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Photochemistry and Electronic Structure of the $(\eta^5\text{-}C_5H_5)_2TiS_5$ Complex

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Abstract: The Cp_2TiS_5 complex (Cp = η^5-C_5H_5) is photochemically quite unreactive. The complex does not react with acetylenes, CO, phosphites, or amines at either high- or low-energy irradiation wavelengths. The complex does react with halocarbons to afford Cp_2TiX_2 (X = halide) and it reacts with organic disulfides (RSSR) to give $Cp_2Ti(SR)_2$ complexes. However, the quantum yields for these reactions are quite low (e.g., $\phi_{366} = 6 \times 10^{-3}$ for the reaction with CCl_4; $\phi_{366} = 2 \times 10^{-3}$ for the reaction with PhSSPh). Flash photolysis of the complex produces a transient that decays by first-order kinetics ($k = 2 \times 10^4$ s^{-1}). The transient is proposed to be a species in which a single Ti–S bond has been cleaved. Rapid reformation of the Ti–S bond is suggested to be the reason for the photochemical inertness of the complex. Self-consistent-field-Xα-scattered-wave calculations show that the lowest energy excited states are S → Ti charge transfer in nature. Cleavage of a Ti–S bond as a primary photoprocess is shown to be consistent with the orbitals involved in these excitations.

As part of our photochemical study of the ligand-to-metal charge-transfer excited states of organometallic complexes, we investigated the reactivity of the S → Ti charge-transfer (CT) excited states of the Cp_2TiS_5 complex. Cp_2TiS_5 was chosen for our initial study of S → M CT reactivity because it is a Ti(IV) complex and will thus have no d–d excited states to interfere with the LMCT excited states. In addition, Cp_2TiS_5 is a logical choice for a first study because it is a well-characterized molecule. Samuel first prepared the complex in 1966 by reacting Cp_2TiCl_2 with $(NH_4)_2S_5$.[1] Several other thermal and photochemical syntheses have since been developed.[2] X-ray crystallographic studies show that in the solid state the six-membered TiS_5 ring is in a chair conformation, analogous to the chair conformer of cyclohexane.[3] The chair structure of the ring is maintained in solution as the Cp rings are inequivalent in the room temperature NMR spectrum of the complex. NMR methods have also been used to measure the activation parameters of the TiS_5 ring-inversion process.[4]

In addition to the structural studies mentioned above, considerable work has been done on the reaction chemistry of the Cp_2TiS_5 complex. Cp_2TiS_5 has been used as an S_5 transfer agent in the synthesis of a variety of sulfur rings, e.g., S_7.[5] Recently, Rauchfuss et al. have published extensive studies on the thermal reactions of Cp_2TiS_5 with phosphines and acetylenes.[6] Finally, we note that Peterson and Dahl performed a Fenske–Hall-type molecular orbital calculation on the Cp_2TiS_5 complex.[7]

Table I. ^{1}H NMR Data

compd	C_5H_5	other resonances	ref
Cp_2TiS_5	6.51, 6.18		*a*, *d*
	6.37, 6.03		*b*, *d*
	5.56, 5.50		*c*, *d*
Cp_2TiCl_2	6.67		*a*, *d*
	6.54		*b*, *d*
	5.91		*c*, *d*
$CpTiCl_3$	7.21		*a*, 16
	7.08, 6.81		*a*, 17
	7.20, 7.11		*a*, 18
	6.22, 5.94		*c*, 18
Cp_2TiBr_2	6.65		*b*, *d*
$Cp_2Ti(SC_6H_5)_2$	6.15	7.61, 7.44, (m, SC_6H_5) 7.25	*a*, *d*
	5.66	7.89, 7.15, (m, SC_6H_5) 6.98	*c*, *d*
$Cp_2Ti(SC_2H_5)_2$	6.21	3.18 (q, SCH_2CH_3) 1.30 (t, SCH_2CH_3)	*a*, *d*
$C_6H_5SSC_6H_5$		7.59 (m) 7.45–7.28 (m)	*a*, *d*
		7.4 (m) 6.92–6.78 (m)	*c*, *d*
$C_2H_5SSC_2H_5$		2.53 (q, SCH_2CH_3) 1.25 (t, SCH_2CH_3)	*a*, 19

[a] ppm in CCl_4. [b] ppm in $BrCCl_3$. [c] ppm in C_6D_6. [d] This work.

Experimental Section

Materials and Methods. All preparative and photochemical reactions were done under an argon or nitrogen atmosphere by using a combination of Schlenk techniques, a Vacuum Atmosphere drybox, and a glovebag. All solvents were of reagent grade, dried over the appropriate drying agent, and distilled under nitrogen.[8] Acetonitrile, benzene, cyclohexane, toluene, and triethylamine were dried over CaH_2. Dichloromethane, chloroform, bromotrichloromethane, and carbon tetrachloride were dried over P_2O_5. Acetone was dried over K_2CO_3. Tetrahydrofuran was dried over $LiAlH_4$. Deuterated NMR solvents were purchased from Aldrich, except chloroform-*d*, which was purchased from Norell Inc. Benzene-d_6 and chloroform-*d* were dried over molecular sieves; acetonitrile-d_3 and Me_2SO-d_6 were purchased in sealed ampules and used as received. Superhydride (lithium triethylborohydride) was purchased from Aldrich as a 1 M solution in THF. Diphenylacetylene, dimethylacetylenedicarboxylate, thiophenol, ethanethiol, triphenylchloromethane, triethyl phosphite, and trimethyl phosphite were purchased from Aldrich and used as received. Diphenyl disulfide was purchased from Aldrich and recrystallized from methanol.[8] Tetrabutylammonium chloride was purchased from Aldrich and recrystallized in the drybox from acetone and anhydrous diethyl ether. Crystalline sulfur was purchased from Fluka Chemical Corp. and used as received. Cp_2TiCl_2 was purchased from Alfa and recrystallized from acetonitrile. $CpTiCl_3$ was purchased from Strem and purified by vacuum sublimation (110 °C, 0.05 mm). Cp_2TiS_5,[2e] $Cp_2Ti(SPh)_2$,[9] $Cp_2Ti(SEt)_2$,[10] and Cp_2TiBr_2[11] were prepared according to published procedures.

Electronic absorption spectra were recorded on a Cary 17 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian XL 200-MHz

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or a Bruker WM 250-MHz instrument. ESR spectra were obtained on a Varian E-line spectrometer. Infrared spectra were obtained with a Perkin-Elmer 621. Flash photolysis experiments were done with a Lambda Physik Excimer Laser (308 nm, 15 ns), as previously described.[12] A 200-W Oriel mercury arc lamp was used for the photochemical experiments and quantum yield measurements. Corning glass filters (3-68, $\lambda > 530$ nm; 3-72, $\lambda > 450$ nm; 7-83, $\lambda = 366$ nm), interference filters from Edmund Scientific, and a potassium chromate filter solution (313 nm)[13] 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 disappearances of Cp_2TiS_5, $Cp_2Ti(SPh)_2$, and $Cp_2Ti(SEt)_2$ were monitored at 490, 545, and 540 nm, respectively. The lamp intensity was measured by ferrioxalate actinometry[14] for wavelengths <400 nm and by Reinecke's salt actinometry[15] for wavelengths >400 nm. In general, photochemical reactions were monitored by ^1H NMR. Reaction products were identified by comparison with spectra of the actual compounds in the appropriate solvents or with reported spectra (Table I). In all experiments, the spectrum of a "dark reaction" was recorded as a control.

Irradiation of Cp_2TiS_5 in CCl_4. (A) A 3.0 mM solution of Cp_2TiS_5 in carbon tetrachloride (1.5 mL) was irradiated ($\lambda > 450$ nm) for 2 h. The color of the solution changed from red to light orange and a small amount of pale yellow precipitate formed. The solution was transferred in a glovebag to the outer cell of a coaxial NMR tube which contained benzene-d_6 in the inner cell for the instrument lock. ^1H NMR δ 6.69 (Cp in Cp_2TiCl_2), 6.51, 6.18 (Cp in Cp_2TiS_5). The amount of Cp_2TiCl_2 formed was approximately equal to the amount of Cp_2TiS_5 still present. (B) A 3.0 mM solution of Cp_2TiS_5 in CCl_4 (1.5 mL) was irradiated in a quartz cuvette at 313 nm for 3 h. The color of the solution did not change. The solution was transferred to a coaxial NMR tube as described above. The spectrum showed that in addition to the products formed by the low-energy irradiation above, $CpTiCl_3$ was also formed. ^1H NMR δ 6.80 (Cp in decomposition product of $CpTiCl_3$) (see Table I), 6.67 (Cp in Cp_2TiCl_2), 6.50, 6.16 (Cp in Cp_2TiS_5). In addition, there were two minor products with resonances at δ 6.69 and 6.65 which formed in both of these experiments.

Irradiation of Cp_2TiS_5 in $BrCCl_3$. A 5.0 mM solution of Cp_2TiS_5 in $BrCCl_3$ (1.5 mL) was irradiated in a quartz cuvette at 313 nm for 2.25 h. The color of the solution changed from dark red to red-orange. The solution was transferred to a coaxial NMR tube as described above. ^1H NMR δ 6.64 (Cp in Cp_2TiBr_2), 6.36, 6.01 (Cp in Cp_2TiS_5). There were also two minor products with resonances at δ 6.58 and 6.48; neither of these is Cp_2TiCl_2 (see Table I).

Irradiation of Cp_2TiS_5 with Ph_3CCl. Cp_2TiS_5, 3.2 mg (9.4×10^{-6} mol), and 21.7 mg (7.8×10^{-5} mol) of Ph_3CCl were dissolved in 1 mL of benzene-d_6. The solution was irradiated at 313 nm for 4 h. The color of the solution changed from dark red to orange, and a small amount of pale yellow precipitate formed. ^1H NMR δ 7.4–7.3, 7.1–6.9 (m, Ph in Ph_3CCl), 6.22, 5.93 (Cp in $CpTiCl_3$, see Table I), 5.91 (Cp in Cp_2TiCl_2), 5.56, 5.50 (Cp in Cp_2TiS_5).

Irradiation of Cp_2TiS_5 with Cl^-. Cp_2TiS_5, 1.4 mg (4.4×10^{-6} mol), and 15 mg (4.7×10^{-5} mol) of Bu_4NCl were dissolved in 1 mL of acetonitrile-d_3. The solution was irradiated at 313 nm for 3.25 h. The solution became slightly cloudy but the ^1H NMR spectrum showed only the Cp resonances for Cp_2TiS_5 and the tetrabutylammonium resonances. There was no resonance for Cp_2TiCl_2.

Irradiation of Cp_2TiS_5 with Acetylenes. (A) Cp_2TiS_5, 3.5 mg (1.0×10^{-5} mol), and 36.1 mg (2.0×10^{-4} mol) of $PhC{\equiv}CPh$ were dissolved in 1 mL of benzene-d_6. The solution was irradiated ($\lambda > 450$ nm) for 3.25 h. The ^1H NMR spectrum of the irradiated solution indicated that there was no photochemical reaction as the only resonances present in the Cp region are due to Cp_2TiS_5. (B) The reaction was repeated with a 30-fold excess of $CH_3O_2CC{\equiv}CCO_2CH_3$. The ^1H NMR spectrum again indicated that there was no photochemical reaction with Cp_2TiS_5.

Irradiation of Cp_2TiS_5 with Phosphites. (A) $P(OCH_3)_3$, 6.7 μL (5.5×10^{-5} mol), was added to 6 mg (1.8×10^{-5} mol) Cp_2TiS_5 in 2 mL of benzene-d_6. (Only 3 equiv of phosphite were added to minimize the thermal abstraction of sulfur by the phosphite.) The solution was irradiated at 313 nm for 2 h. ^1H NMR δ 5.57, 5.50 (Cp in Cp_2TiS_5), 3.27 (d, $J_{P-H} = 10$ Hz, CH_3 in $P(OCH_3)_3$), 3.32 (d, $J_{P-H} = 11$ Hz, CH_3 in $SP(OCH_3)_3$). There was no resonance for $Cp_2Ti[P(OCH_3)_3]_2$: ^1H NMR (C_6D_6) δ 4.42 (t, $J_{P-H} = 2$ Hz, Cp), 2.93 (d, $J_{P-H} = 10$ Hz, CH_3).[20] (B) The reaction was repeated with $P(OC_2H_5)_3$. The ^1H NMR spectrum of the irradiated solution showed that $SP(OC_2H_5)_3$ formed in the photochemical reaction, but there were no new Cp resonances to indicate that the phosphite had coordinated to the titanium.

Irradiation of Cp_2TiS_5 with Amines. (A) Cp_2TiS_5, 4.5 mg (1.3×10^{-5} mol), and 11.7 mg (7.5×10^{-5} mol) of bipyridine were dissolved in 1.5 mL of benzene-d_6. The solution was irradiated at 313 nm for 2.67 h. The ^1H NMR spectrum of the irradiated solution showed only the free bipyridine resonances and the Cp resonances in Cp_2TiS_5. ($Cp_2Ti(bpy)$ is weakly paramagnetic.[21]) (B) Similar reactions were done with pyridine and triethylamine. Again, the ^1H NMR spectra indicated that there was no photochemical reaction of Cp_2TiS_5 with these amines.

Irradiation of Cp_2TiS_5 with CO. This reaction was monitored by infrared spectroscopy. Cp_2TiS_5, 12.8 mg (3.8×10^{-5} mol), was dissolved in 4 mL of benzene. The solution was saturated with carbon monoxide at atmospheric pressure and it was irradiated at 313 nm for a total of 3 h. The infrared spectra of aliquots from the reaction solution were recorded periodically during this time. No bands attributable to coordinated CO were observed. ($Cp_2Ti(CO)_2$, ν(CO) = 1975 and 1897 cm^{-1} [22]). The solvent was removed in vacuo and the residue was dissolved in benzene-d_6. The ^1H NMR spectrum showed only the Cp resonances due to Cp_2TiS_5. ($Cp_2Ti(CO)_2$: ^1H NMR (C_6D_6) δ 4.58 (Cp).[22])

Irradiation of Cp_2TiS_5 with PhSSPh. Cp_2TiS_5, 5.0 mg (1.5×10^{-5} mol), and 55 mg of PhSSPh (2.5×10^{-4} mol) were dissolved in 1.5 mL of benzene-d_6. The solution was irradiated ($\lambda > 450$ nm) for 1.5 h. ^1H NMR δ 7.4, 7.0–6.8 (m, Ph in PhSSPh), 5.657 (Cp in $Cp_2Ti(SPh)_2$), 5.56, 5.49 (Cp in Cp_2TiS_5). The integrated area of the Cp resonance for $Cp_2Ti(SPh)_2$ was approximately 15% of the Cp resonances for Cp_2TiS_5.

Irradiation of $Cp_2Ti(SPh)_2$ in CCl_4. (A) A 6.1 mM solution of $Cp_2Ti(SPh)_2$ (0.5 mL) was irradiated ($\lambda > 530$ nm) for 6 min. The color of the solution changed from dark purple to pale purple. ^1H NMR δ 7.6, 7.45–7.3 (m, Ph in $Cp_2Ti(SPh)_2$), 7.6, 7.45–7.3 (m, Ph in PhSSPh), 6.80 (Cp in $CpTiCl_3$, see Table I), 6.67 (Cp in Cp_2TiCl_2), 6.16 (Cp in $Cp_2Ti(SPh)_2$). The amount of Cp_2TiCl_2 formed was approximately 3 times greater than the amount of $Cp_2Ti(SPh)_2$ still present. (B) A 6.1 mM solution of $Cp_2Ti(SPh)_2$ (0.5 mL) was irradiated ($\lambda > 530$ nm) for 13 min, and the solution turned light yellow. The ^1H NMR spectrum of the irradiated solution showed resonances for Cp_2TiCl_2, $CpTiCl_3$, and PhSSPh. The resonances for $Cp_2Ti(SPh)_2$ were completely gone. In addition, there were two minor products with resonances at δ 6.69 and 6.60 which formed in both of these experiments.

Irradiation of $Cp_2Ti(SPh)_2$ with Cl^-. $Cp_2Ti(SPh)_2$, 2.5 mg (6.3×10^{-6} mol), and 10–15 mg (5–8.5 equiv) of Bu_4NCl were dissolved in 1.5 mL of benzene-d_6 and the solution was irradiated ($\lambda > 530$ nm). After 15 min of irradiation there was no change in the ^1H NMR spectrum. After a total of 3.25 h, the ^1H NMR spectrum showed that PhSSPh and $Cp_2Ti(SPh)_2$ were present, but no Cp_2TiCl_2 had formed. (PhSSPh formed when $Cp_2Ti(SPh)_2$ was irradiated in benzene-d_6.)

Irradiation of $Cp_2Ti(SEt)_2$ in CCl_4. A 9.3 mM solution of $Cp_2Ti(SEt)_2$ (0.5 mL) in CCl_4 was irradiated ($\lambda > 530$ nm) for 10 min. ^1H NMR δ 6.81 (Cp in $CpTiCl_3$, see Table I 6.68 (Cp in Cp_2TiCl_2), 3.4 (q, CH_2 in $CH_3CH_2SSCH_2CH_3$), 1.65 (t, CH_3 in $CH_3CH_2SSCH_2CH_3$). All of the $Cp_2Ti(SEt)_2$ had reacted.

Irradiation of $Cp_2Ti(SEt)_2$ with Cl^-. $Cp_2Ti(SEt)_2$, 1.6 mg (5.3×10^{-6} mol), and 5–7 equiv of Bu_4NCl were dissolved in 1.2 mL of benzene-d_6. The solution was irradiated ($\lambda > 530$ nm) for 1 h. Cp_2TiCl_2 did not form as indicated by ^1H NMR. ($Cp_2Ti(SEt)_2$ was also irradiated with only 5 equiv of CCl_4 in benzene-d_6 and Cp_2TiCl_2 did form in this reaction.)

Results and Discussion

Electronic Spectrum. The electronic spectrum of the Cp_2TiS_5 complex is shown in Figure 1. Because Cp_2TiS_5 is a Ti(IV) complex, the absorption bands must necessarily be of the lig-

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(13) K_2CO_3 (450 mg) and K_2CrO_4 (24 mg) were dissolved in 45 mL of H_2O. The solution, in a 1-cm cell, was used in combination with a Corning glass 7-54 filter to isolate the 313-nm Hg line.

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(17) $CpTiCl_3$ apparently decomposed when it was recrystallized in air from CCl_4, as indicated by the two resonances seen in the ^1H NMR spectrum.

(18) If rigorous precautions are not taken to exclude air and moisture, the resonances at δ 7.106 (CCl_4) and 5.945 (C_6D_6), believed to be due to the hydrolysis product of $CpTiCl_3$, can be seen in the ^1H NMR spectrum.

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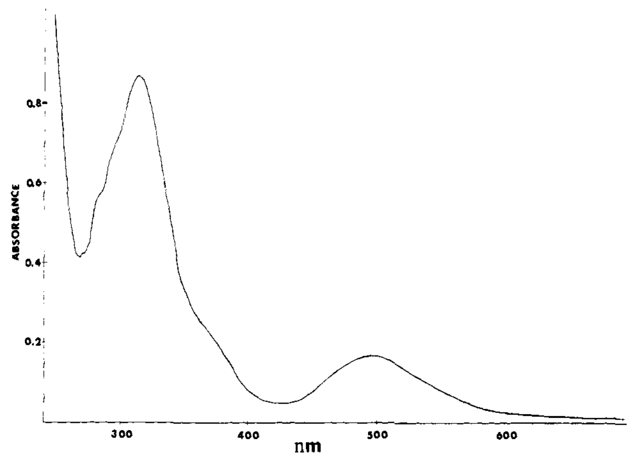


Figure 1. Electronic absorption spectrum of the Cp_2TiS_5 complex in cyclohexane solution (0.3 mM, 1-cm pathlength).

and-to-metal charge-transfer type. Two different types of LMCT transition are possible, either Cp → Ti or S → Ti. Assignment of the bands to either S → Ti or Cp → Ti charge transfer will be made following a discussion of the photochemistry of the Cp_2TiS_5 complex. Note that there is no a priori reason to exclude either assignment for the bands in Figure 1. We recently showed that the Cp → Ti transitions are the lowest energy transitions in the Cp_2TiX_2 (X = Cl, Br) complexes but that an I → Ti charge-transfer transition was lowest in energy in the closely related Cp_2TiI_2 complex.[23] Clearly, there is no rule stating the relative energies of the Cp → Ti and L → Ti charge-transfer bands in Cp_2TiL_2-type complexes.

Photochemical Experiments. Our initial photochemical experiments were designed to test whether a Cp ligand or the S_5 ligand was dissociated from the Cp_2TiS_5 complex upon irradiation. Accordingly, we irradiated the complex with CCl_4 and $BrCCl_3$. The reactions proceeded according to eq 1. (Complete details

$$Cp_2TiS_5 \xrightarrow[XCCl_3]{h\nu} Cp_2TiX_2 \qquad X = Br, Cl \tag{1}$$

for each irradiation including wavelengths, concentrations, and product identification are given in the Experimental Section.) Prolonged irradiation of the CCl_4 solution produced $CpTiCl_3$ by a secondary photolysis.[31a]

$$Cp_2TiCl_2 \xrightarrow[CCl_4]{h\nu} CpTiCl_3 + Cp \tag{2}$$

In the case of the $BrCCl_3$ experiment, no $Cp_2TiBrCl$ or Cp_2TiCl_2 could be detected by NMR. The quantum yields for reaction 1 are very low. In neat CCl_4 ($\simeq 10.3$ M), the quantum yields are 2×10^{-2} (313 nm), 6×10^{-3} (366 nm), and $<10^{-4}$ (546 nm). The reaction with $BrCCl_3$ (1 M in benzene) is slightly more efficient: $\phi = 8 \times 10^{-2}$ (313 nm).

The experiments above clearly show that the S_5 ligand is labilized when the Cp_2TiS_5 complex is irradiated and that the two halide ligands that replace the S_5 ligand must come from different halocarbon molecules. The latter conclusion follows from the observation that Cp_2TiBr_2 forms in the $BrCCl_3$ experiment. Further evidence that the halide ligands are obtained from different halocarbon molecules comes from the observation that irradiation of Cp_2TiS_5 and Ph_3CCl in benzene solution produces Cp_2TiCl_2:

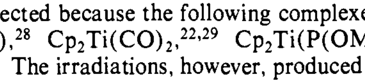
$$Cp_2TiS_5 \xrightarrow[Ph_3CCl]{h\nu} Cp_2TiCl_2 \tag{3}$$

To check for Cp–Ti bond dissociation upon irradiation, Cp_2TiS_5 (3 mM) and the spin-trap nitrosodurene (2 mM) were irradiated in cyclohexane, THF, and 2-MeTHF in the cavity of an ESR spectrometer. The wavelength of irradiation varied from λ > 450, to λ = 313, to λ = unfiltered Hg arc lamp output. No signals attributable to the Cp–nitrosodurene adduct were detected at room temperature or at low temperature (–50 to –80 °C) at any of the irradiation wavelengths. In addition, no signal attributable to a Ti radical could be detected. To test our ability to detect Cp radicals, Cp_2TiCl_2 was irradiated under the same conditions used for Cp_2TiS_5. Cp_2TiCl_2 is known to produce Cp radicals upon irradiation.[24] The four-line pattern of relative intensities 1:2:2:1 at $g \simeq 2.0$ which is characteristic of the Cp–nitrosodurene radical was detected after a few minutes of irradiation.

The formation of Cp_2TiCl_2 in reaction 1 suggests that a Ti(III) intermediate (or a Ti(II) intermediate, see below) is produced by homolytic cleavage of a Ti–S bond. This conclusion follows because Ti(III) species are known to abstract Cl atoms from CCl_4. For example, the reaction in eq 4 is known.[25] Conceivably,

$$Cp_2TiCl + CCl_4 \rightarrow Cp_2TiCl_2 + CCl_3 \tag{4}$$

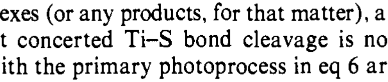
however, the Ti–S bond is heterolytically cleaved (eq 5). To check



(5)

on the possibility of heterolytic cleavage, we irradiated Cp_2TiS_5 with Cl^- in acetonitrile. If heterolytic cleavage is occurring then the expected product is Cp_2TiCl_2. In addition, Cp_2TiCl_2 should presumably form with a much higher quantum yield than in eq 1. However, no Cp_2TiCl_2 or any other complexes could be detected as products of the irradiation of Cp_2TiS_5 with Cl^-. We conclude that heterolytic cleavage of the Ti–S bond is not the primary photoprocess.

As eq 1 shows, the entire S_5 ligand is dissociated from the complex in the reaction of Cp_2TiS_5 with CCl_4.[26] The dissociation could be stepwise (eq 6) or concerted (eq 7). In an attempt to



(6)

$$Cp_2Ti \xrightarrow{h\nu} Cp_2Ti + S_5 \tag{7}$$

distinguish between these pathways, the Cp_2TiS_5 complex was irradiated with PhC≡CPh, CO, $P(OEt)_3$, $P(OMe)_3$, pyridine, NEt_3, and bipyridine. (Phosphines could not be used because they react thermally with the Cp_2TiS_5 complex.) If the titanocene intermediate is forming (eq 7) then reactions with these nucleophiles are expected because the following complexes are known: $Cp_2Ti(C_4Ph_4)$,[28] $Cp_2Ti(CO)_2$,[22,29] $Cp_2Ti(P(OMe)_3)_2$,[20] and $Cp_2Ti(bpy)$.[21] The irradiations, however, produced none of these known complexes (or any products, for that matter), a result which suggests that concerted Ti–S bond cleavage is not occurring. Consistent with the primary photoprocess in eq 6 are the photoreactions of Cp_2TiS_5 with organic disulfides in which irradiation of Cp_2TiS_5 with PhSSPh in benzene produced $Cp_2Ti(SPh)_2$. For comparison, note that Ti(III) complexes react with RSSR to form sulfide complexes, e.g., eq 8.[25]

$$[Cp_2TiCl]_2 + {}^1/_2RSSR \rightarrow Cp_2Ti(Cl)(SR) \qquad R = Me, Et, Ph, CH_2Ph \tag{8}$$

All of the photochemical reactions discussed above are consistent with the proposal that irradiation of the Cp_2TiS_5 complex initially cleaves a single Ti–S bond according to eq 6. The results of flash photolysis experiments also support this conclusion. Flash pho-

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[23] Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639–644.

[24] Tsai, Z.-T.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1979**, *166*, 199.

[25] Coutts, R. S. P.; Surtees, J. R.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1966**, *19*, 1377.

[26] The fate of the S_5 ligand was undetermined. Polysulfide radicals are known to be very reactive and could polymerize or react with the solvent.[27] The formation of a precipitate during irradiation of Cp_2TiS_5 in CCl_4 (see experimental section) is consistent with the formation of some type of polymeric sulfur or simply S_8.

[27] See, for example: Kice, J. L. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, Chapter 6. Schmidt, M. In "Elemental Sulfur"; Meyer, B., Ed.; Interscience Publishers: New York, 1965; Chapter 15.

[28] Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936.

[29] Murray, J. G. *J. Am. Chem. Soc.* **1961**, *83*, 1287.

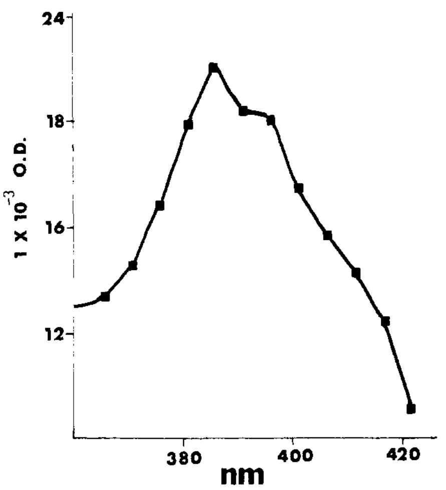
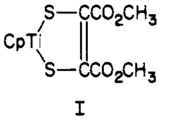


Figure 2. Transient difference absorption spectrum following flash photolysis of Cp_2TiS_5 in benzene. The spectrum was recorded 14 μs after the irradiation.

tolysis (308 nm) of Cp_2TiS_5 in benzene bleaches the Cp_2TiS_5 complex absorption bands at 385 nm (Figure 2). Essentially all of the transient returns to the starting complex following the flash. The return follows first-order kinetics with a rate constant of 2×10^4 s^{-1}. Identical results were obtained in CCl_4 solution (i.e., a transient formed with $\lambda_{max} = 385$ nm, and the rate of transient decay is $\simeq 2 \times 10^4$ s^{-1}). However, a very small amount of bleaching of the Cp_2TiS_5 was observed in CCl_4. Because the intermediate decays by first-order kinetics, we conclude that the intermediate is formed by photochemical cleavage of one bond in the Cp_2TiS_5 complex. (Cleavage of two bonds, e.g., two Ti–S bonds, would produce an intermediate that decayed by second-order kinetics.) There are two possibilities as to which bond is being cleaved photochemically: either a Ti–S bond or a S–S bond. We propose that a Ti–S bond is cleaved because the entire polysulfide ligand is substituted in the photoreactions of the Cp_2TiS_5 complex. Consistent with this proposal is the observation that Cp_2TiS_5 does not react photochemically with $CH_3O_2CC{\equiv}CCO_2CH_3$. If an S–S bond were cleaving, then complex I (a known



I

species) might be one of the expected products.[6] Finally, it is to be noted that although the flash photolysis experiments provide no direct observation for a reaction of the transient with CCl_4 (i.e., the decay rate constant did not increase over that in benzene), there is evidence for a small net reaction. In view of the extremely low quantum yields for reaction with CCl_4, these observations are reasonable.

The question can now be asked if a Ti–S bond is cleaved upon irradiation of the Cp_2TiS_5 complex to produce a very reactive Ti(III) intermediate, why is the complex so unreactive overall? We propose that the unreactivity can be ascribed to the chelating nature of the S_5 ligand. Because the S_5 ligand is a chelate, the cleaved Ti–S bond can efficiently reform, a process that keeps the quantum yield low.[30] (As the flash photolysis results show, the reformation of the Ti–S bond is quite fast.) To test this hypothesis we studied the photochemistry of the $Cp_2Ti(SR)_2$ (R = Et, Ph) complexes. These complexes are similar to the Cp_2TiS_5 complex, but the sulfur ligands are not chelates. The photochemistry of these complexes is qualitatively very similar to that of the Cp_2TiS_5 complex. For example, $Cp_2Ti(SPh)_2$ and $Cp_2Ti(SEt_2)$ react photochemically in CCl_4 to give Cp_2TiCl_2. In addition, neither complex reacts photochemically with Cl^-. However, the $Cp_2Ti(SR)_2$ reactions are much more efficient than their Cp_2TiS_5 counterparts. For example, the quantum yields for the reaction of the $Cp_2Ti(SR)_2$ complexes with CCl_4 at 366 nm are 1.5×10^{-1} and 8.8×10^{-2} for R = Ph and Et, respectively; at 546 nm, the respective quantum yields are 1.3×10^{-2} and 2.2×10^{-3}. Given the qualitative similarities in the reactivities but the greater efficiencies of the $Cp_2Ti(SR)_2$ reactions, we conclude that the lower efficiency of the Cp_2TiS_5 photoreactions can be attributed to the chelating S_5 ligand.

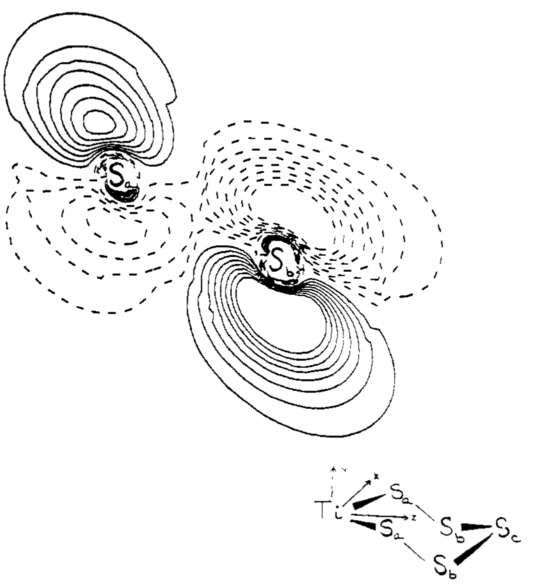
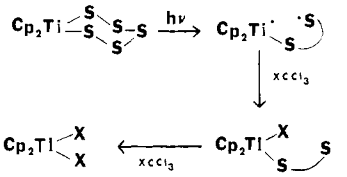


Figure 3. The HOMO orbital in the model complex. The plane shown passes through S_a and S_b, perpendicular to the S_a–S_b–S_b–S_a plane. Solid and broken lines denote contours of opposite sign at values of ±0.01, ±0.02, ±0.03, ±0.04, ±0.06, ±0.07, and ±0.08 $e^{1/2}$ bohr$^{-3/2}$.

Scheme I



This section is best summarized by proposing a mechanism for the reaction of Cp_2TiS_5 with halocarbons. The proposed pathway is shown in Scheme I. The essential features are the initial homolytic cleavage of *one* Ti–S bond to produce a Ti(III) intermediate, followed by X atom abstraction from one halocarbon molecule. Finally, a second X atom is abstracted from a second halocarbon molecule.

Electronic Structure of the Cp_2TiS_5 Complex. In previous studies we and others showed that irradiation into the Cp → Ti charge-transfer bands of the Cp_2TiX_2 (X = Cl, Br) complexes produced Cp radicals.[23,24,31] (The Cp → Ti absorption bands are the lowest energy transitions in these complexes.) Similarly, we also showed that irradiation into the I → Ti CT bands in Cp_2TiI_2 cleaved the I–Ti bond.[32] (The I → Ti CT band is the lowest energy transition in this complex.) On the basis of these results and our observation that a Ti–S bond cleaves when the Cp_2TiS_5 complex is irradiated (λ > 313 nm), it is logical to assign the three lowest energy absorption bands in Figure 1 to S → Ti charge-transfer transitions. We investigated the nature of the sulfur orbitals involved in these transitions by performing a self-consistent-field-Xα-scattered-wave (SCF-Xα-SW) calculation on a model complex with C_s symmetry containing a Ti^{IV}–S_5 ring in

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[30] Houlding, V. H.; Macke, H.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4279.

[31] (a) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *81*, 79. (b) Vitz, E.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1976**, *104*, C33. (c) Vitz, E.; Wagner, P. J.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1976**, *107*, 301. (d) Vitz, E.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1974**, *84*, C16.

[32] Bruce, M. R. M.; Tyler, D. R. *Organometallics*, submitted for publication.

a chair conformation.[33] The results show that the HOMO orbital is primarily a π-type orbital centered on sulfur b and delocalized somewhat on sulfur a (Figure 3). The LUMO orbital is a mixture of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The lowest energy transition (HOMO → LUMO) is thus described as a $S(\pi) \rightarrow Ti$ charge-transfer transition. The photochemistry of the Cp_2TiS_5 complex is essentially wavelength independent. To explain this observation, we must either propose that fast internal conversion to the lowest energy excited state occurs or the absorption bands in the 300–700-nm region are all of the same type (i.e., S → Ti charge transfer). We favor the latter explanation because the Xα calculation predicts that several S → Ti CT bands will occur to lower energy than the first Cp → Ti bands. Accordingly, we qualitatively assign all three absorption bands in the region 300–700 nm as S → Ti bands.

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Registry No. Cp_2TiS_5, 12116-82-4; $Cp_2Ti(SPh)_2$, 1292-47-3; $Cp_2Ti(SEt)_2$, 1291-79-8; Cp_2TiCl_2, 1271-19-8; Cp_2TiBr_2, 1293-73-8; $CpTiCl_3$, 1270-98-0; CCl_4, 56-23-5; $BrCCl_3$, 75-62-7; Ph_3CCl, 76-83-5; Bu_4NCl, 1112-67-0; $PhC{\equiv}CPh$, 501-65-5; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; $P(OCH_3)_3$, 121-45-9; $P(OC_2H_5)_3$, 122-52-1; CO, 630-08-0; PhSSPh, 882-33-7; EtSSEt, 110-81-6; bipyridine, 366-18-7.

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[33] The techniques used in the SCF-Xα-SW calculation have been previously described.[23]

Structures of Two Isomers of $Ir_6(CO)_{16}$

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Abstract: $Ir_6(CO)_{16}$ has been isolated in two different isomeric forms, both of which have been crystallographically characterized. The red isomer is isostructural with $Rh_6(CO)_{16}$, with four face-bridging carbonyl groups. The black isomer, in contrast, has four edge-bridging carbonyl groups, each of them being asymmetrically bonded. For both isomers, a crystallographic 2-fold rotation axis passes through two of the iridium atoms. Crystallographic details: Red isomer of $Ir_6(CO)_{16}$, space group $C2/c$ (monoclinic); $a = 16.656$ (2) Å, $b = 9.761$ (1) Å, $c = 16.776$ (2) Å, $\beta = 118.09$ (1)°, $V = 2406$ Å^3, $Z = 4$; $R = 3.4\%$ for 1508 reflections. Black isomer of $Ir_6(CO)_{16}$, space group $P2/c$ (monoclinic); $a = 13.622$ (5) Å, $b = 12.807$ (4) Å, $c = 18.589$ (5) Å, $\beta = 132.65$ (2)°, $V = 2385$ Å^3, $Z = 4$; $R = 5.1\%$ for 1973 reflections.

One of the landmark papers in organometallic chemistry is the report of the structure of $Rh_6(CO)_{16}$ by Corey, Dahl, and Beck in 1963,[1] which showed for the first time the existence of large (i.e., $n \geq 6$) metal carbonyl clusters.[2] Soon thereafter, the analogous complex $Co_6(CO)_{16}$ was synthesized[3] and shown to be isomorphous with $Rh_6(CO)_{16}$. In this paper we report that the iridium analogue, $Ir_6(CO)_{16}$, exists in two isomeric forms, one of which is isostructural with $Rh_6(CO)_{16}$, while the other one has a different (hitherto unknown) geometry.

Experimental Section

Preparation and Structure Determination of the Red Isomer of $Ir_6(CO)_{16}$. The red isomer of $Ir_6(CO)_{16}$ was originally synthesized by Malatesta and co-workers in 1970 and described as a "highly stable compound, isolable in a very pure state".[4] At that time it was already recognized that this isomer (the only one known then) was isostructural with $Rh_6(CO)_{16}$. Here we describe the results of a full structural analysis of this older compound. The sample used in the X-ray analysis was synthesized according to published procedures.[5] The red isomer of $Rh_6(CO)_{16}$ crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell parameters and other crystallographic details listed in Table I.

Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer by the ω-scan technique, using Mo Kα radiation (λ = 0.7107 Å) with a graphite crystal monochromator in the incident beam. Standard CAD-4 centering, indexing, and data collection programs were used. The lattice parameters and the orientation matrix were refined by least-squares fit using 24 reflections with 7.4° < θ < 16.1°. Intensity data, 2325, were obtained by collecting the ($\pm h,+k,+l$) region of recip-

Table I. Summary of Crystallographic Data and Data Collection Procedures for the Two Isomers of $Ir_6(CO)_{16}$

	red isomer	black isomer
space group	$C2/c$ (monoclinic, No. 15)	$P2/c$ (monoclinic, No. 13)
a, Å	16.656 (2)	13.622 (5)
b, Å	9.761 (1)	12.807 (4)
c, Å	16.776 (2)	18.589 (5)
β, deg	118.09 (1)	132.65 (2)
V, Å^3	2406	2385
ρ(calcd), g cm^{-3}	4.42	4.46
Z	4	4
M_r	1601.4	1601.4
cryst size, mm	0.21 × 0.14 × 0.13	0.20 × 0.25 × 0.45
radtn used	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
μ(Mo Kα), cm^{-1}	330.2	333.2
diffractometer used	Nonius CAD-4	Nicolet/Syntex $P2_1$
scan type	ω	2θ
scan width, deg	$\Delta\omega = 1.6 + 0.35 \tan\theta$	$\Delta 2\theta = 2.0 + [2\theta(K\alpha_2) - 2\theta(K\alpha_1)]$
scan speed, deg min^{-1}	2.5	2.5–15.0
data collctn range	$6° \leq 2\theta \leq 50°$	$3.5° \leq 2\theta \leq 45°$
no. unique data	2246	2954
no. data used in least-squares [$I \geq 3\sigma(I)$]	1508	1973
no. variables	173	281
R	0.034	0.051
R_w	0.039	0.056

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