



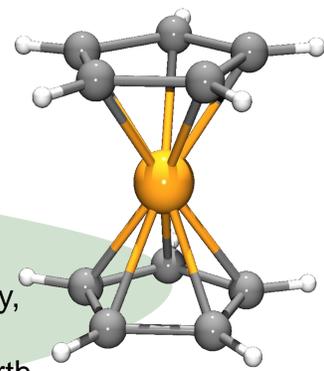
Synthesis, Characterization, Electrochemistry and Calculations of Ferrocenyl-substituted Siloles

Steve W. LEHRICH, Alexander HILDEBRANDT, Tobias RÜFFER,
Marcus KORB, Paul J. LOW† and Heinrich LANG*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry,
Inorganic Chemistry, D-09107 Chemnitz, Germany

†School of Chemistry and Biochemistry, University of Western Australia, Crawley, Perth,
Western Australia, Australia

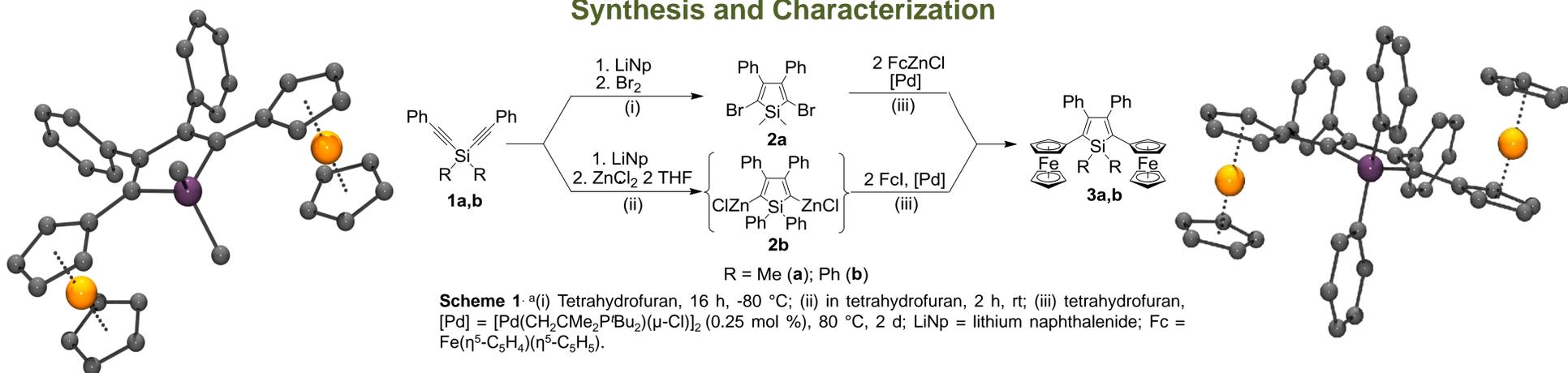
steve-wolfgang.lehrich@chemie.tu-chemnitz.de



Introduction and Motivation

Silacyclopentadienes (siloles) are attractive building blocks for the preparation of conjugated polymers¹ or co-polymers, which show unique conductivity and semiconducting properties attributed to a small band gap (E_g). 1-Silacyclopentadienes have attracted much interest for diverse applications such as new display devices or organic light-emitting diodes (OLEDs), due to the interaction of the σ^* orbital of the Si-C bond with the π^* orbital of the butadiene fragment. 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 light of our recent research on heterocyclopentadienes² and aromatic five-membered heterocycles^{3,4} 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.

Synthesis and Characterization



Electrochemistry

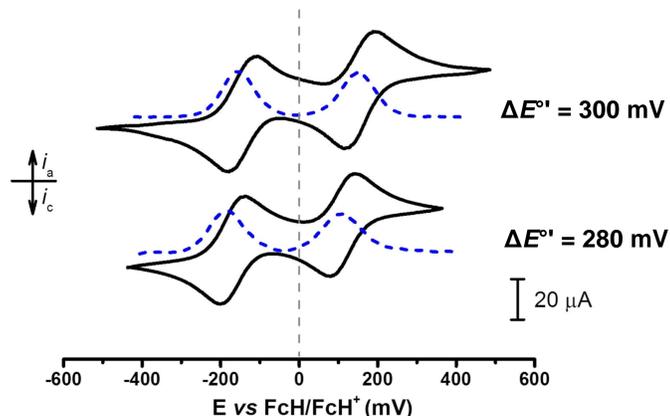


Figure 1. Cyclic voltammograms (solid line) and square wave voltammograms (dotted line) of **3a** and **3b** in dichloromethane solutions (1.0 mmol L⁻¹) at 25 °C (scan rate 100 mV s⁻¹; supporting electrolyte 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄]).

Computational Studies

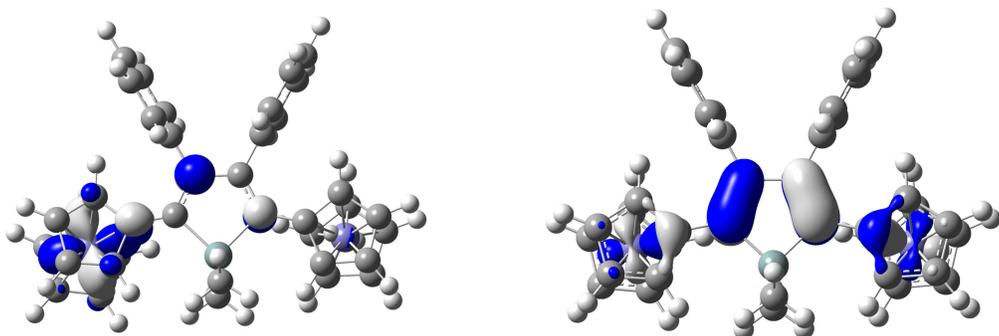


Figure 2. Plot of the β-LUSO of **[3a]⁺** (isocontour value ±0.04 (e/bohr³)^{1/2}).

Figure 3. Plot of the β-HOSO of **[3a]⁺** (isocontour value ±0.04 (e/bohr³)^{1/2}).

The composition of the molecular orbitals supports the MV (mixed valent) 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 2), 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 3).

Spectroelectrochemistry

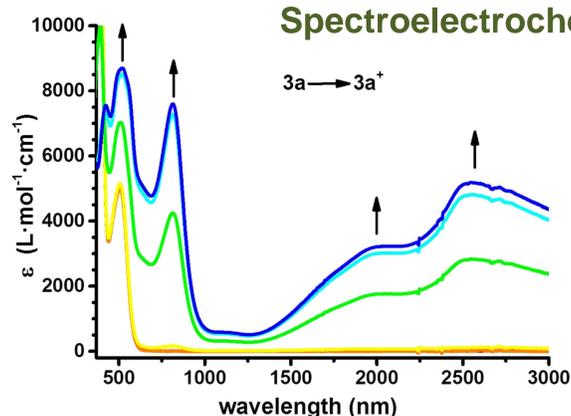


Figure 4. UV-vis/NIR spectra of **[3a]ⁿ⁺** (n = 0, 1, 2) in dichloromethane solution (2.0 mmol L⁻¹) at rising potentials (left: -200 mV to 300 mV, right: 300 mV to 700 mV vs Ag/AgCl) at 25 °C; supporting electrolyte 0.1 mol L⁻¹ of [NⁿBu₄][B(C₆F₅)₄]). Arrows indicates an increase or decrease of absorptions.

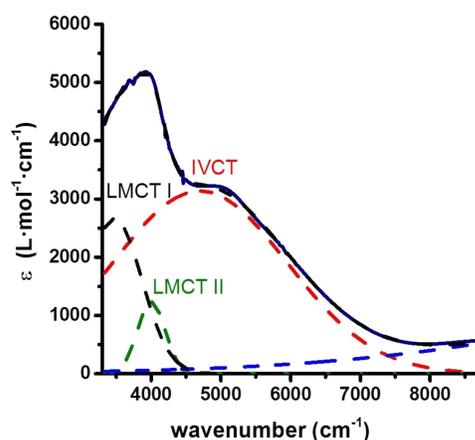


Figure 5. Four band Gaussian deconvolution of the NIR absorption envelope of **[3a]⁺** obtained by spectroelectrochemistry in an OTTE cell.

Spectroelectrochemistry of siloles **3a,b** within the monocation oxidation state shows an IVCT absorption in the NIR region. Deconvolution of this absorption envelope, required four Gaussian-shaped spectral components, consistent with an IVCT transition at 4700 cm⁻¹ (**[3a]⁺**) or 4650 cm⁻¹ (**[3b]⁺**) (**[3a]⁺**: $\epsilon_{max} = 3150$ L mol⁻¹ cm⁻¹, $\Delta\nu_{1/2} = 2950$ cm⁻¹; **[3b]⁺**: $\epsilon_{max} = 2270$ L mol⁻¹ cm⁻¹, $\Delta\nu_{1/2} = 3310$ cm⁻¹) and two LMCT bands. The higher extinction coefficient of the IVCT absorption in **[3a]⁺** might be a consequence of cross-hyperconjugation of the SiMe₂ building block with the butadiene unit. The unexpected strong IVCT interactions allowed to classify siloles **[3a]⁺** and **[3b]⁺** as moderately or moderately to weakly coupled class II system according to the classification system introduced by Robin and Day.

Conclusion

Two types of diferrocenyl-functionalized siloles were synthesized by intramolecular reductive cyclization and following palladium-catalyzed Negishi C,C cross coupling reactions. Their electronic behavior were studied by cyclic and square wave voltammetry showing two individual redox processes for each ferrocenyl unit. Spectroelectrochemical investigations confirmed charge transfer interactions between the individual ferrocenyl termini across the silole linking unit, which are comparable to those found in diferrocenyl phosphole² or diferrocenyl *cis*-butadiene systems⁵.

References and Acknowledgement

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