Vinylogue Mono- and Bimetallic Cationic Sesquifulvalene and Monohydro Sesquifulvalene Complexes for Second Harmonic Generation

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Dedicated to Prof. Dr. Dieter Fenske on the occasion of his 60th birthday

Keywords: Sesquifulvalene / Ruthenium / X-ray structure determination / Hyper-Rayleigh Scattering (HRS) / Second harmonic generation (SHG)

The donor-acceptor complexes with a vinylogue monohydro sesquifulvalene and sesquifulvalene backbone of the type $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}ML](PF_6)_n$ [n = 0: ML = none (**1**), $Cr(CO)_3$ (**2**); n = 1: ML = $Ru(\eta^5\text{-}C_5H_5)$ (**3a**), $Ru(\eta^5\text{-}C_5Me_5)$ (**3b**)] and $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^7\text{-}C_7H_6)\}ML](PF_6)_n$ [n = 1: ML = none (**4**), $Cr(CO)_3$ (**5**); n = 2: ML = $Ru(\eta^5\text{-}C_5H_5)$ (**6a**), $Ru(\eta^5\text{-}C_5Me_5)$ (**6b**)], respectively, have been synthesised, and spectroscopically and structurally characterised. A charge-shift correlation was carried out by means of ^1H NMR spectroscopic studies and an increased ground-state donor-acceptor interaction in the order **5** < **6b** < **4** < **6a** was found. The corresponding donor-acceptor interaction in **3a** and **3b** varies by an insignificant amount. Hyper-Rayleigh scattering (HRS) was applied to determine the first hyperpolarisability β of the mono- and dicationic complexes **3a**–**6b**. The β values obtained for the cationic sesquifulvalene complexes **4**–**6b** are among the largest ever measured for ruthenocenyl containing complexes due to a strong resonance enhancement: the sesquifulvalene complexes **4**–**6a**, **6b** show first hyperpolarisabilities which range between 360 and 700×10^{-30} esu, whereas β for the monohydrosesquifulvalene complexes are considerably lower (75 and 162×10^{-30} esu). For the latter complexes the first hyperpolarisability doubles on going from $Ru(\eta^5\text{-}C_5Me_5)$ (**3b**) to $Ru(\eta^5\text{-}C_5H_5)$ (**3a**) in the acceptor unit.

Introduction

In our studies on mono- and dinuclear sesquifulvalene-type complexes[1] directed to nonlinear optical (NLO) properties of organometallic complexes[2] we have found that cationic ferrocenyl based sesquifulvalene complexes often reveal fluorescence[1c−1e] due to two-photon absorption (TPF)[3] in the hyper-Rayleigh scattering (HRS) experiments, with 1064 nm as the fundamental wavelength. Ruthenocenyl containing sesquifulvalene derivatives are different in that they do not show any TPF in comparable HRS studies, which allows for a reliable determination of the first hyperpolarisability β, a measure of the molecular capability for second harmonic generation (SHG).[2] In order to obtain a better understanding of the donor-acceptor interaction in sesquifulvalene-type complexes, directed to NLO properties, we investigated the ruthenocenyl based congeners in more detail.[4,5] In this work we focussed our interest on the vinylogue sesquifulvalene complexes (**I**) varying the electron-withdrawing force of the tropylium moiety as the electron acceptor (Figure 1). In addition, the cationic monohydro sesquifulvalene complexes **II** are synthesized and investigated, since the coordinated π-bonding system of

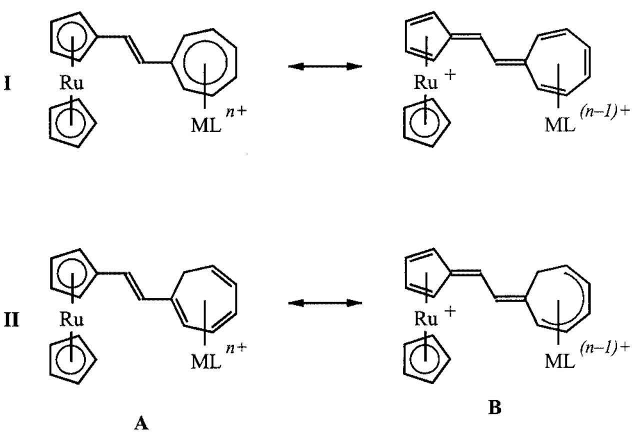

Figure 1. Vinylogue mono- and dinuclear sesquifulvalene (**I**) and monohydro sesquifulvalene (**II**) complexes (**I**: n = 1, ML = none, $Cr(CO)_3$; n = 2, ML = $Ru(\eta^5\text{-}C_5R_5)$, R = H, Me. **II**: n = 1, ML = $Ru(\eta^5\text{-}C_5R_5)$, R = H, Me)

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the cationic acceptor moiety is assumed to be electronically coupled to the ruthenocenyl donor. For both types of complexes the bonding situation can be described in two mesomeric forms, which differ between a bisaromatic (**I**, **A**) and cross-conjugated form (**I**, **B**) and an aromatic-homoaromatic (**II**, **A**) and cross-conjugated-dienyl (**II**, **B**) form, respectively.

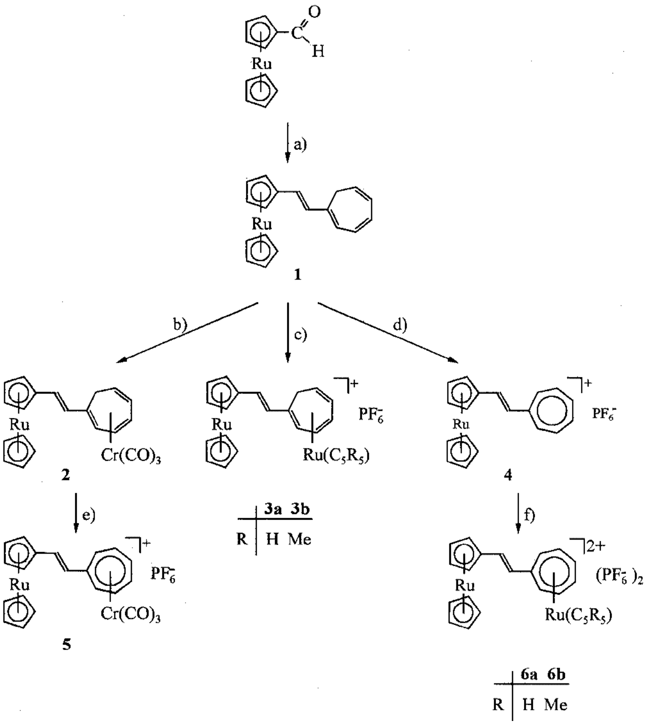
Former investigations on the archetype sesquifulvalene complexes[4,5a] illustrate an increasing SHG effect by reinforced donor-acceptor interaction in the electronic ground state, which is shown by means of NMR spectroscopic data as well as structural data. In terms of a valence bond picture a growing donor-acceptor interaction may be described as an increasing contribution of the cross-conjugated mesomeric form (**B**) to the electronic ground state (Figure 1).

The extension of our NLO studies on organometallic dipolar cationic donor-acceptor complexes to monohydro sesquifulvalene complexes was motivated by the concept that a transition from a homoaromatic to a conjugated-dienyl form (**II**) demands less energy than the loss of aromaticity as shown for the mesomeric forms of **I**. Additionally, mono cationic η^6-cycloheptatriene complexes are expected to be more stable than the corresponding dicationic η^7-cycloheptatrienylium complexes, due to the less electrophilic nature.

Results and Discussion

Synthesis: The cationic dinuclear vinylogue sesquifulvalene and monohydro sesquifulvalene complexes are readily prepared by starting with a Wittig–Horner–Wadsworth–Emmons (WHWE) reaction of the (cyclohepta-1,3,5-trienyl-1-methyl)diethylphosphonate[1d] with *n*BuLi, and formyl ruthenocene[6] (Scheme 1, see a), yielding the mononuclear, monohydro sesquifulvalene complex **1**. The coordination of the neutral unit $Cr(CO)_3$ (Scheme 1, see b) and the cationic half-sandwich moiety $Ru(\eta^5\text{-}C_5R_5)$ (Scheme 1, see c) to the cycloheptatriene ring yields the uncharged and charged dinuclear monohydro sesquifulvalene complexes **2** [ML = $Cr(CO)_3$] and **3** [ML = $Ru(\eta^5\text{-}C_5H_5)$: **3a**; ML = $Ru(\eta^5\text{-}C_5Me_5)$: **3b**], respectively. Hydride abstraction with $[Ph_3C]PF_6$ transforms **1** into the monocationic sesquifulvalene-type complex **4** (Scheme 1, see d), whereas the corresponding reaction with **2** leads to the monocationic, dinuclear sesquifulvalene complex **5** [ML = $Cr(CO)_3$] (Scheme 1, see e). The dicationic complexes **6** [ML = $Ru(\eta^5\text{-}C_5H_5)$: **6a**; ML = $Ru(\eta^5\text{-}C_5Me_5)$: **6b**] are achieved by addition of $[Ru(\eta^5\text{-}C_5R_5)(MeCN)_3]^+$ (R = H, Me) (Scheme 1, see f) to **4**.

The cationic products are complexes that are orange (**3a, 3b**) to dark-red in colour (**4–6a**, **6b**), indicating an increased electronic interaction in the cationic state compared to the neutral monohydro sesquifulvalene starting complex **1,** which has light yellow crystals. The monocationic and dicationic complexes are very soluble in CH_2Cl_2 and $MeNO_2$, respectively. Solutions of **1**, **2**, **3a**, **3b**, **6a** and **6b** are moderately inert in air, whereas **4** and **5** are sensitive to moisture.



Scheme 1. Synthesis of the mono- and dinuclear monohydro sesquifulvalene and sesquifulvalene type complexes **3a** – **6b**: a) THF; *n*BuLi. $C_7H_7CH_2P(O)(OEt)_2$; b) THF, $Cr(CO)_3(EtCN)_3$; c) CH_2Cl_2, $[Ru(\eta^5\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me); d) CH_2Cl_2, $[CPh_3]PF_6$; f) CH_2Cl_2 $[Ru(\eta^5\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me).

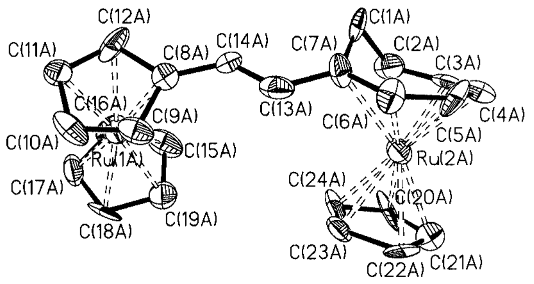


Figure 2. Molecular structure of $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5H_5)]PF_6$ (**3a**) (50% ellipsoids, only one of the two independent complex cations is shown, the hydrogen atoms and the counterion are omitted for clarity).

X-ray Structure Determination: Suitable crystals for X-ray structure analysis were obtained by gas phase diffusion of Et_2O in concentrated solutions of the complexes in CH_2Cl_2 (**3a**, **3b**) and $MeNO_2$ (**6a**). Complex **3a** crystallises as twins. However, the twinning law could not be determined and thus reflexes had to be excluded by hand with $F(\text{obsd.}) \geq 4\,F(\text{calcd.})$ mostly from the *hk*3, *hk*6, etc. planes. In addition a superstructure was found, in which the *a*-axis was tripled resulting in six independent molecules per asymmetric unit. We circumvented the superstructure problem by solving and refining the structure by standard methods using the smaller unit cell. The dinuclear, monocationic monohydro sesquifulvalene complex **3a** crystallises in the monoclinic space group $P2_1/c$, whereas the pentamethylated derivative **3b** crystallises in a triclinic space group $P\bar{1}$. For

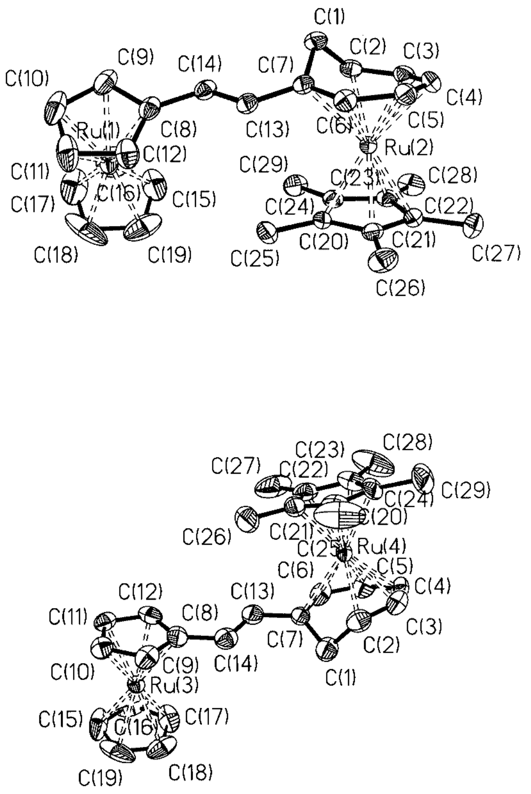


Figure 3. Molecular structures of $[\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5Me_5)]PF_6$ (**3b**). The *cisoid* (top) and *transoid* (bottom) conformers are shown (50% ellipsoids, the hydrogen atoms, the solvent molecules and counterions are omitted for clarity).

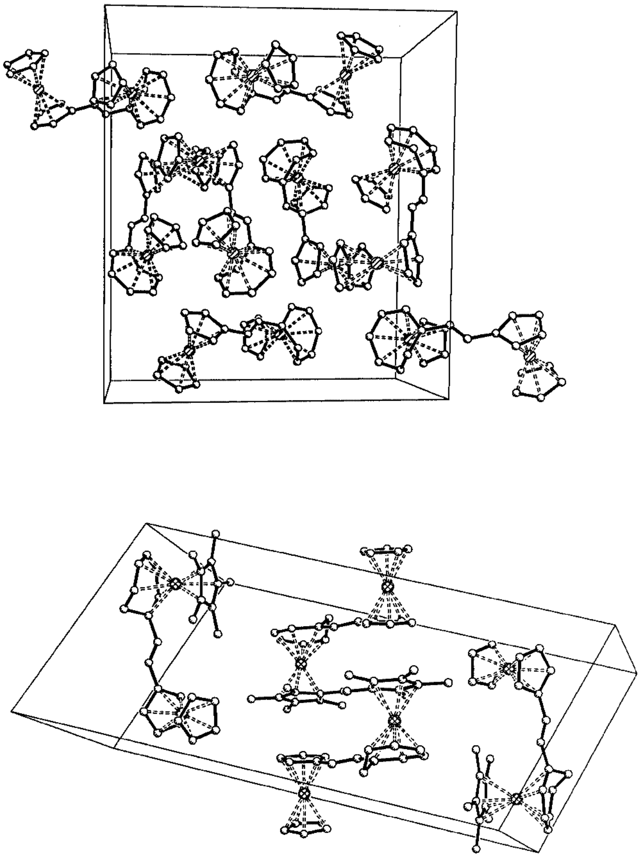


Figure 4. Unit cells of **3a** (top) and **3b** (bottom), illustrating the pairwise arrangements of the two planar chiral enantiomers in pairs (the counterions and solvent molecules are omitted for clarity).

both compounds two independent molecules within the asymmetric unit are found (Figure 2, Figure 3). Since **3a** and **3b** are planar-chiral compounds due to the coordination of the cycloheptatriene ring to a metal centre and its monosubstitution in the proximal position with respect to the sp^3 carbon atom C1, the single crystals are racemic mixtures of both enantiomers. Additionally, for **3b** the solvent molecules $MeNO_2$ and CH_2Cl_2 co-crystallise in a ratio of 2:1. The cations of **3a** and **3b** posses an *E*-configuration, and the sp^3 carbon atom C1 of the seven-membered ring occupies a *trans*-position relative to the hydrogen atom of the neighbouring CH group of the vinyl bridge, which is sterically less demanding. Whereas the monohydro sesquifulvalene cations of **3a** only adopt a *cisoid* conformation in the crystal, the cations of **3b** are packed in a *transoid* and in a *cisoid* conformation (Figure 2, Figure 3, Figure 4). The *transoid* conformation is unprecedented, since all known expanded sesquifulvalene complexes crystallise in a *cisoid* conformation[1] in contrast to the archetype dinuclear sesquifulvalene complexes with directly linked five- and seven-membered rings, which only demonstrate a *transoid* conformation due to steric repulsion.[1a−1c,5a] The *cisoid* complexes of **3a** and **3b** demonstrate a relatively large tilt angle of 47 and 38.1°, respectively, between the best plane of the substituted five-membered ring of the donor moiety and the best plane of the cycloheptatriene ligand defined by the carbon atoms C2−C7; the corresponding tilt angle in the *transoid* conformation only amounts to 20.8°.

The bond lengths and angles of the ruthenocenyl donor moiety are quite similar to those of other ruthenocene derivatives.[6,7]

The cycloheptatriene ligand of the acceptor terminus in **3a** and **3b** adopts a flat boat conformation with a steep bow for the endocyclic methylene group that deflects about 60° from the best plane defined by C2−C7. Similar structural features are known from other cycloheptatriene complexes although with corresponding angles below 50°.[8] The bridging unit C7−C13−C14−C8 does not show any significant deviation from expected bond lengths of sp^2-sp^2 carbon-carbon single and double bonds, indicating only a subtle charge delocalisation in the crystalline state. It is concluded from the bond elongation of more than 10 pm between Ru2 and C7, that a weak donor-acceptor charge equilisation still occurs. This bond elongation indicates electronic communication between the electron donating and accepting termini, which has been found in archetype sesquifulvalene complexes.[1e,5a] Thus, by means of structural data, the electronic ground state of the monohydro sesquifulvalene complexes **3a** and **3b** in the solid state is properly described by the mesomeric form **II**, **A** in Figure 1.

The X-ray structure analysis of the dinuclear dicationic vinylogue sesquifulvalene complex **6a** rendered more diffi-

Table 1. Crystallographic data of $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5H_5)]PF_6$ (**3a**), $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5Me_5)]PF_6$ (**3b**) and $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5H_5)](PF_6)_2$ (**6a**)

	3a	**3b**	**6a**
Empirical formula	$C_{48}H_{46}F_{12}P_2Ru_4$	$C_{29}H_{33}F_6$ P $Ru_2 \times 1/3(CH_3NO_2) \times 2/3\ (CH_2Cl_2)$	$C_{24}H_{22}F_{12}P_2Ru_2 \times (CH_3NO_2)$
Formula mass	1317.07	805.95	863.54
T [K]	153(2)	173(2)	173(2)
λ [pm]	71.073	71.073	71.073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [pm]	1955.0(17)	1174.8(1)	1060.9(2)
b [pm]	1733.5(15)	1179.6(1)	1385.0(1)
c [pm]	1423.2(12)	2379.7(1)	1070.6(2)
α [°]		82.73(1)	80.57(1)
β [°]	96.704(8)	75.81(1)	83.36(1)
γ [°]		75.37(1)	69.29(1)
V [10^6 pm^3]	4790(7)	3057.7(4)	1448.6(4)
Z	8	4	2
$\rho_{calcd.}$ [Mg/m^3]	1.826	1.751	1.980
μ [mm^{-1}]	1.384	1.219	1.257
F (000)	2592	1611	848
Crystal size [mm^3]	0.1 × 0.2 × 0.2	0.6 × 0.4 × 0.3	0.4 × 0.4 × 0.2
Scan range [°]	1.57−25.00	0.88−39.14	1.59−28.73
Index range	$-23 \le h \le 23$ $-20 \le k \le 20$ $-16 \le l \le 16$	$-15 \le h \le 16$ $-16 \le k \le 11$ $-31 \le l \le 32$	$-14 \le h \le 11$ $-18 \le k \le 15$ $-14 \le l \le 12$
Reflections measured	43430	20954	10006
Reflections unique	8120	14884	7063
Rint	0.3217	0.0156	0.0246
Parameters	575	787	445
Reflections $I > 4\ \sigma(I)$	8120[c]	12716	5517
GoF[a]	0.989	1.032	1.030
$R1/wR2$ ($I > 2\sigma(I)$)[b]	0.1127/0.2312	0.0375/0.0886	0.0436/0.1052
$R1/wR2$ (all data)[b]	0.1981/0.2701	0.0469/0.0946	0.0637/0.1153
Resd. min/max. [e-/ Å^3]	−1.453/1.402	−0.819/1.296	−0.957/1.167

[a] GoF (goodness of fit) = $[\Sigma w(F_o^2 - F_c^2)^2/n - p]^{1/2}$ (n = numbers of reflections, p = numbers of parameters). [b] $R1 = \Sigma\|F_o| - |F_c\| / \Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] For refinement all unique reflections were used.

culties due to a disorder in the vinylene bridge (Figure 5), which is commonly observed in vinylogue sesquifulvalene complexes.[1a,1c,1d,9] The best structural solution was obtained by assuming two different molecules in the ratio 3:1. To separate the atoms of the sesquifulvalene ligand restrictions were necessary, which do not allow a more detailed discussion. Nevertheless, the short carbon-carbon bond C13−C14 [132.1(7) pm] differs distinctly from the carbon-carbon bond C8−C14 [145.3(6) pm) and C7−C13 [144.9(6) p], clearly indicating a carbon-carbon double and single bond, respectively.

The structure data of the cyclopentadienyl-ruthenium moieties in **6a** greatly resemble the data of other CpRu units in Ru sandwich compounds (vide supra and ref.[7]). It is worthwhile noting that − as for **3a** and **3b** − the bond length between the Ru2 atom and the bridge-head carbon atom C7 is elongated by more than 10 pm compared with the other Ru−C bond lengths of the $Ru(\eta^7\text{-}C_7H_6)$ moiety.

Spectroscopic Studies: Considering the two different mesomeric forms depicted in Figure 1, it becomes evident that an increasing contribution of the mesomeric form **B** to the ground state of the complexes under study results in a decrease of the bond order of the carbon-carbon bond C13−C14. Hence, spectroscopic properties based on the C,C bond order should be sensitive probes for the examination of the donor-acceptor interaction.[10]

One indicative probe for the C13−C14 bond order is the energy of the C,C stretching vibration of the carbon-carbon bond C13−C14,[10] which differs only marginally for the cycloheptatriene derivatives but the decrease is more pronounced for the tropylium congeners in the order **5** > **6b** > **4** > **6a** (Table 3). Although the energy of the C,C stretching vibration is still representative of a C=C bond, a distinct charge delocalisation can be stated for the electronic ground state of **6a,** in particular, the amount of which can be taken as a measure of the donor-acceptor interaction. From the energy of the stretching mode of the C,C double bond one can conclude that the donor-acceptor interaction is weakest for **1−3** and **5**, and strongest for **6a**, in this series.

This result is in excellent agreement with the NMR spectroscopic data. One NMR probe for the C13−C14 bond order is the *trans* ^{1}H-^{1}H coupling constant of the bridging vinyl group.[10−12] For a real carbon-carbon double bond a *trans*-$^3J(H_\alpha-H_\beta)$ coupling constant of about 16 Hz is expected according to weak donor-acceptor interaction. With increasing charge delocalisation the C13−C14 bond order decreases and hence the ^{1}H-^{1}H coupling constant too;[10] a C,C single bond causes coupling constants of about at least

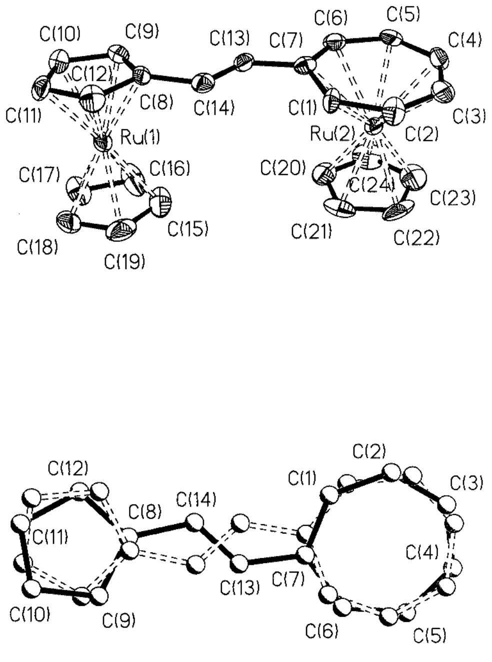


Figure 5. Molecular structure of $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5H_5)](PF_6)_2$ (**6a**) (50% ellipsoids, the hydrogen atoms and counterions are omitted for clarity). The drawing at the bottom demonstrates the disorder of the vinylogue sesquifulvalene ligand.

10 Hz. Whereas for the neutral and monocationic monohydro sesquifulvalene complexes **1**, **2**, **3a**, **3b** the $^3J(H_\alpha{-}H_\beta)$ only varies between 15.8 and 15.6 Hz, indicating a more or less unchanged carbon-carbon double bond, the corresponding coupling constants of the vinylogue sesquifulvalene complexes decrease from 16 Hz for **5** to 15.4 Hz for **4** and **6b** and drops to 13.4 Hz for **6a** (Table 3).

Another NMR probe for donor-acceptor interactions in cationic NLO chromophores under study is the charge-shift correlation of Ru sandwich complexes. A linear dependence between the shift of the cyclopentadienyl proton signals and the charge per sandwich complex in $[(\eta^5\text{-}C_5H_5)Ru(\eta^n\text{-}C_nH_n)]^{m+}$ ($n = 5$, $m = 0$; $n = 6$, $m = 1$; $n = 7$, $m = 2$) is found, which allows the calculation of the actual charge for a sandwich complex containing a $(\eta^5\text{-}C_5H_5)Ru$ unit, when the shift of the signal of the cyclopentadienyl protons is known.[5a,5b] The singlet of the unsubstituted cyclopentadienyl ligand of the metallocene donor and of the $Ru(\eta^5\text{-}C_5H_5)$ unit of the acceptor is taken as the monitoring signal. The corresponding NMR shifts are listed in Table 3, and clearly indicate an increasing positive charge on the metallocene terminus in the order **5** < **6b** < **4** < **6a** for the tropylium derivatives. For **6a** a positive charge of +0.61 is calculated for the ruthenocenyl donor in the ground state which is in good harmony with the diminishing positive charge on the acceptor to +1.44 with respect to the positive charge of +2.0 in $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_7H_7)]^{2+}$ (Table 3). It is worth noting for the studies concerning the $^1H_\alpha$-$^1H_\beta$ coupling constants that the change of the donor-acceptor interaction in this series of complexes is the largest on going from complex **6b** (or, **5**) to **6a**, which is in agreement with the IR spectroscopic studies.

Table 2. Selected interatomic distances [pm] and angles [°] of $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5H_5)]PF_6$ (**3a**), $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5Me_5)]PF_6$ (**3b**) and $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5H_5)](PF_6)_2$ (**6a**).

	3a[a]	**3b** (*cisoid*)	**3b** (*transoid*)	**6a**
C8−C9	148(2)	143.8(5)	140.1(6)	143.0(10)
C9−C10	140(3)	142.1(6)	140.4(6)	141.9(4)
C10−C11	151(3)	141.7(7)	141.5(6)	141.9(4)
C11−C12	141(3)	143.1(5)	142.4(6)	141.9(4)
C12−C8	150(3)	143.2(5)	144.7(6)	143.0(10)
C7−C1	157(3)	151.6(4)	148.5(5)	141.7(10)
C1−C2	159(3)	150.7(4)	148.2(6)	140.9(2)
C2−C3	142(3)	139.4(5)	136.8(6)	140.9(2
C3−C4	144(3)	142.6(5)	139.0(6)	140.9(2
C4−C5	141(3)	142.5(5)	142.2(6)	140.9(2
C5−C6	140(3)	143.3(5)	143.3(6)	140.9(2
C6−C7	153(2)	140.1(4)	145.1(6)	141.7(10)
Ru1−C8	229.7(18)	220.1(3)	220.1(4)	215.2(5)
Ru1−C9	221.2(19)	216.7(4)	219.7(4)	215.9(6)
Ru1−C10	224(2)	217.6(4)	219.1(4)	220.0(6)
Ru1−C11	222(2)	218.0(4)	217.8(4)	218.5(6)
Ru1−C12	222(2)	219.2(4)	217.8(4)	216.5(7)
Ru2−C1	305(2)	292.7(4)	293.4(4)	224.4(6)
Ru2−C2	232(2)	227.4(3)	228.5(4)	222.7(7)
Ru2−C3	202.2(17)	218.8(3)	219.7(4)	224.5(7)
Ru2−C4	225.1(19)	222.2(3)	222.3(4)	224.4(7)
Ru2−C5	226(2)	221.5(3)	220.6(4)	224.9(8)
Ru2−C6	227.0(17)	221.2(3)	222.0(4)	227.4(6)
Ru2−C7	245(2)	238.1(3)	239.2(3)	238.7(5)
C7−C13	147(3)	145.8(4)	146.8(5)	144.9(6)
C13−C14	136(3)	134.3(4)	131.1(6)	132.1(7)
C14−C8	146(2)	145.4(5)	147.5(6)	145.3(6)
$[(C_5H_4)](C2{-}C7)$ [°]	47	38.1(1)	20.8(2)	28.5
[C7,C1,C2]-[C2,C3,C6,C7] [°]	56.8	60.8(3)	61.0(4)	

[a] **3a** crystallises with two different molecules (A and B) within the unit cell. In this table only the data for one molecule (A) is given (see Figure 2). The corresponding data for molecule B are equal to A within the margin of error.

UV/Vis spectroscopic studies were performed with solutions of different polarity such as dichloromethane and nitromethane, to elucidate solvatochromism which gives an indication of the dipole change $\Delta\mu$ between the ground and the excited state,[13] and is thus relevant for the static first hyperpolarisability β_0 according to the two-level approximation.[14]

The electronic excitation spectra of the vinylogue sesquifulvalene complexes **4**−**6a**, **6b** exhibit two intense absorption bands in the visible or near UV region (Figure 6, Table 4). As outlined earlier for metallocene containing donor-acceptor complexes,[1e,5a,12] the high-energy absorption band is assigned to a donor(ligand)−acceptor charge-transfer (D_L-A CT) transition whereas the low energy band is caused by a donor(metal)-acceptor charge-transfer (D_M-A CT) transition. In accordance with other cationic sesquifulvalene donor-acceptor complexes the energy of the D_M-A CT transitions increase when the acceptor unit A changes in the order $(C_7H_6)^+ < [(\eta^7\text{-}C_7H_6)Ru(\eta^5\text{-}C_5H_5)]^{2+} < [(\eta^7\text{-}C_7H_6)Ru(\eta^5\text{-}C_5Me_5)]^{2+} < [(\eta^7\text{-}C_7H_6)Cr(CO)_3]^+$ [1e,5] The

Table 3. Selected IR- and NMR spectroscopic data of the vinylogue sesquifulvalene and monohydro sesquifulvalene complexes $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2A]^{n+}$

A	n		IR[a] $\tilde{\nu}$ (C=C) (cm^{-1})	^{1}H NMR[b] $\delta(C_5H_5)$[c] (ppm)	Charge[d][e]	$\delta(C_5H_5)$[f] (ppm)	Charge[e][g]	$\delta(H_\alpha)$ (ppm)	$\delta(H_\beta)$ (ppm)	$^3J(H_\alpha H_\beta)$ (Hz)	^{13}C NMR[b] $\delta(C_5H_5)$[c] (ppm)	$\delta(C_5H_5)$[f] (ppm)
$(C_7H_7)\}$	0	**1**	1622							15.8		
$(\eta^6\text{-}C_7H_7)\}Cr(CO)_3$	0	**2**	1619							15.6		
$(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5H_5)$	1	**3a**	1624	4.61	+ 0.06	5.35	+ 0.90	6.87	6.40	15.9	72.9	85.3
$(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5Me_5)$	1	**3b**	1619	4.66	+ 0.11			6.89	6.25	15.8	72.5	
$(C_7H_6)\}$	1	**4**	1603	4.78	+ 0.24			8.18	6.78	15.4	74.8	
$(\eta^7\text{-}C_7H_6)\}Cr(CO)_3$	1	**5**	1624	4.65	+ 0.10			7.63	6.81	16.0	73.3	
$(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5H_5)^+$	2	**6a**	1599	5.11	+ 0.61	5.86	+ 1.44	7.55	5.92	13.4	81.9	88.2
$(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5Me_5)^+$	2	**6b**	1609	4.75	+ 0.21			7.98	6.77	15.4	73.9	

[a] KBr pills. [b] CD_3NO_2 solutions. [c] Unsubstituted Cp ligand of the ruthenocenyl donor unit. [d] Charge on the donor unit. [e] Calculated from the charge-shift correlation in ref.[5b] [f] Unsubstituted Cp ligand of the acceptor unit **A**. [g] Charge on the acceptor unit.

Table 4. UV/Vis data of the vinylogue sesquifulvalene and monohydro sesquifulvalene complexes of $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_4A]^{n+}$ and their first hyperpolarisability β determined by HRS.

A	n		λ_{max} (nm) D_L-A CT		$\Delta\tilde{\nu}$ (cm^{-1})	λ_{max} (nm) D_M-A CT		$\Delta\tilde{\nu}$ (cm^{-1})	β[b]	β_0[b][c]
			CH_2Cl_2 (ε)[a]	$MeNO_2$ (ε)[a]		CH_2Cl_2 (ε)[a]	$MeNO_2$ (ε)[a]			
$(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5H_5)$	1	**3a**	–	–		423 (10490)	404 (9410)	−1112(2)	162[d]	50
$(\eta^6\text{-}C_7H_7)\}Ru(\eta^5\text{-}C_5Me_5)$	1	**3b**	–	–		424 (11460)	409 (10225)	−865(2)	75[d] (87)[e]	23 (30)
$(C_7H_6)\}$	1	**4**	480 (16265)	470 (12036)	−443(2)	640 (22559)	600 (16427)	−1042(2)	362[d] (649)[e]	105[f] (120)[f]
$(\eta^7\text{-}C_7H_6)\}Cr(CO)_3$	1	**5**	384 (8730)	< 370	–	533 (8375)	490 (7155)	−1611(2)	497[e]	59[f]
$(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5H_5)$	2	**6a**	> 400 (sh) (10760)	400	–	600 (sh)	560 (4975)	−1190(2)	358[e]	28[f]
$(\eta^7\text{-}C_7H_6)\}Ru(\eta^5\text{-}C_5Me_5)$	2	**6b**	438 (sh)	409 (10580)	−1619(2)	594 (sh)	541 (9280)	−1649(2)	701[e]	17[f]

[a] $M^{-1}cm^{-1}$. [b] Given as units of 10^{-30} esu; as a reference *p*-nitroaniline was used: $\beta(CH_2Cl_2) = 21.6 \times 10^{-30}$ esu,[22] $\beta(MeNO_2) = 34.6 \times 10^{-30}$ esu.[23] [c] Calculated from $\beta_0 = \beta(HRS)\,[(1 - 4\lambda^2_{max}/\lambda^2)(1 - \lambda^2_{max}/\lambda^2)]$.[14] [d] In CH_2Cl_2. [e] In $MeNO_2$. [f] The D_M-A CT transition was taken into account for the calculation of β_0.

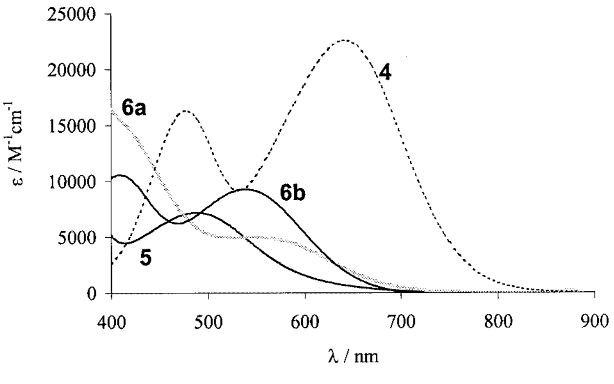


Figure 6. UV/Vis spectra of the vinylogue sesquifulvalene complexes $[(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}(\eta^5\text{-}C_5H_4)C_2H_2(\eta^7\text{-}C_7H_6)\}ML](PF_6)_n$ [n = 1, ML = none (**4**), $Cr(CO)_3$ (**5**); n = 2, ML = $Ru(\eta^5\text{-}C_5R_5)$, R = H (**6a**), Me (**6b**)] obtained from $MeNO_2$ solutions.

extraordinary low-energy shift of the D_M-A CT band of the mononuclear complex **4** compared with the dinuclear species may be explained by the formation of additional molecular orbitals (MO) upon coordination of a metal-ligand fragment to the tropylium unit, thus forming occupied bonding MOs which would be lower in energy, and empty anti-bonding MOs which would be higher in energy compared with the orbitals of the initially uncoordinated tropylium moiety.

The monohydro sesquifulvalene complexes **3a** and **3b** only reveal one intense absorption band with a λ_{max} between 400 and 430 nm (Figure 7). Since the energetically lower lying absorption bands in metallocene containing donor-acceptor complexes are generally explained as a D_M-A CT transition, the low-lying absorption band for **3a** (λ_{max} = 423 nm) and **3b** (λ_{max} = 424 nm) is also assigned to a D_M-A CT transition.

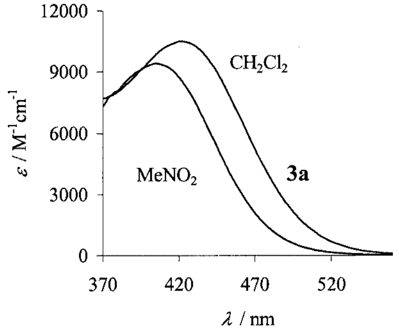


Figure 7. UV/Vis spectra of the vinylogue monohydro sesquifulvalene complex [(η^5-C_5H_5)Ru{μ-(η^5-C_5H_4)C_2H_2(η^6-C_7H_7)}Ru(η^5-C_5H_5)]PF_6 (**3a**) obtained from CH_2Cl_2 and $MeNO_2$ solutions indicating the hypsochromic shift of λ_{max} by increasing solvent polarity.

All of the above mentioned absorption bands undergo considerable negative solvatochromism i.e. hypsochromic shift, with increasing solvent polarity indicating a more localized positive charge in the ground state than in the excited state, or even an inversion of the polarity upon excitation. The extent of the solvatochromism of both of the absorption bands for **4–6a**, **6b** is comparable, indicating a similar change in polarity for both of the CT transitions. Therefore, both CT transitions should contribute considerably to the first hyperpolarisability. The situation is different for **3a** and **3b,** which only reveal one absorption band close to the second harmonic generation. The cut off of the absorption bands around 500 nm warrants a reliable calculation of β_0 for **3a** and **3b**.

NLO Measurements: The low-lying excited states of the sesquifulvalene complexes under study, their facile polarisability as indicated by their strong solvatochromism, and the assignment of the HOMOs and LUMOs to the donor and acceptor orbitals, respectively, make these types of complexes very promising for the second harmonic generation. The cationic nature of the sesquifulvalene complexes requires the hyper-Rayleigh scattering (HRS)[15] as the only method for determining the first hyperpolarisability β, which can be regarded as the molecular capability of doubling the frequency of incoming light. However, a draw-back of the HRS method may be fluorescence due to two-photon absorption.[16–18] Since the realisation of the problem of multiphoton absorption induced fluorescence concerning the determination of the first hyperpolarisability, several techniques have been investigated to overcome this problem. These include long wavelength measurements,[10,19,20] time resolved HRS[19] measurement of the two-photon fluorescence spectrum to abstract the fluorescence contribution to the HRS signal,[21] and, just recently, a high-frequency demodulating technique to suppress the multiphoton fluorescence contribution to the HRS signal.[16] A "low cost" check for the two-photon fluorescence was recently described,[1d,1e] and uses bandpass filters with peak transmittance at different wavelengths, which are introduced in front of the photomultiplier of the HRS set-up. The broad fluorescence signal, which yields the emission maximum at λ/2 of the fundamental wavelength, is easily discerned from the narrow second harmonic signal at λ/2.

In the course of this study no fluorescence was observed (Figure 8). Therefore, for all dipolar mono- and dicationic complexes under study the first hyperpolarisability β was determined by means of HRS (Table 4).

Since the wavelengths of the absorption bands are in close proximity to the wavelength of the SHG signal, the obtained β values are strongly resonance enhanced and are therefore corrected by the dispersion term of the two-level model.[14] It has to be emphasised that the β_0 values for **4**, **5**, **6a** and **6b** are not very reliable, since only the low-energy D_M-A CT transition was taken into account for calculating β_0; the high energy D_L-A CT transition will also contribute to the first hyperpolarisability as indicated by the strong solvatochromism of both CT transitions. However, it is worth noting that the first hyperpolarisability for **4** decreases by almost a factor of two on going from a $MeNO_2$ solution to the less polar CH_2Cl_2 solution, although λ_{max} of the D_L-A CT transition is shifted closer to λ(SHG) for CH_2Cl_2 solutions than for $MeNO_2$ solutions. The opposite is true for the D_M-A CT transition. This behaviour points to larger contributions of the D_M-A CT transition to the β values than the D_L-A CT transition.

The HRS-determined first hyperpolarisability of the vinylogue mono- and dicationic sesquifulvalene complexes **4**, **5**, **6a**, and **6b** (Table 4) belong to the largest values ever obtained for ruthenocenyl containing dipolar NLO chromophores,[24] in particular, when the relatively small molecular mass is taken into account, which is often used as a figure of merit. However, it has to be realized that the first hyperpolarisabilities are strongly resonance enhanced by different contributions of D_L-A CT and D_M-A CT transitions. Therefore, no correlation between the β values of **4**, **5**, **6a** and **6b** and their ground-state donor-acceptor interaction as demonstrated by IR- and NMR spectroscopy, can be stated, although the strongest SHG effect may be expected for **6a** taking into account the ground state donor-acceptor interaction. This can only be proven when λ(SHG) is beyond the cut-off of λ(D_M-A CT).

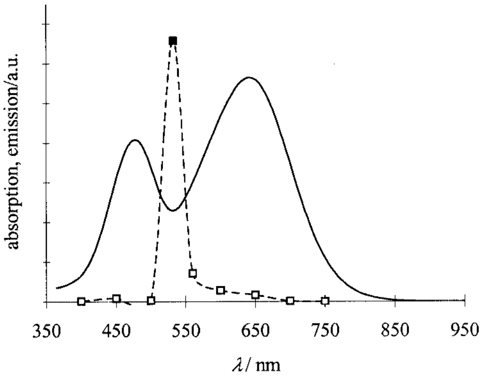


Figure 8. Representative UV/Vis absorption spectrum for vinylogue sesquifulvalene complexes [(η^5-C_5H_5)Ru{μ-(η^5-C_5H_4)C_2H_2(η^7-C_7H_6)}ML]PF_6 (ML: = none: **4**) obtained from CH_2Cl_2 solution (solid line) and the corresponding scattered spectrum obtained from HRS studies (dotted line) indicating only the SHG signal (a.u. = arbitrary units)

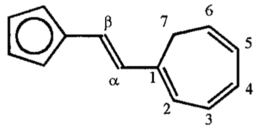
In contrast the cut-off of the absorption band of the D_M-A CT transition of **3a** and **3b** is below λ(SHG), and thus allows a reliable determination of the first hyperpolarisability β, which doubles on going from **3b** (ML = Ru(η^5-C_5Me_5); $\beta = 75 \times 10^{-30}$ esu) to **3a** (ML = Ru(η^5-C_5H_5); $\beta = 162 \times 10^{-30}$esu). This also holds for the β_0 values, since λ_{max} of **3a** and **3b** is almost identical, and is in excellent agreement with the findings from archetype dinuclear sesquifulvalene complexes which also demonstrate a doubling or almost doubling of β and β_0 values when the metal-ligand fragment on the acceptor site is changed from Ru(η^5-C_5Me_5) to Ru(η^5-C_5H_5).[4,5a] The reason for the lack of correlation between the ground-state spectroscopic data and the SHG effect for **3a** and **3b** remains unclear for the time being, and may reflect that the nature of the ground state *and* the excited state determine the SHG effect.

Conclusion

In contrast to ferrocenyl derivatives of vinylogue sesquifulvalene complexes the ruthenocenyl congeners do not show fluorescence, which can be caused by a two photon absorption in HRS experiments with a fundamental wavelength of 1064 nm.[1d,1e] The obtained β values are the highest ever measured for ruthenocenyl containing donor-acceptor NLO chromophores and in particular when they are correlated to the molecular mass of corresponding complexes. However, these β values are strongly resonance enhanced by an energetically low-lying D_M-A CT transition and an energetically higher lying D_L-A CT transition. The different contributions to the resonance enhancement prevent a rationalisation of the NLO property, i.e. the capability of frequency doubling by electronic ground state properties. This is for example the bond order in the olefinic linker between the donor and the acceptor, which can be characterised by the energy of the C=C stretching mode in IR-spectroscopy and $^3J(^1H\text{-}^1H)$ coupling constants between the protons of this double bond. The situation changes for the monohydro sesquifulvalene complexes, which reveal one electronic absorption band with λ_{max} considerably smaller than λ(SHG) and a cut off at about 500 nm. Reliable values for the first hyperpolarisability β have been determined and thus reasonable β_0 values can be calculated. These data confirm the results obtained for dinuclear archetype sesquifulvalene complexes: the first hyperpolarisability is roughly doubled on going from $[Ru(\eta^5\text{-}C_5Me_5)]^+$ to $[Ru(\eta^5\text{-}C_5H_5)]^+$ complex fragments on the acceptor site.

Experimental Section

Manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were saturated with nitrogen, and diethyl ether (Et_2O), tetrahydrofuran (THF), *n*-hexane and toluene were freshly distilled from the appropriate alkali metal or metal alloy. Dichloromethane (CH_2Cl_2) and nitromethane ($MeNO_2$) were dried over calcium hydride. NMR: Varian Gemini 200 BB; Bruker AM 360; measured at 295 K rel. TMS. UV/Vis: Perkin−Elmer Model 554. IR: KBr pills, FT-IR, Perkin−Elmer Model 325. MS: Finnigan MAT 311 A (EI-MS). Elemental analyses: CHN−O-Rapid (Zentrale Elementanalytik, Fachbereich Chemie, Universität Hamburg), Fa. Heraeus. Tropylium hexafluorophosphate (**7**),[25] formyl ruthenocene,[6] triphenylcarbenium hexafluorophosphate/tetrafluoroborate,[26] (tricarbonyl)(trispropionitrile)chromium(0),[27] (trisacetonitrile)(η^5-cyclopentadienyl)ruthenium(II) hexafluorophosphate,[28] (trisacetonitrile)(η^5-pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate,[29] (cylohepta-1,3,5-trienyl-1-methyl)diethylphosphonate[1d] were synthesised according to literature procedures.



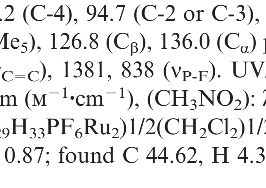
***E*-(1-Ruthenocenyl)(2-cyclohepta-1′,3′,5′-trien-1′-yl)ethene (1), Method A:** A solution of Li*n*Bu in hexane (0.73 mL, 1.6 M in *n*-hexane) was added to a stirred solution of (cyclohepta-1,3,5-trien-1-ylmethyl)(diethyl)phosphonate (270 mg, 1.1 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature. After 30 min of stirring at ambient temperature the reaction mixture was cooled to −78 °C, and formyl ruthenocene (250 mg, 0.96 mmol) dissolved in THF (10 mL) was added dropwise. After warming to room temperature the solvent was evaporated to dryness. The residue was extracted with *n*-hexane and purified by column chromatography (SiO_2, *n*-hexane/Et_2O, 1:1). Isolation of the yellow band yielded 300 mg (90%) of **1** as a light yellow crystalline powder.

Method B (phase-transfer catalysis): A mixture of an aqueous solution of sodium hydroxide (50%, 30 mL), benzene (30 mL), a catalytic amount of [nBu_4N]Br (32 mg, 0.1 mmol), formyl ruthenocene (310 mg, 1.2 mmol) and (cyclohepta-1,3,5-trien-1-yl-methyl)(diethyl)phosphonate (420 mg, 1.7 mmol) was stirred under reflux for 16 h. The progress of the reaction was monitored by TLC. The reaction mixture was extracted by Et_2O, the organic layer dried with $MgSO_4$ and, subsequently, evaporated to dryness. The isolation of the product occurred as described for Method A. Yield (**1**): 198 mg (48%). ^1H NMR ($CDCl_3$): δ = 2.60 (d, *J* = 7.2 Hz, 2 H, H-7), 4.52 (s, 5 H, C_5H_5), 4.59 (t, *J* = 1.8 Hz, 2 H, C_5H_4), 4.81 (t, *J* = 1.8 Hz, 2 H, C_5H_4), 5.41 (m, 1 H, H-6), 6.13 (d, *J* = 4.8 Hz, 1 H, H-2), 6.21 (dd, *J* = 9.2, 5.0 Hz, 1 H, H-5), 6.41 (d, *J* = 15.8 Hz, 1 H, CH=C*H*), 6.53 (d, *J* = 15.8 Hz, 1 H, C*H*=CH), 6.54 (m, 2 H, H-3, H-4), ppm. MS(EI): *m*/*z* (%) = 260 (67) [$M^+ - 88$], 232(100) [$C_{10}H_{10}Ru^+$], 167 (56) [C_5H_5Ru]. $C_{19}H_{18}Ru$ (347.4): calcd. C 65.69, H 5.22; found C 65.52, H 5.55.

***E*-(1-Ruthenocenyl-2-[(tricarbonyl)(η^6-cyclohepta-1′,3′,5′-trien-1′-yl)chromium]ethene (2):** A solution of **1** (90 mg, 0.26 mmol) and $Cr(CO)_3(EtCN)_3$ (78 mg, 0.26 mmol) in THF (20 mL) was stirred overnight at room temperature. The reaction solvent was evaporated in vacuo and the residue extracted with toluene. The toluene extract was filtered and product **2** was precipitated after addition of hexane and cooling to −18 °C. Yield (**2**): 110 mg (88.5%) of a red-violet microcrystalline material. ^1H NMR (C_6D_6): δ = 1.07 (m, 1 H, H-7_{exo}), 2.62 (m, 2 H, H-7_{endo}, H-6), 4.21 (d, *J* = 7.0 Hz, 1 H, H-2), 4.41 (t, *J* = 7.2 Hz, 1 H, H-5), 4.57 (s, 5 H, C_5H_5), 4.67 (s, 2 H, C_5H_4), 4.79 (s, 2 H, C_5H_4), 5.05 (t, *J* = 7.7 Hz, 1 H, H-3), 5.19 (t, *J* = 7.4 Hz, 1 H, H-4), 5.86 (d, *J* = 15.8 Hz, 1 H, CH=C*H*), 6.21 (d, *J* = 15.6 Hz, 1 H, C*H*=CH) ppm. ^{13}C NMR (C_6D_6): δ = 23.0 (C-7), 53.2 (C-6), 68.7 (C_5H_4), 70.7 (C_5H_4), 72.0 (C_5H_5), 75.9 [$C_q(C_5H_4)$], 86.9 (C-1), 96.2 (C-3), 97.5 (C-4), 98.8 (C-2), 100.4 (C-5), 127.5 (C=C), 127.6 (C=C), 232.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 1950 (ν_{CO}), 1898 (ν_{CO}), 1883 (ν_{CO}), 1849 (ν_{CO}), 1618 ($\nu_{C=C}$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 436 (7320), 560 (sh) (1160) nm ($\text{M}^{-1}\cdot\text{cm}^{-1}$). MS (EI): *m/z* (%) = 484 (10) [M^+], 400 (60) [M^+ − 3CO], 347 (100) [M^+ − H-Cr(CO)$_3$. $C_{22}H_{18}O_3CrRu$ (483.5): C 54.66, H 3.75; found C 54.40, H 3.72.

[*E*-(1-Ruthenocenyl-2-{(η^5-cyclopentadienyl)(η^6-cyclohepta-1′,3′,5′-trien-1′-yl)ruthenium}ethene] Hexafluorophosphate (3a): A solution of **1** (171 mg, 0.49 mmol) and [(η^5-C_5H_5)Ru(MeCN)$_3$]PF_6 (213 mg, 0.49 mmol) in CH_2Cl_2 (20 mL) was stirred at ambient temperature. The progress of the reaction was monitored by TLC. When **1** could not be detected any longer (after three days), the product **3a** was precipitated by addition of Et_2O. A recrystallisation was performed by redissolution of crude **3a** and precipitation by slow gas phase diffusion of Et_2O. Yield (**3a**): 170 mg (53%) of orange-coloured microcrystalline material. ^{1}H NMR (CD_3NO_2): δ = 1.28 (dd, *J* = 13.7, 4.9 Hz, 1 H, H-7$_{exo}$), 3.46 (dd, *J* = 13.7, 9.4 Hz, 1 H, H-7$_{endo}$), 4.15 (m, 1 H, H-6), 4.16 (s, 5 H, C_5H_5), 4.75 (t, *J* = 1.8 Hz, C_5H_4), 4.93 (m, 1 H, C_5H_4), 5.07 (m, 1 H, C_5H_4), 5.35 (s, 5 H, C_5H_5), 5.67 (m, 2 H, H-4, H-5), 6.40 (d, *J* = 15.9 Hz, 1 H, H_β), 6.51 (m, 2 H, H-2, H-3), 6.87 (d, *J* = 15.9 Hz, 1 H, H_α) ppm. ^{13}C NMR (CD_3NO_2): δ = 22.6 (C-7), 30.0 (C-6), 56.6 (C-1), 69.8 (C_5H_4), 71.9 (C_5H_4), 72.9 (C_5H_5) 73.0 (C_5H_4), 73.1 (C_5H_4), 85.3 (C_5H_5), 87.2 [$C_q(C_5H_4)$], 89.0, 91.1 (C-4, C-5), 93.8, 95.8 (C-2, C-3), 126.9 (C_β), 135.2 (C_α) ppm. IR (KBr): $\tilde{\nu}$ = 3115, 3058, 2991, 1624 ($\nu_{C=C}$), 1506, 1416, 1101, 834 ($\nu_{P\text{-}F}$), 557 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 423 (10490) nm ($\text{M}^{-1}\text{cm}^{-1}$), ($CH_3NO_2$): λ_{max} (ε) = 404 (9410) nm ($\text{M}^{-1}\text{cm}^{-1}$). $C_{24}H_{23}F_6PRu_2$ (658.6): C 43.77, H 3.52; found C 43.16, H 3.68.

[*E*-(1-Ruthenocenyl-2-{(η^5-pentamethylcyclopentadienyl)(η^6-cyclohepta-1′,3′,5′-trien-1′-yl)ruthenium(II)}ethene] Hexafluorophosphate (3b): A solution of **1** (120 mg, 0.35 mmol) and [η^5-C_5Me_5)Ru(MeCN)$_3$]PF_6 (227 mg, 0.35 mmol) in CH_2Cl_2 (15 mL) was stirred at ambient temperature. The reaction and workup procedure were analogous to that of the synthesis of **3a**. Yield (**3b**): 125 mg (49%) orange-coloured prisms. ^{1}H NMR (CD_3NO_2): δ = 1.24 (dd, *J* = 12.8, 3.5 Hz, 1 H, H-7$_{exo}$) 1.88 (s, 15 H, C_5Me_5), 3.40 (m, 2 H, H-6, H-7$_{endo}$), 4.66 (s, 5 H, C_5H_5), 4.76 (m, 2 H, C_5H_4), 4.93 (m, 1 H, C_5H_4), 5.07 (m, 1 H, C_5H_4), 5.11 (m, 1 H, H-5), 5.18 (dd, *J* = 4.3, 2.6 Hz, 1 H, H-4), 6.18 (m, 2 H, H-2, H-3), 6.25 (d, *J* = 15.8 Hz, 1 H, H_β), 6.89 (d, *J* = 15.8 Hz, 1 H, H_α) ppm. ^{13}C NMR (CD_3NO_2): δ = 10.2 (C_5*Me*$_5$), 23.6 (C-7), 35.7 (C-6), 57.8 (C-1), 69.6 (C_5H_4), 71.7 (C_5H_4), 72.5 (C_5H_5), 72.7 (C_5H_4), 72.8 (C_5H_4), 88.2 [$C_q(C_5H_4)$], 94.2 (C-4), 94.7 (C-2 or C-3), 95.4 (C-5), 97.6 (C-2 or C-3), 99.4 (*C*$_5$Me$_5$), 126.8 (C_β), 136.0 (C_α) ppm. IR (KBr): $\tilde{\nu}$ = 2913, 2860, 1619 ($\nu_{C=C}$), 1381, 838 ($\nu_{P\text{-}F}$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 424 (11460) nm ($\text{M}^{-1}\cdot\text{cm}^{-1}$), ($CH_3NO_2$): λ_{max} (ε) 409 (10225) nm ($\text{M}^{-1}\cdot\text{cm}^{-1}$). ($C_{29}H_{33}PF_6Ru_2$)1/2($CH_2Cl_2$)1/2($CH_3NO_2$) (801.7): C 44.95, H 4.46, N 0.87; found C 44.62, H 4.39, N 1.07.



[*E*-1-Ruthenocenyl-2-(cycloheptatrienylium-1′-yl)ethene] Hexafluorophosphate (4): A solution of [Ph_3C]PF_6 (538 mg, 1.38 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **1** (480 mg, 1.38 mmol) in CH_2Cl_2 (20 mL). After stirring for 30 min the product **4** was precipitated by dilution with Et_2O. Recrystallisation was performed by gas phase diffusion of Et_2O into a concentrated CH_2Cl_2 solution of **4**. Yield: 0.52 g (77%) of a blue-violet crystalline powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.78 (s, 5 H, C_5H_5), 5.24 (s, 4 H, C_5H_4), 6.78 (d, *J* = 15 Hz, 1 H, H_β), 8.18 (d, *J* = 15 Hz, 1 H, H_α,), 8.04−8.23 (m, 4 H, C_7H_6), 8.30−8.35 (d, 2 H, C_7H_6) ppm. ^{13}C NMR (50 MHz, CD_3NO_2): δ = 73.5 (C_5H_4), 74.8 (C_5H_4), 77.7 (C_5H_4), 125.0 (C_β), 147.6 (C_7H_6), 148.6 (C_7H_6), 149.3 (C_7H_6), 152.3 C_α), ppm UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (16270), 640 (22560) nm (M^{-1} cm^{-1}); (CH_3NO_2): λ_{max} (ε) = 470 (12040), 600 (16430) nm (M^{-1} cm^{-1}). MS (FAB): *m/z* (%) = 347 (78%) [M^+ − PF_6]. $C_{19}H_{17}F_6PRu$ (492.0): C 46.34, H 3.48; found C 45.86, H 3.74.

[*E*-1-Ruthenocenyl-2-{(tricarbonyl)(η^7-cycloheptatrienylium-1-yl)-chromium}ethene] Hexafluorophosphate (5): A solution of [Ph_3C]PF_6 (90 mg, 0.23 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **2** (110 mg, 0.23 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After stirring for 30 min the reaction solution was diluted by addition of Et_2O. The precipitation was filtered off and recrystallised by a gas-phase diffusion of Et_2O into a concentrated solution of **5** in $MeNO_2$. Yield (**5**): 70 mg (48.5%) dark red needles. ^{1}H NMR (CD_3NO_2): δ = 4.65 (s, 5 H, C_5H_5), 4.88 (s, 2 H, C_5H_4), 5.13 (s, 2 H, C_5H_4), 6.48 (d, *J* = 9.3 Hz, 2 H, H-2,2′), 6.52 (m, 2 H, H-4,4′),6.80 (m, 2 H, H-3,3′),6.81 (d, *J* = 16.0 Hz, 1 H, H_β), 7.63 (d, *J* = 16.0 Hz, 1 H, H_α) ppm. ^{13}C NMR (CD_3NO_2): δ = 71. 8 (C_5H_4), 73.3 (C_5H_5), 74.3 (C_5H_4), 85.6 [$C_q(C_5H_4)$], 100.4 (C-2,2′),104.7 (C-4,4′),106.0 (C-3,3′),121.5 (C_β), 126.8 (C-1), 142.7 (C_α), 223.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3083, 2064 (ν_{CO}), 2012 (ν_{CO}), 1624 ($\nu_{C=C}$), 1546, 839 ($\nu_{P\text{-}F}$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 384 (8730), 532 (8375) nm (M^{-1}cm^{-1}), (CH_3NO_2): λ_{max} (ε) = 490 (7155) nm ($\text{M}^{-1}\cdot\text{cm}^{-1}$); ($C_{22}H_{17}O_3CrRuPF_6$) 1/2 ($CH_3NO_2$) (627.4): C 41.01, H 2.83, N: 1.06; found C 40.42, H 3.09, N 0.68.

[*E*-1-Ruthenocenyl-2-{(η^5-cyclopentadienyl)(η^7-cycloheptatrienylium-1′-yl)ruthenium(II)}ethene] Bishexafluorophosphate (6a): A solution of **4** (340 mg, 0.7 mmol) and [(η^5-C_5H_5)Ru(MeCN)$_3$]PF_6 (300 mg, 0.7 mmol) in CH_2Cl_2 (40 mL) was stirred overnight at ambient temperature. The precipitated product was filtered off, washed with CH_2Cl_2 and recrystallised from $MeNO_2$/Et_2O. Yield (**6a**): 470 mg (84%) red crystals. ^{1}H NMR (CD_3NO_2): δ = 5.11 (s, 5 H, C_5H_5), 5.38 (t, *J* = 1.8 Hz, 2 H, C_5H_4), 5.83 (t, *J* = 1.8 Hz, 2 H, C_5H_4), 5.86 (s, 5 H, C_5H_5), 5.92 (d, *J* = 13.4 Hz, 1 H, H_β), 6.09 (d, *J* = 9.2 Hz, 2 H, H-2,2′), 6.47 (m, 2 H, H-3,3′), 7.21 (dd, *J* = 5.4, 2.6 Hz, 2 H, H-4,4′), 7.55 (d, *J* = 13.4 Hz, 1 H, H_α) ppm. ^{13}C NMR (CD_3NO_2): δ = 70.5 (C-2,2′), 79.6 (C_5H_4), 81.9 (C_5H_5), 87.2 (C_5H_4), 88.2 (C_5H_5), 96.5 [$C_q(C_5H_4)$], 97.5 (C-3,3′), 99.7 (C-4,4′), 117.4 (C_α), 121.6 (C_β), 138.1 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3121, 1599 ($\nu_{C=C}$), 1541, 1493, 1418, 835 ($\nu_{P\text{-}F}$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 400, 600 (sh) nm, (CH_3NO_2): λ_{max} (ε) = 400 (10760), 560 (4975) nm ($\text{M}^{-1}\cdot\text{cm}^{-1}$). $C_{24}H_{22}Ru_2P_2F_{12}$ (802.5): C 35.92, H 2.76; found C 35.45, H 2.86.

[*E*-1-Ruthenocenyl-2-{η^5-pentamethylcyclopentadienyl)(η^7-cycloheptatrienylium-1′-yl)ruthenium(II)}ethene] Bishexafluorophosphate (6b): The synthesis of **6b** was performed strictly analogously to **6a**. Quantities used: **4** (50 mg, 0.1 mmol), [(η^5-C_5Me_5)Ru(MeCN)$_3$]PF_6 (51 mg, 0.1 mmol), CH_2Cl_2 (10 mL). Yield (**6b**): 64 mg (73%) dark red needles.- ^{1}H NMR (CD_3NO_2): δ = 2.13 (s, 15 H, C_5Me_5), 4.75 (s, 5 H, C_5H_5), 5.05 (t, *J* = 1.7 Hz, 2 H, C_5H_4), 5.24 (t, *J* = 1.7 Hz, 2 H, C_5H_4), 6.77 (d, *J* = 15.4 Hz, 1 H, H_β), 7.20 (m, 2 H, H-3,3′), 7.23 (d, *J* = 8.6 Hz, 2 H, H-2,2′), 7.33 (dd, *J* = 5.5, 3.6 Hz, 2 H, H-4,4′), 7.98 (d, *J* = 15.4 Hz, 1 H, H_α), ppm. ^{13}C NMR (CD_3NO_2): δ = 10.7 (C_5*Me*$_5$), 72.7 (C_5H_4), 73.9 (C_5H_5), 76.0 (C_5H_4), 86.1 [$C_q(C_5H_4)$], 99.1 (C-2,2′), 104.9 (C-3,3′), 105.5 (C-4,4′), 110.3 (*C*$_5$Me$_5$), 116.7 (C_β), 128.6 (C-1), 152.6 (C_α) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 1609 ($\nu_{C=C}$), 1539, 1418, 839 ($\nu_{P\text{-}F}$). UV/Vis (CH_2Cl_2): λ_{max}

(ε) = 438, 594 nm, (CH_3NO_2): λ_{max} (ε) = 409 (10580), 541 (9280) nm ($M^{-1}\cdot cm^{-1}$); ($C_{29}H_{32}Ru_2P_2F_{12}$) 2/3 ($CH_3NO_2$) (914.7): C 38.92, H 3.75, N 1.02 found C 39.29, H 3.75, N 1.48.

X-ray Structure Determination: Crystals suitable for an X-ray structure determination were obtained by gas phase diffusion of Et_2O into a CH_2Cl_2 solution of **3a**, **3b** and into an $MeNO_2$ solution of **6a.** Complex **3b** crystallised with CH_2Cl_2 and $MeNO_2$ molecules. During the isolation of the crystalline product of **3b** it was dissolved once in $MeNO_2$, which may explain the co-crystallisation of $MeNO_2$ molecules. The data were collected with a four-circle diffractometer (**3b**, and **6a**: Hilger and Watts, Mo-K_α; **3a**: Siemens aix, Mo-K_α). All structures were resolved by direct methods (SHELXS-86).[30] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93, SHELXL-97).[31,32] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined by the riding-model method with fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic parameter of their carrier atoms. Weights are optimised in the final refinement cycles.

CCDC-195475 (**3a**) CCCDC-195474 (**3b**) and CCDC-195453 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

HRS Measurements of the First Hyperpolarisabilities: Hyper-Rayleigh scattering measurements were performed with a pulsed Nd:YAG laser at a wavelength of λ = 1064 nm. For the experimental setup see ref.[15b] Solutions of the complexes in CH_2Cl_2 and $MeNO_2$ with concentrations in the range of 10^{-4} to 10^{-6} M were used with *p*-nitroaniline as a reference [$\beta(CH_2Cl_2) = 21.6 \times 10^{-30}$ esu,[22] $\beta(MeNO_2) = 34.6 \times 10^{-30}$ esu].[23] Fluorescence checks were made by replacing the interference filter in front of the photomultiplier tube with filters that have transmittances at 400, 450, 500, 560, 600 and 700 nm.[4]

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 1309/3), by the European Community (COST D4/003/94, TMR FMRX-CT98−0166) and by the Fonds der Chemischen Industrie. We thank the DEGUSSA AG for a donation of $RuCl_3$ and Sartorius GmbH for a donation of microfilters.

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Received August 9, 2002
[I02450]