

Electronic Luminescence Spectra of Charge Transfer States of Titanium(IV) Metallocenes

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Received September 16, 1992*

Many Ti(IV) metallocenes Cp_2TiX_2 and CpTiX_3 ($\text{X} = \text{halogen}$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) exhibit an intense, long-lived charge transfer phosphorescence at 77 K arising from the radiative decay of a $\text{Cp} \rightarrow \text{Ti}$ charge transfer triplet excited state. The phosphorescence band can be shifted systematically by varying X or by replacing Cp with $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$. Trends in the phosphorescence spectra follow closely related trends previously noted in the electronic absorption spectra, photoelectron spectra, and photochemical behavior of these metallocenes. The conspicuous absence of phosphorescence emission in Cp_2TiI_2 and $\text{CpTi}(\text{CH}_3)_2$ correlates with the photochemistry and spectroscopy of these systems; the $\text{Cp} \rightarrow \text{Ti}$ excitation is no longer the lowest energy excitation. Low temperature electronic absorption spectroscopy is utilized to probe the $\text{I} \rightarrow \text{Ti}$ and $\text{Cp} \rightarrow \text{Ti}$ charge transfer excitations of Cp_2TiI_2 . It is proposed that the presence or absence of charge transfer phosphorescence can be used as a diagnostic to determine the relative energy ordering of the valence Cp and X orbitals in Ti(IV) metallocenes.

One of the most intriguing and significant problems in the study of Ti(IV) metallocenes is the identification and characterization of their lowest energy electronic excited states.^{1,2} Ti(IV) metallocenes are formally $3d^0$ complexes whose lowest energy excited states involve transfer of electron density from the ligands to the metal. The key question to be resolved for a given complex is whether the lowest ligand-to-metal-charge transfer (LMCT) excited state of a complex Cp_2TiX_2 or CpTiX_3 is primarily $\text{X} \rightarrow \text{Ti}$ charge transfer or $\text{Cp} \rightarrow \text{Ti}$ charge transfer. Studies based upon photoelectron spectroscopy (PES), electronic absorption spectroscopy, and MO calculations have shown that the $\text{X} \rightarrow \text{Ti}$ and $\text{Cp} \rightarrow \text{Ti}$ charge transfer transitions are very close in energy.^{3,4} Moreover, the relative energies of these transitions can be changed by changing the ligand X or by substituting the Cp ligand with electron releasing groups¹⁻⁴ (e.g., replacing Cp with Cp^*).

This study represents the first systematic application of electronic luminescence spectroscopy to probe the low-lying excited electronic states of a series of Ti(IV) metallocenes.⁵ The general trends in our luminescence data parallel trends observed in earlier electronic absorption and PES studies. However, luminescence spectroscopy is unique among the methods heretofore used in that it directly accesses the lowest spin-forbidden triplet excited state of a Ti(IV) metallocene. This is particularly significant for two reasons. First, this triplet excited state may open the way to new reaction chemistry and photochemistry of Ti(IV) metallocene complexes. Second, the corresponding lowest energy electronic absorption transition, a spin-allowed transition based upon the same orbitals as the triplet emission, is weak and therefore not always easy to observe and identify unambiguously.¹ Luminescence spectroscopy, particularly when used in conjunction with results from PES and electronic absorption spectroscopy, provides a more complete and systematic picture of the low energy excited states of Ti(IV) metallocenes than is afforded by PES and absorption spectroscopy alone.

Experimental Section

All chemicals used in synthesis and spectroscopic analysis were reagent grade. Before use, solvents were distilled and freed from dissolved oxygen by repeated degassing and saturation with inert gas (Ar or N_2). Experiments were carried out in an inert gas atmosphere using standard Schlenk techniques where necessary. Cp_2TiCl_2 , CpTiCl_3 , and Cp^*TiCl_3 were purchased from Aldrich Chemical Co.; Cp^*TiCl_2 was obtained from Strem Chemical Co. These compounds were used without further purification. A sample of $\text{CpCp}^*\text{TiCl}_2$ was donated by Professor Thomas

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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Table I. Electronic Transitions of Phosphorescent Titanium(IV) Metallocenes

metallocene	absorption band ^{a,b}				phosphorescence band ^c		
	cm ⁻¹	M ⁻¹ cm ⁻¹	cm ⁻¹	M ⁻¹ cm ⁻¹	(0-0)/cm ⁻¹	max/cm ⁻¹	$\tau/\mu\text{s}$
Cp ₂ TiF ₂	24 500	432	21 280 (sh) ^d	60	17 200	15 350	730
Cp ₂ TiCl ₂	25 510	2300	19 080	193	16 460	14 880	730
Cp ₂ TiBr ₂ ^e	23 360	3280	18 180	200	15 820	14 620	50
CpCp*TiCl ₂	22 940	2760	18 350 (sh) ^d	290	17 780	14 120	160
Cp* ₂ TiCl ₂	21 490	810	17 180	273	17 780	13 990	230
CpTiCl ₃	25 250	2730	21 050 (sh) ^d	180	18 500	15 300	250
Cp*TiCl ₃	21 830	1340	17 540 (sh) ^d	80	16 320	13 960	190

^a Dichloromethane solutions at room temperature. ^b Other electronic absorption studies of these Ti(IV) metallocenes: Chien,^{1b} Harrigan et al.,^{1c} Bruce et al.,^{1f-h} Mach et al.^{1j} ^c Microcrystalline solid samples at 77 K are excited at 365 nm for luminescence spectra and at 337 nm for luminescence lifetimes. ^d Low energy shoulders are assigned in conjunction with phosphorescence spectra. Band positions and molar absorptivities for these shoulders are approximate. Evidence for these shoulders can be found in earlier electronic absorption studies (see ref 1e). ^e Another band also is observed at 20 410 cm⁻¹ (405 M⁻¹ cm⁻¹) (see ref 1e).

Bitterwolf at the University of Idaho. Cp₂TiF₂ and Cp₂TiI₂ were prepared by the method of Druce et al.⁶ Cp₂TiBr₂ was synthesized using the procedure of Wilkinson and Birmingham for the preparation of Cp₂TiCl₂ with TiBr₄ rather than TiCl₄ as the starting material.⁷ Cp₂Ti(CH₃)₂ was prepared and characterized according to the methods given by Clauss and Bestian.⁸ The compounds Cp₂TiX₂ (X = F, Br, I) were characterized by IR spectroscopy and checked for purity by elemental analysis (Galbraith Analytical Laboratories, Knoxville, TN). Anal. Calcd for Cp₂TiF₂: C, 55.58; H, 4.66; F, 17.58. Found: C, 55.43; H, 4.82; F, 17.50. Calcd for Cp₂TiBr₂: C, 35.55; H, 2.98; Br, 47.29. Found: C, 35.56; H, 3.03; Br, 46.91. Calcd for Cp₂TiI₂: C, 27.81; H, 2.33; I, 58.77. Found: C, 27.90; H, 2.37; I, 57.48.

Electronic absorption spectra were measured on a computer-interfaced Varian-Cary 219 UV-visible spectrophotometer. All quantitative electronic absorption measurements were checked for accuracy and reproducibility on a Hewlett-Packard (HP) 8452A diode array UV-visible spectrophotometer. Matched quartz cells with either 1.00 or 0.10-cm optical path lengths were employed for all measurements in solution at room temperature. Absorption spectra of Ti metallocenes at 77 K were obtained by dissolving a small sample of the compound in a solution of dichloromethane and poly(methyl methacrylate) (PMM) (Aldrich Chemical Co.). The excess dichloromethane was allowed to evaporate, trapping the dispersed molecules of the metallocene in a rigid, transparent PMM plastic matrix. The PMM sample, prepared as a thin film, was suspended in a quartz optical dewar filled with liquid nitrogen (LN₂) at 77 K. The dewar was positioned to allow the sample beam of the Varian-Cary 219 to pass through the PMM film.

Luminescence measurements were performed on microcrystalline metallocene samples sandwiched between quartz plates and sealed with an indium gasket. These samples were housed in a quartz optical dewar filled with LN₂. Ambient temperature luminescence measurements on solid metallocene samples were performed using the same sample holder and dewar, but without LN₂. For frozen solution luminescence studies at 77 K, metallocene samples were dissolved in a 4:1 v/v mixture of freshly distilled and dried ethanol:methanol and placed in a quartz emission tube designed to be held within the LN₂-filled optical dewar.

Luminescence spectra were obtained using the pressure broadened 365-nm band of a 1000-W Hg/Xe arc lamp as the excitation source. The emitted light was collected 90° from the excitation beam, passed into a Kratos GM 252 monochromator (0.25-m focal length, 0.05-nm resolution), and detected by a red-sensitive Hamamatsu 7102 photomultiplier tube (PMT). The PMT output was digitized by computer and corrected with respect to a standard quartz halogen lamp intensity profile. Luminescence lifetimes were measured by exciting the samples with ~10-ns pulses at 337 nm from a PARC Model 2100 nitrogen laser. The emitted light was passed through a monochromator set to the wavelength of the emission maximum and detected by a fast PMT. The decay of the PMT photocurrent was monitored by a HP 54201A digitizing storage oscilloscope. Smoothed luminescence decay curves were obtained by averaging over ~60–80

laser pulses. Oscilloscope data sets were transferred to the computer for least squares data analysis and curve fitting. For lifetimes in the 10²–10³- μs range, lifetime data could be fit to within $\pm 1 \mu\text{s}$. The luminescence lifetime equipment was checked repeatedly for accuracy and reproducibility by measuring the luminescence lifetimes of samples of [Ru(bpy)₃]Cl₂ (Aldrich Chemical Co.) at 77 K and comparing the measured lifetimes to the literature lifetime data for this well-studied complex.⁹

Results and Discussion

Band maxima and, where appropriate, 0–0 band edges for absorption and luminescence, molar absorptivities for absorption, and luminescence lifetime data for each of the luminescent Ti(IV) metallocenes studied are listed in Table I. The primary new finding of this research is that many Ti(IV) metallocenes are intensely luminescent species. Solid samples of luminescent Ti(IV) metallocenes and [Ru(bpy)₃]Cl₂ emit with roughly the same intensity at 77 K. A typical luminescence spectrum at 77 K of a microcrystalline solid Ti(IV) metallocene sample consists of a broad band whose maximum falls within the red to near infrared. The emission band is Stokes shifted ~3000–4000 cm⁻¹ from the corresponding lowest energy band in the absorption spectrum (Figure 1). The emission band shape is typically skewed with a steeper slope on the high energy side than on the low energy side of the band maximum. This same luminescence band shape is observed in solid samples at both room temperature and at 77 K and in 4:1 v/v ethanol:methanol frozen glassy solutions at 77 K.¹⁰ Small shifts in the luminescence bands occur with changing temperature and with changing sample environment at 77 K (Table II). Luminescence lifetimes at 77 K are long (~10²–10³ μs). Trends in the luminescence spectra closely parallel previously reported trends in the electronic absorption spectra, PES data, photochemical reactivities, and MO calculations on Ti(IV) metallocenes.^{1–4} When the luminescence trends are combined with these other experimental and theoretical trends, a much more complete picture of Ti(IV) metallocene electronic structure emerges.

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(10) Alcohols can react with Ti(IV) metallocenes in the very short time interval, typically 15–20 s, between mixing the solution and cooling it to a glassy state at 77 K for luminescence spectroscopy. Care is needed in preparing the glasses and in interpreting their luminescence spectra.

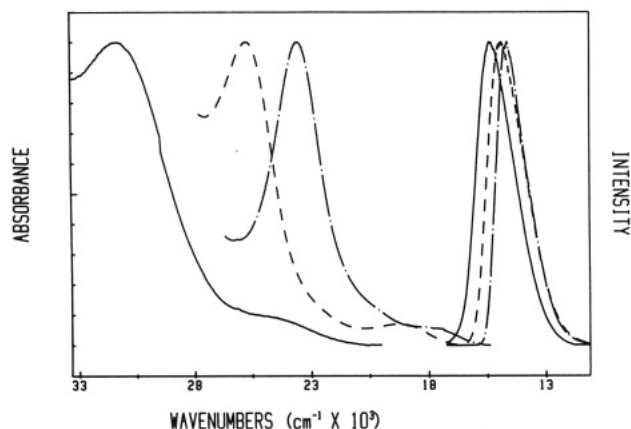


Figure 1. UV-visible absorption spectra and phosphorescence spectra of Cp_2TiF_2 (—), Cp_2TiCl_2 (---), and Cp_2TiBr_2 (-·-·). UV-visible spectra were measured at room temperature in CH_2Cl_2 . Phosphorescence spectra of microcrystalline samples were measured at 77 K with excitation at 365 nm. Spectra are normalized so that maxima appear at full scale.

Table II. Phosphorescence Maxima in cm^{-1} under Different Experimental Conditions

complex	solid (77 K)	solid (room temp)	glass ^a (77 K)
Cp_2TiF_2	15 350		15 550
Cp_2TiCl_2	14 880	14 600	15 020
Cp_2TiBr_2	14 620	14 580	14 410

^a 4:1 v/v ethanol:methanol.

To illustrate trends in the excited electronic states of Ti(IV) metallocenes and to investigate those factors that affect the electronic transitions involving these states, the spectroscopic properties of a number of Ti(IV) metallocenes were studied. The objective was to establish systematic variations in molecular symmetry, molecular structure, choice of monodentate ligand X, and nature and degree of steric and electronic perturbations associated with substituent groups of the Cp ligands. We will divide our discussion of these variations into three sections: (a) variations in X in Cp_2TiX_2 metallocenes, (b) Cp_2TiX_2 vs CpTiX_3 metallocenes, and (c) Cp vs Cp^* metallocenes. These variations can be correlated with spectroscopic trends to arrive at a comprehensive electronic model for Ti(IV) metallocenes. We conclude our discussion by taking a careful look at an alternative Ti(IV) metallocene electronic model from the one we have adopted.

Variations in X. Cp_2TiX_2 Metallocenes. Luminescence spectra at 77 K (Figure 1) of microcrystalline samples of Cp_2TiX_2 (X = F, Cl, Br) show a small, progressive red shift of both the band maxima and the high energy 0-0 band edge as the halogen ligands become larger and less electronegative. However, when X = I or CH_3 no luminescence is observed. This same progressive luminescence red shift pattern is observed in the F, Cl, and Br complexes for microcrystalline samples at ambient temperature and for samples dissolved in ethanol:methanol at 77 K (Table II). Similar energy shift trends were noted by us and by others in the electronic absorption spectra of these complexes (Table I) and in PES data.¹⁻⁴ Our electronic luminescence data readily fit the MO schemes of Bruce et al.,^{1f-h} Condorelli et al.,^{4b} and Cauletti et al.^{4c} if we postulate that the luminescence is a phosphorescence arising from the radiative decay of a ligand-to-metal charge transfer (LMCT) triplet excited state. This triplet state is generated by the promotion of an electron from a Cp

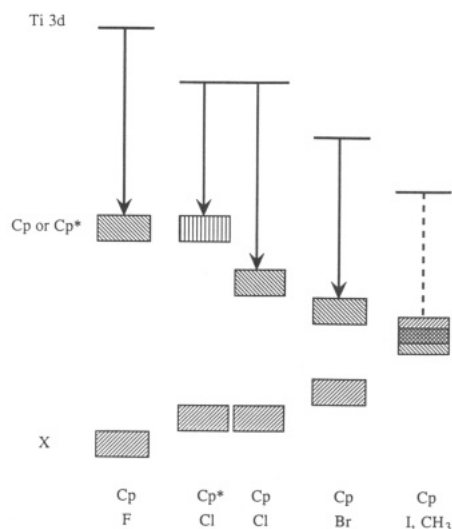


Figure 2. Trends in the MO's of Ti(IV) metallocenes (see refs 1f-h, 4b, and 4c). Note particularly the crossover between the X and Cp MO's when X = I and the effects of Cp vs Cp^* . The down arrows indicate the $\text{Cp} \leftarrow \text{Ti}$ or $\text{Cp}^* \leftarrow \text{Ti}$ radiative decay process leading to phosphorescence. The arrow lengths correlate qualitatively with the phosphorescence transition energies in these metallocenes with the exception of $\text{Cp}^*_2\text{TiCl}_2$ and $\text{CpCp}^*\text{TiCl}_2$. In these systems both steric and electronic effects must be considered to properly evaluate the phosphorescence energy trends. A dotted line connects the LUMO and HOMO of Cp_2TiI_2 and $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ to indicate that no phosphorescence is observed.

π valence orbital to an empty Ti 3d orbital. The phosphorescence occurs as this excited 3d Ti electron returns to the Cp π system. The long luminescence lifetimes observed for these metallocenes (see Table I) provide additional support for the existence of an emitting LMCT triplet excited state. The phosphorescence bands can be shifted by changing the microscopic environment around the emitting metallocene, a common characteristic of charge transfer emission (see Table II).

Both the phosphorescence red shift in the F, Cl, and Br metallocene series and the absence of phosphorescence in the I and CH_3 complexes are readily explained by the MO schemes for bent Ti(IV) metallocenes proposed by Bruce et al.,^{1f-h} Condorelli et al.,^{4b} and Cauletti et al.,^{4c} whose salient features we present in Figure 2 as a part of our general MO scheme for Ti(IV) metallocenes. The Bruce et al. discussion of MO trends in these Ti metallocenes is entirely appropriate for the interpretation of our luminescence results. Specifically, Bruce et al. note that the energy of the Ti LUMO (primarily a mixture of Ti 3d orbitals with some halogen π antibonding character) decreases along the series F to I. The four highest occupied orbitals, including the Cp HOMO, become progressively more stable (decrease in energy) from F to I, but the decrease is not so pronounced as the decrease of the Ti LUMO along this series. The halogen np orbitals increase in energy from F to I. The overall effect is to decrease the Cp HOMO-to-Ti LUMO energy gap as the halogen ligand gets larger and less electronegative; the luminescence therefore red shifts from F to Br (Figure 2). It is gratifying to see that these MO schemes, originally designed to provide a consistent interpretation of photochemical, PES, and electronic absorption data,^{1f-h,4b,c} also correctly predict the observed trends in the luminescence spectra. Bruce et al. make the insightful comment that the orbital trends shown in Figure 2 reflect the reduced π bonding of the

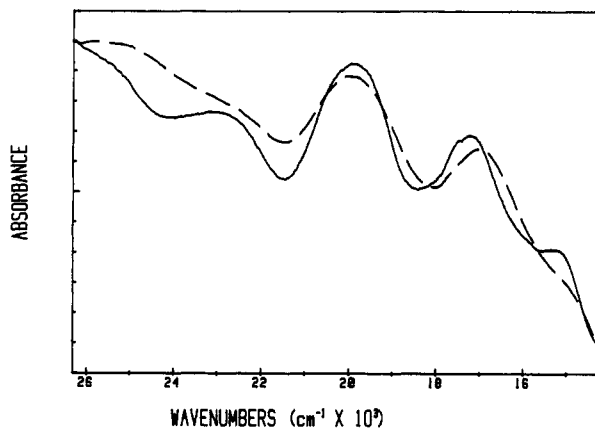


Figure 3. UV-visible absorption spectra of Cp_2TiI_2 at room temperature in CH_2Cl_2 (---) and at 77 K in a transparent PMM plastic matrix (—). The spectra are normalized to facilitate comparison of the band contours at the two temperatures.

halogen p electrons with the d orbitals of Ti upon descending the periodic table in group 17. The virtually identical 730- μs lifetimes of Cp_2TiF_2 and Cp_2TiCl_2 indicate that the photophysical dynamics of the Cp \rightarrow Ti LMCT triplet relaxation process are not influenced by the much lower energy halogen orbitals in these systems. In contrast, the Cp_2TiBr_2 complex exhibits by far the shortest 77 K lifetime (50 μs) of any of the metallocenes studied. We postulate that the order of magnitude reduction in lifetimes as we move from F and Cl to Br is related to the merging of the Br 4p valence orbitals and Cp $p\pi$ valence orbitals (see Figure 2) and the consequent introduction of some halogen orbital character into those states involved in the photophysical decay processes. The presence of an additional low energy band in the electronic absorption spectrum of Cp_2TiBr_2 (see Table I) lends support to this picture. Through these lifetime trends, we see evidence in the Br complex of the eventual emergence of a halogen HOMO in the I complex. The larger Br ligands are also expected to contribute indirectly to the reduction in the lifetime by providing lower energy nonradiative Ti-Br vibrational relaxation pathways for the dissipation of triplet electronic energy.

In Cp_2TiI_2 , the iodine 5p orbitals rise above the Cp orbitals, dramatically reducing the HOMO-to-LUMO energy gap and fundamentally changing its orbital character.^{1f-h} The HOMO is composed of I 5p orbitals, not Cp orbitals. No phosphorescence is observed. As expected, the electronic absorption spectrum of the I complex (Figure 3) is dramatically different from the absorption spectra of the F, Cl, and Br complexes.^{1h} The lowest energy I \rightarrow Ti transition, which appears as a shoulder in the ambient temperature spectrum, becomes much more clearly resolved when the sample is dispersed in a rigid plastic PMM matrix and cooled to 77 K. We follow the assignments of Bruce et al.^{1h} based upon ambient temperature electronic absorption measurements in several solvents and assign the three lowest energy bands in our 77 K spectrum to be I \rightarrow Ti ($\sim 15\,200\text{ cm}^{-1}$), Cp \rightarrow Ti ($\sim 17\,100\text{ cm}^{-1}$), and Cp \rightarrow Ti ($\sim 19\,900\text{ cm}^{-1}$) charge transfer transitions.

The complex $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ also does not phosphoresce. The valence orbital situation is completely analogous to Cp_2TiI_2 . While the LUMO of this dimethyl bent metallocene, like the LUMOs of the dihalogen bent metallocenes,

is predominantly a mixture of Ti 3d orbitals, Bruce et al. show that the highest occupied orbitals are not the Cp $p\pi$ orbitals but orbitals primarily methyl in character with some metal d orbital character.^{1f} The lowest energy electronic absorption transitions for this complex are therefore predicted to be $\text{CH}_3 \rightarrow \text{Ti}$ charge transfer transitions. The important point here is that the lowest energy excited states of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ are not Cp \rightarrow Ti charge transfer states, but states involving the Ti- CH_3 σ orbitals. In fact, the photochemical reactivities of the complexes of Cp_2TiX_2 (X = F, Cl, Br) and of Cp_2TiL_2 (L = I, CH_3) are very different; whereas the Cp-Ti bonds are photochemically cleaved in the Cp_2TiX_2 complexes, the Ti-L bonds are cleaved in the Cp_2TiL_2 complexes.^{1f-h,2} The absence of phosphorescence in $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ and Cp_2TiI_2 is consistent with this photochemical behavior.

Cp_2TiX_2 vs CpTiX_3 Metallocenes. The luminescence behavior of the piano stool complex CpTiCl_3 is quite similar to what we observe in the analogous bent metallocene Cp_2TiCl_2 (Table 1). The emission maximum at $15\,330\text{ cm}^{-1}$ is comparable to the $14\,880\text{-cm}^{-1}$ emission maximum of Cp_2TiCl_2 although the emission bandwidth is considerably broader in the piano stool system. The 0-0 phosphorescence band edge of CpTiCl_3 is shifted to the blue of the 0-0 band edge of Cp_2TiCl_2 . The long luminescence lifetime of CpTiCl_3 at 77 K (250 μs) is indicative of a spin-forbidden charge transfer transition. These facts indicate that the luminescence in this piano stool system is a phosphorescence arising from a Cp \rightarrow Ti charge transfer triplet excited state completely analogous to that of the corresponding bent metallocene Cp_2TiCl_2 . The HOMO is therefore Cp $p\pi$ and the LUMO is Ti 3d, in agreement with earlier PES and MO studies on this system by Terpstra et al.¹¹

Cp vs Cp^* Metallocenes. When we compare the phosphorescence spectra of Cp vs Cp^* Ti(IV) metallocenes we must take into account both the steric and the electronic differences between the Cp and the Cp^* ligands. As expected, the phosphorescence lifetimes of the bulkier, more fluxional Cp^* complexes are shorter than the lifetimes of the corresponding Cp complexes (see Table I). The electron releasing methyl groups raise the Cp^* valence $p\pi$ orbitals, and, in particular, elevate the Cp^* HOMO well above the analogous Cp HOMO.

In the sterically uncrowded piano stool metallocenes, we expect the primary effects of substituting Cp^* for Cp to be electronic in nature. The elevation of the Cp^* HOMO relative to Cp gives rise to a smaller HOMO-to-LUMO gap and a lower excited triplet state energy in Cp^*TiCl_3 than in CpTiCl_3 . Apart from this energy shift, we predict the singlet and triplet potential surfaces of the CpTiCl_3 and Cp^*TiCl_3 complexes to have similar shapes and similar Franck-Condon factors. These predictions are clearly borne out by experiment. We see in Figure 4 that the phosphorescence band contours of CpTiCl_3 and Cp^*TiCl_3 are almost identical but the high energy 0-0 band edge Cp^* complex is red shifted relative to the 0-0 band edge of the Cp complex. In sterically crowded Cp and Cp^* bent metallocenes we expect to find a more complicated situation in which both steric and electronic effects must be considered. Differing steric effects associated with the Cp vs Cp^* ligands make the ground singlet and excited triplet potential surfaces of a Cp_2TiX_2 complex quite different from the singlet and triplet potential surfaces of

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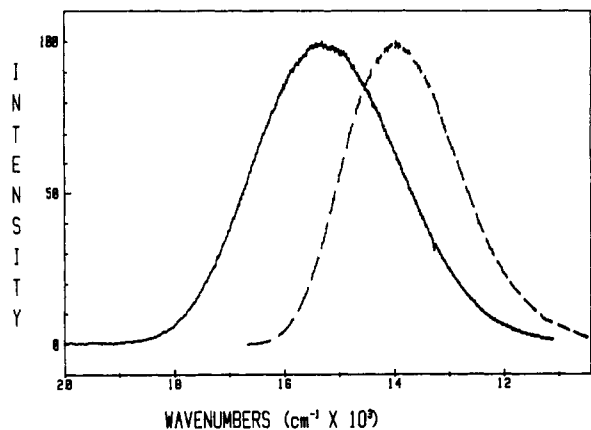


Figure 4. Phosphorescence spectra of microcrystalline samples of CpTiCl_3 (—) and Cp^*TiCl_3 (---) at 77 K with 365-nm excitation. Phosphorescence intensities are normalized so that maxima appear at full scale.

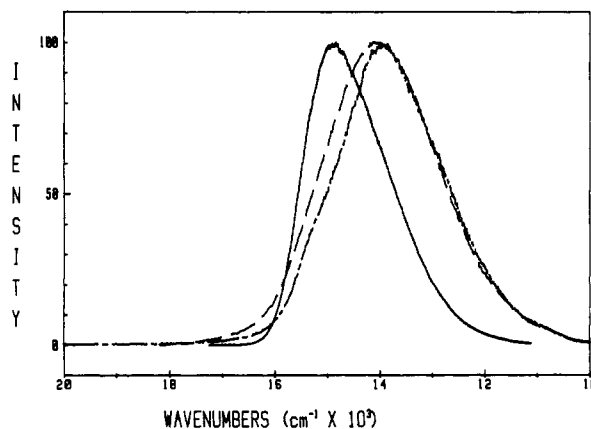


Figure 5. Phosphorescence spectra of microcrystalline samples of Cp_2TiCl_2 (—), $\text{CpCp}^*\text{TiCl}_2$ (---), and $\text{Cp}^*_2\text{TiCl}_2$ (· · ·) at 77 K with 365-nm excitation. Phosphorescence intensities are normalized so that maxima appear at full scale.

the analogous $\text{Cp}^*_2\text{TiX}_2$ complex; the band contours of the phosphorescence spectra of Cp_2TiCl_2 and $\text{Cp}^*_2\text{TiCl}_2$ are therefore expected to differ significantly. This is indeed what we see in Figure 5. Also apparent is the seemingly backward placement of the 0-0 phosphorescence band edge of $\text{Cp}^*_2\text{TiCl}_2$ at higher energy than the 0-0 band edge of the Cp_2TiCl_2 phosphorescence. Steric strain in bent metallocenes with Cp^* ligands clearly competes against the energy-reducing orbital electronic effects of the methyl substituents. It is relevant to note that we were able to induce a pronounced phosphorescence blue shift in a Cp_2TiX_2 ($\text{X} = \text{NCS}$) complex by subjecting it to high pressure in a diamond anvil cell.¹² We postulate that the pressure perturbation reduces the Cp-Ti-Cp angle and drives the Cp ligands into each other, thereby mimicking the steric effects we see under normal ambient pressure conditions in $\text{Cp}^*_2\text{TiCl}_2$. The phosphorescence band contour and 0-0 origin of the mixed ligand complex $\text{CpCp}^*\text{TiCl}_2$ are almost superimposable on the phosphorescence band contour and 0-0 origin of $\text{Cp}^*_2\text{TiCl}_2$ (Figure 5). This suggests that $\text{CpCp}^*\text{TiCl}_2$ is quite similar to $\text{Cp}^*_2\text{TiCl}_2$ both sterically and electronically. We therefore postulate that the emitting triplet of $\text{CpCp}^*\text{TiCl}_2$ arises from the lower energy $\text{Cp}^* \rightarrow \text{Ti}$ orbital excitation rather than the higher energy $\text{Cp} \rightarrow \text{Ti}$ excitation and that similar

ligand steric effects are operative in both the $\text{CpCp}^*\text{TiCl}_2$ and $\text{Cp}^*_2\text{TiCl}_2$ complexes.

Alternative MO Models. It is instructive to evaluate our luminescence results in the context of an alternative electronic model of Cp_2TiX_2 complexes proposed by Petersen et al.^{4a} in which the HOMO is primarily halogen in character. Within this model, the halogen ligand phosphorescence red shift would be interpreted to arise from the increase in the halogen HOMO energy and consequent decrease in the X HOMO-to-Ti LUMO energy gap as X becomes larger and less electronegative. The absence of phosphorescence in the $\text{X} = \text{I}$ complex would therefore be attributed to the predominance of nonradiative decay processes arising from a small HOMO-to-LUMO energy gap. However, neither the dramatic change in the Cp_2TiI_2 electronic absorption spectrum relative to the obviously related electronic absorption spectra of the $\text{X} = \text{F}, \text{Cl},$ and Br complexes nor the significant phosphorescence red shift that occurs when Cp^* is substituted for Cp (*vide infra*) is easily accounted for within the Petersen et al. model. Our luminescence results are more consistently explainable using MO models that, with the exception of Cp_2TiI_2 and $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$, assume a Cp or Cp^* HOMO, such as those of Bruce et al.,^{1f-h} Condorelli et al.,^{4b} and Carlutti et al.^{4c} These Cp/Cp^* HOMO MO models also fit much better with known photochemical and PES results for these metallocenes.¹⁻⁴

Conclusion

Many Ti(IV) metallocenes exhibit an intense, long-lived charge transfer phosphorescence emission at 77 K. This emission arises from the radiative decay of a $\text{Cp} \rightarrow \text{Ti}$ LMCT triplet excited state in both the Cp_2TiX_2 and the CpTiX_3 complexes studied. Phosphorescence emissions from analogous $\text{Cp}^* \rightarrow \text{Ti}$ LMCT triplets are observed in the corresponding Cp^* complexes. Trends in the phosphorescence spectra of different Ti(IV) metallocenes at 77 K correlate almost perfectly with those trends in orbital and state energetics determined by PES, electronic absorption spectroscopy, photochemical studies, and theoretical calculations. However, electronic luminescence spectroscopy is unique within the group of spectroscopic methods used to study Ti(IV) metallocenes in its capacity to access the lowest spin-forbidden triplet state. Within the series of Ti(IV) metallocenes investigated, electronic luminescence spectroscopy provides a rapid and unequivocal answer to the question of whether the $\text{X} \rightarrow \text{Ti}$ or the $\text{Cp} \rightarrow \text{Ti}$ charge transfer excitation is lower in energy. If the metallocene phosphoresces, the $\text{Cp} \rightarrow \text{Ti}$ excitation is the lowest energy transition in the molecule; the HOMO is primarily Cp in character. If the metallocene does not phosphoresce, the $\text{X} \rightarrow \text{Ti}$ excitation is lowest in energy and the HOMO is primarily X in character. Our work suggests that the existence or nonexistence of charge transfer phosphorescence in a Ti(IV) metallocene may be used as a diagnostic to predict probable chemical and photochemical reaction pathways. Phosphorescent Ti(IV) metallocenes are expected to have labile Ti-Cp bonds; nonphosphorescent Ti(IV) metallocenes are expected to have labile Ti-X bonds. Our studies show that the triplet excited state is long-lived in the solid state and in frozen solution at 77 K, but no triplet emission is detectable in solution at room temperature. Triplet phosphorescence emission is present in the solid state at room temperature. From this data we infer that photochemical studies of

(12) Constantopoulos, T.; Clymire, J. W.; Kenney, J. W., III; Chen, Y.; Jas, G. To be published.

these Ti(IV) metallocenes carried out in solution at room temperature have at best fleeting access to a very short-lived transient triplet state, so short lived, in fact, that we cannot detect it with our conventional luminescence spectrophotometer. However, an entirely new class of photochemical experiments in Ti(IV) metallocenes may be possible in solutions at low temperature or in solid state mixtures at both low temperature and room temperature in which a very long-lived LMCT triplet excited state is selectively accessed by other reactants. The observation of phosphorescence from the closely related $3d^0$ compound Cp^*_2ScCl in fluid solution at room temperature suggests that it may also be possible to design Ti(IV) metallocenes whose triplet states are reasonably stable under these conditions.⁵

Acknowledgment. The reviewers' comments and suggestions are gratefully acknowledged. We thank Professor Thomas Bitterwolf at the University of Idaho for

providing a sample of $CpCp^*TiCl_2$ for spectroscopic study. Ms. Paula Blue and Mr. Bayrn McCarty are thanked for performing spectroscopic measurements. It is a pleasure to acknowledge M. Inga S. Kenney's assistance with the synthesis and computer data acquisition. Support for this research was provided by the Llano Estacado Center for Advanced Professional Studies and Research and the College of Liberal Arts and Sciences at Eastern New Mexico University, the Hewlett Packard University Grants Program, and the United States Air Force Office of Scientific Research (UES/AFOSR Contract No. F 49620-85-C-00131 SB5651-0360 P.O. S-760-7MG-019).

Registry No. Supplied By Author. Cp_2TiF_2 , 309-89-7; Cp_2TiCl_2 , 1271-19-8; Cp_2TiBr_2 , 1293-73-8; Cp_2TiI_2 , 12152-92-0; $Cp_2Ti(CH_3)_2$, 1271-66-5; $Cp^*_2TiCl_2$, 11136-36-0; $CpCp^*TiCl_2$, 38496-87-6; $CpTiCl_3$, 1270-98-0; Cp^*TiCl_3 , 12129-06-5.

OM920568J