# STAND-ALONE PROJECT

# FINAL REPORT

| | |
|---|---|
| **Project number** | **P24583-N28** |
| **Project title** | **A New Generation of Iron-based Hydrogenation Catalysts**<br>**Eine neue Generation von Eisen Hydrierungskatalysatoren** |
| **Project leader** | **Karl Kirchner** |
| **Project website** | **http://www.ias.tuwien.ac.at/** |

# I. Summary for public relations work

## 1. Zusammenfassung für die Öffentlichkeitsarbeit

In Summe lieferte dieses Projekt fundamental neue Erkenntnisse im Bereich "*Nachhaltigkeit durch Katalyse mittels unedlen Metallen*", und führte zur Entdeckung neuer effizienter eisenkatalysierter Reaktionen, welche bisher nur mit Edelmetallen möglich waren, umweltfreundlich und nachhaltig sind.

Im Hinblick auf Wirtschaft, Umwelt, und Nachhaltigkeit hinsichtlich Energie werden, ist ein großer Bedarf an der Entdeckung von neuen katalytisch ablaufenden Reaktionen. Wir sind an der katalytischen Reduktion (Hydrierung) von Mehrfachbindungen mittels molekularem Wasserstoff interessiert. Solche Reaktionen spielen eine sehr wichtige Rolle zur Herstellung von Aromastoffen, Parfüms, oder Feinchemikalien, und werden hervorragend durch viele Edelmetalle, wie Ruthenium, Rhodium oder Iridium katalysiert. Allerdings ist es sinnvoll Edelmetalle in diesen Reaktionen aufgrund ihrer limitierten Verfügbarkeit, ihres hohen Preises und ihrer Toxizität durch ökonomischere und umweltfreundlichere Alternativen zu ersetzen. Deshalb war das Hauptziel dieses Projektes neue Verbindungen basierend auf unedlen Metallen zu entwickeln und diese dann als Katalysatoren zu verwenden. Eisen ist in diesem Zusammenhang von besonderem Interesse, da es das häufigste Übergangsmetall in der Erdkruste, praktisch unbegrenzt vorhanden und nicht giftig ist.

Im Zuge dieses Projektes wurden viele neue Eisenverbindungen hergestellt und auch erfolgreich als Katalysatoren, etwa in der Hydrierung von wichtigen Substanzklassen, wie Aldehyde und Ketone zu Alkoholen, eingesetzt. Besonders hervorzuheben ist auch und die effiziente Hydrierung von $CO_2$, einem unerwünschten Treibhausgas, zu Ameisensäure. Es wurde auch versucht, das Know-how der Eisenchemie auf andere Metalle auszudehnen, wie etwa Kobalt, Nickel, Vanadium, und Molybdän. Die Ergebnisse dieses Projektes sind in 11 Publikationen in renommierten und begutachteten wissenschaftlichen Journalen veröffentlicht.

## 2. Summary for public relations work

In sum, this project generated a fundamental understanding of new concepts in the area of *Sustainability through Base Metal Catalysis*. This led to the development of efficient iron-based catalysis in reactions formerly restricted to noble metals, and resulted in the development of new, environmentally benign catalytic processes.

Driven by both public demand and government regulations, pharmaceutical and fine chemical manufacturers are increasingly seeking to replace stoichiometric reagents as well as precious metal based catalysts. This modifications used in synthetic transformations will develop greener, safer, and more cost-effective chemical processes. A process we were interested in was and still is the catalytic hydrogenation of multiple bonds *via* molecular hydrogen. This plays a significant role in modern synthetic organic chemistry for the production of flavors, fragrances and pharmaceuticals and is excellently performed by many transition metal complexes containing noble metals such as ruthenium, rhodium, or iridium. The limited availability of precious metals, their high cost, and their toxicity diminish their attractiveness in the long run. Thus, more economical and environmentally friendly alternatives have to be found which are in line with green chemistry guidelines. In this context, it is important to mention that iron is the most abundant transition metal in the earth crust, ubiquitously available, and non-toxic.

This project aimed at the discovery, development, and implementation of new catalytic methodologies based on iron catalysts which open the door to the sustainable production of pharmaceuticals and fine chemicals (*Sustainability through Base Metal Catalysis*). In the course of this project, we were able to develop well-defined iron-based catalysts for the hydrogenation of aldehydes and ketones to alcohols, which displayed comparable or even higher activity than precious metals. Moreover, these catalysts were also very active for the hydrogenation of $CO_2$, a greenhouse gas, to yield formic acid. In addition, we also started to develop related chemistry with other base metals such as cobalt, nickel, vanadium, and molybdenum. The outcome of this project is documented in 11 publications in highly ranked peer-reviewed journals.

# II. Brief project report

## 1. Report on research work

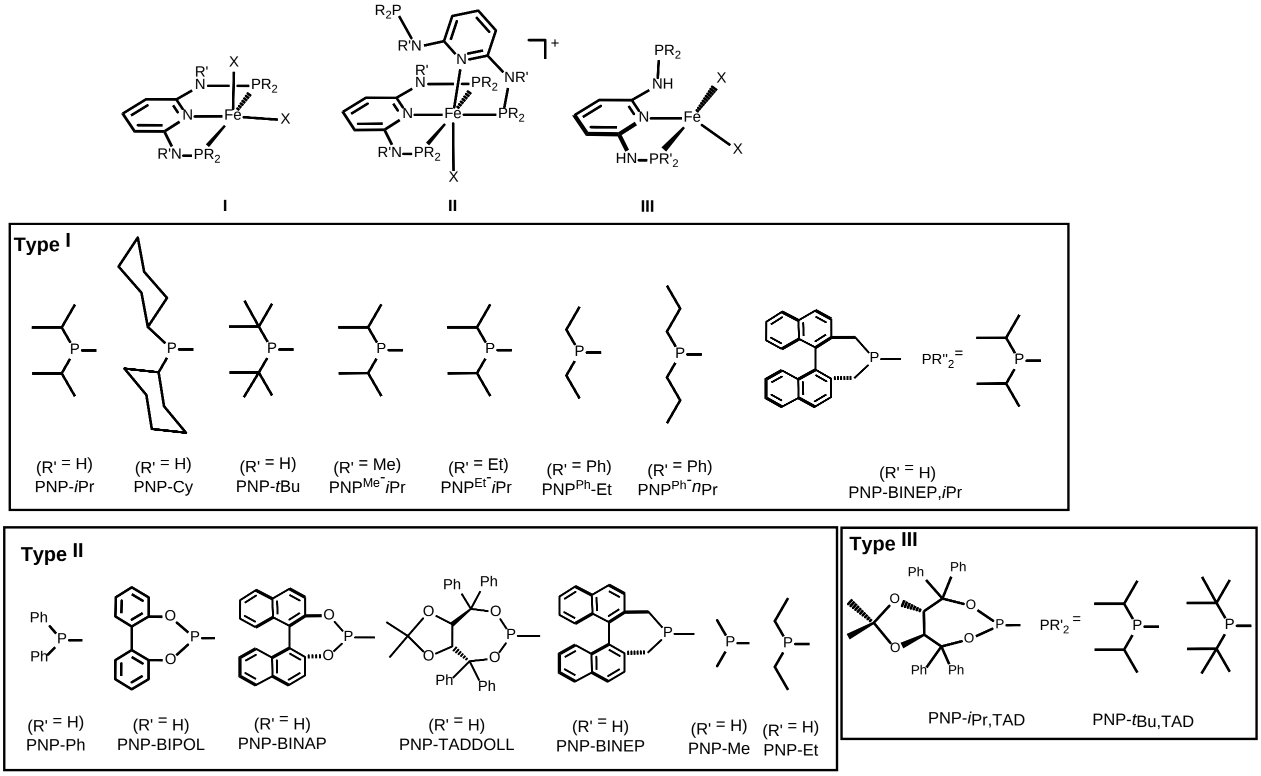
### *1.1 Information on the development of the research project*

The main goal of this project was the modular design of new, inexpensive, and easy-to-handle iron complexes possessing both acidic and basic sites for the subsequent application in homogeneous catalysis. This research originally involved the following specific objectives:

(i) Design and synthesis of a versatile set of ligands (chiral and achiral), including new derivatives of 2,6-diaminopyridine.

(ii) Thorough investigation of the complexation of the new ligands with various sources of iron revealing main patterns in their co-ordination behavior. Determination of the structure, as well as spectral and structural characteristics of the obtained metal complexes and revealing of correlations between these characteristics and the ligand's nature. Of particular relevance is the control of the spin state by the choice of ligands by using CO as co-ligand.

(iii) Extensive application of the novel complexes in the hydrogenation of ketones, aldehydes and related unsaturated substrates. Investigation of the reaction mechanisms (by spectral methods, isolation of intermediates) in order to evaluate key factors responsible for yields.



**Scheme 1** Overview of chiral and achiral tridentate ligands and their iron halide complexes

In this project, we were able to prepare a library of new PNP ligands based on the 2,6-diaminopyridine scaffold with NHR (R = H, alkyl, aryl) linkers and various $PR_2$ moieties (Scheme 1). The presence of NH linkers allows for reversible deprotonation/protonation (metal-ligand cooperation). We prepared also a large number of both achiral and chiral PNP ligands as shown in Scheme1. For two examples of chiral systems their X-ray structures are presented in Fig. 1.

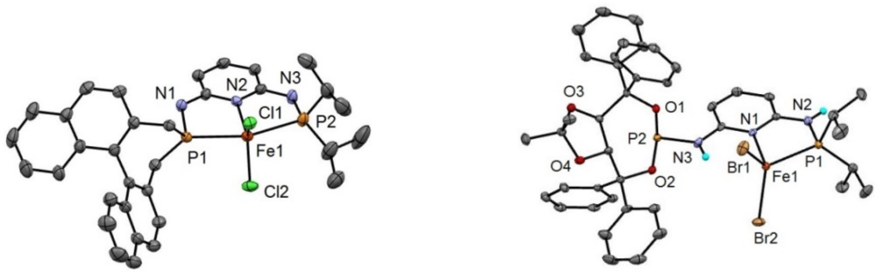
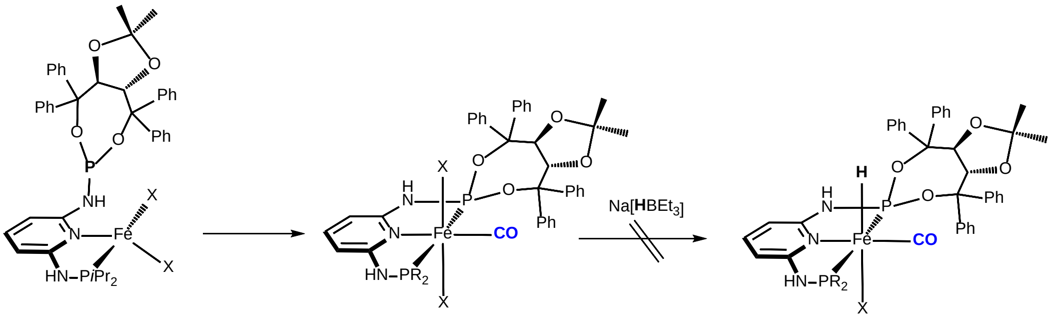


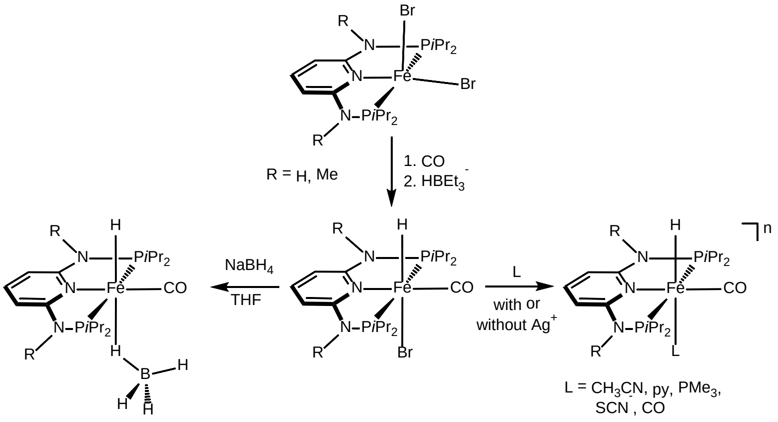
**Figure 1**

All ligands were reacted with anhydrous $FeX_2$ (X = Cl, Br) to give complexes of the types **I**-**III**. It turned out that if the substituents at the phosphorous sites are sterically not demanding enough, irrespective of the stoichiometry, the PNP pincer ligands are coordinated in $\kappa^3$-*P,N,P*- and $\kappa^2$-*P,N*-fashion (Type **II**), while systems with TADDOL were coordinating in $\kappa^2$-*P,N*-fashion (Figure 1, Type **III**). For the preparation of complexes which are active in the hydrogenation of ketones complexes of the type **I** are required. While those of type **II** and **III** do react with CO forming labile mono CO intermediates, they do not react with hydride sources to give hydride complexes (Scheme 2).



**Scheme 2.** Reaction of [Fe($\kappa^3$*P,N,P*-PNP-*i*Pr,TAD)$X_2$] with CO forming *trans*-[Fe($\kappa^3$*P,N,P*-PNP-*i*Pr,TAD)(CO)$X_2$] and attempted reaction with Na[$HBEt_3$].

Type **I** complexes, however, react readily both with CO and hydride donors to give monohydride complexes. This is exemplarily shown for the PNP-*i*Pr and $PNP^{Me}$-*i*Pr systems (Scheme 3). The latter features a NMe linker and is thus not capable of undergoing bifunctional catalysis



**Scheme 3.** Formation of hydride complexes upon treatment of Type **I** complexes with CO and super hydride ($HBEt_3^-$)

This class of Fe(II) PNP pincer hydride complexes [Fe(PNP-*i*Pr)(CO)(H)(L)]$^n$ (n = +1, 0) feature both labile ($Br^-$, $CH_3CN$, $BH_4^-$) and inert (pyridine, $PMe_3$, $SCN^-$, CO) co-ligands. Complexes with labile ligands are efficient catalysts for the hydrogenation of ketones and aldehydes to alcohols under mild conditions. These reactions take place at room temperature with turnover numbers of up to 1540 $h^{-1}$ using five bar hydrogen pressure and seem to involve heterolytic dihydrogen cleavage *via* metal-alkoxide cooperation, with the PNP ligand being not involved in dihydrogen activation. The PNP ligand remains deprotonated throughout the catalytic cycle acting as strongly electron donating anionic ligand. The experimental results complemented by DFT calculations strongly support an inner-sphere mechanism, *i.e.*, insertion of the C=O bond of the carbonyl compound into the Fe-H bond.

If the NH linker is replaced by NMe linkers to suppress any metal ligand co-operation different reactivity was found. Complexes [Fe(PNP$^{Me}$-*i*Pr)(CO)(H)(Br)] and [Fe(PNP$^{Me}$-*i*Pr)$(H)_2$(CO)] were not active for the hydrogenation of ketones, but reduced chemoselectively aldehydes to alcohols. These systems were found to be among of the most efficient catalysts for this process reported to date and constitutes a rare example of a catalytic process which allows selective reduction of aldehydes in presence of ketones and other reducible functionalities. In some cases, TONs and TOFs of up to 80000 and 20000$h^{-1}$, respectively, were reached. Based on stoichiometric experiment and computational studies, a mechanism which proceeds via a *trans*-dihydride intermediate [Fe(PNP$^{Me}$-*i*Pr)$(H)_2$(CO)] is proposed IFig. 2). The structure of the hydride complexes was also confirmed by X-ray crystallography. The yields and chemoselectivities under mild conditions are exceptional compared with previous iron catalysts and even noble metal catalysts. In some cases, full conversion was achieved even at a catalyst to substrate ratio of 1:80000 (12.5 ppm catalyst loading). Accordingly, [Fe(PNP$^{Me}$-*i*Pr)(CO)(H)(Br)] and *trans*-[Fe(PNP$^{Me}$-*i*Pr)$(H)_2$(CO)] are one of the most efficient hydrogenation catalysts for this process to date. The scope of these catalysts is shown in Table 1.

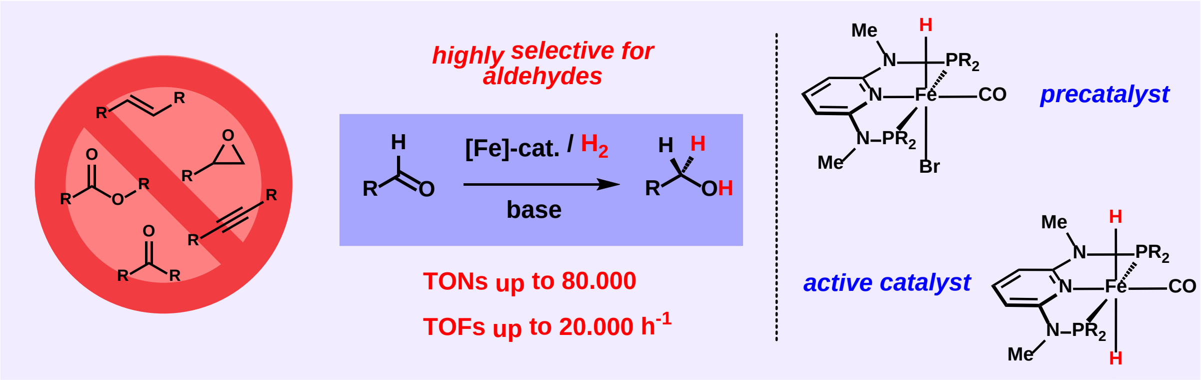
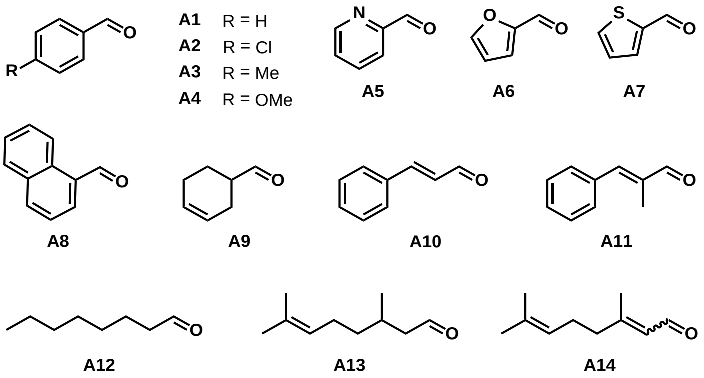


**Figure 2**

**Table 1.** Hydrogenation of aldehydes **A1**-**A14** with catalysts *trans*-[Fe(PNP$^{Me}$-*i*Pr)(CO)(H)$_2$)][a]



| entry | S/C | subst. | conversion (%)[b] | yield (%)[c] |
|---|---|---|---|---|
| 1 | 20000 | **A1** | > 99% | 96% |
| 2 | 20000 | **A2** | > 99% | > 99% |
| 3 | 15000 | **A3** | > 99% | > 99% |
| 4 | 15000 | **A4** | 98% | 98% |
| 5 | 20000 | **A5** | > 99% | 97% |
| 6 | 20000 | **A6** | > 99% | > 99% |
| 7 | 20000 | **A7** | > 99% | > 99% |
| 8 | 10000 | **A8** | 97% | 96% |
| 9 | 10000 | **A9** | 98% | > 99% |
| 10 | 10000 | **A10** | > 99% | > 99% |
| 11[d] | 20000 | **A10** | >99% | >99% |
| 12 | 10000 | **A11** | >99% | >99% |
| 13 | 10000 | **A12** | > 99% | > 99% |
| 14 | 10000 | **A13** | > 99% | 97% |
| 15 | 10000 | **A14** | > 99% | 99% |

Reaction conditions: a) catalyst [Fe(PNP$^{Me}$-*i*Pr)(CO)(H)$_2$)] (0.1-0.2 µmol, 50-100 ppm), aldehyde (2 mmol), DBU (20 µmol, 1.0 mol%), EtOH (1 mL), 30 bar $H_2$; 40°C; 16h b) determined by integration of $^1$H NMR spectra; c) based on integration of $^1$H spectra using mesitylene as internal standard; d) 60 bar $H_2$.

In addition, Fe(II) hydridocarbonyl complexes [Fe(PNP$^{Me}$-*i*Pr)(CO)(H)(Br)] and [Fe(PNP$^{Me}$-*i*Pr)(CO)(H)(Br)] were found to promote the catalytic hydrogenation of carbon dioxide and sodium bicarbonate to formate in protic solvents in the presence of bases, reaching quantitative yields and TONs up to ca. 10000 and 4500, respectively, under mild to moderate reaction conditions starting from as low as 8.5 bar total pressure and 25 °C. NMR and DFT studies highlighted the role of dihydrido- and hydridoformate complexes in catalysis (Fig. 3).

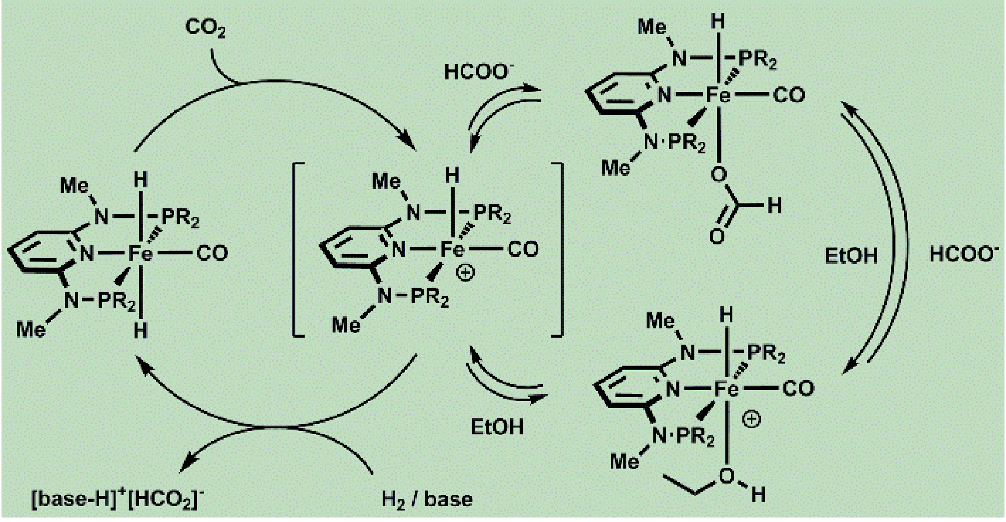


**Figure 3**

The use of $CO_2$ as a C1-source is a matter of great interest due to its high abundance, availability and low cost. In particular, its reduction to HCOOH or derivatives has attracted significant attention in recent years, since it holds the potential for reversible hydrogen storage.

Finally, we extended to use of PNP pincer ligands to other non-precious metals. For instance, the synthesis of a series of vanadium, chromium, and manganese PNP complexes of the types $[M(PNP)Cl_3]$ (M = V, Cr) and $[M(PNP)Cl_2]$ (M = Cr, Mn) is reported. Vanadium and manganese PNP pincer complexes were described for the first time.

Moreover, we also started to explore non-precious metals bearing anionic PCP complexes based on the 1,3-diaminiobenzene scaffold. The review “Non-precious metal complexes with an anionic PCP pincer architecture” provides an overview of the current state-of-the-art revealing that base metals have hardly been studied with PCP ligands. All attempts to prepare iron PCP complexes failed, but we have shown that a PCP pincer ligand based on 1,3-diaminobenzene acts as versatile supporting scaffold in cobalt chemistry. The PCP moiety provides access to a range of Co complexes in formal oxidation states +I, +II, and +III by utilizing the 15e square planar $d^7$ complex $[Co(PCP^{Me}\text{-}i\text{Pr})Cl]$ as synthetic precursor. This complex reacted readily with $NaBH_4$ to afford complexes $[Co(PCP^{Me}\text{-}i\text{Pr})(\eta^2\text{-}BH_4)]$ in high yields. The $\eta^2$-bonding mode of the borohydride ligand was confirmed by IR spectroscopy and X-ray crystallography. Unfortunately this complex was catalytically inactive and did not react with $CO_2$ to give formate complexes as in the case of related known Ni complexes.

Finally, we described the synthesis and reactivity of the first Co(I) pincer complex $[Co(\kappa^3 P,CH,P\text{-}P(CH)P^{Me}\text{-}i\text{Pr})(CO)_2]^+$ featuring an $\eta^2$-$C_{aryl}$-H agostic bond (Fig. 4). This complex was obtained via protonation of the Co(I) complex $[Co(PCP^{Me}\text{-}i\text{Pr})(CO)_2]$. Due to the acidity of the agostic proton treatment with pyridine results in facile deprotonation (C-H bond cleavage), and reformation of $[Co(PCP^{NMe}\text{-}i\text{Pr})(CO)_2]$. Secondly, C-H bond cleavage is achieved upon exposure of $[Co(\eta^3 P,CH,P\text{-}P(CH)P^{NMe}\text{-}i\text{Pr})(CO)_2]^+$ to oxygen or TEMPO to yield the paramagnetic Co(II) PCP complex $[Co(PCP^{NMe}\text{-}i\text{Pr})(CO)_2]^+$. Finally, replacement of one CO ligand in $[Co(\eta^3 P,CH,P\text{-}P(CH)P^{NMe}\text{-}i\text{Pr})(CO)_2]^+$ by CN*t*Bu promotes the rapid oxidative addition of the agostic $\eta^2$-$C_{aryl}$-H bond to give two isomeric hydride complexes of the type $[Co(PCP^{NMe}\text{-}i\text{Pr})(CNt\text{Bu})(CO)(H)]^+$.

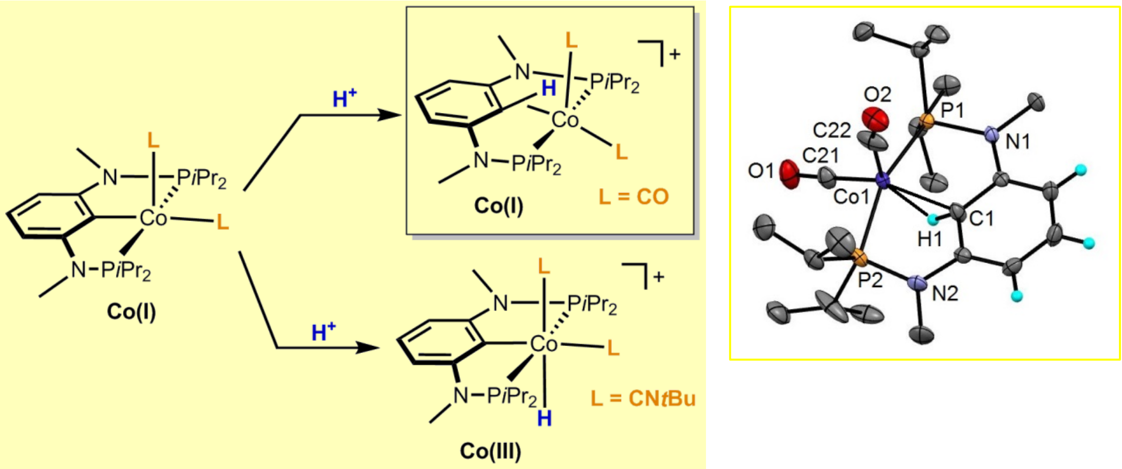


**Figure 4**

### 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. One of them is currently post-doc at Rutgers University, Department of Chemistry and Chemical Biology, USA, in the group of Prof. Alan Goldman

## 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. One of is currently post-doc at Rutgers University, Department of Chemistry and Chemical Biology, USA, in the group of Prof. Alan Goldman, where he will pursue his scientific career as researcher.

## 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

- "Non-precious Metal Pincer Chemistry", University of Toronto, Toronto, Canada, June 12, **2013**.
- "Non-precious Metal Pincer Chemistry", Eberhard Karls Universitaet Tübingen Tübingen, Germany, June 24, **2013**.
- "Non-precious Metal Pincer Chemistry", Center for Research and Advanced Studies of the National Polytechnic Institute (Cinvestav), Mexico City, Mexico, December 2, **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

- "New Chemistry of Non-precious Metal Pincer Complexes", *15th Ferrocene Colloquium"*, Leibniz Universität Hannover, Hannover, Germany, February 6 - 8, **2013**. (plenary lecture)
- "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**.
- "Chemistry Based on Non-precious Metal Pincer Complexes", COST Working Group CM1205, Catalytic Routines for Small Molecule Activation (CARISMA), Tarragona, Spain, March 17 - 20, **2015** (invited)
- "Chemistry Based on Non-precious Metal PNP and PCP Pincer Complexes", EuCheMS 2015 Inorganic Chemistry Conference, Wroclaw, Poland, June 28 – July 1, **2015** (invited).

# III. Attachments

## 1. Scholarly / scientific publications

### *1.1 Peer-reviewed publications / already published*

1. Bichler, B.; Holzhacker, C.; Stöger, B.; Puchberger, M.; Veiros, L. F.; Kirchner, K. "Heterolytic Cleavage of Dihydrogen by an Iron(II) PNP Pincer Complex via Metal-Ligand Cooperation", *Organometallics* **2013***, 32*, 4114-4121 (doi: 10.1021/om400241x). (no OA).
2. Murugesan, S.; Stöger, B.; Carvalho, M. D.; Ferreira, L. P.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. "Synthesis and Reactivity of Four and Five Coordinate Low-spin Co(II) PCP Pincer Complexes and some Ni(II) Analogs", *Organometallics.* **2014***, 33*, 6132-6140 (doi: 10.1021/om5007769). (no OA).
3. **Gorgas, N.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. "Efficient Hydrogenation of Ketones and Aldehydes Catalyzed by Hydride Iron(II) PNP Pincer Complexes - Evidence for an Insertion Mechanism", *Organometallics* 2014, *33*, 6905-6914 (doi: 10.1021/om5009814). (no OA).**
4. Murugesan, S.; Stöger, B.; Veiros, L. F.; Kirchner, K. "Synthesis, Structure, and Reactivity of Co(II) and Ni(II) PCP Pincer Borohydride Complexes", *Organometallics*, **2015***, 34*, 1364-1372 (doi: 10.1021/acs.organomet.5b00075). (no OA).
5. 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 $\kappa^2$*P,N*- and $\kappa^3$*P,N,P*-Bound PNP Pincer Ligands", *Dalton Trans.* **2015**, *44*, 13071-13086 (doi: 10.1039/c5dt00832h). (no OA).
6. Murugesan, S.; Kirchner, K. "Non-precious metal complexes with an anionic PCP pincer architecture", *Dalton Trans.* **2016**, *45*, 4163-439 (doi: 10.1039/c5dt03778f). (no OA).
7. **Murugesan, S.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. "A Cobalt(I) Pincer Complex with an $\eta^2$-$C_{aryl}$-H Agostic Bond - Facile C-H Bond Cleavage through Deprotonation, Radical Abstraction, and Oxidative Addition", *Angew. Chem. Int. Ed.* 2016, *55*, 3045-3048 (doi: 10.1002/anie.201510145). (no OA).**
8. **Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. "Highly Efficient and Selective Hydrogenation of Aldehydes: A Well-Defined Iron(II) Catalyst exhibits Noble Metal Activity", *ACS Catal.* 2016, *6*, 2664-2672 (doi: 10.1021/acscatal.6b00436). (no OA).**
9. Bertini, F.; Gorgas, N.; Stöger, B.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.*;* Gonsalvi, L. "Efficient and Mild Carbon Dioxide Hydrogenation to Formate Catalyzed by Fe(II)-hydridocarbonyl Complexes bearing 2,6-Diaminopyridyl Diphosphine Pincer Ligands", *ACS Catal.* **2016**, *6*, 2889-2893 (doi: 10.1021/acscatal.6b00416). (no OA).
10. "Synthesis and reactivity of BINEPINE-based chiral Fe(II) PNP pincer complexes", Schröder-Holzhacker, C.; Gorgas, N.; Stöger, B.; Kirchner, K. *Monatsh. Chem.* **2016**, *147*, 1023-1030 (doi: s00706-016-1706-x) (OA).
11. Mastalir, M.; Glatz, M.; Stöger, B.; Weil, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. "Synthesis, characterization and reactivity of vanadium, chromium, and manganese PNP pincer complexes", *Inorg. Chim. Acta.* **2016**, in press. (doi: 10.1016/j.ica.2016.02.064). (no OA).

### *1.2 Non peer-reviewed publications / already published*

### *1.3 Planned publications*

| | | | |
|---|---|---|---|
| Author(s) | Glatz, M.; Gorgas, N.; Bichler, B.; Stöger, B.; Carvalho, M. D.; Ferreira, L. P.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. | | |
| Title | Base-Triggered and Ligand Controlled Disproportionation of Fe(II) PNP Pincer Systems to Give Fe(0) and Fe(I) Complexes | | |
| Sources | | | |
| URL (if applicable) | | | |
| Peer Review | yes x | no ☐ | |
| Status | in press/accepted ☐ | submitted ☐ | in preparation x |

## 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)<br>**M** (male) |
| | | **E** | | Extent **E1** **low** (e.g. no joint publications, but mention in acknowledgements or similar);<br>**E2** **medium** (collaboration e.g. with occasional joint publications, exchange of materials or similar, but no longer-term exchange of personnel);<br>**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)<br>**I** **interdisciplinary** (involving two or more disciplines)<br>**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 |
| ITA | M | E2 | W | Luca Gonsalvi | Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici (ICCOM), Florence |

**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 | | B. Bichler | | m |
| Ph.D. theses | | S. Murugesan | | m |
| Ph.D. theses | N. Gorgas | | | m |
| Ph.D. theses | M. Mastalir | | | m |

## 7. Applications for follow-up projects

### *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:<br>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 | Austria | | |
| Funding agency | ERC | | |
| Project number (if applicable) | | | |
| Project type | Advanced Grant | | |
| Title / subject | Sustainability Through Base Metal Catalysis (SUBLIME CATs) | | |
| Status | granted ☐ | pending ☐ | in preparation x |
| 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.