1,3,5-Triferrocenyl-2,4,6-tris(ethynylferrocenyl)-benzene – a new member of the family of multifunctionalised cyclic systems† ‡

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The consecutive synthesis of 1,3,5-triferrocenyl-2,4,6-tris(ethynylferrocenyl)benzene (6c) is described using 1,3,5-C12-2,4,6-I3-C6 (2) as starting compound. Subsequent Sonogashira C,C cross-coupling of 2 with FcC≡CH (3) in the molar ratio of 1 : 4 afforded solely 1,3,5-C12-2,4,6-(FcC≡C)3-C6 (4c) (Fc = Fe(η5-C5H4)2(I′-C5H4)). However, when 2 is reacted with 3 in a 1 : 3 ratio a mixture of 1,3,5-C12-2,4,6-I3-C6 (4a) and 1,3,5-C12-2,4,6-(FcC≡C)3-C6 (4b) is obtained. Negishi C,C cross-coupling of 4c with FcZnCl (5) in the presence of catalytic amounts of [Pd(CH2C(CH3)2P(η5-C5H5))2][μ-Cl]2 gave 1,3,5-C12-5-Fc-2,4,6-(FcC≡C)3-C6 (6a), 1-Cl-3,5-Fc2-2,4,6-(FcC≡C)3-C6 (6b) and 1,3,5-Fc3-2,4,6-(FcC≡C)3-C6 (6c) of which 6b is the main product. Column chromatography allowed the separation of these organometallic species. The structures of 4a,b and 6a in the solid state were determined by single crystal X-ray diffraction showing a π-π interacting dimer (4b) and a complex π-π pattern for 6a. The electrochemical properties of 4a-c and 6a-c were studied by cyclic voltammetry (=CV) and square wave voltammetry (=SWV). It was found that the FcC≡C-substituted benzences 4a-c show only one reversible redox event, indicating a simultaneous oxidation of all ferrocenyl units, whereby 4c is most difficult to oxidise (4a, E°′ = 190, ΔEpa = 71; 4b, E°′ = 195, ΔEpa = 59; 4c, E°′ = 390, ΔEpa = 59 mV). In case of 4c, the oxidation states 4cO+n (n = 2, 3) are destabilised by the partial negative charge of the electronegative chlorine atoms, which compensates the repulsive electrostatic Fc+−Fc+ interactions with attractive electrostatic Fc+−Cl− interactions. When ferrocenyl units are directly attached to the benzene C6 core, organometallic 6a shows three, 6b five and 6c six separated reversible waves highlighting that the FeC units can separately be oxidised. UV-Vis/NIR spectroscopy allowed to determine ICT absorptions (=Inter Valence Charge Transfer) for 6cO+n (n = 1, 2) (n = 1: kmax = 7860 cm−1, εmax = 405 L mol−1 cm−1, Δν1/2 = 7070 cm−1; n = 2: kmax = 9070 cm−1, εmax = 620 L mol−1 cm−1, Δν1/2 = 8010 cm−1) classifying these mixed-valent species as weakly coupled class II systems according to Robin and Day, while for 6a,b only LMCT transitions (=ligand to metal charge transfer) could be detected.

Introduction

Multifunctionalised aromatics and heteroaromatics are fascinating molecules. Besides their uncommon molecular structures, such sterically crowded compounds possess, for example, interesting electronic properties.1 Hence, they can be considered as model systems to study intramolecular electron transfer through π-conjugated carbon-rich organic linking units via the mixed-valence states derived from these multi-metallic compounds. In this respect, the ferrocenyl group is beneficial since the [Fe(η5-C5H4)2] redox couple shows an excellent electrochemical reversibility and high thermal stability.2 The degree of electronic communication among the appropriate metal centers has mostly been explored by electrochemical studies such as cyclic voltammetry (=CV), square wave voltammetry (=SWV) and spectroelectrochemistry (e.g., in situ UV-Vis/NIR spectroscopy). Other relevant applications for reversible multi-step redox systems include their use in the field of catalysis,3 in biological studies4 or as novel molecular electro-active materials.5

Super-crowded ferrocenyl-based organometallic compounds are moreover remarkable species because the expected steric
encumbrance may hinder chemical conjugation between the aromatic core and the ferrocenyl substituents. Representatives of this class of compounds are, for example, ferrocenyl-end-grafted dendrimers\(^7\) in which the intramolecular distance between the ferrocenyls is enlarged by various units such as ethynyl,\(^{6a-c}\) ethyl benzene,\(^{6d-e}\) and ethynyl thiophene\(^6f\) or amidoamine-based dendrimers.\(^7\) Further examples of multi-ferrocenyl organometallic compounds are benzenes,\(^{6b,c,9}\) 5-membered heterocycles\(^{10,11}\) or even covalt\(^{12}\) and manganese\(^{13}\) half-sandwich species with up to six terminal ferrocenyl or ethynyl ferrocenyl entities, \(\text{i.e.} \ (\text{FcC}≡\text{C})_n \text{C}_6, \text{C}_6 \text{F}_6, \text{C}_6 \text{H}_4 \text{(E} = \text{O, S, NPh, NMe}), \text{Co(}η^5\text{-FeC}_4\text{)}(η^5\text{-C}_2\text{H}_5)\text{, and Mn-}(\text{η}^5\text{-FeC}_2\text{)}(\text{CO})_3\). Electrochemical studies revealed that for the respective super-crowded ferrocenyl thiophene significant electrostatic interaction among the four ferrocenyl groups occurs as oxidation progresses. The spectroelectrochemical results showed several UV-Vis and NIR peaks appearing or disappearing between 280 and 3000 nm as this compound is stepwisely oxidised to ultimately generate \([2,3,4,5\text{-FeC}_4\text{]}\text{S}\)\(^+\). For the respective pyrrole compounds electronic interaction between the ferrocenyl/ferrocenium units is evidenced by \(\text{in situ} \ \text{UV-Vis/} \ \text{NIR} \ \text{spectroscopy.}\)\(^{10b}\) In contrast, Vollhardt’s hexa-ethynylferrocenyl benzene\(^2\) and Astruc’s hexa-ethynylferrocenyl benzene\(^6c\) show three separated redox events.

We here enrich this family of perferrocenylated benzenes and describe for the first time the synthesis of multiferrocenyl-substituted benzenes featuring alternating ferrocenyl and ethynyl ferrocenyl functionalities, which represent a combination of the structural motifs of Vollhardt’s\(^9\) and Astruc’s\(^6d,e\) benzenes. The physical and chemical properties of 1,3,5-Cl\(_3\)-2,4,6-(FeC≡C)\(_3\)-C\(_6\), 1,3,5-Cl\(_3\)-2,4,6-(FeC≡C)\(_3\)-Cl\(_6\), 1,3,5-Cl\(_3\)-2,4,6-(FeC≡C)\(_3\)-C\(_6\), and 1,3,5-FeC\(_2\)-2,4,6-(FeC≡C)\(_3\)-C\(_6\) (Fe = Fe(η\(^5\)-C\(_2\)-H\(_5\))(η\(^5\)-C\(_2\)-H\(_5\))) as well as their electrochemical properties will be highlighted.

### Results and discussion

#### Synthesis and characterisation

1,3,5-Trichloro-2,4,6-triiodo-benzene (2),\(^14\) which is accessible by an electrophilic aromatic substitution,\(^15\) was utilised as starting compound for the preparation of 1,3,5-Cl\(_3\)-2,4,6-(FeC≡C)\(_3\)-C\(_6\) (4c) in a Sonogashira C,C cross-coupling reaction\(^16\) (Scheme 1). It appeared that four equivalents of 3 is imperative to the success of the reaction, since with a 1 : 3 stoichiometry of 2 and 3 only the mono- and di-substituted species 1,3,5-Cl\(_2\)-2-(FeC≡C)-4,6-I-C\(_6\) (4a) and 1,3,5-Cl\(_2\)-2,4-(FeC≡C)\(_2\)-6-I-C\(_6\) (4b), respectively, are formed (Scheme 1). Furthermore, the concentration of the palladium catalyst \([\text{PdCl}_2(\text{PPh}_3)_2]\) in the Sonogashira C,C cross-coupling plays a crucial role. For the synthesis of 4c, 1 mol% of the catalyst is required to obtain virtually quantitative yield of 4c (Experimental section), while for the synthesis of 4a and 4b 0.5 mol% of the palladium catalyst is adequate. The separation of 4a from 4b was realised by column chromatography.

The introduction of the ferrocenyl substituents in 4c to give 1,3,5-FeC\(_2\)-2,4,6-(FeC≡C)\(_3\)-C\(_6\) (6c) was realised by the synthetic methodology shown in Scheme 2. The best results were obtained, when 9 eq. of FeZnCl (5) as ferrocenyl source were reacted with 4c under typical Negishi C,C cross-coupling conditions\(^17\) using \([\text{PdCl}_2(\text{CH}_2\text{C(}\text{CH}_3\text{)}\text{)}\text{P(}\text{C}_6\text{H}_{13}\text{)}_2](\text{μ-Cl})_2\) (0.25 mol%) as catalyst (Scheme 2, Experimental section). After appropriate work-up, compounds 6a-c, in which alternating Fe and FeC≡C units are attached to the benzene core, were isolated in the ratio of 1 : 11.2 : 3.6 (= 6a : 6b : 6c) (Scheme 2).

The Fe and FeC≡C multi-substituted benzenes 4a-c and 6a-c (Schemes 1 and 2) were obtained as red (4b, 6b) or orange (4a,c) and 6a,c solids, which dissolve in almost all common organic solvents, including toluene, dichloromethane and tetrahydrofuran. They are stable towards air and moisture in the solid state and in solution.

For comparison (see Spectroelectrochemistry part) 1-FeC≡C-2-FeC\(_6\)\(_4\) (9) has been synthesized starting from 1-Br-2-I-C\(_6\)\(_4\) (7).\(^18\) When 7 was reacted with FeC≡CH (3), then 1-bromo-2-ethylferrocenyl benzene (8) was formed, which on treatment with FeZnCl (5) under typical Negishi C,C cross-coupling conditions gave 9.\(^18\)

Organometallics 4a-c and 6a-c have been identified by elemental analysis, NMR (\(^1\)H, \(^{13}\)C{\(^1\)H}) and IR spectroscopy as well as high resolution ESI-TOF mass spectrometry (Experimental section). In addition, they were analysed electrochemically.
using cyclic voltammetry and square wave voltammetry. Spectroelectrochemistry measurements were carried out to prove if intramolecular electron transfer occurs in the mixed-valent species using *in situ* UV-Vis/NIR spectroscopy.

The $^1$H and $^{13}$C($^1$H) NMR spectroscopic properties of 4a–c and 6a–c correlate with their formulaisations as Fe and FeC≡C multi-functionalised benzenes showing the respective signal patterns for the Fe, C≡C and C$_6$ core building blocks. Most distinctive for the formation of these molecules is the appearance of the expected AA′XX′ signal pattern$^{19}$ for the C$_4$H$_4$ units ($\nu_{\text{HH}} = 1.9$ Hz) and the singlet for the C$_4$H$_5$ moieties (Experimental section). Further characteristic in the $^{13}$C($^1$H) NMR spectra of all complexes are the signals for the ethynyl units, which resonate at ca. 65 ppm (C≡C–C$_6$) and ca. 100 ppm (C≡C–Fc), respectively (Experimental section). 2D experiments such as COSY, HSQC and HMBC were applied to assign the carbon signals in 4a–c and 6a–c unequivocally. Most characteristic in the IR spectrum of all newly synthesised compounds is the appearance of one sharp C–C stretching vibration between 2200 and 2220 cm$^{-1}$, specific for this distinctive unit.$^{20}$

The formation of 4a–c and 6a–c was additionally evidenced from ESI-TOF mass spectrometric investigations. All organometallic compounds show the molecular ion peak [M]$^+$ (Experimental section). Moreover, comparison of the measured isotope patterns (Cl, I) of 4a–c and 6a,b with the calculated ones confirm the elemental composition and charge state.

Furthermore, single crystal X-ray diffraction studies have been carried out to determine the molecular structures of 4a (Fig. 1), 4b (Fig. 2) and 6a (Fig. 3) in the solid state. Suitable single crystals of 4a,b and 6a could be obtained either by crystallisation of 4a and 6a from dichloromethane solutions, or by slow diffusion of n-hexane into a dichloromethane solution containing 4b at ambient temperature (Experimental section). Important bond distances ($\AA$), bond angles (°) and torsion angles (°) are summarised in the captions of Fig. 1–3. For crystal and structure refinement data see ESI.$^\dagger$ Compound 4a crystallises in the triclinic space group $P1$, 4b in the monoclinic space group $C2/c$ and 6a in the orthorhombic space group $Pcnm$.

The asymmetric unit for 4a contains one molecule, whereas half of a dimer of 4b is characteristic for the unit cell. In the case of 6a, two molecules describe the asymmetric unit. The carbon–carbon bond lengths of the benzene cores of 4a,b and 6a in (average 1.394 Å) (Fig. 1–3) are in agreement with the distances found in unsubstituted benzene (1.39 Å).$^{21}$ The $C$, $C$ distances of the ethynyl units agree with $\text{C}\equiv\text{C}$ bond lengths of this type of building blocks (1.20 Å).$^{21}$

The orientation of the cyclopentadienyl rings of the syn-oriented ferrocenyls to the six membered C$_6$ cycle is almost
Fig. 3  ORTEP diagram (50% probability level) of the molecular structure of 6a with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°): Fe1–D1 = 1.623(2), Fe1–D2 = 1.645(2), Fe2–D3 = 1.663(2), Fe2–D4 = 1.642(2), Fe3–D5 = 1.661(2), Fe3–D6 = 1.649(2), Fe4–D7 = 1.643(3), Fe4–D8 = 1.651(3), C1–C7 = 1.514(16), C6–C41 = 1.459(14), C41–C42 = 1.18(2), C42–C43 = 1.45(2), C4–C29 = 1.415(16), C29–C30 = 1.23(2), C30–C31 = 1.42(2), C2–C17 = 1.440(16), C17–C18 = 1.20(2), C18–C19 = 1.43(2), C3–C11 = 1.720(7), C5–C12 = 1.724(7), D1–Fe1–D2 = 175.69(18), D3–Fe2–D4 = 178.07(16), D5–Fe3–D6 = 178.28(17), D7–Fe4–D8 = 179.23(16), C18–C17–C2 = 171.7(14), C30–C29–C4 = 174.1(14), C42–C41–C6 = 173.8(16), C7–C1–C6 = 121.1(7), C7–C1–C2 = 118.8(7); C7–C1–C2–C17 = –13.1(11), C7–C1–C6–C41 = 2.4(11), C11–C3–C4–C29 = –2.5(9), C29–C4–C5–C12 = –1.9(9), C19–C18–C17–C2 = 94.36, C43–C42–C41–C6 = –156.17, C31–C30–C29–C4 = –82.58, (D1, D3, D5, D7 denote the centroid of C$_n$H$_m$, while D2, D4, D6, D8 denote the centroid of C$_n$H$_m$).

Fig. 4  ORTEP diagram (50% probability level) of the molecular structure of 6a, showing intra- (left) and inter-molecular (right) T-shaped π–π interactions between the ferrocenyls. Hydrogen atoms are omitted for clarity. Orange: iron; green: chlorine; blue: distances between two centroids. (Left): 4.784(11) Å; (right): 4.981(13) Å.

coplanar in molecule 4b (3.6(10), 3.5(10)°), however, it somewhat deviates from planarity in 4a (14.6(2)°). All ferrocenyls in 4a,b and 6a possess an eclipsed conformation (4a, –0.8(2)°; 4b, –1.4(2), 1.1(9)°; 6a, 8.5(10), 9.0(11), 2.6(11), 1.8(12)°). The more sterically demanding FeC ≡ C and Fe groups are bonded to the benzene core, the lower is the coplanarity of the ferrocenyls with the C$_n$ unit in 6a. However, for all iron-centroid distances in 4a,b and 6a as well as for all torsion angles, no significant differences occur. Reasons for the orientation of the ferrocenyls in 6a are the T-shaped π–π interactions between two ferrocenyls including intra-molecular (Fig. 4; 4.784(11) Å) as well as inter-molecular ones (Fig. 4; 4.981(13) Å). Furthermore, π–π interactions between the C$_n$H$_m$ moieties with the benzene core (Fig. SI1‡) could be found.

Compound 4b can best be transcribed by the symmetry operation –x, 1 – y, –z, which results in a rectangular shaped dimer (Fig. SI3‡) with parallel displaced π–π interactions between both C$_n$ cycles of 3.615(13) Å. Furthermore, 4b is strongly disordered over two positions (0.6 : 0.4) in which the ferrocenyles of the disordered part correspond to the corners of the rectangle formed by the initial dimer. However, the C$_n$ core is rotated by 45° providing interaction with a third ferrocenyl corner (Fig. SI2 and SI3, ESI†).

Electrochemistry

The redox properties of 4a–c and 6a–c have been determined by cyclic voltammetry (=CV) and square-wave voltammetry (=SWV) (Fig. 5). Dichloromethane solutions containing the respective analyte (1.0 mmol L$^{-1}$) and [Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 mol L$^{-1}$) as supporting electrolyte were used for the measurements. The CV studies have been performed at a
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Fig. 5 Voltammograms of dichloromethane solutions containing 1.0 mmol L\(^{-1}\) of 4a\(\text{--}c\) and 6a\(\text{--}c\) at 25 °C. Supporting electrolyte \([\text{Bu}_4\text{N}]\text{[B(C6F5)4]}\) (0.1 mol L\(^{-1}\)). Left: Cyclic voltammograms (scan rate: 100 mV s\(^{-1}\)). Right: Square-wave voltammograms (step-height: 25 mV; pulse-width: 5 s; amplitude: 5 mV).

### Table 1 Cyclic voltammetry data (voltages vs. FcH/FcH\(^+\)), scan rate 100 mV s\(^{-1}\) at a glassy carbon electrode of 1.0 mmol L\(^{-1}\) solutions of the analytes in dry dichloromethane containing 0.1 mol L\(^{-1}\) of \([\text{Bu}_4\text{N}]\text{[B(C6F5)4]}\) as supporting electrolyte at 25 °C. All potentials are given in [mV]

<table>
<thead>
<tr>
<th>Compd</th>
<th>(E_{\text{p}}^{\text{°}}) (mV)</th>
<th>(\Delta E_p) (mV)</th>
<th>(E_{\text{p}}^{\text{°}\prime}) (mV)</th>
<th>(\Delta E_p^{\prime}) (mV)</th>
<th>(E_{\text{p}}^{\text{°}\prime\prime}) (mV)</th>
<th>(\Delta E_p^{\prime\prime}) (mV)</th>
<th>(\Delta E^{\circ}) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>190 (71)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>185/68/135</td>
</tr>
<tr>
<td>4b</td>
<td>195 (59)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>140/160/85/150</td>
</tr>
<tr>
<td>6c</td>
<td>−80 (75)</td>
<td>70 (68)</td>
<td>220 (69)</td>
<td>420 (65)</td>
<td>530 (63)</td>
<td>660 (147)</td>
<td>150/150/200/110/130</td>
</tr>
</tbody>
</table>

\(E^{\circ}\) = formal potential. \(\Delta E_p\) = difference between oxidation and reduction potential. \(\Delta E^{\circ}\) = potential difference between the redox processes. \(\Delta E_p\) = potential difference between the two redox processes determined by the application of the Richardson and Taube method.\(^{23}\) When using the deconvolution of the redox separation of the oxidation potentials in SWV (Fig. SI4), \(\Delta E^{\circ}\) = 60 mV. Values determined using Square Wave Voltammetry.

The appropriate potential values are given in Table 1. All redox potentials are referenced to the FcH/FcH\(^+\) redox couple (\(E^{\circ}=0\) mV, FcH = Fe(η\(^2\)-C\(_5\)H\(_5\)).\(^{25}\)

From Fig. 5 it can be seen that the cyclic and square wave voltammograms of 4a\(\text{--}c\) show only one reversible redox event irrespective of the number of FcC=\(\equiv\)C units present, evincing the simultaneous oxidation of the Fc groups. Furthermore, it is found that an increasing number of redox-active Fc groups at the benzene core results in a shift of the \(E^{\circ}\) values to higher potentials (4a, \(E^{\circ}=190\) mV; 4b, \(E^{\circ}=195\) mV; 4c, \(E^{\circ}=390\) mV) (Table 1). This indicates that the more FcC=\(\equiv\)C moieties are present, the more difficult is the oxidation of the Fc(n) centres, which is in agreement with the electron withdrawing character of the ferrocenyl ethynyl building blocks. In contrast to 4c, 1,3,5-tris(ethylferrocenyl) benzene (dichloromethane, \([\text{Bu}_4\text{N}]\text{[B(3,5-C\(_5\)H\(_3\)C\(_6\)H\(_5\))\(_3\)]}\) as supporting electrolyte)\(^{6b}\) possesses three well-separated reversible redox events with redox splittings of \(\Delta E^{\circ}=200\) mV and \(\Delta E^{\circ}=170\) mV.\(^{6b}\) Geiger has shown that \([\text{Bu}_4\text{N}]\text{[B(3,5-(CF\(_3\)_2)\(_2\})(C\(_5\)H\(_5\))\(_3\)]}\) and \([\text{Bu}_4\text{N}]\text{[B(C\(_6\)F\(_5\))\(_3\)]}\) possess quite similar ion pairing capabilities in dichloromethane and both these fluorinated borates act as very weak coordinating counter ions, thus it is expected that the appropriate \(\Delta E^{\circ}\) values are similar for both electrolytes.\(^{23}\) Against this background the different redox behaviour of 4c and 1,3,5-tris(ethylferrocenyl) benzene is surprising. On the one hand it could be shown that the electronic communication between the terminal ferrocenyl units is suppressed, when electron poor aromatics are used as bridging systems.\(^{1c,10b,26}\) On the other hand, the electron withdrawing effect of the chlorine atom leads to a partially negative charge, which enables attractive interactions with the neighbouring FcC=\(\equiv\)C units,
suggestions the precipitation of $6c^{6+}$ on the surface of the working electrode, which is not unusual for highly charged ions.\textsuperscript{4,24}

Due to the use of different electrolytes in the electrochemical measurements a comparison with related work is difficult. Vollhardt’s hexaferrocenyl benzene gave only three redox processes consistent of a one ($E'_{1} = -163 \text{ mV}$), a two ($E'_{2} = -32 \text{ mV}$) and a three ($E'_{3} = 222 \text{ mV}$) electron process (dichloromethane, [Bu$_4$N][PF$_6$] as supporting electrolyte).\textsuperscript{5}

However, the use of the classical [PF$_6$]$_{-}$ counter ion compensates most of the electrostatic repulsion by ion-pairing with the analyte. Hence, it is expected that the use of a weakly coordinating anion (= WCA, i.e. [Bu$_4$N][B(C$_6$F$_5$)$_4$]) would probably separate the oxidation of all six ferrocenyl units. In the case of hexakis(ethynylferrocenyl)benzene ($[E'_{1} = -50 \text{ mV}$, $E'_{2} = 170 \text{ mV}$, $E'_{3} = 360 \text{ mV}$; dichloromethane, [Bu$_4$N][B(3,5-(CF$_3$)$_2$-C$_6$H$_4$)$_4$] as supporting electrolyte)]\textsuperscript{6b,c} even the use of WCA electrolytes only resulted in the observation of three reversible redox waves. The combination of both structural motifs, however, led to a well-separated redox behaviour as the ferrocenium units in-between the FeC$=$C moieties of 6c stabilise the mixed-valent forms 6$c^{4−6+}$ by additional repulsive electrostatic interactions.

For a further investigation of the electronic properties of 6a-c \textit{in situ} spectroelectrochemical UV–Vis/NIR measurements have been carried out to prove, if the interactions between the Fe/Fc" groups are solely caused by electrostatic contributions or if an intramolecular electron transfer between the redox-active ferrocenyl moieties \textit{via} the carbon-rich connectivities occurs.

\textbf{Spectroelectrochemistry}

The spectroelectrochemical studies were performed in an OTTLE (= Optically Transparent Thin-Layer Electrochemistry) cell\textsuperscript{12} and the potential was increased stepwisely (step heights: 15 mV, 25 mV, 50 mV or 100 mV) from -200 to 1000 mV vs. Ag/AgCl. Dichloromethane solutions containing 6a, 6b or 6c (0.001 mol L$^{-1}$) and [Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 mol L$^{-1}$) as electrolyte were used at 25 °C. Starting from neutral 6a-c, the stepwise increase of the potential allows the \textit{in situ} generation of cationic 6a−c$n^+$ (n = 1−4 (6a), n = 2 and n = 3 are formed at the same potential; 1−5 (6b); 1−6 (6c)) (Fig. 7, S15 and S16).

For neutral 6a,b, as expected, no absorptions in the NIR region (1000−3000 nm) were observed. Upon subsequent oxidation steadily increasing absorptions with low extinctions ($\epsilon_{\text{max}} = 50–270 \text{ L mol}^{-1} \text{cm}^{-1}$) at 1270 nm (6a$n^+$, n = 1−4) and 1300 nm (6b$n^+$, n = 1−5) were found (Fig. S15 and S16). These absorptions can be assigned to LMCT (=Ligand-to-Metal Charge Transfer) transitions.\textsuperscript{13} In the UV-Vis region (250−750 nm), excitation including the π−π$^*$ transitions of the benzene core as well as the d−d transitions of the Fe substituents could be detected.\textsuperscript{14} Since no IVCT (=Inter-Valence Charge Transfer) absorptions were observed, mainly electrostatic interactions ($\Delta E_\text{ex}$) are responsible for the observed redox splittings between the equally charged redox centres in 6a,b$n^+$ (6a, n = 2−4; 6b, n = 2−5). Therefore, in 6a,b any oxidation state can be classified as class I system according to Robin and Day.\textsuperscript{35}

![Fig. 6 Repulsive (red) and attractive (blue) electrostatic interactions within 1,3,5-tris(ethynylferrocenyl) benzene, 4c$^{++}$ and 6c$^{6+}$](image-url)
However, upon oxidation of 6c, a weak and broad excitation in the NIR region (Fig. 7) was observed of which the band of the dicationic species is hypso- and hyperchromically shifted compared with 6c+.

The physical parameters have been determined by deconvolution of the experimental spectra using three Gaussian-shaped functions (Fig. 7) (6c+, $\nu_{\text{max}} = 7860$ cm$^{-1}$, $\Delta v_{1/2} = 7070$ cm$^{-1}$, $\epsilon_{\text{max}} = 405$ L mol$^{-1}$ cm$^{-1}$; 6c2+, $\nu_{\text{max}} = 9070$ cm$^{-1}$, $\Delta v_{1/2} = 8010$ cm$^{-1}$, $\epsilon_{\text{max}} = 620$ L mol$^{-1}$ cm$^{-1}$). Due to the low absorption in the NIR region detected for 6c+/2+, the compounds can be classified as weakly coupled class II systems according to Robin and Day.15 On further oxidation of 6c2+ to 6c3+ (400 to 1000 mV) this excitation disappeared.

The spectroelectrochemical behaviour of 6c is similar to that of 1,3,5-Fc$_3$C$_6$H$_3$ and 2,4,6-Fc$_3$C$_5$H$_2$N (1,3,5-Fc$_3$C$_6$H$_3$+; $\nu_{\text{max}} = 6970$ cm$^{-1}$, $\Delta v_{1/2} = 6240$ cm$^{-1}$, $\epsilon_{\text{max}} = 35$ L mol$^{-1}$ cm$^{-1}$; 1,3,5-Fc$_3$C$_6$H$_3$2+; $\nu_{\text{max}} = 6590$ cm$^{-1}$, $\Delta v_{1/2} = 6220$ cm$^{-1}$, $\epsilon_{\text{max}} = 105$ L mol$^{-1}$ cm$^{-1}$; 2,4,6-Fc$_3$C$_5$H$_2$N+; $\nu_{\text{max}} = 6010$ cm$^{-1}$, $\Delta v_{1/2} = 7515$ cm$^{-1}$, $\epsilon_{\text{max}} = 30$ L mol$^{-1}$ cm$^{-1}$; 2,4,6-Fc$_3$C$_5$H$_2$N2+; $\nu_{\text{max}} = 6290$ cm$^{-1}$, $\Delta v_{1/2} = 7550$ cm$^{-1}$, $\epsilon_{\text{max}} = 65$ L mol$^{-1}$ cm$^{-1}$).1c

However, upon consecutive oxidation of 1,3,5-Fc$_3$C$_6$H$_3$ a bathochromic shift of the IVCT absorption was observed, while the IVCT transition of 2,4,6-Fc$_3$C$_5$H$_2$N shifts hypsochromically, when oxidation from the mono- to the dicationic species takes place. This indicates that an increasing electron poorness of the aromatic core, caused by the nitrogen atom1c or the electron-withdrawing Fc=C moieties in 6c, is responsible for the shift of the IVCT bands towards higher energy, when the mixed-valent Fe(II)/Fe(II)/Fe(III) species is oxidised to the Fe(II)/Fe(III)/Fe(III) system.

Besides the electronic interaction pathway along the meta-substituted directly bonded ferrocenyl units, an interaction between ortho-substituted Fe and Fe=C moieties seems possible. In this respect, 1-FeC=Fe-2-Fc$_4$H$_4$ (9) has been investigated by in situ UV-Vis/NIR spectroscopy. In contrast to the

Fig. 7 Left: UV-Vis/NIR spectra of 6c at rising potentials vs. Ag/AgCl: left −200 to 245 mV (left top), 245 to 400 mV (left middle), 400 to 1000 mV (bottom). Right: Deconvolution of the NIR absorptions at 245 mV (top) and 400 mV (middle) of in situ generated 6c+ and 6c2+ using three Gaussian-shaped graphs. Measurement conditions: 25 °C, dichloromethane, 0.1 mol L$^{-1}$ [nBu$_4$N][B(C$_6$F$_5$)$_4$] as supporting electrolyte.
UV-Vis/NIR spectrum of 6c**(n = 1, 2)** mixed-valent 9** shows no IVCT but a LMCT absorption at 760 cm** \(^{-1}\)** (Fig. S19**), indicating no electronic interactions between the Fe(II)/Fe(III) centres of the FeC≡C**C** and Fe units. This observation confirms that the charge transfer in 6c**(n = 1, 2)** occurs solely between the directly bonded Fe/Fe**+** termini.

The electron poor character of the benzene core of 6b, caused by the electron-withdrawing effect of the chlorine in position 1, is not capable of facilitating the charge transfer between Fe/Fe**+** in 3,5-positions.

**Conclusion**

A series of (multi)ferrocenyl-substituted benzenes such as 1,3,5-Cl**3-2-(FeC≡C)**C**6** (4a), 1,3,5-Cl**3-2,4-(FeC≡C)**2-6-I-C**6** (4b), 1,3,5-Cl**3-2,4,6-(FeC≡C)**2-C**6 (4c), 1,3,Cl**2-5-Fc-2,4,6-(FeC≡C)**2-C**6 (6a), 1,1-Cl-3,5-Fc-2,4,6-(FeC≡C)**2-C**6 (6b) and 1,3,5-Fc**2-2,4,6-(FeC≡C)**2-C**6 (6c) (4c = Fe(5-Ch2C6)(η**3-C6H5)) have been prepared by palladation-catalysed Sonogashira and Negishi C,C cross-coupling reactions of halogenated aromatics with ethynylferrocene and ethynylferrocene zinc chloride, respectively. The concentration of the [PdCl](η**3-C6H5)] and the amount of FeC≡CH in the Sonogashira C,C cross-coupling plays a crucial role for the formation of 4c. The structures of 4a,b and 6a, in the solid state were determined by single crystal X-ray diffraction analysis. Compound 4b forms a dimeric structure in the solid state, caused by parallel displaced π-π interactions between the centroids of the two C6 cores of this dimer.** For 6a more complex T-shaped π-π interactions, which are of intra- as well as of intermolecular type, occur. The redox properties of 4a-c and 6a-c were studied by cyclic and square wave voltammetry. The ferrocenyl units within compounds 4a-c are oxidised simultaneously. The partial negative charge of the electronegative chlorine atom in between the Fe**+** moieties of 4c**(n = 2)** compensates the repulsive electrostatic Fe**+**-Fe**+** interactions with attractive electrostatic Fe**+**-Cl**-** interactions, destabilising the mixed-valent oxidation states. The absence of these chlorine atoms in 1,3,5-Cl**3-2-(FeC≡C)**C**6 (4a) causes no electronic interactions leading to a separate oxidation of the FcC≡C**C** units. This also explains the different behaviour of 6c, showing six reversible Fe-based one-electron oxidations compared to Astruc’s (FeC≡C**C**6) in which only three redox events have been observed using comparable measurement conditions.

In addition, in situ UV-Vis/NIR studies revealed IVCT excitations in the mixed-valent oxidation states of 6c+ and 6c++ attributed to the Fe(II)/Fe(III) metal centres of the directly bonded ferrocenyl groups. Therefore, the mixed-valent species 6c**(n = 1, 2)** can be classified as weakly coupled class II systems according to Robin and Day.** The spectroscopic characteristics of 6c**(n = 1, 2)** resemble those of 1,3,5-FeC≡C**C**H3 and 2,4,6-FeC≡C**C**H3-Cl**+** demonstrating that the electron transfer occurs between the Fe/Fc**+** groups, while the pathway through the ortho-substituted Fe**+** or FeC≡C**C** units is unsuited for electronic interactions. This was confirmed by in situ UV-Vis/NIR investigations of 1-ethynylferrocenyl-2-ferrocenyl benzene (9) showing no IVCT absorptions in the mixed-valent oxidation state. Class I systems 6a,b showed only LMCT transitions during these measurements.

**Experimental section**

**General conditions**

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Drying of n-hexane, diethyl ether and dichloromethane was performed with a MBrana MB SPS-800 system (double column solvent filtration, working pressure 0.5 bar). Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl, and methanol was purified by distillation from magnesium. Disisopropylamine was purified by distillation from calcium hydride.

**Reagents**

Periodic acid, potassium iodide, 1,3,5-trichlorobenzene (1), triphenylphosphine, copper(i)iodide, BuLi (1.9 M solution in n-pentane), ferrocene, 1-bromo-2-iodo-benzene (7) and KO'Bu were purchased from commercial suppliers and were used without further purification. FeC≡CH (3),** [''Bu[N]-[B(C6F5)3]2** and [PdCl2(PPh3)2]** were prepared according to published procedures. The palladation pre-catalyst [P(η3-C6H4)2]-C(C6H4)-CH2PD(μ-Cl)] was synthesized according to Clark et al.**

**Instruments**

**1**H NMR (500.3 MHz) and **13**C**([1]H) NMR (125.8 MHz) spectra were recorded with a Bruker Avance III 500 spectrometer operating at 298 K in the Fourier transform mode. Chemical shifts are reported in **δ** units (parts per million) using undeuterated solvent residues as internal standard (CDCl3: **1**H at 7.26 ppm and **13**C**([1]H) at 77.16 ppm). Infrared spectra were recorded using a FT-Nicolet IR 200 equipment. The melting points of analytical pure samples (sealed off in nitrogen-purged capillaries) were determined with a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASH91 Series instrument. High-resolution mass spectra were performed with a micrOTOF QII Bruker Daltonite workstation.

**Single crystal X-ray diffraction analysis**

Data for 4a,b and 6a were collected with an Oxford Gemini S diffractometer using graphite-monochromatised Mo Kα
Electrochemistry

Measurements on 1.0 mmol L⁻¹ solutions of the analytes in dry air free dichloromethane containing 0.1 mol L⁻¹ of [Bu₄N]-[B(C₆F₅)₄] as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilising a Radiometer Volta lab PGZ 100 electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilised a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm²), and an Ag/Ag⁺ (0.01 mol L⁻¹ 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 μm and then with a 1/4 μm diamond paste. The reference electrode was built from a silver wire inserted into a solution of 0.01 mol L⁻¹ [AgNO₃] and 0.1 mol L⁻¹ [Bu₄N][B(C₆F₅)₄] in acetonitrile, in a luggin capillary with a vycor tip. This luggin capillary was inserted into a second luggin capillary with a vycor tip filled with a 0.1 mol L⁻¹ dichloromethane solution of [Bu₄N][B(C₆F₅)₄].

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 (Fc/Fc⁺ couple = 220 mV vs. Ag/Ag⁺). Data were then manipulated on a Microsoft Excel worksheet to set the formal redox potentials of the Fc/Fc⁺ couple to E° = 0.000 V. The cyclic voltammograms were taken after typical experiments under the same experimental conditions showed similar results. The cyclic voltammograms were taken after typical experiments under the same experimental conditions showed similar results.

Spectroelectrochemistry

Spectroelectrochemical UV-Vis/NIR measurements of 0.1 (6e) and 2.0 mmol L⁻¹ solutions (6a,b) in dry dichloromethane containing 0.1 mol L⁻¹ of [Bu₄N][B(C₆F₅)₄] as the supporting electrolyte were performed in an OTTLE (= optically transparent thin-layer electrochemistry, quartz windows for UV/Vis-NIR) cell with a Varian Cary 5000 spectrophotometer (UV-Vis/NIR) at 25 °C. Between the spectroscopic measurements the applied potentials have been increased step-wisely using step heights of 15, 25, 50 or 100 mV. At the end of the measurements the analyte was reduced at −500 mV for 15 min and an additional spectrum was recorded to prove the reversibility of the oxidations.

Synthesis of 1,3,5-trichloro-2,4,6-triiodo-benzene (2)

The preparation of compound 2 was carried out using a modified procedure from the literature. To 500 mL concentrated H₂SO₄ periodic acid (30.15 g; 132.3 mmol) was slowly added in small portions (5 g) at ambient temperature. For a complete dissolution of the periodic acid the reaction mixture was stirred vigorously. After adding KI (65.86 g; 411.6 mmol) at 0 °C in small portions (10 g) over 1 h, the resulting deep purple solution was treated with 1,3,5-trichlorobenzene (1) (7.00 g; 38.6 mmol) into three portions (2.33 g) over 25 min at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 96 h. The mixture was poured onto ice (exothermic reaction!) and the precipitate was filtered and washed with H₂O until neutralisation and then washed with methanol (200 mL). The colorless residue was recrystallised from hot tetrahydrofuran affording colorless needle-shaped crystals. Yield: 18.12 g (32.39 mmol, 84% based on 1,3,5-trichlorobenzene (1)); colorless, crystalline solid, soluble in tetrahydrofuran. Anal. calcd for C₁₈H₉FeCl₃I₂·0.08C₆H₁₄: C, 21.35; H, 0.40; I, 46.33. Found: C, 21.18; H, 0.40; I, 46.30. IR data [KBr, cm⁻¹]: ν(C–Cl) 826; ν(C–H) 2930, 3075; ν(Fe–C–Cl) 432. General procedure – synthesis of 4a,b

In a Schlenk flask, 50 mL of degassed diisopropylamine, 6.00 mol% of CuI (65.3 mg, 0.34 mmol) and 0.50 mol% of [PdCl₂(PPh₃)₂] (20 mg, 0.03 mmol) were added and the solution was stirred for 5 min. The reaction mixture was treated with 1.00 g (1.79 mmol) of ethynylferrocene (3) (1.20 g, 5.77 mmol) and 6.00 mol% of PPh₃ (90.0 mg, 0.34 mmol) and then heated to reflux for 24 h, whereby the crimson solution turned orange. After cooling it to room temperature and evaporation of all volatiles, the orange residue was worked-up by column chromatography (column size: 3 × 10 cm, alumina, n-hexane). As eluent a n-hexane-diethyl ether mixture of ratio 20:1 (v/v) was used. The 1st fraction contained ethynylferrocene (3), while from the 2nd fraction 4a and from the 3rd fraction 4b could be isolated. All volatiles were removed under reduced pressure.

1,3,5-Trichloro-2-ethylidyneferrocenyl-4,6-diodo-benzene (4a)

Yield: 40 mg (0.062 mmol, 4% based on 2), orange solid, soluble in dichloromethane. Anal. calcd for C₁₈H₁₃FeCl₂I₂: 36.28 (C, 26.17; H, 1.73). Found: C, 26.17; H, 1.73. IR data [KBr, cm⁻¹]: ν(C–Cl) 826 (s, δ C–H 2930, 3075); ν(Fe–C–Cl) 432. HR-ESI-MS [m/z]: calcd for C₁₈H₁₃FeCl₂I₂: 639.7154, found: 639.7204 [M⁺].
Crystal data for 4a

Single crystals of 4a were obtained by evaporation of a dichloromethane solution containing 4a at 25 °C. C_{30}H_{54}FeCl_{12}I_{2}, M_{r} = 641.25 g mol\(^{-1}\), crystal dimension 0.38 × 0.2 × 0.2 mm, triclinic, P1, \(\alpha = 0.71073\) \(\AA\), \(\beta = 10.1811(8)\) \(\AA\), \(\gamma = 13.7230(8)\) \(\AA\), \(\alpha = 69.747(6)^\circ\), \(\beta = 74.437(6)^\circ\), \(\gamma = 72.227(7)^\circ\), \(V = 912.99(11)\) \(\AA^3\), \(Z = 2\), \(\rho_{\text{calc}} = 2.333 g cm\(^{-3}\), \(\mu = 4.643 mm^{-1}\), \(T = 110 K\), \(\theta_{\text{range}} = 3.03-26.00^\circ\), reflections collected 69,499, independent 3562, \(R_{1} = 0.0243\), \(wR_{2} = 0.0497\) \([I \geq 2\sigma(I)]\).

1,3,5-Trichloro-2,4-bis(ethynylferrocenyl)-6-iodo-benzene (4b)

Yield: 0.333 g (0.46 mmol, 26% based on 2), red-orange solid, soluble in dichloromethane. Anal. calc. for C_{30}H_{54}FeCl_{12}I_{2} (723.42 g mol\(^{-1}\)) [%]: C, 49.91; H, 2.51; found: C, 49.68; H, 2.59. Mp.: 230 °C (decomp.). \(^1\)H NMR [CDCl\(_3\), ppm] \(\delta = 4.28\) (s, 10 H, C\(_2\)H\(_5\)), 4.32 (pt, \(J_{HH} = 1.90 Hz, 4\) H, C\(_2\)H\(_5\)), 4.60 (pt, \(J_{HH} = 1.90 Hz, 4\) H, C\(_2\)H\(_5\)). \(^{13}\)C\(_{\text{H}}\) NMR [CDCl\(_3\), ppm] \(\delta = 63.68\) (FC\(_{\text{Cl}}\) C\(_{6}\)), 69.80 (C\(_{2}\)H\(_5\)), 70.48 (C\(_{2}\)H\(_5\)), 71.12 (C\(_{2}\)H\(_5\)), 80.41 (C\(_{2}\)H\(_5\)), 101.40 (FC\(_{\text{Cl}}\) C\(_{6}\)), 102.35 (C\(_{2}\)H\(_5\)), 122.93 (FC\(_{\text{Cl}}\) C\(_{6}\)), 138.30 (C-Cl), 140.32 (C-Cl, C-1/5), IR data [KBr, cm\(^{-1}\)] \(\nu = 16319\) 16321 | 16323, 1540 (s, C), 70.40 (C 5H5, 5-Fc), 71.45 (C 5H5, 2-Fc), 72.05 (C 5H5, 6-Fc), 122.22 (2-Fc \(C_{6}\)), 122.22 (2-Fc \(C_{6}\)), 138.13 (C-Cl), 143.27 (5-Fc \(C_{6}\)). HR-ESI-MS [m/z]: calecd for C_{30}H_{54}FeCl_{12}I_{2}: 803.9226, found: 803.9227 [M\(^+\)].

General procedure – synthesis of 6a–c

1,3-Dichloro-5-ferrocenyl-2,4,6-tris(ethynylferrocenyl) benzene (6a)

Yield: 0.046 g (0.05 mmol, 3% based on 4c), orange solid, soluble in dichloromethane. Anal. calc. for C_{32}H_{58}FeCl_{2}I (951.13 g mol\(^{-1}\)) [%]: C, 65.49; H, 3.80; found: C, 65.72; H, 4.36. Mp.: 209 °C. \(^1\)H NMR [CDCl\(_3\), ppm] \(\delta = 4.23\) (s, 5 H, C\(_2\)H\(_5\)), 4.30 (s, 10 H, C\(_2\)H\(_5\)), 4.60 (s, 5 H, C\(_2\)H\(_5\)), 4.63 (pt, \(J_{HH} = 1.90 Hz, 2\) H, C\(_2\)H\(_5\)), 4.63 (pt, \(J_{HH} = 1.90 Hz, 2\) H, C\(_2\)H\(_5\)), 4.63 (pt, \(J_{HH} = 1.90 Hz, 2\) H, C\(_2\)H\(_5\)), 4.63 (pt, \(J_{HH} = 1.90 Hz, 2\) H, C\(_2\)H\(_5\)). \(^{13}\)C\(_{\text{H}}\) NMR [CDCl\(_3\), ppm] \(\delta = 64.51\) (2-Fc \(C_{6}\)), 65.30 (4,6-Fc \(C_{6}\)), 68.47 (C\(_2\)H\(_5\)), 69.41 (C\(_2\)H\(_5\)), 69.41 (C\(_2\)H\(_5\)), 70.20 (C\(_2\)H\(_5\)), 70.70 (C\(_2\)H\(_5\)), 70.78 (C\(_2\)H\(_5\)), 71.32 (C\(_2\)H\(_5\)), 71.43 (C\(_2\)H\(_5\)), 71.43 (C\(_2\)H\(_5\)), 71.43 (C\(_2\)H\(_5\)), 101.21 (4,6-Fc \(C_{6}\)), 122.04 (4,6-Fc \(C_{6}\)), 122.22 (2-Fc \(C_{6}\)), 138.13 (C-Cl, C-3), 143.27 (5-Fc \(C_{6}\)). IR data [KBr, cm\(^{-1}\)] \(\nu = 209 16319\) 16321 | 16323, 1540 (s, C), 70.40 (C 5H5, 5-Fc), 71.45 (C 5H5, 2-Fc), 72.05 (C 5H5, 6-Fc), 122.22 (2-Fc \(C_{6}\)), 122.22 (2-Fc \(C_{6}\)), 138.13 (C-Cl, C-3), 143.27 (5-Fc \(C_{6}\)). HR-ESI-MS [m/z]: calecd for C_{32}H_{58}FeCl_{2}I: 953.9593, found: 953.9537 [M\(^+\)].

Crystal data for 6a

Single crystals of 6a were obtained by evaporation of a dichloromethane solution containing 6a at 25 °C. C_{32}H_{58}FeCl_{2}I,
Yield: 0.622 g (0.56 mmol, 35% based on \(4c\)), red solid, soluble in dichloromethane. Anal. calcld for \(C_{62}H_{45}Fe_{5}Cl\) (1104.70 g mol\(^{-1}\)) [%]: C, 67.41; H, 4.11; found: C, 67.25; H, 4.47. Mp.: 148 °C. \(^1\)H NMR [CDCl\(_3\), ppm] \(\delta\): 4.17 (s, 5 H, \(C_5H_5\), 4-FcC), 4.54 (pt, \(J_{HH} = 1.90\) Hz, 4 H, \(C_5H_4\), 3-Fc), 4.71 (pt, \(J_{HH} = 1.90\) Hz, 2 H, \(C_5H_4\), 3-Fc), 72.80 (C\(_5H_4\), Fc), 85.05 (C\(_5H_5\), 4-FcC), 4.32 (s, 10 H, \(C_5H_5\), 3,5-Fc), 4.33 (pt, \(J_{HH} = 1.90\) Hz, 4 H, \(C_5H_4\), 3,5-Fc), 4.46 (pt, \(J_{HH} = 1.90\) Hz, 4 H, \(C_5H_4\), 2,6-FcC=CC), 5.32 (pt, \(J_{HH} = 1.90\) Hz, 4 H, \(C_5H_4\), 3,5,6-Fc), \(^{13}\)C\[^{1}\]H NMR [CDCl3, ppm] \(\delta\): 65.96 (2,6-FcC=CC), 66.45 (4-FcC=CC), 67.80 (C\(_5H_5\), 3,5-Fc), 69.04 (C\(_5H_4\), 4-FcC=CC), 69.30 (C\(_5H_4\), 2,6-FcC=CC), 70.01 (C\(_5H_5\), 4-FcC=CC), 70.19 (C\(_5H_5\), 3,5,5-Fc), 70.30 (C\(_5H_4\), 2,6-FcC=CC), 70.70 (C\(_5H_4\), 4-FcC=CC), 71.42 (C\(_5H_4\), 2,6-FcC=CC), 72.26 (C\(_5H_4\), 3,5-Fc), 83.76 (C\(_5H_5\), 2,6-FcC=CC), 84.44 (C\(_5H_4\), 4-FcC=CC), 88.01 (C\(_5H_5\), 3,5-Fc), 99.57 (4-FcC=CC), 101.03 (2,6-FcC=CC), 121.59 (2,6-FcC=CC), 121.92 (4-FcC=CC), 139.36 (C-Cl, C-1), 143.05 (3,5-Fc-C). IR data [KBr, cm\(^{-1}\)]: \(\nu\): 818 (s, \(\nu_{\text{O=p-C=H}}\)), 1000 (m, \(\nu_{\text{C=O-Cl}}\)), 1386 (m, \(\nu_{\text{C-H}}\)), 1538 (w, \(\nu_{\text{C=C}}\)), 2205 (s, \(\nu_{\text{C=O}}\)), 3084 (w, \(\nu_{\text{C=C}}\)). HR-ESI-MS [m/z]: calcld for \(C_{62}H_{45}Fe_{5}Cl\): 1103.9962; found: 1103.9947 [M\(^{+}\)].

**Notes and references**


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22 This distance was calculated between the Cₛ-plane and the centroid of the transcripted C₆₅-cycle. The displaced Cₛ₅-planar obtain directly stacked atoms that are also in the range of π–π interactions (C₂₋C₃₀ ↓S₁ and C₃₀₋C₂₈ ↓S₁ (3.63Å); centroid-C₂₉ ↓S₁ 3.636Å(12 Å). Symmetry operation for generating equivalent atoms: S = –x, 1 – y, –z. For calculations of displaced π–π-interactions, see: M. O. Simmock, E. F. Valeev and C. D. Sherrill, J. Am. Chem. Soc., 2002, 124, 10887–10893.


