Towards Ferrocyne and Benzyne π-Complexes

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And I saw all the work of the God, how mankind are not able to find out the work that has been done under the sun; however much mankind keep working hard to seek, yet they do not find out. And even if they should say they are wise enough to know, they would be unable to find out.

Ecclesiastes 8:17

Kurzfassung

Auf dem Wege zum Ferrocin und zu Benz-in π-Komplexen.

Im Rahmen der vorliegenden Arbeit wird die Suche nach π-(Arin) Metalkomplexen vorgestellt, dabei wurden die bekannten Konzepte zur Darstellung der Arine auf Ferrocen und (Aren)$Cr(CO)_3$ übertragen. Es wurden Eliminierungsreaktionen an den verschiedenen Halogenbenzolen und Phenylsulfonaten sowie Fragmentierungsreaktionen von 1,2-Ferrocendicarbonsäureanhydrid getestet, auch die Darstellung von Arinen aus Zwitterionen wurde versucht.Bekannt ist, dass die $Cr(CO)_3$-Phenyltriflate unter Einwirkung von Basen keine Eliminierungsreaktionen sondern anionische thia-Fries Umlagerung eingehen. Da die niedrige Elektronendichte im aromatischen Ring, verursacht durch elektronenziehende Eigenschaft der $Cr(CO)_3$-Gruppe, für dieses ungewöhnliche Verhalten verantwortlich gemacht wird, wurden im Rahmen dieser Arbeit zahlreiche elektronenreichere Komplexe dargestellt. Dies wurde zum einen durch Einführung elektronenschiebendener Substituenten wie Methoxy-Gruppen erreicht und zum anderen durch den Ligandenaustausch am Chromatom, initiiert durch UV-Bestrahlung, indem die elektronenziehende CO Liganden durch elektronenreichere Phosphin-Liganden ersetzt wurden.

Des Weiteren wurden Ferrocenyltriflate für entsprechende Untersuchungen herangezogen. Da Ferrocen ein besonders elektronreicher Aromat ist, wurde eine effektive Eliminierung erwartet. Entgegen allen Erwartungen fanden jedoch mit fast quantitativen Ausbeuten die thia-Fries-Umlagerungen statt. Um die elektronendichte in Cyclopentadienylliganden noch weiter zu erhöhen, wurden weitere Ferrocenyltriflate synthetisiert, indem elektronen-liefernde Gruppen wie Methyl und Methoxy eingeführt wurden. Diese extrem elektronenreichen Ferrocenyltriflate gingen jedoch die thia-Fries-Umlagerung mit der gleichen Effektivität ein wie die unsubstituierten Vertreter. Dieses Ergebnis zeigt, dass die Erklärung für dieses Verhalten im Falle des Ferrocens nicht in der Elektronendichte des aromatischen Systems zu suchen ist, sondern mehr auf das gespannte System eines fünfgliedriges Ringes zurückzuführen ist. Die thia-Fries-Umlagerung an 1,1'-Ferrocendiylditriflat führte ausschließlich zur Bildung eines *meso*-Produkts, was offensichtlich ein sehr seltener Fall einer interannularer Stereoinduktion zwischen den Cp-Liganden ist. Während die Metallierung der Halogenferrocene ergebnislos blieb, zeigte das *ortho* lithiierte Fluorbenzol $Cr(CO)_3$ Komplex die erwünschte Reaktivität und lieferte ein Kopplungsprodukt, das als Ergebnis der Eliminierung von LiF gedeutet werden kann. Die UV-Bestrahlung von 1,2-Ferrocendicarbonsäureanhydrid führte zur Bildung des 1,2-Ferrocendiradikals, das formal als Ferrocin betrachtet werden kann.

Schlüsselwörter: (η^6-Arin)tricarbonylchromium(0), Ferrocin, anionische thia-Fries Umlagerung, Ferrocenderivate, Photochemische Reactionen, Interannulare Stereoinduktion

Abstract

Towards Ferrocyne and Benzyne π-Complexes.

In this research project the search for new π aryne metal complexes is presented, in which the known methods for the preparation of arynes were applied to ferrocene and (arene)$Cr(CO)_3$ complexes. The elimination of various halobenzenes and phenyl sulphonates, fragmentation reactions of 1,2-ferrocene dicarboxylic anhydride were tested, and the synthesis from zwitterions was also tried.

It is known that (phenyl triflate)$Cr(CO)_3$ complexes undergo the anionic thia-Fries rearrangement rather than elimination reactions. Since the electron withdrawing nature of the tricarbonylchromium group is the major factor for the anionic thia-Fries rearrangement, the electron density of phenyl triflate tricarbonylchromium complexes was increased via two ways. Firstly, by introduction of electron donating groups at the aromatic system and, secondly, the electron withdrawing carbonyl ligands were substituted by more electron rich triphenyl phosphine ligands, initiated by UV-irradiation.

This result stimulated the idea to try the reaction with a more electron rich ferrocene system with the perspective to obtain ferrocyne or ferrocenediyne. However, treatment of ferrocenyl triflate with different bases gave in an instantaneous reaction products of anionic thia-Fries rearrangements in nearly quantitative yields. This was the first case of this kind of reaction at a five membered ring. In order to increase the electron density in the Cp ligands some even more electron rich ferrocenyl triflates bearing one or more electron donating groups were synthesized, which underwent the thia-Fries rearrangement with the same efficiency as the unsubstituted ferrocenyl triflate. The result shows that this phenomenon cannot only be explained by electronic effects but also by the strain in the five-membered ring. The thia-Fries rearrangement of 1,1'-ferrocendiyl ditriflate exclusively led to the formation of the *meso* product. This is a rare case of an interannular stereoinduction between both Cp ligands.

While the metallation of various haloferrocenes remained unsuccessful, the *ortho*-lithiation of (fluorobenzene)$Cr(CO)_3$ showed the desired reactivity and delivered the coupling product, which can be interpreted as the product of elimination of LiF.

The fragmentation reaction of 1,2-ferrocene dicarboxylic acid anhydride afforded the formation of the 1,2-ferrocene diradical under photochemical reaction conditions, which can be formally regarded as ferrocyne (1,2-didehydroferrocene).

Key words: (η^6-Aryne)tricarbonylchromium(0), Ferrocyne, Anionic thia-Fries Rearrangement, Ferrocene Derivates, Photochemical Reactions, Transannular Stereoinduction

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Abbreviations

Å	Angstrom(s)
aq.	Aqueous
Ar	Aryl
BMS	Borane Dimethylsulphate
Bn	Benzyl
br	Broad (spectral)
Bu	Butyl
t-Bu	*tert*-Butyl
°C	Degrees Celsius
calcd.	Calculated
cat.	Catalyst
cm^{-1}	Wavenumber(s)
^{13}C NMR	^{13}C Nuclear Magnetic Resonance
mCPBA	*meta*-Chloroperbenzoic acid
δ	Chemical Shift (in parts per million downfield from tetramethylsilane)
d	Day(s)
d	Doublet (spectral)
dd	Doublet of Doublet (spectral)
decomp.	Decomposition
DEPT	Distortionless Enhancement by Polarization Transfer
DMF	Dimethylformamide
DMG	Directing Metallating Groups
DIPA	*N,N* Diisopropylamine
ee	Enantiomeric Excess
equiv.	Equivalent
Et	Ethyl
eV	Electron Volt ($1.602*10^{-19}$ J)
g	Gram
h	Hour(s)
^{1}H NMR	^{1}H Nuclear Magnetic Resonance
HOMO	Highest Unoccupied Molecular Orbital
HPLC	High-performance Liquid Chromatography

HRMS	High-resolution Mass Spectrometry
HMQC	Heteronuclear Multiple Quantum Coherence
HMBC	Heteronuclear Multiple Bond Correlation
Hz	Hertz
IR	Infrared
J	Coupling Constant in NMR Spectroscopy
L	Ligand
LDA	Lithium Diisopropylamide
LiTMP	Lithium 2,2,5,5-Tetramethylpiperidine
LUMO	Lowest Unoccupied Molecular Orbital
m	Multiplet (spectral)
m	Medium (IR spectra)
M	Molar (moles per liter)
M^+	Parent Molecular Cation (mass spectrometry)
Me	Methyl
mL	Millilitre(s)
min	Minutes
mmol	Millimol
m. p.	Melting point
MS	Mass spectrometry
m / z	Mass-to-charge Ratio (in mass spectrometry)
μW	Microwave
NMR	Nuclear Magnetic Resonance
Nu	Nucleophile
PE	Petroleum Ether
Ph	Phenyl
ppm	Part(s) per Million
q	Quartet (spectral)
rac	Racemic
s	Singlet (spectral)
s	Sharp (IR spectral)
t	Triplet (spectral)
TBME	*tert*-Butylmethyl Ether
Tf	Trifluoromethanesulfonyl

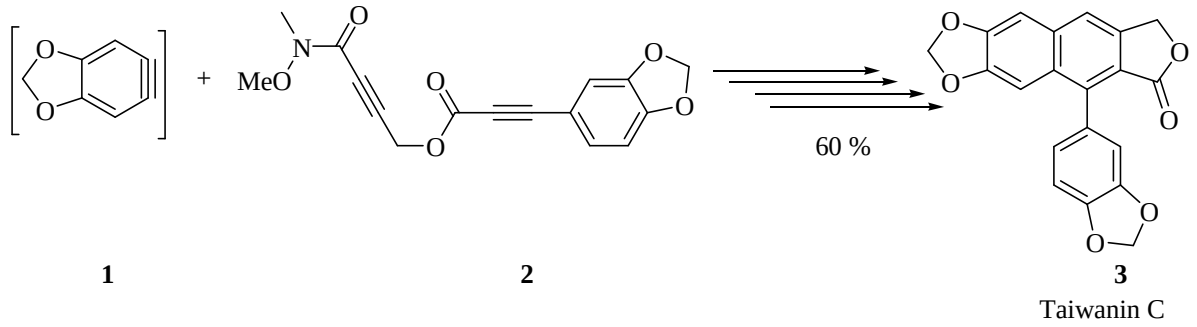
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMEDA	*N*,*N*,*N'*,*N'*-Tetramethylethane-1,2-diamine
TsOH	*para*-Toluenesulfonic acid (tosylic acid)
UV	Ultraviolet
W	Watt
w	weak (IR spectral)

Contents

A. Introduction

1. Arynes: a historical overview

Nowadays arynes play an important role in the modern preparative organic chemistry. They are primarily used for the generation of mono- and polycyclic aromatic hydrocarbons, thus representing a powerful tool for the synthesis of various important compounds for material science, medicine, and other fields.[1] The synthesis of Taiwanin C is an example (*Scheme 1*).

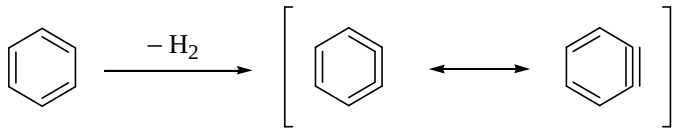


1 **2** **3**
Taiwanin C

Scheme 1. The Synthesis of Taiwanin C (a pharmaceutical for the struggle against tumour cells).[2]

Though arynes represent such a central means in hands of organic chemists, they have not been known for a very long time. Their existence was really postulated only in the 1930s,[3] was proven in the 1950s,[4 - 7] and one more decade has passed before they were systematically applied in syntheses.[8, 9] The reason for such a late development lies in a very high reactivity of these compounds.

Arynes are neutral intermediates in which two adjacent atoms of an aromatic ring lack substituents, leaving thus two aromatic orbitals, which generate two molecular orbitals, π and π^*. The best known representative of the arynes is benzyne (C_6H_4). Nevertheless, this name implies the existence of a rigid triple bond, which is only one part of a resonance formula shown in *Scheme 2*.



4 **4a** **4b**

Scheme 2. Resonance formula of benzyne

The name 1,2-didehydrobenzene is also common and better corresponds to the real structure of the compound, which is usually shown as follows:

4c

One π bond is just a part of the aromatic system, the additional π bond is localised and stands orthogonally to the π orbitals of the aromatic system. As expected, the formal C,C triple bond in benzyne is extensively weaker than in unstrained alkynes as shown by the C≡C stretching vibration (1846 cm^{-1} for benzyne, whereas this band for normal alkynes usually occurs in the range about 2150 cm^{-1}).

Benzyne is sometimes illustrated also as a diradical, while the π bond is homolyticly split.

4d

In the meantime, is **4** one of the most thoroughly examined reactive intermediate, the available experimental data enclose infrared spectroscopy,[10] photoelectron spectroscopy,[11, 12] negative ions photoelectron spectroscopy (NIPES),[13, 14] CID (collision-induced dissociation threshold),[15] microwave spectroscopy[16] and NMR spectroscopy.[17-19] With NIPES detected singlet-triplet splitting amounts to 37.5 kcal mol^{-1},[13] a data, which is also calculated.

The diradical character **4d** is insignificant, the electronic structure is better given as a strained cyclic alkyne or a cumulene,[18] whereas the alkyne character **4b** predominates (*vide infra*).[17]

The high angular strain in **4** is responsible for its high reactivity because of the direct conse-

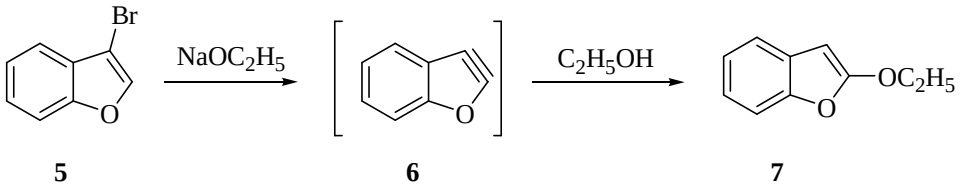
quence for the low lying LUMOs, so that the energy gap between the HOMO and the LUMO is relatively small. For that reason benzynes show the properties of extremely reactive alkynes participating in cycloaddition and *ene* reactions with alkenes. The other reason for the reactivity of benzynes is that the low lying LUMO causes a very high electrophilicity.[19]

Because 1,2-didehydrobenzene and its derivatives are extremely reactive species appearing in chemical processes only as short-lived intermediates, they cannot usually be dedicated directly.

The reason of this extremely high reactivity of arynes remained unrecognized for a long time. Only at the end of the 19th century the first supposition was made concerning the existence of unknown intermediates, with which, under the presumption that they have the substructure of the didehydrobenzene, many experiments could be explained.

Thus a C_6H_4-intermediate was postulated in 1870 for understanding of the origin of biphenyl during the pyrolysis of diphenylmercury.[20] Also the formation of triphenylene and polyphenyl in the Wurtz-Fittig reaction of chlorobenzene was formulated using the 1,2-C_6H_4-diradical as an intermediate.[3, 21]

The generation of didehydroarene with a triple bond was formulated for the first time by Stoermer and Kahlert, who explained the rearrangement of **3** with 2,3-didehydrobenzofuran (**6**) as an intermediate (*Scheme 3*).[22]



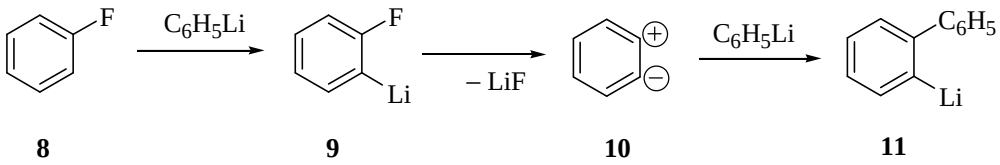
5 **6** **7**

Scheme 3. Formation of 2,3-didehydrobenzofuran (**6**).

In spite of all these first signs no attempt was undertaken until to the half of the 20th century to synthesize and to research didehydroarenes selectively, until two phenomena struck in the investigation of the nucleophilic aromatic substitution.

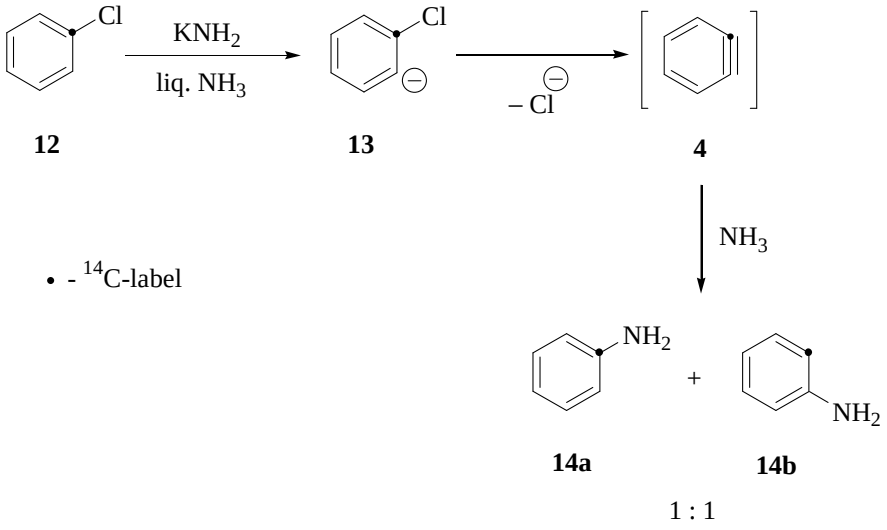
Firstly, phenyl lithium reacted clearly faster with fluorobenzene than with any other halobenzene generating biphenyl.[4] The detection of 2-biphenyllithium (**11**) as the actual product of this reaction led to the hypothesis, that 1,2-didehydrobenzene (**10**) as an intermediate was

formed (*Scheme 4*).[5] The reason for such a reaction path is the higher acidity of *ortho* H atom in fluorobenzene, which results in a higher reaction rate.



Scheme 4

The second phenomenon was that the reaction between chlorobenzene with potassium amide in liquid ammonia led to the formation of two products, which could be distinguished only by use of isotope labelling with ^{14}C in the *ipso* position.[6, 23-25] The formation of both aniline isotopomers (**12a** and **12b**) can be explained only by the appearance of 1,2-didehydrobenzene (**4**) (*Scheme 5*).

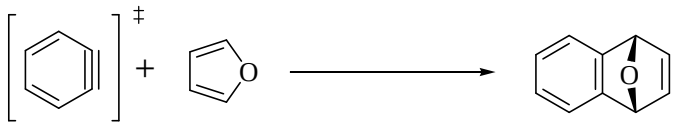


Scheme 5. Formation of two aniline isotopomers

These results confirmed unambiguously the existence of didehydrobenzene and opened a new "age" of the didehydrobenzene chemistry. Different didehydroarenes could be synthesized since then, not only for investigations but selectively for preparative organic chemistry.

The important developments in this period were the confirmation of didehydroaromatic intermediates in the reactions of haloarenes with phenyl lithium by Huisgen[26] and the intercept

tion of 1,2-didehydrobenzene **4** with a diene (furan **15**) generating a cycloaddition product **16** via Diels Alder reactions by Wittig (*Scheme 6*).[27]

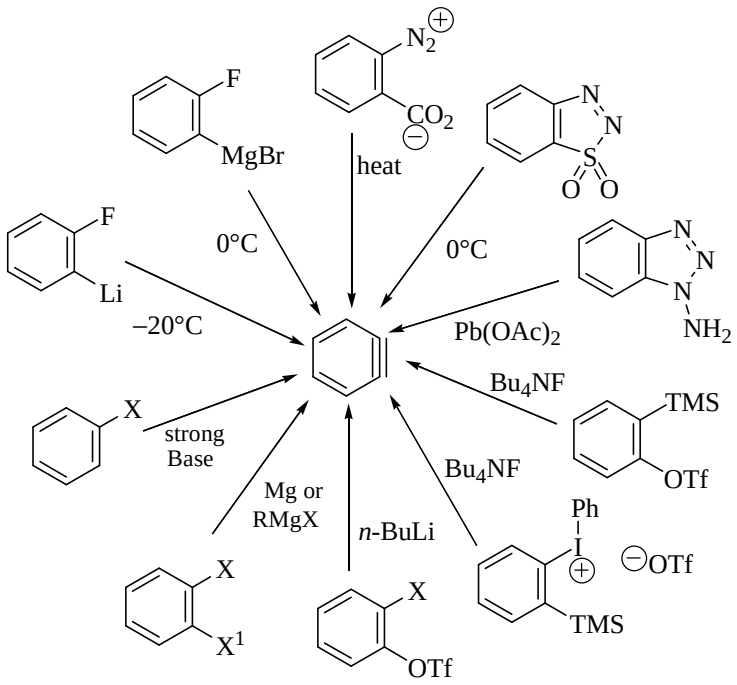


4 **15** **16**

Scheme 6

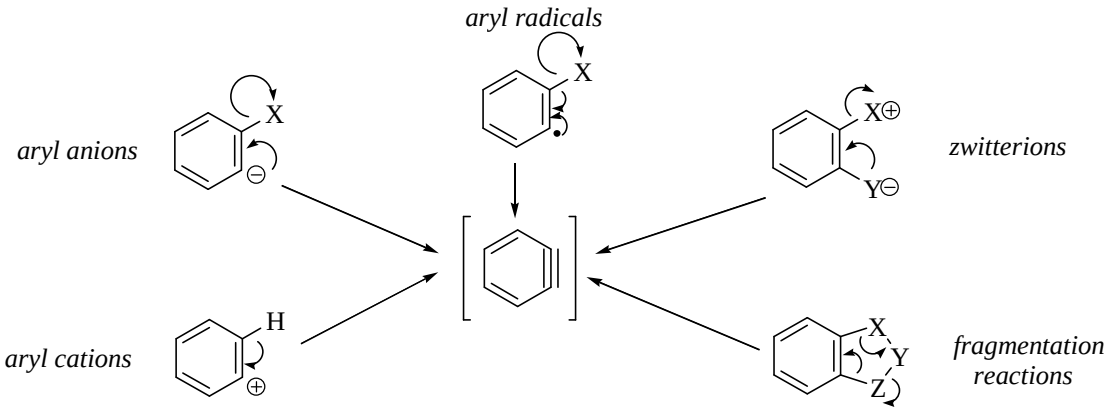
The interest for the 1,2-didehydrobenzene chemistry increased a decade later with the discovery of the possibilities to generate 1,2-didehydrobenzene without use of organometallic reagents. [8, 9]

The methods for the synthesis of didehydroarenes, which were developed in the following decades, are summarised in *Scheme 7*.[27 - 32]



Scheme 7. Possibilities for synthesis of benzyne[33]

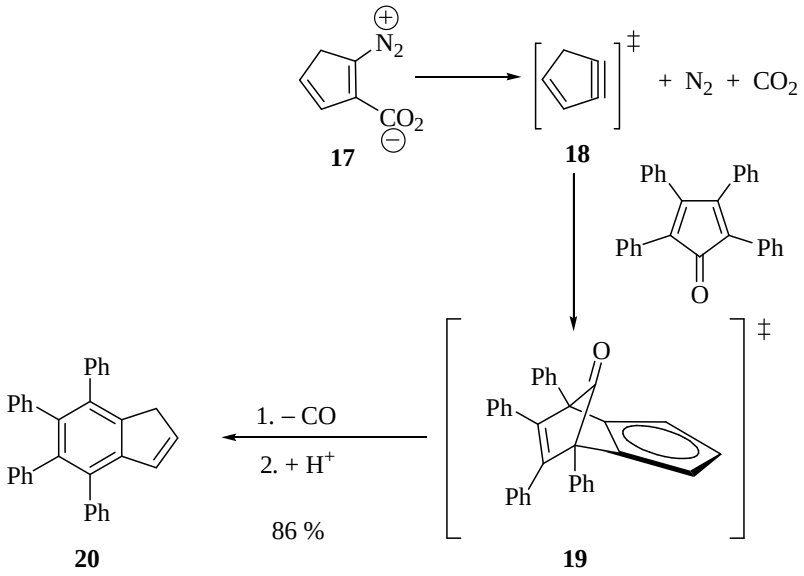
Basically, these various methods can be generalised only in 5 types of reactions. As shown in *Scheme 8* arynes can be generated from aryl anions, aryl cations, aryl radical, zwitterions and by fragmentation reactions.



Scheme 8

Furthermore the methods, which led to benzyne, were adopted in the chemistry of a five-membered aromatic system. In the experiment of Stoermer and Kahlert (*Scheme 3*) 2,3-didehydrobenzofuran was already formed.

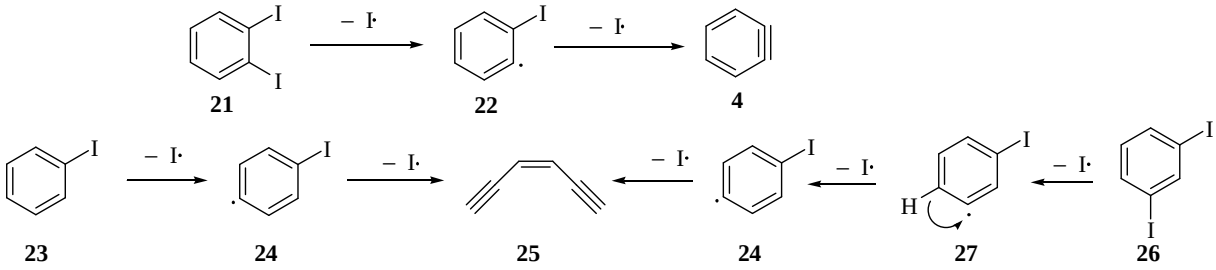
In 1964 G. Wittig managed the synthesis of didehydroindene[34] and in 1970 didehydrocyclopentadienyl was synthesised by Martin and Bloch[35] as an intermediate for a Diels Alder reaction and then converted it successfully (*Scheme 9*).



Scheme 9

Except that arynes have been proved as products of subsequent reaction (Diels-Alder) or in experiments of mark with ^{14}C atoms indirectly, experiments have been undertaken to prove them directly by using spectroscopic identification methods.

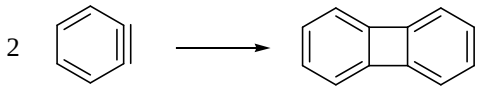
With the investigation of the pyrolysis of three diiodobenzene isomeres Fisher and Lossing detected 1,2-didehydrobenzene mass spectrometrically by measurement of the ionisation potential (*Scheme 10*).[36]



Scheme 10

In all three cases a product was identified with molecular mass *m* / *z* 76. The ionisation potential of **4** amounted to 9.75 eV, while of both other pyrolysis products, identified later as **25**, to 9.46 eV.

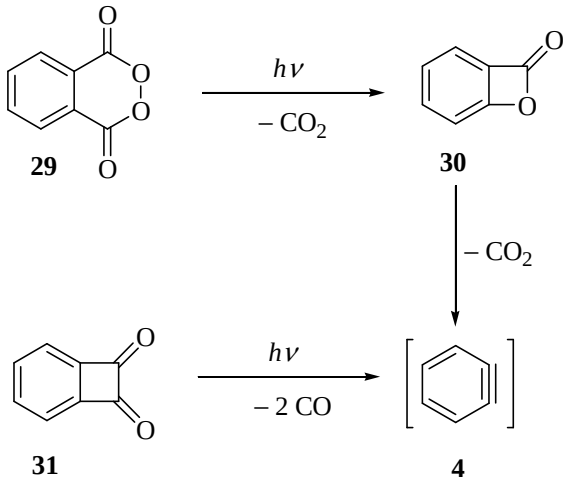
Moreover, in the first pyrolysis a product with *m*/*z* 152 was found, which corresponds to the biphenylene **28** and could be formed only by a [2+2] cycloaddition of two 1,2-didehydro-benzene molecules **4** (*Scheme 11*).



Scheme 11

Also in UV and mass spectrometry experiments **4** could be identified in the gas phase.[37]

The first direct IR-spectroscopic characterisation of 1,2-didehydrobenzene was carried out by Chapman et al. in 1973 with the help of the matrix isolation spectroscopy at very deep temperatures through photolysis of phthaloylperoxide (**34**) and benzocyclobutenedione (**36**) (*Scheme 12*).[38]



Scheme 12

He assigned a band at 2085 cm^{-1} to the C≡C stretching vibration; this allocation was confirmed also several times because of the relatively complicated photochemistry of the involved molecules (*Scheme 13*) severely affected an exact measurement.

However, in 1992 in a more careful investigation of different phthalic anhydride isotopomeres Radziszewski et al. identified the suitable band at 1846 cm^{-1}, which is in a very good agreement with theoretical calculations (1961 cm^{-1}).[10]

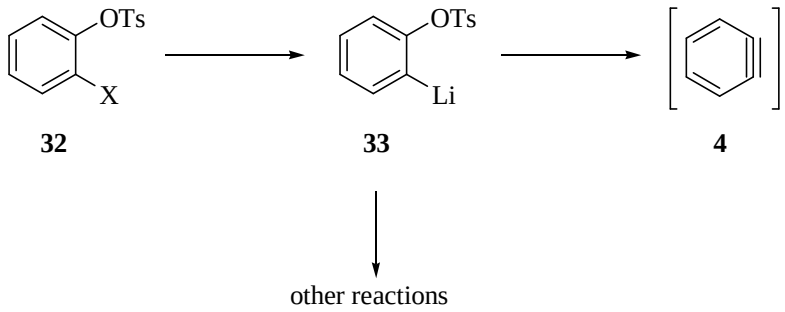
This frequency is closer to the C,C stretching vibration of ethyne (1974 cm^{-1}) as to ethene (1623 cm^{-1}). As expected, the formal C,C triple bond is clearly weaker in **4** than in usual alkynes, its C≡C stretching vibration usually appears in the area about 2150 cm^{-1}. The C≡C stretching vibration of cyclooctyne (the smallest unsubstituted cycloalkyne that can be isolated in a free state) amounts to 2260 / 2206 cm^{-1}.

Based on ^{13}C NMR spectra of **4** in an argon matrix Orendt et al. deduced a Cl-C2 distance of 124 ± 2 pm, indicating a partial triple bond character.[17]

Warmuth performed the first measuring of ^{1}H and ^{13}C NMR spectra of **4**, enclosed in a hemicarcerand.[18] This method allows locking up very reactive molecules in so-called molecular "containers". Furthermore Warmuth et al. determined with quantum-mechanical calculations of magnetic susceptibilities and nucleus-independent chemical shift (NICS) of **4** a Cl-C2-bond length, which lies within the margin of error of 0.02 Å [39] according to the experimental value of Orendt.[17]

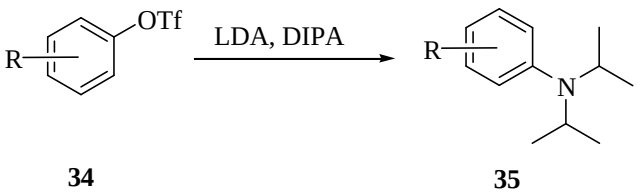
Now, as arynes have been proved and investigated by means of spectrometry, the attention was focused on the formation mechanism of arynes from arenes bearing one or several substituents. Because the effect of the substituents is also vital for electrophilic aromatic substitutions, it was a logical consequence to check the effect of substituents also for elimination reactions.

The first investigations of this kind were carried out by Fleming[40], when he synthesized arynes from phenyltosylates under impact of the sterically hindered base Li-TMP. Nevertheless, yields of benzyne were very low because of the *ortho* lithiation and the following side reactions (*Scheme 13*).



Scheme 13

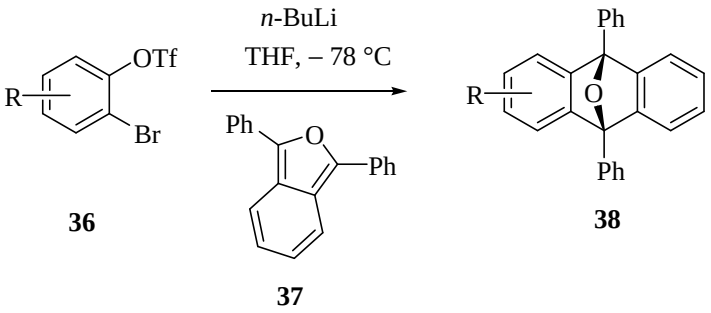
In order to handle this problem, Scott and Wickham[41] used aryltriflates, which do not undergo these annoying side reactions (*Scheme 14*).[42]



Scheme 14

They received yields of *N,N*-diisopropylaniline (**35**) between 67 % and 93 %.

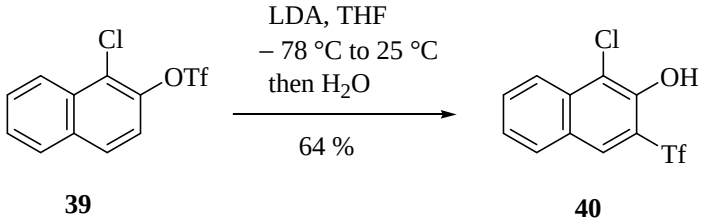
Suzuki used in his experiments *ortho*-haloaryl triflates (**36**) and generated arynes per lithiation with *n*-BuLi. He trapped the arynes with 1,3-diphenylisobenzofuran **37** via Diels-Alder reaction and received the corresponding cycloaddition products (**38**) with yields between 73 % and 93 % (*Scheme 15*).[43]



Scheme 15

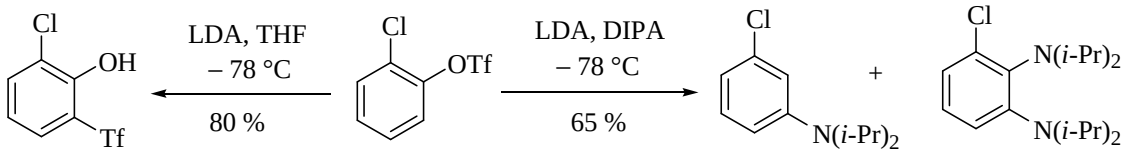
The substituent R in all experiments was an electron-pushing group like methyl, methoxy or phenyl.

The question concerning the influence of electron-withdrawing substituents in reactions of aryltriflates with strong bases was answered for the first time by Guy C. Lloyd-Jones e. al. in 2003.[4] If an aryltriflate with an electron-withdrawing substituent like Cl transacts with such a strong base like LDA, it does not undergo elimination, but an anionic thia-Fries rearrangement (*Scheme 16*).



Scheme 16

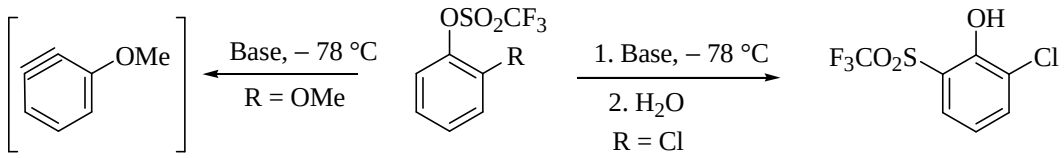
Especially interesting in this work was, that an elimination can occur, if the reaction is carried out in DIPA as a solvent (*Scheme 17*). This is probably a consequence of the formation of aggregates between DIPA and lithiated aryltriflates appearing as intermediates:



41 **42** **43** **44**

Scheme 17

Taking into account this result, the effects of substituents in the benzene ring of the aryltriflates can be summarised as follows (*Scheme 18*).[44]



45 **46** **47**

Scheme 18

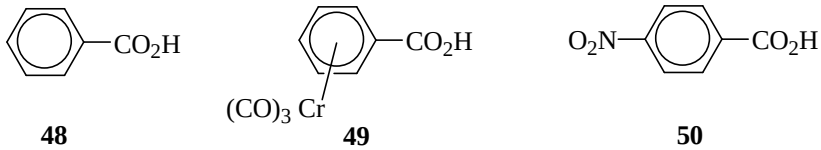
Electron rich aryltriflates undergo elimination reaction, in contrast, electron poor aryltriflates prefer anionic thia-Fries rearrangement.

2. Aryltriflate Metal Complexes

Arenes in transition metal complexes with the form $M(\eta^n\text{-}C_nH_n)_mL_l$ are σ,π-donor-π-acceptor ligands. They often show other properties than in the free state. Iron(II) is valid in general as electron delivering and iron complexes of cyclic π-perimeter like ferrocene are regarded as activated arenes.

Ferrocene shows a stronger aromatic character than benzene,[45] it is very electron rich and undergoes electrophilic aromatic substitutions $3*10^6$ times faster than benzene. Aminoferrocene is more basic than aniline, ferrocenol is less acidic than phenol and ferrocene carboxylic acid is less acidic than benzoic acid.[46, 47]

In contrast, the tricarbonylchromium group in arene tricarbonylchromium complexes is very electron withdrawing and is comparable in this effect to a nitro group in the *para*-position in benzene (*Scheme 19*).[48]

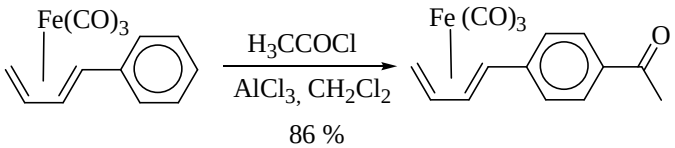


	48	**49**	**50**
pK_a	5.68	4.77	4.48

Scheme 19

The effect of the tricarbonylchromium group arises from three carbonyl ligands, which as strong π-acceptors draw the electron density from the metal toward their π*-orbitals. The metal itself also plays an important role, so chromium(0) is comparatively electron poor.

The comparison of the tricarbonyliron group with the tricarbonylchromium group shows that in contrast to $Cr(CO)_3$ $Fe(CO)_3$ is still electron-pushing as seen from Friedel-Craft-acylation (*Scheme 20*). The acylation occurs in the *para* position.[49]

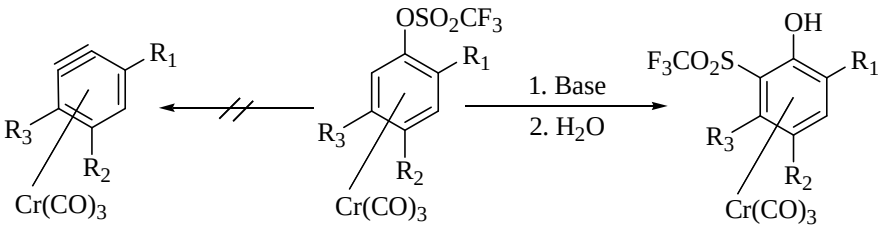


51 **52**

Scheme 20

The comparison of the influence of metals coordinated to arene complexes with the influence of substituents indicates that $Cr(CO)_3$ group will perform the same impact as other withdrawing groups.

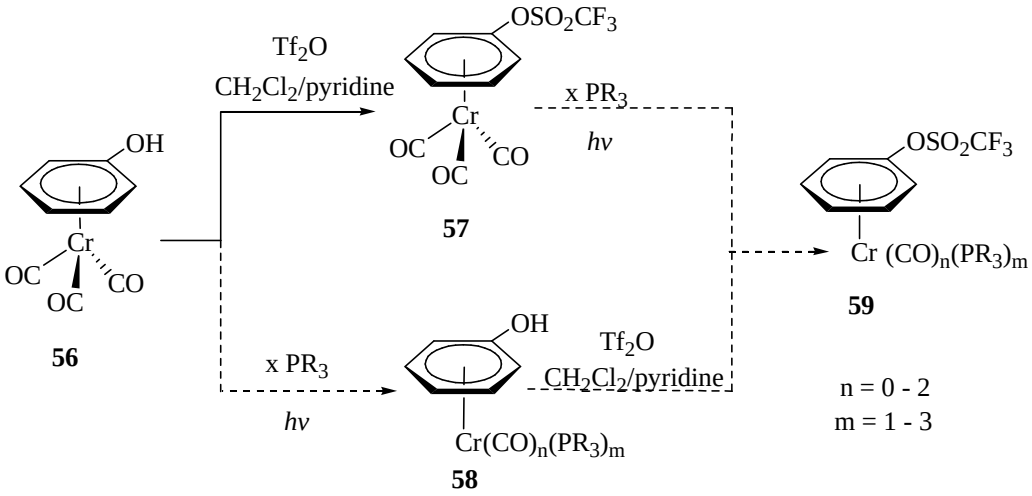
Indeed, this prediction applies in case of the arene tricarbonylchrom complexes and, as shown in *Scheme 21*, the conversion of a tricarbonylchromium complex of phenyltriflate delivers exclusively a product of the anionic thia Fries rearrangement under mild conditions.[50]



53 **54** **55**

Scheme 21

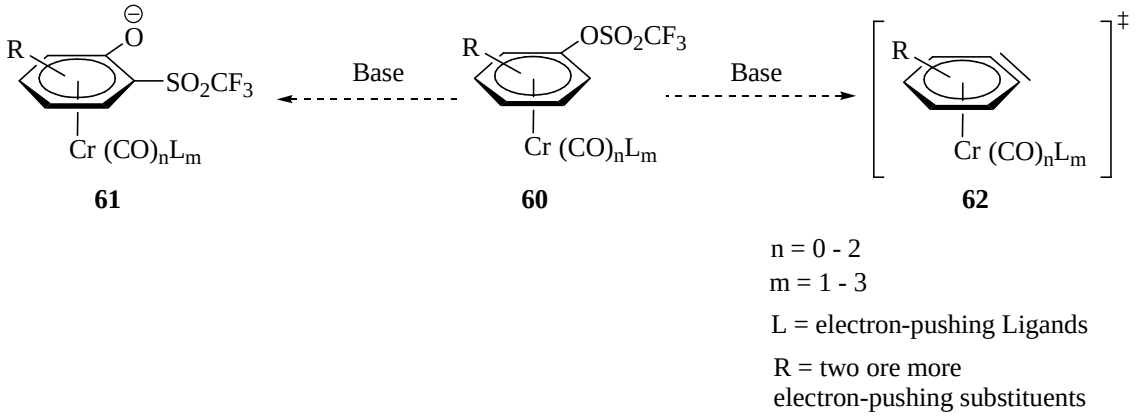
Since the electron poorness in such complexes is caused primarily by carbonyl ligands, it could be possible to increase the electron density in the ring by exchanging of one or several carbonyl ligands by phosphines. The photochemical substitution of carbonyl groups by phosphane ligands in (arene)tricarbonylchromium complexes is well known.[51] Either the known triflate complex **57** undergoes a photochemical exchange or the complex of phenol **56** can be subjected to the ligand exchange generating complexe **58** and then transformed to the corresponding triflate **59** (*Scheme 22).*



Scheme 22

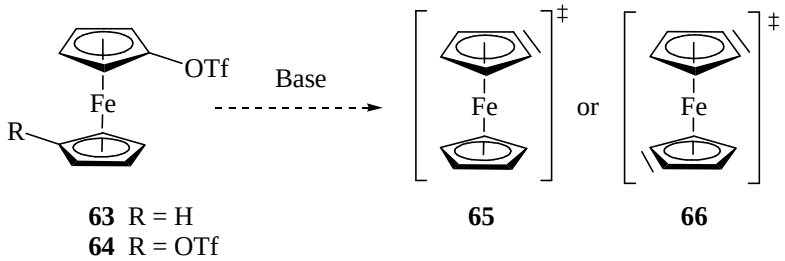
The electron poorness in the tricarbonylchromium complexes could be alternatively encountered by introducing of electron-pushing substituents into the arene ring. It should be mentioned, that our group has already made attempts to generate (aryne) tricarbonylchromium

complexes from phenyltriflates complexes bearing one electron pushing substituent. However all the efforts led to the anionic thia-Fries rearrangement products.[50] Hence the introduction of two or more substituents is required. Also both approaches, the introduction of electron-pushing substituents into the arene ring as well as of electron-pushing ligands, together may not be underestimated (*Scheme 24)*.



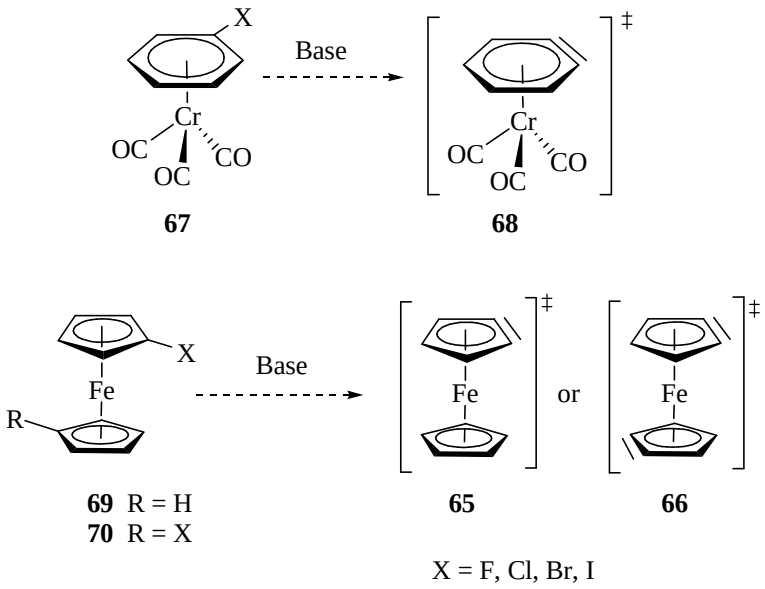
Scheme 24

Because the electron rich phenyltriflates readily undergo elimination reactions (*Scheme 18*), it is also interesting to try such reactions with the more electron rich ferrocene systems **63** and **64** with the perspective to obtain ferrocyne (**65**) or ferrocenediyne (**66**) (*Scheme 25)*.



Scheme 25

Other leaving groups which can not undergo any rearrangements can be used too, in order to initiate the elimination reactions (*Scheme 26)*.



Scheme 26

The objective of this investigation is the synthesis of the unknown aryne π complexes, especially (benzyne) tricarbonyl chromium (**68**), 1,2-didehydroferrocene (**65**) and 1,1',2,2'-tetra- dehydroferrocene (**66**). We expect a very high reactivity of these compounds; therefore they must be trapped by dienes via the Diels-Alder reaction (*Scheme 6*) or by amines (*Scheme 15*) or alcohols (*Scheme 3*). With the absence of such intercepting reagents we expect to found [2+2] cycloaddition products (*Scheme 12*).

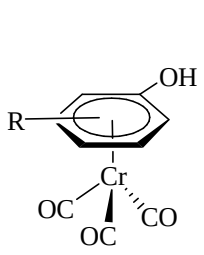
B. Results and discussion

1. Synthesis of arene tricarbonylchromium complexes

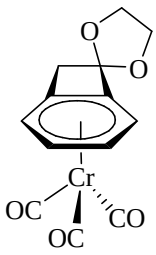
Arene tricarbonylchromium complexes are yellow to red, usually crystalline, sometimes liquid (*vide infra*) compounds that are often stable in the air in the solid state but, in the majority of cases, very sensitive to the light.

1.1 Direct complexation of arenes by hexacarbonylchromium and its derivates

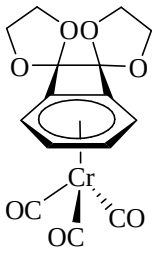
The most common method for the generation of arene tricarbonylchromium complexes is thermolysis of $Cr(CO)_6$ in the presence of excess of an arene in a high-boiling solvent under inert atmosphere (mostly nitrogen or argon). The arene can be used as the solvent with other high-boiling solvents, solvent mixtures are suitable as well. The most commonly established method is the use of mixture of dibutylether and THF (10:1),[53] though dioxane and diglyme can be applied too.[54] The polar-high boiling ether supports the thermolysis, promotes carbonyl dissociation, stabilizes intermediates whereas the reflux of the lower boiling additive brings back sublimed $Cr(CO)_6$ back into the reaction mixture. This method allows the preparation of arene complexes in high yields (80-95 %) with reaction times of typically 2-4 days. Many complexes such as phenol derivates **56**[50], acetals of bezocyclobutenone **71**[55], benzocyclobutendione **72**[56], 1,3-indandione **73**[57], 1,2-indandione **74**[58], 1,2,3-indantrione **75** and **76**[57], *N*-methyl-3,3-dimethoxyisatin **77**[59] and phthalimides **78**[60] have been already synthesized by our group using this procedure (*Scheme 27*).



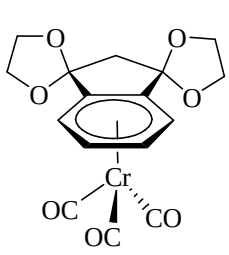
56



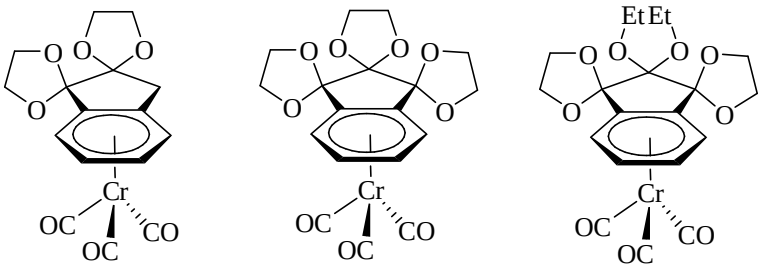
71



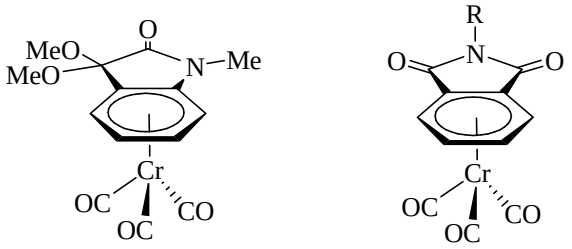
72



73



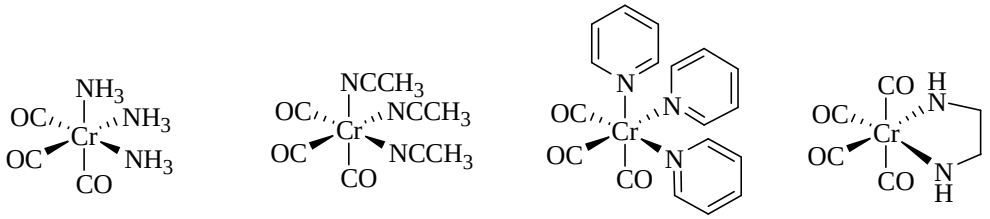
74 **75** **76**



77 **78**

Scheme 27. Complexes **56, 71-78**

Complexation reagents **79-82** (*Scheme 28*) can be used for the generation of complexes, which are synthesized from arenes with heat-sensitive groups. This method makes possible shorter reaction times and lower temperatures.[61]



79 **80** **81** **82**

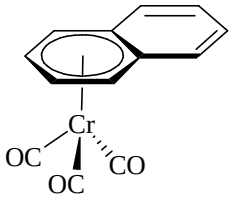
Scheme 28. complexation reagents

Complexation of arenes to $Cr(CO)_6$ can also be carried out photochemically. UV-irradiation of a solution of hexacarbonylchromium and an arene in THF is performed at 25 °C and thus allows the application of thermally sensitive arenes. The yields (15-50 %) are

generally lower than those obtained by usual thermal methods, but the lower reaction temperature compensate it.[62]

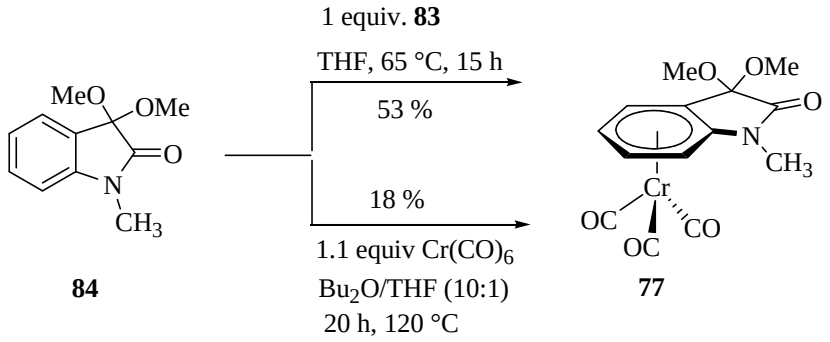
1.2 Complexation via arene exchange

Complexation of arenes can also be carried out by arene exchange using (naphthalene)$Cr(CO)_3$ (Kündig reagent) **83** instead of $Cr(CO)_6$. [63]



83

This method allows the complexation under milder reaction conditions and delivers sometimes even higher yields than the direct complexation with $Cr(CO)_6$. For example, the direct complexation of **84** using $Cr(CO)_6$ provides 18 % yield, while the reaction with Kündig reagent improves the yield up to 53 % (*Scheme 29*).[59]

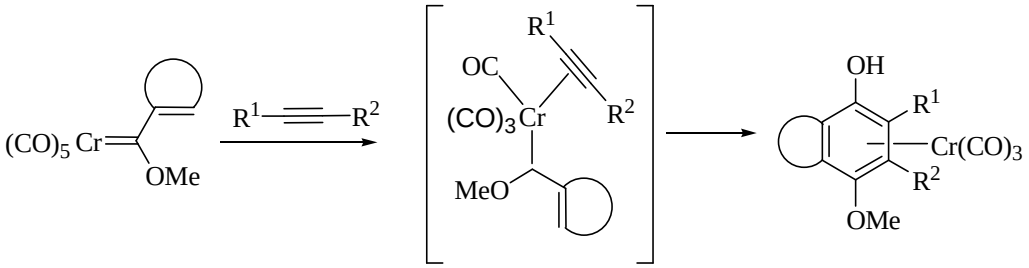


84 **77**

Scheme 29. Complexation reaction of *N*-methyl-3,3-dimethoxyisatin[59]

1.3 Synthesis though intramolecular [3 + 2 + 1] benzannulation of the Fischer cabene complexes

Carbenes are very reactive compounds, but they can be stabilized as complexes of transition metals.[64] These species are divided into two classes: the Fischer-type[65] and the Schrock-type.[66] The Fischer-type complexes such as **85** which contain an unsaturated carbene ligand can add an alkyne under loss of two CO molecules and deliver an alkyne-carbene-carbonyl complex **86**, which, as a reactive intermediate, undergoes a cycloaddition reaction generating an aromatic six-membered ring, π-bonded to the metal **87** (*Scheme 30*).[67-73]

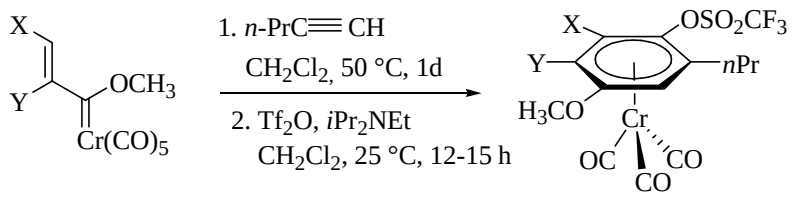


85 **86** **87**

Scheme 30

1.4 Synthesis of (aryltriflate)tricarbonylchromium complexes

Some highly substituted arene-$Cr(CO)_3$ complexes have been synthesized as precursors for palladium-catalyzed cross coupling reactions using Fischer carbenes for the first time by Wulff and co-workers. The highly substituted and air-stable arene-$Cr(CO)_3$ triflate complexes **88a-c** were synthesized in moderate to good yields from carbene complexes **89a-c** and 1-pentyne in a one-pot sequential benzannulation/triflation procedure using triflic anhydride and Hünig's base (*Scheme 31, Table 1*).[52]



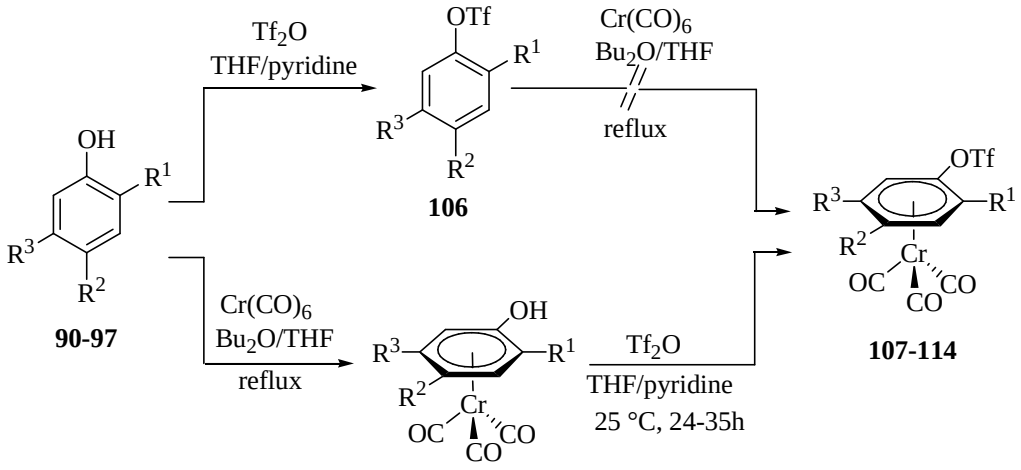
88a-c **89a-c**

Scheme 31

Table 1. Aryltriflate complexes prepared by benzannulation/triflation.[52]

Carbene complexes	X	Y	Aryltriflate complexes (% Yield)
88a	H	$SiMe_3$	**89a** (81 %)
88b	H	CH_3	**89b** (66 %)
88c		$-(CH_2)-$	**89c** (43 %)

Previously our group developed a common and general method using commercially available hexacarbonylchromium and phenols for the preparation of phenyl triflate chromium complexes.[50] This method is based on direct complexation of phenols **90-97** by hexacarbonylchromium. The phenol complexes **98-105** are then converted to the phenyltriflates complexes **107-114**. The direct complexation of phenyl triflates **106** with $Cr(CO)_6$ gave no access to the required complexes (*Scheme 32*).[50]



Scheme 32[50]

The tricarbonylchromium phenol complexes **98-105** were prepared in yields between 48 and 90 % by treatment of phenols **90-97** with hexacarbonylchromium in dibutyl ether / THF (10:1) under reflux for 2-3 days (*Table 2*). They are bright yellow solid compounds susceptible to oxidation and sensitive to light. In general, they should be used as soon as possible in the next reaction since they cannot be stored for a longer period of time. The phenyltriflate complexes **107-114** were synthesized by treatment of the corresponding phenols with triflic anhydride in THF/pyridine (3:1) resulting in 39-88% yield (*Table 2*).

Table 2. Phenol and phenyl triflate tricarbonylchromium complexes.[50]

Entry	R^1	R^2	R^3	Product (yield)	Product (yield)
1	H	H	H	**98** (90 %)	**107** (69 %)
2	H	OMe	H	**99** (73 %)	**108** (75 %)
3	H	Me	H	**100** (65 %)	**109** (72 %)
4	$SiMe_3$	H	H	**101** (48 %)	**110** (39 %)
5	OMe	allyl	H	**102** (88 %)	**111** (88 %)
6	*i*Pr	H	Me	**103** (81 %)	**112** (74 %)
7	Me	H	*i*Pr	**104** (74 %)	**113** (48 %)
8	F	H	H	**105** (78 %)	**114** (53 %)

The reason for low yields in the preparation of complexes **107-114** is the use of THF as solvent, because of side reactions between triflic anhydride and THF.

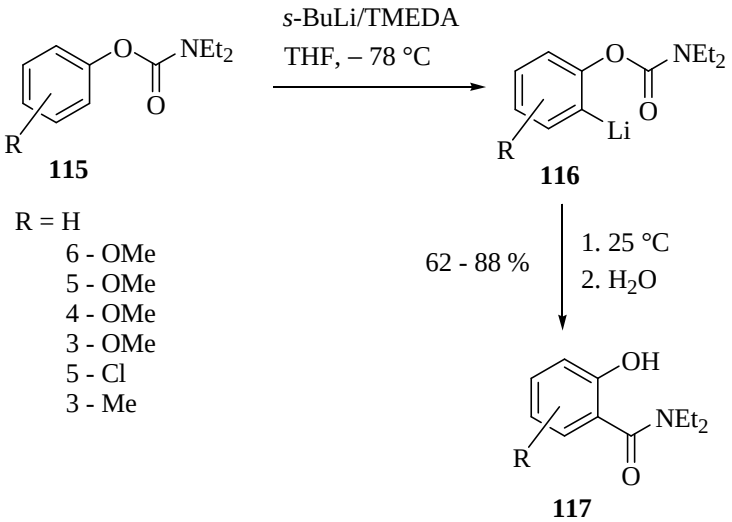
In this work dichloromethylene is used instead of THF, so that the yields of triflates increased up to almost 100 % (*vide infra*). Phenols bearing a methoxy group in the *ortho* position to the OH group (**102** and others) are hardly deprotonated by pyridine, this is presumably due to the hydrogen bonds between the oxygen atom of the methoxy group and the hydrogen atom of the OH group. In these cases stronger bases are required. NaH turned out to be a good reagent for the deprotonation of such compounds and will be used in this work (*vide infra*).

1.5 Anionic thia-Fries rearrangement of (aryltriflate)tricarbonylchromium complexes

The Fries rearrangement is a conversion of phenolic esters into hydroxyaryl ketones catalyzed by protonic acids or Lewis acids at elevated temperatures and thus related to the Friedel-Crafts acylation.[74-76] The thia-Fries rearrangements are effected by a migration of a sulphur atom.[77]

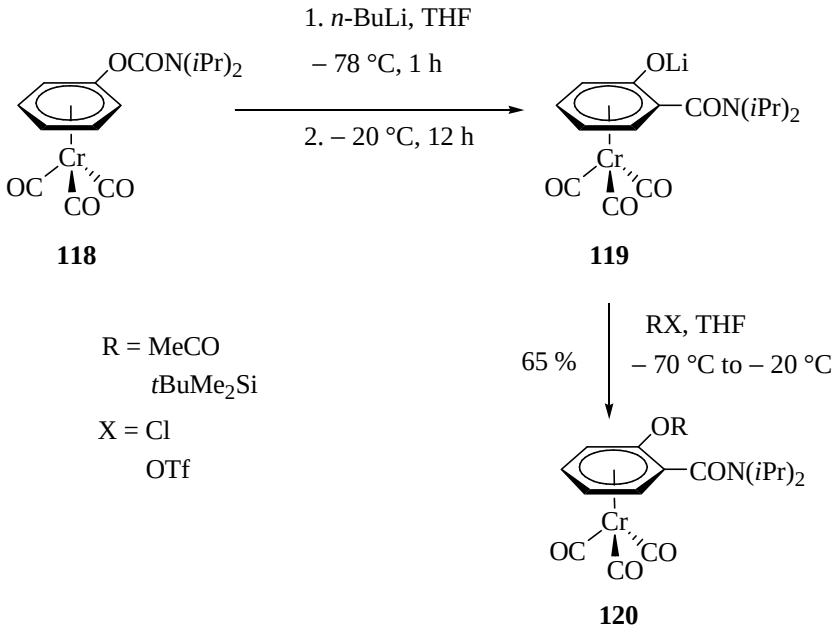
The anionic Fries rearrangements differ from usual Fries rearrangements in reaction conditions and in the mechanism. These reactions are usually carried out at low temperatures (in general at – 78 °C) and in basic medium *via* a different mechanism involving *ortho*-directed metallation and regio-specifically giving the *ortho*-disubstituted aromatics.[78-80]

The anionic Fries rearrangement was reported for the first time by Snieckus and Sibi. They found out that *o*-arylcarbamates are *ortho*-metallated with *s*-BuLi/TMEDA and undergo rearrangement under migration of 1,3-carbamoyl group providing salicylamides in good yields (*Scheme 33*).[80]



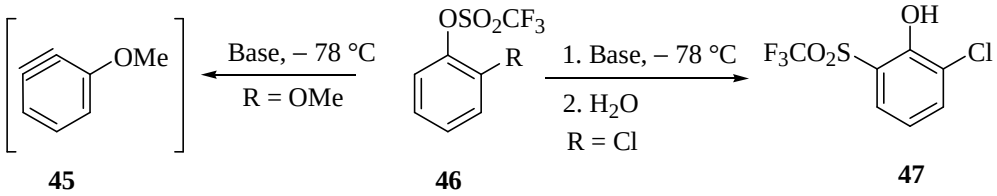
Scheme 33[80]

Kündig described an anionic Fries rearrangement of phenylcarbamate tricarbonylchromium complex **118**.[81] After the lithiation of complex **118** at – 78 °C the reaction mixture was warmed up to – 20 °C, whereby the rearrangement of the carbamoyl group was observed. The generated intermediate anionic phenolate **119** was trapped with electrophiles giving complex **120** in 65 % yield (*Scheme 35*).



Scheme 34[81]

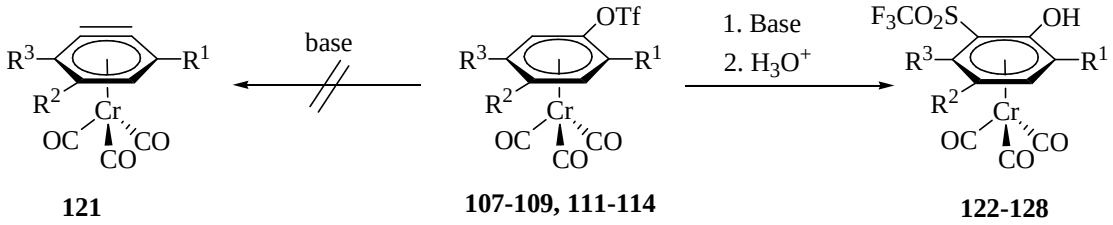
As already mentioned above, the first anionic thia-Fries rearrangement was reported by G. Lloyd-Jones (*vide supra*).[44] He investigated the behaviour of various phenyl triflates toward such strong bases as LDA. He found out that aryl triflates bearing an electron withdrawing group, especially *ortho* to the triflate group, readily undergo the anionic thia-Fries rearrangement. In contrast, phenyl triflates with electron donating groups exclusively undergo elimination reactions with formation benzyne (*Scheme 35*).



Scheme 35[44]

Our group set about to investigate the reactivity of phenyl triflate tricarbonylchromium complexes toward bases. It turned out that the reaction of bases with phenyl triflate tricarbonylchromium complexes exclusively delivers the thia-Fries rearrangement products, wheareas no elimination products were obtained. This result is accord with the report of G. Lloyd-Jones

and the electron withdrawing effects of tricarbonylchromium group (*Scheme 36*), (*Table 3*).[50]



121 **107-109, 111-114** **122-128**

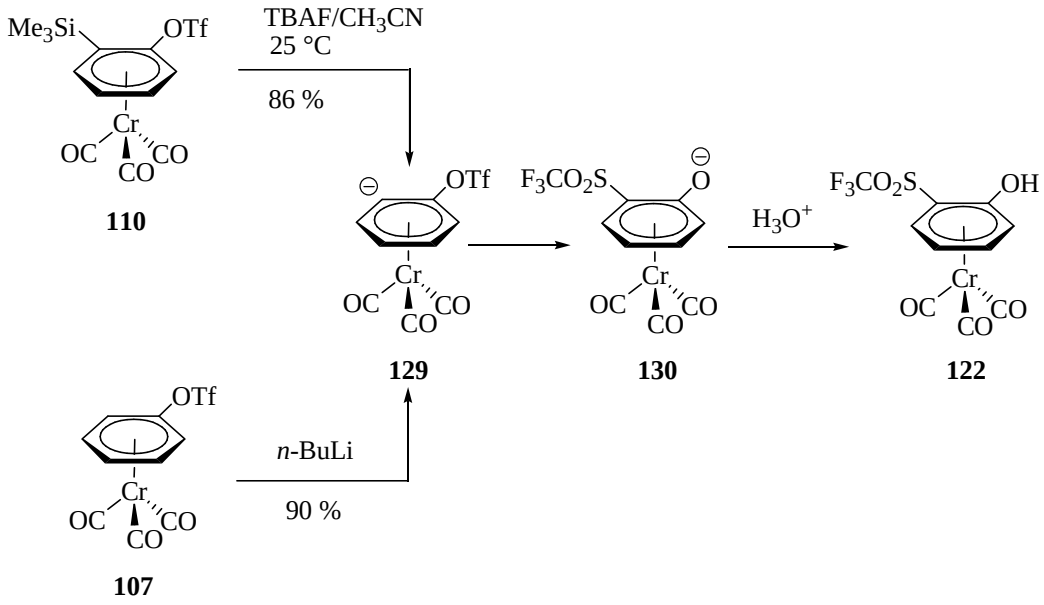
Scheme 36

Table 3. *ortho*-Trifluoromethylsulfonylphenol complexes from phenyl triflate complexes[50]

Entry	R^1	R^2	R^3	Triflate complex	Product (yield)
1	H	H	H	**107**	**122** (90 %)
2	H	OMe	H	**108**	**123** (82 %)
3	H	Me	H	**109**	**124** (94 %)
4	OMe	allyl	H	**111**	**125** (88 %)
5	*i*Pr	H	Me	**112**	**126** (80 %)
6	Me	H	*i*Pr	**113**	**127** (47 %)
7	F	H	H	**114**	**128** (92 %)

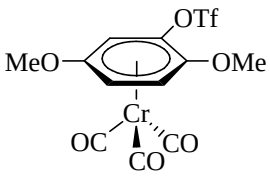
In all these reactions butyllithium was used as the base. In the course of this work it was found that use of LDA instead of butyl lithium afforded much higher yield, in many cases up to almost 100 % (*vide infra*).

In an alternative approach to synthesize a benzyne complex *o*-trimethylsilylphenyl triflate tricarbonylchromium complex (**110)** was treated with tetrabutylammonium fluoride in acetonitrile at 25 °C. Because of the high affinity of silicon to fluorine the trimethylsilyl group was efficiently removed. This led to generation of intermediate **129**, the same intermediate in the treatment of phenyl triflate complex (**107)** with a base. The intermediate **129** instantaneously undergoes a thia-Fries rearrangement affording the phenolate **130**. The following quenching with water generates the thia-Fries rearrangement product **122** (*Scheme 37*).



Scheme 37[50]

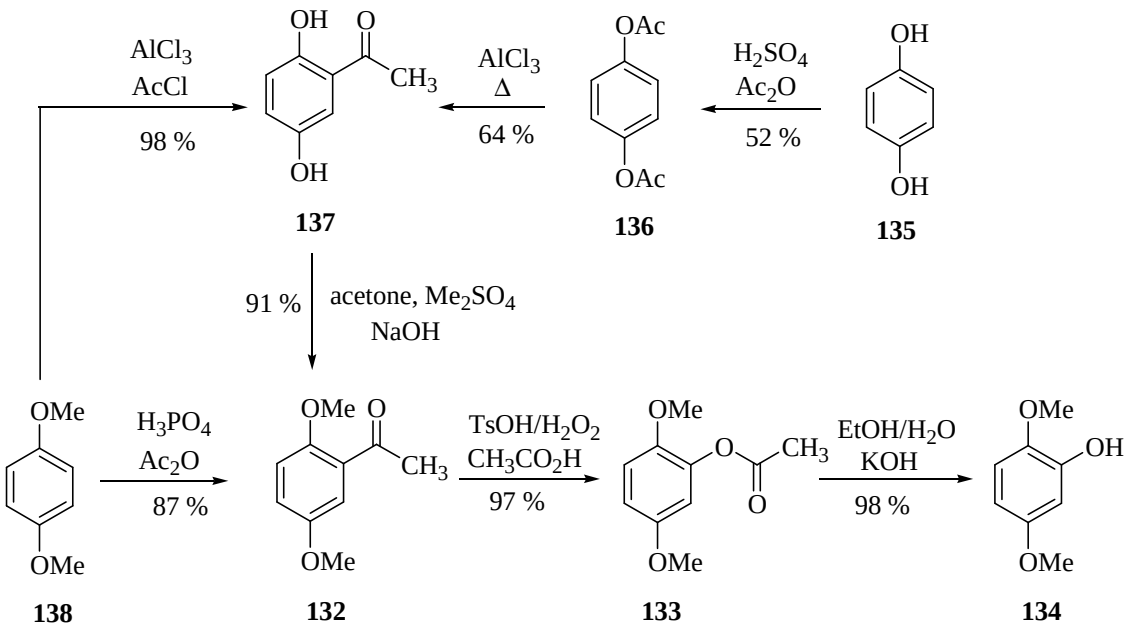
In order to synthesize a benzyne tricarbonylchromium complex, more electron rich phenyl triflate complexes were treated with base. Complex **131** seemed to be very promising.



131

The electron donating methoxy groups make the aromatic ring electron rich. Moreover, the methoxy group in the *meta* position to the triflate group could hinder the rearrangement.

The corresponding phenol **134** is not commercially available and had to be synthesized. The preparation of the phenol **134** was carried out via hydrolysis of the corresponding acetate **133**, which was generated from 1-(2,5-dimethoxy-phenyl)-ethanone **132** via Baeyer-Villiger oxidation (*Scheme 38*).[82]

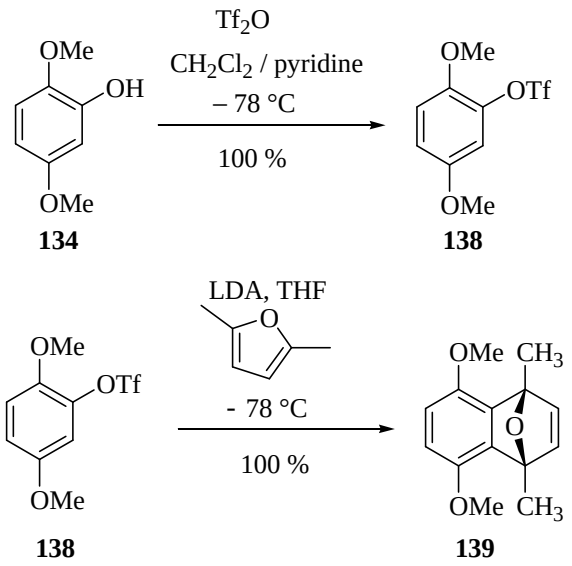


Scheme 38

Two ways are possible to prepare **132**. Hydroquinone (**135**) can be used as starting material and in four steps 1-(2,5-dimethoxy-phenyl)-ethanone (**132**) is obtained in 30 % overall yield. (*Scheme 38*).[83]

The other possibility is the direct Friedel-Crafts acylation of commercial available 1,4-dimethoxy-benzene (**138**). Since the Lewis acids result the demethylation, they should be avoided (*Scheme 38*). So, the generated 1-(2,5-dihydroxy-phenyl)-ethanone (**137**) can be used, of course, in the synthesis of **132** (*Scheme 38*), but we found out that the most efficient method is the direct Friedel-Crafts acylation of 1,4-dimethoxy-benzene (**138**) with phosphoric acid as catalyst. The high yield and one step reaction make this method more useful than the described above (*Scheme 48*).

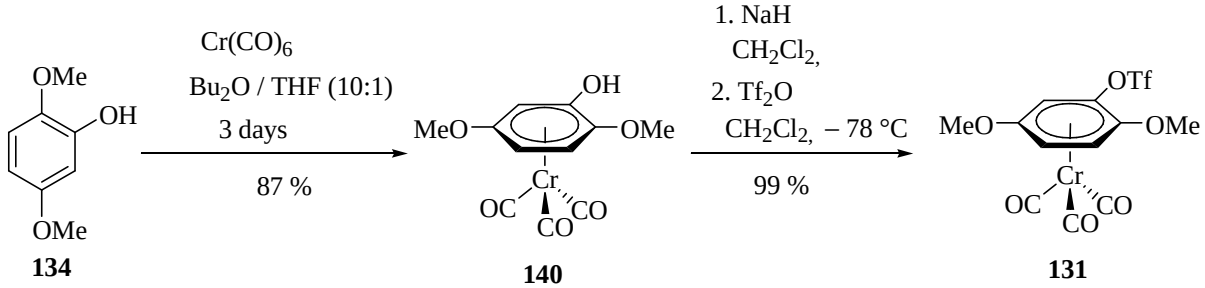
Firstly, the uncomplexed ligand **138**, synthesized from the corresponding phenol **134,** was treated with LDA in the presence of 1,5-dimethylfuran as trapping reagent for benzyne (*Scheme 42*).



Scheme 42

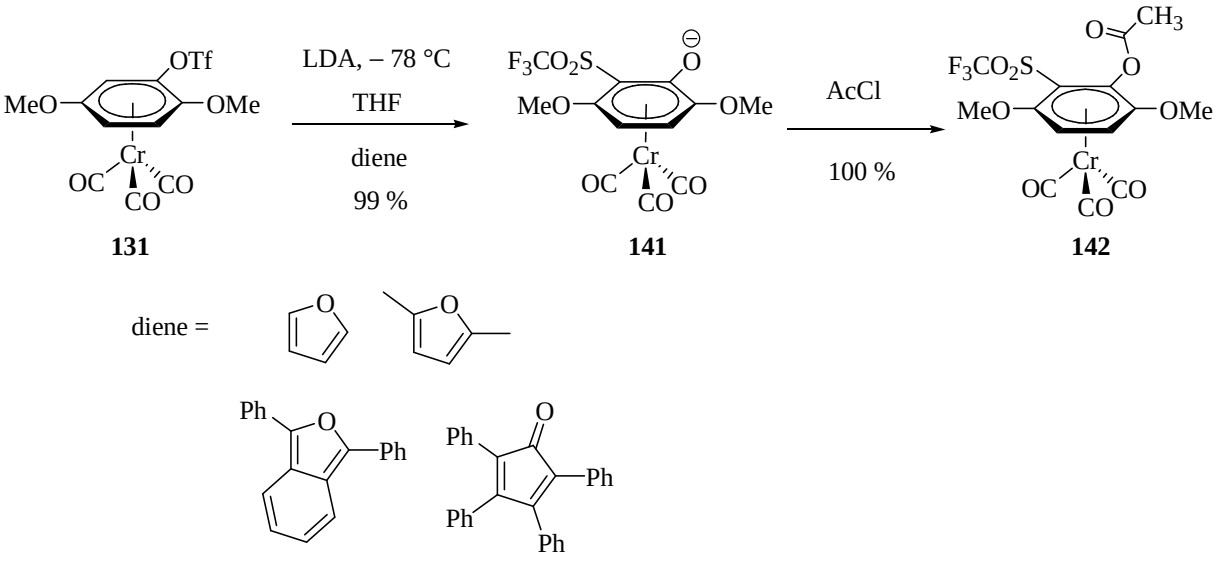
The elimination occurred very efficiently. The cycloaddition product was generated quantitatively at mild conditions and very fast (less than 10 sec. detected via TLC).

The 2,5-dimethoxy-phenyl triflate tricarbonylchromium complex (**131**) was prepared from the corresponding phenol complex **140**, which was generated from the 2,5-dimethoxyphenol (**134**) and $Cr(CO)_6$ in Bu_2O / THF (10:1). Compared to the earlier method of preparing triflate complexes,[50] the use of NaH instead of pyridine and methylene chloride instead of THF improved the yield dramatically (the yield in the earlier method was in range of 39 – 88 %)[50] (*Scheme 43*).



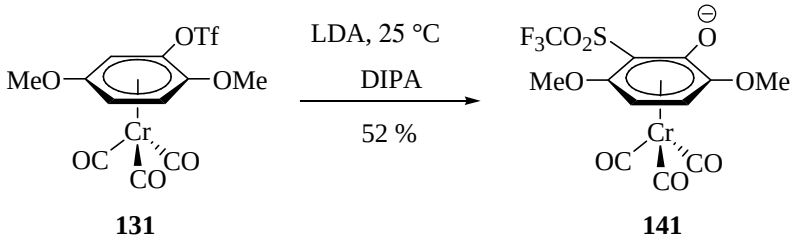
Scheme 43

The triflate tricarbonylchromium complex **131** was treated with LDA in THF at – 78 °C in the presence of various trapping reagents for the possible benzyne. However the reaction leads exclusively to the anionic thia-Fries rearrangement product, no elimination product was observed. The product was characterized as acetate **142**, because the actual rearrangement product **141** is extremely sensitive against oxidation and light (*Scheme 44*).



Scheme 44

The same reaction was also carried out in diisopropyl amine as the solvent. This idea was stimulated by a report of G. Lloyd-Jones, who describes an elimination reaction on an electron poor system in diisopropyl amine (*Scheme 17*).[44] Nevertheless, in case of triflate complex **131**, these conditions did not achieve elimination. Again, only thia-Fries rearrangement product **141** was obtained, but in lower yield. (*Scheme 45*)



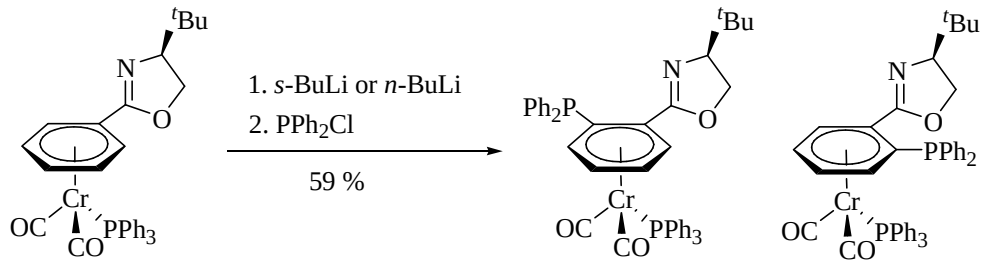
Scheme 45

Since the introduction of electron donating groups does not result in elimination, some triflate complexes were subjected to photochemical ligand exchange, in which one CO was substituted by electron rich phosphines PR_3.

1.6 Photochemical ligand exchange reaction of (aryltriflate)tricarbonylchromium complexes

For various studies quite a number of arene tricarbonylchromium complexes have been subjected to the ligand exchange, in which one CO ligand was substituted by an electron rich phosphines PR_3. These studies include the research of metal-arene rotation barriers,[84-86] investigations of catalytic behaviour of phenanthrene$Cr(CO)_2L$ complexes,[87] steric[88] and electronic[89, 90] effects in synthesis.

In terms of steric and electronic effects, (arene)$Cr(CO)_2PPh_3$ can be used for stereoselective *ortho* lithiation reactions. The less electron deficient, chiral dicarbonyl(triphenylphosphane) chromium oxazoline complexes, unlike the electron poor (arene)$Cr(CO)_3$ complexes, undergo *ortho* lithiation (*Scheme 46*).



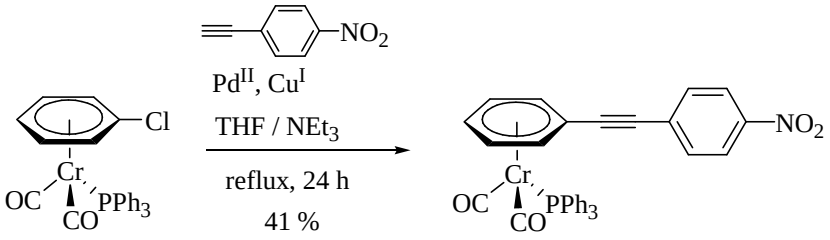
143 **144 a** **144 b**

d.r. 18 1

Scheme 46. Diastereoselective lithiation on dicarbonyl(triphenylphosphane) chromium oxazoline complexes[88]

Another example for the electronic effect of the phosphine ligand is the Sonogashira coupling with the (chlorobenzene)$Cr(CO)_2PPh_3$ complex **145**. Because the substitution of one CO ligand by a phosphane ligand decreases the decline towards the oxidative addition of the pal-

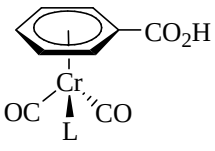
ladium(0) into C-Cl bond, the reaction time must be extended to 24 hours in boiling THF and trietyhalamine, while the same coupling with (chlorobenzene)$Cr(CO)_3$ complex is completed after 3 hours (*Scheme 47*) [89, 90]



145 **146**

Scheme 47. Sonogashira coupling with the (chlorobenzene)$Cr(CO)_2PPh_3$ complex **146**[89]

As already mentioned, the electron density in the arene ring can be detected by measurement of pK_a values of comparable benzoic acids (*vide supra*). The effect of $Cr(CO)_3$ is similar to the electron withdrawing effect of the *para* nitro group.[48] The substitution of CO ligand by phosphines can also cause the increase of pK_a value, and therefore the electron density in the aromatic ring of **147** (*Scheme 48*).



147

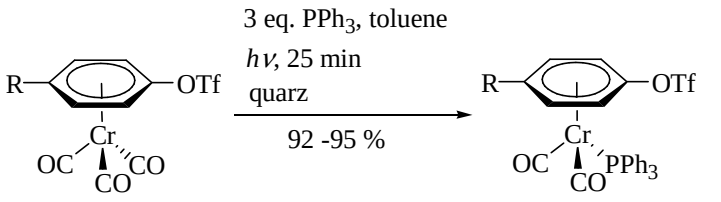
	L	pK_a
para-nitro benzoic acid		4,48
	CO	4,77
	$POMe_3$	5,52
	$POEt_3$	5,62
benzoic acid		5,68
	PPh_3	6,15

Scheme 48. pK_a values of different complexed and non complexed benzoic acid[48, 91]

Because the triphenyl phosphine effects the maximum increase of electron density in arene ring, it seems to be the most adequate ligand for our research, *i. e.* making phenyl triflate

complexes so far electron rich that they undergo elimination reactions instead of the anionic thia-Fries rearrangement.

A couple of mixed ligand complexes of the type (PhOTf)$Cr(CO)_2PPh_3$ were synthesized photochemically, starting from (PhOTf)$Cr(CO)_3$ and 3 equivalents of triphenyl phosphine in toluene or THF. The reaction mixture was irradiated for 25 minutes with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. The reaction progress was monitored by TLC. After the completed consumtion of the starting material (generally ca. 25 minutes) the reaction mixture was irradiated further 20 minutes, and although 3 equiva- lents of triphenyl phosphine were used, no triple or double substitution was observed. Subse- quently the solvent was removed at reduced pressure and the crude product was purified by column chromatography. The products are very stable and can be purified in the air, so that the degassed silica gel, inert atmosphere of argon *etc.* are not necessary (*Scheme 49*).



107 R = H
108 = OMe

148 R = H
149 = OMe

Scheme 49

The new complexes **148** and **149** are deep orange while the starting materials are light yellow. The reason is the extension of the conjugation with triphenyl phosphine. Both mixed ligand complexes are readily identified by inspection of their spectral data. The ^1H NMR, ^{13}C NMR and IR spectral data of **148** and **149** clearly show the powerful electron donating and shielding properties of the phosphine ligand.

In comparison to the tricarbonylchromium complexes **107** and **108** the signals of aromatic protons of **148** and **149** in ^1H NMR reside in higher field (ca. 0.9 ppm), this is caused by the high shielding effect of triphenyl phosphine group. In the ^{13}C NMR all the aromatic signals are also shifted to the higher field (about 3 ppm). Moreover the ^{13}C NMR signal of the carbonyl ligands in (PhOTf)$Cr(CO)_2PPh_3$ are shifted to the higher field even stronger, ca. at 8

ppm. These signals were split to a doublet due to the phosphorous-carbonyl coupling (*Table 4*).

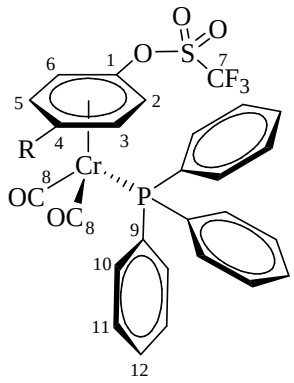


Table 4. The ^{1}H NMR and ^{13}C NMR spectra of triflate tricarbonylchromium complexes and triflate dicarbonyl triphenylphosphine chromium complexes

Substituents	Tricarbonylchromium complexes **107, 108**[50]			Dicarbonyl triphenylphosphine chromium complexes **148, 149**		
	^{1}H NMR	^{13}C NMR		^{1}H NMR	^{13}C NMR	
	3(5)-H, 2(6)-H δ(ppm)	C-3(5), C-2(6) δ(ppm)	$Cr(CO)_3$ δ(ppm)	3(5)-H, 2(6)-H δ(ppm)	C-3(5), C-2(6) δ(ppm)	$Cr(CO)_2PPh_3$ δ(ppm)
R = H	5.46	84.3, 91.3	230.2	5.01	82.1, 90.1	238.5
R = OMe	5.10, 5,72	74.8, 87.4	230.2	4.21, 4.91	71.7, 83.8	238.5

The IR spectra of the complexes **148** and **149** show also the donor ability of the phosphine ligand, which decreases the stretching frequencies of the remaining carbonyl groups in comparison to tricarbonyl chromium complexes **107** and **108**. The reason for this phenomenon is the increasing of the electron density at the carbonyl group caused by the π donor capability of a phosphine ligand leading to the decrease of the stretching frequencies of CO group (*Table 5*)[92]

Table 5. Carbonyl stretching frequencies (cm^{-1}) change after of triphenyl phosphine ligand

Substituents	Tricarbonyl chromium complexes **107, 108**[50]		Dicarbonyl triphenyl phosphine chromium complexes **148, 149**	
R = H	1971	1880	1891	1848
R = OMe	1974	1886	1892	1832

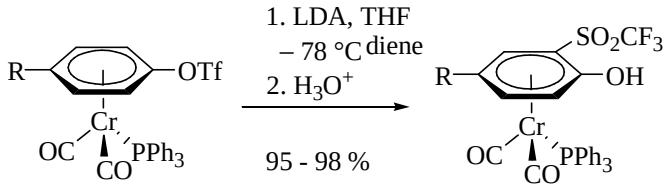
The mass spectra (LC-MS and UPLC-MS) of the complexes **148** and **149** show the molecular ion peak with very low intensity (10 %) because of the instability of such compounds. The base peak is assigned to the free triphenyl phosphine. The peak with the second largest intensity belongs to the $CrPPh_3^+$ moiety. The absence of $PhCr(CO)_2^+$ and $PhCrCO^+$ and the presence of $CrPPh_3^+$ and $PhCrPPh_3^+$ suggests that the Cr-P bond is much stronger than Cr-CO bond. The peak of $PhCr^+$ is also lacking (*Table 6*).

Table 6. The characteristic peaks in the mass spectra (LC-MS) of complexes **148** and **149**

Fragment ions *m/z* (%)

Ion	Assigment	**148**	**149**
a	M^+	596 (10)	626 (10)
b	M^+-CO	568 (5)	598 (6)
c	M^+-2(CO)	540 (25)	570 (20)
d	M^+-PPh_3	334 (0)	363,9 (0)

The complexes **148** and **149** were treated with LDA in THF in the presence of diene or excess of diisobutylamine at – 78 °C. Again, the thia-Fries rearrangement occurred generating complexes **150** and **151** (*Scheme 50*).

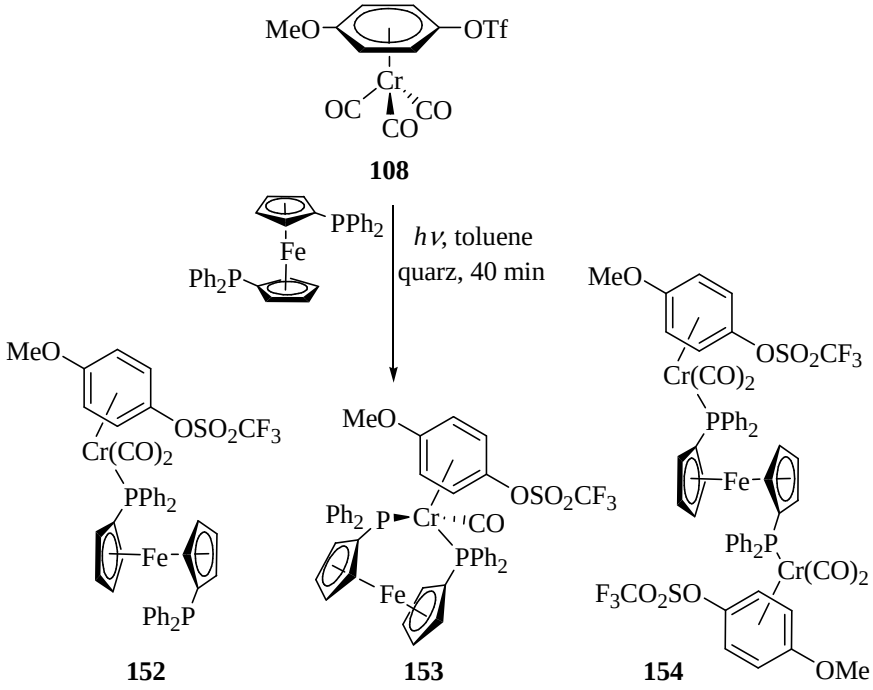


R = H **148** **150**

= OMe **149** **151**

Scheme 50

In the following an attempt to substitute two carbonyl ligands shall be demonstrated. As already mentioned, all efforts to replace two carbonyl ligands by two triphenyl phosphane were unavailing. Although three equivalents of triphenyl phosphane are used in the photochemical ligand exchange reactions, only complexes bearing one triphenyl phosphane **148** and **149** were obtained. On this account we tried the reaction with 1,1'-bis-(diphenylphosphino)ferrocene (dppf) expecting the replacement of two carbonyl ligands by one dppf molecule with the driving force being the increase in entropy (*Scheme 51*).



Scheme 51

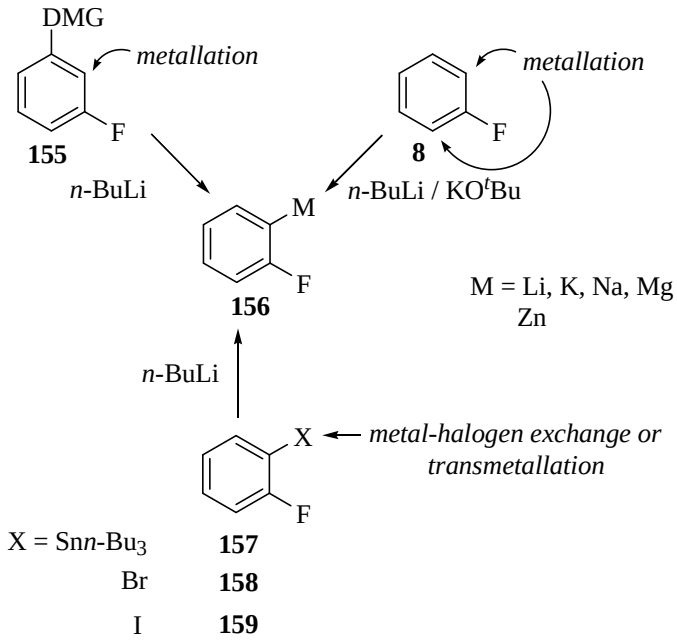
The primary application of dppf is the use as a ligand in catalytic reactions. The phosphorus atoms in dppf can bond to another transition metal centre.[93-95] *A prima facie* it must be possible to bond the chromium atom too.

The reaction was carried out in toluene starting from **108** and 2 equivalents of dppf. The reaction mixture was irradiated for 40 minutes with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. The reaction progress was monitored by the TLC. Theoretically, three compounds can be expected, **152-154** (*Scheme 51*). The trimetallic complex **154** was obtained in ca. 1 % yield and could be identified only by its mass spectrum.

The main product of the reaction was the bimetallic complex **152** in 86 % yield. The desired complex **153** bearing one carbonyl ligand was not obtained.
The compound **152** was fully characterized spectroscopically. It was obtained as a yellow solid, which is very stable to oxidation and could be handled without protecting atmosphere.
Because of the very small amount of the compound **152**, it could not be used for the next reaction.
Since neither the introduction of methoxy groups in the ring nor the ligand exchange with electron donating triphenyl phosphine ligand caused the elimination of phenyl triflate complexes, other good leaving groups were considered, which cannot undergo any rearrangements. Halogens, especially the fluorine, seemed to be very promising.

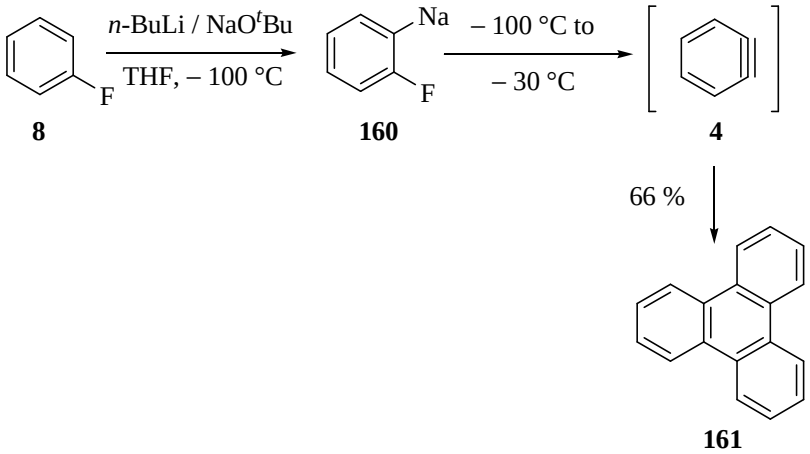
2. Fluorobenzene tricarbonylchromium complexes

Fluorobenzene, which is metallated in the *ortho* position to the fluorine, is a frequently used precursor for synthesis of benzynes. Three reasons are responsible for it. Firstly fluorine is a good leaving group. Secondly, in contrast to sulfonate groups, fluorine does not undergo rearrangement nor hydrolysis. Thirdly fluorine can easily be *ortho*-metallated, without metal-halogen exchange reactions, in contrast to the bromine and iodine.
In general, there are three possibilities for ortho metallation of a fluorobenzene. The fluorine can be used as an *ortho* directing metallating group, thus fluorobenzene can be directly metallated. In this case very reactive metallation systems are required, *e. g. n*-BuLi/KO^{t}Bu. The second possibility is the use of an even stronger *ortho* directing metallating group (*e. g*. oxazoline), which is in the *meta* position to the fluorine. At least, the fluorobenzene should bear a substituent in the *ortho* position, which can be easily exchanged by a metal (*Scheme 52*).



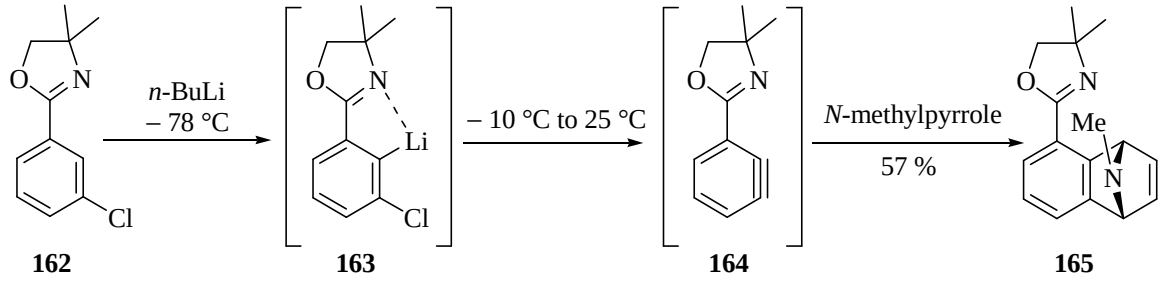
Scheme 52 *ortho* metallation of the fluorobenzene

Using the direct metallation of fluorobenzene **8** with *n*-BuLi/NaO^{t}Bu, triphenylene (**161)** can be synthesized as a result of [2 + 2 + 2] cycloaddition of benzyne **4** in the absence of a diene (Scheme 53).[96]



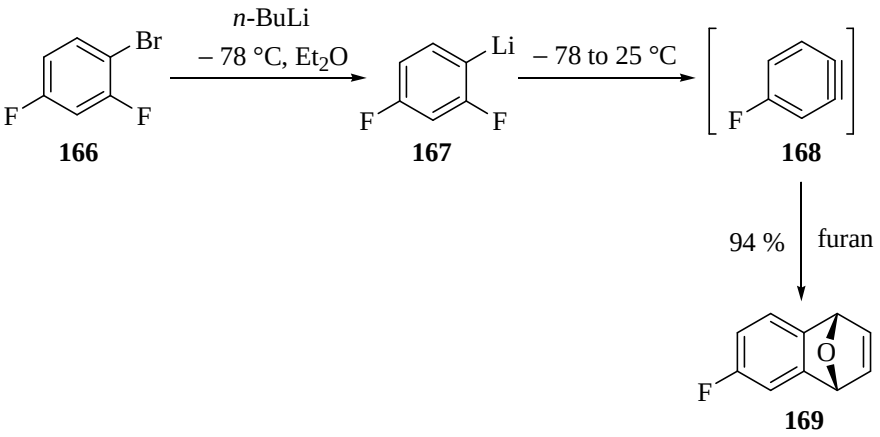
Scheme 53 synthesis of triphenylene[96]

The use of aryl halides with *m*-substituents, which are either electron-drawing or *ortho* directing metallating groups (DMG), allows the regioselective metallation. A. I. Meyers and W. Rieker reported the synthesis of benzyne derived from *m*-chlorophenyl oxazoline (**162**), which is subsequently trapped by *N*-methylpyrrole generating the Diels Alder adduct **165** (*Scheme 54*).[97]



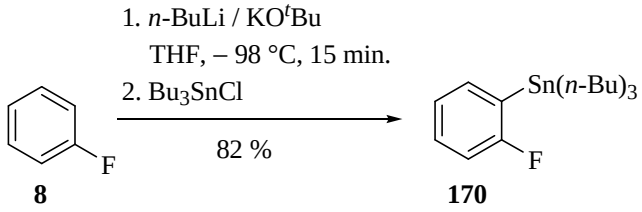
Scheme 54 the synthesis of benzyne derived from *m*-chlorophenyl oxazoline[97]

Although they used chlorobenzene, fluorobenzene would also undergo this reaction. Metallation of 1,2-fluorohalobenzenes with Grignard or alkyllithium is a helpful method to generate arynes. The initial metal halogen exchange also achieves the total regiocontrol. In the presence of more halogens at the ring, the more electropositive halogen exchanges first (*Scheme 55*).[98]



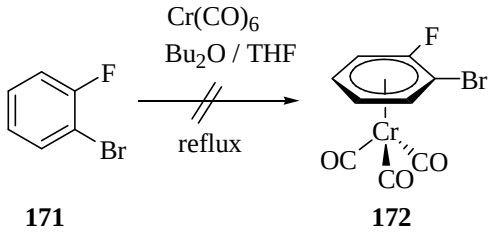
Scheme 55 synthesis of benzyne via metal bromine exchange in 1,2 bromofluorobenzene[98]

We developed a similar possibility for metallation of fluorobenzene via the transmetallation of tributyl(2-fluorophenyl)stannane (**170)**, which was synthesized from fluorobenzene (**8)** (*Scheme 56*).



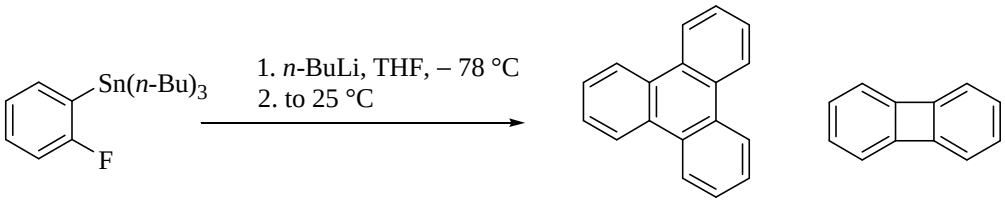
Scheme 56

The advantage of the compound **170** over fluorobenzene (**8**) is the transmetallation at milder conditions, what is more utile for the chemistry with tricarbonylchromium complexes. The other plus of the tributyl-(2-fluoro-phenyl)-stannane (**170**) is the facility for preparation of the corresponding chromium complex, because the bromobenzene tricarbonylchromium complexes can not be generated by the direct arene complexation (*Scheme 57*).



Scheme 57

Before the tributyl(2-fluorophenyl)stannane (**170**) was subjected to the complexation with $Cr(CO)_6$, we tested the trasmetallation with butyl lithium as well in the presence of a diene as without diene. The aim of this experiment was to probe the optimised conditions for the preparation of benzyne. If the reaction was carried out without a trapping reagent, only the triphenylene (**161**) is obtained, and no biphenylene (**28**) was observed (*Scheme 58*). Although in the pyrolysis experiments with phtalic acid anhydride the biphenylene was always obtained as the main product (*vide supra*).



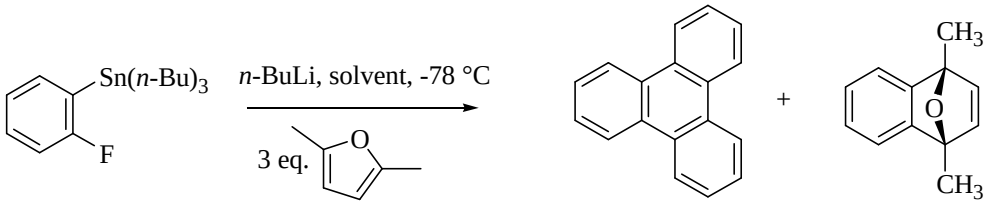
170 **161** **28**

93 % *not observed*

Scheme 58

The yield of **161** in the scheme 58 correspomd to the consumption of **170**.

With the presence of 2,5-dimethylfuran as the trapping regent, we obtained the Diels-Alder adduct **173** and triphenylene (**161**). An interesting result of these experiments was that the kind of the used solvent exerts an influence on the amount of these products. The less polar solvent induces the larger amount of [2 + 4] cycloadduct (*Scheme 59*).

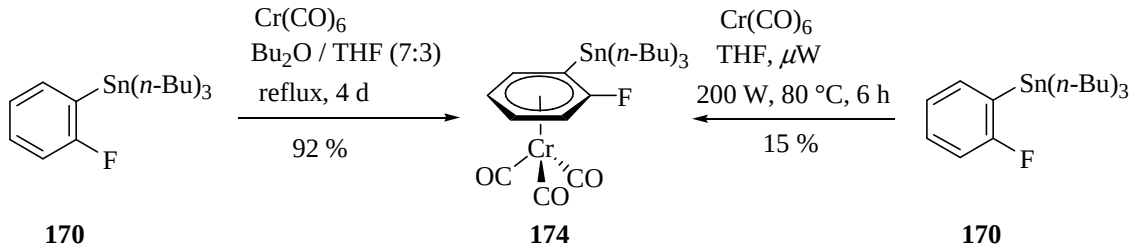


170 **161** **173**

Solvent = THF	83%	17%
n-hexane	28 %	72 %

Scheme 59

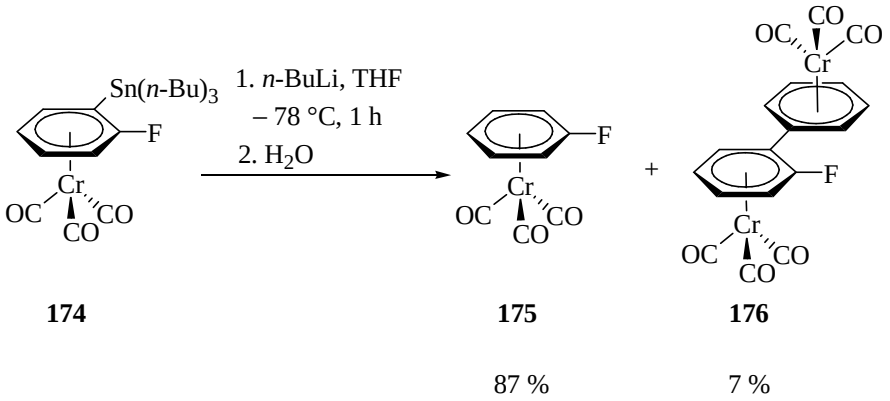
The complexation of **170** was carried out by heating in Bu_2O / THF (7:3) with 1.2 equivalents of $Cr(CO)_6$ for 4 days. These are the best reaction conditions. The usual solvent mixture of Bu_2O / THF (10:1) resulted in lower yield. The attempt to perform the reaction in a micro-wave reactor under the same reaction conditions did not deliver any products. But the use of THF as a solvent causes the generation of the required complex in 15 % yield, what is compensated by short reaction time of 6 hours (*Scheme 60*).



Scheme 60

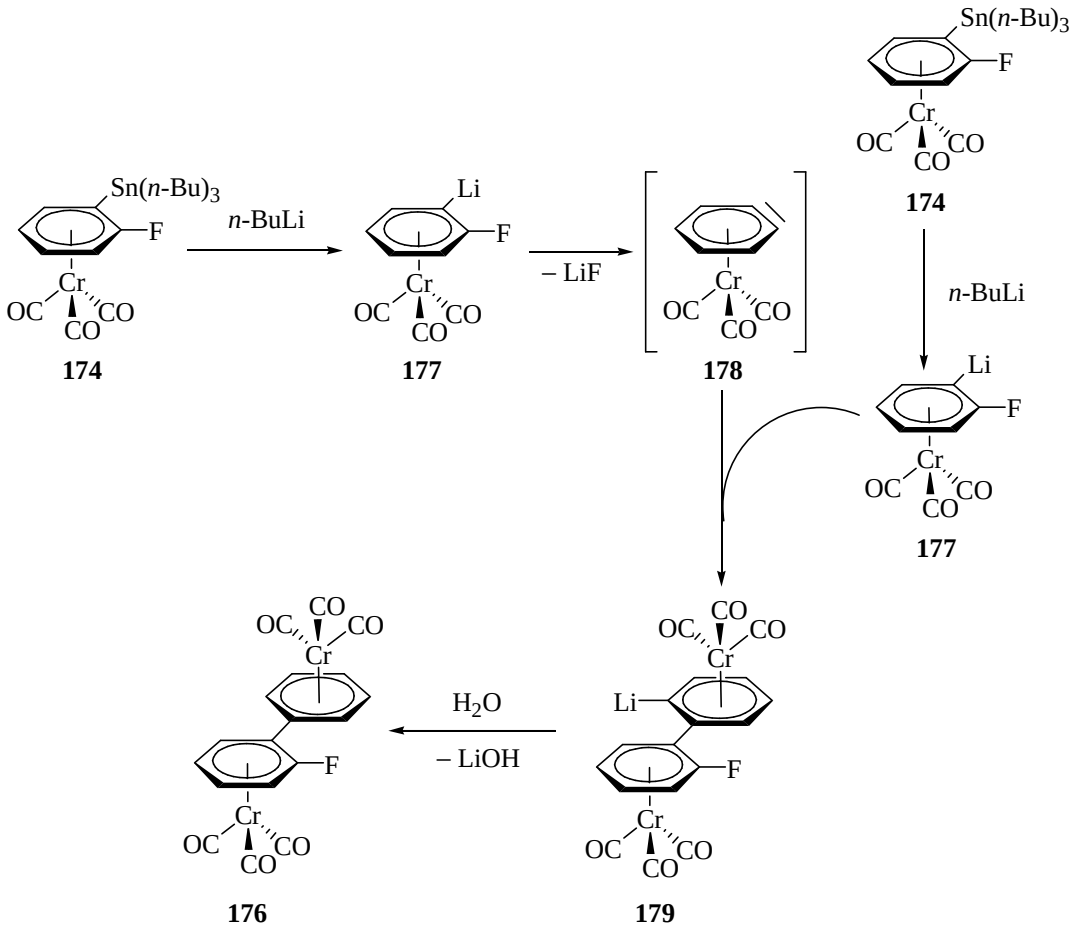
The new complex **174** was obtained as a light yellow viscous liquid. It is very stable and can be purified by column chromatography under air, but it should be stored under inert atmosphere in the dark for a longer period of time.

The complex **174** was subjected to transmetallation with butyl lithium in THF at – 78 °C for 1 hour, warmed up to 25 °C and quenched with water. The main product was fluorobenzene tricarbonylchromium (**175**), which is the result of the transmetallation and subsequent quenching with water (*Scheme 61*).



Scheme 61

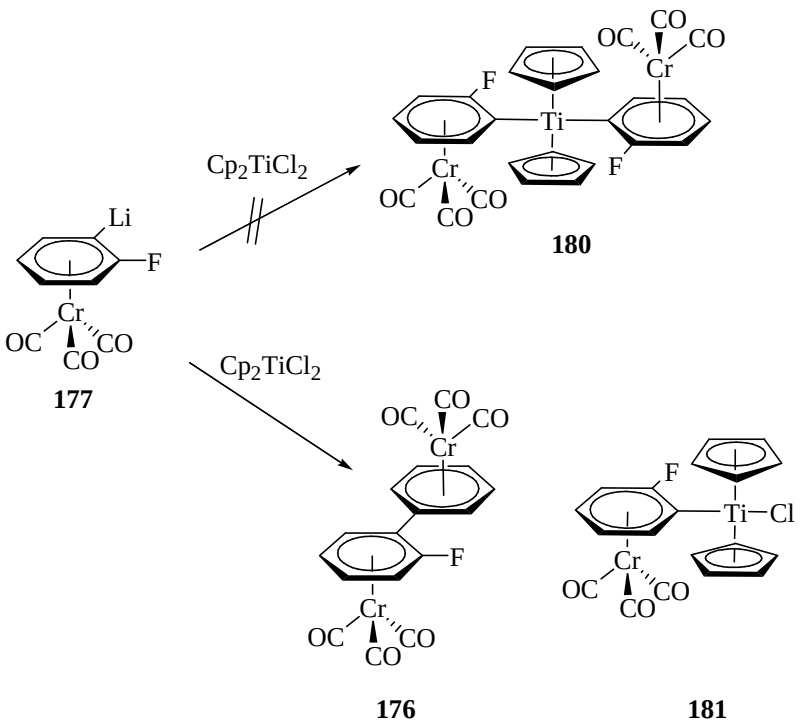
The formation of the product **176** is potentially due to the emergence of the aryne chromium π-complex. This is the first case of formation of this species. The proposed mechanism for the formation of complex **176** is shown in the scheme 62.



Scheme 62

The transmetallation of the tributyl-(2-fluoro-phenyl)-stannane tricarbonylchromium complex (**174**) with butyl lithium leads to the formation of *ortho* metallated fluorobenzene complex **177**. Under release of LiF aryne tricarbonyl chromium is generated, which immediately undergoes an addition with another molecule of **177**. The quenching of the addition product **179** with water delivers the complex **176**.

The complex **176** and its synthesis were already described.[99] The aim of the authors was the synthesis of the heterotrimetallic complex of titanium **180**. Although the analogous reaction with the simple lithiated benzene tricarbonylchromium was successful, the complex **177** did not deliver the desired complex **180**. Instead of that, they obtained bimetallic complex **181** and the complex **176** in very low yield (*Scheme 63*).[99]



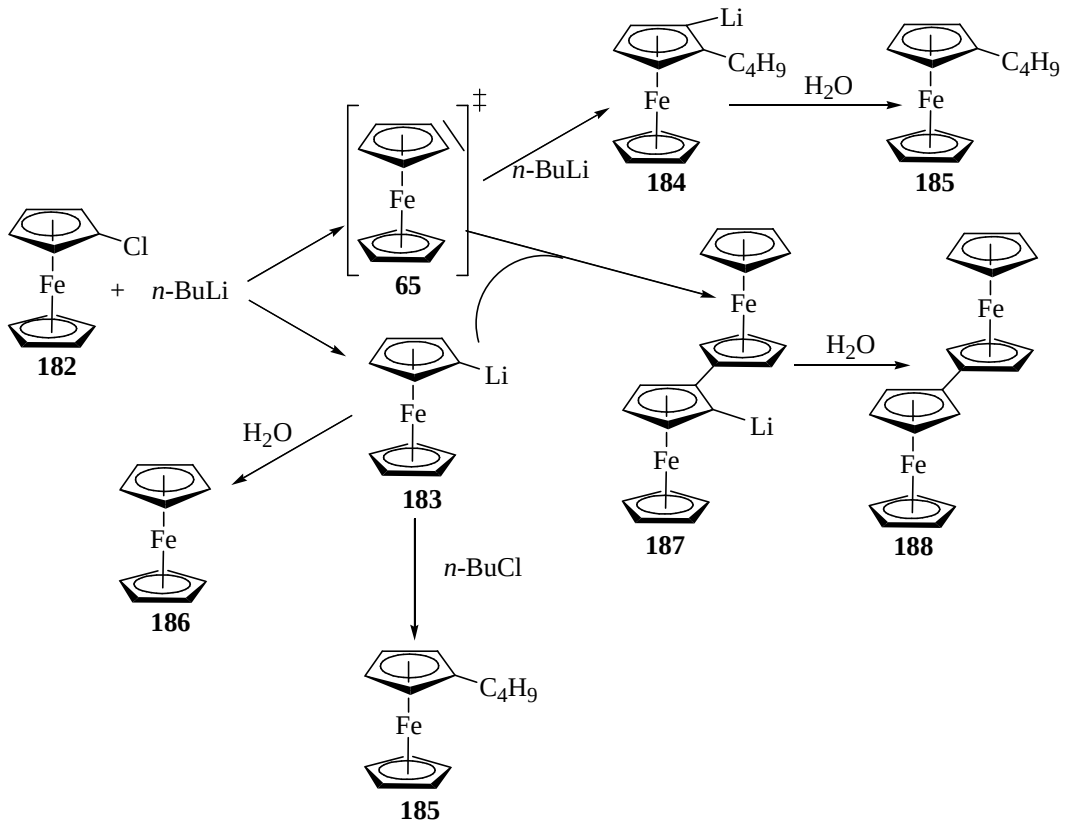
Scheme 63[99]

The authors attribute the formation of **176** to the reaction of lithiated fluorobenzene complex with a non lithiated fluorobenzene complex present in the reaction mixture. They give no consideration to the possible emergence of aryne tricarbonylchromium complex.

3. Ferrocyne and ferrocenyl triflate

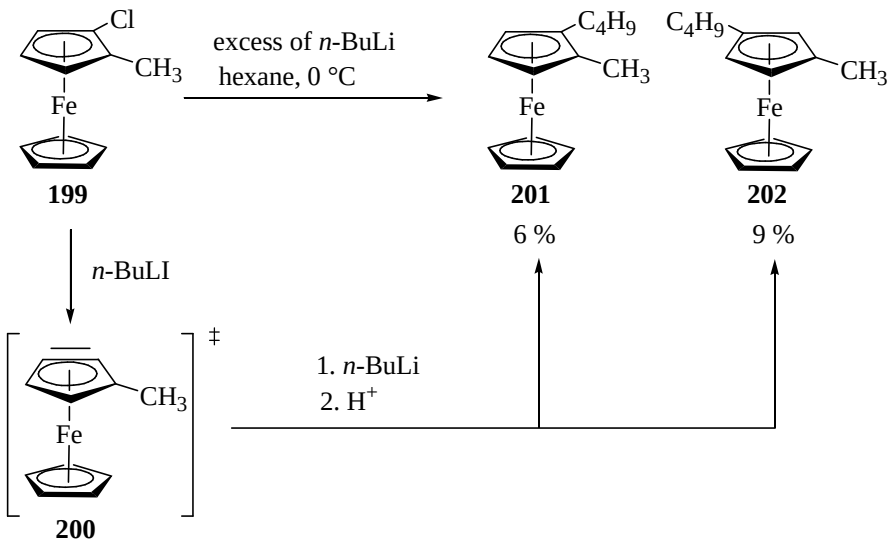
The word “ferrocyne” means by analogy with benzyne the 1,2-didehydroferrocene (**66**) and appeared in the scientific literature for the first time in 1964. Huffman *et. al.* pointed to the possible existence of ferrocyne reporting the similar reaction like Wittig (*Scheme 4*) under use of ferrocene system. They treated the chloroferrocene (**182**) with butyl lithium in hexane/THF, affording butylferrocene (**185**), biferocenyl (**188**) and some minor reaction products.[100]

The formation of butyl ferrocene was explained by addition of butyl lithium to ferrocyne and the formation of biferrocenyl via addition of lithioferrocene to ferrocyne (*Scheme 64*).



Scheme 64. Proposed mechanism for formation of butyl ferrocene (**185**) and biferrocenyl **(188)**[100]

Although this process can be described as a simple Wurtz's Fittig reaction or through radical reactions, the emergence of 1,2-didehydroferrocene cannot be excluded here. In the next report J. W. Huffman and J. F. Cope described another experiment providing the first strong evidence for ferrocyne (**66**). The reaction of 2-methylchloroferrocene with excess of butyl lithium gave a mixture of approximately equal parts of 2-methyl- and 3-methylbutylferrocene (**201** and **202**) (*Scheme 65*).[101]

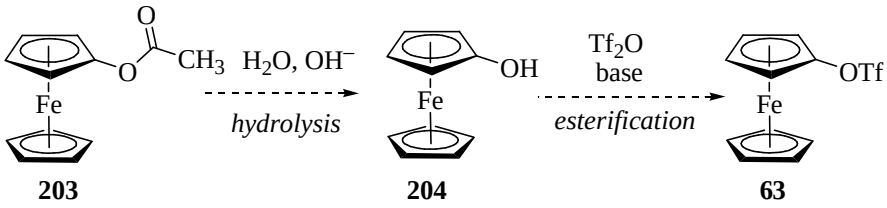


Scheme 65[101]

Our aim is to develop an adequate method for the synthesis of ferrocyne for the preparative scale. Triflate elimination in ferrocenyl triflate seems to be a good possibility for this goal. The *ortho* deprotonation of aryl triflate tricarbonylchromium complexes caused exclusively anionic thia-Fries rearrangement, and no evidence for aryne complex formation was observed. This is due to the electron withdrawing property of $Cr(CO)_3$ group. Since ferrocene derivates are regarded as rather electron rich, we were highly motivated to synthesize ferrocenyltriflates and to subject tthese to *ortho* deprotonation or metallation. We expected an effective formation of ferrocyne (**65**) (1,2-didehydroferrocene) and ferrocenediyne (**66**) (1,1',2,2'-tetra-dehydroferrocene) via elimination of triflate.

3.1 Synthesis of 1-ferrocenyltriflate

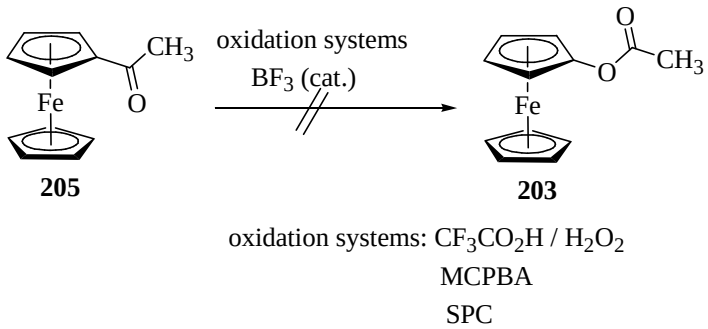
Since the ferrocenyl triflate (**63**) is the ester of the triflic acid, it can be synthesized by esterification of ferrocenol (**204**) by treatment with triflic anhydride in the presence of a base. Ferrocenol can be obtained via hydrolysis of ferrocenyl acetate (**203**) (*Scheme 66*).



203 **204** **63**

Scheme 66

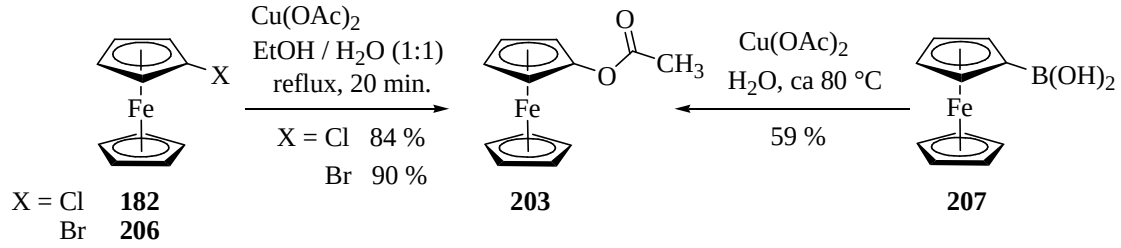
A widely used synthetic method for the preparation of phenyl acetates is the Baeyer-Villiger oxidation of phenyl ketones.[102] Using of peroxytrifluoracetic acid *in situ* prepared from hydrogen peroxide and trifluoracetic acid or the *meta*-chloroperoxybenzoic acid (MCPBA) are the frequently used reagents to perform the reaction. A Lewis acid is mostly used as a catalyst. Olah *et. al*. reported the Baeyer-Villiger oxidation with sodium percarbonate (SPC) in trifluoracetic acid. This system has been found to be a very effective reagent for the Baeyer-Villiger oxidation.[103] Many attempts were undertaken to perform the Baeyer-Villiger oxidation on acetyl ferrocene. Most of them led to the complete decomposition of the complex, so that only inorganic iron (III) compounds were obtained, no ferrocenyl acetate was found (*Scheme 67*).



205 **203**

Scheme 67

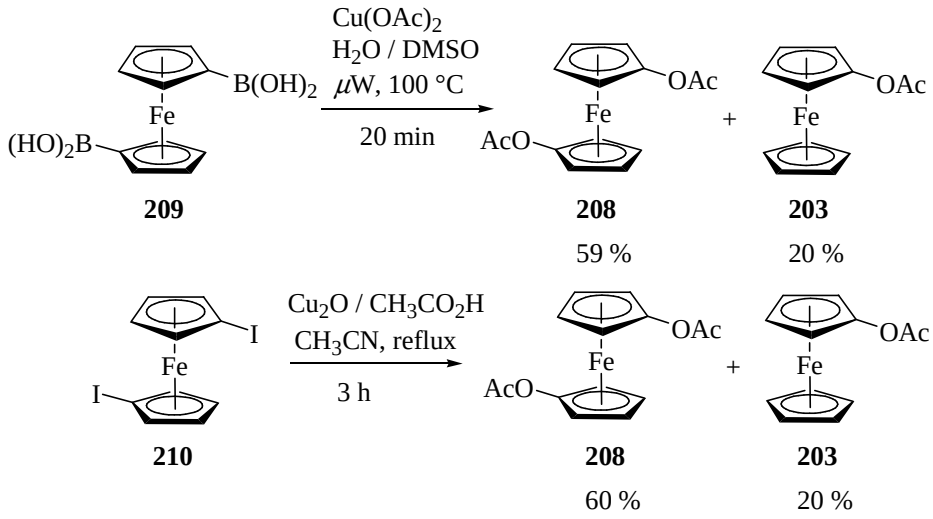
Though, ferrocenyl acetate (**203**) is a known and well investigated compound. Nesmeyanov *et. al.* described the preparation of ferrocenyl acetate from chloroferrocene (**182**) and bromofer- rocene (**206**) or ferrocene boronic acid (**207**) by heating at reflux with $Cu(OAc)_2$ in $EtOH/H_2O$ or in water, respectively (*Scheme 68*).[47]



Scheme 68[47]

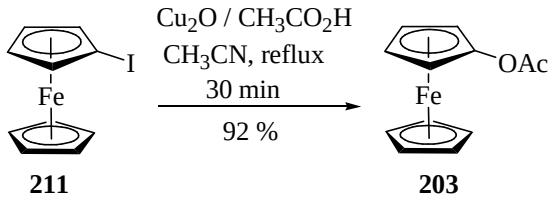
We could increase the yield of ferrocenyl acetate in the preparation from ferrocene boronic acid to 75 % by use of H_2O/DMSO (1:1) mixture as the solvent and under microwave irradiation.

In the course of the preparation of 1,1'-ferrocenediyldiacetate (**208**) (*vide infra*) we found out, that the reaction starting from 1,1'-ferrocenediyldiboronic acid (**209**) gave monoacetate **203** as a valu- able side product in 20 % yield. Alternatively, reaction of 1,1'-diiodoferrocene (**210**) with Cu_2O / acetic acid in CH_3CN afforded **203** in 20% and **208** in 60% yield (*Scheme 69*).



Scheme 69 alternative achievement for ferrocenyl acetate (**203**)

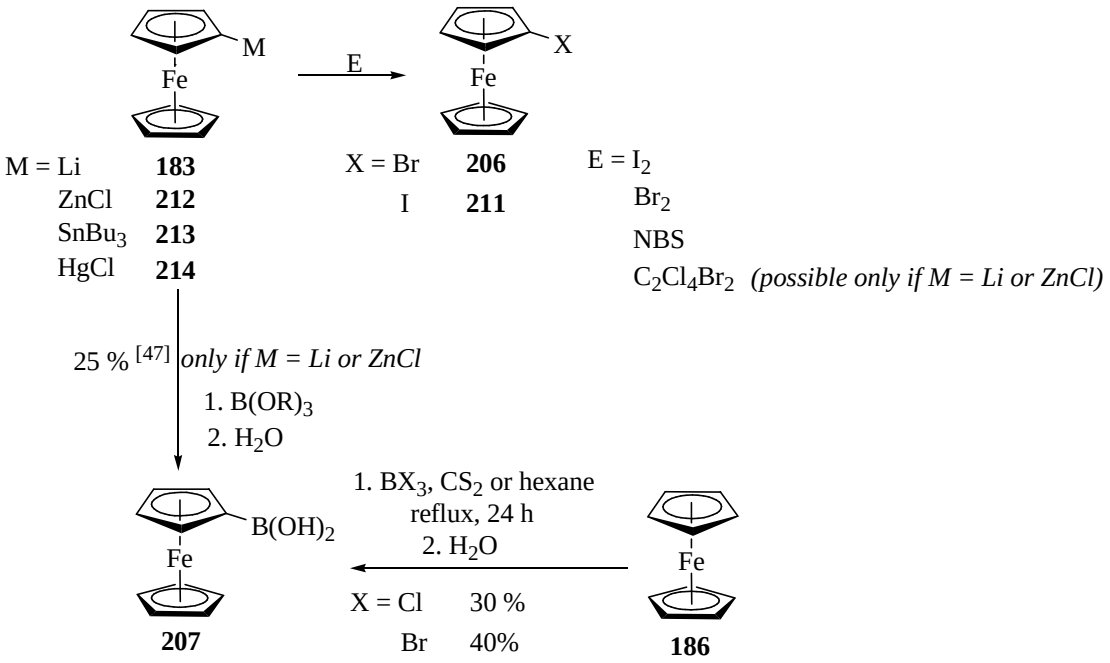
Iodoferrocene (**211**) proved to be the best starting material for the preparation of ferrocenyl acetate (**203**), the reaction delivered the highest yield of all methods (*Scheme 70*).



211 **203**

Scheme 70

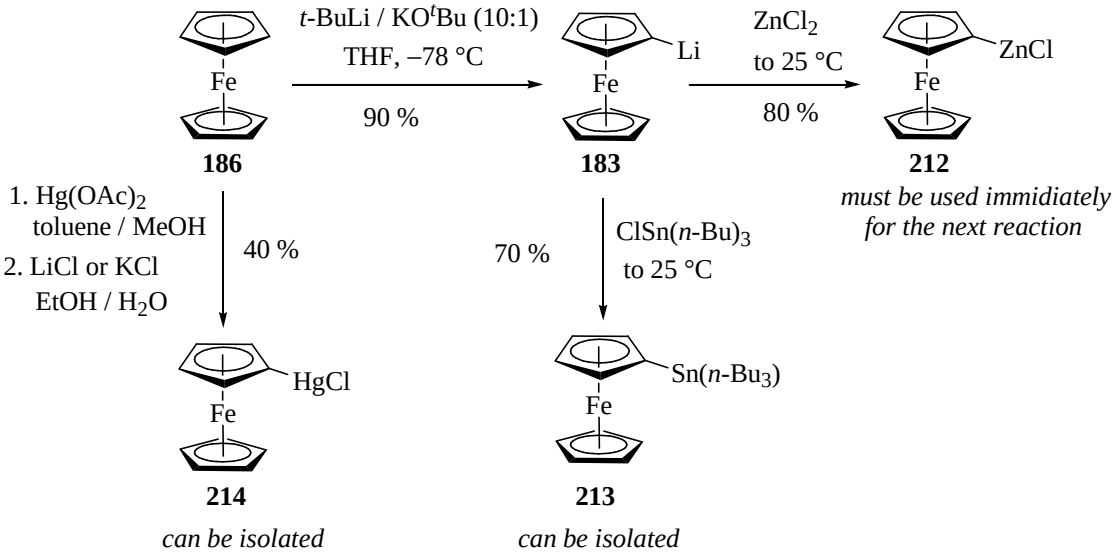
The compounds **206**, **207** and **211** were obtained by treatment of monometallated ferro- cenes by the corresponding electrophiles.[47, 104, 105], Ferrocene boronic acid (**207**) can also be directly generated from ferrocene (**186**) by heating with boron trichloride in hexane or with boron tribromide in CS_2 under reflux and subsequent quenching with water (*Scheme 71*).[100]



Scheme 71[47, 104-107]

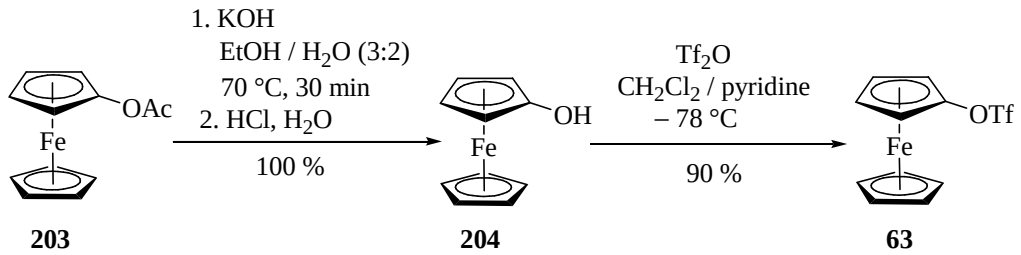
Using of monometallated ferrocenes it should be noted, that the compounds **212** and **213** are synthesized from the lithiated ferrocene **183**,[107] so that the lithiation of ferrocene can not be avoided. The advantage of the compound **212** over lithioferrocene (**183**) is the higher yield of bromoferrocene (**206**) and iodoferrocene (**211**) after addition of the electrophile. The advantage of the compound **213**[104] are also the higher yields of **206** and **211** and the possibility and

purify it before the treatment with electrophile. Chloromercurioferrocene (**214**) is synthesized directly from ferrocene (**186**) by mercuration with $Hg(OAc)_2$ and following treatment with LiCl or KCl (*Scheme 72*) [105]



Scheme 72

Ferrocenyl acetate (**203**) was hydrolyzed. Subsequently, Ferrocenol (**204**) was treated with triflic anhydride in methylene chloride / pyridine affording the new ferrocenyl triflate (**63**) in 90 % yield (*Scheme 73*).



Scheme 73

The new complex **63** was obtained as dark yellow liquid. It is very stable and can be purified by column chromatography under air, but for a long time period it should be stored under protecting atmosphere.

CV-measuring of the ferrocenyl triflate (**63**) shows quasi reversible wave at $E_{1/2}$ = 296.8 mV indicating the Fe^{II}-Fe^{III} redox process, which is in accord with the moderately electron withdrawing effect of the triflate group.[102] In addition, there is a reduction wave at –592.0 mV due to an irreversibe reduction, which we assign to the triflate substituent (*Figure 1*).

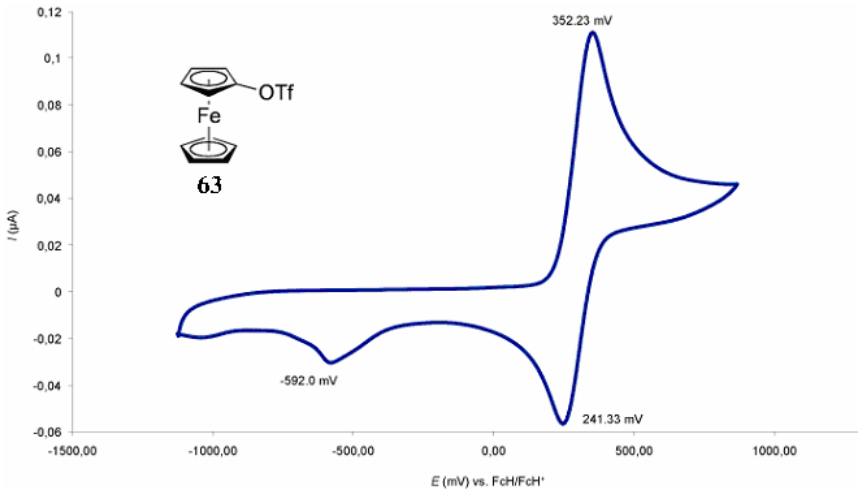
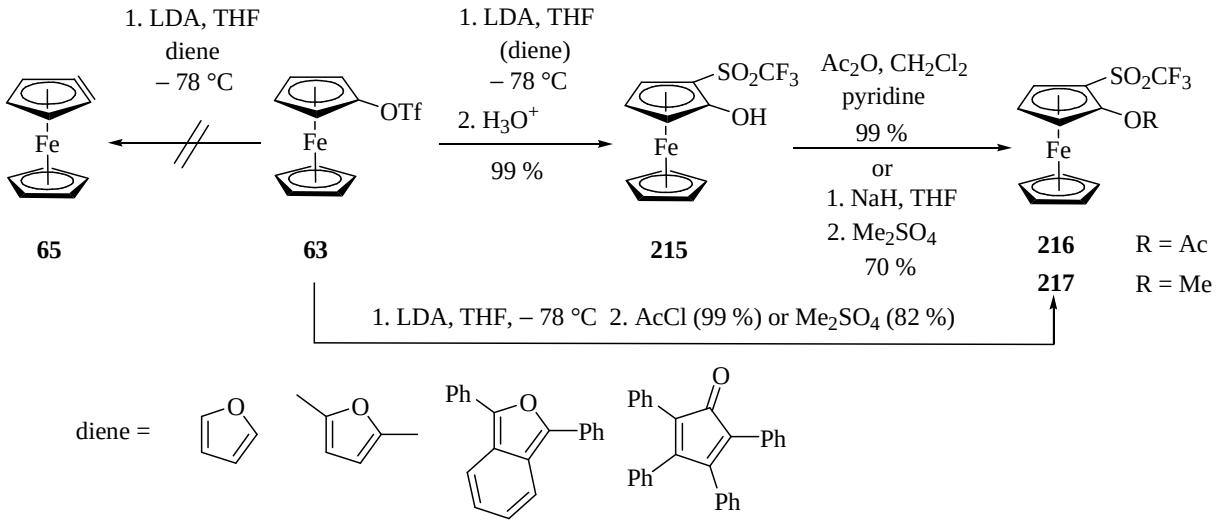


Figure 1 Cyclovoltammogram of **63.** Cyclovoltammetry data (potentials in mV *vs.* FcH/FcH^+, v = 100 mV/s, T = 25 °C, 2 mmol/L, 0.1 mol/L NBu_4PF_6, solvent acetonitrile).

3.2 Anionic thia-Fries rearrangement of 1-ferrocenyl triflate

An *ortho* deprotonation of ferrocenyl triflate **63** with various bases was performed in order to induce triflate elimination with formation of ferrocyne. Several reaction conditions including *in situ* quenching with diverse dienes or access of diisopropyl amine to trap ferrocyne were tested. However, in contrast to our anticipation, no evidence for ferrocyne formation was observed. Instead of that, the anionic thia-Fries rearrangement took place generating 2-(trifluoromethylsulfonyl)ferrocenol (**215**) in high yield (*Scheme 74*).



Scheme 74

Although various bases were used, LDA turned out to be the best option for this procedure generating almost a quantitative yield of the thia-Fries rearrangement product **215**. The efficiency of this reaction exceeded all expectations, because in spite of the more electron rich substrate, ferrocenyl triflate undergoes rather a highly effective anionic thia-Fries rearrangement than triflate elimination. The same result was obtained in the absence of trapping reagents.

Since ferrocenols are known to be susceptible to oxidation,[46, 47, 109] for a comfortable handling **215** can be treated with acetic anhydride/pyridine and with dimethyl sulphate/sodium hydride, affording 2-(trifluoromethylsulfonyl)ferrocenyl acetate (**216**) and 1-methoxy-2-(trifluoromethylsulfonyl)ferrocene (**217**) in 99 % and 70 % yield, respectively. The isolation of intermediate **215** is unnecessary, treatment of the reaction mixture with acetyl chloride or dimethyl sulphate affords **216** and **217** in 99 % and 82 % yield, respectively (*Scheme 71*).The new compounds **215–217** were fully characterized spectroscopically.

The compound **215** differs from **63** in that it bears a trifluoromethylsulfonyl substituent. This circumstance is reflected in the cyclovoltammogram (*Figure 2*).

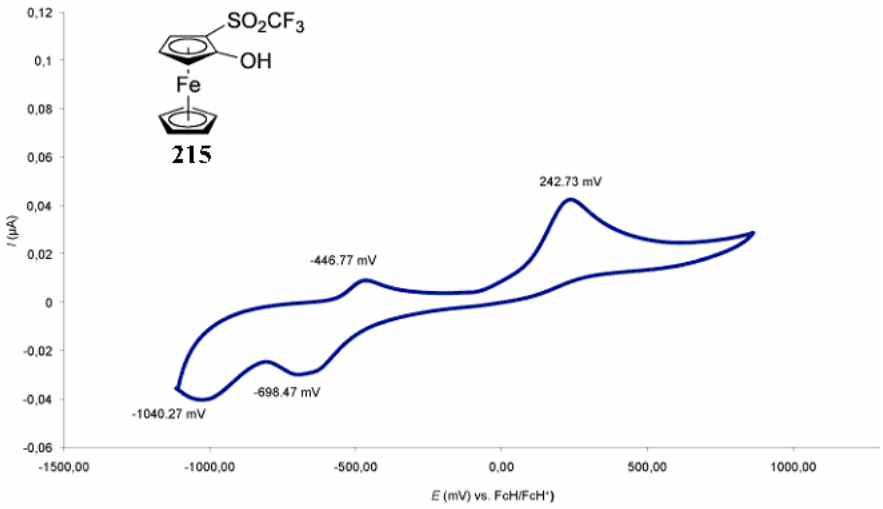
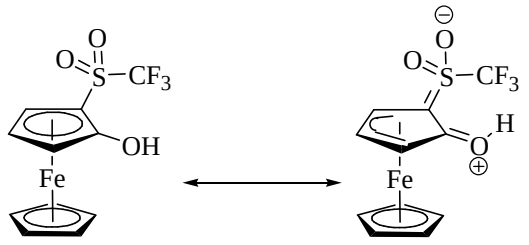


Figure 2 Cyclovoltammogram of **215** Cyclovoltammetry data (potentials in mV *vs.* FcH/FcH^+, *v* = 100 mV/s, *T* = 25 °C, 2 mmol/L, 0.1 mol/L NBu_4PF_6, solvent acetonitrile).

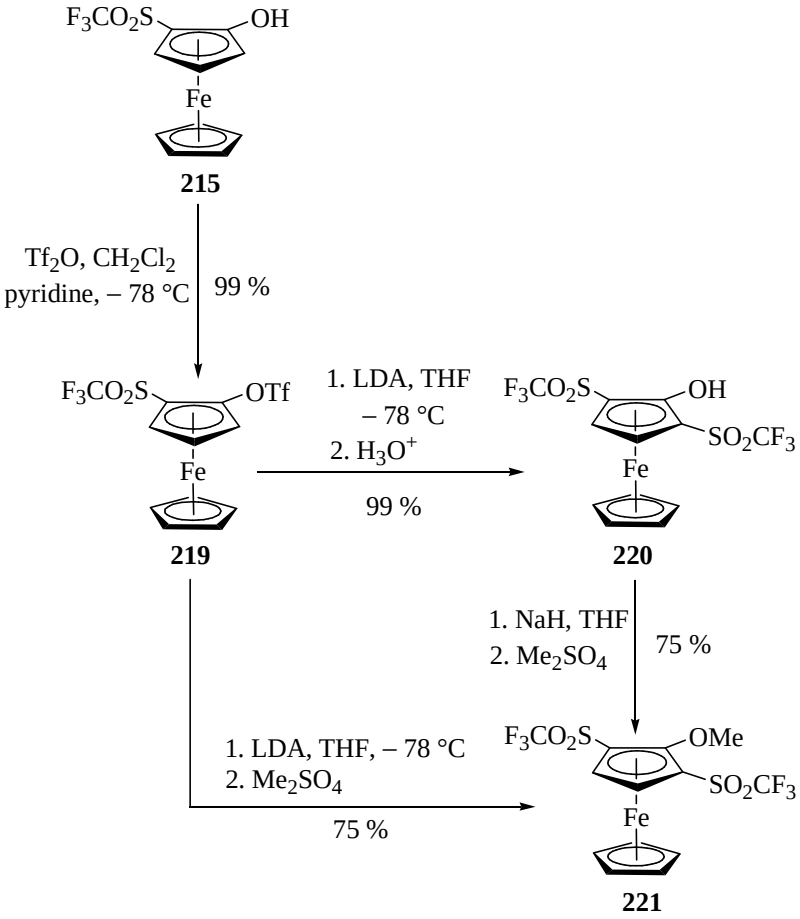
Compound **215** is irreversibly oxidized at E_{pc1} = 242.7 mV, a value smaller than the corresponding one in **63** signifying that the electron withdrawing effect of the trifluoromethylsulfonyl group is partially compensated by the electron deliverance from the hydroxyl substituent. This indicates the ring slipped dipolar, presumably hydrogen-bridged resonance formula **218** (*Scheme 75*). In addition, the cyclovoltammogram shows oxidation and reduction processes at lower potential, which may be attributed to the trifluoromethylsulfonyl group.



215 **218**

Scheme 75 Resonance formulae for **215** and **218**

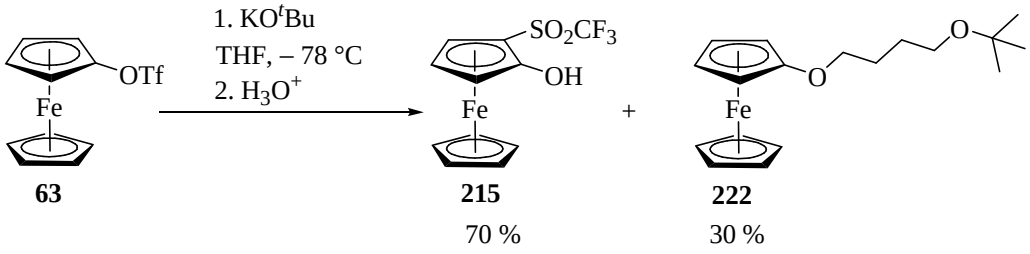
The rearrangement product **215** can be also treated with triflic anhydride in methylene chloride/pyridine generating the much less electron rich triflate **219**, which is obtained in 99 % yield. Following treatment with LDA in THF at −78 °C results in another anionic thia-Fries rearrangement with formation of the symmetric 2,5-bis(trifluoromethylsulfonyl)- ferrocenol (**220**) in nearly quantitative yield. The corresponding methyl ether **221** can either be obtained by *in situ* quench with dimethyl sulphate or by methylation of **220** (*Scheme 76*).



Scheme 76

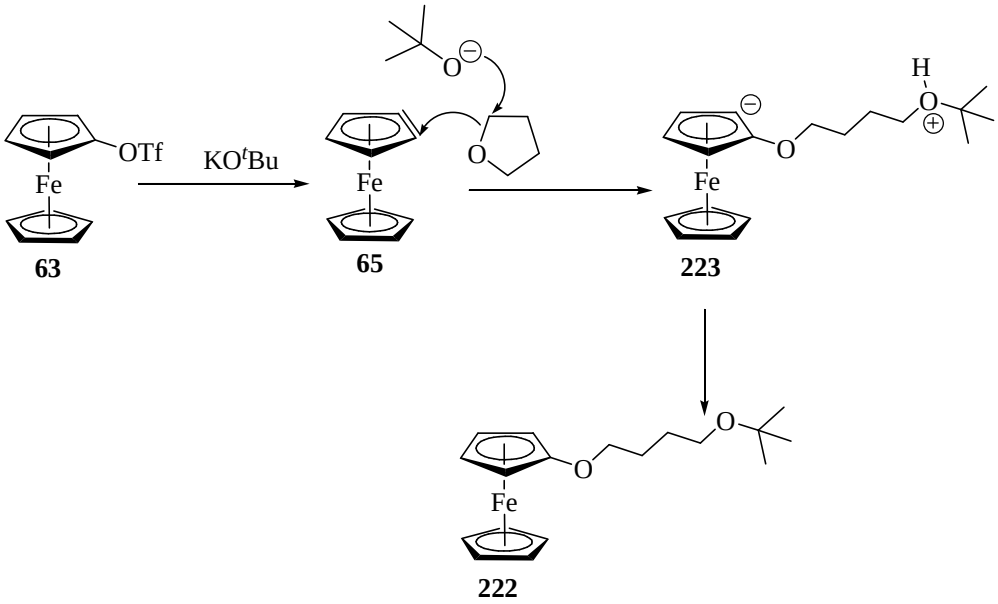
As already mentioned, various bases were used attempting the eliminiation with ferrocenyl triflate, but all efforts led to the same result, namely to the formation of the anionic thia-Fries rearrangement product. The only divergence was the different yields of **215**. A different result was obtained using potassium *tert*-butoxide in THF and potassium methoxide in methanol. Treatment of ferrocenyl triflate with KO^{t}Bu led to the formation of 2-(trifluoromethyl-

sulfonyl)ferrocenol (**215**) with 70 % yield and (4-*tert*-butoxy-butoxy)-ferrocene (**222**) with 30 % yield (*Scheme 77*).



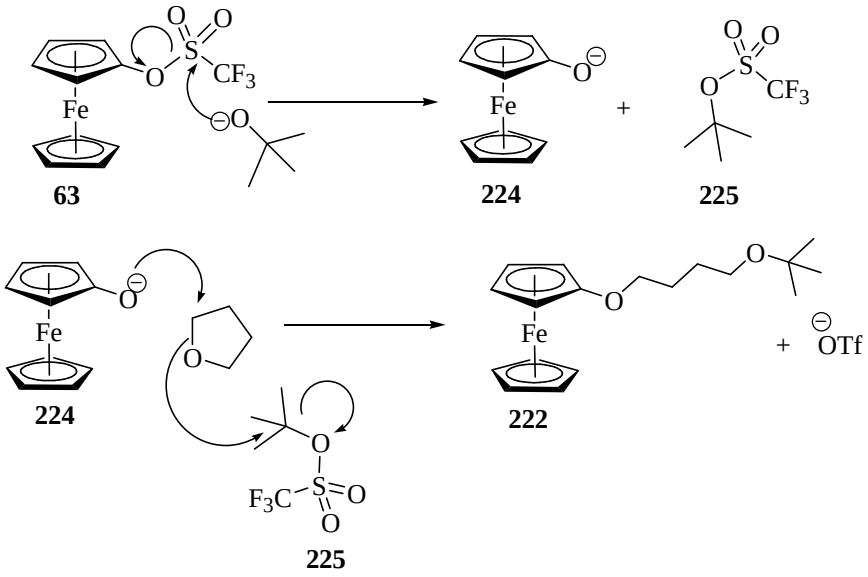
Scheme 77

Obviously, one THF molecule takes part in this process. Two reactions explaining the formation of the compound **222** are conceivable. Firstly, the generation of ferrocyne is open, which is formed via triflate elimination by potassium *tert*-butoxide. Another *tert*-butoxide anion charges the THF in the *ortho* position to the oxygen atom, while the oxygen is adding on the triple bond of the ferrocyne (**65**) generating the zwitterion **223**. After the transfer of the hydrogen (4-*tert*-butoxy-butoxy)-ferrocene (**222**) is generated (*Scheme 78*).



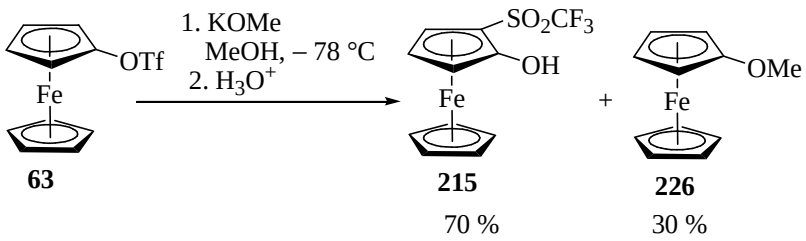
Scheme 78. a proposed mechanism fort he formation of **222**

The other explanation is based on the series of nucleophilic substitutions. The *tert*-butanolate charges the sulphur atom of the triflate group in the ferrocenyl triflate (**63**) and releases a ferrocenolate anion (**224**) generating the *tert* butyl triflate (**225**). The ferocenolate (**224**) attacks a THF molecule in the *ortho* position to the oxygen atom, while the oxygen of the THF attacks the *tert* butyl triflate (**225**) via S_N2 reaction generating (4-*tert*-butoxy-butoxy)-ferrocene (**222**) and triflate anion (*Scheme 79*).



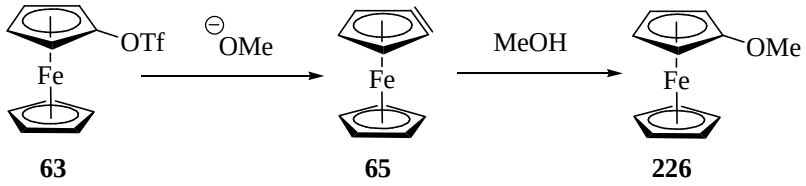
Scheme 79. another proposed mechanism fort he formation of **222**

The similar result was obtained with the treatment of the ferrocenyl triflate with KOMe (or KO^{t}Bu or metallic potassium) in the methanol. Apart from the usual rearrangement product (**215**) methoxy ferrocene (**226**) was obtained (*Scheme 80*).



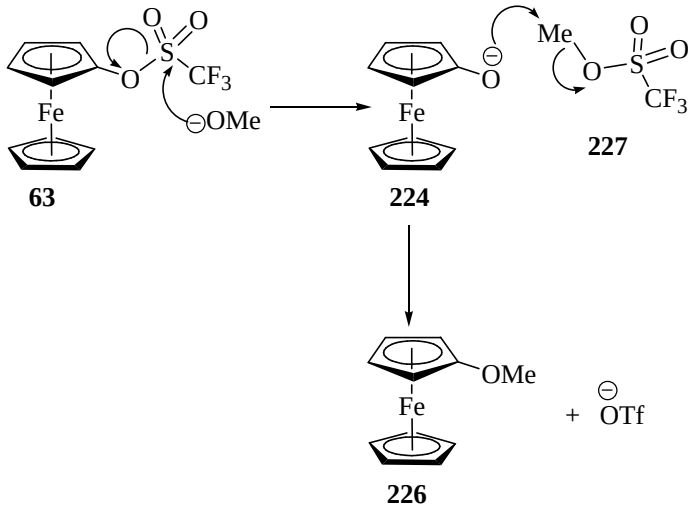
Scheme 80

Again, two reactions explaining the formation of the compound **226** are conceivable. Firstly, ferrocyne (**65**) is generated *via* the triflate elimination induced by the methanolate, which undergoes subsequently an addition with methanol (*Scheme 81*).



Scheme 81

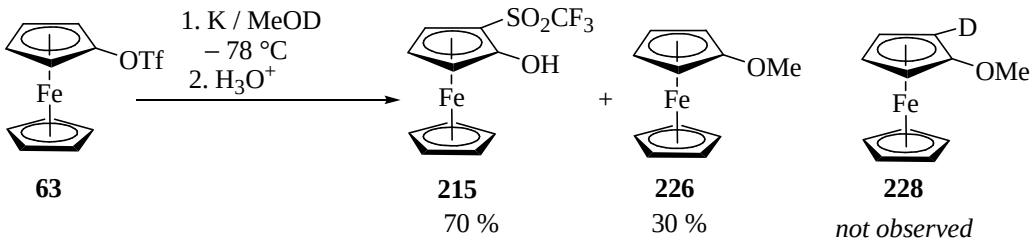
The other explanation is based on the series of nucleophilic substitutions. The methanolate charges the sulphur atom of the triflate group in the ferrocenyl triflate (**63**) and releases a ferocenolate anion (**224**) generating the methyl triflate (**227**), which is attacked by ferrocenolate *via* S_N2 reaction generating methoxy ferrocene (**226**) and triflate anion (*Scheme 82*).



Scheme 82

The *experimentum crucis* in this context is the carrying out of the reaction in the deuterated methanol as the solvent. With appearance of ferrocyne intermediate in the reaction mixture the *ortho* deuterated metoxy ferrocene as the product together with the rearrangement product is to be expected. However, the treatment of the ferrocenyl triflate with metallic potassium in

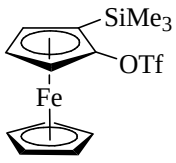
the deuterated methanol delivers the rearrangement product (**215**) and methoxy ferrocene (**226**). The *ortho* deuterated methoxy ferrocene was not observed (*Scheme 83*).



Scheme 83

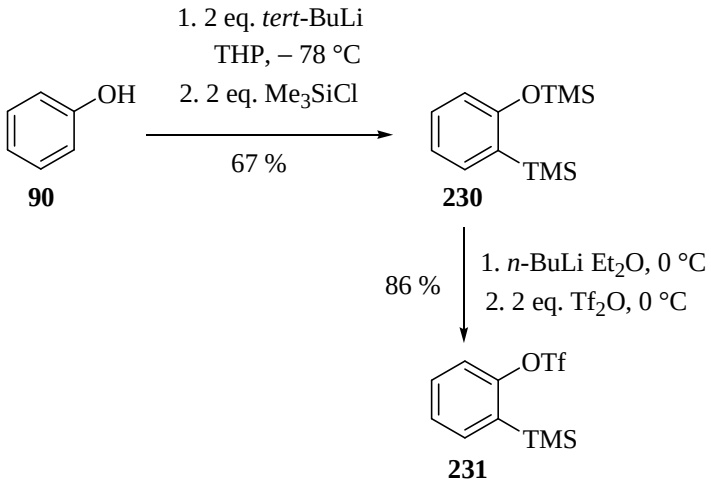
This result leaves no room for doubt, that the reactions with KO^{t}Bu or KOMe are performed only through a series of nucleophilic substitutions generating compounds **222** and **226** and no elimination took place (*Schemes 79 and 82*).

In an alternative approach to synthesize the ferrocyne the *o*-trimethylsilylferrocenyl triflate (**229**) should be used.



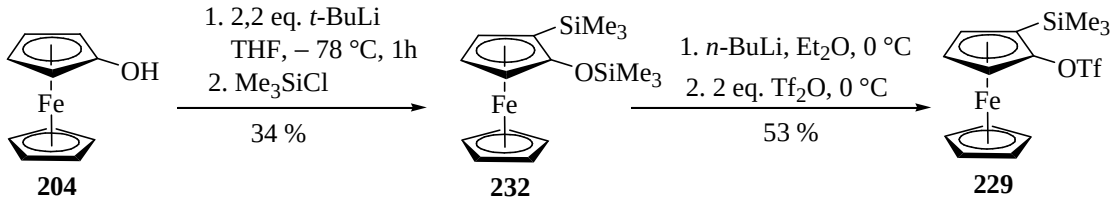
229

The established method for the synthesis of *o*-trimethylsilylphenyl triflate (**231**) is based on the double deprotonation of the phenol (**90**) with *tert* butyl lithium in tetrahydropyrane (THP) and subsequent interception with two equivalent of trimethylsilylchloride, generating the *o*-trimethysilylphenoxytrimethylsilane (**230**),[110, 111] which is treated with excess molar amounts of butyl lithium and subsequently with triflic acid anhydride (*Scheme 84*).[112]



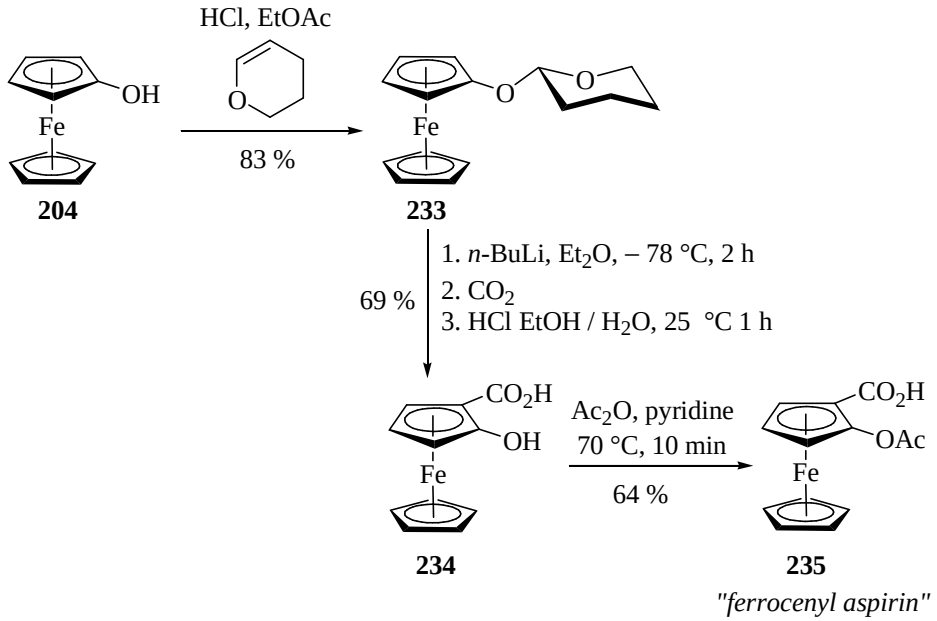
Scheme 84[110-112]

We adopted this method for the synthesis of *o*-trimethylsilylferrocenyl triflate (**229**). However, the yield of the required compound was not really satisfying (*Scheme 85*). This is due to the circumstance, which is always associated with the ferrocene chemistry, namely a part of the used base deprotonates the second Cp-ring.



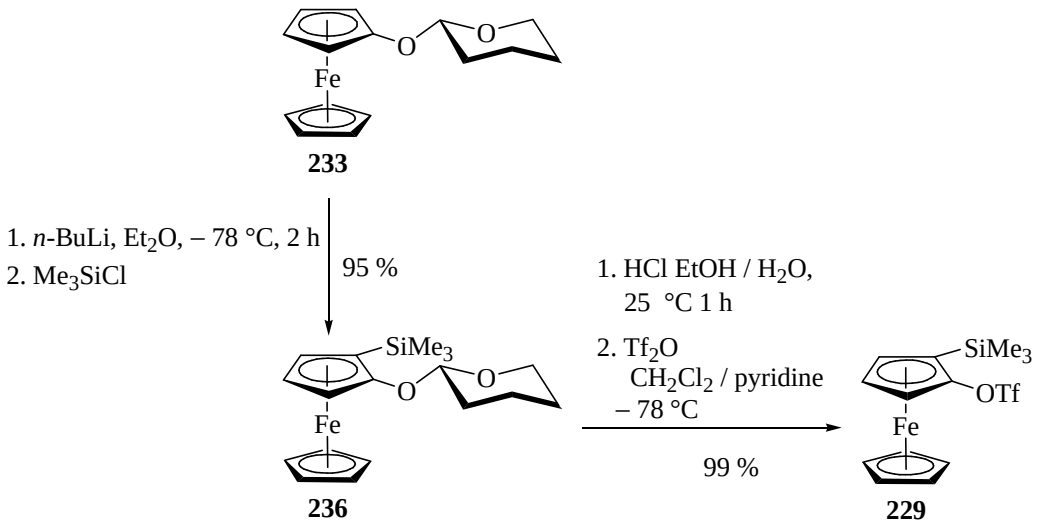
Scheme 85

Rogers *et. al.* reported the synthesis of the "ferrocenyl aspirin". They protected ferrocenol with THP group, which acts not only as a protecting group but also as an excellent *ortho* directing metallating group. After the *ortho* lithiation, following interception with the dry ice and the deprotection of the OH group, the 2-hydroxyferrocenecaboxylic acid (**234**) was obtained, which could be transformed to the required 2-acetoxyferrocenecarboxylic acid (**235**) (*Scheme 86).*[113]



Scheme 86[113]

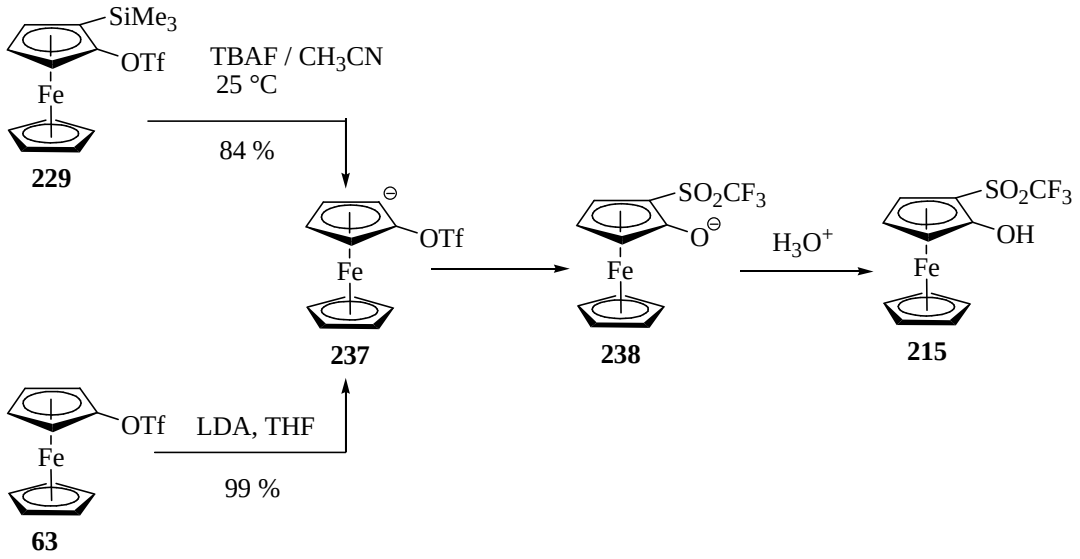
We adopted this procedure for our scope and obtained even higher yields in our reactions. The lithiation of the tetrahydropyran-2-yloxyferrocene (**233**) and the following trapping with Me_3SiCl delivered the trimethyl-[2-(tetrahydro-pyran-2-yloxy)-ferrocenyl]-silane (**236**) in almost quantitative yield. The deprotection and the following esterification with the triflic anhydride are performed with nearby quantitative yield as well generating the required *o*-trimethylsilylferrocenyl triflate (**229**) (*Scheme 87*).



Scheme 87

The new compounds **236** and **229** are fully characterized spectroscopically. The compound **236** is a red solid and compound **229** is a yellow liquid. The both are very stable and can be handled under air.

The *o*-trimethylsilylferrocenyl triflate (**229**) was treated with tetrabutylammonium fluoride in acetonitrile at 25 °C. Because of high affinity of silicon to fluorine the trimethylsilyl group was removed efficiently. This lead to generation of intermediate **237**, the same intermediate in the treatment of ferrocenyl triflate (**63**) with a base. The intermediate **237** undergoes instantaneously thia Fries rearrangement affording the ferrocenolate **238**. The following quenching with water generates the thia Fries rearrangement product **215** (*Scheme 88*).

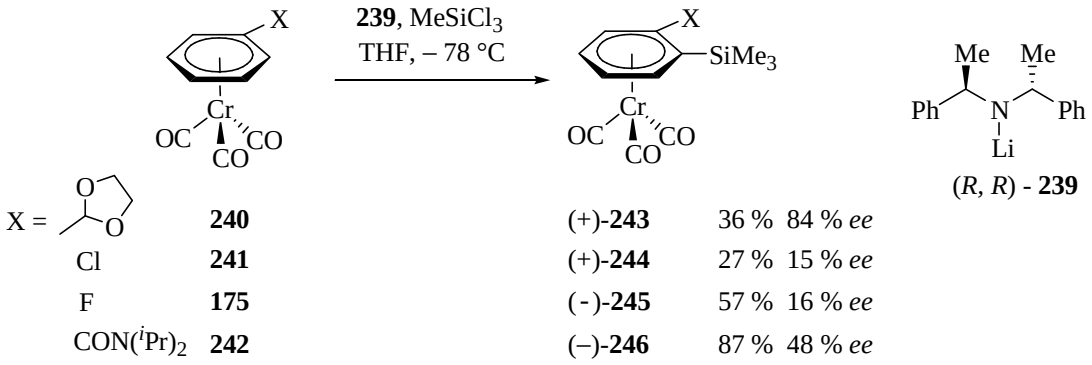


Scheme 88

3.3 Enantioselective ortho-deprotonation of 1-ferrocenyltriflate

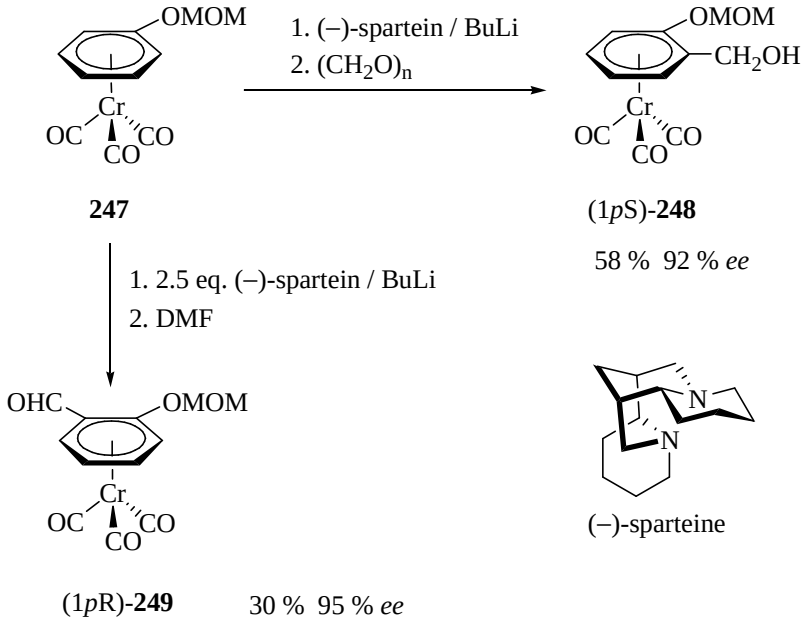
Ferrocenol derivatives **215–217** and **219** are planar chiral[114] and, with respect to the possibility of their use as ligands in asymmetric catalysis, their formation in non racemic form is of prime interest. This requires a differentiation of the two enantiotopic *ortho* protons in **63**. The enantiotopic protons can be distinguished by chiral bases. The one of the frequently used bases for this strategy is the enantiomerically pure lithium amide **239**,[115] which was used by Simpkins for the enantioselective *ortho* deprotonation of (anisole)tricarbonyl chromium fol-

lowed by *in situ* quenching with $MeSiCl_3$ as an electrophile. Enantiomerically enriched tricarbonylchromium complexes were obtained in up 84 % *ee* (Scheme 89).[116]



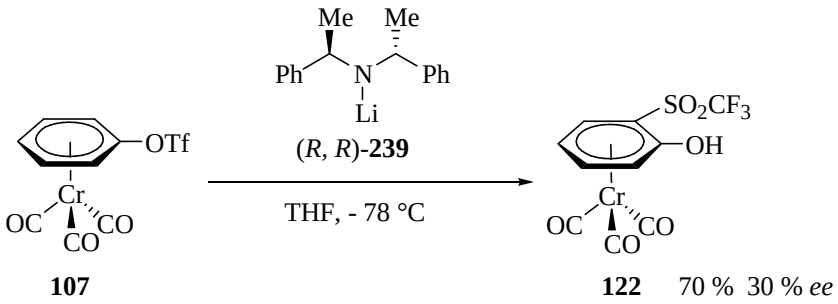
Scheme 89[110]

Widdowson and co-workers describe a successful application of (–)-sparteine / butyl lithium in the enantioselective *ortho* lithiation of complex **247**. After the deprotonation and quenching with an electrophile the planar chiral complex (1*p*S)-**248** was obtained in 58 % yield and 92 % *ee* (Scheme 90).[117] The following research showed, that the use of 2,5 equivalents of (–)-sparteine / butyl lithium can reverse the stereoselectivity, so that (1*p*R)-**249** could be synthesized in 30 % yield and 95 % *ee*.[118]



Scheme 90[118]

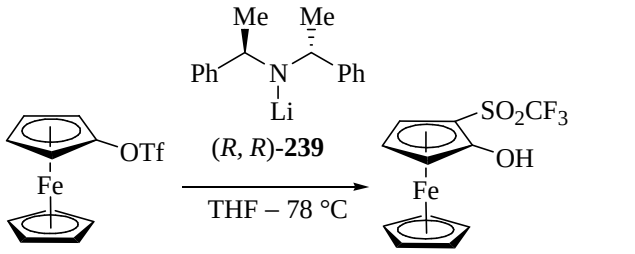
Previously, the enantioselective *ortho* deprotonation on phenyl triflate tricarbonylchromium complexes were adopted by our group. Phenyl triflate complex **107** was treated with lithium-(*R, R*)-di(1-phenylethyl-amide) (Simkins' base). Inspection of the NMR spectra (^{1}H, ^{13}C) of the respective Mosher esters revealed that phenol complex **122** had been obtained in only 30% *ee* (*Scheme 91*).[50]



107 **122** 70 % 30 % *ee*

Scheme 91. enantioselective *ortho* deprotonation of phenyl triflate tricarbonyl chromium[50]

We attempted to achieve the differentiation of enantiotopic *ortho* protons on the ferrocenyl triflate by using lithiated Simpkins' base instead of LDA at − 78 °C gave an only unsatisfactory enantiomeric excess (10% *ee*, determined by NMR of the Mosher esters) (*Scheme 92*).



63 **215** 95 % 10 % *ee*

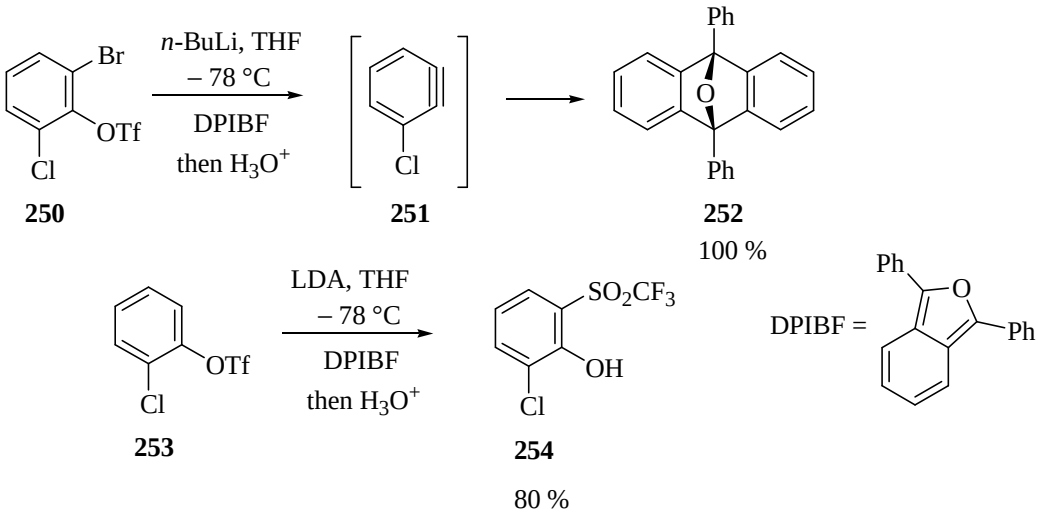
Scheme 92. attempt to achieve the differentiation of enantiotopic *ortho* protons with the Simpkins' base

The extreme low enantioselective excess might be due to a pre-coordination of the chiral base at the Lewis basic oxygen atoms of the triflate group.

(−)-Sparteine / butyl lithium has also been used for the enantioselective deprotonation. This attempt gave no positive results (instead of, a rearrangement product ferrocenol was formed).

3.4 Metallation vs. deprotonation in the ortho-position of phenyltriflates

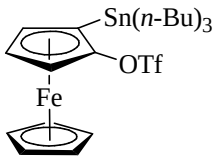
Guy C. Lloyd-Jones *et al.* demonstrated that the differentiation between a metallation and a deprotonation of phenyl triflates plays a crucial role in terms of following reactions.[119] While the deprotonation of phenyl triflates can lead to elimination products as well as the thia-Fries rearrangement products,[44] all examples of *ortho*-metallated aryltriflates (Mg, Zn) generate exclusively arynes.[120-125] For example, the reaction of a phenyl triflate **253**, bearing an electron withdrawing group, with LDA in the presence of 1,3-diphenylisobenzofuran (DPIBF) gave the rearrangement product **254** (80 % yield), while the reaction of the phenyl triflate **250**, bearing the *ortho* bromine, with butyl lithium at – 78 °C resulted in a quantitative aryne generation, as evidenced by the *in situ* trapping with (DPIBF) to give **253** (*Scheme 93*).[119]



Scheme 93[119]

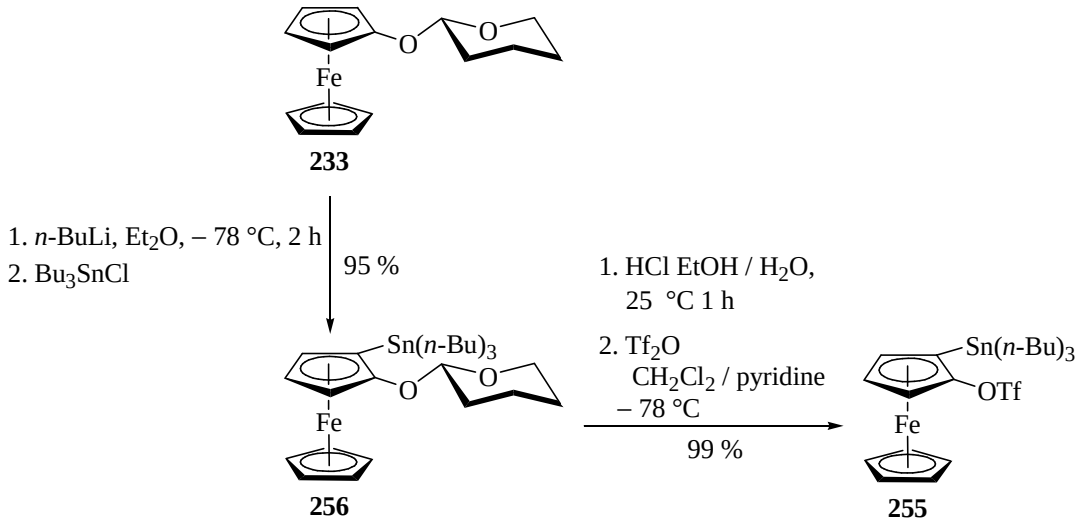
3.4.1 Metallation of ferrocenyltriflate in the *ortho* position

Since all *ortho* metallated phenyl sulphonates (among also triflates) undergo elimination reactions, [119-125] we set about to synthesize the 2-tributylstannyl ferrocenyl triflate (**255**).



255

The same method from the synthesis of the *o*-trimethylsilylferrocenyl triflate (**229**) (*Scheme 87*) was used. The lithiation of the tetrahydropyran-2-yloxyferrocene (**233**) and the following trapping with Bu_3SnCl delivered the tributyl-[2-(tetrahydro-pyran-2-yloxy)-ferrocenyl]-stannane (**256**) in almost quantitative yield. The deprotection and the following esterification with the triflic anhydride are performed with nearby quantitative yield, generating the required 2-tributylstannyl ferrocenyl triflate (**255**) (*Scheme 94*).

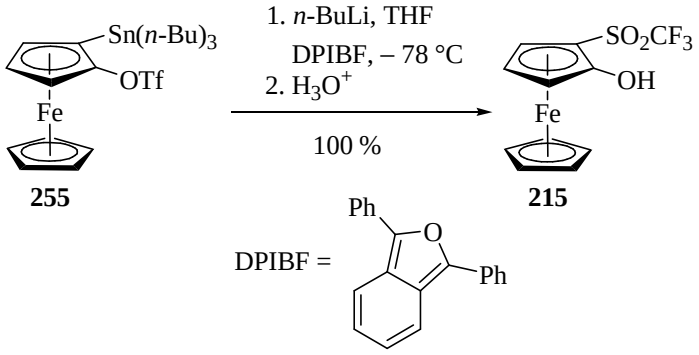


Scheme 94

The new compounds **255** and **256** are fully characterized spectroscopically. Compound **256** is an orange liquid and the compound **255** is a yellow liquid. The both are very stable and can be handled in air.

The tributylstannyl group can be efficiently transmetallated by butyl lithium, so that the *ortho* position to the triflate group is lithiated. This is the essential difference to the previous experiments with ferrocenyl triflate and LDA, in which the *ortho* position was always deprotonated (*vide supra*). In the light of the described divergence between deprotonation and metallation

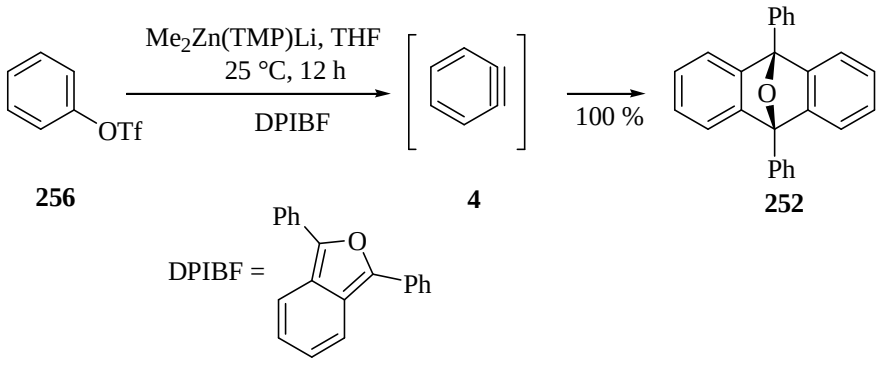
eventually the elimination of the triflate was expected. However, the treatment of 2(-tributylstannyl)ferrocenyl triflate (**255**) with butyl lithium in THF at – 78 °C in the presence of DPIBF quantitatively resulted in the anionic thia-Fries rearrangement product **215** (*Scheme 95*).



Scheme 95

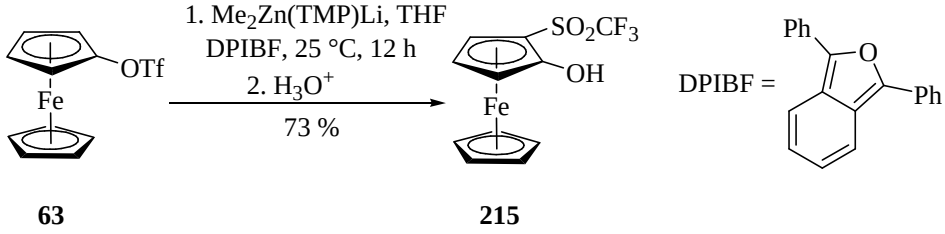
This is the first case that the *ortho* metallation of a phenyl triflate (here, the ferrocenyl triflate) exclusively leads to the rearrangement, while the earlier examples resulted in aryne generation. [119-125]

In an alternative approach to an *o*-metallated ferrocenyl triflate we applied the method, which was presented by M. Uchiyama *et al*. describing the metallation of halobenzenes and phenyl triflates.[123] They used TMP-zincates as very efficient reagents for metallation, which are prepared *in situ* by treatment of $ZnCl_2$ solution in diethyl ether with Li-TMP. The TMP-zincates effectively caused the *o*-metallation quantitatively generating arynes as evidenced by the *in situ* trapping with 1,3-diphenylisobenzofuran (*Scheme 96*).[123]



Scheme 96

This method was executed with ferrocenyl triflate. Again, the treatment of ferrocenyl triflate **63** with the TMP-zincate caused the anionic thia-Fries rearrangement (*Scheme 97*).

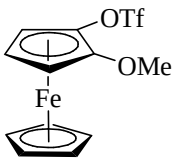


63 **215**

Scheme 97

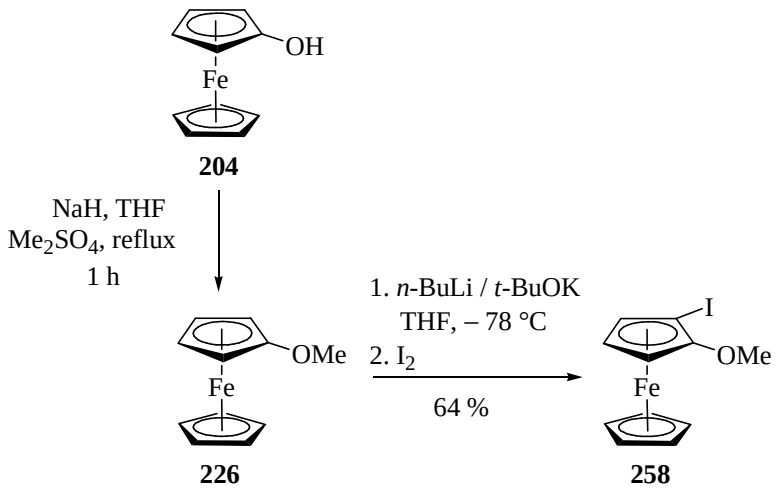
3.5 Syntheses of more electron rich ferrocenyl triflates

In the next step, we synthesized ferrocenyl triflates bearing one or more electron donating groups, in order to increase the electron density in the aromatic system. The introduction of different groups in the ferrocene molecule turned out to be a challenge. The simplest reaction path was the synthesis of the 2-methoxyferrocenyl triflate (**257**)**.**



257

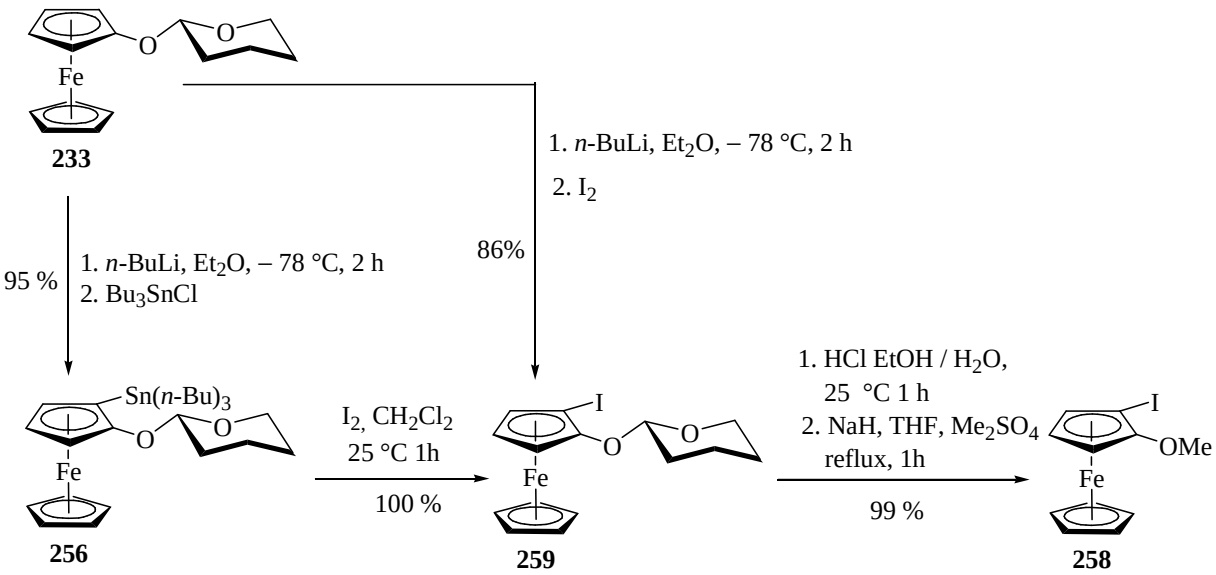
The central compound in this synthesis is 1-iodo-2-methoxyferrocene (**258**), which can be then transformed to 2-methoxyferrocenyl acetate (**260**). There are two alternatives to synthesize this compound. Firstly, methoxyferrocene (**226**) is used as the starting material, which is subjected to *o*-metallation and subsequently trapped by iodine (*Scheme 98*).



Scheme 98

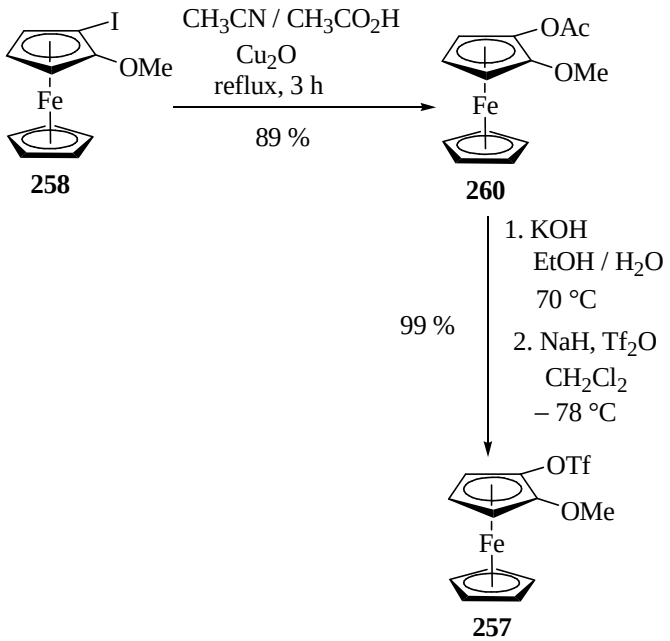
Although this method leads to the required compound (**258**), the low yield leaves a room for improvement. For the better results we applied the method, which we already used for preparation of 2-trimethylsilylferrocenyl triflate (**229**) and 2-tributylstannyl ferrocenyl triflate (**255**) (*Schemes 87 and 94*).

Tributyl-[2-(tetrahydro-pyran-2-yloxy)-phenyl]-stannane (**256**),prepared from **233** was treated with iodine in methylene chloride at 25 °C delivering in quantitative yield 2-(2-iodo-ferrocenoxy)-tetrahydro-pyran (**259**). The deprotection and the following methylation with dimethyl sulphate were performed with nearly quantitative yield generating the required 1-iodo-2-methoxyferrocene (**258**) (*Scheme 99*). The lithiated tetrahydropyran-2-yloxyferrocene (**233**) can also directly be trapped with iodine giving **259**, but the lower yield and problematic separation from **233** make the deviation through **256** much more attractive.



Scheme 99

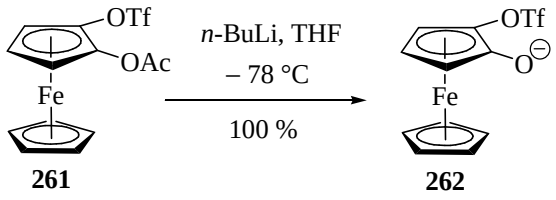
Heating of 1-iodo-2-methoxy ferrocene (**258**) in acetonitrile at reflux with 1.2 equivalents of Cu_2O and 3 equivalents of acetic acid generated the 2-methoxyferrocenyl acetate (**260**) in 89 % yield, which was hydrolyzed and esterificated with triflic anhydride giving the 2-methoxy-ferrocenyl triflate (**257**) (*Scheme 100*).



Scheme 100

The new compounds **257**-**260** were fully characterized spectroscopically. Compounds **257** and **258** are yellow liquids, **259** and **260** are orange solids. In general, they are stable and can be handled in air, but they should be stored in an inert atmosphere for the longer period of time. Compounds **260** and **259** are the first examples of a ferrocene with two vicinal oxygen atoms, thus derivates of 1,2-ferrocenediol.

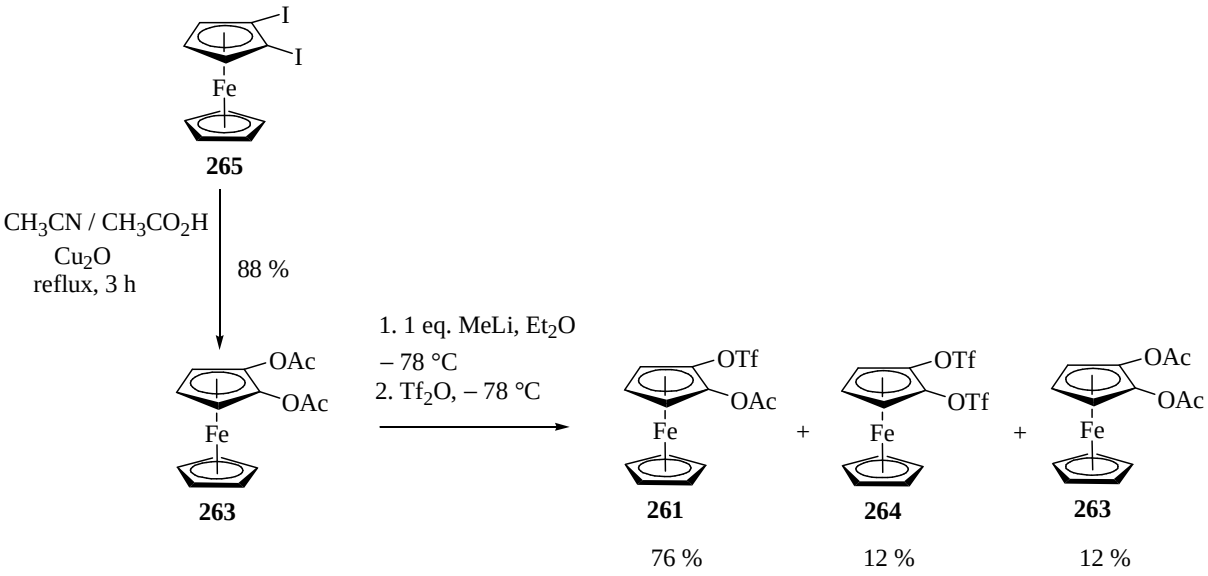
The other even more electron rich ferrocenyl triflate is the 2-trifluoromethanesulfonyloxy-ferrocenolate (**262**), which was generated *in situ* from 2-trifluoromethanesulfonyloxy-ferrocenyl acetate (**261**) (*Scheme 101*).



261 **262**

Scheme 101

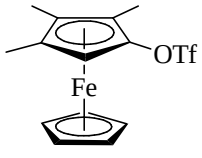
2-Trifluoromethanesulfonyloxy-ferrocenyl acetate (**261**) was synthesized from 2-acetoxy-ferrocenyl acetate (**263**) via a single hydrolysis with one equivalent of methyl lithium. However, the double hydrolysis could not be completely avoided, so that apart from the required product **261** also the 1,2-ferrocenyl diacetate (**263**) was recovered as well as the 1,2-ferrocendiyl ditriflate (**264**) was obtained. The 2-acetoxy-ferrocenyl acetate (**263**) was prepared from 1,2-diiodoferrocene (**265**) (for the synthesis of 1,2-diiodoferrocene *vide infra*) by heating in acetonitrile at reflux in the presence of 2.4 equivalents of Cu_2O and 5 equivalents of acetic acid (*Scheme 102*).



Scheme 102

The new compounds **261**, **263** and **264** were fully characterized. Compound **263** is a yellow solid with a very low melting point (23 °C), compounds **261** and **264** are yellow liquids. In general they are stable and can be handled under air, but they should be stored in an inert atmosphere for the longer period of time. All three compounds are the further examples for ferrocenes with two vicinal oxygen atoms, thus derivates of 1,2-ferrocenediol.

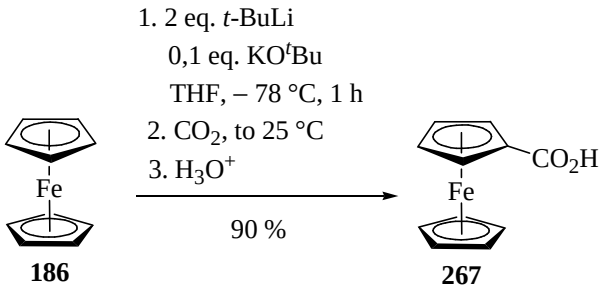
The next electron rich ferrocenyl triflate, was 2,3,4-trimethyl-ferrocenyl triflate (**266**). The three electron donating methyl groups make the aromatic ring electron rich. Moreover, the methyl at C-4 could hinder the rearrangement.



266

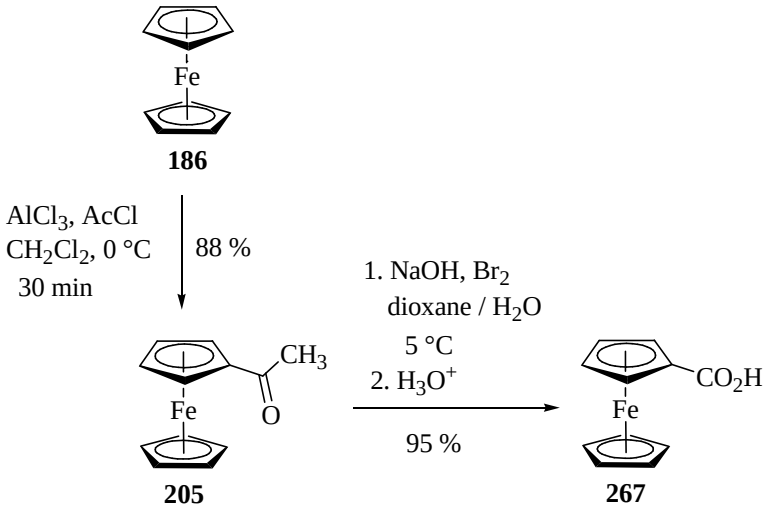
The ferrocene carboxylic acid **267** is the starting material of the choice for the synthesis of **266**. The widely used method for the preparation of **267** is based on the lithiation with a strong base, subsequent interception with the carbon dioxide and the concluding acidification. As far as we are aware, the best method is presented by B. Breit and D. Breuninger.[107] They used for the metallation a mixture of two equivalents of *tert*-butyllithium and 0.1 equivalents

of potassium *tert*-butoxide (known as the Schlosser base). The obtained lithioferrocene was trapped with carbon dioxide to give after acidic work-up ferrocene carboxylic acid (**267**) in 90 % yield (*Scheme 103*).



Scheme 103[107]

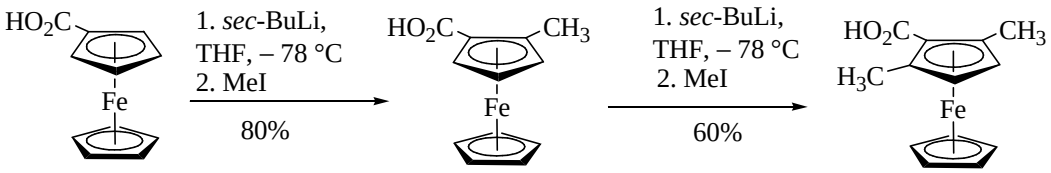
Although this synthesis is very fast and effecient, we developed another method, which allows the preparation of ferrocene carboxylic acid (**267**) in multigram quantities. This method is based on the so called bromoform reaction, which is performed with the acetyl ferrocene (**205**) as the starting material in the dioxane / water (1:1) mixture and with ten equivalents of sodium hydroxide and three equivalents of bromine. Acetyl ferrocene (**205**) is easily accessible from ferrocene (**186**) via Friedel-Crafts acylation (*Scheme 104*).



Scheme 104

This is the first case, that the oxidative cleavage was used with a ferrocene system, which is, probably, due to the fear that the acetyl ferrocene can not withstand such strong oxidation conditions.

The ferrocene carboxylic acid (**267**) can be effectively ortho metallated with two equivalents of *sec* butyl lithium.[107, 126] The adjacent addition of iodomethane gave after acidic work-up the 2-methyl ferrocene carboxylic acid (**268**) in 80 % yield. The repeated procedure delivered the 2,5-dimethyl ferrocene carboxylic acid (**269**) in 60 % yield (*Scheme 105*).



267 **268** **269**

Scheme 105

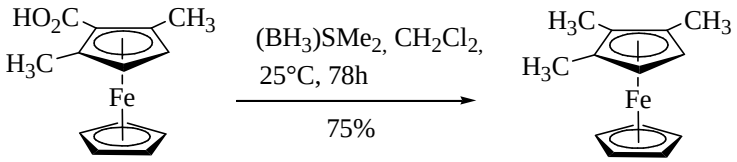
The new compound **269** is fully characterized spectroscopically. It is light orange solid, very stable in air.

Since the carboxylic acid group is electron withdrawing, it can disturb in our effort to design a more electron rich ferrocenyl triflate. Hence it must be removed or reduced. T-Jeong Kim *et al.* presented the borane-dimethyl sulphide (BMS) as a very efficient reducing reagent.[127] They carried out reductive deoxygenation of various ferrocenyl aldehydes, ketones, alcohols, and carboxylic acids into the corresponding alkyl ferrocenes (*Table 7*).[127]

Table 7. reductive deoxygenation of ferrocenyl derivatives by BH_3 SMe_2[127]

entry	substrate	time (h)	product	yield (%)
1	FcCHO	3	$FcCH_3$	95
2	1,1'-$Fc(CHO)_2$	3	1,1'-$Fc(CH_3)_2$	95
3	$FcCOCH_3$	3,5	$FcCH_2CH3$	95
4	FcCOPh	6	$FcCH_2Ph$	93
5	$FcCOCH_2Cl$	30	$Fc(CH_2)_2Cl$	92
6	$FcCOCH_2COCH_3$	30	$Fc(CH_2)_2CH(OH)CH_3$	31
			$Fc(CH_2)_3CH_3$	20
			$FcCH(OH)(CH_2)_2CH_3$	17
7	1,1'-$Fc(CH_2OH)_2$	3	1,1'-$Fc(CH_3)_2$	95
8	$FcCH(OH)CH_3$	3,5	$FcCH_2CH_3$	95
9	$FcCH(OH)CH_2Cl$	8	$FcCH_2CH_2Cl$	92
10	$FcCH(OH)CH_2OH$	3,5	$FcCH_2CH_2OH$	95
12	1,1'-$Fc(CO_2H)_2$	6	1,1'-$Fc(CH_3)_2$	83

This method seems to be ideal for our aim, especially in the light of entry 12 (*Table 7*). The 2,5-dimethyl ferrocene carboxylic acid (**269**) was treated with the two equivalent of BMS in methylene chloride at 25 °C for 78 hours to give the required reduction product **270** in 75 % yield (*Scheme 106*).

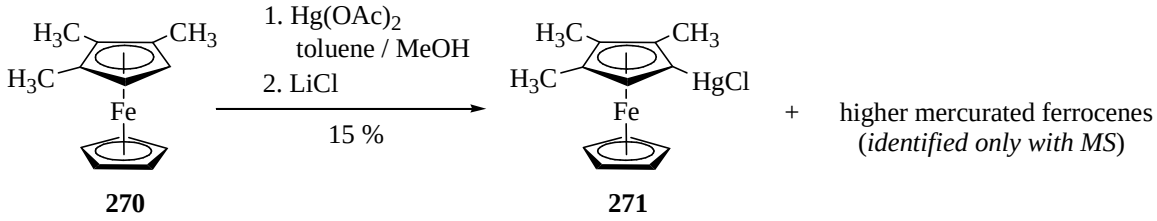


269 **270**

Scheme 106

The new compound **270** is fully characterized spectroscopically. It is light yellow oil, stable in air for a short time and should be stored in a cool under protecting atmosphere.

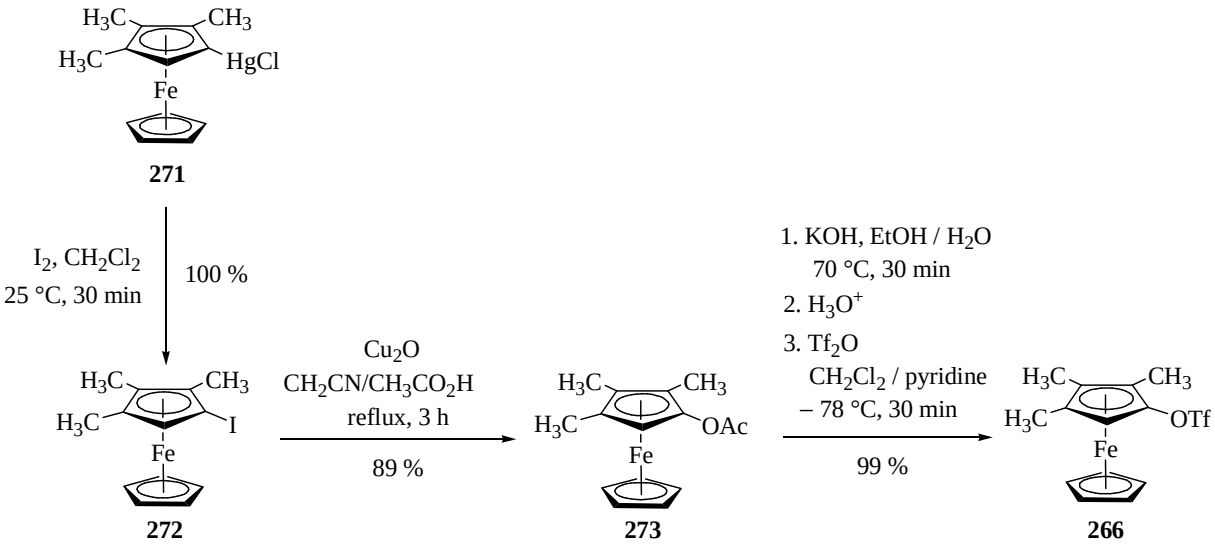
In the next step the 1,2,3-trimethyl ferrocene (**270**) was subjected to the mercuration. Since the mercuration proceeds more readily on the more electron rich arenes,[128-131] we expected the mercuration on the cyclopentadienyl ring bearing the three methyl group. Indeed, the main product of this conversion was the required compound **271**, while many side products were also obtained, which gravely decreased the yield of **271** (*Scheme 107*).



270 **271**

Scheme 107

The mercurated product **271** was treated with iodine in methylene chloride at 25 °C for 30 minutes, the quantitative conversion delivered the 1-iodo-2,3,4-trimethyl ferrocene (**272**), which was heated in acetonitrile under reflux with 1.2 equivalents of Cu_2O and 3 equivalents of acetic acid generating the 2,3,4-trimethyl ferrocenyl acetate (**273**) in 89 % yield , which is, as usually, hydrolyzed and esterificated with triflic anhydride giving quantitatively the 2,3,4-trimethyl ferrocenyl triflate (**266**) (*Scheme 108*).



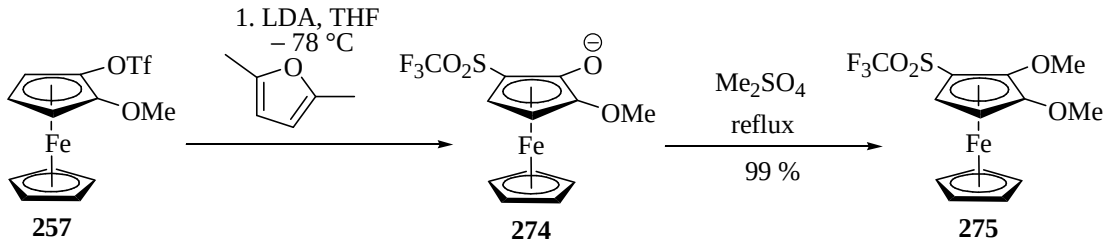
Scheme 108

The new compounds **266**, **271**-**273** are fully identified spectroscopically. The compound **271** is light yellow powder, which is stable in air. The compounds **266**, **272** and **273** were obtained as yellow oils, stable in air for a short time but they should be stored in a cool under protecting atmosphere.

3.6 Anionic thia-Fries rearrangement of more electron rich ferrocenyl triflates

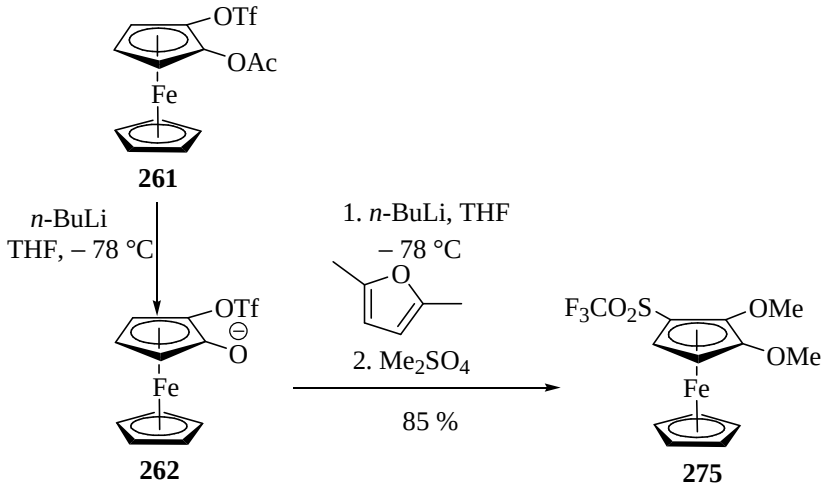
The prepared electron rich ferrocenyl triflates were treated with bases in the presence of dienes, in order to prove their ability to undergo elimination reaction.

The treatment of the 2-methoxy ferrocenyl triflate (**257**) with LDA in THF at – 78 °C in the presence of 2,5-dimethylfuran resulted in the anionic thia-Fries rearrangement generating the 2-methoxy-5-(trifluoromethylsulfonyl)ferrocenolate (**274**), which was methylated delivering the dimethylated anionic thia-Fries rearrangement product **275** (*Scheme 109*).



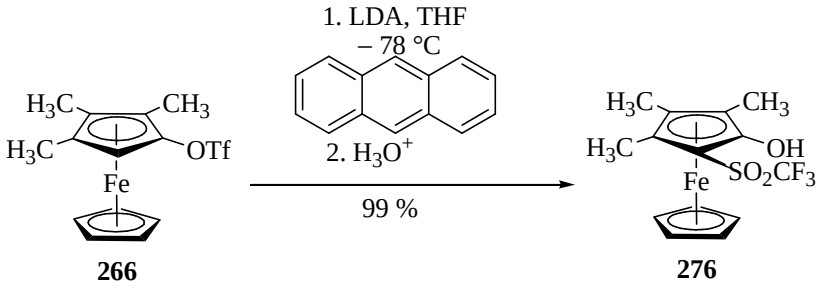
Scheme 109

The 2-trifluoromethanesulfonyloxy-ferrocenolate (**262**), which was generated *in situ* from 2-trifluoromethanesulfonyloxy-ferrocenyl acetate (**261**) was treated with LDA in THF at – 78 °C in the presence of 2,5-dimethylfuran, after the following methylation with dimethyl sulphate 1,2-dimethoxy-5-(trifluoromethylsulfonyl)ferrocene (**275)** was obtained in 85 % yield (*Scheme 110*).



Scheme 111

In the reaction of the 2,3,4-trimethyl-ferrocenyl triflate (**266**) with LDA anthracene was used as the diene, because of the doubt, that the methyl groups of **266** and the methyl groups of 2,5-dimethyl furan or phenyl groups of DPIBF would disturb each other. However, the treatment of the 2,3,4-trimethyl-ferrocenyl triflate (**266**) with LDA in THF at – 78 °C in the presence of anthracene and the following acidification resulted in the anionic thia-Fries rearrangement generating the 2,3,4-trimethyl-5-(trifluoromethylsulfonyl)ferrocenol (**276**) (*Scheme 112*).



266 **276**

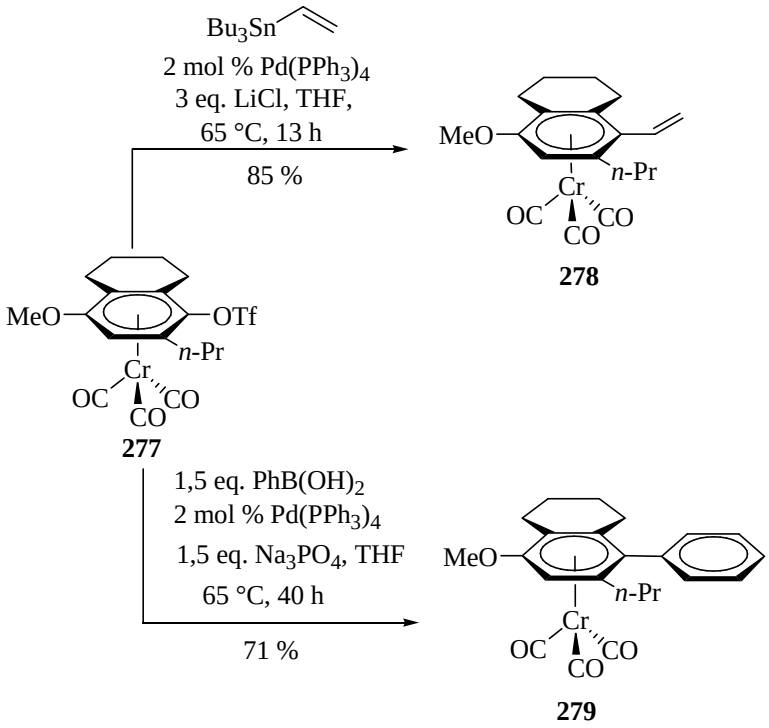
Scheme 112

The new compounds **274-276** are entirely characterized spectroscopically. They are yellow solids, stable in air for a short time but they should be stored in a cool under protecting atmosphere.

3.7 Attempts for palladium(0)-catalyzed cross-coupling of 1-ferrocenyl triflate

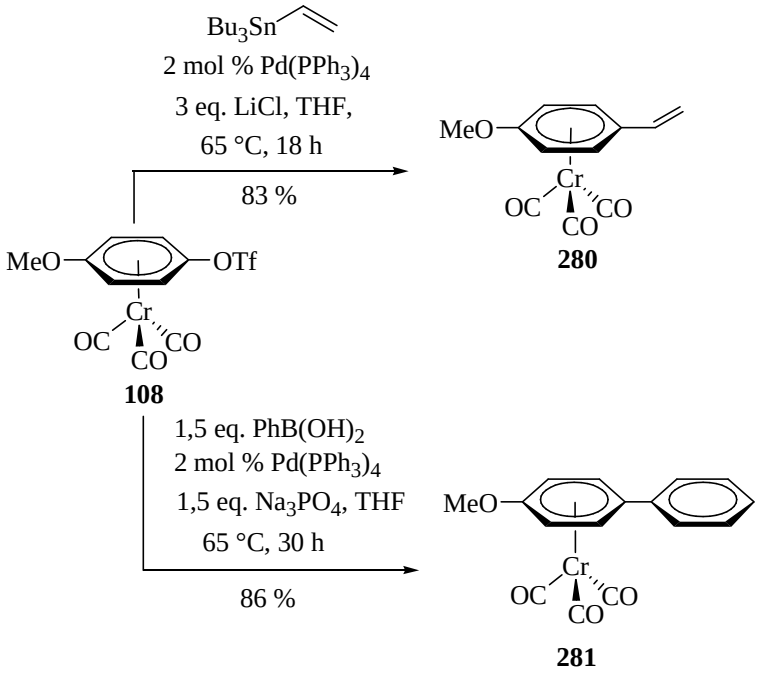
The palladium(0)-catalyzed cross coupling reactions are widely used for the preparation of various arenas, representing thus a powerful tool in the hands of organic chemists. The combination of palladium catalysis and arene tricarbonylchromium complexes gravely enriched this area in the organic preparative chemistry. It has been found that the electron drawing property of $Cr(CO)_3$ group significantly increases the oxidative addition of the palladium(0) into the arene-halogen bond because of the decrease of the π-electron density in the aromatic system. This circumstance makes the palladium(0)-catalyzed cross coupling reactions more

attractive, because they can be carried out faster and at milder conditions. The phenyl triflates tricarbonylchromium complexes are not exceptions. For example, Wulff *et al*. reported that the Stille coupling with electron rich phenyl triflates complexed with tricarbonylchromium proceeded easily and efficiently, while the coupling with the uncomplexed phenyl triflates did not take place at all. The same tricarbonylchromium complexes also readily underwent the Suzuki coupling reaction (*Scheme 113*).



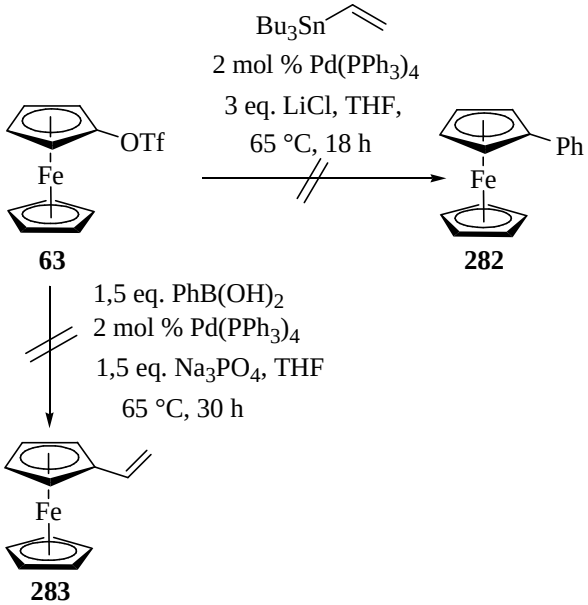
Scheme 113

Previously, some palladium(0)-catalyzed cross coupling reactions of the Suzuki and the Stille type were successfully performed by our group with various phenyl triflate tricarbonylchromium complexes (*Scheme 114*).



Scheme 114

Since ferrocenes are very electron rich arenes (*vide supra*), and the low electron density in the aromatic system is necessary for the successful oxidative addition of palladium, it is a hardly surprising result that no cross coupling reaction with the ferrocenyl triflate took place (*Scheme 115*).

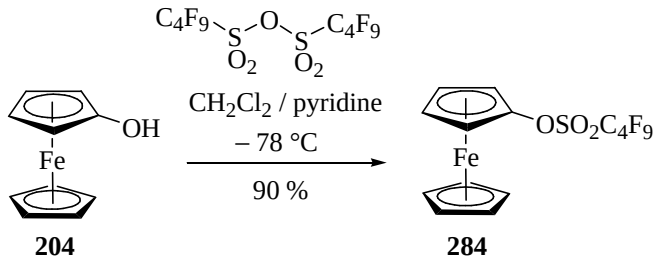


Scheme 115

3.8 Synthesis of ferrocenyl nonaflate and tosylate, and corresponding reactions with bases

Since the ferrocenyl triflates undergo the anionic thia-Fries rearrangement rather than elimination, we considered whether this kind of rearrangement will be extended to other ferrocenyl sulphonates, such as nonafluorobutanesulfonate (nonaflate) or toluenesulfonate (tosylate).

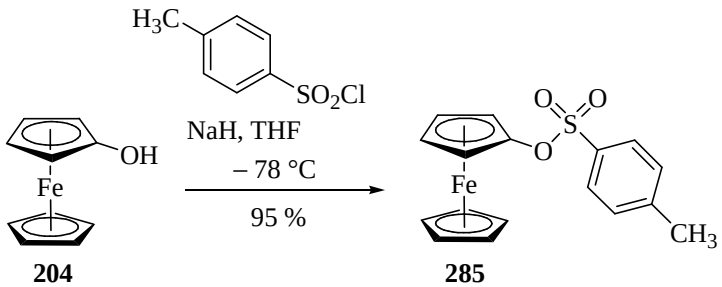
The ferrocenyl nonaflate (**284**) was prepared by treatment of the ferrocenol (**204**) with nonafluorobutanesulfonic anhydride in methylene chloride and pyridine at – 78 °C in 90 % yields (*Scheme 116*).



204 **284**

Scheme 116

The ferrocenyl tosylate (**285**) was obtained in 95 % yield from deprotonated ferrocenol and *p*-toluenesulfonic chloride in THF (*Scheme 117*).

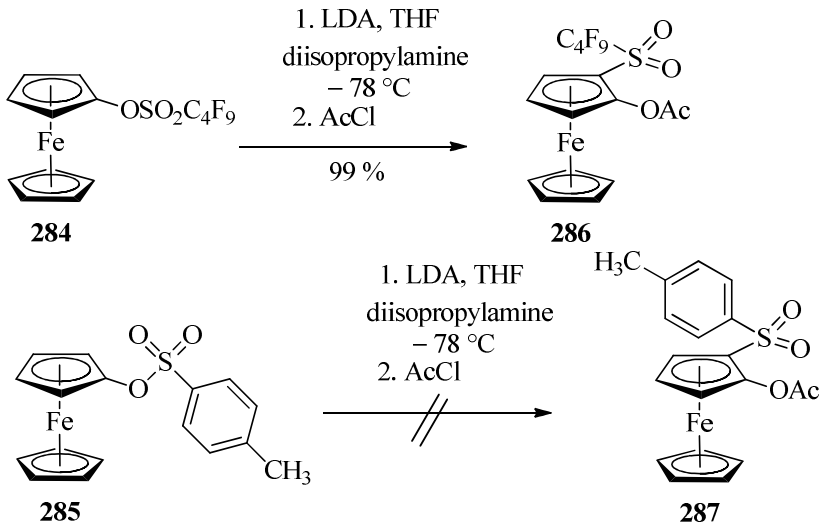


204 **285**

Scheme 117

The new compound **284** and **285** were completely characterized spectroscopically. They are very stable yellow solids.

The treatment of the ferrocenyl nonaflate (**284**) with LDA resulted in the thia-Fries rearrangement delivering the product **286** after the acetylation with acetyl chloride. This was not the case in the reaction with ferrocenyl tosylate. The treatment of ferrocenyl tosylate (**285**) with LDA did not achieve any reaction, only the starting material could be reisolated. The excess of didisopropyl amine was used as a trapping reagent for ferrocyne (*Scheme 118*).

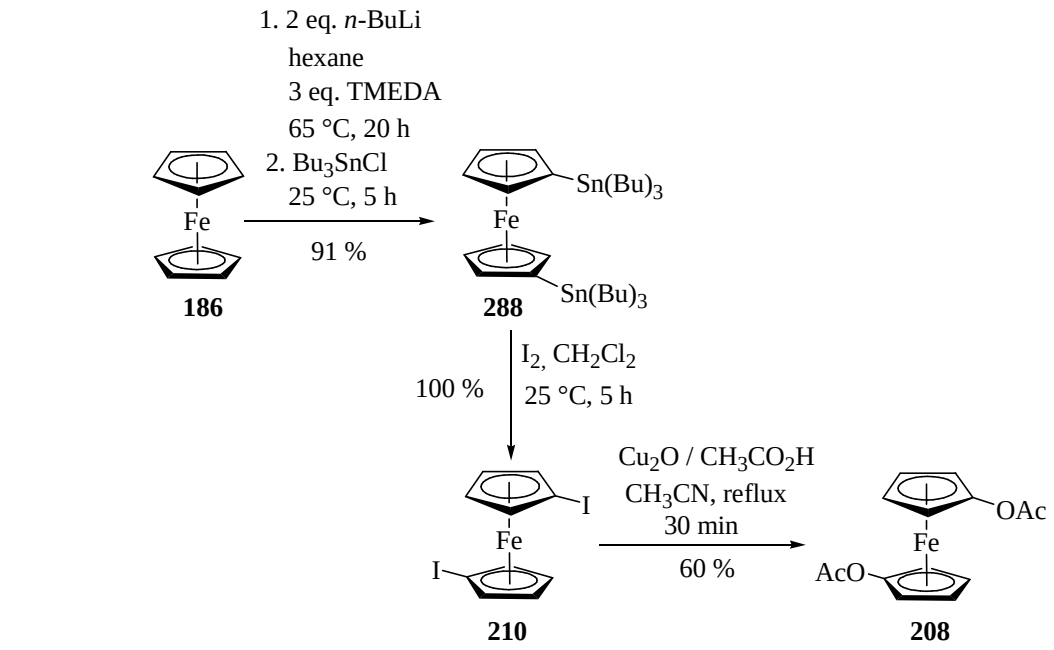


Scheme 118

The ferrocenyl nonaflate (**284**) shows the same property as the ferrocenyl triflate towards the LDA, and no evidence for the formation of ferrocyne could be detected.

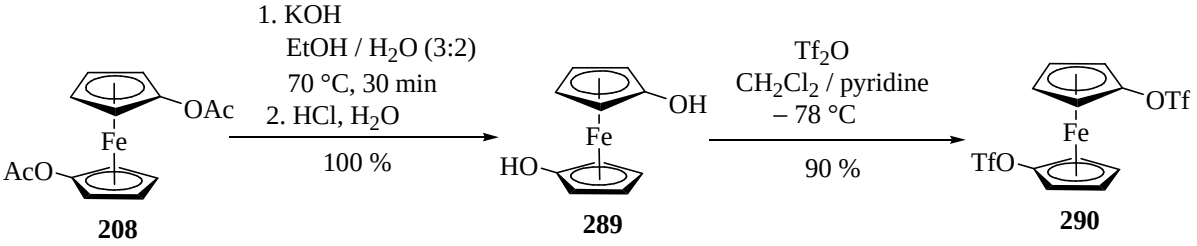
4. 1,1'-ferrocenediyl ditriflate

As already mentioned before, in the best method for preparation of the 1,1'-ferrocenediyl diacetate (**208**) 1,1'-diiodeferrocene (**210**) was used as the starting material (*Scheme 69*), which was synthesized from 1,1'-bis(tributylstannyl) ferrocene (**288**) by treatment with iodine. The 1,1'-bis(tributylstannyl) ferrocene (**288**) was prepared by lithiation of ferrocene with butyl lithium in the presence of tetramethylethylenediamine (TMEDA) and followed by quenching with Bu_3SnCl (*Scheme 119*).



Scheme 119

The 1,1'-ferrocenediyl diacetate (**208**) was hydrolyzed. Ferrocenediol (**289**) was subsequently treated with two equivalents of triflic anhydride in methylene chloride / pyridine affording the new 1,1'-ferrocenediyl ditriflate (**290**) in 90 % yield (*Scheme 120*).



Scheme 120

The new complex **290** was obtained as dark yellow liquid. It is moderatly stable and can be purified by column chromatography in air, but for a long time period it should be stored under protecting atmosphere.

In contrast to **63**, the CV-measurement of the 1,1'-ditriflate **290** shows two irreversible processes: an oxidation wave at 827.5 mV is as signed to the Fe(II)-Fe(III) oxidation, and a reduc-

tion wave at – 370 mV as well as a barely visible shoulder at ca. – 500 mV are, similar to **63**, as signed to the triflate substituents. The higher oxidation potential as compared to **63** is in accord with the fact that **290** is less electron-rich than **63**. In particular, the irreversibility of the oxidation shows that **290** is not simply a higher homologue of **63**, but has distinctly different properties (*Figure 3*).

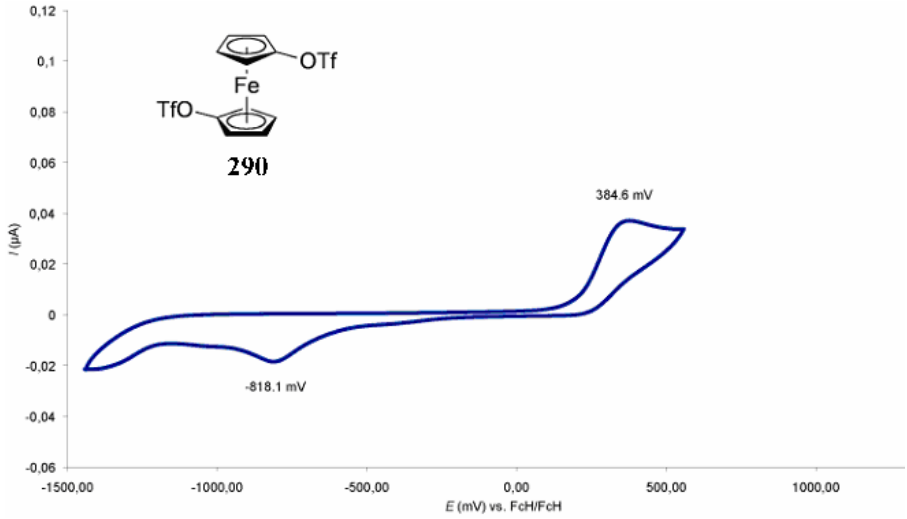
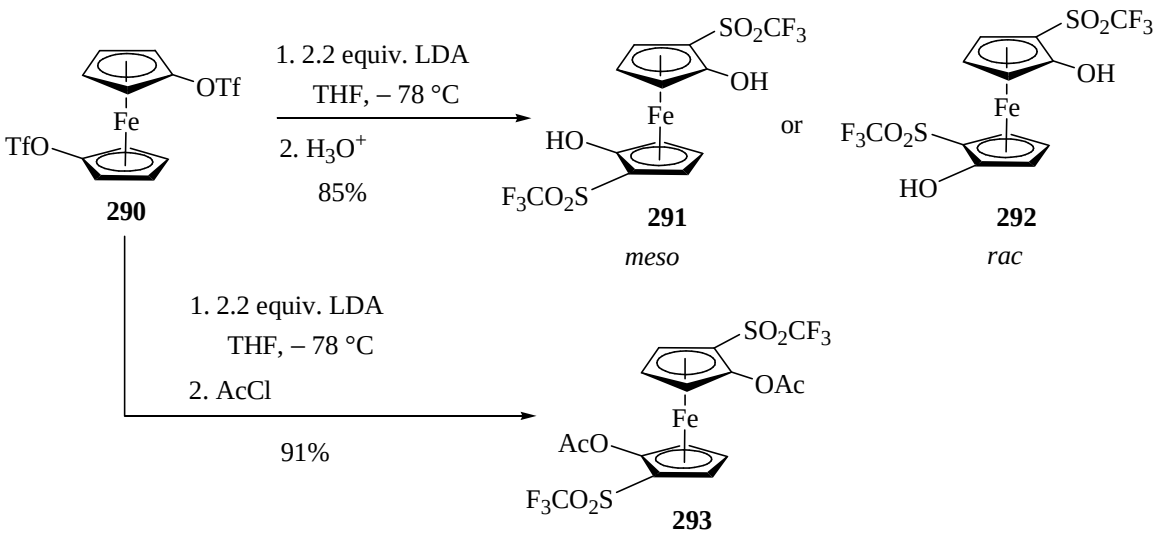


Figure 3 Cyclovoltammogram of **290.** Cyclovoltammetry data (potentials in mV *vs.* FcH/FcH^+, v = 100 mV/s, T = 25 °C, 2 mmol/L, 0.1 mol/L NBu_4PF_6, solvent acetonitrile).

4.1 Anionic thia-Fries rearrangement of 1,1'-Ferrocenediyl ditriflate

The treatment of the 1,1'-ferrocenediyl ditriflate (**290**) with 2.2 equivalents of LDA at – 78 °C led to a double anionic thia-Fries rearrangement in 85 % yield, which could, in principle, afford two diastereomeric rearrangement products **291** and **292** (Scheme 121).



Scheme 121

The ^{1}H NMR data of the rearrangement product shows only one of the two diastereomers, *meso*-**291** and *rac*-**292** (*Figure 4*). The peak at 4.92 ppm is clearly single and attests the existence of only one diastereomer.

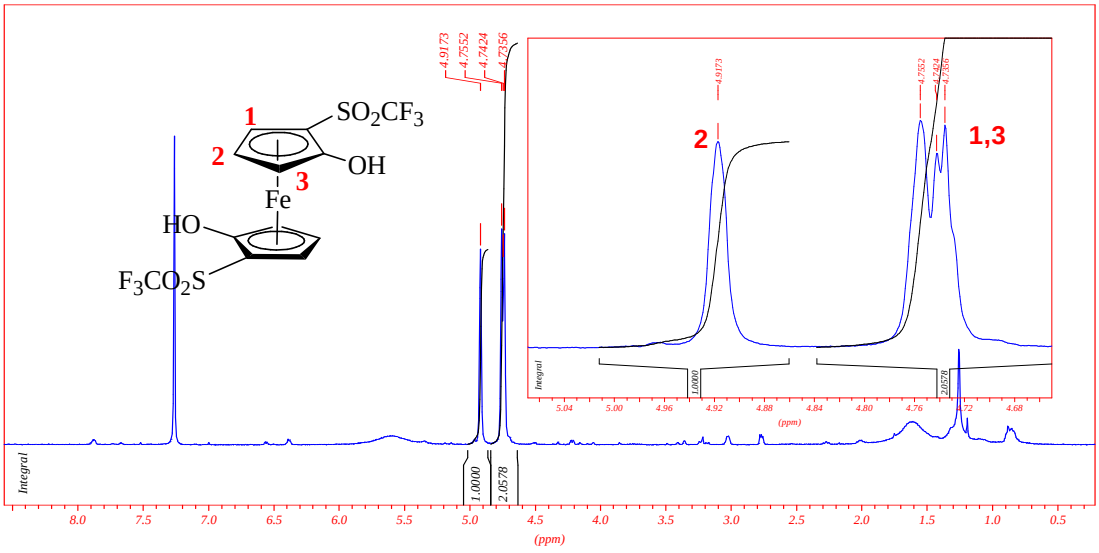


Figure 4. The ^{1}H NMR data of the double rearrangement product

For a more clear ^{1}H NMR spectrum the rearrangement product can be transformed to the corresponding diacetate **293** by quenching of the reaction mixture with acetic chloride instead of with water (*Scheme 121*). The ^{1}H NMR spectrum shows one peak at 2.3 ppm, which belongs

to the methyl group of the acetate group and also clearly attests the existence of only one diastereomer (*Figure 5*).

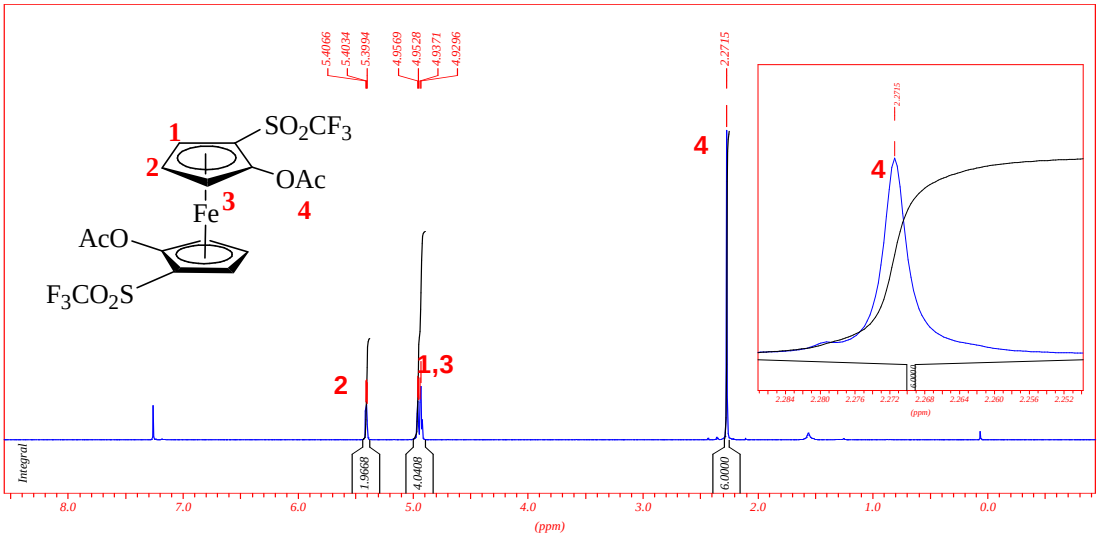


Figure 5. The ^{1}H NMR data of the diacetate **293**

4.2 Identification of the double rearrangement product from 1,1'-ferrocenediyl ditriflate

As the spectroscopic data of the rearrangement product are in accord with either one of the two diastereomers, *meso*-**291** and *rac*-**292**, transformations leading to the products allowing a clear-cut spectroscopic identification were tried. However, in contrast to other ferrocenols, the ferrocene-1,1'-diol formed is a comparatively stable compound. The product was treated with dihalomethanes, acetone/TsOH, dichlorodimethylsilane, or dichlorodimethylstannane in order to obtain a ferrocenophane with either enantiotopic (from **292**) or diastereotopic (from **291**) hydrogen atoms or methyl groups. However, only the starting ferrocene-1,1'-diol was recovered in almost quantitative yields. Also, the treatment with Mosher acid chloride gave no reaction.

The first reflection on the structure of the double rearrangement product was the ^{1}H NMR measurement in the presence of a chiral shift reagent, which shows no signal splitting. This fact suggests the structure corresponding to *meso*-**291.**

The rearrangement product was finally identified by an X-ray crystal structure analysis of the respective diacetate **293** (*Figure 6*). The analysis clearly indicated that the meso product **291** had been formed; no chiral rearrangement product **292** was observed (*Scheme 122*). In the crystal structure of the substituted ferrocene **293** the iron atom occupies a crystallographic inversion centre, affording a staggered conformation of the cyclopentadienyl ligands. Only a *meso* configuration is compatible with the presence of the inversion centre.

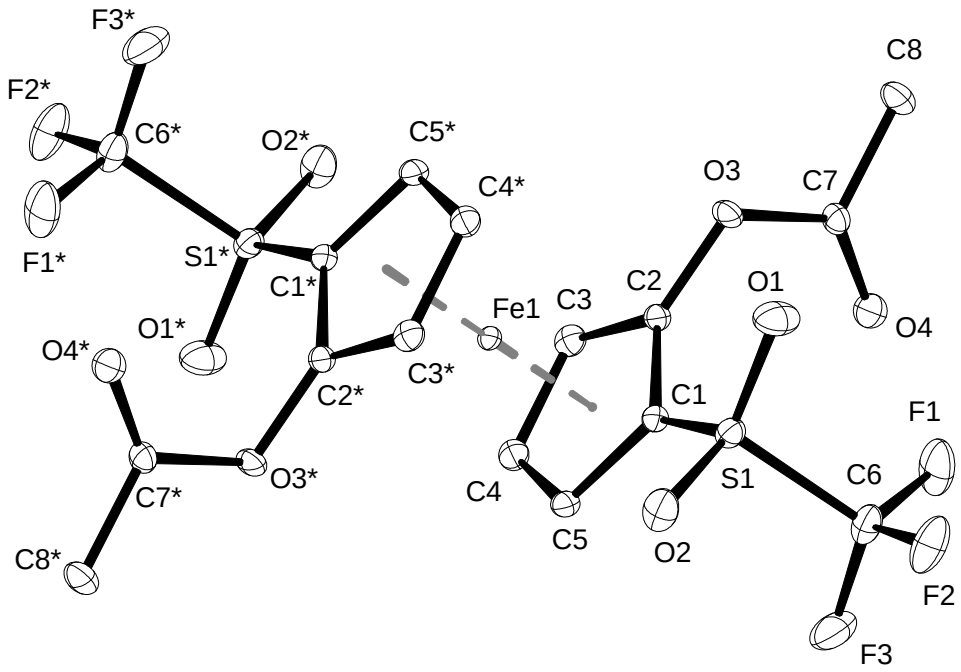
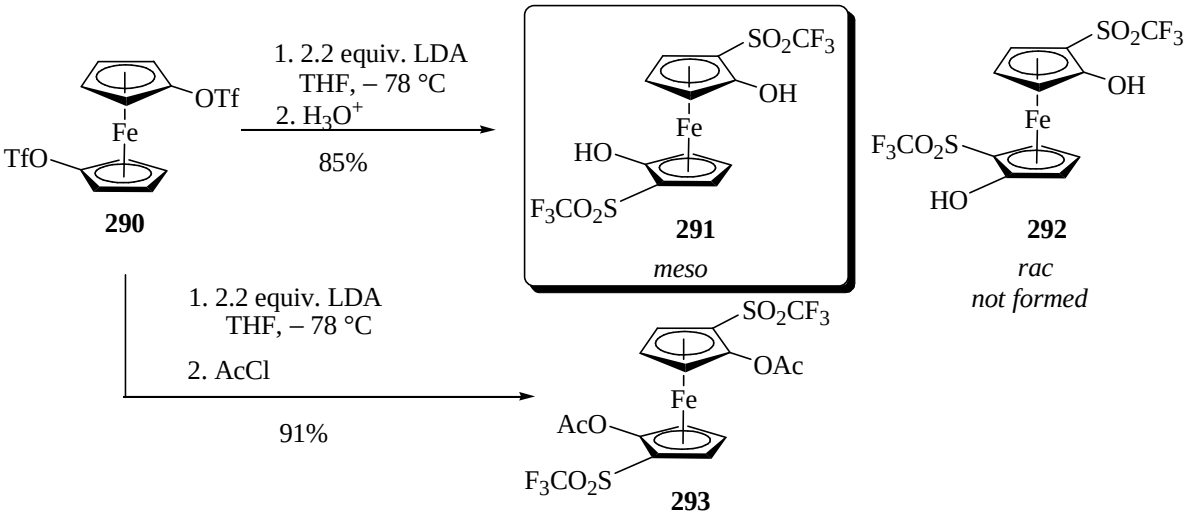
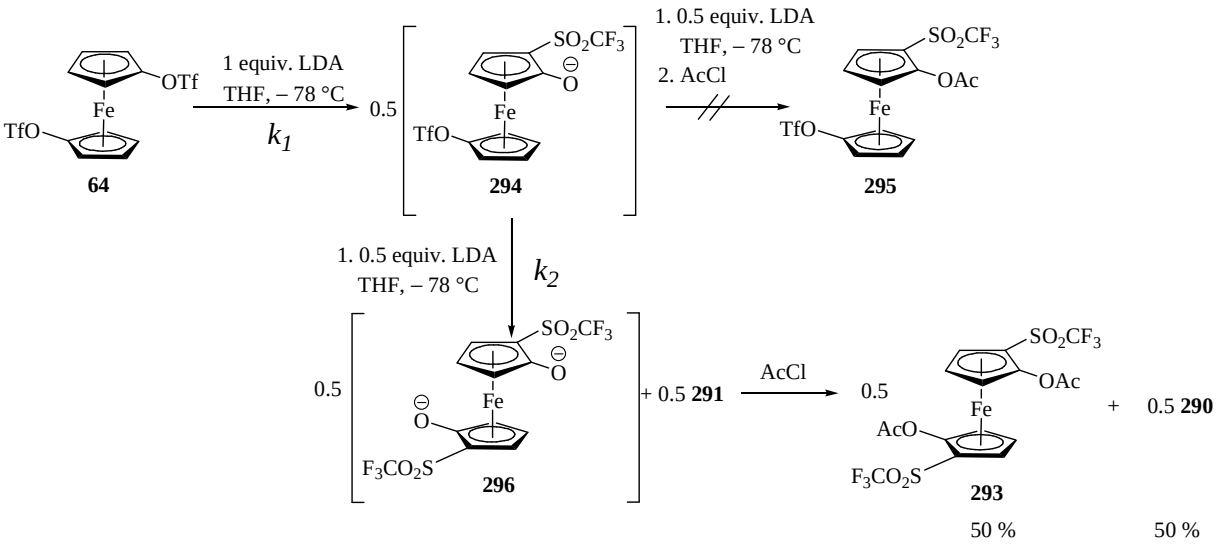


Figure 6. Structure of **293** in the crystal. Selected bond lengths [pm] and angles [°]: Fe1-C1 201.78(10), Fe-C2 203.74(9), Fe-C3 207.19(9), Fe-C4 206.69(9), Fe-C5 204.70(10), C1-S1 172.84(10), S1-O1 142.86(9), S1-O2 143.51(9), S1-C6 185.01(11), C6-F1 132.10(13), C6-F2 132.42(13), C6-F3 133.14(15), C2-O3 137.86(11), O3-C7 138.52(12), C7-O4 119.78(13), C7-C8 149.09(14); C1-S1-C6 103.47(5), O1-S1-O2 121.23(6), C1-S1-O1 111.10(5), C1-S1-O2 109.49(5), C2-O3-C7 114.49(8).



Scheme 122

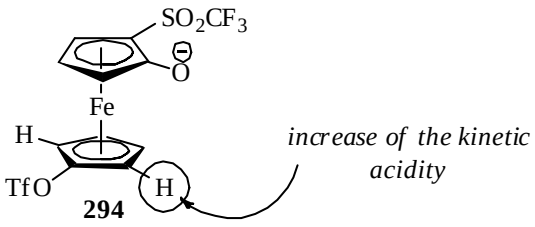
For a better understanding of the remarkably diastereoselective reaction leading from **290** exclusively to **291** we attempted a single anionic thia-Fries rearrangement in order to obtain **294** and subsequently **295** after quenching with acetyl chloride. However, treatment of **290** with 1 equivalent of LDA under otherwise unchanged reaction conditions gave an equimolar mixture of the starting material **290** and the trapped double rearrangement product **293** (*Scheme 123*). This clearly indicates that the second anionic thia-Fries rearrangement leading to **296** is significantly faster than the first one ($k_2 >> k_1$)



Scheme 123. the double thia-Fries rearrangement with 1 equiv. of LDA

The exclusive formation of the *meso* product **291** from **290** with no racemic **292** indicates an unusually high grade of interannular stereoinduction, exerted by the already rearranged cyclopentadienyl ligand in the intermediate **294**. Such an induction is very rare and has first been observed by Vollhardt for a nucleophilic attack at a planar chiral cobaltocenium ion, albeit to a much lesser extent.[132] Jendralla[133] and Snieckus[134] observed stereoselective metalation reactions at ferrocene-1,1'-dicarboxamides using butyllithium / (–)sparteine complexes as a base. Manoury and Balavoine performed diastereoselective deprotonation of 1,1'-disubstituted ferrocenecarboxamides bearing a chiral auxiliary.[135] Ikeda found highly diastereoselective *ortho* metalation of chiral 1,1'-bis(oxazolinyl)ferrocenes.[136] However, in all of these cases it remains unclear if the stereoselectivity observed for the second deprotonation is a result of an interannular stereoinduction or of the present chiral auxiliary.

With regard to the stereoselectivity and the rate of the formation of **291** we envisage two possible explanations. One reason might be that the extremely different electronic nature of the directing substituents in **294** – a highly electron withdrawing trifluoromethylsulfonyl and a highly electron pushing alcoholate – is responsible for this unusual result. In this case, these electronic properties are transferred to the opposite cyclopentadienyl ring via the centrosymmetric e_{1g} orbitals causing thereby a significant increase in kinetic acidity of the proton *ortho* to the triflate substituent (drawn in a cycle) in contrast to the other one.



294

Alternatively one might take into consideration that **294** exists as a complex with the lithium cation coordinated to diisopropylamine, or, after its deprotonation, to LDA. Although the structure and possible dynamics of such an aggregate are not known in detail, it might act as a base abstracting the black or the red proton in **294** in an intramolecular way thereby nicely explaining the rate acceleration of the second rearrangement. If so, steric interactions in a bis-eclipsed ferrocene conformation will prevent abstraction of the proton drawn in black in favor

of the one drawn in red. However, a more profound interpretation of our findings requires a theoretical treatment of the reactions.

As with the triflates **63** and **290**, the cyclovoltammogram of the rearrangement product **291**, which bears a trifluoromethylsulfonyl and a hydroxy substituent at both cyclopentadienyl ligands, differs considerably from the cyclovoltammogram of **215** with this set of substituents at only one of the cyclopentadienyl ligands. Only a rather weak, irreversible oxidation process is observed at a potential of 497.2 mV, reductions comparable to those observed for **215** are found at very low potential (Figure 7). The measurements of the rearrangement products **215** and **291** are accompanied by an irreversible change in color of the sample solution from yellow to red-brown.

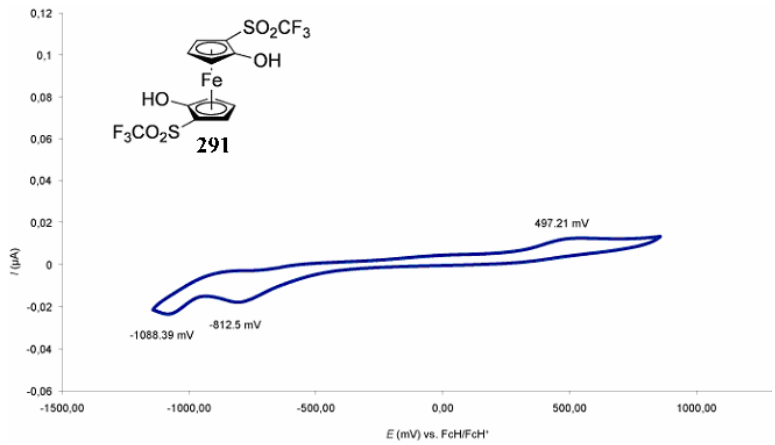


Figure 7 Cyclovoltammogram of **291.** Cyclovoltammetry data (potentials in mV *vs.* FcH/FcH^+, v = 100 mV/s, T = 25 °C, 2 mmol/L, 0.1 mol/L NBu_4PF_6, solvent acetonitrile).

4.3 Chemo enzymatic desymmetrization of *meso*-diols and *meso* diol diacetates

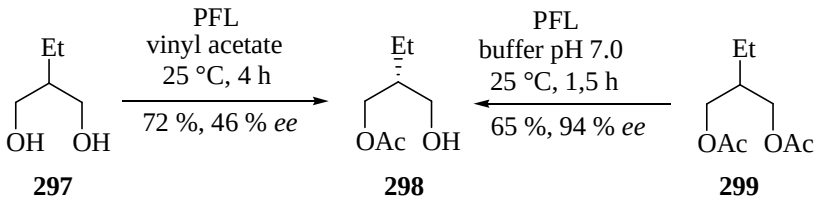
Because of the unique three-dimensional shape, the *meso* compounds **291** and **293** are potentially attractive as ligands for metal complexes. Enantioselective desymmetrization strategies offer most interesting possibilities for the synthesis of enantiopure, chiral derivatives. Functionalization of one of the two hydroxy groups in **291** or hydrolysis of one of the two acetate groups in **293** would give a chiral derivative.

4.3.1 Introduction

Meso and prochiral compounds have in general the presence of either two enantiotopic groups or a planar trigonal group with two enantiotopic faces. In course of the enantioselective enzymatic desymmetrization of a meso or a prochiral compound, the enzymatic reaction takes place faster at one of the enantiotopic groups or faces of the substrate affording the two enantiomers in unequal amounts. This different rate of reaction arises from the different energy of the diastereomeric transition states between the enzyme and the substrate along the reaction coordinate.[137]

Hydrolases are one of the kinds of enzymes most used in synthetic chemistry, which catalyze hydrolysis of *meso* and prochiral alcohols, carboxylic acid esters and anhydrides, and nitriles.

Ester hydrolyses and transesterifications have been successfully used for the desymmetrization of diverse *meso* and prochiral alcohols. Two different methods were developed. Firstly, a *meso* alcohol is subjected to an acylation with vinyl acetate in the presence of an enzyme. Secondly, the diol diacetate is asymmetrically hydrolyzed with an enzyme. For example, Izquierdo and co-workers have successfully desymmetrized the 2-ethylpropane-1,3-diol (**297**) and its diacetate **299** via PFL-catalyzed transesterifications and hydrolysis obtaining the chiral monoacetate (*R*)-**298** (*Scheme 124*).[138]

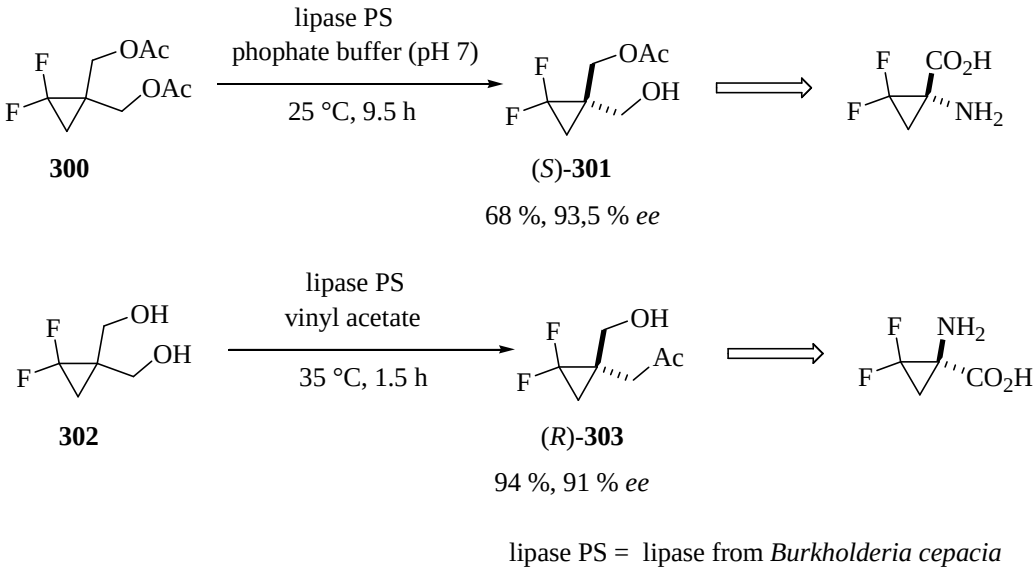


PFL = lipase from *Pseudomonas fluorescens*

Scheme 124[138]

Chiral 1-aminocyclopropane-1-carboxylicacids and their derivatives are interesting synthetic goals because of the possibilities to use them as parts of the sequence of peptides. Both enantiomers of 1-amino-2,2-difluorocyclopropane-1-carboxylicacid have been prepared in high yields and enantiomeric excess using the desymmetrization of [1-(acetoxymethyl)-2,2-

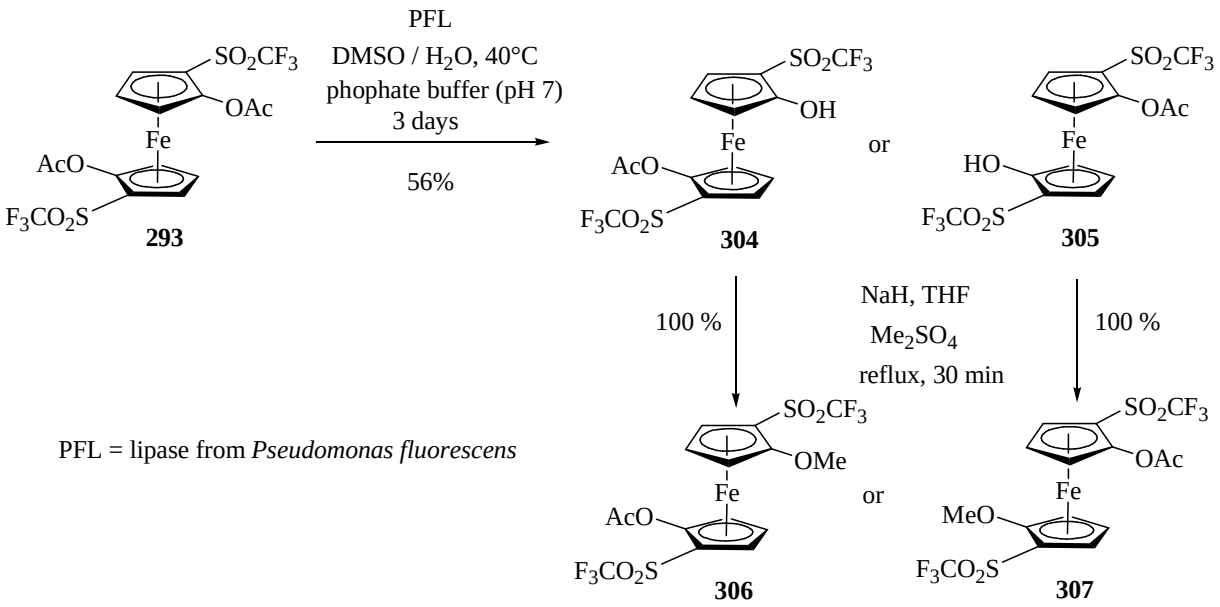
difluorocyclopropyl]methyl acetate (**300**) and the corresponding diol (**302**) by means of a lipase PS-catalyzed hydrolysis and transesterification (*Scheme 125*).[139]



Scheme 125[139]

4.3.2 Chemo enzymatic desymmetrization of the double rearrangement product from 1,1'-ferrocendiyl ditriflate

We tried to adopt the chemo enzymatic desymmetrization with use of the *meso* rearrangement product **291** and the corresponding diacetate **293** under the usual conditions of such reactions, namely with water and water / alcohols mixtures as solvents. The insolubility of **291** and **293** in such systems made the search for other solvents necessary. We obtained the best result with the mixture of DMSO and water (1:1). The reaction was carried out at 40 °C with PFL, as the enzymatic catalyst, for 4 days. We obtained the product with only one hydroxy group. Since the diol **291** was not observed, it may be assumed, that the required desymmetrization indeed took place (*Scheme 126*).



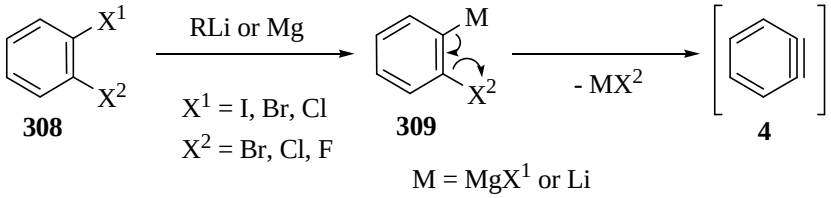
Scheme 126

Because of the high susceptibility of ferrocenols against oxidation (*vide supra*), the generated alcohol was methylated via heating in THF with sodium hydride and dimethyl sulphate under reflux for 30 minutes (*Scheme 126*). The only conclusions reached so far are, that only one of the two possible alcohols **304** and **305** are generated. It was characterized as the methyl ether **306** or **307** by means of ^{1}H NMR and the mass spectrometry. The exactly characterization of this product is still pending.

5. 1,2-Dihaloferrocenes

The *ortho*-metallation of aromatic halides with strong bases is a firmly established route to *o*-arynes.[6,7] The use of fluorobenzene was already discussed (*vide supra*).[96, 98] Chlorine can also act as a leaving group.[97] The already mentioned evidence for the existence of ferrocyne, reported by J. W. Huffman and J. F. Cope, based also on the elimination of chloride by treatment of chloroferrocene with alkyl lithium reagents (*Schemes 64* and *65*).[100, 101] However, although the bromobenzene can also used as a starting material for generation of benzyne, it can not be simply *ortho* metallated with alkyl lithium reagents.

While the treatment of fluoro- or chlorobenzenes with alkyl lithium leads to the ortho lithiation, bromobenzene undergoes under these conditions the halogen-metal exchange. In view of this circumstance the use of 1,2-dibromobenzene or 1-bromo-2-iodo-benzene is necessary. In this case one of two bromine atoms (or the iodine atom) undergoes the halogen-metal exchange with lithium or magnesium generating the beneficial *ortho* lithiated bromobenzene, which is subsequently transformed to the benzyne under release of lithium or magnesium salt (*Scheme 127*).[98, 141]

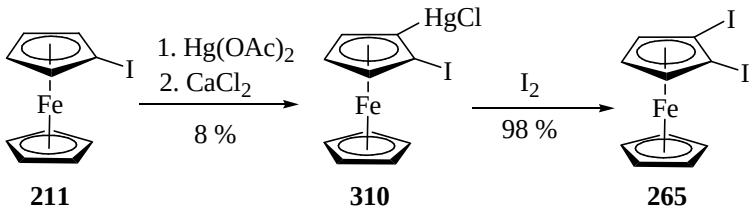


Scheme 127

Fluorine and chlorine can also efficiently used in this method,[98] what we already adopted in our chromium chemistry using the tributylstannyl group for transmetallation and thus for *ortho* lithiation of fluorobenzene and fluorobenzene tricarbonylchromium complexes (*vide Schemes 56, 58, 59, 61* and *62*).

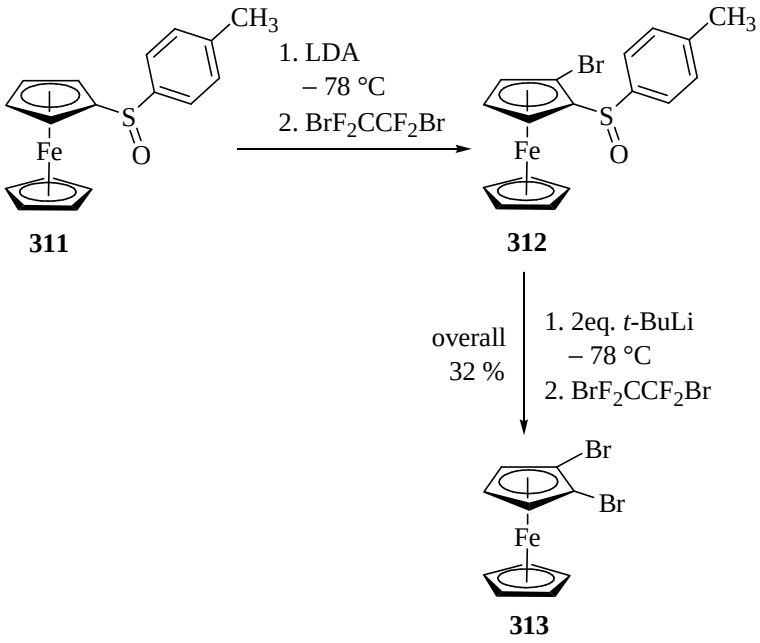
5.1 Synthesis of 1,2-dihaloferrocenes

While there are myriad publications describing the synthesis of 1,1'-dihaloferrocene, the appearance of 1,2-dihaloferrocenes in scientific literature is pretty rare. P. V. Roling and M. D. Rausch reported the preparation of 1,2-diiodoferrocene via mercuration of iodoferrocene followed by treatment with iodine (*Scheme 128*).[142]



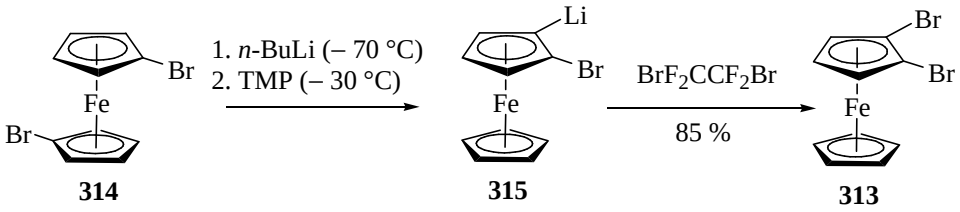
Scheme 128[142]

The extremely low yield of **310** is due to the low regioselectivity of the mercuration reagent. I. R Butler and M. G. B. Drew reported the preparation of 1,2-dibromoferrocene. They treated sulfinylferrocene (**311**) with LDA and quenched with dibromotetrafluoroethane generating the 2-bromo-p-tolylsulfinylferrocene (**312**) in high yield. The subsequent reaction of this compound with 2 equivalents of *tert*-butyl lithium in THF at ca. – 40 °C resulted in the removal of the sulfinyl group to give 1,2-dilithioferrocene, which was treated *in situ* with dibromotetrafluoroethane generating the 1,2-dibromoferrocene (*Scheme 129*).[143]



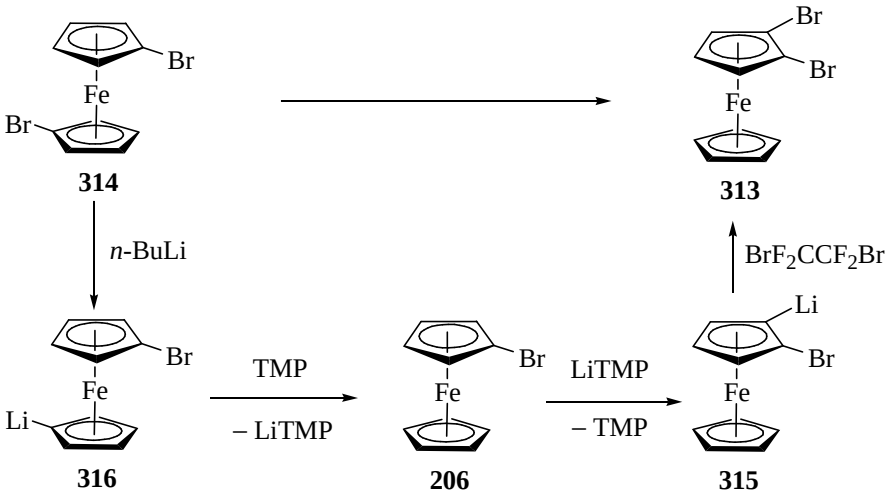
Scheme 129[143]

The authors attribute the relative low yield of the end product to the reactivity of the dilithioferrocene, which undergoes metathesis reactions with transient species in solution.[143] A more advanced method for preparation of 1,2-dibromoferrocene is described by I. R. Butler in a article with the title "*The conversion of 1,1-dibromoferrocene to 1,2-dibromoferrocene: the ferrocene-chemist's dream reaction*"[144] The "dream" of this synthesis is the use of the very easily accessible 1,1-dibromoferrocene, which is converted to the 1,2-dibromoferrocene simply in one-pot reaction with 85 % yield (Scheme 130).



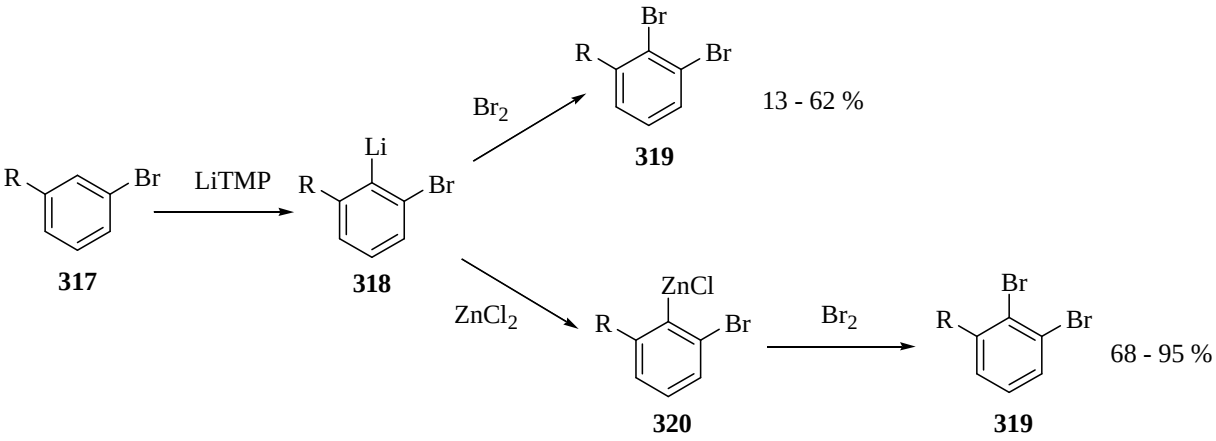
Scheme 130[144]

The 1,1-dibromoferrocene is lithiated in 1'-position via halogen-metal exchange reaction. The mono lithiated bromoferrocene (**316**) is protonated with the 2,2,6,6-tetramethylpiperidine. The generated bromoferrocene (**206**) is metallated by the LTMP and is subsequently trapped with a bromine donating reagent, dibromotetrafluoroethane (*Scheme 131*).



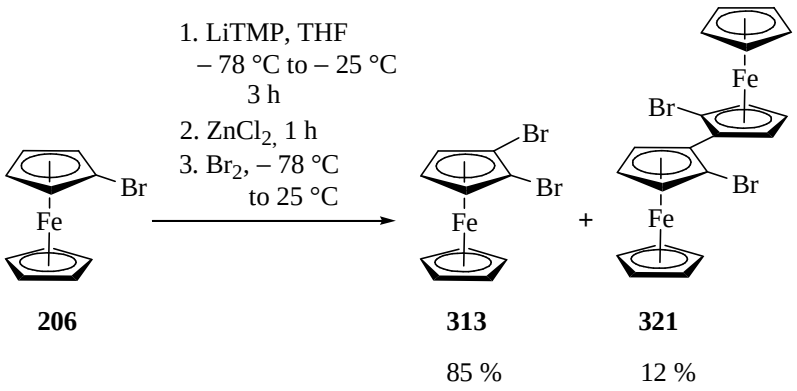
Scheme 131 mechanism of the formation of 1,2-dibromoferrocene from 1,1-dibromoferrocene

K. Menzel an co-workers reported an improvement of the synthesis of 1,2-dibromoarenes via lithium-zinc transmetallation. While the quenching of lithiated arenes with bromine delivers 1,2-dibromoarenes in low to moderate yield, the quenching with bromine of zincated arenes resulted in moderate to high yields (*Scheme 132*).[145]



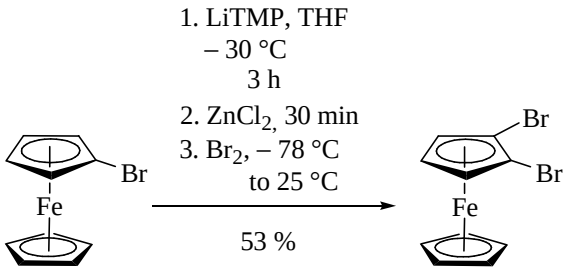
Scheme 132[145]

We combined these two results and developed a new method for the efficient synthesis of 1,2-dibromoferrocene (**313**) from bromoferrocene (**206**). The bromoferrocene is lithiated with LiTMP in THF at – 25 °C for 3 hours and than transmetallated with $ZnCl_2$. The subsequent quenching with bromine at – 78 °C resulted in 90 % yield of 1,2-dibromoferrocene as the main product. The compound **321** was obtained as a by-product in 6 % yield (*Scheme 133*).



Scheme 133

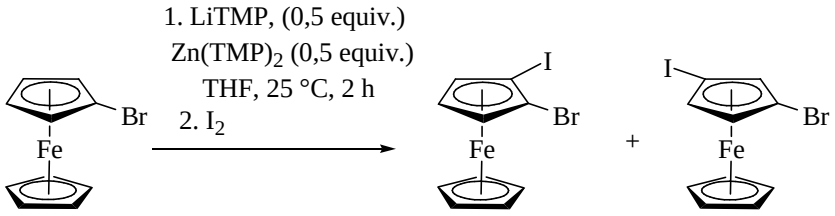
It should be mentioned that during the writing of these lines K.Sünkel and S. Bernhartzeder published a report about the synthesis of 1,2-dibromoferrocene, which is almost identical with our method (*Scheme 134*).[146] However, they obtained **313** in lower yield and the formation of the by-product **321** is not reported (*Scheme 134*).[146]



206 **313**

Scheme 134[146]

F. Mongin *et al.* described an alike method for the preparation of 1-bromo-2-iodo-ferrocene **322** using LiTMP and $Zn(TMP)_2$ at room temperature yielding 1-bromo-3-iodo-ferrocene (**323**) as a by-product (Scheme 135).[147]

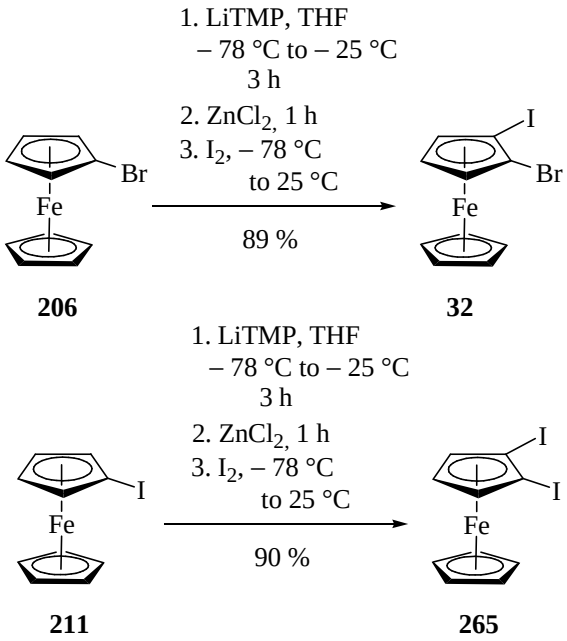


206 **322** **323**

64 % 7 %

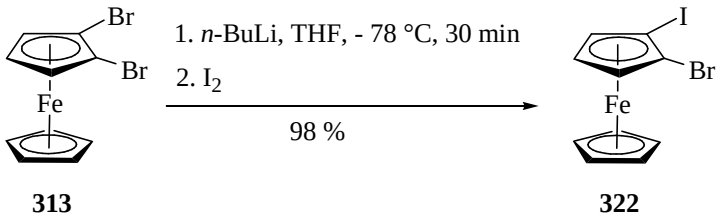
Scheme 135[147]

Using our method we synthesized 1,2-diiodoferrocene **265** and 1-bromo-2-iodo-ferrocene **322** with even higher yields (*Scheme 136*).



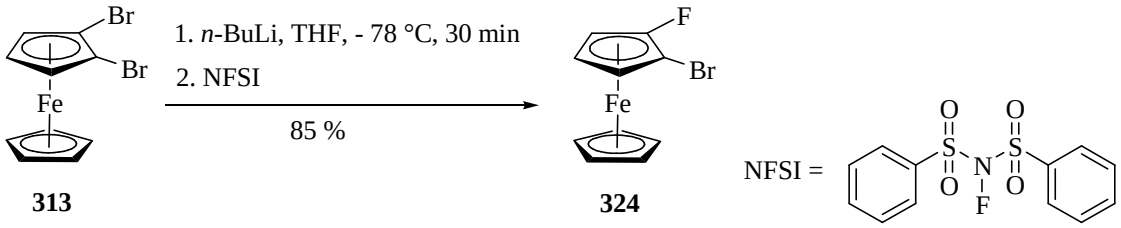
Scheme 136

The 1-bromo-2-iodo-ferrocene **322** can also be synthesized from 1,2-dibromoferrocene (*Scheme 137*).



Scheme 137

In the same manner, the preparation of 1-bromo-2-flioro-ferrocene (**324**) was performed. The 1,2-dibromoferrocene was metallated with one equivalent of butyl lithium and quenched with a fluorinating reagent, *N*-fluorobenzenesulfonimide (*Scheme 138*).



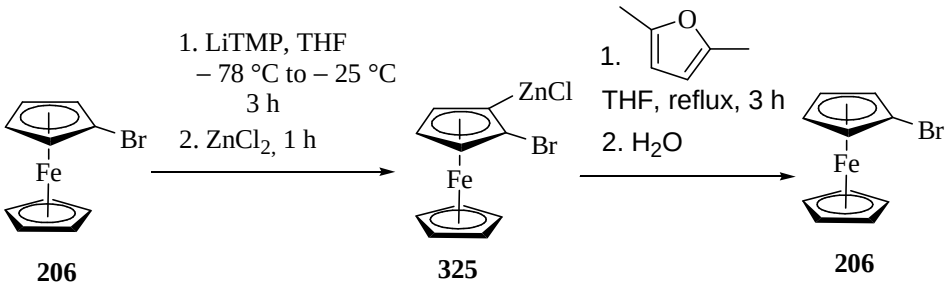
313 **324**

Scheme 138

The new compounds **322** and **324** are fully characterized. The compound **322** is dark yellow oil and the **324** is light yellow solid.

5.1.1 Attempts towards ferrocyne from 1,2 dihaloferrocene and from ortho metallated haloferrocenes

In principle, already the lithiation and the following transmetallation with $ZnCl_2$ of the bromoferrocene delivers the required ortho metallated bromoferrocene, which can be trapped with a diene instead with bromine, in order to intercept the ferrocyne (*Scheme 134*). However, the treatment of the reaction mixture with 2,5-dimethyfuran did not lead to the cycloaddition product. After the quenching with water only the bromoferrocene was recovered (*Scheme 139*).

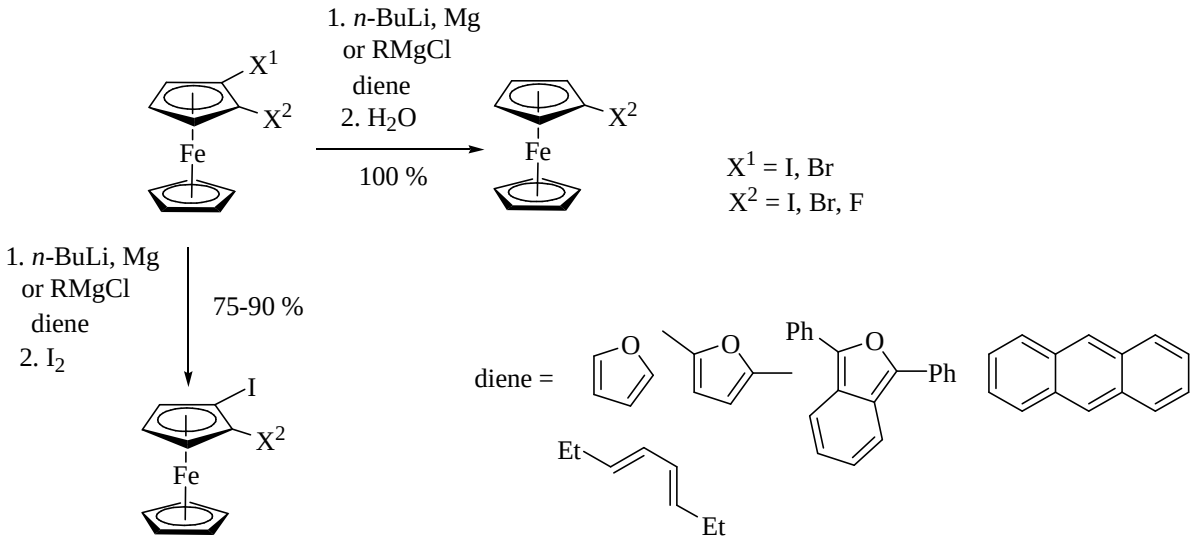


206 **325** **206**

Scheme 139

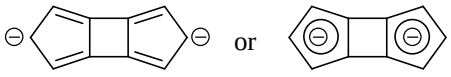
The treatment of **265**, **313**, **322** and **324** with butyl lithium, Grignard reagents and metallic magnesium in the presence of a diene did not result in elimination, instead, only the mono haloferrocenes after quenching with water were obtained. In order to be sure, that the *ortho* metallation indeed took place, the reaction mixtures were also quenched with iodine. The cor-

responding iodoferrocenes were obtained in high yield, attesting thus the successful *ortho* lithiation (*Scheme 140*).



Scheme 140

With respect to our search for the ferrocyne, it is interesting to mention the mass spectra of **265**, **313**, **322** and **324**. All the four mass spectra have the peak of the highest intensity with the mass of 126 *m/z* in common, which corresponds to the 2,5-dihydrocyclobuta-dicyclopentene **326**, the [2 + 2]-cycloaddition product of two 1,2-didehydrocyclopentadienyl anions. The second striking commonality is the peak of 184 *m/z*, the molecular mass of ferrocyne (**65**) or 1,2-ferrocenediradical (*Table 8*).



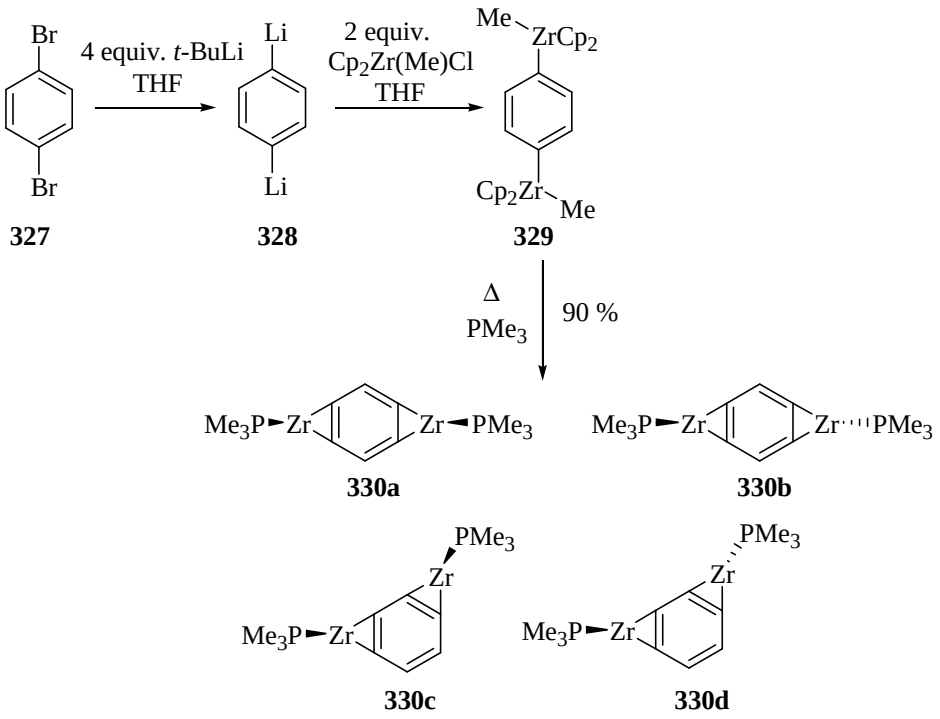
326a **326b**

Table 8. The characteristic peaks in the mass spectra of complexes **265**, **313**, **322** and **324.**

Fragment ions *m/z*

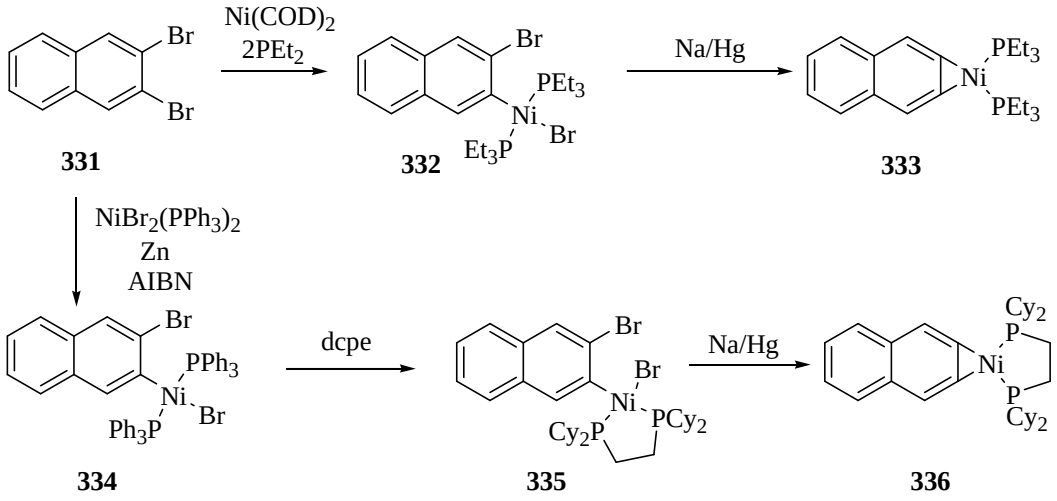
Ion	Assignment	**265**	**313**	**322**	**324**
a	M^+	438 (98)	346 (40)	392 (92)	284 (50)
			344 (75)	390 (99)	282 (52)
			342 (43)		
b	**65**$^+$	184 (25)	184 (25)	184 (29)	184 (16)
c	**326**$^+$	126 (100)	126 (100)	126 (100)	126 (100)

Benzynes can be stabilized as transition metal complexes. This stabilization is based on the deviation of the linearity of the triple bond, whereby the ring strain is mined.[148-153] The usual starting materials for such complexes are halobenzenes. For example, the zirconocene-benzdiyne complex can be synthesized by treatment of 1,4-dilithiobenzene **328** (prepared from 1,4-dibromobenzene) with 2 equivalents of zirconocene (methyl) chloride to give **329** in 90% yield. The subsequent thermolysis of **329** at 70 °C in the presence of excess trimethyl phosphine leads to a mixture of the four isomers **330a**-**330d** (*Scheme 141*).[148]



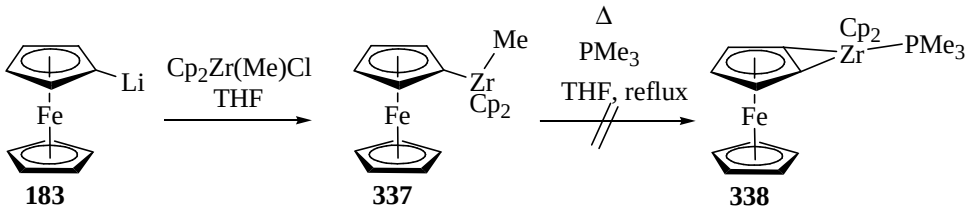
Scheme 141[148]

Also the 1,2-halobenzenes can be used via stepwise lithiation and transmetallation with the transition metal. Oxidative addition of 2,3-dibromonaphthalene to $Ni(COD)_2$ in the presence of triethyl phosphine (2 equivalents) gives the (3-bromonaphthyl)nickel(II) complex **332**. Reduction of **332** with 1% Na-amalgam delivers the aryne-Ni complex **333**. In other approach, the 2,3-dibromonaphthalene is metallated with sonicated zinc in the presence of $NiBr_2(PPh_3)_2$ generating the (3-bromonaphthyl)nickel(II) **334**, which is then heated with dcpe giving the aryne-Ni complex **336** (*Scheme 142*).[152]



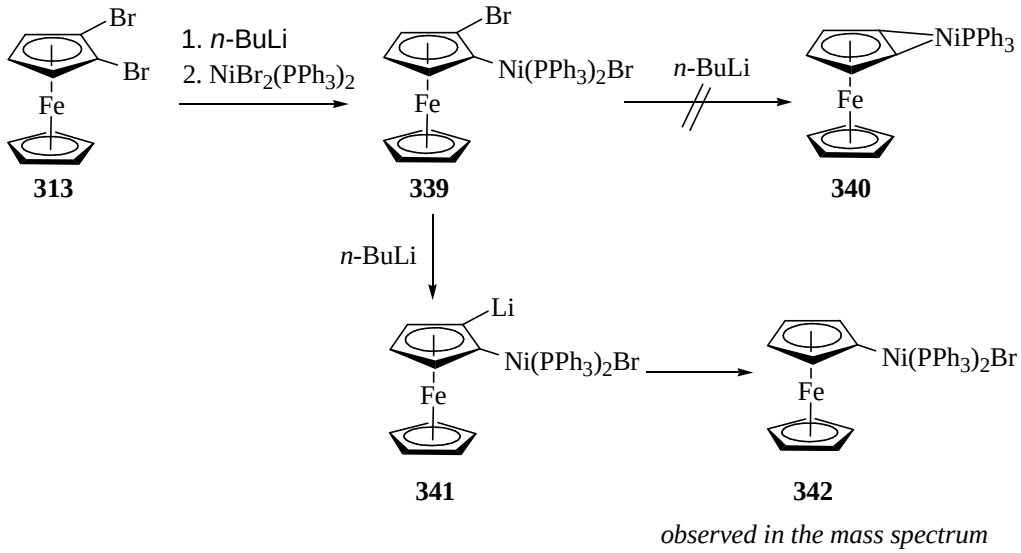
Scheme 142[152]

We attempted to adopt this chemistry for the ferrocene systems toward the synthesis of ferrocyne-Ni complexes or ferrocyne-Zr complexes. In the same manner as shown in the scheme 140 lithioferrocene was treated with zirconocene (methyl) chloride. The immediate colour change of the reaction mixture from orange to deep red shows that the reaction took place. However, the following heating in the presence of trimethyl phosphine shows no progress of the reaction. The mass spectrum of the reaction mixture shows only the compound **337**, meaning, that the crucial step, the elimination reaction, did not took place (*Scheme 143*).



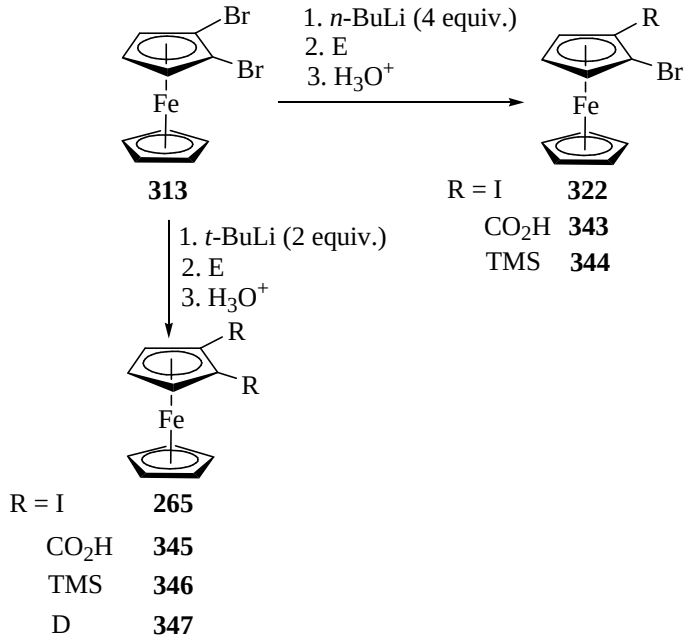
Scheme 143

The corresponding approach to the scheme 141 also brought no satisfying results. The mono lithiation of the 1,2-dibromoferrocene **313** and the following treatment with $NiBr_2(PPh_3)_2$ gave the compound **339**. The second lithiation took place, but did not deliver the required product **340**. The compound **342** was observed in the mass spectrum (*Scheme 144*).



Scheme 144

In an alternative approach to synthesize a ferrocyne-Ni complex we subjected the 1,2-dibromoferrocene to the double lithiation. In order to prove the efficiency of the double lithiation, the 1,2-dilithioferrocene was quenched with different electrophiles (*Scheme 144*).



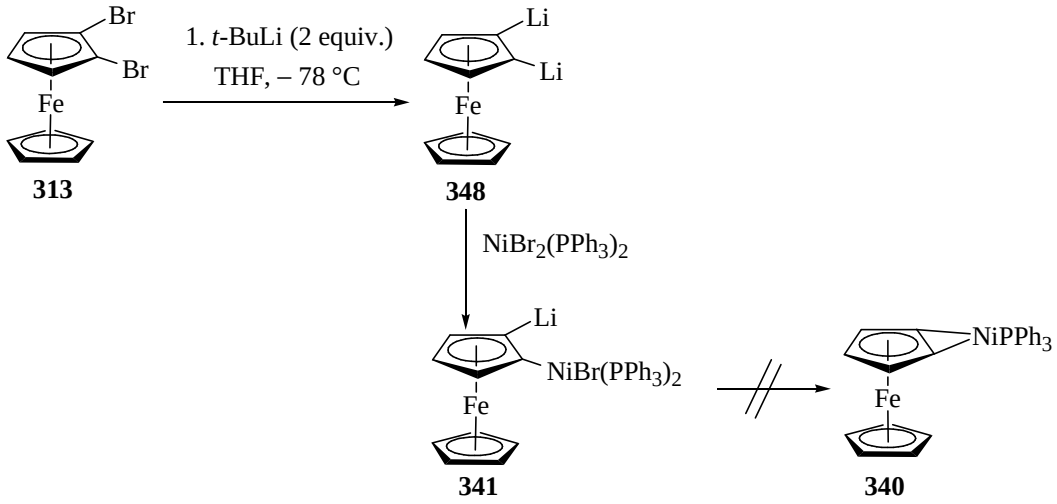
Scheme 145

It turned out that the most suitable lithiation reagent is *tert* butyl lithium, which removed the both bromine atoms generating the 1,2-dilithioferrocene in high yields (with only 2 equivalents). In contrast, even 4 equivalents of butyl lithium were able to remove only one of the both Br atoms (*Scheme 145* and *Table 9*).

Table 9. the double halogen-lithium exchange of 1,2-dibromoferrocene **313** with *tert* butyl lithium

entry	electrophile	R	Generated compound	Yield (%)
1	I_2	I	**265**	78
2	CO_2	CO_2H	**345**	76
3	Me_3SiCl	TMS	**346**	89
4	MeOD	D	**347**	87

The 1,2-dilithioferrocene was treated with $NiBr_2(PPh_3)_2$. Again, only mono transmetallation took place, no ferrocyne-Ni complex was formed (*Scheme 146*).

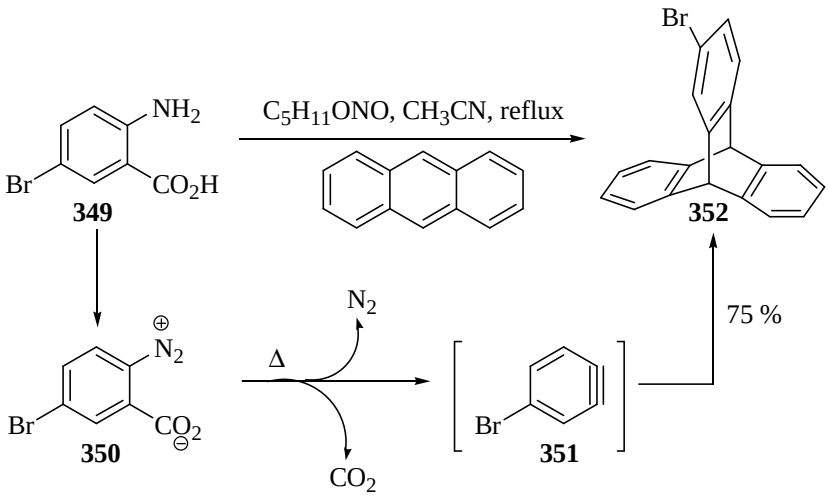


Scheme 146

Although the 1,2-dihalobenzenes are widely used for the preparation of benzynes, this is not the case with 1,2-dihaloferrocenes. The reactions with various metallation reagents delivered only mono- or dimetallated products, no elimination reaction took place and no evidence for formation of ferrocyne was observed. Exceptions are the mass spectra of the 1,2-dihaloferrocenes, which clearly show the molecular masses of ferrocyne (**65**) and 2,5-dihydrocyclobutadicyclopentene **326**, the [2 + 2]-cycloaddition product of two 1,2-didehydrocyclopentadienyl anions. Since this finding can not be used for the synthetical scopes, we feel a vocation to continue our search for ferrocyne.

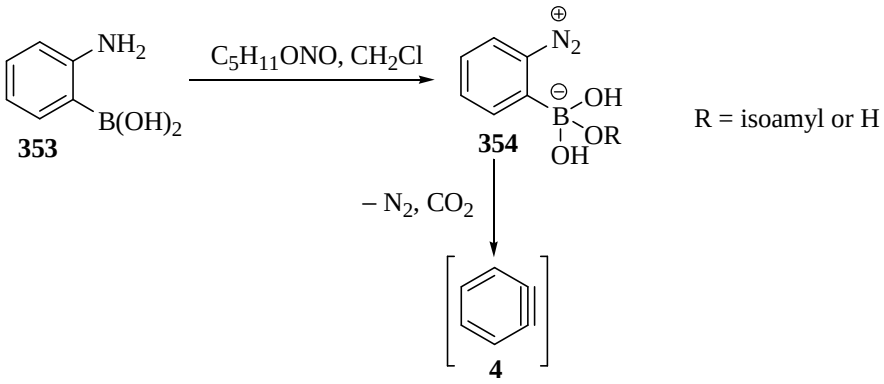
6. Generation of arynes from zwitterions

Arynes may be obtained from zwitterions, mostly generated from anthranilic acids (**349**), which are readily diazotated by alkyl nitrites in aprotic media to give the benzenediazonium-2-carboxylate (**350**). This intermediate undergoes fragmentation to the corresponding aryne (**351**) under release of nitrogen and carbon dioxide (*Schemes 9* and *147*).[32, 35, 154-156]



Scheme 147[32]

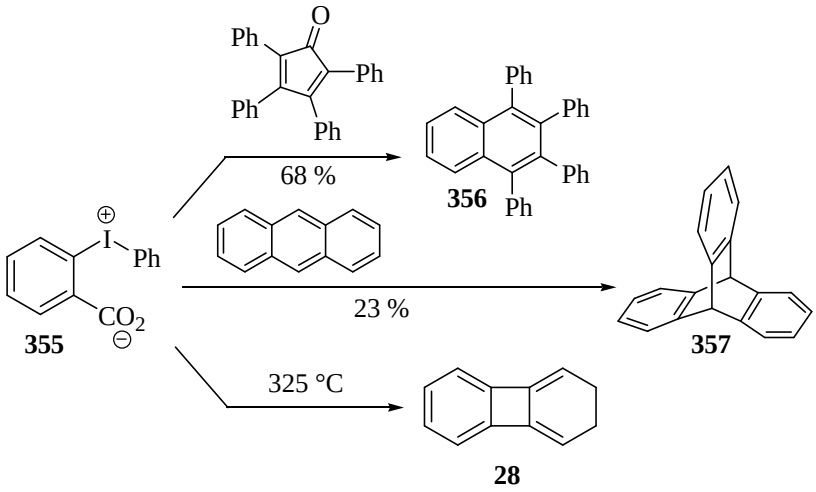
Instead of the carboxylate group every other good leaving group bearing a negative charge can be used. For example, W. Kwalwasser and co-workers reported the preparation of benzyne (**4**) via the aprotic diazotization of *ortho*-aminophenylboronic acid (**353**). Benzyne (**4**) was generated rapidly under similar conditions used for anthranilic acid,[32] and in the presence of anthracene, triptycene was isolated in 45 – 60 % yield (*Scheme 148*).[157]



Scheme 148[157]

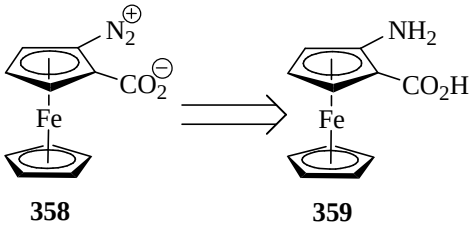
Backwards, instead of the diazonium group every other good leaving group bearing a positive charge can be used. E. Le Goff found, that diphenyliodonium-2-carboxylate (**355**) undergoes a smooth thermal cleavage of carbon dioxide and iodobenzene under aprotic conditions affording benzyne. Refluxing a mixture of **355** and tetraphenylcyclopentadienone in diglyme

for two hours afforded 1,2,3,4-tetraphenylnaphthalene (**356**) in 68 % yield. Under the same conditions anthracene triptycene (**357**) was obtained in 23% yield. Flash pyrolysis of solid **355** at 325 °C afforded biphenylene (**28**) (*Scheme 149*).[158, 159]



Scheme 149[158]

In order to prepare a zwitterion with the ferrocene system, we planned the synthesis of 2-aminoferrocenecarboxylic acid (**359**). The 2-aminoferrocenecarboxylic acid (**359**) could be then oxidized and transformed into the ferrocenediazonium-2-carboxylate (**358**) (*Scheme 150*).

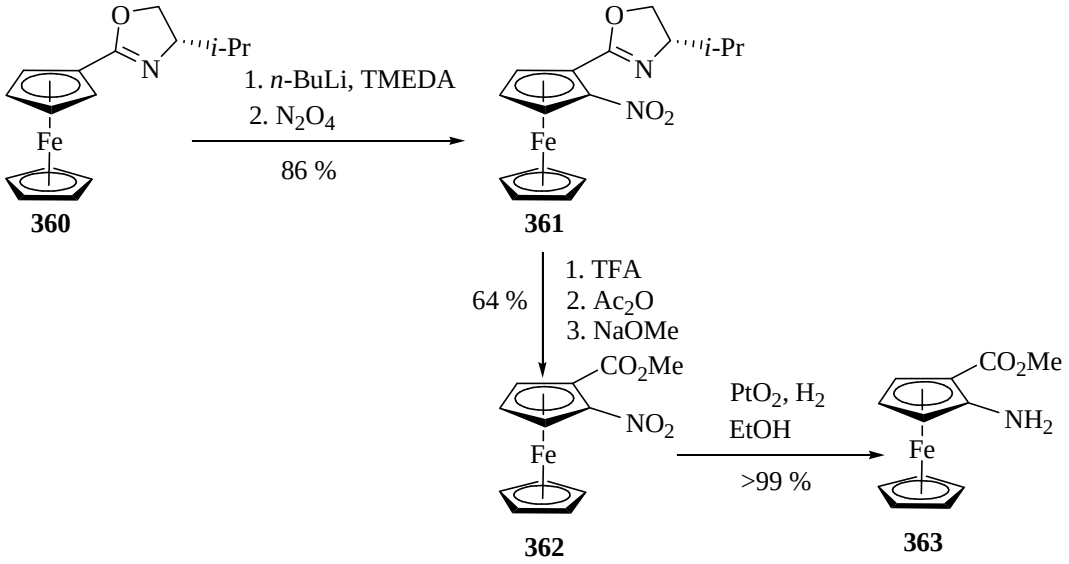


Scheme 150

6.1 Synthesis of 2-aminoferrocenecarboxylic acid

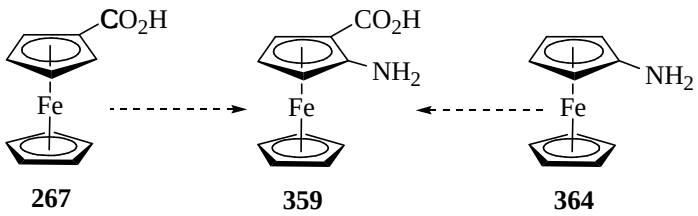
Concerning the scientific literature, the situation with aminoferrocenecarboxylic acids is similar to that with dihaloferrocenes. While there is a myriad of publications describing the

synthesis of 1'-aminoferrocenecarboxylic acids, the appearance of 2-aminoferrocenecarboxylic acids in scientific literature is pretty rare. Indeed, as far as we are aware, the only one publication describing the synthesis of various derivates of the 2-aminoferrocenecarboxylic acid (**359**) is the article of C. J. Richards and co-workers.[160] The *ortho* lithiated ferrocenyloxazoline (**360**) was treated with N_2O_4, giving 2-nitroferrocenyloxazoline (**361**), which was subsequently converted into the derivatives of 2-aminoferrocenecarboxylic acid (*Scheme 151*).[160]



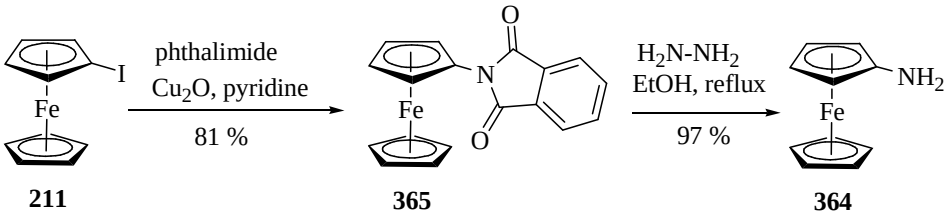
Scheme 151[160]

In order to avoid the toxic and badly to handle nitrogen oxides, we searched for another suitable method for the synthesis of 2-aminoferrocenecarboxylic acid (**359**). In general, there are two possibilities. Firstly, the ferrocene carboxylic acid (**267**) is used as the starting material and is transformed into the 2-aminoferrocenecarboxylic acid (**359**) via introducing of the amino group into the *ortho* position. Secondly, the synthesis is started with aminoferrocene (**364**) and the carboxylic acid group is introduced into the *ortho* position (*Scheme 150*).



Scheme 150

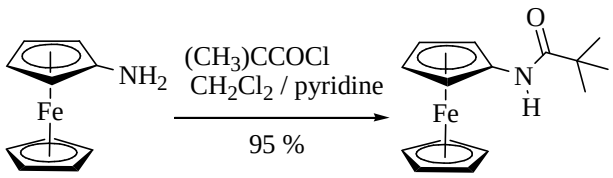
We started our search with the aminoferrocene (**364**). We used the method, which is described by A. Nesmeyanov *et al.*[47] The method is based on the Gabriel synthesis of the *N*-ferrocenyl phthalimide (**365**), which is prepared from iodoferrocene (**211**) and phthalimide via copper mediated coupling (*Scheme 153*).[47, 161-163]



211 **365** **364**

Scheme 153[47, 161-163]

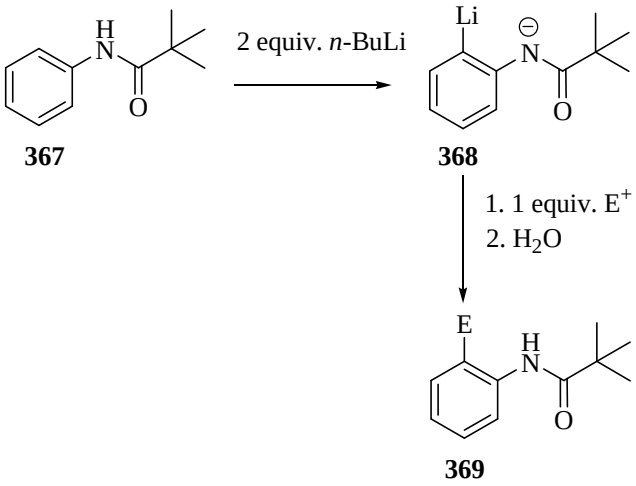
The aminoferrocene (**364**) was subsequently treated with 2,2-dimethyl-propionyl chloride in dimethyl chloride and pyridine obtaining the 2,2-dimethyl-*N*-ferrocenyl-propionamide (**366**) in high yield (*Scheme 154*).



364 **366**

Scheme 154

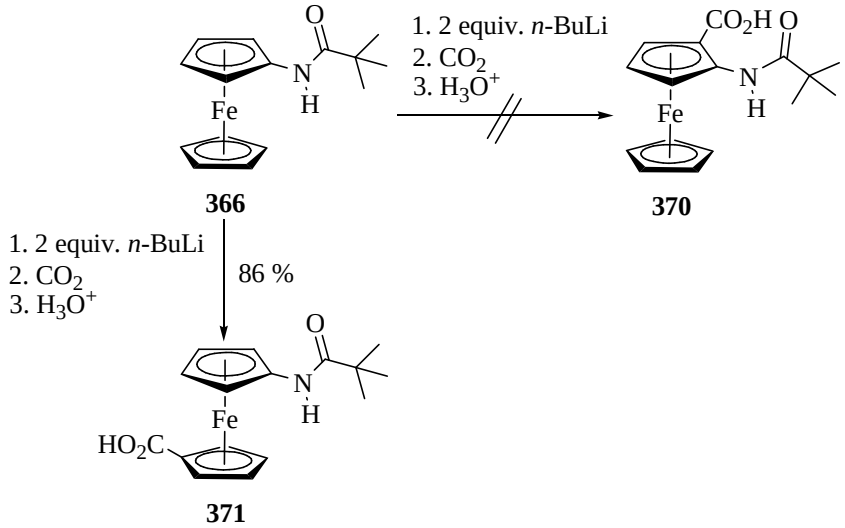
The 2,2-dimethyl-propionamide group is often used as a directing metallating group for the introducing of different groups into the *ortho* position to the amino group. 2,2-Dimethyl-*N*-phenyl-propionamides (**367**) are deprotonated and *ortho* metallated with two equivalents of butyl lithium, whereby the three methyl groups prevent the nucleophilic attack on the carbonyl group. Quenching with one equivalent of the electrophile delivers the required compound **369** (*Scheme 155*).[164-166]



367 **368** **369**

Scheme 155[164-166]

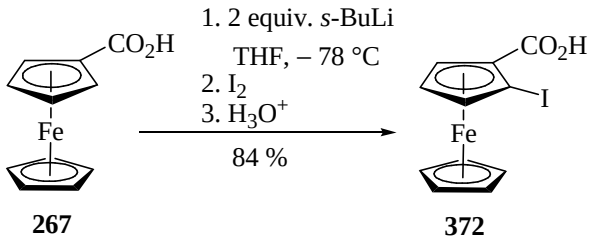
However, in the case of 2,2-dimethyl-*N*-ferrocenyl-propionamide (**366**) the lithiation occurred on the second cyclopentadienyl ring and not on the *ortho* position to the amino group (*Scheme 156*).



366 **370** **371**

Scheme 156

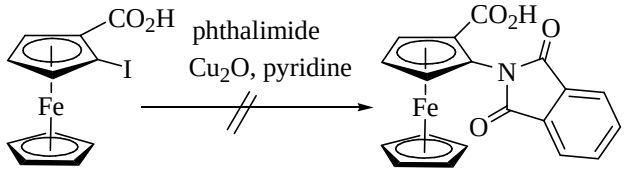
In an alternative approach we started the synthesis with the ferrocene carboxylic acid (**267**), which can be efficiently deprotonated and *ortho* metallated with two equivalents of *sec* butyl lithium.[107] The following trapping with iodine delivered the 2-iodoferrocene carboxylic acid (**372**) in high yield (*Scheme 157*).



267 **372**

Scheme 157

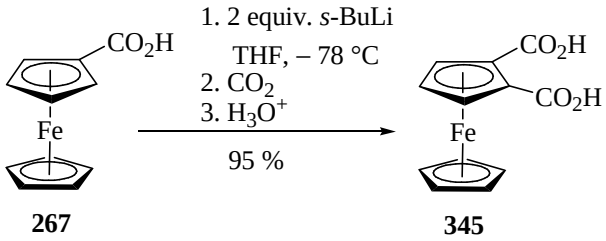
The idea behind this synthesis was the preparation of 2-aminoferrocenecarboxylic acid (**359**) via Gabriel synthesis[47] from *N*-ferrocenyl phthalimide **373**, which shall be generated from the 2-iodoferrocene carboxylic acid (**372**). However, this conversion did not take place (*Scheme 158*).



372 **373**

Scheme 158

The next approach is based on the Curtius rearrangement, which requires a carboxylic acid group. With the same method, which was already successfully used for the preparation of 2-iodoferrocene carboxylic acid (**372**) (*Scheme 156*), allows the synthesis of 1,2-ferrocene dicarboxylic acid (**345**), the ferrocene analogue to the phthalic acid (*Scheme 159*).

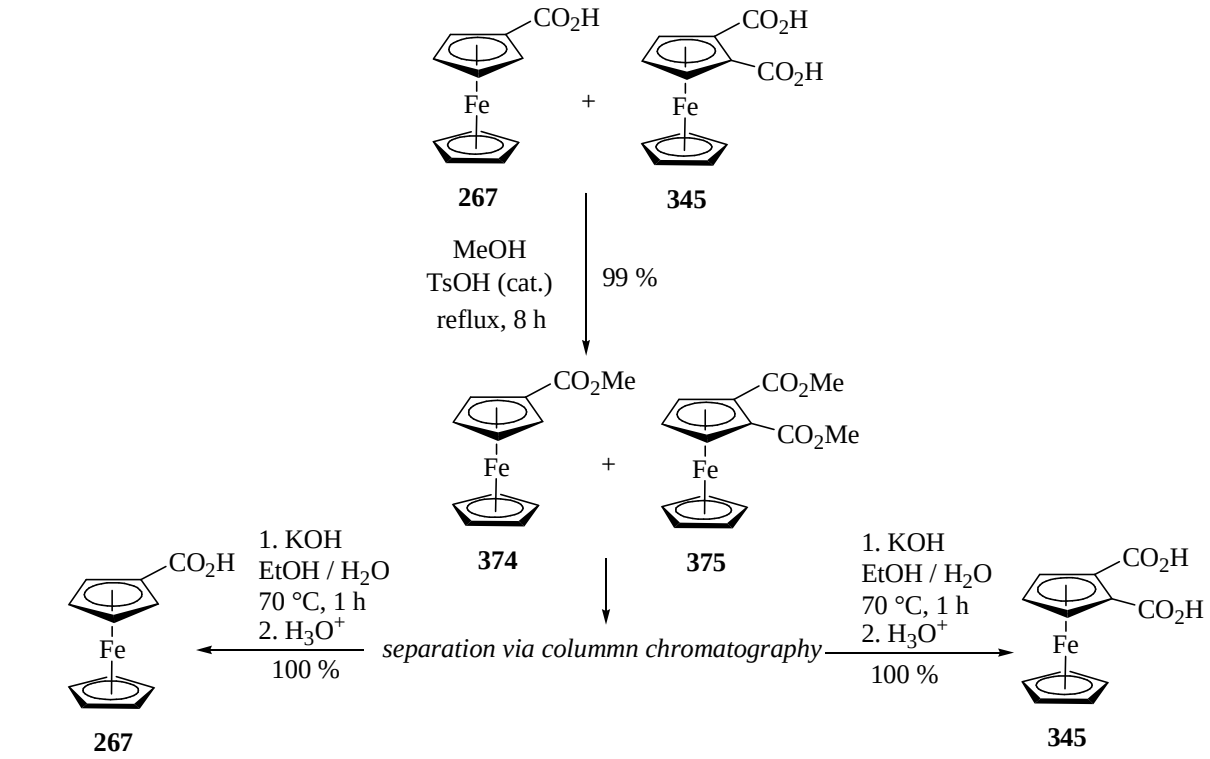


267 **345**

Scheme 159

This method allows the preparation of the 1,2-ferrocene dicarboxylic acid (**345**) in multigram scale. Of course, **345** can be also generated from 1,2-dihaloferrocenes, as already mentioned above (*Scheme 144* and *Table 9*). This method was also used by P. V. Roling and M. D. Rausch.[142] However, our method is more advanced, because of high yields, less reaction steps and working in multigram range.

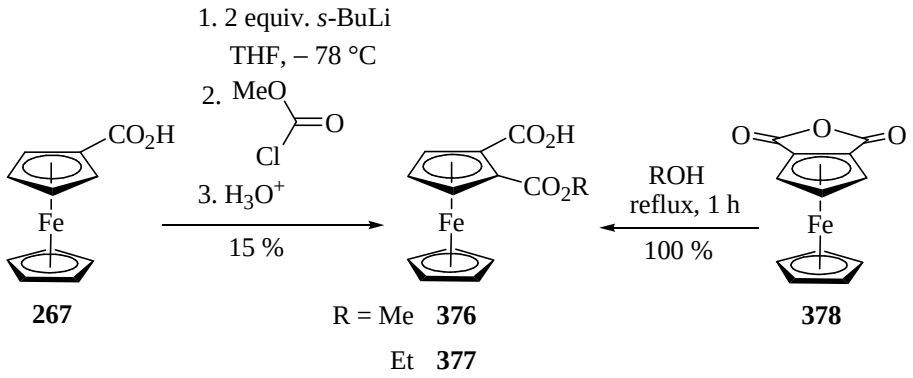
The ferrocene carboxylic acid (**267**) was treated with two equivalents of *sec* butyl lithium at – 78 °C in THF. The following add of dry ice delivered 1,2-ferrocene dicarboxylic acid (**374**) in very high yield. The little trouble, which appeared in this synthesis, is the problematic separation of **374** from **375**. It turned out, that the best solution of this problem is the esterification of both compounds, smooth separation via the column chromatography and the subsequent hydrolysis (*Scheme 160*).



Scheme 160

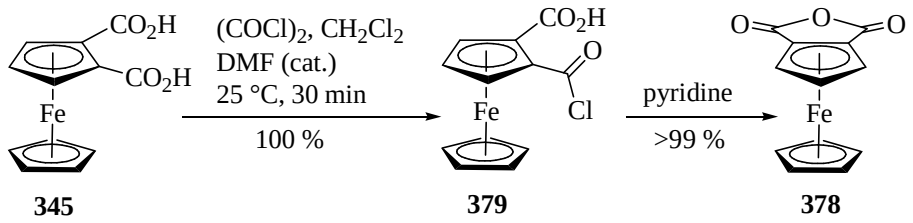
One of the carboxylic groups has to be protected prior to the Curtius rearrangement. Two possibilities are at our disposal. Firstly, the required 1,2-ferrocene dicarboxylic acid mono methyl ester (**376**) can be directly prepared from the ferrocene carboxylic acid (**267**) via *ortho* lithiation and interception with methyl chloroformate giving very low yield of **376.**

The best suitable method is based on the alcoholysis of the 1,2-ferrocene dicarboxylic anhydride (**378**) (*Scheme 161*).



Scheme 161

P. V. Roling and M. D. Rausch describe the preparation of 1,2-ferrocene dicarboxylic anhydride (**378**) via treatment of 1,2-ferrocene dicarboxylic acid (**345**) with *N*,*N*-dicyclohexylcarbodiimide (DCC) in acetone giving **378** in 36 % yield.[142] In our approach we prepared for the first time the 2-chlorocarbonyl-ferrocene carboxylic acid (**379**) by treatment of 1,2-ferrocene dicarboxylic acid (**345**) with oxalyl chloride and catalytic amount of *N*,*N*-dimethylformamide (DMF). The subsequent addition of pyridine delivered the required product **378** in almost quantitative yield (*Scheme 162*).



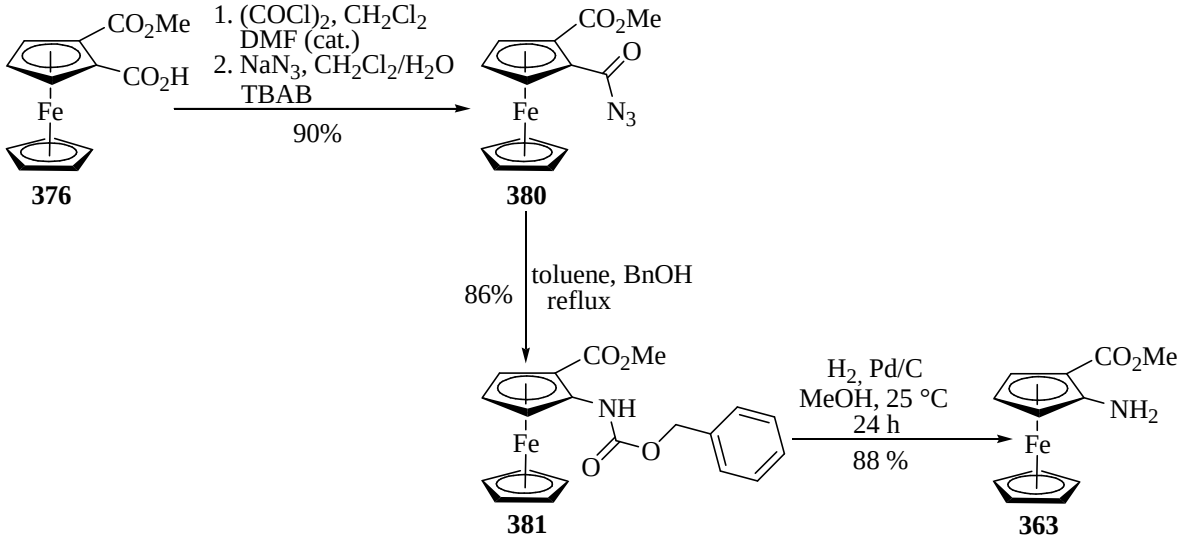
Scheme 162

Remarkably, the 1,2-ferrocene dicarboxylic anhydride (**378**) is very stable against water and alcohols at ambient temperature. In contrast to other anhydrides, the hydrolysis and alcoholy-

sis of **378** occur only via heating under reflux conditions, what is, probably, due to a value ratio of the bond lengths to the angles in this molecule (*Scheme 161*).

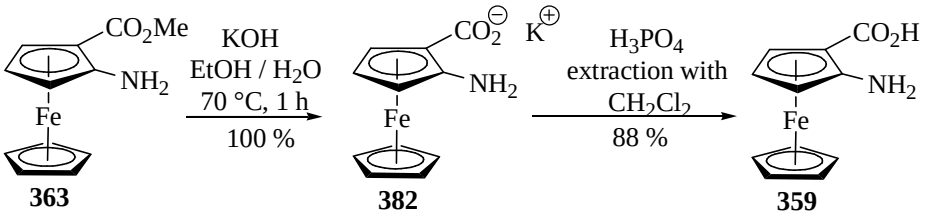
We applied the Curtius rearrangement for the preparation of the aminoferrocene (**364**) described by A. Togni.[167]

The 1,2-ferrocene dicarboxylic acid mono methyl ester (**376**) was treated with oxalyl chloride and catalytic amount of *N*,*N*-dimethylformamide (DMF) in methylene chloride. The subsequent addition of aqueous solution of NaN_3 in the presence of catalytic amount of tetrabutylammonium bromide delivered the acyl azide **380** in 90 % yields. The heating of **380** in toluene in the presence of benzyl alcohol under reflux conditions gave the 2-benzyloxycarbonylamino-ferrocene carboxylic acid methyl ester (**381**), which was then subjected to the catalytic hydrogenation using palladium on charcoal delivering the 2-amino-ferrocene carboxylic acid methyl ester (**363**) (*Scheme 163*).



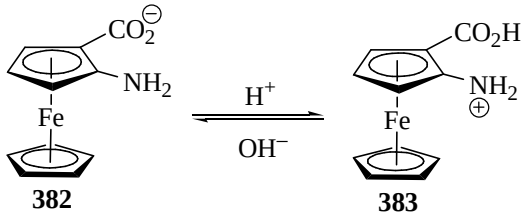
Scheme 163

The salt of the required 2-aminoferrocenecarboxylic acid (**382**) was obtained via hydrolysis of **363** in EtOH / H_2O mixture and potassium hydroxide (*Scheme 164*).



Scheme 164

The problematic situation in this synthesis is obvious: 2-aminoferrocenecarboxylic acid (**359**) is an ampholyte, meaning, that **359** can act either as a base or as an acid, making the efficient extraction from the aqueous solution extremely difficult. As long as the isoelectric point of this aminoacid is not known, it is not possible to convert **359** completely into its neutral form (*Scheme 165*).

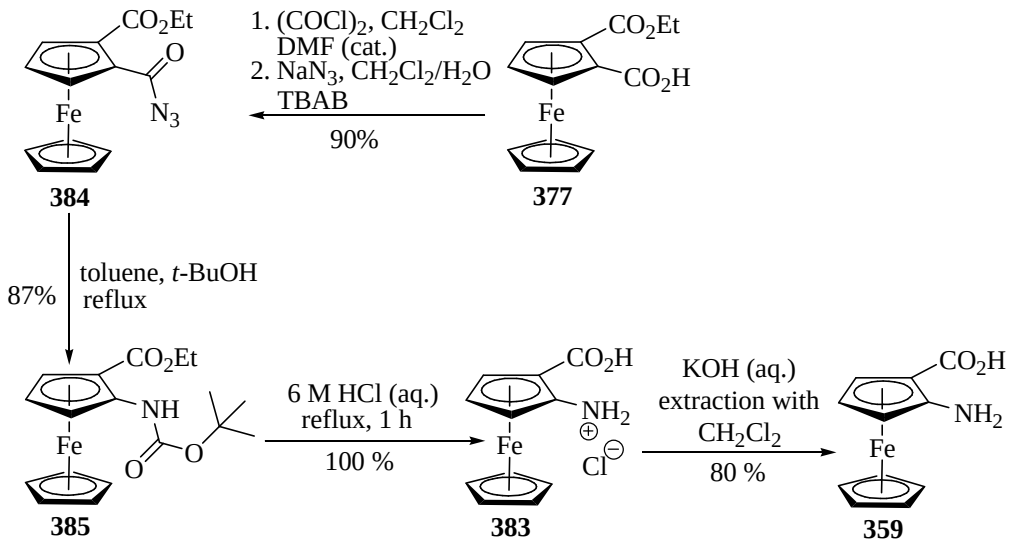


Scheme 165

In order to encounter this problem, to the aqueous solution of **382** was added methylene chloride and under vigorous stirring, the mixture was slowly acidified with phosphoric acid (15 %) until the colour change from deep red to light yellow. The further addition of the acid changes the colour again to deep red. With this procedure 88 % of **359** could be extracted (*Scheme 164*).

In another approach for the synthesis of **359** we used the method for the preparation of the aminoferrocene (**364**) described by V. Rapic and co-workers.[168]

The acyl azide **384** was prepared via the same procedure as the acyl azide **380** (*vide supra*). The heating of **384** in toluene and in the presence of *tert* butanol under reflux gave 2-tert-butoxycarbonylamino-ferrocene carboxylicacid ethyl ester (**385**), which was then deprotected with HCl delivering the chloride salt of the required 2-aminoferrocenecarboxylic acid (**383**) (*Scheme 166*).

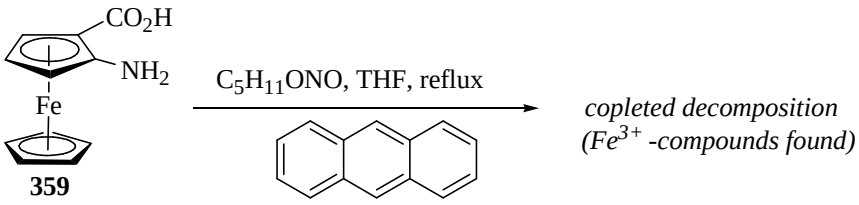


Scheme 166

In the same manner, as described before (*vide supra*), **359** was extracted by slow addition of aqueous solution of potassium hydroxide (1 N) in 80 % yield (*Scheme 166*). The advantage of this method against the described method before is the deprotection of the carboxylic acid group and the amino group in one step via reflux with the aqueous solution of HCl.[169]
The new compound **359** is yellow solid, which is extremely sensitive against the oxidation and should be handled only under protecting atmosphere. Because of the high instability, this compound could be characterized only with ^{1}H NMR and mass spectra.

6.1.1 Attempts towards ferrocyne from 2-aminoferrocenecarboxylic acid

The aprotic diazotization of the 2-aminoferrocenecarboxylic acid **359** was performed in the same manner, which is widely used in the preparation of benzyne via aprotic diazotization of the anthranilic acids.[32, 35, 154-156] A solution of the 2-aminoferrocenecarboxylic acid **359** in THF was added to a refluxing mixture of anthracene and amyl nitrite in methylene chloride. The complete decomposition of **359** was immediately observed. The investigation of the reaction mixture showed only inorganic iron (III) compounds (*Scheme 167*).



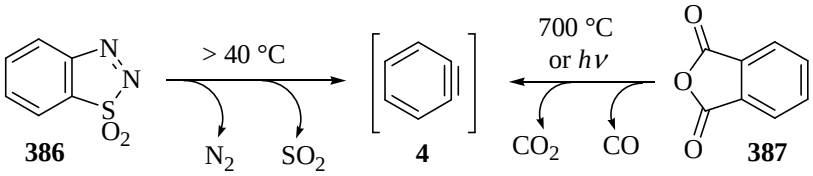
Scheme 167

As already mentioned, **359** is extremely susceptible to oxidation. Obviously, this reaction condition is very destructive for the compound, which is already decomposed under impact of the air.

Although the derivates of the anthranilic acid are widely used for the preparation of benzynes, this is not the case with 2-aminoferrocenecarboxylic acid **359**. The reaction with amyl nitrite leads to the complete decomposition of the complex. Since this attempt did not lead to the required result, we feel a vocation to continue our search for ferrocyne.

7. Generation of arynes via fragmentation reactions

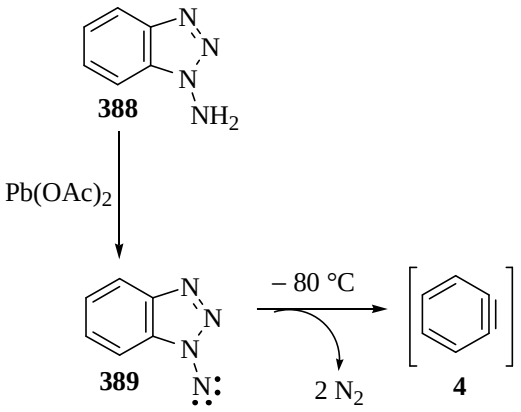
Benzynes can also be prepared by fragmentation of cyclic systems by electronic rearrangements. This kind of reactions is only suitable for compounds bearing functional groups, which are stable against high temperature or irradiation. The high temperature or irradiation are mostly required for initiation of fragmentation reaction (*Schemes 12 and 168*).[38, 170]



Scheme 168[170]

C. W. Rees and C. D. Campbell found a possibility to generate arynes via fragmentation reaction at milder conditions. The oxidation of the 1-aminobenzotriazole with $Pb(OAc)_2$ gives

benzyne at – 80 °C. This reaction is probably based on the generation of an aminonitrene followed by fragmentation under loss of two molecules of nitrogen (*Scheme 169*).[171]



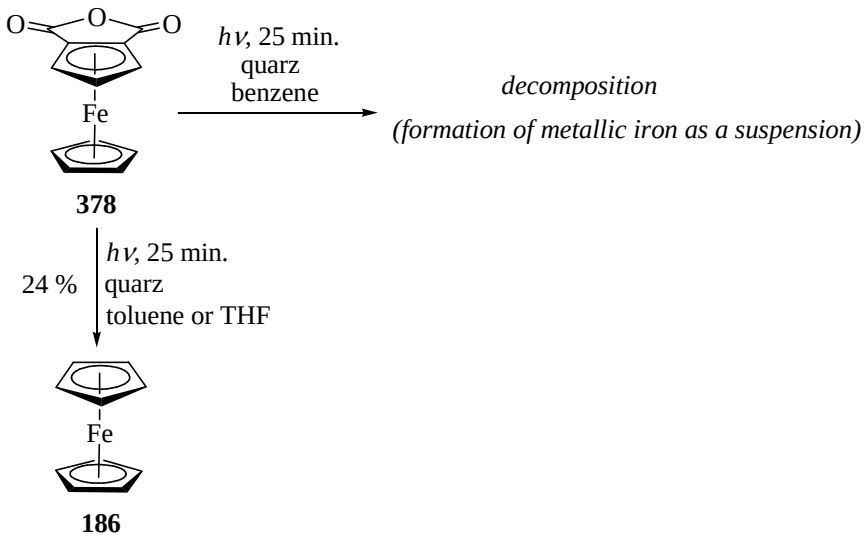
Scheme 169[171]

Because of the sensitivity of ferrocene derivates against oxidation, this reaction is not under consideration for our aim. We planned to subject 1,2-ferrocene dicarboxylic anhydride (**378**) to the fragmentation via heating or irradiation.

7.1 Photochemical fragmentation reaction of 1,2-ferrocene dicarboxylic anhydride

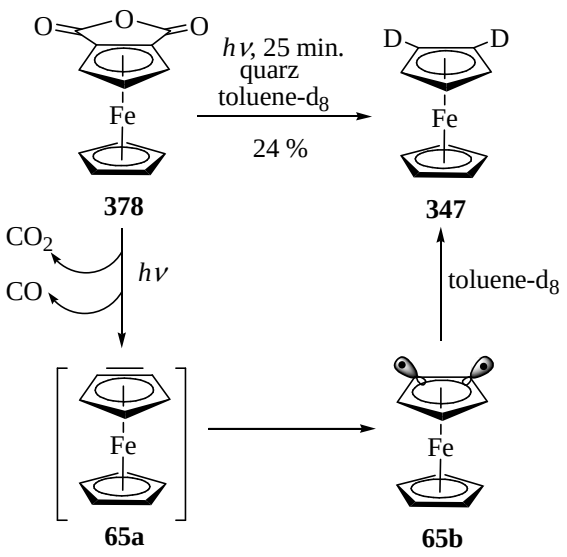
The synthesis of 1,2-ferrocene dicarboxylic anhydride (**378**) was already described (*vide supra*). 1,2-Ferrocene dicarboxylic anhydride (**378**) was subjected to the irradiation with UV light in benzene in the presence of 1,5-dimethylfuran. The reaction mixture was irradiated for 25 minutes with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. After 25 minutes only the complete decomposition of the compound could be determined. Only the metallic iron as suspension was formed. No evidence for the formation of ferrocyne was observed.

Another result was obtained using of toluene and THF as solvent instead of benzene. After 25 minutes of irradiation ferrocene with 24 % yield was found in the reaction mixture (*Scheme 170*).



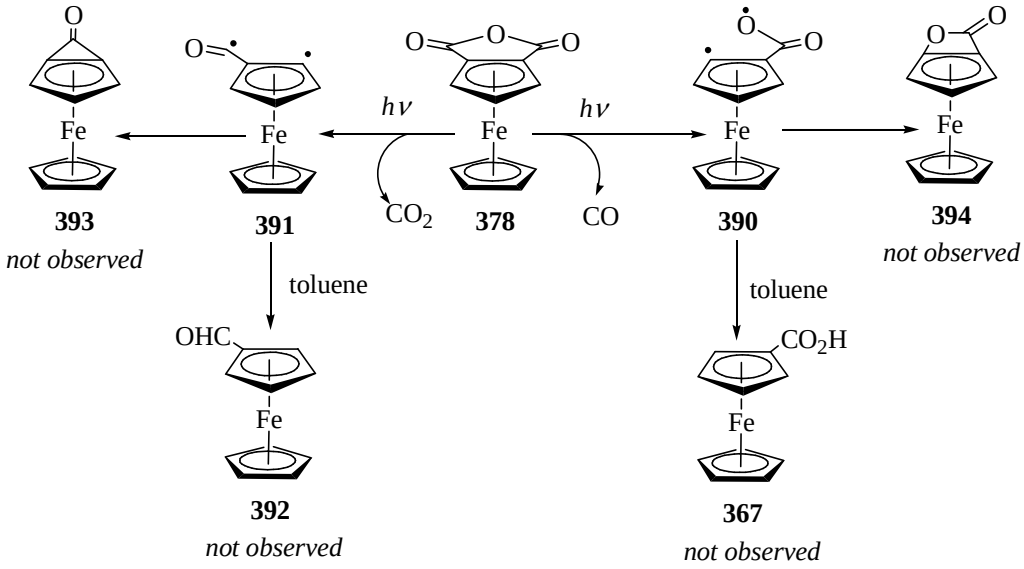
Scheme 170

Obviously, the two hydrogen atom arose from the solvents (or from another molecules **378**). For a better understanding of this conversion, the same reaction was carried out under the same conditions in the deuterated toluene and in the deuterated THF. Instead of ferrocene (**186**) the 1,2-dideuterio ferrocene (**347**) was generated in the same yield. This result clearly shows, that the both H or the both D atoms are delivered indeed by the solvents. Since the both solvents, toluene and THF, are aprotic, this conversion can be only explained by a radical mechanism. The irradiation of 1,2-ferrocene dicarboxylic anhydride (**378**) effects the fragmentation reaction generating ferrocyne (**65**) under release of one carbon dioxide and one carbon monoxide molecules. Because of the high strain of ferrocyne (the strain in ferrocyne must be much higher as the strain in the benzyne), the triple bond undergoes the homolytic splitting generating two vicinal *p*-orbitals with unpaired electrons, thus 1,2-diradical. The 1,2-ferrocene diradical get the both protons or D atoms from the solvent giving the ferrocene or the 1,2-dideuterio ferrocene (*Scheme 171*).



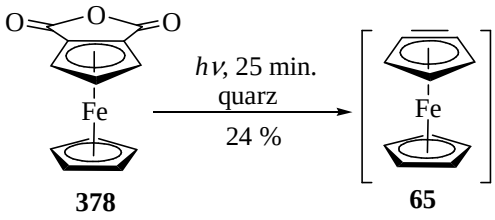
Scheme 171

This procedure can be also explained with a stepwise mechanism. Carbon monoxide and carbon dioxide are released not simultaneously, but probably one by one. In this case the generated intermediates **390** and **391** should also abstract the protons from the solvent, generating the ferrocene aldehyde **392** and the ferrocene carboxylic acid **267** or the compounds **393** and **394** (*Scheme 172*).



Scheme 172

However, neither the compounds **267**, **392**-**394** were found in the reaction mixture. This result clearly suggests the formation of ferrocyne (**65**) by irradiation of the 1,2-ferrocene dicarboxylic anhydride (**378**) (*Scheme 173*).



378 **65**

Scheme 173

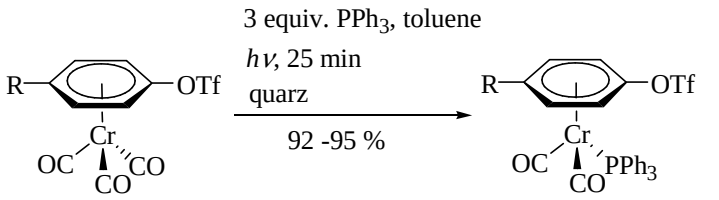
Although the investigation of this conversion is still far from being closed, it is safe to suggest that the fragmentation reaction of the 1,2-ferrocene dicarboxylic anhydride (**378**) indeed works.

C. Summary and outlook

Ferrocyne and η^6-aryne tricarbonylchromium(0) complexes are still unknown.. The attempt to synthesize η^6-aryne tricarbonylchromium(0) complexes from phenyl triflate tricarbonylchromium complexes was already undertaken by our group previously andled to the discovery of the thia-Fries rearrangement at metal complexes.[50] While this was the first case of an anionic thia-Fries rearrangement at a metal complex, Lloyd-Jones had earlier reported such rearrangements for purely organic phenyl triflates.[44] It was found that the anionic thia-Fries rearrangement is preferred in the presence of electron withdrawing substituents, while the elimination to an aryne prevails in electron rich systems.

Having in mind that the electron withdrawing nature of the tricarbonylchromium group was a major factor for the anionic thia-Fries rearrangement to overcome the desired elimination we decided to increase the electron density of phenyl triflate tricarbonylchromium complexes via two ways. Firstly, the electron withdrawing carbonyl ligands should be substituted by more electron rich triphenyl phosphine ligands and secondly, by introducing of electron donating groups into the aromatic system.

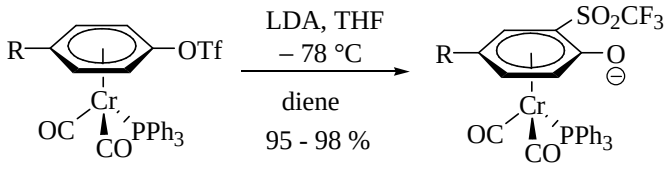
A couple of mixed ligand complexes of the type $(PhOTf)Cr(CO)_2PPh_3$ were synthesized photochemically, starting from $(PhOTf)Cr(CO)_3$ and 3 equivalents of triphenyl phosphine in toluene or THF by irradiation for 25 minutes with a 125 W mercury lamp placed in a quartz tube. Although 3 equivalents of triphenyl phosphine were used, no triple or double substitution was observed. The new complexes of the type $(PhOTf)Cr(CO)_2PPh_3$, which were successfully synthesized in high yield, are very stable against oxidation.



107 R = H
108 = OMe

148 R = H
149 R = OMe

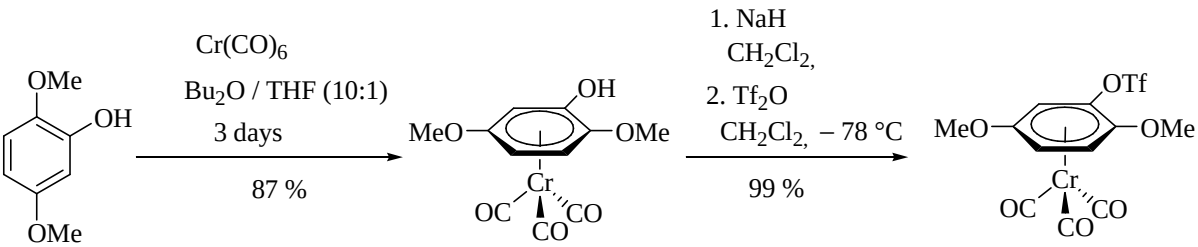
Subsequently, an *ortho* deprotonation of aryl triflate dicarbonyl triphenylphosphine chromium complexes $(PhOTf)Cr(CO)_2PPh_3$ with lithium diisopropylamide in the presence of a diene was carried out to induce the triflate lithium elimination with formation of the respecting aryne complexes. However, in contrast to our expectation no evidence for the formation of aryne complexes was observed. Instead, the corresponding trifluoromethylsulfonyl phenol complexes, products of the anionic thia-Fries rearrangement, were achieved in high yields.



R = H **148** **150**

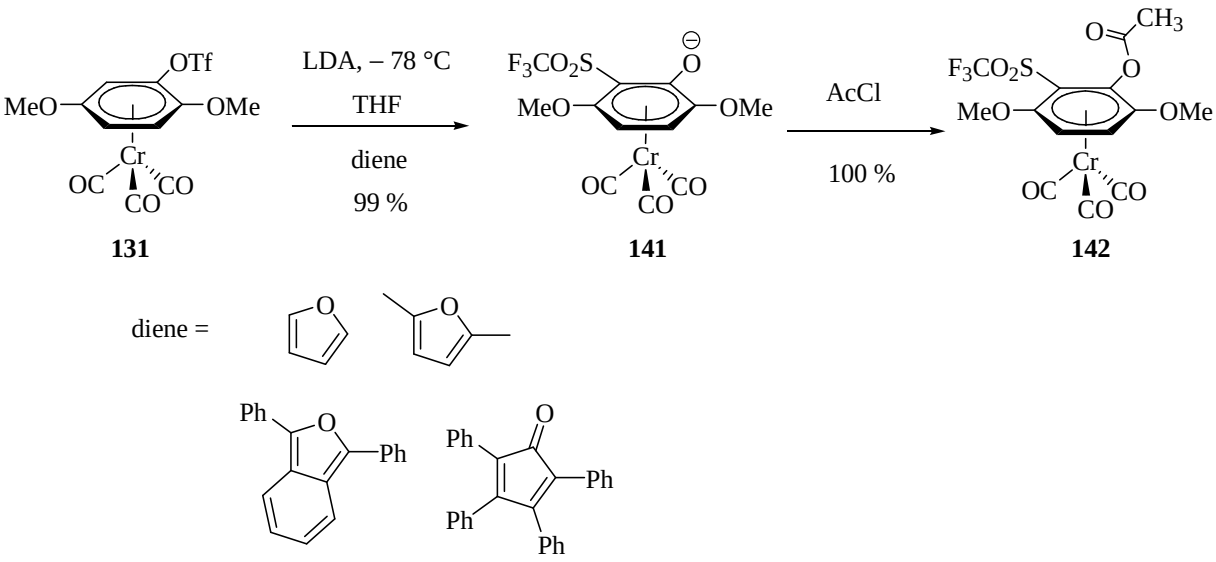
= OMe **149** **151**

In another approach electron donating groups were introduced into the aromatic ring. The 2,5-dimethoxy phenyl triflate tricarbonyl chromium complex was prepared by arene complexation and the following esterification with triflic anhydride in high yield, using the improved synthesis.



134 **140** **131**

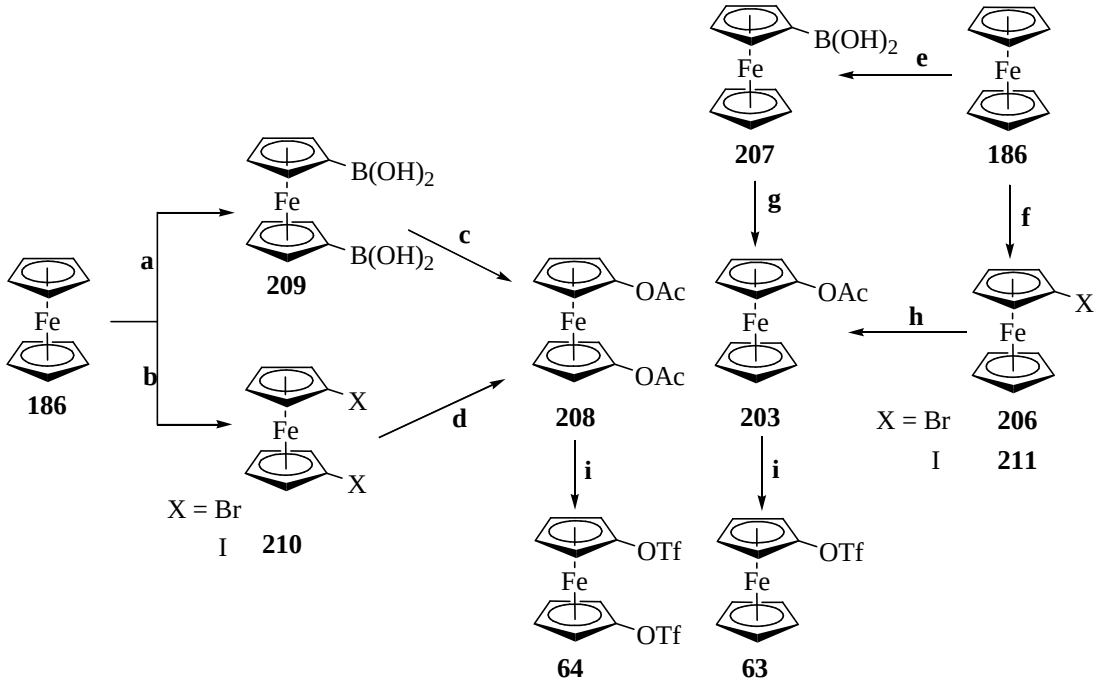
The triflate tricarbonylchromium complex **131** was treated with LDA in THF at – 78 °C in the presence of various trapping reagents for the possible benzyne. Again, the reaction leads exclusively to the anionic thia-Fries rearrangement product, no elimination product was observed.



These results suggest that the electron drawing character of the tricarbonylchromium and the dicarbonylchromium was not vanquished.

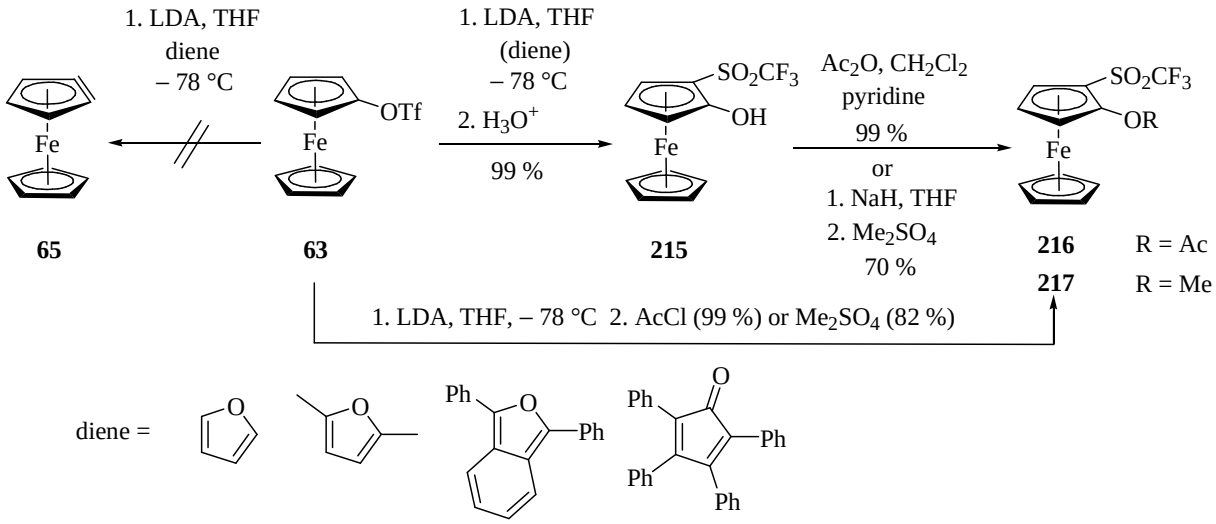
And again, having in mind that the electron withdrawing nature of the tricarbonylchromium group was a major factor for the anionic thia-Fries rearrangement to overcome the desired elimination we concluded that the more electron rich ferrocene system might better be suited for triflate elimination.

The new ferrocenyl triflate (**63**) and 1,1'-ferrocendiyl ditriflate (**64**) were prepared via transesterification from ferrocenyl acetate (**203**) and 1,1'-ferrocendiyl diacetate (**208**) in 90 % yield. Synthesis of **203** and **208** were improved (*Scheme 174*)



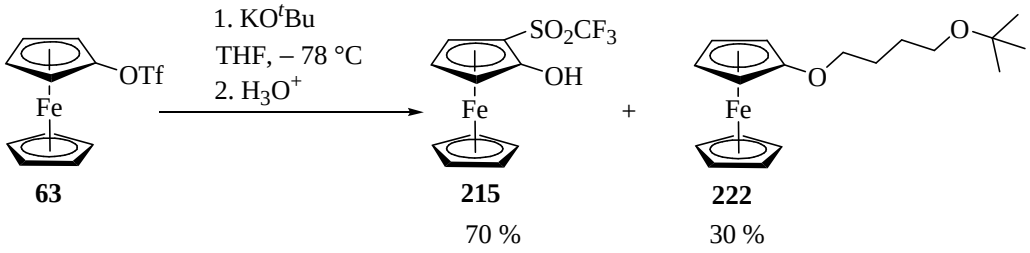
Scheme 174. Synthesis of the ferrocenyl triflate (**63**) and 1,1'-ferrocendiyl ditriflate (**64**) from the ferrocene (**186**): (**a**) TMEDA, *n*-BuLi (2 equiv.), THF, −78 °C then $B(OR)_3$ then water; (**b**) TMEDA, *n*-BuLi (2 equiv.) THF, −78 °C then ClSn(*n*-Bu)$_3$ then I_2 or TMEDA, *n*-BuLi (2 equiv.) then $C_2Cl_4Br_2$; (**c**) and (**g**) $Cu(OAc)_2$, H_2O / DMSO (1:1), μW, 100 °C, 20 min, 200 W; (**d**) and (**h**) with X = Br: $Cu(OAc)_2$, EtOH / H_2O (1:1), reflux 1 h; with X = I: Cu_2O / CH_3CO_2H, CH3CN, reflux 3 h; (**e**) *tert*-BuLi / KO^{t}Bu (10 :1) THF, −78 °C, then $B(OR)_3$ then water; (**f**) *tert*-BuLi / KO^{t}Bu (10 :1) THF, −78 °C, then I_2 or Br_2 or $Hg(OAc)_2$ toluene / MeOH then LiCl then I_2 or NBS; (**i**) KOH EtOH / H_2O, 70 °C, 30 min then Tf_2O, CH_2Cl_2 / pyridine, −78 °C, 30 min.

An *ortho* deprotonation of ferrocenyl triflate **63** with various bases was performed in order to induce triflate elimination with formation of ferrocyne. Several reaction conditions including *in situ* quenching with diverse dienes or excess of diisopropyl amine to trap ferrocyne were tested. However, in contrast to our anticipation, no evidence for ferrocyne formation was observed. Instead of that, the anionic thia-Fries rearrangement took place generating 2-(trifluoromethylsulfonyl)ferrocenol (**215**) in high yield.

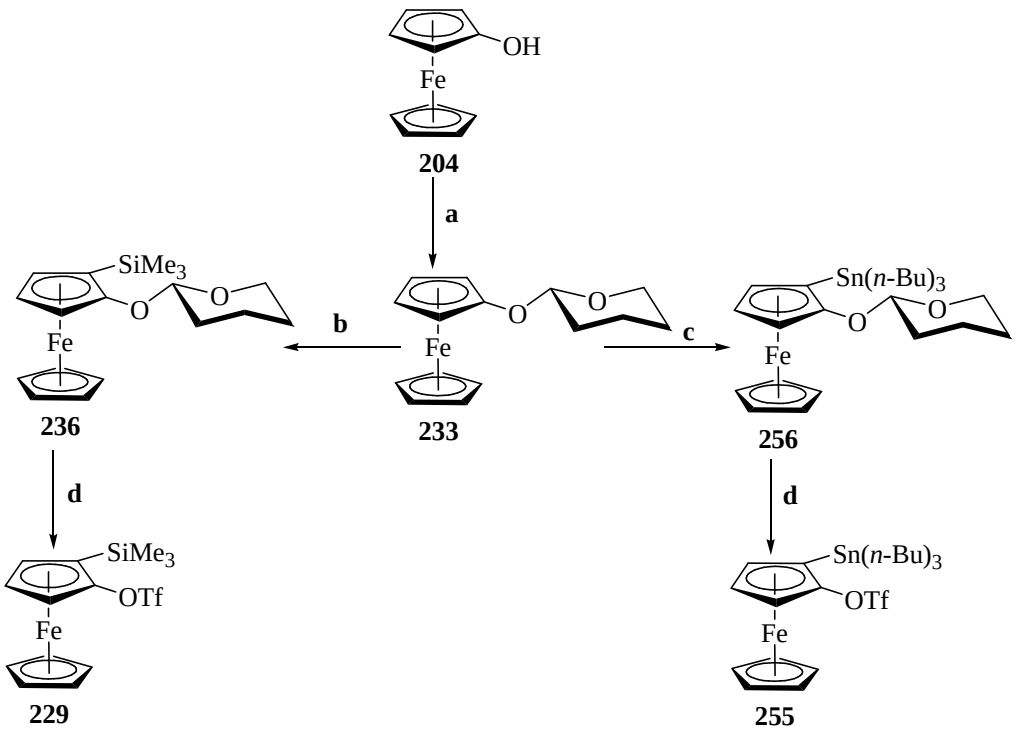


Since ferrocenols are known to be susceptible to oxidation,[46, 47, 109] for a comfortable handling **215** can be treated with acetic anhydride/pyridine and with dimethyl sulphate/sodium hydride, affording 2-(trifluoromethylsulfonyl)ferrocenyl acetate (**216**) and 1-methoxy-2-(trifluoromethylsulfonyl)ferrocene (**217**) in 99 % and 70 % yield, respectively. The isolation of intermediate **215** is unnecessary, treatment of the reaction mixture with acetyl chloride or dimethyl sulphate affords **216** and **217** in 99 % and 82 % yield, respectively.

A different result was obtained using potassium *tert*-butoxide in THF and potassium methoxide in methanol. Treatment of ferrocenyl triflate with KO^{t}Bu led to the formation of 2-(trifluoromethyl-sulfonyl)ferrocenol (**215**) with 70 % yield and (4-*tert*-butoxybutoxy)-ferrocene (**222**) with 30 % yield caused by the THF ring opening.

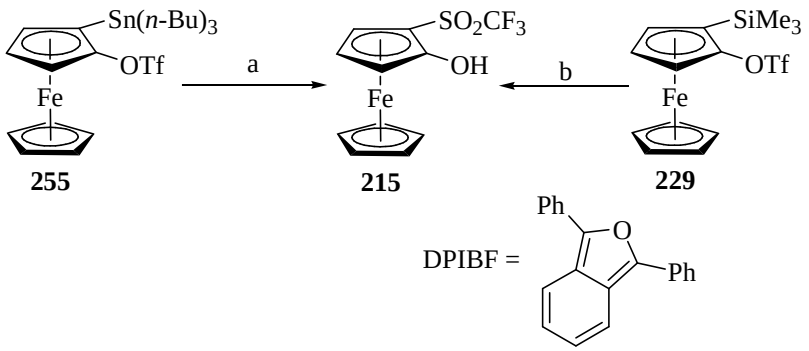


In alternative approaches we synthesized the new *o*-trimethylsilylferrocenyl triflate (**229**) and the new 2-tributylstannyl ferrocenyl triflate (**255**) in high yields starting from the known tetrahydropyran-2-yloxyferrocene (**233**) (*Scheme 175*).

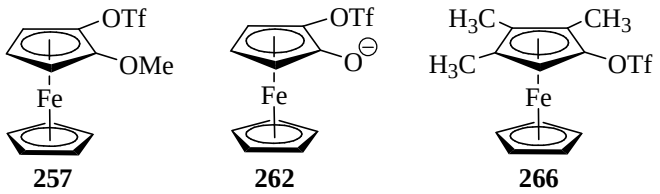


Scheme 175. Synthesis of 2-tributylstannyl ferrocenyl triflate (**255**) and 2-tributylstannyl ferrocenyl triflate (**255**) from the ferrocenol (**204**): (**a**) HCl, EtOAc, 3,4-Dihydro-2*H*-pyran; (**b**) *n*-BuLi, Et_2O, – 78 °C, 2 h then Me_3SiCl; (**c**) *n*-BuLi, Et_2O, – 78 °C, 2 h then Bu_3SnCl; (**d**) HCl, EtOH / H_2O, 25 °C, 1 h then Tf_2O CH_2Cl_2 / pyridine – 78 °C

The *o*-trimethylsilylferrocenyl triflate (**229**) was treated with tetrabutylammonium fluoride in acetonitrile at 25 °C in the presence of DPIBF and the 2-tributylstannyl ferrocenyl triflate (**255**) was treated with butyl lithium in THF at – 78 °C in the presence of DPIBF. In the both cases the reactions resulted in the anionic thia-Fries rearrangement product **215.**

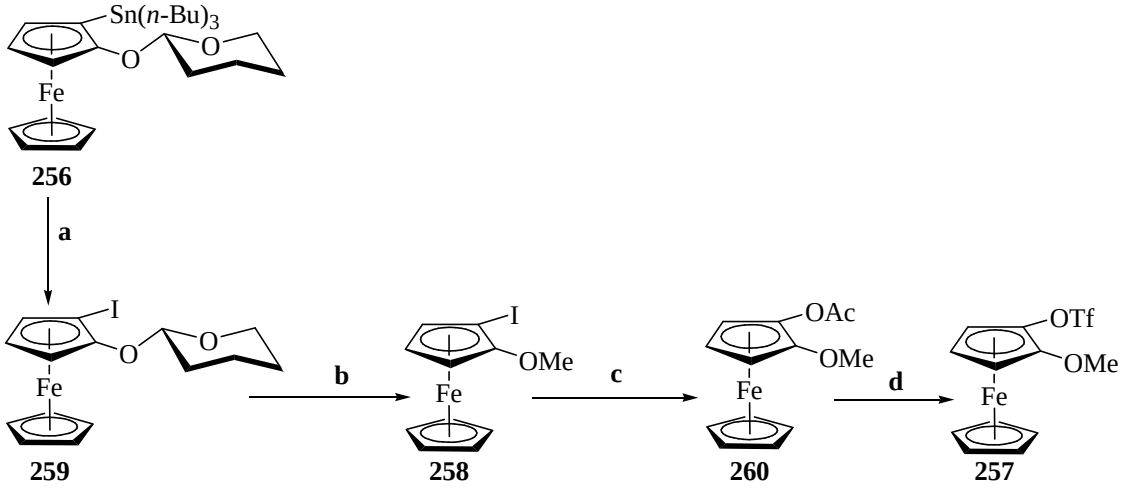


As the next step we synthesized ferrocenyl triflates bearing one or more electron donating groups, in order to increase the electron density in the aromatic system. The introduction of different groups at the ferrocene molecule turned out to be a challenge. The new compounds **257**, **262** and **266** were generated.



257 **262** **266**

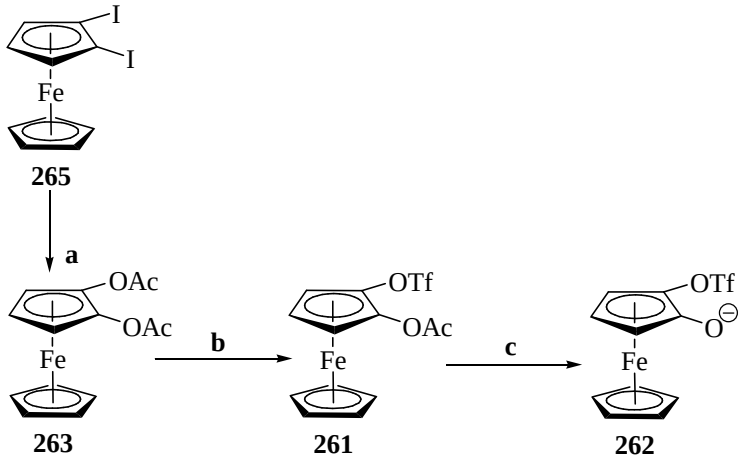
The 2-methoxy ferrocenyl triflate (**257**) was synthesized from the new tributyl-[2-(tetrahydropyran-2-yloxy)phenyl]stannane (**256**) (*vide infra*), over the new 2-(2-iodoferrocenoxy)-tetrahydropyran (**259**), the new 1-iodo-2-methoxyferrocene (**258**) and the new 2-methoxy ferrocenyl acetate (**260**) (*Scheme 176*).



Scheme 176. Synthesis of the 2-methoxy ferrocenyl triflate (**257**): (**a**) I_2, CH_2Cl_2 25 °C 1 h; (**b**) HCl, EtOH / H_2O, 25 °C, 1 h then. NaH, Me_2SO_4, THF reflux, 1 h; (**c**) CH_3CN / CH_3CO_2H, Cu_2O, reflux, 3 h; (**d**) KOH EtOH / H_2O, 70 °C, 30 min then Tf_2O, CH_2Cl_2 / pyridine, –78 °C, 30 min.

The other even more electron rich ferrocenyl triflate is the 2-trifluoromethanesulfonyloxy-ferrocenol anion (**262**), which was generated *in situ* from the new 2-trifluoromethanesulfonyloxy-ferrocenyl acetate (**261**), which was prepared from the new 2-acetoxy-ferrocenyl acetate (**263**) via a single hydrolysis with one equivalent of methyl lithium and following esterification with triflic anhydride. The 2-acetoxy-ferrocenyl acetate (**263**) was

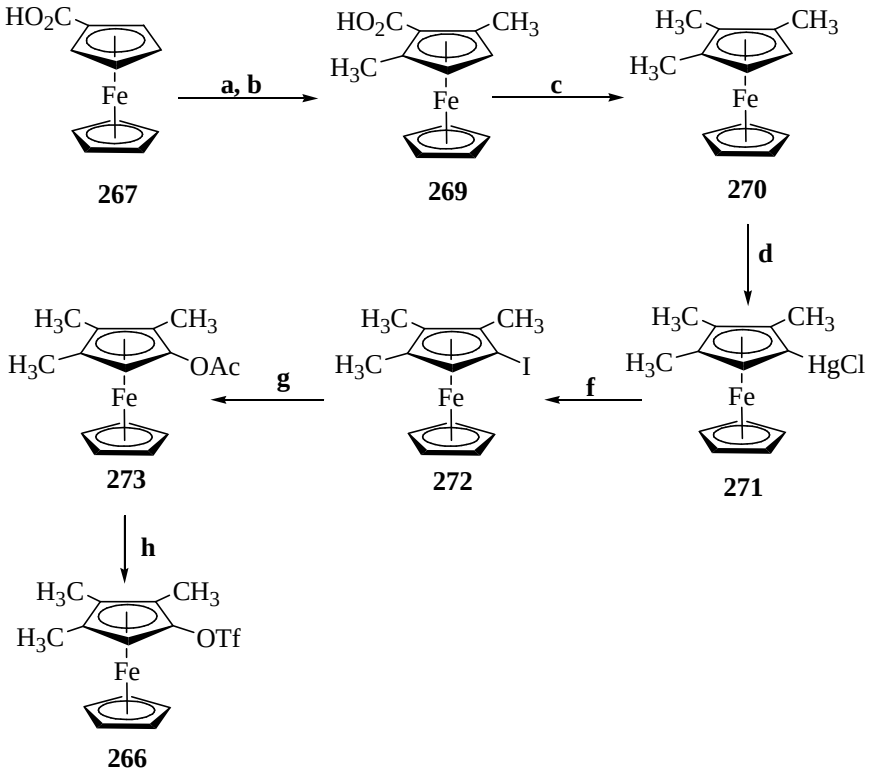
prepared from 1,2-diiodoferrocene (**265**) (for the synthesis of 1,2-diiodoferrocene *vide infra*) by heating in acetonitrile under reflux with 2,4 equivalent of Cu_2O and 5 equivalents acetic acid (*Scheme 177*).



Scheme 177. Synthesis of the 2-trifluoromethanesulfonyloxy-ferrocenol anion (**262**): (**a**) CH_3CN / CH_3CO_2H, Cu_2O, reflux, 3 h; (**b**) MeLi, Et_2O, – 78 °C then Tf_2O; (**c**) *n*-BuLi, THF, – 78 °C.

The next electron rich ferrocenyl triflate, what we synthesized is the 2,3,4-trimethyl-ferrocenyl triflate (**266**). The three electron donating methyl groups make the aromatic ring electron rich. Moreover, the methyl group in the *meta* position to the triflate group could hinder the rearrangement. Starting material for the synthesis of **266** is the ferrocenecarboxylic acid **267.** The ferrocene carboxylic acid (**267**) could be effectively ortho metallated with two equivalents of *sec* butyllithium.[107, 126] The subsequent addition of iodomethane gave after acidic work-up the 2-methylferrocenecarboxylic acid (**268**) in 80 % yield. The repeated procedure delivered the new 2,5-dimethylferrocenecarboxylic acid (**269**) in 60 % yield. The 2,5-dimethylferrocenecarboxylic acid (**269**) was treated with the two equivalent of BMS in methylenechloride at 25 °C for 78 hours to give the required reduction product **270** in 75 %. In the next step the 1,2,3-trimethylferrocene (**270**) was subjected to the mercuration. Since the mercuration proceeds more readily on the more electron rich arenes,[128-131] we expected the mercuration on the cyclopentadienyl ring bearing the three methyl group. Indeed, the main product of this conversion was the required compound **271**, while many side products were also obtained, which gravely decreased the yield of **271**. The mercurated product **271** was treated with iodine in methylenechloride at 25 °C for 30 min, the quantitative conversion

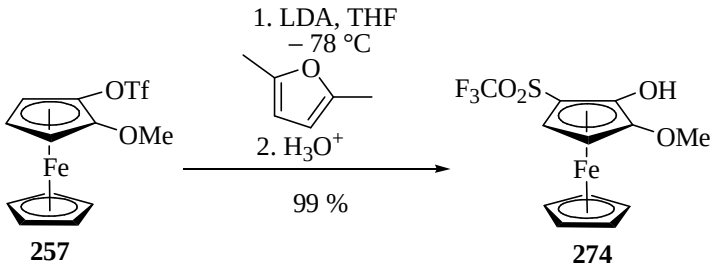
delivered the 1-iodo-2,3,4-trimethylferrocene (**272**), which was heated in acetonitrile under reflux with 1,2 equivalent Cu_2O and 3 equivalents acetic acid generating the 2,3,4-trimethyl ferrocenyl acetate (**273**) in 89 % yield , which is, as usually, hydrolyzed and esterificated with triflic anhydride giving quantitatively the 2,3,4-trimethylferrocenyl triflate (**266**) (*Scheme 178*).



Scheme 178. Synthesis of the 2,3,4-trimethyl-ferrocenyl triflate (**266**): (**a**) *sec*-BuLi, THF, – 78 °C then MeI; (**b**) *sec*-BuLi, THF, – 78 °C then MeI; (**c**) $(BH_3)SMe_2$, CH_2Cl_2, 25 °C, 78 h; (**d**) $Hg(OAc)_2$ toluene / MeOH then LiCl; (**f**) I_2 CH_2Cl_2, 25 °C, 1 h; (**g**) CH_3CN / CH_3CO_2H, Cu_2O, reflux, 3 h; (**h**) KOH EtOH / H_2O, 70 °C, 30 min then Tf_2O, CH_2Cl_2 / pyridine, –78 °C, 30 min.

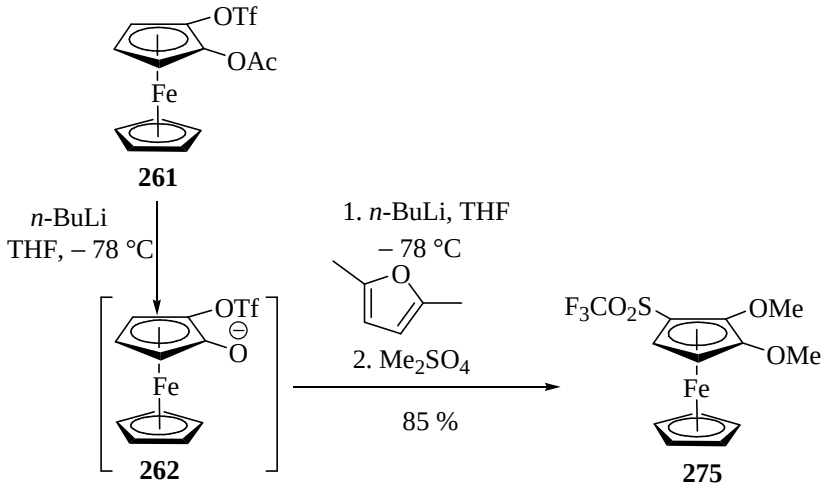
The prepared electron rich ferrocenyl triflates were treated with bases in the presence of dienes, in order to prove their ability to undergo elimination reaction.

The treatment of the 2-methoxy ferrocenyl triflate (**257**) with LDA in THF at – 78 °C in the presence of 2,5-dimethylfuran following acidification resulted the anionic thia-Fries rearrangement generating the 2-methoxy-5-(trifluoromethylsulfonyl)ferrocenol (**274**).



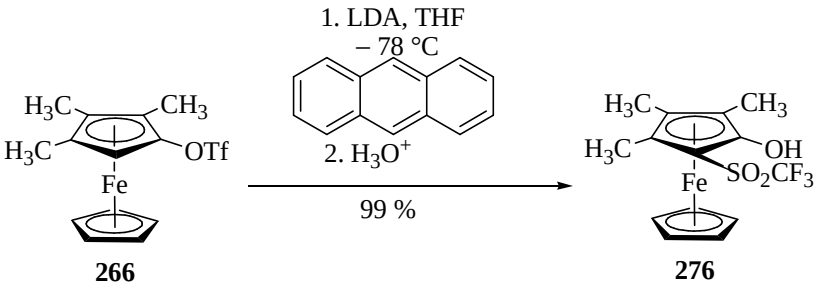
257 **274**

The 2-trifluoromethanesulfonyloxy-ferrocenolate (**262**), which was generated *in situ* from 2-trifluoromethanesulfonyloxy-ferrocenyl acetate (**261**) was treated with LDA in THF at – 78 °C in the presence of 2,5-dimethylfuran, after the following methylation with dimethyl sulphate the dimethylated anionic thia-Fries rearrangement product **275** was obtained in 85 % yield.



261 **262** **275**

In the reaction of the 2,3,4-trimethylferrocenyl triflate (**266**) with LDA anthracene was used as the diene, because of the doubt, if the methyl groups of **266** and the methyl groups of 2,5-dimethyl furan or phenyl groups of DPIBF would disturb each other. However, the treatment of the 2,3,4-trimethyl-ferrocenyl triflate (**266**) with LDA in THF at – 78 °C in the presence of anthracene following acidification resulted the anionic thia-Fries rearrangement generating the 2,3,4-trimethyl-5-(trifluoromethylsulfonyl)ferrocenol (**276**).

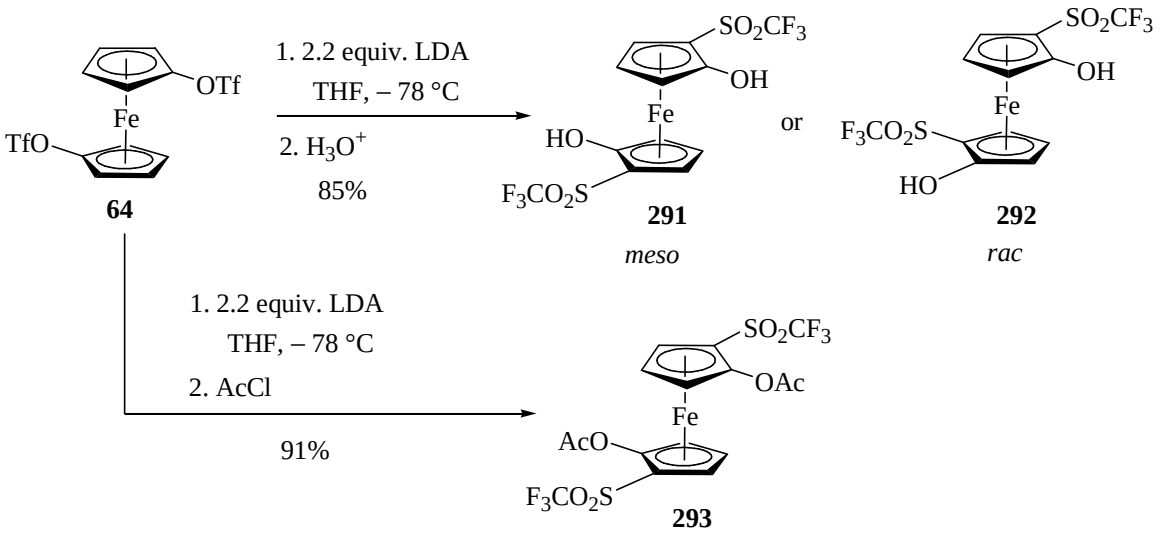


266 **276**

In spite of the more electron rich substrate, ferrocenyl triflate and even more electron rich ferrocenyl triflates undergo a highly efficient anionic thia-Fries rearrangement rather than triflate elimination. This is the first case of an anionic thia-Fries rearrangement at a five-membered ring.

With the extreme efficiency of the anionic thia-Fries rearrangement of ferrocenyl triflate in mind, we turned our attention to the 1,1'-ditriflate **64**. Three possible outcomes could be expected: double elimination, single thia-Fries rearrangement and single elimination, and a double thia-Fries rearrangement at either one of the cyclopentadienyl ligands.

The treatment of the 1,1'-ferrocenediyl ditriflate (**64**) with 2,2 equivalents of LDA at – 78 °C, led a double anionic thia-Fries rearrangement in 85 % yield, which could in principle afford two diastereomeric rearrangement products **291** and **292** (Scheme 121).



64 **291** *meso* **292** *rac* **293**

Remarkably, the reaction takes place with full diastereoselectivity affording only one of the two diastereomers. The rearrangement product was identified by an X-ray crystal structure analysis of the respective diacetate **293**. The analysis clearly indicated that meso product **291**

had been formed; no chiral rearrangement product **292** was observed. In the crystal structure of the substituted ferrocene **293** the iron atom occupies a crystallographic inversion centre, affording a staggered conformation of the cyclopentadienyl ligands. Only a *meso* configuration is compatible with the presence of the inversion centre.

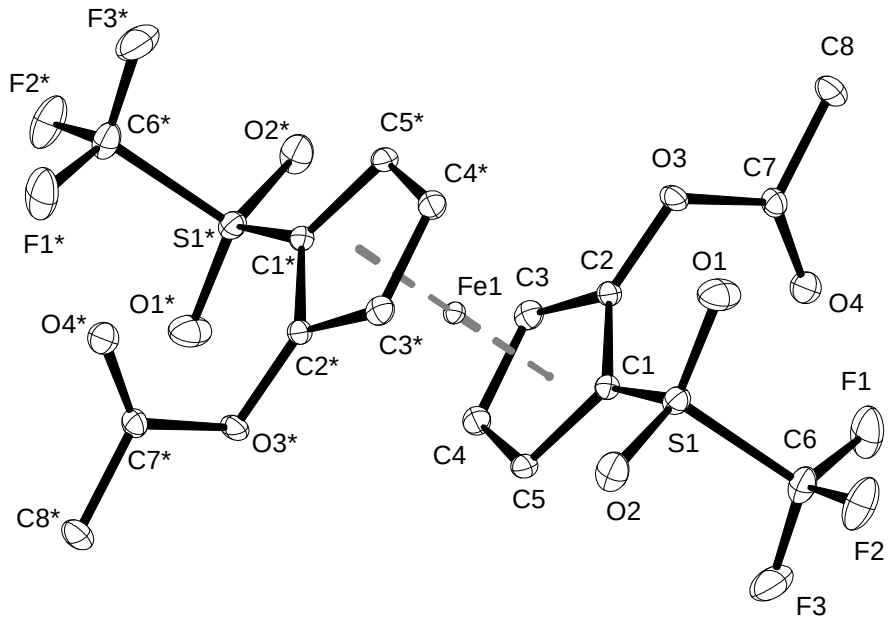
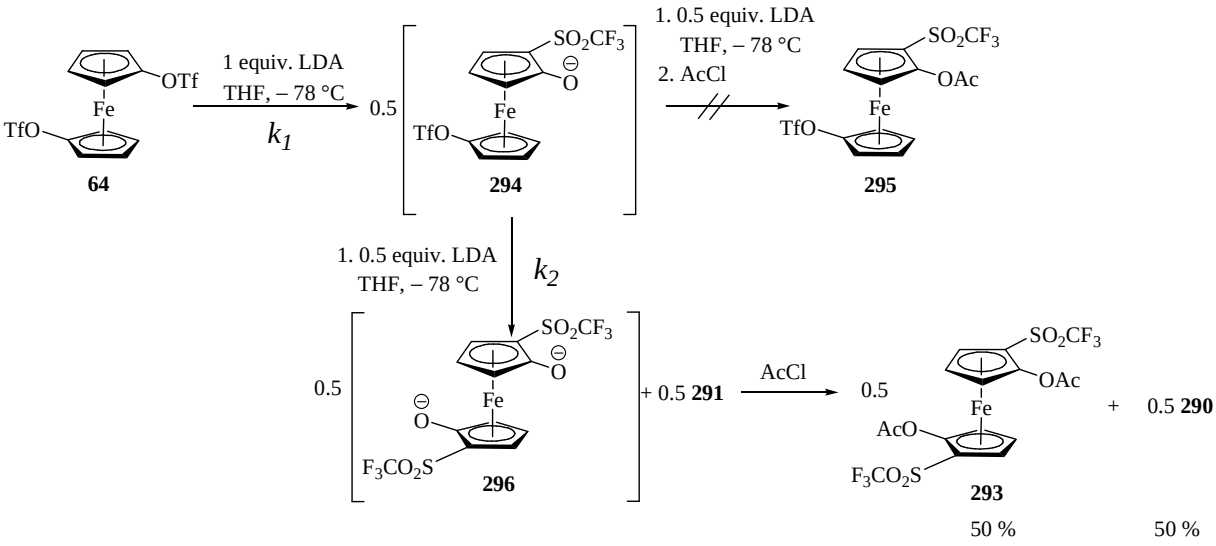


Figure 8

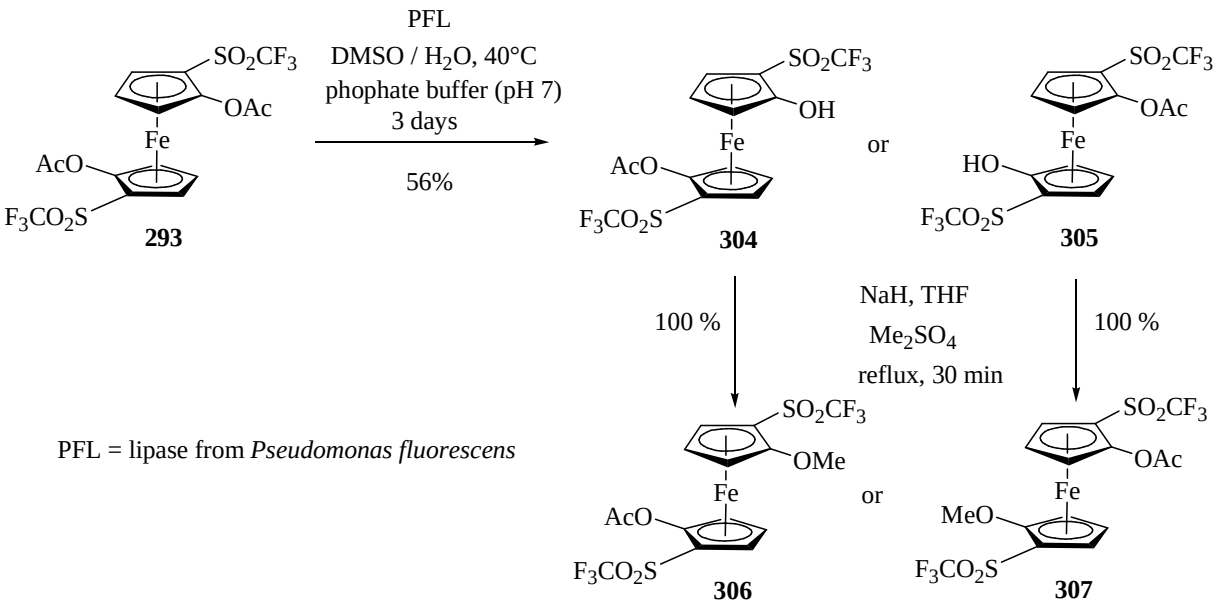
For better understanding the remarkably diastereoselective reaction leading from **290** exclusively to **291** we attempted a single anionic thia-Fries rearrangement in order to obtain **294** and subsequently **295** after quench with acetyl chloride. However, treatment of **290** with 1.0 equiv. of LDA under otherwise unchanged reaction conditions gave a equimolar mixture of starting material **290** and the trapped double rearrangement product **293** (*Scheme 123*). This clearly indicates that the second anionic thia-Fries rearrangement leading to **296** is significantly faster than the first one ($k_2 >> k_1$)



The exclusive formation of *meso* product **291** from **290** with no racemic **292** indicates an unusually high grade of interannular stereoinduction, exerted by the already rearranged cyclopentadienyl ligand in the intermediate **294**.

Because of the unique three-dimensional shape, the *meso* compounds **291** and **293** are potentially attractive as a ligand for metal complexes. Enantioselective desymmetrization strategies offer most interesting possibilities for the synthesis of enantiopure, chiral derivatives. Functionalization of one of the two hydroxy groups in **291** or hydrolysis of one of the two acetate groups in **293** would give a chiral derivative.

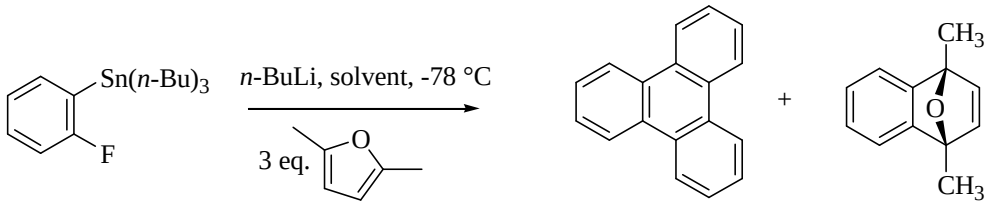
We tried to adopt the chemo enzymatic desymmetrization with use of the *meso* rearrangement product **291** and the corresponding diacetate **293** under the usual conditions of such reactions, namely with water and water / alcohols mixtures as solvents. The insolubility of **291** and **293** in such systems made the searching for other solvents necessary. The best result we obtained with the mixture of DMSO and water (1:1). The reaction was carried out at 40 °C with PFL as the enzymatic catalyst, lasted for 4 days. We obtained a product with only one hydroxy group. Since the diol **291** was not observed, it may be assumed that the required desymmetrization indeed took place.



Because of the high susceptibility of ferrocenols against oxidation (*vide supra*), the generated alcohol was methylated via heating in THF with sodium hydride and dimethyl sulphate under reflux for 30 minutes (*Scheme 126*). The only conclusions reached so far are that only one of the two possible alcohols **304** and **305** is generated. It was characterized as the methyl ether **306** or **307** by means of ^{1}H NMR and mass spectrometry. The exactly characterization of this product is still pending.

In another approach we used halobenzene tricarbonylchromium complexes towards the aryne complexes and haloferrocenes for synthesis of ferrocyne.

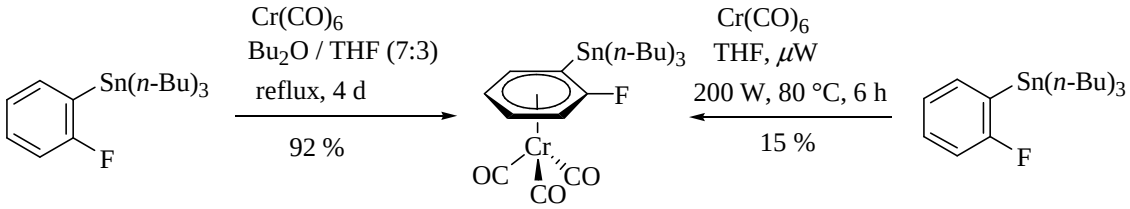
We developed a similar possibility for metallation of fluorobenzene via the transmetallation of tributyl-(2-fluoro-phenyl)-stannane (**170**), which was synthesized from fluorobenzene (**8**). Before the tributyl-(2-fluoro-phenyl)-stannane (**170**) was subjected to the complexation with $Cr(CO)_6$, we tested the trasmetallation with butyl lithium as well in the presence of a diene as without diene. The aim of this experiment was to probe the optimised conditions for the preparation of benzyne. With the presence of 2,5-dimethylfuran as the trapping regent, we obtained the Diels-Alder adduct **173** and triphenylene (**161**). An interesting result of these experiments was that the kind of the used solvent exerts an influence on the amount of these products. The more non polar solvent induces the larger amount of [2 + 4] cycloadduct.



170 **161** **173**

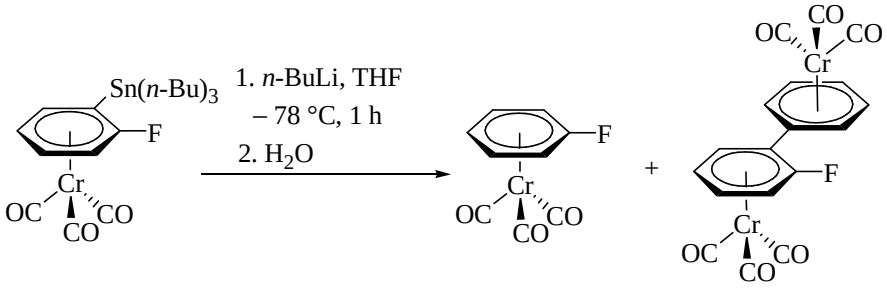
Solvent = THF	83%	17%
n-hexane	28 %	72 %

The complexation of **170** was carried out via heating in Bu_2O / THF (7:3) with 1.2 equivalents of $Cr(CO)_6$ lasted for 4 days. These are the best reaction conditions. The usual solvent mixture of Bu_2O / THF (10:1) resulted lower yield. The attempt to perform the reaction in a micro-wave reactor with the same conditions did not deliver any products. But the use of THF as a solvent causes the generation of the required complex with 15 % yields, what is compensated by short reaction time of 6 hours.



170 **174** **170**

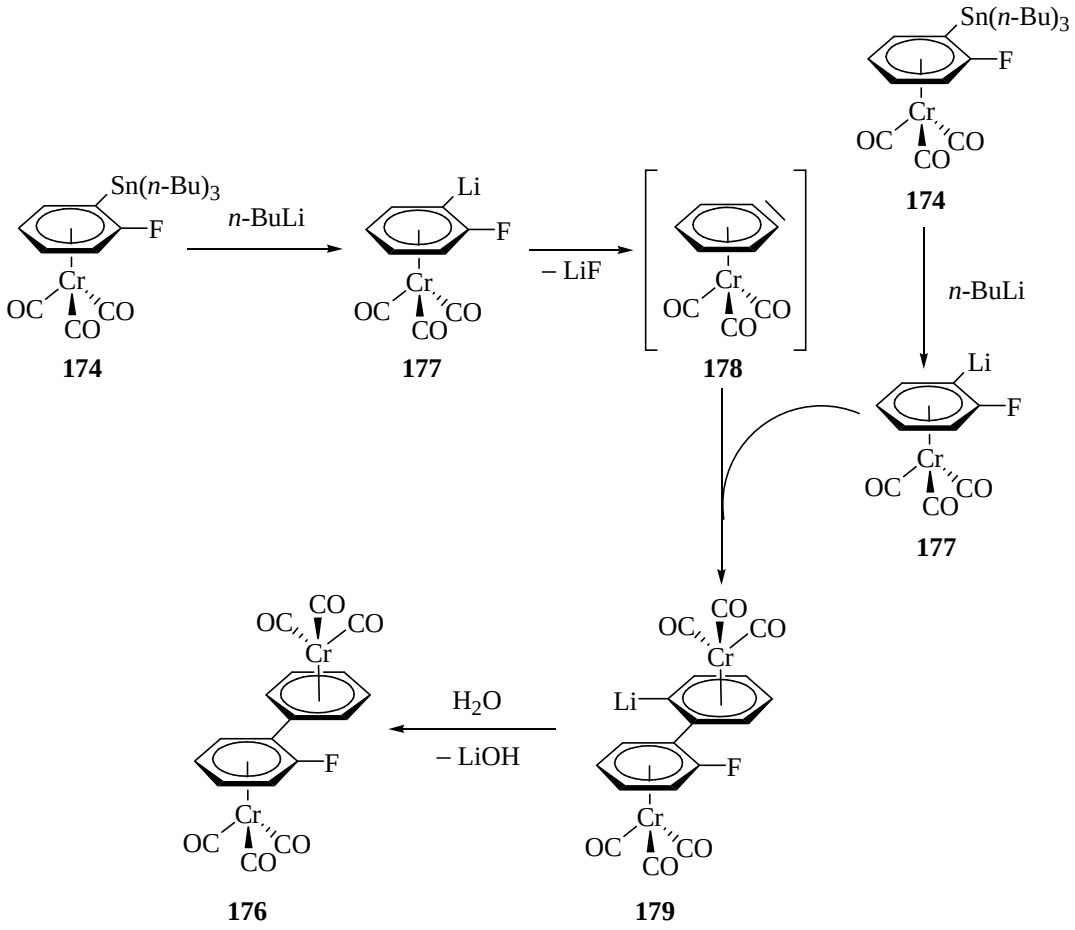
The complex **174** was subjected to transmetallation with butyl lithium in THF at – 78 °C for 1 hour, warmed up to 25 °C and quenched with water. The main product was fluorobenzene tricarbonylchromium (**175**), which is the result of the transmetallation and subsequent quenching with water.



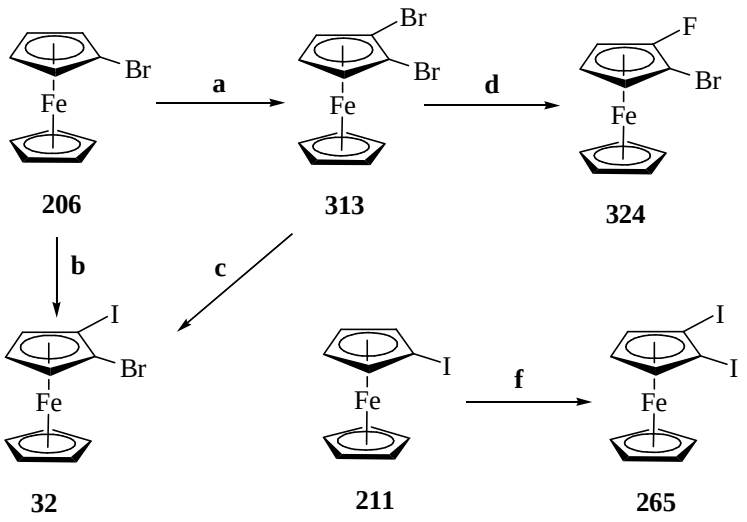
174 **175** **176**

87 %	7 %

The formation of the product **176** is potentially due to the emergence of the aryne chromium π-complex. This is the first case of formation of such species. The proposed mechanism for the formation of complex **176** is shown in the scheme 62.

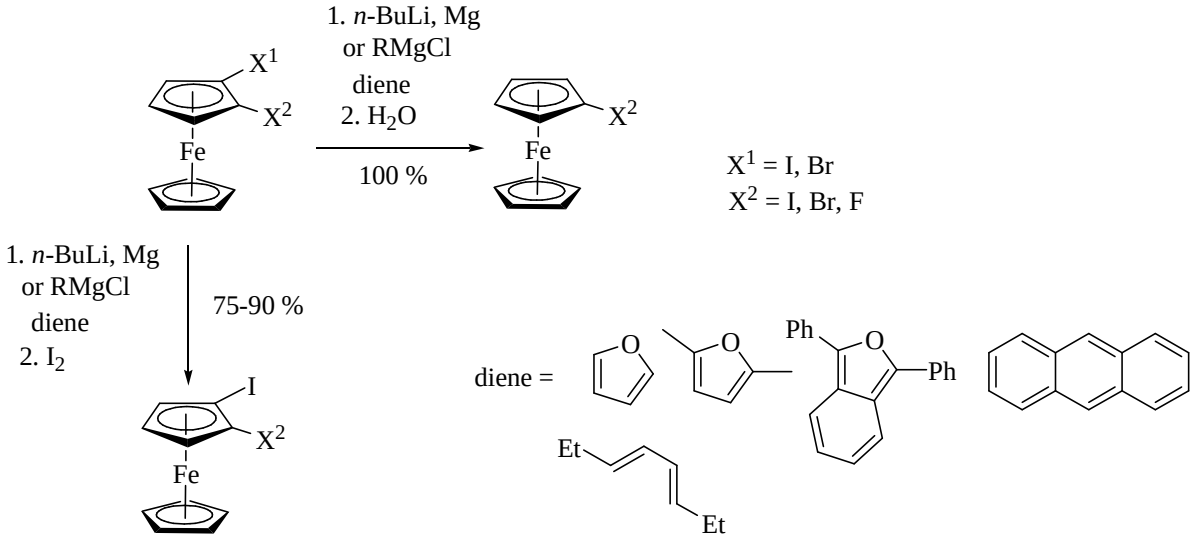


While there are myriad publications describing the synthesis of 1,1'-dihaloferrocene, the appearance of 1,2-dihaloferrocenes in scientific literature is pretty rare. For the preparation of 1,1'-dihaloferrocene we improved an already known method,[144] which allows the synthesis of the required 1,1'-dihaloferrocene in high yield. We prepared the 1,2-dibromoferrocene (**313**) from bromoferrocene (**206**). The bromoferrocene is lithiated with LiTMP in THF at – 25 °C for 3 hours and than transmetallated with $ZnCl_2$. The subsequent quenching with bromine at – 78 °C resulted in 90 % yield of 1,2-dibromoferrocene as the main product. Using this method we synthesized 1,2 diiodoferrocene (**265**) and 1-bromo-2-iodo-ferrocene (**322**) also in higher yields. The new 1-bromo-2-flioro-ferrocene (**324**) was prepared from the 1,2-dibromoferrocene (**313**) (*Scheme 179*).



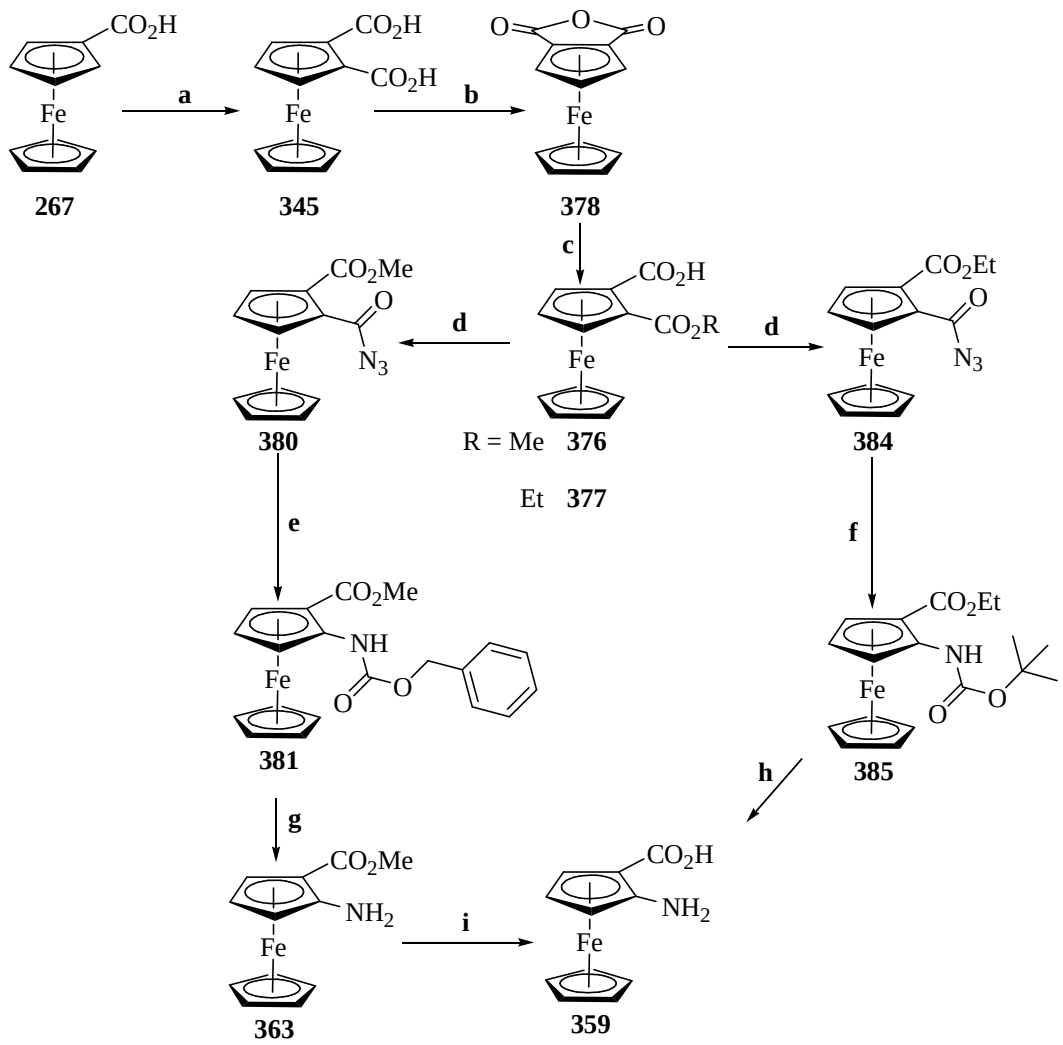
Scheme 179. Synthesis of different 1,2-dihaloferrocenes: (**a**) LiTMP, THF, –30 °C, 3 h then $ZnCl_2$ then Br_2; (**b**) LiTMP, THF, –30 °C, 3 h then $ZnCl_2$ then I_2; (**c**) *n*-BuLi, THF, – 78 °C then I_2; (**d**)) *n*-BuLi, THF, – 78 °C then NFSI; (**f**) LiTMP, THF, –30 °C, 3 h then $ZnCl_2$ then I_2.

The treatment with butyl lithium, Grignard reagents and metallic magnesium of **265**, **313**, **322** and **324** in the presence of a diene did not result elimination, but only the mono haloferrocenes after quenching with water were obtained. In order to be sure, that the ortho metallation indeed took place, the reaction mixtures were also quenched with iodine. The corresponding iodoferrocenes were obtained in high yield, what attests the successful *ortho* lithiation.



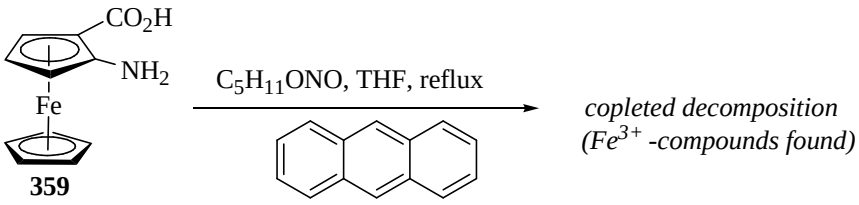
Although the 1,2-dihalobenzenes are widely used for the preparation of benzynes, this is not the case with 1,2-dihaloferrocenes. The reactions with various metallation reagents delivered only mono- or dimetallated products, no elimination reaction took place and no evidence for formation of ferrocyne was observed. Exceptions are the mass spectra of the 1,2-dihaloferrocenes, which clearly show the molecular masses of ferrocyne (**65**) and 2,5-dihydro-cyclobutadicyclopentene, the [2 + 2]-cycloaddition product of two 1,2-didehydrocyclopenta-dienyl anions.

In another approach we tried to prepare the ferrocyne from the zwitterion ferrocenediazonium-2-carboxylate (**358**). During this search we developed a new method for the synthesis of the 2-aminoferrocenecarboxylic acid (**359**). We started with the ferrocene carboxylic acid (**267**) and prepared the 2-ferrocene dicarboxylic acid (**374**) in very high yield by treatment of **267** with two equivalents of *sec* butyl lithium at – 78 °C in THF and the following addition of dry ice. The 2-ferrocene dicarboxylic acid (**374**) was converted into the new 1,2-ferrocene dicarboxylic acid mono methyl ester (**376**) or the new 1,2-ferrocene dicarboxylic acid mono ethyl ester (**377**) via alcoholysis. The following formation of the acyl azide **380**, Curtius' rearrangement and basic or acidic induced deprotection delievered the desired 2-aminoferrocenecarboxylic acid (**359**) (*Scheme 180*).



Scheme 180. Synthesis of the 2-aminoferrocenecarboxylic acid (**359**): (**a**) 2 equiv. *sec*-BuLi, THF, – 78 °C, then CO_2 then H_3O^+; (**b**) oxalyl chloride, CH_2Cl_2, DMF then pyridine; (**c**) EtOH or MeOH reflux, 1 h; (**d**) oxalyl chloride, CH_2Cl_2, DMF then NaN_3 in water, TBAB; (**e**) toluene / BnOH, reflux, 2 h; (**f**) toluene / *tert*-BuOH, reflux, 2 h; (**g**) H_2, Pd / C, MeOH, 24 h; (**h**) 6 M HCl, reflux, 1h then KOH; (**i**) KOH, EtOH / H_2O, 70 °C, 1 h then H_3PO_4.

The aprotic diazotization of the 2-aminoferrocenecarboxylic acid **359** was performed in the same manner, which is widely used in the preparation of benzyne via aprotic diazotization of the anthranilic acids.[32, 35, 154-156] A solution of the 2-aminoferrocenecarboxylic acid **359** in THF was added to a refluxing mixture of anthracene and amyl nitrite in methylene chloride. The completed decomposition of **359** was immediately observed. The investigation of the reaction mixture showed only inorganic iron (III) compounds.



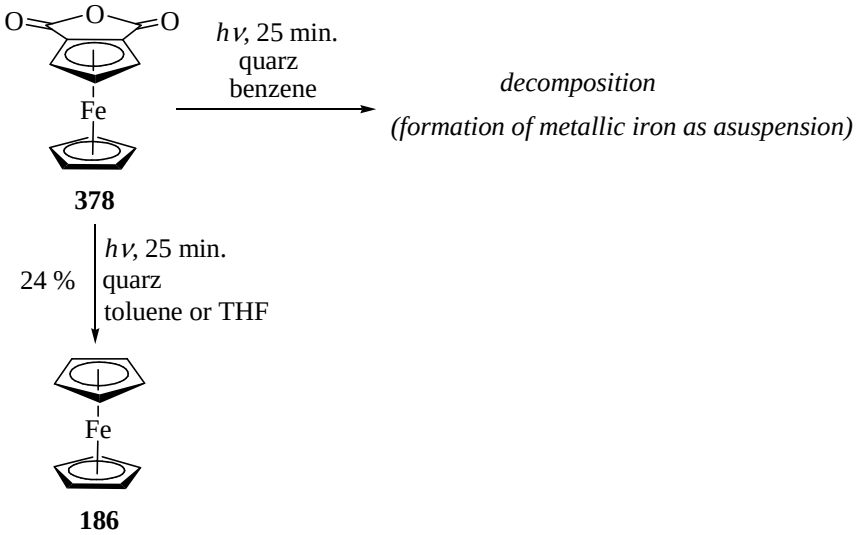
359

Although the derivates of the anthranilic acid are widely used for the preparation of benzynes, this is not the case with 2-aminoferrocenecarboxylic acid **359**. The reaction with amyl nitrite leads to the completed decomposition of the complex.

In the last approach we planed 1,2-ferrocene dicarboxylic anhydride (**378**) to subject to the fragmentation via heating or irradiation.

The 1,2-ferrocene dicarboxylic anhydride (**378**) was subjected to the irradiation with UV light in benzene and in the presence of 1,5-dimethylfuran. The reaction mixture was irradiated for 25 minutes with a 125 W mercury lamp placed in a quartz tub. After the 25 minutes only the completed decomposition of the compound could be determined. Only the metallic iron as a suspension was formed. No evidence for the formation of ferrocyne was observed.

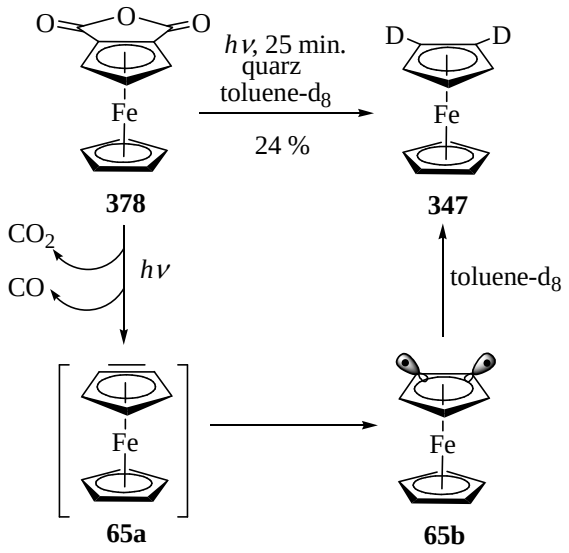
Another result was obtained with using of toluene and THF as the solvent instead of benzene. After 25 minutes of irradiation ferrocene with 24 % yield was found in the reaction mixture.



378

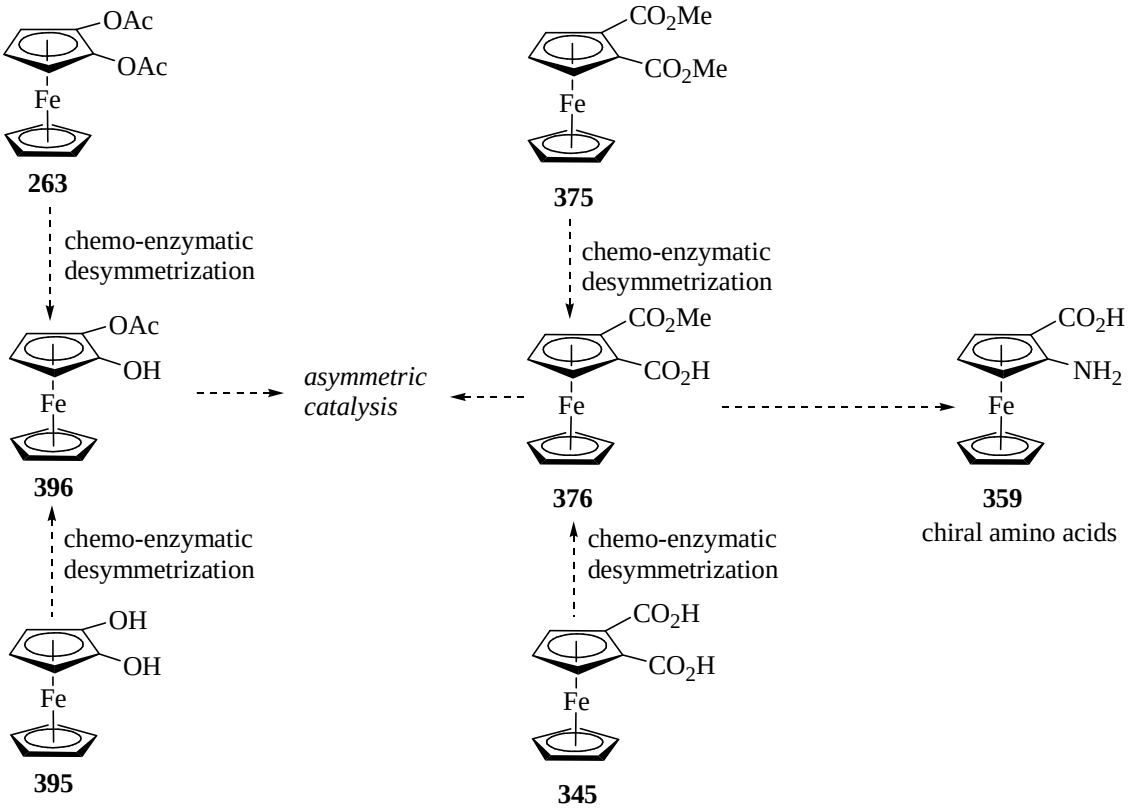
186

For the better understand of this conversion, the same reaction was carried out under the same conditions in the deuterated toluene and in the deuterated THF. Instead of ferrocene (**186**) the 1,2-dideuterio ferrocene (**347**) was generated in the same yield. This result clearly shows, that the both H or the both D atoms are delivered by the solvents. Since the both solvents, toluene and THF, are aprotic, this conversion can be only explained by a radical mechanism. The irradiation of 1,2-ferrocene dicarboxylic anhydride (**378**) effects the fragmentation reaction generating ferrocyne (**65**) under release of one carbon dioxide and one carbon monoxide molecules. Because of the high strain of ferrocyne (the strain in ferrocyne must be much higher as the strain in the benzyne), the triple bond undergoes the homolytic splitting generating two vicinal *p*-orbitals with unpaired electrons, thus 1,2-diradical. The 1,2-ferrocene diradical draw the both protons or D atoms from the solvent giving the ferrocene and the 1,2-dideuterio ferrocene respectively.

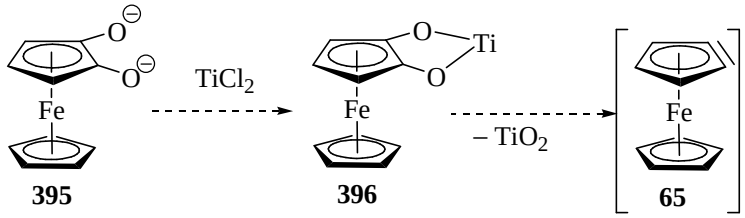


To sum up, the present work was very successful; the planned primary objective to synthesize an aryne tricarbonylchromium complex and the ferrocyne is basically achieved. Although instead of the authentic ferrocyne we obtained the 1,2-dideuterio ferrocene, this molecule can be regarded as ferrocyne. Since the usual elimination reactions of triflate and halides did not work, it can be concluded that ferrocyne is a very instable and very energy rich system, why the ferrocenyl triflates avoid the elimination and undergo readily the anionic thia-Fries rearrangement. Because the haloferrocene do not have this possibility, they do not undergo any reactions.

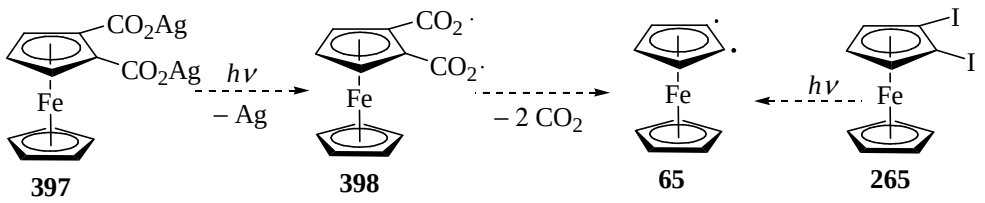
The chemo enzymatic desymmetrization of the *meso* rearrangement product **291** and the corresponding diacetate **293** is really promising and this research has to be followed up. The desymmetrization product **306** or **307** should be fully investigated and can be probably used as an additive in asymmetric synthesis. The new compounds **263**, **375, 395** and known **345** can be also subjected to the chemo enzymatic desymmetrization. The obtained ferrocene derivates with the planar chirality can be used in the asymmetric catalysis too. The chiral compound **376** can be also converted to the chiral amino acid via the described method before.



The 1,2-ferrocene diol can be used for the preparation of ferrocyne via a McMurry like reaction using various titanium reagents.

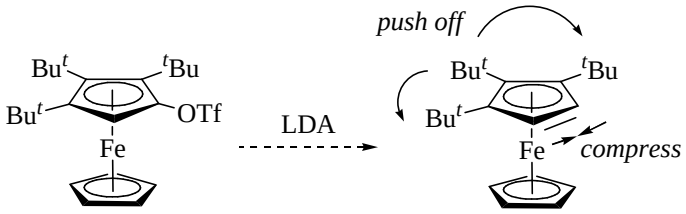


The 1,2-diiodo ferrocene can be irradiated to prepare the 1,2-ferrocene diradical **65b** too. Such radicals can be also generated from the compound **397**, because of the weak bond between the oxygen atom and the silver atom.



397 **398** **65** **265**

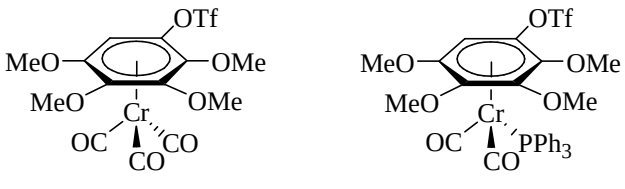
The triflate elimination should not yet be given up. It can be probably performed, if the ratio of bonds length to angles is improved. It can be achieved by introducing of bulky group into the ferrocene molecule (Compounds **399** and **400**)



399 **400**

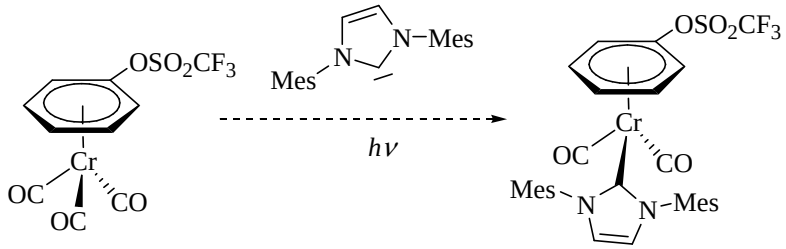
Although we synthesized the aryne tricarbonylchromium complex from the tributyl-(2-fluoro-phenyl)-stannane tricarbonylchromium (**174**), it can be not yet used preparatively and this kind of reaction is still in its infancy. Other reaction conditions such as other solvents, temperature, metallating reagents *etc*. should be tried.

Since the electron withdrawing nature of the tricarbonylchromium group is a major factor for the anionic thia-Fries rearrangement to overcome the desired elimination, it should be tried to prepare further phenyl triflate complexes bearing more electron rich substituents and ligands (**401** and **402**)



401 **402**

The corresponding phenols can be synthesized using methods described in this work. Parallel to phosphine ligands Arduengo carbenes could be also introduced as not less electron pushing ligands **403**.



57 **403**

D. Experimental section

1. General remarks

All operations with involving sensitive compounds were performed in a nitrogen or argon atmosphere using the Schlenk technique. Reaction vessels were heated at reduced pressure with a heat gun and flushed with nitrogen. This procedure was repeated three times. Tetrahydrofuran (THF) and diethyl ether were distilled with sodium wire / benzophenone in a nitrogen atmosphere. Ethanol and methanol were distilled with sodium wire in a nitrogen atmosphere. CH_2Cl_2 and diisopropylamine (DIPA) were distilled from $CaCl_2$ in a nitrogen atmosphere. Petroleum ether (PE) and *tert*-butylmethyl ether (TBME) were dried over $CaCl_2$ and distilled. Unless otherwise noted, chiral compound were obtained as racemates.

Preparative column chromatography was carried out using flash chromatography. For the chromatography of chromium compounds the silica gel (0.04 – 0.063 mm) was degassed by heating with a heat gun at reduced pressure and setting it under normal pressure with argon. All the solvents used for column chromatography were distilled over drying agents and then argonated for ca. 20 min by flushing with a constant argon stream. For the ferrocene chemistry all these procedures were carried out with nitrogen. The silica gel was neutralized with the solvents containing 5 % triethylamine (except the column chromatography of acids and phenols).

Thin layer chromatography (TLC) was carried out using aluminum TLC plates coated with the silica gel $60F_{254}$ from Merck. The detection of substances was done with the help of UV-lamp (λ = 254 nm) or developed with Ce(IV) sulphate reagent.

Infrared spectra (IR) were obtained using the spectrometer Perkin-Elmer FT 1710. The following abbreviations were used to indicate the intensity of absorption bands: br = broad, s = strong, m = medium, w = weak.

Mass spectra (MS) was carried out using a Finnegan AM 400 (ionization potential 70 eV). LC-MS (ESI) mass spectra were recorded on a Micromass LCT with Lock-Spray unit (ESI).

The injection was done in the Loop-modes in a HPLC-Alliance 2695 column. All values are given in atomic units of mass per elemental charge (*m/z*). The intensity is given as a percentage of the base peak.

High resolution mass spectra (HRMS) were recorded with the peak-matching method using perfluorokerosene (PFK) as the internal standard using a VG-Autospec spectrometer (NBA-Matrix) or with the peak–matching method in a Micromass LCT spectrometer with Lock-Spray-Unit (ESI).

^{1}H NMR spectra were measured using instruments Bruker WP 200 (200.1 MHz) and AVS 400 (400.1 MHz) at 25 °C. The chemical shifts refer to residual solvent signals of acetone (δ = 2.05 ppm, chloroform δ = 7.26 ppm, benzene δ = 7.16 ppm) as internal standards. The multiplicity of the peaks were abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

^{13}C NMR spectra were measured using instruments Bruker WP 200 (200.1, 50 MHz) and AVS 400 (400.1, 100 MHz) The chemical shifts refer to residual solvent signals (acetone δ = 29.8 ppm, chloroform δ = 77.2 ppm, benzene δ = 128.1 ppm) as internal standards.

^{31}P NMR spectra were measured using instruments Bruker AVS 400 (162 MHz). A solution of H_3PO_4 30 % in water was used as external reference.

Cyclovoltammetry was performed using Gamry Instruments Reference 600 potentiostat/galvanostat/ZRA with 0.1 mol/L tetrabutylammonium hexafluorophosphate electrolyte in acetonitrile at 25 °C, reference electrode Ag/Ag^+ ($AgNO_3$) electrode in acetonitrile with 0.01 mol/L $AgNO_3$ and 0.1 mol/L tetrabutylammonium hexafluorophosphate. Electrode material for the working and counter electrodes was platinum. The system was calibrated with ferrocene/ferrocinium, and the measured potentialy refer to FcH/FcH^+.

Elemenental analyses were carried out for CHN Rapid (Heraeus) with acetanilide as standard. All values are given as mass percentages.

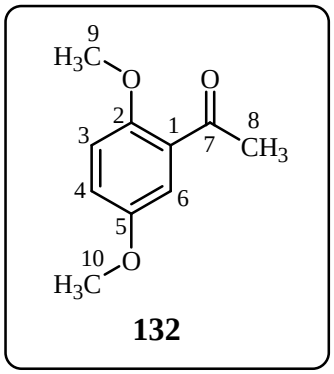
Melting points (m. p.) were determined with Electrothermal IA 9200 Series Digital Melting Point Apparatus.

Photochemical reactions were carried out using apparatus "Labor-UV-Reaktorsystem 1"from UV-Consulting Peschl®, a mercury lamp (TQ-150), 150 W placed in a quartz tube.

Microwave reactor (μW). The microwave reactions were carried out with the Discover® LabMate™ from CEM Corporation.

2. Preparation of arenes

2.1 1-(2,5-Dimethoxyphenyl)ethanone (132)

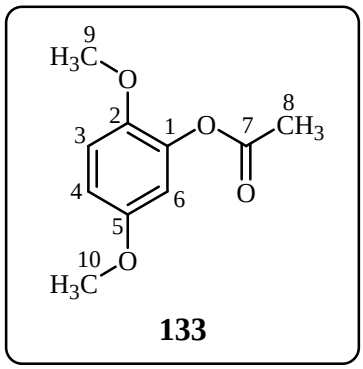


132

1,4-Dimethoxybenzene (5.00 g, 36.0 mmol) was dissolved in acetic anhydride (20 mL). H_3PO_4 (85 %, 7.4 mL) were added to the solution. The reaction mixture was stirred at 65 °C for 30 min. after cooling to 25 °C sodium hydroxide (6.00 g, 150.0 mmol)) in 50 mL water was added. After addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **132** (5.64 g, 31.3 mmol, 87 %) was isolated as a colourless oil, identified by comparison with literature data (^{1}H NMR).[172]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.61 (s, 3H, 8-H), 3.79 (s, 3H, 10-H), 3.87 (s, 3H, 9-H), 6.90 (d, *J* = 9.0 Hz, 1H, 3-H), 7.02 (dd, *J* = 8.9 Hz, 1H, 4-H), 7.28 (d, *J* = 3.2 Hz, 1H, 6-H), ppm.

2.2 2,5-Dimethoxyphenyl acetate (133)[82]

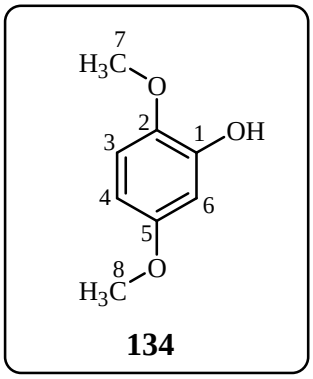


133

1-(2,5-dimethoxyphenyl)ethanone (**132**) (5.64 g, 31.3 mmol) was dissolved in 100 mL acetic acid. H_2O_2 (30 %, 20 mL) and TsOH (1.30 g, 7.3 mmol) were added to the solution. The reaction mixture was stirred at 25 °C for 12 h. Sodium thiosulphate (6.00 g) in water (50 mL) was added. After addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed with water(3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **133** (5.95 g, 30.4 mmol, 97 %) was isolated as colourless solid, identified by comparison with literature data (^{1}H NMR).[82]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.31 (s, 3H, 8-H), 3.75 (s, 3H, 10-H), 3.76 (s, 3H, 9-H), 6.64 (d, *J* = 3.0 Hz, 1H, 3-H), 6.73 (dd, *J* = 9.0 Hz, 1H, 4-H), 6.89 (d, *J* = 8.9 Hz, 1H, 6-H), ppm.

2.3 2,5-Dimethoxyphenol (134)[82]

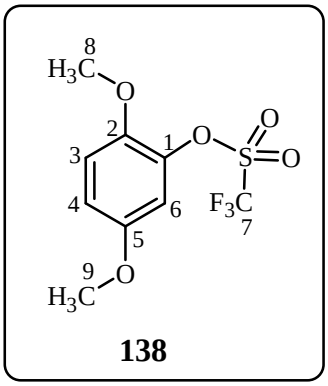


134

Water (40 mL) was added to 2,5-dimethoxyphenyl acetate (**133**) (5.95 g, 30.4 mmol) in ethanol (60 mL) and the mixture was heated to 70 °C. With stirring potassium hydroxide (8.5 g, 150.0 mmol) was added and the mixture was stirred at 70 °C for 30 min. After cooling to 25 °C HCl (37 % aqu., ca. 20 mL) was added with pH control till pH 6. After addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **134** (4.58 g, 29.7 mmol, 98 %) was isolated as colourless oil, identified by comparision wit literature data (^{1}H NMR).[82]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.75(s, 3H, 8-H), 3.84(s, 3H, 7-H), 6.37(dd, J = 9.0 Hz, 1H, 4-H), 6.56(d, J = 2.9 Hz, 1H, 3-H),6.77(d, J = 8.8 Hz, 1H, 6-H),ppm

2.4 2,5-Dimethoxyphenyl triflate (138)

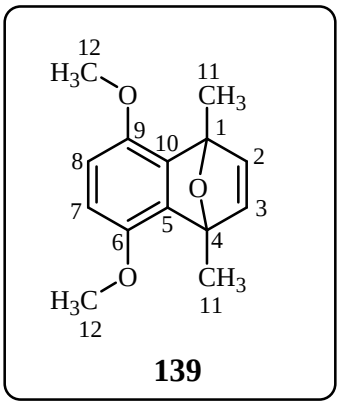


138

2,5-dimethoxy phenol (**134**) (0.82 g, 5.3 mmol) was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (2.1 mL, 26.0 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (1.1 mL, 6.4 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). **138** (1.52 g, 5.3 mmol, 100 %) was isolated as colourless oil

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.78 (s, 3H, 5-OCH_3), 3.87 (s, 3H, 2-OCH_3), 6.78-6.80 (m, 1H, 6-H), 6.84-6.87 (m, 1H, 3-H), 6.94-6.97 (m, 1H, 3-H)ppm.^{13}C NMR (400.1 MHz, $CDCl_3$): δ = 56.1 (C-9), 56.9 (C-8), 109.2 (C-6), 109.5 (C-4), 114.1 (C-3), 118.9 (q, $^1J_{C,F}$ = 320.4 Hz, CF_3), 138.9 (C-1), 145.7 (C-5) 153.7 (C-2)ppm. IR: $\tilde{\nu}$ = 2954 (w), 1597 (w), 1501 (m), 1417 (m), 1302 (w), 1248 (m), 1204 (s), 1169 (m), 1133 (s), 1032 (m), 882 (s), 833 (s) cm^{-1}.HRMS (ESI, acetonitrile):calcd. for $C_9H_9F_3O_5S$286.0123; found 286.0123. $C_{18}H_{23}FeNO_4$(286.01):calcd. C 37.77, H 3.17; found: C 37.65, H 3.34.

2.5 1,4-Dihydro-6,9-dimethoxy-1,4-dimethyl-1,4-epoxynaphthalene (139)

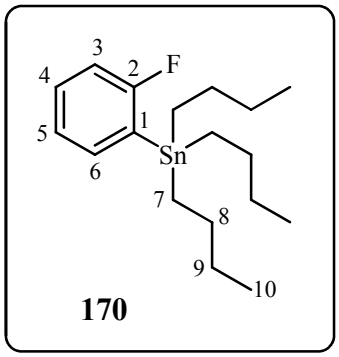


139

At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (1.10 mL, 2.7 mmol) in hexane and diisopropylamine (0.4 mL, 2.7 mmol) in THF (20 mL)] was added dropwise over 40 min to 2,5-dimethoxyphenyl triflate (**138**) (0.76 g, 2.7 mmol) and 2,5-dimethylfuran (1,14 mL, 11 mmol) in THF (20 mL). After warming to 25 °C and acidification by addition of 10 % aq. HCl (until pH 6) CH_2Cl_2 (50 mL) was added. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **139** (0.62 g, 2.7 mmol, 100 %) was isolated as awhite solid.

M. p. 72 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.99 (s, 6H, 11-H), 3.74 (s, 6H, 12-H), 6.54 [s, 2H, 2(3)-H], 6.83 [s, 2H, 7(8)-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 17.2 (C-11), 56.4 (C-12), 89.5 [C-1(4)], 112.0 [C-2(3)] 140.9 [C-5(10)], 147.3 [C-7(8)], 148.4 [C-6(9)] ppm. – IR: $\tilde{\nu}$ = 3787 (w), 2931 (m), 1602 (w), 1490 (s), 1443 (s), 1381 (w), 1294 (w), 1251 (s), 1215 (m), 1177 (m), 1147 (m), 1044 (s), 927 (w), 859 (m) cm^{-1}. – MS (70 eV): *m/z* (%): 232 (37) [M^+], 201 (46) [M^+ – OCH_3], 187 (100) [M^+ – OCH_3 – O], 170 (14) [M^+ – 2OCH_3], 156 (24) [M^+ – 2OCH_3 – O] – HRMS calcd. for $C_{14}H_{16}O_3$: 232.1098; found 232.1098. – Elemental analysis calcd. (%) for $C_{14}H_{16}O_3$: C 72.39, H 6.94; found: C 72.07, H 7.27.

2.6 Tributyl(2-fluorophenyl)stannane (170)

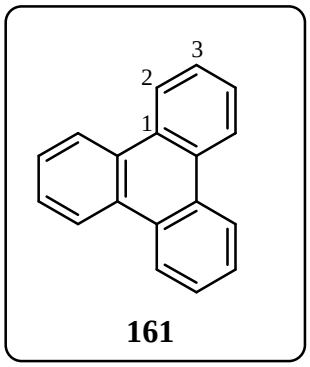


170

Fluorobenzene (10.0 mL, 10.2 g, 106.0 mmol) was dissolved in THF (250 mL), and after addition of KO^{t}Bu (11.9 g, 106.0 mmol) the mixture was cooled to –98 °C. With stirring the solution of *n*-BuLi in hexane (2.5 M, 42.5 mL, 106.0 mmol) was added. The mixture was stirred for 30 min at –98 °C, then $BuSnCl_3$ (95 %, 33.0 mL, 116.0 mmol) was added. After warming to 25 °C and addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE) and distilled (10^{-1} mbar, 145 °C), **170** (33.5 g, 86.9 mmol, 82 %) was isolated as colourless oil

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.17 Hz, 9H, CH_3), 1.07-1.62 (m, 18H, CH_2), 6.95-7.42 (m, 4H, Ph-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, DEPT 135, BB): δ = 10.0 (C-7), 13.8 (C-10), 27.4 (C-9), 29.1 (C-8), 114.4 (m, C-3), 124.2 (m, C-5), 127.0 (d, *J* = 46.0 Hz, C-1), 130.4 (m, C-4), 137.4 (m, C-6), 167.5 (d, *J* = 234.3 Hz, C-2) ppm. – IR: $\tilde{\nu}$ = 3064 (w), 2956 (s), 2922 (s), 2852 (m), 1592 (w), 1572 (w), 1461 (s), 1433 (s), 1377 (w), 1289 (w), 1254 (w), 1200 (s), 1103 (w), 1074 (w), 1052 (w), 1019 (w), 961 (w), 870 (m), 813 (m) cm^{-1}. – MS (70 eV): *m/z* (%): 386 (1) [M^+], 329 (100) [$M^+ - C_4H_9$], 272 (65) [$M^+ - 2C_4H_9$], 214 (88) [$M^+ - 3C_4H_9$]. – HRMS calcd. for $C_{18}H_{31}FSn$: 386.1432; found 386.1429. – Elemental analysis calcd. (%) for $C_{18}H_{31}FSn$: C 56.13, H 8.11; found: C 56.18, H 8.07.

2.7 Triphenylene (161)[96] and 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene(173)[170, 171]

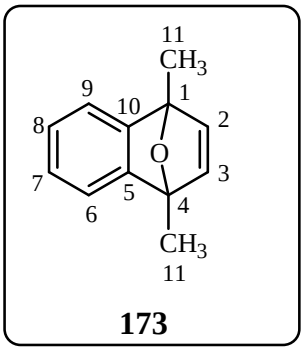


161

At –78 °C *n*-BuLi in hexanes (2.5 M, 1.5 mL, 3.7 mmol) was added to tributyl-(2-fluoro-phenyl)stannane (**170**) (1.0 mL, 1.3 g, 3.5 mmol) and 2,5-dimethylfuran (1.8 mL, 17 mmol) in THF (20 mL). After warming to 25 °C and addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3)

I. **161** (0.22 g, 2.9 mmol, 83 %) was isolated as a white solid, identified by comparison with literature data (^{1}H NMR).[96]

^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.45 (dd, *J* = 9.6 Hz, 6H, 2-H), 8.41 (dd, J = 9.5 Hz, 6H, 3-H) ppm.



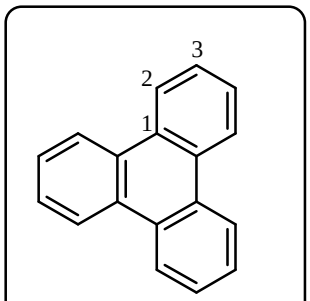
173

II 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene (**173**) (0.1 g, 0.6 mmol, 17 %) was isolated as a colourless oil, identified by comparison with literature data (^{1}H NMR).[170, 171]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.89 (s, 6H, 11-H), 6.77 [s, 2H, 2(3)-H], 6.95-6.99 [m, 2H, 6(9)-H], 7.10-7.15 [m, 2H, 7(8)-H] ppm.

Triphenylene (161)[96] **and 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene(173)**[170, 171]

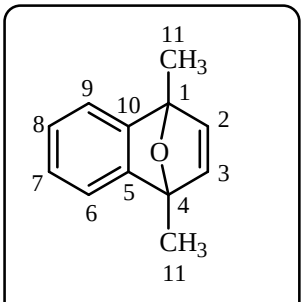
reaction in hexane



161

At –78 °C *n*-BuLi in hexanes (2.5 M, 1.5 mL, 3.7 mmol) was added to tributyl-(2-fluoro-phenyl)stannane (**170**) (1.0 mL, 1.3 g, 3.5 mmol) and 2,5-dimethylfuran (1.8 mL, 17 mmol) in hexane (20 mL). After warming to 25 °C and addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3)

I. **161** (0.07 g, 0.9 mmol, 28 %) was isolated as a white solid, identified by comparison with literature data (^{1}H NMR).[96]

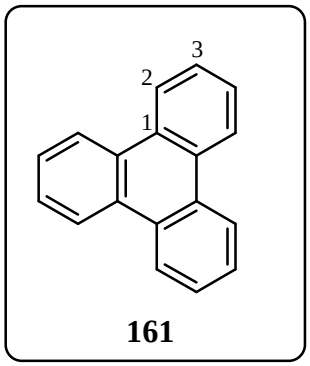


173

II 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene (**173**) (0.43 g, 2.5 mmol, 72 %) was isolated as a colourless oil, identified by comparison with literature data (^{1}H NMR).[170, 171]

Triphenylene (163)[96] **and 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene(175)**[170, 171]

reaction in hexane without dienes

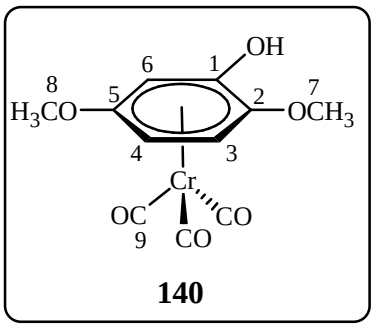


161

At –78 °C *n*-BuLi in hexanes (2.5 M, 1.5 mL, 3.7 mmol) was added to tributyl-(2-fluoro-phenyl)stannane (**170**) (1.0 mL, 1.3 g, 3.5 mmol) in hexane (20 mL). After warming to 25 °C and addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **161** (0.25 g, 3.6 mmol, 93 %) was isolated as a white solid, identified by comparison with literature data (^{1}H NMR).[96]

3. Synthesis of arene tricarbonylchromium complexes

3.1 Tricarbonyl(2,5-dimethoxyphenol)chromium(0) (140)



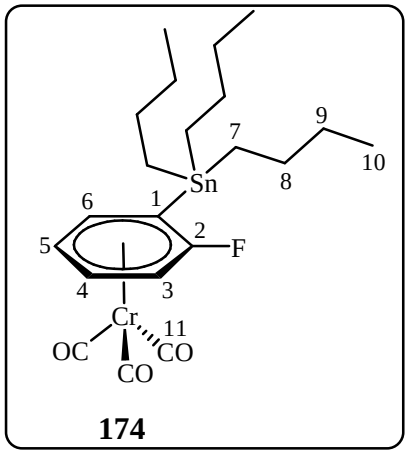
140

2,5-Dimethoxyphenol (**134**) (2.5 g, 16 mmol) and hexacarbonylchromium (4.3 g, 19 mmol) were heated in dibutyl ether and THF (10:1) at reflux for 3 d. After cooling to 25 °C the

rection mixture was carefully filtered through a P4 frit covered with 2 cm thick layer of silica gel. The solvents were removed at reduced pressure and the crude product was purified by flash chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). **140** (4.01 g, 13.9 mmol, 87 %) was isolated as a yellow solid, very sensitive against oxidation and light.

M. p. 47 °C (decomp.). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.68 (s, 3H, 8-H), 3.78 (s, 3H, 7-H), 4.64 (s, 1H, 6-H), 5.37 (s, 1H, 4-H), 5.48 (s, 1H, 3-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 56.1 (C-8), 58.6 (C-7), 68.9 (C-6), 69.6 (C-4), 78.5 (C-3) 122.2 (C-2), 132.9 (C-1), 139.7 (C-5), 234.0 (C-9) ppm. – IR: $\tilde{\nu}$ = 3095 (br), 2946 (w), 1953 (s, CO), 1863 (s, CO), 1521 (w), 1512 (m), 1490 (m), 1257 (m), 1180 (m), 1140 (w), 1088 (w), 1011 (m), 924 (w), 871 (w), 827 (w), 724 (m), 800 (m) cm^{-1} (s). – MS (70 eV): *m/z* (%): 290 (58) [M^+], 262 (16) [M^+ – CO], 234 (65) [M^+ – 2CO], 206 (74) [M^+ – 3CO], 154 (45) [M^+ – $Cr(CO)_3$] – HRMS calcd. for $C_{11}H_{10}CrO_6$: 289.9882; found 289.9874, – Elemental analysis calcd. (%) for $C_{11}H_{10}CrO_6$: C 45.53, H 3.47; found: C 45.18, H 3.07.

3.2 Tricarbonyl[tributyl-(2-fluorophenyl)stannane]chromium(0) (174)



174

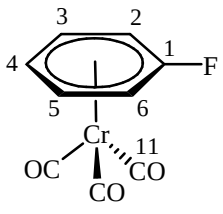
Tributyl(2-fluorophenyl)stannane (**170**) (10.0 mL, 11.7 g, 30.0 mmol) and hexacarbonyl-chromium (8.0 g, 36.0 mmol) were heated in dibutyl ether and THF (7:3) at reflux for 4 days. After cooling to 25 °C the reaction mixture was carefully filtered through a P4 frit covered with 2 cm thick layer of silica gel. The solvents were removed at reduced pressure and the

crude product was purified by flash chromatography (30 x 3 cm, SiO_2, PE). **174** (14.4 g, 27.6 mmol, 92 %) was isolated as a yellow oil, moderately stable against oxidation and light.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.3 Hz, 9H, 10-H), 1.15-1.64 (m, 18H, Bu-H), 4.82-4.86 (m, 1H, Ph-H), 5.30-5.33 (m, 1H, Ph-H), 5.39-5.46 (m, 1H, Ph-H) 5.57-5.61 (m, 1H, Ph-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 11.1 (C-7), 13.7 (C-10), 27.4 (C-9), 28.9 (C-8), 79.7-79.9 (m, C-3), 86.2-86.7 (m, C-5), 87.6-87.8 (m, C-1), 94.7-94.9 (m, C-4), 100.3-100.5 (m, C-6), 149.0-151.5 (m, C-2), 233.0 (C-11) ppm.* – IR: $\tilde{\nu}$ = 2957 (m), 2929 (m), 2860 (m), 1971 (s, CO), 1893 (s, CO), 1462 (m), 1374 (m), 1234 (w), 1199 (w), 1117 (m), 873 (w), 813 (w) cm^{-1}. – MS (70 eV): *m/z* (%): 522 (7) [M^+], 438 (10) [M^+ – 3CO], 386 (15) [M^+ – $Cr(CO)_3$], 329 (100) [M^+ – $Cr(CO)_3$ – Bu], 272 (65) [M^+ – $Cr(CO)_3$ – 2Bu], 215 (83) [M^+ – $Cr(CO)_3$ – 3Bu] – HRMS calcd. for $C_{21}H_{31}CrFO_3Sn$: 522.0684; found 522.0683. – Elemental analysis calcd. (%) for $C_{21}H_{31}CrFO_3Sn$: C 48.40, H 6.00; found: C 48.46, H 5.99.

* The multiplets are due to the coupling between C, Sn and F.

3.3 Tricarbonyl(fluorobenzene)chromium(0) (175)[173] and hexacarbonyl-(2-fluorobiphenyl)η^6:η^6-dichromium[99]



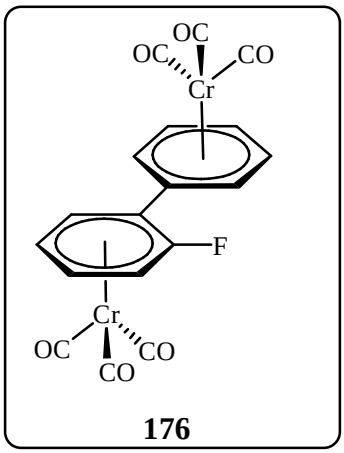
175

At –78 °C *n*-BuLi in hexanes (2.5 M, 0.8 mL, 2.1 mmol) was added to tricarbonyl[tributyl-(2-fluorophenyl)stannane]chromium(0) (**174**) (0.6 mL, 0.97 g, 1.8 mmol) in THF (20 mL). After warming to 25 °C and addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous

$MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3).

I. **175** (0.37 g, 1.6 mmol, 87 %) was isolated as a yellow solid, identified by comparison with literature data (^{1}H NMR).[173]

^{1}H NMR (400.1 MHz, [D_6]benzene): δ = 4.27 (m, 4H, Ph-H), 4.63 (m, 1H, Ph-H) ppm.



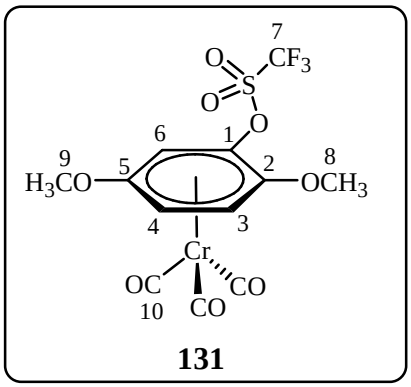
176

II **176** (0.06 g, 0.13 mmol, 7 %) was isolated as a yellow solid, identified by comparison with literature data (^{1}H NMR).[99]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.96 (m, 2H, Ph-H), 5.32 (m, 1H, Ph-H), 5.38 (m, 1H, Ph-H), 5.44 (m, 1H, Ph-H), 5.59 (m, 1H, Ph-H), 5.71 (m, 1H, Ph-H), 5.81 (m, 1H, Ph-H), ppm. - MS (70 eV): *m/z* (%):443 (30) [M^+], 360 (23) [M^+ – 3CO], 332 (20) [M^+ – 4CO], 304 (54) [M^+ – 5CO], 276 (40) [M^+ – 6CO], 224 (87) [M^+ – $Cr(CO)_3$ – 3CO], 172 (10) [M^+ – $Cr(CO)_3$ – $Cr(CO)_3$], 52 (100) [Cr^+].

4 Tricarbonylchromium phenyl triflate complexes

4.1 Tricarbonyl(2,5-dimethoxyphenyl)chromium(0) triflate (131)



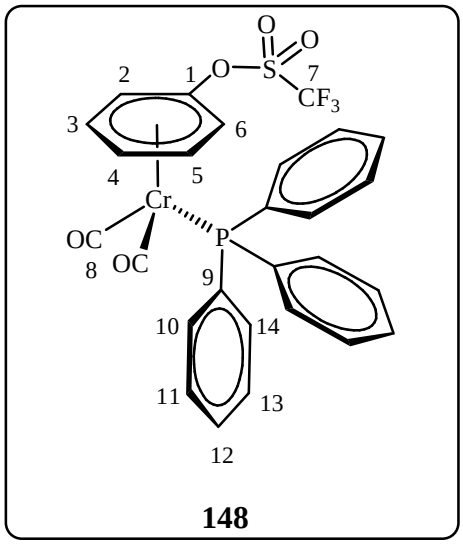
131

Tricarbonyl(2,5-dimethoxyphenol)chromium(0) (**140**) (4.01 g, 13.9 mmol) was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (85 % in oil, 0.56 g, 20.0 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (2.4 mL, 14.2 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **131** (5.8 g, 13.8 mmol, 99 %) was isolated as a yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.69 (s, 3H, 9-H), 3.78 (s, 3H, 8-H), 4.94 (d, J = 5.3 Hz, 1H, 6-H), 5.39-5.44 [m, 2H, 3(4)-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 56.6 (C-9), 58.4 (C-8), 73.4 (C-6), 74.1 (C-4), 75.8 (C-3) 118.6 (q, J = 320.9 Hz, C-7), 123.4 (C-1), 128.8 (C-5) 136.4 (C-2), 231.6 (C-10) ppm – IR: $\tilde{\nu}$ = 3368 (w), 2936 (w), 1978 (s, CO), 1898 (s, CO), 1531 (w), 1524 (m), 1480 (m), 1237 (m), 1191 (m), 1138 (w), 1078 (w), 1005 (m), 918 (w), 861 (w), 819 (w), 734 (m), 700 (m) cm^{-1} (s). – MS (70 eV): *m/z* (%): 422 (12) [M^+], 394 (16) [M^+ – CO], 366 (47) [M^+ – 2CO], 338 (62) [M^+ – 3CO], 286 (44) [M^+ – $Cr(CO)_3$], 286 (23) [M^+ – $Cr(CO)_3$ – SO_2CF_3] – HRMS calcd. for $C_{12}H_9CrF_3O_8S$: 421.9375; found 421.9374. – Elemental analysis calcd. (%) for $C_{12}H_9CrF_3O_8S$: C 34.13, H 2.15; found: C 34.18, H 2.12.

5. Photochemical ligand exchange of the phenyl triflate complexes 107 and 108

5.1 [Dicarbonylphenyltriflate(triphenylphosphine)]chromium(0) (148)

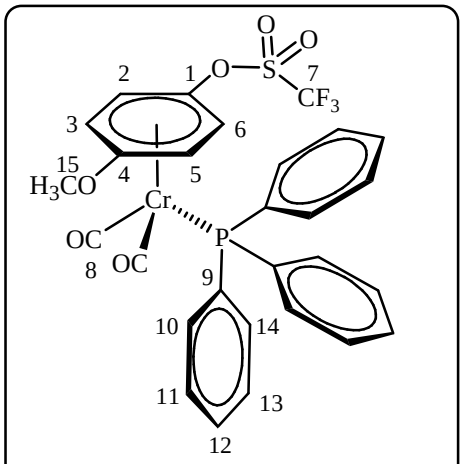


148

Triphenylphophine (6.5 g 24.9 mmol) was added to a solution of tricarbonyl(phenyltriflate)-chromium(0) (**107**)[50] (3.0 g, 8.3 mmol) in toluene (200 mL). The reaction mixture was irradiated for 25 min with a 125 W mercury lamp placed in a quartz tube, which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using a water condenser. The reaction progress was monitored by the TLC. After the completed consumption of the starting material (ca. 25 minutes) the reaction mixture was irradiated for further 20 minutes. The solvent was removed at reduced pressure and the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **148** (4.6 g, 7.6 mmol, 92 %) was isolated as an orange solid.

M. p. 105 °C (decomp.) ^{1}H NMR (400.1 MHz, acetone-d_6): δ = 4.57-4.63 (m 1H, 4-H), 4.97-5.04 [m 2H, 2(6)], 5.09-5.13 [m, 2H, 3(5)-H], 7.42-7.53 [m, 15H, P(C_6H_5)$_3$] ppm.^{13}C NMR (400.1 MHz, acetone-d_6): δ = 80.9 [C-3(5)], 87.9 (C-4), 88.9 [C-2(6)], 118.5 (q, $^{1}J_{C,F}$ = 321.9 Hz, CF_3), 127.9 (d, $^{2}J_{C,P}$ = 9.0 Hz, CPC*C*H), 129.3 (C-PCHCH*C*H) 129.5 (C-1), 132.8 (d, $^{3}J_{C,P}$ = 10.5 Hz, PCH*C*H), 138.3 (d, $^{4}J_{C,P}$ = 35.7 Hz PC), 238.5 (CO) ppm.^{31}P NMR (162 MHz, $CDCl_3$): δ = 87.74 ppm. IR: $\tilde{\nu}$ = 2362 (w), 1920 (s, CO), 1891 (s, CO), 1848 (s, CO), 1480 (w), 1416 (m), 1218 (m), 1125 (m), 1090 (w), 995 (w), 870 (w) cm^{-1}. MS (70 eV): *m/z* (%): 596 (10) [M^+], 568 (5) [M^+ – CO], 540 (25) [M^+ – 2CO], 314 (90) [$CrPPh_3^+$], 263 (100) [PPh_3]. HRMS:calcd. for$C_{27}H_{20}CrF_3O_5PS$596.0126; found 596.0124. $C_{27}H_{20}CrF_3O_5PS$ (596.48):calcd. C 54.37, H 3.38; found: C 54.33, H 3.41.

5.2 [Dicarbonyl(4-methoxyphenyl triflate)triphenylphosphine]chromium(0) (149)



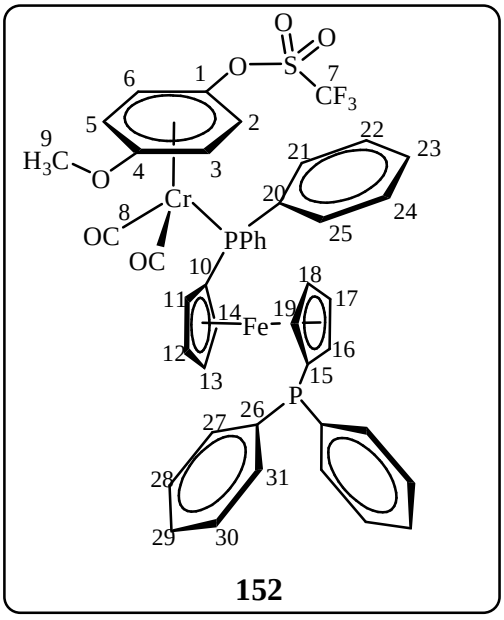
149

Triphenylphophine (6.1 g 23.1 mmol) was added to a solution of tricarbonyl(4-methoxy-phenyl)chromium(0) triflate (**108**)[50] (3.0 g, 7.7 mmol) in toluene (200 mL). The reaction mixture was irradiated for 25 min with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. The reaction progress was monitored by the TLC. After the completed exhaustion of the starting material (generally ca. 25 minutes) the reaction mixture was irradiated further 20 minutes.

The solvent was removed at reduced pressure and the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **149** (4.6 g, 7.3 mmol, 95 %) was isolated as an orange solid.

M. p. 115 °C (decomp.) ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.49 (s, 3H, OCH_3), 4.20-4.21[m, 2H, 3(5)-H], 4.90-4.92 [m, 2H, 2(6)-H], 7.36-7.52[m, 15H, $P(C_6H_5)_3$] ppm.–^{13}C NMR (400.1 MHz, $CDCl_3$): δ = 55.8 (OCH_3), 71.6 [C-3(5)], 83.6 [C-2(6)], 121.7 (q, $^1J_{C,F}$ = 321.2 Hz, CF_3), 122.5 (C-1), 128.3 (d, $^2J_{C,P}$ = 9.6 Hz, PC*C*H), 129.5 (PCCHCH*C*H) 133.1 (d, $^3J_{C,P}$ = 10.9 Hz, PCCH*C*H), 138.6 (d, $^4J_{C,P}$ = 35.4 Hz, PC), 238.5 (d, $^5J_{C,P}$ = 20.8 Hz, CO) ppm.– ^{31}P NMR (162 MHz, $CDCl_3$): δ = 87.73 ppm. IR: $\tilde{\nu}$ = 3059 (w), 1892 (s, CO), 1832 (s, CO), 1504 (m), 1463 (m), 1421 (m), 1244 (m), 1209 (s), 1135 (s), 1088 (m), 1018 (m), 872 (m) cm^{-1}. MS (70 eV): *m/z* (%): 626 (10) [M^+], 598 (6) [M^+ – CO], 570 (20) [M^+ – 2CO], 314 (90) [$CrPPh_3^+$], 263 (100) [PPh_3]. HRMS:calcd. for $C_{28}H_{22}CrF_3O_6PS$ 626.0232; found 626.0233. $C_{28}H_{22}CrF_3O_6PS$ (626.50): C 53.68, H 3.54; found: C 52.83, H 3.43.

5.3 [Dicarbonyl(4-methoxyphenyl)dppf]chromium(0) triflate (152)



152

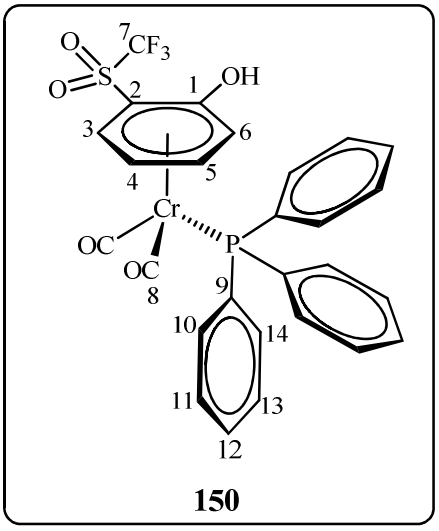
Dppf (0.3 g 0.5 mmol) was added to a solution of tricarbonyl(4-methoxyphenyl)chromium(0) triflate (**108**)[50] (0.1 g, 0.3 mmol) in toluene. The reaction mixture was irradiated for 25 min

with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. The reaction progress was monitored by the TLC. After the completed exhaustion of the starting material (generally ca. 25 minutes) the reaction mixture was irradiated further 20 minutes. The solvent was removed at reduced pressure and the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **152** (0.2 g, 0.2 mmol, 86 %) was isolated as an orange solid. This amount was sufficient only for the mass spectrum.

HRMS (ESI, acetonitrile) calcd. for $C_{44}H_{35}CrF_3FeO_6P_2S$: 918.0336; found 918.0336.

6 Anionic thia-Fries rearrangement of phenyl triflate tricarbonylchromium complexes and dicarbonyltriphenyl phosphinechromium complexes

6.1 [Dicarbonyl(2-trifluoromethylsulfonylphenol)triphenylphosphine]chromium(0) (150)



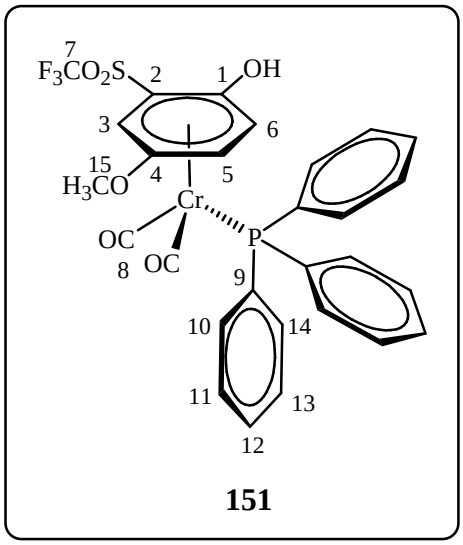
150

At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (1.36 mL, 3.4 mmol) in hexane and diisopropyl amine (1.5 mL, 10.2 mmol) in THF (20 mL)] was added dropwise over 40 min to [dicarbonyl(phenyl)triphenyl phosphine]chromium(0) triflate (**148**) (2.0 g, 3.4 mmol) in THF (20 mL). The colour changed from orange to deep red. After warming to 0 °C and

acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. The solvent was removed at reduced pressure and the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **150** (1.9 g, 3.2 mmol, 95 %) was isolated as a red solid.

M. p. 150 °C (decomp.) ^{1}H NMR (400.1 MHz, acetone-d_6): δ = 4.54 (d, *J* = 5.8 Hz, 1H, 6-H), 4.65(t, *J* = 5.5 Hz, 1H, 4H), 4.99 (q, *J* = 6.7 Hz, 1H, 5-H), 5.74 (d, *J* = 6.0 Hz, 1H, 5-H), 7.43-7.48 [m, 15H, $P(C_6H_5)_3$] ppm.^{13}C NMR (500.1 MHz, acetone-d_6): δ = 76.1 (C-6), 76.2 (C-4), 83.3 (C-2), 90.8 (C-5), 96.1 (C-3), 121.3 (q, $^1J_{C,F}$ = 326.5 Hz, CF_3), 122.6 (C-1), 129.0 (d, $^2J_{C,P}$ = 9.2 Hz, PC*C*H), 130.4 (d, $^3J_{C,P}$ = 1.7 Hz, PCCHCH*C*H), 133.7 (d, $^4J_{C,P}$ = 10.7 Hz, PCCH*C*H), 138.7 (d, $^5J_{C,P}$ = 35.4 Hz PC), 238.9 (d, $^6J_{C,P}$ = 21.4 Hz, CO) ppm– ^{31}P NMR (162 MHz, $CDCl_3$): δ = 85.15 ppm. IR: $\tilde{\nu}$ = 2891 (w), 1883 (s, CO), 1823 (s, CO), 1658 (w), 1504 (s), 1411 (s), 1134 (m), 1008 (m), 997 (m) cm^{-1}.MS (70 eV): *m/z* (%): 540 (10) [M^+ – 2CO], 314 (32) [$CrPPh_3$], 277 (7) [M^+ – 2CO– PPh_3], 262 (100) [PPh_3], 226 (3) [M^+ – 2CO– PPh_3– Cr], 184 (80) [PPh_2], 108 (43) [PPh], 94 (11) [M^+ – 2CO– PPh_3 – Cr – SO_2CF_3], 77 (21) [Ph], 52 (33) [Cr].

6.2 [Dicarbonyl(4-methoxy-2-trifluoromethylsulfonylphenol) triphenyl phosphine]chromium(0) (151)

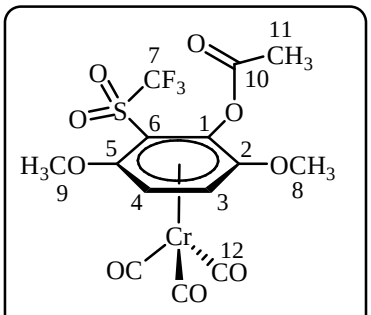


151

At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (1.3 mL, 3.2 mmol) in hexane and diisopropyl amine (1.5 mL, 10.2 mmol) in THF (20 mL)] was added dropwise over 40 min to [dicarbonyl(4-methoxy-phenyl)triphenyl phosphine]chromium(0) triflate (**149**) (2.0 g, 3.2 mmol) in THF (20 mL). The colour changed from orange to deep red. After warming to 0 °C and acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. The solvent was removed at reduced pressure and the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **151** (1.9 g, 3.1 mmol, 98 %) was isolated as a red solid.

M. p. 123 °C (decomp.), ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 3.99-4.01 (m, 1H, 6-H), 4.58-4.61 (m, 1H, 5-H), 5.22 (s, 1H, 3-H), 7.38-7.46 [m, 15H, $P(C_6H_5)_3$]ppm.^{13}C NMR (400.1 MHz, $CDCl_3$): δ = 56.6 (OCH_3), 68.2 (C-2), 70.8 (C-6), 76.7 (C-3), 82.6 (C-5), 125.3 (q, $^{1}J_{C,F}$= 327.8 Hz, CF_3), 121.2 (C-4), 128.7 (C-1), 128.4 (d, $^{2}J_{C,P}$ = 9.2 Hz, PC*C*H), 129.8 (d, $^{3}J_{C,P}$ = 2.0 Hz, PCCHCH*C*H) 133.2 (d, $^{4}J_{C,P}$ = 10.9 Hz, PC), 137.3 (d, $^{5}J_{C,P}$ = 36.3 Hz, PCCH*C*H), 238.0 (d, $^{6}J_{C,P}$ = 20.9 Hz CO) ppm.– ^{31}P NMR (162 MHz, $CDCl_3$): δ = 82.26 ppm. IR: $\tilde{\nu}$ = 2932 (w), 2129 (w), 1916 (s, CO), 1850 (s, CO), 1481 (m), 1432 (m), 1370 (m), 1201 (s), 1122 (m), 1090 (m), 1047 (m), 1024 (m), 895 (m), cm^{-1}.MS (70 eV): *m/z* (%): 570 (11) [M^+ – 2CO], 314 (27) [$CrPPh_3$], 308 (8) [M^+ – 2CO– PPh_3], 262 (100) [PPh_3], 256 (2) [M^+ – 2CO– PPh_3– Cr], 184 (64) [PPh_2], 108 (41) [PPh], 77 (20) [Ph], 52 (35) [Cr].

6.3 Tricarbonyl(2,5-dimethoxy-2-trifluoromethylsufonylphenyl)chromium(0) acetate (142)



142

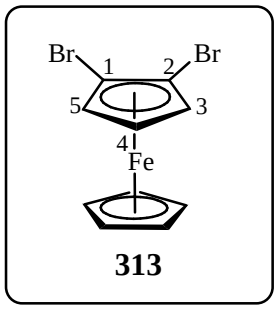
At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (1.0 mL, 2.4 mmol) in hexane and diisopropyl amine (0.8 mL, 5.0 mmol) in THF (20 mL)] was added dropwise over 40 min to tricarbonyl(2,5-dimethoxyphenyl)chromium(0) triflate (**131**) (1.0 g, 2.4 mmol) in THF (20 mL). The colour changed from orange to deep red. After warming to 0 °C acetyl chloride (5 mL) was added. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column

chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). **142** (1.1 g, 2.4 mmol, 99 %) was isolated as a red oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.32 [s, 3H, C(O)CH_3], 3.69 (s, 3H, 2-OCH_3), 3.78 (s, 3H, 5-OCH_3), 4.77 (d, J = 7.1 Hz, 1H, 3-H), 5.79 (d, J = 7.2 Hz, 1H, 4-H) ppm.^{13}C NMR (400.1 MHz, $CDCl_3$): δ = 20.6 [C(O)CH_3], 57.4 (2-OCH_3), 58.6 (5-OCH_3), 65.7 (C-3), 77.9 (C-4), 120.2 (q, $^1J_{C,F}$ = 328.0 Hz, CF_3), 125.2 (C-2), 139.9 (C-5), 168.6 (C-1), 228.9 (CO) ppm.IR: $\tilde{\nu}$ = 3129 (w), 2355 (w), 1985 (s, CO), 1938 (s, CO), 1902 (s, CO), 1785 (m, C=O), 1492 (m), 1426 (m), 1366 (m), 1267 (m), 1207 (s), 1159 (s), 1110 (m), 1060 (m), 1033 (m), 879 (m), 844 (w), cm^{-1}.MS (70 eV): *m/z* (%): 464 (15) [M^+], 436 (17) [M^+ – CO], 408 (25) [M^+ – 2CO], 380 (34) [M^+ – 3CO], 337 (100) [M^+ – 2CO–$COCH_3$]. HRMS:calcd. for $C_{14}H_{11}CrF_3O_9S$463.9481; found 463.9480.$C_{14}H_{11}CrF_3O_9S$ (464.29) C 36.22, H 2.39; found: C 36.23, H 2.42.

7 Preparation of 1.2-dihaloferrocenes

7.1 1,2-Dibromoferrocene (313)[143]



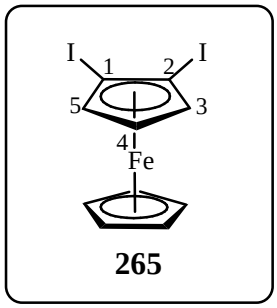
313

At –78 °C LiTMP in THF [prepared from 1.6 M *n*-BuLi (5.2 mL, 8.3 mmol) in hexane and 2,2,5,5-tetramethyl piperidine (1.6 mL, 9.1 mmol) in THF (20 mL)] was added dropwise to bromoferrocene[104, 105] (**206**) (2.00 g, 7.6 mmol) in THF (20 mL). The reaction mixture was warmed to – 25 °C and stirred 3 h. After cooling to – 78 °C a solution of $ZnCl_2$ (0.81 g, 7.6 mmol) in THF (20 mL) was added. The reaction mixture was stirred at – 78 °C 1 h. Br_2 (0.4 mL, 7.6 mmol) was slowly added. The reaction mixture was warmed up to 25 °C. $Na_2S_2O_3$

(1.87 g, 12.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1,2-Dibromoferrocene (**313**) (2.21 g, 6.5 mmol, 85 %) was isolated as red-brown solid, identified by comparison with literature data (^{1}H NMR).[143]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.14 [t. 1H, *J*(H;H) = 2.7 Hz, 4-H], 4.27 (s, 5H, Cp'-H), 4.45 [d, 2H, *J*(H,H) = 2.7 Hz, 3(5)-H] ppm.

7.2 1,2-Diiodoferrocene (265)[142]



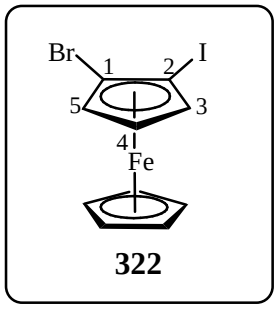
265

At –78 °C LiTMP in THF [prepared from 2.5 M *n*-BuLi (8.2 mL, 20.0 mmol) in hexane and 2,2,5,5-tetramethylpiperidine (3.8 mL, 20.2 mmol) in THF (50 mL)] was added dropwise to iodoferrocene[104, 105] (**211**) (5.80 g, 19.0 mmol) in THF (50 mL). The reaction mixture was warmed to – 25 °C and stirred 3 h. After cooling to – 78 °C a solution of $ZnCl_2$ (2.53 g, 19.0 mmol) in THF (20 mL) was added. The reaction mixture was stirred at – 78 °C 1 h. I_2 (4.72 g, 19.0 mmol) was slowly added. The reaction mixture was warmed up to 25 °C. $Na_2S_2O_3$ (3.74 g, 24.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column

chromatography (30 x 3 cm, SiO_2, PE). 1,2-Diiodoferrocene (**265**) (7.88 g, 18.0 mmol, 90 %) was isolated as red solid, identified by comparison with literature data (^{1}H NMR).[142]

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.19 (s, 5H, Cp'-H), 4.22 [t. 1H, *J*(H;H) = 2.7 Hz, 4-H], 4.51 [d, 2H, *J*(H,H) = 2.7 Hz, 3(5)-H] ppm.

7.3 1-Bromo-2-iodoferrocene (322)



322

Method A:

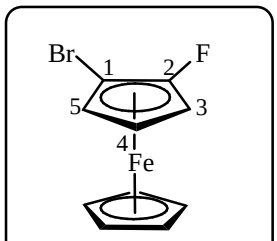
At –78 °C LiTMP in THF [prepared from 1.6 M *n*-BuLi (5.2 mL, 8.3 mmol) in hexane and 2,2,5,5-tetramethylpiperidine (1.6 mL, 9.1 mmol) in THF (20 mL)] was added dropwise to bromoferrocene[104, 105] (**206**) (2.00 g, 7.6 mmol) in THF (20 mL). The reaction mixture was warmed to – 25 °C and stirred 3 h. After cooling to – 78 °C a solution of $ZnCl_2$ (0.81 g, 7.6 mmol) in THF (20 mL) was added. The reaction mixture was stirred at – 78 °C 1 h. I_2 (1.93 g, 7.6 mmol) was slowly added. The reaction mixture was warmed up to 25 °C. $Na_2S_2O_3$ (1.87 g, 12.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1-Bromo-2-iodoferrocene (**322**) (2.64 g, 6.8 mmol, 89 %) was isolated as red-brown solid.

Method B:

At – 78 °C BuLi in hexane (2.5 M, 3.9 mL, 9.8 mmol) was added to a solution of 1,2-dibromoferrocene (**313**) (2 g, 9.8 mmol) in THF (50 mL). The reaction mixture was stirred 30 min. I_2 (2.50 g, 9.8 mmol) was added. The reaction mixture was warmed up to 25 °C. $Na_2S_2O_3$ (1.87 g, 12.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1-Bromo-2-iodoferrocene (**322**) (3.74 g, 9.6 mmol, 98 %) was isolated as red-brown solid.

M. p. 59 °C. – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.19 [t. 1H, *J*(H;H) = 2.7 Hz, 4-H], 4.22 (s, 5H, Cp'-H), 4.42 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H], 4.45 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H]) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 46.4 (Cp), 68.6 (Cp), 69.9 (Cp), 73.8 (Cp), 73.9 (Cp'), 84.8 (Cp) ppm. – IR: $\tilde{\nu}$ = 3095 (w), 1665 (w), 1478 (m), 1464 (s), 1412 (m), 1365 (m), 1368 (m), 1248 (m), 1107 (m), 1073 (m), 1018 (w), 1110 (m), 960 (m), 830 (m), 790 (m). – MS (70 eV): *m/z* (%): 390 (92) [M^+], 310 (5) [M^+ – Br], 263 (12) [M^+ – I], 184 (30) [M^+ – (Br + I)], 126 (100) [$2Cp^{2+}$], 56 (15) [Fe^+]. – HRMS calcd. for $C_{10}H_8BrFeI$: 389.8203; found 389.8201. – Elemental analysis calcd. (%) for $C_{10}H_8BrFeI$: C 30.73, H 2.06; found: C 31.06, H 2.06.

7.4 1-Bromo-2-fluoroferrocene (324)



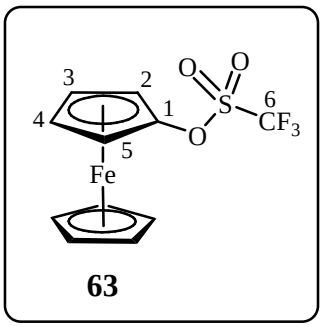
324

At – 78 °C BuLi in hexane (2.5 M, 3.9 mL, 9.8 mmol) was added to a solution of 1,2-dibromoferrocene (**313**) (2 g, 9.8 mmol) in THF (50 mL). The reaction mixture was stirred 30 min. NFSI (3.10 g, 9.8 mmol) was added. The reaction mixture was warmed up to 25 °C. $Na_2S_2O_3$ (1.87 g, 12.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1-Bromo-2-fluoroferrocene (**324**) (2.35 g, 8.3 mmol, 85 %) was isolated as yellow solid.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.80-3.82 (m, 1H, Cp-H), 4.13-4.14 (m, 1H, Cp-H), 4.30 (s, 5H, Cp'-H), 4.32-4.34 (m, 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 54.8 [d, *J*(C,F) = 58.7 Hz, Cp], 59.4 [d, *J*(C,F) = 12,2 Hz, Cp], 63.8 [d, *J*(C,F) = 2,3 Hz, Cp], 66.3 [d, *J*(C,F) = 58,2 Hz, Cp], 72.1 (Cp'), 132.8 [d, *J*(C,F) = 539,2 Hz, C-2] ppm. – IR: $\tilde{\nu}$ = 3098 (w), 1665 (w), 1467 (s), 1411 (m), 1367 (m), 1252 (m), 1107 (m), 1065 (w), 1018 (w), 1002 (m), 973 (m), 822 (m), 799 (m). – MS (70 eV): *m/z* (%): 282 (52) [M^+], 284 (48) [M^+], 263 (3) [M^+-F], 264 (3) [M^+-F], 203 (5) [M^+ – Br], 184 (15) [M^+ – (Br + F)], 126 (100) [$2Cp^{2+}$], 56 (15) [Fe^+] – HRMS calcd. for $C_{10}H_8BrFFe$: 281.9143; found 281.9142.

8 Preparation of ferrocenyl sulfonates

8.1 Ferrocenyl triflate (63)

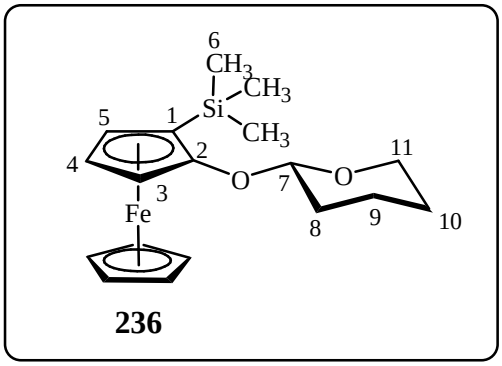


63

Water (40 mL) was added to ferrocenyl acetate[47] (**203**) (0.63 g, 2.6 mmol) in ethanol (60 mL) and the mixture was heated to 70 °C. With stirring potassium hydroxide (0.73 g, 13.0 mmol) was added and the mixture was stirred at 70 °C for 30 min. After cooling to 25 °C oxygen free 37 % aqu. HCl (ca. 2 mL) was added with pH control till pH 6. After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the remaining solid (ferrocenol) was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (1.1 mL, 13.0 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (0.52 mL, 3.1 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL) The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). Ferrocenyl triflate (**63**) (0.78 g, 2.3 mmol, 90 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 4.15 [t, 2H, *J*(H,H) = 1.95 Hz, Cp-H], 4.38 (s, 5H, Cp'-H), 4.68 [t, 2H, *J*(H,H) = 1.88 Hz, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, [D$_6$]acetone, DEPT 90, BB): δ = 61.8 (Cp), 64.9 (Cp), 70.8 (Cp'), 118.6 (q, ^1J(C,F) = 321 Hz, CF_3), 119.2 (C-1) ppm. – IR: $\tilde{\nu}$ = 2927 (w, Cp-H), 1421 (s), 1250 (m), 1205 (s, CF), 1138 (s, CF), 1108 (w), 1021 (w), 1003 (w), 921 (s), 848 (s), 826 (s), 767 (w), 701 (w), 669 cm^{-1} (w). – MS (70 eV): *m/z* (%): 334 (67) [M^+], 201 (84) [M^+ – Tf], 173 (49) [$CpOSO_2CF^+$], 148 (24) [OTf^+], 121 (100) [$FeCp^+$], 95 (9) [$SOCF^+$], 80 (22) [SO_3^+], 64 (24) [SO_2^+], 56 (37) [Fe^+] – HRMS calcd. for $C_{11}H_9F_3FeO_3S$: 333.9574; found 333.9573. – Elemental analysis calcd. (%) for $C_{11}H_9F_3FeO_3S$: C 39.55, H 2.72; found: C 39.46, H 2.61.

8.2 Trimethyl[2-(tetrahydropyran-2-yloxy)ferrocenyl]silane (236)

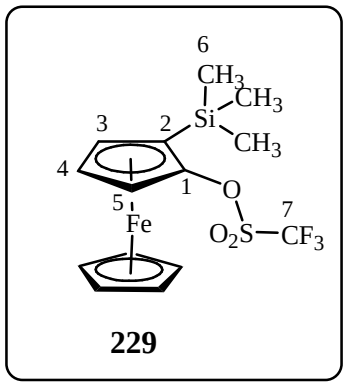


236

To a solution of tetrahydropyran-2-yloxyferrocene (**233**)[113] (1.62 g, 5.7 mmol) in Et_2O (50 mL), *n*-BuLi solution in hexane (2.5 M, 2.5 mL, 6.2 mmol) was added at – 78°C. The reaction mixture was stirred for 2 h. Me_3SiCl (0.78 mL, 6.2 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). Trimethyl[2-(tetrahydro-pyran-2-yloxy)ferrocenyl]silane (**236**) (1.94 g, 5.4 mmol, 95 %) was isolated as an orange oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.28 (s, 9H, 6-H), 1.55-1.89 (m, 6H, THP-H), 3.96 [t, 1H, *J*(H,H) = 2.47 Hz, Cp-H], 4.04-4.18 (m, 8H, Cp'-H, Cp-H, THP-H), 4.42-4.44 (m, 1H, Cp-H), 4.89 [t, 1H, *J*(H,H) = 2.35 Hz, 7-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = -0.1 (C-6), 18.8 (C-9), 25.6 (C-10), 30.8 (C-8), 56.3 (Cp), 59.2 (C-11), 59.8 (Cp), 61.9 (Cp'), 64.6 (Cp), 67.2 (Cp), 99.1 (C-7), 129.0 (C-2) ppm. – IR: $\tilde{\nu}$ = 3092 (w), 2948 (m, Cp-H), 1437 (s), 1412 (s), 1316 (m), 1241 (s), 1201 (w), 1111 (s), 1004 (s), 957 (s), 914 (m), 833 (s), 811 (s), cm^{-1} – MS (70 eV): *m/z* (%): 358 (52) [M^+], 274 (100) [M^+ – THP] – HRMS calcd. for $C_{18}H_{26}FeO_2Si$: 358.1051; found 358.1046. – Elemental analysis calcd. (%) for $C_{18}H_{26}FeO_2Si$: C 60.33, H 7.31; found: C 60.31, H 7.32.

8.3 *o*-Trimethylsilylferrocenyl triflate (229)



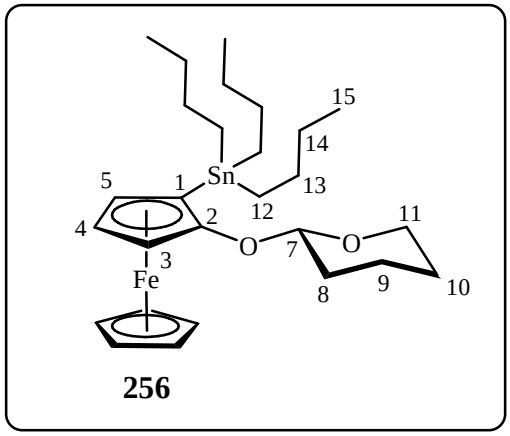
229

Trimethyl[2-(tetrahydropyran-2-yloxy)ferrocenyl]silane (**236**) (1.94 g, 5.4 mmol) was solved in ethanol and 3 *M* hydrochloric acid (30 mL) was added. The mixture was stirred for 1 h and diluted with water (50 mL). After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the remaining solid was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (1.1 mL, 13.0 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (0.52 mL, 6.5 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with

CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). The *o*-trimethylsilylferrocenyl triflate (**229**) (2.17 g, 5.4 mmol, 99 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.33 (s, 9H, 6-H), 3.9 [q, 1H, *J*(H,H) = 1.25 Hz, Cp-H], 4.17 [t, 1H, *J*(H,H) = 2.6 Hz, Cp-H], 4.69 (s, 5H, Cp'-H), 4.69 (s, 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = -0.2 (C-6), 63.1 (Cp), 65.3 (Cp), 66.7 (Cp), 69.4 (Cp), 70.5 (Cp'), 118.5 (q, ^1J(C,F) = 320.4 Hz, CF_3), 123.6 (C-1) ppm. – IR: $\tilde{\nu}$ = 2939 (m, Cp-H), 1429 (s), 1368 (w), 1205 (s), 1130 (s), 935 (s), 844 (s), 820 (s), 833 (s), 811 (s) cm^{-1} – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{17}F_3FeO_3SSi$: 405.9969; found 405.9988. – Elemental analysis calcd. (%) for $C_{14}H_{17}F_3FeO_3SSi$: C 41.39, H 4.22; found: C 41.31, H 4.24.

8.4 Tributyl-[2-(tetrahydro-pyran-2-yloxy)-ferrocenyl]-stannane (256)



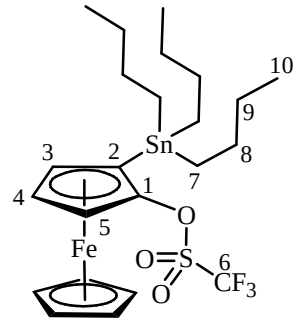
256

To a solution of tetrahydropyran-2-yloxyferrocene (**233**)[113] (2.90 g, 10.2 mmol) in Et_2O (50 mL), *n*-BuLi solution in hexane (2.5 M, 4.5 mL, 11.2 mmol) was added at – 78 °C. The reaction mixture was warmed to 25 °C and stirred for 2 h. The reaction mixture was cooled to – 78 °C and Bu_3SnCl (3.2 mL, 11.2 mmol, 95 %) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude

product was purified by column chromatography (30 x 3 cm, SiO_2, PE). Tributyl[2-(tetrahydropyran-2-yloxy)ferrocenyl]stannane (**256**) (5.59 g, 9.7 mmol, 95 %) was isolated as a red oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 [t, 9H, *J*(H,H) = 7.2, 15-H], 1.05-1.12 (m, 6H, Bu-H), 1.26-1.51 (m, 6H, Bu-H), 1.57-1.90 (m, 12H, Bu-H, THP-H), 3.66-3.71 (m, 2H, THP-H), 3.98 [t, 1H, *J*(H,H) = 2.56 Hz, Cp-H], 4.05-4.09 (m, 2H, THP-H), 4.14 (s, 5H, Cp'-H), 4.35-4.43 (m, 1H, Cp-H), 4.46-4.48 (m, 1H, Cp-H), 4.87 [t, 1H, *J*(H,H) = 2.56 Hz, 7-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 10.5 (C-12), 13.9 (C-15), 18.7 (C-9), 25.6 (C-10), 27.6 (C-14), 29.4 (C-13), 30.7 (C-8), 58.6 (C-11), 61.8 (Cp), 65.2 (Cp), 67.9 (Cp), 68.3 (Cp), 68.8 (Cp'), 99.1 (C-7), 130.0 (C-2) ppm. – IR: $\tilde{\nu}$ = 2953 (s Cp-H), 2924 (s Cp-H), 2871 (m), 2852 (m), 1652 (w), 1435 (s), 1399 (w), 1376 (w), 1355 (w), 1316 (m), 1236 (w), 1202 (m), 1182 (w), 1153 (w), 1113 (s), 1074 (m), 1037 (s), 1020 (s), 999 (s), 987 (m), 844 (m), 832 (s) cm^{-1}. – MS (70 eV): *m/z* (%): 576 (63) [M^+], 519 (23) [M^+ – Bu], 491 (51) [M^+ – THP], 434 (85) [M^+ – (THP + Bu)], 405 (15) [M^+ – 3 Bu], 377 (10) [M^+ – (THP + 2 Bu)], 320 (69) [M^+ – (THP + 3 Bu)], 291 (11) [$SnBu_3^+$], 200 (39) [FcO^+], 120 (16) [Sn^+], 85 (100) [THP^+], 56 (35) [Fe^+]. – HRMS calcd. for $C_{27}H_{44}FeO_2Sn$: 576.1713; found 576.1708. – Elemental analysis calcd. (%) for $C_{27}H_{44}FeO_2Sn$: C 56.38, H 7.71; found: C 54.88, H 7.68.

8.5 2-Tributylstannylferrocenyl triflate (255)

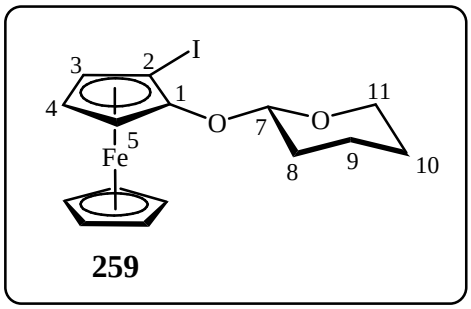


255

Tributyl[2-(tetrahydropyran-2-yloxy)ferrocenyl]stannane (**256**) (1.20 g, 2.1 mmol) was solved in ethanol and 3 *M* hydrochloric acid (30 mL) was added. The mixture was stirred for 1 h and diluted with water (50 mL). After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the remaining solid was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (0.8 mL, 10.0 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (0.42 mL, 2.5 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). 2-Tributylstannyl ferrocenyl triflate (**255**) (1.30 g, 2.1 mmol, 99 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 (t, 9H, *J* = 7.15 Hz, 10-H), 1.04-1.72 [m, 18H, Bu-H], 3.82 [q, 1H, *J*(H,H) = 1.28 Hz, Cp-H], 4.17 [t, 1H, *J*(H,H) = 2.54 Hz, Cp-H], 4.25 (s, 5H, Cp'-H), 4.68 (s, 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = -10.7 (C-7), 13.8 (C-10), 27.5 (C-9), 29.2 (C-8), 53.6 (Cp), 62.0 (Cp), 63.2 (Cp), 67.3 (Cp), 70.2 (Cp'), 118.6 (q, ^1J(C,F) = 320.8 Hz, C-6), 124.9 (C-1) ppm. – IR: $\tilde{\nu}$ = 2957 (m Cp-H), 2924 (m Cp-H), 2854 (m), 1464 (w), 1421 (m), 1315 (m), 1248 (m), 1209 (s), 1141 (s), 1108 (w), 1073 (w), 1028 (w), 1002 (w), 998 (s), 980 (m), 843 (m), cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{23}H_{35}F_3FeO_3SSn$: 624.0630; found 624.0638. – Elemental analysis calcd. (%) for $C_{23}H_{35}F_3FeO_3SSn$: C 44.33, H 5.66; found: C 44.61, H 5.87.

8.6 2-(2-Iodoferrocenoxy)tetrahydropyran (259)

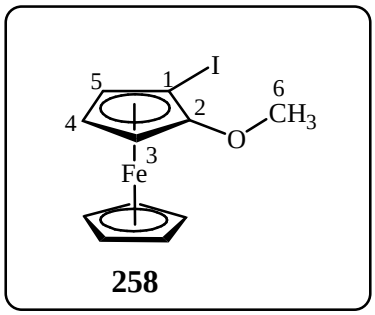


259

To a solution of tributyl[2-(tetrahydropyran-2-yloxy)ferrocenyl]stannane (**256**) (2.00 g, 3.5 mmol) in CH_2Cl_2 (20 mL) was added iodine (1.00 g, 3.9 mmol). The reaction mixture was stirred for 1 h. $Na_2S_2O_3$ (0.55 g, 3.5 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 2-(2-iodoferrocenoxy)tetrahydropyran (**259**) (1.44 g, 3.5 mmol, 100 %) was isolated as red solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.61-2.04 (m, 6H, THP-H), 3.98 [t, 1H, *J*(H,H) = 2.73 Hz, Cp-H], 4.09-4.16 (m, 3H, Cp-H, THP-H), 4.19 (s, Cp'-H), 4.32-4.33 (m, 1H, Cp-H), 4.87 [t, 1H, *J*(H,H) = 3.24 Hz, 7-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 18.9 (C-9), 25.5 (C-10), 30.7 (C-8), 57.5 (C-11), 62.5 (Cp), 63.5 (Cp), 68.4 (Cp), 71.5 (Cp'), 67.2 (Cp), 100.6 (C-7), 122.8 (C-2) ppm. – IR: $\tilde{\nu}$ = 3093 (w), 2941 (m Cp-H), 2871 (m Cp-H), 1456 (s), 1348 (m), 1247 (m), 1202 (m), 1112 (s), 1070 (w), 1026 (s), 972 (s), 970 (s), 906 (s), 872 (m), 815 (s) cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{15}H_{17}FeIO_2$: 411.9623; found 326.8969 (M^+ – THP). – Elemental analysis calcd. (%) for $C_{15}H_{17}FeIO_2$: C 43.72, H 4.16; found: C 43.62, H 4.18.

8.7 1-Iodo-2-methoxy ferrocene (258)



258

Method A:

Methoxyferrocene[47] (**226**) (0.50 g, 2.3 mmol) was dissolved in THF (250 mL), and after addition of KO^{t}Bu (0.26 g, 2.3 mmol) the mixture was cooled to –78 °C. With stirring the solution of *n*-BuLi in hexane (2.5 M, 0.9 mL, 2.3 mmol) was added. The mixture was stirred for 2 h at –78 °C, then I_2 (1.16 g, 4.6 mmol) was added and the reaction mixture was stirred for 30 min. After addition of $Na_2S_2O_3$ (0.47 g, 3.5 mmol) in water (10 mL) the reaction mixture was warmed to 25 °C and stirred for 10 min. After addition of water (50 mL) the mixture was extracted with TBME (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3) 1-iodo-2-methoxyferrocene (**258**) (0.50 g, 1.5 mmol, 64 %) was isolated as a red oil.

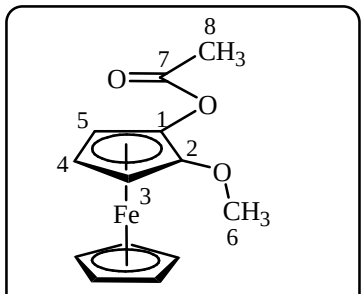
Method B:

2-(2-iodoferrocenoxy)tetrahydropyran (**259**) (1.44 g, 3.5 mmol) was dissolved in ethanol and 3 *M* hydrochloric acid (30 mL) was added. The mixture was stirred for 1 h and diluted with water (50 mL). After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the remaining solid was dissolved in THF (50 mL). At 25 °C NaH (0.18 g, 6.0 mmol, 80 % in mineral oil) was added. The solution was stirred for 1 h at 25 °C the colour changing from light yellow to red. After addition of Me_2SO_4 (0.33 mL, 3.5 mmol) the mixture was heated at reflux 24 h. Then 20 % aqu. KOH (20 mL) was added at 25

°C, and the mixture was heated at reflux for 1 h in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). 1-iodo-2-methoxyferrocene (**258**) (1.19 g, 3.5 mmol, 99 %) was isolated as a red oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.72 (s, 3H, 6-H), 3.94 [t, 1H, *J*(H,H)= 2.60 Hz, Cp-H], 4.07 [q, 1H, *J*(H,H) = 1.29 Hz, Cp-H], 4.16 [s, 1H, Cp-H], 4.19 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 51.8 (C-6), 58.4 (Cp), 62.5 (Cp), 68.6 (Cp), 71.4 (Cp'), 71.5 (Cp), 126.3 (C-2) ppm. – IR: $\tilde{\nu}$ = 3093 (m), 2928 (s Cp-H), 2856 (s Cp-H), 1720 (w), 1483 (s), 1458 (s), 1416 (s), 1369 (m), 1250 (s), 1203 (w), 1108 (m), 1071 (s), 1044 (s), 1020 (s), 975 (m), 947 (m), 908 (m), 872 (w), 816 (s) cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{11}H_{11}FeIO$: 341.9204; found 341.8497. – Elemental analysis calcd. (%) for $C_{11}H_{11}FeIO$: C 38.64, H 3.24; found: C 38.61, H 3.27.

8.8 2-Methoxyferrocenyl acetate (260)



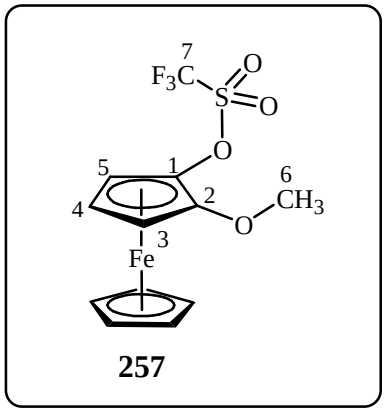
260

To a solution of 1-iodo-2-methoxyferrocene (**258**) (1.19 g, 3.5 mmol) in acetonitrile (50 mL) was added Cu_2O (0.61 g, 4.2 mmol) and acetic acid (0.63 mL, 0.60 g, 10.5 mmol). The reaction mixture was heated at reflux 3 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the

crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-methoxyferrocenyl acetate (**260**) (0.85 g, 3.1 mmol, 89 %) was isolated as a red solid.

M. p. 36 °C, ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.23 (s, 3H, 8-H), 3.65 [t, 1H, *J*(H,H)= 2.88 Hz, Cp-H], 3.69 (s, 3H, 6-H), 3.91 [q, 1H, *J*(H,H) = 1.46 Hz, Cp-H], 4.19 [q, 1H, *J*(H,H) = 1.42 Hz, Cp-H], 4.26 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 21.2 (C-8), 49.7 (C-6), 55.3 (Cp), 57.0 (Cp), 58.27 (Cp), 69.8 (Cp'), 105.1 (C-1), 118.0 (C-2), 169.5 (C-7) ppm. – IR: $\tilde{\nu}$ = 3099 (w), 2940 (m Cp-H), 1755 (s), 1507 (s), 1451 (m), 1422 (m), 1369 (m), 1286 (m), 1202 (s), 1125 (s), 1027 (m), 892 (m), 818 (w) cm^{-1} – MS (70 eV): *m/z* (%): 274 (41) [M^+], 231 (100) [M^+ – Ac], 121 (25) [$FeCp^+$], 56 (22) [Fe^+]. – HRMS calcd. for $C_{13}H_{14}FeO_3$: 274.0292; found 274.0291. – Elemental analysis calcd. (%) for $C_{13}H_{14}FeO_3$: C 56.97, H 5.15; found: C 55.30, H 5.22.

8.9 2-Methoxy ferrocenyl triflate (257)



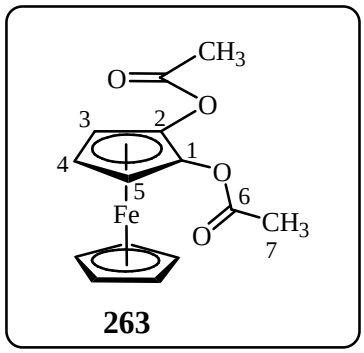
257

Water (40 mL) was added to 2-methoxyferrocenyl acetate (**260**) (0.85 g, 3.1 mmol) in ethanol (60 mL) and the mixture was heated to 70 °C. With stirring potassium hydroxide (0.87 g, 15.5 mmol) was added and the mixture was stirred at 70 °C for 30 min. After cooling to 25 °C oxygen free 37 % aqu. HCl (ca. 4 mL) was added with pH control till pH 6. After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the

remaining solid was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (1.2 mL, 15.5 mmol) the mixture was cooled to –78 °C. With stirring Tf_2O (0.62 mL, 3.7 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). 2-Methoxyferrocenyl triflate (**257**) (1.13 g, 3.1 mmol, 99 %) was isolated as an orange solid.

M. p. 38 °C. – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 3.77 (s, 3H, 6-H), 3.83 [t, 1H, *J*(H,H)= 2.95 Hz, Cp-H], 4.23 [q, 1H, *J*(H,H) = 1.50 Hz, Cp-H], 4.39 (s, 5H, Cp'-H), 4.42 [q, 1H, *J*(H,H) = 1.42 Hz, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, [D_6]acetone, DEPT 90, BB): δ = 51.1 (C-6), 56.6 (Cp), 57.3 (Cp), 58.9 (Cp), 71.4 (Cp'), 110.7 (C-1), 119.5 (q, *J*(C,F) = 320.2 Hz, C-7), 121.1 (C-2) ppm. – IR: $\tilde{\nu}$ = 3398 (w), 2954 (m Cp-H), 1772 (m), 1727 (m), 1514 (m), 1421 (s), 1284 (w), 1212 (s), 1139 (s), 1110 (m), 1043 (m), 992 (w), 861 (m) cm^{-1} – HRMS (ESI, acetonitrile) calcd. for $C_{12}H_{11}F_3FeO_4S$: 363.9680; found 363.9677. – Elemental analysis calcd. (%) for $C_{12}H_{11}F_3FeO_4S$: C 39.58, H 3.04; found: C 39.60, H 3.07.

8.10 1,2-Ferrocenediyl diacetate (263)



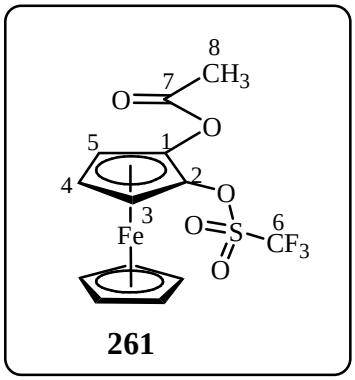
263

To a solution of 1,2-diiodoferrocene (**265**) (0.60 g, 1.4 mmol) in acetonitrile (50 mL) was added Cu_2O (0.48 g, 3.4 mmol) and acetic acid (0.53 mL, 0.51 g, 8.4 mmol). The reaction mixture was heated at reflux 3 h. After addition of water (50 mL) the mixture was extracted

with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 1,2-ferrocenediyl acetate (**263**) (0.37 g, 1.2 mmol, 88 %) was isolated as a red solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.22 (s, 6H, 7-H), 3.81 [t, 1H, *J*(H,H)= 2.92 Hz, 4-H], 4.21 (s, 5H, Cp'-H), 4.34 [d, 2H, *J*(H,H) = 2.95 Hz, 3(5)-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 21.2 (C-7), 57.4 [C-3(5)], 57.7 (C-4), 70.8 (Cp'), 106.8 [C-1(2)], 168.9 (C-6) ppm. – IR: $\tilde{\nu}$ = 3074 (w), 1755 (s), 1480 (m), 1435 (w), 1370 (m), 1278 (w), 1203 (s), 1104 (m), 1029 (m), 1006 (m), 893 (m), 814 (m) cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{14}FeO_4$: 302.0241; found 302.0232. – Elemental analysis calcd. (%) for $C_{14}H_{14}FeO_4$: C 55.66, H 4.67; found: C 55.11, H 4.69.

8.11 2-Trifluoromethanesulfonyloxy-ferrocenyl acetate (261) and 1,2-Ferrocendiyl ditriflate (264)



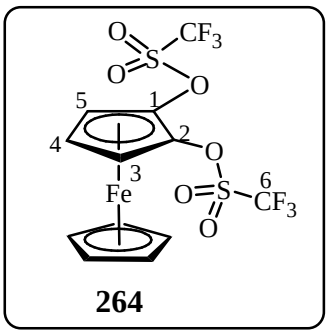
261

To a solution of 1,2-ferrocenediyl diacetate (**263**) (0.19 g, 0.6 mmol) in Et_2O (50 mL) was added a solution of MeLi in hexane (1.6 M, 0.4 mL, 0.6 mmol) at – 78 °C. The reaction mixture was stirred 30 min. With stirring Tf_2O (0.2 mL, 0.8 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at

reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2).

I 2-trifluoromethanesulfonyloxy acetate (**261**) (0.18 g, 0.46 mmol, 76 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 2.24 (s, 3H, 8-H), 4.02 [t, 1H, *J*(H,H)= 3.07 Hz, Cp-H], 4.26 [t, 1H, *J*(H,H) = 3.07 Hz, Cp-H], 4.41-4.43 (m, 6H, Cp'-H, Cp-H).ppm. – ^{13}C NMR (400.1 MHz, [D_6]acetone, DEPT 90, BB): δ = 21.0 (C-8), 57.9 (Cp), 59.1 (Cp), 59.2 (Cp), 72.5 (Cp'), 111.2 (C-2), 111.5 (C-1), 119.5 (q, *J*(C,F) = 320.1 Hz, C-6), 168.8 (C-7) ppm. – HRMS (ESI, acetonitrile) calcd. for $C_{13}H_{11}F_3FeO_5S$: 391.9629; found 391.9610.

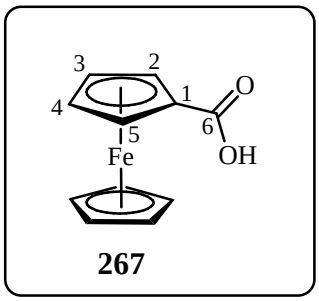


264

II 1,2-Ferrocendiyl ditriflate (**264**) (0.04 g, 0.07 mmol, 12 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 2.24 (s, 3H, 8-H), 4.02 [t, 1H, *J*(H,H)= 3.07 Hz, Cp-H], 4.26 [t, 1H, *J*(H,H) = 3.07 Hz, Cp-H], 4.41-4.43 (m, 6H, Cp'-H, Cp-H). ppm– ^{13}C NMR (400.1 MHz, [D_6]acetone, DEPT 90, BB): δ = 59.7 (Cp), 60.1 (Cp), 73.9 (Cp'), 111.9 [C-1(2)], 119.4 (q, *J*(C,F) = 319.9 Hz, C-6) ppm. – HRMS (ESI, acetonitrile) calcd. for $C_{12}H_8F_6FeO_6S_2$: 481.9016; found 481.9016.

8.12 Ferrocenecarboxylic acid (267)[107]

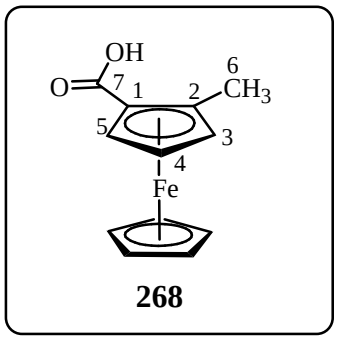


267

At 10 °C a solution of $NaOH/Br_2$ in Water [prepared from 50 mL water, NaOH (36.8 g, 920.0 mmol), and Br_2 (14.1 mL, 275.8 mmol)] was added slowly to a solution of acetylferrocene (**205**) (21 g, 92.1 mmol) in dioxan/water 1:1 (200 mL). During the reaction the temperature should not exceed 10 °C. If a precipitation is forming dioxane has to be added (in general 3 x 20 mL). After addition the reaction mixture was stirred for 1 h. $Na_2S_2O_3$ (7.90 g, 50.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After the solvent removal errocene carboxylic acid (**267**) (20.00 g, 87.5 mmol, 95 %) was isolated as red powder, identified by comparison with literature data (^{1}H NMR).[107]

^{1}H NMR (400.1 MHz, CDCl3): δ = 4.26 [s, 5H, Cp'-H], 4.47 [t, 2H, *J*(H,H) = 1.70 Hz, Cp-H], 4.86 [t, 2H, *J*(H,H) = 2.01 Hz, Cp-H] ppm.

8.13 2-Methylferrocenecarboxylic acid (268)[107, 174, 175]

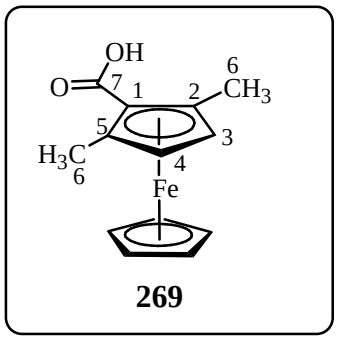


268

Ferrocene carboxylic acid (**267**) (3.0 g, 13.1 mmol) in THF (140 mL) was cooled to – 78 °C. To this clear red solution was added *s*-BuLi (1.6 M in cyclohexane, 16.4 mL, 26.2 mmol) during 10 min and the resulting suspension was stirred until the solid was redissolved (about 2 h). Then MeI (1.86 g, 0.82 mL, 13.1 mmol) was added and the solution was allowed to warm slowly to 25 °C. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-Methylferrocene carboxylic acid (**268**) (2.56 g, 10.5 mmol, 80 %) was isolated as a yellow solid, identified by comparison with literature data (^{1}H NMR).[174, 175]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3H, CH_3), 4.18 (s, 5H, Cp'-H), 4.31 [t, 1H, *J*(H,H) = 2.6 Hz, Cp-H], 4.38 [t, 1H, *J* (H,H) = 1.9 Hz, Cp-H], 4.79 [dd, 1H, *J* (H,H) = 1.6 Hz, *J* (H,H) = 2.6 Hz, Cp-H] ppm.

8.14 2,5-Dimethylferrocene carboxylic acid (269)

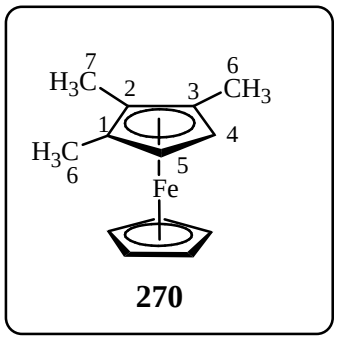


269

2-Methylferrocene carboxylic acid (**268**) (2.56 g, 10.5 mmol) in THF (140 mL) was cooled to – 78 °C. To this red solution was added *s*-BuLi (1.6 M in cyclohexane, 13.2 mL, 21.0 mmol) during 10 min and the resulting suspension was stirred until the solid was redissolved (about 2 h). Then MeI (1.49 g, 0.66 mL, 10.5 mmol) was added and the solution was allowed to warm slowly to 25 °C. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2,5-Dimethylferrocenecarboxylic acid (**269**) (1.63 g, 6.3 mmol, 60 %) was isolated as a yellow solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.56 (s, 6H, CH_3), 4.11 (s, 5H, Cp'-H), 4.25 [s, 2H, 3(4)-H] ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5 (C-6), 67.7 [C-2(5)], 71.4 (Cp'), 72.0 [C-3(4)], 87.8 (C-1), 180.4 (C-7) ppm. – IR: $\tilde{\nu}$ = 2589 (br, OH), 1671 (s, CO), 1435 (m), 1303 (m), 1257 (s), 1102 (m),), 814 (m) cm^{-1} – HRMS (ESI, acetonitrile): calcd. for: $C_{13}H_{14}FeO_2$ 258.0343; found: 258.0341. – Elemental analysis calcd. (%) for $C_{13}H_{14}FeO_2$: C 60.50, H 5.47; found: C 60.55, H 5.56.

8.15 1,2,3-Trimethylferrocene (270)

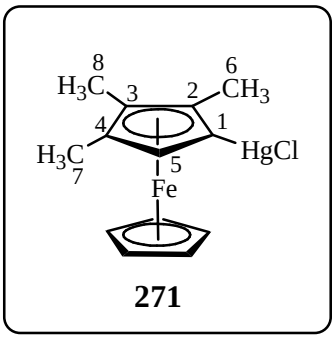


270

To a solution of 2,5-dimethylferrocene carboxylic acid (**269**) (1.63 g, 6.3 mmol) in CH_2Cl_2 (20 mL) was added $BH_3 \cdot SMe_2$ (0.98 g, 1.20 mL, 12.6 mmol). The reaction mixture was stirred at 25 °C for 78 h. After addition of water (50 mL) the mixture was extracted with PE (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1,2,3-Trimethylferrocene (**270**) (1.07 g, 4.7 mmol, 75 %) was isolated as a yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.87 (s, 9H, 6-H, 7-H), 3.94 [s, 7H, 4(5)-H, Cp-H]. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 11.5 (C-7), 13.7 (C-6), 66.7 [C-4(5)], 70.5 (Cp'), 82.9 (C-2), 83.1 [C-1(3)] ppm. – IR: $\tilde{\nu}$ = 3021 (w), 2920 (s, Cp-H), 2854 (Cp-H), 1465 (m), 1382 (m), 1295 (w), 1105 (m), 1029 (m), 1025 (m), 893 (s), cm^{-1} – MS (70 eV): *m/z* (%): 228 (100) [M^+], 213 (8) [$M^+ - CH_3$], 163 (12) [$M^+ - Cp$], 121 (18) [$FeCp^+$], 56 (15) [Fe^+]. – HRMS calcd. for $C_{13}H_{16}Fe$: 228,0601; found 228,0599. – Elemental analysis calcd. (%) for $C_{13}H_{16}Fe$: C 68.45, H 7.07; found: C 68.53, H 7.10.

8.16 2,3,4-Trimethyl(chloromercury)ferrocene (271)

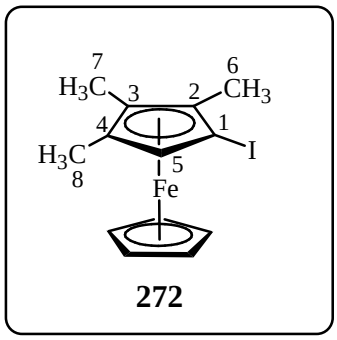


271

To a solution of 1,2,3-trimethylferrocene (1.63 g, 6.3 mmol) in toluene (50 mL) was added a solution of $Hg(OAc)_2$ (2.0 g, 6.3 mmol) in methanol (15 mL). The reaction mixture was stirred at 25 °C 48 h. After this time a solution of LiCl (0.3 g, 7.0 mmol) in 10 mL ethanol/water (1:1) was added and the reaction mixture was stirred at 25 °C 24 h. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the mixture of the desired 2,3,4-trimethyl chloromercuryferrocene (**271**) and higher mercurated compounds was isolated as a light yellow powder, which was used for the next reaction. The full characterization of **271** was not possible. A very small amount of **271** could be isolated by washing of the crude mixture with PE (3 x 100 mL) After removal of PE at reduced pressure, the 2,3,4-trimethyl chloromercury-ferrocene (**271**) was isolated as a yellow powder. This amount was sufficient for the spectroscopic characterization except the ^{13}C NMR and IR.

^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.83 (s, 9H, 6-H, 7-H, 8-H), 4.04 (s, 5H, Cp-H), 4.24 (s, 1H, 5-H) ppm. – MS (70 eV): *m/z* (%): 464 (63) [M^+], 227 (100) [M^+ – HgCl], 121 (60) [$FeCp^+$], 106 (41) [$CpMe_3^+$], 56 (40) [Fe^+], – HRMS calcd. for $C_{13}H_{15}ClFeHg$: 463.9918; found 463.9914. – Elemental analysis calcd. (%) for $C_{13}H_{15}ClFeHg$: C 33.71, H 3.26; found: C 33.76, H 3.06.

8.17 1-Iodo-2,3,4-trimethyl ferrocene (272)

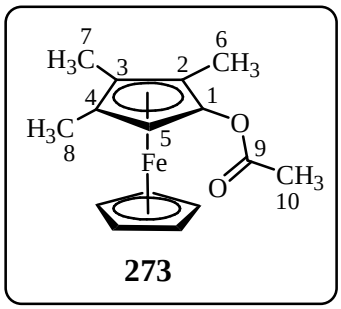


272

To the solution of the mixture of the 2,3,4-trimethyl chloromercuryferrocene (**271**) and higher mercurated compounds (*vide supra*) in CH_2Cl_2 was added I_2 (3.0 g, 11.8 mmol) The reaction mixture was stirred for 1 h. $Na_2S_2O_3$ (1.87 g, 12.0 mmol) in water (10 mL) was added and the reaction mixture was stirred for 10 min. After addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1-Iodo-2,3,4-trimethylferrocene (**272**) [0.33 g, 0.94 mmol, 15 % (reffering to **270** as the starting material)] was isolated as yellow oil.

^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 1.89 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.85 (s, 1H, 5-H), 3.91 (s, 5H, Cp-H). – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 9.3 (C-7), 10.9 (C-6), 13.3 (C-8), 45.2 (C-1), 69.3 (Cp), 70.9 (Cp), 72.6 (Cp'), 72.7 (Cp), 75.7 (Cp) ppm. – IR: $\tilde{\nu}$ = 3086 (w), 2947 (s, Cp-H), 2908 (Cp-H), 1703 (m), 1464 (m), 1378 (m), 1340 (m), 1243 (m), 1144 (w), 1102 (m), 1029 (s), 994 (s), 906 (w), 812 (s) cm^{-1} – HRMS (ESI, acetonitrile) calcd. for $C_{13}H_{15}FeI$: 353.9568; found 353.9565. – Elemental analysis calcd. (%) for $C_{13}H_{16}Fe$: C 44.11, H 4.27; found: C 43.53, H 5.12.

8.18 2,3,4-Trimethylferrocenyl acetate (273)

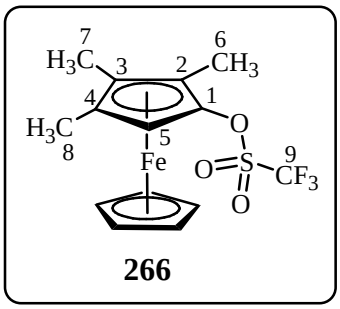


273

To a solution 1-iodo-2,3,4-trimethylferrocene (**272**) (0.33 g, 0.94 mmol) in acetonitrile (50 mL) was added Cu_2O (0.16 g, 1.13 mmol) and acetic acid (0.16 mL, 0.17 g, 2.8 mmol). The reaction mixture was heated at reflux 3 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 7:3). 2,3,4-trimethylferrocenyl acetate (**273**) (0.24 g, 0.84 mmol, 89 %) was isolated as a yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.88 (s, 3H, 8-H), 1.89 [s, 6H, 6(7)-H], 2.19 (s, 3H, 10-H), 3.95 (s, 5H, Cp'-H), 4.19 (s, 1H, 5-H). – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 10.5 (C-8), 11.2 (C-7), 13.0 (C-6), 21.2 (C-10), 60.4 (Cp), 71.4 (Cp'), 75.1 (Cp), 78.1 (Cp), 113.3 (C-1), 170.4 (C-9) ppm. – IR: $\tilde{\nu}$ = 2914 (m, Cp-H), 1753 (s), 1450 (m), 1368 (m), 1208 (s), 1029 (m), 937 (m), 885 (w) cm^{-1} – MS (70 eV): *m/z* (%): 286 (49) [M^+], 244 (100) [M^+ – Ac], 121 (38) [$FeCp^+$], 56 (10) [Fe^+]. – HRMS calcd. for $C_{15}H_{18}FeO_2$: 286.0656; found 286.0658.

8.19 2,3,4-Trimethyl ferrocenyl triflate (266)

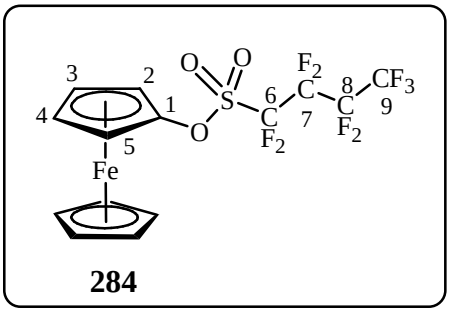


266

To a solution of 2,3,4-trimethylferrocenyl acetate (**273**) (0.24 g, 0.84 mmol) in Et_2O (20 mL) was added a solution of MeLi in hexane (1.6 M, 1.6 mL, 1.0 mmol) at – 78 °C. The reaction mixture was stirred 30 min. With stirring Tf_2O (0.2 mL, 1.8 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). 2,3,4-Trimethylferrocenyl triflate (**266**) (0.31 g, 0.83 mmol, 99 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.87 (s, 3H, 8-H), 1.89 (s, 3H, 7-H), 2.04 (s, 3H, 6-H), 4.05 (s, 5H, Cp'-H), 4.38 (s, 1H, 5-H). – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 10.4 (C-8), 11.0 (C-7), 12.8 (C-6), 59.9 (Cp), 72.2 (Cp'), 75.3 (Cp), 77.4 (Cp), 78.9 (Cp), 118.0 (C-1), 118.6 (q, *J*(C,F) = 320.9 Hz, C-9) ppm. – IR: $\tilde{\nu}$ = 2920 (m, Cp-H), 1418 (s), 1385 (m), 1368 (m), 1243 (m), 1203 (s), 1140 (s), 1106 (m), 1059 (m), 1033 (w), 1001 (w), 940 (s), cm^{-1} – MS (70 eV): *m/z* (%): 376 (45) [M^+], 244 (100) [$M^+ - SO_2CF_3$], 121 (45) [$FeCp^+$], 56 (14) [Fe^+]. – HRMS calcd. for $C_{14}H_{15}F_3FeO_3S$: 376.0043; found 376.0041 – elemental analysis calcd. (%) for $C_{14}H_{15}F_3FeO_3S$: C 44.70, H 4.02; found: C 45.42, H 4.29.

8.20 Ferrocenyl nonaflate (284)

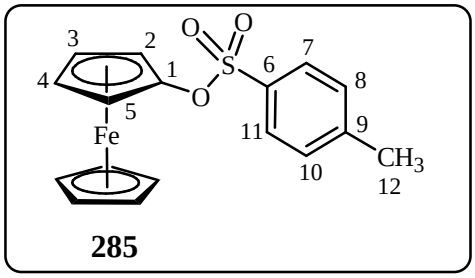


284

Water (40 mL) was added to ferrocenyl acetate[47] (**203**) (1.60 g, 6.5 mmol) in ethanol (60 mL) and the mixture was heated to 70 °C. With stirring potassium hydroxide (1.80 g, 32.0 mmol) was added and the mixture was stirred at 70 °C for 30 min. After cooling to 25 °C oxygen free 37 % aqu. HCl (ca. 4 mL) was added with pH control till pH 6. After addition of CH_2Cl_2 (50 mL) the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of $MgSO_4$ into a Schlenk flask. After solvent removal at reduced pressure the remaining solid was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (1.6 mL, 20.0 mmol) the mixture was cooled to –78 °C. With stirring Nf_2O (3.8 mL, 7.9 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:2). Ferrocenyl nonaflate (**284**) (2.83 g, 5.9 mmol, 90 %) was isolated as a yellow solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.04 [t, 2H, *J*(H,H)= 2.05 Hz, Cp-H], 4.33 (s, 5H, Cp'-H), 4.53 [t, 2H, *J*(H,H) = 1.88 Hz, Cp-H] ppm – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 61.3 (Cp), 61.4 (Cp), 64.2 (Cp'), 106.9-121.5 (m, C_4F_9), 119.6 (C-1) ppm. – IR: $\tilde{\nu}$ = 2600 (w, Cp-H), 1425 (m), 1351 (m), 1291 (w), 1229 (s), 1194 (s), 1142 (s), 1108 (w), 1021 (m), 1005 (m), 980 (s), cm^{-1} – MS (70 eV): *m/z* (%): 484 (56) [M^+], 201 (100) [$M^+ - SO_2C_4F_9$], 121 (45) [$FeCp^+$], 56 (14) [Fe^+]. – HRMS calcd. for $C_{14}H_9F_9FeO_3S$: 483.9478; found 483.9480. – Elemental analysis calcd. (%) for $C_{14}H_9F_9FeO_3S$: C 34.73, H 1.87; found: C 34.94, H 1.97.

8.21 Ferrocenyl tosylate (285)

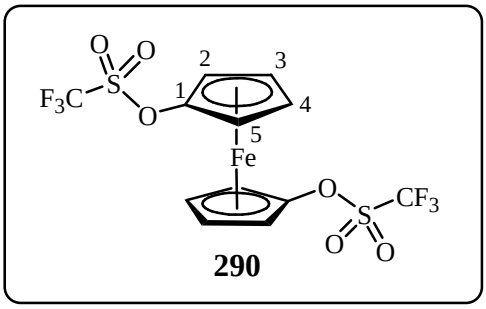


285

To a solution of ferrocenyl acetate[47] (**203**) (1.00 g, 4.1 mmol) in Et_2O (20 mL) was added a solution of MeLi in hexane (1.6 M, 2.8 mL, 4.5 mmol) at – 78 °C. The reaction mixture was stirred 30 min. With stirring TsCl (1.02 g, 4.9 mmol) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). Ferrocenyl tosylate (**285**) (1.39 g, 3.9 mmol, 95 %) was isolated as a light yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.43 (s, 3H, 12-H), 3.87 [t, 2H, *J*(H,H)= 1.95 Hz, Cp-H], 4.17 [t, 2H, *J*(H,H) = 1.91 Hz, Cp-H], 4.23 (s, 5H, Cp'-H), 7.29 [d, 2H, *J*(H,H) = 8.19 Hz, Ph-H], 7.66 [d, 2H, *J*(H,H) = 8.19 Hz, Ph-H] ppm – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 21.9 (C-12), 62.0 (Cp), 63.9 (Cp), 69.9 (Cp'), 127.2 (C-1), 128.8 (Ph), 129.7 (Ph), 130.4 (C-6), 132.1 (C-9) ppm. – IR: $\tilde{\nu}$ = 2364 (w, Cp-H), 1596 (m), 1437 (m), 1366 (s), 1296 (w), 1221 (w), 1174 (s), 1092 (m), 1021 (m), 926 (s), 824 (w), cm^{-1} – MS (70 eV): *m/z* (%): 356 (100) [M^+], 201 (57) [$M^+ - SO_2PhCH_3$], 121 (45) [$FeCp^+$], 91 [$PhCH_3^+$], 80 (14) [CpO^+], 65 (67) [Cp^+], 56 (41) [Fe^+]. – HRMS calcd. for $C_{17}H_{16}FeO_3S$: 356.0170; found 356.0171. – Elemental analysis calcd. (%) for $C_{17}H_{16}FeO_3S$: C 57.32, H 4.53; found: C 57.17, H 4.27.

8.22 1,1'-Ferrocenediyl ditriflate (290)



290

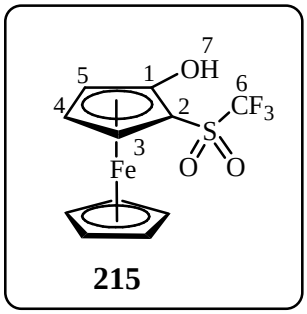
Water (40 mL) was added to 1,1'-ferrocenediyl diacetate[47] (0.61 g, 2.0 mmol) ethanol (60 mL), and the mixture was heated at 70 °C. Potassium hydroxide (1.12 g, 20.0 mmol) was added with stirring, and the mixture was stirred for 30 min at 70 °C. After cooling to 25 °C the mixture was acidified by addition of oxygen free 37 % aqu. HCl (ca. 3.5 mL) under pH control (until pH 6). CH_2Cl_2 (50 mL) was added and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure the remaining solid (1,1'-ferrocenediol) was dissolved in CH_2Cl_2 (50 mL), pyridine (1.6 mL, 20.0 mmol) was added. At –78 °C with stirring Tf_2O (0.8 mL, 4.8 mmol) was added. The mixture was stirred at –78 °C for 30 min, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous

$MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/CH_2Cl_2 8:3). 1,1'-Ferrocenediyl ditriflate (**290**) (0.87 g, 1.8 mmol, 90 %) was isolated as light yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.22 (s, 4H, Cp-H, Cp'-H), 4.69 ppm (s, 4H, Cp-H, Cp'-H) – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 63.3 (Cp), 66.5 (Cp), 118.6 (q, ^1J(C,F) = 321 Hz, CF_3), 118.9 ppm (C-1,1') – IR: $\tilde{\nu}$ = 3127 (w, Cp-H), 1422 (s), 1361 (w), 1252 (m), 1204 (s, CF), 1134 (s, CF), 1022 (m), 921 (s), 831 (s), 768 (w), 704 cm^{-1} (w) – MS (70 eV): *m/z* (%): 482 (34) [M^+], 269 (11) [$FeCpOTf^+$], 155 (100) [$CpOSO_2C^+$], 136 (12) [$FeCpO^+$], 82 (12) [CpO^+], 69 (10) [CF_3^+], 56 (12) [Fe^+]. – HRMS calcd. for $C_{12}H_8F_6FeO_6S_2$: 481.9016; found: 481.9020. – Elemental analysis calcd. (%) for $C_{12}H_8F_6FeO_6S_2$: C 29.89, H 1.67; found: C 30.05, H 1.67.

9 Anionic thia-Fries rearrangement of ferrocenyl sulfonates

9.1 2-(Trifluoromethylsulfonyl)ferrocenol (215)



215

Method A:

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (3.7 mL, 6.0 mmol) in hexane and diisopropylamine (2.6 mL, 18.0 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.0 g, 6.0 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a

Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2-(trifluoromethylsulfonyl)ferrocenol (**215**) was obtained as an orange solid (1.9 g, 5.9 mmol, 99 %).

Method B:

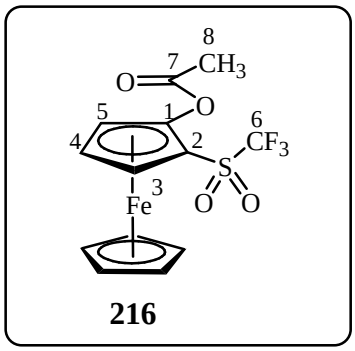
To a solution of 2-tributylstannyl ferrocenyl triflate (**255**) (0.06 g, 0.1 mmol) was added BuLi in hexane (2.5 M, 0.05 mL, 0.12 mmol) at – 78 °C. The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (20 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2-(trifluoromethylsulfonyl)ferrocenol (**215**) was obtained as an orange solid (0.03 g, 0.1 mmol, 99 %).

Method C:

To a solution of *o*-trimethylsilylferrocenyl triflate (**229**) (1.20 g, 2.9 mmol) in acetonitrile (20 mL) was added TBAF (0.78 g, 3.0 mmol) at 25 °C. The reaction mixture was stirred 24 h. After acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (20 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2-(trifluoromethylsulfonyl)ferrocenol (**215**) was obtained as an orange solid (0.81 g, 2.4 mmol, 84 %).

M. p. 72 °C. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.37 (s, 1H, Cp-H), 4.45 (s, 1H, Cp-H), 4.50 (s, 5H, Cp'-H), 4.71 (s, 1H, Cp-H), 5.18 (s, 1H, O-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB, HMQC): δ = 61.9 (Cp), 63.9 (Cp), 66.6 (Cp), 71.3 (C-2), 72.2 (Cp'), 119.4 (q, ^{1}J(C,F) = 324.7 Hz, CF_3), 123.7 (C-1) ppm. – IR: $\tilde{\nu}$ = 3406 (br, O-H), 3103 (w, Cp-H), 1496 (m), 1441 (s), 1384 (w), 1346 (m), 1332 (m), 1264 (m), 1177 (s, CF_3), 1108 (s), 1078 (s), 1032 (w), 1003 (m), 824 (m), 802 (m), 760 (w), 685 cm^{-1} (w). – MS (70 eV): *m/z* (%): 334 (100) [M^+], 333 (10) [M^+ – H], 201 (47) [FcO^+], 173 (12) [O-Cp-SO_2CF^+], 147 (12) [$CpSCF_2^+$], 121 (37) [$CpFe^+$], 95 (10) [$SOCF^+$], 81 (9) [CpO^+], 56 (19) [Fe^+]. – HRMS calcd. for $C_{13}H_{11}F_3FeO_4S$: 333.9574; found 333.9575. – Elemental analysis calcd. (%) for $C_{16}H_{12}F_6FeO_8S_2$: C 39.55, H 2.72; found: C 39.50, H 2.72.

9.2 2-(Trifluoromethylsulfonyl)ferrocenyl acetate (216)



216

Method A:

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (3.7 mL, 6.0 mmol) in hexane and diisopropylamine (2.6 mL, 18.0 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.00 g, 6.0 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure the remaining solid [2-(trifluoromethylsulfonyl)ferrocenol (**215**)] was dissolved in anhydrous CH_2Cl_2 (50 mL), and pyridine (2.2 mL, 26.0 mmol) was added.

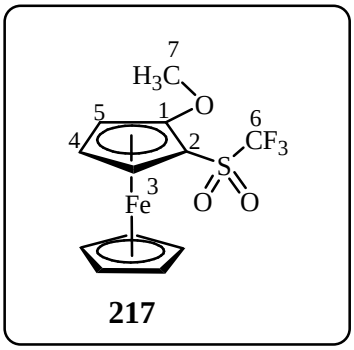
At –78 °C acetic anhydride (0.6 mL, 6.4 mmol) was added dropwise. The mixture was stirred at –78 °C for 30 min, then at 25 °C for 30 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 2-(Trifluoromethylsulfonyl)ferrocenyl acetate (**216**) (2.20 g, 5.9 mmol, 99 %) was isolated as a yellow solid: 2.2 g (5.9 mmol, 99%).

Method B:

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (4.3 mL, 6.9 mmol) in hexane and diisopropylamine (3.0 mL, 20.7 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.30 g, 6.9 mmol) in THF (20 mL). The colour of the mixture changed from light yellow to deep red. Acetyl chloride (0.5 mL, 7.1 mmol) was added, and the colour changed from deep red to yellow. After stirring at 25 °C for 30 min and addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 2-(Trifluoromethylsulfonyl)ferrocenyl acetate (**216**) (2.6 g, 6.8 mmol, 99 %) was isolated as yellow solid.

M. p. 74 °C. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 4.51 [t, J(H,H) = 2.9 Hz, 1H, Cp-H], 4.56 (s, 5H, Cp'-H), 4.59 [q, J(H,H) = 1.5 Hz, 1H, Cp-H], 4.96 [q, J(H,H) = 1.3 Hz, 1H, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 21.0 (CH_3), 67.2 (Cp), 67.5 (Cp), 67.9 (Cp), 68.5 (m, C-2), 72.8 (Cp'), 115.4 (C-1), 119.4 (q, ^1J(C,F) = 325.3 Hz, CF_3), 168.8 (CO) ppm. – IR: $\tilde{\nu}$ = 2924 (w, Cp-H), 1771 (s, C=O), 1443 (m), 1360 (m), 1261 (w), 1246 (w), 1214 (s), 1182 (s, CF_3), 1119 (m), 1079 (m), 1012 (m), 872 (m), 833 (m), 813 (m), 769 (m) cm^{-1}. – MS (70 eV): *m/z* (%): 376 (30) [M^+], 334 (100) [M^+ – Ac], 201 (68) [FcO^+], 173 (24) [O-Cp-SO_2CF^+], 121 (55) [$CpFe^+$], 95 (10) [$SOCF^+$], 81 (15) [CpO^+], 56 (45) [Fe^+]. – HRMS calcd. for $C_{13}H_{11}F_3FeO_4S$: 375.9680; found 375.9679. – Elemental analysis calcd. (%) for $C_{13}H_{11}F_3FeO_4S$: C 41.51, H 2.95; found: C 41.50, H 2.94.

9.3 1-Methoxy-2-(trifluoromethylsulfonyl)ferrocene (217)



217

Method A:

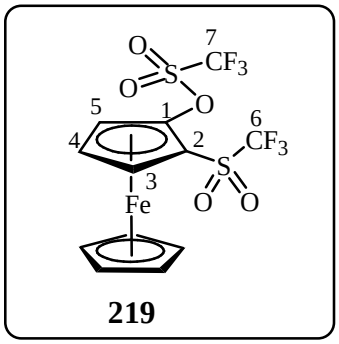
At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (3.6 mL, 5.8 mmol) in hexane and diisopropylamine (2.5 mL, 17.4 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (1.90 g, 5.8 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic phase was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reuced pressure the remaining solid [2-(trifluoromethylsulfonyl)ferrocenol (**215**)] was dissolved in THF (50 mL). At 25 °C NaH (0.18 g, 6.0 mmol, 80 % in mineral oil) was added. The solution was stirred for 1 h at 25 °C the colour changing from light yellow to red. After addition of Me_2SO_4 (0.55 mL, 5.8 mmol) the mixture was heated at reflux 24 h. Then 20 % aqu. KOH (20 mL) was added at 25 °C, and the mixture was heated at reflux for 1 h in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) water the mixture was extracted ethyl acetate (3 x 50 mL). The collected organic layers were washed water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1-Methoxy-2-(trifluoromethylsulfonyl)ferrocene (**217**) (1.42 g, 4.1 mmol, 70 %) was isolated as a red solid.

Method B:

At −78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (3.6 mL, 5.8 mmol) in hexane and diisopropylamine (2.5 mL, 17.4 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (1.90 g, 5.8 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 25 °C Me_2SO_4 (0.55 mL, 5.8 mmol) was added, and the mixture was heated at reflux for 24 h. Then 20 %-KOH (20 mL) in water was added at 25 °C and the mixture was heated at reflux for 1 hour in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) water the mixture was extracted ethyl acetate (3 x 50 mL). The collected organic layers were washed water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1-Methoxy-2-(trifluoromethylsulfonyl)ferrocene (**217**) (1.67 g, 4.8 mmol, 82 %) was isolated as a red solid.

M. p. 66.7 °C. – ^{1}H NMR (400.1 MHz, $CDCl_3$, HMBC): δ = 3.76 (s, 3H, CH_3) 4.34 [t, *J*(H,H) = 2.9 Hz, 1H, Cp-H], 4.47 [q, *J*(H,H) = 1.4 Hz, 1H, Cp-H], 4.5 [q, *J*(H,H) = 1.5 Hz, 1H, Cp-H], 4.52 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB, HMBC): δ = 57.1 (Cp), 58.8 (OCH_3), 65.5 (Cp), 66.1 (C-2), 66.6 (Cp), 71.3 (Cp'), 119.4 (q, ^1J(C,F) = 325.4 Hz, CF_3), 128.1 (C-1) ppm. – IR: $\tilde{\nu}$ = 3120 (w, Cp-H), 2946 (w), 1490 (s), 1463 (w), 1421 (m), 1382 (m), 1361 (s), 1257 (m), 1180 (s, CF_3), 1128 (s), 1088 (s), 1047 (m), 1024 (m), 1005 (m), 969 (m), 827 (m), 800 (m), 760 (w), 676 cm^{-1} (w). – MS (70 eV): *m/z* (%): 348 (100) [M^+], 214 (10) [M^+ – (Cp + CF_3 + CH_3)], 186 (44) [$CpFeCp^+$], 121 (48) [$CpFe^+$], 56 (19) [Fe^+]. – HRMS calcd. for $C_{12}H_{11}F_3FeO_3S$: 347.9730; found 347.9729. – Elemental analysis calcd. (%) for $C_{12}H_{11}F_3FeO_3S$: C 41.40, H 3.18; found: C 41.42, H 3.21.

9.4 2-(Trifluoromethylsulfonyl)ferrocenyl triflate (219)

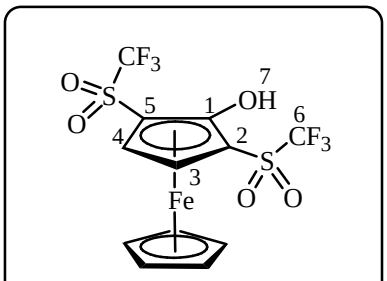


219

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (3.9 mL, 6.3 mmol) in hexane and diisopropylamine (2.7 mL, 18.9 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.10 g, 6.3 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification with oxygen free 10 % HCl (until pH 6), CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure the remaining solid [2-(trifluoromethylsulfonyl)ferrocenol (**215**)] was dissolved in CH_2Cl_2 (50 mL), pyridine (2.3 mL, 27.0 mmol) was added and at –78 °C Tf_2O (1.2 mL, 6.9 mmol) was added dropwise. The mixture was stirred at –78 °C for 30 min, then at 25 °C for 30 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL), the collected organic layers were washed three times with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 2-(trifluoromethylsulfonyl)ferrocenyl triflate (**219**) (2.86 g, 6.2 mmol, 99 %) was isolated as yellow solid.

M. p. 86 °C. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.59 (s, 1H, Cp-H), 4.69 (s, 6H, Cp-H, Cp'-H), 5.04 [s, 1H, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 66.1 (Cp), 68.1 (Cp), 68.8 (Cp), 69.2 (C-2), 74.0 [Cp'], 117.7 (C-1), 118.4 (q, J = 320.3 Hz, C-6, CF_3), 119.4 (q, ^{1}J(C,F) = 324.9 Hz, C-7, CF_3) ppm. – IR: $\tilde{\nu}$ = 3113 (w), 2924 (w), 1421 (s), 1371 (s), 1251 (m), 1217 (s), 1194 (s), 1137 (s), 1122 (s), 1077 (m), 1030 (w), 996 (m), 821 (s), 765 (w), 700 cm^{-1} (w). MS (70 eV): *m/z* (%): 466 (100) [M^+], 333 (87) [M^+–Tf], 200 (49) [M^+ – 2Tf], 172 (26) [O-Cp-SO_2CF^+], 121 (48) [$FeCp^+$], 95 (9) [$SOCF^+$], 56 (49) [Fe^+]. – HRMS calcd. for $C_{12}H_8F_6FeO_5S_2$: 465.9067; found: 465.9070. – Elemental analysis calcd. (%) for $C_{12}H_8F_6FeO_5S_2$: C 30.92, H 1.73; found: C 30.92, H 1.70.

9.5 2,5-Bis(trifluoromethylsulfonyl)- ferrocenol (220)

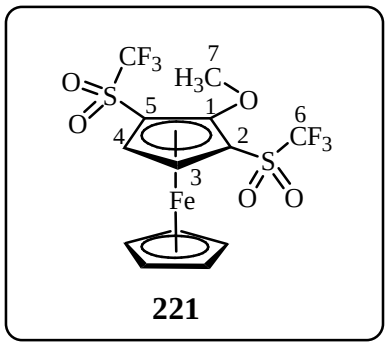


220

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (2.7 mL, 4.4 mmol) in hexane and diisopropylamine (1.9 mL, 13.2 mmol) in THF (20 mL)] was added dropwise over 40 min to 2-(trifluoromethylsulfonyl)ferrocenyl triflate (**219**) (2.05 g, 4.4 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal 2,5-bis(trifluoromethylsulfonyl)ferrocenol (**220**) was isolated as a orange solid (2.00 g, 4.3 mmol, 99 %).

M. p. 140 °C (dec.). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.82 (s, 5H, Cp'-H), 4.87 (s, 2H, Cp-H), 5.83 (s 1H, OH) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB, HMBC): δ = 67.8 (Cp), 68.3 [C-2(5)], 75.1 (Cp'), 119.3 [q, J(C,F) = 324.8 Hz, CF_3], 124.5 (C-1) ppm. – IR: $\tilde{\nu}$ = 3423 (br, O-H), 3115 (w, Cp-H), 2925 (w), 1484 (m), 1394 (w), 1366 (m), 1337 (m), 1198 (s, CF_3), 1179 (s, CF_3), 1146 (s), 1096 (s), 1021 (m), 889 (w), 875 (w), 842 (w), 805 (w), 764 (w), 704 (w), 678 cm^{-1} (m). – MS (70 eV): *m/z* (%): 446 (100) [M^+], 333 (17) [M^+ – (SO_2CF_3 + H)], 138 (38) [$FeCpO^+$], 121 (41) [$CpFe^+$], 95 (5) [$SOCF^+$], 81 (9) [CpO^+], 56 (19) [Fe^+]. – HRMS calcd. for $C_{13}H_{11}F_3FeO_4S$: 465.9067; found 465.9063. – Elemental analysis calcd. (%) for $C_{16}H_{12}F_6FeO_8S_2$: C 30.92, H 1.73; found: C 31.40, H 1.74.

9.6 1-Methoxy-2,5-bis(trifluoromethylsulfonyl)–ferrocene (221)



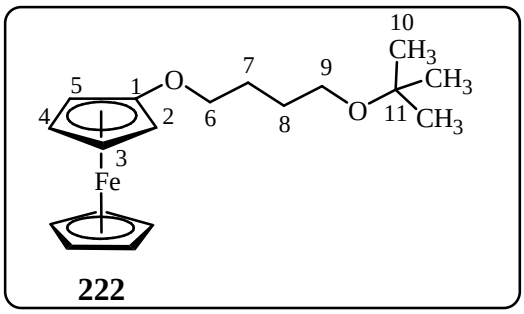
221

At –78 °C LDA in THF [prepared from 1.6 M *n*-BuLi (2.7 mL, 4.4 mmol) in hexane and diisopropylamine (1.9 mL, 13.2 mmol) in THF (20 mL)] was added dropwise over 40 min to 2-(trifluoromethylsulfonyl)ferrocenyl triflate (**219**) (1.8 g, 4.4 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal the remaining solid [2,5-bis(trifluoromethylsulfonyl)ferrocenol (**220**)] was dissolved in THF (50 mL). At 25 °C NaH (0.2 g, 6.0 mmol, 80 % in mineral oil) was added. The solution was stirred for 1 h at 25 °C and the colour changed from light yellow to red. Me_2SO_4 (0.4 mL, 4.4 mmol) was added and the mixture was heated at reflux for 24 h.

20 % aqu. KOH (20 mL) was added, and the mixture was heated at reflux for 1 hour in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1-Methoxy-2,5-bis(trifluoromethylsulfonyl)ferrocene (**221**) (1.6 g, 3.3 mmol, 75%) was isolated as yellow solid.

M. p. 114 °C. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.02 (s, 3H, OCH_3), 4.84 (s, 2H, Cp-H), 4.93 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 67.7 (OCH_3), 69.7 [C-3(4)], 74.1 [C-2(5)], 75.3 (Cp'), 119.4 [q, *J*(C,F) = 325.2 Hz, CF_3], 127.6 (C-1) ppm. – IR: $\tilde{\nu}$ = 3113 (w, Cp-H), 2964 (w), 1471 (m), 1388 (s), 1357 (s), 1382 (m), 1203 (s, CF_3), 1149 (s, CF_3), 1099 (s), 1080 (m), 1030 (m), 964 (m), 849 (m), 821 (w), 768 (w), 766 (w), 677 (w) cm^{-1}. – MS (70 eV): *m/z* (%) = 480 (100) [M^+], 262 (43) [$Cp(SO_2)Tf^+$], 127 (22) [$CpSO_2^+$], 121 (62) [$FeCp^+$], 56 (20) [Fe^+]. – HRMS calcd. for $C_{13}H_{10}F_6FeO_5S_2$: 479.9223; found: 479.9225. – Elemental analysis calcd. (%) for $C_{13}H_{10}F_6FeO_5S_2$: C 32.52, H 2.10; found: C 32.50, H 2.11.

9.7 (4-*Ttert*-Butoxy-butoxy)ferrocene (222)



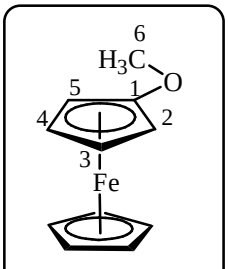
222

At –78 °C KO^{t}Bu (0.67 g, 6.0 mmol) in THF (30 mL) was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.0 g, 6.0 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5

min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2-(trifluoromethylsulfonyl)ferrocenol (**215**) and (4-tert-butoxy-butoxy)-ferrocene (**222**) were separated by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). **215** was obtained with 70 % yield. (4-*tert*Butoxybutoxy)-ferrocene (**222**) was obtained as yellow oil (0.59 g, 1.8 mmol, 30 %).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.20 (s, 9H, 10-H), 1.63-1.70 (m, 2H, 8-H), 1.74-1.81 (m, 2H, 7-H), 3.41 [t, 2H, *J*(HH) = 6.0 Hz, 9-H], 3.77-3.83 (m, 4H, 6-H, Cp-H), 4.07 [t, 2H, *J*(H,H) = 1.98 Hz, Cp-H], 4.18 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 26.7 (C-7), 27.4 (C-8), 27.7 (C-10), 55.4 (C-9), 61.3 (C-11), 61.9 (C-6), 68.5 (Cp'), 70.4 [C-2(5)], 72.7 [C-3(4)], 126.6 (C-1) ppm. – IR: $\tilde{\nu}$ = 3096 (w, Cp-H), 2971 (m, Cp-H), 2870 (m, Cp-H), 1489 (s), 1466 (s), 1391 (w), 1362 (m), 1247 (s), 1197 (s), 1104 (m), 1065 (m), 1020 (m), 1000 (m), 931 (w), 814 (m), 688 (m) cm^{-1}. – MS (70 eV): *m/z* (%) = 330 (17) [M^+], 257 (3) (M^+-O^{t}Bu), 202 (100) [FcO$^+$], 121 (14) [FeCp$^+$], 56 (7) [Fe$^+$]. – HRMS calcd. for $C_{18}H_{26}FeO_2$: 330.1282; found: 330.1281. – Elemental analysis calcd. (%) for $C_{18}H_{26}FeO_2$: C 65.46, H 7.94; found: C 64.45, H 7.68.

9.8 Methoxyferrocene (226)[47]



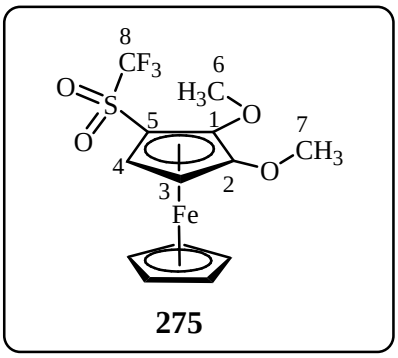
226

At –78 °C KO^{t}Bu (0.67 g, 6.0 mmol) [or K (ca. 0.30 g)], in methanol (30 mL) was added dropwise over 40 min to ferrocenyl triflate (**63**) (2.0 g, 6.0 mmol) in methanol (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the

mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2-(trifluoromethylsulfonyl)ferrocenol (**215**) and methoxyferrocene (**226**) were separated by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). **215** was obtained with 70 % yield. Methoxyferrocene (**226**) was obtained as yellow solid (0.39 g, 1.8 mmol, 30 %), identified by comparison with literature data (^{1}H NMR).[47]

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.65 (s, 3H, 6-H), 3.83 [t, 2H, *J*(H,H) = 3.8 Hz, Cp-H], 4.10 [t, 2H, *J*(HH) = 3.8 Hz, Cp-H], 4.21 (s, 5H, Cp'-H) ppm.

9.9 1,2-dimethoxy-5-(trifluoromethylsulfonyl)ferrocene (275)



275

Method A:

At −78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (0.12 mL, 0.3 mmol) in hexane and diisopropylamine (0.13 mL, 0.9 mmol) in THF (20 mL)] was added dropwise over 40 min to 2-Methoxyferrocenyl triflate (**257**) (0.10 g, 0.3 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 25 °C Me_2SO_4 (0.04 mL, 0.4 mmol) was added, and the mixture was heated at reflux for 24 h. Then 20 %-KOH (20 mL) in water was added at 25 °C and the mixture was heated at reflux for 1 hour in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 10 mL). The collected organic layers were washed water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was

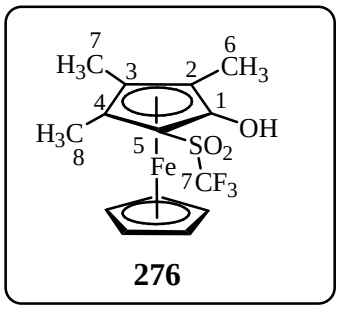
purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1,2-Dimethoxy-5-(trifluoromethylsulfonyl)ferrocene (**275**) (0.10 g, 0.3 mmol, 99 %) was isolated as a red oil.

Method B:

At −78 °C BuLi in hexane (2.5 M, 0.2 mL, 0.51 mmol) was added dropwise over 40 min to 2-trifluoromethanesulfonyloxy acetate (**261**) (0.10 g, 0.26 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 25 °C Me_2SO_4 (0.05 mL, 0.51 mmol) was added, and the mixture was heated at reflux for 24 h. Then 20 %-KOH (20 mL) in water was added at 25 °C and the mixture was heated at reflux for 1 hour in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 10 mL). The collected organic layers were washed water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1,2-Dimethoxy-5-(trifluoromethylsulfonyl)ferrocene (**275**) (0.10 g, 0.26 mmol, 99 %) was isolated as a red oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.71 (s, 3H, OCH_3) 3.92 (s, 3H, OCH_3) 4.28 [d, *J*(H,H) = 3.1 Hz, 1H, Cp-H], 4.33 [d, 1H, *J*(H,H) = 3.1 Hz, 1H, Cp-H], 4.58 (s, 5H, Cp'-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 53.8 (C-6), 58.2 (C-7), 58.9 (Cp), 62.4 (Cp), 72.2 (Cp), 72.3 (Cp'), 114.9 (C-2), 119.3 (C-1), 119.4 [q, *J*(C,F) = 325.4 Hz, CF_3] ppm. – IR: $\tilde{\nu}$ = 2943 (m, Cp-H), 1792 (w), 1710 (w), 1507 (s), 1479 (m), 1425 (m), 1407 (m), 1360 (s), 1290 (m), 1212 (s), 1183 (s), 1150 (m), 1106 (s), 1053 (s), 1026 (m), 982 (m), 914 (m), 828 (m), 700 (m) cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{13}H_{13}F_3FeO_4S$: 377.9836; found 377.9836. – Elemental analysis calcd. (%) for $C_{13}H_{13}F_3FeO_4S$: C 41.29, H 3.47; found: C 41.30, H 3.44.

9.10 2,3,4-Trimethyl-5-(trifluoromethylsulfonyl)ferrocenol (276)

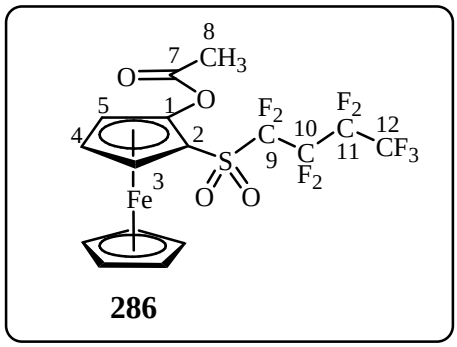


276

At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (0.16 mL, 0.4 mmol) in hexane and diisopropylamine (0.6 mL, 4.0 mmol) in THF (20 mL)] was added dropwise over 40 min to 2,3,4-trimethylferrocenyl triflate (**266**) (0.15 g, 0.4 mmol)in THF (10 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification by addition of oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal at reduced pressure 2,3,4-trimethyl-5-(trifluoromethylsulfonyl)ferro- cenol (**276**) was obtained as an orange solid (0.15 g, 0.4 mmol, 99 %).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.89 (s, 3H, 7-H), 2.01 (s, 3H, 8-H), 2.04 (s, 3H, 6-H), 4.21 (s, 5H, Cp'-H). – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 8.8 (C-6), 11.4 (C-7), 12.7 (C-8), 58.7 (Cp), 73.4 (Cp'), 75.7 (Cp), 78.4 (Cp), 79.3 (Cp), 119.2 (q, ^1J(C,F) = 323.6 Hz, CF_3), 123.1 (C-1) ppm. – IR: $\tilde{\nu}$ = 3406 (br. OH), 2924 (m, Cp-H), 1493 (s), 1451 (s), 1401 (m), 1384 (m), 1257 (m), 1115 (s), 1021 (m), 1003 (s), 824 (m), 805 (m), 773 (w), 720 (m), cm^{-1} – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{15}F_3FeO_3S$: 376.0043; found 376.0041. – Elemental analysis calcd. (%) for $C_{14}H_{15}F_3FeO_3S$: C 44.70, H 4.02; found: C 44.83, H 4.15.

9.11 2-(Nonafluorobutanesulfonyl)ferrocenyl acetate (286)

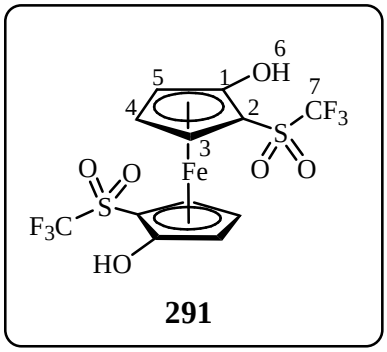


286

At –78 °C LDA in THF [prepared from 2.5 M *n*-BuLi (0.84 mL, 2.1 mmol) in hexane and diisopropylamine (3.0 mL, 20.7 mmol) in THF (20 mL)] was added dropwise over 40 min to ferrocenyl nonaflate (**284**) (1.00 g, 2.1 mmol) in THF (20 mL). The colour of the mixture changed from light yellow to deep red. Acetyl chloride (0.2 mL, 2.5 mmol) was added, and the colour changed from deep red to yellow. After stirring at 25 °C for 30 min and addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) with water and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 2-(Nonafluorobutenesulfonyl)ferrocenyl acetate (**286**) (1.00 g, 2.1 mmol, 99 %) was isolated as yellow oil.

^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 2.20 (s, 3H, 8-H), 4.59 (s, 5H, Cp'-H), 4.69-4.70 (m, 1H, Cp-H), 4.76 (t, 1H, *J*(H,H) = 2.9 Hz, Cp-H), 5.14 [dd, 1H, *J* (H,H) = 2.7 Hz, *J* (H,H) = 2.7 Hz, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 20.9 (C-8), 68.6 (Cp), 69.1 (Cp), 69.6 (Cp), 70.7 (Cp), 73.8 (Cp'), 109.0- 133.3 (m, C_4F_9), 116.4 (C-1), 169.2 (C-7) ppm. – IR: $\tilde{\nu}$ = 2924 (m, Cp-H), 1781 (m), 1444 (m), 1366 (m), 1190 (s), 1187 (s), 1138 (m), 1087 (m), 1013 (m), 875 (w), 833 (w) cm^{-1}. – HRMS (ESI, acetonitrile) calcd. for $C_{16}H_{11}F_9FeO_4S$: 525.9584; found 525.9582. – Elemental analysis calcd. (%) for $C_{14}H_{15}F_3FeO_3S$: C 36.52, H 2.11; found: C 36.47, H 2.15.

9.12 *meso*-2,2'-Bis(trifluoromethylsulfonyl)-1,1'-ferrocenediol (291)

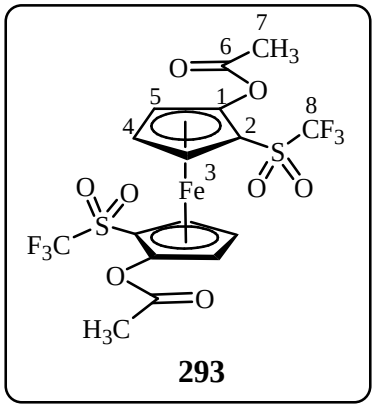


291

At –78 °C a solution of LDA in THF [prepared from 1.6 M *n*-BuLi (5.8 mL, 9.2 mmol) in hexane and diisopropylamine (3 mL, 20.7 mmol) in THF (20 mL)] was added dropwise over 40 min to 1,1'-ferrocenediyl ditriflate (**290**) (2.03 g, 4.2 mmol) in THF (20 mL). The colour changed from light yellow to deep red. After warming to 0 °C and acidification with oxygen free 10 % aqu. HCl (until pH 6) CH_2Cl_2 (50 mL) was added, and the mixture was intensely stirred for 5 min. After phase separation the organic layer was collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of $MgSO_4$. After solvent removal **291** was obtained as a yellow solid (1.74 g, 3.6 mmol, 85 %).

M. p. 145 °C (dec.). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.74 (m, 4H, Cp-H, Cp'-H); 4.92 (s, 2H, Cp-H, Cp'-H); 5.60 (s, 2H, OH) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 64.5 (Cp, Cp'), 64.7 [m, C-2(2')], 67.1 (Cp, Cp'), 70.1 (Cp, Cp'), 119.2 [q, *J*(C,F) = 324.7 Hz, CF_3], 126.1 [C-1(1')] ppm. – IR: $\tilde{\nu}$ = 3386 (br, O-H), 3114 (w, Cp-H), 2924 (w, Cp-H), 1727 (w), 1505 (m), 1434 (m), 1348 (s), 1270 (m), 1188 (s, CF_3), 1109 (s), 1075 (s), 1003 (m), 841 (w), 820 (w), 766 (w), 692 cm^{-1} (w). – MS (70 eV): *m/z* (%): 482 (100) [M^+], 349 (14) [M^+ – Tf)], 218 (12) [M^+ – (2H + 2Tf)], 200 (10) [M^+ – (OH + 2Tf)], 135 (30) [$FeCpO^+$], 95 (15) [$SOCF^+$], 81 (46) [CpO^+], 56 (23) [Fe^+]. – HRMS calcd. for $C_{16}H_{12}F_6FeO_8S_2$: 481.9016; found: 481.9013. – Elemental analysis calcd. (%) for $C_{16}H_{12}F_6FeO_8S_2$: C 29.89, H 1.67; found: C 31.13, H 2.20.

9.13 meso-2,2'-Bis(trifluoromethylsulfonyl)-1,1'-ferrocenediyl diacetate (293)



293

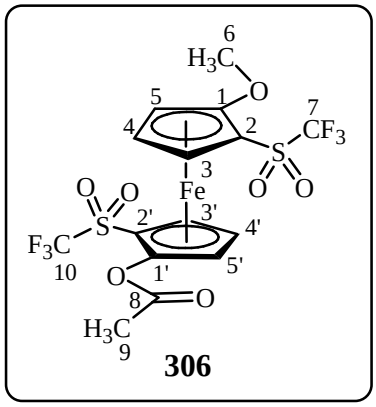
At –78 °C a solution of LDA in THF [prepared from 1.6 M *n*-BuLi (5.8 mL, 9.2 mmol) in hexane and diisopropylamine (3 mL, 20.7 mmol) in THF (20 mL)] was added dropwise over 40 min to 1,1'-ferrocenediyl ditriflate (**290**) (2.03 g, 4.2 mmol) in THF (20 mL). The colour changed from light yellow to deep red. Acetyl chloride (0.9 mL, 12.6 mmol) was added, and the colour changed from red to yellow. The mixture was warmed to 25 °C and was stirred for 30 min. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 50 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 2,2'-di(trifluoromethylsulfonyl)-1,1'-ferrocenyl diacetate (**293**) (2.15 g, 3.8 mmol, 91 %) was isolated as yellow powder. For X-ray structure analysis a sample was recrystallized from toluene.

M. p. 182 °C (dec.). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.27 (s. 3H, CH_3), 4.92 [t, *J*(H,H) = 3.0 Hz, 1H, Cp-H], 4.96 (m, 1H, Cp-H), 5.40 (m 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB, HMQC, HMBC): δ = 20.9 (CH_3), 70.4 (Cp), 71.6 (Cp), 72.1 [C-2(2')], 72.2 (Cp, Cp'), 116.6 [C-1(1')], 119.3 [q, *J*(C,F) = 325.2 Hz, CF_3], 168.1 (C=O) ppm. – IR: $\tilde{\nu}$ = 3133 (w, Cp-H), 1788 (s, C=O), 1454 (m), 1389(w), 1361 (m), 1210 (s), 1173 (s, CF_3), 1120 (s), 1080 (s), 1015 (m), 870 (m), 858 (m), 839 (m), 827 (m), 770(w). – MS (70 eV): *m/z* (%): 566 (7) [M^+], 524 (11) [M^+ – Ac], 482 (100) [M^+ – 2Ac], 349 (10) [M^+ – 2Ac – Tf)], 197 (19) [$CpTf^+$], 135 (10) [$FeCpO^+$], 81 (10) [CpO^+], 56 (7) [Fe^+]. – HRMS calcd. for

$C_{16}H_{12}F_6FeO_8S_2$: 565.9227; found: 565.9229. – Elemental analysis calcd. (%) for $C_{16}H_{12}F_6FeO_8S_2$: C 33.94, H 2.14; found: C 33.31, H 2.08.

10 Chemo enzymatic desymmetrization of meso-2,2'-Bis(trifluoromethylsulfonyl)-1,1'-ferrocenediyl diacetate (291)

10.1 2,2'-Bis(trifluoromethylsulfonyl)-1-methoxy-1'-ferrocenyl acetate (306)



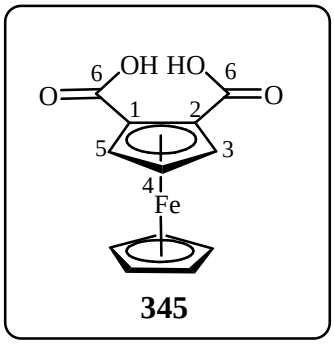
306

A solution of KH_2PO_4 in water (0.5 M, 10 mL) was added to a solution of *meso*-2,2'-di(trifluoromethylsulfonyl)-1,1'-ferrocenyl diacetate (**293**) (0.10 g, 0.18 mmol) in DMSO (20 mL). The reaction mixture was treated with a catalytic amount of PFL and stirred at 40 °C 3 d. After cooling to 25 °C Me_2SO_4 (0.04 mL, 0.4 mmol) was added, and the mixture was heated at reflux for 24 h. Then 20 %-KOH (20 mL) in water was added at 25 °C and the mixture was heated at reflux for 1 hour in order to eliminate unconsumed Me_2SO_4. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 10 mL). The collected organic layers were washed water (3 x 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure. 2,2'-Bis(trifluoromethylsulfonyl)-1-methoxy-1'-ferrocenyl acetate (**306**) was isolated with **293** as a yellow powder. The separation was not possible. The yield of **306** was calculated according to the ^{1}H NMR spectra (56 %).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.34 (s. 3H, 9-H), 3.86 (s, 3H, 6-H), 4.67 (s, 1H, Cp-H), 4.92-4.94 (m, 3H, Cp-H), 5.04 (s, 1H, Cp-H), 5.29 (m, 1H, Cp-H) ppm. – HRMS (ESI, acetonitrile) calcd. for $C_{15}H_{12}F_6FeO_7S_2$: 537.9278; found 537.9348.

11 Preparation of 1,2-ferrocenedicarboxylic acid and its derivates

11.1 1,2-Ferrocenedicarboxylic acid (345)[142]



345

Method A:

Ferrocene carboxylic acid (**267**) (3.0 g, 13.1 mmol) in THF (140 mL) was cooled to – 78 °C. To this clear red solution was added *s*-BuLi (1.6 M in cyclohexane, 16.4 mL, 26.2 mmol) during 10 min and the resulting suspension was stirred until the solid was redissolved (about 2 h). Then a handful of dry ice was added and the solution was allowed to warm slowly to 25 °C. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure 1,2-ferrocene dicarboxylic acid (**345**) [3.41 g, 12.5 mmol, 95 % after hydrolysis of 1,2-dimethoxyferrocene (**375**) (*vide infra*)] was isolated as a red powder.

Method B:

To a solution of 1,2-dibromoferrocene (**313**) (0.5 g, 1.46 mmol) in THF (50 mL) *t*-BuLi solution in hexane (1.6 M, 2.0 mL, 3.2 mmol) was added at – 78°C. The reaction mixture was stirred for 2 h. MeOD (1.0 mL) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with PE (3 x

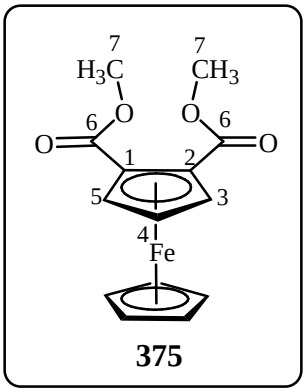
50 mL). Then a handful of dry ice was added and the solution was allowed to warm slowly to 25 °C. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure 1,2-ferrocene dicarboxylic acid (**345**) (0.30 g, 1.1 mmol, 76 %) was isolated as a red powder.

Method C:

Water (40 mL) was added to a solution of 1,2-ferrocene dicarboxylic acid dimethyl ester (**375**) (3.77 g, 12.5 mmol) in ethanol, The mixture was heated to 70 °C and KOH (3.33 g, 59.5 mmol) was added.The mixture was stirred at 70 °C 1h. After addition of water (50 mL) and acidification by addition of 20 % aqu. HCl (until pH 6) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure 1,2-ferrocene dicarboxylic acid (**345**) (3.41 g, 12.5 mmol, 100 %) was isolated as a red powder, identified by comparison with literature data (^{1}H NMR).[142]

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.39 (s. 5H, Cp'-H), 4.81 [t, 1H, *J*(H,H) = 2.8 Hz, 4-H], 5.28 [d, 2H, *J*(H,H) = 2.8 Hz 3(5)-H] ppm.

11.2 1,2-Di(methoxycarbonyl)ferrocene (375)



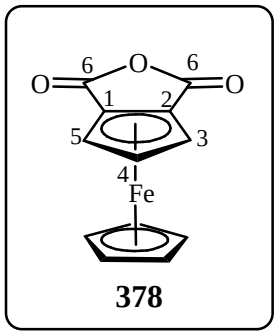
375

This reaction was performed in order to purify the 1,2-ferrocenedicarboxylic acid (**345**) (*vide supra*).

To a solution of the mixture of 1,2-ferrocene dicarboxylic acid (**345**) and carboxylic acid (*vide supra*) in methanol (200 mL) a catalytic amount of TsOH was added. The reaction mixture was heated with reflux 18 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 1,2-Di(methoxycarbonyl)ferrocene (**375**) (3.77 g, 12.5 mmol, 95 %) was isolated as red oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.84 (s. 6H, 7-H), 4.29 (s, 5H, Cp'-H), 4.49 [t, 1H, *J*(H,H) = 2.7 Hz, 4-H], 4.89 [d, 2H, J(H,H) = 2.73 Hz, 3(5)-H], 5.40 (m 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 52.2 (C-7), 71.2 [C-3(5)], 71.9 (Cp'), 74.2 (C-4), 74.3 [C-1(2)], 170.2 (C-6) ppm. – IR: $\tilde{\nu}$ = 2981 (w, Cp-H), 1706 (s, C=O), 1448 (m), 1386(w), 1369 (w), 1348 (w), 1281 (s), 1239 (s), 1174 (s), 1146 (s), 1108 (w), 1071 (m), 1019 (m), 823 (m), 773(m). – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{14}FeO_4$: 302.0241; found 302.0241. – Elemental analysis calcd. (%) for $C_{14}H_{14}FeO_4$: C 55.66, H 4.67; found: C 55.63, H 4.60.

11.3 1,2-Ferrocenedicarboxylic acid anhydride (378)[142]



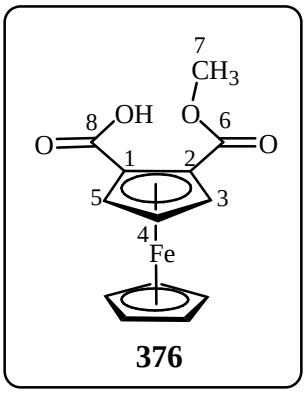
378

Oxalyl chloride (0.31 mL, 3.65 mmol) was added to a solution of 1,2-ferrocene dicarboxylic acid (**345**) (1 g, 3.65 mmol) in Et_2O (50 mL). After addition of two drops of DMF the reaction mixture was stirred at 25 °C 1 h. After solvent removal at reduced pressure the remaining oil

was dissolved in CH_2Cl_2 (50 mL), and after addition of pyridine (1.1 mL, 13.0 mmol) the mixture was stirred at 25 °C 6 h. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, TBME). 1,2-Ferrocene-dicarboxylic acid anhydride (**378**) (0.93 g, 3.65 mmol, 100 %) was isolated as red solid, identified by comparison with literature data (^{1}H NMR).[142]

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.48 (s, 5H, Cp'-H), 4.90 [t, 1H, *J*(H,H) = 2.4 Hz, 4-H], 5.15 [d, 2H, *J* (H,H) = 2.4 Hz, 3(5)-H] ppm.

11.4 2-(Methoxycarbonyl)ferrocenecarboxylic acid (376)

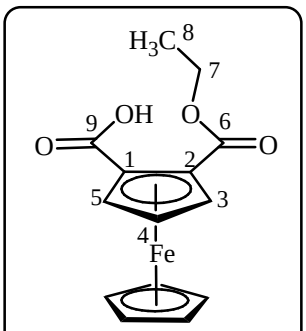


376

A catalytic amount of TsOH was added to asolution of 1,2-Ferrocene dicarboxylic acid anhydride (**378**) (3 g, 11.7 mmol) in methanol (100 mL). The reaction mixture was heated at reflux 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-(Methoxycarbonyl)ferrocenecar- boxylic acid (**376**) (3.38 g, 11.7 mmol, 100 %) was isolated as red solid.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.96 (s. 3H, 7-H), 4.34 (s, 5H, Cp'-H), 4.75 [t, 1H, *J*(H,H) = 2.8 Hz, 4-H], 5.05 [dd, 1H, *J* (H,H) = 2.8 Hz, Cp-H], 5.38 [dd, 1H, *J* (H,H) = 2.8 Hz, Cp-H]) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 53.7 (C-7), 67.5 (Cp), 72.3 (Cp'), 73.6 (Cp), 73.9 (Cp), 75.2 (Cp), 78.3 (Cp), 170.1 (C-6), 177.5 (C-8) ppm. – IR: $\tilde{\nu}$ = 3775 (w), 3699 (w), 3639 (w), 2958 (w, Cp-H), 2678 (w, Cp-H), 1720 (s, C=O), 1626 (br, O-H), 1466 (s), 1411 (s), 1353 (m), 1278 (s), 1205 (m), 1151 (m), 1084 (w), 1013 (m), 932 (w), 870(w). – MS (70 eV): *m/z* (%): 288 (97) [M^+], 184 (52) [M^+ – (CO_2H + CO_2Me)], 81 (10) [CpO^+], 56 (35) [Fe^+]. – HRMS calcd. for $C_{13}H_{12}FeO_4$: 288.0085; found: 288.0086. – Elemental analysis calcd. (%) for $C_{16}H_{12}F_6FeO_8S_2$: C 54.20, H 4.20; found: C 54.16, H 4.57.

11.5 2-(Ethoxycarbonyl)ferrocenecarboxylic acid (377)



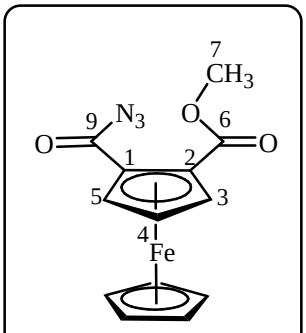
377

A catalytic amount of TsOH was added to asolution of 1,2-Ferrocenedicarboxylic acid anhydride (**378**) (3 g, 11.7 mmol) in ethanol (100 mL). The reaction mixture was heated at reflux 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-(Ethoxycarbonyl)ferrocenecar- boxylic acid (**377**) (3.54 g, 11.7 mmol, 100 %) was isolated as red solid.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.43 [t. 3H, *J*(H;H) = 7.2 Hz, 8-H], 4.34 (s, 5H, Cp'-H), 4.35-4.51 (m, 2H, 7-H), 4.74 [t, 1H, *J*(H,H) = 2.7 Hz, 4-H], 5.06 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H], 5.37 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H]) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 14.4 (C-8), 62.9 (C-7), 67.9 (Cp), 72.3 (Cp'), 73.6 (Cp), 73.9 (Cp), 75.3 (Cp), 77.5 (Cp), 170.2 (C-6), 176.9 (C-9) ppm. – IR: $\tilde{\nu}$ = 2664 (w, Cp-H), 1722 (s, C=O), 1619 (br, O-H), 1478 (m), 1464 (m), 1438 (s), 1411 (m), 1388 (m), 1371 (m), 1346 (m), 1275 (s), 1189 (m), 1151 (m), 1081 (w), 1035 (w), 1022 (m), 852 (m), 822 (m), 770 (m). – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{14}FeO_4$: 302.0241; found 302.0241. – Elemental analysis calcd. (%) for $C_{14}H_{14}FeO_4$: C 55.66, H 4.67; found: C 55.66, H 4.69.

12 Preparation of 2-aminoferrocenecarboxylic acid (359)

12.1 2-(Methoxycarbonyl)ferrocenecarboxylic acid azide (380)



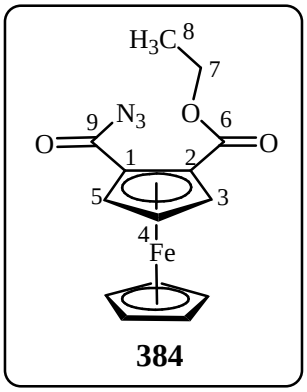
380

Oxalyl chloride (0.7 mL, 8.3 mmol) was added to a solution of 2-(methoxycarbonyl)ferrocenecarboxylic acid (**376**) (2.00 g, 6.9 mmol) in Et_2O (50 mL). After addition of two drops of DMF the reaction mixture was stirred at 25 °C 1 h. After solvent removal at reduced pressure the remaining oil was dissolved in CH_2Cl_2 (50 mL), and after addition of a catalytic amount of Bu_4NBr and a solution of NaN_3 (0.45 g, 6.9 mmol) in water (20 mL) the mixture was stirred at 25 °C 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7).

2-(Methoxycarbonyl)ferrocenecarboxylic acid azide (**380**) (1.94 g, 6.2 mmol, 90 %) was isolated as red solid.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.87 (s, 3H, 7-H), 4.19 (s, 5H, Cp'-H), 4.28 [t, 1H, *J*(H,H) = 2.7 Hz, 4-H], 4.55 [dd, 1H, *J* (H,H) = 2.8 Hz, Cp-H], 5.44 [dd, 1H, *J* (H,H) = 2.5 Hz, Cp-H]) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, BB): δ = 53.7 (C-7), 63.8 (Cp), 65.7 (Cp), 67.3 (Cp), 70.7 (Cp), 70.8 (Cp), 71.2 (Cp'), 153.1 (C-9), 172.8 (C-6) ppm. – IR: $\tilde{\nu}$ = 3334 (w), 2925 (w, Cp-H), 2843 (w, Cp-H), 2138 (s, N=N), 1715 (s, C=O), 1686 (s, C=O), 1537 (s), 1445 (m), 1382 (w), 1376 (w), 1295 (s), 1239 (s), 1193 (m), 1080 (m), 1025 (w), 940 (w), 823 (w), 770 (w), 728 (w). – HRMS (ESI, acetonitrile) calcd. for $C_{13}H_{11}FeN_3O_3$: 313.0150; found 313.0150. – Elemental analysis calcd. (%) for $C_{13}H_{11}FeN_3O_3$: C 49.87, H 3.54, N 13.42; found: C 49.87, H 3.53, N 13.40.

12.2 2-(Ethoxycarbonyl)ferrocenecarboxylic acid azide (384)



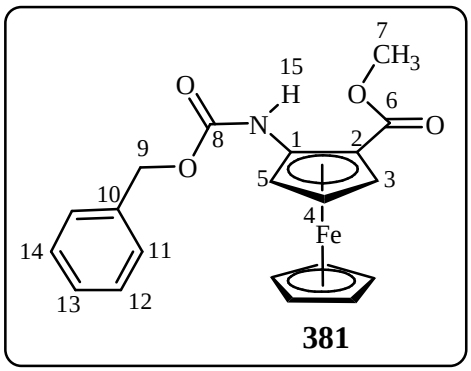
384

Oxalyl chloride (1.00 mL, 3.65 mmol) was added to a solution of 2-(Ethoxycarbonyl)ferrocenecarboxylic acid (**377**) (3.38 g, 11.7 mmol) in Et_2O (50 mL). After addition of two drops of DMF the reaction mixture was stirred at 25 °C 1 h. After solvent removal at reduced pressure the remaining oil was dissolved in CH_2Cl_2 (50 mL), and after addition of a catalytic amount of Bu_4NBr and a solution of NaN_3 (0.76 g, 11.7 mmol) in water (20 mL) the mixture was stirred at 25 °C 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude

product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-(Ethoxycarbonyl)ferrocenecar- boxylic acid azide (**384**) (3.43 g, 10.5 mmol, 90 %) was isolated as red solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.39 [t, 3H, *J*(H,H) = 7.2 Hz, 8-H], 4.19 (s, 5H, Cp'-H), 4.27 [t, 1H, *J*(H,H) = 2.9 Hz, 4-H], 4.28-4.41 (m, 2H, 7-H), 4.56 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H], 5.44 [dd, 1H, *J* (H,H) = 2.5 Hz, Cp-H] ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, BB): δ = 14.7 (C-8), 60.9 (C-7), 63.9 (Cp), 65.6 (Cp), 67.2 (Cp), 70.7 (Cp), 70.8 (Cp), 71.0 (Cp'), 154.2 (C-9), 173.9 (C-6) ppm. – IR: $\tilde{\nu}$ = 3335 (w), 2919 (w, Cp-H), 2850 (w, Cp-H), 2143 (s, N=N), 1716 (s, C=O), 1687 (s, C=O), 1536 (s), 1443 (m), 1379 (w), 1302 (s), 1234 (s), 1191 (m), 1089 (m), 1030 (w), 948 (w), 825 (w), 776 (w), 730 (w). – HRMS (ESI, acetonitrile) calcd. for $C_{14}H_{13}FeN_3O_3$: 327.0306; found 327.0306. – Elemental analysis calcd. (%) for $C_{14}H_{13}FeN_3O_3$: C 51.40, H 4.01, N 12.85; found: C 51.42, H 4.02, N 12.80.

12.3 2-Benzyloxycarbonylaminoferrocenecarboxylic acid methyl ester (381)

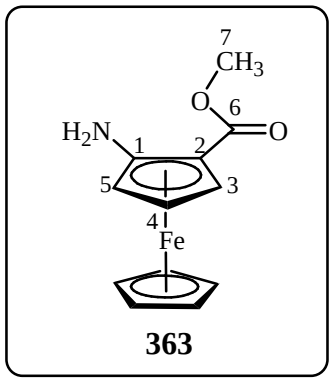


381

Benzyl alcohol (1.3 mL, 12.4 mmol) was added to asolution of 2-(Methoxycarbonyl)ferrocenecarboxylic acid azide (**380**) (1.94 g, 6.2 mmol) in toluene (50 mL). The reaction mixture was heated at reflux 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-Benzyloxycarbonylaminoferrocenecarboxylic acid methyl ester (**381**) (2.09 g, 5.3 mmol, 86 %) was isolated as yellow solid.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.85 (s, 3H, 7-H), 4.15 (s, 5H, Cp'-H), 4.23 [t, 1H, *J*(H,H) = 2.7 Hz, 4-H], 4.52 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H], 5.21 (s, 2H, 9-H), 5.39 (s, 1H, Cp-H), 7.15-7.44 (m, Ph-H), 7.97 (s, 1H, 15-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, BB): δ = 49.6 (C-7), 51.9 (C-9), 58.6 (Cp), 63.1 (Cp), 65.1 (Cp), 66.9 (Cp), 67.1 (Cp), 70.8 (Cp'), 128.2 (Ph), 128.4 (Ph), 128.7 (Ph), 129.2 (Ph), 153.9 (C-8), 174.4 (C-6) ppm. – IR: $\tilde{\nu}$ = 3776 (w), 3699 (w), 3360 (w), 2954 (w, Cp-H), 1727 (s, C=O), 1689 (s, C=O), 1534 (s), 1452 (m), 1415 (w), 1385 (w), 1352 (w), 1300 (s), 1222 (s), 1165 (w), 1102 (m), 1052 (m), 1014 (m), 937 (w). – HRMS (ESI, acetonitrile) calcd. for $C_{20}H_{19}FeNO_4$: 393.0663; found 393.0660. – Elemental analysis calcd. (%) for $C_{14}H_{13}FeN_3O_3$: C 61.09, H 4.87, N 3.56; found: C 60.98, H 4.98, N 3.65.

12.4 2-Amino-1-(methoxycarbonyl)ferrocene (363)[160]

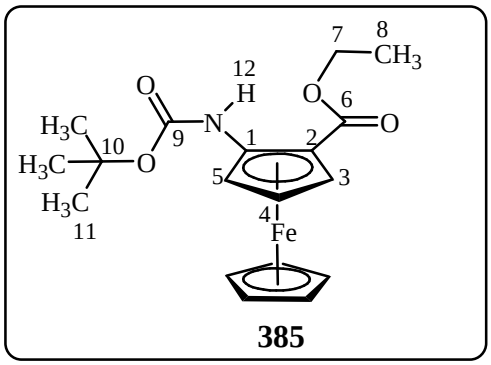


363

A catalytic amount of Pd on activated coal was added to a solution of 2-benzyl-oxycarbonylaminoferrocenecarboxylic acid methyl ester (**381**) (2.09 g, 5.3 mmol) in methanol (50 mL). The reaction mixture was stirred at 25 °C 24 h in H_2 atmosphere. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-Amino-1-(methoxycarbonyl)ferrocene (**363**) (1.21 g, 4.7 mmol, 88 %) was isolated as yellow solid, identified by comparison with literature data (^{1}H NMR).[160]

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.70 (s, 2H, NH_2), 3.85 (s, 3H, 7-H), 4.06 [t, 1H, *J*(H,H) = 2.6 Hz, 4-H], 4.10 (s, 5H, Cp'-H), 4.23 [dd, 1H, *J* (H,H) = 2.6 Hz, Cp-H], 4.46 [dd, 1H, *J* (H,H) = 2.6 Hz, Cp-H] ppm.

12.5 2-tert-Butoxycarbonylaminoferrocenecarboxylicacid ethyl ester (385)

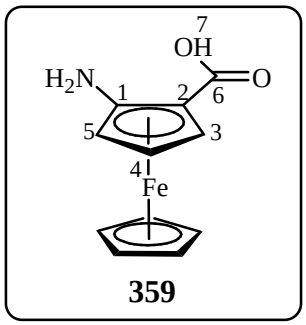


385

tert-Butanol (2.0 mL, 21.0 mmol) was added to a solution of 2-(ethoxycarbonyl)ferrocenecarboxylic acid azide (**384**) (3.43 g, 10.5 mmol) in toluene (50 mL). The reaction mixture was heated at reflux 12 h. After addition of water (50 mL) the mixture was extracted with ethyl acetate (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE/TBME 3:7). 2-tert-Butoxycarbonylamino-ferrocene carboxylicacid ethyl ester (**385**) (3.41 g, 9.2 mmol, 87 %) was isolated as red solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.39 [t, 3H, *J*(H,H) = 7.2 Hz, 8-H], 1.52 (s, 9H, 11-H), 4.16 (s, 5H, Cp'-H), 4.20 [t, 1H, *J*(H,H) = 2.7 Hz, 4-H], 4.24-4.43 (m, 2H, 7-H), 4.50 [dd, 1H, *J* (H,H) = 2.7 Hz, Cp-H], 5.35 (s, 1H, Cp-H), 7.77 (s, 1H, 12-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, BB): δ = 14.7 (C-8), 28.5 (C-11), 29.9 (C-7), 46.4 (C-10), 60.5 (Cp), 62.9 (Cp), 65.0 (Cp), 66.7 (Cp), 70.7 (Cp'), 153.4 (C-9), 169.4 (C-6) ppm. – IR: $\tilde{\nu}$ = 3765 (w), 2979 (w, Cp-H), 1724 (s, C=O), 1688 (s, C=O), 1529 (s), 1443 (m), 1365 (m), 1352 (w), 1286 (s), 1234 (s), 1163 (s), 1099 (m), 1058 (m), 1013 (m), 976 (w) 906 (w), 854 (w). – HRMS (ESI, acetonitrile) calcd. for $C_{18}H_{23}FeNO_4$: 373.0976; found 373.0976. – Elemental analysis calcd. (%) for $C_{18}H_{23}FeNO_4$: C 57.93, H 6.21, N 3.75; found: C 57.65, H 6.35, N 3.86.

12.6 2-Aminoferrocenecarboxylic acid (359)



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Method A:

Water (20 mL) was added to a solution of 2-Amino-1-(methoxycarbonyl)ferrocene (**363**) (1.21 g, 4.7 mmol) in ethanol (30 mL). The mixture was heated to 70 °C and after addition of KOH (0.8 g, 14.1 mmol) was stirred 1 h. After addition of water (50 mL) and neutralization with H_3PO_4 (1 M) the mixture was extracted with CH_2Cl_2 (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, 2-aminoferrocenecarboxylic acid (**359**) (1.01 g, 4.1 mmol, 88 %) was isolated as red solid.

Method B:

Water (20 mL) was added to a solution of 2-*tert*-butoxycarbonylaminoferrocene-carboxylicacid ethyl ester (**385**) (1.00 g, 2.7 mmol) in ethanol (30 mL). After addition of of 20 % aqu. HCl (10 mL) the mixture was stirred at reflux 5 h. After addition of water (50 mL) and neutralization with KOH (1 M) the mixture was extracted with CH_2Cl_2 (3 x 25 mL). The collected organic layers were washed with water (3 x 20 mL) and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, 2-aminoferrocenecarboxylic acid (**359**) (0.53 g, 4.1 mmol, 80 %) was isolated as red solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.19 (s, 5H, Cp'-H), 4.27 [t, 1H, *J*(H,H) = 2.6 Hz, 4-H], 4.56 [dd, 1H, *J* (H,H) = 2.4 Hz, Cp-H], 5.44 [dd, 1H, *J* (H,H) = 2.4 Hz, Cp-H], 8.32 (s, 1H, 7-H) ppm.

13 Irradiation of 1,2-ferrocenedicarboxylic anhydride (378)

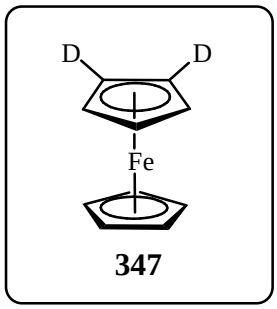
13.1 Irradiation in toluene or THF

1,2-ferrocenedicarboxylic anhydride (**378**) (0.1 g, 0.39 mmol) was dissolved in toluene (in another experiment in THF). The reaction mixture was irradiated for 25 min with a 125 W mercury lamp placed in a quartz tube which was cooled with water. The reaction mixture was continuously flushed with argon and cooled using water condenser. The reaction progress was monitored by the TLC. After the completed exhaustion of the starting material (generally ca. 25 minutes) the irradiation was stopped. The mixture was filtered and the solvent was removed at reduced pressure. Mass spectra and ^{1}H NMR spectra of the crude product were recorded, in witch only ferrocene (**186**) and traces of the starting material were identified. The crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). **186** (0.017 g, 0.09 mmol, 24 %) was isolated.

13.2 Irradiation in benzene

1,2-ferrocene dicarboxylic anhydride (**378**) (0.05 g, 0.19 mmol) was dissolved in benzene in an NMR tube, which was attached to the quartz tube with the 125 W mercury lamp which was cooled with water. The NMR tube was irradiated 10 min. The red cloudy mixture was filtered. The mass and ^{1}H NMR spectra of the colourless filtrate showed only the benzene.

13.3 Irradiation in deuterated toluene and in deuterated THF



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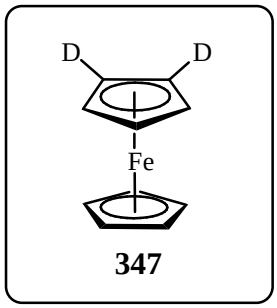
1,2-ferrocene dicarboxylic anhydride (**378**) (0.05 g, 0.19 mmol) was dissolved in deuterated toluene (in another experiment in the deuterated THF) in an NMR tube, which was attached to the quartz tube with the 125 W mercury lamp which was cooled with water. The NMR tube was irradiated 10 min. The red cloudy mixture was filtered. The mass and ^{1}H NMR spectra of the crude product showed the 1,2-dideuterio ferrocene (**347**) and traces of the starting material. The crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). **347** (0.008 g, 0.05 mmol, 24 %) was isolated as an orange solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.1 [d, 2H, *J*(H,H) = 1.71 Hz Cp-H], 4.23 (s, 5H, Cp'-H), 4.41(s, 1H, Cp-H) ppm. – ^{13}C NMR (400.1 MHz, $CDCl_3$, DEPT 90, BB): δ = 67.1-67.2 (m, Cp), 70.2 (Cp), 70.7 (Cp'), 77.7 (Cp) ppm. – IR: $\tilde{\nu}$ = 3097 (w), 2922 (m, Cp-H), 2362 (w), 2116 (w), 1650 (w), 1405 (w), 1259 (m), 1080 (s), 1000 (s), cm^{-1} – MS (LC-MS, ESI): *m/z* (%): 186 (100) [M^+]. – HRMS calcd. for $C_{10}H_8D_2Fe$: 188.0255; found 188.0044

13.4 Synthesis of 1,2-dideuterioferrocene (347) from 1,2-dibromoferrocene (313)



347

This synthesis was performed, in order to compare thus product with the 1,2-dideuterio-ferrocene (**347**) from the irradiation of the 1,2-ferrocenedicarboxylic anhydride (**378**)

To a solution of 1,2-dibromoferrocene (**313**) (0.5 g, 1.46 mmol) in THF (50 mL) *t*-BuLi solution in hexane (1.6 M, 2.0 mL, 3.2 mmol) was added at – 78°C. The reaction mixture was stirred for 2 h. MeOD (1.0 mL) was added. The mixture was stirred for 30 min at –78 °C, then for 30 min at 25 °C. After addition of water (50 mL) the mixture was extracted with PE (3 x 50 mL). The collected organic layers were washed (3 x 20 mL) and dried over anhydrous

$MgSO_4$. After solvent removal at reduced pressure, the crude product was purified by column chromatography (30 x 3 cm, SiO_2, PE). 1,2-dideuterio ferrocene (**347**) (0.24 g, 1.27 mmol, 87 %) was isolated as an orange solid.

All spectra are identical with the spectra of the 1,2-dideuterio ferrocene (**347**) prepared by irradiation of the 1,2-ferrocene dicarboxylic anhydride (**378**).

Feci quod potui, faciant meliora potentes

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