Rate constants accurate to ±10% yield activation values accurate to ±0.5 kJ.

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Registry No. **1a**, 12170-34-2; **1b**, 79816-63-0; **2a**, 94161-38-3; **2b**, 94161-39-4; **3**, 94161-40-7; $Cp_2Ti(SMe)_2Mo(CO)_4$, 94234-84-1; $Li_2[Cp_2TiS_2Mo(CO)_4]$, 94161-41-8; $Cp_2Ti(SCH_2CH_2CO_2CH_3)_2Mo(CO)_4$, 94161-42-9; $Cp_2Ti(SMe)_2$, 12089-78-0; $CpTiCl_3$, 1270-98-0; $CpTi[S_2C_2(CN)_2]_2^-$, 94161-43-0; $(PPN)_2[(MeCp)_2TiS_2Mo(CO)_4]$, 94202-27-4; $Cp_2Ti(SPh)_2$, 1292-47-3; $Cp_2Ti(SePh)_2$, 12290-57-2; Cp_2TiS_5, 12116-82-4; 14-$[(MeCp)_2Ti]_2S_4$, 79816-62-9; $(MeCp)_2TiCl_2$, 1282-40-2; H_2S, 7783-06-4; $C_7H_8Mo(CO)_4$ (C_7H_8 = norbornadiene), 12146-37-1; $C_7H_8W(CO)_4$ (C_7H_8 = norbornadiene), 12129-25-8; $(C_2H_5CN)_3W(CO)_3$, 84580-21-2; $CH_2{=}CHCO_2CH_3$, 96-33-3; $Na_2[S_2C_2(CN)_2]$, 18820-77-4; Ph_2S_2, 882-33-7; Ph_2Se_2, 1666-13-3; S_8, 10544-50-0; $(MeCp)_2TiS_5$, 78614-86-5.

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Electronic Structure and Photochemistry of the $(\eta^5\text{-}C_5H_5)_2TiI_2$ Complex

Mitchell R. M. Bruce and David R. Tyler*

Department of Chemistry, Columbia University, New York, New York 10027

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The photochemistry of the Cp_2TiI_2 (Cp = η^5-C_5H_5) complex can be interpreted in terms of a low-energy I → Ti charge-transfer excited state. Low-energy irradiation ($\lambda > 600$ nm) of unpurged solutions of Cp_2TiI_2 in benzene produces $(Cp_2TiI)_2$ and 0.5 mol of I_2/mol of Cp_2TiI_2 photolyzed. Under similar conditions, photolysis of Cp_2TiI_2 in CCl_4 produces $Cp_2Ti(I)Cl$. In inert-gas-purged solutions, titanocene is formed as well as 1 mol of I_2/mol of Cp_2TiI_2 photolyzed. Under no conditions were nitrosodurene spin-trapped Cp radicals observed by ESR. These results are interpreted in terms of a mechanism involving stepwise loss of I· from the Cp_2TiI_2 complex to produce $(Cp_2TiI)_2$. Further irradiation of this dimer then forms titanocene and more I_2. The electronic spectrum of the Cp_2TiI_2 complex is reported. Previously reported spectra were complicated by the following equilibrium: $Cp_2TiI_2 + nS \rightleftharpoons [(Cp_2Ti(I_{2-n})S_n)^{n+}(nI^-)^{n-}]$ (S = solvent = CH_2Cl_2 or CH_3CN). In benzene, the equilibrium above does not occur to any appreciable extent, while in CH_2Cl_2 $n = 1$ and the equilibrium constant is $K = 3 \times 10^{-3}$ and in CH_3CN $n = 2$ and $K = 2.5 \times 10^{-3}$.

We are interested in the photochemistry of ligand-to-metal charge-transfer excited states as a way of photoreducing organometallic complexes. One aspect of our work involves the study of halide → metal charge-transfer excited states. For that reason, we have been investigating the Cp_2TiX_2 (X = F, Cl, Br, I; Cp = η^5-C_5H_5) complexes. We recently reported the results of self-consistent-field–Xα–scattered-wave (SCF–Xα–SW) molecular orbital calculations on these complexes.[1] Of interest to the photochemistry of these complexes is the calculational result that the lowest energy excited states in the fluoride, chloride, and bromide complexes are Cp → Ti charge-transfer excited states rather than halide → Ti charge transfer. These calculational results are consistent with the known photochemistry: Cp–Ti bond cleavage occurs when the chloride and bromide complexes are irradiated.[2] The calculation could not be used to definitively assign the lowest energy excited state in the Cp_2TiI_2 complex because the Cp → Ti and I → Ti CT transitions have nearly equal energies (within the accuracy of the calculation) in this complex.

A study of the photochemistry of Cp_2TiI_2 seemed worthwhile for three reasons. First, it is likely that the photochemistry would result from the desired halide → Ti charge-transfer excited state. Second, with proper caution we could use the photochemical results to suggest assignments for the low energy excited states of the complex. And third, the close proximity of the I → Ti and Cp → Ti charge-transfer bands might lead to some interesting wavelength dependent photochemistry. This paper reports the results of our photochemical study of the Cp_2TiI_2 complex.

Experimental Section

All manipulations were carried out under argon on a Schlenk line, in a Vacuum Atmospheres glovebox or in a glove bag. Acetonitrile (spectrograde, Kodak), benzene (spectranalyzed, Fisher), carbon tetrachloride (certified, Fisher), chloroform (Amend), methylene chloride (certified, Fisher), and toluene (certified, Fisher) were dried,[3] distilled under nitrogen, and degassed before use. Thallium hexafluorophosphate (Strem Chemicals, Inc.) and C_6D_6 (99.5 atom % D, Aldrich) were used as received. Nitrosodurene was synthesized by a published procedure.[4]

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Nuclear magnetic resonance spectra were obtained on Bruker WM 250 and Varian XL 200 spectrometers. Peak assignments are relative to the appropriate solvent peak: $CHDCl_2$, 5.28; C_6H_6, 7.17. Infrared spectra were recorded with Perkin-Elmer 621 and Perkin-Elmer 983 infrared spectrophotometers. Electronic absorption spectra were obtained with a Cary 17 spectrophotometer. Electron paramagnetic resonance spectra were obtained by using a Varian E-line spectrometer. A 200-W Oriel Co. high-pressure mercury arc lamp was used for the photochemical experiments and quantum yield measurements. Appropriate Corning glass filters and interference filters (Edmund Scientific) were used to isolate the wavelengths for irradiation. Absolute quantum yield measurements were made with the assistance of a Beckman DU spectrophotometer. Solutions were irradiated at room temperature in 1.00-cm quartz cells and were stirred during irradiation. The lamp intensity was measured by Reinecke's salt actinometry.[5] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Titanocene Halides. Bis(cyclopentadienyl)titanium dichloride (Alfa) was recrystallized from acetonitrile. Bis(cyclopentadienyl)titanium dibromide and bis(cyclopentadienyl)titanium diiodide were prepared by the method of Lappert[6] and recrystallized from acetonitrile and/or toluene. The purity of bis(cyclopentadienyl)titanium diiodide was confirmed by infrared spectroscopy,[6] nuclear magnetic resonance spectroscopy,[7] and elemental analysis. Anal. Calcd for $C_{20}H_{20}TiI_2$: C, 27.81; H, 2.33; I, 58.77. Found: C, 27.80; H, 2.31; I, 58.83. Bis(cyclopentadienyl)titanium(III) iodide dimer, $(Cp_2TiI)_2$, was prepared by using Coutts, Wailes, and Martin's method II.[8] The precursors Cp_2TiBH_4[9] and $(Cp_2TiCl)_2$[10] were prepared by literature procedures.

Preparation of $[Cp_2Ti(CH_3CN)_2][PF_6]_2$. A solution of Cp_2TiI_2 (1.0 g, 2.3 mmol) in acetonitrile (50 mL) was treated dropwise at room temperature with a solution of $Tl[PF_6]$ (1.77 g, 5.1 mmol) in acetonitrile (75 mL). The color of the solution immediately changed from brownish to red and was accompanied by the formation of a yellow precipitate (TlI). The solution was allowed to stir for 1 h, then filtered through Celite, and concentrated. Addition of diethyl ether gave red-brown crystals of $[Cp_2Ti(CH_3CN)_2][PF_6]_2$ which were filtered and dried under vacuum at 90 °C for 2 h. The infrared spectrum in the $\nu(C{\equiv}N)$ region showed bands for coordinated acetonitrile (2325, 2288 cm^{-1}; a 31 cm^{-1} blue shift vs. free acetonitrile).[11]

Measurement of Iodine Loss during Photolysis of Cp_2TiI_2 or $(Cp_2TiI)_2$ in Benzene. A known amount of sample (typically $\simeq$5 mg) was introduced into a 500-mL three-necked flask fitted with a Kontes universal adapter and pipet for introduction of argon into the solution, a Kontes gas adapter for removal of gases, and a septum for the introduction of liquids. A dry ice–acetone trap was connected to the gas adapter. Benzene (about 300 mL) was added to the flask, the argon flow turned up to produce turbulent bubbling, and the photolysis begun. Periodically, the photolysis was stopped and the pink solution in the trap was transferred to a volumetric cylinder. Benzene was occasionally added to the flask to replace that lost through vaporization. The contents of the volumetric cylinder were then analyzed for iodine by electronic absorption spectroscopy (λ = 500 nm (ϵ 1040)).[12]

Reaction Stoichiometry. To determine the stoichiometry of the reaction $Cp_2TiI_2 \xrightarrow{h\nu} Cp_2TiI_{2-x} + (x/2)I_2$, the loss of Cp_2TiI_2 was monitored by the decrease in the intensity of the 600-nm peak and the growth of I_2 was monitored by taking the difference between the calculated loss of intensity at 512 nm due to Cp_2TiI_2 disappearance and the actual decrease at 512 nm (ϵ_{I_2} at 512 nm in benzene is 990).

Measurement of the Equilibrium Constant of the Reaction $Cp_2TiI_2 + nS \rightleftharpoons [(Cp_2Ti(I_{2-n})S_n)^{n+}(nI^-)^{n-}]$ (S = Solvent). A solution of Cp_2TiI_2 (0.5–8 mM) in benzene or acetonitrile was prepared and an aliquot (1–2 mL) pipetted into a volumetric flask (10 mL) and capped with a septum. Degassed benzene, methylene chloride, or acetonitrile was then added to the volumetric flask, shaken, and then transferred to a capped quartz cuvette. The electronic absorption spectrum was then obtained. For all solutions, the Cp_2TiI_2 concentration was calculated by using the absorbance maximum between 580 and 610 nm and the molar absorptivity in benzene (ϵ 1800). The $[Cp_2Ti(I_{2-n})^{n+}(nI^-)^{n-}]$ concentration was calculated by the difference in formal vs. actual concentrations measured by the absorbance maximum between 580 and 610 nm. For benzene, the equilibrium constant is $K = 0$; for methylene chloride $n = 1$ and $K = 3 \times 10^{-3}$ ($\pm 2 \times 10^{-3}$); and for acetonitrile $n = 2$ and $K = 2.5 \times 10^{-3}$ ($\pm 1.5 \times 10^{-3}$).

Measurement of the Equilibrium of the Reaction $Cp_2TiI_2 + Cp_2TiCl_2 \rightleftharpoons 2\,Cp_2Ti(I)Cl$. The ^1H NMR spectra of separate Cp_2TiI_2 and Cp_2TiCl_2 solutions in C_6D_6 show the cyclopentadienyl proton resonances at 6.11 and 5.91 ppm, respectively. When these solutions are combined, a third central peak (6.01 ppm) grows in over time until finally the relative intensities of three peaks remain unchanged. We assign the new central peak to $Cp_2Ti(I)Cl$. The equilibrium constant K was found, by integration, to be close to 4, the statistical value for random redistribution. The same equilibrium occurs in 50% benzene/50% carbon tetrachloride except for the positions of the resonance: Cp_2TiI_2, 6.25 ppm; $Cp_2Ti(I)Cl$, 6.14 ppm; Cp_2TiCl_2, 6.03 ppm. These results are analogous to those found by Lappert et al.[6] for $Cp_2TiCl_2 + Cp_2TiBr_2 \rightleftharpoons 2Cp_2Ti(Cl)Br$ and $Cp_2ZrCl_2 + Cp_2ZrBr_2 \rightleftharpoons 2Cp_2Ti(Cl)Br$.

Measurement of the Kinetics of the Reaction $Cp_2TiI_2 + Cp_2TiCl_2 \rightarrow 2\,Cp_2Ti(I)Cl$. The second-order rate constant ($k_{25\,°C}$ = (0.025 ± 0.005) $M^{-1}\,s^{-1}$) was determined by following the changes in $[Cp_2TiI_2]$ and $[Cp_2TiCl_2]$ by ^1H NMR over time and using the expression:[13]

$$k = \left(\frac{1}{t}\right)\left(\frac{1}{[Cp_2TiCl_2]_0 - [Cp_2TiI_2]_0}\right)\ln\left(\frac{[Cp_2TiI_2]_0[Cp_2TiCl_2]_t}{[Cp_2TiCl_2]_0[Cp_2TiI_2]_t}\right)$$

The concentrations of these species at time t were calculated by using an internal standard (benzene). The initial concentrations were calculated by extrapolation to t = zero $[3\text{–}8\ mM]_0$. The back reaction was assumed to be insignificant for the concentrations and time period studied (14–108 min): under these conditions equilibrium takes about 350 min to achieve.

Photolysis of Cp_2TiI_2 in CCl_4/Benzene. A solution of Cp_2TiI_2 (3.0–9.8 mM) in 50% CCl_4/50% C_6D_6 was prepared, and aliquots were transferred to two screw cap NMR tubes. One solution was irradiated (λ > 595 nm) at room temperature (25 °C) for 20–60 min. The other solution was kept in the dark at room temperature during this time. Both tubes were shaken periodically (5–10 min). The ^1H NMR was then recorded. In some cases the ^1H NMR of the thermal blank was recorded both before and after irradiation. The concentrations of titanocene dihalide species were calculated by using an internal standard (benzene). The thermal blank was virtually unchanged while the irradiated sample showed clean quantitative conversion of Cp_2TiI_2 to $Cp_2Ti(I)Cl$ and Cp_2TiCl_2. In a typical experiment irradiation

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(11) These bands immediately disappear upon exposure to the atmosphere. In a Nujol mull, free acetonitrile shows two absorption bands in the $\nu(CN)$ region. A strong band at 2257 cm^{-1} (symmetric $C{\equiv}N$ stretch) and a medium band at 2293 cm^{-1} (combination of symmetric CH_3 deformation and C—C stretching vibrations with borrowed intensity from the symmetric $C{\equiv}N$ stretch). ^1H NMR of the compound in CD_2Cl_2 shows three peaks in the Cp region: δ 6.54 (s, 16%); δ 6.44 (d, 9%); δ 6.38 (s, 74%). We believe the peak at δ 6.38 is $[Cp_2Ti(CH_3CN)_2][(PF_6)_2]$ and that those peaks at δ 6.54 and 6.44 represent molecules having only one CH_3CN per molecule: δ 6.54, 6.44, and 6.38 (10.0 H, C_5H_5) and 1.97 (6.0 H, CH_3CN).

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Table I. Electronic Absorption Spectra of Cp_2TiI_2 in Various Solvents

wavelength[a] (ε)[b]			
benzene[c]	CH_2Cl_2[c]	acetonitrile[c]	CH_2Cl_2[16,17]
665[d] (1×10^3)	665[d]	665[d]	
600 (1.8×10^3)	590	580	595 (6.0×10^2)
512 (2.6×10^3)	505	493	500 (1.5×10^3)
444[d] (1.5×10^3)	445[d]		
363 (5.0×10^3)	360		361 (3.3×10^3)

[a] Wavelength in nm. [b] Extinction coefficient in L mol^{-1} cm^{-1}. [c] This work. [d] Shoulder.

of a 5.8 mM solution of Cp_2TiI_2 in CCl_4/benzene irradiated for 30 min[14] gave Cp_2TiI_2 (δ 6.25; 78%, 4.5 mM), $Cp_2Ti(I)Cl$ (δ 6.14; 19%, 1.1 mM), and Cp_2TiCl_2 (δ 6.03; 3%, 0.17 mM).

Results and Discussion

Electronic Spectrum of Cp_2TiI_2. The synthesis of Cp_2TiI_2 was first reported by Wilkinson and Birmingham in 1954;[15] their product was obtained as dark purple crystals. The crystals melted with decomposition at 319 ± 3 °C, and the chemical properties of Cp_2TiI_2 were reported to be similar to those of Cp_2TiBr_2. The infrared spectrum of the complex was obtained but was not specifically tabulated or shown. The electronic spectrum was also not reported. In 1963, Chien[16] reported the electronic spectrum of Cp_2TiI_2 in dichloromethane using Cp_2TiI_2 prepared by Wilkinson's method (Table I). However, he questioned the reliability of this spectrum because the elemental analysis of Cp_2TiI_2 was not correct; he suggested that the Cp_2TiI_2 was contaminated with $Cp_2Ti(OH)I$. In 1971, Dias reproduced Chien's electronic spectrum using the same solvent and method of synthesis,[17] but he made no mention of the purity of the Cp_2TiI_2.

It was not until 1969 that Lappert et al.[6] reported an improved synthesis of Cp_2TiI_2. Their black product was completely characterized by NMR, infrared spectroscopy, melting point, and elemental analysis, all of which showed the product to be pure. The electronic spectrum was not published, however. Because there is some doubt as to the purity of the Cp_2TiI_2 obtained using Wilkinson's method of preparation, we used material prepared by Lappert's method.[6]

The electronic spectrum of Cp_2TiI_2 is strongly solvent dependent. Figure 1a shows that four features are discernible in the 400–700 nm range in benzene solution (Table I). The spectra in CH_2Cl_2 and CH_3CN are shown in parts b and c, respectively, of Figure 1 and both are clearly different from each other and from the spectrum in benzene (Figure 1a). (Note that the spectra in CH_3CN and CH_2Cl_2 are similar but not identical with the spectra reported by Chien[16] and Dias.[17] See Table I.) The spectra in the three solvents are too dissimilar to attribute the differences only to solvent effects, and we propose that the following equilibrium is important for CH_2Cl_2 and CH_3CN but not for benzene.[18]

$$Cp_2TiI_2 + nS \rightleftharpoons [(Cp_2Ti(I_{2-n})S_n^{\,n+})(nI^-)^{n-}] \qquad (1)$$

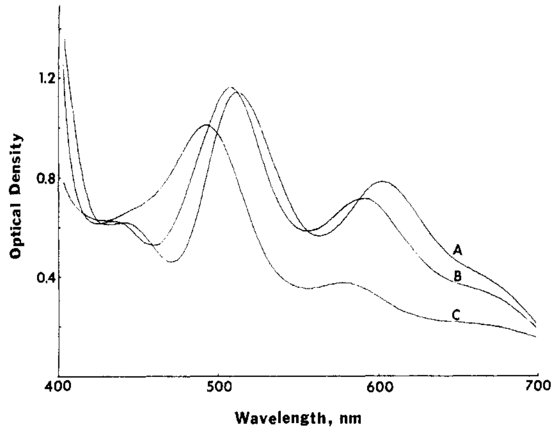

Figure 1. Electronic absorption spectra of Cp_2TiI_2 in various solvents: A, benzene, 4.26×10^{-4} M Cp_2TiI_2; B, dichloromethane, approximately 4.1×10^{-4} M Cp_2TiI_2 and 1.9×10^{-5} M $[(Cp_2Ti(I)CH_2Cl_2)^+(I)^-]$; C, acetonitrile, approximately 2.2×10^{-4} M Cp_2TiI_2 and 2.0×10^{-4} M $[(Cp_2Ti(CH_3CN)_2)^{2+}(I^-)_2^{\,2-}]$. (See Discussion Section for explanation.)

The existence of the equilibrium in eq 1 is supported by three observations. First, we found that the spectrum in a particular solvent (e.g., benzene) could be fully recovered if the solvent was removed, the residue redissolved in another solvent (e.g., CH_3CN), the new solvent removed, and the Cp_2TiI_2 redissolved in the original solvent. This experiment shows that irreversible decomposition of the Cp_2TiI_2 is not occurring in solution, a result which implies an equilibrium. Second, the band intensities for "Cp_2TiI_2" decrease in a going from benzene to dichloromethane to acetonitrile, a progression that coincides with the coordinating ability of these solvents (i.e., the equilibrium is shifted to the right as the coordination ability of the solvent increases). Finally, addition of $TlPF_6$ in CH_3CN to Cp_2TiI_2 in CH_3CN at room temperature immediately produces the insoluble, solvent-coordinated species $[Cp_2Ti(CH_3CN)_2][PF_6]_2$.[19,20] We conclude that the true electronic spectrum of Cp_2TiI_2 is that obtained in benzene solution; because of the equilibrium (eq 1), the spectra obtained in dichloromethane and acetonitrile are not that of pure Cp_2TiI_2. The equilibrium constant for eq 1 was determined to be 3×10^{-3} in CH_2Cl_2 where $n = 1$ and 2.5×10^{-3} in CH_3CN where $n = 2$. The data do not support the separation of the ion pair to any large extent.

The question remains concerning the two additional absorption features at 665 (sh) and 445 nm which we observe but that were not mentioned in the previous studies. The electronic spectrum of solid Cp_2TiI_2 (obtained as a Nujol mull) clearly shows these two shoulders so a solvent effect is ruled out. We note that, in our hands, the electronic spectrum of Cp_2TiI_2 prepared by the method of Wilkinson also did not show these two shoulders. We suggest that the impurity in the Cp_2TiI_2 samples prepared by this original method is masking the two additional features.

The assignments for the bands in the electronic spectrum of Cp_2TiI_2 are discussed in the next section.

Photochemistry of Cp_2TiI_2. Irradiation (λ > 400 nm, λ > 500 nm, or λ > 600 nm) of Cp_2TiI_2 (5×10^{-4} M) in a

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[14] Total time from start of photolysis until end of NMR was 50 min.

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[18] See: Katz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68–79 for analogous results for Cp_2MoX_2 + MeCN → $[Cp_2Mo(NCMe)X]^+$ + X^- (X = Cl, Br, I).

[19] For comparison, note that the analogous reaction with Cp_2MoI_2 requires refluxing for 24 h: $Cp_2MoI_2 + 2TlPF_6 \rightarrow [Cp_2Mo(CH_3CN)_2][(PF_6)_2] + 2TlI$. See: Availes, T.; Green, M. C. H.; Dias, A. R.; Romad, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1367–1371.

[20] Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Sanders: Philadelphia, 1977; p 235 ff.

benzene solution purged by argon produces I_2 and titanocene (eq 2). (Titanocene is not formed in the absence

$$Cp_2TiI_2 \xrightarrow[\substack{\text{benzene}\\ \text{Ar purge}}]{h\nu} \text{“}Cp_2Ti\text{”} + I_2 \qquad (2)$$

of a purge; see below.) I_2 was detected by monitoring the reaction by electronic absorption spectroscopy. The following spectral changes were typically observed: the Cp_2TiI_2 absorption bands at 665 and 600 nm decreased in intensity, the peak at 510 nm decreased more slowly in intensity than the 600- and 665-nm bands, and λ_{max} for the 510-nm band shifted toward 500 nm. Continuing irradiation produced a spectrum that showed no absorption bands at 665 and 600 nm (i.e., all of the Cp_2TiI_2 was gone) but the absorption band at 500 nm was still present. As the electronic spectrum of I_2 in benzene shows a single visible absorption band at 500 nm (ϵ_{max} = 1040 in benzene),[12] it was concluded that I_2 is a product of the photoreaction. Note that all of the iodine originally present in Cp_2TiI_2 can be swept out of the reaction cell during photolysis and trapped as I_2. In a typical experiment, irradiation ($\lambda > 600$ nm) of 3.9 mg of Cp_2TiI_2 (9.0×10^{-6} mol) in benzene for 16 h gave 9.2×10^{-6} mol of I_2. The stoichiometry of reaction 2 is thus confirmed.

When the benzene is removed from the argon-purged and irradiated solution above, an air-sensitive green precipitate is left behind. The infrared spectrum shows it to be very similar to one of the several forms of titanocene.[21] It most closely resembles the black titanocenes reported by Rausch et al. (obtained by the photolysis of $Cp_2Ti(C_6H_5)_2$ in benzene or $Cp_2Ti(CH_3)_2$ in pentane[21i]) in that there are no bands characteristic of bridging hydrides at 1230 cm^{-1}. Instead, there are unsplit bands at 800 and 1015 cm^{-1}, characteristic of a simple metallocene, e.g., $(Cp_2Ti)_x$.[21] An additional strong band at 1260 cm^{-1} was also observed; a weak band at this frequency was also observed by Rausch in the product formed by the photolysis of $Cp_2Ti(C_6H_5)_2$ in benzene.[21g] Our characterization of the titanocene product was hindered by the irreproducibility of its synthesis; the color of the photolysis product, the relative infrared band intensities, and its chemical properties all seem to be dependent on undetermined variables. For example, on one occasion the green residue formed a dark purple solution when it was dissolved in toluene and cooled to −80 °C in an atmosphere of N_2. Upon warming to room temperature and pumping off the toluene and the N_2, the green residue was regenerated. This reactivity with N_2 is characteristic of several forms of titanocene, e.g., $[(\eta\text{-}C_5H_5)_2Ti]_{1-2}$.[21l] Several other photolysis experiments yielded green residues, however, which did not form a purple complex with N_2 in toluene. Van Tamelen et al. reported[21l] two forms of titanocene, $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_x$ and $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2$ that do not react with N_2 in toluene at low temperature. Concerning its other properties, we found that our green residue is not pyrophoric in air. Rausch's black titanocene, formed by the photolysis of $Cp_2Ti(CH_3)_2$[21i] in pentane, is pyrophoric, yet the nearly identical black titanocene formed by the photolysis of $Cp_2Ti(C_6H_5)_2$ in benzene is not pyrophoric.[21g] Finally, very long irradiation times produced a secondary photolysis product, not as yet identified, that shows a strong infrared band at 1735 cm^{-1} and a weak band at 1945 cm^{-1}. The quantum yield (λ = 546 nm) for reaction 2 (in a degassed but unpurged solution) is 1×10^{-4}.

The experiments above show that the photochemistry of the Cp_2TiI_2 complex involves cleavage of the Ti–I bond(s). To check on the possibility of Cp–Ti bond cleavages, we irradiated the Cp_2TiI_2 complex in the presence of the radical spin-trap nitrosodurene. However, irradiation of Cp_2TiI_2 (5×10^{-3} to 5×10^{-4} M) in an ESR tube in chloroform solution containing nitrosodurene (5×10^{-3} to 5×10^{-4} M) did not produce the Cp nitrosodurene adduct. A variety of photolysis conditions were employed: the irradiation wavelength was varied ($\lambda > 254$ to $\lambda > 650$ nm), the temperature of the solution was varied (23 to −100 °C), and both short and long irradiation times were tried (up to 60 min). In none of these cases was the ESR signal of the spin-trapped species observed. Control experiments showed that Cp radicals could be spin-trapped and detected under these photolysis conditions. For example, the Cp_2TiCl_2 and Cp_2TiBr_2 complexes are known to yield Cp radicals on irradiation.[2f] Irradiation of these complexes under the same conditions as those mentioned above produced easily detectable ESR signals attributable to the nitrosodurene spin-trapped Cp radical from which we conclude that irradiation of the Cp_2TiI_2 complex does not lead to Cp–Ti bond cleavage.

The photochemical results above suggest that the lowest energy electronic transition in the Cp_2TiI_2 complex is an I → Ti charge-transfer transition. The failure to trap Cp radicals even upon high-energy irradiation (i.e., we found no evidence of wavelength dependent photochemistry) demonstrates that if there are low energy Cp → Ti CT excited states (as the SCF-Xα calculation predicts) then these states are photochemically inactive (i.e., internal conversion to the lowest energy I → Ti CT state is very fast). Our SCF-Xα calculation showed that the lowest energy I → Ti CT transition (specifically $8b_1 \rightarrow 14a_1$; ${}^1A_1 \rightarrow {}^1B_2$) involved depopulation of an orbital that is Ti–I bonding and population of an orbital that is Ti–I antibonding. Considerable loss of Ti–I bonding is thus expected to occur in this excited state, and it is not surprising that the Ti–I bond breaks. In the Cp_2TiI_2 complex the two lowest energy electronic absorption bands overlap extensively (λ = 600 and λ = 665 (sh) nm). Therefore, we are limited to proposing that one of these is the I → Ti (${}^1A_1 \rightarrow {}^1B_2$) charge-transfer transition responsible for all of the observed photochemistry.

It remains to discuss the mechanism of "titanocene" formation in benzene. Two pathways seem likely, either concerted loss of I_2 (eq 3) or stepwise loss of I· (eq 4).

$$Cp_2TiI_2 \xrightarrow{h\nu} \text{“}Cp_2Ti\text{”} + I_2 \qquad (3)$$

$$\begin{tikzcd} Cp_2TiI_2 \arrow[r, "h\nu"] & Cp_2TiI + I \arrow[d, "h\nu"] \\ & \text{"}Cp_2Ti\text{"} + I \end{tikzcd} \qquad (4)$$

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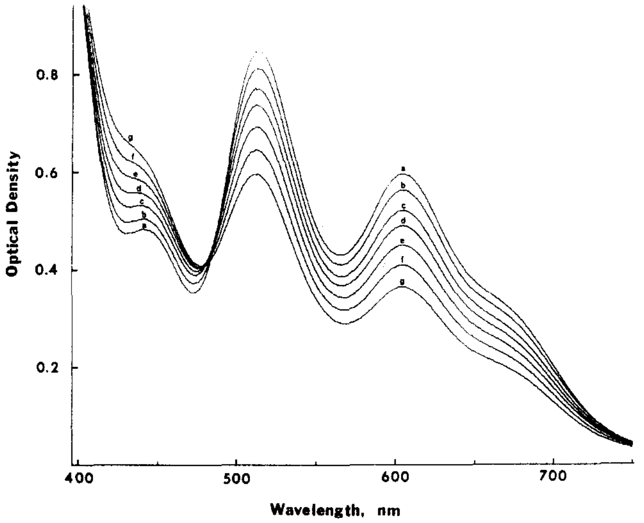

Figure 2. Electronic spectral changes accompanying photolysis ($\lambda > 595$ nm) of Cp_2TiI_2 in C_6D_6/CCl_4 (50:50) to yield $Cp_2Ti(I)Cl$. Irradiation times: (a) 0 s, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, and (g) 60 min. The concentration of Cp_2TiI_2 at $t = 0$ was 3.3×10^{-4} M.

Perhaps the simplest way to establish the stepwise loss of I· would be to show that $(Cp_2TiI)_2$ is formed as the product of Cp_2TiI_2 photolysis. Unfortunately, it is not feasible to spectroscopically characterize $(Cp_2TiI)_2$ in the presence of Cp_2TiI_2 because the electronic spectra of the two complexes are too similar as are their infrared spectra.[8] In addition, $(Cp_2TiI)_2$ is paramagnetic so we could not obtain an NMR spectrum. Finally, room-temperature ESR spectra, even of authentic $(Cp_2TiI)_2$ samples, gave no signals. Because spectroscopic detection of $(Cp_2TiI)_2$ was not feasible, we had to resort to indirect methods to differentiate between the pathways in eq 3 and 4. We favor the mechanism involving stepwise loss of I for the following four reasons: (1) $Cp_2Ti(I)Cl$ forms on photolysis of Cp_2TiI_2 in CCl_4, (2) our stoichiometry study indicates that in unpurged cells, 0.5 mol of I_2 is formed for each mole of Cp_2TiI_2 consumed, (3) titanocene does not form when the photolysis cell is not purged with argon, and (4) irradiation of $(Cp_2TiI)_2$ (the dimerization product of Cp_2TiI) in a purged cell produces titanocene. These points are discussed below.

The photolysis at room temperature ($\lambda > 595$ nm) of Cp_2TiI_2 in carbon tetrachloride/benzene (50%/50%) shows clean conversion of Cp_2TiI_2 to $Cp_2Ti(I)Cl$ (eq 5;

$$Cp_2TiI_2 \xrightarrow[CCl_4/\text{benzene}]{h\nu} Cp_2Ti(I)Cl \qquad (5)$$

Figure 2) as monitored by ^1H NMR and electronic absorption spectroscopy. The quantum yield ($\lambda = 546$ nm) for reaction 5 (in a degassed, unpurged solution) is 1.1×10^{-3}. (Note that this quantum yield is some eleven times larger than that for the photolysis of Cp_2TiI_2 in benzene without carbon tetrachloride.) Eventually, Cp_2TiCl_2 is also formed but only as a minor product. However, the presence of any Cp_2TiCl_2 during the photolysis leads to the question: does the photolysis proceed as written in eq 5 or does the photolysis produce Cp_2TiCl_2 (eq 6) which then reacts with Cp_2TiI_2 producing $Cp_2Ti(I)Cl$ (eq 7)? Reaction

$$Cp_2TiI_2 \xrightarrow[CCl_4/\text{benzene}]{h\nu} Cp_2TiCl_2 \qquad (6)$$

$$Cp_2TiI_2 + Cp_2TiCl_2 \rightleftharpoons 2Cp_2Ti(I)Cl \qquad (7)$$

7 is easily demonstrated by mixing Cp_2TiI_2 and Cp_2TiCl_2 together and observing by ^1H NMR that $Cp_2Ti(I)Cl$ is formed. Eventually, equilibrium is established; the equilibrium constant for eq 7 is 4.

Unfortunately, the equilibrium constant value of 4 precludes differentiating eq 5 from eq 6 and 7 based only on the product distribution. For example if 10% of the Cp_2TiI_2 is converted to Cp_2TiCl_2 (eq 6) and then equilibrium is reached (eq 7) before the ^1H NMR is taken, the relative percentages of species would be Cp_2TiI_2 (81%), $Cp_2Ti(I)Cl$ (18%), and Cp_2TiCl_2 (1%). In other words, the major product observed would still be $Cp_2Ti(I)Cl$, not Cp_2TiCl_2.

In order to differentiate between the pathways in eq 5 and eq 6 and 7, we measured the kinetics of the forward reaction of eq 7 by mixing Cp_2TiI_2 and Cp_2TiCl_2 and monitoring the formation of $Cp_2Ti(I)Cl$ by ^1H NMR. A rate constant of 0.025 M^{-1} s^{-1} was found. This kinetic information allows us to definitively say that the photolysis of Cp_2TiI_2 in carbon tetrachloride/benzene does not occur via eq 6 and 7 but rather via eq 5. In a typical experiment a 5.8 mM Cp_2TiI_2 solution in carbon tetrachloride/benzene was irradiated for 30 min. Total time from the start of photolysis to the end of the ^1H NMR spectrum was 50 min. The final product distribution shows Cp_2TiI_2 (4.5 mM), $Cp_2Ti(I)Cl$ (1.1 mM), and Cp_2TiCl_2 (0.17 mM). To test whether or not eq 6 and 7 are responsible for this product distribution, we can assume that all the $Cp_2Ti(I)Cl$ formed came via eq 7; working backward we can calculate "initial" concentrations for Cp_2TiI_2 (5.1 mM), $Cp_2Ti(I)Cl$ (0 mM), and Cp_2TiCl_2 (0.55 mM). The most exacting condition is to assume that all of the Cp_2TiCl_2 was produced at $t = 0$. Then with use of the rate constant above, we calculate the following product distribution at $t = 50$ min: Cp_2TiI_2 (4.9 mM), $Cp_2Ti(I)Cl$ (0.34 mM), and Cp_2TiCl_2 (0.38 mM). Experimentally, the concentration of $Cp_2Ti(I)Cl$ actually produced is 320% greater and the concentration of Cp_2TiCl_2 actually produced is 55% less than that predicted for eq 6 and 7. Clearly, $Cp_2Ti(I)Cl$ is not formed via reactions 6 and 7; a result consistent with the stepwise loss of I· from Cp_2TiI_2 (eq 4).

The stoichiometry of I_2 formation vs. Cp_2TiI_2 disappearance is also consistent with the stepwise photolytic loss of I· from Cp_2TiI_2. Our measurements clearly indicate the stoichiometry in eq 8. In five separate experiments, a 3.4

$$Cp_2TiI_2 \xrightarrow[\text{benzene}]{h\nu} {}^1/_2I_2 + (Cp_2TiI) \qquad (8)$$

$\times 10^{-4}$ M solution of Cp_2TiI_2 in benzene was irradiated ($\lambda > 490$ nm) for periods up to 5 h and the photolysis monitored by electronic absorption spectroscopy. Analysis of the spectra showed that 0.54 ± 0.16 mol of I_2 are liberated per mole of Cp_2TiI_2 photolyzed.[22] The stoichiometry experiments were done in degassed but unpurged cells; no titanocene product formed under these conditions. This result suggests that the function of the gas purge is to sweep out I_2 and prevent a backreaction with either titanocene or $(Cp_2TiI)_2$.

To demonstrate the conversion of $(Cp_2TiI)_2$ to titanocene (eq 9), we irradiated $(Cp_2TiI)_2$ ($\lambda > 490$ nm; 5×10^{-4} M)

$$(Cp_2TiI)_2 \xrightarrow{h\nu} \text{titanocene} + {}^1/_2I_2 \qquad (9)$$

in benzene. Under closed system conditions no reaction occurred, but when we photolyzed while a rapid stream of argon was bubbled through the reaction cell, a dramatic and rapid change took place and titanocene was formed. Quantitatively, all of the iodine originally present in $(Cp_2TiI)_2$ could be swept out of the reaction cell during

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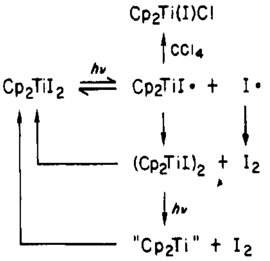
[22] 0.54 represents the mean of 26 data points from five experiments. 0.16 is one standard deviation.

Scheme I



photolysis and trapped as I_2. (In a typical experiment, irradiation ($\lambda > 600$ nm) of 5.12 mg of $(Cp_2TiI)_2$ (8.4×10^{-6} mol) for 13 h produced 8.8×10^{-6} mol of I_2). When the benzene was removed from the irradiated solution, an air-sensitive green precipitate was left behind that was identical with the green precipitate formed when Cp_2TiI_2 is photolyzed in benzene under purging conditions.

In summary, we propose that Cp_2TiI_2 reacts according to the pathway in Scheme I. The key points are (1) the reactivity involves Ti–I bond cleavage and (2) the loss of the iodine atoms is stepwise with the intermediate formation of $(Cp_2TiI)_2$ in benzene or the formation of $Cp_2Ti(I)Cl$ in CCl_4. Iodide loss from $(Cp_2TiI)_2$ to give titanocene is possible with a purge of inert gas through the cell to remove I_2. Otherwise, the I_2 back reacts with the products and no net reaction occurs.

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Registry No. Cp_2TiI_2, 12152-92-0; $Cp_2Ti(I)Cl$, 12116-64-2; $(Cp_2TiI)_2$, 39333-90-9; $[Cp_2Ti(CH_3CN)_2][PF_6]_2$, 94518-22-6; Cp_2TiCl_2, 1271-19-8; Cp_2Ti, 1271-29-0; I_2, 7553-56-2; CH_2Cl_2, 75-09-2; $Tl[PF_6]$, 60969-19-9; acetonitrile, 75-05-8.

η^5-$C_5(CH_3)_5$ vs. η^5-C_5H_5. A Comparison of Electronic Influences for Metallocenes with *fac*-a_3b_2c, *fac*-a_3b_3, and *cis*-a_3b_2 Ligand Geometry Based on ^{59}Co NQR Spectroscopy

E. J. Miller, S. J. Landon, and T. B. Brill*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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^{59}Co NQR data from a series of complexes having *fac*-a_3b_2c, *fac*-a_3b_3, and *cis*-a_3b_2 geometry where a_3 is cyclopentadienyl (Cp) or pentamethylcyclopentadienyl ($CpMe_5$) show that $CpMe_5$ inductively donates more electron density than Cp, but the increase felt by the metal is small (<10%). This finding is consonant with conclusions drawn from photoelectron spectroscopy and MO calculations. The electronic effects in $CpCoI_2c$ complexes (c = unidentate donor ligands) having *fac*-a_3b_2c geometry are linear when $CpMe_5$ replaces Cp and are readily explained. The NQR spectra of $CpCo(bb')C_6H_4$ (b,b′ = O, S, N, Se) complexes having *cis*-a_3b_2 geometry are controlled mostly by the electronegativity of b,b′. Replacing Cp by $CpMe_5$ causes a nonlinear variation in the field gradient implying that the electronic structure of complexes with b = O and S differs somewhat from those with b = N. The temperature dependence of the coupling constant and asymmetry parameter of $CpMe_5Co(CO)_2$ reveals a phase transition at 177 K but does not indicate a change in the "allyl–ene" distortion of the Cp ring. The field gradient at Co in $CpCob_3$ complexes (b = unidentate donor ligand) is more sensitive to b than to replacement of Cp by $CpMe_5$. This sensitivity is utilized to demonstrate that $P(OCH_3)_3$ is a slightly better electron donor than $P(O)(OCH_3)_2^-$.

Introduction

Many situations arise in metallocene chemistry where it is advantageous to replace η^5-C_5H_5 (Cp) with η^5-$C_5(CH_3)_5$ ($CpMe_5$).[1] There is no dispute that the replacement of H by CH_3 alters the steric influence of the Cp ring and the solubility of the resultant complex. An increase in electron density along the metal–$CpMe_5$ bond axis can be expected as a result of inductive donation by CH_3. The basicity of the $CpMe_5^-$ ring toward H^+ is very much greater than that of Cp^-.[2] However, photoelectron spectroscopy studies[1] and MO calculations[3,4] suggest that the electron-releasing nature of the methyl groups is rather small. Moreover, reactions of the $CpMe_5Co^{2+}$ center suggest that the Co(III) site is still quite hard.[5] Differences in the reactivity of Cp vs. alkylated Cp complexes may relate more to the transition-state than the ground-state electronic effects.[6] Another perspective on the redistribution of electron density in metallocenes caused by replacing Cp with $CpMe_5$ as well as by other variations in the molecule evolves from ^{59}Co nuclear quadrupole resonance spectroscopy. Such a study is described here for three ligand geometries and concurs with the previous conclusion that the difference in the inductive electron donation by Cp and $CpMe_5$ is not particularly large.

Cp vs. $CpMe_5$. i. In *fac*-a_3b_2c Complexes. A surprisingly successful model of the electric field gradient (EFG) at cobalt in $CpCoI_2c$ complexes (c = a unidentate ligand) results from viewing the coordination sphere of Co as an octahedron with a geometry of *fac*-a_3b_2c.[7,8] The Cp

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