Synthesis and Luminescence Spectroscopy of a Series of [η^5-CpFe(CO)$_2$] Complexes Containing 1,12-Dicarba-*closo*-dodecaboranyl and -ylene Ligands

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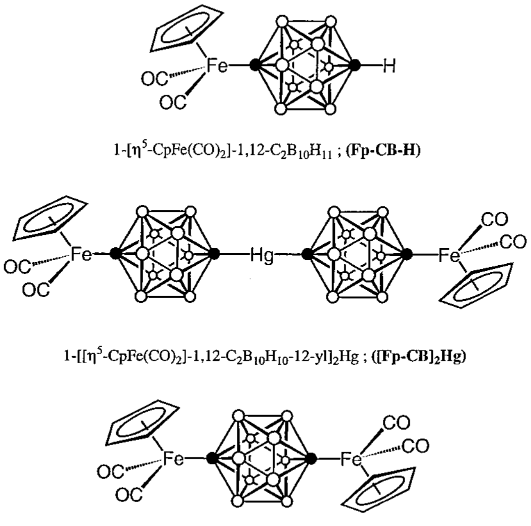
Three new cyclopentadienyliron dicarbonyl compounds, 1-[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{11}$, 1-[[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{10}$-12-yl]$_2$Hg, and 1,12-[η^5-CpFe(CO)$_2$]$_2$-1,12-$C_2B_{10}H_{10}$, composed of 1,12-dicarba-*closo*-dodecaborane as a ligand precursor were synthesized and found to be luminescent. The uncoordinated 1,12-$C_2B_{10}H_{12}$ bridging ligand precursor is luminescent with a band maximum at 25180 cm^{-1}, while the iron complexes luminesce at lower energies in the range 13120−14210 cm^{-1}. The lowest energy excited electronic state in the iron complexes is assigned to a ligand field transition of the iron chromophore. Cyclic voltammetry of 1,12-[η^5-CpFe(CO)$_2$]$_2$-1,12-$C_2B_{10}H_{10}$ displays two discrete one-electron oxidations, and the luminescence maximum is red shifted from that observed in 1-[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{11}$. Both of these observations suggest that the iron-centered chromophores are weakly coupled. In contrast, the 1-[[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{10}$-12-yl]$_2$Hg complex is uncoupled as is evident from the single oxidation process observed with cyclic voltammetry. The extinction coefficient of 1,12-[η^5-CpFe(CO)$_2$]$_2$-1,12-$C_2B_{10}H_{10}$ is six times that of 1-[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{11}$, while the extinction coefficient of 1-[[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{10}$-12-yl]$_2$Hg is only twice that of 1-[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{11}$. These spectroscopic properties are explained in terms of two coupled antiparallel transition dipole moments.

Introduction

The 1,12-dicarba-*closo*-dodecaboran-1,12-ylene moiety (CB) is a high-symmetry bridging ligand that forms covalent bonds with metal centers having two accessible oxidation states. During the course of our studies of such bridged metal systems we discovered that CB complexes with η^5-CpFe(CO)$_2$, Fp, were unexpectedly luminescent. Neither the bridging ligand nor η^5-CpFe(CO)$_2$L compounds with other ligands, L, have previously been reported to luminesce.[1]

The ability of the bifunctional 1,12-$C_2B_{10}H_{10}$-1,12-ylene cage to provide electronic transmission has been qualitatively revealed by Wade et al. in a study of carbon-13 chemical shifts and ultraviolet−visible spectra of various disubstituted 1,12-$C_2B_{10}H_{10}$-1,12-ylene derivatives with organic electron donors and acceptors directly bonded to the terminal carbons of the carborane cage.[2] The use of similar metal-bonded carboranes for this purpose has not been previously described, although η^5-CpFe(CO)$_2$-substituted 1-CH_3-1,2-$C_2B_{10}H_{11}$-2-yl[3] and 1,7-$C_2B_{10}H_{11}$-1-yl[4] are known. In addition, Hawthorne et al. synthesized the smaller cage compound, 1,10-[η^5-CpFe(CO)$_2$]$_2$-1,10-$C_2B_8H_8$.[3] Surprisingly this chemistry has not been extended to include 1,12-$C_2B_{10}H_{12}$. The bridged diferracarborane species under investigation, 1,12-[η^5-CpFe(CO)$_2$]$_2$-1,12-$C_2B_{10}H_{10}$ (Fp-CB-Fp) (Figure 1), was expected to show evidence of electronic communication between the iron centers, and the luminescence spectra were expected to provide evidence for this electronic communication.



1-[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{11}$; **(Fp-CB-H)**

1-[[η^5-CpFe(CO)$_2$]-1,12-$C_2B_{10}H_{10}$-12-yl]$_2$Hg ; **([Fp-CB]$_2$Hg)**

1,12-[η^5-CpFe(CO)$_2$]$_2$-1,12-$C_2B_{10}H_{10}$; **(Fp-CB-Fp)**

Figure 1. Molecular structures, chemical formulas, and abbreviations of the ferracarborane compounds.

In this paper we report the synthesis and luminescence spectra of a series of [η^5-CpFe(CO)$_2$]-*closo*-1,12-$C_2B_{10}H_{10}$-1-yl and -1,-12-ylene derivatives. The lowest excited state is assigned to a ligand field, iron-centered transition based on absorption spectra and their comparison to literature assignments of η^5-CpFe(CO)$_2$X compounds, where X = halogen or methyl, and preresonance Raman spectra. The electronic states of the two η^5-CpFe(CO)$_2$ chromophores are coupled in the Fp-CB-Fp complex. The effect of this coupling on the cyclic voltammetry, extinction coefficients, and luminescence band maxima is compared to the results obtained with the uncoupled Hg compound, [Fp-CB]$_2$Hg.

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Experimental Section

Materials. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Argon gas was dried by passage through a column of reduced chromium oxide on silica. Diethyl ether was dried over sodium benzophenone ketyl and freshly distilled prior to use. *p*-Carborane was obtained from Katchem Ltd. and used as purchased. The η^5-CpFe(CO)$_2$Cl precursor was synthesized according to literature methods.[5] All other chemicals were used as purchased from various sources. Infrared spectra were obtained using a Nicolet Nexus 470 FTIR. All NMR spectra were recorded at room temperature using a Bruker ARX500 spectrometer. The EI and CI mass spectra were obtained on a VG Autospec spectrometer.

Synthesis. 1-[$\boldsymbol{\eta}^5$-CpFe(CO)$_2$]-1,12-C$_2$B$_{10}$H$_{11}$ (Fp-CB-H). To a solution of 1,12-$C_2B_{10}H_{12}$ (1.00 g, 6.93 mmol) in Et_2O (30 mL) was added *n*-BuLi (1.6 M in hexanes, 4.33 mL, 6.93 mmol) dropwise at −78 °C. After warming to room temperature (rt) and stirring for 3 h, the solution was cooled again to −78 °C and η^5-CpFe(CO)$_2$Cl (1.47 g, 6.93 mmol) was added at once. The solution was warmed to rt and stirred for 15 h. The solvent was removed in vacuo and the reddish brown residue redissolved in benzene, extracted with H_2O, and flashed through activated basic alumina (Aldrich, Brockmann I, ∼150 mesh) with petroleum ether/benzene (2:1) as the eluent. The yellow first fraction was collected, and the solvent was removed, leaving the crystalline product Fp-CB-H (1.53 g, 69% yield): FTIR (CCl_4 sol.) 3065, 2961, 2926, 2855, 2607, 2036, 1990 (cm^{-1}); ^{1}H NMR (500 MHz, C_6D_6) δ 3.75 (s, 5H, −Cp), from 3.20 to 1.80 (m, br, 10H, cage BH), 2.17 (s, br, 1H, cage CH); ^{13}C NMR (125 MHz, C_6D_6) δ 214.29, 86.58, 64.67, 63.76; ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, BF_3·Et_2O external) δ −8.53, −12.36 (5:5); HRMS (EI) *m*/*z* calcd for $C_9H_{16}B_{10}FeO_2$ 320.1508 (M$^+$), found 320.1502.

1-[[$\boldsymbol{\eta}^5$-CpFe(CO)$_2$]-1,12-C$_2$B$_{10}$H$_{10}$-12-yl]$_2$Hg ([Fp-CB]$_2$Hg). To a solution of Fp-CB-H (1.06 g, 3.30 mmol) in Et_2O (40 mL) was added *t*-BuLi (1.2 M in pentane, 2.75 mL, 3.30 mmol) dropwise at −78 °C. After warming to rt and being stirred for 5 h, the solution was cooled again to −78 °C, and $HgCl_2$ (0.45 g, 1.65 mmol) was added at once. The solution was then heated at reflux for 24 h. After the solution was allowed to cool to ambient temperature, the solvent was removed in vacuo and the greenish yellow residue was redissolved in benzene, extracted with H_2O, and flashed through activated basic alumina (Aldrich, Brockmann I, ∼150 mesh) with petroleum ether/benzene (2:1) as the eluent. The yellow first fraction was the unreacted starting material Fp-CB-H. The remaining yellow fraction was flashed out of the column with benzene and collected, and the solvent was removed, leaving the powdery product [Fp-CB]$_2$Hg (0.67 g, 48% yield): FTIR (CCl_4 sol.) 2958, 2928, 2856, 2588, 2036, 1990 (cm^{-1}); ^{1}H NMR (500 MHz, C_6D_6) δ 3.71 (s, 10H, −Cp), from 3.30 to 1.70 (m, br, 20H, cage BH); ^{13}C NMR (125 MHz, C_6D_6) δ 214.33, 86.58, 62.11; 61.31 ^{11}B{^{1}H} NMR (160 MHz, C_6H_6, BF_3·Et_2O external) δ −6.25, −9.55 (10:10); ^{199}Hg{^{1}H} NMR (89.6 MHz, C_6H_6, 1.0 M PhHgCl in [D$_6$]-DMSO external) δ −1163; HRMS (CI) *m*/*z* calcd for $C_{18}H_{30}B_{20}Fe_2HgO_4$ 839.2545 (M$^+$), found 839.2600.

1,12-[$\boldsymbol{\eta}^5$-CpFe(CO)$_2$]$_2$-1,12-C$_2$B$_{10}$H$_{10}$ (Fp-CB-Fp). To a solution of Fp-CB-H (0.38 g, 1.19 mmol) in Et_2O (50 mL) was added *t*-BuLi (1.7 M in pentane, 0.70 mL, 1.19 mmol) dropwise at −78 °C. After being warmed to rt and stirred for 3 h, the solution was cooled again to 0 °C, and η^5-CpFe(CO)$_2$Cl (0.28 g, 1.32 mmol) was added at once. The solution was then heated at reflux for 20 h. The solvent was then removed in vacuo at ambient temperature, and the reddish brown residue was redissolved in benzene, extracted with H_2O, and flashed through activated basic alumina (Aldrich, Brockmann I, ∼150 mesh) with petroleum ether/benzene (2:1) as the eluent. The yellow first fraction was the unreacted starting material Fp-CB-H. The remaining yellow fraction was flashed out of the column with benzene and collected, and the solvent was removed, leaving the crystalline product Fp-CB-Fp (0.40 g, 67% yield): FTIR (CCl_4 sol.) 2956, 2928, 2856, 2581, 2033, 1987 (cm^{-1}); ^{1}H NMR (500 MHz, C_6D_6) δ 3.83 (s, 10H, −Cp), from 3.30 to 2.15 (m, br, 10H, cage BH); ^{13}C NMR (125 MHz, C_6D_6) δ 214.74, 86.61, 61.11; ^{11}B{^{1}H} NMR (160 MHz, C_6H_6, BF_3·Et_2O external) δ −7.03 (10); HRMS (CI) *m*/*z* calcd for $C_{16}H_{20}B_{10}Fe_2O_4$ 496.1073 (M$^+$), found 496.1080.

Emission Spectra. Luminescence spectra of powders taken at 10 K were obtained using a Spex 1702 single monochromator equipped with a Hamamatsu S1 photomultiplier tube. The signal was recorded with a Stanford Research System SR400 photon counter and an IBM personal computer. The 350.7 nm line from a Coherent I-300 krypton ion laser at 2 mW was used for excitation. Samples were cooled inside an Air Products closed-cycle helium refrigerator displex equipped with a thermocouple.

Absorption Spectra. Absorption spectra were taken at room temperature using a UV3101 PC Shimadzu spectrophotometer. Samples were dissolved in distilled and degassed methylene chloride in sealed quartz cuvettes

Raman Spectra. Raman (nonresonance) spectra were taken using the 676.4 nm line from a Coherent I-90K krypton ion laser at an excitation power of 40 mW. Spectra were obtained using a Jobin-Yvon 640HR triple monochromator and Princeton Instruments model LN/CCD 1024EUV liquid nitrogen cooled CCD and stored on a PC computer. Resonance Raman spectra were taken using the 457.9 nm line from a Coherent I-90 argon ion laser at an excitation power of 25 mW. Spectra were obtained at room temperature using a Spex 1401 double monochromator equipped with an RCA C31034 photomultiplier tube. Data were collected with a Stanford Research System SR400 photon counter and stored on an IBM PC computer. All Raman and resonance Raman spectra were collected while spinning a pressed pellet containing a mixture of the ferracarborane compounds and KNO_3 (2:1 wt. %) as a reference standard.

Cyclic Voltammetry. Cyclic voltammetry measurements were recorded using a Bioanalytical Systems Inc. CV-27 cyclic voltammograph. Redox potentials of η^5-CpFe(CO)$_2$Cl (Fp-Cl), Fp-CB-H, [Fp-CB]$_2$Hg, and Fp-CB-Fp were measured in CH_3CN solutions containing 100 mM $(Et_4N)^+(PF_6)^-$ as the electrolyte vs Ag/AgCl reference electrode.

Results

Synthesis. Initial attempts to synthesize the monoferracarborane compound, Fp-CB-H, following preparative methods described for analogous compounds[3] led to the desired product in only low yield. The desired product was successfully prepared by reacting the monolithio salt of 1,12-$C_2B_{10}H_{12}$ with η^5-CpFe(CO)$_2$Cl (Fp-Cl) in dry diethyl ether at room temperature. The crude product was purified by flash chromatography through activated basic alumina (Aldrich, Brockmann I, ∼150 mesh) with petroleum ether/benzene (2:1) as the eluent. Unreacted Fp-Cl adheres strongly to the stationary phase and remains on the alumina. Upon removal of solvent, the yellow crystalline product was present in 69% yield and required no further purification. The pure product was easily identified by the ^{11}B{^{1}H} NMR spectrum, which exhibits two resonances of equal integration area at δ −8.53 and −12.36 (5B:5B), as well as by the use of other standard characterization techniques.

The diferracarboranyl mercury compound, [Fp-CB]$_2$Hg, was synthesized by initial lithiation of Fp-CB-H with *tert*-butyllithium in diethyl ether followed by the addition of $^1/_2$ equiv of mercury(II) dichloride and reaction at ambient temperature for 24 h. After a water workup, the product was purified by flash chromatography through activated basic alumina (Aldrich, Brockmann I, ∼150 mesh) with petroleum ether/benzene (2:1) as the eluent to recover the starting material, Fp-CB-H. The yellow product did not elute from the column with this solvent mixture; it was purged from the column with benzene. The mercury-linked product was isolated as a yellow powder in 48% yield. The ^{11}B{^{1}H} NMR spectrum showed two resonances of equal integration area at δ −6.25, −9.55 (10B:10B), while the ^{199}Hg{^{1}H} NMR spectrum contained a single resonance at δ −1163.

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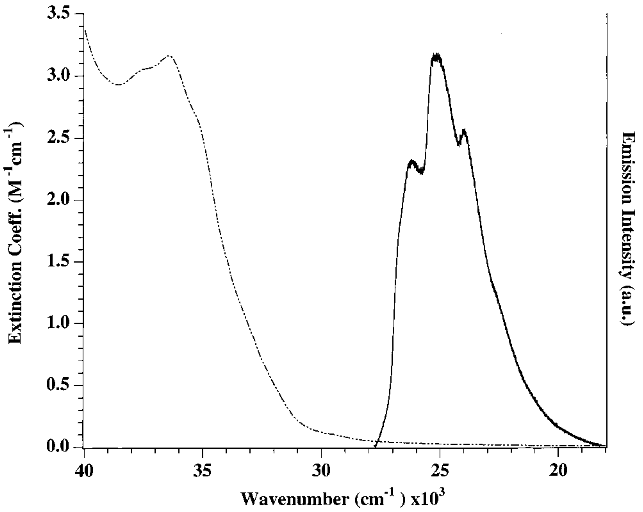

Figure 2. Room temperature absorption spectrum of H-CB-H in CH_2Cl_2 (dash−dotted line) and 15 K emission spectrum (solid line).

Direct synthesis of the diferracarborane compound, Fp-CB-Fp, was attempted by room temperature reaction of the dilithio-1,12-$C_2B_{10}H_{10}$ dianion with 2 equiv of Fp-Cl. This produced only the mono product, Fp-CB-H. Eventually, Fp-CB-Fp was prepared much like the $[Fp\text{-}CB]_2Hg$ compound described above. The precursor, Fp-CB-H, was lithiated with *tert*-butyllithium in diethyl ether followed by the addition of 1 equiv of Fp-Cl and heating at reflux for 20 h. The reaction does not proceed at room temperature. Unreacted Fp-CB-H was removed by flash chromatography through activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with petroleum ether/benzene (2:1) as the eluent, as before. The yellow product did not elute from the column with this solvent mixture; it was purged from the column with benzene, leaving any Fp-Cl behind. The product was isolated as yellow crystals in 67% yield. The $^{11}B\{^1H\}$ NMR spectrum showed one peak at δ −7.03 (10B).

Luminescence Spectra. All of the compounds that were studied are luminescent at low temperatures. The luminescence band maxima of the three ferracarborane complexes are observed at a much lower energy than that of the 1,12-dicarbadodecaborane ligand.

The 10 K emission spectrum of 1,12-$C_2B_{10}H_{12}$, H-CB-H, displayed in Figure 2 (solid line) with a peak maximum at 25180 cm^{-1} shows a resolved vibronic progression with an average spacing of 1110 ± 50 cm^{-1} and a full-width at half-maximum (fwhm) of 4100 cm^{-1}. The 10 K emission spectrum of Fp-CB-H displayed in Figure 3 (top panel) shows a broad unresolved band beginning at approximately 16600 cm^{-1} with a peak maximum at 14210 cm^{-1} and a fwhm of 2200 cm^{-1}. The low-temperature emission spectrum of $[Fp\text{-}CB]_2Hg$ displayed in Figure 3 (middle panel) shows a broad unresolved band beginning at approximately 16200 cm^{-1} with a peak maximum at 13740 cm^{-1} and a fwhm of 2400 cm^{-1}. The low-temperature emission spectrum of Fp-CB-Fp displayed in Figure 3 (bottom panel) shows a broad unresolved band beginning at approximately 16100 cm^{-1} with a peak maximum at 13120 cm^{-1} and a fwhm of 2400 cm^{-1}.

Absorption Spectra. The room temperature solution absorption spectrum of H-CB-H, shown in Figure 2 (dash-dotted line), shows a weakly resolved vibronic progression with an average spacing of 1090 cm^{-1} and a peak maximum at 36430 cm^{-1}. The absorption has a half-width at half-maximum of 2400 cm^{-1} and an extinction coefficient of 3.2 M^{-1} cm^{-1}. A low-intensity shoulder is located to lower energy at 29460 cm^{-1} with an approximate extinction coefficient of 0.1 M^{-1} cm^{-1}.

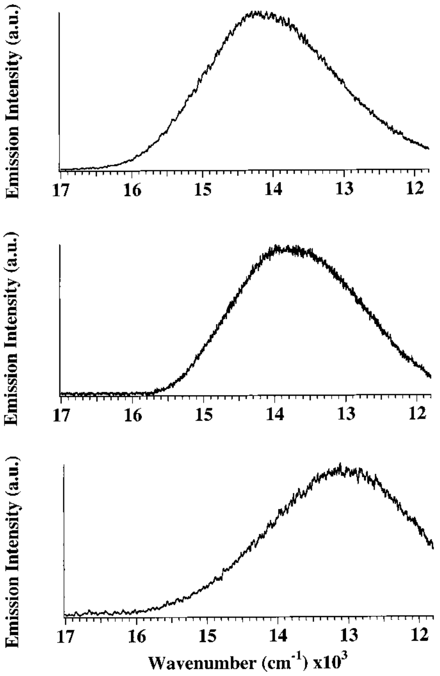

Figure 3. Solid state emission spectra taken at 15 K of Fp-CB-H (top panel), $[Fp\text{-}CB]_2Hg$ (middle panel), and Fp-CB-Fp (bottom panel).

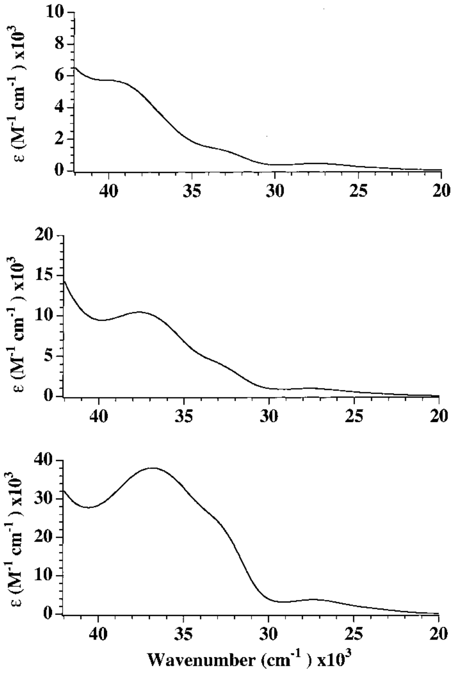

Figure 4. Room temperature absorption spectra of Fp-CB-H (top panel), $[Fp\text{-}CB]_2Hg$ (middle panel), and Fp-CB-Fp (bottom panel) in CH_2Cl_2.

The room temperature solution absorption spectrum of Fp-CB-H, shown in Figure 4 (top panel), shows several broad poorly resolved bands. The lowest energy peak is observed at 27470 cm^{-1} with an extinction coefficient of 590 M^{-1} cm^{-1}, and a less intense shoulder is observed to lower energy at approximately 23950 cm^{-1}. To higher energy an intense peak is observed at 39680 cm^{-1} with an extinction coefficient of 5890 M^{-1} cm^{-1} with a less intense shoulder to lower energy at approximately 33110 cm^{-1}.

Table 1. Emission and Absorption ($\epsilon = M^{-1}\ cm^{-1}$) Energies ($cm^{-1}$) for H-CB-H, Fp-CB-H, [Fp-CB]$_2$Hg, and Fp-CB-Fp

	emission max	fwhm
H-CB-H	25180	4100
Fp-CB-H	14210	2200
[Fp-CB]$_2$Hg	13740	2400
Fp-CB-Fp	13120	2400

	absorption max			
H-CB-H	36500 (3.2)	29150 (sh)		
Fp-CB-H	39680 (5890)	33110 (sh)	27470 (590)	23950 (sh)
[Fp-CB]$_2$Hg	37660 (10790)	32950 (sh)	27430 (1180)	23950 (sh)
Fp-CB-Fp	36830 (38020)	32800 (sh)	27280 (3760)	23950 (sh)

Table 2. Raman Vibrational Frequencies and Excited State Distortions of Fp-CB-H and Fp-CB-Fp

Fp-CB-H		Fp-CB-Fp		
$\hbar\omega$ (cm^{-1})	Δ_i/Δ_{ref}	$\hbar\omega$ (cm^{-1})	Δ_i/Δ_{ref}	assign.
178	1.27	136	1.84	ν(Fe−CB)[a,b]
193	0.603	191	1.19	
217	1.33	215	0.664	
358	1.00	360	1.00	ν(Fe−Cp)[a]
390	0.720	404	0.669	
498	0.341	501	0.292	ν(Fe−CO)[c]

[a] Reference 2. [b] Reference 3. [c] Reference 1.

The room temperature solution absorption spectrum of [Fp-CB]$_2$Hg, shown in Figure 4 (middle panel), also shows several broad unresolved bands. The lowest energy peak is observed at 27430 cm^{-1} with an extinction coefficient of 1180 $M^{-1}\ cm^{-1}$, and a less intense shoulder is observable to lower energy at approximately 23950 cm^{-1}. An intense peak is observed at higher energy at 37660 cm^{-1} with an extinction coefficient of 10790 $M^{-1}\ cm^{-1}$ with a similar shoulder to lower energy at 32950 cm^{-1}.

The room temperature solution absorption spectrum of Fp-CB-Fp, shown in Figure 4 (bottom panel), shows a broad unresolved peak at 27440 cm^{-1} with a measured extinction coefficient of 3760 $M^{-1}\ cm^{-1}$, and a less intense shoulder is observable to lower energy at approximately 23950 cm^{-1}. Similar to the other ferracarborane compounds, an intense peak is observed at 36830 cm^{-1} with an extinction coefficient of 38020 $M^{-1}\ cm^{-1}$ and a shoulder at 32680 cm^{-1}.

A summary of the absorption and emission peak maxima along with the corresponding extinction coefficients is given in Table 1.

Raman Spectra. The preresonance Raman intensities and frequencies of the Fp-CB-H and Fp-CB-Fp compounds that play an important role in the subsequent discussion are listed in Table 2. The numerical factor of importance is the relative intensity of the normal modes, which is related to the excited state distortions multiplied by the vibrational frequencies, $I_k = \Delta_k^2\omega_k^2$. The normal modes with the largest I_k/ω_k^2 values in the Fp-CB-H complex are associated with the 178, 193, 217, 358, 390, and 498 cm^{-1} vibrations. The normal modes with the largest I_k/ω_k^2 values in the Fp-CB-Fp complex are assigned to the 136, 191, 215, 360, 404, and 501 cm^{-1} vibrations.

Cyclic Voltammetry. The measured oxidation potentials vs the Ag/AgCl reference electrode were (+1.29 V) for Fp-Cl, (+1.54 V) for Fp-CB-H, (+1.49 V) for [Fp-CB]$_2$Hg, and (+1.41 V; +1.58 V) for Fp-CB-Fp. These were irreversible oxidation reactions.

Discussion

Luminescence from the title compounds is unexpected because neither metal-containing dicarbadodecaborane derivatives nor η^5-CpFe(CO)$_2$X species have been reported to emit. Since luminescence from these types of compounds is unknown, there are no precedents in the literature concerning the assignment of the luminescent electronic state. The possible assignments of the emission include a dicarbadodecaborane-centered transition, a charge-transfer transition, or a ligand field (d−d) transition. These possibilities are discussed individually below.

1. Assignment of the Lowest Electronic States. A. Ligand-Centered Luminescence from 1,12-Dicarba-*closo*-dodecaborane. The low-temperature emission spectrum of H-CB-H, displayed in Figure 2, shows that the uncoordinated bridging ligand precursor luminesces in the high-energy visible region. The luminescence spectrum overlaps the lowest energy weak-intensity shoulder ($\epsilon \approx 0.1\ M^{-1}\ cm^{-1}$) at about 27000 cm^{-1}.

The lowest energy electronic transitions in H-CB-H are assigned as nonbonding to σ antibonding ($B_{nb} \rightarrow B-C_{\sigma*}$) $^1A_{1g} \rightarrow {}^{1,3}E_{1g}$.[6] Ab initio molecular orbital calculations showed that the HOMO is a nonbonding orbital on boron and that the LUMO is a σ antibonding orbital between carbon and boron. The lowest energy absorption transition is both dipole forbidden and spin forbidden, consistent with its low extinction coefficient. It becomes weakly allowed by vibronic coupling and spin−orbit coupling.[7, 8]

The luminescence spectrum of H-CB-H shows resolved vibronic structure with an average separation of 1110 ± 50 cm^{-1}. This vibronic spacing probably corresponds to a totally symmetric cage stretching vibration.[9−11] In the absorption spectrum of a higher energy excited state, the resolved vibronic bands have a spacing of about 1090 cm^{-1} indicative of a decreased force constant in the excited state.

B. Metal-Centered Luminescence from the Iron Complexes. The ferracarborane complexes luminesce at a much lower energy (in the visible/near-IR region) than the free carborane ligand precursor. The low energies of the band maxima in the luminescence spectra of the iron complexes suggest that the lowest energy excited electronic state is no longer centered on the dicarbadodecaboranyl and -ylene ligands. It is unlikely that substitution of a terminal cage C−H hydrogen by a η^5-CpFe(CO)$_2$ unit lowers the energy of the luminescent state on the ligand by over 10000 cm^{-1}. The red-shifted luminescence of the derivatized cages suggests that the origin of the luminescent excited state involves the η^5-CpFe(CO)$_2$ substituent.

The absorption spectra of Fp-Cl and Fp-CB-H are similar. The lowest energy absorption peak of Fp-Cl, with an absorption maximum at 25700 cm^{-1}, has an extinction coefficient of 565 $M^{-1}\ cm^{-1}$.[12] The lowest energy absorption band of Fp-CB-H has a peak maximum at 27470 cm^{-1} and an extinction coefficient of 590 $M^{-1}\ cm^{-1}$. The similarities between the absorption band energies and extinction coefficients of Fp-Cl and Fp-CB-H suggest that the lowest energy excited state involves the η^5-CpFe(CO)$_2$ unit.

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The similarities in the absorption spectra of Fp-X (X = halogen) and Fp-CB-H indicate that the lowest energy absorption band in the ferracarborane is not a charge-transfer transition involving the metal and carborane cage. The absorption spectra of the Fp-X compounds show minor changes in the band energies upon variation of the X ligand from Cl to Br to I.[12] Furthermore, the extinction coefficients are smaller than expected for charge-transfer transitions.

Spectroscopic studies of Fp-X complexes suggest that the lowest energy transition is primarily ligand field in character.[13−24] Photoelectron ionization spectra were used to assign the highest occupied molecular orbital to an iron 3d antibonding molecular orbital.[15,16] In addition, the extinction coefficient of the lowest energy band in the Fp-Cl absorption spectrum is consistent with ligand field electronic transitions typically exhibiting extinction coefficients on the order of 10^1−10^2 M^{-1} cm^{-1}.[12,25] Although none of these arguments can unambiguously prove that the low-energy absorption band in the ferracarborane species originates from a d−d transition, all of the available evidence supports this assignment.

Further support for this assignment is provided by the preresonance Raman intensities. The intensities are related to the bond length changes that occur when the excited state is populated.[26] The d−d transition is expected to cause changes in the metal−ligand bond distances, and these excited state distortions are estimated by Savin's formula.[27] The largest distortions, listed in Table 2, involve low-frequency metal−ligand normal modes and metal−ligand bonds. The vibrational assignments of Fp-X type compounds and of 1,12-$C_2B_{10}H_{12}$ are well-established in the literature.[9−11,28−30] A more detailed analysis of the distortions is not warranted because the intensities probably include contributions from the higher energy states with larger extinction coefficients. The preresonance enhancement of metal−ligand vibrational modes is consistent with the ligand field assignment, and the lack of significant distortions in ligand-centered normal modes rules against a charge-transfer assignment.

2. Electronic Communication. A. Cyclic Voltammetry. The strongest evidence for electronic communication between the metals is provided by cyclic voltammetry. The oxidation potentials for the compounds containing two iron centers depend upon the identity of the bridging units. If there were no communication, both metals would be oxidized at the same potential, but if they communicate, the second oxidation potential will be significantly different from that of the first. The two-metal system bridged by two CB ligands connected by a mercury atom, [Fp-CB]$_2$Hg, has only one irreversible oxidation potential (+1.49 V). Its value is similar to that of the one-metal reference Fp-CB-H (+1.54 V). However, the two-metal system with one CB bridging ligand, Fp-CB-Fp, shows *two* irreversible oxidation potentials at +1.41 and +1.58 V. These results show that the two metal centers exhibit electronic communication across a single CB ligand.

B. Nonadditivity in the Absorption Spectra. The absorption spectra of the dicarbadodecaborane complexes containing multiple η^5-CpFe(CO)$_2$ units show subtle effects of electronic coupling. The extinction coefficient of the lowest energy peak of the two-metal system separated by two CB ligands and a mercury atom, [Fp-CB]$_2$Hg, is exactly twice that of the one-metal complex, Fp-CB-H. In contrast, the absorption spectrum of the two-metal uncoupled complex with communication between the irons, Fp-CB-Fp, shows a *6-fold* increase in the extinction coefficient. This significant nonlinear increase is a signature of coupling between the metals.

C. Shifts in the Emission Spectra. An interesting feature of the luminescence spectra is the shift to lower energy when the η^5-CpFe(CO)$_2$ chromophores are coupled. The emission spectrum shows that replacement of the terminal −H in Fp-CB-H by the −Hg[CB-Fp] chromophore produces a small shift of 470 cm^{-1}. This shift is probably due to a small change in the ligand field strength of the CB ligand when the Hg is bonded to it. However, replacement of the terminal −H in Fp-CB-H by the −Fp chromophore creates a much larger red shift of 1090 cm^{-1}. This large shift contains a small component derived from the change in the ligand field strength of the CB ligand and a much larger component as a result of the electronic coupling.

Coupling between transition dipole moments is known to cause a red shift in the absorption and emission band maxima.[31] The selection rules governing the direction of the energy shift are related to the relative orientation of the transition dipole moments. In the case of the ferracarborane compounds the transition dipole moments are antiparallel and the lowest energy state resulting from the coupling becomes more allowed.

The dipole moments are aligned antiparallel to each other because Fp-CB-Fp and [Fp-CB]$_2$Hg have a center of symmetry. The solution IR and Raman spectra of Fp-CB-Fp show two mutually exclusive ν(CO) vibrational modes, which implies that the molecular symmetry is C_{2h} and that the dipole moments orientations on each η^5-CpFe(CO)$_2$ chromophore are opposite to each other. The antiparallel dipole moments also account for the increased extinction coefficient in the coupled Fp-CB-Fp compound absorption spectrum compared to that of the [Fp-CB]$_2$Hg compound.

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Summary

A series of η^5-CpFe(CO)$_2$ complexes containing *closo*-dicarbadodecaboranyl and -ylene ligands were synthesized. This new family of ferracarboranes, as well as *p*-carborane itself, luminesce. The luminescence band maximum of *p*-carborane occurs in the blue region of the visible spectrum and is assigned as a nonbonding to antibonding transition, while the emission of the ferracarboranes occurs in the red/near-IR region of the spectrum and is assigned to a metal d−d transition. There is an electronic coupling of the iron-centered chromophores in Fp-CB-Fp, but little to no coupling is found in [Fp-CB]$_2$Hg. Cyclic voltammetry of [Fp-CB]$_2$Hg shows only a single irreversible oxidation reaction while the coupled Fp-CB-Fp system displays two irreversible one-electron oxidations. In addition, the low-energy absorbance spectrum of [Fp-CB]$_2$Hg is the sum of the absorption maxima of two of the Fp-CB-H chromophores, but the absorption maximum of Fp-CB-Fp is six times that of the individual chromophore. The luminescence maximum of Fp-CB-Fp is red shifted by 1090 cm^{-1} from the luminescence maximum of Fp-CB-H. These spectroscopic properties are explained in terms of two coupled antiparallel transition dipole moments.

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