# Bimetallic Sesquifulvalene Complexes—Compounds with Unusually Large Hyperpolarizability $\beta$**

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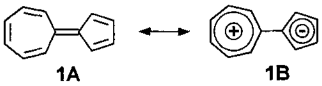
*Dedicated to Prof. Dr. H. Schumann on the occasion of his 60th birthday*

**Abstract**: In order to construct *bimetallic* organometallic donor–acceptor complexes with nonlinear optical (NLO) properties, the bimetallic sesquifulvalene complexes $[\{CpFe(\eta^5\text{-}C_5H_4)\}Z\{\eta^7\text{-}C_7H_6)Cr(CO)_3\}]BF_4$ ($\mathbf{2}BF_4$) have been synthesized with different bridging functions Z (**2a**: Z = –; **2b**: Z = $C_2$; **2c**: Z = $(E)$-$C_2H_2$). X-ray structure determinations show that $\mathbf{2a}BF_4$ and $\mathbf{2c}BF_4$ crystallize in acentric space groups ($P4_1$, $P2_12_12_1$), whereas crystalline $\mathbf{2b}BF_4$ has the centric space group $P2_1/c$. The organometallic fragments in **2a** adopt a *transoid* conformation, those in **2b** and **2c** are *cisoid*. The *cyclo*-$C_5$ and *cyclo*-$C_7$ rings of the sesquifulvalene ligands are almost coplanar; this allows an optimum electronic interaction between the ferrocenyl donor and the $[(\eta^7\text{-}C_7H_6)Cr(CO)_3]^+$ acceptor moiety in the crystalline state. Cyclovoltammetric studies show an electrochemically reversible one-electron oxidation (>0 mV vs. FeH/FcH$^+$, FcH = ferrocene) and an irreversible one-electron reduction ($\leq -900$ mV), which are assigned to the ferrocenyl and $[(\eta^7\text{-}C_7H_6)Cr(CO)_3]^+$ units, respectively. UV/vis spectra reveal low-energy absorptions for **2a–c** at about $\lambda = 600$ nm, showing strong negative solvatochromism. These absorption maxima are related to a charge-transfer excitation between the ferrocenyl and the $[(\eta^7\text{-}C_7H_6)Cr(CO)_3]^+$ groups, indicating considerable nonlinear optical properties. Determination of the first hyperpolarizability $\beta$ by means of hyper Rayleigh scattering yields exceptionally large $\beta$ values: $\beta(\mathbf{2b}) = 570 \times 10^{-30}$ esu and $\beta(\mathbf{2c}) = 320 \times 10^{-30}$ esu. These unexpectedly large $\beta$ values are explained by resonance enhancement.

**Keywords**
bimetallic complexes · NLO materials · sandwich complexes · sesquifulvalenes · solvatochromism

## Introduction

Currently, the most important class of nonlinear optical (NLO) compounds, which show large hyperpolarizabilities and are therefore able, for example, to double the frequency of a laser beam, has the following typical structure: an electron donor **D** is electronically coupled to an electron acceptor **A** by a π bridge.[1–5] Compounds of this type undergo a change in polarity caused by interaction with a strong electric field, which leads, in particular, to large values of the first hyperpolarizability $\beta$ when the change in polarity is coupled with a charge transfer (CT) between the donor and acceptor. Often, such CT states can be represented by a polar resonance structure.[5] This also holds for sesquifulvalene (**1**): although it can be described in terms of two resonance structures of different polarities (Scheme 1), sesquifulvalene behaves like a polyene with alternating bond lengths,[6] and its ground state is thus best described by the apolar resonance structure **1A**. On excitation, charge separation occurs, and the resulting structure is likely to be related to the polar resonance form **1B**.


**1A** **1B**

Scheme 1. Resonance structures of sesquifulvalene.

Calculations of the first hyperpolarizability $\beta$[7, 8] of **1** confirm a change in the dipole moment on excitation, but the high reactivity of **1**[9] prevents the experimental determination of its NLO properties. The objective of this work was to stabilize the aromatic units in **1B** by complexation, for example, as ferrocene and ($\eta^7$-cycloheptatrienylium)tricarbonylchromium units (**2**, Scheme 2), and to introduce various bridging functions Z into the bimetallic sesquifulvalene complexes,[10] in order to modulate the interaction between the donor and acceptor. In addition

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[**] Cooperative effect in π ligand bridged dinuclear complexes, Part 16. Part 15: U. Behrens, J. Heck, M. Maters, G. Frenzen, A. Roelofsen, H. T. Sommerdijk, *J. Organomet. Chem.* **1994**, *475*, 233.

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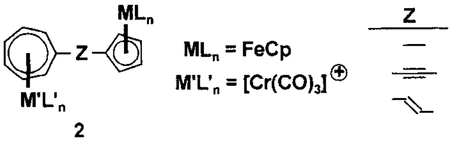
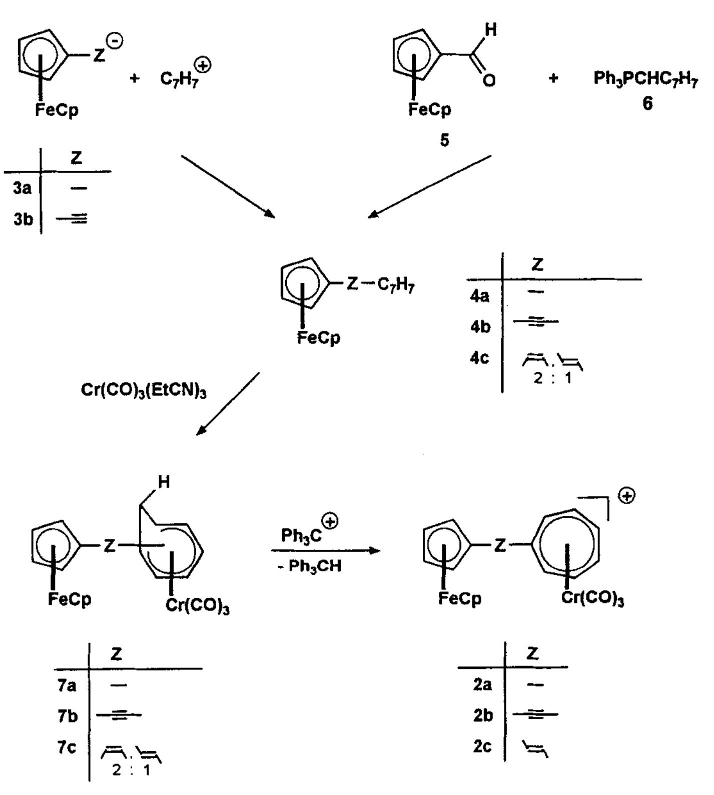


Scheme 2. Bimetallic sesquifulvalene complexes.

to the stabilizing effect of the complexation, we hoped to induce an additional contribution to the first hyperpolarizability $\beta$, due to metal–ligand and ligand–metal charge transfer in the sandwich subunits of the complex.[1]

## Results and Discussion

**Preparation**: Complexes **4a** and **4b**, containing direct (Z = –) and acetylenic links (Z = -C≡C-), respectively, between the subunits, were synthesized by nucleophilic addition of the monolithiated ferrocenyl derivates **3a** or **3b**[11, 12] to the tropylium cation (Scheme 3). The vinylogous product **4c** was obtained by a Wittig reaction between formylferrocene (**5**)[13] and 1,3,5-cycloheptatriene-3-ylmethylidene-$\lambda^5$-phosphane (**6**).[14, 15]



Scheme 3.

The ensuing $Cr(CO)_3$ addition proceeded stereoselectively at the *endo* position with respect to the ferrocenyl moiety.[16] Hence, **7a–c** possess a hydrogen atom at the *exo* position of the coordinated $C_7$ ring, which is essential for successful hydride abstraction to form the desired products **2a–c**. Although a 2:1 mixture of (*Z*)-**7c** to (*E*)-**7c** was used to prepare **2c**, only the (*E*) isomer of **2c** was obtained, in more than 80% yield. Crystals of **2a–c** are stable in air and black to dark green in color. The solutions of **2a–c** in polar solvents are a deep greenish blue.

**X-ray structure analyses:** The X-ray structure analyses of **2a–c** reveal almost coplanar *cyclo*-$C_5$ and *cyclo*-$C_7$ units in the sesquifulvalene ligands (Fig. 1). The maximum deviation from the coplanarity is 16.5(2)°, observed for **2c**. Here, the *cyclo*-$C_5$ and *cyclo*-$C_7$ ligands are twisted out of the ethenediyl plane (C8-C13-C14-C7) by 11.5(4) and 5.2(4)°, respectively. Thus, in the solid state, electronic coupling is greatly facilitated between the donor and the acceptor, even for **2c**. The elongated complexes **2b** and **2c** crystallize in the *cisoid* conformation, whilst the metal–ligand moieties of **2a** are disposed *trans* to one another, possibly for steric reasons. Within experimental error, all the corresponding C–C and C–metal distances in the ferrocene and tricarbonylchromium complex fragments in **2a–c** are identical and as expected. The bond lengths in the π bridge between the *cyclo*-$C_5$ and the *cyclo*-$C_7$ units do not show any anomaly that would suggest a substantial interaction between the two organometallic fragments in the ground state.[17] However, it is worth mentioning that a significant increase in the Cr–C7 bond

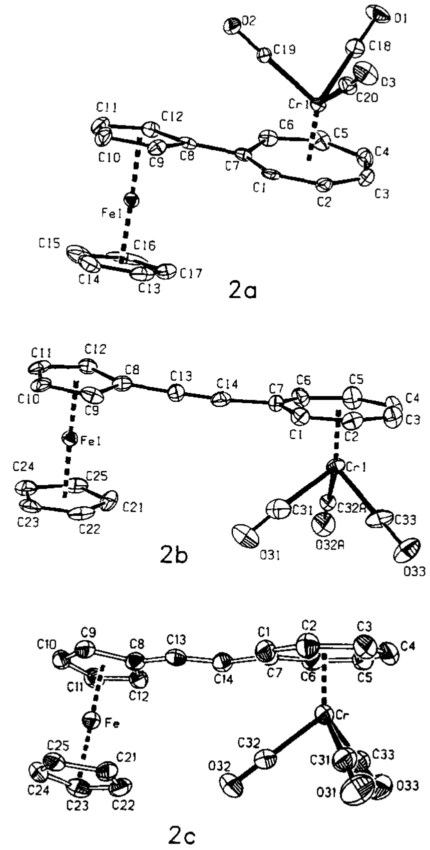


Fig. 1. Molecular structures of **2a–c**. For **2c** the crystal structure depicted was obtained from a crystal grown in $CH_2Cl_2$ (see Experimental Section). The thermal ellipsoids are at the 50% probability level. The hydrogen atoms, counter ions ($BF_4^-$) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] between the *cyclo*-$C_5$ plane and *cyclo*-$C_7$ plane of the sesquifulvalene ligand: **2a**: Cr1–C1 2.241(7), Cr1–C2 2.214(7), Cr1–C3 2.224(9), Cr1–C4 2.228(7), Cr1–C5 2.217(9), Cr1–C6 2.228(8), Cr1–C7 2.320(6), C7–C8 1.451(10), ∢(C1–7)(C8–12) 10.0(4); **2b**: Cr1–C1 2.223(11), Cr1–C2 2.212(10), Cr1–C3 2.209(11), Cr1–C4 2.210(12), Cr1–C5 2.220(11), Cr1–C6 2.237(10), Cr1–C7 2.284(11), C7–C14 1.447(15), C8–C13 1.427(15), ∢(C1–7)(C8–12) 8.3(5); **2c** (obtained from $CH_2Cl_2$ solution): Cr1–C1 2.240(5), Cr1–C2 2.244(5), Cr1–C3 2.252(5), Cr1–C4 2.254(5), Cr1–C5 2.223(5), Cr1–C6 2.264(5), Cr1–C7 2.308(5), C7–C14 1.472(6), C8–C13 1.470(6), C13–C14 1.340(6), ∢(C1–7)(C8–12) 16.5(2); **2c** (obtained from $CHCl_3$ solution, without drawing): Cr1–C1 2.254(8), Cr1–C2 2.227(8), Cr1–C3 2.244(8), Cr1–C4 2.243(9), Cr1–C5 2.215(8), Cr1–C6 2.250(8), Cr–C7 2.358(7), C7–C14 1.439(12), C8–C13 1.462(12), C13–C14 1.347(14), ∢(C1–7)(C8–12) 7.2(5).

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length is observed relative to the remaining Cr–C distances in the *cyclo*-$C_7$ part of the bimetallic complex cations **2a–c** (Fig. 1).[18]

**Redox properties**: Cyclovoltammetric investigations reveal that the shape and maxima of the redox waves of **2a–c** (Fig. 2) are very similar to those of the mononuclear complexes, that is, ferrocene and $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ (**8**) (Table 1): the first oxidation for **2a–c** involves an electrochemically reversible one-electron transfer, with the half-wave potential $E_{1/2}$ showing a slight anodic shift relative to that of ferrocene. In contrast, the first reduction step of **2a–c** displays complete electrochemical irreversibility with a peak potential $E_{pc}$ positioned close to that of **8**. An analysis of the reductive wave ($I_p$ = f($v^{1/2}$)) confirmed that a one-electron reduction had taken place.[19,20] It is thus evident that the character of the HOMO in **2a–c** is defined by the ferrocenyl moiety, whereas the character of the LUMO is mainly determined by the (cycloheptatrienylium)tricarbonylchromium unit. These properties of the bimetallic complexes **2a–c** are expected to favor a change in the polarity upon electronic excitation.

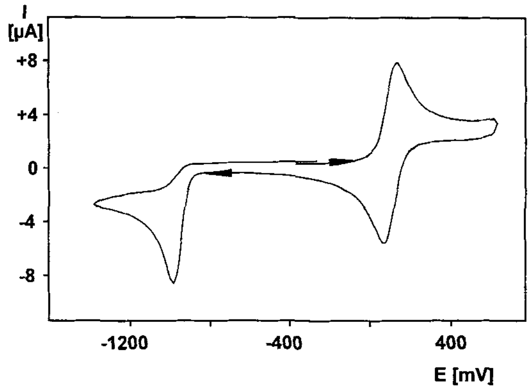


Fig. 2. Representative cyclic voltammogram of the bimetallic sesquifulvalene complexes (here: **2c**, *E* vs. Ag/AgI).

**UV/vis spectra**: The UV/vis spectra of **2a–c** in solution (Fig. 3) confirm our prediction. Pronounced *negative* solvatochromism is observed,[21] in particular for the low-energy absorption about 600 nm (Table 1). This implies a greater polarity for the ground state than for the excited state, or even an inversion of the polarity upon excitation, as depicted by the resonance structures **2A** and **2B** (Scheme 4). The increase of the solvatochromic effect in the order **2a**<**2b**<**2c** corresponds to an increase in the change in dipole moment on photochemical excitation. Solvatochromic absorptions at comparable wavelengths have not been observed for sesquifulvalene,[9] ferrocene,[22] or $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ (**8**).[23] An absorption close to 700 nm has been reported for the structurally characterized cation [(cycloheptatrienylium)ferrocene]$^+$ (**9**).[24] We therefore assign the absorption centered at 600 nm to a charge-transfer excitation between the *cyclo*-$C_5$ and the *cyclo*-$C_7$ complex units, which could be regarded as a transition from the resonance structure **2A** to **2B**. The complex subunits $[(\eta^5$-cyclopentadienyl)-$(\eta^6$-pentafulvene)iron]$^+$[25] and $(\eta^6$-heptafulvene)(tricarbonyl)chromium,[26] which make up the resonance structure **2B**, are stable mononuclear complexes; this indicates that the resonance structure **2B** might indeed have a certain stability.

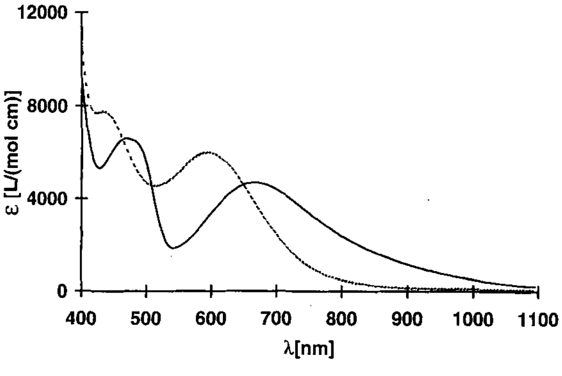
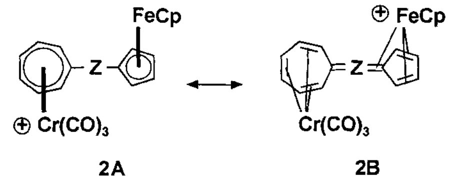


Fig. 3. Representative UV/vis spectra demonstrating the solvatochromic effect in different polar solvents (here **2c**: — $CH_2Cl_2$, ····· acetone).

Table 1. UV/vis and cyclovoltammetric data of the sesquifulvalene complexes **2a**$BF_4$–**2c**$BF_4$ and $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]BF_4$ (**8**) and the first hyperpolarizability *β* of **2b** and **2c**.

| | $\lambda_{max}$/nm [a] $CH_2Cl_2$ | acetone | $\Delta\tilde{\nu}$/cm$^{-1}$ [b] | $E_{1/2}$/V [c] ($\Delta E_p$/mV) | $E_{pc}$/V [c,d] | $\Delta E$/V [e] | $\beta/\times10^{-30}$ esu [f] |
|---|---|---|---|---|---|---|---|
| **2a** | 590 [g] | 570 [g] | 590 | 0.33 (72) | −1.09 | 1.42 | n.o. [h] |
| **2b** | 600 [g] | 560 [g] | 1200 | 0.22 (56) | − 0.90 | 1.12 | 570 |
| **2c** | 670 [i] | 590 [i] | 2000 | 0.11 (64) | − 0.96 | 1.07 | 320 |
| **8** | 420 | | | | −1.06 [j] | | |

[a] Low energy absorption; for further details see Experimental Section. [b] $\tilde{\nu}_{max}(CH_2Cl_2)-\tilde{\nu}_{max}$(acetone). [c] $CH_2Cl_2$ solutions, vs. FcH/FcH$^+$ (FcH = ferrocene). [d] $E_{pc}$ = peak potential of the reduction ($\nu$ = 100 mVs$^{-1}$). [e] $\Delta E = E_{1/2}-E_{pc}$. [f] $CH_2Cl_2$ solution. [g] ca. $10^{-3}$ M. [h] Not observed. [i] ca. $10^{-4}$ M. [j] For more details, see ref. [19,20].



Scheme 4. Resonance structures of the bimetallic sesquifulvalene complexes.

**NLO measurements:** The assumption that the change in dipole moment involves a transition between the two resonance forms **2A** and **2B** can be confirmed, at least for **2b** and **2c**, by investigating the first hyperpolarizability *β* in solution. Owing to the ionic nature of **2a–c**, *β* cannot be determined by means of the traditional EFISH technique (electric field induced second harmonic generation),[1,5] where a strong static electric field is applied to the solution containing the hyperpolarizable compound. Hence, the measurements were carried out using the hyper Rayleigh scattering method,[27a] where a Nd:YAG laser ($\lambda$ = 1064 nm) serves as a light source and the intensity of the frequency-doubled scattered light is measured as a function of the concentration of the NLO chromophore. For **2a** the frequency-doubled light with a wavelength of 532 nm is still in the region of relative strong aborption, and it is therefore impossible to measure the intensity of scattered light. However, the *β* values of **2b** and **2c** by far exceed those measured to date for mono- and bimetallic ferrocene derivates[1,2,28] and are among the highest values ever reported for bimetallic complexes (Table 1); yet larger first hyperpolarizabilities $\beta$ have only been reported for mixed valence hexacoordinated dinuclear Ru complexes.[29]

The unusually large first hyperpolarizability $\beta$ of **2b** and **2c** is attributed to resonance enhancement, which can be explained by means of the two-level model.[30] According to this model, the relationship between the hyperpolarizability $\beta$ and the optical CT excitation is described by Equation (a), where $\mathrm{h}\omega_{\mathrm{CT}}$ = energy of the CT excitation, $\Delta\mu$ = change

$$\begin{aligned}\beta(-2\omega;\omega,\omega) &= \frac{3\,\Delta\mu\,M^2}{(\mathrm{h}\omega_{\mathrm{CT}})^2}\,\frac{\omega_{\mathrm{CT}}^2}{[1-(2\omega)^2(\omega_{\mathrm{CT}}^2)^{-1}][(\omega_{\mathrm{CT}})^2-\omega^2]}\\ &= \beta_{\mathrm{o}}\frac{\omega_{\mathrm{CT}}^2}{[1-(2\omega)^2(\omega_{\mathrm{CT}}^2)^{-1}][(\omega_{\mathrm{CT}})^2-\omega^2]}\end{aligned} \tag{a}$$

of the dipole moment between the ground and excited state, $M$ = electronic transition moment, $\omega$ = frequency of the stimulating laser beam, $\beta_{\mathrm{o}}$ = static hyperpolarizability.

Resonance enhancement becomes important when the frequency of the CT excitation $\omega_{\mathrm{CT}}$ is either close to the frequency $\omega$ of the stimulating laser beam or close to $2\omega$. The latter is the case for **2b** and **2c**. Applying Equation (a) the static hyperpolarizabilty gives $\beta_{\mathrm{o}}(\mathbf{2b}) = 105\times10^{-30}$ esu and $\beta_{\mathrm{o}}(\mathbf{2c}) = 113\times10^{-30}$ esu. These results indicate that the extraordinarily large $\beta$ values for **2b** and **2c** in general and the order $\beta(\mathbf{2b}) > \beta(\mathbf{2c})$ in particular are due to resonance enhancement.

## Conclusion

The concept of using bimetallic organometallic sandwich complexes as NLO chromophores seems to be a very powerful way of developing new materials with unexpectedly high first order hyperpolarizabilities. Our results are not in agreement with other theoretical calculations of the first hyperpolarizability $\beta$, which predict that sandwich compounds do not have a future as efficient NLO chromophores.[2, 31] The present results will encourage us to look for other sesquifulvalene-type bimetallic complexes with enhanced electronic coupling between the donor and acceptor function and increased first hyperpolarizability $\beta$.

## Experimental Section

All manipulations were carried out using standard Schlenk techniques in a dry atmosphere of oxygen-free dinitrogen. The solvents were carefully dried and distilled from the appropriate drying agents prior to use. NMR: Varian Gemini 200BB; measured at 295 K relative to TMS. UV/vis: Perkin-Ellmar Model 554. MS: Finnigan MAT 311A. Elemental analyses: Elementaranalysator CHN-O-Rapid, Fa. Heraeus.

**Ethinylferrocene**: Powdered sodium hydroxide (11 g, 275 mmol) was added to a cooled solution ($T<20$ °C) of (2-formyl-1-chlorovinyl)ferrocene (19 g, 69 mmol) [32] in DMSO (100 mL) and $H_2O$ (5 mL). After being stirred for 30 min, the reaction mixture was diluted with $H_2O$ (500 mL) and extracted with pentane. The pentane extract was evaporated to dryness. Yield: 68–88%.

**(2,4,6-Cycloheptatrien-1-yl)ferrocene (4a)**: Solid $[C_7H_7]BF_4$ (4.40 g, 24.7 mmol) was slowly added to a cooled suspension (− 20 °C) of ferrocenyllithium (LiFc) (4.31 g, 22.4 mmol) [11] in $Et_2O$ (125 mL). After being stirred for 2 h, the reaction mixture was allowed to warm to room temperature, filtered through celite, and evaporated to dryness. Yield: quantitative relative to started LiFc. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.73 (2H, pt, $C_7$ ring), 6.23 (2H, dm, $J$ = 4 Hz, $C_7$ ring), 5.48 (2H, dd, $J$ = 5 Hz, 9 Hz, $C_7$ ring), 4.23 (2H, pt, $C_5H_4$), 4.18 (5H, s, Cp), 4.17 (2H, pt, $C_5H_4$), 2.40 (1H, t, $J$ = 5.4, $C_7$ ring).

**(2,4,6-Cycloheptatrien-1-yl)(ferrocenyl)ethine (4b)**: see ref. [32a].

**(*Z,E*)-1-Ferrocenyl-2-(1,3,5-Cycloheptatrien-3-yl)ethene (4c)**: An equimolar amount of Li*n*Bu (1.6 M in hexane) was added to a cooled suspension (−78 °C) of (1,3,5-cyclo heptatrien-3-yl-methyl)triphenylphosphonium tetrafluoroborate (0.91 g, 2 mmol, **11**) [14, 15] in THF (30 mL). After warming to room temperature, a solution of formylferrocene (0.43 g, 2.0 mmol, **5**) in THF (4 mL) was added. The reaction mixture was stirred for an additional 24 h and evaporated to dryness. The residue was extracted with hexane. Yield: 0.45 g (75%) of a 2:1 mixture of (*Z*):(*E*) isomers. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.50 (3H, m, C*H*=C*H* + $C_7$ ring), 6.43 (1H, d, $J$ = 9.8, $C_7$ ring), 6.22 (1H, dd, $J$ = 9.5, 6.0 Hz, $C_7$ ring), 5.55 (1H, dt, $J$ = 9.8, 7,0 Hz, $C_7$ ring), 5.5 (1H, dt, $J$ = 9.5, 6.7 Hz, $C_7$ ring); 4.40 (2H, m, $C_5H_4$), 4.25 (2H, m, $C_5H_4$), 4.13 (5H, s, Cp), 2.34 (2H, t, $J$ = 6.7 Hz, $C_7$ ring); EI-MS (70 eV): $m/z$ (%) = 302 (100, $M^+$), 237 (43, $M^+$−Cp), 180 (18), 121 (36), 115 (11), 91 (5). Anal (%) calcd for $C_{19}H_{18}Fe$: C 75.52, H 6.00; found C 75.26, H 5.93.

**[{CpFe($\eta^5$-$C_5H_4$)}Z{($\eta^7$-$C_7H_6$)Cr(CO)$_3$}]** (**7a**: Z = –; **7b**: Z = $C_2$; **7c**: Z = (*Z,E*)-$C_2H_2$): In a typical reaction, a mixture of the cycloheptatrienyl compound (5 mmol; **4a**, **4b**, or **4c**) and $Cr(CO)_3(EtCN)_3$ (5 mmol), dissolved in THF (50 mL), was stirred for 20 h. After the solvent was removed in vacuo, the residue was then extracted with hexane, until the hexane extract remained colorless. Quantities used: **4a**, 4.0 g (14.8 mmol); **4b**, 3.16 (10.5 mmol); **4c**, 0.44 g (1.5 mmol).

**7a**: Yield 1.8 g (30%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.96 (2H, m, $C_7$ ring), 4.86 (2H, m, $C_7$ ring), 4.25 (2H, s, $C_5H_4$), 4.17 (2H, s, $C_5H_4$), 4.10 (5H, s, Cp), 3.31 (2H, m, $C_7$ ring), 2.27 (1H, m, $C_7$ ring); IR (THF, KBr): $\tilde{\nu}$ = 1975, 1907, 1885 cm$^{-1}$ ($\tilde{\nu}_{CO}$). Anal (%) calcd for $C_{20}H_{16}O_3CrFe$: C 58.28, H 3,91; found C 58.09, H 4.09;

**7b**: Yield 2.01 g (63%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.01 (2H, m, $C_7$ ring), 4.81 (2H, m, $C_7$ ring), 4.43 (2H, s, $C_5H_4$), 4.23 (5H, s, Cp), 4.19 (2H, s, $C_5H_4$), 3.38 (2H, dd, $C_7$ ring), 2.62 (1H, t, $J$ = 3.0 Hz, $C_7$ ring); IR (THF, KBr): $\tilde{\nu}$ = 1978, 1915, 1889 cm$^{-1}$ ($\tilde{\nu}_{CO}$). Anal (%) calcd for $C_{22}H_{16}O_3CrFe$: C 60.58, H 3.70; found C 59.94, H 4,35.

**7c**: Yield 0.45 g (75%) as a 2:1 (*Z*/*E*) mixture. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.89 (1H, d, $J$ = 15.7 Hz, C*H*=CH), 6.65 (1H, d, $J$ = 15.7 Hz, CH=C*H*), 6.04 (1H, dm, $C_7$ ring), 5.14 (1H, dm, $C_7$ ring), 4.88 (1H, dd, $C_7$ ring), 4.54 (1H, m, $C_5H_4$), 4.42 (1H, m, $C_5H_4$), 4.32 (2H, m, $C_5H_4$), 4.13 (5H, s, Cp), 3.50 (1H, dt, $C_7$ ring), 3.37 (1H, dt, $C_7$ ring), 2.95 (1H, dt, $C_7$ ring), 1.89 (1H, dt, $C_7$ ring); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 129.2 (*C*H=CH), 127.0 (CH=*C*H), 112.9 (ipso-C, $C_7$ ring), 100.0 ($C_7$ ring), 97.9 ($C_7$ ring), 96.4 ($C_7$ ring), 69.5 (Cp), 66.2 ($C_5H_4$), 68.2 ($C_5H_4$), 56.0 ($C_7$ ring), 57.7 ($C_7$ ring), 24.0 ($C_7$ ring); IR (THF, KBr): $\tilde{\nu}$ = 1965, 1894, 1860 cm$^{-1}$ ($\tilde{\nu}_{CO}$); EI-MS (70 eV): $m/z$ (%) = 438 (10, $M^+$), 354 (26, $M^+$−3CO), 302 (100, $M^+$−Cr(CO)$_3$), 237 (38), 180 (22), 121 (29), 115 (8), 91 (5), 65 (6). Anal (%) calcd for $C_{22}H_{18}O_3CrFe$: C 60.30, H 4.14; found C 59.85, H 4.16.

**[{CpFe($\eta^5$-$C_5H_4$)}Z{($\eta^7$-$C_7H_6$)Cr(CO)$_3$}]BF$_4$** (**2a**: Z = –; **2b**: Z = $C_2$; **2c**: Z = (*Z,E*)-$C_2H_2$): A solution of $[Ph_3C]BF_4$ (2 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to a cooled (−78°) solution of **7a**, **7b**, or **7c** (2 mmol). The green reaction mixture was allowed to warm to room temperature and filtered. The product was precipitated from the filtrate by carefully adding $Et_2O$ (20 mL). Quantities used: **7a**, 0.39 g (0.95 mmol); **7b**, 0.85 g (1.95 mmol): **7c**, 0.5 g (1.15 mmol).

**2a**BF$_4$: yield, 0.45 g (95%). $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ = 6.60 (2H, m, $C_7$ ring), 6.33 (2H, dd, $C_7$ ring), 6.21 (2H, d, $C_7$ ring), 4.93 (2H, pt, $C_5H_4$), 4.86 (2H, pt, $C_5H_4$), 4.17 (5H, s, Cp ring); $^{13}$C NMR (50 MHz, $CD_2Cl_2$): $\delta$ = 104.2, 103.1, 98.1 ($C_7$ ring), 75.4 ($C_5H_4$), 72.0 (Cp), 69.7 ($C_5H_4$); IR ($CH_2Cl_2$, KBr): $\tilde{\nu}$ = 2056, 2019 ($\tilde{\nu}_{CO}$), 1056 ($\nu_{B-F}$ in nujol) cm$^{-1}$; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 408 (2600), 443 (sh), 590 (3100) nm ($10^3$ cm$^2$mol$^{-1}$); (acetone): $\lambda_{max}$ ($\varepsilon$) = 400 (1600), 425 (sh), 570 nm ($10^3$ cm$^2$mol$^{-1}$). Anal (%) calcd for $C_{20}H_{15}O_3CrFeBF_4$: C 48.24, H 3.03; found C 47.41, H 3.36.

**2b**BF$_4$: yield, 0.83 g (85%); $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ = 6.68 (2H, m, $C_7$ ring), 6.49 (2H, m, $C_7$ ring). 6.35 (2H, d, $C_7$ ring), 4.64 (2H, pt, $C_5H_4$), 4.46 (2H, pt, $C_5H_4$), 4.26 (5H, s, Cp), 3.70 (1,2-$C_2$*$H_4$*$Cl_2$, recrystallized from 1,2-$C_2H_4Cl_2$); $^{13}$C NMR (50 MHz, [D$_6$]acetone, $\delta$ = 29.9, 206.3, 295 K): $\delta$ = 209.8 (*C*O), 105.5 ($C_7$ ring), 105.4 ($C_7$ ring), 105.3 ($C_7$ ring), 73.3 ($C_5H_4$), 71.1 (Cp), 69.0 ($C_5H_4$); IR ($CH_2Cl_2$, KBr): $\tilde{\nu}$ = 2063, 2026 ($\tilde{\nu}_{CO}$), 2215, 2198, 2170 ($\nu_{C\equiv C}$), 1056 ($\nu_{B-F}$, in nujol) cm$^{-1}$; FAB-MS: $m/z$ (%) = 435 (89, $M^+$), 407 (38, $M^+$−CO), 379 (7, $M^+$−2CO), 367 (24), 351 (83, $M^+$−3CO), 299 (100, $M^+$−Cr(CO)$_3$); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 435 (3100), 600 (3100) nm ($10^3$ cm$^2$mol$^{-1}$); (acetone): $\lambda_{max}$ ($\varepsilon$) = 432 (2800), 560 (2500) nm ($10^3$ cm$^2$mol$^{-1}$). Anal (%) calcd for $C_{22}H_{15}O_3CrFeBF_4 + CH_2Cl_2$: C 45.52, H 2.83; found C 46.08, H 3.06 (the elemental analysis agrees with a formula that incorporates one $CH_2Cl_2$ molecule! This is also supported by the ratio of the intergrals in the $^1$H NMR spectra).

**2c**BF$_4$: yield, 0.39 g (83% with respect to $Ph_3CBF_4$) as pure (*E*) product. $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ = 7.67 (1H, d, $J$ = 15.7 Hz, C*H*=CH), 6.57 (1H, d, $J$ = 15.7 Hz, CH=C*H*), 6.72 (2H, m, $C_7$ ring), 6.35–6.40 (4H, m, $C_7$ ring), 4.82 (2H, pt, $C_5H_4$), 4.73 (2H, pt, $C_5H_4$), 4.35 (5H, s, Cp); $^{13}$C NMR (50 MHz, $CD_2Cl_2$): 211.4 (CO), 145.81 (*C*H=CH), 119.9 (CH=*C*H), 104.80 ($C_7$ ring), 103.1 ($C_7$ ring), 98.6 ($C_7$ ring), 73.9 ($C_5H_4$), 70.3 ($C_5H_4$), 71.5 (Cp). IR (KBr): $\tilde{\nu}$ = 2042, 2007 ($\tilde{\nu}_{CO}$), 1615 ($\tilde{\nu}_{C=C}$), 1056 ($\tilde{\nu}_{B-F}$, in nujol) cm$^{-1}$; FAB-MS: $m/z$ (%) = 437 (100, $M$ +), 409 (44, $M^+$−CO), 372 (16, $M^+$−Cp), 353 (98, $M^+$−3CO), 301 (82, $M^+$−Cr(CO)$_3$); 236 (16), 232 (18); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 385 (11500), 470 (6600), 670 (4700) nm ($10^3$ cm$^2$mol$^{-1}$); (acetone): $\lambda_{max}$ ($\varepsilon$) = 359 (2500), 433 (7700), 594 (6000) nm ($10^3$ cm$^2$mol$^{-1}$). Anal (%) calcd for $C_{22}H_{17}O_3CrFeBF_4$: C 50.43, H 3.27: found C 49.98, H 3.26.

**X-ray structure analysis** (Table 2): Crystals suitable for X-ray structure analyses were obtained by slow diffusion of $Et_2O$ from the gas phase into a $CH_2Cl_2$ solution

Table 2. Crystallographic data of the compounds **2a**$BF_4$, **2b**$BF_4$, **2c**$BF_4$, and **2c**$BF_4(CHCl_3)$

| | **2a**$BF_4$ | **2b**$BF_4$ | **2c**$BF_4$ | **2c**$BF_4(CHCl_3)$ |
|---|---|---|---|---|
| formula | $C_{20}H_{15}CrFeO_3BF_4$ | $C_{22}H_{15}CrFeO_3$-$BF_4$ $(CH_2Cl_2)_2$ | $C_{22}H_{17}CrFeO_3BF_4$ | $C_{22}H_{15}CrFeO_3$-$BF_4$ $(CHCl_3)$ |
| $M_r$ | 497.98 | 691.87 | 524.02 | 643.38 |
| crystal system | tetragonal | monoclinic | triclinic | orthorhombic |
| space group | $P4_1$ | $P2_1/c$ | $P\bar{1}$ | $P2_12_12_1$ |
| $a$/Å | 10.3713(6) | 10.352(2) | 8.056(2) | 8.285(2) |
| $b$/Å | 10.3713(6) | 7.629(2) | 16.264(6) | 28.625(7) |
| $c$/Å | 17.8335(12) | 34.992(13) | 16.259(8) | 10.385(3) |
| $a$/° | – | – | 89.80(4) | – |
| $b$/° | – | 90.61(2) | 89.15(3) | – |
| $\gamma$/° | – | – | 86.01(2) | – |
| $V$/Å$^3$ | 1918.2(2) | 2763.4(14) | 2124.9(14) | 2462.9(10) |
| $Z$ | 4 | 4 | 4 | 4 |
| crystal size/mm$^3$ | $1.0 \times 0.2 \times 0.1$ | $0.05 \times 0.38 \times 0.65$ | $0.1 \times 0.2 \times 0.4$ | $0.5 \times 0.5 \times 0.02$ |
| $T$/K | 150 | 150 | 173 | 173 |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.724 | 1.663 | 1.638 | 1.735 |
| monochromator | graphite | graphite | graphite | graphite |
| abs. coeff./mm$^{-1}$ | 1.38 | 1.36 | 1.25 | 11.9 |
| $F(000)$ | 1000 | 1384 | 1056 | 1288 |
| scan type | $\omega/2\theta$ | $\omega$ | $\omega/2\theta$ | $\omega/2\theta$ |
| $\theta_{min, max}$/° | 2.0–27.5 | 1.2–25.0 | 1.2–25.0 | 2.5–76.0 |
| scan width/° | $0.92 + 0.35 \tan\theta$ | $1.00 + 0.35 \tan\theta$ | $0.80 + 0.35 \tan\theta$ | $1.00 + 0.35 \tan\theta$ |
| index range | $-13 \leq h \leq 0$ | $-13 \leq h \leq 13$ | $0 \leq h \leq 9$ | $-8 \leq h \leq 10$ |
| | $-13 \leq k \leq 13$ | $-9 \leq k \leq 0$ | $-19 \leq k \leq 19$ | $0 \leq k \leq 34$ |
| | $-23 \leq l \leq 0$ | $-45 \leq l \leq 45$ | $-19 \leq l \leq 19$ | $0 \leq l \leq 12$ |
| total reflns | 4994 | 9724 | 8380 | 3938 |
| unique reflns | 2258 | 4818 | 7530 | 3938 |
| obs. reflns $[I > 2\sigma(I)]$ | 1733 | 2668 | 5364 | 3398 |
| parameters | 271 | 342 | 596 | 331 |
| $R1$ | 0.0505 | 0.0996 | 0.0517 | 0.0914 |
| $wR2$ | 0.1219 | 0.2639 | 0.1176 | 0.2395 |
| $w^{-1}$ [a] | $\sigma^2(F_o^2) + (0.0673P)^2$ | $\sigma^2(F_o^2) + (0.1000P)^2$ | $\sigma^2(F_o^2) + (0.0777P)^2$ | $\sigma^2(F_o^2) + (0.2037P)^2$ |
| Flack parameter | + 0.007(41) | – | – | – 0.024(12) |
| $S$ | 0.992 | 1.212 | 1.063 | 1.025 |
| min, max resd/e Å$^{-3}$ | −0.38, 0.75 | −0.73, 1.20 | −0.44, 0.64 | −1.39, 0.91 |

[a] $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

of **2a**$BF_4$–**2c**$BF_4$. For **2c**$BF_4$ an additional crystallization was performed with $CHCl_3$ instead of $CH_2Cl_2$. The data were recorded on four-circle diffractometers (**2a**$BF_4$, **2b**$BF_4$: University of Utrecht, Enraf-Nonius CAD4, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, rotating anode; **2c**$BF_4$, **2c**$BF_4(CHCl_3)$: University of Hamburg, Hilger & Watts, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å and Enraf-Nonius CAD4, $Cu_{K\alpha}$, $\lambda = 1.5418$ Å). The structures of **2a**$BF_4$ and **2b**$BF_4$ were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92) [33]. The structures of **2c**$BF_4$ and **2c**$BF_4(CHCl_3)$ were solved by direct methods (SHELXS-86) [34]. Refinement on $F^2$ was carried out by full-matrix least-square techniques (SHELXL-93) [35]; no observance criterion was applied during refinements. For **2b**$BF_4$ the anion $BF_4^-$ and dichloromethane residues appeared to be disordered but no satisfactory model could be refined. One of the two symmetry-independent cationic sesquifulvalene complexes of **2c**$BF_4$ (crystallized from $CH_2Cl_2$) was disordered. 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 parameter of their carrier atoms. Weights were optimized in the final refinement cycles. Further details of the structure determination (including atomic coordinates, bond lengths and angles, thermal parameters, and thermal motion ellipsoid plots) may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

**Cyclic voltammetry** (CV): For experimental setup see ref. [36]. CV measurements were performed in $CH_2Cl_2$, 0.1 M ($n$Bu$_4$N)$PF_6$ at room temperature: reference electrode $Ag^+/AgI$: working electrode: Pt disk ($d$ = 3 mm); auxiliary electrode: Pt plate (0.6 cm$^2$).

**Hyper Rayleigh scattering**: For experimental setup see ref. [27a]. All measurements were performed at a basic wavelength of $\lambda = 1064$ nm with a the Nd:YAG laser. For all measurements, $CH_2Cl_2$ solutions of **2a–c** were used; p-nitroaniline in $CH_2Cl_2$ was used as reference ($\beta = 21.6 \times 10^{-30}$ esu).

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