# Luminescent $d^0$ Scandocene Complexes: Photophysical Studies and Electronic Structure Calculations on $Cp^*_2ScX$ (X = Cl, I, Me)

Brian W. Pfennig, Mark E. Thompson,* and Andrew B. Bocarsly*

*Department of Chemistry, Frick Laboratories, Princeton University, Princeton, New Jersey 08544*

*Received July 2, 1992*

The room-temperature luminescence and photophysics of a series of early transition metal, first-row organometallic complexes with the general formula $Cp^*_2ScX$ (where Cp* is $\eta_5$-$C_5(CH_3)_5^-$ and X represents a $\sigma$-donating ligand) are reported. Semiempirical molecular orbital calculations using the INDO/S method (ZINDO) have been performed. The calculations were carried out using full $C_5(CH_3)_5^-$ ligands for $Cp^*_2ScX$, X = Cl, I, $CH_3$. The calculations indicate a large amount of metal and ligand orbital mixing in these $d^0$ complexes, with the lowest unoccupied molecular orbitals consisting principally of Sc d-orbitals admixing with the Cp* $\pi$-orbitals. The highest-occupied molecular orbital for the chloride derivative contains primarily Cp* character, while that of the iodide species is mostly halogen in nature. The presence of a lone pair on X is requisite for room-temperature emission to occur, as evidenced by the observation of luminescence for X = $Cl^-$, $I^-$, and NHPh and by the lack of luminescence from $Cp^*_2ScCH_3$ or $Cp^*_2ScCH_2Ph$, under identifical conditions.

## Introduction

Inorganic complexes which emit in fluid solution under ambient conditions represent an important class of molecules in the fields of solar energy conversion, artificial photosynthesis, and photocatalysis.[1] However, the number of luminescent complexes which efficiently emit in fluid solution at room temperature is quite limited.[2] This statement is even more true with respect to organometallic complexes. Principally, room-temperature emission has been associated with the presence of a lowest energy metal d$\pi$ → ligand charge transfer transition, most notably related to a low-spin $d^6$ metal center and a polypyridyl ligand.[3] More recently, long-lived emissive excited states have been reported for metal $p_z$ → metal d transitions in group 10, $d^{10}$ $ML_3$ complexes[4] (L = $PR_3$ or $P(OR)_3$), as well as interligand charge transfer in square planar $d^8$ Pt(II) complexes[5] containing a polypyridyl and a dithiolate in the coordination sphere. Room-temperature emission has also been observed from certain tungsten alkylidyne complexes[6] and is associated with relaxation of a d$\pi$ metal → $\pi^*$ alkylidyne transition, formally a MLCT transition. In all these cases, excited state lifetimes have been found to be relatively long (i.e. 100 ns or longer), opening up the possibility of productive bimolecular photochemistry from the excited state. In the case of the group 10 metal-centered excited states, lifetimes in the microsecond range have been reported at room temperature. Complexes of these types appear to be excellent candidates for chemical processes which allow the productive conversion of optical energy to useful chemical products, via either charge transfer or energy transfer quenching processes.

Unlike the MLCT, metal-centered, or ligand-centered excited states noted above, relatively little information has been reported about the photophysics and photochemistry of organometallic complexes having lowest energy ligand-to-metal charge transfer (LMCT) excited states.[7] Such complexes are interesting because irradiation of the lowest energy LMCT bands of these complexes creates a formal reduction of the metal center (i.e. the excited state is of the form $L^+$–$M^-$). Long-lived LMCT excited states would therefore be expected to be potent reducing agents.[8] Most organometallic complexes, however, possess metals in low oxidation states. For these situations, low-energy MLCT transitions dominate the UV–visible absorption spectrum. One type of organometallic complex containing a metal center in a high oxidation state, which has been extensively investigated, is $Cp_2TiX_2$ (where Cp = $\eta^5$-$C_5H_5^-$ and X = halide).[9] However, these $d^0$ complexes are not emissive under the above state conditions.

We have recently reported[10] the room-temperature luminescence of $Cp_2^*ScX$ (where Cp* = $\eta^5$-$C_5Me_5^-$ and X

---

* To whom correspondence should be addressed.

[1] (a) Balzani, V. Ed. *Supramolecular Photochemistry*; D. Reidel Publishing Co.: Dordrecht, Holland, 1987. (b) Balzani, V. *Pure Appl. Chem.* **1990**, *62*, 1099. (c) Kutal, C. *J. Chem. Educ.* **1983**, *60*, 876.

[2] (a) Geoffrey, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press, Inc.: New York, 1979. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

[3] (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

[4] Casper, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.

[5] Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47.

[6] Bocarsly, A. B.; Cameron, R. E.; Rubin, H.-D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3976.

[7] In addition to the example mentioned in ref 9: Bandy, J. A.; Cloke, G. N.; Cooper, G.; Day, J. P.; Girling, R. B.; Graham, R. G.; Green, J. C.; Grinter, R.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 5039.

[8] For a discussion, see footnote 1 in ref 9d.

[9] (a) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (b) Condorelli, G.; Fragala, I.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311. (c) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61. (d) Bruce, R. M. R.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639.

[10] Pfennig, B. W.; Thompson, M. E.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1989**, *111*, 8947.

[11] Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

[12] Stolz, R. W.; Melson, G. A. *Inorg. Chem.* **1972**, *11*, 1720.

[13] Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

0276-7333/93/2312-0649$04.00/0

= $Cl^-$) in fluid solution. Excitation of the lowest energy transition of this complex (358 nm) leads to emission at 521 nm in a 1:1 (v/v) mixture of isooctane/methylcyclohexane with a room-temperature luminescence lifetime of ~2 μs. Based on the dependence of the emission energy on the nature of the X ligand, the emissive excited state was assigned as LMCT from the *p*-X nonbonding lone pair. We herein report a more detailed description of the photophysical and photochemical properties of $Cp^*_2ScCl$ and analogous derivatives. The photophysical assignments were made with the aid of detailed semiempirical calculations (Zerner's INDO/S—ZINDO),[14a-d] carried out for all of the complexes studied ($Cp_2^*ScX$, X = Cl, I, Me). These ZINDO calculations were carried out on the full complexes; i.e. $C_5Me_5^-$ ligands were used rather than substituting $C_5H_5^-$ or $Cl^-$ ligands for $Cp^{*-}$. The use of Cp* ligands in the calculations gives orbital energies which are close to the experimentally observed values. Moreover, the orbital compositions of the pertinent frontier orbitals, predicted by these MO calculations, are presumably closer to those of the complexes studied, than would be obtained for complexes where the Cp* is approximated by a smaller ligand. The electronic assignments and orbital structure of the complexes are discussed and compared with the their group 4 analogs: $Cp_2TiX_2$, X = halide and alkyl.

## Experimental Section

**Synthesis.** $Cp^*_2ScCl$ was supplied by Drs. John Bercaw and Martin St. Clair or was synthesized according to a modification of the literature method.[11] Anhydrous $ScCl_3$[12] (2.977 g, 19.7 mmol, 1 equiv) was refluxed in freshly distilled xylenes with 6.57 g of LiCp* (46.2 mmol, 2.35 equiv) for several days. The solvent was removed under vacuum, and the resulting precipitate was recrystallized from diethyl ether. $Cp^*_2ScI$ and $Cp^*_2ScNHPh$ were prepared according to the literature methods[13] from $Cp^*_2ScCH_3$. Since the complexes of interest are extremely air- and water-sensitive, all manipulations were carried out on a vacuum line using standard Schlenk techniques or in a glovebox. The solvents employed were obtained from Aldrich and were dried by reflux over the appropriate dessicant, followed by distillation and several freeze–pump cycles on the vacuum line.

**Spectroscopy and Photochemistry.** UV–vis absorption spectroscopy was performed on a HP 8450A diode-array spectrophotometer. Molar absorptivities were determined by least-squares fits to Beer's law plots. Emission spectra were recorded using a Perkin-Elmer Model MPF-66 fluorescence spectrophotometer. Low-temperature spectra (77 K) were obtained using a quartz EPR tube with a screw-tight rubber septum lid immersed in a quartz-tipped Dewar evacuated to $10^{-5}$ Torr and filled with liquid nitrogen. NMR spectra were obtained using a General Electric QE-300 NMR spectrometer or, for the low-temperature experiments, a JEOL GSX 270 NMR spectrometer equipped with a cryostat. Lifetime measurements were measured at 90° to the incident irradiation, using a 337-nm pulsed Molectron UV-400 nitrogen laser as the source and a Hamamatsu R928 PMT monitored by a Tektronics 7704A oscilloscope as the detection system. A 514.5-nm interference filter (600 nm for $Cp^*_2ScNHPh$) was used to eliminate reflected radiation from the laser beam. A Q-switched Nd-YAG laser at 398 nm was employed for the time-resolved spectroscopy, using an OMA detector. Stern–Volmer quenching constants were obtained by plots of the fluorescent intensity versus quencher concentration.

**Table I. Lowest Energy Transitions, Emission Maxima, and Emission Lifetimes for Several $Cp^*_2ScX$ Complexes**

| X | matrix | *T* (K) | excitation max (nm)[a] | emission max (nm) | τ (μs)[b] |
|---|---|---|---|---|---|
| Cl | IO/MCH[c] | 298 | 255, 297, 358, 390 | 521 | 2.0 |
| Cl | IO/MCH | 77 | 348, 412 | 538 | 15.0 |
| Cl | solid | 298 | 320, 365 (sh), 393, 415 | 541 | 6.5 |
| I | solid | 298 | 338, 393, 435 | 555 | |
| NHPh | IO/MCH | 298 | 348, 391 | 600 | 2.0 |
| NHPh | IO/MCH | 77 | 345, 394 | 589 | 5.0 |

[a] Excitation maxima were determined on the basis of excitation profiles of the luminescent complexes with emission monitored at the emission maxima given in column 5. [b] Using 337-nm irradiation; rounded to the nearest 500 ns. [c] IO/MCH represents a 1:1 (v/v) mixture of isooctane and methylcyclohexane.

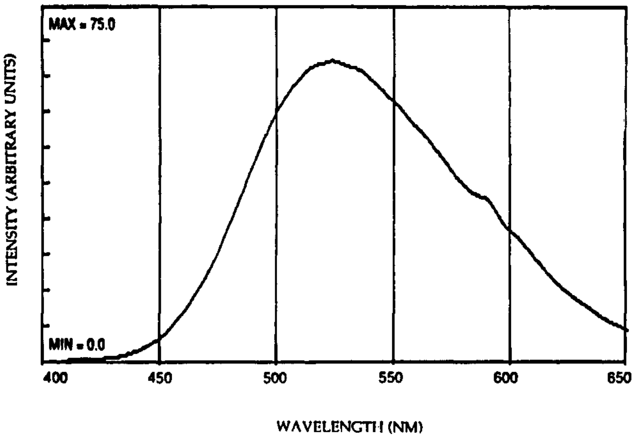

**Figure 1.** Emission spectrum (390-nm excitation) of $Cp^*_2ScCl$ at 298 K in a 1:1 (v:v) mixture of isooctane/methylcyclohexane.

The triplet quenchers employed are listed in the appropriate section. The NMR spectra of a number of the quencher species were taken to ensure their dryness since water rapidly destroys the complex of interest, eventually forming nonluminescent $Sc(OH)_3$. For all of the species tested, there were no NMR peaks attributable to water, indicating that the quenching may genuinely be attributed to the employed compounds. The quantum efficiency of $Cp^*_2ScCl$ was measured relative to that of anthracene (Φ = 0.29) using 366-nm irradiation by ratioing the area of their emission curves under conditions in which the optical densities of the two samples were adjusted to be identical.[10]

**Electronic Structure Calculations.** The semiempirical calculations were carried out using the INDO/S electronic structure formalism developed by Zerner (ZINDO, Zerner's Intermediate Neglect of Differential Overlap Program)[14a-d] with a configuration interaction level of 10 (10 HOMOs and 10 LUMOs). ZINDO calculations were run on a CAChe Worksystem[14e] through a Macintosh[14f] environment. Atom positions for the C, H, Sc, and X atoms of $Cp^*_2ScX$ (X = Cl, I, $CH_3$) were chosen as described in the text. Molecular orbital compositions and transition energies are given in Tables III and IV, respectively.

## Results and Discussion

**Spectroscopic Characterization.** The electronic absorption spectrum of $Cp^*_2ScCl$ in a 1:1 (v/v) isooctane/methylcyclohexane solvent consists of three transitions at 255 nm ($\epsilon = 2500\ M^{-1}\ cm^{-1}$), 297 nm ($\epsilon = 2380\ M^{-1}\ cm^{-1}$), and 358 nm ($\epsilon = 895\ M^{-1}\ cm^{-1}$) with the indicated molar extinction coefficients. The excitation spectrum of this complex provides similar values (Table I), as well as reveals a fourth transition at lower energy (390 nm) which is too weak to be observed in the absorption spectrum. Room-temperature emission (Figure 1) is observed at 521 nm when irradiation is performed at any wavelength for which

---

(14) (a) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728. (b) Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1. (c) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728. (d) Kotzian, M.; Rösch, N.; Schröder, H.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 7687 and references therein. (e) CAChe and the CAChe Worksystem are trademarks of Tektronics, Inc. (f) Macintosh is a trademark of Apple Computer, Inc.

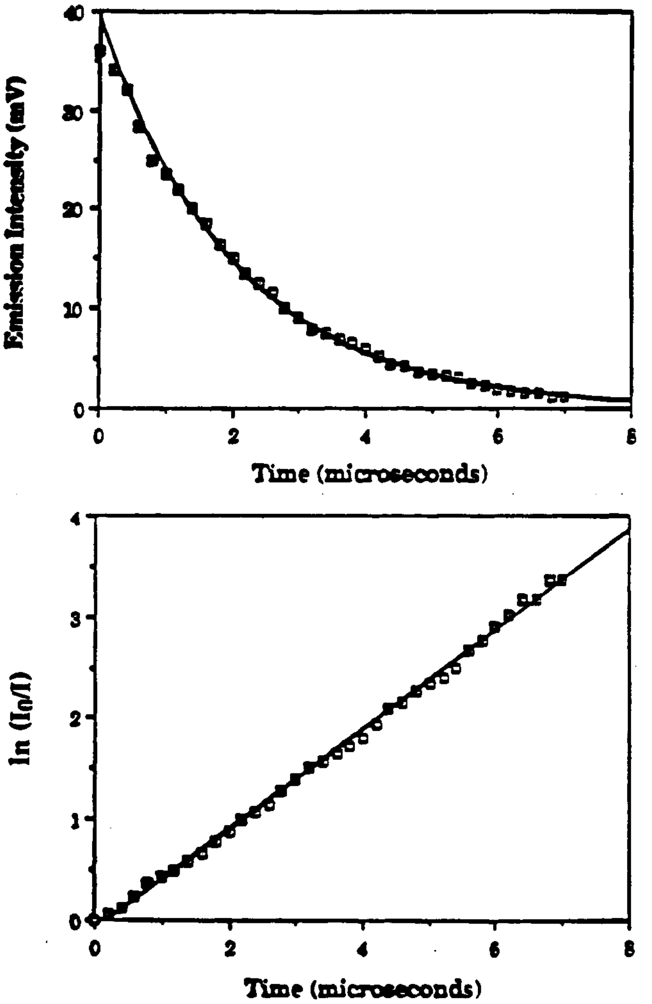

**Figure 2.** Emission decay (337-nm excitation, 514.5-nm emission) of Cp*$_2$ScCl at 298 K in a 1:1 (v:v) mixture of isoctane/methylcyclohexane.

the complex absorbs light. This result is consistent with the hypothesis that the lowest energy excited state is the emissive state and that population of higher-lying excited states generates the emissive state via a nonradiative decay mechanism. The 0–0 energy for this transition was determined to be 449 nm from the overlap of the emission spectrum and the excitation profile. The quantum efficiency for emission using 366-nm excitation was determined to be 0.008.

The excited state decays exponentially (i.e. simple first-order kinetics) when irradiated at 337 nm, as shown in Figure 2, with emission energies and radiative lifetimes in fluid solution, in a frozen matrix (77 K), and in the solid state as listed in Table I. The emission energies of the complex in a frozen organic glass at 77 K and in the solid state (at 298 K) are red-shifted by nearly the same amount from the room-temperature solution maximum. Presumably, this is due to a rigidochromic effect since the shift only depends on the presence of a solid state matrix and is not strongly temperature dependent. A typical rigidochromic interaction, however, leads to a blue shift rather than the red shift that is observed here.[15] The relatively long, room-temperature luminescence lifetime suggests that the 521-nm emission involves a triplet excited state

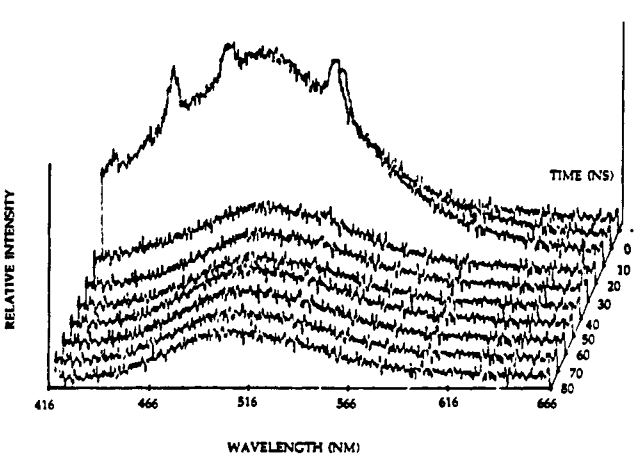

**Figure 3.** Time-resolved spectroscopy of Cp*$_2$ScCl at 298 K in a 1:1 (v:v) mixture of isoctane/methylcyclohexane using 398-nm irradiation.

relaxing to the singlet ground state. This conclusion is supported by the low molar absorptivity of the lowest energy transition (too weak to be observed in the UV–vis spectrum, but clearly visible in the excitation profile). Additionally, no changes in the emission spectrum were observed upon the addition of ethyl iodide to the solution, a molecule which is known to promote intersystem crossing, other than a small blue shift attributable to the increased polarity of the solvent mixture. On the cumulative basis of the above results, the observed emission is assigned as phosphorescence from the lowest energy excited triplet state.

Time-resolved spectroscopy was employed to further characterize the observed emission. Two emissions are observed at room temperature in fluid solution with 398-nm excitation (Figure 3). The first of these occurs at 494 nm with an apparent lifetime of less than 10 ns, while the latter appears at 512 nm with a lifetime on the order of 1 $\mu$s, in agreement with the previously mentioned result. Therefore, the lowest energy emissive state can be assigned as phosphorescence, with fluorescence occurring at 494 nm.

The solvent dependence of the emission energy was examined. The emission energy increases linearly with increasing solvent polarity.[16] This study was restricted to aliphatic hydrocarbons, methylene chloride, and chloroform. Other polar solvents, such as toluene, xylenes, dioxane, THF, and CH$_3$CN, did not show a linear correlation. These species may directly coordinate through the heteroatom (where present) to the scandium center or form $\pi$-complexes with the Cp* rings, thereby complicating the issue.

**Bimolecular Quenching Processes.** Luminescent quenching of Cp*$_2$ScCl is observed with a number of aromatic compounds, showing Stern–Volmer correlations with luminescent intensity as depicted in Figure 4 for toluene. The more common ketone and amine triplet quenchers cannot be employed due to their potential reactivity with the coordinatively-unsaturated complex. The Stern–Volmer quenching constants (Table II) showed no direct correlation with the energy of the triplet states of the employed quenchers. Additionally, the excited state

---

[15] The origin of the rigidochromic effect is associated with restricting the degree of vibrational freedom. This typically leads to an increase in the transition energy, for example see: Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

[16] The polarities of a 1:1 mixture of isooctane/methylcyclohexane, pure methylene chloride, and chloroform are 0.1, 3.1, and 4.1, respectively. Snyder, L. R. *J. Chromatog.* **1974**, *92*, 223. The corresponding emission energies are 19 190, 19 680, and 19 950 cm$^{-1}$, respectively. The linear fit of these points gives an $R^2$ of 0.987.

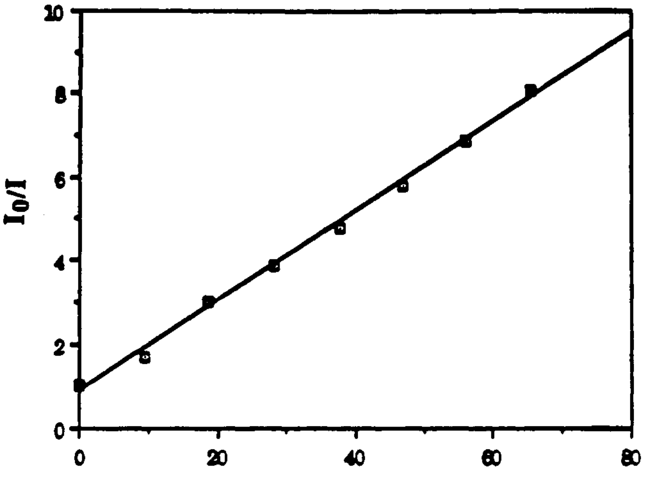

**Figure 4.** Stern–Volmer quenching plot (520-nm emission) for $Cp^*_2ScCl$ at 298 K in a 1:1 (v:v) mixture of isoctane/methylcyclohexane at 390-nm irradiation, using toluene as a quencher.

**Table II. Quenchers, Triplet Energies, and Stern–Volmer Equilibrium Constants for the Quenching of $Cp^*_2ScCl$ at 298 K in a 1:1 (v:v) Mixture of Isoctane/Methylcyclohexane**[a]

| quencher | triplet $E$ ($\times 10^3$ cm$^{-1}$) | $10^6 K_{SV}$ (M$^{-1}$) |
|---|---|---|
| toluene | 28.99 | 110 |
| xylenes | 28.74 | 3.60 |
| $p$-dibromobenzene | 27.78 | 4360 |
| hexamethylbenzene | 27.40 | 2020 |
| 1,2,4,5-tetrachlorobenzene | 26.81 | 25900 |
| hexachlorobenzene | 25.64 | 3720 |
| phenylacetylene | 25.19 | 840 |
| fluorene | 23.75 | 1000 |
| biphenyl | 22.94 | 400 |
| diphenylacetylene | 21.83 | 580 |

[a] 366-nm excitation was employed, with emission monitored at 520 nm.

lifetime of the compound is relatively unchanged even at drastically higher concentrations of quencher for all of the species tested (~10 M). Thus, a static quenching mechanism is indicated. The existence of a static quenching mechanism for $Cp^*_2ScCl$ implies that a nonluminescent complex is formed between the chromophore and the quencher molecule. Direct interaction of the Sc with the majority of the quenchers examined can be excluded, since mechanistic studies have shown that the metal centers of $Cp^*_2ScR$ complexes do not interact with aromatic $\pi$ systems.[11] An interaction between $Cp^*_2ScCl$ and the quenchers used in this study might involve the formation of a $\pi$-complex between the aromatic species and the Cp* ring(s) of the organometallic. Evidence for complexation was sought with both 1,2,4,5-tetrachlorobenzene and toluene as the quenchers using UV–vis spectroscopy and temperature-dependent NMR (+30 to −105 °C). Unfortunately, no spectroscopic features indicative of a chromophore–quencher complex were observed. Of course, this does not rule out the existence of such an interaction.

**Spectral Assignments and Electronic Structure Calculations.** Several of the possible assignments for the emissive transition may be excluded at once upon examination of the electronic configuration of $Cp^*_2ScCl$. Ligand-field and metal-to-ligand charge transfer transitions are impossible since the complex is $d^0$. Additionally, intraligand transitions are generally independent of solvent polarity for nonpolar ligands, such as $Cp^{*-}$ and $Cl^-$. The dependence of the emission energy on solvent polarity thus excludes intraligand transitions. The remaining possibilities are interligand and ligand-to-metal charge transfer. Room-temperature luminescence of the analogy $Cp^*_2ScNHPh$ (solution) and $Cp^*_2ScI$ (solid) yields emission maxima at 600 and 555 nm (see Table I), respectively, conclusively demonstrating that the observed emission is not simply associated with the Cp* ligand. The free ligand ($C_5Me_5H$) is observed to emit at 505 nm with a 580-ns excited state lifetime at 298 K.

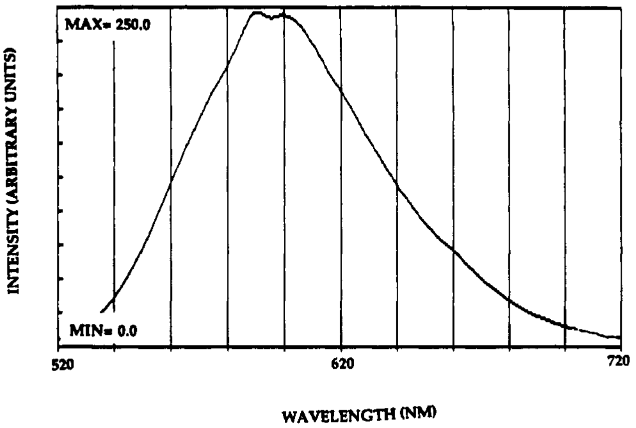

**Figure 5.** Emission spectrum (391-nm excitation) of $Cp^*_2ScNPh$ at 298 K in a 1:1 (v:v) mixture of isoctane/methylcyclohexane.

The emission spectrum for $Cp^*_2ScNHPh$ in fluid solution at 298 K is shown in Figure 5. The lifetime of the phenylamine derivative at 298 K in fluid solution is ~2 μs, identical to that of the chloride species. This emission is blue-shifted to 589 nm at 77 K in a frozen isooctane/methylcyclohexane matrix, and its lifetime is increased by a factor of 2.5 from that at 298 K. Similar blue shifts are observed for other luminescent organometallics upon cooling and have been attributed to a rigidochromic effect (vide supra). The complexes $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2Ph$ (which contain no lone pairs on the X ligand) yielded no observable emission at room temperature in fluid solution. These results are supportive of an assignment of the emissive state as LMCT (from the lone pairs on X).

A limited number of photochemical and electronic structure studies have been performed on the general class of $d^0$ organometallics $Cp_2MX_2$. The photoelectron spectrum of $Cp_2TiCl_2$ has been measured independently by several groups, but was interpreted differently by each group, resulting in one case in a $Cl^-$ highest-occupied molecular orbital,[9a] while in another a Cp HOMO.[9b–c] The photochemistry of this complex was first described by Gray et al.;[17] several studies have followed.[18] Irradiation leads to Cp–Ti bond homolysis, as evidenced by ESR spectroscopy of the trapped Cp radical and the intermediate $CpTiCl_2$ complex. In the presence of a halogenated solvent, the net result is the production of $CpTiCl_2X$. Brubaker et al.[18c] extended this photochemistry into the synthesis of mixed cyclopentadienyl complexes. For example, irradiation of $Cp_2TiCl_2$ with $(Cp\text{-}d_5)_2TiCl_2$ led to the formation of 2 mol of the mixed cyclopentadienyl complex. No evidence for the formation of chloride radicals or the

---

(17) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *81*, 79.

(18) (a) Tsai, Z.-T.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1979**, *166*, 199. (b) Vitz, E.; Wagner, P. J.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1976**, *107*, 301. (c) Vitz, E.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1974**, *82*, C16.

**Table III. Calculated Molecular Orbital Compositions and Energies (eV) for $Cp^*_2ScX$ ($X = Cl^-, I^-, CH_3$)**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $Cp^*_2ScCl$ | | | | | |
| MO | 55 | 56 | 57 | 58 | 59 | HOMO | LUMO | 62 | 63 | 64 | 65 |
| eV | −9.47 | −9.40 | −8.84 | −8.42 | −8.17 | −7.88 | | | | | |
| % Sc (spd) | 4 | 5 | 21 | 16 | 14 | 14 | 90 | 73 | 62 | 25 | 41 |
| % Cp–C (sp) | 4 | 7 | 65 | 67 | 70 | 62 | 7 | 22 | 23 | 68 | 51 |
| % Cp–Me (sp) | 2 | 3 | 5 | 5 | 4 | 3 | 2 | 1 | 1 | 3 | 4 |
| % Cl (sp) | 87 | 82 | 1 | 3 | 3 | 15 | 0 | 3 | 13 | 0 | 1 |
| % H (s) | 2 | 3 | 9 | 9 | 10 | 6 | 1 | 2 | 1 | 4 | 3 |
| | | | | | $Cp^*_2ScI$ | | | | | | |
| MO | 55 | 56 | 57 | 58 | 59 | HOMO | LUMO | 62 | 63 | 64 | 65 |
| eV | −8.95 | −8.58 | −8.33 | −8.25 | −8.18 | −7.14 | | | | | |
| % Sc (spd) | 21 | 17 | 8 | 13 | 19 | 2 | 90 | 74 | 66 | 26 | 42 |
| % Cp–C (sp) | 59 | 52 | 12 | 65 | 44 | 13 | 6 | 20 | 17 | 68 | 51 |
| % Cp–Me (sp) | 5 | 5 | 2 | 5 | 4 | 5 | 2 | 1 | 1 | 3 | 3 |
| % I (sp) | 6 | 19 | 77 | 7 | 29 | 78 | 1 | 3 | 15 | 0 | 1 |
| % H (s) | 9 | 8 | 1 | 11 | 5 | 3 | 1 | 2 | 1 | 4 | 3 |
| | | | | | $Cp^*_2ScCH_3$ | | | | | | |
| MO | 55 | 56 | 57 | 58 | 59 | HOMO | LUMO | 62 | 63 | 64 | 65 |
| eV | −11.54 | −9.66 | −8.68 | −8.29 | −8.07 | −7.84 | | | | | |
| % Sc (spd) | 0 | 25 | 21 | 18 | 15 | 16 | 88 | 68 | 23 | 29 | 40 |
| % Cp–C (sp) | 60 | 7 | 66 | 67 | 71 | 70 | 9 | 26 | 68 | 61 | 50 |
| % Cp–Me (sp) | 23 | 1 | 5 | 4 | 4 | 4 | 1 | 1 | 3 | 4 | 4 |
| % C–Me (sp) | 0 | 57 | 1 | 2 | 0 | 1 | 0 | 0 | 3 | 3 | 3 |
| % H–Me (s) | 0 | 8 | 0 | 0 | 0 | 2 | 0 | 3 | 0 | 1 | 1 |
| % H–Cp* (s) | 17 | 2 | 8 | 8 | 9 | 7 | 1 | 2 | 4 | 3 | 3 |

loss of $Cl^-$ was observed in these systems. The above results have been used to support the latter photoelectron spectroscopic interpretation that the Cp ligand is the HOMO in these complexes. Nevertheless, there has been some controversy in the literature concerning the nature of the photochemically-active state in $Cp_2TiCl_2$. Peterson et al.[9a] calculated (using a nonparameterized Fenske–Hall type molecular orbital method) that the highest filled molecular orbitals for this complex are mainly *p*-Cl in character. However, Tyler et al.[9a] used SCF–X$\alpha$ calculations to conclude that the HOMO is mostly $\pi$-Cp in nature, consistent with the observed photochemical homolysis of the Cp–Ti bond. Thus, at present, it appears that assignment of the lowest energy transition in these species to Cp → Ti LMCT is most generally accepted.

The nature of the lowest energy transition for the entire series of titanocene dihalides, $Cp_2TiX_2$ ($X = F^-, Cl^-$, and $I^-$) has been investigated by both molecular orbital calculations and photoelectron spectroscopy.[9b–d] Three sets of frontier molecular orbitals are of relevance: the lowest-unoccupied MOs (LUMO set) which are mostly metal in character and highest-occupied MO (HOMO) and lower-occupied MO (LOMO) sets which are either Cp or X in character, depending on which halide is employed. As one proceeds down the periodic table from $F^-$ to $I^-$, the energies of the LUMO set decrease due to decreased Ti–X interaction. The Cp set also decreases in energy (though less rapidly than the LUMOs), whereas the halogen set increases in energy due to their decreasing electronegativity. Green[9c] has proposed that these complexes can be separated into three classes of compounds. Class A possesses the Cp orbitals at much higher energy than those of halide character, class C has the halides as the HOMO, and class B has a highly mixed MO diagram, in which the HOMO contains significant amounts of both Cp and X character. Thus, while the lowest energy transition for $Cp_2TiCl_2$ has been assigned as Cp → Ti (class A), $Cp_2TiI_2$ possesses an I → Ti HOMO (class C). These assignments have been confirmed by photoelectron spectroscopy.[9d] Additionally, the latter assignment is supported by photochemical experiments, in which irradiation of $Cp_2TiI_2$ led to Ti–I bond cleavage.[19]

Theoretical calculations have not been reported for group 3 metallocene complexes (i.e. $Cp_2ScX$, X = halide). We have carried out molecular orbital calculations on $Cp^*_2ScX$ ($X = Cl, I, CH_3$) to aid in the assignment of electronic spectra and for comparison to the MO calculations reported for $Cp_2TiX_2$ complexes. MO calculations of this type could be carried out at various levels of sophistication, ranging from extended Hückel to ab initio.[20] For the study reported herein, we chose to use an INDO/S electronic structure formalism developed by Zerner et al. (ZINDO).[14a-d] ZINDO is a good program to use for transition metal complexes, since it was parameterized for all of the first-row transition metals (including scandium) based on electronic spectral data. The end result is that ZINDO does an excellent job in assignment of both absorption and photoelectron spectra of transition metal complexes.[14a–d]

In order for our ZINDO calculations to predict the transition energies as closely as possible, full $C_5(CH_3)_5^-$ ligands were used (rather than $C_5H_5^-$ or $Cl^-$ ligands). Atom positions for the C, H, and Sc atoms of $Cp^*_2ScX$ ($X = Cl, I, CH_3$) were taken from the crystal structure of $Cp^*_2ScCH_3$.[11] Cl was placed along the Sc–$CH_3$ bond vector with a Sc–Cl bond length of 2.41 Å. This Sc–Cl bond length chosen was the average of the three Sc–Cl bond lengths found for $(THF)_3ScCl_2$.[21] The bond length used for the Sc–I bond was 2.81 Å, which was chosen on the basis of the relative ionic radii of $Cl^-$ and $I^-$ (1.81 and 2.20 Å, respectively). The orbital compositions for the top six occupied MOs and the bottom five unoccupied MOs of these complexes are given in Table III. The highest-occupied molecular orbital (HOMO) for each complex is identified in the tables as orbital 60, whereas the lowest-unoccupied molecular orbital (LUMO) corresponds to orbital 61. The remaining orbitals are numbered according

---

(19) Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

(20) Knight, E. T.; Mayers, L. K.; Thompson, M. E. *Organometallics*, in press.

(21) Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1974**, 921.

**Table IV. Lowest Energy Calculated Transition Energies for $Cp^*_2ScCl$ and $Cp^*_2ScI$, Their Primary Character, and Their Calculated Oscillator Strengths (*f*)**

| energy (eV) | energy (nm) | *f* (oscillator strength) | primary character | primary composition |
|---|---|---|---|---|
| | | | $Cp^*_2ScCl$ | |
| 3.66 | 339 | 0.0032 | Cp* → Md | 95% 60 → 61 |
| 4.03 | 308 | 0.0067 | Cp* → Md | 95% 60 → 62 |
| 4.14 | 300 | 0.1011 | Cp* → Md | 82% 59 → 61 |
| 4.23 | 293 | 0.0106 | Cp* → Md | 86% 58 → 61 |
| 4.49 | 276 | 0.0136 | Cp* → Md | 84% 57 → 61 |
| 4.55 | 273 | 0.0476 | Cp* → Md | 69% 59 → 62; 11% 58 → 62 |
| 4.65 | 267 | 0.1019 | Cp* → Md | 82% 58 → 62 |
| 4.92 | 252 | 0.0382 | Cp* → Md | 78% 57 → 62; 14% 60 → 63 |
| 5.09 | 244 | 0.0867 | Cp* → Md | 71% 60 → 63; 16% 57 → 62 |
| 5.29 | 234 | 0.0041 | Cl → Md | 90% 56 → 61 |
| 5.35 | 232 | 0.0023 | Cl → Md | 91% 55 → 61 |
| 5.60 | 221 | 0.0018 | Cl → Md | 73% 56 → 62; 22% 55 → 62 |
| 5.63 | 220 | 0.0069 | Cp* → Md | 82% 59 → 63 |
| 5.68 | 218 | 0.0013 | Cl → Md | 51% 54 → 61, 16% 55 → 62; 24% 58 → 63 |
| | | | $Cp^*_2ScI$ | |
| 3.24 | 383 | 0.0017 | I → Md | 91% 60 → 61 |
| 3.60 | 345 | 0.0016 | I → Md | 93% 60 → 62 |
| 3.80 | 327 | 0.0011 | Cp* → Md | 86% 59 → 61 |
| 4.02 | 308 | 0.0423 | mixture | 42% 58 → 61; 35% 60 → 63; 13% 57 → 61 |
| 4.09 | 303 | 0.0501 | mixture | 40% 60 → 63; 36% 58 → 61; 13% 56 → 61 |
| 4.18 | 296 | 0.0572 | Cp* → Md | 76% 59 → 62; 6% 57 → 62; 6% 58 → 61 |
| 4.22 | 294 | 0.0190 | mixture | 41% 56 → 61; 17% 60 → 63; 17% 57 → 61 |
| 4.42 | 281 | 0.0205 | Cp* → Md | 65% 55 → 61; 15% 56 → 61; 5% 58 → 62 |
| 4.46 | 278 | 0.0403 | Cp* → Md | 78% 58 → 62; 6% 57 → 62; 5% 55 → 61 |
| 4.57 | 271 | 0.0073 | mixture | 50% 57 → 61; 18% 56 → 61; 7% 56 → 62 |
| 4.60 | 270 | 0.0051 | mixture | 62% 56 → 62; 16% 57 → 62; 5% 57 → 61 |
| 4.86 | 255 | 0.0306 | Cp* → Md | 64% 55 → 62; 11% 56 → 62; 10% 57 → 62 |
| 4.94 | 251 | 0.0103 | mixture | 36% 57 → 62; 24% 55 → 62; 15% 59 → 63 |
| 5.18 | 240 | 0.0241 | I → Md | 65% 57 → 63; 21% 59 → 63; 6% 58 → 63 |
| 5.24 | 237 | 0.0126 | Cp* → Md | 89% 54 → 61; 5% 55 → 61 |
| 5.30 | 234 | 0.0106 | Cp* → Md | 80% 58 → 63; 12% 57 → 63 |
| 5.43 | 229 | 0.0803 | Cp* → Md | 49% 56 → 63; 21% 59 → 63; 7% 57 → 63 |
| 5.58 | 222 | 0.1211 | Cp* → Md | 90% 54 → 62 |
| 5.60 | 221 | 0.2506 | Cp* → Md | 38% 56 → 63; 16% 59 → 63; 12% 55 → 63 |

to their energies. Since the complexes of interest possess $C_s$ symmetry (the Cp* rings are staggered and tilted), group theoretical nomenclature for the molecular orbitals would provide no further information about their characters. Configuration interaction (CI) was carried out with the top 10 filled and bottom 10 empty MOs. The calculated energies and oscillator strengths after CI of the lowest energy transitions are given in Table IV.

In agreement with the molecular orbital picture for $Cp_2TiX_2$, the LUMOs for $Cp^*_2ScX$ are primarily 3d Sc in nature, with some mixing of the Cp* ligands and very little halide character. The HOMO (orbital 60) for the chloride derivative is ~70% Cp* and 15% chloride, with the remainder associated with metal d orbitals. High chloride character does not appear until one reaches lower energies (i.e. the fifth and sixth highest filled orbitals, namely orbitals 55 and 56, which contain >80% $Cl^-$ character). In contrast, the iodide analog appears to have a HOMO which is 78% iodide in nature with the penultimate filled MOs containing a good deal of $Cp^*/I^-$ mixing. These results are consistent with those observed for $Cp_2TiX_2$, as discussed above.

As can be seen from Table IV, the two lowest energy, most allowed transitions for $Cp^*_2ScCl$ occur at 267 and 300 nm, in reasonable agreement with those obtained experimentally from the electronic absorption spectrum with molar absorptivities ≥1000 $M^{-1}$ $cm^{-1}$ (255 and 297 nm, respectively). Thus, these two transitions are assigned as the singlet transitions 58 → 62 and 59 → 61, respectively. The compositions of both orbitals 58 and 59 are primarily Cp*, whereas those of 61 and 62 are principally Sc d orbitals. The lowest energy triplet transition was also calculated. It occurs at 350 nm and corresponds to 93% 60 → 61 character. Therefore, on the basis of the semiempirical MO calculations, the lowest energy (and luminescent) transition in this complex is prinicpally Cp* → Sc LMCT, not $Cl^-$ → Sc LMCT, as previously proposed[10] and falling under Green's class A characterization.[9c] However, the small amount of halide p orbital presence is essential for luminescence to occur, as discussed later.

There is considerably more mixing in the complex $Cp^*_2ScI$. The lowest energy transitions with reasonable oscillator strength in this material are predicted to occur at 222, 229, 278, and 305 nm. The transitions which correspond to these energies are listed in Table IV. Most of the lower energy transitions are a mixture of $I^-$ → Sc and Cp* → Sc LMCT character, while the higher energy ones are principally Cp* → Sc. Therefore, the HOMOs of this complex are a mixture of both Cp* and halide composition, placing it into Green's class B category. The lowest energy (calculated) transition (60 → 61) for this complex lies at ~390 nm and is clearly $I^-$ → Sc in character. These results exactly parallel those observed for the $Cp_2TiX_2$ species mentioned above.

In contrast to $Cp_2Ti(CH_3)_2$, however, in which the HOMO is principally Ti–methyl $\sigma$ bonding in nature,[9d] the HOMO calculated for $Cp^*_2ScCH_3$ is ~80% Cp* in composition. The highest energy filled orbital containing a significant percentage of methyl character in this species is the fifth one (orbital 56). The calculated lowest energy transition for this complex (320 nm) is assigned as 60 → 61, or Cp* → Sc LMCT.

As mentioned previously, $Cp^*_2ScCH_3$ is nonluminescent under the stated conditions. This results lends considerable credence to the hypothesis that at least some degree of X lone pair character must be involved in the lowest energy transition in order for luminescence to occur. This is clearly true in the case of the iodide analog, in which the lowest energy transition is $I^- \rightarrow$ Sc LMCT. However, it is more ambiguous for the chloride species since its lowest energy transition is principally Cp* → Sc LMCT. The MO diagrams for X = $Cl^-$ and $CH_3$ are similar in the sense that both contain a Cp* → Sc lowest energy transition and that significant X character is not present until one reaches the fifth highest MO. The fact that the chloride has a room-temperature emissive lifetime of 2 μs, while the methyl derivative is nonluminescent under these conditions, implies that the presence of some nonbonding lone pair character in the HOMO (15% for X = $Cl^-$) is requisite for emission to occur. Additionally, since $Cp^*_2ScCH_3$ is nonluminescent and LMCT excited states are typically accompanied by homolysis of the involved M–L bond, it is predicted that irradiation of this complex at 320 nm will lead to the formation of Cp* radicals.

## Conclusions

In summary, permethyliscandocene halide complexes represent an important new class of room-temperature luminescent organometallics of the early, first-row transition series. The calculated molecular orbital diagrams of these complexes are similar to those proposed by others for the class of compounds with the general formula $Cp_2TiX_2$. Depending on the electronegativity of the appended X ligand, the HOMO ranges from mostly Cp* (for the more electronegative halogens) to mostly X. The limited amount of mixing in the LUMO of these complexes (principally Sc d-orbitals) is likely responsible for the long-lived emission of their LMCT excited states. Although the emissive transition is mostly Cp* → Sc LMCT in the case of $Cp^*_2ScCl$, the presence of some degree of nonbonding lone pair character in the HOMO is apparently necessary for room-temperature luminescence, as evidenced by the total lack of emission for $Cp^*_2ScCH_3$ or $Cp^*_2ScCH_2Ph$ (neither of which possess nonbonding lone pairs) under ambient conditions, despite similar MO schemes for $Cp^*_2ScCl$ and $Cp^*_2ScCH_3$. Therefore, the presence of a nonbonding lone pair from the halogen X ligand is requisite for emission to occur in fluid solution at 298 K for this series of luminescent organometallics.

**Acknowledgment.** This work was supported under Grant No. DE-FG02-85ER 13938 by the Department of Energy, Office of Basic Energy Sciences. B.W.P. is grateful for a General Electric fellowship for most of the duration of this project.

OM920397I