

The (*E*)-2-Ferrocenylethenylcobaltocenium Cation. A Missing Link in Heteronuclear Bimetalloocene-Based Donor–Acceptor Conjugate Chemistry Exhibiting Irregular Solvatochromism

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The new heteronuclear ethene-bridged bimetalloocene ferrocenylethenylcobaltocenium cation (fec-ene-coc⁺), as hexafluorophosphate and chloride, was prepared by Knoevenagel condensation of methylcobaltocenium PF₆ and ferrocenecarbaldehyde. The chloride was obtained by anion exchange. X-ray crystal structure, cyclic voltammetry, and detailed solvatochromism data are reported and compared to those of related bimetalloccenes, namely, the ethyne-bridged fec-yne-coc⁺, the directly linked fec-coc⁺, the new ethene-bridged ruc-ene-coc⁺, and the ethyne-bridged ruc-yne-coc⁺, as well as related termetalloccenes.

Introduction

The ferrocene moiety has been incorporated into a range of organic and organometallic conjugated systems.¹ In the field of linked metalloccenes, donor–acceptor arrangements^{2,3} are of special interest due to their sometimes unusual electrochemical properties⁴ and potential use in nonlinear optics (NLO). Heteronuclear bimetalloccenes derived from Fe, Co, Ni, Ru, Os, and Rh, such as the neutral compounds fec-ruc⁵ and fec-nic⁶ and the cationic species fec-coc⁺,⁷ osc-coc⁺,⁸ ruc-coc⁺,⁸ and fec-rhc⁺,⁹ are logical candidates that fulfill the requirements of donor–acceptor assemblies, although to different degrees. Due to the 18-electron configurations of the individual metalloocene systems, they possess the necessary stability to allow assessment of their optical properties. Also, syntheses of heteronuclear termetalloccenes such as nic-fec-nic,⁶ the cobaltocenium compounds coc⁺-ruc-coc⁺,⁸ coc⁺-osc-coc⁺,⁸ fec-coc⁺-fec,¹⁰ and coc⁺-fec-coc⁺,¹⁰ and the rhodocenium

compounds rhc⁺-fec-rhc⁺ and rhc⁺-fec-coc⁺,⁹ and their electrochemical behavior^{11,12} have been reported. Bisfulvalene (BF) dimetal complexes such as BF(Fe-Ni),⁶ BF(Fe-Co⁺), which is uniquely paramagnetic,^{13–16} and BF(Ru-Co⁺)^{14,16} also belong in this category. Furthermore, fec/ruc and fec/coc⁺ systems with elongated conjugation^{17,18} and conjugatively connected ethene-bridged bi- and quatermetalloccenes,¹⁹ ethyne-bridged fec-yne-coc⁺,^{20,21} and fec-yne-ruc have been described.²² Here, we report on the synthesis and solvatochromic properties of the new compound fec-ene-coc⁺ as well as the analogous ruc-ene-coc⁺ and ruc-yne-coc⁺. None of the aforementioned bimetalloccenes, not even the closely related compounds fec-coc⁺ and fec-yne-coc⁺, have been reported to exhibit visible solvatochromism. Consequently, the new conjugatively bridged bimetalloocene fec-ene-coc⁺ truly represents a missing link in this context, which also opens a long overdue new chapter in solvatochromism.

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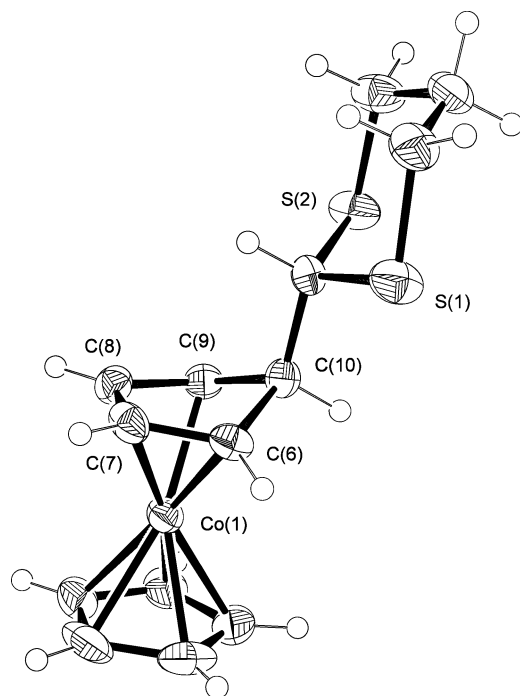
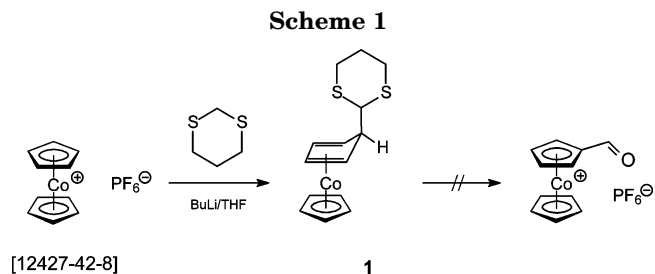


Figure 1. View of the crystal structure of **1** (50% displacement ellipsoids).

Results and Discussion

Synthetic Considerations and Spectroscopic Characterization. Early considerations for the synthesis of *fec-ene-coc*⁺ involved the well-known Seebach methodology,²³ to be followed by hydride abstraction and deprotection using published procedures, but the projected intermediate, dithiane **1**, proved to be a dead end. The crystal structure of **1** (Figure 1) showed the cyclopentadiene C(10)–H to be in the *endo* position relative to the metal center, which, according to the literature,^{10,24} should be abstractable as hydride by trityl cations. However, there were also contradictory reports on the reactivity of *endo* protons.^{25,26} Nonetheless, all attempts to convert the dithiane **1** to the required cobaltoceniumcarbaldehyde were unsuccessful (Scheme 1). Therefore, the planned Wittig olefination could not be put into practice. But fortunately, Knoevenagel condensation²⁷ of methyl cobaltocenium hexafluorophosphate²⁸ with ferrocenecarbaldehyde (Scheme 2) readily yielded the desired 2-ferrocenylethenylcobaltocenium hexafluorophosphate, [*fec-ene-coc*][PF₆] (**2a**). ¹H NMR spectra in DMSO-*d*₆ and dichloromethane-*d*₂ indicated a regular (*E*)-ethene structure with coupling constants of 16 Hz, which was confirmed by X-ray structure analysis. Thus, there was no evidence for a solvent-dependent bisfulvenoid resonance structure^{1,2} contribution. The title compound **2a** was also characterized by ¹³C NMR, IR, and MS. In addition, to improve the solubility of *fec-ene-coc*⁺ in polar solvents, the anion was exchanged to give the chloride **2b**. Next, the preparation



of the new termetallocene [(*fec-ene*)₂coc][PF₆] (**3**) from 1,1'-dimethylcobaltocenium and ferrocenecarbaldehyde by the same process (Scheme 2) suggested itself. The related, new bridged bimetallocene *ruc-ene-coc*⁺ (**4**) was synthesized as hexafluorophosphate and chloride in an analogous manner. Compounds **3** and **4** were shown by ¹H NMR to possess also (*E*)-ethene conformations. Peak assignments for **2** were corroborated by nuclear Overhauser experiments, establishing through-space connectivities between (a) the low-field olefinic doublet and the low-field *coc*⁺ multiplet and (b) the high-field olefinic doublet and the low-field *fec* multiplet. The same pattern was observed in **4**. Finally, *ruc-yne-coc*⁺ (**5**) was obtained from 1-ethynylruthenocene,²⁹ as described for *fec-yne-coc*⁺.²⁰

X-ray Crystal Structures. Two X-ray structures were determined in the course of this work, the most relevant features of which are discussed in the following. In the dithiane **1**, the C(10)–H occupies the *endo* position and the Cp rings are almost eclipsed, but C(10) is bent out of the plane of the remaining four carbon atoms by 32°, as expected for a η^4 -cyclopentadiene complex,³⁰ and the pertinent angle C(6)–C(10)–C(9) is 92.2° (Figure 1). In [*fec-ene-coc*][PF₆] **2a**, the Cp(*fec*) rings are twisted by ~14° and the Cp(*coc*) rings by ~15°, Cp(*fec*) centroid–Fe distances are 1.65 Å, and Cp(*coc*)–Co distances are 1.64 Å. Cp ring–centroid–metal–Cp ring–centroid angles are 178.7° (*fec*) and 179.1° (*coc*). The C(1)–C(2) double bond is tilted out of the Cp(*fec*) plane by a dihedral angle of 12° and out of the Cp(*coc*) plane by 13°. The sp²-carbon angles C(10)–C(1)–C(2) and C(1)–C(2)–C(20) are 125.9° and 124.1°, respectively. The single bond lengths C(1)–C(10) and C(2)–C(20) are 1.466 and 1.460 Å, and the double bond length C(1)–C(2) is 1.315 Å (Figure 2), indicating a regular ethene structure. The Fe–Co distance is 7.13 Å. Short contacts between Cp–H and fluorine atoms are found in the range 2.45 to 2.56 Å. Crystallographic data and structure refinement details of compounds **1** and **2a** are summarized in Table 1.

Cyclic Voltammetry. In *fec-ene-coc*⁺, a quasi-reversible one-electron reduction of Co(III)/Co(II) was observed at $E_{1/2} = -1280$ mV (ΔE_p 90 mV), and the respective oxidation of Fe(II)/Fe(III) was found at $E_{1/2} = 130$ mV (ΔE_p 80 mV) vs Ag/Ag⁺. For comparison, the parent compounds *fec* and *coc*⁺ were measured separately. No significant electrochemical potential shifts were observed in *fec-ene-coc*⁺ compared with the isolated *fec* and *coc*⁺ electrophores. Obviously, the conjugated metallocenes do not influence each other to a measurable degree (Figure 3).

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Scheme 2

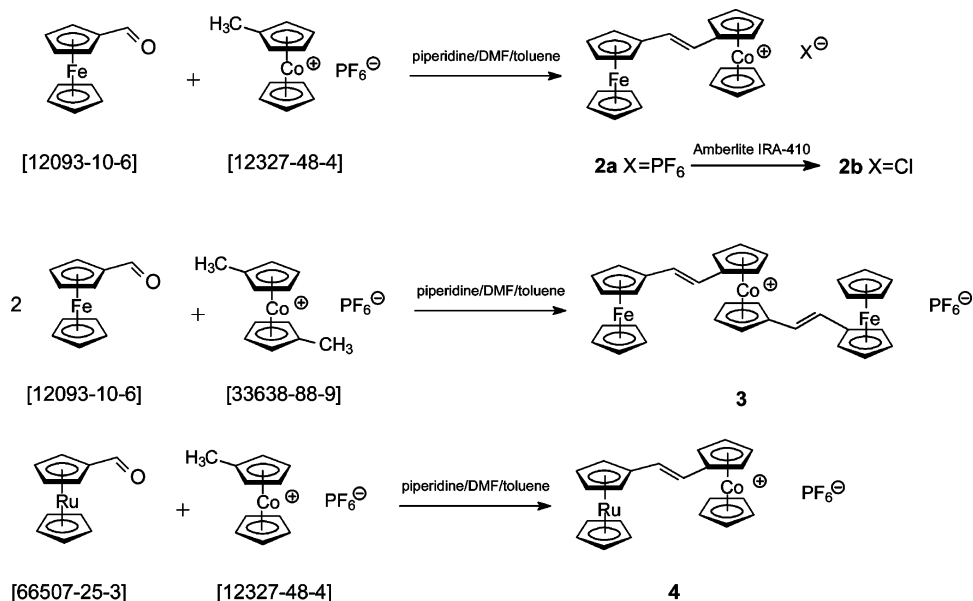
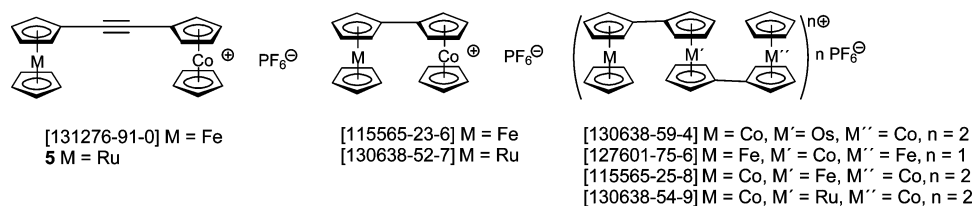


Chart 1



Solvatochromism and Preferential Solvation in Binary Solvent Mixtures. Solvatochromic absorptions have been observed in metallocene-terminated allylium cations³¹ and even in methylene-bridged heteronuclear bi- and termetallocenes.³² Conjugated organic donor-coc⁺ systems²⁷ and a cationic fec-substituted borabenzene Co complex³³ have been reported to exhibit negative solvatochromism, whereas neutral organic acceptor-

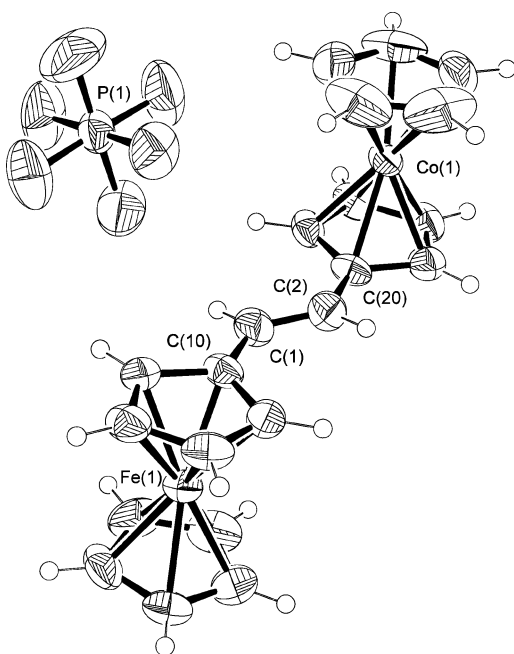


Figure 2. ORTEP plot of the crystal structure of **2a** (50% displacement ellipsoids).

Table 1. Crystallographic Data and Structure Refinement Details of Compounds 1 and 2a

	1	2a
molecular formula	C ₁₄ H ₁₇ CoS ₂	C ₂₂ H ₂₀ CoF ₆ FeP
<i>M_r</i>	308.33	544.13
cryst syst	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P2(1)/c</i>
<i>a</i> , Å	17.173(2)	10.0305(8)
<i>b</i> , Å	8.382(1)	11.3623(5)
<i>c</i> , Å	18.589(3)	18.448(1)
β , deg	96.82(1)	95.909(3)
<i>V</i> , Å ³	2656.8(6)	2091.3(2)
<i>Z</i>	8	4
<i>T</i> , K	218(2)	233(2)
<i>D</i> _{calcd} , g cm ⁻³	1.542	1.728
μ , mm ⁻¹	1.580	1.623
<i>F</i> (000)	1280	1096
color, habit	red block	orange prism
cryst dimens, mm	0.4 × 0.4 × 0.3	0.2 × 0.04 × 0.02
θ range for data collection, deg	2.71–22.98	2.04–21.94
index ranges	–1 ≤ <i>h</i> ≤ 18 –1 ≤ <i>k</i> ≤ 9 –20 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 10 –11 ≤ <i>k</i> ≤ 11 –19 ≤ <i>l</i> ≤ 19
no. of reflns collected	2159	9252
no. of indep reflns	1851	2531
no. of reflns with <i>I</i> > 2σ(<i>I</i>)	1589	1844
no. of data/restraints/params	1783/0/155	2531/0/280
goodness-of-fit on <i>F</i> ²	1.103	1.031
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0293, <i>wR</i> ₂ = 0.0715	<i>R</i> ₁ = 0.0463, <i>wR</i> ₂ = 0.0963
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0386, <i>wR</i> ₂ = 0.0844	<i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.1050

fec systems displayed positive solvatochromism.^{34–38} Therefore, the new conjugatively bridged, cationic heteronuclear bimetalloene fec-ene-coc⁺ (**2**), as a typical

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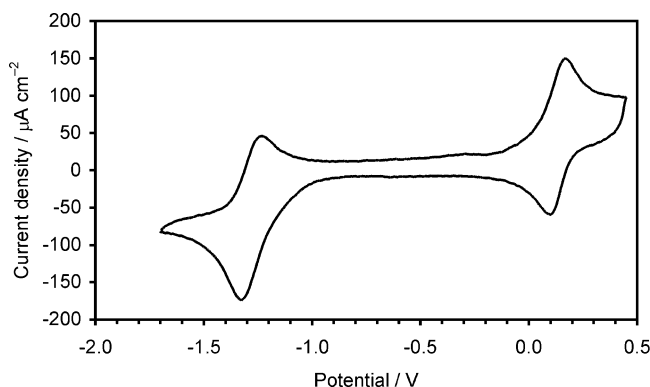


Figure 3. Cyclic voltammogram of [fec-ene-coc][PF₆] (**2a**); 0.5 mM in acetonitrile; *T* 30 °C, scan rate 50 mV s⁻¹. The scale of the potential is referenced to Ag/Ag⁺ (for further details, see the Experimental Section).

donor–acceptor assembly, was also expected to exhibit negative solvatochromism. In the UV–vis range, [fec-ene-coc][PF₆] (**2a**) showed four bands of absorption. However, only the low-energy (LE) absorption (which in accordance with reported assignments is likely a metal-to-metal charge-transfer excitation)³² showed solvent dependence. This compound is red-purple in water, blue in pyridine, and green in 1,2-dichlorobenzene. A wavelength difference between water and 1,2-dichlorobenzene solutions of 71 nm (transition energy ΔE_T 25.7 kJ mol⁻¹; 2140 cm⁻¹) was observed, which is significantly more than in previously reported neutral fec-acceptor systems.^{35,36} In hydroxylic solvents, the corresponding chloride **2b** was used because of the limited solubility of the hexafluorophosphate **2a**. By correlation of the absorption maxima of these two salts in nine different solvents (included in Table 2) with a squared coefficient *r*² of 0.999, it was concluded that the experimental data of both salts could be safely combined to expand the range of applicable solvents. It was also determined that the absorption maxima of [fec-ene-coc]-[PF₆] were not affected by the presence of electrolytes (0.1 M NaCl or NaI in MeOH), excluding the unlikely possibility of halochromism.^{39,40}

It was attempted to correlate the absorption data with known polarity parameters using different models as discussed recently.^{41–43} Transition energies *E*_T were calculated from the wavelengths of the absorption maxima using eq 1.

$$E_T/\text{kJ mol}^{-1} = hcN/\lambda_{\text{max}} = 119\,625/(\lambda_{\text{max}}/\text{nm}) \quad (1)$$

However, use of the most widely applied and recognized primary polarity scales, such as (a) the Kamlet–

Table 2. Electronic LE Absorption Maxima λ_{max} and Transition Energies *E*_T of fec-ene-coc⁺ (2a,b**) in 34 Solvents**

no.	solvent	$\lambda_{\text{max}}/\text{nm}$		<i>E</i> _T /kJ mol ⁻¹	$\bar{\nu}/10^3$ cm ⁻¹
		PF ₆ ⁻	Cl ⁻		
1	water	— ^a	541	221	18.5
2	1- <i>n</i> -butyl-2,3-dimethyl-imidazolium tetrafluoroborate	544	— ^b	220	18.4
3	tri- <i>n</i> -butyl phosphate	545	— ^a	220	18.3
4	<i>N,N</i> -dimethyl acetamide	547	547	219	18.3
5	<i>N,N</i> -dimethyl formamide	547	547	219	18.3
6	acetonitrile	548	548	218	18.3
7	1,2-dimethoxyethane	549	— ^a	218	18.2
8	propionitrile	— ^b	550	218	18.2
9	acetic anhydride	550	— ^a	218	18.2
10	acetone	550	— ^a	217	18.2
11	dimethyl sulfoxide	551	552	217	18.1
12	<i>N</i> -methyl formamide	552	— ^a	217	18.1
13	butan-2-one	552	— ^a	217	18.1
14	acetic acid	553	553	216	18.1
15	tetrahydrofuran	555	— ^a	216	18.0
16	formic acid	556	556	215	18.0
17	methanol	558	558	214	17.9
18	ethanol	— ^a	559	214	17.9
19	hexafluoropropan-2-ol	— ^a	563	213	17.8
20	propan-1-ol	564	564	212	17.7
21	propan-2-ol	— ^a	565	212	17.7
22	2,2,2-trifluoroethanol	567	568	211	17.6
23	<i>N,N</i> -dimethylaniline	569	— ^a	210	17.6
24	benzonitrile	569	— ^a	210	17.6
25	pyridine	572	— ^a	209	17.5
26	nitrobenzene	573	— ^a	209	17.5
27	anisole	579	— ^a	207	17.3
28	benzene	580	— ^a	206	17.2
29	chloroform	588	— ^a	203	17.0
30	chlorobenzene	590	— ^a	203	17.0
31	iodobenzene	590	— ^a	203	16.9
32	dichloromethane	595	— ^a	201	16.8
33	trifluoroacetic acid	— ^a	597	200	16.8
34	1,2-dichlorobenzene	612	— ^a	196	16.3

^a Insoluble. ^b Not available.

Taft model using the dipolarity-polarizability parameter π^* ⁴⁴ (and the partially revised π^* parameters),⁴⁵ the hydrogen bond donor (HBD) α ⁴⁶ and hydrogen bond acceptor (HBA) properties β ,⁴⁷ employing the simplified solvatochromic eq 2,⁴⁸ and using the values compiled by Marcus,⁴³

$$E_T = s\pi^* + a\alpha + b\beta \quad (2)$$

as well as (b) the reaction field approach using refractive index and dielectric constant values,⁴⁹ and (c) the Catalan scale⁵⁰ gave puzzling results (see plots in the Supporting Information).

Of the three models, the best but still quite unsatisfactory correlations were obtained with the Kamlet–

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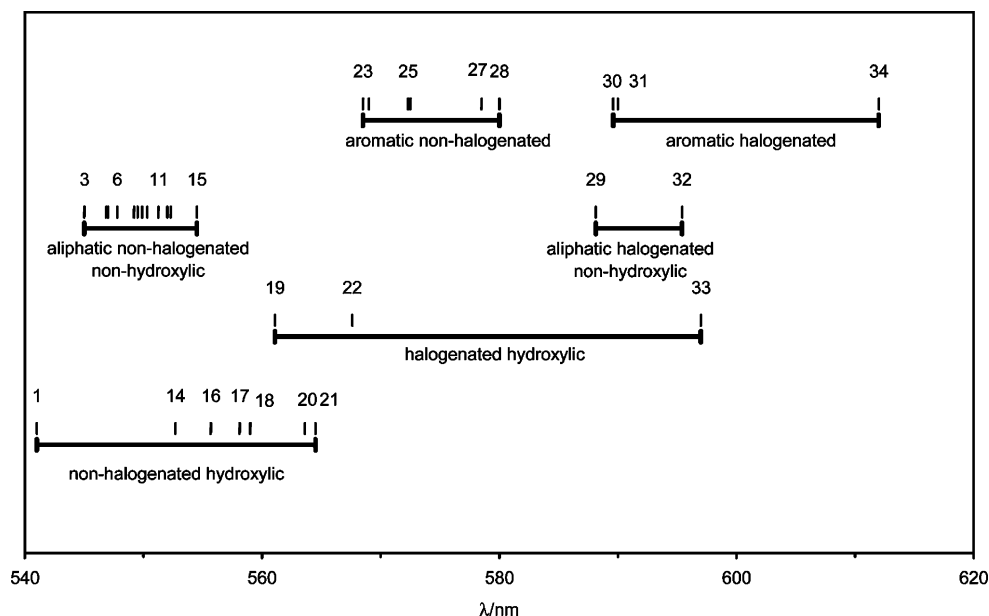


Figure 4. Ranges of visible absorption maxima of fec-ene-coc⁺ (**2**) in different solvent subgroups. The numbers of individual solvents refer to Table 2.

Table 3. Electronic LE Absorption Maxima λ_{\max} of Conjugatively Bridged Metallocenium Cations (fec-ene)₂coc⁺ (3**), ruc-ene-coc⁺ (**4**), ruc-yne-coc⁺ (**5**), and fec-yne-coc⁺ in Six Solvents**

no.	solvent	compound ^a			
		(fec-ene) ₂ coc ⁺ (3) λ_{\max}/nm	ruc-ene-coc ⁺ (4) λ_{\max}/nm	ruc-yne-coc ⁺ (5) λ_{\max}/nm	fec-yne-coc ⁺ [131276-91-0] λ_{\max}/nm
1	water ^b	554	446	415	519
6	acetonitrile	563	456	428	524
17	methanol	572	462	437	526
32	dichloromethane	608	483	459	568
33	trifluoroacetic acid	609	477	— ^c	— ^c
34	1,2-dichlorobenzene	628	496	472	600

^a Hexafluorophosphate was used if not noted otherwise. ^b Chloride. ^c Decomposition.

Taft model for a selection of otherwise appropriate solvents (hydroxylic, HBA, HBD, dipolar, aprotic, aromatic, halogenated), and no meaningful correlations could be established. To avoid this dilemma, subgroups (classes) of solvents were scrutinized separately. Aprotic but dipolar solvents with $\alpha = 0$ cover a wide range of π^* values (e.g., DMSO 1.00, DME 0.53), but absorption maxima of **2** were within an unexpectedly narrow range in these solvents (Figure 4), indicating obviously sensitivity neither to π^* nor to β . From this subgroup of solvents, not even a conclusion about the type of solvatochromism (negative or positive) could be drawn. In addition, compound **2** was observed to be exceptionally sensitive to light in DMSO solution; a color change from purple to blue took place within seconds after exposure to direct sunlight. Only limited success was achieved within the group of aromatic solvents, compound **2** exhibiting definitely no π^* , α , or n_D ²⁰ sensitivity at all and only slight sensitivity toward β (with $r^2 = 0.61$, $n = 10$). Interestingly, linear regression of E_T for the seven nonfluorinated hydroxylic solvents (water, alcohols, carboxylic acids) with π^* gave a satisfactory correlation ($r^2 = 0.94$, $n = 7$), as shown in eq 3.

$$E_T/\text{kJ mol}^{-1} = (205.65 \pm 1.18) + (14.55 \pm 1.75)\pi^* \quad (3)$$

The two fluoro alcohols used here deviate significantly from this correlation. Multiple linear regressions using

α and β in addition to π^* gave slightly better correlations ($r^2 = 0.97$, $n = 7$). However, these correlations are meaningless since the parameters α and β of hydroxylic solvents are inversely self-correlated. It may seem odd to include hydrogen-bonding scales, but the crystal structure of **2** showed short contacts between the Cp-H and the fluorine atoms of the hexafluorophosphate ion and, therefore, weak hydrogen bridges could be possible in solution. A polarizability correction term $d\delta$ to adjust π^* for aromatic and polychloro solvents has been proposed⁵¹ for charged solutes in the case of negative solvatochromism, but the polarizability of fluoro solvents is still questionable and has not been discussed in the literature. However, attempts to apply this term did not succeed in improving any correlation. A specific interaction between metallocene systems and chlorinated solvents has been suggested previously.³¹ No solvatochromic parameters have been published for 1-*n*-butyl-2,3-dimethylimidazolium tetrafluoroborate, and only the π^* value is available for trifluoroacetic acid (TFA). TFA behaved extremely within the subgroup of hydroxylic solvents. The ionic liquid, however, fitted in nicely (polarity tentatively similar to water). All solvents considered together, it was finally concluded that fec-ene-coc⁺ exhibited *negative* solvatochromism, meaning that the wavelength of the absorption maximum de-

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Table 4. Electronic LE Absorption Maxima λ_{\max} of Directly Connected Bi- and Termetalocenium Cations

no.	solvent	compound ^a					
		fec-coc ⁺ [115565-23-6] λ_{\max}/nm	ruc-coc ⁺ [130638-52-7] λ_{\max}/nm	coc ⁺ -osc-coc ⁺ [130638-59-4] λ_{\max}/nm	coc ⁺ -fec-coc ⁺ [115565-25-8] λ_{\max}/nm	coc ⁺ -ruc-coc ⁺ [130638-54-9] λ_{\max}/nm	fec-coc ⁺ -fec [127601-75-6] λ_{\max}/nm
1	water ^b	541	453	443	541	435	539
6	acetonitrile	549	457	455	546	439	546
17	methanol	554	444	458	553	442	554
32	dichloromethane	582	460	469	575	450	577
33	trifluoroacetic acid	585	— ^c	462	565	— ^c	584
34	1,2-dichlorobenzene	592	466	470	587	453	590

^a Hexafluorophosphate was used if not noted otherwise. ^b Chloride. ^c Not available.

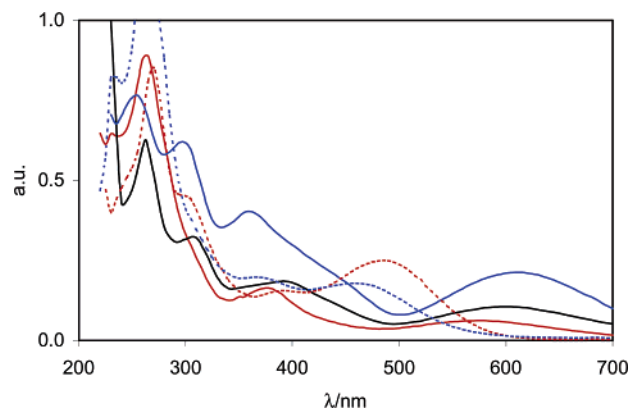


Figure 5. Electronic absorption spectra of fec-ene-coc⁺ (**2**, black), (fec-ene)₂coc⁺ (**3**, blue), fec-yne-coc⁺ [131276-91-0] (red), ruc-ene-coc⁺ (**4**, dashed red), and ruc-yne-coc⁺ (**5**, dashed blue) in dichloromethane.

creases with increasing solvent polarity, indicative of either decreased polarity or even dipole inversion in the excited state of the solute metallocene. The results of these attempts to get at least reasonable assignments of absorption values to solvent subclasses are summarized in Figure 4. Finally, the electronic coupling between the two metal centers⁵² was estimated to be 22 kJ mol⁻¹ (1840 cm⁻¹) in dichloromethane. This supports the general picture where Fe–Co⁺ interactions³² are stronger than Fe–Fe⁺ interactions.⁵³

The ethene-bridged termetalocene (fec-ene)₂coc⁺ (**3**) exhibited basically the same behavior (ΔE_T 25.3 kJ mol⁻¹; 2110 cm⁻¹), as can be seen from the data in Table 3, but poor solubility prevented further investigation. In contrast, the related compound ruc-ene-coc⁺ (**4**) exhibited only one prominent absorption band in the visible region at a comparably short wavelength and only a small shoulder at even lower wavelengths (Figure 5). Nevertheless, this absorption also showed a similar solvent dependence (Table 3). The solvatochromic shift of **4** ($\Delta\lambda$ between water and 1,2-dichlorobenzene: 53 nm) was significantly less than that observed for fec-ene-coc⁺. However, the ΔE_T value of 28.9 kJ mol⁻¹ (2410 cm⁻¹) was larger due to the position of λ_{\max} at shorter wavelengths. At this point, it seems to be appropriate to discuss whether fec or ruc is the stronger donor metallocene. Photoelectron spectra of the parent compounds ferrocene and ruthenocene showed that fec was clearly the stronger donor in an electron-transfer sense, and electrochemical studies of organic acceptor-substi-

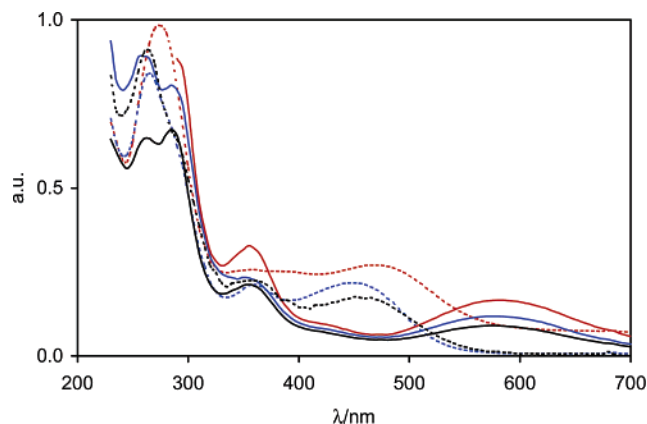


Figure 6. Electronic absorption spectra of fec-coc-fec⁺ [127601-75-6] (blue), coc⁺-fec-coc⁺ [115565-25-8] (black), fec-coc⁺ [115565-23-6] (red), coc⁺-osc-coc⁺ [130638-59-4] (red dashed), coc⁺-ruc-coc⁺ [130638-54-9] (blue dashed), and ruc-coc⁺ [130638-52-7] (black dashed) in dichloromethane.

tuted complexes suggested ruc to be a weaker donor than fec.² In contrast, in 1,3-bis(metalloceanyl)allylium cations, ruc was found to possess superior donor properties.² Thus, which of these metallocenes may be attributed the stronger donor quality obviously depends on the type of conjugation. For further comparison (Table 3, Figure 5), the ethyne-bridged fec-yne-coc⁺ [131276-91-0] (ΔE_T 31.1 kJ mol⁻¹; 2600 cm⁻¹) and the new ruc-yne-coc⁺ (**5**) (the largest ΔE_T of 34.8 kJ mol⁻¹; 2910 cm⁻¹) cations were measured in five representative solvents and displayed comparable solvatochromic behavior. Finally, the directly linked bimetallocenes fec-coc⁺ [115565-23-6] (ΔE_T 19.0 kJ mol⁻¹; 1590 cm⁻¹) and ruc-coc⁺ [130638-52-7] (ΔE_T 7.4 kJ mol⁻¹; 620 cm⁻¹), as well as the termetallocenes coc⁺-osc-coc⁺ [130638-59-4] (ΔE_T 15.5 kJ mol⁻¹; 1300 cm⁻¹), coc⁺-fec-coc⁺ [115565-25-8] (ΔE_T 17.3 kJ mol⁻¹; 1450 cm⁻¹), coc⁺-ruc-coc⁺ [130638-54-9] (ΔE_T 10.9 kJ mol⁻¹; 910 cm⁻¹), and fec-coc⁺-fec [127601-75-6] (ΔE_T 19.2 kJ mol⁻¹; 1600 cm⁻¹), were found to exhibit essentially the same type of solvatochromism. It is interesting that the ethyne-bridged compounds showed a markedly wider range of transition energies than the ethene-bridged analogues, and it is also noteworthy that the directly linked bimetallocenes (especially ruc-coc⁺) displayed a narrower range. The pertinent spectra are shown in Figure 6, and the λ_{\max} data are collected in Table 4.

Solvatochromism in binary solvent mixtures is a useful tool to get insight into the sphere of solvation. When the solute interacts to a different degree with the components of the mixture, this is reflected in the composition of the microsphere of solvation. This phe-

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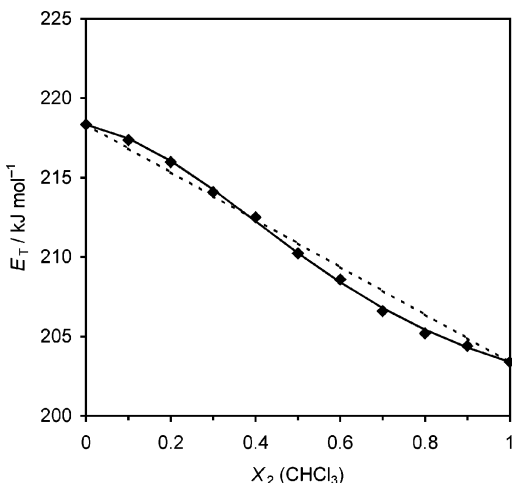


Figure 7. Preferential solvation of [fec-ene-coc][PF₆] (**2a**) in CH₃CN/CHCl₃. The solid line was calculated using eq 6; the dashed line indicates ideal behavior.

nomenon, termed preferential solvation,⁵⁴ denotes the deviation from ideal behavior, i.e., when the observed transition energies vary nonlinearly with the bulk composition (mole fractions X_1 and X_2) of binary mixtures. Moreover, due to strong solvent–solvent interactions, the formation of a solvent structure with properties different from any of the two pure solvents can occur (as experienced by the solute). Assuming that the two solvents (S_1 and S_2) interact in the ratio of 1:1 to form a solvent–cosolvent complex (S_{12}), the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ are defined in eqs 4 and 5.

$$f_{2/1} = \frac{x_2 X_1^2}{x_1 X_2^2} \quad (4)$$

$$f_{12/1} = \frac{x_{12} X_1}{x_1 X_2} \quad (5)$$

Since E_T is sensitive to the proportions of solvents in the solvation microsphere (mole fractions x_1, x_2, x_{12}), but not to their proportions in the bulk solvent, it may be further assumed that the “mixed” solvent S_{12} is formed in the microsphere of solvation of the solute. The resulting eq 6 was found to give excellent fits to the solvatochromic data.⁵⁴

$$E_{T,obs} = E_{T1} + \frac{f_{2/1}(E_{T2} - E_{T1})X_2^2 + f_{12/1}(E_{T12} - E_{T1})X_1X_2}{X_1^2 + f_{2/1}X_2^2 + f_{12/1}X_1X_2} \quad (6)$$

In this model, three parameters (E_{T12} , $f_{2/1}$, $f_{12/1}$) are iterated to fit the calculated with the experimental data by a least-squares method. Here, two mixtures were studied in detail. First, a mixture of typical non-hydroxylic HBA and HBD solvents was used, one of them halogenated; second, a mixture of two solvents was selected in which the solute displays extremely different E_T values, but which are still miscible. The curves obtained are shown in Figures 7 and 8. Thus, in CH₃-

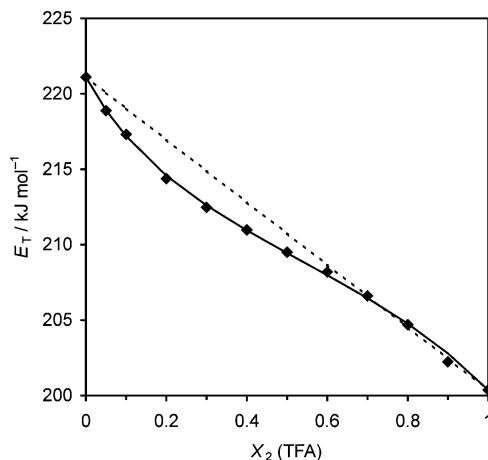


Figure 8. Preferential solvation of [fec-ene-coc][Cl] (**2b**) in H₂O/TFA. The solid line was calculated using eq 6; the dashed line indicates ideal behavior.

CN/CHCl₃ mixtures, fec-ene-coc⁺ displayed a dual behavior, as indicated by the s-shape of the curve, with positive E_T deviations at low CHCl₃ concentrations and negative deviations at high CHCl₃ concentrations. However, these deviations are rather small. The parameters E_{T12} , $f_{2/1}$, and $f_{12/1}$ were determined as 215 nm, 2.18, and 1.56, respectively. In contrast, fec-ene-coc⁺ was preferentially solvated by TFA at low TFA concentrations in H₂O/TFA mixtures, whereas at higher TFA concentrations the behavior became nearly ideal. E_{T12} , $f_{2/1}$, and $f_{12/1}$ were found to be 210 nm, 1.63, and 4.58, respectively. In this case, a marked deviation from ideality was observed, and the intersolvent complex was clearly preferred in the solvation sphere. Wavelengths of the absorption maxima and E_T values in these binary mixtures are deposited as electronic Supporting Information (Table S1).

In summary, these heteronuclear bi- and termetalocenes possess quite irregular but matching solvatochromic properties, and all display negative solvatochromism when a wide range of solvents is considered. Although (or because) these compounds are irregular indicators of solvent polarity, they pose a challenge to established polarity scales, either representing unusual solutes or possibly requiring yet undescribed models of solvation or different kinds of solvation. Anyway, a study of these solvatochromic properties has long been overdue, and the results reported here are fascinating.

Experimental Section

General Comments. Chemicals were purchased from Fluka (Switzerland). Infrared spectra were measured with a Nicolet 510 FT-IR instrument and a Nicolet 5700 FT-IR with an ATR diamond window, and NMR spectra were recorded on a Bruker AC 200 spectrometer using Me₄Si as internal reference (NOE measurements were made on a Varian Gemini 200). UV–vis spectra were recorded at 25 °C on a Shimadzu UV-160A spectrophotometer equipped with a peak detection algorithm, which was calibrated using a solution of holmium perchlorate; all measurements were taken at least in triplicate and averaged. The standard deviation of these measurements was estimated to be ±1.4 nm. Diffraction intensity data were collected on a Siemens P4 instrument via ω -scans (absorption correction by ψ -scans) or a Kappa CCD diffractometer via ϕ - and ω -scans. Cyclic voltammetry experiments were carried out with a Voltalab potentiostat PGZ 301 system using a gold disk

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working electrode (0.03 cm²), a glassy carbon auxiliary electrode, and an Ag/Ag⁺(0.1 M) reference electrode at 30 °C; the scan rate was 50 mV s⁻¹; the solution of the metalloco was approximately 0.5 mM in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. EI mass spectra were measured with a Varian CH7, and HR-FAB mass spectra (Cs gun, 3-nitrobenzyl alcohol matrix) with a Varian MAT 95 spectrometer. Elemental composition was analyzed using a JEOL JXA 8100 electron microprobe. Crystallographic data for this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 267636 (for **1**) and 267637 (for **2a**).

Synthesis of (η^5 -Cyclopentadienyl)-[(η^4 -*exo*-5-(1,3-dithian-2-yl)-1,3-cyclopentadienyl]cobalt(I). To a cooled (-20 °C) solution of 1,3-dithiane (425 mg, 3.53 mmol) in anhydrous THF was added BuLi (2.5 M in hexane, 1.35 mL, 3.37 mmol), and the solution was stirred at -20 °C for 4 h. Cobaltocenium hexafluorophosphate (1.075 g, 3.22 mmol) was added, and the suspension was ultrasonicated for 30 min and stirred overnight at room temperature. After evaporation of the solvent, the residue was continuously extracted with 100 mL of hexane under Ar in a Soxhlet apparatus. The extract was taken to dryness, redissolved in CH₂Cl₂, and filtered through neutral alumina. Evaporation of the solvent yielded the dithiane **1** (668 mg, 67%) as a red solid. IR (KBr, cm⁻¹): ν 3054 (w); 2963 (w); 1423 (m); 1412 (m); 1250 (w); 1261 (s); 1177 (m); 1105 (vs); 1013 (vs); 796 (vs). ¹H NMR (CDCl₃): δ 5.15 (s, 4H, subst. Cp); 4.72 (s, 5H, Cp); 3.76 (s, 1H, *endo*-H); 2.87–2.02 (m, 7H, dithiane). ¹³C NMR (CDCl₃): δ 83.8; 79.0; 74.3; 54.4; 41.1; 29.2; 26.0. Anal. Calcd for C₁₄H₁₇CoS₂: C, 54.53; H, 5.56. Found: C, 54.52; H, 5.57.

Synthesis of (*E*)-2-Ferrocenylethenylcobaltocenium Hexafluorophosphate. A round-bottomed flask flooded with dry nitrogen was charged with methylcobaltocenium hexafluorophosphate (213 mg, 612 μ mol), ferrocenecarbaldehyde (164 mg, 767 μ mol), piperidine (0.30 mL, 3.0 mmol), 1 mL of dimethylformamide, and 15 mL of toluene. The flask was attached to a Dean–Stark trap and heated to reflux for 48 h, protected from light. After allowing the reddish-violet reaction mixture to cool to room temperature, the precipitated product was collected and treated with ether (4 \times 10 mL) in order to remove residual ferrocenecarbaldehyde. Then, the product was dissolved in CH₂Cl₂ (100 mL, bright green solution), extracted with H₂O (2 \times 65 mL) to remove residual methylcobaltocenium hexafluorophosphate, and dried with anhydrous sodium sulfate. After evaporation to dryness, the residue was treated with ether (10 mL) and dried in vacuo, yielding pure [fec-ene-coc]-[PF₆] (**2a**) (185 mg, 56%) as a purple powder. IR (KBr, cm⁻¹): ν 3118 (m); 2962 (w); 2922 (w); 2853 (w); 1633 (s); 1488 (m); 1452 (m); 1416 (m); 1306 (w); 1250 (w); 1195 (w); 1108 (w); 1030 (w); 1101 (w); 970 (w); 930 (w); 876 (m); 856 (s); 830 (vs); 557 (s); 485 (w); 464 (w); 438 (w). UV–vis (CH₂Cl₂, nm) λ_{\max} 262 (log ϵ 4.42); 307 (4.15); 389 (3.87); 595 (3.60). ¹H NMR (DMSO-*d*₆): δ 7.23 (d, 1H, *J* = 16 Hz, fec-CH=CH-coc); 6.46 (d, 1H, *J* = 16 Hz, fec-CH=CH-coc); 6.09 (m, 2H, C2 + C5 coc); 5.83 (m, 2H, C3 + C4 coc); 5.66 (s, 5H, C₅H₅ coc); 4.57 (m, 2H, C2 + C5 fec); 4.45 (m, 2H, C3 + C4 fec); 4.19 (s, 5H, C₅H₅ fec). ¹H NMR (CD₂Cl₂): δ 7.16 (d, 1H, *J* = 16 Hz); 6.33 (d, 1H, *J* = 16 Hz); 5.83 (t, 2H, *J* = 2 Hz); 5.67 (t, 2H, *J* = 2 Hz); 5.51 (s, 5H); 4.55 (t, 2H, *J* = 2 Hz); 4.46 (t, 2H, *J* = 2 Hz); 4.16 (s, 5H). ¹³C NMR (DMSO-*d*₆): δ 136.9; 114.5; 104.6; 85.2; 83.8; 81.1; 79.7; 70.3; 69.4; 67.6. HR-FAB-MS: calcd for C₂₂H₂₀CoFe 399.0241, found 399.02351 (M⁺ of cation). Anal. Calcd for C₂₂H₂₀CoF₆FeP: C, 48.56; H, 3.70. Found: C, 48.62; H, 3.71.

Synthesis of (*E*)-2-Ferrocenylethenylcobaltocenium Chloride. A 50 mg portion of [fec-ene-coc][PF₆] (92 μ mol) was dissolved in 5 mL of MeOH and added to a suspension of 10 g of Amberlite IRA-410 (chloride form) in 10 mL of H₂O. After agitating the mixture in a shaker for 4 h at room temperature, the ion-exchange resin was removed by filtration, and the

filtrate was evaporated to dryness under reduced pressure. To remove traces of residual hexafluorophosphate, the solid residue was again dissolved in 50 mL of H₂O and extracted with CH₂Cl₂ (3 \times 10 mL). Evaporation of the aqueous phase yielded pure [fec-ene-coc][Cl] (**2b**) as a hydrate (18 mg; 44%). IR (neat, cm⁻¹): ν 3441 (w), 3365 (w), 3099 (w); 3065 (w); 3042 (w); 1625 (s); 1489 (w); 1450 (m); 1421 (w); 1413 (w). The chloride was very hygroscopic. Electron microprobe analysis: Fe:Co:Cl = 1:1:1.

Synthesis of (*E,E*)-1,1'-Bis(2-ferrocenylethenyl)cobaltocenium Hexafluorophosphate. 1,1'-Dimethylcobaltocenium hexafluorophosphate (100 mg, 276 μ mol) and ferrocenecarbaldehyde (178 mg, 832 μ mol; 3 equiv) were suspended in 12 mL of toluene, and 1.0 mL of dimethylformamide and piperidine (0.30 mL, 3.0 mmol) were added. The mixture was protected from light and refluxed for 48 h using a Dean–Stark trap. On cooling to room temperature, a dark precipitate was formed. After filtration and subsequent washings with 5 mL of ether and 5 mL of hexane, the solid was dissolved in 50 mL of CH₂Cl₂ and extracted with 50 mL of H₂O. The organic layer was dried (Na₂SO₄) and evaporated to dryness. Drying under vacuum yielded pure [(fec-ene)₂coc][PF₆] (**3**) (110 mg, 53%) as a dark blue powder, mp 122 °C (dec). IR (KBr, cm⁻¹): ν 3107 (w); 1626 (s); 1493 (m); 1454 (m); 1303 (w); 1252 (w); 1106 (m); 1048 (m); 1024 (m); 959 (m); 856 (s); 831 (vs); 736 (m); 556 (m). UV–vis (CH₂Cl₂, nm): λ_{\max} 257 (log ϵ 4.40); 303 (4.09); 356 sh (3.92); 608 (3.56). ¹H NMR (DMSO-*d*₆): δ 7.10 (d, 2H, *J* = 16 Hz, coc-CH=); 6.30 (d, 2H, *J* = 16 Hz, fec-CH=); 5.86 (m, 2H, C2 + C5 coc); 5.65 (m, 2H, C3 + C4 coc); 4.46 (m, 2H, C2 + C5 fec); 4.41 (m, 2H, C3 + C4 fec); 4.16 (s, 10H, Cp fec). ¹³C NMR (DMSO-*d*₆): δ 136.9 (coc-CH=); 114.1 (fec-CH=); 103.9; 84.3; 81.2; 80.2; 70.1 (Cp fec); 69.3; 67.6. HR-FAB-MS: calcd for C₃₄H₃₀CoFe₂ 609.0373, found 609.0376 (M⁺ of cation). Anal. Calcd for C₃₄H₃₀CoF₆Fe₂P: C, 54.15; H, 4.01. Found: C, 54.13; H, 4.01. The chloride was prepared by ion exchange as described above for **2b**. IR (neat, cm⁻¹): ν 3384 (m); 3095 (m); 2960 (w); 2927 (w); 1627 (m); 1452 (w); 1105 (w); 815 (w).

Synthesis of (*E*)-2-Ruthenocenylethenylcobaltocenium Hexafluorophosphate. This compound was prepared from methylcobaltocenium hexafluorophosphate (106 mg, 305 μ mol) and ruthenocenecarbaldehyde (97 mg, 367 μ mol) in a procedure analogous to that described for **2a** to yield compound **4** (137 mg, 76%) as an orange-red powder. IR (neat, cm⁻¹): ν 3116 (m); 1635 (s); 1488 (m); 1452 (m); 1404 (w); 1103 (m); 1036 (m); 971 (m); 831 (vs); 557 (m). UV–vis (CH₂Cl₂, nm) λ_{\max} 262 (log ϵ 4.10); 391 (3.65); 483 (3.86). ¹H NMR (CD₃CN): δ 7.02 (d, 1H, *J* = 16 Hz); 6.35 (d, 1H, *J* = 16 Hz); 5.78 (m, 2H); 5.61 (m, 2H); 5.47 (s, 5H); 4.91 (m, 2H); 4.72 (m, 2H); 4.55 (s, 5H). ¹³C NMR (CD₃CN): δ 136.9; 114.3; 105.9; 86.0; 84.7; 80.4; 72.6; 72.3; 70.4. HR-FAB-MS: calcd for C₂₂H₂₀CoRu 444.9935, found 444.9928 (M⁺ of cation). Anal. Calcd for C₂₂H₂₀CoF₆PRu: C, 44.83; H, 3.42. Found: C, 44.88; H, 3.43. The chloride was prepared by ion exchange as described above. IR (neat, cm⁻¹): ν 3367 (m); 3097 (m); 2951 (w); 2929 (w); 1633 (m); 1452 (w); 1417 (w); 1198 (w); 1101 (w); 1039 (w); 863 (w).

Synthesis of 2-Ruthenocenylethynylcobaltocenium Hexafluorophosphate. [Ruc-yne-coc][PF₆] was prepared according to the analogous procedure for fec-yne-coc⁺,²⁰ starting from ethynylruthenocene, with the exception that the *endo*-hydride intermediate was not isolated. Crude yield: 50 mg, 42% of theory. To obtain an analytically pure sample suitable for UV–vis spectroscopy, the crude [ruc-yne-coc][PF₆] was subjected to anion exchange with Amberlite IRA-4110 resin (Fluka 06433). [Ruc-yne-coc][PF₆] (24 mg) was dissolved in 1 mL of MeOH and added to a suspension of 3 g of dry resin, preswollen and filtered, suspended in 20 mL of H₂O. After shaking the mixture for 15 min, and subsequent ultrasonication for 5 min, the resulting yellow aqueous phase was filtered through a glass sintered frit (G3), and the resin was rinsed with an additional 5 mL of H₂O and filtered through a paper filter. The resulting aqueous solution was extracted two times

with 10 mL of dichloromethane and afterward with 20 mL of diethyl ether. A 15 mL aliquot of the extracted solution was evaporated to dryness (main portion of solvent on a rotary evaporator, 40 °C, then oil pump vacuum line) to yield a dry layer of orange-red product. This was triturated with 10 mL of diethyl ether in an ultrasonication bath to yield a suspension of hydrated [ruc-yne-coc][Cl]. Evaporation of the diethyl ether yielded a free-flowing powder, readily soluble in water and methanol (15 mg). Spectroscopically pure [ruc-yne-coc][PF₆] was obtained by reprecipitation of the chloride from water with an excess of NH₄PF₆ and extracting back the aqueous suspension into CH₂Cl₂, which after drying with sodium sulfate and evaporation gave a sticky residue of the desired hexafluorophosphate salt. Ultrasonication in diethyl ether, decantation, and evaporation gave the product as a red-orange powder in 90% yield. IR (neat, cm⁻¹): ν 3106 (w); 2961 (m); 2924 (m); 2854 (w); 2363 (m); 2342 (m); 1268 (w); 1101 (m); 1027 (m); 833 (m). UV-vis (CH₂Cl₂, nm): λ_{max} 265 (log ϵ 4.77); 367 (3.98); 458 (3.93). ¹H NMR (CDCl₃): δ 5.82; 5.70; 4.94; 4.68; 4.63.

Anal. Calcd for C₂₂H₁₈CoF₆PRu: C, 44.99; H, 3.09. Found: C, 45.01; H, 3.10. The chloride was prepared by ion exchange as a hydrate as described above. IR (neat, cm⁻¹): ν 3327 (w); 2362 (m); 2343 (m); 1647 (w); 1621 (w); 1542 (w); 1101 (w).

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Supporting Information Available: Crystallographic information files (CIF) for **1** and **2a**, visible electron absorption maxima for **2a,b** in binary mixtures. Plots of calculated vs experimental transition energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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