regular coordination geometry around the metal center. The formation of I appears to involve a two-electron reduction of $B_{10}H_{14}$ by Yb to form the $[B_{10}H_{14}]^{2-}$ anion, which then back-donates four electrons to the Yb cation through two three-center two-electron bonds. Coordination of CH_3CN ligands to the ytterbium allows isolation of I as a discrete complex.

The Yb–H–B bridges in I represent the first structurally characterized example of a three-center B–H–Ln interaction. Bridging hydrogen atoms were located, and their positions were refined. The ytterbium–hydrogen distances Yb–H(5) = 2.2 (1) Å and Yb–H(6) = 2.4 (1) Å are effectively equal.

The ^{11}B NMR spectrum of I in CD_3CN indicates that the boron cage remains bonded to the metal in solution.[12] The uncomplexed $[B_{10}H_{14}]^{2-}$ ion has C_{2v} symmetry, and its ^{11}B NMR spectrum consists of four signals of intensity 2(d):4(d):2(t):2(d), corresponding to the 2,4-, 5,7,8,10-, 6,9-, and 1,3-positions, respectively.[13] Complex I has a ^{11}B NMR spectrum that is composed of six signals of intensity 1(d):1(d):4(d):1(d):1(t):2(d). A 2D-COSY ^{11}B NMR analysis showed that the resonances correspond to the 2,4-, 5,7,8,10-, 6,9-, and 1,3-borons in the cage. This spectrum is consistent with a binding of Yb^{2+} to B(6) through a single hydrogen bridge, or bidentate binding with rapid exchange between the H(5) and H(7) sites (Scheme II). Such a spectrum should exhibit seven resonances, but coincidental overlap of the 5,7 and 8,10 boron signals would yield the observed six-line pattern. Such overlap is confirmed from the NMR analysis.

In a typical synthetic procedure, a 1:1 ratio of Ln (1.0 mmol, Yb = 0.173 g, Eu = 0.150 g) to $B_{10}H_{14}$ (1.0 mmol, 0.122 g) reacts in liquid NH_3 (15 mL) at –40 °C to give an insoluble material containing ammonia-solvated Ln^{2+} and reduced B_{10} boron hydride species.[14] Extraction of the solid material with CH_3CN yields yellow (Eu) and orange (Yb) solutions consisting of aceto-nitrile-solvated Ln^{2+} and $[B_{10}H_{14}]^{2-}$ ions.[15] Cooling the Yb^{2+} extract to –30 °C under nitrogen causes I to form as orange crystals (0.149 g, 24% yield). The ammonia-solvated materials (Eu or Yb) decompose when heated to 180 °C in vacuum with elimination of H_2 and NH_3[16] to form the closo borane compounds, grey-green $EuB_{10}H_{10}$ (II) and pea-green $YbB_{10}H_{10}$ (III), respectively. These compounds are formed in stoichiometric yields and in relatively high (ca. 97%) purities.[17]

The closo compounds II and III are primarily ionic solids.[18] Their IR spectra resemble those of the alkali metal salts of $[B_{10}H_{10}]^{2-}$, showing only absorptions due to the boron cage.[19] They are soluble in pyridine, forming bright yellow (Eu) and deep purple (Yb) solutions. The ^{11}B NMR spectrum of III in pyridine-d_5 is very similar to the spectrum observed for free $[B_{10}H_{10}]^{2-}$

(12) ^{11}B NMR data for I in CD_3CN (δ $BF_3\cdot OEt_2$ = 0.00 ppm), with coupling constants, in Hz, in parentheses, are as follows: –4.3, d (109); –7.1, d (126); –20.0, d (111); –25.6, d (113); –32.2, t (98); –40.3, d (132) ppm. Peak integration gives an intensity ratio of approximately 1:1:4:1:1:2, respectively.

(13) Lipscomb, W. N.; Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1972**, *11*, 651.

(14) The ammonia-solvated material is formed along with about 0.36 mol of H_2/mol of $B_{10}H_{14}$.

(15) On the basis of the ^{11}B NMR spectrum of the Yb^{2+} solution, there are also small amounts of the monoanions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ present.

(16) Evolved gases were collected and measured in a calibrated toepler system. The ammonia-solvated solids released 2 mol of H_2/mole of Ln present. There were 4 mol of NH_3/mol of Eu and 2 mol of NH_3/mol of Yb given off from each solid. The evolution of H_2 from the lanthanide deca-borates raises the possibility that a Ln–H intermediate is formed and assists in the transformation of *arachno*-$[B_{10}H_{14}]^{2-}$ to *closo*-$[B_{10}H_{10}]^{2-}$.

(17) Purity is based on the absence of any signals attributed to solvent in the Nujol IR spectra, and the elemental analyses for each. Calcd for $EuB_{10}H_{10}$: Eu, 56.25; B, 40.02; H, 3.73. Obsd: Eu, 55.55; B, 38.21; H, 3.46. Calcd for $YbB_{10}H_{10}$: Yb, 59.42; B, 37.12; H, 3.46. Obsd: Yb, 59.15; B, 35.73; H, 3.40. Each compound contained 0.5% residual N.

(18) Spectral data for II and III, IR (Nujol mull, NaCl plates), in cm^{-1}. $EuB_{10}H_{10}$: 2503 (s), 2456 (vs, br), 1086 (w), 1019 (mw), 974 (w). $YbB_{10}H_{10}$: 2525 (sh), 2456 (vs, br), 1076 (w), 1016 (mw), 974 (w). ^{11}B NMR data for III in pyridine-d_5 (δ $BF_3\cdot OEt_2$ = 0.00 ppm) at 353 K: +0.5, d (136); –27.5, d (102) ppm; relative intensities of 1:4, respectively. B–H coupling of the –27.5 ppm signal is not resolved at temperatures below 353 K. Eu^{2+} compounds are paramagnetic and do not give interpretable NMR spectra.

(19) Muetterties, E. L.; Balthis, J. H.; Chia, Y. T.; Knoth, W. H.; Miller, H. C. *Inorg. Chem.* **1964**, *3*, 444.

$(Rb^+$ salt),[18] indicating that the compound exists as solvent-separated ions in solution.

A New Class of Room Temperature Luminescent Organometallic Complexes: Luminescence and Photophysical Properties of Permethylscandocene Chloride in Fluid Solution

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Received August 10, 1989

The search for organometallic complexes that emit in fluid solution at room temperature has been intensely pursued for the past 35 years because of the importance of an understanding of excited-state properties to the areas of solar energy conversion and photoassisted catalysis.[1] Although extensive studies have been carried out, only complexes consisting of second- or third-row late transition metals have been identified as luminescent under the stated conditions. Usually, such luminescent complexes require the presence of an aromatic amine ligand, ruthenium tris(bi-pyridine) being prototypical; however, a limited number of exceptions to this observation have been recently noted.[2,3] We report here on the photophysics of the d^0 first row transition metal complex Cp^*_2ScCl (Cp^* = pentamethylcyclopentadienyl). To the best of our knowledge, this represents a new class of organometallic transition-metal complexes having no aromatic amine ligands that luminesce at room temperature in fluid solution.

The following UV–vis absorptions were found in solution (1:1 v/v mixture of isooctane and methylcyclohexane) at 298 K (see Figure 1): 39215 cm^{-1} (255 nm, ϵ = 2500 M^{-1} cm^{-1}), 33670 cm^{-1} (297 nm, ϵ = 2400 M^{-1} cm^{-1}), and 27930 cm^{-1}s (358 nm, ϵ = 900 M^{-1} cm^{-1}).[4] A fourth optical transition was too weak to appear by absorption spectroscopy, but was observed in the excitation spectrum at 25640 cm^{-1} (390 nm). Excitation into this lowest energy band produced a broad emission centered at 19230 cm^{-1} (520 nm) with a small shoulder toward the red as shown in Figure 1 (inset). Taking inner filter effects into consideration, this emission is essentially wavelength-independent over the range in which the compound absorbs. Therefore, the lowest energy excited state is taken to be the emissive state. This conclusion is supported, as shown by the overlap between the emission and the foot of the forbidden absorption centered at 390 nm. The

(1) See, for example: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press, Inc.: New York, 1979. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

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

(3) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.

(4) The solvents were obtained from Aldrich and were dried by reflux over the appropriate desiccant, followed by distillation and several freeze–pump cycles on a vacuum line. Molar absorptivities were determined by least-squares fits to Beer's law plots. Since the complex is air- and water-sensitive, all manipulations were carried out by using standard vacuum line techniques or in a glove box.
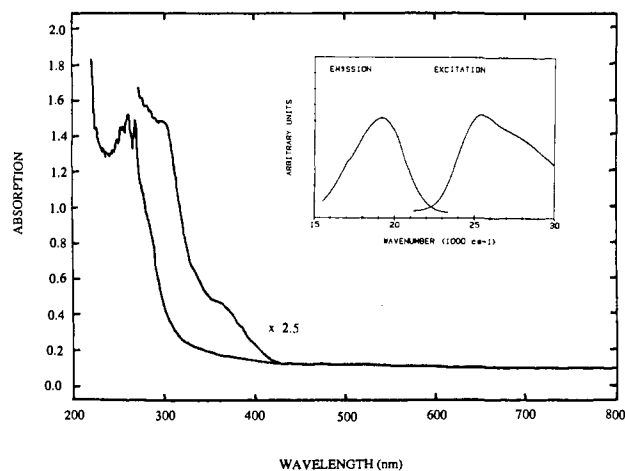
Figure 1. Absorption spectra and (inset) emission (25 640-cm^{-1} excitation) and excitation (19 230-cm^{-1} emission) spectra of permethylscandocene chloride in a 1:1 (v/v) mixture of isooctane and methylcyclohexane at 298 K.

relative luminescent quantum yield with 366-nm excitation was determined to be 0.01.[5] The excited-state lifetimes based on luminescence decay in solution at 298 K, in an isooctane-methylcyclohexane (1:1 v/v) glass at 77 K, and in the solid state at 298 K were found to be 2.0 μs, 15.0 μs, and 6.5 μs, respectively, when excited at 337 nm by using a nitrogen laser.[6] The relatively long apparent lifetime of luminescence at room temperature suggests that emission occurs from a triplet excited state, a conclusion that is further supported by the absence of any significant change in the emission spectrum at 77 K upon the addition of incremental amounts of ethyl iodide as a heavy-atom intersystem crossing agent, as well as by the forbidden nature of this absorption (absent from the UV–vis spectrum, but observed in the excitation profile).

In an effort to understand the nature of the shoulder peak in the emission spectrum, time-resolved spectroscopy was performed by using a Nd:YAG Q-switched laser and an OMA detector. Two emissions were observed and are preliminarily assigned as fluorescence and phosphorescence. The fluorescent lifetime was determined to be less than 10 ns, while the lifetime of phosphorescence was in close agreement with that observed in the luminescence decay experiment mentioned earlier. Furthermore, the emission maximum at short times following the laser pulse was found to be blue-shifted from the maximum at longer times. This result is consistent with the assignment of the lowest energy emissive state as phosphorescence, with the fluorescence occurring at slightly higher energy. The combination and overlap of the two emissions produce the spectrum observed in Figure 1 (inset).

The effect of the energy of emission as a function of polarity of the solvent was also examined. In general, the emission was blue-shifted in more polar chlorocarbon solvents. Possible assignments for the emissive transition are limited in the d^0 complex to intraligand, interligand, or ligand-to-metal charge transfer; the latter two would be expected to show solvent dependence. The assignment is further complicated by the emission of Cp* alone in hexane, which shows an absorption and emission spectrum similar to that of the compound of interest. However, the latter emission has a measured room temperature lifetime of only 580 ns under the same conditions employed to study Cp*$_2$ScCl. Furthermore, it is found that the room temperature luminescence in solution of the corresponding aniline derivative, Cp*$_2$ScNHPh, yields an emission maximum centered around 600 nm, conclusively

demonstrating that the observed emission is not simply associated with the Cp* ligand.

Lauher and Hoffmann[7] have reported a theoretical molecular orbital scheme for bent metallocene hydride complexes. They have suggested for this case that the HOMO is the σ-bonding metal hydride orbital (2a$_1$). Since the 2a$_1$ orbital in Cp*$_2$ScCl should be lower in energy than the nonbonding filled p orbitals on the chloride ligand, we suggest that the HOMO is composed of the chloride lone pairs. Optical transitions from this orbital to the 1a$_1$, 1b$_2$, and 2a$_1$* orbitals respectively are then possible. These orbitals are derived from the metal d orbitals admixing with the Cp* π-system. As a preliminary assignment, we hypothesize that the three transitions observed by absorption spectroscopy are associated with transitions from the p-Cl nonbonding HOMO to the orbitals indicated above. Based on this assignment, the forbidden absorption, which is the source of the luminescence, is assigned to the p-Cl → ^{3}(1a$_1$) transition.[8]

Luminescence quenching was observed with a number of aromatic compounds, showing Stern–Volmer correlations with luminescent intensity as a function of quencher concentration. However, the apparent lifetime of the compound was relatively unchanged even at drastically higher concentrations of quencher. This would indicate that in all cases tested[9] the mechanism of quenching is purely a static one, possibly the formation of a π-complex between the aromatic species and the Cp* ring(s) of the organometallic.

(7) Lauher, J. W.; Hoffmann, R. J. Am. Chem. Soc. **1976,** 98, 1729.
(8) Ligand-to-metal charge-transfer transitions are frequently associated with radical dissociation. It was noted at high N$_2$ laser intensities that the compound of interest decomposes, effecting changes in the Cp* region of the NMR spectra taken in C$_6$D$_6$. However, the nature of the decomposition was not investigated further because the decomposition only occurred at high laser intensities. Nevertheless, one would expect rapid radical recombination for the d^0 complex because of its high Lewis acidity if radicals are indeed formed.
(9) Quenchers employed were toluene, xylenes, biphenyl, 1,2,4,5-tetrachlorobenzene, p-dibromobenzene, hexachlorobenzene, hexamethylbenzene, phenylacetylene, diphenylacetylene, and fluorene. The usual ketone and amine quenching agents could not be employed due to their thermal reactivity with the complex of interest.

Control of Product Distribution by Marcus Type Electron-Transfer Rates for the Radical Pair Generated in Benzylic Ester Photochemistry

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Received February 28, 1989

The solution photochemistry of benzylic compounds with leaving groups (ArCH$_2$–LG) is well known[1–3] to yield products resulting from both ionic (ArCH$_2$$^+$$^-$LG) and radical (ArCH$_2$$^•$ $^•$LG) intermediates. Moreover, it has been recognized that the final composition of the product mixture need not be a direct measure of the initial excited-state bond cleavage process since electron transfer may allow interconversion between the radical pair and the ion pair. In fact, solution redox potentials suggest that the ion pair should be significantly more stable than the radical pair for most of the common leaving groups.[3] We now report results for a series of 1-naphthylmethyl esters, 1,[4] that clearly show that

(5) The quantum efficiency was measured relative to that of anthracene in hexane by adjusting the optical densities of the two samples to be equal and then integrating the area under the respective emission curves. The quantum efficiency of anthracene at 366 nm was assumed to be 0.29 (Parker, A. C. *Photoluminescence of Solutions*; Elsevier Publishing Co.: Amsterdam, The Netherlands, 1968; p 266).
(6) The excited-state decay followed simple first-order kinetics.

(1) Cristol, S. J.; Bindel, T. H. *Organic Photochemistry*; Marcel Dekker: New York, 1983; Vol. 6, p 327.
(2) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985,** 63, 3140.
(3) Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehmbey, C. *Can. J. Chem.* **1987,** 65, 1599.