Multi-functionalized Ferrocenes: “Synthesis and Characterization”
Khaled Al Khalyfeh, Alexander Hildebrandt

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry,
Inorganic Chemistry, D-09107 Chemnitz, Germany
khaled-mohammad.al-khalyfeh@chemie.tu-chemnitz.de

Introduction

One of the major advantages of ferrocenes is the possibility to introduce functional
groups in a straightforward manner. For example, formyl-ferrocene and 1,1′-diformyl-
ferrocene have proven to be valuable starting materials for the introduction of various
functional groups at the ferrocene backbone.[1] Thereby, Wittig and Horner-Wadsworth-
Emmons reactions allow their conversion into vinyl groups. Those vinyl-ferrocenes in turn
have been used as starting material for the generation of ferrocenyl based conducting
and semiconducting polymers.[2] Beside these applications of formyl-ferrocenes their
electronic properties are also highly interesting. In this respect, a possibility to generate a
ferrocenyl species with very high redox potential compared to ferrocene was achieved by
the synthesis of formyl-ferrocenes bearing up to four formyl groups.[3]

Synthesis

Scheme 1. Formylation reaction of diacetal 1 forming aldehydes 2–4; (i) 1.0 equiv.
[PhMgCl] in THF, 4, 0°C for 1 h; (ii) 1.0 equiv. of HCl. 2 mmol.[1] 2.2 mmol of
ferrocene are converted to 2–4. 2 mmol of ferrocene is converted to 2–4 in 95% yield.

Scheme 2. Wittig reaction of aldehydes 3 and 6 forming vinyl ferrocenes 7 and 8; (i) 1.0
equiv. of PPh₃; (ii) 1.0 equiv. of [B(C₆F₅)₄]; (iii) 1.0 equiv. of BuLi. 1 atm for 30 min.

Electrochemistry

Using [PF₆]⁻ within measurements of compound 6 resulted in an irreversible behavior which is most
probably caused by deposition of the compound on the surface of the electrode, whereas, the lower ion-
paring capabilities of weakly coordinating [B(C₆F₅)₄]⁻ minimize this deposition processes.[4] In addition
cooling the samples down to –40 °C helped to prevent side reactions of the monocyclic species
and reversible redox processes have been observed.

X-ray Structure

Parallel displaced π–π interactions between two cyclopentadienyl rings are observed forming 1D chains
along the a-axis where the Cp–Cp distances as short as 3.21 A. The aldehydeic groups adopt as
periplanar conformation (h = 0°) as well as the cyclopentadienyl carbons in both rings are eclipsed.
Oxygen atoms of all aldehyde groups are directed to the opposing direction from each other.

Concept of Application

Cross Linking Polymers

Poly(vinylferrocenes) are in the focus recently as redox active polymers due to their chemical stability and high electrochemical
reversibility. The copolymerization of vinlylferrocenes with ferrocenes bearing two or more vinyl groups introduce additional
cross linking to the polymer and hence alters the physical properties of the electro active material. For example, higher
stability and elasticity are expected.

References and Acknowledgement

Erasmus, J.C. Swarts, H. Lang, Organometallics 29 (2010) 4900–4905. We are grateful to the Fonds der Chemischen Industrie for generous financial support.
Prof. Dr. Heinrich Lang for the supply of laboratory space and equipment, as well as Dieter Schauerschmidt and Marcus Korb for X-ray measurements.

Figure 1. Graphical representation of the structure of compound 6 in the solid state.

Figure 2. Cyclic voltammogram of 6 in dichloromethane; A: using [NBu₄][PF₆] (0.1 mol•L⁻¹) as supporting electrolyte; B: using [NBu₄][B(C₆F₅)₄] (0.1 mol•L⁻¹) as supporting electrolyte at 25 °C (red line) and –40 °C (black line).

Figure 3. Cyclic voltammogram of formyl-1,1′-diformylferrocene, 3 and 6 in DCM; 0.1 mol•L⁻¹ [NBu₄][B(C₆F₅)₄] as supporting electrolyte at –40 °C.

Figure 4. Redox potential of formyl-1,1′-diformyl-1,2-
diformylferrocene, 3 and 6 (black line) and 1, 2 and 4 (red line) in dependency of the number of CHO units.

Conclusion

Multi-functionalized ferrocene have been synthesized using a straightforward
methodology, which included selective mono- or di-ortholithiation of 1,1′-di[(3-dioxan-
yl)ferrocene, subsequent quenching with dimethylformamide and deprotection of
the acetyl moity afford tri- and tetra-formylferrocenes. The respective vinyl derivatives
where synthesized via Wittig reaction. Electrochemical measurements showed that these
electron poor ferrocenes become unstable in the cationic oxidation state. The
irreversible behavior could be prevented by using weakly coordinating supporting
electrolytes and reducing the measurement temperature to –40 °C. Furthermore, a
linear correlation between the number of formyl functionalities and the redox potential
was found.