1,1'-Dialkynylferrocenes: Building Blocks for Molecular Wires by Alkyne Metathesis

Der Naturwissenschaftlichen Fakultät der

Gottfried Wilhelm Leibniz Universität Hannover

zur Erlangung des Grades

Doktor der Naturwissenschaften

Dr. rer. nat.

genehmigte Dissertation

von

Dipl.-Chem. Jingxiang Ma

Geboren am 29.10.1969, in Jiangsu, China

2010

Referent: Prof. Dr. H. Butenschön
Koreferent: Prof. Dr. M. Boysen
Tag der Promotion: 15 September 2010

Hierdurch erkläre ich, dass ich meine Dissertation selbständig verfasst und die benututen Hilfsmittel und Quellen sowie gegebenenfalls die zu hilfeleistungen herangezogenen Institutionen vollständig angegeben habe.

Die Dissertatiion wurde nicht schon als Masterarbeit, Diplomarbeit oder andere prüfungsarbeit verwendet.

Hannover, den 07.07.2010

Die experimentellen Ergebnisse dieser Dissertation wurden in der Zeit von Oktober 2007 bis März 2010 am Institut für Organische Chemie der Leibniz Universität Hannover unter der Leitung von Herrn Prof. Dr. H. Butenschön durchgeführt.

Herrn Prof. Dr. H. Butenschön gilt mein besonderer Dank für die Überlassung des interessanten Themas, die stets freundliche Unterstützung, sowie die gute Betreuung and die vielfältigen Anregungen.

Meinen ehemaligen und jetzigen Kollegen Herrn Dr. Nikolai Vinokurov, Frau Dr. Bianka Muschalek, Frau Dr. Karin Kirleis, Herrn Dr. Ingmar Baugardt, Frau Dr. Stefanie Kohser, Herrn Dr. Osama Habib, Herrn Dr. Ismail Abdelshafy Abdelhamid, Frau Dipl.-Chem. Monika Pfennig, Frau M. Sc. Evelyne Kluser, Herrn Dipl.-Chem. Georg Werner, Herrn cand. Chem. Georg Bender, Herrn cand. Chem. Nico Krauße gilt mein Dank für die gute Zusammenarbeit, die interessanten Diskussionen sowie das angenehme Arbeitsklima.

Frau A. Kandil danke ich für die Hilfe bei organisatorischen Problemen.

Weiterhin möchte ich mich bei allen Mitgliedern der spektroskopischen Abteilung für das Engagement und ihren Hilfe bedanken, insbesondere bei Frau Dagmar Körtje, Frau Monika Rettstadt, sowie bei Dipl.-Chem. Mihail Astratov, Rainer Nöthel, Frau Christine Bartetzko und Dr. Gerald Dräger.

Den Mitgliedern aller Arbeitskreise im Institut für Organische Chemie danke ich für die gute Zusammenarbeit.

Prof. Tamm und Prof. Fürstner danke ich für die freundliche Unterstützung.

Der Deutschen Forschungsgemeinschaft (DFG) gilt mein besonderer Dank für die Vergabe einer Stelle als wissenschaftlicher Mitarbeiter in Rahmen eines DFG-Projekts.

Ein besonderer Dank für die stete Unterstützung gilt meinen Eltern und meiner Frau Miyuki Maekawa.

Zusammenfassung

Der Ersatz von 1,4-Phenylen-Einheiten in molekularen Drähten durch 1,1'-disubstituierte Ferrocen-Bausteine über die Sonogashira-Kupplungsreaktion ist erst kürzlich näher untersucht worden. Auf der Suche nach einer anderen Methode zur Herstellung dieser Schlüsselelemente der Ferrocen-basierten molekularen Drähte, wurde die Alkin-Metathese in Betracht gezogen. Unter Verwendung von $Mo(CO)_6$ und Phenol als Katalysatorsystem sollte 1,1'-Di(1-propinyl)ferrocen (**59**) durch Alkin-Metathese gekuppelt werden. Dabei ergab sich die unvorhergesehene Bildung von [4]Ferrocenophandien-Derivativen. Die Reaktionen von 1,1'-Dialkinylferrocen mit einer Vielzahl von Phenolen in der Anwesenheit sowie in Abwesenheit von $Mo(CO)_6$ erbrachte gute bis sehr gute Ausbeuten der Phenoxy[4]ferrocenophandiene. Eine ähnliche Reaktivität wurde mit Thiophenol und Essigsäure beobachtet, wobei Verbindungen **72** und **73** erzeugt werden. Die Reaktion unter basischen Bedingungen führte zu der Bildung von [4]Ferrocenophan **75**. Die erhaltenen Phenoxy[4]ferrocenophandiene zeigten dynamisches Verhalten als Ergebnis einer Verdrehung der Kohlenstoffbrücke, was durch temperaturabhängige ^{1}H- und ^{13}C-NMR-Spektroskopie gezeigt wurde. Die Kristallstruktur von **60** bestätigte diese Annahme. Als Reaktionsmechanismus wird ein Vinylkation-Intermediat postuliert, dessen Auftreten durch Untersuchung von Massenspekten der hergestellten Verbindung unterstützt wird.

Unter Verwendung des Molybdän-basierten Fürstner-Katalysators **58**, ein verhältnismäßig stabiler Katalysator für Alkin-Metathese, haben wir erfolgreich die Ferrocen-basierten molekularen Drähte **114**, **116** und **118** hergestellt.

Unser Interesse galt auch der Ein-Elektron-Oxidation von Triferrocenylmethan-Derivativen. Die Kristallstruktur von Triferrocenylmethanol-Hexafluorophosphat (**120**) zeigte klar, dass eine Ferrocenyl-Gruppe oxidiert wurde. Das Cyclovoltammogram und ^{57}Fe-Mössbauer-Effekt-Spektrum von **120** bei 91.5 K wurden untersucht. In Zusammenarbeit mit einer Gruppe der Unversität Bern wurden die Ferrocen-basierten molekularen Drähte **15**, **116**, **123** und **124** durch Sonogashira-Kupplungsreaktion dargestellt.

[4]Ferrocenophandiene, Alkin-Metathese, Molekulare Drähte

Abstract

Replacement of 1,4-phenylene moieties in molecular wires by 1,1'-disubstituted ferrocene units via Sonogashira coupling reaction has been extensively investigated recently. In the search for a different tool for the construction of the key elements of ferrocene-based molecular wires we considered alkyne cross metathesis to be of interest. Using $Mo(CO)_6$ and phenol as catalyst system we attempted to couple 1,1'-di(1-propynyl)ferrocene (**59**) by alkyne metathesis, which resulted in unanticipated formation of [4]ferrocenophanediene derivatives. The reaction of some 1,1'-dialkynylferrocenes with a variety of phenols in the presence as well as in the absence of $Mo(CO)_6$ yields good to high yields of phenoxy[4]ferrocenophanedienes. Similar reactivity was observed with a thiophenol and with acetic acid to generate compounds **72** and **73**. Reaction under basic conditions led to the formation of the [4]ferrocenophanone **75**. The phenoxy[4]ferroceno-phanedienes obtained show dynamic behavior as a result of a torsional twist of the carbon bridge as indicated by the ^{1}H and ^{13}C NMR spectra. The crystal structure of **60** confirmed the result. The reaction mechanism is discussed. A vinyl cation intermediate is postulated, whose relative stability is evident from the mass spectra of the compounds prepared.

Using Fürstner molybdenum-based catalyst **58**, a relatively stable catalyst for cross-coupling alkyne metathesis, we have successfully obtained some ferrocene based molecular wires **114**, **116** and **118**.

We are also interested in one-electron-oxidation of triferrocenylmethane derivatives. The crystal structure of triferrocenylmethanol hexafluorophosphate (**120**) showed clearly that one ferrocenyl group was oxidized. The cyclovoltammogram and ^{57}Fe Mössbauer effect spectrum of **120** at 91.5 K were investigated.

After the demand of a group from University of Bern, ferrocene-based molecular wires, **15**, **116**, **123** and **124**, have been prepared by using Sonogashira cross-coupling reaction.

[4]Ferrocenophanediene, Alkyne Metathesis, Molecular wire

Abbreviations

Å	Angstrom
aq.	Aqueous
APT	Attached Proton Test (in NMR spectroscopy)
Ar	Aryl
atm	Atmosphere(s)
ATR	Attenuated Total Reflection
br	Broad (in NMR spectroscopy)
Bu	Butyl
BuLi	n-Butyllithium
tert-Bu	*tert*-Butyl
°C	Degrees Celsius
calcd	Calculated
cat.	Catalyst
cm^{-1}	Wavenumber(s)
^{13}C NMR	^{13}C Nuclear Magnetic Resonance
CV	Cyclic Voltammetry
Cp	Cyclopentadienyl (C_5H_5)
δ	Chemical Shift (in parts per million downfield from tetramethylsilane)
d	Doublet (in NMR spectroscopy)
decomp.	Decomposition
DME	1,2-Dimethoxyethane
equiv	Equivalent
$E_{1/2}$	Half Potential
Et	Ethyl
Fc	Ferrocene(s)
g	Gramm
^{1}H NMR	^{1}H Nuclear Magnetic Resonance
Hz	Hertz
h	Hour(s)
IR	Infrared
J	Coupling Constant (in NMR spectroscopy)
$LiAlH_4$	Lithium aluminium hydride

LiHMDS	Lithium *N,N*-di(trimethylsilyl)amide
Me	Methyl
MeOH	Methanol
MHz	Megahertz
mL	Milliliter(s)
min	Minute(s)
mmol	Millimol
m.p.	Melting Point
MS	Mass Spectrometry
m/z	Mass-to-charge Ratio (in mass spectrometry)
µW	Microwave
NMR	Nuclear Magnetic Resonance
PE	Petroleum ether
Ph	Phenyl
ppm	Part per Million (in NMR spectroscopy)
i-Pr	*iso*-Propyl
q	Quartet (in NMR spectroscopy)
s	Singlet (in NMR spectroscopy)
THF	Tetrahydrofuran
TMEDA	*N,N,N',N'*-Tetramethylethane-1,2-diamine
TMSCl	Trimethylsilyl chloride
t	Triplet (in NMR spectroscopy)
TBME	*tert*-Butylmethyl Ether
TLC	Thin-layer Chromatography
V	Volt

Table of Contents

1 Introduction

1.1 Moore's Law

"The complexity for minimum component costs has increased at a rate of roughly a factor of two per year... Certainly over the short term this rate can be expected to continue, if not to increase. Over the longer term, the rate of increase is a bit more uncertain, although there is no reason to believe it will not remain nearly constant for at least 10 years. That means by 1975, the number of components per integrated circuit for minimum cost will be 65,000. I believe that such a large circuit can be built on a single wafer."

Moore's original statement that transistor counts had doubled every year appeared in his publication "Cramming more components onto integrated circuits", *Electronics Magazine* 19 April 1965.[1] In 1975 Gorden E. Moore, who co-founded the Intel Corporation, altered his prediction, popularly known as *Moore's Law*, which stated that the number of transistors on a chip will double about every two years.[2] Despite the popular misconception, Gordon Moore insisted on that he did not predict a doubling "every 18 months", but David House, his Intel colleague, had concluded that the integrated circuits would double in performance every 18 months in the light of the increasing performance of transistors.

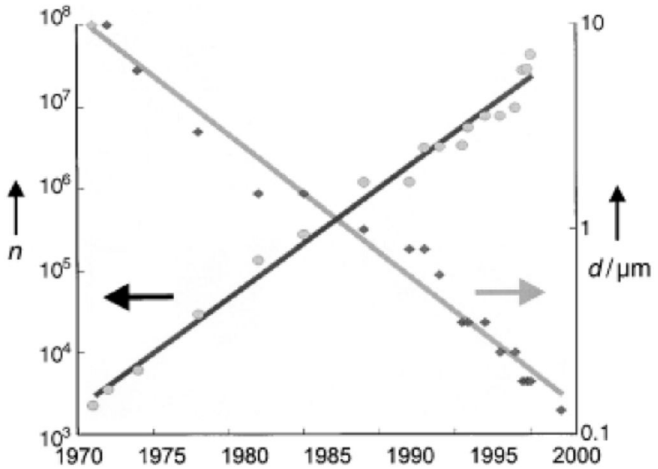


Figure 1. Moore's Law – the development of the number of transistors per square centimeter (n) and the component size (d) between 1970 and 2000.[3]

Since Moore first formulated this prediction in 1965, Moore's Law has become the guiding principle of progress in electronics and computing technology. Figure 1 shows that the development of the transistors proved the predictive power of the statement. The capabilities of many electronic devices are strongly linked to Moore's Law: processing speed, memory capacity and sensors. All of these are improving at roughly exponential rates as well.

1.2 Limitation of Moore's Law

The prediction has proved to be accurate enough that it has become a solid-state electronics industry target. The silicon industry has been following Moore's Law and the transistor sizes on chips has been miniaturizing exponentially.[4] The first integrated circuits contained only a few transistors. In January 1995, the Digital Alpha 21164 microprocessor had 9.3 million transistors. Six years later, a state of the art microprocessor contained more than 40 million transistors.[5] The characteristic sizes are around 100 nanometers, and the trend is believed to continue for the far future.

In 2003 Intel predicted the end of Moore's Law would come between 2013 and 2018 with 16 nanometer manufacturing processes and 5 nanometer gates, due to quantum tunneling.[6] On the contrary to the above described results and expectations, it was also pointed out that further increase of the integration density of computer chips may face a physical limit, abrupt and major complications due to false bit occurrences generated by thermal fluctuations (Johnson-Nyquist noise). [7] The expected range of sizes where serious problems will emerge is around 40 nanometer and below.[8] At the serious miniaturization of integrated chips, the problems will be expected.

On 13 April 2005, in an interview Gordon Moore stated that the law cannot be sustained indefinitely. He also noted that transistors would eventually reach the limits of miniaturization at atomic levels.

1.3 Molecular Electronics - A possible Solution for Traditional Semiconductor Materials

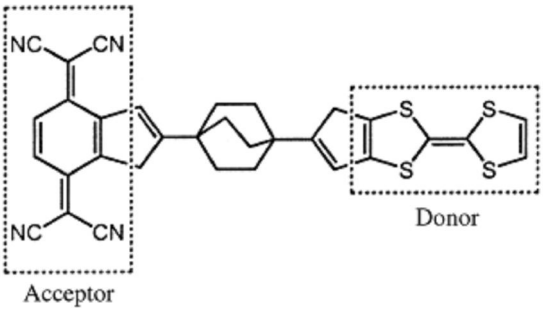
The ongoing exponential miniaturization of silicon based electronic devices is nicely demonstrated by with Moore's Law. The process approaches physical limitations such as

charge leakage through insulating silicon layers three or less silicon atoms thick.[9] These physical limitations cannot be overcome by more sophisticated engineering, but require conceptually new electronics. It is expected that the ultimate integrated circuits will reach the molecular or atomic level. In 1959 Richard Feynman stated in a lecture as follows:

"I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements – and by little, I mean little. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand ngstroms across…there is plenty of room to make them smaller. There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now. In fact, there may be certain advantages."[10]

Due to the electronic properties, some single molecules were regarded as an alternative for silicon based devices. In the past decades many achievements have been reported in this field, which is known as molecular electronics.[11]

Molecular electronics has been defined as technology utilizing single molecules, small groups of molecules, carbon nanotubes, or nanoscale metallic or semiconductor wires to perform electronic functions.[3] The molecular electronic components include transistor, rectifier, wire and so on. In the 1970s Aviram and Ratner reported the first theoretical and experimental result in this field. They successfully prepared and characterized molecule **1** as rectifier, which has a donor and an acceptor moieties (Scheme 1).[12]

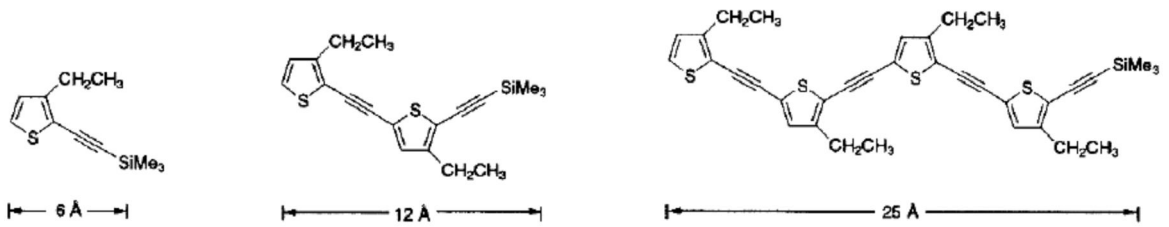


1

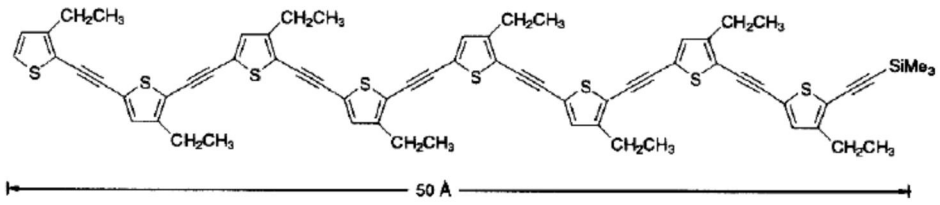
Scheme 1.

1.4 Molecular Wires

To connect the molecular electronic components, the molecular-scale wires are required. They are usually extended conjugated π systems. Due to the important characteristics, the molecular wire has been focused on linear, conjugated oligomers, for instance, molecules **2**-**5** (Scheme 2).[10]



2 **3** **4**



5

Scheme 2.

Molecular wires should be designed so that they can be attached to the surface of metals by covalent bonds. In many cases, the self-assembled monolayers (SAMs) attached via the thiol groups to gold surface (Figure 2). The thiol group and its precursors, the thioacetyl group, the (*tert*-butoxyl)sulfanoyl group, are usually termed as alligator clips. Since the lability of thiol groups, molecular wires are often prepared with thioacetyl groups or (*tert*-butoxyl)sulfanoyl groups as the tail groups (Scheme 3), which can change to thiol groups under acidic condition.[11] Alkyl substituents such as the ethyl groups in **6** are used to increase the solubility in organic solvents. Functional groups such as the nitro and amino groups in **7** can be used to tune the electronic properties of the molecular wire, e.g., by pH or by an external electric field.

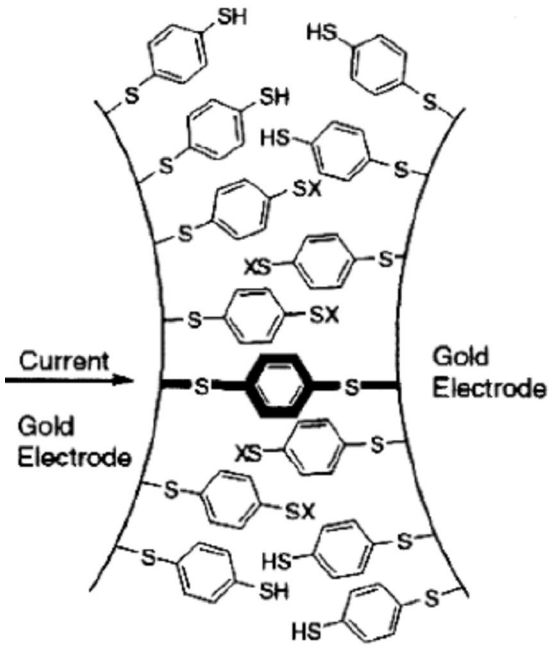
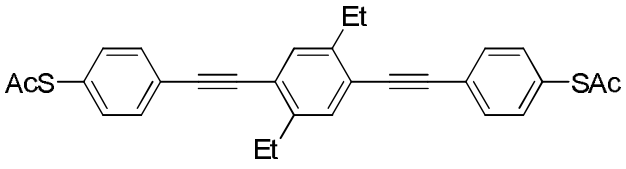
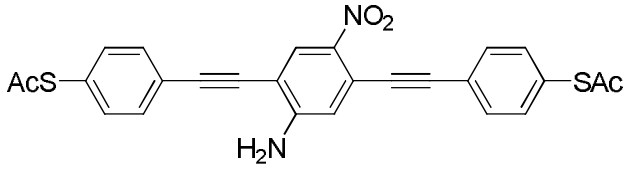


Figure 2. a benzene-1,4-dithiolate molecule between two Au electrodes



6



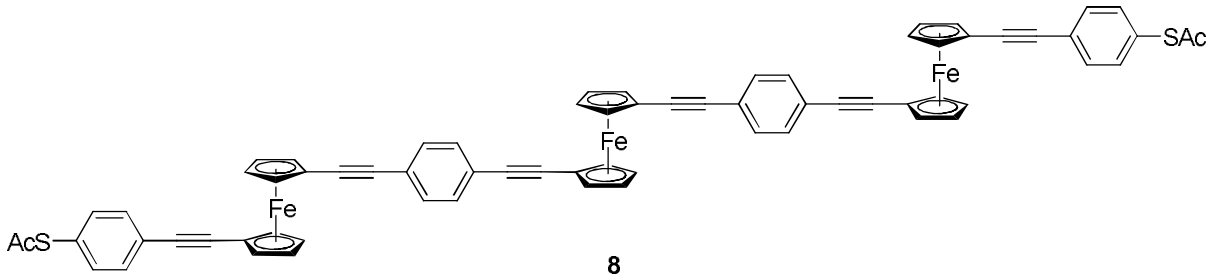
7

Scheme 3.

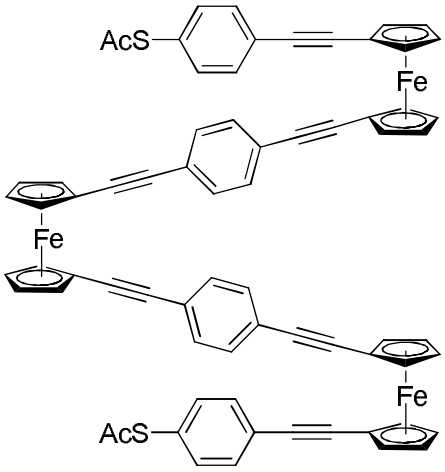
1.5 Molecular Wires based on Ferrocene

Most conventional molecular wires such as **6** and **7** are oligophenyleneethynylene (OPE) type wires with two dimensional rigid structures.[13, 14] As such they are prone to π,π stacking

making it somewhat difficult to assign physical properties to precisely one molecule of the type investigated. In addition the rigidity causes a fixed wire length, which might or might not ideally fit between electrodes. In the context of our interest in molecular wires, novel molecular wires have been designed, in which some - not all – of the 1,4-phenylene moieties are replaced by 1,1'-disubstituted ferrocene groups. The idea is that the three dimensional structure of ferrocene derivatives in contrast to OPEs should make π,π stacking less likely. Additionally, the easily possible rotation around the Cp-Fe-Cp axis should in a hinge-like way allow for some limited conformational flexibility of the wires, comparable to a foldable ruler. These principles are illustrated by conformations **8** and **9** of a molecular wire containing three ferrocene moieties (Scheme 4).[15]



8

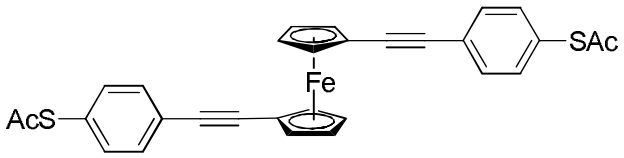


9

Scheme 4.

Attempts to resolve these issues by replacing some of the 1,4-phenylene or 2,5-thiophenylene units by 1,1'-ferrocenylene moieties have been investigated.[17-20] A first representative of

ferrocene containing molecular wires **10** was prepared starting from 1,1'-bis(trimethyl-silylethynyl)ferrocene (Scheme 5).[16]

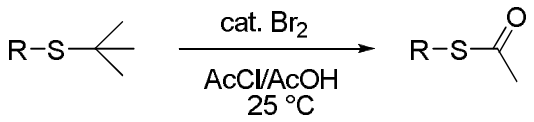


10

Scheme 5.

In many molecular wires thioacetyl end groups serve as protected thiol "allogator clips". Our investigations showed, however, that the thioacetyl group is relatively sensitive and often precluded the synthesis of longer molecular wires. Recently Mayor reported that the less sensitive *tert*-butylthio group could easily be transformed into a thioacetyl group.[21] Therefore some ferrocene based molecular wires have been prepared from suitable building blocks bearing *tert*-butylthio alligator clips.

The facile and efficient conversion of a *tert*-butyl protecting group to an acetyl protecting group for thiols can take place by catalytic amounts of bromine in acetyl chloride and the presence of acetic acid (Scheme 6). [21]



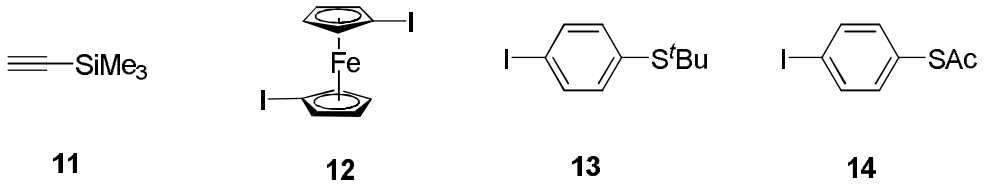
Scheme 6. Bromine catalyzed conversion of a tert-butyl thiol into an acetyl protected thiol. [21]

The synthesis of the above mentioned molecular wires widely relies on repetitive Sonogashira coupling reactions of a small number of suitable building blocks. The Sonogashira coupling reaction is among the most commonly used reactions for the connection of alkynyl groups to arenes. However, the reaction not always gives satisfactory results.[22] In search for a different tool for the construction of the key element of molecular wires we considered alkyne cross metathesis to be of interest.

2 Results and Discussion

2.1 Synthesis of Ferrocene-based Molecular Wires via Sonogashira Coupling Reaction[15]

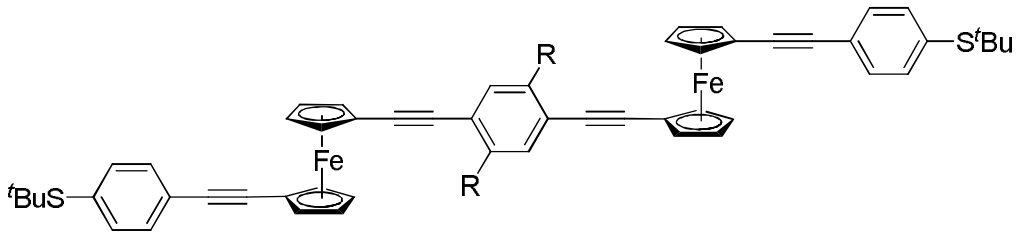
The ferrocene based molecular wires with triple bonds directly attached to the ferrocene moieties have been constructed by repetitive reactions using a rather limited number of building blocks and coupling reactions such as Sonogashira-Hagihara coupling,[15, 18] or the palladium catalyzed Stille coupling of alkynylstannanes with aryl halides.[16] The limited building blocks in the context of our research include trimethylsilylethyne (**11**), 1,1'-diiodoferrocene (**12**),[23] 1-*tert*-butylsulfanyl-4-iodobenzene (**13**), 1-iodo-4-thioacetylbenzene (**14**) (Scheme 6). [21]



11 **12** **13** **14**

Scheme 7.

For the synthesis of **10** 1,1'-diiodoferrocene (**12**) was coupled with **11** affording 1,1'-bis(trimethylsilylethynyl)ferrocene,[15] which upon treatment with methyllithium followed by tributylchlorostanne was transmetallated to give the corresponding stannyl compound. Subsequent Stille coupling finally afforded **10**.[16] In the sequence the use of **11** was necessary, because 1,1'-diethynylferrocene came out to be unstable under the reaction conditions.[24,25]
Having prepared a molecular wire with one ferrocene moiety we became interested in the construction of molecular wires with two ferrocene hinges. In particular, the synthesis of **15** and **16** was envisaged (Scheme 8).

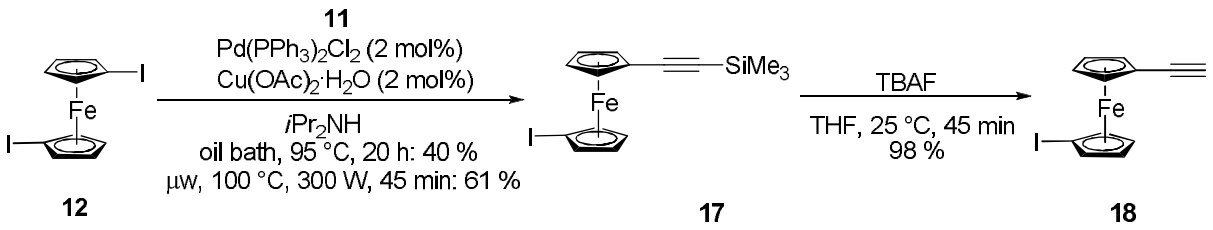


15: R = H
16: R = OMe

Scheme 8.

15 is the parent system of molecular wires with two ferrocene hinges separated by a 1,4-diethynylphenylene moiety, and **16** is the first representative with a functionalized spacer. In addition, **16** offers the possibility of an oxidation with formation of the respective quinine derivative,[26] which deserves interest with respect to its redox properties in the hydroquinone as well as in the ferrocene moieties.

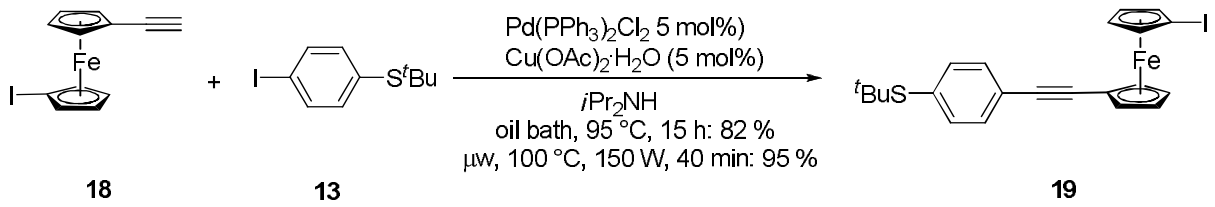
The synthesis of **15** and **16** started from 1,1'-diiodoferrocene (**12**), which was alkynylated with trimethylsilylethyne (**11**) in a Sonogashira coupling reaction to give the unsymmetrically substituted ferrocene building block **17**.[27] While conventional heating of the reaction in an oil bath for 20 h at 95 °C afforded **17** in 40 % yield, the application of microwave heating for 45 min afforded **17** in an improved yield of 61 %. Subsequent desilylation with tetrabutylammonium fluoride in THF at 25 °C gave 1-ethynyl-1'-iodoferrocene (**18**) in 98 % yield (Scheme 9). **18** has earlier been prepared by Butler by a less convenient route in 23 % yield.[28]



Scheme 9.

Subsequent Sonogashira coupling of **18** with 1-*tert*-butylsulfanyl-4-iodobenzene (**13**), which was obtained in 82 % yield from commercially available pepsyl chloride,[29] afforded **19** in 82 % yield with conventional heating for 15 h at 95 °C and in 95 % yield under microwave

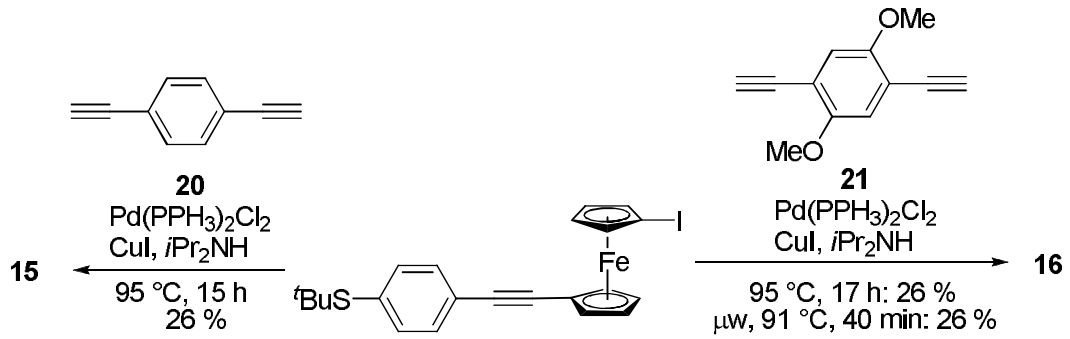
irradiation at 100 °C for 40 min (Scheme 10). Alternatively, **19** was obtained by Sonogashira coupling of 1,1'-diiodoferrocene (12) and 1-*tert*-butylsulfanyl-4-ethynylbenzene[28] in 36 % yield.



18 **13** **19**

Scheme 10.

Double Sonogashira coupling of **19** with commercially available 1,4-diethynylbenzene (**20**) afforded **15** in 26 % yield corresponding to a 51 % yield per coupling step. Alternatively, the corresponding reaction with 1,4-diethynyl-2,5-dimethoxybenzene (**21**)[26] afforded **16** in 24 % yield with conventional heating at 95 °C for 17 h, microwave heating for 40 min at 91 °C gave a slightly higher yield of 26 % (Scheme 11).



19

Scheme 11.

The electrochemical behavior of **16** was investigated by cyclic voltammetry (CV). The respective plot (Figure 2) shows one almost reversible redox process at $E_{1/2}$ ca. 0.27 V versus FcH/FcH$^+$ at three scan rates. The redox process observed presumably indicates the reversible oxidation to the corresponding ferrocenium ion. The CV data are given in Table 1.

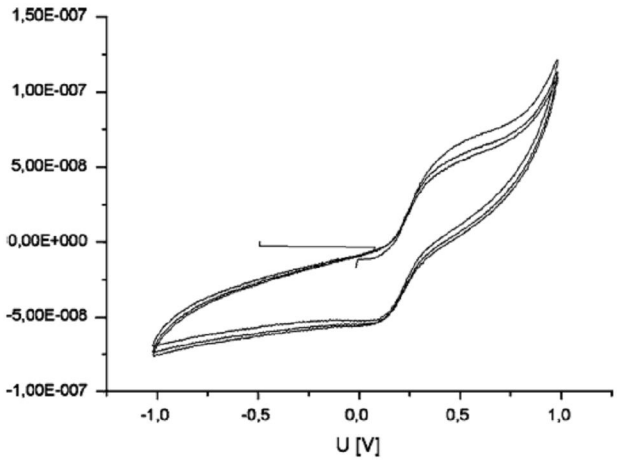


Figure 2. Cyclovoltammogram of **16**, For conditions see Table 1. [15]

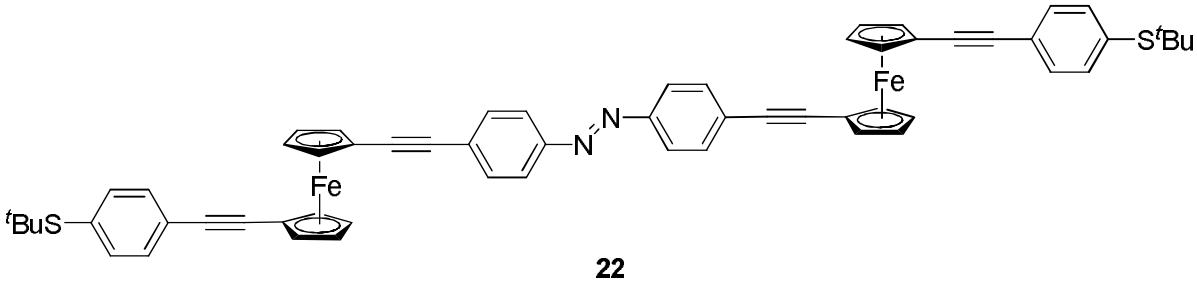
Table 1. CV data of **16** (0.2 mol/L Bu_4NPF_6 in CH_2Cl_2, c = 0.0005 mol/L, T = 293 K, 100 mV/s, potential versus FcH/FcH^+)[15]

V [mV/s]	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]
500	0.149	0.379	0.230	0.264
200	0.154	0.387	0.233	0.271
100	0.149	0.381	0.232	0.265

Another interesting molecular wire is **22** (Scheme 12), which was prepared from 4,4'-diethynylazobenzene[30-32] in 39 % yield under microwave heating for 40 min at 91 °C. **22** has an extended delocalized π system including an azobenzene moiety, which can be photochemically switched from the *trans* to the *cis* configuration. This change should be reflected in the electronic properties of the wire.

The possibility of a photochemical *trans*-*cis*-isomerization is indicated by the UV spectra obtained. Figure 3 shows the UV spectrum of solid **22** with the respective transitions indicated. Figure 4 shows the change in the UV spectrum upon irradiation with 0.0, .05, 12.5, 17.5, 35.5 and 50.5 min of irradiation. The decrease at the π-π* band indicates a decrease of the *trans* isomer due to photoisomerization.

The cyclic voltammogram of **22** is given in Figure 5 and the data are collected in Table 2. The



22

Scheme 12.

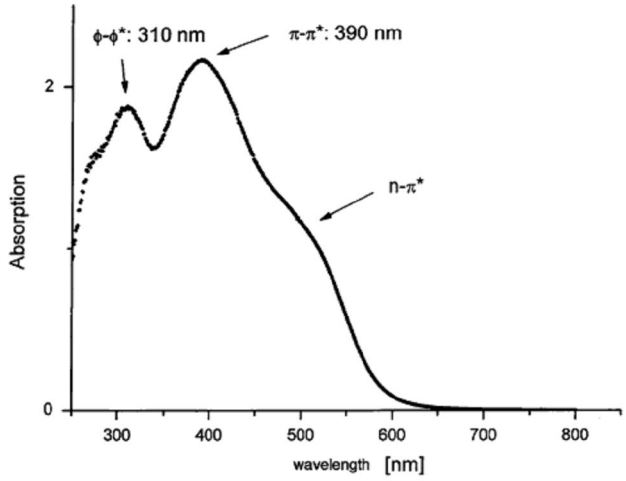


Figure 3. UV-VIS spectrum of solid **22**. [15]

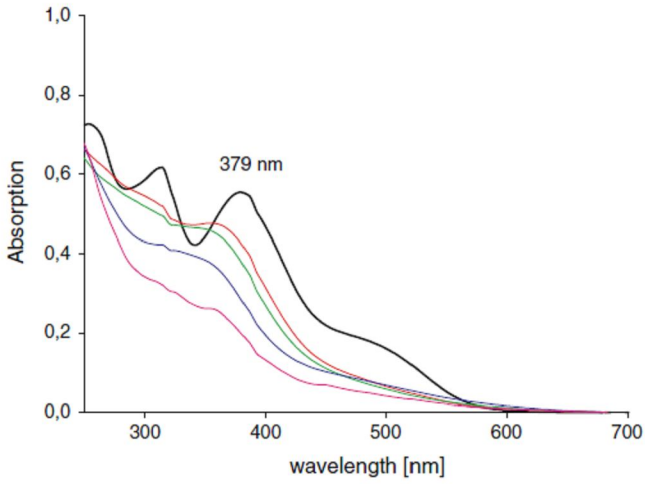


Figure 4. UV-VIS spectrum of **22** in $CDCl_3$: Original (black), irradiation for 0.5 min (below black), 12.5 min (red), 17.5 min (green), 35.5 (blue), 50.5 min (pink)-decrease indicated by arrow (I = 100 mW/cm^2; λ = 360 ± 50 nm). [15]

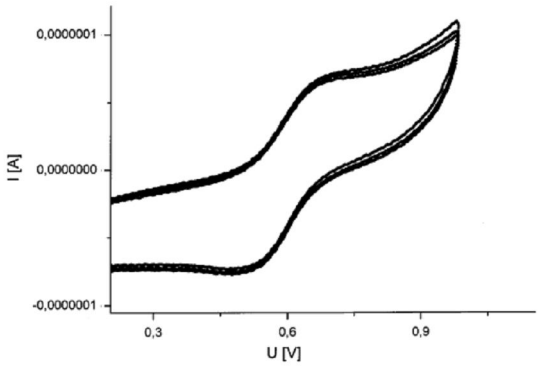


Figure 5. Cyclovoltammogram of **22**. For condition see Table 2.[15]

Table 2. CV data of **22** (0.2 mol/L Bu_4NPF_6 in CH_2Cl_2, c = 0.0005 mol/L, T = 293 K, 100 mV/s, potential versus FcH/FcH^+)[15]

Scan	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]
1	0.711	0.495	0.216	0.603
2	0.713	0.494	0.219	0.604
3	0.712	0.495	0.217	0.604

cyclovoltammogram resembles that of **16** in that it shows a reversible oxidation. As with **16** this presumably results from the oxidation to the corresponding ferrocenium species.

Although the CV results should not be over-interpreted, the fact that only one redox process is observed for **16** and for **22** seems to indicate that the oxidation product contains two equivalent ferrocene/ferrocenium moieties (Fc-Fc^+, Fc^+-Fc), otherwise one would expect to observe two different redox processes, namely one for the oxidation to the Fc-Fc^+ product and a second one for the subsequent oxidation to the Fc^+-Fc product. Consequently the CV results are in accord with a charge delocalization between the ferrocene moieties in **16** and in **22**. Further electrochemical investigations are planned for the hydroquinone/quinine redox couple to be obtained from **16** by phenyl ether hydrolysis to the corresponding hydroquinone, which is expected to show interesting interactions with the ferrocene/ferrocenium redox couple attached to it.

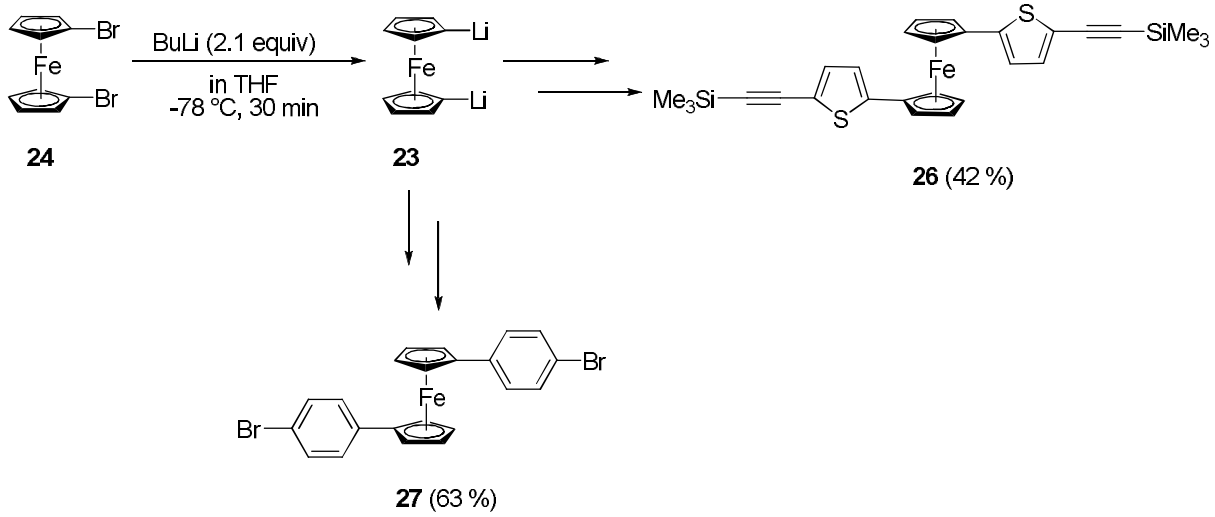
The molecular wires with two ferrocene hinges have been presented. The compounds bear *tert*-butylsulfanyl end groups, which night be transformed to thioacetyl groups by the method of Mayor.[21] In particular, compound **22** deserves interest, because in addition to its nature as

a molecular wire, this compound contains a spacer allowing photoisomerization and should therefore have some potential for the optical manipulation of its electronic properties.

2.2 Synthesis of 1,1'-Dilithioferrocene (23)

In the chemistry of 1,1'-disubstituted ferrocene, as a versatile nucleophile, 1,1'-dilithioferrocene (**23**) is usually utilized, which was prepared by treatment of either 1,1'-dibromoferrocene (**24**) [20] (Scheme 12) or ferrocene (**25**) [33,34] (Scheme 13) with butyllithium. In order to compare the two methods for synthesis of 1,1'-dilithioferrocene (**23**), the compounds **26**, **27** and **28** were prepared respectively by using 1,1'-dibromoferrocene (**24**) or ferrocene (**25**) as starting material.

The lithiation of **24** might be finished within 30 min at -78 °C. 1,1'-Dibromoferrocene can be prepared according to the literature[35] and is also commercially available, but rather expensive.

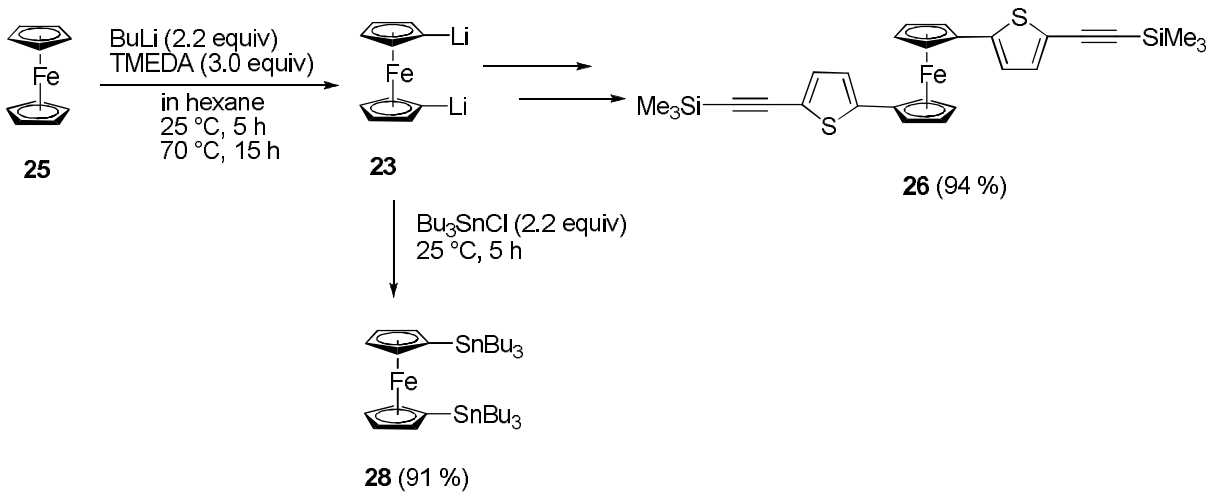


Scheme 13.

The different parameters influencing lithiation of **25** with butyllithium had been intensively investigated. The optimal reaction condition was obtained as followed: BuLi (2.2 equiv), TMEDA (3.0 euqiv), hexane as solvent, 5 h at 25 °C, 15 h at 70 °C. The yields of **26** and **28** showed that the formation of **23** is more 94 % under the above mentioned reaction condition

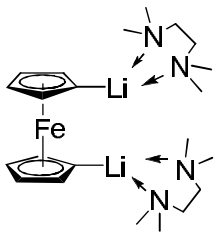
(Scheme 14). Here TMEDA acts as chelating reagent for **23**, 1,1'-dilithioferrocene · 2TMEDA (**29**) was isolated as an orange solid (Scheme 15).[36]

The reaction temperature influences remarkably the dilithiation of ferrocene (**25**) with butyllithium. Compared with heating at boiling point, the yield of **28** is only 45 % at 25 °C overnight.[37]



25 **23** **26** (94 %) **28** (91 %)

Scheme 14.



29

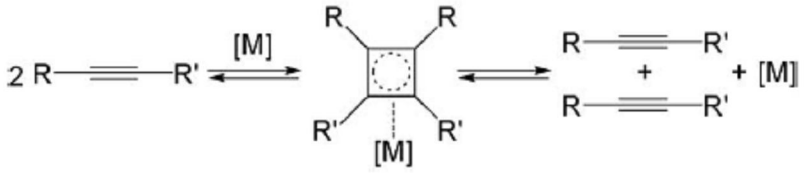
Scheme 15.

2.3 Alkyne Metathesis

In the past decades, as one of the primary tools of carbon-carbon double bond formation, the transition-metal-catalyzed alkene metathesis has intensively been studied and applied in organic chemistry. The method is increasingly replacing the other such as Wittig reaction and McMurry coupling reaction. Schrock[38], Grubbs[39] and others[40] have developed active and

efficient catalysts for olefin metathesis that are also commercially available. In terms of both activity and tolerance to functional groups, this pathway has made a great contribution to organic synthesis and polymer chemistry. However, one disadvantage of alkene metathesis is that mixtures of (*E*)- and (*Z*)-isomers are usually obtained,[40a,b] therefore much attention has been paid to an alternative: *alkyne metathesis*, which refers to the mutual exchange of the alkynyl units between non-terminal acetylene derivatives.[41]

The first triple bond metathesis reaction was reported by Pennella et al in 1968.[42] The reaction of pent-2-yne was studied from 200 to 450 °C. In the presence of the catalyst, 6-8 % tungsten trioxide on silica, pent-2-yne yielded but-2-yne and hex-3-yne. The mechanism was suggested on the basis of the formation of cyclobutadiene-tungsten complexes (Scheme 16).

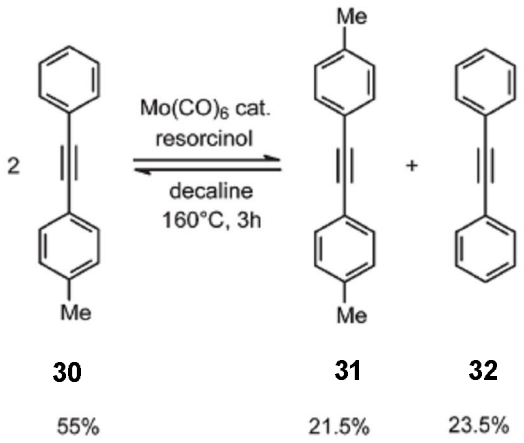


Scheme 16.

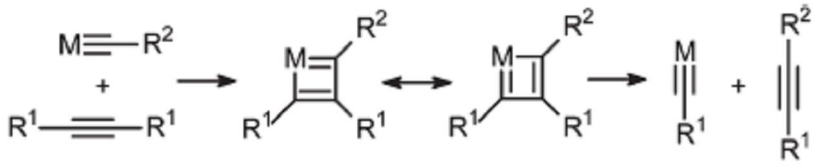
Due to the very high reaction temperature, this condition is hardly relevant for organic synthesis. Thereafter, different tungsten- or molybdenum-based catalytically active catalyst systems have been developed.[43-47]

2.3.1 $Mo(CO)_6$ and Phenol as Classical Catalyst systems

Mortreux initially investigated Molybdenum hexacarbonyl as catalyst for alkyne metathesis.[48] In 1974, he reported the first successful reaction catalyzed by a homogeneous mixture of $Mo(CO)_6$ and resorcinol in decaline as solvent at 160 °C (Scheme 17).[43] The catalytically active species was formed in situ from these precursors. One year later, Katz et al. suggested that metal carbynes likely account for the catalytic mechanism in a sequence of [2+2] cycloaddition and cycloreversion (Scheme 18).[49]



Scheme 17.

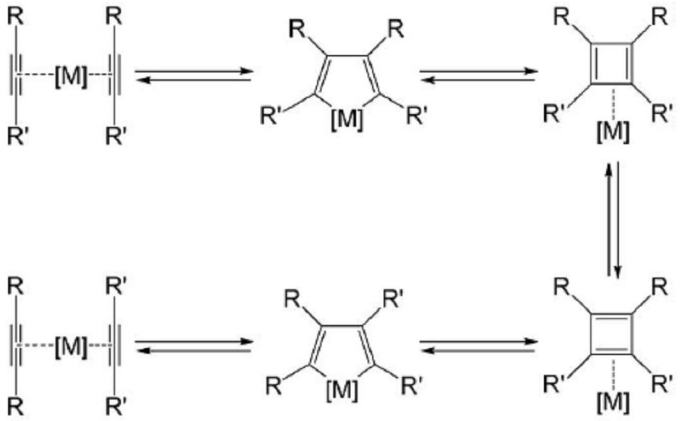


Scheme 18.

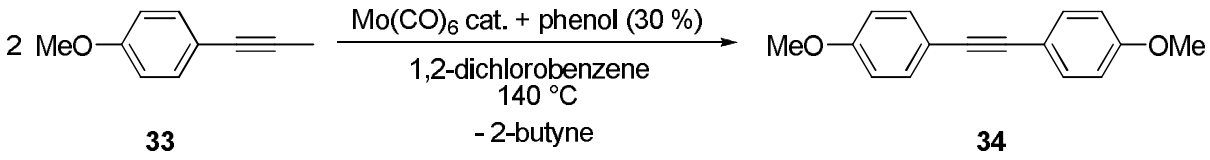
This mechanism was later experimentally established by Schrock using high valent metal alkylidynes.[44] Some tungstenacyclobutadiene complexes formed by the [2+2] cycloaddition of alkylidynes and alkynes were isolated and characterized, which have been proved to be catalytically active intermediates.[50]

As an alternative mechanism, Mori et al. also suggested that the formation of metallacyclopentadiene and the isomerization of cyclobutadiene-metal complexes were the key points (Scheme 19). This proposal resulted from the reaction of *ortho*-hydroxyphenyl substituted alkynes, which led to trimerization product.[51]

The "Mortreux systems" have gained widespread application due to the facile utilization of $Mo(CO)_6$ and phenols, entirely stable, inexpensive and commercially available reagents; besides, no rigorously purified solvents and inert atmosphere were required.[41] The most convenient reactions are conducted using $Mo(CO)_6$ and 4-chlorophenol in high boiling solvents (Scheme 20).[52]



Scheme 19.



Scheme 20.

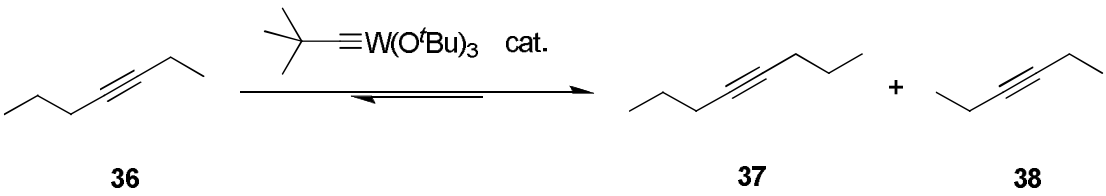
In 2004 Grela et al. reported an improved approach, where 1 equiv 2-fluorophenol and chlorobenzene as solvent were utilized.[46] This "instant" catalyst system has been successfully applied to alkyne cross metathesis (ACM),[46] homometathesis (HM),[46] ring closing alkyne metathesis (RCAM)[46, 53,54] and polymerization[55].

2.3.2 A well-defined Schrock Catalyst: Tri-*tert*-butoxytungsten Neopentylidyne (35)

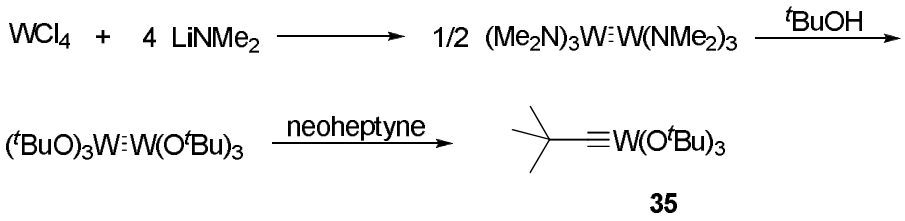
On the basis of the earlier work by Fischer, who obtained a mixture of tolane, phenyl-*p*-tolylacetylene and diparatolylacetylene by mixing $Br(CO)_4Cr{\equiv}CPh$ and $Br(CO)_4Cr{\equiv}CPhMe$ at 40 °C,[56] tremendous efforts were made for synthesis of high oxidation state metallacarbynes, which had been previously suggested as potential active species for alkyne metathesis.[48] In a series of investigations, Schrock et al. found that the high valent metal alkylidyne complexes are catalytically active. He successfully obtained the first well-defined

catalyst, (^{t}BuO)$_3$C≡WC^{t}Bu, which transformed hept-3-yne (**36**) to the mixture of oct-4-yne (**37**) and hex-3-yne (**38**) at 25 °C (Scheme 21).[44]

Most applications of Schrock alkylidyne complex **35** require fairly mild conditions, even at ambient temperature. Synthesis of **35** from (^{t}BuO)$_3$W≡W(O^{t}Bu)$_3$[57] and neoheptyne (Scheme 22) is the most convenient approach.

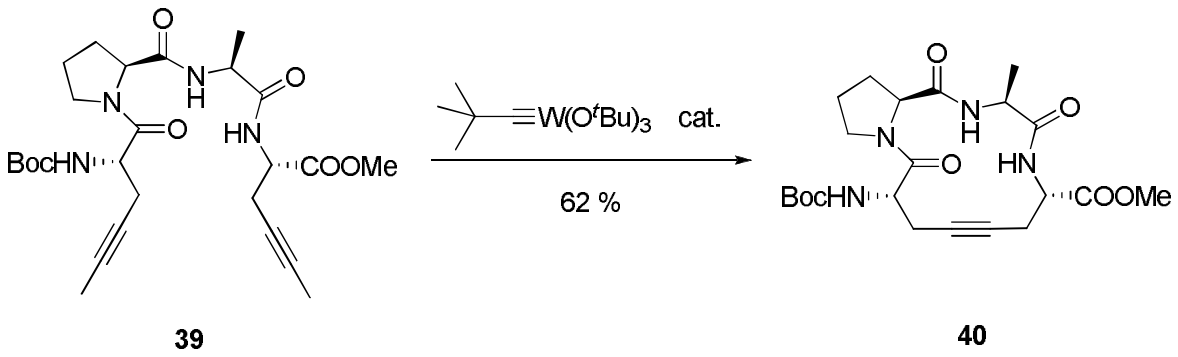


Scheme 21.



Scheme 22.

As the most favored Schrock alkylidyne catalyst, **35**, has been utilized not only for formations of cycloalkynes,[41] cross metathesis products from simple acetylene derivatives[44,51a] and polymers,[58] but also for syntheses of hetreocycles[59] and metalla-macrocycles.[60] Using **35** as catalyst, ring-closing alkyne metathesis has been applied to synthesis of conformationally restricted peptidic β-turn mimetics (Scheme 23).[61]

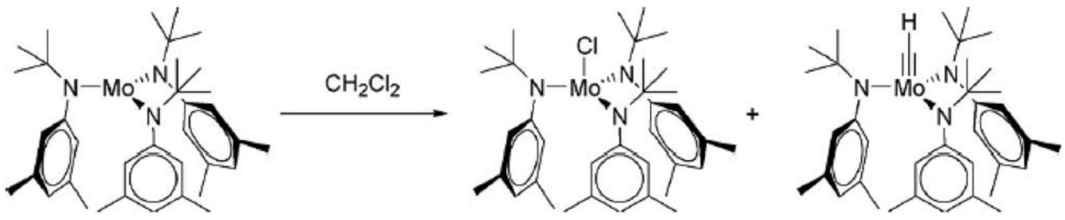


39 **40**

Scheme 23.

2.3.3 Trisamidomolybdenum based Catalyst (41)

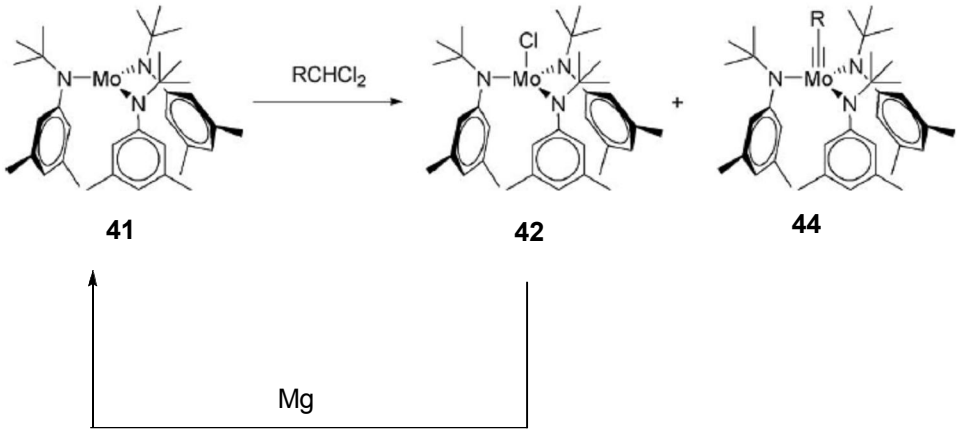
Fürstner and coworkers studied the development of a novel catalyst, which is tolerant against the functional groups. Based on the work of Cummins related to nitrogen activation with trisamidomolybdenum species,[62] an active catalyst, Mo[N(*t*Bu)(Ar)]$_3$-CH_2Cl_2-system (Ar = 3,5-dimethylphenyl), was reported.[45] Complex **41** showed no catalysis for alkyne metathesis by itself. When mixed with CH_2Cl_2, two derivatives, ClMo[N(*t*Bu)(Ar)]$_3$ (**42**) and HC≡Mo[N(*t*Bu)(Ar)]$_3$ (**43**), were obtained in this process (Scheme 24).[63] The both complexes were isolated and characterized.[63] The catalytic competence of **42** and **43** were investigated, the results showed that the methylidyne carbyne **43** did not induce any catalysis, whereas **42** owned catalytic activity.[64] Similarly, treatment of **41** with $CHCl_3$, CCl_4, CH_2Br_2, CH_2I_2, $C_6H_5CHCl_2$, $C_6H_5CH_2Cl$, Me_3SiCl also resulted in formation of catalytically active species for alkyne metathesis.[45] Most importantly, the **41**-CH_2Cl_2 system was fully active in the presence of the following functional groups: acetal, amide, carbonate, enoate, ester, ketone, silyl ether, sulfone and various metal centers.[63]



41 **42** **43**

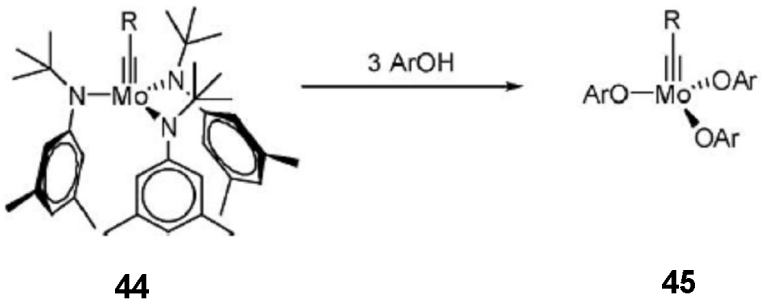
Scheme 24. Production of **42** and **43** from **41**.

In 2003 Moore and coworkers reported an improvement of the catalytic behavior of this catalyst system.[65] *gem*-Dihalides such as 1,1-dichloropropane were utilized to activate the precatalyst **41**, the molybdenum chloride complexe **42** and the non-terminal molybdenum alkylidyne **44** were formed. Addition of magnesium allowed to reduce the continuously formed chloro complex **42** and to produce the metallacarbyne species quantitatively (Scheme 25). The terminal group has an influence on the catalytic effect. Compared with methyl group, the catalyst with ethyl group has superior activity.[65b]



Scheme 25.

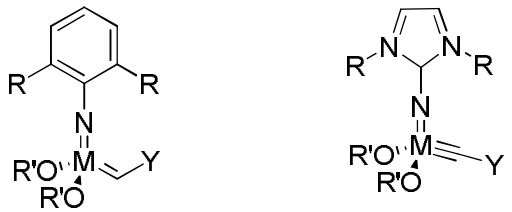
44 have also been used as precursors for phenoxymolybdenum carbyne **45** (Scheme 26). Using **45** as catalyst, the alkyne metathesis reactions could be carried out even at ambient temperature. [66b]



Scheme 26. Preparation of **45** via phenolysis of **44**.

2.3.4 Well-defined Imidazolin-2-iminato Tungsten Alkylidyne Complexes

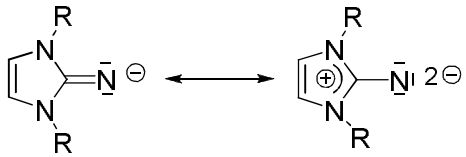
Most recently, Tamm and coworkers successfully developed a novel active well-defined catalyst for alkyne metathesis by introducing a new design strategy.[47] This idea was drawn from the most active alkene metathesis catalysts, molybdenum and tungsten based imido alkylidene complexes **46**, from which these alkyne metathesis catalysts **47** were designed (Scheme 27).[47]



46 **47**

Scheme 27. Design strategy for catalysts **47**.

Complexes **47** were designed by using monoanionic imidazolin-2-iminato ligands **48**, which can be described as the two limiting resonance structures (Scheme 28).[66] Substitution of the arylimido ligand in the alkene complexes **46** by a dinegative imidazolin-2-imide resulted in the concurrent conversion of metal-carbon double bond into a triple bond to afford alkylidyne complexes **47**. It has been demonstrated that alkoxide ligands with electron-withdrawing substituents such as R' = $CMe(CF_3)_2$, are beneficial for catalytic performance, since they increase the electrophilicity of the metal center.

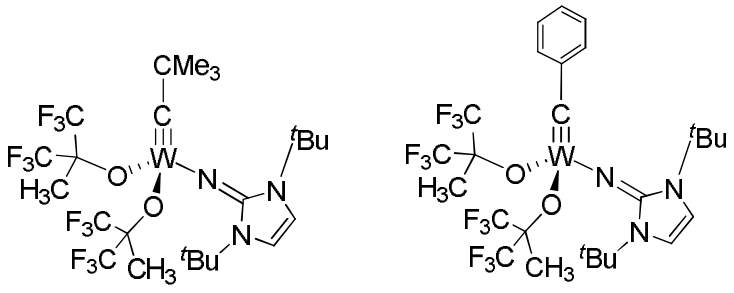


48

Scheme 28. Two limiting resonance structures of **48**.

Starting from the readily available complex, $Me_3CC{\equiv}W[OCMe(CF_3)_2]_3(dme)$, where the tungsten center is stabilized by dimethoxyethane (dme).[67] Treatment of this complex with the

lithium reagent (ImN)Li, obtained from the lithiation of 1,3-di-tert-butylimidazolin-2-imine (ImNH) with methyllithium, gave the catalytically active tungsten alkylidyne complex **48**, $Me_3CC{\equiv}W[OCMe(CF_3)_2]_3(ImN)$ (Scheme 29).[47] Moreover, catalyst **49** was successfully prepared.[68]



Scheme 29. Catalysts **49** and **50**.

The reactivity of **49** was intensively investigated by treatment of 1-phenylpropyne (**51**) in hexane. This reaction was carried out at room temperature and reduced pressure (350 mbar). In the presence of 1 mol% catalyst **50**, the product, diphenylacetylene (**52**), was obtained in greater than 90 % yield after 30 min (Scheme 30). The catalytic activity of **49** was compared with the most widely used catalyst **35** by treatment of 1-(2-methylphenyl)propyne in hexane. The results showed that at room temperature the catalytic performance of **49** is superior, whereas **35** is unable to catalyze this homodimerization reaction.[47] Under the same reaction condition, a relatively sophisticated cyclophanes were prepared via ring-closing alkyne transformation.[69]

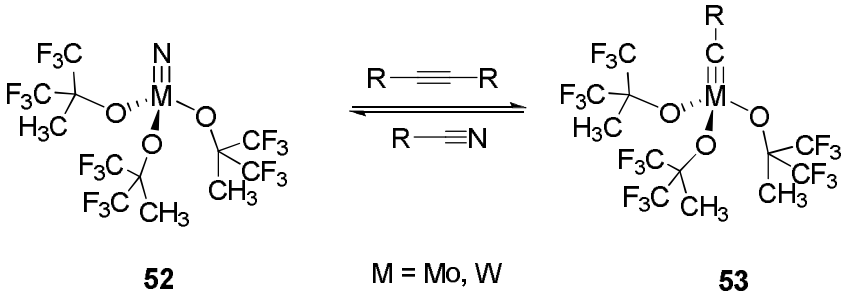
Scheme 30. Cross alkyne metathesis of **51**.

The other catalytic imidazolin-2-iminato tungsten alkylidyne complexe, **50**, has also been experimentally and theoretically investigated.[70]

2.3.5 Molybdenum Nitride Complex *(58)*[72]

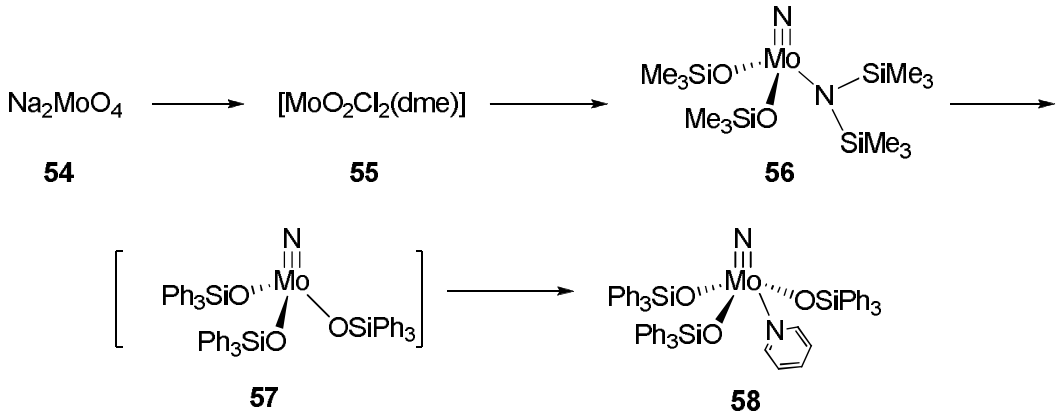
Several molybdenum-based catalyst systems have been developed, for example, $Mo(CO)_6$-phenol, and $Mo[N(tBu)(Ar)]_3$-CH_2Cl_2-system (Ar = 3,5-dimethylphenyl). The Mortreux system catalyzed alkyne metathesis relied on the use of catalysts generated in situ from $Mo(CO)_6$ and phenols. Although the procedure is operationally simple, sometimes high temperature is required, which may be unsuitable for synthesis of natural products. The latter has superior tolerance with functional groups such as nitrogen heterocycles, divalent sulfur, or ether. Despite the mentioned advantages for application, **41** is very sensitive against air and moisture, it must be carefully handled under argon, since this complex has capability to activate many small molecules such as nitrogen.[62]

Fürstner and coworkers have aimed at the development of new molybdenum-based catalysts, which are relatively stable, highly catalytically active and tolerant with functional groups. Inspired by the discovery that nitride complex **52** was treated with alkynes to afford the corresponding metal alkylidynes **53** (Scheme 31),[71] a novel catalyst was prepared (Scheme 32).[72]



52 **53**

Scheme 31.



Scheme 32. Preparation of catalyst **58**.

Compared with **53**, a more convenient complex **56** was prepared. The commercially available sodium molybdate (**54**) was heated with Me_3SiCl in DME to give the intermediate **55**, which was treated with LiHMDS to afford complex **56**. As stated by Fürstner, the combination of **56** and triphenylsilanol was found to be catalytically active for alkyne metathesis.[72]

Treatment of **56** with 3 equiv triphenylsilanol and 5 equiv pyridine afforded complex **58** as a light yellow solid, which showed catalytic performance for alkyne metathesis. This alkylidyne molybdenum complex (**58**) has been intensively investigated. [72] The results revealed that the activity is as superior as the combination of **56** and Ph_3SiOH. Compared with the other well-defined catalysts, complex **58** is tolerant with many functional groups and relatively stable under air, it can be handled in the air for a short time.

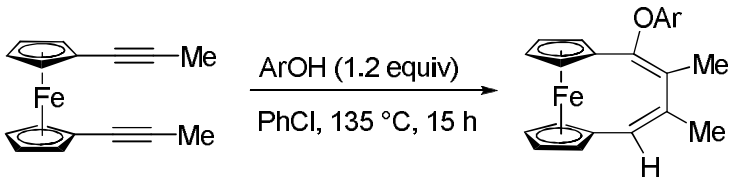
2.4 Synthesis of Phenoxy[4]ferrocenophanedienes

Recently Stepnicka and Kotora reported the results of alkyne metathesis starting from (1-propynyl)ferrocene (**103**).[73,74] Here we show some results of our attempts to couple 1,1'-dipropynylferrocene (**59**) by alkyne metathesis, which resulted in an unanticipated formation of [4]ferrocenophanediene derivatives.

Due to available undesired reaction paths such as polymerization reactions terminal alkynes are usually not suitable for alkyne metathesis.[38,75] In order to generate a volatile product in addition to the desired coupling product 1-propynyl compounds are often used giving 2-butyne as the removable volatile thereby shifting the equilibrium to the product side. Therefore our study started from 1,1'-di(1-propynyl)ferrocene (**59**).[76] Because of the ready

availability of the catalyst we decided to test the Mortreux catalyst system, essentially using hexacarbonylmolybdenum and a phenol derivative in a solvent with a high boiling point.[43,77-80] The reaction, which would involve metallacyclobutadiene intermediates,[49] was expected to yield oligo(1,1'-ferrocenylidene)ethynylenes. However, in contrast to our expectation the reaction of diyne **59** with 1.2 equiv. of 4-chlorophenol *in the presence as well as in the absence of hexacarbonylmolybdenum* in chlorobenzene at 135°C afforded [4]ferrocenophanediene **60** in up to 84 % yield as a result of a transannular addition reaction. Subsequently it was found that a number of other phenols react in the same way to give derivatives **60-71**, clearly showing the generality of this reaction, results are summarized in table 1.

Table 3. Transannular addition of phenols ArOH to 1,1'-di(1-propynyl)ferrocene(**59**)[a]



59 **60-71**

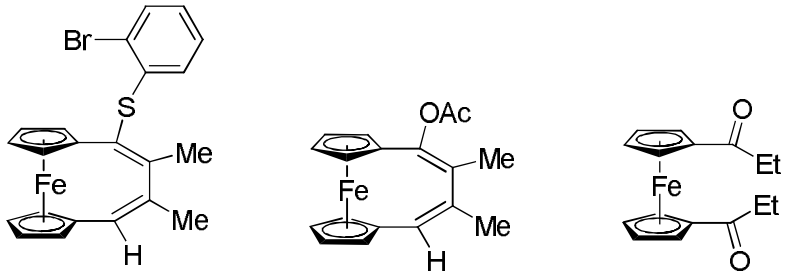
Entry	ArOH	Product	Yield[%]
1	4-chlorophenol	**60**	84
2	3-chlorophenol	**61**	92
3	2,4-dichlorophenol	**62**	99
4	2-fluorophenol	**63**	75
5	4-iodophenol	**64**	99
6	4-nitrophenol	**65**	91
7	phenol	**66**	57
8	4-methylphenol	**67**	86
9	4-methoxyphenol	**68**	89
10	2-methoxyphenol	**69**	84
11	2-isopropoxyphenol	**70**	39
12	4-aminophenol	**71**	65

[a]: 1.0 mmol of 1, 1.2 mmol of phenol derivative in 20 mL of chlorobenzene, 15 h, 135°C

The phenols used include electron poor ones such as halophenols (entries 1-5) or 4-nitrophenol (entry 6) as well as the unsubstituted phenol (entry 7) and electron rich ones such as alkyl or alkoxyphenols (entries 8-11) or 4-aminophenol (entry 12). While the yield of the reaction with 2-isopropoxyphenol is only moderate, presumably for steric reasons, the yields of the other reactions are good to excellent, 4-iodophenol and 2,4-dichlorophenol giving essentially quantitative amounts of product.

The constitutions and relative configurations of the products were determined spectroscopically. As a representative example the data of the 4-chlorophenol adduct **60** are discussed (entry 1): The monoaddition is evident from the mass spectrum as well as from the ^{13}C NMR spectrum showing the signals for the tertiary olefinic carbon atom at δ = 124.2, and those for the quarternary olefinic carbon atoms at δ = 124.3, 126.2, and 136.5 ppm. ^{1}H NMR signals assigned to the two methyl groups appear at δ = 1.85 (s, 3H) and at 1.95 (d, 3H, J = 1.4 Hz) ppm. The ^{1}H NMR signal assigned to the olefinic proton appears as a two line signal with a separation of 1.0 Hz with slight shoulders, we presume that this is a quartet with the less intense outer two lines being covered as a result of the small coupling constant. The *E* configuration of the double bond bearing the phenoxy substituent in the representative case of **63** has also been established by NOE measurement, which shows a 14 % increase at the signal at δ = 6.14 (br s, 1H, CH=C) ppm upon irradiation at δ = 1.97 (d, 3H, J = 0.7 Hz, CH=C-CH_3) ppm. All other analytical data are in full accord with the assigned formulas. In accord with the assignments made, treatment of **60** with hydrochloric acid afforded the corresponding ketone **75** in 40 % yield.

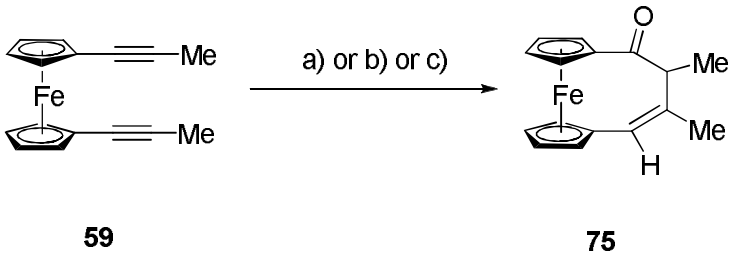
To check in how far a sulfur analogue would undergo the reaction, **59** was treated with 2-bromothiophenol under the same reaction conditions. Ferrocenophane **72** was obtained in 31 % yield. As the acidity of the phenols was considered a factor in the addition reaction we also checked if a carboxylic acid would add in the same manner. Treatment of **59** with acetic acid under otherwise unchanged reaction conditions indeed resulted in the transannular addition affording enol ester **73** in 44 % yield. Reaction of **59** with a stronger carboxylic acid, trifluoracetic acid, however, resulted in the formation of 1,1'-dipropanoylferrocene (**74**)[81] in 58 % yield after chromatographic work up instead of the corresponding adduct.



72 (31 %) **73** (44 %) **74** (58 %)

Scheme 33.

The reaction conditions were modified by replacing the solvent chlorobenzene by *N*,*N*-dimethylfomamide (DMF), which is known to decompose slowly at elevated temperatures with formation of dimethylamine rendering the reaction conditions more basic. When **59** was heated at 157 °C in DMF in the presence of 5 equiv. of 4-chlorophenol for 15 h, a different result was obtained. Instead of the phenyl enol ether **60** the unsaturated [4]ferrocenophanone **75** was obtained in 57 % yield. Alternatively, **75** was obtained in 38 % yield, when **59** was treated with 2.4 equiv. of 4-iodophenol in DMF with microwave heating at 157°C for 30 min. Finally, heating **59** with 5 equiv. of water in DMF for 20 h at 157°C afforded **75** in 72 % yield (Scheme 34).

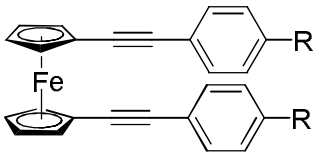


59 **75**

Scheme 34. a) 4-Chlorophenol (5 equiv), DMF, 157 °C, 20 h, 57 %. b). 4-Iodophenol (2.4 equiv), DMF, µW, 157 °C, 38 %. c). H_2O (5 equiv), DMF, 157 °C, 20 h, 72 %.

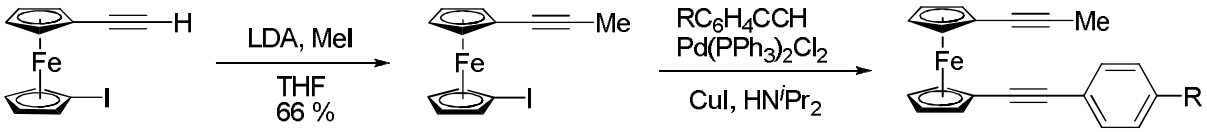
In order to get a better insight into the reaction the alkynyl substituents in the starting material were also varied. 1,1'-Di(phenylethynyl)ferrocene (**76**) was prepared by a published procedure,[82] and 1,1'-di(4-*tert*-butylsulfanylphenylethynyl)ferrocene (**77**) was obtained in 33 % yield from 1,1'-diiodoferrocene by a Sonogashira coupling reaction (Scheme 35). Treatment of 1-ethynyl-1-iodoferrocene[15] (**18**) with lithium diisopropylamide (LDA)

followed by iodomethane afforded 1-iodo-1'-(1-propynyl)ferrocene (**78**) in 66 % yield. Subsequent Sonogashira coupling reactions with phenylethyne or with 4-(*tert*-butylsulfanyl)-phenylethyne gave mixed 1,1'-dialkynylferrocenes **79** and **80** in 85 % and 46 % yield, respectively (Scheme 36).



76: R = H
77: R = S^{t}Bu (33 %)

Scheme 35.

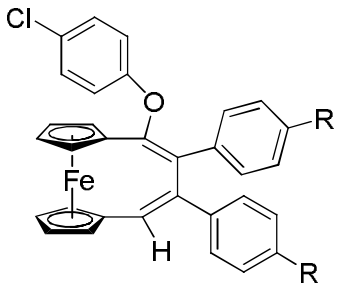


18 **78**

79: R = H (85 %)
80: R = S^{t}Bu (46 %)

Scheme 36.

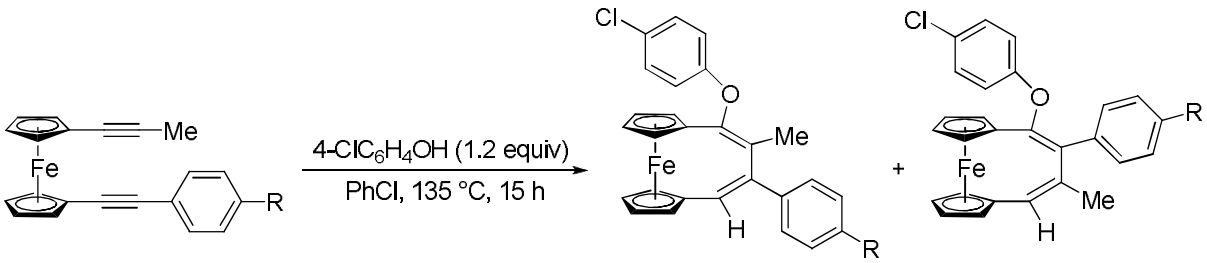
Treatment of the symmetrically disubstituted ferrocenes **76** and **77** with 4-chlorophenol under the usual reaction conditions resulted in the formation of ferrocenophanes **81** and **82** in 59 % and 46 % yield. Although the yields obtained in these cases were not as high as with **59** as starting material, the reactions clearly indicate the general nature of the reaction with respect to the alkynyl substituents.



81: R = H (59 %)
82: R = S^{t}Bu (46 %)

Scheme 37.

The corresponding reaction of the unsymmetrically 1,1'-dialkynylated ferrocenes **79** and **80** resulted in product mixtures **83**/**84** (36 % / 42 % yield) and **85**/**86** (47 % / 29 % yield) (Scheme 38). While the over all yields of ferrocenophanes are almost the same in both cases, the product ratios indicate that the triple bonds in **79** are hardly differentiated by the attacking nucleophile while the electron delivering *tert*-butylsulfanylphenyl substituent in **80** renders the triple bond next to it less prone to nucleophilic attack.



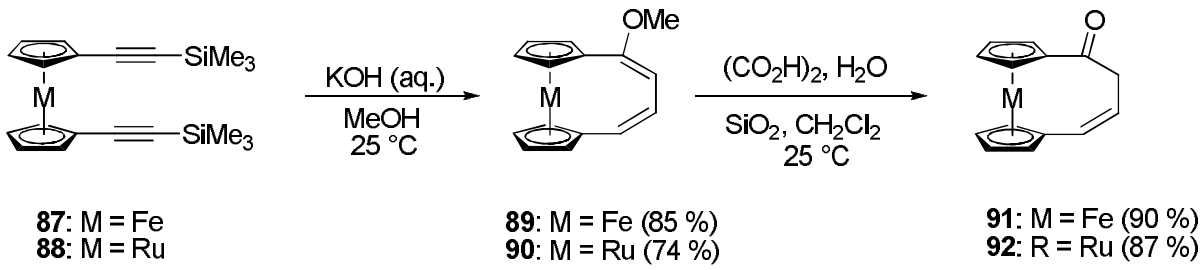
79: R = H (85 %)
80: R = S^{t}Bu (46 %)

83: R = H (36 %)
85: R = S^{t}Bu (47 %)

84: R = H (42 %)
86: R = S^{t}Bu (29 %)

Scheme 38.

Pudelski and Callstrom have published on a related reaction. It was reported that 1,1'-Bis(trimethylsilylethynyl)ferrocene (**87**) and -ruthenocene (**88**) react with methanol in the presence of aqueous KOH with formation of methyl enol ethers **89** and **90**, respectively (Scheme 39). Subsequent enol ether hydrolysis afforded ketones **91** and **92**.[24,83]



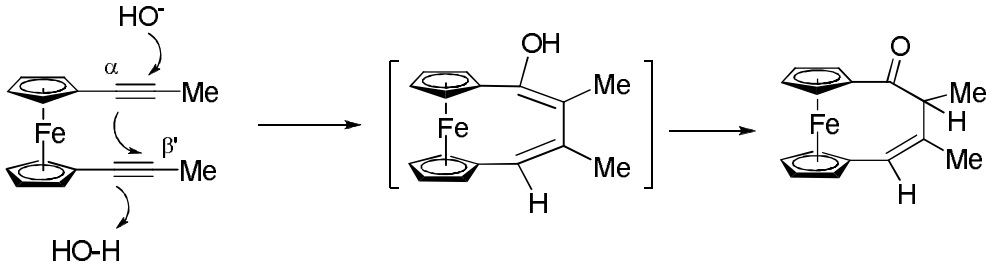
87: M = Fe
88: M = Ru

89: M = Fe (85 %)
90: M = Ru (74 %)

91: M = Fe (90 %)
92: R = Ru (87 %)

Scheme 39.

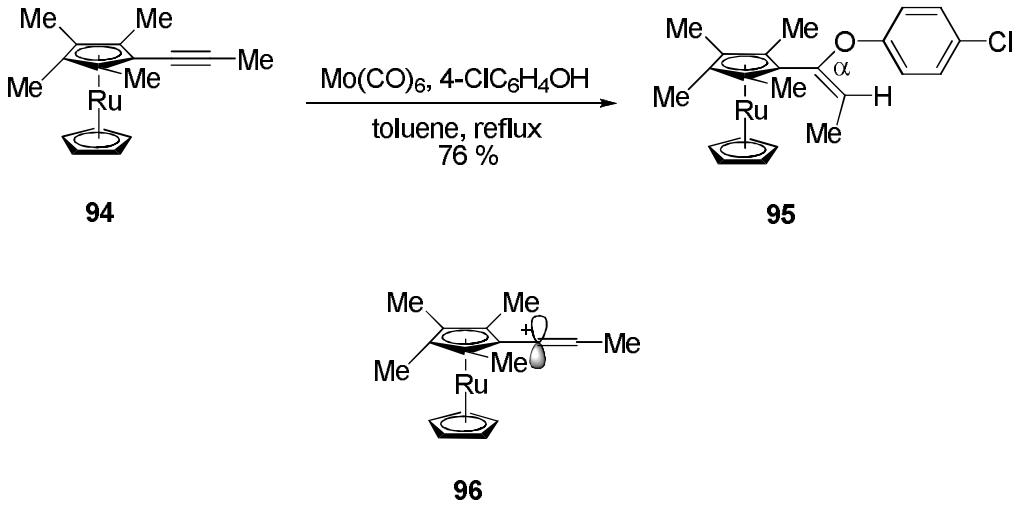
The authors explain their result by a subsequent protiodesilylation generating 1,1'-diethynylmetallocenes. In a concerted process a nucleophilic attack of methoxide at α-C induces a nucleophilic transannular attack at β'-C followed by protonation. Considering this reasonable mechanism to be operative in the reactions of **59** under basic reaction conditions would involve a hydroxide attack at **59** leading to the intermediate enol **93**, which subsequently enolized to the observed ketone **75** (Scheme 40).



59 **93** **75**

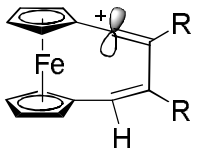
Scheme 40.

Although the mechanism proposed by Pudelski and Callstrom seems reasonable for basic reaction conditions, this is not necessarily the case for the reaction under acidic reaction conditions given in the presence of phenols or a weak acid such as acetic acid. In this context we note a recent publication of Sato *et al.* describing the reaction of 1-(1-propynyl)-2,3,4,5-tetramethylruthenocene (**94**) with $Mo(CO)_6$ and 4-chlorophenol in refluxing toluene to give *syn* adduct **95** in 76 % yield (Scheme 41).[84] The authors do not give a mechanistic explanation for this result.



Scheme 41.

Because of the high degree of substitution of ruthenocene derivative **94** steric reasons for the observed regioselectivity seem unlikely. If these were operative, one would expect the opposite regioisomer. In order to consider electronic factors a comparison of the pK_a values of ferrocene carboxylic acid (5.72) and ruthenocene carboxylic acid (5.43) reveals the ruthenocenyl substituent to be less electron rich as compared to the ferrocenyl group, which is in accord with comparing electrophilic substitution investigations.[85] To estimate the electronic influence of the methyl substituents in **94** one might compare the pK_a values[86] of benzoic acid (4.204) with that of 3-methylbenzoic acid (4.25) and that of 3,5-dimethylbenzoic acid (4.32) to see that there is a small electron delivering effect, which in the case of **94** will presumably result in an electron density of the 2,3,4,5-tetramethylruthenocenyl fragment comparable to that of the ferrocenyl group. Given the fact that resonance stabilized ferrocenylvinyl cations have been observed,[87,88] and taking the geometry of these into account, we consider vinyl cation **96** a reasonable intermediate in the addition of 4-chlorophenol to **94** resulting from a protonation of the triple bond in **94** from the face opposite to the CpRu moiety. The electronic stabilization of the vinyl cation **96** with an *sp* hybridized cationic center results in a hindered rotation around the Me_4C_5–C^+ bond, facilitating an attack of the phenol at the empty *p* orbital in **96** from the face opposite to the CpRu moiety, too. As a result of this over all *syn* addition the *E* double bond observed in **95** is formed. With respect to the proposed vinyl cation intermediate **96** data from Table 4 are instructive, which lists the relative intensities of MS peaks assigned to vinyl cation fragments **97** resulting from a fragmentation of the respective phenolate substituent for 19 compounds of this work.



97

Scheme 42.

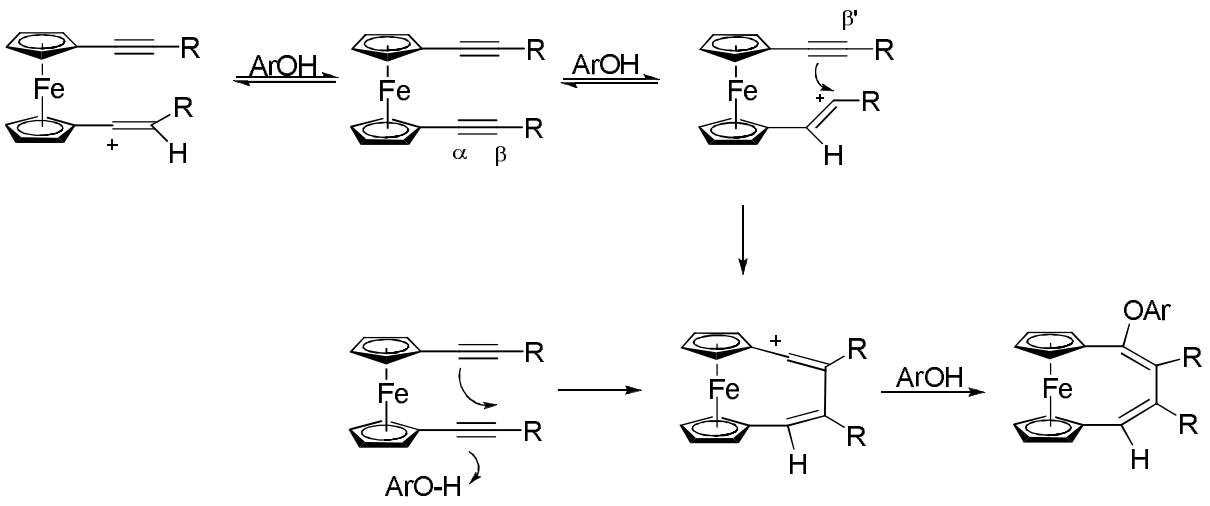
Remarkably, 11 out of 19 entries indicate vinyl cation **97** to be the most abundant cation (base peak, 100 %), in the mass spectra of three other entries **97** is among the most prominent peaks (entries 2, 6, 16), and in two entries it has more than 50 % of the base peak intensity (entries 7, 19). These data clearly reflect the remarkable stability of vinyl cations **97** and support the proposed intermediacy of **96** in the formation of **95**.

Table 4. Relative MS peak intensities of **97** and base peaks (100 %).[a]

Entry	Compd.	R	R'	Rel. MS Peak Intensity [%]	*m/z* Base Peak (100 %)
1	**60**	Me	Me	100	263 [M^+ – (4-ClC_6H_4O)]
2	**61**	Me	Me	85	390 [M^+]
3	**62**	Me	Me	100	263 [M^+ – ($C_6H_3Cl_2O$)],
4	**63**	Me	Me	100	263 [M^+ – (2-FC_6H_4O)]
5	**64**	Me	Me	45	224 [Fc-$CCCH_3$],
6	**65**	Me	Me	94	401 [M^+],
7	**66**	Me	Me	69	356 [M^+]
8	**67**	Me	Me	100	263 [M^+ – (4-$CH_3C_6H_4O$)],
9	**68**	Me	Me	100	263 [M^+ – (4-$H_3COC_6H_4O$)]
10	**69**	Me	Me	100	263 [M^+ – (2-$H_3OC_6H_4O$)]
11	**70**	Me	Me	100	263 [M^+ – (2-($iPrOC_6H_4O$)]
12	**71**	Me	Me	100	263 [M^+ – (4-$H_2NC_6H_4O$)],
13	**72**	Me	Me	100	263 [M^+ – (2-BrC_6H_4S)]
14	**81**	Ph	Ph	100	387 [M^+ – ClC_6H_4O],
15	**82**	4-*t*BuSC_6H_4	4-*t*BuSC_6H_4	14	690 [M^+ (^{35}Cl)],
16	**83**	Me	Ph	93	452 [M^+ (^{35}Cl)]
17	**84**	Ph	Me	100	325 [M^+ – ClC_6H_4O]
18	**85**	Me	4-*t*BuSC_6H_4	17	540 [M^+ (^{35}Cl)],
19	**86**	4-*t*BuSC_6H_4	Me	52	540 [M^+ (^{35}Cl)]

[a]: 70 eV; for full fragmentation patterns see experimental part.

A reaction mechanism for the transannular addition of phenols to 1,1'-dialkynylferrocenes should take into account the moderately acidic reaction conditions rendering a nucleophilic attack of a phenol at a triple bond unlikely. On the other hand, a protonation of one of the triple bonds would preferentially take place at C_β with formation of the ferrocenyl stabilized α-vinyl cation.[89,90] This, however, cannot directly undergo the transannular addition at the remaining triple bond with formation of the observed [4]ferrocenophanediene derivatives. Although 1,2-hydride shifts are known in vinyl cations, such a process, which would avoid a re-formation of the triple bond, seems unlikely here, because these shifts usually occur with formation of the more stable vinyl cation.[91-93] Therefore two possible explanations for the formation of [4]ferrocenophanediene derivatives might be considered (Scheme 43). First, one might envisage a *reversible* protonation at C_β and, to a lesser extent, at C_α with formation of a less stabilized cationic center at C_β, which subsequently *irreversibly* attacks $C_{\beta'}$ to give the ferrocenyl stabilized vinyl cation **97**. Alternatively a concerted reaction path might be considered, which circumvents the unfavorable β-cationic intermediate by a direct formation of **97**. In either case **97** will react with ArOH to give the observed products.



97

R = Me, Ph, 4-^{t}BuSC$_6$H$_4$O

Scheme 43.

We were able to obtain a crystal structure analysis of **60**, which confirmed the assigned constitution (Figure 6). The structure clearly shows a distorted ferrocene moiety with C-Fe

bond lengths ranging from 2.011 (Fe-C6) and 2.022 pm (Fe-C1) for the substituted cyclopentadienyl carbon atoms up to 2.088 pm for Fe-C9. The cyclopentadienyl ligands adopt a staggered conformation and deviate from parallelism by ca. 12.4°, and the angle between the centers of the cyclopentadienyl rings and the iron atom is ca. 172.0°. As can be seen from figure 1 (right), the carbon chain connecting the cyclopentadienyl moieties is helically distorted as indicated by torsional angles C14-C13-C12-C11 (–50.6°) and C22-C13-C12-C21 (–49.0°) rendering the molecule chiral in the solid state.

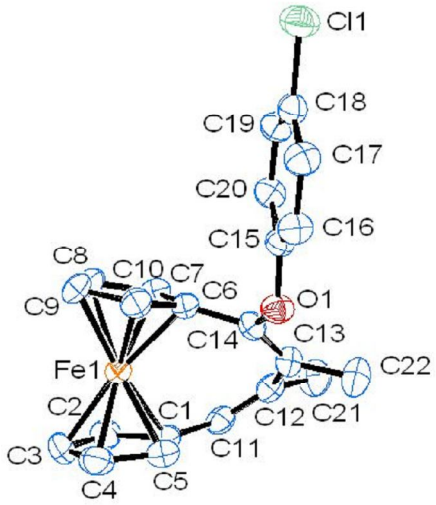


Figure 6. Structure of **60** in the crystal.[94] Selected bond lengths [pm], bond angles [°] and torsional angles [°]: Fe-C1 202.2(4), Fe-C2 205.9(4), Fe-C3 208.8(4), Fe-C4 207.5(4), Fe-C5 202.7(4), Fe-C6 201.1(3), Fe-C7 203.8(4), Fe-C8 206.3(4), Fe-C9 208.4(3), Fe-C10 205.4(4), C1-C2 144.6(5), C1-C5 142.9(6), C1-C11 147.1(5), C2-C3 142.4(7), C3-C4 142.7(7), C4-C5 142.5(6), C6-C7 143.2(5), C6-C10 144.7(5), C6-C14 147.3(5), C7-C8 142.7(6), C8-C9 142.2(6), C9-C10 142.5(5), C11-C12 133.8(6), C12-C13 1.498(5), C12-C21 151.3(7), C13-C14 1.343(5), C13-C22 1.508(6), C14-O1 1.414(4); C1-C11-C12 130.1(4), C11-C12-C13 127.0(3), C11-C12-C21 118.3(4), C13-C12-C21 114.7(3), C12-C13-C14 125.9(3), C12-C13-C22 114.9(3), C14-C13-C22 119.2(3), C6-C14-C13 130.5(3), C6-C14-O1 112.8(3), C13-C14-O1 116.3(3); C2-C1-C11-C12 137.4(4), C5-C1-C11-C12 –35.0(7), C1-C11-C12-C13 4.4(7), C14-C13-C12-C11 –50.6(6), C22-C13-C12-C21 –49.0(5), C12-C13-C14-C6 1.6(6).

Some ^{1}H and ^{13}C NMR spectra of the [4]ferrocenophane derivatives indicate dynamic behavior in solution. While the dimethyl compounds **60-74** show reasonably sharp absorption peaks in their NMR spectra, alkylaryl substituted compounds **83-86** show some broadening of

the ferrocenyl ^{1}H NMR signals. The ^{1}H NMR spectra of diaryl compounds **81** and **82** show broad, unresolved signals for their ferrocenyl protons, and the ^{13}C NMR spectra show sharp peaks for the quarternary ferrocenyl carbon atoms, while the eight ferrocenyl CH absorptions appear as a broad, unresolved absorption.

As a representative example, the temperature dependent ^{1}H NMR spectra of **82** are shown in figure 7 for the ferrocenyl protons in the temperature range from 223 to 323 K. The plot shows eight distinct but unresolved multiplets for the eight ferrocenyl protons at low temperature. These appear in two goups of four signals each, presumably signals for 2-H, 5-H, 2'-H, and 5'-H in one group and for 3-H, 4-H, 3'-H, and 4'-H in the other. At elevated temperature the resulting four broad singlets likewise form two groups of two signals each. The coalescence temperature was determined to 283 K. The chemical shift differences $\Delta\nu$ are not equal for each pair of signals and range between 309 and 490 Hz at 400 MHz. Application of the approximation solution[95] results in an estimated free energy of the activation $\Delta G^{\neq}$ = 53-54 kJ/mol. In addition, dynamic NMR simulations (DNMR) were performed for the determination of rate constants and the corresponding free energies of activation as a function of temperature.[96] The calculated values of $\Delta G^{\neq}$ are between 51-54 kJ/mol over the whole temperature range, and the change in entropy of the process is at 30 J/K·mol. An activation energy E_a of 62 kJ/mol was obtained by fitting the rate constants according to the Arrhenius equation.

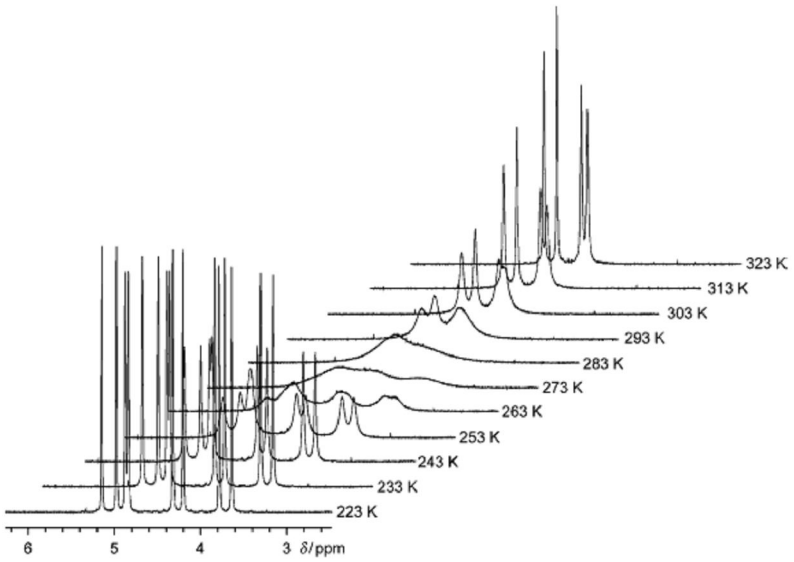


Figure 7. Ferrocenyl ^{1}H NMR ($CDCl_3$, 400 MHz) spectra signals of **82** between 223 and 323 K.

The signals in the ^{13}C NMR spectra are much less resolved than in the corresponding ^{1}H NMR spectra, even at 223 and 323 K. However, the coalescence temperature is the same with 283 K. At low temperature seven signals are observed for the eight ferrocenyl *C*H, one with double intensity. The two quarternary ferrocenyl carbon atoms do not show any dynamic behavior.

With the structure of **60** in mind (Figure 6) we assign the dynamic process observed to a rotation around the C12-C13 bond, which occurs along with a rotation around the cyclopentadienyl-iron-cyclopentadienyl axis. This process represents a racemization of the chiral conformation as given in Figure 8. The process appears to be highly dependent on the substitution pattern at C12 and C13. Obviously the methyl groups at **60-74** do not significantly prevent the racemization to occur. The presence of one of the somewhat larger aryl substituents in **83-86** raises the activation energy of the process as indicated by some line broadening of the ^{1}H NMR signals of the ferrocenyl protons at 298 K. When both, C12 and C13, bear aryl substituents the activation energy of the process is sufficiently high as to allow for coalescence phenomena to be observed at temperatures accessible by routine NMR measurements. That the quarternary ferrocenyl carbon atoms do not show coalescence is due to the fact that in contrast to the ferrocenyl *CH* groups each of these is unique.

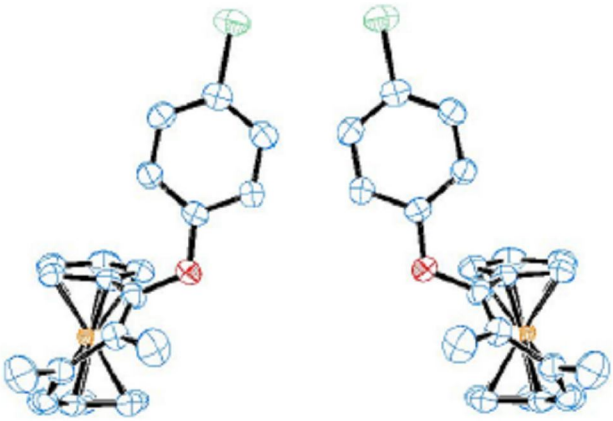
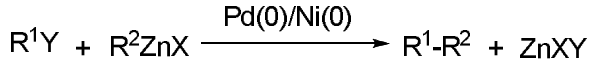


Figure 8. Side view of **60** in the crystal with the C12-C13 bond in front. This Figure shows the enantiomeric conformations and was generated from the structure in Figure 6 to clarify the dynamic racemization process causing the coalescence observed for **81** and **82**.

2.5 Negishi Cross-Coupling Reaction[97-99]

For synthesis of ferrocene-based building blocks **26** and **27**,[20] Negishi cross-coupling reaction was utilized. In order to improve the yields of them, the optimal reaction conditions were investigated.

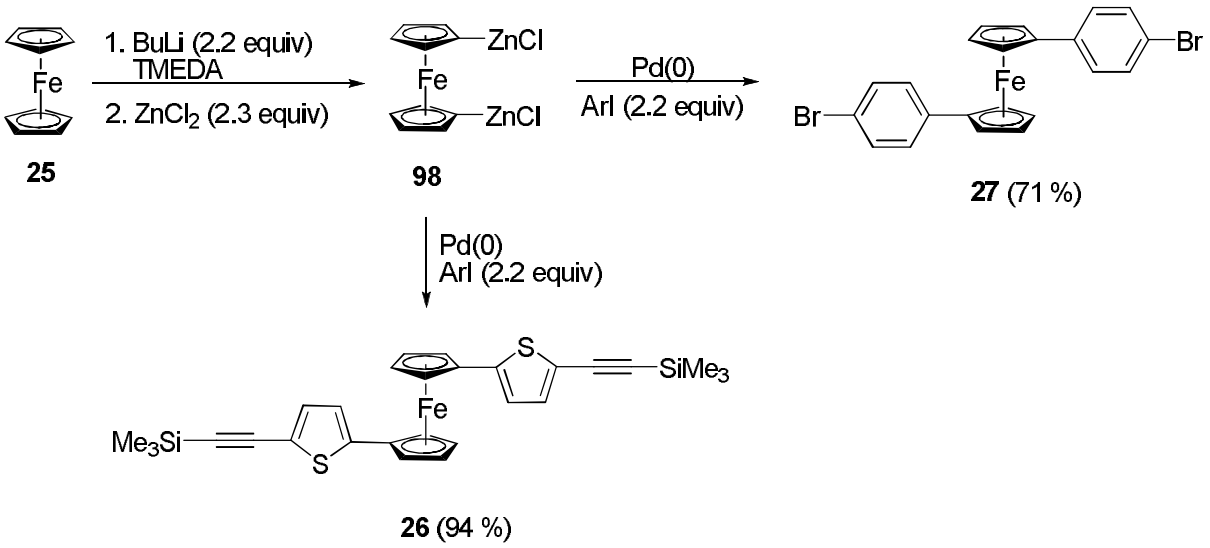
Since 1977 the Negishi cross-coupling reaction[97] has become one of the most straightforward methods for carbon-carbon bond formation, which affords unsymmetric biaryls in good yields from arylhalides with arylzinc reagents in the presence of catalytic amount of Ni(0) or Pd(0) (Scheme 44).[98] This method has broad scope, and is not restricted to the preparation of biaryls.[99]



X,Y = halogen
R^1 = alkenyl, aryl, allylic, benzylic, propargylic
R^2 = alkenyl, aryl, alkynyl, alkyl, benzylic, allylic

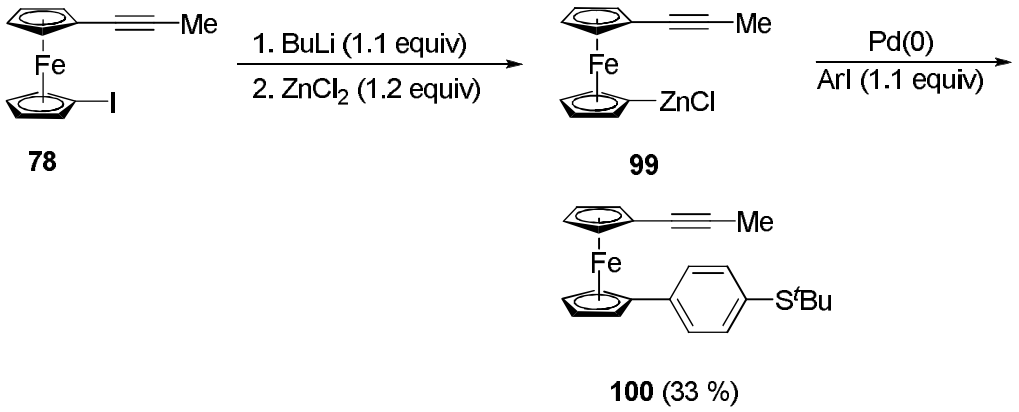
Scheme 44.

Some ferrocene-based building blocks are of interest in synthesis of molecular wires via cross-coupling alkyne metathesis. **26** and **27**[20] were successfully obtained by utilizing Negishi coupling reaction from ferrocene with 2-iodo-5-(trimethylsilylethynyl)thiophene and 1-bromo-4-iodobenzene in 94 % and 71 % yields (Scheme 45). Whereas, under the similar reaction condition without TMEDA as base, compound **101** was prepared in merely 33 % yield (Scheme 46).



25 **98** **27** (71 %) **26** (94 %)

Scheme 45.



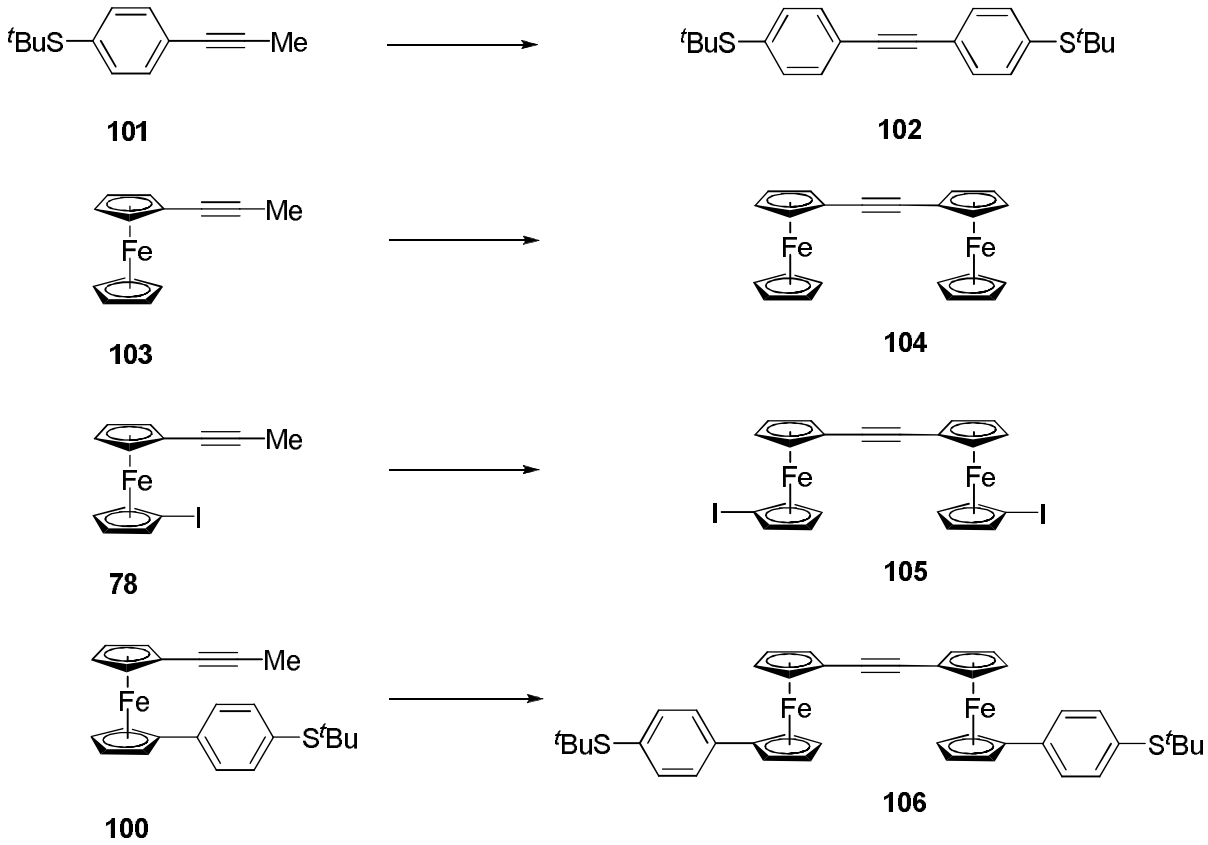
78 **99** **100** (33 %)

Scheme 46.

With the help of Stille coupling method, the first ferrocene-based molecular wire **10** was obtained. Compared with Stille method, Negishi coupling reaction utilizes a cheap reagent, zinc chloride, and the ferrocene-based products are much more easily purified. **101** was regarded as the substrate, which has potential to afford the simplest molecular wire (**106**) with two ferrocene hinges via alkyne metathesis.

2.6 Dimerization of Ferrocene-based Compounds via Alkyne Metathesis

Among the alkyne metathesis catalysts above mentioned, the Mortreux system is most favored due to the ease at application. As co-catalyst 4-chlorophenol or 2-fluorophenol is usually utilized. According to Grela[46] molybdenum hexacarbonyl and 2-fluorophenol system is more active for preparation of natural products. In 2003 the $Mo(CO)_6$ and 4-chlorophenol system was reported to be used as catalyst to afford the first ferrocene-based alkyne metathesis product **104**.[73] To compare the catalytic effects of the two catalyst systems, they were applied to the synthesis of some ferrocene-based compounds (Scheme 47). The results (Table 5) showed that the $Mo(CO)_6$ (0.1 equiv) and 2-fluorophenol (1 equiv) system is much more active than the other system, as expected. Under the same reaction conditions, the influences of the amount of phenols and solvents have been investigated. The yields showed that more 4-chlorophenol (1 equiv) and chlorbenzene as solvent are not helpful in giving more products even at higher temperature.



Scheme 47.

Table 5. Comparison of $Mo(CO)_6$ with different phenol as catalyst system.

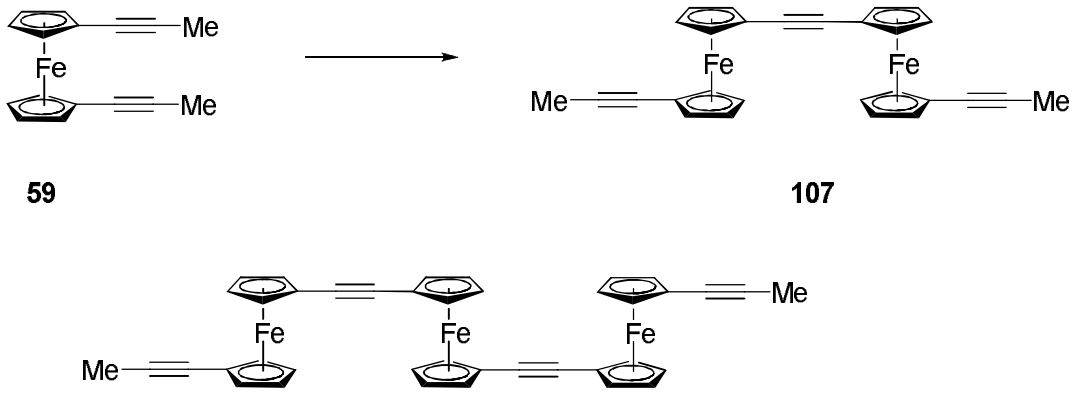
Product	Yield [%][a]	Yield [%][b]
102	12	46
104	40[73]	59
105	20	35
106	34	45

[a]: $Mo(CO)_6$ (0.1 equiv), 4-chlorophenol (0.3 equiv), in toluene, 120 °C, 12 h.

[b]: $Mo(CO)_6$ (0.1 equiv), 4-fluorophenol (1.0 equiv), in chlorobenzene, 132 °C, 12 h.

Using Mortreux catalyst system, **106** was successfully obtained as the first molecular wire with two ferrocene hinges via alkyne metathesis, in 34 % or 45 % yield (Table 5). Although there are these described advantages of Mortreux catalyst system, it is difficult to purify the products and to recover the rest of the ferrocene-based substrates due to molybdenum hexacarbonyl. Catalysts **49** and **50** were also investigated, we failed to get the compounds **102**, **104**, **105** and **106**.

Due to easy preparation and excellent tolerance with functional groups[72] the catalyst **58** has been intensively investigated. The study started from 1,1'-di(1-propynyl)ferrocene (**59**) using catalyst **58** (20 mol %).[72] In an oil bath no reaction was observed at 80 °C after 12 h, and at 110 °C overnight. Then the reaction was carried out under microwave irradiation in the presence of catalyst **58**, the product **107** was received in 29 % yield under the following reaction condition (Scheme 47). Using 7 mol% catalyst **49**, being heated in an oil bath for 12 h at 100 °C, afforded **107** in 10 % yield. To improve the yield of **107**, the temperature was elevated to 120 °C, after 24 h, besides 19 % compound **107** as main product, **108** was obtained as byproduct, which was identified by ^{1}H NMR (200 MHz) (Scheme 48). Compared with catalyst **58**, catalyst **49** makes the purification much easy, after chromatography using silica gel, most of the rest substrate **59** was received, and the purity of the products is satisfactory. Under the same reaction conditions the catalyst **50** was also investigated, the result showed that catalyst **50** is inactive for substrate **59**, all the starting material was received.



59 **107**

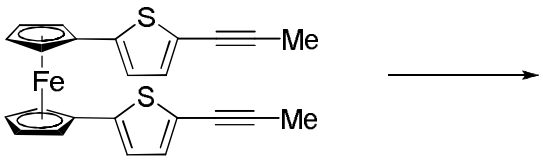
108

a). μw, 120 °C, 250 W, 120 min,catalyst **58** (20 mol%): 29 %;
b). oil bath, 100 °C, 12 h, catalyst **49** (7 mol%): 10 %;
c). oil bath, 120 °C, 24 h, catalyst **49** (5 mol%): 19 %, and **108** (2 %).

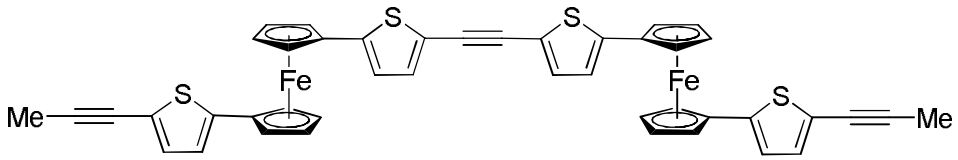
Scheme 48.

Substrate **109** and **111** were investigated in the presence of Mortreux catalyst system, $Mo(CO)_6$ (10 mol %)and 4-chlorophenol (30 mol %), and toluene as solvent. After 15 h at 120 °C only starting materials **109** (25 %) and **111** (31 %) were recovered.

In an oil bath at 80 °C catalyst **58** showed no catalytic activity for substrate **109**. Dimerization of **109** was performed under microwave irradiation. The optimized reaction condition is to utilize microwave (105 °C, 200 W, 120 min), product **110** was obtained in 14 % yield (Scheme 49).



109

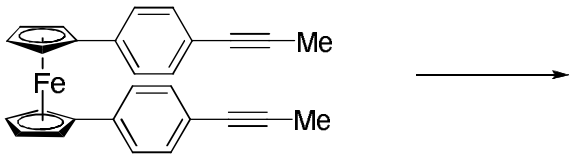


110

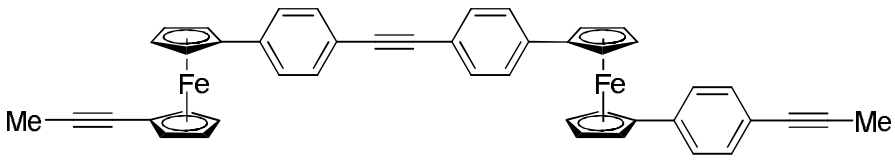
μw, 105 °C, 200 W, 120 min,catalyst **58** (20 mol%):14 %.

Scheme 49.

Under microwave irradiation, in the presence of catalyst **58**, substrate **111** dimerized to afford **112** in 11 % yield. Using **111** as starting material, catalysts **49** and **50** were also investigated. The reactions were carried out in an oil bath at 100 °C for 12 h. **49** showed no catalytic effect for this compound. Whereas with **50** (2 mol %) as catalyst, the product **112** was obtained in 6 % yield (Scheme 50). According to Tamm and coworker,[69] **49** is more catalytically active than **50** for alkyne metathesis.



111



112

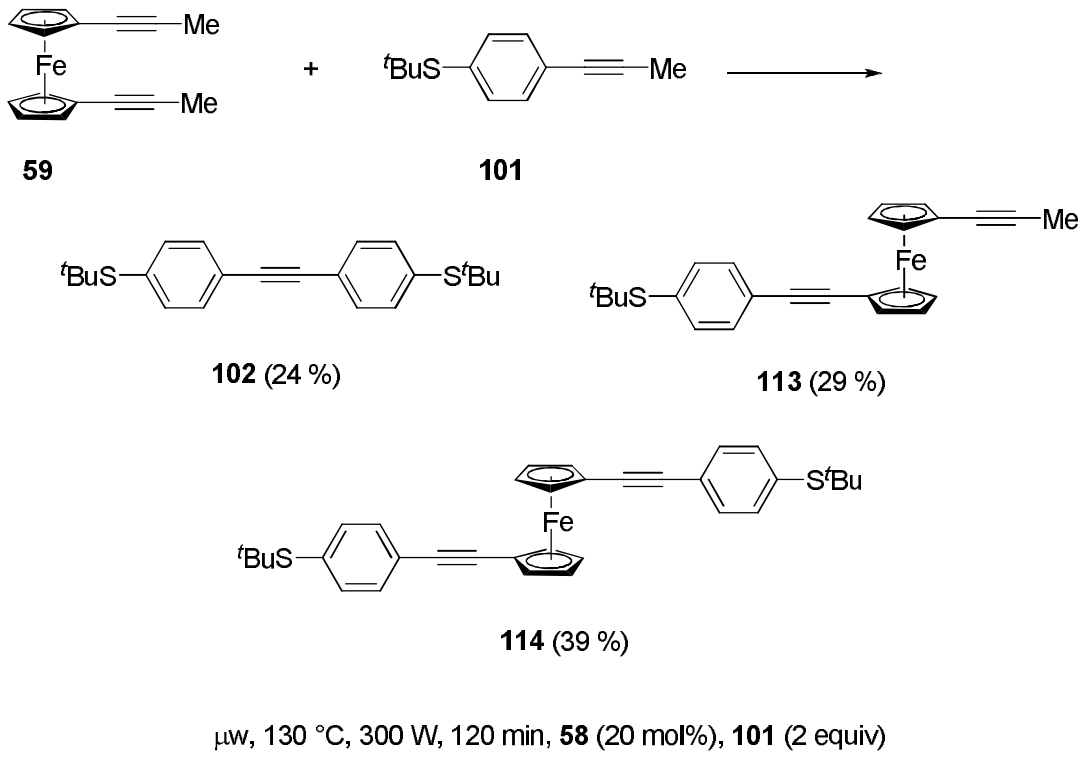
a). μw, 130 °C, 200 W, 120 min,catalyst **58** (20 mol%): 11 %;
b). oil bath, 100 °C, 12 h, catalyst **50** (2 mol%): 6 %.

Scheme 50.

In the presence of **58** (20 mol %), the reactions, which take **59**, **109** and **111** as starting materials, were performed at first in an oil bath at 130 °C. After about 2 h, red solids were formed, which are insoluble in toluene or dichloromethane even at boiling points, and only trace amount of **107**, **110** and **112** were found. Under microwave irradiation (130 °C, 300 W), the same phenomena were observed. The red solids might be polymers.

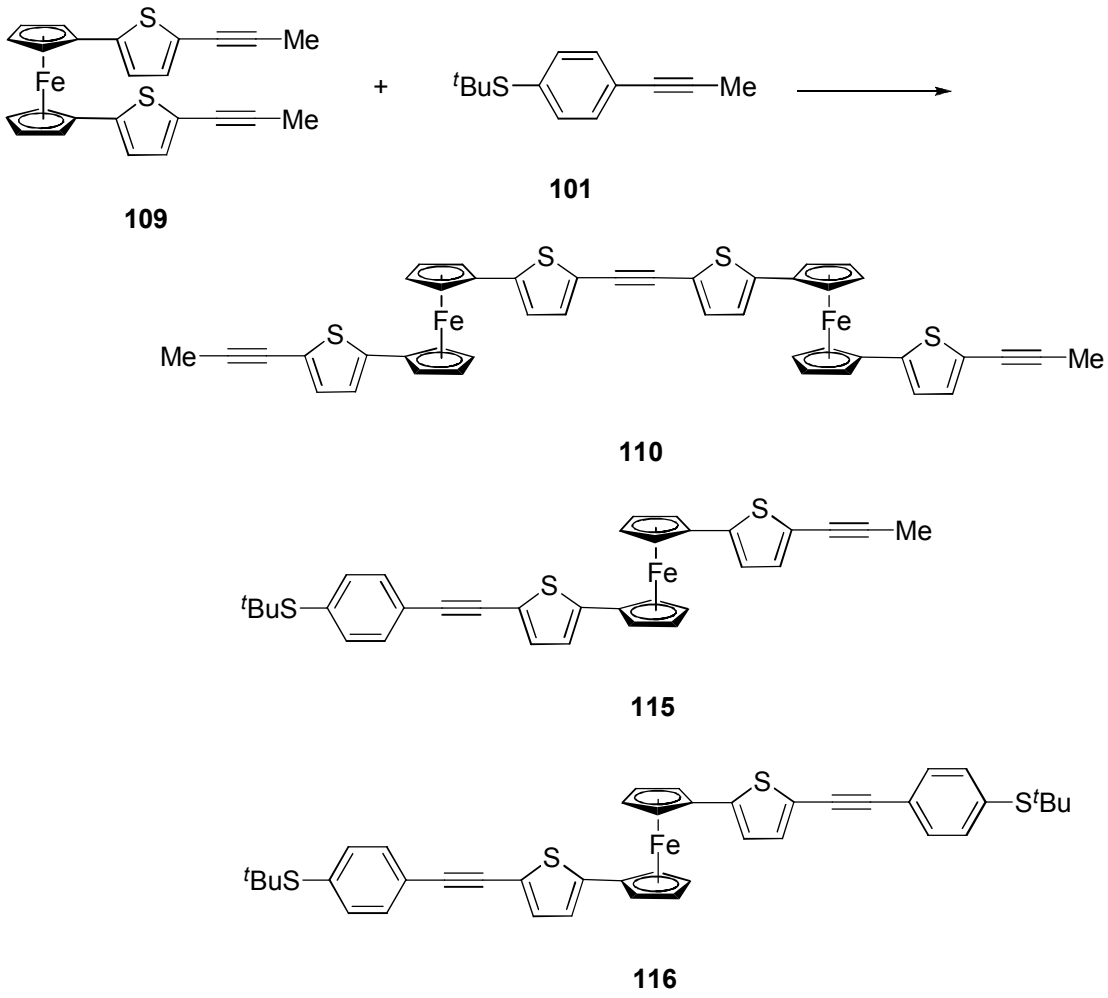
2.7 Synthesis of Ferrocene-based molecular Wires using Alkyne Metathesis

With the help of cross-coupling reactions (Stille,[16] Negisgi[19] and Sonogashira[15,20]) some ferrocene-based molecular wires have been prepared in our group. The cross-coupling alkyne metathesis is an alternative, interesting method. As mentioned before,[100] the Mortreux catalyst system is unsuitable for 1,1'-dialkynylferrocene derivatives. Catalyst **58** was intensively investigated in this field. This work started from 1,1'-di(1-propynyl)ferrocene (**59**) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**101**). The mixture was heated by microwave irradiation (130 °C, 300 W, 120 min.). Besides ferrocene-based mono-cross-coupling product (**113**) and molecular wire (**114**), the homo-dimerization product (**102**) of **101** was also isolated (Scheme 51).



Scheme 51.

To study the influence of heating methods, compound **109** was treated with **101** in the presence of catalyst **58** (20 mol %) (Scheme 52). All the ferrocene-based products were isolated. The results are listed in Table 6. While being heated in oil bath for 15 h at 120 °C, merely dimer **110** of substrate **109**, and mono-cross-coupling product **115** were generated. Higher temperature (130 °C, oil bath) caused generation of possible polymer as red solid in hot toluene. The reaction was repeated under microwave irradiation. At 110 °C and 200 W, 12 % dimer **110** and 13 % molecular wire **116** were obtained. Whereas at lower temperature (105 °C, 200 W), the yields of **110** and **116** were reduced to 9 % and 7 %, but the mono-cross-coupling product **115** was obtained in 29 % yield.



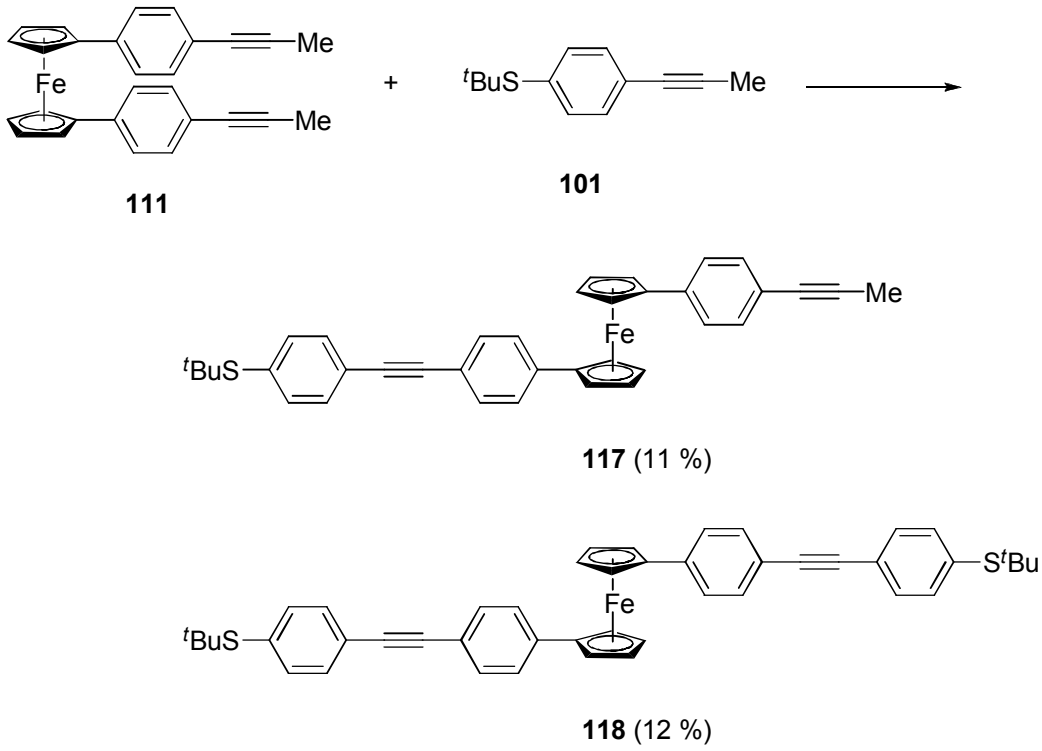
Scheme 52.

Table 6. Comparison of yields by using catalyst **58** in toluene as solvent.[a]

Condition	Yield [%] (**110**)	Yield [%] (**115**)	Yield [%] (**116**)
oil bath, 120 °C, 15 h	44	8	0
μw, 110 °C, 200 W, 120 min	12	0	13
μw, 105 °C, 200 W, 120 min	9	29	7

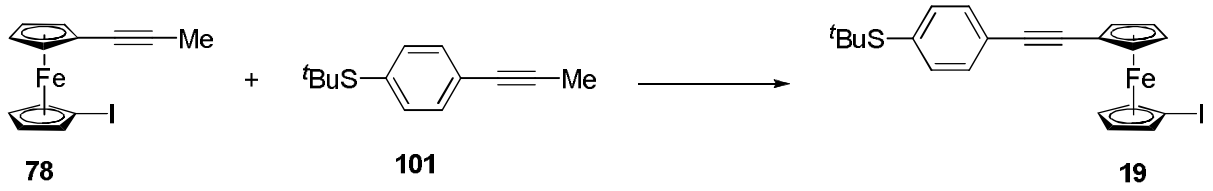
a: catalyst **58** (20 mol %), **101** (2 equiv).

By treatment of compound **111** with **101** (2 equiv) in the presence of catalyst **58** (20 mol %), products **117** and **118**[20] were obtained in 11 % and 12 % yields (Scheme 53).



Scheme 53.

Compound **19** is an important building block for synthesis of ferrocene-based molecular wires,[15,20] which was usually prepared by Sonogashira coupling reaction.[15] **19** has also been generated by using cross-coupling alkyne metathesis. Compound **78** was treated with **101** by microwave irradiation to afford **19** as product in 55 % yield.



Scheme 54.

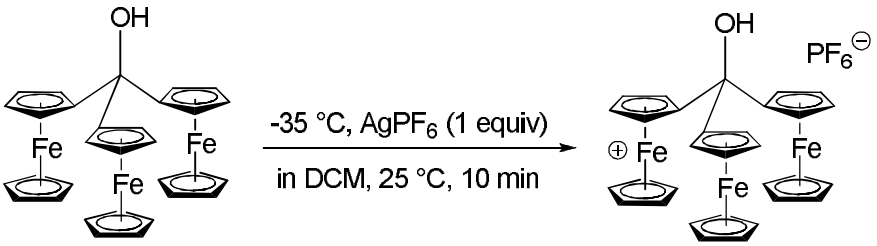
The results suggested that the molybdenum-based catalyst **58** is a suitable for preparation of ferrocene-based molecular wires. At high temperature it is possible to produce the unknown

red solids, which might be polymers. Comparison with the tungsten-based catalysts **49** and **50**, with which no ferrocene-based molecular wires were obtained, **58** is much active and tolerant with many functional groups.

Compared with Mortreux catalyst system and catalyst **58**, with catalysts **49** and **50**, the workup is much easier, besides products, almost the rest of substrates were recovered.

2.8 Synthesis of Triferrocenylmethanol Hexafluorophosphate (120)

In late 1960s Allen et al[101] began to study the electronic interactions between metal centers in mixed-valent (MV) compounds. One electron oxidation products of the compounds with one or two ferrocene moieties, were prepared and characterized by cyclovoltammogram, Mössbauer spectroscopy and X-ray crystallography.[102,103] Compared with the investigation of the three-iron-center compounds with *meta* connections around a central phenylene ring,[104] we are also interested in the one electron oxidation products of triferrocenylmethane derivatives with respect to spin/charge delocalization and transport. The oxidation product (**120**) was obtained from triferrocenylmethanol (**119**) with $AgPF_6$ (Scheme 55). Recrystallization in dichloromethane at 25 °C afforded a dark green crystal.



119 **120** (97 %)

Scheme 55.

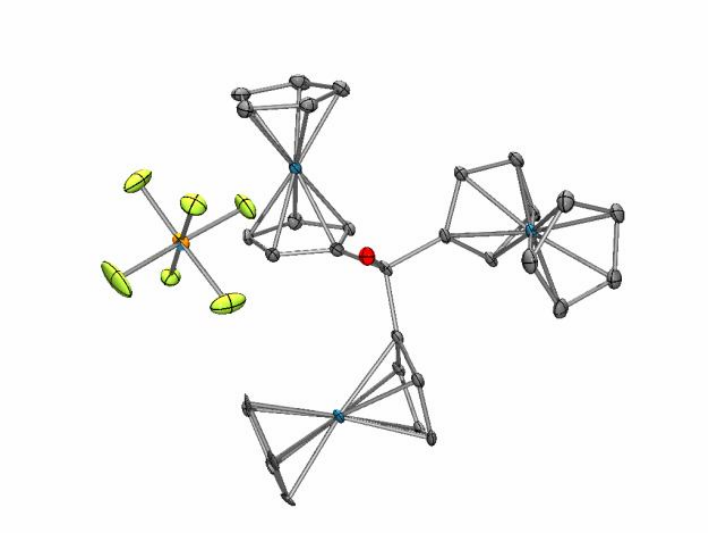


Figure 9. Structure of **120** in the crystal. Selected bond lengths [pm] and angles [°]: Fe(1)-C(14) 2.040(5), Fe(1)-C(18) 2.045(4), Fe(1)-C(13) 2.052(5), Fe(1)-C(15) 2.054(5), Fe(1)-C(12) 2.054(5), Fe(1)-C(10) 2.055(4), Fe(1)-C(11) 2.057(4), Fe(1)-C(17) 2.059(5), Fe(1)-C(19) 2.060(5), Fe(1)-C(16) 2.061(5), Fe(2)-C(22) 2.077(4), Fe(2)-C(23) 2.085(5), Fe(2)-C(26) 2.086(5), Fe(2)-C(25) 2.100(4), Fe(2)-C(27) 2.100(5), Fe(2)-C(24), 2.104(4), Fe(2)-C(21) 2.106(4), Fe(2)-C(29) 2.111(4), Fe(2)-C(28) 2.111(4), Fe(2)-C(20) 2.134(4), Fe(3)-C(31) 2.037(4), Fe(3)-C(39) 2.042(5), Fe(3)-C(32) 2.044(5), Fe(3)-C(34) 2.051(5), Fe(3)-C(38) 2.052(5), Fe(3)-C(33) 2.054(5), Fe(3)-C(37) 2.054(5), Fe(3)-C(36) 2.056(5), Fe(3)-C(30) 2.060(5), Fe(3)-C(35) 2.061(5), O-C 1.427(5); O-C-C(10) 111.1(4).

In the crystal structure of triferrocenylmethanol derivative **120** one ferrocene moiety has relatively longer bond lengths than those of the other two, it indicates that this iron center was oxidized.

The electrochemical properties of **120** was investigated by cyclovoltammetry (CV) and compared with unoxidized **119**. Both of the cyclovoltammograms seem to be quasi-reversible oxidation-reduction waves, which are in accord with the redox processes of the ferrocene moieties (Figure 10), and the respective data are listed in Table 7. The fact that three redox processes were observed for **119** and **120** indicates that the oxidation products contain three different ferrocene/ferrocenium moieties. For complexes **119** and **120**, two of the oxidation reactions take place at positive potentials relative to ferrocene/ferrocenium, and all the ΔE values are almost identical, but **120** has relatively higher $E_{1/2}$ respectively than **119**.

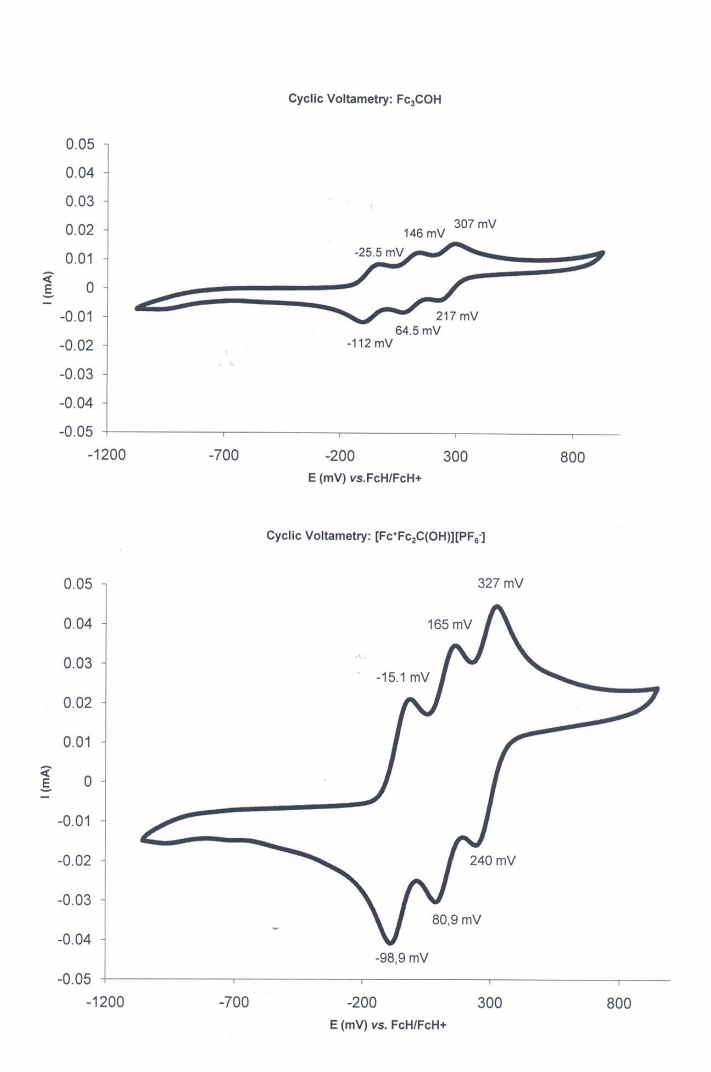


Figure 10. Cyclovoltammograms of **119** (*top*) and **120** (*bottom*). Potential vs. FcH/FcH^+. For further details see Table 7.

Table 7. Cyclovoltammetry data of **119** and **120** (potentials in V *vs* Fc/Fc^+, v = 100 mV/s, T = 25 °C, 2 mmol/L, 0.1 mol/L Bu_4NPF_6 in acetonitrile).

compound	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]
119	0.307	0.217	0.090	0.262
	0.146	0.065	0.081	0.106
	−0.026	−0.112	0.086	−0.069
120	0.327	0.240	0.087	0.284
	0.165	0.081	0.084	0.123
	−0.015	−0.099	0.084	−0.059

^{57}Fe Mössbauer effect spectroscopy has been widely applied to explain the delocalization of electrons in molecular systems that contain two or more iron atoms due to the characteristic property concerning the dynamics of electron exchange among two or more sites.[105] Figure 11 shows three different iron sites of compound **120**, which was measured by Prof. Herber. Two of them have isomer shifts and quadrupole splitting similar to what have been found in unoxidized triferrocenylmethanol. The major component of this pair corresponds to the two unoxidized iron atoms in the complex. The minor component might be unreacted starting material in which all three iron sites are identical.

The third site clearly corresponds to the oxidized iron atom and gives rise to a broad line with a somewhat smaller isomer shift and a negative quadrupole splitting. The line is indicative of a spin-lattice relaxation site and the relaxation rate might be dependent on temperature.

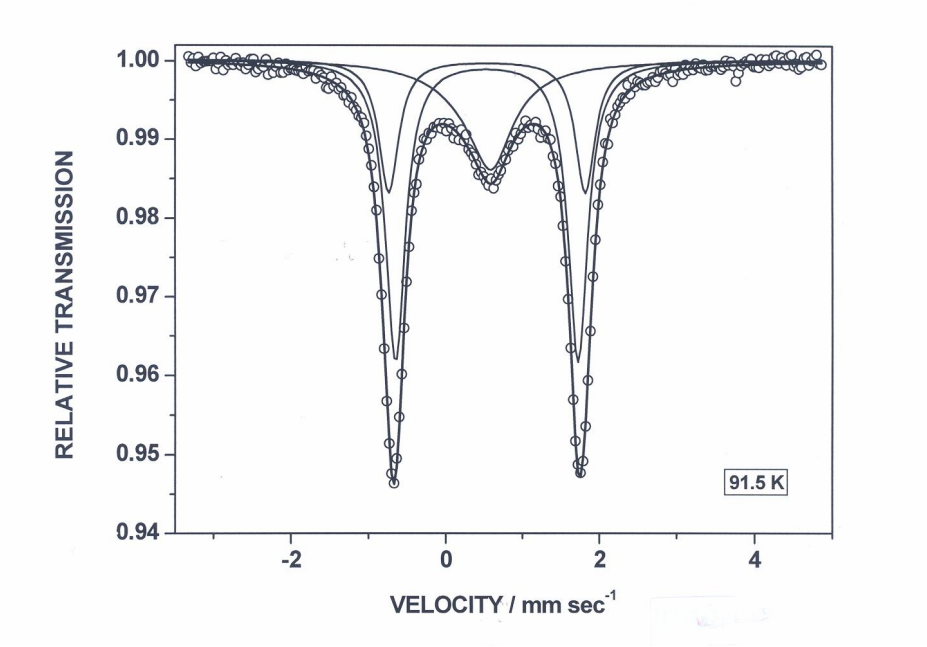
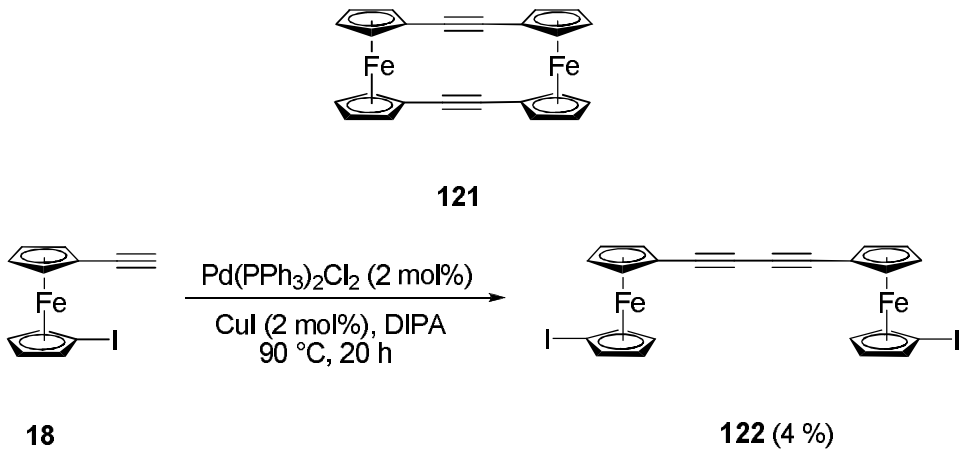


Figure 11. ^{57}Fe Mössbauer effect spectrum of **120** at 91.5 K.

2.9 Synthesis of 1,4-Di(1'-iodoferrocenyl)-buta-1,3-diyne (122)

[2,2]Ferrocenophane-1,13-diyne (**121**) was first prepared by Rosenblum and coworkers in 1970.[105] Synthesis of **121** using alkyne metathesis cross-coupling reactions has been investigated by us. This work started with 1,1'-di(1-propynyl)ferrocene (**59**) using **58** as alkyne metathesis catalyst. Instead of the expected **121**, dimer **107**, even trimer **108** was

obtained. Under typical Sonogashira coupling condition substrate **18** was treated to afford only **122** in 4 % yield, which was reported previously together with **121** (Scheme 56).[105]



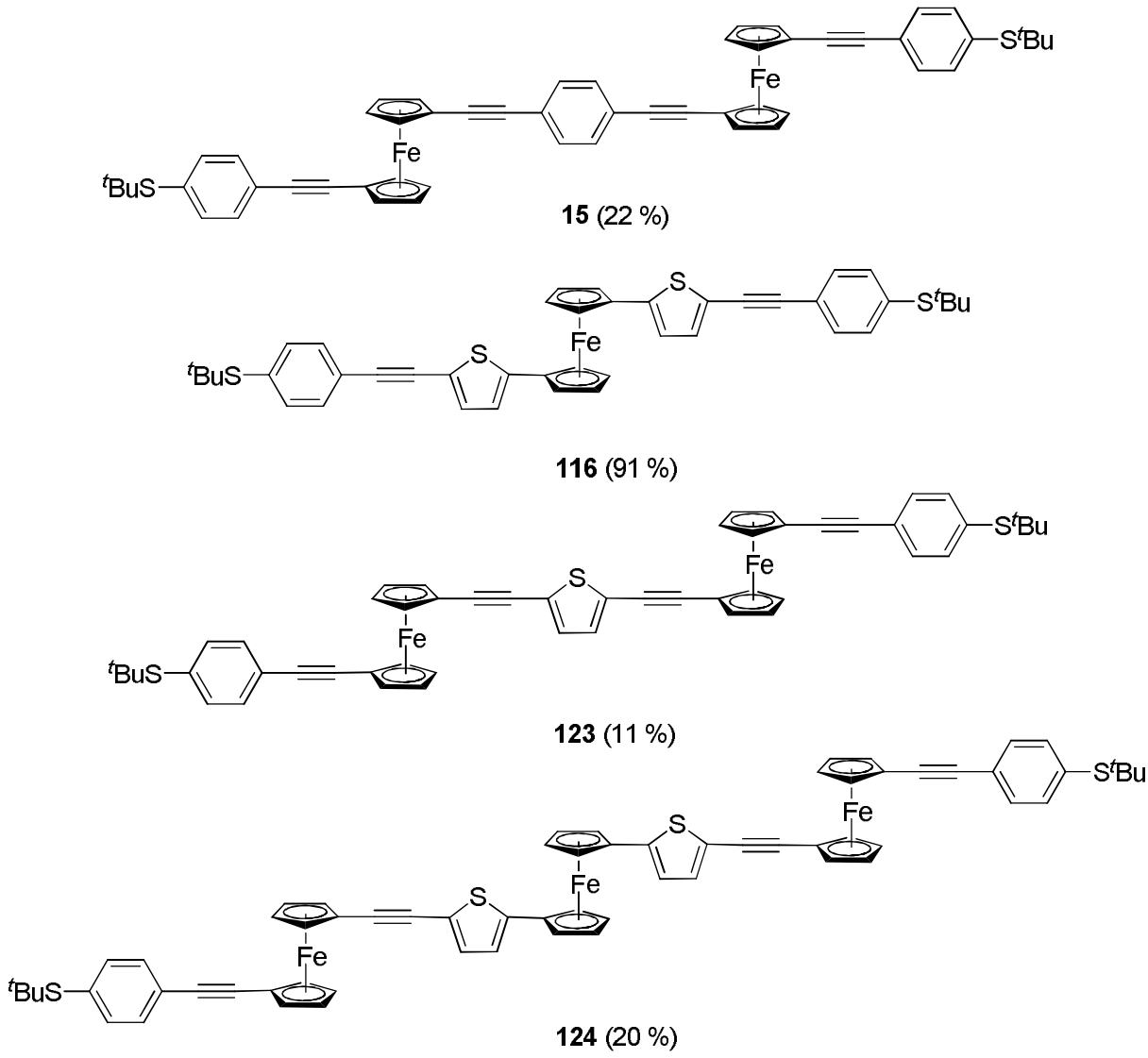
Scheme 56.

2.10 Synthesis of Ferrocene-based molecular Wires

The group of Prof. Wandlowski form University of Bern is interested in the molecular wires containing ferrocene as redox-active unit (Scheme 57).[15,20] Single molecule electron transport characteristics of these molecular wires will be explored under electrochemical conditions employing an STM-based "stretching approach". These experiments will provide new insight into single molecule electron transport properties of ferrocene unit in different oxidation states and will be compared with ongoing conductance studies with "inert" OPE-type molecule rods. Due to Cp-Fe-Cp unit(s) the family of these molecules also exhibits a certain conformational flexibility, the relations between single molecule conductance and (i) length of the molecular wire respective (ii) conformation. The ferrocene unit enables minimizing π-π stacking of the molecular wires in solution. Comparison of conductance studies with ferrocene free molecular wires will provide new insight on the role or importance of π-π stacking in single and/or multi-molecule junctions.

All the following four molecular wires were prepared according to Sonogashira coupling reaction. The reactions were carried out under microwave irradiation: 100 °C, 300 W, RAMP 15 min, HOLD 120 min, Open vessel.

Under the mentioned conditions, diyne was treated with 2.4 equiv **19** to give **124** in 8 % yield, which is just as much as reported.[20] Whereas, treatment of diyne with 3.0 equiv **19** afforded **124** in 20 % yield.

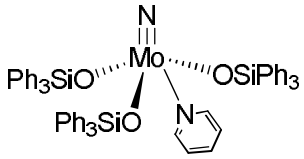


Scheme 57.

3 Summary and Outlook

3.1 Synthesis of ferrocene based molecular wires by alkyne metathesis

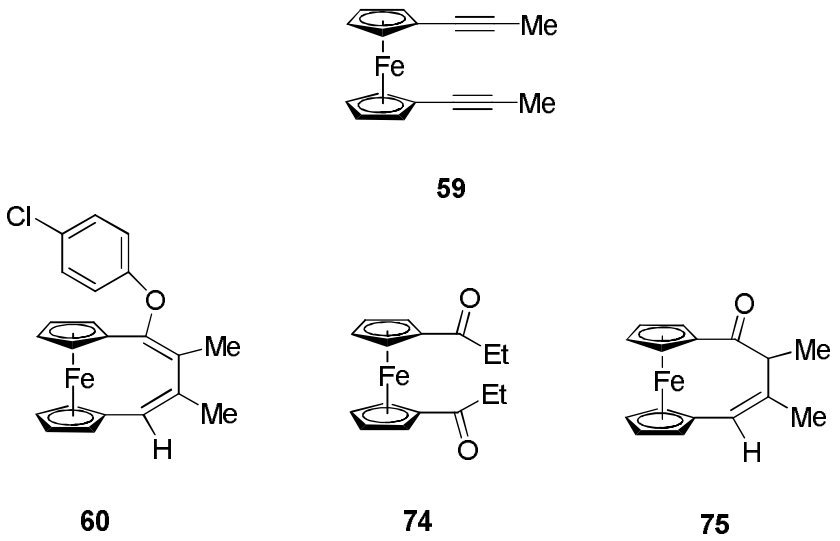
The ferrocene-based molecular wires were mainly constructed by Sonogashira,[15] Stille[16] and Negishi[20] coupling reactions of a limited number of building blocks. As an alternative tool, alkyne metathesis has been investigated. Two catalyst systems, the Mortreux catalyst system ($Mo(CO)_6$ and phenol) and the Fürstner catalyst **58** were applied.



58

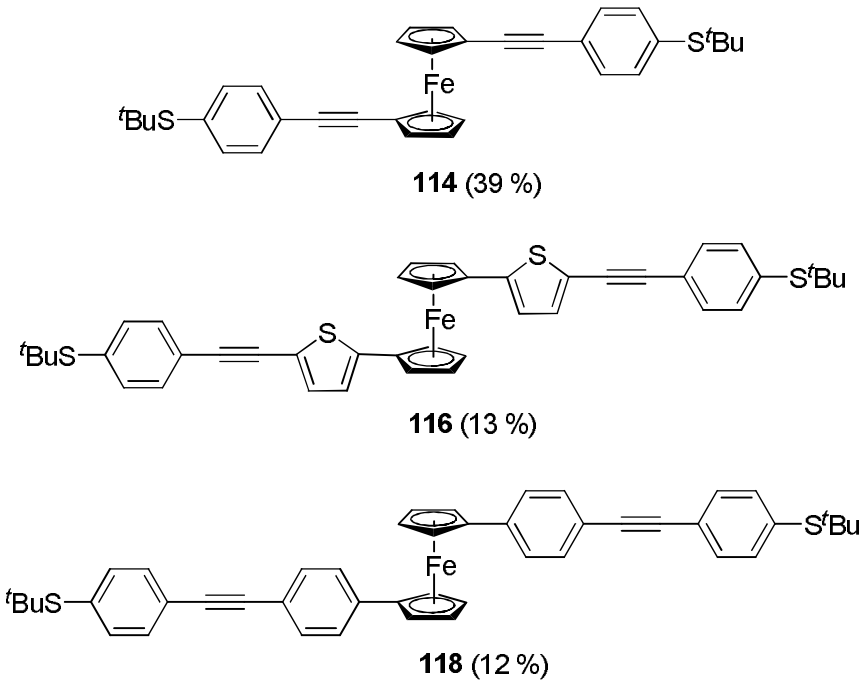
Scheme 58.

The "Mortreux system" has gained relatively widespread use due to its ease of application. The reagents are cheap, commercially available and stable; the reactions can be performed without the requirement for rigorously purified solvents and inert atmosphere. Attempts originally directed toward alkyne metathesis reactions of 1,1'-di(1-propynyl)ferrocene (**59**) under Mortreux reaction conditions led to an unanticipated transannular phenol addition, which takes place in the presence as well as in the absence of molybdenum hexacarbonyl and results in the formation of phenoxy[4]ferrocenophanediene **60**. The reaction is also observed with a thiophenol or with a weak acid such as acetic acid, whereas treatment with a strong acid (F_3CCO_2H) causes formation of 1,1'-dipropanoylferrocene (**74**). Reaction under basic reaction conditions led to the formation of the [4]ferrocenophanone (**75**). Under the same reaction condition, the other 1,1'-dialkynylferrocenes were treated with 4-chlorophenol to yield the corresponding phenoxy[4]ferrocenophanedienes. The [4]ferrocenophanedienes with aryl substituents show NMR spectroscopic coalescence in solution, presumably resulting from conformational switches of the helically distorted moleculaes.



Scheme 59.

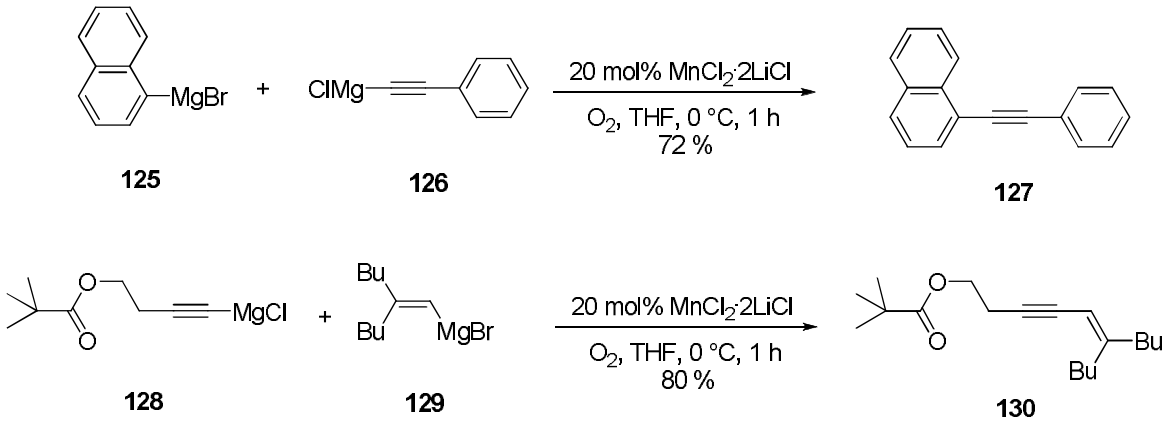
The cross-coupling alkyne metathesis is an alternative, interesting method. Catalyst **58** has been intensively investigated in this field. Attempts using catalyst **58** (20 mol %) under microwave irradiation afforded ferrocene-based molecular wires **114**, **116** and **118**.



Scheme 60.

3.2 Synthesis of ferrocene based molecular wires by manganese-catalyzed oxidative cross coupling

In 2009 Cahiez and coworkers reported the manganese-catalyzed oxidative cross coupling of Grignard reagents with oxygen as an oxidant.[106] In the presence of 20 mol % of $MnCl_2 \cdot 2LiCl$ and oxygen, treatment of aryl magnesium bromides with alkynyl magnesium chlorides afforded the cross heterocoupling products **127** and **130** in good yields (Scheme 61).

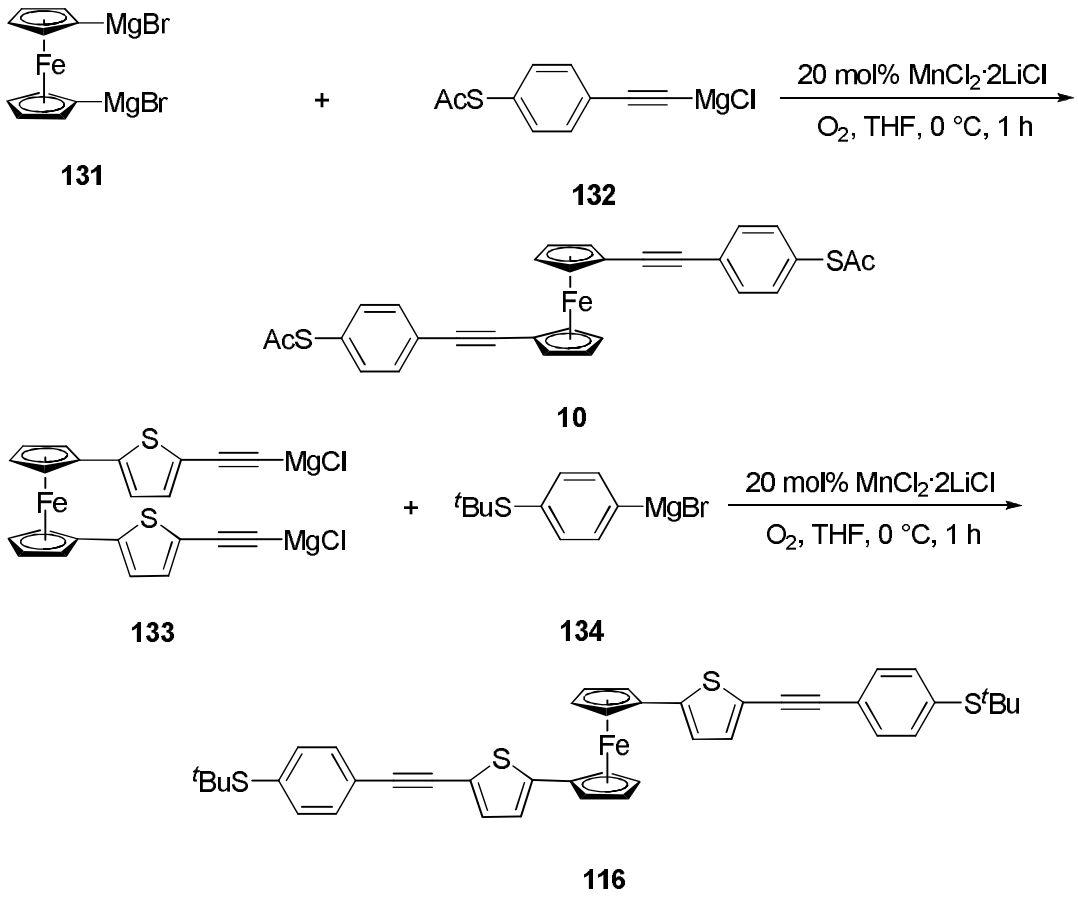


Scheme 61.

In many cases, the manganese-catalyzed oxidative cross coupling of alkynyl, alkenyl and aryl magnesium halides with alkynyl magnesium halides give preferentially the heterocoupling products, and the presence of various functional groups (ester, nitrile, etc.) is tolerated.

We anticipate that such a new general procedure may be useful for the synthesis of ferrocene-based molecular wires. Accordingly, this new method will be applied to ferrocene derivatives and the ferrocene based molecular wires might be obtained as manganese-catalyzed oxidative cross heterocoupling products.

To achieve this, the ferrocenyl 1,1'-di-Grignard reagent **131** will be treated with alkynyl magnesium chloride reagents obtained from molecular wire building blocks in the presence of 20 mol% of $MnCl_2 \cdot 2LiCl$ and oxygen to give the respective heterocoupling products **10** and **116** (Scheme 62).



Scheme 62.

After establishment of the method by synthesis of the molecular wires described above, it will be applied to preparation of longer and also branched ferrocene-based molecular wires.

4 Experimental Part

4.1 General

All operations involving air- or moisture-sensitive compounds were carried out in argon or nitrogen as the inert gas, using standard, Schlenk techniques. All glassware was heated at reduced pressure and filled with inert gas. This procedure was repeated three times. The following solvents were distilled before use under a slight positive pressure of nitrogen or argon. Tetrahydrofuran, diethyl ether, dimethoxyethane and hexane were dried over sodium/potassium alloy/benzophenone and distilled. Dichloromethane, diisopropylamine and toluene were dried over calcium hydride. Anhydrous chlorobenzene was purchased (Fluka) and used as delivered. *N*,*N*-dimethylformamide was obtained from an M. Braun Solvent Purification System.

^{1}H and ^{13}C NMR spectra were obtained with Bruker AVS 200 (^{1}H: 200 MHz) and AVS 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) instruments. Chemical shifts δ refer to δ_{TMS} = 0 ppm or to residual solvent signals. Signal multiplicities are abbreviated as s (singulet), d (doublet), t (triplet), q (quartet), m (multiplet). Primary, secondary, tertiary and quarternary carbon atom signals were identified as such by the APT and DEPT techniques.

IR spectra were obtained with Perkin-Elmer instruments FT-IR 580 and 1170. Signal characteristics are abbreviated as s (strong), m (medium), w (weak), and br (broad).

Mass spectra were obtained with a Micromass LC-TOF-MS instrument with lockspray source and direct injection with an ionization potential of 70 eV. **HR-MS** spectra were carried out using a VG-Autospec spectrometer (peak matching with perfluorokerosin; NBA Matrix), Micromass LCT spectrometer with Lock-Spray-Unit (ESI).

Analytical TLC was performed with Merck 60F-254 silica gel thin layer plates.

Column chromatography was done with J. T. Baker silica gel (60 µm) as the stationary phase.

Melting points were determined with the Electro thermal IA 9200.

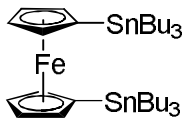
Elemental analysis (EA) Microanalyses was conducted with an Elemental Vario EL instrument with acetamide as standard. All values are given as mass percentages.

Microwave oven (μW) Reactions under microwave irradiation (μW) were performed with a CEM Discover^{TM} Labmate reactor under nitrogen ("open vessel") using the ChemDriver software. The temperature was monitored by means of an IR sensor.

Cyclic Voltammetry (CV) measurement was performed with a Gamry Instruments Reference 600 potentiostat/galvanostat/ZRA with 0.1 mol/L tetrabutylammonium hexafluorophosphonate electrolyte in acetonitrile at 25 °C. Ag/Ag^+ ($AgNO_3$) was used as the reference electrode in acetonitrile with 0.01 mol/L $AgNO_3$ and 0.1 mol/L tetrabutylammonium hexafluorophosphonate. Platinum was used for the working and counter electrode. The system was calibrated with ferrocene/ferrocenium and the values measured are referenced to Fc/Fc^+.

4.2 Synthesis of 1,1'-Di(1-propynyl)ferrocene (59)

4.2.1 1,1'-Bis(tributylstannyl)ferrocene (28)[34,107]



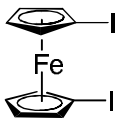
28

Ferrocene (**25**) (2.00 g, 10.7 mmol) was dissolved in hexane (60 mL). TMEDA (4.8 mL, 32.2 mmol) added. At –78 °C BuLi (1.6 M in hexane, 14.8 mL, 23.5 mmol) was added dropwise. The solution was stirred for 5 h at 25 °C, and then heated for 15 h at 70 °C. At 0 °C tributyltin chloride (tech. grade 90 %, 7.1 mL, 23.5 mmol) was added and the mixture was stirred for 5 h at 25 °C.

The white solid was filtered off and washed with hexane. The solution was washed with H_2O (30 mL) and then dried over magnesium sulfate. The solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel deactivated with 5

% triethylamine, hexane) to give **28** as a dark red oil (7.46 g, 9.8 mmol, 91 %), identified by comparison with literature data (^{1}H NMR).[107]

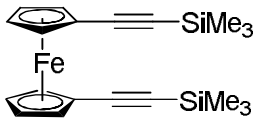
4.2.2 1,1'-Diiodoferrocene (12)[23]



12

1,1'-Bis(tributylstannyl)ferrocene (**28**) (4.84 g, 6.3 mmol) was dissolved in dichloromethane (50 mL). Iodine (3.52 g, 13.9 mmol) was added and the mixture was stirred for 20 h at 25 °C. After addition of $Na_2S_2O_3$ solution (1.27 g, 8.0 mmol, in 20 mL H_2O) and stirring for 5 min, the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure the residue was dissolved in methanol (40 mL). Potassium fluoride (1.40 g, 24.1 mmol) was added. The formed solid was filtered off. The solvent was removed at reduced pressure, and the residue was dissolved in diethyl ether (40 mL) again, and filtered through celite (3 cm). After solvent removal, the residue is purified by column chromatography (30 x 3 cm, silica gel deactivated with 5 % triethylamine, petroleum ether) to give **12** as a dark red oil (2.75 g, 6.3 mmol, 99 %), identified by comparison with literature data (^{1}H NMR).[23]

4.2.3 1,1'-Bis(trimethylsilylethynyl)ferrocene (137)[83]



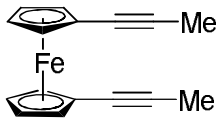
137

Microwave heating: 1,1'-diiodoferrocene (**12**) (3.33 g, 7.6 mmol) was dissolved in diisopropylamine (40 mL). After addition of trimethylsilylethyne (2.7 mL, 19.0 mmol), $Pd(PPh_3)_2Cl_2$ (53 mg, 0.1 mmol, 1 mol %) and CuI (15 mg, 0.1 mmol, 1 mol%) the flask was subjected to microwave irradiation (100

°C, 300 W, 15 min RAMP, 30 min HOLD, open vessel). After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 8:1) to give (**137**) (2.65 g, 7.0 mmol, 92 %) as a dark red solid.

Conventional heating: 1,1'-diiodoferrocene (**12**) (1.09 g, 2.5 mmol) was dissolved in diisopropylamine (15 mL). After addition of trimethylsilylethyne (0.9 mL, 6.2 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol, 2 mol %) and CuI (10 mg, 0.05 mmol, 2 mol %), the mixture was heated at reflux (oil bath 90 °C) for 20 h. After cooling to 25 °C, the suspension was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 8:1) to give **138** (0.69 g, 1.8 mmol, 73 %) as a dark red solid, identified by comparison with literature data (^{1}H NMR).[83]

4.2.4 1,1'-Di(1-propynyl)ferrocene (59)[108]



59

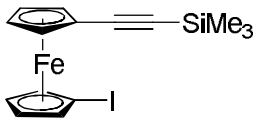
1,1'-Bis(trimethylsilylethynyl)ferrocene (**137**) (1.13 g, 3.0 mmol) was dissolved in tetrahydrofuran (30 mL). At –78 °C MeLi (1.6 M in diethyl ether, 5.6 mL, 9.0 mmol) was added dropwise and the mixture was stirred for 20 h at 25 °C. After addition of iodomethane (0.8 mL, 12.0 mmol) at –78 °C, the solution was stirred for 1 h at 25 °C. After addition of water (20 mL) and stirring for 5 min, the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine (30 mL) and then dried over magnesium sulfate. After removal of solvent at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **59** (0.60 g, 2.3 mmol, 76 %) as a orange solid, which was recrystallized from hexane/dichloromethane (3:1) as a dark red crystal (m. p. 142.2-143.6 °C).

IR (ATR): $\tilde{\nu}$ = 3087 (m) cm^{-1}, 2912 (m), 2849 (m), 2227 (w), 1666 (w), 1463 (m), 1436 (m), 1379 (m), 1262 (m), 1207 (w), 1058 (s), 1030 (s), 982 (s), 871 (s), 853 (s), 816 (s). – ^{1}H NMR

($CDCl_3$, 400 MHz): δ = 1.95 (s, 6H, CH_3), 4.16 (AA'BB', 4H, H_{Fc}), 4.34 (AA'BB', 4H, H_{Fc}) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.5 (CH_3), 67.9 ($CCCH_3$), 70.1 ($C_{Fc}H$), 72.3 ($C_{Fc}H$), 76.4 ($C_{Fc}C$), 82.4 ($CCCH_3$) ppm. – MS (70 eV): *m/z* (%) = 263 (22) [$(M+1)^+$], 262 (100) [M^+], 261 (19), 260 (35), 205 (14), 204 (16), 203 (42), 202 (19), 190 (17), 189 (19), 165 (14), 159 (21), 56 (10) [Fe^+]. – HRMS ($C_{16}H_{14}Fe$) calcd. 262.0445, found 262.0444. – Anal. ($C_{16}H_{14}Fe$): Calcd. C 71.31, H 5.38; found C 71.13, H 5.48.

4.3 Synthesis of 1-Ethynyl-1'-iodoferrocene (18)[15]

4.3.1 1-Iodo-1'-(trimethylsilylethynyl)ferrocene (17)[15]

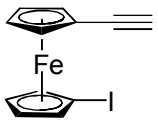


17

Conventional heating: 1,1'-Diiodoferrocene (**12**) (1.96 g, 4.5 mmol) was dissolved in diisopropylamine (40 mL). After addition of trimethylsilylethyne (0.37 g, 3.8 mmol), $Pd(PPh_3)_2Cl_2$ (65 mg, 0.09 mmol, 2 mol%) and $Cu(OAc)_2 \cdot H_2O$ (19 mg, 0.09 mmol, 2 mol%) the solution was heated at reflux (oil bath 95 °C) for 20 h. After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, hexane) to give **17** (0.62 g, 1.5 mmol, 40 %) as a dark red oil.

Microwave heating: 1,1'-Diiodoferrocene (0.56 g, 1.3 mmol) and trimethylsilylethyne (0.12 g, 1.2 mmol) was dissolved in diisopropylamine (40 mL). After addition of $Pd(PPh_3)_2Cl_2$ (18 mg, 0.05 mmol, 4 mol%) and $Cu(OAc)_2 \cdot H_2O$ (5 mg, 0.02 mmol, 2 mol%) the flask was subjected to microwave irradiation (100 °C, 300 W, 15 min RAMP, 30 min HOLD, open vessel). After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, hexane) to give **17** (0.30 g, 0.7 mmol, 61 %) as a dark red oil, identified by comparison with literature data (^{1}H NMR).[15]

4.3.2 1-Ethynyl-1'-iodoferrocene (18)[15]



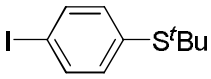
18

Method 1: Tetrabutylammonium fluoride (8.0 mL, 1M in THF, 8.0 mmol) was added to a solution of 1-Iodo-1'-(trimethylsilylethynyl)ferrocene (**17**) (1.62 g, 4.0 mmol) in dichloromethane (50 mL). The mixture became immediately dark. After stirring at 25 °C for 45 min the solvent was removed at reduced pressure and the residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/ dichloromethane 4:1). **18** (1.30 g, 3.9 mmol, 98 %) was obtained as a dark red oil.

Method 2: Potassium carbonate (3.23 g, 23.4 mmol),) was added to a solution of 1-Iodo-1'-(trimethylsilylethynyl)ferrocene (**17**) (3.18 g, 7.8 mmol) in methanol (50 mL), the mixture was stirred for 20 h at 25 °C. After addition of dichloromethane (30 mL) and water (30 mL) the suspension was stirred for 5 min at 25 °C. The layers were separated and the aqueous layer was extracted with dichloromethane (30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After solvent removal at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/ dichloromethane 4:1). **18** (2.45 g, 7.3 mmol, 94 %) was obtained as a dark red oil, identified by comparison with literature data (^{1}H NMR).[15]

4.4 Synthesis of 1-(*tert*-butylsulfanyl)-4-ethynylbenzene (139)[15,29]

4.4.1 1-(*tert*-Butylsulfanyl)-4-iodobenzene (13)[15]

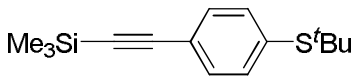


13

4-Iodophenylsulfonyl chloride (2.00 g, 6.4 mmol) and dimethylacetamide (1.72 g, 19.8 mmol) in 1,2-dichloroethane was added to zinc dust (1.45 g, 22.2 mmol) and dichlorodimethylsilane (3.00 g, 23.2 mmol) n 1,2-dichloroethane (40 mL). The mixture was heated at 75 °C for 4 h.

After cooling to 45 °C *tert*-butylchloride (1.83 g, 19.8 mmol) was added, and the mixture was stirred at this temperature for another 10 h. After cooling to 25 °C water (30 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were dried over magnesium sulfate. After filtration and solvent removal at reduced pressure a yellow liquid was obtained, which was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether). Compound **13** (1.54 g, 5.3 mmol, 82 %) was obtained as a colorless shiny crystal, identified by comparison with literature data (^{1}H NMR).[15]

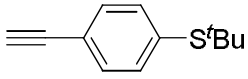
4.4.2 1-(*tert*-Butylsulfanyl)-4-(trimethylsilylethynyl)benzene (138)[29]



138

1-(*tert*-Butylsulfanyl)-4-iodobenzene (**13**) (3.00 g, 10.3 mmol) was dissolved in tetrahydrofuran (50 mL). After addition of trimethylsilylethyne (2.2 mL, 15.4 mmol), diisopropylamine (20 mL), $Pd(PPh_3)_2Cl_2$ (72 mg, 0.1 mmol, 1 mol %) and CuI (20 mg, 0.1 mmol, 1 mol %) the solution was heated at reflux (oil bath 80 °C) for 20 h. After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 6:1) to give **138** (2.48 g, 9.4 mmol, 92 %) as a light yellow oil, identified by comparison with literature data (^{1}H NMR).[29]

4.4.3 1-(*tert*-Butylsulfanyl)-4-ethynylbenzene (139)[29]



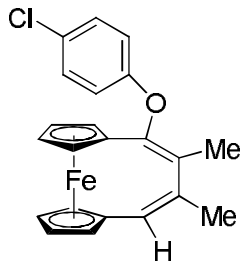
139

1-(*tert*-Butylsulfanyl)-4-(trimethylsilylethynyl)benzene (**138**) (2.48 g, 9.4 mmol) was dissolved in methanol (40 mL). After addition of potassium carbonate (3.90 g, 28.3 mmol) the mixture was stirred for 20 h at 25 °C. Dichloromethane (50 mL) and water (30 mL) were added. After 5 min stirring the layers were separated and the aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine and dried over $MgSO_4$. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1). **139** (1.70 g, 9.0 mmol, 95 %) was obtained as a light yellow oil, identified by comparison with literature data (^{1}H NMR).[29]

4.5 Synthesis of Phenoxy[4]ferrocenophanedienes[100]

General Procedure 1 (**GP 1**): A solution of 1,1'-di(1-propynyl)ferrocene (**59**)[108] (262 mg, 1.0 mmol) and the phenol (1.2 mmol) in chlorobenzene (20 mL) is heated at reflux (oil bath 135 °C) for 15 h. After cooling to 25 °C, the solvent is removed at reduced pressure. The residue is purified by column chromatography (30 x 3 cm, silica gel, hexane/dichloromethane 4:1) to give the product as a dark red solid. The product is recrystallized from hexane/dichloromethane (3:1).

4.5.1 1,1'-[1-(4-Chlorophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (60)



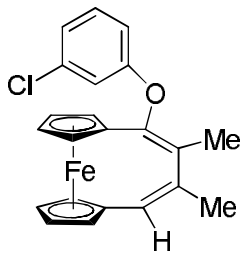
60

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 154 mg (1.2 mmol) of 4-chlorophenol; 331 mg (0.8 mmol, 84 %) of **60** as a dark red crystal (m. p. 180.5-182.1 °C).

IR (ATR): $\tilde{\nu}$ = 3050 (w) cm^{-1}, 2916 (w), 1640 (m), 1589 (m), 1486 (s), 1445 (m), 1281 (w), 1261 (w), 1243 (s), 1163 (m), 1124 (m), 1086 (m), 1069 (s), 1026 (s), 1009 (m), 910 (w), 846 (m), 821 (s), 803 (s), 721 (w), 666 (m). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.85 [s, 3H, C(OAr)=CCH_3], 1.95 (d, 3H, J = 1.4 Hz, CH=C-CH_3), 4.12 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.42 (m, 4H, H_{Fc}), 6.13 (q, 1H, ^4J = 1.0 Hz, CH=C), 6.71 (m, 2H, $H_{Ar.}$), 7.12 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=CCH_3], 25.1 (CH=CCH_3), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 70.7 (C_{Fc}H), 74.5 (C_{Fc}C), 77.8 (C_{Fc}C), 117.1 (C_{Ar}H), 124.2 (CH=C), 124.3 [C(OAr)=CCH$_3$], 126.2 (CH=C), 129.3 (C_{Ar}H), 136.5 (C_{qAr}), 145.3 [C(OAr)=CCH$_3$], 155.1 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 392 (29) [$(M+2)^+$], 391 (22) [$(M+1)^+$], 390 (82) [M^+], 298 (18) [M^+ – 2H], 263 (100) [M^+ – (4-ClC_6H_4O)], 261 (23) [M^+ – (4-ClC_6H_4O) – 2H], 121 (20) [$(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+$]. - HRMS ($C_{22}H_{19}FeClO$): Calcd. 390.0474, found 390.0472. - Anal. ($C_{22}H_{19}FeClO$): Calcd. C 67.63, H 4.90, found C 67.72, H 5.07.

Crystal Structure analysis:[94] Single crystals were obtained by crystallization from hexane / dichloromethane (3:1) at 25 °C. Empirical formula $C_{22}H_{19}ClFeO$, formula weight 390.69 g/mol, crystal system monoclinic, space group P 2_1/n, unit cell dimensions a = 8.544(2), b = 10.045(2), c = 20.630(6) Å, α = 90º, β = 96.04(3)º, γ = 90º, V = 1760.7(8) $Å^3$, Z = 4, $d_{calc.}$ =1.474 g/cm^3, μ = 1.014 mm^{-1}, crystal size 0.25 x 0.21 x 0.19 mm, F (000) = 808, STOE IPDS one-axis diffractometer with imaging plate detector, T = 294 K, $Mo_{K\alpha}$ radiation (λ= 0.71073 Å), θ-range 2.71 to 25.76º, reflections collected / unique 21139 / 3430 [R(int) = 0.060], completeness of data θ = 26.1 (97.8%), index ranges –10≤ h ≤ 10, –12≤ k ≤ 12, –25 ≤ l ≤ 25, empirical absorption correction (multi-scan), no extinction correction, direct methods, full-matrix least-squares refinement on F^2, goodness-of-fit on F^2 = 0.964, R_1 = 0.0463 (I > 2σ_I), wR_2 = 0.1175, R-indices [all data] R_1 = 0.0690 , wR_2 = 0.1259, final difference electron density 0.352 and –0.500 e$Å^{-3}$.

4.5.2 1,1'-[1-(3-Chlorophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (61)

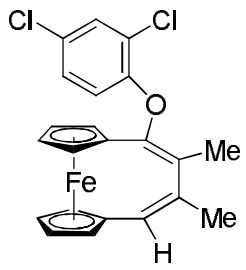


61

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 154 mg (1.2 mmol) of 3-chlorophenol; 359 mg (0.9 mmol, 92 %) of **61** as a dark red crystal (m. p. 140.7-142.6 °C).

IR (ATR): $\tilde{\nu}$ = 3100 (w) cm^{-1}, 2916 (w), 1589 (s), 1473 (s), 1453 (m), 1432 (m), 1304 (s), 1269 (s), 1224 (s), 1119 (s), 1061 (s), 1024 (s), 994 (m), 915 (s), 881 (m), 846 (s), 820 (m), 803 (s), 780 (s), 691 (m), 681 (s). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.85 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^{4}J = 1.4 Hz, CH=C-CH_3), 4.14 + 4.17 (AA'BB', 2 x 2H, H_{Fc}), 4.42 + 4.44 (AA'BB', 2 x 2H, H_{Fc}), 6.14 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.67 (m, 1H, H_{Ar}), 6.80 (m, 1H, H_{Ar}), 6.86 (m, 1H, H_{Ar}), 7.08 (m, 1H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.8 [C(OAr)=C*C*H_3], 25.0 (CH=C*C*H_3), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 70.7 (C_{Fc}H), 74.4 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 114.2 (C_{Ar}H), 116.3 (C_{Ar}H), 121.5 (C_{Ar}H), 124.3 (*C*H=C), 124.5 [C(OAr)=*C*CH_3], 130.1 (C_{Ar}H), 134.8 (C_{qAr}), 136.5 (CH=*C*), 145.1 [*C*(OAr)=CCH_3], 157.3 (OC_{qAr}) ppm. -MS (70 eV): *m/z* (%) = 392 (60) [$(M+2)^+$], 391 (48) [$(M+1)^+$], 390 (100) [M^+], 264 (23), 263 (85) [M^+ – (3-ClC_6H_4O)], 261 (20) [M^+ – (3-ClC_6H_4O) – 2H], 121 (26) [(Cp-CH=C(OH)-CH_3)$^+$], 56 (18) [Fe^+]. - HRMS ($C_{22}H_{19}FeClO$): Calcd. 390.0474, found 390.0475. - Anal. ($C_{22}H_{19}FeClO$): Calcd. C 67.63, H 4.90, found C 67.50, H 5.04.

4.5.3 1,1'-[1-(2,4-Dichlorophenoxy)- 2,3-dimethyl-1,3-butadienylene]ferrocene (62)

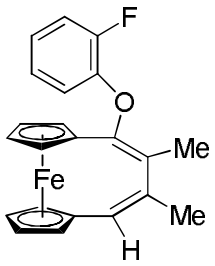


62

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 196 mg (1.2 mmol) of 2,4-dichlorophenol; 420 mg (1.00 mmol, 99 %) of **62** as a dark red solid (m. p. 102.7-103.4 °C).

IR (ATR): $\tilde{\nu}$ = 3070 (w) cm^{-1}, 2915 (w), 1647 (w), 1582 (w), 1472 (s), 1445 (m), 1389 (w), 1250 (s), 1233 (s), 1113 (m), 1098 (s), 1064 (s), 1024 (s), 927 (w), 907 (w), 856 (s), 841 (s), 804 (s), 753 (s), 709 (m), 695 (m). – ^{1}H- NMR ($CDCl_3$, 400 MHz): δ = 1.87 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^{4}J = 1.4 Hz, CH=C-CH_3), 4.13 + 4.18 (AA'BB', 2 x 2H, H_{Fc}), 4.46 (m, 4H, H_{Fc}), 6.14 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.47 (d, 1H, H_{Ar}), 6.95 (m, 1H, H_{Ar}), 7.32 (d, 1H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=C*C*H$_3$], 25.1 (CH=C*C*H$_3$), 70.2 (C_{Fc}H), 70.3 (C_{Fc}H), 70.4 (C_{Fc}H), 70.7 (C_{Fc}H), 74.1 (*C*$_{Fc}$C), 77.7 (*C*$_{Fc}$C), 116.5 (C_{Ar}H), 123.4 [C(OAr)=*C*CH$_3$], 124.5 (*C*H=C), 124.7 (C_{Ar}), 126.3 (CH=*C*), 127.5 (C_{Ar}H), 129.9 (C_{Ar}H), 136.2 (C_{qAr}), 145.6 [*C*(OAr)=CCH$_3$], 150.9 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 426 (51) [$(M+2)^+$], 425 (22) [$(M+1)^+$], 424 (69) [M^+], 277 (20), 264 (32), 263 (100) [M^+ – ($C_6H_3Cl_2O$)], 261 (26) [M^+ – ($C_6H_3Cl_2O$) – 2H], 205 (18), 191 (21), 121 (22) [(Cp-CH=C(OH)-CH_3)$^+$], 56 (15) [Fe^+]. - HRMS ($C_{22}H_{18}FeCl_2O$): Calcd. 424.0084, found 424.0085. - Anal. ($C_{22}H_{18}FeCl_2O$): Calcd. C 62.15, H 4.27, found C 62.30, H 4.35.

4.5.4 1,1'-[1-(2-Fluorophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (63)

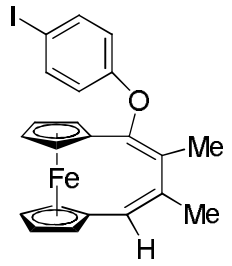


63

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 134 mg (1.2 mmol) of 2-fluorophenol; 280 mg (0.8 mmol, 75 %) of **63** as a dark red crystal (m. p. 143.5-144.9°C).

IR (ATR): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 2921 (m), 2854 (w), 1608 (m), 1497 (s), 1454 (m), 1254 (s), 1197 (s), 1119 (s), 1101 (s), 1055 (s), 1023 (s), 926 (m), 907 (s), 857 (m), 834 (s), 800 (s), 777 (m), 746 (s), 720 (w), 700 (w). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.91 [s, 3H, C(OAr)=CH_3], 1.97 (d, 3H, ^{4}J = 0.7 Hz, CH=C-CH_3), 4.12 + 4.17 (AA'BB', 2 x 2H, H_{Fc}), 4.46 + 4.49 (AA'BB', 2 x 2H, H_{Fc}), 6.14 (br s, 1H, CH=C), 6.62 (m, 1H, H_{Ar}), 6.83 (m, 2H, H_{Ar}), 7.05 (m, 1H, H_{Ar}) ppm. NOE: Irradiation at δ = 1.97 (d, 3H, J = 0.7 Hz, CH=C-CH_3) ppm causes 14 % increase at δ = 6.14 (br s, 1H, CH=C) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=C*C*H_3], 25.1 (CH=C*C*H_3), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.3 (C_{Fc}H), 70.7 (C_{Fc}H), 74.4 (*C*$_{Fc}$C), 77.7 (*C*$_{Fc}$C), 116.4 (C_{Ar}H), 116.9 (C_{Ar}H), 121.7 (C_{Ar}H), 124.1 (*C*H=C), 124.4 (C_{Ar}H), 136.4 [C(OAr)=*C*CH$_3$], 144.4 (CH=*C*), 145.5 (C_{Ar}), 151.3 [*C*(OAr)=CCH$_3$], 153.7 (OC_{Ar}) ppm. - MS (70 eV): *m/z* (%) = 375 (36) [$(M+1)^+$], 374 (99) [M^+], 282 (28), 277 (17), 264 (26), 263 (100) [M^+ – (2-FC_6H_4O)], 261 (27) [M^+ – (2-FC_6H_4O) – 2H], 205 (20), 203 (18), 191 (18) , 121 (24) [(Cp-CH=C(OH)-CH_3)$^+$]. - HRMS ($C_{22}H_{19}FeFO$): Calcd. 374.0769, found 374.0770. - Anal. ($C_{22}H_{19}FeFO$): Calcd. C 70.61, H 5.12, found C 70.66, H 5.30.

4.5.5 1,1'-[1-(4-Iodophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (64)

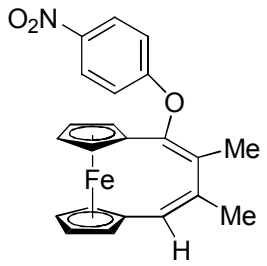


64

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 266 mg (1.2 mmol) of 4-iodophenol; 481 mg (1.0 mmol, 99 %) of **64** as dark red crystals (m. p. 187.5-188.5 °C).

IR (ATR): $\tilde{\nu}$ = 3010 (w) cm^{-1}, 2920 (w), 1793 (w), 1637 (w), 1582 (m), 1480 (s), 1456 (w), 1374 (w), 1275 (w), 1259 (w), 1227 (s), 1169 (m), 1120 (m), 1055 (m), 1024 (m), 1003 (m), 999 (w), 871 (w), 845 (w), 816 (s), 804 (s), 662 (w). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.84 [s, 3H, C(OAr)=CCH_3], 1.95 (d, 3H, ^{4}J = 1.7 Hz, CH=C-CH_3), 4.13 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.42 (q, 4H, H_{Fc}), 6.13 (d, 1H, J = 1.0 Hz, CH=C), 6.57 (m, 2H, H_{Ar}), 7.44 (m, 2H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=C*C*H_3], 25.1 (CH=C*C*H_3), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 70.7 (C_{Fc}H), 74.4 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 83.6 (C_{qAr}), 118.2 (C_{Ar}H), 124.2 (*C*H=C), 124.3 [C(OAr)=*C*CH$_3$], 136.5 (CH=*C*), 138.2 (C_{Ar}H), 145.2 [*C*(OAr)=CCH$_3$], 156.5 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 483 (13) [$(M+1)^+$], 482 (47) [M^+], 360 (13), 263 (45) [M^+ – (4-IC_6H_4O)], 261 (11) [M^+ – (4-IC_6H_4O) – 2H], 224 (100) [Fc-CCCH$_3$], 158 (15), 121 (24) [$(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+$], 56 (27) [$Fe^+$]. - HRMS ($C_{22}H_{19}FeIO$): Calcd. 481.9830, found 481.9833. - Anal. ($C_{22}H_{19}FeIO$): Calcd. C 54.81, H 3.97, found C 54.98, H 4.07.

4.5.6 1,1'-[1-(4-Nitrophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (65)

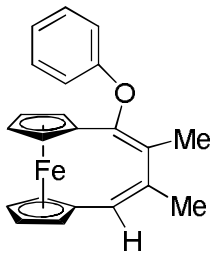


65

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 167 mg (1.2 mmol) of 4-nitrophenol; 365 mg (0.9 mmol, 91 %) of **65** as a dark red crystal (m. p. 188.6-189.5 °C).

IR (ATR): $\tilde{\nu}$ = 3073 (w) cm^{-1}, 2925 (w), 1644 (w), 1604 (m), 1587 (s), 1512 (s), 1488 (s), 1444 (m), 1375 (w), 1338 (s), 1253 (s), 1161 (s), 1110 (s), 1057 (s), 1025 (s), 954 (w), 927 (w), 908 (m), 862 (m), 847 (s), 835 (s), 798 (s), 752 (s), 716 (s), 686 (m), 663 (m). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.84 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^{4}J = 1.4 Hz, CH=C-CH_3), 4.15 + 4.19 (AA'BB', 2 x 2H, H_{Fc}), 4.44 (m, 4H, H_{Fc}), 6.16 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.86 (m, 2H, H_{Ar}), 8.09 (m, 2H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.8 [C(OAr)=C*C*H_3], 25.0 (CH=C*C*H_3), 70.3 (C_{Fc}H), 70.4 (C_{Fc}H), 70.5 (C_{Fc}H), 70.8 (C_{Fc}H), 74.0 (*C*$_{Fc}$C), 77.7 (*C*$_{Fc}$C), 115.9 (C_{Ar}H), 124.6 (*C*H=C), 125.0 (C_{qAr}), 125.8 (C_{Ar}H), 136.0 [C(OAr)=*C*CH$_3$], 142.0 (CH=*C*), 145.2 [*C*(OAr)=CCH$_3$], 161.8 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 402 (35) [$(M+1)^+$], 401 (100) [M^+], 264 (20), 263 (94) [M^+ – (*p*-$O_2NC_6H_4O$)], 261 (20) [M^+ – (*p*-$O_2NC_6H_4O$) – 2H], 205 (21), 203 (19), 121 (24) [$(Cp\text{-}CH=C(OH)\text{-}CH_3)^+$]. – HRMS ($C_{22}H_{19}FeNO_3$): Calcd. 401.0714, found 401.0712. Anal. ($C_{22}H_{19}FeNO_3$): Calcd. C 65.86, H 4.77, N 3.49, found C 65.74, H 4.82, N 3.52.

4.5.7 1,1'-(1-Phenoxy-2,3-dimethyl-1,3-butadienylene)ferrocene (66)

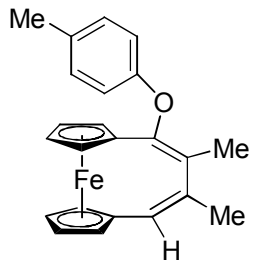


66

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 113 mg (1.2 mmol) of phenol; 203 mg (0.6 mmol, 57 %) of **66** as a dark red crystal (m. p. 167.6-168.5 °C).

IR (ATR): $\tilde{\nu}$ = 3073 (w) cm^{-1}, 2925 (w), 1644 (w), 1604 (m), 1587 (s), 1512 (s), 1488 (s), 1444 (m), 1375 (w), 1338 (s), 1253 (s), 1161 (s), 1110 (s), 1057 (s), 1025 (s), 9154 (w), 927 (w), 908 (m), 862 (m), 847 (s), 835 (s), 798 (s), 752 (s), 716 (s), 686 (m), 663 (m). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.87 [s, 3H, C(OAr)=CCH_3], 1.97 (d, 3H, ^{4}J = 1.7 Hz, CH=C-CH_3), 4.12 + 4.17 (AA´BB´, 2 x 2H, H_{Fc}), 4.45 (m, 4H, H_{Fc}), 6.14 (q, 1H, ^{4}J = 1.4 Hz, CH=C), 6.81 (m, 2H, H_{Ar}), 6.87 (m, 1H, H_{Ar}), 7.17 (m, 2H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.8 [C(OAr)=C*C*H_3], 25.1 (CH=C*C*H_3), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.9 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 115.8 (C_{Ar}H), 121.2 (*C*H=C), 124.0 [C(OAr)=*C*CH_3], 124.1 (C_{Ar}H), 129.4 (C_{Ar}H), 136.7 (CH=*C*), 145.3 (*C*(OAr)=CCH_3), 156.5 (OC_{qAr}) ppm. -MS (70 eV): *m/z* (%) = 357 (25) [$(M+1)^+$], 356 (100) [M^+], 264 (30), 263 (69) [$M^+ - (C_6H_5O)$], 261 (15) [$M^+ - (C_6H_5O) - 2H$], 205 (10), 203 (11), 121 (16) [$(Cp\text{-}CH=C(OH)\text{-}CH_3)^+$], 77 (13), 56 (11). - HRMS ($C_{22}H_{20}FeO$) Calcd. 356.0864, found 356.0865. - Anal. ($C_{22}H_{20}FeO$): Calcd. C 74.17, H 5.66, found C 73.98, H 5.74.

4.5.8 1,1'-[1-(4-Methylphenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (67)

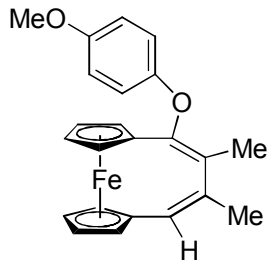


67

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 130 mg (1.2 mmol) of 4-aminophenol; 320 mg (0.9 mmol, 86 %) of **67** as a dark red crystal (m. p. 170.7-172.2 °C).

IR (ATR): $\tilde{\nu}$ = 3005 (w) cm^{-1}, 2970 (w), 1607 (m), 1504 (s), 1435 (m), 1261 (m), 1238 (m), 1218 (s), 1165 (m), 1123 (s), 1104 (m), 1066 (s), 1057 (s), 1023 (s), 928 (w), 906 (m), 862 (m), 831 (s), 806 (s), 800 (s), 756 (w), 716 (m). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.88 [s, 3H, C(OAr)=CCH_3], 1.97 (d, 3H, ^{4}J = 1.7 Hz, CH=C-CH_3), 2.21 (s, 3H, $ArCH_3$), 4.11 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.44 (m, 4H, H_{Fc}), 6.13 (q, 2H, ^{4}J = 1.4 Hz, C*H*=C), 6.69 (d, 2H, H_{Ar}), 6.97 (d, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=C*C*H_3], 20.5 (Ar*C*H_3), 25.1 (CH=C*C*H_3), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.9 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 115.6 (C_{Ar}H), 123.8 [C(OAr)=*C*CH_3], 124.1 (*C*H=C), 129.8 (C_{Ar}H), 130.4 (C_{qAr}), 136.8 (CH=*C*), 145.4 [*C*(OAr)=CCH_3], 154.4 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 371 (23) [$(M+1)^+$], 370 (85) [M^+], 278 (28), 277 (17), 264 (20), 263 (100) [M^+ – (4-$CH_3C_6H_4O$)], 261 (22) [M^+ –(4-$CH_3C_6H_4O$) – 2H], 121 (21) [(Cp-CH=C(OH)-CH_3)$^+$], 86 (48), 84 (73), 56 (10) [Fe^+]. - HRMS ($C_{23}H_{22}FeO$): Calcd. 370.1020, found 370.1018. - Anal. ($C_{23}H_{22}FeO$): Calcd. C 74.61 H 5.99, found C 74.41, H 5.98.

4.5.9 1,1'-[1-(4-Methoxyphenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (68)

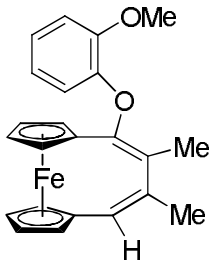


68

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 148 mg (1.2 mmol) of 4-methoxyphenol; 344 mg (0.9 mmol, 89 %) of **68** as a dark red crystal (m. p. 138.8-139.7 °C).

IR (ATR): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 2939 (w), 1637 (w), 1501 (s), 1451 (m), 1377 (w), 1266 (w), 1207 (s), 1180 (m), 1127 (m), 1103 (w), 1070 (m), 1039 (s), 1025 (s), 910 (w), 857 (w), 845 (m), 822 (s), 801 (s), 753 (s), 712 (m), 700 (m). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.89 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^{4}J = 1.4 Hz, CH=C-CH_3), 3.69 (s, 3H, OCH_3), 4.11 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.43 (m, 4H, H_{Fc}), 6.12 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.72 (s, 4H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 [C(OAr)=C*C*H_3], 25.1 (CH=C*C*H_3), 55.6 (O*C*H_3), 69.9 (C_{Fc}H), 70.0 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.8 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 114.6 (C_{Ar}H), 116.6 (C_{Ar}H), 123.7 [C(OAr)=*C*CH_3], 124.0 (*C*H=C), 136.8 (CH=*C*), 145.7 (C_{qAr}), 150.5 [*C*(OAr)=CCH_3], 154.1 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 387 (18) [$(M+1)^+$], 386 (67) [M^+], 294 (22), 291 (26), 278 (23), 277 (98) [M^+ – 4-H_3C=C_4H_4 + 2], 264 (24), 263 (100) [M^+ – (4-$H_3COC_6H_4O$)], 261 (19) [M^+ – (4-$H_3COC_6H_4O$) – 2H], 203 (18), 121 (25) [(Cp-CH=C(OH)-CH_3)$^+$], 56 (16) [Fe^+]. - HRMS ($C_{23}H_{22}FeO_2$): Calcd. 386.0969, found 386.0968. - Anal. ($C_{23}H_{22}FeO_2$): Calcd. C 71.52, H 5.74, found C 71.36, H 5.78.

4.5.10 1,1'-[1-(2-Methoxyphenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (69)

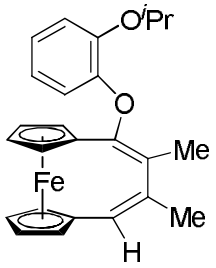


69

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 148 mg (1.2 mmol) of 2-methoxyphenol; 322 mg (0.8 mmol, 84 %) of **69** as a dark red crystal (m. p. 83.6-84.8 °C).

IR (ATR): $\tilde{\nu}$ = 3095 (w) cm^{-1}, 2970 (w), 1587 (w), 1495 (m), 1451 (m), 1373 (w), 1247 (s), 1210 (m), 1177 (w), 1127 (s), 1117 (s), 1067 (m), 1046 (w), 1026 (w), 951 (s), 910 (m), 862 (w), 839 (w), 815 (m), 778 (w), 734 (s). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.90 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^{4}J = 1.4 Hz, CH=C-CH_3), 3.95 (s, 3H, OCH_3), 4.10 + 4.14 (AA'BB', 2 x 2H, H_{Fc}), 4.50 (m, 4H, H_{Fc}), 6.12 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.54 (m, 1H, C_{Ar}), 6.70 (m, 1H, C_{Ar}), 6.82 (m, 2H, C_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.8 [C(OAr)=C*C*H_3], 25.2 (CH=C*C*H_3), 56.0 (O*C*H_3), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.3 (C_{Fc}H), 70.6 (C_{Fc}H), 75.0 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 111.9 (C_{Ar}H), 115.5 (C_{Ar}H), 120.7 (C_{Ar}H), 121.7 (C_{Ar}H), 124.1 [C(OAr)=*C*CH$_3$], 124.2 (*C*H=C), 136.6 (C_{qAr}), 145.6 (CH=*C*), 146.0 [*C*(OAr)=CCH$_3$], 149.3 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 387 (30) [$(M+1)^+$], 386 (92) [M^+], 294 (9), 277 (14), 264 (28), 263 (100) [M^+ – (2-$H_3OC_6H_4O$)], 261 (22) [M^+ – (2-$H_3OC_6H_4O$) – 2H], 205 (19), 203 (17), 121 (24) [(Cp-CH=C(OH)-CH_3)$^+$], 86 (53), 84 (80), 56 (15) [Fe^+]. - HRMS ($C_{23}H_{22}FeO_2$): Calcd. 386.0969, found 386.0967. - Anal. ($C_{23}H_{22}FeO_2$): Calcd. C 71.52, H 5.74, found C 71.33, H 5.86.

4.5.11 1,1'-[1-(2-*iso*-Propoxyphenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (70)

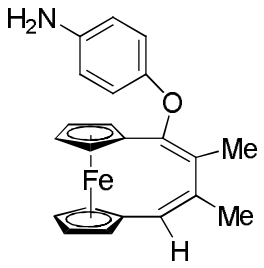


70

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 183 mg (1.2 mmol) of 2-(isopropoxy)phenol; 162 mg (0.4 mmol, 39 %) of **70** as a dark red solid (m. p. 86.6-87.9°C).

IR (ATR): $\tilde{\nu}$ = 3080 (w) cm^{-1}, 2973 (m), 1588 (m), 1495 (s), 1451 (m), 1284 (w), 1247 (s), 1211 (s), 1277 (m), 1127 (s), 1117 (s), 1067 (m), 1046 (m), 1026 (m), 951 (s), 910 (m), 863 (m), 815 (m), 779 (w), 746 (s), 734 (s). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.45 [d, 6H, ^3J = 6.1 Hz, OCH(CH_3)$_2$], 1.90 [s, 3H, C(OAr)=CCH_3], 1.96 (d, 3H, ^4J = 1.4 Hz, CH=CCH_3), 4.09 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.46 + 4.50 (AA'BB', 2 x 2H, H_{Fc}), 4.59 [hept, 1H, OC*H*(CH_3)$_2$], 6.12 (q, 1H, J = 1.4 Hz CH=C), 6.57 (m, 1H, H_{Ar}), 6.72 (m, 1H, H_{Ar}), 6.80 (m, 1H, H_{Ar}), 6.88 (m, 1H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.9 [C(OAr)=C*C*H$_3$], 22.4 [OCH(*C*H$_3$)$_2$], 25.2 (CH=C*C*H$_3$), 69.9 (C_{Fc}H), 70.0 (C_{Fc}H), 70.4 (C_{Fc}H), 70.6 (C_{Fc}H), 72.0 [O*C*H(CH_3)$_2$], 75.1 (C_{Fc}C), 77.8 (C_{Fc}C), 116.2 (C_{Ar}H), 117.1 (C_{Ar}H), 121.2 (C_{Ar}H), 121.7 (C_{Ar}H), 123.5 [C(OAr)=*C*CH$_3$], 124.0 (*C*H=C), 136.8 (C_{qAr}), 146.2 (CH=*C*), 147.2 [*C*(OAr)=CCH$_3$], 147.7 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 415 (23) [$(M+1)^+$], 414 (75) [M^+], 264 (35), 263 (100) [M^+ – (2-($iPrOC_6H_4O$)], 261 (22) [M^+ – (2-$iPrOC_6H_4O$) – 2H], 205 (18), 203 (17), 191 (11), 121 (18) [(Cp-CH=C(OH)-CH_3)$^+$], 56 (9) [Fe^+]. - HRMS ($C_{25}H_{26}FeO_2$) Calcd. 414.1482, found 414.1481. - Anal. ($C_{25}H_{26}FeO_2$): Calcd. C 72.47, H 6.33, found C 72.21, H 6.39.

4.5.12 1,1'-[1-(4-Aminophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (71)

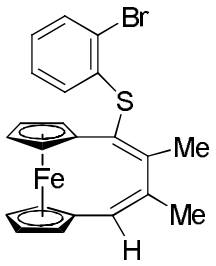


71

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 132 mg (1.2 mmol) of 4-aminophenol; 242 mg (0.7 mmol, 65 %) of **71** as a dark red crystal (m. p. 185.9-186.9 °C).

IR (ATR): $\tilde{\nu}$ = 3070 (w) cm^{-1}, 2920 (w), 1748 (w), 1610 (m), 1505 (s), 1437 (m), 1372 (w), 1260 (m), 1214 (s), 1164 (w), 1125 (m), 1069 (m), 1055 (m), 1024 (m), 927 (w), 908 (m), 861 (m), 829 (s), 801 (s), 770 (w), 721 (w). – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.89 [s, 3H, C(OAr)=CH_3], 1.96 (d, 3H, J = 1.4 Hz, CH=CCH_3), 3.33 (s, 2H, NH_2), 4.10 + 4.14 (AA'BB', 2 x 2H, H_{Fc}), 4.42 (m, 4H, H_{Fc}), 6.11 (q, 1H, ^{4}J = 1.0 Hz, CH=C), 6.61 (m, 4H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 (C(OAr)=CCH_3), 25.2 (CH=CCH_3), 69.9 ($C_{Fc}H$), 70.0 ($C_{Fc}H$), 70.6 ($C_{Fc}H$), 70.7 ($C_{Fc}H$), 74.9 ($C_{Fc}C$), 77.9 ($C_{Fc}C$), 116.2 ($C_{Ar}H$), 116.8 ($C_{Ar}H$), 123.4 (C(OAr)=CCH_3), 123.9 (CH=C), 136.9 (C_{qAr}), 140.3 (CH=C), 145.2 (C(OAr)=CCH_3), 149.4 (OC_{qAr}) ppm. -MS (70 eV): *m/z* (%) = 372 (12) [$(M+1)^+$], 371 (43) [M^+], 277 (13), 264 (24), 263 (100) [M^+ – (4-$H_2NC_6H_4O$)], 261 (20) [M^+ – (4-$H_2NC_6H_4O$)– 2H], 205 (12), 203 (12), 121 (16) [(Cp-CH=C(OH)-CH_3)$^+$], 57 (20), 56 (14) [Fe^+]. - HRMS ($C_{22}H_{21}FeNO$): Calcd. 371.0973, found 371.0972. - Anal. ($C_{22}H_{21}FeNO$): Calcd. C 71.17, H 5.70, N 3.77, found C 70.80, H 5.75, N 3.83.

4.5.13 1,1'-[1-(2-Bromothiophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (72)

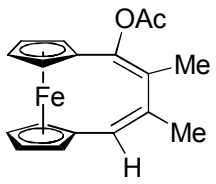


72

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 227 mg (1.2 mmol) of 2-bromothiohenol; 140 mg (0.3 mmol, 31 %) of **72** as a dark red solid (m. p. 107.7-109.5 °C).

IR (ATR): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 2962 (w), 1629 (w), 1572 (m), 1445 (s), 1425 (m), 1367 (w), 1325 (w), 1241 (m), 1103 (w), 1050 (m), 1035 (m), 1017 (s), 945 (w), 888 (w), 853 (s), 841 (s), 821 (m), 796 (s), 752 (s), 712 (s), 684 (w), 660 (w). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.01 (d, 3H, ^{4}J = 1.4 Hz, C=C-CH_3), 2.19 [s, 3H, C(SAr)=CCH_3], 4.08 + 4.16 (AA'BB', 2 x 2H, H_{Fc}), 4.35 + 4.41 (AA'BB', 2 x 2H, H_{Fc}), 6.15 (q, 1H, ^{4}J = 1.4 Hz, CH=C), 6.84 (m, 2H, H_{Ar}), 7.01 (m, 1H, H_{Ar}), 7.42 (m, 1H, H_{Ar}). - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 22.7 [C(SAr)=CCH_3], 24.9 (C=CCH_3), 69.9 (C_{Fc}H), 70.4 (C_{Fc}H), 70.8 (C_{Fc}H), 72.5 (C_{Fc}H), 76.6 (C_{Fc}C), 79.7 (C_{Fc}C), 122.0 [C(OAr)=CCH$_3$], 124.9 (CH=C), 126.0 (C_{Ar}H), 127.2 (C_{Ar}H), 127.9 (C_{qAr}), 129.0 (C_{Ar}H), 132.6 ($C_{A}H_r$), 137.4 (CH=C), 137.6 [C(SAr)=CCH$_3$], 143.8 (SC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 452 (34) [M(^{81}Br)$^{+}$], 451 (9) [(M+1)$^{+}$], 450 (36) [M(^{79}Br)$^{+}$], 264 (24), 263 (100) [M^{+} – (2-BrC_6H_4S)], 261 (14) [M^{+} – (2-BrC_6H_4S) – 2H], 205 (8), 192 (13), 191 (18), 189 (10), 165 (12), 108 (12), 57 (17), 56 (16) [Fe^{+}]. - HRMS ($C_{22}H_{19}$FeBrS): Calcd. 449.9740, found 449.9737. – Anal. ($C_{22}H_{19}$FeBrS): Calcd. C 58.56, H 4.24, found C 58.63, H 4.38.

4.5.14 1,1'-(1-Acetoxy-2,3-dimethyl-1,3-butadienylene)ferrocene (73)

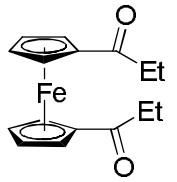


73

GP 1, 262 mg (1.0 mmol) of 1,1'-di(1-propynyl)ferrocene (**59**), 72 mg (1.2 mmol) of acetic acid; 150 mg (0.4 mmol, 44 %) of **73** as a dark red solid (m. p. 106.6-108.0 °C).

IR (ATR): $\tilde{\nu}$ = 3080 (w) cm^{-1}, 2922 (m), 2854 (w), 2077 (w), 1750 (s), 1648 (w), 1437 (m), 1369 (s), 1202 (s), 1113 (s), 1060 (s), 1022 (s), 918 (m), 859 (m), 836 (m), 806 (s), 745 (w), 727 (m), 660 (m). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.75 [s, 3H, C(OAc)=CCH_3], 1.91 (d, 3H, ^4J = 1.4 Hz, CH=CCH_3), 2.19 (s, 3H, OCOCH_3), 4.16 (m, 4H, H_{Fc}), 4.45 (m, 4H, H_{Fc}), 6.10 (q, 1H, ^4J = 1.0 Hz, CH=C) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 16.2 [C(OAc)=CCH_3], 20.8 (C=CCH_3), 24.7 (OCOCH_3), 69.5 (C_{Fc}H), 70.0 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 75.5 (C_{Fc}C), 77.6 (C_{Fc}C), 124.2 [C(OAc)=CCH$_3$], 124.5 (CH=C), 135.9 (CH=C), 143.5 [C(OAc)=CCH$_3$], 168.5 (OCOCH$_3$) ppm. - MS (70 eV): *m/z* (%) = 323 (17) [$(M+1)^+$], 322 (92) [M^+], 281 (20), 280 (100) [$M^+ - H_2C=C=O$], 279 (30), 251 (25), 129 (16), 121 (16) [$(Cp\text{-}CH=C(OH)\text{-}CH_3)^+$], 86 (13), 84 (20), 56 (13) [Fe^+]. - HRMS ($C_{18}H_{18}FeO_2$): Calcd. 322.0656, found 322.0655. Anal. ($C_{18}H_{18}FeO_2$): Calcd. C 67.10, H 5.63, found C 67.02, H 5.81.

4.5.15 1,1'-Dipropanoylferrocene (74)[109]



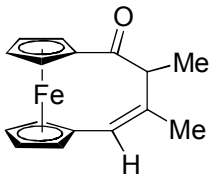
74

1,1'-Di(1-propynyl)ferrocene (**59**) (262 mg, 1.0 mmol) and trifluoracetic acid (0.054 mL, 1.2 mmol) in chlorobenzene (20 mL) was heated at reflux (oil bath 132 °C) for 15 h. After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel deactivated with 5 % triethylamine, PE/EE 4:1) to give **74** (172 mg, 0.58 mmol, 58 %) as a dark red crystal (m. p. 47.8-49.2 °C).

IR (ATR): $\tilde{\nu}$ = 3081 (w) cm^{-1}, 2967 (w), 2935 (m), 2910 (w), 2876 (w), 1668 (s), 1456 (s), 1414 (s), 1398 (m), 1372 (s), 1337 (s), 1240 (s), 1101 (s), 1048 (s), 1025 (s), 964 (m), 884 (m),

863 (m), 850 (w), 826 (m), 807 (s). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.17 (t, 6H, ^{3}J = 7.2 Hz, CH_3), 2.66 (q, 4H, ^{3}J = 7.2 Hz, CH_2), 4.46 + 4.76 (AA'BB', 2x4H, H_{Fc}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 8.1 ($COCH_2CH_3$), 32.9 ($COCH_2CH_3$), 70.4 ($C_{Fc}H$), 73.2 ($C_{Fc}H$), 80.2 ($C_{Fc}C$), 204.0 (CO) ppm. - MS (70 eV): *m/z* (%) = 299 (47) [$(M+1)^+$], 298 (100) [M^+], 296 (16), 213 (62) [$FcCO^+$], 186 (18) [FcH], 185 (27), 129 (26), 121 (66) [(Cp-CH=C(OH)-$CH_3)^+$], 120 (19), 94 (13), 56 (34) [Fe^+]. - HRMS ($C_{16}H_{18}FeO_2$): Calcd. 298.0656, found 298.0658. - Anal. ($C_{16}H_{18}FeO_2$): Calcd. C 64.45, H 6.09, found C 64.18, H 6.15.

4.5.16 1,1'-(2,3-Dimethyl-4-oxo-1-butenylene)ferrocene (75)



75

a) 1,1'-Di(1-propynyl)ferrocene (**59**) (262 mg, 1.0 mmol) and 4-chlorophenol (648 mg, 5.0 mmol) in *N*,*N*-dimethylformamide (20 mL) was heated at reflux (oil bath 157 °C) for 15 h. After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/dichloromethane 4:1) to give **75** (160 mg, 0.6 mmol, 57 %) as light yellow crystals (m. p. 154.0-154.9 °C).

b). 1,1'-Di(1-propynyl)ferrocene (**59**) (131 mg, 0.5 mmol) and 4-iodophenol (266 mg, 1.2 mmol) in *N*,*N*-dimethylformamide (3 mL) was subjected to microwave irradiation (157 °C, 300 W, 5 min RAMP, 30 min HOLD, CEM Discover). After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/dichloromethane 4:1) to give **75** (53 mg, 0.2 mmol, 38 %).

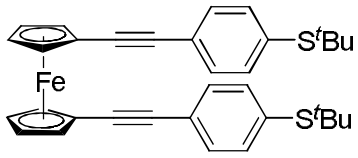
c). 1,1'-Di(1-propynyl)ferrocene (**59**) (131 mg, 0.5 mmol) and H_2O (45 mg, 2.5 mmol) in DMF (10 mL) was heated at reflux (oil bath 157 °C) for 15 h. After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/dichloromethane 4:1) to give **75** (101 mg, 0.4 mmol, 72 %).

d) 1,1'-[1-(4-Chlorophenoxy)-2,3-dimethyl-1,3-butadienylene]ferrocene (**60**) (149 mg, 0.38 mmol) was dissolved in THF (10 mL) and water (2 mL). 2 N HCl (2 mL) was added. The

solution was stirred at 65 °C for 12 h. After cooling to 25 °C water (10 mL) was added, and the solution was extracted with dichloromethane (3 x 10 mL). The organic layer was washed with 1 N NaOH (25 mL) to remove 4-chlorophenol, and dried over magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/ethyl acetate 4:1) to give **75** (42 mg, 0.15 mmol, 40 %).

IR (ATR): $\tilde{\nu}$ = 3080 (w) cm^{-1}, 2917 (w), 1666 (s, C=O), 1644 (s), 1456 (w), 1440 (s), 1374 (s), 1286 (w), 1232 (s), 1212 (w), 1167 (w), 1049 (s), 1028 (s), 987 (w), 970 (m), 930 (m), 879 (m), 862 (m), 847 (m), 819 (s), 743 (w). - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32 (d, 3H, ^3J = 7.2 Hz, CHC*H*$_3$), 2.01 (d, 3H, ^4J = 1.7 Hz, C=C-CH$_3$), 4.12 (m, 2H, H_{Fc}), 4.19 (m, 1H, H_{Fc}), 4.36 (m, 1H, H_{Fc}), 4.42 (m, 1H, H_{Fc}), 4.52 (m, 1H, H_{Fc}), 4.57 (m, 1H, H_{Fc}), 4.62 (q, 1H, ^3J = 6.8 Hz, C*H*CH$_3$), 4.74 (m, 1H, H_{Fc}), 5.74 (q, 1H, ^4J = 1.5 Hz, CH=C) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 13.8 (CH*C*H$_3$), 21.9 (C=C*C*H$_3$), 44.9 (*C*HCH$_3$), 67.1 (C_{Fc}H), 68.8 (C_{Fc}H), 69.3 (C_{Fc}H), 69.5 (C_{Fc}H), 69.9 (C_{Fc}H), 72.4 (C_{Fc}H), 72.7 (C_{Fc}H), 74.3 (C_{Fc}H), 77.3 (*C*$_{Fc}$C), 87.7 (*C*$_{Fc}$C), 117.9 (*C*H=C), 144.8 (CH=*C*), 209.7 (*C*O) ppm. - MS (70 eV): *m/z* (%) = 281 (31) [$(M+1)^+$], 280 (100) [M^+], 252 (57) [M^+ – CO], 251 (20), 237 (38) [M^+ – CO – CH_3], 186 (24), 121 (21), 115 (18), 56 (37) [Fe^+]. - HRMS ($C_{16}H_{16}FeO$) Calcd. 280.0551, found 280.0552. Anal. ($C_{16}H_{16}FeO$): Calcd. C 68.60, H 5.76, found C 68.59, H 5.88.

4.5.17 1,1'-Di[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocene (77)



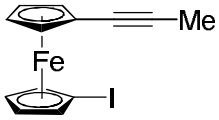
77

1,1'-Diiodoferrocene (**12**) (253 mg, 0.6 mmol) and 1-(*tert*-butylsulfanyl)-4-ethynylbenzene (**139**) (263 mg, 1.4 mmol) were dissolved in diisopropylamine (15 mL). After addition of $Pd(PPh_3)_2Cl_2$ (12 mg, 0.02 mmol, 3 mol%) and CuI (4 mg, 0.02 mmol, 2 mol%) the solution was heated at reflux (oil bath 95 °C) for 18 h. After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After

solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, hexane/dichloromethane 2:1) to give **77** (97 mg, 0.2 mmol, 33 %) as an orange solid (m. p. 162.2-163.0 °C).

IR (ATR): $\tilde{\nu}$ = 3104 (w), 2966 (m), 2924 (m), 2859 (m), 2223 (m, C≡C), 1681 (w), 1588 (m), 1489 (s), 1466 (s), 1392 (m), 1365 (s), 1293 (w), 1261 (w), 1205 (w), 1164 (s), 1100 (s), 1039 (w), 1028 (s), 1017 (s), 917 (s), 854 (w), 841 (s), 820 (s), 724(m) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32 [s, 18H, $C(CH_3)_3$], 4.36 + 4.58 (AA'BB', 2x4H, $C_{Fc}H$), 7.44 (m, 8H, $C_{Ar}H$). - ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 31.0 [$C(CH_3)_3$], 46.3 [$C(CH_3)_3$], 66.7 ($C_{Fc}C$), 71.1 ($C_{Fc}H$), 73.1 ($C_{Fc}H$), 86.1 (*C*C), 89.0 (*C*C), 124.1 (C_{qAr}), 131.3 ($C_{Ar}H$), 132.5 (C_{qAr}), 137.2 ($C_{Ar}H$). - MS (70 eV): *m/z* (%) = 564 (18) [$(M+2)^+$], 563 (39) [$(M+1)^+$], 562 (100) [M^+], 450 (34), 449 (19), 448 (17), 57 (62), 56 (14) [Fe^+]. - HRMS ($C_{34}H_{34}FeS_2$): Calcd. 562.1451, found 562.1453. - Anal. ($C_{34}H_{34}FeS_2$): Calcd. C 72.58, H 6.09, found C 72.61, H 6.46.

4.5.18 1-Iodo-1'-(1-propynyl)ferrocene (78)



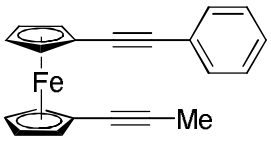
78

At –78 °C freshly prepared lithium diisopropylamide (6.4 mmol, 1.1 equiv.) in 10 mL of tetrahydrofuran was added to the mixture of 1-ethynyl-1'-iodoferrocene (**18**) (1.954 g, 5.8 mmol) and iodo-methane (1.47 mL, 23.3 mmol) in tetrahydrofuran (40 mL). The mixture was stirred for 1 h at this temperature and then for 1 h at 25 °C. Water (30 mL) was added, and the mixture was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine and dried over magnesium sulfate. After filtration and solvent removal at reduced pressure, a dark red liquid was obtained, which was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) **78** (1.39 g, 3.9 mmol, 66 %) was obtained as a dark red solid (m. p. 52.2 – 53.5 °C).

IR (ATR): $\tilde{\nu}$ = 3097 (m), 2909 (m), 2216 (w, C≡C), 1674 (m), 1463 (m), 1401 (m), 1377 (m), 1343 (m), 1263 (m), 1207 (w), 1137 (m), 1063 (m), 1025 (s), 1009 (m), 980 (m), 877 (m),

861 (s), 842 (s), 822 (s) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.96 (s, 3H, CC*CH*$_3$), 4.15 + 4.18 (AA'BB', 2 x 2H, H_{Fc}), 4.32 + 4.40 (AA'BB', 2 x 2H, H_{Fc}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 4.5 (CH_3), 41.1 ($C_{Fc}I$), 68.8 ($C_{Fc}C$), 70.7 ($C_{Fc}H$), 71.4 ($C_{Fc}H$), 73.6 ($C_{Fc}H$), 76.0 ($C_{Fc}H$), 76.1 (C*C*CH$_3$), 83.1 (*C*CCH$_3$) ppm. - MS (70 eV): *m/z* (%) = 351 (29) [$(M+1)^+$], 350 (100) [M^+], 348 (11), 183 (11), 167 (27), 166 (25), 165 (42), 152 (16), 77 (15), 56 (21) [Fe^+]. - HRMS ($C_{13}H_{11}FeI$): Calcd. 349.9255; found 349.9257. - Anal. ($C_{13}H_{11}FeI$): Calcd. C 44.61, H 3.17; found C 44.59, H 3.02.

4.5.19 1-(Phenylethynyl)-1'-(1-propynyl)ferrocene (79)



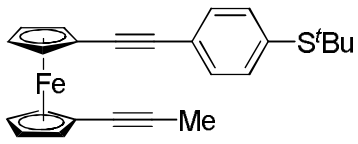
79

$Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol, 3 mol%) and CuI (6 mg, 0.03 mmol, 3 mol%) were added to a solution of 1-iodo-1'-(1-propynyl)ferrocene (**78**) (350 mg, 1.0 mmol) and phenylethyne (123 mg, 1.2 mmol) in diisopropylamine (15 mL). The mixture was stirred at reflux (oil bath 90 °C) for 20 h. After cooling to 25 °C the mixture was filtered through a 3 cm thick layer of silica, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1). **79** (275 mg, 0.8 mmol, 85 %) was obtained as a red shiny crystal (m. p. 115.0 – 116.8 °C).

IR (ATR): $\tilde{\nu}$ = 3094 (w), 2923 (w), 2362 (w, C≡C), 2208 (w, C≡C), 1598 (w), 1497 (m), 1459 (w), 1440 (w), 1377 (w), 1296 (w), 1260 (w), 1205 (w), 1162 (w), 1071 (w), 1053 (w), 1028 (s), 981 (w), 919 (m), 898 (w), 875 (w), 861 (w), 844 (w), 821 (s), 756 (s), 690 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.85 (s, 3H, CH_3), 4.22 + 4.28 (AA'BB', 2 x 2H, H_{Fc}), 4.40 + 4.50 (AA'BB', 2 x 2H, H_{Fc}), 7.31 (m, 3H, H_{Ar}), 7.34 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (CH_3), 66.7 ($C_{Fc}C$), 68.4 ($C_{Fc}C$), 70.2 ($C_{Fc}H$), 70.7 ($C_{Fc}H$), 72.5 ($C_{Fc}H$), 72.7 ($C_{Fc}H$), 76.1 (CC), 82.8 (CC), 86.4 (CC), 87.4 (CC), 124.0 (C_{qAr}), 127.6 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 131.4 ($C_{Ar}H$) ppm. - MS (70 eV): *m/z* (%) = 325 (25) [$(M+1)^+$], 324 (100) [M^+], 165

(17), 56 (9) [Fe^+]. - HRMS ($C_{21}H_{16}Fe$): Calcd. 324.0601; found 324.0600. - Anal. ($C_{21}H_{16}Fe$): Calcd. C 77.80, H 4.97; found C 77.70, H 4.99.

4.5.20 1-[4-(*tert*-Butylsulfanyl)phenylethynyl]-1'-(1-propynyl)ferrocene (80)

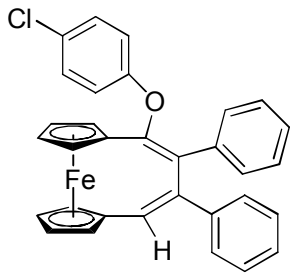


80

$Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol, 3 mol%) and CuI (8 mg, 0.04 mmol, 3 mol%) were added to a solution of 1-iodo-1'-(1-propynyl)ferrocene (**78**) (420 mg, 1.2 mmol) and 1-(*tert*-butylsulfanyl)-4-ethynylbenzene (**139**) (274 mg, 1.4 mmol) in diisopropylamine (15 mL). The mixture was stirred at reflux (oil bath 90 °C) for 48 hours. After cooling to 25 °C the mixture was filtered through a 3 cm thick layer of silica, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1). **80** (230 mg, 0.6 mmol, 46 %) was obtained as a red solid (m. p. 99.0 – 100.7 °C).

IR (ATR): $\tilde{\nu}$ = 3095 (w), 2958 (m), 2230 (m, C≡C), 2207 (m, C≡C), 1668 (w), 1589 (m), 1490 (m), 1456 (m), 1394 (m), 1363 (s), 1298 (w), 1263 (w), 1207 (w), 1164 (s), 1096 (m), 1065 (w), 1032 (s), 1014 (m), 923 (m), 875 (m), 831 (s), 820 (s), 724 (w), 666 (w) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.29 [s, 9H, $C(CH_3)_3$], 1.83 (s, 3H, $CCCH_3$), 4.21 + 4.28 (AA'BB', 2 x 2H, H_{Fc}), 4.39 + 4.50 (AA'BB', 2 x 2H, H_{Fc}), 7.46 (m, 4H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 ($C(CH_3)_3$), 30.9 ($CCCH_3$), 46.3 ($C(CH_3)_3$), 66.4 ($C_{Fc}C$), 68.6 ($C_{Fc}C$) 70.2 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 72.5 ($C_{Fc}H$), 72.7 ($C_{Fc}H$), 76.0 (CC), 82.8 (CC), 85.9 (CC), 89.2 (CC), 124.4 (C_{Ar}), 131.2 ($C_{Ar}H$), 132.4 (C_{qAr}), 137.2 ($C_{Ar}H$) ppm. - MS (70 eV): *m/z* (%) = 413 (30) [$(M+1)^+$], 412 (100) [M^+], 357 (20), 356 (77), 355 (13), 265 (12), 57 (40) [Fe^+]. - HRMS ($C_{25}H_{24}FeS$): Calcd. 412.0948, found 412.095. - Anal. ($C_{25}H_{24}FeS$): Calcd. C 72.82, H 5.87, found C 72.89, H 6.07.

4.5.21 1,1´-[1-(4-Chlorophenoxy)-2,3-diphenyl-1,3-butadienylene]ferrocene (81)

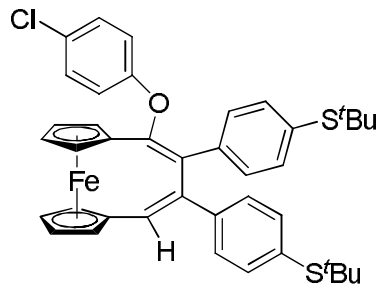


81

GP 1, 193 mg (0.5 mmol) of 1,1'-di(phenylethynyl)ferrocene(**76**)[84] 78 mg (0.6 mmol) of 4-chlorophenol; 153 mg (0.30 mmol, 59 %) of **81** as a red solid (m. p. 245 °C, dec.).

IR (ATR): $\tilde{\nu}$ = 3020 (w), 2925 (w), 1878 (w), 1623 (m), 1586 (m), 1483 (s), 1444 (m), 1403 (w), 1380 (w), 1328 (w), 1290 (w), 1225 (m), 1214 (s), 1159 (m), 1101 (m), 1085 (s), 1059 (m), 1026 (s), 1008 (m), 931 (w), 911 (w), 899 (m), 869 (m), 843 (w), 830 (s), 810 (s), 762 (s), 723 (s), 698 (s), 673 (m) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 4.26 (br. 4H, H_{Fc}), 4.60 + 4.74 (AA'BB', 2 x 2H, H_{Fc}), 6.80 (s, 1H, CH=C), 6.88 (m, 2H, H_{Ar}), 7.10 (m, 4H, H_{Ar}), 7.22 (m, 6H, H_{Ar}), 7.37 (m, 2H, H_{Ar}) ppm. - ^{1}H-NMR ($CDCl_3$, 400 MHz, –50 °C): δ = 3.62 (br s, H_{Fc}), 3.77 (br s, H_{Fc}), 4.21 (br s, H_{Fc}), 4.31 (br s, H_{Fc}), 4.80 (br s, H_{Fc}), 4.84 (br s, H_{Fc}), 4.95 (br s, H_{Fc}), 5.14 (br s, H_{Fc}), 6.83 (s, 1H, CH=C), 6.91 (m, 2H, H_{Ar}), 7.11 (m, 4H, H_{Ar}), 7.18 (m, 6H, H_{Ar}), 7.39 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 70.5 ($C_{Fc}H$), 70.8 ($C_{Fc}C$), 71.0 ($C_{Fc}H$), 73.5 ($C_{Fc}H$), 77.1 ($C_{Fc}C$), 77.2 ($C_{Fc}H$), 118.0 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 126.8 ($C_{Ar}C$), 126.9 ($C_{Ar}H$), 127.4 ($C_{Ar}C$), 127.8 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 130.8 (*C*H=C), 138.7 (C(OAr)=*C*), 141.1 ($C_{Ar}C$), 143.1 (CH=*C*), 149.3 (*C*(OAr)=C), 156.2 (OC_{qAr}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz, –50 °C): δ = 67.2 ($C_{Fc}H$), 67.7 ($C_{Fc}H$), 68.0 ($C_{Fc}H$), 68.5 ($C_{Fc}H$), 72.8 ($C_{Fc}C$), 74.0 ($C_{Fc}H$), 74.4 ($C_{Fc}H$), 75.3 ($C_{Fc}H$), 75.9 ($C_{Fc}H$), 76.6 ($C_{Fc}C$), 117.9 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 126.76 ($C_{Ar}C$), 126.86 ($C_{Ar}H$), 126.92 ($C_{Fc}H$), 127.8 ($C_{Ar}C$), 127.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 131.1 (*C*H=C), 138.2 (C(OAr)=*C*), 140.2 ($C_{Ar}C$), 142.6 (CH=*C*), 149.1 (*C*(OAr)=C), 155.7 (OC_{qAr}) ppm. -MS (70 eV): *m/z* (%) = 516 (31) [M^+ (^{37}Cl)], 515 (30) [$(M+1)^+$], 514 (80) [M^+ (^{35}Cl)], 388 (30), 387 (100) [$M^+ - ClC_6H_4O$], 386 (61), 310 (18), 265 (12), 253(15), 252 (19), 165 (24), 56 (11) [Fe^+]. - HRMS ($C_{32}H_{23}Fe^{35}ClO$): Calcd. 514.0787, found 514.0790. Anal. ($C_{32}H_{23}ClFeO$): Calcd. C 74.66, H 4.50, found C 74.47, H 4.85.

4.5.22 1,1'-{1-(4-Chlorophenoxy)-2,3-di[4-(*tert*-butylsulfanyl)phenyl]-1,3-buta-dienylene}ferrocene (82)



82

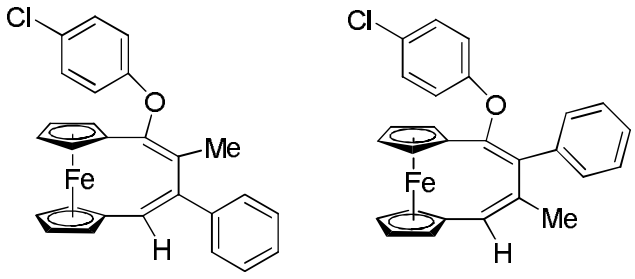
GP 1, 164 mg (0.3 mmol) of 1,1'-Di[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocene (**77**), 50 mg (0.4 mmol) of 4-chlorophenol; 101 mg (0.2 mmol, 46 %) of **82** as a light red solid (m. p. 252 °C, dec.).

IR (ATR): $\tilde{\nu}$ = 3020 (w), 2959 (m), 1619 (m), 1588 (m), 1485 (s), 1454 (m), 1392 (w), 1362 (m), 1267 (m), 1255 (m), 1217 (s), 1166 (m), 1102 (m), 1089 (s), 1055 (w), 1039 (m), 1029 (m), 1013 (s), 934 (w), 915 (w), 901 (m), 875 (w), 851 (m), 832 (s), 803 (s), 790 (m), 751 (m), 725 (m), 712 (w), 684 (w), 670 (m) cm^{-1}. - ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 1.13 [s, 9H, $C(CH_3)_3$], 1.18 [s, 9H, $C(CH_3)_3$], 4.3 (br m, 4H, H_{Fc}), 4.60 (br m, 2H, H_{Fc}), 4.75 (br m, 2H, H_{Fc}), 6.84 (s, 1H, CH=C), 6.86 (m, 2H, H_{Ar}), 7.13 (m, 2H, H_{Ar}), 7.23 (m, 4H, H_{Ar}), 7.28 (m, 2H, H_{Ar}), 7.33 (m, 2H, H_{Ar}) ppm. - ^{1}H-NMR ($CDCl_3$, 400 MHz, –50 °C): δ = 1.13 [s, 9H, $C(CH_3)_3$], 1.18 [s, 9H, $C(CH_3)_3$], 3.63 (br s, 1H, H_{Fc}), 3.78 (br s, 1H, H_{Fc}), 4.19 (br s, 1H, H_{Fc}), 4.31 (br s, 1H, H_{Fc}), 4.83 (br s, 1H, H_{Fc}), 4.87 (br s, 1H, H_{Fc}), 4.97 (br s, 1H, H_{Fc}), 5.14 (br s, 1H, H_{Fc}), 6.87 (s, 1H, CH=C), 6.89 (m, 2H, H_{Ar}), 7.15 (m, 2H, H_{Ar}), 7.24 (m, 4H, H_{Ar}), 7.30 (m, 2H, H_{Ar}), 7.35 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 30.8 [C(CH_3)$_3$], 30.9 [C(CH_3)$_3$], 45.8 [C(CH_3)$_3$], 45.9 [C(CH_3)$_3$], 71-72.3 (br, 8 $C_{Fc}H$), 73.2 ($C_{Fc}C$), 76.7 ($C_{Fc}C$), 118.0 ($C_{Ar}H$), 126.6 ($C_{Ar}H$), 126.9 ($C_{Ar}C$), 127.0 ($C_{Ar}C$), 128.4 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 130.7 (CH=C), 131.0 [C(OAr)=C], 131.5($C_{Ar}H$), 136.9 ($C_{Ar}H$), 137.2 ($C_{Ar}H$), 139.4 (CH=C), 140.4 (C_{qAr}), 143.6 (C_{qAr}), 150.3 [C(OAr)=C], 156.0 (OC_{qAr}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz, –50 °C, C,H-COSY): δ = 30.4 [2 C(CH_3)$_3$], 46.0 [2 C(CH_3)$_3$], 67.2 ($C_{Fc}H$), 68.0 (2 $C_{Fc}H$), 68.7 ($C_{Fc}H$), 72.4 ($C_{Fc}C$), 74.3 ($C_{Fc}H$), 74.7 ($C_{Fc}H$), 75.5 ($C_{Fc}H$), 76.0 ($C_{Fc}H$), 76.2 ($C_{Fc}C$), 118.0 ($C_{Ar}H$), 126.1 ($C_{Ar}H$), 126.2 ($C_{Ar}C$), 126.7 ($C_{Ar}C$), 128.0 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 129.7 (CH=C), 129.8 [C(OAr)=C], 132.0 ($C_{Ar}H$), 137.2 ($C_{Ar}H$), 137.4

($C_{Ar}H$), 139.0 (CH=*C*), 139.4 (C_{qAr}), 143.2 (C_{qAr}), 150.1 [*C*(OAr)=C], 155.4 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 692 (51) [M^+ (^{37}Cl)], 691 (47) [$(M+1)^+$], 690 (100) [M^+ (^{35}Cl)], 563 (14) [$M^+ - ClC_6H_4O$], 474 (27), 450 (25), 419 (26), 418 (84), 417 (24), 327 (16), 326 (17), 57 (49). - HRMS ($C_{40}H_{33}FeClOS_2$): Calcd. 690.1480, found 690.1263. - Anal. ($C_{40}H_{39}ClFeOS_2$): Calcd. C 69.51, H 5.69, found C 69.66, H 6.00.

Variable-temperature (VT) NMR spectroscopy measurements: First, ^1H and ^{13}C NMR spectra of the product (15 $mgmL^{-1}$, $CDCl_3$, TMS, Bruker DPX 400 MHz spectrometer) were recorded at 295 °C. VT experiments were conducted in the temperature range 223-323 K in 10 K steps. The free energy of activation ($\Delta G^{\neq}$) was estimated from the coalescence temperature (T_c) and $\Delta\nu$ of the respective resonance: $\Delta G^{\neq}(T_c) = RT_c(22.96+\ln(T_c/\Delta\nu)$.[97] For the simulation of NMR spectra the DNMR line-shape tool of the TOPSPIN 2.1 software was used.[98] The simulations were performed in the range of δ = 2.5 to 6 ppm. Two spin systems were defined, one for each ferrocenyl ring (δ = 3.63, 4.19, 4.83, 4.97 ppm and δ = 3.78, 4.31, 4.87, 5.14 ppm). At each temperature the line-broadening factor was estimated from the half width of the olefinic proton at δ = 6.84 (s, 1H). Coupling constants were fitted in the spectrum recorded at 223 K. In the simulations at higher temperatures the coupling constants were set to be constant. At each temperature the rate constant was first approximated. Then the intensities and the chemical shifts were fitted alternately. Finally, a fit was performed on all parameters. All simulated spectra had an overlap of more than 96 % with the original spectra.

4.5.23 1,1´-[1-(4-Chlorophenoxy)-2-methyl-3-phenyl-1,3-butadienylene]ferrocene (83) and 1,1´-[1-(4-Chlorophenoxy)-3-methyl-2-phenyl-1,3-butadienylene]ferrocene (84)



83 **84**

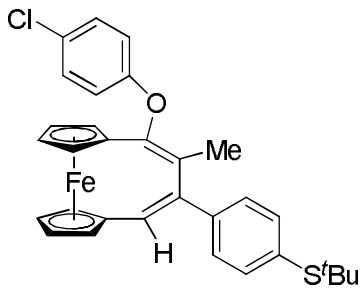
GP 1, 133 mg (0.4 mmol) of 1-(Phenylethynyl)-1'-(1-propynyl)ferrocene (**79**), 65 mg (0.5 mmol) of 4-chlorophenol; column chromatography (30 x 3 cm, silica gel, petrol

ether/dichloromethane 4:1). I. R_f = 0.41: 66 mg (0.15 mmol, 36 %) of **83** as a red solid (m. p. 152.0 – 153.5 °C), II. R_f = 0.35: 77 mg (0.17 mmol, 42 %) of **84** as a red crystal (m. p. 228 °C, dec.).

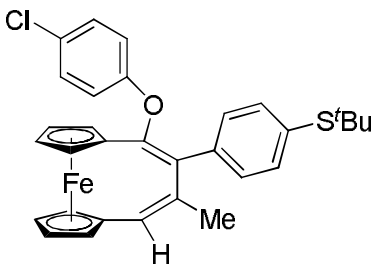
84: IR (ATR): $\tilde{\nu}$ = 3054 (w), 2922 (w), 2851 (w), 1639 (w), 1590 (s), 1486 (s), 1440 (m), 1375 (w), 1308 (w), 1280 (w), 1260 (m), 1227 (s), 1172 (w), 1157 (m), 1098 (m), 1084 (s), 1052 (m), 1041 (m), 1024 (s), 1009 (m), 959 (w), 920 (w), 897 (m), 867 (m), 839 (w), 821 (s), 808 (s), 776 (s), 724 (s), 700 (s) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.72 (s, 3H, CH_3), 4.16 + 4.27 (AA'BB', 2 x 2H, H_{Fc}), 4.53 + 4.57 (AA'BB', 2 x 2H, H_{Fc}), 6.54 (s, 1H, CH=C), 6.83 (m, 2H, H_{Ar}), 7.18 (m, 2H, H_{Ar}), 7.32 (m, 1H, H_{Ar}), 7.34 (m, 4H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz, DEPT): δ = 17.4 (CH_3), 70.5 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.5 ($C_{Fc}H$), 74.0 ($C_{Fc}C$), 77.2 ($C_{Fc}H$), 77.3 ($C_{Fc}C$), 117.2 ($C_{Ar}H$), 122.8 [C(OAr)=$C$$CH_3$], 126.4 ($C_{Ar}H$), 126.5 ($C_{qAr}$), 127.2 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 129.5 ($C$H=C), 142.3 (CH=$C$), 143.3 ($C_{qAr}$), 148.1 ($C$(OAr)=$CCH_3$), 157.3 ($OC_{qAr}$) ppm. - MS (70 eV): *m/z* (%) = 454 (37) [M^+ (^{37}Cl)], 453 (31) [$(M+1)^+$], 452 (100) [M^+ (^{35}Cl)], 326 (23), 325 (93) [M^+ – ClC_6H_4O], 324 (28), 310 (43), 265 (10), 253(11), 252 (14), 165 (11), 56 (8) [Fe^+]. - HRMS ($C_{27}H_{21}Fe^{35}ClO$): Calcd. 452.0630, found 452.0628. Anal. ($C_{27}H_{21}ClFeO$): Calcd. C 71.63, H 4.68, found C 71.51, H 4.62.

85: IR (ATR): $\tilde{\nu}$ = 3081 (w), 2946 (w), 1615 (w), 1590 (s), 1485 (s), 1437 (m), 1379 (w), 1316 (w), 1284 (w), 1256 (m), 1228 (s), 1165 (m), 1102 (m), 1088 (s), 1046 (w), 1026 (s), 1007 (m), 975 (w), 915 (m), 876 (w), 852 (m), 825 (s), 804 (s), 760 (s), 744 (w), 723 (w), 700 (s), 667 (s) cm^{-1}. – ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.71 (d, 3H, ^4J = 1.4 Hz, CH_3), 4.20 (m, 4H, H_{Fc}), 4.49 + 4.59 (AA'BB', 2 x 2H, H_{Fc}), 6.32 (q, 1H, ^4J = 1.4 Hz, CH=CCH_3), 6.75 (m, 2H, H_{Ar}), 7.14 (m, 2H, H_{Ar}), 7.21 (m, 4H, H_{Ar}), 7.24 (m, 1H, H_{Ar}) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.1 (CH=C$C$$H_3$), 70.5 ($C_{Fc}H$), 70.6 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.1 ($C_{Fc}H$), 73.8 ($C_{Fc}C$), 77.8 ($C_{Fc}C$), 117.9 ($C_{Ar}H$), 126.2 ($C_{Ar}H$), 126.5 (C(OAr)=$C$Ar), 126.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 129.4 ($C$H=C), 136.2 (CH=$C$), 139.0 ($C_{qAr}$), 146.7 ($C$(OAr)=CAr), 156.1 ($OC_{qAr}$) ppm. - MS (70 eV): *m/z* (%) = 454 (37) [M^+ (^{37}Cl)], 453 (31) [$(M+1)^+$], 452 (99) [M^+ (^{35}Cl)], 326 (26), 325 (100) [M^+ – ClC_6H_4O], 324 (21), 310 (21), 253 (11), 252 (14), 165 (12), 111 (16), 56 (13) [Fe^+]. - HRMS ($C_{27}H_{21}Fe^{35}ClO$): Calcd. 452.0630, found 452.0628. - Anal. ($C_{27}H_{21}ClFeO$): Calcd. C 71.63, H 4.68, found C 70.85, H 4.62.

4.5.24 1,1´-{2-[4-(*tert*-Butylsulfanyl)phenyl]-1-(4-chlorophenoxy)-3-methyl-1,3-butadienylene}ferrocene (85) and 1,1´-{3-[4-(*tert*-Butylsulfanyl)phenyl]-1-(4-chlorophenoxy)-2-methyl-1,3-butadienylene}ferrocene (86)



85



86

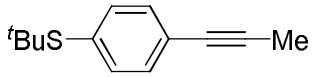
GP 1, 206 mg (0.5 mmol) of 1-[4-(*tert*-butylsulfanyl)phenylethynyl]-1´-(1-propynyl)ferrocene (**80**), 78 mg (0.6 mmol) of 4-chlorophenol; column chromatography (30 x 3 cm, silica gel, petroleum ether/ dichloromethane 4:1). I. R_f = 0.31: 126 mg (0.2 mmol, 47 %) of **85** as a dark red solid (m. p. 152.9 – 153.4 °C), II. R_f = 0.26: 79 mg (0.2 mmol, 29 %) of **86** as a dark red crystal (m. p. 184.9 – 186.2 °C).

86: IR (ATR): $\tilde{\nu}$ = 3094 (w), 2957 (m), 2920 (m), 2856 (m), 1645 (w), 1587 (m), 1483 (s), 1455 (m), 1396 (w), 1363 (m), 1265 (m), 1240 (m), 1223 (s), 1160 (m), 1101 (m), 1085 (s), 1057 (m), 1044 (m), 1026 (m), 1009 (m), 960 (w), 896 (m), 871 (w), 859 (w), 848 (w), 833 (s), 818 (s), 806 (s), 751 (w), 721 (w), 660 (m) cm^{-1}. - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.34 [s, 9H, $C(CH_3)_3$], 1.72 (s, 3H, $C{=}CCH_3$), 4.17 + 4.28 (AA'BB', 2 x 2H, H_{Fc}), 4.52 + 4.58 (AA'BB', 2 x 2H, H_{Fc}), 6.59 (s, 1H, CH=C), 6.82 (m, 2H, H_{Ar}), 7.19 (m, 2H, H_{Ar}), 7.33 (m, 2H, H_{Ar}), 7.52 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.5 ($CH{=}C\mathit{C}H_3$), 31.0 [$C(\mathit{C}H_3)_3$], 46.1 [$\mathit{C}(CH_3)_3$], 70.6 ($C_{Fc}H$), 71.0 ($C_{Fc}H$), 71.5 ($C_{Fc}C$), 71.6 ($\mathit{C}_{Fc}H$), 73.9 ($C_{Fc}C$), 77.2 ($\mathit{C}_{Fc}H$), 117.2 ($C_{Ar}H$), 122.5 [$C(OAr){=}\mathit{C}_{Ar}$], 126.4 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.4 ($\mathit{C}_{Ar}C$), 129.5 ($C_{Ar}H$), 131.5 ($\mathit{C}_{Ar}C$), 137.6 ($CH{=}\mathit{C}$), 141.6 ($\mathit{C}H{=}C$), 143.7 (C_{qAr}), 148.2 [$\mathit{C}(OAr){=}CAr$], 155.1 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 542 (42) [M^+ (^{37}Cl)], 541 (37) [$(M+1)^+$], 540 (100) [M^+ (^{35}Cl)], 413 (17) [$M^+ - ClC_6H_4O$], 357 (23), 356 (16), 324 (33), 265 (11), 57 (60), 56 (8) [Fe^+]. - HRMS ($C_{31}H_{29}{}^{35}ClFeOS$): Calcd. 540.0977, found 540.0981. Anal. ($C_{31}H_{29}ClFeOS$): Calcd. C 68.83, H 5.40, found C 69.20, H 5.84.

87: IR (ATR): $\tilde{\nu}$ = 3095 (w), 2962 (m), 2919 (w), 1617 (w), 1588 (m), 1485 (s), 1447 (m), 1362 (m), 1332 (w), 1296 (w), 1281 (w), 1253 (m), 1227 (s), 1170 (m), 1101 (m), 1086 (s), 1045 (m), 1027 (s), 1010 (s), 977 (m), 913 (m), 849 (m), 821 (s), 805 (s), 738 (w), 702 (m), 669 (m) cm^{-1}. - ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.29 (s, 9H, $C(CH_3)_3$), 1.70 (d, 3H, ^4J = 1.4 Hz, C=CCH_3), 4.20 (m, 4H, H_{Fc}), 4.48 + 4.58 (AA'BB', 2 x 2H, H_{Fc}), 6.33 (q, 1H, ^4J = 1.0 Hz, CH=C), 6.75 (m, 2H, H_{Ar}), 7.16 (m, 4H, H_{Ar}), 7.41 (m, 2H, H_{Ar}) ppm. - ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.1 (CH=C*C*H_3), 31.0 [C(*C*H_3)$_3$], 46.0 [*C*(CH_3)$_3$], 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 70.8 (C_{Fc}H), 71.1 (*C*$_{Fc}$H), 73.6 (C_{Fc}C), 77.6 (*C*$_{Fc}$C), 117.9 (C_{Ar}H), 126.5 (C_{Ar}H), 126.6 [C(OAr)=*C*$_{Ar}$], 128.2 (C_{Ar}H), 128.9 (*C*$_{Ar}$C), 129.4 (C_{Ar}H), 131.0 (*C*$_{Ar}$C), 135.9 (CH=*C*), 137.2 (*C*H=C), 139.6 (C_{qAr}), 147.3 [*C*(OAr)=CAr], 156.0 (OC_{qAr}) ppm. - MS (70 eV): *m/z* (%) = 542 (42) [M^+ (^{37}Cl)], 541 (38) [$(M+1)^+$], 540 (100) [M^+ (^{35}Cl)], 413 (52) [$M^+ - ClC_6H_4O$], 412 (67), 357 (48), 356 (65), 265 (16), 57 (58), 56 (11) [Fe^+]. - HRMS ($C_{31}H_{29}{}^{35}ClFeOS$): Calcd. 540.0977, found 540.0982. - Anal. ($C_{31}H_{29}ClFeOS$): Calcd. C 68.83, H 5.40, found C 68.79, H 5.62.

4.6 Alkynes Metathesis

4.6.1 1-(*tert*-Butylsulfanyl)-4-(1-propynyl)benzene (101)[108]

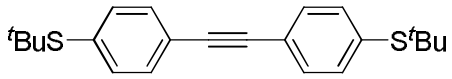


101

1-(*tert*-Butylsulfanyl)-4-(trimethylsilylethynyl)benzene (**139**) (0.69 g, 2.6 mmol) was dissolved in tetrahydrofuran (30 mL). At -78 °C MeLi (1.6 M in diethyl ether, 2.5 mL, 3.9 mmol) was added dropwise and stirred for 20 h at 25 °C. After addition of iodomethane (0.3 mL, 5.3 mmol) at −78 °C, the solution was stirred for 5 h at 25 °C. Water (20 mL) was added and stirred for 5 min. The layers were separated. The aqueous layer was extracted with dichloromethane (3 x 20 mL). The collected organic layers were washed with brine (20 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **101** (0.49 g, 2.4 mmol, 91 %) as a white solid, which was recrystallized from hexane/dichloromethane (3:1) as a colorless crystal (m. p. 82.0 – 83.5 °C).

IR (ATR): $\tilde{\nu}$ = 3041 (w), 2960 (m), 2921 (m), 2855 (m), 2251 (w) 1692 (w), 1590 (w), 1486 (s), 1470 (m), 1393 (w), 1375 (w), 1363 (s), 1263 (w), 1169 (m), 1151 (s), 1096 (w), 1019 (w), 970 (w), 934 (w), 845 (s), 745 (w) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (s, 9H, C(CH_3)$_3$), 2.08 (s, 3H, CH_3), 7.35 + 7.46 (AA'BB', 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (*C*H_3), 30.9 (C(*C*H_3)$_3$), 46.2 (*C*(CH$_3$)$_3$), 79.2 (*C*C), 87.5 (C*C*), 124.5 (C_{Ar}C), 131.4 (C_{Ar}H), 132.2 (C_{Ar}C), 137.2 (C_{Ar}H) ppm. – MS (70 eV): *m/z* (%) = 204 (26) [M^+], 149 (15), 148 (100), 147 (31), 115 (32), 57 (27) [tBu$^+$].- HRMS ($C_{13}H_{16}S$): Calcd. 204.0973, found 204.0974. – Anal. ($C_{13}H_{16}S$): Calcd. C 76.41, H 7.89; found C 76.45, H 7.67.

4.6.2 Bis(4-*tert*-butylsulfanylphenyl)ethyne (102)[46]

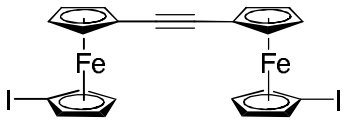


102

1-(*tert*-Butylsulfanyl)-4-(1-propynyl)benzene (**101**) (0.20 g, 1.0 mmol) was dissolved in chlorobenzene (20 mL). After addition of $Mo(CO)_6$ (13 mg, 0.05 mmol, 5 mol %) and 2-fluorophenol (112 mg, 1 mmol) the solution was heated at reflux (oil bath 132 °C) for 4 h. After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **102** (63 mg, 0.2 mmol, 36 %) as a colorless shiny crystal (m. p. 113.5-115.0 °C).

IR (ATR): $\tilde{\nu}$ = 3054 (w), 2958 (s), 2920 (s), 2853 (s), 2108 (w), 1594 (m), 1497 (m), 1457 (s), 1397 (m), 1361 (s), 1310 (w), 1292 (w), 1263 (w), 1163 (s), 1105 (m), 1093 (m), 1012 (s), 934 (w), 839 (s), 831 (s), 736 (w), 721 (m) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (s, 9H, C(CH_3)$_3$), 7.49 (m, 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 31.3 (C(*C*H$_3$)$_3$), 46.8 (*C*(CH$_3$)$_3$), 90.1 (*C*C), 123.7 (C_{Ar}C), 131.8 (C_{Ar}H), 133.8 (C_{Ar}C), 137.5 (C_{Ar}H) ppm. – MS (70 eV): *m/z* (%) = 355 (10) [$(M+1)^+$], 354 (38) [M^+], 298 (10), 244 (17), 243 (30), 242 (100), 241 (36), 208 (14), 165 (9), 57 (55) [tBu$^+$].- HRMS ($C_{22}H_{26}S_2$): Calcd. 354.1476, found 354.1474. – Anal. ($C_{22}H_{26}S_2$): Calcd. C 74.52, H 7.39; found C 74.63, H 7.99.

4.6.3 Bis(1'-iodoferrocenyl)ethyne (105)[46]

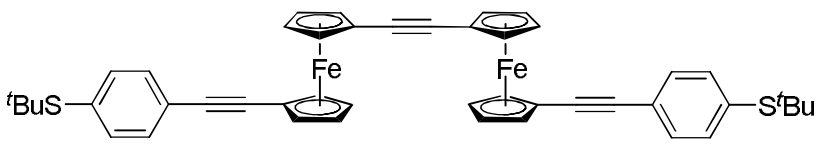


105

1-Iodo-1'-(1-propynyl)ferrocene (**78**) (0.35 g, 1.0 mmol) was dissolved in chlorobenzene (10 mL). After addition of $Mo(CO)_6$ (26 mg, 0.10 mmol, 10 mol %) and 2-fluorophenol (112 mg, 1 mmol) the solution was heated at reflux (oil bath 132 °C) for 15 h. After cooling to 25 °C, the solvent was removed at reduced pressure. The residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **105** (113 mg, 0.2 mmol, 35 %) as a orange crystal (m. p. 128.4 -130.1 °C).

IR (ATR): $\tilde{\nu}$ = 3101 (m), 2918 (m), 2849 (m), 2216 (w), 1631 (w), 1500 (w), 1403 (m), 1378 (m), 1347 (s), 1287 (m), 1202 (m), 1138 (m), 1057 (m), 1043 (m), 0128 (m), 1010 (s), 935 (s), 861 (s), 833 (s), 803 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.24 (m, 4H, H_{Fc}), 4.44 (m, 4H, H_{Fc}) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 40.9 ($C_{Fc}I$), 68.2 ($C_{Fc}C$), 71.0 ($C_{Fc}H$), 71.8 ($C_{Fc}H$), 74.1 ($C_{Fc}H$), 76.4 ($C_{Fc}H$), 84.0 (*C*C) ppm. – MS (70 eV): *m/z* (%) = 647 (11) [$(M+1)^+$], 646 (100) [M^+], 644 (11), 350 (10), 336 (11), 290 (14), 288 (14), 216 (14), 215 (26), 189 (10), 85 (14), 83 (16), 71 (12), 57 (23), 56 (13) [Fe^+]. - HRMS ($C_{22}H_{16}Fe_2I_2$): Calcd. 645.8040; found 645.8045. - Anal. ($C_{22}H_{16}Fe_2I_2$): Calcd. C 40.91, H 2.50; found C 41.49, H 2.79.

4.6.4 Bis{1'-[(4-*tert*-butylsulfanylphenyl)ethynyl]ferrocenyl}ethyne (140)



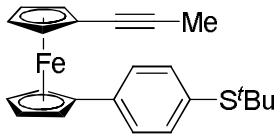
140

Bis(1'-iodoferrocenyl)ethyne (**105**) (187 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-ethynylbenzene (**139**) (133 mg, 0.7 mmol) were dissolved in THF (20 mL). After addition of

diisopropylamine (20 mL), $Pd(PPh_3)_2Cl_2$ (11 mg, 0.02 mmol, 5 mol%) and CuI (3 mg, 0.02 mmol, 5 mol%) the solution was heated at reflux (oil bath 90 °C) for 20 h. After cooling to 25 °C, the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 2:1) to give **140** (36 mg, 0.05 mmol, 16 %) as an orange solid (m. p. 179.5 -181.0 °C).

IR (ATR): $\tilde{\nu}$ = 3095 (w), 2957 (m), 2921 (m), 2858 (m), 2207 (m), 1589 (w), 1492 (m), 1455 (m), 1392 (w), 1362 (m), 1292 (w), 1201 (w), 1161 (m), 1098 (w), 1047 (w), 1026 (m), 1016 (m), 937 (m), 923 (m), 832 (s), 817 (s) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.29 (s, 18H, C(CH_3)$_3$), 4.26 (m, 4H, H_{Fc}), 4.29 (m, 4H, H_{Fc}), 4.44 (m, 4H, H_{Fc}), 4.51 (m, 4H, H_{Fc}), 7.43 (m, 8H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 31.0 (C(*C*H_3)$_3$), 46.3 (*C*(CH$_3$)$_3$), 66.4 (*C*$_{Fc}$C), 67.8 (*C*$_{Fc}$C), 70.7 (C$_{Fc}$H), 71.1 (C$_{Fc}$H), 72.9 (C$_{Fc}$H), 73.2 (C$_{Fc}$H), 83.9 (C*C*), 85.9 (*C*C), 89.2 (C*C*), 124.2 (*C*$_{Ar}$C), 131.3 (*C*$_{Ar}$H), 132.4 (*C*$_{Ar}$C), 137.2 (*C*$_{Ar}$H) ppm. – MS (70 eV): *m/z* (%) = 462 (10), 97 (6), 83 (6), 71 (7), 69 (7), 57 (24), 56 (100), 55 8459, 53 812), 51 (11) - HRMS ($C_{46}H_{42}Fe_2S_2$): Calcd. 770.1427; found 770.1437. - Anal. ($C_{46}H_{42}Fe_2S_2$): Calcd. C 71.69, H 5.49; found C 71.89, H 5.69.

4.6.5 1-(4-*tert*-Butylsulfanylphenyl)-1'-(1-propynyl)ferrocene (100)[20]



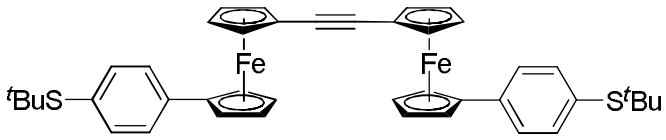
100

1-Iod-1'-(1-propynyl)ferrocen (**78**) (0.70 g, 2.0 mmol) was dissolved in tetrahydrofuran (30 mL). At -78 °C BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol) was slowly dropped and stirred for 1 h at this temperature. At 0 °C zinc chloride (0.33 g, 2.4 mmol, in 10 mL tetrahydrofuran) was added. The solution was stirred for 30 min. at 0 °C, then 1 h at 25 °C. 1-(*tert*-Butylsulfanyl)-4-iodobenzene (**13**) (0.64 g, 2.2 mmol) and Pd(0) (5 mol %) were added at 0 °C. [in situ: at 0 °C, $Pd(PPh_3)_2Cl_2$ (75 mg, 0.1 mmol) in tetrahydrofuran (5 mL), DIBAL-H (20 % in toluene, 0.2 mL, 0.2 mmol), 10 min.] The solution was stirred for 15 h at 85 °C. After cooling to 25 °C NaOH (1 M in water, 10 mL) was added and stirred for 5 min.. The

layers were separated. The aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **100** (254 mg, 0.7 mmol, 33 %) as a dark red solid (m. p. 86.1 – 87.8 °C).

IR (ATR): $\tilde{\nu}$ = 3068 (w), 2966 (m), 2911 (m), 2856 (m), 2359 (w), 1596 (s), 1508 (m), 1468 (m), 1455 (m), 1409 (w), 1386 (w), 1362 (s), 1280 (w), 1266 (w), 1166 (s), 1103 (m), 1075 (w), 1059 (w), 1036 (s), 1016 (s), 981 (w), 932 (w), 886 (s), 849 (w), 831 (s), 814 (s), 733 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (s, 9H, C(CH_3)$_3$), 1.83 (s, 3H, CH_3), 4.02 (m, 2H, H_{Fc}), 4.18 (m, 2H, H_{Fc}), 4.37 (m, 2H, H_{Fc}), 4.64 (m, 2H, H_{Fc}), 7.44 (m, 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (CH_3), 31.0 (C(CH_3)$_3$), 45.9 (C(CH_3)$_3$), 68.0 (C_{Fc}H), 69.7 (C_{Fc}H), 70.9 (C_{Fc}H), 72.5 (C_{Fc}H), 76.2 (C_{Fc}C), 77.2 (C_{Fc}C), 82.4 (CC), 85.4 (CC), 126.2 (C_{Ar}H), 129.8 (C_{Ar}C), 137.4 (C_{Ar}H), 138.8 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 389 (22) [(M+1)$^+$], 388 (100) [M$^+$], 333 (24), 332 (100), 331 (8), 330 (8), 298 (9), 171 (8), 139 (12), 57 (45), 56 (10) [Fe$^+$]. - HRMS ($C_{23}H_{24}FeS$): Calcd. 388.0948; found 388.0951. - Anal. ($C_{23}H_{24}FeS$): Calcd. C 71.13, H 6.23; found C 70.99, H 6.48.

4.6.6 Bis[1'-(4-*tert*-butylsulfanylphenyl)ferrocenyl]ethyne (106)[73]



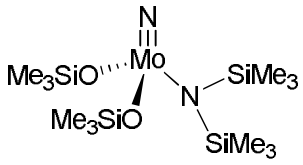
106

1-(4-*tert*-Butylsulfanylphenyl)-1'-(1-propynyl)ferrocene (**100**) (97 mg, 0.3 mmol) was dissolved in toluene (10 mL). After addition of $Mo(CO)_6$ (6 mg, 0.03 mmol, 10 mol %) and 4-chlorophenol (10 mg, 0.08 mmol) the solution was heated at reflux (oil bath 120 °C) for 20 h. After cooling to 25 °C, NaOH (1 M in water, 10 mL) was added and stirred for 5 min.. The mixture was extracted with dichloromethane (3 x 10 mL). The collected organic layers were washed with brine (10 mL), and then dried over magnesium sulfate.After removal of the solvent at reduced pressure the residue was purified by column chromatography (30 x 3 cm,

silica gel, petroleum ether/dichloromethane 2:1) to give **106** (31 mg, 0.04 mmol, 34 %) as an orange solid (m. p. 198.2 -200.1 °C).

IR (ATR): $\tilde{\nu}$ = 3068 (w), 2954 (s), 2920 (s), 2853 (s), 2162 (w), 1597 (m), 1509 (m), 1449 (m), 1409 (w), 1385 (w), 1364 (s), 1278 (m), 1167 (s), 1103 (m), 1076 (w), 1049 (m), 1039 (s), 936 (s), 885 (s), 849 (w), 831 (s), 808 (s) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (s, 18H, C(C*H*$_3$)$_3$), 4.10 (m, 4H, H_{Fc}), 4.23 (m, 4H, H_{Fc}), 4.40 (m, 4H, H_{Fc}), 4.64 (m, 4H, H_{Fc}), 7.46 (m, 8H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 31.0 (C(*C*H$_3$)$_3$), 45.9 (*C*(CH$_3$)$_3$), 67.1 (C_{Fc}C), 68.5 (C_{Fc}H), 70.4 (C_{Fc}H), 71.3 (C_{Fc}H), 72.8 (*C*$_{Fc}$H), 84.0 (*C*$_{Fc}$H), 85.5 (*C*C), 126.2 (*C*$_{Ar}$H), 130.0 (*C*$_{Ar}$C), 137.5 (*C*$_{Ar}$H), 139.2 (*C*$_{Ar}$C) ppm. – MS (70 eV): *m/z* (%) = 725 (7), 724 (23), 723 (52) [(M+1)$^+$], 722 (100) [M$^+$], 721 (6), 720 (13), 666 (8), 610 (11), 608 (6), 438 (7), 437 (21), 436 (50), 434 (8), 305 (11), 57 (20). - HRMS ($C_{42}H_{42}Fe_2S_2$): Calcd. 722.1427; found 722.1774.

4.6.7 [(*N*,*N*-Trimethylsilyl)amino]-bis(trimethylsilyloxy)molybdenum nitride (56)[72]

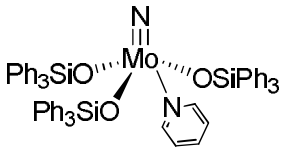


56

Me_3SiCl (24 mL, 189 mmol) was added to a suspension of Na_2MoO_4 (9.80 g, 47.2 mmol) in dimethoxyethane (300 mL) under argon and the mixture was stirred for 16 h at reflux (oil bath 110 °C). After removal of the solvents, the blue residue was suspended in hexane (200 mL). $LiN(SiMe_3)_2$ (15.92 g, 95.2 mmol, in 80 mL hexane) was added to the suspension of the blue residue. The mixture was stirred for 2 h at 25 °C.

The suspension was filtered through celite (2 cm) under argon. After evaporation of solvent, the residue was purified by distillation at reduced pressure (0.3 mbar) to give **56** (15.41 g, 34.3 mmol, 73 %, b. p. = 72-74 °C) as a light yellow liquid.

4.6.8 Pyridinyl-tri(triphenylsilyloxy)molybdenum nitride (58)[72]

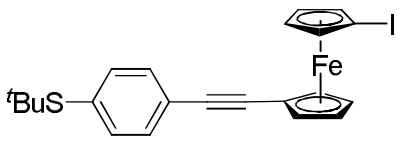


58

56 (4.82 g, 10.8 mmol) was dissolved in toluene (120 mL). After addition of Ph_3SiOH (8.91 g, 32.3 mmol) the solution was stirred for 30 min at 80 °C. After cooling to 25 °C and addition of pyridine (4.3 mL, 53.7 mmol) the mixture was stirred for 20 h at 25 °C. After removal of the solvent, the residue was dried for 2 h at reduced pressure (0.5 mbar). The light yellow solid was suspended in toluene (60 mL) and stirred for 10 min at 80 °C. After cooling to 25 °C, the solvent was removed and **58** was dried for 2 h at reduced pressure (0.5 mbar) as a light yellow solid (8.15 g, 8.03 mmol, 75 %).

General Procedure 2 (**GP 2**): Catalyst **58** (50 mg, 0.05 mmol, 20 mol %) was dissolved in toluene (10 mL). After addition of the starting material(s), the flask was subjected to microwave irradiation (Open Vessel). After cooling to 25 °C the solution was filtered through a 3 cm thick layer of silica gel and then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel deactivated with 5 % triethylamine, petroleum ether/dichloromethane 2:1).

4.6.9 1-[(4-*tert*-Butylsulfanyl)phenylethynyl]-1'-iodoferrocene (19)[15]

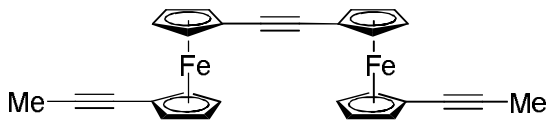


19

GP 2, 1-Iodo-1'-(1-propynyl)ferrocene (**59**) (88 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**101**) (51 mg, 0.3 mmol), 130 °C, 300 W, 30 min RAMP, 120 min

HOLD, **19** (69 mg, 0,1 mmol, 55 %) as a dark red solid, identified by comparison with literature data (^{1}H NMR).[15]

4.6.10 Bis[1'-(1-propynyl)ferrocenyl]ethyne (107)

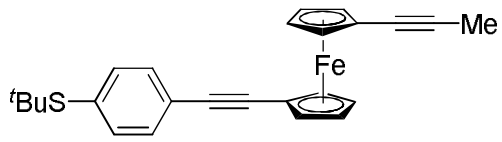


107

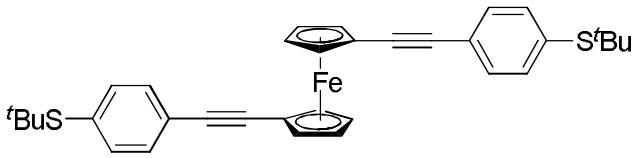
GP 2, 1,1'-di(1-propynyl)ferrocene (**59**) (66 mg, 0.3 mmol), 120 °C, 250 W, 30 min RAMP, 120 min HOLD, **107** (17 mg, 0,04 mmol, 29 %) as a red solid (m. p. 181.0 -182.5 °C).

IR (ATR): $\tilde{\nu}$ = 3099 (w), 2966 (m), 2919 (s), 2850 (m), 2232 (w), 1719 (w), 1494 (m), 1463 (m), 1378 (w), 1265 (m), 1202 (m), 1057 (m), 1043 (m), 1026 (s), 982 (m), 935 (s), 873 (m), 848 (s), 822 (s), 735 (m) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.91 (s, 6H, CH_3), 4.21 (m, 4H, H_{Fc}), 4.24 (m, 4H, H_{Fc}), 4.37 (m, 4H, H_{Fc}), 4.45 (m, 4H, H_{Fc}) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.5 (*C*H$_3$), 67.5 (C*C*CH$_3$), 68.0 (*C*$_{Fc}$C), 70.4 (C$_{Fc}$H), 70.5 (C$_{Fc}$H), 72.6 (C$_{Fc}$H), 72.7 (C$_{Fc}$H), 76.4 (*C*$_{Fc}$C), 82.6 (*C*CCH$_3$), 83.8 (*C*C) ppm. – MS (70 eV): *m/z* (%) = 471 (37) [(M+1)$^+$], 470 (100) [M$^+$], 468 (14), 235 (8), 86 (10), 84 (14), 81 (9), 57 (11), 56 (16) [Fe$^+$]. - HRMS ($C_{28}H_{22}Fe_2$): Calcd. 470.0420; found 470.0417. - Anal. ($C_{28}H_{22}Fe_2$): Calcd. C 71.53, H 4.72; found C 71.53, H 5.15.

4.6.11 1-[4-(*tert*-Butylsulfanyl)phenylethynyl]-1´-(1-propynyl)ferrocene (113) and 1,1'-Di[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocene (114)



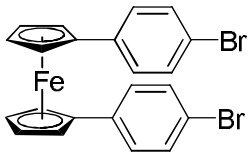
113



114

GP 2, 1,1'-di(1-propynyl)ferrocene (**59**) (66 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**101**) (102 mg, 0.5 mmol), 130 °C, 300 W, 30 min RAMP, 120 min HOLD, **113** (30 mg, 0.07 mmol, 29 %) as a red solid and **114** (50 mg, 0.1 mmol, 39 %) as an orange solid. Compounds **113** and **114** were identified by comparison with literature data (^{1}H NMR).[100]

4.6.12 1,1'-Di(4-bromophenyl)ferrocene (27)[20]

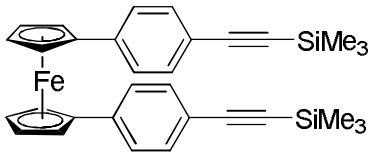


27

Ferrocene (**25**) (1.00 g, 5.35 mmol) was dissolved in hexane (20 mL). TMEDA (2.4 mL, 16.1 mmol) was added. At −78 °C BuLi (1.6 M in hexane, 7.4 mL, 12.3 mmol) was dropped slowly. The mixture was stirred for 5 h at 25 °C and for 15 h at reflux (oil bath 70 °C). At 0 °C zinc chloride (1.67 g, 12.3 mmol, in 20 mL tetrahydrofuran) was added. The solution was stirred for 30 min. at 0 °C, then 1 h at 25 °C. 1-Bromo-4-iodobenzene (3.47 g, 12.3 mmol) and Pd(0) (2 mol %) were added at 0 °C. [in situ: at 0 °C, $Pd(PPh_3)_2Cl_2$ (75 mg, 0.1 mmol) in tetrahydrofuran (10 mL), DIBAL-H (20 % in toluene, 0.2 mL, 0.2 mmol), 10 min.] The

solution was stirred for 4h at 25 °C and for 15 h at 65 °C. After cooling to 25 °C NaOH (1 M in water, 25 mL) was added and stirred for 5 min. The layers were separated. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The collected organic layers were washed with brine (50 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **27** (1.89 g, 3.81 mmol, 71 %) as an orange solid, identified by comparison with literature data (^{1}H NMR).[20]

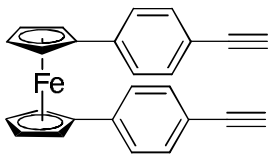
4.6.13 1,1'-Bis[4-(trimethylsilylethynyl)phenyl]ferrocene (140)[20]



140

1,1´-Di(4-bromophenyl)ferrocene (**27**) (496 mg, 1.0 mmol) was dissolved in diisopropylamine (30 mL). After addition of trimethylsilylethyne (0.3 mL, 2.4 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol, 3 mol%) and CuI (6 mg, 0.03 mmol, 3 mol%), the solution was heated at reflux (oil bath 90 °C) for 20 h. After cooling to 25 °C, the suspension was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 9:1) to give **140** (395 mg, 0.74 mmol, 74 %) as an orange solid, identified by comparison with literature data (^{1}H NMR).[20]

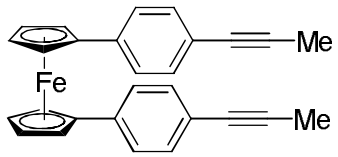
4.6.14 1,1'-Bis(4-ethynylphenyl)ferrocene (141)[20]



141

1,1´-Bis[4-(trimethylsilylethynyl)phenyl]ferrocene (**140**) (851 mg, 1.6 mmol) was suspended in methanol (30 mL). After addition of potassium carbonate (1.33 g, 9.6 mmol), the mixture was stirred for 15 h at 25 °C. Dichloromethane (30 mL) and water (30 mL) were added and the suspension was stirred for 5 min. at 25 °C. The layers were separated. The aqueous layer was extracted with dichloromethane (30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/ dichloromethane 3:1) to give **141** (554 mg, 1.4 mmol, 90 %) as an orange solid, identified by comparison with literature data (^{1}H NMR).[20]

4.6.15 1,1'-Bis[4-(1-propynyl)phenyl]ferrocene (111)[108]



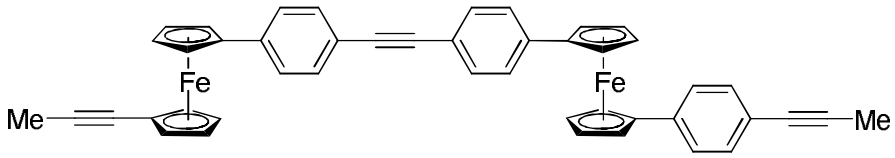
111

1,1'-Bis(4-ethynylphenyl)ferrocene (**141**) (924 mg, 2.4 mmol) was dissolved in tetrahydrofuran (50 mL). At –78 °C BuLi (1.6 M in hexane, 3.3 mL, 5.3 mmol) was dropped slowly and stirred for 1 h. After addition of iodomethane (1.2 mL, 19.0 mmol) at -78 °C, the solution was stirred for 3 h at 25 °C. Water (30 mL) was added and the mixture was stirred for 5 min. After separation of the layers, the aqueous layer was extracted with dichloromethane (3 x 30 mL). The collected organic layers were washed with brine and dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 3:1) to give **111** (894 mg, 2.2 mmol, 90 %) as a red solid (m. p. 186.7–188.3 °C).

IR (ATR): $\tilde{\nu}$ = 3084 (w), 2914 (w), 2850 (m), 2243 (w), 1605 (w), 1523 (s), 1454 (m), 1415 (w), 1386 (w), 1279 (m), 1210 (w), 1106 (m), 1084 (m), 1032 (s), 1005 (w), 967 (w), 888 (s), 848 (m), 832 (s), 810 (s), 728 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.08 (s, 6H, CH_3), 4.22 (m, 4H, H_{Fc}), 4.41 (m, 4H, H_{Fc}), 7.18 (m, 4H, arom. H), 7.23 (m, 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (CH_3), 68.0 (C_{Fc}H), 70.7 (C_{Fc}H), 80.0 (C_{Fc}C), 85.2

(*C*C), 85.7 (C*C*), 121.3 (C_{Ar}C), 125.6 (C_{Ar}H), 131.4 (C_{Ar}H), 137.6 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 416 (9), 415 (48) [$(M+1)^+$], 414 (100) [M^+], 413 (6), 412 (11), 179 (29), 178 (17), 152 (11), 57 (9), 56 (7) [Fe^+]. - HRMS ($C_{28}H_{22}Fe$): Calcd. 414.1071; found 414.1072. - Anal. ($C_{28}H_{22}Fe$): Calcd. C 81.17, H 5.35; found C 80.96, H 5.35.

4.6.16 Bis{4-{1'-[4-(1-propynyl)phenyl]ferrocenyl}phenyl}ethyne (112)

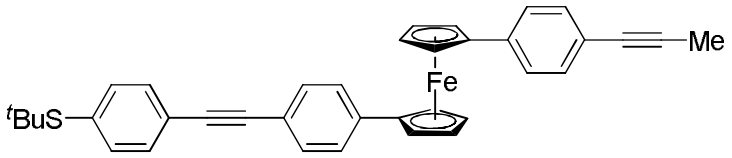


112

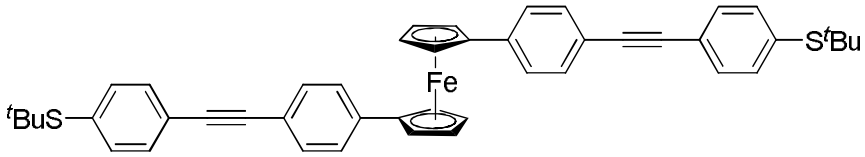
GP 2, 1,1'-Bis[4-(1-propynyl)phenyl]ferrocene (**111**) (103 mg, 0.3 mmol), 130 °C, 200 W, 30 min RAMP, 120 min HOLD, **112** (11 mg, 0,01 mmol, 11 %) as an orange solid (m. p. 258.0 °C, dec.).

IR (ATR): $\tilde{\nu}$ = 3104 (w), 2921 (m), 2850 (m), 2223 (w), 1910 (w), 1604 (w), 1524 (s), 1454 (m), 1416 (w), 1386 (w), 1280 (m), 1209 (w), 1183 (w), 1108 (m), 1084 (m), 1033 (s), 1018 (w), 880 (s), 848 (s), 838 (s), 818 (s), 730 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.04 (s, 6H, CH_3), 4.25 (m, 8H, H_{Fc}), 4.45 (m, 8H, H_{Fc}), 7.25 (m, 8H, arom. H), 7.38 (m, 8H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (CH_3), 68.0 (C_{Fc}H), 68.1 (C_{Fc}H), 69.5 (C_{Fc}H), 69.6 (C_{Fc}H), 70.7 (C_{Fc}C), 70.8 (C_{Fc}C), 85.1 (*C*C), 85.4 (*C*C), 90.2 (C*C*), 120.7 (C_{Ar}C), 120.8 (C_{Ar}C), 125.6 (C_{Ar}C), 125.7 (C_{Ar}H), 125.9 (C_{Ar}H), 131.4 (C_{Ar}H), 131.5 (C_{Ar}H), 138.9 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 776 (18), 775 (57) [$(M+1)^+$], 774 (100) [M^+], 772 (13), 388 (14), 387 (39), 386 (6), 179 (6), 178 (5), 84 (8). - HRMS ($C_{52}H_{38}Fe_2$): Calcd. 774.1672; found 4774.1677. - Anal. ($C_{52}H_{38}Fe_2$): Calcd. C 80.63, H 4.95; found C 81.09, H 4.98.

4.6.17 1-{4-[4-(*tert*-Butylsulfanyl)phenylethynyl]phenyl}-1´-[4-(1-propynyl)phenyl]-ferrocene (117) and 1,1'-Di{4-[4-(*tert*-butylsulfanyl)phenylethynyl]phenyl}ferrocene (118)



117

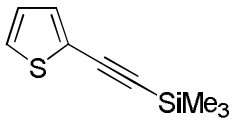


118

GP 2, 1,1´-Bis[4-(1-propynyl)phenyl]ferrocene (**111**) (104 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**101**) (102 mg, 0.5 mmol), 130 °C, 300 W, 30 min RAMP, 120 min HOLD, **117** (16 mg, 0.03 mmol, 11 %) as an orange solid (m. p. 187.3–188.5 °C) and **118** (21 mg, 0.03 mmol, 12 %) as an orange solid. **118** was identified by comparison with literature data (^{1}H NMR).[20]

117: IR (ATR): $\tilde{\nu}$ = 3095 (w), 2946 (s), 2921 (s), 2852 (s), 2216 (w), 1588 (w), 1524 (m), 1454 (s), 1377 (w), 1362 (w), 1260 (s), 1165 (m), 1082 (s), 1033 (s), 1016 (s), 878 (m), 824 (s), 811 (s), 797 (s), 784 (s), 730 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.31 (s, 9H, C(CH_3)$_3$), 2.02 (s, 3H, CH_3), 4.25 (m, 4H, H_{Fc}), 4.45 (m, 4H, H_{Fc}), 7.16(m, 2H, arom. H), 7.22 (m, 4H, arom. H), 7.34 (m, 2H, arom. H) 7.53 (m, 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 (*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$), 46.4 (*C*(CH$_3$)$_3$), 67.9 (C_{Fc}H), 68.0 (C_{Fc}H), 70.6 (C_{Fc}H), 70.8 (C_{Fc}H), 80.0 (C*C*), 85.0 (C_{Fc}C), 85.4 (C_{Fc}C), 85.8 (*C*C), 88.9 (C*C*), 91.4 (*C*C), 120.1 (C_{Ar}C), 121.3 (C_{Ar}C), 124.0 (C_{Ar}C), 125.6 (C_{Ar}H), 125.7 (C_{Ar}H), 131.4 (C_{Ar}H), 131.5 (C_{Ar}H), 131.6 (C_{Ar}H), 133.0 (C_{Ar}C), 137.2 (C_{Ar}H) 137.3 (C_{Ar}C), 138.6 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 566 (17), 564 (43) [(M+1)$^+$], 564 (100) [M$^+$], 509 (13), 508 (34), 57 (33). - HRMS ($C_{37}H_{32}FeS$): Calcd. 564.1574; found 564.1570. - Anal. ($C_{37}H_{32}FeS$): Calcd. C 78.72, H 5.71; found C 78.22, H 5.95.

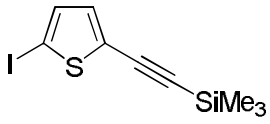
4.6.18 2-(Trimethylsilylethynyl)thiophene (142)[110, 111]



142

2-Bromothiophene (2.04 g, 20.0 mmol) was dissolved in tetrahydrofuran (50 mL). After addition of trimethylsilylethyne (3.4 mL, 24.0 mmol), diisopropylamine (20 mL), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol, 1 mol%) and CuI (40 mg, 0.2 mmol, 1 mol%), the solution was heated at reflux (oil bath 70 °C) for 20 h. After cooling to 25 °C, the suspension was filtered through a 2 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether) to give **142** (3.51 g, 19.5 mmol, 95 %) as a colorless oil, identified by comparison with literature data (^{1}H NMR).[110]

4.6.19 2-Iodo-5-(trimethylsilylethynyl]thiophene (143)[111,112]

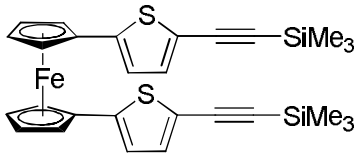


143

Diisopropylamine (1.2 mL, 8.4 mmol) was dissolved in diethyl ether (10 mL). At -78 °C n-BuLi (1.6 M in hexane, 4.8 mL, 7.7 mmol) was dropped slowly and was stirred for 15 min. at -78°C, for 30 min. at 0 °C. 2-(trimethylsilyl)ethynyl-thiophene (**142**) (0.69 g, 3.8 mmol, in 5 mL diethyl ether) was added at -78 °C and stirred for 15 min at 0 °C. Iodine (2.12 g, 8.4 mmol, in 20 mL diethyl ether) was added at -78 °C and stirred overnight at 25 °C.

Water (20 mL) was added and the mixture was stirred for 10 min. After separation of the layers, the aqueous layer was extracted with diethyl ether (20 mL). The collected organic layer was washed with $Na_2S_2O_3$ solution (1M in water, 10 mL) and brine (20 mL), dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether) to give **143** (0.90 g, 2.9 mmol, 77 %) as a light yellow oil, identified by comparison with literature (^{1}H NMR).[112]

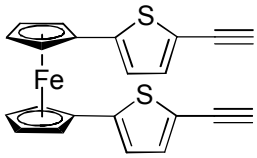
4.6.20 1,1'-Di[2-(4-trimethylsilylethynyl)thiophenyl]ferrocene (144)[20]



144

Ferrocene (**25**) (882 mg, 4.7 mmol) was dissolved in hexane (20 mL). TMEDA (2.1 mL, 14.2 mmol) was added. At -78 °C n-BuLi (1.6 M in hexane, 6.5 mL, 10.4 mmol) was dropped slowly. The mixture was stirred for 4 h at 25 °C and for 15 h at reflux (oil bath 70 °C). At 0 °C zinc chloride (1.49 g, 10.9 mmol, in 20 mL tetrahydrofuran) was added. The solution was stirred for 30 min. at 0 °C, then 1 h at 25 °C. 2-Iodo-5-[(trimethylsilyl)ethynyl]thiophene (**143**) (3.19 g, 10.4 mmol) and Pd(0) (5 mol %) were added at 0 °C. [in situ: at 0 °C, $Pd(PPh_3)_2Cl_2$ (166 mg, 0.2 mmol) in tetrahydrofuran (10 mL), DIBAL-H (20 % in toluene, 0.4 mL, 0.5 mmol), 10 min.] The solution was stirred for 4h at 25 °C and for 15 h at 75 °C. After cooling to 25 °C, the solvents were evaporated at reduced pressure. Dichloromethane (50 mL) was added and stirred for 5 min. The suspension was washed with water (2 x 50 mL) and brine (30 mL), dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 9:1) to give **144** (2.41 g, 4.4 mmol, 94 %) as a dark red solid, identified by comparison with literature data (^{1}H NMR).[20]

4.6.21 1,1'-Di[2-(4-ethynyl)thiophenyl]ferrocene (145)[20]

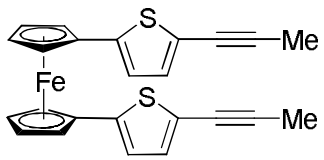


145

1,1´-Di{2-[4-(trimethylsilyl)ethynyl]thiophenyl}ferrocene (**144**) (2.41g, 4.4 mmol) was suspended in methanol (50 mL). After addition of potassium carbonate (3.68 g, 26.6 mmol), the mixture was stirred for 20 h at 25 °C. Dichloromethane (50 mL) and water (50 mL) were

added and the suspension was stirred for 5 min. at 25 °C. The layers were separated. The aqueous layer was extracted with dichloromethane (50 mL). The collected organic layers were washed with brine (30 mL), and dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/ dichloromethane 3:1) to give **145** (1.61g, 4.0 mmol, 91 %) as a dark red solid, identified by comparison with literature data (^{1}H NMR).[20]

4.6.22 1,1'-Di{2-[4-(1-propynyl)]thiophenyl}ferrocene (109)[108]



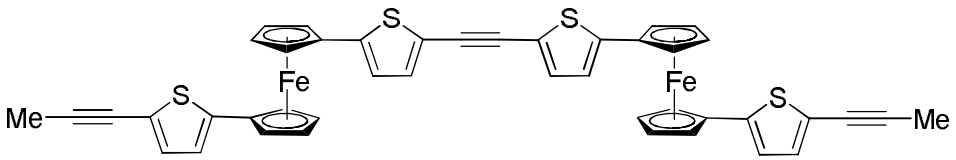
109

1,1´-Di[2-(4-ethynyl)thiophenyl]ferrocene (**145**) (1.00 g, 2.5 mmol) was dissolved in tetrahydrofuran (40 mL). At –78 °C BuLi (1.6 M in hexane, 3.5 mL, 5.5 mmol) was dropped slowly and stirred for 1 h. After addition of iodomethane (1.3 mL, 20.1 mmol) at -78 °C, the solution was stirred for 2 h at 25 °C. Water (20 mL) was added and the mixture was stirred for 5 min. After separation of the layers, the aqueous layer was extracted with dichloromethane (30 mL). The collected organic layers were washed with brine (30 mL) and dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel deactivated with 5 % triethylamine, petroleum ether/dichloromethane 4:1) to give **109** (769 mg, 1.8 mmol, 72 %) as a red solid (m. p. 118.5–120.0 °C).

IR (ATR): $\tilde{\nu}$ = 3081 (w), 2908 (w), 2843 (m), 2340 (w), 2189 (w), 2074 (w), 2040 (w), 1978 (w), 1752 (w), 1546 (w), 1489 (w), 1427 (m), 1389 (w), 1373 (w), 1268 (w), 1232 (w), 1199 (w), 1188 (w), 1070 (w), 1044 (w), 1029 (s), 973 (m), 929 (m), 865 (m), 811 (s), 784 (s), 753 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (s, 6H, CH_3), 4.21 (m, 4H, H_{Fc}), 4.41 (m, 4H, H_{Fc}), 6.66 (d, J = 3.8, 2H, arom. H), 6.88 (d, J = 3.8, 2H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.8 (CH_3), 68.5 (C_{Fc}H), 70.8 (C_{Fc}H), 73.4 (C_{Fc}C), 80.8 (*C*C), 90.0 (C*C*), 121.4 (C_{Ar}C), 122.1 (C_{Ar}H), 131.5 (C_{Ar}H), 142.3 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 428 (14), 427 (29) [(M+1)$^+$], 426 (100) [M$^+$], 424 (6), 185 (13), 184 (7), 152 (10), 57 (7), 56

(7) [Fe^+]. - HRMS ($C_{24}H_{18}FeS_2$): Calcd. 426.0199; found 426.0201. - Anal. ($C_{24}H_{18}FeS_2$): Calcd. C 67.61, H 4.26; found C 67.58, H 4.39.

4.6.23 Bis{2-{5-{1'-{2-[5-(1-propynyl)]thiophenyl}ferrocenyl}}thiophenyl}ethyne (110)

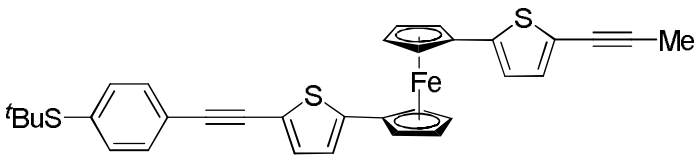


110

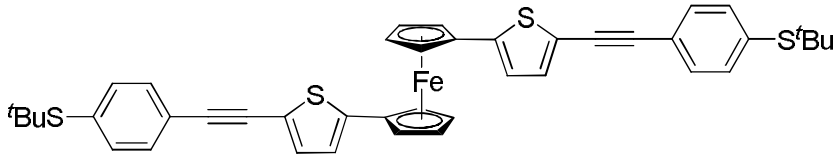
GP 2, 1,1´-Di{2-[4-(1-propynyl)]thiophenyl}ferrocene (**109**) (106 mg, 0.3 mmol), 105 °C, 200 W, 30 min RAMP, 120 min HOLD, **110** (14 mg, 0.02 mmol, 14 %) as a red solid (m. p. 172.2 – 173.6 °C).

IR (ATR): $\tilde{\nu}$ = 3081 (w), 2959 (m), 2919 (m), 2851 (m), 2189 (w), 1753 (w), 1543 (w), 1428 (m), 1364 (w), 1262 (w), 1202 (m), 1071 (w), 1044(m), 1030 (s), 958 (s), 918 (w), 851 (m), 797 (s), 743 (w), 730 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.08 (s, 6H, CH_3), 4.24 (m, 8H, H_{Fc}), 4.44 (m, 8H, H_{Fc}), 6.68 (d, J = 3.8, 2H, arom. H), 6.73 (d, J = 3.8, 2H, arom. H), 6.89 (d, J = 3.8, 2H, arom. H), 7.04 (d, J = 3.8, 1H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.7 (CH_3), 68.5 ($C_{Fc}H$), 68.6 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.0 ($C_{Fc}H$), 73.4 ($C_{Fc}C$), 80.6 ($C_{Fc}C$), 81.0 (*C*C), 87.1 (C*C*), 90.2 (*C*C), 120.3 ($C_{Ar}C$), 121.5 ($C_{Ar}C$), 122.2 ($C_{Ar}H$), 122.5 ($C_{Ar}H$), 131.5 ($C_{Ar}H$), 132.6 ($C_{Ar}H$), 142.1 ($C_{Ar}C$), 144.2 ($C_{Ar}C$) ppm. – MS (70 eV): *m/z* (%) = 577 (31), 576 (76), 520 (26), 388 (34), 330 (34), 186 (29), 185 (24), 111 (22), 97 (36), 95 (26), 85 (28), 83 (38), 81 (26), 71 (40), 69 (43), 57 (100), 56 (46), 55 (53). - HRMS ($C_{44}H_{30}Fe_2S_4$): Calcd. 797.9929; found 797.9911. - Anal. ($C_{44}H_{30}Fe_2S_4$): Calcd. C 66.17, H 3.79; found C 66.73, H 4.58.

4.6.24 1-{2-{5-[4-(*tert*-Butylsulfanyl)phenylethynyl]thiophenyl}}-1'-{2-[5-(1-propynyl)] thiophenyl}ferrocene (115) and 1,1'-Di{2-{5-[4-(*tert*-Butylsulfanyl)phenylethynyl]thiophenyl}}ferrocene (116)



115



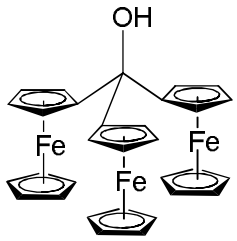
116

GP 2, 1,1´-Di{2-[4-(1-propynyl)]thiophenyl}ferrocene (**109**) (53 mg, 0.1 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**101**) (51 mg, 0.2 mmol), 110 °C, 200 W, 30 min RAMP, 120 min HOLD, **115** (15 mg, 0.03 mmol, 20 %) as an orange solid (m. p. 111.5–113.1 °C) and **116** (12 mg, 0.02 mmol, 13 %) as an orange solid. **116** was identified by comparison with literature data (^{1}H NMR).[20]

115: IR (ATR): $\tilde{\nu}$ = 3081 (w), 2958 (w), 2920 (w), 2852 (w), 2189 (m), 1588 (w), 1469 (m), 1455 (w), 1427 (m), 1391 (w), 1363 (m), 1247 (w), 1214 (m), 1199 (w), 1185 (w), 1167 (m), 1098 (w), 1071 (w), 1039 (w), 1030 (m), 1014 (w), 973 (m), 838 (m), 811 (s), 770 (s), 730 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.31 (s, 9H, C(CH_3)$_3$), 2.05 (s, 6H, CH_3), 4.24 (m, 4H, H_{Fc}), 4.44 (m, 4H, H_{Fc}), 6.66 (d, J = 3.8, 1H, arom. H), 6.73 (d, J = 3.8, 1H, arom. H), 6.88 (d, J = 3.8, 1H, arom. H), 7.05 (d, J = 3.8, 1H, arom. H), 7.50 (m, 4H, arom. H) ppm. – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 4.7 (*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$), 46.4 (*C*(CH$_3$)$_3$), 68.5 (C_{Fc}H), 68.6 (C_{Fc}H), 70.7 (C_{Fc}H), 70.9 (C_{Fc}H), 73.4 (C_{Fc}C), 80.5 (C_{Fc}C), 81.0 (*C*C), 85.0 (C*C*), 90.1 (*C*C), 92.7 (C*C*), 120.1 (C_{Ar}C), 121.5 (C_{Ar}C), 122.2 (C_{Ar}H), 122.4 (C_{Ar}H), 123.6 (C_{Ar}C), 131.1 (C_{Ar}H), 131.5 (C_{Ar}H), 132.8 (C_{Ar}H), 133.1 (C_{Ar}C), 137.2 (C_{Ar}H), 142.0 (C_{Ar}C), 144.3 (C_{Ar}C) ppm. – MS (70 eV): *m/z* (%) = 578 (22), 577 (41) [(M+1)$^+$], 576 (100) [M$^+$], 521 (14), 520 (38), 57 (27). - HRMS ($C_{33}H_{28}FeS_3$): Calcd. 576.0703; found 576.0699. - Anal. ($C_{24}H_{18}FeS_2$): Calcd. C 68.74, H 4.89; found C 69.05, H 5.20.

4.7 Triferrocenylmethane Derivatives

4.7.1 Triferrocenylmethanol (119)[113,114]



119

Ferrocene (**25**) (2.00 g, 10.7 mmol) was dissolved in the mixture of hexane (5 mL) and tetrahydrofuran, stirred for 30 min at 25 °C. At 0 °C t-BuLi (1.6 M in pentane, 6.4 mL, 10.2 mmol) was added dropwise, the mixture was stirred for 1 h at 0 °C. At this temperature after addition of freshly distilled ethyl chloroformate (0.15 mL, 1.6 mmol) the solution was stirred for 1 h at 25 °C. At 0 °C methanol (20 mL) was added. The mixture was diluted with dichloromethane (50 mL), washed with water (3 x 20 mL) and dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (silica gel deactivated with 5 % triethylamine, petroleum ether/trichloromethane 3:1) to give **119** (633 mg, 1.1 mmol, 68 %) as a red crystal, identified by comparison with literature data (^{1}H NMR).[113]

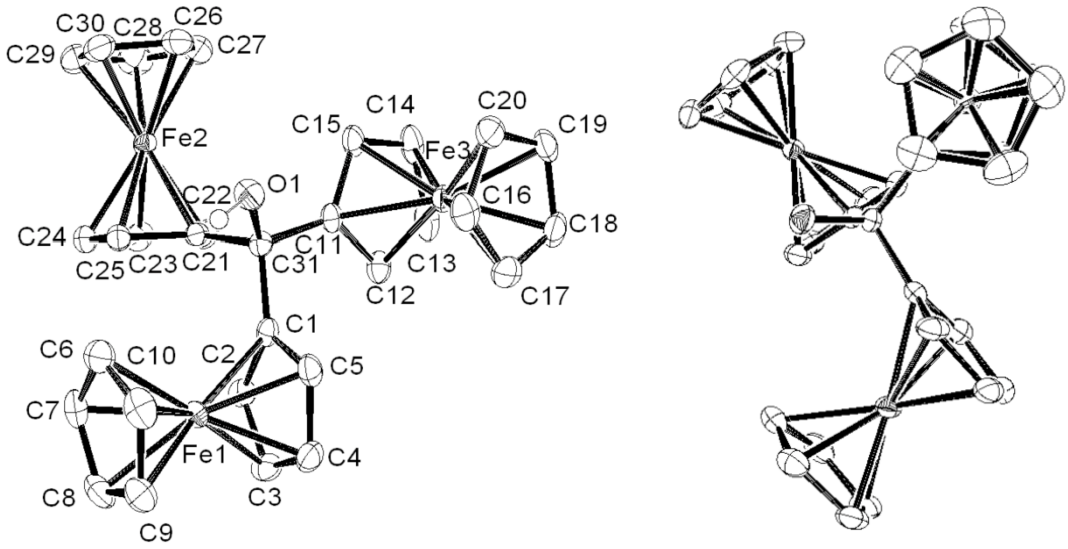


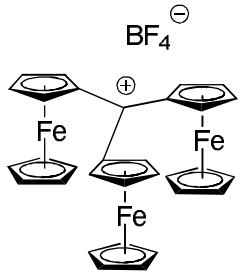
Figure 12.[115] Left: ORTEP drawing of **119** at 173 K.[116] Ellipsoids are shown as 50 % probability level. Right: Perspective view indicating the orthogonal orientation of the ferrocene units. Hydrogen atoms are omitted for clarity. Selected bond lengths [´], bond angles [°] and torsional angles [°]: C1-C2 1.427(4), C1-C5 1.426(5), C1-C31 1.521(3), C2-C3 1.408(4) C3-C4 1.428(6), C4-C5 1.419(5), C11-C31 1.518(4), C21-C31 1.531(5), C31-O1 1.426(4),; C1-C31-C11 109.2(2), C1-C31-C21 108.3(2), C11-C31-O1 111.0(2), C1-C31-O1 110.9(2), C11-C31-O1 109.1(2), C21-C31-O1 111.0(2); C2-C1-C31-C11 –92.6(3), C5-C1-C31-C11 78.5(4), C5-C1-C31-C21 –163.9(3).

Crystal structure analysis:[116] Single crystal was obtained from hexane/dichloromethane (3:1) at 25 °C. A single crystal (size = 0.23 x 0.17 x 0.14 mm^3) was attached to a glass fiber with epoxy glue, and transferred to a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite monochromator and using $Mo_{K\alpha}$ radiation (λ = 0.71073 ´). The system was controlled by a pentium-based PC running the SMART software package.[117] Data sets were collected at 295 K and on the same crystal at 173 K. The crystal was maintained at this temperature by means of a Bruker KRYOFLEX nitrogen cryostat. Immediately after collection, the raw data frames were transferred to a second PC for intergration and reduction by the SAINT program package.[118] The structure was solved and refined by the SHELXTL software package.[114] Crystal data for T = 173(1) K: Empirical formula $C_{31}H_{28}OFe_3$, formula weight 584.08 g mol^{-1}; crystal system monoclinic; space group *Ia*, Z = 4, unit cell dimensions a = 11.237(1), b = 18.810(2), c = 12.292(1) ´; β = 112.845(1); V = 2394.2(3) $´^3$; $d_{calc.}$ = 1.650 g cm^{-3}; μ = 1.851, empirical absorption correction (multi-scan Bruker SADABS V2.05),

T_{min} = 0.676, T_{max} = 0.782, reflections collected/unique 13254/5460, R_{int} = 0.027, direct methods, full matrix least squares refinement on F^2, R_1 = 0.0310 ($I > 2\sigma_I$), wR_2 = 0.0710, goodness-of-fit on F^2 = 1.093, final difference electron density 0.57 and –0.30 eÅ^{-3}, completeness of data 98.2 %, Flack parameter 0.034(13),

Crystal data for T = 295(1) K: Empirical formula $C_{31}H_{28}OFe_3$, formula weight 584.08 g mol^{-1}; crystal system monoclinic; space group *Ia*, Z = 4, unit cell dimensions a = 11.237(1), b = 18.810(2), c = 12.292(1) ´; β = 112.845(1); V = 2394.2(3) ´^{3}; $d_{calc.}$ = 1.620 g cm^{-3}; μ = 1.817, empirical absorption correction (multi-scan Bruker SADABS V2.05), T_{min} = 0.6800, T_{max} = 0.7850, reflections collected/unique 13510/5548, R_{int} = 0.027, direct methods, full matrix least squares refinement on F^2, R_1 = 0.0385 ($I > 2\sigma_I$), wR_2 = 0.0892, goodness-of-fit on F^2 = 1.115, final difference electron density 0.48 and –0.27 eÅ^{-3}, completeness of data 98.4 %, Flack parameter 0.036(17),

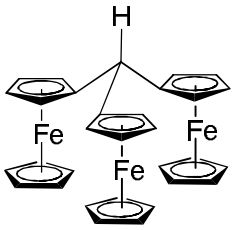
4.7.2 Triferrocenylmethyl tetrafluoroborate (144)[113]



144

Triferrocenylmethanol (**119**) (0.30 g, 0.5 mmol) was suspended in THF (10 mL). At 25 °C Ph_3CBF_4 (0.19 g, 0.6 mmol) was added. The mixture was stirred for 4 h at this temperature. Then the solvent was removed. The remaining solid was washed with hexane (4 x 20 mL). The dark green solid was obtained as product (**144**) and dried under high vacuum (0.26 g, 0.4 mmol, 78 %), identified by comparison with literature data (^{1}H NMR).[113] Recrystallization in hexane/dichloromethane (3:1) at –30 °C afforded a dark green crystal.

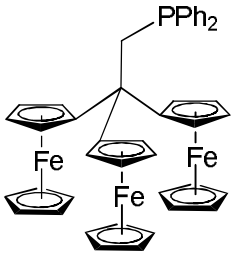
4.7.3 Triferrocenylmethane (145)[113]



145

At −78 °C **144** (0.50 g, 0.8 mmol) was added to the suspension of $LiAlH_4$ (0.87 g, 23.0 mmol) in tetrahydrofuran (50 mL) and the mixture was stirred for 1 h at 25 °C and heated for 12 h at 65 °C. At 0 °C water (50 mL) was added dropwise, and then extracted with dichloromethane (30 mL x 3). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel deactivated with 5 % triethylamine, petroleum ether/dichloromethane 4:1) to give **145** (0.33 g, 0.6 mmol, 75 %) as an orange solid, identified by comparison with literature data (^{1}H NMR).[113] Recrystallization took place from hexane/dichloromethane (3:1) to yield a red crystal,

4.7.4 Diphenyl(2,2,2-triferrocenylethyl)phosphine (146)[119]

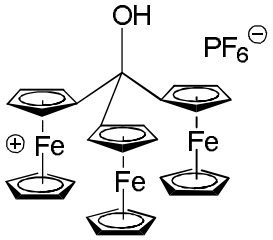


146

At 25 °C Ph_3CBF_4 (0.32 g, 1.0 mmol) was added to a suspension of triferrocenylmethanol (**119**) (0.51 g, 0.9 mmol) in diethyl ether (40 mL) and stirred for 2 h. The dark green precipitate was washed with diethyl ether (30 mL x 3) and dissolved in tetrahydrofuran (40 mL). At −78 °C to the solution lithiomethyldiphenylphosphine borane complex [in situ, at −78 °C s-BuLi (1.3 M, 1.4 mL, 1.8mmol) was added dropwise to the solution of Ph_2MePBH_3

(0.34 g, 1.6 mmol) itetrahydrofuran (5 mL)] was added. At 25 °C the mixture was stirred for 2 h. After addition of degassed Et_2NH (25 mL), the mixture was stirred for 2 d at 25 °C. After removal of the volatiles at reduced pressure dichloromethane (20 mL) was added. Ammonium salts was removed by filtration through celite. Removal of solvent at reduced pressure resulted in the formation of **146** as an orange solid (0.48 g, 0.63 mmol, 72 %), which was washed with ice-cold methanol. **146** was identified by comparison with literature data (^{1}H NMR).[119]

4.7.5 Triferrocenylmethanol hexafluorophosphate (120)[103]



120

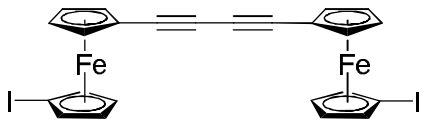
Triferrocenylmethanol (**119**) (58.4 mg, 0.1 mmol) was dissolved in dichloromethane (10 mL). At –35 °C the solution of $AgPF_6$ (25.2 mg, 0.1 mmol) in dichloromethane (2 mL) was added and the color of the solution changed from light red to dark green. The mixture was stirred for 10 min at 25 °C. The formed silver was filtered off through celite and washed with dichloromethane. After removal of solvent at reduced pressure, **120** was obtained as a dark green solid (71 mg, 0.1 mmol, 97 %). Recrystallization form dichloromethane at 25 °C gave a dark green crystal (m. p. 178.2–179.2 °C).

IR (ATR): $\tilde{\nu}$ = 3108 (w), 3088 (w), 2927 (w), 2364 (w), 2324 (w), 2269 (w), 2234 (w), 2175 (w), 2163 (w), 1996 (w), 1740 (w), 1558 (w), 1423 8w), 1391 (w), 1343 (w), 1303 (w), 1262 (w), 1212 (w), 1106 (m), 1060 (w), 1035 8w), 1003 (m), 838 (s), 730 (s) cm^{-1}. – MS (70 eV): *m/z* (%) = 584 (20), 583 (49), 582 (100), 398 (27), 302 (11), 287 (27), 236 (30), 84 (11), 73 (28), 71 (12), 69 (14), 57 (47), 55 (19).

Crystal structure analysis: Single crystal was obtained from dichloromethane at 25 °C. $C_{32}H_{30}Cl_2F_6Fe_3OP$; M_r = 813.98 g mol^{-1}; crystal system monoclinic; space group *Pc*; *a* =

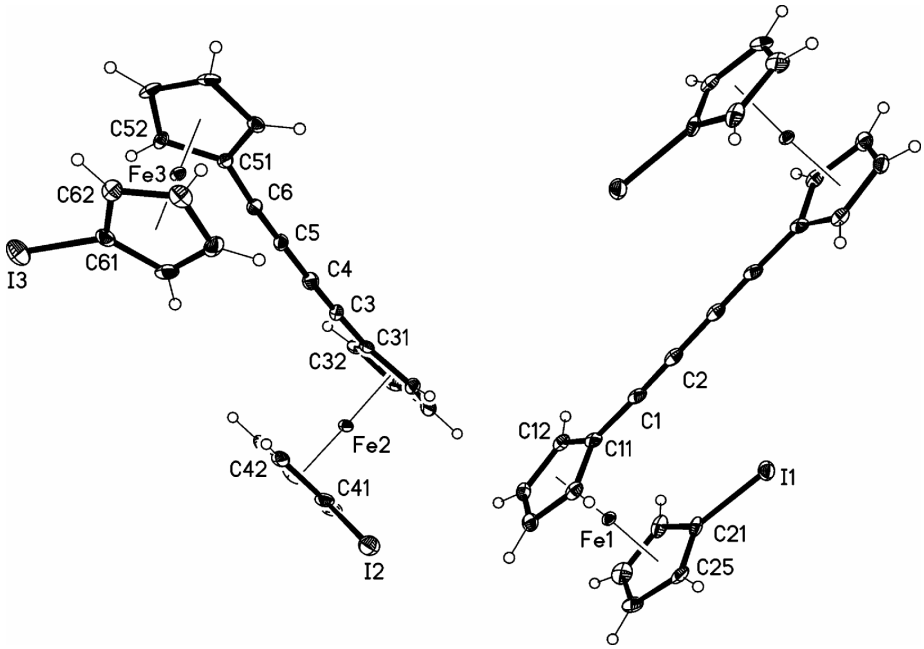
10.7296(2), b = 25.7495(4), c = 11.2096(2) Å; α = 90, β = 97.289(2), γ = 90°; V = 3071.98(9) Å^3; Z = 4; ρ = 1.760 g cm^{-3}; μ = 13.874 mm^{-1}; crystal size 0.12 x 0.10 x 0.90 mm^3; F(000) = 1644; STOE IPDS one-axis diffractometer with imaging plate detector; T = 100(2) K; $Mo_{K\alpha}$ radiation (λ = 0.71073 Å): θ range 3.43 to 76.00°; reflections collected/unique 43728/10257 (R(int) = 0.0537); completeness of data θ = 72.50° (99.9 %); index ranges -13≤h≤11, -32≤k≤32, -13≤l≤14; empirical absorption correction (multi-scan), no extinction correction, direct methods, full-matrix least-squares refinement on F^2, goodness-of-fit on F^2 = 1.091, R_1 = 0.0429 ($I > 2\sigma_I$), wR_2 = 0.1098, R-indices [all data] R_1 = 0.0464 , wR_2 = 0.1115, final difference electron density 0.882 and –0.749 eÅ^{-3}.

4.8 To synthesis of 1,4-Di(1'-iodoferrocenyl)-buta-1,3-diyne (122)[105]



122

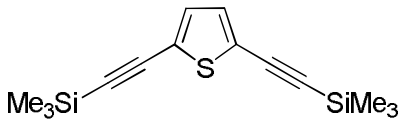
1-Ethynyl-1'-iodoferrocene (**18**) (495 mg, 1.5 mmol) was dissolved in diisopropylamine (20 mL). After addition of $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol, 2 mol%) and CuI (6 mg, 0.03 mmol, 2 mol%) the solution was heated at reflux (oil bath 90 °C) for 20 h. After cooling to 25 °C the solution was filtered through a 5 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/dichloromethane 4:1) to give **122** (18 mg, 0.03 mmol, 4 %) as a dark red solid, which was recrystallized in hexane/dichloromethane (3:1) to give a dark red crystal, identified by x-ray structure.



Crystal structure analysis: Single crystal was obtained from the mixture of hexane and dichloromethane at 25 °C. $C_{24}H_{16}Fe_2I_2$; M_r = 669.87 g mol^{-1}; crystal system triclinic; space group *P(-1)*; a = 6.3179(2), b = 14.6514(5), c = 17.7513(6) ´; α = 69.566(3), β = 83.056(3), γ = 87.001(3)°; V = 1528.39(9) ´^{3}; Z = 3; ρ = 2.183 g cm^{-3}; μ = 4.461 mm^{-1}; crystal size 0.40 x 0.35 x 0.20 mm^3; F(000) = 954; STOE IPDS one-axis diffractometer with imaging plate detector; T = 100(2) K; $Mo_{K\alpha}$ radiation (λ = 0.71073 ´): θ range 2.23 to 30.03°; reflections collected/unique 64726/8743 (R(int) = 0.0300); completeness of data θ = 30.03° (98.0 %); index ranges -8≤h≤8, -20≤k≤20, -24≤l≤24; empirical absorption correction (multi-scan), no extinction correction, direct methods, full-matrix least-squares refinement on F^2, goodness-of-fit on F^2 = 1.082, R_1 = 0.0386 ($I > 2\sigma_I$), wR_2 = 0.1095, R-indices [all data] R_1 = 0.0460 , wR_2 = 0.1119, final difference electron density 2.081 and –2.878 eÅ^{-3}.

4.9 Synthesis of ferrocene-based molecular wires

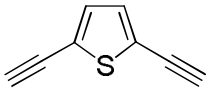
4.9.1 2,5-Bis(trimethylsilylethynyl)thiophene (147)[120]



147

2-Iodo-5-[(trimethylsilyl)ethynyl]thiophene (**143**) (1.53 g, 5.0 mmol) was dissolved in tetrahydrofuran (30 mL). After addition of trimethylsilylacetylene (0.8 mL, 6.0 mmol), diisopropylamine (15 mL), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol, 2 mol%) and CuI (20 mg, 0.1 mmol, 2 mol%), the solution was heated at reflux (oil bath 70 °C) for 20 h. After cooling to 25 °C, the suspension was filtered through a 2 cm thick layer of silica gel, which was then washed with *tert*-Butyl methyl ether. After solvent removal at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether) to give **147** (1.38 g, 5.0 mmol, 100 %) as a light yellow solid, identified by comparison with literature data (^{1}H NMR).[120]

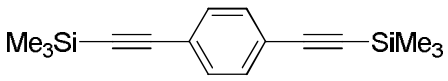
4.9.2 2,5-Diethynylthiophene (148)[120]



148

2,5-Bis[(trimethylsilyl)ethynyl]thiophene (**147**) (1.38 g, 5.0 mmol) was suspended in methanol (50 mL). After addition of potassium carbonate (4.14 g, 30.0 mmol), the mixture was stirred for 20 h at 25 °C. Dichloromethane (30 mL) and water (30 mL) were added and the suspension was stirred for 5 min at 25 °C. The layers were separated. The aqueous layer was extracted with dichloromethane (30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether/ dichloromethane 4:1) to give **148** (0.61 g, 4.6 mmol, 92 %) as an orange dark red oil, identified by comparison with literature data (^{1}H NMR).[120]

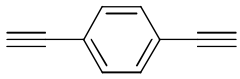
4.9.3 1,4-Bis[(trimethylsilyl)ethynyl]benzene (149)[26]



149

1,4-Diiodobenzene (3.30 g, 10.0 mmol) was dissolved in tetrahydrofuran (50 mL). After addition of trimethylsilylethyne (2.9 mL, 21.0 mmol), diisopropylamine (20 mL), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol, 1 mol%) and CuI (20 mg, 0.1 mmol, 1 mol%), the solution was heated at reflux (oil bath 70 °C) for 20 h. After cooling to 25 °C, the suspension was filtered through a 2 cm thick layer of silica gel, which was then washed with *tert*-Butyl methyl ether. After solvent removal at reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether) to give **149** (2.60 g, 9.9 mmol, 99 %) as a colorless crystal, identified by comparison with literature data (^{1}H NMR).[26]

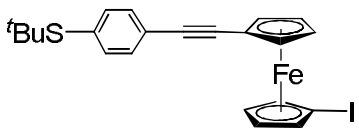
4.9.4 1,4-Diethynylbenzene (20)[26]



20

1,4-Bis[(trimethylsilyl)ethynyl]benzene (**149**) (3.75 g, 13.9 mmol) was dissolved in methanol (50 mL). After addition of potassium carbonate (5.74 g, 41.6 mmol), the mixture was stirred for 20 h at 25 °C. Dichloromethane (50 mL) and water (50 mL) were added and the suspension was stirred for 5 min at 25 °C. The layers were separated. The aqueous layer was extracted with dichloromethane (30 mL). The collected organic layers were washed with brine (30 mL), and then dried over magnesium sulfate. After removal of solvent at reduced pressure, the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether) to give **20** (0.61 g, 4.6 mmol, 92 %) as a shiny colorless crystal, identified by comparison with literature data (^{1}H NMR).[26]

4.9.5 1-[(4-*tert*-Butylsulfanyl)phenylethynyl]-1'-iodoferrocene (19)[15]

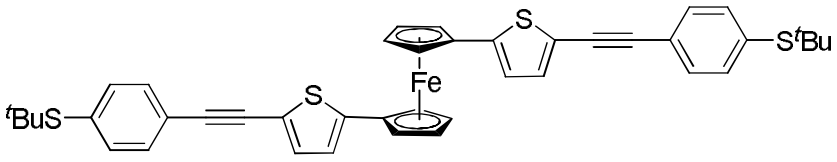


19

$Pd(PPh_3)_2Cl_2$ (100 mg, 0.14 mmol, 5 mol%) and $Cu(OAc)_2 \cdot H_2O$ (27 mg, 0.14 mmol, 5 mol%) were added to a solution of 1-ethynyl-1'-iodoferrocene (**18**) (2.12 g, 6.3 mmol) and 1-(*tert*-butylsulfanyl)-4-iodobenzene (**13**) (2.02 g, 6.9 mmol) in diisopropylamine (40 mL) and subjected to microwave irradiation (100 °C, 200 W, 15 min RAMP, 50 min HOLD, open vessel). After cooling to 25 °C the mixture was filtered through a 3 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, silica gel, petroleum ether /dichloromethane 4:1). **19** (3.02 g, 6.0 mmol, 96 %) was obtained as a dark red solid, identified by comparison with literature data (^{1}H NMR).[15]

General Procedure 3 (**GP 3**): The starting materials were dissolved in diisopropylamine (30 mL), After addition of $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol, 5 mol%) and CuI (10 mg, 0.05 mmol, 5 mol%), the flask was subjected to microwave irradiation (100 °C, 300 W, RAMP 15 min, HOLD 120 min, open vessel). After cooling to 25 °C the mixture was filtered through a 3 cm thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (30 x 3 cm, deactivated silica gel, petroleum ether /dichloromethane 2:1).

4.9.6 1,1'-Bis{5-[4-(*tert*-butyisulfanyl)phenylethynyl]-2-thienyl}ferrocene (116)[20]

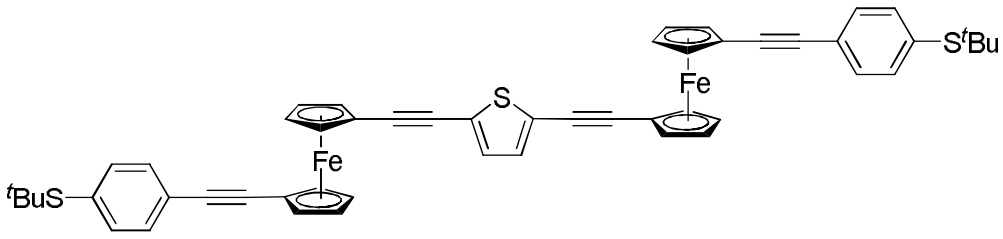


116

GP 3, 1,1´-Di[2-(4-ethynyl)thiophenyl]ferrocene (**145**) (398 mg, 1.0 mmol) and 1-(*tert*-butylsulfan-yl)-4-iodobenzene (**13**) (642 mg, 2.2 mmol), 91 %(661 mg, 0.9 mmol). **116** was obtained as a orange solid, identified by comparison with literature data (^{1}H NMR).[20]

.

4.9.7 1,4-Bis{1'-[(4-*tert*-butylsulfanyl)phenylethynyl]ferrocenylethynyl}thiophene (123)[15]

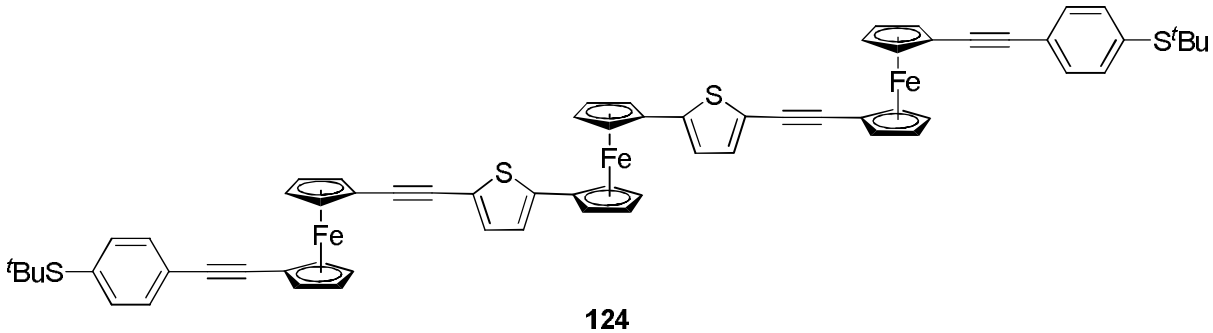


123

GP3, 2,5-Diethynyl-thiophene (**147**) (0.13 g, 1.0 mmol) and 1-[(4-*tert*-Butylsulfanyl)phenyl-ethynyl]-1'-iodoferrocene (**19**) (1.10 g, 2.2 mmol), 11 % (100 mg, 0.1 mmol). **123** was obtained as a dark red solid (m. p. 173.6-174.8 °C).

IR (ATR): $\tilde{\nu}$ = 3095 (w), 2957 (m), 2918 (w), 2893 (w), 2857 (w), 2203 (m), 1663 (w), 1589 (w), 1538 (w), 1491 (m), 1470 (w), 1455 (m), 1393 (m), 1364 (s), 1294 (w), 1249 (w), 1206 (w), 1163 (s), 1099 (w), 1030 (s), 1015 (m), 926 (s), 912 (s), 851 (s), 838 (s), 824 (s), 743 (w) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (s, 18H, C(CH_3)$_3$), 4.35 (m, 8H, H_{Fc}), 4.57 (m, 8H, H_{Fc}), 6.91 (s, 2H, arom. H), 7.40 (m, 4H, arom. H), 7.45 (m, 4H, arom. H) ppm. . – ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 31.0 (C(*C*H$_3$)$_3$), 46.3 (*C*(CH$_3$)$_3$), 66.3 (C_{Fc}C), 66.9 (C_{Fc}C), 71.1 (C_{Fc}H), 71.3 (C_{Fc}H), 72.9 (C_{Fc}H), 73.0 (C_{Fc}H), 79.5 (*C*C), 86.3 (C*C*), 88.8 (*C*C), 92.1 (C*C*), 124.1 (C_{Ar}C), 124.5 (C_{Ar}C), 131.1 (C_{Ar}H), 131.3 (C_{Ar}H), 132.5 (C_{Ar}C), 137.1 (C_{Ar}H) ppm. – MS (70 eV): *m/z* (%) = 198 (15), 57 (19), 56 (100) 55 (49), 53 (15), 51 (13). - HRMS ($C_{52}H_{44}Fe_2S_3$): Calcd. 876.1304, found 876.1278.

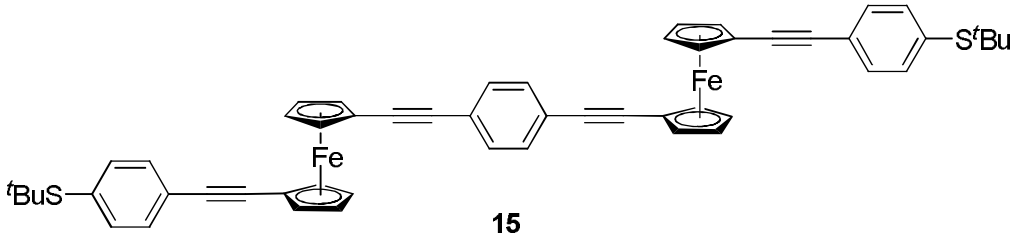
4.9.8 1,1'-Bis{5-{1'-[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocen-1-ylethnyl}-2-thiwnyl}-ferrocene (124)[20]



124

GP3, 1,1´-Di[2-(4-ethynyl)thiophenyl]ferrocene (**145**) (0.40 g, 1.0 mmol) and 1-[(4-*tert*-Butyl-sulfanyl)phenylethynyl]-1'-iodoferrocene (**19**) (1.50 g, 3.0 mmol), 20 % (0.23 g, 0.2 mmol). **124** was obtained as a orange solid, identified by comparison with literature data (^{1}H NMR).[20]

4.9.9 1,4-Bis{1'-[(4-*tert*-butylsulfanyl)phenylethynyl]ferrocenylethynyl}benzene (15)[15]



15

GP3, 1,4-Diethynylbenzene (**20**) (126 mg, 1.0 mmol) and 1-[(4-*tert*-Butylsulfanyl)phenyl-ethynyl]-1'-iodoferrocene (**19**) (1.10 g, 2.2 mmol), 22 % (0.20 g, 0.2 mmol) **15** was obtained as a orange solid, i dentified by comparison with literature data (^{1}H NMR).[15]

5 Bibliography

[1] G. E. Moore, *Electronics* **1965**. *38*. 114-117.

[2] G. E. Moore, *Tech. Dig. Int. Electron Devices Meet*. **1975**, 11-13.

[3] C. B. Gorman, R. L. Carroll, *Angew. Chem*. **2002**, *114*, 4556-4579; *Angew. Chem. Int. Ed. Engl*. **2002**, *41*, 4378-4400.

[4] International Technology Roadmap for Semiconductors, Semiconductor Industry Association, **2001**.

[5] J.-B. Waldner, (**2008**). *Nanocomputers and Swarm Intelligence*. London: ISTE John Wiley & Sons, pp. 44-45.

[6] M. Kanellos (2003-12-01). "Intel scientists find wall for Moore's Law". Retrieved 2009-03-19, http://news.cnet.com/2100-1008-5112061.html

[7] a). J. B. Johson, *Phys. Rev.* **1928**, *32*, 97-109; b). H. Nyquist, *Phys. Rev.* **1928**, *32*, 110-113.

[8] L. B. Kish, *Phys Lett. A* **2002**, *305*, 144-149.

[9] P. A. *Science* **1999**, *285*, 2079.

[10] Richard Feynman gave this talk entitled "There's plenty of room at the Bottom" on December 29th **1959**, at the annual meeting of the American Physical Society at the California Institute of Technology.

[11] J. M. Tour, Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming, World Scientific, New Jersey, **2003**, pp. 36.

[12] A. Aviram, M. A. Ratner, *Chem. Phys. Lett*. **1974**, *29*, 277-283.

[13] J. M. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang, I. Campbell, *Chem. Eur. J.* **2001**, *7*, 5118-5134.

[14] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252-254.

[15] J. Ma, M. Vollamnn, H. Menzel, S. Pohle, H. Butenschön, *J. Inorg. Organomet. Polym.* **2008**, *18*, 41-50.

[16] M. Vollmann, H. Butenschön, *C. R. Chimie*, **2005**, *8*, 1282-1285.

[17] C. Engtrakul, L. R. Sita, *Nano Lett.* **2001**, *10*, 541-549.

[18] S. A. Getty, C. Engtrakul, L. Wang, R. Liu, S.-H., Ke, H. U. Baranger, W. Yang, M. S. Fuhrer, L. R. Sita, *Phys. Rev. B* **2005**, *71*, 241401/1-241401/4.

[19] C. Engtrakul, L. R. Sita, *Organometallics* **2008**, *27*, 927-937.

[20] I. Baumgardt, H. Butenschön, *Eur. J. Org. Chem.* **2010**, 1076-1087.

[21] A. Blaszczyk, M. Elbing, M. Mayor, *Org. Biomol. Chem.* **2004**, *2*, 2722-2724.

[22] J. A. Marsden, M. M. Haley in *Metal-Catlyzed Cross-Coupling Reactions, Vol. 1* (Eds. A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, 317-394.

[23] I. R. Butler, S. B. Wilkes, S. J. Mcdonald, L. J. Hobson, A. Taralp, C. P. Wilde, *Polyhedron* **1993**, *12*, 129-131.

[24] J. K. Pudelski, M. R. Callstrom, *Organometallics* **1992**, *11*, 2757-2759.

[25] M. Buchmeiser, H. Schottenberger, *J. Organomet. Chem.* **1992**, *436*, 223-230.

[26] S. M. Dirk, D. W. Price, S. Chanteau, D. V. Kosynkin, J. M. Tour, *Tetrahedron* **2001**, *57*, 5109-5121.

[27] T.-Y. Dong, D. W. Chang, S.-F. Lin, M.-C. Lin, Y.-S. Wen, L. Lee, *Organometallics* **2006**, *25*, 2018-2024.

[28] I. R. Butler, A. L. Boyes, G. Kelly, S. C. Quayle, T. Herzig, J. Szewczyk, *Inorg. Chem. Commun.* **1999**, *2*, 403-406.

[29] M. Mayer, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer, *Angew. Chem*. **2003**, *115*, 6014-6018; *Angew. Chem. Int. Ed.* **2003**, *42*, 5834-5838.

[30] J. Yin, G.-A. Yu, J. Guan, F. Mei, S. H. Liu, *J. Organomet. Chem.* **2005**, *690*, 4265-4271.

[31] L.-X. Liao, F. Stellacci, D. V. McGrath, *J. Am. Chem. Soc.* **2004**, *126*, 2181-2185.

[32] D. Grebel-Köhler, D. Liu, S. De Feyter, V. Enkelmann, T. Weil, C. Engles, C. Samyn, K. Müllen, F. C. De Schryver, *Macromolecules* **2003**, *36*, 578-590.

[33] J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, J. C. Smart, *J. Organomet. Chem.* **1971**, *27*, 241-249.

[34] M. D. Rausch, D. J. Ciappenelli, *J. Organomet. Chem.* **1967**, *10*, 127-136.

[35] R. F. Kovar, M. D. Rausch, H. Rosenberg, *Organomet. Chem. Synth.* **1970**/**1971**, *1*, 173-181.

[36] M. D. Rausch, G. A. Moser, C. F. Meade, *J. Organomet. Chem.* **1973**, *51*, 1-11.

[37] I. Baumgardt, *Dissertation*, Leibniz Universität Hannover, **2008**.

[38] R. R. Schrock, *Polyhedron* **1995**, *14*, 3177-3195.

[39] R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413-4450.

[40] a). A. Fürstner, K. Grela, *Angew. Chem*. **2000**, *112*, 1292-1294; *Angew. Chem. , Int. Ed.* **2000**, *39*, 1234-1236; b). A. Fürstner, C. Mathes, K. Grela, *Chem. Commun.* **2001**, *12*, 1057-1059; c). A. Fürstner, K. Langemann, *J. Org. Chem.* **1996**, *61*, 8746-

8749; d). R. R. Schrock, A. Hoveyda, , *Angew. Chem*. **2003**, *115*, 4740-4782; *Angew. Chem. , Int. Ed.* **2003**, *42*, 4592-4633.

[41] A. Fürstner, C. Mathes, P. W. Davies, *Chem. Commun.* **2005**, *18*, 2307-2320.

[42] F. Pennella, R. L. Banks, G. C. Bailey, *Chem. Commun.* **1968**, *23*, 1548-1549.

[43] A. Mortreux, M. Blanchard, *J. Chem. Soc. Chem. Commun*. **1974**, *19*, 786-787.

[44] J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am .Chem. Soc*. **1981**, *103*, 3932-3934.

[45] A. Fürstner, C. Mathes, C. W. Lehmann, *J. Am .Chem. Soc*. **1999**, *121*, 9453-9454.

[46] V. Sashuk, J. Ingatowska, K. Grela, *J. Org. Chem.* **2004**, *69*, 7748-7751.

[47] S. Beer, C. G. Hrib, P. G. Jones, K. Brandhorst, J. Grunenberg, M. Tamm, *Angew. Chem*. **2007**, *119*, 9047-9051; *Angew. Chem. Int. Ed.* **2007**, *46*, 8890-8894.

[48] A. Mortreux, O. Coutelier, *J. Mol. Cat. A: Chem.* **2006**, *254*, 96-104.

[49] T. J. Katz, J. McGinnis, *J. Am .Chem. Soc*. **1975**, *97*, 1592-1594.

[50] S. F. Pedersen, R. R. Schrock, M. R. Churchill, H. J. Wasserman, *J. Am .Chem. Soc*. **1982**, *104*, 6808-6809.

[51] a). N. Kaneta, T. Hirai, M. Mori, *Chem. Lett.* **1995**, *24*, 627-628; b). N. Kaneta, K. Hikichi, S. Asaka, M. Uemura, M. Mori, *Chem. Lett.* **1995**, *24*, 1055-1056.

[52] N. G. Pschirer, U. H. Bunz, *Tetrahedron Lett.*, **1999**, *40*, 2481-2484.

[53] K. Grela, J. Ignatowska, *Org. Lett.* **2002**, *4*, 3747-3749.

[54] N. G. Pschirer, W. Fu, R. D. Adams, U. H. Bunz, *Chem. Commun*. **2000**, *1*, 87-88.

[55] a). U. H. Bunz *Acc. Chem. Res*. **2001**, *34*, 998-1010; b). N. G. Pschirer, U. H. Bunz, *Macromolecules* **2000**, *33*, 3961-3964; c). G. Brizius, N. G. Pschirer, W. Steffen, K. Stitzer, H. C. zur Loye, U. H. Bunz, *J. Am. Chem. Soc*. **2000**, *122*, 12435-12440.

[56] E. O. Fischer, R. Ruhs, D. Plabst, *Z. Naturforsch, Teil B, 32 B*, **1977**, *7*. 802.

[57] M. Aklyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, P. E. Fanwick, *Inorg. Chem*. **1979**, *18*, 2266-2270.

[58] a). S. A. Krouse, R. R. Schrock, *Macromolecules* **1989**, *22*, 2569-2576; b). K. Weiss, A. Michel, E. M. Auth, U. H. Bunz, T. Mangel, K. Müllen, *Angew.Chem*. **1997**, *109*, 522-525; *Angew. Chem. Int. Ed.* **1997**, *36*, 506-509.

[59] A. Fürstner, A.-S. Castanet, K. Radkowski, C. W. Lehmann, *J. Org. Chem.* **2003**, *68*, 1521-1528.

[60] E. B. Bauer, S. Szafert, F. Hampel, J. A. Gladysz, *Organometallics* **2003**, *22*, 2184-2186.

[61] M. Ijsselstijn, B. Aguilera, G. A. van der Marel, J. H. Van Boom, F. L. Van Delft,

H. E. Schoemaker, H. S. Overkleeft, F. P. J. T. Rutjes, M. Overhand, *Tetrahedron Lett.* **2004**, *45*, 4379-4382.

[62] C. C. Cummins, *Chem. Commun*. **1998**, *17*, 1777-1786.

[63] A. Fürstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.* **2001**, *7*, 5299-5317.

[64] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145-179.

[65] a). W. Zhang, S. Kraft, J. S. Moore, *Chem. Commun.* **2003**, *7*, 832-833; b). W. Zhang, S. Kraft, J. S. Moore, *J. Am .Chem. Soc.* **2004**, *126*, 329-335; c). J. M. Blackwell, J. S. Figueroa, F. H. Stephens, C. C. Cummins, *Organometallics* **2003**, *22*, 3351-3353.

[66] M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol, Chem.* **2007**, *5*, 523-530.

[67] J. H. Freundenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold, J. F. Ziller, *Organometallics* **1984**, *3*, 1563-1573.

[68] B. Haberlag, X. Wu, K. Brandhorst, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2010**, im press, DOI: 10.1002/chem.201000597.

[69] S. Beer, K. Brandhorst, J. Grunenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Org. Lett.* **2008**, *10*, 981-984.

[70] S. Beer, K. Brandhorst, C. G. Hrib, X. Wu, B. Haberlag, J. Grunenberg, P. G. Jones, M. Tamm, *Organometallics* **2009**, *28*, 1534-1545

[71] a). A. M. Geyer, E. S. Wiedner, J. B. Gary, R. L. Gdula, N. C. Kuhlmann, M. J. A. Johnson, B. D. Dunietz, J. W. Kampf, *J. Am. Chem. Soc*. **2008**, *130*, 8984-8999; b). R. L. Gdula, M. J .A. Johnson, *J. Am. Chem. Soc*. **2006**, *128*, 9614 – 9615.

[72] M. Bindl, R. Stade, E. K. Heilmann, A. Picot, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2009**, *131*, 9468-9470.

[73] M. Kotora, D. Necas, P. Stepnicka, *Collect. Czech. Chem. Commun.* **2003**, *68*, 1897-1903.

[74] T. Bobula, J. Hudlicky, P. Novak, R. Gyepes, I. Cisarova, P. Stepnicka, M. Kotora, *Eur. J. Inorg. Chem.* **2008**, *25*, 3911-3920.

[75] R. R. Schrock, *Acc. Chem. Res.* **1986**, *19*, 342-348.

[76] G. Doisneau, G. Balavoine and T. Fillebeen-Khan, *J. Organomet. Chem.* **1992**, *425* 113-117.

[77] A. Mortreux, N. Dy. M. Blanchard, B. *J. Mol. Catal.* **1976**, *1*, 101-109.

[78] A. Bencheick, M. Petit, A. Mortreux, F. Petit, *J. Mol. Catal.* **1982**, *15*, 93-101.

[79] A. Mortreux, J. C. Delgrange, M. Blanchard, B. Lubochinsky, *J. Mol. Catal.* **1977**,

2, 73-82.

[80] A. Mortreux, F. Petit, A. Blanchard, *J. Mol. Catal*. **1980**, *8*, 97-106.

[81] W. G. Jary, A. K. Mahler, T. Purkathofer, J. Baumgartner, *J. Organomet. Chem.* **2001**, *629*, 208-212.

[82] S. L. Ingaham, M. S. Khan, J. Lewis, N. J. Long, P. R. Raithby, *J. Organomet. Chem.* **1994**, *470*, 153-159.

[83] J. K. Pudelski, M. R. Callstrom, *Organometallics* **1994**, *13*, 3095-3109.

[84] M. Sato, Y. Kubota, Y. Kawata, T. Fujihara, K. unoura, A. Oyama, *Chem. Eur. J.* **2006**, *12*, 2282-2292.

[85] M. D. Rausch, E. O. Fischer, H. Grubert, *J. Am. Chem. Soc.* **1960**, *82*, 76-82.

[86] *Handbook of Chemistry and Physics*, 88th ed. (Ed.: D. R. Lide), CRC, Boca Raton, **2007-2008**.

[87] T. S. Abram, W. E. Watts, *J. Chem. Soc. Chem. Commun.* **1974**, 857-858.

[88] E. W. Koch, H. U. Siehl, M. Hanack, *Tetrahedron Lett.* **1985**, *26*, 1493-1496.

[89] T. S. Abram, W. E. Watts, *J. Chem. Soc. Perkin Trans. 1* **1977**, 1522-1526.

[90] T. S. Abram, W. E. Watts, *J. Chem. Soc. Perkin Trans. 1* **1977**, 1527-1531.

[91] K. P. Jäckel, M. Hanack, *Tetarhedron Lett.* **1974**, *15*, 1637-1640.

[92] C. C. Lee, E. C. F. Ko, *J. Org. Chem.* **1975**, *40*, 2132-2133.

[93] K. P. Jäckel, M. Hanack, *Chem. Ber.* **1977**, *110*, 199-207.

[94] CCDC-744855 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. J. Ma, B. Kühn, T. Hackl, H. Butenschön, *Chem. Eur. J.* **2010**, *16*, 1859-1870.

[95] H. Günther, *NMR Spectroscopie,* 2nd ed., Thieme, Stuttgart, **1983**, p. 229.

[96] Topspin 2.1, Patchlevel 3, Bruker Biospin, **2008**.

[97] E. Negishi, A. O. King, N. Okukado, *J. Org. Chem.* **1977**, *42*, 1821-1823.

[98] a). E. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340-348; b). J. E. Milne, S. L. Buchwald, *J. Am .Chem. Soc.* **2004**, *126*, 13028-13032; c). V. B. Phapale, D. J. Cardenas, *Chem. Soc. Rev.* **2009**, *38*, 1598-1607.

[99] S. Superchi, N. Sotomayor, G. Miao, B. Joseph, V. Snieckus, *Tetrahedron Lett.* **1996**, *37*, 6057-6060.

[100] J. Ma, B. Kühn, T. Hackl, H. Butenschön, *Chem. Eur. J.* **2010**, *16*, 1859-1870.

[101] a). G. C. Allen, N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 357-389; b). N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391-344; c). M. B. Robin, P. Day, *Adv. Inorg. Chem.*

Radiochem. **1967**, *10*, 247-422.

[102] K. Kowalski, M. Linseis, R. F. Winter, M. Zabel, S. Zalis, H. Kelm, H.-J. Krüger, B. Sarkar, W. Kaim, *Organometallics* **2009**, *28*, 4196-4209.

[103] K. Venkatasubbaiah, A. Doshi, I. Nowik, R. H. Herber, A. L. Rheingold, F. Jäkle, *Chem. Eur. J.* **2008**, *14*, 444-458.

[104] T. Weyland, K. Costuas, L. Toupet, J.-F. Halet, C. Lapinte, *Organometallics* **2000**, *19*, 4228-4239.

[105] M. Rosenblum, N. M. Brawn, D. Ciappenelli, *J. Organomet. Chem.* **1970**, *24*, 469-477.

[106] G. Cahiez, C. Duplais, J. Buendia, *Angew.Chem*. **2009**, *121*, 6859-6862; *Angew. Chem. Int. Ed.* **2009**, *48*, 6731-6734.

[107] M. E. Wright, *Organometallics* **1990**, *9*, 853-856.

[108] G. Doisneau, G. Balavoine T. Fillebeen-Khan, *J. Organomet. Chem.* **1992**, *425*, 113-117.

[109] W. G. Jary, A. K. Mahler, T. Purkathofer, J. Baumgartner, *J. Organomet. Chem.* **2001**, *629*, 208-212.

[110] D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1376-1387.

[111] E. Viola, C. L. Sterzo, F. Trezzi, *Organometallics* **1996**, *15*, 4352-4354.

[112] G. R. Li, X. H. Wang, J. Li, X. J. Zhao, F. S. Wang, *Tetrahedron* **2006**, *62*, 2576-2582.

[113] J. R. Garabatos-Perera, R. Wartchow, H. Butenschön, *J. Organomet. Chem.* **2004**, *689*, 3541-3549.

[114] *SHEÖXTL-NT V6.1*, Bruker AXS GmbH, D-76181 Karlsruhe, Germany, **2002**.

[115] S. Cohen, J. Ma, H. Butenschön, R. H. Herber, *Dalton Trans.* **2009**, 6606-6609.

[116] CCDC-725397 (T = 173 K) and CCDC-725398 (T = 295 K) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. S. Cohen, J. Ma, H. Butenschön, R. H. Herber, *Dalton Trans.* **2009**, 6606-6609.

[117] *SMART-NT V5.6*, Bruker AXS GmbH, D-76181 Karlsruhe, Germany, **2002**.

[118] *SAINT-NT V5.0*, Bruker AXS GmbH, D-76181 Karlsruhe, Germany, **2002**.

[119] J. R. Garabatos-Perera, H. Butenschön, *J. Organomet. Chem.* **2008**, *693*, 359-360.

[120] J. Lewis, N. J. Long, P. R. Raithby, G. P. Shields, W. Y. Wong, M. Younus, *J. Chem. Soc., Dalton Trans.* **1997**, 4283-4288.

Curriculum Vitae

Personal Information:

Name: Jingxiang Ma
Sex: Male
Date of Birth: 10.29.1969
Place of Birth: Jiangsu, P.R.China
Marital Status: married
E-mail: jingxiangma@googlemail.com

Education:

09/1976 – 07/1982 Daying Primary School
09/1982 – 07/1988 Paoche Secondary School
09/1988 – 07/1991 University Nanjing, College of Medicine
09/1997 – 09/1999 University Suzhou, Department of Chemistry
10/2000 – 08/2007 Leibniz University Hannover, Institute of Organic Chemistry
Master's thesis: Synthesis of Ferrocene-based Molecular Wires Via Sonogashira Coupling Reaction
10/2007 –09/2010 Leibniz University Hannover, Institute of Organic Chemistry
Doctor's thesis: 1,1'-Dialkynylferrocenes: Building Blocks for Molecular Wires by Alkyne Metathesis

Work Experiences:

08/1991 – 08/1997 Suzhou Nr. 4 Hospital, China
Research subject: Trace elements and Cancers

Publications:

1. New Molecular Wires with Two Ferrocene Hinges, J. Ma, M. Vollmann, H. Menzel, S. Pohle, H. Butenschön, *J. Inorg. Organomet. Polym.* 2008, *18*, 41 – 50.
2. Metal Atom Dynamics in Four Triferrocenylmethane Derivatives and the Crystal Structure of Fc_3COH, S. Cohen, J. Ma, H. Butenschön, R. H. Herber, *Dolton Trans*. **2009**, 6606 – 6609.
3. Transannular Addition of Phenols to 1,1'-Dialkynylferrocenes: Unanticipated Formation Of Phenoxy[4]ferrocenophanedienes, J. Ma, B. Kühn, T. Hackl, H. Butenschön, *Chem*. Eur. *J.* 2010, *16*, 1859 – 1870.