STAND-ALONE PROJECT

FINAL REPORT

Project number	**P24202-N17**
Project title	**Carbonylation of Coordinatively Unsaturated Iron Complexes** **Carbonylierung koordinativ ungesättigter Eisenverbindungen**
Project leader	**Karl Kirchner**
Project website	**http://www.ias.tuwien.ac.at/**

I. Summary for public relations work

1. Zusammenfassung für die Öffentlichkeitsarbeit

Die Reaktivität von Übergangsmetallkomplexen gegenüber kleinen Molekülen ist ein wichtiges Gebiet der metallorganischen Chemie. Durch die steigenden Energiepreise und die begrenzten Vorräte an fossilen Brennstoffen ist die Umwandlung kleiner Moleküle wie CO, H_2, N_2, oder CO_2 in komplexe Chemikalien ein wichtiger Schritt in Richtung nachhaltige Chemie. Um effizientere Prozesse zu entwickeln, ist ein Verständnis der Koordinations- und Bindungseigenschaften von Übergangsmetallen gegenüber solchen Molekülen sehr wichtig, was typischerweise durch Untersuchungen der Wechselwirkung von bestimmten Substratmolekülen mit Metallzentren in unterschiedlichen Spin- und oxidationszuständen erreicht wird. In diesem Zusammenhang ist CO als wichtiges Molekül hervorzuheben. In Kombination mit Eisen ist es in verschiedenen industriellen Prozessen, wie der Wassergasreaktion, wo CO in CO_2 und H_2 umgewandelt wird, oder der Fischer-Tropsch Reaktion, wo es in flüssige lineare Kohlenwasserstoffe umgewandelt wird, von Bedeutung. Außerdem spielt CO Koordination an Eisen eine wichtige Rolle in der Natur.

Da CO äußerst toxisch für Menschen ist, wäre überdies die Entwicklung neuer CO Sensoren von großer Wichtigkeit. Nachteile von vielen neuen optochemischen Verbindungen ist die relative hohe Nachweisgrenze von CO, die Interferenzen mit Sauerstoff und anderen Luftinhaltsstoffen, als auch die hohen Kosten von Edelmetallen, welche typischerweise als Sensoren verwendet werden.

Das Ziel dieses Projektes ist koordinativ ungesättigte high-spin Fe(II) Verbindungen herzustellen und deren Reaktivität gegenüber CO zu untersuchen, um einen tieferen Einblick in die elektronischen Eigenschaften derartiger Komplex zu erhalten. Solche Untersuchungen sind sehr wichtig, da es dadurch möglich sein sollte auch schwerer zu aktivierende Substrate wie Wasserstoff zu binden und zu aktivieren, wie etwa in [Fe]-Hydrogenasen. Derartige Untersuchungen sind auch nützlich für die Entwicklung von Eisencarbenkatalysatoren für die Olefinmetathese, da Carben Liganden viele Ähnlichkeiten zu CO aufweisen. Außerdem könnten diese Untersuchungen zur Entwicklung von neuen CO Gassensoren führen.

Deshalb ist die Entwicklung von neuen wohldefinierten umweltfreundlichen Eisenkatalysatoren, die eine vergleichbare Aktivität aufweisen wie Edelmetallkatalysatoren, äußerst wichtig. Eisen ist das häufigste Übergangsmetall in der Erdkruste, praktisch unbegrenzt vorhanden, ungiftig, und sehr billig.

2. Summary for public relations work

In sum, this project generated a fundamental understanding of new concepts in the area of Reactivity of *Base Metal Complexes towards Small Molecules*. This led to the development of efficient iron-based complexes which were used in catalytic reactions formerly restricted to noble metals, and resulted in the development of new, environmentally benign catalytic processes.

Iron is the most abundant transition metal in the earth crust, essentially non-toxic, inexpensive, and ubiquitously available. Accordingly, such investigations are important for the rational design of well-defined iron catalysts.

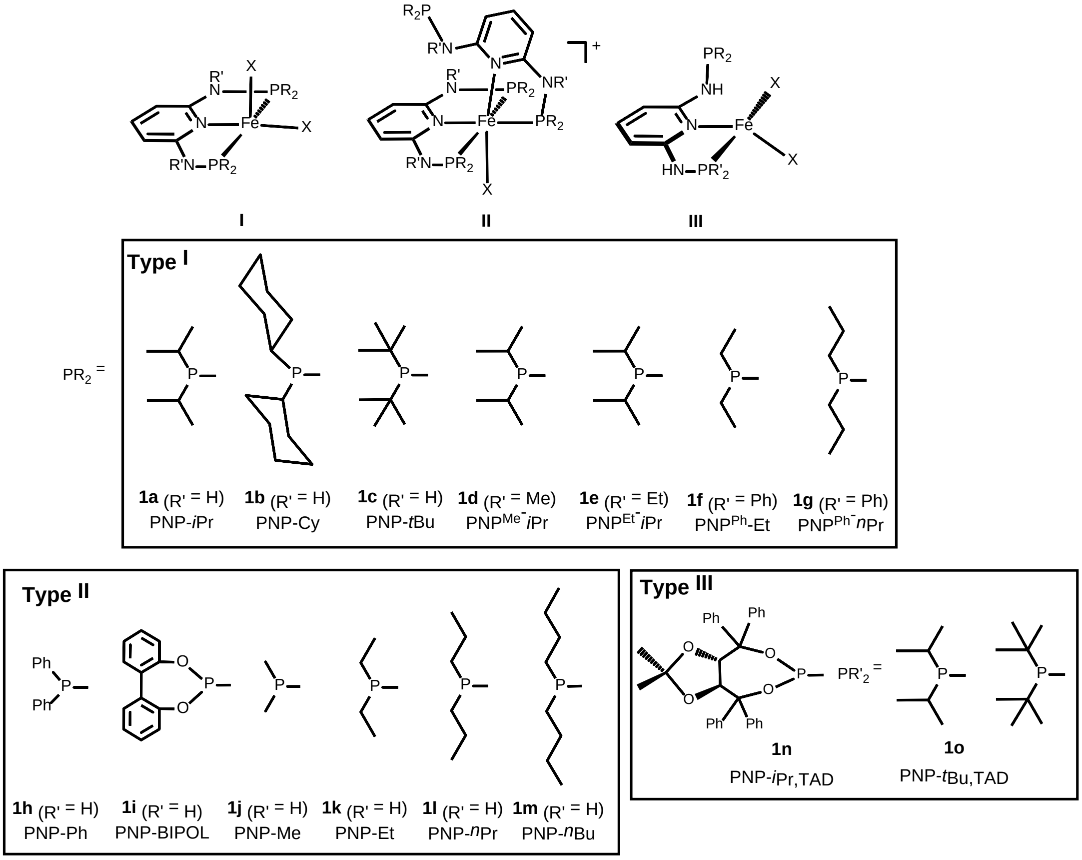
The reactivity of transition metal complexes towards small molecules is an increasingly important topic in organometallic chemistry. With energy prices on the rise and limited supplies of fossil fuels, transformations that involve incorporating small molecules such as CO, H_2, N_2, or CO_2 into complex chemicals can prove valuable in developing more sustainable chemistry. In order to achieve more efficient processes, it is important to understand the bonding and coordination properties of transition metals to such small molecules. The objective was to obtain insights into their electronic properties and features that may allow the coordination and functionalization of more challenging substrates such as dihydrogen or carbenes as well as to find new materials which may possess potential for catalytic applications and/or CO gas sensing in future investigations. Moreover, this study may be useful for the future synthesis of iron complexes containing alkylidene ligands – which are electronically very similar to CO - as olefin metathesis catalysts, an as yet illusive reaction as iron is concerned.

II. Brief project report

1. Report on research work

1.1 Information on the development of the research project

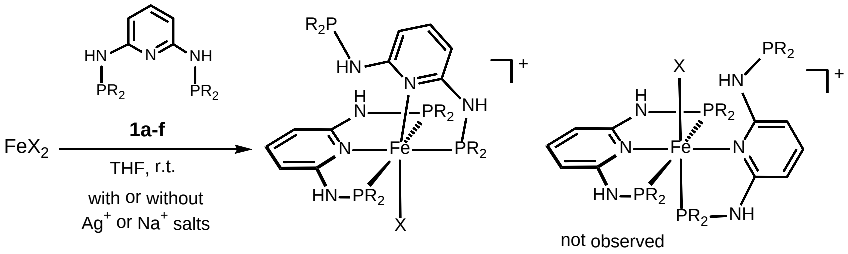
The objective of the underlying project was to prepare a series of coordinatively unsaturated high spin Fe(II) compounds and to study their reactivity of towards carbon monoxide. Such investigations provide useful insights into the electronic properties and reactivity patterns of high spin iron complexes (e.g. spin block and spin acceleration effects) that may allow the coordination and functionalization of more challenging substrates such as dinitrogen In addition, these investigations could have lead also to new chromogenic CO sensing materials. Notwithstanding this, the present study is important for the development of more environmentally friendly and sustainable reactions. Iron is the most abundant transition metal in the earth crust, essentially non-toxic, inexpensive, and ubiquitously available. Accordingly, such investigations are an important aid for the rational design of well-defined iron catalysts.



Scheme 1 Overview of PNP ligands (labeling of complexes refers to letters of ligands depicted here) and classification of their reaction behavior with FeX_2 (X = Cl, Br).

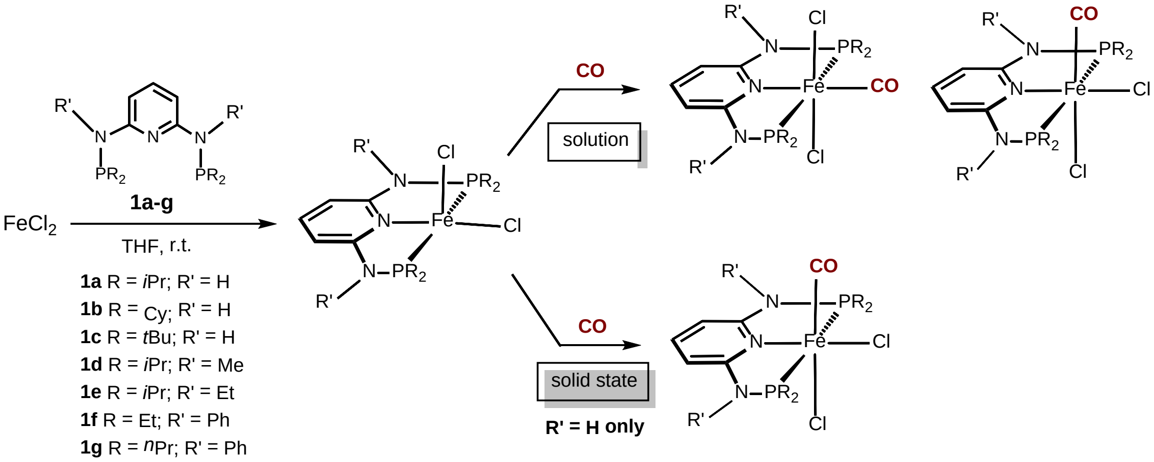
We investigated the reaction of iron(II) halides with a series of PNP pincer ligands based on the 2,6-diaminopyridine scaffold (Scheme 1). The building blocks had to be prepared via microwave assisted copper catalyzed amination of halopyridines. The steric bulk of PNP ligands prepared thus far decrease in the order PNP-*t*Bu (130) > PNP^{Me}-*i*Pr (120) ≈ PNP^{Ph}-*n*Pr ≈ PNP^{Ph}-Et (120) > PNP-*i*Pr (115) > PNP^{Me}-Ph (105)> PNP-*n*Bu ≈ PNP-

*n*Pr ≈ PNP-Et ≈ PNP-Ph (100) > PNP-BIPOL (95) > PNP-Me (90). With PNP ligands which are sterically less demanding than PNP-*i*Pr complexes of the type [Fe(k^3-*P,N,P*-PNP)(k^2-*P,N*-PNP)X]$^+$ (X = Cl, Br) were formed (Scheme 2), while with the bulkier ligands pentacoordinate complexes [Fe(k^3-*P,N,P*-PNP)X$_2$] were obtained. In the case of the first, the PNP pincer ligands are coordinated in k^3-*P,N,P*- and k^2-*P,N*-fashion, respectively, and adopt a strongly distorted octahedral geometry as established by X-ray crystallography. Obviously related to these distortions is their reactivity undergoing, upon halide dissociation, a facile rearrangement reaction to give the dicationic complexes [Fe(k^3-*P,N,P*-PNP)$_2$]$^{2+}$ where now both PNP ligands are bound in k^3-*P,N,P*-fashion. This reaction proceeds only in the case of the smaller PNP ligands (PNP-Ph, PNP-BIPOL, PNP-Me), while with the bulkier ones (PNP-*n*Bu, PNP-*n*Pr, PNP-Et) the presence of a halide scavenger is required. The outcome of these investigation strongly suggests that the formation and reactivity of [Fe(k^3-*P,N,P*-PNP)(k^2-*P,N*-PNP)X]$^+$ complexes is controlled by the steric bulk of the PNP ligands rather than their electronic properties.



Scheme 2

We have also prepared *trans*- and *cis*-[Fe(k^3*P,N,P*-PNP)(CO)Cl$_2$] complexes bearing both sterically demanding and small PNP ligands based on the 2,6-diaminopyridine scaffold where the aromatic pyridine ring and the phosphine PR$_2$ moieties are connected via NH, N-alkyl, or N-aryl linkers (Scheme 3). In the case of bulky PNP ligands, with the exception of complexes



Scheme 3

with P*t*Bu$_2$ units, these complexes are obtained upon treatment of [Fe(k^3*P,N,P*-PNP)Cl$_2$] with CO in THF or CH$_2$Cl$_2$ solutions. On the other hand, with small PNP ligands such complexes are not directly accessible due to the formation of [Fe(k^3*P,N,P*-PNP)(k^2*P,N*-PNP)Cl]Cl. These complexes turned out to be substitutionally labile liberating the k^2-*P,N*-bound PNP ligand in the presence of CO to yield the desired complexes [Fe(k^3*P,N,P*-PNP)(CO)Cl$_2$] but in yields <50%. High yields of [Fe(k^3*P,N,P*-PNP)(CO)Cl$_2$] could be achieved by reacting anhydrous FeCl$_2$ with 1 equiv of the respective PNP ligands under a CO atmosphere. For structural and reactivity comparisons we also prepared the related complex [Fe(k^3*P,N,P*-PNP-Ph)(k^2*P,N*-PN-Ph)Cl]$^+$ where the pyridine moiety of the PN-Ph lacks a substituent in the second *ortho* position. This complex does not react with CO. In the solid state, complexes [Fe(k^3*P,N,P*-PNP)Cl$_2$] with NH linkers are also converted quantitatively into *trans*- or *cis*-[Fe(k^3*P,N,P*-PNP)(CO)(Cl)$_2$] upon treatment with CO as indicated by a color change of the material and by IR monitoring. On the other hand, all complexes with NMe, NEt, and NPh linkers did not react with CO. Finally, in order to rationalize why most [Fe(k^3*P,N,P*-PNP)Cl$_2$] complexes react readily with CO, but not those with *t*Bu substituents, the addition of CO to [Fe(k^3*P,N,P*-PNP-*i*Pr)Cl$_2$] and [Fe(k^3*P,N,P*-PNP-*t*Bu)Cl$_2$] was investigated by means of DFT calculations revealing an thermodynamically unfavorable process in case of the latter.

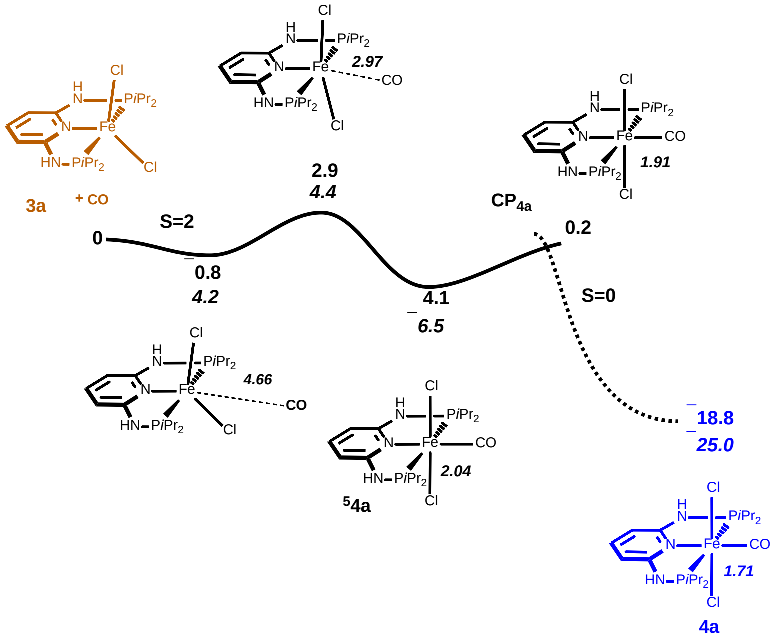


Figure 1. Energy profile (OPBE) for the addition of CO to [Fe(k^3*P,N,P*-PNP-*i*Pr)Cl$_2$]. The energy values (kcal/mol) are referred to the separated reagents and the values in italics represent free energy corrected for dispersion effects (DFT-D3). The plain curve corresponds to the spin-quintuplet PES (S = 2), and the dashed curve to the spin-singlet PES (S = 0). The Fe-C(CO) distance (Å) along the reaction coordinate is indicated.

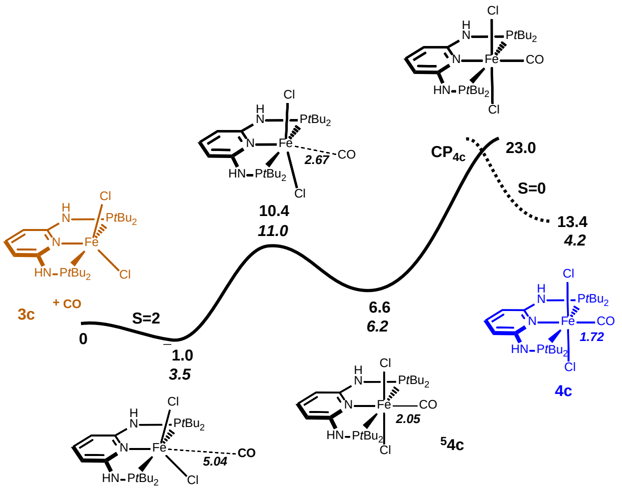
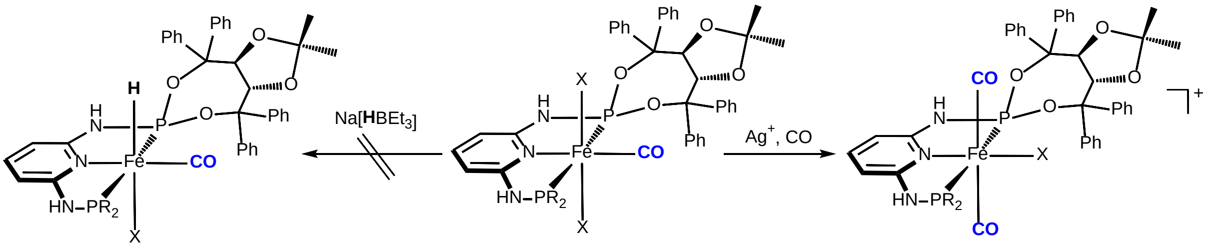


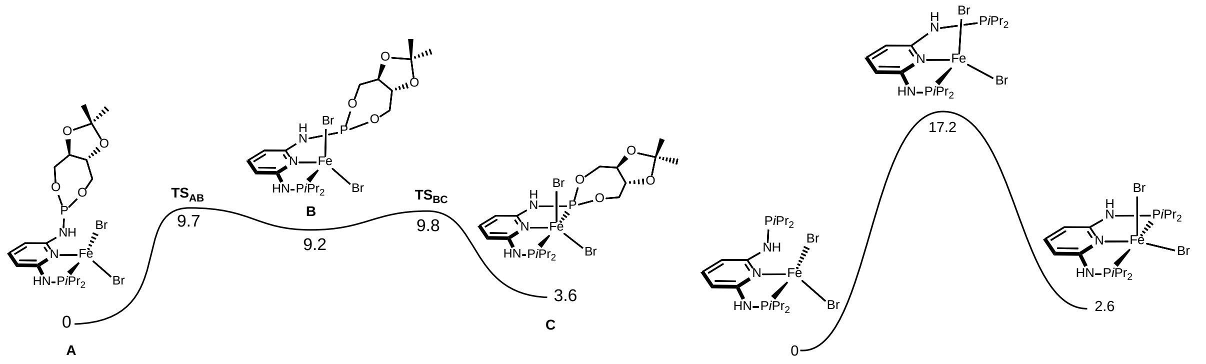
Figure 2. Energy profile (OPBE) for the addition of CO to [Fe(k^3*P,N,P*-PNP-*t*Bu)Cl$_2$]. The energy values (kcal/mol) are referred to the separated reagents and the values in italics represent free energy corrected for dispersion effects (DFT-D3). The plain curve corresponds to the spin-quintuplet PES (*S* = 2), and the dashed curve to the spin-singlet PES (*S* = 0). The Fe–C(CO) distance (Å) along the reaction coordinate is indicated.

We have prepared several Fe(II) complexes of the general formula [Fe(PNP-R,TAD)X$_2$] (R = *i*Pr, *t*Bu; X = Cl, Br) bearing asymmetric chiral pincer ligands based on *R,R*-TADDOL (TAD). In the solid state, as shown by X-ray crystallography, Mössbauer and IR spectroscopy, these complexes adopt a tetrahedral geometry with the PNP ligand coordinated in k^2*P,N*-fashion with the TAD arm being not coordinated. All complexes are paramagnetic with a quintet ground state. In solution there are equilibria between [Fe(k^3*P,N,P*-PNP-R,TAD)X$_2$] and [Fe(k^2*P,N*-PNP-R,TAD)X$_2$] complexes and the PNP-R,TAD ligand is hemilabile. DFT calculations indicate that the rearrangement of the pincer ligands is an accessible process and, thus, equilibria between the four-coordinated species and their five-coordinated counterparts is expected to occur. Addition of CO to [Fe(PNP-*i*Pr,TAD)X$_2$] in solution yields the diamagnetic octahedral complexes *trans*-[Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)(CO)X$_2$], which react further with Ag$^+$ salts in the presence of CO to give the cationic complexes *trans*-[Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)(CO)$_2$X]$^+$. Complexes bearing *t*Bu substituents do not react with CO. Moreover, in the solid state none of the tetrahedral complexes are able to bind CO. Addition of CO most likely takes place at the five coordinate complex [Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)X$_2$]. The mechanism for this process was investigated by DFT and the most favorable path obtained corresponds to the rearrangement of the pincer ligand first from a k^2*P,N*- to a k^3*P,N,P*-coordination mode followed by CO coordination to [Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)X$_2$]. The alternative path with a reversed order of the two processes is competitive and the possible occurrence of both at the same time may not be discarded. Heating solid



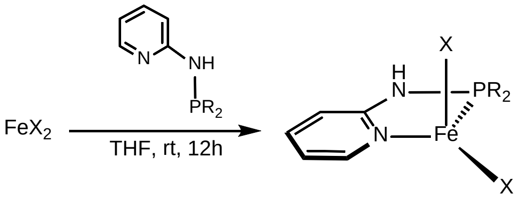
Scheme 4

samples of *trans*-[Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)$(CO)_2X]^+$ at 100°C under vacuum leads to regeneration of complex [Fe(k^2*P,N*-PNP-*i*Pr,TAD)X_2]. Loss of CO is slow with about 80% conversion after 2h. Mössbauer measurements show no evidence for the formation of [Fe(k^3*P,N,P*-PNP-*i*Pr,TAD)X_2] suggesting that at higher temperatures the PNP ligands are flexible enough to change their coordination modes also in the solid state.



Scheme 5. Energy profile (kcal/mol) for the rearrangement between κ^2*P,N* and κ^3*P,N,P* in [Fe(PNP-*i*Pr,TAD')Br_2] and comparison with [Fe(PNP-*i*Pr)Br_2].

Moreover, we have prepared stable coordinatively unsaturated 14e and 16e iron(II) complexes of the types [Fe(EN-*i*Pr)X_2] (E = P, S, Se; X = Cl, Br) and [Fe(ON-*i*Pr)$_2$X]X, respectively, containing bidentate EN ligands based on 2-aminopyridine. Mössbauer spectroscopy and magnetization studies confirmed their high spin nature with magnetic moments very close to 4.9 μ_B reflecting the expected four unpaired d-electrons in all these compounds.

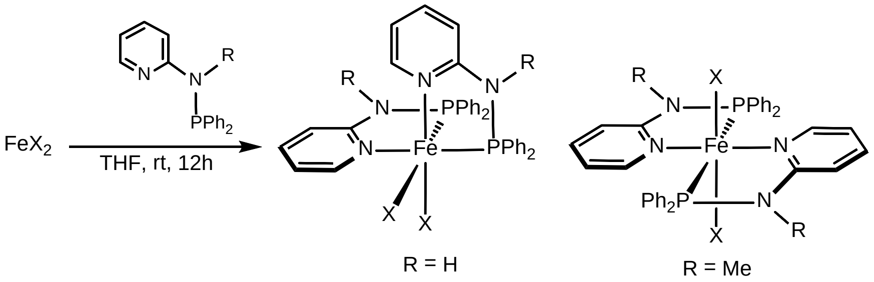


Scheme 6

Despite their relatively low formal electron count neither the tetrahedral 14e complexes [Fe(EN-*i*Pr)X_2] nor the square pyramidal 16e complexes [Fe(ON-*i*Pr)$_2$X]X reacted with CO at ambient temperature. IR monitoring at low temperature (-50 to 0°C) revealed that [Fe(PN-*i*Pr)X_2] reversibly added CO to give, in the case of X = Cl, the paramagnetic monocarbonyl species [Fe(PN-*i*Pr)(CO)Cl_2], and, in the case of X = Br, the low-spin dicarbonyl complexes *cis,trans*- and *cis,cis*-[Fe(PN-*i*Pr)$(CO)_2Br_2$]. The *cis,trans* isomer, although thermodynamically slightly more stable than the *cis,cis* complex, is kinetically labile and releases readily CO at ambient temperature to reform [Fe(PN-*i*Pr)Br_2]. The *cis,cis* isomer, on the other hand, is stable with respect to CO release due to a spin-block effect, i.e., prior to CO dissociation an energetically unfavorable spin state change has to occur. The complex *cis,cis*-[Fe(PN-*i*Pr)$(CO)_2Br_2$] could be obtained in a different way by reacting *cis*-[Fe$(CO)_4Br_2$] with PN-*i*Pr. The mechanisms for the formation of *cis,trans*- and *cis,cis*-[Fe(PN-*i*Pr)$(CO)_2Br_2$] were deduced from DFT calculations and are in full agreement with experimental findings.

The outcome of a reaction of CO addition to iron complexes is closely related to the nature of the reagent, i.e., the unsaturated iron complex. Both geometry and coordination number are important to determine the success of the reaction, the key factor being the overall ligand field of the ensemble of ligands in the reactant. The stronger the ligand field, the easier will be CO addition with formation of the low spin product. In fact, the effect of strong ligands on the energy balance of the reaction is two-fold. On the one hand strong field ligands stabilize the low spin product, and, on the other hand, they will destabilize the unsaturated high spin complex with respect to its low spin form, thus favoring the "spin-forbidden" reaction. In general, P-donor ligands generate a stronger ligand field than N-donor ligands. Within this group, the ligand field strength seems to decrease in the order amidinates > imines > amines. In the present study, the reactivity towards CO follows the order ON-*i*Pr < SN-*i*Pr ≈ SeN-*i*Pr < PN-*i*Pr < PP.

We have prepared stable octahedral 18e iron(II) complexes of the general formula [Fe(PN^R-Ph)$_2$X$_2$] (R = H, Me) by reacting anhydrous FeX$_2$ with 2 equivs of PN^R-Ph ligands. Tetrahedral complexes of the type [Fe(PN^R-Ph)X$_2$] as in the case of the bulkier PN-*i*Pr and PN-*t*Bu ligands were not formed. ^{57}Fe Mössbauer spectroscopy and magnetization studies confirmed their high spin nature with magnetic moments very close to 4.9 μ_B at room temperature reflecting the expected four unpaired d-electrons in all these compounds. While in the case of the PN^H-Ph ligand a S = 2 to S = 0 spin crossover was observed at low temperatures, complexes with the N-methylated analog PN^{Me}-Ph maintain the high spin state also at low temperatures. It should be emphasized that this is the first example of spin crossover in this type of complexes with heterodifunctional PN ligands. Accordingly, complexes [Fe(PN^H-Ph)$_2$X$_2$] and [Fe(PN^{Me}-Ph)$_2$X$_2$] adopt different coordination geometries.



Scheme 7

For complexes of the general formula [Fe(PN^R-Ph)$_2$X$_2$] in principle five different coordination isomers are conceivable. While in [Fe(PN^{Me}-Ph)X$_2$] all donor atoms of the two PN^{Me}-Ph ligands are *trans* to one another, i.e., a *trans-Cl,P,N*-geometry is adopted, in [Fe(PN^H-Ph)X$_2$] the PN ligands most likely exhibit a *cis-Cl,P,N*-arrangement. The structural assignments are based on reactivity studies and various experimental data derived from ^{57}Fe Mössbauer spectroscopy, SQUID magnetometry, UV/Vis, Raman, and ESI-MS as well as theoretical considerations by means of DFT and TDDFT calculations. In the case of [Fe(PN^{Me}-Ph)Cl$_2$] the geometry is unequivocally established by X-ray crystallography. Moreover, in contrast to [Fe(PN^{Me}-Ph)$_2$X$_2$], [Fe(PN^H-Ph)$_2$X$_2$] is very labile and undergoes rearrangement reactions. In CH$_3$OH the diamagnetic dicationic complex [Fe(PN^H-Ph)$_3$]$^{2+}$ is formed *via* the intermediacy of *cis-P,N*-[Fe(κ^2-*P,N*-PN^H-Ph)$_2$(κ^1-*P*-PN^H-Ph)(X)]$^+$ where one PN ligand is coordinated in κ^1-*P*-fashion. This reaction involves an intermolecular ligand transfer. In CH$_3$CN the diamagnetic dicationic complex *cis-N,P,N*-[Fe(PN^H-Ph)$_2$(CH$_3$CN)$_2$]$^{2+}$ is formed as major isomer where the two halide ligands are replaced by CH$_3$CN. In sum, this dual theoretical/experimental approach provides a consistent picture of the chemistry of complexes [Fe(PN^H-Ph)$_2$X$_2$] and[Fe(PN^{Me}-Ph)$_2$X$_2$] with respect to their geometries and electronic properties.

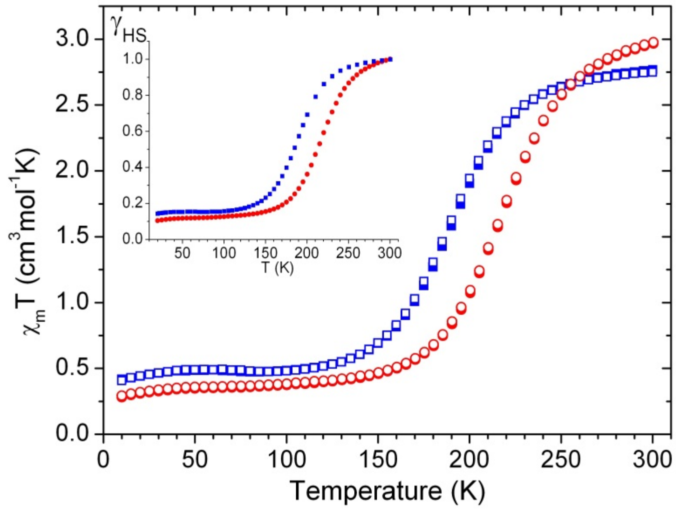


Figure 3. Temperature dependence of $\chi_m T$ for [Fe(PN^H-Ph)$_2$Cl$_2$] (blue squares) and [Fe(PN^H-Ph)$_2$Br$_2$] (red circles) upon cooling (solid symbols) and warming (open symbols). The inset shows the temperature variation of the HS Fe(II) mole fraction for both compounds, assuming that at 300 K there is only HS.

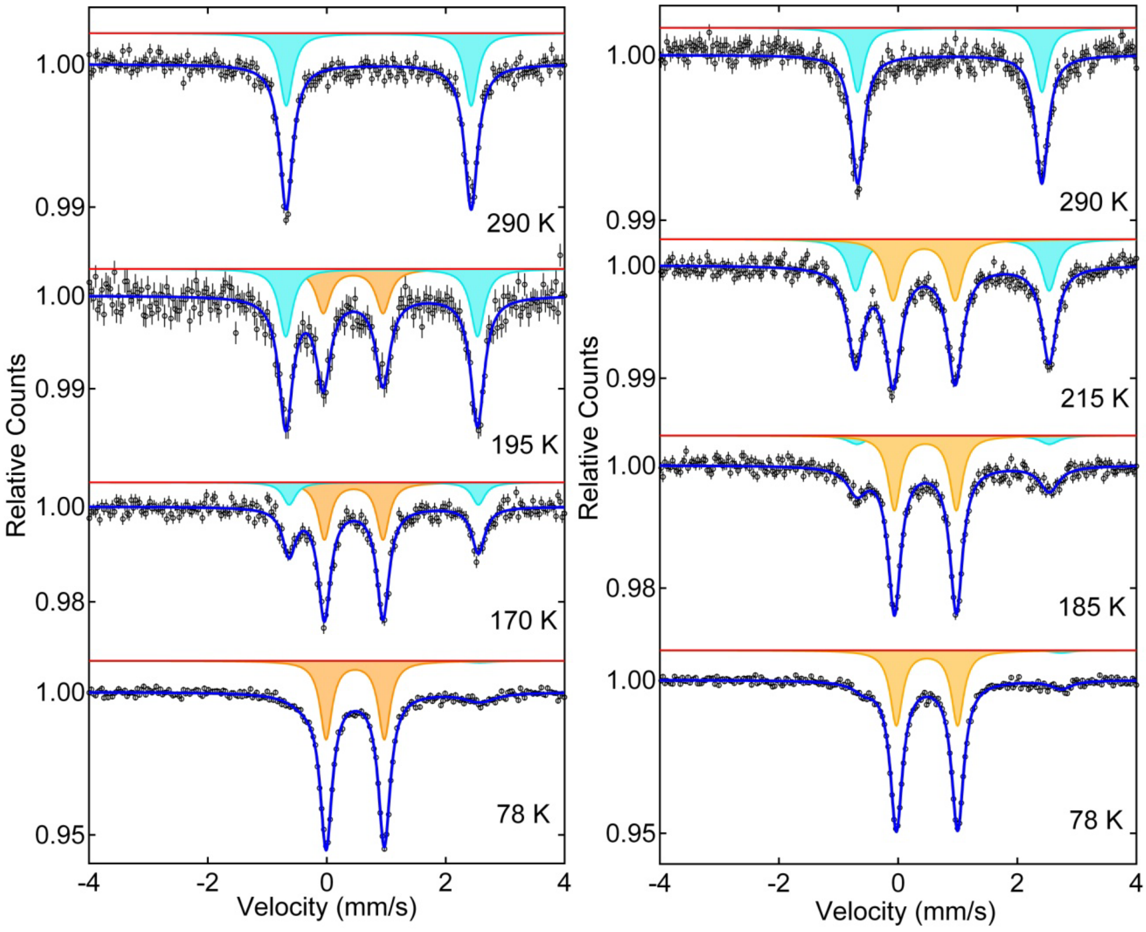
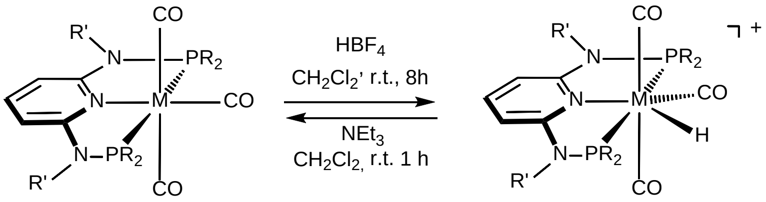


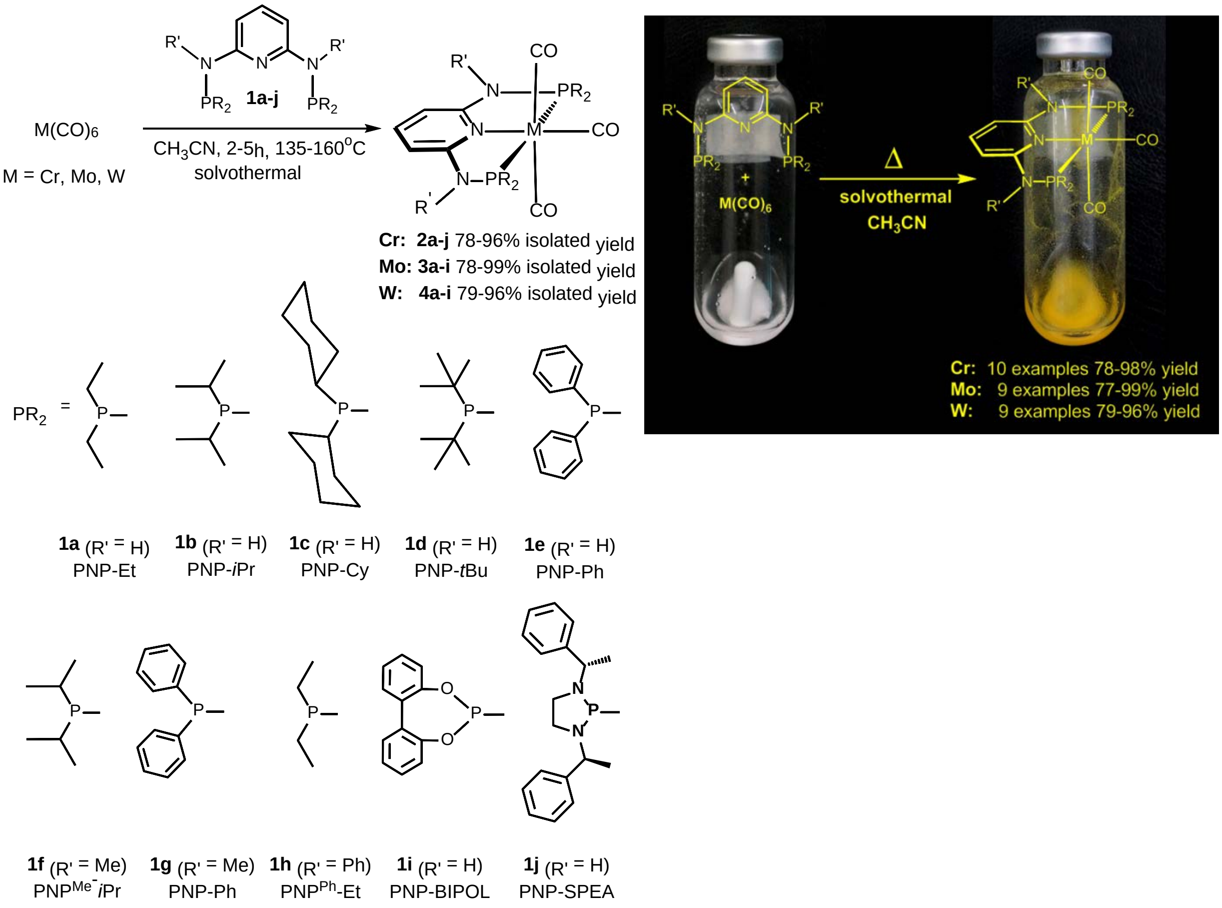
Figure 4. Temperature dependence of ^{57}Fe Mössbauer spectra of [Fe(PN^H-Ph)$_2$Cl$_2$] (left) and [Fe(PN^H-Ph)$_2$Br$_2$] (right).

Finally, we extended to use of PNP pincer ligands to other non-precious metals. For instance, the synthesis of a series of molybdenum and tungsten PNP complexes of the types [M(PNP)(CO)$_3$]. Mo(0) and W(0) complexes [M(PNP)CO)$_3$] as well as seven coordinate cationic hydridocarbonyl and halocarbonyl Mo(II) and W(II) complexes of the type [M(PNP)(CO)$_3$Br]$^+$ and [M(PNP)(CO)$_3$H]$^+$ featuring PNP pincer ligands based on 2,6-diaminopyridine were prepared and fully characterized. The synthesis of Mo(0) complexes [Mo(PNP)CO)$_3$] was accomplished by treatment of [Mo(CO)$_3$(CH$_3$CN)$_3$] with the respective PNP ligands. Addition of HBF$_4$ to [M(PNP)(CO)$_3$] resulted in protonation at the tungsten and molybdenum centers to formally generate Mo(II) and W(II) hydride complexes [M(PNP)(CO)$_3$H]$^+$. The protonation is fully reversible and upon addition of NEt$_3$ as base the Mo(0) and W(0) complexes [M(PNP)(CO)$_3$] are reformed quantitatively.



Scheme 8

We also demonstrated that the solvothermal synthesis technique presented provides a powerful, simple and practical synthetic method to afford group six PNP pincer carbonyl complexes of the type [M(PNP)(CO)$_3$] (M = Cr, Mo, W) in high isolated yields in a short time. As Cr and W complexes are concerned, these complexes are not readily accessible with conventional methods.



Scheme 9

1.2 Most important results and brief description of their significance:

- This project generated a fundamental understanding of new concepts in the area of *Sustainability through Base Metal Catalysis* and led to the development of efficient iron-based catalysts
- In the course of this project, we were able to develop well-defined iron-based catalysts of comparable or even higher activity in the hydrogenation of ketones, aldehydes and CO_2
- New Co PCP pincer systems in oxidation states 0, +I, +II, and +III were prepared and fully characterized exhibiting promising properties.

1.3 Information on the execution of the project, use of available funds and changes to the original project plan relating to the following:

- This project was carried out within about 3.5 years. Funding was carefully used and sufficient for the successful completion of this project.
- Four PhD students were involved in this project pursuing different topics.

2. Personnel development – Importance of the project for the research careers of those involved (including the project leader)

- This project helped to significantly improve the scientific standing of the PI in the organometallic and organic community. Moreover, this project resulted and will result in the award of four PhD theses.

3. Effects of the project beyond the scientific field

- The development of base metal catalysts and their implementation catalytic processes may constitute an environmentally benign alternative to critical resources.

4. Other important aspects (lectures)

Lectures Given at Universities

- “Iron PNP Pincer Complexes and Catalysis – The Importance of Ligand Field Strength, Spin State, and Geometry”, Center for Research and Advanced Studies of the National Polytechnic Institute (Cinvestav), Puebla, Mexico, December 6, **2013**.
- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, Kyushu University, Kasuga City, Japan, July 7, **2014**.
- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, University Jaume I, Castellon, Spain, May 19, **2015**.
- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, University of Valladolid, Valladolid, Spain, May 21, **2015**.
- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, University of Castilla-La Mancha, Ciudad Real, Spain, May 25, **2015.**
- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, Institute for Chemical Research (IIQ) (Juan Campora), Sevilla, Spain, May 26, **2015**.

- “Chemistry based on Non-precious Metal PNP and PCP Pincer Complexes”, University of Zaragoza, Zaragoza, Spain, May 28, **2015**.
- “Chemistry based on Non-precious Metal Pincer Complexes”, University of Wroclaw, Wroclaw, Poland, June 6, **2015**.

Lectures Given at Conferences

- “Small Molecule Activation with Non-precious Metal Pincer Complexes”, COST Working Group CM1205, Catalytic Routines for Small Molecule Activation (CARISMA), Venice, Italy, May 5 - 8, **2014**.
- “Small Molecule Activation with Non-precious Metal PNP and PCP Pincer Complexes”, *26th International Conference on Organometallic Chemistry*, Fukuoka, Japan, July 13-18, **2014**. (invited)$_{(20)}$

III. Attachments

1. Scholarly / scientific publications

1.1 Peer-reviewed publications / already published

1. Öztopcu, Ö.; Stöger, B.; Mereiter, K.; Kirchner, K. "Reactivity of Iron Complexes containing Monodentate Aminophosphine Ligands - Formation of Four-membered Carboxamido-Phospha-Metallacycles", *J. Organomet. Chem.* **2013**, *735*, 80-87 (doi: 10.1016/j.jorganchem.2013.03.027) (no OA).
2. **Öztopcu, Ö.; Holzhacker, C.; Puchberger, M.; Weil, M.; Mereiter, K.; Veiros, L. F.; Kirchner, K. "Synthesis and Characterization of Hydridocarbonyl Molybdenum and Tungsten PNP Pincer Complexes",** ***Organometallics*** **2013,** ***32*****, 3042-3052 (doi: 10.1021/om400254k) (no OA).**
3. de Aguiar, S. R. M. M.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Puchberger, M.; Veiros, L. F.; Kirchner, K. "A Complete Series of Halocarbonyl Molybdenum PNP Pincer Complexes – Unexpected Differences between NH and NMe Spacers", *J. Organomet. Chem.* **2014**, *760*, 74-83 (doi: 10.1016/j.jorganchem.2013.12.018) (no OA).
4. Holzhacker, C.; Calhorda, M. J.; Gil, A.; Carvalho, M. D.; Ferreira, L. P.; Mereiter, K.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Kirchner, K. "Four- and Five Coordinate High-Spin Iron(II) Complexes bearing Bidentate Soft/Hard SN Ligands based on 2-Aminopyridine", *Polyhedron* **2014**, *81*, 45-55 (doi: 10.1016/j.poly.2014.05.052) (no OA).
5. Holzhacker, C.; Calhorda, M. J.; Gil, A.; Carvalho, M. D.; Ferreira, L. P.; Stöger, B.; Mereiter, K.; Weil, M.; Pittenauer, E.; Allmaier, G.; Müller, D.; Weinberger, P.; Kirchner, K. "Six-coordinate High-Spin Iron(II) Complexes with Bidentate PN Ligands based on 2-Aminopyridine – New Spin Crossover Systems", *Dalton Trans.* **2014**, *43*, 11152-11164 (doi: 10.1039/c4dt00186a). (no OA)
6. de Aguiar, S. R. M. M.; Öztopcu, Ö.; Stöger, B.; Mereiter, K.; Veiros, L. F.; Pittenauer, E.; Allmaier, G.; Kirchner, K. "Coordinatively Unsaturated Halocarbonyl Molybdenum PNP Pincer Complexes", *Dalton Trans.* **2014**, *43*, 14669-14679 (doi: 10.1039/c4dt01932f). (no OA)
7. Bichler, B.; Glatz, M.; Stöger, B.; Mereiter, K.; Veiros, L. F.; Kirchner, K. "An iron(II) complex featuring κ^3 and labile κ^2-bound PNP pincer ligands – striking differences between CH_2 and NH spacers", *Dalton Trans* **2014***, 43*, 14517-14519 (doi: 10.1039/c4dt01933d). (no OA)
8. **Glatz, M.; Bichler, B.; Mastalir, M.; Stöger, B.; Mereiter, K.; Weil, M.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. "Iron(II) complexes featuring κ^3 and κ^2-bound PNP pincer ligands - the significance of sterics",** ***Dalton Trans.*** **2015*****, 44*****, 281-294** (doi: **10.1039/c4dt02866j). (no OA).**

9. Holzhacker, C.; Stöger, B.; Carvalho, M. D.; Ferreira, L. P.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Realista, S.; Gil, A.; Calhorda, M. J.; Müller, D.; Kirchner, K. "Synthesis and Reactivity of Taddol-Based Chiral Fe(II) PNP Pincer Complexes – Solution Equilibria between κ^2*P,N*- and κ^3*P,N,P*-Bound PNP Pincer Ligands", *Dalton Trans.* **2015**, *44*, 13071-13086 (doi: 10.1039/c5dt00832h). (no OA).
10. Glatz, M.; Holzhacker, C.; Bichler, B.; Mastalir, M.; Stöger, B.; Mereiter, K.; Weil, M., Veiros, L. F.; Mösch-Zanetti, N. C.; Kirchner, K. "Fe^{II} Carbonyl Complexes Featuring Small to Bulky PNP Pincer Ligands - Facile Substitution of κ^2*P,N*-Bound PNP Ligands by Carbon Monoxide", *Eur. J. Inorg. Chem.* **2015**, 5053-5065 (doi: 10.1002/ejic.201500646). (no OA).
11. Mastalir, M.; Rosenberg, E. E.; Kirchner, K. "A practical synthesis of substituted 2,6-diaminopyridines *via* microwave-assisted copper-catalyzed amination of halopyridines", *Tetrahedron* **2015**, *71*, 8104-8110 (doi: 10.1016/j.tet.2015.08.042). (no OA).
12. Mastalir, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. "2,6-Diamination of substituted pyridines via heterogeneous Chichibabin reaction", *Tetrahedron Lett.* **2016**, *57*, 333-336 (doi: /10.1016/j.tetlet.2015.12.013). (no OA).
13. **Mastalir, M.; Glatz, M.; de Aguiar, S. R. M. M.; Stöger, B.; Kirchner, K. "A Convenient Solvothermal Synthesis of Group 6 PNP Pincer Tricarbonyl Complexes", *Organometallics* 2016, *35*, 229-232 (doi: 10.1021/acs.organomet.5b00940). (no OA).**
14. Mastalir, M.; Schweinzer, C.; Weil, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. "A chromium tricarbonyl complex featuring the 4,6-bis(diphenyl-phosphinomethyl)dibenzothiophene (PSP^{Ph}) ligand", *Monatsh. Chem.* **2016**, *147*, 1183-1187 (doi: s00706-016-1707-9). (OA).
15. Schröder-Holzhacker, C.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. "High-spin iron(II) complexes with mono-phosphorylated 2,6-diaminopyridine ligands", *Monatsh. Chem.* **2016**, *147*, 1539-1545 (doi: s00706-016-1731-9). (OA)

1.2 Non peer-reviewed publications / already published

1.3 Planned publications

Author(s)			
Title			
Sources			
URL (if applicable)			
Peer Review	yes ☐	no ☐	
Status	in press/accepted ☐	submitted ☐	in preparation ☐

2. Most important academic awards

3. Information on results relevant to commercial applications

Type of commercial application		
Subject / title of the invention / discovery		
Short description of the invention / discovery		
Year		
Status	granted ☐	pending ☐
Application reference (or patent number)		

4. Publications for the general public and other publications

	national	**International**
Self-authored publications on the www		
Editorial contributions in the media		
(Participatory) contributions within science communication		
Popular science contributions		

5. Development of collaborations

N				Nationality of collaboration partner (please use the ISO-3-letter country code)
	G			Gender **F (**female) **M** (male)
		E		Extent **E1** **low** (e.g. no joint publications, but mention in acknowledgements or similar); **E2** **medium** (collaboration e.g. with occasional joint publications, exchange of materials or similar, but no longer-term exchange of personnel); **E3** **high** (extensive collaboration with mutual hosting of group members for research stays, regular joint publications, etc.)
			D	Discipline **W** **within the discipline** (within the same scientific field) **I** **interdisciplinary** (involving two or more disciplines) **T** **transdisciplinary** (collaborations outside the sciences)

N	**G**	**E**	**D**	**Name**	**Institution**
PRT	M	E2	W	Luis F. Veiros	Instituto Superior Técnico, Universidade de Lisboa
PRT	F	E2	W	Maria J. Calhorda	Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa
AUT	M	E2	W	Berthold Stöger	Institute of Chemical Technologies and Analytics, Vienna University of Technology
AUT	M	E2	W	Ernst Pittenauer	Institute of Chemical Technologies and Analytics, Vienna University of Technology

Note: General scientific contact and occasional meetings should not be considered collaborations for the purposes of this report.

6. Development of human resources in the course of the project

	In progress	**Completed**	**Gender**	
			f	**m**
Ph.D. theses		C. Holzhacker		m
Ph.D. theses		Ö. Öztopcu		m
Ph.D. theses	S. R. M. M. de Aguiar		f	
Ph.D. theses	M. Mastalir		m	

7. Applications for follow-up projects

(Please indicate the status of each project and the funding organisation)

7.1 Applications for follow-up projects (FWF projects)

Please indicate the project type (e.g. stand-alone project, SFB, DK, etc.)

Project number (if applicable)	P28866-N34		
Project type	Stand-alone project		
Title / subject	Environmentally Benign Catalytic Reactions Based on Iron		
Status	granted x	pending ☐	in preparation ☐
Application reference (if a patent is applied)			

7.2 Applications for follow-up projects (Other national projects)

(e.g. FFG, CD Laboratory, K-plus centres, funding from the Austrian central bank [OeNB], Austrian federal government, provincial agencies, provincial government or similar sources)

Funding agency	Please choose an item: Wählen Sie ein Element aus.		
Other national funding agencies			
Project number (if applicable)			
Project type			
Title / subject			
Status	granted ☐	pending ☐	in preparation ☐
Total costs (granted)			

7.3 Applications for follow-up projects (international projects) (e.g. EU, ERC or other international funding agencies)

Country			
Funding agency	Please choose an item: Wählen Sie ein Element aus.		
Project number (if applicable)			
Project type			
Title / subject			
Status	granted ☐	pending ☐	in preparation ☐
Total costs (granted)			

IV. Cooperation with the FWF

Please rate the following aspects with regard to your interaction with the FWF. Please provide any **additional comments (explanations)** on the supplementary sheet with a reference to the corresponding question/aspect.

Scale:
-2 highly unsatisfactory
-1 unsatisfactory
0 appropriate
+1 satisfactory
+2 highly satisfactory
X not used

Rules
(i.e. guidelines for: funding programme, application, use of resources, reports)

Rating

Application guidelines	Length	**2**
	Clarity	**2**
	Intelligibility	**2**

Procedures (submission, review, decision)

	Advising	**1**
	Duration of procedure	**2**
	Transparency	**1**

Project support

Advising	Availability	**x**
	Level of detail	**x**
	Intelligibility	**x**

Financial transactions (credit transfers, equipment purchases, personnel management)	**2**

Reporting / review / exploitation

	Effort	**x**
	Transparency	**x**
	Support in PR work / exploitation	**x**

Comments on cooperation/interaction with the FWF:

Personal of the FWF was always very friendly, supportive, helpful and very professional in answering questions.