,η^1-cyclopentadienyl intermediate are known for some titanocene species.[80] Brintzinger and Bartell[81] have shown that an electronic transition from ligand e_{1g} π-orbitals to a titanium a_{1g} orbital leads to a distortion of e_{1g} symmetry.* A $\eta^5 \rightarrow \eta^1$ distortion has this symmetry. Thus the electronic transition which probably results from irradiation with 313 nm light is one which promotes a η^5 to η^1 bonding rearrangement.

In light of the present experimental results, it is reasonable to propose reduction in bond order from η^5 (to η^1 as a limiting case) as the first step in both the methanolysis and ligand exchange reactions of titanocene dichloride. The coordination number of titanium is thus reduced, allowing the attack of the entering group. The suggested

---

*Notations appropriate to D_{5d} symmetry were used because the titanocene system was treated as a perturbed ferrocene system.

mechanism is illustrated in Figure 12.

It must be noted that reduction of the coordination sphere may not be necessary for ligand substitution. Titanocene monochloride forms a 1:1.5 bipyridine adduct which must have a coordination number of at least 5, while Coutts and Wailes[58] suggest a coordination number of 6. Attack of the entering group could thus occur before, or in concert with, cleavage of the leaving group bonds. These pathways are probably experimentally indistinguishable from the suggested one.

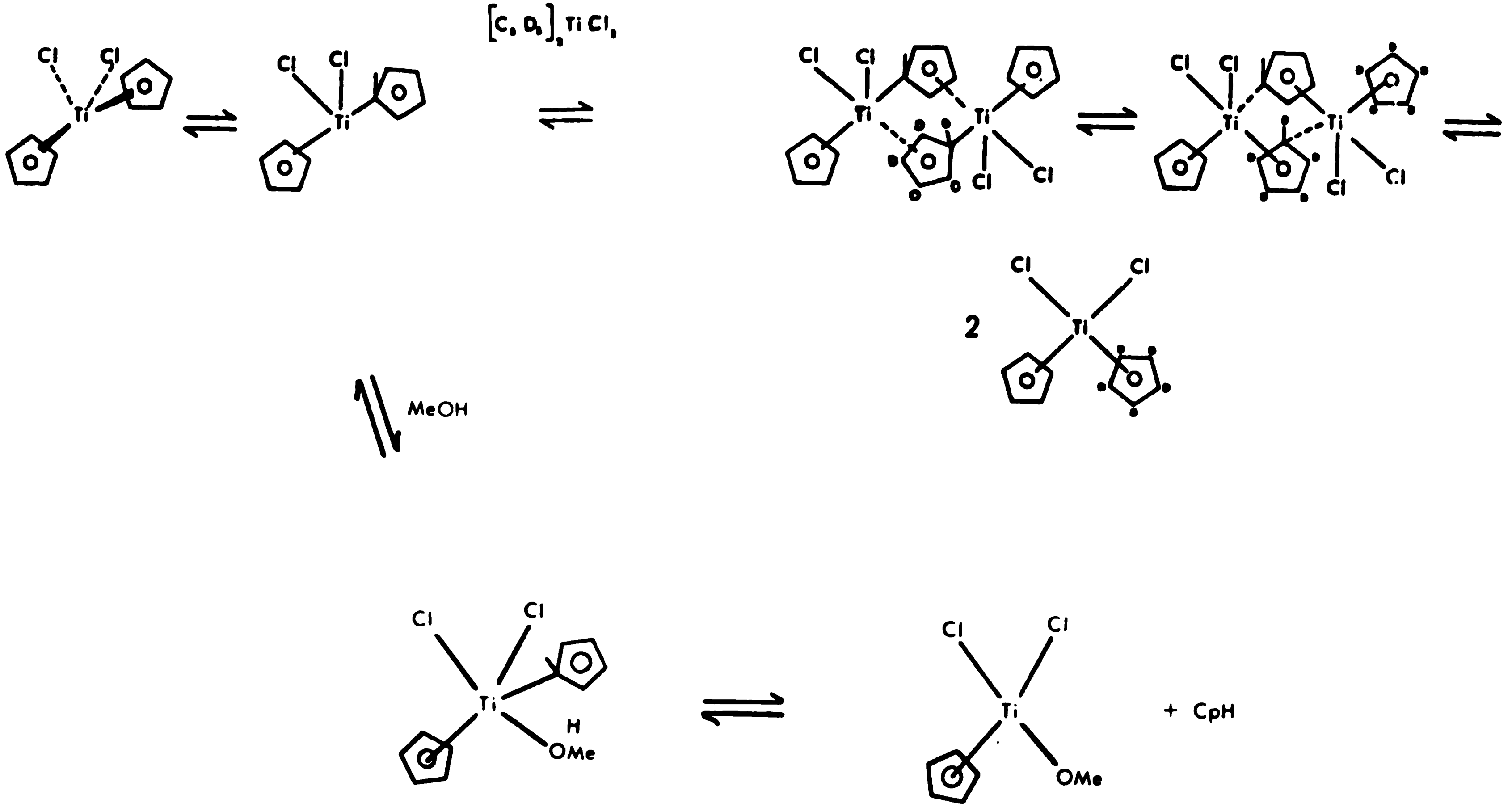


Figure 12. Proposed mechanism for photolytic reactions of titanocene dichloride.

SUMMARY

The present research has demonstrated the importance of photolytic processes in the chemistry of titanocene dichloride. Specifically, the η^5-cyclopentadienyl ligand exchange between molecules of titanocene dichloride and between titanocene dichloride and monochloride, and the methanolysis of titanocene dichloride are photolytic. A mechanism based on photolytic reduction of the bond order of the η^5-cyclopentadienyl to titanium bond has been proposed as the initial step of these processes.

The discovery of the photolytic activity of titanocene derivatives indicates a new dimension which must be controlled in all related work, and which, it is hoped, will be exploited to yield novel results in further work.

APPENDICES

APPENDIX A

THE HALIDE EXCHANGE BETWEEN TITANOCENE DICHLORIDE AND TITANOCENE DIBROMIDE

A benzene solution initially 3.7×10^{-3} *M* in titanocene dichloride and 1.4×10^{-3} *M* in titanocene dibromide contained the mixed halide complex in the same molar ratio after 18 hours irradiation as it did when immediately frozen in the dark and evaporated to dryness. Thus the halogen exchange is rapid and thermal. An equilibrium constant of 0.5 was found for the reaction,

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + (\eta^5\text{-}C_5H_5)_2TiBr_2 \rightleftarrows 2\ (\eta^5\text{-}C_5H_5)_2TiClBr$$

Experimental

Titanocene dibromide was prepared by a new method, which involved treating the titanocene hydride polymer[54] in toluene with HBr at -70^{c}. The sublimed product melted at 305°C. All other materials were prepared and/or purified in the usual manner. Separate solutions of titanocene dibromide and titanocene dichloride in about 75 ml of benzene were mixed in the dark. One aliquot (*ca.* 30 ml) was frozen and the solvent was sublimed in the dark, and the mass spectrum of the titanocene derivative was obtained. The remainder of the exchange solution was sealed into pyrex culture tubes in the usual manner and mounted in the photolysis apparatus. The samples were photolyzed for up to 18 hours (over which time the intensity was about 0.010 einsteins/liter hr), evaporated to dryness, and the mass spectrum was obtained.

Discussion

The mass spectra of the photolyzed and unphotolyzed samples were identical. The main peaks are shown in Figure 13. It appears that halide ligands on titanocene dihalides are thermally labile, in contrast to the cyclopentadienyl ligands.

The equilibrium constant was calculated from the intensities of the product and reactant peaks in the proper ratio. The sum of the intensities of all peaks in the peak manifold of the species of interest was taken to be proportional to the concentration of that species, and an equilibrium constant of 0.5 was calculated for the reaction:

$$K = 0.5 = \frac{[(\eta^5\text{-}C_5H_5)_2TiClBr]^2}{[(\eta^5\text{-}C_5H_5)_2TiCl_2]\,[(\eta^5\text{-}C_5H_5)_2TiBr_2]}$$

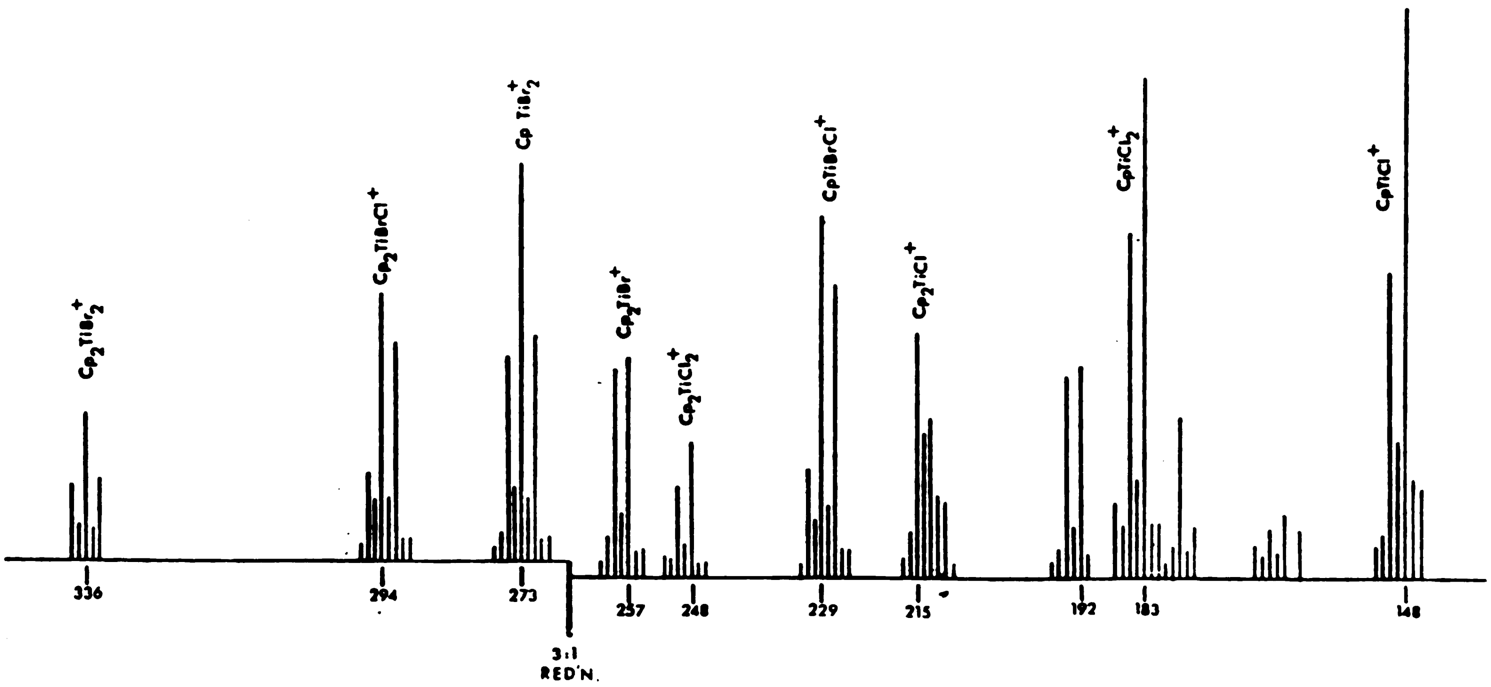


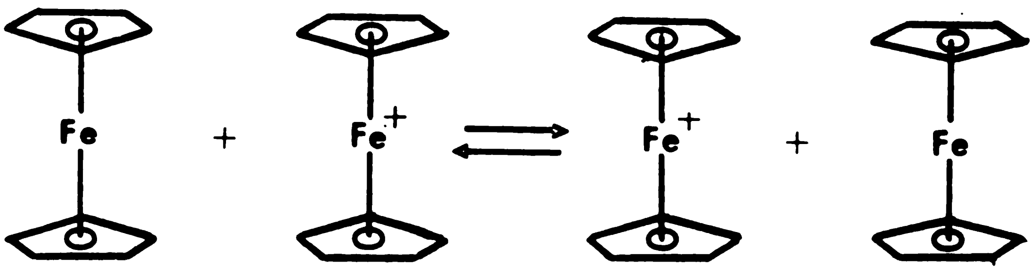
Figure 13. Mass spectrum of the halide exchange product.

APPENDIX B

THE ELECTRON EXCHANGE BETWEEN BIS(ARENE)CHROMIUM COMPLEXES AND THEIR CATIONS

I. Introduction

Recent interest in measuring the rate of electron exchange between sandwich complexes and the corresponding cations (obtained by one electron oxidation of the complex) has been intense. The electron exchange between ferrocene and the ferricenium ion,



is typical of this class of reaction, and has been studied extensively.

The first study of electron exchange in a sandwich complex system was done by Voigt and Katz in 1958.[82] The exchange between bis(cyclopentadienyl)cobalt(II) and bis(cyclopentadienyl)cobalt(III) was found to be "very fast."

In 1960, D. R. Stranks did a tracer study of the ferrocene-ferricenium exchange by using stopped flow techniques. By cooling methanol solutions of the reactants to -70°, he was able[83] to estimate the exchange rate constant at 1.7×10^6 $\underline{M}^{-1}$ sec^{-1}.

In 1963, Dietrich and Wahl studied the same system by nmr line-broadening techniques.[84] They established that the rate constant for the reaction in acetone at room temperature was greater than 10^5 $\underline{M}^{-1}sec^{-1}$.

The acceleration of the diffusion of ferricenium ions through a solution of ferrocene in alcohol by the electron exchange process was used by I. Ruff, _et al_. in 1971 to determine a rate constant of greater than 1.5×10^{9} $\underline{M}^{-1}$ sec^{-1} at room temperature.[85]

Recently, Espenson and Pladziewicz used the Marcus relation for outer sphere electron transfer to calculate the rate of self-exchange between ferrocene and ferricenium from data on the rate of mixed exchange reaction (_i_. _e_. between bis(methylcyclopentadienyl)iron(II) and ferricenium cation). These experiments were done in tetrahydrofuran-water mixtures and yielded a calculated value of 5.7×10^{6} $\underline{M}^{-1}$ sec^{-1} for the rate constant for electron exchange between ferrocene and ferricenium ion.[86]

The results on the ferrocene system are not consistent. The esr linebroadening technique cannot be applied to the ferrocene system because of the short relaxation time characteristic of the ferricenium cation[87] so further corroboration of the results above seems unlikely.

The isoelectronic and isostructural bis(benzene)chromium(0) (abbreviated bz_2Cr) - bis(benzene)chromium(I) [abbreviated $bz_2Cr(I)$] system escapes the difficulty of short relaxation time, and is a tantalizing system for electron exchange studies for this and a myriad of other reasons: Molecular orbital bonding schemes are highly refined.[88-90] A polarographic wave is obtained at -0.97 V _vs_. SCE regardless of the direction of approach, which reflects the necessary reversibility.[91-94] Methyl derivatives, like bis(toluene)chromium, have more negative reduction potentials, while phenyl derivatives, like bis(1,3,5-triphenyl)-chromium, have more positive reduction potentials.[95-97] Good theoretical correlation is obtained between the reduction potential and the localization of the highest occupied molecular orbital (HOMO) predicted by substituent effects,[98] and correlations with exchange rates would be interesting. The core sandwich structure remains essentially the same through the series of derivatives,[99] so free energy changes related to electronic reorganization and inner sphere solvent effects can be eliminated for theoretical treatment. The fact that one of the reactants is neutral allows further simplification in theoretical calculations of the exchange rate, since coulombic interaction is nonexistent. Theory has not dealt extensively with ion-molecule reactions in solution.

Finally, the electron exchange would necessarily be simple, because associated chemical reaction of the ligands, ion transfer, or atom transfer are unlikely. The chemistry of $bz_2Cr(0)$ and $bz_2Cr(I)$ is well known, and has been reviewed several times.[100, 101] The ultraviolet[102-104] and infrared[105] spectra have been analyzed. The structure has been studied thoroughly[106-110] and the symmetry established as D_{6h}. The esr spectrum is reminiscent of those of organic arene radicals, with 3.6 G hyperfine due to arene protons and similarly narrow hyperfine due to ^{53}Cr.[111-113]

For these reasons, the electron exchange between $bz_2Cr(0)$ and $bz_2Cr(I)$ was studied, first by tracer techniques which established a lower limit on the rate constant, second by esr linewidth measurements, and finally by the nmr technique.

II. Quenched-Flow Study of the Electron Exchange Between Bis(benzene)-chromium(0) and Bis(benzene)chromium(I).

A quenched-flow experiment established the lower limit of 4 x 10^3 $\underline{M}^{-1}$ sec^{-1} for the rate constant for the electron exchange between $bz_2Cr(0)$ and $bz_2Cr(I)$ in dimethyl sulfoxide. A 1.0 x 10^{-2} $\underline{M}$ solution of $bz_2Cr(0)$ was rapidly mixed with a 9.8 x 10^{-3} $\underline{M}$ solution of bis-(benzene)chromium iodide, bz_2CrI, containing ^{51}Cr at a specific activity of 5.3 x 10^5 cpm/mmole. The molecule was separated from the cation after a 0.07 second reaction time by spraying the exchange solution into water at 0°C. The $bz_2Cr(0)$ precipitated immediately and was removed by filtration. The specific activity of the initially inactive complex indicated that equilibrium with respect to exchange had been reached.

It was found that bz_2CrI undergoes Szilard-Chalmers reactions when it is bombarded with neutrons. The product of the Szilard-Chalmers reaction does not oxidize $bz_2Cr(0)$, so electron transfer experiments run with tracer prepared by neutron bombardment of bz_2CrI indicate that no exchange occurs. A true measurement of the exchange rate between $bz_2Cr(0)$ and $bz_2Cr(I)$ can be made only if the tracer is prepared from $^{51}CrCl_3$.

Experimental

A. Preparation of Materials

The $bz_2{}^{51}CrI$ tracer was prepared from anhydrous chromium chloride which was bombarded *ca*. 1 h with a neutron flux of 2 x 10^{12} neutrons/cm^2-sec in the MSU/TRIGA Reactor to give an activity of 2.8 x 10^5 cps/mg. The high chlorine and ^{55}Cr activity which resulted was allowed to decay before the samples were handled. The bz_2CrI was prepared by sealing the active $^{51}CrCl_3$ in a pyrex tube of about 100 ml capacity with sublimed $AlCl_3$, aluminum powder, and benzene. The tube was rotated in an oven following the Friedel Crafts preparative method of Fischer.[114] It was purified by recrystallization from an aqueous solution of KI. The zerovalent bz_2Cr was prepared by a similar method, except that a final step involving reduction of the product with $Na_2S_2O_4$ was required,[115] and the product was purified by vacuum sublimation.

Dimethylsulfoxide was vacuum distilled from CaO at low temperature to avoid decomposition. Water was distilled from $KMnO_4$ and then vacuum distilled to remove air.

B. Gamma Counting Procedures

Solvent was evaporated from or added to samples obtained from the separated exchange mixture to yield solutions of about 1 ml volume, and they were sealed in 15 mm pyrex test tubes.

The 0.32 MeV gamma radiation from the ^{51}Cr ($t_{1/2} = 27.8$ d) isotopic tracer was counted by use of a sodium iodide scintillation detector (Packard Model 1212 WSP) and a Nuclear Data Series 130, 512 Channel Analyzer/Computer that automatically integrated the channels corresponding to the sample peak to give an output of total counts (sample plus background) for those channels. The background activity was calculated by adding the counts registered by the three channels before the first of the integrated channels, and the three after the last of the integrated channels and dividing by 6 to give an estimate of the average number of background counts per channel. This average was multiplied by the number of channels integrated to give the total background count and was subtracted from the total counts output.

About 10^4 counts were recorded for most samples, and the measured activity was adjusted for decay between collection time and counting time.

C. Quantitative Analysis of Chromium

The dimethylsulfoxide solutions of bz_2Cr and bz_2CrI were washed from the counting ampoules with 2 ml benzene, 2 ml methanol, 1 ml concentrated H_2SO_4, and 4-5 ml concentrated HCl. The solution was heated for several hours to digest the organometallics (and most of the DMSO). The samples turned green in this time. Sodium hydroxide (5 M) was then added to make the samples basic, and 10 ml of 30% H_2O_2 was added. The samples turned yellow immediately as the chromium was oxidized to Cr(VI). They were boiled for 1-2 hours to destroy excess peroxide, diluted to known volumes, and added to quartz, 1 cm cells so that the absorbance at 372 nm could be accurately measured on a Cary Model 14 Spectrophotometer.

A calibration solution was prepared by dissolving 0.0303 g $K_2Cr_2O_7$ in 0.05 M KOH to make 1.00 liter of solution with an absorbance of 1.0.

D. The Szilard-Chalmers Reaction of Bis(benzene)chromium Iodide

Bz_2CrI prepared from $^{51}CrCl_3$ was split into two samples, one of which was subjected to further neutron bombardment. Both samples were dissolved in air free water, and added under nitrogen to 15 x 1 cm columns of Dowex 50WX4 cation exchange resin. Dilute, air free hydrochloric acid was added to the columns as needed, and aliquots of about 1 ml volume were collected. The sample subjected to the second bombardment separated on the column to give a high specific activity fraction (aliquots 25 - 28) as well as a fraction common to both samples (aliquots 36 - 40) which had a specific activity nearly identical to that of the bz_2CrI prepared from $^{51}CrCl_3$.

If DMSO solutions of neutron-bombarded bz_2CrI were added to the exchange column without strict air exclusion, nearly all the activity was retained in the first few centimeters of resin even after 50 ml of elutate was collected. This top layer of the column turned green slowly during the elution. A yellow solution, identical in appearance to bz_2CrI solutions, but which contained no chromium, was obtained in aliquots 27 - 75 of elutate.

E. Quenched-Flow Experiments

A diagram of the quenched-flow apparatus is shown in Figure 14. A pneumatic plunger, driven by compressed air at 50 psi operated two sample syringes which could be filled with the reactant solutions under nitrogen. The mixing chamber was designed to give high turbulence. The time of the plunging stroke (0.4 seconds) was measured by using a Heath Universal Analog Computer with a Heath Timer Module which was activated by microswitches at the extremes of plunger travel. The reaction time was calculated as follows: Since the apparatus delivered 15.6 ml of solution in 0.4 seconds, it delivers 39 ml/sec. The volume of the apparatus from the mixing chamber to the outlet in the quench solution was 2.8 ml. It follows that the reaction time was 2.8/39 = 0.07 seconds.

Schlenk flasks containing the DMSO solutions of reactants under nitrogen, and the quench of air-free water, were attached to the apparatus without admitting air. The plunger was activated to mix the reactants and spray them into the quench. The quench mixture was immediately filtered, and the respective samples were prepared for counting as

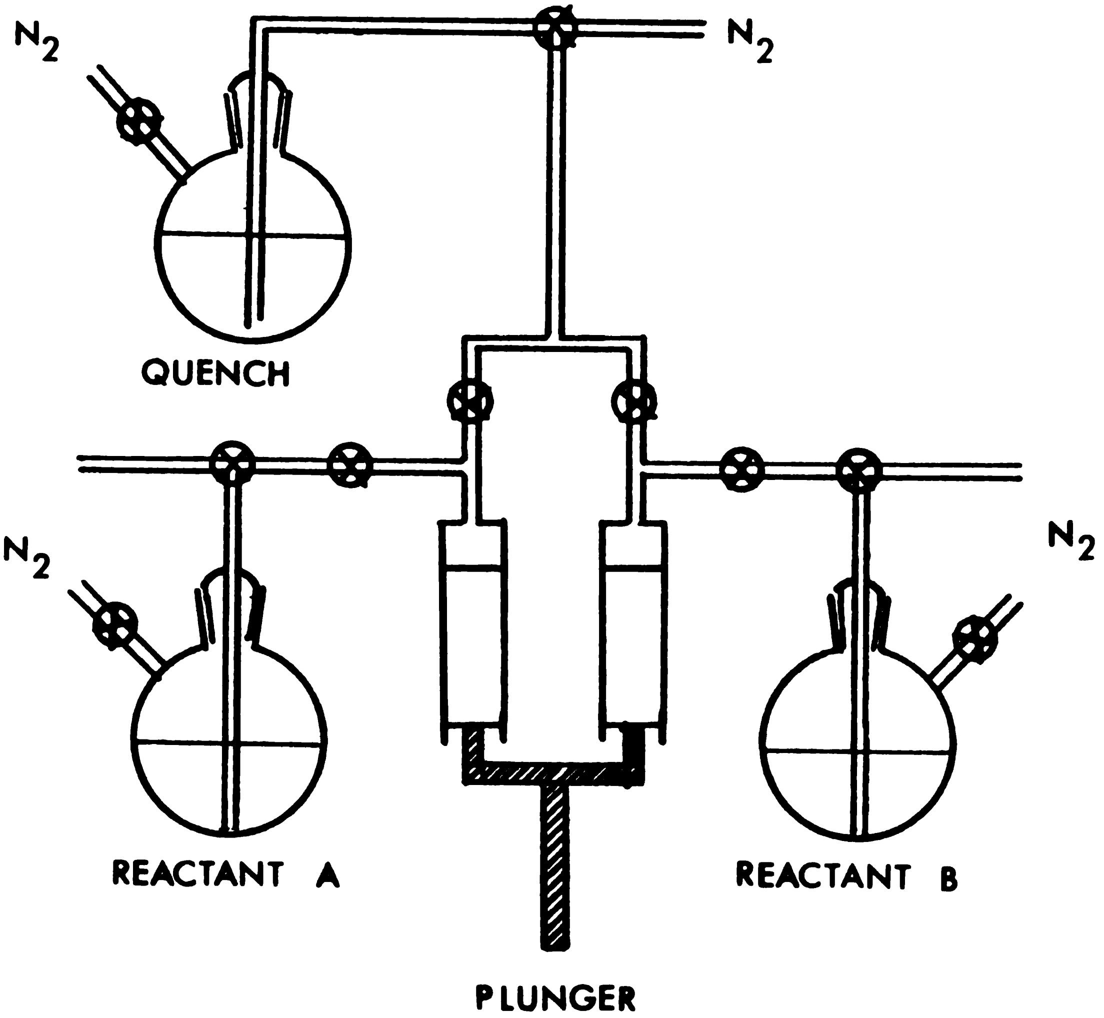


Figure 14. Quenched-flow apparatus.

previously detailed. A t_∞ sample was obtained by activating the plunger to deliver a sample which was not separated (quenched). Instead, this sample was subjected directly to counting and analysis to determine the total amount of chromium and the total activity. From these totals, a specific activity can be calculated which should be equal to the specific activity of either species in the exchange solution at equilibrium.

Discussion

The rate constant for the electron exchange can be calculated from the standard equation,

$$k = \frac{0.693}{(t_{1/2})\ ([bz_2Cr(0)] + [bz_2Cr(I)])}$$

In the exchange experiment, the sum of the concentrations of the reactants, $([bz_2Cr(0)] + [bz_2Cr(I)])$ was 9.9×10^{-3} $\underline{M}$. If the reaction time (in which the reaction reached completion) is assumed to be at least four times the half life, $t_{1/2}$, then the rate constant is greater than 4×10^{3} $\underline{M}^{-1}$ sec^{-1}. Pertinent data for the exchange experiment are displayed in Table 5. Some error arose from difficulties in decomposing the organometallic compounds and DMSO in the quantitative determination of chromium. The expected, well resolved esr spectra were obtained for the bz_2CrI and oxidized $bz_2Cr(0)$ recovered from the quench mixture.

The exchange was checked by preparing the $bz_2{}^{51}Cr(0)$ tracer (rather than $bz_2{}^{51}CrI$ tracer) and measuring the activity of the (initially inactive) bz_2CrI after mixing and separating the reactants. The exchange

Table 5. Quenched-flow exchange experimental data.

Sample Description	Chromium, mmoles x 10^3	Activity, cpm x 10^{-3}	Specific Activity cpm/mmole	Comments
1.0 ml t_∞ sample	9.0	1.91	2.1×10^5	$[Cr] = 9.0 \times 10^{-3}$ $\underline{M}$
2.0 ml $bz_2Cr(0)$ solution	20	0.0	0.0	$[Cr] = 1.0 \times 10^{-2}$ $\underline{M}$
2.0 ml bz_2CrI solution	20	9.1	4.6×10^5	$[Cr] = 1.0 \times 10^{-2}$ $\underline{M}$
Aqueous filtrate from quench mixture	11	1.8	1.6×10^5	
Precipitate from quench mixture	13	2.3	1.8×10^5	

was complete in less than 30 seconds, the shortest time checked in this "reverse direction" of exchange.

Exchange experiments run with $bz_2{}^{51}CrI$ tracer prepared by neutron bombardment of bz_2CrI (rather than from $^{51}CrCl_3$) showed no exchange. This proved to be a consequence of a Szilard-Chalmers reaction of bz_2CrI that resulted in a product that did not oxidize $bz_2Cr(0)$. The presence of the Szilard-Chalmers product was proved by preparing a sample of bz_2CrI from $^{51}CrCl_3$, dividing the bz_2CrI into two samples, and subjecting one to further neutron bombardment. When aqueous solutions of both samples were added to Dowex 50WX4 ion exchange columns, the sample which was subjected to the second bombardment separated to give a high specific activity fraction as well as a fraction common to both samples with a specific activity nearly identical to that of the bz_2CrI prepared from $^{51}CrCl_3$. The high specific activity fraction (Szilard-Chalmers product) was unstable in air, and no characterization was attempted.

III. Study of the Electron Exchange Between Bis(arene)chromium Complexes and Their Cations by ESR Technique

The width of esr signals is a measure of the lifetime of the electron in a particular state. The rate of processes that change this lifetime may be studied by determining the effect of the process on the esr linewidth.[116-120] Electron exchange is, of course, such a process. The method developed by Weissman[121] was applied to the study of the electron exchange in the systems $bz_2Cr(0)$ - $bz_2Cr(I)$ and bis(biphenyl)-chromium(0) - bis(biphenyl)chromium(I), $biph_2Cr(0)$ - $biph_2Cr(I)$, in dimethylsulfoxide and benzene.

While results were often consistent within a particular experiment, sets of experiments in which historical factors (methods of sample preparation, of material purification, etc.) were varied were often inconsistent. In some experiments the concentration of the complex could be increased from zero to near the level of saturation without affecting the linewidth of the esr signal of the cation present; in others, broadening did occur in the expected way. If the Weissman method was applied, the rate constant for $\text{biph}_2\text{Cr(0)}$ - $\text{biph}_2\text{Cr(I)}$ electron exchange was calculated to be 3.4×10^9 $\underline{M}^{-1}$ sec^{-1} in benzene and 2.7×10^9 $\underline{M}^{-1}$ sec^{-1} in DMSO. In some experiments broadening occured to the extent that all hyperfine structure collapsed.

Because of its occasional absence, however, it is likely that broadening was due to a state perturbing process (other than electron exchange) that occurs at a frequency near that corresponding to the separation of the hyperfine components of the signal, which is due to (or promoted by) species other than the bis(arene)chromium complexes and their cations. If the broadening is spurious, then the experiments showing no broadening limit the rate constant for the electron exchange to $k < 3 \times 10^8$ $\underline{M}^{-1}$ sec^{-1}, and the experiments showing broadening are irrelevant.

In a search for possible complicating processes, it was found that biph_2CrI undergoes photodecomposition *via* a CTTM (charge transfer to metal) transition that resulted in production of iodine and (probably) $\text{biph}_2\text{Cr(0)}$.

To allow study of the electron exchange between bis(arene)chromium molecules and the corresponding cations in benzene, a new compound, bis(benzene)chromium tetrabutylaluminate, was prepared. This compound had high solubility in benzene. The preparative method appears to be one of general utility for creating benzene-soluble ionic species.

Experimental

A. Preparation and Purification of Materials

Bis(benzene)chromium and its univalent cation were prepared as in the previous experiment. Bis(biphenyl)chromium(0) and bis(biphenyl)-chromium iodide were prepared by standard techniques.[122] Solvents were purified as in the previous experiments.

Bis(benzene)chromium tetrabutylaluminate was prepared by adding a solution of sodium tetrabutylaluminate (0.4 g in 10 ml benzene) to a suspension of bz_2CrI (0.1 - 0.5 g) in benzene (10 ml). Additions must be made dropwise and with adequate stirring to prevent reduction of the complex. The resulting solution was filtered and evaporated. The product was triturated with ether, and further purified by subliming foreign matter from it under high vacuum. The yellow product is soluble in benzene.

Sodium tetrabutylaluminate[123] was prepared by adding 50 ml of tributylaluminum and 10 g. of sodium to 125 ml of n-heptane in a 250 ml Morton flask, then heating the mixture slowly to reflux temperature. A sodium dispersion was produced by high speed stirring of the reaction mixture. The mixture was allowed to reflux for two hours, then it was filtered and cooled to yield the product which was then recrystallized from pentane.

B. Exchange Experiments

The exchange solutions were prepared in the glove box by preparing a solution of the complex cation (typically 10^{-4} M), dividing it in half, and saturating one half with the zerovalent complex. Exchange solutions with varying concentrations of zerovalent complex, but constant in cation concentration, could then be prepared by mixing the portions.

Samples were added, in the glove box, to 3 mm esr tubes with glass microstopcocks. Tube size variation was checked by use of a standard paramagnetic solution and corrected for if necessary. Esr spectra were obtained by use of a Varian E-4 esr spectrophotometer with a variable temperature controller. Stability was excellent over many hours, as the peak intensity for stable samples remained constant over the span of each experiment.

Weissman's method[121] was applied to the central peak of the bis(arene)chromium(I) spectrum centered at g = 1.99. The unbroadened spectrum of $bz_2Cr(I)$ had hyperfine splitting of 3.6 G, while the spectrum of $biph_2Cr(I)$ had hyperfine of 1.2 G.

C. Photochemistry of Bis(biphenyl)chromium Iodide

A solution of $biph_2CrI$ in benzene which gave the expected esr signal and a peak at 365 nm in the visible spectrum was divided in half. Half was exposed to intense but indirect sunlight for 20 minutes while the other half remained in the spectrophotometer cell compartment. The exposed sample had no esr signal and no peak at 365 nm. Instead, peaks had grown in at 500 and 300 nm, indicating the presence of I_2 in benzene. No change occured in the sample that remained in the spectrophotometer cell compartment, but when the samples were mixed the absorbance of the

365 nm peak rose from the initial value of 0.4 to 0.6. Addition of I_2 to a solution of $biph_2Cr(0)$ in benzene caused an intense esr signal, typical of $biph_2CrI$, to appear.

Results and Discussion

Occasionally, experiments yielded data which indicated a monotonic decrease in the intensity (or increase in the linewidth) of the esr spectrum of the bis(arene)chromium cation with the addition of the respective zerovalent complex. Figure 15 shows the effects on the spectrum of $biph_2CrI$ (2.8×10^{-4} $\underline{M}$ in DMSO) of the addition of $biph_2Cr(0)$ to give concentrations of 0, 0.5, 1.0, 1.5, 2.0, and 3.0×10^{-3} $\underline{M}$, respectively. The Weissman plot, shown in Figure 16, allows the calculation of a rate constant for the electron exchange of 2.7×10^{9} $\underline{M}^{-1}$ sec^{-1}. Measuring the spectrum at 23° and 50° revealed an inverse temperature dependence (higher temperatures gave less broadening) for the broadening. The hyperfine structure collapsed completely at high concentrations of added $biph_2Cr(0)$ and high temperature (75°).

Other experiments that spanned the concentration ranges of the experiments above showed no linewidth changes on addition of $biph_2Cr(0)$. The same result was obtained for analogous experiments involving the $bz_2Cr(0)$ - bz_2CrI exchange, where the concentration of bz_2CrI was 2.5×10^{-3} $\underline{M}$ and $bz_2Cr(0)$ was varied up to 5×10^{-3} $\underline{M}$. At the higher complex concentrations in one experiment carried out with $bz_2Cr(0)$ and $bz_2CrAlBu_4$ [bis(benzene)chromium tetrabutylaluminate] in benzene, further splitting of the hyperfine structure into doublets was observed, as shown in Figure 17 and 18. It should be noted that what might be

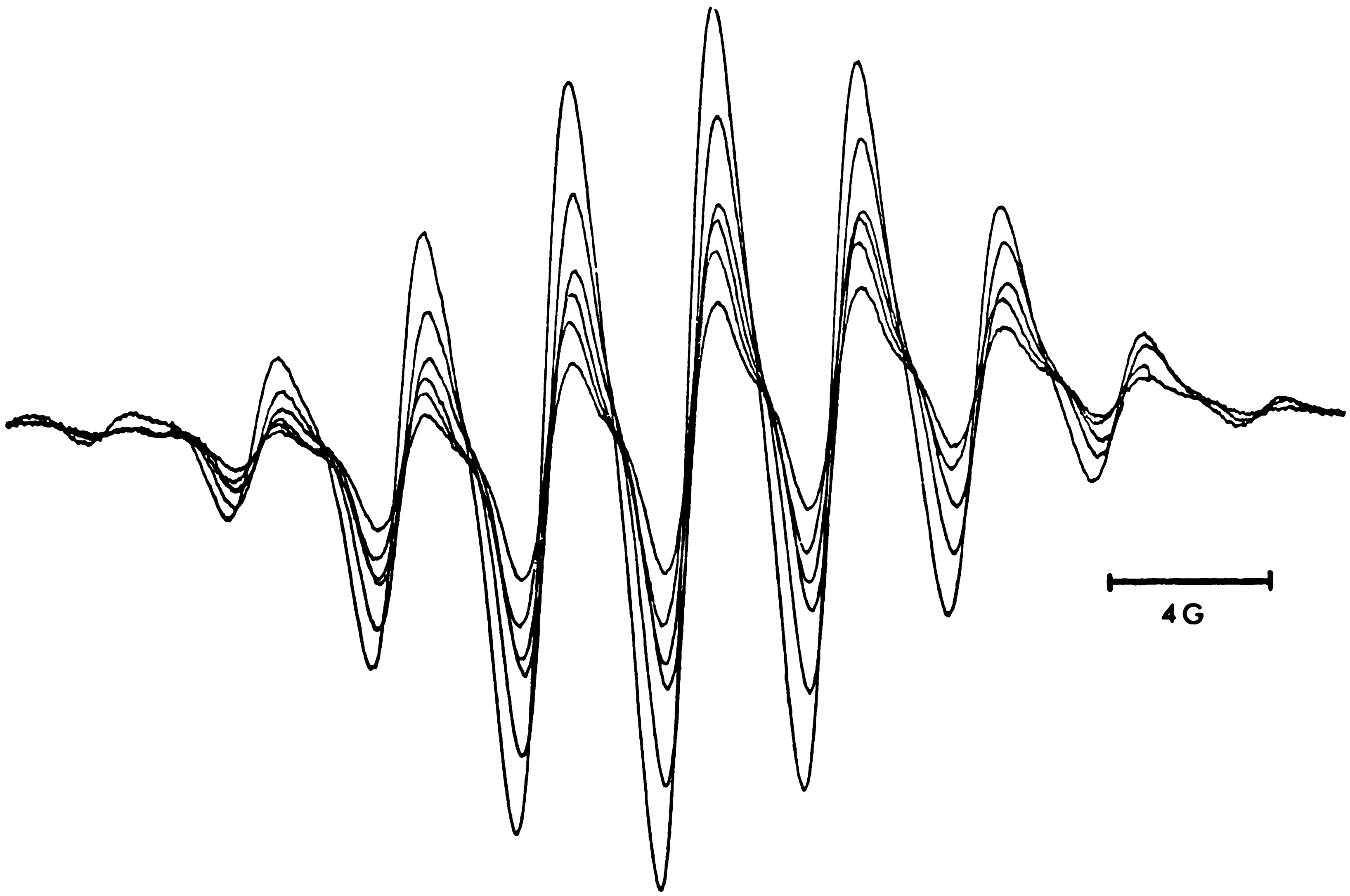


Figure 15. Exchange broadened esr spectrum of bis(biphenyl)chromium iodide.

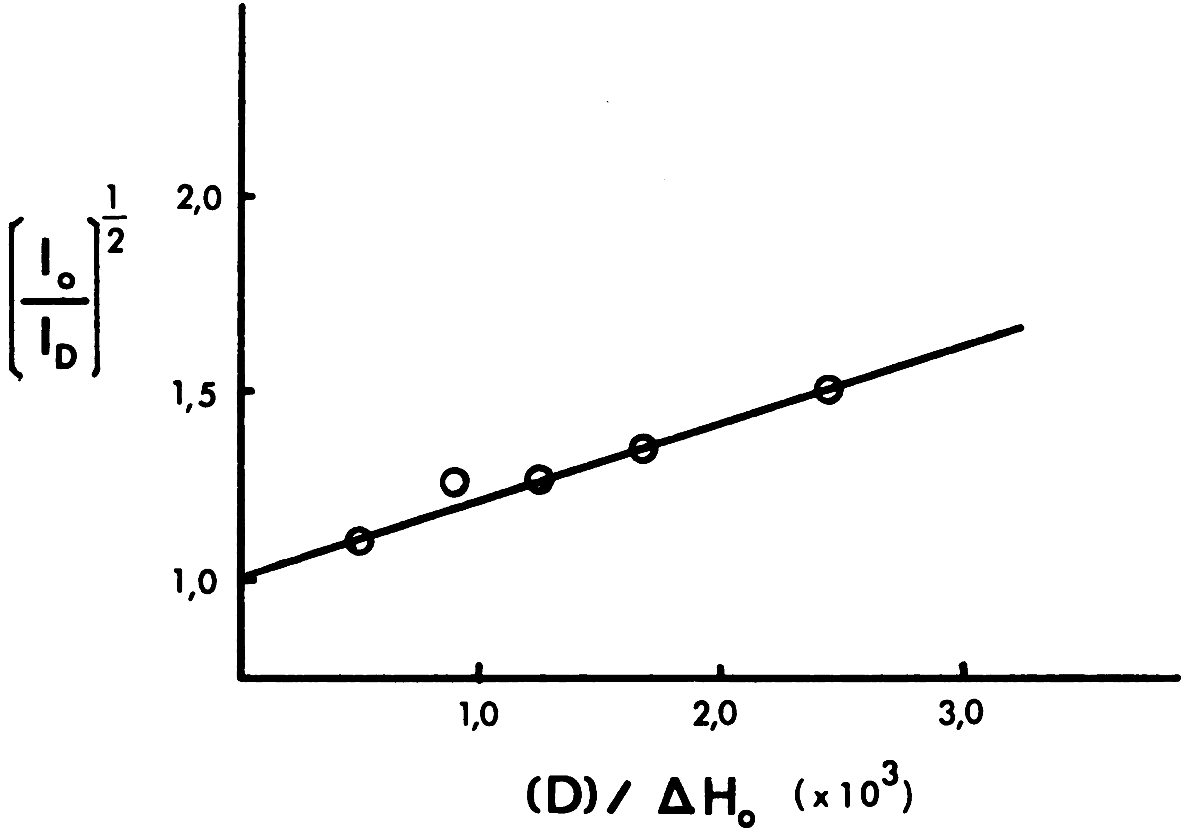


Figure 16. Weissman plot for electron exchange between bis(biphenyl)chromium(0) and its univalent cation.

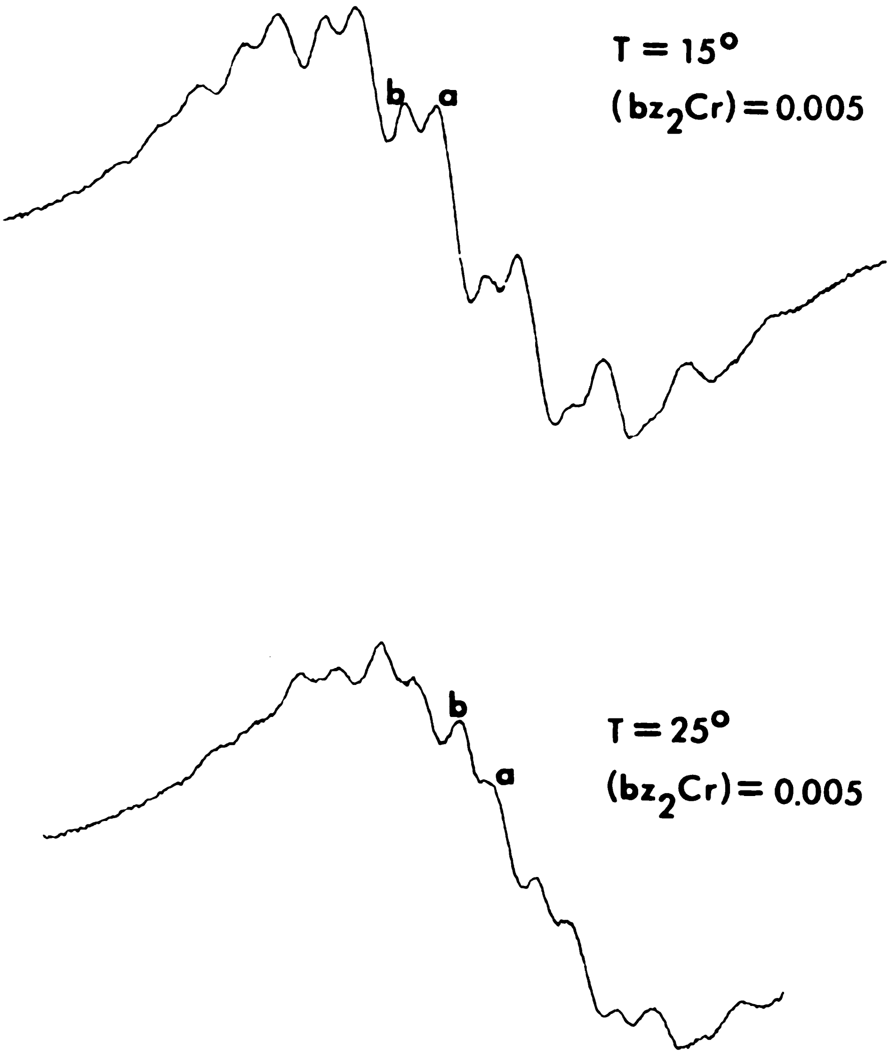


Figure 17. Exchange broadened esr spectra of bis(benzene)chromium(I).

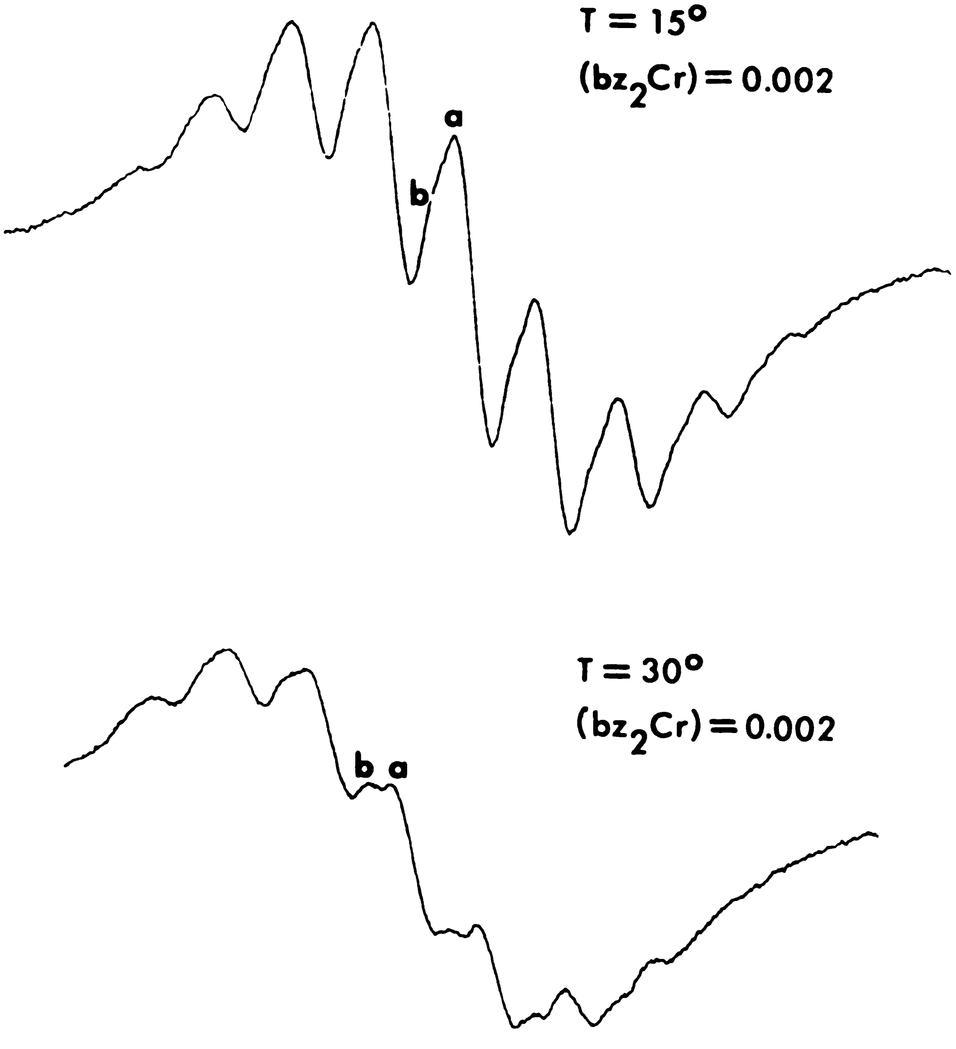


Figure 18. Exchange broadened spectra of bis(benzene)chromium(I).

interpreted as common anisotropy in Figure 15 could also be interpreted as the onset of the additional splitting of the hyperfine which is apparent in Figures 17 and 18. The splitting pattern shown in Figures 17 and 18 has never been reported (even though the esr spectra of bis(arene)chromium cations have been thoroughly investigated), and is difficult to reproduce. It may be evidence for a species which broadens the esr spectrum in the absence of electron exchange. The following observations were made: Increasing the concentration of the zerovalent complex increased the intensity of the set of peaks with the higher g value (see, for example, Figure 17A and Figure 18A), as did increasing the temperature (see Figures 17A and 17B).

The bis(benzene)chromium tetrabutylaluminate which was used to allow the study of the $bz_2Cr(0)$ - $bz_2Cr(I)$ exchange in benzene is a novel species that is paramagnetic (the usual $bz_2Cr(I)$ esr signal is obtained) yet soluble in benzene. The tetrabutylaluminate ion will combine with ferricenium cation to give a benzene soluble species which has an esr signal with hyperfine splitting. Because of the characteristically short relaxation time for ferricenium, no hyperfine splitting was observed in previous work in which solvents other than benzene were used.

Several facts suggest that the broadening observed in the esr signal for bis(arene)chromium(I) when bis(arene)chromium(0) is added in solution is due to processes other than intermolecular electron exchange. First, some broadening occurs even for frozen solutions, suggesting that the mechanism is intramolecular. Second, broadening was not reproducible for solutions which had the same concentrations of reactants, so it probably was a result of a species whose concentration was not intentionally controlled. Finally, the solutions were of a very low concentration compared to those required for the esr study of other rapid electron exchange systems. The concentrations used, however, were near the maximum possible because of the inherent solubilities of the species, and because the cation concentration should not exceed 10^{-3} $\underline{M}$ to prevent spin-spin interactions.

The result of no broadening can be used to eliminate certain ranges of possible values for the rate constant. If the broadening of the nominally 3.6 G $bz_2Cr(I)$ hyperfine were considered "unobservable" if less than 0.1 G, and the concentration of $bz_2Cr(0)$ was varied from zero to 5×10^{-3} $\underline{M}$ without causing observable broadening, then the rate constant would be less than 3×10^{8} $\underline{M}^{-1}$ sec^{-1} according to the equation,[118]

$$k = \sqrt{3}\,\pi(2.83 \times 10^{6}) \left[\frac{(\Delta H)_{exch}}{[bz_2Cr(0)]}\right]$$

where $(\Delta H)_{exch}$ is the increase in linewidth due to exchange.[121]

IV. Study of the Electron Exchange Between Bis(arene)chromium Complexes and Their Cations by NMR Technique

If a proton is located on a molecule that is undergoing electron exchange with others, the proton will experience a "paramagnetic pulse" each time the (usually diamagnetic) molecule accepts an electron from another and so becomes momentarily paramagnetic.[124] The line shape of the nmr signal is affected by the frequency of the pulses (and the intensity of the hyperfine interaction). The nmr technique of measuring the rate of electron exchange stems from the broadening of the nmr spectrum of a diamagnetic compound when minute amounts of the exchangeing paramagnetic compound are added.[125-127] This technique has been applied successfully to many systems, including inorganic,[128-131] organometallic,[132] and organic[133, 134] ones.

The nmr technique was applied to the study of electron exchange between $bz_2Cr(0)$ and $bz_2CrAlBu_4$ in benzene. As in the esr experiments, lineshapes appeared to be sensitive to competing processes to the extent that electron exchange broadening was usually masked by more pronounced spurious broadening effects.

Experimental

$Bz_2Cr(0)$ was dissolved in benzene to give an approximately 2 x 10^{-2} *M* solution. This solution was divided into halves, and $bz_2CrAlBu_4$ was dissolved in one half to give approximately the concentration desired (the exact concentration was determined later by the usual spectrophotometric method, or by the intensity of the esr signal). Exchange solutions with constant concentration of $bz_2Cr(0)$ but varying amounts of the cation could then be prepared by mixing the two solutions. The esr spectrum of each exchange solution was checked to determine whether the cation signal was resolved into the expected hyperfine pattern, a prerequisite for the application of the nmr method.[130]

The nmr spectrum of the exchange solution was obtained by use of a Varian A56-60 nmr spectrometer with a temperature controller. The linewidth of the $bz_2Cr(0)$ peak at $\delta = 4.3$ was measured for solutions containing various concentrations of $bz_2Cr(I)$. The natural linewidth of the peak was about 1.0 cps.

Results and Discussion

The broadening observed for the exchange systems studied was inexplicable in terms of only the $bz_2Cr(0)$ and $bz_2Cr(I)$ concentrations. For instance, extreme broadening was observed for initially narrow peaks as a result of slight air exposure of the $bz_2Cr(0)$ solution. The amount of complex oxidized by this treatment was insufficient to give an esr signal. If, however, $bz_2Cr(I)$ was added to solutions of $bz_2Cr(0)$ in amounts large enough to give a clear esr signal, there was often no broadening whatsoever. It is difficult to determine the cause of the spurious broadening, because the amount of material necessary to change the linewidth drastically is minute. The extreme sensitivity of these systems to oxygen and light are apparently only a small part of the difficulty.

Broadening was an artifact of many experimental variables. For instance, if a previously cleaned and dried nmr tube was filled with $bz_2Cr(0)$ solution and capped with a teflon pressure cap, mere inversion of the tube broadened the spectrum. Flame sealing of tubes was not attempted because it broadened the esr spectra of $bz_2Cr(I)$ solutions

contained in the tubes.

The data for three samples are displayed in Table 6. Regular trends in the amount of broadening with added cation were always obliterated by competing effects as noted above, so although the exchange probably belongs in the "weak pulse" category, no definite classification can be made, and thus no information can be extracted with certainty from the data. Since it is very probable that the frequency of exchange is in the nmr range for some of the concentrations studied, it is perhaps most reasonable to propose that results of "no broadening" were misinterpretations of experiments where some degree of exchange narrowing actually occured. The natural linewidth, and the progressive broadening and then narrowing of the signal due to exchange, may very well have escaped observation because of the acute experimental difficulties.

Table 6. NMR linewidths for exchange solutions.

$[bz_2Cr(0)]$ $\underline{M} \times 10^2$	$[bz_2Cr(I)]$ $\underline{M} \times 10^3$	Linewidth at half max. (cps)
1.9	0.0	1.0
2.2	0.48	1.0
1.9	1.6	10.0

APPENDIX C

THE ELECTRON EXCHANGE BETWEEN TITANOCENE DICHLORIDE AND TITANOCENE MONOCHLORIDE

Tetrahydrofuran solutions initially 2.4×10^{-3} $\underline{M}$ in (D-10)titanocene dichloride and 1.0×10^{-2} $\underline{M}$ in titanocene monochloride show complete mixing of the (D-10) tracer between the (III) and (IV) oxidation states within the time of mixing and separation, typically less than one minute. This indicates that the electron exchange,

$$(\eta^5\text{-}C_5H_5)_2TiCl + (\eta^5\text{-}C_5D_5)_2TiCl_2 \rightleftarrows (\eta^5\text{-}C_5D_5)_2TiCl + (\eta^5\text{-}C_5H_5)_2TiCl_2$$

is immeasurably fast when studied by this technique.

Experimental

Titanocene dichloride and titanocene monochloride were prepared and purified as described previously. Tetrahydrofuran (THF) was distilled from CaH_2 and then from sodium benzophenone. 2,2'-bipyridine was obtained from Eastman Organic Chemicals and used without further purification.

The apparatus that was used for the exchange experiments is shown in Figure 19. Flask A contained a solution of (D-10)titanocene dichloride (50 mg) in THF (40 ml), flask B contained a solution of titanocene monochloride (0.20 g) in THF (40 ml), and flask C contained excess 2,2'-bipyridine in THF (20 ml). To effect the mixing, argon was supplied through stopcock "a" to flask A at about 10 torr pressure, and a vacuum

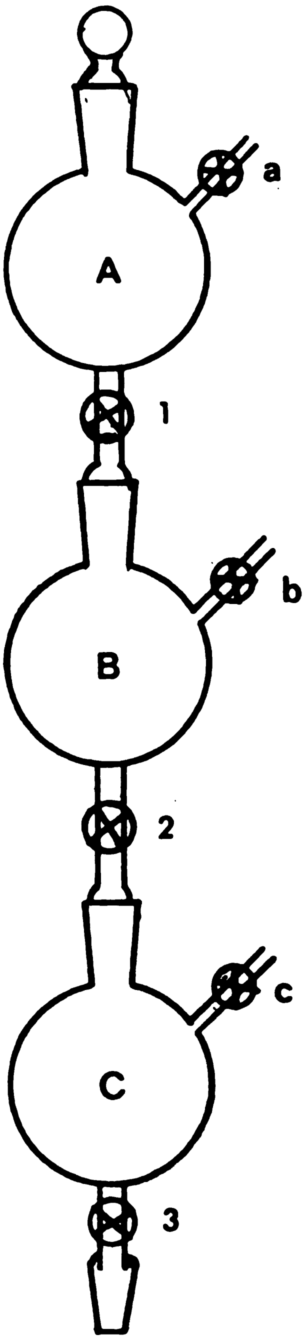


Figure 19. Apparatus for electron exchange experiment.

was applied to flasks B and C. Stopcock 1 was opened to cause turbulent mixing of the reactant solutions. Stopcock 2 was opened after ca. 5 seconds so that all but 10 ml of the reaction mixture was added to the bipyridine solution. A flocculent blue precipitate formed and could be vacuum filtered quickly by opening stopcock 3 which led to a filter tube. The filtrate was evaporated to dryness and sublimed before the mass spectrum was obtained. The precipitate was dissolved in a minimum (1-2 ml) of air free water and treated with HCl gas. The titanocene dichloride solution which resulted after an hour or so was evaporated to dryness and sublimed before the mass spectrum was obtained. A t_∞ sample was obtained by treating 10 ml of the reaction mixture with HCl gas, evaporating it to dryness, and subliming the resulting titanocene dichloride. A mass spectrum of this pure material was obtained.

Discussion

The mass spectrum of the titanocene dichloride species present in the exchange solution at the time of quenching is shown in Figure 20. A mass spectrum identical to that shown in Figure 20 was obtained for the t_∞ sample, indicating that the electron exchange was complete in less than 1 minute. If this is assumed to be at least 4 $t_{1/2}$, the rate constant is greater than $4 \times 10^{2}\ \underline{M}^{-1}\ \mathrm{sec}^{-1}$ as calculated by using the equation,

$$k = \frac{\ln 2}{t_{1/2}([(\eta^5\text{-}C_5H_5)_2TiCl] + [(\eta^5\text{-}C_5D_5)_2TiCl_2])}$$

The reaction mixture had a uv-visible absorption spectrum identical to a combination of the spectra of the individual reactants, and the

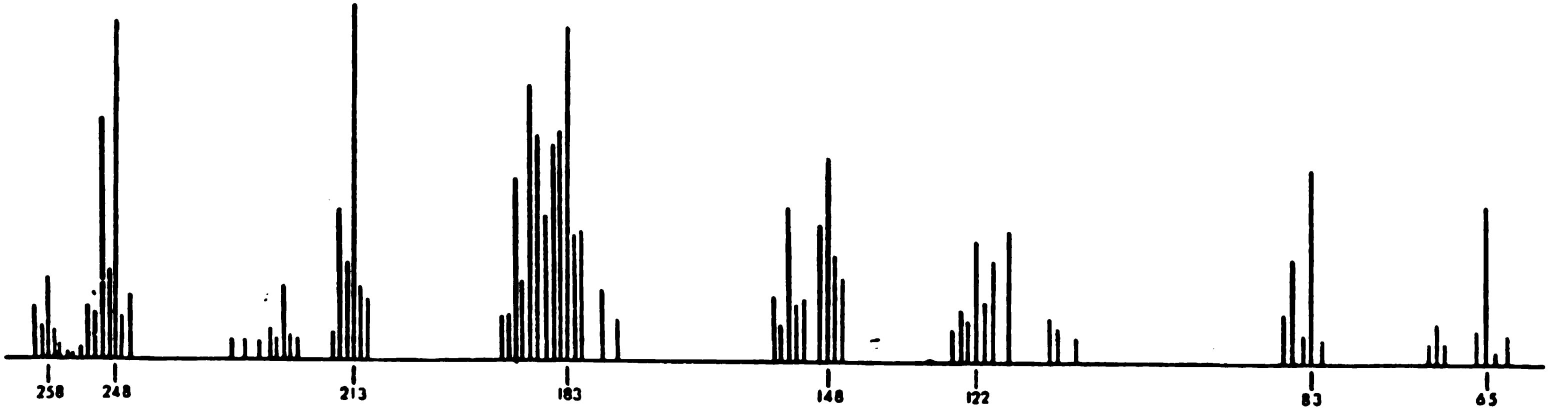


Figure 20. Mass spectrum of titanocene dichloride from electron exchange solution.

esr spectrum of the reaction mixture was identical to that of titanocene monochloride. The clean electron exchange between titanocene dichloride and titanocene monochloride demonstrates the reversibility of the reduction of titanocene dichloride, which had come into doubt as a result of polarographic studies.[22-24]

There is little hope of improving on the experimental procedure used to study the rate of exchange by tracer techniques. The limiting factor is the slow precipitation of the titanocene monochloride-bipyridine adduct, which takes at least 30 seconds. Furthermore, species that precipitate the $(\eta^5\text{-}C_5H_5)_2Ti(III)$ species from aqueous solutions usually precipitate the $(\eta^5\text{-}C_5H_5)_2Ti(IV)$ species as well. These species include sulfate, phosphate, carbonate, phthalate, oxalate, picrate, and other ions. Sodium tetraphenylborate forms a blue precipitate with $(\eta^5\text{-}C_5H_5)_2\text{-}Ti(III)$, but reacts with titanocene dichloride to give biphenyl and triphenylboron (identified by mass spectra) according to the equation,[135]

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + NaB\Phi_4 \rightarrow NaCl + \Phi_3B + \Phi_2 + \text{reduced titanium species}$$

There is one procedure that might allow the measurement of the rate of exchange by tracer techniques. Titanocene monochloride probably exists as a solvated monomer in THF,[136] even though it is known to be dimeric in the solid form[79] and in benzene solution.[55] In aqueous solution, the complex does show the conductance of a 1:1 electrolyte[137] and it exists as a solvated monomeric cation. If titanocene monochloride is a monomer in THF, slower electron exchange might be encountered if benzene exchange solutions were studied. It would be interesting to see if the additional structural rearrangement that would be required for electron exchange between the titanocene monochloride <u>dimer</u> and titanocene dichloride would decrease the rate of that process enough to make it measurable by tracer techniques.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Alt, H., and M. D. Rausch, J. Amer. Chem. Soc., 96, 5936 (1974).

2. Rubezhov, A. Z., and S. P. Gubin, "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Eds., Academic Press, New York, 1972, Vol. 9, p. 347.

3. Wilkinson, G., F. A. Cotton, and J. M. Birmingham, J. Inorg. Nucl. Chem., 2, 95 (1956).

4. Maitlis, P. M., J. Amer. Chem. Soc., 85, 1887 (1963).

5. Efraty, A., J. Organometal. Chem., 57, 1 (1973).

6. Rubezhov, A. Z., and S. P. Gubin, "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Eds., Academic Press, New York, 1972, Vol. 9, p. 347.

7. Basolo, F., and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1967.

8. Langford, C. H., and H. B. Gray, "Ligand Substitution Processes," The Benjamin Co., New York, 1965.

9. Gow, A., and H. Heinemann, J. Phys. Chem., 64, 1574 (1960).

10. Cramer, R., Inorg. Chem., 4, 445 (1965).

11. Pearson, R. G., and M. M. Anderson, Angew. Chem., 4, 281 (1965).

12. Nesmeyanov, A. N., A. Z. Rubezhov, and S. P. Gubin, J. Organometal. Chem., 16, 163 (1969).

13. Cossee, P., Rec. Trav. Chim Pays-Bas, 85, 1151 (1966).

14. Green, M., *et al.*, Chem. Commun., 1973, 97.

15. Strohmeier, W., Angew. Chem., 3, 730 (1964).

16. Strohmeier, W., and D. v.Hobe, Z. Naturforsch., B, 18, 981 (1963).

17. King, R. B., and M. B. Bisnette, Inorg. Chem., 6, 469 (1967).

18. Efraty, A., J. Organometal. Chem., 57, 19 (1973).

19. Nesmeyanov, A. N., *et al.*, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1962, 1481.

20. Nesmeyanov, A. N., *et al.*, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, **12**, 2146 (1961).

21. Maitlis, P. M., *et al.*, J. Amer. Chem. Soc., **87**, 719 (1965).

22. Hsiung, H., and G. H. Brown, J. Electrochem. Soc., **110**, 1035 (1963).

23. Dessey, R. E., and R. B. King, J. Amer. Chem. Soc., **88**, 5112 (1966).

24. Gubin, S. P., and S. A. Smirnova, J. Organometal. Chem., **20**, 229 (1969).

25. Coutts, R. S. P., P. C. Wailes, and R. L. Martin, J. Organometal. Chem., **57**, 375 (1973).

26. Coutts, R. S. P., and P. C. Wailes, "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Eds., Academic Press, New York, 1970, Vol. 9, p. 135.

27. Birmingham, J. M.,"Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Eds., Academic Press, New York, 1964, Vol. 2, p. 365.

28. Salzmann, J. J., and P. Mosimann, Helv. Chim. Acta, **50**, 1831 (1967).

29. Watt, G. W., *et al.*, J. Amer. Chem. Soc., **88**, 1138 (1966).

30. Fischer, A. K., and G. Wilkinson, J. Inorg. Nucl. Chem., **2**, 149 (1956).

31. Brintzinger, H. H., *et al.*, J. Amer. Chem. Soc., **92**, 6182 (1970).

32. Davison, A., and S. S. Wreford, J. Amer. Chem. Soc., **96**, 3017 (1974).

33. Bercaw, S. E., R. N. Marvich, L. G. Bell, and H. H. Brintzinger, J. Amer. Chem. Soc., **94**, 1219 (1972).

34. Baye, L. J., Syn. Inorg. Metal-Org. Chem., **2**, 47 (1972).

35. Gorsich, R. D., J. Amer. Chem. Soc., **80**, 5744 (1958).

36. Balzani, V., and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, 1970.

37. Adamson, A. W., Coord. Chem. Rev., **3**, 169 (1968).

38. Adamson, A. W., Rec. Chem. Progress, **29**, 191 (1968).

39. Adamson, A. W., *et al.*, Chem. Rev., **68**, 541 (1968).

40. Fleischauer, P. D., A. W. Adamson, and G. Sartori, "Progress in Inorganic Chemistry," S. J. Lippard, Ed., Interscience Publishers, New York, 1972, Vol. 17, part 2, p. 1.

41. Fleischauer, P. D., and P. Fleischauer, Chem. Rev., 70, 199 (1970).

42. Wehry, E. E., Quart. Rev. (London), 21, 213 (1967).

43. Endicott, J. F., Israel J. Chem., 8, 209 (1970).

44. Ford, P. C., J. D. Petersen, and R. E. Hintze, Coord. Chem. Rev., 14, 67 (1974).

45. Bozak, R. E., "Advances in Photochemistry," J. N. Pitts, G. S. Hammond, and W. A. Noyes, Eds., John Wiley and Sons, New York, 1971, Vol. 8, p. 227.

46. Tyerman, W. J. R., et al., Chem. Commun., 497 (1967).

47. Natarajan, P., and A. W. Adamson, J. Amer. Chem. Soc., 93, 5599 (1971).

48. Nesmeyanov, A. N., et al., Dokl. Akad. Nauk SSSR, 155, 1130 (1964).

49. Herzog, S., and J. Dehnert, Z. Chem., 4, 1 (1964).

50. Aquasorb is P_2O_5 supported on an inert matrix, marketed by Mallinckrodt Chemical Works, St. Louis, Mo.

51. Broadbent, A. D., J. Chem. Educ., 44, 145 (1967).

52. Brintzinger, H. H., and R. H. Marvich, J. Amer. Chem. Soc. 93, 2048 (1971).

53. Clauss, K., and H. Bestian, Justus Liebigs Ann. Chem., 654, 8 (1962).

54. Brintzinger, H. H., et al., J. Amer. Chem. Soc., 94, 1219 (1972).

55. Coutts, R. S. P., P. C. Wailes, and R. L. Martin, J. Organometal. Chem., 47, 375 (1973).

56. Wagner, P. J., J. Amer. Chem. Soc., 89, 5898 (1967).

57. Moses, F. G., R. S. H. Liu, and B. M. Monroe, Mol. Photochem., 1, 245 (1969).

58. Coutts, R. S. P., and P. C. Wailes, Aust. J. Chem., 21, 2199 (1968).

59. Dillard, J. G., and R. W. Kiser, J. Organometal. Chem., 16, 265 (1969).

60. Nesmeyanov, A. N., et al., J. Organometal. Chem., 61, 225 (1973).

61. Takegami, Y., et al., Bull. Chem. Soc. Jap., 41, 2637 (1968).

62. McKay, H. A. C., Nature, 148, 997 (1938).

63. Friedlander, G., J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed., Wiley, New York, 1955, p. 198.

64. Hoeschele, J. D., Ph.D. Thesis, Michigan State University, 1969, p. 78.

65. Friedlander, G., J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed., Wiley, New York, 1955, p. 202.

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

67. Nesmeyanov, A. N., O. V. Nogina, and A. M. Berlin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1961, 804.

68. Nesmeyanov, A. N., O. V. Nogina, A. M. Berlin, A. S. Girshovich, and G. V. Shatalov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1961, 2146.

69. Nesmeyanov, A. N., O. V. Nogina, and V. A. Bubovitskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1962, 1481.

70. Nesmeyanov, A. N., G. G. Bvoryantseva, Y. N. Sheinker, O. V. Nogina, N. A. Lasareva, and V. A. Bubovitskii, Dokl. Akad. Nauk SSSR, 161, 603 (1965).

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

72. Nesmeyanov, A. N., V. A. Dubovitskii, O. V. Nogina, and V. N. Bochkarev, Dokl. Akad. Nauk SSSR, 165, 125 (1965).

73. Nesmeyanov, A. N., O. V. Nogina, N. A. Lazareva, and V. A. Dubovitskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1967, 808.

74. Nesmeyanov, A. N., O. V. Nogina, and V. A. Dubovitskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1968, 527.

75. Nesmeyanov, A. N., O. V. Nogina, B. V. Lokshin, and V. A. Dubovitskii, Dokl. Akad. Nauk SSSR, 182, 844 (1968).

76. Gorsich, R. D., J. Amer. Chem. Soc., 82, 4211 (1960).

77. Beynon, J. H., "Mass Spectrometry," Elsevier Publishing Co., New York, 1960, p. 298.

78. Green, J. C., M. L. H. Green, and C. K. Prout, Chem. Commun., 1972, 421.

79. Martin, R. L., and G. Winter, J. Chem. Soc. A, 1965, 4709.

80. Brintzinger, H. H., and L. S. Bartell, J. Amer. Chem. Soc., 92,

6182 (1970).

81. Brintzinger, H. H., and L. S. Bartell, J. Amer. Chem. Soc., 92, 1105 (1970).

82. Voigt, A. F., and S. Katz, Dissertation Abstracts, 19, 2242 (1959).

83. Stranks, D. R., Discuss. Faraday Soc., 29, 73 (1960).

84. Wahl, A. C., and M. W. Dietrich, J. Chem. Phys., 38, 1591 (1963).

85. Ruff, I., V. J. Friedrich, K. Demeter, and K. Csillag, J. Phys. Chem., 75, 3303 (1971).

86. Espenson, J. H., and J. R. Pladziewicz, J. Amer. Chem. Soc., 95, 56 (1973).

87. Prins, R., and F. J. Reinders, J. Amer. Chem. Soc., 91, 4929 (1969).

88. Cotton, F. A., "Chemical Applications of Group Theory," John Wiley and Sons, New York, 1967, p. 174.

89. Bhustorovich, E. M., and M. E. Dyatkina, Zh. Neorg. Khim., 6, 493 (1961).

90. Hillier, I. H., and R. M. Canadine, Discuss. Faraday Soc., 1969, 27.

91. Dessy, R. E., R. B. King, and M. Waldrop, J. Amer. Chem. Soc., 88, 5112 (1966).

92. Dessy, R. E., and R. L. Pohl, J. Amer. Chem. Soc., 90, 2005 (1968).

93. Furlani, C., and E. O. Fischer, Z. Electrochem., 61, 481 (1957).

94. Nesmeyanov, et al., J. Organometal. Chem., 20, 169 (1969).

95. Korshunov, A., et al., Dokl. Akad. Nauk SSSR, 122, 769 (1958).

96. Furlani, C., and G. Sartori, Ric. Sci., 28, 973 (1958).

97. Vertyulina, L. N., et al., Zh. Obschch. Khim., 33, 285 (1963).

98. Vlcek, A. A., Z. Anorg. Allg. Chem., 334, 205 (1964).

99. Vlcek, A. A., Z. Anorg. Allg. Chem., 104, 109 (1960).

100. Cotton, F. A., Chem. Rev., 55, 551 (1955).

101. Zeiss, H., P. J. Wheatley, and H. J. S. Winkler, "Benzenoid Metal Complexes," Ronald Press, New York, 1966.

102. Sohn, Y. S., D. N. Hendricksen, and H. B. Gray, J. Amer. Chem. Soc., 93, 3603 (1971).

103. Berry, R. S., J. Chem. Phys., 35, 2025 (1961).

104. Levy, D. A., and L. E. Orgel, Mol. Phys., 4, 93 (1961).

105. Fritz, H. P., and J. Manchot, J. Organometal. Chem., 2, 8 (1964).

106. Jellinek, F., J. Organometal. Chem., 5, 490 (1966).

107. Cotton, F. A., J. Amer. Chem. Soc., 85, 1543 (1963).

108. Haaland, A., Acta Chem. Scand., 19, 41 (1965).

109. Schafer, L., J. F. Southern, S. J. Cyvin, and J. Brunvoll, J. Organometal. Chem. 24, C13 (1970).

110. Cyvin, S. J., J. Brunvoll, and L. Schafer, J. Chem. Phys., 54, 1517 (1971).

111. Olive, G. H., and S. Olive, Z. Phys. Chem., 56, 223 (1967).

112. Hausser, K. H., Naturwissenschaften, 48, 666 (1964).

113. Vetchinkin, S. I., et al., Opt. Spektrosk., 8, 71 (1960).

114. Fischer, E. O., and W. Hafner, Z. Anorg. Allg. Chem., 286, 9 (1956).

115. Fischer, E. O., in "Inorganic Syntheses," E. G. Rochow, Ed., McGraw Hill Book Co., Inc., New York, 1960, Vol. 6, p. 132.

116. Hudson, A., and G. R. Luckhurst, Chem. Rev., 1969, 191.

117. Weissman, S. I., Z. Electrochem., 64, 47 (1960).

118. Chang, R., J. Chem. Educ., 47, 563 (1970).

119. Currin, J. D., Phys. Rev., 126, 1995 (1962).

120. Weissman, S. I., J. Amer. Chem. Soc., 84, 4269 (1962).

121. Weissman, S. I., and R. L. Ward, J. Amer. Chem. Soc., 79, 2086 (1957).

122. Brauer, G., Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 2, Academic Press, New York, p. 1396.

123. Hohn, E. G., J. A. Olander, and M. C. Day, J. Phys. Chem., 73, 3880 (1969).

124. McConnell, H. M., and S. B. Berger, J. Chem. Phys., 27, 230 (1957).

125. Johnson, C. S., "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press, New York, 1965, Vol 1, p. 33.

126. Sack, R. A., Mol. Phys., 1, 163 (1958).

127. Bloembergen, N., E. M. Purcell, and R. V. Pound, Phys. Rev., 73, 679 (1948).

128. McConnell, H. M., and H. E. Weaver, J. Chem. Phys., 25, 307 (1956).

129. Myers, O. E., and Sheppard, J. C., J. Amer. Chem. Soc., 83, 4739 (1961).

130. McConnell, H. M., and C. R. Giuliano, J. Inorg. Nucl. Chem., 9, 171 (1959).

131. Britt, A. D., and W. M. Yen, J. Amer. Chem. Soc. 83, 4516 (1961).

132. Bietrich, M. W., and A. C. Wahl, J. Chem. Phys., 38, 1591 (1963).

133. DeBoer, E., and C. MacLean, J. Chem. Phys., 44, 1334 (1966).

134. Bruce, C. R., R. E. Norberg, and S. I. Weissman, J. Chem. Phys., 24, 473 (1956).

135. Gerrard, W., "The Organic Chemistry of Boron," Academic Press, New York, 1961, p. 110.

136. Raynor, J. B., and A. W. L. Ball, Inorg. Chem. Acta, 7, 315 (1973).

137. Wilkinson, G., and J. M. Birmingham, J. Amer. Chem. Soc., 76, 4281 (1954).