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Chiral Ferrocene Phosphanyl-carboxylic Ligands
Chirální ferrocenové fosfanyl-karboxylové ligandy

Ph.D. Thesis/Dizertační práce

Praha 2008

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List of publications of the author in impacted journals:

- 1) P. Štěpnička, M. Lamač, I. Císařová *Polyhedron* **2004**, *23*, 921.
- 2) M. Lamač, I. Císařová, P. Štěpnička *J. Organomet. Chem.* **2005**, *690*, 4285.
- 3) M. Lamač, P. Štěpnička *Inorg. Chem. Commun.* **2006**, *9*, 319.
- 4) M. Lamač, I. Císařová, P. Štěpnička *Eur. J. Inorg. Chem.* **2007**, 2274.
- 5) J. Kühnert, M. Lamač, T. Ruffer, B. Walfort, P. Štěpnička, H. Lang *J. Organomet. Chem.* **2007**, *692*, 4303.
- 6) M. Lamač, I. Císařová, P. Štěpnička *Collect. Czech. Chem. Commun.* **2007**, *72*, 985.
- 7) M. Lamač, J. Tauchman, I. Císařová, P. Štěpnička *Organometallics* **2007**, *26*, 5042.
- 8) P. Štěpnička, M. Lamač, I. Císařová *J. Organomet. Chem.* **2008**, *693*, 446.
- 9) C. Bianchini, A. Meli, W. Oberhauser, A. M. Segarra, E. Passaglia, M. Lamač, P. Štěpnička *Eur. J. Inorg. Chem.*, **2008**, 441.
- 10) J. Kühnert, M. Lamač, J. Demel, A. Nicolai, H. Lang, P. Štěpnička *J. Mol. Catal. A: Chem.* **2008**, *285*, 41.
- 11) J. Kühnert, I. Císařová, M. Lamač, P. Štěpnička *Dalton Trans.* **2008**, 2454.
- 12) P. Štěpnička, M. Zábranský, M. Lamač, I. Císařová, P. Němec *J. Organomet. Chem.* **2008**, *693*, 1779.
- 13) M. Lamač, J. Cvačka, P. Štěpnička *J. Organomet. Chem.* **2008**, *693*, 3430.
- 14) P. Štěpnička, M. Zábranský, I. Císařová, M. Lamač *J. Organomet. Chem.* **2008**, in press.

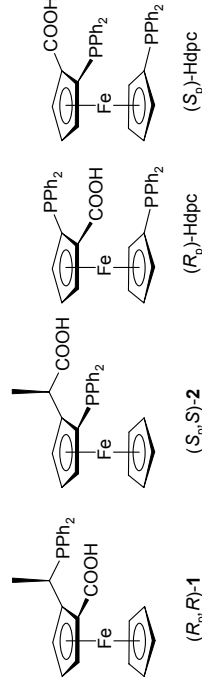
Moreover ...

- co-authored a chapter entitled: "Synthesis and Catalytic Use of Planar Chiral and Polydentate Ferrocene Donors" in: *Ferrocenes: Ligands, Materials and Biomolecules*, P. Štěpnička (Ed.), Wiley, Chichester, 2008.
- the work included in the thesis has been presented at international conferences (three oral presentations, two posters) or national meetings (three oral presentations, one poster)

Summary

The presented thesis was aimed at the synthesis, characterisation, and studies into coordination and catalytic properties of new ferrocene-based phosphanyl-carboxylic ligands (Scheme 1). These hybrid ligands suitably extend the range of derivatives known up-to-date. The combination of phosphorus and oxygen donor atoms allows them to coordinate many transition metals in various modes. Besides, the compounds studied possess planar chirality, optionally accompanied by additional chirality centres present in the attached substituents. Appropriate synthetic protocols were designed and utilised in order to effectively prepare these novel chiral ferrocene ligands in optically pure form. In view of successful applications of many chiral ferrocene derivatives in catalysis,¹ the prepared compounds were tested in palladium-mediated enantioselective allylic alkylation.²

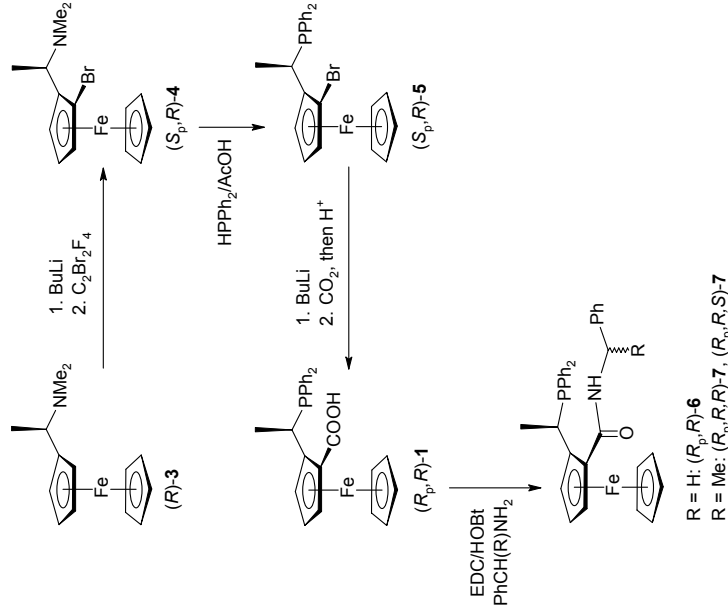
The acids (*R_p,R*)-**1** and (*R_p*)/(*S_p*)-Hdpc (Scheme 1) were prepared by the described synthetic procedures in optically pure form either by the approach involving the functionalisation of a derivative bearing chiral *ortho*-directing group, or by the resolution of a racemic product via temporary attachment of a chiral auxiliary and separation of the diastereoisomeric intermediates.



(*R_p*)-2-[(*R*)-1-(diphenylphosphany)ethyl]ferrocenecarboxylic acid (**1**), a ligand combining planar and central chirality, was synthesised as depicted in Scheme 2. Acid **1** is a homologue to the previously reported racemic 2-[(diphenylphosphany)methyl]ferrocenecarboxylic acid.³ Synthesis of **1** began with diastereoselective *ortho*-lithiation and bromination of chiral amine **3**. The resulting bromo-amine **4** was subsequently phosphorylated as previously described by Giambastiani et al.⁴ In the last step, bromide **5** was lithiated and the intermediate immediately carboxylated with an excess of solid carbon dioxide, to give, after acidification and work-up, acid **1**. In addition, an alternative route to the devised involving protection of the phosphane group through its conversion to the corresponding phosphane sulfide.

Modifications at both functional groups in **1** afforded a series of closely related derivatives. Apart from the above mentioned phosphane sulphide, also phosphane oxide was

prepared and its solid state structure determined by X-ray diffraction. Finally, amidation of the carboxyl group with both achiral and chiral amines yielded amides **6** and **7**, respectively.



Scheme 2 (EDC = *N*-ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide, HOBt = 1-hydroxybenzotriazole)

In order to study coordination properties of **1** and the related compounds, some rhodium and palladium complexes were prepared. Firstly, a bridge-cleavage of $[\{\text{Rh}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)_2\}_2]$ with **1** gave complex **8** (Scheme 3) featuring *P*-monodentate **1**. Compound **8** underwent smooth conversion to phosphanyl-carboxylate complex **9** upon treatment with silica gel or alumina. *O,P*-Chelating coordination of the phosphanyl-carboxylate was also achieved in the rhodium(I) complex **10** that resulted from acid-base displacement of acetylacetonate (acac) ligand in $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$. Solid-state structures of complexes **8** and **10** were determined by single-crystal X-ray diffraction. The coordination behaviour of amides was probed on palladium(II). Thus, amide **6** displaced the cycloocta-1,5-diene (cod) ligand in $[\text{PdCl}(\text{Me})(\text{cod})]$, affording the chelate complex **11**, the crystal structure of which was established by the X-ray diffraction.

Abstract: Interaction of (S_p) -2-(diphenylphosphino)ferrocenecarboxylic acid [(S_p)-**1**] with *N,N'*-dicyclohexylcarbodiimide (DCC) and *N*-ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide (EDC) have been investigated in order to study the reacting system itself and to characterise side-products typically arising during the diimide-promoted condensation of acid (S_p)-**1** with nucleophiles. The reaction between (S_p)-**1** and DCC was found to give preferentially the respective urea derivative in the absence of a base, and (S_p)-2-(diphenylphosphino)ferrocenecarboxylic anhydride [(S_p, S_p)-**3**] when the same reaction was performed in the presence of 4-(dimethylamino)pyridine (DMAP). With EDC, the preference for a reaction pathway was less pronounced: whereas the reaction without the base afforded exclusively the corresponding urea, that in the presence of DMAP yielded a mixture of the urea and anhydride (S_p, S_p)-**3**.

6) M. Lamač, I. Čisafová, P. Štěpnička: "Preparation of planar-chiral carboxylated dpfp analogues, a study into their coordination behavior and application to palladium-catalyzed asymmetric allylic alkylation" – submitted for publication in *Organometallics*

Abstract: A novel polar dpfp derivative possessing only planar chirality, 1',2'-bis(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpc) has been synthesized in racemic form and resolved to pure enantiomers via diastereomeric esters with D-glucose diacetone ((R_p)- and (S_p)-**3**). The enantiomer (R_p)-Hdpc was further converted to a series of *N*-substituted amides. All donors were studied as ligands to enantioselective allylic alkylation of racemic (*E*)-1,3-diphenylprop-2-en-1-yl acetate or carbonate with dialkyl malonates, showing high activity and good enantioselectivity (ee's up to 80 %). The obtained catalytic results were rationalized in view of structural data (NMR and X-ray crystallography) for (η^3 -allyl)palladium(II) complex (R_p)- $[\text{Pd}(\eta^3\text{-1,3-Ph}_2\text{C}_3\text{H}_3)\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5\text{-1-(CONHCH}_2\text{Ph)}_2\text{-2-(PPH}_2\text{-}\kappa\text{P})\})\text{ClO}_4$ (**17**), serving as a model of the plausible reaction intermediate, and the results reported for some related ligands. The available data indicate that the reaction course is governed largely by steric factors and planar chirality at the ferrocene unit, the amide substituent having only minor influence. A further study into coordination properties of Hdpc led to isolation of $[\text{PdCl}_2(\text{Hdpc-}\kappa^2\text{P,P'})]$ (**12**) and $[\{\text{Pd}(\mu\text{-Cl})(\text{Hdpc-}\kappa^2\text{P,P'})\}_2]$ (**13**). The close structural relationship between dpfp and Hdpc was corroborated by X-ray diffraction analysis of *rac*-Hdpc, methyl ester of (R_p)-Hdpc ((R_p)-**5**), glycoside (R_p)-**3**, and the solvated complex **12-Me}_2\text{CO}**.

diffraction. Catalytic properties of **1** and the amides were probed in enantioselective rhodium-catalyzed hydrogenation and palladium-catalyzed asymmetric allylic alkylation.

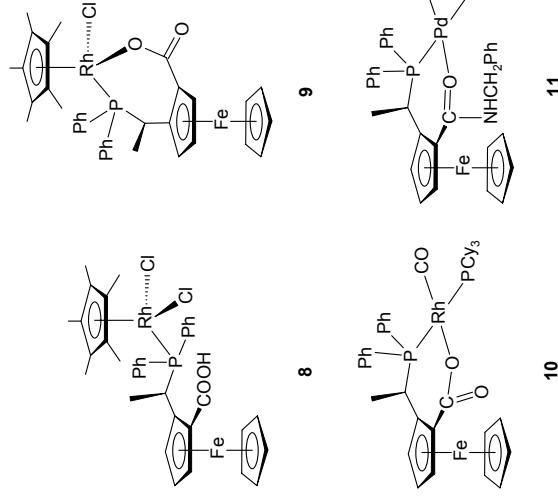
3) M. Lamač, I. Císařová, P. Štěpnička: "Stereoselective methylation of 1-(diphenylphosphanyl)-2-[(methoxycarbonyl)methyl]ferrocene. The crystal structures of the methylated ester and its palladium(II) complex with an auxiliary 2-[(dimethylamino)methyl]phenyl ligand." *Collect. Czech. Chem. Commun.* **2007**, *72*, 985.

Abstract: Treatment of racemic 1-(diphenylphosphanyl)-2-[(methoxycarbonyl)methyl]ferrocene successively with $\text{NaN}(\text{SiMe}_3)_2$ and methyl iodide gives the C-alkylated product, 1-(diphenylphosphanyl)-2-[1-(methoxycarbonyl)ethyl]ferrocene (**6**) as a mixture of diastereoisomers in ca. 10:1 ratio, from which the major (S_p/R_p)-diastereoisomer is easily isolated by crystallisation. Ester (S_p/R_p)-**6** reacts with $[\text{L}^{\text{NC}}\text{Pd}(\text{NCMMe}_2)\text{ClO}_4]$ ($\text{L}^{\text{NC}} = 2$ -[(dimethylamino- κ^N)phenyl- κ^C]) to give the cationic bis-chelate complex (S_p/R_p)-**9** [$\text{L}^{\text{NC}}\text{Pd}(\text{6-}\kappa^2\text{O,P})\text{ClO}_4$]. The structures of (S_p/R_p)-**6** and **9** have been determined by single-crystal X-ray diffraction. Hydrolysis of ester **6** to the corresponding carboxylic acid proved to be difficult, complicated by racemisation at the newly created stereogenic carbon atom and oxidation of the phosphane group.

4) M. Lamač, J. Tauchman, I. Císařová, P. Štěpnička: "Preparation of Chiral Phosphinoferrocene Carboxamide Ligands and Their Application to Palladium-Catalyzed Asymmetric Allylic Alkylation" *Organometallics* **2007**, *26*, 5042.

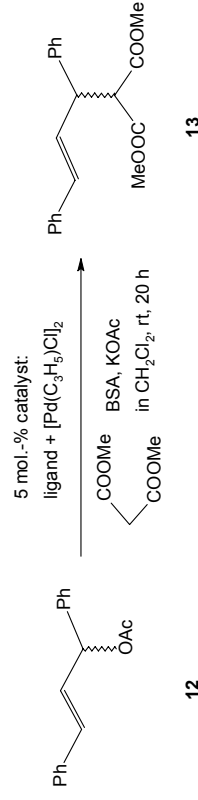
Abstract: A series of phosphinoferrocene-carboxamides bearing achiral (benzyl) and chiral [(R_p)- and (S_p)-1-phenylethyl] substituents at the amide nitrogen has been prepared from 1'-(diphenylphosphino)ferrocenecarboxylic acid (Hdppf) and (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid (S_p -**1**) and tested as ligands for enantioselective allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate. At room temperature, the alkylation reactions proceeded with complete conversions and ee's up to 90%, the most efficient being the planar-only chiral ligand (S_p)-2-(diphenylphosphino)-1-(N -benzylcarbamoyl)ferrocene ((S_p)-**2**). The crystal structures of (S_p)-**2** and cationic (η^3 -allyl)palladium(II) complex $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})\{(\text{S}_p)\text{-2-}\kappa^2\text{O,P}\}\text{ClO}_4]$ ((S_p)-**8**) have been determined by single-crystal X-ray diffraction and confronted with the solution NMR data to provide an insight into the mechanism of chiral discrimination.

5) M. Lamač, J. Cvačka, P. Štěpnička: "The reaction of (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid with carbodiimide reagents: Characterisation of the acid anhydride and urea products" *J. Organomet. Chem.* **2008**, *693*, 3430.



Scheme 3

Catalytic properties of the newly prepared ligands (acid **1**, and its amides **6** and **7**) were probed in palladium-catalyzed allylic alkylation of racemic (E)-1,3-diphenylprop-2-en-1-yl acetate (**12**) with dimethyl malonate anion (Scheme 4). The results summarised in Table 1 indicate only modest asymmetric induction and a considerable difference between free acid and its amides.



Scheme 4 Asymmetric allylic alkylation (BSA = N,O -bis(trimethylsilyl)acetamide)

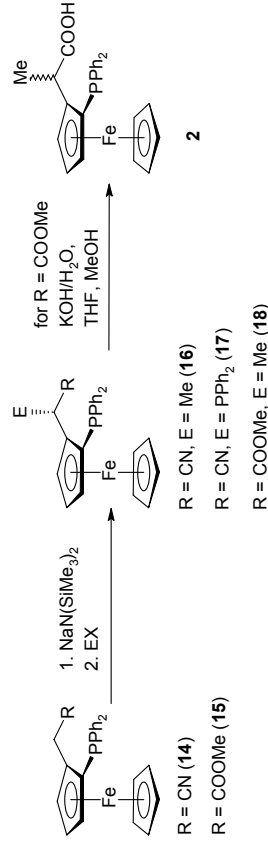
Table 1

Entry	Ligand	conversion (isolated yield) [%] ^[a]	ee [%] (configuration) ^[b]
1	(R_p,R)- 1	100 (94)	10 (S)
2	(R_p,R)- 6	55	41 (R)
3	(R_p,R,R)- 7	42	43 (R)
4	(R_p,R,S)- 7	22	35 (R)

[a] Conversion determined by ^1H NMR spectroscopy.

[b] Absolute configuration assigned on the basis of sign of the optical rotation.

The following work was focused on the preparation of (*S*)-2-[(*S*_p)-2-(diphenylphosphanyl)ferrocenyl]propionic acid (**2**), a homologue to previously prepared [2-(diphenylphosphanyl)ferrocenyl]acetic acid.⁵ The application of synthetic procedure similar to the preparation of the homologous compound was not successful due to different reactivity of some reaction intermediates. Instead, an alternative approach had to be used, leading to racemic but diastereomerically pure products. It was found, that α -deprotonation of racemic [2-(diphenylphosphanyl)ferrocenyl]acetonitrile (**14**) or ester **15** with NaN(SiMe₃)₂ proceeds with high diastereoselectivity, and this opens a route to products **16-18** via a subsequent reactions of the formed carbanion with electrophiles (Scheme 5). The resulting ester **18** was utilised in the preparation of the cationic chelate palladium complex, (*S*,*R*_p)/(*R*,*S*_p)-[(C₆H₄CH₂NMe₂- κ^2 -C¹,*P*)Pd(**18**- κ^2 -O,*P*)]ClO₄, featuring an *ortho*-metalated auxiliary ligand. Unfortunately, the hydrolysis of nitriles was entirely unsuccessful, while in the case of ester **18**, it was complicated by racemisation at the newly created stereogenic carbon atom and by concomitant oxidation of the phosphanyl group.



Scheme 5

In view of the previous results, the following work was devoted to the preparation of amides from the known ferrocene based phosphanyl-carboxylic acids and their testing as ligands for asymmetric allylic alkylation (Scheme 4). Thus, a series of ligands comprising (*S*_p)-2-(diphenylphosphanyl)ferrocenecarboxylic acid (**19**),⁶ its amides (**20**, Scheme 6), as well as two other *C*-chiral amides (**21**) derived from Hdpf (1'-(diphenylphosphanyl)ferrocenecarboxylic acid)⁷ was studied. The results (summarised in Table 2) clearly indicated the dominant role of planar chirality on the stereoselectivity of the alkylation reaction, as amides **21** exhibited no stereogenic induction at all while their planar chiral counterparts gave moderate to good *ee*'s. Subsequent modification of the reaction conditions allowed for *ee* as high as 90 % with ligand **20a**. The suggested reaction mechanism for this ligand was confronted with the NMR spectroscopic and X-ray structural data of the model complex [Pd-(η^3 -1,3-Ph₂C₃H₃)(*S*_p)-**20a**- κ^2 -O,*P*}]ClO₄ (**22**).

Published articles/manuscripts included in the thesis

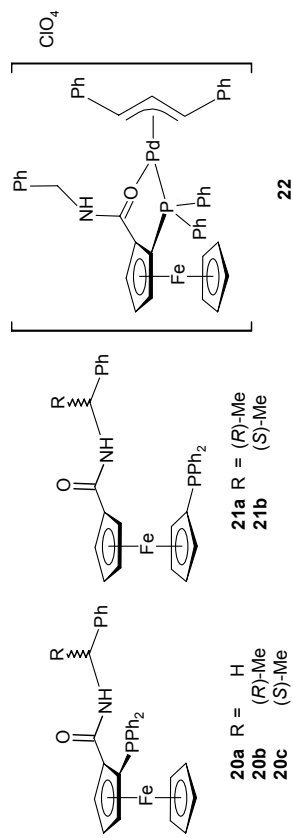
- 1) M. Lamač, P. Štěpnička: "Stereoselective alkylation of [2-(diphenylphosphino)ferrocenyl]acetonitrile" *Inorg. Chem. Commun.* **2006**, *9*, 319.

Abstract: Deprotonation of racemic [2-(diphenylphosphino)ferrocenyl]acetonitrile (**1**) with NaN(SiMe₃)₂ in THF followed by reaction with electrophiles MeI and Ph₂PCl affords the substituted nitriles, 2-[2-(diphenylphosphino)ferrocenyl]propionitrile (**2a**) and 2-(diphenylphosphino)-[2-(diphenylphosphino)ferrocenyl]acetonitrile (**2b**), respectively. Whereas the former reaction yields a 15:1 mixture of isomers differing in configuration at the alkylated α -carbon from which the major diastereoisomer can be isolated by simple recrystallization, the latter gives **2b** as a single diastereoisomer. The dominating product of the methylation reaction was characterized by X-ray diffraction analysis as (*S*,*R*_p/*R*,*S*_p)-**2a**, which is in accordance with the possible access of the electrophile towards deprotonated **1**.

- 2) M. Lamač, I. Čisarová, P. Štěpnička: "Synthesis, Coordination and Catalytic Utilization of Novel Ferrocene Phosphanylcarboxylic Ligands Combining Planar and Central Chirality" *Eur. J. Inorg. Chem.* **2007**, 2274.

Abstract: Chiral ferrocene phosphanylcarboxylic acid, (*R*,*R*_p)-2-[1-(diphenylphosphanyl)-ethyl]ferrocenecarboxylic acid (**1**), was prepared together with its selected derivatives obtained by modification (a) at the phosphane moiety (P-oxide (**5**) and P-sulfide (**4**)), and (b) at the carboxyl group (amides with benzyl (**6**) and (*R*)- or (*S*)-1-phenylethyl substituents ((*R*)-**7** and (*S*)-**7**) at the amide nitrogen). Acid **1** and amide **6** were studied as ligands in rhodium and palladium complexes, respectively. Thus, bridge-cleavage of [{Rh(μ -Cl)(η^5 -C₅Me₅)₂] with **1** gave [RhCl(η^5 -C₅Me₅)(**1**- κ *P*)] (**9**) featuring P-monodentate **1**, which underwent smooth conversion to phosphanylcarboxylate complex [RhCl(η^5 -C₅Me₅){Fe(η^5 -C₃H₃(η^5 -C₃H₃-1-CH(Me)PPh₂-2-COO- κ^2 -O,*P*)} (**10**) upon treatment with silica gel or alumina. Yet another O,*P*-chelating complex, [Rh{Fe(η^5 -C₅H₅(η^5 -C₅H₅-1-CH(Me)PPh₂-2-COO- κ^2 -O,*P*)}(CO)(PCy₃)] (**11**), was obtained directly via acid-base displacement of acetylacetonate from [Rh(acac)(CO)(PCy₃)] and **1**. Amide **6** reacted with [{Pd(μ -Cl)(η^3 -C₃H₃)₂] to give the expected phosphane complex [PdCl(η^3 -C₃H₃)(**6**- κ *P*)] (**12**) while the replacement of cyclooctadiene (cod) ligand in [PdCl(Me)(cod)] afforded the chelate complex [PdCl(Me)(**6**- κ^2 -O,*P*)] (**13**). All compounds were characterized by spectral methods and the solid-state structures of **5**, **9**, **11**, **13**, (*R*,*S*_p)-2-[1-(diphenylphosphoryl)ethyl]-1-[*N*-(*R*)-(1-phenylethyl)carbamoyl]ferrocene (*R*)-**8**, phosphane oxide from (*R*)-**7**), and of the synthetic precursors (*R*,*S*_p)-2-[1-(diphenylphosphanyl)ethyl]bromoferrocene (**2**) and (*R*,*S*_p)-2-[1-(diphenylthiophosphoryl)ethyl]bromoferrocene (**3**) were determined by single-crystal X-ray

- (a) J. M. Longmire, B. Wang, X. Zhang *Tetrahedron Lett.* **2000**, *41*, 5435. (b) P. Štěpnička *New. J. Chem.* **2002**, *26*, 567. (c) S.-L. You, X.-L. Hou, L.-X. Dai, B.-X. Cao, J. Sun *Chem. Commun.* **2000**, 1933.
- J. Podlaha, P. Štěpnička, I. Čisárová, J. Ludvík *Organometallics* **1996**, *15*, 543.
- 2,2'-Bis(difénylfosfanyl)ferrocen-1,1'-dikarboxylová kyselina je známa pouze ve formě svých esterů a amidů: (a) W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda *Tetrahedron Lett.* **1996**, *37*, 7995. (b) W. Zhang, T. Shimanuki, T. Kida, Y. Nakatsuji, I. Ikeda *J. Org. Chem.* **1999**, *64*, 6247. (c) R. Laufer, U. Veith, N. J. Taylor, V. Snieckus *Org. Lett.* **2000**, *2*, 629.
- I. R. Butler, S. Müssig, M. Plath *Inorg. Chem. Commun.* **1999**, *2*, 424.
- (a) B. Schetter, B. Speiser *J. Organomet. Chem.* **2004**, *689*, 1472. (b) A. Cooke, A. Radhi, N. Boden, R. J. Bushby, Z. Lu, S. Brown, S. L. Heath *Tetrahedron* **2000**, *56*, 3385. (c) B. Schetter *Z. Anorg. Chem.* **2004**, *630*, 1074. (d) K. Heinze, M. Schlenker *Eur. J. Inorg. Chem.* **2004**, 2974.



Scheme 6

Table 2

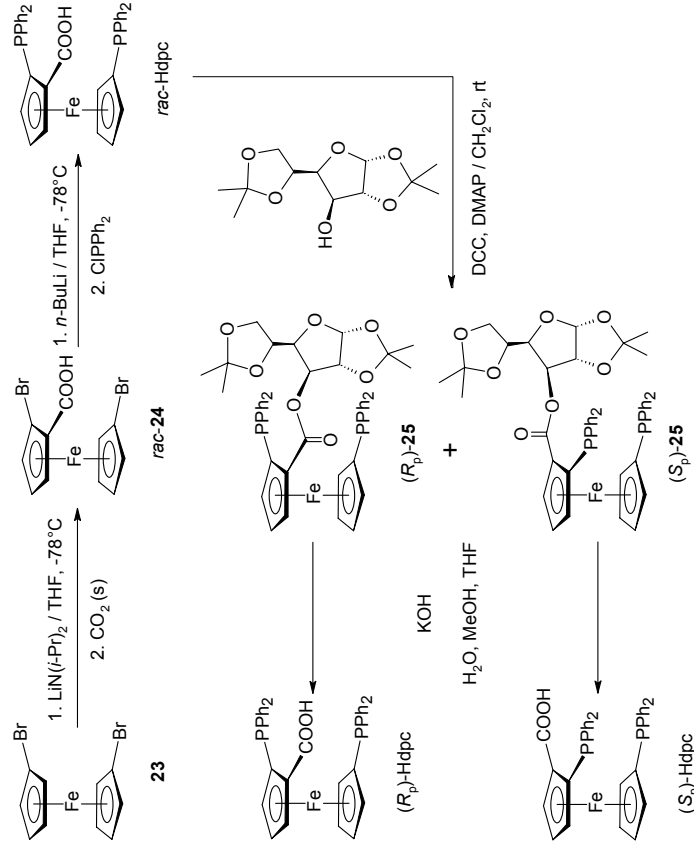
Entry	Ligand	T (°C)	Time (h)	Additive	Conversion (%) ^[a]	ee (%) [config.] ^[b]
1	(S _p)- 19	22	20	KOAc	100 (91)	50 [R]
2	(S _p)- 20a	22	20	KOAc	100 (91)	58 [R]
3	(R _s ,S _p)- 20b	22	20	KOAc	100 (97)	49 [R]
4	(S _s ,S _p)- 20c	22	20	KOAc	100 (95)	21 [R]
5	(R)- 21a	22	20	KOAc	100 (90)	0
6	(S)- 21b	22	20	KOAc	100 (92)	0
7	(S _p)- 20a	22	20	none	85	90 [R]
8	(S _p)- 20a	22	20	LiOAc	100	48 [R]
9	(S _p)- 20a	22	20	NaOAc	100	84 [R]
10	(S _p)- 20a	0	42	NaOAc	41	88 [R]
11	(S _p)- 20a	22	20	KOAc	100	58 [R]
12	(S _p)- 20a	22	20	RbOAc	100	44 [R]
13	(S _p)- 20a	22	20	CsOAc	100	49 [R]

[a] Conversion determined by ¹H NMR spectroscopy.

[b] Absolute configuration assigned on the basis of sign of the optical rotation.

As a next step in the exploration of carboxyphosphane ligands, a *monocarboxylated* dppf derivative (dppf = 1,1'-bis(diphenylphosphanyl)ferrocene), 1',2'-bis(diphenylphosphanyl)ferrocene-1-carboxylic acid (Hdpc) was prepared and studied. Hdpc fills the gap left between Hdppf, its planar chiral isomer (S_p)-2-(diphenylphosphanyl)ferrocenecarboxylic acid (**19**), and C₂-symmetric 2,2'-bis(diphenylphosphanyl)ferrocene-1,1'-dicarboxylic acid.⁸ The preparation of Hdpc (Scheme 7) starts with the readily available 1,1'-dibromoferrocene (**23**), which is *ortho*-lithiated and carboxylated to yield racemic acid **24**, as previously

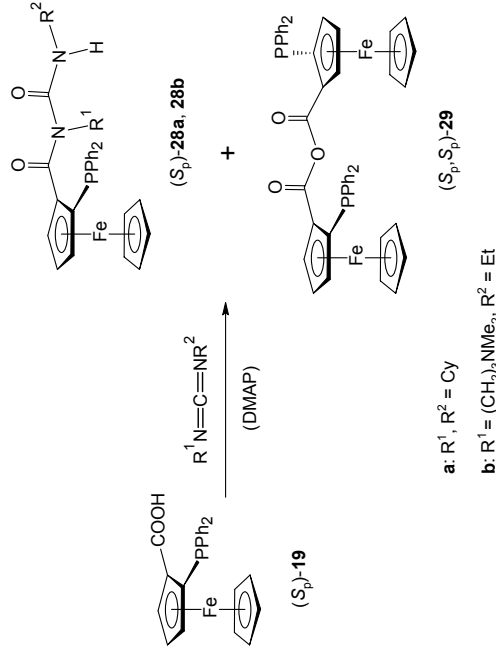
described by Butler et al.⁹ After another metalation step and subsequent phosphorylation, the racemic Hdpc was obtained, which was resolved to its enantiomers via diastereomeric esters with D-glucose diacetone. The diastereomeric glycosides **25** were prepared by the carbodiimide promoted coupling of Hdpc to 1,2:5,6-diisopropylidene-D-glucofuranose (glucose diacetone) in the presence of 4-(dimethylamino)pyridine and separated by combined chromatography and crystallisation. Subsequently, the glycosides were hydrolysed to give the corresponding Hdpc enantiomers. The solid-state structures of *rac*-Hdpc, the glucofuranoside (*R_p*)-**25**, and the methyl ester (*R_p*)-Medpc (resulting as a by-product during hydrolysis of the glycoside) were determined by the X-ray diffraction analysis.



Scheme 7 (DCC = *N,N*-dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine)

The coordination properties of racemic Hdpc were probed in palladium(II) complexes. The complex *rac*-[PdCl₂(Hdpc-κ²-P:P')] resulted from the reaction of *rac*-Hdpc with [PdCl₂(cod)], and its solid-state structure was determined. The complex also served as a precursor for the chloride-bridged dimer [(μ-Cl)₂{Pd(Hdpc-κ²-P:P')}₂](BF₄)₂ that was obtained upon chloride abstraction with the silver salt as a mixture of *rac*- and *meso*-isomers.

v přítomnosti 4-(dimethylamino)pyridinu (DMAP) jako báze vzniká příslušný anhydrid kyseliny **29**, který je dominantním produktem v případě DCC, zatímco reakce s použitím EDC dává vzniknout směsi anhydridů s močovinovým derivátem. Na základě popsaných pozorování byl navržen pravděpodobný mechanismus reakce, který je rovněž ve shodě se závěry dříve publikovaných studií týkajících se příbuzných sloučenin.¹⁰



Scheme 13 (DMAP = 4-(dimethylamino)pyridin, Cy = cyklohexyl)

Literatura:

1. Zevrubné přehledy tematicky: (a) *Ferrocenes: Ligands, Materials and Biomolecules*, P. Štěpnička (Ed.), Wiley, Chichester, 2008. (b) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, A. Togni, T. Hayashi (Ed.), VCH, Weinheim, 1995.
2. Přehledné články: (a) T. Hayashi: *Asymmetric Allylic Substitution and Grignard Cross-coupling in Catalytic Asymmetric Synthesis*, ed. I. Ojima, kap. 7.1, 325-365, VCH, New York 1993. (b) B. M. Trost, D. L. Van Vranken *Chem. Rev.* **1996**, 96, 395. (c) B. M. Trost, M. L. Crawley *Chem. Rev.* **2003**, 103, 2921. (d) B. M. Trost *J. Org. Chem.* **2004**, 69, 5813.
3. M. Lamač, I. Čísařová, P. Štěpnička *J. Organomet. Chem.* **2005**, 690, 4285.
4. P. Barbaro, C. Bianchini, G. Giambastiani *Synthesis* **2005**, 2445.
5. P. Štěpnička, I. Čísařová *Organometallics* **2003**, 22, 1728.

Tabulka 3 Asymetrická allylová alkylace s ligandy (*R_p*)-Hdpc, **25**, **26**.^[a]

reakce	ligand	ee (%) [konfig.]
1	(<i>R_p</i>)-Hdpc	+54 [R]
2	(<i>R_p</i>)- 25	+65 [R]
3	(<i>S_p</i>)- 25	-60 [S]
4	(<i>R_p</i>)- 26a	+60 [R]
5	(<i>R_p</i>)- 26b	+55 [R]
6	(<i>R,R</i>)- 26c	+67 [R]
7	(<i>S,S</i>)- 26d	+60 [R]
8	(<i>R_p</i>)- 26e	+58 [R]
9	(<i>R_p</i>)- 26f	+58 [R]
10	komplex ^[b]	+49 [R]

[a] Konverze ve všech případech kvantitativní po 20 h.

[b] Reakce provedena s použitím komplexu (*R_p*)-**27**.

Tabulka 4 Optimalizace reakčních podmínek pro ligand (*S,S*)-**26c**^a

reakce	T (°C)	báze	ee (%) [konfig.]
1	22	LiOAc	+52 [R]
2	22	NaOAc	+67 [R]
3	22	KOAc	+66 [R]
4	22	RbOAc	+68 [R]
5	22	CsOAc	+68 [R]
6	22	–	+57 [R]
7	0	NaOAc	+67 [R]
8 ^b	22	NaOAc	+65 [R]
9 ^c	22	NaOAc	+80 [R]

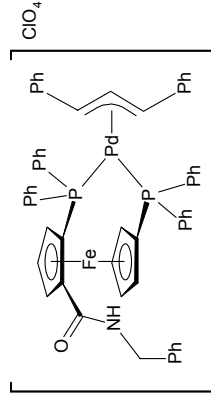
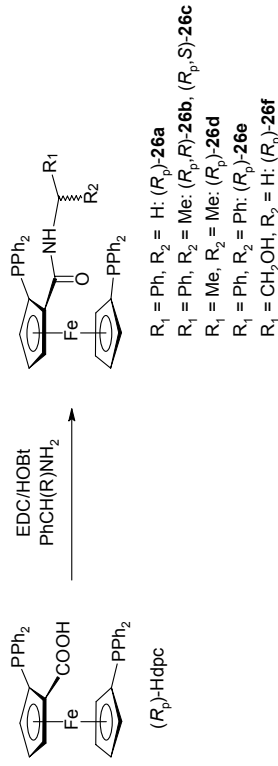
[a] Konverze byly kvantitativní kromě reakce 9 (93 %).

[b] Reakce byla provedena s ethyl-(*E*)-1,3-difenyprop-2-en-1-yl karbonátem.

[c] Reakce byla provedena s di-*t*-butyl malonátem jako nukleofilem.

Jako další příspěvek k problematice popisované v této práci byla studována reaktivita v systémech fosfanyl-karboxylová kyselina/karbodiimid. Cílem bylo optimalizovat reakční podmínky a zamezit vzniku nežádoucích vedlejších produktů při přípravách derivátů karboxylových kyselin – esterů a amidů. Jako zástupce první skupiny reaktantů byla zvolena (*S_p*)-2-(difenyfosfanyl)ferrocenkarboxylová kyselina a dva běžně používané karbodiimidy: *N*-ethyl-*N'*-[3-(dimethylamino)propyl]karbodiimid (EDC) a *N,N'*-dicyklohexylkarbodiimid (DCC). Bylo zjištěno, že reakce bez přítomnosti báze a nukleofilu poskytuje přednostně substituované *N*-acylmočoviny (**28**, schema 9) v případě obou diimidů. Naopak

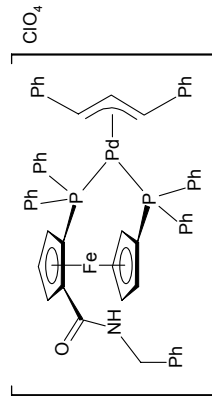
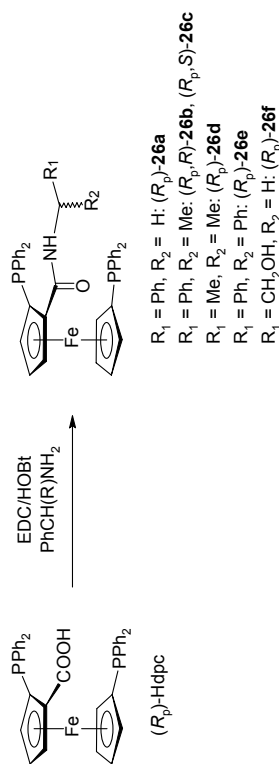
Furthermore, (*R_p*)-Hdpc was converted to a series of secondary amides with substituents at the amide nitrogen differing in steric properties and, optionally, also in chirality of the side chain (**26**, Scheme 8). As a model for the anticipated intermediate in allylic substitution reaction, the cationic η³-1,3-diphenylallyl complex (**27**) was prepared and its structure determined by X-ray diffraction.

**Scheme 8** (EDC = *N*-ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide, HOBT = 1-hydroxybenzotriazole)

The catalytic tests (for results, see Tables 3 and 4) were performed again on the palladium mediated asymmetric allylic alkylation of (*E*)-1,3-diphenylprop-2-en-1-yl acetate (or ethyl-(*E*)-1,3-diphenylprop-2-en-1-yl carbonate), using dimethyl (or di-*t*-butyl) malonate/base as the nucleophile, and 3 mol.-% of the catalyst formed *in situ* from the corresponding ligand and {Pd(μ-Cl)(η³-C₃H₅)₂}.

All amides of the series, as well as the parent acid Hdpc and the diastereomeric glycosides were involved in the testing, which revealed only minor differences in the selectivity of the reaction caused predominantly by steric factors. The *ee* values observed for the whole series of ligands were moderate, while the highest value of 80 % was obtained with the more sterically demanding nucleophile, di-*t*-butyl malonate.

Dále byla (*R_p*)-Hdpc převedena na sérii sekundárních amidů (**26**, schema 8) se substituenty s různými sterickými vlastnostmi a případně chiralitou. Jako model s předpokládanou strukturou reakčního intermediátu allylové substituce byl připraven kationtový komplex **27** s η³-1,3-difenylallylovým ligandem, jehož struktura byla určena rentgenovou difrakcí.



Schema 12 (EDC = *N*-ethyl-*N'*-[3-(dimethylamino)propyl]karbodiimid, HOBT = 1-hydroxybenzotriazol)

Katalytické testy byly provedeny opět v palladiem katalyzované asymetrické allylové alkykaci (*E*)-1,3-difenylprop-2-en-1-yl-acetátu (nebo ethyl-(*E*)-1,3-difenylprop-2-en-1-yl-karbonátu) za použití dimethyl- (nebo di-*t*-butyl-) malonátu/báze jako nukleofilu a 3 mol.-% katalyzátoru vytvořeného *in situ* z příslušného ligandu a dimerního prekurzoru [$\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)_2\}_2$].

Celá série amidů, stejně jako výchozí kyselina Hdpc a diastereomerní glykosidy byly testovány v uvedené reakci. Výsledky ukázaly jen poměrně malé rozdíly v selektivě, způsobené především sterickými faktory. Hodnoty enantiomerních přebytků pozorované v sérii ligandů dosahovaly průměrných hodnot, přičemž nejlepší výsledek (80 % *ee*) byl dosažen se stericky náročným nukleofilem, di-*t*-butyl-malonátem.

Table 3 Asymmetric allylic alkylation with ligands (*R_p*)-Hdpc, **25**, **26**.^[a]

entry	ligand	ee (%) [config]
1	(<i>R_p</i>)-Hdpc	+54 [<i>R</i>]
2	(<i>R_p</i>)- 25	+65 [<i>R</i>]
3	(<i>S_p</i>)- 25	-60 [<i>S</i>]
4	(<i>R_p</i>)- 26a	+60 [<i>R</i>]
5	(<i>R_p</i>)- 26b	+55 [<i>R</i>]
6	(<i>R,R</i>)- 26c	+67 [<i>R</i>]
7	(<i>S,R</i>)- 26d	+60 [<i>R</i>]
8	(<i>R_p</i>)- 26e	+58 [<i>R</i>]
9	(<i>R_p</i>)- 26f	+58 [<i>R</i>]
10	complex ^[b]	+49 [<i>R</i>]

[a] In all cases, conversions were quantitative after 20 h.

[b] The reaction was performed in the presence of the complex (*R_p*)-**27**.

Table 4 Optimisation of the Reaction Conditions with Ligand (*S,R_p*)-**26c**^a

entry	<i>T</i> (°C)	base	ee (%) [config]
1	22	LiOAc	+52 [<i>R</i>]
2	22	NaOAc	+67 [<i>R</i>]
3	22	KOAc	+66 [<i>R</i>]
4	22	RbOAc	+68 [<i>R</i>]
5	22	CsOAc	+68 [<i>R</i>]
6	22	none	+57 [<i>R</i>]
7	0	NaOAc	+67 [<i>R</i>]
8 ^b	22	NaOAc	+65 [<i>R</i>]
9 ^c	22	NaOAc	+80 [<i>R</i>]

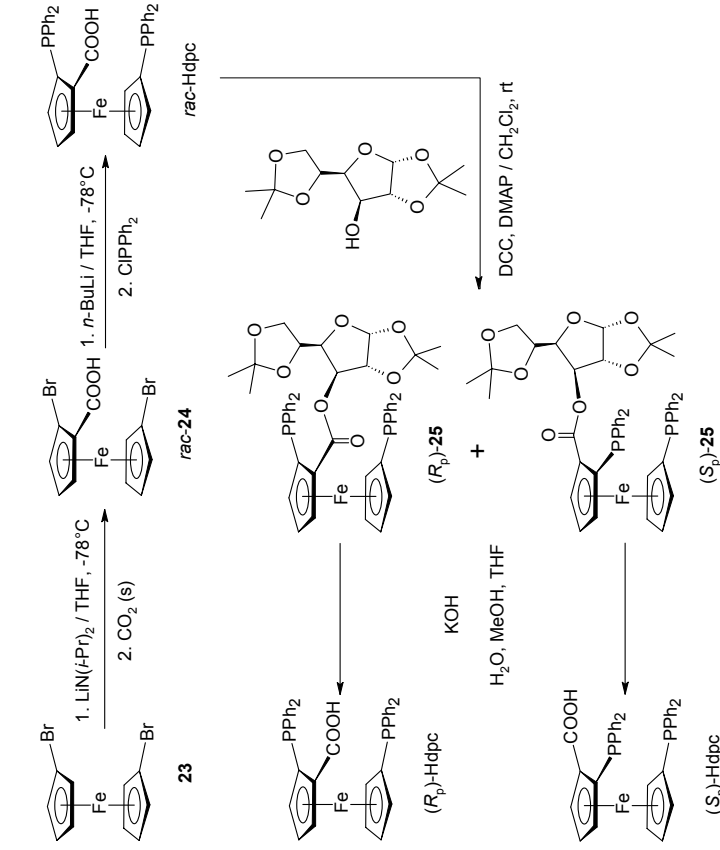
[a] The conversions were quantitative with the exception of entry 9 (93 %).

[b] The reaction was performed with ethyl-(*E*)-1,3-difenylprop-2-en-1-yl carbonate.

[c] The reaction was performed with di-*t*-butyl malonate as the nucleophile.

As an additional contribution to the topic of this thesis, the reactivity in systems phosphanyl-carboxylic acid/carbodiimide was explored in order to optimise the reaction conditions and to avoid the formation of ferrocenyl ureas as undesired side-products during the preparation of carboxylic acid derivatives – esters and amides. As the studied subject, (*S_p*)-2-(diphenylphosphanyl)ferrocenecarboxylic acid (**19**) and two commonly used carbodiimides: *N*-ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide (EDC) and *N,N'*-

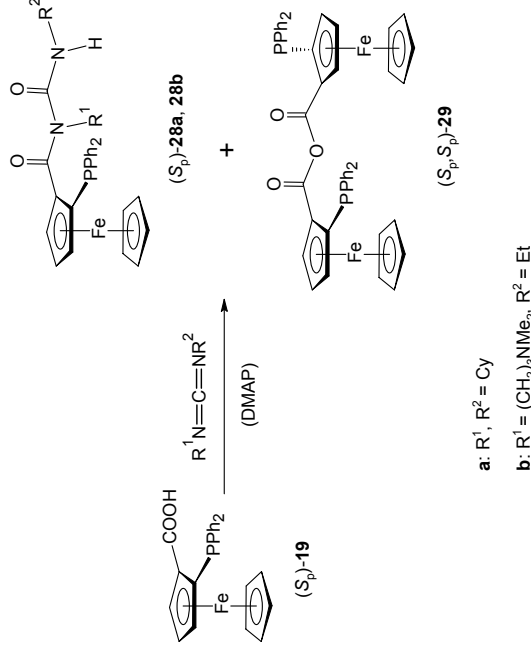
fosfanylaci byla získána racemická Hdpc, která byla následně rozštěpena na enantiomery přes diastereomerní estery s diacetonidem D-glukózy. Diastereomerní glykosidy **25** byly připraveny reakcí Hdpc s 1,2:5,6-diisopropyliden-D-glukofuranosou za přítomnosti *N,N'*-dicyklohexylcarbodiimidu a 4-(dimethylamino)pyridinu a následně separovány kombinací chromatografie a krystalizace. Glykosidy byly hydrolyzovány za vzniku příslušných enantiomerů kyseliny Hdpc. Krystalové struktury racemické Hdpc, glukofuranosidu (*R_p*)-**25** a methylesteru (*R_p*)-Medpc (vzniklého jako vedlejší produkt během hydrolyzy glykosidu **25**) byly určeny rentgenovou difrakcí.



Scheme 11 (DCC = *N,N'*-dicyklohexylcarbodiimid, DMAP = 4-(dimethylamino)pyridin)

Koordináční vlastnosti racemické Hdpc byly zkoumány v palladnatých komplexech. Komplex *rac*-[PdCl₂(Hdpc-κ²-*P,P'*)] vznikl reakcí *rac*-Hdpc s [PdCl₂(cod)], a jeho struktura v pevné fázi byla stanovena. Tento komplex rovněž posloužil jako prekurzor pro přípravu můstkového dimerního komplexu [(μ-Cl)₂{Pd(Hdpc-κ²-*P,P'*)₂](BF₄)₂, který vznikl abstrakcí chloridového ligandu stříbrnou solí jako směs *rac*- a *meso*- izomerů.

dicyklohexylcarbodiimid (DCC) were selected. It was found that the reaction in the absence of a base and any nucleophile yielded predominantly the *N*-acylurea derivative (**28**, Scheme 9) for both diimides. On the other hand, in the presence of 4-(dimethylamino)pyridine (DMAP) as a base, the reaction gave preferentially the corresponding acid anhydride **29**, which was the dominating product in the case of DCC, while EDC afforded a mixture of anhydride with the urea derivative. Based on the observed results a plausible reaction mechanism was suggested, which is also in accordance with the conclusions reported previously for related compounds.¹⁰

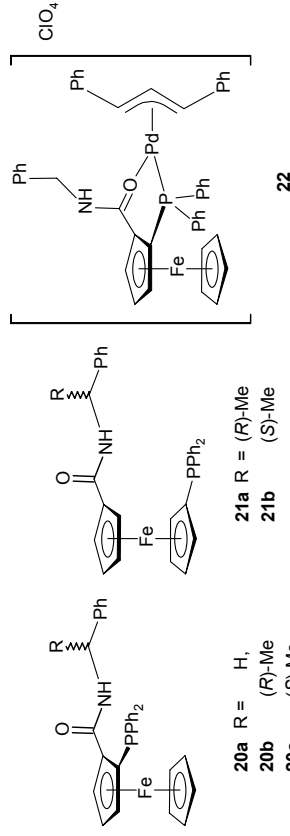


Scheme 9 (DMAP = 4-(dimethylamino)pyridine, Cy = cyclohexyl)

References:

1. For a comprehensive overview of the topic, see: (a) *Ferrocenes: Ligands, Materials and Biomolecules*, P. Štěpnička (Ed.), Wiley, Chichester, 2008. (b) *Ferrocenes: Homogeneous Catalysis*, *Organic Synthesis, Materials Science*, A. Togni, T. Hayashi (Eds.), VCH, Weinheim, 1995.
2. Reviews: (a) T. Hayashi: *Asymmetric Allylic Substitution and Grignard Cross-Coupling in Catalytic Asymmetric Synthesis*, ed. I. Ojima, ch. 7.1, 325-365, VCH, New York 1993. (b) B. M. Trost, D. L. Van Vranken *Chem. Rev.* **1996**, *96*, 395. (c) B. M. Trost, M. L. Crawley *Chem. Rev.* **2003**, *103*, 2921. (d) B. M. Trost *J. Org. Chem.* **2004**, *69*, 5813.
3. M. Lamač, I. Čisarová, P. Štěpnička *J. Organomet. Chem.* **2005**, *690*, 4285.

4. P. Barbaro, C. Bianchini, G. Giambastiani *Synthesis* **2005**, 2445.
5. P. Štěpnička, I. Čiřařová *Organometallics* **2003**, *22*, 1728.
6. (a) J. M. Longmire, B. Wang, X. Zhang *Tetrahedron Lett.* **2000**, *41*, 5435. (b) P. Štěpnička *New J. Chem.* **2002**, *26*, 567. (c) S.-L. You, X.-L. Hou, L.-X. Dai, B.-X. Cao, J. Sun *Chem. Commun.* **2000**, 1933.
7. J. Podlaha, P. Štěpnička, I. Čiřařová, J. Ludvík *Organometallics* **1996**, *15*, 543.
8. 2,2'-Bis(diphenylphosphanyl)ferrocene-1,1'-dicarboxylic acid is known only in the form of its esters and amides: (a) W. Zhang, T. Kida, Y. Nakatsujii, I. Ikeda *Tetrahedron Lett.* **1996**, *37*, 7995. (b) W. Zhang, T. Shimanuki, T. Kida, Y. Nakatsujii, I. Ikeda *J. Org. Chem.* **1999**, *64*, 6247. (c) R. Laufer, U. Veith, N. J. Taylor, V. Snieckus *Org. Lett.* **2000**, *2*, 629.
9. I. R. Butler, S. Müssig, M. Plath *Inorg. Chem. Commun.* **1999**, *2*, 424.
10. (a) B. Schetter, B. Speiser *J. Organomet. Chem.* **2004**, *689*, 1472. (b) A. Cooke, A. Radhi, N. Boden, R. J. Bushby, Z. Lu, S. Brown, S. L. Heath *Tetrahedron* **2000**, *56*, 3385. (c) B. Schetter *Z. Anorg. Chem.* **2004**, *630*, 1074. (d) K. Heinze, M. Schlenker *Eur. J. Inorg. Chem.* **2004**, 2974.



Scheme 6

Tabulka 2

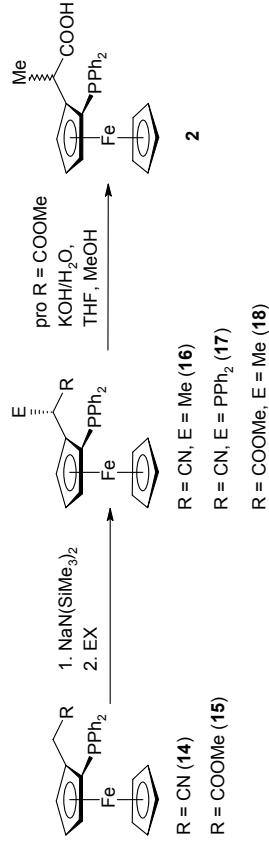
reakce	ligand	T (°C)	čas (h)	aditivum	konverze (%) ^[a]	ee (%) ^[b]
1	(S _p)- 19	22	20	KOAc	100 (91)	50 [R]
2	(S _p)- 20a	22	20	KOAc	100 (91)	58 [R]
3	(R,S _p)- 20b	22	20	KOAc	100 (97)	49 [R]
4	(S,S _p)- 20c	22	20	KOAc	100 (95)	21 [R]
5	(R)- 21a	22	20	KOAc	100 (90)	0
6	(S)- 21b	22	20	KOAc	100 (92)	0
7	(S _p)- 20a	22	20	–	85	90 [R]
8	(S _p)- 20a	22	20	LiOAc	100	48 [R]
9	(S _p)- 20a	22	20	NaOAc	100	84 [R]
10	(S _p)- 20a	0	42	NaOAc	41	88 [R]
11	(S _p)- 20a	22	20	KOAc	100	58 [R]
12	(S _p)- 20a	22	20	RbOAc	100	44 [R]
13	(S _p)- 20a	22	20	CsOAc	100	49 [R]

[a] Konverze určena ¹H NMR spektroskopii.

[b] Absolutní konfigurace určena na základě znaménka optické rotace produktu.

Dalším krokem ve studiu karboxyfosfanových ligandů se stala příprava monokarboxylovaného derivátu dppf (dppf = 1,1'-bis(difenylofosfanyl)ferrocen), 1',2'-bis(difenylofosfanyl)ferrocen-1-karboxylové kyseliny (Hdpc). Připravená Hdpc představuje poslední chybějící členek mezi Hdpf, jejím planárně chirálním isomerem (S_p)-2-(difenylofosfanyl)ferrocenkarboxylovou kyselinou a C₂-symetrickou 2,2'-bis(difenylofosfanyl)ferrocen-1,1'-dikarboxylovou kyselinou.⁸ Synéza Hdpc (schema 7) vychází z dostupného 1,1'-dibromferrocenu (**23**), který byl *ortho*-lithován a karboxylován za vzniku racemické kyseliny **24**, jak bylo popsáno dříve Butlerem a kol.⁹ Po další metalaci a

Další část práce byla zaměřena na přípravu (*S*)-2-[(*S_p*)-2-(difenylofosfanyl)-ferrocenylo]propionové kyseliny (**2**), homologu dříve připravené [2-(difenylofosfanyl)-ferrocenylo]octové kyseliny.⁵ Použití analogických postupů jako u homologické látky však v tomto případě nebylo úspěšné, vinou rozdílné reaktivity některých meziproduktů. Jako alternativa byl vyvinut postup vedoucí k racemickému, avšak diastereomerně čistým produktům. Bylo zjištěno, že α -deprotonace racemického [2-(difenylofosfanyl)-ferrocenylo]acetonnitrilu (**14**) nebo příbuzného esteru **15** za použití $\text{NaN}(\text{SiMe}_3)_2$ probíhá s vysokou diastereoselektivitou a otevírá tak cestu k produktům **16-18** prostřednictvím následných reakcí vzniklého karbaniontu s elektrofilu (schema 5). Vzniklý ester **18** byl dále použit při přípravě iontového palladnatého komplexu, (*S_p*/*R_p*/*S_p*)-[(*C*₆H₄CH₂NMe₂- κ^2 -*C*₁,*P*)Pd(**18**- κ^2 -*O*,*P*)]ClO₄ s *ortho*-metalovaným *N,N*-dimethyl(benzyl)aminovým ligandem. Následná hydrolyza nitrilů byla bohužel zcela neúspěšná, zatímco v případě esteru **18** vedla sice k požadovanému produktu, ale pouze za cenu racemizace na vzniklém chirálním centru, nebo oxidace fosfanylové skupiny.



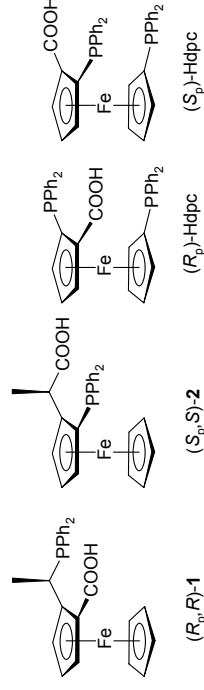
Schema 5

V následující části práce byla skupina látek testovaných v asymetrické allylové alkylationi rozšířena o amidy známých ferrocenových fosfanyl-karboxylových kyselin. Pro testy byly připraveny (*S_p*)-2-(difenylofosfanyl)ferrocenkarboxylová kyselina (**19**),⁶ její amidy (**20**, schema 6), a dva další chirální amidy (**21**) odvozené od 1'-(difenylofosfanyl)-ferrocenkarboxylové kyseliny (Hdpc).⁷ Výsledky jednoznačně potvrdily dominantní roli planární chiralita na stereoselektivitu reakce. Amidy **21** nevykazovaly žádnou asymetrickou indukci, zatímco jejich planárně chirální izomery poskytovaly průměrně či dobré enantiomerní přebytky (*ee*). Následná modifikace reakčních podmínek vedla k *ee* až 90 % s ligandem **20a**. Navržený mechanismus reakce pro tento ligand byl konfrontován s informacemi, které poskytla NMR spektroskopie a rentgenostrukturální analýza pro modelový komplex $[\text{Pd}(\eta^3\text{-1,3-Ph}_2\text{C}_3\text{H}_3)\{(\text{S}_p)\text{-20a-}\kappa^2\text{O,P}\}]\text{ClO}_4$ (**22**).

Shrnutí

Předkládaná dizertační práce byla zaměřena na přípravu, charakterizaci a studium koordinačních a katalytických vlastností nových ferrocenových fosfanyl-karboxylových ligandů (Schema 1). Tyto látky vhodným způsobem rozšiřují spektrum dosud známých sloučenin, které tvoří skupinu variabilních hybridních ligandů. Jelikož jsou vybaveny fosforovými a kyslíkovými donorovými atomy, mohou se koordinovat k různým kovům a v různých modech. Navíc disponují planární chiralitou, která je v některých případech kombinována s dalším chirálním centrem na připojených substituentech. Syntetické postupy vedoucí k jejich přípravě byly navrženy a použity tak, aby bylo možno efektivním způsobem získat tyto chirální ligandy v opticky čisté formě. Vzhledem k úspěšnému využití mnoha chirálních ferrocenových derivátů v optice čisté formě,¹ připravené látky byly testovány v enantioselektivní allylové alkylationi katalyzované komplexy palladia.²

Kyseliny (*R_p*,*R*)-**1** a (*R_p*)/(*S_p*)-Hdpc byly připraveny níže popsanými postupy v opticky čisté formě, buď za použití metod vycházejících z derivátů s chirální *ortho*-dirigující skupinou, nebo rozštěpením racemické směsi produktu cestou dočasně zavedení další chirální skupiny a následné separace diastereomerních meziproduktů.

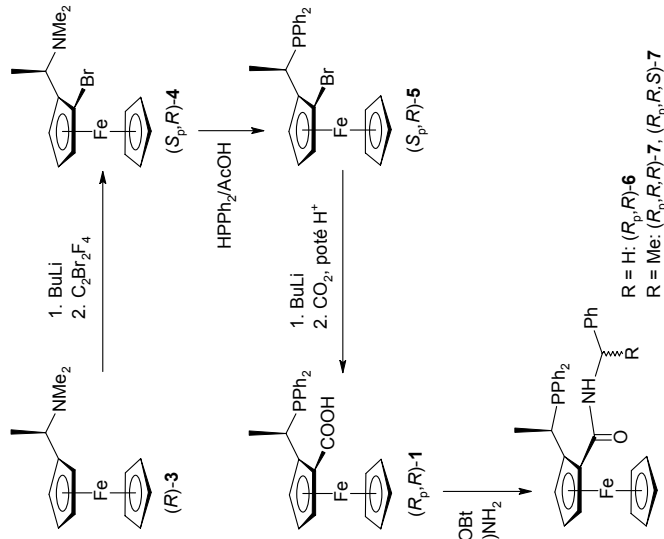


Schema 1

(*R_p*)-2-[(*R*)-1-(difenylofosfanyl)ethyl]ferrocenkarboxylová kyselina (**1**), ligand kombinující planární a centrální chiralitu, byl syntetizován postupem naznačeným ve Schematu 2. Kyselina **1** je homologem dříve popsané racemické 2-[(difenylofosfanyl)methyl]-ferrocenkarboxylové kyseliny.³ Její syntéza byla zahájena diastereoselektivní *ortho*-lithiací a následnou bromací chirálního aminu **3**, následovanou fosfanylací brom-aminu **4**, jak bylo dříve popsáno Giambastianim a kol.⁴ V posledním kroku byl bromid **5** lithiován a vzniklý intermediát přímo karboxylován nadbytkem pevného CO₂. Po následném okyselení a zpracování reakční směsi byla získána kyselina **1**. Mimo to byla vyvinuta alternativní cesta, která zahrnuje chránění fosfanové skupiny převodem na příslušný fosfanylthioester.

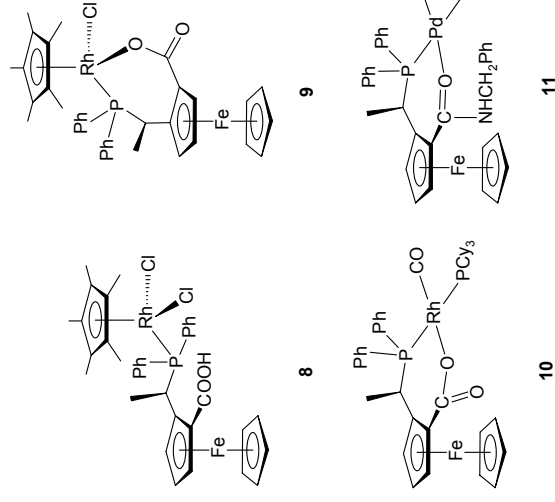
Modifikace obou funkčních skupin v látce **1** poskytly sérii příbuzných derivátů. Vedle zmíněného fosfanylthioesteru byl připraven také fosfanoxid, jehož struktura v pevné fázi byla

určena rentgenovou difrakcí. Dále byly reakcí karboxylové skupiny s aminy nesoucími chirální i achirální substituenty připraveny amidy **6** a **7**.



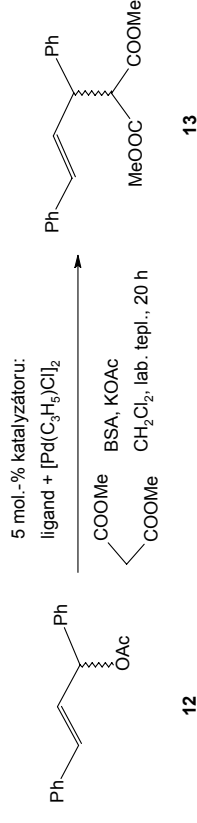
Scheme 10 (EDC = *N*-ethyl-*N'*-[3-(dimethylamino)propyl]karbodiimid, HOBt = 1-hydroxybenzotriazol)

Pro studium koordinačních vlastností ligandu **1** a odvozených látek byly připraveny některé komplexy rhodia a palladia. Štěpením můstkového komplexu $[\{\text{Rh}(\mu\text{-Cl})\text{Cl}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2]$ za přítomnosti látky **1** vznikl rhoditý komplex **8** (Schema 3) obsahující *P*-monodentátně kordinovanou kyselinu **1**. Komplex **8** působením silikagelu nebo neutrální aluminy ochotně přecházel na fosfanyl-karboxylátový komplex **9**. *O,P*-Chelatující koordinace fosfanyl-karboxylátu bylo rovněž dosaženo v rhodném komplexu **10**, který hladce vznikl acidobazickou výměnou acetylacetonátového ligandu (acac) ve výchozím komplexu $[\text{Rh}(\text{acac})\text{CO}(\text{PCy}_3)]$. Struktury komplexů **8** a **10** byly určeny difrakcí rentgenova záření. Koordinační chování amidů bylo testováno v palladnatých komplexech. Amid **6** nahradil koordinovaný cyclookta-1,5-dien (cod) ve výchozím $[\text{PdCl}(\text{Me})(\text{cod})]$ za vzniku chelátového komplexu **11**, jehož krystalová struktura byla určena rentgenovou difrakcí.



Scheme 3

Katalytické schopnosti nově připravených ligandů (kyseliny **1** a amidů **6** a **7**) byly testovány v palladiem katalyzované allylové alkylaci racemického (*E*)-1,3-difenylprop-2-en-1-yl-acetátu (**12**) dimethyl-malonátem (Schema 4). Výsledky uvedené v Tabulce 1 vykazují pouze průměrnou asymetrickou indukci, avšak značné rozdíly mezi kyselinou a jejími amidy.



Scheme 4 Asymetrická allylová alkylace (BSA = *N,O*-bis(trimethylsilyl)acetamid).

Tabulka 1

ligand	konverze (izol. výtěžek) [%] ^[a]	ee [%] (konfigurace) ^[b]
1 (<i>R_p,R</i>)- 1	100 (94)	10 (<i>S</i>)
2 (<i>R_p,R</i>)- 6	55	41 (<i>R</i>)
3 (<i>R_p,R,R</i>)- 7	42	43 (<i>R</i>)
4 (<i>R_p,R,S</i>)- 7	22	35 (<i>R</i>)

[a] Konverze určena ¹H NMR spektroskopii.

[b] Absolutní konfigurace určena na základě znaménka optické rotace produktu.