Synthesis, Characterization, Electrochemistry and Computational Studies of Ferrocenyl-substituted Siloles

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Supporting Information Placeholder

ABSTRACT: Ferrocenylsiloles of the type 2,5-Fc₂-3,4-Ph₂-C₄SiR₂ (**3a**, R = Me; **3b**, R = Ph) have been prepared by reductive cyclization from diethynyl silanes, followed by ferrocenylation using the Negishi C,C cross coupling protocol with the silole ring serving as either the vinyl halogenide species or as zinc organic component and the complementary functionality introduced on the ferrocenyl moiety. The electrochemical behavior of these silacyclic-bridged bis(ferrocenyl) complexes was investigated by cyclic and square wave voltammetry, and the nature of the redox products studied by *in situ* UV-vis/NIR spectroelectrochemical measurements. Each of **3a** and **3b** undergoes two sequential ferrocenyl-based redox processes, the separation of each ($\|E^o = \|E_2^o - \|E_1^o = 300 \text{ mV (3a); } 280 \text{ mV (3b)}$) is in the range of structural similar systems such as 2,5-diferrocenyl-1-phenyl-1H-phosphole (280 mV) and 2,5-diferrocenylfuran (290 mV). Interestingly, the more electron-rich silole **3b**, compared to **3a**, shows a modestly lower redox separation between the individual ferrocenyl oxidation processes, which may be due to the capacity of this group to shield the effect of an adjacent positive charge. An inter-valence charge transfer (IVCT) absorption was found in the *in situ* NIR measurements for **[3a]⁺** and **[3b]⁺**, the analysis of which is consistent with a moderate electronic interaction between the iron atoms through the *cis*-diene-like fragment of the silole bridge, and allowing description as Robin and Day class II mixed-valence systems. These conclusions are supported by results from quantum chemical calculations, which also reveal the likely presence of a range of molecular conformations in solution.

INTRODUCTION

Silicon-containing metalloles (metallacyclopentadienes) are useful structural and electronic building blocks that can be used as monomers for the preparation of conjugated polymers^{1,2} or co-polymers.^{3,4} For example, Tamao has presented an π conjugated thiophene silole co-polymer,⁵ whilst polysilole (PS) or silole-containing co-polymers, which are linked through the 2,5-position exhibit unique conductivity and semiconducting properties attributed to the small band gap (E_g),⁶⁻⁸ with computational studies indicating that PS has an even smaller band gap than other five-membered polyheterocycles such as polythiophene (PT, $E_g = 2.10 \text{ eV}$) and polypyrrole (PP, $E_g = 2.85 \text{ eV}$).^{7,10} These properties make silicon-containing metalloles interesting motifs for use in the design of organic semiconductors. In addition, due to the high electron mobility and high photoluminescence quantum yields, 1-silacyclopentadienes have attracted much interest for a diverse range of other materials applications such as new display devices or in organic light-emitting diodes (OLEDs), according to the interaction of the $\|$ * orbital of the Si-C bond with the π^* orbital of the butadiene fragment.¹¹⁻¹⁴

In order to gain a deeper insight into the electron transfer process that can be propagated through a single repeating unit of such polymers, and in the light of our recent research on heterocyclopentadienes¹⁵⁻¹⁷ and aromatic five-membered heterocycles¹⁸⁻²³ we became interested in siloles as π conjugated

bridging units between two redox-active ferrocenyl termini. Herein, we present the synthesis and structural characterization of siloles of type 2,5-Fc₂-3,4-Ph₂-C₄SiR₂ (R = Me, Ph), together with an electrochemical study of their redox chemistry and spectroelectrochemical investigation of the redox products. Computational calculations were carried out to enhance our understanding of the electronic structure of the compound in different oxidation states.

RESULTS AND DISCUSSION

Synthesis and Characterisation. Silacyclopentadienes **2a** and **2b** were synthesized by intramolecular reductive cyclization from dimethyl-bis(phenylethynyl)silane (**1a**) and diphenyl-bis(phenylethynyl)silane (**1b**) with lithium naphthalenide followed by bromination with elemental bromine, forming dibromide **2a**, or the reaction with [ZnCl₂-2thf] giving the zinc organic species **2b** (Scheme 1). Applying Negishi-ferrocenylation conditions, the reaction of **2a** with FcZnCl (Fc = Fe($\|$ ⁵-C₅H₄)($\|$ ⁵-C₅H₅)) as ferrocenyl source and [Pd(CH₂CMe₂P^tBu₂)(μ -Cl)]₂ as precatalyst gave silole **3a**. The analog coupling of 2,5-Br₂-3,4-Ph₂-C₄SiPh₂ with ferrocenyl zinc chloride did not result in the formation of desired **3b**. The synthesis of **3b** was realized by a Negishi C,C cross-coupling reaction using iodoferrocene as ferrocenyl source, while the application of bromoferrocene was unsuccessful. After appropriate work up (Experimental Section), molecules **3a** and **3b** were obtained in moderate (**3a**) to low (**3b**) yield as dark red solids.

Scheme 1 Synthesis of **3a** and **3b** using Negishi Conditions^a

^a(i) Tetrahydrofuran, 16 h, -80 °C; (ii) in tetrahydrofuran, 2 h, rt; (iii) tetrahydrofuran, [Pd] = [Pd(CH₂CMe₂P^tBu₂)(μ-Cl)]₂ (0.25 mol %), 80 °C, 2 d; LiNp = lithium naphthalenide; Fc = Fe(η⁵-C₅H₅)(η⁵-C₅H₅).

Siloles **3a,b** are stable towards air, light and moisture in the solid state and in solution and were each characterized by elemental analysis, UV-vis, IR and NMR (¹H, ¹³C{¹H}, ²⁹Si{¹H}) spectroscopy and mass spectrometry. The molecular structure of **3a** and **3b** in the solid state was determined by single crystal X-ray structure analysis. The electrochemical behavior of **3a,b** was examined by cyclic voltammetry (CV), square wave voltammetry (SWV) and *in situ* UV-vis/NIR spectroelectrochemistry. Furthermore, DFT calculations were carried out to support the conclusions drawn from the spectroscopic measurements and enhance the understanding of the underlying electronic structures of [3a,b]ⁿ⁺ (n = 0, 1, 2).

The ¹H NMR spectra of **3a,b** show the characteristic pattern for the two equivalent ferrocenyl groups with one singlet (C₅H₅) and two pseudotriplets (C₅H₄) with *J* = 1.90 Hz, the latter characteristic for AA'XX' spin systems.²⁴ The signal of the C₅H₅ group is found at 4.06 ppm for **3a** and 3.52 ppm for **3b**. The ¹³C{¹H} and ²⁹Si{¹H} NMR spectra show typical resonances corresponding to the heterocyclic core and the methyl- and the phenyl-groups (Experimental Section).²⁵ High resolution mass spectrometry (HRMS) displays an anticipated *m/z* peak of 630.1298 for **3a** and 754.1425 for **3b**.

Single crystals of **3a** and **3b** in form of 3b·2CH₂Cl₂ suitable for X-ray diffraction analysis could be obtained by diffusion of *n*-hexane into a dichloromethane solution containing either **3a** or **3b** at ambient temperature. The molecular structures of **3a** and **3b** in the solid state together with selected bond distances (Å) and bond angles (°) are shown in Figure 1.

Molecule **3a** crystallizes in the orthorhombic space group *Pbca* with C₁ symmetry and **3b** in the monoclinic space group *P2₁/n* with two dichloromethane molecules. In contrast to **3a**, silole **3b** possesses a C₂ symmetry axis going through the Si1 atom and the middle of the C2-C2' bond (Figure 1). For **3a**, the ferrocenyl groups are oriented in *syn*-fashion, and are located on the same side of the silacycle, while in **3b** an *anti*-conformation is observed, similar to the structure determined for other bis(ferrocenyl)metallocycles.¹⁵ In the case of **3b**, the *anti*-configuration is apparently stabilized by intramolecular π interactions^{26,27} between the ferrocenyl moieties and the phenyl groups pendant to the silicon atom (Figure 2). These π interactions also seem to cause the high-field shift of the C₅H₅ protons of **3b** when compared with **3a** (**3a**: 4.06 ppm; **3b**: 3.52 ppm).

Figure 1. ORTEP diagram (50% probability level) of the molecular structure of **3a** (left) and **3b** (right) with the atom-numbering scheme. The sign $\propto$ indicates interplanar angles between calculated mean planes of atoms adjoining differently coloured areas. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles ($^\circ$), and torsion angles ($^\circ$): **3a**: Si1-C1 = 1.8787(16), C1-C2 = 1.359(2), C1-C7 = 1.463(2), Si1-C4 = 1.8817(16), Si1-C5 = 1.8710(17), Si1-C6 = 1.8692(17), C2-C3 = 1.498(2), C2-C27 = 1.494(2), C3-C33 = 1.494(2), C3-C4 = 1.360(2), C4-C17 = 1.462(2), average D-Fe = 1.649; C2-C1-Si1 = 107.31 (11) C1-Si1-C4 = 92.26(7), average D-Fe-D = 177.43. **3b**: Si-C1 = 1.871(4), C1-C2 = 1.353(5), C1-C7 = 1.463(5), Si-C5 = 1.870(3), C2-C2A = 1.507(6), C2-C27 = 1.491(5), average D-Fe = 1.648; C2-C1-Si1 = 107.0 (2) C1-Si1-C1A = 93.0(2), average D-Fe-D = 177.4. D denotes the centroid of C₅H₄ or C₅H₅. Symmetry operation for generating equivalent atoms: ' = $-x + \frac{1}{2}, y, -z + \frac{5}{2}$.

Figure 2. Ball-and-stick model of the molecular structure of **3b** displaying intramolecular π interactions between the aromatic C₅H₅ and Ph_{Si} functionalities. All hydrogen atoms are omitted for clarity. The sign $\propto$ refers to the calculated interplanar angle and D to the distance of the geometrical centroids of π interacting aromatic units. Symmetry operation for generating equivalent atoms: ' = $-x + \frac{1}{2}, y, -z + \frac{5}{2}$.

In **3a,b** the bond distances within the central SiC₄ heterocyclic silole cores each display the same short-long alternation, consistent with the valence bond description of the silacyclopentadiene (Scheme 1, Figure 1), whilst the distances between the silacyle and the ferrocenyl *ipso* carbon atoms are indistinguishable (**3a** 1.436(2), 1.432(2); **3b** 1.436(5) Å). Furthermore, the bond distances of the silole core of **3a,b** are identical to those reported for 1,1,2,3,4,5-hexaphenylsilole^{28,29} and 1,1-dimethyl-2,3,4,5-tetraphenylsilole,³⁰ respectively. These observations might indicate that the substitution of the 2,3,4,5-bonded phenyl groups by ferrocenyl moieties or the Si-bonded phenyl groups by methyl groups have a negligible influence on structural parameters.

The ferrocenyl ligands are almost coplanar with the heterocyclic core (torsion angles of the C₅H₄ plane to the silacyclopentadiene unit: **3a**, 2.07(3) $^\circ$ for Fe1, 2.88(3) $^\circ$ for Fe2; **3b**, 3.5 $^\circ$ for Fe1 and Fe1'). In **3a,b** the phenyls in 3,4-position are almost orthogonal to the heterocyclic core (torsion angles of the phenyl plane to the silacyclopentadiene unit: **3a**, 88.49(6) $^\circ$, 82.47(6) $^\circ$; **3b**, 81.8 $^\circ$). The conformation of the cyclopentadienyls in all ferrocenyl ligands are almost eclipsed (**3a**, -7.64(11) $^\circ$ for Fe1 and 0.80(10) $^\circ$ for Fe2; **3b**, -2.30 $^\circ$ for Fe1). In both compounds, **3a** and **3b**, the central SiC₄ cores are planar with the silicon atom possessing, as expected, a tetrahedral environment.³¹

Figure 3. Left: experimental ^1H NMR spectra of **3b** between 2.36 and 4.05 ppm.; dichloromethane- d_2 ; at various temperatures; Right: simulated ^1H NMR spectra of **3b** with different exchange rates. Protons in α, α' -position of the C_5H_4 ring are marked with an asterisk.

Given the stabilization of the ferrocenyls' orientation by π interactions with the phenyl substituents at the silicon atom the free rotation around the silole-ferrocenyl carbon-carbon bond could be reduced by cooling NMR samples of **3b** to $-100\text{ }^\circ\text{C}$. The exchange rates of those protons can be determined by line-shape-fitting of the NMR spectra at the appropriate temperatures (Figure 3). The activation parameters of the rotations could be quantified from the exchange rates in graphical analysis according to Eyring^{32,33} to $\Delta H^\ddagger = 38.6 (\pm 1.5) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 18.2 (\pm 7) \text{ J mol}^{-1} \text{ K}^{-1}$ (Supporting Information Figure SI16). Comparison with similar rotation energy barriers in 2,3,4,5-tetraferrocenyl-*N*-phenyl-1-*H*-pyrrole ($\Delta H^\ddagger = 26.8 (\pm 1.2) \text{ kJ mol}^{-1}$ / $\Delta S^\ddagger = -94.1 (\pm 4.5) \text{ J mol}^{-1} \text{ K}^{-1}$)¹⁹ showed that the activation enthalpy of **3b** is ca. 12 kJ mol^{-1} higher, which in part may be attributed to the T-shaped π - π interaction (Figure 2). Sherrill and coworkers showed in 2002 that such aromatic T-shaped interactions can reach stabilization energies of $9 - 12 \text{ kJ mol}^{-1}$ for the benzene dimer.²⁶ Furthermore, in contrast to 2,3,4,5-tetraferrocenyl-*N*-phenyl-1-*H*-pyrrole¹⁹ the activation entropy of the ferrocenyl rotation in **3b** is positive. This is generally the case, when the transition state exhibits more degrees of freedom than the ground state. The π - π interaction not only hinders the rotation of the ferrocenyls, but also limits the freedom of rotation for the C_5H_5 rings and the phenyl groups. Therefore, the ground states of the rotation around the silole-ferrocenyl carbon-carbon bond could be considered entropically unfavourable hence resulting in a positive activation entropy. The observations of dynamic NMR studies not only support the crystallographic determined π - π interaction but also showed that even in solution especially at low temperatures a rotation barrier of the ferrocenyls is present and should be taken into consideration. Please, note that, due to the absence of π - π interaction in **3a** no rotation barrier could be observed at temperatures down to $-100\text{ }^\circ\text{C}$ (Supporting information Figure SI17).

Electrochemistry. The electrochemical properties of **3a,b** were investigated by cyclic voltammetry (CV), square wave voltammetry (SWV) (Figure 4) and the nature of the redox products was explored in more detail by *in situ* UV-vis/NIR spectroelectrochemistry (Figure 5). The voltammetric measurements were carried out in dry dichloromethane solutions of $[\text{N}^+\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.1 mol L^{-1}), the latter being chosen to

minimize ion pairing effects^{34–36} (examples for application of $[\text{N}^+\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte within electrochemical measurements see references^{15,19,22,37–41}). Cyclic voltammetry studies were performed at $25\text{ }^\circ\text{C}$ with a scan rate of 100 mV s^{-1} . All potentials are referenced to the FcH/FcH^+ ($\text{FcH} = \text{Fc}(\text{C}_5\text{H}_5)_2$) redox couple ($E^\circ = 0.0 \text{ mV}$).⁴²

Chart 1. Selected Diferrocenyl Molecules for Comparison

Table 1. Cyclic Voltammetry Data of **3a,b** and **4-8** for Comparison

Compd.	E_1° [mV] ^a ($ E_p $ [mV]) ^c	E_2° [mV] ^b ($ E_p $ [mV]) ^c	$ E^\circ $ [mV] ^d
3a ^c	-145 (72)	155 (74)	300
3b ^c	-170 (64)	110 (68)	280
4 ^{f, 43}	-35	90	225
5 ^{e, 44}	-94 (65)	166 (65)	260
6 ^{e, 15}	-110 (72)	170 (80)	280
7 ^{e, 44}	-152 (60)	138 (63)	290
8 ^{e, 44}	-206 (65)	204 (65)	410

^a E° = formal potential of first redox process. ^b E_1° = formal potential of second redox process. ^c $|E_p|$ = difference between oxidation and reduction potentials. ^d $|E^\circ|$ = potential difference between the two ferrocenyl-related redox processes. ^ePotentials vs FcH/FcH^+ , scan rate 100 mV s^{-1} at a glassy-carbon electrode of 1.0 mmol L^{-1} solutions in dry dichloromethane containing 0.1 mol L^{-1} of $[\text{N}^+\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte at $25\text{ }^\circ\text{C}$. ^fmeasured in $[\text{Bu}_4\text{N}][\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)]$ (0.1 M) in dichloromethane working electrode, Pt; reference electrode, Ag/AgI , referenced to FcH/FcH^+ ; scan rate, 50 mV/s .

The ferrocenyl substituents in **3a,b** are oxidized separately showing two reversible redox events with a redox separation ($\|E^{\text{ox}} = \|E_2^{\text{ox}} - \|E_1^{\text{ox}}$) of 300 mV (**3a**) and 280 mV (**3b**), respectively, which indicates some through-bond or through-space electronic interactions between the ferrocenyl/ferrocenium termini (Table 1, Figure 4). While for 1,1-dimethyl-2,3,4,5-tetraphenyl-silacyclopentadiene irreversible oxidation ($E_{\text{pa}} = 1482$ mV) and reduction ($E_{\text{pc}} = -2174$ mV) processes have been observed by Tracy³¹, compounds **3a,b** showed no such redox events within the measured potential range (-2500 – 1800 mV). Within the series of bis(ferrocenyl) complexes featuring five-membered aromatic heterocyclic bridges, such as **5**³⁶, **7**³⁵ and **8**¹⁹ (Chart 1) it could be shown that the separation of the two ferrocenyl redox waves depends on the electronic characteristics of the bridging moiety. The more electron-rich the bridging group, the lower (less positive) the first ferrocenyl oxidation (E_1^{ox}) potential process becomes and hence electron-rich heterocycles show higher $\|E^{\text{ox}}$ values (Table 1). The C_4Si bridging unit within silole **3b** donates more electron density towards the ferrocenyl moieties when compared with **3a** and thus those ferrocenyls are more easily oxidized (**3a**: $E_1^{\text{ox}} = -145$ mV, **3b**: $E_1^{\text{ox}} = -170$ mV); however, **3b** possesses the lower redox separation (**3a**, 300 mV; **3b**, 280 mV), which is in contrast to the trends revealed by other members of this five-membered heterocyclic family (Table 1). The discrepancy between the observed and expected electrochemical behavior of **3a** and **3b** might be explained by the influence of the cross-hyperconjugation of the SiMe_2 moiety to the butadiene system.^{12,46–49} Due to the involvement of the silicon atom in the π conjugation, the electronic interactions between the respective iron centers might be increased, leading to some additional stabilization of the mono-oxidized redox product $[\mathbf{3a}]^+$ relative to $[\mathbf{3b}]^+$. In order to explore this hypothesis, the IVCT transitions within the mixed-valent cations $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ have been studied using spectroelectrochemical methods.

Figure 4. Cyclic voltammograms (solid line) and square wave voltammograms (dotted line) of **3a** and **3b** in dichloromethane solutions (1.0 mmol L⁻¹) at 25 °C (scan rate 100 mV s⁻¹; supporting electrolyte 0.1 mol L⁻¹ of $[\text{N}^{\text{Bu}}_4][\text{B}(\text{C}_6\text{F}_5)_4]$).

Spectroelectrochemistry. Spectroelectrochemical studies were performed in an optically transparent thin-layer electrochemistry (OTTLE) cell containing 2.0 mmol L⁻¹ of **3a** or **3b** and 0.1 mol L⁻¹ of $[\text{N}^{\text{Bu}}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as the supporting electrolyte, with stepwise increase of the applied potential from -200 to 700 mV vs Ag/AgCl. The potential was increased using varying step heights of 25, 50 and 100 mV. This procedure allowed the sequential *in situ* generation of $[\mathbf{3a,b}]^+$ and $[\mathbf{3a,b}]^{2+}$ (Figure 5). In their charge neutral,

Fe(II/II) state, siloles **3a,b** are, as expected, transparent in the NIR region, while broad intensive transitions (IVCT and LMCT) could be observed as **3a,b** were oxidized to $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ by increasing the applied potential. Deconvolution of this absorption envelope, required four Gaussian-shaped spectral components, consistent with an IVCT transition at 4700 cm⁻¹ ($[\mathbf{3a}]^+$) or 4650 cm⁻¹ ($[\mathbf{3b}]^+$) ($[\mathbf{3a}]^+$: $\|_{\text{max}} = 3150$ L mol⁻¹ cm⁻¹, $\|_{1/2} = 2950$ cm⁻¹; $[\mathbf{3b}]^+$: $\|_{\text{max}} = 2270$ L mol⁻¹ cm⁻¹, $\|_{1/2} = 3310$ cm⁻¹) and two LMCT bands at 3470 cm⁻¹ and 4000 cm⁻¹ ($[\mathbf{3a}]^+$) and 3460 cm⁻¹ and 3930 cm⁻¹ ($[\mathbf{3b}]^+$) (Table 2, Figure 6). The fourth component was used to simulate the low energy edge of higher energy absorptions that protrude into the NIR region. Due to the sp³ character of the silicon atom, the silole fragment C_4Si is rather comparable to a *cis*-diene system.⁴³ However, the intensity of the IVCT absorption found in $[\mathbf{3a}]^+$ exceeds those found in mixed valence $[\mathbf{6}]^{+15}$ and $[\mathbf{4}]^{+43}$ while the IVCT characteristics ($\|_{\text{max}}$, $\|_{1/2}$) of $[\mathbf{3b}]^+$ are very similar to those of the diene analog $[\mathbf{4}]^+$. The higher extinction coefficient of the IVCT absorption in $[\mathbf{3a}]^+$ might be a consequence of cross-hyperconjugation of the SiMe_2 building block with the butadiene unit causing involvement of the sp³ hybridized silicon atom in the π conjugated system, a phenomenon that has been described in, for example, methyl- and H-substituted siloles.^{12,46–49} The fact that the IVCT transition associated with $[\mathbf{3b}]^+$ is less intense and broader than that of $[\mathbf{3a}]^+$ demonstrates a weaker electronic coupling between the redox centers. In support of this, we note that although $\|E^{\text{ox}}$ depends on many factors, including ion-pairing energies, solvation factors, magnetic effects and metal-ligand bonding variations in different oxidation states, in addition to statistic and electrostatic terms,^{50,51} these are not expected to be substantively different in **3a**/ $[\mathbf{3a}]^+$ vs **3b**/ $[\mathbf{3b}]^+$. Hence, the smaller $\|E^{\text{ox}}$ value observed for **3b** (see above electrochemistry) is also consistent with a smaller contribution of the resonance term. Comparison of the characteristics of the IVCT transition of $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ with those from other aromatic five-membered heterocycles revealed that the $\|_{1/2}$ values for $[\mathbf{5}]^+$,^{21,45,52} $[\mathbf{6}]^+$,¹⁵ $[\mathbf{7}]^+$,⁴⁴ $[\mathbf{8}]^+$ ^{44,53,54} are smaller (2300 – 2400 cm⁻¹) than those of $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$, while the intensities are within the same range. Phosphole $[\mathbf{6}]^+$,¹⁵ which is similar to siloles **3a,b** also contains a non-aromatic five membered heterocycle showing IVCT absorptions with $\|_{1/2}$ values comparable to $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$, respectively.

Table 2. NIR Data of the Absorptions of Siloles $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$.^a

Compd.		ϵ_{max} (cm ⁻¹) (ϵ (L mol ⁻¹ cm ⁻¹))	$\epsilon_{1/2}$ (cm ⁻¹)	$(\epsilon_{1/2})_{\text{theo}}$ (cm ⁻¹)	H_{ab} (cm ⁻¹) ^b <i>ga</i> conformation	H_{ab} (cm ⁻¹) ^b <i>anti</i> conformation
3a ⁺	IVCT	4700 (3150)	2950	3300	542	500
	I LMCT	3470 (2650)	950			
	II LMCT	4000 (1250)	450			
3b ⁺	IVCT	4650 (2250)	3300	3300	482	445
	I LMCT	3460 (1450)	800			
	II LMCT	3930 (800)	450			

^a In dry dichloromethane containing 0.1 mol L⁻¹ of $[\text{N}^{\text{Bu}}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte at 25 °C. ^b H_{ab} was calculated according to equation 1 with $r_{\text{ab,syn}} = 7.9438$ Å and $r_{\text{ab,anti}} = 8.6074$ Å.

$$H_{\text{ab}} = 2.06 \cdot 10^{-2} \cdot \frac{\sqrt{\nu_{\text{max}} \cdot \epsilon_{\text{max}} \cdot \Delta \nu_{1/2}}}{r_{\text{ab}}} \quad (1)$$

The electronic coupling parameter H_{ab} can be calculated according to Hush's two state model for a class II system as shown in Eq 1, where r_{ab} is the effective electron transfer distance between the two redox active sites, which is notoriously hard to determine experimentally^{51,55-58}. Therefore, the crystallographic Fe-Fe distances were used to estimate H_{ab} . Since the ferrocenyl substituents within **3a,b** can adopt both, a *syn*- and an *anti*-conformation, H_{ab} was calculated using crystallographic data derived from **3a** representing the *syn*-orientation ($r_{ab,syn} = 7.9438$ (18) Å) and *anti*-oriented **3b** ($r_{ab,anti} = 8.6074$ (9) Å). Please, note that the effective electron transfer distance is expected to be shorter than the geometric Fe-Fe distances and hence H_{ab} might be underestimated.⁵⁴ As expected, due to the lower r_{ab} value H_{ab} is higher for the *syn*-conformation for both molecules [**3a**]⁺ and [**3b**]⁺, when compared with the respective *anti*-conformer (Table 2). Silole [**3a**]⁺ exhibits higher H_{ab} values when compared with [**3b**]⁺, nevertheless, the determined values are quite similar showing that there are only minor differences in the electronic coupling caused by the different substitution on the silicon atom.

The unexpected strong IVCT interactions allowed to classify siloles [**3a**]⁺ and [**3b**]⁺ as moderately or moderately to weakly coupled class II system, respectively, according to the classification system introduced by Robin and Day.⁵⁸

Figure 5. UV-vis/NIR spectra of [**3a**]ⁿ⁺ ($n = 0, 1, 2$) in dichloromethane solution (2.0 mmol L⁻¹) at rising potentials (top: -200 mV to 300 mV, bottom: 300 mV to 700 mV vs Ag/AgCl) at 25 °C; supporting electrolyte 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄]. Arrows indicate an increase or decrease of absorptions.

Figure 6. Four band Gaussian deconvolution of the NIR absorption envelope of [**3a**]⁺ obtained by spectroelectrochemistry in an OTTE cell.

Further oxidation of [**3a**]⁺ and [**3b**]⁺ to the dications [**3a**]²⁺ and [**3b**]²⁺ leads to a disappearance of the IVCT bands as homo-valent Fe(III/III) species are formed. In association with this, two MLCT transitions are emerged at ca. 1000 nm (10000 cm⁻¹). The LMCT bands that are determined for [**3a**]⁺ and [**3b**]⁺ can also be found in dications [**3a**]²⁺ and [**3b**]²⁺ exhibiting a decreased intensity (ca. 200 L mol⁻¹ cm⁻¹) (Supporting Information).

Computational Studies. To explore the electronic structures of [**3a,b**]ⁿ⁺ ($n = 0, 1, 2$) in more detail, the computational model systems *syn*-[**3a**']ⁿ⁺, *anti*-[**3a**']ⁿ⁺ and *anti*-[**3b**']ⁿ⁺ (where the prime (') nomenclature is introduced to distinguish the computational from real system) were analyzed (B3LYP using Dunning's all-electron valence double zeta (D95V) for C and H atoms, and the Los Alamos ECP/double zeta valence basis set on Fe and Si (LANL2DZ) and a CPCM-dichloromethane solvent model). Tables of orbital energy and composition are given in the supporting information, together with the results from benchmarking studies carried out on **3a**' using 3-21G* (all atoms), and 6-31G** (H, C, Si) / LANL2DZ (Fe) basis sets which reveal no structural or electronic differences of any significance to the results reported in the main body of the paper.

Figure 7. The atom labelling scheme of **3a**.

The optimized geometry of *syn*-**3a**' compares very well with that determined crystallographically for **3a** (Figure 7, Table 3), and differs little from that of *anti*-**3a**', which lies only +0.37 kJ/mol lower in energy. The optimized geometries of the *syn*- and *anti*-conformer of **3a**' both exhibit pronounced bond-length alternation in the silacyclopentadiene ring, and significant *cis*-diene-like character in the bridging moiety linking the two ferrocenyl fragments, in a manner entirely analogous to the crystallographically determined structures of **3a,b** and other heterocyclic bridged bis(ferrocenyl) complexes. In both

computational models as well as the crystallographically determined structures, the C1-C15, silacyclopentadiene and C6-C65 rings are essentially co-planar, whilst the geometry at Si is distorted from idealized tetrahedral by the inclusion within the C₄Si ring. The HOMO of *syn*-**3a'** features a substantial (ca. 42%) character from the *cis*-butadiene-like portion of the silacycle, admixed with contributions from the ferrocenyl substituents (ca. 28% each) (Figure 8). There is negligible contribution from both the SiMe₂ fragment and the phenyl groups, the latter being oriented approximately perpendicularly to the plane of the silacycle. The electronic structure varies little as a function of the relative disposition of the ferrocenyl moieties across the silacyclic ring, and the composition and energy of the frontier orbitals of the *anti*-conformer *anti*-**3a** are essentially the same as those described for the *syn*-form (Supporting Information).

Figure 8. Plot of the HOMO of **3a'** (isocontour value ± 0.04 (e/bohr³)^{1/2}).

Table 3. Selected Bond Lengths (Å), Bond and Torsion Angles (°) from the Crystallographically Determined Structure of **3a** and the Optimized Geometry of Models [**3a'**]ⁿ⁺ (n = 0, 1, 2).

		3a	<i>syn</i> - 3a'	<i>anti</i> - 3a'	<i>syn</i> -[3a'] ⁺	<i>anti</i> -[3a'] ⁺	<i>anti</i> -[3b'] ⁺	<i>syn</i> -T-[3a'] ²⁺	<i>anti</i> -T-[3a'] ²⁺
a Cp ₁ is the mid- poin t of the C1- C15 cyclo pent adie nyl ring.	Fe-Cp ₁ ^a	1.647	1.730	1.730	1.800	1.799	1.795	1.798	1.798
	Fe-Cp ₆ ^b	1.648	1.730	1.732	1.731	1.731	1.730	1.796	1.798
	C1-C2	1.462	1.467	1.467	1.445	1.445	1.447	1.457	1.458
	C2-C3	1.360	1.380	1.380	1.395	1.394	1.391	1.386	1.386
	C3-C4	1.498	1.507	1.507	1.487	1.487	1.490	1.497	1.498
	C4-C5	1.359	1.380	1.380	1.390	1.390	1.387	1.386	1.386
	C5-C6	1.463	1.467	1.467	1.458	1.458	1.457	1.457	1.458
	C2-Si	1.882	1.904	1.905	1.902	1.902	1.901	1.906	1.906
b Cp ₂ is the mid- poin t of the C6- C65 cyclopentadienyl ring.	C5-Si	1.879	1.904	1.905	1.909	1.909	1.910	1.906	1.906
	C1-C2-C3	127.12	127.97	127.88	126.50	126.71	126.94	126.47	126.44
	C2-C3-C4	116.33	116.43	116.43	116.70	116.67	116.74	116.00	115.99
	C3-C4-C5	116.66	116.43	116.43	115.93	115.97	116.06	115.98	115.99
	C4-C5-C6	126.84	127.97	127.88	127.80	127.67	127.83	126.70	126.44
	C2-Si-C5	92.26	91.85	91.86	91.16	91.16	91.30	90.73	90.76
	CH ₃ -Si-CH ₃	109.07	111.11	110.89	111.68	111.62	111.71 ^c	112.42	112.09
	C12-C1-C2-Si	-1.68	-0.88	1.24	4.55	2.68	1.83	2.41	2.90
	C62-C6-C5-Si	0.11	0.84	1.25	2.40	0.88	1.14	4.39	2.91

C65 cyclopentadienyl ring. ^c Read (*ipso*-C)-Si-(*ipso*-C)

The mono-cation *syn*-[**3a'**]⁺ displays a number of structural and orbital features that are entirely consistent with the description of this species as an Fe(II/III) mixed-valence (MV) complex. The C1-C2 bond is rather shorter in the monocation (1.445 Å) than in the neutral (1.467 Å), although the C5-C6 bond lengths are more consistent between the two oxidation states (**3a'** 1.467; [**3a'**]⁺ 1.458 Å), whilst within the silacyclopentadiene ring, the bond length alternation is modestly less pronounced (Table 3), giving rise to a valence bond description with more cumulenic character in the diene-like backbone. There is also a substantial elongation of the Fe-Cp^a distance in [**3a'**]⁺ compared with **3a'**, consistent with the oxidation of this site. However, there is little variation in the local geometry at the silicon center. The composition of the molecular orbitals also supports the MV description of [**3a'**]⁺, with the β-LUSO in [**3a'**]⁺ essentially localized (80 %) on one ferrocenyl

center and a small contribution (14 %) from the diene-like backbone (Figure 9), whilst the β-HOSO has more character derived from the other ferrocenyl moiety (58 %) and the diene (30 %) with 10 % arising from the formally oxidized ferrocenyl center (Figure 10).

Figure 9. Plot of the $\bar{\text{L}}\text{USO}$ of $[\mathbf{3a}']^+$ (isocontour value ± 0.04 (e/bohr^3) $^{1/2}$).

Figure 10. Plot of the $\bar{\text{H}}\text{OSO}$ of $[\mathbf{3a}']^+$ (isocontour value ± 0.04 (e/bohr^3) $^{1/2}$).

Interestingly, $\text{anti-}[\mathbf{3a}']^+$ is essentially isoenergetic with the syn- isomer, lying barely 0.65 kJ/mol lower in energy. This together with the virtually barrierless rotation determined from the dynamic NMR studies, indicates that solutions of $[\mathbf{3a}]^+$ contain more than one conformer. The key bond lengths and angles of $\text{anti-}[\mathbf{3a}']^+$ are to all intents identical to those of the syn- isomer, and there would also therefore appear to be little by way of net reorganization energy in the interconversion of the two conformers. The composition of the $\bar{\text{L}}\text{USO}$ and $\bar{\text{L}}\text{HOSO}$ in $\text{anti-}[\mathbf{3a}']^+$ is, perhaps surprisingly, almost indistinguishable from that of the syn- conformer, with the $\bar{\text{L}}\text{USO}$ being largely localized on one ferrocenyl moiety (81%) and the diene (14%) with the $\bar{\text{L}}\text{HOSO}$ again exhibiting more diene-like character (Fc 59%, diene 30%, Fc $^+$ 10%) and being somewhat more delocalized.

In order to probe the possible conformational and chemical differences of the mixed-valence complexes $[\mathbf{2,5-Fc_2-3,4-Ph_2-C_4SiR_2}]^+$ further, the complex $\text{anti-}[\mathbf{3b}']^+$ was also modelled. The presence of the phenyl substituents made essentially no change to the core geometry of the cis-diene-like $\text{Fc}^+-\text{C}=\text{CPh}-\text{CPh}=\text{C-Fc}$ fragment, when compared with syn- or $\text{anti-}[\mathbf{3a}']^+$ (Table 3), although the ferrocenyls are slightly distorted from co-planarity ($\text{Fe-Cp}_1\cdots\text{Fe-Cp}_2$: $\text{anti-}[\mathbf{3b}']^+$ -172.00° ; $\text{anti-}[\mathbf{3a}']^+$ -175.25° Me_2). This minor geometric variation, and the impact on the electronic structure, is potentially interesting with regards the suggestions of a degree of attenuation of the coupling between the ferrocenyl moieties through the 1,1,3,4-tetraphenylsilacyclopentadiene scaffold of $[\mathbf{3b}]^+$ vs $[\mathbf{3a}]^+$ made on the basis of the electrochemical and NIR data. Whilst the $\bar{\text{L}}\text{USO}$ of this lowest energy geometry of $\text{anti-}[\mathbf{3b}']^+$ exhibits the same composition as in syn- and $\text{anti-}[\mathbf{3a}']^+$

(Fc $^+$ 80 %, diene 15%, Fc 4 %), the diene contribution to the $\bar{\text{L}}\text{HOSO}$ in $\text{anti-}[\mathbf{3b}']^+$ is somewhat smaller (Fc 65 %, diene, 25 %, Fc $^+$ 8 %). Given that the IVCT transition is approximated in terms of the $\bar{\text{L}}\text{HOSO} \rightarrow \bar{\text{L}}\text{USO}$ transition, the lower overlap between these orbitals may be responsible for the modestly weaker coupling. Such suggestions must be tempered against the relatively high barriers to rotation about the C1-C2 and C5-C6 bonds determined by dynamic NMR arising from the T-shaped π - π interactions, and taken in light of the likely conformational distribution in solution. The notion that the SiPh_2 moiety presents a steric barrier to the optimal co-planar arrangement of the ferrocenyl and silacyclic moieties, would be consistent with the modestly weaker coupling observed in $[\mathbf{3b}]^+$ than in $[\mathbf{3a}]^+$.

As an aside, we note that at the level of theory employed, a local minimum with a *symmetric* (i.e. delocalized or class III) electronic structure was also found for $\text{anti-}[\mathbf{3a}']^+$, which differs only slightly in individual bond lengths and is only 14 kJ/mol higher in energy than the class II form described above (Supporting Information). Given the well-known over-estimation of delocalized electronic structures from the B3LYP functional, it is not appropriate to base any substantive comment on the apparently low energy difference between the class II and class III forms of $\text{anti-}[\mathbf{3a}']^+$. However, the point to note is not that the B3LYP hybrid functional identifies a structure with a delocalized electronic structure, but rather that there are only very subtle changes in bond length required to pass between class II and class III in these complexes (a point that is implicit in the thermal barrier to electron transfer associated with class II complexes).

The dication $\text{syn-}[\mathbf{3a}']^{2+}$ proved to be substantially more stable in the triplet (or high-spin, HS) ground state ($\bar{\text{E}}_{\text{T,S}}: -118.6$ kJ/mol $[\mathbf{3}']^{2+}$), and consequently the discussions here are restricted to this state. The molecular geometry of $\text{HS-}[\mathbf{3a}']^{2+}$ reflects the homovalent nature of the two iron centers, with essentially identical geometric parameters observed in each half of the dication, and a restoration of the more pronounced bond-length alternation in the cis-diene backbone (Table 3). The dication is therefore well described as two ferrocenium moieties pendant to the silacycle.

CONCLUSION

The synthesis of 2,5-diferrocenyl-3,4-diphenyl siloles bearing methyl (**3a**) or phenyl (**3b**) groups at the silicon atom are realized by a reductive cyclization reaction of dimethyl- or diphenyl-bis(phenylethynyl)silane with lithium naphthalenide. The ferrocenyl substituents are introduced to the silole ring by Negishi C,C cross-coupling reactions, whereas the siloles ring either was applied as vinyl halogenide or as zinc organic component. Electrochemical investigations showed that the ferrocenyl units of both synthesized siloles can be oxidized separately. In contrast to findings among the series of aromatic diferrocenyl five-membered heterocycles,^{15,18,19,44,45} the more electron-rich siloles showed a lower redox separation between the individual ferrocenyl oxidation processes. Spectroelectrochemical investigations confirmed electron charge transfer interactions between the individual ferrocenyl termini across the silole linking unit, which are comparable to those found in diferrocenyl phosphole¹⁵ or diferrocenyl cis-butadiene systems⁴³, arguing that the C_4 chain at the molecule's backbone mediates the electronic coupling. Molecules $[\mathbf{3a,b}]^+$ can be characterized as moderate or moderate to weakly coupled class II species according to Robin and Day. Despite being more electron-rich, **3b** $^+$ showed less intense IVCT absorptions than dimethyl-silole **3a** $^+$, which may be due to steric interactions. DFT calculations are consistent with the class II mixed valence

description of [3a,b]⁺, with the apparent low differences in energy between *syn* and *anti* conformations suggesting a distribution of molecular geometries, and hence variation in electronic coupling, in solution.

EXPERIMENTAL SECTION

General conditions. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran were purified by distillation from sodium/benzophenone ketyl. For column chromatography alumina with a particle size of 90 μm (standard, Merck KGaA) was used.

Reagents. 2,5-Dibromo-1,1-dimethyl-3,4-diphenyl-1H-silole⁵⁹ and diphenylbis(phenylethynyl)-silane⁶⁰ were prepared in analogy to published procedures. [NⁿBu₄][B(C₆F₅)₄] was prepared by metathesis of lithium tetrakis(pentafluorophenyl)borate etherate (Boulder Scientific) with tetra-*n*-butylammonium bromide according to reference,³⁵ [P(C₄H₉)₂C(CH₃)₂CH₂Pd(μ-Cl)]₂^{61,62} and iodoferrocene^{63,64} were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Instrumentation. Infrared spectra were recorded using 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 (CHCl₃) = 7.26 ppm; ¹³C{¹H} NMR: δ (CHCl₃) = CDCl₃, d 77.16 ppm, ²⁹Si{¹H} NMR: δ (TMS) = 0.00 ppm). The melting points were determined using 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. UV-vis spectra were recorded with a THERMO Genesys 6 spectrometer.

X-ray Diffraction: Data were collected with an Oxford Gemini S diffractometer at 110 K using Mo-K α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least square procedures on F².^{65,66} All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions.

Electrochemistry. Electrochemical measurements on 1.0 mmol L⁻¹ solutions of the analytes in dry air free dichloromethane containing 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. 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⁻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 a 1/4 μm 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(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 [NⁿBu₄][B(C₆F₅)₄] solution in dichloromethane.³⁶ 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.⁴² When

decamethylferrocene was used as an internal standard, the experimentally measured potential was converted into *E* vs FcH/FcH⁺ by addition of 1619 mV.⁶⁷ Data were then manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH⁺ couple to $E^{\circ} = 0.0$ V. Ferrocene itself showed a redox potential of 220 mV vs. Ag/Ag⁺ ($E_p = 61$ mV) within our measurements.^{68,69} The cyclic voltammograms, which are depicted (Figure 4), were taken after typical two scans and are considered to be steady state cyclic voltammograms in which the signal pattern differs not from the initial sweep.

Spectroelectrochemistry. UV-vis/NIR measurements were carried out in an OTTE (optically thin layer electrochemistry) cell with quartz windows similar to that described previously⁷⁰ in dry dichloromethane solutions containing 2.0 mmol L⁻¹ analyte and 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)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 Pt-mesh auxiliary electrode are melt-sealed into a polyethylene spacer. The values obtained by deconvolution could be reproduced within $\epsilon_{\text{max}} = 100$ L mol⁻¹ cm⁻¹, $\epsilon_{\text{max}} = 50$ cm⁻¹ and $\epsilon_{1/2} = 50$ 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.

Computational chemistry. Calculations were carried out with the Gaussian 09⁷¹ package, with GaussView 5.0.8⁷² and GaussSum3.0⁷³ used to further analyse the results. All geometries were optimized with the B3LYP functional, using the LAN2DZ basis set on Fe, and 6-31G** on all other atoms, with a CPCM (dichloromethane) solvent model. All optimized geometries were confirmed as true minima by absence of imaginary frequencies.

Synthesis of 2,5-diferrocenyl-1,1-dimethyl-3,4-diphenyl-1H-silole (3a). To a solution of 9.52 mmol ferrocenyl zinc chloride in 40 mL of tetrahydrofuran, prepared by monolithiation of ferrocene (1.95 g, 10.47 mmol)⁷⁴ followed by addition of [ZnCl₂·2thf] (4.23 g, 15.08 mmol) at -80 °C, was added 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole (2.0 g, 10.47 mmol) in a single portion at 25 °C. To the solution was added 16.3 mg of (24 μmol) [P(C₄H₉)₂C(CH₃)₂CH₂Pd(μ-Cl)]₂ and the mixture was stirred for 2 d at 80 °C. After evaporation of all volatiles, the precipitate was dissolved in 70 mL of diethyl ether and washed three times with 60 mL portions of water. The organic phase was dried over MgSO₄ and all volatiles were removed. The remaining crude solid was purified by column chromatography (column size 20 x 4 cm, on alumina) using a *n*-hexane-dichloromethane mixture of ratio 2:1 (v/v) as eluent. All volatiles were removed under reduced pressure and the wine-red solid was crystallized from *n*-hexane at 68 °C. Yield: 35 % (based on 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole). Anal. Calcd for C₃₈H₃₄Fe₂Si (M = 630.45 g mol⁻¹): C 72.39, H 5.44; found: C 71.89, H 5.38. Mp: 275 °C decomp.. IR (KBr, in cm⁻¹): 3087 (w), 3076 (m), 3056 (m), 3022 (m), 2947 (w), 2923 (w), 1682 (w), 1442 (m), 1241 (s), 1106 (s), 1000 (s), 793 (s), 745 (s), 702 (s), 506 (s). ¹H NMR (CDCl₃, δ in ppm): 0.73 (s, 6H, CH₃), 3.71 (pt, *J*_{HH} = 1.89 Hz, 4H, C₅H₄), 4.06 (s, 10H, C₅H₅), 4.10 (pt, *J*_{HH} = 1.89 Hz, 4H, C₅H₄), 6.96-7.00 (m, 4H, *o*-C₆H₅), 7.09-7.14 (m, 2H, *p*-C₆H₅) 7.18-7.22 (m, 4H, *m*-C₆H₅). ¹³C{¹H} NMR (CDCl₃, δ in ppm): -1.0 (CH₃), 68.6 (C₅H₄), 68.7 (C₅H₄), 69.5 (C₅H₅), 83.3 (*i*-C₅H₄), 126.4 (*o*-C₆H₅), 128.0 (*m*-C₆H₅), 129.3 (*p*-C₆H₅), 134.8 (2,5-C₄Si), 141.6 (*i*-C₆H₅), 152.6 (3,4-C₄Si). ²⁹Si{¹H} NMR (CDCl₃, δ in ppm): 5.70 (s, Si). UV-vis: 391 nm (12057 L mol⁻¹ cm⁻¹), 507 nm (5073 L mol⁻¹ cm⁻¹). HRMS (ESI-TOF, *m/z*): calcd. for C₃₈H₃₄Fe₂Si: 630.1129; found 630.1198 [M]⁺. Crystal Data for **3b**: C₃₈H₃₄Fe₂Si,

$M_r = 630.44 \text{ g mol}^{-1}$, orthorhombic, $P b c a$, $\beta = 0.71073^\circ$, $a = 13.036(5) \text{ \AA}$, $b = 19.934(5) \text{ \AA}$, $c = 22.598(5) \text{ \AA}$, $V = 5872(3) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.426 \text{ g cm}^{-3}$, $\mu = 1.023 \text{ mm}^{-1}$, $T = 110 \text{ K}$, θ range 3.13 – 26.00° , 56340 reflections collected, 5734 independent reflections ($R_{\text{int}} = 0.0338$), $R1 = 0.0258$, $wR2 = 0.0635$ ($I > 2\sigma(I)$).

Synthesis of 2,5-diferrocenyl-1,1,3,4-tetraphenyl-1H-silole (3b). Lithium naphthalenide was prepared by stirring 84.5 mg (12.18 mmol) of lithium with 1.56 g (12.18 mmol) of naphthalene in 10 mL of dry tetrahydrofuran at room temperature for 18 h. To this solution were added 1.17 g (3.04 mmol) of (diphenylbis(phenylethynyl)silane in a single portion and the mixture was stirred for 1 h. Afterward, 3.41 g (12.18 mmol) of $[\text{ZnCl}_2 \cdot 2\text{thf}]$ was added in a single portion at 0°C , 10 mL of dry tetrahydrofuran were added and the mixture was stirred again for 1 h. Iodoferrocene (1.97 g (6.33 mmol)) and 12 mg (17.5 μmol) of $[\text{P}(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{Pd}(\text{Cl})_2]$ were added and the reaction mixture was stirred for 2 d at 80°C . After evaporation of all volatiles, the solid material was dissolved in 40 mL of diethyl ether and washed three times with 30 mL portions of water. The organic phase was dried over MgSO_4 and all volatiles were removed. The remaining crude solid was purified by column chromatography (column size $20 \times 2 \text{ cm}$, on alumina) using a n -hexane-dichloromethane mixture of ratio 4:1 (v/v) as eluent. All volatiles were removed under reduced pressure and the wine-red solid was crystallized from n -hexane at 68°C . Yield: 12 % (based on diphenylbis(phenylethynyl)silane). $\text{C}_{48}\text{H}_{38}\text{Fe}_2\text{Si}$ ($M = 754.59 \text{ g mol}^{-1}$). Mp: 280°C decomp.. IR (KBr, in cm^{-1}): 3089 (w), 3070 (m), 3048 (m), 3021 (m), 1594 (w), 1557 (m), 1483 (m), 1429 (m), 1267 (s), 1112 (s), 1105 (s) 1000 (s), 819 (s), 770 (s) 735 (s), 706 (s), 504 (s). ^1H NMR (CDCl_3 , δ in ppm): 3.52 (s, 10H, C_5H_5), 3.57 (pt, $J_{\text{HH}} = 1.89 \text{ Hz}$, 4H, C_5H_4), 3.95 (pt, $J_{\text{HH}} = 1.89 \text{ Hz}$, 4H, C_5H_4), 7.06–7.09 (m, 4H, $o\text{-C}_6\text{H}_5$), 7.13–7.17 (m, 2H, $p\text{-C}_6\text{H}_5$), 7.22–7.26 (m, 4H, $m\text{-C}_6\text{H}_5$), 7.52–7.55 (m, 6H, $\text{Si-C}_6\text{H}_5$), 8.00–8.03 (m, 4H, $\text{Si-C}_6\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ in ppm): 68.6 (C_5H_4), 69.5 (C_5H_5), 69.5 (C_5H_4), 82.8 ($i\text{-C-C}_5\text{H}_4$), 126.6 ($\text{C-}o\text{-C}_6\text{H}_5$), 128.1 ($\text{C-C}_6\text{H}_5$), 128.6 ($\text{Si-C}_6\text{H}_5$), 129.4 ($\text{C-C}_6\text{H}_5$), 130.5 ($\text{Si-C}_6\text{H}_5$), 133.5 (C_6H_5), 133.8 (C_6H_5), 136.8 ($\text{Si-C}_6\text{H}_5$), 141.6 ($i\text{-C}_6\text{H}_5$), 154.8 ($3,4\text{-C}_4\text{Si}$). UV-vis: 398 nm (11846 $\text{L mol}^{-1} \text{ cm}^{-1}$), 523 nm (5297 $\text{L mol}^{-1} \text{ cm}^{-1}$). HRMS (ESI-TOF, m/z): calcd. for $\text{C}_{48}\text{H}_{38}\text{Fe}_2\text{Si}$: 754.1442; found 754.1425 [M] $^+$.

Crystal Data for 3b: $\text{C}_{48}\text{H}_{38}\text{Fe}_2\text{Si} \cdot 2\text{CH}_2\text{Cl}_2$, $M_r = 924.42 \text{ g mol}^{-1}$, monoclinic, $P2_1/n$, $a = 13.1115(4) \text{ \AA}$, $b = 10.8183(4) \text{ \AA}$, $c = 14.8040(4) \text{ \AA}$, $V = 2073.56(12) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.481 \text{ g cm}^{-3}$, $\mu = 1.023 \text{ mm}^{-1}$, $T = 110 \text{ K}$, θ range 2.942 – 24.997° , 8460 reflections collected, 3644 independent reflections ($R_{\text{int}} = 0.0205$), $R1 = 0.0520$, $wR2 = 0.1284$ ($I > 2\sigma(I)$).

ASSOCIATED CONTENT

Supporting Information

Figures, Tables, and CIF files giving further (spectro)-electrochemical spectra, computational data, and crystallographic data for **3a** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data of **3a** and **3b** are also available from the Cambridge Crystallographic Database as file numbers CCDC 981390 (**3a**) and 981391 (**3b**).

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Notes

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