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1. MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL DECOMPOSITION OF DIPHENYLPERMETHYLTITANOCENE AND -ZIRCONOCENE 11. A POLYMER-SUPPORTED DICHLORO(CYCLOPENTADIENYL)-RHODIUM (III) CATALYST III. THERMOCHEMICAL DECOMPOSITION OF DINEOPENTYLPERMETHYLTITANOCENE IV. HEMOGENEOUS REDUCTION OF CARBON MONOXIDE

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# I. MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL DECOMPOSITION OF DIPHENYLPERMETHYLTITANOCENE AND -ZIRCONOCENE

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# IV. HOMOGENEOUS REDUCTION OF CARBON MONOXIDE

BY

Hsueh-Sung Tung

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# ABSTRACT

## I. MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL DECOMPOSITION OF DIPHENYLPERMETHYLTITANOCENE AND -ZIRCONOCENE

## II. A POLYMER-SUPPORTED DICHLORO(CYCLOPENTADIENYL)-RHODIUM(III) CATALYST

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## IV. HOMOGENEOUS REDUCTION OF CARBON MONOXIDE

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## I

Qualitative investigations of the mechanisms of photochemical decomposition of diphenylpermethyltitanocene and -zirconocene have been made. Reductive elimination as well as homolytic cleavage of metal-carbon $\sigma$-bonds are the two major pathways for photodecomposition of the diphenylpermethylmetallocenes. When benzene-$d_6$ was used as the solvent for photolysis of diphenylpermethyltitanocene, biphenyl-$d_0$ and biphenyl-$d_5$ were found in a ratio of 36/1, indicating that reductive elimination was the much more favorable process. But in the case of diphenylpermethylzirconocene, biphenyl-$d_0$ and biphenyl-$d_5$ were in a ratio of 1/3, suggesting that the homolytic photocleavage of the $\sigma$-bonds was predominant.

In the presence of carbon monoxide, moderately large amounts of the dicarbonylpermethylmetallocenes were found, suggesting that the permethylmetallocenes were the intermediates. The discovery of pentamethylcyclopentadiene and 2,3,4,5-tetramethylfulvene in the recovered solvent indicated further photodecomposition of permethylmetallocene. Consequently a more stable intermediate, $[(C_5Me_5)(C_5Me_4CH_2)M]$, is proposed. An oligomeric material was found to be the major final product after photolysis of the title compounds. Although the structure of the oligomeric material remained undetermined, it was believed to be mainly $[(C_5Me_5)-(C_5Me_4CH_2)M]$ as unit block, because of the finding of pentamethylcyclopentadiene and 2,3,4,5-tetramethylfulvene in a ratio of 1 : 1.3.

Small amounts of $N_2$ were absorbed by the photolyzed solution of the title compounds although the hydrogenation of olefins was not appreciable. Nitrogen-15 NMR measurement of the $N_2$-complexes as well as an ESR spin trapping experiment with the photolyzed complexes were also made in this study.

## II

The insoluble dichloro(cyclopentadienyl)rhodium(III) complex was successfully anchored to 20% divinylbenzene crosslinked polystyrene by treating polymer-attached cyclopentadiene directly with rhodium trichloride trihydrate. Polymer-supported dichloro(cyclopentadienyl)rhodium(III) proved to be a good hydrogenation catalyst for olefins as well as arenes in the presence of excess triethylamine under 110 psig $H_2$ and at 70° C. It could also catalyze the isomerization of allylbenzene in the absence of triethylamine at 85° C. Under 80 psig pressure of CO + $H_2$ (1/1) in the presence of triethylamine, this polymer-supported catalyst can be easily converted into the polymer-supported dicarbonyl(cyclopentadienyl)rhodium(I) catalyst. Mechanisms for the catalyst-preparation, hydrogenation and isomerization were also discussed.

## III

Thermal decomposition of dineopentylpermethyltitanocene produced methane (5.1%), ethylene (4.2%), isobutylene (15%), neopentane (75%) and trace amounts of $C_3$ and $C_4$ hydrocarbons. A titanametallacycle and a titanium-carbene complexes are proposed as intermediates following $\gamma$-hydrogen elimination. Deuterium tracer experiments indicated that the hydrogen-abstraction of the titanium-carbene complex to produce

methane was from the solvent, and not from the cyclopentadienyl rings.

## IV

Transition metal carbonyls were used as catalysts to hydrogenate carbon monoxide in the presence of a base under pressures of 40 to 960 psig at various temperatures. Although the catalytic reaction was not achieved, some interesting reductions of carbonyl ligands on the metal carbonyls were discovered. An aluminum hydride derivative was found to reduce carbon monoxide rapidly at 90° C to produce methane. Sodium hydroxide could initiate the reduction of carbonyl ligands of hexacarbonyltungsten at 150° C under the pressure of CO and $H_2$ in the presence of hexamethyldisiloxane. A mechanism is proposed for this reaction.

To my parents and Ying

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H. S. T.

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# PART I

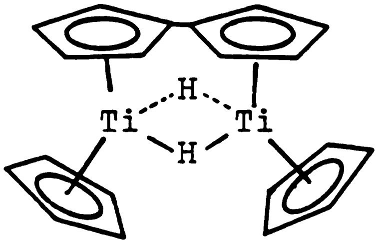
## MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL DECOMPOSITION OF DIPHENYLPERMETHYLTITANOCENE AND -ZIRCONOCENE

# PART I

## INTRODUCTION

Since the discovery of ferrocene in 1951[1], the remarkable "sandwich" structure as well as its extraordinary thermal stability provided the initial impetus for the immense and continuing research effort on ferrocene[2] and related compounds. Bis-$\eta^5$-cyclopentadienyl complexes of iron, vanadium, chromium, mangnese, cobalt, and nickel are fairly stable and can be readily prepared by standard methods of organometallic synthesis[3,4]. In contrast, bis($\eta^5$-cyclopentadienyl)titanium(II) appeared to be extremely reactive and, hence, instability of the monomeric $(\eta^5\text{-}C_5H_5)_2Ti$ species lies in its carbenoid-type behavior[5,6]. The structure and nature of titanocene had been a subject of argument for a long period of time[7,8], since the first report of preparation of the titanocene by Fischer and wilkinson in 1956[9]. Strong reducing reagents, such as magnesium[10] or sodium[11] had been reported to reduce titanium (IV) to titanium(II). Electrochemical reduction of titanocene dichloride could destroy the Ti-Cl bonds, leaving the $\pi$-bonds of titanium to cyclopentadienyl ligand intact[12-14]. However, the nature of titanocene varied with the methods of preparation[7-14]; thus, the parent titanocene $(\eta^5\text{-}C_5H_5)_2Ti$, the dimer $[(\eta^5\text{-}C_5H_5)_2Ti]_2$, or its rearranged product

$[(\eta^5\text{-}C_5H_5)(\mu\text{-}C_5H_4)TiH]_x$ was believed to be the possible formula of titanocene. An attempt to isolate titanocene ended with a relatively inert dimer, $\mu$-($\eta^5$:$\eta^5$-fulvalene)-di-$\mu$-hydrido-bis($\eta$-cyclopentadienyltitanium) (1)[8]. But another titanocene dimer, $\mu$-($\eta^1$:$\eta^5$-cyclopentadienyl)-tris-($\eta$-cyclopentadienyl)dititanium(Ti-Ti) (2), prepared by the low-temperature reduction of $(C_5H_5)_2TiCl_2$ with potassium naphthalene, was also reported by Pez[16].



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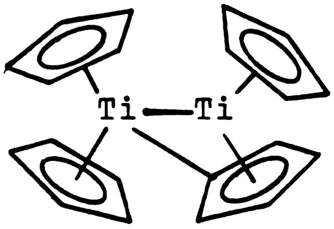

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Despite all these uncertainties about titanocene, there were some characteristic reactions exhibited by this metastable species. These observed characteristics are summarized below in Fig. 1[7,11,17-20]. In addition, Van Tamelen et al.[21] also reported the catalytic ability of titanocene to hydrogenate olefins. And the polymerization of acetylene was catalyzed by titanocene, which was obtained from the reduction of $Cp_2TiCl_2$ by sodium amalgam, according to Yokokawa and Azuma[22]. Presumably, the metastable titanocene(II) was either the intermediate or the catalyst in all these reactions. In the absence of hydrogen, two ethylene molecules seemed to stablize the titanocene. An equilibrium between the ethylene coordinated titanocene and

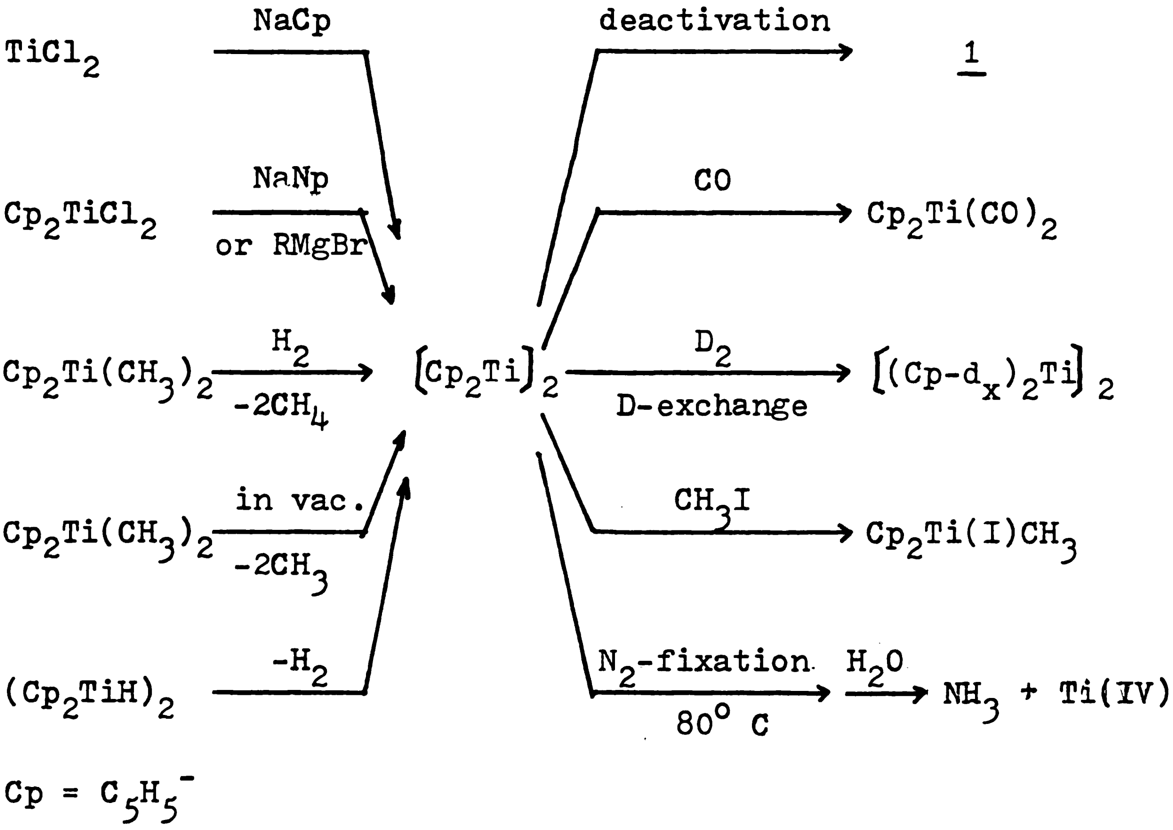
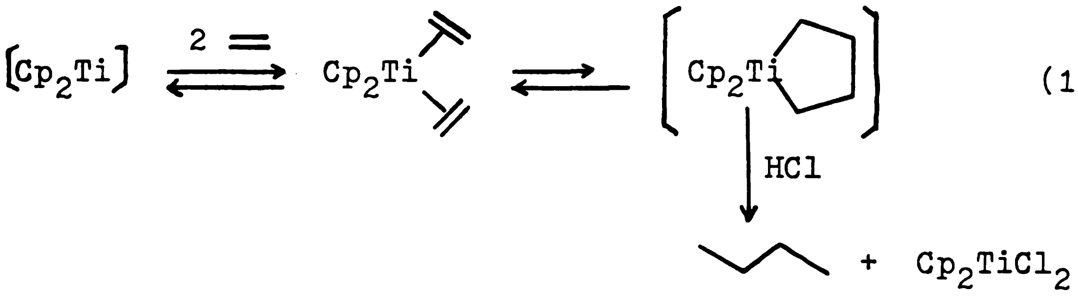


Figure 1 Nonphotochemical preparations and reactions of titanocene

a metallocycle, 1,4-tetramethylene-bis(cyclopentadienyl)titanium(IV), was established (Eq. 1)[23].

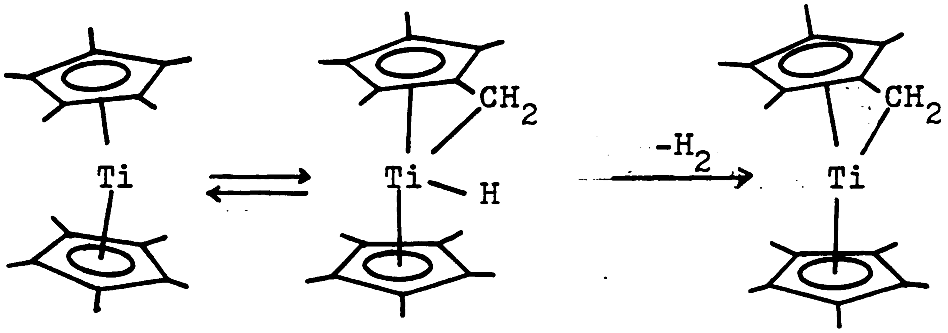


(1)

Subsquent decomposition of the metallocycle would produce butene, although the isolation of the 1,4-tetramethylene-bis(cyclopentadienyl)titanium(IV) has not been successful.

Because of the similar but less reactive nature of zirconocene compared with titanocene, much less attention had been given to it[24]. The only important catalytic feature of zirconium is probably Ziegler-Natta type polymerization catalysis[25]. However, advantage has been taken of the relative stability and lower reactivity of zirconocene in order to investigate certain zirconocene-related intermediates and, hence, to understand the titanium-analog which is intrinsically difficult to study because of its extreme instability. For example, the successful X-ray crystallographic and NMR dynamic studies of the dinitrogen complex of permethylzirconocene dimer have clearly explained the similar properties for the titanium-analog[26].

Cyclopentadienide anion has an aromatic sextet of $\pi$-electrons which makes it a stable $\pi$-bond ligand for most organometallic compounds. It exhibits extreme stability for Group VIII metal "sandwich" compounds. But for the early transition metals such as Ti and Zr, the ring-H atoms become labile. Ring-H abstraction has resulted in dimerization among the rings and the metals, for instance, compounds (1) and (2). Such dimerization usually are irreversible and deactivate the active monomer. In view of this problem, 1,2,3,4,5-pentamethylcyclopentadienide anion has been used as an analogous ligand[18,26]. Five methyl groups on the ring can not only prevent the dimerization or polymerization among the rings but also improve the solubility of its ligated organometallic compounds in various organic solvents. Therefore, the importance of the pentamethyl-cyclopentadienyl group as a ligand has increased. Permethyltitanocene was reported to be much more stable than the analogous titanocene, according to Bercaw[27]. However, prolonged storage of this species at room temperature still resulted in its decomposition to compound (3) (Eq. 2) with the evolution of hydrogen.



(2)

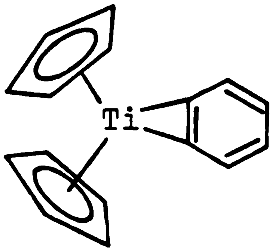
3

Studies of the chemistry of transition metal alkyls have increased dramatically in recent years because of the recognition that the metal-carbon bond in metal alkyls is inherently strong and that decomposition does not readily occur by simple homolytic cleavage. In addition, the understanding of the stability and degradation of the metal alkyls could help to disclose the mystery of catalytic behavior of such organometallic compounds[24,28]. Beta-hydrogen elimination is the low-energy and, hence, the most common pathway causing decomposition of the metal-carbon bond, and often responsible for the relative instability of these transition metal alkyls. Much attention has been given to alkyl ligands which do not have β-hydrogen, such as methyl, neopentyl, benzyl, etc. But the interaction between the metal d-orbital and the π-electron cloud makes the phenyl group a special ligand and stablizes these metal alkyls.

Preparations of diphenyl[29] and dimethyl[30] derivatives of titanocene were reported as early as 1955, whereas the similar derivatives of zirconocene were not reported until 1973[31]. Scattered reports of the basic reactions of dialkyl and diaryl titanocenes were found in the literature[19,32]. A quantitative amount of titanocene dichloride was found when the dialkyl reacted with hydrogen chloride gas (Eq. 3).

$$Cp_2TiR_2 \xrightarrow{HCl} Cp_2TiCl_2 + 2\ RH \qquad (3)$$

Thermal decomposition of these alkyl[33] and aryl[34-47]



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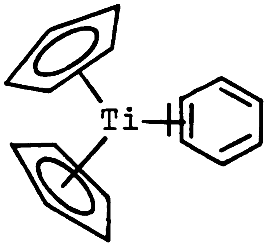
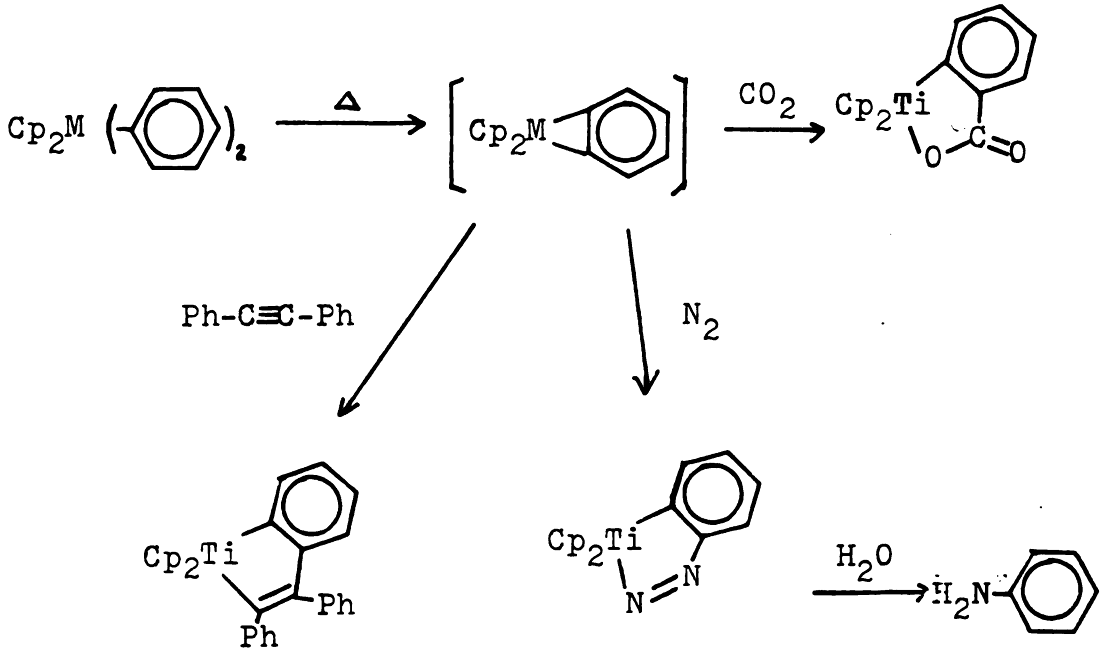


5

derivatives was one of the major areas being investigated. Beta-hydrogen elimination was believed to be the predominant pathway to generate an intermediate o-phenylene (4) or benzyne (5) derivative of titanocene and zirconocene. The observations from thermochemical decomposition of diaryl titanocene and zirconocene are summarized below in Fig. 2.



M = Ti or Zr

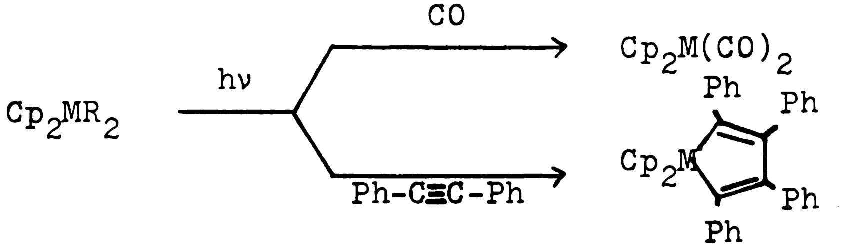
Figure 2 Thermal decomposition of diaryl titanocene and zirconocene

Photochemical properties of the dialkyl and diaryl derivatives of titanocene and zirconocene **have** not been examined as extensively as thermolysis[48]. The earliest study of photochemical degradation of diphenyltitanocene was very brief by Razuvaev et al.[32] in 1961. These investigators reported that titanocene dichloride was produced upon photolysis of diphenyltitanocene in chloroform for 50-60 h. Benzene and a very small amount of biphenyl were also obtained. However, no chlorobenzene or cyclopentadiene could be detected. Harrigan et al. first reported in 1974[49] that dimethyltitanocene was photosensitive. When dimethyltitanocene was photolyzed in degassed chloroform solution, a product mixture of $Cp_2Ti(CH_3)Cl$ , $Cp_2TiCl_2$ , and $CpTiCl_3$ was obtained. About the same time, Rausch and Alt[50] studied the photolysis of dimethyl derivatives of titanocene, zirconocene, and hafnocene in somewhat more detail. "Black titanocene" and methane were reported to be the major products from the photolysis of dimethyltitanocene. This "black titanocene" was not identical to the "titanocene" characterized by the other workers[7-14]. Corresponding metallocenes were also reported to be one of the products from the photolysis of dimethyl derivatives of zirconocene and hafnocene (Eq. 4).

$$Cp_2M(CH_3)_2 \xrightarrow{h\nu} \text{"}Cp_2M\text{"} + 2CH_4. \qquad (4)$$

M=Ti, Zr, Hf

In the presence of carbon monoxide and diphenylacetylene, the photochemically-generated metallocenes produced the corresponding adducts, dicarbonylmetallocenes and 1,1-bis($\eta^5$-cyclopentadienyl)-2,3,4,5-tetraphenylmetallanoles[51] (Eq. 5).

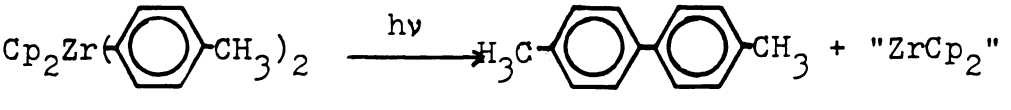


(5)

Three years later, Peng and Brubaker[52] examined the photolysis of diphenyltitanocene and suggested that benzene, biphenyl and an oligomeric material formulated as $[Ti(\eta^5-C_5H_5)_2H]_x$ were produced (Eq. 6). However, Rausch

$$Cp_2Ti(C_6H_6)_2 \xrightarrow{h\nu} [Cp_2TiH]_x + C_6H_6 + Ph\text{-}Ph \qquad (6)$$

et al.[53] reported that irradiation of diphenyltitanocene in benzene-$d_6$ solution produced black titanocene", a 1/1 ratio of biphenyl-$d_0$ and biphenyl-$d_5$. With the di-paratolyl analog, a mixture of toluene, 4-methylbiphenyl, and 4,4'-dimethylbiphenyl were obtained upon photolysis. In contrast to the chemistry observed with diaryltitanocenes, Erker[46] had suggested that photolysis of diarylzirconocene led only to coupling of the aryl ligands (Eq. 7).



(7)

The nearly-quantitative yield of 4,4'-dimethylbiphenyl from photolysis of di-para-tolyzirconocene in benzene solution seemed to raise a question about Zr-tolyl homolysis to produce tolyl radicals.

There were discrepancies among these studies. Furthermore, hydrogenation of ethylene and 1-hexene, which was reported to be catalytic at low temperature over titanocene generated from other methods[21], proved in this laboratory not to be appreciable in the presence of photolyzed diphenyltitanocene[125]. Isomerization of allylbenzene was not observed. These observations clearly indicate the necessity for additional mechanistic studies in these systems.

Since bis(pentamethylcyclopentadienyl) derivatives of titanium and zirconium had proved to be useful congeners to their bis(cyclopentadienyl)analogues by virtue of enhanced stability, solubility, and crystallinity[25,27], investigations into the mechanistic aspects of diphenylpermethyltitanocene (6) and -zirconocene (7) upon photolysis have been made in this study.

# EXPERIMENTAL

## 1. Material

Reagent grade solvents were used. Benzene, toluene, xylene and tetrahydrofuran (THF) were distilled over sodium-benzophenone under argon. Hexane, n-pentane and other saturated hydrocarbons were refluxed over calcium hydride at least overnight and freshly distilled prior to use. Diethyl ether and 1,2-dimethoxyethane were refluxed and distilled from lithium aluminum hydride. Petroleum ether (30-60° C) was distilled from lithium aluminum hydride into "titanocene"[18] and transferred under vaccum into the reaction flask immediately before use. Hydrogen, carbon monoxide, *cis*,*trans*-2-butene and hydrogen chloride were purified grade from Matheson. Phenyl lithium, methyl lithium, 1-hexene, cyclohexene, allyl benzene and ethyl acetate were purchased from Alrich Chemical Co.. Titanocene dichloride and zirconium tetrachloride were obtained from Alfa Ventron Corp. while zirconocene dichloride was purchased from Arapahoe Chemical Co. and sublimed at 150-180° C. All the other regular chemicals were obtained from Fischer Scientific Co., J. T. Baker Chemical Co. and Mallinckrodt, Inc. respectively. Packing material used for gas chromatography, such as Porapak Q, Durapak and Molecular Sieve 5A etc. were purchased from Water Associates, Inc. or Altech Associates.

Purified grade nitrogen and argon from Matheson were further deoxygenated by passing through columns of activated BASF catalyst R 3-11 and Aquasorb (Mallinckrodt). Benzene-$d_6$, 99.5% deterium, and toluene-$d_8$, 99%, were also purchased from Aldrich Chemical Co. and further purified by distillation from sodium. N-15 (95%) enriched nitrogen gas was obtained from Merk & Co., Inc..

## 2. General techniques and equipments

Schlenk-tubes and a vacuum line were used to handle the air and moisture-sensitive compounds. Where necessary transfers were made in an argon or nitrogen-filled glove box.

Proton NMR spectra were obtained by use of a Varian T-60 spectrometer and a Bruker WM 250 when necessary. Nitrogen-15 NMR spectra were measured on a Bruker WH 180 multinuclei spectrometer. Electron spin resonance (ESR) spectra were obtained by use of a Varian E-4 spectrometer. IR spectra were measured on a Perkin-Elmer 457 or 237B spectrometer. Mass spectra were obtained by use of a Hitachi Perkin Elmer RMU-6 mass spectrometer or Finnigan 400 spectrometer with an INCOS data system. Varian model 920 TCD (thermoconductivity detector) and 1400 FID (flame ionization detector) gas chromatographs were used to analyze organic products. A Hanovia 1000 watt high pressure mercury arc lamp was used to provide a source of UV light when photolysis was conducted in the Varian E-4 spectrometer. A Hanovia medium pressure 450 W mercury lamp with quartz well was used as a UV light source for bench-top reactions. All the bench-top reaction vessels for photolysis were Pyrex Schlenk tubes, so the UV wavelength range used was greater than 300 nm. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

## 3. Preparation of diphenyltitanocene

Diphenyltitanocene was prepared by a modification of the method of Summers et al.[29].

Titanocene dichloride (9.17 g) was suspended in 170 mL diethyl ether in a 500 mL 3-neck flask under argon. Phenyl lithium (1.67 M; 47 mL) was added slowly over a period of 3 h. The mixture was stirred one hour longer. Then, the solution was cooled to -30° C and 30 μL methanol was added to destroy the excess amount of phenyl lithium. While the solution was warmed slowly to room temperature, the solvent and excess amount of methanol were removed in a vacuum. Fresh diethyl ether was added to extract the residue and the solution was filtered under argon. The orange-yellow, solid diphenyltitanocene can be crystallized at -78° C and isolated under argon. The yield is about 95%. It may be recrystallized from methylene chloride and petroleum ether solution if necessary.

## 4. Preparation of diphenylzirconocene

Diphenylzirconocene was prepared by following the reported method[31]. Fifteen g zirconocene dichloride was suspended in 300 mL diethyl ether. Sixty four mL 1.67 M phenyl lithium was added in from an addition funnel at -40° C in a period of 1 h. The solution was stirred for another hour while temperature was raised slowly to 0° C. The solvent was removed under reduced pressure. The remaining residue was washed with 50 mL of freshly distilled pentane and decanted. The residue was then extracted by 300 mL ether. The resulting solution was filtered under argon. When the volume of the filtrate was reduced, pale diphenylzirconocene was crystallized and obtained by filtration under argon. The IR spectrum was similar to that reported. The $Cp_2ZrCl_2$ was stored in dry box and appeared to be less stable than diphenyltitanocene.

## 5. Synthesis of 1,2,3,4,5-pentamethylcyclopentadiene

Cis,trans-2-butene was used as starting material to synthesize 1,2,3,4,5-pentamethylcyclopentadiene. The synthetic sequence is shown in Fig. 3.

### A. Preparation of 2,3-dibromobutane

Bromine was dissolved in 300 mL 90% acetic acid. Cis,trans-2-butene was bubbled through the solution, being stirred vigorously at 3-5° C. After the solution was decolorized, more bromine was added. This cycle was continued until the solution separated into two layers. A concentrated NaOH solution was prepared to neutralize this solution until the pH was approximately

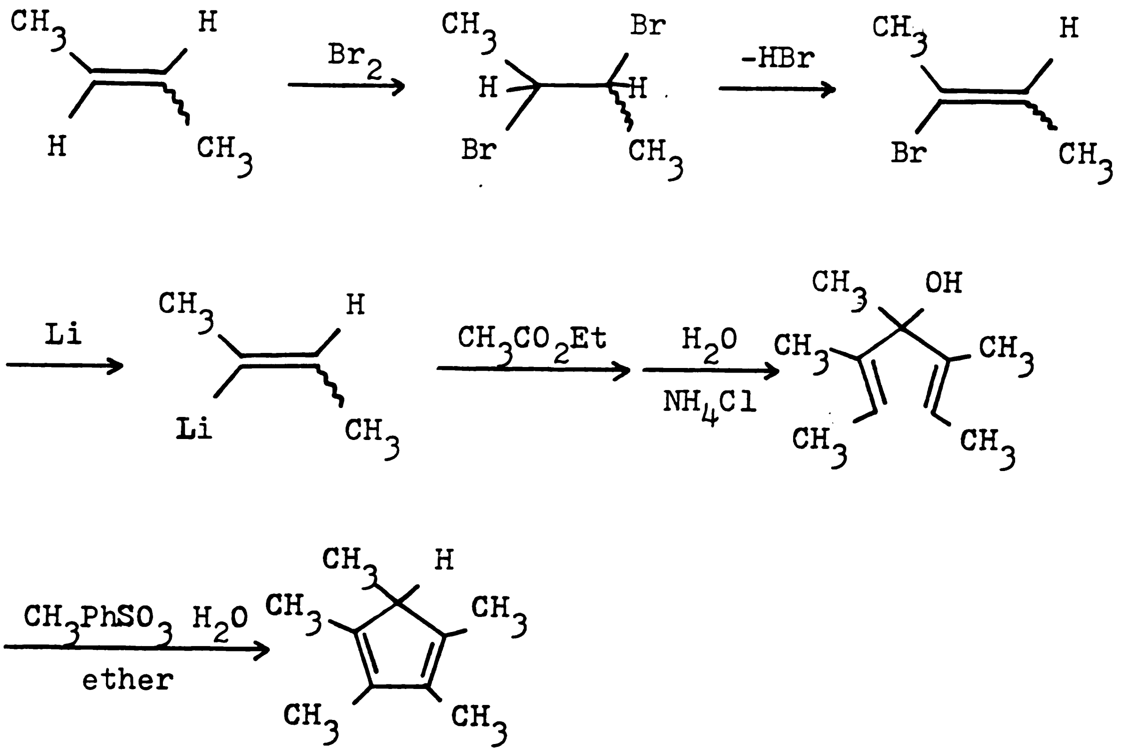


Figure 3 Scheme of synthesis of 1,2,3,4,5-pentamethylcyclopentadiene

7. If solid sodium acetate precipated out, the solution was diluted until no solid remained. Then, the two layers were separated. The water layer was extracted twice with ether. The organic layer was combined with the ether solution and dried over anhydrous sodium sulfate. Ether was then removed by rotary evaporation.

## B. Preparation of 2-bromo-2-butene

2-Bromo-2-butene was prepared by dehydrobromination of 2,3-dibromobutane[54].

Eighty g analytical grade KOH was dissolved in 370 mL methanol. Previously prepared 2,3-dibromobutane (240 g), without further purification, was added slowly to the KOH-methanol solution in order to maintain a gentle reflux. White crystals of potassium bromide precipitated during the reaction, a mechanical stirrer was used when necessary to keep the solution well-stirred. The resulting mixture was cooled and diluted with 4 L of distilled water, and neutralized with concentrated HCl. The organic layer was separated and water layer was extracted twice with ether. The organic layer and ether solution were combined and dried over anhydrous $Na_2SO_4$. After ether was removed by rotary evaporation, the solution was distilled. Purified cis and trans-2-bromo-2-butene was collected at 82-92° C. Yield was about 80%. The $^1H$ NMR of the final product shows three multiplets at 1.6 ppm, 2.2 ppm, and 5.6 ppm from TMS.

## C. Preparation of 1,2,3,4,5-pentamethylcyclopentadiene[55]

Three L freshly distilled diethyl ether was used to suspend 21 g finely-cut lithium wire in a 5 L 3-neck flask. About one fifth of 200 g of previously prepared 2-bromo-2-butene was added to the ether solution through an addition funnel. The solution was well stirred and after the reflux began, the rest of 2-bromo-2-butene was added slowly to maintain the gentle reflux. After the addition was completed, the solution was stirred for an additional hour and, then, 66 g ethyl acetate, diluted with an equal volume of ether, was added dropwise. The remaining lithium was removed before the resulting milky solution was poured into 2 L water saturated with $NH_4Cl$. The ether layer was separated and water layer was extracted three times with ether. The combined ether solution was dried over anhydrous $Na_2SO_4$. Ether was then removed under reduced pressure.

Di-s-2-butenylmethylcarbinol prepared from the above was quickly added to a suspended mixture of 13 g p-toluenesulfonic acid monohydrate and 300 mL ether. Vigorous reflux began immediately and two layers formed. The mixture was stirred until it was cool, then was poured into a solution of 7 g $Na_2CO_3$ in a 800 mL saturated aqueous $NaHCO_3$ solution. The ether layer was separated, and water layer was extracted three times with ether. The combined ether solution was dried over anhydrous $Na_2SO_4$. Then, ether was removed by rotary evaporation. The product was first purified by transferring it into another flask in a vacuum at room temperature, and then vacuum (15 torr) distilled at 70-75° C. The yield was about 75 %. The $^1H$ NMR spectrum of the product shows one doublet (1.01 ppm), two singlets (1.77 ppm; 1.81 ppm) and one quartet (2.48 ppm). The mass spectrum has a parent peak at m/z = 136 and major fragments at 121, 105, 93, 91, 79, 77, etc.

### 6. Preparation of bis($\eta^5$-pentamethylcyclopentadienyl)titanium dichloride[18,27]

Finely divided sodium (2.3 g) and two small crystals of $Fe(NO_3)_3 \cdot 9H_2O$ were put in a 1000 mL flask under argon. Liquid ammonia (500 mL) was condensed into this flask at -78° C. The solution was warmed slowly to -33°C and stirred until the blue color changed to light gray. Above prepared 1,2,3,4,5-pentamethylcyclopentadiene (12 g) was added into the sodium amide-liquid ammonia suspension by syringe, and the mixture was stirred at this temperature for 2 h. The ammonia was then removed <u>in vacuo</u>. Freshly distilled 1,2-dimethoxyethane (200 mL) was added by syringe to the flask to dissolve the sodium pentamethylcyclopentadienide. The solution was filtered under argon and transferred by syringe onto 5 g of anhydrous $TiCl_3$ at -80° C. The mixture was allowed to warm slowly to room temperature, then heated to 80° C for 20 h. Concentrated aqueous HCl (50 mL) was added to the suspension at -20° C. Red-brown crystals precipitated. Chloroform (250 mL) was added and the chloroform-1,2-dimethyoxyethane layer was separated and dried over anhydrous $Na_2SO_4$. The chloroform and 1,2-diemthyoxyethane were removed under reduced pressure and the by-product, $[C_5(CH_3)_5]TiCl_3$, was extracted from the residue by HCl-saturated petroleum ether in Soxhlet extractor. The product, $[C_5(CH_3)_5]_2TiCl_2$, was extracted from the residue by an HCl-saturated $CCl_4$ solution in the same apparatus. The solution of $CCl_4$ was cooled in ice bath for a few hours, the dark brown, needle-like product was collected by suction filtration. The product may be recrystallized in HCl-saturated chloroform, and well formed crystals are dark purple. The mass spectrum of the product shows a parent peak at m/z = 388 and major fragments at 353, 253, 217, 213, 135, etc. The $^1H$ NMR shows a singlet at 1.99 ppm from TMS. The yield was about 40%.

### 7. Preparation of bis($\eta^5$-pentamethylcyclopentadienyl)zirconium[26]

1,2,3,4,5-pentamethylcyclopentadiene (20.4 g) was syringed into 300 mL freshly distilled 1,2-dimethyoxyethane in a 500 mL flask. After the solution was cooled to -80° C, *n*-butyllithium (1.6 *M*; 93.8 mL) was added by a syringe. The mixture was warmed slowly to room temperature and stirred for another 30 min. Then, it was cooled to -80° C again and 16 g zirconium tetrachloride was added. This mixture was warmed to room temperature and refluxed for 3 d. Solvent was removed under reduced pressure. Chloroform (250 mL) was added to the pale brown residue and, subsequently, 100 mL of 6 *M* HCl was added. The chloroform layer was separated and aqueous layer was washed twice with chloroform. The combined chloroform solution was dried over anhydrous $Na_2SO_4$, then concentrated to approximately 50 mL. Petroleum ether (200 mL, 60-110° C) was added and solvent slowly removed by rotary evaporation to leave about 50 mL. The concentrated solution was cooled and pale yellow crystals were filtered out and washed with cool petroleum ether. The yield was about 50%. The $^1H$ NMR spectrum in $CDCl_3$ of the product had a singlet at 2.0 ppm. Mass spectrum exhibited a parent peak at m/z = 432 and major fragments are at 394, 297, 255, 136, 135, etc.

### 8. Preparation of diphenylpermethyltitanocene

The method used to prepare diphenylpermethyltitanocene is similar to that for diphenyltitanocene.

In a typical reaction, 1 g bis($\eta^5$-pentamethylcyclopentadienyl)titanium dichloride was crushed to a powder and suspended in 40 mL of diethyl ether. Phenyllithium (1.5 M; 3.5 mL) was added by syringe slowly under argon at room temperature. The mixture was then stirred at room temperature for additional 5 h. Methanol (9 μL) was added to the mixture at -40° C to destroy the excess amount of phenyllithium. Solvent was then removed under reduced pressure. Residue was extracted by 400 mL ether and the mixture was filtered under argon. Ether was removed by use of a vacuum line. Diphenylpermethyltitanocene was a paste-like compound and very photosensitive. Prolonged storage in room light at room temperature led to the formation of a paramagnetic species which showed the same ESR signal as that from photolysis of this compound. The $^1H$ NMR spectrum of the newly-prepared diphenylpermethyltitanocene in $CDCl_3$ shows the expected signals: singlet (1.65 ppm), singlet (7.16 ppm).

### 9. Preparation of diphenylpermethylzirconocene

The method used to prepare diphenylpermethylzirconocene is similar to that for diphenylzirconocene.

In a typical reaction, 5.3 g bis($\eta^5$-pentamethylcyclopentadienyl)zirconium dichloride was suspended in 80 mL diethyl ether. Phenyllithium (1.5 M; 16.5 mL) was added under argon at -40° C. The mixture was then warmed slowly to room temperature and stirred for another hour. Solvent was removed under reduced pressure. The residue was extracted with 80 mL of ether and filtered under argon. Pale yellow solid of diphenylpermethylzirconocene was obtained in 60% yield and it may be recrystallized from ether again. The $^1H$ NMR spectrum in benzene-$d_6$ shows two singlets: 1.72 ppm (ring methyl groups) and 7.16 ppm (phenyl hydrogens). Elemental analysis indicated: H, 7.57%; C, 73.7%; Zr, 18.8%; calculated wt% of $H_{40}C_{32}Zr$ are: H, 7.76; C, 74.5; Zr, 17.7.

### 10. Preparation of dimethylpermethylzirconocene

Method used to synthesize dimethylpermethylzirconocene was similar to that for dimethylzirconocene[31].

Bis($\eta^5$-pentamethylcyclopentadienyl)zirconium dichloride (1 g) was suspended in 20 mL diethyl ether under argon at

-20° C. Methyllithium (1.84 M; 2.52 mL) was syringed into the reaction flask slowly with vigorous stirring. The temperature was then allowed to raise to room temperature slowly and stirred for another 30 min. Solvent was then removed under reduced pressure and residue was sublimed at 90° C ($10^{-3}$ torr). White solid of dimethylpermethylzirconocene was obtained with a yield of 70%.

### 11. Decomposition of photochemically-generated titanocene from diphenyltitanocene by HCl

Diphenyltitanocene (0.13 g) was dissolved in 70 mL of toluene in a Schlenk tube under $N_2$. This solution was cooled to -25° C and photolyzed for 3 h. A dark greenish brown solution resulted and was cooled to -78° C for 48 h. A dark greenish black solid layer was found at the bottom of the Schlenk tube. The solvent was removed by syringe and the solid layer was rinsed twice with 10 mL *n*-pentane and once with 10 mL isobutane at -78° C. Then, it was dried in a vacuum and suspended with 1 mL freshly distilled *n*-pentane. While HCl gas was bubbled through this mixture, the color changed to brown. After it was warmed slowly to room temperature, the solvent was removed under reduced pressure. A dark purple solid was obtained and sublimed at 45° C to 50° C for 48 h. A batch (16%) of yellow crystals was obtained. It was identified as $CpTiCl_3$ by mass spectrum (parent peak at $m/z = 218$). Continued sublimation of the residue at 150-160° C generated a batch (6.1%) of red crystals which was identified as $Cp_2TiCl_2$. The remaining brown residue (78%) was unidentified; mass spectrum showed a parent peak at m/z = 582; elemental analysis: C, 49%; H, 6.4%; Cl, 9.7%; Ti, 34.7%.

### 12. Photolysis of diphenylpermethyltitanocene in benzene-$d_6$

A benzene-$d_6$ solution (8.5 mL) of diphenylpermethyltitanocene (0.04 $\underset{\sim}{M}$) was placed in a Schlenk tube under prepurified nitrogen gas. This solution was photolyzed and stirred for 3 h in a water bath which was maintained around $25^{o}$ C. At the end of irradiation, the solvent was recovered by use of a vacuum line. GC-Mass spectroscopic analysis of this recovered solvent indicated that very small amounts of 2,3,4,5-tetramethylfulvene (Mass spectrum: m/z = 134, 119, 103, 91, 77, etc; $^1$H NMR: three singlets, 1.84, 1.89, 5.47 ppm from TMS) and 1,2,3,4,5-pentamethylcyclopentadiene were also recovered. The residue left in the Schlenk tube was dissolved in freshly distilled hexanes, and decomposed by stirring in air for several hours. The mixture was filtered and hexane solution obtained was analyzed by GC-MS. Biphenyl-$d_0$ ($M^+$ = 154) and biphenyl-$d_5$ ($M^+$ = 159) were found in a ratio of 36/1. Relatively large amounts of 2,3,4,5-tetramethylfulvene and 1,2,3,4,5-pentamethylcyclopentadiene were also detected in a ratio of 1/1.3. The total amount of biphenyl recovered was determined by GC analysis (10% SE-30) as 9.4 mg.

### 13. Photolysis of diphenylpermethyltitanocene in toluene at -10° C

A toluene solution (10 mL) of diphenylpermethyltitanocene (0.04 M) was placed in the same Schlenk tube as that used above in a isopropanol bath at -10° C. After 3 h irradiation, the mixture was warmed to room temperature. Solvent was removed under reduced pressure. The resulting residue was extracted by hexanes and decomposed in air. After filtration, the hexane solution was analyzed by GC-MS. Only a trace amount of phenyltoluene was detected besides the product of biphenyl, 2,3,4,5-tetramethylfulvene and 1,2,3,4,5-pentamethylcyclopentadiene.

### 14. Photolysis of diphenylpermethyltitanocene in the presence of carbon monoxide

A toluene solution (10 mL) of diphenylpermethyltitanocene (0.04 M) was introduced by a syringe into the Schlenk tube under nitrogen. The tube was degassed and charged with carbon monoxide, this cycle was repeated for three times. The mixture was photolyzed and stirred at room temperature for 3 h and then cooled to -80° C overnight. A yellow-brown solid layer precipitated and toluene solution was removed by syringe. The solid was washed twice with n-pentane, and dried in vacuum at room temperature. Dicarbonylpermethyltitanocene was collected with a yield of 15% after sublimation of the dry solid at 80-90° C, $10^{-3}$ torr. The IR spectrum shows two strong carbonyl absorptions at 1930 and 1850

$cm^{-1}$.

### 15. Photolysis of diphenylpermethyltitanocene in the presence of ethylene

A *n*-pentane solution (42 mL) of diphenylpermethyltitanocene (0.01 *M*) was transferred into a glass pressure bottle under argon. The pressure bottle was degassed and charged with ethylene gas three times, and then the solution was saturated with ethylene and pressurized to 35 psig. The mixture was irradiated and stirred at -20° C for 2.5 h. A dark green solution resulted and cooled to -78° C with continuing stirring for additional 24 h. This mixture was then treated with excess amount of HCl gas at this temperature. In a short period of time, the color of the solution changed from dark green to brown with some brown solid formed. The analyses of the gas phase product was conducted on a FID GC with Durapak as column (20' x 1/8"). Butane and ethane were found with yields of 2.2% and 1.5% based on Ti respectively.

### 16. Hydrogenation of 1-hexene over photochemically-generated titanium species

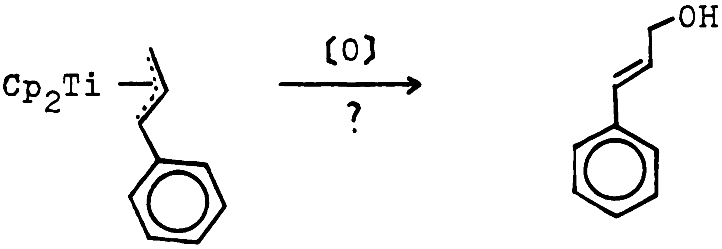
Ten mL of a benzene solution of diphenylpermethyltitanocene (0.055 *M*) was saturated with $H_2$ gas at 1 atm in a Schlenk tube. After 3 h irradiation, a brown solution was obtained and 1 mL of freshly-distilled 1-hexene was added. The solution was stirred at 1 atm of $H_2$ for 12 h and analyzed by GC, Carbowax 20 M (25' x 1/4"). A trace amount of hexane was found.

The same experiment was carried out with diphenyltitanocene starting material, and no appreciable amount of hydrogenated product was found. Nor was hydrogenated product for substrate of acetylene or ethylene instead of 1-hexene.

## 17. Isomerization of allylbenzene over photochemically-generated titanium species

$Cp_2TiPh_2$ (0.125 g) was dissolved in 10 mL of THF and 1 mL of allylbenzene. After irradiation of this mixture under Ar at room temperature for 2 h, a dark green solution was resulted. Analysis of this solution by GC showed no appreciable amount of isomerized product.

Elution of this dark green solution through a silica gel column by hexane led to the decomposition of this dark green solution. A pale yellow band was collected. After removal of the most amount of solvent, a concentrated yellow solution was obtained. Analysis of this solution by GC-MS showed that biphenyl and very small amount of 1-phenyl-propen-3-ol were present. The latter was expected to be the oxidized product from the intermediate of π-allyl-titanocene (**Eq.** 8). However, the attempt to isolate the π-allyl intermediate was not successful. Since there was only very small amount of 1-phenyl-propen-3-ol detected, no further attempt was made to obtain this product.



Similar experiment was performed under $H_2$ atmosphere instead of Ar -- no isomerized product was foune.

18. <u>Polymerization of styrene over photochemically-generated titanium species</u>

$Cp_2TiPh_2$ (0.08 g) was either dissolved in 10 mL of styrene or 6 mL styrene and 20 mL toluene. The mixture was photolyzed under argon at room temperature for 2 h. The resulted dark green solution was exposed to air until their color changed to yellow, and then filtered into large amount

Table 1 Polystyrene obtained from photolysis of $Cp_2TiPh_2$ in styrene

| $Cp_2TiPh_2$ | Styrene | Polymer | Net polymer/mmole $Cp_2TiPh_2$ |
|---|---|---|---|
| 0 g | 4 mL | 0.022 g | -- |
| 0.08 g | 10 mL | 0.102 g | 0.1 g |
| 0.08 g | 6 mL in 20 mL of toluene | 0.075 g | 0.1 g |

of methanol[56]. Polystyrene was collected by filtering this methanol solution. The results, after substracting a blank test are listed in Table 1. The polymerization was believed to be initiated by the radicals formed from photocleavage of diphenyltitanocene[57].

## 19. Photolysis of diphenylpermethylzirconocene in benzene-$d_6$

A benzene-$d_6$ solution of diphenylpermethylzirconocene (8.8 mL; 0.077 $\underset{\sim}{M}$) was photolyzed for 47 min under the same conditions and equipment as those for diphenylpermethyltitanocene (Part 12 of this section). The solution turned purple-red. The extraction process by hexanes and analytical methods used were also the same. A very small amount of 2,3,4,5-tetramethylfulvene and 1,2,3,4,5-pentamethylcyclopentadiene were also found in the recovered benzene-$d_6$ solvent. The ratio of biphenyl-$d_0$ and biphenyl-$d_5$ was 1/3. Total amount of biphenyl found was 0.056 mmole. The $^1$H NMR spectrum of the recovered benzene-$d_6$ solvent also showed a significant absorption in the vicinity of benzene (7.2 ppm). Quantitative $^1$H NMR analysis by using cyclohexane as internal standard showed 0.36 mmole of benzene present. GC-MS analysis of this recovered benzene-$d_6$ solvent showed the presence of benzene ($M^+ = 78$) and benzene-$d_1$ ($M^+ = 79$), while the mass spectrum of recovered benzene-$d_6$ solvent from unphotolyzed original solution did not show the peaks at 78 and 79 mass units.

Again, the ratio of 2,3,4,5-tetramethylfulvene and 1,2,3,4,5-pentamethylcyclopentadiene in the hexane extract was 1/1.2. When a much more dilute benzene-$d_6$ solution of diphenylpermethylzirconocene (0.0093 M) was used, the ratio of biphenyl-$d_0$ to biphenyl-$d_5$ was 1/10.

## 20. Stepwise photolysis of diphenylpermethylzirconocene in benzene-$d_6$

All the procedures and equipment were the same as above, except the solution was photolyzed for 12 min, then stirred for 30 min without light, and then photolyzed for additional 35 min. After 12 min irradiation, the color of the solution turned dark red, and changed to light brown gradually when it was stirred for 30 min. Dark purple-red color again appeared after 35 min continued irradiation.

The same hexane-extraction procedure was used, and the ratio of biphenyl-$d_0$ to biphenyl-$d_5$ was 1/4.

## 21. Photolysis of diphenylpermethylzirconocene in the presence of carbon monoxide

A toluene solution (10 mL) of diphenylpermethylzirconocene (0.07 M) was photolyzed under an atmosphere of carbon monoxide for 2 h. The mixture was stirred for an additional hour after extinguishing the light. It was cooled to -80° C overnight. Purple brown crystals precipitated. Toluene was removed by syringe. Crystals were washed with n-pentane twice, and then dried in a vacuum. The IR (Nujol Mull) spectrum of the solid showed strong absorptions at 1942, 1850 $cm^{-1}$. The yield of dicarbonylpermethylzirconocene was about 25%.

## 22. Photolysis of dimethylpermethylzirconocene in toluene

A toluene solution (10 mL) of dimethylpermethylzirconocene (0.04 M) was photolyzed under argon for 2 h. The analysis of the gaseous products evolved showed that methane was the only product and no ethane was detected. FID GC with a column of Durapak (20' x 1/8') was used.

## 23. $N_2$-absorption by photochemically-generated titanium and zirconium species

In a typical reaction, the toluene solution of diphenylpermethyltitanocene (0.04 M; 40 mL) was photolyzed under prepurified nitrogen at -20° C for 2 h. The resulting solution was cooled to -78° C and stirred vigorously, $N_2$-absorption was measured with a mercury buret installed together with an oil bubbler. The net absorption of nitrogen gas was 2 mL (approximately 0.08 mmole; 5% based on Ti) obtained by substraction of the $N_2$-absorption by a 60 mL toluene blank at -78° C.

A similar experiment was conducted for a benzene solution of diphenylpermethylzirconocene (0.07 M; 10 mL). The photolysis was performed at room temperature for 2 h, and $N_2$-absorption was measured at room temperature by comparing with a blank. About 2 mL of nitrogen gas was absorbed (11%

in terms of number of moles of Zr).

## 24. Measurement of $^{15}N$ NMR of $N_2$-titanium and zirconium complexes

A broad band probe (17.7-39 MHz) with N-15 preamplifier was used to measure the $^{15}N$ NMR (18.25 MHz) spectra of $N_2$-metal complexes on Bruker WH 180 NMR spectrometer. The sample (about 10 mL; concentration varied from 0.04-0.07 M) was introduced by a syringe into a small tube (O.D. 17 mm x 72 mm) through a septum. Nitrogen-15 enriched $N_2$ was then charged in by a gas-tight syringe. The solution in the small tube was irradiated for 2-3 h and, then, placed into a 20 mm (O.D.) NMR tube which was used for the measurement of spectra. The measurement for the toluene solution of diphenylpermethyltitanocene was usually performed at -60° C, and 7° C for the benzene solution of diphenylpermethylzirconocene.

## 25. Electron spin resonance studies of photolyses of diphenyl derivatives of metallocenes

A Pyrex tube (4 mm O.D.) was used as the container for the ESR measurement. The tube was first degassed and then sample solution was added by a syringe. The tube and the sample solution was degassed again and sealed under argon. A Hanovia 1000 W high pressure compact arc lamp with a 4 cm water filter was used as light source. A UV light beam was aimed at the cavity of a Varian E-4 spectrometer in which the sample tube was mounted. ESR spectra could be obtained during the irradiation. DPPH (2,2-diphenyl-1-picryhydrazyl, g = 2.0037 ± 0.0002) was used for magnetic field calibration for the measurement of g values.

### 26. <u>ESR spectra of a photolyzed toluene solution of diphenylzirconocene</u>

When a saturated toluene solution was photolyzed in the E-4 spectrometer, an ESR signal, a doublet (Fig. 4a; similar to an overlapping signal of two singlets) was obtained. The color of the solution changed to black-blue and a precipitate of the same color formed. This signal persisted for days after extinguishing the light. However, when a doubly-diluted toluene solution was photolyzed under exactly the same conditions, only was a clean singlet signal was obtained (Fig. 4b). The signal only lasted for 5 min. Attempts to explain these observations were not successful.

### 27. <u>Spin trap experiment for photolysis of diphenylpermethyltitanocene</u>

Previously prepared nitrosodurene[58] was used as spin trapping agent. Excess amounts of nitrosodurene were mixed with a toluene solution (0.01 M) of diphenylpermethyltitanocene in a 4 mm ESR tube. Upon photolysis of this mixture on ESR spectrometer, a triplet signal was obtained (Fig. 6). The intensity of this triplet grew rapidly while irradiation

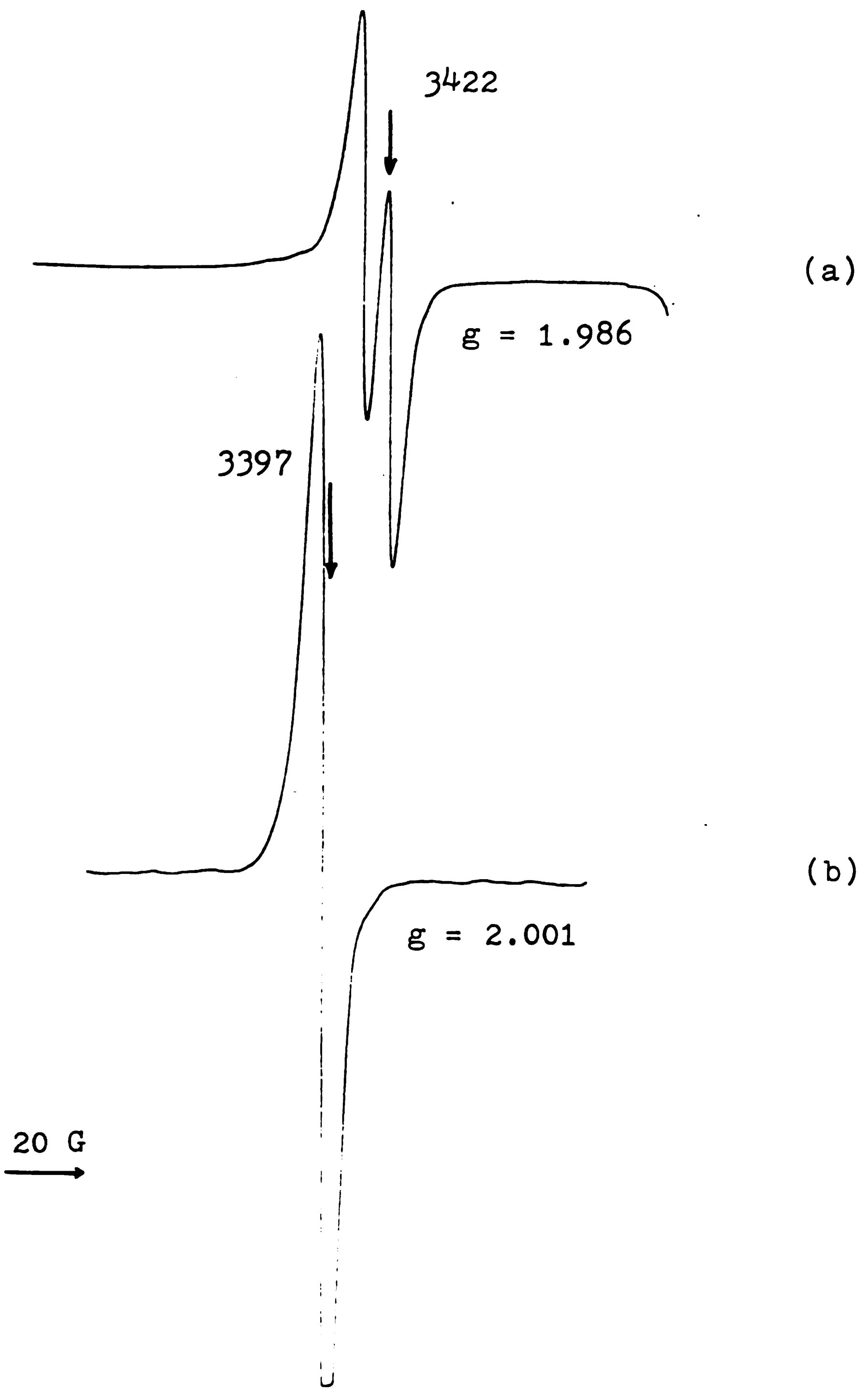


Figure 4 ESR spectra of photolyzed samples at room temperature: (a) saturated toluene solution of diphenylzirconocene, (b) doubly-diluted the same solution.

continued. The signal also lasted for days after extinguishing the light.

### 28. Preparation of μ-dinitrogenbis[phenyldicyclopentadienyltitanium(III)]

μ-Dinitrogenbis[phenyldicyclopentadienyltitanium(III)] was obtained by following the published method[59].

Titanocene dichloride (2 g) was suspended in 40 mL diethyl ether in a 100 mL flask under argon. To this mixture 8 mL of ether solution of i-$C_3H_7MgCl$ (1 M) was added slowly by syringe at -20° C. The solution was then warmed to room temperature and stirred for 30 min. It was again cooled to -20° C and stirred vigorously while an ether solution of $C_6H_5MgBr$ (11.8 mL; 0.68 M) was added dropwise. The solvent was then removed at -20° C. The residue was stirred with 40 mL toluene under argon at a temperature below 0° C. The resulting solution was filtered under argon and transferred to an evacuated NMR tube. Then, $^{15}N$-enriched $N_2$ was charged into the tube, the color of the solution changed to dark blue.

### 29. Photolysis of diphenylpermethylzirconocene over sodium amalgam

A benzene solution of diphenylpermethylzirconocene (0.07 M; 40 mL) was introduced by use of a syringe into a Schlenk tube containing excess amounts of 40% sodium amalgam under nitrogen. The mixture was photolyzed and stirred vigorously at room temperature for 1 h. The color of the solution changed from light yellow to dark red, then brown. The UV lamp was extinguished, and the solution was stored at room temperature for 3 d. A purple red color was generated at the surface of the sodium amalgam. When the solution was stirred vigorously under nitrogen, the color of the entire solution changed to purple red in two hours. But stirring overnight changed the color of the solution to purple-brown. Attempts to isolate the dinitrogenzirconium complex was not successful[26].

# RESULTS AND DISCUSSION

## 1. Photolyses of diphenyltitanocene

When a toluene solution of diphenyltitanocene was photolyzed under $N_2$ at -25° C for 3 h, a dark greenish brown solution resulted. After the solution was cooled to -78° C, dark greenish black crystals precipitated. Decomposition of this solid by HCl generated a batch of dark purple crystals. Fractional sublimation showed that $CpTiCl_3$ (16%), $CpTiCl_2$ (6.1%), and an unknown oligomeric material (78%) comprised this dark purple crystals. This result suggested that an oligomeric material was probably the major product from the photolysis of diphenyltitanocene.

When a THF solution of diphenyltitanocene was photolyzed in the presence of allylbenzene at room temperature for 2 h, a dark green solution resulted. No isomerized product was found. But when the dark green solution was eluted through a silica gel column by hexane, a pale yellow band was collected. Analysis of this solution showed that biphenyl and very small amount of 1-phenyl-propen-3-ol were present. The latter was presumed to be the oxidized product from the corresponding $\pi$-allyl-titanocene (Eq. 8, p. 27) and suggested that $\pi$-allyl-titanocene was probably an intermediate in the photolysis of $Cp_2TiPh_2$ in the presence of allylbenzene. However, the attempt to isolate the $\pi$-allyl intermediate was not successful.

Photolysis of a toluene solution of $Cp_2TiPh_2$ in the presence of styrene at room temperature for 2 h produced small amount of polystyrene (Table 1, p. 27). The polymerization of styrene was probably initiated by the radicals[57] generated from the photolytic homolysis of diphenyltitanocene.

## 2. Photolyses of diphenylpermethyltitanocene (6)

When (6) was photolyzed in a solution of benzene-$d_6$ at room temperature for 3 h, biphenyl-$d_0$ and biphenyl-$d_5$ was found in a ratio of 36/1 which suggested that reductive elimination (Path B in Fig. 5) had taken place predominantly. No biphenyl-$d_{10}$ was detected, and implied that the exchange of phenyl group in (6) with the solvent molecules had not happened.

After exposing the resulting red-brown solution to 1 atm of $H_2$ gas, the color of the solution changed to light brown. There was no indication of the formation of permethyltitanocene dihydride[18,60]. Upon addition of 1-hexene to this solution, stirred for 12 h under 1 atm of $H_2$, no hydrogenated product was found. But when (6) was photolyzed in the presence of CO under similar conditions, dicarbonylpermethyltitanocene (13) was collected (15% yield). On the other hand, in the recovered solvent, 2,3,4,5-tetramethylfulvene (11) and pentamethylcyclopentadiene (12) were detected in very small amounts. These observations suggested that permethyltitanocene (8) was one of the products, but

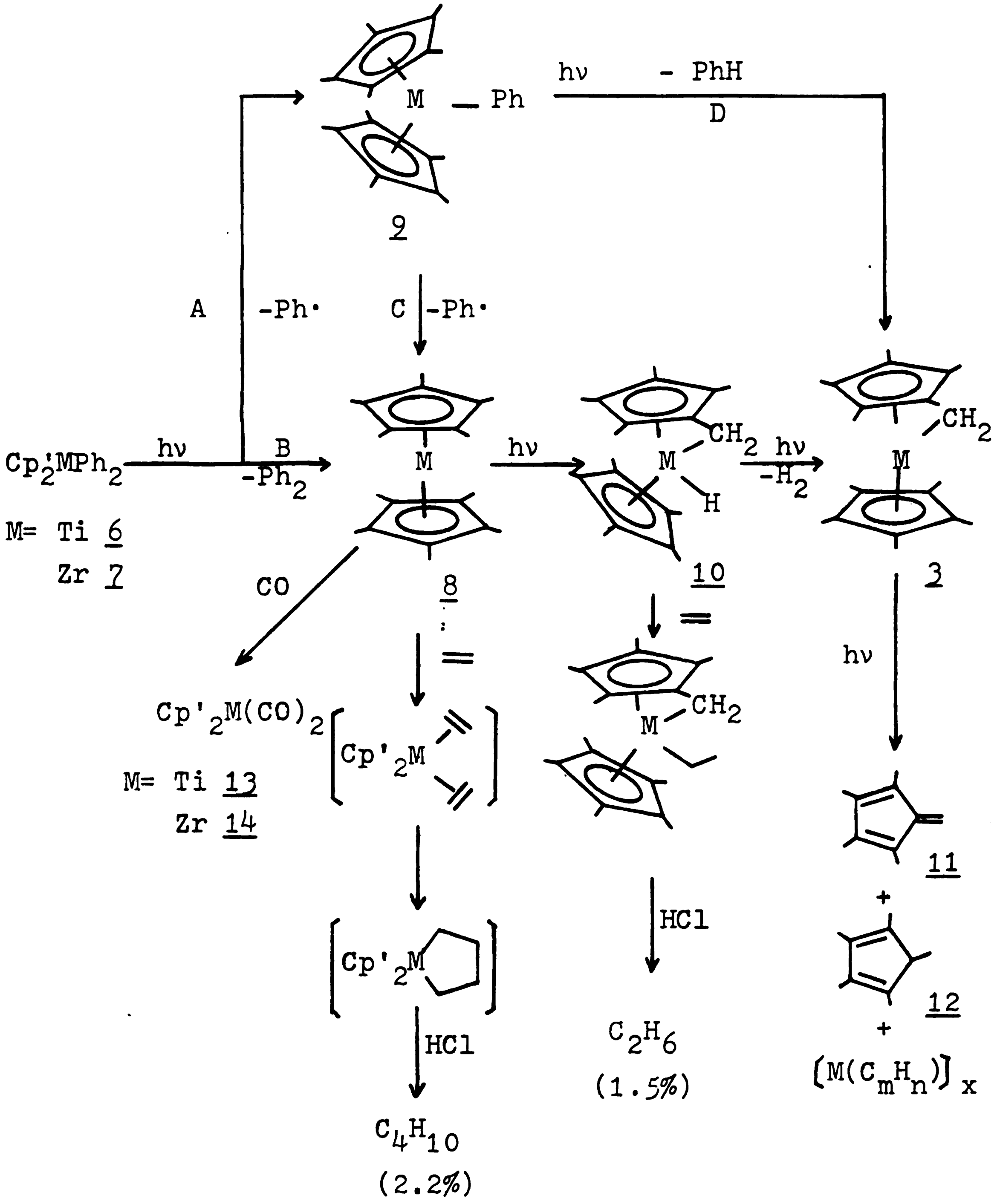
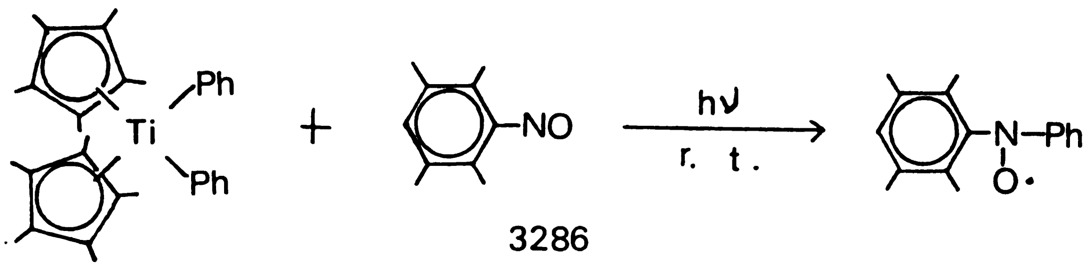


Figure 5 Mechanism of the photodecomposition of diphenylpermethyltitanocene and -zirconocene

further irradiation could still affect it and cleave the metal-ring π-bond. According to the published data[27], (8) was not quite stable at ambient temperature. It went on to abstract a hydrogen atom from the ring-methyl groups and formed a relatively stable compound (3) (see Fig. 5). Considering the conditions of photolysis, not only the ambient temperature but also the UV light could force (8) to change into (3). In particular, compounds (11) and (12) are more like those cleaved from (3) rather than (8); reductive elimination to form 2,3,4,5-tetramethylfulvene and/or homolysis of the metal-ring π-bond followed by H-abstraction from solvent to form pentamethylcyclopentadiene. Therefore, it seemed reasonable to assume that (8) was only an intermediate that could be trapped in the presence of a strong π-acid such as carbon monoxide, otherwise it would decompose to (3), and further degradation could take place (see below). The metal-containing species after degradation of (3) would be expected to be extremely reactive and probably could initiate oligomerization among the other molecules. This expectation can rationalize the formation of a large amount of oligomeric material obtained from decomposition of the resulting residue with HCl gas after photolysis. The weight ratio of the oligomeric material to the recovered permethyltitanocene dichloride was 5/1. In addition, when the residue obtained after photolysis was dissolved in hexane and then decomposed in air, relatively large amount of (11) and (12) were found. The ratio of these products was 1/1.3. It seems reasonable that (3) was the major unit composing the oligomeric material. There might be some amount of (3) existing in the residue, but an attempt to sublime (3) was not successful.

When an n-pentane solution of (6) was photolyzed under a pressure of 35 psig of ethylene at -20° C for 3 h, a dark green solution was obtained. Upon decomposition of this solution by HCl gas at -78° C, butane was found in 2.2% yield. The metallocycle, which was formed by cyclizing two molecules of ethylene as shown in Fig. 5, was believed to be the precursor of butane before decomposition by HCl[23,61]. Ethane was another product found from the same reaction. The formation of ethane suggested that there was a metal hydride species present during the course of photolysis, presumably, intermediate (10) (metal hydride could also be generated from the H-abstraction of (8) from solvent). Ethylene could insert into metal hydride easily, subsequent decomposition by HCl released the ethyl ligand as ethane, as described in Fig. 5.

Reductive elimination predominated the photochemical decomposition of (6). The stepwise homolysis of the metal-phenyl $\sigma$-bond (Path A in Fig. 5) was minimal, even at low temperature. A toluene solution of (6) was photolyzed at -10° C, biphenyl was detected as a major product and only a trace amount of phenyl toluene found. However, a homolytic process to produce phenyl radicals did occur, as was confirmed by the spin trapping experiment. When a toluene



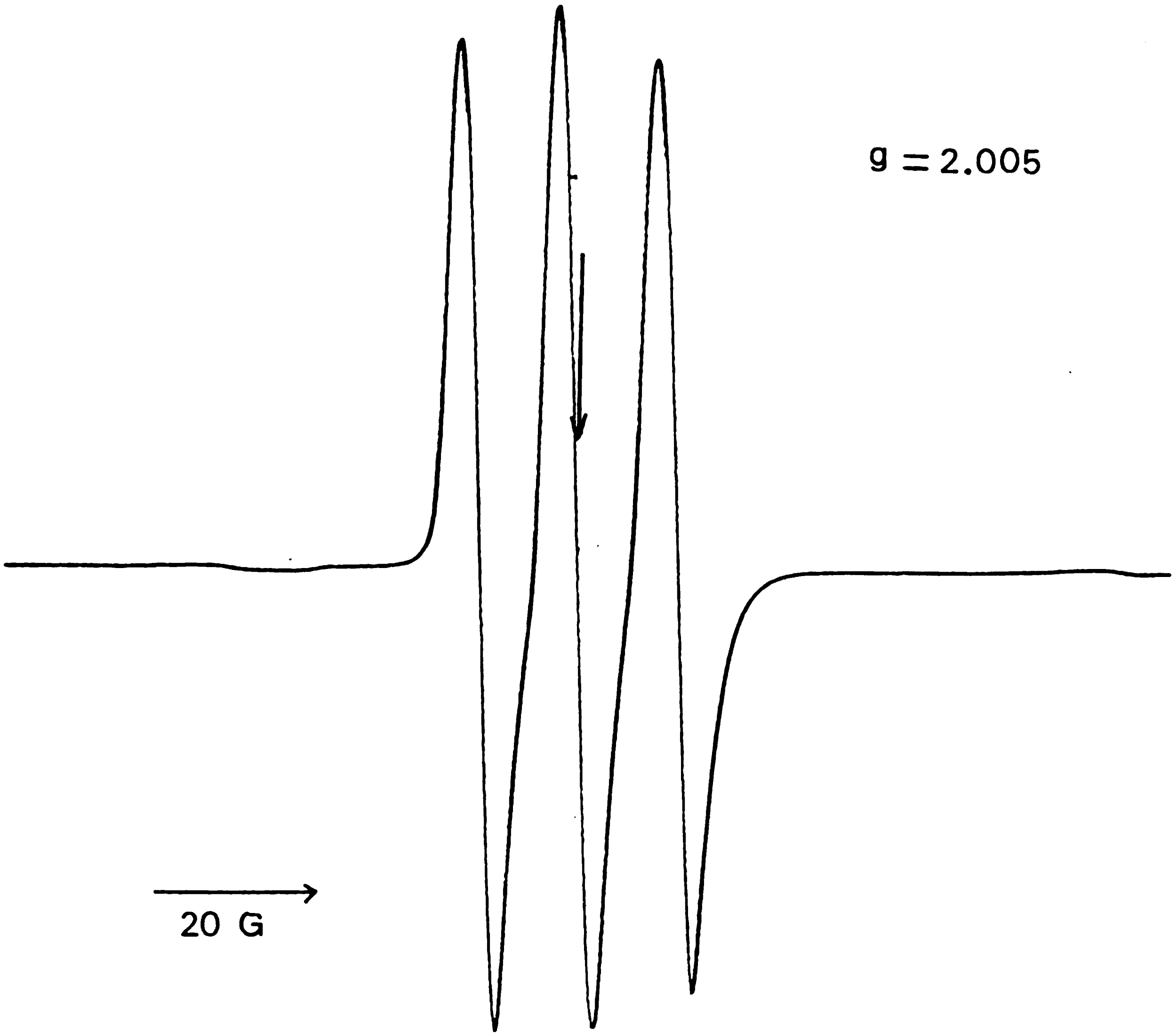


Figure 6 ESR spectrum of photolysis of (6)
in the presence of nitrosodurene

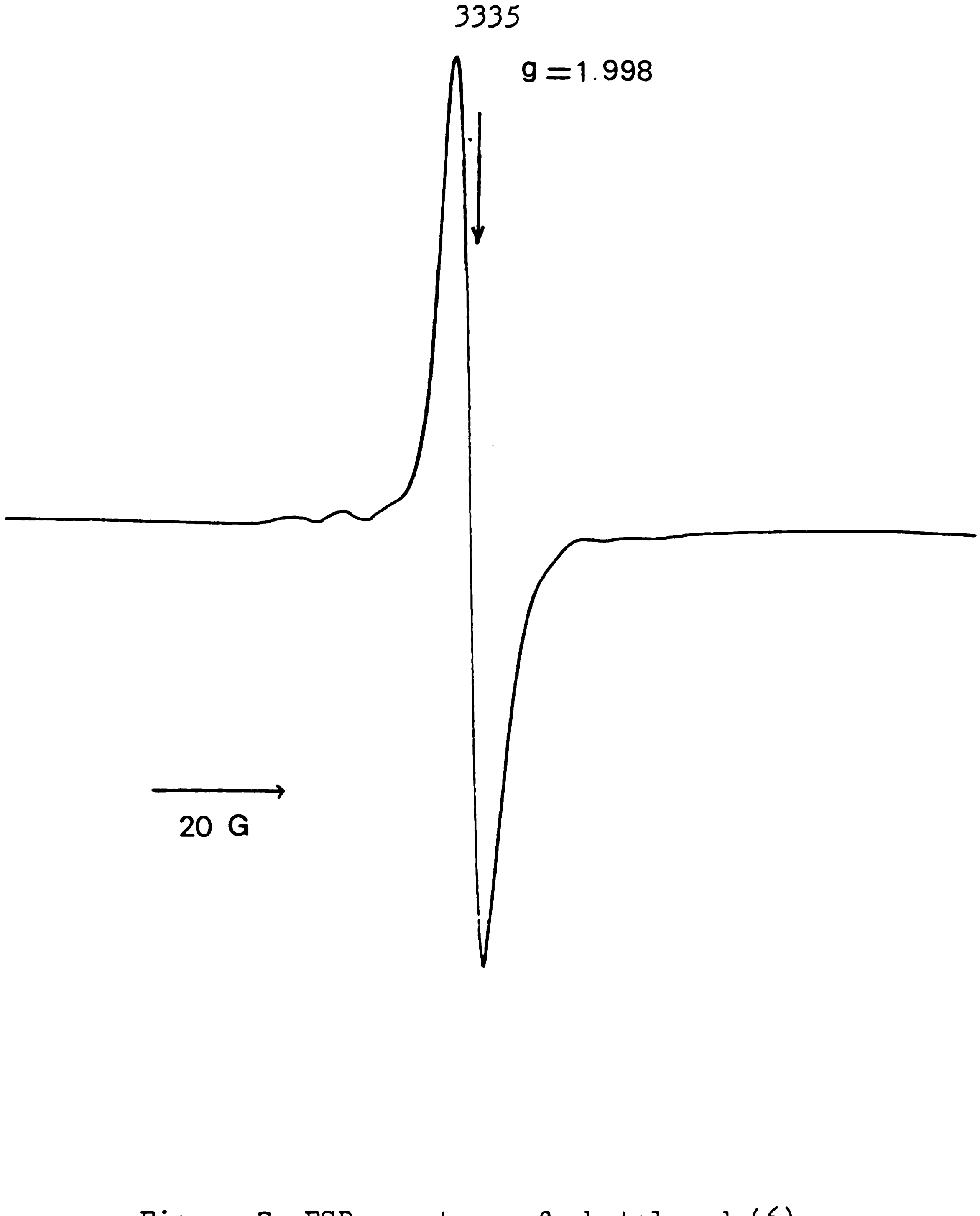


Figure 7 ESR spectrum of photolyzed (6) in toluene at room temperature

solution of (6) was photolyzed in an ESR spectrometer in the presence of nitrosodurene, 2,3,5,6-tetramethylphenyl phenyl nitroxide was found. It showed a triplet ESR signal with $g = 2.005$, $a_N = 12$ G[62] (Fig. 6). Without nitrosodurene, a singlet at $g = 1.998$ was shown (Fig. 7) together with small satellites attributable to hyperfine interaction with Ti isotopes ($^{47}$Ti and $^{49}$Ti, nuclear spin of 5/2 and 7/2 present in natural abundance of 7.75 and 5.51%, respectively). The singlet stayed the same throughout the entire three hours irradiation, it also lasted for at least three days after the light was extinguished. Since photochemical degradation of (6) seems to favor reductive elimination and permethyltitanocene is not stable at room temperature[27], the assignment of the compound (3) as being responsible for this singlet seems logical. Compound (3) is a paramagnetic species of Ti(III).

### 3. Photolyses of diphenylpermethylzirconocene (7)

When (7) was photolyzed in benzene-$d_6$ solution for 47 min. The color of the solution changed from light yellow to purple red. Biphenyl-$d_0$ and biphenyl-$d_5$ were found in a ratio of 1/3, which suggested that the stepwise homolysis of Zr-phenyl σ-bond (Path A in Fig. 5) was predominant. Again, there was no biphenyl-$d_{10}$ detected. Similar to the photolysis of (6), dicarbonylpermethylzirconocene was isolated (25% yield) when (7) was photolyzed in the presence of CO. 2,3,4,5-Tetramethylfulvene and pentamethylcyclopentadiene were also found in the recovered solvent as well as in the hexane after the photolyzed-residue decomposed in air. These observations indicate that the proposed mechanism in Fig. 5 is also applicable to the photochemical decomposition of (7).

The NMR spectrum of the recovered benzene-$d_6$ solvent showed a singlet at the chemical shift of benzene. GC-MS analysis of the same recovered solvent confirmed that mass 78 (benzene) and 79 (benzene-$d_1$) were present in a ratio of 3.8/1. Benzene-$d_1$ was probably obtained from the deuterium-abstraction from solvent molecules by phenyl radicals generated from Path A and C in Fig. 5. The detection of nondeuterated benzene indicates that Path D (H-abstraction from the methyl groups on the rings) is operative.

Nevertheless, the exchange reaction (Eq. 9) of newly produced permethylzirconocene with the starting material (7) is also a possible pathway for the generation of monophenylpermethylzirconocene. When a two-step photolytic process

$$Cp'_2ZrPh_2 + Cp'_2Zr \longrightarrow 2\ Cp'_2ZrPh \qquad (9)$$

was used with the same benzene-$d_6$ solution of (7) (more precisely, the solution was irradiated for 12 min, then stirred for 30 min without light and then photolyzed for another 35 min), the ratio of biphenyl-$d_0$ to biphenyl-$d_5$ changed to 1/4. The larger amount of biphenyl-$d_5$ formed revealed that more monophenylpermethylzirconocene had

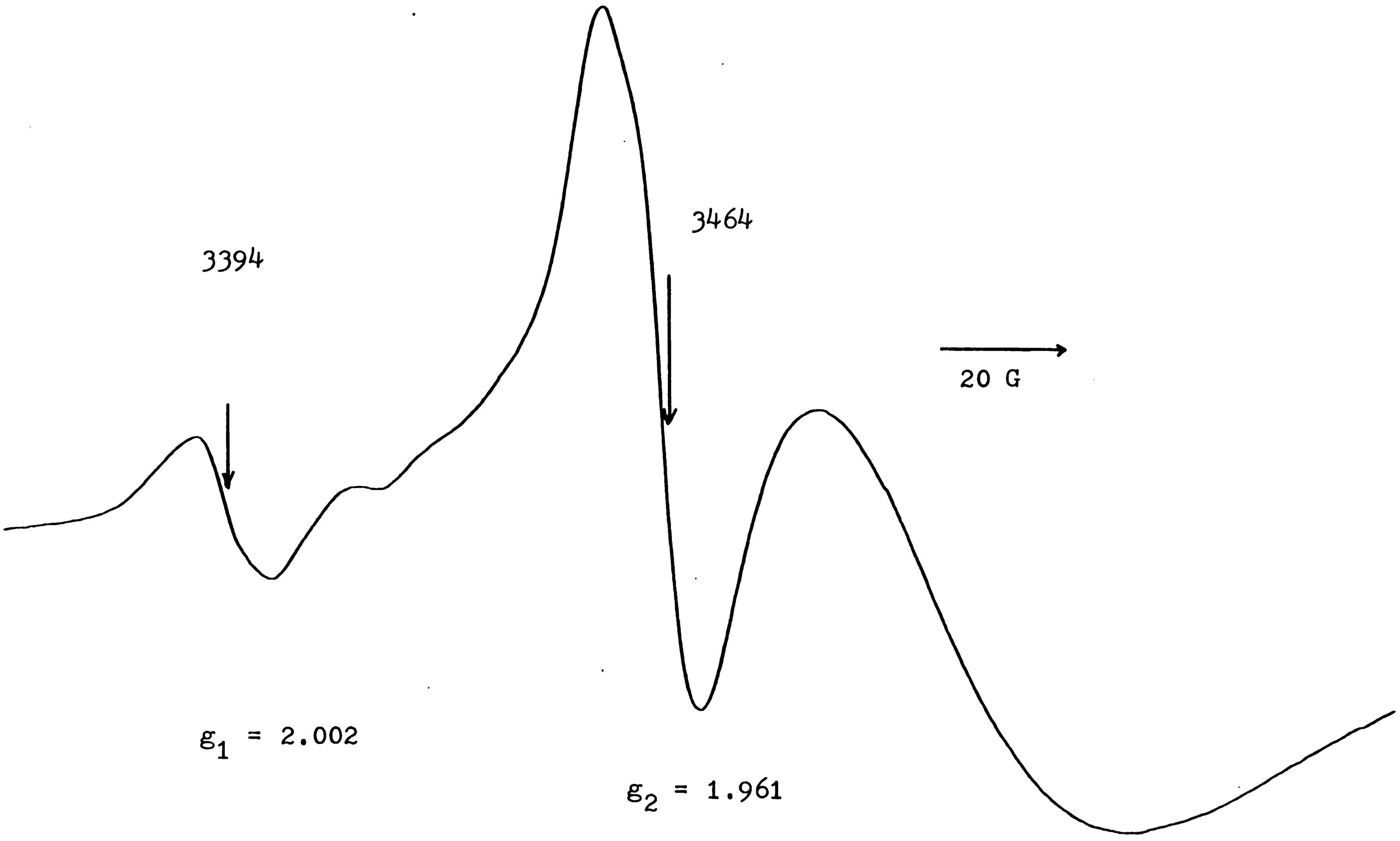


Figure 8 ESR spectrum of photolyzed (7) in benzene at room temperature

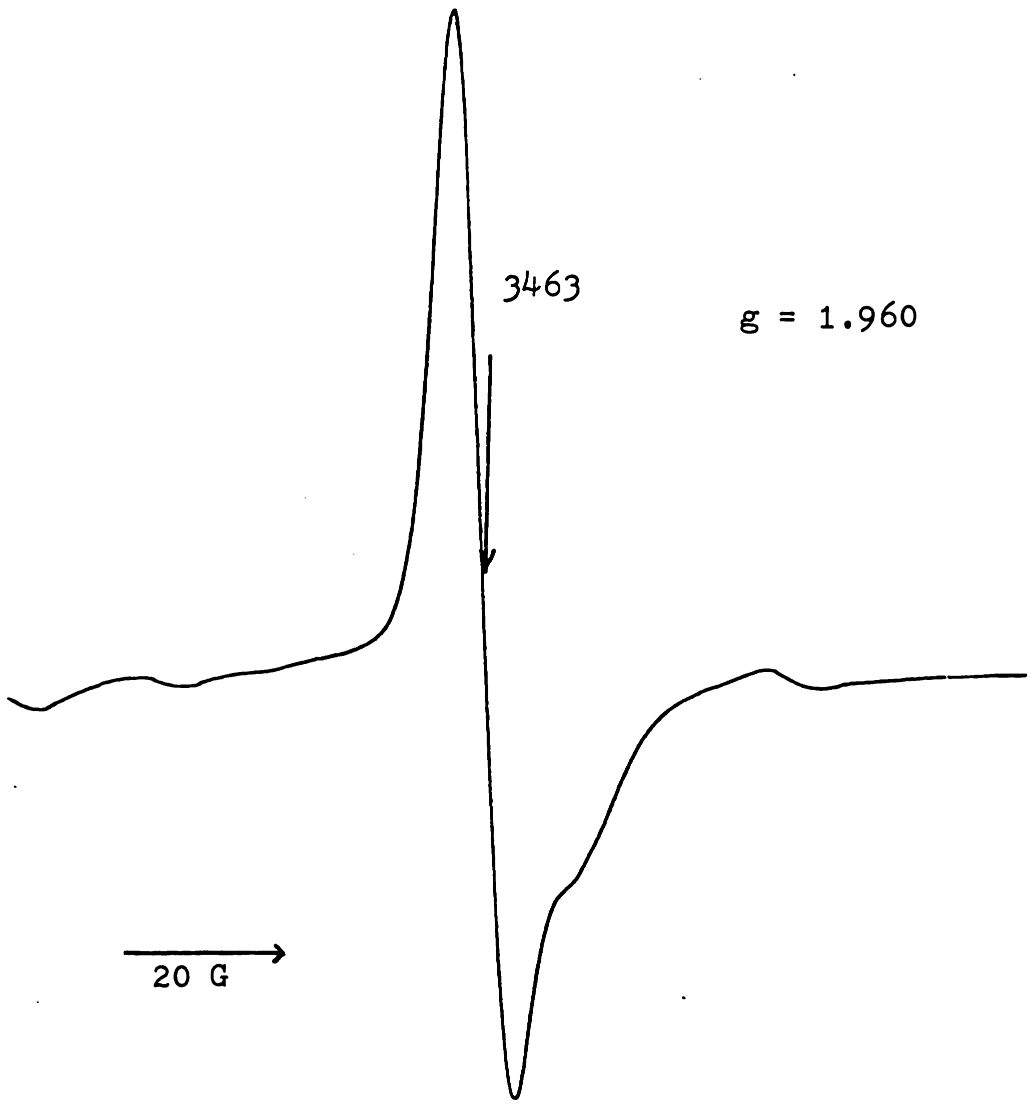


Figure 9 ESR spectrum of photolyzed (7) in benzene at room temperature after extinguishing the light and mixing

formed under these conditions. It implied that the exchange reaction of Eq. 9 did exist. But the amount of increase of biphenyl-$d_5$ was relatively small ($4/5 - 3/4 = 1/20$), and suggested that the exchange reaction did not dominate the whole process and Path A in Fig. 5 was still a predominant mechanism for photolysis of (7).

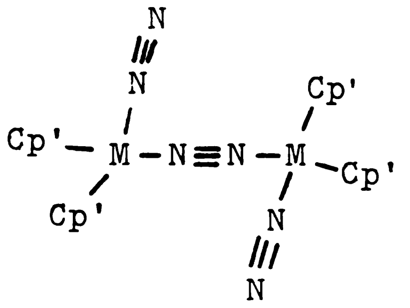
Irradiation of a benzene-$d_6$ solution of (7) in an ESR spectrometer showed a complex signal (Fig. 8). Apparently, more than one paramagnetic species was generated, consistent with the proposed mechanism. After extinguishing the UV light, the sample was shaken until the color of the solution was uniform. The spectrum was a singlet (Fig. 9). Presumably the exchange reaction was complete, and the signal was presumed to be due to monophenylpermethylzirconocene.

### 4. Nitrogen fixation of photochemically-generated active species

A small amount of $N_2$ gas was absorbed when a toluene solution of diphenyltitanocene was photolyzed under nitrogen at -20° C. Nitrogen-15 NMR at -60° C showed two singlets, one at 40 ppm upfield of conc. nitric acid which was determined to be the free $^{15}N_2$ molecules dissolved in toluene at that temperature by a blank experiment, another at 48 ppm downfield of conc. nitric acid. When (6) was photolyzed under the same conditions, there were also two singlets. Again, the upfield singlet was the free $^{15}N_2$, the downfield singlet was expected to be a similar species to that obtained from photolysis of diphenyltitanocene under $N_2$, but it appeared at 3 ppm downfield from conc. nitric acid. The upfield shift of this singlet is probably attributable to the ten electron-donating methyl groups on the two pentamethylcyclopentadienyl ligands. This spectrum proved that the $N_2$-fixed compound was not (15) which should have three signals, one singlet and two doublets[27]. This evidence confirmed that permethyltitanocene (8) was not the final product of photolysis of (6).

In a separate experiment, compound (16), which is a $N_2$-fixed compound from monophenyltitanocene, was prepared as reported by Teuben et al[59,63,64]. Nitrogen-15 NMR showed a singlet at 88 ppm upfield of conc. nitric acid. Thus (16) was not the nitrogen-containing compound from the photolysis of diphenyltitanocene. It could be inferred that the $N_2$-fixed compound from photolysis of (6) was not the analog of (16).

Unfortunately, all the attempts to isolate these $N_2$-containing compounds failed, because of their extreme



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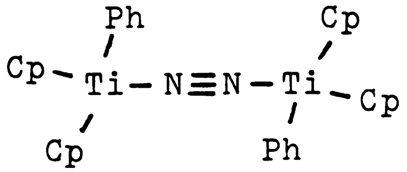

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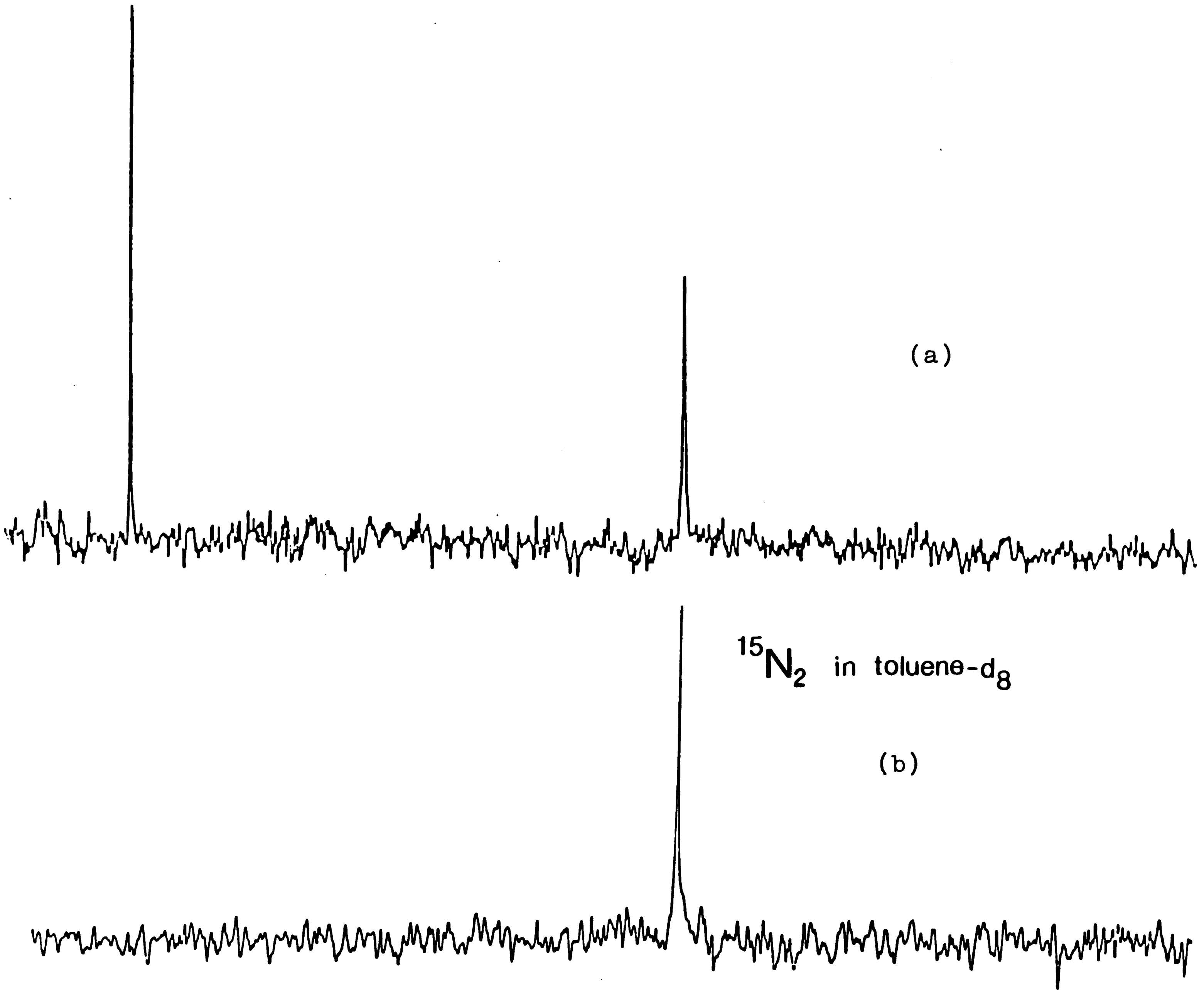
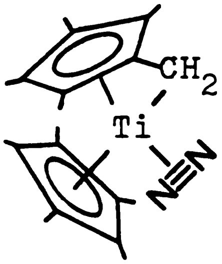


Figure 10 (a) $^{15}N$ NMR of $^{15}N_2$-Ti(III) complex in toluene-$d_8$ at -60° C
(b) Free $^{15}N_2$ gas in toluene-$d_8$ at -60° C

instability and very small concentration (inferred from the long period of time needed to obtain a spectrum even in a $^{15}$N-enriched sample). Since the monomethyl[65] and monophenyl[59] derivatives of titanocene have demonstrated an ability to absorb $N_2$, it seems reasonable to assign the structure of the $N_2$-Ti(III), to a side-on monomer (17)[66] or dimer (18).



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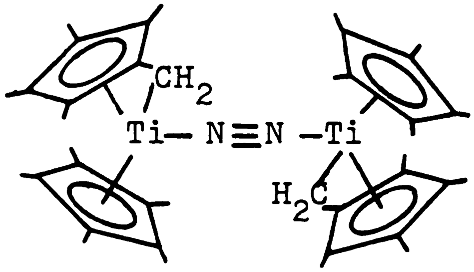

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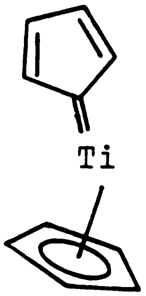
A small amount of $N_2$ gas was also absorbed when (7) was photolyzed at room temperature. Measurement of $^{15}$N NMR on a $^{15}$N-enriched sample did not show any signal. Isolation of the $N_2$-Zr compound (15) by following the published method[26] was not successful. This also implied that permethylzirconocene was not the final product of photolysis of (7).

# CONCLUSIONS

Photochemical decomposition of diphenylpermethyl titanocene and zirconocene seems to follow two general patterns: reductive elimination and stepwise homolysis. Percentage distributions in these two different pathways vary from Ti to Zr as well as with the ligands. Compared with the previous studies[53], the extent of reductive elimination is improved from approximately 50% (referred to the ratio of biphenyl-$d_0$ to -$d_5$) for diphenyltitanocene to 97% for diphenylpermethyltitanocene. Steric hindrance of ten methyl-substituents is believed to be responsible for this improvement. In the similar cases with zirconium, because of a much bigger nucleus of Zr, the effect of steric hindrance is not expected to be as serious. In the case of diphenylpermethylzirconocene, at least 75% of the decomposition pathways favors stepwise homolysis. It seems reasonable to believe that for the less sterically-hindered diphenylzirconocene, the stepwise homolysis should predominate in contrast to the results reported by Erker[46].

The proposed intermediates were based on the findings of photocleaved ligand derivatives, such as pentamethylcyclopentadiene and 2,3,4,5-tetramethylfulvene. Although the Ti-Cp $\pi$-bond is thermally stable, the photocleavage of this $\pi$-bond is known[49,67]. The formation of a Cp radical was found to be the primary process of photolysis with $Cp_2TiCl_2$[68]. The reason that none of the previous studies of the photolyses of the dimethyl[50,69] or diphenyl[32,52,53] derivatives of titanocene have reported the detection of the photocleaved ligand is probably the high reactivity and difficulty of isolation of the relatively unstable cyclopentadiene, and/or the possible formation of the extremely reactive intermediate (19), according to the mechanism proposed above.



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Compound (19) is a carbene-like species. It would probably undergo dimerization and/or oligomerization immediately following it's formation. Nevertheless, small amounts of $CpTiCl_3$ found from the HCl decomposition of the "black titanocene" photochemically-generated from dimethyl[69] and diphenyl titanocene give other evidence of possible photocleavage of Cp-Ti $\pi$-bond.

# PART II

# A POLYMER-SUPPORTED DICHLORO(CYCLOPENTADIENYL)-RHODIUM(III) CATALYST

# PART II

## INTRODUCTION

### A. Polymer-supported catalysts

In general, catalysts are classified as homogeneous or heterogeneous. Transition metals play an important role in both classes, and the following discussed catalysts concern only the transition metal catalysts.

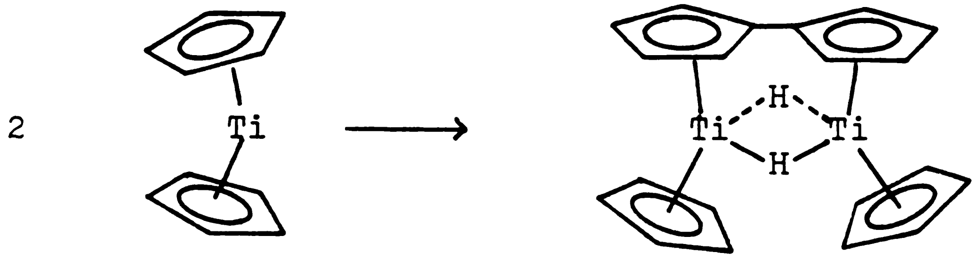
Homogeneous catalysts, comprised of discrete, soluble metal complexes, are in most cases more active and operate at lower temperatures and pressures than their heterogeneous counterparts. The catalytic site in homogeneous systems is the individual metal nucleus, but in heterogeneous systems it is the bulky surface of a group (or groups) of metal nuclei (or metal crystallite). The metal center activity in a homogeneous system is controlled by supporting ligands. In heterogeneous systems the metal centers are either a part of the support surface, or part of a surface metal crystallite. When a homogeneous catalyst is attached to an insoluble support through a covalent bond, the complex becomes heterogeneous when considered at the bulk level but is essentially identical to a soluble analog on a molecular level. Consequently, the catalyst will show properties somewhere between the two major classes. This new class of covalent bone-supported catalysts has been called "hybrid-phase catalysts"[70].

Varieties of chemically inert supports have been used for hybrid-phase catalysts, such as silica gel, alumina, zeolite, crosslinked and noncrosslinked polystyrene, polymethacrylate, polyvinylchloride, etc. Crosslinked polystyrene, available with a wide range of crosslink densities, surface areas, and porosities, has received the most attention as an organic support. The polymer backbone is basically chemically inert[71,72], but it has poor mechanical and thermal stabilities and poor heat-transfer properties.

The obvious advantages of the hybrid-phase systems are to retain the higher selectivity and activity of homogeneous catalysts, overcome the problem of catalyst separation from the reaction products, and prevent the loss of possibly expensive catalytic materials and contamination of products. In some particular cases, the homogeneous catalysts are unsaturated intermediates which have a tendency to dimerize or oligomerize and become deactivated. When such homogeneous catalysts are anchored on a rigid support, the frame structure of the rigid support can immobilize the catalytic species and prevent the association of the unsaturated catalytic intermediate, thus preserving all the potential catalytic activity. Therefore, these supported-catalysts could exhibit a higher catalytic activity than the corresponding homogeneous catalysts.

For example, palladium amine complexes were reported by Haag and Whitehurst[73] to catalyze the carbonylation of allyl chloride. The activity of the homogeneous catalyst soom reached a maximum when its concentration was raised. This is because of the parrallel increase of mutual interactions among palladium atoms, leading to aggregation and formation of catalytically inactive oligomeric species. Such an aggregation was prevented when the palladium complexes were anchored on a rigid polymer. The catalytic activity of the supported catalyst increased linearly with the amount of palladium used.

Brubaker, Grubbs and coworkers[74-76] had also reported a perfect example of activation of a homogeneous catalyst by anchoring on a support. Titanocene, obtained from reduction of titanocene dichloride by various strong reducing agents, was believed to be a hydrogenation catalyst for olefins. However, the catalytic effect was not very high, because the titanocene tended to dimerize and form a relatively inactive species (Eq. 1). The attachment of titanocene to crosslinked polystyrene provided an isolation of each titanocene species from one another and, hence, prevented the dimerization and preserved the catalytic activity of titanocene. Therefore,



(1)

the polymer-supported titanocene catalyst exhibited a much greater activity for hydrogenation of olefins than the corresponding homogeneous species.

Beside all the positive factors mentioned above, one can also expect some disadvantages from the polymer-supported catalysts. The use of polymer raises the question of diffusion of the substrate from the bulk solution to the catalytic centers, through the pore channels of the polymer. Diffusion barriers are associated with substrate size, polymer crosslinking, swelling power of the solvent and relative substrate and polymer polarities. On the other hand, the attachment of the catalyst on the polymer brings the catalytic centers much closer to each other (although not close enough to interact with each other) than the corresponding homogeneous system. For a stereoselective polymer-supported catalyst, the stereoselectivity could be reduced from that of the corresponding homogeneous analog because the chances of random attacks by the sterically congested catalytic centers have been largely increased. Rhodium(I) hydrogenation catalysts attached to 2% crosslinked polystyrene showed decreased reduction rates as olefin size increased or as solvent swelling power decreased[77]. These effects are mostly associated with diffusion limitations and become more important as catalyst activity increases[78].

In order to attach the catalysts to a polymer, the polymer has to be first functionalized with suitable ligands.

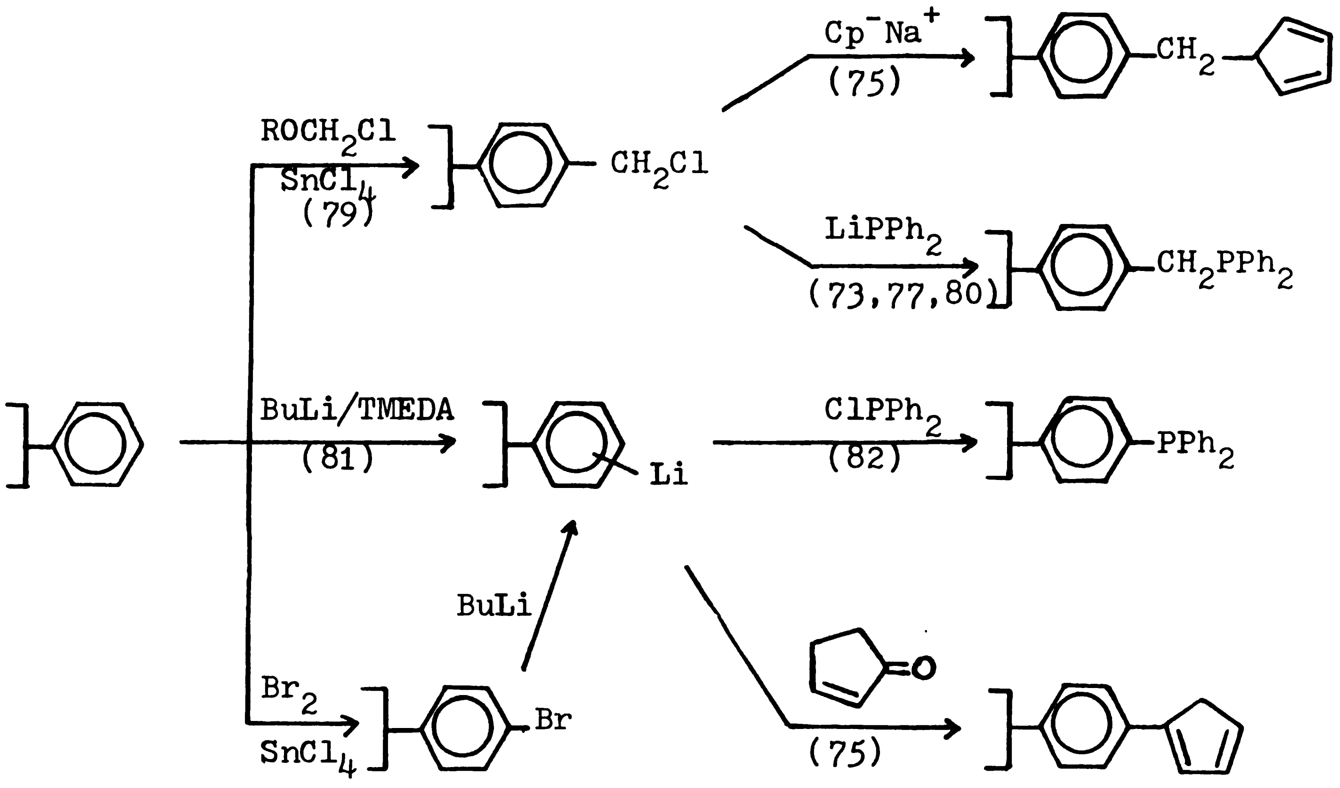
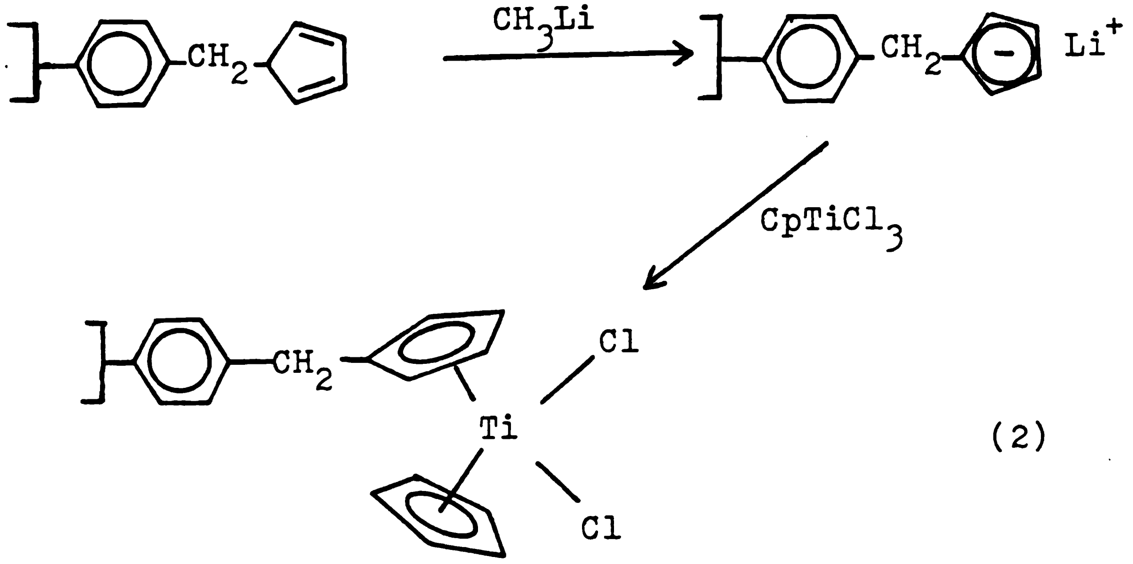


Figure 11 Functionalization of polystyrene with ligands

The ideal ligands used to bind a metal complex to a support should be chemically inert under the reaction conditions and form a nonlabile link between metal complex and support. Numerous techniques have been developed for functionalization of polystyrene, and some of them are summarized in Fig. 11[70]. Among these techniques, the chloromethylating method (first method in Fig. 11)can generate the most uniformly functionalized polymer and the extent of chloromethylation can be controlled so that only approximately one in ten benzene rings is chloromethylated. However, the starting material, chloromethyl ethyl ether, is potentially carcinogenic[83].

Because of these well-developed methods of attaching a cyclopentadiene ring to the polystyrene, a variety of transition metal complexes which are ligated by cyclopentadienide anion can be anchored on the polystyrene. In order to achieve this purpose, usually a strong base, such as methyllithium or butyllithium, is needed to generate a polymer-bound cyclopentadienide anion. Subsequent addition of the desired metal chloride can successfully attach the metal to the polymer (Eq. 2). The X-ray fluorescene microprobe scan has indicated that the titanium and chloride are evenly distributed across a cross section of the beads and not confined to the surface of the material[83].

Because of the excellent catalytic activity of rhodium complexes, attempts have been made to attach most of the homogeneous rhodium catalysts to rigid polymers. Although phosphines are normally labile ligands in catalyst systems



(2)

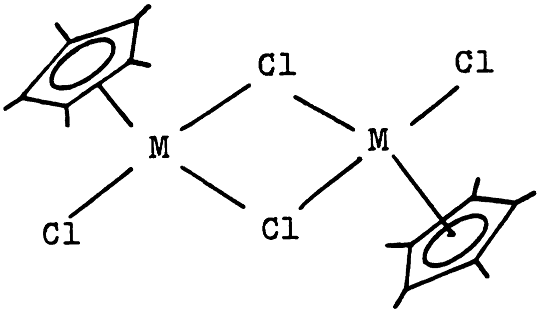
and are easily oxidized, they are the optimum supporting ligands for rhodium complexes. In fact, more than 90% of the reported hybrid-phase rhodium complexes are linked through phosphine[70]. In this work, a rhodium catalyst has been successfully attached to 20% divinylbenzene crosslinked polystyrene through a cyclopentadienyl ligand.

## B. Catalytic hydrogenation of aromatic ring

As early as in 1904, Sabatier and Senderens[84] had discovered the catalytic hydrogenation of aromatic systems by nickel metal. Since then, the developments of metals and metal oxides as hydrogenation catalysts of arenes have been significantly advanced, and utilized in present industrial technology[85,86]. However, like most of the other heterogeneous catalytic systems, the mechanisms of these hydrogenations are still not well defined, relatively high temperatures and pressures are employed, and the lack of chemoselectivity and stereoselectivity are observed.

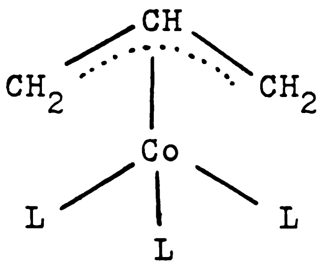
In contrast, homogeneous catalysts for hydrogenations of aromatic systems have been discovered recently, and only four of them have been characterized.

Maitlis and coworkers have reported the synthesis[87] of pentamethylcyclopentadienylrhodium (1) and -iridium (2) halides and have studied their catalytic activities toward olefins[88,89] and aromatic rings[90]. These complexes were isolated as dimers. The rhodium complex (1), in the presence of triethylamine as a cocatalyst, catalyzes olefin hydrogenation and aromatic hydrogenation at 50° C and 50 atm of hydrogen. The reactions are highly stereoselective and cis-isomers are the major products. But no catalytic isomerization of olefins by these complexes has been reported.



M = Rh <u>1</u>
Ir <u>2</u>

Muetterties and coworkers[91] have shown that π-allyl cobalt phosphite complexes (3) can catalyze homogeneous hydrogenation of aromatics and olefins with almost equal efficiency at room temperature and low pressures (1-3 atm). The catalytic hydrogenations of arenes are exclusively <u>cis</u>-stereoselective[92]. Unfortunately, the catalyst is

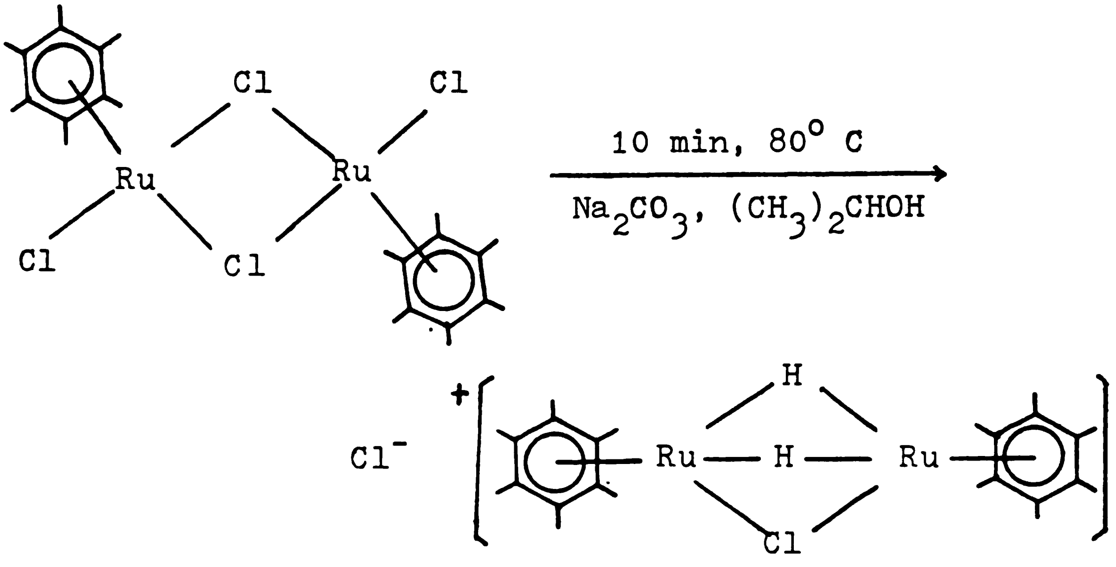


$L = P(OCH_3)_3$

3

readily deactivated due to irreversible hydrogenolysis of the π-allyl ligand to propene.

Bennett and coworkers have[93] indicated that the ruthenium(II) complex $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ is easily converted



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to a purple dinuclear hydride catalyst (4). This catalyst is reported to be highly active toward hydrogenations of aromatics at $50^{o}$ C and 50 atm of hydrogen. The reactions are not stereoselective.

Dichloro(cyclopentadienyl)rhodium(III) (5) was first synthesized by Maitlis et al.[87], along with the analogous dichloro(pentamethylcyclopentadienyl)rhodium(III)dimer (1). In contrast to (1), (5) is amorphous and insolubile in all but powerfully coordinating solvents and is probably polymeric. Reliable and reproducible synthesis of $[Rh(C_5H_5)Cl_2]_n$ is difficult[94] and (5) has never been reported as a catalyst in homogeneous system. The unsubstituted cyclopentadienyl ligand could be responsible for the insolubility. The aforementioned dimerization or oligomerization among the cyclopentadienyl ligands (Eq. 1) could be the main reason for the polymeric nature of (5). If one could attach (5) to a polymer in order to immobilize the individual molecule, the dimerization or oligomerization among the cyclopentadienyl rings would be prevented. The problem of the insolubility of (5) would be solved and a new hybrid-phase catalyst would be produced.

In this work, compound (5) was successfully attached to the 20% divinyl benzene crosslinked polystyrene beads by treating the cyclopentadienylpolystyrene beads directly with $RhCl_3 \cdot 3H_2O$. The polymer-supported dichloro(cyclopentadienyl)rhodium(III) (6) proved to be a good hydrogenation as well as an isomerization catalyst. It was also found that

(6) was easily converted to a polymer-supported cyclopentadienylrhodium dicarbonyl catalyst under mild conditions.

# EXPERIMENTAL

## 1. General

Purification of all solvents and general chemicals were the same as those in the experimental section of Part I. Spectroscopic instruments, vacuum techniques and the inert atmosphere box were also the same.

1,4-Cyclohexadiene and cis,trans-β-methylstyrene(propenylbenzene) were purchased from Aldrich Chemical Co.. Allylbenzene was dried through an activated alumina column and distilled under vacuum. Ortho-xylene was refluxed over sodium and distilled under reduced pressure. Acetophenone was dried over $CaCl_2$ for several days, then distilled under reduced pressure and stored in the dark under argon. Triethylamine hydrochloride was obtained from the reaction of triethylamine with HCl gas. Rhodium·trichloride trihydrate was purchased from Strem Chemicals Inc. The 20% cross-linked polystyrene-divinylbenzene copolymer beads were a gift from the Dow Chemical Co. and were washed to remove impurities before use. They were washed with 10% aqueous HCl, 10% aqueous NaOH, $H_2O$, $H_2O$-$CH_3OH$ (1:1), $CH_3OH$, $CH_3OH$-$CH_2Cl_2$ and benzene and then dried in a vacuum[95]. Polymer-supported samples used for IR measurements were prepared by crushing the polymer beads in a ball mill and mulling the powder with dry nujol in a glovebox. IR spectra were recorded under a $N_2$ atmosphere. A glass pressure bottle purchased from Lab Glass Inc. was installed with a 4-way adapter, a needle valve, a ball valve and a pressure gauge (0-200 psig). This bottle was used for conducting catalytic hydrogenations.

### 2. Preparation of polymer-supported dichloro($\eta^5$-cyclopentadienyl)rhodium(III) catalyst

In a typical reaction, 2 g of the previously prepared[95,96] 20% crosslinked polystyrene-cyclopentadiene beads (approximately 1 mmol $C_5H_5$ per g beads) was suspended in 30 mL methanol. A 10 mL methanol solution of $RhCl_3 \cdot 3H_2O$ (0.11 g) was added to this suspended mixture at room temperature. This mixture was then refluxed for a week. In the first two days, the dark red solution of $RhCl_3 \cdot 3H_2O$ was decolorized rapidly. The solution turned colorless at the end of a week and the color of the polymer beads changed from pale yellow to brick-brown. The solvent was then removed by a syringe and the polymer beads were washed three times by fresh methanol. The removed solvent was concentrated to 3-5 mL and diluted with an equal volume of distilled water. A white precipitate was found upon addition of aqueous $AgNO_3$ to this solution. Acidity was observed when the solution was tested with pH paper. The color of beads was very uniform if the beads were originally prepared from chloromethylation (the first method in Fig.11, p. 57). Some of the uncolorized beads were found in a batch of beads that was originally prepared from bromination (the last method in Fig.11, p.57). Elemental analysis of the polymer-supported rhodium complex showed 2% loading of Rh on the polymer with a Rh/Cl mole ratio of 1/2.2)

### 3. Catalytic hydrogenation

In a typical reaction, about 0.4 g beads of polymer-supported dichloro(cyclopentadienyl)rhodium(III) was placed in a glass pressure bottle. The pressure bottle was then degassed three times by use of a vacuum line and charged with $H_2$. A large excess of substrate (1-hexene, benzene, o-xylene, or acetophenone) and 0.3 mL triethylamine were introduced into the bottle by syringes. The pressure of $H_2$ was then increased to 110 psig at room temperature. The pressure bottle was then put into an oil bath at 70° C. The solution was stirred vigorously throughoutthe hydrogenation. The pressure was increased slightly at the beginning of the hydrogenation and then dropped gradually until the reaction was finished. The pressure changes were recorded at time intervals of 2-4 h and plotted in Fig. 13. The extents of hydrogenation were confirmed by quantitative analyses of the final products on a TCD GC with column of 10% Carbowax 20M (25' x 1/4") or 10% SE-30 (10' x 1/4"). Qualitative analyses of the products were determined by a GC-MS with an INCOS data system. The turnover rates were calculated from the slopes in the first two hours of hydrogenation from the plot of pressure vs. time (Fig. 13). All substrates used were in approximately equal excess in terms of reducible double bonds. In the case of 1-hexene, a catalytic reaction without triethylamine was also observed. The catalytic hydrogenation was not appreciable in the absence of triethylamine for the other substrates used in this work under the similar conditions.

Triethylamine hydrochloride was isolated from the resulting solution after the hydrogenation. It was identified by comparison of the IR spectrum with that of the authentic sample. The color of the beads changed to black after the hydrogenation. The nujol mull IR spectrum of the ground black beads showed a moderate absorption at 1960 $cm^{-1}$ and suggested the presence of terminal Rh-hydride. The color of the resulting beads returned to brown after the black beads were soaked in chloroform for overnight. The catalytic activity of the recovered beads had only decreased slightly. There were no black particles found in the solution during the course of catalytic hydrogenation.

### 4. Isomerization of allylbenzene

Polymer-supported dichloro(cyclopentadienyl)rhodium(III) (0.23 g) was first placed into a 100 mL flask. The flask was degassed and the atmosphere was replaced by prepurified $N_2$. Allylbenzene (6 mL) was introduced to the flask by a syringe. The flask was then put into an oil bath at 85° C. The pressure of $N_2$ was kept constant (1 atm) and the mixture was stirred vigorously throughout the isomerization. A sample of about 0.2 mL was withdrawn by a syringe at different time intervals (more often at the beginning of the reaction). Analysis were performed on a TCD GC with a column of Carbowax 20M (25' x 1/4"). The isomerized products, cis and trans-propenylbenzene (β-methylstyrene) were determined by comparison with authentic samples. Percent compositions of the sampled mixture were plotted against time (Fig. 2). The total conversion of allylbenzene to cis and trans-propenylbenzene leveled off at 90% after 40 h. Trans-propenylbenzene was the major product and leveled off at 75%. The proportion of cis-propenylbenzene seemed to reach equilibrium at an early stage of isomerization. The color of the beads remained the same throughout the entire reaction.

In a separate experiment, exactly the same conditions and equipment were used. At the beginning stage (30 min) of the isomerization, 0.2 mL triethylamine was added to the reaction flask by a syringe. The same analytic steps were used for next 20 h. No isomerized products was found after the addition of triethylamine. After the removal of polymer beads and substrate under reduced pressure, very small amount of $Et_3NHCl$ was detected.

### 5. Disproportionation of 1,4-cyclohexadiene

Polymer-supported Rh(III) (0.16 g) was transferred to a 100 mL flask. The flask was degassed and $N_2$ was introduced in at 1 atmosphere pressure. 1,4-Cyclohexadiene (4 mL) was then added into the flask by a syringe. The mixture was stirred in an oil bath at 75° C. Samples were withdrawn and analyzed every 10 h. After 70 h, small amounts of cyclohexane, cyclohexene and benzene were formed as determined by GC (Carbowax 20M, 25' x 1/4") and only about 1% of 1,4-cyclohexadiene was consumed.

### 6. Preparation of polymer-supported cyclopentadienylrhodium dicarbonyl catalyst

Polymer-supported dichloro(cyclopentadienyl)rhodium(III) (0.4 g) was transferred into a glass pressure bottle. The bottle was than degassed and $H_2$ gas was introduced. Ten mL prepurified hexane and 0.3 mL triethylamine were introduced into the bottle by syringe. The pressure bottle was then charged with 40 psig CO and 40 psig $H_2$. The mixture was stirred vigorously and heated in an oil bath at 80° C for a week. The color of the beads changed from brick-brown to black then dark brown. IR spectrum (nujol mull) of the newly produced beads showed two strong absorption bands at 2040 and 1980 $cm^{-1}$. After removal of the solvent, small amount of $Et_3NHCl$ was detected.

# RESULTS AND DISCUSSION

## 1. Polymer-supported dichloro(cyclopentadienyl)rhodium(III) (6)

The coventional way to prepare polymer-bound cyclopentadienyl-metal catalysts is to prepare a polymer-bound cyclopentadienide lithium first by using a strong base to react with the Cp-polymer. This method is not applicable for the preparation of (6), because of the total insolubility of anhydrous $RhCl_3$. If, instead, the soluble salt of $RhCl_3 \cdot 3H_2O$ is used, the polymer-bound cyclopentadienide would be destroyed by the water in the hydrated compound. However, when $RhCl_3 \cdot 3H_2O$ was dissolved in methanol and refluxed with Cp-polymer for a week, the dark red solution turned clear and HCl was formed. The acidity and the presence of $Cl^-$ were detected by litmus paper and a $AgNO_3$ solution respectively. The resulting polymer beads were brick-brown like (5)[87]. The reaction probably involved the coordination of $RhCl_3$ first with the two double bonds of cyclopentadiene ring, then a hydrogen-abstraction occurred to form a more stable cyclopentadienide anion ligand coordinated with Rh. Subsequently (or perhaps simultaneously), 1 mol of HCl was released to produce (6) as in Figure 12. The result of microanalyses showed 2% loading of Rh on polymer with a Rh/Cl ratio of 1/2.2.

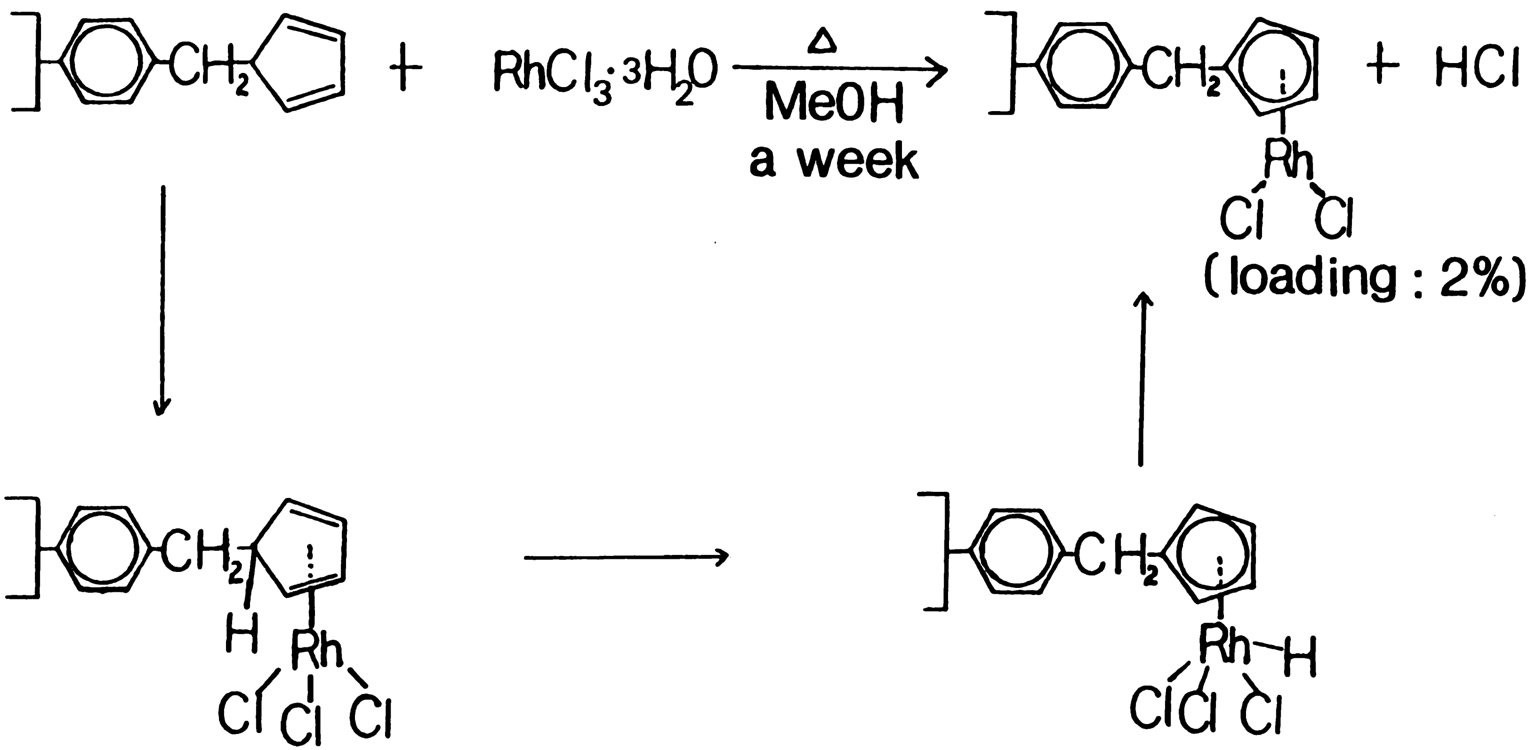
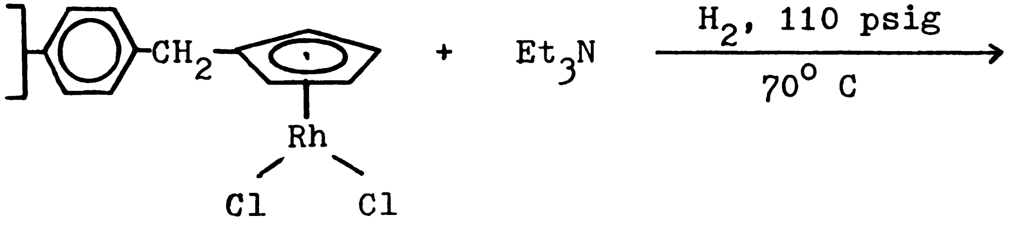


Figure 12 Preparation of polymer-supported dichloro(cyclopendienyl)rhodium(III) catalyst

2. Catalytic hydrogenation

Benzene, o-xylene, acetophenone, and 1-hexene were chosen as substrates for catalytic hydrogenation over (6) in the presence of an excess of $Et_3N$ ($Et_3N/Rh$ = 30/1) under 110 psig of $H_2$ at $70^{\circ}$ C. The results are shown in Table 2. The catalyst was still active without $Et_3N$ in the case of 1-hexene, but the hydrogenation rate had been lowered by about one third. The turnover rate was expressed in mol of $H_2$-uptake per mol Rh per hour. The extent of hydrogenation was confirmed by product analyses. In the case of o-xylene, although trans-1,2-dimethylcyclohexane is 1.8 kcal/mole more stable than the cis-isomer[98], the cis-isomer was the predominant product and indicated that the hydrogenation catalyzed by (6) was stereoselective. Acetophenone was hydrogenated to three different products: cyclohexyl methyl ketone (48%), ethyl benzene (45%), and 1-phenyl ethanol (7%). It indicated that the aromatic ring and carbonyl group were almost equally competitive in the catalytic hydrogenation. The pressure drop of $H_2$ for these reactions was plotted against time (Fig.13) and showed that electron-withdrawing substituents on the benzene ring slowed down the reaction rate more than donating groups. It may suggest that sizes of substrates (steric factor) and the hydrophobic nature of the polymer support play important roles in the mass transport, which is the dominant factor in comparing the hydrogenation in and out of the polymer matrices. The reason that the presence of $Et_3N$ enhanced the hydrogenation rate

Table 2 Catalytic hydrogenation of alkenes and arenes over polymer-supported dichloro(cyclopentadienyl)rhodium(III)



1 30

| Substrate | Turnovers/hr | Product composition |
|---|---|---|
| 1-hexene | 253 | n-hexane ( > 99%)<br>2-hexene (trace) |
| 1-hexene ( no $Et_3N$) | 169 | n-hexane ( >99%)<br>2-hexene (trace) |
| benzene | 59.3 | cyclohexane (100%) |
| o-xylene | 35.6 | *cis*-1,2-dimethylcyclohexane (66%)<br>*trans*-1,2-dimethylcyclohexane (34%) |
| acetophenone | 20.0 | cyclohexyl methyl ketone (48%)<br>ethyl benzene (45%)<br>1-phenyl ethanol (7%) |

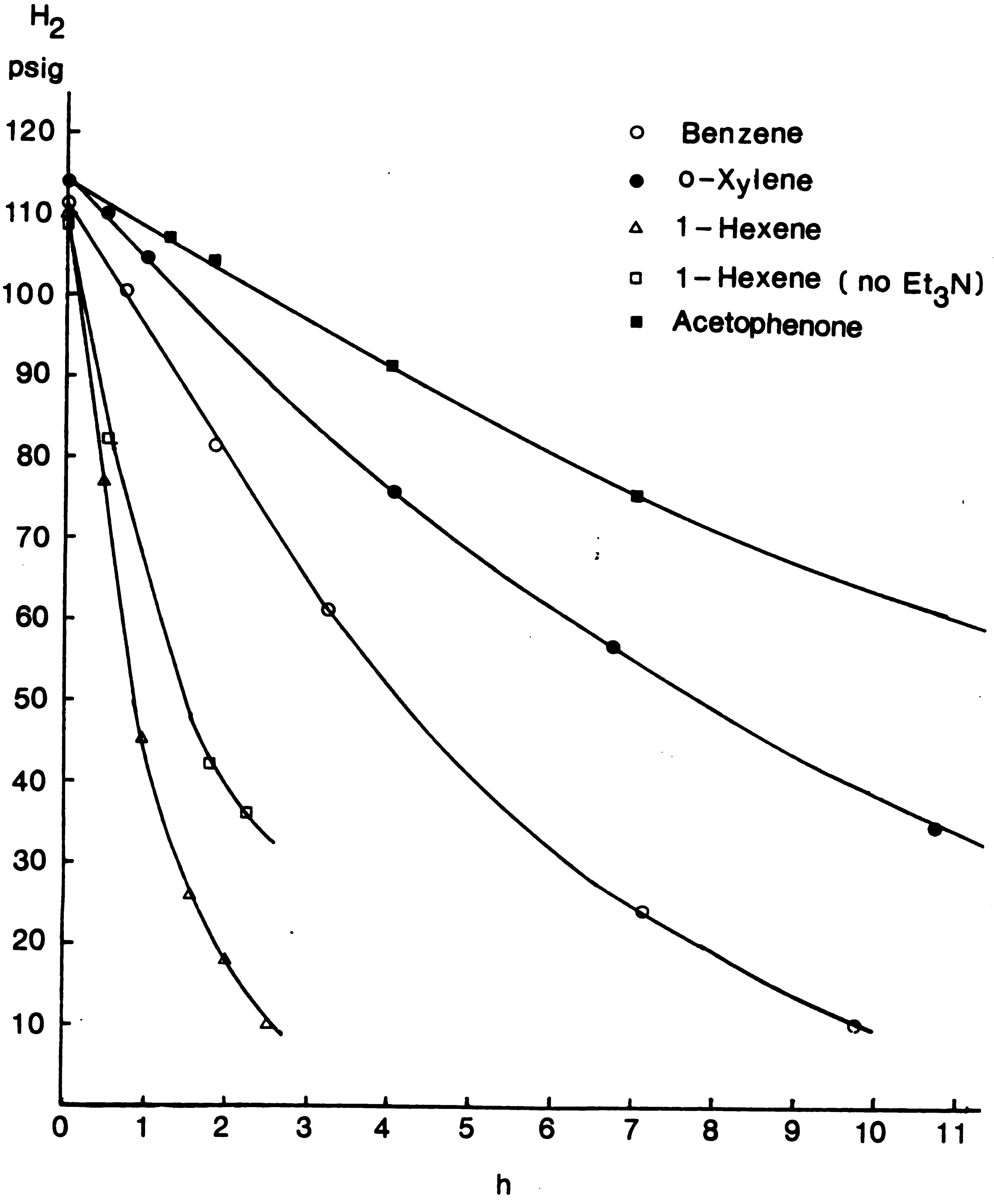


Figure 13 Catalytic hydrogenation of alkenes and arenes with polymer-supported Rh(III) complex: $H_2$(psig) vs. h

can be rationalized by Figure 14. The catalytic center of Rh can insert into a molecule of $H_2$ at the beginning stage of hydrogenation to form an 18 electron unstable intermediate (or transition state), then $Et_3N$ aids in the release a mole of HCl as $Et_3NHCl$. The resulting Rh hydride is a necessary and reactive intermediate as was confirmed by IR absorption at 1960 $cm^{-1}$ [97]. $Et_3NHCl$ was isolated and identified after the hydrogenation had been completed. In the absence of triethyl amine, the release of HCl is necessary in order for the hydrogenation to occur. Since it is a reversible reaction, the rate of hydrogenation is obviously slower than that in the presence of $Et_3N$.

The Rh hydride beads are black, but the possible presence of black Rh metal was excluded by the observation that the color returns to brown after soaking the black beads in chloroform overnight. The stereoselective hydrogenation of o-xylene is another important observation which helps rule out the possibility of Rh(0) formation.

### 3. Isomerization of allyl benzene

Allyl benzene was used as the substrate to demonstrate the isomerization ability of the catalyst (6) at 85° C. The result is shown in Fig. 15. Two isomerized products were found, cis and trans-propenyl benzene. The conversion of allyl benzene leveled at 90% after 40 h. The predominant product was trans-propenyl benzene and leveled at 75%. The color of the polymer-bound catalyst remained unchanged

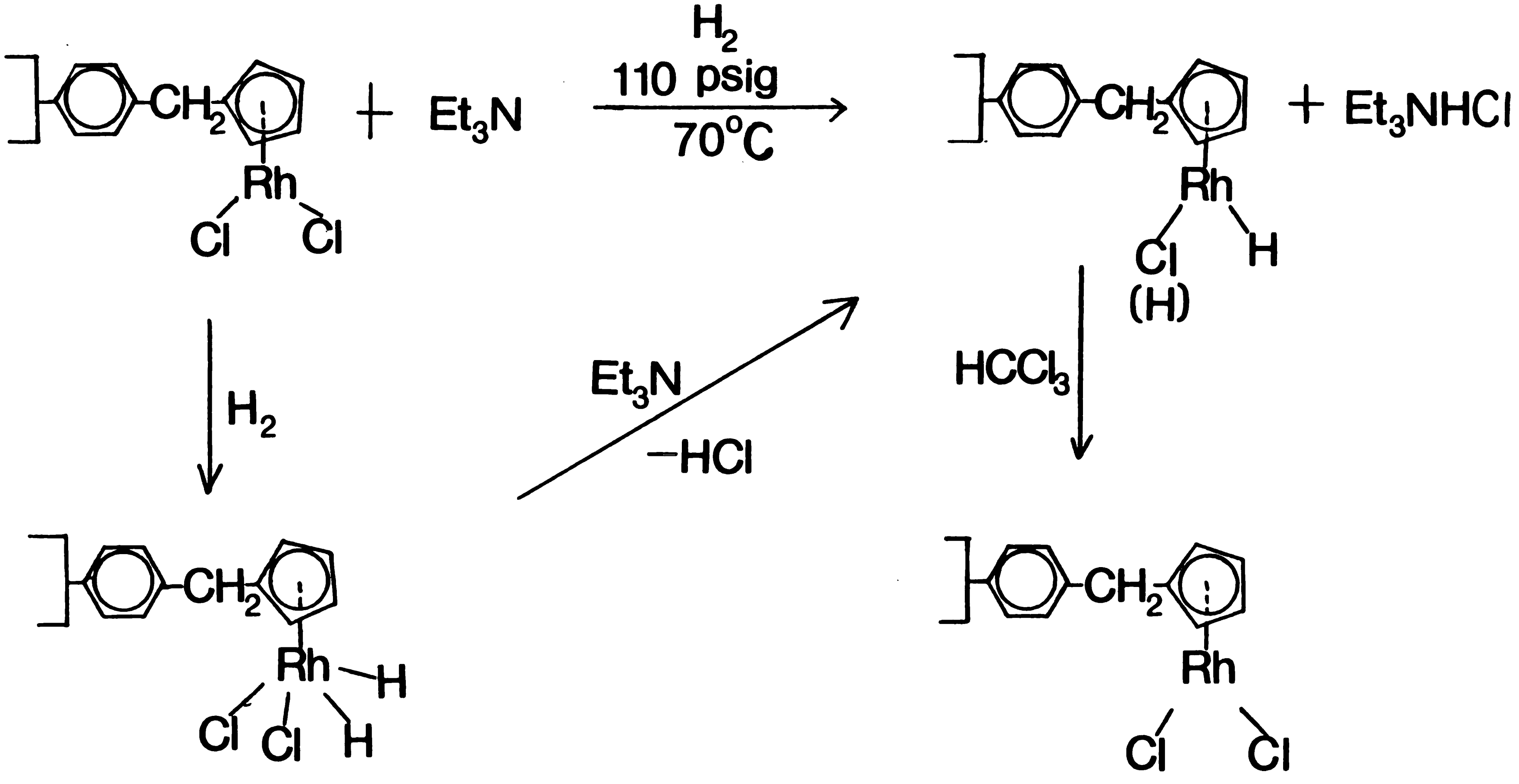


Figure 14 Scheme for the formation of Rh-hydride from the reaction of polymer-supported Rh(III) complex with $H_2$ in the presence of triethylamine

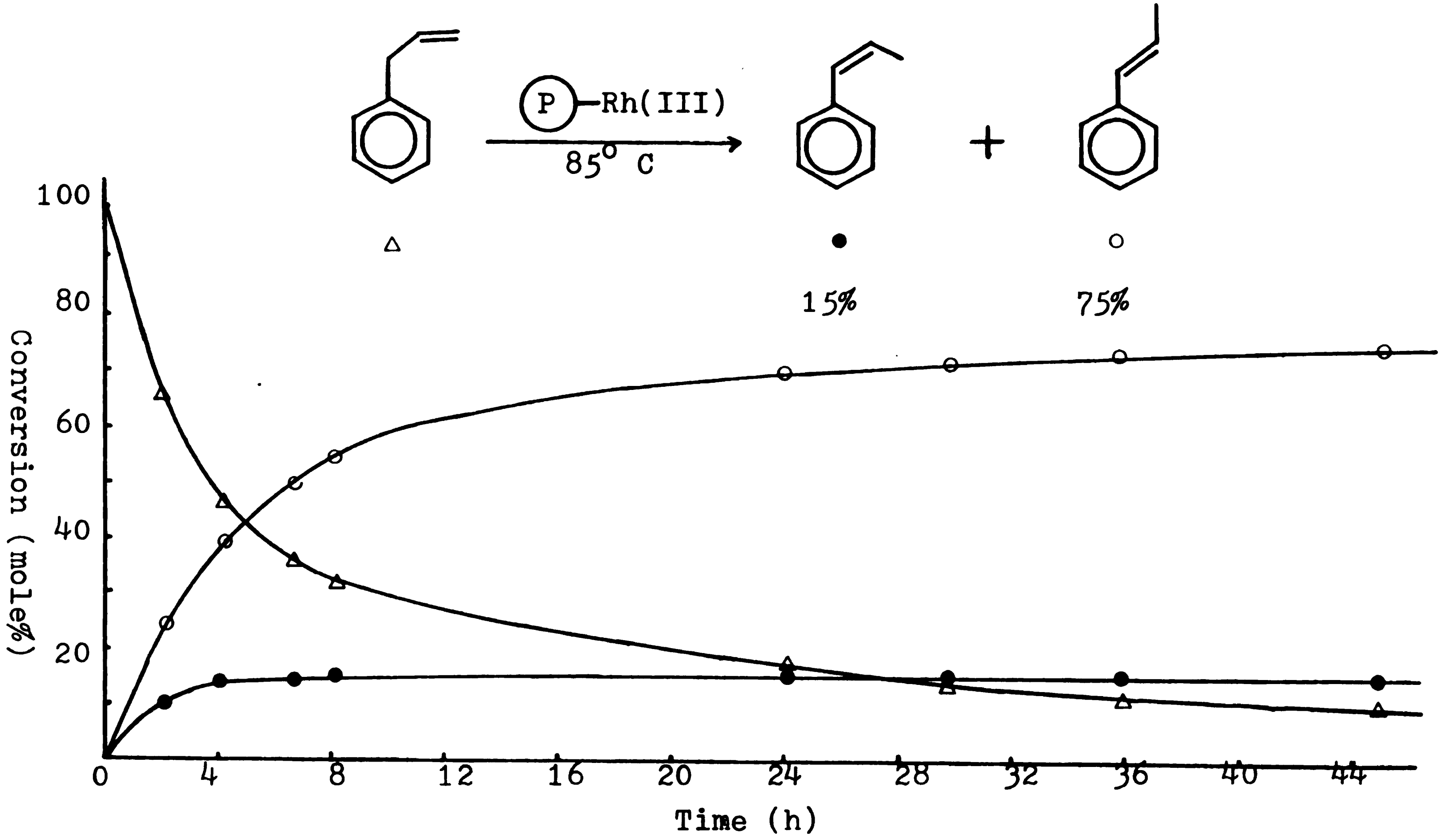


Figure15 Catalytic isomerization of allylbenzene with polymer-supported Rh(III) complex

throughout the reaction period.

The addition of $Et_3N$ to the reaction vessel stopped the isomerization immediately. This phenomenum can be rationalized as in Figure 16. This isomerization was initiated with insertion of the Rh catalytic center into the allylic hydrogen-carbon bond followed by the return of the hydrogen to the γ-carbon which led to a rearrangement of the double bond to form propenyl benzenes (β-methyl styrenes). In the presence of $Et_3N$, the HCl on the metal hydride intermediate (or transition state) was irreversibly removed by $Et_3N$ as $Et_3NHCl$ which was identified. As a result, the isomerization cycle could not be completed and the catalytic centers were spent.

### 4. Preparation of polymer-supported cyclopentadienyl rhodium dicarbonyl catalyst (7)

Compound (7) has been reported a good catalyst[99]. It was prepared by treating polymer-bound cyclopentadienide lithium with the chlororhodium dicarbonyl dimer (Figure 17a).

Since a strong base is involved in this preparation, it might have reduced some Rh complex to the metallic form[95]. However, when (6) was placed in a pressure bottle with 80 psig $H_2$ and CO (1/1) in the presence of excess $Et_3N$ and heated at 80° C for 1 week, the color of the beads changed from brick-brown to dark brown. The IR spectrum of this polymer-bound species showed two strong CO-stretching bands at 2040 and 1980 $cm^{-1}$ which suggested that catalyst (7) was

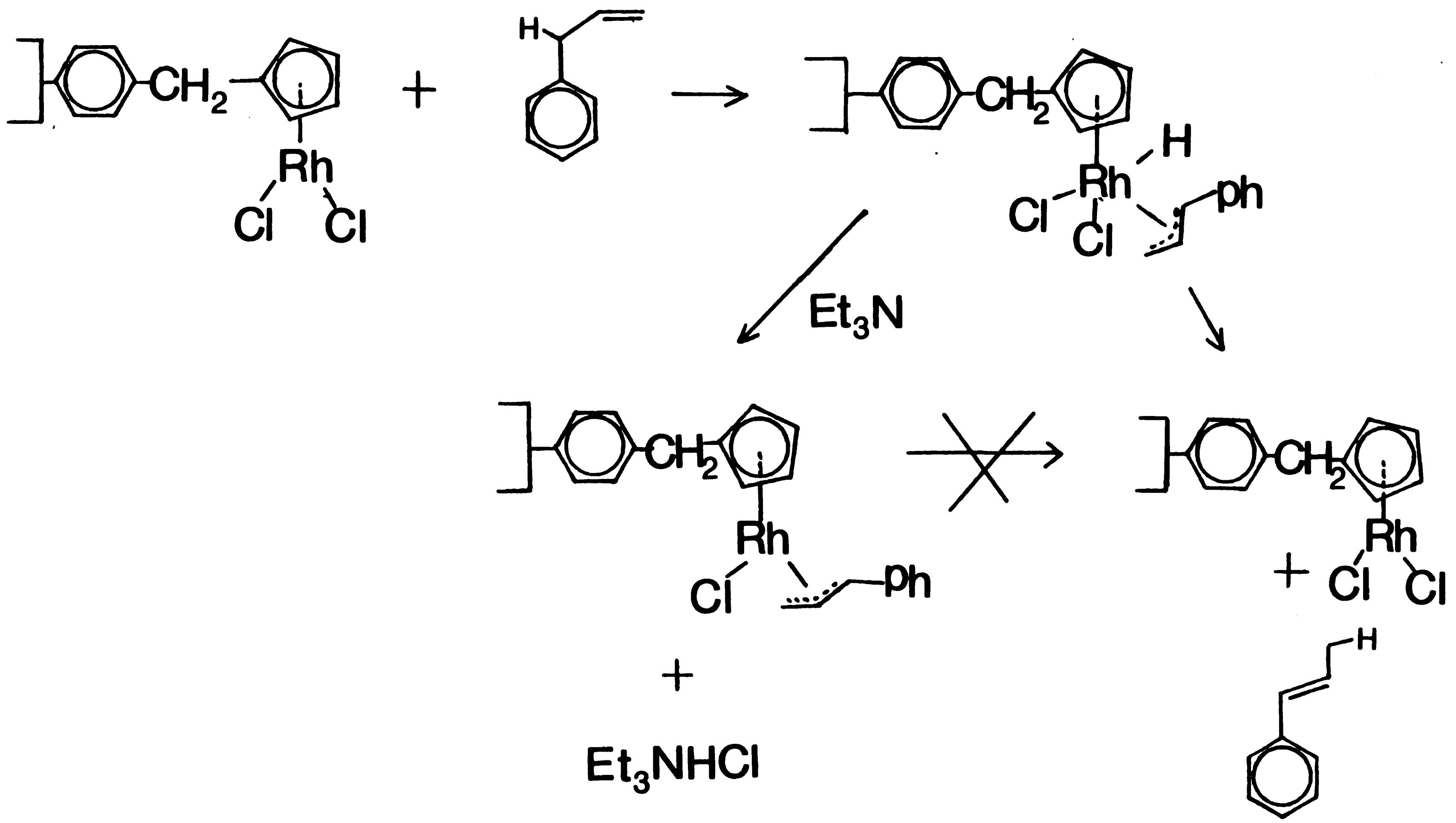
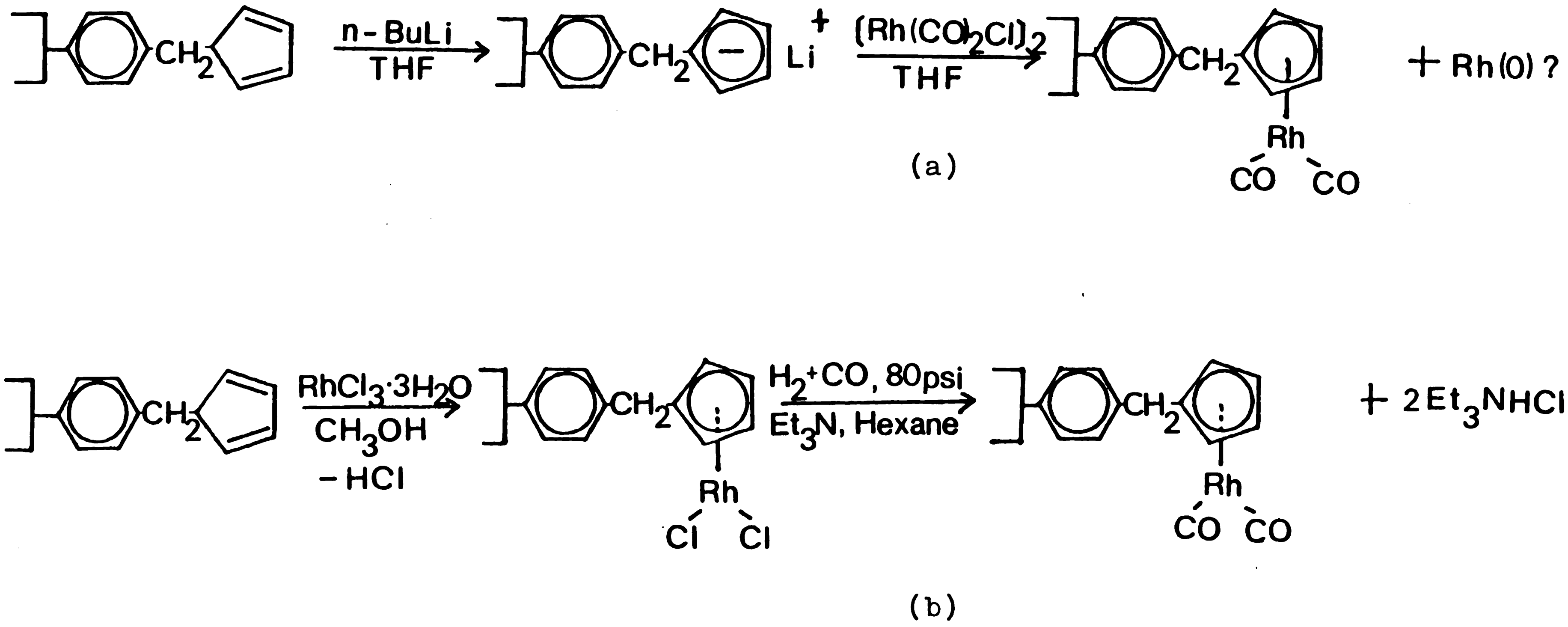


Figure 16 The termination of catalytic isomerization of allylbenzene with polymer-supported Rh(III) complex by triethylamine



IR $\nu_{CO}$ : 2040, 1980 cm$^{-1}$

Figure 17 Preparation of polymer-supported dicarbonyl(cyclopentadienyl)rhodium catalyst from (a) polymer-bond cyclopentadienide lithium and dicarbonylchlororhodium dimer (b) polymer-supported Rh(III) complex

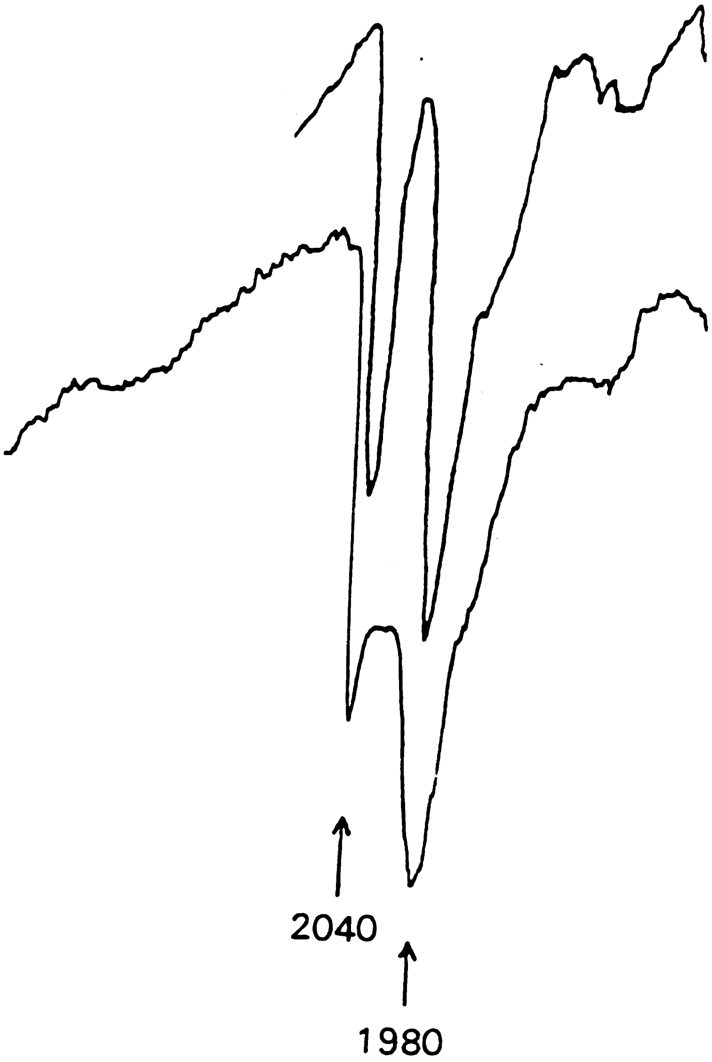
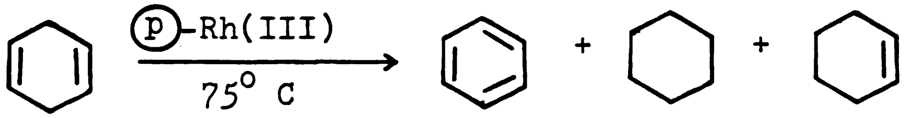


Figure 18 IR spectrum of polymer-supported dicarbonyl-(cyclopentadienyl)rhodium catalyst

formed[95,99]. Again, $Et_3NHCl$ was found in the solution. This approach (Fig.17b) generated a new method of preparing (7) without risking the formation of metallic rhodium.

## 5. Disproportionation of 1,4-cyclohexadiene

1,4-Cyclohexadiene was stirred together with (6) at 75° C for 70 h. Only about 1% of the substrate had disproportionated to benzene, cyclohexane and trace amounts of cyclohexene. Raising the reaction temperature above the boiling point of 1,4-cyclohexadiene may increase the disproportionation rate, but is not very convenient.



# PART III

# THERMOCHEMICAL DECOMPOSITION OF DINEOPENTYLPERMETHYLTITANOCENE

# PART III

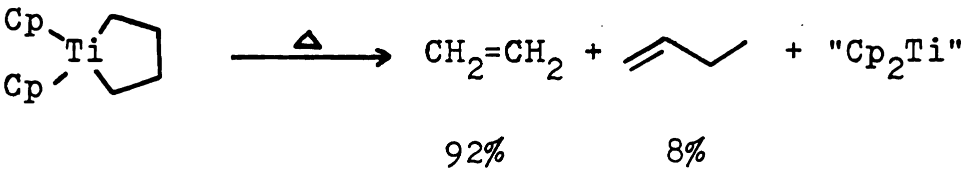
## INTRODUCTION

Transition metal alkyls are often thermally unstable and their thermal instability is frequently the characteristic that makes them catalytically important. Metal-carbon bond breaking may formally be uni- or bimolecular. A unimolecular process involves either (a) migration of a substituent from the alkyl group to the metal (α, β, etc., ekunubatuib) or (b) homolytic cleavage of metal-carbon bond[28].

Beta-hydrogen elimination dominates the thermal decomposition of metal alkyls[28]. The best-studied example is the thermal decomposition of di-*n*-butyl-bis(triphenyl phosphine)-platium(II)[100]. The products of thermolysis are n-butane, 1-butene, and a complex of platinum(0). The decomposition has been proposed to take place by intramolecular β-hydrogen elimination process.

Alpha-hydrogen elimination involves migration of a hydrogen from the α-carbon to the metal with formation of a carbenic fragment which may remain coordinated to the metal. It is generally less well established than β-hydrogen elimination. The best example of α-hydrogen elimination is in the pentaneopentyltantalum complex. The neopentylidene ligand forms by abstraction of a neopentyl α-proton by a neighboring neopentyl group in the sterically crowded penta(neopentyl) intermediate[101,102].

In addition to α, and β-hydrogen elimination, a different elimination which involves carbon-carbon bond cleavage in the thermal decomposition of metallocycles can occur. 1,4-Tetramethylene bis(cyclopentadienyl)titanium(IV) has been reported to decompose to produce ethylene in good yield[103,106]. No reductive elimination was found and β-hydrogen elimination (formation of 1-butene) occurred to the extent of only 8%.



In this work, studies of the thermochemical decomposition of dineopentylpermethyltitanocene have been made. The mechanism of this decomposition is proposed to proceed by γ-hydrogen elimination, followed by the formation of a metallocycle. A metalcarbene is also shown to be one of the intermediates.

# EXPERIMENTAL

## 1. General

Common solvents, general techniques and instruments are the same as those in the experimental section of Part I. Schlenk tubes, a glove box and a vacuum line were also used for conducting this experiment.

Methane and propane used for standard gases are purchased from Linde Division, Union Carbide Corp. and Phillips Petroleum Company respectively. 1-Chloro-2,2-dimethylpropane was obtained from City Chemical Corporation. Sodium cyclopentadienide-$d_5$ was previously prepared[107].

## 2. Preparation of neopentyllithium[102]

Finely divided lithium wire (6 g) was suspended in 200 mL freshly distilled hexane under argon. 1-Chloro-2,2-dimethylpropane (20 g) was added to the mixture by use of a syringe. The mixture was stirred and refluxed under argon for a week. The resulting solution was filtered under argon and the volume of the solution was reduced to half by use of a vacuum line. White crystals of $LiCH_2CMe_3$ were collected by filtration of the cooled solution, under argon, and stored in a glove box. The yield was about 80%.

## 3. Preparation of dineopentylpermethyltitanocene

Crystals of dichloropermethyltitanocene (0.1 g) were ground to a powder and suspended in 40 mL diethylether.

In a separate flask, 50 mg neopentyllithium was dissolved in 25 mL ether. The latter solution was added, by use of a syringe, to the former under argon at -78° C. The mixture was stirred vigorously and warmed to room temperature slowly, and then stirred for an additional 20 min at room temperature. The mixture was cooled again to -30° C and 20 μL methanol was introduced to destroy excess neopentyllithium. The solvent and excess methanol was removed under reduced pressure at -30° C. The resulting residue was extracted with 50 mL freshly distilled n-pentane and the solution was filtered through a fritted Schlenk tube with cooling jacket at -78° C. A clear orange-yellow solution was obtained. An attempt to crystalize dineopentylpermethyltitanocene was not successful. But the decomposition of this solution by HCl at -78° C produced dichloropermethyltitanocene and neopentane in a ratio of 1/2. The percentage recovery of dichloropermethyltitanocene was greater that 95%.

### 4. Thermal decomposition of dineopentylpermethyltitanocene

The above pentane solution of dineopentylpermethyltitanocene was transferred by a syringe into a glass pressure bottle under argon. Pentane was removed under reduced pressure. The orange residue was dissolved in 20 mL freshly distilled toluene at -78° C. The pressure bottle was warmed to room temperature slowly before it was put into an oil bath of 80° C. The toluene solution of dineopentylpermethyltitanocene was stirred vigorously under argon at

80° C for 24 h. Gas products were analyzed by FID GC with a column of Durapak (20' x 1/8") at 60° C. Methane (5.1%), ethylene (4.2%), isobutylene (15%) and neopentane (75%) were found together with trace amounts of $C_3$ and $C_4$ hydrocarbons.

When toluene-$d_8$ was used as a solvent, a large amount of $CH_2D_2$ was detected as methane by GC-MS.

## 5. Preparation of perdeuterotitanocene dichloride

Sodium cyclopentadienide-$d_5$ (18 g) was dissolved in 120 mL THF under argon. The solution was added to 10 mL (17 g) titanium tetrachloride by use of a syringe at -30° C. The mixture was stirred vigorously and refluxed overnight. The solvent was removed under reduced pressure. The residue was transferred into a thimble in a Soxhlet extractor. HCl-saturated chloroform was used as the extracting solvent. Upon cooling of the chloroform solution, $(C_5D_5)_2TiCl_2$ was collected by filtration. The yield was approximately 50%. The mass spectrum of the red crystals showed major peaks at $m/z = 258$ ($M^{+\cdot}$), 223, 188, 153, 118, 83, 70.

## 6. Preparation of dineopentylperdeuterotitanocene

Perdeuterotitanocene dichloride (0.52 g) was suspended in 50 mL diethylether under argon. An ether solution of neopentyllithium (100 mL; 0.34 g) was introduced into the mixture at -78° C. The solution was warmed slowly to 0° C and stirred at this temperature for two additional hours.

The solvent was removed *in vacuo*. The residue was extracted by freshly distilled *n*-pentane (50 mL). The mixture was filtered under argon at -78° C.

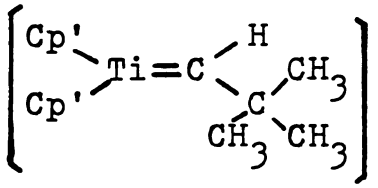
### 7. Thermal decomposition of dineopentylperdeuterotitanocene

The above freshly-prepared solution was transferred into a glass pressure bottle under argon at -78° C. The solvent was removed at low temperature in vacuo. Freshly-distilled toluene (40 mL) was introduced by using a syringe at -78° C. The solution was first warmed to room temperature slowly and then heated to 80° C for 24 h. The mass spectroscopic analysis of the gaseous products did not indicate the presence of $CH_2D_2$.

# RESULTS AND DISCUSSION

Thermolysis of a toluene solution of dineopentylpermethyltitanocene (1) at 80° C produces methane (5.1%), ethylene (4.2%), isobutylene (15%) and neopentane (75%). There are also trace amount of $C_3$ and $C_4$ hydrocarbons found, but no direct reductive elimination product, 2,2,5,5-tetramethylhexane, was detected.

Alpha and γ-hydrogen elimination are the only two possible pathways in this case, in addition to the homolytic cleavage of the Ti-carbon bond. Alpha-hydrogen elimination will lead to a Ti-carbene intermediate (2). But in an attempt to trap the carbene by cyclohexene in the thermolysis of dineopentyltitanocene, norcarene was the only product[95]. The absence of substituted norcarene suggested that (2) was not present, but the presence of norcarene suggested the presence of the simple unsubstituted carbene.



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Gama-hydrogen elimination seems to be a plausible mechanism to form methylene complex via a metallocycle (Figure 19). Subsequent cleavage of one of the carbon-carbon bonds in the metallocycle produces isobutylene, one of the major products,

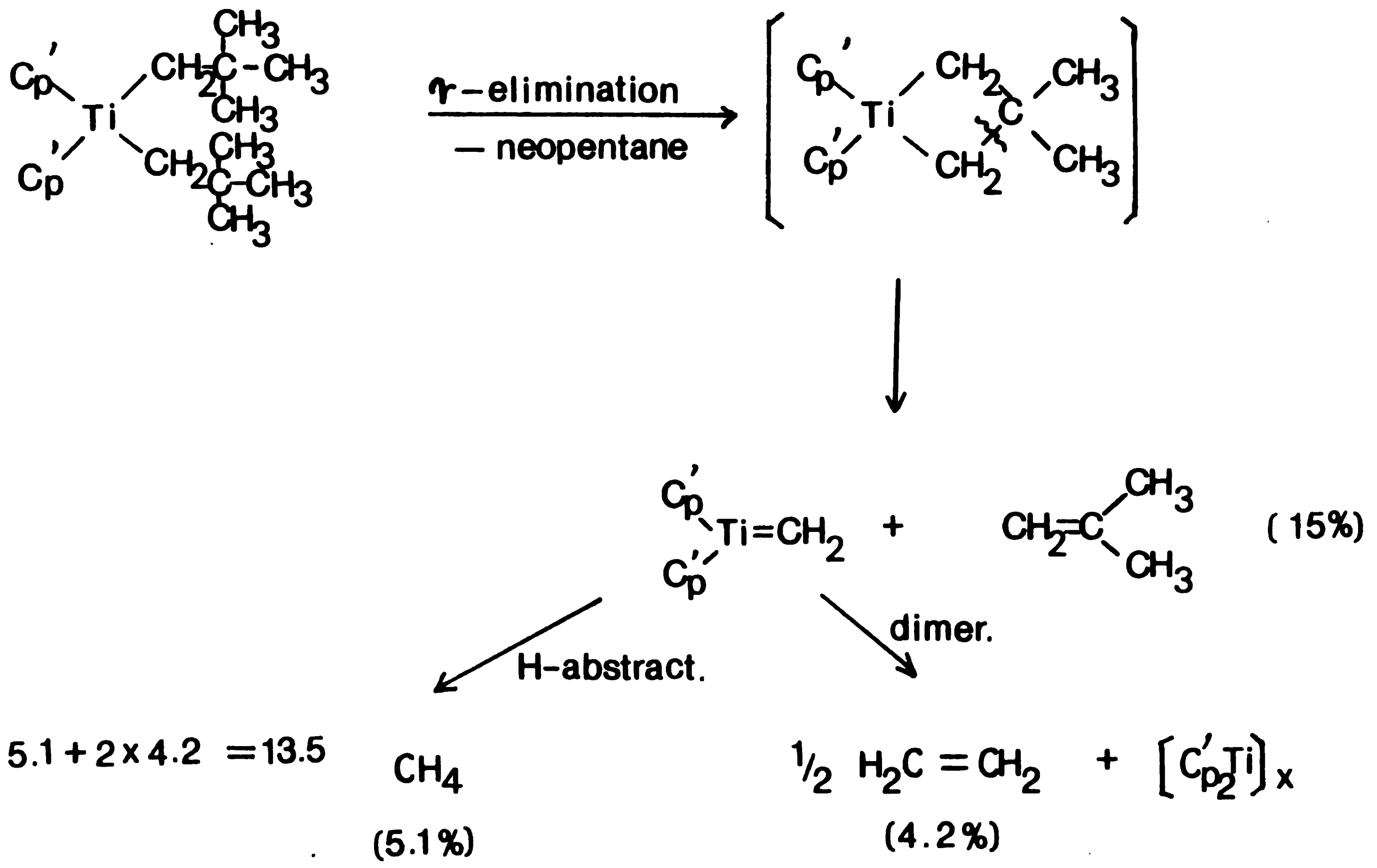


Figure 19 Mechanism for the thermal decomposition of dineopenylpermethyltitanocene

and a $Ti=CH_2$. A carbon-13 NMR study of the thermally-decomposed solution of dineopentyltitanocene[95] showed a singlet at 356 ppm from TMS at -50° C, which is characteristic evidence for a Ti-carbene.

Ethylene is expected to be formed by dimerization of 2 moles of a metal-carbene[120]. Methane is produced by H-abstraction from either the cyclopentadienyl rings or the solvent. A perdeuterated sample was made, $(C_5D_5)_2Ti[CH_2C(CH_3)]_2$, in order to trace the H-source. There was no deuterium in the methane produced from this system. However, when (1) was thermally decomposed in toluene-$d_8$, a large amount of $CD_2H_2$ was found in the methane, clearly indicating that the H-abstraction by the metal-carbene in this system is from the solvent.

According to this mechanism (Fig.19), the number of moles of isobutylene formed should be equal to that of metal carbene which wubsquently produces methane and ethylene. So, the sum of the percentage of methane and ethylene should be equal to that of isobutylene, that is, $5.1 + 4.2 \times 2 = 13.5$. The small difference, 1.5%, could represent the amount of metal carbene which is oligomerized to produced the trace amounts of $C_3$ and $C_4$.

The solution analysis did not reveal the product from direct reductive elimination, which is in agreement with the orbital symmetry approach of B. Akermark et al.[108], who showed that reductive elimination was symmetry forbidden thermally for $d^0$ transition metal dialkyls.

# PART IV

# HOMOGENEOUS REDUCTION OF CARBON MONOXIDE

# PART IV

## INTRODUCTION

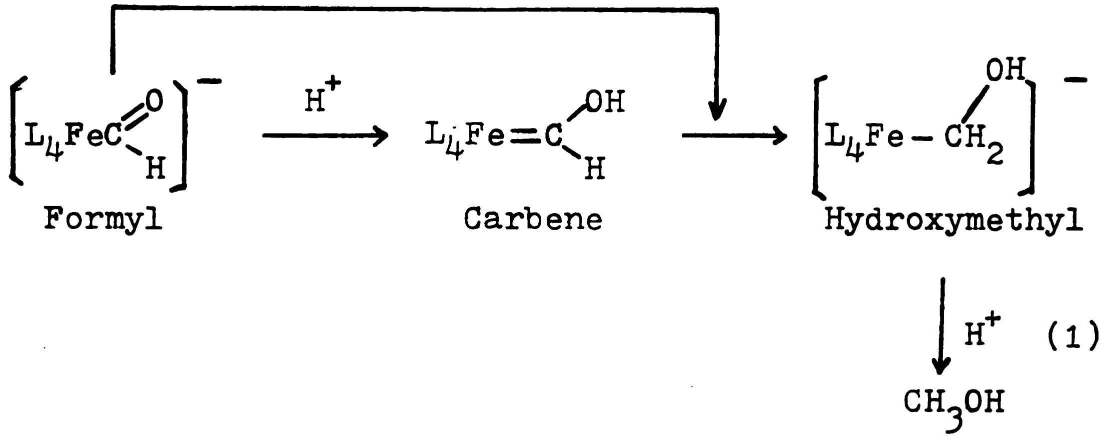
The diminishing world supply of petroleum has now made the conservation of energy a prime goal of the chemical industry. Additional problems are arising in switching from petroleum to coal as the major source of hydrocarbon raw material. The ready availability of carbon monoxide from coal together with its reactivity towards transition metals and its facile insertion into metal-carbon bonds has made it an attractive material for industrial organic syntheses.

The synthesis of hydrocarbons from carbon monoxide and hydrogen has been studied for the past five decades. Fischer-Tropsch[109,110] synthesis has been one of the most successful catalytic systems developed to produce high molecular weight hydrocarbons from carbon monoxide and hydrogen. It enabled Germany to obtain large quantities of gasoline and diesel fuels from carbon monoxide derived from coal during World War II. Because of the current shortage and high price of crude oil, there has been a renewed interest in Fischer-Tropsch, methane and methanol syntheses from carbon monoxide using heterogeneous catalysts. Research to develop the homogeneous analogs was the recent activity in the past three years. The successful developments in the homogeneous models of such heterogeneous systems could enable us to understand better the mechanisms of these systems and, hence, improve the catalytic conditions in both homogeneous and heterogeneous systems.

Muetterties[111] has reported the catalytic conversion of CO and $H_2$ to methane and ethane over an iridium carbonyl cluster in molten NaCl/2$AlCl_3$ at 180° C. The mononuclear $HCo(CO)_4$ has been reported by Feder and Rathke[112] to catalyze the reaction of an equimolar mixture of $H_2$ and CO to alcohols and formates. The reaction was carried out in benzene at 200° C and 300 atm and the conversion rates were very low. Bradley[113] reported that CO was catalytically hydrogenated to methanol and methyl formate at 1300 atm and 250° C by ruthenium carbonyls. The remarkable selectivity of certain rhodium carbonyls in the conversion of CO and $H_2$ to ethylene glycol[114] clearly demonstrates the potential utility of homogeneous catalyst.

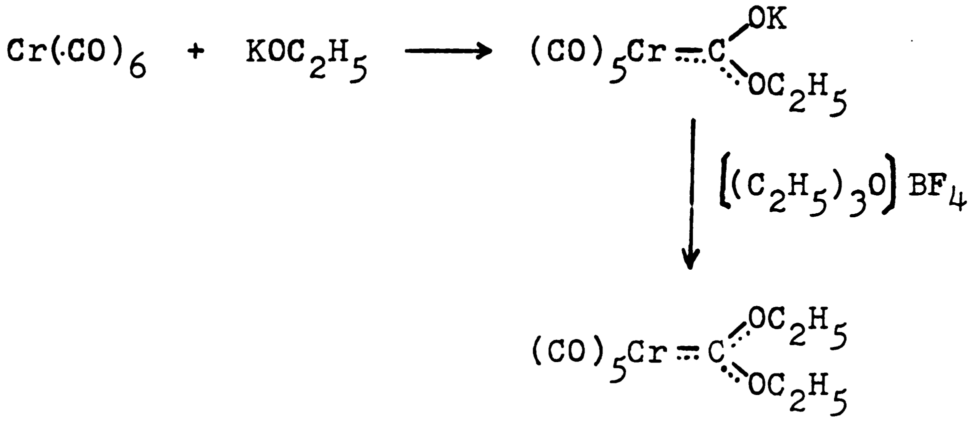
Stoichiometric reductions of carbon monoxide have also been reported by a number of research groups. Caulton and coworkers[115] reported that methane was produced when a toluene solution of $Cp_2Ti(CO)_2$ is treated with a mixture of $H_2$ and CO (3:1, 1 atm) at 150° C. Schwartz and Shoer[116] reported that DIBAH (i-$Bu_2AlH$) reduced CO in the presence of $Cp_2ZrCl_2$ at room temperature to give, on hydrolysis, a mixture of linear aliphatic alcohols. Bercaw and coworkers[117] have stoichiometrically hydrogenated CO to methanol (upon hydrolysis) with dicarbonylpermethylzirconocene at 25° C and 1.5 atm $H_2$ pressure. A formyl complex was proposed as an intermediate in the reaction.

Transition-metal formyl (CHO) and hydroxymethyl ($CH_2OH$) complexes have been believed to be the intermediates in the metal catalyzed reduction of CO by $H_2$. Casey and coworkers[118] have demonstrated hydride donation reactions of iron formyl complexes (Eq. 1). According to this work, a metal-carbene seems to be another possible intermediate for CO reduction.



(1)

Fischer and coworkers[119] reported that a Cr-carbene complex was produced when a strong base, such as potassium

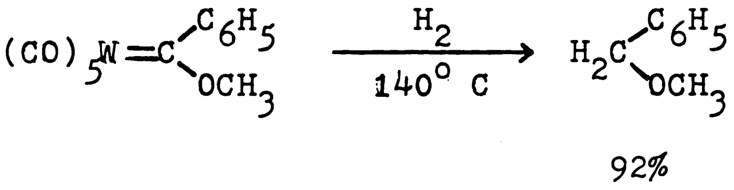


(2)

ethoxide, reacted with hexacarbonylchromium (Eq. 2). Since the carbon of the coordinated carbonyl is the most positive center, the nucleophilic addition occurs directly on the carbonyl-carbon.

The final product was isolated, although the yield was rather low. The intermediate metal-carbene was believed to exist in fairly high concentration.

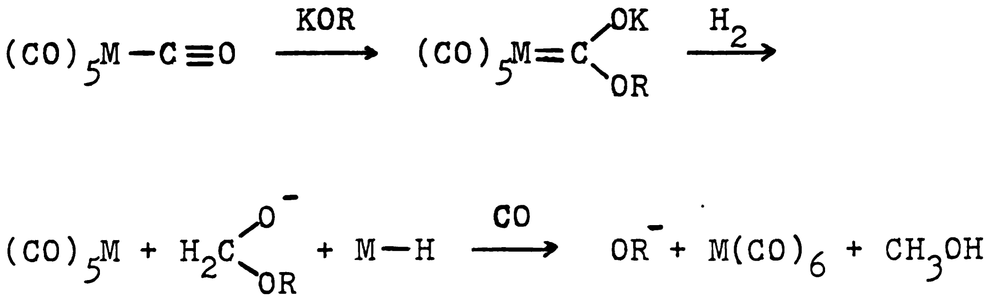
A reductive cleavage of some tungsten carbene complexes with $H_2$ has been observed by Casey[120] (Eq. 3). When a decalin solution of the phenylmethoxycarbenetungsten complex reacted with 1.8 atm of $H_2$ at 140° C for 5 h, benzylmethylether (92%) was produced.



$$(CO)_5W{=}C\begin{matrix}\nearrow C_6H_5\\ \searrow OCH_3\end{matrix} \xrightarrow[140^\circ\ C]{H_2} H_2C\begin{matrix}\nearrow C_6H_5\\ \searrow OCH_3\end{matrix} \qquad (3)$$

92%

From the above information, a system could be designed to bring about catalytic hydrogenation of CO by using metal carbonyls (especially molybdenum and tungsten hexacarbonyls)



$$(CO)_5M-C\equiv O \xrightarrow{KOR} (CO)_5M{=}C\begin{matrix}\nearrow OK\\ \searrow OR\end{matrix} \xrightarrow{H_2}$$

$$(CO)_5M + H_2C\begin{matrix}\nearrow O^-\\ \searrow OR\end{matrix} + M-H \xrightarrow{CO} OR^- + M(CO)_6 + CH_3OH \qquad (4)$$

as catalysts. Metal hexacarbonyl could be attacked by the base on the carbonyl carbon to form the corresponding metalcarbene. Under a pressure of $H_2$, the heteroatom-substituted metalcarbene could be reductively cleaved into an unsaturated pentacarbonylmetal complex and an ester anion. In the presence of CO, the metal hexacarbonyl would be recovered from the reaction of the pentacarbonylmetal complex with an equimolar amount of CO. The unsaturated metal complex could form the corresponding metal hydride from $H_2$ under pressure at an elevated temperature. Such a metal hydride could further reduce the ester anion and generate the base and methanol. The starting materials, the metal hexacarbonyl and base, are recovered at the end of the reaction sequence. Carbon monoxide and hydrogen are the materials consumed. Thus, a catalytic cycle of hydrogenation of CO could be established.

# EXPERIMENTAL

## 1. General

The general materials, techniques and instruments are the same as the experimental section in Part I. In addition to the glass pressure bottle, a high pressure autoclave was used as a hydrogenation reactor where necessary.

1,2-Bis(2-methoxyethoxy)ethane, $CH_3(OCH_2CH_2)_3OCH_3$, used as a solvent was refluxed in lithium aluminum hydride and distilled under reduced pressure at 150° C. Deuterium gas was purchased from Linde Division, Union Carbide Corp.. Red-al, a 3.4 M solution of sodium bis(2-methoxyethoxy)-aluminum hydride in toluene, was obtained from Aldrich Chemical Co.. Hexamethyldistannane and all the potassium alkoxides were also purchased from Aldrich Chemical Co.. All metal carbonyls and bis(chlorodicarbonylrhodium) were bought from Strem Chemical Company. The composition of deuteromethanes ($CD_4$, $CD_3H$, $CD_2H_2$, and $CDH_3$) were determined by use of a Hitachi Perkin Elmer RMU-6 mass spectrometer. GC column of 5% Triton X-305 on Chromosorb T (12' x 1/4") was used to analyze the low molecular weight alcohols.

## 2. Preparation of trimethylstannyllithium reagent[121]

A THF solution (10 mL) of hexamethyldistannane (0.3 mL) was cooled to -20° C. Methyllithium (0.69 mL; 1 mmole) was added to it slowly by use of a syringe under argon. The mixture was stirred for 30 min at -20° C. Trimethylstannyllithium was produced with a yield greater than 95% and used without isolation.

3. Preparation of sodium deuteroxide

Sodium methoxide was dissolved in large excess $D_2O$. The solution was distilled to dryness. A batch of white solid NaOD was obtained.

4. General procedure for hydrogenation of carbon monoxide

Metal carbonyls were first dissolved in a solvent under $N_2$. After the solution became homogeneous, excess amount of base was added. Then, the pressure bottle was degassed three times, and CO and $H_2$ were charged into the bottle at the desired pressure. The pressure reactor was placed in an oil bath, and the reactions were carried out at different temperatures for 24-48 h.

Gas products were analyzed by GC with columns of Porapak Q and Durapak at 60-70° C. A GC column of Molecular Sieve 5A was also used at 50° C if necessary.

Liquid products were usually analyzed after hydrolysis of the reacted solution. GC columns, such as DC 550, Carbowax 20M and Triton X-305 were used.

# RESULTS AND DISCUSSION

Mononuclear metal carbonyl complexes and multinuclear metal carbonyl clusters were used as homogeneous catalysts in the attempts to catalyze the hydrogenation of carbon monoxide. The reaction conditions were varied in different experiments. Pressures of CO and $H_2$ ranged from 40 to 960 psig. Temperatures were varied from 75 to 150° C. A strong base was used in most of these reactions in order to initiate the catalytic reaction. The results of these reactions are summarized in Table 3.

In the presence of a strong base, such as potassium alkoxide, neither mononuclear metal carbonyls (entries 1, 10, 15) nor metalclusters (entries 3, 4) had any effect on the hydrogenation of carbon monoxide. Upon addition of a strong reducing agent, $NaBH_4$, hexacarbonylmolybdenum was still inactive (entry 2). However, when Red-al (a hydride derivative of aluminum)was used as solvent (or cocatalyst) in the presence of rutheniumcarbonyl (entry 5), 15% methane and small amounts of ethylene and ethane were found as gas products. Small amounts of $CH_3OH$ were also detected after hydrolysis of the reacted solution. The presence of a base, potassium <u>t</u>-butoxide, seemed not to affect the reaction. But when deuterium gas was used instead of $H_2$, only monodeuteromethane was found in a small amount ($CH_3D/CH_4 = 2/3$). This result indicates that carbon monoxide was mainly reduced by the aluminum hydride derivative, not by hydrogen gas.

Table 3 Hydrogenation of CO over metal carbonyls

| Seq. # | Catalyst | Solvent + Cocatalyst | Base | B[a]/M | Press. (psig)[b] CO + $H_2$ | Temp. (°C) | Products |
|---|---|---|---|---|---|---|---|
| 1 | $Mo(CO)_6$ | THF | t-BuOK | 1 | 20 + 40 | 75 | — |
| 2 | $Mo(CO)_6$ | THF + $NaBH_4$ | EtOK | 1 | 10 + 30 | 120 | — |
| 3 | $Rh_2Cl_2(CO)_4$ | THF | EtOK | 3 | 15 + 40 | 120 | — |
| 4 | $Ru_3(CO)_{12}$ | THF | EtOK | 20 | 10 + 30 | 130 | — |
| 5 | $Ru_3(CO)_{12}$ | 3.6 M Red-al[c] in THF | — | — | 20 + 40 | 90 | 15% $CH_4$<br>(s)[d] $C_2H_4$ + $C_2H_6$<br>(s) $CH_3OH$[e] |
| 6[f] | $Ru_3(CO)_{12}$ | 3.6 M Red-al in THF | — | — | 20 + 40 | 90 | large quantity $CH_4$ |
| 7 | $Ru_3(CO)_{12}$ | 3.6 M Red-al in THF | — | — | 20 + 40($D_2$) | 90 | $CH_3D/CH_4$ = 4/6 |
| 8 | $Ru_3(CO)_{12}$ | 3.6 M Red-al in THF | t-BuOK | 20 | 20 + 40 | 90 | 16% $CH_4$<br>(s) $C_2H_4$ + $C_2H_6$<br>(s) $CH_3OH$[e] |
| 9 | $Ru_3(CO)_{12}$ | dioxane<br>+<br>ex. $Al(OCHMe_2)_3$ | t-BuOK | 20 | 22 + 50 | 115 | trace $CH_4$ |

(continued on next page)

(continued for Table 3)

| Seq. # | Catalyst | Solvent + Cocatalyst | Base | $B^a/M$ | Press.(psig)$^b$ CO + $H_2$ | Temp. ($^oC$) | Products |
|---|---|---|---|---|---|---|---|
| 10 | $Fe(CO)_5$ | dioxane<br>+<br>ex. $Al(OCHMe_2)_3$ | t-BuOK | 10 | 20 + 42 | 135 | – |
| 11 | $W(CO)_6$ | THF | $(CH_3)_3SnLi$ | 1 | 30 + 40($D_2$) | 110 | 2% $CH_4$+trace $CD_4$ |
| 12$^g$ | $W(CO)_6$ | $CH_3(OCH_2CH_2)_3OCH_3$<br>+<br>ex. $[(Me)_3Si]_2O$ | NaOH | 125 | 20 + 30 | 150 | 70% $CH_4$ |
| 13$^g$ | $W(CO)_6$ | $CH_3(OCH_2CH_2)_3OCH_3$<br>+<br>ex. $[(Me)_3Si]_2O$ | NaOH | 125 | 20 + 30($D_2$) | 150 | $CD_4$:$CD_2H_2$:$CH_3D$:$CH_4$<br>1 : 3 : 5 : 40 |
| 14$^g$ | $W(CO)_6$ | $CH_3(OCH_2CH_2)_3OCH_3$<br>+<br>ex. $[(Me)_3Si]_2O$ | NaOD | 125 | 20 + 30 | 150 | $CD_4$:$CH_4$<br>1 : 4 |
| 15 | $W(CO)_6$ | $CH_3(OCH_2CH_2)_3OCH_3$ | t-BuOK | 5 | 150 + 810 | 100 | – |

a. Base to metal ratio. b. Pressures listed are measured at room temperature.

c. Red-al is $Na[(CH_3OCH_2CH_2O)_2AlH_2]$. d. (s) indicates small amount.

e. $CH_3OH$ was detected after the hydrolysis of the solution.

f. This solution was saturated with CO (equivalent to 40 psig CO) before the reaction.

g. Reactions were run for 12 h. The other reactions were for 24 h.

Comparison with a blank (same conditions without $Ru_3(CO)_{12}$), revealed that the ruthenium carbonyl cluster had little effect on this reaction. Replacement of aluminum isopropoxide for the Red-al (entry 9) led to production of only a trace amount of methane. In addition, a metallic nucleophile, $(CH_3)_3Sn^-$, seemed to have little effect (entry 11).

However, in the presence of a cocatalyst (hexamethyldisiloxane), sodium hydroxide seemed to initiate the hydrogenation of CO over hexacarbonyltungsten. A large quantity of methane was produced (entry 12). But the deterium-tracer experiment (entry 13) indicated that only about 2% methane was obtained from hydrogen gas. The majority of methane was probably generated from the degradation of solvent and/or cocatalyst, or the reduction of carbonyl ligands in the presence of NaOH. In another reaction, sodium hydroxide was replaced by NaOD. About 20% $CD_4$ was found as methane. These results suggested that the base, NaOH, play a major role, although the reaction was not catalytic. A mechanism is proposed as in Fig.20 to rationalize the reaction. Hydroxide anion can add to the carbonyl-carbon to form a tungsten anion. A proton-shift follows to form a tungsten hydride. In the absence of hexamethyldisiloxane the tungsten formate ion could decompose to $CO_2$ and a metal hydride anion[122]. Hexamethyldisiloxane could react with the carboxyl oxygen to form a more stable neutral complex. Then, the intramolecular reduction could take place to produce a metal formyl complex. The further reduction (inter- or intramolecular) by

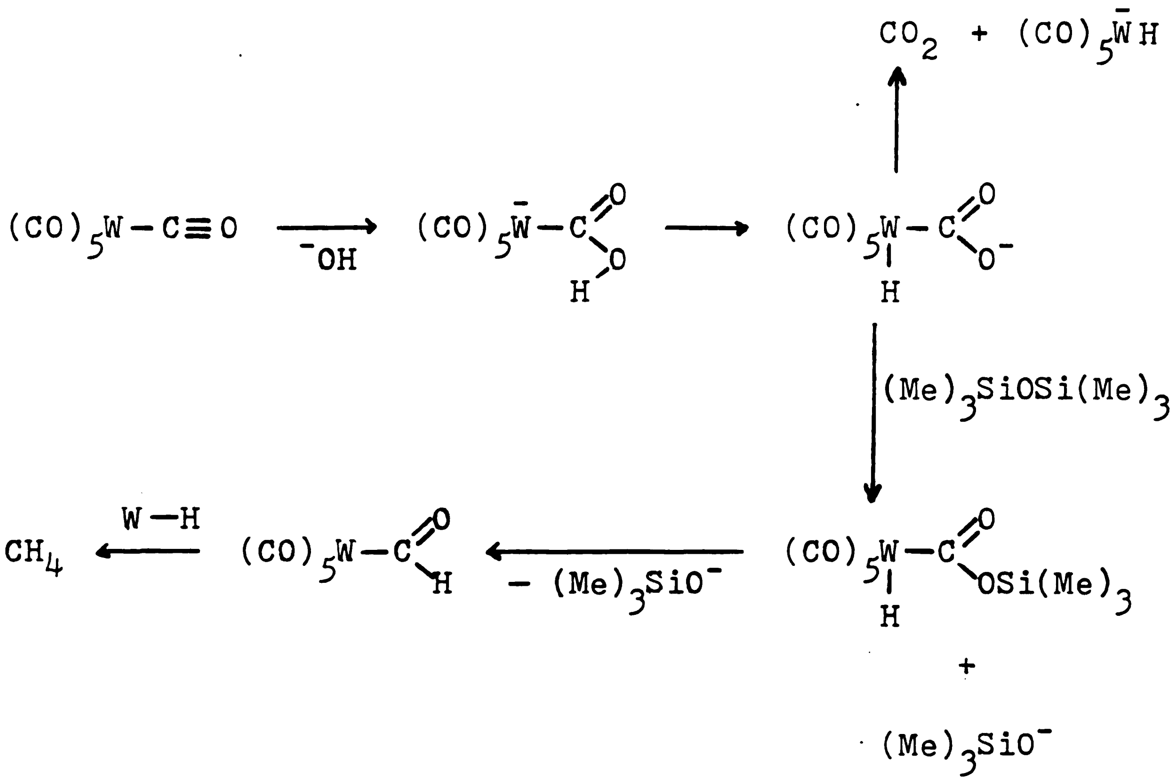


Figure 20 Scheme of reduction of carbonyl ligand in metal carbonyl complex initiated by hydroxide ion

other metal hydrides can produce the final product, methane.

In general, the catalytic approach for hydrogenation of CO with metal carbonyl complexes as catalysts was unsuccessful. But the discovery of the stoichiometric reduction of the carbonyl group initiated by NaOH in a metal carbonyl complex could further support the proposed mechanism for the catalytic water-gas shift reaction with metal carbonyl complexes[122-124].

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