Inorg. Chem. **2001,** *40,* 7047−7053 **7047**

Fe^{II}-to-Co^{III} Charge-Transfer Transitions in Methylene-Bridged Metallocene Salts

Stephen Barlow[†]

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U.K.

Received June 22, 2001

Four compounds have been studied which contain ferrocene or octamethylferrocene donors linked by CH_2 bridges to cobaltocenium or pentamethylcobaltocenium acceptors. The electronic spectra of these compounds cannot be accounted for by superposition of those of the constituent metallocenes; in each case, a low-energy solvatochromic absorption is observed, the energy of which parallels the difference in electrode potentials between the iron and cobalt centers. This absorption is assigned to Fe^{II}-to-Co^{III} charge transfer; analysis using Hush theory gives delocalization parameters V and α in the ranges 46−130 meV and 0.019−0.069, respectively, indicating much stronger coupling between the metal centers than in structurally similar ferrocene/ferrocenium systems.

Introduction

Intervalent charge-transfer (IVCT) transitions are a feature of class II mixed-valence compounds.[1,2] There has been considerable interest in the study of these transitions since Hush developed the theory linking optical electron transfer with the Marcus theory of thermal electron transfer.[3] Besides the insights they afford into electron-transfer processes, studies of IVCT have also led to exploitation in nonlinear optics; low-lying charge-transfer states with strong coupling to the ground state are associated with large first hyperpolarizabilities.[4] For example, $[(CO)_5Mo^0{-}\mu\text{-}CN{-}Ru^{III}(NH_3)_5]^{2+}$ shows a prominent Mo^0-to-Ru^{III} transition at 693 nm (14 400 cm^{-1}) and has a first hyperpolarizability of 225×10^{-30} esu.[5]

Ferrocene−ferrocenium mixed-valence systems have been much studied;[6] the IVCT (Fe^{II}-to-Fe^{III}) absorptions are found in the energy range ca. 4500−8500 cm^{-1}. Generally transitions are observed only when the two ferrocenes are joined directly (as in biferrocenium salts)[7] or by a conjugated bridge (such as −CH═CH−).[8] In general, transitions are not observed in species with saturated bridges such as $[Fc_2CH_2]^+$ (Fc = ferrocenyl),[9] $[Fc_3B]^+$,[9] $[Fc_3P]^+$,[9] $[Fc_2S]^+$,[10] $[Fc_2Se]^+$,[11,12] and the cations of [1^2]ferrocenophanes;[13] i.e., these species are class I. However, weak IVCT transitions have been observed in a few saturated systems including $[Fc_2SiMe_2]^+$,[14] $[Fc_3CH]^+$,[9] and the zwitterionic $[Fc_4B]$.[15] In the latter two cases, the electronic mixing leading to IVCT has been attributed to the effects of steric crowding, leading to close metal−metal approaches.

The syntheses of the trimetallic **Fe2CoA**[16] and the tetrametallic **Fe3Co**[17] (Figure 1) have recently been reported, and the purple color of these species has been noted. This color would be unexpected from the superposition of spectra of the constituent ferrocene (orange), octamethylferrocene (yellow-orange), and cobaltocenium (yellow) chromophores. This paper describes investigations of the electronic spectra of **Fe2CoA** and **Fe3Co**, together with those of two new related compounds, **FeCo** and **Fe2CoB**, and shows that the unexpected color of these compounds may be attributed to Fe^{II}-to-Co^{III} IVCT.

Experimental Section

Cyclic voltammetry was carried out with a CH Instruments CHI600A electrochemical analyzer, using a cell with Pt wire auxiliary and pseudoreference electrodes and a glassy carbon working electrode. Measurements were made under a nitrogen atmosphere on deoxygenated solutions, ca. 10^{-4} M in sample and 0.1 M in $[^nBu_4N]^+[PF_6]^-$, in solvent freshly distilled from CaH_2 (or, in the case of THF, from K). Potentials were referenced to $[FeCp_2]^+/FeCp_2$ (Cp = η^5-cyclopentadienyl) by addition of $FeCp_2$, $FeCp''_2$ (Cp'' = η^5-tetramethylcyclopentadienyl)[18] (the potential of which was measured as −445 mV vs $[FeCp_2]^+/FeCp_2$ in CH_2Cl_2, −410 mV in MeCN, −360 in THF, and −430 mV in PhCN), or bis(heptamethylindenyl)iron[19] (−785 mV vs $[FeCp_2]^+/FeCp_2$ in CH_2Cl_2, −715 mV in MeCN) to the cell (the choice of internal reference being made to avoid overlap of sample and reference peaks). The error in the reported potentials is estimated (from the reproducibility of the

---

[†] Present address: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

(1) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247−422.
(2) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357−389.
(3) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391−444.
(4) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664−2668.
(5) Denning, R. G. *J. Mater. Chem.* **1995**, *5*, 365−378 and references therein.
(6) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637−669 and references therein.
(7) Cowan, D. O.; Le Vanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1−7 and references therein.
(8) Barlow, S.; Marder, S. R. *Chem. Commun.* **2000**, 1555−1562 and references therein.
(9) Delgado Peña, F.; Talham, D. R.; Cowan, D. O. *J. Organomet. Chem.* **1983**, *253*, C43−C46.
(10) O'Connor Salazar, D. C.; Cowan, D. O. *J. Organomet. Chem.* **1991**, *408*, 227−231.
(11) Shu, P.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 1849−1852.
(12) Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 2293−2301.
(13) It was initially reported that [1.1]ferrocenophanium shows an absorption at 750 nm (ϵ = 3 350 M^{-1} cm^{-1}), with a suggestion that this is the IVCT band (Morrison, W. H.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331−2346). Subsequent work shows [1.1]ferrocenophanium species do not show IVCT bands and suggests materials initially believed to be these species were contaminated with ferrocenophane-based carbocation species (Moore, M. F.; Wilson, S. R.; Hendrickson, D. N.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1984**, *23*, 2918−2920).
(14) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683−12695.
(15) Cowan, D. O.; Shu, P.; Hedberg, F. L.; Rossi, M.; Kistenmacher, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1304−1306.
(16) Barlow, S.; Murphy, V. J.; Evans, J. S. O.; O'Hare, D. *Organometallics* **1995**, *14*, 3461−3474.
(17) Barlow, S.; O'Hare, D. *Organometallics* **1996**, *15*, 3885−3890.
(18) Schmitt, G.; Ozman, S. *Chem.-Ztg.* **1976**, *100*, 143.
(19) O'Hare, D.; Green, J. C.; Marder, T.; Collins, S.; Stringer, G.; Kakkar, A. K.; Kaltsoyannis, N.; Kuhn, A.; Lewis, R.; Mehnert, C.; Scott, P.; Kurmoo, M.; Pugh, S. *Organometallics* **1992**, *11*, 48−55.

10.1021/ic010666+ CCC: $20.00

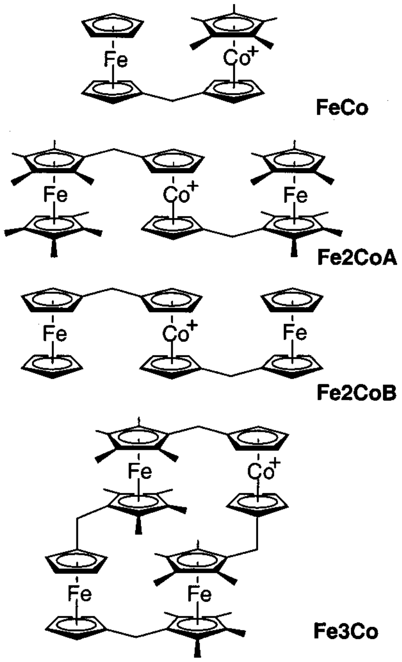

Figure 1. Structures of ferrocene−cobaltocenium compounds described in this work. In each case the counterion is hexafluorophosphate.

measurements) to be ca. ±5 mV; the errors in potentials referenced indirectly to $[FeCp_2]^+/FeCp_2$ and in $\Delta E_{1/2}$ values are, therefore, ca. ±10 mV. UV−vis−NIR spectra were recorded using 1 cm quartz cells and a GBC Instruments Cintra 10 spectrometer. $[Cp^*CoBr]_2$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl),[20] **Fe2CoA**,[16] and **Fe3Co**[17] were prepared as described in the literature. $[CoCpCp^*]^+[PF_6]^-$ was prepared by a modification of the literature procedure;[21] its identity and purity were checked by NMR spectroscopy [^{1}H NMR (300 MHz, acetonitrile-d_3) δ 5.20 (s, 5H, CH), 2.02 (s, 15H, CH_3); ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 98.8 (quat), 87.5 (CH), 11.0 (CH_3)]. $LiAlH_4$ was purified before use by extraction into dry diethyl ether, filtration, and solvent removal under reduced pressure. Other compounds were obtained commercially and used without further purification or prepared as described below. Solvents were dried when necessary by distillation from sodium (toluene), sodium−benzophenone (diethyl ether), potassium (THF), or CaH_2 (pyridine-d_5).

6-Ferrocenylfulvene and Lithium (Ferrocenylmethyl)cyclopentadienide. 6-Ferrocenylfulvene was synthesized in an analogous method to that previously described for 6-ferrocenyl-6-methylfulvene;[16] cyclopentadiene (25 mL, ca. 250 mmol) was added to a solution of KOH (8.6 g, 153 mmol) in ethanol (70 mL). The resulting mixture was added to a stirred solution of FcCHO (9.32 g, 44 mmol) in ethanol (65 mL). After 2.5 h, TLC showed the reaction to be complete and the reaction mixture was transferred to a separating funnel along with water (200 mL) and diethyl ether (200 mL). The layers were separated, and the aqueous layer was back-extracted with 2 × 100 mL of diethyl ether. The combined ether layers were washed with 2 × 100 mL of 2 M NaCl solution, dried on $MgSO_4$, filtered, and evaporated under reduced pressure to yield a deep red oil, the ^{1}H NMR spectrum of which was in accordance with literature data for 6-ferrocenylfulvene.[22] The oil was obtained in essentially quantitative yield. The fulvene was dried in a vacuum for a further 15 h to remove traces of ethanol; this resulted in slight decomposition to afford some ether-insoluble orange solid (630 mg) (the instability of the fulvene has previously been noted[23]). The remaining fulvene was, therefore, extracted into dry diethyl ether (150 mL). To the stirred ether extracts was added a solution of $LiAlH_4$ (1.67 g, 44 mmol) in dry diethyl ether (140 mL). An orange precipitate soon formed. After 20 h the precipitate was collected on a frit, washed with dry diethyl ether (3 × 100 mL), and dried for 24 h in a vacuum to afford solvent-free NMR-pure lithium salt (9.37 g, 35 mmol, 80% from FcCHO) as an orange air-sensitive solid: ^{1}H NMR (300 MHz, pyridine-d_5) δ 6.32 (apparent t, $J = 2.6$ Hz, 2H, C_5H_4Li), 6.24 (apparent t, $J = 2.6$ Hz, 2H, C_5H_4Li), 4.36 (apparent t, $J = 1.8$ Hz, 2H, C_5H_4Fe), 4.21 (s, 5H, C_5H_5Fe), 4.07 (apparent t, $J = 1.8$ Hz, 2H, C_5H_4Fe), 3.91 (s, 2H, CH_2); ^{13}C NMR (75 MHz, pyridine-d_5) δ 121.1 (C_5H_4Li quat), 104.6 (C_5H_4Li CH), 103.6 (C_5H_4Li CH), 93.9 (C_5H_4Fe quat), 69.8 (C_5H_4Fe CH), 69.4 (C_5H_5Fe), 67.6 (C_5H_4Fe quat), 32.0 (CH_2).

1-(Ferrocenylmethyl)-1′,2′,3′,4′,5′-pentamethylcobaltocenium Hexafluorophosphate (FeCo). A solution of lithium (ferrocenylmethyl)cyclopentadienide (410 mg, 1.52 mmol) in THF (20 mL) was added dropwise to a stirred solution of $[Cp^*CoBr]_2$ (410 mg, 0.75 mmol) in THF (10 mL). After 20 h, the solvent was removed under reduced pressure. The residue was extracted with dry toluene; the extracts were filtered through Celite and reduced in volume (to ca. 40 mL) under reduced pressure. A solution of ammonium hexafluorophosphate (500 mg, 3 mmol) in dry THF (40 mL) was then added dropwise to the stirred toluene extracts. After 45 h, the resulting orange precipitate was collected on a frit, washed with water (100 mL), THF (5 mL), and diethyl ether (100 mL), and dried under vacuum to afford pure air-stable product (585 mg, 0.97 mmol, 64%): ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 5.13 (apparent t, $J =$ ca. 2 Hz, 2H, C_5H_4Co), 5.07 (apparent t, $J =$ ca. 2 Hz, 2H, C_5H_4Co), 4.12 (s, 5H, C_5H_5Fe), 4.09 (apparent t, $J = 2$ Hz, C_5H_4Fe), 4.06 (apparent t, $J = 2$ Hz, C_5H_4Fe), 3.31 (s, 2H, CH_2), 2.01 (s, 15H, CH_3); ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 104.4 (C_5H_4Co quat.), 98.4 (C_5Me_5 quat), 87.7 (C_5H_4Co CH), 87.5 (C_5H_4Fe quat), 86.2 (C_5H_4Co CH), 70.0 (C_5H_5Fe), 69.3 (C_5H_4Fe CH), 69.1 (C_5H_4Fe CH), 26.9 (CH_2), 10.7 (CH_3); MS (electrospray, MeOH) *m*/*z* 457. Anal. Calcd for $C_{26}H_{30}CoF_6FeP$: C, 51.85; H, 5.02. Found: C, 51.96; H, 5.62.

1,1′-Bis(ferrocenylmethyl)cobaltocenium Hexafluorophosphate (Fe2CoB). A solution of lithium (ferrocenylmethyl)cyclopentadienide (695 mg, 2.57 mmol) in dry THF (25 mL) was added dropwise to a stirred solution of anhydrous cobalt(II) bromide (285 mg, 1.30 mmol) in dry THF (25 mL). After 10 h, the solvent was removed and the residue extracted and oxidized in a way analogous to that used to prepare **FeCo**. The product was obtained as an air-stable red powder (485 mg, 0.66 mmol, 51%): ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 5.43 (apparent s, 4H, C_5H_4Co), 4.18 (m, 4H, C_5H_4Fe), 4.16 (m, 2H, C_5H_4Fe), 4.15 (s, 10H, C_5H_5Fe), 3.44 (s, 4H, CH_2); ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 107.8 (C_5H_4Co quat), 85.3 (C_5H_4Fe quat), 84.0 (C_5H_4Co CH), 83.8 (C_5H_4Co CH), 68.8 (C_5H_5Fe), 68.4 (C_5H_4Fe CH), 68.0 (C_5H_4Fe CH), 27.5 (CH_2); MS (electrospray, MeOH) *m*/*z* 585. Anal. Calcd for $C_{32}H_{30}CoF_6Fe_2P$: C, 52.64; H, 4.14. Found: C, 52.86; H, 4.27.

Results

The previously reported compounds **Fe2CoA**[16] and **Fe3Co**,[17] together with the new compounds **FeCo** and **Fe2CoB** (Figure 1), were investigated by UV−vis spectroscopy (Table 1) and cyclic voltammetry (Table 2); data for $FeCp_2$, $FeCp''_2$, $[CoCp_2]^+[PF_6]^-$, and $[CoCpCp^*]^+[PF_6]^-$ ($Cp = \eta^5$-cyclopentadienyl; $Cp'' = \eta^5$-tetramethylcyclopentadienyl; $Cp^* = \eta^5$-pentamethylcyclopentadienyl) were also acquired for comparison.[24]

---

(20) Koelle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980−987.

(21) Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem. Suppl.* **1982**, 230−240.

(22) Rausch, M. D.; Wang, Y.-P. *Organometallics* **1991**, *10*, 1438−1443.

(23) Cassens, A.; Eilbracht, P.; Mueller-Westerhoff, U. T.; Nazzal, A.; Neuenschwander, M.; Prössdorf, W. *J. Organomet. Chem.* **1981**, *205*, C17−C20.

(24) Potentials for the model compounds have previously been reported and are similar to those reported here; they are given here (vs $[FeCp_2]^+/FeCp_2$) for comparison. $[FeCp''_2]^+/FeCp''_2$: −400 mV in MeCN (Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7578−7584); −340 mV in MeCN (Miller, J. S.; Glatzhofer, D. T.; O'Hare, D. M.; Reiff, W. M.; Chakraborty, A.; Epstein, A. J. *Inorg. Chem.* **1989**, *28*, 2930−2939); −445 mV in CH_2Cl_2 (ref 35). $[CoCp_2]^+/CoCp_2$: −1330 mV in CH_2Cl_2 (Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.); −1350 mV in CH_2Cl_2 (Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640−641). $[CoCpCp^*]^+/CoCpCp^*$: −1655 in EtCN (Hudeczek, P.; Köhler, F. H.; Bergerat, P.; Khan, O. *Chem. Eur. J.* **1991**, *5*, 70−78).

Table 1. UV−Vis Data for Bridged Ferrocene/Cobaltocenium Systems and for the Parent Metallocenes

compd	λ_{max}/nm ($\epsilon_{max}{}^{a}$/M^{-1} cm^{-1}) acetonitrile	dichloromethane
FeCo	200 (65 000), 286 (43 000), 332 (1 700), 409 (860)	272 (33 000), 426 (710), sh 502 (560)
Fe2CoA	218 (58 000), 271 (33 000), sh 308 (7 500), 572 (700)	273 (38 000), sh 310 (7600), 637 (710)
Fe2CoB	200 (95 000), 272 (32 000), 423 (910), sh 482 (720)	287 (39 000), sh 345 (1500), 417 (800), sh 508 (550)
Fe3Co	206 (99 000), 269 (44 000), 325 (4 300), 579 (980)	271 (50 000), 369 (3400), 655 (1100)
$FeCp_2{}^{b}$	200 (45 000), 326 (58), 442 (96)	327 (52), 442 (97)
$FeCp''_2{}^{b}$	218 (32 000), sh 285 (2400), 427 (130)	sh 283 (3700), 427 (130)
$[CoCp_2]^+[PF_6]^{-\ b}$	262 (27 000), 301 (830), 405 (170)	264 (30 000), 302 (970), 405 (210)
$[CoCpCp^*]^+[PF_6]^{-\ b}$	281 (35 000), sh 329 (1000), 397 (300)	283 (38 000), sh 327 (1200), 398 (350)

[a] Absorbtivity refers to moles of polymetallic molecular species rather than to each Fe−Co interaction. [b] Cp = η^5-cyclopentadienyl; Cp″ = η^5-tetramethylcyclopentadienyl; Cp* = η^5-pentamethylcyclopentadienyl.

Table 2. Electrochemical Potentials (mV vs $[FeCp_2]^+/FeCp_2$), with Relative Peak Intensities in Parenthesis,[a] for Linked Ferrocene/Cobaltocenium Systems and for the Parent Metallocenes

compd	acetonitrile $E_{1/2}$ (Fe^{III}/Fe^{II})	$E_{1/2}$ (Co^{III}/Co^{II})	$\Delta E_{1/2}{}^{b}$	dichloromethane $E_{1/2}$ (Fe^{III}/Fe^{II})	$E_{1/2}$ (Co^{III}/Co^{II})	$\Delta E_{1/2}{}^{b}$
FeCo	+45 (1)	−1665 (1)	1710	+5 (1)	−1675 (1)	1680
Fe2CoA	−325 (2)	−1420 (1)	1095	−385 (2)	−1415 (1)	1030
Fe2CoB	+60 (2)	−1420 (1)	1480	+10 (2)	−1435 (1)	1445
Fe3Co	+100 (1), −320 (2)[c]	−1420 (1)	1100	+60 (1), −380 (2)[c]	−1415 (1)	1035
$FeCp_2{}^{d}$	0			0		
$FeCp''_2{}^{d}$	−410			−445		
$[CoCp_2]^+[PF_6]^{-\ d}$		−1310			−1320	
$[CoCpCp^*]^+[PF_6]^{-\ d}$		−1630			−1625	

[a] **FeCo** contains one Fe^{II} center, while **Fe2CoA** and **Fe2CoB** contain two equivalent Fe^{II} centers, and **Fe3Co** contains three Fe^{II} centers of two types. [b] Difference between the lowest Fe^{III}/Fe^{II} potential and the Co^{III}/Co^{II} potential. [c] The more negative potential is assigned to the methylated ferrocene units by analogy with the model compounds and in accordance with the peak intensities. [d] Cp = η^5-cyclopentadienyl; Cp″ = η^5-tetramethylcyclopentadienyl; Cp* = η^5-pentamethylcyclopentadienyl.

Electrochemistry. Cyclic voltammetry showed quasi-reversible redox processes for all the ferrocene and cobaltocene constituents of the molecules; these were readily assigned by comparison with mononuclear complexes. Separations between anodic and cathoodic peaks ($E_{ox} - E_{red}$) for both Fe^{III}/Fe^{II} and Co^{III}/Co^{II} couples were in all cases essentially the same as those for the internal reference metallocenes and fell in the range between the ideal value of 59 and ca. 70 mV. Anodic and cathodic currents were equal, except for the Co^{III}/Co^{II} couples in dichloromethane where the oxidation currents were somewhat smaller than those for reduction (I_{ox}/I_{red} = ca. 0.7), presumably indicating some instability of the Co^{II} species in this solvent. The half-wave potentials, $E_{1/2} = 0.5(E_{ox} + E_{red})$, are summarized in Table 2. The differences between the potentials of the Co^{III}/Co^{II} couples of the polymetallic species and those of the parent cobaltocenium are attributable to the electron-donating effect of the alkyl substituents. The ferrocenyl units of **Fe2CoB** and **FeCo** are, however, slightly *less* readily oxidized than ferrocene itself, and the octamethylferrocenyl groups of **Fe2CoA** and **Fe3Co** are less readily oxidized than octamethylferrocene, despite the presence of additional alkyl substituents (the bridging CH_2 groups), each of which would be expected to lead to shifts to negative potential of 50−60 mV.[25−27] The positive shifts can be attributed to the effect of the attached cobaltocenium ion on the ferrocenyl group, this interaction potentially consisting of both resonance and electrostatic (repulsion of like-charged metal centers) contributions.[28] The electrostatic contribution will presumably be similar to that for the class I (no IVCT band[9]) $[Fc_2CH_2]^+$ cation, where the separation between successive oxidations, $\Delta E_{1/2}$, is 170 mV in acetonitrile.[29,30] The combination of the effect of alkyl groups with the estimated electrostatic contribution is broadly consistent with the observed positive shifts of the Fe^{III}/Fe^{II} potentials in acetonitrile, indicating little contribution to $\Delta E_{1/2}$ from the resonance interaction, consistent with little ground-state delocalization. The effect of the cobaltocenium units upon the ferrocene moieties is somewhat smaller in dichloromethane than in acetonitrile. Further measurements for **Fe2CoB** in tetrahydrofuran (the Fe^{III}/Fe^{II} couple is observed at −15 mV vs $[FeCp_2]^+/FeCp_2$, and the Co^{III}/Co^{II} couple, at −1415 mV) and benzonitrile (+40 and −1430 mV vs $[FeCp_2]^+/FeCp_2$) suggest consistently larger electrostatic effects in solvents of higher dielectric constant; this behavior has previously been found for a variety of class I and II linked ferrocene systems[31−36] but is at variance with the prediction of the dielectric continuum model that the electrostatic contribution to $\Delta E_{1/2}$ is inversely proportional to the solvent dielectric constant.[37]

---

(25) Hoh, G. L. K.; McEwen, W. E.; Kleinberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3949−3953.

(26) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470−1472.

(27) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882−1893.

(28) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273−325 and references therein.

(29) Morrison, W. H.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998−2004.

(30) For a symmetrical system such as $[Fc_2CH_2]^+$, there is an additional entropic contribution of +(*RT*/*F*) ln 4, which arises from the degeneracy of $Fe^{II}-Fe^{III}$ and $Fe^{III}-Fe^{II}$ molecules. This entropic factor will be responsible for ca. +40 mV of the observed $\Delta E_{1/2}$ in $[Fc_2CH_2]^+$ but will be absent in the present Fe/Co compounds.

(31) Atzkern, H.; Huber, B.; Köhler, F. H.; Müller, G.; Müller, R. *Organometallics* 1991, *10*, 238−244.

(32) Hudezcek, P.; Köhler, F. H. *Organometallics* **1992**, *11*, 1773−1775.

(33) Rittinger, S.; Buchholz, D.; Delville-Desbois, M. H.; Linarès, J.; Varret, F.; Boese, R.; Zsolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454−1456.

(34) Floris, B.; Tagliatesta, P. *J. Chem. Res., Synop.* **1993**, 42−43.

(35) Mendiratta, A.; Barlow, S.; Day, M. W.; Marder, S. R. *Organometallics* **1999**, *18*, 454−456.

(36) Although $\Delta E_{1/2}$ values for linked metallocene systems are generally larger in more polar solvents, there are exceptions: $\Delta E_{1/2}$ values of 195 and 150 mV in CH_2Cl_2 and MeCN, respectively, have been reported for 1,8-diferrocenylnaphthalene (Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539−547).

Table 3. Parameters Relating to the IVCT Bands of Ferrocene/Cobaltocenium Systems

	acetonitrile				dichloromethane			
	FeCo	**Fe2CoA**	**Fe2CoB**	**Fe3Co**	**FeCo**	**Fe2CoA**	**Fe2CoB**	**Fe3Co**
$\bar{\nu}_{max}$ ($\epsilon_{max}{}^{a}$)/10^3 cm^{-1} (M^{-1} cm^{-1})	*g*	17.48 (352)	20.49 (240)	17.27 (491)	20.33 (462)	15.70 (355)	19.42 (208)	15.27 (545)
$\Delta\bar{\nu}_{1/2}$(exptl)/10^3 cm^{-1}		6.90	4.58^f	5.74	4.94^f	6.60	4.65^f	6.38
$\Delta G^{\circ\ b}$/10^3 cm^{-1}	13.79	8.83	11.94	8.87	13.55	8.31	11.66	8.35
λ^c/10^3 cm^{-1}		8.65	8.55	8.40	6.78	7.39	7.76	6.92
$\Delta\bar{\nu}_{1/2}$(Hush)^d/10^3 cm^{-1}		4.47	4.45	4.41	3.96	4.13	4.23	4.00
V^e/10^3 cm^{-1}		0.56−0.94	0.41−0.68	0.69−1.00	0.59−0.98	0.52−0.87	0.32−0.62	0.63−1.05
V^e/meV		70−116	5−85	75−125	73−122	65−108	46−77	78−130
α^e		0.032−0.054	0.020−0.033	0.035−0.058	0.029−0.048	0.033−0.056	0.019−0.032	0.041−0.069

^{a} For the species where two Fe^{II} donor moieties are attached to the same cobaltocenium, the value of ϵ_{max} quoted here is that relevant to each individual Fe^{II}−Co^{III} interaction; this was taken to be half the molecular value, on the basis of the assumption that the two interactions are more or less independent. ^{b} Estimated from $\Delta E_{1/2}$. ^{c} Estimated from eq 1. ^{d} Calculated from eq 5. ^{e} Quoted as minimum and maximum possible values obtained from eqs 2 and 3, assuming r in the range 4.5−7.5 Å. ^{f} Estimated minimum bandwidth assuming a symmetrical band; actual width could not be determined due to severe overlap with other absorptions on the high-energy side. Derived parameters (V and α) are therefore likely to be somewhat underestimated. ^{g} Not determined due to severe overlap with d−d transitions.

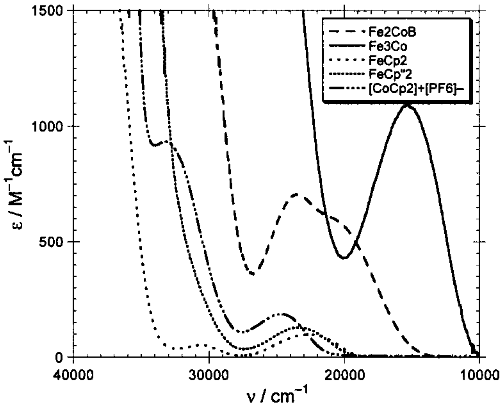

Figure 2. Electronic spectra of **Fe2CoA** and **Fe3Co** in CH_2Cl_2 compared with the spectra of the relevant parent metallocenes.

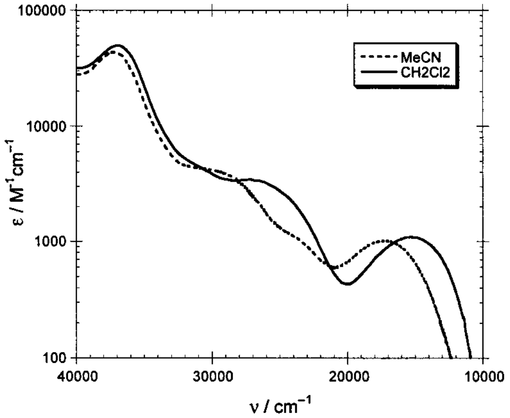

Figure 3. Solvatochromism of the UV−vis−near-IR spectrum of **Fe3Co**.

Electronic Spectra: General Features. The UV−vis spectra (Table 1) are clearly inconsistent with the superposition of those of the constituent metallocenes (Figure 2). For **Fe2CoA** and **Fe3Co** in particular there is a prominent band at much lower energy than the d−d transitions of ferrocenes or cobaltoceniums. This band is clearly that leading to the unusual color of these species. The spectrum of red **Fe2CoB** also shows absorption at lower energy than the parent metallocenes, although now there is considerable overlap with the energies expected for the d−d transitions. Nevertheless, it was possible to determine the position and approximate shape of this low-energy band by subtracting ferrocene and cobaltocenium spectra.[38] For orange **FeCo** the overlap problems were more significant, especially in acetonitrile. The details of these low-energy transitions are tabulated in Table 3, together with parameters arising from their analysis in terms of Hush theory (vide infra), on the basis of the assumption that these are IVCT bands. Significantly, and in contrast to the d−d transitions, the low-energy bands show marked solvatochromism, being substantially red-shifted (by 1000−2000 cm^{-1}) on moving from acetonitrile to dichloromethane (shown in Figure 3 for **Fe3Co**). **Fe2CoA** and **Fe2CoB** were studied in a wider range of solvents (determination of $\bar{\nu}_{max}$ was not possible for **FeCo** in all solvents due to overlap of the IVCT with other transitions, while **Fe3Co** is not soluble in such a wide range of solvents as the two trimetallics); the values of $\bar{\nu}_{max}$ are plotted against $1/n^2 - 1/D$, where n is the refractive index and D the dielectric constant, in Figure 4.[39,40] A linear relationship is expected for typical class II IVCT bands.[41,42] Although the overall trend is as expected, the relationship in the present compounds is clearly subject to complications (for example, peaks are more red-shifted in dichloromethane than might be expected from the magnitude of $1/n^2 - 1/D$ alone).[43] Nevertheless, the strong solvent dependence is consistent with a CT origin for the low-energy bands of these species; on the basis of this and other evidence (vide infra), these bands are assigned to Fe^{II}−Co^{III} IVCT. In addition, the compounds also show solvatochromic absorptions at higher energy which cannot be explained by the superposition of features of the constituent metallocene moieties. These transitions are tentatively assigned to CT transitions from the highest cyclopentadienyl-based level

---

(37) Ferrere, S.; Elliott, C. M. *Inorg. Chem.* **1995**, *34*, 5818−5824.

(38) The intensities of the subtracted spectra were multiplied relative to those of the parent metallocenes to account for the reduced symmetries in the Fe−Co compounds. The factors by which the intensities were increased were determined by trial and error so that the low-energy CT band acquired a reasonable profile. The correction is not perfect of course, as the d−d transitions may occur at slightly different energies relative to the parent metallocenes.

(39) Values of $1/n^2 - 1/D$ were taken from the following: *CRC Handbook of Chemistry and Physics*, 58th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1978. Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233−4241.

(40) In fact, it is λ, as determined by eq 1, that is predicted to show linear dependence upon $1/n^2 - 1/D$. Nevertheless, our electrochemical measurements show the main contribution to variations in $\Delta E_{1/2}$ between solvents is the interaction between the Fe and Co centers, an interaction which should be corrected for in determining ΔG^o from eq 1. Therefore, in this case it seems valid to assume the true ΔG^o is approximately constant with solvent polarity and, therefore, that plotting $\bar{\nu}_{max}$ against $1/n^2 - 1/D$ is valid.

(41) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1−73.

(42) However, in the case of ruthenium amine mixed-valence species, the donor number is more important than $1/n^2 - 1/D$ (Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233−4241).

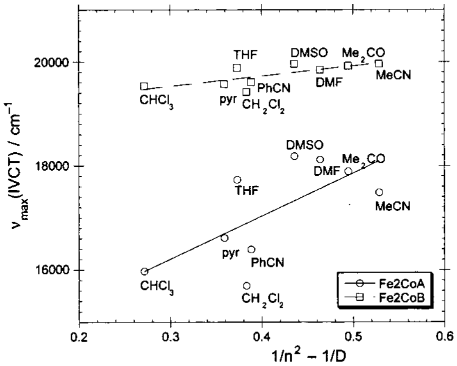

Figure 4. Variation in the IVCT peak maxima with solvent polarity (*n* and *D* are refractive index and dielectric constant respectively; see ref 39 for sources of values) for **Fe2CoA** and **Fe2CoB**. The lines are provided as a guide to the eye.

of the ferrocene donors to the cobaltocenium LUMO. For example, for **Fe3Co** (Figure 3) this absorption is ca. 12 000 cm^{-1} higher in energy than the low-energy IVCT; this is roughly consistent with the difference in energy between the highest metal-based and highest Cp*-based orbitals of $FeCp^*_2$.[44] The assignment of this higher energy band parallels that for compounds of the form Fc($CH{=}CH)_nA$, where A is a π-acceptor, for which the two solvatochromic transitions have been attributed to Fe-to-A CT (the lower energy band) and "π"-to-A CT, "π" being a combination of cyclopentadienyl and alkene orbitals.[45] However, in the present compounds overlap with other absorptions precludes a more detailed analysis. The intense features found at the UV end of the spectra are similar to those of the parent metallocenes. For example, the intense more-or-less solvent-independent transition seen at ca. 37 000 cm^{-1} for **Fe3Co** (Figure 3) is characterized by an energy and absorptivity similar to those for the ligand-to-metal CT band of the cobaltocenium ion.[46]

Electronic Spectra: Analysis of the Low-Energy Band. The plausibility of assigning the low-energy bands of the present compounds as Fe^{II}-to-Co^{III} IVCT was assessed by consideration of the energies of these bands. Hush theory[3] indicates that for a class II mixed-valence system with two identical redox centers (e.g. the biferrocenium ion) the energy of the IVCT transition, $\bar{\nu}_{max}$, is equal to the sum of the inner and outer-sphere reorganization energies, λ (Figure 5a). Where the two redox centers are inequivalent, the relationship is given by

$$\bar{\nu}_{max} = \lambda + \Delta G^\circ \quad (1)$$

where ΔG° is the free-energy difference between the zero-level vibrational states of the ground and excited electronic states (Figure 5b). ΔG° can be estimated by the difference in electrode potentials between the two redox centers. If one assumes that the oxidation potential of one center is unaffected by the oxidation state of the other, the magnitude of ΔG° is obtained by converting the electrochemical value of $\Delta E_{1/2}$ into energy units. As discussed in the electrochemistry section, the cobaltocenium centers do affect the Fe^{III}/Fe^{II} potentials. However, no correction has been made for this effect; the effect is relatively small (ca. 10% of $\Delta E_{1/2}$) and not readily estimated accurately (although it appears to be the main factor leading to different values of $\Delta E_{1/2}$ in different solvents). Combining the experimentally determined $\bar{\nu}_{max}$ with the electrochemical estimate of ΔG° gives reorganization energies in the range 6780−8650 cm^{-1}. The full set of values is given in Table 3, and the data are presented graphically in Figure 6. Figure 6 shows that the $\bar{\nu}_{max}$ and ΔG° are related in the manner suggested by eq 1 and that the reorganization energy is consistently larger in acetonitrile than in dichloromethane. It has previously been found (from bond-length and vibrational data) that the $[CoCp_2]^+/CoCp_2$ system has reorganization parameters almost identical to those of its iron analogue.[47] Hence, values of λ in the current systems would be expected to be similar to those in linked ferrocenium/ferrocene mixed-valence systems. Thus is indeed the case; values of $\bar{\nu}_{max}$, and therefore λ, for a variety of ferrocenium/ferrocene mixed-valence species fall in the range 4520−8470 cm^{-1}. Thus, both the variation in $\bar{\nu}_{max}$ with $\Delta E_{1/2}$ (Figure 6) and the deduced values of λ (Table 3) are consistent with the assignment of the low-energy features of the present compounds as Fe^{II}-to-Co^{III} IVCT bands.

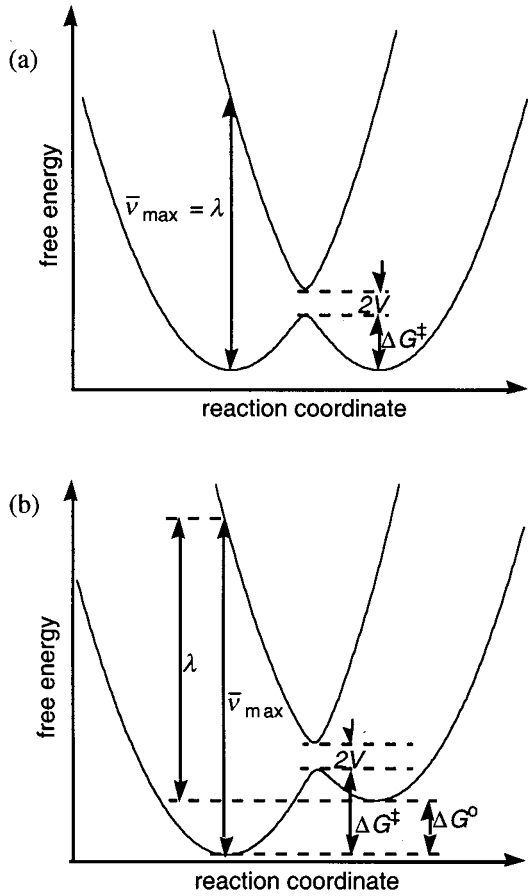

Figure 5. Potential wells representing (a) symmetrical and (b) unsymmetrical class II mixed-valence systems.

---

(43) Several other studies have found chlorinated solvents to have larger effects on charge-transfer type bands of metallocene derivatives than might be expected from the solvent polarity alone, perhaps reflecting some sort of specific interaction between the metallocene species and the solvent. These effects may be seen in the metal-to-acceptor and π-to-acceptor CT bands of $Mc(CH{=}CH)_nA$ (Mc = Fc, Fc″, ruthenocenyl; A = π-acceptor) NLO dyes (Supporting Information for ref 45), the metal-to-π^* and π-to-π^* CT transitions of $[Mc(CH)_3Mc]^+$ cations (Barlow, S.; Henling, L. M.; Day, M. W.; Schaefer, W. P.; Green, J. C.; Hascall, T.; Marder, S. R. Submitted), and the IVCT band of $[FcN{=}NFc]^+$ (Kurosawa, M.; Nankawa, T.; Matsuda, T.; Kubo, K.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **1999**, *38*, 5113−5123).

(44) Cauletti, C.; Green, J. C.; Kelly, M. R.; Robbins, J.; Smart, J. C. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327−353.

(45) Barlow, S.; Bunting, H. E.; Ringham, C.; Green, J. C.; Bublitz, G. U.; Boxer, S. G.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **1999**, *121*, 3715−3723.

(46) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603−3612.

(47) Nielson, R. M.; Govin, M. N.; McManis, G. E.; Weaver, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1745−1749.

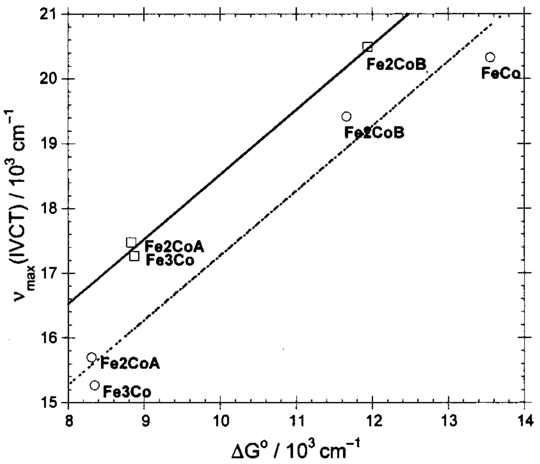

Figure 6. Correlation between the electrochemically determined value of $\Delta G°$ and the low-energy absorption maximum of the $Fe^{II}-Co^{III}$ mixed-valence compounds in MeCN (squares, solid line) and CH_2Cl_2 (circles, broken line). The lines have the equation $\nu_{max} = \Delta G° + \lambda$, thus assuming a constant λ for each solvent.

Hush theory[3] also allows the electronic coupling between the two metal centers to be estimated via

$$V = \frac{\sqrt{4.5 \times 10^{-4}\, \epsilon_{max} \Delta\bar{\nu}_{1/2} \bar{\nu}_{max}}}{r} \tag{2}$$

where V is the electronic coupling (cm^{-1}), r is the separation between donor and acceptor centers (Å), and $\Delta\bar{\nu}_{1/2}$ (cm^{-1}), $\bar{\nu}_{max}$ (cm^{-1}), and ϵ_{max} (M^{-1} cm^{-1}) are width at half-height, absorption maximum, and maximum extinction coefficient respectively for the IVCT band. V can be related to the ground-state delocalization coefficient, α, by

$$\alpha = V/\bar{\nu}_{max} \tag{3}$$

α being defined according to

$$\psi = (1 - \alpha^2)^{0.5}\phi_A + \alpha\phi_B \tag{4}$$

where ψ is the ground-state wavefunction and ϕ_A and ϕ_B are the wavefunctions for the completely localized extreme structures, in the present compounds corresponding to Fe^{II}/Co^{III} and Fe^{III}/Co^{II}, respectively. V and α were estimated for the compounds in both acetonitrile and dichloromethane and are tabulated in Table 3. One problem that arises in analyzing the data using eq 2 is in estimating an appropriate value of the metal−metal distance, r. Metallocene systems with XR_2 bridges are extremely conformationally flexible, as shown by molecular mechanics studies of CMe_2- and $SiMe_2$-bridged ferrocene systems.[48−50] Moreover, gas-phase minimum energy conformations[49,50] typically have M−M separations rather different from those determined crystallographically[14,16,48,51−53] or modeled[49,50] in the solid-state structures; thus, X-ray crystallography would not necessarily afford values of r relevant to solution behavior. Thus, we have quoted minimum and maximum values for V and α, on the basis of the assumption that, by analogy with the modeling in refs 49 and 50, r must fall within the range 4.5−7.5 Å.

Hush theory[3] also relates the width of a IVCT band to the reorganization energy, and hence to the IVCT energy, via

$$\Delta\bar{\nu}_{1/2} = \sqrt{2310\lambda} \tag{5}$$

The observation of experimental $\Delta\bar{\nu}_{1/2}$ lower than predicted by eq 5 is often taken to indicate a class III mixed-valence system, while class II systems typically show bandwidths 30−40% in excess of the Hush prediction (due to various contributory factors overlooked in Hush's treatment).[41] Thus, Table 3 also compares experimental and predicted values of $\Delta\bar{\nu}_{1/2}$; the comparison is clearly consistent with the identification of the low-energy absorption of this class of compounds as class II mixed-valence IVCT bands.

Discussion

The magnitude of the delocalization parameters, α, indicates that the present compounds are reasonably localized toward the Fe^{II}/Co^{III} extreme. Nevertheless, the values of α and V are surprisingly large, being of magnitude comparable to those found in biferrocenium (α = 0.09, V = 62 meV),[9] [*E*-FcCH═CHFc]$^+$ (α = 0.1, V = 61 meV),[54] [FcC≡CFc]$^+$ (α = 0.07, V = 56 meV),[55] and $[Fc_2SiMe_2]^+$ (α = 0.02, V = 23 meV),[14] and are considerably in excess of those found for ferrocenium−ferrocene systems with a single unsaturated bridging carbon atom (for $[Fc_2C{=}CH_2]^+$, α = 0.004, V = 3 meV[9]) or with a saturated carbon bridge (for $[Fc_2CH_2]^+$, no IVCT observed; for $[Fc_3CH]^+$, α = 0.004, V = 3 meV[9]).[56] Thus, the $Fe^{II}-Co^{III}$ interaction is much stronger than in structurally similar $Fe^{II}-Fe^{III}$ systems. Although ferrocene and cobaltocenium derivatives abound, there are surprisingly few studies of systems incorporating both of these moieties and even fewer where $Fe^{II}-Co^{III}$ interactions are discussed. The closest literature parallel to the present compounds is the $[(FcCHPhC_5H_4)_2Co]^+$ cation,[57] but neither its electronic spectrum nor its color was reported. The colors reported for 1,1′-bis(ferrocenyl)cobaltocenium (intense blue-violet),[58] 1,1′-bis(cobaltoceniumyl)ferrocene (intense red-violet),[58] [FcC≡CCc]$^+$ (Cc = cobaltocenyl) (dark purple),[59] and a variety of molecules comprising cobaltocenium directly linked to ruthenocene or osmocene (orange)[60] may well be due to M^{II}-to-Co^{III} IVCT, but the spectra have not been reported.[61] [FcC≡C(1,4-C_6H_4)C≡C(1,4-C_6H_4)C≡CCc]$^+$ has been reported to be deep orange, but the details of the UV−vis spectra were not given.[62] It should also be noted that another $Fe^{II}-Co^{III}$ mixed-

---

(48) Pannell, K. H.; Dementiev, V. V.; Li, H.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644−3650.

(49) Barlow, S.; Rohl, A. L.; O'Hare, D. *Chem. Commun.* **1996**, 257−260.

(50) Barlow, S.; Rohl, A. L.; Shi, S.; Freeman, C. M.; O'Hare, D. *J. Am. Chem. Soc.* **1996**, *118*, 7578−7592.

(51) Lough, A. J.; Manners, I.; Rulkens, R. *Acta Crystallogr.* **1994**, *C50*, 1667−1669.

(52) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797−798.

(53) Barlow, S.; O'Hare, D. *Acta Crystallogr.* **1996**, *C53*, 578−581.

(54) Ribou, A. C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735−3740.

(55) Le Vanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700−2704.

(56) The parameters for the present ferrocene/cobaltocenium compounds and for ferrocene/ferrocenium mixed-valence systems can also be compared to those for bridged $[(NH)_3Ru(\mu\text{-}L)Ru(NH_3)_5]^{5+}$ complexes: For L = 4,4-bipyridyl, V = 48 meV and α = 0.04 and, for L = *E*-bis(4-pyridyl)ethene, V = 38 meV and α = 0.03, while, for the saturated-bridged species with L = bis(4-pyridyl)methane, V = 12 meV and α = 0.009 (Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125−3134).

(57) Knox, G. R.; Munro, J. D.; Pauson, P. L.; Smith, G. H.; Watts, W. E. *J. Chem. Soc.* **1961**, 4619−4624.

(58) Rieker, C.; Ingram, G.; Jaitner, P.; Schottenberger, H.; Schwarzhans, K. E. *J. Organomet. Chem.* **1990**, *381*, 127−133.

(59) Wildschek, M.; Rieker, C.; Jaitner, P.; Schottenberger, H.; Schwarzhans, K. E. *J. Organomet. Chem.* **1990**, *396*, 355−361.

(60) Ingram, G.; Jaitner, P.; Schwarzhans, K. E. *Z. Naturforsch.* **1990**, *45B*, 781−784.

valence species containing a Co^{III} moiety isoelectronic with cobaltocenium, the (1-ferrocenyl-η^6-borabenzene)(η^5-cyclopentadienyl)cobalt cation, exhibits a solvatochromic absorption with λ_{max} in the region 585−650 nm (ϵ_{max} 1640−2000 M^{-1} cm^{-1}) and an associated first hyperpolarizability of 90×10^{-30} esu.[63] Although the authors attributed this transition to Fe-to-π^* charge transfer, the ESR spectrum of its reduced $Fe^{II}-Co^{II}$ form suggests there is considerable cobalt character to the LUMO.

Although $Fe^{II}-Co^{III}$ metallocene systems have been little studied, data for several dinuclear $Co^{II}-Co^{III}$ metallocene systems indicate increased M−M interactions relative to their $Fe^{II}-Fe^{III}$ analogues. The electronic spectra of the bicobaltocenium mixed-valence ion have been studied in detail, suggesting this species to be at least on the class II/class III borderline, while biferrocenium was found to be class II with $\alpha = 0.09$.[64] In other systems, less direct electrochemical evidence is available; the separation between the successive oxidations of the two metal centers in the dicobalt compounds is generally larger than for the diiron analogues.[32,33,65−67] The greater electronic coupling in dicobalt systems can be attributed to the greater ligand character of the cobaltocenium LUMO/cobaltocene SOMO (mainly d_{xz}/d_{yz}, but with significant M−Cp π-antibonding character), relative to that of ferrocenium SOMO/ferrocene HOMO ($d_{xy}/d_{x^2-y^2}$, with some M−Cp δ-bonding character). This explanation has also been advanced to account for the much greater rates of electron exchange found for $[CoCp_2]^+/CoCp_2$ and $[CoCp^*{}_2]^+/CoCp^*{}_2$ relative to those for the analogous iron systems.[47,68] Presumably, then, it is the nature of the cobaltocenium LUMO that accounts for the enhanced strength of $Fe^{II}-Co^{III}$ coupling in the present compounds relative to that for $Fe^{II}-Fe^{III}$ metallocene systems.

In summary, compounds in which ferrocene and cobaltocenium units are bridged by CH_2 groups have been shown to exhibit IVCT bands in the visible part of the spectrum. These have been shown to correspond to much stronger interaction between donor and acceptor than in analogous ferrocene/ferrocenium systems. Even stronger interactions may be anticipated in systems with different bridging groups or with different donors linked to the cobaltocenium acceptor.

Acknowledgment. The author is grateful to Simon Jones for LiCp*, Colin Sparrow for recording electrospray mass spectra, Bob Denning for some helpful discussion, and a reviewer for some helpful suggestions.

IC010666+

---

(61) In addition to the simple metallocene systems discussed here, several other more complex Fe−Co metallocene systems have been studied including the 34 electron $[Cp^*Fe(\mu{:}\eta{:}^5\eta^5\text{-pentalene})CoCp^*]^+$ cation (Manriquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182−6193), which seems to be an unsymmetrical class III system, and the bis(fulvalene)ironcobalt cation, which, remarkably, is paramagnetic (Schwarzhans, K. E.; Schottenberger, H. *Z. Naturforsch.* **1983**, *38B*, 1493−1496).

(62) Nock, H.; Buchmeiser, M.; Polin, J.; Lukasser, J.; Jaitner, P.; Schottenberger, H. *Mol. Cryst. Liq. Cryst.* **1993**, *235*, 237−244.

(63) Hagenau, U.; Heck, J.; Hendrickx, E.; Persoons, A.; Schuld, T.; Wong, H. *Inorg. Chem.* **1996**, *35*, 7863−7866.

(64) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, *27*, 1827−1829.

(65) Schottenberger, H.; Rieker, C.; Obendorf, D. *Electrochim. Acta* **1993**, *38*, 1527−1533.

(66) Wadepohl, H.; Leith, C. W.; Paffen, F. J.; Pritzkow, H. *Chem. Ber.* **1995**, *128*, 317−320.

(67) The reverse is true for species such as $Cp^*M(\mu{:}\eta{:}^5\eta^5\text{-L})MCp^*$, where L = pentalene or indacene (Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Barra, C.; Gonzalez, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6596−8. Manriquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182−6193). However, bimetallic complexes of these ligands typically show very different properties from the parent metallocenes due to their triple-decker-like delocalized bonding (Garland, M. T.; Saillard, J.-Y.; Chávez, I.; Oëleckers, B.; Manríquez, J.-M. *J. Mol. Struct.* **1997**, *390*, 199−208).

(68) Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441−3450.