(1-Ferrocenyl-η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(1+): A New Heterobimetallic Basic NLO Chromophore[§,‖]

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The heterobimetallic cationic NLO chromophore (1-ferrocenyl-η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(1+) ([{1-((η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$))-η^6-BC$_5$H$_5$}Co(η^5-C$_5$H$_5$)]$^+$, **1**$^+$) has been synthesized by reaction of FcBBr$_2$ and cobaltocene and subsequent oxidation with FeCl$_3$. The neutral bimetallic compound **1** is paramagnetic and exhibits an ESR spectrum similar to that of the mononuclear 19-valence-electron complex Co(1-Ph-η^6-borabenzene)$_2$. Complex **1**-PF$_6$ crystallizes in monoclinic space group $P2_1/c$ with $a = 10.541(3)$ Å, $b = 17.647(5)$ Å, $c = 10.965(3)$ Å, $\beta = 96.38(2)°$, $Z = 4$, and $V = 2027.0(10)$ Å^3. NMR data for the oxidized diamagnetic cation **1**$^+$ indicate that the positive charge is predominantly localized on the (borabenzene)cobalt moiety. The X-ray structure determination of **1**-PF$_6$ shows the two sandwich units in mutually *trans* positions. The structural data denote an increased electronic interaction between the donating ferrocenyl group and the borabenzene unit. A cyclic voltammetric study of **1**-PF$_6$ or **1** reveals three reversible redox couples ($-1/0$, $0/+1$, $+1/+2$), resembling those of the mononuclear parent compounds, although the redox potentials are slightly shifted due to the mutual influence of the electron-donating and -accepting properties of the different sandwich units. The UV−vis spectrum of **1**$^+$ confirms the enhanced donor−acceptor interaction by a strong, negative solvatochromic absorption about $\lambda = 600$ nm which is assigned to a charge-transfer transition. The determination of the first hyperpolarizability β by means of hyper Rayleigh scattering yields $(90 \pm 30) \times 10^{-30}$ esu, which is unexpectedly high in the face of the directly coupled donor−acceptor pair.

Introduction

The concept of heterobimetallic organometallic complexes for NLO chromophores has shown great potential in the development of new materials with unexpected high first-order hyperpolarizabilities β.[1] In our search for other promising organometallic donor−acceptor combinations, we have chosen the cation (η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(1+) as an electron acceptor. Its electron-accepting capability is reinforced by two effects: first, by the cationic nature of the Co complex and, second, by the π-acidity of the boron center (see Chart 1). Additionally, this cation has several advantages for future applications: (i) it could be used as a redox-switched NLO chromophore because complexes containing borabenzene ligands are easier to reduce than the corresponding Cp complexes,[2] and (ii) borabezene cations are very stable in air.[2a]

Experimental Section

All manipulations were carried out using standard Schlenk techniques in a dry atmosphere of oxygen-free nitrogen. The solvents were carefully dried and distilled from the appropriate drying agents prior to use. Instrumentation: NMR, Varian Gemini 200 BB, measured at

Chart 1

a)   **b)**
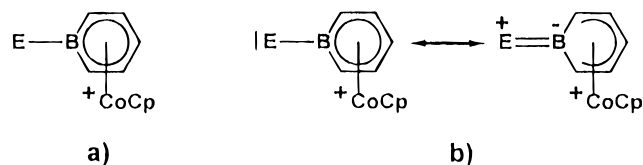
295 K relative to TMS; UV−vis, Perkin-Elmer Model 554; MS, Finnigan MAT 311A; ESR, Bruker ESP 300; elemental analysis, Heraens CHN-O-Rapid.

Cyclic Voltammetry. An Amel System 5000 was used. The measurements were performed in CH$_3$CN with 0.2 M [n-Bu$_4$N]ClO$_4$ as supporting electrolyte, ca. 10^{-3} M **1** and **1**-PF$_6$, a Pt-wire working electrode, a Ag/Ag$^+$ (0.1 M AgNO$_3$ CH$_3$CN) reference electrode, and a Pt-plate (0.6 mm^2) auxiliary electrode. The given potentials are referenced against $E_{1/2}$(FcH/FcH$^+$) = 0 V (FcH = ferrocene).

X-ray Structure Analysis of 1-PF$_6$. Suitable crystals were grown from slow diffusion of Et$_2$O in a concentrated solution of **1**-PF$_6$ in CH$_2$Cl$_2$. Crystal data and details of the structure determination are collected in Table 1. The structure was solved by direct methods (SHELXS-86).[3] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELX-93);[4] no observance criteria were applied during refinements. For the anion PF$_6^-$, residues were disordered and could be refined with two statistically weighted PF$_6^-$ units. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic thermal parameters of the carrier atoms. Weights were optimized in the final refinement cycles.

Hyper Rayleigh Scattering. For the experimental setup, see ref 5a. The measurements were performed at a fundamental wavelength of 1064 nm with a Nd:YAG laser; CH$_2$Cl$_2$ solutions were used for the

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[§] Dedicated to Prof. Dr. E. Weiss on the occasion of his 70th birthday.
[‖] Cooperative Effects in π-Ligand-Bridged Dinuclear Complexes. 19. Part 18: van den Berg, W.; Boot, L.; Joosen, H.; van der Linden, J. G. M.; Bosman, W. P.; de Gelder, R.; Beurskens, P. T.; Heck, J.; Gal, A. W. *Inorg. Chem.*, submitted for publication.
[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.
(1) Behrens, U.; Brussaard, H.; Hagenau, U.; Heck, J.; Hendrickx, E.; Körnich, J.; van der Linden, J. G. M.; Persoons, A.; Spek, A. L.; Veldman, N.; Voss, B.; Wong H. *Chem. Eur. J.* **1996**, *2*, 98−103.
(2) (a) Herberich, G. E.; Koch, W.; Lueken, H. *J. Organomet. Chem.* **1978**, *160*, 17−23. (b) Koelle, U. *J. Organomet. Chem.* **1978**, *152*, 225−228.

(3) Sheldrick, G. M. SHELXS-86: Program for crystal structure determination. University of Göttingen, Germany, 1986.
(4) Sheldrick, G. M. SHELXL-93: Program for crystal structure refinement. University of Göttingen, Germany, 1993.

Table 1. Crystal Data and Structure Refinement Details for **1**-PF$_6$[a]

empirical formula	C$_{20}$H$_{19}$BCoF$_6$FeP
fw	529.91
temp, K	293(2)
λ(Mo Kα), Å	0.710 73
cryst system	monoclinic
space group	$P2_1$/c
a, Å	10.541(3)
b, Å	17.647(5)
c, Å	10.965(3)
β, deg	96.38(2)
V, Å^3	2027.0(10)
Z	4
d(calc), Mg/m^3	1.736
abs coeff μ, mm^{-1}	1.671
F(000)	1064
cryst size, mm^3	0.3 × 0.35 × 0.35
2θ range, deg	2.26 ≤ θ ≤ 30.08
index ranges	−2 ≤ h ≤ 14,
	−2 ≤ k ≤ 24
	−15 ≤ l ≤ 15
no. of data collcd	8543
no. of data refined	5942
GOF on F2	1.111
R [$I > 2\sigma(I)$]	$R_1 = 0.0588$, w$R_2 = 0.1394$
R indices (all data)	$R_1 = 0.0805$, w$R_2 = 0.1576$

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 1.43P]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

measurements, and *p*-nitroaniline in CH$_2$Cl$_2$ was used as the reference ($\beta = 21.6 \times 10^{-30}$ esu). Because **1**$^+$ absorbs appreciably at ~532 nm, corrections were performed as suggested in ref 5b; the corrected β value is given in Table 5.
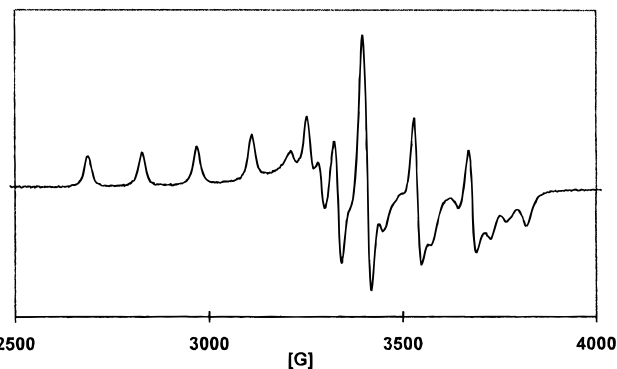
FcBBr$_2$ (Fc = ferrocenyl) was prepared by the method described in the literature,[6] and BBr$_3$ was purchased from Merck.

Synthesis of 1. A solution of 2.5 g (13.2 mmol) of CoCp$_2$ in 50 mL of toluene was added to a stirred, cooled (−50 °C) solution of 1.75 g (4.92 mmol) of FcBBr$_2$ in 50 mL of toluene. The reaction mixture was allowed to warm to room temperature and filtered. The filtrate was evaporated to dryness, and the residue was dissolved in a minimum amount of a 1:1 toluene−hexane mixture. The dark red solution was chromatographed on alumina (14% H$_2$O). The main fraction (violet) yielded 0.79 g (42%) of **1**. EI-MS: *m/z* (%) = 385 (3.8, M$^+$, ^{11}B), 384 (1, M$^+$, ^{10}B), 370 (3.1, M$^+$ − 15), 189 (60, CoCp$_2^+$), 186 (6, FeCp$_2^+$), 124 (27, CoCp$^+$), 121 (47, FeCp$^+$), 98 (7.3), 92 (7), 91 (100), 65 (20), 63 (11), 59 (13), 51 (10). Anal. Calcd for C$_{20}$H$_{19}$-BCoFe (M_r 387.94): C, 62.40; H, 5.97. Found: C, 62.87; H, 5.2.

Synthesis of 1-PF$_6$. A 0.95 g (2.5 mmol) quantity of **1** was dissolved in 40 mL of Et$_2$O and 20 mL of H$_2$O, and, during rigorous stirring, 80 mg (0.30 mmol) of FeCl$_3$·6H$_2$O was added in small portions. The dark-blue water layer was removed, and a sufficient amount of NH$_4$PF$_6$ was added to precipitate the desired product **1**-PF$_6$. Yield: 0.98 g (75%). ^{1}H NMR (200 MHz, acetone-d_6, relative to TMS): δ = 3.95 (5H, FeCp), 4.67 (2H, pt (pt = pseudotriplet), C$_5$H$_4$), 4.68 (2H, pt, C$_5$H$_4$), 5.81 (2H, d, $^3J_{^1H-^1H}$ = 9.3 Hz, H11, H15), 5.96 (5H, CoCp), 6.86 (2H, dd, $^3J_{^1H-^1H}$ = 6 Hz, 9.3 Hz, H12, H14), 7.15 (1H, t, $^3J_{^1H-^1H}$ = 6 Hz, H13). ^{13}C NMR (50 MHz, acetone-d_6, relative to TMS): δ = 69.3 (FeCp), 74.0 (C$_5$H$_4$), 74.3 (C$_5$H$_4$), 87.7 (CoCp), 90.4 (C13), 91.5 (br, C11, C15), 106.5 (C12, C14). Anal. Calcd for C$_{20}$H$_{19}$BCoF$_6$FeP (M_r 529.89): C, 45.33; H, 3.61. Found: C, 44.95; H, 3.65.

Results and Discussion
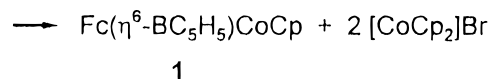
The first report of the synthesis of an (η^6-borabenzene)(η^5-cyclopentadienyl)cobalt complex was published by Herberich and co-workers.[7] According to this report, the heterobimetallic

(5) (a) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285−3289. (b) Laidlaw, W. M.; Denning, R. G.; Verbiest, T. ; Chauchard, E.; Persoons, A. *Nature* **1993**, *363*, 58−60.
(6) Ruf, W.; Fueller M.; Siebert, W. *J. Organomet. Chem.* **1974**, *64*, C45.
(7) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem.* **1970**, *82*, 838− 839; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 805. Herberich, G. E.; Greiss, G. *Chem. Ber.* **1972**, *105*, 3413−3423.

Figure 1. Frozen solution EPR spectrum of **1** (X-band, 2-MTHF, T = 115 K).

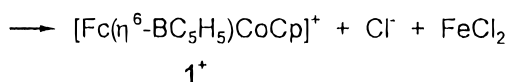**Table 2.** EPR Data^a of Frozen-Solution Spectrum of **1**

compd	g_x[b]	g_y[b]	g_z[b]	A_x(^{59}Co)[c]	A_y(^{59}Co)[c]	A_z(^{59}Co)[c]
1	2.116(1)	2.031(1)	1.875(1)	142(1)	28(1)	36(1)
2[d]	2.1378(3)	2.0240(5)	1.9340(3)	141.7(4)	31.3(10)	48.4(4)

^{a} Determined from a fitted X-band spectrum (2-MTHF, T = 115 K. ^{b} The axis notation is in accordance with that for Co(η^6-C$_5$H$_5$BPh)$_2$ (**2**) from ref 8b. ^{c} 10^{-4} cm^{-1}. ^{d} Taken from ref 8b.

sandwich complex **1** is obtained in acceptable yields (eq 1). Upon oxidation with FeCl$_3$, the desired donor−acceptor pair **1**$^+$ is formed (eq 2). Whereas solutions of the neutral

$$\text{FcBBr}_2 + 3\ \text{CoCp}_2 \qquad (1)$$

$$\longrightarrow \text{Fc}(\eta^6\text{-BC}_5\text{H}_5)\text{CoCp} + 2\ [\text{CoCp}_2]\text{Br}$$
$$\mathbf{1}$$

Fc = ferrocenyl

$$\text{Fc}(\eta^6\text{-BC}_5\text{H}_5)\text{CoCp} + \text{FeCl}_3 \qquad (2)$$

$$\longrightarrow [\text{Fc}(\eta^6\text{-BC}_5\text{H}_5)\text{CoCp}]^+ + \text{Cl}^- + \text{FeCl}_2$$
$$\mathbf{1^+}$$

paramagnetic complex **1** are deeply red, solutions of diamagnetic **1**$^+$ are dark blue or dark greenish blue depending on the polarity of the solvent.

ESR spectra of solutions of **1** are only obtainable at low temperatures (Figure 1), indicating a rapid electron spin relaxation, which is typical for 19-valence-electron (19-ve) sandwich type cobalt complexes. Accordingly, a rhombic **g** tensor is found for **1** with the corresponding three different ^{59}Co hyperfine coupling constants (Table 2). A more detailed inspection of the ESR data for **1** reveals their resemblance to ESR data for other 19-ve borabenzene complexes.[8]

The diamagnetic cation **1**$^+$ was studied by means of NMR spectroscopy. The shifts of the ^{1}H NMR signals of **1**$^+$ are comparable to those of monosubstituted ferrocenes (δ(C$_5$H$_5$) = 3.95 ppm; δ(C$_5$H$_4$) = 4.67, 4.68 ppm) and the cation [(1-R-η^6-borabenzene)(η^5-cyclopentadienyl)Co]$^+$ (δ(C$_5$H$_5$) = 5.96 ppm; δ(C$_5$H$_5$B) = 5.81, 6.86, 7.15 ppm).[7] Hence, the ^{1}H NMR data indicate that the positive charge in the electronic ground state of **1**$^+$ is predominantly located on the borabenzene complex fragment.

(8) (a) Herberich, G. E.; Lund, T.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1975**, 985−990. (b) Kühne, R. O. Ph.D. thesis, University of Zürich, 1986; pp 189−286.
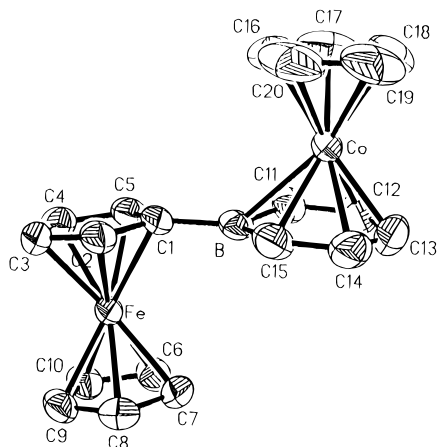
Figure 2. Molecular structure of **1**$^+$ as obtained from X-ray structure analysis. Hydrogen atoms are omitted for clarity. The atoms are represented as 50% probability thermal ellipsoids.

Table 3. Selected Bond Lengths (Å) for **1**-PF$_6$

Fe−C1	2.053(3)	Co−B	2.307(4)
Fe−C2	2.038(3)	Co−C11	2.112(4)
Fe−C3	2.047(4)	Co−C12	2.055(4)
Fe−C4	2.049(4)	Co−C13	2.044(4)
Fe−C5	2.043(4)	Co−C14	2.062(4)
Fe−C6	2.043(4)	Co−C15	2.111(4)
Fe−C7	2.054(4)	Co−C16	1.992(5)
Fe−C8	2.048(4)	Co−C17	1.997(5)
Fe−C9	2.036(4)	Co−C18	2.028(5)
Fe−C10	2.035(3)	Co−C19	2.026(5)
		Co−C20	2.001(5)
C1−B	1.535(5)	C11−B	1.531(6)
C1−C2	1.431(5)	C15−B	1.528(6)
C2−C3	1.425(6)	C11−C12	1.405(6)
C3−C4	1.384(7)	C12−C13	1.379(8)
C4−C5	1.412(6)	C13−C14	1.397(8)
C5−C1	1.429(5)	C14−C15	1.393(6)

An X-ray structure analysis of **1**-PF$_6$ reveals a *trans* conformation for the two sandwich moieties (Figure 2, Table 3). The Fe−C$_{Cp}$ and Co−C$_{Cp}$ distances are quite normal. However, the Co−C$_{borabenzene}$ bond lengths shorten distinctly upon oxidation compared to those of the neutral 19-ve complex bis(1-phenyl-η^6-borabenzene)cobalt (**2**),[9] whereas a slight Co−B bond lengthening becomes apparent (Co−B: 2.283(5) Å in **2**, 2.307(4) Å in **1**-PF$_6$). Normally, a metal−boron bond shortening can be recognized upon going from a 19-ve to an 18-ve borabenzene complex.[10] Additionally, the distance between the boron atom and the *ipso*-C atom of the ferrocenyl substituent (1.535(5) Å) is slightly shortened, whereas the B−C bond lengths within the borabenzene ligand are slightly elongated, compared to the corresponding B−C bond distances in other borabenzene complexes.[9−11] These effects point to a slight diminution of the Co−B interaction and to a weak increase in the ferrocenyl−boron interaction.

An enhanced interaction between the boron atom and the ferrocenyl moiety also seems to be indicated by the tilt angle of 7° enclosed by the C$_{ipso}$−B bond vector and the adjacent Cp plane. Such tilt angles are characteristic for boron-substituted metallocenes and have been correlated to the Lewis acidity of the boron center.[12] This Lewis acidity could facilitate a weak π-bonding interaction between the ferrocenyl substituent and the boron atom of the borabenzene ligand (compare Chart 1b).
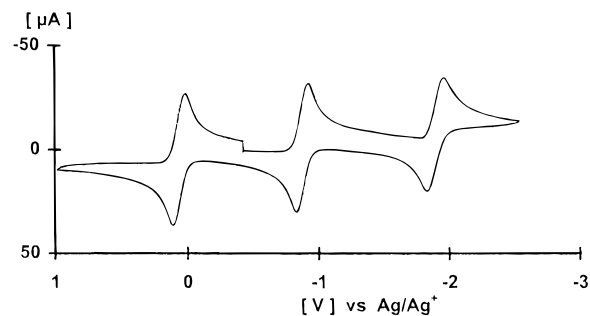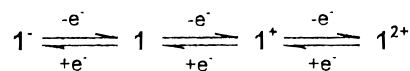
(9) Huttner, G.; Krieg, B.; Gartzke, W. *Chem. Ber.* **1972**, *105*, 3424−3436.

(10) Herberich, G. E.; Klein, W.; Spaniol, T. P. *Organometallics* **1993**, *12*, 2660−2667.

(11) Huttner, G.; Gartzke, W. *Chem. Ber.* **1974**, *107*, 3786−3799.

(12) Appel, A.; Nöth, H.; Schmidt, M. *Chem. Ber.* **1995**, *128*, 621−626

Figure 3. Cyclic voltammogram of **1**-PF$_6$. The scale of the potential is referenced to Ag/Ag$^+$ (for further details, see the Experimental Section and Table 2).

Table 4. Cyclic Voltammetric Data[a] for **1**-PF$_6$

redox couple	$E_{1/2}$, V[b]	ΔE, mV	i_{pc}/i_{pa}
+2/+1	0.05	65	1.0
+1/0	−0.88	63	1.0
0/−1	−1.90	76[c]	1.1

[a] Obtained from CH$_3$CN solutions; 293 K (for further details see Experimental Section); equilibrium potentials E_{eq}(**1**-PF$_6$) = −0.71 V, E_{eq}(**1**) = −1.20 V *vs* FcH/FcH$^+$. [b] *Vs* FcH/FcH$^+$. [c] See ref 13.

Scheme 1

$$\mathbf{1^-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathbf{1} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathbf{1^+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathbf{1^{2+}}$$

In order to obtain deeper insight into the mutual electronic influence of both organometallic sandwich units, cyclic voltammetric measurements were performed. The cyclic voltammogram of **1**-PF$_6$ (Figure 3, Table 4) shows three well separated reversible redox waves. Two of them are electrochemically reversible one-electron transfers, while the peak potentials of the redox couple 0/−1 slightly depend on the scan rate. The differences in the peak potentials ΔE for the couples +2/+1 and +1/0 are comparable to the theoretical values of $\Delta E = 59$ mV and are independent of the scan rate v within 1 decade. In contrast, the ΔE values of the redox wave 0/−1 increase slightly from 66 mV ($v = 20$ mV/s) to 88 mV ($v = 400$ mV/s), whereas the ratio of the peak currents remains $i_{pc}/i_{pa} \approx 1$, indicating chemical reversibility. The same cyclic voltammogram is recorded for the neutral complex **1**. However, the equilibrium potentials of **1** and **1**$^+$ are quite different (see Table 2). The redox properties are summarized by the redox cascade shown in Scheme 1.

The redox behavior of **1**-PF$_6$ resembles to a great degree that of the mononuclear sandwich moieties: the potential of the redox couple +2/+1 is anodically shifted about 50 mV with respect to the FcH/FcH$^+$ couple (FcH = ferrocene), whereas the $E_{1/2}$ of the couple 0/+1 is cathodically shifted about 60 mV with respect to [(1-phenyl-η^6-borabenzene)(η^5-cyclopentadienyl)Co]$^+$ (**3**$^+$).[13] Obviously, the redox pairs obtained for **1**-PF$_6$ can be assigned to the ferrocenyl part (*viz.* +2/+1) and the borabenzene complex unit (*viz.* +1/0, 0/−1), respectively.

A particular interaction between the ferrocenyl moiety and the cationic borabenzene complex unit in **1**$^+$ can be shown by means of UV−vis spectra (Figure 4). The two absorption maxima below $\lambda = 450$ nm, which only slightly depend on the solvent polarity, are assigned to metal-to-ligand charge transfer in accordance with other 18-ve sandwich type complexes.[14]

(13) The shift of the potential has been calculated with respect to the redox potential of **3** and CoCp$_2$ as given in ref 2b, taking into account that $E_{1/2}$(CoCp$_2$/CoCp$_2^+$) = −1.33 V *vs* FeH/FeH$^+$, which has been obtained in our system.
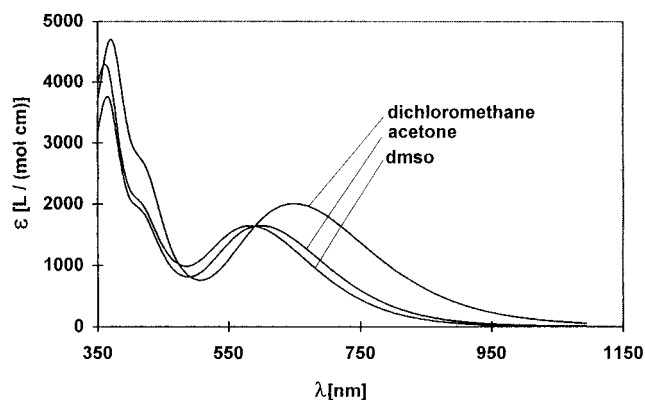
Figure 4. UV–vis spectra of **1**-PF$_6$, in CH$_2$Cl$_2$, acetone and dmso.

Scheme 2
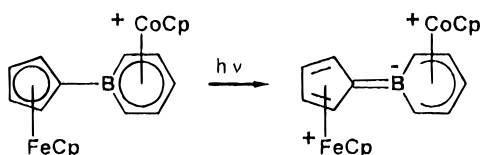
Table 5. UV–Vis Data for **1**-PF$_6$[a] and the First Hyperpolarizability β

solvent	λ_{max}[b] (ϵ)	λ_{max}[b,c]	λ_{max}[b] (ϵ)	$\Delta\nu$[d]	$10^{-30}\beta$, esu
CH$_2$Cl$_2$	370 (4700)	410 (sh)	650 (2000)		90 ± 30
acetone	365 (3700)	405 (sh)	600 (1650)	1282	
dmso	360 (4300)	405 (sh)	585 (1640)	1709	

[a] 5.66 × 10^{-4} M **1**-PF$_6$. [b] In nm. [c] sh = shoulder. [d] Relative to λ_{max}(CH$_2$Cl$_2$) in cm^{-1}.

Additionally, a fairly strong, clearly solvatochromic absorption band is recorded at about $\lambda = 600$ nm. A comparable absorption maximum is not reported for the mononuclear sandwich moieties. The UV–vis spectra of **1**-PF$_6$ are very similar to those of the heterobimetallic sesquifulvalene complexes[1] and accordingly, we interpret this long-wavelength absorption to be a charge transfer between the ferrocenyl moiety and the borabenzene complex unit as described in Scheme 2. The influence of the polarity of the solvent on the position of λ_{max} corroborates this interpretation (Figure 4, Table 5). The hypsochromic shift upon increasing polarity of the solvent (negative solvatochromism) demonstrates a decrease of the dipole moment of **1**$^+$ in the excited state, as shown in Figure 5, or even an inversion of the dipole moment.[15]

The most important property of **1**$^+$, which originates from the change of the dipole moment upon irradiation, is the first hyperpolarizability β of **1**$^+$, determined by means of hyper Rayleigh scattering.[5] The β value obtained is 90×10^{-30} esu, which to be appreciated properly must be compared with those of other directly coupled donor–acceptor pairs like the cationic sesquifulvalene complexes (ferrocenyl-η^7-cycloheptatrienylium)-tricarbonylchromium(1+) and ferrocenylcycloheptatrienylium-(1+), which are similar electronic systems. However, these di- and monometallic sesquifulvalene-type complexes do not show any measurable first hyperpolarizability β.[1,16] Nevertheless, when the donor and acceptor groups in heterobimetallic sesquifulvalene complexes are separated by one ethynediyl or ethenediyl bridge only, surprisingly high first hyperpolarizabilities are obtainable.[1] Hence, combinations of ferrocene and (η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(1+) seem to be encouraging NLO chromophores with respect to very high β values, if it is possible to separate both functions by unsaturated linkers. This is currently under investigation by our group. Taking into account the thermal stability of ferrocene and (η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(1+) and their insensitivity to air, NLO chromophores containing these sandwich units as electron-donating and -accepting groups are promising candidates for applications in Langmuir–Blodgett films because of their amphiphilic nature and for applications in polymers since the sandwich moieties are easily substituted with polymerizable groups.[17]

Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1**-PF$_6$ and the experimental and fitted ESR spectra of **1** (14 pages). Ordering information is given on any current masthead page.

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(14) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227–7232.

(15) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Verlagsgesellschaft: Weinheim, Germany, 1988.

(16) Brussaard, H. C.; Heck J.; Hendrickx, E.; Persoons, A. Unpublished results.

(17) Gonsalves, K. E.; Chen, X. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH Verlagsgesellschaft: Weinheim, Germany, 1995; p 497 ff.