



Doctoral Thesis

Planar-chirale Aminoferrocene: Bausteine zur Synthese neuartiger Amidinato- und Carbenliganden für die asymmetrische Katalyse

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Synthese neuartiger Amidinato- und
Carbenliganden für die Asymmetrische Katalyse

ABHANDLUNG
zur Erlangung des Titels

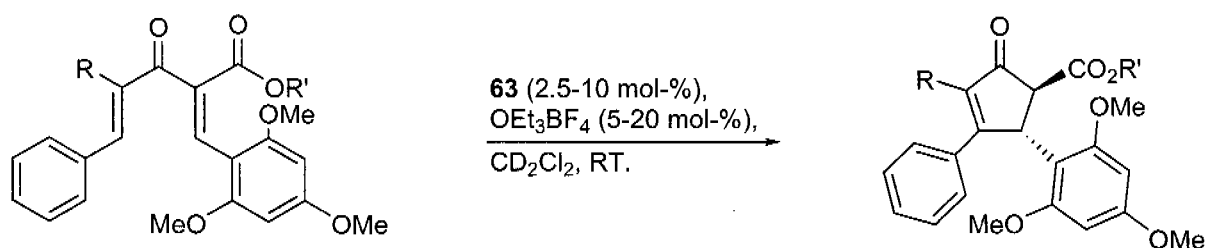
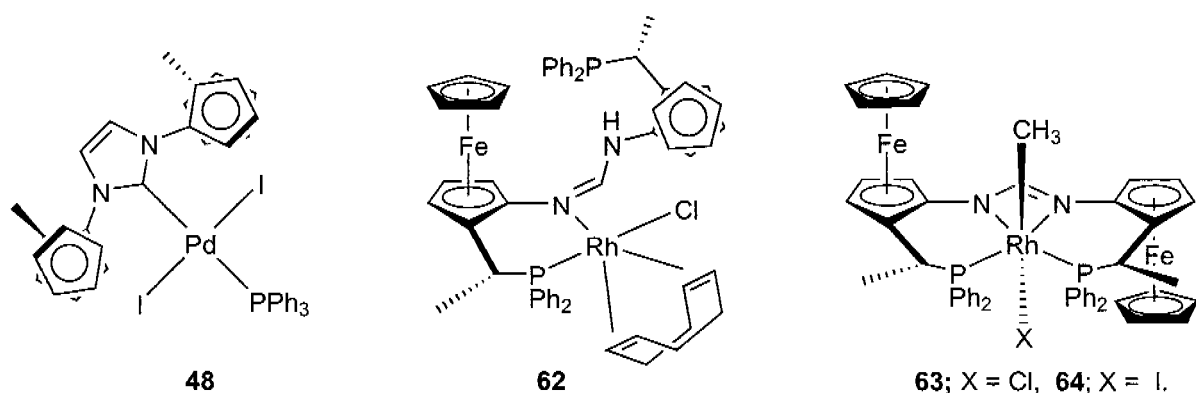
DOKTOR DER NATURWISSENSCHAFTEN
der
EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE ZÜRICH

vorgelegt von
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Dipl. Chem. ETH
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Angenommen auf Antrag von:
Prof. Dr. Antonio Togni, Referent
Prof. Dr. Andreas Pfaltz, Korreferent

Zürich, 2006

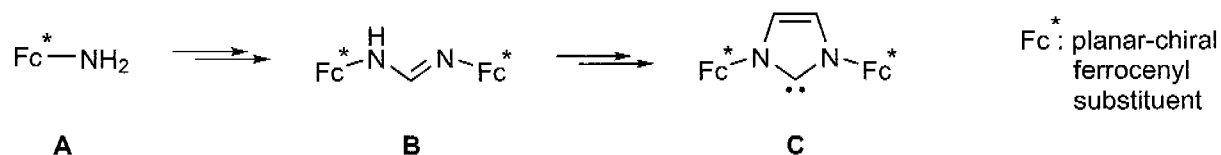
Zwei spezifische Derivate von Aminoferrocenen stellen die C_2 -symmetrischen Liganden des Pd(II)-Komplexes **48** sowie der Rh(I)- und Rh(III)-Komplexe **62-64** dar. So wurden mithilfe des Pd(II)-Komplexes **48** und verwandter Verbindungen die Koordinationseigenschaften monodentater N,N' -bisferrocenylierter N-Heterocyclischer Carbene untersucht, woraus auch ein neuartiger Syntheseweg für sterisch anspruchsvolle Carbenliganden resultierte (*Kapitel 3*). Insbesondere jedoch zeigte sich, dass Komplexe des Typs von **48** als Katalysatoren für Pd-katalysierte asymmetrischen Amid-Cyclisierungen nach *Buchwald* und *Hartwig* verwendet werden können, wobei jedoch ebenfalls klar wurde, dass die Realisierung vorteilhafter Enantioselektivitäten nur bei einer weiteren Einschränkung der rotatorischen Freiheitsgrade des Carbenliganden erwartet werden darf. Eine Möglichkeit diesem Problem Herr zu werden besteht grundsätzlich in der Verwendung von Chelatliganden; Rh-Komplexe wie die Verbindungen **62-64** zeugen nicht nur von der reichen, in weiten Teilen noch unerforschten Koordinationschemie des Amidin-/Amidinatoliganden, sie besitzen auch einiges Potential in der Aktivierung von E-H-Bindungen (E = Element) und machen *Lewis*-Säuren zugänglich, welche unser oben erwähntes geometrisches Konzept aufs trefflichste veranschaulichen (*Kapitel 4*). Ein Beispiel dafür bildet die katalytische asymmetrische *Nazarov*-Cyclisierung von β -Ketoestern, eine asymmetrisch-katalytische Umsetzung, für welche bisher keine Literaturpräzedenz besteht (*Kapitel 5*).



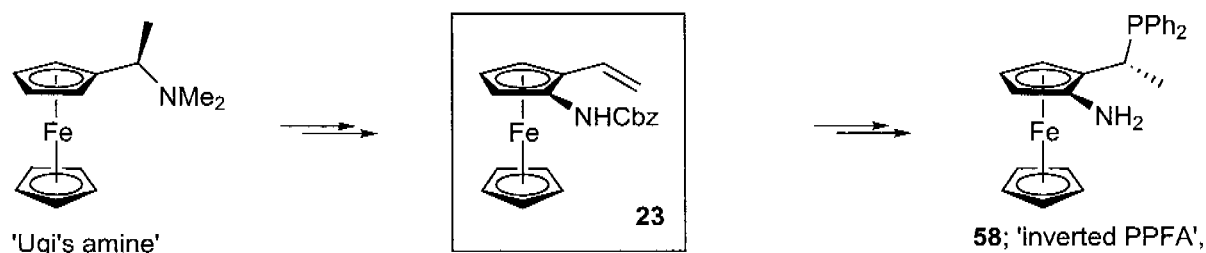
Umsätze: **quantitativ**; Enantiomerenüberschüsse: **bis 18%**.

ABSTRACT

The present thesis deals with establishing a generally applicable synthetic access to planar-chiral aminoferrocenes **A** and with the conversion of the latter to novel, C_2 -symmetrical amidinato- **B** and carbene ligands **C** for asymmetric catalysis. As we were not

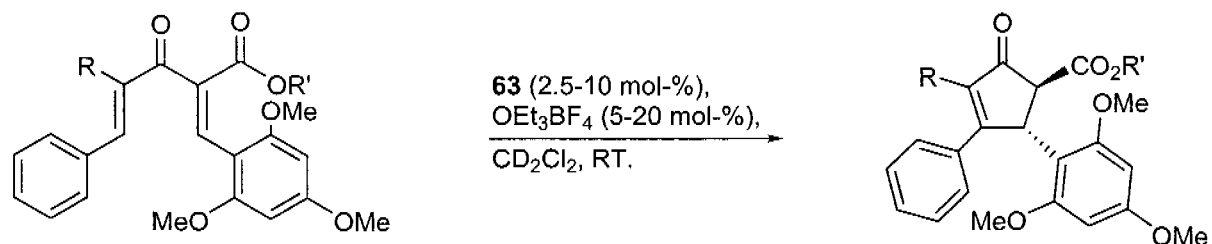
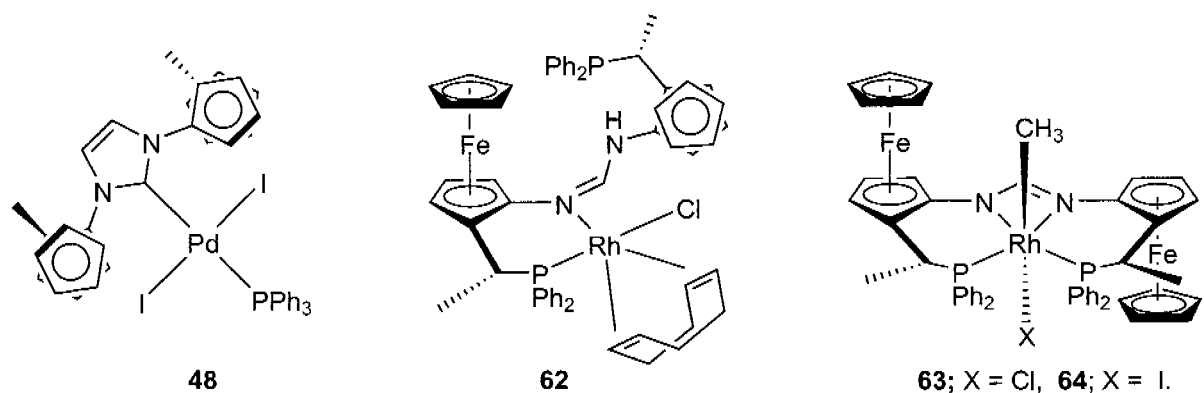


concerned with modifying or optimizing a specific catalytic application, our efforts focused on creating a synthetic building block according to the general formula **A** and on its use for preparing novel bisferrocenyl ligands. The syntheses of latter were based on a geometrical concept, which deals with the specific sterical characteristics of C_2 -symmetrical bisferrocenyl ligands (*chapter 1*). The vinylferrocene **23** proved to be an ideal synthetic intermediate for accessing aminoferrocene based ligands; not only could it be synthesized from the commercially available 'Ugi's amine' [(*R*)-1-ferrocenyl-*N,N'*-dimethylethylamine] (*chapter 2*),



it could also be converted to the phosphine **58**, with the highly diastereoselective addition of diphenylphosphine being the key reaction step of its synthesis. Compound **58** can be described as 'inverted PPFA', with PPFA [(*R*)-*N,N*-dimethyl-1[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethylamine] which is well-known as a synthetic intermediate in the preparation of many successful ferrocenyl ligands. The rich chemistry of polarized olefins allows for proposing the vinyl ferrocene **23** as a general building block for ferrocene chemistry; not only could we realize a diastereoselective addition of a heterocycle to the vinyl functionality, published results with non-chiral vinyl-ferrocenes also show, that such ferrocene derivatives react in cycloaddition reactions and in asymmetric dihydroxylations or oxidative cleavages reactions.

The C_2 -symmetrical ligands in the Pd(II)-complex **48** and in the Rh(I)- and Rh(III)-complexes **62-64** are both derivatives of aminoferrocenes and thereby representatives of the ligand class studied here. Based on a novel synthetic access to sterically hindered carbene ligands, we investigated the coordination chemistry as well as the conformations of monodentate N,N' -bisferrocenylated N -heterocyclic carbenes (*chapter 3*). We found, that complexes such as **48** are active catalysts in asymmetric amide-cyclizations such as developed by *Buchwald* and *Hartwig*, although enantioselectivities are low. This suggests, that more favorable results can only be achieved by reducing the rotatory degrees of freedom of the ligand system. One possibility of solving this problem bases on the use of chelating ligands; Rh-complexes such as the compounds **62-64** not only shed light on the still sparsely explored coordination chemistry of amphoteric amidines as amidine/amidinato-ligands, they also form more rigid structures. Most importantly, corresponding Rh(I)-compounds show potential for the activation of E–H-bonds (E = element), which makes them potential catalysts for hydroamination, hydrosilylation and related reactions (*chapter 4*). The Rh(III)-compounds, on the other hand, can be turned into *Lewis*-acids such as could be shown in the first catalytic asymmetric *Nazarov*-Cyclization of β -ketoesters (*chapter 5*).



conversions: **quantitative**; enantiomeric excesses: up to **18%**.