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Mono- and dinuclear sesquifulvalene complexes, organometallic materials with large nonlinear optical properties

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Abstract

Currently, the most important class of nonlinear optical (NLO) compounds providing second harmonic generation (SHG) comprises of electron donating and accepting groups which are electronically coupled. These kinds of dipolar compounds have potential in photonic applications. In this article the synthesis and the NLO activities of dipolar mono- and dinuclear sandwich-like complexes are reviewed. These structures are composed of

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sesquifulvalenes and metal–ligand fragments ML_n and $M'L'_n$ which stabilize the aromatic units of the sesquifulvalene moiety. In these complexes the five-membered ring of the sesquifulvalene complexes is coordinated to $ML_n = Fe(C_5H_5)$, $Fe(C_5Me_5)$, $Ru(C_5H_5)$ and $Co(C_4Ar_4)$ and acts as an electron donor; hence, its electron donating capability is varied by changing the ML_n entity. The electron withdrawing capability of the seven-membered ring is changed by the coordination of $Cr(CO)_3$ and $RuCp^+$ or by keeping it uncoordinated. In addition, cationic borabenzene complexes are introduced as electron accepting groups. The electronic communication between the donor and acceptor is facilitated by a direct coupling or by introducing acetylenic and olefinic bridges between the donor and acceptor, e.g. *E*-1,2-ethendiyl, *E*,*E*-1,3-diendiyl, *E*,*E*,*E*,-1,5-triendiyl, 2,5-thiendiyl, 2,5′-dithiendiyl. Structural as well as UV–vis spectroscopic studies indicate a distinct mutual influence of the donor and the acceptor of the sesquifulvalene complexes. The NLO properties of these mono- and dinuclear sandwich-type complexes are studied by means of hyper-Rayleigh scattering experiments. They prove that most of the ferrocenyl derivatives demonstrate fluorescence in the region of the SHG due to two-photon absorption whereas all of the ruthenium congeners show SHG which is quantified by determination of the first hyperpolarizability. The measured β-values are large and their magnitude can be partly explained by resonance enhancement. Taking the two-level model into account the calculated values of the static hyperpolarizability are still very large indicating that mono- and bimetallic sesquifulvalene complexes are powerful NLO-chromophores.

Keywords: NLO materials; Solvatochromism; Electrochemistry; Sesquifulvalenes; Sandwich complexes; Bimetallic complexes

1. Introduction

Materials showing nonlinear optical (NLO) properties have potential application in photonic devices, i.e. for optical data acquisition, storage, transmission and processing. The most prominent NLO features are frequency doubling or even tripling (second and third harmonic generation (SHG and THG)) of incident light, and the linear electro-optical effect (Pockels-effect) which describes the change of the refractive index of matter with the strength of an applied external electric field [1].

The origin of the NLO properties of matter composed of molecules is due to an induced molecular polarization μ_{ind} which can be described by a power series:

$$\mu_{ind} = \alpha E + 1/2!\beta E^2 + 1/3!\gamma E^3 + \ldots \tag{1}$$

where α is the polarizability, and β and γ, the first and second hyperpolarizabilites; α is related to the refractive index, whereas β and γ are a measure of the molecular capability for frequency doubling (SHG) or tripling (THG). Our interest is currently focused on the design of organometallic molecules suitable for SHG characterized by the first hyperpolarizability β. The most important class of compounds capable of frequency doubling are formed by an electron donor(D), an acceptor(A) and a π-bridge providing the electronic communication between the donor and acceptor. Such D-π-A compounds are highly polarizable and experimental studies on this kind of organic and polymer compounds indeed reveal large first hyperpolarizabilities [1,2]. A simplified theoretical approach to calculate the first hyperpolarizability β elucidates the correlation between the molecular electronic properties of compounds and β. This so called two-level-approximation [3,4] takes into account the ground state and one excited state, e.g. the charge-transfer (CT) state, which have different polarities:

$$\beta(-2\omega;\omega,\omega)=\frac{3\Delta\mu_{eg}M^2}{(\hbar\,\omega_{eg})^2}\,\frac{\omega_{eg}^2}{\left(1-\frac{4\omega^2}{\omega_{eg}^2}\right)(\omega_{eg}^2-\omega^2)} \tag{2}$$

where $\Delta\mu_{eg}$ is the change in the dipole moment between the ground and the CT state, M^2 is the electronic transition moment which is directly correlated to the oscillator strength, $\hbar\omega_{eg}$ is the energy of the optical transition between the ground and CT state (in a simplified model the electronic excitation from the HOMO to the LUMO), ω_{eg} is the circular frequency of the optical transition, and ω is the fundamental circular frequency of the incident radiation.

From Eq. (2) it becomes evident that the value for $\beta(-2\omega;\omega;\omega)$ gets very large when the frequency of the stimulating light ω or the frequency of the second harmonic 2ω approaches the frequency ω_{eg} of the electronic transition ($\omega\rightarrow\omega_{eg}$, or $2\omega\rightarrow\omega_{eg}$). Very often this resonance enhancement dominates the first hyperpolarizability and renders difficulties in comparing the intrinsic first hyperpolarizabilities of different compounds. Therefore, given the experimental data $\beta(-2\omega;\omega,\omega)$, ω_{eg} and ω the static (intrinsic) first hyperpolarizability β_0 ($\omega\rightarrow 0$) can be calculated (Eq. (3)) [4], which is independent of the frequency of the incident light.

$$\beta_0=\frac{3\Delta\mu_{eg}M^2}{(\hbar\omega_{eg})^2} \tag{3}$$

Eq. (3) predicts that large, frequency independent first hyperpolarizabilities are obtained for compounds undergoing:

- a low energy CT transition ΔE_{eg}, which can immediately be taken from UV–vis spectra. A small HOMO-LUMO gap will provide low energy shifted CT transitions;
- a large transition moment M^2 which is directly correlated with the oscillator strength which can be calculated from the integral intensity of the CT band (simply spoken, the extinction coefficient ε should be large);
- a large change in dipole moment $\Delta\mu_{eg,}$ which is indicated by a pronounced solvatochromism of the CT transition [5].

Since the dipole moment equals the charge times distance, significant changes of the dipole may be expected from elongated conjugated π-systems terminated by a strong donor and a strong acceptor when the charge is transferred from the donor to the acceptor upon excitation. However, it has to be mentioned explicitly that the two-level model is a rough guide because it only takes into account the ground and one excited state, and it is valid only off-resonance. Nevertheless, the two state model gives valuable clues to molecular design of NLO compounds with the D-π-A motif. In particular, organic chemists were previously successful in synthesizing D-π-A compounds with extremely large first hyperpolarizabilities as shown in Fig. 1.

Whereas the study of organic compounds directed to NLO properties started about 25 years ago with the work of Davydov et al. [7], the introduction of metals into NLO chromophores was first referred by Green et al. in 1987 [8]. These results were the motivation for organometallic and coordination chemists to create new NLO chromophores [9]. That the donating or accepting capability of organometallic moieties or more generally coordination complexes are indeed able to compete with organic groups can be seen in Table 1 showing a selection of historical examples of organometallic NLO chromophores.

The special features of metal coordinated donors or acceptors are the following:

- the low lying excited states, which can give considerable contributions to the first hyperpolarizability;
- the stability of the metal centers in different oxidation states, e.g. ferrocene ⇔ ferrocenium, which enables the switching of the NLO property;
- 3d metals can often easily be substituted with 4d and 5d metals to tune the donating and accepting capability;
- from organometallic and coordination chemistry a rich variation of the ligand sphere is available.

The search for new types of NLO chromophores containing metal centers functioning in a donating and/or accepting role has opened a new dimension of research in organometallic and coordination chemistry [9]. Table 2 represents a

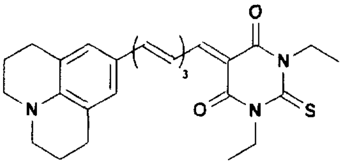
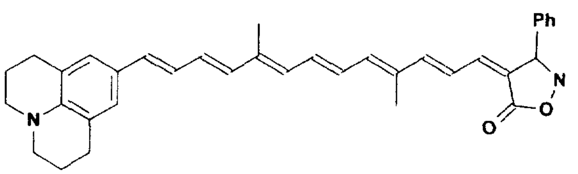
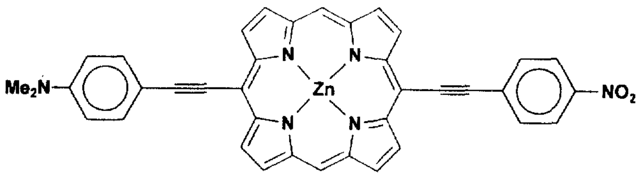
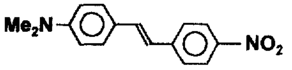
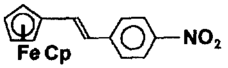
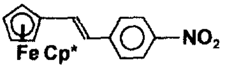
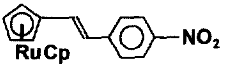
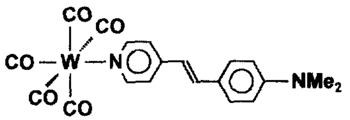
	β	β_0	ref.
	(x 10^{-30} esu)		
	2169	911	6b
	1781	849	6b
	4933	800	6a

Fig. 1. Selected examples of organic D-π-A compounds showing extremely large first hyperpolarizabilities [6].

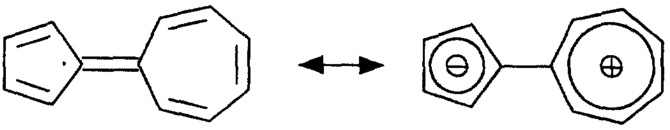
Table 1
Some 'historical' examples of organometallic D-π-A NLO chromophores in comparison to an organic congener

	β (x 10^{-30} esu)	Reference
	73	[10a]
	31	[10b]
	40	[10b]
	12	[10b]
	60	[11a, b]

λ = 1.91 μm

collection of the most frequently used organometallic and coordination compounds as electron releasing and withdrawing moieties in NLO chromophores.

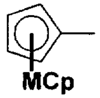
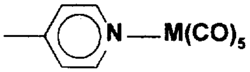
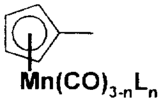
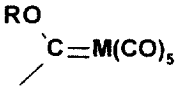
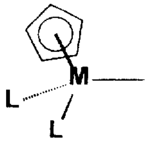
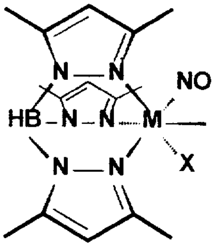
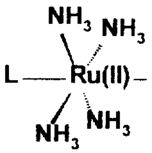
Our approach to organometallic NLO chromophores has been to synthesize sesquifulvalene and related sandwich type complexes, and to investigate their NLO properties. Very often the CT states which are very important for high β values (vide supra), can be represented by a polar resonance structure [1a]. This also holds for sesquifulvalene (**1**): although it can be described in terms of two resonance structures of different polarities (Scheme 1), sequifulvalene behaves like a polyene with alternating bond lengths [18], and its ground state is thus best described by the



1A **1B**

Scheme 1. Resonance structures of sesquifulvalene.

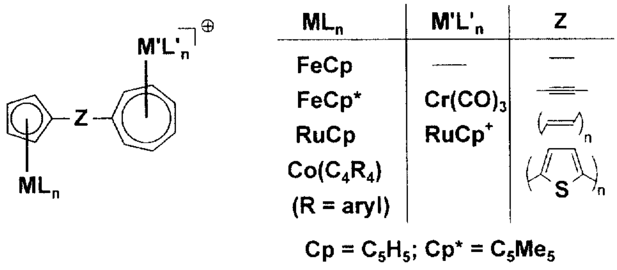
Table 2
Examples of the most frequently used organometallic and coordination compounds in NLO chromophores [2,8,11–17]

Donor	Reference	Acceptor	Reference
	[2, 8]		[11a, b] [13d, 14]
	[12]		[15a, b]
 M = Fe, Ru; L = PR_3	[13]	 M = Mo, W; X = Hal	[17]
	[16]		

nonpolar resonance structure **1A**. Upon excitation charge separation occurs and the resulting structure is likely to be related to the polar resonance form **1B**.

Calculation of the first hyperpolarizability β [19,20] of **1** confirm a change in the dipole moment on excitation, but the high reactivity of **1** [21] prevents the experimental determination of its NLO properties. The objective of our work was to stabilize the aromatic units in **1B** by complexation (Scheme 2), and to introduce various bridging functions Z into the sesquifulvalene complexes in order to modulate the interaction between the donor and the acceptor (**2a**).

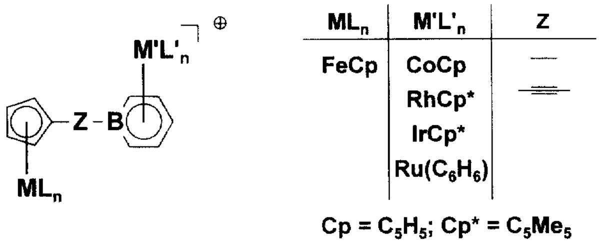
It was proposed that the five-membered ring in **2a** could be stabilized by coordination to (η^5-cyclopentadienyl)iron and -ruthenium and to (η^4-cyclobutadiene)cobalt fragments. The seven-membered ring could be uncoordinated as a free tropylium cation or could be bound to $Cr(CO)_3$ or $RuCp^+$. Therefore, the neutral five-membered ring unit of the sesquifulvalene complexes would act as an electron donor whereas the seven-membered ring moiety remained cationic, and would behave as an electron accepting group. Such a molecular arrangement creates a dipolar structure in the ground state, which could change upon excitation.



ML_n	$M'L'_n$	Z
FeCp	—	—
FeCp*	$Cr(CO)_3$	$\equiv$
RuCp	$RuCp^+$	
$Co(C_4R_4)$ (R = aryl)		

$Cp = C_5H_5$; $Cp^* = C_5Me_5$

2a



ML_n	$M'L'_n$	Z
FeCp	CoCp	—
	RhCp*	$\equiv$
	IrCp*	
	$Ru(C_6H_6)$	

$Cp = C_5H_5$; $Cp^* = C_5Me_5$

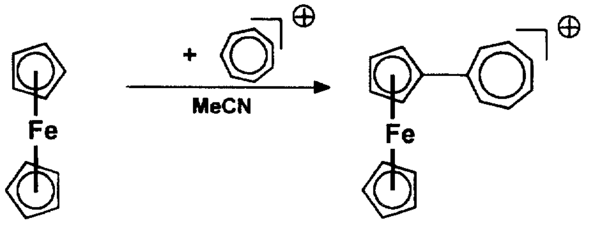
2b

Scheme 2. Mono- and bimetallic sesquifulvalene (**2a**) and borabenzene complexes (**2b**) with D-π-A motif ($M'L'_n$ = — : no further coordination at the seven-membered ring; Z = — : direct linkage of the five- and seven-membered rings).

In addition, attempts were made to employ cationic borabenzene complexes as electron accepting groups which were linked to donating ferrocenyl units via the boron atom (**2b**).

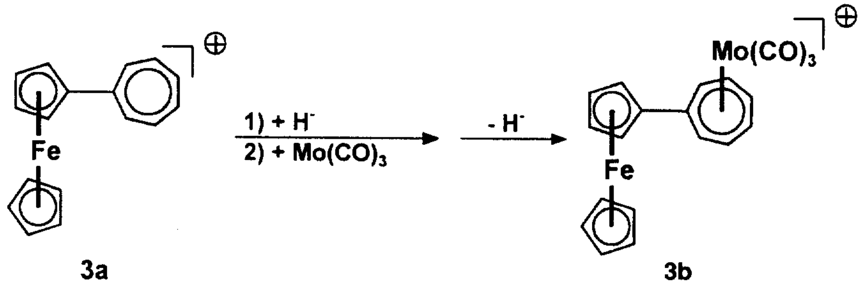
2. Results

When we started our work on dipolar mono- and dinuclear sesquifulvalene complexes only a brief note on two derivatives had been published:



3a

Scheme 3. Formation of the monometallic sesquifulvalene complex **3a** according to Ref. [22].



Scheme 4. Formation of the heterobimetallic FeMo sesquifulvalene complex **3b** according to Ref. [22].

$ML_n = FeCp$; $M'L'_n = -$ (**3a**) and $M'L'_n = Mo(CO)_3$ (**3b**) [22]

The synthetic route towards **3a** and **3b** was via the electrophilic substitution of ferrocene by the tropylium cation (Scheme 3).

Subsequent hydride and $Mo(CO)_3$ addition and finally hydride abstraction yielded **3b** (Scheme 4)

Our experience with the electrophilic substitution reaction was a low yield of **3a** containing paramagnetic impurities which were difficult to remove. Therefore, we prefered the nucleophilic addition of monolithiated ferrocene [23] to the tropylium cation yielding the neutral complex **4a** (Scheme 5, a).

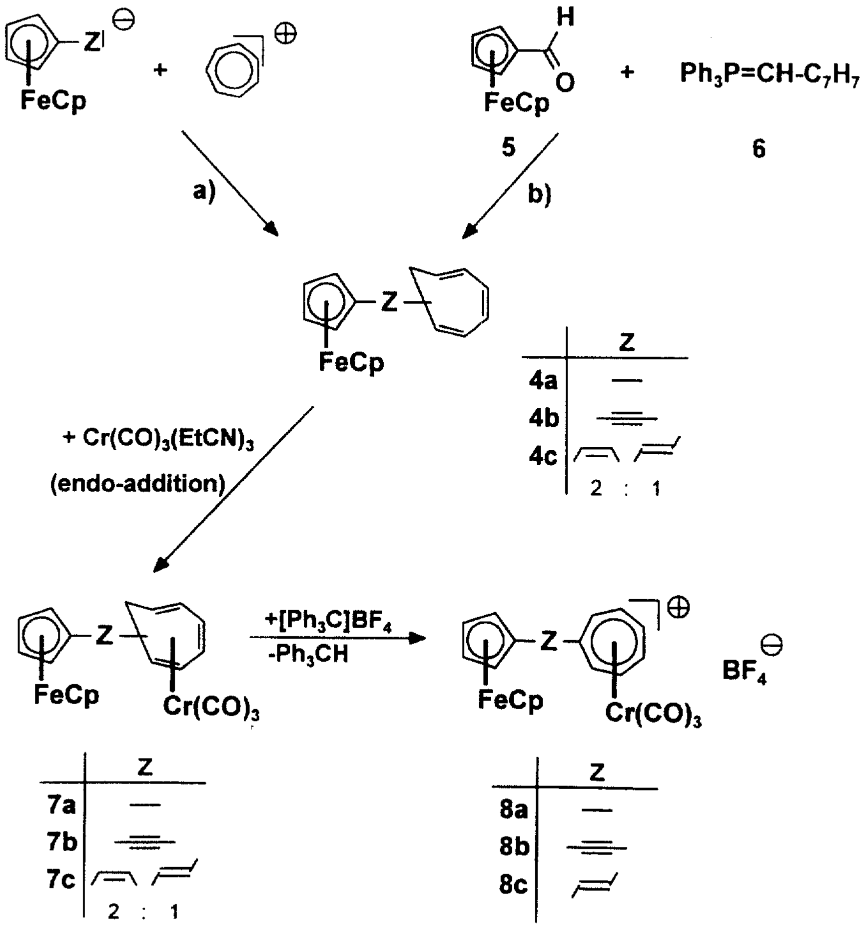
The nucleophilic addition to the tropylium cation was also successful with the ferrocenylacetylide anion [24] to introduce an ethyndiyl spacer between the five- and seven-membered ring in **4b** (Scheme 5, a). The vinylogous product **4c** was obtained by a Wittig reaction between formylferrocene (**5**) [25] and 1,3,5-cycloheptatriene-3-ylmethylidene-λ^5-phosphane (**6**) [26] (Scheme 5, b)

The ensuing $Cr(CO)_3$ addition proceeded stereoselectively at the *endo* position with respect to the ferrocenyl moiety (Scheme 5) [24]. Hence, **7a–c** possess a hydrogen atom in the *exo* position of the coordinated C_7 ring, which is essential for successful hydride abstraction to form the desired products **8a–c**. Although a 2:1 mixture of (*E*, Z)-**7c** was used to prepare **8c**, only the *E* isomer of **8c** was obtained, in more than 80% yield. It is interesting to note that crystals and solutions of **7a–c** are red coloured whereas upon hydride elimination the colour changes dramatically to deep greenish-blue. This observation gives a first hint of a remarkable donor–acceptor (DA) interaction in these bimetallic sesquifulvalene complexes. Additional indications about the DA interaction in the ground state were expected from X-ray structure analyses.

The molecular structures of **8a–c** reveal almost coplanar *cyclo*-C_5 and *cyclo*-C_7 units in the sequifulvalene ligands (Fig. 2). Thus in the solid state electronic coupling is greatly facilitated between the donor and acceptor. It is striking that the directly coupled dinuclear complex **8a** is fixed in a *transoid* conformation whereas the more separated derivatives **8b** and **c** adopt a *cisoid* conformation [24]. These structural peculiarities are regularly found in these kinds of complexes (see below).

Whereas most of the C–C and C–metal bond lengths are very typical within experimental error, a significant increase in the Cr–C7 bond length (228–236 pm) is observed relative to the remaining Cr–C (221–225 pm) distances in the *cyclo*-C_7 part of the bimetallic complex cations **8a**–**c**. A comparable elongation of the corresponding bond is found in tricarbonyl(methoxy-η^7-tropylium)chromium [27] indicating a certain degree of electronic communication with the substituent connected to the seven-membered ring complex.

An important method revealing indications about the nature and relative energies of the HOMO and the LUMO is the electrochemistry. Cyclic voltammetry investigations illustrate that the shape and maxima of the redox waves for **8a**–**c** (Fig. 3) are very similar to those of the mononuclear complexes, that is ferrocene and $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ (Table 3): the first oxidation for **8a**–**c** involves an electro-



Scheme 5. Synthetic routes to prepare the bimetallic sesquifulvalene complexes **8a**–**c**.

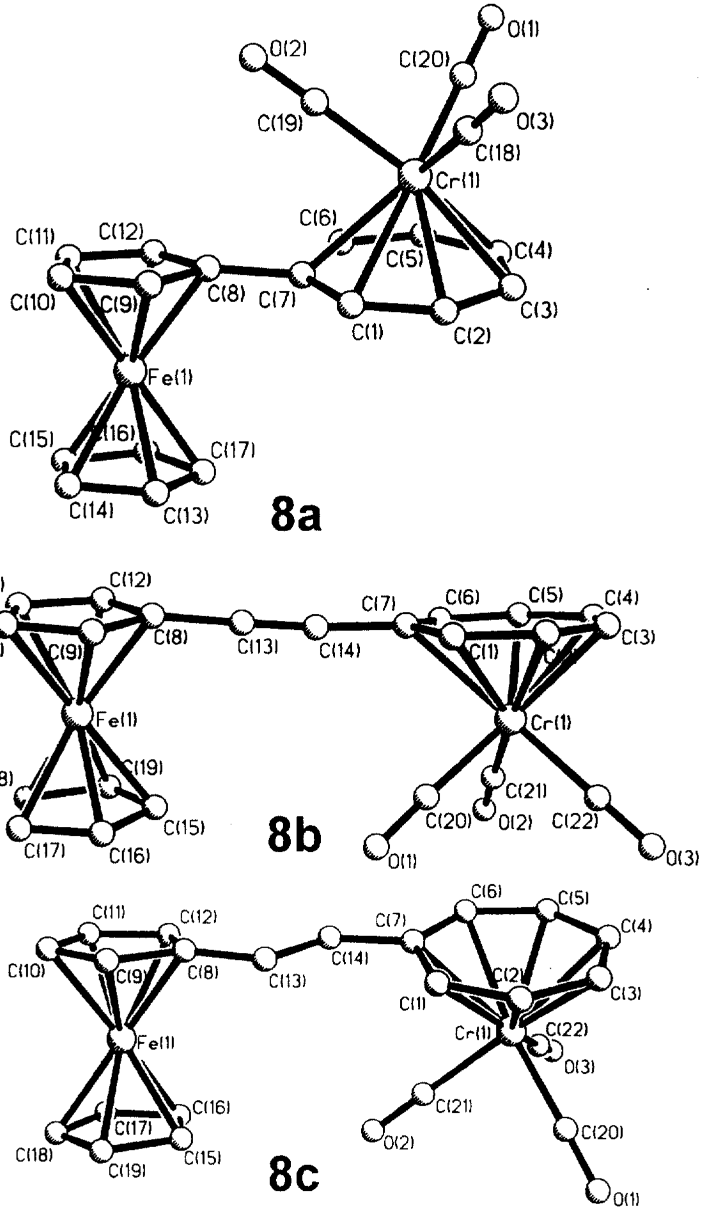


Fig. 2. Molecular structures of **8a**–**c**. (the hydrogen atoms, counter ions (BF_4^-) and solvent molecules are omitted for clarity) [24].

chemically 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 **8a**–**c**, which also involves a one-electron transfer, displays complete

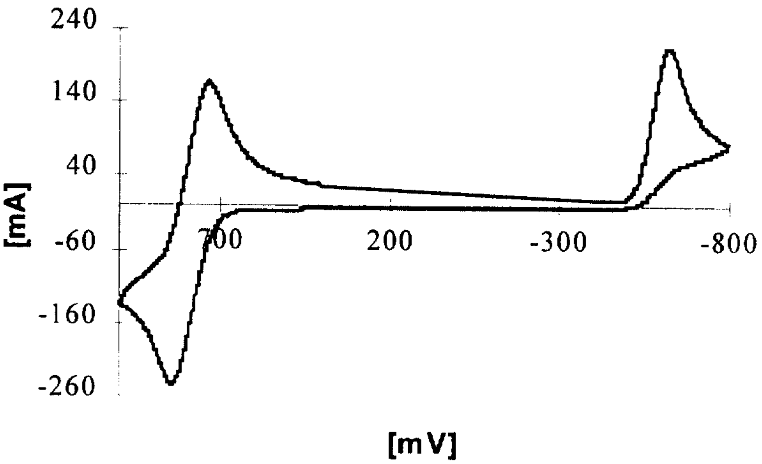


Fig. 3. Representative cyclic voltammogram of bimetallic sesquifulvalene complexes (here **8a**, CH_2Cl_2, E vs. Ag | AgI) [24].

electrochemical irreversibility with a peak potential E_{pc} positioned close to that of $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ ($E_p = -1.20$ V vs. FcH/FcH$^+$, see also Table 4 and Ref. [28]). It is thus evident that the character of the HOMO in **8a–c** is defined by the ferrocenyl moiety, whereas the character of the LUMO is mainly determined by the (tricarbonyl)tropyliumchromium unit.

Table 3
UV–vis and cyclic voltammetry data of the bimetallic sesquifulvalene complexes **8a–c** and the first hyperpolarizability β of **8b** and **c** determined by HRS

	λ_{max} (nm) [a]		$\Delta\tilde{\nu}$ (cm^{-1}) [b]	$E_{1/2}$ (V) [c] ΔE_p (mV)	E_{pc} (V) [c,d]	ΔE (V) [e]	$\beta \times 10^{-30}$esu [f]	$\beta_0 \times 10^{-30}$esu
	CH_2Cl_2	Acetone						
8a	590 [g]	570 [g]	590	0.33 (72)	−1.09	1.42	n.o. [h]	–
8b	600 [g]	560 [g]	1200	0.22 (56)	−0.90	1.12	570	105
8c	670 [i]	590 [i]	2000	0.11 (64)	−0.96	1.07	320	113

[a] Low energy absorption.

[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 (v = 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.

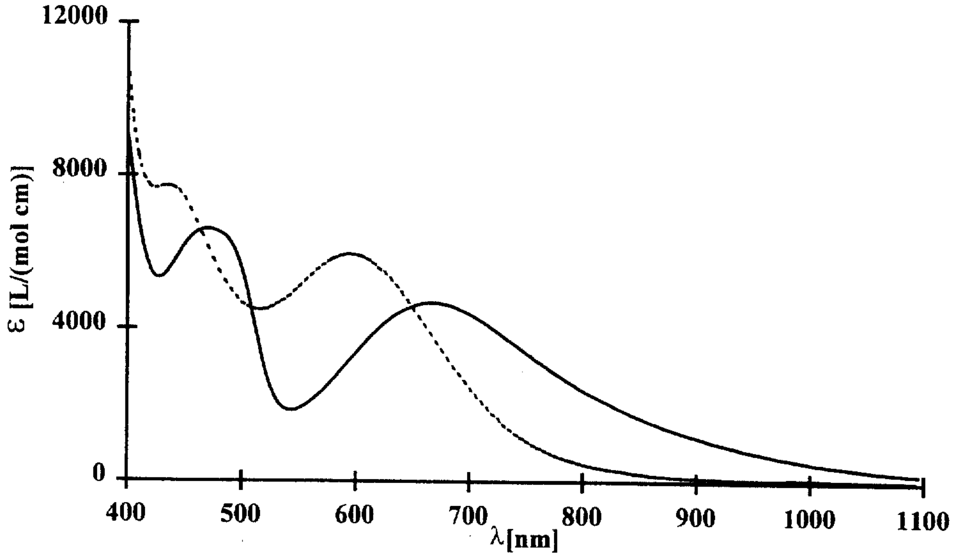


Fig. 4. Representative UV–vis spectra demonstrating the solvatochromic effect in different polar solvents (here **8c**: CH_2Cl_2 (solid line) and acetone (dotted line)) [36].

The UV–vis specra of solutions of **8a–c** and in general most ferrocenyl complexes exhibit two intense CT bands in the range of 300–800 nm. Both bands exhibit *negative* solvatochromism [29] indicated by a hypsochromic shift of the absorption band going from a less polar (E_T (CH_2Cl_2) = 0.309) to a more polar solvent (E_T (acetone) = 0.355) [29] (Fig. 4). The strongest *negative* solvatochromism is observed for the low energy transition at $\lambda > 600$ nm (Table 3). The increase of the solvatochromic effect in the order **8a** > **8b** > **8c** corresponds to an increase in the change in dipole moment on photochemical excitation. Therefore, the low energy transition has been assigned to a charge transfer transition from the *cyclo*-C_5 donor to the *cyclo*-C_7 acceptor as depicted in Scheme 6. The negative solvatochromism implies a greater polarity for the ground state than for the excited state, or even an inversion of the polarity upon excitation as shown in **8B** (Scheme 6).

The complex subunits [(η^5-cyclopentadienyl)(η^6-pentafulvene)iron]$^+$ [30] and (η^6-heptafulvene)(tricarbonyl)chromium [31], which make up the bonding situation in **8B**, are stable mononuclear complexes, and this indicates that **8B** might indeed have a certain stability. The assumption that the change in dipole moment involves a transition between two resonance forms **8A** and **8B** could be confirmed, at least for **8b** and **8c** by investigating the first hyperpolarizability β in solution. In principle the first hyperpolarizability β of the ionic bimetallic sesquifulvalene complexes cannot be determined by the EFISH technique, because a strong static electric field has to be applied to the solution containing the hyperpolarizable compound during the measurements. The only applicable method to determine β for ionic compounds in solution is the hyper-Rayleigh scattering (HRS) [32], which does not require an external electric field to remove the average centrosymmetry of the solution. The HRS method takes advantage of the temporal and spatial deviation from the average centrosymmetry due to fluctuations.

During the HRS experiment a dissolved sample of the NLO chromophore is irradiated with a laser beam of the intensity $I(\omega)$, and the intensity of the frequency-doubled scattered light $I(2\omega)$ is recorded as a function of $I(\omega)$. The dependence of the ratio $I(2\omega)/I(\omega)^2$ from the concentration of the NLO chromophore referred against a standard leads to the β(HRS) value (Fig. 5) [32].

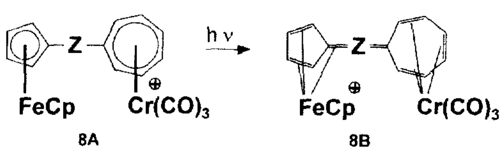
However, the first hyperpolarizability β is a second rank tensor with 27 tensor elements which, from theoretical considerations, are reduced to ten independent components. Molecular symmetry at last determines the number of independent components. In case of CT molecules, as in the present study, the β value determined by means of HRS is approximately β_{zzz} [33].

The determined β (HRS) values of **8b** and **c** are listed in Table 3. Additionally the values of the static hyperpolarizability β_0 were calculated according to Eq. (3), which assume the low energy transition to be responsible for DA transfer. For **8a**, the frequency doubled light with a wavelength of 532 nm is still in the region of relatively strong absorption, and it is therefore impossible to measure the intensity of scattered light. However, the β and β_0 values of **8b** and **c** considerably exceeded those measured to date for mono- and bimetallic ferrocene derivatives [2].

These results encouraged us to study the class of sesquifulvalene complexes more systematically with respect to the NLO properties.

2.1. Changing the electron acceptor

Since carbon monoxide complexes very often tend to photolability we made some attempts to introduce sandwich like, non-carbonyl containing electron withdrawing groups. First, the cation (η^6-borabenzene)(η^5-cyclopentadienyl)-cobalt(1+) was chosen 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. Additionally, this cation has several advantages for further 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 and (ii), borabenzene cations are very stable in air [34].



Scheme 6. Donor–acceptor charge transfer (DA-CT) in bimetallic sesquifulvalene complexes.

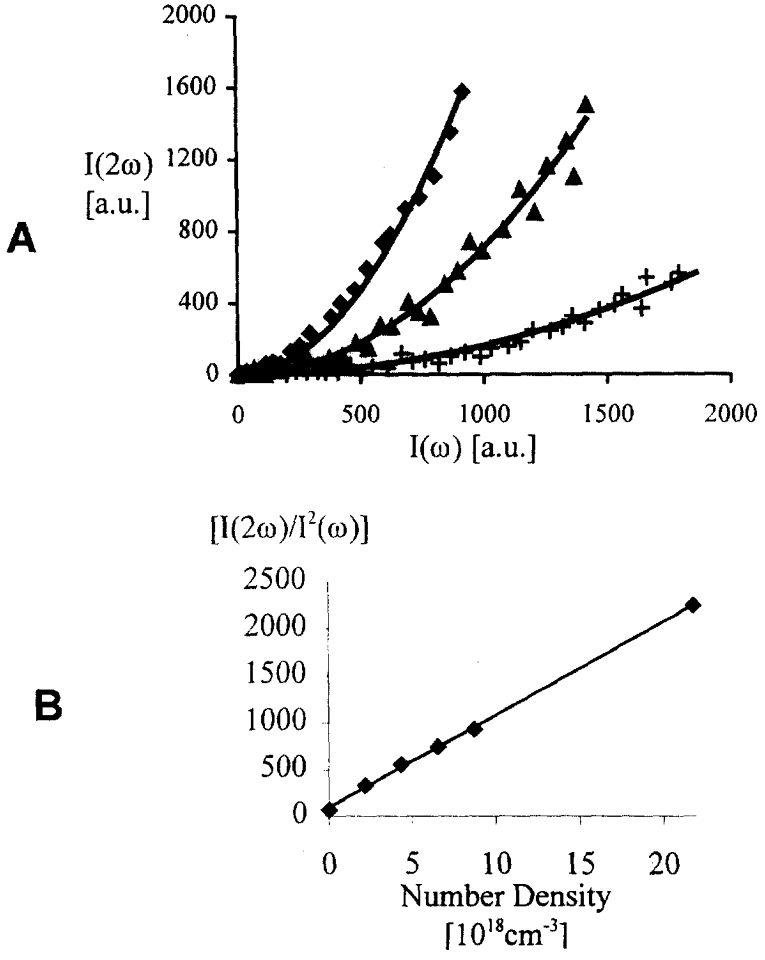


Fig. 5. Graphical presentation of $I(2\omega)=f(I(\omega))$ (**A**), and $I(2\omega)/I(\omega)^2=f$(concentration of NLO chromophore) (**B**) (data obtained from solutions of *p*-nitroaniline in CH_2Cl_2).

According to the ring expansion reaction of the cyclopentadienyl ligand in cobaltocene published by Herberich et al. [34a] the neutral, paramagnetic ferrocenyl substituted borabenzene complex **9** was obtained which could be oxidized by $FeCl_3$ or $[FeCp_2]^+$ (Scheme 7) to the monocation **10** [35].

Again, a dramatic colour change occurs when burgundy-red coloured **9** is oxidized to the DA complex cation **10** which results in a deeply blue–green solution. The enhanced stability and inertness of **10** with respect to chromium-containing congeners has been proven from DMSO and acetone solution and thermogravimetry: dilute DMSO solutions of **10** keep their colour under nitrogen for several hours whereas **8a–c** immediately lose their color when dissolved in DMSO;

acetone solutions of **10** can be stored in a beaker over night under air revealing black crystals of **10PF$_6$** whereas solutions of **8a–c** decompose under comparable conditions within a few minutes. In a thermogravimetric experiment the crystalline material decompose at about 200°C whereas the tropylium species decomposes at least 50°C lower [36].

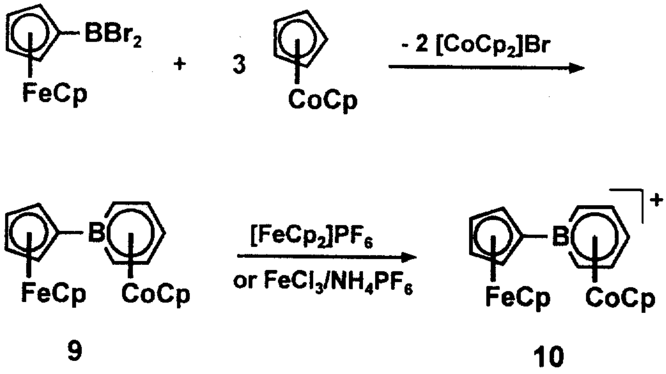
Another goal of our investigations of organometallic sandwich type DA systems was to enhance the accepting capability by using a dicationic sandwich-type electron acceptor like $[(\eta^7\text{-}C_7H_7)Ru(\eta^5\text{-}C_5H_5)]^{2+}$. The synthesis of the dicationic tropylium complex was first published by Mann et al. [37] by adding the cationic half-sandwich complex $[CpRu(MeCN)_3]^+$ to tropylium cation. Applying this synthetic method to metallocenyl-substituted tropylium cations immediately reveals the desired dicationic DA complex **11** (Scheme 8A) as a microcrystalline precipitate.

Similarly, it was possible to prepare the vinylogous derivative of **11** when **4c** was taken as the starting material (see Scheme 5). In Scheme 8B the synthetic procedure for the bimetallic dicationic complex **13** is shown.

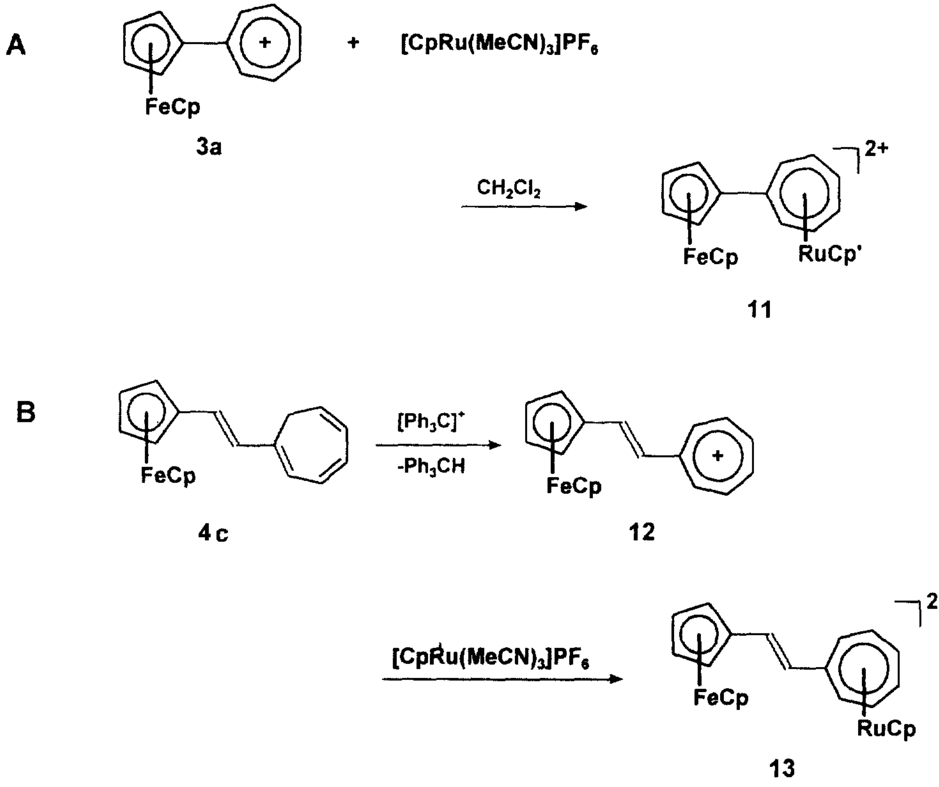
2.2. Changing the electron donor

The intention to modify the electron accepting and donating capability is not only to enhance the DA interplay for increasing the first hyperpolarizability but also to be able to modulate the DA communication to obtain a deeper insight and understanding into the origin of the NLO properties of these types of organometallic compounds.

The first step was to modify the ferrocenyl donor by increasing methylation. Whereas the influence of the permethylation of the distal Cp ligand on ferrocene (the Cp ligand which is not directly connected to the π-bridge) is well known from earlier work [10], nothing was yet known about the electronic effect of a nonamethylation of the ferrocenyl moiety in D-π-A complexes. As the starting mate-



Scheme 7. Synthesis of the heterobimetallic borabenzene complex **10**.



Scheme 8. Synthesis of the dicationic bimetallic sesquifulvalene complexes **11** and **13**.

rial for the elongated sesquifulvalene complexes with a penta- and nonamethylated ferrocenyl donor the corresponding carbaldehydes were synthesized which subsequently were subjected to a Wittig–Horner–Emmons (WHE) reaction affording exclusively the (*E*)-product. The ensuing $Cr(CO)_3$ addition yields the precursor complexes **15a** and **b** suitable for the hydride abstraction (Scheme 9).

In the case of the pentamethylated product **15a**, hydride abstraction with $[Ph_3C]^+$ affords the desired cationic complex **16** whereas the reaction of the nonamethylated complex **15b** with the trityl cation yields the ferrocenyl-oxidized product **17**. The corresponding reaction with the ethynediyl bridged compounds **14b** and **15c** also produces ferrocenyl oxidized, paramagnetic complexes (**18** and **19**), which can be confirmed also by X-ray structure analysis (Fig. 6) [36].

The molecular structure of **19** demonstrates the exclusivity of the *endo*-addition of the $Cr(CO)_3$ fragment.

Another option to modulate the donating ability was the use of a ruthenocenyl in place of the ferrocenyl terminus which from earlier work is known [10] to be a less electron releasing group according to an increased electronegativity of a ruthenocenyl substitutent compared to ferrocenyl [38]. The synthesis of the ruthenocenyl containing sesquifulvalene complexes is quite similar to that of the ferrocene derivatives shown before in Schemes 5 and 9 and uses monolithiated ruthenocene [39] as starting material [10].

Whereas nitromethane solutions of the ferrocenyl derivatives **12** and **13** are deep green–blue ($\lambda_{max} = 725 - 765$ nm), the color of the corresponding solutions of the Ru congeners **21a-c**, **22** and **23** are intense violet ($\lambda_{max} < 600$ nm). This blue shift of the DA charge transfer in the ruthenocenyl derivatives compared to the ferrocenyl containing complexes reflect the lower electron releasing ability of the donor.

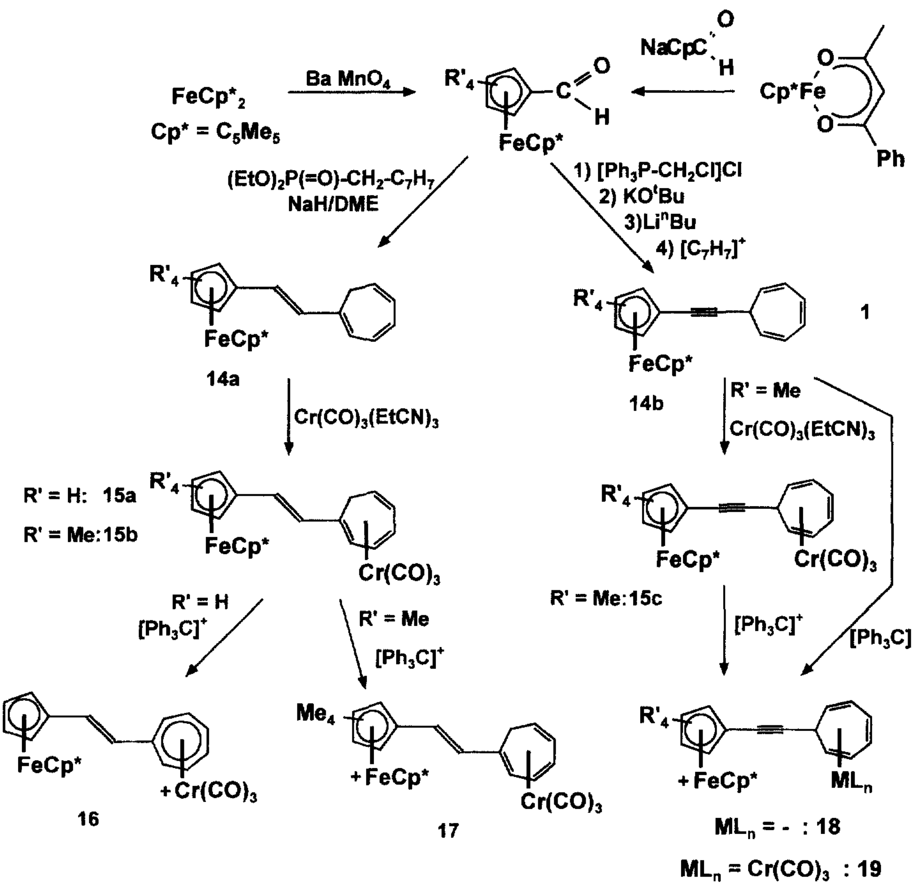
With the (η^4-cyclobutadiene)(η^5-cyclopentadiendiyl)cobalt [40] unit a new organometallic electron donating group was introduced into the D-π-A systems [41]. The motivation to use this sandwich entity as an electron donor was the easy manipulation of the electronic properties of this unit by modifying the electronic demand of the *p*-substitutents of the aryl groups linked to the cyclobutadiene ligand (see Scheme 11). The reaction sequence is compatible to that shown in Schemes 9 and 10. In addition, the stability of the uncoordinated tropylium cation **25a** (see also Schemes 8 and 10) enabled us to synthesize the dicationic bimetallic complex **25d** as well. Whereas the dication **25d** is sufficiently robust to be studied thoroughly when kept under inert atmosphere, the complex **25c** is light sensitive and the $Cr(CO)_3$ fragment is easily cleaved upon standing in sunlight.

2.3. Changing the π-bridge

Former HRS studies on the ethenediyl bridged heterodinuclear complex **8c** revealed a large first hyperpolarizability *β*. Since it is well known from dipolar organic NLO chromophores that increasing the number of π-bonds by one between the donor and acceptor enlarges the experimental *β* value by a factor of 1.5–2 [2], the introduction of additional double bonds between the five- and seven-membered rings of the sesquifulvalene complexes appeared to be a most promising endeavour to improve the NLO properties

. The starting complex for the introduction of two and three double bonds again was formyl ferrocene which underwent a WHE reaction with (ethoxycarbonylmethyl)diethylphosphonate [42]. Subsequent reduction of the formed ester by $Li[AlH_4]$, and oxidation with $Ba[MnO_4]$ led to the vinylogous carbaldehyde which was either connected to the cycloheptatrienyl compound (Scheme 12a) or further subjected to the above reaction sequence to form the dienyl formyl derivative (Scheme 12b). The formation of the cationic dipolar NLO chromophores proceeded via the usual treatment with $[Ph_3C][PF_6]$ [36].

However, three conjugated double bonds cause an enhanced reactivity of the neutral and dipolar complexes **27** and **28**, respectively, which makes the full characterization of **28** more difficult with respect to the NLO properties. The introduction of methyl substitutents into the π-bridge would lead to more



Scheme 9. Synthetic route to methylated bimetallic sesquifulvalene complexes.

stabilisation as is found in carotinoids and retinal derivatives or in other organic NLO chromophores [43].

Another preparatively convenient method to improve the inertness of extended π-bridges in dipolar NLO chromophores is the use of thiene-2,5-diyl as π-linkers [44]. These types of complexes have been synthesized starting

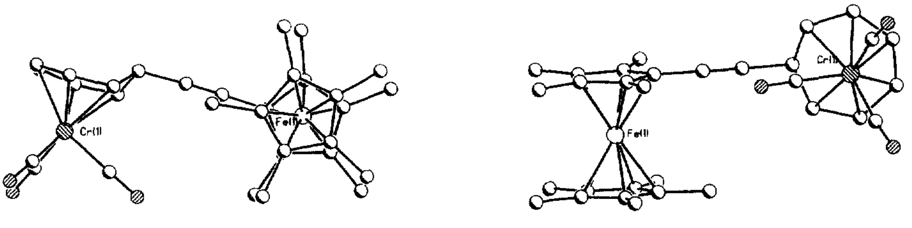
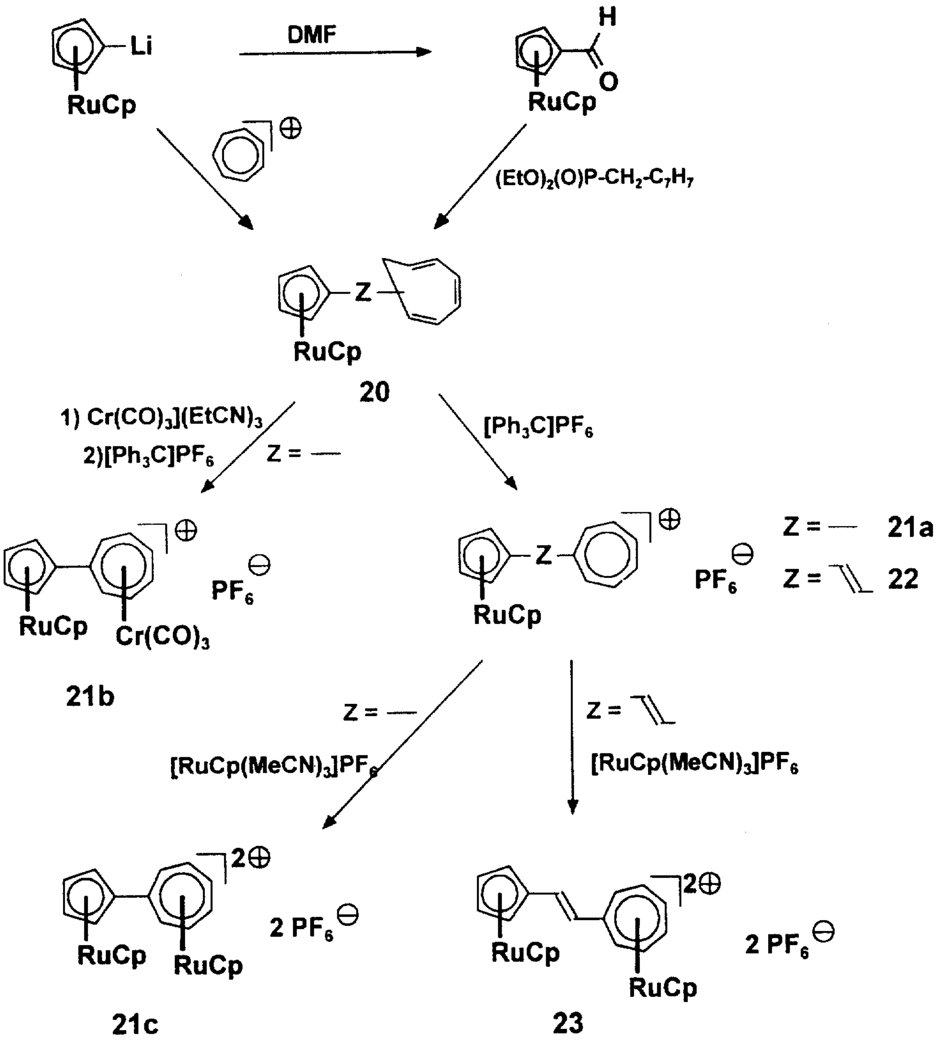


Fig. 6. Molecular structure of the paramagnetic cation of the nonamethylated bimetallic complex **19** [36].



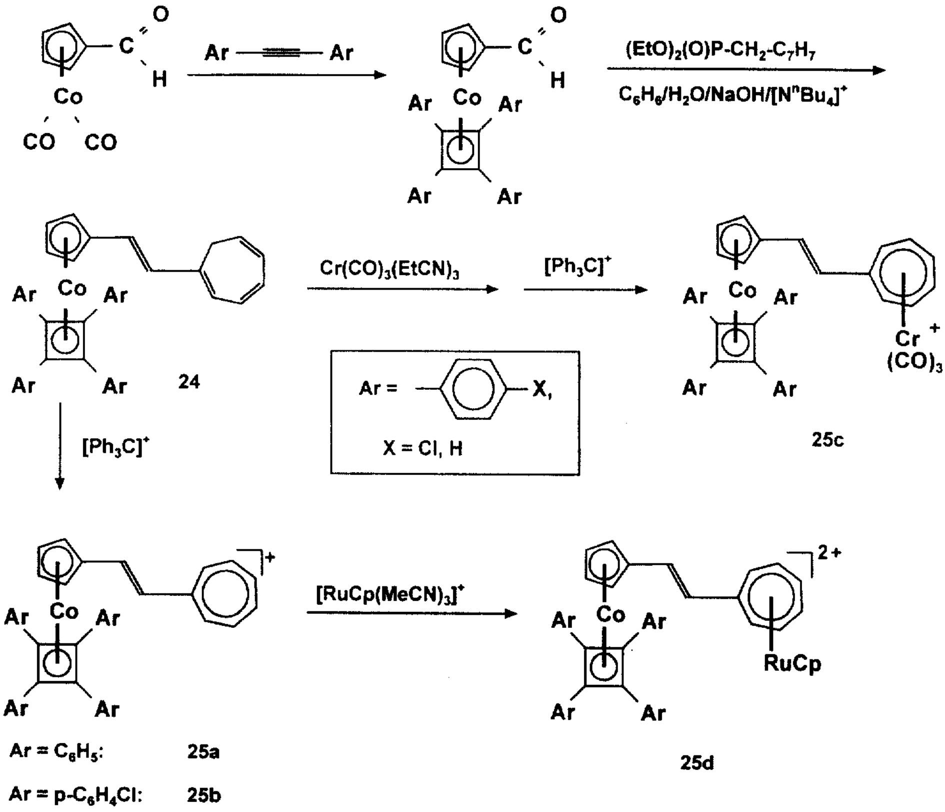
Scheme 10. Synthetic route to ruthenocenyl containing sesquifulvalene complexes.

from 2,5-dibromothiophene as shown in Scheme 13A. Br–Li exchange and subsequent nucleophilic additions led to the formation of 2-bromo-5-cycloheptatrienylthiophene (**29**). Complex **29** was either allowed to react with ferrocenyl zinc chloride in a cross-coupling reaction affording the desired monothiophene species **30**, or was subjected to a Ni catalyzed cross-coupling reaction with the bromo thiophene Grignard reagent resulting in the formation of the bithiophene derivative **33** (Scheme 13B). **33** was lithiated, followed by a Li–Zn exchange and cross-coupled with ferrocene. The procedure to generate the cationic dipolar complexes **31a–c** and **34** was performed as before [36].

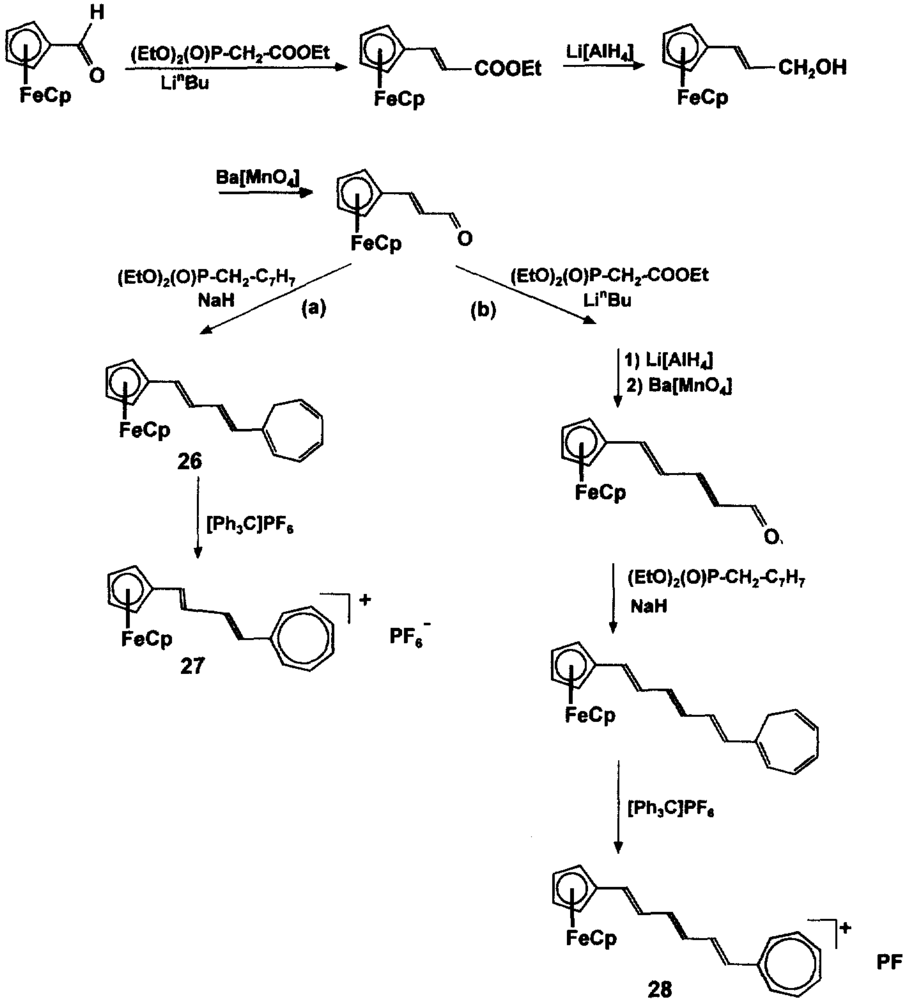
The introduction of an ethyndiyl bridge between the donor and a borabenzene ligand was successfully performed by nucleophilic substitution of the PMe_3 group in the zwitterion **36** [45]. Subsequent Li | Tl exchange [46] and addition of a half-sandwich unit (i.e. $Ru(C_6H_6)$, RhCp*, IrCp*) revealed the ethyndiyl linked DA complex **37a–c** with a cationic borabenzene complex as the electron accepting group (Scheme 14) [47].

2.4. Redox properties

The ferrocenyl containing compounds reveal an electrochemically reversible one-electron oxidation (see Fig. 3) which is slightly anodically shifted with respect to ferrocene. The amount of the anodic shift depends on the length of the π-linker and the nature of the electron withdrawing ability of the tropylium moiety (Table 4). The coordination to the $Cr(CO)_3$ fragment induces in the weakest effect whereas



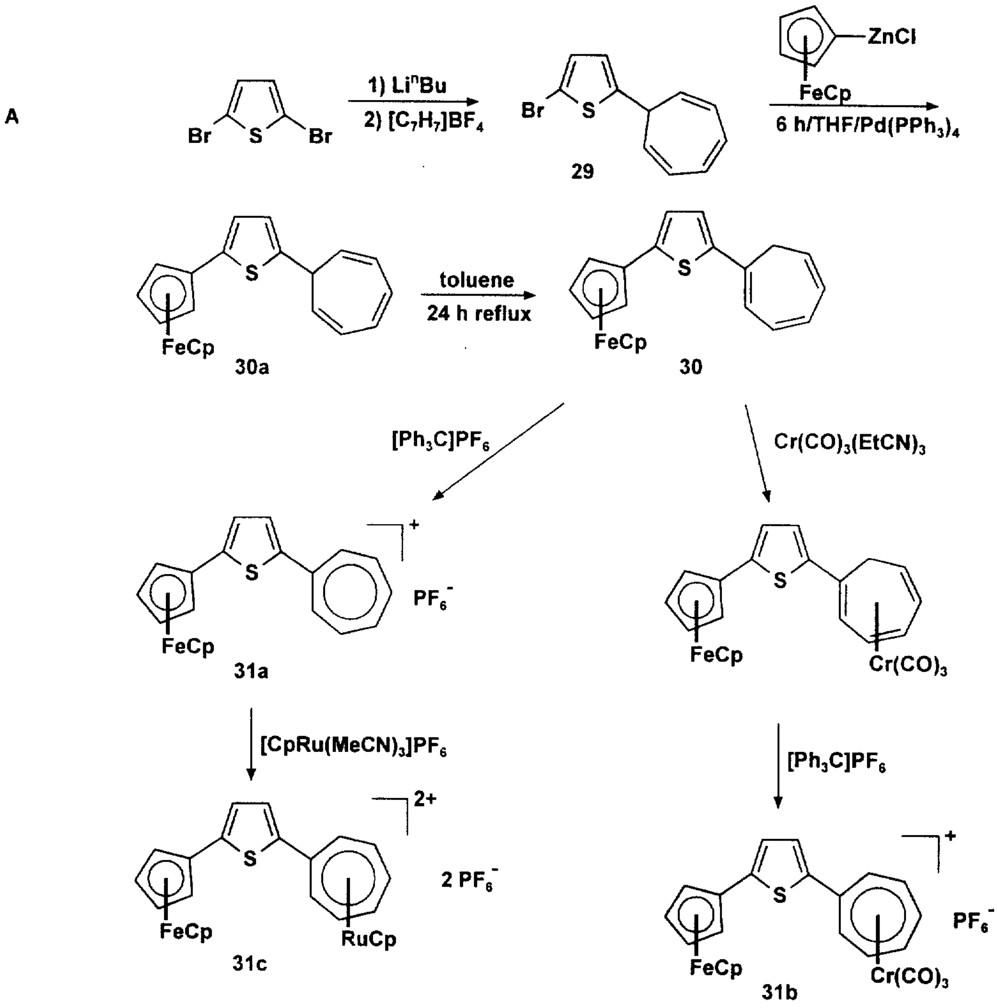
Scheme 11. Synthesis of (tetraaryl-η^4-cyclobutadiene)cobalt complexes of vinylogue sesquifulvalene complexes.



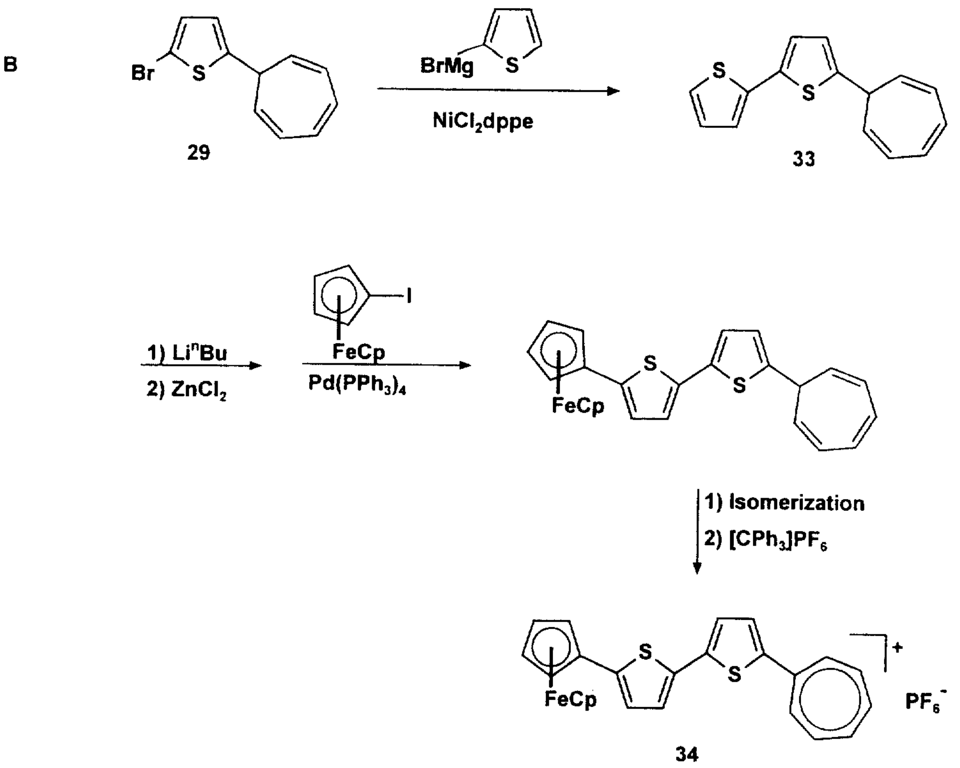
Scheme 12. Extension of the number of double bonds between the five- and seven membered rings in sesquifulvalene complexes.

the influence of the uncoordinated or RuCp$^+$ coordinated tropylium entity are similar in the oxidation potential. The reduction of the sesquifulvalene complexes occur in an irreversible one-electron transfer and at very similar potentials as reported from the unsubstituted mononuclear tropylium and tropylium complexes; the peak potential E_{pc} depends on the length of the π-connection, and the nature of the tropylium moiety: E_{pc} distinctly decreases in the order $M'L'_n = Cr(CO)_3 < - <$ RuCp$^+$. The same order is found for the difference ΔE between the oxidation and reduction step. Comparable trends in the redox behaviour are observed for the ruthenocenyl and (η^4-cyclobutadiene)(η^5-cyclopentadienediyl)cobalt containing complexes, although the oxidation step normally is 400–600 mV more anodically shifted, and includes an irreversible two electron transfer step, as expected from the results of the corresponding mononuclear sandwich complexes [37,48]. For the CoRu complex **25d**, the oxidation is split into two not clearly resolved waves indicating two subsequent one-electron transfer steps.

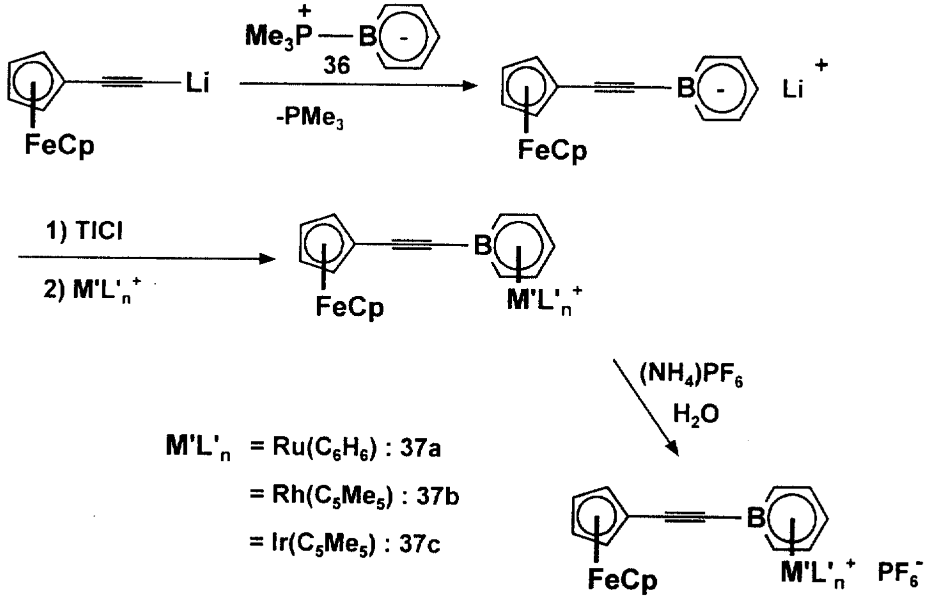
The mutual electronic influence, although less pronounced, is also found for the bimetallic borabenzene complex **10**. This complex even reveals three electrochemically reversible one-electron redox couples, one redox couple $+1/+2$ which



Scheme 13. Synthetic route for preparing mono- (**A**) and bithiophene (**B**) bridged sesquifulvalene complexes.



Scheme 13. (*Continued*)



$M'L'_n$ = $Ru(C_6H_6)$: 37a
= $Rh(C_5Me_5)$: 37b
= $Ir(C_5Me_5)$: 37c

Scheme 14. Synthesis of the ethyndiyl bridged borabenzene complex.

potential is 50 mV anodically shifted with respect to unsubstituted ferrocene and two redox couples $+1/0$ and $0/-1$ (Fig. 7). The potential of the redox couple $+1/0$ is about 60 mV cathodically shifted with respect to [(1-phenyl-η^6-borabenzene)(η^5-cyclopentadienyl)cobalt]$^+$ [34b]. The redox potentials allow the assignment of the ferrocenyl part (viz. $+2/+1$) and borabenzene complex moiety (viz $+1/0$, $0/-1$).

Table 4
Redox properties of mono- and dinuclear sesquifulvalene complexes of the general form in Scheme 2 [a]

ML_n	$M'L'_n$	Z		$E_{1/2}$ [b,c]	E_{pc} [b,c,d]	ΔE [d]
FeCp [e]	$Cr(CO)_3$	–	**8a**	0.33	−1.09	1.42
FeCp [e]	–	–	**3a**	0.40	−0.82	1.22
FeCp [f]	$RuCp^+$	–	**11**	0.44	−0.61	1.05
FeCp [e]	$Cr(CO)_3$	*E*–CH=CH–	**8c**	0.11	−0.96	1.07
FeCp [e]	–	*E*–CH=CH–	**12**	0.22	−0.68	0.90
FeCp [f]	$RuCp^+$	*E*–CH=CH–	**13**	0.19	−0.55	0.72
FeCp [f]	–	*E*,*E*–(CH=CH–)$_2$	**27**	0.15	−0.65	0.80
FeCp [f]	$Cr(CO)_3$	(C_4H_2S)	**31b**	0.12	−1.00	1.12
FeCp [f]	–	(C_4H_2S)	**31a**	0.20	−0.66	0.82
FeCp [f]	$RuCp^+$	(C_4H_2S)	**31c**	0.19	ND [l]	
FeCp [f]	–	$(C_4H_2S)_2$	**34**	0.10	−0.62	0.72
RuCp [f]	$Cr(CO)_3$	–	**21b**	1.03	−1.27	2.3
RuCp [f]	–	–	**21a**	1.12	0.85	1.97
RuCp [g]	$RuCp^+$	–	**21c**	0.67	−0.75	1.42
RuCp [f]	–	*E*–CH=CH–	**22**	0.61 [i]	−0.68	1.29
RuCp [f]	$RuCp^+$	*E*–CH=CH–	**23**	0.90 [i]	−0.64	1.54
CoCbd [f,h]	$Cr(CO)_3$	*E*–CH=CH–	**25c**	0.58 [i]	−0.98	1.56
CoCbd [f,h]	–	*E*–CH=CH–	**25a**	0.65 [i]	−0.68	1.33
CoCbd [f,h]	RuCp	*E*–CH=CH–	**25d**	0.46 [j]	−0.57	1.03
				0.61 [j]		1.18
$RuCp_2$ [f]				0.61 [i]		
$[(C_7H_7)Ru(Cp)](PF_6)_2$ [f]				0.60 [k]	−0.63 [m]	
$[(C_7H_7)]PF_6$ [f]					−0.63 [m]	
$[(C_7H_7)Cr(CO)_3]PF_6$ [f]					−1.20 [n]	

[a] For more experimental details see Ref. [35].

[b] Versus $[FeCp_2] | [FeCp_2]^+$.

[c] In Volt.

[d] Irreversible one-electron reduction, scan rate 100 mV.

[e] In CH_2Cl_2.

[f] In $MeNO_2$.

[g] In MeCN.

[h] Cbd = 1,2,3,4-tetraphenylcyclobutadien.

[i] Irreversible oxidation.

[j] Not clearly resolved waves.

[k] Our result, other data see Ref [48].

[l] Not determined.

[m] Our result, other data see Ref. [37].

[n] See also Ref. [28].

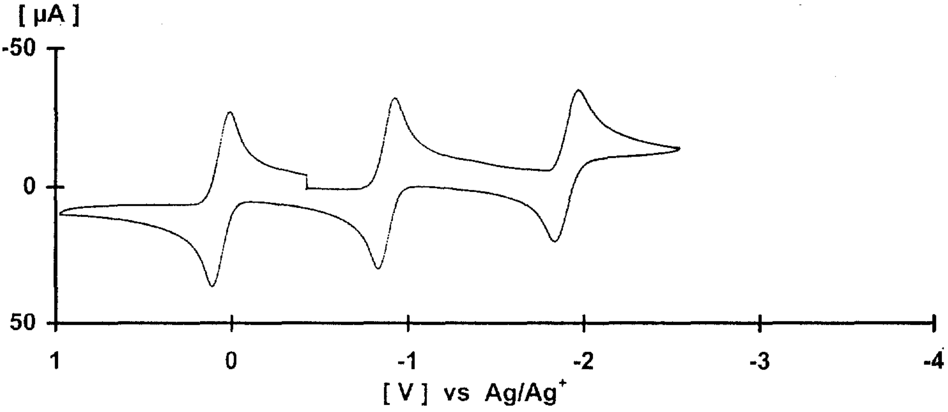


Fig. 7. Cyclic voltammogram of the ferrocenyl borabenzene complex **10** (CH_3CN) [35].

The electrochemical data show that in the sesquifulvalene complexes the nature of the HOMO is dominated by the neutral donating sandwich units whereas the character of the LUMO is determined by the cationic C_7-moiety. This constellation favours a dipole change upon electronic excitation from the HOMO to the LUMO and ΔE is a relative measure of the energy gaps between the HOMO and the LUMO.

2.5. Solvatochromism studies

The UV–vis spectra of the complexes under study are comparable in that the spectra consist of two absorption bands in the visible region with the exception of

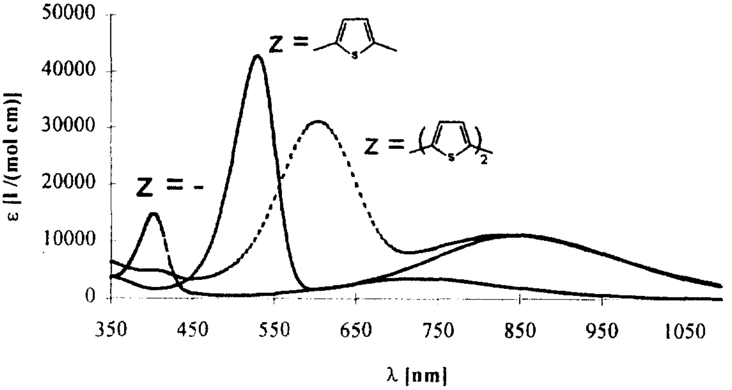


Fig. 8. UV–vis spectra of mononuclear sesquifulvalene complexes as depicted in Scheme 2 with none ($z = -$), one ($z = C_4H_2S$) and two ($z = (C_4H_2S)_2$) thiophene linkers between the seven- and five-membered rings measured in CH_2Cl_2 [36].

Table 5
UV–vis data of the mono- and bimetallic sesquifulvalene and borabenzene complexes of the general form shown in Scheme 2

ML_n	$M'L'_n$	Z		LL-CT λ_{max} [a] (ε) [b]		$\Delta\tilde{\nu}$ [c]	DA-CT λ_{max} [a] (ε) [b]		$\Delta\tilde{\nu}$ [c]
				CH_2Cl_2	$MeNO_2$		CH_2Cl_2	$MeNO_2$	
FeCp	$Cr(CO)_3$	–	**8a**	408 (2600)	395 (5280)	−807	590 (3100)	574 (4880)	−473
FeCp	–		**3a**	400 (14710)	395 (13360)	−316	726 (3565)	700 (3330)	−511
FeCp	$RuCp^+$	–	**11**	–	[e]		–	614 (5270)	
FeCp	$Cr(CO)_3$	*E*–CH=CH–	**8c**	470 (6600)	450 (4940)	−946	665 (4690)	610 (3960)	−1356
FeCp	–	*E*–CH=CH–	**12**	490 (39440)	470 (24360)	−868	816 (13350)	765 (9510)	−817
FeCp	$RuCp^+$	*E*–CH=CH–	**13**	–	480 (5970)		–	725 (2100)	
FeCp*	$Cr(CO)_3$	*E*–CH=CH–	**16**	475 (8590)	450 (6530)	−1170	755 (5540)	705 (2700)	−939
FeCp	–	*E, E*–$(CH=CH)_2$–	**27**	560 (37380)	520 (24860)	−1373	865 (18090)	780 (12770)	−1260
FeCp	–	*E, E, E*–$(CH=CH)_3$–	**28**	620 (32040)	510	−3214	906 (20200)	715	−2557
FeCp	$Cr(CO)_3$	(C_4H_2S)	**31b**	475 (18825)	460 (9275)	−686	645 (11745)	590 (6740)	−1445
FeCp	–	(C_4H_2S)	**31a**	530 (42870)	510 (33690)	−740	845 (11210)	760 (9470)	−1324
FeCp	$RuCp^+$	(C_4H_2S)	**31c**	–	480 (6850)		–	735 (2020)	
FeCp	–	$(C_4H_2S)_2$	**34**	618 (31130)	560 (27800)	−1676	844 (11210)	700 (9820)	−2437
RuCp	$Cr(CO)_3$	–	**21b**	412 (5100)	[e]		486 (3990)	458 (5260)	−1258
RuCp	–	–	**21a**	410 (14020)	398 (6660)	−740	560 (7360)	536 (3250)	−800
RuCp	$RuCp^+$	–	**21c**	–	[e]		–	462 (5820)	
RuCp	–	*E*–CH=CH–	**22**	477 (16270)	455 (12040)	−1014	642 (22560)	600 (20345)	−1040
RuCp	$RuCp^+$	*E*–CH=CH–	**23**	–	[e]		–	546 (4975)	
CoCbd	–	*E*–CH=CH–	**25a**	455 (22100)	432 (14870)	−1170	720 (23940)	670 (16300)	−1040
CoCbdCl [d]	–	*E*–CH=CH–	**25b**	450 (358709	428 (15393)	−1142	702 (35660)	650 (15335)	−1140
CoCbd	RuCp	*E*–CH=CH–	**25d**	–	406 (11816)		–	622 (8758)	
FeCp	CoBBz	–	**10**	410 (sh)	405 (sh) [f)]	−300	650 (2000)	585 [f] (1640)	1709

[a] In nm.

[b] In l $mol^{-1}cm^{-1}$.

[c] In cm^{-1}.

[d] CoCbdCl: Ar = *p*-C_6H_4Cl (see Scheme 11) (Ref. [41]).

[e] λ_{max} < 370nm.

[f] In dmso.

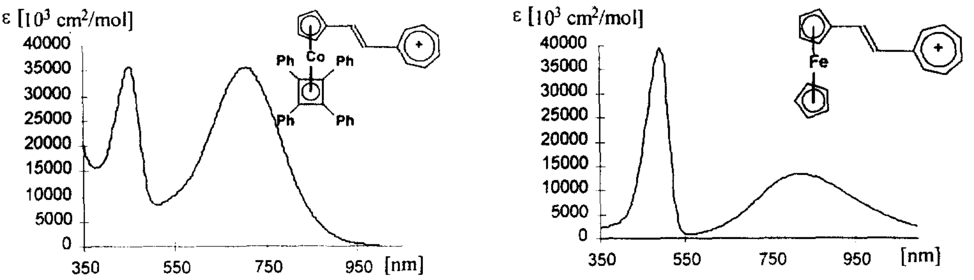


Fig. 9. UV–vis spectrum of the mononuclear vinylogue sesquifulvalene complex **25a** (right), with a tetraphenylcyclobutadiene cobalt as electron-donor moiety in comparison to the ferrocenyl congener **12** (left)(CH_2Cl_2) [41].

the ruthenocenyl containing complexes whose high energy absorption bands are shifted towards the near UV (Table 5). As can be seen from Table 5, the electronic excitations are governed by a strong negative solvatochromism, which is typically more pronounced for the low energy absorption, indicating strong dipole changes between the ground and excited state.

Fig. 8 nicely demonstrates the influence of the length of the π-bridge linking the donor and acceptor: whereas the short wavelength absorption band is considerably red shifted, the low energy absorption band seems to move to a certain limit. This behaviour is in accordance to the assignment of this absorption band to a donor–acceptor charge-transfer (DA-CT) transition. As can be deduced from the electrochemistry data, the oxidation potential of the ferrocenyl donor continuously approaches the potential of free ferrocene the longer the π-bridge becomes; correspondingly, the reduction potential of the acceptor more and more resembles that of the unsubstituted tropylium cation or tropylium complex. In conclusion, the energy difference between the donor (HOMO) and the acceptor orbital (LUMO) has to reach a constant value with increasing length of the π-bridge connecting the five- and seven-membered rings, and thus, the excitation energy reaches a limiting value as well. The assignment of the low energy absorption to the DA-CT transition is also in accordance to the rule of organic dyes that unusual long-wave-length absorptions always are to be expected when the HOMO and the LUMO are located in different parts of the molecule [49]. Additionally, this assignment is corroborated by the dependence of the positions of the absorption bands from the nature of the donor: the absorption band at higher energy is considerably less influenced than the low lying absorption band upon changing the donating capability as shown in the series of ethenediyl-bridged complexes **8c**, **16**, **12** and **22**. We therefore suppose that the higher-lying absorption is due to an interligand π–π* transition (LL-CT), which also agrees with the dramatic shift caused by the coordination of the $Cr(CO)_3$ fragments to the *cyclo*-C_7-membered cation. The assignment of the higher-lying absorption band to a LL-CT transition as well agrees to theoretical calculations of acceptor substituted ferrocene derivatives [10].

In the case of the tetraarylcyclobutadiene cobalt moiety (**25a** and **b**), a comparable pattern in the UV–vis spectra can be observed (Fig. 9) [41]. However, the low energy DA-transitions have a molar extinction coefficient which is more than three times larger than that of the corresponding cyclopentadienyl iron derivatives (see **8c** and **13**). Additionally, a small but distinct hypsochromic shift occurs on going from **25a** to **b** showing the electronic effect of the *p*-substituents in the aryl functions of the cyclobutadiene ligand.

2.6. Structural results

A very important result of the studies about structural parameters and molecular factors governing the NLO properties, in particular the first hyperpolarizabilit β, is the correlation between the bond length alternation (BLA) of olefinic bridged D-π-A systems and (i) the dipole change between the ground and the excited CT state $\Delta\mu_{eg}$; (ii) the electronic transition moment M^2 of the CT transition, and (iii) the energy ΔE of the CT transition [50–52]. In Fig. 10, the correlation between $\Delta\mu_{eg}$, M^2, ΔE^{-2}, the hyperpolarizability β and the BLA is shown (Fig. 10).

However, from a couple of the presented sesquifulvalene-type complexes we were able to prepare an X-ray structure analysis. But in many cases, the accuracy of the structural analysis, which is absolutely necessary for the discussion of a structure-property relationship was hampered by the poor quality of the crystals. Nevertheless, some characteristic structural features of this type of complexes could be formulated.

Most of the complexes except **8a** [24], **8c** [20] and **21b** [53] crystallize in a centrosymmetric space group and hence could not be used for NLO studies in the solid state concerning the first hyperpolarizability. Without any exception all archetype dinuclear sesquifulvalene complexes (without an additional π-spacer, Z = –) including the dinuclear borabenzene complex **10** adopt a transoid conformation, independent of the electronic nature of the donor and the acceptor. For example, the borabenzene cation **10** and the dication **21c** are shown in Fig. 11. In

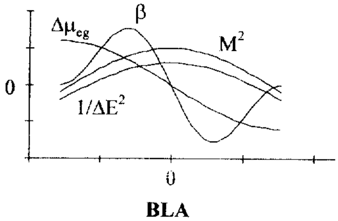


Fig. 10. Relationship of the bond length alternation (BLA) with the dipole change $\Delta\mu_{eg}$ between the ground and the CT state, the electronic transition moment M^2, the reciprocal CT transition energy, and the first hyperpolarizability β according to Refs. [50–52].

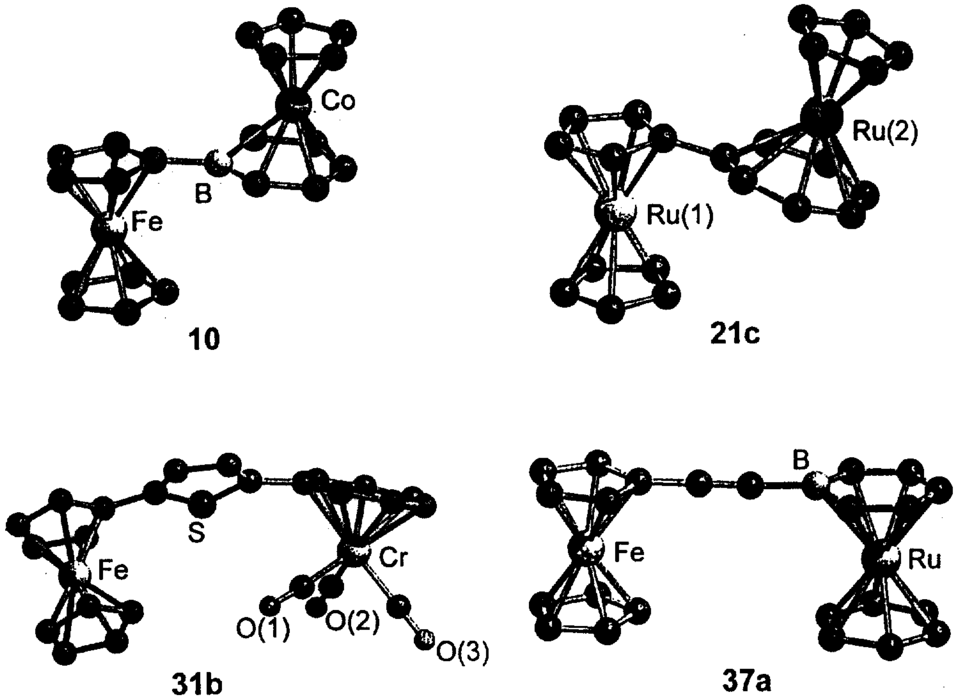


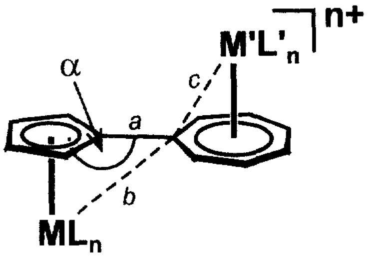
Fig. 11. Molecular structures of the borabenzene complex cations **10** [35] and **37a** [53] and of the sesquifulvalene complex cations **21c** [53] and **31b** [36].

contrast to it, all of the dinuclear complexes containing an additional π-linker between the donor and acceptor always take a cisoid conformation (compare also Fig. 4, **8b** and **c**). In Fig. 11, the molecular structure of the thiophen-2,5-diyl linked derivative of the dinuclear sesquifulvalene complex **31b** and the molecular structure of a borabenzene D-π-A complex **37** with an ethyndiyl spacer is shown. Therefore the transoid conformation of the sesquifulvalene complexes without an additional π-spacer presumably will be a consequence of the steric demand of the organometallic termini. In the case of the mono- and dinuclear archetypal sesquifulvalene complexes we were successful in obtaining molecular structures of two whole series with sufficient accuracy. These results suggest that we can detect the influence of the donor and acceptor sites on each other not only by electronic spectroscopy and cyclic voltammetry, but also by molecular structure analysis.

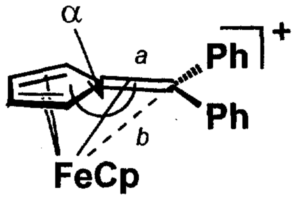
Five different geometrical parameters clearly indicate the structural change as a result of the electron withdrawing ability of the cationic *cyclo*-C_7-moiety (Table 6): (i) the bond length *a* between the five- and seven-membered ring, (ii) the angle α enclosed by the vector which bisects the five-membered ring and contains the bridge-head atom of the Cp ring, and the bonding vector of the bridging bond between the five and seven-membered rings, (iii) the nonbonding distance *b* between the *ipso*-carbon atom of the seven-membered ring and the metal atom of the donor, and (iv) the bond length *c* between the *ipso*-carbon of the seven-membered ring and the metal center of the tropylium complex compared to the other metal–carbon bond lengths of the tropylium complex (see schematic picture in Table 6). The geometrical parameters α and *b* decrease in the order of $M'L'_n = Cr(CO)_3 > - >$ $RuCp^+$ and approach the corresponding values of the cationic fulvene complex (Table 6): the metallocene unit more and more resembles the fulvene complex moiety [30], where the positive charge is localized on the iron center.

This tendency of the metallocene unit concerning the bonding mode of the Cp ring with increasing electron withdrawing ability of the acceptor moiety agrees with the C–C bond length *a* which is somewhat shorter than expected for a sp^2–sp^2

Table 6
Selected geometrical parameters in mono- and bimetallic sesquifulvalene complexes **A** and in the mononuclear fulvene complex **B**



A



B

ML_n	$M'L'_n$		*a* [c] (pm)	*b* [d] (pm)	*c* [e] (pm)	*d* [f] (pm)	α (°)
FeCp	$Cr(CO)_3$	**8a**	145.1(10)	305.0(7)	232.0(6)	221.4(7)–224.1(7)	176.5
FeCp	–	**3a**	145.9(6)	296.7(10)	–	–	175.5
FeCp	$RuCp^+$	**11**	144.0(10)	290.0(10)	244.1(10)	222.2(11)–227.4(10)	167.5
RuCp	$Cr(CO)_3$	**21b**	146.3(9)	318.1	233.0(7)	223.5(7)–227.1(6)	178.6
RuCp	–	**21a**	147.2(7)	311.3(5)	–	–	174.0
RuCp	$RuCp^+$	**21c**	144.9(4)	293.6(3)	246.2(3)	222.6(3)–228.1(3)	165.7
FeCp	CoCp [b]	**10**	153.5(5)	–	230.7(4)	204.4(4)–211.2(4)	173.0
FeCp [a]	–		141.6(9)	271.5(6)	–	–	159.3

[a] Fulvene complex.

[b] Borabenzene complex.

[c] Length of the bridging bond between the five- and seven membered rings.

[d] Nonbonding distance between the metal center of the metallocene and the bridge-head carbon atom of the seven-membered ring.

[e] Distance between the metal center of the tropylium moiety and the bridge-head carbon atom of the seven membered ring.

[f] The largest and the smallest metal center-carbon atom distances in the tropylium moiety, except the distance *c*.

carbon–carbon single bond, and an increase in the bond length *c* between the metal center of the tropylium complex and the bridging carbon atom of the tropylium ligand: the extend of the bond elongation of *c* in the dicationic RuCp species is about twice as large as in the monocationic $Cr(CO)_3$ entity.

Similar structural effects — although to a lesser extent—are also observable for the cationic borabenzene complex **10**. The remarkable structural features of **10** are the lengthening of Co–B bond (230.7(4) pm) and shortening of the B–C(ferrocenyl) bond (153.5(5) pm) compared to other neutral (borabenzene)cobalt complexes [54]. In addition a tilt angle of 7° which encloses the B–C(ferrocenyl) bond vector and the vector bisecting the adjacent Cp plane, is observed. Such tilt angles are characteristic for boron substituted metallocenes wherein a Lewis acidity of the boron centers can be assumed [55].

These results imply an increasing electron with drawing ability in the order $Cr(CO)_3 < - < RuCp^+$ in accordance to the electrochemical results.

2.7. Nonlinear optical studies

The low lying excited states, the facile polarizability and the assignment of the HOMO and LUMO to donor and acceptor orbitals, respectively, make sesquifulvalene type complexes most promising NLO candidates. Therefore we subjected these complexes to HRS studies. However, an intrinsic shortcoming of this method is fluorescence due to two-photon absorption [33,56,57].

From the two-level approximation to calculate the first hyperpolarizability β, it becomes clear that β increases when the energy difference between the ground and the excited state decreases. Nevertheless, in an HRS experiment, the excited state will not be populated but the uptake of two photons of the frequency ω and the instantaneous emission of one photon of 2ω will be more probable the more the energy of 2ω ($E_{2\omega}$) approaches the energy of the excited state (E_{CT}). When $E_{2\omega}$ equals E_{CT}, the CT state can be populated by the absorption of two photons, whereupon relaxation can occur by means of fluorescence, which may affect considerable intensity at the frequency of the HRS signal (Fig. 12) and falsifies the measured intensity at $\lambda/2$ due to second harmonic generation.

In order to check for fluorescence enhancement we introduced special filters with a transmittance at different wave lengths at the entrance to the photomultiplier [32]. A fluorescence signal should have a considerable broad line width and a maximum of the emission band which casually only occur at $\lambda/2$. In sharp contrast to it the line width of the HRS signal is very small and the maximum has to be fixed. In our investigations we used a Q-switched Nd:YAG laser with $\lambda = 1064$ nm and detect the intensity of the scattered light at $\lambda = 532$ nm to determine the first hyperpolarizability as well as at $\lambda = 400, 450, 500, 560, 600, 650$ and 700 nm to get indications of fluorescence.

In Fig. 13 corresponding absorption and emission spectra of the reference *p*-nitroaniline (*p*NA) are shown corroborating the emission characteristic of the

Table 7
Experimental first hyperpolarizability β [a] and static first hyperpolarizability β_0 (calc. from Eq. (3)) of sesquifulvalene complexes tested as nonfluorescent, and examples from the literature for comparison

ML_n	$M'L'_n$		Z	λ_{max} (nm)	$\beta \times 10^{30}$ (esu)	$\beta_0 \times 10^{30}$ (esu)	Ref.
FeCp	$RuCp^+$	**11**	–	615	125 [b]	28	
RuCp	–	**21a**	–	536	378 [b]	4	
RuCp	$Cr(CO)_3$	**21b**	–	458	167 [b]	35	
RuCp	$RuCp^+$	**21c**	–	462	264 [b]	53	
RuCp	–	**22**	*E*–CH=CH–	600	649 [b]	120	
RuCp	$RuCp^+$	**23**	*E*–CH=CH–	549	358 [b]	17	
$Cp(Ph_3P)_2Ru$	$Ru(NH_3)_5^{3+}$		–C≡N–	716	157 [b]	69	[58]
$Ind(Ph_3P)_2Ru$	$W(CO)_5$		–C≡N–	392	40 [c]	15	[59]
$Cp(Ph_3P)_2Ru$	p-$C_6H_4NO_2$		–C≡C–C_6H_4-4-*E*–CH=CH–	476	1455 [d]	232	[13a]
$Ind(Ph_3P)_2Ru$	$W(CO)_5$		–C≡C–(*E*)–CH=CH–C_6H_4-4-C≡N	456	700 [c]	150	[59]

[a] Determined by hyper-Rayleigh scattering.

[b] Measured in $MeNO_2$, reference: pNA ($\beta = 34.6 \times 10^{-30}$ esu).

[c] Measured in CH_2Cl_2, reference: pNA ($\beta = 21.6 \times 10^{-30}$ esu).

[d] Measured in thf, reference: pNA ($\beta = 21.4 \times 10^{-30}$ esu).

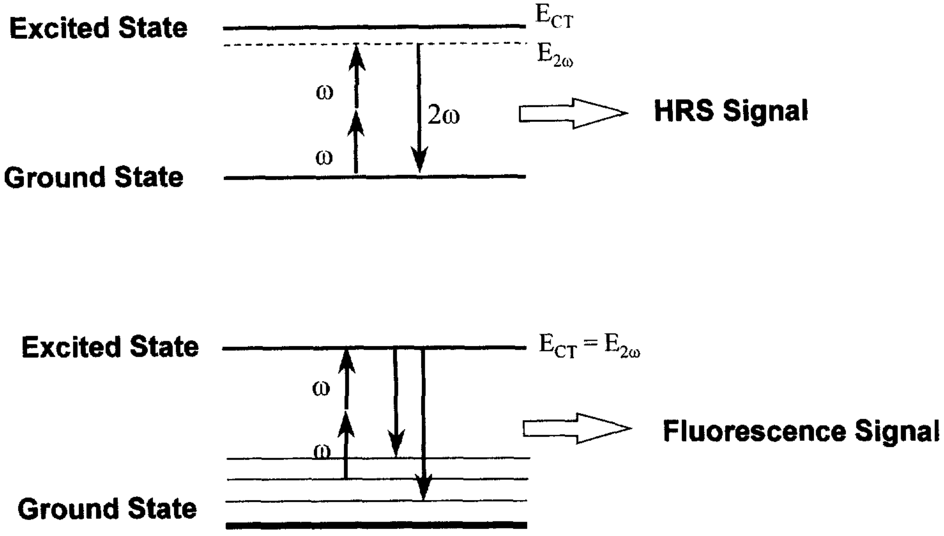


Fig. 12. Schematic drawing of the origin of the HRS and the fluorescence signal.

HRS signal of the second harmonic. Comparable HRS signals are recorded for the ruthenocenyl containing sesquifulvalene complexes **21c** and **23** as shown in Fig. 14. In contrast most of the ferrocenyl containing derivatives reveal broader emission spectra with a maximum not at $\lambda = 532$ nm (Fig. 15), indicating that these ferrocene derivatives show fluorescence due to two-photon absorption.

In Table 7, the determined β values of the nonfluorescent complexes are shown. Several features of the estimations of β and β_0 values are remarkable: (i) the closer the DA-CT maximum approaches the position of the HRS signal, the less reliable the β_0 values are: the directly coupled DA-complex (**21c**) shows a larger β_0 value than the olefinic bridged congener **23**; (ii) as expected from organic NLO chro mophores, the first hyperpolarizability increases with increasing chainlength (compare **21a** and **22**): although a stronger resonance enhancement takes place in **21a**, β of **22** is almost twice as large; (iii) the more the ruthenocenyl entity resembles a fulvene-like structure, the larger the β_0 value is (compare **21b** and **21c**); (iv) the β and β_0 value of **22** determined from CH_2Cl_2 and the $MeNO_2$ solutions confirm the long wavelength absorption as the CT absorption band which makes the largest contribution to the first hyperpolarizability: upon changing the solvent from CH_2Cl_2 to $MeNO_2$ both absorption bands undergo a distinct blue shift, which brings the low energy DA absorption band closer to the HRS signal whereas the so called LL-CT absorption band is shifted further away.

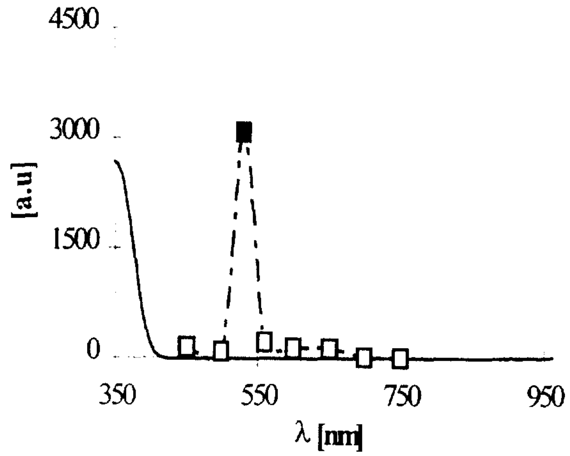


Fig. 13. Absorption and emission spectra of the HRS reference *p*-nitroanilin (*p*NA) (irradiation wavelength $\lambda = 1064$ nm).

Compared to other organometallic mono- and dinuclear NLO chromophores with extended π-linkers the results are very promising in regard of the short D–A distance in the sesquifulvalene type complexes (Table 7). Our results also are in contrast to the theoretical calculations of the first hyperpolarizabilities, which predict that sandwich compounds do not have a future in efficient NLO chromophores because of a poor electronic coupling between the electron releasing metal center and the π-system linking the donor and the acceptor in D-π-A systems [60].

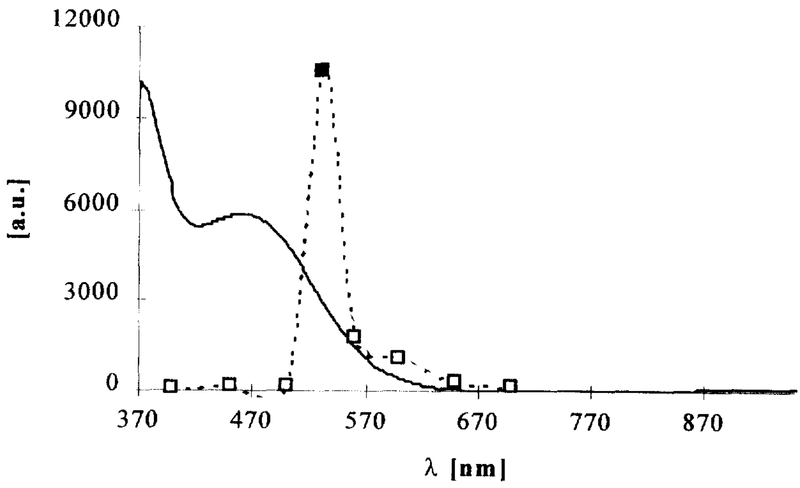


Fig. 14. Absorption and emission spectra of the diruthenium sesquifulvalene complexes **21c** and **22** (irradiation wavelength $\lambda = 1064$ nm).

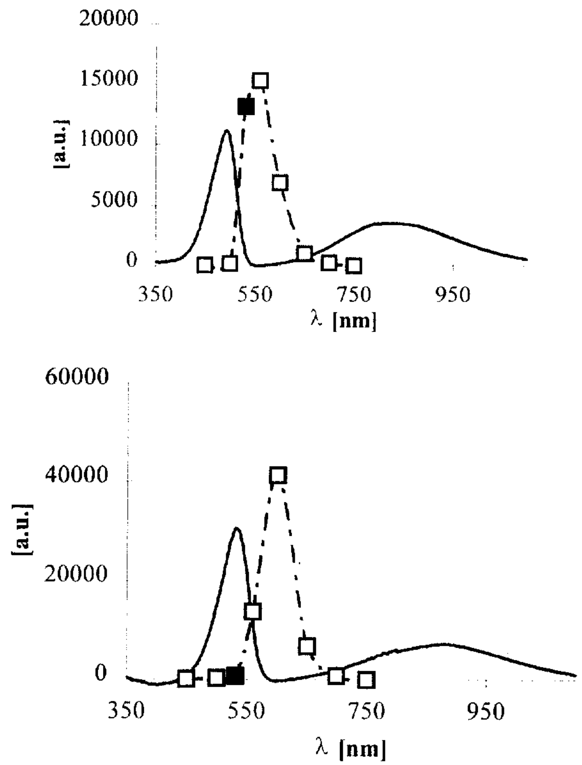


Fig. 15. Absorption and emission spectra of the ferrocenyl containing sesquifulvalene complexes **12** and **31a** (irradiation wavelength $\lambda = 1064$ nm).

3. Conclusions

Multifarious synthetic feasibilities opened a cornucopia of different mono- and dinuclear dipolar sesquifulvalene type complexes, whose application as NLO chromophores appears to be a successful concept. Despite the relatively short dipole lengths strong NLO effects can be obtained which are very promising with respect to longer π-linkers between the neutral donating sandwich and the cationic acceptor group of the seven-membered ring moiety or borabenzene complex.

The feasible chemical variations of the electronic properties of the donors and acceptors as well as of the π-bridge present the possibility of modulating the NLO properties involving the results of the first hyperpolarizability β and of the influence on the two-photon absorption. The two-photon fluorescence is observed in particular for mononuclear ferrocenyl derivatives showing low-lying DA-CT and LL-CT transitions, and is not necessarily a disadvantage because of its potential use, e.g. in NIR detector devices.

Since the chemical modification of metallocenes, particularly ferrocene, is straight forward [61], the linkage of the sesquifulvalene type NLO chromophores to polymers or liquid crystalline phases is quite obvious. On the other hand the presented cationic complexes are amphiphilic. Therefore, the complexes which are not moisture sensitive like the borabenzene species, can be used for Langmuir–Blodgett films.

Acknowledgements

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