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Polární ligandy odvozené od fosfinoferrocenového hydrazidu

Polar ligands derived from a phosphinoferrocene hydrazide

Bakalářská práce

Vedoucí bakalářské práce: Prof. RNDr. Petr Štěpnička, Ph.D.

Praha, 2014

Prohlášení:

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V Praze, 30.05.2014 Tomáš Vašíček

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Shrnutí

Název práce: Polární ligandy odvozené od fosfinoferocenového hydrazidu

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Tato práce popisuje syntézy tří nových ligandů odvozených od fosfinoferrocenového hydrazidu, viz. 1´-(difenylfosfino)ferrocen-1-karbohydrazidu. Za účelem přípravy těchto látek s nejvyšším výtěžkem a čistotou, byly reakční podmínky optimalizovány změnami reakčních časů a teplot. Nově připravené sloučeniny nesoucí prodloužené polární skupiny byly charakterizovány NMR spektroskopií, hmotnostní spektrometrií, infračervenou spektroskopií a elementární analýzou. Pomocí rentgenové difrakční analýzy byla určena molekulová struktura 1'-(difenylfosfino)-1-{[2-(aminokarbonyl)hydrazino]-karbonyl}ferrocenu.

Klíčová slova: Ferrocen, Fosfiny, Hydrazidy

Abstract

Title: Polar ligands derived from a phosphinoferrocene hydrazide

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This thesis describes the syntheses of three new ligands derived from a phosphinoferrocene hydrazide, namely 1´-(diphenylphosphino)ferrocene-1-carbohydrazide. The reaction conditions were optimized by varying the reaction time and temperature in order to achieve high yields and purity of the products. Newly prepared compounds that bear extended polar groups were characterized by NMR spectroscopy, mass spectrometry, infrared spectroscopy and by elemental analysis. Additionally, the molecular structure of 1'-(diphenylphosphino)-1-{[2-(aminocarbonyl)hydrazino]-carbonyl}ferrocene (**8**) was determined by X-ray diffraction analysis.

Key words: Ferrocene, Phosphines, Hydrazides

Table of Contents

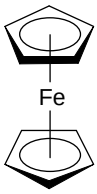
1. Introduction

One of the most important areas of chemical research lies within the study and development of new catalytic systems. Such catalytic systems are expected to meet the demands of rising number and variety of organic transformations, ever increasing demand for production of fine chemicals with the expectation to satisfy the requirements of environmental issues and economic interests. While thinking about developing a new catalyst, one needs to take into the account catalysts' activity and selectivity towards the products as well as the availability of catalyst. Practical aspect is nowadays paid also to the combination of positive features found in homogeneous and heterogeneous classes of catalysts. Although the difficulties with separation and less efficient reuse of homogeneous catalysts remains to be an undeniable fact, the importance of careful designing a homogeneous catalyst has not yet been fully matched in the field of heterogeneous catalysis. Synthesis of new ligands with the desired characteristics are aimed to control coordination of the active metal centre through various electronic and steric properties of the ligands.

Prominent group of ligands that have gained a wide-range application in transition-metal catalyzed reactions is found within the group of metallocenes. Metallocenes are subclass to a broad group of the so-called sandwich compounds, on which pedestal stands the molecule of ferrocene since the majority of metallocene-based ligands is based on ferrocene scaffold.

Ferrocene was discovered in 1951, independently by two research groups. While working on fulvalene synthesis, Kealy and Pauson found that their proposed reaction between cyclopentadienylmagnesium bromide and iron(III) chloride led to then unknown crystalline product of $C_{10}H_{10}Fe$ composition.[1] This orange, air-stable product was found to be remarkably stable, which wasn't however a feature characteristic for typical organometallic compounds of this time. Group led by Samuel A. Miller intended to prepare organic amines by direct reaction of nitrogen with hydrocarbons in the presence of iron catalyst. As the hot cyclopentadiene vapor was passing through iron catalyst, orange crystals of the same composition were formed.[2] Both groups failed to determine the correct structure that would correspond with the noted extraordinary stability of ferrocene. Interestingly enough, structure of ferrocene **I** (Figure **1.1.**) was soon solved also by two independently working groups. Wilkinson et al. interpreted an infrared spectrum and explained diamagnetism of ferrocene whereas Fischer's group simply carried out a simple crystal X-ray diffraction analysis.[3,4]

Fischer's and Wilkinson's striking suggestion made earlier about the existence of compounds that may contain bonds between metal atoms and whole molecule was confirmed. The proposed structure of ferrocene in which two cyclopentadienyl rings are facing each other while connected via iron atom by pentahaptic covalent bond was reported and soon afterward confirmed by X-ray crystallography.



I

Figure 1.1. Structure of ferrocene.

The establishment of a new concept of viewing chemical bonding in organometallic chemistry, further derivatization and extensions to other metallocene structures in following years ensured that Wilkinson and Fischer were jointly awarded a Nobel Prize in Chemisty 1973 for „their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds."[5]

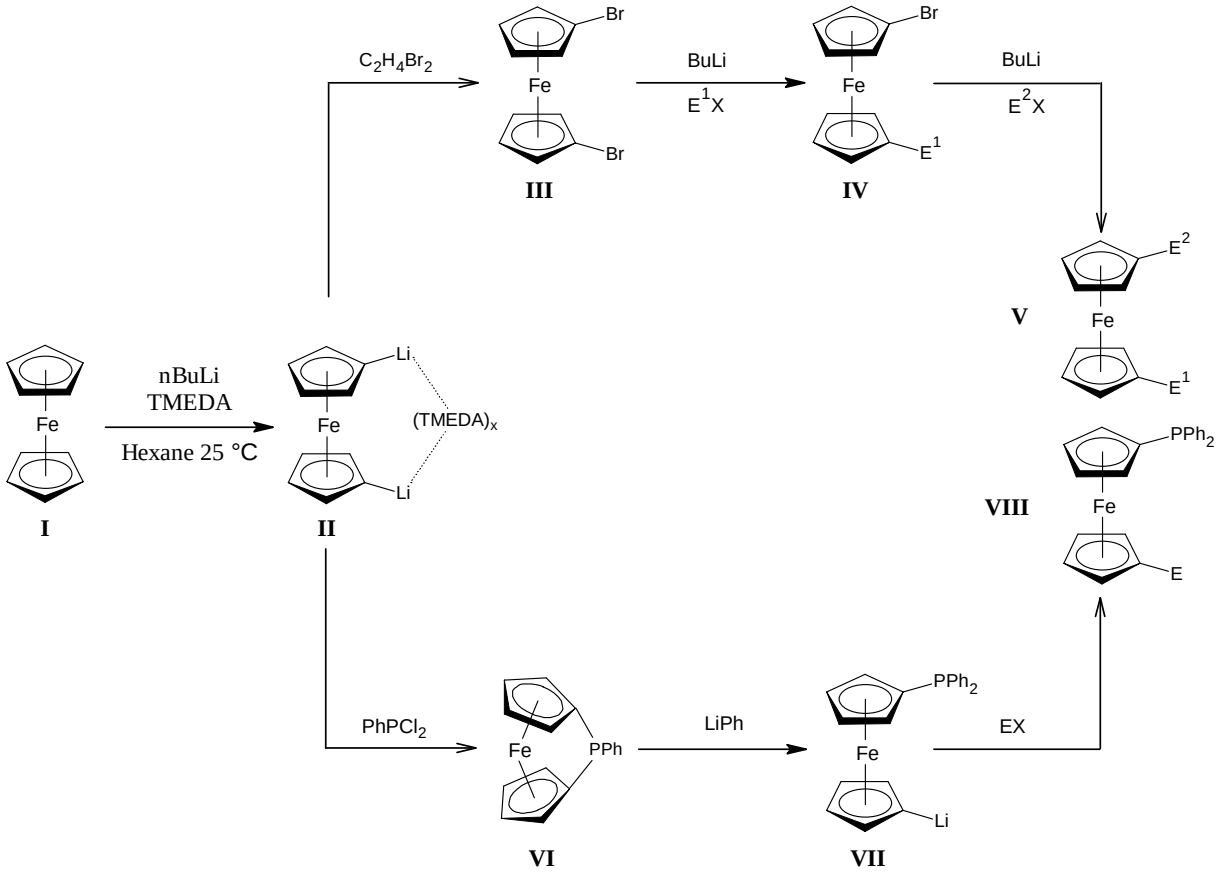
Since that time ferrocene and ferrocene-based molecules have been the object of the intense research and found many applications ranging from the field of analytical chemistry (molecular recognition, ion sensing)[6] and material development (polymer design, magnetic materials, fuel additives)[7] to coordination chemistry (homogeneous catalysis in stereoselective and asymmetric transformantions), electrochemistry (electron-transfer processes), biochemistry (design of functionalized peptides)[8] and even medicinal chemistry (drug design) [9].

Aromatic character of ferrocene stems from the fact that each cyclopentadienyl ring provides 6π electrons, iron in 2+ oxidation state another 6d electrons, thus stable 18 electron configuration is attained. It is important to note that ferrocene reacts in electrophilic substitutions roughly million times faster than benzene and readily undergoes Friedel-Crafts alkylation, acylation and produces organometallic structures via lithiation and mecruration. Formyl functional group can be attached via conventional Vilsmeier-Haack reaction, ferrocene also undergoes readily Mannich amminomethylation.[10] On the other hand, ferrocene is rather sensitive to oxidation and is converted to ferrocenium cation with a incomitant color change from orange to blue. Therefore, when incorporating electrophilic

substituent, it needs to possess no sign of the oxidative character that would lead to a deep red ferrocenium salt, if concentrated, rather than providing desired product.

Not surprising is that electrophilic substitution can take place on both of the identical electron rich cyclopentadienyl rings providing heteroanular disubstituted products. Most common synthetic routes towards asymmetric 1,1'-disubstituted ferrocene derivatives are based on sequential lithiation and functionalization approach (Scheme **1.1.**).[11]

The first synthetic route involves preparation of 1,1'-dibromoferrocene (**III**) from ferrocene via the reaction intermediate (**II**) in the presence of TMEDA and *n*-butyllithium that reacts with 1,2-dibromoethane to give 1,1'-dibromoferrocene (**III**). Reacting **III** with one molar equivalent of electrophilic reagent provides monosubstituted derivative (**IV**) that can be readily converted to a 1,1'-disubstituted derivative (**V**) via a subsequent electrophilic substitution/functionalization.



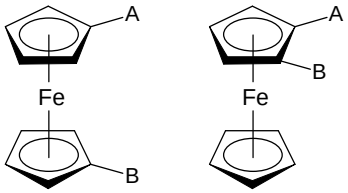
Scheme 1.1. Two synthetic routes towards 1,1'-disubstituted ferrocene derivatives.

Second synthetic route is based on ring opening of 1-phenyl-1-phospha-[1]ferrocenophane (**VI**) that is accessible from 1,1'-dilithioferrocene–TMEDA intermediate (**II**) and

dichlorophenylphosphine. The ring opening of ferrocenophane frame (**VI**) by reaction with phenyllithium produces monolithiated derivative bearing diphenylphosphine group (**VII**) that can be further reacted with electrophilic reagents to provide 1,1'-disubstituted derivatives (**VIII**).

The use of ferrocene-based ligands is naturally based on specific properties of the ferrocene molecule such as adequate rigidity of the unique ring system, conjugation and easy derivatization, steric bulkiness governing stereo- and enantio- selectivity.[12]

A class of the ferrocene derivatives that receives attention to successful and frequent catalytic use are ferrocene phosphines. Generally speaking, ferrocene phosphines are the derivatives of tertiary phosphine, group of organophosphorous compounds having the general formula PX_3. Phosphine ligands span from simple monodentate[13] to multidentate[14] donors including a class of mixed-donor compounds possessing nitrogen, oxygen or sulfur within the structure of ligand. Such a variety of possible structure types led to the development of phosphinoferrocenes as a class with special electronic and steric properties.[15,16] The phosphinoferrocene donors are predominantly represented by 1,1'-disubstituted and 1,2-disubstituted derivatives, although monodentate phosphinoferrocenyl donors found their application in the field of homogeneous catalysis, too.



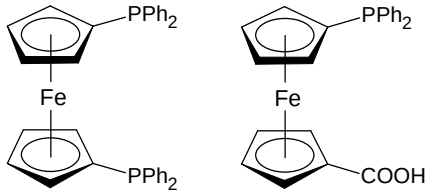
IX **X**

Figure 1.2. Disubstituted 1,1'- (**IX**) and 1,2'- (**X**) asymmetric ferrocene derivatives.

One of the first phosphinoferrocene ligands, synthesized with the application in catalysis, was 1,1'-bis(diphenylphosphino)ferrocene (dppf, Figure **1.3.**).[17] This archetypal representative of the symmetric 1,1'-diphosphinoferrocene ligands shows flexibility in molecular conformation when we realize that the observed values of bite angles range from 90° to 120° which in turn alters its' steric and electronic properties.[18]

A typical representative of the 1,1'-unsymmetric phosphanylferrocene hybrid ligands is 1'-(diphenylphosphino)ferrocene-1-carboxylic acid (**XII)** (Hdpf, Figure **1.3.**) that can be easily

synthesized from the lithiated intermediate (**II)** that is reacted in situ with the excess of solid carbon dioxide and the reaction mixture subsequently acidified.[19]



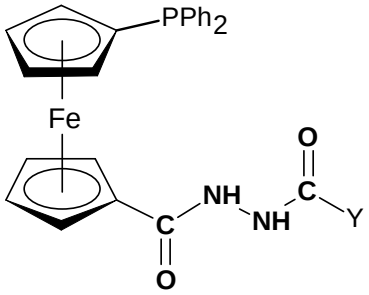
XI **XII**

Figure 1.3. The 1,1'-disubstituted ferrocene derivatives; Dppf (**XI**) and Hdpf (**XII**).

The electronegativity of X substituents, covalently bonded to phosphorus atom, are the means by which donating and steric properties are controlled. Substitutent X with a greater electronegativity tends to withdraw electron density from the phosphorous atom more, which causes the ligand to behave as less effective σ-donor. Just as the electron density is withdrawn from the phosphorous atom with a lone pair a simultaneous contraction of 3d orbitals takes place which causes lowering of their energy level. Due to this very fact, d orbitals of phosphorous atom take part in $d_\pi - d_\pi$ interaction and PX_3 becomes a π–acceptor. Thus, if atoms exhibiting high electronegativities (ex. PF_3) are bonded as substituents to the phosphorous atom in PX_3 the resulting compound will indicate strong π–acceptor behavior. On the other hand, in the case of alkyl and aryl substituents that possess donating capability, the resulting phosphine ligand will behave as a strong σ-donor. Pearson's Hard and Soft Acid and Base concept (HSAB) classifies phosphines as soft Lewis bases, which can be expected to have a high affinity toward soft metals from the right-hand corner of d-block such as ruthenium, rhodium, platinum, palladium, mercury for instance.[20]

Additional applications become possible when phosphino-ferrocene derivatives contain another substituent with hard donor atom. These hard atoms, typically oxygen, nitrogen, phosphorous coordinate to the metal atom in a distinctly different way than phosphorous atom in phosphine group. The ligands combining hard and soft donor moieties are called hybrid ligands, and are capable of hemilabile coordination.[21,22] While phosphine group is bonded strongly to a soft metal atom, ligand's functional group with the hard atom interacts with the metal relatively weakly thus offering an opportunity for a substrate with a higher affinity towards the metal atom to replace the hard donor atom within the coordination sphere and undergo a chemical reaction. After the product of a catalyzed reaction is formed and released from a coordination sphere, hemilabile coordination is restored again as weak interaction

between hard donor group and metal is observed again. Structures of polar phosphinoferrocene ligands reported in this thesis contain CONHNHCO moiety attached to a (diphenylphosphino)ferrocene fragment from one side and to remaining group Y on the other.



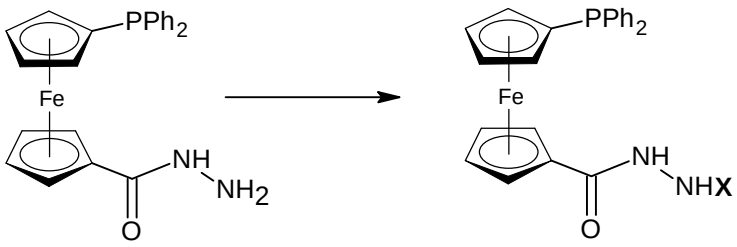
where **Y** = NH_2 ; $N(CH_3)_2$; NCH_2CH_3

Figure 1.4. Reported polar phosphinoferrocene ligands with CONHNHCO moiety.

The presence of carbonyl and amide groups in this moiety is the basis for the polar attributes these ligands have.

1.1 Aims of the thesis

The aim of this thesis was to prepare and optimize the synthesis of new ligands derived from 1´-(diphenylphosphino)ferrocene-1-carbohydrazide. The preparation of three such hydrazide derivatives bearing extended polar groups is reported in this thesis along with their characterization by the available spectroscopic and diffraction techniques.



X = $CONH_2$, $CON(CH_3)_2$, $CONHCH_2CH_3$.

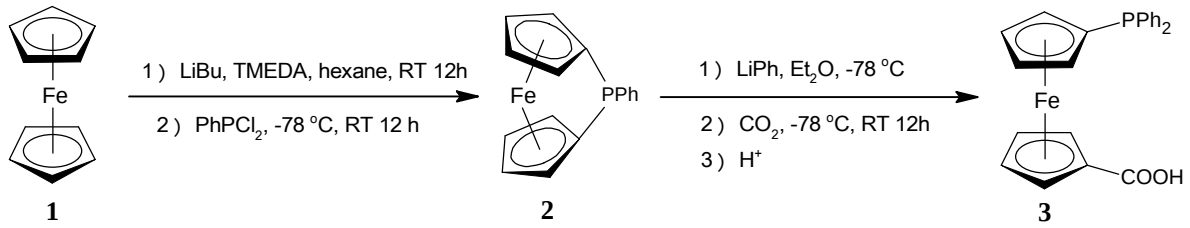
2. Results and Discussion

2.1 Synthesis of phosphinoferrocene hydrazides

The starting material for the synthesis of the modified 1'-(diphenylphosphino)ferrocene hydrazides **8**, **9** and **10** was 1'-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)** that was prepared according to the literature.[23]

Firstly, ferrocene **1** was introduced into an inert atmosphere and reacted butyllithium in the presence of *N,N,N',N'*-tetramethyl-1,2-diaminoethane in distilled hexane. Thus, reaction intermediate (**II**) in Scheme **1.1.** was formed and subsequently reacted with dichlorophenylphosphine in a precooled CO_2/ethanol cold bath (–78 °C) to give ferrocenophane **2**. After stirring overnight, reaction was quenched by addition of distilled water. Reaction mixture was washed with hexane, brine and then dried and evaporated to dryness. Purity and identity of resulting product was confirmed by ^{1}H and ^{31}P NMR spectra. This reaction provided 1-phenyl-1-phospha-[1]ferrocenophane (**2**) in 28 % yield.

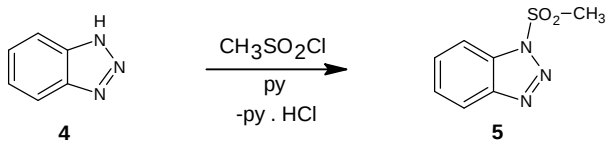
Ferrocenophane (**2**) did undergo ring opening process[24] upon addition of 1.1 molar equivalent of phenyllithium in dry diethyl ether at –78 °C under argon atmosphere. Portion-wise addition of crushed dry ice led to formation of Lidpf as a fine yellow precipitate, that was extracted with aqueous NaOH and washed with diethyl ether. Aqueous phase was thoroughly cooled in an ice water bath and acidified by the addition of phosphoric acid. The separated acid **3** was filtered and washed with a cold diluted phosphoric acid and distilled water on a Büchner funnel to afford a crude product that was dissolved in a hot acetic acid and left to crystallize. The crystalline acid was identified by measuring ^{1}H and ^{31}P NMR spectra. Orange-red crystalline solid was isolated in a good yield (57 %).



1 **2** **3**

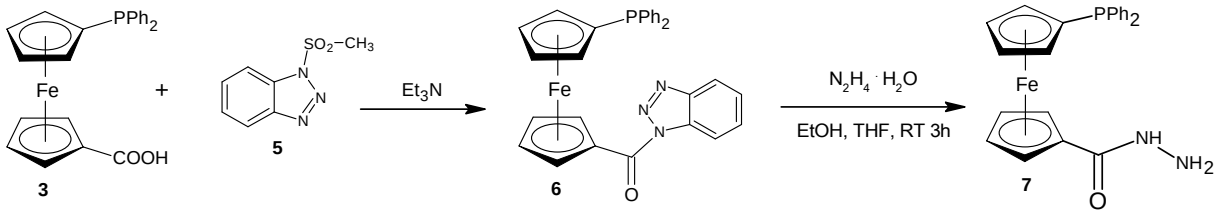
Scheme 2.1. Synthesis of Hdpf (**3**).

For the purpose of synthesis of hydrazide **7**, benzotriazole (**4**) was dissolved in a mixture of dry toluene and pyridine, cooled in an ice bath and reacted with methanesulfonyl chloride (1.2 eqv.). Formation of white precipitate was observed as the reaction was allowed to proceed at room temperature for 12 hours. The resulting white precipitate was washed and dried to give a white crystalline solid in a good yield (77 %). The purity of 1-(methanesulfonyl)-1*H*-1,2,3-benzotriazole (**5**) and the structure was confirmed by ^{1}H NMR spectra and comparison with the data found in literature.



Scheme 2.2. Synthesis of methylsulfonyl reagent (**5**).

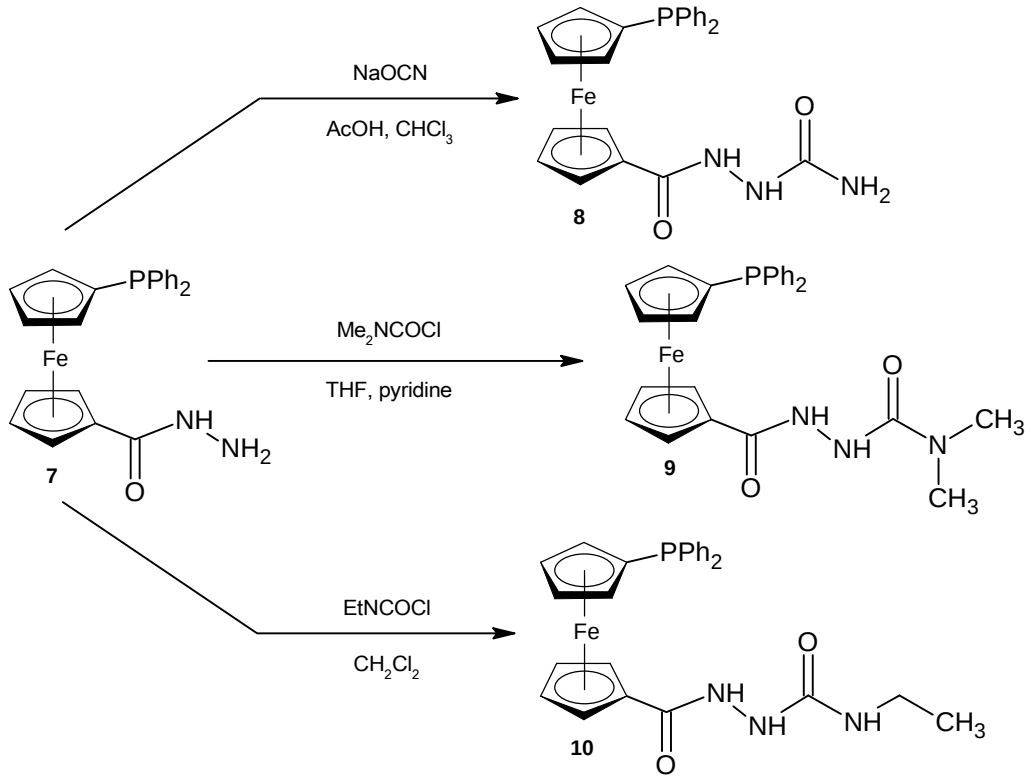
Benzotriazolyl derivative (**6**) was obtained by reacting Hdpf (**3**) with the stoichiometric amount of 1-(methanesulfonyl)-1*H*-1,2,3-benzotriazole (**5**) in THF and triethylamine as a base under the argon atmosphere and reflux conditions for 8 hours. Reaction mixture, dissolved in chloroform, was then washed with distilled water, dried and evaporated to dryness, passed through a short column of silica gel in dichloromethane. The reaction product was identified by consistent ^{1}H and ^{31}P NMR data and was used in the subsequent reaction step in which the triazole derivative (**6**) was treated with an excess of hydrazine monohydrate in a mixture of dry ethanol and THF. Color of the reaction mixture turned from deep red to orange almost immediately upon the addition indicating the formation of **7**. The reaction mixture was stirred for 3 hours at room temperature, evaporated and then extracted with sodium hydroxide. After drying, reaction product was further purified by flash column chromatography. This reaction procedure afforded 1'-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)** as an orange solid in a good yield (78.0 %).



Scheme 2.3. Synthetic route towards hydrazide (**7**).

All of the newly synthesized 1'-(diphenylphosphino)ferrocene hydrazides **8**,**9** and **10**, reported in this thesis were prepared from 1'-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)**. The syntheses were carried out under the inert atmosphere of argon and with the

exclusion of the direct sunlight. The crude products of these syntheses were further purified by flash column chromatography on silica gel (MeOH/CH_2Cl_2 1:20 by volume).



Scheme 2.4. Synthesis of 1'-(diphenylphosphino)ferrocene hydrazides **8**, **9** and **10** bearing extended polar groups.

Firstly, hydrazide **7** was reacted with the sodium isocyanate (1.2 eqv.) in a mixture of acetic acid and chloroform as a solvent. Reaction conditions were found by an optimization and so the reaction was performed at 0 °C for 2 hours and then at room temperature for 8 hours. After drying and purification by chromatography, orange solid in a very good yield (88 %) was obtained. Single crystals of hydrazide **8** were isolated by crystallization from hot ethyl acetate solution and further studied by X-ray diffraction analysis.

Starting hydrazide **7** was also reacted with two molar equivalents of *N*,*N*-dimethylcarbamoyl chloride in the presence of pyridine and THF. After cooling and stirring for 2 hours, the reaction mixture was heated to 60 °C and then kept under reflux conditions for 6 hours. Its' color changed to deep orange upon refluxing. After the normal purification, hydrazide **9** was obtained as a dark orange powder in a very good yield (94 %).

Finally, the starting hydrazide **7** was reacted with 1.5 molar equivalents of ethyl isocyanate in dry dichloromethane. No color change was observed, but yellow clumps of the product begun to form almost immediately after mixing the reactants. After washing and purifying the resulting reaction mixture, hydrazide **10** was isolated in a 79 % yield along with a minor amount of corresponding phosphine oxide (4 %).

2.2 NMR spectra

Nuclear magnetic resonance spectroscopy was used as a tool to identify all the synthesized substances and confirm their purity. The newly synthesized hydrazides **8**, **9** and **10** were characterized by ^{1}H, ^{13}C and ^{31}P NMR. All three hydrazides show similar chemical shifts for the ferrocene protons that are found within the range δ_H 4.11–4.77 ppm. Aromatic rings of diphenylphosphine group are found as a multiplet integrating to ten hydrogens at δ_H 7.28–7.40 ppm.

The terminal –NH_2 amine group in hydrazide **8** is observed as a singlet with a chemical shift of δ_H 5.89 ppm. Two amide hydrogens in a CONHNHCO moiety are observed as a pair of dublets at 7.78 and 9.43 ppm with $^{3}J_{HH}$ = 1.6 Hz.

The presence of two methyl groups in hydrazide **9** is confirmed by the presence of a sharp singlet peak at δ_H 2.95 ppm. Two amide hydrogens in a CONHNHCO moiety are observed as a pair of dublets at 7.09 and 8.08 ppm with $^{3}J_{HH}$ = 4.0 Hz and $^{3}J_{HH}$ = 2.0 Hz.

Hydrazide **10** was distinguished from its' structural isomer (hydrazide **9**) by the signals due to the presence of ethyl group confirmed by the combination of triplet found at 0.99 ppm and quintet at 3.05 ppm. The CONHNHCO moiety is manifested by the presence of two dublets due to non-equivalent NH groups at δ_H 7.73 ppm and 9.44 ppm. Secondary amide hydrogen, connected to ethyl group is found as a triplet at δ_H 6.26 ppm.

In ^{31}P{^{1}H} NMR spectra the hydrazides display singlets at δ_P –18.2 ppm (hydrazides **8**, **10**). The signal of hydrazide **9** is seen at δ_P –17.0 ppm.

When analyzing the ^{13}C NMR spectra, common features of all three hydrazides were found. The signals of the ferrocene carbons range from δ_C 69.37 ppm to 77.83 ppm. Signals of the PPh_2 group are found at δ_C 128.95 ppm to 139.32 ppm. The carbonyl resonances are detected by the presence of singlets at δ_C 158.94 ppm and 168.71 ppm for **8**, δ_C 157.70 ppm and 169.94 ppm for **9** and δ_C 158.11 ppm and 168.79 ppm for **10**. Hydrazide **9** showed one signal of the

methyl group (δ_C 36.22 ppm). On the other hand, hydrazide **10** was found to have two distinctive signals with a low chemical shift (δ_C 16.24 ppm and 34.69 ppm) that confirmed two different carbon atoms in the ethyl group.

2.3 IR spectra

The infrared spectra of hydrazides **8**, **9** and **10** contain some characteristic bands that allow me to identify the functional groups in the molecules of hydrazides. The sharp N–H stretching bands near 3335 cm^{-1} is found in all the mentioned hydrazides as well as C=O stretching bands within 1680–1660 cm^{-1}.[25]

Hydrazide **8** absorbs at 3373 cm^{-1} (apparent dublet) and also possesses a broad NH_2 scissoring band at 1605 cm^{-1}. Stretching bands of two carbonyl functional groups are found at 1659 cm^{-1} and 1698 cm^{-1}. IR spectrum of hydrazide **9** has two peaks at 1632 cm^{-1} and 1661 cm^{-1} referring to two carbonyl functional groups and an apparent doublet at 3213 cm^{-1}.

Hydrazide **10** shows a sharp N–H stretching bands at 3356, 3292 and 3245 cm^{-1}.Two carbonyl functional groups absorb strongly at 1700 and 1624 cm^{-1}.

2.4 Mass spectra

The ions detected by electrospray ionization mass spectrometry were found by the addition of sodium ($[M + Na]^+$) and potassium cation ($[M + K]^+$). Such ions were predominantly detected in mass spectrometry of hydrazides **8**, **9** and **10**.

2.5 X-ray diffraction analysis

Single crystals of hydrazide **8** suitable for X-ray diffraction analysis experiment were grown by crystallization from a hot ethyl acetate solution (orange plate, 0.56 × 0.27 × 0.11 mm^3). The compound crystalizes in monoclinic crystal system with the symmetry of the $P2_1/c$ space group and four formula units per the elementary cell. The molecule **8** as seen in this crystal structure is depicted in Figure **2.1.**

Ferrocene core in **8** adopts the standard geometry usual for sandwich compounds with typically small tilting of 3.49(10)°. (Table **2.1.**).

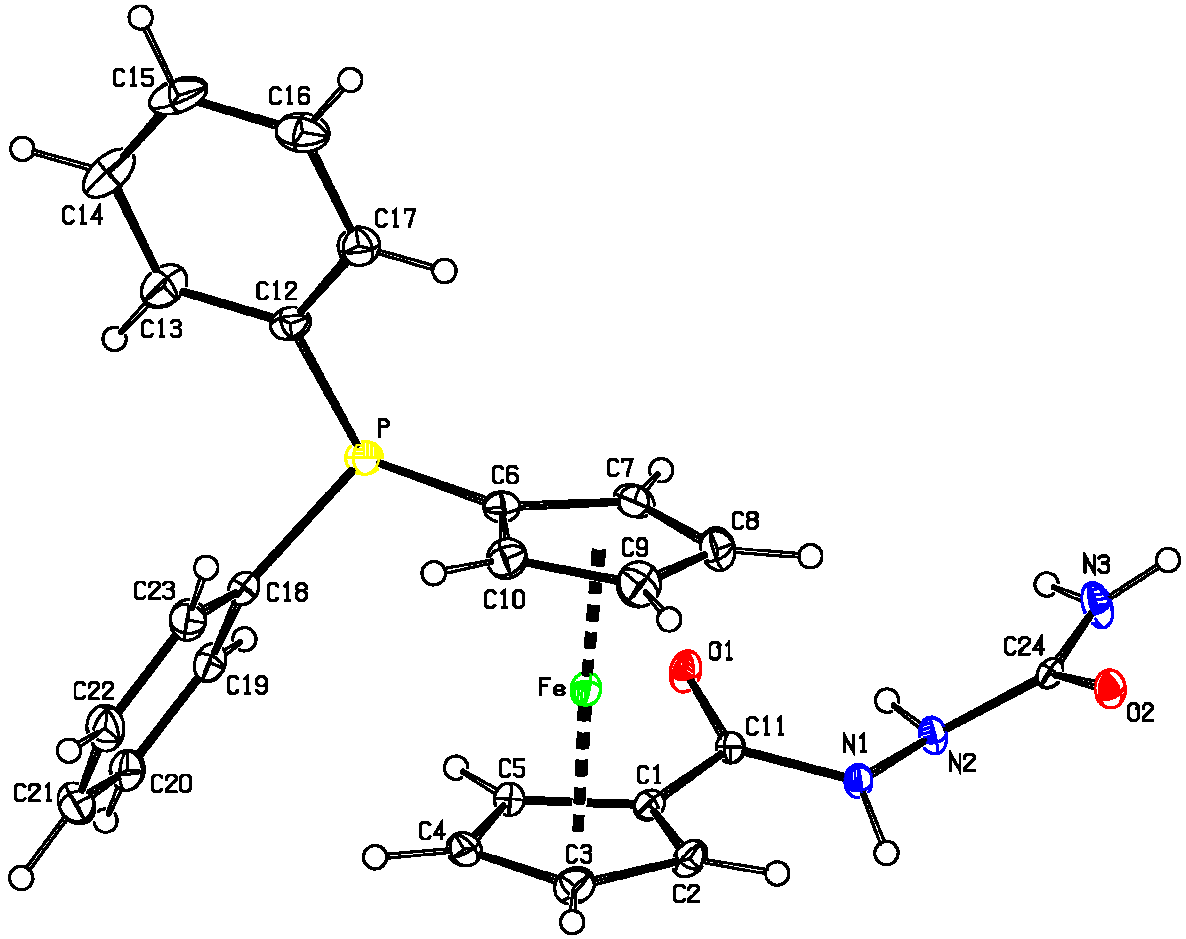


Figure **2.1.** The view of the molecular structure of hydrazide **8**. Displacement ellipsoids enclose the 30% probability level.

The torsion angle C1-Cg1-Cg2-C6 is 92.82(12)° which corresponds to anticlinal conformation of the substituents at the ferrocene unit. The hydrazide functional group addopts the standard geometry with the torsion angle O1-C11-N1-N2 being 6.2(2)°. On the other hand, the torsion angle C11-N1-N2-C24 is 130.58(15)°.

The conformation of the hydrazide moiety is susceptible to the hydrogen bonding that is observed in the crystal packing of this compound. Intermolecular interactions involved within the structure of hydrazide **8** are listed in Table **2.2.**. There are four main intermolecular hydrogen bonding interactions detected in the structure of hydrazide **8**. Two of these hydrogen bonds are formed by the terminal $–NH_2$ amide group (donor) that interacts with oxygen atoms from both carbonyl groups (acceptor).

Table 2.1. Selected bond lengths and angles for **8** [Å,°].

parameter	**8**
Fe-Cg1	1.6507(8)
Fe-Cg2	1.6494(8)
Cp1-Cp2	3.49(10)
C1-C11	1.472(2)
C11-O1	1.2358(19)
C11-N1	1.348(2)
N1-N2	1.3978(18)
N2-C24	1.3762(19)
C24-O2	1.2408(17)
C24-N3	1.334(2)
C11-N1-N2	116.40(12)
N1-N2-C24	118.70(12)
N2-C24-N3	114.04(13)
O2-C24-N3	122.31(13)
O2-C24-N2	118.70(12)
N1-N2-C24	116.40(12)
O1-C11-N1-N2	6.2(2)
C11-N1-N2-C24	130.58(15)
C1-Cg1-Cg2-C6	92.82(12)

[a] Cp1 = C1-C5 and Cp2 = C6-C10 and Cg1 ang Cg2 are geometrical centers of rings Cp1 and Cp2.

The other two hydrogen bonds are formed between the hydrazide functional groups (donor) and the atom of oxygen of both carbonyl groups (acceptor).

The last interaction included in Table **2.2.** (C2–H2⋯O2,V) is probably the weakest and may be thus considered as the potentional hydrogen interaction due to the relatively acute angle ∠CHO.

Table 2.2. Parameters of intermolecular interactions in **8**.

interaction	bond	bond length [Å]	angle [°]
	D–H⋯A	D⋯A	∠ DHA
I	N1–H1N⋯O2	3.0112(16)	173
II	N2–H2N⋯O1	2.9692(16)	152
III	N3–H3N⋯O2	2.9147(18)	172
IV	N3–H4N⋯O1	2.8768(17)	151
V	C2–H2⋯O2	3.260(2)	128

Although a relatively short distance (2.6223(17) Å) between atoms N2 and O1 could indicate an intramolecular hydrogen bond, the corresponding angle ∠NHO is relatively acute and speaks against such contact.

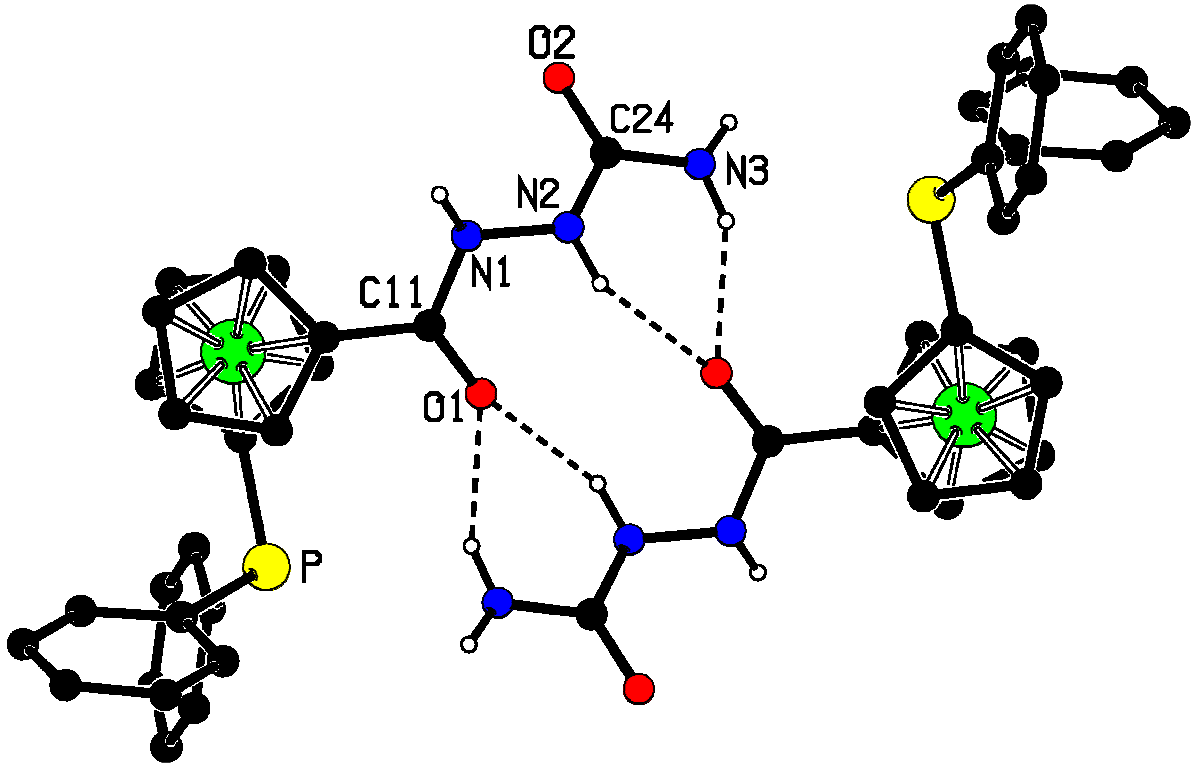


Figure 2.2. Centrosymmetric dimer of hydrazide **8**. (Hydrogen atoms of CH groups were omitted for clarity, dashed lines are the representation of hydrogen bonds).

Two of the previously mentioned hydrogen bonds (II, IV) bind centrosymmetric dimer in the crystal structure of **8** (Figure **2.2.**). These dimers are interlinked via further hydrogen bonding interactions (I, III, V) into layers parallel with the *bc* plane. Neighbouring layers interact with each other via van der Waals interactions between diphenylphosphino moieties and ferrocene cores. A part of such a layer is depicted in Figure **2.3.**.

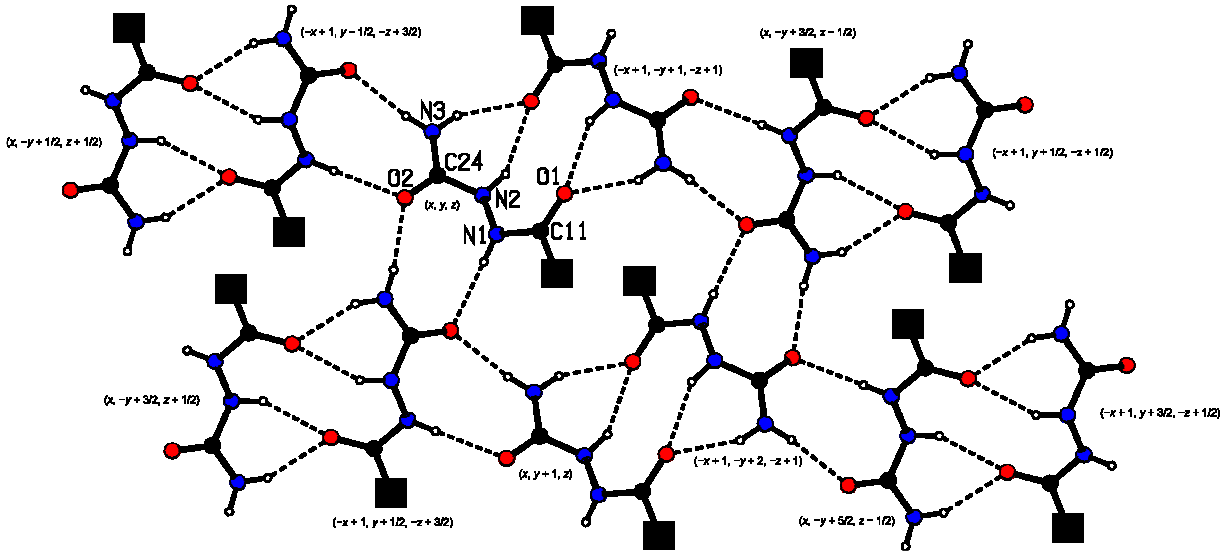
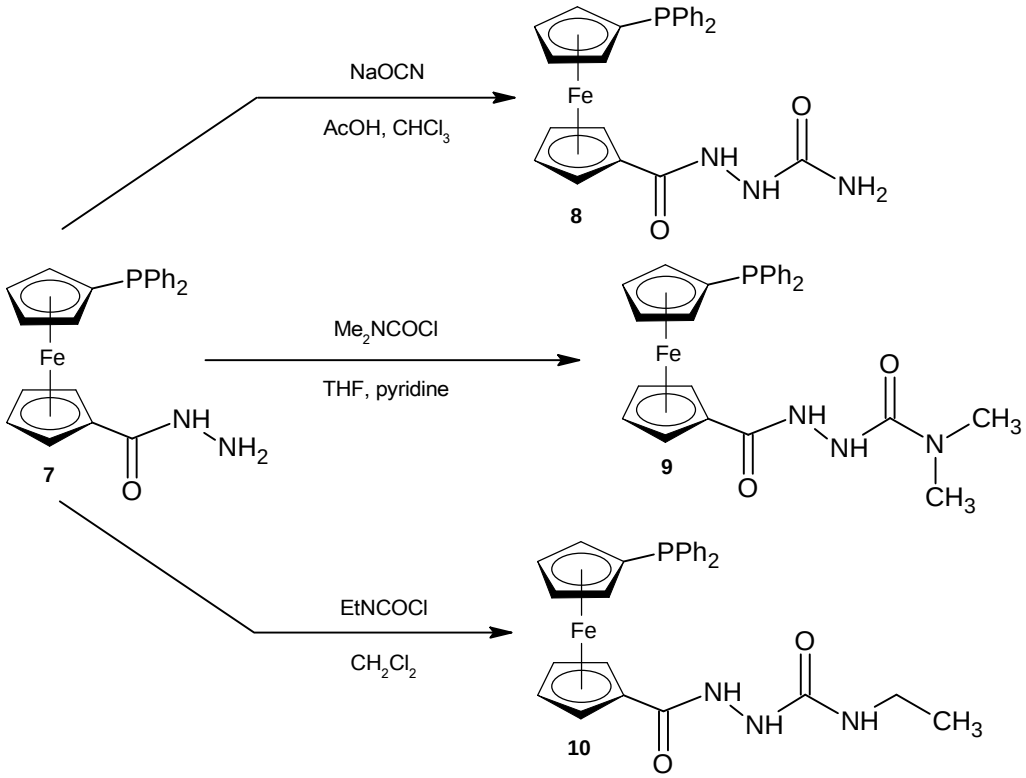


Figure 2.3. Section of the hydrogen bonded system in the crystal structure of 8 (Hydrogen atoms of CH groups were omitted for clarity and the black squares represent C1 atom of the ferrocene moiety, symmetry codes are given).

3. Summary

This thesis describes the syntheses of three new ligands derived from a phosphinoferrocene hydrazide, namely 1´-(diphenylphosphino)ferrocene-1-carbohydrazide. The reaction conditions were optimized by varying the reaction time and temperature in order to achieve high yields and purity of the products. Newly prepared compounds that bear extended polar groups were characterized by NMR spectroscopy, mass spectrometry, infrared spectroscopy and by elemental analysis. Additionally, the molecular structure of 1'-(diphenylphosphino)-1-{[2-(aminocarbonyl)hydrazino]-carbonyl}ferrocene (**8**) was determined by X-ray diffraction analysis.



Scheme 3.1. Synthesized polar ligands **8**, **9** and **10** derived from phosphinoferrocene hydrazide (**7**).

4. Experimental Section

4.1 General Comments

4.1.1 Chemicals

Solvents used in syntheses reported in this thesis (chloroform, dichloromethane, diethylether, tetrahydrofuran, acetic acid, toluene, pyridine, hexane, ethylacetate, ethanol) were obtained from Lachner and Sigma-Aldrich. Dichloromethane and chloroform were dried over anhydrous potassium carbonate and distilled. Toluene was distilled from sodium metal, pyridine and TMEDA were distilled from sodium hydroxide and potassium hydroxide, respectively. Triethylamine was purified by distillation from anhydrous potassium carbonate. Other solvents used for crystallizations and in chromatography were used as received without any additional purification. Other chemicals (ferrocene, *n*-butyllithium, phenyllithium, dichlorophenylphosphine, methanesulfonyl chloride, hydrazine monohydrate, sodium cyanate, *N*,*N*-dimethylcarbamoyl chloride, ethylisocyanate) were purchased from Sigma-Aldrich and Fluka and were not additionally purified.

4.1.2 Analytical Methods

Nuclear magnetic resonance spectra

^{1}H, ^{13}C and ^{31}P NMR spectra were measured with a Varian Unity Inova 400 spectrometer at 298 K. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or to external 85% H_3PO_4 (^{31}P). The spectra were recorded in $CDCl_3$ or in d_6-DMSO.

Infrared spectra

Infrared spectra were recorded with an FT IR Nicolet Magna 760 instrument within the mid-infrared (4000-400 cm^{-1}) region. The samples were thoroughly grinded, suspended in Nujol and analyzed as a thin film between KBr plates.

Mass spectra

Low-resolution electrospray ionization (ESI) mass spectra were obtained with an Esquire 3000 (Bruker) spectrometer. The samples were dissolved in HPLC grade methanol.

X-ray diffraction analysis

Diffraction data were collected with a Bruker APEX2 CCD image plate diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) using graphite monochromatized MoKα radiation (λ=0.71073 Å) and were analyzed with the program package included in the software of diffractometer. Some crystallographic data are summarized in Table **4.1.**.

The structures were solved by direct methods (SHELXS97[26]) and refined by full-matrix least squares procedure based on F^2 (SHELXL97[26]). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms residing on the nitrogens were identified on difference electron density maps and refined as "riding atoms". Hydrogens in the CH_n groups were inserted in their calculated positions and refined similarly. Geometric parameters such as bond lengths, dihedral angles and structural drawings were obtained with a recent version of PLATON program.[27]

Table 4.1. Crystallographic data, data collection and structure refinement parameters for **8.**[a]

Formula	$C_{24}H_{22}FeN_3O_2P$
M [g·mol^{-1}]	471.27
Crystal system	monoclinic
Symmetry space group	$P2_1/c$
a [Å]	15.7717(4)
b [Å]	7.7650(2)
c [Å]	17.1706(4)
β[deg]	93.6980(10)
V [Å^3]	2098.46(9)
Z	4
D_{calc} [g·cm^{-3}]	1.492
μ (Mo Kα) [mm^{-1}]	0.822
Diffractions total	34164
Unique/observed[b] diffractions	4812/4179
R_{int} (%)[c]	0.0303
R(observed data) (%)[b,d]	0.0373
R, wR (all data) (%)[d]	0.0772
Δρ (e·Å^{-3})	0.635, –0.280

[a] Common details: T = 150(2) K.

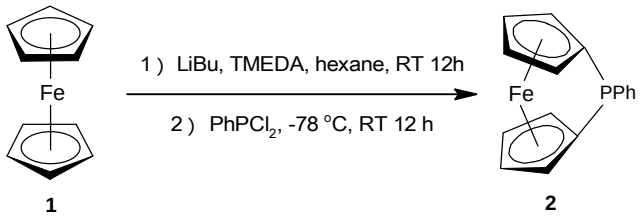
[b] Diffractions with $I_O > 2\sigma(I_O)$.

[c] $R_{int} = \Sigma\left|F_O^2 - F_O^2(mean)\right| / \Sigma F_O^2$, where $F_O^2(mean)$ is the average intensity of symmetry-equivalent diffractions.

[d] $R_{int} = \Sigma\left||F_O| - |F_C|\right| / \Sigma|F_O|$, w$R$ = $\left[\Sigma\left\{w\left(F_O^2 - F_C^2\right)^2\right\} / \Sigma w\left(F_o^2\right)^2\right]^{\frac{1}{2}}$.

4.2 Synthesis of Hdpf

4.2.1 Synthesis of 1-phenyl-1-phospha-[1]ferrocenophane (**2**)[19]



Three-necked round-bottom reaction flask was charged with ferrocene **(1)** (18.6 g, 100 mmol) and put under argon atmosphere. Dry hexane (400 mL) was added dropwise, followed by the introduction of freshly distilled *N,N,N',N'*-tetramethyl-1,2-diaminoethane. The resulting mixture was stirred before 2.5M solution of *n*-butyl lithium in hexane (96 mL, 240 mmol) was slowly introduced into the reaction flask. The ferrocene dissolved and the reaction mixture turned red during the addition. The reaction was allowed to stir for an hour after which time it was left to stand overnight.

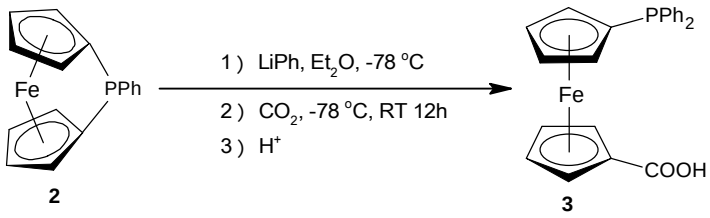
Two distinct layers were formed, the upper phase consisting of deep-orange liquid was removed from the reaction mixture by carefully removing it via a double ended syringe needle. Immediately thereafter, 400 mL of hexane was quickly added dropwise and the reaction mixture was immersed into an CO_2/ethanol cold bath (–78 °C). After cooling for 15 minutes, dichlorophenylphosphine (11.0 mL, 81 mmol) was added stepwise to a vigorously stirred reaction mixture within the space of 20 minutes under the argon atmosphere. The resultant mixture was stirred in the cooling bath for 30 minutes and then at room temperature overnight.

The reaction mixture was quenched by adding 50 mL of distilled water, stirred for an hour and transferred to a separatory funnel. Rusty-red organic phase was left there, while water phase was washed with hexane and then washings were combined with the original organic phase. The combined organic phases were washed with distilled water, then with brine and

dried over magnesium sulfate for 30 minutes, filtered and evaporated to dryness. Thus prepared 1-phenyl-1-phospha-[1]ferrocenophane **(2)** (8.223 g, 28 %) was characterized by ^{1}H and ^{31}P NMR spectroscopy and immediately used for the subsequent synthesis.

Characterization. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.40 (m, 4 H, fc), 4.48 (m , 2 H, fc), 4.65 (m, 2 H, fc), 7.29-7.68 (m, 5 H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ +11.1 (s). The data were consistent with the literature data.

4.2.2 Synthesis of 1'-(diphenylphosphino)ferrocenecarboxylic acid (**3**)[19]



Two-neck round bottom reaction flask containing 1-phenyl-1-phospha-[1]ferrocenophane **(2)** (8.220 g, 28.1 mmol) was flushed with argon and immersed into a cold CO_2/ethanol bath (–78 °C). Then, dry diethylether (250 mL) was injected, stirring begun and 1.8 M phenyllithium in dibutylether (17.3 ml, 31 mmol) was added carefully. Reaction mixture was stirred and cooled at –78 °C for 30 minutes, then stirred for another 30 minutes at room temperature, followed by cooling in the CO_2/ethanol bath again.

Reaction flask was equipped with a bubbler and the freshly crushed dry ice was added portion-wise into the reaction mixture which resulted into the formation of Lidpf as a fine yellow dense precipitate. During this procedure, argon atmosphere was maintained and the reaction flask was cooled. After 15 minutes of cooling, the reaction was left to proceed at room temperature overnight.

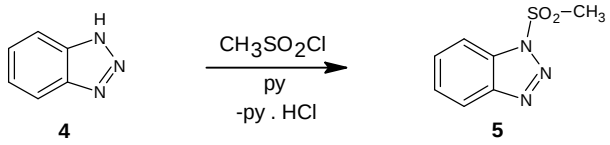
Yellow mixture was extracted four times with 25 mL aqueous NaOH (w = 0.05) and the aqueous phases were washed with diethyl ether. The bottom red aqueous layer was separated from the organic phase. Cold water bath was prepared and the beaker containing the combined aqueous and crushed ice was immersed into it. An aqueous solution of phosphoric acid (pH ca. 1) was added dropwise. Brown clumps of precipitate that formed were filtered out on a Büchner funnel and washed twice with 25 mL of aqueous solution of phosphoric acid (w = 0.01). The crude product was dissolved in a hot diluted acetic acid (w = 0.80), and the

solution was left to cool slowly over the following 48 hours. The resulting needle-like orange-red crystals were filtered off, carefully washed with distilled water, and dried in a vacuum dessicator over NaOH. The residue from first crystallization was recrystallized from hot acetic acid and second and third crops provided some additional portion of Hdpf, which was isolated similarly. Orange-red crystalline solid was isolated with a total 57 % yield (6.603 g).

Characterization. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.18 (apparent q, *J'* = 1.8 Hz, 2 H, fc), 4.34 (apparent t, *J'* = 2.1 Hz, 2 H, fc), 4.46 (apparent t, *J'* = 2.1 Hz, 2 H, fc), 4.77 (apparent t, *J'* = ^{31}P{^{1}H} NMR ($CDCl_3$): δ –17.6 (s). The data were consistent with the literature.

4.3 Synthesis of Hydrazide **7**

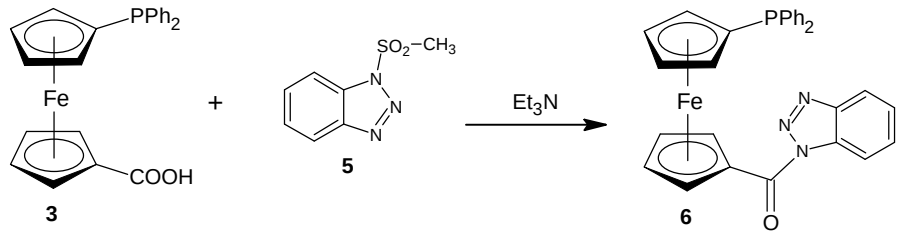
4.3.1 Synthesis of 1-(methanesulfonyl)-1*H*-1,2,3-benzotriazole (**5**)[28]



Under argon atmosphere, benzotriazole (**4**) (11.916 g, 100 mmol) was mixed with 12.0 mL of dry pyridine and 80 mL of dry toluene. Meanwile, methanesulfonyl chloride (9.5 mL, 123 mmol) was dissolved in 10 mL of dry toluene and the solution was added dropwise into reaction flask that was cooled in an ice water bath (4 °C) prior to the introduction of the methanesulfonyl reagent. After 15 minutes, cloudy white precipitate began to form. The reaction mixture was stirred overnight (12 h) before the resulting white precipitate was dissolved by addition 100 mL of water and 150 mL of ethyl acetate. The organic layer was isolated, washed with brine and dried over magnesium sulfate for 30 minutes. The drying agent was filtered off and the organic phase was evaporated to dryness. Product (15.198 g, 77 %) was isolated as a white crystalline solid whose structure and purity was confirmed by ^{1}H NMR spectroscopy.

Characterization. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 3 H, CH_3), 7.51-7.57 (m, 1 H, C_6H_4), 7.66-7.72 (m, 1 H, C_6H_4), 8.02 (td, J_{HH} = 8.4, 1.0 Hz, 1H, C_6H_4), 8.16 (td, J_{HH} = 8.4, 1.0 Hz, 1H, C_6H_4).

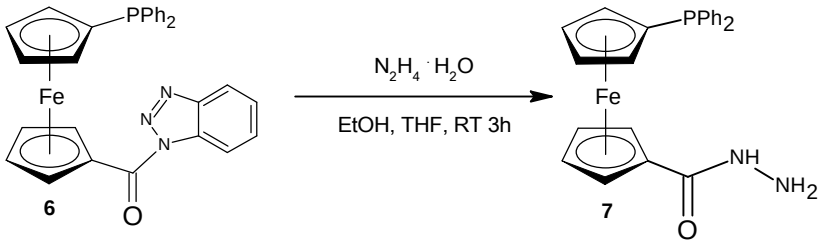
4.3.2 Synthesis of 1-[1'-(diphenylphosphino)ferrocene-1-carbonyl]-1*H*-1,2,3-benzotriazole (**6**)[23]



Freshly synthesized 1-(methanesulfonyl)-1*H*-1,2,3-benzotriazole **(5)** (2.821 g, 6.81 mmol) and the stoichiometric amount of solid Hdpf (1.3427 g, 6.81 mmol) were charged to 100mL two-neck round bottom flask under an argon atmosphere. The content of reaction flask was dissolved in dry tetrahydrofuran (30 mL) that was injected via a syringe followed by triethylamine (1.42 ml, 10.2 mmol). The reaction mixture was stirred and heated under reflux conditions (82 °C) for 8 hours. After cooling the reaction mixture, the solvents were evaporated under vacuum and the residue was dissolved in 35 mL of dry chloroform. The extract was washed with distilled water, dried over magnesium sulfate and evaporated. The residue was redissolved in dichloromethane and filtered through a short column (ca. 2 cm) of silica gel in dichloromethane. After evaporation to dryness and purity confirmation by ^{1}H and ^{31}P NMR, deep-red product **6** was collected and used immediately in the subsequent reaction step.

Characterization. ^{1}H NMR (300 MHz, $CDCl_3$): 4.15 (apparent q , *J'* = 1.8 Hz, 2 H, fc), 4.42 (apparent t, *J'* = 1.8 Hz, 2 H, fc), 4.58 (apparent t, *J'* = 2.0 Hz, 2 H, fc), 5.45 (apparent t, *J'* = 2.0 Hz, 2 H, fc), 7.26-7.54 (m, 1 H, C_6H_4), 7.63-7.67 (m, 1 H, C_6H_4), 8.15 (td, J_{HH} = 8.4, 1.0 Hz, 1H, C_6H_4), 8.35 (td, J_{HH} = 8.3, 1.0 Hz, 1H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –17.9 (s). The data were consistent with the literature.

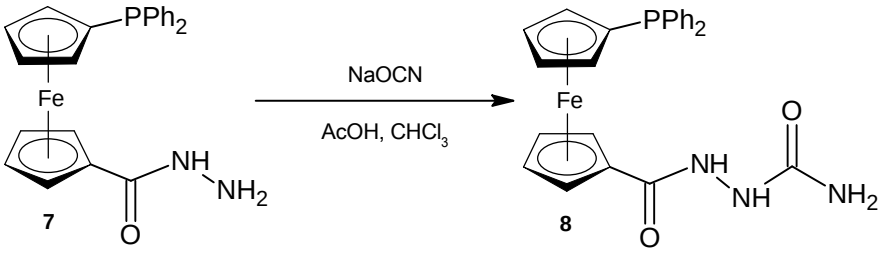
4.3.3 Synthesis of 1'-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)**[23]



Triazole derivative **(6)** was immediately put under argon atmosphere and dissolved in a mixture of 6 mL of ethanol and 11 mL of dry tetrahydrofuran. Sufficient excess of hydrazine monohydrate (7.0 ml, 136 mmol) was added dropwise into the reaction flask. The color of the mixture changed from deep red to orange almost immediately upon the addition. The reaction mixture was stirred for 3 h at room temperature. Solvents were evaporated under vacuum, the residue was dissolved in ethyl acetate and extracted three times with 25 mL of 2 M sodium hydroxide. The organic layer was dried over magnesium sulfate, filtered and evaporated. The crude product was purified by flash column chromatography over silica gel ($MeOH/CH_2Cl_2$ 1:10 by volume), evaporated and dried in a vacuum desiccator. This procedure afforded hydrazide **(7)** as an orange solid (2.275 g, 78.0 %).

Characterization. ^1H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 2 H, NH_2), 4.10 (apparent q , *J'* = 1.8 Hz, 2 H, fc), 4.24 (apparent t, *J'* = 1.8 Hz, 2 H, fc), 4.43 (apparent t, *J'* = 2.0 Hz, 2 H, fc), 4.57 (apparent t, *J'* = 2.0 Hz, 2 H, fc), 6.97 (s, 1 H, NH), 7.30-7.39 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –17.2 (s). The data were consistent with the literature.

4.4 Synthesis of 1'-(diphenylphosphino)-1-{[2-(aminocarbonyl)hydrazino]-carbonyl}ferrocene **(8)**

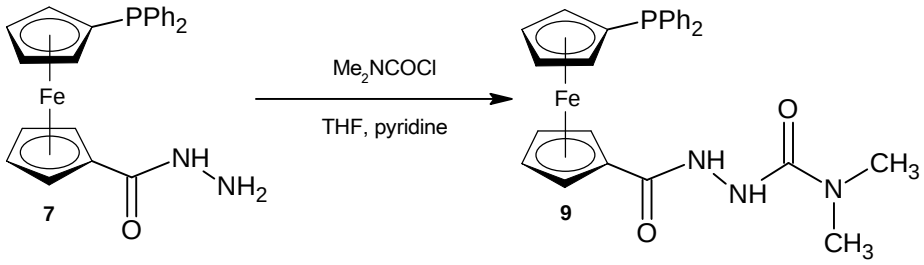


Under argon 1'-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)** (431 mg, 1.01 mmol) was dissolved in 6.0 mL of $CHCl_3$ and the solution was cooled in an ice bath. Solid sodium cyanate (78.5 mg, 1.21 mmol) was introduced, followed by a dropwise addition of cold acetic acid (427 mg, 7.11 mmol). Additional 5.0 mL of $CHCl_3$ were used to wash the remaining reactants into reaction mixture. The reaction was left to proceed at 0 °C for 2 hours and then at room temperature for 8 h. The reaction mixture was evaporated to dryness and the residue was dissolved in 5 mL of ($MeOH/CH_2Cl_2$ 1:20 by volume). The crude product was purified by flash column chromatography on silica gel in the same solvent mixture. Evaporation of the

major band afforded the product as an orange solid (416 mg, 88%). Single crystals of **(8)** were isolated by crystallization from hot ethyl acetate solution.

^{1}H NMR (400 MHz, d_6-DMSO): δ 4.12 (apparent q, *J'* = 1.9 Hz, 2 H, fc), 4.16 (apparent t, *J'* = 1.9 Hz, 2 H, fc), 4.56 (apparent t, *J'* = 1.7 Hz, 2 H, fc), 4.77 (apparent t, *J'* = 1.9 Hz, 2 H, fc), 5.89 (s, 1 H, NH), 7.28-7.39 (m, 10 H, PPh_2), 7.78 (d, $^{3}J_{HH}$ = 1.6 Hz, 1 H, NH), 9.43 (d, $^{3}J_{HH}$ = 1.6 Hz, 1 H, NH). ^{31}P{^{1}H} NMR (d_6-DMSO): δ –18.2 (s). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 69.37 (s, 2 C, CH fc), 71.91 (s, 2 C, CH fc), 73.58 (d, $^{3}J_{PC}$ = 4 Hz, 2 C, CH fc), 74.10 (d, $^{2}J_{PC}$ = 15 Hz, 2 C, CH fc), 75.10 (s, 1 C, *C*–CO fc), 77.06 (d, $^{1}J_{PC}$ = 9 Hz, 1 C, *C*–P fc), 128.95 (d, $^{3}J_{PC}$ = 7 Hz, 4 C, CH_m PPh_2), 129.29 (s, 2 C, CH_p PPh_2), 133.67 (d, $^{2}J_{PC}$ = 20 Hz, 4 C, CH_o PPh_2), 139.07 (d, $^{1}J_{PC}$ = 11 Hz, 2 C, C_{ipso} PPh_2), 158.94 (s, 1 C, C=O), 168.71 (s, 1 C, C=O). ESI MS: *m/z* = 494.1 $[M + Na]^+$, 510.1 $[M + K]^+$. IR (Nujol, cm^{-1}): 3373 m, 3284 m, 3242 w, 3198 m, 3113 w, 3072 w, 3052 w, 2726 w, 2679 w, 1698 s, 1659 s, 1605 s, 1585 w, 1564 w, 1501 s, 1307 w, 1217 w, 1195 w, 1178 w, 1162 m, 1125 w, 1099 m, 1067 m, 1054 w, 1033 m, 997 w, 860 w, 837 m, 819 m, 757 s, 741 m, 705 w, 698 s, 634 w, 597 w, 568 w, 529 w, 508 m, 456 m, 468 w, 455 m, 427 w, 419 m. Elemental analysis calculated for $C_{24}H_{22}FeN_3O_2P$ (MW 470.28): C 61.16, H 4.71, N 8.92 %. Found C 60.72, H 4.73, N 8.52 %.

4.5 Preparation of 1'-(diphenylphosphino)-1-{[2-[(dimethylamino)carbonyl]-hydrazino]carbonyl}ferrocene **(9)**

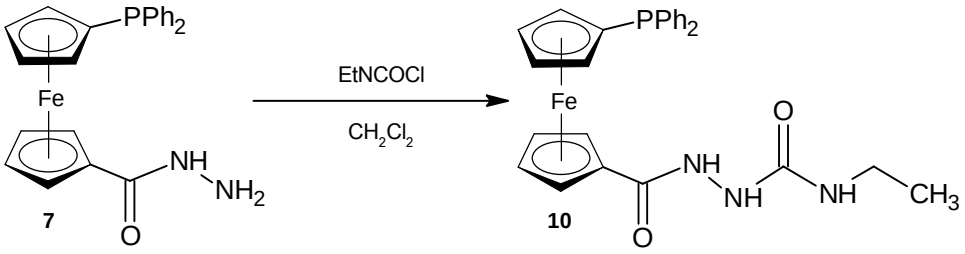


1´-(Diphenylphosphino)ferrocene-1-carbohydrazide **(7)** (428 mg, 1.00 mmol) was introduced into a 50mL reaction flask, dissolved in 5 mL of CH_2Cl_2 and the flask was placed into an ice bath (0 °C). A solution of *N*,*N*-dimethylcarbamoyl chloride (180 µL, 1.97 mmol) in 2 mL of THF was added dropwise followed by pyridine (0.80 ml, 10.0 mmol) diluted with another 4.0 mL of THF. Reaction mixture was cooled for 2 hours and then heated to 60 °C for 6 h under a reflux condenser. The color of the mixture changed to deep orange upon refluxing. The reaction mixture was evaporated to dryness, residue was taken up with 20 mL of

dichloromethane and the extract was washed with distilled water. The organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel ($MeOH/CH_2Cl_2$ 1:20 by volume) to give 1'-(diphenylphosphino)-1-{[2-[(dimethylamino)carbonyl]hydrazino]carbonyl}ferrocene **(9)** as a dark orange powder (469 mg, 94%).

^{1}H NMR (400 MHz, d_6-DMSO): δ 2.95 (s, 6 H, 2 CH_3), 4.21-4.24 (m , 4 H, fc), 4.54 (apparent t, *J'* = 1.8 Hz, 2 H, fc), 4.65 (apparent t, *J'* = 1.9 Hz, 2 H, fc), 7.09 (d, $^3J_{HH}$ = 4.0 Hz, 1 H, NH), 7.28-7.40 (m, 10 H, PPh_2), 8.08 (d, $^3J_{HH}$ = 2.0 Hz, 1 H, NH). $^{31}P\{^1H\}$ NMR (d_6-DMSO): δ –17.0 (s). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 36.22 (s, 2 C, $N(CH_3)_2$), 69.74 (s, 2 C, CH fc), 72.52 (s, 2 C, CH fc), 73.75 (d, $^3J_{PC}$ = 4 Hz, 2 C, CH fc), 74.15 (s, 1 C, *C*–CO fc), 74.97 (d, $^2J_{PC}$ = 15 Hz, 2 C, CH fc), 77.83 (d, $^1J_{PC}$ = 9 Hz, 1 C, *C*–P fc), 128.97 (d, $^3J_{PC}$ = 7 Hz, 4 C, CH_m PPh_2), 129.41 (s, 2 C, CH_p PPh_2), 134.26 (d, $^2J_{PC}$ = 20 Hz, 4 C, CH_o PPh_2), 139.32 (d, $^1J_{PC}$ = 10 Hz, 2 C, C_{ipso} PPh_2), 157.70 (s, 1 C, C=O), 169.94 (s, 1 C, C=O). ESI MS: *m*/*z* = 522.1 $[M + Na]^+$, 538.3 $[M + K]^+$. IR (Nujol, cm^{-1}): *v* = 3213 m, 3049 w, 2954 w, 2726 w, 1661 m, 1632 m, 1551 m, 1433 w, 1349 w, 1327 w, 1256 w, 1183 m, 1160 w, 1069 w, 1025 w, 936 w, 834 w, 744 m, 698 m, 574 s, 491 m. Elemental analysis calculated for $C_{26}H_{26}FeN_3O_2P$ (MW 499.32): C 62.54, H 5.25, N 8.42 %. Found C 60.35, H 4.94, N 7.85 %.

4.6 Synthesis of 1'-(diphenylphosphino)-1-{[2-[(ethylamino)carbonyl) hydrazino]-carbonyl}ferrocene **(10)**



A solution of 1´-(diphenylphosphino)ferrocene-1-carbohydrazide **(7)** (601 mg, 1.40 mmol) in 6.0 mL of CH_2Cl_2 was treated with ethyl isocyanate (170 μL, 2.10 mmol) in a 50mL reaction flask under argon atmosphere, protected from direct sunlight. No immediate color change was observed but slowly, after 15 minutes of stirring, yellow clumps began to form. Another 5.0 mL of dry CH_2Cl_2 was added into reaction mixture and the mixture was left stirring for 9 hours. Then, it was quenched by adding 15 mL of saturated $NaHCO_3$ and stirring for 10

minutes, extracted with CH_2Cl_2 and washed with distilled water. The purified organic phase was dried over $MgSO_4$, evaporated to dryness. Flash chromatography on silica gel (MeOH/CH_2Cl_2 1:20 by volume) was performed in order to isolate not only desired 1'-(diphenylphosphino)-1-{[2-[(ethylamino)carbonyl)hydrazino]carbonyl}ferrocene **(10)** (552 mg, 79 %) but also the corresponding phosphineoxide (25 mg, 4 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 3.05 (q, $^3J_{HH}$ = 6.6 Hz, 2 H, CH_2), 4.11 (apparent q, *J'* = 1.8 Hz, 2 H, fc), 4.16 (apparent t, *J'* = 1.9 Hz, 2 H, fc), 4.56 (apparent t, *J'* = 1.8 Hz, 2 H, fc), 4.77 (apparent t, *J'* = 1.9 Hz, 2 H, fc), 6.26 (t, $^3J_{HH}$ = 5.6 Hz, 1 H, NH), 7.28-7.39 (m, 10 H, PPh_2), 7.73 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, NH), 9.44 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, NH). ^{31}P{^{1}H} NMR (d_6-DMSO): δ –18.2 (s). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 16.24 (s, 1 C, CH_3), 34.69 (s, 1 C, CH_2), 70.19 (s, 2 C, CH fc), 72.68 (s, 2 C, CH fc), 74.36 (d, $^3J_{PC}$ = 4 Hz, 2 C, CH fc), 74.81 (d, $^2J_{PC}$ = 14 Hz, 2 C, CH fc), 75.88 (s, 1 C, *C*–CO fc), 77.83 (d, $^1J_{PC}$ = 7 Hz, 1 C, *C*–P fc), 128.96 (d, $^3J_{PC}$ = 7 Hz, 4 C, CH_m PPh_2), 129.30 (s, 2 C, CH_p PPh_2), 133.67 (d, $^2J_{PC}$ = 20 Hz, 4 C, CH_o PPh_2), 139.09 (d, $^1J_{PC}$ = 10 Hz, 2 C, C_{ipso} PPh_2), 158.11 (s, 1 C, C=O), 168.79 (s, 1 C, C=O). ESI MS: *m*/*z* = 522.2 $[M + Na]^+$, 538.3 $[M + K]^+$. IR (Nujol, cm^{-1}): *ν* = 3356 m, 3292 m, 3245 b, 3077 w, 1700 s, 1624 s, 1586 s, 1538 b, 1432 w, 1347 w, 1320 m, 1245 m, 1221 w, 1195 w, 1164 m, 1066 w, 1027 m, 935 m, 854 w, 842 w, 824 w, 747 s, 740 s, 693 m, 638 w, 584 w, 515 m, 496 m, 475 m, 453 m, 422 w. Elemental analysis calculated for $C_{26}H_{26}FeN_3O_2P$ (MW 499.32): C 62.54, H 5.25, N 8.42 %. Found C 62.38, H 5.34, N 7.91 %.

5. Attachments

5.1 Crystallographic data

Table 5.1. Fractional coordinates for hydrazide **8**.

Atom	*x*	*y*	*z*	U_{izo}
Fe	0.730015(14)	0.94228(3)	0.573107(13)	0.01982(8)
P	0.81228(3)	0.79719(5)	0.40535(3)	0.02306(10)
O1	0.55441(8)	0.67831(14)	0.50596(6)	0.0239(3)
O2	0.51838(7)	0.48118(14)	0.74673(6)	0.0222(2)
N1	0.51969(8)	0.72248(16)	0.62963(7)	0.0186(3)
N2	0.47136(9)	0.57155(16)	0.62432(7)	0.0191(3)
N3	0.45273(10)	0.29379(18)	0.66140(8)	0.0265(3)
C1	0.60150(10)	0.93762(19)	0.56774(9)	0.0186(3)
C2	0.63304(10)	1.0323(2)	0.63478(10)	0.0231(3)
C3	0.68069(11)	1.1736(2)	0.60793(11)	0.0273(4)
C4	0.67888(11)	1.1668(2)	0.52534(10)	0.0255(4)
C5	0.63024(10)	1.0216(2)	0.50012(9)	0.0206(3)
C6	0.81664(10)	0.8134(2)	0.51108(10)	0.0243(3)
C7	0.77055(11)	0.6968(2)	0.55790(11)	0.0281(4)
C8	0.78509(12)	0.7460(3)	0.63737(11)	0.0341(4)
C9	0.83951(12)	0.8912(3)	0.64032(11)	0.0343(4)
C10	0.85900(11)	0.9324(2)	0.56338(11)	0.0285(4)
C11	0.55694(10)	0.7709(2)	0.56460(9)	0.0175(3)
C12	0.92359(11)	0.7603(2)	0.38549(10)	0.0247(4)
C13	0.94592(13)	0.7860(3)	0.30938(11)	0.0361 (4)
C14	1.02465(14)	0.7354(3)	0.28652(13)	0.0458(5)
C15	0.98339(11)	0.6867(2)	0.43851(11)	0.0308(4)
C16	1.08248(13)	0.6593(3)	0.33880(14)	0.0421(5)
C17	1.06237(12)	0.6361(3)	0.41485(13)	0.0375(5)
C18	0.79779(11)	1.0201(2)	0.37238(9)	0.0229(3)
C19	0.72226(11)	1.0567(2)	0.32849(10)	0.0254(4)
C20	0.70237(12)	1.2240(2)	0.30566(10)	0.0306(4)
C21	0.75808(14)	1.3553(2)	0.32586(11)	0.0354(4)
C22	0.83448(13)	1.3201(2)	0.36724(11)	0.0345(4)
C23	0.85486(12)	1.1525(2)	0.38986(10)	0.0282(4)
C24	0.48501(10)	0.44766(19)	0.68106(8)	0.0172(3)

Table 5.2. Anisotropic displacement for hydrazide **8**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.02072(13)	0.01996(12)	0.01915(12)	0.00122(9)	0.00415(9)	-0.00116(9)
P	0.0210(2)	0.0204(2)	0.0280(2)	-0.00100(17)	0.00332(16)	0.00023(16)
O1	0.0352(7)	0.0230(6)	0.0140(5)	-0.0041(4)	0.0050(5)	-0.0073(5)
O2	0.0330(6)	0.0203(6)	0.0133(5)	-0.0007(4)	0.0016(4)	-0.0027(5)
N1	0.0275(7)	0.0141(6)	0.0146(6)	-0.0012(5)	0.0048(5)	-0.0029(5)
N2	0.0272(7)	0.0158(6)	0.0143(6)	0.0009(5)	0.0010(5)	-0.0049(5)
N3	0.0451(9)	0.0188(7)	0.0150(7)	0.0023(5)	-0.0030(6)	-0.0069(6)
C1	0.0204(8)	0.0181(7)	0.0177(7)	-0.0010(6)	0.0052(6)	0.0006(6)
C2	0.0253(8)	0.0240(8)	0.0206(8)	-0.0054(6)	0.0074(6)	-0.0039(7)
C3	0.0295(9)	0.0203(8)	0.0330(9)	-0.0073(7)	0.0091(7)	-0.0054(7)
C4	0.0272(9)	0.0170(7)	0.0332(9)	0.0028(7)	0.0097(7)	0.0000(7)
C5	0.0226(8)	0.0195(7)	0.0201(8)	0.0026(6)	0.0053(6)	0.0012(6)
C6	0.0209(8)	0.0236(8)	0.0291(9)	0.0033(7)	0.0057(7)	0.0064(7)
C7	0.0253(9)	0.0204(8)	0.0389(10)	0.0047(7)	0.0046(7)	0.0049(7)
C8	0.0350(10)	0.0370(10)	0.0309(10)	0.0070(8)	0.0068(8)	0.0136(8)
C9	0.0300(10)	0.0434(11)	0.0287(9)	0.0034(8)	-0.0039(8)	0.0035(8)
C10	0.0214(8)	0.0323(9)	0.0318(9)	0.0021(7)	0.0024(7)	0.0000(7)
C11	0.0201(7)	0.0180(7)	0.0147(7)	0.0013(6)	0.0018(6)	0.0017(6)
C12	0.0235(8)	0.0210(8)	0.0301(9)	-0.0057(7)	0.0051(7)	-0.0003(6)
C13	0.0324(10)	0.0469(12)	0.0293(10)	-0.0059(9)	0.0050(8)	0.0036(9)
C14	0.0403(12)	0.0611(14)	0.0376(11)	-0.0143(10)	0.0159(9)	0.0006(11)
C15	0.0281(9)	0.0289(9)	0.0357(10)	0.0005(8)	0.0044(7)	0.0017(7)
C16	0.0246(10)	0.0417(11)	0.0616(14)	-0.0174(10)	0.0151(9)	0.0017(8)
C17	0.0247(9)	0.0326(10)	0.0550(13)	-0.0035(9)	0.0006(9)	0.0031(8)
C18	0.0269(8)	0.0228(8)	0.0199(8)	0.0012(6)	0.0088(6)	0.0029(7)
C19	0.0280(9)	0.0287(9)	0.0202(8)	0.0014(7)	0.0075(7)	-0.0005(7)
C20	0.0362(10)	0.0345(10)	0.0216(8)	0.0059(7)	0.0062(7)	0.0070(8)
C21	0.0531(12)	0.0262(9)	0.0277(9)	0.0053(7)	0.0075(8)	0.0060(9)
C22	0.0481(12)	0.0255(9)	0.0307(10)	-0.0006(7)	0.0090(8)	-0.0074(8)
C23	0.0316(9)	0.0284(9)	0.0250(9)	0.0010(7)	0.0047(7)	-0.0019(7)
C24	0.0207(7)	0.0178(7)	0.0140(7)	0.0001(6)	0.0068(6)	0.0013(6)

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