Departement für Chemie, Institut für Organische Chemie
Universität Freiburg (Schweiz)

Development of iron catalysts for hydrogenation and polymerization

DISSERTATION

Zur Erlangung der Würde eines *Doctor rerum naturalium* der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Freiburg (Schweiz)

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Zusammenfassung

Im Rahmen der vorliegenden Arbeit wurden eine Reihe von neuen, einfach herzustellenden Eisenhydrierkatalysatoren eingeführt. Verschiedenste Aspekte dieser neuen Hydrierkatalysatoren wie Eisenquelle, Aktivierungsmittel, Substrate und Effizienz wurden untersucht.

Ein ligandfreier Katalysator, hergestellt aus einer Eisen(II)chlorid-Suspension aktiviert mit Diisobutylaluminiumhydrid (DIBAH), weist die grösste Aktivität auf. Alle Arten von C-C-Doppelbindungen wie mono-, di- oder trisubstituierte, acyclische oder cyclische, isolierte oder konjugierte Doppelbindungen sowie Alkine werden von diesem Katalysator unter milden Bedingungen (3 bar Wasserstoffdruck, Raumtemperatur) in kurzer Zeit quantitativ hydriert. Sowohl TON wie auch TOF steigen mit zunehmender Menge Aktivierungsmittel, bis bei einem Verhältnis $FeCl_2$/DIBAH 1:8 mit TON = 1900 und TOF = 125 h^{-1} der effizienteste Katalysator erhalten wird. Mit Ausnahme von Ethern und Aminen verhindert die Verwendung eines starken Reduktionsmittels zur Aktivierung die Hydrierung von funktionalisierten Olefinen. In Abwesenheit von Wasserstoff H_2 konnte katalytische Aktivität für Alkinpolymerisierungs- und Alkincyclotrimerisierungsreaktionen nachgewiesen werden. Ferner kann dieser Katalysator zur Polymerisierung von Acetylen eingesetzt werden.

Bei dem Versuch, die in diesen Fällen katalytisch aktive Spezies zu identifizieren fand man einen homogenen Präkatalysator, welcher erstaunliche Effizienz aufweist (TOF > 340 h^{-1}). Abgeleitet von der angenommenen Struktur dieses Präkatalysators wurden eine Reihe von Allylbenzylether synthetisiert, welche als Liganden getestet wurden. Die entsprechenden Katalysatoren, erhalten durch Aktivierung mit Alkyllithiumreagenzien, weisen Alkenhydrier- und Ethylenoligomerisierungs-aktivität auf.

Abstract

In the scope of this work, a series of new, easy to prepare iron hydrogenation catalysts have been introduced. Different aspects of this new hydrogenation catalysts such as iron source, activation reagent, substrates and efficiency were investigated.

A ligand-free catalyst, prepared from an iron(II) chloride suspension activated with diisobutylaluminiumhydride (DIBAH), showed the highest activity. With this catalyst all kind of C-C double bonds like mono-, di- or trisubstituted, acyclic or cyclic, isolated or conjugated double bonds as well as alkynes were hydrogenated quantitatively under mild conditions (3 bar hydrogen pressure, room temperature) within short time. Both TON and TOF scale with the added amount of activation reagent up to a 1:8 $FeCl_2$/DIBAH ratio furnishing the most active catalyst with TON = 1900 and TOF = 125 in this case. With the exception of ethers and amines, the use of strong reducing agents as activators prevents the hydrogenation of functionalized olefins. In absence of hydrogen H_2, catalytic activity for alkyne polymerization and cyclotrimerization was observed. Furthermore, this catalyst is able to promote the polymerization of acetylene.

Attempts to identify the catalytic active species led to the development of a homogeneous precatalyst showing an amazing efficiency (TOF > 340 h^{-1}). Derived from the assumed structure of this precatalyst, a series of allylbenzylethers were synthesized and tested as ligands. The corresponding catalysts, obtained by activation with alkyllithium reagents, display alkene hydrogenation and ethylene oligomerization activity.

Abbreviations

Ac	Acetyl
Bn	Benzyl
bpy	2,2′-Bipyridine
Bz	Benzoyl
CHT	Cycloheptatriene
COD	1,5-Cyclooctadiene
COE	Cyclooctene
COSY	Correlated spectroscopy
DAD	1,4-Diazadiene
DAT	2,5-Diazatriene
de	Diastereomeric excess
DFT	Density functional theory
DIBAH	Diisobutylaluminiumhydride
ee	Enantiomeric excess
EI	Electron impact
ENB	5-Ethylidene-2-norbornene
ESI	Electrospray ionisation
Et	Ethyl
FAB	Fast atom bombardement
GC	Gas chromatography
HETCOR	Heteronuclear correlation
HMB	Hexamethylbenzene
HPB	Hexaphenylbenzene
^{i}Pr	Isopropyl
LAH	Lithiumaluminiumhydride
M	Molar
Me	Methyl
MMAO	Modified methylaluminoxan
MS	Mass spectroscopy

NBD	Norbornadiene
NMR	Nuclear magnetic resonance
PES	Potential energy surface
Ph	Phenyl
SEM	Scanning electron microscope
THF	Tetrahydrofuran
TOF	Turn-over frequency
TON	Turn-over number
UV-Vis	Ultraviolet-visible
VCH	4-Vinylcyclohexene

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Theoretical part

1. Introduction

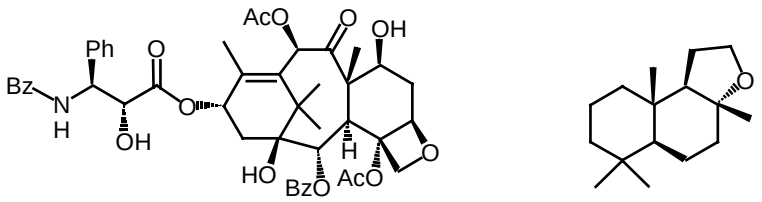
Organometallic catalysts have a tremendous importance in the field of modern organic synthesis. Many processes only take place when metal complexes offer new reaction pathways. The organic ligands complexed to the metal allow to tune the reactivity of the metal and are responsible for the chemo- and stereoselective outcome of the catalyzed reaction.

Among the large variety of transition metals which were used as catalysts iron plays a special role. In contrast to toxic metals (i.e. Cr, Os, Co..), iron is a physiologically and environmentally friendly metal. The few toxic iron compounds can easily be oxidized or hydrolysed to harmless iron salts. And the large aboundance of iron in earth's crust (4.5 %, second most after aluminium) renders it a very cheap metal source compared to those which were mainly used for catalytic processes (i. e. Pt, Pd, Ru…). Its low costs offers the possibility to engage iron in stoichiometric manner.

Despite these obvious advantages only few iron complexes are used for synthetic applications. Among them, iron carbonyl complexes and ferrocene derivatives are the most prominent examples. In the case of ferrocene derivatives, the metal plays only a secondary role, the importance of these compounds arises from the structural motif of the sandwich complex. A large variety of bidentate *P,P*-, *P,N*- and *N,N*-ligands containing the ferrocene moiety are applied to transition metal-catalyzed reactions such as asymmetric hydrogenations, hydrosilylations, cross-couplings, cycloadditions and aldol reactions. Iron carbonyls are mainly used to modify the reactivity of coordinated olefin ligands and to facilitate unusual transformations. They can act as protecting group for conjugated dienes. Furthermore, the iron carbonyl fragment exerts also directing effects in stereoselective reactions rendering it a stereocontrolling element.

In the group of Prof. Jenny we are interested in stoichiometric and catalytic applications of different iron compounds. The various iron complexes studied have found interesting uses. Thus, iron carbonyl complexes are employed stoichiometrically to control the stereochemistry in the synthesis of Taxol®, one of the most promising anticancer agents with antileukemic and tumor inhibitory

properties. An electronically mimic of a cyclopentadienyliron complex can act as promotor in the cyclization of homofarnesol. Ambrox® is obtained in good diastereoselectivity, a highly valuable parfumery compound registered by Firmenich. Another type of iron compounds is used for the hydrogenation of olefins: After activation diimineiron complexes are able to catalyze the reduction of mono-, di- and trisubstituted alkenes with molecular hydrogen under mild conditions.



Taxol Ambrox

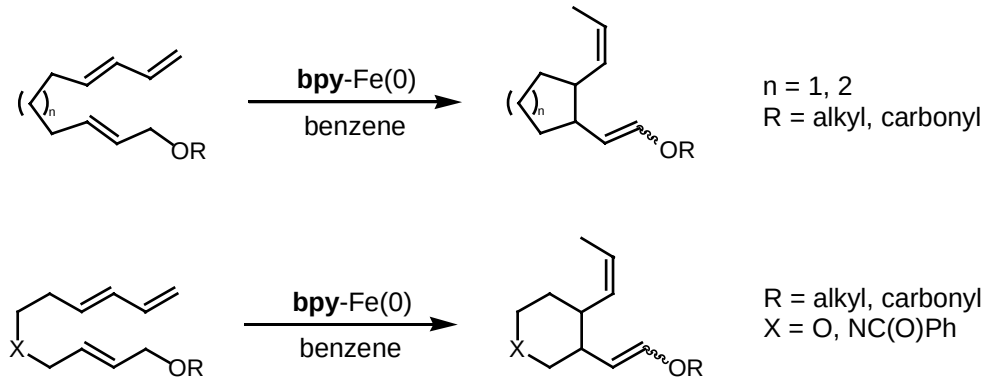
Chart 1: Structures of Taxol® and Ambrox®

The aim of this work was to investigate the diimineiron hydrogenation catalyst with regard to the mechanism and to explore rationally new chiral ligands and activation methods to facilitate stereocontroled hydrogenations and to allow the presence of functional groups in the substrates during the catalytic reaction. When the hydrogenation is sufficiently understood the catalyst should be applied to the polymerization of alkynes and, in a later stage, to the polymerization of olefins.

2. Iron catalysts for carbon-carbon bond formation

2.1 Carbocyclization catalysts

A Fe^0 catalyst developed by TAKACS is able to promote intramolecular [4+2] ene carbocyclization reactions of acyclic triene ethers and esters. Originally the same catalyst is used for the intermolecular formal ene reactions of 1,3-dienes with allylic ethers.[1]



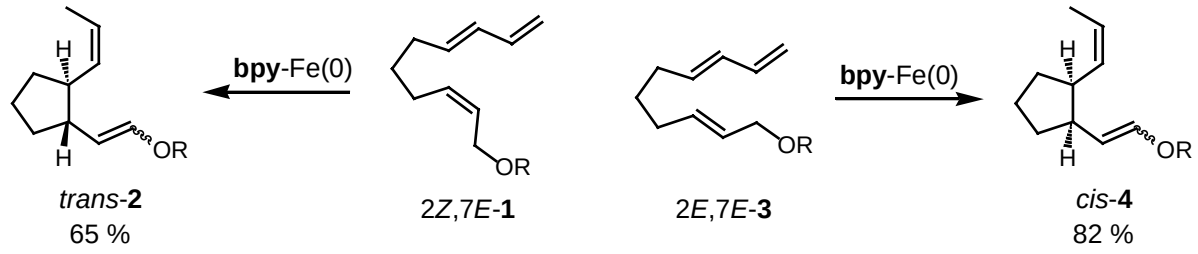
Scheme 1: General scheme of the carbocyclization reaction

The soluble iron(0) complexes are conveniently prepared *in situ* via reduction of Fe(II) or Fe(III) salts (usually the chlorides or acetyl acetonates) by Grignard or trialkylaluminium reagents. Thus, an active "**bpy**-Fe(0)L_n" catalyst is obtained by treatment of Fe(III)$(acac)_3$ with triethylaluminium in benzene in the presence of 2,2'-bipyridine (**bpy**) and an additive such as furan. Apparently the additive serves to stabilize intermediate catalyst complexes.

Suitable substrates for the carbocyclization reaction are 2,7,9- and 2,8,10-triene ethers and esters. The iron(0) catalyst has been applied for the construction of cyclopentyl, cyclohexyl, tetrahydropyranyl[2] and N-acylpiperidinyl[3] rings from these triene precursors. Functional groups are only tolerated in the substrates when they are not attacked by the reducing reagent. Hence the substrates can bear ether, silylether and trisubstituted amine functionalities, and ester groups without hydrogen in α-position

are tolerated too. Substrates with more substituted double bonds react much slower, trisubstituted double bonds have to carry an electronwithdrawing substituent to ensure the cyclization reaction.

This iron(0) catalyzed carbocyclization shows interesting stereoselectivity properties. The *E*/*Z*-geometry of the $\Delta_{2,3}$-double bond offers a means to control the *cis*/*trans*-disposition of the vicinal substituents in the cyclic product by simple diastereoselection. The (2*Z*,7*E*)-triene **1** gives rise to the *trans*-disubstituted product **2**, while the geometric isomer (2*E*,7*E*)-triene **3** gives rise to the *cis*-disubstituted cyclopentane **4**.



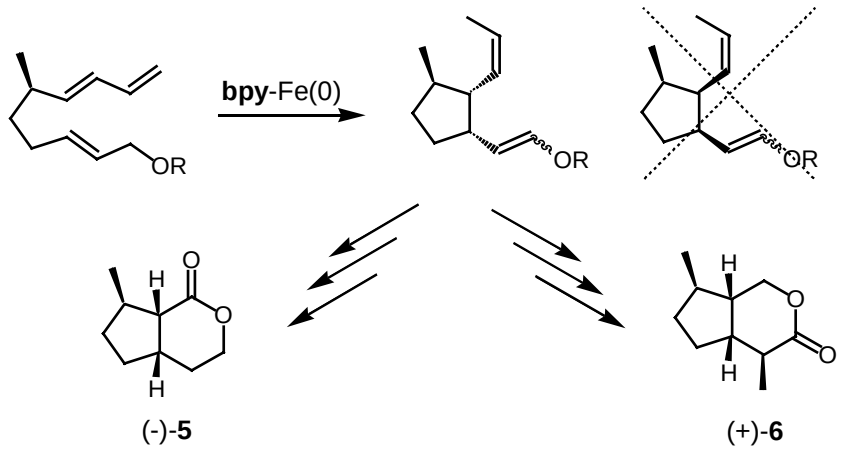
Scheme 2: Regioselectivity of the carbocyclization reaction

This stereocontrol apparently arises from facial discrimination in the complexation of the $\Delta_{2,3}$-double bond. Stereospecific *syn*-oxidative cyclization then sets the *cis*- or *trans*-relative stereochemistry observed in the final carbocycles.[4] The same diastereoselectivity is also observed in the cyclization reactions to six-membered rings.

Changing the diene geometry from *E* to *Z* have the effect of reversing the sense of diastereoselectivity in the cyclized products. However, the iron-catalyzed *Z*-to-*E* diene isomerization is usually faster than the ene carbocyclization process and only *trans*-disubstituted carbocycles are obtained in most cases.

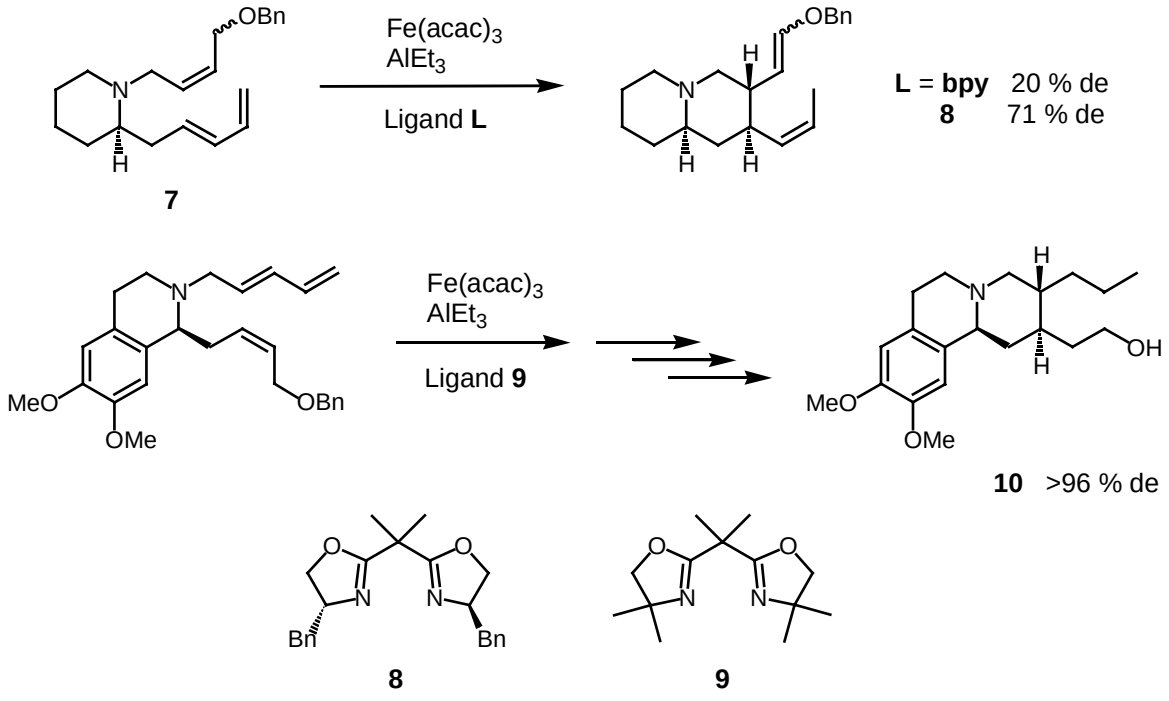
A further element of stereocontrol is obtained by the introduction of a chiral center in the tether of the triene substrates. High stereoinduction enables to control the relative stereochemistry of three contiguous asymmetric centers, and one of two possible diastereomers is formed almost exclusively.[5] This stereoselective cyclization

strategy is applied in the enantioselective syntheses of the two iridoid monoterpenes (-)-mitsugashiwalactone (**5**) and (+)-isoiridomyrmecin (**6**).[6]



Scheme 3: Diastereoselectivity of the carbocyclization reaction

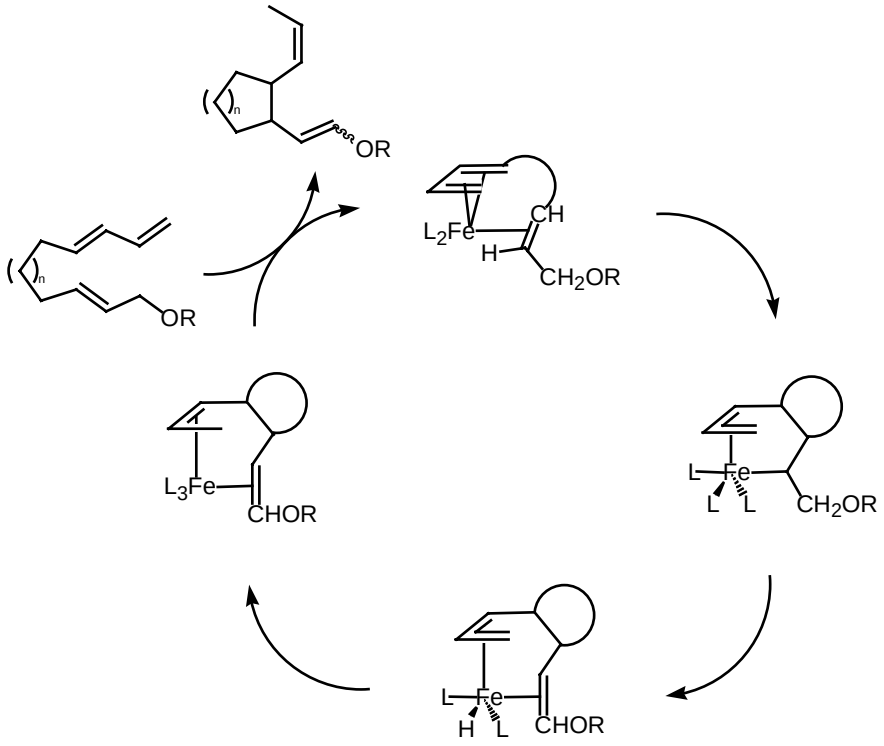
The same iron(0) catalyzed cyclization reaction can be used for the construction of bicyclic ring systems. The choice of a correct ligand is important to obtain high diastereoselectivities in these cases.[7]



Scheme 4: Influence of ligands on the diastereoselectivity

The piperidinetriene **7** is cyclized with only 20 % diastereomeric excess (de) in presence of **bpy** as ligand, whereas the use of the chiral bisoxazoline **8** as ligand yielded 71 % de under the same conditions. In the stereoselective synthesis of methylprotoemetinol (**10**) excellent diastereoselectivity is obtained with the achiral bisoxazoline ligand **9**.[8]

The mechanism proposed by TAKACS involves initial formation of an iron(0) diene-olefin complex, which undergoes oxidative cyclization to a π-allyl σ-alkyl iron(II) complex. β-Hydride elimination takes place from this intermediate complex, followed by reductive elimination to a di-π-ene complex. Ligand exchange of the product with a new triene molecule closes the catalytic cycle. Two coordination sites are always occupied by the didentate diimine ligand, a further ligand to stabilize unsaturated complexes is provided by the presence of an additive.

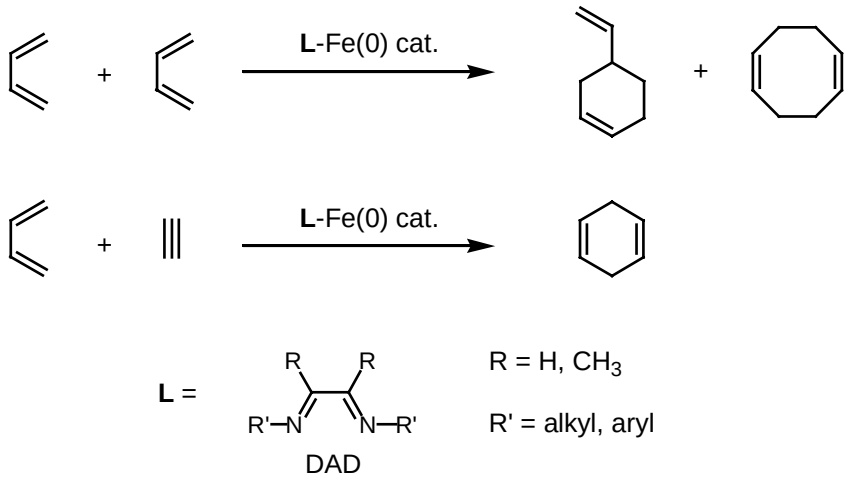


Scheme 5: Proposed mechanism for the carbocyclization

2.2 Cycloaddition catalysts

2.2.1 Diene dimerization catalysts

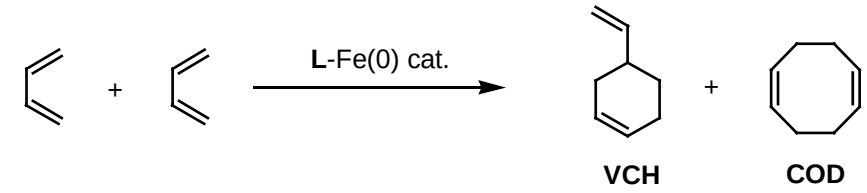
TOMDIECK introduced a (diimine)iron catalyst for [4+4] and [4+2] cycloaddition reactions.[9] 1,3-Dienes cyclodimerize to the 1,5-cyclooctadiene derivatives or in a Diels-Alder reaction to the cyclohexene products. Cyclohexadiene products are obtained when 1,3-dienes are reacted with alkynes. The active catalyst for these cyclization reactions is generated upon treatment of a diazadiene-iron(II)chloride adduct with a Grignard or a trialkylaluminium reagent. (Diimine)Fe(II)$(NO)_2$ complexes can be used as catalyst precursors too.[10] The use of (diazadiene)$_2$Fe(0) complexes or Fe(acac)$_3$/diimine mixtures as precatalysts require elevated temperatures (90 °C) to generate the active catalyst. The reactivity of the catalyst depends on the substituents R' in the ligand. Whereas N,N-dialkyldiimine ligands are successfully employed for all the investigated cyclization reactions, N,N-diaryldiimine ligands are not active in the Diels-Alder reaction with alkynes.



Scheme 6: Diene cycloaddition reactions

The steric bulk in the diimine ligand and the reaction temperature are important for the chemo- and stereoselective outcome of the cyclizations. This behaviour can be observed in the cyclodimerization of 1,3-butadiene to 4-vinylcyclohexene (**VCH**) and

1,5-cyclooctadiene (**COD**) using N-menthylpyridylimine ligands.[11] Whereas the simplest ligand (R = H) gives 69 % of **VCH** with only 24 % enatiomeric excess (ee) at room temperature, 80 % of **VCH** with 47 % ee is obtained when the cycloaddition is carried out at 5 °C. Increasing the steric bulk in the menthyl moiety rises the ee of the **VCH** product, but the chemoselectivity changes in favour of the achiral **COD**.



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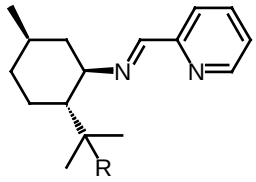
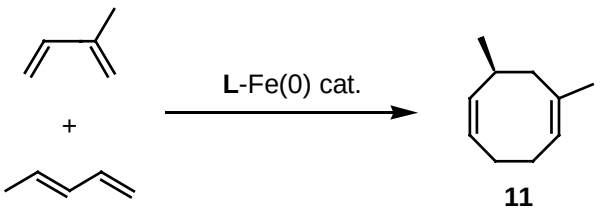


	T [°C]	**VCH** (% ee)	**COD**
R = H	RT	69 % (24)	31 %
R = H	5	80 % (47)	20 %
R = Me	RT	49 % (56)	51 %
R = Ph	RT	33 % (62)	67 %

Scheme 7: Chemoselectivity of the diene dimerization

The property of bulky ligands to rise the enantioselectivity in the product and to favour the formation of the **COD** product is used for the stereoselective synthesis of optical active cyclooctadiene products.[12] The [4+4] codimerization of isoprene and *trans*-piperylene with an iron catalyst bearing a bulky bis(menthylimine) ligand furnishes 89 % of the corresponding chiral cyclooctadiene derivative **11** with 61 % ee.



11

89 % (61 % ee)

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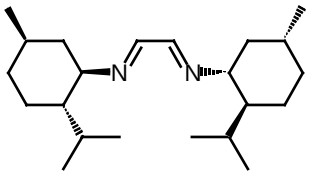
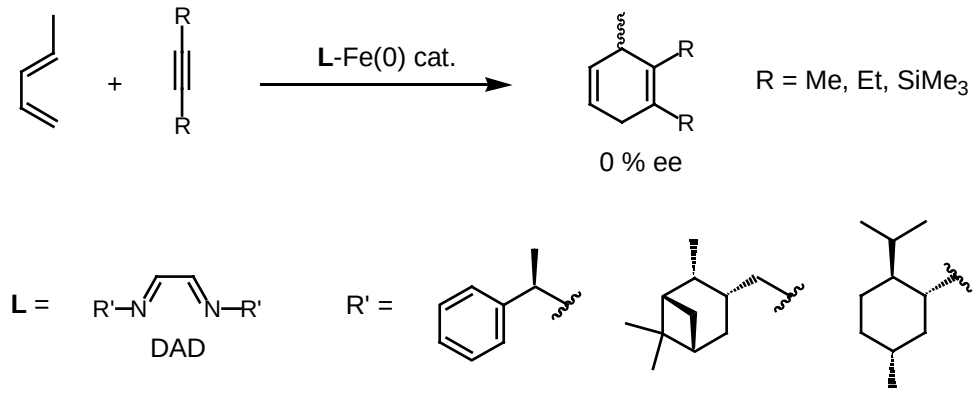


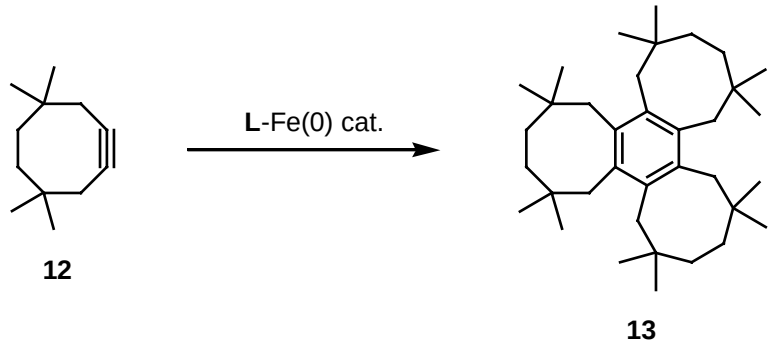
Scheme 8: Enantioselective diene cycloaddition

In Diels-Alder reactions of *trans*-piperylene and alkynes, cyclohexadiene products with an asymmetric center are formed. In these reactions no asymmetric induction is obtained using chiral diimine ligands.



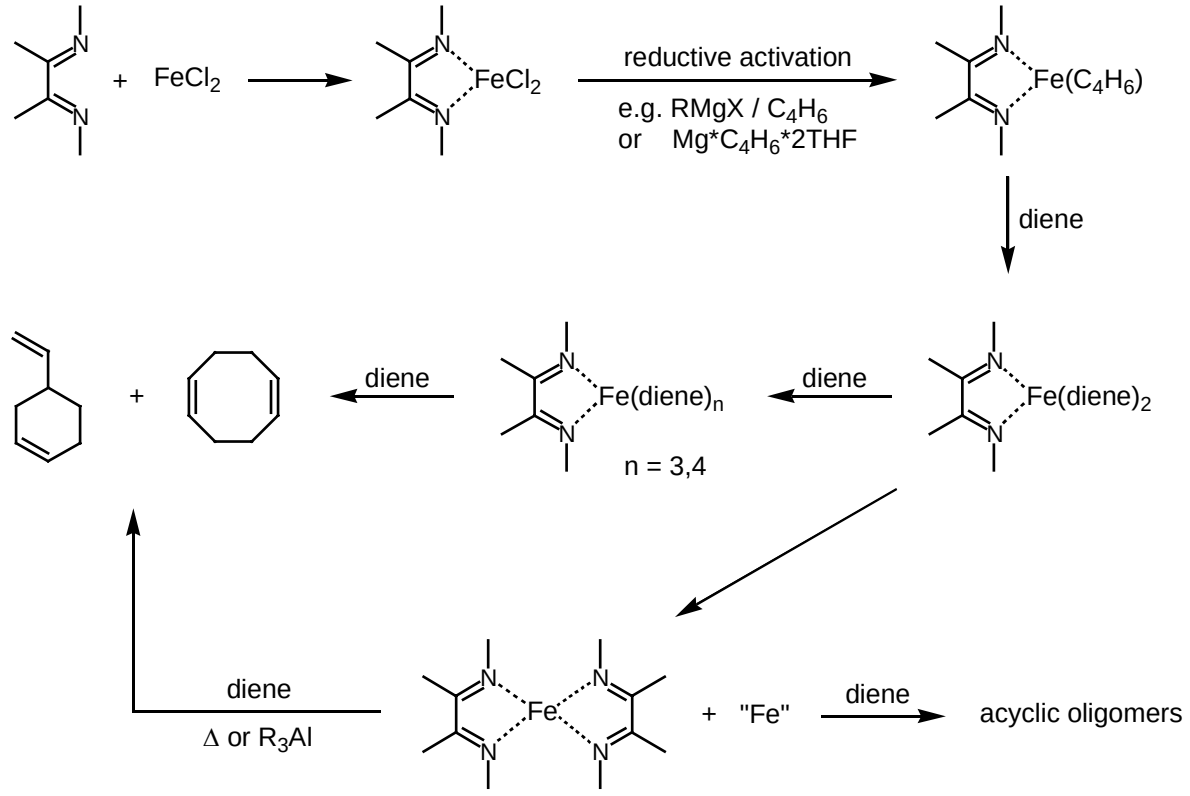
Scheme 9: Diels-Alder cycloaddition

In these [4+2] cycloadditions only unfunctionalized acyclic dienes and alkynes can be used as substrates. Cyclic and sterically crowded dienes don't react even at elevated temperatures. When the strained cyclooctyne **12** is engaged, [2+2+2] cyclo-trimerization occurs and the benzene derivative **13** is obtained as only product.



Scheme 10: Cyclotrimerization side reaction

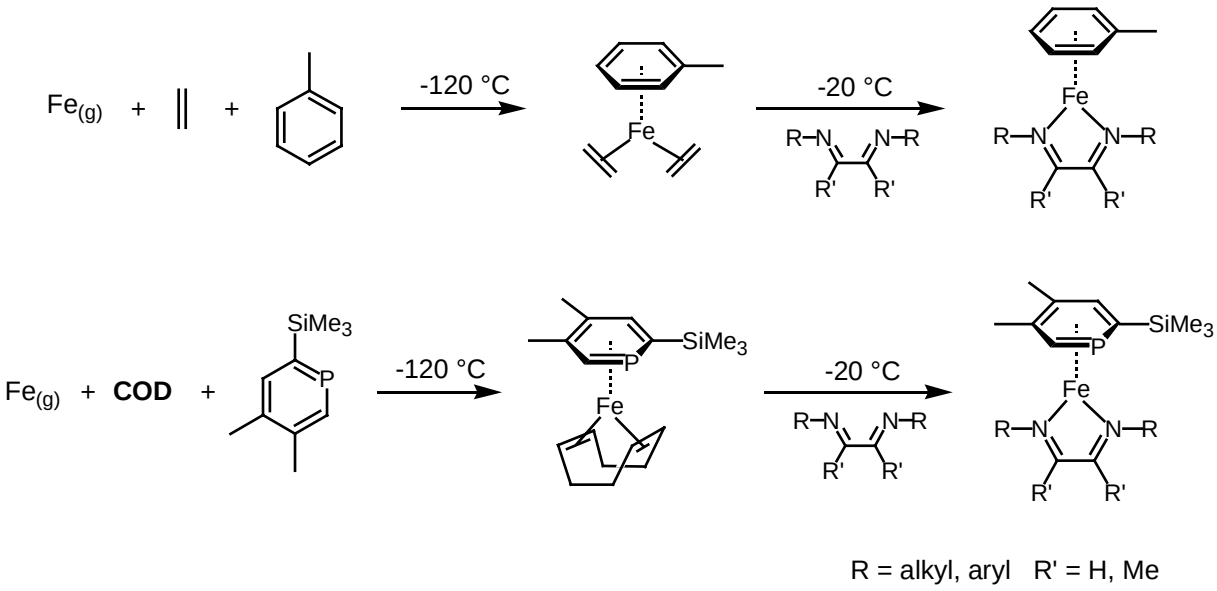
No detailed mechanism is given for these cycloaddition reactions. TOMDIECK isolated (diazadiene)$_2$iron(0) complexes after the reduction of the diazadiene-iron(II)chloride adducts with Grignard reagents or alkali metals,[13] so he suggested a (diimine)iron(0) species to be the active catalyst.



Scheme 11: Proposed mechanism for the diene cycloaddition

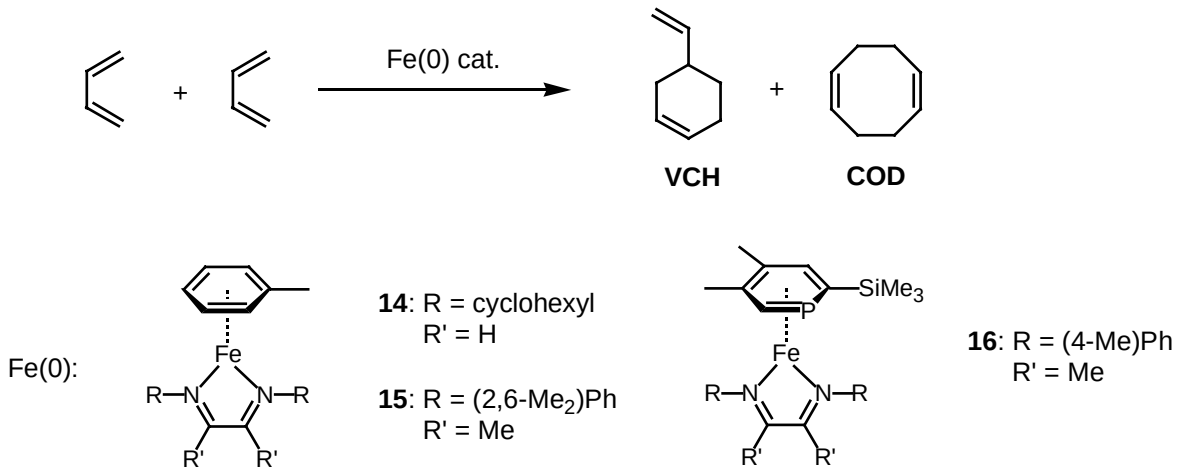
Another type of diimine iron catalysts, i.e. (diimine)(η⁶-toluene)iron(0) and (diimine)(η⁶-2-trimethylsilyl-4,5-dimethylphosphinine)iron(0) complexes are reported by ZENNECK to catalyze the cyclodimerization reaction of 1,3-butadiene.[14] The (diimine)(η⁶-arene)iron(0) catalyst precursors syntheses are quite demanding. A bis(alkene)(toluene)iron(0) complex is obtained by co-condensation of iron vapor, ethylene and toluene.[15] Alkene ligand exchange in the resulting bis(ethene)(η⁶-toluene)Fe(0) with the diazadiene ligands at very low temperature gives the (diazadiene)(η⁶-toluene)iron(0) catalyst precursor complexes. The same metal vapor cocondensation procedure can be applied for the synthesis of the phosphinine complexes, but **COD** is used as alkene instead of ethylene in this case. Alternatively the bis(**COD**)(phosphinine)iron(0) complexe can be obtained by *in situ* reaction of the phosphinine ring with the highly reactive **COD**$_2$Fe[16] complex. Alkene ligand exchange in bis(**COD**)(phosphinine)iron(0) with the diimine ligands gives the

desired (diimine)(η⁶-2-trimethylsilyl-4,5-dimethylphosphinine)-iron(0) catalyst precursors.



Scheme 12: Syntheses of (diimine)(arene)iron(0) complexes

The active catalysts are generated then by treatment of the (diazadiene)(η⁶-arene)iron(0) precursors with an ethylaluminoxan $(Et_2AlOEt)_2$ cocatalyst. 1,3-Butadiene is cyclodimerized in presence of the active catalyst to **VCH** and **COD** analogous to TOMDIECK's catalysts. The main difference is the lower reactivity of the (diimine)(η⁶-arene)iron(0) complexes as compared to the (diazadiene)Fe(0) catalysts, the cyclodimerization reaction requires elevated temperatures (120 °C) for the (η⁶-arene)iron(0) catalysts to occur. The toluene complexes **14** and **15** display higher reactivity as compared to the phosphinine species **16** explained by a stronger Fe-phosphinine interaction hampering the formation of the active catalyst. Good chemoselectivity in favour of the [4+4] cycloaddition product **COD** is obtained for both types of arene complexes.



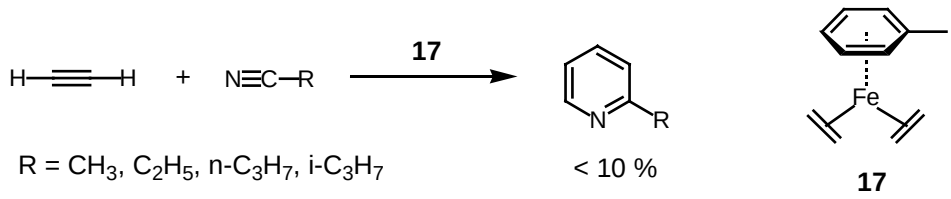
Scheme 13: Butadiene cyclodimerization

Table 1: Efficiency and chemoselectivity of the butadiene cyclodimerization

Entry	Catalyst	TON **VCH**	TON **COD**	**COD** selectivity
1	**14**	240	972	80 %
2	**15**	130	1479	92 %
3	**16**	54	94	64 %

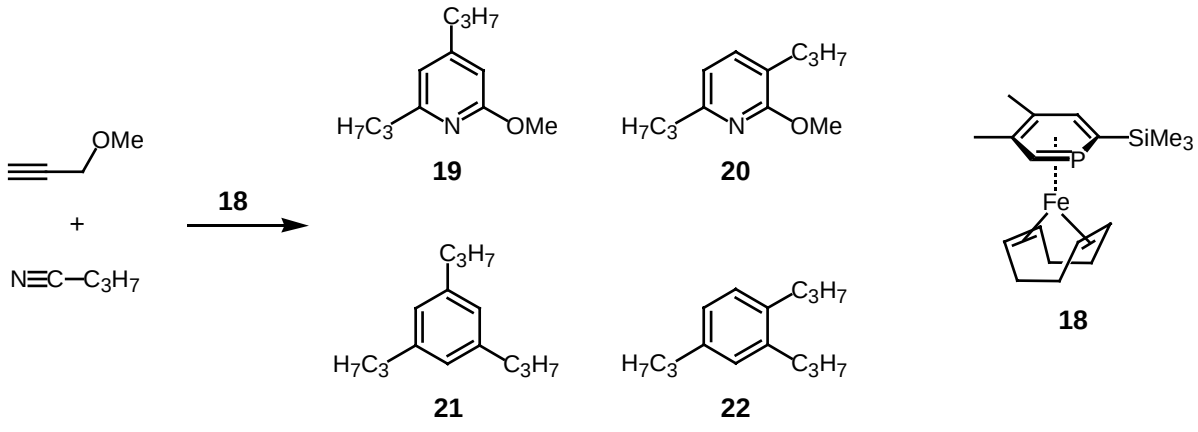
2.2.2 Alkyne trimerization catalysts

The bis(alkene)(η^6-arene)iron(0) complexes of ZENNECK are active catalysts for [2+2+2] cycloaddition reactions at room temperature. The bis(ethene)(η^6-toluene)Fe(0) complex **17** cyclotrimerizes alkynes to the corresponding benzene derivatives under formation of a new η^6-arene ligand.[17] The benzene product is liberated then by decomposition of the resulting (η^6-arene)(η^6-toluene)Fe(0) complex and consequently the reaction is not catalytic in iron. Catalytic activity is observed for the [2+2+2] cocyclotrimerization of acetylene with unfunctionalized alkyl nitriles, but in these cases the resulting pyridines are isolated only in poor quantity.[18]



Scheme 14: Cycloaddition reaction to pyridines

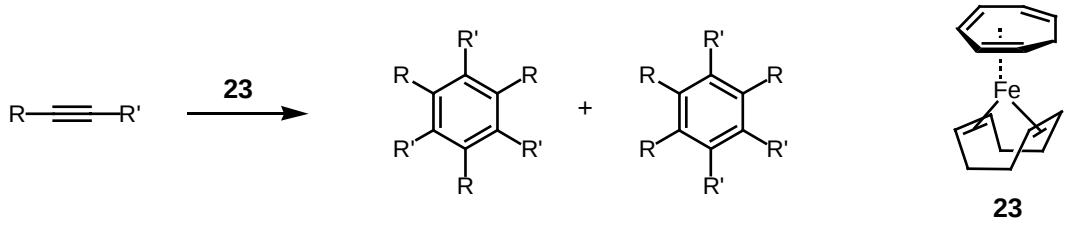
This pyridine formation is catalyzed more efficiently by the (**COD**)(η⁶-2-trimethylsilyl-4,5-dimethylphosphinine)iron(0) complex **18**.[19] The cycloaddition of propargylmethylether with an excess of butyronitrile results in the formation of two isomeric pyridine derivatives **19** and **20** along with the two isomeric benzene derivatives **21** and **22**. The symmetric 2,4,6-substituted pyridine derivative **19** is preferred over the 2,3,6-derivative **20**, but the symmetric 1,3,5-substituted benzene derivative **21** is produced in lower yield than the asymmetric **22**; however, this regioselectivity is not very pronounced (ca. 3:2). Diazines or triazines have not been identified in the reaction mixtures. The chemoselectivity of this reaction depends on the substrate concentrations and favours the formation of the benzene products. A TON of 160 for pyridine formation with a chemoselectivity of 0.69 are found as best values for this cotrimerization.



Scheme 15: Chemo- and regioselectivity in the cycloaddition to pyridines

Recently a new alkyne cyclotrimerization catalyst is described by BRESCHI.[20] The (η⁶-cycloheptatriene)(η⁴-**COD**)Fe(0) complex **23** easily catalyzes the cyclotrimerization of

terminal and internal alkynes to the benzene derivatives at room temperature. **23** is obtained by metal vapor cocondensation synthesis like the before mentioned complexes **17** and **18**. **23** displays the same η^6, η^4 coordination of the ligands as **17** and **18**, but in this case a nonaromatic triene ligand instead of an arene ligand is involved. A wide range of alkynes can be reacted with catalyst **23**. The corresponding benzenes are obtained in high yield, but only small regioselectivity was observed for unsymmetrically substituted alkynes. A quite high TOF of 5.4 h^{-1} was assessed for the reaction of 2-butyne indicating an efficient catalyst for such cyclotrimerization reactions.



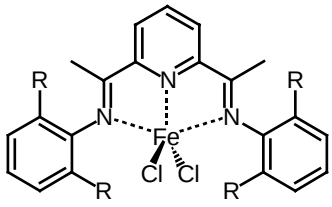
R = H; R' = $(CH_2)_3CH_3$, $C(CH_3)_3$, C_6H_5, $Si(CH_3)_3$
R, R' = CH_3, C_6H_5

Scheme 16: Cyclotrimerization of alkynes

2.3 Olefin polymerization catalysts

Only five years ago BROOKHART[21] and GIBSON[22] independently described a new iron catalyst bearing tridentate 2,6-bis(arylimino)pyridyl ligands for the polymerization of ethylene. The catalyst precursor complexes are prepared by treatment of $FeCl_2$ with the 2,6-bis(imino)pyridines. The active catalyst is generated *in situ* by the addition of modified methylaluminoxane (MMAO, ≥ 300 equiv.) in presence of ethylene. These catalysts produce essentially highly linear polyethylene, no branching is observed. However, the polymer molecular weight markly depends on ethylene pressure, nature of ligand and concentration of activator. Increasing the ethylene pressure or the steric bulk of the *ortho* substituents in the aryl part increases the molecular weight of the resulting polyethylene. Using large amounts of activator leads to broadened polydispersity and lower molecular weight. The turnover

frequencies (TOF) increase with ethylene pressure. TOFs up to 10^7 h^{-1} can be achieved at 60 °C and 40 bar C_2H_4 pressure. These activities are comparable to the most active Ziegler-Natta systems.[23]



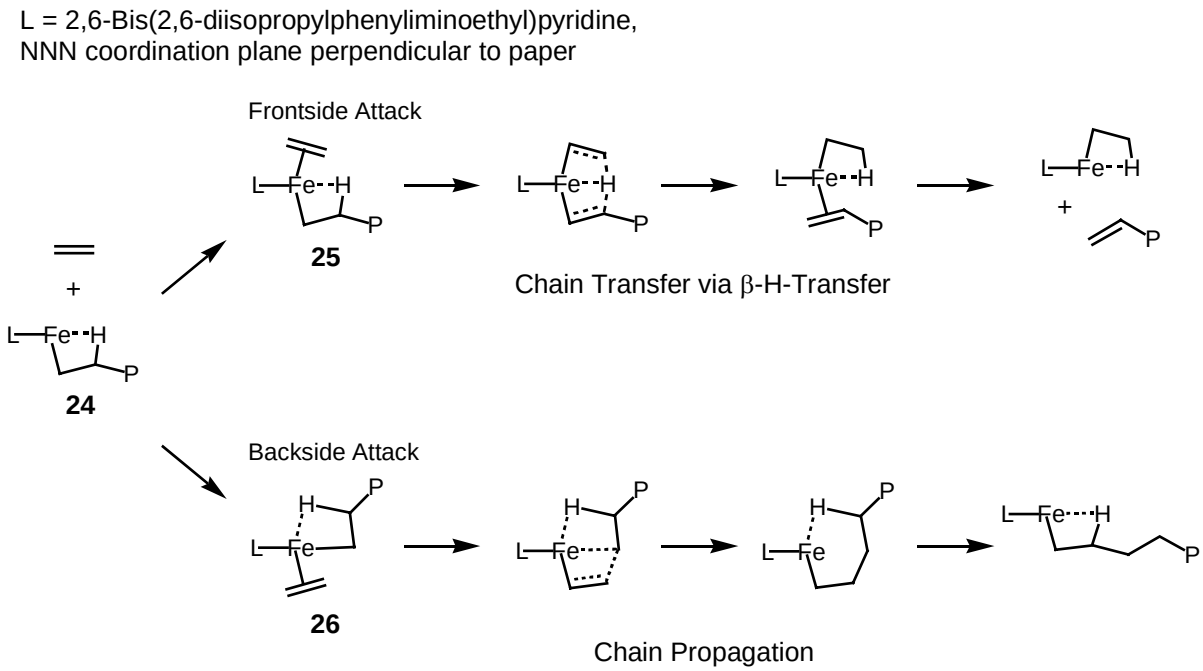
Activity in [g $mmol^{-1}$ bar^{-1} h^{-1}]		
R	Activity	Mw PE
Me	570	29000
^{i}Pr	1170	203000

Chart 2: Ethylene polymerization catalyst

The 2,6-bis(arylimino)pyridine can also be complexed with other metals such as Ni[24] or Co[25] to provide catalyst precursors. Again, active polymerization catalysts are obtained by activation with MMAO, but the corresponding iron catalysts are always superior in their polymerization activity.

The mechanism of the polymerization is discussed by ZIEGLER refering on an extensive theoretical study based on DFT and combined DFT/MM calculation methods.[26] In analogy to other olefin polymerization catalysts a cationic iron-σ-alkyl complex **24** is assumed as the active Fe(II) species. This resting state adopts a conformation with the C_α atom in an axial position and an agostic β-hydrogen bound to the metal trans to the pyridine nitrogen. Two ethylene complexes are located on the PES (potential energy surface) that are readily accessible by ethylene uptake of the iron(II) alkyl complex **24**. Chain propagation occurs through the backside complex **26**, which is reached from an axial ethylene approach from the same side of the iron-nitrogen coordination plane as the C_α atom. Insertion takes place from **26** with a modest energy barrier. The chain propagation is driven by a strong thermodynamic force with an exothermicity of 27.9 kcal/mol. The rate-determining step is the capture of ethylene by **24** with an energy barrier of 7.1 kcal/mol. The other (frontside) complex **25** is responsible for chain termination. **25** is formed by an attack of ethylene from above the iron-nitrogen coordination plane trans to the C_α atom. Steric bulk helps to suppress the formation of the termination precursor **25** by

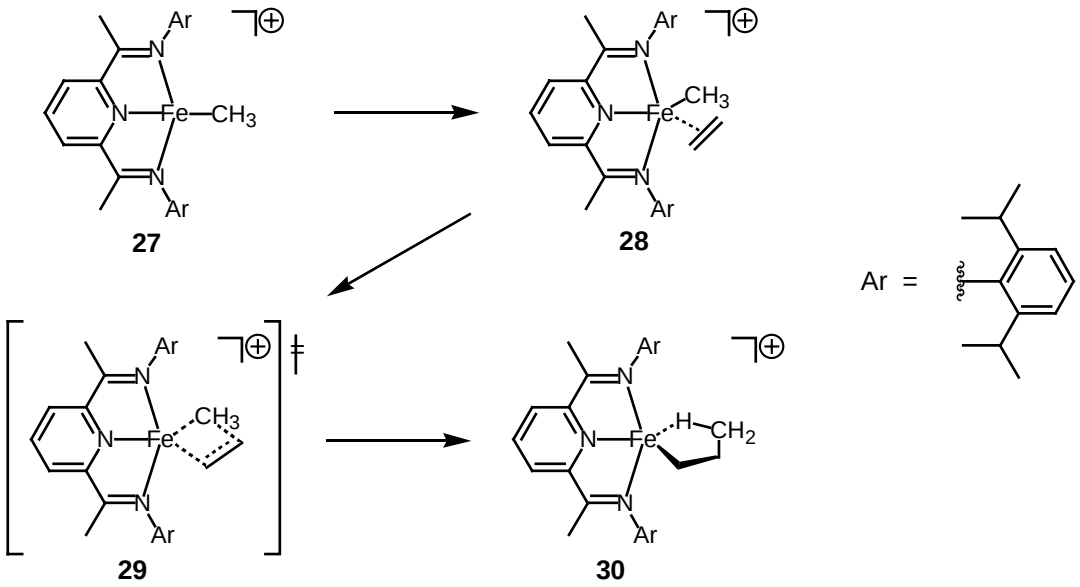
destabilizing the ethylene complexation energy, and the propagation precursor **26** can now be formed in competition with **25**.



Scheme 17: Calculated mechanism for the ethylene polymerization by ZIEGLER

In an *ab initio* study of the same catalyst, GOULD calculated the energies of four assumed key structures of the polymerization.[27] In this approach the chain propagation proceeds from the cationic iron(II)-σ-methyl complex **27**. Ethylene uptake leads to complex **28** with a binding energy of 38.9 kcal/mol. The low insertion barrier of 2.5 kcal/mol facilitates the insertion process to complex **30**. The high propagation energy of 52.6 kcal/mol can't be compared to ZIEGLER's results because the calculated structures are incompatible.

Neutral Fe(II) complexes rather than cationic intermediates are suggested to be the active species by TALZI,[28] whereas evidence for the presence of iron solely in the +3 oxidation state is found by BRITOVSEK from Mössbauer and ESR spectroscopy.[29]



Scheme 18: Calculated mechanism for the ethylene polymerization by GOULD

Together with alkyl substituted phenyl groups on the imine nitrogen atoms of the bis(imino)pyridines, ligands with other substituents on the imines are introduced. Amongst them are bulky, alkyl-free aromatic groups such as naphthyl or pyrenyl,[30] substituted N-heterocycles[31] and bulky tertiary amines[32] leading to bis(hydrazone)-pyridine ligands, and phosphino groups.[33]

The ethylene polymerization is also feasible with supported bis(imino)pyridyliron(II) catalysts. Heterogenized catalysts are obtained by either immobilizing the catalyst precursor[34] or the activator.[35] Other activators than MMAO, mainly trialkyl-aluminium reagents, can be used to form the active catalysts.[36] Careful choice of the activator and the reaction conditions provides catalysts which are able to polymerize propylene[37] and other olefins such as norbornene.[38]

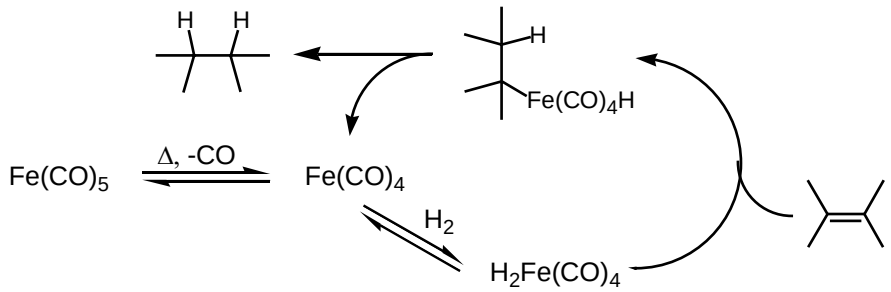
The importance of these 2,6-bis(imino)pyridineiron(II) complexes as ethylene polymerization catalysts can be seen in the rapidly growing number of publications concerning such compounds. In view of all the ligands reported so far for this purpose, structural singularity is displayed by the first generation catalyst with the bis(2,6-diisopropylphenylimino)pyridine ligand. This property appears in the by far most efficient catalyst, since any change in the ligand will deteriorate of even kill the catalytic activity.

3. Iron hydrogenation catalysts

A large number of hydrogenation catalysts with transition metals are known. Besides the classical heterogeneous metal catalysts, complexes containing mainly Pd,[39] Rh,[40] Ru,[41] Ir,[42] Ni,[43] Co,[44] Ti[45] and Cr[46] are reported to be efficient hydrogenation catalysts for the reduction with molecular hydrogen. Over the last ten years many other transition metals[47] were introduced for catalytic hydrogenations.
In contrast to the great variety of applications for these metals only few examples of iron hydrogenation catalysts have been described so far.[48] In addition to the limited number of substrates which can be hydrogenated these reactions often require high H_2 pressures (30 - 100 bar) and/or elevated temperatures (150 - 180 °C).

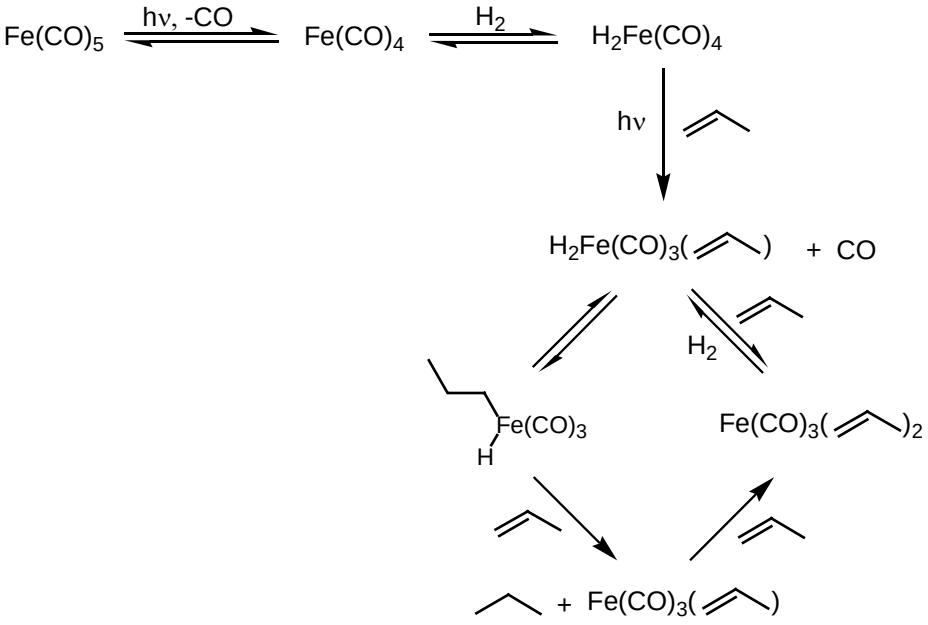
3.1 Carbonyliron(0) catalysts

Ironpentacarbonyl, known especially for its olefin isomerization activity, also has found limited use as hydrogenation catalyst. At high temperatures (>180 °C) and hydrogen pressures (>200 bar), $Fe(CO)_5$ catalyzes the hydrogenation of unsaturated fatty acid esters.[49] The catalysis is explained by formation of the thermally unstable $H_2Fe(CO)_4$ complex, which is a strong reducing agent. Irreversible insertion of the dihydride iron complex into a substrate double bond followed by reductive elimination leads to the hydrogenated products and coordinatively unsaturated $Fe(CO)_4$, which is stabilized by addition of H_2 regenerating the dihydride species.



Scheme 19: Thermally activated ironpentacarbonyl as hydrogenation catalyst

Simple alkenes such as propylene and cyclopentene are hydrogenated under near-UV irradiation of $Fe(CO)_5$ at RT and 1 bar H_2.[50] A slightly different mechanism is proposed for this photocatalyzed hydrogenation of alkenes. As in the previous case the dihydride tetracarbonyliron complex is formed, but the continuous irradiation causes loss of a further carbonyl ligand and coordination of the alkene substrate to the active $H_2Fe(CO)_3$(alkene) species. The catalytic cycle proceeds then via insertion in the coordinated double bond followed by irreversible reductive elimination of the alkane product. The intermediate tricarbonyliron fragment is stabilized by coordination of a new alkene molecule. The active catalyst is regenerated by exchange of an alkene ligand with H_2.



Scheme 20: Photochemically activated ironpentacarbonyl as hydrogenation catalyst

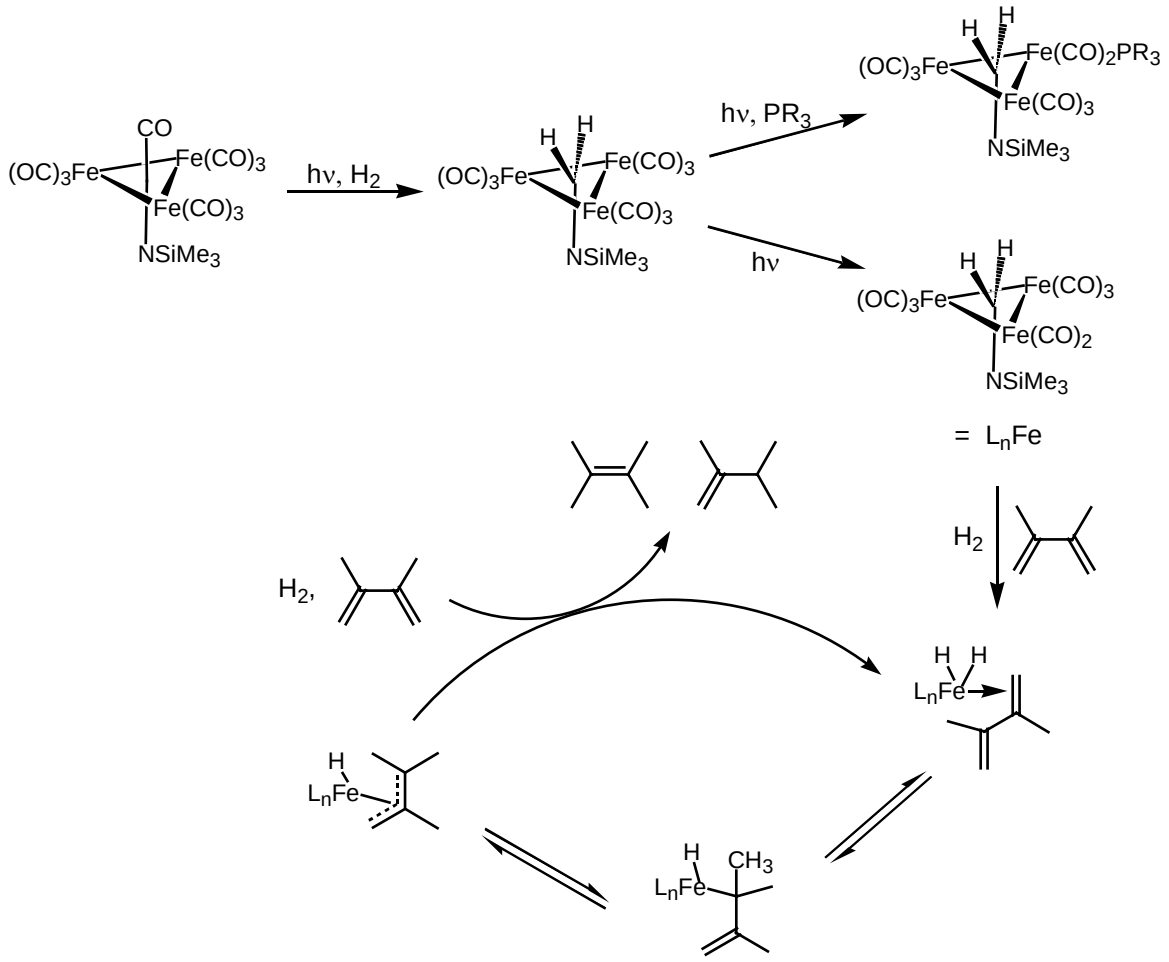
Stoichiometric hydrogenation activity for selected aldehydes and ketones is obtained with $Fe(CO)_5$ in NEt_3.[51] Benzaldehyde and butyraldehyde as well as acetone and acetophenone are hydrogenated successfully whereas benzophenone failed to react. Under the same conditions N-benzylideneaniline is hydrogenated to N-benzylaniline.[52] These reactions proceed most probably via a heterolytic mechanism.

Treatment of iron(III)trisacetylacetonate with trisisobutylaluminium in 1-hexene or cyclohexene gives an active, soluble Ziegler-type catalyst,[53] which hydrogenates the solvent at ~4 bar hydrogen pressure.

A phenyllithium activated $Fe_4S_4Cl_4^{2-}$ cluster exhibits catalytic activity in the hydrogenation of stilbene and the four isomeric octenes.[54] The hydrogenation efficiency in the formation of octane is strongly dependent on the molar ratio of phenyllithium to $Fe_4S_4Cl_4^{2-}$ cluster. Thus the most active catalyst is obtained when 8 equivalents PhLi are used for activation.

The photochemical reaction of the trinuclear $Fe_3(CO)_{10}NSi(CH_3)_3$ complex under hydrogen atmosphere leads to substitution of the capping carbonyl ligand by two hydrogens.[55] The resulting dihydride complex acts as catalyst precursor in the photochemical hydrogenation of acrylic acid and propionic acid methylesters, 2,3-diemethylbutadiene, cyclobutene, cyclobutenedicarboxylic acid dimethylester and cyclobutenedicarboxylic acid anhydride. The postulated mechanism for the 2,3-dimethylbutadiene hydrogenation is depicted in scheme 21.

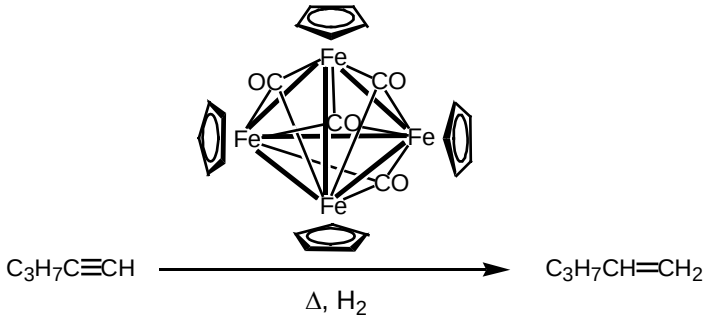
The active catalyst is obtained by irradiation of the dihydride $H_2Fe_3(CO)_9$ $NSi(CH_3)_3$ causing loss of a further CO ligand. The free coordination site can be occupied by a phosphine ligand PR_3, but these complexes show only poor catalytic activity. In presence of a substrate the unsaturated complex is stabilized by π-coordination of the C-C double bond followed by hydrogen atom transfer to the hydrideiron-σ-alkyl complex. In the case of the butadiene derivative the reductive elimination of the alkane product occurs from the π-allyl complex as indicated by the presence of both ene isomers in the product mixture. The catalytic cycle doesn't need continuous irradiation, but then the hydrogenation proceeds less efficient due to desactivation of the catalyst by CO coordination or formation of photolabile dimers.



Scheme 21: Trinuclear ironcarbonyl cluster as hydrogenation catalyst

The $[(^5\eta\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$ cluster represents another interesting hydrogenation catalyst.[56] The cluster catalyzes the selective hydrogenation of alkynes to cis-alkenes, terminal activated carbon-carbon double bonds to alkanes and aryl nitro groups to the aniline derivatives at 100-140 °C and 7-70 bar hydrogen pressure. Turnover numbers (TON) up to 1400 are attained with this catalyst. No mechanistic details are given, but the reported results suggest that the cluster itself functions as active catalyst. Fragmentation to $(^5\eta\text{-}C_5H_5)Fe(CO)_2H$ appears to be ruled out since $[(^5\eta\text{-}C_5H_5)Fe(CO)_2]_2$, which gives this iron hydride when heated in hydrogen atmosphere, was not active in 1-pentyne hydrogenation. Furthermore the cluster is reisolated in >95 % yield after the hydrogenation reactions. But the authors did not take into account that other fragments such as $(^5\eta\text{-}C_5H_5)Fe$ or $(^5\eta\text{-}C_5H_5)Fe(CO)$ can be

formed and act as active catalysts leaving the rest of the cluster intact. At the end of the hydrogenation the fragments could recombine to rebuild the tetranuclear cluster.



Scheme 22: Tetranuclear cyclopentadienylironcarbonyl cluster as hydrogenation catalyst

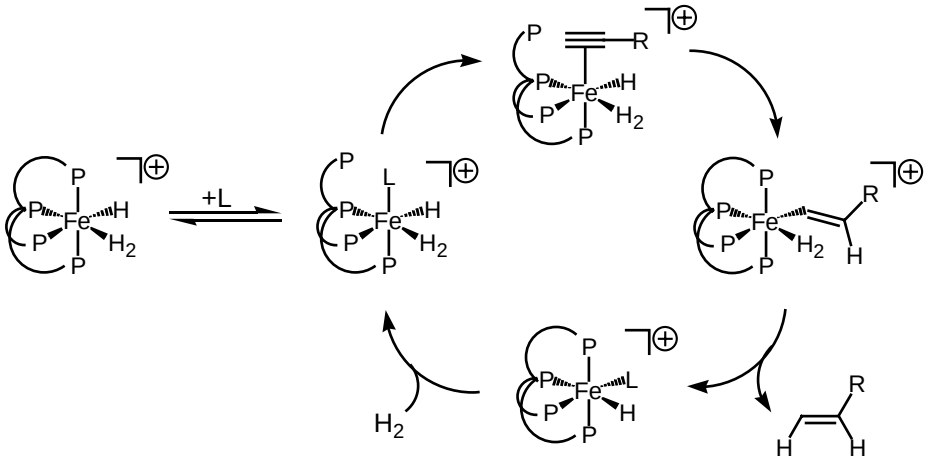
3.2 Iron(II) catalysts with a tripodal phosphine ligand

BIANCHINI reported the hydride iron complexes $[(PP_3)Fe(H)(N_2)]BPh_4$ and $[(PP_3)Fe(H)(H_2)]BPh_4$ to catalyze selectively the homogeneous hydrogenation of terminal alkynes to alkenes under mild conditions (RT-60 °C, 1 bar H_2) in THF (PP_3 = $P(CH_2CH_2PPh_2)_3$).[57] No reaction takes places with disubstituted alkynes, and no appreciable formation of alkanes is observed. The conversion decreases by increasing the bulkiness of the alkyne substituent in the substrate.

The cationic dinitrogen complex $[(PP_3)Fe(H)(N_2)]BPh_4$ can be converted upon treatment with H_2 to the nonclassical trihydride complex $[(PP_3)Fe(H)(H_2)]BPh_4$, which acts as active catalyst.[58]

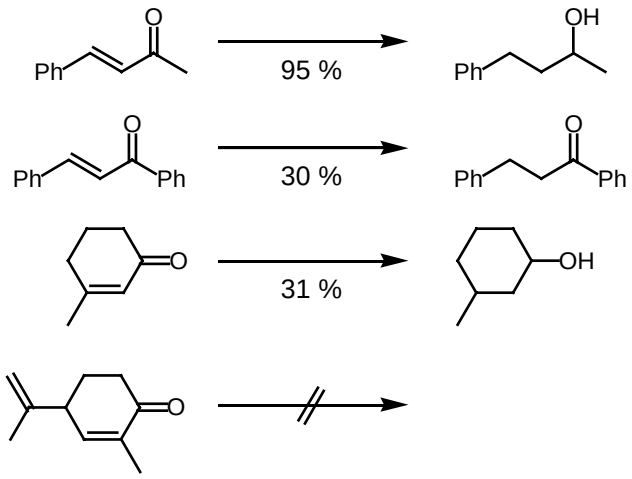
The octahedral $^2\eta$-dihydrogen iron(II) complex reacts with a terminal alkyne to give the corresponding σ-alkynyl complex. As no H_2 evolution is observed, the dihydrogen ligand remains coordinated to the iron and a terminal phosphine arm is unfastened to create a free coordination site. The σ-alkynyl inserts across the Fe-H bond forming a σ-alkenyl $^2\eta$-dihydrogen intermediate. The elimination step to liberate the vinyl product is still unclear. An oxidative addition of H_2 to iron(II) to give a classical dihydride iron(IV) complex followed by reductive elimination of the alkene seems highly improbable considering the very low tendency of iron(II) to be oxidized to iron(IV). A fast intramolecular acid/base reaction is proposed therefore

involving the acidic $^2\eta$-H_2 and the basic σ-vinyl ligand mutually *cis* disposed. The unsaturated intermediate can be stabilized by a solvent molecule L until coordination of H_2 regenerates the *cis*-hydride $^2\eta$-dihydrogen iron(II) complex.



Scheme 23: Hydrogenation mechanism proposed by BIANCHINI

The $^2\eta$-dihydrogen complex $[(PP_3)Fe(H)(H_2)]BPh_4$ is also an efficient catalyst precursor for the homogeneous reduction of α,β-unsaturated ketones via hydrogen-transfer from secondary alcohols.[59] The reactions are performed using either isopropanol or cyclopentanol as hydrogen donors in THF or dioxane as solvent. In this hydrogen-transfer reduction the vacant coordination site for the incoming ketone is provided by H_2 dissociation from the starting complex. Together with the iron(II) complex, the *cis*-hydride $^2\eta$-dihydrogen ruthenium(II) and osmium(II) complexes can be employed as catalyst precursors. Depending on the steric and electronic factors of the substrates, the corresponding α,β-unsaturated alcohol, the saturated ketone or the saturated alcohol is obtained chemoselectively. No reaction is observed when the substrate bears an alkyl substituent in α-position.



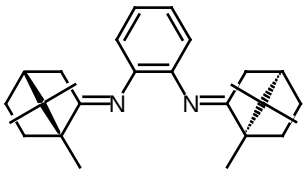
Scheme 24: Hydrogen-transfer reduction

3.3 Diimineiron(II) catalysts

During his thesis in our group, SIEBER introduced a new olefin hydrogenation catalyst based on diimineiron(II) complexes.[60] The active catalyst is prepared by addition of a precatalyst solution to an activator suspension. The precatalyst solution is obtained from a diimine ligand and iron(II)dichloride stirred overnight in benzene, the activator suspension in THF contained a reducing reagent, a substrate and a dummy ligand if needed. All hydrogenations are conducted under mild conditions at RT and 3 bar hydrogen. He investigated different ligands, alkene substrates and activators, and he proposed a mechanism for the hydrogenation. These results are summerized in the following section and represent the starting point of our work.

3.3.1 Diimine ligands

A range of nitrogen-containing ligands mainly of diimine type with a 1,4-diaza-1,3-diene (DAD) or a 2,4-diaza-1,3,5-triene (DAT) substructure were synthesized, complexed and tested for hydrogenation. The used DAT-type ligands **31-33** have a phenylene-1,2-diimine structure. The series from bisoxazoline **34**, pyridineoxazoline **35** to bipyridine **36**, acenaphthenequinonediimines **37-39** and campherquinone-diimines **40-43** belongs to the DAD-type.



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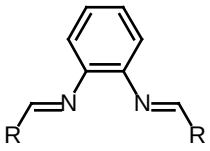
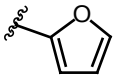
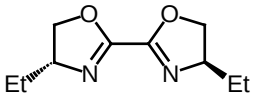


32 R = Ph

33 R = 

Scheme 26: Diazatriene (DAT) ligands which give active catalysts



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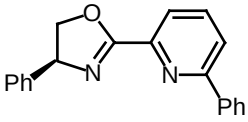

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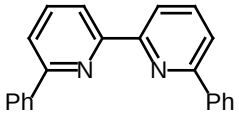

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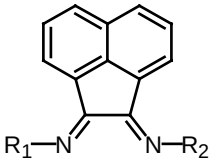
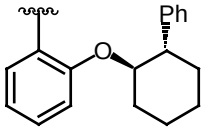
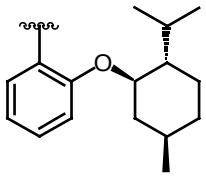
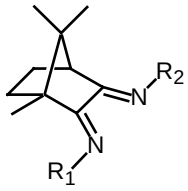


37 R_1, R_2 = Ph

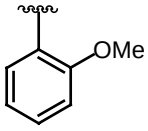
38 R_1 = Ph, R_2 = 

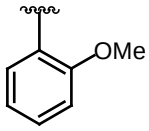
39 R_1 = Ph, R_2 = 



40 R_1, R_2 = Ph

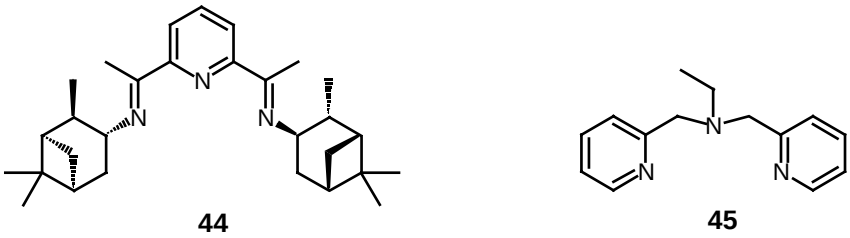
41 R_1 = Ph, R_2 = 1-Naphthyl

42 R_1 = 1-Naphthyl, R_2 = 

43 R_1, R_2 = 

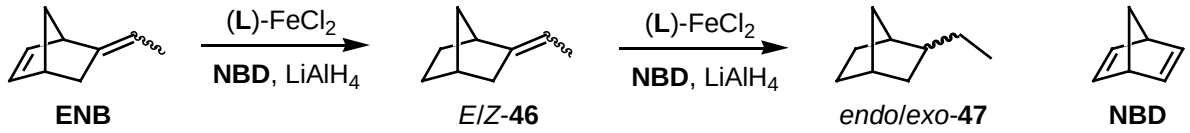
Scheme 27: Diazadiene (DAD) ligands which give active catalysts

A few tridentate ligands, namely **44** and **45** differ from the DAD or DAT motif. The bis(imino)pyridine **44** is derived from BROOKHART's ligands. The bis(pyridine)amine **45** is an example of a non-conjugated ligand.



Scheme 28: Other ligands which give active catalysts

All these ligands are reacted with $FeCl_2$ to form precatalyst complexes, which gave active catalysts for the hydrogenation of 5-ethylidene-2-norbornene (**ENB**) in presence of the additive norbornadiene (**NBD**) upon activation with $LiAlH_4$.



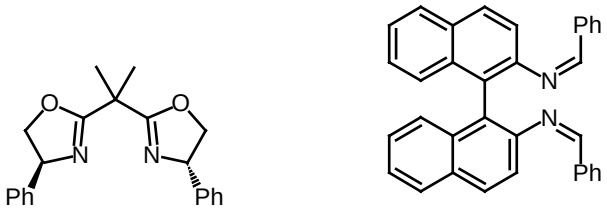
Scheme 29: Hydrogenation of **ENB**

Table 2: Ligand dependence on the conversion in **ENB** hydrogenation

Entry	Ligand **L**	Time [h]	Conversion to **47**
1	**37**	125	21 %
2	**40**	144	52 %
3	**34**	219	84 %
4	**35**	98	66 %
5	**36**	112	92 %
6	**31**	90	88 %
7	**32**	125	81 %

Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/LAH 1:4, RT, 3 bar hydrogen pressure.

The non-conjugated dioxazoline **48** and the binaphthol-derived diimine **49** turned out to be inactive for this hydrogenation.

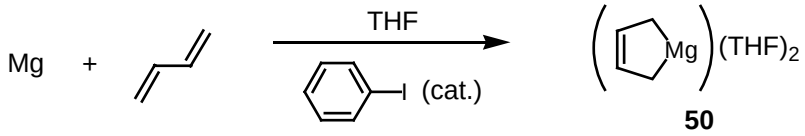


48 **49**

Scheme 30: Ligands which don't give active catalysts

3.3.2 Activation reagents

In the first hydrogenation experiments the tetrahydrofuran-magnesium-butadiene complex **50**[61] was used as activation reagent and active catalysts were obtained. But the preparation of **50** is toilsome and the complex is not isolated, so the engaged quantity of **50** remains unknown.



50

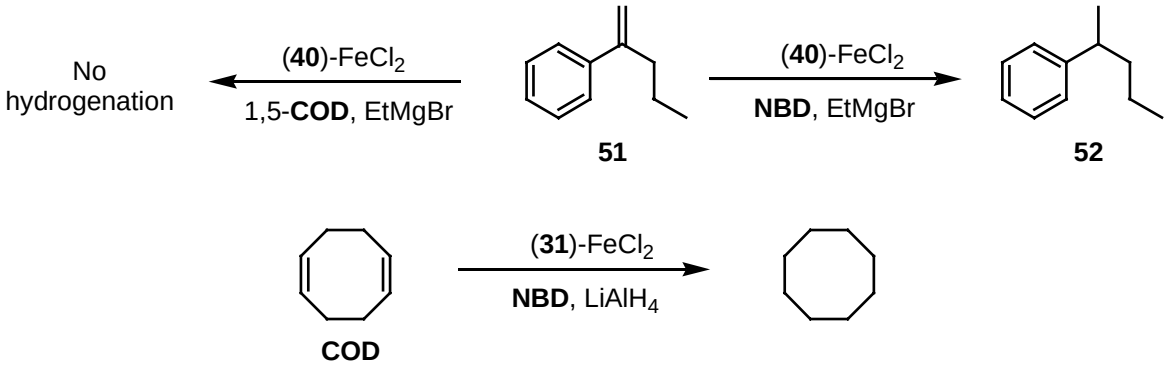
Scheme 31: Preparation of tetrahydrofuran-magnesium-butadiene complex **50**

An alternative was found in simple Grignard reagents such as ethylmagnesiumbromide, which are easy to prepare and the concentration of the reagent can be estimated. Preliminary hydrogenation experiments failed to furnish an active catalyst when the precatalyst was activated with EtMgBr. This behaviour was attributed to the need of an additional 'dummy ligand' as present in **50** with butadiene. Therefore, norbornadiene (**NBD**) was added to the precatalyst solutions before activation and indeed, active catalysts were obtained in this case. Most hydrogenations were carried out with $LiAlH_4$ activated catalysts. The reactions show similar behaviour as the hydrogenations with EtMgBr activation, and the additive **NBD** is necessary too. Depending on the ligand used for precatalyst formation, also BuLi can be used as activator.

Several other reagents tested are not able to generate an active catalyst for the hydrogenation. Among them are weaker hydride donors such as sodium borohydride and sodium hydride, bases like triethylamine and sodium hydroxyde, a magnesium-anthracene complex[62] or the powerful reductant metallic Zn powder.

3.3.3 Additives

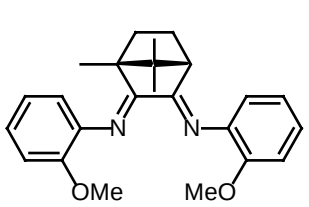
As mentioned above the hydrogenations with the diimineiron(II) complexes activated with $LiAlH_4$ or EtMgBr always required a diene dummy ligand present in the reaction mixture to ensure catalytic hydrogenation activity. Sieber supposed that the supplementary diene acts as stabilizing ligand for coordinatively unsaturated catalyst intermediates. But not all dienes, which usually are good ligands for transition metals, are suitable as additives for this purpose. This behaviour is illustrated comparing **NBD** and 1,5-cyclooctadiene (**COD**) as dummy ligands. No hydrogenated product **52** or eventually cyclooctane are found when **NBD** is replaced with **COD** in EtMgBr activated reactions. In contrast, the use of **COD** as substrate and **NBD** as additive resulted in an active hydrogenation and cyclooctane was obtained quantitatively.



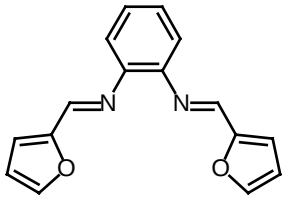
Scheme 32: Influence of the additive on the hydrogenation

The problem of the additional diene ligand is circumvented using ligands with more than two ligating sites. The ligands **43** and **33** display in addition to the diimine fragment two supplementary oxygen atoms for coordination resulting in a potential

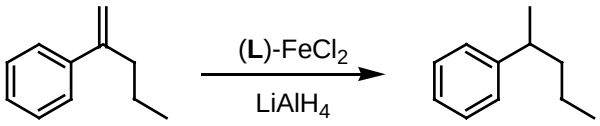
tetradentate ligand. Activation of precatalysts prepared from either **43** or **33** with LAH in absence of **NBD** furnished active catalysts for the hydrogenation of **51**, but no further investigations concerning this property of tetradentate ligands were made.



43



33



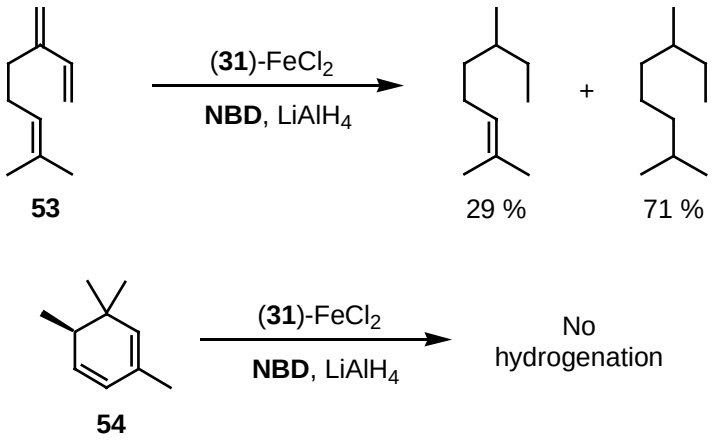
51 **52**

L	Time [h]	Conversion [%]
43	66	100
33	8	91

Scheme 33: Hydrogenation of **51** with tetradentate ligands

3.3.4 Substrates

Alkene substrates with different substitution patterns at the double bond are hydrogenated successfully with the diimineiron(II) catalyst. Substrates containing vinyl-, 1,1- or 1,2-disubstituted as well as trisubstituted C-C double bonds reacted to the corresponding alkanes. In the case of myrcene (**53**), a substrate with conjugated double bonds is hydrogenated, whereas diene **54** remained unchanged under the same conditions. Unfortunately incomplete conversion was obtained in almost all the hydrogenation experiments performed by SIEBER.



Scheme 29: Hydrogenation of conjugated olefins

The diimineiron(II) catalysts were also tested for the hydrogenation of functionalized substrates such as α,β-unsaturated esters, unsaturated alcohols or carbonyl groups. Acetoaceticacid ethyl ester, itaconic acid, cinnamonic alcohol and geraniol failed to be hydrogenated probably due to the reducing agent used as activator reacting more likely with the substrate than with the precatalyst. Unsaturated methoxyphenylethers such as aenethol (**55**) or **56** and **57** respectively are hydrogenated to the reduced products, while other ethers like geranylbenzyl- and geranylmethylether **58** are not touched using the same reaction conditions.

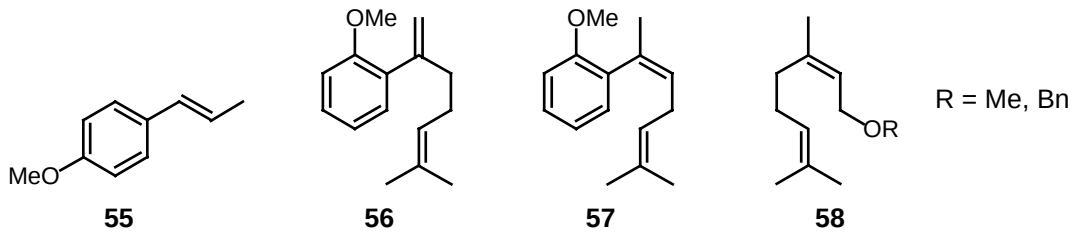
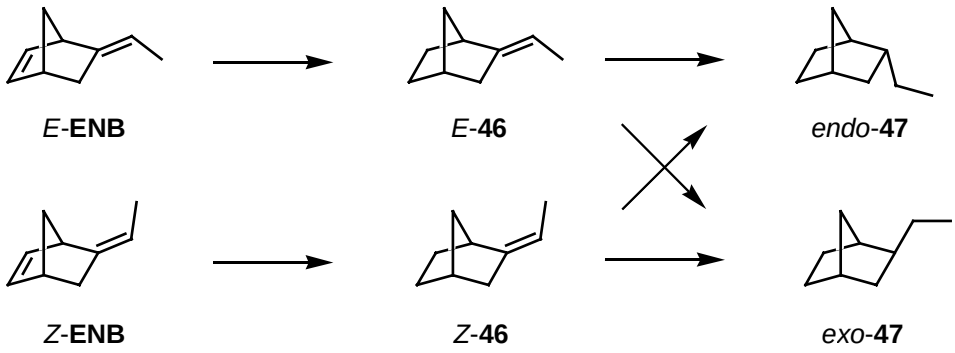


Chart 7: Ether substrates

3.3.5 Chemo- and stereoselectivity

Chemoselectivity is observed when alkenes with differently substituted double bonds are engaged as substrates as in the case of **ENB**. Independently of the catalyst precursor (**L**)-$FeCl_2$ the less substituted C=C bond is always converted faster.

However, a small influence of the ligand **L** is seen in the hydrogenation of **ENB**. **ENB** is commercially available in racemic form as an approximatively 3 : 1 mixture of *E*- and *Z*-isomers.



Scheme 30: Hydrogenation of **ENB**

Hydrogenation of the cyclic double bond led to *E*- and *Z*-5-ethylidene-2-norbornane (**46**) with almost the same *E*/*Z* ratio. But the minor isomer *Z*-**46** reacts faster to the products as seen at the growing *E*/*Z* ratio in favour of the *E*-isomer. Little *endo*/*exo* stereoselectivity (7 % at most) is observed in the final 5-ethyl-2-norbornane (**47**). Catalysts prepared with DAD ligands give more of the *exo* isomer while catalysts with DAT ligands furnish more of *endo*-**47**.

Table 3: Ligand dependence on the regioselectivity in **ENB** hydrogenation

Entry	Ligand	*E*/*Z* ratio of **46** (at % conversion)	*Endo*/*exo* ratio of **47** (at % conversion)
1	**34**	14.8 (79 %)	0.92 (84 %)
2	**40**	4.5 (14 %)	0.88 (56 %)
3	**37**	5.4 (21 %)	1.02 (21 %)
4	**36**	14.8 (79 %)	0.79 (92 %)
5	**31**	6.8 (63 %)	1.32 (89 %)
6	**32**	7.6 (37 %)	1.18 (51 %)

Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/LAH 1:4, RT, 3 bar hydrogen pressure.

Despite the use of various chiral ligands, no asymmetric induction in hydrogenations of prochiral substrates (or kinetic resolution in the case of **ENB**) is obtained with these diimineiron(II) catalysts.

3.3.6 Kinetics

Apart from small regioselectivity effects, the diimine ligands affect the reaction rate of the hydrogenation. This behaviour can be observed again with **ENB** as substrate and is reflected in the turn-over frequencies (TOF) of the catalysts. As the hydrogenation rate for the disubstituted double bond in **ENB** is much higher than the rate for the trisubstituted C=C bond, two independent TOF can be determined. These TOF assess also the efficiency of the diimineiron catalyst.

Table 4: Ligand dependence on the turn-over frequencies in **ENB** hydrogenation

Entry	Ligand	1. TOF [h^{-1}]	2. TOF [h^{-1}]	Ratio 1. TOF / 2. TOF
1	**40**	1.9	< 0.01	> 190
2	**34**	3.9	0.10	39
3	**35**	5.2	0.06	87
4	**36**	10.8	0.23	47
5	**31**	4.2	0.11	38
6	**32**	8.5	0.21	40
7	**45**	0.6	0.03	20

Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/LAH 1:4, RT, 3 bar hydrogen pressure.

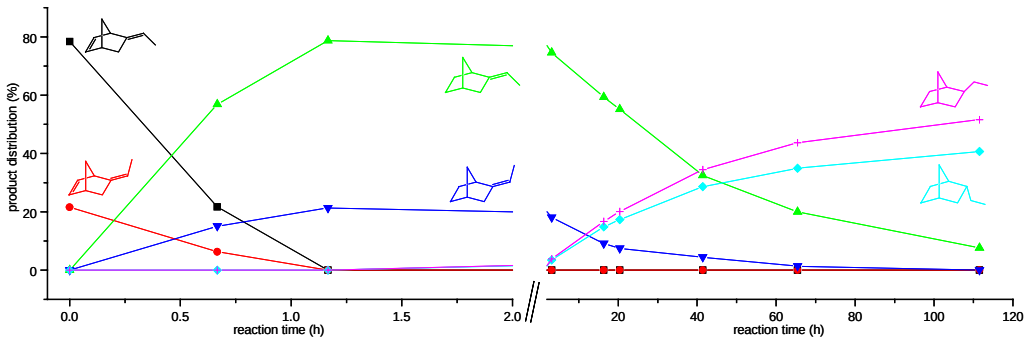
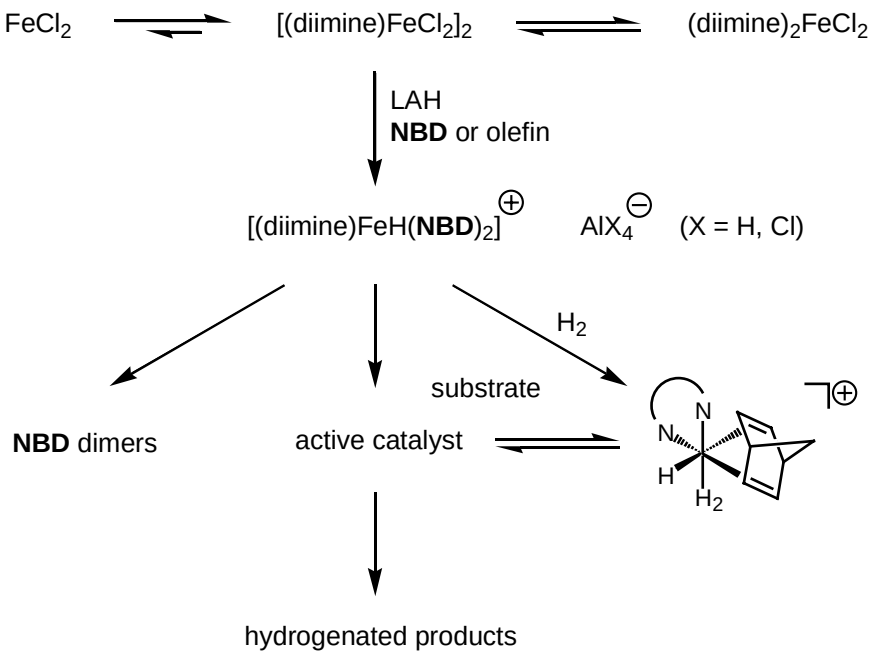


Figure 1: Rate and product distribution of **ENB** hydrogenation

3.3.7 Mechanism

SIEBER proposed also a mechanism for the hydrogenation with the diimineiron complexes based on his own results and the already mentioned results from BIANCHINI, BROOKHART, ZIEGLER and TOMDIECK.

Activation of a diimineirondichloride dimer with an hydride donor gives a cationic σ-hydride precatalyst, which is stabilized by an additive. In the case of **NBD**, one of the **NBD** molecules has to be coordinated with both π-bonds whereas the second one has to be bound only in η^2-manner to satisfy the iron coordination sphere in this cationic complex. In the absence of hydrogen, this complex is active for the dimerization of the coordinated olefin ligand, e. g. **NBD**. The active hydrogenation catalyst is formed by exchange of the stabilizing ligand with the substrate and coordination of dihydrogen. The catalytic cycle proceeds then through an σ-hydride η^2-dihydrogen complex like in BIANCHINI's mechanism.



Scheme 31: Proposed mechanism by SIEBER

4. Thesis project

The initial objective of this work was the further development of the diimineiron(II) catalyst system as presented by SIEBER in his thesis.

Several investigations and optimizations of this catalytic system were intended:

- One of the most important points to be solved is the question of the mechanism for the hydrogenation with the diimineiron(II) catalyst. SIEBER proposed a mechanism based on analogy, but no evidence for this proposition is given in his thesis. Therefore, the isolation and characterization of a precatalyst complex becomes indispensable to have a more precise idea about the possible structural disposition in the active species. The knowledge of the catalyst structure would permit to make rational optimizations of the catalyst. Isolation of a precatalyst complex would also allow to engage a well-defined quantity of catalyst with determined structure, because up to now the precatalysts are generated and activated *in situ*.
- Improvements of the catalytic system are also envisaged concerning the activator. The reagents used by SIEBER for the activation of the precatalysts all have a disadvantage: as they are strong reducing or nucleophilic agents nearly no functional groups are tolerated in the olefin substrates limiting thereby drasticly the possibilities of application. This problem should be circumvented by using other reagents as activators. Together with reductors such as BuLi or DIBAH, chloride abstractors like silver salts should be tested to generate the active species. Chloride abstractors as activators would have the advantage not to interfere with functionalities such as carbonyl groups.
- Also the preparation of the catalytically active mixture would allow possible optimizations. Up to now, the precatalyst is generated and activated *in situ* in presence of the substrate. If the active catalyst is generated in absence of the substrate, the reductive activation would not interfere with functional groups in the substrate anymore.

- Probably the most common way to modify the catalyst behaviour is displayed by variation of the ligands. Different approaches are conceivable for this purpose. Modification of the existing ligands tested by SIEBER can alter the donor properties or the steric environment of these ligands and thus, the reactivity of the catalyst complex can change. And as the synthesis of new DAD- and DAT-type ligands is easy to accomplish, a broad range of diimine ligands can be imagined as potential new ligands. With the knowledge of the structure of the catalyst, chiral ligands should be designed which allow enantioselective hydrogenations. Further interest concerns tetradentate ligands because SIEBER could perform the hydrogenation without additive using such ligands.
- Finally as additives have to be considered as undesired side products in the reaction mixture, the property of tetradentate ligands to furnish active hydrogenation catalysts when the additive is left out should be generalized.

Unfortunately, the objectives had to be changed almost completely with the first results (see chapter 5). Instead of developing the diimineiron(II) catalyst, the attention was directed to the exploration of the newly found "ligand-free" iron catalyst system with regard to applicability and efficiency. The scope and limitation in terms of substrates, activation reagents and iron sources was investigated. This new catalyst was also preliminarily tested in other reactions than hydrogenations such as polymerizations and cycloadditions. It was tried to elucidate the origin of the catalytic activity by precatalyst isolation attempts. This leads to the proposition of an (arene)iron(II) precatalyst structure from which other iron complexes are derived and tested as hydrogenation catalysts.

II

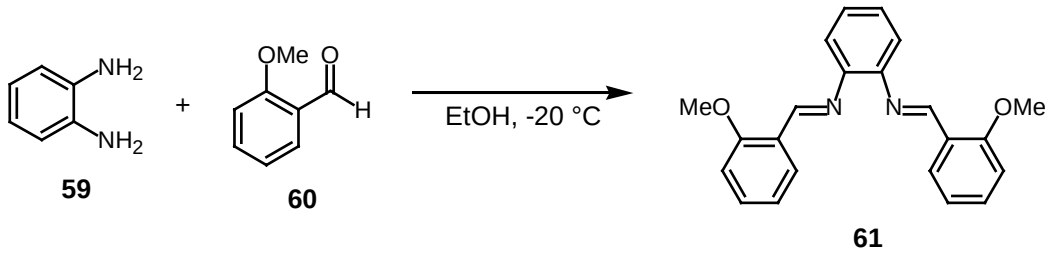
Results and discussion

5. 1,2-Phenylenediimine ligands

All the tetradentate ligands used by SIEBER did not need the presence of a supplementary stabilizing olefin ligand during the hydrogenation. This property should be examined in more details to generalize the role of the dummy ligand and to get insight into the mechanistic pathway of the hydrogenation by isolation of a potential precatalyst. For this reason the synthesis of the *o*-methoxy-substituted benzylidenediamine **61** was envisaged.

5.1 Ligand syntheses

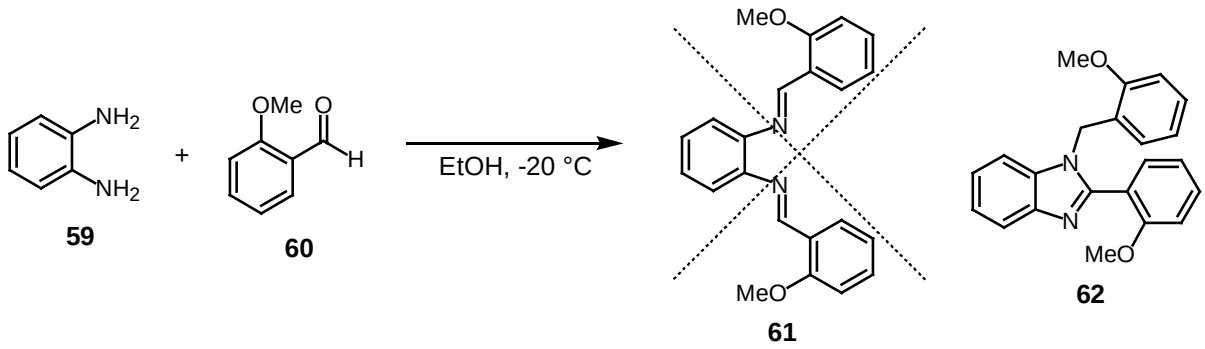
The synthesis of **61** was carried out following the procedure used by SIEBER for the synthesis of all the other Schiff base ligands. The condensation of 2 equivalents *o*-methoxy-benzaldehyde (**60**) with *o*-phenylenediamine (**59**) at low temperature in EtOH afforded 60 % of a product first considered as **61**.



Scheme 32: Assumed formation of diimine **61**

MS analysis of the compound revealed the correct molecular mass, but the NMR spectra showed too many signals for such a symmetrical structure. *E*/*Z* isomerism at the imine groups could explain the large number of signals, but other features such as the absence of signals in the imine region and the presence of a singlet at δ = 5.2 ppm in the ^{1}H-spectrum, as well as the presence of a methylene carbon in the ^{13}C-spectrum did not match with a phenylenedialdimine structure.

Finally a careful analysis of the COSY and HETCOR spectra allowed to elucidate the correct structure: a cyclized benzimidazole **62**. Comparison of the simulated spectra of **61** and **62** confirmed nicely the benzimidazole structure of the product.



Scheme 33: Synthesis of benzimidazole **62**

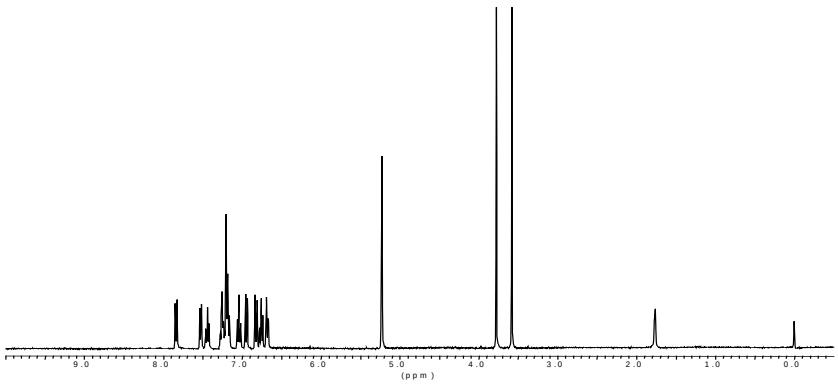


Figure 2: ^{1}H-NMR spectra of the product from the condensation of **59** and **60**

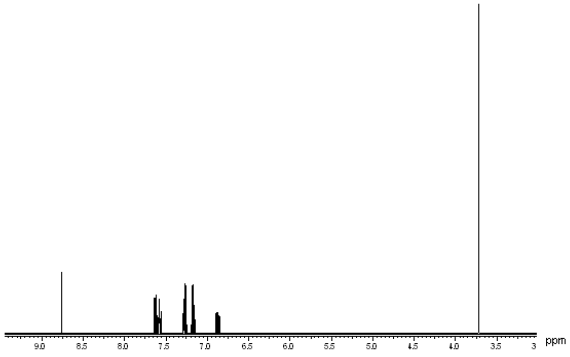


Figure 3: Simulated ^{1}H-NMR spectrum of **61**

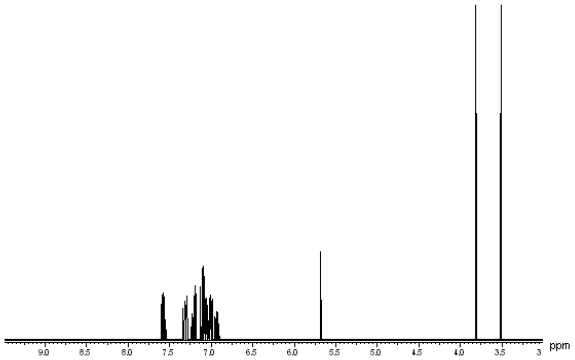
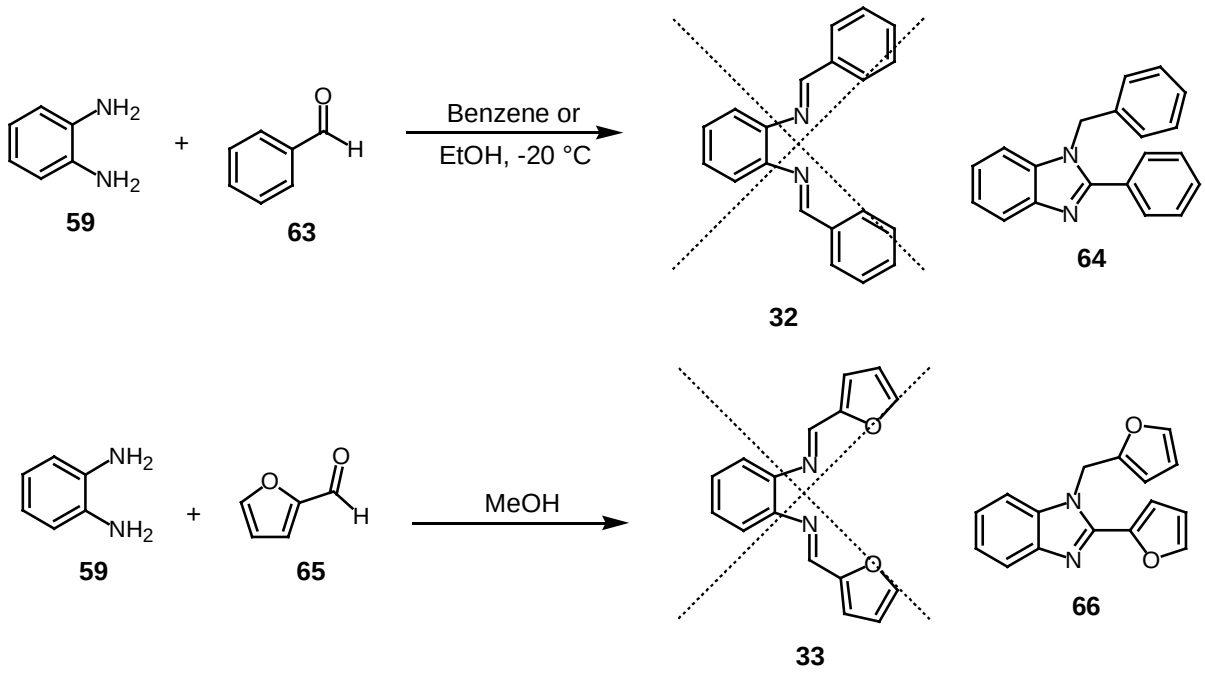


Figure 4: Simulated ^{1}H-NMR spectrum of **62**

Reexamination of the description of the spectra of the Schiff bases **32** and **33** given by SIEBER led to the conclusion that they were also of the benzimidazole type. Therefore the syntheses of these compounds were repeated under the same conditions as described.[60] Indeed in both cases only the benzimidazoles **64** and **66** could be isolated. Solvent change from EtOH to the aprotic benzene and the use of molecular sieves led to the same result, thus the ring closure and the subsequent shift of a proton is not due to the presence of protic solvent.



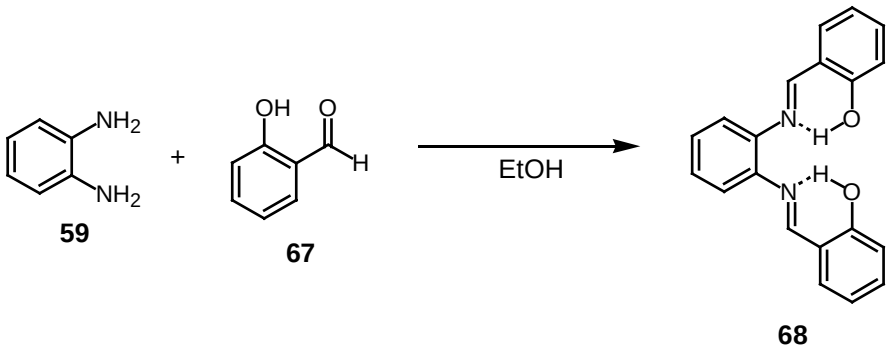
Scheme 34: Syntheses of benzimidazoles **64** and **66**

Already 30 years ago HO reported the formation of these benzimidazoles instead of the desired phenylenediimine **32** in the reaction of **59** and benzaldehyde via intramolecular cyclization of **32** or oxidation of a benzimidazoline intermediate.[63] After thourough study of the reaction he comes to the conlusion that the phenylenediimines are just reactive transient intermediates if formed at all. Despite the report of HO several authors described recently the use of $FeCl_2$ complexes with phenylenediimine ligands in structural[64] and hydrolysis[65] studies as well as ethylene oligomerization catalyst.[66] In these cases **32** was synthesized according to the original procedure of HINSBERG[67] or slightly modified procedures used for *para*-

substituted aldehydes.[68] As the reaction conditions in these syntheses are almost identical to those leading to the benzimidazole **64** these results have to be regarded with caution. In addition the reported analytical data elemental analysis and MS are identical for **32** and **64**, so no structural conclusion can be taken.

Also in the case of the furfurylidenephenylenediamine **33** there are doubts about the accuracy of the reported literature. MUKHOPADHYAY described the synthesis of **33**, the complexation with $CoCl_2$ and the use of this complex as catalyst to convert allylic alcohols to allylic amides.[69] The characterization of the ligand **33** was made by ^{1}H-NMR. The reported proton chemical shifts seem to be correct except a pretty low chemical shift of 7.6 ppm for the imine protons. A closer look revealed that all these reported signals can be found in the spectrum of the benzimidazole derivative **66**. Furthermore the synthesis of **33** was repeated under exactly the same conditions as described and still only the benzimidazole **66** could be isolated.

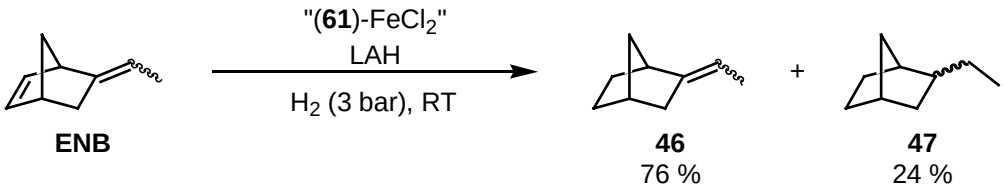
From all the different aldehydes reported only the condensation of **59** with salicylaldehyde derivatives appear to furnish the desired phenylenediimines. As the *m*- and *p*-hydroxy analogs afforded exclusivly the benzimidazoles, apparently the *o*-hydroxy groups are stabilizing the open form by intramolecular hydrogen bridges preventing ring closure furnishing the phenylenediimine **68**.[70]



Scheme 35: Synthesis of phenylenediimine **68**

5.2 Complexation of benzimidazoles with iron(II)chloride

Obviously these benzimidazoles could no longer be regarded as bidentate diimine ligands in the sense introduced by SIEBER. Nevertheless catalytic hydrogenation activity was observed when **32** and **33** were used as ligands following SIEBER's procedure for the hydrogenation of **ENB** and 2-phenylpentene.[60] Assuming the wrong structure, **61** was tested under the same conditions as for the other ligands for the hydrogenation of **ENB**. After stirring **61** and $FeCl_2$ overnight, **ENB** was added and the suspension was activated with LAH. Within 24 h the cyclic double bond was entirely reduced. At the end of the reaction 24 % was converted to the completely hydrogenated product **47**.

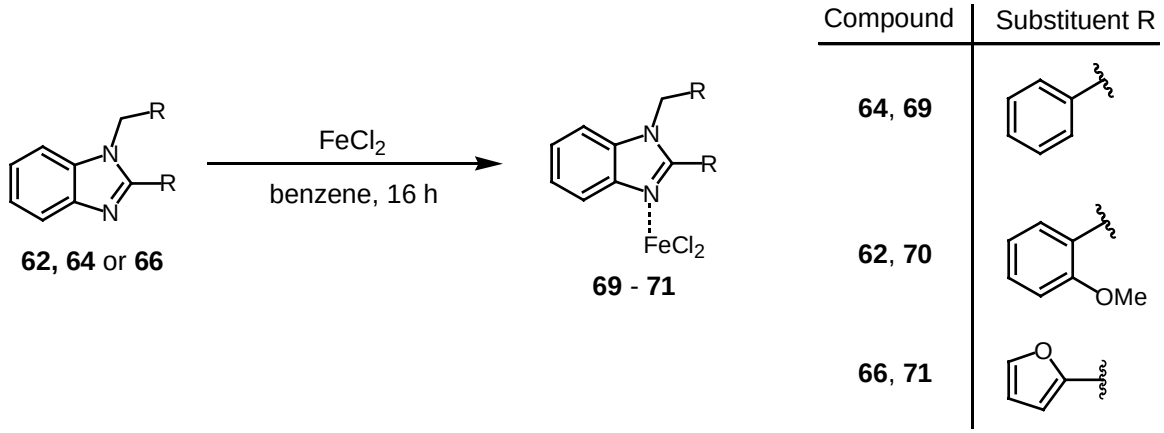


Scheme 36: Hydrogenation of **ENB**

One of the most interesting questions arising from the wrong structure of the ligands is at what species the hydrogenation is due to. The postulated mechanism for this hydrogenation can only be correct when the complexation occurs under ring opening of the imidazole moiety to generate the assumed precatalyst.

Therefore the three benzimidazoles **62**, **64** and **66** were submitted to complexation with $FeCl_2$. The same conditions were used as to form the precatalysts in the previous hydrogenations. Before the mixture was set under hydrogenation conditions, the precatalyst was isolated to determine the constitution of the ligand in the precatalyst. After stirring the ligands in presence of $FeCl_2$ in benzene overnight the precipitates were isolated by filtration. In all the cases ^{1}H-NMR study of the isolated products showed slightly shifted signals for the benzimidazole ligands, but the complexes were decomposed and the shift arose from paramagnetic inpurities.

The benzimidazole signals indicated that no ring opening takes place during the complexation reaction.



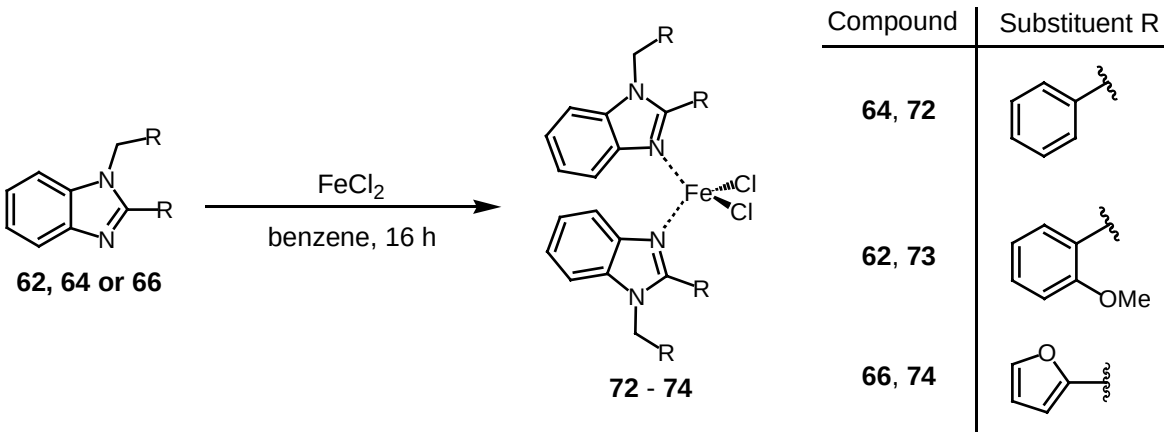
Scheme 37: Complexation of benzimidazoles with $FeCl_2$

More difficult to answer is the question of the exact composition and the structure of the complexes. Structures can be imagined where 2 or even more ligands were attached to the metal to saturate the coordination sphere. Among the mass signals for the free ligand and the $(\mathbf{L})FeCl^{+}$ fragment in the ESI-MS, other signals for compounds with higher masses were found. Thus the most intense signal corresponds always to a monocharged species with two ligands per iron and one chlorine $(\mathbf{L})_2FeCl^{+}$, but also a mass signal for a doubly charged fragment with three ligands and one iron $(\mathbf{L})_3Fe^{2+}$ is present in all cases. It's not absolutly clear if these fragments arise from aggregation in the spectrometer or if corresponding complexes were present in the isolated products already. The NMR spectra allow no conclusion either because only broad signals from the ligand are visible.

Useful indications can be found in literature. Benzimidazole ligands were used to complex different metals such as Cu(II),[71] Ni(II)[72] and even Fe(II).[73] In all the described cases elemental analysis of the complexes revealed a composition with two benzimidazole molecules attached to one metal atom. IR studies of these complexes supported that the benzimidazole ligands are all coordinated only via the unsaturated nitrogen atom to the different metals since there are no other donor sites available in the ligands. The same type of coordination was observerd for Ru(II)

complexes,[74] where only one benzimidazole molecule is complexed to the metal and the remaining coordination site is occupied by an η^6-arene ligand.

Taking these reports into account also we can propose a structure for the main complex where two benzimidazole molecules were coordinated through the unsaturated nitrogen atom of the imidazole ring to the central iron atom, probably arranged in a distorted tetrahedral geometry analogous to the reported complexes.[73]



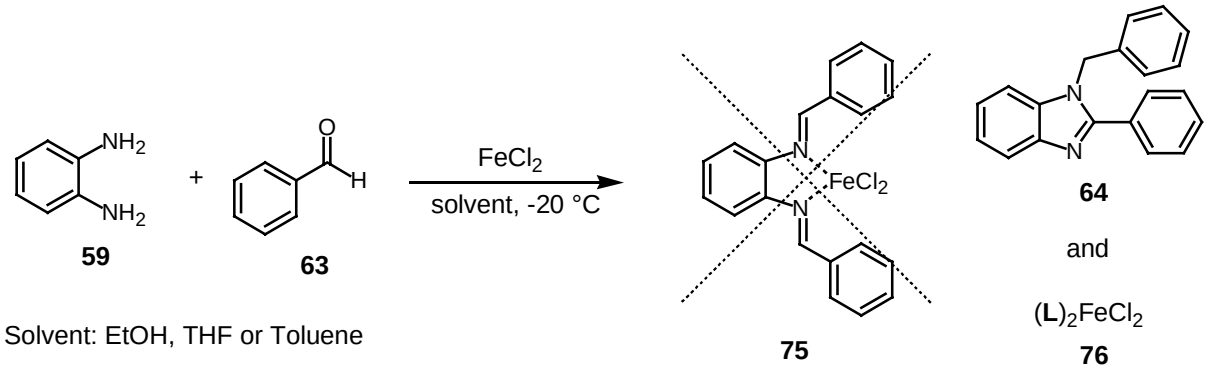
Scheme 38: Complexation of benzimidazoles with $FeCl_2$

All attempts to obtain crystals by recrystallisation for a X-ray analysis failed. Either the complexes were not soluble in apolar solvents such as pentane, toluene or ether, or they decomposed in more polar solvents such as acetone, alcohols or THF.

5.3 Template synthesis of phenylenediimines

Despite the repeated mentions of phenylenediimines in literature it was not possible to obtain this structure but only the cyclized benzimidazoles. So a last approach was tried to synthesize the desired phenylenediimines by the assistance of a templating metal. As we were particulary interested in the iron complex the reaction was carried out first in the presence of $FeCl_2$.

The diamine **59** and $FeCl_2$ were suspended in the solvent at low temperature and stirred for about one hour, then the aldehyde **63** was added. The precipitate formed was filtered and analyzed, and also the resulting solution was examined as well.



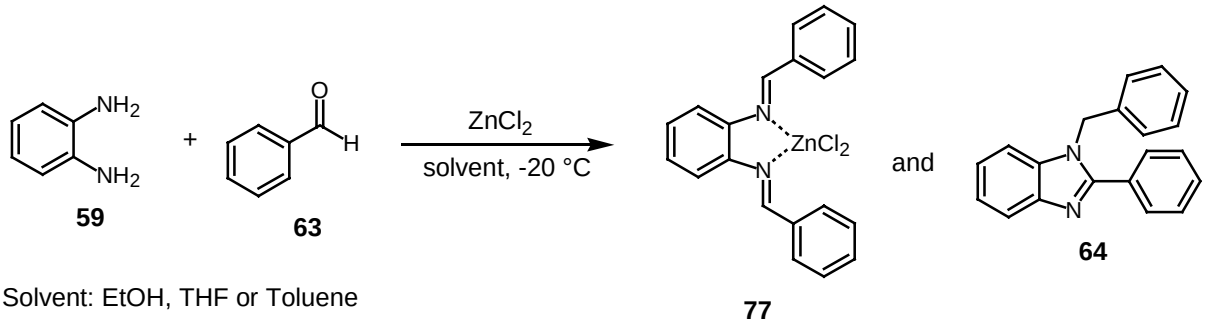
Scheme 39: $FeCl_2$-templated condensation of **59** and **63**

In all these approaches no trace of a phenylenediimine iron complex was found. When EtOH was used as solvent the bendzimidazole **64** along with some small amount of complex **76** was obtained, and when the reaction was carried out in THF unreacted benzaldehyde was reisolated. In toluene a green complex appeared but fast degradation occurred. The isolation of unchanged benzaldehyde (**63**) in this approach supposes more likely the formation of a phenylenediamine-iron adduct than of complex **75** or other known products.

Table 5: Metal-templated condensation of **59** and **63**

Entry	Metal	Solvent	Products
1	$FeCl_2$	Toluene	**63**
2	$FeCl_2$	THF	**63**
3	$FeCl_2$	EtOH	**64**, **76**
4	$ZnCl_2$	Toluene	**64**, unidentified complex
5	$ZnCl_2$	THF	**64**
6	$ZnCl_2$	EtOH	**64**, **77**

Zinc was also tested as templating metal. The reaction was carried out under the same conditions for the different solvents with $ZnCl_2$ instead of $FeCl_2$.



Scheme 40: $ZnCl_2$-templated condensation of **59** and **63**

When toluene or THF were used as solvents mainly the benzimidazole **64** along with some amounts of unreacted aldehyde **63** was obtained. In the case of EtOH as solvent a yellowish precipitate was isolated. The ^{1}H-NMR analysis showed clearly the signals for the zinc complex **77** with the desired phenylenediimine ligand, and MS spectroscopy confirmed the complexed nature of **32**.

All attempts to obtain the free ligand **32** by decomplexation of **77** or by use of catalytic amounts of $ZnCl_2$ for the condensation failed. The resulting reaction mixtures consisted mainly of imidazole **64** and the starting products **59** and **63**.

6. Bis(pyridylmethyl)amine ligands

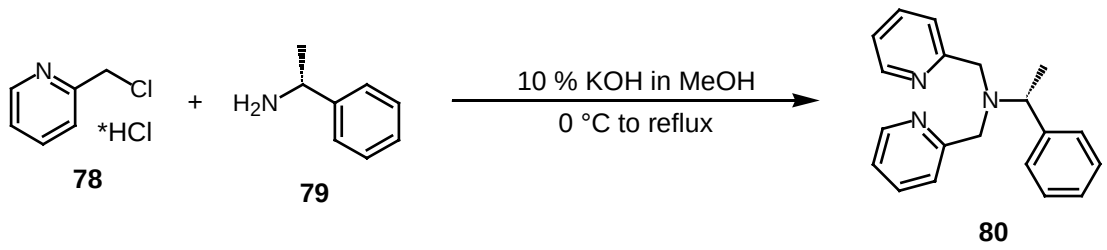
Bis(2-pyridylmethyl)amines are an interesting type of tridentate ligands for different reasons. They show similar geometrical features as BROOKHART's pyridine diimine ligands but display much more flexibility. They can not only coordinate in a meridional fashion, also a facial arrangement around the metal center is conceivable. Indeed, both coordination modes were found recently in isolated bis(pyridylmethyl)ethylamine iron(II) chloride complexes[75] depending on further substitution at the pyridine rings. When the ligand is coordinated facial, the complex has a dimeric structure with distorted octahedral geometry while coordinated meridional the complex is present in monomeric form with a distorted trigonal bipyramidal geometry.

One hydrogenation experiment was performed by SIEBER with a bis(pyridylmethyl)ethylamine iron(II) chloride complex. The conversion of the substrate was comparable to the diimine iron catalysts, but in contrast the hydrogenation proceeded much slower in this case. Two new bis(pyridylmethyl)amines were synthesized to get insight in the mechanistics of the hydrogenation with a precatalyst of this type.

6.1 Ligand syntheses

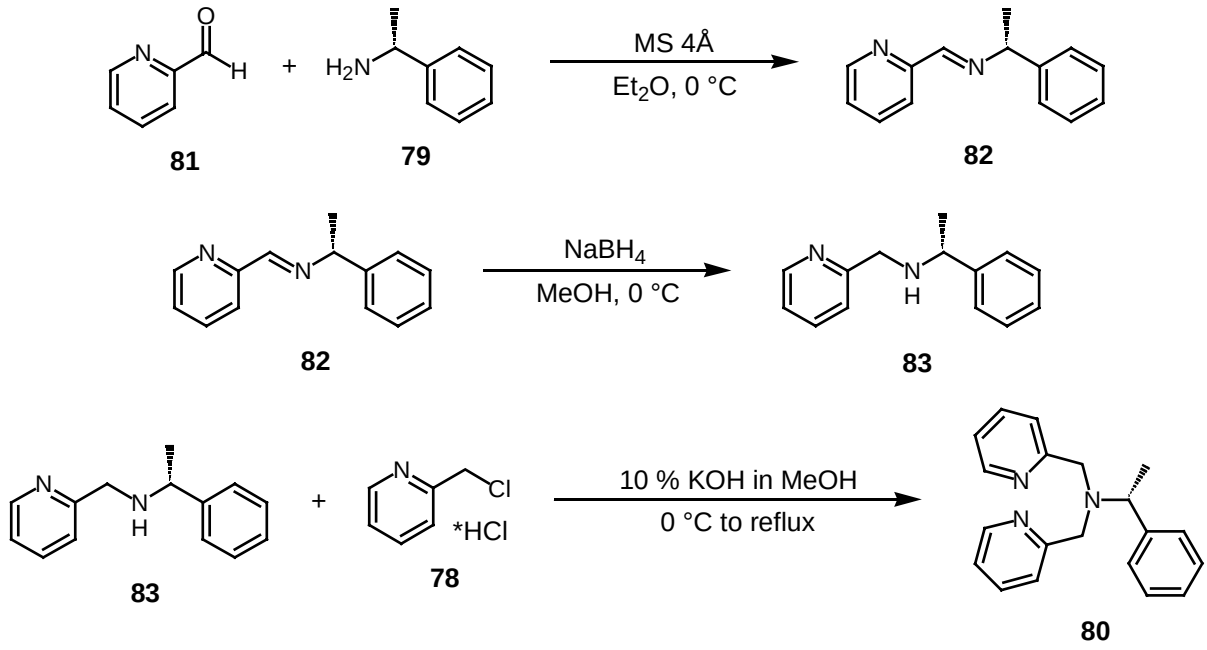
Originally the ethylamine ligand was synthesized under basic conditions from 2-picolyl chloride (**78**) and the corresponding amine compound.[76] The same method was applied for the synthesis of the chiral bis(2-pyridylmethyl)phenylethylamine (**80**).

Analysis of the reaction mixture after the described reaction time of one hour revealed that the reaction is by no means finished and only very low conversion to amine **80** was observed. A longer reaction time raised the yield of **80** only little, but the number and amount of side products increased significantly. Isolation of **80** turned out to be difficult, the amine degrades on silica and can't be washed out from Alox.



Scheme 41: Synthesis of bis(pyridylmethyl)amine **80**

Therefore an alternative way with better conversion and easier workup was searched and found in a three step procedure where the two 2-pyridylmethyl moities were introduced independently.



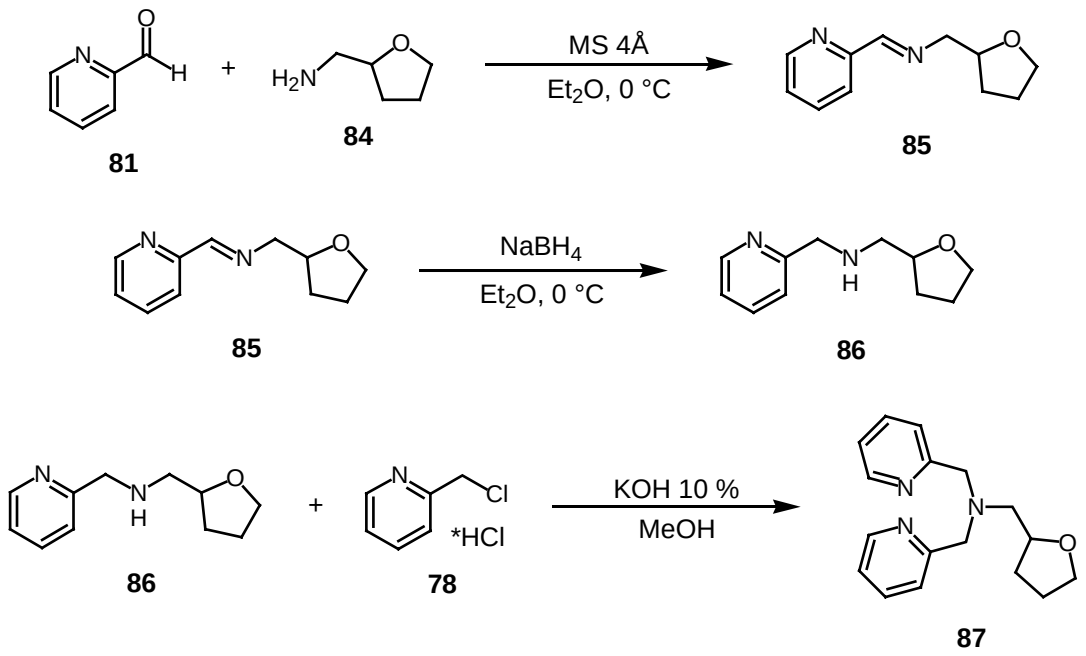
Scheme 42: Three-step synthesis of bis(pyridylmethyl)amine **80**

Pyridine 2-carbaldehyde (**81**) was condensed at low temperature in presence of molecular sieves 4Å with the corresponding chiral amine **79**. The resulting imine was reduced with $NaBH_4$ in deoxygenated MeOH affording the monosubstituted (2-pyridylmethyl)phenylethylamine **83** in good yield (65 %) for both steps.

Finally a slightly modified procedure[77] allowed, after optimization of the reaction conditions, to obtain the desired amine **80** in reasonable yield. Picolyl chloride **78** was first treated with 1 equivalent of methanolic base and the solution was filtered to

remove the chloride salt. After addition of amine **83** to the filtered solution methanolic KOH was added under slight warming over a 2 h period in such a way that the pH of the reaction mixture remained ≤ 9. Purification of the product was achieved by distillation in a very high vacuum (120 °C, $2 \cdot 10^{-6}$ bar). At higher temperatures (> 130 °C) **80** decomposed.

The same reaction sequence was used for the synthesis of a racemic tetradentate bis(2-pyridylmethyl)amine ligand starting from racemic tetrahydrofurfurylamine (**84**). The potential tetradenticity renders this ligand similar to the PP_3 ligand [PP_3: $P(CH_2CH_2PPh_2)_3$] used by BIANCHINI for the hydrogenation of terminal alkynes in the iron(II) hydride dihydrogen complex $[(PP_3)Fe(H)(H_2)]BPh_4$.[57-59] In this case the desired amine **87** was obtained in 62 % overall yield.



81 **84** **85** **85** **86** **86** **78** **87**

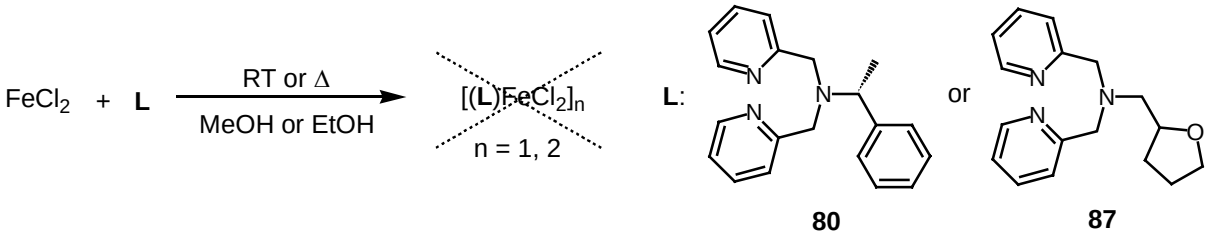
Scheme 43: Three-step synthesis of bis(pyridylmethyl)amine **87**

This 3-step procedure displays an improvement compared to the original method. Though more steps are involved, all reactions proceed fast and the workups are easy with a good overall yield. Furthermore the independent introduction of the pyridylmethyl part should allow to introduce, together with one unsubstituted pyridine ring, other ligating moities such as pyridines with different substitution

patterns or even other N-heterocycles when the pyridine aldehyde **81** is replaced by another appropriate aldehyde.

6.2 Complexation of bis(pyridylmethyl)amines with iron(II)chloride

As crystal structures from Fe(II) complexes with this bis(pyridylmethyl)amine type ligands are known it was tried to repeat the complexation under the described conditions[75] with the ligands **80** and **87** in order to obtain an isolated, characterized precatalyst for the hydrogenation.



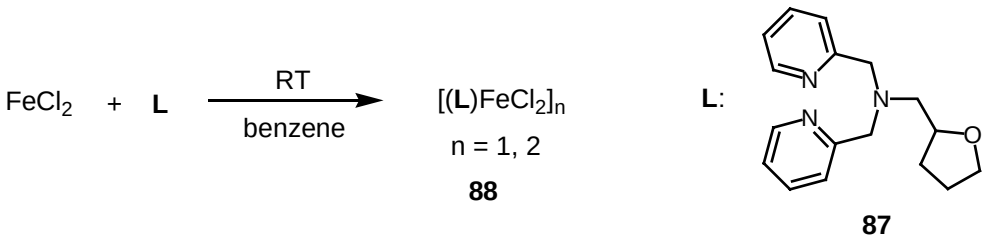
Scheme 44: Complexation of bis(pyridylmethyl)amines **80** and **87** in alcohols

The complexation was carried out under inert conditions once in MeOH and once in EtOH, first at reflux temperature and then at room temperature, but in both cases only a red, rusty solid was formed indicating oxidation of the iron species. The ligand was reisolated unchanged.

The same procedures in alcoholic solvents were applied for the complexation of the tetrahydrofurfurylamine ligand **87**, but as with ligand **80** fast degradation occurred and no complex was obtained.

Hence the solvent was changed to the aprotic, apolar benzene and the complexation was repeated with ligand **87**. When the reaction was heated to reflux, the same degradation was observed as in the previous cases. When the complexation was carried out at RT overnight, a bright yellow precipitate appeared after short time. Isolation of this product furnished an air-sensitive complex. The instability of the complex prevented NMR measurements, but ESI analysis in acetone solution could be performed. At 30 V capillary voltage only the mass signal (**87**)$FeCl^+$ for the

monomeric complex [(**87**)$FeCl_2$] was present while at lower capillary voltage (10 V) also other signals appeared, among them the mass fragment (**87**)$_2Fe_2Cl_3^+$ for the dimeric complex as the most intense signal. All attempts to obtain suitable crystals for X-ray measurements failed because of insolubility or degradation of the complex.



Scheme 45: Complexation of bis(pyridylmethyl)amine **87** in benzene

Finally no reliable conclusion could be drawn about the structure of the complex, i.e. monomeric or dimeric form and coordination geometry of the ligand. The quite clean ESI spectrum at 30 V capillary voltage with the (**87**)$FeCl^+$ fragment suggests that the other fragments at 10 V capillary voltage arose from aggregation reactions in the spectrometer. Consequently a monomeric structure is proposed, supported by the tetradenticity of the ligand which facilitates the coordination of the oxygen to replace the bridging chlorine atom in case of facial coordination mode. The geometry the ligand is occupying in the complex remains unclear, two possibilities are depicted below.

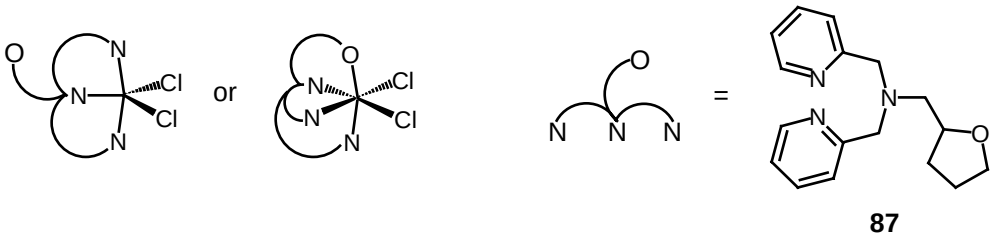
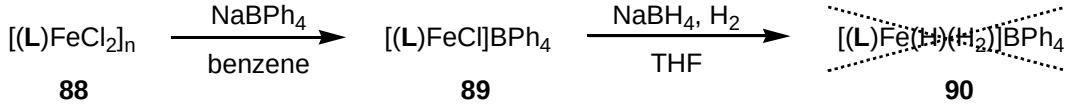


Figure 5: Two possible structure of complex **88**

Since no crystals were obtained and the structure could not be determined it was decided to synthesize the hydride dihydrogen complex [(**87**)Fe(H)(H_2)]BPh_4 (**90**) in

analogy to BIANCHINI's catalyst which is described to be exceptionally stable.[78] The precursor [(**87**)FeCl]BPh_4 (**89**), obtained by treatment of **88** with $NaBPh_4$,[79] was reacted with $NaBH_4$ under hydrogen atmosphere.



Scheme 46: Attempted synthesis of complex **90**

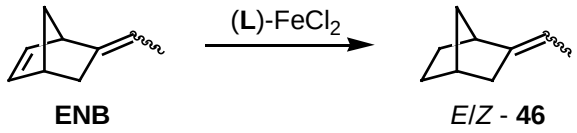
The reaction of **88** with $NaBPh_4$ afforded complex **89** as grey-yellow powder in good yield. The higher stability of **89** as compared to **88** allowed to measure the ^{1}H-NMR spectra but no interpretation was possible because of the intense signals for the aromatic protons of the tetraphenylborate and extensive signal broadening arising from some paramagnetic impurities or the high spin nature of the complex. In the ESI spectra the same behaviour as for **88** was observed: At high capillary voltage the spectrum showed mainly the signal for the (**87**)FeCl$^+$ fragment whereas at low capillary voltage many different fragments were present.

Some unsuccsessful attempts were made to synthesize the hydride dihydrogen complex **90**. Following the described procedures[78, 79] for similar complexes furnished only unchanged complex **89**, no BIANCHINI-type catalyst precursor complex was obtained.

6.3 Hydrogenations with bis(pyridylmethyl)amineiron complexes

Though the hydrido dihydrogen complex [(**87**)Fe(H)(H_2)]BPh_4 (**90**) could not be obtained, hydrogenation experiments were carried out using the ligands **80** and **87**. First SIEBER's protocol was followed meaning the same conditions for precatalyst preparation were involved as for the formation of [(**87**)$FeCl_2$]$_n$ (n = 1, 2) and hence the [(**L**)$FeCl_2$]$_n$ complexes (**L** = **80** or **87**, n = 1, 2) can be assumed in these hydrogenations as the *in situ* prepared precatalysts. A few reactions were also carried out with the

isolated complex **89** as catalyst precursor. All hydrogenations were performed at RT under 3 bar H_2 pressure.



Scheme 47: Hydrogenation of **ENB**

Table 6: Hydrogenation experiments with bis(pyridylmethyl)amineiron catalysts

Entry	Solvent	Precursor	Activation	Substrate	Duration [h]	Conversion
1	Benzene	**80**, $FeCl_2$	LAH	**ENB** (**NBD**)	24	100 %
2	Benzene	**80**, $FeCl_2$	LAH	**ENB**	150	100 %
3	Benzene	**87**, $FeCl_2$	LAH	**ENB** (**NBD**)	24	100 %
4	Benzene	**87**, $FeCl_2$	LAH	**ENB**	150	100 %
5	Benzene	**87**, $FeCl_2$	$NaBH_4$	**ENB** (**NBD**)	150	no conversion
6	Benzene	**87**, $FeCl_2$	$NaBH_4$	**ENB**	150	no conversion
7	Benzene	**87**, $FeCl_2$	^{s}BuLi	**ENB** (**NBD**)	16	100 %
8	Benzene	**87**, $FeCl_2$	^{s}BuLi	**ENB**	16	95 %
9	Benzene	**87**, $FeCl_2$	DIBAH	**ENB** (**NBD**)	150	no conversion
10	Benzene	**87**, $FeCl_2$	DIBAH	**ENB**	16	47 %
11	THF	**89**	$NaBH_4$	**ENB** (**NBD**)	150	no conversion
12	THF	**89**	$NaBH_4$	**ENB**	150	no conversion
13	THF	**89**	$NaBH_4$	**COE**	24	5 %

Reaction conditions: substrate 0.5 M, 10 mol% catalyst, iron/activator 1:4, RT, 3 bar hydrogen pressure.

In the hydrogenations activated with LAH (entries 1–4) the additive **NBD** has a considerable effect, in contrast to the choice of the tri- or tetradentate ligand. In presence of **NBD** the reactions started right after activation and the cyclic double bond of **ENB** was reduced within a day. When no supplementary **NBD** was added the **ENB** was found unchanged after one day, but after a longer period of time the substrate was reduced completely to the monoolefin. An inverse effect was observed for diisobutylaluminiumhydride (DIBAH) activated hydrogenations (entries 9 and

10). The presence of **NBD** prevented any hydrogenation of the substrate even after long reaction times, whereas a modest conversion of 47 % was obtained for the reaction without **NBD** after short time but the reaction had stopped at this stage already. Fast hydrogenation was obtained with ^{s}BuLi activated reaction mixtures. In both cases (entries 7 and 8) **ENB** was hydrogenated to the monoolefin within 16 h. In absence of **NBD** the conversion was not totally quantitative, some small amount of unreacted **ENB** was detected. The use of $NaBH_4$ as activation agent did not lead to an active catalyst for **ENB** reductions at all, no conversion was observed in these experiments (entries 5 and 6, 11 and 12). The other substrate cyclooctene (**COE**) was converted to 5 % (entry 13). This small conversion is surprising because in all the other hydrogenation experiments with $NaBH_4$ activation during this work no hydrogenation activity was observed. In all the hydrogenations the exocyclic double bond of **ENB** was not reduced even after long reaction periods.

A few preliminary ethylene polymerization experiments were made with complex **89** as catalyst precursor. But when the reaction mixture was activated with $NaBH_4$, **89** was reisolated unchanged, and the use of MMAO led to decomposition of the complex.

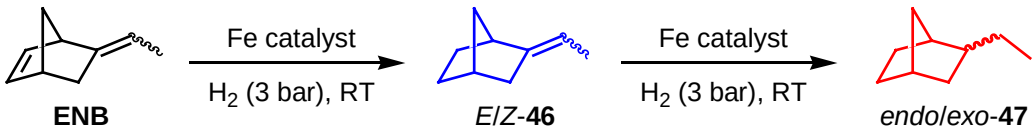
Despite the quite promising hydrogenation results obtained with the bis(pyridylmethyl)amineiron(II) catalyst precursors, the exploration of these complexes as catalysts was abandoned. The attention was directed to the investigation of the “ligand-free” iron catalyst, which was discovered at the same time.

7. “Ligand-free” hydrogenation catalysts

It was surprising that the catalytic hydrogenation occurred with the benzimidazoles as ligands, because they don’t fit in the mechanistic scheme proposed by SIEBER. Therefore other species than the assumed diimine complexes must be responsible for the catalytic activity.

7.1 Activation reagents

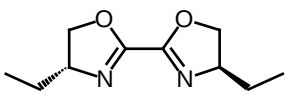
As the isolation and characterization of the real catalytic species is a difficult or even impossible task, information about the origin of the catalytic activity was sought by systematic variation of the composition of the reaction mixture. The influences of the bisoxazoline ligand **34** and the stabilizing substrate **NBD** were investigated in the hydrogenation of **ENB** for several activation reagents. All catalysts were prepared from $FeCl_2$ in benzene. A dark slurry usually indicated the formation of an active catalyst.



ENB *E*/*Z*-**46** *endo*/*exo*-**47**

Scheme 48: Hydrogenation of **ENB**

Ligand:

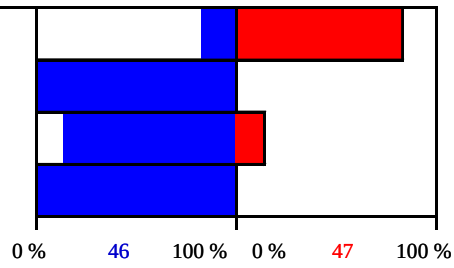


34

Chart 8: Ligand used for the hydrogenation of **ENB**

Table 7: $LiAlH_4$ activated hydrogenation of **ENB**

Activator/Time	Ligand **34**	**NBD**	Conversion
	Yes	Yes	
LAH	Yes	No	
16 h	No	Yes	
	No	No	



Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/activator 1:4, RT, 3 bar hydrogen pressure.

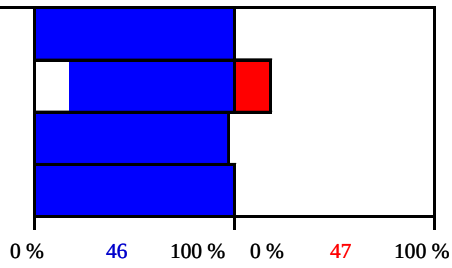
Interesting results were obtained in the experiments with LAH activation. Firstly, the hydrogenation takes place also in absence of the bisoxazoline ligand. However, it has to be noted, that a much longer induction period was observed in these reactions: after 24 h no hydrogenated product was found whereas in the presence of bisoxazoline **34** the hydrogenation started right after addition of the activation agent and the cyclic double bond was reduced completely within a few hours. The hydrogenation of the exocyclic double bond proceeded then much slower as compared to the first reduction. The final conversions are similar for these reactions. Furthermore the presence of a supplementary stabilizing olefin such as **NBD** is not necessary either for the reaction, the only effect of this additive is a higher conversion, the trisubstituted double bond was not touched in its absence.

As in the previous cases with DAD or DAT ligands, no active hydrogenation catalyst was obtained in all the experiments with $NaBH_4$ as activator independent of the reaction mixture composition.

In order to find an activation reagent which furnishes an active catalyst only in presence of diimine ligands, other common reducing agents such as ^{s}BuLi and DIBAH were tested under the same conditions as the metal hydrides. An active catalyst is formed in all the hydrogenation experiments performed with ^{s}BuLi or DIBAH activation.

Table 8: ^{s}BuLi activated hydrogenation of **ENB**

Activator/Time	Ligand **34**	**NBD**	Conversion
	Yes	Yes	
sec-BuLi	Yes	No	
16 h	No	Yes	
	No	No	

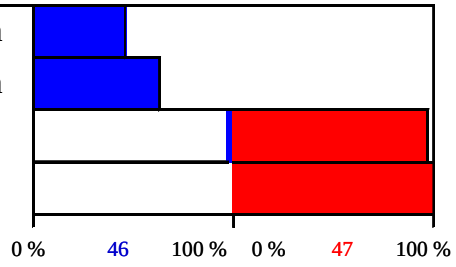


Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/activator 1:4, RT, 3 bar hydrogen pressure.

The influence of the ligand **34** and the additive **NBD** on the conversion and the reaction rate in the hydrogenation of **ENB** is negligible when ^{s}BuLi was used as activator. Within 16 h quantitative hydrogenation of the more reactive double bond is observed, but the catalyst is already degraded at this time under all conditions.

Table 9: DIBAH activated hydrogenation of **ENB**

Activator	Ligand **34**	**NBD**	Time	Conversion
	Yes	Yes	144 h	
DIBAH	Yes	No	144 h	
	No	Yes	16 h	
	No	No	16 h	



Reaction conditions: **ENB** 0.5 M in benzene, **NBD** 0.5 M, 10 mol% catalyst, iron/ligand 1:1, iron/activator 1:4, RT, 3 bar hydrogen pressure.

The most surprising result was obtained for DIBAH activated hydrogenation experiments. On the one hand the most active catalyst was generated within the series lacking a diimine ligand. The substrate was hydrogenated to the completely reduced *exo*/*endo* product mixture within a short time. On the other hand the lowest conversion was obtained for the reactions in presence of the ligand. In addition a long induction period, similar as for the LAH activated hydrogenation without ligands, was observed. Furthermore, the reaction proceeded slowly and only partial hydrogenation of the more reactive double bond was found even at very long reaction times. As in the case of the ^{s}BuLi activated reactions, a slightly higher conversion was observed in absence of **NBD**.

Especially the results obtained in the hydrogenations without ligand were unexpected. As no diimineiron complex is present, other species must be responsible for the catalytic hydrogenation activity. The dark heterogeneous slurry mixture suggests the formation of colloidal iron clusters which may be the active catalysts. It can be seen that the different hydride donors LAH, $NaBH_4$ and DIBAH furnish catalysts with different activity suggesting that different active species are formed in these hydrogenations. In the case of ^{s}BuLi activation, iron-ate complexes (^{s}BuFeCl, $^{s}Bu_2Fe$, $^{s}Bu_3FeLi$, $^{s}Bu_4FeLi_2$) may be generated as reported by KAUFFMANN.[80] This compounds are known to promote cross-coupling reactions, hence they may also be able to catalyze the hydrogenation reaction.

7.2 Role of the iron source

Besides anhydrous iron(II) chloride a range of iron species in different oxidation states are able to serve as catalyst precursors in the absence of diimine ligands. Again the hydrogenation of **ENB** served as test reaction. In a typical hydrogenation experiment the substrate followed by an activator is added to the catalyst precursor suspension under hydrogen atmosphere at RT.

Table 10: Hydrogenation of **ENB** with different iron sources

Entry	Iron source	Product yield		
		DIBAH activation (**46** : **47**)	^{s}BuLi activation (**46** : **47**)	MeLi activation (**46** : **47**)
1	$Fe(II)Cl_2$	0 : 100	100 : 0	12 : 0
2	Fe(0)	97 : 0	2 : 0	no conversion
3	$Fe(III)(ac)_3$	74 : 0	10 : 0	no conversion
4	$Fe(III)(acac)_3$	no conversion	32 : 0	no conversion

Reaction conditions: **ENB** 0.5 M in benzene, 10 mol% catalyst, iron/activator 1:4, RT, 3 bar hydrogen pressure, 40 h.

The catalyst mixtures prepared from $Fe(II)Cl_2$ were the most effective ones leading in all the cases to the highest conversions. A less active catalyst is obtained when metallic iron(0) in form of a fine powder activated with DIBAH was used. A similar

reactivity was observed for iron(III) trisacetate as catalyst precursor. The alkyllithium activators, i. e. ^{s}BuLi and MeLi, proved to be inefficient in these cases. Surprisingly the related iron(III) salt tris(2,4-pentanedionato) ferrate fails to be activated by DIBAH, whereas BuLi leads to a marginaly active catalyst. This finding corroborates the result of SLOAN who obtained an active hydrogenation catalyst from $Fe(III)(acac)_3$ and trisisobutylaluminium.[53] In our case, the similar reagent ^{s}BuLi also furnished an active catalyst, whereas the hydride donor DIBAH failed to activate $Fe(III)(acac)_3$. It strongly suggests that DIBAH reacts in a different way with iron compounds as compared to trialkylaluminium and alkyllithium reagents.

7.3 Substrate range

Within all the precatalysts tested, mixtures generated from $FeCl_2$ and activated by DIBAH furnished the most active catalyst. To generalize the utility of this catalyst a range of olefins with different substitution patterns were investigated. Typical hydrogenation experiments were carried out on 0.5 M substrate solutions in benzene under 3 bar hydrogen pressure for 16 h in the presence of 10 mol% catalyst prepared from a 1:1 molar ratio of $FeCl_2$ and DIBAH.

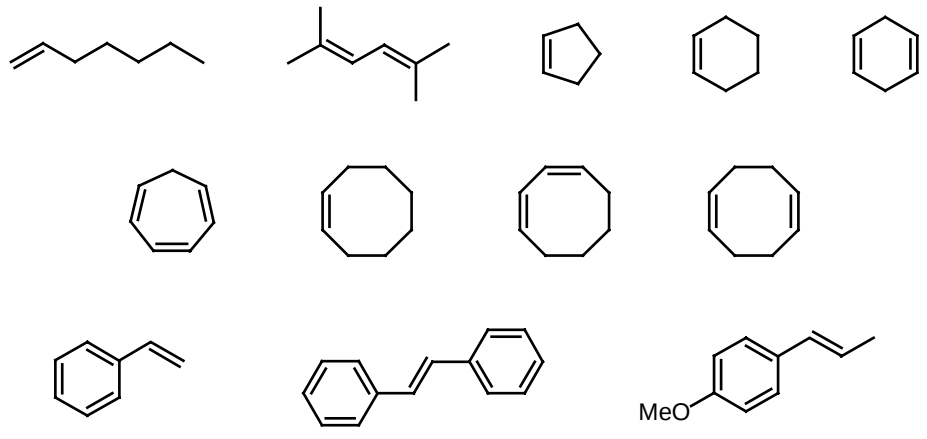
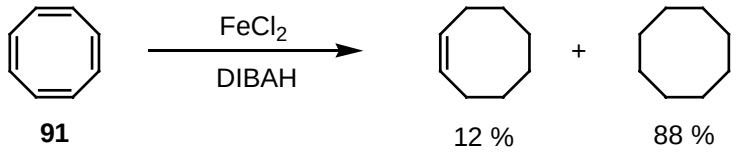


Chart 9: Substrates which were hydrogenated quantitatively (iron/DIBAH 1:1)

Almost all the investigated alkene substrates containing acylic and cyclic, isolated and conjugated mono-, di- and trisubstituted double bonds were reduced

quantitatively. Only in the case of cyclooctatetraene (**91**) 12 % of **COE** was found together with the totally reduced cyclooctane.



Scheme 49: Hydrogenation of tetraene **91**

Vinyl and allyl ethers as well as allyl amines reacted only when the DIBAH amount was raised to an 8fold excess with respect to iron. This finding does not contrast SIEBER's work since in his case, he obtained no hydrogenation using a 4fold excess of LAH with respect to the precatalyst.

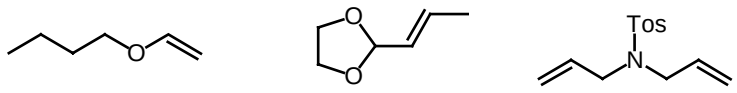
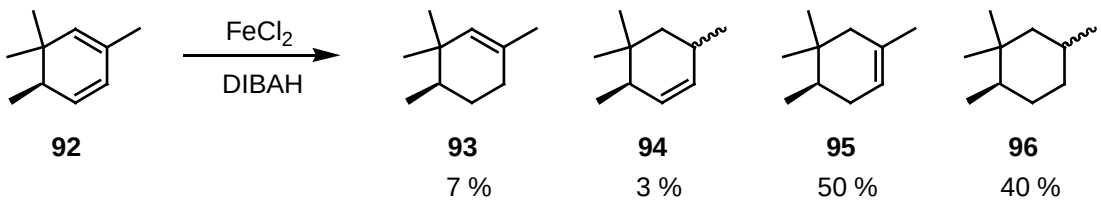


Chart 10: Substrates which were hydrogenated quantitatively (iron/DIBAH 1:8)

Double bond isomerization was observed as a competing reaction only in the case of the tetramethylcyclohexadiene substrate **92**. The expected product 1,3,3,4-tetramethylcyclohexene (**93**), a desired intermediate in the synthesis of γ-irone,[81] was obtained in only 7 % whereas the completely reduced cyclohexane **96** and the isomerized 1,4,5,5-tetramethylcyclohexene **95** were found as major products.



Scheme 50: Hydrogenation of hexadiene **92**

A special property of the catalytic system is the ability to reduce also alkynes. Tolane (**97**), cyclooctyne and 4-octyne were hydrogenated to the corresponding alkanes provided that an excess of activation reagent (Fe/DIBAH ≥ 1:4) was used again. Terminal alkynes like 1-pentyne and 1-hexyne produced highly viscous reaction mixtures indicating oligo- or polymerization side reactions, but after some additional time the viscosity decreased and the reduced alkanes were found together with a small amount of side products.

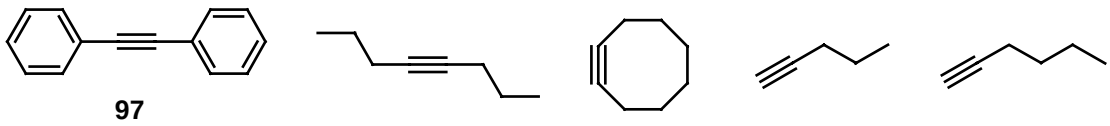
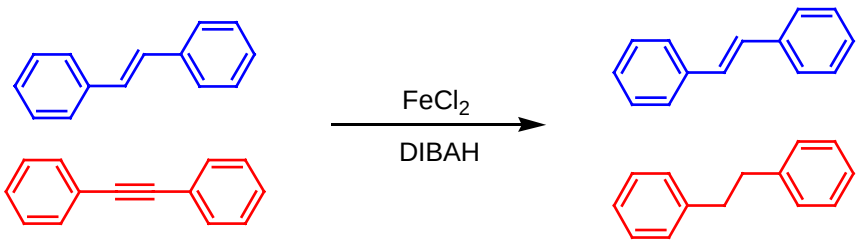
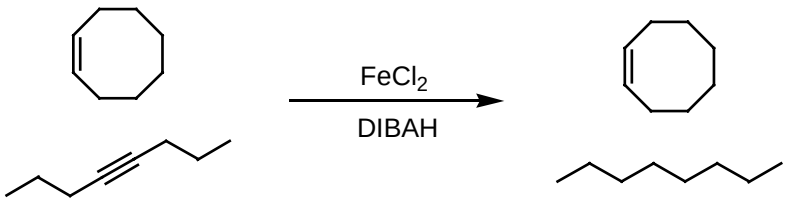


Chart 11: Alkynes which were hydrogenated quantitatively (iron/DIBAH 1:8)

The fact that a larger quantity of activation reagent is necessary to ensure the hydrogenation of alkynes than for the hydrogenation of alkenes seems to open a possible way for the chemoselective reduction of C=C bonds in presence of C-C triple bonds, a transformation which is not possible up to now. For this reason competition experiments were carried out where both alkenes and alkynes were present in the reaction mixture. First the different yne/ene couples were reacted with a catalyst generated with a 1:1 and a 1:2 iron/DIBAH ratio. In the case of the tolane/stilbene and the 4-octyne/cyclooctene couples no hydrogenation at all was observed. Using the most efficient catalyst generated with a 1:8 iron/DIBAH ratio led to the hydrogenation of the yne components to the completely reduced alkane products. Astonishingly the respective alkenes remained unchanged in these reactions.



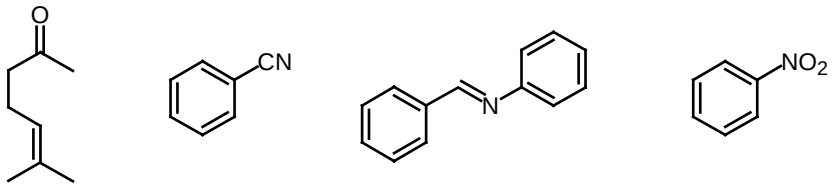
Scheme 51: Competitive tolane/stilbene hydrogenation



Scheme 52: Competitive cyclooctyne/4-octyne hydrogenation

Furthermore, the cyclooctyne/cyclooctene mixture polymerized very fast even at a 1:1 iron/DIBAH ratio (see chapter 8.1). Therefore this catalyst is not able to reduce chemoselectively alkenes in presence of alkynes.

Again, the reduction of olefins containing carbonyl groups such as 6-methyl-5-hepten-2-one (**98**) failed because in these cases the activation reagent reacts with the substrate instead of forming a catalyst. Attempts to hydrogenate substrates bearing functional groups other than C-C multiple bonds such as nitriles (benzonitrile), imines (N-benzylideneaniline) or nitro groups (nitrobenzene) failed too. As imines have been found to complex the catalyst precursor, excess of them as substrate masks all the iron and prevents the formation of the active hydrogenation catalyst. The same behaviour is inferred for the other functional groups.

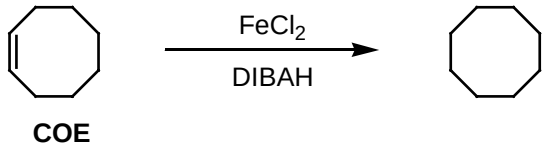


98

Chart 12: Substrates which were not hydrogenated

7.4 Hydrogenation efficiency

The catalytic efficiency of the $FeCl_2$/DIBAH system was assessed by measuring the TON (turn-over number) and TOF (turn-over frequency) for the hydrogenation of cyclooctene (**COE**). The TON reflects how many substrate molecules are transformed by one catalyst molecule before it desactivates, and the TOF shows how many substrate molecules are transformed by one catalyst molecule within a defined time (normally one hour).



Scheme 53: Hydrogenation of **COE**

Table 11: TON and TOF for **COE** hydrogenation

Entry	$FeCl_2$/DIBAH ratio	TON	TOF [h^{-1}]
1	1 : 1	158	28
2	1 : 2	236	27
3	1 : 4	726	30
4	1 : 6	1170	36
5	1 : 8	1859	124
6	1 : 10	1595	63
7	1 : 12	1485	69
8	1 : 14	1543	67
9	1 : 16	2047	109

Reaction conditions: substrate 0.25 M in benzene, 0.01 mol% catalyst, RT, 3 bar hydrogen pressure.

The results clearly show a strong dependence on the iron/DIBAH ratio. For both TON and TOF an 1:8 iron/DIBAH ratio turned out to generate the most active catalyst. The TON scales with the amounts of added DIBAH up to 8 equivalents, then decreases with further increasing DIBAH amounts and finally raises again up to > 2000 for a multiple of 8 equivalents DIBAH. A similar behaviour was observed for

the turn-over frequency. The higher efficiency of a catalyst prepared with an iron/DIBAH ratio of 1:8 as compared to catalysts generated with other iron/DIBAH ratios is even more pronounced for the TOF.

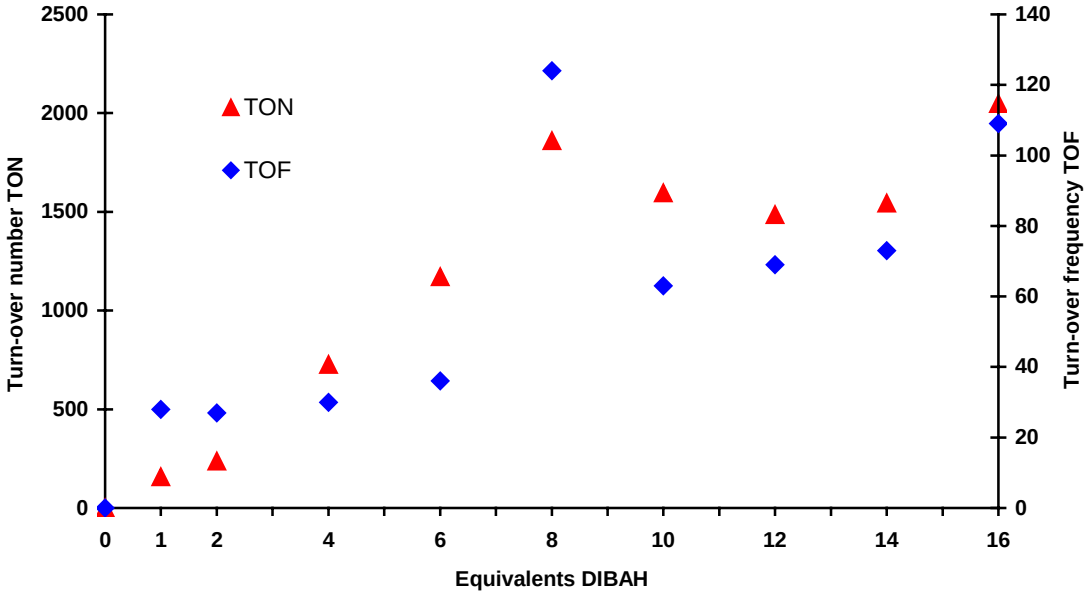
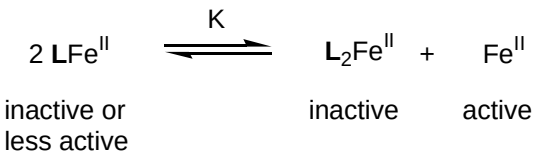


Figure 6: TON and TOF of **COE** hydrogenation for increasing iron/DIBAH ratios

The $FeCl_2$/DIBAH catalyst system displays pretty good efficiency compared to the catalysts discussed in the theoretical part. The TOF for any iron/DIBAH ratio is at least a factor 2 higher than for SIEBER's most active catalyst (10.8 h^{-1}), for the most active iron/DIBAH ratio the TOF (124 h^{-1}) is even 10 times higher. A possible explanation for this efficiency difference can be given taking in account the formation of a 1:1 mixture of $\mathbf{L}_2Fe$ and "free" Fe(II) in equilibrium with a **L**Fe species in presence of bidentate ligands **L**.



Scheme 54: Equilibrium between ligands **L** and iron(II)

The **L**$_2$Fe species is inactive, mainly the free iron(II) leads to the active catalyst. The **L**Fe species is either inactive too or at least much less active as compared to the free iron. The dependence of the equilibrium constant K on the ligand **L** explains why the different ligands furnished more or less active catalysts in SIEBER's case. For the ligands which don't give an active catalyst (**48**, **49**), the equilibrium is entirely shifted to **L**Fe.

The best TON (1859) is comparable to the values given for the tetranuclear ironcarbonyl cluster hydrogenation catalyst (1400)[56] (see page 23) or for the 1,3-butadiene cycloaddition with the (diimine)(arene)Fe(0) catalyst (1479)[14] (see page 14).

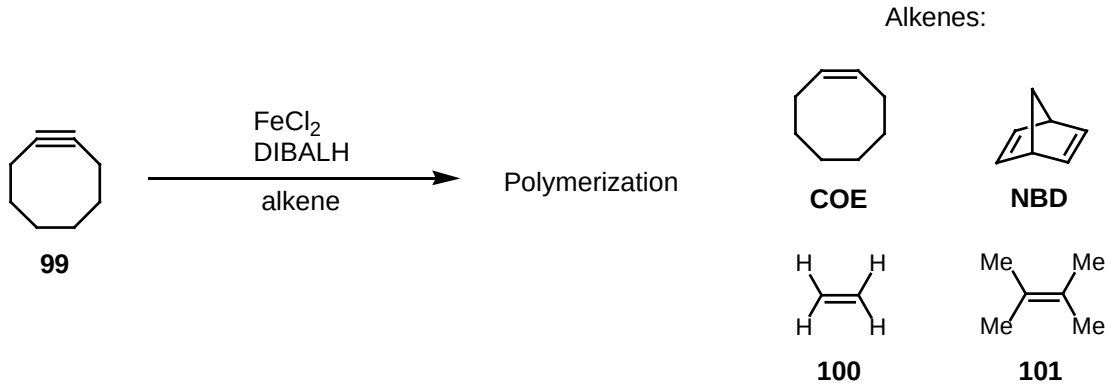
A special behaviour was observed carrying out the hydrogenation with a 1:1 $FeCl_2$/DIBAH ratio. At the end of the reaction, the hydrogenation can be restarted by addition of another portion of activation reagent. This procedure can be repeated several times and the global TON scales with every DIBAH addition. A TON of 686 was found for 4 repetitive DIBAH additions which is comparable to the TON for the 1:4 $FeCl_2$/DIBAH ratio (726).

8. Other reactions mediated by the $FeCl_2$/DIBAH catalyst

8.1 Polymerization of alkynes

In the competitive hydrogenation experiment involving cyclooctyne (**99**) and cyclooctene (**COE**) no hydrogenation was observed but the mixture polymerized and a hard, brittle polymer was obtained.

As hydrogenation of **99** was observed under hydrogen atmosphere in the absence of an alkene, several olefin substrates were tested if they promote this polymerization of cyclooctyne. The experiments were carried out under nitrogen atmosphere by activation of a benzene suspension containing $FeCl_2$ as precatalyst, cyclooctyne and 10 mol% of a supplementary alkene such as **NBD**, ethylene (**100**) or tetramethylethylene (**101**) using the 1:1 iron/DIBAH catalyst. It has to be noted that in the absence of this supplementary alkene no reaction occurred at this iron/DIBAH ratio.



Scheme 55: Polymerization of **99**

All tested alkenes were able to promote the polymerization of **99** in a very fast exothermal reaction. The resulting product is insoluble, it just swells in certain solvents. The polymer contains more or less iron contaminations from the catalyst, but the insolubility of the product prevents purification. The polymers arising from different experiments differ in their appearances in the dry and the swollen state, but

no information about the structure or the composition of the products could be obtained because of their insolubility.

In order to produce purer polymer, the amount of catalyst in the polymerization reaction was reduced. Indeed less iron contamination was incorporated in the polymer, but the reaction proceeded slower and less polymer product was isolated (see chapter 8.3). The isolated product was pure enough and suitable for solid state NMR measurements using the ^{13}C-CP-MAS technique (Cross Polarization - Magic Angle Spinning).

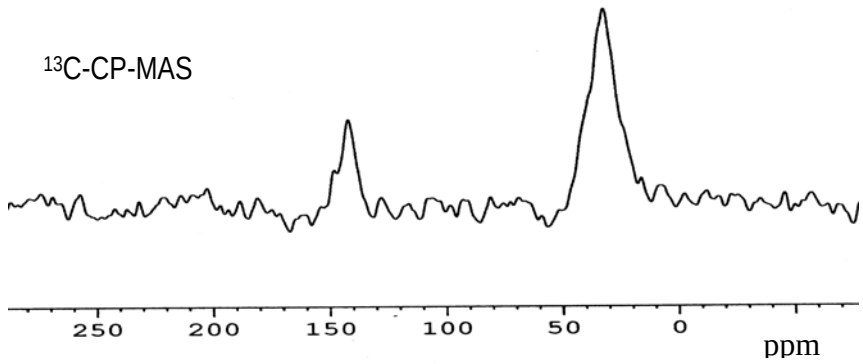
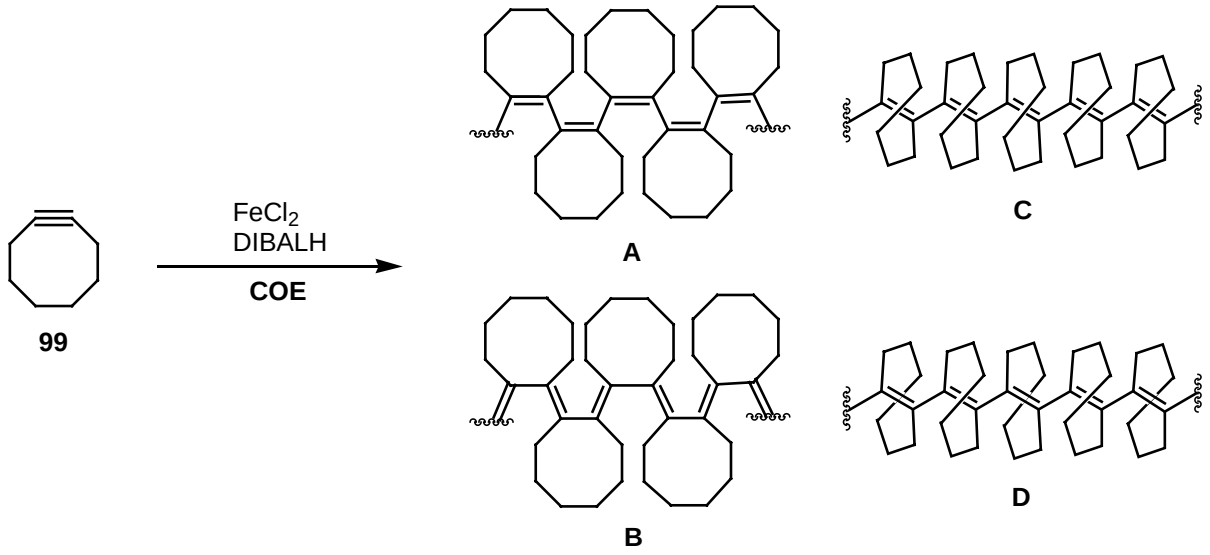


Figure 7: ^{13}C-CP-MAS-NMR spectra of the polymer product

Two signals were found in the spectrum. The large signal at ~30 ppm indicates alkyl carbons whereas the signal at ~140 ppm shows the presence of sp^2 carbons. Together with an estimated ratio of 3:1 for the integrals of the signals a polyacetylenic structure can be deduced. The rather broad lines indicate an amorphous material. Four different structures can be drawn which match with this proposition. First the polymerization can occur in either cis or trans fashion yielding a cis or trans polymer. Furthermore a double bond shift out of the cyclooctane ring is conceivable. But it is impossible to determine the regioselectivity of the polymerization and whether the polymer shows an isotactic or an atactic structure. Calculations using a simple force field indicate a distorted structure **A** at lowest energy. No coplanarity and therefore no conjugation between the double bonds is present due to steric hinderance between the rings.



Scheme 56: Possible structures of the cyclooctyne-polymer

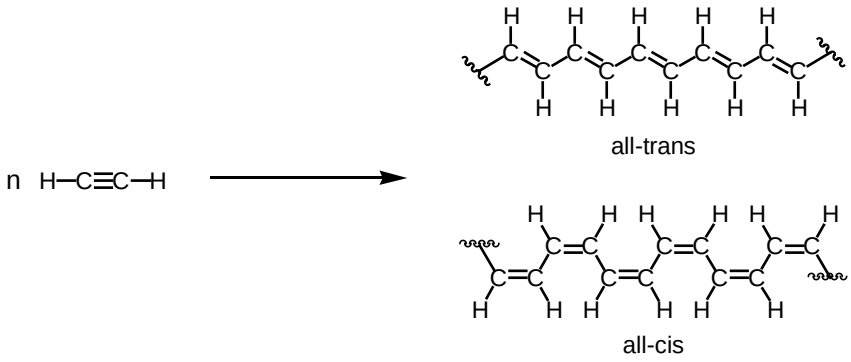
Attempts to polymerize less reactive alkynes than **99** with its strained triple bond such as tolane **97** or 4-octyne with the 1:1 iron/DIBAH catalyst were not successful even in presence of an alkene additive. As for the hydrogenation no reaction takes place at all and the substrates remain untouched. When the most active mixture iron/DIBAH 1:8 was used in the reaction with **97**, cyclotrimerization instead of polymerization occurred (see chapter 8.3).

Terminal alkynes i.e. 1-pentyne and 1-hexyne were also submitted to the polymerization conditions used before. The resulting reaction mixtures were highly viscous indicating that a polymerization or oligomerization reaction occurred. But the solutions became again fluid after some hours and no solid was formed like in the cyclooctyne case. The viscosity may have two possible reasons: one possibility is that the polymer chain is formed and several chains coagulated, but it is also conceivable that in the presence of terminal alkynes a sort of iron-aluminium-alkyne gel is formed (the same viscosity behaviour is observed in the hydrogenation experiments with 1-pentyne). Several attempts to isolate a polymer from these reactions failed. But as the reaction mixture was always filtered over Alox to eliminate the iron contaminations, the polymer got probably stucked on the top of the Alox filter, if formed at all. For both substrates indications for the formation of

the corresponding cyclotrimers were found with the appearance of aromatic signals in the ^{1}H-NMR spectra of the residues (see chapter 8.3).

8.2 Polymerization of acetylene

Probably the most interesting alkyne to polymerize is acetylene. Polyacetylene is the most representative one-dimensional organic conductor.[82] It exhibits a remarkable increase in electrical conductivity upon chemical doping with an electron donor or acceptor.[83] A variety of synthetic routes have been described for polyacetylene.[84] The most widely used method for preparing high-quality, free-standing films of polyacetylene is the polymerization of acetylene by Ziegler-Natta catalysts. Among these catalysts a combination of $Ti(OR)_4$-R_3Al is usually used as standard, but also an example of an iron Ziegler-Natta catalyst, i.e. $Fe(acac)_3$-Et_3Al is reported to polymerize acetylene.[85] The importance of polyacetylene and conducting conjugated polyenes in general is documented by the Nobel prize 2000 awarded to SHIRAKAWA,[86] MACDIARMID[87] and HEEGER[88] for the discovery and development of metallic conductivity in polyacetylene and other organic polymers.



Scheme 57: Polymerization of acetylene

The ability of our iron/DIBAH system to catalyze the acetylene polymerization reaction was checked in a few experiments. It has to be noted that our lacking of appropriate equipment and experience for this kind of reactions prevented the

synthesis of free-standing polymer films, and only simple qualitative experiments were performed. Nevertheless interesting results were obtained in these attempts.

The reactions were carried out under very mild conditions (0.5 bar acetylene pressure, RT) in either benzene or hexane solution. The catalyst was generated from an iron source activated by one equivalent of DIBAH as cocatalyst. The color of the reaction mixture turned to rose-violet when the active catalyst species was formed.

Table 12: Acetylene polymerization experiments

Entry	Solvent	Concentration of cocatalyst [10^{-3} M]	Iron source	Polymerization activity
1	Benzene	25	$FeCl_2$ ($2.5 \cdot 10^{-2}$ M)	+++
2	Benzene	5	$FeCl_2$ ($0.5 \cdot 10^{-2}$ M)	+
3	Benzene	10	Iron foil	++
4	Benzene	10	Teflon plate heated in $Fe(CO)_5$	++
5	Benzene	10	MALDI target (stainless steel plate)	-
6	Hexane	25	$FeCl_2$ ($2.5 \cdot 10^{-2}$ M)	+++
7	Hexane	5	$FeCl_2$ ($0.5 \cdot 10^{-2}$ M)	+
8	Hexane	10	Iron foil	++
9	Hexane	10	Teflon plate heated in $Fe(CO)_5$	+

Reaction conditions: 20 mL solvent, RT, 0.5 bar acetylene pressure.

First only a small difference in the polymerization activity was observed between benzene and hexane.

As already known for Ziegler-Natta catalysts,[ito] the outcome of the polymerization was depending on the catalyst concentration. At a catalyst concentration of $25 \cdot 10^{-3}$ M a bulky heap of a black product sticking on the glasswall of the Schlenk tube was obtained, whereas at a lower concentration of $5 \cdot 10^{-3}$ M the same material was formed but in much smaller quanitity in the shape of flakes. The proof of a successful polymerization of acetylene to polyacetylene was furnished with resonance Raman spectroscopy. Polyacetylene shows two Raman bands at around 1060 cm^{-1} and 1500

cm^{-1} which are assigned to the double bond stretching mode (ν_1) and to the single bond stretching mode (ν_3) of *trans*-polyacetylene.[89] The exact Raman shifts depend on the conjugation length of the polyacetylene:[90] the smaller the wave number, the longer the conjugation length. So a Raman resonance of 1485 cm^{-1} infers a conjugated chain length of about 25, whereas a wave number of 1460 cm^{-1} is deduced for infinite conjugation.[91] In our case the Raman spectra of the obtained black bulk material exhibited two intense bands at 1084 cm^{-1} and 1473 cm^{-1} respectively suggesting that the conjugation length of our polyacetylene is more than 50.[92] The morphology of the polymer is revealed by scanning electron microscope imaging (SEM). The images showed nicely the densely packed dreads of polyacetylene fibrils the material was consisted of.

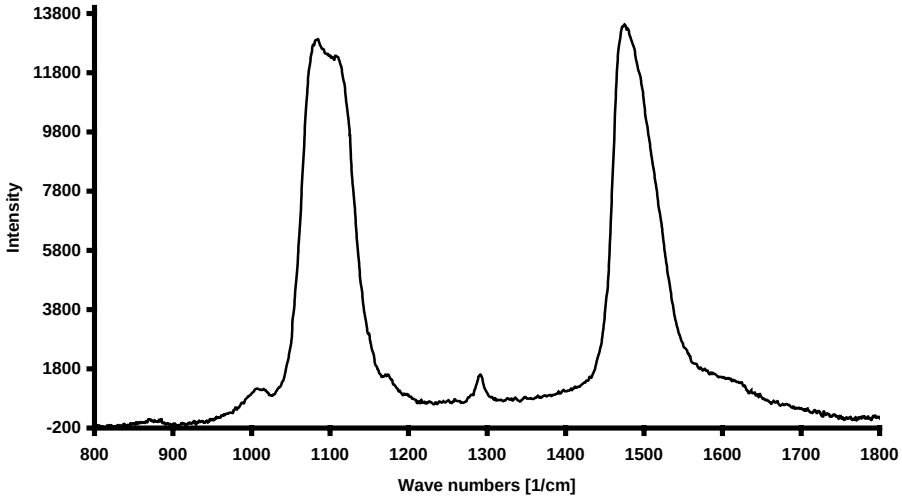


Figure 8: Raman spectra of the polymer product (table 10, entry 1)

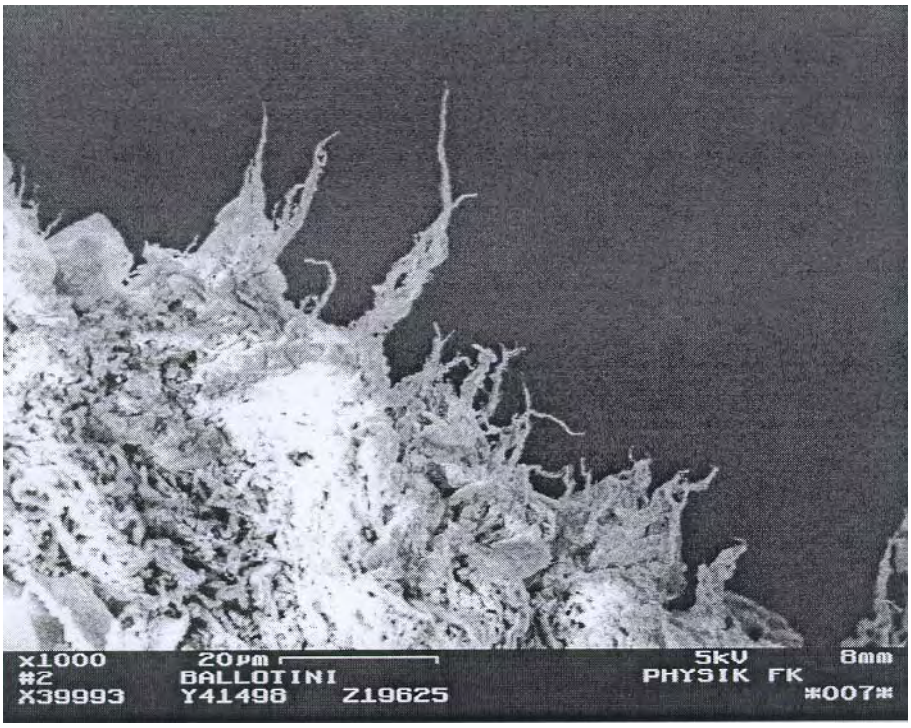


Figure 9: SEM image of polymer dreads (table 10, entry 1)

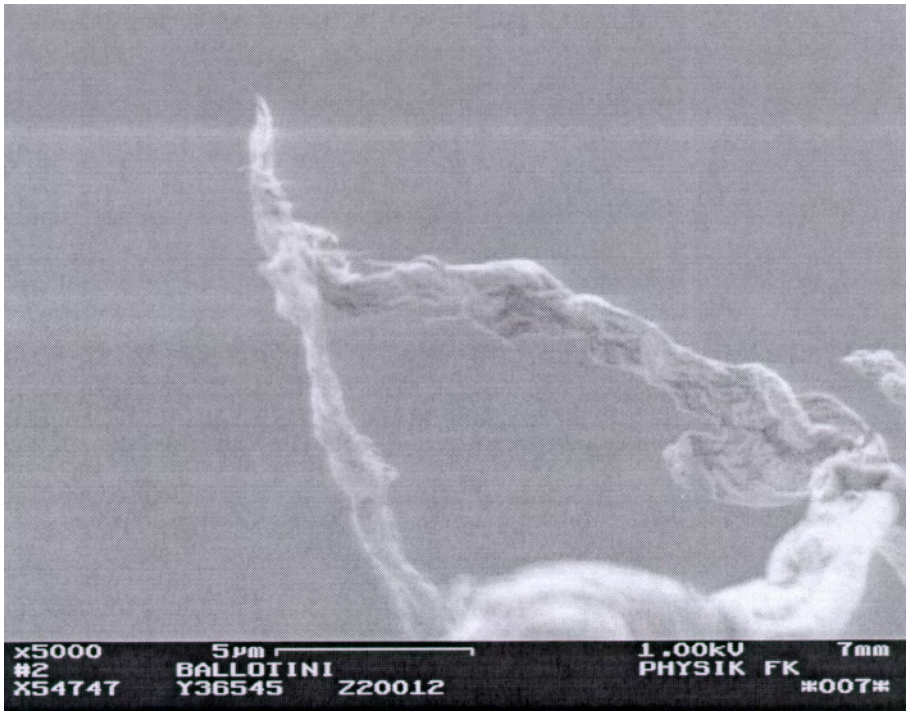


Figure 10: SEM image of single polymer dreads (table 10, entry 1)

From the hydrogenation experiments with the $FeCl_2$/DIBAH catalyst it was known that iron species other than $FeCl_2$ can serve as precatalysts. So it was tried to coat an iron foil with a polyacetylene film. In this case a metallic iron(0) foil was used as precatalyst and indeed, an active catalyst was generated upon activation. Together with few fluffy polyacetylene flakes in the solution the iron foil was found coated with a layer of black material. The SEM imaging then showed not a film, but more likely several layers of irregularly folded polyacetylene films adsorbed on the foil.

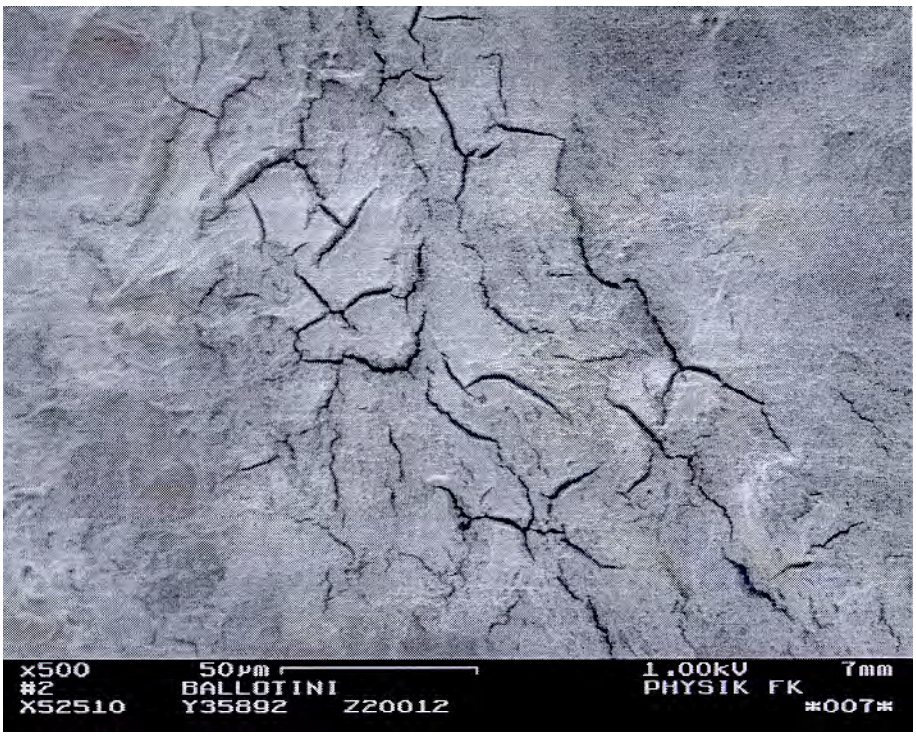


Figure 11: SEM image of polyacetylene layer on iron foil

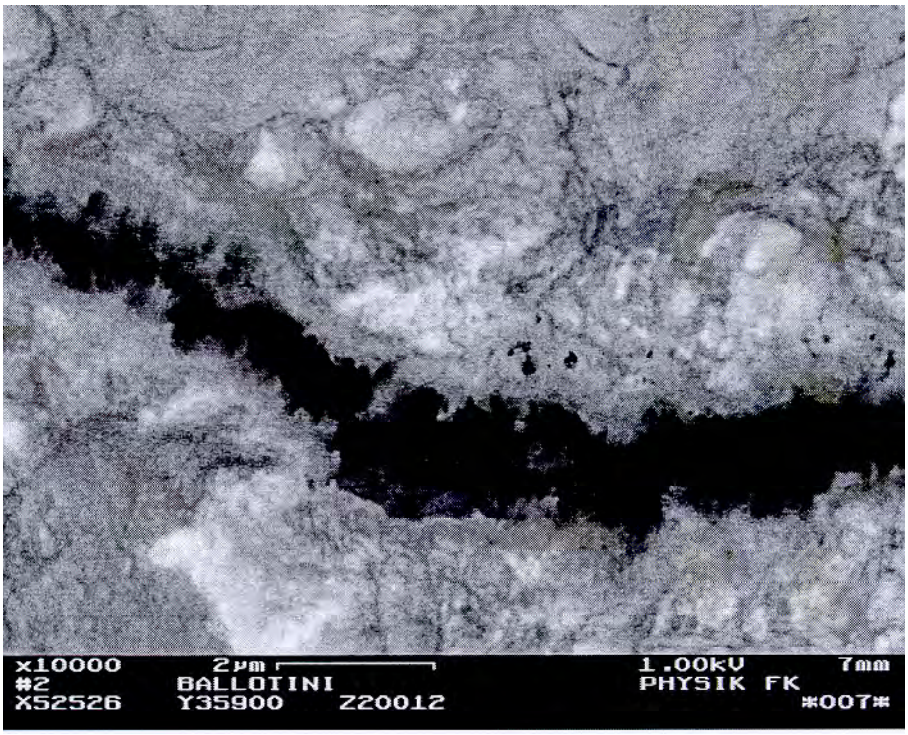


Figure 12: SEM image of polyacetylene layer on iron foil (magnification)

Analyzing the surface of the coating by Raman spectroscopy revealed the same *trans*-polyacetylene resonances as in the previous product. But depending on the exact excitation point on the coating surface two new bands around 1250 cm^{-1} and 1540 cm^{-1} appeared. These bands got more intense when the excitation was not focused on the surface but inside the layer stack. At a certain point near the iron support two resonances at 1341 cm^{-1} and 1566 cm^{-1} respectively were found exclusively in the spectrum.

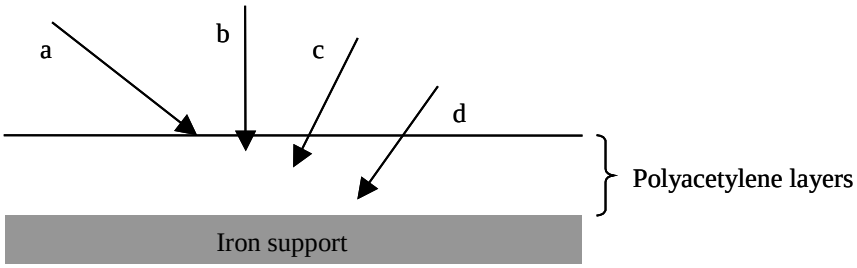


Figure 13: Schematic representation of the different excitation points

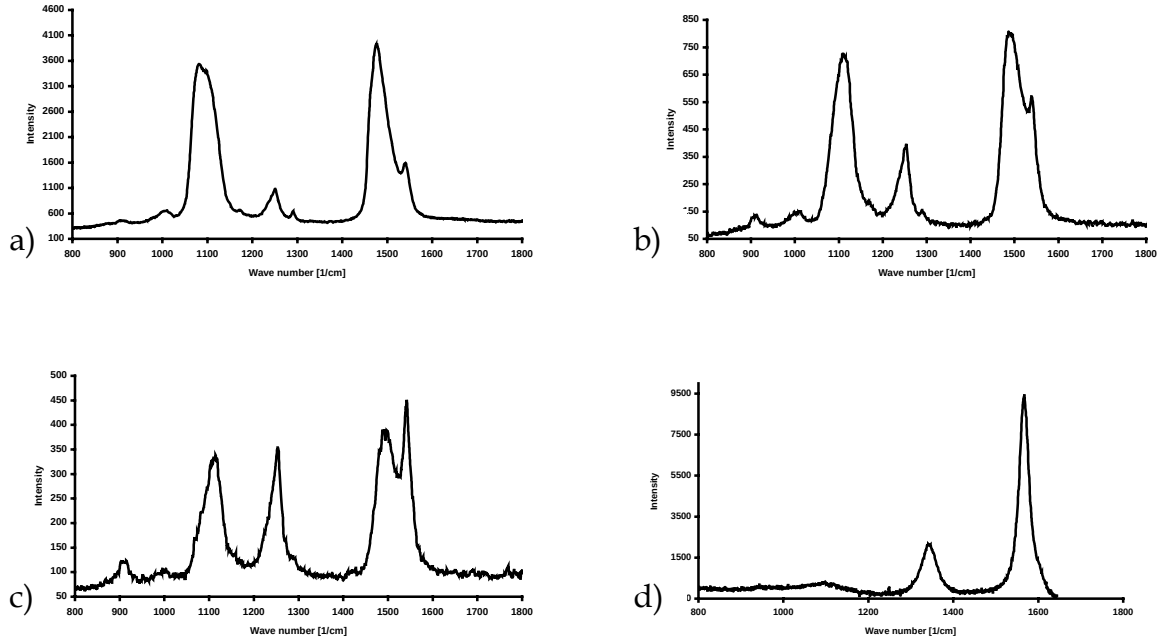


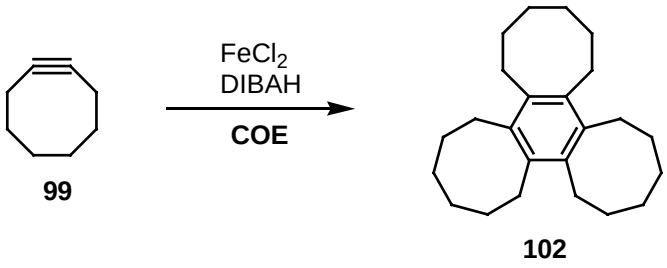
Figure 14: Raman spectra for different excitation points showing the appearance of the *cis*-polyacetylene bands (figures a-c) and the graphitic bands (figure d) (table 10, entry 3)

The two resonances at 1250 cm^{-1} and 1540 cm^{-1} can be attributed to *cis*-polyacetylene, those at 1341 cm^{-1} and 1566 cm^{-1} respectively to graphitic structures in the polymer.[93] The same resonances were also found in Raman spectra of carbon nanotubes.[94] Like polyacetylene, carbon nanotubes attracted enormous interest since their discovery in 1991 by IIJIMA[95] because of their electronic and mechanical properties.[96] Today several methods, all using harsh conditions are known for producing nanotubes[97] involving laser vaporization of metal-doped carbon targets,[98] arc evaporation of metal-doped carbon electrodes[99] and decomposition of carbon-containing molecules such as C_2H_4, CO[100] or CH_4 on supported metal particles.[101] An optimized iron/DIBAH catalyst offers now a potentially unique possibility to synthesize nanotubes in solution under mild conditions from acetylene. The ability of the catalyst to promote such a reaction is in principle demonstrated by the presence of the graphitic material in the polyacetylene coating. To circumvent the problem of forcing a graphite sheet to adopt a tube-like shape, the nanotubes could be grown on an appropriate template such as a [0_n]-paracyclophane derivative having already the necessary cyclic structure.

Another attempt to coat a support in order to obtain a better polyacetylene film was made using a teflon piece. This piece was heated in ironpentacarbonyl for two hours and then dried under inert atmosphere. By this procedure some $Fe(CO)_5$ diffused in the teflon piece which was partially decomposed and used as precatalyst. Activation of the prepared support with DIBAH led to a polymerization catalyst with only low activity. Few black polyacetylene flakes were formed, but no film or layer as in the iron foil case was obtained.

8.3 Cyclotrimerization of alkynes

In the polymerization attempts of the alkynes indications were found that cyclotrimerization instead of polymerization takes place. So the scope of the iron chloride/DIBAH catalyst to promote the cyclotrimerization of alkynes was investigated shortly. The reaction mixtures were prepared by suspending the substrate and $FeCl_2$ in the solvent followed by addition of DIBAH. In these cases a 1:4 Fe/Al catalyst was used.



Scheme 58: Cyclotrimerization of cyclooctyne (**99**)

The reactive cyclooctyne (**99**) was reacted under more diluted conditions as compared to the polymerization experiments to favour the cyclotrimerization. The concentration of the catalyst was lowered from $2{,}5 \cdot 10^{-2}$ M to $5 \cdot 10^{-3}$ M resulting in the preferential formation of the aromatic trimer **102** over the polymer, which was still observed as side product in this reaction. The polymer formation was almost entirely suppressed when hexane was used as solvent instead of benzene. In all these reactions 5 mol% of an additional alkene had to be added to ensure the generation of

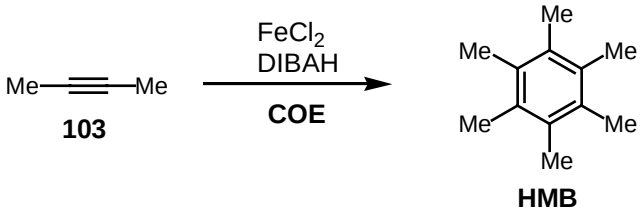
an active catalyst. Omitting cyclooctene **COE** used for this reason prevented the reaction to occur.

Table 13: Cyclotrimerization of cyclooctyne (**99**)

Entry	Solvent	Concentration of catalyst [10^{-3} M]	Additive	Result
1	Toluene	25	**COE**	Polymer
2	Toluene	5	**COE**	Polymer and cyclotrimer **102** (13 %)
3	Toluene	5	-	No reaction
4	Hexane	5	**COE**	Cyclotrimer **102** (62 %)

Reaction conditions: **99** 0.5 M, 10 mol% additive, iron/DIBAH 1:1, RT.

The less reactive 2-butyne (**103**) was submitted to the cyclotrimerization reaction using the same conditions as in the previous case (table 11, entry 2). The corresponding trimer hexamethylbenzene (**HMB**) was isolated in good yield (71 %).



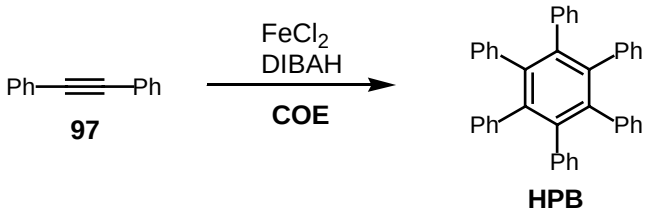
Scheme 59: Cyclotrimerization of 2-butyne (**103**)

Diphenylacetylene (**97**) turned out to be even less reactive towards the Fe/Al catalyst. At room temperature no reaction took place at all. Only when the reaction mixture was heated to reflux prior to activation some conversion to hexaphenylbenzene (**HPB**) was observed. Just a small difference was noted comparing toluene and hexane as solvents, the latter gives a little better conversion. Surprisingly the most promising result was obtained in the absence of an alkene which was necessary in the cyclooctyne case to ensure a reaction. Purification of **HPB** was difficult because of its poor solubility so the product still contained some iron inpurities.

Table 14: Cyclotrimerization of tolane (**97**)

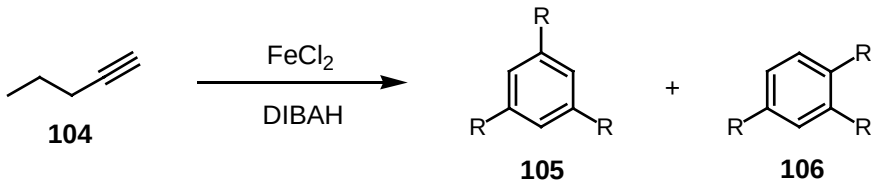
Entry	Solvent	T [°C]	Additive	Conversion
1	Toluene	RT	**COE**	No reaction
2	Toluene	75[a]	**COE**	< 10 %
3	Hexane	RT	**COE**	No reaction
4	Hexane	75[a]	**COE**	< 10 %
5	Hexane	75[a]	**-**	~35 %

Reaction conditions: **97** 0.5 M, 10 mol% catalyst, 5 mol% additive, iron/DIBAH 1:4.
a: Preheated before activation, continuous heating during the reaction



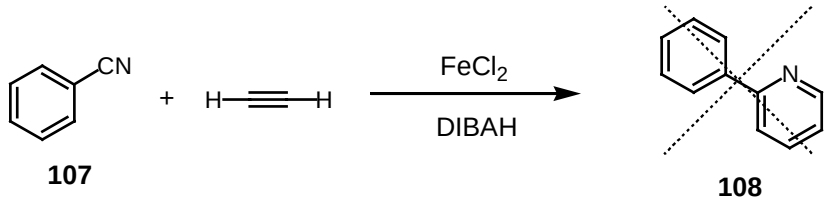
Scheme 60: Cyclotrimerization of tolane (**97**)

The cyclotrimerization of terminal alkynes or disubstituted alkynes with two different groups displays the possibility for the formation of two regioisomers. A few experiments were made with 1-pentyne (**104**) as substrate to check whether regioselectivity is obtainable with the iron/DIBALH catalyst in this case. The reaction was carried out in toluene as well as in hexane solution. As in the polymerization attempts, the reaction mixture became very viscous at the beginning and then turned fluid again. Small quantities of both regioisomeric cyclotrimers **105** and **106** were detected in the product residue after the work-up, but only poor regioselectivity (**105**/**106** 1.5) was observed. The viscosity of the reaction mixture indicated a poly- or oligomerization to occur, and the same problems may arise in the isolation of the products as in the polymerization experiments.



Scheme 61: Cyclotrimerization of 1-pentyne (**104**)

It was also tried to incorporate other functional groups than C-C triple bonds in the cyclotrimer in order to obtain heterocycles. For this reason benzonitrile (**107**) was engaged under acetylene atmosphere in presence of the iron/DIBAH 1:4 catalyst. Unfortunately this reaction failed, neither the 2-substituted pyridine **108** nor polyacetylene could be detected in the reaction mixture. This observation confirms the previous failure in the attempted hydrogenation experiment. The nitrile obviously complexes iron too strongly.



Scheme 62: Attempted cocyclotrimerization of benzonitrile (**107**) and acetylene

9. Homogeneous precatalyst

On the search of the catalytic active species a hydrogenation experiment was performed where the $FeCl_2$-benzene suspension was filtered immediately after the addition of **ENB** and DIBAH prior to pressurizing the mixture with hydrogen in order to exclude the presence of heterogeneous colloidal iron. The slightly yellow solution still showed catalytic activity, 8 % **ENB** was found reduced to the monoolefin **46**. This homogeneous hydrogenation activity attracted our interest and the question arose whether the activity could be raised. The iron(II) chloride was therefore suspended in benzene overnight to dissolve more of the iron salt, then the suspension was filtered and the homogeneous solution was set under hydrogen pressure upon addition of substrate and activator. In this case, 14 % **ENB** was converted to **46**. In a further attempt the stirring of the $FeCl_2$-suspension overnight was performed in toluene as solvent. This raised the conversion to 53 % of **46**.

As iron(II)chloride is almost insoluble in benzene or toluene, the dissolution has to be favoured by the formation of a new complex species. This proposition was supported by the results obtained with UV-Vis spectroscopy. The comparision of the UV-Vis spectra of the homogeneous yellow solution in toluene with the spectra of $FeCl_2$ and $FeCl_3$ in THF solutions revealed that contrary to the single absorption maxima shown by the dissolved iron chlorides in THF (329 nm for $FeCl_2$, 344 nm for $FeCl_3$) a twin absorption band with maxima at 315 nm and 358 nm, respectively. The double absorption clearly indicates the presence of a new complex species. As only $FeCl_2$ and toluene (or benzene, respectively) were present in the mixture, a dimeric toluene-$FeCl_2$ structure **109** was assumed in analogy to the (cymene)$RuCl_2$ dimer, a common starting material in ruthenium chemistry.

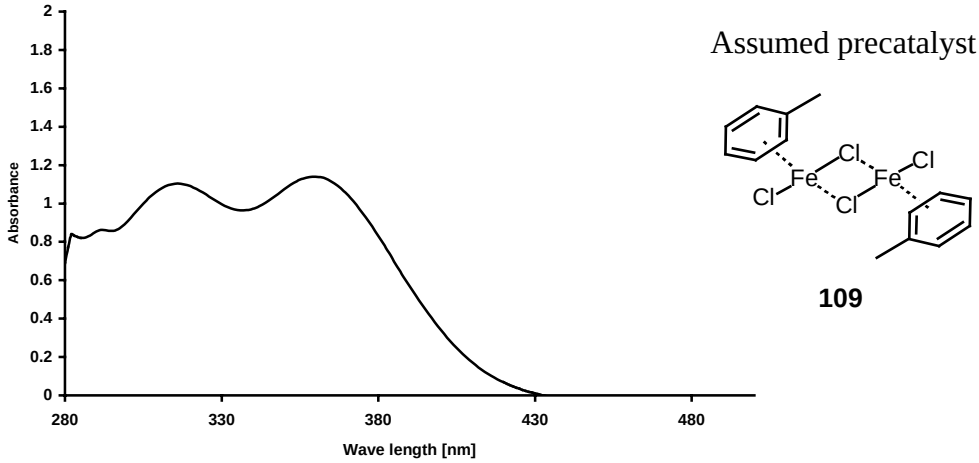


Figure 15: UV-Vis spectra of assumed toluene-$FeCl_2$ dimer **109** precatalyst

In the further experiments with this homogeneous species the presence of the double absorption in the UV-Vis spectra was taken as confirmation for the formation of the desired precatalyst **109**. The conversion to this complex was estimated from the UV-Vis absorbance.

9.1 Precatalyst isolation attempts

Many attempts were made to optimize and improve the synthesis of the assumed complex **109** in order to isolate characterizable amounts of this compound, but two major problems arising during these experiments prevented this intention. A first problem was the reproductibility of the reactions: even two absolutly identical preparations did not lead to the same result. Furthermore only poor solubility (presumably in equilibrium with the uncomplexed $FeCl_2$) was observed for the assumed complex **109**. Hence, large quantities of solvent and a big excess of iron(II) chloride had to be used to obtain reasonable amounts of compound **109**. Only 5 mg of the assumed complex were isolated out of 500 mL of a saturated toluene solution as the best result. The several approaches performed are summerized below and focus on the best results.

- The temperature plays an important role in this complexation. First, the reaction was carried out at RT, but when the mixture was heated, a better conversion was observed. Carrying out the reaction at reflux temperature (111 °C) however, much degraded iron is present in the suspension in this case. The best temperature with the highest conversion for this precatalyst formation was found at 80 °C, decomposition did not take place at this temperature.

- In all cases a lot of unreacted iron(II) chloride remained in the reaction mixture. It was tried to circumvent this problem with the aid of a Soxhlet apparatus. When the extraction was performed at reflux temperature, only decomposed iron was found in the reaction mixture probably due to the elevated temperature. Carrying out the reaction at 80 °C under a slight vacuum to ensure refluxing of the solvent only led to the isolation of uncomplexed, unreacted $FeCl_2$.
  Another possibility to improve the reactivity of iron(II) chloride was checked carrying out the reaction in an ultrasonic bath. But the $FeCl_2$ grains only became smaller, the complexation did not proceeded better with this aid.

- It was also tried to use other arenes than toluene to check whether a better conversion to the arene-$FeCl_2$ complex could be obtained by this approach. For this reason the more electronrich mesitylene was investigated. In this case the $FeCl_2$ decomposed faster than with toluene, a reaction at elevated temperature was not possible. At RT, a reaction took place revealing two weak bands in the UV-Vis spectra, but the conversion was much lower as compared to the reaction with toluene at RT.
  Some attempts were made using cymene to form the assumed complex in analogy to the (cymene)$RuCl_2$ dimer. But with this arene, the UV-Vis spectra never showed the double absorption, and only degraded iron was obtained by this approach. The same result is obtained when solvent mixtures such as benzene/toluene, toluene/mesitylene or toluene/cymene were used for the reaction.

- In order to eliminate all disturbing influences (such as O_2 in the solvent), the solvent was degased with nitrogen prior to the iron(II) chloride addition. The conversion to the assumed complex went up significantly using this pretreatment. The by far best result for all these complexation attempts was obtained using this finding: first, the toluene was degased before the reaction, then nitrogen was bubbled through the reaction mixture every hour for 15 min during the reaction. By this way the highest absorption was obtained in the UV-Vis spectra.

  In the first attempts, isolation of the complex was tried by evaporation of the solvent at RT under reduced pressure from a solution where the double absorption was observed. But only very poor quantities of a yellow product together with decomposed iron residues were obtained in these cases. Therefore, in a second attempt the solvent was evaporated at 80 °C under a permanent stream of nitrogen. In this case about 5 mg of the product could be isolated from 500 mL toluene solution. The UV-Vis spectra of this isolated product redissolved in THF still showed the expected two maximas indicating that the complex survived this prodcedure. It has to be noted, however, that the absorption around 360 nm is slightly shifted to 363 nm in THF as compared to 358 nm in toluene. A concentration of about $4 \cdot 10^{-4}$ was estimated from these experiments. Other analyses such as NMR or MS measurements were not successful, the product decomposed during the measurements. Nevertheless, regarding all the findings up to now, the idea of a new precatalyst structure arose where a N_2 molecule is coordinated to the iron. Hence, the bathochromic shift of the absorption in THF solution would be due to an exchange of the labile nitrogen ligand with a THF molecule.

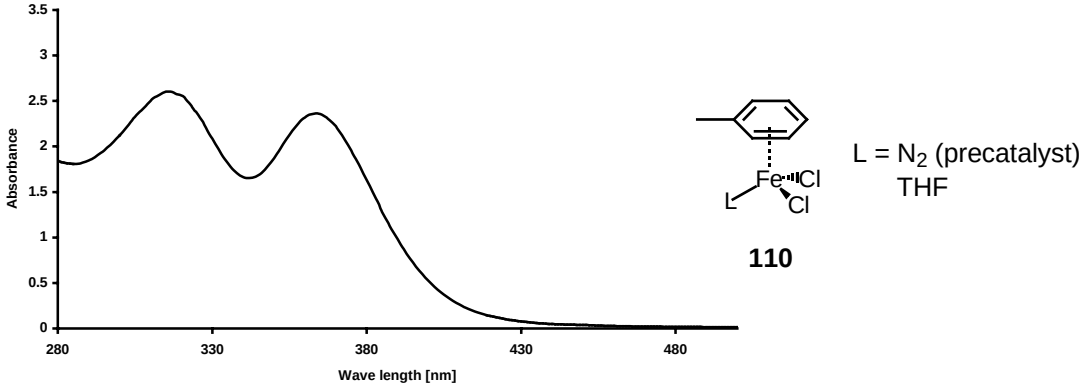


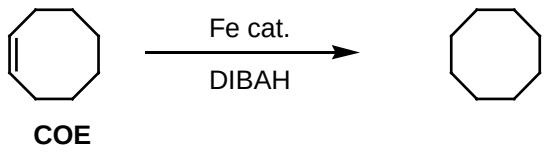
Figure 16: UV-Vis spectra of assumed precatalyst **110** in THF

This assumption is supported by the result obtained when argon instead of nitrogen was used to degase the reaction mixture. In this case, no reaction took place at all, only a weak single absorption for $FeCl_2$ was observed in the UV-Vis spectra. This result led also to the assumption that N_2 has to be involved in the complex formation and hence coordinates to the metal. Furthermore the first assumed dimer precatalyst **109** does not explain these findings supporting the idea of structure **110**.

- A last series of experiments was made derived from the assumed complex **109**. It was tried to incorporate other simple molecules with π-bonds such as ethylene and isobutylene instead of nitrogen. In these cases, the double bands appeared too, but the absorption showed only a modest conversion as compared to the N_2 complexations. As compared to the N_2 case, the absorption maxima at 315 nm remained while the second absorption maxima was slightly shifted to bathochromic wave lengths (ethylene 360 nm, isobutylene 361 nm). It was also observed that the resulting solutions swiftly degraded indicating less stable complexes than in the nitrogen case. This behaviour was more pronounced for isobutylene maybe due to steric effects.

9.2 Hydrogenation activity

To have an idea about the efficiency of this homogeneous precatalyst the assessment of the TON and TOF of this catalyst system was envisaged. As not enough quantity of the assumed precatalyst **110** could be isolated, the iron content in the homogeneous solution had to be determined by other means in order to measure the efficiency. For this reason a $FeCl_2$ -toluene solution displaying the two absorptions was examined by atomic absorption spectroscopy. The iron concentration of the solution was determined by this way to be $7.5 \cdot 10^{-4}$ M yielding an ε of about 7800 L mol^{-1} cm^{-1}. This solution with now known iron concentration was used to assess the TON and TOF of the hydrogenation of **COE** for different iron/DIBAH ratios.



Scheme 63: Hydrogenation of **COE**

Table 15: TON for **COE** hydrogenation

Entry	Fe/DIBAH ratio	TON
1	1 : 2	331
2	1 : 4	340
3	1 : 8	338
4	1 : 12	348
5	1 : 16	341
6	1 : 50	371

Reaction conditions: 5 mL catalyst solution, iron/substrate 1:10000, RT, 3 bar hydrogen pressure.

A different TON behaviour was obtained for this homogeneous catalyst compared to the slurry case. The TON of ~340 is independent of the iron/DIBAH ratio, the small variations remain within the error limit. The TON did not raise significantly even for very large amounts of activation reagent. Despite the higher TON obtained for the

slurry catalyst at elevated iron/DIBAH ratios, this homogeneous precatalyst is by far superior as compared to a 1:2 iron/DIBAH ratio in the heterogeneous case. The assessment of the TOF could only be made approximately. As the reaction already had stopped after one hour, the real TOF must be higher than the determined TON/hour value. Nevertheless it has to be added that a TOF of > 331 h^{-1} indicates a very efficient hydrogenation catalyst, which hydrogenates about 3-10 times faster than the slurry catalyst system.

These findings imply that in the slurry case (see chapter 7.4), mainly the same homogeneous precatalyst is responsible for the formation of the active catalyst. Other inactive species may be formed in competition with the active catalyst. More of the precatalyst is generated and activated with scaling amounts of DIBAH up to 8 equivalents. Also the result obtained with repetitive DIBAH addition corroborates this assumption, because the large excess of $FeCl_2$ present in these cases allow to generate new active catalyst upon subsequent additions of activator.

10. Allylbenzylether ligands

Since the isolation and characterization of the presumed $FeCl_2$ -toluene precatalyst **110** could not be achieved, a new type of ligand was designed inspired from the supposed structure of **110**. These ligands should help to diminish the stability problems arising in the formation and isolation of the presumed $FeCl_2$ -toluene precatalyst. Therefore the required monodentate π-bonded ligand was tethered to the aryl moiety via an ether link resulting in a pincer-like allyl benzyl ligand. The linkage should prevent the dissociation of the weakly coordinated ene ligand from the metal by the chelation effect. Deprotonation of the allyl group forms an allyl anion which is known to be a good ligand, consequently the stability of the resulting complex should raise even more. Furthermore the main goal of this work i.e. introducing an homogeneous stereoselective iron hydrogenation catalyst still exists and stereoselective processes can only occur in presence of chiral ligands. The allyl benzyl ethers display the possibility to be modified chirally either in the aryl or the allyl part.

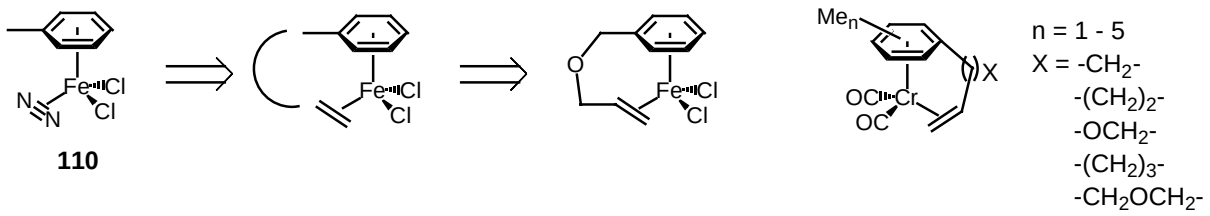


Figure 17: Development of allyl benzyl ligands, example of chromium complex

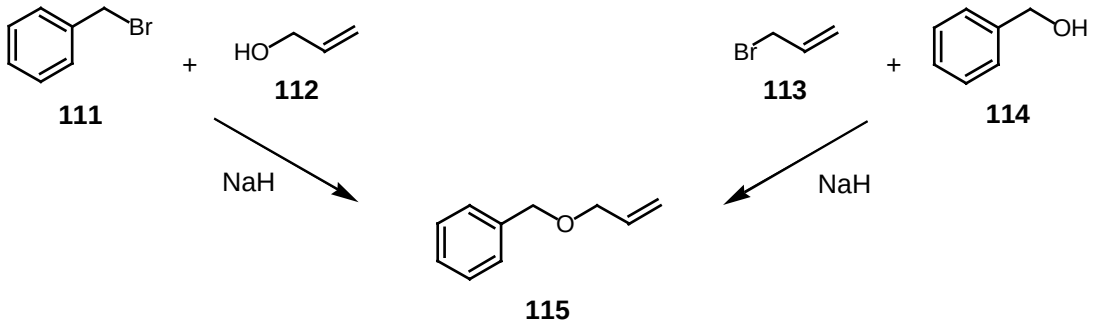
About 35 years ago NESMEYANOV described chromium complexes with similar ligands.[102] He mainly used various alkenylarenes with different alkyl chain lengths and methyl substitution in the arenes to synthesize alkenylarenedicarbonyl-chromium complexes[103] by photolysis of the tricarbonyl chromium precursors where only the arene is complexed to the metal. In the same way he obtained chromium complexes with phenyl and benzyl alkenyl ethers.[104] Ligands with one to

three linking atoms between aryl and double bond form stable complexes while ligands with longer alkyl chains don't form complexes anymore.

These ligands are easily accessible from readily available starting materials. A deprotonated benzyl alcohol derivative reacts with an allyl halide in a nucleophilic substitution reaction to the corresponding allyl benzyl ether compound. Alternativly the same product can be obtained when the substrates with reversed functionality (i.e. benzyl halide and allyl alcohol) were used as starting materials. A range of these ligands with different substitution patterns for the allyl double bond was synthesized.

10.1 Ligand syntheses

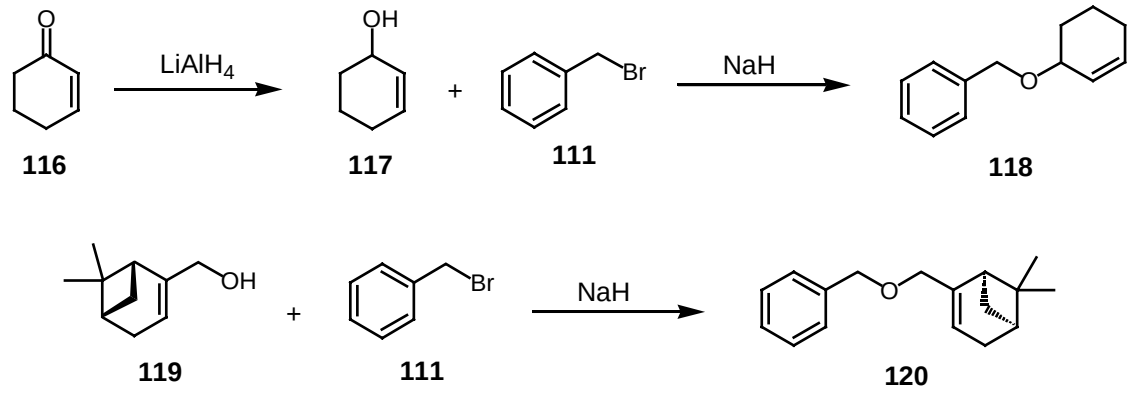
The syntheses were carried out following a slightly modified procedure as described by ARNDT.[105] Deprotonation of the alcohol with NaH in a DMF solution and subsequent addition of catalytic amounts of KI and the halide compound furnished the desired allyl benzyl ether. Usually benzyl bromide (**111**) was added to a deprotonated allyl alcohol (**112**). The simplest represant of these ligands, allyl benzyl ether (**115**), was also synthesized from benzyl alcohol (**114**) and allyl bromide (**113**). But only a small amount of ether **115** was produced under this conditions, 82 % of benzyl alcohol was reisolated unreacted.



Scheme 64: Synthesis of allyl benzyl ether (**115**)

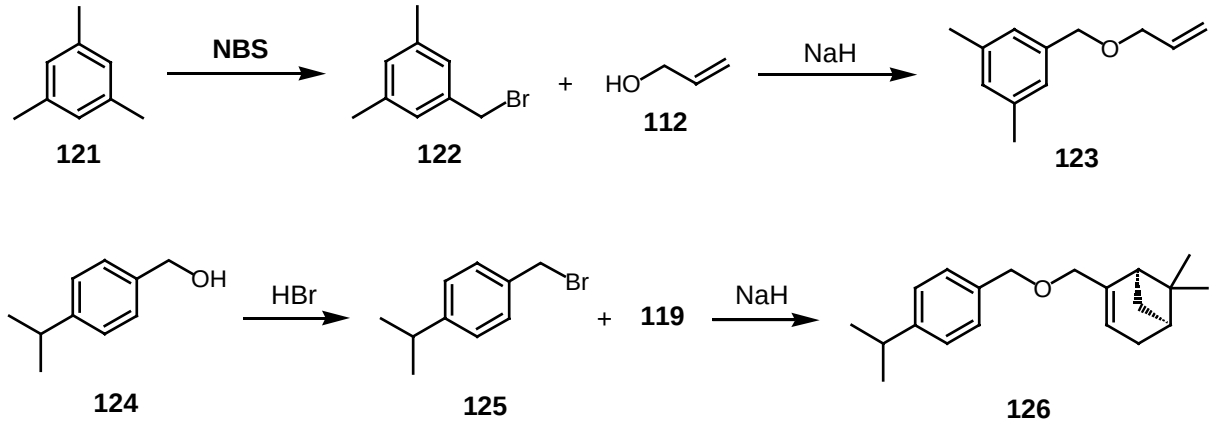
The benzyl halide/allyl alcohol combination was therefore used for the further syntheses of these ethers. Benzyl bromide (**111**) was reacted with 2-cyclohexen-1-ol

(**117**) and the optical active myrtenol (**119**), and the corresponding allyl benzyl ethers **118** and **120** were isolated in good yields (> 75 %).



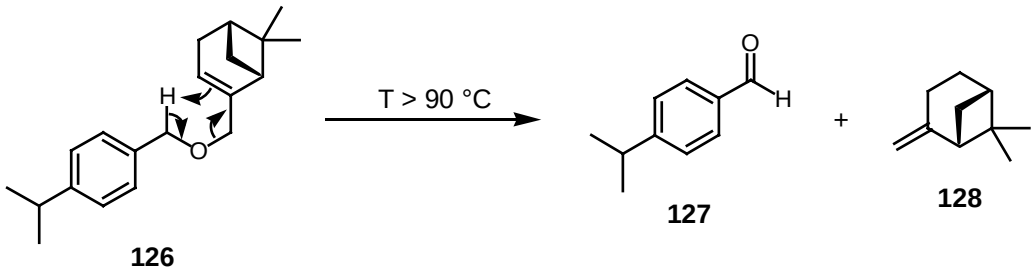
Scheme 65: Syntheses of benzyl ethers **118** and **120**

Variation of the aryl part was achieved when alkyl substituted benzyl bromides were reacted with allyl alcohols. Reaction of *meta*-disubstituted benzyl bromide **122**, obtained by radical bromination from mesitylene (**121**) and *N*-bromosuccinimide (**NBS**),[106] with allyl alcohol **112** afforded ether **123** in modest yield (30 %). Ether **126** was synthesized from myrtenol (**119**) and 4-isopropyl benzyl bromide (**125**), obtainable via S_N2-reaction of 4-isopropylbenzyl alcohol (**124**) and HBr.



Scheme 66: Syntheses of benzyl ethers **123** and **126**

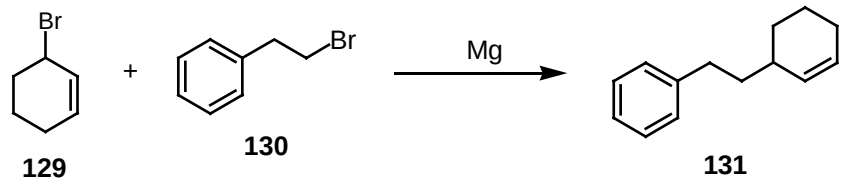
The purification of ether **126** turned out to be tricky. **126** can not be separated from the starting products by extraction, and it decomposes by a sort of retro-Claisen rearrangement on silica or at elevated temperatures (> 90 °C) into the benzyl aldehyde **127** and β-pinene (**128**).



Scheme 67: Decomposition of benzyl ether **126**

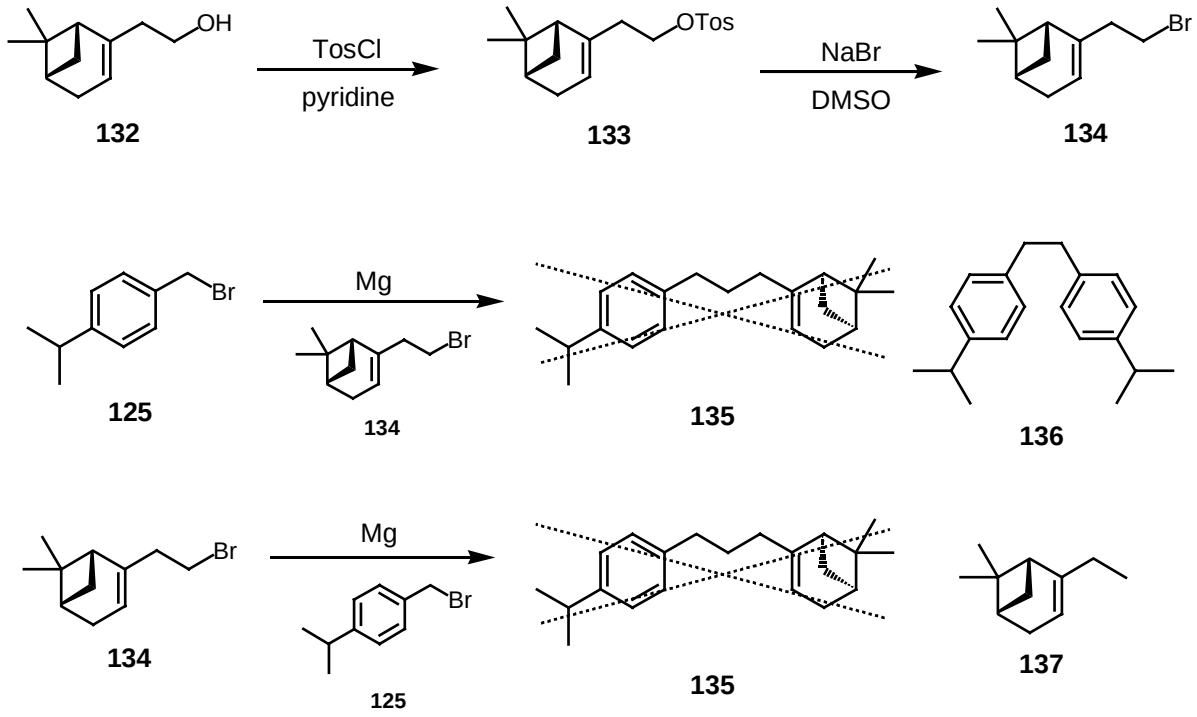
Finally pure ether **126** was obtained when the nucleophilic substitution was carried out with a slight excess of myrtenol (**119**). Alcohol **119** can be separated from the product by distillation at 85 °C in a ~10^{-5} bar vacuo. The residue consists of pure **126** in 56 % yield.

The synthesis of two oxygen-free alkenylarene derivatives by Grignard cross coupling reaction was envisaged to compare their behaviour as ligands in the catalytic hydrogenation with the allyl benzyl ether ligands.
The reaction of phenetyl bromide (**130**) and magnesium produced the Grignard reagent which was subsequently coupled with 3-bromocyclohexene (**129**) affording the alkenyl analogue **131** of ether **118** in modest yield.



Scheme 68: Synthesis of phenylalkenyl **131**

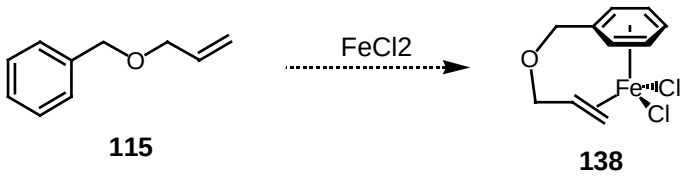
Coupling attempts to synthesize the myrtenyl ether carbon analogue **135** via the Grignard cross coupling reaction were not successful. When the benzyl bromide compound **125** was used to form the Grignard reactive only the bibenzyl **136** was isolated due to homocoupling. When bromide **134**, obtained from nopol (**132**) via tosylation followed by substitution with NaBr, was reacted with magnesium the Grignard reagent was formed, but no coupling took place upon addition of **125** and only unreacted bromide **125** as well as the dehydroxylated nopol derivative **137** were isolated after hydrolysis. Presumably the desired cross coupling could be attained by use of a nickel catalyst.



Scheme 69: Attempted syntheses of phenylalkenyl **135**

10.2 Complexation of allylbenzylether ligands with iron(II)chloride

In order to obtain an isolated allylbenzyliron precatalyst for the catalytic reactions, it was briefly tried in several approaches to isolate such an assumed allylbenzylether-iron complex. Ligands **115** and **126** were reacted therefore with iron(II) chloride varying solvent and temperature.



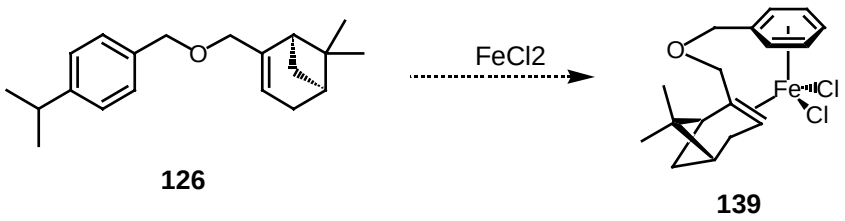
115 **138**

Scheme 70: Attempted synthesis of iron complex **138**

A first approach was made with a solvent-free complexation attempt. $FeCl_2$ was mixed with an excess of ether ligand **115** as solvent therefore. But the mixture solidified like polymerized. All isolation attempts of this material failed: Filtration of the material furnished a grey solid which decomposed quickly by oxidation. Dissolution of the solid reaction mixture with either pentane or toluene led to a slurry out of which the ligand was isolated unchanged, but no complex or polymerization product was found. When the solid reaction mixture stood for longer time under inert atmosphere, it became fluid again. At this stage the iron was degraded and **115** was recovered unchanged.

A second approach with the use of either toluene or THF as solvent for the complexation reaction was not an improvement. The yellow toluene solution showed weakly two absorptions in the UV-Vis spectra similar to the assumed $FeCl_2$-toluene complex **110**, but the complex solution showed decomposition, so no further characterization or isolation was possible. In THF the $FeCl_2$ simply dissolved but no complexation took place.

Another series of complexation experiments was performed with ligand **126** to obtain an isolated allylbenzylether iron complex. Apart from the ususally tested solvents toluene and THF, the complexation was tried in other solvents like butanol, the solvent of choice for the preparation of BROOKHART's bis(imino)pyridineiron polymerization catalysts, and dimethoxyethane.



126 **139**

Scheme 71: Attempted synthesis of iron complex **139**

The most promising approach was obtained in toluene solution at room temperature (entry 1). Mixing the ligand **126** with iron chloride for several days at room temperature resulted in a yellow solution with a lot of unreacted $FeCl_2$. This rest was filtered off and the solvent was evaporated under a stream of nitrogen. Washing off the residual ligand with pentane afforded a yellow oily product which was analyzed. In the UV-Vis spectra the two bands with maximas at 313 and 358 nm suggest the presence of the desired complex. NMR measurements were not possible due to decomposition. The ESI-MS showed two signals for iron compounds (552.1 and 732.3), but the isotope patterns of these signals indicated 4 chlorines. The mass difference of 178.2 between the two signals correspond exactly to the ligand **126**.

Table 16: Conditions for the complexation of **126**

Entry	Solvent	T [°C]
1	Toluene	RT
2	Toluene	55
3	THF	RT
4	THF	55
5	Butanol	RT
6	Dimethoxyethane	80

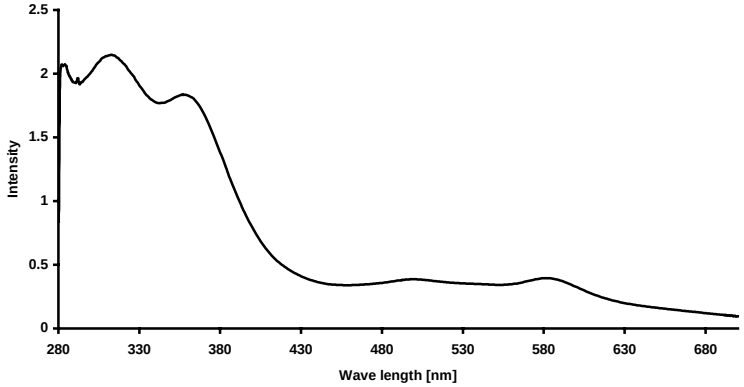


Figure 18: UV-Vis spectra of presumed complex **139**

Despite all these indications no suitable structure propositions for these masses were found. Several attempts were made to produce more of this compound using the same procedure, but like in the case of the homogeneous toluene-iron chloride complex **110** the reaction was not reproducable and the outcome varied every time. Heating up the reaction suspension was not an improvement for this complexation. In contrast to the isolated ether, **126** decomposed in presence of the metal already at a temperature of 55 °C.

Another approach was made with THF as solvent. In contrast to the complexation attempts in toluene, the $FeCl_2$ reacted completely within few hours resulting in a red-brown solution. Evaporation of the solvent led to separation of an oily brown product which decomposed immediately. A diffusion crystallization attempt with pentane to crystallize this product was not successful. Oily brown drops were separated from the solution, but as before this product decomposed immediately upon isolation. It's not clear therefore whether this product was really a complex compound or not, since the UV-Vis spectra of the complexation mixture showed only one absorption band which can be attributed to $FeCl_2$.

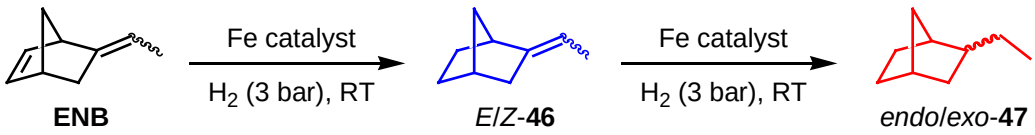
In butanol the iron(II) chloride dissolved without any problems and it seemed as complexation occurred. The color of the solution changed with the addition of **126**, but no complexation was indicated in the UV-Vis spectra. Attempts to separate any complex compound from the reaction solution by extraction with toluene, diffusion crystallization with pentane or destillation of the solvent failed, the iron was found always degraded.

In the least polar solvent dimethoxyethane the iron(II) chloride did not dissolve at all and so no reaction took place even at reflux temperature. $FeCl_2$ as well as ether **126** were reisolated.

10.3 Catalytic reactions with allylbenzyletheriron complexes

10.3.1 Hydrogenation experiments

Some preliminary experiments were performed with the allyl benzyl ethers as ligands for the catalytic hydrogenation of **ENB**. Different precatalyst preparations and activation reagents were investigated.



ENB *E/Z*-**46** *endo/exo*-**47**

Scheme 72: Hydrogenation of **ENB**

Preparation A:

The first precatalyst preparation consisted in deprotonation of the allyl ligands **115**, **120, 123** or **126** with ^{s}BuLi at 0 °C in cyclohexane solution followed by addition of an iron(II) chloride suspension in a small volume of THF. Then the substrate was added and the mixture was set under 3 bar hydrogen pressure prior to the activation step.

No hydrogenation activity is observed in both blank experiments pointing out the presence of the ligand as well as the activation step are necessary for these hydrogenations (entries 1 and 2 versus entry 3). Only a small influence of the ether ligand was observed for ^{n}BuLi activated hydrogenations. The ligand with the less substituted allyl group **115** showed the best activity with small conversion of the trisubstituted C=C bond, whereas with the other ether ligands the hydrogenation stopped when the cyclic double bond was reduced.

Table 17: Hydrogenations using preparation A

Entry	Ligand	Activator	Conversion
1	**115**	-	No conversion
2	-	^{n}BuLi	No conversion
3	**115**	^{n}BuLi	*E*/*Z*-**46** 92 % *endo*/*exo*-**47** 8 %
4	**115**	DIBAH	*E*/*Z*-**46** 100 %
5	**115**	LAH	No conversion
6	**120**	^{n}BuLi	*E*/*Z*-**46** 100 %
7	**120**	DIBAH	No conversion
8	**120**	LAH	*E*/*Z*-**46** 35 %
9	**120**	MMAO	No conversion
10	**126**	^{n}BuLi	*E*/*Z*-**46** 100 %
11	**126**	DIBAH	No conversion
12	**123**	^{n}BuLi	No conversion
13	**123**	DIBAH	No conversion

Reaction conditions: Ligand 0.05 M in cyclohexane, 0.5 mmol $FeCl_2$ in 2 mL THF, **ENB** 0.5 M, iron/activator 1:4, RT, 3 bar H_2 pressure, 40 h.

The hydride donors DIBAH and LAH showed a different behaviour with respect to the ligand: good hydrogenation activity for DIBAH activated reaction was obtained with ligand **115**, while no hydrogenation was observed in case of LAH activation. The behaviour is inversed for ethers with bulkier allyl groups. Whereas the activation with DIBAH led not to an active catalyst, modest conversion was found for LAH activation in this case.

Reactions with ligand **123** bearing *meta*-substituents in the phenyl ring of the benzyl part did not furnished an active catalyst at all using neither ^{n}BuLi nor DIBAH activation.

Preparation B:

Another series of hydrogenation experiments was performed with precatalysts prepared similar to the ones mentioned above except that the suspension was filtered before the addition of the activtor. In that way the reaction solution was

homogeneous and no free $FeCl_2$ was present to generate other active catalysts upon activation.

Table 18: Hydrogenations using preparation B

Entry	Ligand	Activator	Conversion
1	-	^{n}BuLi	No conversion
2	**118**	-	No conversion
3	**118**	^{n}BuLi	*E*/*Z*-**46** 100 %
4	**118**	MeLi	*E*/*Z*-**46** 100 %
5	**118**	DIBAH	No conversion
6	**118**	LAH	No conversion
7	**118**	$LiBH_4$	No conversion
8	**131**	^{n}BuLi	*E*/*Z*-**46** 66 %
9	**120**	^{n}BuLi	No conversion

Reaction conditions: Ligand 0.05 M in cyclohexane, 0.5 mmol ^{s}BuLi, 0.5 mmol $FeCl_2$ in 2 mL THF, **ENB** 0.5 M, iron/activator 1:4, RT, 3 bar H_2 pressure, 40 h.

Again the blank experiments showed no hydrogenation of **ENB**. Both alkyllithium activators were able to generate the active catalysts, the less reactive C=C bond was completely hydrogenated. The use of the carbon analogue **131** of ether **118** also led to an active catalyst upon ^{n}BuLi activation, but the conversion is lower as compared to the reaction with the ether analogue.

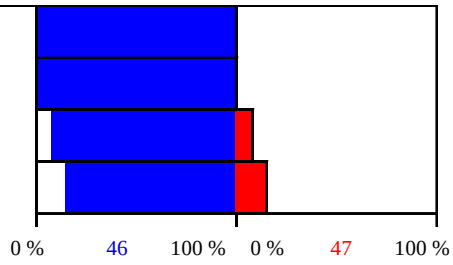
The use of hydride donors as activators was not successful, no hydrogenation of **ENB** occurred. In contrast to preparation A, no hydrogenation activity was observed when ligand **120** was used in this case.

Preparation C:

A different precatalyst preparation was used for reactions with ligand **126**. $FeCl_2$ and ether **126** were suspended in toluene and stirred for several hours. The resulting mixtures were activated with alkyl lithium reagents and used for the hydrogenation of **ENB**. Especially these hydrogenation results have to be regarded with caution because the active catalyst also could be generated from free iron chloride present in the mixture and the reducing agent.

Table 19: ^{n}BuLi activated hydrogenation of **ENB** using preparation C

Activator	Fe/Li ratio	Time	Conversion
n-BuLi	1 : 1	16 h	
	1 : 5	16 h	
		40 h	
		75 h	

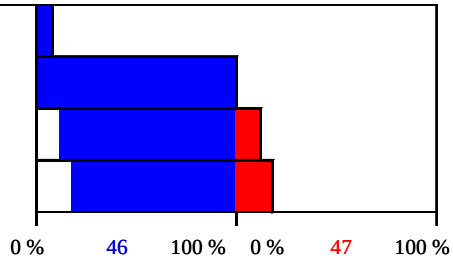


Reaction conditions: **ENB** 0.5 M in toluene, 10 mol% catalyst, RT, 3 bar H_2 pressure.

The activation of the precatalyst with one equivalent of ^{n}BuLi generated an active catalyst. The cyclic C=C bond was hydrogenated in short time, but the exocyclic double bond remained untouched. In contrast activation of the precatalyst with one equivalent of MeLi led to only poor conversion of **ENB**, not even 10 % of the more reactive double bond was found hydrogenated. However, similar activity as in the ^{n}BuLi case was observed for the catalysts obtained with a 1:5 iron chloride/alkyl lithium ratio. After complete reduction of the disubstituted double bond the hydrogenation rate slowed down for the trisubstituted C=C bond until the reaction stopped at about 15 % conversion to the totally reduced *endo* and *exo* isomers.

Table 20: MeLi activated hydrogenation of **ENB** using preparation C

Activator	Fe/Li ratio	Time	Conversion
MeLi	1 : 1	16 h	
	1 : 5	16 h	
		40 h	
		75 h	



Reaction conditions: **ENB** 0.5 M in toluene, 10 mol% catalyst, RT, 3 bar H_2 pressure.

10.3.2 Ethylene polymerization experiments

During the development of the catalysts it was always briefly tried to apply the catalysts also to the polymerization of ethylene. As very similar mechanisms are presumed for hydrogenation and polymerization respectively, a catalyst displaying hydrogenation activity can be imagined as potentially active polymerization catalyst too. The most promising results were obtained with this allylbenzyletheriron catalyst system.

The ethylene polymerization experiments were carried out with the catalyst generated from 5 equivalents of alkyl lithium reagent or a large excess of MMAO (~300 equivalents) added to a **126**-$FeCl_2$ suspension. At low ethene pressure no reaction took place for all MMAO, BuLi and MeLi activated reactions. Whereas the catalyst obtained by BuLi activation also showed no activity towards ethylene at high pressure, MeLi activation led to an active catalyst. No ethylene polymer was produced but pentene was detected by GC indicating just an oligomerization reaction.

Table 21: Ethylene polymerization experiments

Entry	Activator	Pressure [bar]	T [°C]	Result
1	MMAO	0.5	RT	No reaction
2	^{n}BuLi	0.5	RT	No reaction
3	^{n}BuLi	50	RT	No reaction
4	^{n}BuLi	50	80	No reaction
5	MeLi	0.5	RT	No reaction
6	MeLi	50	RT	Oligomerization (pentene)
7	MeLi	50	80	Oligomerization (pentene)

Reaction conditions: Catalyst 0.5 M in toluene, iron/activator 1:4.

The fact that pentene was found in the MeLi activated high pressure polymerization reactions supports a potential ethylene polymerization capacity of this catalyst. In the present case the termination step may become favoured over chain growth at a length of 4-5 carbons in the growing polymer chain. The butyl rest may be already to long to serve as starting group for chain growth and therefore no activity was observed in case of ^{n}BuLi activation. As steric hindrance of the ligands plays an important role in these polymerizations,[26] increasing the steric bulk of **126** could favour the chain growth and polymerization would be obtained.

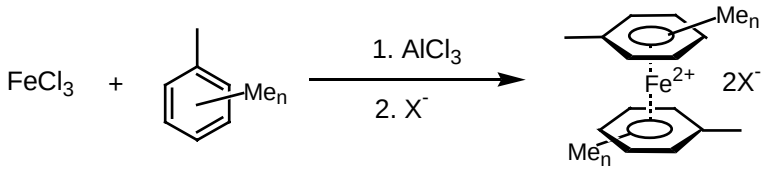
11. Bis(arene)iron(II) complexes as catalyst precursors?

As the isolation of an assumed $FeCl_2$–arene precatalyst complex **109**, **110**, **138** or **139** was not achieved, a different approach to such an isolated iron(II) catalyst precursor was envisaged. Since bis(η^6-arene)iron(II) complexes display structural similarity with the coordinated arene ligand like the assumed precatalysts, they were investigated as catalyst precursors for the hydrogenation.

11.1 Complex syntheses

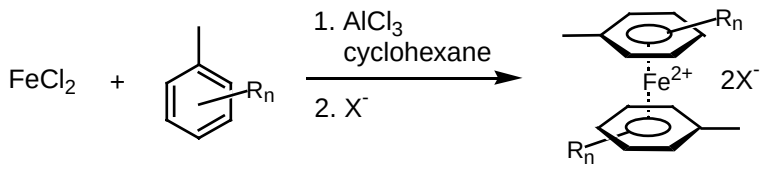
These bisareneiron(II) complexes were prepared according to two different procedures.

Method A: The first procedure consisting in treatment of $FeBr_2$ with $AlCl_3$ in the refluxing aromatic hydrocarbon was originally introduced by FISCHER,[107] but a modified procedure reported by HELLING[108] was applied in this case to synthesize these complexes. Thus, $FeCl_3$ was refluxed in an excess of the corresponding arene. After solvolysis the orange-red bisareneiron(II) cation was extracted in water and finally precipitated adding an appropriate counterion to the solution.



Scheme 73: Synthesis of bis(arene)iron(II)$^{2+}$ complexes (method A)

Method B: For the second approach another improved procedure from HELLING[109] was used for the preparation of the bis(η^6-arene)Fe^{2+} complexes. In this case $FeCl_2$ was treated with $AlCl_3$ in the presence of the aromatic ligand in refluxing cyclohexane solution. Isolation of the desired complexes was achieved by the same work-up procedure as for method A.



Scheme 74: Synthesis of bis(arene)iron(II)$^{2+}$ complexes (method B)

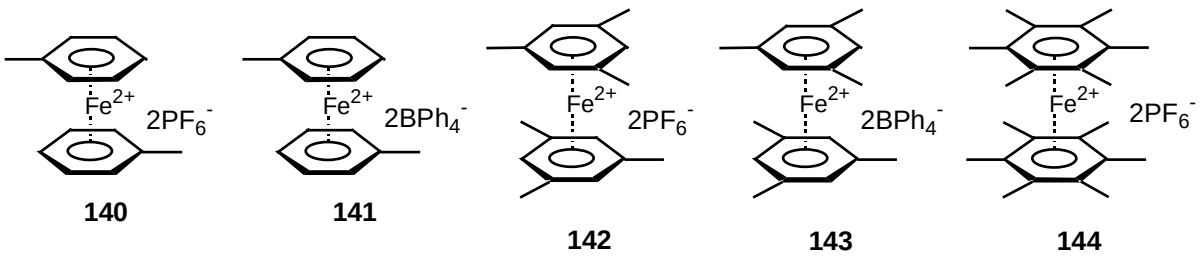
The complexations were carried out each time with toluene and mesitylene as arene ligands, cymene, hexamethylbenzene (**HMB**) and hexaphenylbenzene (**HPB**) were reacted only according to method B.

Table 22: Synthesis of bis(arene)iron(II)$^{2+}$ complexes

Entry	Arene	Method	Counterion	Yield [%]
1	Toluene	A	NH_4PF_6	64
2	Toluene	B	NH_4PF_6	47
3	Toluene	A	$NaBPh_4$	44
4	Toluene	B	$NaBPh_4$	38
5	Toluene	A	$NaBF_4$	-
6	Toluene	A	$AgSO_3CF_3$	-
7	Mesitylene	A	NH_4PF_6	82
8	Mesitylene	B	NH_4PF_6	56
9	Mesitylene	A	$NaBPh_4$	67
10	Mesitylene	B	$NaBPh_4$	52
11	**HMB**	B	NH_4PF_6	61
12	**HMB**	B	$NaBPh_4$	43
13	Cymene	B	NH_4PF_6	-
14	**HPB**	B	$NaBPh_4$	-

All the preparations with a PF_6^- counterion gave the more stable complexes as compared to BPh_4^- complexes which decomposed slowly on air. When BF_4^- was added as counterion the complexe did not precipitate even when the solvent was reduced by distillation. The addition of triflate $SO_3CF_3^-$ caused decomposition of the iron(II) cation. Regarding the yields, method A seemed to be superior to method B. But when the reaction was carried out at elevated temperature as in case of method

A, isomerizations and side reactions in form of methylation/demethylation reactions occurred.[110] This behaviour was most pronounced in the complexations to mesitylene complexes. Evidence for the formation of $(C_6H_3(CH_3)_3)(C_6H_2(CH_3)_4)Fe^{2+}$, $(C_6H_3(CH_3)_3)(C_6H(CH_3)_5)Fe^{2+}$ and $(C_6H_2(CH_3)_4)(C_6H(CH_3)_5)Fe^{2+}$ was found in the ^{1}H-NMR and mass spectra. Conducting the complexation at lower temperature suppressed the isomerization side reaction and led exclusively to the bis(mesitylene)iron^{2+} cation. The complexation of the arenes cymene and **HPB** failed probably due to steric hindrance. These results correspond to the observation that the complexation of bulkier arenes such as nonylbenzene and 1,3,5-triisopropylbenzene did not take place.[111] In fact, only complexes with methylsubstituted arene ligands were described in literature.

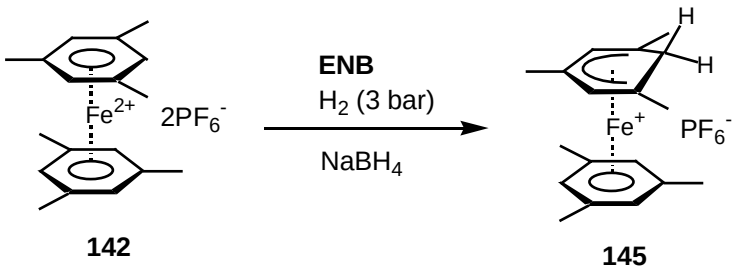


140 **141** **142** **143** **144**

Chart 13: Synthesized bis(arene)iron(II)$^{2+}$ complexes

11.2 Ligand exchange reactions/Hydrogenation experiments

The bis(arene)iron(II) complexes could only serve as catalyst precursors if they can be activated. It is known that the treatment of these complexes with reducing agents such as metal hydrides, alkyllithium and trialkylaluminium reagents affords not neutral bis(arene)iron(0) complexes, but reductive nucleophilic addition at one of the arene rings leading to (η^6-arene)(η^5-cyclohexadienyl)iron(I) complexes occurs instead.[112] This reactivity is maintained when the reaction is carried out under hydrogenation conditions, i.e. $NaBH_4$ was added to **142** in presence of **ENB** as substrate under hydrogen atmosphere (3 bar). The hydride added to the mesitylene ring at an unsubstituted position but no hydrogenation occurred.

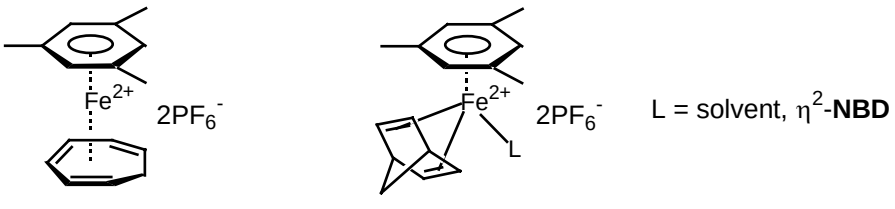


142 **145**

Scheme 75: Reaction of **142** with $NaBH_4$ under hydrogenation conditions

Thus, an approach was envisaged where an arene ring is exchanged with an appropriate ligand prior to the activation step to suppress the nucleophilic addition side reaction. These ligand substitution attempts were carried out with the complexes **142** and **144** under irradiation.

A first try to replace a mesitylene ring in **142** by **HMB** in benzene or acetonitrile was not successful, only the starting bis(mesitylene)iron complex was reisolated. However, the reaction of **142** with cycloheptatriene (**CHT**) in CH_3CN led to a yellow complex product, but all attempts to isolate and characterize this product failed, it decomposed rapidly during work-up. Out of the residue, **CHT** was isolated unchanged. A similar behaviour was observed when **NBD** was used as ligand. A yellow product appeared, but degradation occurred rapidly and **NBD** was reisolated from the residue. As acetonitrile is known to be a ligand for iron, a control experiment was performed in absence of an additional olefin ligand where CH_3CN is used as solvent as well as substituting ligand. In this case, no reaction occurred at all, complex **142** was reisolated indicating that in the former reactions, the formation of the yellow product is mainly caused by the presence of the diene or triene ligand.



146 **147**

Chart 14: Possible structures of formed complexes

So the exchange reactions with **CHT** and **NBD** were repeated under hydrogen atmosphere (0.5 bar) to provide either an additional ligand for stabilizing this product or a source of hydrogen for hydrogenating the olefin ligand. The yellow product appeared again, but no improvement of the stability of this compound was attained by these attempts because isolation always failed due to decomposition. Furthermore, the olefin ligands were not hydrogenated under these conditions.

The reactions with **CHT** and **NBD** were carried out with complex **144** assuming that the usually higher stability of **HMB** complexes compared to arene complexes with less methyl substituents in the arene rings should help to obtain an isolable complex. But in this case, the reactivity of **144** was found to be different from **142**. The color of these reaction mixtures turned to violet each, followed by decoloration of the solution and the appearance of a white precipitate. A violet color usually indicates $19e^-$ $Fe(I)^+$ complexes,[113] but the reaction could not be stopped at this stage. The precipitate was identified as **HMB**, and the olefins **CHT** and **NBD** were found unchanged in the reaction residue. The same behaviour was observed for the reaction with the monoolefin ethylene, decomposition led only to free **HMB** in this approach. When the diimine **34** was engaged for the ligand exchange reaction with **144**, no reaction occurred at all and the starting materials were reisolated.

These results led us conclude that the bis(arene)iron(II) complexes were not suitable as catalyst precursors for our purpose.

12. Conclusion and outlook

Various investigations were performed during this work concerning iron catalysts. The initial objective of further developing the hydrogenation catalyst introduced by SIEBER had to be changed after the first results to the development of a newly found "ligand-free" iron catalysts. As such a catalyst was not known before, this work became extremly exploratory in nature with still many open questions. Nevertheless, interesting results were obtained concerning this new catalyst system.

Different aspects of the ligand-free slurry catalyst such as iron source, substrate range, activation reagents and efficiency were investigated. A series of iron compounds in different oxidation states (Fe(0), Fe(II), Fe(III)) are able to serve as catalyst precursors. The activity of the catalysts is depending on the activation agent (alkyllithium, hydride donor).

A catalyst prepared from an iron(II)chloride suspension activated with DIBAH displayed the highest activity. A large variety of alkenes were hydrogenated quantitatively with this catalyst in short time under mild conditions (3 bar hydrogen pressure, RT). Mono-, di- and trisubstituted, cyclic and acyclic, isolated and conjugated C-C double bonds reacted without problems, but also vinyl and allyl ethers and amines could be hydrogenated. With the exception of ethers and amines, the need for a strong reducing or alkylating agent prevents the hydrogenation of functionalized olefins. However, the catalyst is able to hydrogenate alkynes to the completely reduced products.

The efficiency of the system was assessed by the TON and TOF the hydrogenation for cyclooctene. The TON as well as the TOF scaled with the amounts of activation reagent up to a $FeCl_2$/DIBAH ratio of 1:8, where the most active catalyst was obtained with a TON = 1900 and a TOF = 125 h^{-1} indicating a quite efficient catalyst. The catalyst is simple and easy to prepare, the determined efficiency renders it interesting for industrial applications. Hence, preliminary experiments were performed at Ciba Specialty Chemicals in Basel to apply the catalyst for their purpose, but the choosen, functionalized substrates did not react in these cases.

The $FeCl_2$/DIBAH catalyst is not only active for the hydrogenation of carbon-carbon double bonds, in absence of molecular hydrogen catalytic activity in alkyne polymerization and alkyne cyclotrimerization reactions were observed. Depending on the reaction conditions and the alkyne substrate, either polymerization or cyclotrimerization occurs. These reactions were investigated only in a preliminary manner, however, and optimization of the reaction conditions could lead to a powerful cyclotrimerization and/or polymerization catalyst.

Another interesting reactivity of the catalyst was found with the ability to polymerize acetylene. The polyacetylenic structure of the product was proven with Raman spectroscopy and the morphology of the obtained material was revealed by SEM imaging. Furthermore, indications for graphitic structures were found. Especially these findings led to the idea of synthesizing nanotubes in solution under mild conditions from acetylene. The ability of the catalyst to promote such a reaction is in principle demonstrated by the presence of the graphitic material in the polyacetylenic product. To circumvent the problem of forcing a graphite sheet to adopt a tube-like shape, the nanotubes could be grown from a corresponding template such as a $[0_n]$-paracyclophane derivative having already the necessary cyclic structure. But the synthesis of such a $[0_n]$-paracyclophane is yet a difficult task which was not achieved up to now. Appropriate work is in progress in the group of Prof. Jenny.

Attempts to characterize the catalytic active species led to the development of a homogeneous precatalyst. The hydrogenation efficiency of this homogeneous catalyst is even higher than the efficiency of the previously investigated slurry catalyst, a TOF > 340 h^{-1} was assessed in this case. An (arene)(**L**)$FeCl_2$ structure (**L** = N_2, THF) is proposed for the precatalyst based on the results obtained with UV-Vis spectroscopy.

Furthermore, a series of allylbenzylethers were synthesized derived from the assumed structure of the homogeneous precatalyst and tested as ligands for $FeCl_2$ in the hydrogenation of olefins. Indeed it was found that these precatalysts catalyze the hydrogenation reaction upon activation with an alkyllithium reagent. Moreover, this catalyst system promotes the oligomerization of ethylene under high ethylene

pressure conditions. As in the previous cases, the isolation of a catalyst precursor complex failed with these ligands due to stability problems.
Attempts to use bisareneiron(0) complexes as catalyst precursors were not successful, these compounds could not be activated and therefore they are not suitable for this purpose and have to be ruled out as possible structure of the precatalyst.

In spite of the results obtained in this work, the hydrogenation catalyst system described by SIEBER should not be discarded. Optimization of this system is still an interesting task, but attention has to be paid to several points. First, it is really necessary to ensure that the ligands remain coordinated to the metal during the activation and to avoid the presence of free Fe(II) species in order to have the possibility to perform stereoselective hydrogenations. Isolated precatalysts with known structures should be engaged therefore, and the type of activation must be choosen carefully. The same holds when new ligands are tested for this purpose. Also in this case, the isolation of a precatalyst becomes necessary in order to rationally optimize the hydrogenation performance of such new catalysts.

Although the initial objective of introducing stereoselective iron catalyzed reactions could not be achieved, this work is important as basis for further investigations on iron hydrogenation and polymerization catalysts. Moreover, the results obtained within this work led the basis of several other projects.

III

Experimental part

General

Chemical products and reagents were provided by Fluka, Merck, Acros, Aldrich or Riedl-de-Haën and used, unless otherwise stated, without further purification. Solvents were treated after common methods prior to use: ether, pentane, THF, benzene and toluene were dried and destilled over sodium; ethyl acetate, dichloromethane and chloroform were dried and destilled over phosphorus pentoxide.
Anhydrous $FeCl_2$ (> 98 %) was purchased from either Riedl-de-Haën or Aldrich. DIBAH 1 M in toluene and DIBAH 1 M in cyclohexane were provided from Aldrich, BuLi 1.6 M in pentane and MeLi 1.6 M in ether were obtained from Acros.

High pressure ethylene polymerization experiments were carried out with the assistance of Dr. Christian Müller in the group of Prof. Piet van Leeuwen at the University of Amsterdam.

TLC analyses were performed with *Merck Silikagel 60 F_{254}*-coated aluminium foils. The products were revealed with UV-light (254 nm) or by spraying with either a $KMnO_4$-solution or a HNO_3/KSCN combination. Column chromatographic separations were done using *Merck silica gel 60, 70-230 mesh ASTM* or *Merck silica gel 60, 230-400 mesh ASTM*.

NMR spectra were recorded either on a *Varian Gemini 200* (^{1}H: 200 MHz / ^{13}C: 50 MHz), on a *Bruker AM 360* (^{1}H: 360 MHz / ^{13}C: 90 MHz) or on a *Bruker Avance DRX-500* (^{1}H: 500 MHz / ^{13}C: 125 MHz). Chemical shifts are given in ppm relative to TMS for CDCl3 or the residual proton signal of the deuterated solvent used. Coupling constants J are given in Hz. The signals were attributed using APT, COSY and HETCOR techniques.
Solid-state NMR spectra were recorded on a *Bruker Avance 300* (^{13}C: 75.4 MHz) equipped with a *MAS* probe head (University of Lausanne).

UV/Vis-spectra were acquired on a *Perkin-Elmer Lambda 40* diode array spectrophotometer.

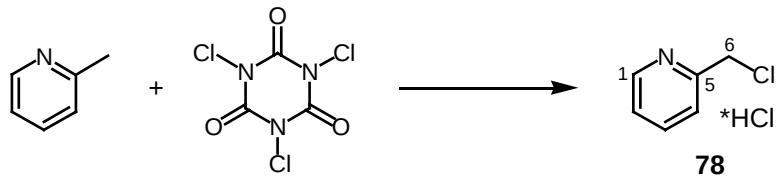
Raman spectra were measured on a *Dilor Labram1 300* spectrometer with the assistance of Dr. Jean-Nicolas Aebischer (UAS Fribourg).

Mass spectra were recorded either on a *Vacuum Generators Micromass VG 70/70E* (FAB ionisation) or on a *HP 5988A Quadrupol* (EI ionisation, 70 eV) mass spectrometer. ESI and high resolution mass spectra were measured on a *Bruker FTMS 4.7T BioAPEX* mass spectrometer.

GC analyses were carried out on a *FISONS Instruments HRGC MEGA 2 Series* equipped with a *OPTIMA-1701* column (0.25 μm, 25 m x 0.32 mm; Marcherey-Nagel). GC/MS analyses were carried out on a *ThermoQuest Finnigan VOYAGER GC/MS Trace GC 2000 Series* equipped with a *Optima-5-MS* column (0.25 μm, 30 m x 0.25 mm; Marcherey-Nagel).

13. Ligand syntheses

2-Picolyl chloride hydrochloride (78)

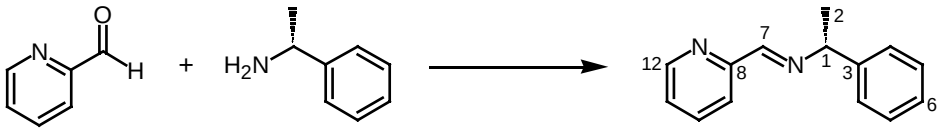


78

Picolyl chloride **78** was synthesized according to the literature procedure.[114]
A solution of 2-picoline (56.6 mL, 0.57 mol) and DMF (4 mL, 0.055 mol) in $CHCl_3$ (220 mL) was heated to reflux, then triisocyanuric acid (TCC) (80 g, 0.345 mol) was added in portions so that the reaction mixture remained refluxing without heating. After further heating for 2 h at reflux the solution was allowed to cool to RT. The mixture was filtered, washed with NaOH 5 % (26 mL) and dried over $MgSO_4$. Then gaseous HCl (40 mL H_2SO_4 + 43 g NH_4Cl) was introduced to the solution during 2 h. The $CHCl_3$ was evaporated and under vigorously stirring acetone (65 mL) was added. The solution was kept in an icebath for 2 d. The precipitate was filtered and dried yielding **78** (41.5 g, 44 %) as white-brown crystals.

^{1}H-NMR (360 MHz, D_2O): 4.85 (s, 1H, HCl), 5.07 (s, 2H, $H_2C(6)$), 8.05 (t, 1H, HC(2)), 8.19 (d, 1H, HC(4)), 8.64 (t, 1H, HC(3)), 8.83 (d, 1H, HC(1)).
MS (FAB): 128 (M^++H, 100), 92 (66).

1-Phenyl-*N*-(pyridin-2-ylmethylidene)ethan-1-amine (82)



82

Imine **82** was synthesized according to a modified literature procedure.[115]

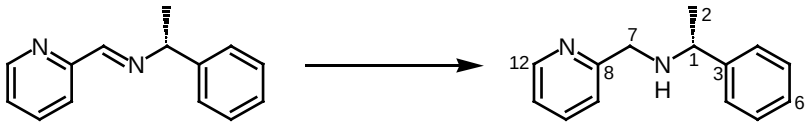
A round-bottom flask containing molecular sieves 4Å (~5 g) was charged under nitrogen with a solution of freshly destilled 2-pyridinecarboxaldehyde (2.9 mL, 30 mmol) in Et_2O (30 mL). 1-Phenylethylamine (3.8 mL, 30 mmol) was added dropwise at 0 °C and the mixture was stirred at RT for 2 h. The mixture was filtered and the solvent was evaporated yielding **82** (5.1 g, 81 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.61 (d, 3H, J = 6.71, H_3C(2)), 4.63 (q, 1H, J = 6.71, HC(1)), 7.23 – 7.36 (m, 4H, HC(5), HC(6), HC(11)), 7.43 (d, 2H, J = 8.22, HC(4)), 7.74 (dxt, 1H, J = 7.68, 1.41, HC(9)), 8.09 (d, 1H, J = 7.68, HC(10)), 8.46 (s, 1H, HC(7)), 8.63 (d, 1H, J = 4.72, HC(12)).

^{13}C-NMR (50.3 MHz, $CDCl_3$): 25.1 (CH_3, C(2)), 70.1 (CH, C(1)), 121.9 (CH, C(11)), 125.2 (CH, C(9)), 127.2 (CH, C(4)), 127.5 (CH, C(6)), 129.0 (CH, C(5)), 137.0 (CH, C(10)), 145.1 (C, C(3)), 149.8 (CH, C(12)), 155.3 (C, C(8)), 160.9 (CH, C(7)).

MS (EI): 210 (M^+, 24), 195 (100), 168 (37), 133 (36), 105 (100), 92 (82), 77 (97).

1-Phenyl-*N*-(pyridin-2-ylmethyl)ethan-1-amine (83)

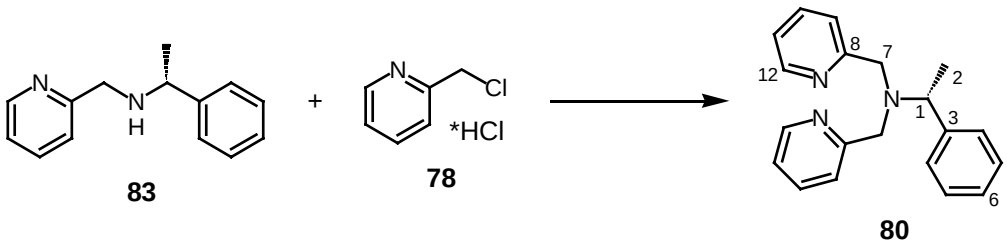


82 **83**

Amine **83** was synthesized according to a modified literature procedure.[116]
Degased MeOH (20 mL) was cooled to 0 °C under nitrogen atmosphere and imine **82** (2.1 g, 10 mmol) was added. Under a slight stream of nitrogen $NaBH_4$ (409 mg, 10.8 mmol) was added in portions and the mixture was stirred for ½ h at 0 °C. The solution was allowed to warm to RT and was stirred for further 3 h. The reaction was quenched with H_2O and extracted with 3 times Et_2O. The organic phase was washed with saturated NaCl solution, dried over $MgSO_4$ and the solvent was evaporated affording **83** (1.68 g, 79 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.41 (d, 3H, J = 6.58, $H_3C(2)$), 3.75 (s, 2H, $H_2C(7)$), 3.82 (q, 1H, J = 6.58, HC(1)), 7.14 (dxt, 1H, J = 4.88, 1.83 HC(11)), 7.19 (d, 1H, J = 7.94, HC(9)), 7.22 – 7.26 (m, 2H, HC(4)), 7.31 – 7.38 (m, 3H, HC(5), HC(6)), 7.60 (dxt, 1H, J = 7.94, 1.83, HC(10)), 8.55 (d, 1H, J = 4.88, HC(12)).
^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.4 (CH_3, C(2)), 53.0 (CH_2, C(7)), 58.0 (CH, C(1)), 121.8 (CH, C(11)), 122.3 (CH, C(9)), 126.7 (CH, C(4)), 126.9 (CH, C(6)), 128.4 (CH, C(5)), 136.2 (CH, C(10)), 145.3 (C, C(3)), 149.2 (CH, C(12)), 159.7 (C, C(8)).

1-Phenyl-*N*,*N*-bis(pyridin-2-ylmethyl)ethan-1-amine (80)

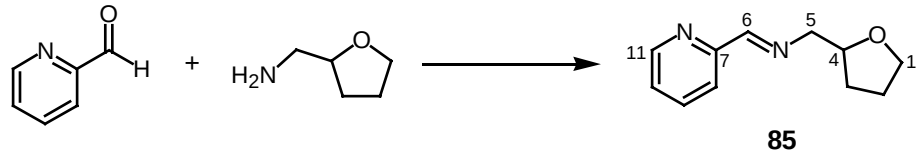


83 **78** **80**

Amine **80** was synthesized according to a modified literature procedure.[117]
To MeOH (10 mL) at 0 °C was added picolyl chloride **78** (400 mg, 2.4 mmol). A menthanolic KOH solution (10 %) (5 mL) was added and the mixture was stirred for 1h. After filtration the solution was allowed to warm to RT. Amine **83** (500 mg, 2.35 mmol) was added and the mixture was heated to reflux for 2 d. During this time a methanolic KOH solution (10 %) (5 mL) was added in small portions (pH ≤ 9). Then the solvent was evaporated and the residue was dissolved in CH_2Cl_2. The precipitate was filtered and the solvent was evaporated. The side products were eliminated by destillation (≤ 160 °C, 10^{-4} bar) yielding **80** (0.455 mg, 63 %) as yellow, viscous oil.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.49 (d, 3H, J = 6.71, $H_3C(2)$), 3.75 (d, 2H, J = 14.65, $H_aC(7)$), 3.91 (d, 2H, J = 14.65, $H_bC(7)$), 3.98 (q, 1H, J = 6.71, HC(1)), 7.12 (dxt, 2H, J = 4.88, 1.22, HC(11)), 7.23 (m, 1H, HC(6)), 7.33 (t, 2H, J = 7.33, HC(5)), 7.45 (d, 2H, J = 7.33, HC(4)), 7.56 (d, 2H, J = 7.63, HC(9)), 7.64 (dxt, 2H, J = 7.63, 1.83, HC(10)), 8.48 (d, 2H, J = 4.88, HC(12)).
^{13}C-NMR (50.3 MHz, $CDCl_3$): 14.9 (CH_3, C(2)), 56.4 (CH_2, C(7)), 58.6 (CH, C(1)), 121.8 (CH, C(11)), 122.8 (CH, C(9)), 126.9 (CH, C(6)), 127.9 (CH, C(4)), 128.1 (CH, C(5)), 136.3 (CH, C(10)), 143.4 (C, C(3)), 148.7 (CH, C(12)), 160.4 (C, C(8)).

_N_-(Pyridin-2-ylmethylidene)-_N_-(tetrahydrofuran-2-ylmethyl)amine (85)



85

Imine **85** was synthesized according to a modified literature procedure.[115]

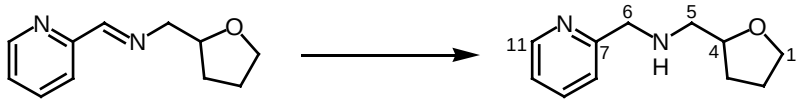
A round-bottom flask containing molecular sieves 4Å (~5 g) was charged under nitrogen with a solution of freshly destilled 2-pyridinecarboxaldehyde (5.8 mL, 61 mmol) in Et_2O (50 mL). Tetrahydrofurfurylamine (6.3 mL, 61 mmol) was added dropwise at 0 °C and the mixture was stirred first for 2 h at 0 °C, then for 1 h at RT. The mixture was filtered and the solvent was evaporated affording **85** (11.4 g, 99 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.73 (m, 1H, HC(4)), 1.87 – 2.10 (m, 4H, $H_2C(2)$, $H_2C(3)$), 3.78 (m, 2H, $H_2C(5)$), 3.89 (txd, 1H, J = 8.24, 6.71, $H_aC(1)$), 4.26 (qxd, 1H, J = 6.71, 5.18, $H_bC(1)$), 7.31 (dxdxd, 1H, J = 6.11, 4.88, 1.22, HC(10)), 7.73 (txd, 1H, J = 7.33, 1.53, HC(9)), 8.02 (txd, 1H, J = 7.93, 1.22, HC(8)), 8.41 (s, 1H, HC(6)), 8.64 (dxdxd, 1H, J = 4.88, 1.53, 0.92, HC(11)).

^{13}C-NMR (50.3 MHz, $CDCl_3$): 26.2 (CH_2, C(2)),, 29.9 (CH_2, C(3)), 66.1 (CH_2, C(5)), 68.7 (CH_2, C(1)), 78.7 (CH, C(4)), 121.7 (CH, C(10)), 125.1 (CH, C(8)), 136.8 (CH, C(9)), 149.8 (CH, C(11)), 155.0 (C, C(7)), 163.8 (CH, C(6)).

MS (EI): 191 (M^++H, 100), 173 (9), 131 (11), 119 (95), 92 (38), 78 (11), 71 (62), 65 (37).

_N_-(Pyridin-2-ylmethyl)-_N_-(tetrahydrofuran-2-ylmethyl)amine (86)

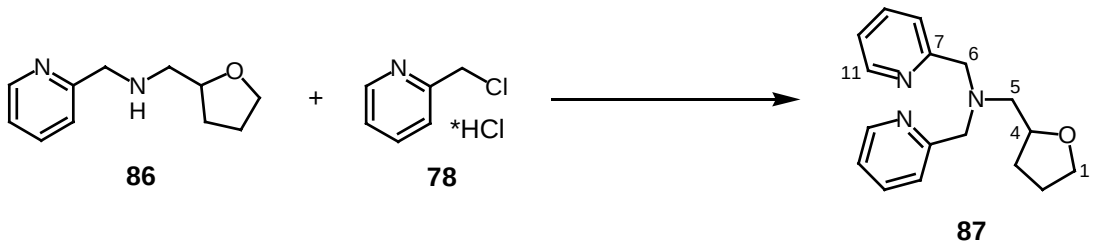


85 **86**

Amine **86** was synthesized according to a modified literature procedure.[116]
Degased MeOH (50 mL) was cooled under nitrogen atmosphere to 0 °C and imine **85** (5 g, 26.3 mmol) was added. Under a slight stream of nitrogen $NaBH_4$ (1.3 g, 34.2 mmol) was added and the mixture was stirred first for 1 h at 0 °C, then for 2 h at RT. The reaction was quenched with ice water and extracted with 3 times CH_2Cl_2. The combined organic phases were washed with saturated NaCl solution, dried over $MgSO_4$ and the solvent was evaporated yielding **86** (4.9 g, 97 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.56 (m, 1H, $H_aC(3)$), 1.82 – 2.02 (m, 3H, $H_2C(2)$, $H_bC(3)$), 2.15 (b, 1H, HN), 2.69 (dxd, 1H, J = 11.29, 7.02, $H_aC(5)$), 2.73 (dxd, 1H, J = 11.29, 3.97, $H_bC(5)$), 3.74 (txd, 1H, J = 8.54, 6.71, $H_aC(1)$), 3.84 (txd, 1H, J = 8.24, 6.71, $H_bC(1)$), 3.94 (s, 2H, $H_2C(6)$), 4.04 (qxd, 1H, J = 7.19, 4.42, HC(4)), 7.14 (dxdxd, 2H, J = 7.02, 4.89, 0.61, HC(10)), 7.32 (d, 2H, J = 7.93, HC(8)), 7.63 (txd, 2H, J = 7.63, 1.83, HC(9)), 8.53 (dxd, 2H, J = 4.88, 1.83, 0.92, HC(11)).
^{13}C-NMR (50.3 MHz, $CDCl_3$): 25.6 (CH_2, C(2)), 29.2 (CH_2, C(3)), 53.8 (CH_2, C(5)), 55.2 (CH_2, C(6)), 67.8 (CH_2, C(1)), 78.2 (CH, C(4)), 121.7 (CH, C(10)), 122.0 (CH, C(8)), 136.2 (CH, C(9)), 149.0 (CH, C(11)), 159.8 (C, C(7)).
MS (EI): 193 (M^++H, 89), 121 (100), 93 (96), 71 (12), 65 (58).

_N,N_-Bis(pyridin-2-ylmethyl)-_N_-(tetrahydrofuran-2-ylmethyl)amine (87)

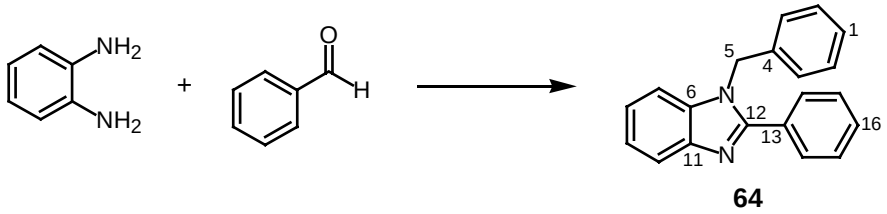


86 **78** **87**

Amine **87** was synthesized according to a modified literature procedure.[117]
To MeOH (50 mL) cooled to 0 °C was added picolyl chloride **78** (6.3 g, 38.2 mmol). A methanolic KOH solution (10 %) (20 mL) was added and the mixture was stirred for 1h. After filtration of the solution amine **86** (4.9 g, 25.9 mmol) was added and the mixture was stirred first at 0 °C for 4 h, then heated to 50 °C for 2 d. During this time a methanolic KOH solution (10 %) (20 mL) was added in small portions (pH ≤ 9). Then the solvent was evaporated and the residue was dissolved in CH_2Cl_2. The precipitate was filtered and the solvent was evaporated. The product was purified by destillation (150 °C, 10^{-5} bar) yielding **87** (4.75 g, 65 %) as yellow, highly viscous oil.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.80 (m, 2H, $H_2C(2)$), 1.93 (m, 2H, $H_2C(3)$), 2.65 (dxd, 1H, J = 13.42, 4.58, $H_aC(5)$), 2.73 (dxd, 1H, J = 13.42, 7.02, $H_bC(5)$), 3.75 (txdxd, 2H, J = 14.95, 8.23, 6.71, HC(1)), 3.89 (d, 2H, J = 14.65, $H_aC(6)$), 3.98 (d, 2H, J = 14.65, $H_bC(6)$), 4.12 (qxd, 1H, J = 7.02, 4.58, HC(4)), 7.14 (dxd, 2H, J = 4.88, 1.52, HC(10)), 7.58 (d, 2H, J = 7.94, HC(8)), 7.65 (txd, 2H, J = 7.63, 1.83, HC(9)), 8.51 (dxd, 2H, J = 4.88, 0.92, HC(11)).
^{13}C-NMR (50.3 MHz, $CDCl_3$): 25.3 (CH_2, C(2)),, 29.9 (CH_2, C(3)), 58.6 (CH_2, C(5)), 60.8 (CH_2, C(6)), 67.8 (CH_2, C(1)), 77.6 (CH, C(4)), 121.9 (CH, C(10)), 123.1 (CH, C(8)), 136.3 (CH, C(9)), 148.8 (CH, C(11)), 159.5 (C, C(7)).

1-Benzyl-2-phenyl-1*H*-benzimidazole (64)



64

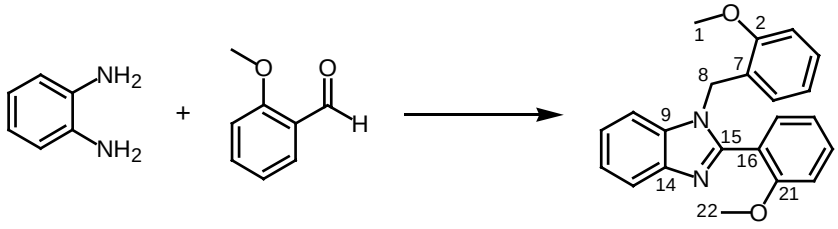
o-Phenylenediamine (5 g, 46 mmol) was suspended in EtOH (10 mL) and the mixture was cooled to –20 °C. Freshly destilled benzaldehyde (9.35 mL, 92 mmol) in EtOH (5 mL) was added and the solution was stirred for 2.5 h. Then the solvent was evaporated and the residue was mixed with Et_2O. The precipitate formed was filtered, the solvent was evaporated and the obtained product was dried under reduced pressure yielding **64** (7.88 g, 60 %) as white-yellow powder.

^{1}H-NMR (360 MHz, $CDCl_3$): 5.41 (s, 2H, $H_2C(5)$), 7.00 (d, 1H, J = 5.90, HC(7)), 7.15 – 7.19 (m, 2H, HC(1), HC(16)), 7.20 – 7.26 (m, 3H, HC(2), HC(9)), 7.37 – 7.43 (m, 3H, HC(8), HC(15)), 7.63 (d, 2H, J = 5.51, HC(3)), 7.74 (d, 1H, J = 5.15, HC(10)), 8.15 (d, 2H, J = 4.93, HC(14)).

^{13}C-NMR (90.6 MHz, $CDCl_3$): 48.4 (CH_2, C(5)), 110.5 (CH, C(10)), 120.0 (CH, C(1)), 122.7 (CH, C(8)), 123.0 (CH, C(6)), 126.0 (CH, C(16)), 126.7 (CH, C(7)), 127.8 (C, C(4)), 128.7 (CH, C(2)),129.0 (CH, C(15)), 129.3 (CH, C(9)), 129.9 (CH, C(3)), 130.1 (CH, C(14)), 136.0 (C, C(13)), 143.1 (C, C(11)), 154.2 (C, C(12)).

MS (EI): 284 (M^+, 100), 207 (13), 194 (48), 152 (13), 105 (19), 91 (98), 77 (20), 65 (28).

1-(2-Methoxybenzyl)-2-(2-methoxyphenyl)-1*H*-benzimidazole (62)

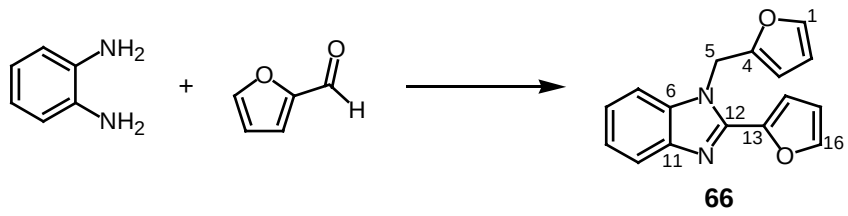


62

o-Phenylenediamine (2 g, 18.5 mmol) was suspended in EtOH (10 mL) and the mixture was cooled to –20 °C. *o*-Methoxybenzaldehyde (7.55 g, 55.5 mmol) in EtOH (5 mL) was added and the solution was stirred during 4 h while warming to RT. After heating shortly at reflux, the solvent was evaporated and the residue was mixed with Et_2O. The precipitate formed was filtered, washed with Et_2O and dried under reduced pressure yielding **62** (3.18 g, 50 %) as white powder.

^{1}H-NMR (500 MHz, $CDCl_3$): 3.58 (s, 3H, $H_3C(1)$), 3.78 (s, 3H, $H_3C(22)$), 5.23 (s, 2H, $H_2C(8)$), 6.68 (txdxd, 1H, J = 7.48, 1.62, 0.76, HC(10)), 6.76 (txd, 1H, J = 7.48, 1.07, HC(11)), 6.83 (dxd, 1H, J = 8.24, 0.92, HC(13)), 6.95 (dxd, 1H, J = 8.40, 0.76, HC(3)), 7.04 (txd, 1H, J = 7.48, 1.07, HC(5)), 7.17 (dxdxd, 1H, J = 8.16, 7.48, 1.76, HC(12)), 7.18 (dxdxd, 1H, J = 8.11, 6.65, 1.17, HC(19)), 7.21 (dxdxd, 1H, J = 8.11, 1.68, 0.76, HC(20)), 7.26 (dxdxd, 1H, J = 8.00, 6.61, 1.55, HC(18)), 7.44 (dxdxd, 1H, J = 8.40, 7.48, 1.83, HC(4)), 7.53 (dxd, 1H, J = 7.47, 1.83, HC(6)), 7.84 (txd, 1H, J = 7.93, 0.93, HC(17)).
^{13}C-NMR (125.8 MHz, $CDCl_3$): 43.7 (CH_2, C(8)), 55.4 (CH_3, C(1)), 55.5 (CH_3, C(22)), 110.5 (CH, C(13)), 111.3 (CH, C(20)), 111.4 (CH, C(3)), 120.5 (CH, C(17)), 120.5 (C, C(7)), 121.0 (CH, C(11)), 121.4 (CH, C(5)), 122.6 (CH, C(18)), 123.0 (CH, C(19)), 125.2 (C, C(16)), 128.4 (CH, C(10)), 129.0 (CH, C(12)), 132.1 (CH, C(4)), 133.1 (CH, C(6)), 136.3 (C, C(9)), 144.2 (C, C(14)), 153.3 (C, C(2)), 157.4 (C, C(21)), 158.5 (C, C(15)).
MS (EI): 344 (M^+, 17), 223 (48), 121 (72), 91 (100), 77 (20), 65 (28).

2-(2-Furyl)-1-(2-furylmethyl)-1*H*-benzimidazole (66)



66

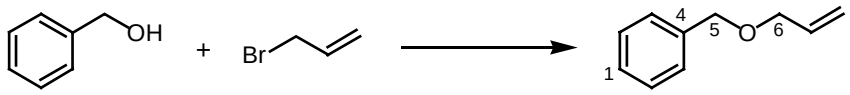
In a round-bottom flask fitted with a Dean-Stark trap and a condenser was placed *o*-phenylenediamine (2 g, 18.5 mmol) and *p*-toluenesulfonic acid monohydrate (0.35 g, 1.85 mmol) in benzene (60 mL). Freshly destilled 2-furaldehyde (3.8 mL, 46.2 mmol) was added and the mixture was heated to reflux for 2 d. After evaporation of the solvent, the residue was dissolved in few CH_2Cl_2 and submitted to a column chromatography (SiO_2, Et_2O/pentane 4:1). The product fraction was recrystallized from Et_2O affording **66** (2.25 g, 46 %) as brown-reddish crystals.

^{1}H-NMR (360 MHz, $CDCl_3$): 5.59 (s, 2H, $H_2C(5)$), 6.20 (d, 1H, J = 3.24, HC(3)), 6.24 (dxd, 1H, J = 3.24, 1.83, HC(2)), 6.56 (dxd, 1H, J = 3.48, 1.72, HC(15)), 7.18 (d, 1H, J = 3.48, HC(14)), 7.25 (m, 2H, HC(7), HC(9)), 7.29 (d, 1H, J = 1.83, HC(1)), 7.46 (m, 1H, HC(10)), 7.60 (t, 1H, J = 1.72, HC(16)), 7.76 (m, 1H, J = , HC(8)).

^{13}C-NMR (90.6 MHz, $CDCl_3$): 41.6 (CH_2, C(5)), 108.3 (CH, C(3)), 109.0 (CH, C(10)), 110.4 (CH, C(2)), 112.0 (CH, C(15)), 112.8 (CH, C(14)), 119.7 (CH, C(8)), 122.8 (CH, C(7)), 123.2 (CH, C(9)), 135.4 (CH, C(11)), 142.6 (CH, C(1)), 142.9 (C, C(12)), 143.9 (CH, C(16)), 145.3 (C, C(4)), 149.5(C, C(13)).

MS (EI): 264 (M^+, 79), 183 (9), 90 (9), 81 (100), 53 (9).

Allyl benzyl ether (115)

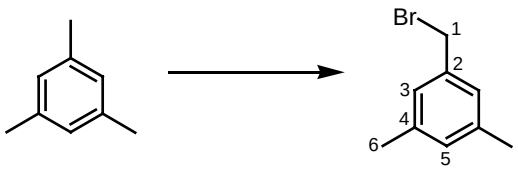


115

Ether **115** was synthesized according to a modified literature procedure.[105]
A two-necked flask equipped with a bubbler was charged with sodium hydride (55 % in mineral oil, washed 3 times with pentane) (6.3 g, 264 mmol) and freshly destilled DMF (150 mL). To this suspension benzyl alcohol (17.1 mL, 132 mmol) was added dropwise during ½ h. Stirring was continued until gas evolution ceased. After addition of potassium iodide (5 g, 30 mmol), a solution of allyl bromide (12.7 mL, 150 mmol) in DMF (10 mL) was added over a period of 40 min. The viscous suspension was stirred overnight. The resulting mixture was pourred into H_2O (700 mL), NaCl (60 g) was added and the aqueous layer was extracted 3 times with Et_2O. The combined organic phases were washed 2 times with H_2O, dried over $MgSO_4$ and the solvent was removed in vacuo yielding **115** (19.2 g, 98 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 4.03 (d, 2H, J = 5.91, $H_2C(6)$), 4.52 (s, 2H, $H_2C(5)$), 5.20 (dxd, 1H, J = 10.45, 1.82, $H_{trans}C(8)$), 5.30 (dxd, 1H, J = 17.26, 1.82, $H_{cis}C(8)$), 5.96 (txdxd, 1H, J = 17.26, 10.45, 5.91, HC(7)), 7.35 (m, 5H, HC(1), HC(2), HC(3)).
^{13}C-NMR (75.3 MHz, $CDCl_3$): 71.7 (CH_2, C(6)), 72.6 (CH_2, C(5)), 118.2 (CH_2, C(8)), 127.5 (CH, C(1)), 128.1 (CH, C(3)), 128.9 (CH, C(2)), 135.6 (CH, C(7)), 139.2 (C, C(4)).
MS (EI): 147 (M^+-H, 5), 107 (22), 105 (19), 91 (100), 79 (17).

3,5-Dimethylbenzyl bromide (122)



122

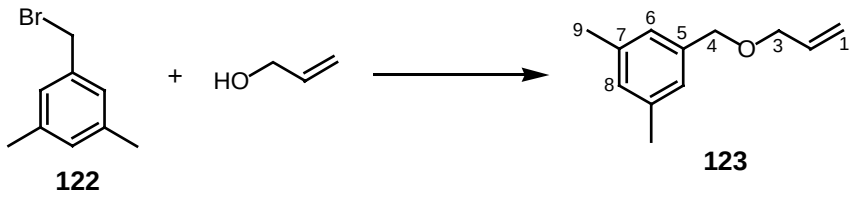
Bromide **122** was synthesized according to the literature procedure.[106]

A mixture of mesitylene (6.9 mL, 50 mmol), *N*-bromosuccinimide (8.9 g, 50 mmol) and benzoyl peroxide (0.5 g, 2 mmol) in CCl_4 (150 mL) was heated to reflux for 24 h. The suspension was filtered and the solvent was removed under reduced pressure. The residue was submitted to a destillation (130 °C, $2*10^{-1}$ bar) affording **122** (5.04 g, 51 %) as colorless liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 2.30 (s, 6H, $H_3C(6)$), 4.43 (s, 2H, $H_2C(1)$), 6.92 (s, 1H, HC(5)), 7.00 (s, 1H, HC(3)).

^{13}C-NMR (90.6 MHz, $CDCl_3$): 21.6 (CH_3, C(6)), 34.3 (CH_2, C(1)), 127.2 (CH, C(3)), 130.6 (CH, C(5)), 138.1 (C, C(2)), 138.9 (C, C(4)).

Allyl 3,5-dimethylphenetyl ether (123)

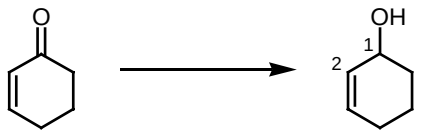


122 **123**

Ether **123** was synthesized according to a modified literature procedure.[105]
A two-necked flask equipped with a bubbler was charged with sodium hydride (55 % in mineral oil, washed 3 times with pentane) (0.53 g, 22.3 mmol) and THF (30 mL). To this suspension allyl alcohol (0.8 mL, 11.1 mmol) was added dropwise over a 10 min period. Stirring was continued until gas evolution ceased. After addition of potassium iodide (0.4 g, 2.5 mmol), bromide **122** (2.5 g, 12.7 mmol) was added over a 10 min period. The resulting suspension was stirred overnight and then mixed with H_2O (25 mL) and saturated NaCl solution (15 mL). The aqueous layer was extracted 3 times with Et_2O and the combined organic phases were washed first with saturated NaCl solution, then with H_2O. After drying over $MgSO_4$, the solvent was removed in vacuo. Destillation (85 °C, $2*10^{-1}$ bar) of the residue afforded yellow, liquid **123** (1.05 g, 47 %).

^{1}H-NMR (360 MHz, $CDCl_3$): 2.31 (s, 6H, $H_3C(9)$), 4.02 (txd, 2H, J = 5.90, 1.36, $H_2C(3)$), 4.45 (s, 2H, $H_2C(4)$), 5.21 (dxd, 1H, J = 10.44, 1.36, $H_{trans}C(1)$), 5.31 (dxd, 1H, J = 17.26, 1.36, $H_{cis}C(1)$), 5.96 (txdxd, 1H, J = 17.26, 10.44, 5.90, HC(2)), 6.93 (s, 1H, HC(8)), 6.97 (s, 2H, HC(6)).
^{13}C-NMR (90.6 MHz, $CDCl_3$): 21.7 (CH_3, C(9)), 71.6 (CH_2, C(3)), 72.6 (CH_2, C(4)), 117.1 (CH_2, C(1)), 126.1 (CH, C(6)), 129.7 (CH, C(8)), 135.3 (CH, C(2)), 138.4 (C, C(7)), 138.5 (C, C(5)).
MS (EI): 175 (M^+-H, 19), 133 (32), 119 (100), 105 (31), 92 (16).

2-Cyclohexen-1-ol (117)

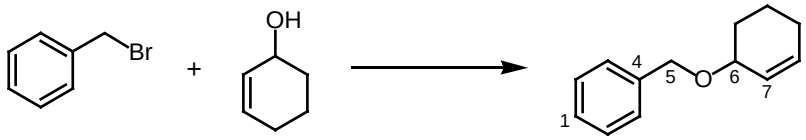


117

To a suspension of $LiAlH_4$ (1.42 g, 37.5 mmol) in Et_2O (10 mL) under nitrogen atmosphere, a solution of 2-cyclohexen-1-one (9.65 mL, 100 mmol) in Et_2O (20 mL) was added dropwise under cooling during 30 min. Then the mixture was heated to reflux for 1 h. After cooling to 0 °C the mixture was hydrolysed carefully with H_2O (50 mL). The precipitate was dissolved with HCl 2 M (20 mL) and H_2SO_4 4 M (10 mL) and the layers were separated. The aqueous phase was extracted 3 times with Et_2O and the combined organic phases were washed twice with a saturated NaCl solution. After drying over $MgSO_4$, the solvent was removed in vacuo affording colorless, liquid **117** (8.96 g, 91 %).

^{1}H-NMR (360 MHz, $CDCl_3$): 1.50 – 2.10 (m, 6H, $H_2C(4)$, $H_2C(5)$, $H_2C(6)$), 4.19 (b, 1H, HC(1)), 5.74 (mxd, 1H, J = 9.99, HC(3)), 5.84 (mxd, 1H, J = 9.99, HC(2)).

Benzyl 2-cyclohexen-1-yl ether (118)

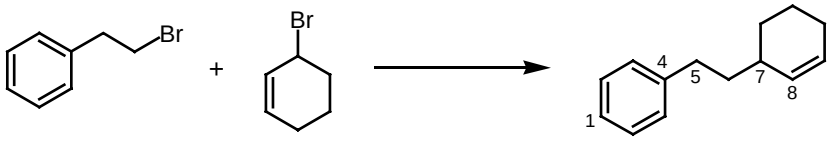


117 **118**

Ether **118** was synthesized according to a modified literature procedure.[105]
A two-necked flask equipped with a bubbler was charged with sodium hydride (55 % in mineral oil, washed 3 times with pentane) (3.4 g, 135 mmol) and THF (80 mL). To this suspension alcohol **117** (6.67 mL, 68 mmol) was added dropwise over a 15 min period. Stirring was continued until gas evolution ceased. After addition of potassium iodide (2.6 g, 15.5 mmol), benzyl bromide (9.3 mL, 77 mmol) was added over a 15 min period. The resulting suspension was stirred overnight and then mixed with H_2O (50 mL) and saturated NaCl solution (30 mL). The aqueous layer was extracted 3 times with Et_2O and the combined organic phases were washed first with saturated NaCl solution, then with H_2O. After drying over $MgSO_4$, the solvent was removed in vacuo. The side products were eliminated by destillation (≤ 100 °C, $2*10^{-1}$ bar) yielding slightly yellow, liquid **118** (9.36 g, 73 %).

^{1}H-NMR (360 MHz, $CDCl_3$): 1.52 – 2.06 (m, 6H, $H_2C(9)$, $H_2C(10)$, $H_2C(11)$), 3.95 (b, 1H, HC(6)), 4.54 (d, 1H, J = 12.04, $H_aC(5)$), 4.61 (d, 1H, J = 12.04, $H_bC(5)$), 5.79 – 5.88 (m, 2H, HC(7), HC(8)), 7.24 – 7.37 (m, 5H, HC(1), HC(2), HC(3)).
^{13}C-NMR (90.6 MHz, $CDCl_3$): 19.7 (CH_2, C(9)), 25.7 (CH_2, C(10)), 28.8 (CH_2, C(11)), 70.5 (CH_2, C(5)), 72.6 (CH, C(6)), 127.8 (CH, C(1)), 128.1 (CH, C(3)), 128.2 (CH, C(7)), 128.8 (CH, C(2)), 131.4 (CH, C(8)), 139.5 (C, C(4)).
MS (EI): 170 (M^+-H_2O, 7), 97 (31), 91 (100), 79 (35), 77 (24), 69 (40), 65 (28).

1-(2-(2-Cyclohexen-1-yl)ethyl)benzene (131)



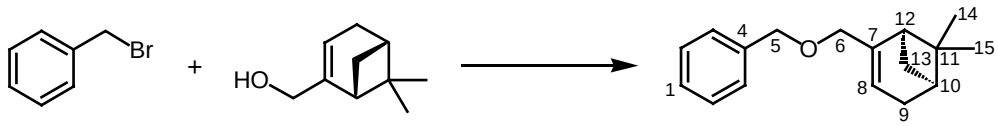
131

A dry two-necked flask fitted with reflux condenser and an addition funnel was charged under nitrogen atmosphere with magnesium turnings (1.25 g, 51.4 mmol) and Et_2O (75 mL). A solution of phenethyl bromide (6.75 mL, 50 mmol) in Et_2O (5 mL) was added in such a way that the reaction mixture was kept slightly boiling. After complete addition the suspension was added dropwise to a solution of 3-bromocyclohexene (5.78 mL, 50 mmol) in Et_2O (25 mL) at reflux over a 45 min period and stirred for further 1.5 h at reflux. After cooling to RT the mixture was quenched carefully with ice water. The layers were separated and the aqueous phase was extracted 3 times with Et_2O. The combined organic phases were washed with a saturated NaCl solution, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by destillation (90 °C, $2*10^{-1}$ bar) yielding **131** (4.5 g, 48 %) as slightly yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.28 (m, 1H, $H_aC(12)$), 1.52 (m, 1H, $H_aC(11)$), 1.55 – 170 (m, 2H, $H_2C(6)$), 1.75 (m, 1H, $H_bC(11)$), 1.83 (m, 1H, $H_bC(12)$), 1.97 (m, 2H, $H_2C(10)$), 2.10 (m, 1H, HC(7)), 2.66 (m, 2H, $H_2C(5)$), 5.62 (m, 1H, HC(8)), 5.69 (m, 1H, HC(9)), 7.18 (m, 3H, HC(1), HC(3)), 7.27 (m, 2H, HC(2)).

^{13}C-NMR (90.6 MHz, $CDCl_3$): 22.0 (CH_2, C(11)), 25.9 (CH_2, C(10)), 29.5 (CH_2, C(12)), 33.8 (CH_2, C(5)), 35.2 (CH, C(7)), 38.8 (CH_2, C(6)), 126.1 (CH, C(1)), 127.6 (CH, C(9)), 128.8 (CH, C(2)), 128.9 (CH, C(3)), 132.2 (CH, C(8)), 143.3 (C, C(4)).

Benzyl (6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)methyl ether (120)

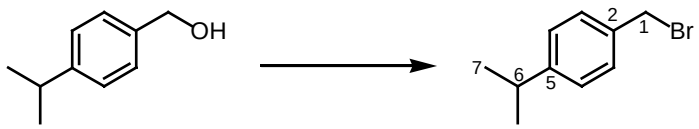


120

Ether **120** was synthesized according to a modified literature procedure.[105]
A two-necked flask equipped with a bubbler was charged with sodium hydride (55 % in mineral oil, washed 3x with pentane) (1.1 g, 44 mmol) and THF (25 mL). To this suspension (-)-myrtenol (3.4 mL, 22 mmol) was added dropwise over a 20 min period. The mixture was further stirred until gas evolution ceased. After addition of potassium iodide (0.83 g, 5 mmol), a solution of benzyl bromide (3 mL, 25 mmol) in THF (5 mL) was added over a 10 min period. The resulting suspension was stirred overnight and then mixed with H_2O (50 mL) and saturated NaCl solution (30 mL). The aqueous layer was extracted 3 times with Et_2O and the combined organic phases were washed first with saturated NaCl solution, then with H_2O. After drying over $MgSO_4$, the solvent was removed in vacuo affording **120** (5.03 g, 94 %) as yellow liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 0.86 (s, 3H, H_3C(14)), 1.20 (d, 1H, J = 8.63, H_aC(13)), 1.29 (s, 3H, H_3C(15)), 2.11 (b, 1H, HC(10)), 2.22 (m, 1H, HC(12)), 2.27 (b, 1H, H_aC(9)), 2.31 (b, 1H, H_bC(9)), 2.40 (txd, 1H, J = 8.63, 5.91, H_bC(13)), 3.89 (d, 2H, J = 1.36, H_2C(6)), 4.47 (s, 2H, H_2C(5)), 5.53 (b, 1H, J = 1.36, HC(8)), 7.33 (m, 5H, HC(1), HC(2), HC(3)).
^{13}C-NMR (90.6 MHz, $CDCl_3$): 21.6 (CH_3, C(14)), 26.8 (CH_3, C(15)), 31.8 (CH_2, C(9)), 32.1 (CH_2, C(13)), 38.5 (C, C(11)), 41.5 (CH, C(10)), 43.9 (CH, C(12)), 72.1 (CH_2, C(5)), 73.6 (CH_2, C(6)), 120.5 (CH, C(8)), 127.9 (CH, C(1)), 128.1 (CH, C(3)), 128.8 (CH, C(2)), 136.2 (C, C(7)), 145.9 (C, C(4)).
MS (FAB): 241 (M^+-H, 5), 136 (24), 119 (13), 107 (22), 91 (100), 79 (59).

4-Isopropylbenzyl bromide (125)

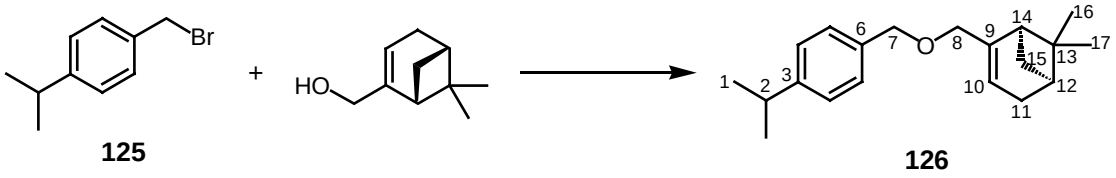


125

Bromide **125** was synthesized according to a modified literature procedure.[118]
A mixture of 4-isopropylbenzyl alcohol (15.3 mL, 0.1 mol) in hydrobromic acid 48 % (60 mL, 0.5 mol) was heated to 70 °C for ½ h. The layers were separated and the aqueous phase was extracted once with heptane. The combined organic phases were dried and the solvent was evaporated under reduced pressure yielding **125** (20.8 g, 98 %) as slightly orange liquid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.24 (d, 6H, J = 7.20, H_3C(7)), 2.90 ('heptett', 1H, J = 7.20, HC(6)), 4.49 (s, 2H, H_2C(2)), 7.19 (d, 2H, J = 8.18, HC(4)), 7.31 (d, 2H, J = 8.18, HC(3)).
^{13}C-NMR (90.6 MHz, $CDCl_3$): 24.3 (CH_3, C(7)), 34.2 (CH_2, C(1)), 34.3 (CH, C(6)), 127.3 (CH, C(4)), 129.5 (CH, C(3)), 135.6 (C, C(2)), 149.7 (C, C(5)).

(6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)methyl 4-isopropylbenzyl ether (126)



125 **126**

Ether **126** was synthesized according to a modified literature procedure.[105]

A two-necked flask equipped with a bubbler was charged with sodium hydride (55 % in mineral oil, washed 3 times with pentane) (0.85 g, 36 mmol) and dry DMF (50 mL). To this suspension (-)-myrtenol (4.6 g, 30 mmol) was added dropwise over a 20 min period. Stirring was continued until gas evolution ceased. After addition of potassium iodide (1 g, 6 mmol), benzyl bromide **125** (7 g, 33 mmol) was added over a 15 min period. The resulting suspension was stirred overnight and then mixed with H_2O (50 mL) and saturated NaCl solution (30 mL). The aqueous layer was extracted 3 times with Et_2O and the combined organic phases were washed with H_2O. After drying over $MgSO_4$, the solvent was removed in vacuo affording **126** (7.75 g, 91 %) as orange-yellow liquid.

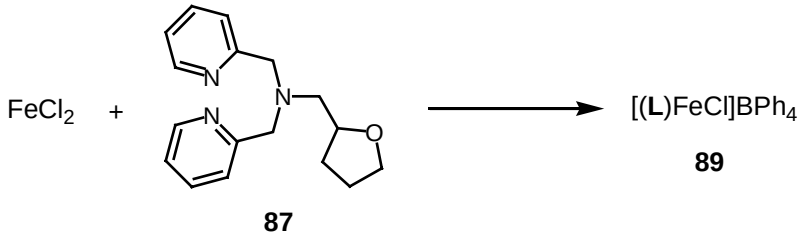
^{1}H-NMR (360 MHz, $CDCl_3$): 0.86 (s, 3H, $H_3C(16)$), 1.20 (d, 1H, J = 8.17, $H_aC(15)$), 1.24 (d, 6H, J = 6.81, $H_3C(1)$), 1.29 (s, 3H, $H_3C(17)$), 2.11 (m, 1H, HC(12)), 2.22 (m, 1H, HC(14)), 2.27 (m, 1H, $H_aC(11)$), 2.31 (m, 1H, $H_bC(11)$), 2.40 (txd, 1H, J = 8.17, 5.90, $H_bC(15)$), 2.90 ('heptett', 1H, J = 6.81, HC(2)), 3.88 (d, 2H, J = 1.36, $H_2C(8)$), 4.43 (s, 2H, $H_2C(7)$), 5.52 (m, 1H, J = 1.36, HC(10)), 7.19 (d, 2H, J = 7.73, HC(4)), 7.25 (d, 2H, J = 7.73, HC(5)).

^{13}C-NMR (90.6 MHz, $CDCl_3$): 21.5 (CH_3, C(16)), 24.5 (CH_3, C(1)), 26.7 (CH_3, C(17)), 31.7 (CH_2, C(11)), 32.0 (CH_2, C(15)), 34.3 (CH ,C(2)), 38.5 (C, C(13)), 41.3 (CH, C(12)), 45.7 (CH, C(14)), 71.9 (CH_2, C(7)), 73.5 (CH_2, C(8)), 120.4 (CH, C(10)), 126.8 (CH, C(4)), 128.2 (CH, C(5)), 136.4 (C, C(9)), 145.9 (C, C(6)), 148.6 (C, C(3)).

MS (CI): 285 (M^++H, 27), 267 (100), 178 (43), 135 (35), 57 (71).

14. Complex syntheses

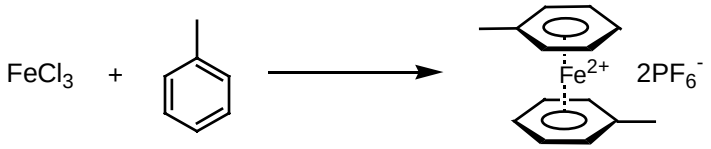
Bis(pyridylmethyl)amineiron tetraphenylborate complex 89



To a suspension of anhydrous iron(II) chloride (445 mg, 3.5 mmol) in benzene (5 mL) under nitrogen atmosphere was added dropwise a solution of amine **87** (1 g, 3.5 mmol) in benzene (10 mL). The mixture was stirred overnight. Then a suspension of sodium tetraphenylborate (1.2 g, 3.5 mmol) in benzene (10 mL) was added and the reaction mixture was stirred for 24 h. The precipitate was filtered and dried furnishing yellow complex **89** (1.21 g, 84 %).

Bis(toluene)iron hexafluorophosphate (140)

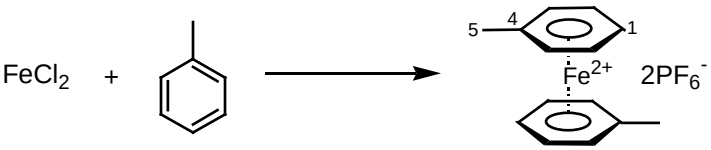
Method A



140

Complex **140** was synthesized according to the literature procedure.[helling]
Anhydrous iron(III) chloride (1.6 g, 10 mmol) was placed under nitrogen atmosphere and dissolved in toluene (20 mL). After addition of aluminium chloride (2.7 g, 20 mmol) the mixture was heated under vigorous stirring to reflux overnight. The mixture was allowed to cool to RT and was further cooled to –50 °C. At this temperature a 4:1 methanol/water solution (25 mL) was added and the mixture was stirred for 10 min. Water was added until the phases could be separated. To the aqueous phase was added progressively a saturated solution of ammonium hexafluorophosphate (3.25 g, 20 mmol) in water, the precipitate was filtered and dried yielding orange complex **140** (3.4 g, 64 %).

Method B



140

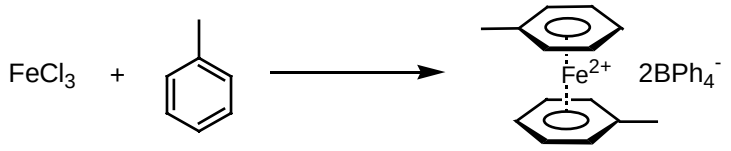
Complex **140** was synthesized according to the literature procedure.[helling2]
Anhydrous iron(II) chloride (1.25 g, 10 mmol) was placed under nitrogen atmosphere and suspended in cyclohexane (20 mL). After addition of toluene (2.7 mL, 25 mmol) aluminium chloride (4.25 g, 32 mmol) was added under vigorous stirring and the mixture was heated to reflux for 3 h. Then the mixture was allowed to cool to RT and carefully quenched at 0 °C with water (30 mL). The layers were separated and a

saturated solution of ammonium hexafluorophosphate (3.25 g, 20 mmol) in water was added progressively to the aqueous phase. The precipitate was filtered and dried affording orange complex **140** (1.33 g, 25 %).

^{1}H-NMR (360 MHz, CD_3CN): 2.59 (s, 6H, $H_3C(5)$), 6.84 (b, 6H, HC(1), HC(3)), 7.21 (b, 4H, HC(2)).
^{13}C-NMR (75.3 MHz, CD_3CN): 19.9 (CH_3, C(5)), 92.5 (CH, C(1)), 93.6 (CH, C(3)), 93.8 (CH, C(2)), 113.8 (C, C(4)).
MS (ESI): 385.03 (M^+-PF_6).

Bis(toluene)iron tetraphenylborate (141)

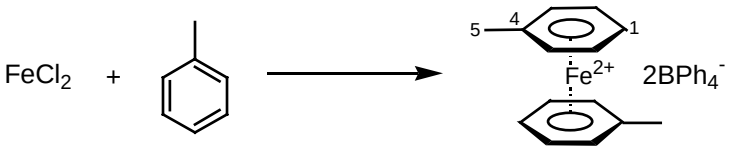
Method A



141

Complex **141** was synthesized according to the literature procedure.[helling]
Anhydrous iron(III) chloride (1.6 g, 10 mmol) was placed under nitrogen atmosphere and dissolved in toluene (20 mL). After addition of aluminium chloride (2.7 g, 20 mmol) the mixture was heated under vigorous stirring to reflux overnight. The mixture was allowed to cool to RT and was further cooled to –50 °C. At this temperature a 4:1 methanol/water solution (25 mL) was added and the mixture was stirred for 10 min. Water was added until the phases could be separated. To the aqueous phase was added progressively a saturated solution of sodium tetraphenylborate (6.85 g, 20 mmol) in water, the precipitate was filtered and dried yielding dark orange complex **141** (3.87 g, 44 %).

Method B



141

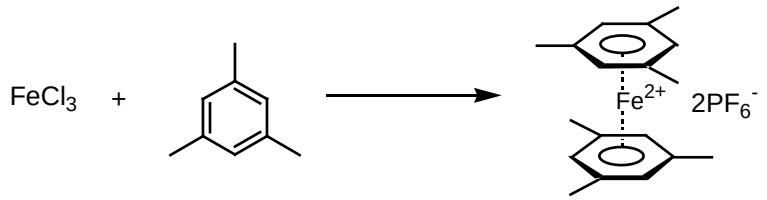
Complex **141** was synthesized according to the literature procedure.[helling2]
Anhydrous iron(II) chloride (1.25 g, 10 mmol) was placed under nitrogen atmosphere and suspended in cyclohexane (20 mL). After addition of toluene (2.7 mL, 25 mmol) aluminium chloride (4.25 g, 32 mmol) was added under vigorous stirring and the mixture was heated to reflux for 3 h. Then the mixture was allowed to cool to RT and carefully quenched at 0 °C with water (30 mL). The layers were separated and a

saturated solution of sodium tetraphenylborate (6.85 g, 20 mmol) in water was added progressively to the aqueous phase. The precipitate was filtered and dried affording dark orange complex **141** (3.34 g, 38 %).

^{1}H-NMR (360 MHz, CD_3CN): 2.46 (s, 6H, H_3C(5)), 6.79 (b, 14H, HC(1), HC(3), *p*-PhB), 6.96 (b, 16H, *o*-PhB), 7.24 (b, 20H, HC(2), *m*-PhB).

Bis(mesitylene)iron hexafluorophosphate (142)

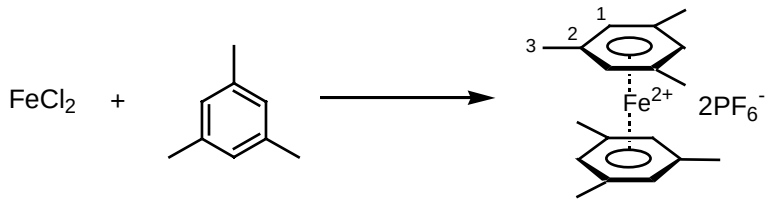
Method A



142

Complex **142** was synthesized according to the literature procedure.[helling]
Anhydrous iron(III) chloride (1.6 g, 10 mmol) was placed under nitrogen atmosphere and dissolved in mesitylene (20 mL). After addition of aluminium chloride (2.7 g, 20 mmol) the mixture was heated under vigorous stirring to reflux overnight. The mixture was allowed to cool to RT and was further cooled to –50 °C. At this temperature a 4:1 methanol/water solution (25 mL) was added and the mixture was stirred for 10 min. Water was added until the phases could be separated. To the aqueous phase was added progressively a saturated solution of ammonium hexafluorophosphate (3.25 g, 20 mmol) in water, the precipitate was filtered and dried yielding red complex **142** (4.8 g, 82 %).

Method B



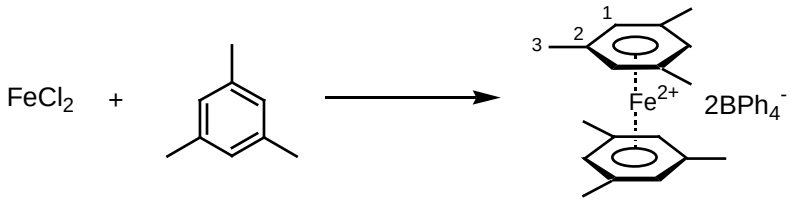
142

Complex **142** was synthesized according to the literature procedure.[helling2]
Anhydrous iron(II) chloride (1.25 g, 10 mmol) was placed under nitrogen atmosphere and suspended in cyclohexane (20 mL). After addition of mesitylene (4.7 mL, 25 mmol), aluminium chloride (4.25 g, 32 mmol) was added under vigorous stirring and the mixture was heated to reflux for 3 h. Then the mixture was allowed to cool to RT

and carefully quenched at 0 °C with water (30 mL). The layers were separated and a saturated solution of ammonium hexafluorophosphate (3.25 g, 20 mmol) in water was added progressively to the aqueous phase. The precipitate was filtered and dried affording red complex **142** (5.0 g, 86 %).

^{1}H-NMR (360 MHz, CD_3CN): 2.55 (s, 18H, H_3C(3)), 6.46 (s, 6H, HC(1)).
^{13}C-NMR (75.3 MHz, CD_3CN): 20.0 (CH_3, C(3)), 91.8 (CH, C(1)), 113.2 (C, C(2)).
MS (ESI): 441.10 (M^+-PF_6).

Bis(mesitylene)iron tetraphenylborate (143)

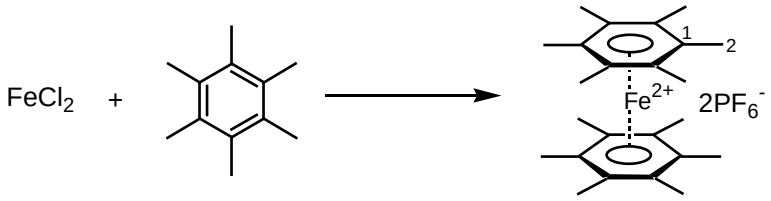


143

Complex **143** was synthesized according to the literature procedure.[helling2]
Anhydrous iron(II) chloride (1.25 g, 10 mmol) was placed under nitrogen atmosphere and suspended in cyclohexane (20 mL). After addition of mesitylene (4.7 mL, 25 mmol), aluminium chloride (4.25 g, 32 mmol) was added under vigorous stirring and the mixture was heated to reflux for 3 h. Then the mixture was allowed to cool to RT and carefully quenched at 0 °C with water (30 mL). The layers were separated and a saturated solution of sodium tetraphenylborate (6.85 g, 20 mmol) in water was added progressively to the aqueous phase. The precipitate was filtered and dried yielding dark red complex **143** (6.1 g, 65 %).

^{1}H-NMR (360 MHz, CD_3CN): 2.41 (s, 18H, H_3C(3)), 6.23 (s, 6H, HC(1)), 6.82 (b, 8H, *p*-PhB), 6.97 (b, 16H, *o*-PhB), 7.26 (b, 16H, *m*-PhB).
MS (ESI): 296.13 (M^+-$2BPh_4$ (formaly Fe^+)).

Bis(hexamethylbenzene)iron hexafluorophosphate (144)

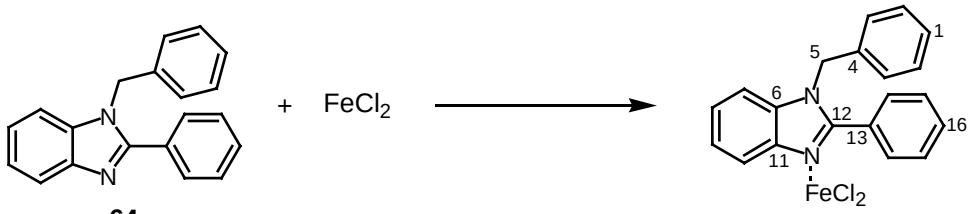


144

Complex **144** was synthesized according to the literature procedure.[helling2]
Anhydrous iron(II) chloride (1.25 g, 10 mmol) was placed under nitrogen atmosphere and suspended in cyclohexane (20 mL). After addition of hexamethylbenzene (4.05 g, 25 mmol), aluminium chloride (4.25 g, 32 mmol) was added under vigorous stirring and the mixture was heated to reflux for 4 h. Then the mixture was allowed to cool to RT and carefully quenched at 0 °C with water (30 mL). The layers were separated and a saturated solution of ammonium hexafluorophosphate (3.25 g, 20 mmol) in water was added progressively to the aqueous phase. The precipitate was filtered and dried affording pink complex **144** (4.1 g, 61 %).

^{1}*H-NMR* (360 MHz, CD_3CN): 2.26 (s, 18H, H_3C(2)).
^{13}*C-NMR* (75.3 MHz, CD_3CN): 16.3 (CH_3, C(2)), 118.4 (C, C(1)).

Benzylbenzimidazoleiron complex 69

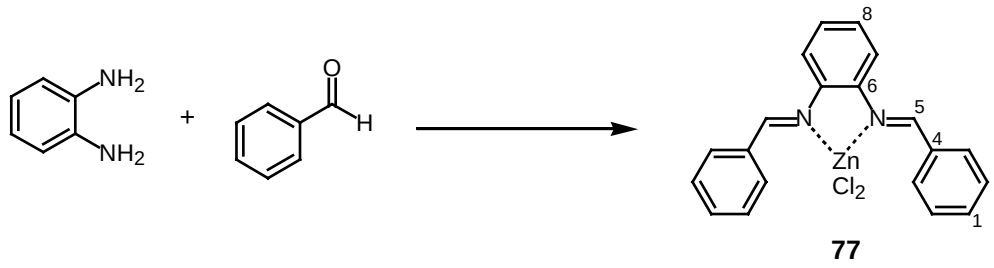


64 **69**

Anhydrous iron(II) chloride (126 mg, 1 mmol) and benzimidazole **64** (284 mg, 1 mmol) were placed under nitrogen atmosphere and benzene (15 mL) was added. The mixture was stirred at RT for 4 h. The precipitate was filtered and dried affording **69** (395 mg, 96 %) as white powder.

^{1}H-NMR (360 MHz, MeOD): 5.49 (s, 2H, H_2C(5)), 6.96 (b, 2H, HC(2)), 7.22 (b, 6H, HC(7), HC(8), HC(9), HC(10), HC(15)), 7.35 (b, 1H, HC(1)), 7.47 (b, 3H, HC(3), HC(16)), 7.62 (b, 2H, HC(14)).
MS (ESI): 375.04 (M^+-Cl).

Phenylenediiminezinc complex 77

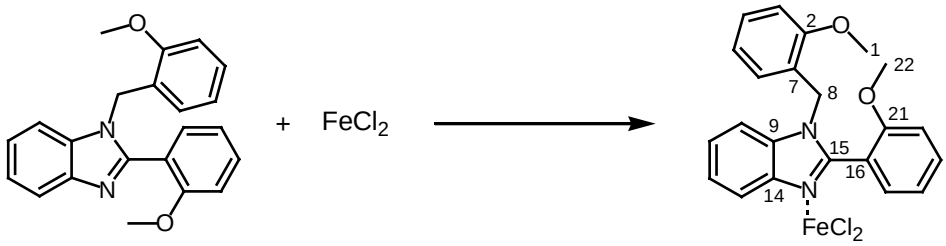


77

Phenylene-1,2-diamine (1.08 g, 10 mmol) and zinc chloride (1.36 g, 10 mmol) were placed under nitrogen atmosphere and toluene (25 mL) was added. The solution was cooled to 0 °C and benzaldehyde (2.53 mL, 25 mmol) was added dropwise during 30 min. After further stirring at 0 °C for 4 h the precipitate was filtered and dried yielding **77** (3.93 g, 93 %) as yellowish-white powder.

^{1}H-NMR (360 MHz, $CDCl_3$): 7.50 – 7.66 (m, 10H, HC(1), HC(2), HC(7), HC(8)), 8.18 (d, 4H, J = 7.27, HC(3)), 8.95 (s, 2H, HC(5)).
MS (ESI): 667.18 (**32**$_2$ZnCl$^+$).

Methoxybenzylbenzimidazoleiron complex 70

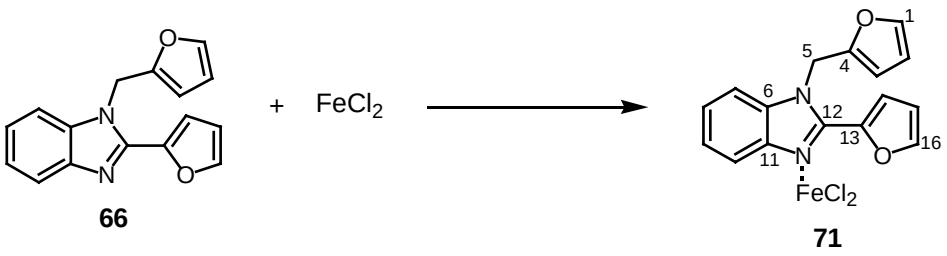


62 **70**

Anhydrous iron(II) chloride (126 mg, 1 mmol) and benzimidazole **62** (344 mg, 1 mmol) were placed under nitrogen atmosphere and benzene (15 mL) was added. The mixture was stirred at RT for 6 h. The precipitate was filtered and dried yielding **70** (396 mg, 84 %) as white powder.

^{1}H-NMR (360 MHz, MeOD): 3.43 (s, 6H, H_3C(1), H_3C(22)), 5.17 (s, 2H, H_2C(8)), 6.52 (d, 1H, HC(10)), 6.58 (t, 1H, HC(11)), 6.72 (d, 1H, HC(13)), 6.92 (t, 1H, HC(12)), 6.98 (d, 1H, HC(3)), 7.03 (t, 1H, HC(5)), 7.10 – 7.18 (m, 2H, HC(18), HC(20)), 7.28 (m, 2H, HC(4), HC(6)), 7.39 (t, 1H, HC(19)), 7.49 (b, 1H, HC(17)).
MS (ESI): 435.07 (M^+-Cl).

Furanylbenzimidazoleiron complex 71



66 **71**

Anhydrous iron(II) chloride (126 mg, 1 mmol) and benzimidazole **66** (264 mg, 1 mmol) were placed under nitrogen atmosphere and benzene (15 mL) was added. The mixture was stirred at RT overnight. The precipitate was filtered and dried affording complex **71** (258 mg, 66 %) as white powder.

^{1}H-NMR (360 MHz, MeOD): 5.52 (s, 2H, $H_2C(5)$), 6.08 (b, 1H, HC(2)), 6.12 (b, 1H, HC(3)), 6.52 (b, 1H, HC(1)), 7.05 (b, 3H, HC(7), HC(8), HC(9)), 7.14 (b, 1H, HC(10)), 7.37 (b, 1H, HC(15)), 7.45 (b, 1H, HC(14)), 7.59 (b, 1H, HC(16)).
MS (ESI): 355.00 (M^+-Cl).

15. General procedures for catalytic reactions

General procedure for hydrogenations according to SIEBER's method

In a dry Schlenk tube were placed a ligand (0.5 mmol) and anhydrous iron(II) chloride (0.5 mmol) under nitrogen atmosphere. Benzene (10 mL) was added and the mixture was stirred under light exclusion overnight. To this mixture was transferred a benzene suspension (10 mL) containing a substrate (5 mmol), an additive (5 mmol) (optional) and an activation reagent (2 mmol), and the resulting reaction mixture was set under 3 bar hydrogen pressure. At the end of the hydrogenation reaction, the suspension was filtered over Alox and the solvent was evaporated under reduced pressure. The residue was purified by destillation to furnish the hydrogenated product.
The Schlenk tube can be stoppered with a septum so that analytical samples can be taken during the hydrogenation without pressure release.

General procedure for hydrogenations with the 'ligand-free' catalyst system

In a dry Schlenk tube was suspended anhydrous iron(II) chloride (0.5 mmol) in the solvent (10 mL) under nitrogen atmosphere. The mixture was stirred for half an hour, then a substrate (5 mmol) was added. The suspension was set under 3 bar hydrogen pressure and the activation reagent (1-8 equivalents) was added. At the end of the hydrogenation reaction, the suspension was filtered over Alox and the solvent was evaporated under reduced pressure. The residue was purified by destillation to furnish the hydrogenated product.
The Schlenk tube can be stoppered with a septum so that analytical samples can be taken during the hydrogenation without pressure release.

Procedure A for hydrogenations with the allylbenzyletheriron catalyst system

In a dry Schlenk tube was placed a ligand (0.5 mmol) in cyclohexane (10 mL) under nitrogen atmosphere. The solution was cooled to 0 °C and ^{s}BuLi 1.6 M (0.5 mmol) in pentane was added slowly. The mixture was stirred for 15 min, then a suspension of anhydrous $FeCl_2$ (0.5 mmol) in THF (2.5 mL) was added. **ENB** (5 mmol) was added subsequently, the mixture was set under 3 bar hydrogen pressure and the activation reagent (0.5 mmol) was added. At the end of the hydrogenation reaction, the mixture was filtered over Alox and the solvent was evaporated under reduced pressure. The residue was purified by destillation to furnish the hydrogenated product.
The Schlenk tube can be stoppered with a septum so that analytical samples can be taken during the hydrogenation without pressure release.

Procedure B for hydrogenations with the allylbenzyletheriron catalyst system

In a dry Schlenk tube was placed a ligand (0.5 mmol) in cyclohexane (10 mL) under nitrogen atmosphere. The solution was cooled to 0 °C and ^{s}BuLi 1.6 M (0.5 mmol) in pentane was added slowly. The mixture was stirred for 15 min, then a suspension of anhydrous $FeCl_2$ (0.5 mmol) in THF (2.5 mL) was added. The mixture was filtered, **ENB** (5 mmol) was added subsequently to the solution, the mixture was set under 3 bar hydrogen pressure and the activation reagent (0.5 mmol) was added. At the end of the hydrogenation reaction, the mixture was filtered over Alox and the solvent was evaporated under reduced pressure. The residue was purified by destillation to furnish the hydrogenated product.
The Schlenk tube can be stoppered with a septum so that analytical samples can be taken during the hydrogenation without pressure release.

Procedure C for hydrogenations with the allylbenzyletheriron catalyst system

In a dry Schlenk tube were placed a ligand (0.5 mmol) and anhydrous $FeCl_2$ (0.5 mmol) in toluene (10 mL) under nitrogen atmosphere. The suspension was stirred for 4 h, then **ENB** (5 mmol) was added. The mixture was set under 3 bar hydrogen pressure and an alkyllithium reagent (0.5-2.5 mmol) was added. At the end of the hydrogenation reaction, the mixture was filtered over Alox and the solvent was evaporated under reduced pressure. The residue was purified by destillation to furnish the hydrogenated product.
The Schlenk tube can be stoppered with a septum so that analytical samples can be taken during the hydrogenation without pressure release.

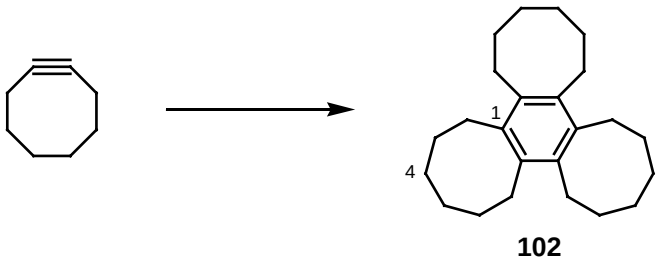
Polymerization of cyclooctyne

In a dry Schlenk tube were suspended anhydrous iron(II) chloride (63 mg, 0.5 mmol), cyclooctyne (1.08 g, 10 mmol) and cyclooctene (53 mg, 0.5 mmol) in toluene (10 mL) under nitrogen atmosphere. DIBAH 1 M (0.5 mL, 0.5 mmol) in toluene was added and the mixture polymerized rapidly in an exothermal reaction. The resulting material was filtered and dried furnishing a hard, brittle polymer.

Polymerization of acetylene

In a dry Schlenk tube was placed an iron source (1-10 mmol) under acetylene atmosphere and toluene (10 mL) was added. DIBAH 1 M (8 equivalents) in toluene was added and the mixture was stirred under 0.5 bar acetylene pressure. The resulting material was filtered and dried furnishing a black, hard polymer.

Cyclotrimerization of cyclooctyne

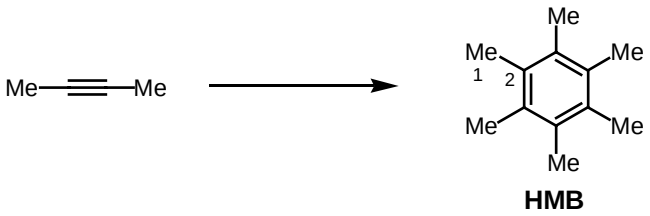


102

In a dry Schlenk tube were suspended anhydrous iron(II) chloride (63 mg, 0.5 mmol), cyclooctyne (1.08 g, 10 mmol) and cyclooctene (53 mg, 0.5 mmol) in toluene (50 mL) under nitrogen atmosphere. DIBAH 1 M (0.5 mL, 0.5 mmol) in toluene was added and the reaction mixture was stirred for 1 h. The resulting suspension was filtered over Alox and the solvent was evaporated under reduced pressure yielding benzene derivative **102** (2.01 g, 62 %) as white solid.

^{1}H-NMR (360 MHz, $CDCl_3$): 1.36 (b, 12H, $H_2C(4)$), 1.66 (b, 12H, $H_2C(3)$), 2.86 (b, 12H, $H_2C(2)$).
^{13}C-NMR (75.3 MHz, $CDCl_3$): 27.2 (CH_2, C(4)), 28.4 (CH_2, C(3)), 31.7 (CH_2, C(2)), 136.2 (C, C(1)).
MS (EI): 324 (M^+, 100), 295 (33), 281 (90), 253 (19), 239 (19), 225 (23), 211 (21), 185 (23), 171 (20), 143 (18), 129 (22), 91 (18).

Cyclotrimerization of 2-butyne



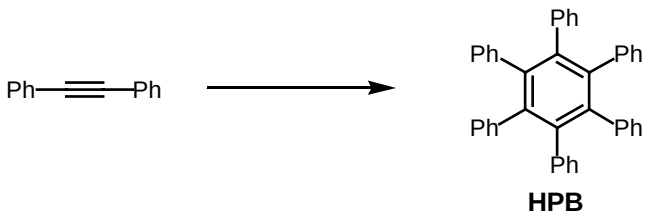
HMB

In a dry Schlenk tube were suspended anhydrous iron(II) chloride (63 mg, 0.5 mmol), 2-butyne (0.79 mL, 10 mmol) and cyclooctene (53 mg, 0.5 mmol) in toluene (10 mL) under nitrogen atmosphere. DIBAH 1 M (0.5 mL, 0.5 mmol) in toluene was added and the reaction mixture was stirred for 1 h. The resulting suspension was filtered over Alox and the solvent was evaporated under reduced pressure yielding benzene derivative **HMB** (1.15 g, 71 %) as white solid.

^{1}H-NMR (360 MHz, $CDCl_3$): 2.22 (s, 18H, $H_3C(1)$).

^{13}C-NMR (75.3 MHz, $CDCl_3$): 16.7 (CH_3, C(1)), 131.9 (C, C(2)).

Cyclotrimerization of diphenylacetylene (tolane)



HPB

In a dry Schlenk tube were suspended iron(II) chloride (126 mg, 1 mmol) and diphenylacetylene (5.35 g, 10 mmol) in hexane (10 mL) under nitrogen atmosphere. DIBAH 1 M (4 mL, 4 mmol) in toluene was added and the reaction mixture was heated to reflux for 5 h. The resulting suspension was filtered over Alox and the solvent was evaporated under reduced pressure yielding benzene derivative **HPB** (1.87 g, 35 %) as brown-white solid.

^{1}*H-NMR* (360 MHz, $CDCl_3$): 6.84 (b, 30H, H-Ph).

IV

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16. References

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