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Photochemical Decomposition of (Diphenyl)bis(η^5-cyclopentadienyl)titanium, (Diphenyl)bis(η^5-pentamethylcyclopentadienyl)titanium and the Zirconium Analogs

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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 σ-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 found in a ratio of 1/3, indicating that the homolytic photocleavage of the σ-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 another intermediate, $[(C_5Me_5)(C_5Me_4CH_2)M]$*, is proposed. An oligomeric material was found to be the major metal containing product after the photolyses.*

Introduction

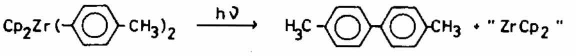
Razuvaev, *et al.* [1] studied the photochemical decomposition of bis(phenyl)bis(η^5-cyclopentadienyl)titanium(IV) in 1961 and reported that titanocene dichloride was produced upon photolysis of diphenyltitanocene in chloroform for 50–60 h. Benzene and a very small amount of biphenyl were also obtained. However, no chlorobenzene or cyclopentadiene could be detected. Harrigan, Hammond and Gray [2] first reported in 1974 that dimethyltitanocene was photosensitive. When dimethyltitanocene was photolyzed in a 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 [3] 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 [4–11]. Corresponding metallocenes were also reported to be among the products from the photolysis of dimethyl derivatives of zirconocene and hafnocene.

$$Cp_2M(CH_3)_2 \xrightarrow{h\nu} \text{'}Cp_2M\text{'} + 2CH_4$$

$$M = Ti, Zr, Hf$$

In the presence of carbon monoxide and diphenylacetylene, the photochemically-generated metallocenes produced the corresponding adducts, dicarbonylmetallocenes and 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylmetallacyclopentadienes [12].

Three years later, Peng and Brubaker [13] examined the photolysis of diphenyltitanocene and suggested that benzene, biphenyl and an oligomeric material formulated as $[Ti(\eta^5\text{-}C_5H_5)_2H]_x$ were produced. However, Rausch, *et al.* [14] reported that irradiation of diphenyltitanocene in benzene-d_6 solution produced 'black titanocene', and 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 [15] suggested that photolysis of diarylzirconocene led only to coupling of the aryl ligands.



The nearly-quantitative yield of 4,4′-dimethylbiphenyl from photolysis of di-tolyzirconocene in

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benzene solution seemed to raise a question about Zr-tolyl homolysis to produce tolyl radicals.

Hydrogenation of ethylene and 1-hexene, reported to be catalytic at low temperature over titanocene generated by other methods [1c] and by photolysis of diphenyltitanocene [17], was not found, and indicated the necessity of additional mechanistic studies.

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 [18, 19], investigations into the mechanistic aspects of the photolysis of diphenylpermethyltitanocene (*1*) and zirconocene (*2*) have been undertaken.

Experimental

Materials

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 ℃) was distilled from lithium aluminum hydride and transferred under vacuum into reaction flasks immediately before use. Hydrogen, carbon monoxide, *cis, trans*-2-butene and hydrogen chloride were purified grade from Matheson Chemical Co. Phenyl lithium, methyl lithium, 1-hexene, cyclohexene, allyl benzene and ethyl acetate were purchased from Aldrich Chemical Co.. Titanocene dichloride and zirconium tetrachloride were obtained from the Alfa Division of Ventron Corp. while zirconocene dichloride was purchased from Arapahoe Chemical Co. and sublimed at 150–180 ℃. 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 Waters Associates, Inc. and 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.

General Techniques and Apparatus

Schlenk-tubes and a vacuum lines 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. Electron spin resonance (ESR) spectra were obtained by use of a Varian E-4 spectrometer. IR spectra were measured by Perkin-Elmer 457 or 237B spectrometers. 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 a 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. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of Diphenylmetallocenes

Diphenyltitanocene was prepared by a modification of the method of Summers, *et al.* [20].

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 ℃ and 30 μL methanol was added to destroy the excess of phenyl lithium. While the solution was warmed slowly to room temperature, the solvent and excess 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 was crystallized at −78 ℃ and isolated under argon. The yield was about 95%. It may be recrystallized from methylene chloride and petroleum ether solution, if necessary.

Diphenylzirconocene was prepared by the reported method [21]. The Cp_2ZrPh_2 was stored in a dry box and appeared to be less stable than Cp_2TiPh_2.

The bis(η^5-pentamethylcyclopentadienyl)titanium dichloride [19, 22] was prepared by modification of previously known methods [20, 21].

Bis(η^5-pentamethylcyclopentadienyl)zirconium was prepared as previously reported [23], and was verified by ^{1}H NMR, IR and mass spectra.

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

In a typical reaction, 1 g bis(η^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 slowly by syringe under argon at room temperature. The mixture was then stirred at room temperature for an additional 5 h. Methanol (9 μL) was added to the mixture at –40 °C to destroy the excess phenyllithium. The solvent was then removed under reduced pressure. The residue was extracted with 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 that appeared in photolysis of it. The ^{1}H NMR spectrum of the newly-prepared diphenylpermethyltitanocene in $CDCl_3$ showed the expected signals: singlet (1.65 ppm), singlet (7.16 ppm).

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

In a typical reaction, 5.3 g bis(η^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 diphenylpermethylzirconocene was obtained in 60% yield and it was recrystallized from ether. The ^{1}H 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 for $H_{40}C_{32}Zr$: H, 7.76; C, 74.5; Zr, 17.7.

Dimethylpermethylzirconocene was prepared by the method previously reported [19].

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%.

Photolysis of Diphenylpermethyltitanocene in Benzene-d_6

A benzene-d_6 solution (8.5 mL) of diphenylpermethyltitanocene (0.04 *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 at ca. 25 °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 hexane, and decomposed by stirring in air for several hours. The mixture was filtered and the 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), 9.4 mg.

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 in addition to biphenyl, 2,3,4,5-tetramethylfulvene and 1,2,3,4,5-pentamethylcyclopentadiene.

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}.

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 an excess of HCl gas at this temperature. In a short period of time, the color of the solution changed from dark green to brown and some brown solid formed. The analyses of the gas phase product was conducted on a FID GC with Durapak as column (20′ × 1/8″). Butane and ethane were found with yields of 2.2% and 1.5% respectively based on Ti.

Polymerization of Styrene over Photochemically-Generated Titanium Species

A sample of 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 resulting dark green solution was exposed to air until the color changed to yellow, and then filtered into an excess of methanol [20]. Polystyrene was collected by filtering this methanol solution. The results, after substracting a blank are listed in Table I. The polymerization was believed to be initiated by the radicals formed from photocleavage of diphenyltitanocene [24].

Photolysis of Diphenylpermethylzirconocene in Benzene-d_6

A benzene-d_6 solution of diphenylpermethylzirconocene (8.8 mL; 0.077 *M*) was photolyzed for 47 min under the same conditions and equipment as those for diphenylpermethyltitanocene (above). The solution turned purple-red. The extraction process by hexane 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 mmol. The ^1H NMR spectrum of the recovered benzene-d_6 solvent also showed a significant absorption in the vicinity of benzene (7.2 ppm). Quantitative ^1H NMR analysis by using cyclohexane as internal standard showed 0.36 mmol 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.

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 in the dark, and then photolyzed for an additional 35 min. After a 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 of continued irradiation.

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

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 and 1850 cm^{-1}. The yield of dicarbonylpermethylzirconocene was about 25%.

TABLE I. Polystyrene Obtained from Photolysis of Cp_2TiPh_2 in Styrene.

Cp_2TiPh_2	Styrene	Polymer	Net polymer/mmol Cp_2TiPh_2
0.00 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

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′ × 1/8′) was used.

Electron Spin Resonance Studies of Photolyses of Diphenyl 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, $g = 2.0037 \pm 0.0002$) was used for magnetic field calibration for the measurement of g values.

When a saturated toluene solution of diphenylzirconocene was photolyzed in the E-4 spectrometer, an ESR signal, a doublet (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 a clean singlet signal was obtained at $g = 2.001$. The signal only lasted for 5 min. Attempts to explain these observations were not successful.

Spin Trapping Experiment for Photolysis of Diphenylpermethyltitanocene

Previously prepared nitrosodurene [25] 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 in the ESR spectrometer, a triplet signal was obtained. The intensity of this triplet grew rapidly while irradiation continued. That signal persisted for days after the irradiation had ended.

Results and Discussion

Photolyses of Diphenylmetallocenes and Diphenylpermethylmetallocenes

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 the dark purple crystals. This result suggested that an oligomeric material was probably the major product from the photolysis of diphenyltitanocene.

Photolysis of a tolune solution of Cp_2TiPh_2 in the presence of styrene at room temperature for 2 h produced a small amount of polystyrene (Table I). The polymerization of styrene was probably initiated by the radicals [24] generated from the photolytic homolysis of diphenyltitanocene.

When (*1*) was photolyzed in a solution of benzene-d_6 at room temperature for 3 h, biphenyl-d_0 and biphenyl-d_5 were found in a ratio of 36/1 which suggested that reductive elimination (Path B in the reaction scheme) had been predominant. No biphenyl-d_{10} was detected, and implied that exchange of phenyl groups in (*1*) with the solvent molecules had not occurred.

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 [23, 24]. A sample of 1-hexene was added to this solution, which was stirred for 12 h under 1 atm of H_2, and no hydrogenated product was found. But when (*1*) was photolyzed in the presence of CO under similar conditions, dicarbonylpermethyltitanocene was collected (15% yield). On the other hand, 2,3,4,5-tetramethylfulvene and pentamethylcyclopentadiene were detected in very small amounts in the recovered solvent. These observations suggested that permethyltitanocene was one of the products, but further irradiation could still affect it and cleave the metal—ring π-bond. According to the published data [19], (*3*) is not stable at ambient temperatures. It abstracted a hydrogen atom from the ring-methyl groups and formed a relatively stable compound (*6*). Considering the conditions of photolysis, not only temperature, but also the UV light could force (*3*) to change into (*6*). In particular, compounds (*7*) and (*8*) are more like those cleaved from (*5*) rather than (*3*). 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 must occur. Therefore, it seemed reasonable to assume that (*3*) was only an intermediate that could be trapped in the presence of a strong π-acid such as carbon monoxide, otherwise it decomposed to (*6*), and further degradation could take place. The metal-containing species after degradation of (*6*) would be expected to be extremely reactive and probably could initiate oligomerization among the other molecules, and can account for 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 phtotolysis was dissolved in hexane and then decomposed in air, relatively large amounts of (*7*) and (*8*) were found. The ratio of these products was 1/1.3. It seems reasonable that (*6*) was the major part of the oligomeric material. There might be some (*6*) in the' residue, but an attempt to sublime (*6*) was not successful.

When an n-pentane solution of (*1*) 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 a 2.2% yield. The metallacycle, which was formed by cyclizing two molecules of ethylene as shown in the mechanistic scheme, was believed to be the precursor of butane [29, 30]. Ethane was also found in the same reaction. The formation of ethane suggested that there was a metal hydride species present during the course of photolysis, presumably, intermediate (*5*) (metal hydride could also be generated from the H-abstraction of (*3*) from solvent). Ethylene can insert into metal hydride easily and subsequent decomposition by HCl would release the ethyl ligand as ethane, as described in the reaction scheme.

Reductive elimination predominated in the photochemical decomposition of (*1*). The stepwise homolysis of the metalphenyl σ-bond (path) was minimal, even at low temperature. A toluene solution of (*1*) 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 solution of (*1*) was photolyzed in an ESR spectrometer in the presence of nitrosodurene, 2,3,4,5-tetramethylphenyl phenyl nitroxide was found. It showed a triplet ESR signal with g = 0.225, a_N = 12 G[62] (Fig. 1). Without nitrosodurene, a singlet at g = 1.998 was found together with small satellites attributable to hyperfine interaction with Ti isotopes (^{47}Ti and ^{49}Ti, I = 5/2 and 7/2, present in natural abundances 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 (*1*) seems to favor reductive elimination and permethyltitanocene is not stable at room temperature [19], the assignment of the compound (*6*) as being responsible for this singlet seems logical. Compound (*6*) is paramagnetic.

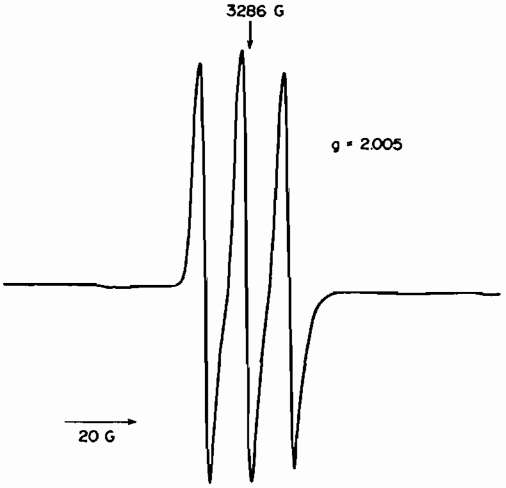
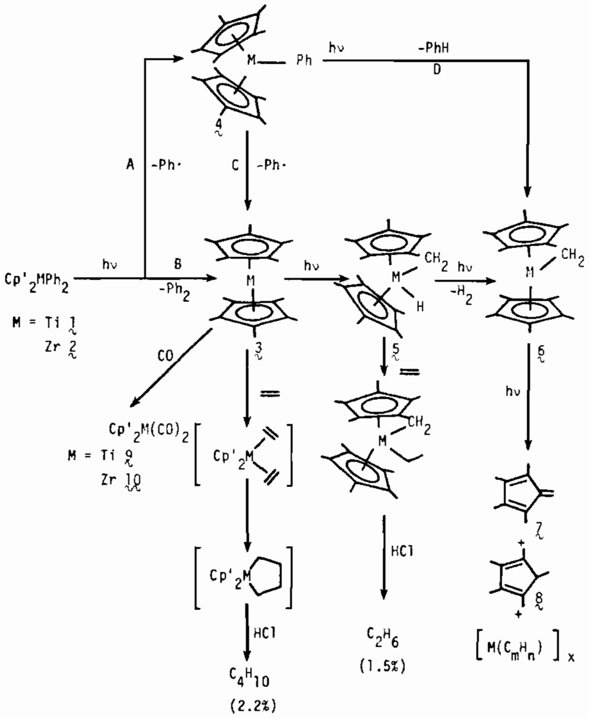


Fig. 1. ESR spectrum in the photolysis of (*1*) in the presence of nitrosodurene.



When (*2*) 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 the Zr–phenyl σ-bond (Path A) was predominant. Again, there was no biphenyl-d_{10} detected. Similar to the photolysis of (*1*), dicarbonylpermethylzirconocene was isolated (25% yield) when (*2*) was photolyzed in the presence of CO. Some 2,3,4,5-tetramethylfulvene and pentamethylcyclopentadiene were also found in the recovered solvent as well as in the hexane after the photolysis residue decomposed in air. These observations indicate that the proposed mechanism is also applicable to the photochemical decomposition of (*2*).

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. The detection of nondeuterated benzene indicates that Path D (H-abstraction from the methyl groups on the rings) occurs.

Nevertheless, the exchange reaction of newly produced permethylzirconocene with the starting material (*2*) is also a possible pathway for the generation of monophenylpermethylzirconocene. When a two-step photolytic process was used

$$Cp'_2ZrPh_2 + Cp'_2Zr \longrightarrow 2Cp'_2ZrPh$$

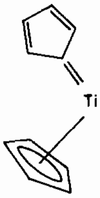
with the same benzene-d_6 solution of (*2*) (more precisely, the solution was irradiated for 12 min, then stirred for 30 min without light and then photolyzed for another 35 min), the ratio of biphenyl-d_0 to biphenyl-d_5 changed to 1/4. The larger amount of biphenyl-d_5 formed revealed that more monophenylpermethylzirconocene had formed under these conditions. It implied that the exchange reaction did occur. But the amount of increase of biphenyl-d_5 was relatively small ($4/5 - 3/4 = 1/20$), and showed that the exchange reaction did not dominate the process and Path A was still predominant for the photolysis of (*2*).

Irradiation of a benzene-d_6 solution of (*2*) in an ESR spectrometer showed a complex signal. 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. Presumably the exchange reaction was complete, and the signal was probably due to monophenylpermethylzirconocene.

Conclusion

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 [14], the extent of reductive elimination is enhanced 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. 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 large. In the case of diphenylpermethylzirconocene, at least 75% of the decomposition pathways involves stepwise homolysis. It seems reasonable that for the less sterically-hindered diphenylzirconocene, the stepwise homolysis predominates.

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 π-bond is thermally stable, the photocleavage of this π-bond is known [2, 26]. The formation of a Cp radical was found to be the primary process of photolysis of Cp_2TiCl_2 [27]. The reason that none of the previous studies of the photolyses of the dimethyl [3, 28] or diphenyl [1, 13, 14] 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 an extremely reactive intermediate.



This is a carbene-like species and would probably undergo dimerization and/or oligomerization immediately following its formation. Nevertheless, small amounts of $CpTiCl_3$ found after the HCl decomposition of the 'black titanocene' photochemically-generated from dimethyl- [28] and diphenyltitanocene gives additional evidence of the photocleavage of Cp–Ti π-bond.

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