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Novel Ferrocenyl Monotrifluoromethylphosphine Ligands Combining Three Elements of Chirality

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presented by
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dedicated to

Guilhem and my parents Marie-Claire and Jean-Claude

The greatest glory in living lies not in never falling, but in rising every time we fall.

Nelson Mandela

Acknowledgement

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Publications and Presentations

Part of the work described in this thesis has been published:

Novel Ferrocenyl Monotrifluoromethylphosphine Ligands Combining Three Elements of Chirality, A. Sondenecker, A. Togni, *in preparation*.

Poster presentations at international conferences:

"Catalytic Electrophilic Amination of ß-Ketoester", XVII EuChemMS Conference on Organometallic Chemistry, Sofia, Bulgary, September 1st-6th, 2007.

"Towards Chiral Trifluoromethylphosphines for Asymmetric Catalysis", 16th International Symposium on Homogeneous Catalysis, Florence, Italy, July 6th-11th, 2008.

"Novel Type of Chiral Ferrocenyl Trifluoromethylphosphines", XVIII EuChemMS Conference on Organometallic Chemistry, Gothenburg, Sweden, June 22nd-25th, 2009.

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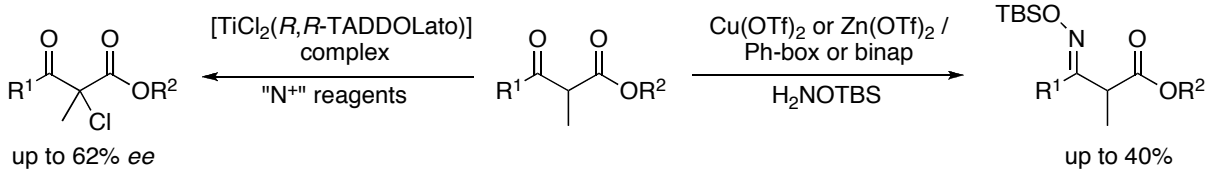
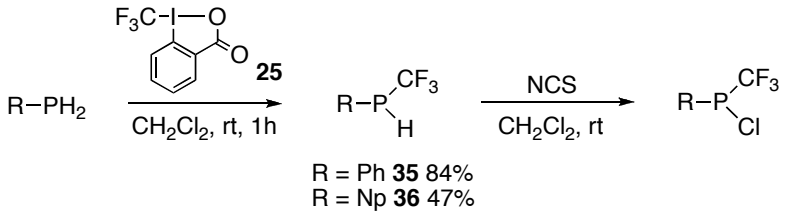
Abstract

The first part of the thesis describes the synthetic efforts toward α-amino acids via titanium-catalyzed electrophilic amination of ß-keto esters in analogy to the electrophilic halogenation, sulfenylation and hydroxylation established in our group. Despite extensive screening of the reaction conditions, the use of the [$TiCl_2$(*R,R*-TADDOLato)] complex as the catalyst for the electrophilic amination proved fruitless as it exclusively acted as a chloride donor yielding chlorinated ß-keto esters.

In order to avoid the transfer of the chloride onto the substrate several chloride free catalysts were tested. Interestingly, no conversion could be observed for the majority of metals used. Only the use of zinc (II) or copper (II) salts led to the consumption of the starting material resulting, however, in the formation of oximes. This transformation represents the first metal-catalyzed synthesis of ß-oxime esters starting from ß-keto esters.

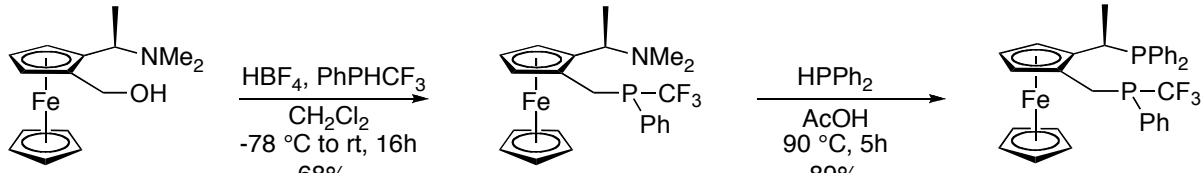


The second part of this work deals with the synthesis of a new kind of chiral 1,2-disubstituted ferrocenyl bisphosphines possessing a stereogenic phosphorus atom bearing a trifluoromethyl group. Although the first synthetic approach toward the target molecules via reaction of the lithiated ferrocene derivatives with halo(trifluoromethyl)phosphines failed, we established an efficient methodology for the synthesis of the prerequisite halo(trifluoromethyl)phosphines. Primary phosphines were thus subjected to electrophilic trifluoromethylation by reagent **25** based on hypervalent λ^3-organoiodine compounds developed in our group yielding the secondary monotrifluoromethylphosphines. Their subsequent treatment with *N*-chlorosuccinimide (NCS) in the presence of 10 mol% Ti catalyst resulted in an instantaneous, clean and quantitative reaction. This is a new catalyzed synthesis of chlorophosphines from corresponding secondary phosphines.



R	cat.	t	conv.
Ph (**37**)	-	24h	11%
Ph (**37**)	$CpTiCl_3$	5 min	quant.
Np (**38**)	$CpTiCl_3$	5 min	quant.

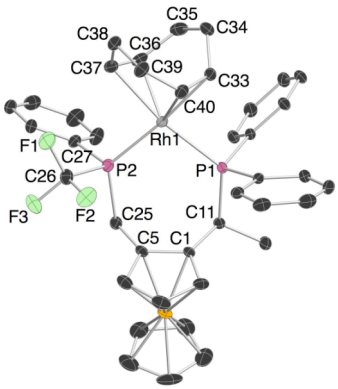
After modification of our synthetic strategy, a new class of chiral ferrocenyl bisphosphine ligands was achieved via a short two-step procedure with high modularity starting from the amino alcohol **52**. Nucleophilic substitution of the alcohol functionality by a secondary trifluoromethylphosphine in the presence of HBF_4 followed by a nucleophilic replacement of the dimethylamino group by diphenylphosphine in acetic acid furnished the novel ferrocenyl monotrifluoromethylphosphine ligands combining three elements of chirality.



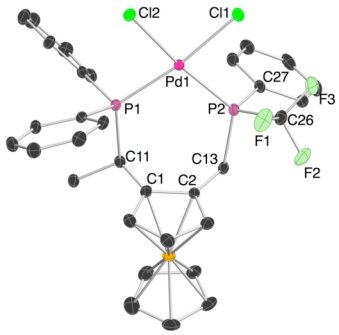
(R,S_{Fc})-**52** ($R,S_{Fc},R_P/S_P$)-**49** ($R,R_{Fc},R_P/S_P$)-**54**

Diastereomeric forms of **54** are separable by chromatographic techniques or fractional crystallization.

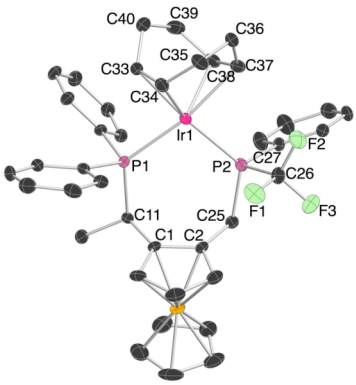
Cationic rhodium(I) and iridium(I) as well as neutral palladium(II) complexes containing the bisphosphine **54** were prepared and fully characterized by 1D- and 2D-NMR techniques and by X-ray crystallography. The structural features of these complexes are discussed with focus on the CF_3 moiety.



[Rh(cod)**54**]BF_4 (**57**)



[$Pd(Cl)_2$**54**] (**58**)

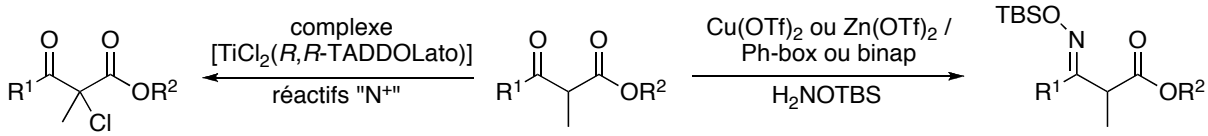


[Ir(cod)**54**]BF_4 (**61**)

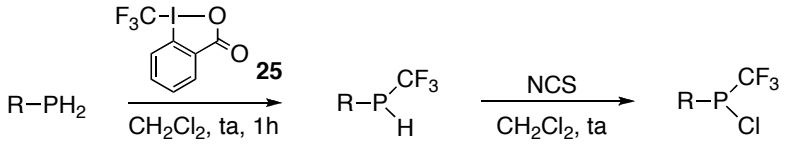
Résumé

La première partie de cette thèse décrit l'effort déployé pour la synthèse d'acides α-aminés via l'amination électrophile de ß-cétoesters catalysée avec du titane par analogie à l'halogénation, la sulfonation et l'hydroxylation électrophiles développées dans notre groupe pour les mêmes substrats. Malgré l'exploration extensive de très nombreuses conditions réactionnelles, l'utilisation du catalyseur [$TiCl_2$(*R,R*-TADDOLato)] pour l'amination électrophile s'est avéré stérile aboutissant à la chloration en α des ß-cétoesters utilisés.

Afin d'éviter le transfert de chlore au substrat, d'autres catalyseurs sans atome de chlore ont été utilisés. Curieusement, aucune conversion n'a été observée pour la majorité des métaux testés. La consommation du produit de départ a pu être observé avec l'utilisation de sel de zinc(II) ou de cuivre(II) résultant en la formation d'oximes. Cette transformation représente la première synthèse catalysée par des métaux de transition de ß-oximesters à partir de ß-cétoesters.

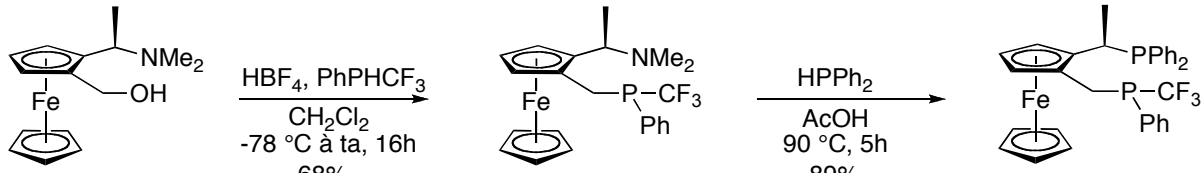


Dans un second temps, la synthèse d'un nouveau type de ferrocène bisphosphines chirales 1,2-disubstitués comportant un atome de phosphore stéréogénique contenant un groupe trifluoromethyle a été développée. Bien que la première approche vers la molécule cible, via la réaction du dérivé ferrocène lithié avec une chloro(trifluoromethyl)phosphine ait échoué, nous avons établi une autre méthodologie efficace pour la synthèse de chloro(trifluoromethyl)phosphines. Les phosphines secondaires monotrifluorométhylées ont été synthétisées, dans un premier lieu, par la réaction de la phosphine primaire correspondante avec le réactif éléctrophile trifluorométhylé **25** basé sur le composé λ^3-organoiodé hypervalent développé dans notre groupe. Puis, un traitement avec le *N*-chlorosuccinimide (NCS) combiné à 10% de catalyseur de titane a produit une réaction instantanée, propre et quantitative. Ceci constitue une nouvelle synthèse de chlorophosphines à partir des phosphines secondaires correspondantes.



R	cat.	t	conv.
Ph (**37**)	-	24h	11%
Ph (**37**)	$CpTiCl_3$	5 min	quant.
Np (**38**)	$CpTiCl_3$	5 min	quant.

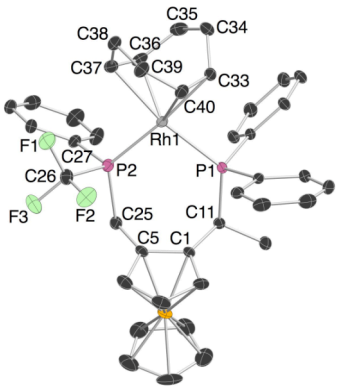
Après avoir changé de stratégie de synthèse, une nouvelle classe de ligands ferrocène bisphosphine chiraux ont été obtenu avec une grande modularité à partir de l'amino-alcool **52** via une procédure en deux étapes. Une substitution nucléophile de la fonction alcool par une phosphine secondaire trifluorométhylée en présence de HBF_4, puis un remplacement nucléophile du groupe diméthylamine par un groupe diphénylphosphine dans de l'acide acétique a fourni un nouveau type de ligand ferrocène phosphine monotrifluorométhylé combinant trois éléments de chiralité.



(R,S_{Fc})-**52** $(R,S_{Fc},R_P/S_P)$-**49** $(R,R_{Fc},R_P/S_P)$-**54**

La séparation des deux diastéréoisomères de **54** s'est avérée fructueuse par des techniques chromatographiques ou par cristallisation.

Deux complexes cationiques de rhodium(I) et iridium(I) ainsi qu'un complexe neutre de palladium(II) contenant la bisphosphine **54** ont été préparé et charactérisés par des spectroscopies RMN 1D et 2D et par cristallographie. Les particularités structurales de ces complexes seront discutées en se concentrant sur le groupement CF_3.



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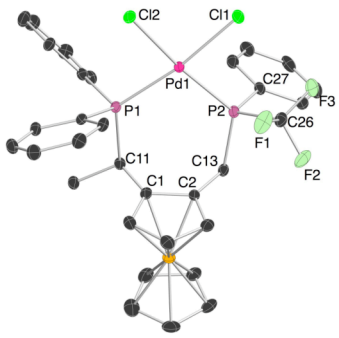

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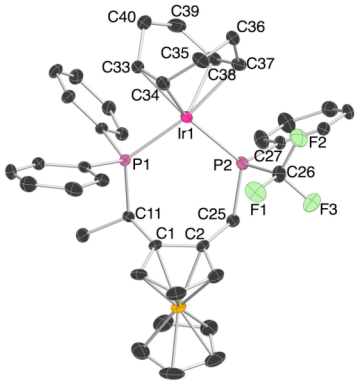
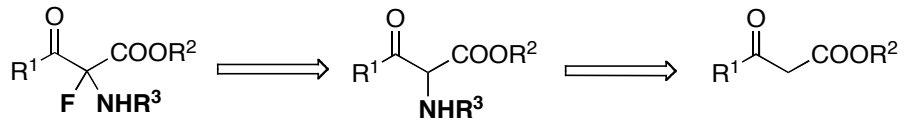


[Ir(cod)**54**]BF_4 (**61**)

1. Electrophilic Amination of ß-Keto Esters

The synthesis of α-halogenated α-amino acids can probably be placed somewhere between a challenge and a dream. This new class of compounds should be a powerful tool, with many applications to problems in the field of the life sciences. Fluorine would probably be the best choice of halogen because of the strength of the C-F bond relative to the other C-X bonds. *Takeuchi*, who dedicated most of his previous work to this topic, stated "I knew well that most organic chemists would think that a structure having both a halogen - a good leaving group - and an amino, hydroxyl, or thiol group, with readily removed protons, on the same carbon atom could not exist. In spite of this, the synthesis of α-halogenated α-amino acids has remained my dream." And so far, it remained a dream because *Takeuchi* failed at the last stage of reactions to isolate the α-fluoro α-amino acid itself.[1]

Despite these somewhat discouraging sentiments, it was believed that different approaches towards α-fluoro α-amino acids could lead to the goal. The first chapter of this thesis describe the attempt to perform enantioselective electrophilic amination on ß-keto esters affording α-amino acids. Following the chemistry developed in our group in the last 10 years, fluorine could be introduced via the titanium-catalyzed reaction at the same carbon atom to finally afford the desired α-fluoro α-amino acids.



α-fluoro α-amino acids α-amino acids ß-keto ester

1.1 Introduction

The aim of this introduction is to highlight the exceptional role of α-amino acids in organic chemistry. In the first section of this chapter, the biological and synthetic importance of α-amino acids and α-fluoro α-amino acids will be described. It is an exciting story to see how chemists and biologists have inspired each other to build up the field of fluorinated amino acids. In the following part, reagents for electrophilic fluorination will be compared and methods for metal- catalyzed enantioselective electrophilic fluorination will be discussed including the Ti(TADDOLato) catalyst developed in our group. The third part is related to the electrophilic amination of ß-keto ester. Electrophilic amination, especially asymmetric amination is of particular interest, therefore, nucleophilic or radical-based amination methods will not be discussed. Electrophilic aminating reagents will be presented by listing them

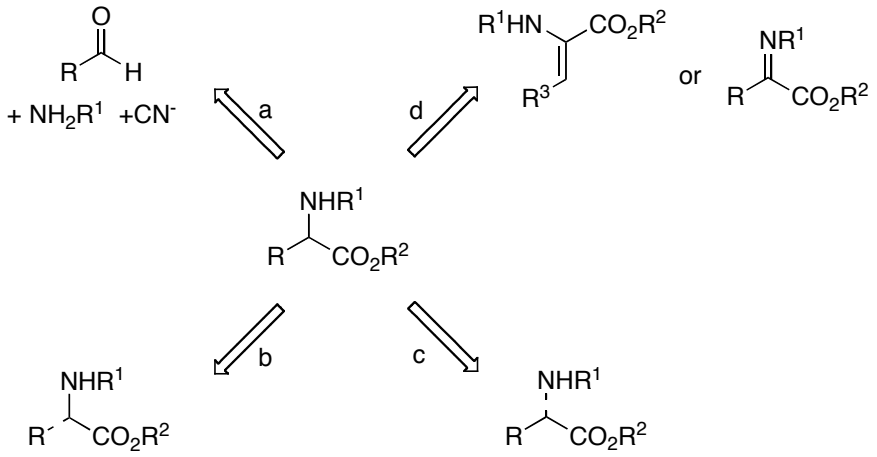
according to their structure, and some quite rare examples of metal-catalyzed enantioselective electrophilic amination will be discussed. Before the conclusion, section 1.1.4 will combine the two previous topics, describing the consecutive catalytic electrophilic fluorination/amination.

1.1.1 Amino Acids

1.1.1.1 α-Amino Acids

The interest in amino acids (AAs) and their derivatives has existed for many years. More than 700 amino acids have already been found in nature and their number is continuously growing. Optically active α- and ß-amino acids are fundamental building blocks for the preparation of pharmaceutical and agrochemical target molecules, such as, peptides, proteins and many other natural products.[2,3] Furthermore, amino acids are extensively used as chiral starting materials, auxiliaries and catalysts in modern organic synthesis.[4] There are four main approaches to obtain optically active amino acids, namely biotechnological methods, chemical synthesis using compounds from the chiral pool, resolution of a racemic mixture, and asymmetric synthesis. Catalytic asymmetric synthesis may be carried out by the use of chiral reagents or auxiliaries and have clear advantages since a catalytic amount of chiral material can produce large quantities of enantiomerically enriched or enantiopure products.
Several different catalytic asymmetric approaches to α-amino acids involving carbon-carbon, carbon-nitrogen, and carbon-hydrogen bond forming reactions have been developed (Scheme 1, paths a-d).[5]

Recent publications have highlighted catalytic asymmetric Strecker reactions[6] (path a) and catalytic asymmetric hydrogenation of dehydroamino acids[7] (path d). Several advances involving carbon-carbon bond forming events have emerged for the catalytic asymmetric synthesis of α-amino acids[8] (path b), and also for asymmetric carbon-nitrogen bond forming reactions (path c).

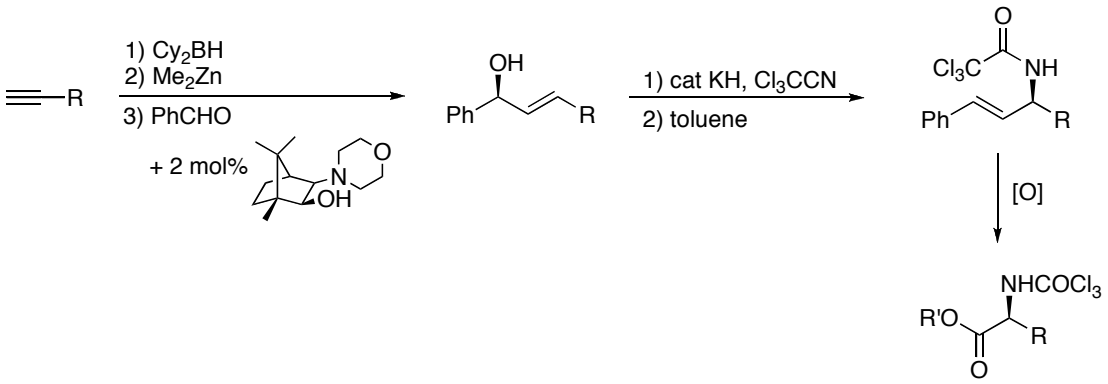


Scheme 1: Methods for the synthesis of α-amino acids.

Catalytic Asymmetric Carbon-Nitrogen Bond-Forming Reactions

- Nucleophilic Amination

The generation of α-amino acids by introducing the NH_2 group through the use of nucleophilic aminating reagents is generally based on S_N2 substitutions. Chirality is introduced prior to the nucleophilic amination. Versatile intermediates for this purpose are chiral epoxides and chiral α-halo or α-hydroxy carboxylates.[9] *Walsh* and co-workers disclosed an efficient and highly enantioselective synthesis for protected α-amino acids from terminal alkynes (Scheme 2).[10]



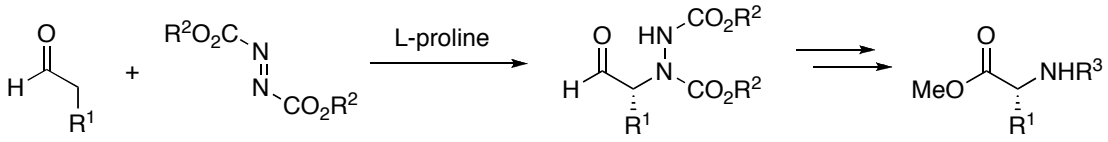
Scheme 2: Catalytic asymmetric synthesis of α-amino acids from terminal alkynes.

Asymmetric vinylation of benzaldehyde with terminal alkynes catalyzed by 2 mol% of a camphor derived amino alcohol gave allylic alcohols in high yields (65-94%) and

enantioselectivities (88-97% *ee*), which were converted to the protected allylic amines by an Overman [3,3]-sigmatropic rearrangement. Then, oxidative cleavage of the allylic amines gave the desired amino acids in good yields (57-92%) without loss of optical purity. An attractive feature of this method is that it provides entry to nonproteinogenic α-amino acids containing bulky substituents, such as *tert*-leucine, and (1-adamantyl)glycine (>99% *ee*)

- Electrophilic Amination

Asymmetric electrophilic amination of enolates is a relatively uncommon approach to amino acids because of the paucity of electrophilic source of nitrogen. In 2002, the research groups of *Jørgensen* and *List* independently reported the L-proline-catalyzed asymmetric α-amination of unmodified aldehydes with azodicarboxylates as nitrogen source (Scheme 3).[11] The corresponding chiral α-aminated adducts were obtained in high yields with excellent enantioselectivities (89-97 % *ee*).



Scheme 3: L-proline-catalyzed asymmetric α-amination of aldehydes.

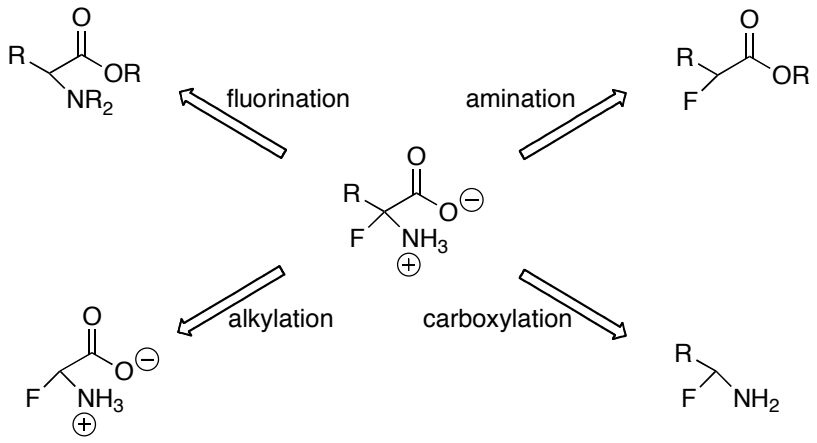
A very attractive aspect of the α-amination reaction is that it provides an easy access to optically active α-amino acid derivatives through oxidation of the aminated adducts.

1.1.1.2 Fluorinated Amino Acids

The synthesis of “unusual” amino acids has continued to develop at tremendous pace over the past 50 years, producing an incredible range of structurally exotic and novel compounds. The man-made area of fluorine-containing amino acids (FAAs) takes the most important place in the family of “unusual” amino acids.[12] Biologists and medicinal chemists have been quick to seize on the opportunities opened up by the unique basic physico-chemical properties of fluorinated amino acids. It is a field to which both chemists and biologists have contributed significantly. The present brisk activity in the field, with the surprises that often emerge from research in this area, led Professor *D. Seebach* to coin a new term: *Flustrates* (*Flu*orine-containing sub*strates*).

Fluorine is one of the most abundant elements on earth, yet it occurs extremely rarely in biological compounds. Due to the specific properties of the fluorine atom, including its small steric size, high electronegativity, carbon-fluorine bond strength, the sensitivity of ^{19}F NMR spectroscopy along with large ^{19}F-^{1}H coupling constants, etc., the introduction of fluorine atom(s) into many biologically active molecules can bring about remarkable and profound changes in their physical, chemical and biological properties.[13] Thus, fluorine-containing amino acids and large molecules derived from them have enjoyed widespread bioorganic applications such as biological tracers, mechanistic probes, enzyme inhibitors and medical applications including control of blood pressure, allergies, and tumor growth.[14] Moreover, fluorinated amino acids have recently emerged as valuable building blocks for the design of hyperstable protein folds as well as directing highly specific protein-protein interaction.[15,16] At the same time, protein design and engineering of fluorinated amino acids have also achieved remarkable progress.[17] For all of these reasons, fluorinated amino acids have been the subjects of intensive synthetic research activities and some related reviews[18] and a book[12] in this area have been published recently.

The great interest in the synthesis and development of bioactive compounds as single enantiomers is due to the final acknowledgement of the relevance of chirality to biological activity.[19] Examples in which the property of a compound is strongly related to a given absolute configuration can be drawn from several different classes of products, such as drugs, pheromones, food additives, perfumes and crop protection agents. Considering that most fluorine-containing amino acids have been designed and synthesized as compounds with potential biological activity, the development of efficient methods for preparing pure enantiomers becomes a requirement for their biological evaluation.
In order to synthesize α-fluorinated α-amino acids, four different synthetic approaches can be used to give the desired target compound, having a quaternary carbon with four different substituents (Scheme 4).



Scheme 4: Synthetic routes to lead to α-fluorinated α-amino acids.

Approaches to related structural motifs (ß-keto esters, ß-keto phosphonates, etc) via fluorination and amination have received much attention in the last years and substantial progress has been made in the catalytic enantioselective introduction of fluorine and nitrogen. Specific introductions to those two pathways will be presented below.

1.1.2 Electrophilic Fluorination

1.1.2.1 Reagents for Electrophilic Fluorination

For carbon-fluorine bond formation, many suitable carbon nucleophiles are available, such as ß-keto esters, enolates of monocarbonyl compounds, etc. Finding sources of electrophilic fluorine, "F^+" is more problematic due to the fact that such reagents must either contain groups that withdraw electron-density from fluorine, an excellent leaving group directly attached to fluorine, or a combination of both.[20] Instead of using F_2,[21] CF_3OF,[22] CH_3COOF,[23] etc. as electrophilic sources of fluorine, which were shown to be toxic, highly oxidizing and some even explosive, fluorination can be done using safe and easy-to-handle N-F reagents (Figure 1).[24]

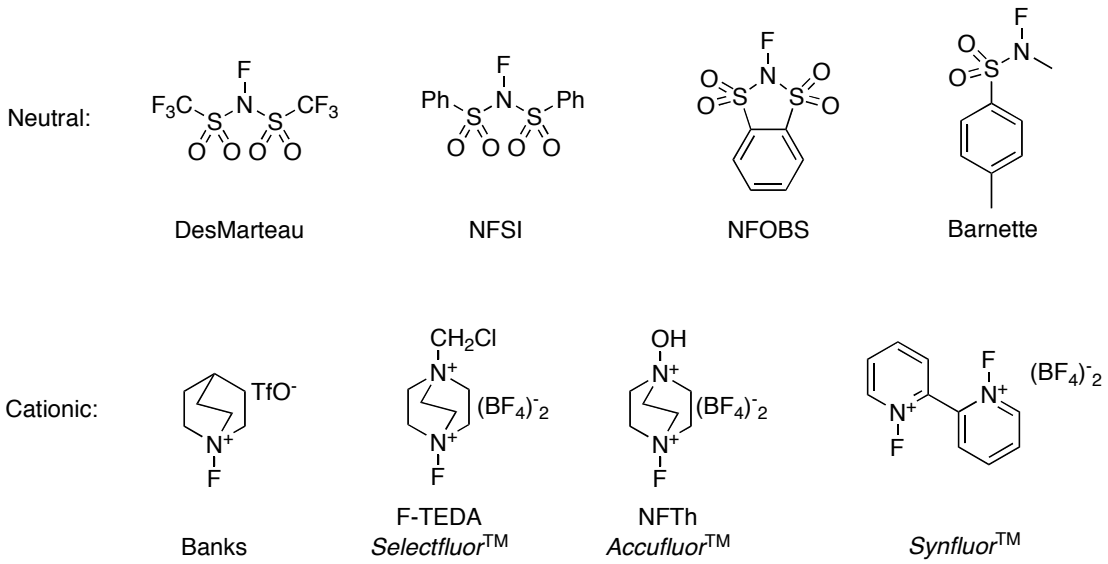


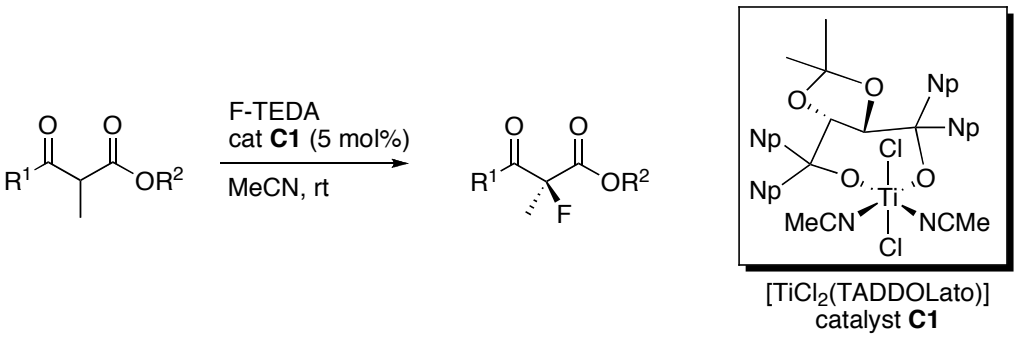
Figure 1: Neutral and cationic N-F fluorinating reagents.

Today, the most widely used among such reagents are *N*-fluorobenzenesulfonimide (NFSI)[25] and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane (F-TEDA, Selectfluor).[26] Most of the fluorinating agents mentioned above are commercially available except *N*-fluoro perfluoroalkylsulfonimide. In general, the cationic ammonium/iminium reagents are more powerful fluorinating agents than the neutral ones, with the exception of $(CF_3SO_2)_2NF$.

1.1.2.2 Metal-Catalyzed Enantioselective Electrophilic Fluorinations

Titanium(IV) TADDOLato Catalysts

During his Ph.D. thesis in our group, *Lukas Hintermann* studied the enantioselective fluorination of ß-keto esters catalyzed by chiral Ti(TADDOLato) complexes. He found that with 5 mol% of the [$TiCl_2$(*R,R*-TADDOLato)] complex **C1** as catalyst, a quite fast reaction of racemic ß-keto esters with F-TEDA took place (quantitative conversion in less than 5 h), yielding the fluoro-ß-keto esters in good yields (between 80% and 95%) and with up to 90% *ee* (Scheme 5).[27] The reactions have been conducted at room temperature with a slight excess of saturated F-TEDA solution in acetonitrile.



Scheme 5: Catalytic enantioselective fluorination of ß-keto esters with F-TEDA and [$TiCl_2$(*R,R*-TADDOLato)] complex **C1** as catalyst.

The steric bulk of the catalyst is important with regard to the stereoselectivity. Thus, the best enantioselectivities for all substrates under study were obtained by using catalyst **C1**, bearing 1-naphthyl groups (Figure 2).

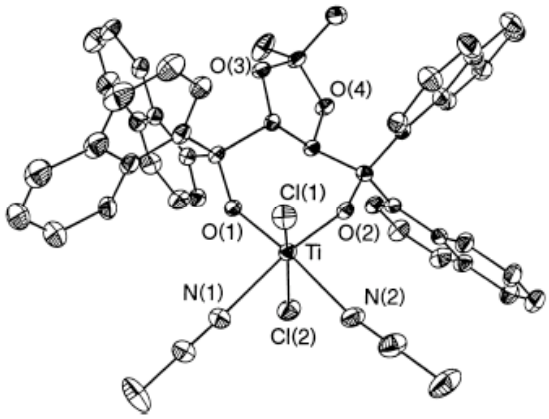
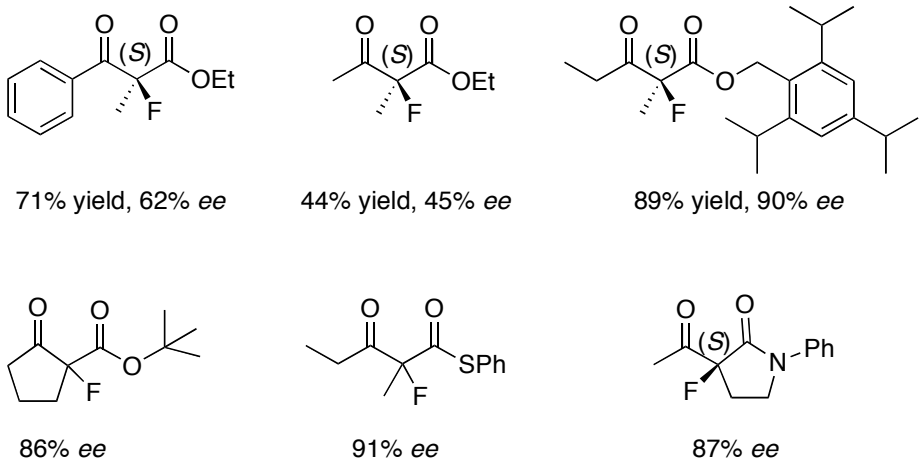


Figure 2: ORTEP view of [$TiCl_2$(TADDOLato)($MeCN)_2$] complex **C1**. H-atoms and solvent of crystallization are omitted for clarity.

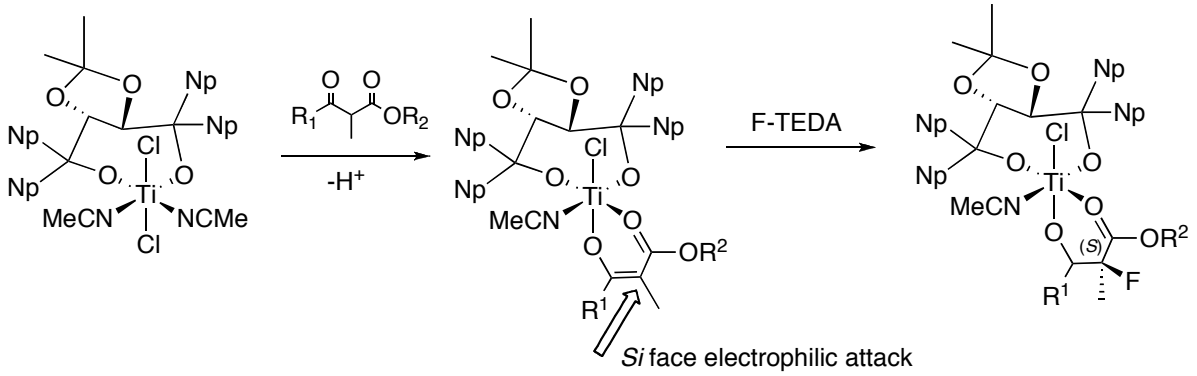
Also the nature of the ester group clearly influences enantioselectivity; bulky ester groups lead to an increase of stereoselectiviy, whereas steric bulk in the 2-position decreases the selectivity (Scheme 6). Later on, the substrate scope of the reaction was successfully extended to ß-keto thioesters[28] and ß-keto amides[29] (with NFSI as fluorinated agent). This level of stereoselectivity compares favourably with the highest enantioselectivity obtained by using chiral enantiopure fluorinating agents.



Scheme 6: Selected results of catalytic enantioselective fluorination reactions using [$TiCl_2$(TADDOLato)] complex (**C1**).

Further synthesis and characterization of [$TiCl_2$(diolato)(solvent)$_2$] complexes showed that the first choice of MeCN seemed to be the most suitable.[30] Firstly, the presence of excess sterically undemanding MeCN ligands assures coordinative saturation and, thus, makes the dichlorotitanium entity less susceptible towards hydrolysis. Still, the strength of coordination of MeCN is not too high to prevent ligand exchanges with substrates (and thus catalytic processes) to take place. Secondly, the coordination of solvents may contribute in converting polymeric metal species into mononuclear, crystalline complexes of defined composition. These may be useful as catalyst precursors that are easy to handle. The stable complex **C1** is an easily prepared catalyst precursor.

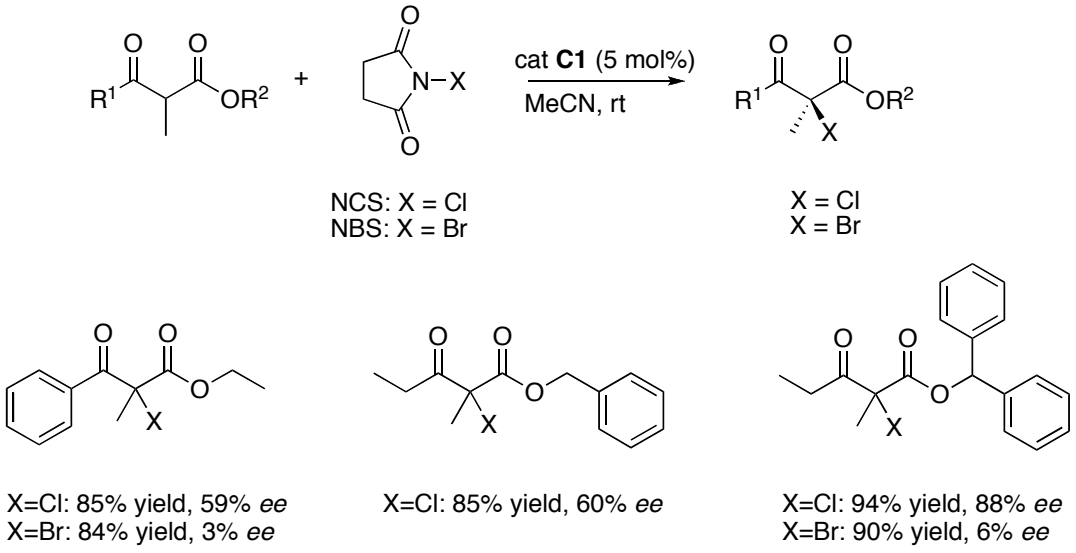
As a mechanistic hypothesis, it was postulated that the ß-keto ester coordinates to the catalyst as an enolate and substitutes one of the two chlorides and one of the acetonitrile molecules (Scheme 7).[31]



Scheme 7: Proposed mechanism for the Ti-catalyzed asymmetric fluorination reaction.

To understand the origin of enantioselectivity and to elucidate the detailed mechanism of the fluorination step, density functional theory (DFT) as well as quantum mechanical/molecular mechanical (QM/MM) calculations were performed. It was found that the most stable diastereoisomeric complex has the remaining chloride ligand in axial position, and the acetonitrile in the equatorial plane defined by the Ti center and the two TADDOL oxygens. The enolate binds with the ester oxygen in equatorial position, which leads to a complete shielding of its *re* face by the naphthyl group of the *R*-configured TADDOL. This diastereoisomer can be attacked by F-TEDA only from the unshielded *si* face of the enolate, in accordance with the experimentally observed (*S*) configuration of the fluorinated product. Meanwhile the key intermediate has been isolated and characterized and the mechanism has been corroborated by kinetics measurements.[32]

This enantioselective fluorination of ß-keto ester was generalized to enantioselective chlorination and bromination of ß-keto ester using the same [$TiCl_2$(*R,R*-TADDOLato)] complex as catalyst.[33] *N*-Chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS) were chosen as the electrophilic chlorination and bromination agents, respectively (Scheme 8).



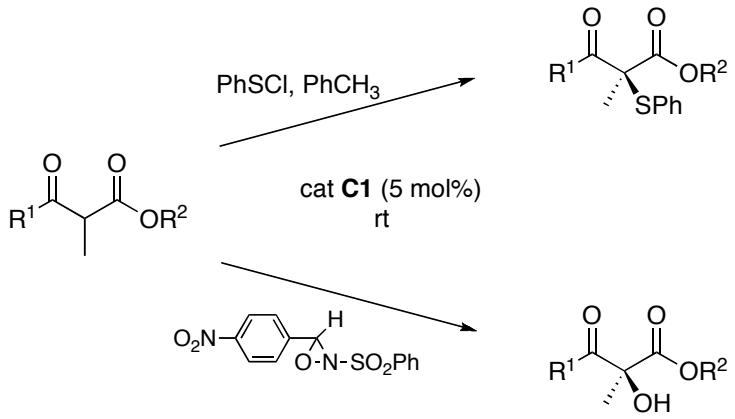
Scheme 8: Catalytic enantioselective chlorination and bromination of ß-keto esters with NCS or NBS and the [$TiCl_2$(*R,R*-TADDOLato)] complex **C1** as catalyst.

This new catalytic halogenation of ß-keto esters proceeds smoothly at room temperature in the presence of 5 mol% of catalyst **C1**, to afford chlorinated or brominated products as oily materials in good to almost quantitative isolated yields.

As well as for the fluorination, inspection of the data provided by Scheme 8 indicated that the enantioselectivity and rate of the chlorination reaction depends on a subtle interplay between steric properties of catalyst and substrate. Thus, it appeared that sterically demanding substituents on the ester group increased the *ee* values of the product up to 88% *ee*.
Despite the excellent yield (incomplete conversion was observed due to the catalyst decomposition) of the bromination reaction, the most striking feature observed was the dramatic drop in enantioselectivity as compared to the corresponding catalytic chlorination of the same substrate. In the HPLC chromatograms of the raw bromination products, minor amounts of the corresponding chlorinated products were detected, showing that Cl ligands from the catalyst **C1** are available to undergo the corresponding halogenation reactions under the reaction conditions applied.

Concerning the mechanistic study, as well as for the fluorination, it was shown that the role of the catalyst consists in triggering the enolization of the ß-keto ester substrate *via* complexation of the Ti-atom in the chelating fashion. This activation process is followed by an external stereoselective attack by the electrophilic halogenating agent.

In 2004, *Marjan Jereb* and *Patrick Toullec*, from our group, published works to carry on this study about electrophilic atom-transfer reactions using [$TiCl_2$(TADDOLato)] complex **C1**.[34,35] New catalytic and asymmetric carbon-sulfur bond and carbon-oxygen bond forming reactions were found using ß-keto esters as substrates (Scheme 9).



Scheme 9: Catalytic enantioselective sulfenylation and hydroxylation of ß-keto esters with phenylsulfenyl chloride and 2-(phenylsulfonyl)-3-(4-nitrophenyl)oxaziridine, respectively, and [$TiCl_2$(*R,R*-TADDOLato)] **C1** as catalyst.

As well as for halogenation, changing substituents in position R^1 or R^2 plays a key role in influencing the enantioselectivity, the bulkiness of the ester group being crucial. For these reasons, using a methyl group in position R^1 and a 1,1,2-trimethylpropyl group in position R^2 leads to the best results for the sulfenylation, with up to 82% yield and 97% *ee*. With regard to hydroxylation, 2-*tert*-butoxycarbonyl cyclopentanone gave the highest enantioselectivity with up to 94% *ee* and 97% yield.

Other Metal Catalysts

In the last years, a number of other systems were reported for the electrophilic fluorination of 1,3-dicarbonyl compounds (Table 1) but the basic principle remained very similar.

Table 1: Selected catalysts for the electrophilic fluorination of 1,3-dicarbonyl compounds.

Fluorinated agent	Catalyst	*ee*	Ref.
NFSI	$[Pd(binap)(H_2O)]^{2+}$	> 90%	*Sodeoka*[36]
NFSI	$[Cu(Ph\text{-}box)](OTf)_2$	up to 85%	*Cahard*[37], *Shibata*[38]
NFSI	$[Ni(Ph\text{-}dbfox)](ClO_4)_2$	up to 99%	*Shibata*[38]
NFSI	$[Zn(Ph\text{-}dbfox)](ClO_4)_2$	up to 99%	*Shibata*[39]
NFPY	Al(III)/Li/binol	up to 67%	*Cahard*[40]
NFPY	$[Sc(\text{-}F_8bnp)_3]$	up to 88%	*Inanaga*[41]
NFSI	$[Ni(NNN)](ClO_4)_2$	up to 94%	*Iwasa*[42]
NFSI	$[Ru(OEt_2)_2(PNNP)](PF_6)_2$	up to 92%	*Becker*[43]

1.1.3 Electrophilic Amination

1.1.3.1 Reagents for Electrophilic Amination

Electrophilic amination is an important synthetic reaction in which an electrophilic nitrogen carried by the reagent is transferred to a nucleophilic atom of the substrate to form the new Nu-N bond in the product.[44] This methodology provides an important route for C-N bond formation in organic synthesis. The direct C-N bond-forming reactions using electrophilic aminating reagents also constitute one of the simplest procedures for the construction of a stereogenic carbon center bearing to an amino group.

The introduction of a nitrogen functionality adjacent to a carbonyl group using electrophilic aminating reagents is a topical area of research, particularly with respect to the synthesis of α-amino acids, esters and ketones. The biological and synthetic importance of racemic and enantiopure α-amino acids has stimulated the development of numerous methods[45,46] for their synthesis and, among these, electrophilic amination is one of the most important and general methods for the direct formation of optically active α-amino acids.

The electrophilic aminating reagents used in the synthesis of α-aminocarbonyl compounds and nitriles are summarized in Scheme 10.

Electrophilic aminating reagents for α-carbanions of carbonyl compounds			
↳ ***sp^3N containing reagents***		***sp^2N contaning reagents*** ↵	
➢ N-haloamines	H_2N-X	➢ Arenediazonium salts	ArN_2X
➢ O-Substituted hydroxylamines	H_2N-OR; H_2N-OCOR; H_2N-OSO_2Ar; H_2N-$OP(O)Ar_2$; $HN(SiMe_3)(OSiMe_3)$	➢ Azides	R-N_3
		➢ Diazene dicarboxylates	$R^1OOCN{=}NCOOR^2$
		➢ α-chloronitroso compounds	$R_2C(Cl)NO$
➢ Oxaziridines		➢ Hypervalent iodine	

Scheme 10: Electrophilic aminating reagents.

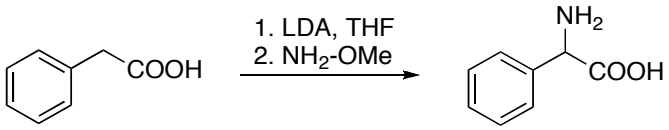
N-Haloamines (H_2N-X)

In the 70th, *Kovacic* and co-workers reviewed the synthesis and the reactivity of *N*-haloamines.[47] This class of compounds has not been utilized extensively for amination procedures because of their instability and cumbersome preparation, leading to unreproducible yields. Only the monochloroamine was used for enolate amination and a few examples have been reported.[48,49]

O-alkyl and *O*-aryl hydroxylamines (H_2N-OR)

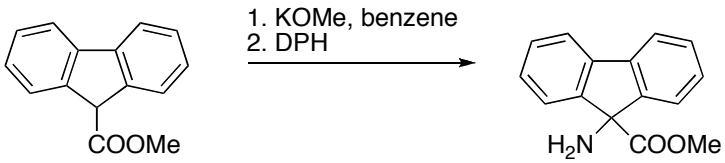
O-Methylhydroxylamine (methoxyamine) and *O*-(2,4-dinitrophenyl)hydroxylamine (DPH) are the most extensively used *O*-organyl hydroxylamine type reagents for electrophilic amination of carbanions. A review covering part of the topic was published by *Tamura* and co-workers.[50]

In order to prepare a series of α-aminocarboxylic acids, the amination of α-lithiated carboxylic acids was investigated by *Yamada* and co-workers (Scheme 11).[48]



Scheme 11: Amination with *O*-methylhydroxylamine (methoxyamine).

The use of *O*-(2,4-dinitrophenyl)hydroxylamine as an aminating reagent for enolates was first studied by *Sheradsky* and co-workers in the amination of methyl 9-fluorene carboxylate (Scheme 12).[51]

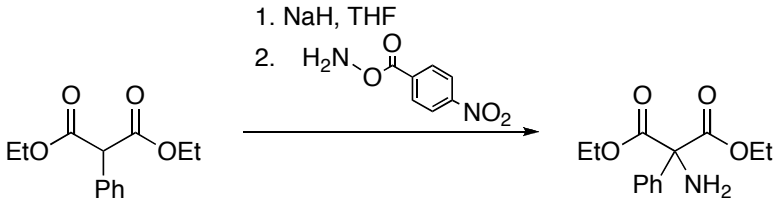


Scheme 12: Amination with *O*-(2,4-dinitrophenyl)hydroxylamine (DPH).

At the end of the 70ies, *Radhakrishna* and co-workers converted the sodium enolates of substituted diethyl malonates into α-aminocarboxylic acids in good yields by amination with DPH followed by hydrolysis and decarboxylation.[52] The method was also found to be useful in the amination of various ester enolates and the amination yield was found to decrease with increasing basicity of the enolate.

O-acyl hydroxylamines (H_2N-OCOR)

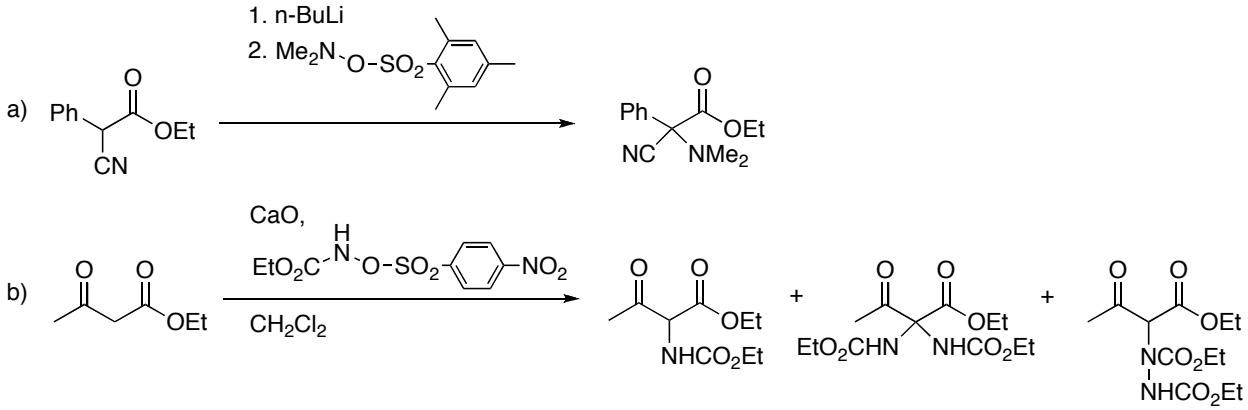
O-acylhydroxylamine are generally unstable with the exception of the 2,4,6-trimethylbenzoyl derivatives, which are reported to give only traces of amination product in their reaction with an α-lithiated carboxylic acid.[49] *Smulik* and *Vedejs* have proved *O*-(4-nitrobenzoyl)-hydroxylamine to be quite effective for amination of stabilized enolates (Scheme 13).[53]



Scheme 13: Amination with *O*-(4-nitrobenzoyl)hydroxylamine.

O-sulfonyl hydroxylamine (H_2N-OSO_2Ar)

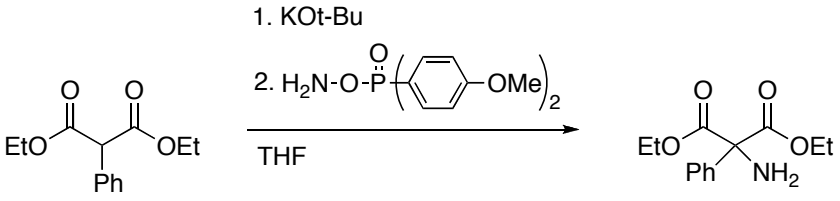
Methods for the preparation of *O*-(arenesulphonyl)hydroxylamine and their *N*-mono and *N,N*-diorganyl-substituted derivatives have been reviewed.[47] Amination of the lithium enolate of ethyl phenylcyanoacetate with the *N,N*-dimethyl derivative of *O*-(mesitylenesulfonyl) hydroxylamine was reported to give a high yield of the α-aminated product (Scheme 14a).[54] *N*-alkoxycarbonyl *O*-(arenesulfonyl)-hydroxylamines are useful aminating reagents since they can be easily prepared[55] and can be stored at 0 °C for many months without decomposition, arenesulfonyloxy groups are good leaving groups and alkoxycarbonyl groups are widely used[56] and easily removable protecting groups for amino functions.[57] *Pellacani* and co-workers reacted ß-oxo esters with *N*-ethoxylcarbonyl *O*-(4-nitrobenzenesulfonyl) hydroxylamine (NH(COOEt)ONs) in the presence of CaO and aminated products were obtained (Scheme 14b).[58] Depending on the relative amounts of the reagent and the reaction time, ethyl acetylacetate can be easily monoaminated or bisaminated. Its monoalkylated derivate, however, gave an *N*-aminated compound as the second product.



Scheme 14: Amination with *O*-(arenesulphonyl)hydroxylamine.

O-phosphinyl hydroxylamine (H_2N-OP(O)Ar_2)

In 2003, *Smulik* and *Vedejs* have shown that *O*-[di-(4-methoxyphenyl)phosphinyl]-hydroxylamine reacts efficiently with enolates derived from malonates, phenylacetates and phenylacetonitriles at -78 °C (Scheme 15).[53]

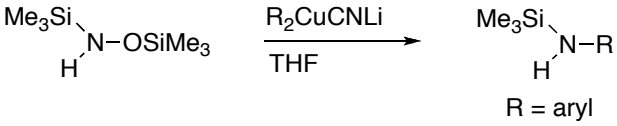


Scheme 15: Amination of 1,3-diketone derivatives with *O*-(di-4-methoxyphenylphosphinyl)-hydroxylamine.

The *O*-[di-(4-methoxyphenyl)phosphinyl]hydroxylamine shown in Scheme 15 was found to be more soluble than the *O*-(diphenylphosphinyl)hydroxylamine and sufficiently reactive for use in electrophilic amination at low temperature.

Bis (trimethylsilyl) hydroxylamine ($HN(SiMe_3)(OSiMe_3)$)

N,O-Bis(trimethylsilyl)hydroxylamine was reported to be an efficient and mild reagent for aryl cuprates (Scheme 16).[59] Yields between 58% and 90% were obtained, depending on the substrate.



Scheme 16: Amination of aromatic cuprates with $NH(SiMe_3)(OSiMe_3)$.

Oxaziridines

Oxaziridines are attacked by nucleophiles at either the oxygen or nitrogen atoms, depending upon the nature of the nucleophile and the substituents on the oxaziridine, especially at the nitrogen atom. *N*-alkyl, *N*-aryl, *N*-acyl, *N*-alkoxycarbonyl (*N*-COOR), *N*-carboxamido (*N*-$CONR_2$) oxaziridines have been used as electrophilic nitrogen transfer reagents to

C-nucleophiles. The preparation and utilization of oxaziridines as electrophilic aminating reagents have been extensively reviewed by *Vidal* and co-workers.

Different oxaziridine derivatives have been reported to perform amination:

- Cyclohexanespiro-3'-oxaziridine for amination of various nucleophiles[60] and carbanions.[61]
- *N*-Alkoxycarbonyloxaziridines have been used as aminating reagents for enolates[62] and for chiral enolates of ketones.[63]
- *N*-carboxamidoaziridines for the amination of enolates.[64]
- Chiral N-H oxaziridine derived from camphor and fenchone have been prepared and have been used for asymmetric nitrogen transfer to enolates.[65]

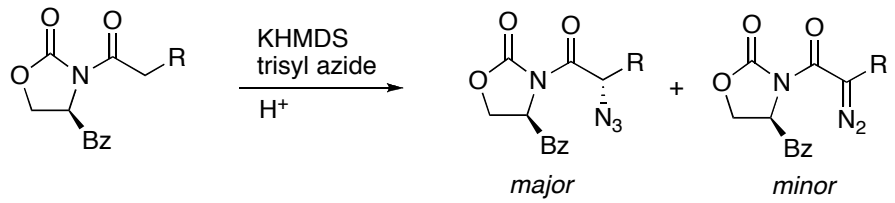
Arenediazonium salts (ArN_2X)

Arenediazonium salts were used as the electrophilic nitrogen source for active methylene compounds in protic media and also for lithium and silyl enolates. The reaction of ß-dicarbonyl compounds with $[C_6H_5N_2]^+Cl^-$ in alkaline solution is known as the Japp-Klingemann reaction.[66] The hydrazono or azo esters can be easily reduced to the α-amino acid esters and hydrolyzed to the α-amino acids.

Azides ($R\text{-}N_3$)

Organic azides have found their numerous applications in the electrophilic amination of carbanions, and methods for their preparation have been reviewed by *Scriven* and *Turnbull*.[67] Methods for the electrophilic azide transfer to enolates and eniminates are, however, still limited. The problem related to the use of azides is that these reagents also function as diazo transfer reagents.[68] For this reason, the reaction parameters in the synthesis of α-azidocarbonyl compounds using sulfonyl azides were modified in all attempts to maximize the azide introduction with minimal competing diazo transfer. So far, *p*-toluensulfonyl azide (tosyl azide), *p*-nitrobenzenesulfonyl azide (nosyl azide) and 2,4,6-triisopropyl-benzenesulfonyl azide (trisyl azide) were used for electrophilic azidation of enolates and eniminates.

Evans and co-workers have explored the azidation of chiral carboximide enolates systematically and developed a method for the synthesis of enantiomeric α-amino acids.[69] A chiral oxazolidinone group was needed for the diastereoselective introduction of the azide. Enolization was accomplished with potassium hexamethyldisilazide (KHMDS) (Scheme 17).



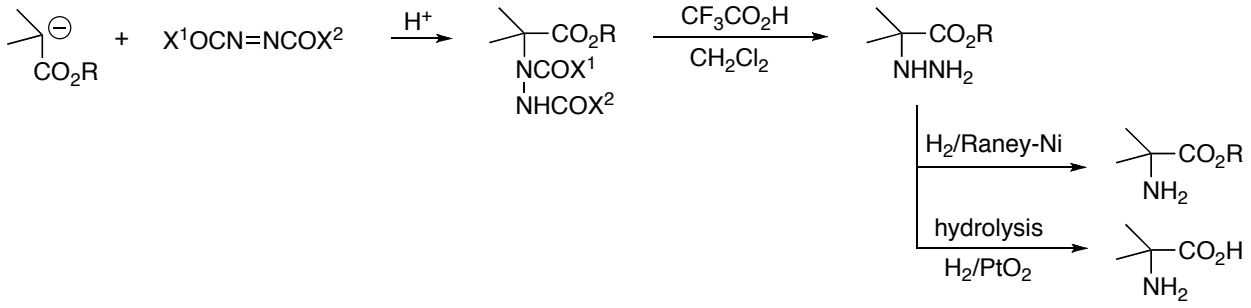
Scheme 17: Enantioselective introduction of an azide.

The yield of the azide transfer product increases at the expense of the competing diazo transfer product when:

- the enolate counterion becomes more electropositive (Li << Na < K)
- the transfer reagent becomes more electron rich and sterically demanding (nosyl < tolyl < trisyl)
- glacial acetic acid is used instead of the more reactive trifluoroacetic acid or silylating agents, TMSCl or TMSOTf, for quenching.

Diazene dicarboxylate ($R^1OOCN=NCOOR^2$)

Diazene dicarboxylates are stable and commercially available reagents. Due to its high reactivity, di-*t*-butyl azodicarboxylate (EtOOCN=NCOOEt) is the most frequently used reagent. A number of methods are available for clean removal of the *t*-butoxycarbonyl group[70] in addition to methods for N-N bond cleavage. Removal of the N-acyl groups (via hydrolysis by trifluoroacetic acid), followed by hydrogenolysis of the α-hydrazino adducts with Raney-Ni or with Pt is the most common route for the synthesis of α-amino esters and α-amino acids, respectively (Scheme 18).

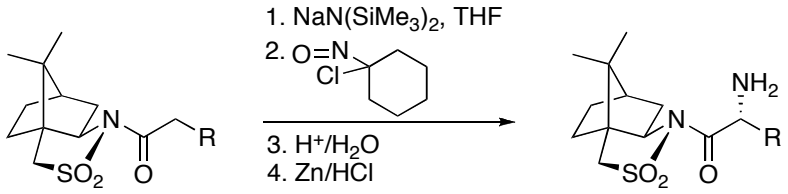


Scheme 18: Amination of enolates with diazene dicarboxylates.

α-Chloronitroso compounds ($R_2C(Cl)NO$)

Oppolzer and co-workers offered successful solutions for asymmetric electrophilic transfer to ketone and carboxylic amide enolates by using achiral or chiral α-chloronitroso-cycloalkanes.[71]

1-Chloro-1-nitrosocyclohexane was used for the amination of chiral carboxamides, which are converted to enantiomerically pure α-amino acids (Scheme 19).



Scheme 19: Asymmetric amination of chiral carboxymides.

Hypervalent iodine

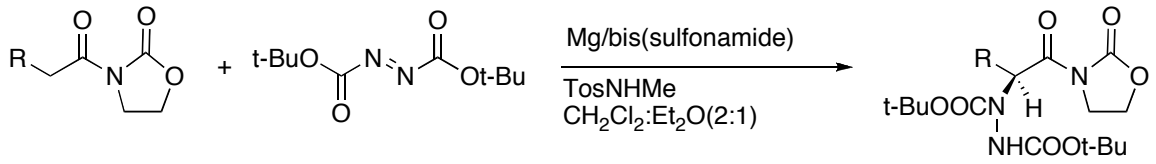
A hypervalent iodine compound, (*N*-tosylimino)phenyliodinane, was also efficiently used for the electrophilic amination of achiral and chiral α-tosylaminoketones.[72] (*N*-Tosylimino)phenyl- iodinane acts as a nitrene precursor and reacts with a C=C bond to form an aziridine. Following the aziridination of the enol derivatives, ring opening of the aziridine intermediate affords the corresponding α-aminocarbonyl compound.

Evans[73] and *Jacobsen*[74] extended the scope of the aziridination process independently by using chiral copper catalysts in the reaction with styrene and cinnamate derivatives and developed an asymmetric metal-catalyzed aziridination method.

1.1.2.2 Metal-Catalyzed Enantioselective Electrophilic Aminations

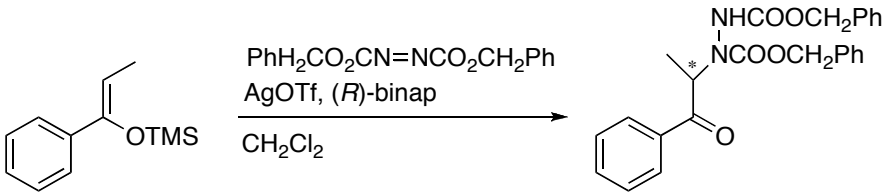
Asymmetric amination of silyl enol esters with enantiomeric excesses up to 92% was reported by *Sudalai*.[75] Chloramine-T was used as source of nitrogen and cinchona alkaloid derivatives ($(DHQD)_2$-CLB: dihydroquinidine-*p*-chlorobenzoate) as chiral ligands of osmium tetroxide. The conditions correspond to those of the asymmetric Sharpless aminohydroxylation.

In 1997, *Evans* and co-workers reported an asymmetric α-amination of *N*-acyloxazolidinones with diazene dicarboxylates using a chiral magnesium bis(sulfonamide) complex $Mg(NR^*_2)_2$ and obtained enantiomeric excesses up to 99% (Scheme 20).[76]



Scheme 20: Asymmetric amination using Mg complexes.

Kobayashi and co-workers investigated transition metal catalysis in the amination of silyl enolates with dibenzyl azodicarboxylate (DBzAD).[77] They observed that copper and silver triflates have a higher catalytic activity than other transition metals. Preliminary results with silver/(*R*)-binap as catalyst gave good enantioselectivities of up to 86% *ee* (Scheme 21).



Scheme 21: Ag triflates-catalyzed amination of silyl enol ethers.

Carrying on with the asymmetric amination of silyl enolates, *Evans* used chiral copper (II) Lewis acid catalysts based on a box-ligand also with diazene carboxylate derivatives.[78] The selectivities were up to 99% enantiomeric excess (Figure 3).

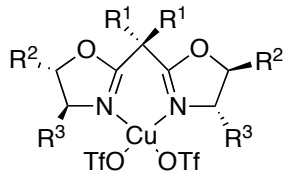
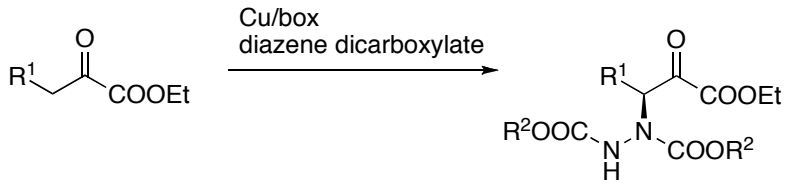


Figure 3: Chiral bisoxazoline copper(II) complex (Cu/box).

In 2002, a very attractive use of diazene dicarboxylates for the asymmetric α-amination of carbonyl compounds involving the preparation of catalytic chiral enolate derivatives was

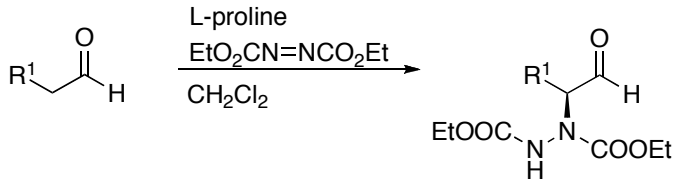
reported by *Jørgensen*.[79] The use of chiral box-based copper(II)triflate catalysts for the amination of ß-keto esters allowed to obtain high selectivities (up to 99% *ee*).



Scheme 22: Cu/box-catalysed amination of esters.

Since that report, the use of azene dicarboxylates in asymmetric catalytic amination has experienced a boost: ß-keto esters have been aminated with the Cu/box-system[80], as well as ß-keto phosphonates with a chiral palladium complex[81]; achiral amination of ketones was performed with a manganese catalyst[82]; aromatic compounds were aminated with azene dicarboxylates using scandium triflate[83] and zirconium tetrachloride as catalysts.[84]

More recently, also the organocatalytic approach showed interesting solutions for the asymmetric amination with diazene dicarboxylates: *List*,[85] *Jørgensen* (Scheme 23)[86] and *Bräse*[87] independently reported the L-proline-catalyzed amination of aldehydes or ketones. Other groups have found similar systems by replacement of the organocatalyst with other proline-derivatives.[88] In 2003, *Duthaler* published a short review on the subject.[89]



Scheme 23: Organocatalytic asymmetric α-amination of carbonyl compound using L-proline (*ee* between 84-99%).

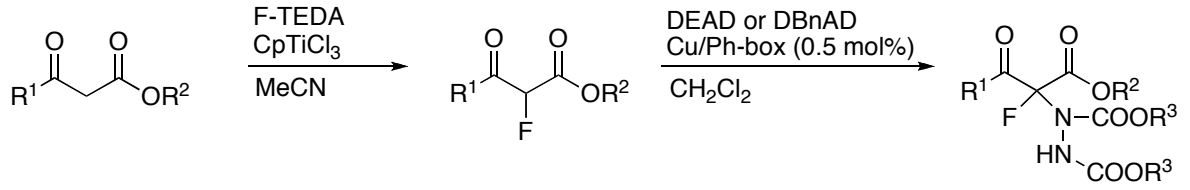
Asymmetric aminations via enantiopure diazene dicarboxylates were accomplished by *Vederas*[90] and *Brimble*.[91] *Oppolzer* reported the use of an enantiopure camphor-based ester giving enantioselectivities up to 99.7% *ee*.[92]

1.1.4 Consecutive Catalytic Electrophilic Fluorination / Amination

In 2006, *Dominique Huber* combined the field of fluorination and amination of ß-keto esters in a publication called: "*Consecutive catalytic electrophilic fluorination/amination of ß-keto esters: toward α-fluoro-α-amino acids?*".[93]

Fluorination/amination

In order to do so, he combined the previous work done in our group on the monofluorination with Selectfluor as a fluorine source catalyzed by $CpTiCl_3$ with *Jørgensen's* strategy for the amination process by azodicarboxylate (DEAD) or di-benzylazodicarboxylate (DBnAD) as aminating agent catalyzed by a copper/box catalyst (Scheme 24).

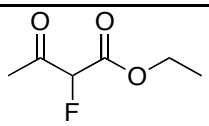
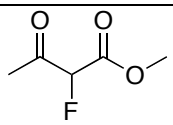
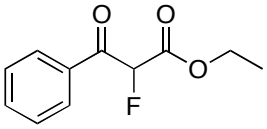


Scheme 24: Monofluorination of ß-keto esters followed by amination.

The ratio of mono *vs*. difluorinated product (>8:1), as well as the yields (>40%) were comparable to those previously reported.
For the amination of α-monofluoro ß-keto esters, full conversion and enantiomeric excess between 81% and 94% were observed after a reaction time of two days, which were comparable to those of the standard amination reaction. Isolated yields were up to 95% (Table 2).

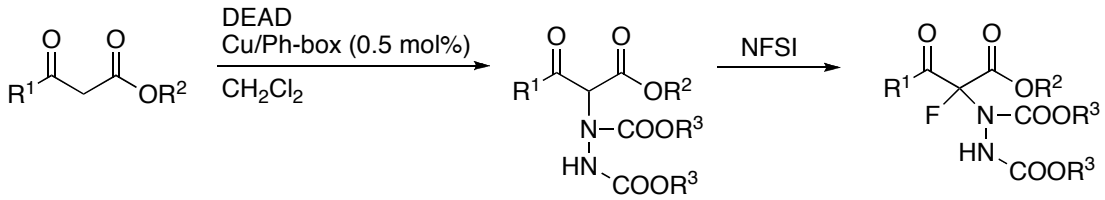
The best results were obtained when water-free $Cu(OTf)_2$ and the Ph-box ligand were used. The use of $Cu(OTf)_2$ and Ph-box, which was stored under air, lowered the enantioselectivity of the reaction.

Table 2: Amination of α-monofluoro ß-keto esters with Cu/Ph-box.

Substrate	Aminating agent	Yield [%]	Selectivity [% *ee*]
	DEAD	90	93
	DBnAD	73	91
	DEAD	94	94
	DBnAD	95	92
	DEAD	85	87
	DBnAD	78	81

Amination/fluorination

The amination followed by fluorination with NFSI as investigated with Cu/Ph-box as catalyst, DEAD as aminating agent and CH_2Cl_2 as solvent (Scheme 25).[94]

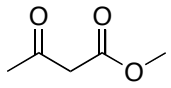
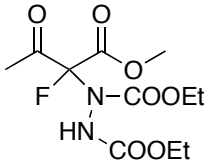
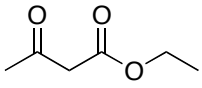
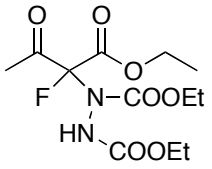


Scheme 25: Amination of ß-keto esters followed by fluorination.

After an amination reaction time of two days, 90% conversion was observed and the enantiomeric excess was in a range of 60% (Table 3). When the aminated products were isolated, they showed full enolization in the solid state whereas in solution, only 50% were enolized.

The fluorination showed to be very slow. After 4 days, only 80% conversion was obtained.

Table 3: Amination of ß-keto esters with Cu/Ph-box and DEAD followed by fluorination with NFSI.

Substrate	Products	Yield [%]	Selectivity [% *ee*]
		63	65
		n.d.	57

Mechanistic consideration and reduction attempts

Surprisingly, the same major isomer was observed for the consecutive one-pot fluorination / amination as well as for the consecutive one-pot amination / fluorination: HPLC measurements showed a major isomer eluting first in both case.

Several methods have been described for the cleavage of N-N bonds.[95] None of the method described gave the desired products; either no conversion was observed or in the case of using SmI_2, full conversion to defluorinated products occured.
The reduction of the hydrazine compounds proved to be a major problem. The N-N bond cleavage of these α-fluoro α-hydrazino compounds seems to be rather difficult.
It seems to be of great interest to find a method for the enantioselective introduction of only a single protected nitrogen as such methods are still vastly underdeveloped.

1.1.5 Objectives of this Part of the Thesis

Our group has shown that the well-known *Lewis* acidic [$TiCl_2$(TADDOLato)] complexes are suitable catalysts for the electrophilic halogenation, sulfenylation and hydroxylation of ß-keto esters. These new catalytic reactions offer a mild method for the generation of a new stereogenic centers by carbon-halogen, carbon-sulfur or carbon-oxygen bond formation.

Continuing these efforts, one goal of the present thesis was to extend these [$TiCl_2$(TADDOLato)]-catalyzed electrophilic halogenation, sulfenylation and hydroxylation to

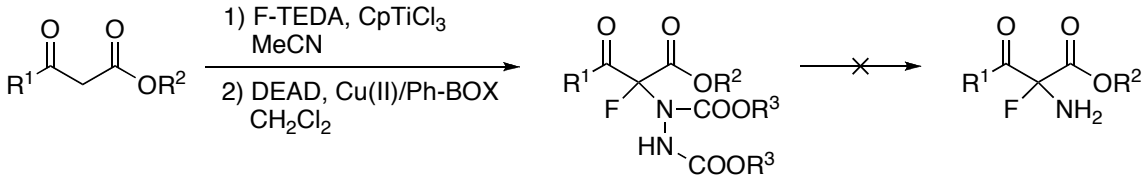
an electrophilic amination by a single-nitrogen transfer reagent in order to obtain α-amino acids, as substrates for a fluorination reaction using the same catalyst in an one-pot reaction to obtain α-fluorinated α-amino acids.

This electrophilic amination would also give an alternative to *Dominique Huber*'s trouble concerning the N-N bond cleavage he observed on the α-fluoro α-hydrazino compounds.

1.2 Results and Discussion

1.2.1 Introduction

Analogously to the heterodihalogenation of ß-keto esters, *Dominique Huber* carried out consecutive fluorination and amination in two steps.[93] The cleavage of the N-N bond of the α-fluoro α-hydrazino ß-keto esters was attempted under various conditions, however with no success (Scheme 26).

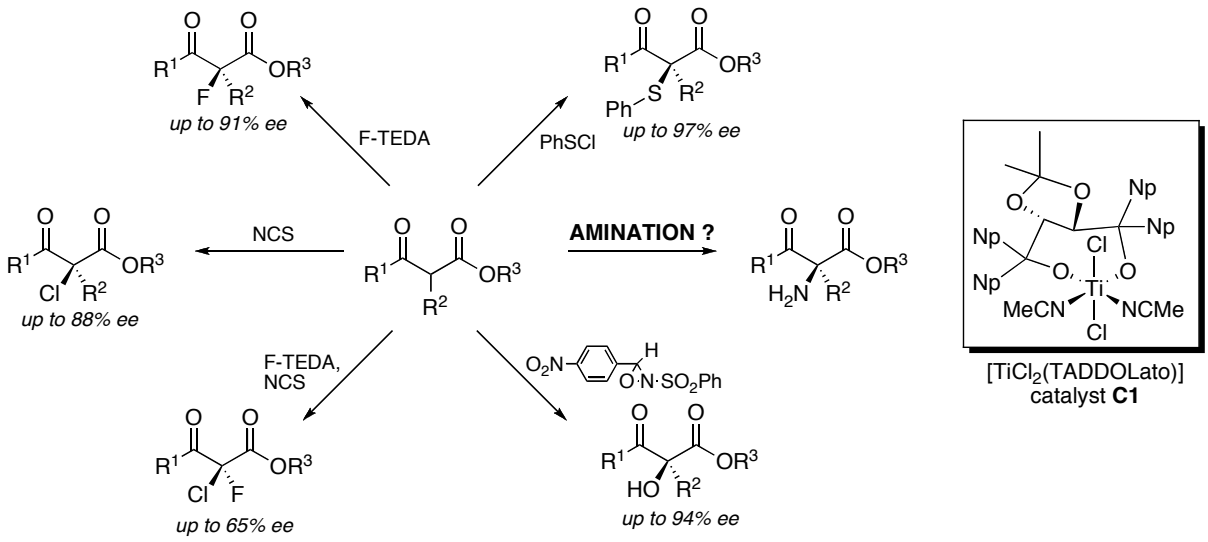


Scheme 26: One-pot fluorination / amination followed by the attempted reduction.

In order to solve this problem, new catalytic systems and aminating reagents had to be screened.

1.2.1.1 Catalytic System

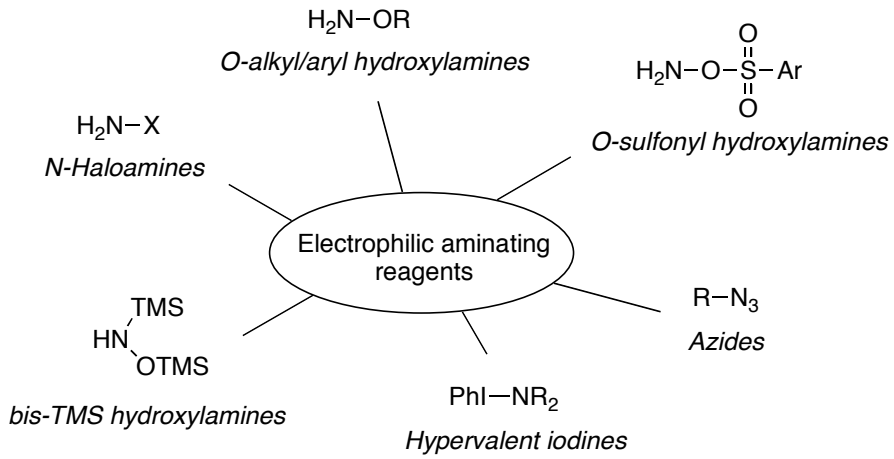
As shown above, the [$TiCl_2$(TADDOLato)] complex showed to be the catalyst of choice for the enantioselective electrophilic halogenation (fluorination[27], chlorination[33] and bromination[33]) as well as for the enantioselective electrophilic sulfenylation[34] and hydroxylation.[35] The new idea consist in the electrophilic amination of ß-keto esters with electrophilic amination reagents under the conditions of [Ti(TADDOLato)] catalysis (Scheme 27).



Scheme 27: Enantioselective transfer reactions of halogens, oxygen and sulfur electrophilic reagents to ß-keto-esters.

1.2.1.2 Aminating Reagents

In order to avoid the problem of the cleavage of the N-N bond, the best suited reagent leading to a C-N bond formation have to be identified. Some compounds, which behave as "$^{+}NR_2$" equivalents, are selected and presented in Scheme 28.



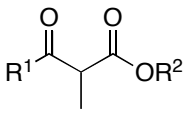
Scheme 28: Selected electrophilic aminating reagents.

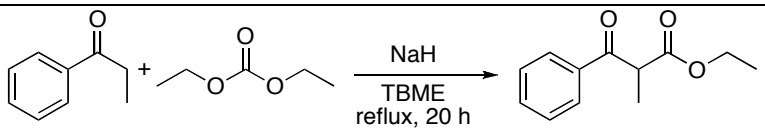
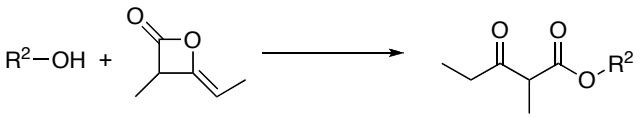
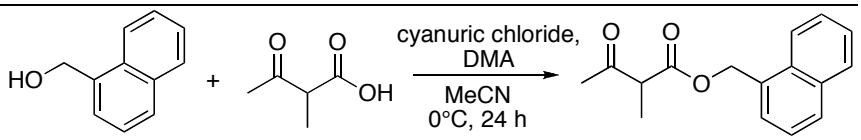
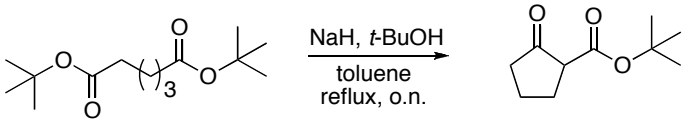
1.2.2 Synthesis of the Reagents

1.2.2.1 ß-Keto Ester

The unsubstituted substrates for amination were either commercially available (**S1**) or synthesized (**S2-S8**). ß-Keto esters were prepared as reported in *Lukas Hintermann*'s thesis (Table 4).[96]

Table 4: Assignment and synthesis of structures **S1-S8**.

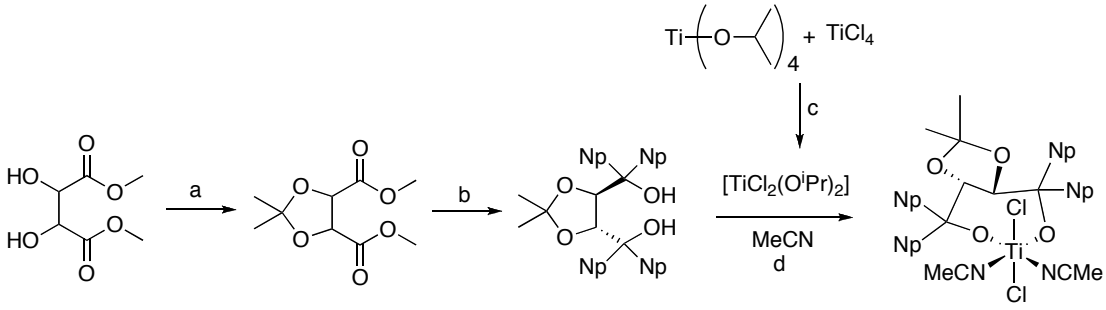


	R^1	R^2	**Synthesis**
S1	Me	Et	commercially available
S2	Ph	Et	
S3	Et	Ph	
S4	Et	Bn	
S5	Et	$CH(Ph)_2$	
S6	Et	$CH_2Ph(^iPr)_3$	
S7	Me	CH_2Np	
S8		^{t}Bu	

The synthesis of the ß-keto esters **S3-S6** proceeded via reaction of the alcohol R^2OH with the methylketene dimer, prepared previously. Regarding the quality of the methylketene dimer, which is known to dimerize to 6-acetyl-3,5-dimethyl-3-propionyl-2H-pyran-2,4(3H)-dione upon storage, the yield of the prepared ß-keto esters varied between 80% and 95%.[97]

1.2.2.2 $TiCl_2$(TADDOLato) Complex

The fully characterized [$TiCl_2$(*R,R*-TADDOLato)] complex **C1** was developed and applied in asymmetric halogenation, hydroxylation and sulfenylation of ß-keto ester in our group. The *R,R*-enantiomeric form of the complex was prepared according to reported procedures and used throughout this work (Scheme 29).[98,30]



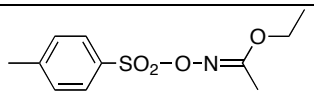
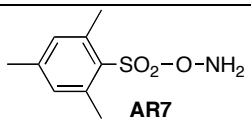
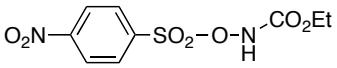
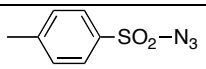
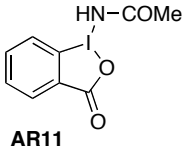
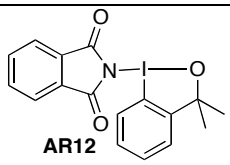
Scheme 29: Synthesis of [$TiCl_2$(*R,R*-TADDOLato)] complex **C1**. a) $BF_3 \cdot OEt_2$, acetone, rt, 24 h; b) Mg, 1-bromonaphtalene, THF, rt to reflux, overnight; c) hexane, rt, 6 h; d) MeCN, rt, 2 h.

1.2.2.3 Aminating Reagents

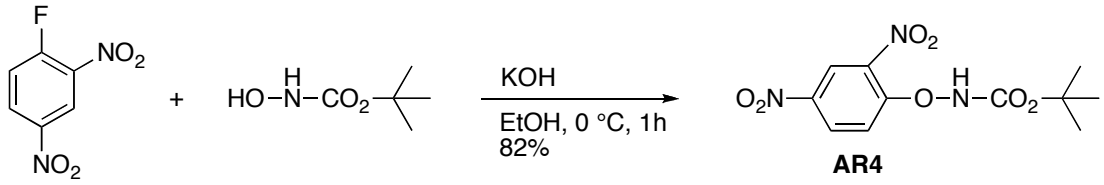
The aminating reagents were either commercially available (**AR1**, **AR2**, **AR3**, **AR5**, **AR6**, **AR9**) or synthesized (**AR4**, **AR7**, **AR8**, **AR10**, **AR11**, **AR12**). The used reagents are summarized in Table 5.

Table 5: Aminating reagents **AR1-AR12**.

***N*-chloroamine**	**AR1**: chloramine T
bis-TMS-hydroxylamine	**AR2**
***O*-alkyl/aryl hydroxylamine**	**AR3** $H_2N-OCH_3 \cdot HCl$ **AR4** **AR5**

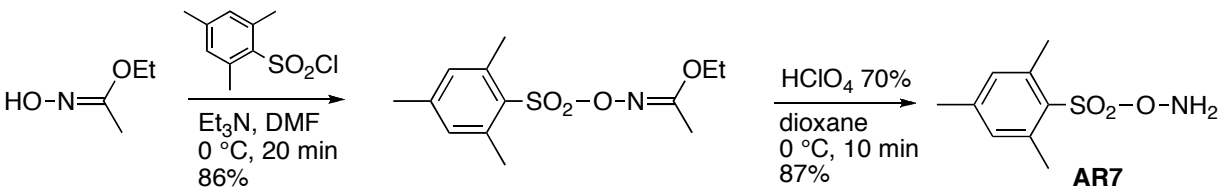
***O*-sulfonyl hydroxylamine**	 **AR6**  **AR7**  **AR8**
azides	NaN_3 **AR9**  **AR10**
hypervalent iodine	 **AR11**  **AR12**

t-Butyl *N*-2,4-dinitrophenyloxycarbamate **AR4** is synthesized in good yield (Scheme 30). The synthesis is based on the reaction of suitably activated aryl halide with *N*-hydroxy-carbamates.[99] The use of *N*-hydroxyurethane revealed itself as a failure due to the sensitivity of the N-O bond toward the hydrolytic conditions employed. On the other hand, the use of *t*-butyl *N*-hydroxycarbamate yielded the desired *t*-butyl *N*-aryloxycarbamate.



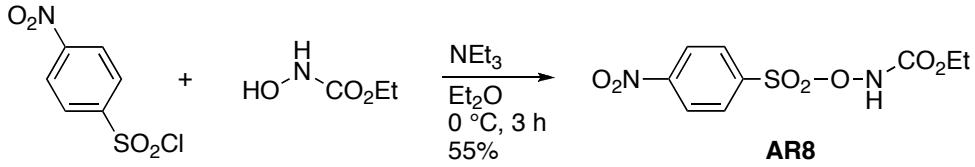
Scheme 30: Synthesis of *t*-butyl *N*-2,4-dinitrophenyloxycarbamate **AR4**.

Ethyl *O*-(mesitylenesulfonyl)acetohydroxamate, prepared from the readily accessible ethyl hydroxamate and mesitylenesulfonyl chloride, were treated with 70% perchloric acid at 0 °C for 10 min to yield crystalline *O*-mesitylenesulfonyl hydroxylamine **AR7** in high yield (Scheme 31).[100] **AR7** is quite stable and can be kept in a freezer for several weeks. The products obtained by this method contain between 20-30% of water (estimated by iodometry) but, if necessary, they can be recrystallized from petroleum ether.



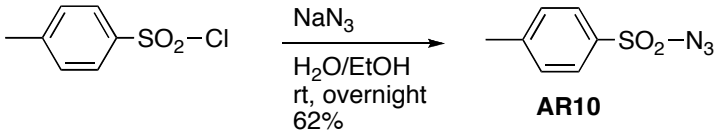
Scheme 31: Synthesis of *O*-mesitylenesulfonyl hydroxylamine **AR7**.

Ethyl *N*-*p*-nitrophenylsulfonyloxycarbamate **AR8** is prepared from *N*-hydroxyurethan and *p*-nitro- benzenesulfonyl chloride in 57% yield,[101] together with *N,O*-di-*p*-nitrobenzene-sulfonyl- hydroxyurethan (Scheme 32). **AR8** is soluble in more polar organic solvents and is converted to its anion by weak bases, such as triethylamine.



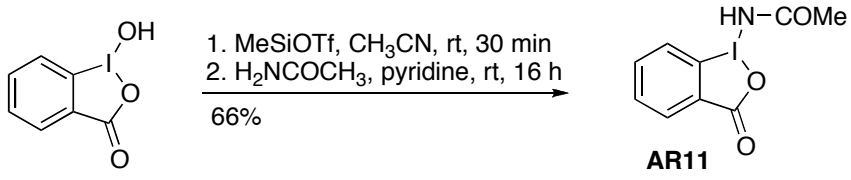
Scheme 32: Synthesis of *N*-*p*-nitrobenzenesulfonoxyurethan **AR8**.

The reaction of *p*-toluenesulfonyl chloride with sodium azide **AR9** in a 1:4 mixture of water/ethanol afforded *p*-tosyl azide **AR10** in 62% yield (Scheme 33).



Scheme 33: Synthesis of *p*-tosyl azide **AR10**.

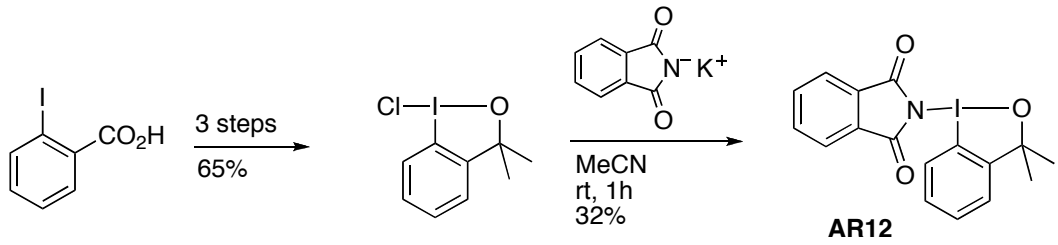
Amidobenziodoxoles can be conveniently prepared in one step from the commercial 2-iodosylbenzoic acid, trimethylsilyltriflate and the appropriate amide.[102] Acetamide benziodoxole **AR11**, prepared with the corresponding acetamide, is isolated as thermally stable, white microcrystalline solid (Scheme 34).



Scheme 34: Synthesis of acetamide benziodoxole **AR11**.

The second hypervalent iodine compound, 1-phtalimide-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole **AR12**, was synthesized following the procedure developed in our group for the trifluoromethylation of 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole.[103] Interestingly, the sequence starting from chloride could be performed in a one step protocol. The previous

sequence for the synthesis of the chloride precursor, starting from 2-iodobenzoic acid, is very well suited to be adapted as a large scale process, since the only purification steps involved are two distillations and two crystallizations in an overall yield of 65%. In our case, dry potassium phthalimide was mixed with 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole in acetonitrile to yield the desired **AR12** (Scheme 35).



Scheme 35: Synthesis of 1-phtalimide-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole **AR12**.

This new compound could be the starting point for a new class of electrophilic aminating reagent based on hypervalent λ^3-organoiodine.

1.2.3 Attempted Catalytic Enantioselective Amination using the Ti(TADDOLato) Complex

We initiated our investigations by reacting the selected ß-keto ester **S2** with the aminating reagents described above using 10 mol% of [$TiCl_2$(*R,R*-TADDOLato)] complex as catalyst. Depending on the aminating agent, two reaction scenarios were observed: either no conversion occurred or a new product was formed in low yield (Figure 4). Its structure could not be unambiguously confirmed by ^{1}H NMR. Although it suggested substitution of the α-proton (the *quartet* of the α-proton (*CH*) disappeared and the *doublet* of the CH_3 on the α-carbon turned into a *singlet*, Figure 4), the definite proof for the presence of the amino group as a substituent at the alpha atom could not be provided by NMR analysis.

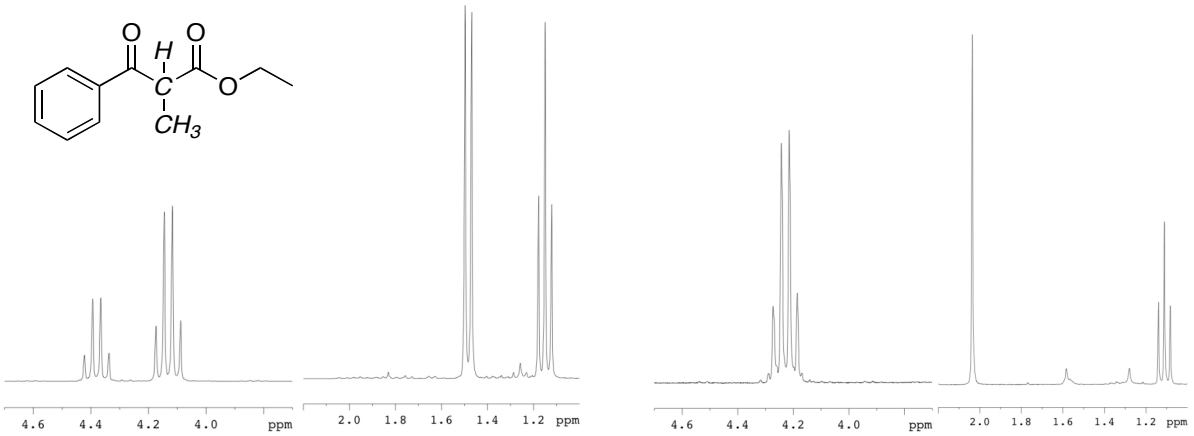
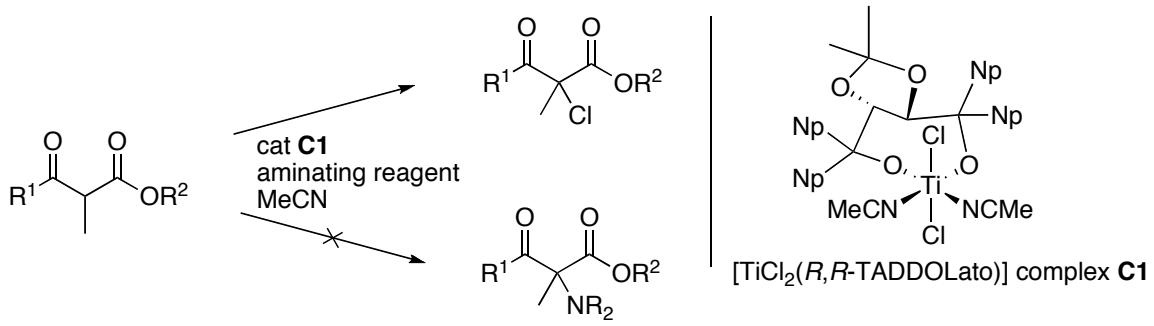


Figure 4: ^{1}H-NMR of the ß-keto ester **S2** and of the reaction mixture.

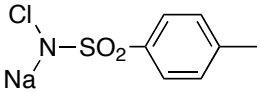
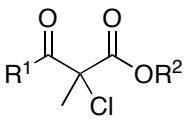
Only after further analytical inspection (HPLC, GC-MS and EI-MS), we could conclude that, unfortunately, no product of an amination reaction was formed but, surprisingly, chlorination took place exclusively (Scheme 36).

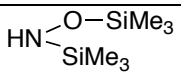
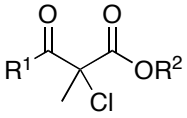
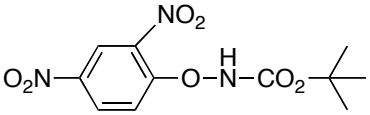
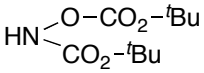
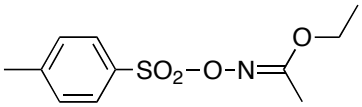
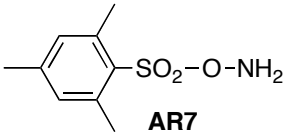
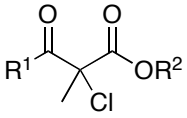
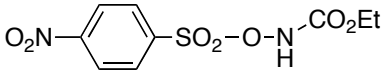
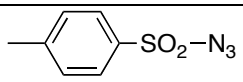
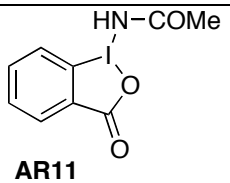
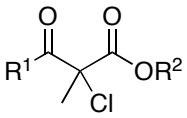
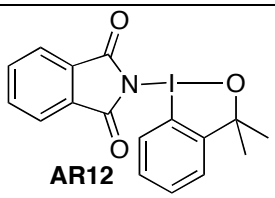


Scheme 36: Two possibilities of reactions with [$TiCl_2$(*R,R*-TADDOLato)] complex.

The outcome of the attempted aminations based on the aminating reagent is given in Table 6 (chlorination as side-reaction vs no reaction).

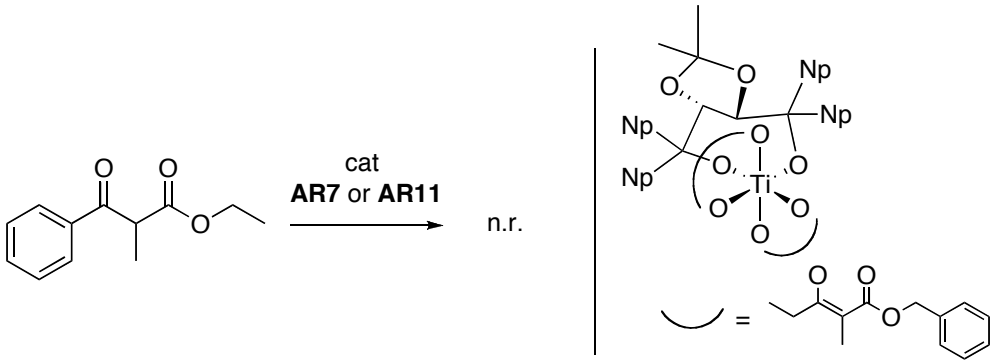
Table 6: Chlorination of ß-keto ester **S2** with selected aminating reagents in the presence of 10 mol% of [$TiCl_2$(*R,R*-TADDOLato)] catalyst **C1**.

Entry	Aminating reagents	Products
1	*N*-Haloamine  **AR1**: chloramine T	 yield[a]: 42% *ee*[b]: rac.

Entry	Aminating reagents		Products
2	Bis-TMS-hydroxylamine	 **AR2**	n.r.
3	*O*-alkyl/aryl hydroxylamine	 **AR3**	 yield[a]: 30% *ee*[b]: rac.
4		 **AR4**	n.r.
5		 **AR5**	n.r.
6	*O*-sulfonyl hydroxylamine	 **AR6**	n.r.
7		 **AR7**	 yield[a]: 17% *ee*[b]: 62%
8		 **AR8**	degradation
9	Azides	 **AR9**	n.r.
10		 **AR10**	n.r.
11	Hypervalent iodine compounds	 **AR11**	 yield[a]: 7% *ee*[b]: rac.
12		 **AR12**	n.r.

[a] Isolated yields; [b] *ee* measured by chiral HPLC

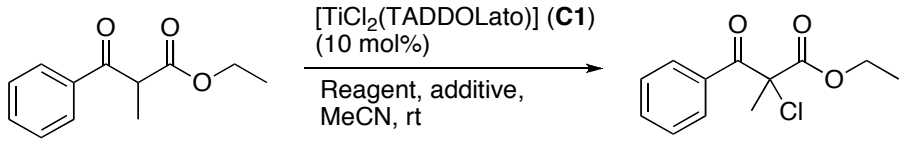
While in the case of the aminating reagents **AR1** and **AR3** the source of the chlorine atom could not be unambiguously determined, the formation of the chlorinated product in the presence of a chlorine-free aminating reagent could be only explained by the transfer of chlorine from the Ti-catalyst to the substrate. This is also in agreement with the fact that with 10 mol% [$TiCl_2$(*R,R*-TADDOLato)], the theoretical yield of 20% of chlorinated product was never exceeded (17% with **AR7**, 7% with **AR11**). Further evidence for our hypothesis was provided by the experiment with a chloride free Ti catalyst, as we observed no chlorinated product (Scheme 37). Entry 7 showed an interesting result with an *ee* up to 62%, which is a higher enantiomeric excess than the one reported using the same substrate and the same [$TiCl_2$(*R,R*-TADDOLato)] catalyst but with NCS as chlorinating reagent.[33]

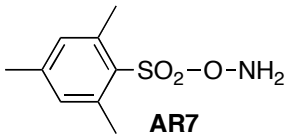
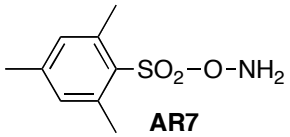


Scheme 37: Reaction carried out with a chloride free Ti catalyst.

We reasoned that the addition of a chloride source should increase the extent of the catalytic chlorination. Interestingly, this is not the case. When one equivalent of NaCl is added to the catalytic chlorination of **S2** with NCS, basically the same result is observed as without additive (Table 7, entry 1 and 3). Interestingly, for our new *O*-sulfonyl hydroxylamine **AR7** system, the yield decreased slightly upon adding one equivalent of NaCl whereas the *ee* increased significantly growing from 62% *ee* without additive up to 79% *ee* with one equivalent of chloride salt (runs 2 and 4).

Table 7: Influence of additives on the catalytic chlorination of **S2**.



Entry	Reagent	Additive (1 eq)	Time [h]	Yield[a] [%]	*ee*[b] [%]
1	NCS	-	1.5	91	54
2	 **AR7**	-	18	17	62
3	NCS	NaCl	2	90	54
4	 **AR7**	NaCl	18	12	79

[a] Isolated yields; [b] *ee* measured by chiral HPLC

As the [$TiCl_2$(*R,R*-TADDOLato)] catalyst is a source for the formation of an electrophilic chlorinating agent, other chlorides free catalysts should be tested in order to see if the amination proceeds.

1.2.4 Variation of the Catalytically Active Metal

Trying to reach the goal of the amination of ß-keto esters, another approach was chosen. *O*-(*tert*-Butyldimethylsilyl)hydroxylamine ($TBSONH_2$) was used as the potential aminating agent and several selected complexes were tested. When the catalyst was prepared from $Pd(OAc)_2$, $Mg(OTf)_2$, AgOTf or CuOTf and equimolar amount of (*S,S*)-Ph-box or binap as ligand, the reaction did not take place and degradation products could be observed. On the other hand, in the case of $Zn(OTf)_2$ or $Cu(OTf)_2$ in combination with (*S,S*)-Ph-box or binap ligands, HPLC confirmed a complete consumption of the starting material. The resulted product was isolated in 40% yield. GC combined with ESI-MS analysis revealed a formation of a new compound as a mixture of two isomers (RT = 21.9 min and 22.7 min; MW = 335.5 $gmol^{-1}$, Figure 5).

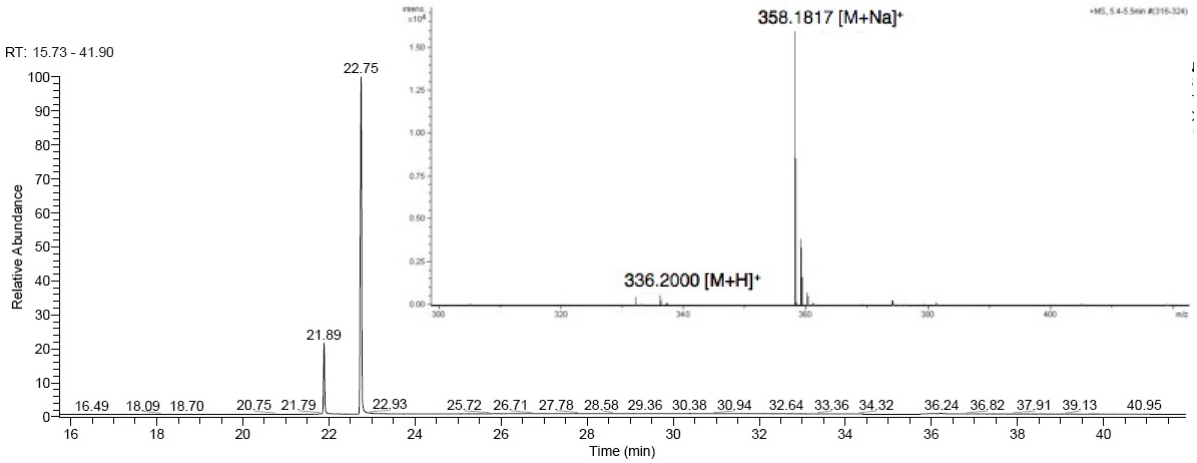
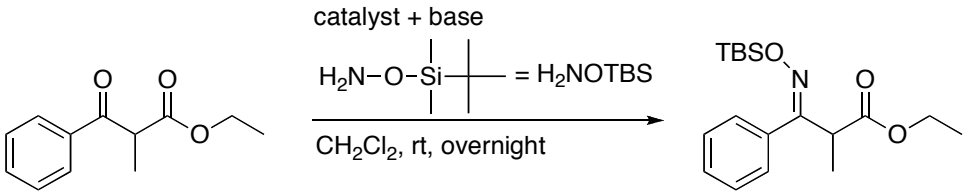


Figure 5: Two different isomers resulting from the reaction of ß-keto ester **S2** with $TBSONH_2$ catalysed with Cu/box detected by GC and ESI-MS

After extensive NMR studies, we could conclude that the catalytic electrophilic amination of ß-keto ester did not proceed. The corresponding ß-oxime ester was formed as a mixture of E/Z-isomers (7.9:1) (Table 8).

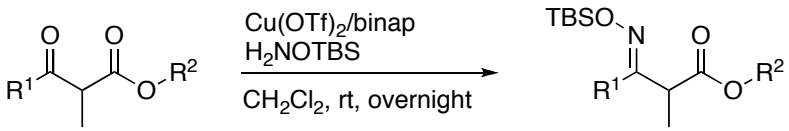
Table 8: Oximation of ethyl 2-methyl-3-oxo-phenylpropanoate (**S2**) with $TBSONH_2$.



Catalyst	Base	Yield [%]
-	-	
Pd(OAc)	Ph-box, binap	
$Mg(OTf)_2$	Ph-box, binap	no conversion
AgOTf	Ph-box, binap	
CuOTf	Ph-box, binap	
$Zn(OTf)_2$	Ph-box	trace
	binap	7
$Cu(OTf)_2$	Ph-box	30
	binap	40

Using ethyl 2-methyl-3-oxo-phenylpropanoate (**S2**) as substrate, the best result was found using $Cu(OTf)_2$ as catalyst combined with binap ligand to obtain a yield of 40%.
Changing the structure of the ß-keto ester to benzyl 2-methyl-3-oxo-pentanoate **S4** resulted in a slightly increased yield of 42% (Table 9).

Table 9: Oximation of differently substituted ß-keto ester.



Substrate	R^1	R^2	Yield [%]
S2	Ph	Et	40
S4	Et	Bn	42
S5	Et	$CH_2(Ph)_2$	39
S6	Et	$CH_2Ph(^iPr)_3$	24
S7	Me	CH_2Np	21

This novel strategy represents the first metal-catalyzed synthesis of O-TBS oximes from ketones.

1.3 Conclusions

In summary, we attempted the electrophilic amination of ß-keto esters using a variety of aminating agents and catalysts. However, the desired product could never be observed and this project had to be discontinued.

We also synthesized a new electrophilic aminating reagent **AR12** based on hypervalent λ^3-organoiodine compound inspired by the work done in our group on similar organoiodine reagents used as a source of electrophilic CF_3.[103] Further experiments should be performed to determine its potential as electrophilic aminating reagent.

The [$TiCl_2$(*R,R*-TADDOLato)] complex proved not to be the catalyst of choice for the electrophilic amination of ß-keto esters, despite several conditions tested. Instead, its use as a catalyst in combination with several different aminating agents (**AR1**- **AR12**) resulted either in no conversion or the formation of chlorinated product. As described previously in our group,[33] the [$TiCl_2$(*R,R*-TADDOLato)] catalyst acted as a source of chloride, due to its two chloride ligands. Although only some preliminary experiments were performed, more studies with a chloride free titanium catalyst should be tried in the future.

In order to avoid this chloride transfer process, several other metals were analyzed. *O*-(*tert*-butyldimethylsilyl)hydroxylamine ($TBSONH_2$) was chosen as the standard aminating reagent and palladium, magnesium, silver, copper (I and II) and zinc were screened using either Ph-box or binap as ligands. Interestingly, no conversion could be observed for the majority of these metals but using zinc or copper (II) resulted in the formation of the oxime product in moderate yield (up to 40%). This new way to produce ß-oxime esters constitutes the first metal-catalyzed reaction starting from ß-keto esters.

1.4 References

[1] Y. Takeuchi, *J. Fluorine Chem.* **2000**, *105*, 215.

[2] J-A. Ma, *Angew. Chem. Int. Ed.* **2003**, *42*, 4290.

[3] For α-amino acids: a) G. C. Barrett, *Chemistry and Biochemistry of the Amino Acids,* Chapman and Hall, London, **1985**; b) J. H. Jones, *Amino Acids and Peptides, Vol. 23*, The Royal Society of Chemistry, London, **1992** (Specialist Periodical Report). For ß-amino acids: c) "The Chemistry and Biology of ß-Amino Acids": (Ed: W. J. Hoekstra), *Curr. Med. Chem.* **1999**, *6*, 905-1004; d) C. A. Bewley, D. J. Faulkner, *Angew. Chem. Int. Ed.* **1998**, *37*, 2162; e) A. H. Berks, *Tetrahedron* **1996**, *52*, 331.

[4] J. Seyden-Penne, *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*, Wiley, New York, **1995**.

[5] Reviews: a) R. M. Williams, *Synthesis of Optically Active α-Amino Acids*, Pergamon, Oxford, **1989**; b) T. Wirth, *Angew. Chem. Int. Ed.* **1997**, *36*, 225; c) C. Cativiela, M. D. Diaz-de-Villegas, *Tetrahedron: Asymmetry* **1998**, *9*, 3517; d) C. Cativiela, M. D. Diaz-de-Villegas, *Tetrahedron: Asymmetry* **2000**, *11*, 645.

[6] L. Yet, *Angew. Chem. Int. Ed.* **2001**, *40*, 875.

[7] Highlight: K. Rossen, *Angew. Chem. Int. Ed.* **2001**, *40*, 4611. Review: R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40.

[8] a) B. M. Trost, *Chem. Pharm. Bull.* **2002***, 50*, 1; b) E. J. Corey, F. Xu, M. C. Noe, *J. Am. Chem. Soc.* **1997**, *119*, 12414; c) Y. N. Belokon, K. A. Kochetkov, T. D. Churkina, N. S. Ikonnikov, O. V. Larionov, S. R. Harutyunyan, S. Vyskocil, M. North, H. B. Kagan, *Angew. Chem. Int. Ed.* **2001**, *40*, 1948; d) K. Juhl, N. Gathergood, K. A. Jorgensen, *Angew. Chem. Int. Ed.* **2001**, *40*, 2995.

[9] R. O. Duthaler, *Tetrahedron* **1994**, *50*, 1539.

[10] Y. K. Chen, A. E. Lurain, P. J. Walsh, *J. Am. Chem. Soc.* **2002**, *124*, 12225.

[11] a) A. Bogevig, K. Huhl, N. Kumaragurubaran, W. Zhang, K. A. Jorgensen, *Angew. Chem. Int. Ed.* **2002**, *41*, 1790; b) B. List, *J. Am. Chem. Soc.* **2002**, *124*, 5656.

[12] V. P. Kukhar, V. A. Soloshonok, *Fluorine Containing Amino Acids: Synthesis and Properties*; Wiley: New York, **1995**.

[13] a) In *Organofluorine Chemistry: Principles and Commercial Applications;* R. E. Banks, B. E. Smart, J. C. Tatlow, Eds.; Plenum: New York, **1994**; b) J. T. Welch, S. Eswaraksrishnan, *Fluorine in Bioorganic Chemistry;* Wiley: New York, **1991**; c) In *Organofluorine Chemicals and Their Industrial Applications;* R. E. Ed; Ellis Harwood: New York, **1979**.

[14] R. Filler, Y. Kobayashi, L. M. Yagupolskii, *Biomedical Aspects of Fluorine Chemistry*; Elsevier: Amsterdam, **1993**.

[15] N. C. Yoder, K. Kumar, *Chem. Soc. Rev.* **2002**, *31*, 335.

[16] E. N. G. Marsh, *Chem. Biol.* **2000**, *7*, 153.

[17] a) B. Bilgiçer, A. Fichera, K. Kumar, *J. Am. Chem. Soc.* **2001**, *123*, 4393; b) C. Renner, S. Alefelder, J. H. Bae, N. Budisa, R. Huber, L. Moroder, *Angew. Chem. Int. Ed.* **2001**, *40*, 923; c) M. Sani, L. Bruché, G. Chiva, S. Frustero, J. Piera, A. Volonterio, M. Zanda, *Angew. Chem. Int. Ed.* **2003**, *42*, 2060.

[18] a) V. Tolman, *Amino Acids*, **1996**, *11*, 15; b) A. Sutherland, C. L. Willis, *Nat. Prod. Rep.* **2000**, *17*, 621; c) R. Dave, B. Badet, P. Meffre, *Amino Acids* **2003**, *24*, 245; d) T. Katagiri, K. Uneyama, *Chirality* **2003**, *15*, 4.

[19] R. Crossley, *Tetrahedron* **1992**, *48*, 8155.

[20] J. A. Wilkinson, *Chem. Rev.* **1992**, *92*, 505.

[21] S. Rozen, *Acc. Chem. Res.* **1996**, *29*, 243.

[22] D. H. R. Barton, L. S. Godinho, R. H. Hesse, M. M. Pechet, *Chem. Commun.* **1968**, 804.

[23] O. Lerman, S. Rozen, *J. Org. Chem.* **1983**, *48*, 724.

[24] G. S. Lal, G. P. Pez, R. G. Syvret, *Chem. Rev.* **1996**, *96*, 1737.

[25] E. Differding, H. Ofner, *Synlett* **1991**, 187.

[26] a) R. E. Banks, M. K. Beshesh, S. N. Mohialdin-Khaffaf, I. Sharif, *J. Chem. Soc. Perkin Trans. 1* **1996**, 2069; b) R. E. Banks, S. N. Mohialdin-Khaffaf, G. S. Lal, I. Sharif, R. B. Syvret, *J. Chem. Soc. Chem. Commun.* **1992**, 595.

[27] a) L. Hintermann, A. Togni, *Angew. Chem. Int. Ed.* **2000**, *39*, 4359; b) A. Togni, A. Mezzetti, P. Barthazy, C. Becker, I. Devillers, R. Frantz, L. Hintermann, M. Perseghini, M. Sanna, *Chimia* **2001**, *55*, 801.

[28] M. Perseghini, M. ETH, Ph. D. Thesis No. 15195, Zürich, Switzerland, 2003.

[29] M. Perseghini, M. Massaccesi, Y. Liu, A. Togni, *Tetrahedron* **2006**, *62*, 7180.

[30] L. Hintermann, D. Broggini, A. Togni, *Helv. Chim. Acta* **2002**, *85*, 1597.

[31] S. Piana, I. Devillers, A. Togni, U. Röthlisberger, *Angew. Chem. Int. Ed.* **2002**, *41*, 979.

[32] M. Viciu, A. Togni, unpublished results.

[33] L Hintermann, A. Togni, *Helv. Chim. Acta* **2000**, *83*, 2425.

[34] a) M. Jereb, A. Togni, *Org. Lett.* **2005**, *7*, 4041; b) M. Jereb, A. Togni, *Chem. Eur. J.* **2007**, *13*, 9384.

[35] P. Y. Toullec, C. Bonaccorsi, A. Mezzetti, A. Togni, *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101* 5810.

[36] a) M. Sodeoka, Y. Hamashima, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 941; b) Y. Hamashima, M. Sodeoka, *Synlett* **2006**, 1467.

[37] J-A. Ma, D. Cahard, *Tetrahedron: Asymmetry* **2004**, *15*, 1007.

[38] N. Shibata, T. Ishimaru, T. Nagai, J. Kohno, T. Toru, *Synlett* **2004**, 1703.

[39] D. S. Reddy, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem. Int. Ed.* **2008**, *47*, 164.

[40] J-A. Ma, D. Cahard, *J. Fluorine Chem.* **2004**, *125*, 1357.

[41] S. Suzuki, H. Furuno, Y. Yokoyama, J. Inanaga, *Tetrahedron: Asymmetry* **2006**, *17*, 504.

[42] K. Shibatomi, Y. Tsuzuki, S. Nakata, Y. Sumikawa, S. Iwasa, *Synlett* **2007**, 551.

[43] a) C. Becker, ETH, Ph. D. Thesis No 15699, Zürich, Switzerland, 2004; b) M. Althaus, C. Becker, A. Togni, A. Mezzetti, *Organometallics* **2007**, *26*, 5902.

[44] E. Erdik, *Tetrahedron* **2004**, *60*, 8747.

[45] In *Modern Amination Methods*, Ricci, A., Ed.; Wiley-VCH: Weinheim, **2000**.

[46] R. M. Williams, J. A. Hendrix, *Chem. Rev.* **1992**, *92*, 889.

[47] P. Kovacic, M.K. Lowery, K. W. Field, *Chem Rev.* **1970**, *70*, 639.

[48] S. Yamada, T. Oguri, T. Shioiri, *J. Chem. Soc. Chem. Commun.* **1972**, 623.

[49] T. Oguri, T. Shioiri, S. Yamada, *Chem. Pharm. Bull.* **1975**, 23167.

[50] Y. Tamura, J. Minamikawa, M. Ikeda, *Synthesis* **1977**, 1.

[51] a) T. Sheradsky, G. Salemnick, Z. Nir, *Tetrahedron* **1972**, *28*, 3833; b) T. Sheradsky, Z. Nir, *Tetrahedron Lett.* **1969**, 77.

[52] A. S. Radhakrishna, G. M. Loudon, M. J. Miller, *J. Org. Chem.* **1979**, *44*, 4836.

[53] J. A. Smulik, A. Vedejs, *Org. Lett.* **2003**, *5*, 4187.

[54] G. Boche, N. Mayer, M. Bernheim, K. Wagner, *Angew. Chem. Int. Ed.* **1978**, *17*, 687.

[55] L. A. Carpino, C. A. Giza, B. A. Carpino, *J. Am. Chem. Soc.* **1959**, *81*, 955.

[56] a) T. W. Greene, P. G. M. Wuts, In *Protective Groups in Organic Synthesis,* 2nd ed.; Wiley: New York, 1991; p 327. b) P. J. Kocienski, In *Protecting Groups,* Georg Thieme: Stuttgart, 1994; p 192.

[57] N. S. Shaikh, A. S. Gajare, V. H. Deshpande, A. V. Bedekar, *Tetrahedron Lett.* **2000***, 41*, 385.

[58] M. Barani, S. Fioravanti, L. Pellacani, P. A. Tardella, *Tetrahedron* **1994**, *50*, 11235.

[59] A. Casarini, P. Dembech, D. Lazzari, E. Marini, G. Reginato, A. Ricci, G. Seconi, *J. Org. Chem.* **1993**, *58*, 5620.

[60] S. Andrea, E. Schmitz, *Synthesis* **1991**, 327.

[61] S. Andrea, E. Schmitz, J-P. Wulf, B. Schutz, *Liebigs Ann. Chem.* **1992**, 239.

[62] J. Vidal, L. Gay, S. Steron, A. Collet, *J. Org. Chem.* **1993**, *58*, 4791.

[63] D. Enders, C. Poiesz, R. Joseph, *Tetrahedron: Asymmetry* **1998**, *9*, 3709.

[64] A. Armstrong, M. A. Atkin, S. Swallow, *Tetrahedron Lett.* **2000***, 41*, 2247.

[65] a) P. C. B. Page, V. L. Murrel, C. Limousin, D. D. P. Laffan, D. Bethell, A. M. Z. Slawin, T. A. D. Smith, *J. Org. Chem.* **2000***, 65*, 4204. b) P. C. B. Page, C. Limousin, V. L. Murrel, *J. Org. Chem.* **2002***, 67*, 7787.

[66] R. R. Phillips, *Org. React.* **1959**, *10*, 143.

[67] E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988***, 88*, 298.

[68] M. Regitz, G. Mass, In *Diazo Compounds, Properties and Synthesis,* Academic: New York, 1986; Chapter 13.

[69] a) D. A. Evans, T. C. Britton, *J. Am. Chem. Soc.* **1987**, *109*, 6881; b) D. A. Evans, T. C. Britton, J. A. Ellman, R. L. Dorow, *J. Am. Chem. Soc.* **1990**, *112*, 4011; c) D. A. Evans, D. A. Evrard, S. D. Rychnovsky, T. Früh, W. G. Whittingham, K. M. Devries, *Tetrahedron Lett.* **1992**, *33*, 1189.

[70] N. S. Shaika, A. S. Gajare, V. H. Deshpande, A. V. Bedekar, *Tetrahedron Lett.* **2000**, *41*, 385.

[71] a) W. Oppolzer, O. Tamura, *Tetrahedron Lett.* **1990**, *31*,991. b) W. Oppolzer, O. Tamura, G. Sundarababu, M. Signer, *J. Am. Chem. Soc.* **1992**, *114*, 5900.

[72] D. A. Evans, M. A. Faul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, *116*, 2742.

[73] D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.* **1993**, *115*, 5328.

[74] Z. Liz, J. Conser, E. N. Jacobsen, *J. Am. Chem. Soc.* **1993**, *115*, 5326.

[75] P. Phukan, A. Sudalai, *Tetrahedron: Asymmetry* **1998**, *9*, 1001.

[76] D. A. Evans, S. G. Nelson, *J. Am. Chem. Soc.* **1997**, *119*, 6452.

[77] Y. Yamashita, H. Ishitani, S. Kobayashi, *Can. J. Chem.* **2000**, *78*, 666.

[78] D. A. Evans, D. S. Johnson, *Org. Lett.* **1999**, *1*, 595.

[79] a) K. Juhl, K. A. Jorgenson, *J. Am. Chem. Soc.* **2002**, *124*, 2420. b) M. Marigo, J. Juhl, K. A. Jorgenson, *Angew. Chem. Int. Ed.* **2003**, *42*, 1367.

[80] a) M. Marigo, N. Kumaragurubaran, K. A. Jorgensen, *Synthesis* **2005***, 6*, 957. b) Y. K. Kang, D. Y. Kim, *Tetraheron Lett.* **2006**, *47*, 4565.

[81] S. Min Kim, H. R. Kim, D. Y. Kim, D. Y. Kim, *Org. Lett.* **2005**, *7*, 2309.

[82] G. Dessole, L. Bernardi, B. F. Bonini, E. Capito, M. Fochi, R. P. Herrera, A. Ricci, G. Cahiez, *J. Org. Chem.* **2004**, *24*, 8525.

[83] J. S. Yadav, B. V. S. Reddy, G. Veerendhar, R. S. Rao, K. Nagaiah, *Chem. Lett.* **2002**, *3*, 318.

[84] S. Bombek, F. Pozgan, M. Kocebar, S. Polanc, *J. Org. Chem.* **2004**, *69*, 2224.

[85] B. List, *J. Am. Chem. Soc.* **2002**, *124*, 5656.

[86] a) N. Kumaragurubaran, K. Juhl, W. Zhuang, A. Bogevig, K. A. Jorgensen, *J. Am. Chem. Soc.* **2002**, *124*, 6254. c) A. Bogevig, K. Juhl, N. Kumaragurubaran, W. Zhuang, K. A. Jorgensen, *Angew. Chem. Int. Ed.* **2002***, 41*, 1790.

[87] H. Vogh, S. Vanderheiden, S. Bräse, *Chem. Comm.* **2003**, 2448.

[88] a) C. Thomassigny, D. Prim, C. Greck, *Tetrahedron Lett.* **2006**, *47*, 1117. b) N. Dahlin, A Bogevig, H. Adolfsson, *Adv. Synth. Catal.* **2004**, *346*, 1101.

[89] R. O. Duthaler, *Angew. Chem. Int. Ed.* **2003**, *42*, 975.

[90] J. M. Harris, E. A. Bolessa, A. J. Mendonca, S. Feng, J. C. Vederas, *J. Chem. Soc. Perkin Trans. 1,* **1995**, 1945.

[91] M. A. Brimble, C. K. Y. Lee, *Tetrahedron: Asymmetry* **1998**, *9*, 873.

[92] W. Oppolzer, R. Moretti, *Helv. Chim. Acta,* **1986**, *69*, 1923.

[93] D. P. Huber, K. Stanek, A. Togni, *Tetrahedron: Asymmetry* **2006**, *17*, 658.

[94] D. P. Huber, ETH, Ph. D. Thesis No 16761, Zürich, Switzerland, 2006.

[95] a) Hydrogenation with Raney-Ni: B. J. Fitzsimmons, Y. Leblanc, J. Rokach, *J. Am. Chem. Soc.* **1987**, *109*, 285; b) PtO_2 or Pd based catalysts: E. J. Corey, R. J. McCaully, H. S. Sachdew, *J. Am. Chem. Soc.* **1970**, *92*, 2476; SmI_2: M. J. Burk, J. E. Feaster, *J. Am. Chem. Soc.* **1992**, *114*, 6266; oxidation with magnesium: R. Fernandez, A. Ferrete, J. M. Llera, A. Magiz, E. Martin-Zamora, E. Diez, J. M. Lassaletta, *Chem. Eur. J.* **2004**, *10*, 737.

[96] L. Hintermann, M. ETH, Ph. D. Thesis No. 13892, Zürich, Switzerland, 2000.

[97] J. A. Hyatt, P. L. Feldman, R. J. Clement, *J. Org. Chem.* **1984**, *49*, 105.

[98] A. K. Beck, B. Bastani, D. A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi, L. La Vecchia, *Chimia* **1991**, *45*, 238.

[99] T. Sheradsky, G. Salemnick, Z. Nir, *Tetrahedron* **1972**, *28*, 3833.

[100] Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, M. Ikeda, *J. Org. Chem.* **1973**, *38*, 1239.

[101] W. Lwowski, T. J. Maricich, *J. Am. Chem. Soc.* **1965**, *87*, 3630.

[102] V. V. Zhdankin, M. McSherry, B. Mismash, J. T. Bolz, J. K. Woodward, R. M. Arbit, S. Erickson, *Tetrahedron Lett.* **1997**, *38*, 21.

[103] a) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579; b) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754; c) P. Eisenberger, M. ETH, Ph. D. Thesis No. 17371, Zürich, Switzerland, 2007.

2. Chiral Ferrocenyl Trifluoromethylphosphine Ligands - A New Class of Ligands for Asymmetric Catalysis

2.1 Introduction

One of the most active current areas of chemical research is centered on how to synthesize handed (chiral) compounds in a selective manner, rather than as mixtures of mirror-image forms (enantiomers) with different three-dimensional structures (stereochemistries). Nature points the way in this endeavour: the two enantiomers of a given biomolecule can exhibit dramatically different biological activities, and enzymes have therefore evolved to catalyze reactions with exquisite selectivity for the formation of one enantiomeric form over the other.[1] Drawing inspiration from these natural catalysts, chemists have developed a variety of synthetic small-molecule catalysts, consisting of a transition metal ion and a chiral organic environment (organometallic ligand), that can achieve levels of selectivity approaching, and in some case matching, those observed in enzymatic reactions.

2.1.1 Chiral Organometallic Ligands - an Innovative Concept

The importance of processes catalyzed by transition metals was highlighted by two Nobel Prizes in chemistry during the last decade; in 2001, *Noyori*[2] and *Knowles*[3] "for their work on enantioselective catalyzed hydrogenation reactions" and *Sharpless*[4] "for his work on chirally catalyzed oxidation reactions" and 4 years later, in 2005, *Chauvin*,[5] *Grubbs*[6] and *Schrock*[7] "for the development of the metathesis method in organic synthesis".

William S. Knowles, a pioneer in small molecule asymmetric catalysis, made the following key observation in his Nobel address: "When we started this work we expected these man-made systems to have a highly specific match between substrate and ligand, just like enzymes. Generally, in our hands and in the hands of those that followed us, a good candidate has been useful for quite a range of applications".[3] Surprisingly, certain classes of synthetic catalysts are enantioselective over a wide range of different reactions. Such catalysts may be called, according to *Jacobsen*, "privileged structures", in the same manner that the term has been applied in pharmaceutical research to compound classes that are active against a number of different biological targets (Figure 6).[8]

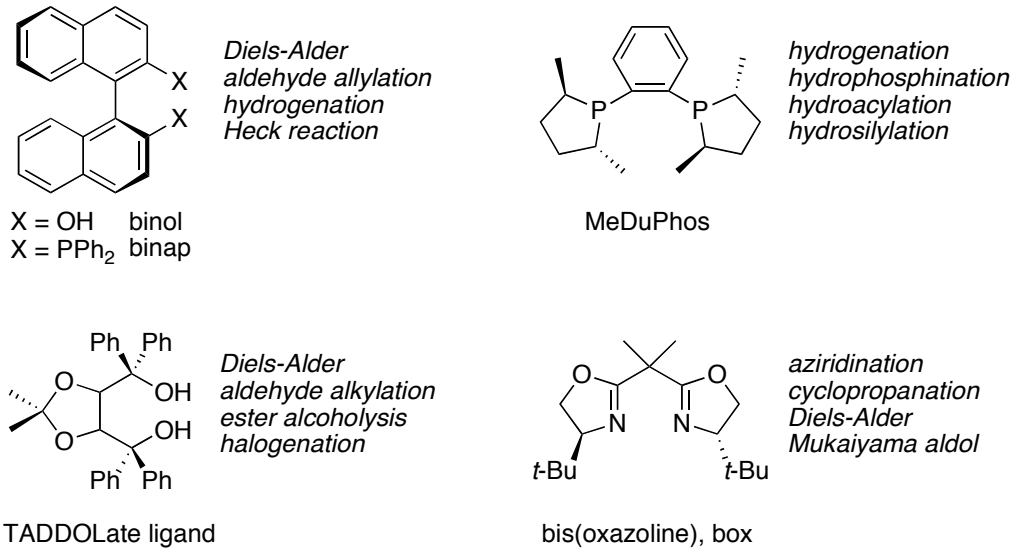


Figure 6: Examples of "privileged chiral ligands" and their applications in asymmetric catalysis.

The story behind the discovery of these structures is different in each case. For instance, binol and binap are completely synthetic molecules developed to exploit the axial symmetry induced by the restricted rotation around the biaryl bond. The design of TADDOL was driven by practical considerations, derived from tartaric acid, the least expensive chiral starting material with two-fold symmetry available from natural source. Bis(oxazoline) ligands were inspired by the ligand framework of vitamin B12.

It is not immediately clear what structural features account for the broad applicability of privileged structures across so many different reaction types, but some trends can be discerned. For instance, the most "privileged catalysts" possess rigid structures with multiple oxygen-, nitrogen-, or phosphorus-containing functional groups that allow them to bind strongly to several metal centers.

Chiral bidentate ligands have shown over the years a high modularity and a broad applicability in catalysis including important industrial applications. The success of chiral bisphosphine ligands and the tradition of our research group in developing very versatile chiral bidentate bisphosphine ligands based on ferrocene for applications in asymmetric catalysis motivated further research in this area.

2.1.2 Chiral Ferrocenes - a Versatile Class of Ligands for Asymmetric Catalysis

Since the discovery of ferrocene in 1951,[9] its fascinating sandwich structure has captured the imagination of chemists, to the point of being nowadays among the most important structural motifs in organometallic chemistry, materials science, and, especially, catalysis (Figure 7).

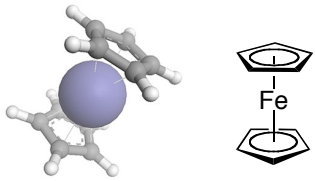


Figure 7: Sandwich structure of $Fe(C_5H_5)_2$ ferrocene.

Furthermore, the applications of ferrocene compounds are not only a subject of steady interest in academia, but also in industry. A quite remarkable example of the great utility of chiral ferrocene ligands in the industrial production of optically active compounds is the synthesis of a precursor for the herbicide (*S*)-Metolachlor by an Ir-Xyliphos-catalyzed asymmetric hydrogenation reaction.[10] This process is extremely effective and presently constitutes the largest-scale enantioselective catalytic process in industry[11] (turnover numbers (TONs) of 2 000 000 and turnover frequencies (TOFs) of > 400 000 h^{-1}, at more than 10 000 tons per annum).

In addition to its unique structure, ferrocene has ideal properties such as low price, thermal stability, and high tolerance to moisture, oxygen, and many types of reagents. Interestingly, its behavior as an electron-rich aromatic compound in electrophilic aromatic substitutions, its facile lithiation (at the 1 position) and dilithiation (at the 1,1'-positions) (Figure 8), and the extraordinary ability to stabilize carbocations at the benzylic-like position are key chemical properties that provide very practical ways for the synthesis of functionalized and substituted ferrocenes.

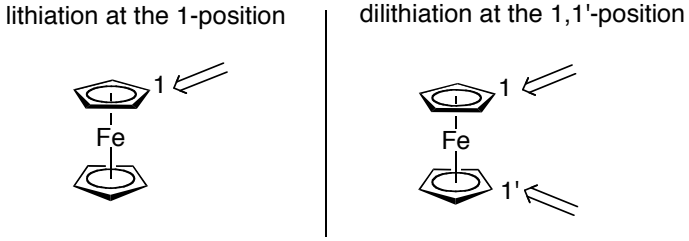


Figure 8: Electrophilic aromatic substitution (lithiation and dilithiation) of ferrocene.

Unlike 1,1'-disubstitution, a very interesting structural feature in ferrocene chemistry is that compounds substituted at positions 1 and 2 with different groups are chiral because of the loss of the plane of symmetry of ferrocene (planar chirality). For instance, the ligand *N,N*-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]ethylamine (ppfa) (see Figure 9), synthesized by *Hayashi* and *Kumada* in 1974 by *ortho* lithiation of enantiopure (*R*)-*N,N*-dimethyl-1-ferrocenylethylamine (Ugi's amine **1**) and reaction with chlorodiphenylphosphine, was the first reported example of a planar-chiral enantiopure ferrocenyl phosphine and will be discussed more in details below.[12]

The discovery of ppfa and its high efficiency as a chiral ligand in some transition-metal-mediated reactions was a landmark in the development of chiral 1,2-disubstituted ferrocene ligands for asymmetric catalysis. Years later, in the 1990s, three breakthrough achievements were

- the synthesis of the Josiphos family of bisphosphine ferrocene ligands by S_N1-type reaction of the dimethylamino group on the Ugi's amine-derived ligands with secondary phosphines (reported by *Togni* and co-workers)[13]
- the straightforward preparation of ferrocenyl phosphine-oxazolines (Fc-Phox ligands) by diastereoselective *ortho* lithiation/phosphinylation of chiral ferrocenyl oxazolines (independently reported by the groups of *Richards,*[14] *Sammakia*[15] and *Uemura*[16])
- the development of the 1,5-bisphosphine Taniaphos (*Knochel* and co-workers[17])

Since the first monograph reported by *Hayashi* in 1995 on the synthesis and applications of chiral ferrocenes in asymmetric catalysis,[18] a set of reports by *Kagan*,[19] *Richards*,[20] *Togni*,[21] *Santelli*[22] and *Hou*[23] covering different aspects of chiral ferrocene ligands have been published. Furthermore, the reviews of *Lemaire*[24] and *Guiry*[25] on chiral nitrogen-containing ligands include the case of ferrocenyl ligands bearing nitrogen donor atoms. More recently, books[26] in this area have been printed and reviews include a compilation on chiral ferrocenyl oxazolines reported in 2003 by *Bryce* and *Sutcliffe*,[27] a comprehensive review on chiral ferrocenyl phosphines disclosed by *Colacot*,[28] a general report on the synthesis and catalytic applications of chiral ferrocene ligands presented by *Gibson* and *Long*[29] in 2004 and a review on applications of chiral ferrocene ligands in asymmetric catalysis by *Carretero* in 2006[30] have been published.

2.1.2.1 Structural Variety of Chiral Ferrocenyl Ligands

In recent years an amazing number of various chiral ferrocene ligands have been used in asymmetric catalysis. Figure 9 shows some of the most relevant families of ferrocenyl ligands, with their current simplified names, organized according to the substitution at the ferrocene backbone and the nature of the coordinating heteroatoms.

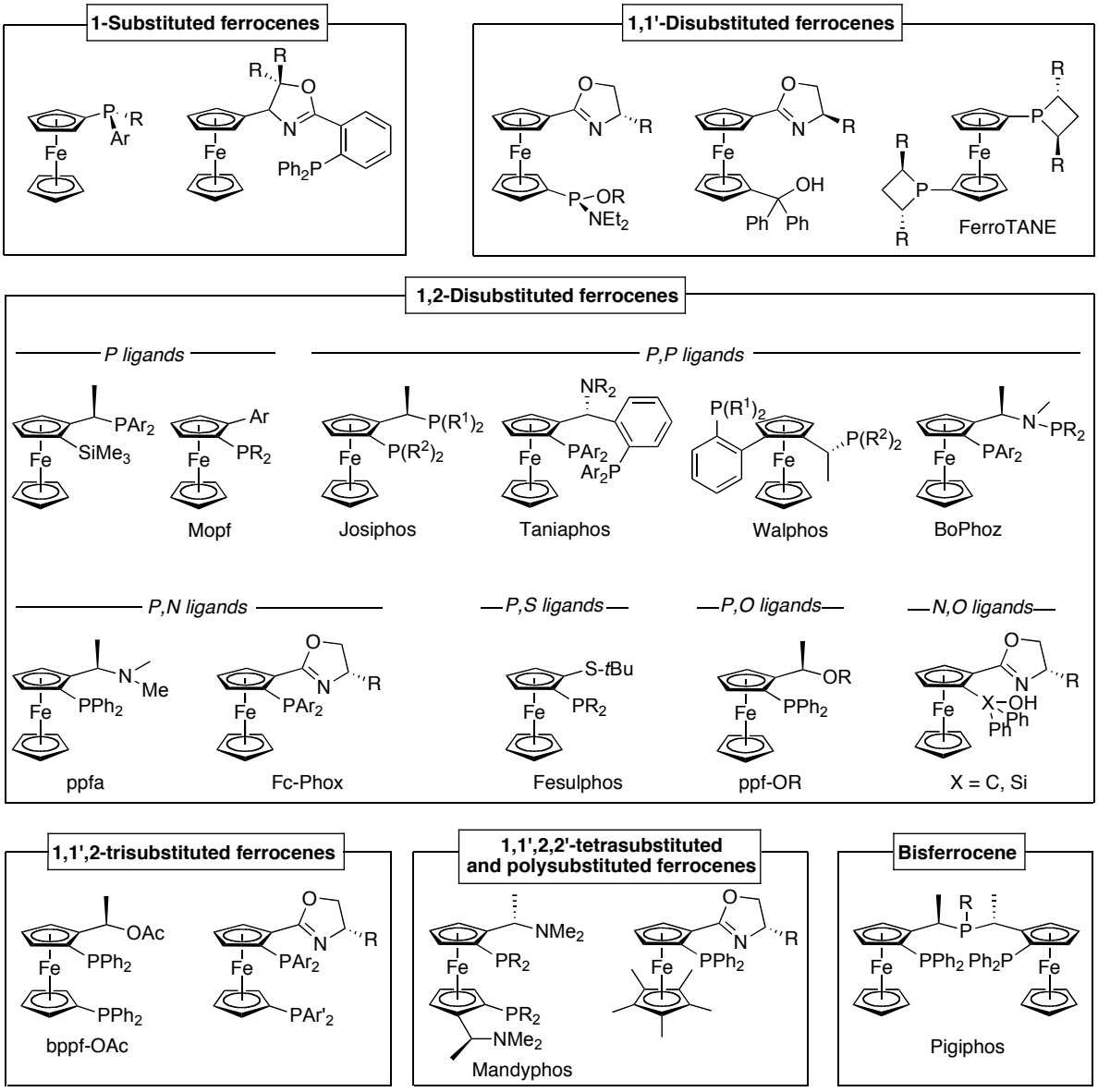


Figure 9: Representative families of chiral ferrocenyl ligands.

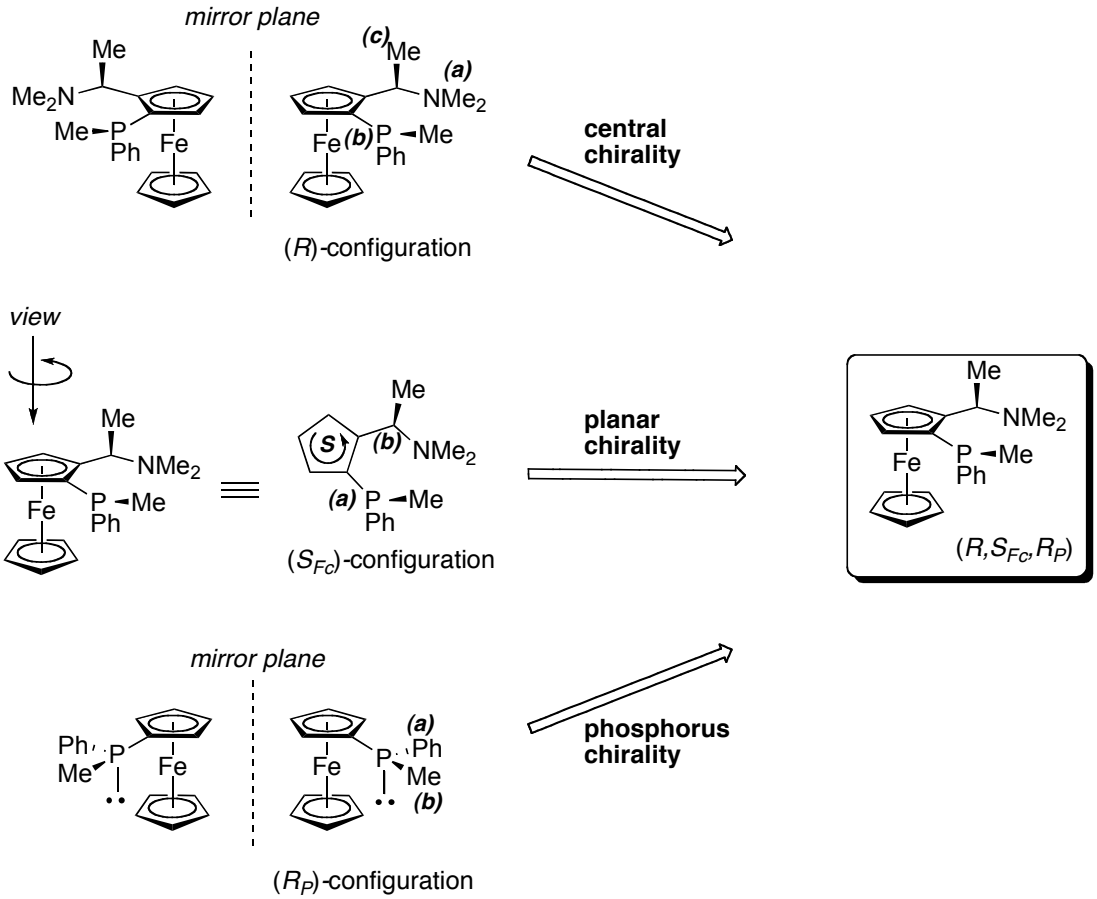
As a result of the high chemical stability of the ferrocene backbone and the existence of a variety of general methods for its fictionalization, from a structural point of view a vast array of substitution patterns have been applied in the preparation of chiral ferrocene catalysts, including 1-substituted, 1,1'-disustituted, 1,2-disubstituted, 1,1',2-trisubstituted and

1,1',2,2'-tetrasubstituted ferrocenes as well as polysubstituted ferrocenes and bisferrocenes. On the other hand, the nature of the substitution can be also varied. Substituents with appropriately located metal-coordinating phosphorus and/or nitrogen atoms represent the most common alternative (P,P and P,N ligands), although sulfur (P,S ligands) and oxygen substituents (P,O ligands) are also known.

2.1.2.2 Stereochemistry of Chiral Ferrocenyl Ligands

The classical CIP rules introduced by *Cahn, Ingold* and *Prelog*[31] can be applied to ferrocene derivatives with planar chirality but a simpler rule was proposed in 1967 by *Schlögl*[32] and accepted as a standard rule for planar chiral metallocenes.
The rule for the assignment of absolute configuration is simple and states that "the observer looks along the principal axis of the molecule so that the more highly substituted ring is directed towards him, whereby the priority of the groups are decisive. The substituents are then, as usual, arranged in decreasing order of priority according to the sequence rule. The choice of symbol (*R*) or (*S*) depends on the resulting direction (clockwise or counterclockwise)."

Different chirality units can be present such as carbon-centered chirality, planar chirality and phosphorus chirality. This simultaneous presence poses nomenclature problems. The convention emerged during the last years uses a "p" subscript for the planar and a "P" subscript for the phosphorus chirality and priority sequence "central > planar > phosphorus chirality" is generally used when defining metallocenes containing more than one stereogenic unit. To avoid mix-ups, planar chirality will be symbolized in this chapter with "Fc" subscript, Fc referring to the ferrocene plane. Scheme 38 shows an example to clarify the different rules used for chiral metallocenes.



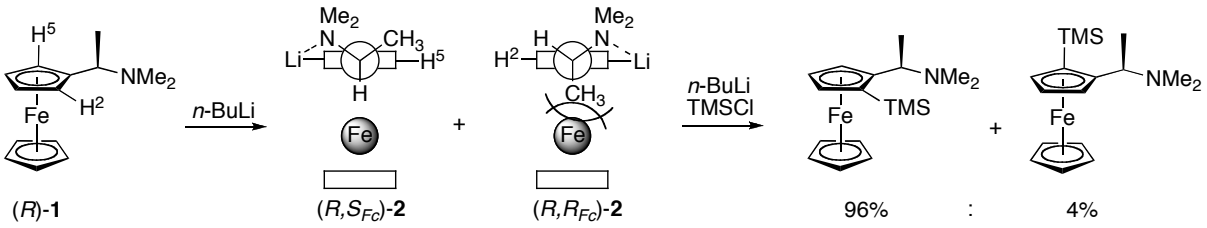
Scheme 38: Determination of central and phosphorus chirality (CIP rule) and planar chirality (according to *Schlögl*).

2.1.2.3 Chiral 1,2-Disubstituted Ferrocenyl Ligands

Special attention is deserved by planar-chiral ferrocenes with 1,2-disubstitution, which have emerged as a first structural ligand motif in metal-catalyzed asymmetric reactions and constitute undoubtedly the most studied substitution pattern for ferrocene ligands.

The pioneering work of *Ugi* in 1970[33] was the first report on the preparation of the ferrocene derivatives with planar chirality based on the diastereoselective *ortho* lithiation of 1-substituted ferrocenes. The development of a chiral tertiary amine, nowadays known as Ugi's amine **1**, containing a stereogenic directing group, gave 96:4 *d.r.* after deprotonation with *n*-BuLi and in situ trapping of the Li-species (**2**) with an electrophile (for instance TMSCl) (Scheme 39). Taking into account a Li-N interaction in the metallated intermediate, one recognizes the unfavorable steric interaction of the methyl group with the ferrocene core in

one of the two diastereoisomers. This is the origin of the differentiation between the two diastereotopic *ortho*-positions upon metallation.

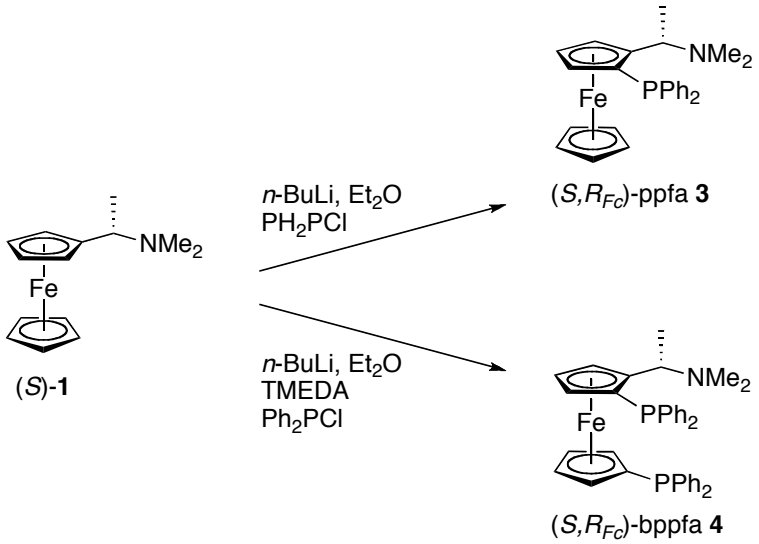


Scheme 39: Highly diastereoselective ortho-lithiation of Ugi's amine **1**.

X-ray analysis of the obtained products showed the selective formation of the *S* planar-chiral derivative starting from Ugi's amine (*R*)-**1** giving a (R,S_{Fc})-configured product.[34] *Ugi* introduced the term "*stereorelating synthesis*" to describe this behavior: the steric course of the reaction provides a reliable correlation of the configurations of the products and the starting materials. Diastereomeric ratio of up to 97:3 were also obtained when replacing the α-methyl group with ethyl, pentyl, phenyl, *o*-tolyl and 2-naphtyl substituents. Other chiral ferrocenes like *e.g.* menthyl-substituted ferrocenylamines were on the contrary found to be sterically too hindered and when subjected to lithiation with *n*-BuLi variable amounts of different products were obtained with low selectivities.[35]

In 1974, *Hayashi* and *Kumada* reported the utilization of chlorodiphenylphosphine as electrophile reacting with the Li-species **2** and synthesized the first 1,2-disubstituted P,N ferrocene ligand: 2-(diphenylphosphino)-1-(*N,N*,-dimethylaminoethyl) ferrocene **3**, the most commonly named ppfa (Scheme 40).[12]
The use of two equivalents of ^{n}BuLi in the presence of TMEDA gave the 1,1'-dilithiated species in a highly diastereoselective manner. The subsequent addition of two equivalents of chloro(diphenyl)phosphine afforded the 1,2,1'-substituted bppfa **4**.

The two enantiomerically pure compounds obtained, **3** and **4**, are the first examples of planar-chiral derivatives with applications as ligands in asymmetric homogeneous catalysis.

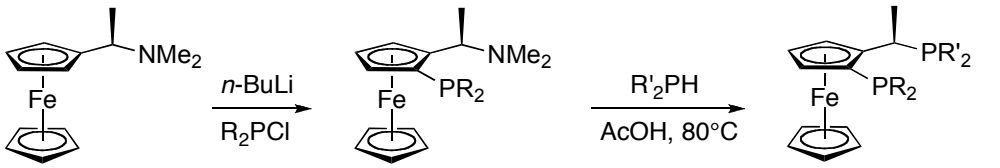


Scheme 40: Preparation of chiral ferrocenyl phosphine and bisphosphine ligands, respectively (S,R_{Fc})-ppfa **3** and (S,R_{Fc})-bppfa **4**.

In addition to Ugi's amine, a good number of chiral *ortho*-directing groups have been progressively described, such as sulfoxides,[36] acetals,[37] oxazolines,[14-16] azepines,[38] pyrrolidines,[39] hydrazones,[40] sulfoximines,[41] *O*-methyl ephedrine derivatives,[42] imidazolines,[43] phosphine oxides,[44] and oxazaphospholidines.[45]

2.1.2.4 Chiral 1,2-Disubstituted Ferrocenyl Bisphosphine Ligands

The Josiphos ligands constitute one of the most versatile and successful ligand families because of the wide variety of ligands available thanks to the introduction of the two phosphino groups in consecutive steps with very high yields. In the first step, a PR_2 fragment is introduced via diastereoselective *ortho*-lithiation of **1** and subsequent treatment with an electrophilic chloro(diaryl)phosphine. Then, the dimethylamino group in **3** is substituted by a phosphine with retention of configuration at the stereogenic C-center as demonstrated by *Ugi* and co-workers (Scheme 41).[46] About 150 different Josiphos ligands have been prepared and 40 derivatives are available in a ligand kit for screening and on a multi-kilogram scale for production.[47]

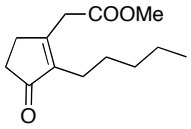
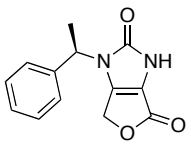
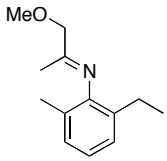
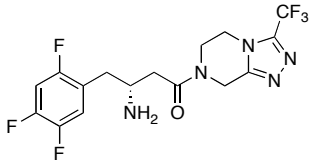


(*R*)-**1** (*R,S*$_{Fc}$)-ppfa **3** (*R,S*$_{Fc}$)-Josiphos **5**

Scheme 41: Synthesis of the well-known Josiphos ligand family **5**.

The most successful ligands are listed in Table 10. Catalytic applications of the Josiphos ligand family have been reviewed up to 2002 by *Pugin* and co-workers.[48] For this reason, only four examples of the most important processes are provided here. The most important application is undoubtedly the Ir/**5c**-catalyzed hydrogenation of a hindered N-aryl imine of methoxyacetone, the largest known enantioselective process operated for the enantioselective production of the herbicide (*S*)-Metolachlor.[49]

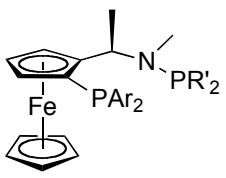
Table 10: Representative applications and industrial applications of Josiphos ligands.

	R	R'	Important applications	Industrial applications	
5a	Ph	Cy	hydrogenation of enamide; allylic alkylations; Michael additions; hydroboration; PMHS reduction of C=C	Jasmonate process 	Ru/**5a**: 90% *ee* TON 2000 TOF 200 h^{-1} *Firmenich*
5b	Ph	*t*-Bu	opening of oxabicycles	Biotin process 	Rh/**5b**: 99% *ee* TON 2000 *Lonza*
5c	Ph	3,5-Xyl	methoxycarboxylation	Metolachlor process 	Ir/**5c**: 80% *ee* TON 2000000 TOF >400000 h^{-1} *Ciba-Geigy/ Solvias*
5d	Ph	*t*-Bu	hydrogenation	Sitaglipin process 	Rh/**5d**: >99% *ee* *Merck/Solvias*

The hydrogenation of a tetrasubstituted olefin was the key step for two production processes developed for the synthesis of methyl dihydrojasmonate by Firmenich[50] and of biotin by Lonza,[51] respectively. Synthesis of sitagliptin, a potent and selective inhibitor for the treatment of type 2 diabetes mellitus (T2DM) has been developed by Merck and Solvias using Rh/**5d** catalyst.[52]

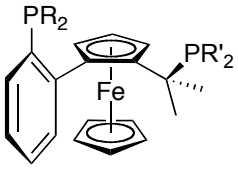
The Josiphos backbone has been covalently attached to organic or inorganic polymeric supports, and modified by the introduction of hydrophilic groups (to make the ligands water soluble) or imidazolium tags (in order to immobilise the ligand to ionic liquids).[53,54]

Using the same methodology, new ligand classes were developed in recent years showing a high level of modularity and good catalytic results.



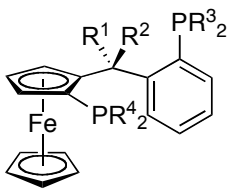
BoPhoz **6**

Similar to Josiphos, BoPhoz **6** is a modular ligand class with a PAr_2 group on the Cp ring and an aminophosphine at the side chain. Its preparation starts from ppfa and leads via acetate to a secondary amine. Coupling of the amino group with chlorophosphines affords BoPhoz **6**.[55] This new kind of bisphosphine ligands is very effective for the Rh-catalyzed hydrogenation of a variety of activated C=C bonds such as enamides (*ee* 96-99%) and itaconates (*ee* 80-99%).[55]



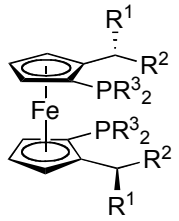
Walphos **7**

Modular Walphos ligands **7** form eight-membered metallacycles due to the additional phenyl ring attached to the cyclopentadienyl fragment. Its preparation starts from Ugi's amine **1** reacting via Negishi coupling reaction with 2-bromoiodobenzene leading to the enantiomerically pure bromo intermediate.[56] A subsequent lithiation of the bromide followed by quenching with the appropriate R_2PCl results in the formation of the corresponding tertiary phosphine. To prevent a ring closure, the phosphine must be protected as phosphine oxide before carrying on with the nucleophilic substitution of the dimethylamino with various R'_2PH. Finally, reduction yields the Walphos ligands **7**. Walphos ligands proved efficient for various Rh-catalyzed enantioselective hydrogenations of dehydroamino and itaconic acid derivatives (*ee* 92-95%) as well as Ru-catalyzed hydrogenations of ß-keto esters (*ee* 91-95%) and acetylacetone (*ee* 99.5%).[56,57]



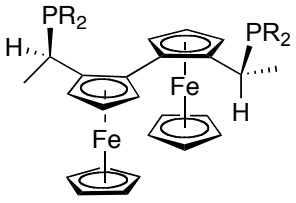
Taniaphos **8**

Taniaphos ligands **8** have an additional phenyl ring inserted at the side chain of Ugi's amine. Besides the two phosphine moieties, the substituents at the stereogenic center can also be varied and, up to now, three generations with different substituents types (R^1 = $N(alkyl)_2$ and R^2 = H for the first generation;[58] R^1 = H or MeO and R^2 = H or MeO for the second generation;[59] R^1 = H and R^2 = alkyl for the third generation[60]) have been prepared. The nature of both phosphine moieties (R^3, R^4) and the substituents at the stereogenic center (R^1, R^2) has strong but not systematic effect on the catalytic performance. With very few exceptions, relatively electron rich all-aryl substituted derivatives (R^3, R^4 = Ph, Xyl, MeO-Xyl) gave the best performance for hydrogenation reaction.



Ferriphos/ Mandyphos **9**

Ferriphos/mandyphos are bidentate analogs of ppfa. The synthesis of such ligands starts from a diamine analogous to Ugi's amine, which is dilithiated and halogenated to give a dibromide as a single diastereoisomer.[61] Direct substitution of the two dimethylamino groups with diorganozincs in the presence of acetyl chloride gives a dibromo intermediate, which is treated with *n*-BuLi and $ClPR^3_2$ to provide Ferriphos/Mandyphos **9**. Screening results indicate high enantioselectivities in Rh-catalyzed hydrogenation of dehydro aminoacid derivatives (*ee* 95-99%) and Ru-catalyzed hydrogenation of tiglic acid (*ee* 97%).[62]



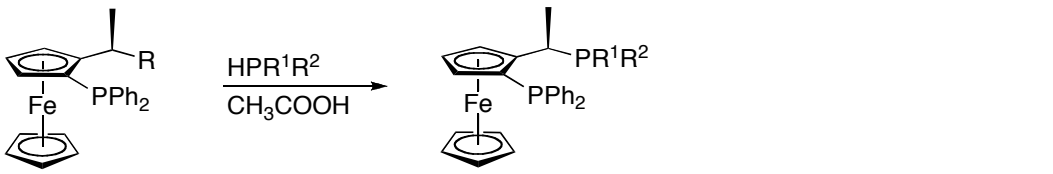
TRAP **10**

The TRAP ligands **10** form nine-membered chelate rings and were conceived as *trans*-chelating bisphosphines. The synthesis starts with the 2-iodo derivative of Ugi's amine, which is converted to tertiary phosphine and then oxidized to the corresponding phosphine oxide.[63] Homocoupling with activated copper powder without solvent affords the phosphine oxide bisferrocene, which is finally reduced to give TRAP **10**. The choice of R strongly affects the level of enantioselectivity and sometimes even the sense of induction. The Rh-catalyzed hydrogenation of MAA and itaconates gives enantioselectivities of 92-96% if carried out at pressures of 0.5-1 bar.[64]

2.1.2.5 Chiral 1,2-Disubstituted Ferrocene Having a Stereogenic Phosphorus Atom

To the selective preparation of 1,2-disubstituted ferrocenyl bisphosphine ligands displaying a stereogenic phosphorus atom much less attention has been paid than to the ferrocene-based ligands (Josiphos, Taniaphos, etc) which incorporate both carbon-centered chirality and planar chirality. However, in theory, the former derivatives might provide a superior class of ligands for asymmetric catalysis by virtue of bringing the chiral environment into the closest possible proximity to the catalytic center. The paucity of examples undoubtedly reflects the difficulties in the synthesis of P-chiral phosphines.

The first 1,2-disubstituted ferrocenyl ligands with a stereogenic phosphorus atom on the ethyl moiety were reported by *Togni* and *Spindler*.[65] These new ligands of type **11** are easily obtained as diastereoisomeric mixture (1:1) by the reaction of the acetate **12** or the amine **13** with a slight excess of a secondary chiral phosphine in glacial acetic acid at 50-60 °C (Scheme 42). The possibility of varying the phosphino groups in a chiral chelating bisphosphine, independently from one another and in such an easy way, opened new avenues of exploration addressing the important issue of steric and electronic effects of ligands used in asymmetric catalysis. Structural study provided evidence that **11** behaves as a conformationally rather rigid ligand. Because the two ligating fragments are not equal, the two ligands in *trans* position should display different reactivities, and hence stereochemical control.



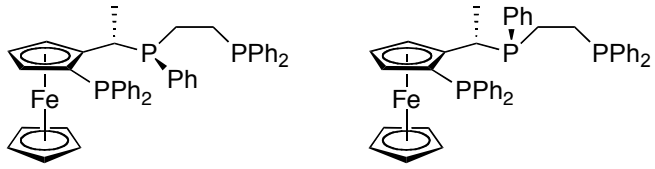
12 (R = OAc)
13 (R = NMe_2)

(R,S_{Fc},R_p) or (R,S_{Fc},S_p)-**11a** (R^1 = Ph, R^2 = 2-OMe-Ph)
(R,S_{Fc},R_p) or (R,S_{Fc},S_p)-**11b** (R^1 = Ph, R^2 = Cy)

Scheme 42: New chiral ferrocenylphosphines **11** for asymmetric catalysis.

Eight years later, in 2002, *Barbaro* and co-workers reported the first tridentate phosphine ferrocenyl ligand combining planar, phosphorus and carbon chirality.[66] These two new diastereomerically pure tridentate phosphine ligands P3Chir **14** and **15** (Figure 10) have been prepared from the reaction of (R,S_{Fc})-ppfa with racemic $C_6H_5P(H)CH_2CH_2P(O)(C_6H_5)_2$ in acetic acid to give a 1:1 mixture of diastereoisomers having opposite absolute configuration

at phosphorus. Treatment of this mixture with borane dimethyl sulfide afforded the pure (R,S_{Fc},S_P) and (R,S_{Fc},R_P) phosphine oxide-diborane adducts in good yields after separation by flash chromatography. One pot reduction ($CeCl_3$, $NaBH_4$, $LiAlH_4$) / deboronation reactions of the two stereoisomers gave pure **14** and **15**. The X-ray crystal structure of **14** proved the reduction step to proceed with retention of configuration at all stereocenters.

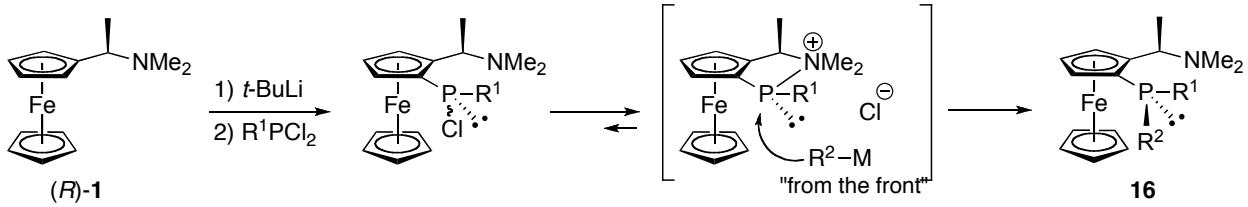


(R,S_{Fc},S_P)-P3Chir **14** (R,S_{Fc},R_P)-P3Chir **15**

Figure 10: Newly developed tridentate phosphine ferrocenyl ligands **14** and **15** combining planar, phosphorus and carbon chirality.

The two new tridentate phosphine ligands P3Chir were unprecedented molecular assemblies and the synthetic procedure enabled a large-scale preparation in excellent overall yields using cheap and commercially available reagents through simple manipulations.

More recently, *Chen* showed a highly stereoselective and modular synthesis of ferrocene-based P-chiral ligands thanks to the special properties of Ugi's amine.[67] The idea was that - contrary to almost all ferrocene-based planar chiral phosphine ligands that are synthesized by chiral group-directed diastereoselective *ortho*-lithiation[68] or enantioselective lithiation[69] followed by reaction with a *monochloro*phosphine – ferrocene-based P-chiral phosphine could be synthesized by reaction of a *dichloro*phosphine with a chiral lithiated ferrocene, followed by a second organometallic reagent. Thus, (*R*)-Ugi's amine **1** was lithiated with *t*-BuLi, followed by reaction with different dichlorophosphines R^1PCl_2 and then reacted with organometallic compounds R^2M to afford a single diastereoisomer **16** in high yield (Scheme 43). The simple and straightforward reaction mechanism can be explained as follows. For the substrates bearing groups which are strong Lewis bases (such as the dimethylamino unit in Ugi's amine), a five-membered cyclic, quaternary ammonium salt intermediate is formed and then the organometallic compound RM attacks from the side opposite to the nitrogen atom in the intermediate to give the products, as shown in Scheme 43.



R^1	R^2	M	Yield [%]	Configuration
Ph	*o*-An	Li	91	(R,S_{Fc},S_P)-**16a**
Ph	1-Np	MgBr	83	(R,S_{Fc},S_P)-**16b**
Cy	Ph	MgBr	95	(R,S_{Fc},S_P)-**16c**
Ph	Cy	MgCl	92	(R,S_{Fc},R_P)-**16d**

Scheme 43: Strategy for the synthesis of P-chiral phosphines.

Further modification of the amino group in **16** led to the preparation of *e.g.* Josiphos, BoPhoz or Taniaphos analogs containing a P-stereogenic center.

The results from asymmetric hydrogenation reaction of α-dehydroamino acid derivatives showed that the introduction of P-chirality into ferrocene-based phosphine ligands enhances the enantioselective discrimination produced by the corresponding Rh-catalyst when the planar chirality, carbon chirality and the chirality at phosphorus are matched.

2.1.3 Ferrocene Bisphosphine Ligands and the Trifluoromethyl Group - an Unexplored Field

Fluorine is a magic element: with its small steric size, it is able to bring about dramatic, and often unexpected, changes in physico-chemical properties, reactivity and biological features of organic molecules. Fluorine is not a rare element on the earth's crust, in fact it ranks 13th on the abundance list.[70] However, only about ten natural monofluorinated organic molecules have been hitherto described, moreover in a very limited amount.[71] Thus, one can safely state that fluoroorganic molecules are nearly exclusively "man-made".

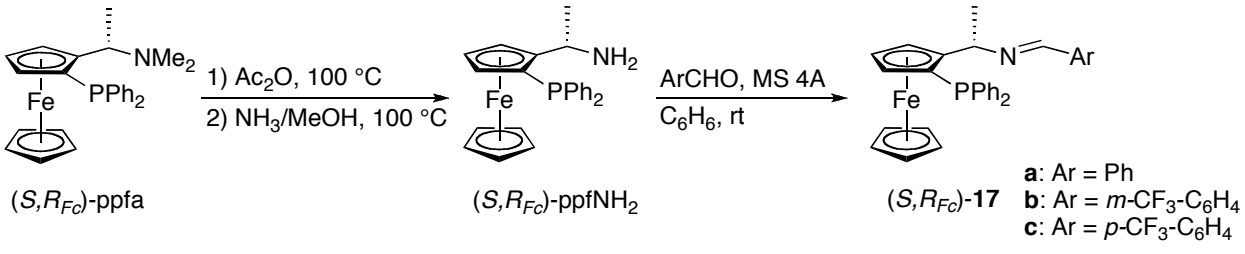
One of the most studied functional group containing fluorine is probably the small trifluoromethyl group (-CF_3). It has a significant electronegativity that is often described as being intermediate between the electronegativity of fluorine (Pauling electronegativity: 3.98) and chlorine (Pauling electronegativity: 3.16).[72] For this reason, trifluoromethyl-substituted compounds are often strong acids, such as trifluoromethanesulfonic acid and trifluoroacetic

acid. In other cases, the trifluoromethyl group is employed to lower the basicity of organic compounds or to confer distinctive solvation properties (e.g. trifluoroethanol).
The trifluoromethyl group occurs in certain organic molecules used as drugs[73] (e.g. *Prevacid*, gastrointestinal disorders, *Tap Pharmaceutical and Taked Pharmaceutical,* Nr. 8 in the best-selling prescription drugs in 2005; *Prozac*, depression, *Eli Lilly*, Nr. 184) and used as agrochemicals[74] (e.g. *Flurazole*, herbicide safener, *Monsanto*; *Metaflumizone*, insecticide, *BASF*). From a synthetic point of view, the modification of ligands with strong electron-withdrawing CF_3 group may result in promising catalytic performance.

2.1.3.1 Chiral 1,2-Disubstituted Ferrocenyl Ligands Containing CF_3 Groups

A particular advantage of the class of 1,2-disubstituted ferrocenyl ligands is the fact that the two substituents (P and N in the case of P,N ligands or P and P in the case of P,P ligands) can be modified sequentially. This means that a large number of different ligands can be prepared with a relatively small synthetic effort. Moreover, their electronic and steric properties can be varied easily and thereby be tuned to the needs of a specific transformation, adding for instance a CF_3 group, typically to phenyl substituents.

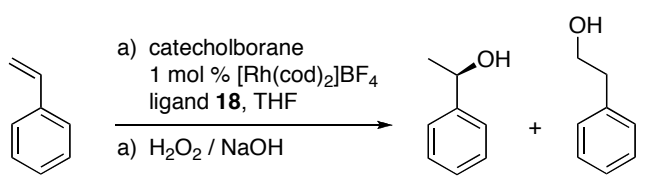
In 1995, *Hayashi* and co-workers published new chiral ferrocenyl phosphine ligands containing an imino group at the ferrocenylmethyl position (Scheme 44).[75] Replacement of the dimethylamino group on (S,R_{Fc})-ppfa by an acetoxy group gave (S,R_{Fc})-ppfOAc, which was substituted with an amino group by the reaction with a large excess of ammonia in methanol at 100 °C to yield (S,R_{Fc})-ppfNH_2. Treatment of the amino derivative with benzaldehyde, *m*-trifluoromethylbenzaldehyde and *p*-trifluoromethylbenzaldehyde in benzene in the presence of molecular sieves at room temperature gave (S,R_{Fc})-**17a**, (S,R_{Fc})-**17b** and (S,R_{Fc})-**17c**, respectively, in good yields.

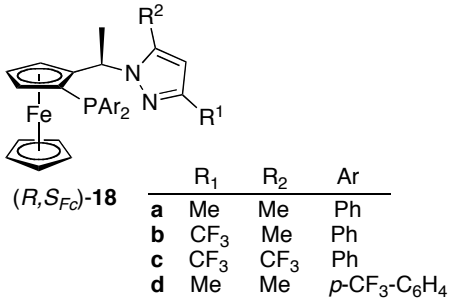


Scheme 44: Synthesis of chiral ferrocenyl phosphine-imine ligands **17**.

Ferrocenyl phosphine-imine ligands **17** were examined in the Rh-catalyzed asymmetric hydrosilylation of prochiral ketones with diphenylsilane. A slightly higher enantioselectivity was observed in the reaction with ligands **17b** and **17c**, which were derived from aldehydes containing electron-withdrawing groups on the phenyl ring. Moreover, it was observed that the hydrosilylation was faster with those ligands (< 10 min vs 1h for ligand **17a**).

The same year, the work of *Anita Schnyder*, in our group, on P,N ligands of type **18**, incorporating a phosphine and a pyrazole showed interesting catalytic characteristics for the Rh-catalyzed hydroboration of styrenes with catecholborane due to the electronic properties of trifluoromethyl substituents (Scheme 45).[76] Compared to some known systems,[77] [Rh(cod)**18**]BF_4 proved to be less regioselective and afforded relatively high amounts of the achiral linear alcohol. On the other hand, in the case of **18d**, which bears the electron-withdrawing trifluoromethyl group on the phenyl ring attached to the phosphine, the enantioselectivity for the desired branched alcohol reached 98% *ee*, an unprecedented value for this particular reaction.





(R,S_{Fc})-**18**

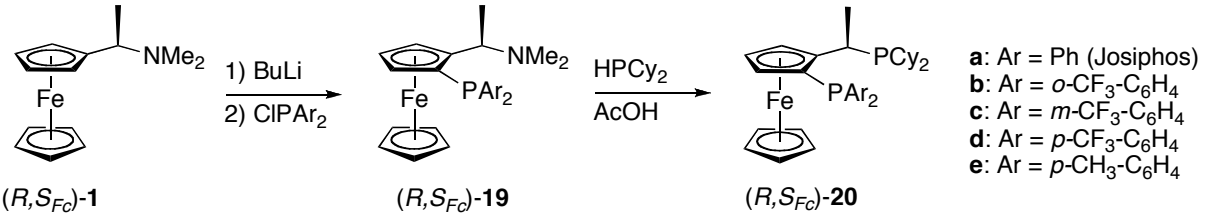
	R_1	R_2	Ar
a	Me	Me	Ph
b	CF_3	Me	Ph
c	CF_3	CF_3	Ph
d	Me	Me	*p*-CF_3-C_6H_4

Scheme 45: [Rh(cod)**18**]BF_4 catalyzed hydroboration of styrene with catecholborane.

While the use of ligands **18b** and **18c**, bearing the CF_3 fragments on the pyrazole resulted in lower enantioselectivities of 43% and 33%, respectively, one could observe that the different electronic properties of the pyrazole and phosphine fragments exert opposite influences: high enantioselectivities were obtained when the N-ligand was a good σ-*donor* and the P-ligand a good π-*acceptor*.

A few years later, *Céline Gambs*, in our group, published the synthesis of a series of chiral 1,2-disubstituted ferrocenyl bisphosphine ligands of type **20** derived from Josiphos, where the electronic properties of the ligand are systematically varied (Scheme 46).[78] The planar-chiral ferrocenyl bisphosphine ligands of type **20** were prepared by the same two-step

procedure described previously for the synthesis of Josiphos analogs.[76] The *ortho*-lithiation of **1** and the subsequent treatment with diaryl(chloro)phosphine was followed by the introduction of the cyclohexylphosphine fragment by nucleophilic substitution of the dimethylamino group of **19**.

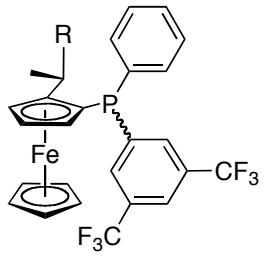


(R,S_{Fc})-**1** (R,S_{Fc})-**19** (R,S_{Fc})-**20**

Scheme 46: Synthesis of chiral ferrocenyl bisphosphine ligands of type **20**, derived from Josiphos.

The electronic effects of ligands **20** were studied in enantioselective copolymerization of carbon monoxide and propene.[79] Pd^{II} systems combined with sterically very similar ferrocenyl ligands **20a-e** (except 20b) produced almost completely isotactic copolymers from propene and CO in a highly enantioselective fashion. Only small variations in enantioface discrimination were observed, whereas drastic changes in catalytic activity were noted by changing the electronic properties of the PAr_2 substituent.

Interestingly, upon reaction of the racemic chlorophosphine $ClPPh[3,5\text{-}(CF_3)_2C_6H_3]$ with the lithiated form of Ugi's amine **1**, the corresponding diastereoisomeric products **19f$_a$** and **19f$_b$**, containing a stereogenic P-atom, were formed in equal amounts and separation could be performed by column chromatography (Figure 11).[78] Unfortunately, when the diastereoisomerically pure **19f$_b$** was reacted at 100 °C with $HPCy_2$ in AcOH it did not retain completely its stereochemical integrity, as partial epimerization (*ca.* 20%, as ascertained by ^{31}P NMR spectroscopy) at the P-atom occurred, due to the high temperature required for the reaction. Attempts to separate the pairs of diastereoisomeric ferrocenyl bisphosphines **20f$_a$** and **20f$_b$** failed and the chemistry with this new P-stereogenic phosphine was not pursued.



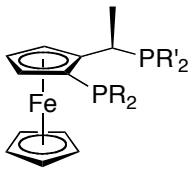
(R,S_{Fc})-**19f$_{a,b}$** R = NMe_2
(R,S_{Fc})-**20f$_{a,b}$** R = PCy_2

Figure 11: New diastereoisomers **19f** and **20f**, containing a stereogenic P-atom.

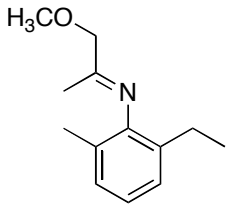
The same year, *Blaser and Spindler*, from *Solvias AG*, reported a study of the Ir-catalyzed hydrogenation of *N*-aryl imines. The results for the hydrogenation of MEA imine are collected in Table 11. Two conclusions could be drawn from the use of Josiphos-like ligands **21**: (a) the presence of one CF_3 group on the R or R' position (ligand **21b** and **21c**) increased the enantioselectivity; (b) the presence of a CF_3 group both on the R and R' position (ligand **21d**) significantly decreased the enantioselectivity.

Table 11: Hydrogenation of MEA imine catalyzed with Ir-R_2PFc-PR'_2 catalysts.

	Ligands		**Conv.**	***ee***
	R	**R'**	**[%]**	**[%]**
21a	Ph	Cy	65	61
21b	4-CF_3-C_6H_4	Ph	100	81
21c	Ph	4-CF_3-C_6H_4	-	81
21d	4-CF_3-C_6H_4	4-CF_3-C_6H_4	-	69



(R,S_{Fc})-**21**



MEA imine

However, the catalyst activities varied drastically and the optimal combination of R and R' groups on the ferrocenyl backbone was different for each substrate. No explanations could be found for this observation.

2.1.3.2 Ferrocenyl Bisphosphine Ligands Having a Stereogenic P-CF_3 Group

Due to the difficulty in synthesizing trifluoromethylphosphines, no 1,2-disubstituted ferrocenyl Josiphos containing the CF_3 group directly attached to phosphorus has ever been prepared. *Grobe* and co-workers in the 80's described the syntheses of several catalysts containing the

structural unit $F_3CP{=}CF_2$[80] or $F_3CP(SCH_2CH_2S)$[81] ligands. Some articles have appeared concerning bidentate bis(trifluoromethyl)phosphine ligands.[82] Several examples are depicted in Figure 12.

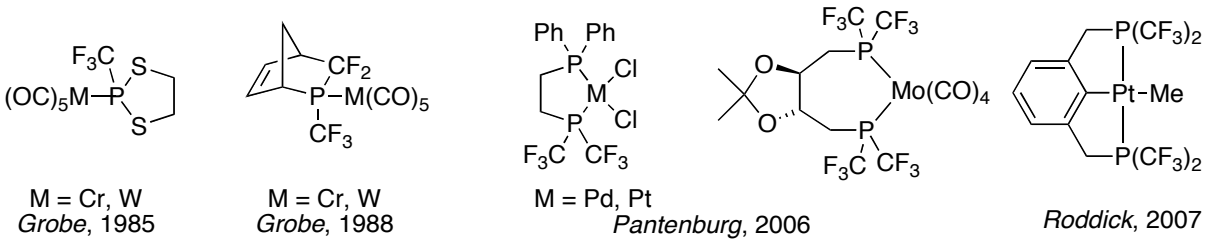
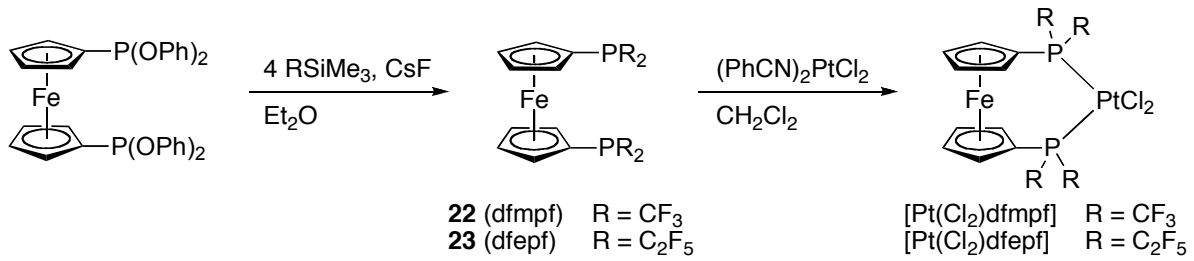


Figure 12: Examples of catalysts made up of trifluoromethylphosphine ligands.

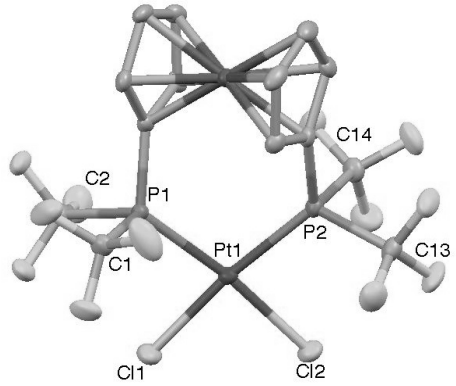
The body of work by the *Roddick* group on the $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe)[83] suggests that the chemistry of other bisphosphines of different bulkiness, electronic properties, and bite angles would be an area worthy of investigation. Indeed, *Cundari* and co-workers have announced, "Analysis of the most common alkyl and aryl phosphines in experimental usage suggests that the complexes are quite similar stereoelectronically. Indeed, apart from $P(CF_3)_3$, it is interesting just how similar the commonly studied phosphines are."[84] Clearly this analysis can be extended to bisphosphines, since none of the known (perfluoroalkyl)-bisphosphines have an exceptionally large cone angle.[83,85]

Therefore, it was of interest to synthesize a strongly electron withdrawing bisphosphine of larger bite angle, since there is a rarity of ligands with such a combination of properties. With respect to electron-withdrawing ferrocenyl bisphosphine ligands, *Beletskaya* and co-workers have recently reported the synthesis of the (perfluoroaryl)bisphosphine $[Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2]$.[86] Two years later, in 2008, *Caffyn* and co-workers reported the synthesis of the first perfluoroalkyl-sustituted ferrocenylbisphosphines ligands $[Fe\{\eta^5\text{-}C_5H_4P(CF_3)_2\}_2]$ (dfmpf, **22**) and $[Fe\{\eta^5\text{-}C_5H_4P(C_2F_5)_2\}_2]$ (dfepf, **23**).[87] Using the methodology which they had previously developed for the synthesis of perfluoroalkyl mono- and bisphosphine,[88] **22** and **23** were isolated in 66% and 71% yield after the reaction of $[Fe\{\eta^5\text{-}C_5H_4P(OPh)_2\}_2]$ with CsF and 4 equivalents of CF_3SiMe_3 or $C_2F_5SiMe_3$, respectively (Scheme 47).



Scheme 47: Synthesis of 1,1'-bis(bis(trifluoromethyl)phosphino)ferrocene, dfmpf **22** and 1,1'-bis(bis(pentafluoroethyl)phosphino)ferrocene, dfepf **23**.

The coordination of **22** to platinum was studied, thereby revealing interesting properties. The geometry around the metal in [Pt(Cl_2)dfmpf] is distorted square planar (Figure 13). From the X-ray crystal structure analysis and in agreement with Tolman's formula, the maximum cone angle was estimated as 126°, which means that dfmpf is a wider-cone-angle ligand than $(CF_3)_2PCH_2CH_2P(CF_3)_2$ (120°) and almost as wide as $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (129°).



	b. distances [Å]		b. angles [°]
Pt1-P1	2.2411(7)	P2-Pt1-P1	101.00(2)
Pt1-P2	2.2397(7)	Cl1-Pt1-Cl2	87.43(3)
Pt1-Cl1	2.3060(8)	C1-P1-C2	98.2(2)
Pt1-Cl2	2.3112(7)	C13-P2-C14	99.3(1)

Figure 13: Mercury representation of the solid state structure of [Pt(Cl_2)dfmpf] (50% probability ellipsoids). Selected bond distances and angles.[88]

Interestingly, a difference between the structure of [Pt(Cl_2)dfmpf] and the one of [Pt(Cl_2)dfepf] is that the ferrocenyl core in [Pt(Cl_2)dfepf] is more twisted and the P-Pt-P bite angle increases to 102.95(4)°. The larger steric demand of the dfepf ligand is reflected by a larger calculated maximum cone angle of 154° (± 5-10%), which is significantly larger than 129° for $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$. Consequently, dfepf constitutes the bulkiest chelating bidentate(perfluoroalkyl)-bisphosphine known so far.

P-chiral mono-trifluoromethylated ferrocenyl bisphosphine ligands are so far unknown, and besides the synthetic challenge beyond those kinds of molecules, they might possess interesting properties concerning asymmetric catalysis.

2.1.4 Objectives of this Part of the Thesis

The previous sections have emphasized the potential significance of P-chiral mono-trifluoromethylated ferrocenyl bisphosphine ligands. As this area is unexplored, the synthetic challenge behind those kinds of molecules is of utmost importance. Therefore, we formulated the following goals for this part of the thesis:

1) Synthesis and characterization of a novel type of chiral 1,2-disubstituted ferrocenyl trifluoromethylphosphine ligands, with the focus on the development of a new general route for the preparation of enantiomerically pure P-chiral trifluoromethylphosphines.

2) Synthesis, structure and coordination properties of new catalysts based on complexes of transition metals with new trifluoromethylphosphine ligands and their application in asymmetric catalysis.

2.2 Results and Discussion

2.2.1 Introduction

Recently, in our laboratories, *Patrick Eisenberger* and *Iris Kieltsch* developed a new class of trifluoromethylating reagents **24** and **25** based on hypervalent λ^3-organoiodine compounds that can be used as a source of electrophilic CF_3.[89] Compounds **24** and **25** can be synthesized in a relatively simple and inexpensive fashion and they showed good to excellent reactivity toward several classes of nucleophiles (Figure 14) mainly, C-centered nucleophiles[89] (carbonyl compounds such as ß-keto esters and α-nitro esters), S-centered nucleophiles[89] (thiols), O-centered nucleophiles[90] (alcohols, sulfonate) and P-centered nucleophiles (essentially secondary phosphine).[91]

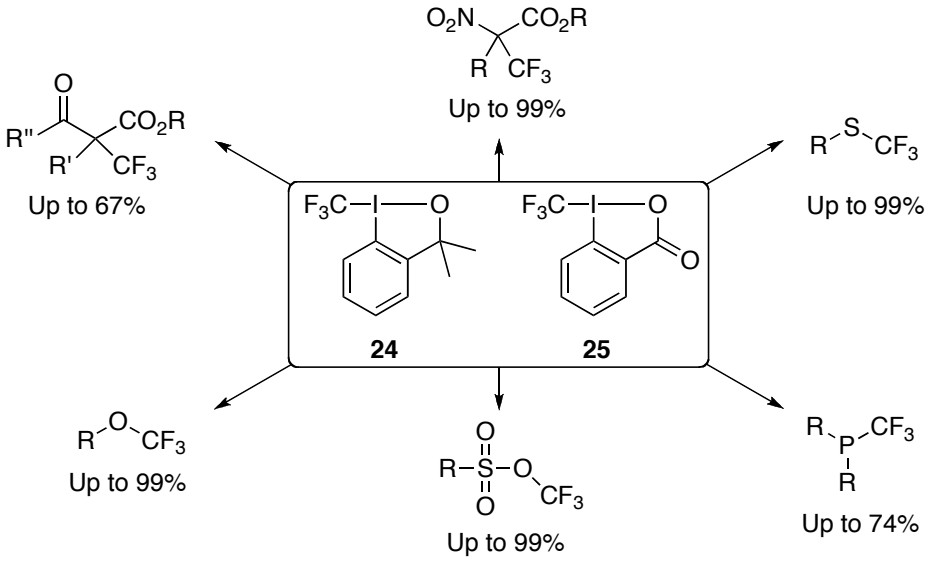
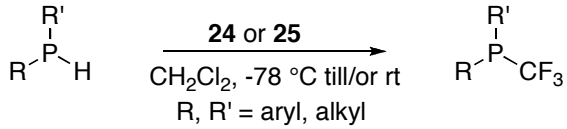


Figure 14: Electrophilic trifluoromethylation of C-, S-, O- and P-centered nucleophiles developed in the *Togni* group.

Regarding the topic of this thesis' chapter, we will focus on the formal exchange of a H^+ with CF_3^+ at the phosphorus atom of a phosphine.[91] The synthesis of the desired disubstituted (trifluoromethyl)phosphine is obtained by mixing equimolar amounts of either one of the reagents **24** or **25** and a disubstituted phosphine at ambient or at low temperature in CH_2Cl_2 (Table 12). The general procedure was developed for the synthesis of the model compound diphenyl(trifluoromethyl)phosphine (entry 3) to yield up to 78% after purification by column

chromatography. Similarly, the sterically more demanding dicyclohexylphosphine reacted under the same conditions (entry 1) and was isolated as the corresponding phosphine sulfide after stirring with S_8 to avoid rapid oxidation during work-up and isolation. Interestingly, the *P*-trimethylsilylated derivative (entry 4) underwent trifluoromethylation under the same condition in comparable yield.

Table 12: Electrophilic trifluoromethylation of phosphine using λ^3-iodane **24** or **25**.



Entry	Substrate	Product	Reagent	Yield [%]
1	Cy_2PH	$Cy_2(CF_3)P{=}S$[a]	**24**	52
2	$CyPH_2$	$CyPH(CF_3)$	**25**	54[b,c]
3	Ph_2PH	$Ph_2P(CF_3)$	**25**	78
4	$Ph_2P(SiMe_3)$	$Ph_2P(CF_3)$	**25**	92[b]
5	$PhPH_2$	$PhPH(CF_3)$	**25**	84[b]
6	$(p\text{-Tol})_2PH$	$(p\text{-Tol})_2P(CF_3)$	**25**	78

[a] S_8 as oxidant. [b] Conversion calculated based on ^{19}F NMR spectroscopy with $PhCF_3$ as internal reference. [c] Sum of $CyPH(CF_3)$ and $CyPH_2(CF_3)^+$.

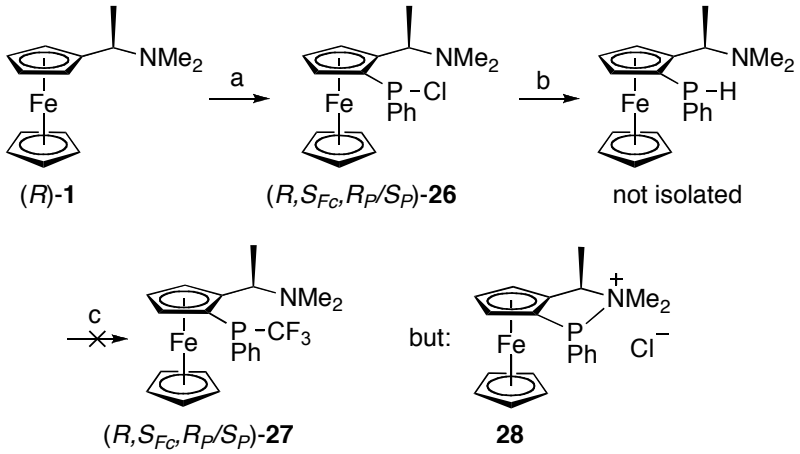
Two experiments using primary phosphines were conducted under the same condition (entries 2 and 5) using equimolar amounts of **25** in CD_2Cl_2 at ambient temperature to yield, interestingly, the corresponding monotrifluoromethylated phosphines exclusively. This constitutes a direct and very convenient synthesis of secondary racemic *P*-trifluoromethylated phosphines.

Some more recent studies showed that mixing primary phosphines with two equivalents of **25** and equimolar amount of the base DBU in CD_2Cl_2 afforded the corresponding ditrifluoromethylated phosphines.

2.2.2 Attempted Syntheses

In the following preliminary experiments, we tried several reactions to obtain our target molecule, the P-CF_3 analog of Josiphos.

In a first attempt, our strategy was based on the *ortho*-lithiation of (*R*)-Ugi's amine (**1**) with ^{t}BuLi and reaction with dichlorophenylphosphine (Scheme 48). Then, reduction of the phosphine with lithium aluminium hydride ($LiAlH_4$) followed by the electrophilic trifluoromethylation of the secondary phosphine using the hypervalent iodine-CF_3 reagent **24** developed in our group should afford the desired dimethylamino P-CF_3 analog of Josiphos. Unfortunately, the formal exchange of the H^+ with the CF_3^+ at the phosphorus atom of the phosphine did not proceed. The NMR analysis revealed the formation of a five membered cyclic quaternary ammonium salt **28** as the main product.



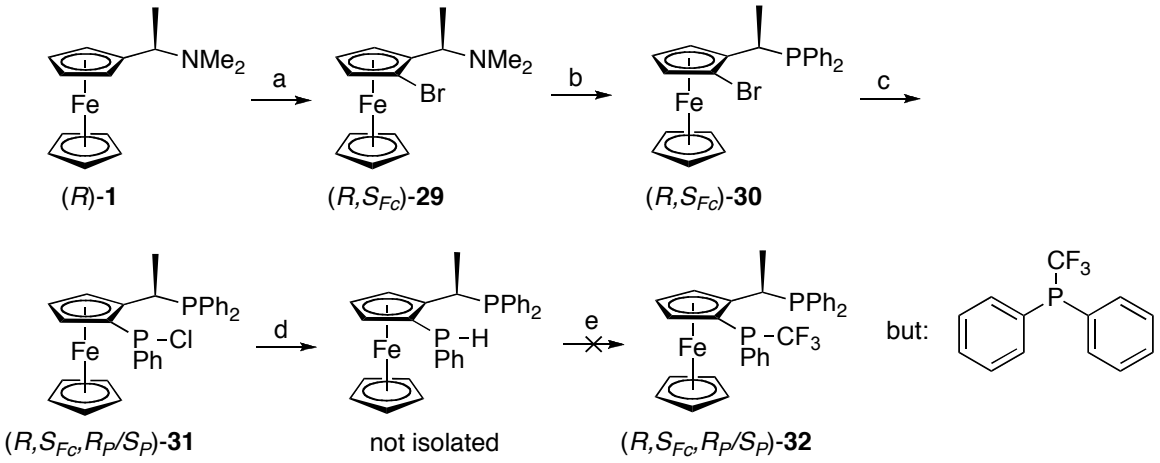
Scheme 48: First attempted synthesis of the P-CF_3 Josiphos analog. a) ^{t}BuLi, $PhPCl_2$, Et_2O, -78 °C to rt, overnight. b) $LiAlH_4$, Et_2O, -78 °C to rt, overnight. c) trifluoromethylating reagent **24**, CH_2Cl_2, -78 °C to rt, overnight.

This result parallels what *Chen* and co-workers reported in the synthesis of ferrocene-based P-chiral phosphine ligands (cf. section 2.1.2.5).[67] *Ortho*-lithiation was performed on Ugi's amine following by addition of a dichlorophosphine R^1PCl_2. As in Chen's case where Cl acted as a leaving group on the phosphorus atom, our team have recently discovered that also a CF_3 group can act as a leaving group yielding the five-membered cyclic diphosphine (P-P bond) when a secondary phosphine acts as nucleophile intramolecularly.[92]

As a consequence of this failed attempt, we considered that the replacement of the dimethylamino group by the phenylphosphine may prevent the formation of the cyclized product (Scheme 49). The synthesis started with the preparation of the known *o*-Br-Ugi's amine **29** by diastereoselective *ortho*-lithiation of (*R*)-Ugi's amine **1** with ^{s}BuLi and reaction with 1,2-dibromotetrachloroethane as the formal Br^+ source. Nucleophilic substitution of the NMe_2-group in **29** with diphenylphosphine $HPPh_2$[93] in acetic acid required elevated

temperatures due to the deactivating effect of the bromine substituents, but gave the desired product (R,S_{Fc})-**30** in good yield and a relatively short reaction time.

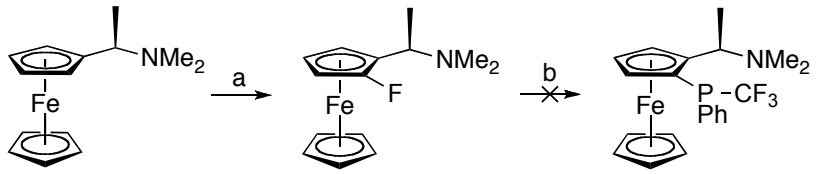
The phosphine unit was then introduced by nucleophilic attack of an *in situ* generated Fc-Li species on dichloro(phenyl)phosphine. Following the same procedure as above, reduction of the phosphine followed by electrophilic trifluoromethylation of **32** should have afforded the P-CF_3 analog of Josiphos. However, no desired compound was observed, instead, diphenyl(trifluoromethyl)phosphine and vinyl ferrocene were detected indicating an elimination reaction.



Scheme 49: Second attempted synthesis of the P-CF_3 Josiphos analog. a) ^{s}BuLi, -78 °C to rt, 1h and $(BrCl_2C)_2$, -78 °C to rt, overnight. b) $HPPh_2$, AcOH, 110 °C, 3h. c) ^{n}BuLi, $PhPCl_2$, Et_2O, -78 °C to rt, overnight. d) $LiAlH_4$, Et_2O, -78 °C to rt, overnight. e) trifluoromethylating reagent **24**, CH_2Cl_2, -78 °C to rt, overnight.

As *Yudin* and co-workers reported recently nucleophilic substitution on tetrafluoro(naphthalene) derivatives,[94] F-Ugi's amine* was thought to be a suited starting material for an analogous reaction. *o*-F-Ugi's amine **33** was synthesized applying the already described *ortho*-lithiation with ^{s}BuLi followed by the reaction with *N*-fluorobenzenesulfonimide (NFSI) as the formal F^+ source. With **33** in hands, the direct coupling reaction using the deprotonated form of phenyl(trifluoromethyl)phosphine as a nucleophile was attempted (Scheme 50). However, the formation of the desired P-CF_3 analog of ppfa was not observed when monitoring the reaction by means of NMR spectroscopy.

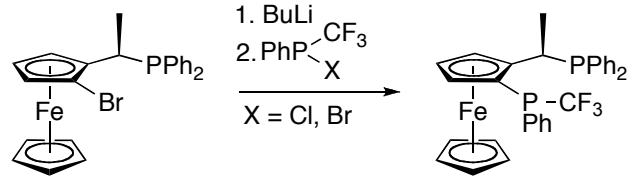
* a common compound in our group but yet to be published.



(*R*)-**1** (*R,S*$_{Fc}$)-**33** (*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**27**

Scheme 50: Third attempted synthesis of the P-CF_3 Josiphos analog. a) ^{s}BuLi, NFSI, Et_2O, -78 °C to rt, overnight. b) ^{n}BuLi, $PhPH(CF_3)$, THF, -78 °C to rt, overnight.

Carrying on with our reasoning, we pursued the idea to react the lithiated species derived from the (*S*$_{Fc}$)-1-bromo-2-[(*R*)-1-(diphenylphosphino)ethyl]ferrocene **30** with halo(phenyl)-(trifluoromethyl)phosphine in order to obtain the desired ligand in one step (Scheme 51).



(*R,S*$_{Fc}$)-**30** (*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**32**

Scheme 51: The proposal for the fourth attempt of the synthesis of the P-CF_3 Josiphos analog (**30**).

Whereas synthesis of compound (*R,S*$_{Fc}$)-**30** is known and reported with good yield,[93] the first challenge was the preparation of halo(trifluoromethyl)phosphines, a new class of compounds.

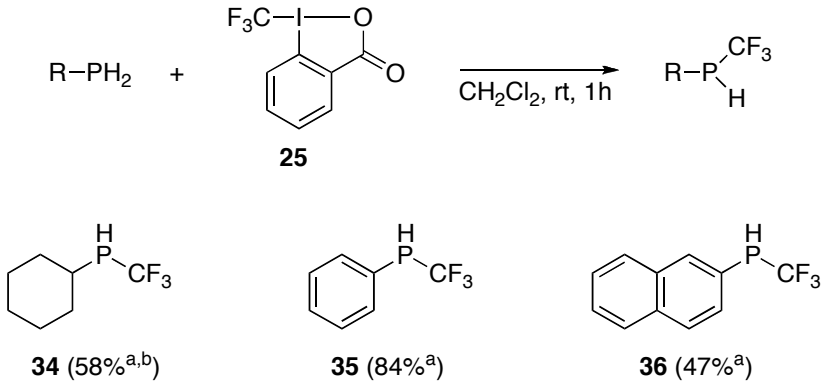
2.2.2.1 Synthesis of Halo(trifluoromethyl)phosphines

The straightforward approach to such compounds was conceived as following: first, a mono trifluoromethylation of a primary phosphine followed by the halogenation of the resulting secondary phosphine.

Trifluoromethylation of Primary Phosphines

As detailed previously, secondary and tertiary phosphines containing only a single CF_3-substituent can be accessed using hypervalent electrophilic I-CF_3 compounds.[89] Interestingly, mixing a primary phosphine with equimolar amounts of hypervalent iodine

derivative **25** in DCM at ambient temperature results in the formation of the corresponding monotrifluoromethylated phosphines, exclusively (Scheme 52).



Scheme 52: Trifluoromethylation of primary phosphines using hypervalent iodine reagent **25**. [a] conversion based on the comparison of the ratio of the integrals of the product signal to the signal of the internal standard, Ph-CF_3, in the ^{19}F NMR spectrum. [b] Sum of $CyPH(CF_3)$ and $CyPH_2(CF_3)^+$.

Being extremely sensitive to oxidation, these monotrifluoromethylated phosphines were synthesized in the glove-box and used in the next step without further purification.

Halogenation of Monotrifluoromethylated Phosphines

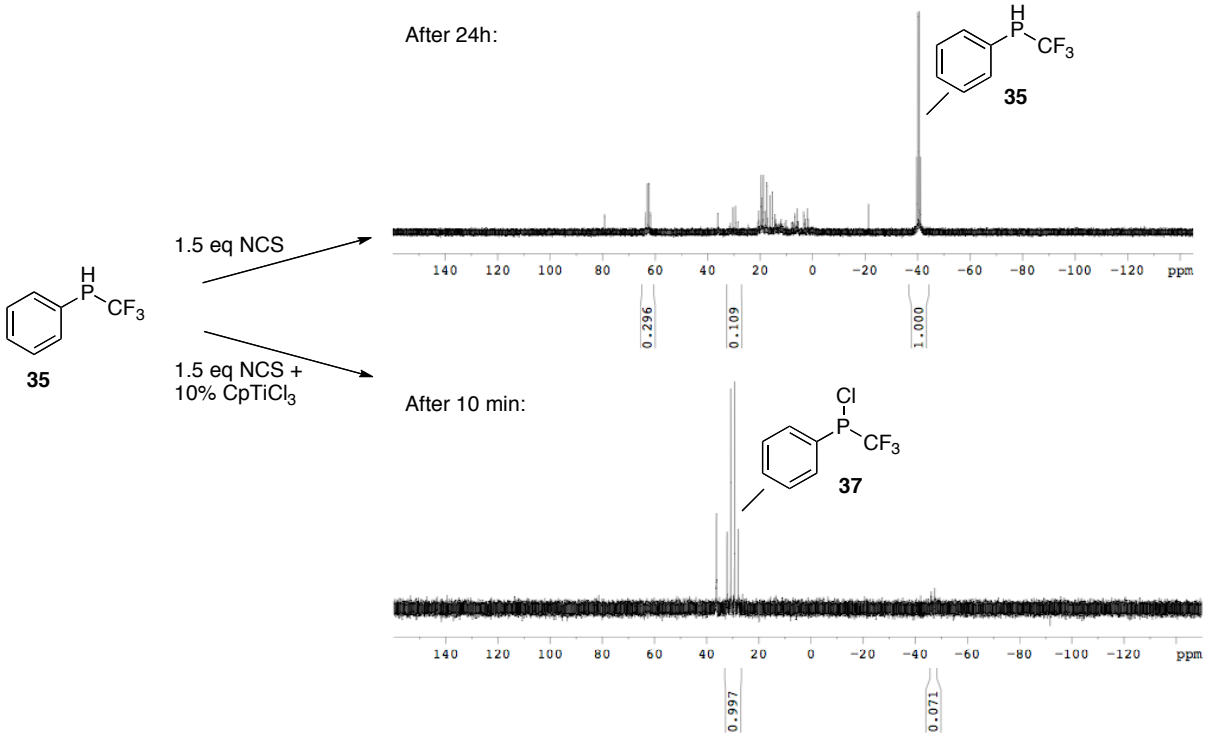
To use these secondary monotrifluoromethylated phosphines as reagents according to our plan, we proceeded with their transformation into the corresponding halophosphines.

Having in mind the catalytic enantioselective chlorination and bromination of ß-ketoesters performed by *Lukas Hintermann* in our group and described in Chapter 1 (Scheme 53),[95] we spontaneously chose NCS as chlorinating agent and NBS for bromination.

Scheme 53: Catalytic enantioselective chlorination and bromination of ß-ketoesters with NCS or NBS and [$TiCl_2$(*R,R*-TADDOLato)] as catalyst.

For the first time ever, this method was applied to phosphorus substrates and showed that secondary monotrifluoromethylated phosphines can be converted to the corresponding chlorides upon reaction with NCS although with very low conversion.

By analogy to the situation involving ß-keto esters, these reactions required the presence of a Ti catalyst. Indeed, when 10 mol% of cyclopentadienyltitanium (IV) trichloride ($CpTiCl_3$) was added to the secondary phosphine, the reaction took place cleanly and instantaneously while without titanium, only 11% conversion could be detected after 24h (Scheme 54).



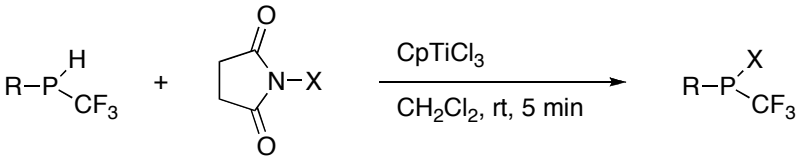
Scheme 54: ^{31}P-NMR spectroscopic observations of chlorination of phenyl(trifluoromethyl)phosphine catalyzed without and with Ti catalyst.

In spite of the fact that it wasn't possible to completely purify the product, a simple hexane extraction removes more than 80% of the by-products.

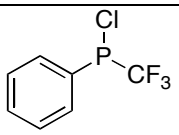
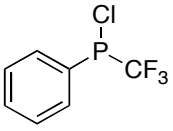
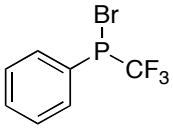
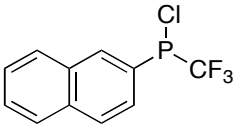
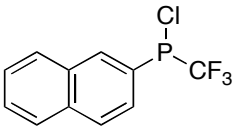
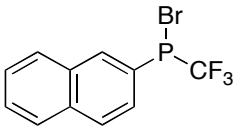
The reaction was then extended to the corresponding bromination using NBS as reagent, in order to obtain bromo(phenyl)(trifluoromethyl)phosphine. Interestingly, after 5 min reaction time at room temperature, the formation of two major new compounds could be detected in the ^{31}P and ^{19}F NMR spectra. Analysis of the spectra indicated that these two products corresponded to bromo- and chloro- (phenyl)(trifluoromethyl)phosphine, respectively, in a ratio of 1 to 1.4. This striking observation indicates that Cl ligands from the Ti catalyst were

prone to undergo halogen-exchange reactions under the reaction conditions applied. Similar trends were observed also in the case of chlorination and bromination of naphtyl(trifluoromethyl)phosphine (Table 13).

Table 13: Chlorination and bromination of (phenyl)- and (naphtyl)-(trifluoromethyl)phosphine.



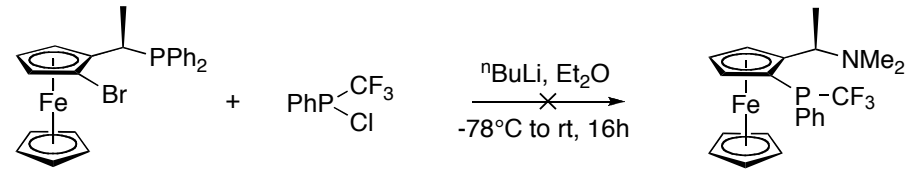
NCS: X = Cl
NBS: X = Br

	R	Reagent	Product / Conversion
1	Ph	NCS	 **37** conv[a]: quant.
2	Ph	NBS	 **37**  **38** conv[b]: quant. 1(Br)/1.4(Cl)[c]
3	Np	NCS	 **39** conv[a]: quant.
4	Np	NBS	 **39**  **40** conv[b]: quant. 1(Br)/1.4(Cl)[c]

[a] conversion based on the ^{19}F and ^{31}P NMR spectrum. [b] conversion based on the ^{19}F and ^{31}P NMR spectrum; incorporation of Cl from the catalyst. [c] molar ratio of the bromo- vs the chloro-compounds based on the ^{19}F and ^{31}P NMR spectrum.

Attempts to Synthesize the Trifluoromethylated Analog of Josiphos

Coming back to our initial goal to synthesize a PCF_3 analog of Josiphos, halogeno(trifluoromethyl)phosphines were reacted together with the lithiated intermediate (*R,S*$_{Fc}$)-**30** but again, the formation of the product was not detected (Scheme 55).

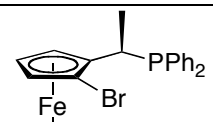
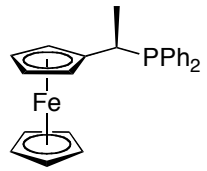


(R,S_{Fc})-**30** **37** ($R,S_{Fc},R_P/S_P$)-**27**

Scheme 55: Attempted substitution reaction of (R,S_{Fc})-**30** with chloro(phenyl)(trifluoromethyl)phosphine.

Several phosphines were tested under different conditions but with no success. The results are compiled in Table 14.

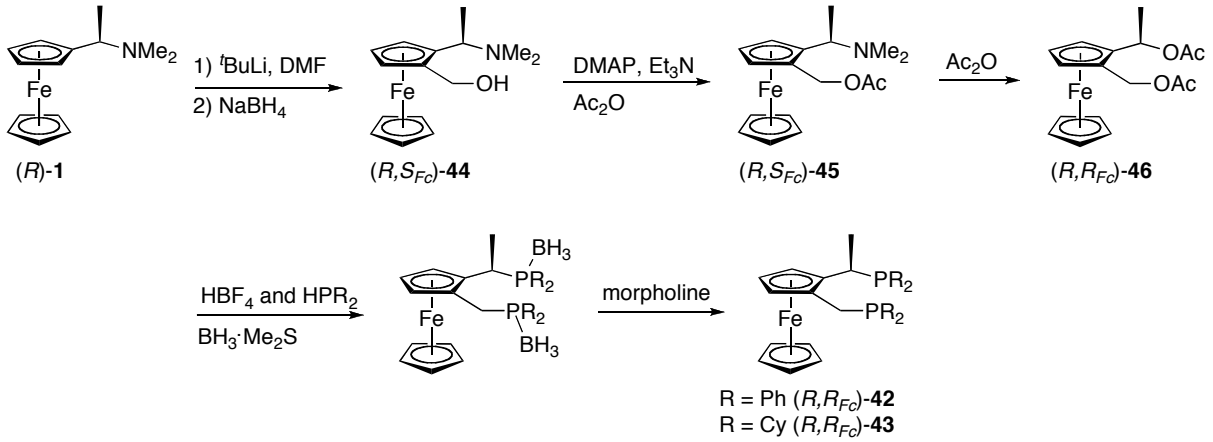
Table 14: Various conditions for the nucleophilic substitution of **30** and **41**.

	Substrate	Reagent	Conditions	Observation
1	 (R,S_{Fc})-**30**	$PPh(CF_3)Cl$ (**37**)	^nBuLi, Et_2O -78 °C to rt, overnight	n.r.
2		$PPh(CF_3)Cl$ (**37**) + $PPh(CF_3)Br$ (**38**)	^nBuLi, Et_2O -78 °C to rt, overnight	n.r.
3	 (R)-**41**	$PPh(CF_3)Cl$ (**37**)	^nBuLi, Et_2O -78 °C to rt, overnight	n.r.
4		$PPh(CF_3)Cl$ (**37**)	^nBuLi, Et_2O -78 °C to reflux, overnight	n.r.
5		$PPh(CF_3)Cl$ (**37**) + $PPh(CF_3)Br$ (**38**)	^nBuLi, Et_2O -78 °C to reflux, overnight	n.r.

2.2.3 New Ferrocenyl Bisphosphines Ligands - Combination of Carbon-Centered Chirality, Planar Chirality and Phosphorus Chirality

Recently, *Pélinski* and co-workers reported a new class of 1,2 disubstituted chiral ferrocenyl bisphosphines for asymmetric transfer hydrogenation of acetophenone.[96] Following a similar procedure as described by *Fukuzawa* and co-workers,[97] the ferrocenyl bisphosphines (R,R_{Fc})-**42** and (R,R_{Fc})-**43** have been synthesized from (*R*)-Ugi's amine (**1**) (Scheme 56). *Ortho*-lithiation of (*R*)-**1** by *t*-BuLi followed by addition of DMF and subsequent reduction of

the corresponding aldehyde by $NaBH_4$ led to (R,R_{Fc})-**44** in an overall yield of 88%. The acylation of the alcohol group was carried out in acetic anhydride in the presence of DMAP and Et_3N at room temperature to give (R,R_{Fc})-**45** in 95% yield. Substitution of the dimethylamino group by an acetoxy residue was then performed in the presence of acetic anhydride at 100 °C providing (R,R_{Fc})-**46** in 72% yield.



Scheme 56: Synthesis of a new class of ferrocenyl bisphosphine (**42** and **43**).

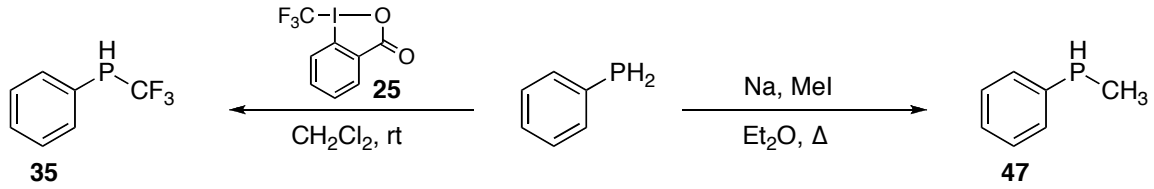
The diacetoxyferrocene **46** was then converted into bisphosphines in the presence of HBF_4 followed by addition of HPR_2 in CH_2Cl_2 at room temperature. For the sake of facile purification by column chromatography on silica gel, the bisphosphine was protected as borane adduct. Subsequent deprotection by morpholine yielded (R,R_{Fc})-**42** and (R,R_{Fc})-**43** in 80 and 50% yield, respectively, and was carried out prior to their use in catalysis.
Pélinsky showed that **42** may be used in the Ru-catalyzed transfer hydrogenation of acetophenone, giving an enantiomeric excess of up to 64%.

2.2.3.1 Synthesis of New Ligands

The general synthesis of the new ferrocenyl trifluoromethylphosphine reported here started from the enantiomerically pure (*R*)-Ugi's amine **1** and gave the desired ligands in four steps using different kinds of secondary phosphines as nucleophiles for the introduction of the phosphorus functionality.
The "standard" procedure developed by *Pélinski* and co-workers will be used and revisited to simplify the method for the introduction of a phosphine in the *ortho* position of Ugi's amine

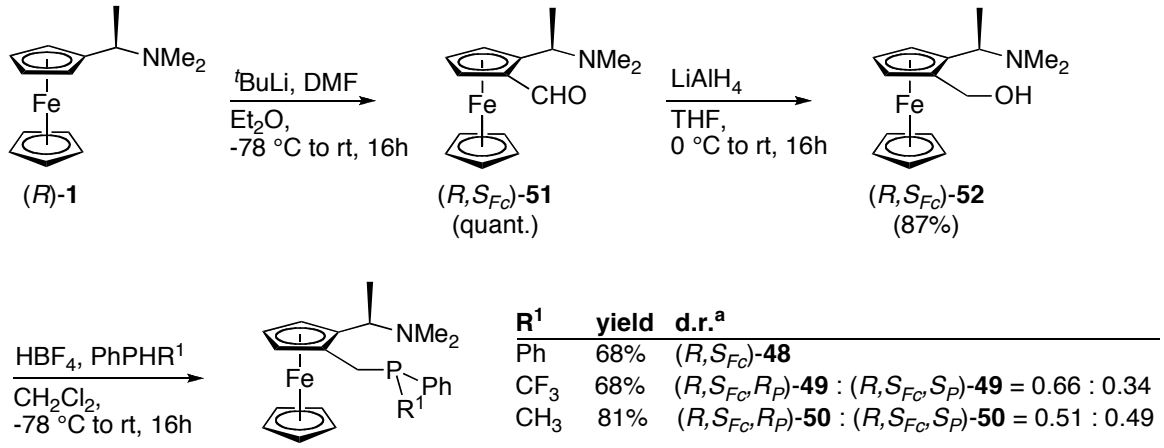
and as a last step, the dimethylamino group will be substituted by a secondary phosphine in order to obtain a new kind of ferrocenyl bisphosphine ligands.

To perform the synthesis as delineated above, the secondary phosphine Ph_2PH, $PhPH(CF_3)$ and $PhPH(CH_3)$ were required. The commercially available Ph_2PH from *Strem Chemicals* was used without further purification. $PhPH(CF_3)$ **35** was synthesized in the glovebox according to the procedure described above, by reacting phenylphosphine with the hypervalent iodine-CF_3 reagent **25** in CH_2Cl_2 and was used without further purification. Finally, $PhPH(CH_3)$ **47** was synthesized according to the two step procedure described by *Schindlbauer* in 1959.[98] First, addition of phenylphosphine to a suspension of sodium in Et_2O and refluxing for one hour, followed by the addition of iodomethane at room temperature (exothermic reaction) and refluxing the reaction mixture for 30 min. The methyl(phenyl)phosphine **47** was purified by filtration and distillation (Scheme 57).



Scheme 57: Synthesis of the (phenyl)(trifluoromethyl)phosphine **35** and the methyl(phenyl)phosphine **47**.

The syntheses of the ferrocenyl monophosphines **48**, **49** and **50** starting from (*R*)-Ugi's amine are depicted in Scheme 58. Diastereoselective *ortho*-lithiation of (*R*)-**1** with ^{t}BuLi followed by the addition of *N,N*-dimethylformamide (DMF) and reduction of the aldehyde (*R,S*$_{Fc}$)-**51** by $LiAlH_4$ led to the desired alcohol (*R,S*$_{Fc}$)-**52** in an overall yield of 87% over two steps. The alcohol function was then transformed to the substituted phenylphosphine in the presence of HBF_4 followed by the addition of Ph_2PH, $PhPH(CF_3)$ **35** or $PhPH(CH_3)$ **47**, respectively, at -78 °C providing the aminophosphines **48**, **49** and **50** in good yields. The two diastereoisomers of **49** and **50** turned out to be readily separable (*vide infra*).



R^1	yield	d.r.[a]
Ph	68%	(R,S_{Fc})-**48**
CF_3	68%	(R,S_{Fc},R_P)-**49** : (R,S_{Fc},S_P)-**49** = 0.66 : 0.34
CH_3	81%	(R,S_{Fc},R_P)-**50** : (R,S_{Fc},S_P)-**50** = 0.51 : 0.49

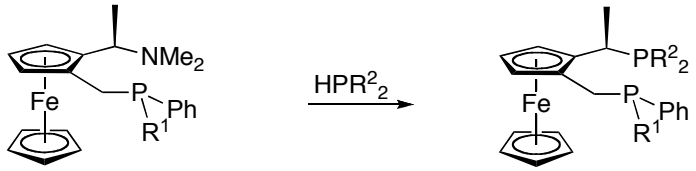
Scheme 58: Highly modular preparation of chiral ferrocenyl aminophosphines starting from (*R*)-Ugi's amine (**1**). [a] Distereomeric ratio determined by ^{31}P NMR spectroscopy.

Standard nucleophilic substitution of NMe_2-group by PPh_2 or PCy_2 was performed in acetic acid at 90 °C for 5h or at 110 °C for 3h to obtain the desired bisphosphines in good to very good yields (entries 1-5, Table 15). Reaction with enantiomerically pure ($R,S_{Fc,}S_P$)-**49** or ($R,S_{Fc,}R_P$)-**49**, afforded ($R,R_{Fc,}S_P$)-**54** or ($R,R_{Fc,}R_P$)-**54**, respectively in better yields (up to 93%).

Surprisingly, no conversion could be observed by reacting the aminophosphine **50** under these conditions. Variation of reaction conditions revealed 90% conversion after 3h at 90 °C when trifluoroacetic acid (TFA) was used as solvent instead of the traditional acetic acid (entry 6).

It is interesting to note that all the aminophosphines and the bisphosphines prepared were stable under the conditions of an aqueous work-up and column chromatography. The only problems appeared during the isolation and purification of the bisphosphine **56**, which turned out to be air sensitive; work-up and purification of the product by flash chromatography were then performed under inert conditions using degassed solvents and the product was stored in a glove-box.

Table 15: Bisphosphine ligands **53**, **54**, **55** and **56** are readily prepared from the corresponding aminophosphines in a one step procedure by a nucleophilic substitution.



	Substrate		Conditions	Product			Yield [%]
	R^1			R^1	R^2		
1	Ph	(*R,S*$_{Fc}$)-**48**	AcOH, 110 °C, 3h	Ph	Ph	(*R,R*$_{Fc}$)-**53**	72
2	CF_3	(*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**49**	AcOH, 90 °C, 5h	CF_3	Ph	(*R,R*$_{Fc}$,*R*$_P$/*S*$_P$)-**54**	89
3	CF_3	(*R,S*$_{Fc}$,*R*$_P$)-**49**	AcOH, 90 °C, 5h	CF_3	Ph	(*R,R*$_{Fc}$,*R*$_P$)-**54**	93
4	CF_3	(*R,S*$_{Fc}$,*S*$_P$)-**49**	AcOH, 90 °C, 5h	CF_3	Ph	(*R,R*$_{Fc}$,*S*$_P$)-**54**	92
5	CF_3	(*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**49**	AcOH, 90 °C, 5h	CF_3	Cy	(*R,R*$_{Fc}$,*R*$_P$/*S*$_P$)-**55**	91
6	CH_3	(*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**50**	TFA, 90 °C, 3h	CH_3	Ph	(*R,R*$_{Fc}$,*R*$_P$/*S*$_P$)-**56**	65

2.2.3.2 Ligand Characterization

Ligands (*R,S*$_{Fc}$)-**48** and (*R,R*$_{Fc}$)-**53** were fully characterized with the NMR spectroscopic characteristics following the expected pattern. The attempted crystallization proved successful, the orange microcrystals were, however, not suitable for X-ray analysis.

The characterization of dimethylamino methyl(phenyl)phosphine **50** proved complicated because of the two inseparable diastereoisomers (*R,S*$_{Fc}$,*S*$_P$) and (*R,S*$_{Fc}$,*R*$_P$). NMR analyses were therefore quite laborious due to the two sets of signals. Similarly, all attempts to separate the diastereoisomeric mixture of the bisphosphine (*R,R*$_{Fc}$,*R*$_P$/*S*$_P$), even by means of HPLC proved fruitless.

The trifluoromethylated ligands **49**, **54** and **55** show characteristic structural and spectroscopic features, which deserve further discussion.

The first amino phosphine ferrocenyl ligand containing a chiral trifluoromethylated phosphine (*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**49** was isolated in 68% yield starting from the alcohol (*R,S*$_{Fc}$)-**52**. We were delighted that the attempts to separate the two diastereoisomers on chiral HPLC happened to be successful. Using a Chiralcel OJ column, (*R,S*$_{Fc}$,*R*$_P$)-**49** was found to be the major product (66%) and (*R,S*$_{Fc}$,*S*$_P$)-**49** appeared to be present in 34%. Preparative HPLC was then

performed on small amounts of product (10 to 50 mg) yielding enantiomerically pure forms of **49** (Figure 15). Further investigations showed that the easiest way to perform this separation is a "simple" crystallization from hot methanol. While (*R,S*$_{Fc}$,*R*$_P$)-**49** forms orange crystals, (*R,S*$_{Fc}$,*S*$_P$)-**49** remains in the methanol phase.

a) b)

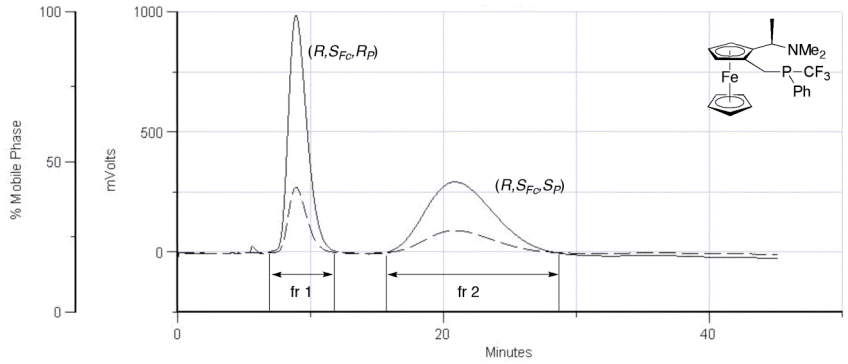


Figure 15: a) Preparative HPLC, chiralcel OJ, hexane:^{i}PrOH 98:2, 15 mL/min, 10-50 mg. b) Picture of a crystalline sample of (*R,S*$_{Fc}$,*R*$_P$)-**49** together with a MeOH solution of (*R,S*$_{Fc}$,*S*$_P$)-**49**.

As expected, the nucleophilic substitution of the dimethylamino group in (*R,S*$_{Fc}$,*R*$_P$/*S*$_P$)-**49** with diphenylphosphine or dicyclohexylphosphine occured with retention of configuration. Because no epimerization took place, reaction of (*R,S*$_{Fc}$,*R*$_P$)-**49** with $HPPh_2$ yielded (*R,R*$_{Fc}$,*R*$_P$)-**54** as orange microcrystalline compound in 93% yield. Similarly, (*R,S*$_{Fc}$,*S*$_P$)-**49** reacted with $HPPh_2$ affording (*R,R*$_{Fc}$,*S*$_P$)-**54** as orange oily product in 90% yield. On the other hand, the reaction of the diastereoisomeric mixture of **49** with both secondary phosphines $HPPH_2$ and $HPCy_2$, yielded the diastereoisomeric mixture of **54** or **55**, respectively, which were easy to separate by crystallization from hot MeOH.

The stereogenic P atom in ligand **54** is configurationally stable. In fact, heating (*R,R*$_{Fc}$,*R*$_P$)-**54** in d^8-toluol for 3 days at 100 °C did not lead to any detectable epimerization, as monitored by ^{31}P NMR spectroscopy.

NMR Investigation in Solution

The main efforts were directed towards the characterization of the new (*R,S*$_{Fc}$/*R*$_{Fc}$,*R*$_P$/*S*$_P$)-(trifluoromethyl)phosphine ligand **49**, **54** and **55.** Especially **49** and **54** were studied in $CDCl_3$ solution by NMR using 1D [^{1}H-, ^{31}P{^{1}H}-, ^{19}F-, ^{13}C- and ^{13}C{^{19}F}-INEPT] and 2D-techniques [^{1}H,^{13}C-HMQC, ^{1}H,^{13}C-HMBC, ^{1}H,^{1}H-COSY, ^{19}F,^{13}C-HMQC, ev. ^{1}H,^{31}P-HMQC].

A preliminary analysis of the 1D-spectra usually gave information about the relative amount of the two diastereoisomers. $^{31}P\{^1H\}$- and ^{19}F-NMR spectra were particularly helpful providing quick information on the diastereoisomer and P,F- coupling. The ^1H assignment of the aliphatic protons was important as we could easily detect the $J_{H,H}$ but also the $J_{P,H}$. Interestingly, as it is depicted in Figure 16 for (R,R_{Fc},R_P)-**54**, each of the two diasterotopic protons of the methylene spacer appeared as two different signal, one being a *doublet* (2.48 ppm) with a $^2J_{H,H}$ of 15 Hz and the other one being a *doublet of doublet* (1.96 ppm) featuring also a coupling to the phosphorus atom ($^2J_{H,H}$ = 15 Hz $^2J_{P,H}$ = 7 Hz).

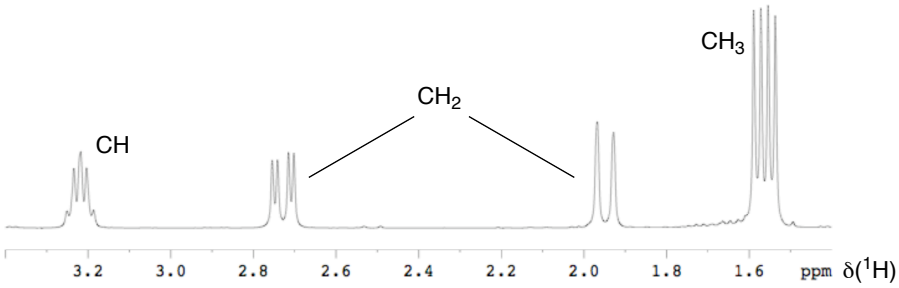


Figure 16: ^1H-NMR spectrum (300.1 MHz, $CDCl_3$) of ligand (R,R_{Fc},R_P)-**54** in the aliphatic area showing a *doublet of doublet* for the methyl group, a *doublet* and a *doublet of doublet* for the methylene spacer and an overlapped *quartet of doublet* for the methine group.

Because the carbon of the CF_3 substituent displayed only a very low intensity signal in the ^{13}C-NMR spectrum (Figure 17), ^{19}F coupled INEPT and $^{13}C,^{19}F$-HMQC analyses were performed to confirm our hypothesis that the carbon of the trifluoromethyl substituent should appear as a *quartet of doublet* due to its spin-spin coupling with the three fluorine atoms (*quartet*) and the phosphorus atom (*doublet*).

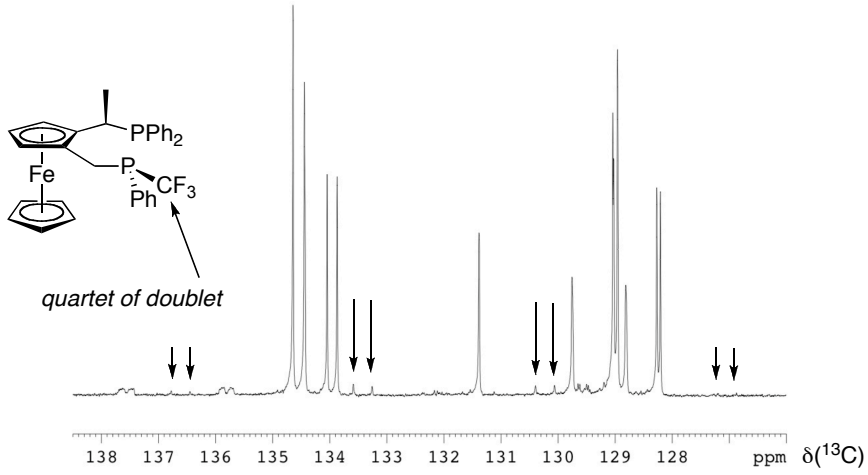


Figure 17: $^{13}C\{^1H\}$-NMR spectrum (100.6 MHz, $CDCl_3$) of ligand (R,R_{Fc},R_P)-**54** showing the *quartet of doublet* (arrows) of the trifluoromethyl substituent at 131.8 ppm.

The $^{13}C\{^{1}H\}$-NMR ^{19}F coupled spectrum obtained using the INEPT pulse sequence confirms the presence of a P-CF_3 moiety in the molecule (Figure 18). The idea behind the INEPT pulse sequence is to selectively invert the lines of the ^{19}FX *quartet* by using a phase cycling. If instead of using a $^{19}F(90°)_y$ pulse as the final ^{19}F pulse, a $^{19}F(90°)_{-y}$ pulse is used, the phase of the ^{19}F *quartet* is reversed. Phase cycling of the receiver permits addition or subtraction of the spectra. The resulting ^{19}F coupled X spectrum does not have the usual 1 : 3 : 3 : 1 *quartet* intensity, but rather the (-1) : (-1) : 1 : 1 *quartet* intensity. Because carbon is also coupling with the adjacent phosphorus atom, each signal of the *quartet* is doubled giving the expected *quartet of doublet*. In order to be able to ^{19}F decouple, the pulse sequence has to be extended. This is because in a ^{19}F coupled INEPT spectrum there is as much positive intensity as negative intensity. The result of the decoupling is to give zero intensity. INEPT was chosen (rather than DEPT) in order to observe the valuable ^{13}C, ^{31}P and ^{13}C, ^{19}F coupling constants. The large value of $^{1}J_{F,C}$ = 321 Hz and $^{1}J_{P,C}$ = 33 Hz confirmed the *quartet of doublet* multiplicity of the carbon of the CF_3 group shown by the arrows in Figure 17.

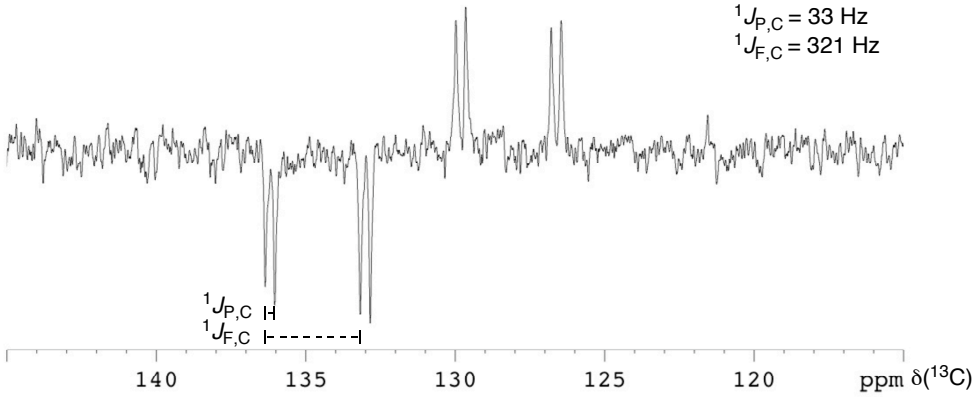


Figure 18: ^{19}F coupled INEPT NMR spectrum (100.6 MHz, $CDCl_3$) of ligand (*R,R*$_{Fc}$,*R*$_P$)-**54** showing a (-1) : (-1) : 1 : 1 *quartet* at 131.8 ppm.

Inverse detection as carried out by the $^{13}C,^{19}F$-HMQC experiment, is also a powerful tool to confirm the structure of a molecule by detecting insensitive nuclei attached to sensitive nuclei. The method uses the sensitivity of the sensitive nucleus, here ^{19}F, to observe other spin-coupled nuclei. The HMQC plot of ligand **54**, tuned for *J*(CF), is shown in Figure 19, illustrating an enlargement of the spectral region between -58.4 and -59.8 ppm on the ^{19}F scale in order to highlight the coupling pattern of the trifluoromethyl group.

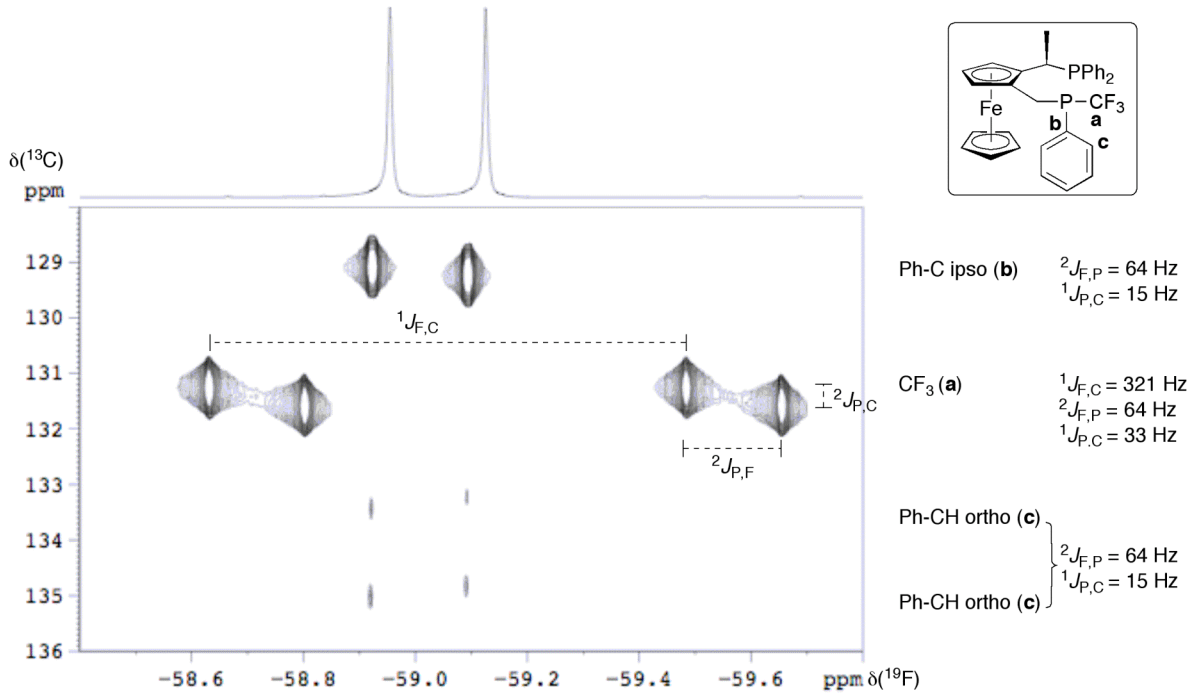


Figure 19: $^{13}C,^{19}F$-HMQC NMR spectrum (376 MHz, $CDCl_3$) of ligand (R,R_{Fc},R_P)-**54**.

A coupling with the *ipso* and the two *ortho* carbons of the phenyl attached at the phosphorus can be observed with the expected $^1J_{F,P}$ of 64 Hz and $^2J_{P,C}$ of 15 Hz. The carbon atom of the CF_3 group can be easily identified showing the same coupling constant as in the ^{19}F coupled INEPT NMR spectrum plus a new $^2J_{F,P}$ of 64 Hz.

X-Ray Crystal Structural Characterization

Finally, X-ray analyses also provided information concerning the nature of the bonding present in free bisphosphines. Crystals of ligands (R,S_{Fc},R_P)-**49** and (S,R_{Fc},S_P)-**49** as well as (R,R_{Fc},R_P)-**54** and (S,S_{Fc},S_P)- **54** were grown by diffusion of *n*-hexane into a CH_2Cl_2 solution.

These new ferrocenyl ligands **49** and **54** represent the first crystallographic analyses (based on the Cambridge Structure Database) of chiral ferrocenyl ligand containing a PCF_3 unit.
As mostly observed in compounds derived from Ugi's amine, the nitrogen atom (N1 in **49**) or the phosphorus atom (P2 in **54**) attached to C11 is in a pseudo-axial position with respect to the ferrocene core as indicated by the torsion angles C1C2C15P1 = 80.3° and C2C1C11N1 = -64.4° for **49** and C5C1C11C12 = 73.7° for **54**.[99]

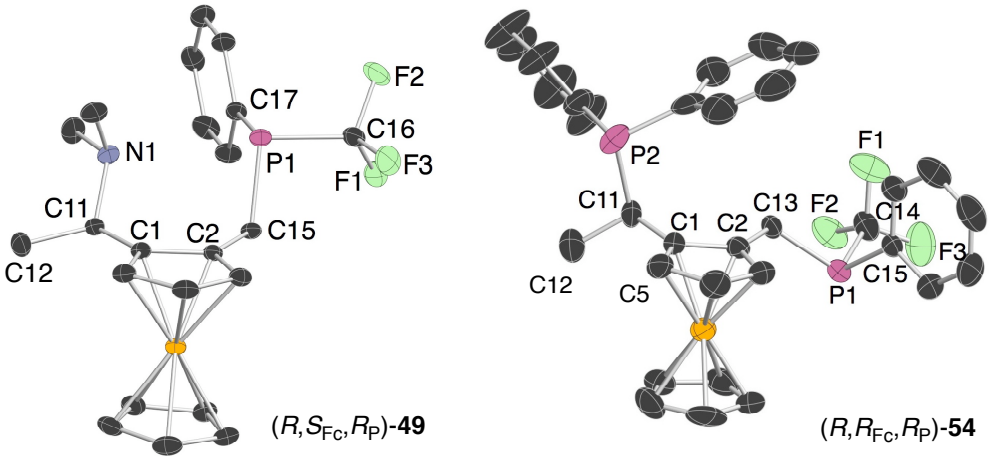


Figure 20: ORTEP representation of the molecular structure of ligand (*R,S*$_{Fc}$,*R*$_P$)-**49** (left) and ligand (*R,R*$_{Fc}$,*R*$_P$)-**54** (right). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): (*R,R*$_{Fc}$,*R*$_P$)-**49**: P1-C16: 1.8809(13); P1-C17: 1.8262(12); C16-F1: 1.3444(15); C16-F2: 1.3513(14); C16-F3: 1.3540(14); C15-P1-C16: 96.34(5); C15-P1-C17: 106.26(5); C16-P1-C17: 95.71(5); C1-C11-N1: 108.34(9); C1-C11-C12: 112.19(10); N1-C11-C12: 115.44(10). (*R,R*$_{Fc}$,*R*$_P$)-**54**: P1-C14: 1.866(5); P1-C15: 1.830(4); C14-F1: 1.341(6); C14-F2: 1.361(6); C14-F3: 1.347(5); C13-P1-C14: 96.0(2); C13-P1-C15: 103.7(2); C14-P1-C15: 97.9(2); C1-C11-P2: 106.7(4); C1-C11-C12: 113.5(4); P2-C11-C12: 106.8(3).

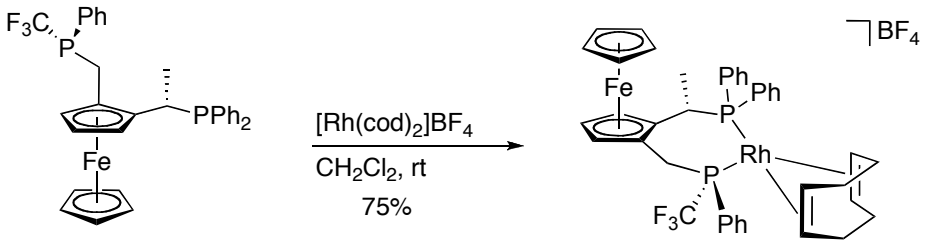
As a consequence of Bent's rule,[100] which claims that the electronegative substituents "prefer" hybrid orbitals with less s-character and the electropositive substituents "prefer" hybrid orbitals with more s-character, the lone pair at phosphorus bearing an electronegative CF_3 group is in the orbital with increased s-character. In the absence of obvious steric effects, the valence angle generally decreases as the electronegativity of the substituent increases. The sum of bond angles around P1 (297.6°) is significantly smaller than around P2 (306.2°).

Focussing on the bisphosphines (*R,R*$_{Fc}$,*R*$_P$)-**54** and (*S,S*$_{Fc}$,*S*$_P$)-**54**, analysis of the phosphorus-carbon bond distance within the PCF_3 framework of the uncoordinated bisphosphine are 1.866(5) Å and 1.856(4) Å, respectively Unfortunately, it was not possible to compare the data with the methylphosphine analog (*R,R*$_{Fc}$,*R*$_P$/*S*$_P$)-**56** as crystals suitable for X-ray analysis were not obtained.

2.2.4 Complexes with P^P*CF_3 Ferrocenyl Ligands

2.2.4.1 Cationic [Rh(P^P*CF_3)cod]$^+$ Complex - Synthesis and Characterization

A cationic Rh^I complex was prepared in a simple procedure by reaction of ligand (*S,S*$_{Fc}$,*S*$_P$)-**54** at room temperature with [Rh(cod)$_2$]BF_4 in dichloromethane (Scheme 59).



(*S,S*$_{Fc}$,*S*$_P$)-**54** **57**

Scheme 59: Synthesis of the cationic Rh^I complex **57** with ligand (*S,S*$_{Fc}$,*S*$_P$)-**54**.

Analysis of the isolated complex **57** gave important information on the steric and electronic properties of the new trifluoromethylphosphine ligand (*S,S*$_{Fc}$,*S*$_P$)-**54**. The coordinated cod ligand can be investigated from a structural point of view both by NMR techniques and by X-ray crystallography.

The $^{31}P\{^1H\}$-NMR spectrum of compound **57** in $CDCl_3$ solution proved unambiguously that the desired [Rh(cod)**54**]BF_4 complex had been obtained. Figure 21 highlights three main features of the spectra:

- since rhodium has one NMR active isotope with 100% natural abundance (^{103}Rh), the expected split of the multiplicity was observed (the *doublet* of the diphenylphosphine turned into a *doublet of doublet* and the *quartet of doublet* of the (phenyl)(trifluoromethyl)phosphine was replaced by a *quartet of doublet of doublet*). An interesting, but not surprising, fact is that the $^1J_{P,Rh}$ is by 24 Hz larger for the trifluoromethylphosphine than for the diphenylphosphine substituent. This reflects the higher s-character of the P lone pair of the CF_3 group.
- when phosphines are coordinated to rhodium, an expected shift of the resonances to higher field is observed (a difference of +17 ppm for the diphenylphosphine and +44 ppm for the (phenyl)(trifluoromethyl)phosphine)

- coupling constants between the two phosphine substituents ($J_{P,P}$) in the Rh-complex appeared to be 8 times larger than in the free ligand. This represent a significant difference from Josiphos where a $J_{P,P}$ of 30 Hz could be observed for the free as well as for the coordinated ligand.[101]

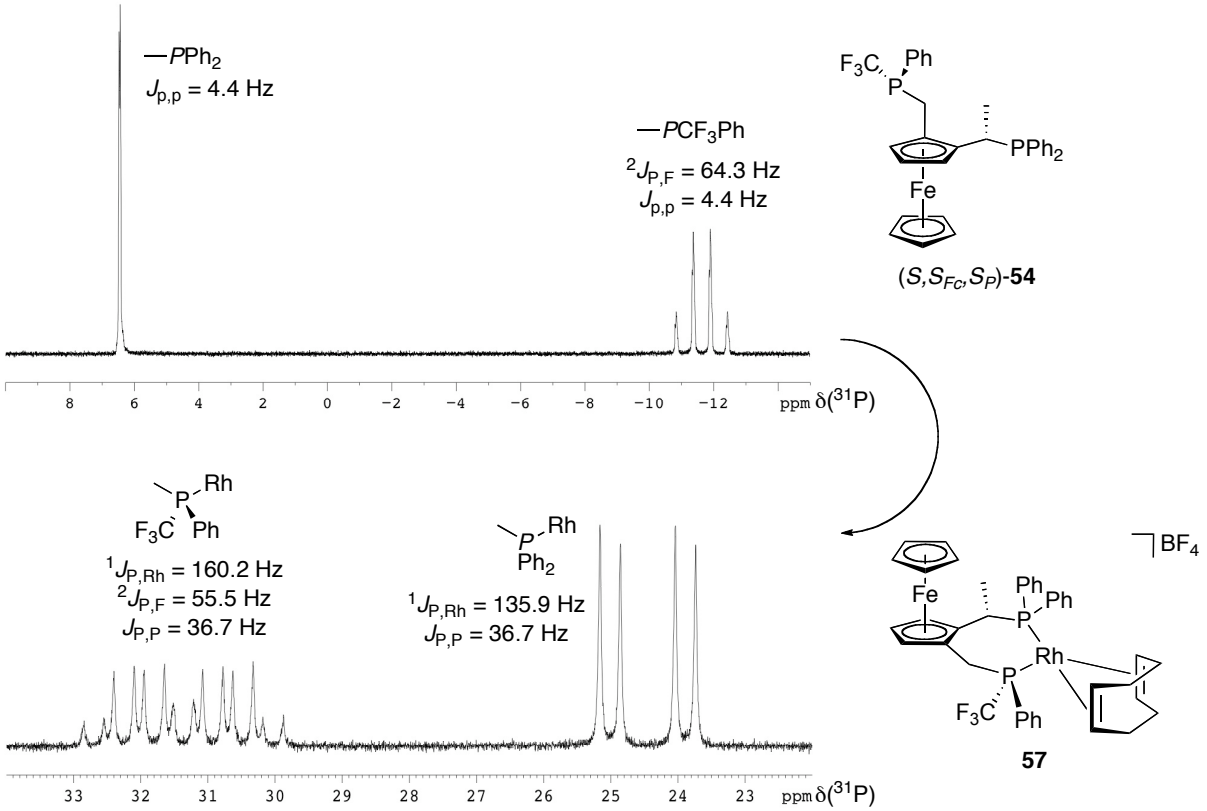


Figure 21: $^{31}P\{^{1}H\}$ NMR spectrum (121.5 MHz, $CDCl_3$) of ligand (S,S_{Fc},S_P)-**54** and Rh complex **57** showing chemical shifts and coupling parameters of both phosphines.

Single crystals suitable for X-ray analysis were obtained for the [Rh(cod)**54**]BF_4 complex **57** by diffusion of *n*-hexane in a dichloromethane solution. An ORTEP representation of the crystal structure of **57** is given in Figure 22.

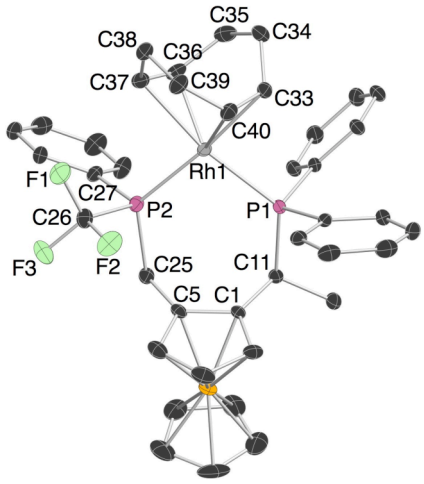
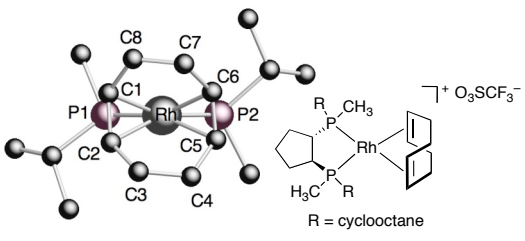
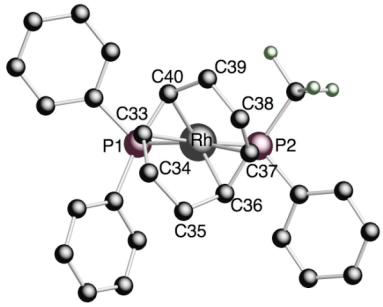


Figure 22: ORTEP representation of the molecular structure of [Rh(cod)**54**]BF_4 (**57**). Hydrogen atoms and the BF_4 anion are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond angles (°): C25-P2-C26: 97.89(9); C25-P2-C27: 102.84 (9); C26-P2-C27: 103.82(9).

[Rh(cod)**54**]BF_4 has a crystal packing, which seems to be predominantly determined by Van der Waals' interactions between the bulky cations. The rhodium cation is a 16 valence electron species, somewhat distorted square planar complex, the vertices (atoms, points) of the square planar being occupied by the phosphorus atoms and by the 2 η^2-bonded double bonds of 1,5-cyclooctadiene. Figure 23 depicts the coordination sphere around rhodium; on the left hand side, a nearly perfect square planar geometry is shown[102] with the Rh-P bonds being essentially coplanar with the midpoints of the Rh-C=C_{cod} whereas on the right hand side, the distorted square planar complex **57** is presented. A possible interpretation of the deviation from square-planar geometry for **57** can be a possible sterically induced twisting of the COD ligand.



[Rh(cod)C_5H_8{P(CH_3)(C_8H_{15}-*cyclo*)}$_2$]O_3SCF_3

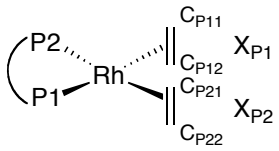


[Rh(cod)**54**]BF_4 (**57**)

Figure 23: Ball-and-stick representations of the molecular structure of **57** compared with that of [Rh(cod)C_5H_8{P(CH_3)(C_8H_{15}-*cyclo*)}$_2$]O_3SCF_3,[102] an other Rh complex containing a P-stereogenic ligand. Only the coordination sphere around rhodium is shown for clarity.

A search in the CSD database for crystal structures of seven-membered ring bisphosphino $Rh(cod)L_2$ complexes delivered a few examples. For comparison, $[Rh(cod)(LL)]^+$; with LL = 1,4-bis(diphenylphosphino)butane (dppb)[103] was chosen. It is interesting to analyze the geometrical parameters concerning the coordination sphere around rhodium in the two cases. The relevant bond lengths and angles are summarized in Table 16.

Table 16: Structural data concerning the coordination sphere around rhodium in crystals of [Rh(cod)(**54**)]BF_4 (**57**) and [Rh(cod)(dppb)]BF_4.[103] Distances are given in [Å] and angles in [°]. Standard deviations are given in parentheses.



	[Rh(cod)(**54**)]BF_4	[Rh(cod)(dppb)]BF_4[103]
Rh-P1	2.3100(5)	2.318
Rh-P2[a]	2.2679(4)	2.343
Rh-C_{P11}	2.280(2)	2.266
Rh-C_{P12}	2.191(2)	2.253
Rh-C_{P21}	2.225(2)	2.221
Rh-C_{P22}	2.277(2)	2.220
C_{P11}-C_{P12}	1.386(3)	1.336
C_{P21}-C_{P22}	1.378(3)	1.336
< P1-Rh1-P2	99.21(2)	90.73

[a] For complex [Rh(cod)(**54**)]BF_4, P2 belonging to the *P*$PhCF_3$ group.

The Rh-P1 distance is comparable to those found in similar complexes $[Rh(cod)(LL)]^+$; for instance, for [Rh(cod)(dppb)]BF_4 the mean value is 2.318 Å. On the other hand, the Rh-P2 distance is significantly shorter due to the CF_3 substituent and reflects again the increased s-character of the p lone-pair, making the phosphine a weaker σ-donor and a better π-acceptor (Figure 22).[100] Interestingly, the Rh-C_{cod} bonds reflect the difference between Rh-P1 and Rh-P2 in such manner that the longest Rh-C_{cod} bond is trans to the shortest Rh-P bond (2.126 Å for the centroid between Rh-C_{P21}-C_{P22} and 2.143 Å for the centroid between Rh-C_{P11}-C_{P12}).

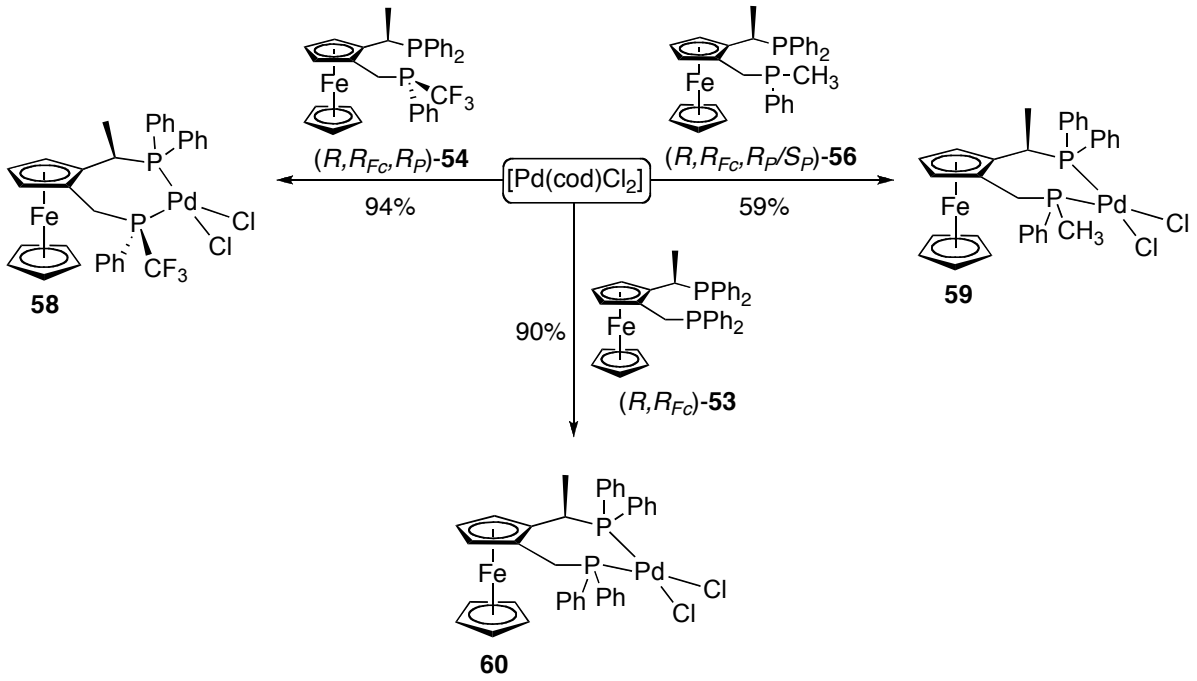
In the dppb analog there is a seven-membered chelate ring and the P-Rh-P angle is 90.73°. In our compound there is a seven-membered metallocycle fused with a five membered ferrocene ring; this implies an increased rigidity of the metallocycle reflected by the larger P-Rh-P angle (99.2°).

The distances between rhodium and the double-bond centers of cod are 2.126 and 2.143 Å and are on the long end of the range 2.00-2.14 Å found in heavy-metal complexes with cod. This lengthening probably results from the π-back donation from the metal and also reflects the trans influence of the phosphine ligands. The coordinated double bonds C_{P21}-C_{P22} and C_{P11}-C_{P12} have lengths of 1.378(3) and 1.386(3) Å, respectively, compared to an uncoordinated olefinic distance of 1.34 Å. The average coordinated olefin bond length of cod in $[Rh(cod)Cl]_2$ is 1.44(7) Å. The "similarity" of these bond lengths in our complex with those in uncoordinated cod is consistent with the lengths of the Rh-C bonds (average 2.250 Å), which indicate a weak bonding of the cod ligand. Carbon-carbon single bond distances range from 1.529 to 1.540 Å, values typical for cod bonded to heavy metal.

The seven-membered chelate ring has a boat conformation, with the CH_2 and the CHMe group in the P1-Rh-P2 plane (the out-of plane displacement of CHMe and CH_2 being only 0.029 and 0.173 Å respectively). The conformations of seven-membered rings of this type have been discussed by *Kagan* and co-workers examining the structure of the complex $[Fe(\eta^5\text{-Cp})(diop)I]$.[104] The analysis was based on the comparison with the conformations of cycloheptane, and cannot be simply extended to our complex since the bisphosphine differs from diop as it does not possess a C_2 symmetry. The structural data for diop complexes indicate a preferred chair conformation, but examples of boat conformation are also known.

2.2.4.2 [Pd(P^P*CF_3)Cl_2] Complex- Synthesis and Characterization

Pd^{II} complexes **58**, **59** and **60** were prepared by reaction of the bisphosphines (*R,*R_{Fc}*,*R_P)-**54**, (*R,*R_{Fc}*,*R_P)-**56** and (*R,*R_{Fc})-**53**, respectively, with $[Pd(cod)Cl_2]$ in CH_2Cl_2 at room temperature for 90 min (Scheme 60). Reactions proceeded without problems and the formation of the desired complexes could be observed by NMR.



Scheme 60: Synthesis of the neutral complexes [Pd(Cl)$_2$**54**] (**58**), [Pd(Cl)$_2$**56**] (**59**) and [Pd(Cl)$_2$**53**] (**60**).

Complexes **58** and **60** were then easily obtained by precipitation with *n*-pentane giving an air stable compound, whereas complex **59** was found to be more sensitive. The synthesis of **59** was performed with the mixture of the two diastereoisomers (*R,R*$_{Fc}$*,R*$_P$*/S*$_P$)-**56**. The complex was purified by flash chromatography under nitrogen and the separation of the two diastereoisomers of **59** was attempted by several common methods but without success.

^{31}P{^{1}H}-NMR spectra of complexes **58** and **59** confirmed the coordination of the ligands by the coordination chemical shifts of the two phosphorus atoms of approximately +30 ppm for the -PPh$_2$ and +50 ppm for the stereogenic -PPhCF$_3$ and -PPhCH$_3$.

The aliphatic area of the ^{1}H-NMR spectra of complexes **58** and **59** shows interesting features concerning the methylene spacer. Figure 24 shows a selection of the spectra between 2.9 and 4.1 ppm. One of the two diastereotopic protons of the CH$_2$ groups resonates at approximately the same chemical shift of around 3.5 ppm for both complexes. Interestingly, the other proton appears for both complexes as *triplet of doublets* with a $^2J_{H,H}$ = ~15 Hz and a $^2J_{P,H}$ = ~2.5 Hz but with a chemical shift difference of +0.9 ppm for complex **58** as compared to complex **59**. This difference can be attributed to the neighbouring phosphine bearing in

one case an electron donating methyl group and an electron withdrawing trifluoromethyl group in the other case.

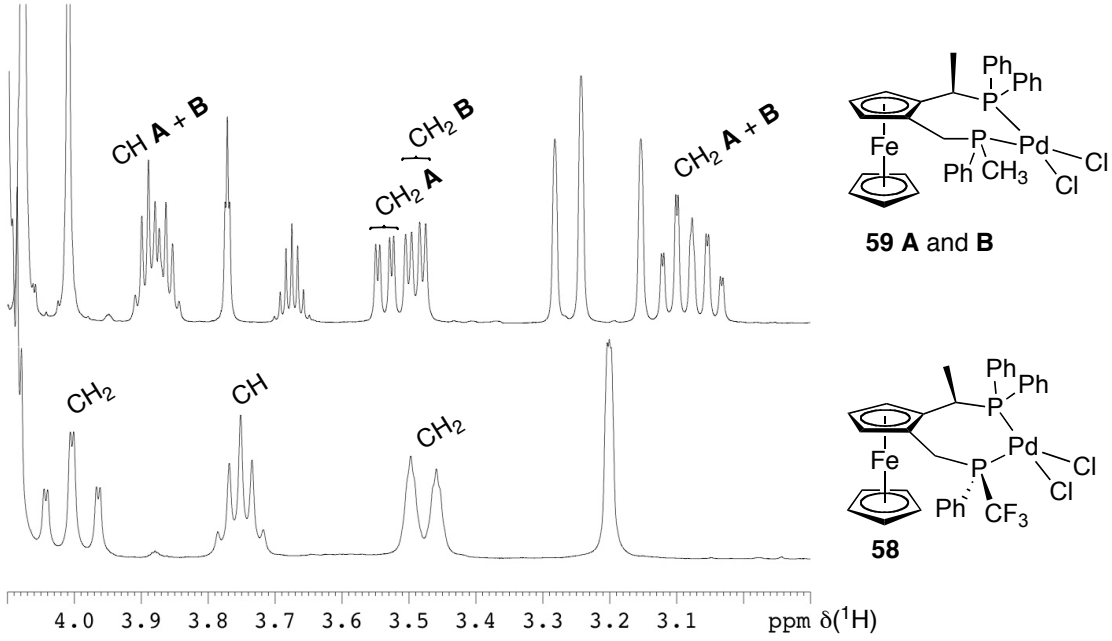


Figure 24: ^{1}H-NMR spectra (400.1 MHz, CD_2Cl_2) obtained for **58** and for the two diastereoisomers **A** and **B** of **59**.

Aromatic protons as well as methyl protons came at the same chemical shifts for both complexes and could be assigned without too much difficulty; of course, the diastereoisomeric mixture of **59** show two more *doublets* assigned to the three protons of the methylphosphine.

Crystals suitable for an X-ray measurement were easily obtained for complex **58**, which crystallized from CH_2Cl_2/*n*-hexane. Also the complex **59** gave a small crystal from CH_2Cl_2/^{i}-PrOH, which could be measured by X-ray. Although the quality of the measurement was not excellent, we could conclude that only the [Pd(Cl)$_2$(*R,R*$_{Fc}$,*R*$_P$)-**56**] diastereoisomer selectively crystallized under these conditions. Unfortunately, complex **60** could only be obtained as an oily material so no crystals could be grown. Ellipsoid and ball-and-stick representations showing the crystal structures of the two complexes **58** and **59** are shown in Figure 25 and a summary of structural parameters is given in Table 17.

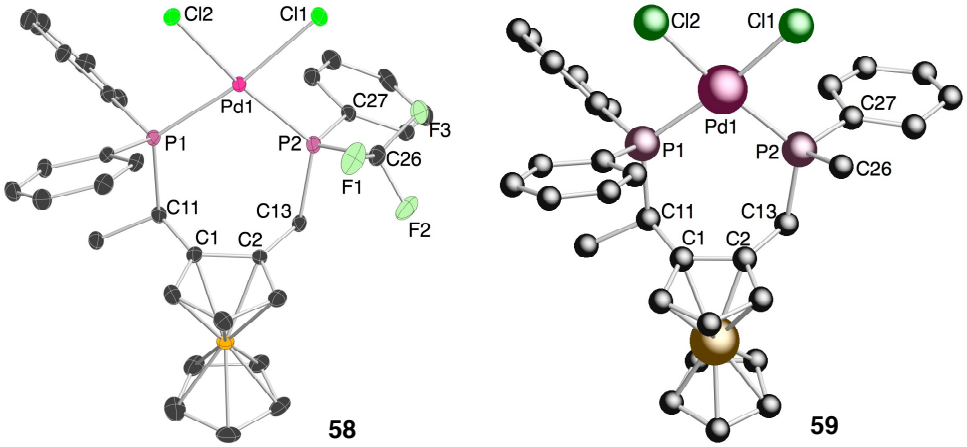


Figure 25: ORTEP and ball-and-stick representations of the molecular structure of [Pd(Cl)$_2$**54**] (**58**) and [Pd(Cl)$_2$**53**] (**59**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 30% probability.

Concentrating first on the general aspects concerning complexes **58** and **59**, we can observe that although having P^P ligands with different electronic and steric properties, both complexes show some common features. The first important one is the conformation of the coordinated ligand. **59** was synthesized starting from a diastereoisomeric ligand mixture but we were lucky enough to obtain in crystalline form the diastereoisomer having the same confiuration as complex **58**. Despite the different CIP priority of CH_3 and CF_3, the CIP descriptors for P2 remain the same in the two complexes.

Table 17: Summary of the relevant crystallographic data describing the geometry of the neutral palladium complexes **58** and **59**. Distances are given in (Å) and angles in (°). Standard deviations are given in parentheses.

	58	**59**
Pd-Cl1	2.3416(9)	2.343(5)
Pd-Cl2	2.3252(7)	2.344(5)
Pd-P1	2.2793(7)	2.267(4)
Pd-P2	2.2537(7)	2.260(5)
< P1-Rh1-P2	102.69(3)	102.9(2)
< C27-P2-C26	104.48(16)	106.3(9)
< C13-P2-C26	99.50(15)	102.8(8)
< C13-P2-C27	102.61(14)	101.9(8)

Complex **58** and **59** differ from each other by the presence of a different substituent at stereogenic phosphorus (CF_3 in complex **58** while complex **59** bears a methyl substituent).
The P-Pd-P bite angle is approximately the same, namely 102°, for the two bisphosphino ferrocenyl ligands, whereas for the dppb analog [Pd(Cl)$_2$(dppb)],[105] the mean value is 94.36(6)° due to the flexibility of this ligand.
The methyl substituent does not have a significant influence on the bond lengths of compound **59** as both Pd-P bonds are around 2.26 Å and the Pd-Cl distances amount to 2.34 Å. As already observed for [Rh(cod)(**54**)]BF_4, the presence of a trifluoromethyl substituent on the phosphorus significantly shortens the corresponding Pd-P bond (2.2537 Å vs. 2.2793 Å for Pd-P1). The diminished trans influence of P2 in complex **58** leads to a shorter Pd-Cl2 bond.

The coordination around the palladium atom is a bit different. Whereas complex **59** is ideally squared planar (∑ all angles around Pd: 360°), complex **58** is almost ideally squared planar with a sum of all angles around palladium at 362°, showing the chloro ligands deviating from the P1-Pd-P2 plane (Figure 26).

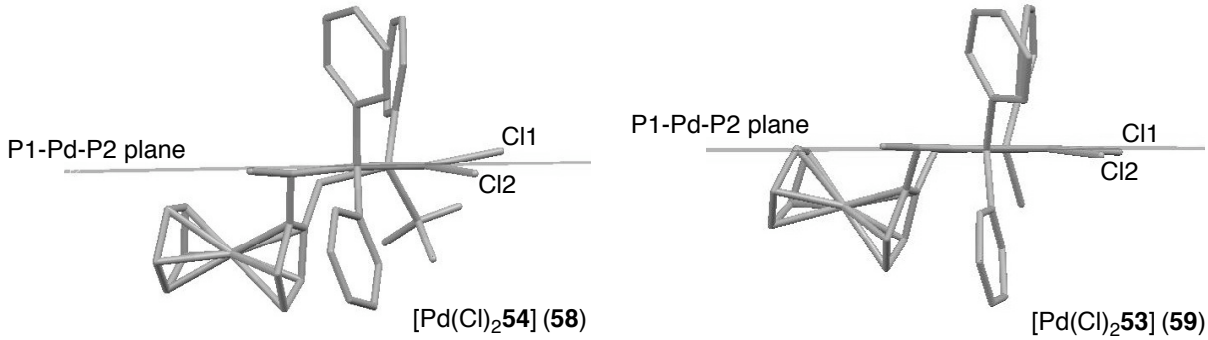
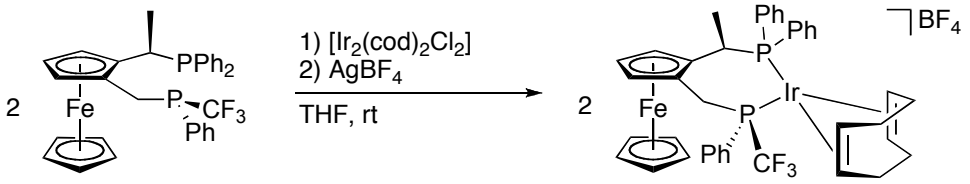


Figure 26: Capped sticks representations of the molecular structure of [Pd(Cl)$_2$**54**] (**58**) and [Pd(Cl)$_2$**53**] (**59**). Hydrogen atoms (except P-CH_3) are omitted for clarity. Distance between the P1-Pd-P2 plane and the two chloro ligands (Å) for **58**: Pd plane-Cl1: 0.358; Pd plane-Cl2: 0.238 and for **59**: Pd plane-Cl1: 0.107; Pd plane-Cl2: 0.180.

2.2.4.3 Cationic [Ir(P^P*CF_3)cod]$^+$ Complex - Synthesis and Characterization

We prepared the cationic Ir^I complex **61** by reaction of two equivalents of the bidentate chiral trifluoromethylphenylphosphine (*R,R*$_{Fc}$,*R*$_P$)-**54** with [Ir_2(cod)$_2$$Cl_2$] in THF followed by anion metathesis with $AgBF_4$ (Scheme 61). The reaction proceeded smoothly and complex **61** was

then easily obtained by filtration over alox and precipitation with *n*-pentane giving an air stable compound.



(*R*,R_{Fc},R_P)-**54** **61**

Scheme 61: Synthesis of the cationic complex [Ir(cod)**54**]BF_4 (**61**).

The $^{31}P\{^1H\}$-NMR spectrum showed a *doublet* at -0.51 ppm (-PPh_2) and a *quartet of doublet* at -4.26 ppm (-P(CF_3)Ph) confirming the formation of a single product. 2D-NMR studies were performed and the $^1H,^1H$-COSY NMR spectrum is presented in Figure 27. The homonuclear phase sensitive COSY experiment of complex **61** shows exchange signals for the CH_3 and the CH group, the cod CH_2 and cod CH, the three Cp-H protons and the CH_2 from the methylene spacer. This NMR spectrum represent a typical 2D $^1H,^1H$-COSY for Rh, Pd and Ir complexes with ligand **54** and represents a useful tool for the structural determination in solution.

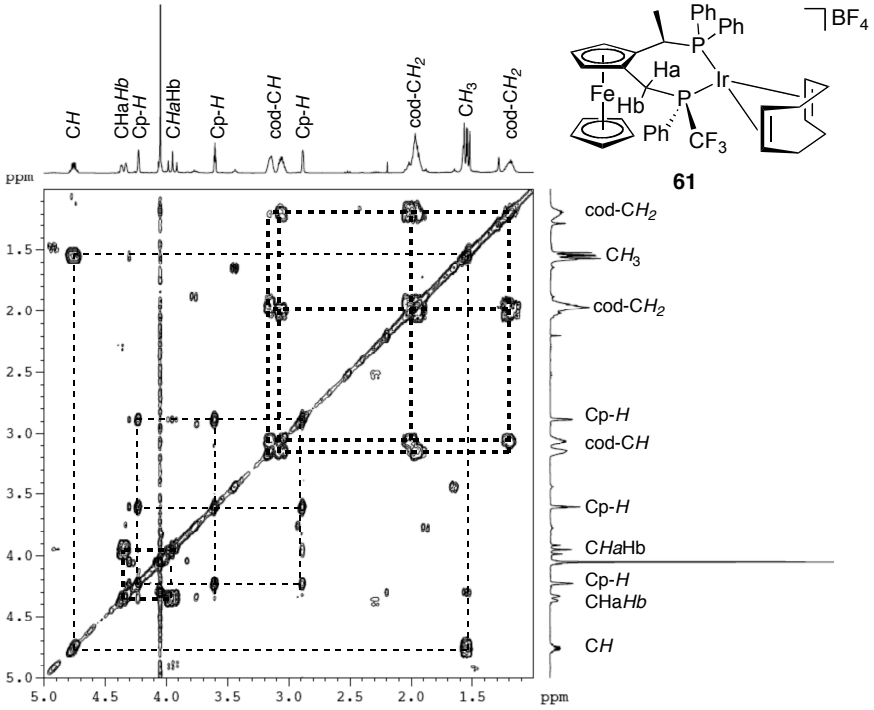


Figure 27: Section of a phase-sensitive $^1H,^1H$-COSY NMR spectrum (400.1 MHz, $CDCl_3$) of [Ir(cod)**54**]BF_4 complex (**61**) showing the exchange signals found in the low field (δ between 1 and 5 ppm).

For comparison, a ^{1}H-NMR spectrum of the free ligand (*R,R*$_{Fc}$,*R*$_P$)-**54** showed for the C*H*Me an overlapped *quartet of doublet* whereas, in the Ir-complex, the same multiplicity could be observed but at higher frequencies (from 3.35 ppm for **54** to 4.76 ppm for **61**).

As observed for [Rh(cod)**54**]BF_4 (**57**), the X-ray crystal structure of complex [Ir(cod)**54**]BF_4 (**61**), shows a somewhat distorted square planar geometry, the vertices of the square plane being occupied by the phosphorus atoms and by the 2 η^2-bonded double bonds of 1,5-cyclooctadiene (Figure 28).

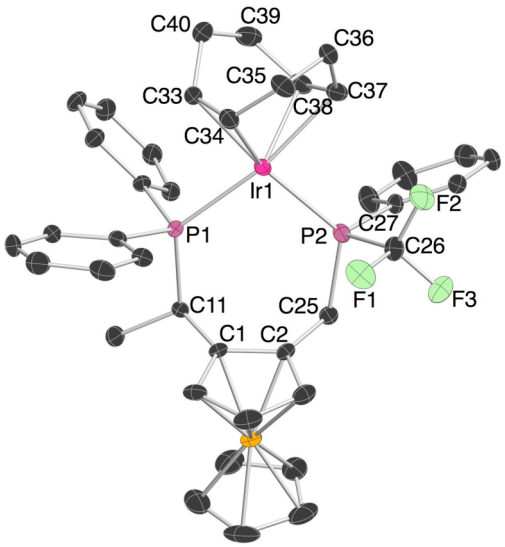
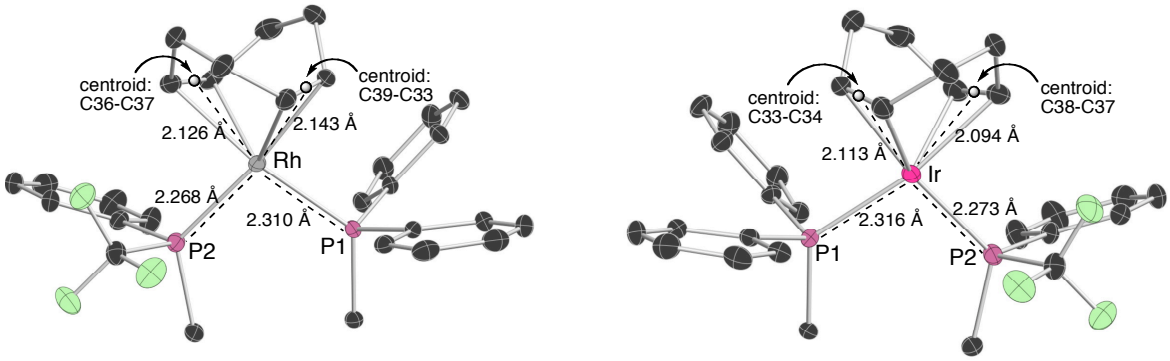


Figure 28: ORTEP representation of the molecular structure of [Ir(cod)**54**]BF_4 (**61**). Hydrogen atoms and the BF_4 anion are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (°): Ir-P1: 2.3162(6); Ir-P2: 2.2731(6); Ir-C33: 2.251(2); Ir-C34: 2.198(3); Ir-C37: 2.257(3); Ir-C38: 2.157(3); C33-C34: 1390(4); C37-C38: 1.402(4); P1-Ir-P2: 100.58(2); C25-P2-C26: 98.20(13); C25-P2-C27: 103.10(12); C26-P2-C27: 103.99(13).

As observed for the [Rh(cod)**54**]BF_4 (**57**), the iridium-phosphorus bond distances are influenced by the trifluoromethyl group. The distance Ir-P2 (2.2731(6) Å) is significantly shorter than Ir-P1 (2.3162(6) Å). Similar considerations as for **57** can be applied for the bonding parameters of the cod ligand (Figure 29). Indeed, the longest Ir-C_{cod} centroid bond is trans to the shortest Ir-P2 bond, and the shortest Ir-C_{cod} centroid bond is trans to the longest Ir-P1 bond.



[Rh(cod)**54**]BF_4 (**57**) [Ir(cod)**54**]BF_4 (**61**)

Figure 29: Sections of the crystal structures of [Rh(cod)**54**]BF_4 (**57**) and [Ir(cod)**54**]BF_4 (**61**) showing the similar trends in bond distances and angles around the metal centers. Hydrogen atoms and the BF_4 anion are omitted for clarity. Thermal ellipsoids are set at 30% probability.

The significantly shorter distance of Ir-P2 can be explained by the higher s-orbital character of the lone pair at the phosphorus atom. According to Bent's rule[100] the electron-withdrawing trifluoromethyl group will form a bond with phosphorus atom via an orbital with higher *p* character (see similar arguments put forward in the case of ligands **54**). Consequently, the orbital, constituting the lone pair, will gain more *s* character. The phosphorus atom is thus forced to approach closer in order to overlap more efficiently with the metal resulting in a shorter Ir-P2 bond length. One has to keep in mind that although the bond is shorter, it is not necessarily stronger. Furthermore, the degree of pyramidalization at P2 is slightly decreased in **57** and **61**, as compared to the situation in the free ligand.

2.3 Conclusion and Outlook

In this chapter, three main projects have been presented and discussed. All of them are still in development. Nevertheless, they show promising features and should be further investigated in the future.

- **Chiral Halogeno(trifluoromethyl)phosphines**

Based on *Eisenberger's* and *Kieltsch's* strategy, we were able to trifluoromethylate primary phosphines by a convenient method using a new class of electrophilic trifluoromethylating reagent based on hypervalent λ^3-organoiodine. The obtained secondary monotrifluoromethylphosphines were reacted with a halogenating agent (NCS or NBS). Surprisingly, the addition of 10% of a Ti catalyst ($CpTiCl_3$) resulted in an instantaneous and clean reaction. This new method does not require complex purification (only a simple *n*-hexane extraction) and provide quantitative yield of the desired halogeno(trifluoromethyl)phosphines.
This method for the halogenation of secondary trifluoromethylphosphines constitutes the first metal-catalyzed reaction of this type proceeding in quantitative yields with an easy purification of the target compounds.

- **Chiral Ferrocenyl Trifluoromethylphosphine Ligands**

A new class of chiral ferrocenyl bisphosphine ligands characterized by a short synthetic pathway and high modularity has been developed. The ligands are obtained in a two step procedure starting from the amino alcohol **52**, starting with the nucleophilic substitution of the alcohol function by PPh_2 or a P-chiral phosphine group in the presence of HBF_4, followed by the nucleophilic substitution of the dimethylamino group by diphenylphosphine in acetic acid. These novel ligands are the first ferrocenyl bisphosphine ligands combining a planar and a central chirality as well as a phosphorus chirality, bearing a CF_3 group at the phosphorus atom. Moreover, stereoselective modification of the methylene spacer between the phosphine and the ferrocenyl backbone would allow the introduction of an additional stereogenic center

- **Complexes with P^P*CF_3 Ferrocenyl Ligands**

Isolated complexes [Rh(cod)**54**]BF_4, [Ir(cod)**54**]BF_4 and [Pd$(Cl)_2$(**54-56**)] were investigated by X-ray analysis of single crystals and 2D-NMR techniques showing several interesting features. The metal-P(CF_3)Ph bond distances were *e.g.* found to be always shorter than the metal-P$(Ph)_2$ bond, this reflecting the electronic effect of the CF_3 group.

The development of a series of new ferrocenyl P-chiral bisphosphines gives the possibility of testing them as ligands for transition-metal-catalyzed reactions. Their electronic properties, as investigated here on isolated and characterized complexes should reflect differences of the catalytic properties due to the electron-withdrawing group CF_3, as compared to CH_3.
Preliminary results of the Rh-catalyzed enantioselective hydrogenation of dimethyl itaconate did not so far confirm the monotrifluoromethylated phosphine ligands as being superior to more traditional phosphine ligands. Their further application in asymmetric catalysis is still investigated in our laboratories.

2.4 References

[1] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691.

[2] R. Noyori, *Angew. Chem. Int. Ed.* **2002**, *41*, 2008.

[3] W. S. Knowles, *Angew. Chem. Int. Ed.* **2002**, *41*, 1999.

[4] K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2024.

[5] Y. Chauvin, *Angew. Chem. Int. Ed.* **2006**, *45*, 3740.

[6] R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760.

[7] R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, *45*, 3748.

[8] B. E. Evans, *J. Med. Chem.* **1998**, *31*, 2235.

[9] T. J. Kealy, P. L Pauson, *Nature* **1951**, *168*, 1039.

[10] M. Breuer, K. Ditrich, T. Habicher, B. Hauer, M. Kebeler, R. Stürmer, T. Zelinsky, *Angew. Chem. Int. Ed.* **2004**, *43*, 788.

[11] H.-U. Blaser, W. Brieden, B. Pugin, F. Spindler, M. Studer, A. Togni, *Top. Catal.* **2002**, *19*, 3.

[12] T. Hayashi, K. Yamamoto, K. Kumada, *Tetrahedron Lett.* **1974**, 4405.

[13] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijiani, *J. Am. Chem. Soc.* **1994**, *116*, 4062.

[14] C. J. Richards, T. Damalidis, D. E. Hibbs, M. B. Hursthouse, *Synlett* **1995**, 74.

[15] T. Sammakia, H. A. Latham, D. R. Schaad, *J. Org. Chem.* **1995**, *60*, 10.

[16] Y. Nishibayashi, S. Uemura, *Synlett* **1995**, 79.

[17] T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel, *Angew. Chem. Int. Ed.* **1999**, *38*, 3212.

[18] T. Hayashi in *Ferrocenes. Homogeneous Catalysis, Organic Synthesis, Material Science* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**, pp. 105-142.

[19] H. B. Kagan, O. Riant, *Adv. Asymmetric Synth.* **1997**, *2*, 189.

[20] C. F. Richards, A. J. Lock, *Tetrahedron: Asymmetry* **1998**, *9*, 2377.

[21] A. Togni in *Metallocenes* (Eds.: A. Togni, R. L. Haltermann), Wiley, New York, **1998**, pp 685-721.

[22] D. Laurenti, M. Santelli, *Org. Prep. Proced. Int.* **1999**, *31*, 245.

[23] L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng, X.-L. Hou, *Acc. Chem. Res.* **2003**, *36*, 659.

[24] F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159.

[25] a) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* **2004**, *346*, 497; b) H. A. McManus, P. J. Guiry, *Chem. Rev.* **2004**, *104*, 4151.

[26] a) *Ferrocenes. Homogeneous Catalysis, Organic Synthesis, Material Science* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**; b) *Metallocenes* (Eds.: A. Togni, R. L. Haltermann), Wiley, New York, **1998**; c) *Ferrocenes. Ligands, Materials and Biomolecules* (Eds.: P. Stepnicka), Wiley, West Sussex, **2008**.

[27] O. B. Sutcliffe, M. R. Bryce, *Tetrahedron: Asymmetry* **2003**, *14*, 2297.

[28] T. J. Colacot, *Chem. Rev.* **2003**, *103*, 3101.

[29] R. C. J. Atkinson, V. C. Gibson, N. J. Long, *Chem. Soc. Rev.* **2004**, *33*, 313.

[30] R. G. Arrayas, J. Adrio, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 7674.

[31] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed.* **1966**, *5*, 385.

[32] K. Schlögl, *Top. Stereochem.* **1967**, *1*, 39.

[33] D. Markarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **1970**, *92*, 5389.

[34] a) L. F. Battelle, R. Bau, I. K. Ugi, R. T. Oyakawa, G. W. Gokel, *Angew. Chem. Int. Ed.* **1972**, *11*, 138; b) L. F. Battelle, R. Bau, G. W. Gokel, R. T. Oyakawa, I. K. Ugi, *J. Am. Chem. Soc.* **1973**, *95*, 482.

[35] N. Deus, D. Robles, R. Herrmann, *J. Organomet. Chem.* **1990**, *386*, 253.

[36] a) F. Rebière, O. Riant, L. Ricard, H. B. Kagan, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 568; b) N. M. Lagneau, Y. Chen, P. M. Robben, H.-S. Sin, K. Tasaku, J-S. Chen, P. D. Robinson, D. H. Hua, *Tetrahedron* **1998**, *54*, 7301.

[37] a) O. Riant, O. Samuel, H. B. Kagan, *J. Am. Chem. Soc.* **1993**, *115*, 5835; b) H. Wölfle, H. Kopacka, K. Wurst, K.-H. Ongania, H.-H. Görtz, P. Preishuber-Pflügl, B. Bildstein, *J. Organomet. Chem.* **2006**, *691*, 1197.

[38] M. Wildhalm, K. Mereiter, M. Bourghida, *Tetrahedron: Asymmetry* **1998**, *9*, 2983.

[39] a) Y. Farrell, R. Goddard, P. J. Guiry, *J. Org. Chem.* **2002**, *67*, 4209; b) C. Ganter, T. Wagner, *Chem. Ber.* **1995**, *128*, 1157.

[40] a) D. Enders, P. Peters, R. Lochtman, G. Raabe, *Angew. Chem. Int. Ed.* **1999**, *38*, 2421; b) D. Enders, R. Peters, R. Lochtman, J. Runsink, *Eur. J. Org. Chem.* **2000**, 2839.

[41] C. Bolm, M. Kesselgruber, K. Muniz, G. Raabe, *Organometallics* **2000**, *19*, 1648.

[42] L. Xiao, R. Kitzler, W. Weissensteiner, *J. Org. Chem.* **2001**, *66*, 8912.

[43] R. Peters, D. F. Fischer, *Org. Lett.* **2005**, *7*, 4137.

[44] U. Nettekoven, M. Widhalm, P. C. J. Kamer, P. W. N. M. Van Leeuwen, K. Mereiter, M. Lutz, A. Spek, *Organometallics* **2000**, *19*, 2299.

[45] D. Vinci, N. Mateus, S. Wu, F. Hancock, A. Steiner, J. Xiao, *Org. Lett.* **2006**, *8*, 215.

[46] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **1970**, *92*, 5389.

[47] See ref 26c, pp. 205.

[48] H-U. Blaser, W. Brieden, B. Pugin, *Top. Catal.* **2002**, *19*, 3.

[49] a) H-U. Blaser, *Adv. Synth. Catal.* **2002**, *344*, 17; b) H. U. Blaser, H. P. Buser, K. Coers, R. Hanreich, H. P. Jalett, E. Jelsch, B. Pugin, H. D. Schneider, F. Spindler, A. Wegmann, *Chimia* **1999**, *53*, 275.

[50] a) D. A. Dobbs, K. P. M. Vanhessche, E. Brazi, V. Rautenstrauch, J.-Y. Lenoir, J.-P. Genet, J. Wiles, S. H. Bergens, *Angew. Chem. Int. Ed.* **2000**, *39*, 1992; b) D. Dobbs, K. Vanhessche, V. Rautenstrauch, WO 98/52687, **1997**, assigned to Firmenich.

[51] a) R. Imwinkelried, *Chimia* **1997**, *51*, 300; b) J. McGarrity, F. Spindler, R. Fuchs, M. Eyer, EP624587, **1994**, assigned to Lonza AG.

[52] K. B. Hansen, Y. Hsiao, F. Xu, N. Rivera, A. Clausen, M. Kubryk, S. Krska, T. Rosner, B. Simmons, J. Balsells, N. Ikemoto, Y. Sun, F. Spindler, C. Malan, E. J. J. Grabowski, J. D. Amstrong, , *J. Am. Chem. Soc.* **2009**, *131*, 8798.

[53] a) X. Feng, B. Pugin, E. Küsters, *Adv. Synth. Catal.* **2007**, *349*, 1803; b) B. Pugin, H. Landert, F. Spindler, H-U. Blaser, *Adv. Synth. Catal.* **2002**, *344*, 974; c) C. Köllner, B. Pugin, A. Togni, *J. Am. Chem. Soc.* **1998**, *120*, 10274.

[54] R. Šebesta, M. Mečiarová, V. Poláčková, E. Veverková, I. Kmentová, E. Gajdošíková, J. Cvengroš, R. Buffa, V. Gajda, *Collect. Czech. Chem. Commun.* **2007**, *72*, 1057.

[55] a) N. W. Boaz, D. D. Debenham, E. B. Mackenzie, S. E. Large, *Org. Lett.* **2002**, *4*, 2421; b) N. W. Boaz, E. B. Mackenzie, S. D. Debenham, *J. Org. Chem.* **2005**, *70*, 1872.

[56] a) T. Sturm, L. Xiao, W. Weissensteiner, *Chimia* **2001**, *55*, 688; b) T. Sturm, W. Weissensteiner, F. Spindler, *Adv. Synth. Catal.* **2003**, *345*, 160.

[57] Solvias AG, unpublished screening results.

[58] a) T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel, *Angew. Chem. Int. Ed.* **1999**, *38*, 3212; b) T. Ireland, K. Trappe, G. Grossheimann, P. Knochel, *Chem Eur. J.* **2002**, *8*, 843.

[59] M. Lotz, K. Polborn, P. Knochel, *Angew. Chem. Int. Ed.* **2002**, *41*, 4708; b) W. Chen, S. M. Roberts, J. Whittall, A. Steiner, *Chem. Commun.* **2006**, 2916.

[60] K. Tappe, P. Knochel, *Tetrahedron: Asymmetry* **2004**, *15*, 91.

[61] J. Almena Perea, A. Börner, P. Knochel, *Tetrahedron Lett.* **1998**, *39*, 8073.

[62] F. Spindler, C. Malan, M. Lotz, *Tetrahedron: Asymmetry* **2004**, *15*, 2299.

[63] M. Sawamura, H. Hamashima, Y. Ito, *Tetrahedron: Asymmetry* **1991**, *2*, 593.

[64] M. Sawamura, H. Hamashima, M. Sugawara, *Organometallics* **1995**, *14*, 4549.

[65] A. Togni, C. Breutel, M. C. Soares, N. Zanetti, T. Gerfin, V. Gramlich, F. Spindler, G. Rihs, *Inorg. Chim. Acta* **1994**, *222*, 213.

[66] P. Barbaro, C. Bianchini, G. Giambastiani, A. Togni, *Chem. Commun.* **2002**, 2672.

[67] a) W. Chen, W. Mbafor, S. M. Roberts, J. Whittall, *J. Am. Chem. Soc.* **2006**, *128*, 3922; b) W. Chen, S. M. Roberts, J. Whittall, A. Steiner, *Chem. Commun.* **2006**, 2916.

[68] a) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. M. Konishi, K. Yamamoto, M. Kumada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138; b) O. Riant, O. Samuel, T. Flessner, S. Taudien, H. B. Kagan, *J. Org. Chem.* **1997**, *62*, 6733; c) R. Kitzler, L. Xiao, W. Weissensteiner, *Tetrahedron: Asymmetry* **2000**, *11*, 3459.

[69] a) Y. Nishibayashi, Y. Arikawa, K. Ohe, S. Uemura, *J. Org. Chem.* **1996**, *61*, 1172; b) H. Jendralla, E. Paulus, *Synlett* **1997**, 471.

[70] C. Dong, F. Huang, H. Deng, C. Schaffrath, J. B. Spencer, D. O'Hagan, J. H. Naismith, *Nature* **2004**, *427*, 561.

[71] D. O'Hagan, D. B. Harper, *J. Fluorine Chem.* **1999**, *100*, 127.

[72] J. E. True, T. D. Thomas, R. W. Winter, G. L. Gard, *Inorg. Chem.* **2003**, *42*, 4437.

[73] MedAd News **2006**, *25* (Nr 6), 22.

[74] Data from *The e-Pesticide Manua,* Ed. C. D. S. Tomlin, 13th edition, Ver. 3.2, 2005/06. BCPC, http://www.bcpc.org/epm.

[75] T. Hayashi, C. Hayashi, Y. Uozumi, *Tetrahedron: Asymmetry* **1995**, *6*, 2503.

[76] A. Schnyder, L. Hintermann, A. Togni, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 931.

[77] J. M. Brown, D. I. Hulmes, T. P. Layzell, *J. Chem. Soc. Chem. Commun.* **1993**, 1673.

[78] C. Gambs, G. Consiglio, A. Togni, *Helv. Chim. Acta* **2001**, *84*, 3105.

[79] C. Gambs, S. Chaloupka, G. Consiglio, A. Togni, *Angew. Chem. Int. Ed.* **2000**, *39*, 2486.

[80] a) J. Grobe, D. Le Van, W. Meyring, B. Krebs, M. Dartmann, *J. Organomet. Chem.* **1988**, *340*, 143; b) J. Grobe, D. Le Van, W. Meyring, B. Krebs, M. Dartmann, *J. Organomet. Chem.* **1988**, *346*, 361.

[81] a) J. Grobe, D. Le Van, J. Szameitat, *J. Organomet. Chem.* **1985**, *289*, 341; b) J. Grobe, D. Le Van, W. Meyring, *J. Organomet. Chem.* **1986**, *307*, 327.

[82] a) J. Grobe, M. Köhne-Wächter, D. Le Van, *J. Organomet. Chem.* **1985**, *280*, 331; b) B. Hoge, C. Thösen, I. Pantenburg, *Chem. Eur. J.* **2006**, *12*, 9019; c) J. J. Adams, A. Lau, N. Arulsamy, D. M. Roddick, *Inorg. Chem.* **2007**, *46*, 11328;

[83] M. F. Ernst, D. M. Roddick, *Inorg. Chem.* **1989**, *28*, 1624.

[84] K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **2003**, *125*, 4318.

[85] I. G. Phillips, R. G. Ball, R. G. Cavell, *Inorg. Chem.* **1988**, *27*, 4038.

[86] O. V. Gusev, T. A. Peganova, A. M. Kalsin, N. V. Vologdin, P. V. Petrovskii, K. A. Lyssenko, A. V. Tsvetkov, I. P. Beletskaya, *Organometallics* **2006**, *25*, 2750.

[87] E. J. Velazco, A. J. M. Caffyn, *Organometallics* **2008**, *27*, 2402.

[88] M. B. Murphy-Jolly, L. C. Lewis, A. J. M. Caffyn, *Chem. Commun.* **2005**, 4479.

[89] a) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579; b) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754.

[90] R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann, A. Togni, *Angew. Chem. Int. Ed.* **2009**, *48*, 4332.

[91] P. Eisenberger, I. Kieltsch, N. Armanino, A. Togni, *Chem. Commun.* **2008**, 1575.

[92] J. Bürgler, ETH, planned Ph.D. Thesis, Zürich, Switzerland.

[93] G. Pioda, ETH, Ph. D. Thesis No 13405, Zürich, Switzerland, 1999.

[94] S. Yekta, L. Cheung, A. K. Yudin, *Tetrahedron Lett.* **2007**, *48*, 8048.

[95] L. Hintermann, A. Togni, *Helv. Chim. Acta* **2000**, *83*, 2425.

[96] J. Cabou, J. Brocard, L. Pélinski, *Tetrahedron Lett.* **2005**, *46*, 1185.

[97] S.-I. Fukuzawa, D. Tsuchiya, K. Sasamoto, K. Hiramo, M. Ohtaguchi, *Eur. J. Org. Chem.* **2000**, 2877.

[98] F. Pass, E. Steininger, H. Schindlbauer, *Monatsh. Chem.* **1959**, *90*, 792.

[99] For a general discussion of conformational aspects of ferrocenyl ligands, see *Metallocenes* (Eds.: A. Togni, R. L. Haltermann), Wiley, New York, **1998**, chapter 11.

[100] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

[101] Josiphos free ligand: A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062; [Rh(cod)josiphos]BF_4: M. Valentini, K. Selvakumar, M. Wörle, P. S. Pregosin, *J. Organomet. Chem.* **1999**, *587*, 244.

[102] L. Dahlenburg, V. Kurth, *J. Organomet. Chem.* **1999**, *585*, 315.

[103] M. P. Anderson, L. H. Pignolet, *Inorg. Chem.* **1981**, *20*, 4101.

[104] H. B. Kagan, *J. Organomet. Chem.*, **1980**, *187*, 125.

[105] V. D. Makhaev, Z. M. Dzhabieva, S. V. Konovalikhin, O. A. D'Yachenko, G. P. Belov, *Koord. Khim. (Russ) (Coord. Chem)* **1996**, *22*, 598.

3. Experimental part

3.1 General Remarks

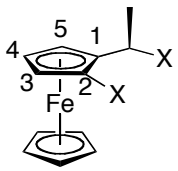
Chemicals

All solvents used for synthetic purpose were of "puriss. p. a." grade, purchased from *Fluka, Merck, J. T. Baker* or *Scharlau Chemie*. The solvents for air- or moisture-sensitive manipulations were freshly distilled from an appropriate drying agent under argon (EtOH from Na/diethyl phthalate; toluene from Na; CH_2Cl_2 and 1,2-dichloroethane from CaH_2; Et_2O and THF from Na/benzophenone; hexane from Na/benzophenone/tetraglyme; pentane from Na/benzophenone/diglyme). Deuterated solvents for NMR spectroscopy were purchased from *Cambridge Isotope Laboratories* (CD_2Cl_2) or *Armar Chemicals* ($CDCl_3$). For sensitive compounds, solvents as well as deuterated solvents were degassed by three freeze-pump-thaw cycles.
All commercial chemicals were obtained in "puriss. p. a." grade from *Fluka, Aldrich, Acros, ABCR, VWR* or *Strem Chemicals* and metal precursors from Johnson Matthey and were used without further purification, unless stated otherwise.

Instruments and Techniques

All manipulations with air- or moisture-sensitive materials were carried out at a vacuum/argon line with standard *Schlenk* techniques, or in a glovebox (*MBRAUN* MB-150B-GII) under an atmosphere of purified nitrogen.
High vacuum: generated by a *Vacuumbrand* RZ5 vacuum pump. A vacuum of better than $5 \cdot 10^{-4}$ mbar was possible. Vacuum detector: uncalibrated *Leybold* thermovacTM20 was used.
Rotavapor: *Büchi* Rotavapor R-200, Vacuum Controller V-800, Heating Bath B-490. The temperature of the heating bath was kept at or below 40 °C.
TLC: SiO_2 *Merck 60-F254*. UV-detection at 254 nm or aluminium oxide *Merck 60-F254*. UV-detection at 254 nm (mentioned). Stains: mostaïne (0.4 g $Ce(SO_4)_2 \cdot 4H_2O$, 10.0 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 10 mL H_2SO_4 conc., 180 mL water), $KMnO_4$ (1.0 g $KMnO_4$, 2.0 g Na_2CO_3, 100 mL water).
Preparative TLC (PTLC): SiO_2 *Merck 60-F254*. UV-detection at 254 nm. 2mm.
Flash chromatography (FC): SiO_2: *Fluka* Silica gel 60, particle size 0.04-0.063 nm. Air pressure < 0.3 bar. Al_2O_3: *Fluka* Aluminium oxide for Chromatography, particle size 0.05-0.15 nm, pH 7.0±0.5 (mentioned).

NMR: The ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectra were recorded on the following instruments (frequencies in MHz): *Bruker Avance* 700, 500, 400, 300, 250 or 200 spectrometers operating at the given spectrometer frequency. The samples were measured as solutions (if not otherwise stated) in the given solvent at room temperature and in non-spinning mode. ^{1}H and ^{13}C positive chemical shift δ (in ppm) are downfield from tetramethylsilane (TMS), and are referenced to the residual solvent signal. ^{19}F NMR signals are referenced to external $CFCl_3$, and ^{31}P NMR signals to external 85% H_3PO_4. Coupling constants *J* are given in Hertz. If not specified, *J* represents $J_{H,H}$. The multiplicity is denoted by the following abbreviations: *s*: singlet; *d*: doublet; *t*: triplet; *q*: quartet; *sept*: septet; *m*: multiplet; *br*: broad. When possible, Cp-atoms were arbitrarily numbered as shown.



High pressure liquid chromatography (HPLC) : *Agilent Series* 1100 or *Hewlett-Packard* 1050 Series: UV detectors (210, 230 and 254 nm); columns: OD-H (0.46 x 25, corn size 5μm), OJ (0.46 x 25, corn size 5μm); eluent: hexane and ^{i}PrOH. Conditions are given in the order: instrument type, column type, hexane:^{i}PrOH ratio, flow [mL/min], retention times [min].

Preparative HPLC: A *Gilson* system with the modules *306 Pump, 806 Mnometric Module, UV/VIS-156* detector and *FC 204 Fraction Collector* was used. Column: *Chiralcel OJ* (25 cm x 2 cm, particle size 5 μm).

Gas chromatography-mass spectroscopy (GC-MS): *Thermo Finnigan Trace GC;* column: *Zebron ZB-5* (30 m x 0.25 mm, film 0.25 μm). Inlet: Split injector (42mL/min, 200 °C). Carrier: Helium (1.2 L/min). *Thermo Finnigan Trace MS*; EI-M; diagnostic peaks are given as *m/z* and the intensities in % of the base peak.

Mass Spectroscopy (HiRes-MS): High-resolution mass spectra were measured by the MS-Service of the "Laboratorium für organische Chemie der ETHZ". The signals are given as mass per charge number (m/z) and the intensity in % of the basis peak in the form m/z (intensity, fragment).

Melting point (M.p).: A *Gallenkamp Griffin MPA-350.BM2.5* melting point apparatus was used to determine melting points, which are uncorrected.

Elemental analysis (EA): Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich); all measurements are within a deviation of ± 0.4% of the calculated values.

Crystallography: X-ray structural measurements were carried out by *Raphael Aardoom* and *Katrin Niedermann* on a *Bruker* CCD diffractometer: *Bruker* SMART PLATFORM, with CCD detector, graphite monochromator, Mo K_α (0.71073 Å) radiation and a low-temperature device (200 K). The single crystals were mounted in perfluoropolyalkylether oil on the top of a

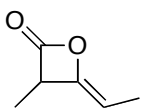
glass fiber and fixed with epoxidic glue. All calculations were performed on PC systems with SHELXTL (ver. 6.12) and SHELXL-97. The structures were solved either by Patterson or direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined freely with anisotropic displacement parameters. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model for the X-ray structures. Moreover, an empirical absorption correction using SADABS (ver. 2.03) was applied to all structures. Model plots were made with Crystal Maker for Mac.

3.2 Chapter 1: Electrophilic Amination of ß-Keto Esters

3.2.1 Substrates

Methylketene dimer

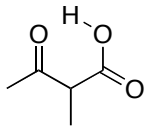
Synthesis adapted from *Sauer*[1,2]



To a solution of propinyl chloride (8 mL, 92 mmol) in Et_2O (150 mL), triethylamine (p.a) (12.8 mL, 9.30 mg, 92 mmol) was added during 30 min under vigorous stirring. A white precipitate appeared quickly. After 2 d of stirring at rt, the mixture was filtered and the suspension washed with 50 mL Et_2O. The yellow residue was purified by vacuum distillation (0.32 mbar, b.p. 50-54°C) giving the methylketene dimer as a colourless liquid. Yield: 2.06 g (37%), from which 7% were propionyl chloride hydride (^{1}H-NMR).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 4.74 (*qd*, 1 H, *J* = 7.0 Hz, *J* = 1.2 Hz, C*H*CH_3), 3.97 (*q*, 1 H, *J* = 7.5 Hz, C*H*CH_3), 1.62 (*d*, 3 H, *J* = 7.0 Hz, CH C*H*$_3$), 1.35 (*d*, 3 H, *J* = 7.5 Hz, CH C*H*$_3$).

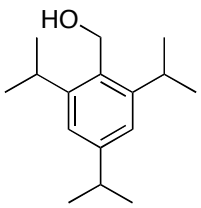
2-Methyl-3-oxobutanoic acid



To a solution of KOH (2.86 g, 51.0 mmol) in water (100 mL), ethyl-2-methyl acetoacetate (7.1 mL, 7.17 mg, 50.0 mmol) was added. The reaction mixture was stirred at rt for 3 d. The impurities were extracted with TBME (2 x 150 mL). The aqueous phase was treated with H_2SO_4 (1.4 mL in ice water) and the product extracted with TBME (4 x 50 mL). The combined organic phases were dried ($MgSO_4$) and the solvent evaporated to give 2-methyl-3-oxobutanoic acid as a colourless oil. Yield: 3.07 g (53%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.59 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH_3), 2.32 (*s*, 3 H, C*H*$_3$CO), 1.41 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$).

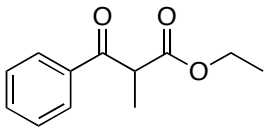
2,4,6-Triisopropylbenzyl alcohol[3]



To a suspension of $LiAlH_4$ (721 mg, 19.0 mmol) in Et_2O (40 mL), a solution of 2,4,6-triisopropylbenzoyl chloride (4.00 g, 15.0 mmol) in Et_2O (40 mL) was added dropwise at the rate to maintain gentle reflux. After stirring for 1.5 h, the reaction was quenched with Na_2SO_4 (sat., 30 mL) and extracted with Et_2O. Evaporation of the solvent gave pure 2,4,6-triisopropylbenzyl alcohol as a white solid. Yield: 2.87 g (82%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.03 (*s*, 2 H, Ar-*H*), 4.77 (*s*, 2 H, C*H*$_2$OH) 3.10 (*sept*, 2 H, *J* = 6.8 Hz, C*H*$(CH_3)_2$), 2.90 (*sept*, 1 H, *J* = 6.9 Hz, C*H*$(CH_3)_2$), 1.28 (*d*, 12 H, *J* = 6.8 Hz, CH$(CH_3)_2$), 1.27 (*d*, 6 H, *J* = 6.9 Hz, CH$(CH_3)_2$).

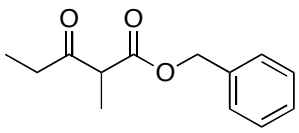
2-Methyl-3-oxo-3-phenyl-propionic acid ethyl ester (S2)[4]



NaH (15g, 375 mmol, 60% suspension in oil) was washed with TBME (3 x 30 mL), suspended in TBME (300 mL) and diethyl carbonate (60 mL, 493 mmol). The suspension was heated to reflux and a portion of propiophenone (5 mL of 40 mL, total of 301 mmol) was added. The reaction mixture was stirred under reflux overnight and then, cooled at 0 °C for 1 h. The solid which precipitated from the yellow solution was collected by filtration, washed with TBME (2 x 50 mL) and pentane (2 x 50 mL), and dried *in vacuo*. The yellow solid was then suspended in TBME (300 mL) and treated with acetic acid (10 weight-% aqueous solution) to complete neutralization (pH ~ 7). The organic phase was washed with $NaHCO_3$ (sat., 200 mL), NaCl (sat., 200 mL). Evaporation of the solvent gave the crude product, which was purified by vacuum distillation (0.23 mbar, b.p. 95 °C) giving pure **S2** as a colourless liquid. Yield: 32.45 g (51%).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.99 - 7.95 (*m*, 2 H, Ph-*H*), 7.60 - 7.54 (*m*, 1 H, Ph-*H*), 7.49 - 7.33 (*m*, 2 H, Ph-*H*), 4.37 (*q*, 1 H, *J* = 7.08 Hz, C*H*CH_3), 4.13 (*q*, 2 H, *J* = 7.12 Hz, C*H*$_2$$CH_3$), 1.47 (*d*, 3 H, *J* = 7.08 Hz, CHC*H*$_3$), 1.15 (*t*, 3 H, *J* = 7.12 Hz, CH_2C*H*$_3$).

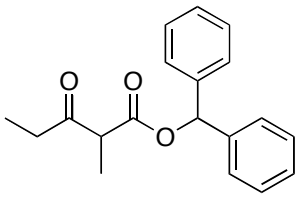
2-Methyl-3-oxo-pentanoic acid benzyl ester (S4)[5]



To a solution of benzyl alcohol (3.2 mL, 3.33 g, 31.0 mmol) and imidazole (2.11 g, 31.0 mmol) in MeCN (10 mL), methylketene dimer (3.82 g, 34.1 mmol) was added dropwise at 0 °C. After stirring for 30 min, TFA (2.3 mL, 3.53 g, 31.0 mmol) was added slowly. After stirring for 20 h at rt, the reaction mixture was quenched with $NaHCO_3$ (sat., 15 mL) and extracted with TBME (3 x 10 mL). The combined organic phases were washed with NaCl (sat., 25 mL), dried (Na_2SO_4) and filtered over Al_2O_3. Evaporation of the solvent gave the crude product, which was purified by FC on SiO_2 with hexane/TBME 15:1 as eluents, affording pure **S4** as a colourless oil. Yield: 6.18 g (90%).

TLC (hexane/TBME 5:1): R_f = 0.30. **^{1}H NMR** (200.1 MHz, $CDCl_3$): δ 7.41 - 7.30 (*m*, 5 H, Ph-*H*), 5.21 (*s*, 2 H, OC*H*$_2$Ph), 3.62 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH_3), 2.58 (*q*, 1 H, *J* = 7.2 Hz, C*H*$_2$$CH_3$), 2.54 (*q*, 1 H, *J* = 7.2 Hz, C*H*$_2$$CH_3$), 1.40 (*d*, 3 H, *J* = 7.2 Hz, CHC*H*$_3$), 1.07 (*t*, 3 H, *J* = 7.2 Hz, CH_2C*H*$_3$).

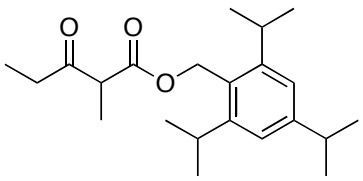
2-Methyl-3-oxo-pentanoic acid diphenylmethyl ester (S5)[6]



To a solution of methylketene dimer (1.32 g, 11.8 mmol) in CH_2Cl_2 (4 mL), diphenylmethanol (1.84 g, 9.99 mmol) was added. After complete dissolution, 4-pyrrolidinopyridine (50 mg, 0.34 mmol) was added slowly at 0 °C and the reaction mixture was refluxed for 1 h. The yellow solution was stirred for 36 h and the solvent evaporated. Purification was performed by FC on SiO_2 with hexane/TBME 10:1 (dry packed) as eluents, affording pure **S5** as a colourless oil. Yield: 2.85 g (80%).

TLC (hexane/TBME 5:1): R_f = 0.49. **^{1}H NMR** (250.1 MHz, $CDCl_3$): δ 7.41 - 7.28 (*m*, 10 H, Ph-*H*), 6.93 (*s*, 1 H, Ph_2CH), 3.65 (*q*, 1 H, *J* = 7.3 Hz, $CHCH_3$), 2.49 (*q*, 2 H, *J* = 7.3 Hz, CH_2CH_3), 1.41 (*d*, 3 H, *J* = 7.3 Hz, $CHCH_3$), 1.03 (*t*, 3 H, *J* = 7.3 Hz, CH_2CH_3).

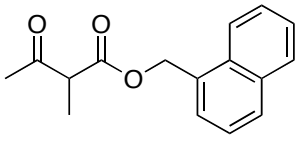
2-Methyl-3-oxo-pentanoic acid 2,4,6-triisopropyl-benzyl ester (S6)[6]



To a solution of 2,4,6-triisopropylbenzyl alcohol (1.68 g, 7.6 mmol) and methylketene dimer (1.01 g, 8.8 mmol) in CH_2Cl_2 (5mL), imidazole (0.59 g, 8.7 mmol) was added in portions while cooling with a water bath. After cooling to -15 °C (ice/EtOH), TFA (0.65 mL, 0.99 g, 8.8 mmol) was added dropwise. The resulting suspension was stirred overnight before quenching with water and extracting with TBME. The combined organic phases were washed with HCl (0.1 M) and water, and then dried over Na_2SO_4. After evaporation of the solvent, the resulting crude material was purified by FC on SiO_2 with hexane/TBME 30:1 to 20:1 as eluents, affording pure **S6** as a colourless oil. Yield: 2.29 g (85%).

TLC (hexane/TBME 25:1): R_f = 0.07. **^{1}H NMR** (200.1 MHz, $CDCl_3$): δ 7.06 (*s*, 2 H, Ar-*H*), 5.32 (*d*, 1 H, *J* = 12.2 Hz, OCH_2Ar), 5.30 (*d*, 1 H, *J* = 12.2 Hz, OCH_2Ar), 3.54 (*q*, 1 H, *J* = 7.1 Hz, $CHCH_3$), 3.18 (*sept*, 2 H, *J* = 6.8 Hz, $CH(CH_3)_2$), 2.91 (*sept*, 1 H, *J* = 6.9 Hz, $CH(CH_3)_2$), 2.46 - 2.64 (*m*, 2 H, CH_2CH_3), 1.36 (*d*, 3 H, *J* = 7.1 Hz, $CHCH_3$), 1.28 (*d*, 6 H, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.26 (*d*, 6 H, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.24 (*d*, 6 H, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.05 (*t*, 3 H, *J* = 7.2 Hz, CH_2CH_3).

2-Methyl-3-oxo-pentanoic acid naphtalen-1-ylmethyl ester (S7)[2]



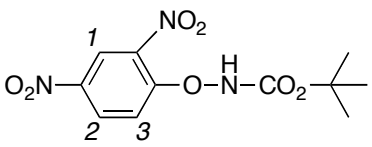
To a solution of 1-naphthylmethyl alcohol (2.01 g, 12.7 mmol), cyanuric chloride (1.19 g, 64.5 mmol) and 2-methyl-3-oxobutanoic acid (2.11 g, 18.2 mmol) in MeCN (5 mL), N,N-dimethylaniline (1.90 mL, 1.81 g, 14.9 mmol) was added slowly at 0 °C. The

greenish suspension was stirred for 1 d before quenching with water (200 mL) and extracting with TBME (3 x 50 mL). The yellow organic phases were washed with HCl (0.2 M) and water. After evaporation of the solvent, the resulting crude material was purified by FC on SiO_2 with hexane/TBME 10:1 (dry packed) as eluents, affording pure **S7** as a colourless oil. Yield: 2.66 g (82%).

TLC (hexane/TBME 5:1): R_f = 0.23. **^{1}H NMR** (200.1 MHz, $CDCl_3$): δ 8.06 - 8.01 (*m*, 1 H, Ar-*H*), 7.95 - 7.89 (*m*, 2 H, Ar-*H*), 7.66 - 7.30 (*m*, 4 H, Ar-*H*), 5.68 (*s*, 2 H, OC*H*$_2$Ar), 3.59 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH_3), 2.18 (*s*, 3 H, C*H*$_3$CO), 1.41 (*d*, 3 H, *J* = 7.2 Hz, CHC*H*$_3$).

3.2.2 Aminating Reagents

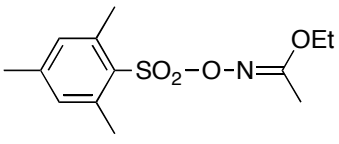
t-Butyl *N*-2,4-dinitrophenyloxycarbamate (AR4)[7]



2,4-Dinitrofluorobenzene (4.09 g, 22.0 mmol) was added slowly to an ice-cooled stirred solution of *tert*-butyl *N*-hydroxycarbamate (3.00 g, 22.0 mmol) and KOH (1.23 g, 22.0 mmol) in absolute ethanol (45 mL). The solution, which turned deep red was stirred for 1h and AcOH was added until the colour became pale yellow. Pouring into cold water (450 mL) yielded a yellow solid, which was collected by filtration and crystallized from EtOAc/hexane to give **AR4** as very pale yellow crystals. Yield: 5.39 g (82%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.86 (*d*, 1 H, *J* = 2.7 Hz, Ar-*H*$_1$), 8.46 (*dd*, 1 H, *J* = 2.7, 9.3 Hz, Ar-*H*$_2$), 7.74 (*d*, 1 H, *J* = 9.3 Hz, Ar-*H*$_3$), 1.52 (*s*, 9 H, C*H*$_3$).

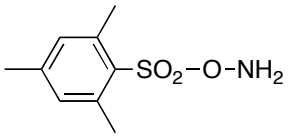
Ethyl *O*-(mesitylenesulfonyl)acetohydroxamate[8]



2-Mesitylenesulfonyl chloride (10.32 g, 47.2 mmol) was added to a solution of ethyl acetohydroxamate (4.87 g, 47.2 mmol) and triethylamine (6.6 mL, 47.2 mmol) in DMF (18 mL) in portions under stirring and ice cooling. When the addition was complete, the reaction was poured into ice water. A white precipitate was filtered off and recrystallized from hexane to give the ethyl *O*-(mesitylenesulfonyl)acetohydroxamate as colourless needles. Yield: 11.64 g (86%).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 6.99 (*s*, 2 H, Ar-*H*), 3.93 (*q*, 2 H, *J* = 7.2 Hz, C*H*$_2$CH$_3$), 2.67 (*s*, 6 H, Ar-C*H*$_3$), 2.34 (*s*, 3 H, Ar-C*H*$_3$), 2.07 (*s*, 3 H, C*H*$_3$), 1.21 (*t*, 3 H, *J* = 7.2 Hz, CH$_2$C*H*$_3$).

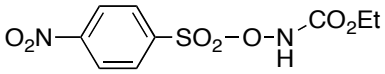
O-mesitylenesulfonyl hydroxylamine (AR7)[8]



To a solution of ethyl *O*-(mesitylenesulfonyl)acetohydroxamate (10.12 g, 35.0 mmol) in dioxane (8 mL), 70% perchloric acid (3.4 mL) was added dropwise with stirring at 0 °C over 10 min. The reaction mixture was poured into ice water to give a white solid, which was filtered off and washed with water. Although the product thus obtained still contains 20% of water, it can be obtained as a dry solid simply by extraction with methylene chloride. The solid was dissolved in ether and precipitated by the addition of hexane to give **AR7** as white needles. Yield: 6.51 g (87%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 6.61 (*s*, 2 H, Ar-*H*), 2.39 (*s*, 6 H, Ar-C*H*$_3$), 2.01 (*s*, 3 H, Ar-C*H*$_3$).

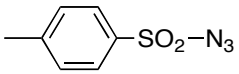
Ethyl *N*-*p*-nitrophenylsulfonyloxycarbamate (AR8)[9]



p-Nitrobenzenesulfonyl chloride (2.10 g, 9.5 mmol) was added slowly to a ice cooled solution of *N*-hydroxyurethan (1.00 g, 9.5 mmol) dissolved in Et_2O (14 mL). A solution of triethylamine (1.13 mL, 8.1 mmol) in Et_2O (1.5 mL) was added slowly from an addition funnel at such a rate as to keep the mixture acidic at all time. After addition, the reaction mixture was stirred for 3 h and filtered to remove a precipitate containing *N,O*-di-*p*-nitrobenzenesulfonylhydroxyurethan as the by-product. The yellow ether filtrate was evaporated to dryness to yield a cream-white solid, which was purified by FC on SiO_2 with hexane/EtOAc 2:1 as eluents, affording pure **AR8** as a cream-white solid. Yield: 1.52 g (55%).

TLC (hexane/EtOAc 2:1): R_f = 0.35. **^{1}H NMR** (250.1 MHz, $CDCl_3$): δ 8.44 (*d*, 2 H, *J* = 8.8 Hz, Ar-*H*), 8.24 (*d*, 2 H, *J* = 8.8 Hz, Ar-*H*), 4.11 (*q*, 2 H, *J* = 7.1 Hz, C*H*$_2$CH$_3$), 1.18 (*t*, 3 H, *J* = 7.1 Hz, CH$_2$C*H*$_3$).

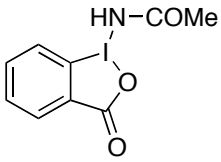
p-Tosyl azide (AR10)



p-Toluenesulfonyl chloride (2.40 g, 12.6 mmol) was added to a stirred solution of sodium azide (1.02 g, 15.7 mmol), in a mixture of 1 mL of water and 14 mL of absolute EtOH. The resulting mixture was stirred overnight. After this time, water (15 mL) was added and the resulting slurry was extracted with Et_2O. The combined organic phases were dried over Na_2SO_4. After evaporation of the solvent, pure **AR10** was obtained as a colourless oil. Yield: 1.92 g (62%).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.87 (*d*, 2 H, *J* = 8.0 Hz, Ar-*H*), 7.43 (*d*, 2 H, *J* = 8.0 Hz, Ar-*H*), 2.51 (*s*, 3 H, Ar-C*H*$_3$).

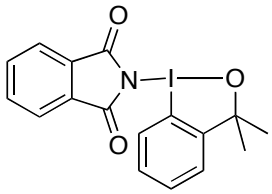
1-Acetamido benziodoxolone (AR11)[10]



To a stirred suspension of 2-iodosylbenzoic acid (1.05 g, 4.0 mmol) in MeCN (15 mL), trimethylsilyl triflate (0.85 mL, 4.4 mmol) was added at rt. The reaction mixture was stirred 30 min and pyridine (0.32 mL, 4.0 mmol) and acetamide (472 mg, 8.0 mmol) were added. The resulting mixture was additionally stirred overnight. The precipitate was filtered, washed with anhydrous acetone (10 mL) and dried in vacuo to afford pure **AR11** as a white solid. Yield: 801 mg (66%).

^{1}H NMR (300.1 MHz, $CDCl_3$ + CF_3CO_2D): δ 8.39 (*dd*, 1 H, *J* = 1.8, 7.8 Hz, Ar-*H*), 8.23-8.17 (*m*, 2 H, Ar-*H*), 7.91 (*td*, 1 H, *J* = 0.9, 7.8 Hz, ar-*H*), 2.33 (*s*, 3 H, C*H*$_3$).

1-Phtalimide-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (AR12)



To dry potassium chloride (1.65 g, 8.9 mmol), 1-chloro-1,3-dihydro-3,3-dimethylbenziodoxole (1.55 g, 5.24 mmol) in MeCN (13 mL) was added slowly. The resulting white suspension was stirred for 1 h, filtered under argon (canula) and washed with further MeCN (3 x 4 mL). The obtained clear, yellow solution was evaporated to dryness and the residue dried in vacuo to give pure **AR12** as a yellowish solid. Yield: 682 mg (32%).

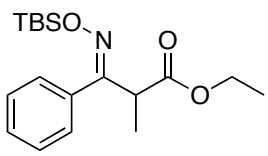
^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.60-7.47 (*m*, 4 H, Ar-*H*), 7.28-6.90 (*m*, 4 H, Ar-*H*), 1.33 (*s*, 6 H, C(C*H*$_3$)$_2$).

3.2.3 Catalytic Oximation of ß-Keto Esters

General Procedure

In an oven dried *Schlenk*-flask equipped with a magnetic stirring bar, copper trifluoromethanesulfonate (9 mg, 0.025 mmol) and binap ligand (9.2 mg, 0.026 mmol) were added under nitrogen atmosphere (glove box). The mixture was stirred under vacuum for 1 h and filled with Ar. CH_2Cl_2 (2 mL) was added, and the green solution was stirred for 2 h. ß-keto ester (0.5 mmol) and *O*-(*tert*-butyldimethylsilyl)hydroxylamine (1 mmol) were added and the reaction was monitored by TLC. After completion, the solvent was evaporated under reduced pressure and the oily residue was subjected to FC on SiO_2. Yields refer to isolated products unless otherwise stated.

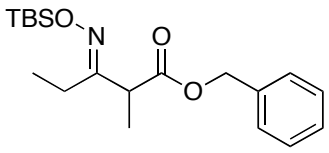
3-[*tert*-Butyldimethylsilanyloxyimino]-2-methyl-3-phenyl-propionic acid ethyl ester (O2)



Prepared according to the general procedure from ß-keto ester **S2** (103 mg, 0.5 mmol). Purification by FC on SiO_2 with hexane/TBME 20:1 as eluents afforded pure **O2** as a colourless oil. Yield: 67 mg (40%). The ^{1}H NMR spectrum showed the presence of two isomers (**A** and **B**) in the ratio **A**:**B** = 7.9:1.

TLC (hexane/TBME 5:1): R_f = 0.7. **^{1}H NMR** (300.1 MHz, $CDCl_3$): Diastereoisomer **A**: δ 7.66 - 7.63 (*m*, 2 H, Ph-*H*), 7.41 - 7.36 (*m*, 3 H, Ph-*H*), 4.20 - 4.10 (*m*, 2 H, *J* = 7.2 Hz, C*H*$_2$CH$_3$), 4.01 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 1.51 (*d*, 3 H, *J* = 7.2 Hz, CHC*H*$_3$), 1.19 (*t*, 3 H, *J* = 7.2 Hz, CH$_2$C*H*$_3$), 1.03 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.27 (*s*, 6 H, Si(C*H*$_3$)$_2$). Diastereoisomer **B**: δ 7.66 - 7.63 (*m*, 2 H, Ph-*H*), 7.41 - 7.36 (*m*, 3 H, Ph-*H*), 4.20 - 4.10 (*m*, 2 H, *J* = 7.2, Hz C*H*$_2$CH$_3$), 3.78 (*q*, 1 H, J = 7.2 Hz, C*H*CH$_3$), 1.42 (*d*, 3 H, *J* = 7.2 Hz, CHC*H*$_3$), 1.23 (*t*, 3 H, *J* = 7.2 Hz, CH$_2$C*H*$_3$), 0.09 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.26 (*s*, 6 H, Si(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): Diastereoisomer **A**: δ 172.23 (*s*, *C*O), 160.61 (*s*, *C*N), 135.68 (*s*, Ph-*C*), 129.14 (s, Ph-*C*H), 128.43 (*s*, Ph-*C*H), 126.62 (*s,* Ph-*C*H), 60.61 (*s*, *C*H$_2$CH$_3$), 39.54 (*s*, *C*HCH$_3$), 26.02 (*s*, SiC(*C*H$_3$)$_3$), 18.10 (*s*, Si*C*(CH$_3$)$_3$), 14.07 (*s*, CH$_2$*C*H$_3$), 13.16 (*s*, CH*C*H$_3$), -5.20 (*s*, Si(*C*H$_3$)$_2$). **MS (ESI)**: m/z: calcd for $C_{18}H_{29}NO_3Si$: 336.3 ([M]$^+$); found: 358.2 (100, [M+Na]$^+$), 336.3 (35, [M]$^+$). **GC-MS** : t_R = 21.89, 22.75 min.

3-[*tert*-Butyldimethylsilanyloxyimino]-2-methyl-pentanoic acid benzyl ester (O4)

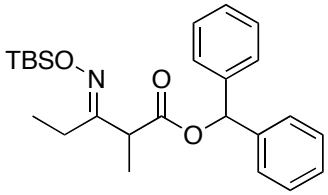


Prepared according to the general procedure from ß-keto ester **S4** (110 mg, 0.5 mmol). Purification by FC on SiO_2 with hexane/TBME 20:1 as eluents afforded pure **O4** as a colourless oil. Yield: 73 mg (42%). The ^{1}H NMR spectrum showed the presence of two isomers (**A** and **B**) in the ratio **A**: **B** = 4.1:1.

TLC (hexane/TBME 10:1): R_f = 0.5. **^{1}H NMR** (300.1 MHz, $CDCl_3$): Diastereoisomer **A**: δ 7.38 - 7.33 (*m*, 5 H, Ph-*H*), 5.17 (*s*, 2 H, C*H*$_2$Ph), 3.77 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 2.30 (*q*, 2 H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.37 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$), 1.15 (*t*, 3 H, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 0.98 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.20 (*s*, 6 H, Si(C*H*$_3$)$_2$). Diastereoisomer **B**: δ 7.38 - 7.33 (*m*, 5 H, Ph-*H*), 5.15 (*s*, 2 H, C*H*$_2$Ph), 3.50 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 2.40 (*q*, 2 H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.41 (*d*, 3 H, *J* = 7.2 Hz, CHC*H*$_3$), 1.09 (*t*, 3 H, *J* = 7.6 Hz, CH$_2$C*H*$_3$), 0.99 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.19 (*s*, 6 H, Si(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): Diastereoisomer **A**: δ 172.17 (*s*, *C*O), 162.36 (*s*, *C*N), 136.12 (*s*, Ph-*C*), 128.45 (*s*, Ph-*C*H), 128.03 (*s*, Ph-*C*H), 127.94 (*s*, Ph-*C*H), 66.28 (*s*, *C*H$_2$Ph), 39.73 (*s*, *C*HCH$_3$), 26.45 (s, *C*H$_2$CH$_3$), 26.04 (*s*, SiC(*C*H$_3$)$_3$), 18.08 (*s*,

Si*C*(CH_3)$_3$), 12.94 (*s*, CH*C*H_3), 10.65 (*s*, CH_2*C*H_3), -5.27 (*s*, Si(*C*H_3)$_2$). Diastereoisomer **B**: δ 172.56 (*s*, *C*O), 163.84 (*s*, *C*N), 135.89 (*s*, Ph-*C*), 128.50 (*s*, Ph-*C*H), 128.16 (*s*, Ph-*C*H), 128.10 (*s*, Ph-*C*H), 66.52 (*s*, *C*H_2Ph), 44.88 (*s*, *C*HCH$_3$), 26.13 (*s*, SiC(*C*H_3)$_3$), 20.79 (*s*, Si*C*(CH_3)$_3$), 14.56 (*s*, CH*C*H_3), 10.46 (*s*, CH_2*C*H_3), -5.31 (*s*, Si(*C*H_3)$_2$). **MS (ESI)**: m/z: calcd for $C_{19}H_{31}NO_3Si$: 350.5 ([M]$^+$); found: 372.3 (100, [M+Na]$^+$), 350.4 (10, [M]$^+$). **GC-MS**: t_R = 23.92, 24.17 min.

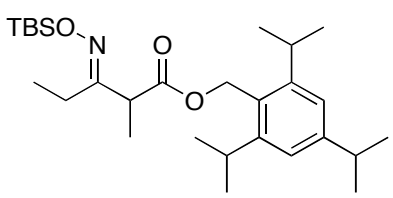
3-[*tert*-Butyldimethylsilanyloxyimino]-2-methyl-pentanoic acid diphenylmethyl ester (O5)



Prepared according to the general procedure from ß-keto ester **S5** (148 mg, 0.5 mmol). Purification by FC on SiO_2 with hexane/TBME 20:1 as eluents afforded pure **O5** as a colourless oil. Yield: 83 mg (39%). The ^{1}H NMR spectrum showed the presence of two isomers (**A** and **B**) in the ratio **A**:**B** = 2.5:1.

TLC (hexane/TBME 5:1): R_f = 0.7. **^{1}H NMR** (300.1 MHz, $CDCl_3$): Diastereoisomer **A**: δ 7.35 - 7.28 (*m*, 10 H, Ph-*H*), 6.88 (*s*, 1 H, C*H*Ph_2), 3.86 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH_3), 2.33 (*q*, 2 H, *J* = 7.4 Hz, C$H_2$$CH_3$), 1.33 (*d*, 3 H, *J* = 7.2 Hz, CH*C*H_3), 1.11 (*t*, 3 H, *J* = 7.4 Hz, CH_2CH_3), 0.89 (*s*, 9 H, SiC(CH_3)$_3$), 0.21 (*s*, 6 H, Si(CH_3)$_2$). Diastereoisomer **B**: δ 7.35 - 7.28 (*m*, 10 H, Ph-*H*), 6.88 (*s*, 1 H, C*H*Ph_2), 3.63 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH_3), 2.40 (*q*, 2 H, *J* = 7.6 Hz, C$H_2$$CH_3$), 1.39 (*d*, 3 H, *J* = 7.2 Hz, CH*C*H_3) 1.06 (*t*, 3 H, *J* = 7.6 Hz, CH_2CH_3), 1.01 (*s*, 9 H, SiC(CH_3)$_3$), 0.26 (*s*, 6 H, Si(CH_3)$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): Diastereoisomer **A**: δ 171.23 (*s*, *C*O), 162.14 (*s*, *C*N), 140.68 (*s*, Ph-*C*), 140.35 (*s*, Ph-*C*), 128.51 (*s*, Ph-*C*H), 128.41 (*s*, Ph-*C*H), 127.91 (*s*, Ph-*C*H), 127.74 (*s*, Ph-*C*H), 127.31 (*s*, Ph-*C*H), 127.02 (*s*, Ph-*C*H), 76.86 (*s*, *C*HPh_2), 39.67 (*s*, *C*HCH$_3$), 26.28 (*s*, *C*H_2CH$_3$), 26.08 (*s*, SiC(*C*H_3)$_3$), 18.11 (*s*, Si*C*(CH_3)$_3$), 12.91 (*s*, CH*C*H_3), 10.71 (*s*, CH_2*C*H_3), -5.23 (*s*, Si(*C*H_3)$_2$). Diastereomer **B**: δ 171.76 (*s*, *C*O), 163.69 (*s*, *C*N), 140.28 (*s*, Ph-*C*), 140.18 (*s*, Ph-*C*), 128.54 (*s*, Ph-*C*H), 128.49 (*s*, Ph-*C*H), 127.95 (*s*, Ph-*C*H), 127.15 (*s*, Ph-*C*H), 127.11 (*s*, Ph-*C*H), 127.01 (*s*, Ph-*C*H), 77.28 (*s*, *C*HPh_2), 45.28 (*s*, *C*HCH$_3$), 26.19 (*s*, *C*H_2CH$_3$), 20.92 (*s*, SiC(*C*H_3)$_3$), 18.20 (*s*, Si*C*(CH_3)$_3$), 14.50 (*s*, CH*C*H_3), 10.49 (*s*, CH_2*C*H_3), -5.18 (*s*, Si(*C*H_3)$_2$). **MS (ESI)**: m/z: calcd for $C_{25}H_{35}NO_3Si$: 426.2 ([M]$^+$); found: 426.2 (100, [M]$^+$), 448.2 (85, [M+Na]$^+$). **GC-MS**: t_R = 29.33, 29.84 min.

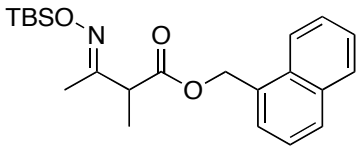
3-[*tert*-Butyldimethylsilanyloxyimino]-2-methyl-pentanoic acid 2,4,6-triisopropyl benzyl ester (O6)



Prepared according to the general procedure from ß-keto ester **S6** (173 mg, 0.5 mmol). Purification by FC on SiO_2 with hexane/TBME as eluents afforded pure **O6** as a colourless oil. Yield: 57 mg (24%). The ^{1}H NMR spectrum showed the presence of two isomers (**A** and **B**) in the ratio **A**:**B** = 3.2:1.

^{1}H NMR (300.1 MHz, $CDCl_3$): Diastereoisomer **A**: δ 7.12 (*s*, 2 H, Ar-*H*), 5.47 (*d*, 1 H, *J* = 12.2 Hz, C*H*$_2$Ar), 5.17 (*d*, 1 H, *J* = 12.2 Hz, C*H*$_2$Ar), 3.82 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 3.29 (*sept*, 2 H, *J* = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.97 (*sept*, 1 H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 2.32 (*q*, 2 H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.39 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$), 1.34 (*d*, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.32 (*d*, 12 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.14 (*t*, 3 H, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 1.00 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.21 (*s*, 6 H, Si(C*H*$_3$)$_2$). Diastereoisomer **B**: δ 7.12 (*s*, 2 H, Ar-*H*), 5.41 (*d*, 1 H, *J* = 12.3 Hz, C*H*$_2$Ar), 5.27 (*d*, 1 H, *J* = 12.3 Hz, C*H*$_2$Ar), 3.48 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 3.29 (*sept*, 2 H, *J* = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.97 (*sept*, 1 H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 2.32 (*q*, 2 H, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.43 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$), 1.34 (*d*, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.32 (*d*, 12 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.13 (*t*, 3 H, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 1.00 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.21 (*s*, 6 H, Si(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): Diastereomer **A**: δ 172.54 (*s*, *C*O), 162.06 (*s*, *C*N), 149.46 (*s*, Ar-*C*), 148.89 (*s*, Ar-*C*), 126.66 (*s*, Ar-*C*), 121.08 (*s*, Ar-*C*H), 59.51 (*s*, *C*H$_2$Ar), 39.76 (*s*, *C*HCH$_3$), 34.42 (*s*, *C*H(CH$_3$)$_2$), 29.42 (*s*, *C*H(CH$_3$)$_2$), 26.29 (*s*, *C*H$_2$CH$_3$), 26.04 (*s*, SiC(*C*H$_3$)$_3$), 24.44 (*s*, CH(*C*H$_3$)$_2$), 24.01 (*s*, CH(*C*H$_3$)$_2$), 18.08 (*s*, Si*C*(*C*H$_3$)$_3$), 13.17 (*s*, CH*C*H$_3$), 10.41 (*s*, CH$_2$*C*H$_3$), -5.32 (*s*, Si(*C*H$_3$)$_3$). Diastereoisomer **B**: δ 172.99 (*s*, *C*O), 163.66 (*s*, *C*N), 149.60 (*s*, Ar-*C*), 148.89 (*s*, Ar-*C*), 126.44 (*s*, Ar-*C*), 121.13 (*s*, Ar-*C*H), 59.77 (*s*, *C*H$_2$Ar), 44.96 (*s*, *C*HCH$_3$), 34.42 (*s*, *C*H(CH$_3$)$_2$), 29.46 (*s*, *C*H(CH$_3$)$_2$), 26.11 (*s*, SiC(*C*H$_3$)$_3$), 24.44 (*s*, CH(*C*H$_3$)$_2$), 24.01 (*s*, CH(*C*H$_3$)$_2$), 20.85 (*s*, *C*H$_2$CH$_3$), 18.11 (*s*, Si*C*(CH$_3$)$_3$), 14.70 (*s*, CH*C*H$_3$), 10.49 (*s*, CH$_2$*C*H$_3$), -5.32 (*s*, Si(*C*H$_3$)$_3$). **MS (ESI)**: m/z: calcd for $C_{28}H_{49}NO_3Si$: 476.2 ([M]$^+$); found: 498.3 (100, [M+Na]$^+$), 476.3 (40, [M]$^+$). **GC-MS**: t_R = 28.71, 29.15 min.

3-[*tert*-Butyldimethylsilanyloxyimino]-2-methyl-pentanoic acid naphthalen-1-yl methyl ester (O7)



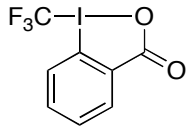
Prepared according to the general procedure from ß-keto ester **S7** (128 mg, 0.5 mmol). Purification by FC on SiO_2 with hexane/TBME 20:1 as eluents afforded pure **O7** as a colourless oil. Yield: 40 mg (21%). The ^{1}H NMR spectrum showed the presence of two isomers (**A** and **B**) in the ratio **A**:**B** = 1.5:1.

TLC (hexane/TBME 10:1): R_f = 0.48. **^{1}H NMR** (300.1 MHz, $CDCl_3$): Diastereoisomer **A**: δ 8.03 - 7.98 (*m*, 1 H, Ar-*H*), 7.92 - 7.86 (*m*, 2 H, Ar-*H*), 7.60 - 7.44 (*m*, 4 H, Ar-*H*), 5.62 (*s*, 2 H, C*H*$_2$Ar), 3.48 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 1.82 (*s*, 3 H, *CH*$_3$C=N), 1.37 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$), 0.91 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.14 (*s*, 6 H, Si(C*H*$_3$)$_2$). Diastereoisomer **B**: δ 8.03 - 7.98 (*m*, 1 H, Ar-*H*), 7.92 - 7.86 (*m*, 2 H, Ar-*H*), 7.60 - 7.44 (*m*, 4 H, Ar-*H*), 5.59 (*s*, 2 H, C*H*$_2$Ar), 4.07 (*q*, 1 H, *J* = 7.2 Hz, C*H*CH$_3$), 1.84 (*s*, 3 H, *CH*$_3$C=N), 1.32 (*d*, 3 H, *J* = 7.2 Hz, CH*CH*$_3$), 0.90 (*s*, 9 H, SiC(C*H*$_3$)$_3$), 0.12 (*s*, 6 H, Si(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): Diastereomer **A**: δ 172.63 (*s*, *C*O), 159.84 (*s*, *C*N), 133.72 (*s*, Ar-*C*), 131.58 (*s*, Ar-*C*), 131.30 (*s*, Ar-*C*), 129.26 (*s*, Ar-*C*H), 128.69 (*s*, Ar-*C*H), 127.37 (*s*, Ar-*C*H), 126.53 (*s*, Ar-*C*H), 125.92 (*s*, Ar-*C*H), 125.23 (*s*, Ar-*C*H), 123.52 (*s*, Ar-*C*H), 64.99 (*s*, *C*H$_2$Ar), 45.88 (*s*, *C*HCH$_3$), 26.04 (*s*, SiC(*C*H$_3$)$_3$), 18.11 (*s*, Si*C*(CH$_3$)$_3$), 17.68 (*s*, *C*H$_3$C=N), 14.37 (*s*, CH*C*H$_3$), -5.31 (*s*, Si(*C*H$_3$)$_2$). Diastereomer **B**: δ 172.33 (*s*, *C*O), 158.83 (*s*, *C*N), 133.70 (*s*, Ar-*C*), 131.60 (*s*, Ar-*C*), 131.42 (*s*, Ar-*C*), 129.18 (*s*, Ar-*C*H), 128.66 (*s*, Ar-*C*H), 127.25 (*s*, Ar-*C*H), 126.49 (*s*, Ar-*C*H), 125.90 (*s*, Ar-*C*H), 125.23 (*s*, Ar-*C*H), 123.57 (*s*, Ar-*C*H), 64.82 (*s*, *C*H$_2$Ar), 39.28 (*s*, *C*HCH$_3$), 25.96 (*s*, SiC(*C*H$_3$)$_3$), 18.00 (*s*, Si*C*(CH$_3$)$_3$), 13.06 (*s*, *C*H$_3$C=N), 12.14 (*s*, CH*C*H$_3$), -5.34 (*s*, Si(*C*H$_3$)$_2$). **MS (ESI)**: m/z: calcd for $C_{22}H_{31}NO_3Si$: 385.2 ([M]$^+$); found: 408.3 (100, [M+Na]$^+$), 386.3 (20, [M]$^+$). **GC-MS**: t_R = 28.86, 29.40 min.

3.3 Chapter 2: Chiral Ferrocenyl Trifluoromethylphosphine Ligands

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one was synthesized following reported procedures.[11] Several metal complexes were prepared and kindly provided by *Kyrill Stanek*, an other member of the group: $[Rh(cod)_2]BF_4$, $[Pd(cod)Cl_2]$,[12] $[Ir_2(cod)_2Cl_2]$[13]

1-Trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (25)[14]



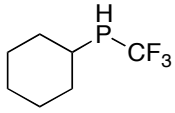
1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (6.00 g, 21.1 mmol) was refluxed in Ac_2O for a few minutes until a clear solution was obtained. Upon cooling, white crystals began to separate and cooling was continued to -20 °C for 4 h. The solution was decanted and the crystals were dried under HV for 24 hours under stirring. The resulting white powder was identified as 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one. It was dissolved in dry MeCN (50 mL) under Argon. $TMSCF_3$ (4.5 mL, 30.4 mmol) followed by dry CsF (50 mg, 0.33 mmol) was added and the suspension was vigorously stirred at rt for 22 h. The solvent was evaporated under reduced pressure and the brown residue was purified by FC with CH_2Cl_2/MeOH 15:1 as eluents, affording pure compound **25** as a white solid. Yield: 5.65 g (79% over 2 steps, 76% from 2-iodo benzoic acid). NMR data was in agreement with the reported data.[14]

3.3.1 Mono(trifluoromethyl)halogeno Phosphines

1. General procedure for the trifluoromethylation of primary phosphines

The primary phosphine (0.2 mmol) was added to a solution of 1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (**25**) (0.2 mmol) in CH_2Cl_2 (0.5 mL) in the glove-box. The reaction mixture was stirred at rt. After 1h, the starting materials were found to be consumed, based on the ^{19}F- and $^{31}P\{^1H\}$ NMR spectroscopy. Conversions were based on the comparison of the ratio of the integrals of the product signal to the signal of the internal standard $PhCF_3$ in the ^{19}F NMR spectrum. The compounds were not isolated as pure materials but used for further transformation immediately after preparation.

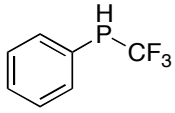
Cyclohexyl(trifluoromethyl)phosphine (34)



Prepared according to the general procedure from cyclohexylphosphine (26.5 μL, 0.2 mmol). Conversion: 58% (23% of product **34** and 35% of its protonated form $CyP(CF_3)H_2^+$ **34**H^+).

^{19}F NMR (188.3 MHz, CD_2Cl_2): δ -42.00 (*dt*, $^2J_{F,P}$ = 45.5 Hz, $^3J_{F,H}$ = 12.3 Hz, PC*F*$_3$ **34**H^+), -48.65 (*dd*, $^2J_{F,P}$ = 49.3 Hz, $^3J_{F,H}$ = 12.0 Hz, PC*F*$_3$ **34**). **^{31}P{^{1}H} NMR** (80.0 MHz, CD_2Cl_2): δ -123.46 (*q*, $^2J_{P,F}$ = 45.5 Hz, *P*CF_3 **34**H^+), -38.22 (*q*, $^2J_{P,F}$ = 49.3 Hz, *P*CF_3 **34**).

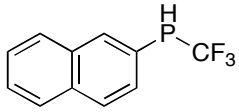
Phenyl(trifluoromethyl)phosphine (35)



Prepared according to the general procedure from phenylphosphine (22.0 μL, 0.2 mmol). Conversion: 84%.

^{19}F NMR (188.3 MHz, CD_2Cl_2): δ -52.15 (*dd*, $^2J_{F,P}$ = 57.5 Hz, $^3J_{F,H}$ = 11.5 Hz, PC*F*$_3$). **^{31}P{^{1}H} NMR** (80.0 MHz, CD_2Cl_2): δ -40.38 (*q*, $^2J_{P,F}$ = 57.5 Hz, *P*CF_3).

Naphthyl(trifluoromethyl)phosphine (36)



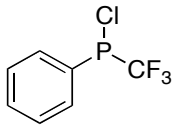
Prepared according to the general procedure from naphtylphosphine (38 mg, 0.2 mmol). Conversion: 47%.

^{19}F NMR (188.3 MHz, CD_2Cl_2): δ -51.76 (*dd*, $^2J_{F,P}$ = 57.4 Hz, $^3J_{F,H}$ = 11.3 Hz, PC*F*$_3$). **^{31}P{^{1}H} NMR** (80.0 MHz, CD_2Cl_2): δ -40.51 (*q*, $^2J_{P,F}$ = 57.4 Hz, *P*CF_3).

2. General procedure for the halogenation (chlorination or bromination) of (mono)trifluoromethylated phosphines

A catalytic amount of $TiCpCl_3$ (0.02 mmol) was added to a mixture of monotrifluoromethylated phosphine (0.2 mmol) in CH_2Cl_2 (0.5 mL). After dissolution of the metal complex, the halogenating agent (NCS or NBS) (0.3 mmol) was added, and the reaction mixture was stirred for 10 min. Evaporation of the solvent followed by a *n*-hexane extraction removed more than 80% of the by-products. Conversions were determined by ^{31}P NMR spectroscopy as the ratio between the product and the sum of the starting material and product.

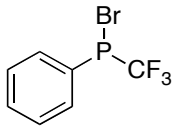
Chloro(phenyl)(trifluoromethyl)phosphine (37)



Prepared according to the general procedure from phenyl(trifluoromethyl)phosphine (**35**) (35 mg, 0.2 mmol) with NCS as halogenating agent. Conversion: quant.

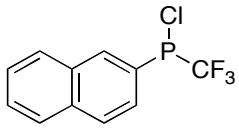
^{19}F NMR (188.3 MHz, CD_2Cl_2): δ -74.44 (*d*, $^2J_{F,P}$ = 114.6 Hz, PC*F*$_3$). **^{31}P{^{1}H} NMR** (80.0 MHz, CD_2Cl_2): δ 29.89 (*q*, $^2J_{P,F}$ = 114.6 Hz, *P*CF_3).

Bromo(phenyl)(trifluoromethyl)phosphine (38)



Prepared according to the general procedure from phenyl(trifluoromethyl) phosphine (**35**) (35 mg, 0.2 mmol) with NBS as halogenating agent. Conversion: quant. Molar ratio of the bromo- vs the chloro-compounds based on the ^{19}F and ^{31}P NMR spectrum: 1 (Br) / 1.4 (Cl).

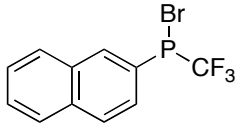
Chloro(naphthyl)(trifluoromethyl)phosphine (39)



Prepared according to the general procedure from naphtyl(trifluoromethyl) phosphine (**36**) (46 mg, 0.2 mmol) with NCS as halogenating agent. Conversion: quant.

^{19}F NMR (188.3 MHz, CD_2Cl_2): δ -74.86 (*d*, $^2J_{F,P}$ = 111.5 Hz, PC*F*$_3$). **^{31}P{^{1}H} NMR** (80.0 MHz, CD_2Cl_2): δ -19.29 (*q*, $^2J_{P,F}$ = 111.5 Hz, *P*CF_3).

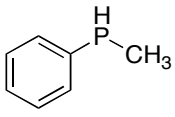
Bromo(naphthyl)(trifluoromethyl)phosphine (40)



Prepared according to the general procedure from naphtyl(trifluoromethyl) phosphine (**36**) (46 mg, 0.2 mmol) with NBS as halogenating agent. Conversion: quant. Molar ratio of the bromo- vs the chloro-compounds based on the ^{19}F and ^{31}P NMR spectrum: 1 (Br) / 1.4 (Cl).

3.3.2 New Ferrocenyl Bisphosphine Ligands

Methylphenylphosphine (47)

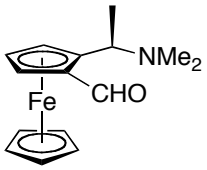


To a suspension of Na (1.05 g, 45.50 mmol) in Et_2O (25 mL), H_2PPh (5 mL, 45.50 mmol) was added via cannula to give a yellow suspension, which was heated for 1 h at reflux (35 °C). After cooling down to rt, MeI (2.83 mL, 45.46 mmol) was added, giving a white suspension in an exothermic reaction. After heating another 30 min at reflux, the white suspension was filtered via cannula filter and then distilled under vacuum, affording **47** as a colorless liquid. Yield: 4.90 g (87%).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.57 - 7.51 (*m*, 2 H, Ph-*H*), 7.39 - 7.29 (*m*, 3 H, Ph-*H*), 1.44 (*d*, 3 H, $^2J_{P,H}$ = 2.9 Hz, C*H*$_3$). **^{31}P{^{1}H} NMR** (101.3 MHz, $CDCl_3$): δ -70.54 (*s*, *P*H). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 136.99 (*d*, $^1J_{P,C}$ = 9.9 Hz, Ph-*C ipso*), 132.79 (*d*, $^2J_{P,C}$ = 16.0 Hz,

Ph-*C*H *ortho*), 128.46 (*d*, $^3J_{P,C}$ = 5.9 Hz, Ph-*C*H *meta*), 128.07 (*d*, $^4J_{P,C}$ = 1.3 Hz, Ph-*C*H *para*), 6.29 (*d*, $^1J_{P,C}$ = 11.7 Hz, *C*H_3).

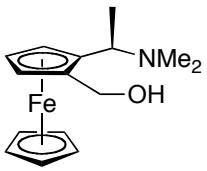
1-[(*R*)-Dimethylaminoethy]-2-(S_{Fc})-formylferrocene (51)[15]



To a cooled (-78 °C) solution of (*R*)-Ugi amine (1.62 g, 6.3 mmol) in Et_2O (20 mL) was added dropwise a solution of *tert*-BuLi (4.9 mL, 7.9 mmol, 1.6 M in pentane). The red reaction mixture was stirred for 30 min at -78 °C followed by 2 h at 0 °C. The reaction temperature was kept at 0 °C and *N,N*-dimethylformamide (0.97 mL, 919 mg, 12.6 mmol) was added. The temperature was raised to rt and stirring continued for 16 h at this temperature. The reaction was quenched with water (25 mL) and Et_2O was added. The phases were separated and the aqueous phase was extracted 3 times with Et_2O (20 mL). The combined organic phases were washed with NaCl (sat., 25 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by FC on SiO_2 with hexane/Et_2O/Et_3N 10:5:1 as eluents, affording pure **51** as a brown oil. Yield: 1.80 g (quant.).

TLC (hexane/Et_2O/Et_3N 10:5:1): R_f = 0.15. **^{1}H NMR** (250.1 MHz, $CDCl_3$): δ 10.01 (*s*, 1 H, C*H*O), 4.69 (*s*, 1 H, Cp-*H*), 4.46 - 4.44 (*m*, 2 H, Cp-*H*), 4.06 (*s*, 5 H, Cp'-*H'*), 4.00 (*q*, 1 H, *J* = 6.8 Hz C*H*CH_3), 1.97 (*s*, 6 H, (N(CH_3)$_2$), 1.35 (*d*, 3 H, *J* = 6.8 Hz, CHCH_3). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 193.07 (*C*HO), 91.38 (Cp-*C*), 72.28 (Cp-*C*H), 71.14 (Cp-*C*H), 70.21 (Cp'-*C*H'), 69.27 (Cp-*C*H), 68.88 (Cp-*C*), 55.38 (*C*HCH_3), 40.23 (N(*C*H_3)$_2$), 14.32 (CH*C*H_3).

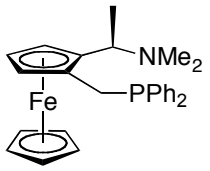
1-[(*R*)-Dimethylaminoethy]-2-(S_{Fc})-hydroxymethylferrocene (52)[15]



$LiAlH_4$ (357 mg, 9.4 mmol) was added to a cooled (<0 °C) solution of (R,S_{Fc})-**51** (1.79 g, 6.3 mmol) in THF (20 mL) in one portion. The green-yellow reaction mixture was allowed to warm at rt and stirred for 16 h. The reaction was quenched with Na_2CO_3 (sat., 50 mL) and Et_2O was added. The phases were separated and the aqueous phase was extracted 3 times with Et_2O (40 mL). The combined organic phases were washed with brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the pure **52** as an orange solid. Yield: 1.56 g (87%).

^{1}H NMR (250.1 MHz, $CDCl_3$): δ 6.50 (*br s*, 1 H, O*H*), 4.77 (*d*, 1 H, *J* = 12.1 Hz, CH_2OH), 4.18 - 4.04 (*m*, 4 H, Cp-*H* and C*H*CH_3), 4.03 (*s*, 5 H, Cp'-*H'*), 2.13 (*s*, 6 H, (N(CH_3)$_2$), 1.26 (*d*, 3 H, *J* = 6.8 Hz, CHCH_3). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 90.26 (Cp-*C*), 87.18 (Cp-*C*), 69.77 (Cp-*C*H), 68.97 (Cp-*C*H'), 67.43 (Cp-*C*H), 65.29 (Cp-*C*H), 60.19 (*C*H_2OH), 57.46 (*C*HCH_3), 38.76 (N(*C*H_3)$_2$), 6.90 (CH*C*H_3).

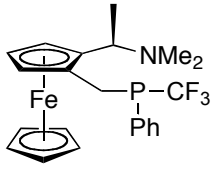
1-[(*R*)-Dimethylaminoethy]-2-(S_{Fc})-diphenylphosphinomethylferrocene (48)



A solution of fluoroboric acid (4.4 mL, 2.1 mmol, 51-57% in diethylether) was added dropwise to a cooled (-78 °C) solution of 1-[(*R*)-dimethylaminoethy]-2-(R_{Fc})-hydroxymethylferrocene (**52**) (591 mg, 2.1 mmol) in CH_2Cl_2 (6 mL). The red reaction mixture was stirred for 10 min at -78 °C and diphenylphosphine (0.43 mL, 2.5 mmol) was added dropwise at the same temperature. The temperature was raised to rt and stirred for 16 h. The reaction was quenched with Na_2CO_3 (sat., 50 mL) and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (30 mL). The combined organic phases were washed with brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by PTLC on basic Alox with hexane/TBME 10:1 as eluents, affording pure **48** as an orange oil. Yield: 720 mg (77%)

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.54 - 7.44 (*m*, 4 H, Ph-*H*), 7.39 - 7.30 (*m*, 6 H, Ph-*H*), 4.09 - 4.07 (*m*, 1 H, Cp-*H5*), 4.05 (*s*, 5 H, Cp'-*H'*), 3.96 (*t*, 1 H, *J* = 2.3 Hz, Cp-*H4*), 3.90 - 3.83 (*m*, 2 H, ^3J = 6.7 Hz, Cp-*H3* + C*H*CH_3), 3.31 (*dd*, 1 H, *J* = 14.9 Hz, $^2J_{P,H}$ = 2.3 Hz, CH_2), 3.20 (*dd*, 1 H, *J* = 14.9 Hz, $^2J_{P,H}$ = 1.3 Hz, CH_2), 2.13 (*s*, 6 H, N(CH_3)$_2$), 1.40 (*d*, 3 H, *J* = 6.7 Hz, CHCH_3). **^{31}P{^{1}H} NMR** (101.3 MHz, $CDCl_3$): δ -15.15 (*s*, *P*Ph_2). **^{13}C{^{1}H} NMR** (62.9 MHz, $CDCl_3$): δ 140.11 (*d*, $^1J_{P,C}$ = 15.8 Hz, Ph-*C ipso*), 139.86 (*d*, $^1J_{P,C}$ = 16.5 Hz, Ph-*C ipso*), 133.43 (*d*, $^2J_{P,C}$ = 20.0 Hz, Ph-*C*H *ortho*), 132.44 (*d*, $^2J_{P,C}$ = 18.2 Hz, Ph-*C*H *ortho*), 128.76 (*s*, Ph-*C*H *para*), 128.46 (*d*, $^3J_{P,C}$ = 12.2 Hz, Ph-*C*H *meta*), 128.45 (*s*, Ph-*C*H *para*), 128.32 (*d*, $^3J_{P,C}$ = 15.8 Hz, Ph-*C*H *meta*), 89.13 (*d*, $^3J_{P,C}$ = 4.0 Hz, Cp-*C1*), 84.80 (*d*, $^2J_{P,C}$ = 16.3 Hz, Cp-*C2*), 69.64 (*d*, $J_{P,C}$ = 0.9 Hz, Cp'-*C*H'), 69.10 (*d*, $^3J_{P,C}$ = 9.0 Hz, Cp-*C*H*3*), 66.39 (*d*, $^4J_{P,C}$ = 0.8 Hz, Cp-*C*H*5*), 65.43 (*s*, Cp-*C*H*4*), 56.87 (*s*, *C*HCH_3), 40.57 (*d*, $J_{P,C}$ = 1.1 Hz, N(*C*H_3)$_2$), 28.42 (*d*, $^1J_{P,C}$ = 14.7 Hz, *C*H_2), 12.02 (*s*, CH*C*H_3). **HRMS (EI)**: m/z: calcd for $C_{27}H_{30}FeNP$: 455.1460 ([M]$^+$); found: 455.1459 (22, [M]$^+$), 410.0892 (100, [M-N$(CH_3)_2$]$^+$), 225.0359 (50, [M-PPh_2- N$(CH_3)_2$]$^+$).

1-[(*R*)-Dimethylaminoethy]-2-(S_{Fc})-[(R_P/S_P)-trifluoromethylphenylphosphino]methyl-ferrocene (49)



A solution of fluoroboric acid (1.7 mL, 0.8 mmol, 51-57 % in diethylether) was added dropwise to a cooled (-78 °C) solution of 1-[(*R*)-dimethylaminoethy]-2-(R_{Fc})-hydroxymethylferrocene (**52**) (230 mg, 0.8 mmol) in CH_2Cl_2 (2.5 mL). The red reaction mixture was stirred for 10 min at -78 °C and phenyl(trifluoromethyl)phosphine (**35**) (~ 100 mg, 0.8 mmol) was added dropwise at the same temperature. The temperature was raised to rt and stirred for 16 h. The reaction was quenched with Na_2CO_3 (sat., 50 mL) and CH_2Cl_2 was added. The phases were

separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (30 mL). The combined organic phases were washed with brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by PTLC on basic Alox with hexane/TBME 10:1 as eluents, affording pure **49** as an orange oil. Yield: 243 mg (68%) of the 2 diastereoisomers.

Separation of the 2 diastereoisomers was performed by preparative HPLC using chiralcel OJ column, hexane:^{i}PrOH 98:2, 15 mL/min, 10-50 mg or by crystallization in hot MeOH, affording pure (R,S_{FC},S_P)-**49** as an orange oil and pure (R,S_{FC},S_P)-**49** as an orange solid.

Diastereoisomeric ratio from ^{31}P NMR spectroscopy: **A** (R,S_{FC},S_P):**B** (R,S_{FC},R_P)= 0.34 : 0.66.

Diastereoisomer **A**: (R,S_{Fc},S_P)-**49**

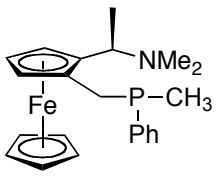
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.79 - 7.74 (*m*, 2 H, Ph-*H*), 7.52 - 7.46 (*m*, 3 H, Ph-*H*), 4.09 (*s*, 1 H, Cp-*H*), 4.01 (*s*, 5 H, Cp'-*H'*), 3.97 - 3.01 (*m*, 2 H, Cp-*H* and C*H*CH_3), 3.80 (*s*, 1 H, Cp-*H*), 3.38 (*dd*, 1 H, *J* = 14.5 Hz, $^{2}J_{P,H}$ = 6.6 Hz, CH_2), 3.20 (*d*, 1 H, *J* = 14.5 Hz, CH_2), 2.13 (*s*, 6 H, N(CH_3)$_2$), 1.34 (*d*, 3 H, *J* = 6.7 Hz, CHCH_3). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -58.83 (*d*, $^{2}J_{P,F}$ = 61.9 Hz, CF_3). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ -10.69 (*q*, $^{2}J_{F,P}$ = 61.9 Hz, *P*). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 134.65 (*dq*, $^{2}J_{P,C}$ = 22.5 Hz, $^{4}J_{F,C}$ = 0.7 Hz, Ph-*C*H *ortho*), 130.90 (*d*, $^{4}J_{P,C}$ = 1.0 Hz, Ph-*C*H *para*), 130.19 (*d*, $^{1}J_{P,C}$ = 19.4 Hz, Ph-*C ipso*), 131.61 (*dq*, $^{1}J_{F,C}$ = 321.6 Hz, $^{1}J_{P,C}$ = 39.3 Hz, *C*F_3), 128.60 (*d*, $^{3}J_{P,C}$ = 8.2 Hz, Ph-*C*H *meta*), 89.33 (*d*, $^{3}J_{P,C}$ = 3.1 Hz, Cp-*C*), 82.31 (*d*, $^{2}J_{P,C}$ = 19.7 Hz, Cp-*C*), 69.46 (*s,* Cp'-*C*H'), 68.93 (*d*, $^{3}J_{P,C}$ = 6.1 Hz, Cp-*C*H), 66.67 (*s*, Cp-*C*H), 65.50 (*s*, Cp-*C*H), 57.02 (*s*, *C*HCH_3), 39.81 (*d*, $J_{P,C}$ = 1.6 Hz, N(*C*H_3)$_2$), 22.35 (*qd*, $^{1}J_{P,C}$ = 13.8 Hz, $^{3}J_{F,C}$ = 3.6 Hz, *C*H_2), 9.98 (*s*, CH*C*H_3). **MS (EI)**: m/z: calcd for $C_{22}H_{25}NF_3PFe$: 447.26 ([M]$^+$); found: 447.10 (38, [M]$^+$), 402.04 (93, [M-N$(CH_3)_2$]), 333.05 (100). **EA**: calcd. for $C_{22}H_{25}NF_3PFe$ (447.26): C, 59.08; H, 5.63; N, 3.13; F, 12.74; found: C, 59.12; H, 5.64; N, 3.13; F, 12.59

Diastereoisomer **B**: (R,S_{Fc},R_P)-**49**

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.76 - 7.71 (*m*, 2 H, Ph-*H*), 7.48 - 7.46 (*m*, 3 H, Ph-*H*), 4.15 (*br s*, 2 H, Cp-*H*), 4.11 (*s*, 5 H, Cp'-*H'*), 4.07 (*m*, 1 H, Cp-*H*), 3.89 (*q*, 1 H, *J* = 6.7 Hz, C*H*CH_3), 3.32 (*dd*, 1 H, *J* = 14.7 Hz, $^{2}J_{P,H}$ = 4.0 Hz, CH_2), 3.22 (*dd*, 1 H, *J* = 14.7 Hz, $^{2}J_{P,H}$ = 5.3 Hz, CH_2), 1.89 (*s*, 6 H, N(CH_3)$_2$), 1.28 (*d*, 3 H, *J* = 6.7 Hz, CHCH_3). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -59.40 (*d*, $^{2}J_{P,F}$ = 60.5 Hz, CF_3). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ -7.70 (*q*, $^{2}J_{F,P}$ = 60.5 Hz, *P*). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 133.93 (*d*, $^{2}J_{P,C}$ = 21.6 Hz, Ph-*C*H *ortho*), 132.40 (*dq*, $^{1}J_{F,C}$ = 322.4 Hz, $^{1}J_{P,C}$ = 40.6 Hz, *C*F_3), 131.13 (*dd*, $^{1}J_{P,C}$ = 16.2 Hz, $^{3}J_{F,C}$ = 3.8 Hz, Ph-*C ipso*), 130.50 (*d*, $^{4}J_{P,C}$ = 1.0 Hz, Ph-*C*H *para*), 128.52 (*d*, $^{3}J_{P,C}$ = 7.9 Hz, Ph-*C*H *meta*), 88.83 (*d*, $^{3}J_{P,C}$ = 2.8 Hz, Cp-*C1*), 84.07 (*d*, $^{2}J_{P,C}$ = 24.6 Hz, Cp-*C2*), 69.48 (*s,* Cp'-*C*H'), 68.90 (*d*, $^{3}J_{P,C}$ = 5.0 Hz, Cp-*C*H), 66.77 (*s*, Cp-*C*H), 65.50 (*s*, Cp-*C*H), 57.24 (*s*, *C*HCH_3), 39.44 (*d*,

$J_{P,C}$ = 1.5 Hz, N(*C*H$_3$)$_2$), 21.93 (*qd*, $^1J_{P,C}$ = 11.5 Hz, ^3J(C,F) = 3.5 Hz, *C*H$_2$), 8.42 (*s*, CH*C*H$_3$). **MS (EI)**: m/z: calcd for $C_{22}H_{25}NF_3PFe$: 447.26 ([M]$^+$); found: 447.10 (38, [M]$^+$), 402.04 (93, [M-N(CH$_3$)$_2$]), 333.05 (100). **EA**: calcd. for $C_{22}H_{25}NF_3PFe$ (447.26): C, 59.08; H, 5.63; N, 3.13; F, 12.74; found: C, 58.8; H, 5.67; N, 3.05; F, 12.47.

1-[(*R*)-Dimethylaminoethy]-2-(*S$_{Fc}$*)-[(*R$_P$*/*S$_P$*)-methylphenylphosphino]methylferrocene (50)



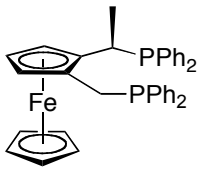
A solution of fluoroboric acid (2.6 mL, 1.2 mmol, 51-57% in diethylether) was added dropwise to a cooled (-78 °C) solution of 1-[(*R*)-dimethylaminoethy]-2-(*R$_{Fc}$*)-hydroxymethylferrocene (**52**) (350 mg, 1.2 mmol) in CH_2Cl_2 (4 mL). The red reaction mixture was stirred for 10 min at -78 °C and methylphenylphosphine (**47**) (0.18, 1.4 mmol) was added dropwise at the same temperature. The temperature was raised to rt and stirred for 16 h. The reaction was quenched with Na_2CO_3 (sat., 70 mL) and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (50 mL). The combined organic phases were washed with brine (70 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by FC with hexane/EtOAc/Et_3N 10:2:0.2 as eluents, affording pure **50** as an orange oil. Yield: 370 mg (81%) of the two diastereoisomers.

Diastereoisomeric ratio from ^{31}P NMR spectroscopy: **A**:**B** = 0.49 : 0.51.

^{1}H NMR (700.1 MHz, $CDCl_3$): δ 7.64 - 7.62 (*m*, 1.02 H, Ph-*H ortho* **B**), 7.57 - 7.55 (*m*, 0.98 H, Ph-*H ortho* **A**), 7.45 - 7.42 (*m*, 1.02 H, Ph-*H meta* **B**), 7.41 - 7.39 (*m*, 1.49 H, Ph-*H meta* **A** + Ph-*H para* **B**), 7.36 - 7.34 (*m*, 0.49 H, Ph-*H para* **A**), 4.14 (*br s*, 0.51 H, Cp-*H3* **B**), 4.10 (*br s*, 1.0 H, Cp-*H5* **A** + Cp-*H5* **B**), 4.06 (*s*, 2.45 H, Cp'-*H'* **A**), 4.05 - 4.04 (*m*, 0.51 H, Cp-*H4* **B**), 4.02 (*s*, 3.04 H, Cp'-*H'* **B** + Cp-*H4* **A**), 3.95 (*br s*, 0.49 H, Cp-*H3* **A**), 3.87 - 3.83 (*m*, 1.0 H, C*H*CH$_3$ **A** + C*H*CH$_3$ **B**), 3.01 (*d*, 0.49 H, *J* = 15.0 Hz, C*H$_2$* **A**), 2.93 (*d*, 0.51 H, *J* = 14.3 Hz, C*H$_2$* **B**), 2.84 (*dd*, 0.51 H, *J* = 14.1 Hz, $^2J_{P,H}$ = 3.4 Hz, C*H$_2$* **B**), 2.78 (*dd*, 0.49 H, *J* = 14.1 Hz, $^2J_{P,H}$ = 1.6 Hz, C*H$_2$* **A**), 2.17 (*s*, 3.06 H, N(C*H$_3$*)$_2$ **B**), 2.16 (*s*, 2.94 H, N(C*H$_3$*)$_2$ **A**), 1.41 (*d*, 1.47 H, *J* = 6.7 Hz, CHC*H$_3$* **A**), 1.39 (*d*, 1.53 H, *J* = 6.7 Hz, CHC*H$_3$* **B**), 1.36 (*d*, 1.47 H, $^1J_{P,H}$ = 3.9 Hz, PC*H$_3$* **A**), 1.34 (*d*, 1.53 H, $^1J_{P,H}$ = 3.7 Hz, PC*H$_3$* **B**). **^{31}P{^{1}H} NMR** (283.4 MHz, $CDCl_3$): δ -31.95 (*s*, *P*CH$_3$ **B**), -32.43 (*s*, *P*CH$_3$ **A**). **^{13}C{^{1}H} NMR** (176.0 MHz, $CDCl_3$): δ 141.88 (*d*, $^1J_{P,C}$ = 32.9 Hz, Ph-*C ipso* **A**), 141.79 (*d*, $^1J_{P,C}$ = 31.6 Hz, Ph-*C ipso* **B**), 131.83 (*d*, $^2J_{P,C}$ = 19.1 Hz, Ph-*C*H *ortho* **B**), 131.24 (*d*, $^2J_{P,C}$ = 17.9 Hz, Ph-*C*H *ortho* **A**), 128.56 (*s*, Ph-*C*H *para* **B**), 128.33 (*d*, $^3J_{P,C}$ = 6.7 Hz, Ph-*C*H *meta* **B**), 128.29 (*d*, $^3J_{P,C}$ = 5.9 Hz, Ph-*C*H *meta* **A**), 128.06 (*s*, Ph-*C*H para **A**), 89.29 (*d*, $^3J_{P,C}$ = 2.8 Hz, Cp-*C1* **B**), 89.24 (*d*, $^3J_{P,C}$ = 1.9 Hz, Cp-*C1* **A**),

85.06 (*d*, $^{2}J_{P,C}$ = 15.0 Hz, Cp-*C2* **B**), 84.83 (*d*, $^{2}J_{P,C}$ = 11.0 Hz, Cp-*C2* **A**), 69.54 (*d*, $J_{P,C}$ = 0.5 Hz, Cp'-*C*H*'* **B**), 69.51 (*d*, $J_{P,C}$ = 0.8 Hz, Cp'-*C*H*'* **A**), 68.58 (*d*, $^{3}J_{P,C}$ = 9.2 Hz, Cp-*C*H*3* **B**), 68.41 (*d*, $^{3}J_{P,C}$ = 6.5 Hz, Cp-*C*H*3* **A**), 66.38 (*s*, Cp-*C*H*5* **A**), 66.28 (*s*, Cp-*C*H*5* **B**), 65.40 (*s*, Cp-*C*H*4* **B**), 65.34 (*s*, Cp-*C*H*4* **A**), 56.75 (*s*, *C*HCH$_3$ **A**), 56.63 (*s*, *C*HCH$_3$ **B**), 40.41 (*d*, $J_{P,C}$ = 1.0 Hz, N(*C*H$_3$)$_2$ **A**), 40.24 (*s*, N(*C*H$_3$)$_2$ **B**), 30.55 (*d*, $^{1}J_{P,C}$ = 13.2 Hz, *C*H$_2$ **B**), 30.52 (*d*, $^{1}J_{P,C}$ = 15.0 Hz, *C*H$_2$ **A**), 12.14 (*d*, $^{1}J_{P,C}$ = 15.3 Hz, P*C*H$_3$ **A**), 12.07 (*d*, $^{1}J_{P,C}$ = 15.0 Hz, P*C*H$_3$ **B**), 11.57 (*s*, CH*C*H$_3$ **A**), 10.83 (*s*, CH*C*H$_3$ **B**). **HRMS (EI)**: m/z: calcd for $C_{22}H_{28}NPFe$: 393.3012 ([M]$^+$); found: 393.1300 (56, [M]$^+$), 348.0789 (100, [M-N(CH$_3$)$_2$]$^+$), 224.9915 (100, [M-PPh$_2$CH$_3$N(CH$_3$)$_2$]$^+$).

1-[(*R*)-Diphenylphosphinoethyl]- 2-(R_{Fc})-diphenylphosphinomethylferrocene (53)

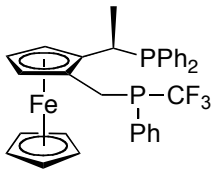


(*R,R*$_{Fc}$)-**48** (720 mg, 1.58 mmol) was dissolved in degassed AcOH (3.0 mL) resulting in an orange-red homogeneous solution. After the addition of diphenylphosphine (358 μL, 2.06 mmol) at rt, the reaction mixture was stirred for 3 h in a preheated oil bath at 110 °C. The resulting dark orange mixture was quenched with Na_2CO_3 (sat., 70 mL) and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (50 mL). The combined organic phases were washed with brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by FC with hexane/EtOAc/NEt$_3$ 20:0.3:0.3 as eluents, affording pure **53** as an orange foamy solid. Yield: 679.2 mg (72%)

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.58 - 7.52 (*m*, 3 H, Ph-*H*), 7.43 - 7.12 (*m*, 14 H, Ph-*H*), 7.07 - 7.01 (*m*, 3 H, Ph-*H*), 4.13 (*s*, 5 H, Cp'-*H'*), 4.05 (*s*, 1 H, Cp-*H5*), 4.00 (*t*, 1 H, *J* = 2.7 Hz, Cp-*H4*), 3.80 (*s*, 1 H, Cp-*H3*), 3.37 (*qd*, 1 H, *J* = 14.0 Hz, $^{2}J_{P,H}$ = 6.9 Hz, C*H*CH$_3$), 2.61 (*d*, 1 H, *J* = 15.4 Hz, C*H*$_2$), 2.11 (*dd*, 1 H, *J* = 15.4 Hz, $^{2}J_{P,H}$ = 4.3 Hz, C*H*$_2$), 1.56 (*dd*, 3 H, *J* = 14.0 Hz, $^{3}J_{P,H}$ = 7.0 Hz, CHC*H*$_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ 5.79 (*d*, $J_{P,P}$ = 4.1 Hz, CHCH$_3$*P*Ph$_2$), -18.21 (*d*, $J_{P,P}$ = 4.1 Hz, CH$_2$*P*Ph$_2$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 140.40 (*d*, $^{1}J_{P,C}$ = 14.8 Hz, Ph-*C ipso*), 139.23 (*d*, $^{1}J_{P,C}$ = 15.5 Hz, Ph-*C ipso*), 137.69 (*d*, $^{1}J_{P,C}$ = 17.7 Hz, Ph-*C ipso*), 135.87 (*d*, $^{1}J_{P,C}$ = 16.9 Hz, Ph-*C ipso*), 134.36 (*d*, $^{2}J_{P,C}$ = 20.0 Hz, Ph-*C*H *ortho*), 133.31 (*d*, $^{2}J_{P,C}$ = 17.4 Hz, Ph-*C*H *ortho*), 133.08 (*d*, $^{2}J_{P,C}$ = 20.1 Hz, Ph-*C*H *ortho*), 132.55 (*d*, $^{2}J_{P,C}$ = 18.6 Hz, Ph-*C*H *ortho*), 129.11 (*d*, $^{4}J_{P,C}$ = 0.6 Hz, Ph-*C*H *para*), 128.60 (*d*, $^{4}J_{P,C}$ = 0.5 Hz, Ph-*C*H *para*), 128.36 (*d*, $^{3}J_{P,C}$ = 7.0 Hz, Ph-*C*H *meta*), 128.26 (*s*, Ph-*C*H *meta*), 128.19 (*d*, $^{3}J_{P,C}$ = 6.4 Hz, Ph-*C*H *meta*), 127.82 (*d*, $^{3}J_{P,C}$ = 6.1 Hz, Ph-*C*H *meta*), 91.29 (*dd*, $^{2}J_{P,C}$ = 16.8 Hz, $^{3}J_{P,C}$ = 5.8 Hz, Cp-*C1*), 83.90 (*dd*, $^{2}J_{P,C}$ = 13.6 Hz, $^{3}J_{P,C}$ = 1.9 Hz, Cp-*C2*), 69.16 (*d*, $J_{P,C}$ = 2.1 Hz, Cp'-*C*H*'*), 68.32 (*d*, $^{3}J_{P,C}$ = 9.9 Hz, Cp-*C*H*3*), 66.01 (*dd*, $^{3}J_{P,C}$ = 6.2 Hz, $^{4}J_{P,C}$ = 1.5 Hz, Cp-*C*H*5*), 65.61 (*s*, Cp-*C*H*4*), 29.73 (*d*, $^{1}J_{P,C}$ = 14.5 Hz, *C*HCH$_3$), 27.05 (*dd*,

$^1J_{P,C}$ = 13.7 Hz, $J_{P,C}$ = 1.5 Hz, *C*H_2), 19.28 (*d*, $^2J_{P,C}$ = 18.6 Hz, CH*C*H_3). **HRMS (EI)**: m/z: calcd for $C_{37}H_{34}P_2Fe$: 596.1502 ([M]$^+$); found: 596.1478 (7, [M]$^+$), 411.0978 (47), 183.0381 (100).

1-[(*R*)-Diphenylphosphinoethyl]-2-(R_{Fc})-[(R_P/S_P)-trifluoromethylphenylphosphino]-methyl-ferrocene (54)



(*R,*S_{Fc},R_P/S_P)-**49** (78 mg, 0.17 mmol) was dissolved in degassed AcOH (0.7 mL), resulting in an orange-red homogeneous solution. After the addition of diphenylphosphine (39 μL, 0.22 mmol) at rt, the reaction mixture was stirred for 5 h in a preheated oil bath at 90 °C. The resulting dark orange mixture was quenched with Na_2CO_3 (sat., 10 mL) and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (5 mL). The combined organic phases were washed with brine (10 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified by FC with hexane/TBME 10:1 as eluents, affording pure **54** as an orange oil. Yield: 89.5 mg (89%) of the 2 diastereoisomers.

Reaction with enantiomerically pure (*R,*$S_{Fc,}S_P$)-**49** or (*R,*$S_{Fc,}R_P$)-**49**, afforded (*R,*$R_{Fc,}S_P$)-**54** or (*R,*$R_{Fc,}R_P$)-**54**, respectively in better yields (up to 93%).

Separation of the 2 diastereoisomers was performed by crystallization in hot MeOH affording pure (*R,*$R_{Fc,}S_P$)-**54** as an orange oil and pure (*R,*$R_{Fc,}R_P$)-**54** as an orange solid.

Diastereoisomeric ratio from ^{31}P NMR spectroscopy: **A** (*R,*$R_{Fc,}S_P$):**B** (*R,*$R_{Fc,}R_P$)= 0.34 : 0.66.

Diastereoisomer **A**: (*R,*$R_{Fc,}S_P$)-**54**

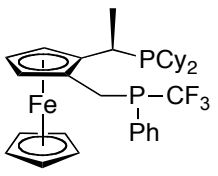
^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.75 - 7.72 (*m*, 2 H, Ph-*H*), 7.60 - 7.51 (*m*, 5 H, Ph-*H*), 7.47 - 7.46 (*m*, 3 H, Ph-*H*), 7.31 - 7.28 (*m*, 1 H, Ph-*H*), 7.23 - 7.19 (*m*, 2 H, Ph-*H*), 7.03 - 7.00 (*m*, 2 H, Ph-*H*), 4.16 - 4.15 (*m*, 2 H, Cp-*H*), 4.11 (*s*, 1 H, Cp-*H*), 4.02 (*s*, 5 H, Cp'-*H'*), 3.22 (*qd*, 1 H, ^3J = 14.1 Hz, $^2J_{P,H}$ = 6.7 Hz, C*H*CH_3), 2.72 (*dd*, 1 H, *J* = 15.9 Hz, $^2J_{P,H}$ = 5.3 Hz*,* C*H*$_2$), 1.95 (*d*, 1 H, *J* = 15.9 Hz, C*H*$_2$), 1.56 (*dd*, 3 H, *J* = 14.1 Hz, $^3J_{P,H}$ = 7.0 Hz*,* CHC*H*$_3$). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -58.23 (*d*, $^2J_{P,F}$ = 64.6 Hz, C*F*$_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ 6.27 (*d*, $J_{P,P}$ = 8.3 Hz, *P*Ph_2), -10.34 (*qd*, $^2J_{F,P}$ = 64.6 Hz, $J_{P,P}$ = 8.3 Hz, *P*$PhCF_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 137.43 (*qd*, $^1J_{P,C}$ = 16.7 Hz, PPh_2-*C ipso*), 135.82 (*qd*, $^1J_{P,C}$ = 16.7 Hz, PPh_2-*C ipso*), 135.06 (*d*, $^2J_{P,C}$ = 22.6 Hz, $PPhCF_3$-*C*H *ortho*), 134.74 (*d*, $^2J_{P,C}$ = 19.9 Hz, PPh_2-*C*H *ortho*), 133.50 (*d*, $^2J_{P,C}$ = 17.1 Hz, PPh_2-*C*H *ortho*), 131.66 (*qd*, $^1J_{F,C}$ = 321.2 Hz, $^1J_{P,C}$ = 34.9 Hz, *C*F_3), 131.65 (*d*, $^4J_{P,C}$ = 1.1 Hz, Ph-*C*H *para*), 130.50 (*qd*, $^1J_{P,C}$ = 13.9 Hz, $^3J_{F,C}$ = 3.4 Hz, $PPhCF_3$-*C ipso*), 129.69 (*s*, Ph-*C*H *para*), 129.25 (*d*, $^3J_{P,C}$ = 8.4 Hz, Ph-*C*H *meta*), 128.95 (*s*, Ph-*C*H *para*), 128.89 (*d*, $^3J_{P,C}$ = 7.1 Hz, Ph-*C*H *meta*), 128.27 (*d*, $^3J_{P,C}$ = 6.1 Hz, Ph-*C*H *meta*), 91.79 (*dd*, $^2J_{P,C}$ = 16.5 Hz, $^3J_{P,C}$ = 6.2 Hz, Cp-*C1*), 82.81 (*dd*, $^2J_{P,C}$ = 17.8 Hz, $^3J_{P,C}$ = 1.8 Hz,

Cp-*C2*), 69.41 (*d*, $J_{P,C}$ = 1.6 Hz, Cp'-*C*H'), 68.28 (*d*, $^3J_{P,C}$ = 12.1 Hz, Cp-*C3*), 66.85 (*dd*, $^3J_{P,C}$ = 6.1 Hz, $^4J_{P,C}$ = 1.8 Hz, Cp-*C5*), 66.60 (*s*, Cp-*C4*), 30.39 (*d*, $^1J_{P,C}$ = 14.8 Hz, *C*HCH$_3$), 21.51 (*qd*, $^1J_{P,C}$ = 11.6 Hz, $^3J_{F,C}$ = 3.2 Hz, *C*H$_2$), 19.67 (*d*, $^2J_{P,C}$ = 18.7 Hz, CH*C*H$_3$). **HRMS (EI)**: m/z: calcd for $C_{32}H_{29}F_3P_2Fe$: 588.3680 ([M]$^+$); found: 588.1043 (11, [M]$^+$), 519.1074 (13, [M-CF$_3$]), 403.0460 (100, [M-PPh$_2$]). **EA**: calcd. for $C_{32}H_{29}F_3P_2Fe$ (588.37): C, 65.32; H, 4.97; found: C, 65.04; H, 5.12.

Diastereoisomer **B**: (*R,R*$_{Fc}$,*R*$_P$)-**54**

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.65 - 7.61 (*m*, 2 H, Ph-*H*), 7.54 - 7.41 (*m*, 8 H, Ph- *H*), 7.30 - 7.25 (*m*, 1 H, Ph-*H*), 7.19 - 7.13 (*m*, 2 H, Ph-*H*), 7.02 - 6.97 (*m*, 2 H, Ph-*H*), 4.18 (*s*, 5 H, Cp'-*H'*), 4.15 (*s*, 1 H, Cp-*H5*), 4.03 - 3.99 (*m*, 1 H, Cp-*H4*), 3.50 (*s*, 1 H, Cp-*H3*), 3.35 (*qd*, 1 H, ^3J = 14.6 Hz, $^2J_{P,H}$ = 6.3 Hz, C*H*CH$_3$), 2.48 (*d*, 1 H, *J* = 15.6 Hz, C*H*$_2$), 1.96 (*dd*, 1 H, *J* = 15.6 Hz, $^2J_{P,H}$ = 6.6 Hz, C*H*$_2$), 1.60 (*dd*, 3 H, *J* = 14.6 Hz, $^3J_{P,H}$ = 6.6 Hz, CHC*H*$_3$). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -59.01 (*d*, $^2J_{P,F}$ = 64.3 Hz, C*F*$_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ 6.45 (*d*, $J_{P,P}$ = 4.4 Hz, *P*Ph$_2$), -11.63 (*qd*, $^2J_{F,P}$ = 64.3 Hz, $J_{P,P}$ = 4.4 Hz, *P*PhCF$_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 137.56 (*qd*, $^1J_{P,C}$ = 17.5 Hz, PPh$_2$-*C ipso*), 135.79 (*qd*, $^1J_{P,C}$ = 16.7 Hz, PPh$_2$-*C ipso*), 134.55 (*d*, $^2J_{P,C}$ = 20.1 Hz, PPh$_2$-*C*H *ortho*), 133.95 (*d*, $^2J_{P,C}$ = 17.6 Hz, PPhCF$_3$-*C*H *ortho*), 131.84 (*qd*, $^1J_{F,C}$ = 321.1 Hz, $^1J_{P,C}$ = 33.1 Hz, *C*F$_3$), 131.38 (*s*, Ph-*C*H *para*), 129.75 (*s*, Ph-*C*H *para*), 129.57 (*qd*, $^1J_{P,C}$ = 15.1 Hz, $^3J_{F,C}$ = 3.4 Hz, PPhCF$_3$-*C ipso*), 129.00 (*d*, $^3J_{P,C}$ = 6.4 Hz, Ph-*C*H *meta*), 128.81 (*s*, Ph-*C*H *para*), 128.24 (*d*, $^3J_{P,C}$ = 6.2 Hz, Ph-*C*H *meta*), 91.92 (*dd*, $^2J_{P,C}$ = 15.5 Hz, $^3J_{P,C}$ = 6.6 Hz, Cp-*C1*), 81.78 (*dd*, $^2J_{P,C}$ = 13.9 Hz, $^3J_{P,C}$ = 1.6 Hz, Cp-*C2*), 69.58 (*d*, $J_{P,C}$ = 2.5 Hz, Cp'-*C*H'), 67.96 (*d*, $^3J_{P,C}$ = 8.0 Hz, Cp-*C3*), 66.55 (*dd*, $^3J_{P,C}$ = 5.7 Hz, $^4J_{P,C}$ = 1.8 Hz, Cp-*C5*), 66.46 (*s*, Cp-*C4*), 30.25 (*d*, $^1J_{P,C}$ = 13.9 Hz, *C*HCH$_3$), 20.00 (*qd*, $^1J_{P,C}$ = 11.2 Hz, $^3J_{F,C}$ = 3.4 Hz, *C*H$_2$), 19.72 (*d*, $^2J_{P,C}$ = 20.3 Hz, CH*C*H$_3$). **HRMS (EI)**: m/z: calcd for $C_{32}H_{29}F_3P_2Fe$: 588.3680 ([M]$^+$); found: 588.1043 (11, [M]$^+$), 519.1074 (13, [M-CF$_3$]), 403.0460 (100, [M-PPh$_2$]). **EA**: calcd. for $C_{32}H_{29}F_3P_2Fe$ (588.37): C, 65.32; H, 4.97; found: C, 65.08; H, 5.24.

1-[(*R*)-Dicyclohexylphosphinoethyl]-2-(*R*$_{Fc}$)-[(*R*$_P$/*S*$_P$)-trifluoromethylphenylphosphino]-methyl-ferrocene (55)

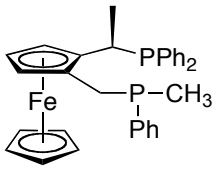


(*R,S*$_{Fc}$,*R*$_P$)-**49** (520 mg, 1.16 mmol) was dissolved in degassed AcOH (5.0 mL), resulting in an orange-red homogeneous solution. After the addition of dicyclohexylphosphine (306 μL, 1.51 mmol) at rt, the reaction mixture was stirred for 5 h in a preheated oil bath at 90 °C. The resulting dark orange mixture was quenched with Na_2CO_3 (sat., 70 mL) and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2 (50 mL).

The combined organic phases were washed with brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was filtered over silica gel in the glovebox with CH_2Cl_2 as eluent, affording pure (*R,R*$_{Fc}$*,R*$_P$)-**55** as an orange oil. Yield: 735 mg (91%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.77 (*t*, 2 H, *J* = 7.6 Hz, Ph-*H ortho*), 7.50 - 7.44 (*m*, 3 H, Ph-*H meta* and Ph-*H para*), 4.13 (*s*, 5 H, Cp'-*H'*), 4.09 (*s*, 1 H, Cp-*H5*), 3.99 - 3.96 (*m*, 1 H, Cp-*H4*), 3.89 (*s*, 1 H, Cp-*H3*), 3.39 (*dd*, 1 H, *J* = 15.4 Hz, $^2J_{P,H}$ = 5.8 Hz, C*H*$_2$), 3.23 (*d*, 1 H, *J* = 15.4 Hz, C*H*$_2$), 2.92 (*q*, 1 H, ^3J = 7.1 Hz, C*H*CH$_3$), 1.74 - 1.64 (*m*, 11 H, Cy-*H*), 1.59 - 1.54 (*m,* 3 H, CHC*H*$_3$), 1.29 - 1.00 (*m*, 11 H, Cy-*H*). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -58.76 (*d*, $^2J_{P,F}$ = 62.0 Hz, C*F*$_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ 9.94 (*d*, $J_{P,P}$ = 37.4 Hz, *P*Cy$_2$), -11.55 (*qd*, $^2J_{F,P}$ = 62.0 Hz, $J_{P,P}$ = 37.4 Hz, *P*PhCF$_3$). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ 134.33 (*d*, $^2J_{P,C}$ = 20.8 Hz, Ph-*C*H *ortho*), 130.64 (*s*, Ph-*C*H *para*), 128.59 (*d*, $^3J_{P,C}$ = 7.6 Hz, Ph-*C*H *meta*), 81.18 (*dd*, $^2J_{P,C}$ = 18.9 Hz, $^3J_{P,C}$ = 2.9 Hz, Cp-*C1*), 69.37 (*d*, $J_{P,C}$ = 1.7 Hz, Cp'-*C*H'), 69.35 (*dd*, $^2J_{P,C}$ = 19.6 Hz, $^3J_{P,C}$ = 2.1 Hz, Cp-*C2*), 68.29 (*d*, $J_{P,C}$ = 7.0 Hz, Cp-*C3*), 66.22 - 66.13 (*m*, Cp-*C5*), 65.23 (*s*, Cp-*C4*), 33.10 - 26.35 (*m*, Cy-*C*H$_2$ and Cy-*C*), 26.28 (*d*, $^1J_{P,C}$ = 1.07 Hz, *C*HCH$_3$), 21.69 - 21.52 (*m*, *C*H$_2$), 15.80 (*d*, $^2J_{P,C}$ = 1.68 Hz, CH*C*H$_3$). **HRMS (EI)**: m/z: calcd for $C_{32}H_{41}F_3P_2Fe$: 600.2030 ([M]$^+$); found: 600.1895 (1, [M]$^+$), 531.2032 (100, [M-CF_3]), 402.9937 (63, [M-PCy_2]), 224.9912 (40, [M-$P_2Cy_2PhCF_3$]).

1-[(*R*)-Diphenylphosphinoethyl]-2-(*R*$_{Fc}$)-[(*R*$_P$/*S*$_P$)-methylphenylphosphino]methyl-ferrocene (56)



(*R,S*$_{Fc}$*,R*$_P$/*S*$_P$)-**50** (440 mg, 1.12 mmol) was dissolved in TFA (0.7 mL) resulting in an orange-red homogeneous solution. After the addition of diphenylphosphine (253 μL, 1.46 mmol) at rt, the reaction mixture was stirred for 5 h in a preheated oil bath at 90 °C. The resulting dark orange mixture was evaporated and gave the crude product, which was purified by FC with hexane/EtOAc/Et_3N 20:0.3:0.3 as eluents, affording pure **56** as an orange oil. Yield: 468 mg (79%) of the two diastereoisomers.

Diastereoisomeric ratio from ^{31}P NMR spectroscopy: **A**:**B** = 0.48 : 0.52.

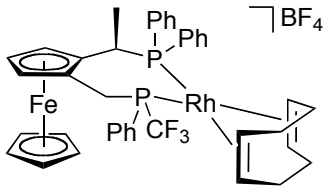
^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.61 - 7.51 (*m*, 3 H, Ph-*H*), 7.45 - 7.36 (*m*, 7H, Ph-*H*), 7.29 - 7.15 (*m*, 3 H, Ph-*H*), 7.12 - 7.06 (*m*, 1 H, Ph-*H*), 7.04 – 6.97 (*m*, 1 H, Ph-*H*), 4.18 (*s*, 2.40 H, Cp'-*H'* **A**), 4.16 - 4.13 (*m*, 0.80 H, Cp-*H*), 4.10 (*t*, 0.70 H, *J* = 2.6 Hz, Cp-*H*), 4.06 (*s*, 2.60 H, Cp'-*H'* **B**), 4.03 - 4.01 (*m*, 1.0 H, Cp-*H*), 3.86 - 3.84 (*m*, 0.50 H, Cp-*H*), 3.41 (*qd*, 0.48 H, *J* = 6.8 Hz, $^2J_{P,H}$ = 4.1 Hz, C*H*CH$_3$ **A**), 3.30 (*qd*, 0.52 H, *J* = 7.0 Hz, $^2J_{P,H}$ = 4.7 Hz, C*H*CH$_3$ **B**), 2.49 (*dd*, 0.48 H, *J* = 15.3 Hz, $^2J_{P,H}$ = 0.9 Hz, C*H*$_2$ **A**), 2.36 (*dd*, 0.52 H, *J* = 15.3 Hz, $^2J_{P,H}$ = 0.8 Hz,

C*H*$_2$ **B**), 2.01 (*d*, 0.52 H, *J* = 2.5 Hz, C*H*$_2$ **B**), 1.95 (*d*, 0.48 H, *J* = 2.5 Hz, C*H*$_2$ **A**), 1.59 (*dd*, 1.44 H, *J* = 6.8 Hz, $^3J_{P,H}$ = 3.5 Hz, CHC*H*$_3$ **A**), 1.53 (*dd*, 1.56 H, *J* = 7.0 Hz, $^3J_{P,H}$ = 4.3 Hz, CHC*H*$_3$ **B**), 1.28 (*d*, 1.56 H, $^2J_{P,H}$ = 4.0 Hz, PC*H*$_3$ **B**), 1.20 (*d*, 1.44 H, $^2J_{P,H}$ = 3.8 Hz, PC*H*$_3$ **A**). **^{31}P{^{1}H} NMR** (101.3 MHz, $CDCl_3$): δ 5.76 (*d*, $J_{P,P}$ = 9.6 Hz, *P*Ph$_2$ **B**), 5.74, (*d*, $J_{P,P}$ = 4.6 Hz, *P*Ph$_2$ **A**), -36.90 (*d*, $J_{P,P}$ = 9.6 Hz, *P*CH$_3$ **B**), -38.33 (*d*, $J_{P,P}$ = 4.6 Hz, *P*CH$_3$ **A**). **HRMS (EI)**: m/z: calcd for $C_{32}H_{32}P_2Fe$: 534.1287 ([M]$^+$); found: 534.1326 (15, [M]$^+$), 349.0823 (100, [M-PPh$_2$]$^+$), 226.0446 (5, [M-PPh$_2$PPhMe]$^+$).

3.3.3 Complexes with P^P Ferrocenyl Ligands

[Rh(cod)(54-κ^2*P,P'*)]BF$_4$ (57)

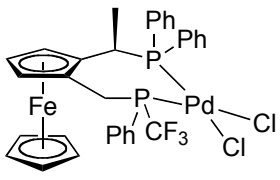
A solution of (*S,S$_{Fc}$,S$_P$*)-**54** (61 mg, 0.10 mmol) and [Rh(cod)$_2$]BF$_4$ (40 mg, 0.09 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 1 h. One third of the solvent was evaporated and hexane was added. The microcrystalline solid was filtered off in the air, washed with cold hexane and dried in vacuo, affording pure **57** as a red microcrystalline that turned out to be air-sensitive. Yield: 64 mg (75%).



^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.04 - 7.98 (*m*, 2 H, Ph-*H*), 7.85 - 7.79 (*m*, 2 H, Ph-*H*), 7.74 - 7.43 (*m*, 11 H, Ph-*H*), 5.15 (*br s*, 2 H, cod-C*H*), 4.65 (*br s*, 2H, cod-C*H*), 4.30 - 4.25 (*m*, 3H, cod-C*H* and Cp-*H*), 4.13 (*s*, 5 H, Cp'-*H'*), 4.09 - 4.04 (*m*, 2 H, cod-C*H*), 3.89 (*s*, 1 H, Cp-*H*), 3.64 - 3.54 (*m*, 1 H, C*H*CH$_3$), 3.27 (*s*, 1 H, Cp-*H*), 2.18 - 1.92 (*m*, 10 H, cod-C*H*$_2$ and 2 C*H*$_2$), 1.39 - 1.33 (dd, 3 H, *J* = 12.7 Hz, $J_{P,H}$ = 6.7 Hz, CHC*H*$_3$). **^{19}F NMR** (188.3 MHz, $CDCl_3$): δ -53.43 (*d*, $^2J_{P,F}$ = 53.0 Hz, C*F*$_3$), -154.04 (*s*, B*F*$_4$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ 32.91 (*qdd*, $^1J_{Rh,P}$ = 161.1 Hz, $^2J_{F,P}$ = 53.0 Hz, $J_{P,P}$ = 36.7 Hz, *P*PhCF$_3$), 24.02 (*dd*, $^1J_{Rh,P}$ = 135.9 Hz, $J_{P,P}$ = 36.7 Hz, *P*Ph$_2$). **MS (HiResMALDI)**: m/z: calcd for $C_{32}H_{29}F_3P_2Fe$: 886.26 ([M$^+$]), 799.10 ([M-BF$_4$]$^+$); found: 799.1048 ([M-BF$_4$]$^+$).

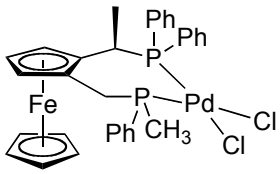
[PdCl$_2$(54-κ^2*P,P'*)] (58)

[Pd(cod)Cl_2] (31 mg, 0.11 mmol) was added in one portion to a solution of (*R,R$_{Fc}$,R$_P$*)-**54** (70 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) and the resulting red mixture was stirred at rt for 2 h. The precipitated complex was filtered off in air, washed with cold hexane and dried in vacuo, affording pure **58** as an orange microcrystalline solid. Yield: 82 mg (94%).



^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 8.08 - 8.03 (*m*, 2 H, $PPhCF_3$-*H ortho*), 7.90 - 7.85 (*m*, 2 H, PPh_2-*H ortho*), 7.73 - 7.69 (*m*, 1 H, $PPhCF_3$-*H para*), 7.67 - 7.57 (*m*, 8 H, 2 $PPhCF_3$-*H meta* and 2 PPh_2-*H meta* and 2 PPh_2-*H ortho* and 2 PPh_2-*H para*), 7.49 - 7.44 (*m*, 2 H, PPh_2-*H meta*), 4.51 (*s*, 1 H, Cp-*H3*), 4.10 (*s*, 5 H, Cp'-*H'*), 4.09 – 4.08 (*m*, 1H, Cp-*H4*), 4.00 (*td*, 1 H, ^{2}J = 15.7 Hz, $^{2}J_{P,H}$ = 2.2 Hz, C*H*$_2$), 3.75 (*qd*, 1 H, ^{3}J = 13.5 Hz, $^{2}J_{P,H}$ = 6.8 Hz, C*H*CH_3), 3.48 (*d*, 1 H, ^{2}J = 15.7 Hz, C*H*$_2$), 3.20 (*s*, 1 H, Cp-*H5*), 1.34 (*dd*, 3 H, ^{3}J = 13.5 Hz, $^{3}J_{P,H}$ = 6.9 Hz, CHC*H*$_3$). **^{19}F NMR** (376.5 MHz, CD_2Cl_2): δ -50.45 (*d*, $^{2}J_{P,F}$ = 66.6 Hz, C*F*$_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, CD_2Cl_2): δ 36.95 (*qd*, $^{2}J_{F,P}$ = 66.6 Hz, $J_{P,P}$ = 2.2 Hz, *P*$PHCF_3$), 32.83 (*d*, $J_{P,P}$ = 2.2 Hz, *P*Ph_2). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 2 PPh_2-*C ipso* + *C1* + *C2 could not be seen*): δ 136.51 (*d*, $^{2}J_{P,C}$ = 10.5 Hz, PPh_2-*C*H *ortho*), 134.33 (*qd*, $^{2}J_{P,C}$ = 12.8 Hz, $^{4}J_{F,C}$ = 1.0 Hz, $PPhCF_3$-*C*H *ortho*), 133.35 (*d*, $^{4}J_{P,C}$ = 3.0 Hz, $PPhCF_3$-*C*H *para*), 132.73 (*d*, $^{2}J_{P,C}$ = 8.5 Hz, PPh_2-*C*H *ortho*), 132.03 (*d*, $^{4}J_{P,C}$ = 2.7 Hz, PPh_2-*C*H *para*), 131.62 (*d*, $^{4}J_{P,C}$ = 3.0 Hz, PPh_2-*C*H *para*), 129.61 (*d*, $^{3}J_{P,C}$ = 11.6 Hz, $PPhCF_3$-*C*H *meta*), 129.23 (*d*, $^{3}J_{P,C}$ = 10.5 Hz, PPh_2-*C*H *meta*), 127.88 (*d*, $^{3}J_{P,C}$ = 11.6 Hz, PPh_2-*C*H *meta*), 125.90 ($^{1}J_{F,C}$ = 68.5 Hz, $PPhCF_3$-*C ipso*), 124.44 ($^{1}J_{F,C}$ = 321.5P Hz, $^{1}J_{P,C}$ = 72.9 Hz, $^{2}J_{F,P}$ = 66.6 Hz, *C*F_3), 70.07 (*s*, Cp'-*C*H'), 69.83 (*s*, Cp-*C3*), 68.15 (*d*, $^{3}J_{P,C}$ = 1.8 Hz, Cp-*C5*), 67.50 (*s*, Cp-*C4*), 33.72 (*ddd*, *J* = 21.5 Hz, *J* = 4.1 Hz, *J* = 0.5 Hz, *C*HCH_3), 29.82 (*d*, $^{1}J_{P,C}$ = 18.3 Hz, *C*H_2), 16.50 (*dd*, *J* = 5.0 Hz, *J* = 0.5 Hz, CH*C*H_3). **MS (HiResMALDI)**: m/z: calcd for $C_{32}H_{29}Cl_2F_3FeP_2Pd$: 765.94 ([M$^+$]); found: 832.02 (22), 788.45 (8, [M+Na]$^+$), 759.27 (100), 729.51 (12, [M-Cl]$^+$), 694.38 (12, [M-Cl_2]$^+$).

[$PdCl_2$(56-κ^2*P,P'*)] (59)



[Pd(cod)Cl_2] (24 mg, 0.08 mmol) was added in one portion to a solution of (*R,R$_{Fc}$,R$_P$/S$_P$*)-**56** (50 mg, 0.09 mmol) in CH_2Cl_2 (2 mL) and the resulting red mixture was stirred at rt for 2 h. After evaporation of the solvent, the orange solid was purified by FC with CH_2Cl_2/MeOH 10:0.1 as eluents, affording pure **59** as an orange solid. Yield: 39 mg (59%) of the two diastereoisomers.

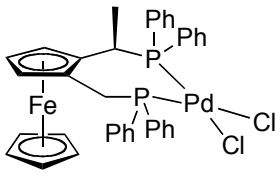
Diastereoisomeric ratio from ^{31}P NMR spectroscopy: **A**:**B** = 0.41 : 0.59.

On a small scale, crystallization from CH_2Cl_2/*n*-hexane afforded crystals of pure [$PdCl_2$(**56**-κ^2*P,P'*)] suitable for X-ray analysis.

^{1}H NMR (CD_2Cl_2, 700.1 MHz): *δ* 8.04 - 7.98 (*m*, 2 H, PPh_2-*H ortho* **B** + PPh_2-*H ortho* **A**), 7.87 - 7.84 (*m*, 1.18 H, $PPhCH_3$-*H ortho* **B**), 7.80 - 7.74 (*m*, 1.64 H, PPh_2-*H ortho* **A +** $PPhCF_3$-*H ortho* **A**), 7.68 - 7.57 (*m*, 6.18 H, PPh_2-*H ortho* **B** + PPh_2-*H meta* **B** + 2 PPh_2-*H para* **B** + $PPhCH_3$-*H para* **B** + PPh_2-*H meta* **A** + 2 PPh_2-*H para* **A** + $PPhCH_3$-*H para* **A**), 7.55 - 7.49 (*m*, 2.82 H, PPh_2-*H meta* **A** + $PPhCH_3$-*H meta* **A** + $PPhCH_3$-*H meta* **B**), 7.47 - 7.45 (*m*, 1.18 H,

PPh_2-*H meta* **B**), 4.34 (*br s*, 0.59 H, *J* = 1.1 Hz, Cp-*H3* **B**), 4.08 (*t*, 0.59 H, *J* = 2.4 Hz, Cp-*H4* **B**), 4.07 (*s*, 2.95 H, Cp'-*H'* **B**), 4.01 (*s*, 2.05 H, Cp'-*H'* **A**), 3.91 - 3.84 (*m*, 1 H, C*H*CH_3 **A** + **B**), 3.77 (*t*, 0.41 H, *J* = 2.5 Hz, Cp-*H4* **A**), 3.54 (*dd*, 0.41 H, *J* = 14.5 Hz, $^2J_{P,H}$ = 4.4 Hz, CH_2 **A**), 3.49 (*dd*, 0.59 H, *J* = 15.0 Hz, $^2J_{P,H}$ = 6.2 Hz, CH_2 **B**), 3.28 (*br s*, 0.41 H, Cp-*H5* **A**), 3.24 (*br s*, 0.59 H, Cp-*H5* **B**), 3.15 (*br s*, 0.41 H, Cp-*H3* **A**), 3.10 (*td*, 0.59 H, *J* = 15.0 Hz, $^2J_{P,H}$ = 2.7 Hz, CH_2 **B**), 3.05 (*td*, 0.41 H, *J* = 14.5 Hz, $^2J_{P,H}$ = 2.9 Hz, CH_2 **A**), 2.26 (*d*, 1.23 H, $^2J_{P,H}$ = 11.2 Hz, PCH_3 **A**), 2.23 (*d*, 1.77 H, $^2J_{P,H}$ = 11.4 Hz, PCH_3 **B**), 1.36 (*dd*, 1.23 H, *J* = 12.9 Hz, $^2J_{P,H}$ = 7.0 Hz, CHCH_3 **A**), 1.34 (*dd*, 1.77 H, *J* = 12.9 Hz, $^2J_{P,H}$ = 6.8 Hz, CHCH_3 **B**). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$, 162.0 MHz): *δ* 33.66 (*d*, $J_{P,P}$ = 2.2 Hz, *P*Ph_2 **A**), 33.52 (*d*, $J_{P,P}$ = 2.5 Hz, *P*Ph_2 **B**), 15.53 (*d*, $J_{P,P}$ = 2.5 Hz, *P*$PhCH_3$ **B**), 13.87 (*d*, $J_{P,P}$ = 2.2 Hz, *P*$PhCH_3$ **A**). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 176.0 MHz, 1 PPh_2-*C ipso* **A** and 1 PPh_2-*C ipso* **B** could not be seen): *δ* 136.28 (*d*, $^2J_{P,C}$ = 10.8 Hz, PPh_2-*C*H *ortho* **A**), 136.01 (*d*, $^2J_{P,C}$ = 10.8 Hz, PPh_2-*C*H *ortho* **B**), 133.21 ($PPhCH_3$-*C ipso* **A**), 133.06 ($PPhCH_3$-*C ipso* **B**), 132.74 (*d*, $^2J_{P,C}$ = 10.8 Hz, $PPhCH_3$-*C*H *ortho* **A**), 132.66 (*d*, $^2J_{P,C}$ = 8.3 Hz, PPh_2-*C*H *ortho* **A**), 132.50 (*d*, $^2J_{P,C}$ = 8.1 Hz, PPh_2-*C*H *ortho* **B**), 131.79 (*d*, $^2J_{P,C}$ = 10.8 Hz, $PPhCH_3$-*C*H *ortho* **B**), 131.43 (*d*, $^4J_{P,C}$ = 2.7 Hz, PPh_2-*C*H *para* **A**), 131.28 (*d*, $^4J_{P,C}$ = 2.7 Hz, PPh_2-*C*H *para* **B**), 131.12 (*d*, $^4J_{P,C}$ = 2.7 Hz, PPh_2-*C*H *para* **B**), 130.96 (*d*, $^4J_{P,C}$ = 2.7 Hz, $PPhCH_3$-*C*H *para* **B**), 130.93 (*d*, $^4J_{P,C}$ = 2.7 Hz, PPh_2-*C*H *para* **A**), 130.77 (*d*, $^4J_{P,C}$ = 2.7 Hz, $PPhCH_3$-*C*H *para* **A**), 128.77 (*d*, $^3J_{P,C}$ = 11.0 Hz, $PPhCH_3$-*C*H *meta* **B**), 128.75 (*d*, $^3J_{P,C}$ = 9.9 Hz, PPh_2-*C*H *meta* **B**), 128.48 (*d*, $^3J_{P,C}$ = 10.2 Hz, PPh_2-*C*H *meta* **A**), 128.12 (*d*, $^3J_{P,C}$ = 11.3 Hz, $PPhCH_3$-*C*H *meta* **A**), 127.47 (*d*, $^3J_{P,C}$ = 11.3 Hz, PPh_2-*C*H *meta* **A**), 127.29 (*d*, $^3J_{P,C}$ = 11.3 Hz, PPh_2-*C*H *meta* **B**), 126.17 (PPh_2-*C ipso* **B**), 126.03 (PPh_2-*C ipso* **A**), 85.15 (Cp-*C1* **B**), 84.74 (Cp-*C1* **A**), 77.76 (Cp-*C2* **B**), 77.56 (Cp-*C2* **A**), 69.54 (*s*, Cp'-*C*H' **B**), 69.39 (*s*, Cp'-*C*H' **A**), 69.15 (*d*, $^4J_{P,C}$ = 1.1 Hz, Cp-*C*H*5* **A**), 68.76 (*d*, $^4J_{P,C}$ = 1.3 Hz, Cp-*C*H*3* **B**), 67.64 (*d*, $^4J_{P,C}$ = 1.6 Hz, Cp-*C*H*5* **B**), 67.18 (*d*, $^4J_{P,C}$ = 2.2 Hz, Cp-*C*H*3* **A**), 66.76 (*s*, Cp-*C*H*4* **B**), 66.01 (*s*, Cp-*C*H*4* **A**), 33.32 (*C*H_2 **B**), 33.17 (*C*H_2 **A**), 32.96 (*C*HCH_3 **A**), 32.57 (*C*HCH_3 **B**), 15.96 (*dd*, *J* = 5.4 Hz, $^3J_{P,C}$ = 0.5 Hz, CH*C*H_3 **A**), 15.92 (*dd*, *J* = 5.6 Hz, $^3J_{P,C}$ = 0.5 Hz, CH*C*H_3 **B**), 14.20 (*d*, $^1J_{P,C}$ = 34.9 Hz, CH*C*H_3 **A**), 13.88 (*d*, $^1J_{P,C}$ = 38.4 Hz, CH*C*H_3 **B**). **MS (HiResMALDI)**: m/z: calculated for $C_{32}H_{32}Cl_2FeP_2Pd$: 675.00 ($[M\text{-}Cl]^+$); found: 675.00 (23, $[M\text{-}Cl]^+$), 705.07 (100).

[$PdCl_2$(53-κ^2*P,P'*)] (60)

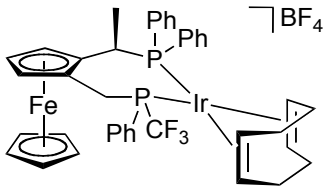


[$PdCl_2$cod] (32 mg, 0.11 mmol) was added in one portion to a solution of (*R,S$_{Fc}$*)-**53** (71 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) and the resulting red mixture was stirred at rt for 2 h. The complex was precipitated, filtered off in air, washed with cold hexane and dried in

vacuo, affording pure **60** as an orange microcrystalline solid. Yield: 76 mg (90%).

^{1}H NMR (700.1 MHz, CD_2Cl_2): δ 8.01 - 7.97 (*m*, 4 H, Ph-*H*), 7.91 - 7.89 (*m*, 2 H, Ph-*H*), 7.76 - 7.74 (*m*, 2 H, Ph-*H*), 7.63 - 7.55 (*m*, 10 H, Ph-*H*), 7.50 - 7.47 (*m*, 2 H, Ph-*H*), 4.02 (*s*, 5 H, Cp'-*H'*), 3.94 - 3.90 (*m*, 1 H, C*H*CH_3), 3.85 (*t*, 1 H, *J* = 2.1 Hz, Cp-*H4*), 3.83 (*dd*, 1H, *J* = 14.2 Hz, *J* = 4.6 Hz, CH_2), 3.52 - 3.47 (*m*, 2 H, Cp-*H3* + CH_2), 3.19 (*s*, 1 H, Cp-*H5*), 1.36 (*dd*, 3 H, ^3J = 12.6 Hz, $^3J_{P,H}$ = 6.8 Hz, CHCH_3). **^{31}P{^{1}H} NMR** (121.5 MHz, CD_2Cl_2): δ 32.47 (*d*, $J_{P,P}$ = 2.4 Hz, $CHCH_3PPh_2$), 20.39 (*d*, $J_{P,P}$ = 2.4 Hz, CH_2PPh_2). **^{13}C{^{1}H} NMR** (176.0 MHz, CD_2Cl_2): δ 136.16 (*d*, $^2J_{P,C}$ = 10.5 Hz, Ph-*C*H *ortho*), 134.49 (*d*, $^2J_{P,C}$ = 10.5 Hz, Ph-*C*H *ortho*), 133.50 (*d*, $^2J_{P,C}$ = 9.9 Hz, Ph-*C*H *ortho*), 132.52 (*d*, $^2J_{P,C}$ = 8.6 Hz, Ph-*C*H *ortho*), 132.07 (*d*, $^1J_{P,C}$ = 59.4 Hz, Ph-*C ipso*), 131.34 (*d*, $^4J_{P,C}$ = 3.0 Hz, Ph-*C*H *para*), 131.18 (*d*, $^4J_{P,C}$ = 3.0 Hz, Ph-*C*H *para*), 131.06 (*d*, $^4J_{P,C}$ = 2.8 Hz, Ph-*C*H *para*), 131.05 (*d*, $^1J_{P,C}$ = 51.3 Hz, Ph-*C ipso*), 130.85 (*d*, $^4J_{P,C}$ = 2.7 Hz, Ph-*C*H *para*), 129.64 (*d*, $^1J_{P,C}$ = 47.6 Hz, Ph-*C ipso*), 128.63 (*d*, $^3J_{P,C}$ = 10.2 Hz, Ph-*C*H *meta*), 128.60 (*d*, $^3J_{P,C}$ = 10.8 Hz, Ph-*C*H *meta*), 128.10 (*d*, $^3J_{P,C}$ = 11.3 Hz, Ph-*C*H *meta*), 127.36 (*d*, $^3J_{P,C}$ = 11.5 Hz, Ph-*C*H *meta*), 126.21 (d, $^1J_{P,C}$ = 56.4 Hz, Ph-*C ipso*), 85.32 (*d*, $^2J_{P,C}$ = 6.7 Hz, Cp-*C1*), 77.55 (*d*, $^2J_{P,C}$ = 5.3 Hz, Cp-*C2*), 69.45 (*s*, Cp'-*C*H'), 69.28 (*s*, Cp-*C3*), 67.32 (*d*, $^3J_{P,C}$ = 1.6 Hz, Cp-*C5*), 66.30 (*s*, Cp-*C4*), 33.18 (*m*, *J* = 68.5 Hz, *J* = 24.0 Hz, *J* = 3.7 Hz, *C*HCH_3 + *C*H_2), 15.98 (*d*, $^2J_{P,C}$ = 5.6 Hz, CH*C*H_3). **MS (HiResMALDI)**: m/z: calcd for $C_{37}H_{34}Cl_2FeP_2Pd$: 773.77 ([M^+]); found: 840.08 (100), 767.22 (61), 737.02 (46, [M-Cl]$^+$), 701.05 (21, [M-Cl_2]$^+$).

[Ir(cod)(54-κ^2*P,P'*)]BF_4 (61)



Silver (I) tetrafluoroborate (17 mg, 0.09 mmol) was added in one portion to a solution of $[Ir_2(cod)_2Cl_2]$ (28 mg, 0.04 mmol) in THF (0.7 mL) and the resulting orange mixture was stirred at rt in a glove-box for 45 min. The mixture was then filtered over celite (filtration of AgCl) yielding an orange solution, which turned black upon addition of (*R,R$_{Fc}$,R$_P$*)-**54** (50 mg, 0.09 mmol). The reaction mixture was stirred overnight. Evaporation of the solvent gave the crude product, which was filtrated over alox with CH_2Cl_2 as eluent, affording pure **61** as a yellow microcrystalline solid. Yield: 97 mg (24%).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.14 - 8.10 (*m*, 2 H, Ph-*H*), 7.85 - 7.80 (*m*, 2 H, Ph-*H*), 7.58 - 7.51 (*m*, 3 H, Ph-*H*), 7.49 - 7.44 (*m*, 2 H, Ph-*H*), 7.42 - 7.35 (*m*, 2 H, Ph-*H*), 7.24 - 7.20 (*m*, 2 H, Ph-*H*), 7.16 - 7.12 (*m*, 2 H, Ph-*H*), 4.76 (*qd*, 1 H, *J* = 7.2 Hz, $^2J_{P,H}$ = 4.0 Hz, C*H*CH_3), 4.35 (*d*, 1H, *J* = 13.7 Hz, CH_2), 4.23 (*s*, 1 H, Cp-*H*), 4.04 (*s*, 5 H, Cp'-*H'*), 3.95 (*t*, 1 H, *J* = 13.7 Hz, CH_2), 3.60 (*t*, 1 H, *J* = 2.5 Hz, Cp-*H*), 3.17 - 3.13 (*m*, 2 H, cod-C*H*), 3.08 - 3.02 (*m*, 2 H, cod-C*H*), 2.88 (*s*, 1 H, Cp-*H*), 2.03 - 1.91 (*m*, 7 H, cod-CH_2), 1.54 (*dd*, 3 H, $^3J_{P,H}$ = 10.1 Hz, *J* = 7.2

Hz, CHC*H*$_3$), 1.23 - 1.15 (*m*, 3 H, cod-C*H*$_2$). **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -53.86 (*d*, $^2J_{P,F}$ = 39.7 Hz, C*F*$_3$), -155.23 (*s*, B*F*$_4$). **^{31}P{^{1}H} NMR** (121.5 MHz, $CDCl_3$): δ -0.51 (*d*, $J_{P,P}$ = 12.4 Hz, *P*Ph$_2$), -4.26 (*qd*, $^2J_{F,P}$ = 39.7 Hz, $J_{P,P}$ = 12.4 Hz, *P*PhCF$_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 138.71 (*d*, $J_{P,C}$ = 10.0 Hz, Ph-*C*), 138.41 (*d*, $J_{P,C}$ = 10.7 Hz, Ph-*C*), 135.55 (*d*, $J_{P,C}$ = 10.3 Hz, Ph-*C*H), 133.16 (*d*, $J_{P,C}$ = 10.7 Hz, Ph-*C*H), 130.66 (*dd*, $J_{P,C}$ = 26.0 Hz, $J_{P,C}$ = 2.1 Hz, Ph-*C*H), 128.61 (*qd*, $J_{P,C}$ = 17.4 Hz, $J_{F,C}$ = 1.6 Hz, Ph-*C*), 128.37 (*d*, $J_{P,C}$ = 9.4 Hz, Ph-*C*H), 128.04 (*s*, Ph-*C*H), 127.96 (*s*, Ph-*C*H), 127.72 (*d*, $J_{P,C}$ = 9.4 Hz, Ph-*C*H), 90.04 (*dd*, $J_{P,C}$ = 8.7 Hz, $J_{P,C}$ = 1.4 Hz, Cp-*C1*), 78.67 (*dd*, $J_{P,C}$ = 8.9 Hz, $J_{P,C}$ = 1.8 Hz, Cp-*C2*), 70.87 (*s*, Cp-*C*H), 69.80 (*s*, 5 Cp'-*C*H'), 67.26 (*d*, $J_{P,C}$ = 1.4 Hz, Cp-*C*H), 66.26 (*s*, Cp-*C*H), 64.77 (*dd*, $J_{P,C}$ = 14.6 Hz, $J_{P,C}$ = 1.6 Hz, cod-*C*H), 64.07 (*dd*, $J_{P,C}$ = 14.2 Hz, $J_{P,C}$ = 0.7 Hz, cod-*C*H), 36.55 (*d*, $J_{P,C}$ = 6.2 Hz, cod-*C*H$_2$), 29.91 (*dd*, $J_{P,C}$ = 4.1 Hz, $J_{P,C}$ = 1.1 Hz, cod-*C*H$_2$), 29.19 (*dd*, $J_{P,C}$ = 14.9 Hz, $J_{P,C}$ = 1.8 Hz, *C*HCH$_3$), 26.00 (*d*, $J_{P,C}$ = 16.2 Hz, *C*H$_2$), 16.24 (*d*, $J_{P,C}$ = 6.2 Hz, CH*C*H$_3$).

3.4 References

[1] J. C. Sauer, *J. Am. Chem. Soc.* **1947**, *69*, 2444.

[2] L. Hintermann, ETH, Ph.D Thesis No. 13892, Zürich, Switzerland, 2000.

[3] G. J. Dozeman, J. F. Timothy, J. C. Walker, *Org. Process. Res. Dev.* **1997**, *1*, 137.

[4] E. E. Royals, D. G. Turpin, *J. Am. Chem. Soc.* **1954**, *76*, 5452.

[5] M. Taniguchi, K. Koga, S. Yamada, *Chem. Pharm. Bull.* **1972**, *20*, 1438.

[6] A. Nudelman, R. Kelner, N. Broida, H. E. Gottlieb, *Synthesis* **1989**, 387.

[7] T. Sheradsky, G. Salemnick, Z. Nir, *Tetrahedron* **1972**, *28*, 3833.

[8] Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, M. Ikeda, *J. Org. Chem.* **1973**, *38*, 1239.

[9] W. Lwowski, T. J. Maricich, *J. Am. Chem. Soc.* **1965**, *87*, 3630.

[10] V. V. Zhdankin, M. McSherry, B. Mismash, J. T. Bolz, J. K. Woodward, R. M. Arbit, S. Erickson, *Tetrahedron Lett.* **1997**, *38*, 21.

[11] P. Kazmierczak, L. Skulski, L. Kraszkiewicz, *Molecules* **2001**, *6*, 881.

[12] D. Drew, J. R. Doyle, *Inorg. Synth.* **1990**, *28*, 346.

[13] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.* **1974**, *15*, 18.

[14] a) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579; b) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754.

[15] S-i. Fukuzawa, D. Tsuchiya, K.Sasamoto, K. Hirano, M. Ohtaguchi, *Eur. J. Org. Chem.* **2000**, 2877.

4. Appendix

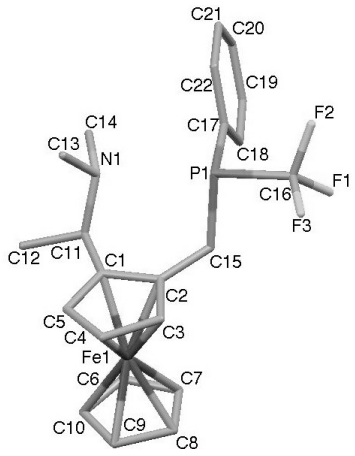
4.1 List of Abbreviations

Ac	**ac**etyl
acac	**ac**etyl**ac**etonate
Ar	**ar**yl
binap	2,2'-**bi**s(diphenylphosphino)-1,1'-bi**na**phthyl
box	**b**is**ox**azoline
cod	1,5-**c**yclo**o**cta**d**iene
conv.	**con**version
cosy	homonuclear **co**rrelation **s**pectroscop**y**
Cp	**c**yclo**p**entadienyl
Cy	**cy**clohexyl
d	**d**ay
DBU	1,8-**d**iaza**b**icyclo[5.4.0]**u**ndec-7-en
DEPT	**d**istortionless **e**nhancement by **p**olarization **t**ransfer
DFT	**d**ensity **f**unctional **t**heory
DMAP	4-**d**i**m**ethyl**a**mino**p**yridine
DMF	**d**i**m**ethyl**f**ormamide
DPH	*O*-(2,4-**d**initro**p**henyl)**h**ydroxylamine
d.r.	**d**iastereomeric **r**atio
EA	**e**lemental **a**nalysis
ee	**e**nantiomeric **e**xcess
ESI	**e**lectro**s**pray **i**onization
Et	**et**hyl
FAAs	**f**luorine-containing **a**mino **a**cids
FC	**f**lash **c**hromatography
F-TEDA	1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane
GC	**g**as **c**hromatography
h	**h**our
HMBC	**h**eteronuclear **m**ultiple **b**ond **c**orrelation experiment
HMQC	**h**eteronuclear **m**ultiple-**q**uantum **c**oherence experiment
HPLC	**h**igh **p**ressure **l**iquid **c**hromatography
INEPT	**i**nsensitive **n**uclei **e**nhanced by **p**olarization **t**ransfer
^{i}Pr	***iso*-pr**opyl

MALDI	**m**atrix-**a**ssisted **l**aser **d**esorption/**i**onization
Me	**me**thyl
MEA imine	*N*-(2-ethyl-6-methylphenyl)-*N*-(1'-**m**ethoxymethyl)-**e**thylidene-**a**mine
min	**min**ute
M.p.	**m**elting **p**oint
MS	**m**ass **s**pectrometry
NFSI	**N**-**f**luorobenzene**s**ulfon**i**mide
NMR	**n**uclear **m**agnetic **r**esonance
NOESY	**n**uclear **O**verhauser **e**ffect **s**pectroscop**y**
Np	**n**a**p**hthyl
n.r.	**n**o **r**eaction
Ph	**ph**enyl
ppm	**p**arts **p**er **m**illion
PTLC	**p**reparative **t**hin **l**ayer **c**hromatography
QM/MM	**q**uantum **m**echanical/**m**olecular **m**echanical
rac	***rac***emic
rt	**r**oom **t**emperature
sat.	**sat**urated
TADDOL	$\alpha,\alpha,\alpha',\alpha'$-**t**etra-**a**ryl-2,2-**d**imethyl-1,3-**d**ioxolane-4,5-dimethan**ol**
t-Bu	***tert*-bu**tyl
TBME	***tert*-b**utyl**m**ethyl**e**ther
TBS	***tert*-b**utyldimethyl**s**ilyl
TFA	**t**ri**f**luoro**a**cetic acid
THF	**t**etra**h**ydro**f**uran
TLC	**t**hin **l**ayer **c**hromatography
TMEDA	*N,N,N',N'*-**t**etra**m**ethyl**e**thylene**d**i**a**mine
Xyl	**xyl**yl

4.2 Crystallographic Data

4.2.1 1-[(*R*)-Dimethylaminoethy]-2-(S_{Fc})-[(R_P)-trifluoromethylphenylphosphino]methyl-ferrocene (49)



Crystal Data and Structure Refinement:

Empirical formula	$C_{22}H_{25}F_3FeNP$
Formula weight	447.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2(1)
Unit cell dimensions	a = 10.3568(6) Å
	alpha = 90°
	b = 12.3974(7) Å
	beta = 96.678(2)°
	c = 15.8685(9)Å
	gamma = 90°
Volume	2023.7(2) $Å^3$
Z, Calculated density	4, 1.468 Mg/m^3
Absorption coefficient	0.858 mm^{-1}
F(000)	928
Crystal size	0.46 x 0.39 x 0.29 mm
Theta range for data collection	2.09 to 28.36°
Limiting indices	-13<=h<=13, -16<=k<=16, -21<=l<=21
Reflections collected / unique	53039 / 5053 [R(int) = 0.0322]
Completeness to theta = 26.37	99.8%
Absorption correction	Empirical
Max. and min. transmission	0.7889 and 0.6946
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5053 / 0 / 256
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0701
R indices (all data)	R1 = 0.0277, wR2 = 0.0709
Largest diff. peak and hole	0.458 and -0.220 $e·Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3):

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Fe(1)	3262(1)	9001(1)	1285(1)	14(1)	C(9)	1664(1)	9672(1)	596(1)	24(1)
P(1)	7492(1)	7534(1)	2122(1)	15(1)	C(10)	1906(1)	10170(1)	1406(1)	26(1)
F(1)	8943(1)	8224(1)	875(1)	29(1)	C(11)	4867(1)	8953(1)	3128(1)	17(1)
F(2)	9566(1)	6722(1)	1470(1)	30(1)	C(12)	3853(1)	9275(1)	3711(1)	27(1)
F(3)	7821(1)	6784(1)	580(1)	33(1)	C(13)	5591(1)	7257(1)	3834(1)	30(1)
N(1)	5973(1)	8308(1)	3532(1)	19(1)	C(14)	6728(1)	8904(1)	4212(1)	31(1)
C(1)	4271(1)	8361(1)	2351(1)	16(1)	C(15)	6311(1)	8499(1)	1550(1)	16(1)
C(2)	4942(1)	8161(1)	1627(1)	15(1)	C(16)	8504(1)	7328(1)	1225(1)	21(1)
C(3)	4093(1)	7562(1)	1023(1)	18(1)	C(17)	8690(1)	8356(1)	2769(1)	17(1)
C(4)	2899(1)	7389(1)	1375(1)	20(1)	C(18)	8857(1)	9467(1)	2693(1)	22(1)
C(5)	3011(1)	7878(1)	2193(1)	19(1)	C(19)	9760(1)	10013(1)	3256(1)	26(1)
C(6)	3176(1)	10628(1)	1483(1)	22(1)	C(20)	10523(1)	9456(1)	3889(1)	26(1)
C(7)	3723(1)	10408(1)	716(1)	19(1)	C(21)	10394(1)	8343(1)	3955(1)	25(1)
C(8)	2788(1)	9814(1)	170(1)	21(1)	C(22)	9472(1)	7803(1)	3404(1)	20(1)

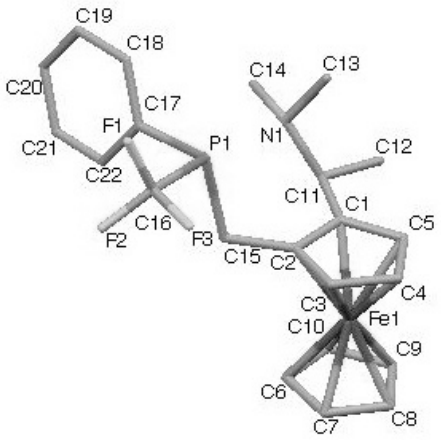
Bond lengths (Å). Calculated distances to hydrogen atoms are omitted:

Bond	Å	Bond	Å	Bond	Å
Fe(1)-C(5)	2.0414(11)	F(1)-C(16)	1.3444(15)	C(6)-C(10)	1.4249(19)
Fe(1)-C(4)	2.0422(12)	F(2)-C(16)	1.3513(14)	C(6)-C(7)	1.4258(17)
Fe(1)-C(10)	2.0425(12)	F(3)-C(16)	1.3540(14)	C(7)-C(8)	1.4272(17)
Fe(1)-C(1)	2.0429(11)	N(1)-C(14)	1.4576(16)	C(8)-C(9)	1.4229(17)
Fe(1)-C(6)	2.0443(12)	N(1)-C(13)	1.4588(17)	C(9)-C(10)	1.423(2)
Fe(1)-C(3)	2.0446(11)	N(1)-C(11)	1.4807(14)	C(11)-C(12)	1.5307(16)
Fe(1)-C(7)	2.0456(11)	C(1)-C(5)	1.4316(15)	C(17)-C(18)	1.3958(17)
Fe(1)-C(8)	2.0464(12)	C(1)-C(2)	1.4324(15)	C(17)-C(22)	1.3968(16)
Fe(1)-C(2)	2.0466(11)	C(1)-C(11)	1.5042(16)	C(18)-C(19)	1.3913(17)
Fe(1)-C(9)	2.0500(12)	C(2)-C(3)	1.4309(15)	C(19)-C(20)	1.3883(19)
P(1)-C(17)	1.8262(12)	C(2)-C(15)	1.4965(15)	C(20)-C(21)	1.391(2)
P(1)-C(15)	1.8678(11)	C(3)-C(4)	1.4309(16)	C(21)-C(22)	1.3896(17)
P(1)-C(16)	1.8809(13)	C(4)-C(5)	1.4246(17)		

Bond angles (°). Angles involving hydrogen atoms are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(5)-Fe(1)-C(4)	40.83(5)	C(8)-Fe(1)-C(2)	126.21(5)	C(4)-C(5)-Fe(1)	69.61(7)
C(5)-Fe(1)-C(10)	105.81(5)	C(5)-Fe(1)-C(9)	119.48(5)	C(1)-C(5)-Fe(1)	69.54(6)
C(4)-Fe(1)-C(10)	123.64(5)	C(4)-Fe(1)-C(9)	106.90(5)	C(10)-C(6)-C(7)	107.78(11)
C(5)-Fe(1)-C(1)	41.04(4)	C(10)-Fe(1)-C(9)	40.68(6)	C(10)-C(6)-Fe(1)	69.53(7)
C(4)-Fe(1)-C(1)	69.05(5)	C(1)-Fe(1)-C(9)	54.54(5)	C(7)-C(6)-Fe(1)	69.65(7)
C(10)-Fe(1)-C(1)	119.27(5)	C(6)-Fe(1)-C(9)	68.61(5)	C(6)-C(7)-C(8)	107.97(11)
C(5)-Fe(1)-C(6)	123.59(5)	C(3)-Fe(1)-C(9)	125.31(5)	C(6)-C(7)-Fe(1)	69.55(7)
C(4)-Fe(1)-C(6)	160.61(5)	C(7)-Fe(1)-C(9)	68.54(5)	C(8)-C(7)-Fe(1)	69.62(6)
C(10)-Fe(1)-C(6)	40.81(5)	C(8)-Fe(1)-C(9)	40.65(5)	C(9)-C(8)-C(7)	108.03(11)
C(1)-Fe(1)-C(6)	106.45(5)	C(2)-Fe(1)-C(9)	162.99(5)	C(9)-C(8)-Fe(1)	69.81(7)
C(5)-Fe(1)-C(3)	68.86(5)	C(17)-P(1)-C(15)	106.26(5)	C(7)-C(8)-Fe(1)	69.56(7)
C(4)-Fe(1)-C(3)	40.99(5)	C(17)-P(1)-C(16)	95.71(5)	C(10)-C(9)-C(8)	107.95(11)
C(10)-Fe(1)-C(3)	161.55(5)	C(15)-P(1)-C(16)	96.34(5)	C(10)-C(9)-Fe(1)	69.38(7)
C(1)-Fe(1)-C(3)	69.05(5)	C(14)-N(1)-C(13)	110.66(11)	C(8)-C(9)-Fe(1)	69.54(7)
C(6)-Fe(1)-C(3)	156.74(5)	C(14)-N(1)-C(11)	111.58(10)	C(9)-C(10)-C(6)	108.27(11)
C(5)-Fe(1)-C(7)	161.46(5)	C(13)-N(1)-C(11)	113.47(10)	C(9)-C(10)-Fe(1)	69.94(7)
C(4)-Fe(1)-C(7)	156.90(5)	C(5)-C(1)-C(2)	107.71(10)	C(6)-C(10)-Fe(1)	69.66(7)
C(10)-Fe(1)-C(7)	68.58(5)	C(5)-C(1)-C(11)	128.83(10)	N(1)-C(11)-C(1)	108.34(9)
C(1)-Fe(1)-C(7)	124.97(5)	C(2)-C(1)-C(11)	123.44(10)	N(1)-C(11)-C(12)	115.44(10)
C(6)-Fe(1)-C(7)	40.81(5)	C(5)-C(1)-Fe(1)	69.43(6)	C(1)-C(11)-C(12)	112.19(10)
C(3)-Fe(1)-C(7)	121.94(5)	C(2)-C(1)-Fe(1)	69.64(6)	C(2)-C(15)-P(1)	110.78(7)
C(5)-Fe(1)-C(8)	155.34(5)	C(11)-C(1)-Fe(1)	127.68(8)	F(1)-C(16)-F(2)	105.99(10)
C(4)-Fe(1)-C(8)	121.01(5)	C(3)-C(2)-C(1)	108.01(10)	F(1)-C(16)-F(3)	105.78(10)
C(10)-Fe(1)-C(8)	68.50(5)	C(3)-C(2)-C(15)	127.24(10)	F(2)-C(16)-F(3)	106.10(10)
C(1)-Fe(1)-C(8)	162.89(5)	C(1)-C(2)-C(15)	124.72(10)	F(1)-C(16)-P(1)	116.42(8)
C(6)-Fe(1)-C(8)	68.69(5)	C(3)-C(2)-Fe(1)	69.45(6)	F(2)-C(16)-P(1)	111.33(8)
C(3)-Fe(1)-C(8)	108.56(5)	C(1)-C(2)-Fe(1)	69.36(6)	F(3)-C(16)-P(1)	110.56(9)
C(7)-Fe(1)-C(8)	40.83(5)	C(15)-C(2)-Fe(1)	128.39(8)	C(18)-C(17)-C(22)	118.65(11)
C(5)-Fe(1)-C(2)	68.90(4)	C(4)-C(3)-C(2)	107.97(10)	C(18)-C(17)-P(1)	125.79(9)
C(4)-Fe(1)-C(2)	68.96(5)	C(4)-C(3)-Fe(1)	69.41(6)	C(22)-C(17)-P(1)	115.55(9)
C(10)-Fe(1)-C(2)	155.36(5)	C(2)-C(3)-Fe(1)	69.60(6)	C(19)-C(18)-C(17)	120.36(11)
C(1)-Fe(1)-C(2)	41.01(4)	C(5)-C(4)-C(3)	108.00(10)	C(20)-C(19)-C(18)	120.44(12)
C(6)-Fe(1)-C(2)	120.79(5)	C(5)-C(4)-Fe(1)	69.56(7)	C(19)-C(20)-C(21)	119.74(11)
C(3)-Fe(1)-C(2)	40.94(4)	C(3)-C(4)-Fe(1)	69.60(6)	C(22)-C(21)-C(20)	119.71(11)
C(7)-Fe(1)-C(2)	108.41(5)	C(4)-C(5)-C(1)	108.31(10)	C(21)-C(22)-C(17)	121.07(12)

4.2.2 1-[(*S*)-Dimethylaminoethy]-2-(R_{Fc})-[(S_P)-trifluoromethylphenylphosphino]methyl-ferrocene (49)



Crystal Data and Structure Refinement:

Empirical formula	$C_{22}H_{25}F_3FeNP$
Formula weight	447.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2(1)
Unit cell dimensions	a = 10.2602(8) Å
	alpha = 90°
	b = 9.9858(8) Å
	beta = 108.207(2)°
	c = 10.7056(8) Å
	gamma = 90°
Volume	1041.94(14) $Å^3$
Z, Calculated density	2, 1.426 Mg/m^3
Absorption coefficient	0.834 mm^{-1}
F(000)	464
Crystal size	0.43 x 0.34 x 0.17 mm
Theta range for data collection	2.00 to 28.28°
Limiting indices	-13<=h<=13, -13<=k<=13, -14<=l<=14
Reflections collected / unique	27424 / 5150 [R(int) = 0.0285]
Completeness to theta = 26.37	100.0%
Absorption correction	Empirical
Max. and min. transmission	0.8692 and 0.7178
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5150 / 1 / 253
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0227, wR2 = 0.0561
R indices (all data)	R1 = 0.0232, wR2 = 0.0563
Largest diff. peak and hole	0.513 and -0.156 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3):

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Fe(1)	1232(1)	2751(1)	1599(1)	14(1)	C(9)	1133(2)	1376(2)	154(1)	26(1)
P(1)	3001(1)	4146(1)	6062(1)	15(1)	C(10)	2479(2)	1412(2)	1073(1)	26(1)
F(1)	3625(1)	6459(1)	7391(1)	30(1)	C(11)	1877(1)	991(1)	4209(1)	17(1)
F(2)	4756(1)	6243(1)	6016(1)	25(1)	C(12)	1062(2)	-307(2)	3796(2)	24(1)
F(3)	2600(1)	6701(1)	5309(1)	27(1)	C(13)	1012(2)	1493(2)	6042(2)	29(1)
N(1)	2228(1)	1340(1)	5626(1)	20(1)	C(14)	3178(2)	371(2)	6455(2)	32(1)
C(1)	1161(1)	2171(1)	3408(1)	15(1)	C(15)	3135(1)	3859(1)	4383(1)	15(1)
C(2)	1751(1)	3474(1)	3477(1)	14(1)	C(16)	3543(1)	5953(1)	6207(1)	19(1)
C(3)	767(1)	4328(1)	2596(1)	16(1)	C(17)	4607(1)	3484(1)	7179(1)	18(1)
C(4)	-432(1)	3561(2)	1989(1)	18(1)	C(18)	4638(2)	3250(2)	8473(2)	28(1)
C(5)	-197(1)	2232(1)	2490(1)	18(1)	C(19)	5799(2)	2695(2)	9381(1)	35(1)
C(6)	2991(1)	2728(2)	1095(1)	25(1)	C(20)	6921(2)	2362(2)	9001(2)	29(1)
C(7)	1970(2)	3513(2)	184(2)	26(1)	C(21)	6903(1)	2585(2)	7718(2)	24(1)
C(8)	824(2)	2679(2)	-397(1)	27(1)	C(22)	5755(1)	3155(1)	6812(1)	19(1)

Bond lengths (Å). Calculated distances to hydrogen atoms are omitted:

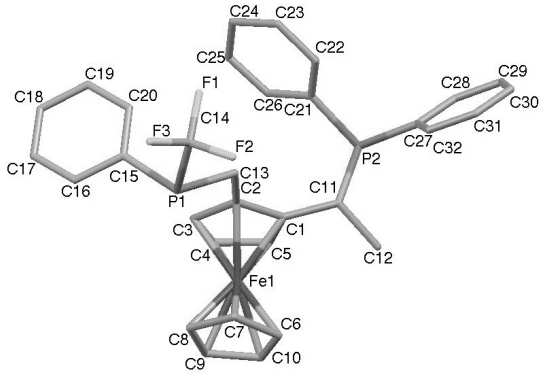
Bond	Å	Bond	Å	Bond	Å
Fe(1)-C(6)	2.0396(13)	F(1)-C(16)	1.3431(16)	C(6)-C(10)	1.413(3)
Fe(1)-C(7)	2.0403(15)	F(2)-C(16)	1.3535(17)	C(6)-C(7)	1.423(2)
Fe(1)-C(3)	2.0407(13)	F(3)-C(16)	1.3553(16)	C(7)-C(8)	1.416(2)
Fe(1)-C(2)	2.0439(13)	N(1)-C(13)	1.458(2)	C(8)-C(9)	1.424(3)
Fe(1)-C(1)	2.0441(13)	N(1)-C(14)	1.4605(19)	C(9)-C(10)	1.424(2)
Fe(1)-C(4)	2.0463(13)	N(1)-C(11)	1.4871(18)	C(11)-C(12)	1.5304(19)
Fe(1)-C(8)	2.0464(13)	C(1)-C(2)	1.4270(18)	C(17)-C(22)	1.393(2)
Fe(1)-C(9)	2.0474(15)	C(1)-C(5)	1.4332(19)	C(17)-C(18)	1.3948(19)
Fe(1)-C(10)	2.0482(15)	C(1)-C(11)	1.5072(18)	C(18)-C(19)	1.395(2)
Fe(1)-C(5)	2.0494(14)	C(2)-C(3)	1.4286(17)	C(19)-C(20)	1.377(2)
P(1)-C(17)	1.8312(14)	C(2)-C(15)	1.4986(18)	C(20)-C(21)	1.385(2)
P(1)-C(15)	1.8673(13)	C(3)-C(4)	1.4223(19)	C(21)-C(22)	1.3915(19)
P(1)-C(16)	1.8805(15)	C(4)-C(5)	1.423(2)		

Bond angles (°). Angles involving hydrogen atoms are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(6)-Fe(1)-C(7)	40.82(6)	C(9)-Fe(1)-C(10)	40.68(6)	C(4)-C(5)-Fe(1)	69.55(8)
C(6)-Fe(1)-C(3)	121.21(7)	C(6)-Fe(1)-C(5)	160.23(6)	C(1)-C(5)-Fe(1)	69.31(8)
C(7)-Fe(1)-C(3)	107.60(6)	C(7)-Fe(1)-C(5)	157.69(6)	C(10)-C(6)-C(7)	108.10(13)
C(6)-Fe(1)-C(2)	106.51(5)	C(3)-Fe(1)-C(5)	68.51(6)	C(10)-C(6)-Fe(1)	70.11(8)
C(7)-Fe(1)-C(2)	123.74(6)	C(2)-Fe(1)-C(5)	68.65(5)	C(7)-C(6)-Fe(1)	69.62(8)
C(3)-Fe(1)-C(2)	40.94(5)	C(1)-Fe(1)-C(5)	40.99(5)	C(8)-C(7)-C(6)	108.05(15)
C(6)-Fe(1)-C(1)	122.94(6)	C(4)-Fe(1)-C(5)	40.67(6)	C(8)-C(7)-Fe(1)	69.96(8)
C(7)-Fe(1)-C(1)	160.07(6)	C(8)-Fe(1)-C(5)	122.33(6)	C(6)-C(7)-Fe(1)	69.56(8)
C(3)-Fe(1)-C(1)	68.89(5)	C(9)-Fe(1)-C(5)	107.96(6)	C(7)-C(8)-C(9)	107.98(13)
C(2)-Fe(1)-C(1)	40.86(5)	C(10)-Fe(1)-C(5)	124.19(6)	C(7)-C(8)-Fe(1)	69.50(8)
C(6)-Fe(1)-C(4)	157.27(7)	C(17)-P(1)-C(15)	104.55(6)	C(9)-C(8)-Fe(1)	69.69(8)
C(7)-Fe(1)-C(4)	122.07(6)	C(17)-P(1)-C(16)	96.31(6)	C(10)-C(9)-C(8)	107.79(14)
C(3)-Fe(1)-C(4)	40.73(5)	C(15)-P(1)-C(16)	96.77(6)	C(10)-C(9)-Fe(1)	69.69(8)
C(2)-Fe(1)-C(4)	68.74(5)	C(13)-N(1)-C(14)	110.87(13)	C(8)-C(9)-Fe(1)	69.61(9)
C(1)-Fe(1)-C(4)	68.90(5)	C(13)-N(1)-C(11)	112.24(12)	C(6)-C(10)-C(9)	108.09(14)
C(6)-Fe(1)-C(8)	68.42(6)	C(14)-N(1)-C(11)	111.53(12)	C(6)-C(10)-Fe(1)	69.45(8)
C(7)-Fe(1)-C(8)	40.54(7)	C(2)-C(1)-C(5)	107.60(11)	C(9)-C(10)-Fe(1)	69.63(8)
C(3)-Fe(1)-C(8)	124.64(7)	C(2)-C(1)-C(11)	124.08(11)	N(1)-C(11)-C(1)	108.46(11)
C(2)-Fe(1)-C(8)	160.90(7)	C(5)-C(1)-C(11)	128.30(12)	N(1)-C(11)-C(12)	115.47(12)
C(1)-Fe(1)-C(8)	157.39(7)	C(2)-C(1)-Fe(1)	69.56(7)	C(1)-C(11)-C(12)	111.88(11)
C(4)-Fe(1)-C(8)	108.40(6)	C(5)-C(1)-Fe(1)	69.70(8)	C(2)-C(15)-P(1)	108.78(9)
C(6)-Fe(1)-C(9)	68.36(7)	C(11)-C(1)-Fe(1)	127.27(10)	F(1)-C(16)-F(2)	105.82(11)
C(7)-Fe(1)-C(9)	68.38(7)	C(1)-C(2)-C(3)	108.01(11)	F(1)-C(16)-F(3)	106.39(11)
C(3)-Fe(1)-C(9)	161.52(6)	C(1)-C(2)-C(15)	124.61(11)	F(2)-C(16)-F(3)	105.18(11)
C(2)-Fe(1)-C(9)	156.37(6)	C(3)-C(2)-C(15)	127.30(12)	F(1)-C(16)-P(1)	111.62(10)
C(1)-Fe(1)-C(9)	121.16(6)	C(1)-C(2)-Fe(1)	69.58(8)	F(2)-C(16)-P(1)	117.06(10)
C(4)-Fe(1)-C(9)	124.88(6)	C(3)-C(2)-Fe(1)	69.41(7)	F(3)-C(16)-P(1)	110.06(9)
C(8)-Fe(1)-C(9)	40.70(8)	C(15)-C(2)-Fe(1)	129.06(9)	C(22)-C(17)-C(18)	118.81(13)
C(6)-Fe(1)-C(10)	40.44(8)	C(4)-C(3)-C(2)	108.19(12)	C(22)-C(17)-P(1)	124.66(10)
C(7)-Fe(1)-C(10)	68.31(6)	C(4)-C(3)-Fe(1)	69.85(8)	C(18)-C(17)-P(1)	116.48(11)
C(3)-Fe(1)-C(10)	156.35(6)	C(2)-C(3)-Fe(1)	69.65(7)	C(17)-C(18)-C(19)	120.53(14)
C(2)-Fe(1)-C(10)	120.52(6)	C(3)-C(4)-C(5)	108.00(11)	C(20)-C(19)-C(18)	120.02(14)
C(1)-Fe(1)-C(10)	106.59(6)	C(3)-C(4)-Fe(1)	69.42(7)	C(19)-C(20)-C(21)	120.03(14)
C(4)-Fe(1)-C(10)	161.25(6)	C(5)-C(4)-Fe(1)	69.78(8)	C(20)-C(21)-C(22)	120.21(14)
C(8)-Fe(1)-C(10)	68.36(6)	C(4)-C(5)-C(1)	108.20(12)	C(21)-C(22)-C(17)	120.38(13)

4.2.3 1-[(*R*)-Diphenylphosphinoethyl]-2-(R_{Fc})-[(R_P)-trifluoromethylphenylphosphino]-methyl-ferrocene (54)

Crystal Data and Structure Refinement:



Empirical formula	$C_{32}H_{29}F_3FeP_2$
Formula weight	588.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2
Unit cell dimensions	a = 18.476(4) Å
	alpha = 90°
	b = 8.0691(16) Å
	beta = 93.595(3)°
	c = 19.428(4) Å
	gamma = 90°
Volume	2890.6(10) $Å^3$
Z, Calculated density	4, 1.352 Mg/m^3
Absorption coefficient	0.671 mm^{-1}
F(000)	1216
Crystal size	0.35 x 0.33 x 0.29 mm
Theta range for data collection	2.10 to 26.37°
Limiting indices	-23<=h<=23, -10<=k<=10, -24<=l<=24
Reflections collected / unique	9472 / 5085 [R(int) = 0.0580
Completeness to theta = 26.37	86.0%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5085 / 1 / 343
Goodness-of-fit on F^2	0.894
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.0913
R indices (all data)	R1 = 0.0770, wR2 = 0.0987
Largest diff. peak and hole	0.486 and -0.256 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3):

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Fe(1)	6461(1)	10345(1)	8709(1)	36(1)	C(14)	3602(2)	9976(6)	7813(3)	44(1)
P(1)	4420(1)	9673(1)	8414(1)	32(1)	C(15)	4227(2)	7553(5)	8684(2)	31(1)
P(2)	6741(1)	8629(2)	6386(1)	48(1)	C(16)	4135(3)	7262(6)	9380(3)	43(1)
F(1)	3481(2)	8860(4)	7308(2)	58(1)	C(17)	4006(3)	5681(7)	9614(3)	58(2)
F(2)	3644(2)	11452(4)	7479(2)	57(1)	C(18)	3988(3)	4382(7)	9167(3)	59(2)
F(3)	2996(1)	10054(5)	8163(2)	72(1)	C(19)	4080(3)	4648(7)	8480(3)	55(2)
C(1)	6487(2)	9435(6)	7717(2)	34(1)	C(20)	4210(3)	6209(6)	8244(3)	45(1)
C(2)	5824(2)	8968(6)	8025(2)	32(1)	C(21)	5947(3)	7271(7)	6404(3)	53(2)
C(3)	6022(3)	8044(6)	8631(3)	38(1)	C(22)	5315(4)	7418(8)	6011(3)	69(2)
C(4)	6764(3)	7938(8)	8693(3)	49(1)	C(23)	4758(5)	6309(11)	6061(4)	100(3)
C(5)	7066(3)	8810(7)	8130(2)	45(1)	C(24)	4827(5)	4961(10)	6529(4)	100(3)
C(6)	6586(3)	12903(8)	8719(3)	53(2)	C(25)	5465(5)	4825(9)	6921(4)	92(2)
C(7)	5911(3)	12422(7)	8970(4)	56(2)	C(26)	6026(4)	5915(7)	6853(4)	67(2)
C(8)	6044(3)	11394(7)	9543(3)	54(2)	C(27)	6563(3)	9743(7)	5562(2)	52(1)
C(9)	6803(4)	11202(8)	9661(3)	66(2)	C(28)	6938(4)	9194(8)	5013(3)	73(2)
C(10)	7124(3)	12176(7)	9137(3)	60(2)	C(29)	6864(4)	9987(11)	4378(3)	98(3)
C(11)	6541(2)	10291(8)	7031(2)	40(1)	C(30)	6406(4)	11306(10)	4292(3)	85(2)
C(12)	7158(3)	11543(8)	7027(3)	64(2)	C(31)	6043(4)	11851(10)	4817(4)	84(2)
C(13)	5069(2)	9394(6)	7735(2)	32(1)	C(32)	6109(4)	11062(9)	5447(3)	76(2)

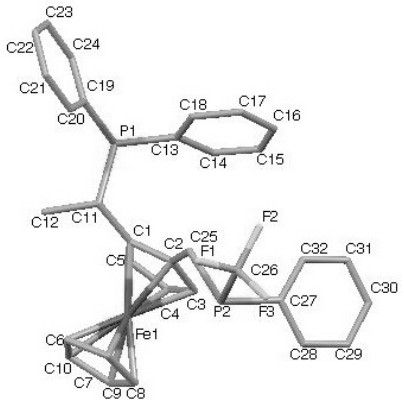
Bond lengths (Å). Calculated distances to hydrogen atoms are omitted:

Bond	Å	Bond	Å	Bond	Å
Fe(1)-C(8)	2.022(5)	F(2)-C(14)	1.361(6)	C(16)-C(17)	1.380(7)
Fe(1)-C(4)	2.022(6)	F(3)-C(14)	1.347(5)	C(17)-C(18)	1.359(8)
Fe(1)-C(3)	2.028(5)	C(1)-C(5)	1.391(6)	C(18)-C(19)	1.373(8)
Fe(1)-C(9)	2.037(5)	C(1)-C(2)	1.447(6)	C(19)-C(20)	1.366(7)
Fe(1)-C(7)	2.040(6)	C(1)-C(11)	1.510(6)	C(21)-C(22)	1.361(8)
Fe(1)-C(2)	2.047(4)	C(2)-C(3)	1.421(6)	C(21)-C(26)	1.401(8)
Fe(1)-C(5)	2.052(5)	C(2)-C(13)	1.510(6)	C(22)-C(23)	1.371(9)
Fe(1)-C(10)	2.061(5)	C(3)-C(4)	1.371(7)	C(23)-C(24)	1.418(11)
Fe(1)-C(1)	2.065(4)	C(4)-C(5)	1.442(7)	C(24)-C(25)	1.367(11)
Fe(1)-C(6)	2.077(6)	C(6)-C(10)	1.374(8)	C(25)-C(26)	1.371(9)
P(1)-C(15)	1.830(4)	C(6)-C(7)	1.421(8)	C(27)-C(32)	1.366(7)
P(1)-C(13)	1.852(4)	C(7)-C(8)	1.397(8)	C(27)-C(28)	1.381(7)
P(1)-C(14)	1.866(5)	C(8)-C(9)	1.415(9)	C(28)-C(29)	1.390(8)
P(2)-C(21)	1.833(6)	C(9)-C(10)	1.443(8)	C(29)-C(30)	1.364(10)
P(2)-C(27)	1.846(5)	C(11)-C(12)	1.524(7)	C(30)-C(31)	1.331(10)
P(2)-C(11)	1.888(6)	C(15)-C(20)	1.380(6)	C(31)-C(32)	1.378(8)
F(1)-C(14)	1.341(6)	C(15)-C(16)	1.392(6)		

Bond angles (°). Angles involving hydrogen atoms are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(8)-Fe(1)-C(4)	122.3(2)	C(2)-Fe(1)-C(6)	127.2(2)	C(8)-C(9)-Fe(1)	69.0(3)
C(8)-Fe(1)-C(3)	105.8(2)	C(5)-Fe(1)-C(6)	122.7(2)	C(10)-C(9)-Fe(1)	70.3(3)
C(4)-Fe(1)-C(3)	39.6(2)	C(10)-Fe(1)-C(6)	38.8(2)	C(6)-C(10)-C(9)	109.6(5)
C(8)-Fe(1)-C(9)	40.8(2)	C(1)-Fe(1)-C(6)	110.7(2)	C(6)-C(10)-Fe(1)	71.2(3)
C(4)-Fe(1)-C(9)	105.6(2)	C(15)-P(1)-C(13)	103.7(2)	C(9)-C(10)-Fe(1)	68.5(3)
C(3)-Fe(1)-C(9)	118.6(2)	C(15)-P(1)-C(14)	97.9(2)	C(1)-C(11)-C(12)	113.5(4)
C(8)-Fe(1)-C(7)	40.2(2)	C(13)-P(1)-C(14)	96.0(2)	C(1)-C(11)-P(2)	106.7(4)
C(4)-Fe(1)-C(7)	159.3(2)	C(21)-P(2)-C(27)	102.0(3)	C(12)-C(11)-P(2)	106.8(3)
C(3)-Fe(1)-C(7)	124.6(2)	C(21)-P(2)-C(11)	102.8(2)	C(2)-C(13)-P(1)	112.7(3)
C(9)-Fe(1)-C(7)	68.1(3)	C(27)-P(2)-C(11)	101.4(2)	F(1)-C(14)-F(3)	107.1(4)
C(8)-Fe(1)-C(2)	121.0(2)	C(5)-C(1)-C(2)	108.0(4)	F(1)-C(14)-F(2)	104.5(4)
C(4)-Fe(1)-C(2)	67.5(2)	C(5)-C(1)-C(11)	125.7(4)	F(3)-C(14)-F(2)	105.9(4)
C(3)-Fe(1)-C(2)	40.82(19)	C(2)-C(1)-C(11)	126.1(4)	F(1)-C(14)-P(1)	117.5(3)
C(9)-Fe(1)-C(2)	155.0(2)	C(5)-C(1)-Fe(1)	69.7(3)	F(3)-C(14)-P(1)	110.9(4)
C(7)-Fe(1)-C(2)	109.4(2)	C(2)-C(1)-Fe(1)	68.7(2)	F(2)-C(14)-P(1)	110.2(3)
C(8)-Fe(1)-C(5)	160.0(2)	C(11)-C(1)-Fe(1)	131.9(3)	C(20)-C(15)-C(16)	117.9(4)
C(4)-Fe(1)-C(5)	41.5(2)	C(3)-C(2)-C(1)	107.4(4)	C(20)-C(15)-P(1)	123.7(4)
C(3)-Fe(1)-C(5)	68.6(2)	C(3)-C(2)-C(13)	127.7(4)	C(16)-C(15)-P(1)	118.3(4)
C(9)-Fe(1)-C(5)	123.6(2)	C(1)-C(2)-C(13)	124.9(4)	C(17)-C(16)-C(15)	120.6(5)
C(7)-Fe(1)-C(5)	158.3(3)	C(3)-C(2)-Fe(1)	68.9(3)	C(18)-C(17)-C(16)	120.0(5)
C(2)-Fe(1)-C(5)	68.13(18)	C(1)-C(2)-Fe(1)	70.1(2)	C(17)-C(18)-C(19)	120.0(5)
C(8)-Fe(1)-C(10)	67.9(2)	C(13)-C(2)-Fe(1)	126.8(3)	C(20)-C(19)-C(18)	120.3(6)
C(4)-Fe(1)-C(10)	122.5(2)	C(4)-C(3)-C(2)	108.0(5)	C(19)-C(20)-C(15)	121.0(5)
C(3)-Fe(1)-C(10)	155.7(2)	C(4)-C(3)-Fe(1)	70.0(3)	C(22)-C(21)-C(26)	118.0(6)
C(9)-Fe(1)-C(10)	41.2(2)	C(2)-C(3)-Fe(1)	70.3(3)	C(22)-C(21)-P(2)	126.7(5)
C(7)-Fe(1)-C(10)	66.6(2)	C(3)-C(4)-C(5)	109.6(5)	C(26)-C(21)-P(2)	115.3(5)
C(2)-Fe(1)-C(10)	162.6(2)	C(3)-C(4)-Fe(1)	70.5(3)	C(21)-C(22)-C(23)	121.7(7)
C(5)-Fe(1)-C(10)	108.8(2)	C(5)-C(4)-Fe(1)	70.4(3)	C(22)-C(23)-C(24)	120.6(8)
C(8)-Fe(1)-C(1)	158.2(2)	C(1)-C(5)-C(4)	107.0(4)	C(25)-C(24)-C(23)	117.3(7)
C(4)-Fe(1)-C(1)	67.7(2)	C(1)-C(5)-Fe(1)	70.8(3)	C(24)-C(25)-C(26)	121.7(8)
C(3)-Fe(1)-C(1)	68.72(18)	C(4)-C(5)-Fe(1)	68.2(3)	C(25)-C(26)-C(21)	120.8(7)
C(9)-Fe(1)-C(1)	160.6(2)	C(10)-C(6)-C(7)	107.4(6)	C(32)-C(27)-C(28)	117.2(5)
C(7)-Fe(1)-C(1)	124.4(2)	C(10)-C(6)-Fe(1)	70.0(3)	C(32)-C(27)-P(2)	126.5(4)
C(2)-Fe(1)-C(1)	41.19(16)	C(7)-C(6)-Fe(1)	68.4(3)	C(28)-C(27)-P(2)	116.3(4)
C(5)-Fe(1)-C(1)	39.50(17)	C(8)-C(7)-C(6)	108.7(5)	C(27)-C(28)-C(29)	120.8(6)
C(10)-Fe(1)-C(1)	125.7(2)	C(8)-C(7)-Fe(1)	69.2(3)	C(30)-C(29)-C(28)	119.6(6)
C(8)-Fe(1)-C(6)	68.0(2)	C(6)-C(7)-Fe(1)	71.2(3)	C(31)-C(30)-C(29)	120.2(6)
C(4)-Fe(1)-C(6)	157.5(2)	C(7)-C(8)-C(9)	108.5(5)	C(30)-C(31)-C(32)	120.5(7)
C(3)-Fe(1)-C(6)	162.7(2)	C(7)-C(8)-Fe(1)	70.6(3)	C(27)-C(32)-C(31)	121.6(6)
C(9)-Fe(1)-C(6)	68.0(2)	C(9)-C(8)-Fe(1)	70.2(3)		
C(7)-Fe(1)-C(6)	40.4(2)	C(8)-C(9)-C(10)	105.8(5)		

4.2.4 1-[(*S*)-Diphenylphosphinoethyl]-2-(S_{Fc})-[(S_P)-trifluoromethylphenylphosphino]-methyl-ferrocene (54)



Crystal Data and Structure Refinement:

Empirical formula	$C_{32}H_{29}F_3FeP_2$
Formula weight	588.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2
Unit cell dimensions	a = 18.6376(12) Å
	alpha = 90°
	b = 8.1112(5) Å
	beta = 93.840(2)°
	c = 19.4332(12) Å
	gamma = 90°
Volume	2931.2(3) $Å^3$
Z, Calculated density	4, 1.333 Mg/m^3
Absorption coefficient	0.662 mm^{-1}
F(000)	1216
Crystal size	0.29 x 0.28 x 0.17 mm
Theta range for data collection	1.05 to 28.31°
Limiting indices	-24<=h<=24, -10<=k<=10, -25<=l<=25
Reflections collected / unique	15385 / 7221 [R(int) = 0.0661]
Completeness to theta = 26.37	100.0%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7221 / 1 / 343
Goodness-of-fit on F^2	0.702
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.0593
R indices (all data)	R1 = 0.1257, wR2 = 0.0732
Largest diff. peak and hole	0.484 and -0.295 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3):

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Fe(1)	1492(1)	1866(1)	3721(1)	62(1)	C(14)	1040(3)	6245(8)	1836(3)	107(2)
P(1)	1759(1)	3507(2)	1390(1)	81(1)	C(15)	486(5)	7320(8)	1883(4)	140(3)
P(2)	-535(1)	2560(1)	3420(1)	56(1)	C(16)	-129(5)	7093(12)	1482(4)	160(4)
F(1)	-1306(1)	786(3)	2488(1)	94(1)	C(17)	-210(4)	5803(11)	1044(3)	154(3)
F(2)	-1481(1)	3341(3)	2322(1)	92(1)	C(18)	349(4)	4686(7)	1010(3)	115(2)
F(3)	-1944(1)	2155(4)	3162(1)	114(1)	C(19)	1578(2)	2397(7)	582(2)	82(2)
C(1)	1504(2)	2741(5)	2732(2)	53(1)	C(20)	1146(3)	1083(8)	468(3)	112(2)
C(2)	861(2)	3210(5)	3033(2)	53(1)	C(21)	1054(3)	283(8)	-165(3)	135(2)
C(3)	1057(2)	4137(5)	3623(2)	61(1)	C(22)	1399(4)	834(9)	-700(3)	135(2)
C(4)	1801(3)	4263(5)	3695(2)	72(1)	C(23)	1848(3)	2134(9)	-611(3)	145(3)
C(5)	2086(2)	3377(5)	3151(2)	68(1)	C(24)	1937(3)	2923(7)	33(3)	113(2)
C(6)	1613(4)	-643(6)	3750(3)	85(2)	C(25)	104(2)	2806(4)	2749(2)	53(1)
C(7)	964(3)	-192(7)	3994(3)	89(2)	C(26)	-1342(2)	2227(6)	2824(2)	70(1)
C(8)	1091(4)	819(7)	4551(3)	101(2)	C(27)	-723(2)	4662(5)	3673(2)	50(1)
C(9)	1843(4)	1023(7)	4655(3)	110(2)	C(28)	-836(2)	4959(6)	4359(2)	72(1)
C(10)	2153(3)	113(8)	4153(4)	103(2)	C(29)	-962(2)	6556(8)	4583(3)	90(2)
C(11)	1559(2)	1918(6)	2047(2)	63(1)	C(30)	-974(3)	7810(7)	4135(3)	92(2)
C(12)	2174(2)	639(6)	2050(2)	104(2)	C(31)	-874(2)	7546(7)	3462(3)	90(2)
C(13)	977(3)	4872(6)	1401(3)	82(2)	C(32)	-745(2)	5972(6)	3239(2)	73(1)

Bond lengths (Å). Calculated distances to hydrogen atoms are omitted:

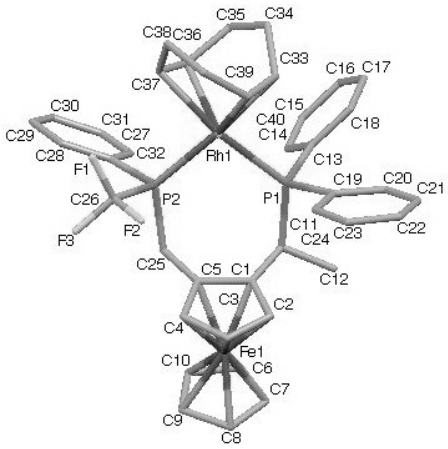
Bond	Å	Bond	Å	Bond	Å
Fe(1)-C(9)	2.008(5)	F(2)-C(26)	1.341(4)	C(14)-C(15)	1.360(7)
Fe(1)-C(8)	2.010(4)	F(3)-C(26)	1.338(4)	C(15)-C(16)	1.356(8)
Fe(1)-C(3)	2.016(4)	C(1)-C(5)	1.409(5)	C(16)-C(17)	1.351(9)
Fe(1)-C(7)	2.026(5)	C(1)-C(2)	1.421(4)	C(17)-C(18)	1.386(7)
Fe(1)-C(10)	2.027(5)	C(1)-C(11)	1.500(5)	C(19)-C(20)	1.346(6)
Fe(1)-C(5)	2.029(4)	C(2)-C(3)	1.399(5)	C(19)-C(24)	1.365(5)
Fe(1)-C(4)	2.029(4)	C(2)-C(25)	1.516(4)	C(20)-C(21)	1.392(6)
Fe(1)-C(2)	2.037(4)	C(3)-C(4)	1.388(5)	C(21)-C(22)	1.336(7)
Fe(1)-C(6)	2.048(5)	C(4)-C(5)	1.412(5)	C(22)-C(23)	1.350(7)
Fe(1)-C(1)	2.051(4)	C(6)-C(7)	1.377(6)	C(23)-C(24)	1.405(6)
P(1)-C(19)	1.820(5)	C(6)-C(10)	1.378(7)	C(27)-C(32)	1.356(5)
P(1)-C(13)	1.831(5)	C(7)-C(8)	1.365(6)	C(27)-C(28)	1.384(5)
P(1)-C(11)	1.869(4)	C(8)-C(9)	1.414(6)	C(28)-C(29)	1.392(6)
P(2)-C(27)	1.815(4)	C(9)-C(10)	1.380(6)	C(29)-C(30)	1.338(6)
P(2)-C(25)	1.834(3)	C(11)-C(12)	1.546(5)	C(30)-C(31)	1.351(6)
P(2)-C(26)	1.856(4)	C(13)-C(18)	1.359(6)	C(31)-C(32)	1.374(5)
F(1)-C(26)	1.343(5)	C(13)-C(14)	1.399(6)		

Bond angles (°). Angles involving hydrogen atoms are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(9)-Fe(1)-C(8)	41.20(18)	C(5)-Fe(1)-C(1)	40.41(13)		
C(9)-Fe(1)-C(3)	120.1(2)	C(4)-Fe(1)-C(1)	67.93(17)	C(10)-C(9)-Fe(1)	70.8(3)
C(8)-Fe(1)-C(3)	107.04(19)	C(2)-Fe(1)-C(1)	40.68(12)	C(8)-C(9)-Fe(1)	69.5(3)
C(9)-Fe(1)-C(7)	67.5(2)	C(6)-Fe(1)-C(1)	111.19(18)	C(6)-C(10)-C(9)	108.4(5)
C(8)-Fe(1)-C(7)	39.52(18)	C(19)-P(1)-C(13)	102.0(2)	C(6)-C(10)-Fe(1)	71.1(3)
C(3)-Fe(1)-C(7)	125.33(19)	C(19)-P(1)-C(11)	102.3(2)	C(9)-C(10)-Fe(1)	69.2(3)
C(9)-Fe(1)-C(10)	40.00(18)	C(13)-P(1)-C(11)	102.34(18)	C(1)-C(11)-C(12)	112.9(3)
C(8)-Fe(1)-C(10)	67.6(2)	C(27)-P(2)-C(25)	103.71(17)	C(1)-C(11)-P(1)	109.1(3)
C(3)-Fe(1)-C(10)	155.4(3)	C(27)-P(2)-C(26)	98.18(19)	C(12)-C(11)-P(1)	106.5(2)
C(7)-Fe(1)-C(10)	66.8(2)	C(25)-P(2)-C(26)	96.33(18)	C(18)-C(13)-C(14)	117.5(5)
C(9)-Fe(1)-C(5)	122.8(2)	C(5)-C(1)-C(2)	107.5(4)	C(18)-C(13)-P(1)	125.6(5)
C(8)-Fe(1)-C(5)	159.8(3)	C(5)-C(1)-C(11)	125.6(3)	C(14)-C(13)-P(1)	116.9(5)
C(3)-Fe(1)-C(5)	68.13(17)	C(2)-C(1)-C(11)	126.4(3)	C(15)-C(14)-C(13)	121.2(6)
C(7)-Fe(1)-C(5)	158.8(2)	C(5)-C(1)-Fe(1)	69.0(2)	C(16)-C(15)-C(14)	119.4(8)
C(10)-Fe(1)-C(5)	108.12(19)	C(2)-C(1)-Fe(1)	69.1(2)	C(17)-C(16)-C(15)	121.5(9)
C(9)-Fe(1)-C(4)	105.8(2)	C(11)-C(1)-Fe(1)	133.2(3)	C(16)-C(17)-C(18)	118.9(8)
C(8)-Fe(1)-C(4)	123.1(2)	C(3)-C(2)-C(1)	107.5(3)	C(13)-C(18)-C(17)	121.5(6)
C(3)-Fe(1)-C(4)	40.14(15)	C(3)-C(2)-C(25)	126.8(4)	C(20)-C(19)-C(24)	115.9(5)
C(7)-Fe(1)-C(4)	159.9(2)	C(1)-C(2)-C(25)	125.7(3)	C(20)-C(19)-P(1)	127.4(4)
C(10)-Fe(1)-C(4)	121.1(2)	C(3)-C(2)-Fe(1)	69.0(2)	C(24)-C(19)-P(1)	116.6(4)
C(5)-Fe(1)-C(4)	40.71(15)	C(1)-C(2)-Fe(1)	70.2(2)	C(19)-C(20)-C(21)	123.5(5)
C(9)-Fe(1)-C(2)	156.2(3)	C(25)-C(2)-Fe(1)	127.2(3)	C(22)-C(21)-C(20)	119.7(6)
C(8)-Fe(1)-C(2)	121.6(2)	C(4)-C(3)-C(2)	109.1(4)	C(21)-C(22)-C(23)	119.2(7)
C(3)-Fe(1)-C(2)	40.38(14)	C(4)-C(3)-Fe(1)	70.4(3)	C(22)-C(23)-C(24)	120.3(6)
C(7)-Fe(1)-C(2)	110.13(18)	C(2)-C(3)-Fe(1)	70.6(2)	C(19)-C(24)-C(23)	121.3(5)
C(10)-Fe(1)-C(2)	162.9(2)	C(3)-C(4)-C(5)	108.1(4)	C(2)-C(25)-P(2)	113.5(2)
C(5)-Fe(1)-C(2)	68.32(15)	C(3)-C(4)-Fe(1)	69.4(2)	F(3)-C(26)-F(2)	105.0(4)
C(4)-Fe(1)-C(2)	67.88(17)	C(5)-C(4)-Fe(1)	69.6(3)	F(3)-C(26)-F(1)	105.7(4)
C(9)-Fe(1)-C(6)	66.9(2)	C(1)-C(5)-C(4)	107.8(4)	F(2)-C(26)-F(1)	104.2(4)
C(8)-Fe(1)-C(6)	66.68(19)	C(1)-C(5)-Fe(1)	70.6(2)	F(3)-C(26)-P(2)	111.8(3)
C(3)-Fe(1)-C(6)	162.4(2)	C(4)-C(5)-Fe(1)	69.7(2)	F(2)-C(26)-P(2)	117.7(3)
C(7)-Fe(1)-C(6)	39.50(17)	C(7)-C(6)-C(10)	108.1(5)	F(1)-C(26)-P(2)	111.4(3)
C(10)-Fe(1)-C(6)	39.53(19)	C(7)-C(6)-Fe(1)	69.4(3)	C(32)-C(27)-C(28)	117.6(4)
C(5)-Fe(1)-C(6)	123.5(2)	C(10)-C(6)-Fe(1)	69.4(3)	C(32)-C(27)-P(2)	124.4(3)
C(4)-Fe(1)-C(6)	157.2(2)	C(8)-C(7)-C(6)	108.9(5)	C(28)-C(27)-P(2)	118.0(3)
C(2)-Fe(1)-C(6)	127.4(2)	C(8)-C(7)-Fe(1)	69.6(3)	C(27)-C(28)-C(29)	120.2(4)
C(9)-Fe(1)-C(1)	160.3(3)	C(6)-C(7)-Fe(1)	71.1(3)	C(30)-C(29)-C(28)	120.0(5)
C(8)-Fe(1)-C(1)	157.8(2)	C(7)-C(8)-C(9)	107.5(5)	C(29)-C(30)-C(31)	120.8(5)
C(3)-Fe(1)-C(1)	67.98(15)	C(7)-C(8)-Fe(1)	70.9(3)	C(30)-C(31)-C(32)	119.4(5)
C(7)-Fe(1)-C(1)	124.5(2)	C(9)-C(8)-Fe(1)	69.3(3)	C(27)-C(32)-C(31)	122.0(5)
C(10)-Fe(1)-C(1)	125.9(2)	C(10)-C(9)-C(8)	107.1(5)		

4.2.5 [Rh(cod)(54-κ²*P,P'*)]BF_4 (57)

Crystal Data and Structure Refinement:



Empirical formula	$C_{41}H_{43}BCl_2F_7FeP_2Rh$
Formula weight	971.16
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.9481(3) Å alpha = 90° b = 18.8617(5) Å beta = 90° c = 21.3985(6) Å gamma = 90°
Volume	4015.2(2) $Å^3$
Z, Calculated density	4, 1.607 Mg/m^3
Absorption coefficient	1.048 mm^{-1}
F(000)	1968
Crystal size	0.345 x 0.33 x 0.168 mm
Theta range for data collection	1.44 to 33.15°
Limiting indices	-15<=h<=15, -28<=k<=27, -32<=l<=32
Reflections collected / unique	143472 / 15301 [R(int) = 0.0863]
Completeness to theta = 26.37	99.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15301 / 0 / 524
Goodness-of-fit on F^2	0.940
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0610
R indices (all data)	R1 = 0.0356, wR2 = 0.0622
Largest diff. peak and hole	1.232 and -0.604 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3). Disordered CH_2Cl_2 molecules are omitted:

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Rh(1)	4960(1)	650(1)	1971(1)	14(1)	C(23)	3593(2)	1647(1)	-173(1)	23(1)
Fe(1)	2021(1)	-1391(1)	440(1)	17(1)	C(24)	3653(2)	1255(1)	375(1)	17(1)
P(1)	2866(1)	763(1)	1515(1)	12(1)	C(25)	3922(2)	-1154(1)	1593(1)	18(1)
P(2)	5135(1)	-549(1)	1969(1)	15(1)	C(26)	6665(2)	-801(1)	1495(1)	21(1)
F(1)	7818(1)	-546(1)	1720(1)	28(1)	C(27)	5426(2)	-966(1)	2722(1)	17(1)
F(2)	6548(1)	-556(1)	910(1)	31(1)	C(28)	6642(2)	-1256(1)	2926(1)	20(1)
F(3)	6820(1)	-1510(1)	1449(1)	28(1)	C(29)	6726(2)	-1533(1)	3530(1)	24(1)
C(1)	2527(2)	-422(1)	794(1)	13(1)	C(30)	5625(2)	-1527(1)	3922(1)	26(1)
C(2)	2425(2)	-388(1)	129(1)	19(1)	C(31)	4422(2)	-1240(1)	3717(1)	28(1)
C(3)	3354(2)	-882(1)	-125(1)	24(1)	C(32)	4327(2)	-952(1)	3122(1)	24(1)
C(4)	4041(2)	-1218(1)	372(1)	22(1)	C(33)	5054(2)	1857(1)	1971(1)	19(1)
C(5)	3529(2)	-943(1)	946(1)	15(1)	C(34)	5337(2)	2124(1)	2626(1)	26(1)
C(6)	329(2)	-1733(1)	896(1)	32(1)	C(35)	5231(2)	1535(1)	3121(1)	26(1)
C(7)	59(3)	-1628(1)	257(1)	40(1)	C(36)	5732(2)	819(1)	2918(1)	22(1)
C(8)	912(3)	-2066(1)	-93(1)	42(1)	C(37)	6867(2)	683(1)	2562(1)	21(1)
C(9)	1727(3)	-2452(1)	329(1)	36(1)	C(38)	7830(2)	1245(1)	2325(1)	22(1)
C(10)	1368(2)	-2241(1)	943(1)	31(1)	C(39)	7471(2)	1503(1)	1669(1)	24(1)
C(11)	1779(2)	6(1)	1266(1)	15(1)	C(40)	5987(2)	1588(1)	1558(1)	20(1)
C(12)	393(2)	254(1)	1043(1)	23(1)	F(4)	1134(1)	9104(1)	3368(1)	33(1)
C(13)	1961(2)	1112(1)	2191(1)	14(1)	F(5A)	-155(3)	8781(1)	2521(1)	47(1)
C(14)	1562(2)	615(1)	2644(1)	17(1)	F(6A)	1768(2)	8194(1)	2710(1)	39(1)
C(15)	969(2)	838(1)	3198(1)	21(1)	F(7A)	9(4)	8061(2)	3369(2)	39(1)
C(16)	769(2)	1555(1)	3310(1)	22(1)	F(6B)	1660(30)	8036(11)	3099(16)	110(11)
C(17)	1158(2)	2051(1)	2864(1)	20(1)	F(5B)	910(30)	8748(9)	2460(6)	87(10)
C(18)	1742(2)	1834(1)	2308(1)	17(1)	F(7B)	-370(30)	8270(19)	3253(17)	101(12)
C(19)	2721(2)	1363(1)	853(1)	14(1)	B(1)	686(2)	8540(1)	2994(1)	25(1)
C(20)	1711(2)	1874(1)	776(1)	20(1)	Cl(1S)	7137(1)	10729(1)	9977(1)	38(1)
C(21)	1687(2)	2277(1)	231(1)	26(1)	Cl(2S)	7095(1)	9393(1)	9272(1)	60(1)
C(22)	2619(2)	2167(1)	-239(1)	28(1)	C(1S)	6330(3)	10214(2)	9418(2)	51(1)

Bond lengths (Å). Calculated distances to hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Bond	Å	Bond	Å	Bond	Å
Rh(1)-C(36)	2.1909(19)	F(3)-C(26)	1.350(2)	C(22)-C(23)	1.385(3)
Rh(1)-C(40)	2.2252(19)	C(1)-C(2)	1.429(3)	C(23)-C(24)	1.389(3)
Rh(1)-P(2)	2.2679(4)	C(1)-C(5)	1.436(3)	C(27)-C(32)	1.387(3)
Rh(1)-C(33)	2.2774(16)	C(1)-C(11)	1.492(2)	C(27)-C(28)	1.397(3)
Rh(1)-C(37)	2.2804(18)	C(2)-C(3)	1.420(3)	C(28)-C(29)	1.397(3)
Rh(1)-P(1)	2.3100(5)	C(3)-C(4)	1.414(3)	C(29)-C(30)	1.380(3)
Fe(1)-C(8)	2.034(2)	C(4)-C(5)	1.428(3)	C(30)-C(31)	1.386(3)
Fe(1)-C(5)	2.0344(19)	C(5)-C(25)	1.493(3)	C(31)-C(32)	1.388(3)
Fe(1)-C(3)	2.036(2)	C(6)-C(7)	1.406(4)	C(33)-C(40)	1.378(3)
Fe(1)-C(9)	2.037(2)	C(6)-C(10)	1.413(3)	C(33)-C(34)	1.515(3)
Fe(1)-C(10)	2.037(2)	C(7)-C(8)	1.402(4)	C(34)-C(35)	1.540(3)
Fe(1)-C(7)	2.039(3)	C(8)-C(9)	1.414(4)	C(35)-C(36)	1.503(3)
Fe(1)-C(4)	2.042(2)	C(9)-C(10)	1.419(4)	C(36)-C(37)	1.386(3)
Fe(1)-C(1)	2.0418(17)	C(11)-C(12)	1.532(3)	C(37)-C(38)	1.516(3)
Fe(1)-C(2)	2.0461(18)	C(13)-C(18)	1.402(3)	C(38)-C(39)	1.529(3)
Fe(1)-C(6)	2.049(2)	C(13)-C(14)	1.407(3)	C(39)-C(40)	1.504(3)
P(1)-C(19)	1.8190(18)	C(14)-C(15)	1.388(3)	F(4)-B(1)	1.404(3)
P(1)-C(13)	1.8257(18)	C(15)-C(16)	1.388(3)	F(5A)-B(1)	1.390(3)
P(1)-C(11)	1.8689(18)	C(16)-C(17)	1.391(3)	F(6A)-B(1)	1.397(3)
P(2)-C(27)	1.8187(19)	C(17)-C(18)	1.385(3)	F(7A)-B(1)	1.383(4)
P(2)-C(25)	1.8460(19)	C(19)-C(24)	1.395(3)	F(6B)-B(1)	1.374(18)
P(2)-C(26)	1.890(2)	C(19)-C(20)	1.402(3)	F(5B)-B(1)	1.228(13)
F(1)-C(26)	1.334(2)	C(20)-C(21)	1.392(3)	F(7B)-B(1)	1.30(3)
F(2)-C(26)	1.339(2)	C(21)-C(22)	1.383(3)		

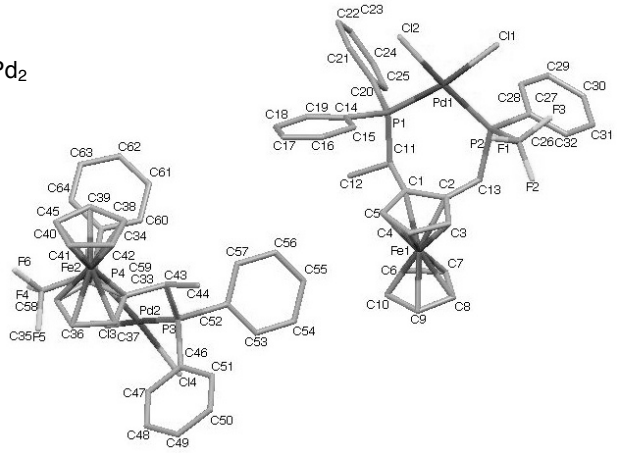
Bond angles (°). Angles involving hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(36)-Rh(1)-C(40)	95.23(7)	C(19)-P(1)-C(13)	110.73(8)	C(24)-C(19)-P(1)	115.31(13)
C(36)-Rh(1)-P(2)	96.89(6)	C(19)-P(1)-C(11)	101.95(8)	C(20)-C(19)-P(1)	125.17(14)
C(40)-Rh(1)-P(2)	139.16(5)	C(13)-P(1)-C(11)	102.48(8)	C(21)-C(20)-C(19)	119.10(19)
C(36)-Rh(1)-C(33)	80.79(7)	C(19)-P(1)-Rh(1)	117.23(6)	C(22)-C(21)-C(20)	121.01(19)
C(40)-Rh(1)-C(33)	35.63(7)	C(13)-P(1)-Rh(1)	98.26(6)	C(21)-C(22)-C(23)	120.08(19)
P(2)-Rh(1)-C(33)	173.25(5)	C(11)-P(1)-Rh(1)	124.86(6)	C(22)-C(23)-C(24)	119.5(2)
C(36)-Rh(1)-C(37)	36.05(8)	C(27)-P(2)-C(25)	102.84(9)	C(23)-C(24)-C(19)	120.86(18)
C(40)-Rh(1)-C(37)	79.47(7)	C(27)-P(2)-C(26)	103.82(9)	C(5)-C(25)-P(2)	114.17(13)
P(2)-Rh(1)-C(37)	87.95(5)	C(25)-P(2)-C(26)	97.89(9)	F(1)-C(26)-F(2)	106.78(15)
C(33)-Rh(1)-C(37)	86.48(7)	C(27)-P(2)-Rh(1)	116.26(6)	F(1)-C(26)-F(3)	106.55(15)
C(36)-Rh(1)-P(1)	133.85(6)	C(25)-P(2)-Rh(1)	124.59(6)	F(2)-C(26)-F(3)	106.52(16)
C(40)-Rh(1)-P(1)	99.98(5)	C(26)-P(2)-Rh(1)	108.28(6)	F(1)-C(26)-P(2)	114.05(14)
P(2)-Rh(1)-P(1)	99.214(16)	C(2)-C(1)-C(5)	107.77(16)	F(2)-C(26)-P(2)	110.18(13)
C(33)-Rh(1)-P(1)	86.86(5)	C(2)-C(1)-C(11)	127.92(17)	F(3)-C(26)-P(2)	112.32(13)
C(37)-Rh(1)-P(1)	168.99(5)	C(5)-C(1)-C(11)	124.29(16)	C(32)-C(27)-C(28)	119.92(18)
C(8)-Fe(1)-C(5)	163.42(11)	C(2)-C(1)-Fe(1)	69.70(10)	C(32)-C(27)-P(2)	114.34(14)
C(8)-Fe(1)-C(3)	108.40(10)	C(5)-C(1)-Fe(1)	69.10(10)	C(28)-C(27)-P(2)	125.67(15)
C(5)-Fe(1)-C(3)	68.81(8)	C(11)-C(1)-Fe(1)	127.76(12)	C(27)-C(28)-C(29)	119.09(19)
C(8)-Fe(1)-C(9)	40.67(11)	C(3)-C(2)-C(1)	107.74(17)	C(30)-C(29)-C(28)	120.83(19)
C(5)-Fe(1)-C(9)	125.25(9)	C(3)-C(2)-Fe(1)	69.26(11)	C(29)-C(30)-C(31)	119.73(19)
C(3)-Fe(1)-C(9)	119.20(10)	C(1)-C(2)-Fe(1)	69.37(10)	C(30)-C(31)-C(32)	120.2(2)
C(8)-Fe(1)-C(10)	68.34(10)	C(4)-C(3)-C(2)	108.80(17)	C(27)-C(32)-C(31)	120.25(19)
C(5)-Fe(1)-C(10)	106.36(9)	C(4)-C(3)-Fe(1)	69.93(11)	C(40)-C(33)-C(34)	126.21(19)
C(3)-Fe(1)-C(10)	153.23(10)	C(2)-C(3)-Fe(1)	70.03(11)	C(40)-C(33)-Rh(1)	70.12(10)
C(9)-Fe(1)-C(10)	40.78(11)	C(3)-C(4)-C(5)	108.07(17)	C(34)-C(33)-Rh(1)	109.91(12)
C(8)-Fe(1)-C(7)	40.27(12)	C(3)-C(4)-Fe(1)	69.49(12)	C(33)-C(34)-C(35)	112.58(16)
C(5)-Fe(1)-C(7)	154.00(10)	C(5)-C(4)-Fe(1)	69.22(11)	C(36)-C(35)-C(34)	115.21(16)
C(3)-Fe(1)-C(7)	127.78(10)	C(4)-C(5)-C(1)	107.62(17)	C(37)-C(36)-C(35)	126.55(19)
C(9)-Fe(1)-C(7)	68.00(10)	C(4)-C(5)-C(25)	127.38(17)	C(37)-C(36)-Rh(1)	75.49(11)
C(10)-Fe(1)-C(7)	67.94(9)	C(1)-C(5)-C(25)	124.99(16)	C(35)-C(36)-Rh(1)	106.41(13)
C(8)-Fe(1)-C(4)	126.40(11)	C(4)-C(5)-Fe(1)	69.77(11)	C(36)-C(37)-C(38)	124.64(19)
C(5)-Fe(1)-C(4)	41.01(8)	C(1)-C(5)-Fe(1)	69.65(10)	C(36)-C(37)-Rh(1)	68.45(11)
C(3)-Fe(1)-C(4)	40.57(9)	C(25)-C(5)-Fe(1)	125.08(13)	C(38)-C(37)-Rh(1)	111.05(12)
C(9)-Fe(1)-C(4)	106.85(9)	C(7)-C(6)-C(10)	107.8(2)	C(37)-C(38)-C(39)	112.43(16)
C(10)-Fe(1)-C(4)	118.52(9)	C(7)-C(6)-Fe(1)	69.53(15)	C(40)-C(39)-C(38)	114.09(17)

C(7)-Fe(1)-C(4)	164.39(10)	C(10)-C(6)-Fe(1)	69.31(13)	C(33)-C(40)-C(39)	126.77(19)
C(8)-Fe(1)-C(1)	154.44(10)	C(8)-C(7)-C(6)	108.7(2)	C(33)-C(40)-Rh(1)	74.25(11)
C(5)-Fe(1)-C(1)	41.25(7)	C(8)-C(7)-Fe(1)	69.66(15)	C(39)-C(40)-Rh(1)	107.65(13)
C(3)-Fe(1)-C(1)	68.71(7)	C(6)-C(7)-Fe(1)	70.24(14)	F(5B)-B(1)-F(7B)	132.5(17)
C(9)-Fe(1)-C(1)	163.46(10)	C(7)-C(8)-C(9)	108.0(2)	F(5B)-B(1)-F(6B)	104.1(17)
C(10)-Fe(1)-C(1)	125.96(9)	C(7)-C(8)-Fe(1)	70.07(14)	F(7B)-B(1)-F(6B)	103.2(18)
C(7)-Fe(1)-C(1)	120.20(9)	C(9)-C(8)-Fe(1)	69.76(13)	F(5B)-B(1)-F(7A)	147.0(9)
C(4)-Fe(1)-C(1)	68.94(7)	C(8)-C(9)-C(10)	107.6(2)	F(7B)-B(1)-F(7A)	25.7(17)
C(8)-Fe(1)-C(2)	120.18(9)	C(8)-C(9)-Fe(1)	69.58(13)	F(6B)-B(1)-F(7A)	78.1(17)
C(5)-Fe(1)-C(2)	69.10(7)	C(10)-C(9)-Fe(1)	69.62(12)	F(5B)-B(1)-F(5A)	48.0(14)
C(3)-Fe(1)-C(2)	40.71(9)	C(6)-C(10)-C(9)	107.9(2)	F(7B)-B(1)-F(5A)	87.2(17)
C(9)-Fe(1)-C(2)	154.01(10)	C(6)-C(10)-Fe(1)	70.22(13)	F(6B)-B(1)-F(5A)	140.3(12)
C(10)-Fe(1)-C(2)	164.27(9)	C(9)-C(10)-Fe(1)	69.60(13)	F(7A)-B(1)-F(5A)	110.1(2)
C(7)-Fe(1)-C(2)	109.13(9)	C(1)-C(11)-C(12)	113.79(15)	F(5B)-B(1)-F(6A)	66.6(13)
C(4)-Fe(1)-C(2)	68.62(8)	C(1)-C(11)-P(1)	108.53(12)	F(7B)-B(1)-F(6A)	129.0(16)
C(1)-Fe(1)-C(2)	40.92(7)	C(12)-C(11)-P(1)	112.06(12)	F(6B)-B(1)-F(6A)	37.5(16)
C(8)-Fe(1)-C(6)	67.94(11)	C(18)-C(13)-C(14)	118.71(17)	F(7A)-B(1)-F(6A)	108.8(3)
C(5)-Fe(1)-C(6)	118.96(9)	C(18)-C(13)-P(1)	124.67(14)	F(5A)-B(1)-F(6A)	107.5(2)
C(3)-Fe(1)-C(6)	165.06(10)	C(14)-C(13)-P(1)	116.41(13)	F(5B)-B(1)-F(4)	103.2(7)
C(9)-Fe(1)-C(6)	68.20(10)	C(15)-C(14)-C(13)	120.38(18)	F(7B)-B(1)-F(4)	108.2(14)
C(10)-Fe(1)-C(6)	40.48(10)	C(16)-C(15)-C(14)	120.30(19)	F(6B)-B(1)-F(4)	102.0(8)
C(7)-Fe(1)-C(6)	40.23(11)	C(15)-C(16)-C(17)	119.76(18)	F(7A)-B(1)-F(4)	108.6(3)
C(4)-Fe(1)-C(6)	153.28(10)	C(18)-C(17)-C(16)	120.47(18)	F(5A)-B(1)-F(4)	111.0(2)
C(1)-Fe(1)-C(6)	107.94(8)	C(17)-C(18)-C(13)	120.38(18)	F(6A)-B(1)-F(4)	110.89(19)
C(2)-Fe(1)-C(6)	127.40(9)	C(24)-C(19)-C(20)	119.37(17)		

4.2.6 [$PdCl_2$(54-κ^2*P,P'*)] (58)

Crystal Data and Structure Refinement:



Empirical formula	$C_{67}H_{62}Cl_{10}F_6Fe_2P_4Pd_2$
Formula weight	1784.05
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 11.4081(6) Å
	alpha = 90°
	b = 13.8454(7) Å
	beta = 102.865(2)°
	c = 22.8429(12) Å
	gamma = 90°
Volume	3517.5(3) $Å^3$
Z, Calculated density	2, 1.684 Mg/m^3
Absorption coefficient	1.435 mm^{-1}
F(000)	1784
Crystal size	0.46 x 0.17 x 0.12 mm
Theta range for data collection	0.91 to 34.35°
Limiting indices	-18<=h<=18, -21<=k<=21, -36<=l<=36
Reflections collected / unique	132944 / 29465 [R(int) = 0.0979]
Completeness to theta = 26.37	100.0%
Absorption correction	Empirical
Max. and min. transmission	0.8466 and 0.5600
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	29465 / 1 / 820
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.0923
R indices (all data)	R1 = 0.0557, wR2 = 0.0969
Largest diff. peak and hole	1.599 and -0.926 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3). Disordered CH_2Cl_2 molecules are omitted:

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Pd(1)	1011(1)	5427(1)	9917(1)	11(1)	Pd(2)	-245(1)	8261(1)	4376(1)	11(1)
Fe(1)	2321(1)	8783(1)	8789(1)	15(1)	Fe(2)	1600(1)	4810(1)	3563(1)	14(1)
Cl(1)	1814(1)	4596(1)	10809(1)	22(1)	Cl(3)	-2059(1)	9111(1)	4081(1)	20(1)
Cl(2)	240(1)	3976(1)	9482(1)	18(1)	Cl(4)	702(1)	9699(1)	4727(1)	18(1)
P(1)	-116(1)	6122(1)	9073(1)	12(1)	P(3)	1572(1)	7570(1)	4782(1)	12(1)
P(2)	2046(1)	6690(1)	10397(1)	13(1)	P(4)	-1339(1)	6974(1)	3973(1)	13(1)
F(1)	3939(2)	5727(2)	10170(1)	33(1)	F(4)	-3238(2)	7664(2)	3131(1)	28(1)
F(2)	4423(2)	7103(2)	10582(1)	29(1)	F(5)	-1501(2)	7801(2)	2907(1)	31(1)
F(3)	4055(2)	5926(2)	11120(1)	31(1)	F(6)	-2399(2)	6428(2)	2844(1)	26(1)
C(1)	1403(3)	7546(2)	8890(1)	14(1)	C(33)	1635(3)	6089(2)	4013(1)	14(1)
C(2)	2346(3)	7720(2)	9405(1)	13(1)	C(34)	480(3)	5925(2)	3627(1)	14(1)
C(3)	3458(3)	7738(2)	9214(2)	18(1)	C(35)	629(3)	5846(2)	3022(2)	17(1)
C(4)	3202(3)	7582(3)	8586(2)	21(1)	C(36)	1875(3)	5956(2)	3036(2)	19(1)
C(5)	1940(3)	7462(2)	8380(1)	18(1)	C(37)	2492(3)	6107(2)	3641(2)	17(1)
C(6)	1131(4)	9901(3)	8624(3)	38(1)	C(38)	1982(3)	3767(2)	4213(2)	22(1)
C(7)	1960(5)	10035(3)	9188(2)	34(1)	C(39)	798(3)	3640(2)	3855(2)	19(1)
C(8)	3112(4)	10080(3)	9075(3)	42(1)	C(40)	895(3)	3498(2)	3248(2)	23(1)
C(9)	3044(5)	9977(3)	8471(3)	49(1)	C(41)	2120(4)	3534(3)	3230(2)	28(1)
C(10)	1839(6)	9867(3)	8186(2)	46(1)	C(42)	2802(3)	3704(2)	3828(2)	27(1)
C(11)	98(3)	7420(2)	8908(1)	14(1)	C(43)	1835(3)	6257(2)	4674(1)	14(1)
C(12)	-781(3)	7759(2)	8339(1)	18(1)	C(44)	3076(3)	5929(2)	5024(2)	17(1)
C(13)	2152(3)	7852(2)	10024(1)	15(1)	C(45)	-641(3)	5818(2)	3856(1)	15(1)
C(14)	0(3)	5548(2)	8371(1)	16(1)	C(46)	2795(3)	8129(2)	4512(1)	14(1)
C(15)	1121(3)	5190(2)	8319(2)	20(1)	C(47)	2548(3)	8511(2)	3932(1)	16(1)
C(16)	1289(4)	4879(3)	7761(2)	26(1)	C(48)	3477(3)	8803(3)	3673(2)	21(1)
C(17)	345(4)	4926(3)	7259(2)	27(1)	C(49)	4672(3)	8706(3)	3987(2)	23(1)
C(18)	-757(4)	5269(2)	7313(2)	26(1)	C(50)	4922(3)	8342(2)	4564(2)	20(1)
C(19)	-952(3)	5572(2)	7863(1)	19(1)	C(51)	3988(3)	8065(2)	4832(1)	15(1)
C(20)	-1675(3)	6042(2)	9139(1)	15(1)	C(52)	1878(3)	7704(2)	5591(1)	14(1)
C(21)	-2348(3)	5209(2)	8960(2)	19(1)	C(53)	2502(3)	8514(2)	5869(1)	16(1)
C(22)	-3536(3)	5153(3)	9019(2)	24(1)	C(54)	2721(3)	8614(3)	6493(2)	21(1)
C(23)	-4068(3)	5929(3)	9249(2)	26(1)	C(55)	2300(3)	7921(3)	6839(2)	23(1)
C(24)	-3393(3)	6750(3)	9429(2)	26(1)	C(56)	1664(3)	7125(2)	6562(2)	20(1)
C(25)	-2199(3)	6809(2)	9379(2)	20(1)	C(57)	1452(3)	7013(2)	5940(1)	16(1)
C(26)	3699(3)	6337(2)	10584(2)	21(1)	C(58)	-2180(3)	7241(2)	3173(2)	18(1)
C(27)	1742(3)	7052(2)	11105(1)	17(1)	C(59)	-2459(3)	6608(2)	4376(1)	15(1)
C(28)	607(3)	6860(2)	11213(2)	21(1)	C(60)	-2192(3)	6780(2)	4992(2)	17(1)
C(29)	282(4)	7239(3)	11717(2)	31(1)	C(61)	-2895(3)	6378(2)	5353(2)	21(1)
C(30)	1092(5)	7804(3)	12113(2)	39(1)	C(62)	-3860(3)	5794(2)	5095(2)	22(1)
C(31)	2216(5)	7982(3)	12016(2)	39(1)	C(63)	-4143(3)	5633(2)	4482(2)	23(1)
C(32)	2566(4)	7614(3)	11514(2)	29(1)	C(64)	-3452(3)	6034(2)	4118(2)	18(1)

Bond lengths (Å). Calculated distances to hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Bond	Å	Bond	Å	Bond	Å
Pd(1)-P(2)	2.2537(8)	C(14)-C(19)	1.402(4)	P(4)-C(58)	1.903(3)
Pd(1)-P(1)	2.2793(8)	C(15)-C(16)	1.398(5)	F(4)-C(58)	1.326(4)
Pd(1)-Cl(2)	2.3253(8)	C(16)-C(17)	1.389(6)	F(5)-C(58)	1.334(4)
Pd(1)-Cl(1)	2.3416(8)	C(17)-C(18)	1.375(6)	F(6)-C(58)	1.345(4)
Fe(1)-C(10)	2.028(4)	C(18)-C(19)	1.388(5)	C(33)-C(37)	1.431(4)
Fe(1)-C(6)	2.038(4)	C(20)-C(25)	1.390(4)	C(33)-C(34)	1.431(4)
Fe(1)-C(3)	2.039(3)	C(20)-C(21)	1.395(4)	C(33)-C(43)	1.496(4)
Fe(1)-C(7)	2.042(4)	C(21)-C(22)	1.394(5)	C(34)-C(35)	1.435(4)
Fe(1)-C(1)	2.047(3)	C(22)-C(23)	1.393(6)	C(34)-C(45)	1.493(4)
Fe(1)-C(4)	2.049(3)	C(23)-C(24)	1.382(6)	C(35)-C(36)	1.423(5)
Fe(1)-C(8)	2.050(4)	C(24)-C(25)	1.395(5)	C(36)-C(37)	1.419(5)
Fe(1)-C(9)	2.052(4)	C(27)-C(28)	1.396(5)	C(38)-C(42)	1.423(6)
Fe(1)-C(5)	2.057(3)	C(27)-C(32)	1.404(5)	C(38)-C(39)	1.425(5)
P(1)-C(20)	1.821(3)	C(28)-C(29)	1.389(5)	C(39)-C(40)	1.429(5)
P(1)-C(14)	1.822(3)	C(29)-C(30)	1.383(7)	C(40)-C(41)	1.408(5)
P(1)-C(11)	1.864(3)	C(30)-C(31)	1.372(8)	C(41)-C(42)	1.432(6)
P(2)-C(27)	1.799(3)	C(31)-C(32)	1.392(6)	C(43)-C(44)	1.532(4)

P(2)-C(13)	1.838(3)	Pd(2)-P(4)	2.2512(8)	C(46)-C(47)	1.394(4)
P(2)-C(26)	1.901(3)	Pd(2)-P(3)	2.2845(8)	C(46)-C(51)	1.398(4)
F(1)-C(26)	1.340(4)	Pd(2)-Cl(4)	2.3208(8)	C(47)-C(48)	1.384(4)
F(2)-C(26)	1.345(4)	Pd(2)-Cl(3)	2.3452(8)	C(48)-C(49)	1.399(5)
F(3)-C(26)	1.329(4)	Fe(2)-C(34)	2.030(3)	C(49)-C(50)	1.379(5)
C(1)-C(2)	1.427(4)	Fe(2)-C(33)	2.043(3)	C(50)-C(51)	1.396(4)
C(1)-C(5)	1.437(4)	Fe(2)-C(39)	2.044(3)	C(52)-C(57)	1.400(4)
C(1)-C(11)	1.508(4)	Fe(2)-C(38)	2.046(3)	C(52)-C(53)	1.403(4)
C(2)-C(3)	1.431(4)	Fe(2)-C(35)	2.050(3)	C(53)-C(54)	1.397(5)
C(2)-C(13)	1.492(4)	Fe(2)-C(40)	2.051(3)	C(54)-C(55)	1.395(5)
C(3)-C(4)	1.416(5)	Fe(2)-C(37)	2.052(3)	C(55)-C(56)	1.391(5)
C(4)-C(5)	1.421(5)	Fe(2)-C(42)	2.055(3)	C(56)-C(57)	1.395(5)
C(6)-C(10)	1.419(7)	Fe(2)-C(36)	2.058(3)	C(59)-C(60)	1.393(5)
C(6)-C(7)	1.430(7)	Fe(2)-C(41)	2.062(3)	C(59)-C(64)	1.402(4)
C(7)-C(8)	1.396(7)	P(3)-C(52)	1.812(3)	C(60)-C(61)	1.389(5)
C(8)-C(9)	1.373(9)	P(3)-C(46)	1.820(3)	C(61)-C(62)	1.386(5)
C(9)-C(10)	1.393(8)	P(3)-C(43)	1.867(3)	C(62)-C(63)	1.383(5)
C(11)-C(12)	1.529(4)	P(4)-C(59)	1.805(3)	C(63)-C(64)	1.385(5)
C(14)-C(15)	1.401(5)	P(4)-C(45)	1.834(3)		

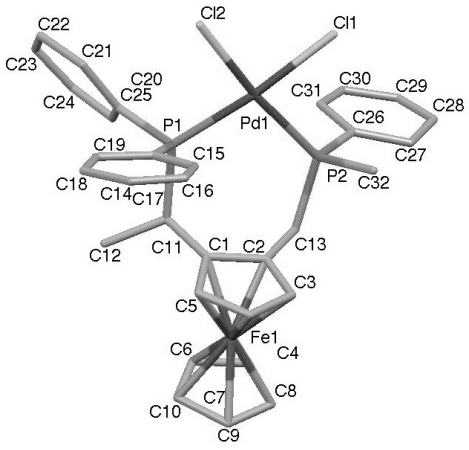
Bond angles (°). Angles involving hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
P(2)-Pd(1)-P(1)	102.69(3)	C(6)-C(7)-Fe(1)	69.3(2)	C(38)-Fe(2)-C(41)	68.34(15)
P(2)-Pd(1)-Cl(2)	170.31(3)	C(9)-C(8)-C(7)	109.7(4)	C(35)-Fe(2)-C(41)	122.54(15)
P(1)-Pd(1)-Cl(2)	85.07(3)	C(9)-C(8)-Fe(1)	70.5(3)	C(40)-Fe(2)-C(41)	40.03(15)
P(2)-Pd(1)-Cl(1)	84.09(3)	C(7)-C(8)-Fe(1)	69.7(2)	C(37)-Fe(2)-C(41)	127.13(14)
P(1)-Pd(1)-Cl(1)	168.95(3)	C(8)-C(9)-C(10)	108.0(4)	C(42)-Fe(2)-C(41)	40.70(17)
Cl(2)-Pd(1)-Cl(1)	89.18(3)	C(8)-C(9)-Fe(1)	70.4(2)	C(36)-Fe(2)-C(41)	110.55(15)
C(10)-Fe(1)-C(2)	165.0(2)	C(10)-C(9)-Fe(1)	69.1(3)	C(52)-P(3)-C(46)	108.36(14)
C(10)-Fe(1)-C(6)	40.9(2)	C(9)-C(10)-C(6)	109.0(4)	C(52)-P(3)-C(43)	103.55(13)
C(2)-Fe(1)-C(6)	125.74(17)	C(9)-C(10)-Fe(1)	71.0(3)	C(46)-P(3)-C(43)	102.22(13)
C(10)-Fe(1)-C(3)	153.6(2)	C(6)-C(10)-Fe(1)	69.9(2)	C(52)-P(3)-Pd(2)	108.81(10)
C(2)-Fe(1)-C(3)	41.16(12)	C(1)-C(11)-C(12)	113.9(2)	C(46)-P(3)-Pd(2)	112.23(10)
C(6)-Fe(1)-C(3)	162.56(18)	C(1)-C(11)-P(1)	107.0(2)	C(43)-P(3)-Pd(2)	120.80(10)
C(10)-Fe(1)-C(7)	67.89(18)	C(12)-C(11)-P(1)	112.2(2)	C(59)-P(4)-C(45)	101.98(14)
C(2)-Fe(1)-C(7)	106.22(14)	C(2)-C(13)-P(2)	111.8(2)	C(59)-P(4)-C(58)	106.35(14)
C(6)-Fe(1)-C(7)	41.0(2)	C(15)-C(14)-C(19)	119.5(3)	C(45)-P(4)-C(58)	99.90(14)
C(3)-Fe(1)-C(7)	124.08(17)	C(15)-C(14)-P(1)	118.4(2)	C(59)-P(4)-Pd(2)	113.92(10)
C(10)-Fe(1)-C(1)	128.8(2)	C(19)-C(14)-P(1)	121.6(2)	C(45)-P(4)-Pd(2)	122.11(10)
C(2)-Fe(1)-C(1)	40.97(12)	C(16)-C(15)-C(14)	120.0(3)	C(58)-P(4)-Pd(2)	110.74(10)
C(6)-Fe(1)-C(1)	108.61(15)	C(17)-C(16)-C(15)	119.9(3)	C(37)-C(33)-C(34)	107.2(3)
C(3)-Fe(1)-C(1)	68.92(12)	C(18)-C(17)-C(16)	120.0(3)	C(37)-C(33)-C(43)	128.8(3)
C(7)-Fe(1)-C(1)	120.05(15)	C(17)-C(18)-C(19)	121.2(3)	C(34)-C(33)-C(43)	124.0(3)
C(10)-Fe(1)-C(4)	121.27(17)	C(18)-C(19)-C(14)	119.4(3)	C(37)-C(33)-Fe(2)	69.89(17)
C(2)-Fe(1)-C(4)	68.72(12)	C(25)-C(20)-C(21)	119.4(3)	C(34)-C(33)-Fe(2)	68.96(16)
C(6)-Fe(1)-C(4)	156.13(18)	C(25)-C(20)-P(1)	120.0(2)	C(43)-C(33)-Fe(2)	128.6(2)
C(3)-Fe(1)-C(4)	40.53(14)	C(21)-C(20)-P(1)	120.7(2)	C(33)-C(34)-C(35)	108.3(3)
C(7)-Fe(1)-C(4)	161.41(18)	C(22)-C(21)-C(20)	120.0(3)	C(33)-C(34)-C(45)	122.9(3)
C(1)-Fe(1)-C(4)	68.63(12)	C(23)-C(22)-C(21)	120.6(3)	C(35)-C(34)-C(45)	128.7(3)
C(10)-Fe(1)-C(8)	66.5(2)	C(24)-C(23)-C(22)	119.1(3)	C(33)-C(34)-Fe(2)	69.91(16)
C(2)-Fe(1)-C(8)	118.46(18)	C(23)-C(24)-C(25)	120.9(3)	C(35)-C(34)-Fe(2)	70.17(17)
C(6)-Fe(1)-C(8)	67.78(17)	C(20)-C(25)-C(24)	120.1(3)	C(45)-C(34)-Fe(2)	123.5(2)
C(3)-Fe(1)-C(8)	106.37(16)	F(3)-C(26)-F(1)	108.2(3)	C(36)-C(35)-C(34)	107.6(3)
C(7)-Fe(1)-C(8)	39.9(2)	F(3)-C(26)-F(2)	106.2(3)	C(36)-C(35)-Fe(2)	70.02(18)
C(1)-Fe(1)-C(8)	153.75(19)	F(1)-C(26)-F(2)	105.7(3)	C(34)-C(35)-Fe(2)	68.66(17)
C(4)-Fe(1)-C(8)	125.46(17)	F(3)-C(26)-P(2)	113.7(2)	C(37)-C(36)-C(35)	108.3(3)
C(10)-Fe(1)-C(9)	39.9(2)	F(1)-C(26)-P(2)	110.6(2)	C(37)-C(36)-Fe(2)	69.57(18)
C(2)-Fe(1)-C(9)	152.2(2)	F(2)-C(26)-P(2)	112.1(2)	C(35)-C(36)-Fe(2)	69.45(18)
C(6)-Fe(1)-C(9)	68.08(19)	C(28)-C(27)-C(32)	119.9(3)	C(36)-C(37)-C(33)	108.6(3)
C(3)-Fe(1)-C(9)	118.49(18)	C(28)-C(27)-P(2)	118.5(2)	C(36)-C(37)-Fe(2)	70.03(18)
C(7)-Fe(1)-C(9)	67.1(2)	C(32)-C(27)-P(2)	121.2(3)	C(33)-C(37)-Fe(2)	69.21(17)
C(1)-Fe(1)-C(9)	166.0(2)	C(29)-C(28)-C(27)	120.2(4)	C(42)-C(38)-C(39)	107.9(3)
C(4)-Fe(1)-C(9)	108.51(17)	C(30)-C(29)-C(28)	119.6(4)	C(42)-C(38)-Fe(2)	70.0(2)
C(8)-Fe(1)-C(9)	39.1(2)	C(31)-C(30)-C(29)	120.5(4)	C(39)-C(38)-Fe(2)	69.52(18)

C(10)-Fe(1)-C(5)	110.59(17)	C(30)-C(31)-C(32)	121.2(4)	C(38)-C(39)-C(40)	107.7(3)
C(2)-Fe(1)-C(5)	68.85(12)	C(31)-C(32)-C(27)	118.6(4)	C(38)-C(39)-Fe(2)	69.69(19)
C(6)-Fe(1)-C(5)	121.77(16)	P(4)-Pd(2)-P(3)	101.81(3)	C(40)-C(39)-Fe(2)	69.86(18)
C(3)-Fe(1)-C(5)	68.45(13)	P(4)-Pd(2)-Cl(4)	173.26(3)	C(41)-C(40)-C(39)	108.4(3)
C(7)-Fe(1)-C(5)	156.13(17)	P(3)-Pd(2)-Cl(4)	84.77(3)	C(41)-C(40)-Fe(2)	70.4(2)
C(1)-Fe(1)-C(5)	40.98(12)	P(4)-Pd(2)-Cl(3)	84.61(3)	C(39)-C(40)-Fe(2)	69.30(18)
C(4)-Fe(1)-C(5)	40.50(14)	P(3)-Pd(2)-Cl(3)	171.83(3)	C(40)-C(41)-C(42)	108.1(3)
C(8)-Fe(1)-C(5)	163.26(19)	Cl(4)-Pd(2)-Cl(3)	88.96(3)	C(40)-C(41)-Fe(2)	69.57(19)
C(9)-Fe(1)-C(5)	128.1(2)	C(34)-Fe(2)-C(33)	41.13(12)	C(42)-C(41)-Fe(2)	69.4(2)
C(20)-P(1)-C(14)	108.06(14)	C(34)-Fe(2)-C(39)	104.14(13)	C(38)-C(42)-C(41)	107.9(3)
C(20)-P(1)-C(11)	104.47(14)	C(33)-Fe(2)-C(39)	118.89(13)	C(38)-C(42)-Fe(2)	69.38(19)
C(14)-P(1)-C(11)	101.78(14)	C(34)-Fe(2)-C(38)	121.34(13)	C(41)-C(42)-Fe(2)	69.9(2)
C(20)-P(1)-Pd(1)	106.37(10)	C(33)-Fe(2)-C(38)	105.66(13)	C(33)-C(43)-C(44)	113.3(2)
C(14)-P(1)-Pd(1)	115.03(10)	C(39)-Fe(2)-C(38)	40.79(14)	C(33)-C(43)-P(3)	106.98(19)
C(11)-P(1)-Pd(1)	120.25(10)	C(34)-Fe(2)-C(35)	41.17(12)	C(44)-C(43)-P(3)	112.1(2)
C(27)-P(2)-C(13)	102.61(14)	C(33)-Fe(2)-C(35)	69.15(12)	C(34)-C(45)-P(4)	113.4(2)
C(27)-P(2)-C(26)	104.48(16)	C(39)-Fe(2)-C(35)	122.02(14)	C(47)-C(46)-C(51)	119.3(3)
C(13)-P(2)-C(26)	99.50(15)	C(38)-Fe(2)-C(35)	158.45(14)	C(47)-C(46)-P(3)	118.4(2)
C(27)-P(2)-Pd(1)	117.91(11)	C(34)-Fe(2)-C(40)	119.67(14)	C(51)-C(46)-P(3)	121.7(2)
C(13)-P(2)-Pd(1)	122.40(10)	C(33)-Fe(2)-C(40)	155.01(13)	C(48)-C(47)-C(46)	120.3(3)
C(26)-P(2)-Pd(1)	107.19(11)	C(39)-Fe(2)-C(40)	40.84(14)	C(47)-C(48)-C(49)	120.3(3)
C(2)-C(1)-C(5)	107.6(3)	C(38)-Fe(2)-C(40)	68.47(14)	C(50)-C(49)-C(48)	119.7(3)
C(2)-C(1)-C(11)	124.4(3)	C(35)-Fe(2)-C(40)	106.93(14)	C(49)-C(50)-C(51)	120.3(3)
C(5)-C(1)-C(11)	127.9(3)	C(34)-Fe(2)-C(37)	68.68(12)	C(50)-C(51)-C(46)	120.1(3)
C(2)-C(1)-Fe(1)	68.93(17)	C(33)-Fe(2)-C(37)	40.90(12)	C(57)-C(52)-C(53)	119.6(3)
C(5)-C(1)-Fe(1)	69.87(18)	C(39)-Fe(2)-C(37)	156.16(13)	C(57)-C(52)-P(3)	119.9(2)
C(11)-C(1)-Fe(1)	129.3(2)	C(38)-Fe(2)-C(37)	122.21(13)	C(53)-C(52)-P(3)	120.5(2)
C(1)-C(2)-C(3)	108.0(3)	C(35)-Fe(2)-C(37)	68.35(13)	C(54)-C(53)-C(52)	119.9(3)
C(1)-C(2)-C(13)	124.0(3)	C(40)-Fe(2)-C(37)	162.46(13)	C(55)-C(54)-C(53)	120.2(3)
C(3)-C(2)-C(13)	128.0(3)	C(34)-Fe(2)-C(42)	159.28(15)	C(56)-C(55)-C(54)	119.9(3)
C(1)-C(2)-Fe(1)	70.11(17)	C(33)-Fe(2)-C(42)	124.15(15)	C(55)-C(56)-C(57)	120.4(3)
C(3)-C(2)-Fe(1)	69.69(17)	C(39)-Fe(2)-C(42)	68.37(14)	C(56)-C(57)-C(52)	120.0(3)
C(13)-C(2)-Fe(1)	125.8(2)	C(38)-Fe(2)-C(42)	40.59(15)	F(4)-C(58)-F(5)	108.8(3)
C(4)-C(3)-C(2)	108.0(3)	C(35)-Fe(2)-C(42)	159.11(15)	F(4)-C(58)-F(6)	106.1(3)
C(4)-C(3)-Fe(1)	70.11(19)	C(40)-Fe(2)-C(42)	68.07(15)	F(5)-C(58)-F(6)	106.7(3)
C(2)-C(3)-Fe(1)	69.15(16)	C(37)-Fe(2)-C(42)	109.94(14)	F(4)-C(58)-P(4)	114.2(2)
C(3)-C(4)-C(5)	108.6(3)	C(34)-Fe(2)-C(36)	68.66(13)	F(5)-C(58)-P(4)	109.3(2)
C(3)-C(4)-Fe(1)	69.36(18)	C(33)-Fe(2)-C(36)	68.71(13)	F(6)-C(58)-P(4)	111.4(2)
C(5)-C(4)-Fe(1)	70.06(19)	C(39)-Fe(2)-C(36)	160.01(14)	C(60)-C(59)-C(64)	119.8(3)
C(4)-C(5)-C(1)	107.8(3)	C(38)-Fe(2)-C(36)	158.85(14)	C(60)-C(59)-P(4)	116.5(2)
C(4)-C(5)-Fe(1)	69.44(19)	C(35)-Fe(2)-C(36)	40.53(13)	C(64)-C(59)-P(4)	122.9(2)
C(1)-C(5)-Fe(1)	69.15(18)	C(40)-Fe(2)-C(36)	125.24(14)	C(61)-C(60)-C(59)	120.4(3)
C(10)-C(6)-C(7)	105.8(4)	C(37)-Fe(2)-C(36)	40.40(13)	C(62)-C(61)-C(60)	119.3(3)
C(10)-C(6)-Fe(1)	69.2(2)	C(42)-Fe(2)-C(36)	124.61(14)	C(63)-C(62)-C(61)	120.6(3)
C(7)-C(6)-Fe(1)	69.6(2)	C(34)-Fe(2)-C(41)	156.27(15)	C(62)-C(63)-C(64)	120.6(3)
C(8)-C(7)-C(6)	107.5(4)	C(33)-Fe(2)-C(41)	162.36(15)	C(63)-C(64)-C(59)	119.3(3)
C(8)-C(7)-Fe(1)	70.4(3)	C(39)-Fe(2)-C(41)	68.16(15)		

4.2.7 [$PdCl_2$(56-κ^2*P,P'*)] (59)

Crystal Data and Structure Refinement:



Empirical formula	$C_{33}H_{34}Cl_4FeP_2Pd$
Formula weight	796.59
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 11.189(6) Å alpha = 90° b = 14.344(8) Å beta = 90° c = 20.863(11) Å gamma = 90°
Volume	3348(3) $Å^3$
Z, Calculated density	4, 1.580 Mg/m^3
Absorption coefficient	1.408 mm^{-1}
F(000)	1608
Crystal size	0.306 x 0.068 x 0.038 mm
Theta range for data collection	1.72 to 28.46°
Limiting indices	-14<=h<=14, -18<=k<=19, -27<=l<=27
Reflections collected / unique	23169 / 8383 [R(int) = 0.2490]
Completeness to theta = 26.37	99.6%
Absorption correction	Not measured
Max. and min. transmission	0.9485 and 0.6726
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8383 / 246 / 372
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.1380, wR2 = 0.1985
R indices (all data)	R1 = 0.2379, wR2 = 0.2387
Largest diff. peak and hole	1.791 and -1.378 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3). Disordered CH_2Cl_2 molecules are omitted:

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Pd(1)	6039(1)	685(1)	2355(1)	19(1)	C(1)	7022(15)	2914(10)	1362(8)	21(4)
Fe(1)	7945(2)	4120(2)	1394(1)	28(1)	C(25)	3134(16)	2048(12)	1628(8)	26(4)
Cl(2)	5242(4)	-620(3)	1832(2)	35(1)	C(2)	7680(13)	2994(10)	1947(7)	10(3)
P(1)	5452(4)	1453(3)	1459(2)	17(1)	C(27)	7050(30)	2240(20)	4263(17)	126(13)
P(2)	6996(4)	1802(3)	2921(2)	25(1)	C(11)	5736(14)	2726(10)	1327(8)	20(4)
Cl(1)	6608(5)	-298(3)	3198(2)	36(1)	C(20)	3877(17)	1353(11)	1345(8)	24(4)
C(15)	7411(13)	703(12)	897(7)	19(4)	C(9)	8650(20)	5366(14)	1114(10)	48(6)
C(26)	6390(17)	2007(12)	3703(9)	32(5)	C(21)	3337(15)	574(13)	1023(8)	29(4)
C(4)	9038(17)	3053(10)	1131(7)	18(4)	C(24)	1930(16)	1951(11)	1564(8)	27(4)
C(5)	7931(17)	2956(11)	854(9)	28(4)	C(22)	2061(18)	535(14)	965(9)	39(5)
C(3)	8912(18)	3076(11)	1797(8)	25(4)	C(7)	7370(16)	5194(11)	1946(9)	26(4)
C(12)	5202(17)	3096(13)	679(9)	34(5)	C(6)	6734(15)	5143(10)	1412(8)	20(4)
C(19)	5787(16)	845(12)	180(8)	31(5)	C(32)	8543(18)	1454(13)	3040(10)	44(6)
C(16)	8148(16)	340(10)	413(8)	21(4)	C(10)	7453(18)	5263(12)	888(9)	34(5)
C(8)	8650(20)	5324(14)	1742(11)	50(6)	C(31)	5135(19)	2063(13)	3778(10)	42(6)
C(14)	6290(14)	927(10)	797(7)	15(4)	C(29)	5280(30)	2465(19)	4861(14)	77(8)
C(13)	7140(13)	3004(9)	2603(7)	13(3)	C(23)	1370(20)	1243(14)	1225(10)	52(6)
C(18)	6507(18)	520(13)	-335(9)	42(6)	C(30)	4650(20)	2289(17)	4320(12)	69(8)
C(17)	7710(18)	274(12)	-188(9)	35(5)	C(28)	6480(30)	2350(20)	4856(11)	11(12)

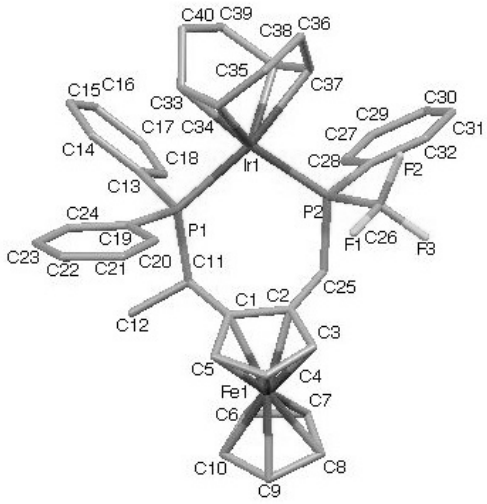
Bond lengths (Å). Calculated distances to hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Bond	Å	Bond	Å	Bond	Å
Pd(1)-P(2)	2.260(5)	P(2)-C(26)	1.790(19)	C(13)-C(2)	1.50(2)
Pd(1)-P(1)	2.266(5)	P(2)-C(32)	1.82(2)	C(18)-C(17)	1.43(3)
Pd(1)-Cl(1)	2.343(5)	P(2)-C(13)	1.855(14)	C(1)-C(2)	1.43(2)
Pd(1)-Cl(2)	2.344(5)	C(15)-C(14)	1.31(2)	C(1)-C(11)	1.47(2)
Fe(1)-C(6)	1.998(15)	C(15)-C(16)	1.40(2)	C(25)-C(24)	1.36(2)
Fe(1)-C(2)	2.007(14)	C(26)-C(31)	1.42(3)	C(25)-C(20)	1.43(2)
Fe(1)-C(5)	2.014(17)	C(26)-C(27)	1.42(4)	C(27)-C(28)	1.40(4)
Fe(1)-C(1)	2.016(16)	C(4)-C(5)	1.37(2)	C(20)-C(21)	1.44(2)
Fe(1)-C(10)	2.026(18)	C(4)-C(3)	1.40(2)	C(9)-C(10)	1.43(3)
Fe(1)-C(7)	2.029(17)	C(5)-C(1)	1.47(2)	C(21)-C(22)	1.43(2)
Fe(1)-C(3)	2.029(17)	C(3)-C(2)	1.42(2)	C(24)-C(23)	1.38(2)
Fe(1)-C(8)	2.03(2)	C(12)-C(11)	1.57(2)	C(22)-C(23)	1.38(3)
Fe(1)-C(4)	2.034(16)	C(19)-C(14)	1.41(2)	C(7)-C(6)	1.32(2)
Fe(1)-C(9)	2.04(2)	C(19)-C(18)	1.42(2)	C(6)-C(10)	1.37(2)
P(1)-C(20)	1.784(19)	C(16)-C(17)	1.35(2)	C(31)-C(30)	1.29(3)
P(1)-C(14)	1.831(15)	C(8)-C(9)	1.31(3)	C(29)-C(30)	1.35(3)
P(1)-C(11)	1.874(15)	C(8)-C(7)	1.50(3)	C(29)-C(28)	1.36(4)

Bond angles (°). Angles involving hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
P(2)-Pd(1)-P(1)	102.96(17)	C(2)-Fe(1)-C(9)	158.0(8)	C(19)-C(18)-C(17)	117.1(18)
P(2)-Pd(1)-Cl(1)	84.56(18)	C(5)-Fe(1)-C(9)	124.8(8)	C(16)-C(17)-C(18)	121.6(19)
P(1)-Pd(1)-Cl(1)	172.05(18)	C(1)-Fe(1)-C(9)	160.3(8)	C(2)-C(1)-C(11)	124.3(15)
P(2)-Pd(1)-Cl(2)	171.85(19)	C(10)-Fe(1)-C(9)	41.1(7)	C(2)-C(1)-C(5)	104.8(14)
P(1)-Pd(1)-Cl(2)	83.93(17)	C(7)-Fe(1)-C(9)	67.6(8)	C(11)-C(1)-C(5)	130.5(16)
Cl(1)-Pd(1)-Cl(2)	88.38(18)	C(3)-Fe(1)-C(9)	124.0(8)	C(2)-C(1)-Fe(1)	68.9(9)
C(6)-Fe(1)-C(2)	118.7(6)	C(8)-Fe(1)-C(9)	37.6(7)	C(11)-C(1)-Fe(1)	131.5(11)
C(6)-Fe(1)-C(5)	127.9(7)	C(4)-Fe(1)-C(9)	110.4(8)	C(5)-C(1)-Fe(1)	68.5(9)
C(2)-Fe(1)-C(5)	69.7(6)	C(20)-P(1)-C(14)	111.8(8)	C(24)-C(25)-C(20)	117.7(17)
C(6)-Fe(1)-C(1)	106.5(7)	C(20)-P(1)-C(11)	103.1(7)	C(3)-C(2)-C(1)	108.6(14)
C(2)-Fe(1)-C(1)	41.6(6)	C(14)-P(1)-C(11)	101.7(7)	C(3)-C(2)-C(13)	126.4(14)
C(5)-Fe(1)-C(1)	42.8(7)	C(20)-P(1)-Pd(1)	110.9(6)	C(1)-C(2)-C(13)	125.0(13)
C(6)-Fe(1)-C(10)	39.7(7)	C(14)-P(1)-Pd(1)	105.8(5)	C(3)-C(2)-Fe(1)	70.3(9)
C(2)-Fe(1)-C(10)	155.6(7)	C(11)-P(1)-Pd(1)	123.1(5)	C(1)-C(2)-Fe(1)	69.5(9)
C(5)-Fe(1)-C(10)	112.2(7)	C(26)-P(2)-C(32)	106.3(9)	C(13)-C(2)-Fe(1)	125.3(10)
C(1)-Fe(1)-C(10)	122.6(7)	C(26)-P(2)-C(13)	101.9(8)	C(28)-C(27)-C(26)	121(3)
C(6)-Fe(1)-C(7)	38.4(7)	C(32)-P(2)-C(13)	102.8(8)	C(1)-C(11)-C(12)	110.8(14)
C(2)-Fe(1)-C(7)	103.8(6)	C(26)-P(2)-Pd(1)	114.4(6)	C(1)-C(11)-P(1)	109.7(11)
C(5)-Fe(1)-C(7)	160.8(7)	C(32)-P(2)-Pd(1)	109.1(7)	C(12)-C(11)-P(1)	113.0(11)
C(1)-Fe(1)-C(7)	120.5(7)	C(13)-P(2)-Pd(1)	120.8(5)	C(25)-C(20)-C(21)	119.5(17)
C(10)-Fe(1)-C(7)	66.1(7)	C(14)-C(15)-C(16)	122.6(16)	C(25)-C(20)-P(1)	117.7(13)
C(6)-Fe(1)-C(3)	153.6(7)	C(31)-C(26)-C(27)	114(2)	C(21)-C(20)-P(1)	122.7(13)
C(2)-Fe(1)-C(3)	41.1(6)	C(31)-C(26)-P(2)	119.0(16)	C(8)-C(9)-C(10)	109(2)
C(5)-Fe(1)-C(3)	67.9(7)	C(27)-C(26)-P(2)	126(2)	C(8)-C(9)-Fe(1)	70.9(13)
C(1)-Fe(1)-C(3)	69.7(7)	C(5)-C(4)-C(3)	109.2(17)	C(10)-C(9)-Fe(1)	68.9(11)
C(10)-Fe(1)-C(3)	163.3(8)	C(5)-C(4)-Fe(1)	69.4(10)	C(22)-C(21)-C(20)	119.2(17)
C(7)-Fe(1)-C(3)	119.6(7)	C(3)-C(4)-Fe(1)	69.7(10)	C(25)-C(24)-C(23)	124.8(18)
C(6)-Fe(1)-C(8)	68.3(8)	C(4)-C(5)-C(1)	109.0(15)	C(23)-C(22)-C(21)	119.6(19)
C(2)-Fe(1)-C(8)	122.4(8)	C(4)-C(5)-Fe(1)	71.0(10)	C(6)-C(7)-C(8)	106.2(17)
C(5)-Fe(1)-C(8)	155.2(8)	C(1)-C(5)-Fe(1)	68.7(9)	C(6)-C(7)-Fe(1)	69.6(10)
C(1)-Fe(1)-C(8)	159.9(8)	C(4)-C(3)-C(2)	108.4(17)	C(8)-C(7)-Fe(1)	68.4(10)
C(10)-Fe(1)-C(8)	66.6(8)	C(4)-C(3)-Fe(1)	70.1(10)	C(7)-C(6)-C(10)	110.4(17)
C(7)-Fe(1)-C(8)	43.4(7)	C(2)-C(3)-Fe(1)	68.6(9)	C(7)-C(6)-Fe(1)	72.1(10)
C(3)-Fe(1)-C(8)	105.9(8)	C(14)-C(19)-C(18)	119.4(17)	C(10)-C(6)-Fe(1)	71.2(10)
C(6)-Fe(1)-C(4)	164.9(7)	C(17)-C(16)-C(15)	118.8(17)	C(6)-C(10)-C(9)	107.5(18)
C(2)-Fe(1)-C(4)	68.8(6)	C(9)-C(8)-C(7)	107(2)	C(6)-C(10)-Fe(1)	69.0(10)
C(5)-Fe(1)-C(4)	39.7(7)	C(9)-C(8)-Fe(1)	71.5(13)	C(9)-C(10)-Fe(1)	69.9(11)
C(1)-Fe(1)-C(4)	69.8(7)	C(7)-C(8)-Fe(1)	68.2(10)	C(30)-C(31)-C(26)	122(2)
C(10)-Fe(1)-C(4)	129.2(7)	C(15)-C(14)-C(19)	120.4(15)	C(30)-C(29)-C(28)	119(3)
C(7)-Fe(1)-C(4)	156.3(7)	C(15)-C(14)-P(1)	118.1(12)	C(24)-C(23)-C(22)	119(2)
C(3)-Fe(1)-C(4)	40.2(6)	C(19)-C(14)-P(1)	121.3(12)	C(31)-C(30)-C(29)	124(3)
C(8)-Fe(1)-C(4)	120.2(8)	C(2)-C(13)-P(2)	110.7(10)	C(29)-C(28)-C(27)	118(4)

4.2.8 [Ir(cod)(54-κ²*P,P'*)]BF_4 (61)



Crystal Data and Structure Refinement:

Empirical formula	$C_{41}H_{43}BCl_2F_7FeIrP_2$
Formula weight	1060.45
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.9694(5) Å alpha = 90° b = 18.8436(10) Å beta = 90° c = 21.3522(12) Å gamma = 90°
Volume	4011.2(4) $Å^3$
Z, Calculated density	4, 1.756 Mg/m^3
Absorption coefficient	3.952 mm^{-1}
F(000)	2096
Crystal size	0.28 x 0.22 x 0.16 mm
Theta range for data collection	1.44 to 31.52°
Limiting indices	-14<=h<=14, -27<=k<=27, -31<=l<=31
Reflections collected / unique	132798 / 13379 [R(int) = 0.0608]
Completeness to theta = 26.37	100.0%
Absorption correction	Empirical
Max. and min. transmission	0.5758 and 0.4041
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13379 / 0 / 496
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0595
R indices (all data)	R1 = 0.0276, wR2 = 0.0605
Largest diff. peak and hole	2.928 and -0.555 e·$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters U_{eq} ($Å^2$ x 10^3). Disordered CH_2Cl_2 molecules are omitted:

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Ir(1)	5048(1)	9363(1)	3039(1)	16(1)	C(20)	6351(3)	8744(1)	4625(1)	19(1)
Fe(1)	7974(1)	11391(1)	4566(1)	18(1)	C(21)	6411(3)	8348(2)	5172(1)	25(1)
P(1)	7153(1)	9235(1)	3484(1)	13(1)	C(22)	7379(4)	7829(2)	5239(2)	31(1)
P(2)	4847(1)	10565(1)	3039(1)	16(1)	C(23)	8320(3)	7723(2)	4775(2)	28(1)
F(1)	3443(2)	10579(1)	4102(1)	32(1)	C(24)	8298(3)	8127(2)	4228(1)	21(1)
F(2)	2170(2)	10564(1)	3288(1)	30(1)	C(25)	6067(3)	11162(1)	3414(1)	19(1)
F(3)	3181(2)	11528(1)	3552(1)	30(1)	C(26)	3320(3)	10819(2)	3516(1)	22(1)
C(1)	7470(2)	10425(1)	4210(1)	14(1)	C(27)	4561(3)	10980(1)	2285(1)	19(1)
C(2)	6469(3)	10942(1)	4063(1)	16(1)	C(28)	5665(3)	10969(2)	1890(2)	27(1)
C(3)	5963(3)	11219(2)	4639(1)	22(1)	C(29)	5573(3)	11251(2)	1284(2)	31(1)
C(4)	6652(3)	10872(2)	5137(1)	26(1)	C(30)	4370(3)	11536(2)	1081(2)	28(1)
C(5)	7578(3)	10384(1)	4877(1)	20(1)	C(31)	3269(3)	11541(2)	1470(1)	25(1)
C(6)	9650(3)	11738(2)	4106(2)	34(1)	C(32)	3351(3)	11267(1)	2077(1)	21(1)
C(7)	8619(3)	12243(2)	4063(2)	31(1)	C(33)	4979(3)	8169(1)	3023(1)	21(1)
C(8)	8262(4)	12453(2)	4684(2)	37(1)	C(34)	4032(3)	8433(2)	3440(1)	21(1)
C(9)	9088(5)	12065(2)	5105(2)	44(1)	C(35)	2547(3)	8482(2)	3327(1)	26(1)
C(10)	9931(4)	11624(2)	4747(2)	40(1)	C(36)	2188(3)	8766(2)	2677(2)	24(1)
C(11)	8216(3)	9994(1)	3734(1)	15(1)	C(37)	3158(3)	9333(2)	2457(1)	23(1)
C(12)	9610(3)	9753(2)	3952(2)	24(1)	C(38)	4311(3)	9203(2)	2099(1)	23(1)
C(13)	8074(3)	8887(2)	2808(1)	16(1)	C(39)	4765(3)	8483(2)	1874(1)	29(1)
C(14)	8278(3)	8166(2)	2693(1)	21(1)	C(40)	4681(3)	7893(2)	2372(2)	27(1)
C(15)	8873(3)	7949(2)	2134(1)	23(1)	F(4)	10015(3)	1921(1)	1640(1)	48(1)
C(16)	9260(3)	8446(2)	1690(1)	24(1)	F(5)	10133(4)	1199(2)	2480(1)	65(1)
C(17)	9061(3)	9161(2)	1801(1)	23(1)	F(6)	8243(3)	1803(2)	2294(2)	54(1)
C(18)	8465(3)	9385(2)	2360(1)	19(1)	F(7)	8842(2)	893(1)	1625(1)	35(1)
C(19)	7292(3)	8635(1)	4146(1)	17(1)	B(1)	9313(3)	1450(2)	2002(2)	29(1)

Bond lengths (Å). Calculated distances to hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Bond	Å	Bond	Å	Bond	Å
Ir(1)-C(38)	2.157(3)	F(2)-C(26)	1.334(3)	C(20)-C(21)	1.388(4)
Ir(1)-C(34)	2.198(3)	F(3)-C(26)	1.346(3)	C(21)-C(22)	1.381(5)
Ir(1)-C(33)	2.251(2)	C(1)-C(2)	1.429(4)	C(22)-C(23)	1.379(5)
Ir(1)-C(37)	2.257(3)	C(1)-C(5)	1.431(4)	C(23)-C(24)	1.393(4)
Ir(1)-P(2)	2.2731(6)	C(1)-C(11)	1.499(3)	C(27)-C(28)	1.387(4)
Ir(1)-P(1)	2.3162(6)	C(2)-C(3)	1.428(4)	C(27)-C(32)	1.394(4)
Fe(1)-C(2)	2.031(3)	C(2)-C(25)	1.500(4)	C(28)-C(29)	1.401(4)
Fe(1)-C(1)	2.035(2)	C(3)-C(4)	1.425(5)	C(29)-C(30)	1.384(5)
Fe(1)-C(7)	2.036(3)	C(4)-C(5)	1.416(4)	C(30)-C(31)	1.377(5)
Fe(1)-C(10)	2.037(4)	C(6)-C(7)	1.403(5)	C(31)-C(32)	1.398(4)
Fe(1)-C(3)	2.037(3)	C(6)-C(10)	1.414(5)	C(33)-C(34)	1.390(4)
Fe(1)-C(8)	2.038(3)	C(7)-C(8)	1.429(6)	C(33)-C(40)	1.513(4)
Fe(1)-C(9)	2.042(3)	C(8)-C(9)	1.423(6)	C(34)-C(35)	1.503(4)
Fe(1)-C(4)	2.043(3)	C(9)-C(10)	1.408(6)	C(35)-C(36)	1.531(4)
Fe(1)-C(6)	2.047(3)	C(11)-C(12)	1.535(4)	C(36)-C(37)	1.515(4)
Fe(1)-C(5)	2.048(3)	C(13)-C(18)	1.394(4)	C(37)-C(38)	1.402(4)
P(1)-C(19)	1.815(3)	C(13)-C(14)	1.395(4)	C(38)-C(39)	1.510(4)
P(1)-C(13)	1.832(3)	C(14)-C(15)	1.395(4)	C(39)-C(40)	1.542(5)
P(1)-C(11)	1.859(3)	C(15)-C(16)	1.388(4)	F(4)-B(1)	1.370(4)
P(2)-C(27)	1.814(3)	C(16)-C(17)	1.382(4)	F(5)-B(1)	1.390(5)
P(2)-C(25)	1.841(3)	C(17)-C(18)	1.399(4)	F(6)-B(1)	1.403(5)
P(2)-C(26)	1.893(3)	C(19)-C(24)	1.398(4)	F(7)-B(1)	1.403(4)
F(1)-C(26)	1.336(3)	C(19)-C(20)	1.403(4)		

Bond angles (°). Angles involving hydrogen atoms and disordered CH_2Cl_2 molecules are omitted:

Angle	deg (°)	Angle	deg (°)	Angle	deg (°)
C(38)-Ir(1)-C(34)	95.41(11)	C(3)-Fe(1)-C(5)	68.81(12)	C(1)-C(11)-P(1)	109.19(17)
C(38)-Ir(1)-C(33)	80.56(10)	C(8)-Fe(1)-C(5)	153.79(14)	C(12)-C(11)-P(1)	112.04(18)
C(34)-Ir(1)-C(33)	36.40(11)	C(9)-Fe(1)-C(5)	119.89(14)	C(18)-C(13)-C(14)	119.5(2)
C(38)-Ir(1)-C(37)	36.94(11)	C(4)-Fe(1)-C(5)	40.51(12)	C(18)-C(13)-P(1)	116.1(2)
C(34)-Ir(1)-C(37)	79.03(10)	C(6)-Fe(1)-C(5)	127.54(13)	C(14)-C(13)-P(1)	124.0(2)
C(33)-Ir(1)-C(37)	86.61(11)	C(19)-P(1)-C(13)	110.63(12)	C(15)-C(14)-C(13)	119.9(3)
C(38)-Ir(1)-P(2)	96.28(8)	C(19)-P(1)-C(11)	102.28(12)	C(16)-C(15)-C(14)	120.3(3)
C(34)-Ir(1)-P(2)	138.89(8)	C(13)-P(1)-C(11)	102.42(12)	C(17)-C(16)-C(15)	120.0(3)
C(33)-Ir(1)-P(2)	173.15(7)	C(19)-P(1)-Ir(1)	116.98(9)	C(16)-C(17)-C(18)	120.1(3)
C(37)-Ir(1)-P(2)	87.24(8)	C(13)-P(1)-Ir(1)	99.70(9)	C(13)-C(18)-C(17)	120.1(3)
C(38)-Ir(1)-P(1)	132.49(8)	C(11)-P(1)-Ir(1)	123.63(8)	C(24)-C(19)-C(20)	119.2(2)
C(34)-Ir(1)-P(1)	100.04(7)	C(27)-P(2)-C(25)	103.10(12)	C(24)-C(19)-P(1)	125.4(2)
C(33)-Ir(1)-P(1)	85.96(8)	C(27)-P(2)-C(26)	103.99(13)	C(20)-C(19)-P(1)	115.21(19)
C(37)-Ir(1)-P(1)	168.31(8)	C(25)-P(2)-C(26)	98.20(13)	C(21)-C(20)-C(19)	120.4(3)
P(2)-Ir(1)-P(1)	100.58(2)	C(27)-P(2)-Ir(1)	116.33(9)	C(22)-C(21)-C(20)	119.8(3)
C(2)-Fe(1)-C(1)	41.15(10)	C(25)-P(2)-Ir(1)	123.43(9)	C(23)-C(22)-C(21)	120.3(3)
C(2)-Fe(1)-C(7)	106.39(12)	C(26)-P(2)-Ir(1)	108.87(9)	C(22)-C(23)-C(24)	120.8(3)
C(1)-Fe(1)-C(7)	125.83(13)	C(2)-C(1)-C(5)	108.0(2)	C(23)-C(24)-C(19)	119.4(3)
C(2)-Fe(1)-C(10)	153.88(14)	C(2)-C(1)-C(11)	124.5(2)	C(2)-C(25)-P(2)	114.17(18)
C(1)-Fe(1)-C(10)	120.02(13)	C(5)-C(1)-C(11)	127.5(2)	F(2)-C(26)-F(1)	107.3(2)
C(7)-Fe(1)-C(10)	68.11(13)	C(2)-C(1)-Fe(1)	69.25(14)	F(2)-C(26)-F(3)	106.9(2)
C(2)-Fe(1)-C(3)	41.09(11)	C(5)-C(1)-Fe(1)	69.97(14)	F(1)-C(26)-F(3)	107.0(2)
C(1)-Fe(1)-C(3)	69.08(10)	C(11)-C(1)-Fe(1)	127.97(17)	F(2)-C(26)-P(2)	113.8(2)
C(7)-Fe(1)-C(3)	118.43(13)	C(3)-C(2)-C(1)	107.9(2)	F(1)-C(26)-P(2)	110.09(19)
C(10)-Fe(1)-C(3)	164.37(15)	C(3)-C(2)-C(25)	126.9(2)	F(3)-C(26)-P(2)	111.45(19)
C(2)-Fe(1)-C(8)	125.34(14)	C(1)-C(2)-C(25)	125.3(2)	C(28)-C(27)-C(32)	119.9(2)
C(1)-Fe(1)-C(8)	163.53(14)	C(3)-C(2)-Fe(1)	69.69(16)	C(28)-C(27)-P(2)	114.2(2)
C(7)-Fe(1)-C(8)	41.07(16)	C(1)-C(2)-Fe(1)	69.60(14)	C(32)-C(27)-P(2)	125.9(2)
C(10)-Fe(1)-C(8)	68.27(15)	C(25)-C(2)-Fe(1)	124.82(18)	C(27)-C(28)-C(29)	120.2(3)
C(3)-Fe(1)-C(8)	106.59(14)	C(4)-C(3)-C(2)	107.7(2)	C(30)-C(29)-C(28)	119.6(3)
C(2)-Fe(1)-C(9)	163.61(16)	C(4)-C(3)-Fe(1)	69.81(17)	C(31)-C(30)-C(29)	120.3(3)
C(1)-Fe(1)-C(9)	154.28(15)	C(2)-C(3)-Fe(1)	69.22(15)	C(30)-C(31)-C(32)	120.7(3)
C(7)-Fe(1)-C(9)	68.63(15)	C(5)-C(4)-C(3)	108.7(2)	C(27)-C(32)-C(31)	119.3(3)
C(10)-Fe(1)-C(9)	40.38(18)	C(5)-C(4)-Fe(1)	69.92(16)	C(34)-C(33)-C(40)	125.3(3)
C(3)-Fe(1)-C(9)	126.28(16)	C(3)-C(4)-Fe(1)	69.32(16)	C(34)-C(33)-Ir(1)	69.74(15)
C(8)-Fe(1)-C(9)	40.82(17)	C(4)-C(5)-C(1)	107.8(3)	C(40)-C(33)-Ir(1)	111.39(18)

C(2)-Fe(1)-C(4)	68.87(11)	C(4)-C(5)-Fe(1)	69.57(16)	C(33)-C(34)-C(35)	126.1(3)
C(1)-Fe(1)-C(4)	68.65(11)	C(1)-C(5)-Fe(1)	69.02(14)	C(33)-C(34)-Ir(1)	73.86(16)
C(7)-Fe(1)-C(4)	153.55(14)	C(7)-C(6)-C(10)	108.1(3)	C(35)-C(34)-Ir(1)	110.05(19)
C(10)-Fe(1)-C(4)	127.50(14)	C(7)-C(6)-Fe(1)	69.46(19)	C(C(37)-C(36)-C(35)	112.2(2)
C(3)-Fe(1)-C(4)	40.87(13)	C(10)-C(6)-Fe(1)	69.4(2)	C(38)-C(37)-C(36)	124.7(3)
C(8)-Fe(1)-C(4)	119.16(14)	C(6)-C(7)-C(8)	108.1(3)	C(38)-C(37)-Ir(1)	67.66(15)
C(9)-Fe(1)-C(4)	108.22(15)	C(6)-C(7)-Fe(1)	70.34(18)	C(36)-C(37)-Ir(1)	112.36(18)
C(2)-Fe(1)-C(6)	118.82(13)	C(8)-C(7)-Fe(1)	69.56(19)	C(37)-C(38)-C(39)	125.2(3)
C(1)-Fe(1)-C(6)	107.93(12)	C(9)-C(8)-C(7)	107.4(3)	C(37)-C(38)-Ir(1)	75.40(16)
C(7)-Fe(1)-C(6)	40.20(14)	C(9)-C(8)-Fe(1)	69.72(19)	C(39)-C(38)-Ir(1)	108.69(19)
C(10)-Fe(1)-C(6)	40.50(16)	C(7)-C(8)-Fe(1)	69.37(17)	C(38)-C(39)-C(40)	114.3(2)
C(3)-Fe(1)-C(6)	152.99(14)	C(10)-C(9)-C(8)	107.8(3)	C(33)-C(40)-C(39)	112.0(2)
C(8)-Fe(1)-C(6)	68.29(15)	C(10)-C(9)-Fe(1)	69.6(2)	F(4)-B(1)-F(5)	109.5(3)
C(9)-Fe(1)-C(6)	68.15(16)	C(8)-C(9)-Fe(1)	69.46(19)	F(4)-B(1)-F(6)	109.4(3)
C(4)-Fe(1)-C(6)	165.05(15)	C(9)-C(10)-C(6)	108.6(3)	F(5)-B(1)-F(6)	106.5(3)
C(2)-Fe(1)-C(5)	69.10(11)	C(9)-C(10)-Fe(1)	70.0(2)	F(4)-B(1)-F(7)	109.4(3)
C(1)-Fe(1)-C(5)	41.02(10)	C(6)-C(10)-Fe(1)	70.15(19)	F(5)-B(1)-F(7)	111.3(3)
C(7)-Fe(1)-C(5)	164.18(14)	C(1)-C(11)-C(12)	113.8(2)	F(6)-B(1)-F(7)	110.7(3)
C(10)-Fe(1)-C(5)	108.87(13)				

Curriculum Vitae

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06/2005 - 12/2005 **CIBA Sc, Basel, Switzerland**. Industrial internship in the division of process research and development (Dr. A. Hafner).

10/2004 - 05/2005 **Laboratory of Chemistry, Université de Neuchâtel, Switzerland**.
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