

# Synthesis and characterization of dinuclear monohydro sesquifulvalene complexes with potential NLO properties

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## Abstract

*E*-1-(1''-hydroxycarbonylferrocen-1'-yl)-2-(cycloheptatrienyl)ethene (**4**) was synthesized by using selective transmetallation reactions. Reaction of **4** with [Cp\*Ru(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>) revealed the vinylogue monohydro sesquifulvalene complex *E*-1-(1''-hydroxycarbonylferrocen-1'-yl)-2-((1'''-6'''-η-cyclohepta-1''',3''',5'''-trien-1'''-yl)(η<sup>5</sup>-pentamethylcyclopentadienyl)ruthenium(II))ethene hexafluorophosphate (**5**). X-ray structure analysis demonstrates that complex **5** crystallizes in the triclinic space group *P*1̄, which forms discrete dimers via two hydrogen bonds between the carboxylic functions. Reaction of complex **5** with triethylamine or NaHCO<sub>3</sub> generated a new organometallic zwitterion *E*-1-(1''-oxycarbonylferrocen-1'-yl)-2-((1'''-6'''-η-cyclohepta-1''',3''',5'''-trien-1'''-yl)(η<sup>5</sup>-pentamethylcyclopentadienyl)ruthenium(II))ethene (**6**), which was characterized by UV, IR, and NMR spectra.

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**Keywords:** Dinuclear sesquifulvalene complex; UV–Vis spectra; Crystal structure; Zwitterion; Ferrocene; Ruthenium

## 1. Introduction

Since the first organometallic complex with an excellent second harmonic generation (SHG) was published by Green et al. [1], the interest in organometallic complexes concerning non-linear optical (NLO) properties has been greatly developed [2]. Most organometallic compounds revealing considerably strong SHG response, illustrate the following features: (i) dipolar structure composed of an electron donating (D) and electron accepting (A) group; (ii) a rich variation of the ligand sphere including a π-system, which facilitates an electronic communication between donating and accepting unit; (iii) excited states of low energy providing a facile electron transfer between the different parts of the molecule. This charge-transfer (CT) transition is an important feature of chromophores suitable for molecular materials with NLO properties e.g., SHG [2g]. In our group, several series of mono- and dinuclear dipolar sesquifulvalene type organometallic com-

plexes have been synthesized, which exhibit good SHG effects [3]. The previous strategies on preparing molecular SHG material have thus far focussed on modifications of different moieties (e.g., electron acceptor and π-linker) in a sesquifulvalene complex without considering the development of intermolecular interaction.

The second-order NLO susceptibility ( $\chi^2$ ) of bulk materials requires a non-centrosymmetric arrangement of the dipolar chromophores, which may be obtained by intermolecular interactions, e.g., hydrogen bonds, counter ion variations or coulomb attraction between zwitterionic modified dipoles [4]. On the basis of our recently prepared dipolar NLO compounds [3], we try to design and synthesize novel bifunctional sesquifulvalene complexes in order to investigate the influence of weak intermolecular interaction on crystal packing and NLO properties

In this paper, we describe the synthesis of a bifunctionalized ferrocenyl based dinuclear sesquifulvalene complex, and investigate the transformation between the cationic D–A complex and zwitterion by deprotonation. The corresponding characterization and properties of the novel complexes will also be reported.

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## 2. Results and discussion

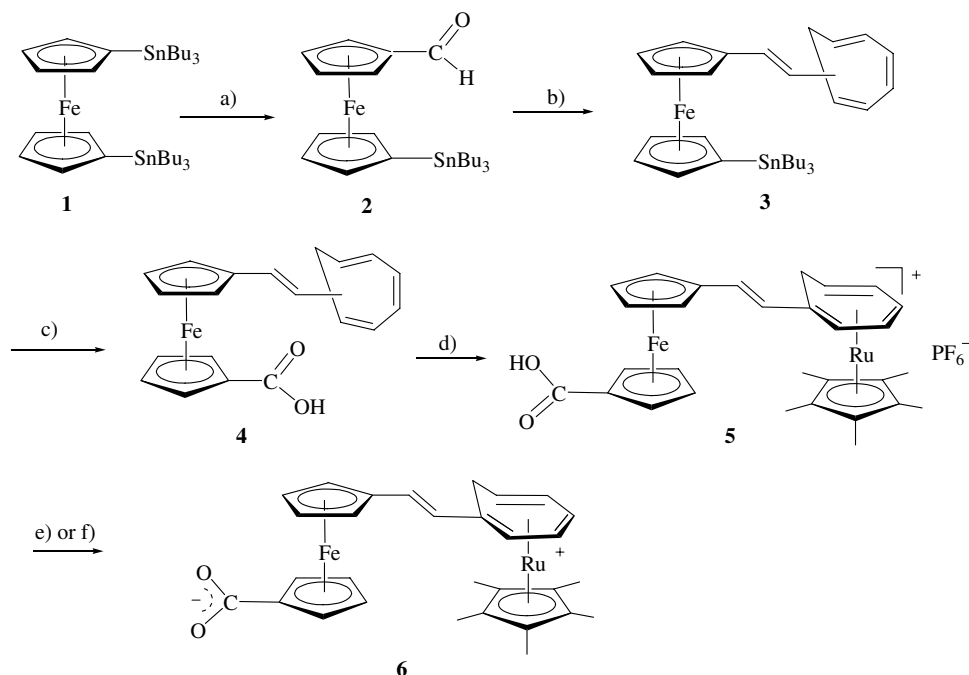
### 2.1. Synthesis

Using selective transmetalation reactions, complex **1** was easily monolithiated with one equivalent of *Lin*Bu, and after treating with DMF, the formyl ferrocene **2** (Scheme 1(a)) was achieved [5]. An effective Wittig–Horner–Wadsworth–Emmons (WHWE) reaction of complex **2** with (cycloheptatrienylmethyl)diethylphosphonate, which was first treated with *Lin*Bu, afforded the vinyllogue monohydro sesquiifulvalene complex **3** (Scheme 1(b)) [6]. Complex **3** was lithiated with one equivalent of *Lin*Bu, and then treated with an excess amount of solid CO<sub>2</sub>; the subsequent acidification gained complex **4** in a high yield (Scheme 1(c)). Addition of [Cp\**Ru*(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>] to a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 1(d)) immediately caused a color change from red to purple, indicating the formation of a new heterobimetallic complex **5** (Scheme 1(d)). Further purification was performed by diffusion of Et<sub>2</sub>O into the concentrated solution of **5** in CH<sub>2</sub>Cl<sub>2</sub>. In order to obtain the zwitterionic complex **6**, two different attempts were conducted. First, to a solution of **5** in CH<sub>2</sub>Cl<sub>2</sub> was added triethylamine (Scheme 1(e)). After stirring overnight, the reaction mixture was filtered. The solvent and excess of triethylamine were removed in vacuo. A further purification was carried out by slow diffusion of Et<sub>2</sub>O into a solution of **6** in CH<sub>2</sub>Cl<sub>2</sub>, where upon triethylammonium hexafluorophosphate was precipitated as colorless crystals. The supernatant layer was separated. After removal of the solvent, complex **6** was obtained as a purple powder. In a second

attempt, (Scheme 1(f)) NaHCO<sub>3</sub> was used, taking into account that NaPF<sub>6</sub> is easily precipitated from the solution. A solvent mixture of CH<sub>2</sub>Cl<sub>2</sub> and methanol was adopted to improve the reaction of NaHCO<sub>3</sub> with complex **5**. After stirring at room temperature for 12 h, the solvent was removed and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub>. After removal of the solvent, the product was obtained in high yield. However, attempts to obtain single crystals of complex **6** suitable for X-ray structure analysis have thus far been unsuccessful.

### 2.2. X-ray structure analysis

Suitable crystals of **5** for X-ray structure analysis were obtained by gas phase diffusion of diethyl ether into a solution of complex **5** in CH<sub>2</sub>Cl<sub>2</sub>. Crystal data and structure refinement data are given in Table 1, and selected bond lengths and angles are presented in Table 2. This molecule crystallizes in the triclinic space group *P* $\bar{1}$  with two independent molecules within the unit cell. Compound **5** forms discrete dimers whose monomers reveal a *cisoid* conformation as expected for ethene linked donor and acceptor sandwich complexes (Fig. 1). The  $\pi$ -linker displays an *E*-configuration quite similar to the ruthenocene congener without the carboxylic function (Fig. 2) [3d]. The carboxylic function is positioned distal with respect to the Cp\**Ru* moiety. The endocyclic sp<sup>3</sup> carbon atom C7 of the cycloheptatriene ring occupies the sterically less demanding *trans*-position relative to the hydrogen atom of the neighboring CH group of the vinyl bridge. A tilt angle of 27.1 (2)° is found between the best plane of the substituted five-mem-



Scheme 1. (a) 1. THF, *Lin*Bu, 2. DMF; (b) THF, (Et<sub>2</sub>O)<sub>2</sub>P(O)CH<sub>2</sub>C<sub>7</sub>H<sub>7</sub>, *Lin*Bu; (c) THF, *Lin*Bu, dry ice; (d) CH<sub>2</sub>Cl<sub>2</sub>, [Cp\**Ru*(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>]; (e) CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N; (f) C<sub>2</sub>H<sub>5</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>, NaHCO<sub>3</sub>.

Table 1  
Crystallographic data of **5** · 2CH<sub>2</sub>Cl<sub>2</sub>

<b>5</b> · 2CH <sub>2</sub> Cl <sub>2</sub>	
Empirical formula	C <sub>32</sub> H <sub>37</sub> Cl <sub>4</sub> F <sub>6</sub> FeO <sub>2</sub> PRu
Formula mass	897.31
<i>T</i> (K)	153 (2)
$\lambda$ (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.670 (3)
<i>b</i> (Å)	11.751 (3)
<i>c</i> (Å)	13.753 (3)
$\alpha$ (°)	96.957 (3)
$\beta$ (°)	97.074 (4)
$\gamma$ (°)	106.869 (4)
<i>V</i> (10 <sup>3</sup> Å <sup>3</sup> )	1766.5 (8)
<i>Z</i>	2
$\rho_{\text{calcd.}}$ (Mg/m <sup>3</sup> )	1.687
Absolute coefficient (mm <sup>-1</sup> )	1.247
<i>F</i> (000)	872
Crystal size (mm <sup>3</sup> )	0.1 × 0.2 × 0.5
Scan range (°)	2.18–25.08
Index range	−13 ≤ <i>h</i> ≤ 13, −13 ≤ <i>k</i> ≤ 13, −16 ≤ <i>l</i> ≤ 16
Reflections measured	16219
Reflections unique	6211
<i>R</i> <sub>int</sub>	0.0644
Parameters	428
Reflections <i>I</i> > 4σ( <i>I</i> )	4085
GoF <sup>a</sup>	0.939
<i>R</i> 1/ <i>wR</i> 2 [ <i>I</i> > 2( <i>I</i> )]	0.0574/0.1353
<i>R</i> 1/ <i>wR</i> 2 (all data) <sup>b</sup>	0.0945/0.1477
Residual minimum/maximum [e/Å <sup>3</sup> ]	−0.878/1.131

<sup>a</sup> (GoF (goodness-of-fit) =  $[\sum(wF_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  (*n* = number of reflections, *p* = numbers of parameters).

<sup>b</sup> *R*1 =  $\sum||F_o| - |F_c||/|F_o|$ ; *wR*2 =  $[\sum w(F_o^2 - F_c^2)^2 / \{w(F_o^2)_2\}]^{1/2}$ .

Table 2  
Selected bond lengths [Å] and angles [°] for **5** · 2CH<sub>2</sub>Cl<sub>2</sub>

Ru1–C <sub>Cp</sub> <sup>a</sup>	2.185 (6)– 2.402 (6)	Fe2–C <sub>Cp</sub> <sup>b</sup>	2.007 (6)– 2.080 (6)
C30–O1	1.267 (8)	C30–O2	1.269 (8)
C2–C3	1.413 (9)	C18–C30	1.466 (10)
C4–C3	1.435 (9)	C2–C1	1.413 (9)
C4–C5	1.421 (10)	C5–C6	1.399 (10)
C6–C7	1.502 (9)	C1–C7	1.507 (8)
C8–C13	1.458 (9)	C1–C14	1.438 (8)
C14–C13	1.336 (8)	O1–O2	2.622 (9)
C6–C7–C1	104.8 (5)	C14–C1–C7	120.8 (5)
C5–C6–C7	120.5 (6)	C5–C4–C3	126.1 (6)
C6–C5–C4	125.1 (6)	C2–C3–C4	128.3 (6)
C14–C13–C1	126.2 (6)	C2–C1–C14	119.0 (5)
C3–C2–C1	104.8 (5)	C2–C1–C7	118.1 (5)
C12–C8–C14	128.6 (6)	C9–C8–C13	124.4 (6)
C13–C14–C8	125.9 (6)	O1–C30–C18	117.5 (7)
O1–C30–O2	123.5 (7)	O2–C30–C18	118.8 (7)

<sup>a</sup> The carbon atoms in the pentamethylcyclopentadienyl ring.

<sup>b</sup> The carbon atoms in the cyclopentadienyl rings.

bered ring of the ferrocene donor terminus and the best plane of the cycloheptatriene moiety defined by the carbon atoms C1–C6, which is considerably smaller than those val-

ues found in similar structures (47.0(1)° and 38.1(1)°) [3d]. The tilt angle between the best plane C1–C6 of the cycloheptatriene ligand, and the best plane of the Cp\* ring defined by C20–C24 is quite small (1.6(1)°), whereas, the tilt angle between the two five-membered rings of the ferrocene moiety amounts to 6.1(2)°. The carboxylic function is tilted only about 10° with respect to the bound cyclopentadienyl ring. Within experimental error, all of the corresponding C–O, C–C and C–metal distances in the ferrocene and Ru sandwich moiety do not present any unexpected features. The same is true for the hexafluorophosphate anion and dichloromethane solvent molecules.

The dinuclear cationic complex **5** is a planar chiral complex due to the coordination of the cycloheptatriene ring to the ruthenium atom and its monosubstitution in the proximal position with respect to the sp<sup>3</sup> carbon atom C7. The two enantiomers of the cationic complex **5** are dimerized via a double hydrogen bond and both cations are related by a center of symmetry. The O...O distance of 2.622(9) Å is in the range found in most structures containing carboxylic acids dimerized via hydrogen bonds [7]. The hydrogen bonds in the cationic dimers of complex **5** demonstrate similar structural features as in other ferrocenyl carboxylic acids [7b–d]. The two C–O distances of the carboxylic groups (1.267(8), 1.269(8) Å) are the same, within the margin of error, and do not allow a more detailed discussion about the nature of the hydrogen bond.

### 2.3. Spectroscopic properties

The assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals of **4–6** was performed by using the splitting pattern of the <sup>1</sup>H NMR spectra and <sup>1</sup>H–<sup>13</sup>C correlation spectroscopy. A comparison of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** and **5** clearly indicates the effect of the coordination of a [Cp\*Ru]<sup>+</sup> fragment to a cycloheptatriene ligand [3d]. Whereas in **4** the resonance signals of H1 and H2 of the vinyl bridge, and H3''' and H4''' of the cycloheptatriene are superimposed at about 6.5 ppm as well as the signals of H5''' and H2''' at 6.2 ppm, they are well separated in the <sup>1</sup>H NMR spectra of **5** and **6**. For **5**, the corresponding signals are found at 4.90 (H5'''), 5.09 (H2''') and 5.94 (H3''', H4'''), 6.06 (H1) and 6.74 (H2) ppm. Upon deprotonation, these signals are shifted to a small extent to: 4.93, 5.40, 6.02, 6.21 and 6.92 ppm, respectively. A comparable influence on the relative positions of the resonance signals is also observed in the <sup>13</sup>C NMR spectra of **4** and **5**. A peculiarity of compound **4** should be mentioned: two isomers **A** and **B** were produced in the ratio of 1:3 (as indicated by <sup>1</sup>H NMR spectra), which differ in the position of the endocyclic methylene group of the cycloheptatriene moiety (Fig. 3).

The resonance signal at 12.4 ppm in the <sup>1</sup>H NMR spectrum of **5** indicates the existence of the carboxylic acid group, which is not observed for **6** in agreement with a deprotonated state. As outlined in our previous papers, NMR spectroscopic properties of a vinylene bridge should be sensitive probes for the examination of the donor and

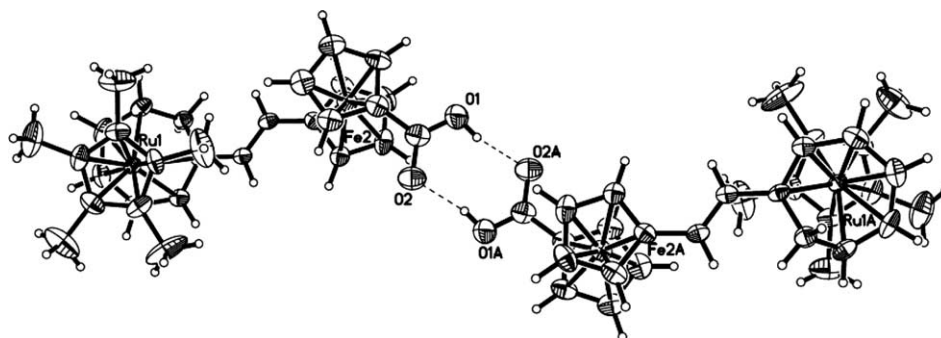


Fig. 1. Perspective view of the dimer of **5**; Hydrogen bonds are drawn as dotted lines.

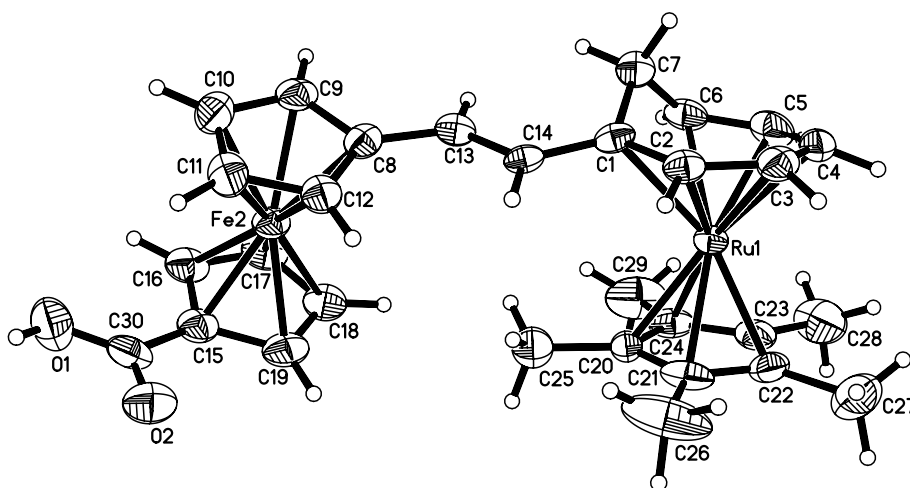


Fig. 2. Molecular structure of complex **5** (50% ellipsoids; solvent molecules of  $\text{CH}_2\text{Cl}_2$  and  $\text{PF}_6$  counter ion are omitted for clarity).

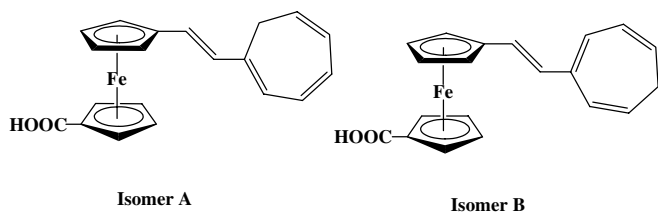


Fig. 3. Different isomers of **4** obtained after the WHWE reaction.

acceptor interaction [3d]. For a carbon–carbon double bond, a  $^3J$  (H1–H2) coupling constant of about 14.8 Hz for complex **5** is observed, and about 16.0 Hz for complex **6**. The  $^1\text{H}$ – $^1\text{H}$  coupling constant of the bridging vinyl group should commonly correspond to the energy of the C–C stretching vibration, which can be taken as a measure of charge delocalization in the electronic ground state of the compound. Unfortunately, no evidence from IR spectra can be obtained for complex **5** and **6** because the signal of the stretching mode of the C,C double bond completely overlaps with the band of the CO stretching mode of the carboxylate function in both cases.

However, the marginal increase of the coupling constant  $^3J$  (H1–H2) of **6** compared to **5** demonstrates a slightly larger bond length alternation in the  $\pi$ -bridge of **6** [3d] and thus a smaller donor–acceptor interaction in the electronic ground state for **6** than for **5**, which is not yet well understood.

Due to the effect of the conjugation of the carboxylic function of the electron rich ferrocene unit, the IR spectrum of **5** reveals a strong absorption band at  $\tilde{\nu} = 1672 \text{ cm}^{-1}$  for the CO stretching vibration. After deprotonation, the CO absorption band shifts to a lower wave number of  $1613 \text{ cm}^{-1}$ . On the other hand, a strong absorption band of the OH stretching vibration can be observed at  $\tilde{\nu} = 3470 \text{ cm}^{-1}$  for complex **5**, but not for the zwitterion **6**.

UV–Vis spectroscopic properties of complexes **4–6** were investigated in  $\text{CH}_2\text{Cl}_2$  (Table 3). The UV–Vis spectrum of complex **4** exhibits two absorption bands at 343 and 462 nm. In complexes **5** and **6**, three intense absorption bands are observed. The high energy absorption bands at 333 and 393 nm for **5** (334 and 392 nm for **6**) are attributed to donor(ligand)–acceptor charge-transfer transition ( $\text{D}_L\text{–A CT}$ ) according to the literature [3]. The low-lying absorp-

Table 3  
UV/Vis data of complexes **4–6**<sup>a</sup>

Complex	D <sub>L</sub> -A CT $\lambda_{\max}^b$ ( $\epsilon$ ) <sup>c</sup>	D <sub>M</sub> -A CT $\lambda_{\max}^b$ ( $\epsilon$ ) <sup>c</sup>
<b>4</b>	339 (24820)	460 (2097)
<b>5</b>	333 (5079)	393 (3492)
<b>6</b>	334 (4856)	392 (3222)

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> In nm.

<sup>c</sup> In M<sup>-1</sup> cm<sup>-1</sup>.

tion band at  $\lambda_{\max} = 487$  nm for complex **5** and  $\lambda_{\max} = 507$  nm (see Table 3) for **6** are assigned to donor(-metal)-acceptor (D<sub>M</sub>-A) CT transitions, since a corresponding absorption band does not appear in complex **4**. This assignment is in harmony with other ferrocene containing donor-acceptor complexes [3d].

Preliminary studies showed that progressive addition of triethylamine to a solution of **5** (Fig. 4) causes a slight red shift of the lower lying absorption band from  $\lambda = 487$  to 507 nm accompanied by an obvious increase in absorption. An isosbestic point seems to appear at  $\lambda = 435$  nm under low molar ratios of triethylamine to complex **5**. However, it does not hold for the addition of a larger excess of triethylamine, which causes a weak hypsochromic shift of the D<sub>M</sub>-A CT transition. Apparently, an equilibrium between complex **5**, triethylamine and complex **6** occurs at lower triethylamine concentrations. Since triethylamine is dipolar, and interacts strongly with charged molecules, it is reasonable to deduce that the slight hypsochromic effect stems from the excess amount of triethylamine, which is usually observed in charged D- $\pi$ -A systems [3] (Fig. 4). For comparison, UV-Vis spectra of complex **4** were recorded under comparable conditions, but obviously no changes for the positions of the absorption maxima  $\lambda_{\max}$  as well as for the absorption coefficients were observed.

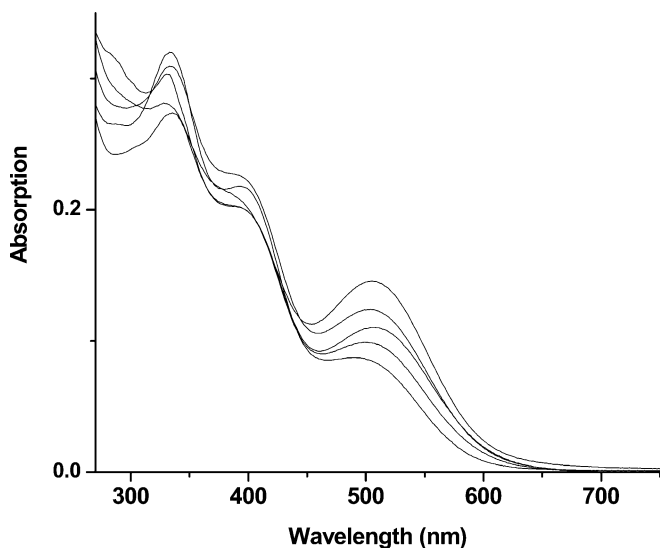


Fig. 4. Absorption spectra of complex **5** ( $1.27 \times 10^{-4}$  M) with different concentrations of triethylamine. From bottom at 487 nm to top at 507 nm, triethylamine (M): 0,  $1.26 \times 10^{-4}$ ,  $2.52 \times 10^{-4}$ ,  $2.52 \times 10^{-3}$ ,  $5.04 \times 10^{-3}$ .

Table 4  
Redox potentials<sup>a</sup> of complexes **5** and **6**

Complex	$E_{1/2}^b$	$E_{pc}^c$	$\Delta E$
<b>5</b>	0.26	-1.61	1.87
<b>6</b>	0.24	-1.61	1.85

<sup>a</sup> In volts vs. [FeCp<sub>2</sub>]/[FeCp<sub>2</sub>]<sup>+</sup>; scan rate: 200 mV/s, 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Electrochemically reversible one-electron oxidation.

<sup>c</sup> Irreversible one-electron reduction.

Cyclic voltammetric measurements of **5** reveal an electrochemically reversible one-electron oxidation as expected for ferrocene derivatives. These measurements show an essential anodic shift with respect to unsubstituted ferrocene (Table 4), caused by the electron-withdrawing ability of the carboxylic acid group and the positively charged Cp<sup>\*</sup>Ru moiety. In addition, an irreversible one-electron reduction process occurs at -1.61 V (vs. FcH/FcH<sup>+</sup>), which is related to the reduction of the cycloheptatriene moiety [8]. A similar electrochemistry behavior was observed for complex **6** (Table 4). The electrochemical data for complex **5** and **6** indicate that the nature of the HOMO is dominated by the donating ferrocenyl unit, whereas the character of the LUMO is determined by the Cp<sup>\*</sup>Ru entity. This combination favors a dipole change upon electronic excitation from the HOMO to the LUMO.

#### 2.4. NLO properties

Attempts to study non-linear optical properties of **5** and **6** were made using hyper Rayleigh scattering (HRS) measurements with a stimulating wavelength of  $\lambda = 1064$  nm [9]. They were performed with CH<sub>2</sub>Cl<sub>2</sub> solutions of complex **5** and MeCN solutions of complex **6**. However, no SHG signal could be observed for complex **5**. This is probably due to the broad absorption band of the D<sub>M</sub>-A CT transition beyond 500 nm and a weak SHG signal at 532 nm. Since the D<sub>M</sub>-A CT absorption of **6** has an even greater shift towards the wavelength of the second harmonic, and the corresponding extinction coefficient increases by a factor of two, **6** also exhibited no frequency doubled signal in the HRS experiment.

### 3. Conclusion

The mononuclear complex *E*-1-(1''-hydroxycarbonylferrocen-1'-yl)-2-(cycloheptatrienyl)ethene (**4**) was synthesized by using selective transmetallation reactions. Reaction of **4** with [Cp<sup>\*</sup>Ru(CH<sub>3</sub>CN)<sub>3</sub>](PF<sub>6</sub>) revealed the new monohydro sesquifulvalene complex *E*-1-(1''-hydroxycarbonylferrocen-1'-yl)-2-((1'''-6'''- $\eta$ -cyclohepta-1''',3''',5'''-trien-1'''-yl)-( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium(II))ethene hexafluorophosphate (**5**). Complex **5** crystallizes in the space group *P*1 with two molecules linked together by two hydrogen bonds between two carboxylate groups. Preliminary NMR spectra, IR spectra and UV-Vis spectro-

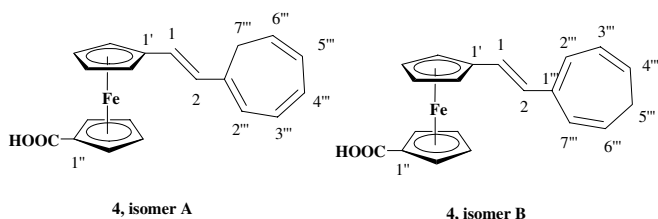
scopic results indicate the formation of the zwitterionic congener **6** upon reaction of triethylamine or  $\text{NaHCO}_3$  with complex **5**. However, we were unable to crystallize the zwitterion **6** for X-ray structure analysis. The studies of bimetallic organometallic zwitterionic species concerning NLO properties are in progress.

## 4. Experimental section

### 4.1. General procedures

Manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether ( $\text{Et}_2\text{O}$ ) were freshly distilled from the appropriate alkali metal or metal alloy. Ethanol was dried over magnesium metal and distilled under  $\text{N}_2$ . *N,N*-dimethylformamide (DMF) was purified by distillation from molecular sieves 4 Å. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and triethylamine were dried over  $\text{CaH}_2$  and distilled under  $\text{N}_2$ . UV–Vis: Perkin–Elmer Model 554. IR: Perkin–Elmer FT-IR 1720X spectrophotometer. NMR: Bruker AM 400, Varian Gemini 200 BB. Elemental analyses: CHN–O–Rapid, Fa. Heraeus (Zentrale Elementanalytik, Fachbereich Chemie, Universität Hamburg). 1,1'-Bis(tri-*n*-butylstannyl)ferrocene and 1'-(tri-*n*-butylstannyl)-1-ferrocene-carboxaldehyde [5], (cyclohepta-1,3,5-trien-1-ylmethyl)-diethylphosphonate [3e],  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3](\text{PF}_6)$  [10] and 1-(1''-tributylstannylferrocen-1'-yl)-2-(cycloheptatrienyl)ethene (**3**) [6] were synthesized according to the literature procedures.

### 4.2. 1-(1''-Hydroxylcarbonylferrocen-1'-yl)-2-(cycloheptatrienyl)ethene (**4**)

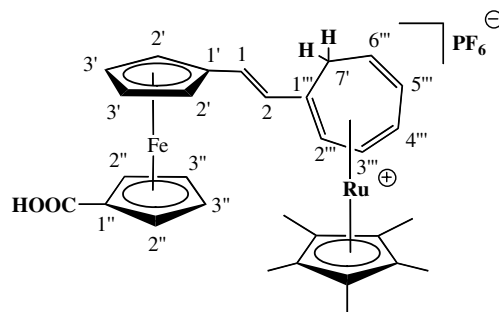


LinBu (0.5 mL, 0.87 mmol, 1.6 M in hexane) was added to a solution of **3** (0.50 g, 0.84 mmol) in THF (10 mL) and stirred at  $-78^\circ\text{C}$  for 30 min. The mixture was poured under vigorous stirring onto a mixture of finely crushed dry ice (1.0 g, 22.5 mmol) and anhydrous diethyl ether (30 mL). The reaction mixture was allowed to warm to room temperature. After 2 h stirring, the reaction mixture was acidified with a small volume of concentrated hydrochloric acid, and then was extracted with dichloromethane ( $3 \times 20$  mL). The organic layers were combined and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent in vacuo, the residue was washed with

hexane ( $3 \times 20$  mL). The pure product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . Yield: 0.24 g (83%) red needles.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.31 (t,  $J = 6.6$  Hz, 2H,  $\text{H}5'$ , isomer **A**), 2.65 (d,  $J = 7.0$  Hz, 2H,  $\text{H}7'$ , isomer **B**), 4.32 (t,  $J = 2.0$  Hz, 2H, Cp), 4.40 (t,  $J = 2.0$  Hz, 2H, Cp), 4.46 (t,  $J = 2.0$  Hz, 2H, Cp), 4.79 (t,  $J = 2.0$  Hz, 2H, Cp), 5.45–5.50 (m,  $\text{C}_7\text{H}_7$ ), 6.20 (m, 2H,  $\text{H}2''$ ,  $\text{H}5'''$ ) 6.4–6.6 (m,  $\text{C}_7\text{H}_7$ , H1, H2).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 28.2 ( $\text{C}7'$ ), 68.7 (Cp), 71.3 (Cp), 72.0 (Cp), 73.4 (Cp), 83.2 (*ipso*-Cp), 123.1 ( $\text{C}_7\text{H}_7$ ), 125.7 ( $\text{C}_7\text{H}_7$ ), 128.0 ( $\text{C}_7\text{H}_7$ ), 130.0 ( $\text{C}_7\text{H}_7$ ), 130.4 (C1), 131.0 (C2), 132.4 (*ipso*-C-1'), 176.6 (COOH). Anal. Calcd. for ( $\text{C}_{20}\text{H}_{18}\text{FeO}_2$ ) (346.07): C, 69.39; H, 5.24; Found: C, 68.80; H, 5.31%.

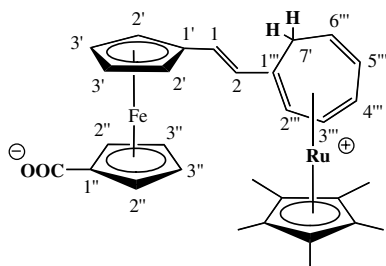
### 4.3. E-1-(1''-hydroxycarbonylferrocen-1'-yl)-2-[(1'''-6'''- $\eta$ -cyclohepta-1''',3''',5'''-trien-1'''-yl)( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium(II)]ethene-hexafluorophosphate (**5**)



To a solution of **4** (0.30 g, 0.87 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added solid  $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3](\text{PF}_6)$  (0.38 g, 0.87 mmol). The reaction mixture was stirred overnight. The solution was concentrated to 10 mL in vacuo, and then dry diethyl ether (5 mL) was added. After filtration, the crude product was precipitated by addition of more  $\text{Et}_2\text{O}$  and stored at  $-20^\circ\text{C}$ . After filtration, the pure product was obtained by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  as deep purple microcrystalline material. Yield: 0.36 g (51%).

$^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ): 1.29 (dd,  $J = 13.2$  Hz, 2.2 Hz, 1H,  $\text{H}7'''_{\text{exo}}$ ), 1.74 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 3.25 (m, 2H,  $\text{H}6'''$ ,  $\text{H}7'''_{\text{endo}}$ ), 4.43 (m, 1H, Cp), 4.52–4.56 (m, 4H, Cp), 4.67 (m, 1H, Cp), 4.81 (m, 2H, Cp), 4.90 (m, 1H,  $\text{H}5'''$ ), 5.09 (dd,  $J = 5.6$  Hz, 1H,  $\text{H}2'''$ ), 5.94 (m, 2H,  $\text{H}3'''$ ,  $\text{H}4'''$ ), 6.06 (d,  $J = 14.8$  Hz, 1H, H1), 6.74 (d,  $J = 14.8$  Hz, 1H, H2), 12.32 (s, 1H, COOH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ): 10.6 ( $\text{C}_5\text{Me}_5$ ), 23.7 ( $\text{C}7'''$ ), 35.3 ( $\text{C}6'''$ ), 57.6 ( $\text{C}1'''$ ), 67.8 (Cp), 72.1 (Cp), 72.3 (Cp), 72.8 (Cp), 72.9 (Cp), 73.2 (Cp), 73.9 (Cp), 74.3 (Cp), 83.7 (*ipso*-Cp), 93.9 ( $\text{C}4'''$ ), 94.4 ( $\text{C}2'''$  or  $\text{C}3'''$ ), 94.6 ( $\text{C}5'''$ ), 97.0 ( $\text{C}3'''$  or  $\text{C}2'''$ ), 98.6 ( $\text{C}_5\text{Me}_5$ ), 127.4 (C1), 134.2 (C2), 176.4 (C=O). Anal. Calcd. for  $\text{C}_{31}\text{H}_{35}\text{FeRuO}_2\text{PF}_6\text{Cl}_2$  (812.41): C, 45.83; H, 4.34. Found: C, 45.47; H, 4.19%.

4.4. *E*-1-(1''-oxycarbonylferrocen-1'-yl) {(1'''-6'''-η-cyclohepta-1''',3''',5'''-trien-1'''-yl) (η<sup>5</sup>-pentamethylcyclopentadienyl)ruthenium(II)} ethene (**6**)



**Method A:** Triethylamine (0.065 g, 1.1 mmol) was added to a solution of **5** (0.16 g, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After stirring overnight, the reaction mixture was filtered. The solvent and excess of triethylamine were removed in vacuo. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> again. By slow diffusion of Et<sub>2</sub>O into this solution, triethylammonium hexafluorophosphate was formed as colorless crystals. The solution was separated, the solvent was removed and a crude product was obtained as a purple powder still contaminated with triethylammonium hexafluorophosphate.

**Method B:** Compound **5** (0.26 g, 0.36 mmol) was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:4), and dried NaHCO<sub>3</sub> powder (33 mg, 0.39 mmol) was added. The reaction mixture was stirred for one day. After removal of the solvent in vacuo, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered. The solution was concentrated and the product was purified by recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Yield: 0.188 g (90%).

<sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 1.29 (dd, *J* = 13.2 Hz, 2.2 Hz, 1H, H7<sup>'''</sup><sub>exo</sub>), 1.78 (s, 15H, C<sub>5</sub>M<sub>5</sub>), 3.43 (m, 2H, H6<sup>'''</sup>, H7<sup>'''</sup><sub>endo</sub>), 4.40 (m, 1H, Cp), 4.47 (m, 3H, Cp), 4.54 (m, 1H, Cp), 4.67 (m, 2H, Cp), 4.75 (m, 1H, Cp), 4.93 (t, *J* = 6.0 Hz, 1H, H5<sup>'''</sup>), 5.40 (dd, *J* = 5.6 Hz, 1H, H2<sup>'''</sup>), 6.03 (m, 2H, H3<sup>'''</sup>, H4<sup>'''</sup>), 6.20 (d, *J* = 16.0 Hz, 1H, H1), 6.93 (d, *J* = 16.0 Hz, 1H, H2). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 10.4 (C<sub>5</sub>Me<sub>5</sub>), 24.0 (C7<sup>'''</sup>), 35.4 (C6<sup>'''</sup>), 58.8 (C1<sup>'''</sup>), 69.4 (Cp), 71.8 (Cp), 72.0 (Cp), 72.8 (Cp), 73.0 (Cp), 73.3 (Cp), 73.4 (Cp), 74.3 (Cp), 84.0 (*ipso*-Cp), 94.0 (C2<sup>'''</sup>), 94.1 (C5<sup>'''</sup>), 94.3 (C3<sup>'''</sup>), 96.7 (C4<sup>'''</sup>), 98.0 (C<sub>5</sub>Me<sub>5</sub>), 127.5 (C1), 135.6 (C2), 181.3 (C=O). Complex **6** is air sensitive, a correct elemental analysis could not be obtained.

#### 4.5. Cyclic voltammetry

The measurements of cyclic voltammetry were carried out in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with 0.4 M [N(*n*Bu)<sub>4</sub>]PF<sub>6</sub> as supporting electrolyte at scan rates from 100 to 500 mV/s. An Amel 5000 system was used with a Pt wire as the working electrode and a Pt plate as the auxiliary electrode. The potentials were measured against Ag/Ag<sup>+</sup> and are referenced against E<sub>1/2</sub>([Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]/[Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>) = 0.

#### 4.6. X-ray crystallography

The red single crystal of **5** · 2CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray structure determination was obtained by gas-phase diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex **5**. The single crystal was covered with an inert oil and cooled to 153 K with a cold nitrogen gas flow. The measurement was made on a Bruker axis SMART, and a CCD system was used with graphite-monochromated Mo K<sub>α</sub> radiation (λ = 0.71069 Å). Data were corrected for Lorentz and polarization effects. The structure was solved by direct method (program SHELXS 97) and refined by the full-matrix least-squares method on all F<sup>2</sup> data using the SHELXL 97 programs [11]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were fixed at calculated positions and included at the final stage of refinements with fixed parameters. No absorption corrections were applied. Two independent molecules of CH<sub>2</sub>Cl<sub>2</sub> are presented within the asymmetric unit. For more information, see Table 1.

#### 5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-231734. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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