PART ONE
INTERCHANGE OF MONOHAPTO- AND PENTAHAPTOCYCLOPENTADIENYL RINGS IN EARLY TRANSITION METAL METALLOCENE SYSTEMS

PART TWO
A NEW ROUTE TO PREPARING POLYMER-ATTACHED METALLOCENE DERIVATIVES

PART THREE
CYCLOPENTADIENYL LIGAND EXCHANGE REACTIONS IN SELECTED SYSTEMS

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This is to certify that the

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(1) INTERCHANGE OF MONOHAPTO- AND PENTAHAPTO
CYCLOPENTADIENYL RINGS IN SOME EARLY TRANSITION
METAL METALLOCENE SYSTEMS (2) A NEW ROUTE TO
PREPARING POLYMER-ATTACHED METALLOCENE DERIVATIVES
(3) CYCLOPENTADIENYL LIGAND EXCHANGE REACTIONS IN
SELECTED SYSTEMS

presented by

John Guo-shuh Lee

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ABSTRACT

PART ONE

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PART ONE

PMR and mass spectral analysis have been used to study the interchange of pentahapto-bonded cyclopentadienyl rings with monohapto-bonded cyclopentadienyl rings in the compounds $(C_5H_5)_4M$ (M = Ti, Zr, Hf, Nb, Ta, Mo, and W) and $(C_5H_5)_3V$ or monohapto-bonded benzylcyclopentadienyl rings in the compounds $(C_6H_5CH_2C_5H_4)(C_5H_5)_2MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo, and W). As soon as the Cp_4M (or Cp_3MCl) species are generated (indicated by a color change), the exchange occurs and the equilibrium is established. As reported, no such interchange was observed in $(C_5H_5)_4Mo$ on the PMR time scale; however, it does occur after a longer time.

John Guo-shuh Lee

PART TWO

New methods of attaching transition metals to polymers have been studied. The metallocene dichlorides of Ti, Zr, Hf, V, Nb, Ta, Mo, and W have been attached to polystyrene divinylbenzene beads by facile exchange reactions instead of the previous synthetic routes involving synthesis of monocyclopentadienyl metal halides.

PART THREE

Cyclopentadienyl ligands have been exchanged between molecules of metallocene dichloride (M = V and Hf) in benzene solely by photochemical process. The exchange of cyclopentadienyl ligands between molecules of vanadocene monochloride (vanadocene or chromocene) occurs by both thermal and photochemical processes.

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BY

John Guo-shuh Lee

A THESIS

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To My Parents

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PART ONE

INTERCHANGE OF MONOHAPTO- AND PENTAHAPTOCYCLOPENTADIENYL RINGS IN SOME EARLY TRANSITION METAL METALLOCENE SYSTEMS

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INTRODUCTION

Ligand sigma-pi rearrangements have been observed for almost all of the transition metals with a variety of ligands. The rearrangements are not only of interest in the field of organometallic chemistry but are also involved in such industrially important processes as the Ziegler-Natta polymerization of olefins, the oxo process (hydroformylation of olefins), and in homogeneous catalysis in general.

Interchange of η^1-C_5H_5 and η^5-C_5H_5 rings was first observed in temperature-dependent PMR studies of $(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2Ti$ [1] . This work and subsequent investigations of three other Cp_4M (M = Zr, Hf, and Mo) [2-4] systems demonstrated that only the molybenum complex does not undergo rapid ring interchange at ambient temperatures. Through the use of labelled Cp compounds (C_5D_5 in Cp_4M and $C_6H_5CH_2C_5H_4$ in Cp_3MCl systems), the interchange reactions in some d^0 to d^2 metallocenes were investigated. The results show that the interchange of monohapto- and pentahaptocyclopentadienyl rings occurs in all the systems studied.

RESULTS AND DISCUSSION

A. Interchange of Monohapto- and Pentahaptocyclopentadienyl Rings in Cp_4M (M = Ti, Zr, Hf, Nb, Ta, Mo, and W) Systems

The compounds $(C_5H_5)_{2-n}(C_5D_5)_{2+n}M$, where n = 0, 1, 2, and M = Ti, Zr, Hf, Nb, Ta, Mo, and W; were prepared from the corresponding $(C_5H_5)_2MCl_2$ [abbreviated M(A)] and two moles of NaC_5D_5 (or TlC_5D_5 for Mo system). Excess NaC_5D_5 was used for the Nb and Ta compounds. When the resultant products were treated with gaseous HCl, σ-bonded Cp^- was replaced by Cl^-, and a mixture of $(C_5H_5)_{2-n}(C_5D_5)_nMCl_2$ [abbreviated M(B)] was isolated. The PMR data for the cyclopentadienyl protons of M(A) and M(B) (M = Ti, Zr, and Hf) are listed in Table 1.

Table 1. PMR Results of Ti(A), Ti(B), Zr(A), Zr(B), Hf(A), and Hf(B) [in THF with Equal Concentrations of M(A) and M(B)]

Metallocene Dichloride	C_5H_5(ppm)	Peak Ratio M(A)/M(B)* Expected	Found
Titanocene Dichloride	6.6	2	2.12
Zirconocene Dichloride	6.62	2	1.89
Hafnocene Dichloride	6.52	2	1.95

*M(A) = $(C_5H_5)_2MCl_2$

M(B) = $(C_5H_5)_2MCl_2$, $(C_5H_5)(C_5D_5)MCl_2$, and $(C_5D_5)_2MCl_2$.

The ratio of the peak areas M(A)/M(B) [M = Ti, Zr, and Hf] for two different equimolar solutions based on absolute ^{1}H nmr intergration is ca. 2 and suggests that essentially half of the C_5H_5 ring were replaced by C_5D_5 rings. The mass spectrographic data of M(A) and M(B) (M = Ti, Zr, Hf, Nb, Ta, Mo, and W; Table 2, 3, and 4) are consistent with there being a mixture of $C_{10}D_{10}MCl_2$, $C_{10}D_5H_5MCl_2$, and $C_{10}H_{10}MCl_2$ as expected if initially η^1-bonded C_5D_5 rings were interchanged with η^5-bonded C_5H_5 rings. My results confirm the fast exchange expected in d^0 systems. With the intermediately bonded ring concept proposed by Cotton [3,4] fast ring interchange in d^1 systems can also be explained. As reported [4], no such interchange was observed in $(C_5H_5)_4Mo$ on the PMR time scale, since it has an eighteen electron configuration in its ground state and would have to go through a high-energy, intermediately bonded state in order to exchange the ring. However, this interchange is observed in my experiments which encompass a longer period of time. The PMR spectrum of $(C_5H_5)_2(C_5D_5)_2Mo$ (prepared from either $(C_5H_5)_2MoI_2$ and two moles of TlC_5D_5 or from $(C_5D_5)_2MoI_2$ and two moles of TlC_5H_5), was measured. The spectrum (toluene-d^8) consisted of two very sharp singlets at δ 3.83 and δ 3.94 with equal intensities. With no interchange, only one of these two singlets should be observed in the PMR spectra [4]. Attempts to determine the rate of interchange were unsuccessful since by the time the Cp_4Mo species were generated (indicated by a violet color), the interchange had occurred and the equilibrium had been established.

Table 2. Mass Spectrographic Data for Ti(A), Ti(B), Zr(A), Zr(B), Hf(A), and Hf(B).
(based on Ti,48; Zr,90; Hf,180; Cl,35)

	Ti(A)	Ti(B)		Zr(A)	Zr(B)		Hf(A)	Hf(B)	Ion
m/e	Rel.	int.(%)	m/e	Rel.	int.(%)	m/e	Rel.	int.(%)	M = Ti, Zr, Hf
258	0	14	300	0	28	390	0	24	$C_{10}D_{10}MCl_2^+$
253	0	30	295	0	50	385	0	49	$C_{10}D_5H_5MCl_2^+$
248	86	17	290	51	25	380	35	25	$C_{10}H_{10}MCl_2^+$
223	0	9	265	0	9	355	0	12	$C_{10}D_{10}MCl^+$
218	0	20	260	0	15	350	0	23	$C_{10}D_5H_5MCl^+$
213	75	12	255	20	8	345	10	16	$C_{10}H_{10}MCl^+$
188	0	90	230	0	100	320	0	95	$C_5D_5MCl_2^+$
183	100	100	225	100	95	315	100	100	$C_5H_5MCl_2^+$
160	0	0	202	0	28	292	0	23	$C_3D_3MCl_2^+$
157	0	0	199	15	26	289	27	35	$C_3H_3MCl_2^+$
153	0	45	195	0	20	285	0	5	$C_5D_5MCl^+$
148	80	50	190	10	20	280	5	3	$C_5H_5MCl^+$

Note: M(A) = $(C_5H_5)_2MCl_2$

M(B) = $(C_5H_5)(C_5D_5)MCl_2$, $(C_5H_5)_2MCl_2$, and $(C_5D_5)_2MCl_2$.

Table 3. Mass Spectrographic Data for Nb(A), Nb(B), Ta(A), and Ta(B). (based on Nb,93; Ta,181; Cl,35)

m/e	Nb(A) Rel. int.(%)	Nb(B) Rel. int.(%)	m/e	Ta(A) Rel. int.(%)	Ta(B) Rel. int.(%)	Ion M = Nb, Ta
303	0	60	391	0	63	$C_{10}D_{10}MCl_2^+$
298	0	42	386	0	20	$C_{10}D_5H_5MCl_2^+$
293	87	10	381	90	0	$C_{10}H_{10}MCl_2^+$
284	0	11	372	0	38	$C_{10}D_{10}MOCl^+$
279	0	8	367	0	18	$C_{10}D_5H_5MOCl^+$
274	13	3	362	10	0	$C_{10}H_{10}MOCl^+$
268	0	20	356	0	30	$C_{10}D_{10}MCl^+$
263	0	15	351	0	25	$C_{10}D_5H_5MCl^+$
258	30	5	346	16	5	$C_{10}H_{10}MCl^+$
233	0	100	321	0	100	$C_5D_5MCl_2^+$
228	100	35	316	100	17	$C_5H_5MCl_2^+$
198	0	18	286			$C_5D_5MCl^+$
193	10	5	281			$C_5H_5MCl^+$

Note: Excess NaC_5D_5 was used in this study.

Table 4. Mass Spectrographic Data for M(A) and M(B) (M = Mo and W). (based on Mo,95; W,184; Cl,35)

m/e	Mo(A) Rel. int.(%)	Mo(B)* Rel. int.(%)	m/e	W(A) Rel Int.(%)	W(B) Rel Int.(%)	Ion M = Mo, W
305	1	9	394	0	45	$C_{10}D_{10}MCl_2^+$
300	2	15	389	0	80	$C_{10}D_5H_5MCl_2^+$
295	25	7	384	85	42	$C_{10}H_{10}MCl_2^+$
270	0	55	359	0	27	$C_{10}D_{10}MCl^+$
265	1	100	354	0	55	$C_{10}D_5H_5MCl^+$
260	100	44	349	53	25	$C_{10}H_{10}MCl^+$
235	2	27	324	2	100	$C_5D_5MCl_2^+$, $C_{10}D_{10}M^+$
230	32	52	319	100	97	$C_5H_5MCl_2^+$, $C_{10}D_5H_5M^+$
225	33	20	314	8	5	$C_{10}H_{10}M^+$
200	3	65				$C_5D_5MCl^+$
195	95	70				$C_5H_5MCl^+$

*From the reaction of $(C_5H_5)_2MoI_2$ and TlC_5D_5

B. Interchange of Monohapto- and Pentahaptocyclopentadienyl Rings in Cp_4V, Cp_3V, and Cp_2V

Since it appears that Cp_4V cannot be prepared [5], the interchange reactions of Cp_2V and Cp_3V were chosen for study. The compound, $(C_5H_5)_2(C_5D_5)V$, was prepared from $(C_5H_5)_2VCl$ and one mole of NaC_5D_5. When the mixture of compounds was heated, σ-bonded Cp was eliminated and exchange products $(C_5H_5)_2V$, $(C_5H_5)(C_5D_5)V$, and $(C_5D_5)_2V$ were isolated by sublimation. Mass spectrographic data confirmed the exchange (Table 5.). When vanadocene was treated with NaC_5D_5 in excess, ring substitution to give mostly $(C_5D_5)_2V$ was observed by the mass spectra of the final products (Table 5.).

C. Interchange of Monohapto- and Pentahaptocyclopentadienyl Rings in Cp_3MCl (M = Ti, Zr, Hf, Nb, Ta, Mo, and W) systems

$(C_5H_5)_2(C_5H_4CH_2C_6H_5)MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo, and W) were prepared from the corresponding metallocene dichloride and one mole of sodium (or lithium) benzylcyclopentadienide. The interchange follows the reaction scheme in Figure 1.

Exchange products of $(C_6H_5CH_2C_5H_4)_n(C_5H_5)_{2-n}MCl_2$ (n = 0, 1, and 2) were isolated and the PMR spectral data for M = Ti, Zr, and Hf are listed in Table 6. The presence of C_6H_5- and $-CH_2$- protons are good indications of the ring exchange reactions.

The mass spectrographic data for M = Ti, Zr, Hf, Nb, Ta, Mo, and W reveal the presence of either the parent peaks of $(C_5H_5)(C_5H_4CH_2C_6H_5)MCl_2$, or their fregments. (Table 7-9). These data suggest the interchange of the rings. By the same scheme vanadocene dichloride was tested and no ring interchange was detected from the PMR and mass spectra, nor was any starting material, vanadocene dichloride, recovered.

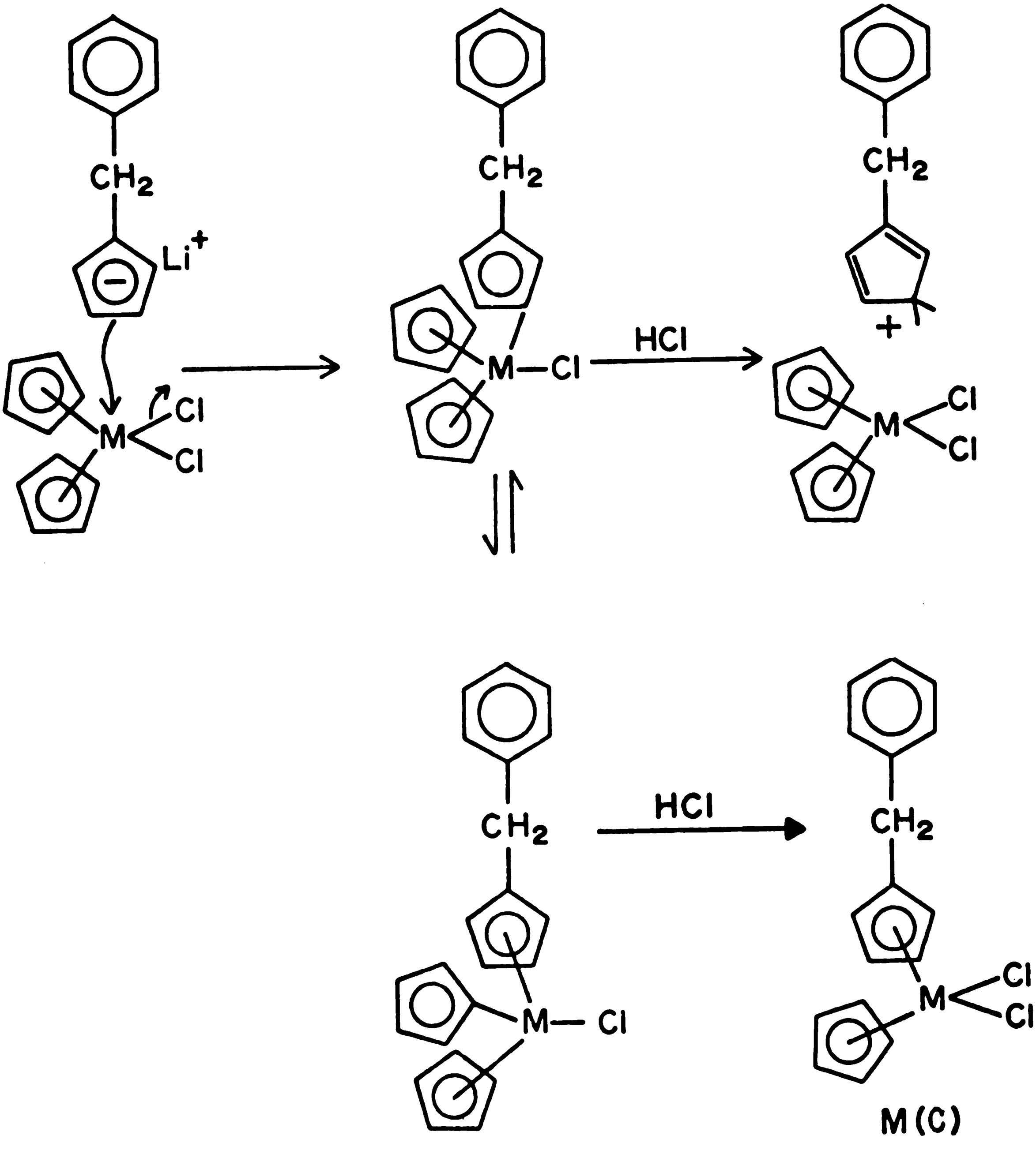

Figure 1. Scheme for Sigma-pi Ring Interchanges in Cp_3MCl Systems

Table 5. Mass Spectrographic Data for V(A) and V(B).
(based on V,51; Cl,35)

m/e	V(A) Rel. int(%)	V(B1)	V(B2)	V(B3)	Ion
		Rel. int.(%)			
191	0	53	100	100	$C_{10}D_{10}V^+$
186	0	95	15	4	$C_{10}D_5H_5V^+$
181	84	100	5	2	$C_{10}H_{10}V^+$
121	0	65	85	80	$C_5D_5V^+$
116	100	97	12	4	$C_5H_5V^+$

Note: V(B1): sublimation product from $(C_5H_5)_2VCl$ and NaC_5D_5.

V(B2): product isolated from the reaction between $(C_5H_5)_2V$ and excess NaC_5D_5 with 15 minutes stirring.

V(B3): stirring for 4 days, all others same as B.

Table 6. PMR Data for Ti(C), Zr(C), and Hf(C),
$M(C) = (C_5H_5)_{2-n}(C_6H_5CH_2C_5H_4)_nMCl_2$

M(C)	Cp-	Rel. Int. C_6H_5-	$-CH_2-$
Ti(C)	6.48(18)	7.2(9)	4.1(1)
Zr(C)	6.2(3.2)	7.05(1)	3.95(0)
Hf(C)	6.35(12)	7.15(7)	4.05(1)

Table 7. Mass Spectrographic Data for Ti(A), Ti(C), Zr(A), Zr(C), Hf(A), and Hf(C).
$[(C_5H_5)(C_6H_5CH_2C_5H_4)MCl_2 = P, (M = Ti, Zr, and Hf)]$
(based on Ti,48; Zr,90; Hf,180; Cl,35)

	Ti(A)	Ti(C)		Zr(A)	Zr(C)		Hf(A)	Hf(C)	
m/e	Rel.	int.(%)	m/e	Rel.	int(%)	m/e	Rel.	int(%)	Ion
338	0	0	380	0	7	470	0	40	P^+
302	0	5	344	0	6	434	0	0	$(P-HCl)^+$
273	0	9	315	0	14	405	0	100	$(P-C_5H_5)^+$
248	86	29	290	51	44	380	35	25	$C_{10}H_{10}MCl_2^+$
237	0	4	279	0	0	369	0	0	$(P-HCl-C_5H_5)^+$
213	75	30	255	20	50	345	10	53	$C_{10}H_{10}MCl^+$
183	100	100	225	100	100	315	100	50	$C_5H_5MCl_2^+$
148	80	65	190	0	0	280	0	0	$C_5H_5MCl^+$

Table 8. Mass Spectrographic Data for Nb(A), Nb(C), Ta(A), and Ta(C).
$[(C_5H_5)(C_6H_5CH_2C_5H_4)MCl_2 = P, (M = Nb and Ta)]$
(based on Nb,93; Ta,181; Cl,35)

	Nb(A)	Nb(C)		Ta(A)	Ta(C)	
m/e	Rel.	int.(%)	m/e	Rel.	int.(%)	Ion
383	0	11	471	0	27	P^+
347	0	11	435	0	12	$(P-HCl)^+$
318	0	0	406	0	7	$(P-C_5H_5)^+$
293	87	80	381	90	65	$C_{10}H_{10}MCl_2^+$
274	13	55	362	10	13	$C_{10}H_{10}MOCl^+$
258	30	30	346	16	12	$C_{10}H_{10}MCl^+$
228	100	100	316	100	100	$C_5H_5MCl_2^+$

Table 9. Mass Spectrographic Data for Mo(A), Mo(C), W(A), and W(C). [$(C_5H_5)(C_6H_5CH_2C_5H_4)MCl_2$ = P, (M = Mo and W)] (based on Mo,95; W,184; Cl,35)

m/e	Mo(A) Rel.	Mo(C) int.(%)	m/e	W(A) Rel.	W(C) int.(%)	Ion
385	0	0	474	0	3	P^+
349	0	7	428	0	7	$(P-HCl)^+$
320	0	0	409	0	0	$(P-C_5H_5)^+$
315	0	3	404	0	3	$(P-Cl_2)^+$
295	25	15	384	85	80	$C_{10}H_{10}MCl_2^+$
260	100	100	349	53	88	$C_{10}H_{10}MCl^+$
230	20	21	319	100	100	$C_5H_5MCl_2^+$
225	35	35	314	8	15	$C_{10}H_{10}M^+$
204	9	11	293	50	55	$C_3H_3MCl_2^+$
195	95	100	284	15	20	$C_5H_5MCl^+$

Note: M(C) is a mixture of $(C_5H_5)_{2-n}(C_6H_5CH_2C_5H_4)_nMCl_2$, n = 0, 1, 2.

EXPERIMENTAL

A. General

Oxygen and moisture were excluded from the reaction mixtures by thoroughly drying the glassware and reagents, and by manipulating the reagents under dry argon or in a vacuum in Schlenk-type apparatus.

D_2O was purchased from J. T. Baker Chemical Co. Tl_2SO_4 and the metal chlorides ($TiCl_4$, $ZrCl_4$, $HfCl_4$, VCl_3, VCl_4, $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6) were purchased from Alfa Products.

Vanadocene, vanadocene monchloride [6], and the metallocene dichlorides of Ti, Zr, Hf, V, Nb, Ta, Mo, and W were prepared as previously reported [7-12]. C_5D_6 [13], $C_6H_5CH_2C_5H_5$ [14] and their lithium salts, $(C_5H_5)_2MoI_2$ [4] and TlC_5D_5 [4] were also prepared by known methods.

PMR spectra were obtained by using a Varian T-60 NMR spectrometer and by using TMS as a reference. The mass spectra were obtained by use of a Perkin Elmer model RMU-6 mass spectrometer.

B. Preparation of $(C_5H_5)_2(C_5D_5)_2M$ (M = Ti, Zr, Hf, and V) and Their Reactions with Gaseous HCl

$(C_5H_5)_2MCl_2$ (0.01 mole) was mixed with the benzene suspension of NaC_5D_5 (0.02 moles). The reaction mixture was stirred for 15 minutes, and the filtrate obtained after separation of the sodium chloride was evaporated to dryness. This residue of $(C_5H_5)_2(C_5D_5)_2M$ was then redissolved in toluene, the flask partially evacuated and then refilled with gaseous HCl. After stirring for 30 minutes, the solvent was removed under reduced pressure, and the products, M(B), were purified by vacuum sublimation ($145^o/10^{-2}$ torr).

C. Preparation of $(C_5H_5)_2(C_5D_5)V$ and Its Thermal Decomposition Products

$(C_5H_5)_2VCl$ (3.4×10^{-3} moles) was mixed with 60 ml of THF at 0°, and 11.5 ml of NaC_5D_5 (1 ml = 0.39×10^{-3} moles) in THF and stirred for 15 minutes. The solvent was removed in a vacuum and then 100 ml of cold ether (0°) was added. The mixture was stirred for 15 minutes, filtered and concentrated to 40 ml. On slow cooling to -78°, $(C_5H_5)_2(C_5D_5)V$ separated as black crystals. When the compound was heated to 75°, the mixture of $(C_5H_5)_2V$, $(C_5H_5)(C_5D_5)V$, and $(C_5D_5)_2V$ were sublimed.

D. Cyclopentadiene Ring Exchange between Vanadocene and NaC_5D_5

$(C_5H_5)_2V$ in THF was treated with NaC_5D_5 in large excess for 15 minutes (another trial was allowed to react for 4 days). The reaction mixture was evaporated to dryness and blue crystals of $(C_5H_5)_2V$, $(C_5D_5)_2V$, and $(C_5H_5)(C_5D_5)V$ were isolated upon sublimation ($70°/10^{-2}$ torr).

E. Preparation of $(C_5H_5)_{4-n}(C_5D_5)_nM$ (M = Nb and Ta) and Their Reactions with Gaseous HCl

$(C_5H_5)_2MCl_2$ was treated with excess NaC_5D_5 in THF. The mixtures, which became red in four hours, were stirred an additional 12 hours, the solvent removed at reduced pressure and the residue evaporated to dryness. Dry ether was added and the mixture stirred for an additional hour. The red filtrate of $(C_5H_5)_{4-n}(C_5D_5)_nM$ was separated from the salt residue, the flask was partially evacuated and refilled with gaseous HCl, after which the mixture immediately became dark colored. Two hours later, the supernatant, clear, etheral solution was decanted, and the residue was evaporated to dryness. The M(B) component was sublimed at $280°/10^{-2}$ torr.

F. Preparation of $(C_5H_5)_2(C_5D_5)_2M$ (M = Mo and W) and Their Reactions with Gaseous HCl

$(C_5H_5)_2MoI_2$ [or $(C_5D_5)_2MoI_2$] (0.01 mole) was mixed with TlC_5D_5 [or TlC_5H_5] (0.02 moles) in THF. After 12 hours, a yellow precipitate of thallium(I) iodide had formed and the color of the solution changed from green to red. The resultant violet solution that formed after an additional 60 hours was reduced to dryness in a vacuum and the dry residue extracted with 200 ml of toluene. The red filtrate of $(C_5H_5)_2(C_5D_5)_2Mo$ was separated and the reaction with HCl carried out as above. The green residues of Mo(B) were filtered and dried in vacuum.

G. Preparation of $(C_6H_5CH_2C_5H_4)(C_5H_5)_2MCl$ (M = Ti, Zr, Hf, Nb, Ta, Mo, and W) and Their Reactions with Gaseous HCl

$(C_5H_5)_2MCl_2$ (0.5 g) was suspended in toluene, and then a stoichiometric amount of sodium (or lithium) benzylcyclopentadienide was added. The reaction times varied: 30 minutes for Ti, Zr, and Hf; 6 hours for Nb and Ta; 4 days for Mo and W. The filtrate was separated from the residues, and it was treated with HCl. The mixtures of M(C) (M = Mo and W) were precipitated and were separated and dried in vacuum, while the others (M = Ti, Zr, Hf, Nb, and Ta) were simply dried in vacuum and purified by vacuum sublimation.

PART TWO

A NEW ROUTE TO PREPARING POLYMER-ATTACHED METALLOCENE DERIVATIVES

INTRODUCTION

Conventional heterogeneous catalysts, although widely used industrially, generally suffer from the disadvantages that (1) design and improvement are difficult because the active sites are not welldefined, (2) only a small percentage of the active components are accessible and effective, and (3) the control that can be exerted over the composition and structure of the active sites is relatively limited. In contrast, homogeneous transition metal catalysts are not only structurally better defined, but the steric and electronic environment of the catalytic active site can often be varied widely and in a systematic manner so that the course and rate of the reaction may be precisely controlled.

However, homogeneous catalysts have so far found only limited use, chiefly because of the difficulty of their separation from the reaction products. Making homogeneous transition metal catalysts insoluble by attachment to immobile supports such as silica [15-18], clay [19], or polymeric material [20-41] is a significant step in improving their industrial applicability. While the solid-support technique obviously prevents the loss of possibly expensive materials and contamination of reaction products, the method also offers the opportunity to prepare a new class of catalyst systems with other desirable properties. Several different types of transition metal compounds have been bound to a various polymeric material, mostly polystyrene-divinyl benzene copolymers. Manassen [42] has suggested that, when a catalyst is attached to a polymer chain, there may be adventitious changes due to the introduction of preferred orientations, a change stereochemistry about the metal atom, steric crowding, or a change in the equilibrium between the catalyst metal and its ligands. Patchornik and Krans [43] have pointed out that when a catalyst is bound to a cross-linked insoluble polymer, its motion is restricted, and if the molecules of catalyst are bound at an appropriate distance, a situation approaching infinite dilution may be reached. Reaction on such a catalyst may be more rapid than one in which the catalyst molecules are free. For instance, the polymer-supported catalysts have been demonstrated to have selectivity towards molecules of different bulk and polarity. Also, the attachment of a saturated complex that is a potential catalyst to a rigid support, followed by reductive elimination of a ligand, should produce higher concentration of monomeric coordinatively unsaturated species than is obtained in solution. This would then be reflected in the increase in catalytic activity of that complex as compared to a similar non-attached complex under the same conditions as have been reported by Brubaker and co-workers [39-41] .

In this research, a new route to preparing polymer-attached metallocene derivatives has been developed (Figure 2). By using this route, metallocene dichlorides of Ti, Zr, Hf, V, Nb, Ta, Mo, and W have been attached to polystyrenedivinylbenzene beads.

If the catalyst is heterogenized by linking it to a polymer, the catalytic as well as the support part must be able to stand whatever temperature is necessary for the reaction which is to be conducted, so it is important to use ligands which coordinate strongly and give thermally stable complexes. Putting methylene bridged titanocene dichloride on the support takes advantage of the fact that chelate complexes are more stable, inert, and less labile. This species would be expected to react like titanocene dichloride, but to be more stable.

RESULTS AND DISCUSSION

A. A New Route to Preparing Polymer Attached Metallocene Derivatives

The metallocene dichlorides of Ti, Zr, Hf, Nb, Ta, Mo, and W have been attached to the polymer according to a new route (Figure 2). It has been determined that there is sigma-pi interchange of ligands in $(C_5H_5)_3MCl$ (PART ONE) by use of $C_6H_5CH_2C_5H_4^-$ for one of the ligands. Following that observation, polymer-attached $(C_5H_5)_3MCl$ was synthesized from $(C_5H_5)_2MCl_2$ and polymer-attached $C_5H_5^-$, its Cp rings allowed to interchange, and then converted it to polymer attached metallocene dichloride by treatment with HCl. This procedure leads to the polymer supported metallocene dichloride at two thirds of the original concentration of the $(C_5H_5)_3MCl$, but provides a much more facile route to its preparation than the use of $(C_5H_5)MCl_3$ and the polymer-attached $C_5H_5^-$ (Figure 3). Further, it is very difficult to prepare monocyclopentadienyl halide derivatives of many metals - zirconium, hafnium, niobium, tantalum, molybdenum, and tungsten monocyclopentadienyl halides are all very difficult to prepare and purify - and so this reaction provides a means of making the polymer-attached metallocene dichlorides for those metals.

Because no direct ring exchange was detected (page 8) between benzylcyclopentadienide anion and vanadocene dichloride, the attachment procedure is different for vanadocene dichloride. Since we do know that the cyclopentadienide anion will displace a bound ring in

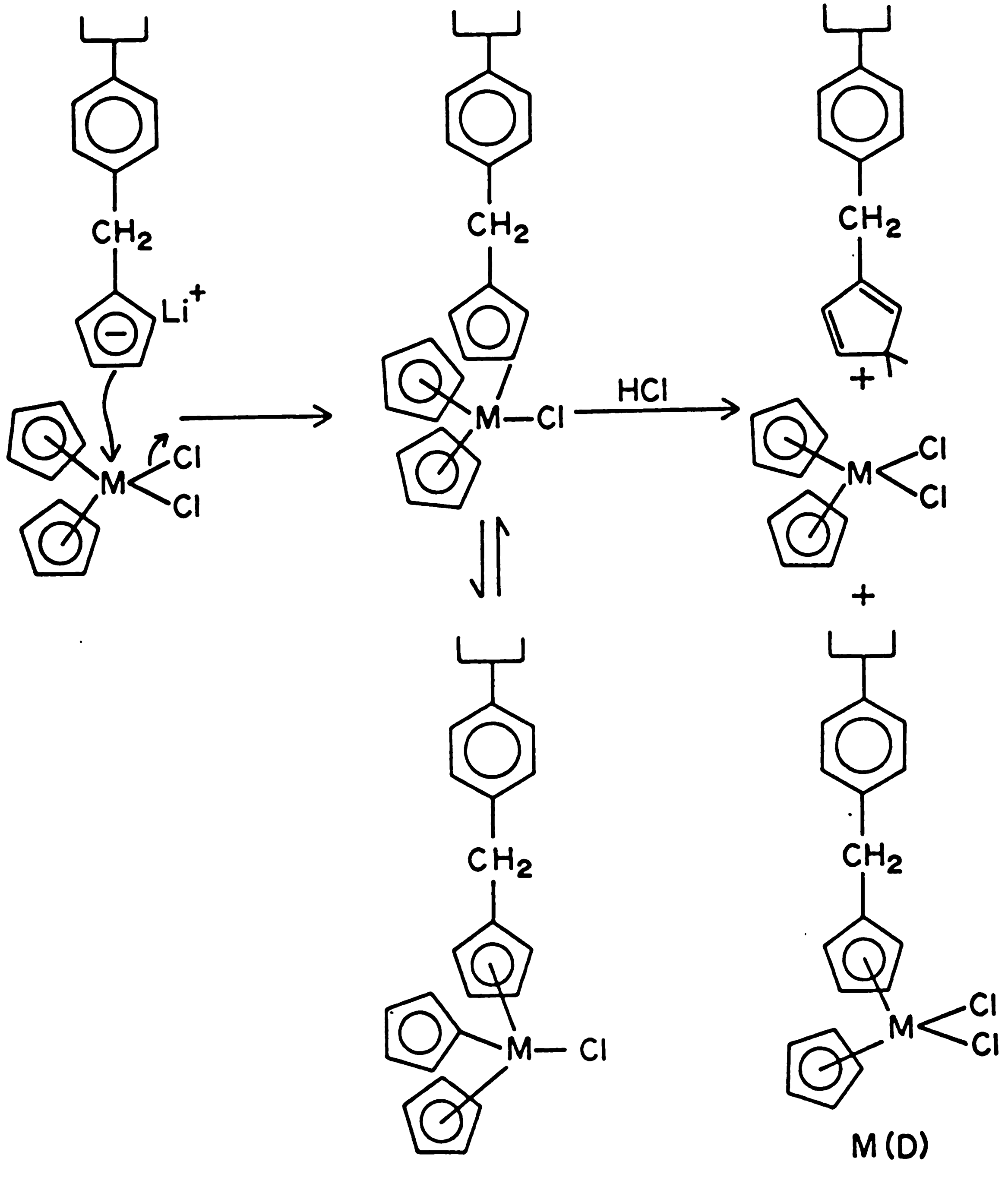

Figure 2. Scheme for the Preparation of Polymer Supported Metallocene Dichloride by a New Route

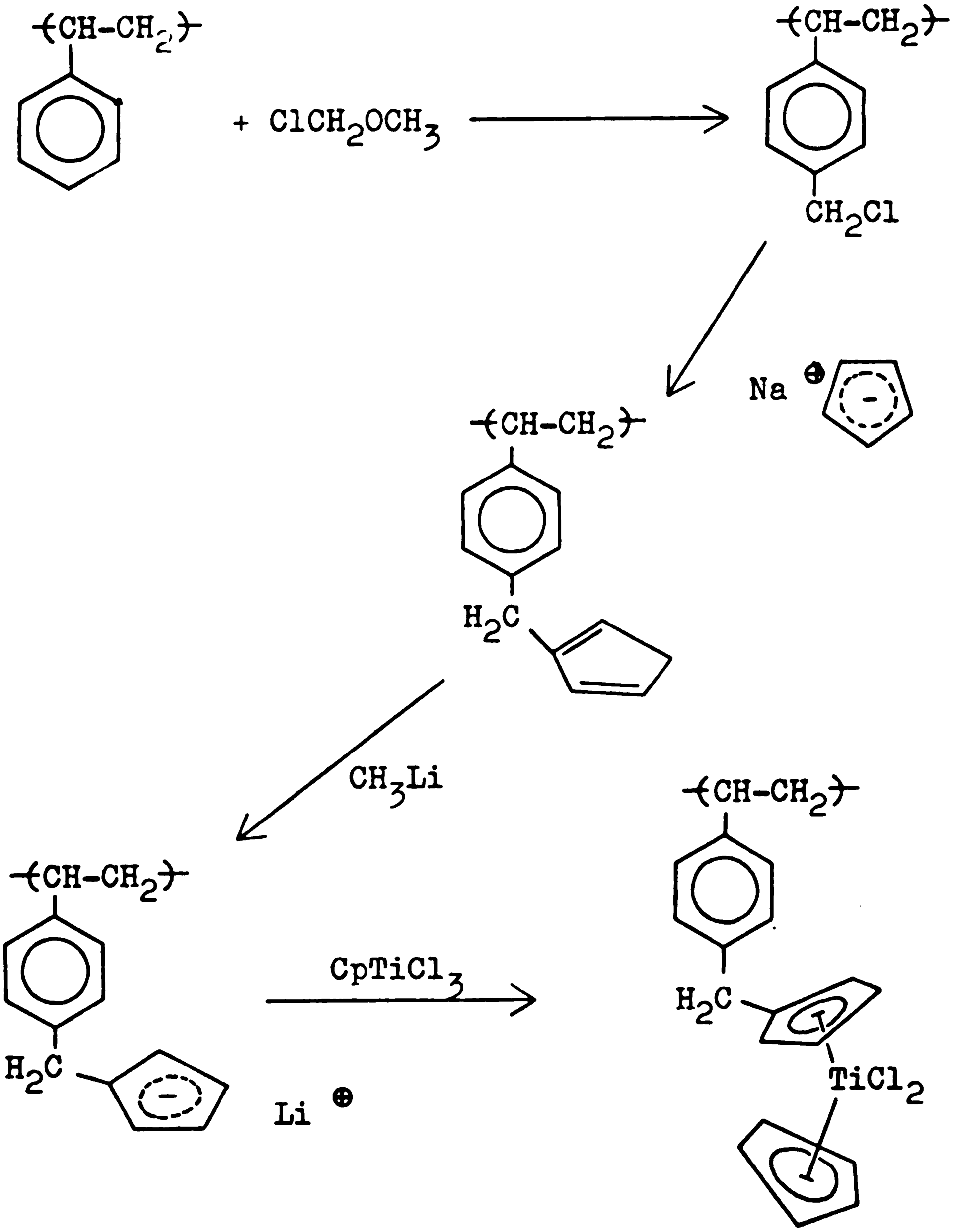

Figure 3. Scheme for the Preparation of Polymer Supported Titanocene Dichloride (ref. 14)

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vanadocene, this behavior can be used to attach the complex to the beads. After this product was treated with HCl vanadocene monochloride was generated it was then further oxidized by air/HCl mixture to vanadocene dichloride [6].

The analytical results of the metals and chloride concentrations of the supported metallocene dichlorides are listed in Table 10.

Table 10.

Analytical Results for The Polymer Supported Metallocene Dichloride

Attached Species	Concentration (mmole/g beads) Metal	Chloride	Ratio Expected	Found
Ti(D)	0.1	0.21	2	2.1
Zr(D)	0.19	0.45	2	2.4
Hf(D)	0.11	0.26	2	2.3
V(D)	0.048	0.109	2	2.3
Nb(D)	0.11	0.22	2	2.0
Ta(D)	0.4	0.92	2	2.3
Mo(D)	0.1	0.24	2	2.4
W(D)	0.12	0.23	2	1.9
BTi(a)	0.15	0.33	2	2.2
BTi(b)	0.12	0.28	2	2.3

Note: $M(D) = (-C_5H_4)M(C_5H_5)Cl_2$

In general, they are in reasonable agreement with the expected results. Since the beads are not totally inert to the gaseous HCl, the metal to chloride ratio may increase, if the reaction time is too long. However; usually the replacement reactions are fast, and keeping the reaction times less than 2 hours leads to the desired products. ESR spectral data of attached vanadocene and niobocene dichloride (Figures 4 and 5) were identical with those reported for nonattached species [7].

B. Polymer Supported Methylene Bridged Titanocene Dichloride

In the supported methylene bridged titanocene dichloride, characteristics of the supported catalyst which prevent the loss of metal, avoid contamination of product, etc., were imporved (compared with regular supported titanocene dichloride), for the following reasons:

(1) Higher thermal and photolytic stability.

The methylene bridged cyclopentadienyl ligands prefer pentahapto bonding to the metal [44], and usually pentahapto bonded rings are difficult to displace.

(2) Retention of higher catalytic activity.

Even if cleavage of one of the Cp rings occurs in Cp_2TiCl_2 and $CpTiCl_2R$ (in which R has substituded a Cp ring) is generated, the metal will still be attached on the polymer and act as an active catalyst in the next cycle.

Supported methylene bridged titanocene dichlorides were prepared according to Figures 6 and 7.

There are at least two advantages to these synthetic routes. First is the faster reaction rate. As soon as the first chlorine atom in the metal chloride derivatives is replaced by an incoming Cp anion the second chlorine atom is rapidly replaced by the other linked anion near by. Second is the retention of the loading in the reaction between Cp_2TiCl_2 and Cp anion beads. After treatment with HCl, the concentration of the originally attached Cp_4Ti is less likely to decrease, since

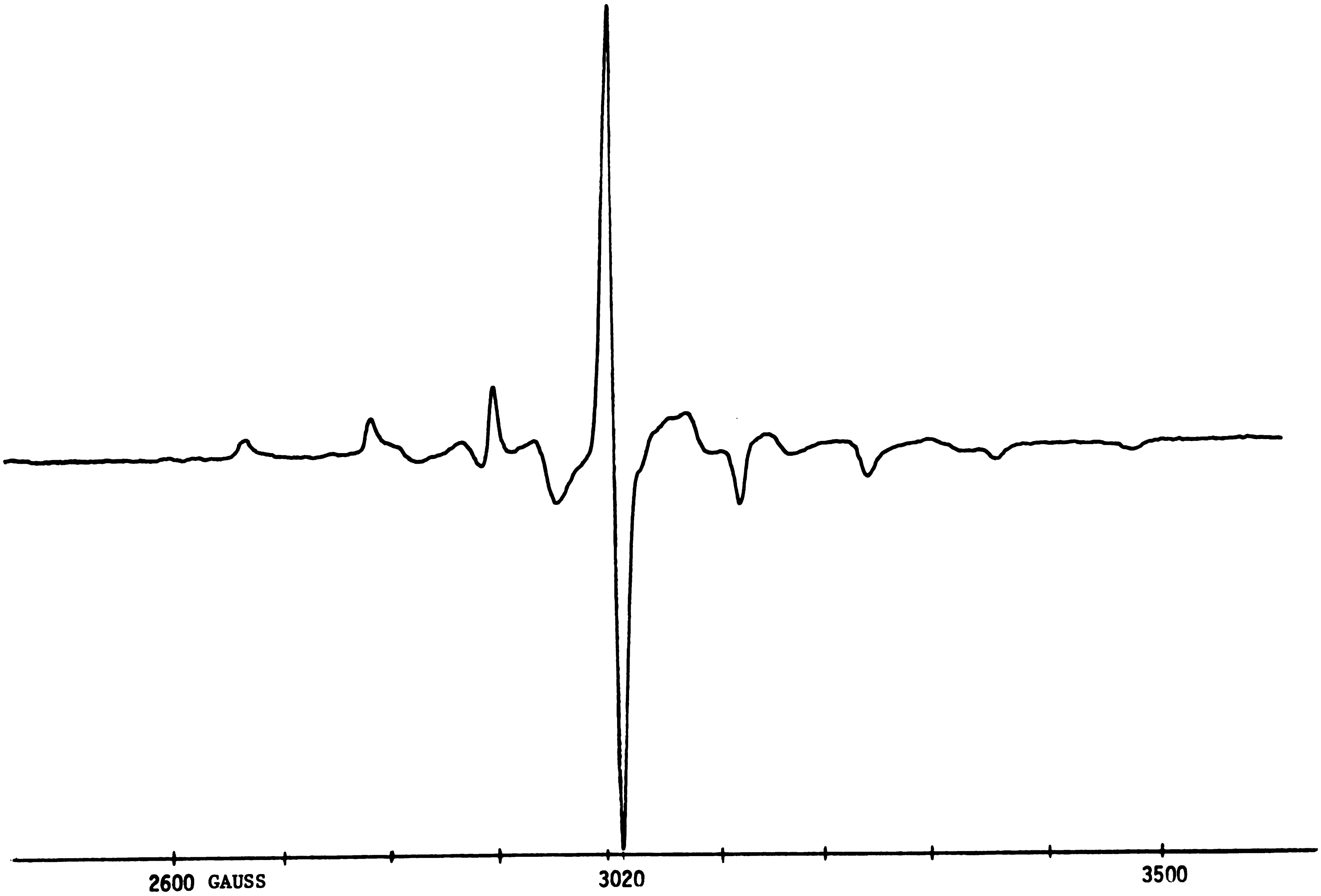


Figure 4. ESR Spectrum of Supported Vanadocene Dichloride

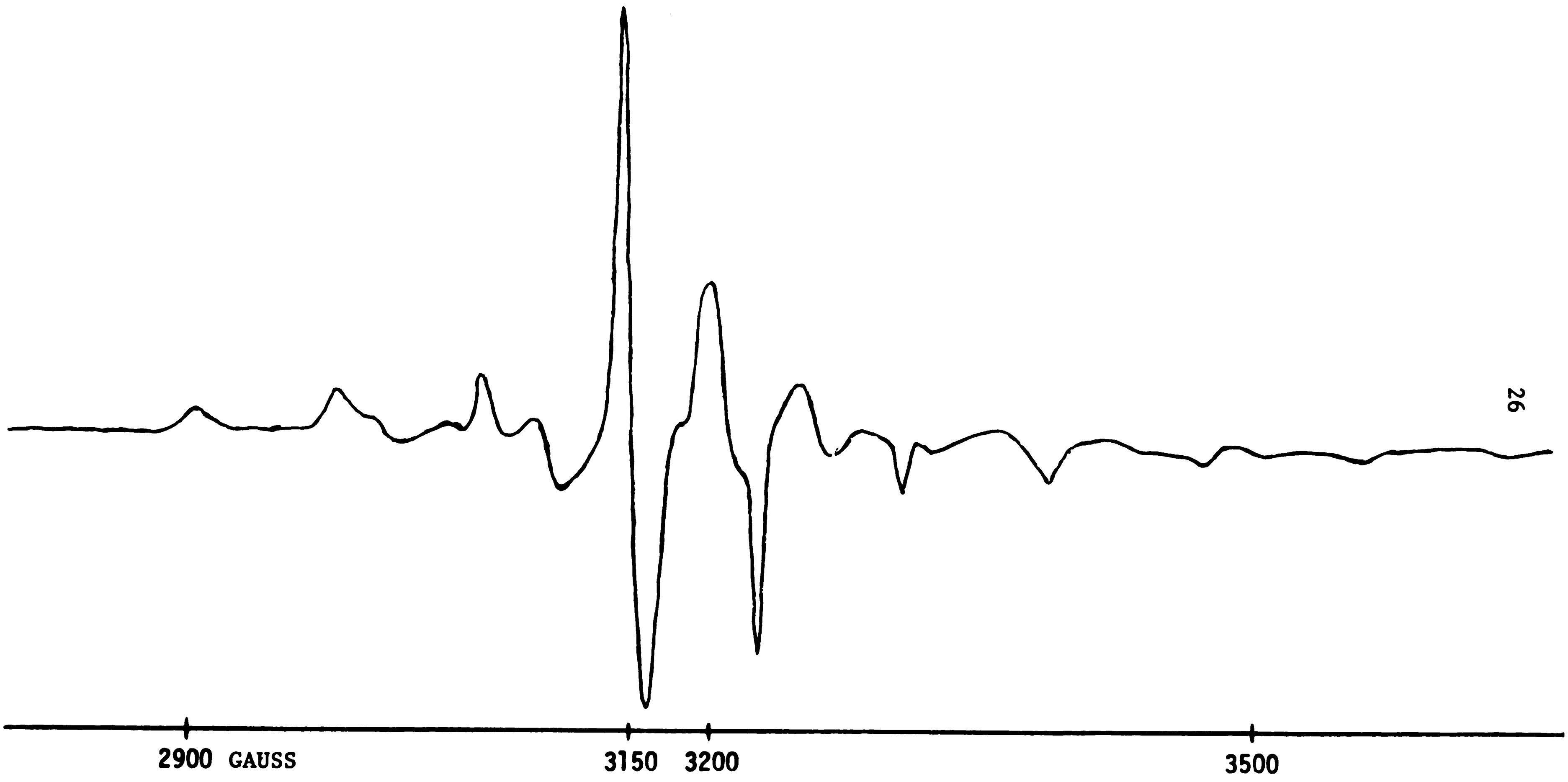


Figure 5. ESR Spectrum of Supported Niobocene Dichloride

the polymer attached methylene bridged Cp ligands prefer to be pi-bonded. That makes (B) more stable than (A) in the sigma-pi equilbrium, and therefore only the free Cp ligands in (B) will be substituted by Cl^- (Figure 6 and 7).

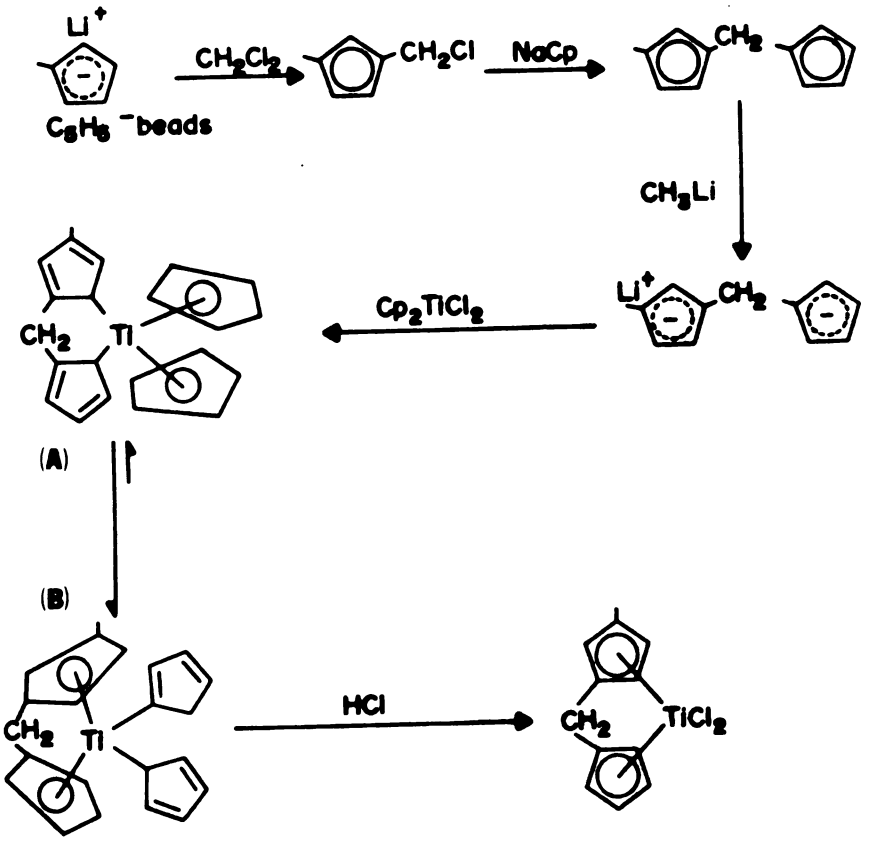


Figure 6. Scheme for the Preparation of Polymer Supported Methylene Bridged Titanocene Dichloride (a)

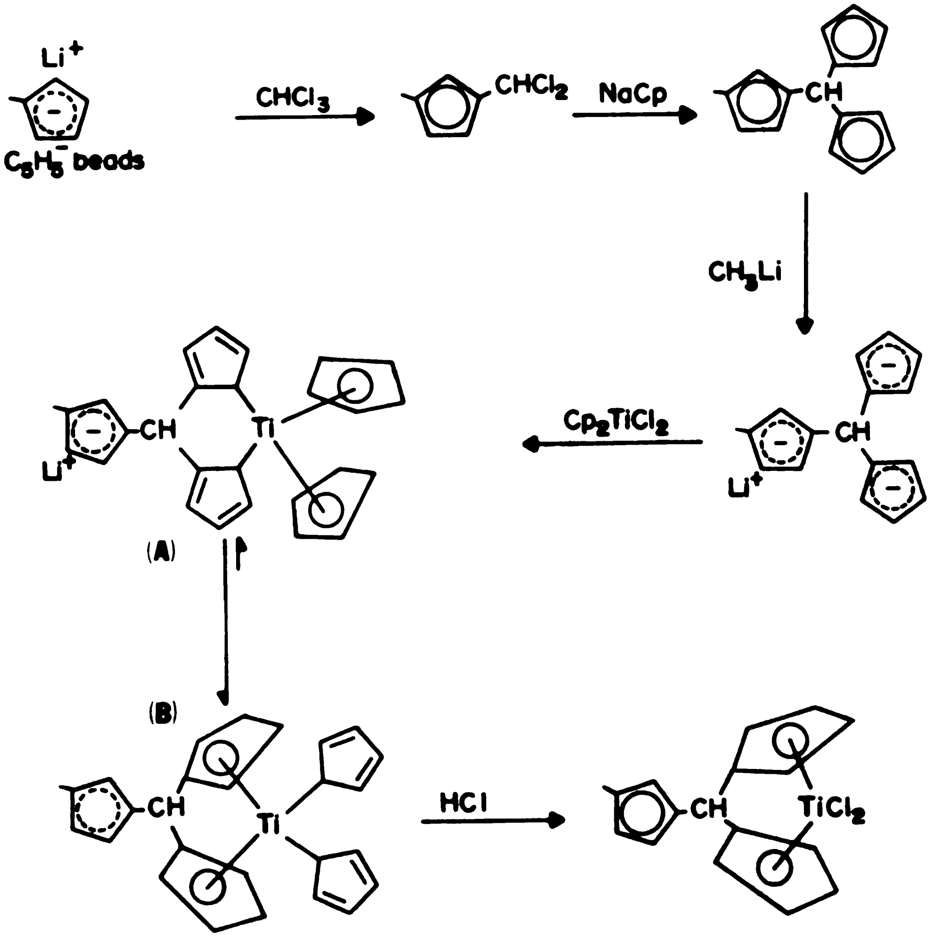


Figure 7. Scheme for the Preparation of Polymer Supported Methylene Bridged Titanocene Dichloride (b)

EXPERIMENTAL

A. General

General experimental techniques, sources of common chemicals and analytical instruments used in this work have been described in the EXPERIMENTAL section of PART ONE.

Cp beads (20% crosslinked polystyrene-divinylbenzene copolymer) were supplied by C. P. Lau, B. H. Chang and J. Ray of this Department.

The metal and chloride analysis of the polymer-attached complexes was obtained as previously described [39-41]. Titanium, hafnium, vanadium, niobium, tantalum, molybdenum and tungsten were determined by decomposition of the polymer (0.5 g) with three drops of concentrated H_2SO_4 and heating over a very low flame, and then by ignition of the metal containing polymer at 900^o (600^o for Mo and W) for 12 hours. The residue was weighed as the oxide. Metal complexed chloride was removed by digestion of the polymer samples in 2 N KOH solution at 100^oC for 12 hours. Chloride was determined by the Volhard method following acidification of the aqueous supernatant. The ESR spectra were recorded by use of a Varian E-4 ESR spectrometer.

B. Preparation of Anion Beads

The polymer attached cyclopentadienide beads (1 g) in THF were treated with excess CH_3Li in ether for 3 days. Excess CH_3Li was removed by thorough washing with THF (40 ml x 5 times). For the attachment of Ti and Hf, the lithium salt of the anion beads was kept in THF, but for all the others, the dry beads were stored in an argon filled dry box.

C. Preparation of the Polymer Supported Metallocene Dichlorides of Ti, Zr and Hf

A toluene solution of the metallocene dichloride was added to the anion beads (THF suspension), stirred for 2 days, and the beads were then treated with HCl. The color of the beads immediately changed from dark brown to red for the Ti species and yellow to cream for Hf,Zr species. After stirring for 5 hours, the solvent was removed and the beads were washed with $CHCl_3$ and THF until the washings were freed of metallocene dichloride and lithium chloride. The beads were then dried in vacuum.

D. Preparation of the Polymer Supported Metallocene Dichlorides of Nb, Ta, Mo, and W

Excess metallocene dichlorides of niobium, tantalum, molybdenum and tungsten were added to anion beads in dry box, and then 100 ml of THF was added to the mixture. After the flask was removed from the dry box, the mixture was stirred for 6 days, and then the flask was partially evacuated and refilled with HCl as above. The color of the beads changed from red to brown-black for niobium and tantalum and to green for molybdenum and tungsten species. Through the same washing procedures, the beads were dried in vacuum. (Ta beads are air sensitive).

E. Preparation of the Polymer Supported Vanadocene Dichloride

Excess vanadocene was mixed with the anion beads in 100 ml of THF, for 6 days. The atmosphere over the beads was then replaced with HCl gas as above. The color of the beads changed from dark blue to light blue in 10 minutes, as expected for the attached vanadocene monochloride. Five hours later, the whole mixture was exposed to the air and the attached species was oxidized to green vanadocene dichloride beads. The solution was decanted, the beads were washed with THF as above, and dried in vacuum.

F. Preparation of the Polymer Supported Methylene Bridged Titanocene Dichloride

Cyclopentadienide anion beads were treated with either (a) CH_2Cl_2 or (b) $CHCl_3$, and yellow beads of $-CpCHCl_2$, or $-CpCH_2Cl$ were formed immediately. The resulting beads were washed with THF and then treated with excess NaCp. After being stirred for 24 hours, NaCl and the excess NaCp were removed by thorough washing with THF. CH_3Li was added, and the mixture stirred for two days. Excess CH_3Li was removed with THF washes. Then the anion beads [product from both (a) and (b)] were treated with Cp_2TiCl_2 in THF and then treated with gaseous HCl. Bridged titanocene dichlorides were formed, washed with THF and then dried.

PART THREE

CYCLOPENTADIENYL LIGAND EXCHANGE REACTIONS IN SELECTED SYSTEMS

INTRODUCTION

The photochemistry of organometallic compounds of early transition metals has received considerable attention. Hunt and Winter [45] and McFarlane and Tindall [46] reported the observation of photoreduction of titanium(IV) alkoxides. Harrigan, Hammond, and Gray [47] found that the irradiation of cyclopentadienyl derivatives of titanium(IV) in solvents containing halogen atoms leads to photolysis and abstraction of halogens. The photochemical reactions of dimethyl derivatives of titanocene, zirconocene, and hafnocene were studied by Ald and Rausch [48]. Laine and Ford [49] reported that photolysis of neutral bimetallic complexes such as $(\eta^5\text{-CpW(CO)}_3)_2$ and $(\eta^5\text{-CpMo(CO)}_3)_2$ leads to homolytic metal-metal bond cleavage to give reactive organometallic radical species. The interest in such species derives in part from their potential roles in the synthesis of new organometallic complexes [50-52] and from possible usage in certain homogeneous catalytic processes [53, 54].

In our laboratory, the first photoexchange of cyclopentadienyl rings has been reported for d^0 systems [55,57]. Irradiation of a 1 : 1 benzene solution of titanocene dichloride/(D-10)titanocene dichloride with 313 nm wavelength light produced the exchange of the cyclopentadienyl ligand. Later it was expanded to the other metal systems [56,58]. The mechanism proposed by Vitz the photoexchange reactions of the cyclopentadienyl ligands between titanocene dichloride

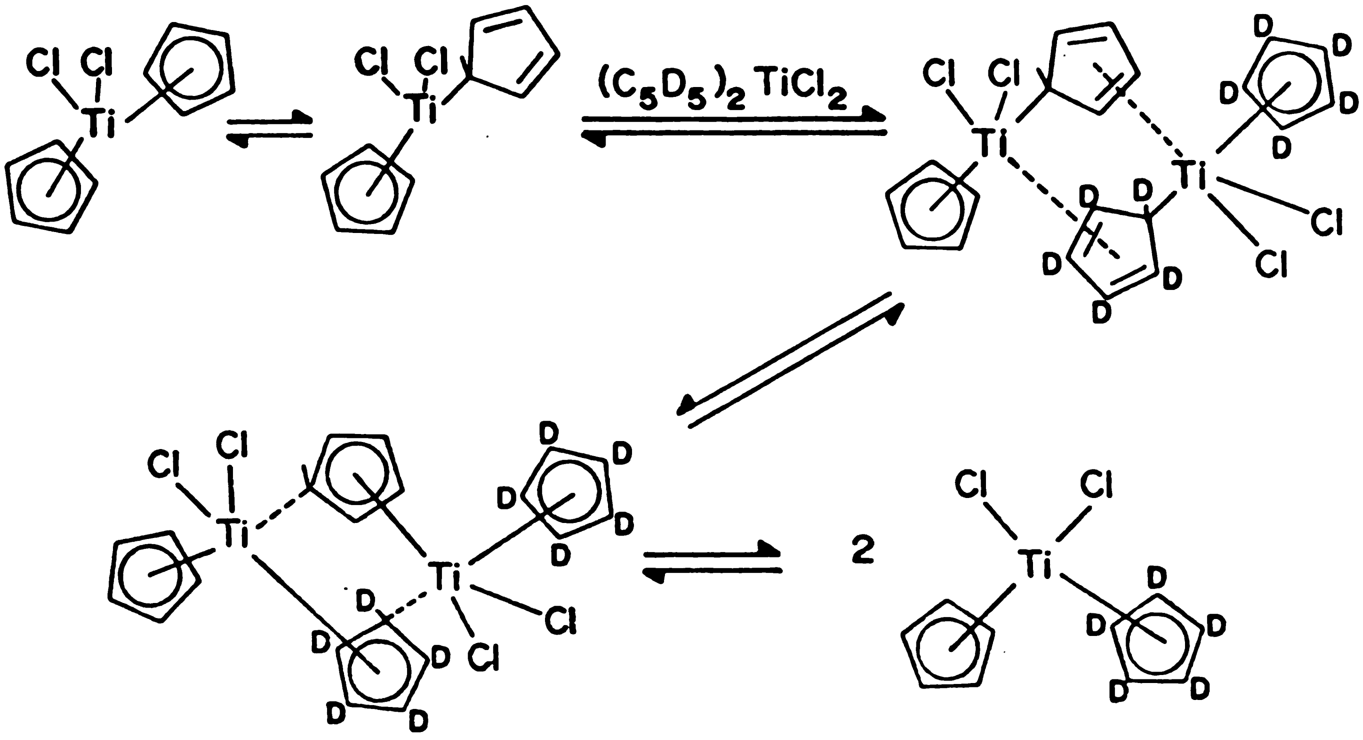


Figure 8. Proposed Mechanism for Photolytic Ligand Exchange Reactions of Titanocene Dichloride[60]

molecules on the basis of fundamental group theoretical and chemical considerations is given in Figure 8.

At the same time, Harrigan, et. al. propose a mechanism for the photocleavage of Cp_2TiCl_2 to generate $CpTiCl_2$ in neat benzene[47] which may well explain the Cp exchange reaction between $(C_5H_5)_2TiCl_2$ and $(C_5D_5)_2TiCl_2$. Harrigan said that the formation of $CpTiCl_2$ radical as a distinct intermediate prior to reaction with solvent is supported by neglibible effect of solvent concentration on the quantum yield and the order of magnitude increase in quantum yield upon permethylation of the cyclopentadienide ring. This latter effect was seen as a decreased probability of ring-metal bond reformation due to greatly increased steric hindrance. Additionally, he suggested that the formation of $CpTiCl_2$ in neat benzene in very low quantum yield indicates that reductive dissociation is an open reaction pathway and that recombination of the cyclopentadienyl radical with $CpTiCl_2$ is as expected, quite efficient.

In order to clarify the role of $CpTiCl_2$, a series of reactions under the conditions where the presence of $CpTiCl_2$ intermediate seems probable was reviewed (Figure 9).

$$\mathrm{CpTiCl_2} \quad + \quad \begin{array}{lcl} \mathrm{Br_2\ (Cl_2)} & \text{————————} & \mathrm{CpTiCl_2Br\ (CpTiCl_3)}\ \text{[61]} \\ \mathrm{CHCl_3\ (CCl_4,\ HCl)} & \text{————} & \mathrm{CpTiCl_3}\ \text{[47]} \\ \mathrm{MeOH} & \text{————————} & \mathrm{CpTiCl_2(OCH_3)}\ \text{[60]},\ \mathrm{CpTiCl_3} \\ \mathrm{CBr_4} & \text{————————} & \mathrm{CpTiCl_2Br,\ CpTiCl_3} \end{array}$$

Figure 9. Reaction Scheme for the $CpTiCl_2$ Intermediate

In the case of Br_2 (or Cl_2), the Br (or Cl) radical which is thermally generated initiates the formation of $CpTiCl_2$ intermediate by the abstraction of one Cp ring (giving CpX, X = Cl, Br, CpX may further react with X_2 to give $C_5H_5X_5$ as side product) and then reacted with Br_2 (or Cl_2) to give $CpTiCl_2X$. In all the other cases, the $CpTiCl_2$ which is generated by the photolysis of titanocene dichloride solutions abstracts a halogen atom to give the desired product. All these results are favor a $CpTiCl_2$ intermediate which was proposed by Harrigen and *et*. *al*..

Base on $CpTiCl_2$ intermediate, another photolytic ligand exchange pathway can be proposed (Figure 10).

$$(C_5H_5)_2TiCl_2 \xrightarrow{h\nu} (C_5H_5)^{\cdot} + (C_5H_5)TiCl_2$$

$$(C_5D_5)_2TiCl_2 \xrightarrow{h\nu} (C_5D_5)^{\cdot} + (C_5D_5)TiCl_2$$

$$(C_5H_5)^{\cdot} + (C_5D_5)_2TiCl_2 \longrightarrow (C_5H_5)(C_5D_5)TiCl_2 + (C_5D_5)^{\cdot}$$

$$(C_5D_5)^{\cdot} + (C_5H_5)_2TiCl_2 \longrightarrow (C_5H_5)(C_5D_5)TiCl_2 + (C_5H_5)^{\cdot}$$

$$(C_5H_5)^{\cdot} + (C_5D_5)TiCl_2 \xrightarrow{fast} (C_5H_5)(C_5D_5)TiCl_2$$

$$(C_5D_5)^{\cdot} + (C_5H_5)TiCl_2 \xrightarrow{fast} (C_5H_5)(C_5D_5)TiCl_2$$

Figure 10. Proposed Mechanism for the Photolytic Exchange Reactions of Titanocene Dichloride (based on Photolytic cleavage to give cyclopentadienyl radicals)

All the possible radical abstraction or combination process other than these are associated with decomposition. In the abscence of such decomposition, the recombination of the $CpTiCl_2$ and Cp radical has to be faster than any other processes. The exact nature of the $CpTiCl_2$ is not fully understood at this moment. A comprehensive study of the formation of $CpTiCl_2$ and the different types of reactions it can undergo is under investigation in our laboratory.

Substitution of pi-bonded ligands in general has received much attention. Information on ligand substitution mechanisms should enable us more profoundly to understand homogeneous catalysis by transition metal complexes. In 1956, Wilkinson, Cotton, and Birmingham [59] reported the first pi-ligand transfer reaction in which ferrocene was prepared from chromocene and ferrous chloride. In 1974 Rettig, *et. al.* [13], reported pi-ligand transfer reactions in (a) the reaction of LiC_5D_5 with MCp_2 in THF, M = V, Cr, Mn, Fe, Co, and Ni; and (b) the reaction of $Ni(C_5D_5)_2$ with MCp_2 (M = V, Cr, Co) in benzene. Here I wish to report my results of cyclopentadienyl ligands exchange in various systems. Cp rings are exchanged between molecules of vanadocene, chromocene or vanadocene monochloride and their analogs by a thermal process; however, this exchange can be enhanced by uv irradiation. In hafnocene dichloride and vanadocene dichloride and their perdeutoanalogs, the exchange occurs exclusively by photochemical process.

RESULTS AND DISCUSSION

A. Photolytic Cyclopentadienyl Ligand Exchange between Vanadocene Monochloride and Perdeutero Vanadocene Monochloride

When benzene solutions containing a vanadocene monochloride/(D-10)vanadocene monochloride mixture were irradicated with 313 nm light (Intensity equal to 0.0025 Ei/liter-hour) intermolecular exchange of the cyclopentadienyl rings occurs. Table 11 shows the pertinent peaks in the mass spectrum of samples irradiated for varying times. The peak at m/e = 221, corresponding to (D-5)vanadocene monochloride, increases relative to the peaks at m/e = 216 and 226, the D-0 and D-10 species, respectively, as photolysis time increases.

The possibility of hydrogen-deuterium exchange rather that cyclopentadienyl exchange is ruled out because there is a constant ratio of all peaks between m/e = 60 and 71 in both photolyzed and unphotolyzed samples. The ratio of the intensities of the m/e = 221 and 216 peaks I_{221}/I_{216}, is computed for each irradiation time. The fraction of exchange, F, is calculated on the basis of an equilbrium value of 1.88. For each sample, a plot of ln(1-F) vs. photolysis time was made, the most probable slope calculated by a standard least squares treatment of data, and the rate calculated by using the McKay equation [62] (Figure 11). The quantum yield, calculated by dividing the exchange rate (1.1×10^{-4} M/hr.) by the light intensity (2.5×10^{-3} Ei/liter-hr) is 0.044 mol/Ei.

The equilibrium constant for the reaction:

$$(\eta^5\text{-}C_5H_5)_2VCl + (\eta^5\text{-}C_5D_5)_2VCl \rightleftarrows 2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5D_5)VCl$$

Table 11. Mass Spectrographic Data for The Perdeuterovanadocene Monochloride/Vanadocene Monochloride Ligand Exchange.

Time(hr)	m/e = 216	221	226	65	66	67	68	69	70	71	$I/_{221}/I_{226}$	F
0	85	1.5	100	85	100	32	20	32	60	58	0.015	0.008
10	90	23	100	90	100	32	16	40	70	64	0.23	0.12
20	92	45	100	81	100	32	21	32	63	57	0.45	0.24
30	89	70	100	78	100	39	24	46	58	70	0.70	0.37
40	90	88	100	82	100	35	20	41	62	66	0.88	0.47
50	94	110	100	84	100	34	18	40	65	62	1.10	0.59
60	92	128	100	85	100	33	19	36	68	64	1.28	0.68
70	87	141	100	87	100	36	20	34	68	66	1.41	0.74
80	90	157	100	82	100	34	18	36	70	65	1.57	0.83
90	88	178	100	86	100	36	17	44	65	60	1.78	0.94
120	91	189	100	82	100	37	18	43	69	64	1.88	1.0

Note: % thermal-exchange has been substracted from normalized intensity.

Table 12. Cyclopentadienyl Ligand Exchange between Vanadocene Compounds of Different Oxidation States.

Compounds	Exchange Results	
	a*	b*
$(C_5H_5)_2VCl/(CH_3C_5H_4)_2VCl_2$	1%	5%
$(C_5H_5)_2V/(CH_3C_5H_4)_2VCl_2$	3%	30%
$(C_5H_5)_2V/(CH_3C_5H_4)_2VCl$	5%	50%

*a : room temperature, 24 hours

b : 70°, 24 hours

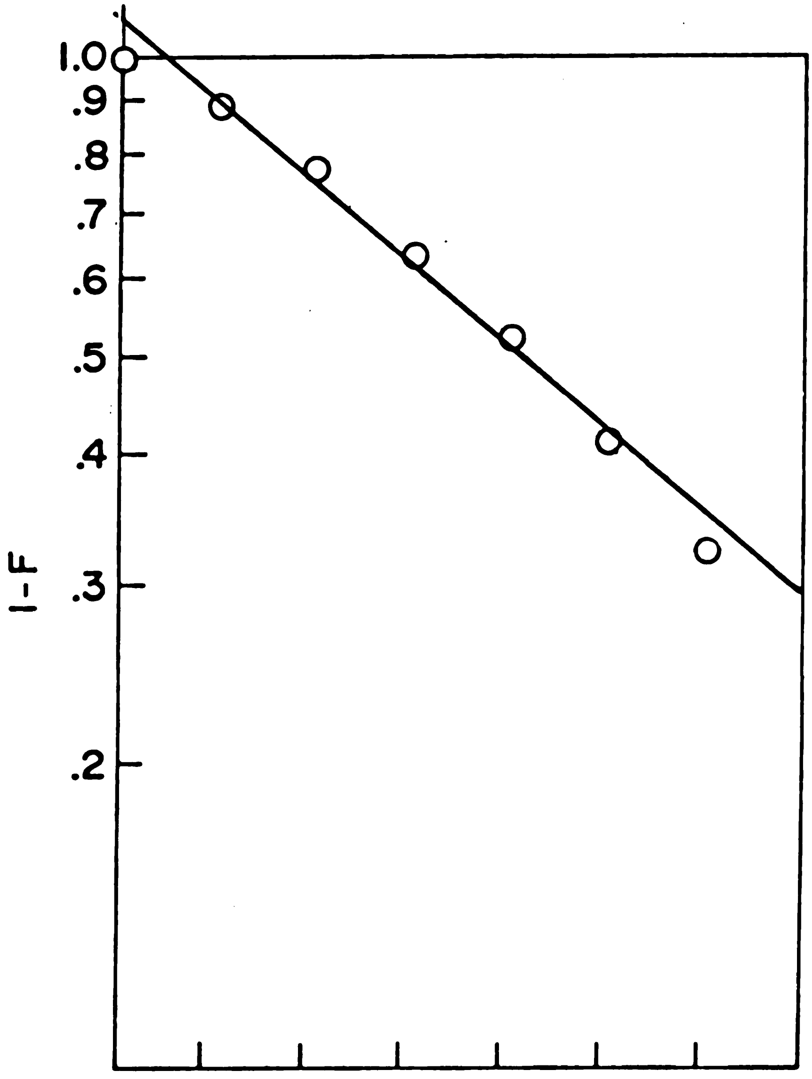


Figure 11. McKay Plot for Perdeuterovanadocene Monochloride/ Vanadocene Monochloride

calculated from the intensities of the exchange peaks in the mass spectrum at time t was $K = (I_{221})^2/(I_{226})(I_{216}) = 4.$ $(t \rightarrow \infty)$.

The exchange of cyclopentadienyl ligands is not solely a photochemical process. 10% thermal exchange is observed when the sample solution is stirred in the dark at room temperature for one week (about 0.5% for every 12 hours). At higher temperatures, the thermal exchange is even faster.

B. Cyclopentadienyl Ring Exchanges - Miscellaneous

Thermal cyclopentadienyl ligand exchange has also been observed in vanadocene/(D-10)vanadocene and chromocene/(D-10)chromocene. It can be enhanced by either increasing the temperature or by irradiating with uv light.

Like all the metallocene dichlorides, ligand exchange in hafnocene dichloride/(D-10)hafnocene dichloride and vanadocene/(D-10)vanadocene dichloride occurs only by a photochemical process.

Rapid photolytic Cp ring exchange was found as expected in the vanadocene/(D-10)vanadocene system.

We did observe side reactions in the following compounds. More than 20% of the vanadocene dichloride or hafnocene dichloride photolytically decomposed during the 24 hours photolysis at 313 nm required to reach exchange equilbrium.

The exchange of the cyclopentadienyl ligand in the three possible binary combinations of Cp_2V, Cp_2VCl, and Cp_2VCl_2 were studied. The results are listed on Table 12. Irradiating the reaction mixtures by all wavelength light always enhances the reactions, and Cp exchange rates increase with decreasing metal oxidation states.

The photolytic ring exchange reactions were not able to be detected in the mixed metallocene systems of $(C_5H_5)_2/(CH_3C_5H_4)_2VCl$ or $((C_5H_5)_2TiCl)_2/(CH_3C_5H_4)_2VCl$. The thermal exchange does occur in $(C_5H_5)_2Cr/(CH_3C_5H_4)_2VCl$ and $(C_5H_5)_2Cr/(C_5D_5)_2V$ systems.

C. Possible Mechanism

There are two possible mechanisms which can be used to explain the photolytic cyclopentadienyl ligand exchange reactions between H-10 and D-10 metallocene dichlorides. First, the bimolecular bridging mechanism which was proposed by Vitz on the basis of fundamental group theoretical and chemical considerations, is shown in Figure 8.

Second, the photodissociation and recombination mechanism suggested by Harrigan's experiments, in which $CpTiCl_2$ in neat benzene, can be generated from the direct photocleavage of the Cp_2TiCl_2, then rapidly recombine with a cyclopentadiene radical to regenerate titanocene dichloride, is shown in Figure 10. In this pathway, however, there is an equal chance for $CpTiCl_2$ to recombine with a perdeuterocyclopentadiene radical to generate the exchange species.

Certainly more study is needed to evaluate the relative importance of these two possible pathways.

EXPERIMENTAL

A. General

General experimental techniques, sources of common chemicals and analytical instruments used in this work have been described in the EXPERIMENTAL section of PART ONE. $CrCl_3$ was purchased from Alfa Product. Chromocene was prepared as previous reported [63], and its cyclopentadienyl-d_{10} metallocene analog was similarly prepared.

The two filter solutions for the isolation of 313 nm light were: (1) 0.002 $\underline{M}$ K_2CrO_4 in 0.07 $\underline{M}$ K_2CO_3 (1 cm) and (2) 0.96 $\underline{M}$ $CoSO_4$ (1.9 cm) [60].

Each benzene solution, containing a metallocene compound (10^{-3} $\underline{M}$) and its analog (10^{-3} $\underline{M}$), was irradiated by 313 nm light in merry-go-round photolysis apparatus. The irradiated samples were analyzed by mass spectrometry (Perkin Elmer RMU-6 Mass Spectrometer). Valerophenone actinomers were used to determine the lamp intensity [60]. These solutions, irradiated under essentially the same condition as the exchange solutions, were analyzed by gas chromatography.

B. Photolytic Cyclopentadienyl Ligand Exchange between Vanadocene Monochloride and (D-10)Vanadocene Monochloride

Weighed amounts of vanadocene monochloride and perdeuterovanadocene monochloride were stirred with benzene in 50 ml volumetric flasks in a glove box under argon. The solutions were stirred thoroughly and diluted to 200 ml to give 1.1×10^{-2} $\underline{M}$ vanadocene monochloride and

1.2×10^{-2} $\underline{M}$ (D-10)vanadocene monochloride. After mixing the two in dim light 3 ml aliquots were added to the 13 mm culture tubes to make about 60 samples. The tubes were securely stoppered under argon and sealed with an oxypropane torch. Twenty-four exchange samples and six actinomers were mounted in the merry-go-round photolysis apparatus equipped with a medium-pressure mecury lamp centered with 313 nm light filter solution. The temperature of photolysis was kept at 25°. The equipment has been described previously [60]. After measured periods of irradiation, four samples and one actinometer were withdrawn. The samples were pooled, evaporated to dryness, and sublimed at 80° before analyzing by mass spectrometry. The actinometer was analyzed by gas chromatography.

C. Photolytic Cycopentadienyl Ligand Exchange between Hafnocene Dichloride and (D-10)Hafnocene Dichloride

The procedure was the same as described as above. A mixture of 1.5×10^{-2} $\underline{M}$ in hafnocene dichloride and 1.2×10^{-2} $\underline{M}$ in (D-10)hafnocene dichloride was used.

D. Thermal and Photolytic Cyclopentadienyl Ligand Exchange between the H-10 and D-10 analogues of Cp_2V, Cp_2Cr and of Cp_2VCl_2

The procedure was the same as described above. The concentration of vanadocene dichloride and its analog is about 2×10^{-4} $\underline{M}$. The concentration of vanadocene, chromocene and their analogues were close to 10^{-2} $\underline{M}$.

E. Thermal and Photolytic Cyclopentadienyl Ligand Exchange in The Three Possible Binary Combinations of Cp_2V, Cp_2VCl and Cp_2VCl_2

Weighed amounts of vanadocene and bis-(methylcyclopentadienyl) vanadium monochloride were stirred with benzene in 100 ml volumetric flasks in a glove box under argon. The solutions were then mixed thoroughly to give 5.2 x 10^{-2} M vanadocene and 3.7 x 10^{-2} M bis(methylcyclopentadienyl) vanadium monochloride. Half of the solution was stirred in the dark, while the other half was stirred and heated to 70°. After 24 hours, the solvent was removed and the samples were analyzed by mass spectrometry. Similar procedures were carried out in the study of the $(C_5H_5)_2V/(CH_3C_5H_4)_2VCl_2$, and $(C_5H_5)_2VCl/(CH_3C_5H_4)_2VCl_2$ systems.

F. Thermal and Photolytic Cyclopentadienyl Ligand Exchange in the Mixed Metallocene Systems of $(C_5H_5)_2Cr/(C_5D_5)_2V$, $(C_5H_5)_2Cr/(CH_3C_5H_4)_2VCl$, and $(CH_3C_5H_4)_2VCl/((C_5H_5)_2TiCl)_2$

The procedure was the same as described above.

G. Quantum Yield Determination

The quantum yield for each ligand exchange process was determined by applying the approach of McKay analysis [62] on the mass spectrographic data. It was calculated from the exchange rate and light intensity.

The mass spectrum of vanadocene monochloride has a well characterized mass spectrum with a parent ion peak at m/e = 251. 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. Figure 12 and 13 show the mass spectra of the two derivatives. In the mass spectrum of an unphotolyzed mixture of vanadocene monochloride and its perdeutero-analog there are peaks at 216 and 226 with associated manifolds due to the isotopes ^{37}Cl, ^{35}Cl, ^{51}V, ^{12}C, and ^{13}C. The peak at m/e = 221 is zero for the unphotolyzed mixture. Photolyzed samples show increased intensity of the 221 peak (Figure 14), which corresponds

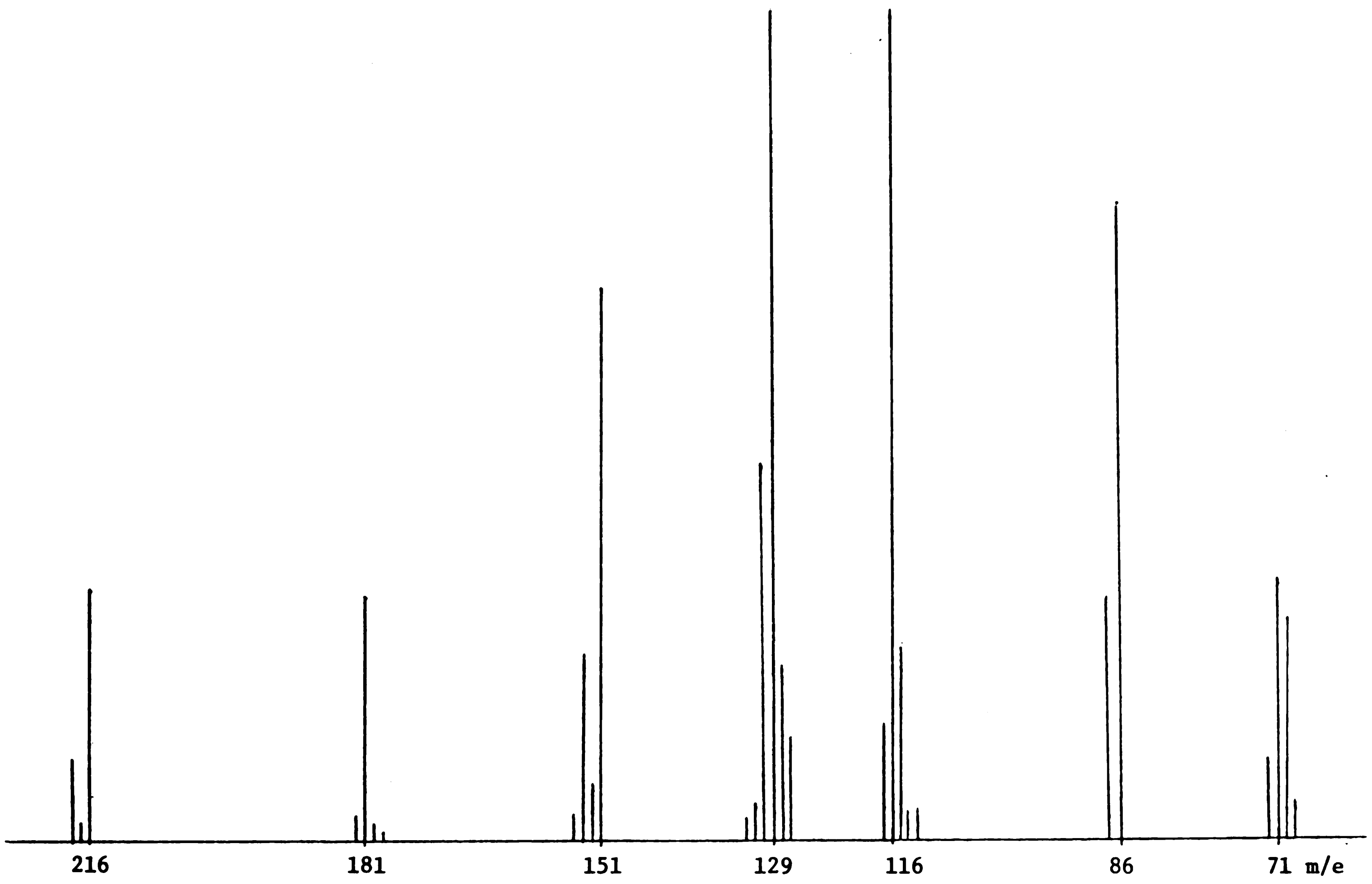


Figure 12. Mass Spectrum of Vanadocene Monochloride

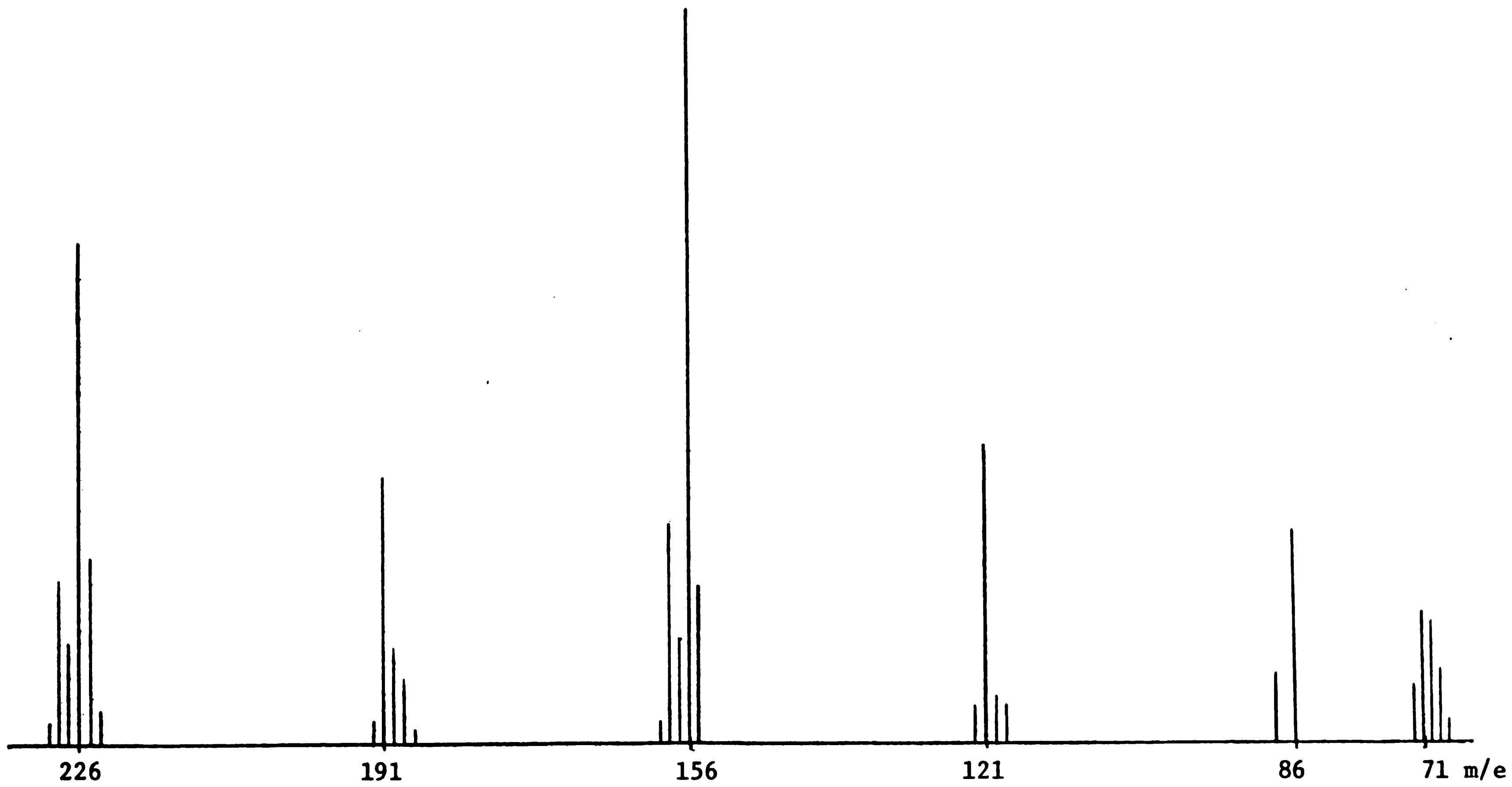
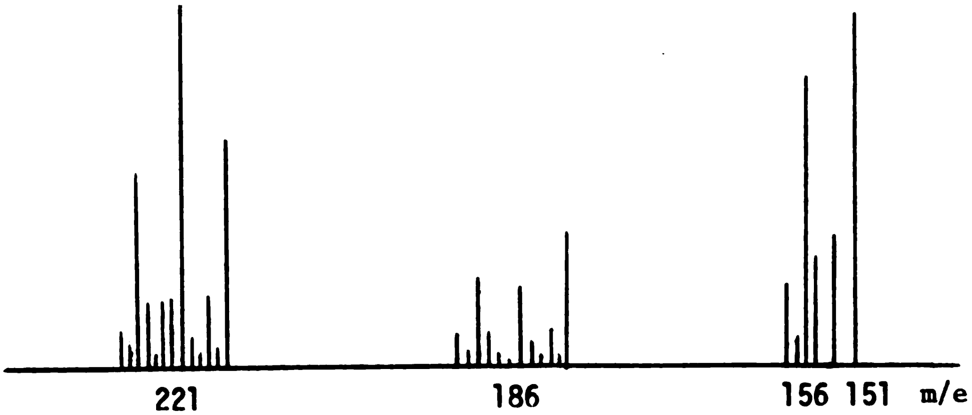
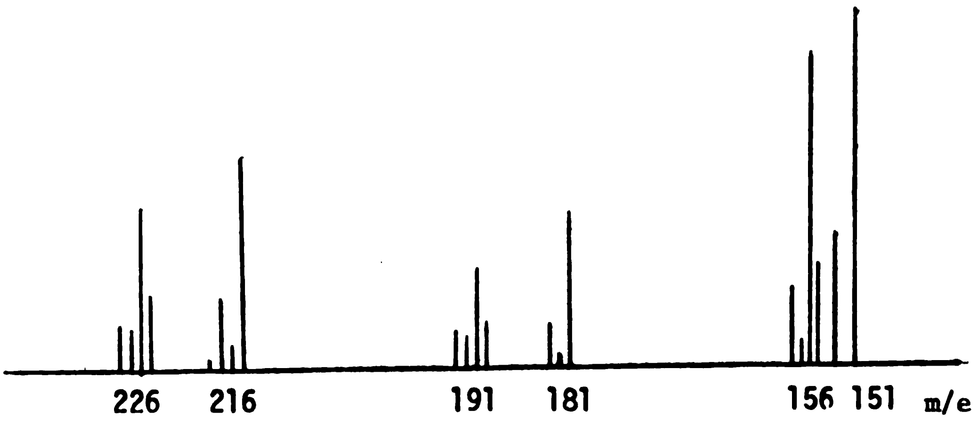


Figure 13. Mass Spectrum of (D-10)Vanadocene Monochloride



A. At t_{∞}



B. At t_0

Figure 14. Mass Spectra of Exchange Mixtures

to $(C_5H_5)(C_5D_5)VCl^+$. The ratio of the peaks at m/e = 221, and 226 for various periods irradiation reflects the extent of exchange.

The logarithmic form of the McKay equation [62], as applied to the exchange system, is as follows:

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

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

$$F = \frac{(I_{221/226})_t}{(I_{221/226})_\infty}$$

where $I_{221/226}$ is the ratio of the peaks at m/e = 221 and 226.

The plot of ln(1-F) vs photolysis time (Figure 11), had a slope of -0.019, which was determined by a linear squares treatment of the data.

From the slope and from the concentration of Cp_2VCl (1.1×10^{-2} $\underline{M}$) and $(C_5D_5)_2VCl$ (1.2×10^{-2} $\underline{M}$), the exchange rate, R, was computed as 1.1×10^{-4} $\underline{M}$/hr (or 3×10^{-8} $\underline{M}$/sec).

The quantum yield, computed directly from the experimentally observed exchange rate R (1.1×10^{-5} $\underline{M}$/hr) and corresponding absorbed intensity I (0.0025 Ei/liter-hr), can be generally expressed as [60] :

$$\Phi = \frac{R\ (\text{mol/liter-hr})}{I\ (\text{Ei/liter-hr})}$$

and has the value of 0.044 mol/Ei.

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