Journal of Organometallic Chemistry xxx (2017) 1-9



Contents lists available at ScienceDirect

Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

From diferrocenyl-cyclopropenone to diferrocenyl-cyclopropenylium cations and triferrocenylpropenones: An electrochemical study \star

Steve W. Lehrich, Alexander Hildebrandt, Marcus Korb, Heinrich Lang*

Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Anorganische Chemie, D-09107 Chemnitz, Germany

ARTICLE INFO

Article history: Received 26 January 2017 Received in revised form 7 March 2017 Accepted 8 March 2017 Available online xxx

Keywords: Ferrocenvl Cyclopropenone Cyclopropenylium Solid state structure (Spectro)Electrochemistry

ABSTRACT

The reaction of 2,3-diferrocenylcyclopropenone (1) with the electrophiles H[BF4] and [Et₃O][BF4], respectively, produced the corresponding cyclopropenylium cations [Fc₂C₃OH][BF₄] (2) and [Fc₂C₃OEt] $[BF_4]$ (3) (Fc = Fe(η^5 -C₅H₄)(η^5 -C₅H₅)). Reacting 3 with HNEt₂ afforded the NEt₂-functionalized species [Fc₂C₃NEt₂][BF₄] (**4**). However, when **2** was reacted with nucleophiles such as FcLi a ring opening of the C₃ cycle was observed and *E*- and *Z*-1,2,3-triferrocenylpropenones *Z*-**5** and *E*-**5** were formed. Crystallization of a dichloromethane solution containing $\mathbf{3}$, layered with hexane, gave the BF₃ adduct of diferrocenylcyclopropenone 6 at the interphase. The molecular solid state structures of Z-5, E-5 and 6 were determined by single crystal X-ray diffraction. Compound E-5 possesses a helical chirality and crystallizes in an enantiopure form. The electronic properties of the ferrocenyl-substituted cyclopropenylium cations **2–4** and of the triferrocenyl- α , β -unsaturated ketones Z-5 and E-5 were studied by cyclic voltammetry and square wave voltammetry. In comparison to the cyclopropenone derivative 1, the ferrocenyl oxidation processes of the cyclopropenylium cations 2 and 3 are shifted towards higher potentials, which is caused by the lower electron density of the strained C_3 rings. Compound 4 decomposes during the electrochemical measurements. Furthermore, it could be shown that E/Z isomerism has only small effects on the electronic properties of the triferrocenyl- $\alpha_{,\beta}$ -unsaturated ketones. Spectroelectrochemical UV -Vis/NIR measurements carried out on 1 and Z-5 and E-5 confirmed electron-transfer interactions within the 2,3-diferrocenylcyclopropenone and the 1,2,3-triferrocenyl- α , β -unsaturated ketones. However, the cyclopropenylium cations 2 and 3 show no long time stability under oxidative conditions.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Since the first preparation of triphenylcyclopropenylium perchlorate [1], cyclopropenylium cations as the smallest member of Hückel aromatic systems have been studied intensively [2]. Cyclopropenylium ions possess a high reactivity due to their strained ring system. On the other hand, the aromatic stabilization induces a considerable thermodynamic stability [2,3]. The chemistry of cyclopropenones is follows by the presence of zwitterionic mesomeric structures that contain the aromatic cyclopropenylium motif (Fig. 1), which causes the high polarity of the molecule and enhances the stability of the strained system [2,4,5]. Thermolysis or nucleophilic attack at the $C_3(=0)$ ring cause ring opening, allowing, for example, to prepare five- or six-membered nitrogen-containing

Dedicated to Prof. Dr. John A. Gladysz on the occasion of his 65th birthday.

Corresponding author.

E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang).

http://dx.doi.org/10.1016/j.jorganchem.2017.03.018 0022-328X/© 2017 Elsevier B.V. All rights reserved. heterocycles [6,7]. Cyclopropenones can also act as a three-carbon building block to elongate the nucleophiles added [8].

Ferrocenyl-substituted cyclopropenones allow to introduce iron atoms in a large number of different organic compounds [8]. In this respect, especially extended conjugated metal-containing systems are of great interest because they can be used as model compounds for molecular wires [8-12]. Furthermore, the electron-donating nature of ferrocenyl functionalities on the cyclopropenone system enhances their stability by delocalizing the positive charge [3,13,14]. Another benefit of using ferrocenyls in cyclopropenone chemistry is the in situ generation of mixed-valent compounds through oxidation of one of the two ferrocenyl units and hence the possibility to study the charge transfer behaviour through the aromatic C₃ framework. This family of compounds can be considered as enrichment of well-studied diferrocenyl-functionalized 5membered heterocycles [15-24].

Herein, we report the charge transfer between ferrocenyl/ferrocenium moieties via 2π -aromatic strained C₃ ring systems in

respective mixed-valent compounds. In addition, the reaction chemistry of diferrocenylcyclopropenone towards FcLi to give 1,2,3triferrocenylprop-2-enones and their electrochemical and spectroelectrochemical characteristics are discussed.



Fig. 1. Mesomeric structures of cyclopropenones [2].

2. Results and discussion

2.1. Synthesis

Diferrocenylcyclopropenone (1) (Scheme 1) was prepared by Friedel-Crafts alkylation of ferrocene with tetrachlorocyclopropane in the presence of AlCl₃ [3,13]. The synthesis of the cyclopropenylium salts **2–4** (Scheme 1) was performed according to published procedures [4,5,25]. During crystallization of **3** from a hexane/dichloromethane mixture at ambient temperature it was observed that at the hexane ad-layer a minor number of single crystals of **6** grew, most likely due to a trace of BF₃ present in the Et₃OBF₄ reagent. The solid state molecular structure of **6** is discussed in the Supporting Information (Fig. SI5). To prepare **6** in a straightforward manner, diferrocenylcyclopropenone (1) was subsequently treated with trifluoroborane etherate in tetrahydrofuran. However, instead of neutral **1**•BF₃, cationic **2** was isolated (Scheme 1), tracing the *in situ* formation of HBF₄.

Klimova et al. described the nucleophilic attack of phenyl- or methyl-lithium on diferrocenyl-substituted cyclopropenes [26]. In this respect, compound **1** was treated with ferrocenyllithium, producing *Z*- and *E*-1,2,3-triferrocenylprop-2-enone (*Z*-**5**, *E*-**5**) (Scheme 1).

Compounds **1** and *Z-*/*E*-**5** are stable towards air, light and moisture both in the solid state and in solution. The cyclo-propenylium cations **2**–**4** are best isolated using anhydrous solvents under inert conditions and are preferably stored under argon atmosphere, whereas aerobic conditions led to a slow decomposition of the respective compounds.

2.2. Characterization

The identity of organometallic compounds **1–5** was confirmed by IR and NMR (¹H, ¹³C{¹H}) spectroscopy. The observed infrared bands of **1** at 1849 cm⁻¹, 1817 cm⁻¹ and 1614 cm⁻¹ are diagnostic for the cyclopropenone structure motif [3]. The change of the characteristic carbonyl stretching vibrations in **1** as well as the occurrence of v_{B-F} vibrations (1060 - 1170 cm⁻¹) in IR spectroscopy could be used to monitoring the progress of the reactions.

1,2,3-Triferrocenylprop-2-enones *Z-/E*-**5** were additionally characterized by high resolution mass spectrometry, elemental analysis (Materials and Methods) and single crystal X-ray structure analysis (Fig. 2).

The electrochemical behavior of 1-5 was studied by cyclic voltammetry (CV) and square wave voltammetry (SWV). In addition, for compounds 1 and *Z-/E-5 in situ* UV–Vis/NIR spectroelectrochemistry measurements were carried out.

The molecular structures of *Z*-**5** and *E*-**5** (Fig. 2) in the solid state have been determined by single crystal X-ray diffraction analysis. Suitable crystals of *Z*-/*E*-**5** were obtained by solvent evaporation at ambient temperature. They crystallize in the *non*-centrosymmetric orthorhombic space group $Pca2_1$ (*Z*-**5**) (absolute structure parameter [27] = 0.022(16)) and the *non*-centrosymmetric *Sohncke* space group [28] $P2_1$ (*E*-**5**) (absolute structure parameter [27] = 0.06(4)) with one molecule in the asymmetric unit.

The ferrocenyl groups of *Z*-**5** and *E*-**5** are attached to the carbonyl carbon atom and the α - and β -position of the ethylene unit (Fig. 2. Scheme 1). The C1–O1. C1–C2 and C2–C3 bond lengths are in the range for related compounds, *i. e.* 2.3-diferrocenvl-1-phenvl-prop-2-enone or [Fc-COCH=CH-Anth] derivatives (Anth = antracenyl) [29–41]. Due to the steric interaction for a *cis*-substitution pattern, the ferrocenyls at the olefin group resulted in an increased bending out of the vinylic plane by $10.5(7)^{\circ}$ for Z-5, in contrast to $173.2(19)^{\circ}$ for E-5, as evidenced by the C14-C2-C3-C24 torsion angle. To avoid an interaction of the hydrogen atoms of the Fe2-and Fe3labeled ferrocenyls in Z-5, they are rotated out of plane of the C-C=C vinyl unit by 31.9(5) ° for the Fe2 entity and by 47.2(4) ° for the Fe3 moiety. For E-5, the trans-substitution avoids the steric interaction between the two ferrocenyls and reduces the rotation out of the olefin plane to 22.8(14) and 21.3(17) °, respectively. In contrast to Z-5 with an anti-orientation, the ferrocenyls in E-5 are rotated in a syn-coplanar fashion towards each other with a plane



Scheme 1. Synthesis of cyclopropenylium salts 2-4, diferrocenylcyclopropenone BF₃ complex 6 and 1,2,3-triferrocenylprop-2-enones Z-5 and E-5.

S.W. Lehrich et al. / Journal of Organometallic Chemistry xxx (2017) 1-9



Fig. 2. ORTEPs (50% probability level) of the molecular structure of Z-5 (left) and E-5 (right) with the atom numbering scheme. Left (Z-5): Hydrogen atoms and a disordered $C_{5}H_5$ ring (0.43:0.57 occupancy ratio) have been omitted for clarity. Selected bond distances (Å) and torsion angles (°): C1=O1 1.218(5), C1-C2 1.502(6), C2=C3 1.343(6), O1-C1-C2-C3 132.2(4). Right (E-5): Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and torsion angles (°): O1=C1 1.231(14), C1-C2 1.514(17), C2=C3 1.295(17), O1-C1-C2-C3 123.2(13).

intersection of 5.0(7) °. The Fe1 cyclopentadienyls are rather coplanar with the attached O=C–C moiety with 3.0(5) ° for Z-**5** and 12.5(7) ° for E-**5**.

Regarding the α , β -unsaturated moiety, a *trans* orientation of both double bonds is observed, whereas the interactions of the attached ferrocenyls rotate the C=O and C=C bonds out of coplanarity around the C1–C2 single bond by 47.8(4) ° to avoid interactions of the C8 and C3 hydrogen atoms in *Z*-**5**. For *E*-**5**, the torsion angle increases to 56.8(13) ° to avoid the interaction of the C28 und C5 hydrogen atoms.

The C4–C1–C2–C3–C24 atoms of *E*-**5** form a helical structural motif in the solid state (Fig. SI8). The crystallization in the *non*-centrosymmetric *Sohncke* space group $P2_1$, which does not contain the respective enantiomer, allows the assigned of the absolute conformation to be the *M* isomer within the used single crystal [42].

2.3. Electrochemistry

The electrochemical properties of **1–4**, *Z*-**5** and *E*-**5** were investigated by cyclic voltammetry (CV) and square-wave voltammetry (SWV) (Fig. 3; for data of **3** see Supporting Information Fig. SI10). The charge transfer behavior of **[1]**⁺, [*Z*-**5**]^{+/2+} and [*E*-**5**]^{+/2+} was additionally studied by *in situ* UV–Vis/NIR spectroelectrochemistry (Figs. 4–7, and Figs. SI12–SI13), while it was found that **[2]**⁺, **[3]**⁺ and **[4]**⁺ were not stable under oxidative conditions in multi-cyclic measurements. The electrochemical studies were carried out in anhydrous dichloromethane solutions containing [^{*n*}Bu₄N][B(C₆F₅)₄] (0.1 mol·L⁻¹) as supporting electrolyte under inert conditions (Materials and Methods) **[43]**. The weak coordinating electrolyte [^{*n*}Bu₄N][B(C₆F₅)₄] was used, since it is known to stabilize highly charged species and minimize ion pairing effects **[44–46]**. The cyclic voltammetry measurements were performed at 25 °C. All potentials are referenced to the FcH/FcH⁺ (FcH = Fe(η ⁵-

 $(C_5H_5)_2$) redox couple [47]. The CV data at a scan rate of 100 mV s⁻¹ are summarized in Table 1.

The ferrocenyl units in **1**, **2**, *Z*-**5** and *E*-**5** can be oxidized separately. Compounds **1** and **2** show two and *Z*-**5** and *E*-**5** three consecutive reversible one-electron redox processes for the redox active termini in the CV as well as in the SWV (Fig. 5). While for **3** in the initial scans two reversible oxidation events are characteristic, multi-cyclic experiments demonstrated the low electrochemical stabilities of $[3]^+/[3]^{2+}$. The two ferrocenyl-related oxidation events are in close proximity and therefore the better resolved SWV data are given in Table 1 (Supporting Information, Fig. SI10). Compound **4** was not stable in electrochemical measurements and hence after the first cycle no defined redox processes could be detected, which is most probably caused by a contamination of the electrode surface with decomposition products. The low electron density and the chemically less stable amine functionality in **4** might be responsible for rapid decomposition after oxidation.

Compound **1** shows under the applied measurement conditions a half-wave potential separation of 250 mV. Klimova et al. described that **1** absorbs on the platinum electrode, when $[N^nBu_4]$ [PF₆] in dichloromethane was used as electrolyte. However, by changing the electrolyte from $[N^nBu_4]$ [PF₆] to weakly coordinating $[^nBu_4N]$ [B(C₆F₅)₄], two reversible one-electron processes with a redox separation of 260 mV were found, which is in agreement with our measurements [25].

The cyclopropenylium species **2** showed higher redox potentials in comparison with neutral **1**, which is caused by the electronwithdrawing effect of the cationic 2π aromatic C₃ ring system. The separation between the 1st and 2nd redox event is decreased by 35 mV ($\Delta E^{\circ'} = 215$ mV) (Table 1). The trend that a lower electron density within the bridging system often corresponds to a lower electronic coupling has been established on various examples of π bridged diferrocenes [16,19,51,52], *i. e.* in a series of 2,5-

S.W. Lehrich et al. / Journal of Organometallic Chemistry xxx (2017) 1-9



Fig. 3. Cyclic voltammograms (solid lines: scan rate 100 mV s⁻¹) and square-wave voltammograms (dotted lines: step-height 25 mV, pulse-width 5 s, amplitude 5 mV) of **1** and **2** (left) and *Z*-**5** and *E*-**5** (right) in dichloromethane solutions (1.0 mmol L⁻¹) at 25 °C measured with glassy carbon working electrode. Supporting electrolyte 0.1 mol L⁻¹ of [NⁿBu₄] [B(C₆F₅)₄]).



Fig. 4. Left: UV–Vis/NIR spectra of Z-5 in dichloromethane solution (2.0 mmol L⁻¹) at rising potentials (-200 mV–1300 mV vs Ag/AgCl) at 25 °C; supporting electrolyte 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄]. Right: UV–Vis/NIR spectral changes of Z-5 to *in situ* generated [Z-5]⁺ and [Z-5]²⁺.



Fig. 5. Three band Gaussian deconvolution of the NIR absorption envelope of [Z-5]⁺ (left) and [Z-5]²⁺ (right) obtained by spectroelectrochemistry in an OTTLE cell.

diferrocenyl-1-phenyl-1*H*-pyrroles [51] and in 3,4-di-*N*-substituted 2,5-diferrocenyl thiophenes [19]. For the α,β -unsaturated carbonyl compounds *Z*-**5** and *E*-**5** the assignment of the individual oxidation processes of the three ferrocenyls could be achieved by comparison with similar building blocks from literature (Chart 1). A comparison of various vinylferrocenes with acylferrocenes shows that the electron-withdrawing effect of the carbonyl group leads to a decreased electron density at the CO-bonded ferrocenyl and hence this unit is oxidized at higher potentials (see, for example, ace-tylferrocene **10**, $E^{\circ\prime} = 280$ mV; vinyl ferrocenes **11–13**, $E^{\circ\prime} \approx -75$ mV). Therefore, it is reasonable to assume that the CO-bonded ferrocenyl termini in *Z*/*E*-**5** are oxidized last. Mesomeric

stabilization in α , β -unsaturated carbonyl compounds leads to an enhanced electron density at the α carbon, while the β -position is electron deficient [53]. Following this principle, we assume that the 1st oxidation takes place at the ferrocenyl unit in α -position to the carbonyl functionality, while the β -ferrocenyl is oxidized subsequently.

Paramagnetic ¹H NMR studies on partially oxidized analytes can be used to determine the sequence of the ferrocenyl oxidations [54,55]. Therefore, ¹H NMR studies of *E*-**5** were carried out by subsequent dropwise addition of a solution of "Magic Blue" (= tris-(4-bromophenyl)aminium hexachloroantimonate; 20 mmol in CH₃CN) as oxidant (Supporting Information, Fig. SI11). From these

S.W. Lehrich et al. / Journal of Organometallic Chemistry xxx (2017) 1-9



Fig. 6. UV–Vis/NIR spectra of *E*-**5** in dichloromethane solution (2.0 mmol L^{-1}) at rising potentials (-200 mV–1200 mV vs Ag/AgCl) at 25 °C; supporting electrolyte 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4$.

5]^{+/2+} typical absorptions in the UV–Vis (inner ferrocenyl related MLCT/DMSO-*d*₆ and π^* - π^* transitions) [19,57,58] and in the NIR region (IVCT = inter valence charge transfer) could be detected (Figs. 4–7 and Figs. SI12–SI13). A spectral simulation of the NIR absorptions with three Gaussian-shaped functions was performed to determine the physical parameters (wavenumber ($\bar{\nu}_{max}$), extinction coefficient (ϵ_{max}) and full width at half maximum ($\Delta \tilde{\nu}_{1/2}$)) of the charge transfer excitations (Figs. 5 and 7 and Fig. SI12, Table 2).

Cyclopropenone **1** shows a weak IVCT absorption at 5300 cm⁻¹ ($e_{\text{max}} = 220 \text{ L mol}^{-1} \text{ cm}^{-1}$, $\Delta \nu_{1/2} = 4750 \text{ cm}^{-1}$). The redox separation ΔE° ' of 250 mV for **1** seems to be mainly a result of electrostatic interactions.

Organometallic compounds $[Z-5]^{+/2+}$ and $[E-5]^{+/2+}$ showed IVCT transitions in both oxidation states + and 2+ (Figs. 4 and 6 and Fig. SI13). The IVCT absorption after mono-oxidation was found at 6060 cm⁻¹ (= 1650 nm) (ϵ_{max} = 400 L mol⁻¹ cm⁻¹, $\Delta v_{1/2}$ = 4560 cm⁻¹) for $[Z-5]^+$ and 4810 cm⁻¹ (= 2079 nm)



Fig. 7. Three band Gaussian deconvolution of the NIR absorption envelope of [E-5]⁺ (left) and [E-5]²⁺ (right) obtained by spectroelectrochemistry in an OTTLE cell.

measurements it can be concluded that the carbonyl bound ferrocenyl is oxidized last, while a distinction between the α - and β ferrocenyl was not possible, which might be due to partial charge delocalization between those two ferrocenyl units. This result confirms the statement made earlier.

The Z/E isomerism seems to have no significance for the first two consecutive oxidation processes, which is in accordance with the vinylferrocenes **11–13** (Chart 1) [50]. However, the closer proximity of the *E-β*-ferrocenyl unit toward the CO-bonded ferrocenyl leads to higher electrostatic repulsion in the *E*-isomer and hence, the 3rd redox potential is increased from 490 mV (*Z*-**5**) to 560 mV (*E*-**5**). While for other examples an oxidation-mediated isomerization of vinyl ferrocenes is reported [50], we found no evidence for such behavior in our electrochemical measurements.

In order to get a deeper insight into the charge transfer behavior in **1**, *Z*-**5** and *E*-**5**, *in situ* UV–Vis/NIR spectroelectrochemical measurements were performed (Figs 4 and 6, Figs. SI12 and SI13) in an optically transparent thin-layer electrochemical [56] (= OTTLE) cell containing 2.0 mmol·L⁻¹ of the analyte and 0.1 mol·L⁻¹ of [^{*n*}Bu₄N] [B(C₆F₅)₄] as supporting electrolyte with a stepwise increase of the applied potential from –200 to 1200 mV vs Ag/AgCl. The sequential *in situ* generation of the mixed-valent species was performed by increasing potentials using varying step heights of 25, 50 and 100 mV. In the homo-valent neutral state, molecules **1**, *Z*-**5** and *E*-**5** are, as expected, transparent in the near infrared (NIR). During *in situ* generation of the mixed-valent species [**1**]⁺, [*Z*-**5**]^{+/2+} and [*E*- $(\varepsilon_{\text{max}} = 870 \text{ L mol}^{-1} \text{ cm}^{-1}, \Delta v_{1/2} = 4170 \text{ cm}^{-1})$ for $[E-5]^+$. After subsequent oxidation to the dicationic mixed-valent species, a bathochromic shift of the IVCT band to 5130 cm⁻¹ (= 1949 nm) $(\varepsilon_{\text{max}} = 540 \text{ L mol}^{-1} \text{ cm}^{-1}, \Delta v_{1/2} = 4970 \text{ cm}^{-1})$ for $[Z-5]^{2+}$ and a hypochromic shift to 6000 cm^{-1} (= 1667 nm) $(\varepsilon_{\text{max}} = 190 \text{ L mol}^{-1} \text{ cm}^{-1}, \Delta v_{1/2} = 5690 \text{ cm}^{-1})$ for $[E-5]^{2+}$ was observed. Since the first oxidation takes place at the ferrocenyl in α position, two electron-transfer pathways from the two other ferrocenyls are possible. It could be shown that the electronic coupling in E-vinyl-diferrocenes is stronger than in the corresponding Zisomers [50]. The same result was observed of $[E-5]^+$ and $[Z-5]^+$, since the oscillator strength of the IVCT absorption (f), which represents the strength of the charge transfer, for mono-cationic $[E-5]^+$ is higher than for $[Z-5]^+$ (Table 2). However, after the second oxidation only the transfer path from the CO-ferrocenyl is possible. In this case the enhanced steric strain for the E-isomer, as evinced by the higher torsion between the carbonyl and the vinyl functionality (see X-ray discussion), hinders the conjugation between the redox active termini. As a result, only a very weak IVCT band was observed for the *E*-isomer, while strong electronic coupling was found in the Z-analog (Figs. 4–7, Table 2). The relatively weak bands at ca. 4000 cm^{-1} can be assigned to interconfigurational (IC) transition bands, which are normally forbidden, but gain intensity through spin-orbit coupling and metal-ligand mixing. This observation is often found in ferrocenium complexes [19,59,60].

6

Table 1

Cyclic Voltammetry Data of **1–3**, *Z***-5**, *E***-5** and **7–13** for comparison. All potentials are given in (mV).

Compd.	$E_1^{\circ}^{a}$ $(\Delta E_p)^{d}$	$E_2^{\circ'^{\mathbf{b}}}$ $(\Delta E_p)^{\mathbf{d}}$	$E_3^{\circ} C^{\circ}$ $(\Delta E_p)^{d}$	ΔE° "
1	255 (64)	505 (70)		250
1 ^f	330 (91) ^f	590 (115) ^f		260
2	425 (62)	640 (95)		215
3 ^g	420	510		90
Z- 5	-75 (70)	290 (71)	490 (73)	365/200
E- 5	-60 (60)	275 (60)	560 (75)	335/285
7 ^h 8 ⁱ 9 ^j 10 ^j	110 ^h -65 (70) -55 280	235 ^h 430 (72)		125 ^h 495
11 ^k	-67 ^k	89 ^k	159 ^k	
12 ^k	-77 ^k	93 ^k	170 ^k	
13 ^k	-90 ^k	82 ^k	172 ^k	

Potentials vs FcH/FcH⁺ (FcH = $Fe(\eta^5-C_5H_5)_2$), scan rate 100 mV s⁻¹ at a glassycarbon electrode of 1.0 mmol L⁻¹ solutions in anhydrous dichloromethane containing 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 25 °C.

^a $E_1^{\circ'}$ = formal potential of 1st redox process.

^b $E_{2^{\circ}}$ = formal potential of 2nd redox process.

^c $E_{3^{\circ}}$ = formal potential of 3rd redox process.

^d ΔE_{p} = difference between oxidation and reduction potentials.

 $^e~\Delta E^{\rm cr}$ = potential difference between the two ferrocenyl-related redox processes. $^f~Data$ taken from literature, potentials converted to FcH/FcH⁺ by adding –0.42 V

[25].

^g Potentials from square-wave voltammogram (dotted line: step-height 25 mV, pulse-width 5 s, amplitude 5 mV).

^h Electrolyte $[N^nBu_4][B(3,5-C_6H_3(CF_3)_2)_4]$, scan rate 50 mV s⁻¹, reference electrode Ag/Agl, potentials vs FcH/FcH⁺ [11].

ⁱ From reference [48].

^j From reference [49].

^k In nitrobenzene, electrolyte [NⁿBu₄][PF₆], scan rate 200 mV s⁻¹, reference electrode Ag/AgCN, potentials converted to FcH/FcH⁺ by adding of -125 mV [50].



Chart 1. Selected ferrocene species for comparison of the electrochemical data.

3. Conclusion

Cyclopropenylium cations 2-4 have been prepared starting from 2,3-diferrocenylcyclopropenone (1) [4,5,25]. The strained C₃ ring system in 1 could be cleaved by a nucleophilic attack of ferrocenyl lithium at the carbonyl carbon atom. The ring opened products were obtained as separable isomeric mixtures of 1,2,3triferrocenylpropenones *E*-5 and *Z*-5. Both the *E*- and *Z*-isomer could be crystallized and the molecular solid-state structures were determined by single crystal X-ray diffraction. The single crystals

showed for *E*-**5** a helical chirality crystallizing in an enantiopure form. In addition, from a dichloromethane solution of **3**, which was layered with hexane, single crystals of 6, a cyclopropenone species complexing one molecule of BF₃, could be obtained. The electrochemical behavior of 1-5 have been determined by cyclic voltammetry and square wave voltammetry. It was found that the redox splitting between the ferrocenvl units is decreased for the cyclopropenvlium compounds 2 and 3, when compared with cyclopropenone 1. All cyclopropenylium molecules decompose upon oxidation in multi-cyclic experiments and hence are not stable under oxidative conditions. The well-resolved three ferrocenyl-centered oxidations of *E*-**5** ($E_1^{\circ'} = -60$ mV, $E_2^{\circ'} = 275$ mV and $E_3^{\circ'} = 560$ mV) and Z-5 at ($E_1^{\circ'} = -75$ mV, $E_2^{\circ'} = 290$ mV and $E_3^{\circ'} = 490$ mV) allowed for an assignment of the individual redox events to the respective ferrocenyl units by comparison with similar literature known compounds (Chart 1, Electrochemistry). It is shown that solely the 3rd oxidation process is influenced in a significant way by the *E*/*Z* isomerism, whereby the closer proximity of the β -ferrocenyl and the CO-ferrocenyl in *E*-**5** led to an increase of electrostatic interactions and hence the 3rd oxidation is shifted towards higher potentials (*Z*-**5**, $E_3^{\circ \prime} = 490$ mV; *E*-5, $E_{3^{\circ}}$ = 560 mV). In situ UV–Vis/NIR spectroelectrochemical measurements on compounds 1 and Z-/E-5 evince the charge transfer behavior between the ferrocenyls. The analysis of the IVCT bands allowed the classification of these two compounds as weakly coupled Robin and Day class II systems [62].

4. Materials and methods

4.1. General data

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl. Hexane was purified with a MBRAUN SBS-800 purification system. Dichloromethane was purified by distillation from CaH₂. For column chromatography alumina with a particle size of 90 μ m (standard, Merck KgaA) or silica with a particle size of 40–60 μ m (230–400 mesh (ASTM), Fa. Macherey-Nagel) were used. As filtration support celite (Riedel de Häen) was applied.

4.2. Instrumentation

Infrared spectra were recorded with a FT-Nicolet IR 200 equipment. The ¹H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the ¹³C{¹H} NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent as reference signal (¹H NMR: δ (CDCl₃) = 7.26 ppm; ¹³C{¹H} NMR: δ (CDCl₃) = 77.16 ppm). The melting points were determined with a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were performed with a Thermo FlashEA 1112 Series instrument. High resolution mass spectra were recorded using a micrOTOF QII Bruker Daltonite workstation.

Paramagnetic ¹H NMR studies were performed in CDCl₃ with dropwise adding of "Magic Blue" (tris-(4-bromophenyl)aminium hexachloroantimonate; 20 mmol in CH₃CN) as oxidant and measuring a ¹H NMR spectra after each drop.

4.3. X-ray diffraction

Data were collected with an Oxford Gemini S diffractometer at 120 K for *E*-**5**, *Z*-**5** and at 110 K for **6** (for more details for **6** see Supporting Information) using Mo K_{α} (λ = 0.71073 Å) radiation. The

S.W. Lehrich et al. / Journal of Organometallic Chemistry xxx (2017) 1-9

Table 2

NIR data of the absorp	otions of [1] ⁺ , [E-5	^{+/2+} and	[Z-5] ^{+/2+} .	a
wint uata of the absorp		, [L-J	anu	[2-3]	•

Compd.	${\scriptstyle ilde{ u}}_{ m max}(m cm^{-1})\ (arepsilon(Lmol^{-1} m cm^{-1}))$	- ⁻¹))	$\Delta \tilde{\nu}_{1/2} \ (\mathrm{cm}^{-1})$	$(\Delta \tilde{\nu}_{1/2})_{\text{theo}}{}^{\text{b}}(\text{cm}^{-1})$	$f \cdot 10^{-3c} ({ m cm}^{-1})$
[1]+	IVCT	5300 (220)	4750	3500	4.8
	IC	3710 (40)	360		
[Z-5] ⁺	IVCT	6060 (400)	4560	3740	8.4
	IC	3860 (80)	660		
[Z-5] ²⁺	IVCT	5130 (540)	4970	3440	12.3
	IC	3770 (130)	640		
[E- 5]+	IVCT	4810 (870)	4170	3330	16.7
	IC	3640 (340)	740		
[E- 5] ²⁺	IVCT	6000 (190)	5690	3720	5.0
	IC	3800 (80)	720		

^a In dichloromethane solutions containing 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C.

^b Calculated with equation $(\Delta \tilde{\nu}_{1/2})_{theo} = (2310 \ \tilde{\nu} \ max)^{1/2}$ according to the Hush relationship for weakly coupled systems [61]. ^c Calculated with equation $f = 4.6 \cdot 10^{-9} \cdot \varepsilon \cdot \Delta \tilde{\nu}_{1/2}$.

structures were solved by direct methods and refined by fullmatrix least square procedures on F² with SHELXL-2013 [63,64]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions. Graphics of the molecular structures have been created by using ORTEP [65].

Crystal Data for *E*-**5**: $C_{33}H_{28}Fe_{3}O$, $M_r = 608.10$ g mol⁻¹, monoclinic, P2₁, a = 12.890(11) Å, b = 5.805(5) Å, c = 17.414(16) Å, $\beta = 109.071(9)$ °, V = 1231.5(2) Å³, Z = 2, $\rho_{calcd} = 1.640$ g m⁻³, $\mu = 1.770 \text{ mm}^{-1}$, T = 120(1) K, θ range $3.345-24.991^{\circ}$, 3800 reflections collected, 3800 independent reflections ($R_{int} = 0.0463$), R1 = 0.0636, wR2 = 0.1513 ($I > 2\sigma(I)$).

Crystal Data for Z-**5**: $C_{33}H_{28}Fe_3O$, $M_r = 608.10$ g mol⁻¹, orthorhombic, $Pca2_1$, a = 23.167(11) Å, b = 5.811(2) Å, c = 18.164(16) Å, V = 2445.2(15) Å³, Z = 4, $\rho_{calcd} = 1.652$ g m⁻³, $\mu = 1.783$ mm⁻¹, T = 120 K, θ range 3.506–24.997°, 3141 reflections collected, 3141 independent reflections (*R*_{int} = 0.0383), *R*1 = 0.0250, *wR*2 = 0.0543 $(I > 2\sigma(I)).$

4.4. Electrochemistry

Electrochemical measurements on 1.0 mmol L⁻¹ solutions of the analyte in anhydrous, air free dichloromethane containing 0.1 mol·L⁻¹ of $[N^n Bu_4][B(C_6 F_5)_4]$ as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a Radiometer Voltalab PGZ 100 electrochemical workstation combined with a personal computer [66–68]. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm²) and an Ag/Ag⁺ (0.01 mol·L⁻ AgNO₃) reference electrode mounted on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 μ m and then with a 1/4 μ m diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol·L⁻¹ [AgNO₃] and 0.1 mol·L⁻¹ [NⁿBu₄][B(C_6F_5)₄] in acetonitrile in a Luggin capillary with a CoralPor tip. This Luggin capillary was inserted into a second Luggin capillary with a CoralPor tip filled with a 0.1 mol \cdot L⁻¹ $[N^{n}Bu_{4}][B(C_{6}F_{5})_{4}]$ solution in dichloromethane. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Experimentally, potentials were referenced against an Ag/Ag⁺ reference electrode but results are presented referenced against ferrocene as an internal standard as required by IUPAC [69]. When decamethylferrocene was used as an internal standard, the experimentally measured potentials were converted into E vs FcH/ FcH^+ by setting the Fc^*/Fc^{*+} ($Fc^* = Fe(\eta^5-C_5Me_5)_2$) potential to -614 mV [70,71]. Ferrocene itself showed a redox potential of 220 mV vs Ag/Ag⁺ ($\Delta E_p = 61$ mV) within the measurements [72,73]. The cyclic voltammograms, which are depicted in Fig. 5, Fig. SI9 and Fig. SI10 were taken after typically three scans and are considered to be steady state cyclic voltammograms in which the signal pattern differs not from the initial sweep.

UV-Vis/NIR measurements were carried out in an OTTLE (= optically thin-layer electrochemical) cell with quartz windows similar to that described previously [56] in anhydrous dichloromethane solutions containing $2.0 \text{ mmol} \cdot L^{-1}$ analyte and 0.1 mol·L⁻¹ of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte using a Varian Cary 5000 spectrophotometer at 25 °C. The working electrode Pt-mesh, the AgCl coated Ag wire for reference and the Ptmesh auxiliary electrode are melt-sealed into a polyethylene foil. The values obtained by deconvolution could be reproduced within $\varepsilon_{\text{max}} = 100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, $\nu_{\text{max}} = 50 \text{ cm}^{-1}$ and $\Delta \nu_{1/2} = 50 \text{ cm}^{-1}$. Between the spectroscopic measurements the applied potentials have been increased step-wisely using step heights of 25, 50 or 100 mV. At the end of the measurements the analyte was reduced at -400 mV for 30 min and an additional spectrum was recorded to prove the reversibility of the oxidations.

4.5. Reagents

 $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$ was prepared by metathesis of lithium tetrakis(pentafluorophenyl)borate etherate (Boulder Scientific) with tetra-*n*-butylammonium bromide according to reference [45]. All other chemicals were purchased from commercial suppliers and were used without further purification. Compounds 1-4 were synthesized according to published procedures [3–5,13,25].

4.6. Synthesis

Z- and E-1,2,3-triferrocenylprop-2-enone (Z-5/E-5). Ferrocene (0.4 g, 2.13 mmol) and KO^tBu (30 mg, 0.27 mmol) were dissolved in 40 mL of tetrahydrofuran and the mixture was cooled to -80 °C. ^tBuLi (2.2 mL, 4.26 mmol, 1.9 M solution in pentane) was added dropwise via a syringe and the reaction mixture was stirred for 1 h during warming up to 0 °C. Then compound **1** (0.9 g, 2.13 mmol) dissolved in 20 mL of tetrahydrofuran was added dropwise via a syringe and the reaction solution was stirred at ambient temperature for 12 h. After evaporation of all volatiles in vacuum, 20 mL of water and 60 mL of dichloromethane were added and the organic phase was extracted twice each with 40 mL of water. The resulting organic phase was dried over MgSO4 and all volatiles were removed. The crude product was purified by column chromatography (column size: 20 × 3 cm, silica) using a hexanedichloromethane mixture of ratio 1:1 (v/v) as eluent. The third

8

fraction was (*E*)-1,2,3-triferrocenylprop-2-enone (*E*-**5**) and the fourth fraction (*Z*)-1,2,3-triferrocenylprop-2-enone (*Z*-**5**). Removing of all volatiles under reduced pressure gave dark red solids. The isomeric ratio is 1:1.

(*E*)-1,2,3-triferrocenylprop-2-enone (*E*-**5**): Yield of *E*-**5**: 135 mg (0.22 mmol, 10% based on 1). Anal. Calcd. for C₃₃H₂₈Fe₃O $(M = 608.11 \text{ g} \cdot \text{mol}^{-1})$: C 65.18, H 4.64; found: C 64.41, H 4.93 (Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.). Mp.: >200 °C decomposition. IR (KBr, in cm^{-1}): 3088 (m, v_{C-H}), 2954 (w), 1635 (s, $v_{C}=_0$), 1615 (m), 1450 (m), 1410 (w), 1374 (m), 1265 (w), 1244 (m), 1105 (m), 1094 (m), 1048 (m), 1029 (m), 1000 (m, δ_{C-H} , C₅H₄), 821 (s, π_{C-H} , C₅H₅), 516 (s, C₅H₄ ring tilt). ¹H NMR (CDCl₃, δ in ppm): 4.01 (s, 5 H, C₅H₅), 4.17 (s, 5 H, C₅H₅), 4.17 (pt (= pseudo triplett), $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.24 (s, 5 H, C_5H_5), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.31 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.36 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.46 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.60 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 6.70 (s, 1 H, C=CH). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 66.5 (C₅H₄), 68.6 (C₅H₄), 69.3 (C₅H₄), 69.4 (C₅H₅), 69.5 (C₅H₄), 69.9 (C₅H₅), 70.2 (C₅H₅), 70.6 (C₅H₄), 71.9 (C₅H₄), 80.3 (ⁱC-C₅H₄), 82.0 (ⁱC-C₅H₄), 85.1 (ⁱC-C₅H₄), 124.6 (C=CH), 136.3 (C=CH), 202.5 (C=O). HRMS (ESI-TOF, m/z): calcd. for C₃₃H₂₈Fe₃O: 608.0188; found 608.0135 [M]⁺.

(Z)-1,2,3-triferrocenylprop-2-enone (Z-5): Yield of Z-5: 135 mg (0.22 mmol, 10% based on 1). Anal. Calcd. for C₃₃H₂₈Fe₃O $(M = 608.11 \text{ g} \cdot \text{mol}^{-1})$: C 65.18, H 4.64; found: C 64.65, H 4.99. Mp.: 176 °C. IR (KBr, in cm⁻¹): 3093 (m, v_{C-H}), 2959 (w), 2923 (w), 2852 (w), 1635 (s, $v_c = 0$), 1615 (m), 1439 (m), 1410 (w), 1376 (m), 1272 (m), 1246 (m), 1106 (m), 1094 (m), 1046 (m), 1031 (m), 1001 (m, δ_{C-H} , C₅H₄), 820 (s, π_{C-H} , C₅H₅), 526 (w, C₅H₄ ring tilt). ¹H NMR (CDCl₃, δ in ppm): 3.92 (s, 5 H, C₅H₅), 4.13 (s, 5 H, C₅H₅), 4.20 (pt, $J_{\rm HH} = 1.9$ Hz, 2 H, C₅H₄), 4.25 (pt, $J_{\rm HH} = 1.9$ Hz, 2 H, C₅H₄), 4.30 (pt, $J_{\rm HH} = 1.9$ Hz, 2 H, C₅H₄), 4.35 (s, 5 H, C₅H₅), 4.41 (pt, $J_{\rm HH} = 1.9$ Hz, 2 H, C_5H_4), 4.61 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.94 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.28 (s, 1 H, =CH). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 68.3 (C₅H₄), 69.2 (C₅H₅), 69.3 (C₅H₄), 69.5 (C₅H₅), 70.1 (C₅H₄), 70.2 (C₅H₄), 70.3 (C₅H₅), 71.3 (C₅H₄), 72.2 (C₅H₄), 79.1 (¹C-C₅H₄), 79.2 (¹C-C₅H₄), 80.1 (¹C-C₅H₄), 131.0 (C=CH), 136.2 (C=CH), 200.6 (C=O). HRMS (ESI-TOF, *m/z*): calcd. for C₃₃H₂₈Fe₃O: 608.0188; found 608 0.0148 [M]⁺.

Acknowledgment

We thank Julia A. Kronawitt for her support in lab. We are grateful to the Fonds der Chemischen Industrie for generous financial support. M.K. thanks the Fonds der Chemischen Industrie for a Chemiefonds fellowship.

Appendix A. Supplementary data

Figures, Tables, and CIF files giving further (spectro)electrochemical spectra, NMR spectra, and crystallographic data. This material is available free of charge *via* the Internet at http://dx.doi. org/.

Crystallographic data of *Z*-/*E*-**5** and **6** are also available from the Cambridge Crystallographic Database as file numbers 1518178 (*Z*-**5**), 1518177 (*E*-**5**) and CCDC 1518176 (**6**).

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.03.018.

References

- [1] R. Breslow, J. Am. Chem. Soc. 79 (1957) 5318.
- [2] K. Komatsu, T. Kitagawa, Chem. Rev. 103 (2003) 1371.
- [3] I. Agranat, E. Aharon-Shalom, J. Am. Chem. Soc. 97 (1975) 3829.

- [4] T. Klimova Berestneva, E.I. Klimova, J.M. Méndez Stivalet, S. Hernández-Ortega, M. Martínez García, Eur. J. Org. Chem. (2005) 4406.
 [5] E.I. Klimova, T.K. Berestneva, S.H. Ortega, D.M. Iturbide, A.G. Marquez,
- [5] L.I. KIIIIIOVA, I.K. BERESTIEVA, S.H. UTEGA, D.M. ITUTDIDE, A.G. MARQUEZ, M.M. García, J. Organomet. Chem. 690 (2005) 3333.
- [6] T. Eicher, D. Lerch, Tetrahedron Lett. 21 (1980) 3751.
- [7] S. Yoneda, H. Hirai, Z. Yoshida, Chem. Lett. 46 (1976) 1051.
- [8] T. Berestneva, E. Klimova, M. Flores-Alamo, L. Backinowsky, M. García, Synth. (Stuttg) (2006) 3706.
- [9] U. Pfaff, A. Hildebrandt, D. Schaarschmidt, T. Rüffer, P.J. Low, H. Lang, Organometallics 32 (2013) 6106.
- [10] F. Paul, C. Lapinte, Coord. Chem. Rev. 178-180 (1998) 431.
- [11] Y. Li, M. Josowicz, L.M. Tolbert, J. Am. Chem. Soc. 132 (2010) 10374.
- [12] M.D. Ward, Chem. Soc. Rev. 24 (1995) 121.
- [13] I. Agranat, E. Aharon-Shalom, Tetrahedron 35 (1979) 733.
- [14] R. Hauser, D. Lednicer, Angew. Chem. Int. Ed. Engl. 11 (1972) 1025.
 [15] A. Hildebrandt, H. Lang, Organometallics 32 (2013) 5640.
- [16] A. Hildebrandt, U. Pfaff, H. Lang, Rev. Inorg. Chem. 31 (2011) 111.
- [17] S.W. Lehrich, A. Hildebrandt, T. Rüffer, M. Korb, P.J. Low, H. Lang, Organo-
- metallics 33 (2014) 4836. [18] D. Miesel, A. Hildebrandt, M. Korb, P.J. Low, H. Lang, Organometallics 32
- (2013) 2993.
 [19] J.M. Speck, M. Korb, A. Schade, S. Spange, H. Lang, Organometallics 34 (2015)
- 3788.
 D. Missel A. Hildshards M. Keit, H. Leng, L. C. Statistics of Control (2012)
- [20] D. Miesel, A. Hildebrandt, M. Korb, H. Lang, J. Organomet. Chem. 803 (2016) 104.
- [21] K. Kaleta, A. Hildebrandt, F. Strehler, P. Arndt, H. Jiao, A. Spannenberg, H. Lang, U. Rosenthal, Angew. Chem. - Int. Ed. 50 (2011) 11248.
- [22] K. Kaleta, F. Strehler, A. Hildebrandt, T. Beweries, P. Arndt, T. Rüffer, A. Spannenberg, H. Lang, U. Rosenthal, Chem. Eur. J. 18 (2012) 12672.
- [23] B. van der Westhuizen, J.M. Speck, M. Korb, D.I. Bezuidenhout, H. Lang, J. Organomet. Chem. 772–773 (2014) 18.
- [24] S.W. Lehrich, A. Hildebrandt, M. Korb, H. Lang, J. Organomet. Chem. 792 (2015) 37.
- [25] E.I. Klimova, T. Klimova Berestneva, L.R. Ramirez, A. Cinquantini, M. Corsini, P. Zanello, S. Hernández-Ortega, M.M. García, Eur. J. Org. Chem. (2003) 4265.
- [26] E.I. Klimova, T. Klimova, S.H. Ortega, M.E. Rabell, L.R. Ramírez, M.M. García, J. Organomet. Chem. 689 (2004) 2395.
 [27] H. Flack, A.G. Gutti, Mag. Gatt, A. 202 (2002) 275.
- [27] H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876.
- [28] J.J. Burckhardt, R. Haüy, Die Symmetrie Der Kristalle, Birkhäuser, Basel, Schweiz, 1988.
- [29] L.N. Sobenina, M.V. Markova, D.N. Tomilin, E.V. Tret'yakov, V.I. Ovcharenko, A.I. Mikhaleva, B.A. Trofimov, Russ. J. Org. Chem. 49 (2013) 1241.
- [30] I.R. Butler, P.N. Horton, M.B. Hursthouse, Crystal Structure Report Archive, vol. 912, University of Southampton, 2002.
- [31] I.R. Butler, S.J. Coles, M.B. Hursthouse, Crystal Structure Report Archive, vol. 907, University of Southampton, 2002.
- [32] E.I. Klimova, E.A. Vázquez López, J.M. Martínez Mendoza, L.R. Ramírez, M.F. Alamo, L.V. Backinowsky, J. Heterocycl. Chem. 46 (2009) 484.
- [33] Y. Jung, K.I. Son, Y.E. Oh, D.Y. Noh, Polyhedron 27 (2008) 861.
- [34] D.I. Méndez, E. Klimova, T. Klimova, L. Fernando, S.O. Hernández, M.G. Martínez, J. Organomet. Chem. 679 (2003) 10.
- [35] A.C. Coleman, C. Long, A. Meetsma, B.L. Feringa, W.R. Browne, M.T. Pryce, Dalton Trans. (2009) 7885.
- [36] Z. Jin, A. Huo, T. Liu, Y. Hu, J. Liu, J. Fang, J. Organomet. Chem. 690 (2005) 1226.
 [37] B. Delavaux-Nicot, J. Maynadié, D. Lavabre, C. Lepetit, B. Donnadieu, Eur. J. Inorg. Chem. 2 (2005) 2493.
- [38] E.I. Klimova, T. Klimova Berestneva, R. a. Toscano, J.M. Méndez Stivalet, M. Martínez Garcia, Synth. Commun. 37 (2007) 889.
- [39] J.J.C. Erasmus, G.J. Lamprecht, J.C. Swarts, A. Roodt, Å. Oskarsson, Acta Crystallogr. Sect. C Cryst. Struct. Commun. 52 (1996) 3000.
- [40] C.A. Pugh, M.W. Lufaso, M. Zeller, T.R. Wagner, L.S. Curtin, J. Organomet. Chem. 691 (2006) 680.
- [41] G. Laus, H. Schottenberger, J. Lukasser, K. Wurst, J. Schütz, K.H. Ongania, L. Zsolnai, J. Organomet. Chem. 690 (2005) 691.
- [42] J.J. Burckhardt, Die Symmetrie Der Kristalle, Birkhäuser Verlag, Basel, Switzerland, 1988.
- [43] W.E. Geiger, F. Barrière, Acc. Chem. Res. 43 (2010) 1030.
- [44] H.J. Gericke, N.I. Barnard, E. Erasmus, J.C. Swarts, M.J. Cook, M.S.A. Aquino, Inorg. Chim. Acta 363 (2010) 2222.
- [45] R.J. LeSuer, C. Buttolph, W.E. Geiger, Anal. Chem. 76 (2004) 6395.
- [46] F. Barriere, Organometallics 33 (2014) 5046.
- 47] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.
- [49] J.M. Speck, M. Korb, T. Rüffer, A. Hildebrandt, H. Lang, Organometallics 33 (2014) 4813.
 - [50] Y.J. Chen, D.-S. Pan, C.-F. Chiu, J.-X. Su, S.J. Lin, Inorg. Chem. 39 (2000) 953.
 - [51] A. Hildebrandt, H. Lang, Dalton Trans. 40 (2011) 11831.
 - [52] R.F. Winter, Organometallics 33 (2014) 4517.
 - [53] N.L. Allinger, M.P. Cava, D.C. de Jongh, C.R. Johnson, N.A. Lebel, C.L. Stevens, Organische Chemie, Walter de Gruyter, Berlin, 1980.
 - [54] D. Siebler, M. Linseis, T. Gasi, L.M. Carrella, R.F. Winter, C. Förster, K. Heinze, Chem.-A Eur. J. 17 (2011) 4540.
 - [55] C. Förster, P. Veit, V. Ksenofontov, K. Heinze, Chem. Commun. 51 (2015) 1514.
 - [56] M. Krejcik, M. Danek, F. Hartl, J. Electroanal. Chem. 317 (1991) 179.

S.W. Lehrich et al. / Journal of Organometallic Chemistry xxx (2017) 1-9

- [57] D.M. Duggan, D.N. Hendrickson, Inorg. Chem. 14 (1975) 955.
- [57] D.M. Duggar, D.M. Hendrickson, H.B. Gray, J. Am. Chem. Soc. (1971) 3603.
 [59] Y. Li, M. Josowicz, L.M. Tolbert, J. Am. Chem. Soc. 132 (2010) 10374.
 [60] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, Chem. Rev. 101 (2001) 2655.
- [61] N.S. Hush, Electrochim. Acta 13 (1968) 1005.
- [62] M.B. Robin, P. Day, Adv. Inorg. Chem. Radiochem 10 (1968) 247.

- [62] M.B. RODII, P. Day, Adv. morg. Chen. Radiochem 10 (1968) 247.
 [63] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.
 [64] G.M. Sheldrick, SHELXL-97, Progr. Crystal Struct, Refinement University, 1997.
 [65] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849.
 [66] H.J. Gericke, N.I. Barnard, E. Erasmus, J.C. Swarts, M.J. Cook, M. a. S. Aquino,

Inorg. Chim. Acta 363 (2010) 2222.

- [67] F. Barrière, W.E. Geiger, J. Am. Chem. Soc. 128 (2006) 3980.
 [68] F. Barrière, N. Camire, W.E. Geiger, U.T. Mueller-Westerhoff, R. Sanders, J. Am. Chem. Soc. 124 (2002) 7262.
- [69] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.
- [70] A. Nafady, W.E. Geiger, Organometallics (2008) 5624.
 [71] I. Noviandri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, L. Phillips, J. Phys. Chem. B 103 (1999) 6713.
- [72] J.A. Ruiz, M.-C. Daniel, D. Astruc, Can. J. Chem. 84 (2006) 288.
 [73] J. Ruiz, D. Astruc, C. R. Acad. Sci. Paris, T. 1, Ser. II C. 1 (1998) 21.