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Photochemical Consequences of the Manipulation of the Lowest Energy Excited States by Substitution of the Cp (Cp = η^5-C_5H_5) Ligands in Cp_2TiX_2 (X = Br, I) Complexes

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Photoelectron spectroscopic studies and molecular orbital calculations show that the lowest energy X → Ti and Cp → Ti charge-transfer transitions are close in energy in the Cp_2TiBr_2 and Cp_2TiI_2 complexes. In the Cp_2TiI_2 complex the I → Ti CT band is of lower energy than the Cp → Ti CT band, but the relative energies of these transitions can be reversed by substituting electron-releasing groups on the Cp rings. Thus, the $Cp^*{}_2TiI_2$ (Cp^* = η^5-$C_5(CH_3)_5$) complex has a lowest energy Cp → Ti CT excited state. The different lowest energy excited states in the Cp_2TiI_2 and $Cp^*{}_2TiI_2$ complexes are reflected in the photochemistry and electronic spectra of these molecules: Ti–I bond cleavage occurs upon irradiation of the Cp_2TiI_2 complex, but Ti–Cp bond cleavage results when the $Cp^*{}_2TiI_2$ complex is irradiated. The electronic spectra and photochemical reactivities of the $(MeCp)_2TiI_2$ and $Cp^{tms}{}_2TiI_2$ (Cp^{tms} = η^5-$C_5H_4Si(CH_3)_3$) complexes are essentially identical with those of the Cp_2TiI_2 complex. In the Cp_2TiBr_2 complex, the Cp → Ti CT excited-state energy is lower than the Br → Ti CT state energy. An attempt to reverse these relative energies by substituting the C(O)OCH$_3$ electron-withdrawing group on the Cp rings was unsuccessful. The electronic spectra and the photochemical reactivities of the Cp_2TiBr_2 and $Cp^{mc}{}_2TiBr_2$ (Cp^{mc} = η^5-$C_5H_4(C(O)OCH_3)$) complexes are identical; Cp–Ti bond cleavage occurs upon irradiation.

Introduction

A clear picture has emerged concerning the relative energies of the halide and cyclopentadienyl molecular orbitals in the Cp_2TiX_2 (X = F, Cl, Br, I; Cp = η^5-C_5H_5) complexes.[1-9] Figure 1 is a simplified molecular orbital diagram showing the relative energies of the Ti, halide, and Cp orbitals for these complexes; this figure is based on photoelectron spectroscopic studies[2] and SCF–Xα–SW molecular orbital calculations.[9] The line next to Ti represents the five unoccupied titanium d orbitals, while the lines next to Cp and X represent the set of occupied molecular orbitals of Cp and X character, respectively. The HOMO changes in character from primarily Cp in Cp_2TiF_2, Cp_2TiCl_2, and Cp_2TiBr_2 to primarily iodine in Cp_2TiI_2. Consistent with this diagram is the different photochemistry observed for these complexes: Cp radicals form when Cp_2TiCl_2 and Cp_2TiBr_2 are irradiated[3-6] while iodine atoms are produced when Cp_2TiI_2 is irradiated. Because the Cp and halide molecular orbitals are close in energy in the bromine and iodide complexes, we wondered whether the relative energies of the Cp and halide molecular orbitals could be reversed by appropriately substituting the Cp ligands. To answer this question, we placed electron-withdrawing substituents on the Cp ligands in Cp_2TiBr_2 and electron-donating substituents on the Cp ligands in Cp_2TiI_2. We hoped that this "electronic tuning" would lead to a change in the primary photoprocess of the substituted complexes by changing the character of the HOMO orbital and, thus, of the lowest energy excited state. The demonstration of such an effect has significance, in that the manipulation of molecular orbital energy levels is often cited as being very important for the optimization of catalytic systems.[10]

Experimental Section

Materials and Methods. All preparative and photochemical reactions were carried out under an argon or nitrogen atmosphere by using Schlenk techniques or a Vacuum Atmospheres drybox. All solvents were reagent grade and were dried over the appropriate drying agent and distilled under nitrogen.[11] $(MeCp)_2TiCl_2$ (Pressure Chemicals), chlorotrimethylsilane (Aldrich), *n*-butyllithium (Aldrich), $TiCl_4$ (Aldrich), BBr_3 (Aldrich, Gold Label), and dimethyl carbonate (Aldrich) were used as received. BI_3 (Aldrich) was purified[12] and nitrosodurene synthesized[13] by published procedures.

Electronic absorption spectra were recorded by use of a Cary 17 spectrophotometer. ^1H NMR spectra were obtained by use of a Varian XL-200 or a Bruker WM-250 instrument. ESR spectra were obtained by use of a Varian E-line spectrometer. Infrared spectra were obtained by use of a Perkin-Elmer 621 or a Perkin-Elmer 983 instrument. A 200-W Oriel high-pressure mercury arc lamp was used for the photochemical experiments and quantum yield measurements. A CS 2-62 Corning glass filter ($\lambda > 595$ nm) was used for all of the irradiations. Irradiation by using a CS 2-64 ($\lambda > 650$ nm) filter gave the same results as the CS 2-62 filter. However, experiments with the former filter frequently took up to 7 h; the latter filter was used in our experiments because it allows considerably more radiation to pass, and the irradiation times were therefore shortened. (Note that no wavelength-dependent photochemistry has ever been reported for any titanocene dihalide complex.) 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.[14] In general, photochemical reactions were monitored by ^1H NMR. Halide analyses were performed gravimetrically following precipitation as silver halide by addition of an aqueous solution of silver nitrate after digestion in nitric acid (acetone/H_2O).[15] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Unsubstituted Titanocene Halides: Cp_2TiX_2 (X = Cl, Br, I). Cp_2TiCl_2 (Alfa or Aldrich) was recrystallized from acetonitrile or benzene. Cp_2TiBr_2 and Cp_2TiI_2 were prepared by the method of Lappert et al.[12] and recrystallized from acetonitrile or toluene. The purity of the titanocene dihalides was confirmed by comparison of reported infrared,[12] electronic absorption,[1,7] and NMR[16] spectra.

General Synthetic Technique for Substituted Titanocene Halides. Lappert's general procedure[12] for preparing the halide-exchange products

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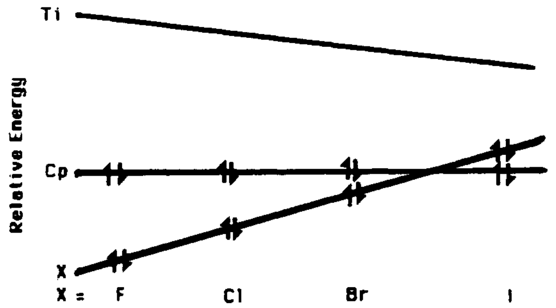

Figure 1. Simplified molecular orbital diagram of Cp_2TiX_2 complexes (X = F, Cl, Br, I) showing the relative energies of the Ti, Cp, and halide molecular orbitals. See Figure 2 in ref 9 for the complete set of molecular orbital diagrams.

Table I. ^1H NMR Data

compd	δ(H) C_5H_5	δ(H) other	solvent	ref
Cp_2TiCl_2	5.91		*a*	
Cp_2TiBr_2	5.98		*a*	
Cp_2TiI_2	6.08		*a*	
$CpTiCl_3$	7.25		*b*	17
$CpTiBr_3$	7.29		*b*	17
$CpTiI_3$	7.11		*b*	17
$MeCp_2TiI_2$	6.86 (t), 6.45 (t)	2.42	*d*	
$Cp^{mc}{}_2TiCl_2$	6.87 (t), 5.94 (t)	3.45	*a*	
$Cp^{mc}{}_2TiBr_2$	7.21 (m), 6.70 (m)	3.80	*b*	
$Cp^{mc}{}_2TiBr_2$	7.00 (m), 6.22 (m)	3.53	*c*	
$Cp^{mc}TiCl_3$	6.72 (t), 5.81 (t)	3.36	*a*	
$Cp^{tms}{}_2TiCl_2$	6.48 (t), 5.92 (t)	0.36	*a*	
$Cp^{tms}{}_2TiI_2$	6.97 (t), 6.27 (t)	0.26	*a*	
$Cp^{tms}TiCl_3$	6.48 (t), 6.18 (t)	0.14	*a*	
$Cp^{tms}TiI_3$	6.80 (t), 6.33 (t)	0.14	*a*	
$Cp^*{}_2TiCl_2$		1.86	*a*	
$Cp^*{}_2TiCl_2$		2.00	*d*	
Cp^*TiCl_3		2.37	*d*	
$Cp^*{}_2Ti(I)Cl$		1.95	*a*	
$Cp^*{}_2TiI_2$		2.06	*a*	
Cp^*TiI_3		2.09	*a*	

^{a} C_6D_6. ^{b} CD_3CN. ^{c} 50%/50% CCl_4/C_6D_6. ^{d} $CDCl_3$.

of Cp_2MCl_2 (M = Ti, Hf, Zr) complexes is easily extended to substituted cyclopentadienyl (Cp′) titanocene dichlorides (eq 1; X = Br, I). The

$$Cp'_2TiCl_2 + BX_3 \rightarrow Cp'_2TiX_2 + BCl_2X \qquad (1)$$

products are usually analytically pure because boron trihalides are easily removed under vacuum. Impurities that exist are either due to an incomplete reaction or the reaction going too far and forming $Cp'TiX_3$. That $Cp'TiX_3$ is a byproduct can be demonstrated by independent synthesis of the species. $Cp'TiCl_3$ is made by reacting 1 equiv of $TiCl_4$ with 1 equiv of Cp'_2TiCl_2. Further reaction of $Cp'TiCl_3$ (1 equiv) with the corresponding boron trihalide (1 equiv) affords $Cp'TiBr_3$ or $Cp'TiI_3$. In addition, adding LiCp′ to the $Cp'TiX_3$ affords Cp'_2TiX_2 (eq 2).

$$Cp'TiX_3 + LiCp' \rightarrow Cp'_2TiX_2 + LiX \qquad (2)$$

The preparations of substituted (cyclopentadienyl)titanocene dihalide complexes are included below when a specific workup was required or as generalized examples. Identification of new Cp'_2TiX_2 and $Cp'TiX_3$ complexes was made by using ^1H NMR (see Table I[17]).

Preparation of Bis((methoxycarbonyl)cyclopentadienyl)titanium Dihalides ($Cp^{mc}{}_2TiCl_2$ and $Cp^{mc}{}_2TiBr_2$; Cp^{mc} = η^5-$C_5H_4C(O)OCH_3$). $NaCp^{mc}$ was prepared by using dimethyl carbonate.[18] $TiCl_4$ (2.24 g, 1.2 × 10^{-2} mol) in benzene (40 mL) was added dropwise over 30 min to $NaCp^{mc}$ (3.70 g, 2.5 × 10^{-2} mol) in benzene (60 mL). Within 2 h, the solution turned deep red and a white-tan precipitate formed. The reaction was allowed to continue overnight, after which the solution was filtered leaving a brown precipitate and a burgundy-colored filtrate. The precipitate was rinsed with 400 mL benzene. The filtrates were combined and the solvent removed in vacuo, leaving a reddish brown oil. Benzene (30 mL) was added to redissolve the oil. The solvent was slowly removed in vacuo (≈half the original volume of benzene) until orange crystals were observed. The solution was filtered and dried, yielding $Cp^{mc}{}_2TiCl_2$ (310 mg, 7%). For NMR data see Table I. IR (Nujol mull): ν(C≡O) = 1722 cm^{-1}.[19] Anal. Calcd for $C_{14}H_{14}O_4TiCl_2$: Cl, 19. Found: Cl, 18.

$Cp^{mc}{}_2TiCl_2$ (0.195 g, 5.3 × 10^{-4} mol) was stirred in CH_2Cl_2 (30 mL) giving an orange slurry. BI_3 (2.0 mL, 1.0 M in CH_2Cl_2) was diluted with CH_2Cl_2 (8 × 10^{-2} M), and then 8.0 mL of the diluted solution was added to the orange slurry. The mixture immediately turned dark red. The reaction was allowed to continue for 10 min after which time the solvent was removed in vacuo, yielding large burgundy-colored crystals (205 mg, 85%). For NMR data see Table I. IR (Nujol mull): ν(C≡O) = 1724 cm^{-1}.

Preparation of Bis((trimethylsilyl)cyclopentadienyl)titanium Dihalides ($Cp^{tms}{}_2TiCl_2$ and $Cp^{tms}{}_2TiI_2$; Cp^{tms} = η^5-$C_5H_4Si(CH_3)_3$). Cp^{tms} and $LiCp^{tms}$ were prepared by using the methods of Kraihanzel and Losee[20] and Lappert,[12] respectively. A solution of $TiCl_4$ (1.3 mL, 11.8 mmol) in benzene (60 mL) was added dropwise over 30 min to $LiCp^{tms}$ (3.66 g, 25.3 mmol) in benzene (100 mL). The solution darkened during this period from light tan/brown to dark red. The solution was stirred overnight, then filtered, washed (benzene), and dried, yielding $Cp^{tms}{}_2TiCl_2$ (4.55 g, 11.5 mmol, 98%). For NMR data see Table I.

BI_3 (0.5 g, 1.3 mmol) in benzene (10 mL) was added to a solution of $Cp^{tms}{}_2TiCl_2$ (0.5 g, 1.3 mmol) over 5 min. The dark red solution turned red-black. The reaction was allowed to stir for 5 min, and then the solvent was removed in vacuo, yielding dark black crystals. For NMR data see Table I. Anal. Calcd for $C_{16}H_{26}Si_2TiI_2$: C, 33.4; H, 4.55; I, 44.0. Found: C, 32.5; H, 4.72; I, 42.0.

Preparation of Bis(pentamethylcyclopentadienyl)titanium Diiodide ($Cp^*{}_2TiI_2$; Cp^* = η^5-$C_5(CH_3)_5$). $Cp^*{}_2TiCl_2$ (Strem, 0.39 g, 0.77 mmole in CH_2Cl_2 (20 mL) was stirred while a solution of boron triiodide (0.322 g, 0.85 mmol) in CH_2Cl_2 (30 mL) was added dropwise. The solution color turned from bright red to deep purple almost immediately. The solution was stirred for 15 min at room temperature and then the solvent was removed *in vacuo* affording dark black crystals of $Cp^*{}_2TiI_2$ (*90%). For NMR data see Table I.

Measurement of Halogen Loss during Photolysis of Cp'_2TiX_2 (X = Br, I) in Benzene. A known amount of sample (typically ≈5 mg) was introduced into a 500-mL three-necked flask fitted with a Kontes universal adapter and a 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 (≈300 mL) was added to the flask, the argon flow turned up to produce turbulent bubbling, and the irradiation ($\lambda > 595$ nm) begun. Periodically, the irradiation was stopped and the 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 or bromine by electronic absorption spectroscopy (for iodine; λ = 500 nm (ϵ = 1040 M^{-1} cm^{-1});[21] for bromine, λ = 400 nm ($\epsilon \approx$ 175 M^{-1} cm^{-1}).[21]

Photolysis of Cp'_2TiX_2 (X = Br, Cl) in Halocarbon/Benzene Solutions. A solution of Cp'_2TiX_2 (3.0–9.8 mM) in halocarbon/C_6D_1 (50%/50%) was prepared, and aliquots were transferred to two screw-cap NMR tubes. One solution was irradiated ($\lambda > 595$ 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 (every 5–10 min). The ^1H NMR spectra were then recorded. The ^1H NMR of the thermal blank was recorded both before and after irradiation. The concentrations of the titanocene dihalides were calculated by using benzene as an internal standard.

Nitrosodurene Spin-Trapping Experiments. A solution of the complex (5 × 10^{-3} to 5 × 10^{-4} M) to be tested was prepared in an appropriate solvent with the nitrosodurene (5 × 10^{-3} to 5 × 10^{-4} M), placed in a ESR tube and sealed. The tube was then placed in the ESR spectrometer cavity and a baseline taken at the temperature to be investigated (−23 to −100 °C). The solution was then irradiated (in the ESR cavity) by using an appropriate wavelength cutoff filter. Spectra were recorded while the sample was being irradiated. The irradiations lasted up to 60 min.

Results and Discussion

When electron-withdrawing groups are placed on the Cp ligands in Cp_2TiBr_2, the overall effect will be to stabilize those molecular

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Table II. Summary of Photolysis Experiments for $Cp^{sub}_2TiX_2$ Complexes

complex	photochemistry: ESR Cp-ND[a] signal?	halogen evolved?	other reacns
Cp_2TiBr_2	yes	no	$Cp_2TiBr_2 \xrightarrow[CCl_4]{h\nu} CpTi(Br_2)Cl$
$Cp^{mc}_2TiBr_2$	yes	no	$Cp^{mc}_2TiBr_2 + Cp_2TiBr_2 \xrightarrow{h\nu} 2Cp^{mc}CpTiBr_2$
Cp_2TiI_2	no	yes, I_2	$Cp_2TiI_2 \xrightarrow[CCl_4]{h\nu} Cp_2Ti(I)Cl$
$MeCp_2TiI_2$	no	yes, I_2	
$Cp^{tms}_2TiI_2$	no	yes, I_2	
$Cp^*_2TiI_2$	yes	no	$Cp^*_2TiI_2 \xrightarrow[CHI_3]{h\nu} Cp^*TiI_3$

[a] Presence of the ESR cyclopentadienyl–nitrosodurene (ND) spin adduct.

Table III. Electronic Absorption Spectra of Titanocene Dihalide Complexes

complex	λ, nm (ε M^{-1} cm^{-1})		
Cp_2TiF_2[a,26]	322 (4100)	392 (400)	
Cp_2TiCl_2[b]	388 (2200)	516 (200)	
$MeCp_2TiCl_2$[b]	390	523	
$Cp^{mc}_2TiCl_2$[b]	389	514	
$Cp^{tms}_2TiCl_2$[b]	390	530	
Cp_2TiBr_2[a,26]	429 (3400)	549 (250)	
$Cp^{mc}_2TiBr_2$[b]	436	545	
Cp_2TiI_2[b]	512 (2600)	595 (720)	665 sh (390)
$(MeCp)_2TiI_2$[b]	505	595	660 sh
$Cp^{tms}_2TiI_2$[b]	505 sh	600 sh	
$Cp^*_2TiI_2$[b]	523 (2900)	600 sh (1200)	

[a] In methylene chloride. [b] In benzene.

orbitals that are primarily Cp in character. If sufficient stabilization occurs, the relative ordering of bromine and Cp orbitals may change, resulting in a different HOMO. This reversal in energies would have the overall effect of changing the character of the lowest energy excited state and, in turn, the primary photoprocess. The same argument can be made for changing the HOMO in Cp_2TiI_2 except that electron-donating groups are used instead of electron-withdrawing groups. Recent photoelectron spectroscopic studies have quantified this effect in related complexes.[22,23] For example, the vertical ionization energies of $Cp'MX_3$ complexes (Cp′ = Cp, $CH_3C_5H_4$, or $(CH_3)_5C_5$; M = Ti, Zr, Hf; X = Cl, Br) were measured and it was found that permethylation of Cp (in $CpTiCl_3$) decreases the ionization energies of the Cp e molecular orbital by 0.92 eV with respect to the unsubstituted Cp complex. The halide molecular orbitals also decrease in energy but by much less (≈0.38 eV). Thus, the overall effect in the permethylated complex is to destabilize the Cp* molecular orbitals by 0.54 eV vs. the halide molecular orbitals.

The complexes that were synthesized and investigated photochemically in our study are given in Table II. (The $(MeCp)_2TiI_2$ complex is the only Cp-substituted bromide or iodide complex whose synthesis has been previously reported.[24]) Two complementary photochemical experiments were used to determine whether Cp ligands or halide ligands are dissociated during photolysis of the Cp'_2TiX_2 complexes. The first was an ESR spin-trapping experiment that used the spin-trapping reagent nitrosodurene to determine whether Cp radicals were formed during the irradiation. The second technique was a quantitative measure of the amount of halogen evolved during the irradiation (see Experimental Section for details).

Irradiation (λ > 595 nm) of unsubstituted Cp_2TiBr_2 in the presence of nitrosodurene shows an easily detectable ESR signal at room temperature (1:2:2:1; $g = 2.007$) and halogen-trapping experiments indicated that no bromine gas was released upon irradiation. In addition, photolysis of Cp_2TiBr_2 in the presence of carbon tetrachloride shows evidence (by NMR) of the formation of $CpTiBr_2Cl$.[1] These results are consistent with a Cp → Ti charge-transer lowest energy excited state.[25] Substitution by the electron-withdrawing methoxycarbonyl group on the Cp ligands in Cp_2TiBr_2 should stabilize the Cp ligands in comparison with the unsubstituted complex. However, the irradiation of $Cp^{mc}_2TiBr_2$ results in a photochemistry which is identical with that of the Cp_2TiBr_2 complex; i.e., no bromine forms and the Cp^{mc}–nitrosodurene adduct is observed by ESR (1:2:2:1; $g = 2.014$). We conclude that the methoxycarbonyl group does not stabilize the Cp molecular orbitals enough to reverse the relative energies of the Cp and Br orbitals. Therefore, the character of the lowest energy excited state is not changed, and the primary photoprocess remains Cp–Ti bond cleavage. The inability of the methoxycarbonyl group to change the electronic structure of the Cp_2TiBr_2 complex significantly is reflected in the electronic spectra of the two complexes: they are essentially identical (Table III).

Recall that the photochemistry of the Cp_2TiI_2 complex is very different from that of the fluoride, chloride, and bromide complexes.[7] Irradiation of Cp_2TiI_2 in the presence of nitrosodurene does not produce the Cp–nitrosodurene adduct, and halogen-trapping at low temperature showed that iodine is released. In fact, all of the iodine originally present in the Cp_2TiI_2 complex can be trapped and detected as molecular iodine.[7] In addition, NMR experiments showed that the photolysis of Cp_2TiI_2 in the presence of carbon tetrachloride forms $Cp_2Ti(I)Cl$.[7] These results are consistent with a primary photoprocess which is Ti–I bond cleavage and a lowest energy I → Ti charge-transfer excited state.[25]

Methyl and trimethylsilyl substituents on the Cp ligands in Cp_2TiI_2 should destabilize the Cp ligands in comparison with the unsubstituted complex.[23] However, irradiation of $(MeCp)_2TiI_2$ or $Cp^{tms}_2TiI_2$ results in a photochemistry which is identical with that of Cp_2TiI_2; i.e., molecular iodine is evolved and the Cp–nitrosodurene spin adduct is not observed. Therefore, it appears that substitution by a single methyl or trimethylsilyl group does not significantly destabilize the Cp′ molecular orbitals relative to the iodine molecular orbitals. The inability of the methyl and trimethylsilyl groups to significantly alter the electronic structure of the Cp_2TiI_2 complex is again reflected in the electronic spectra of the complexes: the Cp_2TiI_2, $(MeCp)_2TiI_2$, and $Cp^{tms}_2TiI_2$ complexes have spectra that are all essentially identical (Table III).

Photolysis of $Cp^*_2TiI_2$, however, does result in photochemistry which is quite different from that of the Cp_2TiI_2 complex. Halogen-trapping experiments (up to 5 h; λ > 595 nm) indicate that no molecular iodine is released upon irradiation of $Cp^*_2TiI_2$. ESR spin-trapping experiments with nitrosodurene are consistent with the formation of Cp* because a triplet with $g = 2.00$ is observed at room temperature. In addition, irradiation of $Cp^*_2TiI_2$ in the presence of iodoform forms Cp^*TiI_3, identified by comparison to an authentic sample. These results are consistent with photodissociation of Cp from the complex, implying a lowest energy Cp* → Ti charge-transfer excited state. Thus, it appears that substitution of Cp by five methyl groups reverses the relative energies of the Cp* → Ti and I → Ti CT bands in the Cp_2TiI_2 and $Cp^*_2TiI_2$ complexes. The switch in relative energies is reflected in the electronic spectra of these complexes. The discussion that follows examines this point and discusses the electronic spectra

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(25) SCF-Xα-SW molecular orbital calculations[9] showed that irradiation of Cp_2TiX_2 (X = F, Cl, Br) weakens the Ti–Cp bond because the lowest energy transition is Cp → Ti charge-transfer and a Ti–Cp bonding orbital is depopulated in the lowest energy excited state ($10b_2 \rightarrow 14a_1$; $^1A_1 \rightarrow {}^1B_2$). In contrast, irradiation of Cp_2TiI_2 at low energy weakens the Ti–I bond because (1) the lowest energy transition is I → Ti charge transfer and (2) a Ti–I bonding orbital is depopulated ($8b_1 \rightarrow 14a_1$; $^1A_1 \rightarrow {}^1B_1$).

(26) Dias, A. N. *Rev. Port. Quim.* **1971**, *13*, 222–235.

Figure 2. Electronic spectra of Cp_2TiI_2 (---) and $Cp^*{}_2TiI_2$ (—) in benzene solution. The absorbance scale is relative; see Table III for ϵ values.

of the Cp_2TiX_2 complexes in general.

The electronic spectra of the Cp_2TiX_2 (X = F, Cl, Br, I) complexes are summarized in Table III. (The spectra of the fluoride, chloride, and bromide complexes are pictured in Figure 1 of ref 1. The spectrum of the iodide complex is shown in Figure 2 of this paper. Both figures are helpful in understanding the discussion that follows.) The spectra of the fluoride, chloride, and bromide complexes are similar in that there is a weak band at lowest energy and an intense band at higher energy. Both bands in these complexes have been previously assigned as Cp → Ti charge-transfer bands.[9] Note the red shift in both bands along the series Cp_2TiF_2, Cp_2TiCl_2, and Cp_2TiBr_2. (The reason for the red shift has been previously discussed.[9]) The intense band is also clearly present in the iodide complex; it has approximately the same extinction coefficient ($\epsilon = 2600\ M^{-1}\ cm^{-1}$) as the intense bands in the fluoride, chloride, and bromide complexes, and it falls into the red-shifted pattern in the sequence fluoride (322 nm), chloride (388 nm), bromide (429 nm), and iodide (512 nm). It is logical therefore to assign the intense band at 512 nm in the iodide complex as a Cp → Ti CT band.

The electronic spectrum of the Cp_2TiI_2 complex differs from those of the other titanocene dihalide complexes by having two features to lower energy of the intense Cp → Ti CT band (Figure 2). Specifically, the Cp_2TiI_2 complex has a band at 595 nm and a shoulder at 665 nm. Either of these features falls into the red-shifted pattern of the weak bands in the other complexes (fluoride, 392 nm; chloride, 516 nm; bromide, 549 nm), and, thus, on the basis of this trend, it is not possible to conclude which of the two features is the counterpart of the weak, lowest energy bands in the other complexes. However, the distinctly different photochemical behavior of the Cp_2TiI_2 complex compared with the other complexes suggests that the lowest energy excited state in the iodide complex is I → Ti CT rather than Cp → Ti CT in character. PES[8] and SCF–Xα–SW molecular orbital calculations[9] also support our assignment of an I → Ti CT transition to the 665-nm shoulder. Consequently, the band at 595 nm is assigned as the counterpart of the Cp → Ti (lowest energy) bands in the other titanocene dihalide complexes. Additional support for these assignments can be drawn from a comparison of the spectra of Cp_2TiI_2 and $Cp^*{}_2TiI_2$. As Figure 2 shows, the shoulder at 665 nm in the electronic spectrum of Cp_2TiI_2 is absent in the spectrum of $Cp^*{}_2TiI_2$; however, the band at 595 nm is still present (as a shoulder at ≈600 nm) in the $Cp^*{}_2TiI_2$ complex. We suggest that substitution of the Cp ligands by five methyl groups raises the energy of the I → Ti CT transition, and, hence, it is no longer observable. (Similarly, the lowest energy Cp → Ti CT band should red shift in going from Cp_2TiI_2 to $Cp^*{}_2TiI_2$. Although it is difficult to locate the exact position of the low-energy shoulder (at ≈600 nm) in the $Cp^*{}_2TiI_2$ complex, it seems certain that any red shift is small.) In summary, our assignments of the electrtonic spectra of the Cp_2TiI_2 and $Cp^*{}_2TiI_2$ complexes are given as follows. For Cp_2TiI_2: 512 nm, Cp → Ti CT; 595 nm, Cp → Ti CT; 665 nm, I → Ti CT. For $Cp^*{}_2TiI_2$: 523 nm, Cp → Ti CT; 600 nm, Cp → Ti CT.

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Registry No. $Cp^{mc}{}_2TiCl_2$, 88242-71-1; $NaCp^{mc}$, 102261-46-1; $TiCl_4$, 7550-45-0; $LiCp^{tms}$, 76514-39-1; $Cp^{tms}{}_2TiCl_2$, 59307-41-4; BI_3, 13517-10-7; $Cp^{tms}{}_2TiI_2$, 82696-63-7; $Cp^*{}_2TiI_2$, 102261-42-7; $Cp^*{}_2TiCl_2$, 11136-36-0; Cp_2TiCl_2, 1271-19-8; Cp_2TiBr_2, 1293-73-8; Cp_2TiI_2, 12152-92-0; $(MeCp)_2TiI_2$, 72622-33-4; $Cp^{mc}{}_2TiBr_2$, 102261-43-8; Cp^*TiCl_3, 12129-06-5; $Cp^{mc}TiCl_3$, 102261-44-9; Cp^*TiI_3, 102261-45-0; $Cp^{tms}TiI_3$, 75583-72-1; $(MeCp)_2TiCl_2$, 1282-40-2.