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Photochemical Generation of Reactive Titanium(II) Species

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Photolysis of diphenyl titanocene, resulting in loss of phenyl groups is a generally useful approach to the generation of coordinatively unsaturated complex species. The low temperature nuclear magnetic resonance and electron paramagnetic resonance methods were utilized to investigate the transient titanocene.

Isolation and characterization of electron deficient intermediates were attempted. The green $[(\eta^5\text{-}C_5H_5)_2TiH]_x$ *polymer was obtained in solid state, which was converted to the dark green transient* $(\eta^5\text{-}C_5H_5)_2Ti$ *species in benzene and tetrahydrofuran at low temperatures.*

Some stable titanocene adducts were prepared quantitatively by photolysis of diphenyl titanocene in the presence of carbon monoxide and diphenylacetylene. Presumably, $(\pi\text{-}C_5H_5)_2Ti(II)$ *is the intermediate in these reactions and thus photolysis is a convenient method for synthesis of titanocene derivatives.*

Introduction

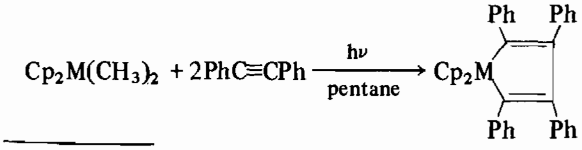
As early as 1915 Benrath [1] observed the photoreduction of alcoholic solutions of titanium tetrachloride. Hunt and Winter [2] found that titanium haloalkoxides were suitable for photoreduction to titanium(III) complexes.

Dimethyl derivatives of titanocene, zirconocene, hafnocene decompose readily on photolysis with homolytic cleavage of the methyl-metal bond [3]:

$$Cp_2M(CH_3)_2 \xrightarrow[\text{solvent}]{h\nu} Cp_2M + 2CH_3\cdot$$

where M = Ti, Zr, Hf

In pentane the methyl radicals ultimately form CH_4. All spectroscopic evidence indicates the presence of only π-bonded cyclopentadienyl rings in the diamagnetic, pyrophoric residues. In the presence of diphenylacetylene, metallocycles were produced:



Carbon monoxide formed $Cp_2Ti(CO)_2$ with the titanium residue. It is also possible to form stable adducts with various substances such as hydrogen, nitrogen, nitric oxide, hydrochloric acid, and olefins as well as acetylenes.

Photolysis of dialkyltitanocene compounds Cp_2TiR_2 (R = CH_3, $CH_2C_6H_5$) in the presence of elemental sulfur produces titanocene pentasulfide Cp_2TiS_5 along with other organic polysulfides [4].

The photolysis of bis(fluorenyl)dimethylzirconium in solution [5] leads to cleavage of the methyl groups, with the formation of methane and a bis(fluorenyl)zirconium compound – possibly polynuclear.

This work is an investigation of the chemical behavior of bis(cyclopentadienyl)diphenyltitanium. Convenient ways to generate and isolate titanocene were sought both at ambient and at low temperatures. These reactions have provided a method for preparing new organometallic compounds of titanium.

Experimental

Standard Schlenck-tube and high-vacuum techniques were used for handling the highly air-sensitive compounds in this work [1, 6].

The esr spectra were recorded by use of a Varian E-4 esr spectrometer and the instrument was calibrated with diphenylpicrylhydrazyl in potassium chloride and peroxylamine disulfonate. A Hanovia 100 watt high pressure mercury arc lamp with a focusing lens was used to provide a point source of uv light.

Reagent grade diethyl ether, tetrahydrofuran (THF), petroleum ether (b.p. 30–60 °C), benzene, toluene, and hexane were refluxed continuously over appropriate drying agents and distilled immediately before use. Prepurified argon was further purified by passing it through an activated copper (BTS) catalyst and subsequently through Aquasorb (containing phosphorus pentoxide). Carbon monoxide was Matheson prepurified grade. Diphenylacetylene was recrystallized from alcohol. Bis(cyclopentadienyl)diphenyltitanium was prepared by a modification of the published method [7]. After

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Figure 1a. Esr spectrum of Cp_2TiPh_2 for 18 min irradiation in THF at –60 °C.

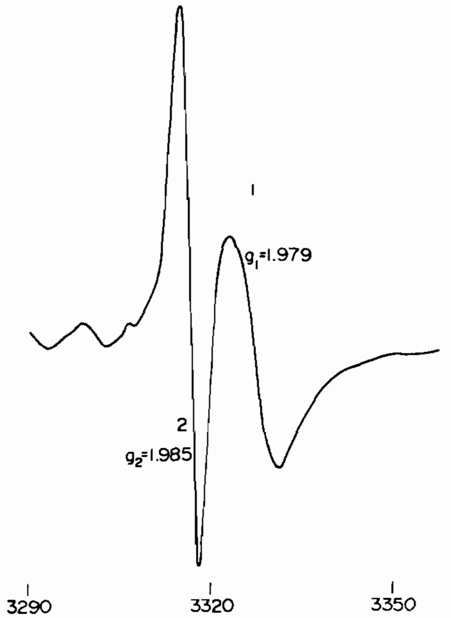


Figure 1b. Esr spectrum of Cp_2TiPh_2 for 55 min irradiation in THF at –60 °C.

reaction of Cp_2TiCl_2 with two equivalents of phenyl lithium, the solvent was removed under reduced pressure. The residue was extracted with methylene chloride and diethyl ether and was recrystallized from diethyl ether. Yellow–organge crystals were obtained in 70% yield.

Photolysis of bis(cyclopentadienyl)diphenyltitanium(IV) in various organic solvents at room temperature and low temperature was carried out in the absence or in the presence of reagents such as carbon monoxide, carbon dioxide, carbon tetrachloride and diphenylacetylene. Photolysis procedures have been described previously [8].

Photolysis products were identified by proton nmr, ir, and mass spectroscopy. Titanium content of samples was determined as the oxide, after destruction of the compound (by hydrolysis and ignition).

Products were separated by sublimation or silica gel, column chromatography.

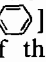
Results and Discussion

The photolysis of bis(cyclopentadienyl)diphenyltitanium in benzene produced biphenyl, benzene, and titanocene:

$$Cp_2TiPh_2 \longrightarrow [Cp_2Ti]_2 + C_6H_6 + C_6H_5\text{–}C_6H_5$$

A free radical mechanism is likely since the radical coupling product biphenyl is formed in detectable amounts and radical termination reactions like the abstraction of hydrogen from the solvent or the other phenyl group to give benzene nearly quantitatively is also observed. The production of benzene was established by photolysis of Cp_2TiPh_2 in benzene-d_6 solution for different periods and the intensity of the peak of benzene protons in the nmr spectrum increases gradually and reaches a limiting value in 2 to 3 hr. The formation of biphenyl suggests that the reduction of Cp_2TiPh_2 might lead directly to Cp_2-Ti(II) or its dimer as a reaction intermediate. It is also possible that the photoreduction follows some more complicated reaction pathways.

The identification of $[Cp_2TiH]_x$ from the photoreduction of Cp_2TiPh_2 in various organic solvents was made by its ir spectrum and titanium analysis [9].

Esr was applied to trace the course of the photoreduction of Cp_2TiPh_2 in THF solution at low temperatures. A complex signal was observed at a field of about 3320 gauss for an initial period of 30 minutes' irradiation at –60 °C. Figure 1a. Through the intermediate stages, the esr spectrum of the solution consisted of two signals [10], $[Cp_2Ti \cdot Solv]$ or $[Cp_2Ti^{II} \longleftarrow$ ] are probably responsible for the appearance of the singlet at g = 1.979. The singlet (Fig. 1b) with g = 1.985 probably is due to species of the type $[Cp_2Ti \cdot Solv]_2$, which were described previously [11]. At temperatures above –60 °C, the intensity of the one signal at high field increased gradually as irradiation was continued (Fig. 1c, d).

A similar appearance to that of Fig. 1b was seen in the esr spectrum when the solution was allowed to warm to room temperature and the irradiation was stopped. The dependence of the intensity of the first signal on temperature suggests that the disappearance of this signal is related to the process of dimerizing the complex [10]:

Figure 1c. Esr spectrum of Cp_2TiPh_2 for 55 min irradiation in THF at –60 °C and 3 min at –40 °C.

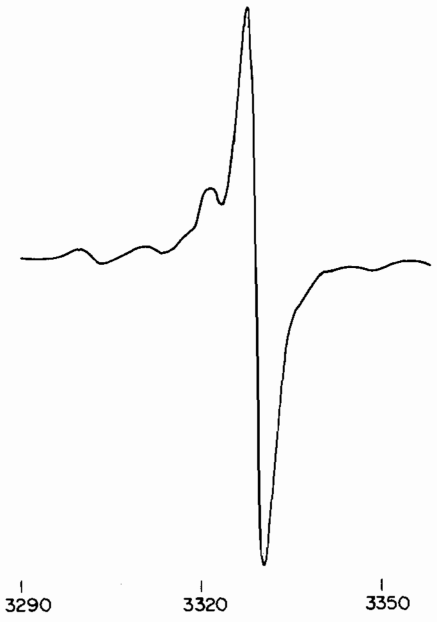


Figure 1d. Esr spectrum of Cp_2TiPh_2 for 55 min irradiation in THF at –60 °C and 5 min at –20 °C.

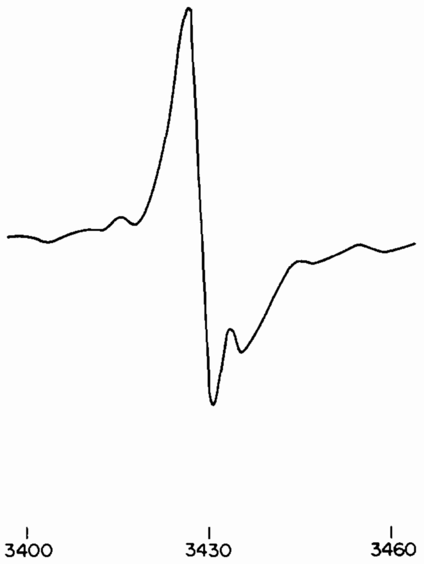


Figure 2a. Esr spectrum of Cp_2TiPh_2 for 8 min irradiation in THF at room temperature.

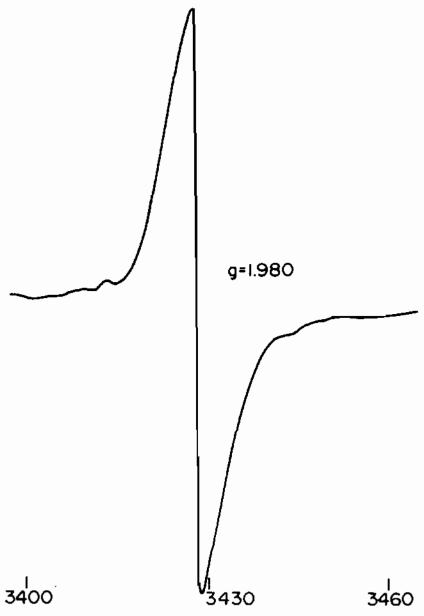
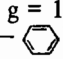


Figure 2b. Esr spectrum of Cp_2TiPh_2 for 27 min irradiation in THF at rroom temperature.

$$2[Cp_2Ti\cdot Solv] \rightleftarrows [Cp_2Ti\cdot Solv]_2$$

When the solution temperature is lowered, dimerization of titanium reduction products occurs.

When the sample solution was irradiated at room temperature for 10 minutes, a singlet at g = 1.986 appeared. When cooled to –60 °C, an esr spectrum similar to that of Fig. 1a appeared. As irradiation time was extended to 30 minutes in THF at –60 °C, the esr spectrum consisted of a triplet. The hydride bridged titanium species would be responsible for this triplet centered at g = 1.986, with one of the triplet peaks superimposed on the singlet at g = 1.979 (probably $[Cp_2Ti\cdot Solv]$ or $[Cp_2Ti^{II} \longleftarrow$ ]).

The esr spectra recorded in the course of photoreduction of bis(cyclopentadienyl)diphenyltitanium in THF at room temperature are shown in Fig. 2a–c. A singlet at g = 1.980 appears after 27 minutes irradiation (Fig. 2b). By continuing the irradiating at room temperature, $[Cp_2TiH\cdot THF]$ is observed in Fig. 2c. The signal is split by two non-equivalent hydrogen atoms. A main doublet splitting of 4.8

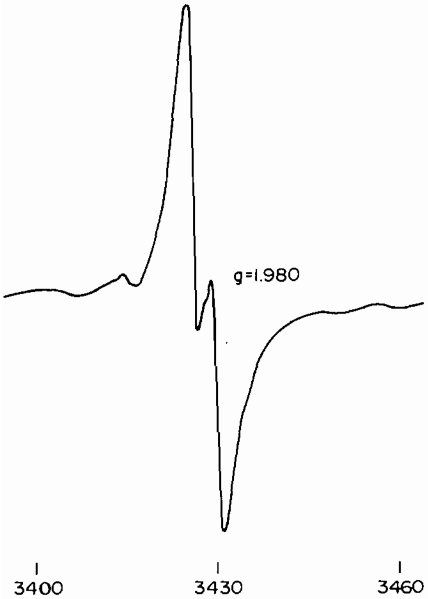


Figure 2c. Esr spectrum of Cp_2TiPh_2 for 50 min irradiation in THF at room temperature.

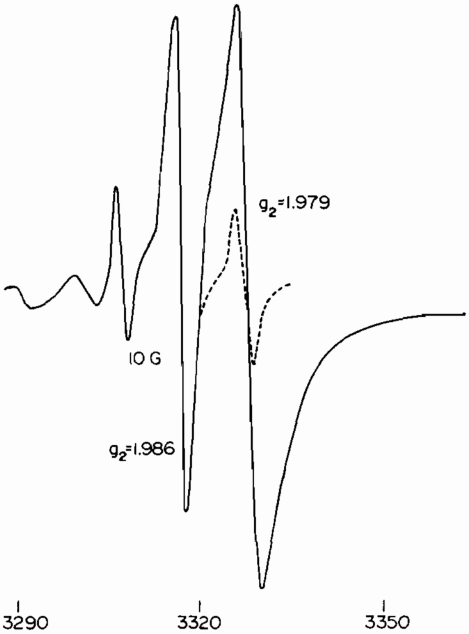
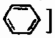


Figure 2d. Esr spectrum of Cp_2TiPh_2 for 10 min irradiation in THF at room temperature and then 30 min at −60 °C.

gauss is in turn split (1.5 gauss) by a second hydrogen atom. Both signals exist for less than 10 minutes at room temperature.

These esr spectra indicate that the photochemical reaction of Cp_2TiPh_2 in solution produces the solvated monohydride titanium species or the phenylene titanium complexes, $[Cp_2Ti^{II} \longleftarrow$ ], in which one of the originally σ-bonded phenyl ligands might be promoted to π-allylic transition state by interaction of π-electron system of the phenyl group with a vacant metal orbital. This type of σ–π rearrangement has been reported for other transition-metal phenyl derivatives [12]. The second step of this photoreduction apparently results in titanium(II), Cp_2Ti as the reaction intermediate.

The isolated $[Cp_2TiH]_x$ is a convenient source of a highly reactive form of titanocene. When the hydride is suspended and stirred in benzene or THF, a species of the composition of $[Cp_2Ti]_2$ results [13]:

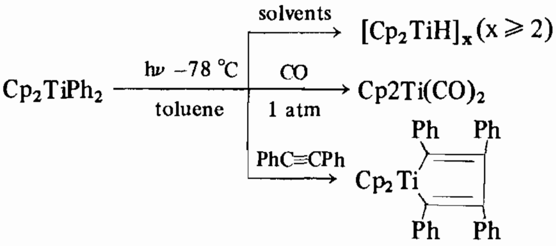
$$[Cp_2TiH]_x \xrightarrow{\text{solvent}} [Cp_2Ti]_2 + H_2$$

The postulated intermediate $[Cp_2Ti]_2$ exhibits a striking analogy in its reaction patterns to those of a carbene. Stable titanocene adducts can be formed from the reactions of $[Cp_2TiH]_x$ with various substrates.

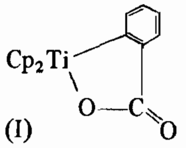
An oxidation–reduction reaction has been reported [14] in which an interaction of titanocene with diphenylacetylene leads to the formation of an adduct, $Cp_2Ti[C_2(C_6H_5)_2]_2$, heterocyclo-1,1-dicyclopentadienyl-2,3,4,5,-tetraphenyl-1-titanacyclopentadiene, which is air stable at room temperature.

The ir spectrum of the red adduct, $Cp_2Ti(CO)_2$, shows two very strong bands at 1975 and 1897 cm^{-1} in Nujol, which are characteristic of C–O stretches. The photolysis reaction provides a simpler synthesis of $Cp_2Ti(CO)_2$, with a higher yield than previously reported [15]. The latter requires the use of high pressure and temperature. Our results are to be compared with those reported [16] for the carbonylation of Cp_2TiPh_2, which gave good yields of benzophenone, but carbonyltitanium was not isolated.

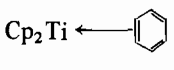
The photoreactions of bis(cyclopentadienyl)diphenyltitanium with various reagents are summarized below. In the absence of other reagents, the irradiation of Cp_2TiPh_2 only gave titanocene monohydride polymer. Many stable titanocene adducts have been obtained in the presence of reagents:



The photoreaction of Cp_2TiPh_2 with carbon dioxide in our hands did not lead to carboxylation of the phenyl ring to form metallocycle (I) as previously reported [14] and probably suggests that either the



(I)

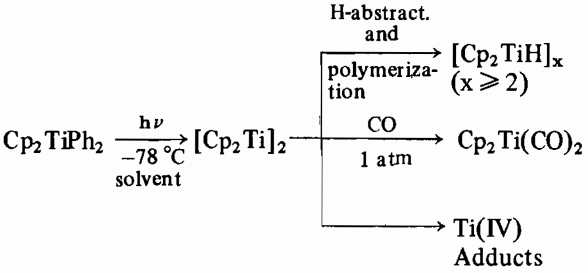


(II)

intermediate phenylene titanium complex(II) does not exist (or its concentration is too low).

Possible Mechanism

The above experimental results seem to be best explained by the formation of a reactive metallocene by photodissociation of the phenyl ligands. The reactive intermediate might then react either by attacking the available substrates to form a stable adduct, or by dimerization or oligomerization to form titanocene monohydride:



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

$$Cp_2TiPh_2 \xrightarrow[-78\,^{\circ}C]{h\nu} Cp_2Ti + 2C_6H_5\bullet \qquad \text{(dissociation)}$$

$$Cp_2Ti + \text{Solvent} \longrightarrow [Cp_2TiH]_x \qquad \text{(abstraction)}$$

$$C_6H_5\bullet + \text{Solvent} \longrightarrow C_6H_6 \qquad \text{(abstraction)}$$

$$C_6H_5\bullet + C_6H_5\bullet \longrightarrow C_6H_5{-}C_6H_5 \qquad \text{(coupling)}$$

$$Cp_2Ti + \text{bases} \longrightarrow \text{Ti(IV) Adducts}$$

All of the previous photolysis products were characterized by comparing their proton nmr and ir or mass spectra with those previously reported. They were obtained without evidence of other side reactions. The photolysis pathways can be used as convenient new routes to synthesize titanocene derivatives.

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