

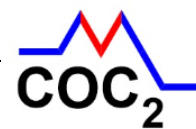
31st Colloquy on Organometallic Chemistry for Catalysis

September 11 – September 13, 2023

Bayreuth * Germany

Book of Abstracts





Program

General information I: Plenary Lecture (PL) 50 min + 5 min discussion, Key Note Lecture (KN) 40 min + 5 min discussion, (Invited Lecture) IL 30 min + 5 min discussion, Oral Contribution (OC) 20 min + 5 min discussion

Day 1 (11.09.2023) morning session: 9.00 am - 12.25 am

Session chair: Sjoerd Harder

General Information II: 9.00- 9.05
am

PL 9.05 -10 am

KN1 10.00-10.45 am

Rhett Kempe

Matthias Beller: *“Catalysis – a key technology for sustainable chemistry and energy technologies”*

Qiang Liu: *“Bimetallic synergy in catalytic hydrogenation of polar unsaturated bonds”*

Coffee break 10.45 - 11.15 am

IL1 11.15-11.50 am

IL2 11.50-12.25 am

Jean-Baptiste Sortais: *“Hydrogenation of esters promoted by bidentate NHC-based manganese catalysts”*

Nadia Mösch-Zanetti: *“Elucidating the role of amine donors in manganese catalyzed transfer hydrogenation”*

Break including lunch and social interaction (Options: hiking, sightseeing, golf, please sign in for planning) 12.25 am - 3.30 pm

Day 1 (11.09.2023) afternoon session: 3.30 pm - 6.25 pm,

Session chair: Qiang Liu

KN2 3.30-4.15 pm

IL3 4.15-4.50 pm

IL4 4.50-5.15 pm

IL5 5.15-5.50 pm

IL6 5.50-6.25 pm

Sjoerd Harder: *“Alkene and arene hydrogenation catalysis: boosting main group metal hydrides with a pinch of iron powder”*

Shoubhik Das: *“Is it homogeneous or is it heterogeneous?”*

Rakesh Maiti: *“Super-oxidizing Covalent Triazine Framework (CTF) for Anti-Markovnikov Hydro-carboxylation and Hydroamination of Styrenes.”*

Jarl Ivar van der Vlugt: *“Iron-catalyzed C(sp³)-H Amination”*

Jie Liu: *“Electrocatalytic hydrogenative reactions”*

Poster session, Franconian “Brotzeit” and beer: 6.30 pm – 10.00 pm maximum

Day 2 (12.09.2023) morning session: 9.00 am - 12.25 am

Session chair: Grzegorz Hreczycho

KN3 9.00-9.45 am

Karl Kirchner: *"Catalytic applications of iron and manganese alkyl complexes"*

IL7 9.45-10.20 am

Dragos-Adrian Rosca: *"Adventures in cycloaddition chemistry with iron complexes: the enabling role of redox-active ligands"*

OC1 10.20-10.45 am

Heiko Schratzberger: *"Transfer-Semihydrogenation of Alkynes catalyzed by an Iron(II) PCP Dicarbonyl Alkyl Complex"*

Coffee break 10.45 - 11.15 am

IL8 11.15-11.50 am

Krzysztof Kuciński: *"Silylacetylenes: Synthesis and Applications"*

IL9 11.50-12.25 am

Johann Hlina: *"Heterobimetallic Rare-Earth/Transition Metal Complexes in Hydrofunctionalisation Catalysis"*

Break including lunch and social interaction (Options: hiking, sightseeing, golf, please sign in for planning) 12.25 am - 3.30 pm

Day 2 (12.09.2023) afternoon session: 3.30 pm – 6.30 pm,

Session chair: Karl Kirchner

KN4 3.30-4.15 pm

Moshe Kol: *"Environmentally-friendly polymers via catalyst design"*

IL10 4.15-4.50 pm

Christoph Topf: *"(Transfer) Hydrogenation Reactions with Chromium- and Tungsten-Based Organometallics"*

IL11 4.50-5.15 pm

Slawomir Szafert: *"Organic and organometallic species derived from 1-haloalkynes"*

OC2 5.15-5.40 pm

Stephanie Bastin: *"Chiral, L-shape N-heterobicyclic carbene ligands for asymmetric gold(I) catalysis"*

OC3 5.40-6.05 pm

Xianle Rong: *"Cobalt-Catalyzed Desymmetric Isomerization of Exocyclic Olefins"*

Poster session, dinner and beer: 6.05 pm – 10.00 pm maximum

Day 3 (13.09.2023) morning session: 9.00 am - 12.25 am

Session chair: Moshe Kol

KN5 9.00-9.45 am

Grzegorz Hreczycho: *“Cobalt complexes as Earth-abundant catalysts in the synthesis of organometallic compounds”*

OC4 9.45-10.05 am

Daniel Zobernig: *“NHC-Based Manganese (I) PCP Complexes for Hydrogenation and Hydrofunctionalization Reactions”*

OC5 10.05-10.25 am

Fabian Lukas: *“Synthesis of a branched α -olefin via tetramerization of ethylene and homopolymers thereof”*

Coffee break 10.25 - 11.15 am

IL12 11.15-11.45 am

Robert Wolf: *“Counterion Effect in Cobalt-Catalyzed Alkene Hydrogenation”*

OC6 11.45-12.05 am

Martin Schlagbauer: *„Selective C-alkylations“*

General information III “Good bye”
12.30-12.40 pm

Rhett Kempe

Plenary & Keynote Lectures

PL **“Catalysis – a key technology for sustainable chemistry and energy technologies”**
Matthias Beller



KN1 **“Bimetallic synergy in catalytic hydrogenation of polar unsaturated bonds”**
Qiang Liu



KN2 **“Alkene and arene hydrogenation catalysis: boosting main group metal hydrides with a pinch of iron powder”**
Sjoerd Harder



KN3 **“Catalytic applications of iron and manganese alkyl complexes”**
Karl Kirchner

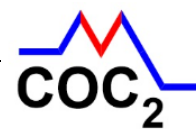


KN4 **“Environmentally-friendly polymers via catalyst design”**
Moshe Kol



KN5 **“Cobalt complexes as Earth-abundant catalysts in the synthesis of organometallic compounds”**
Grzegorz Hreczycho





Lectures

**Catalysis – a key technology for sustainable
chemistry (and energy technologies)**

Matthias Beller

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The cost-effective and waste-free synthesis of materials, life science goods and all kinds of organic products require efficient chemical transformations. In this regard, development of more active and selective catalysts constitutes a key factor for achieving improved processes and providing the basis for a sustainable chemical industry. Despite continuous advancements in all areas of catalysis, still organic syntheses as well as the industrial production of most chemicals can be improved significantly in terms of sustainability and efficiency.

In the talk, the principle of cooperative catalysis will be shown in the context of modern palladium catalysts for carbonylation reactions. By rational design novel ligands and complexes have been synthesized, which allow for unprecedented efficiency in such transformations. Both industrially relevant processes as well as interesting carbonylation reactions for modern organic synthesis will be presented.

Furthermore, it will be shown how new and improved homogeneous catalysts can be developed using the phenomenon of cooperative catalysis as a guideline. Several examples which demonstrate the potential of such catalytic processes with non-noble metal complexes will be presented.

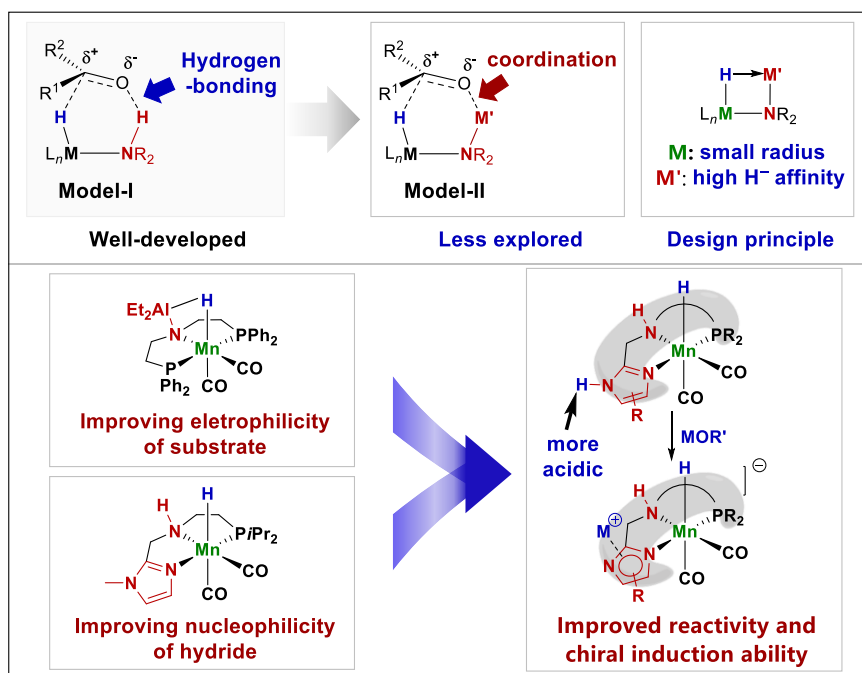
Bimetallic Synergy in Catalytic Hydrogenation of Polar Unsaturated Compounds

Qiang Liu

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Recently, we developed a more reactive intermediate, amidato M-H complex ($M'N-MH$), in catalytic hydrogenation reactions by changing the proton of the amino group of the corresponding amino M-H complex ($HN-MH$) into a Lewis acidic metal cation to establish a new activation mode, namely bimetallic synergetic hydride transfer. This coordination interaction between M' with polar unsaturated substrates significantly enhanced the electrophilicity of substrates. The strength of this coordination interaction is easily-tunable and is also expected to better shape the conformation and chiral environment towards a more effective stereoselectivity control. Based on this novel bimetallic synergetic reaction model, we realized the asymmetric hydrogenation of a series of *N*-heterocyclic compounds, such as quinolines, indoles and quinoxalines in high efficiency and selectivity. A high TON of over 70,000 has been achieved, which is the highest TON yet obtained from an asymmetric hydrogenation reaction via earth-abundant metal catalysis. Moreover, a stereodivergent asymmetric hydrogenation reaction has also been realized for the first time, providing concise access to all the stereoisomers of products from the same substrates.



Literature:

- [1] C. Liu, X. Liu, Q. Liu*, *Chem* **2023**, accepted.
- [2] Y. Wang, S. Liu, H. Yang, H. Li, Y. Lan*, Q. Liu*, *Nat. Chem.* **2022**, *14*, 1233.
- [3] C. Liu, M. Wang, Y. Xu, Y. Li, Q. Liu*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202814.
- [4] C. Liu, M. Wang, S. Liu, Y. Wang, Y. Peng, Y. Lan*, Q. Liu*, *Angew. Chem. Int. Ed.* **2021**, *60*, 5108.
- [5] Y. Wang, L. Zhu, Z. Shao, G. Li, Y. Lan*, Q. Liu*, *J. Am. Chem. Soc.* **2019**, *141*, 17337.

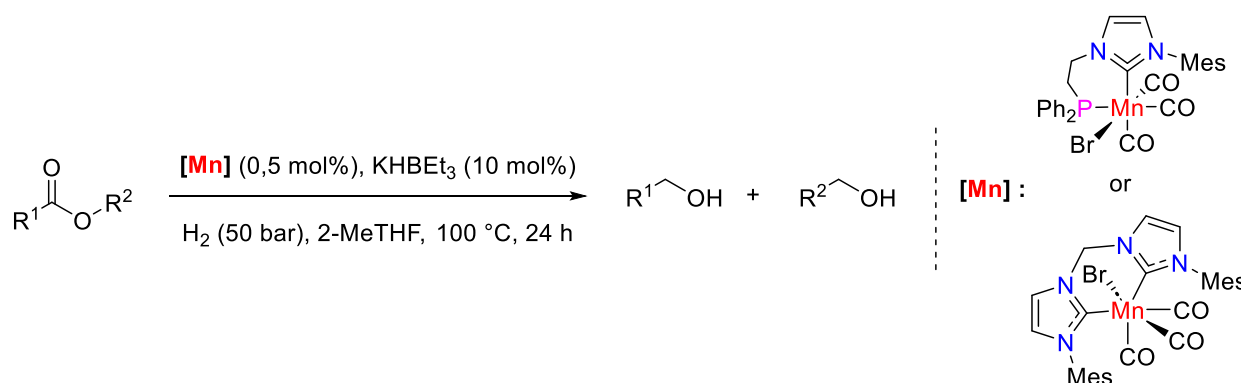
Hydrogenation of esters promoted by bidentate NHC-based manganese catalysts

Romane Pointis, Karim Azouzi, Lucie Pedussaut, Ruqaya Buhaibeh, Stéphanie Bastin,

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Alcohols are highly valuable synthetic intermediates for the production of pharmaceutical, agrochemical and fine chemical products. Therefore, carboxylic esters, considered as an important class of natural products, are interesting candidates to produce alcohols through their reduction. Hydrogenation catalyzed by transition metal complexes is a well-known method for the reduction of carboxylic esters. Although noble metals are known to be highly efficient in this category of transformation, their scarcity and potential toxicity have prompted chemists to seek a more sustainable alternative: the use of more environmentally friendly and inexpensive Earth-abundant transition metal of the first row such as iron and manganese.^[1] In the literature, the catalysts developed so far are mainly based on tridentate ligands involved in a metal-ligand cooperativity.^[2]

In this context, we have focused our research on the development of a catalytic system based on a manganese complex carrying a bidentate NHC-phosphine and NHC-NHC ligand,^[3,4] which is not a priori capable of inducing metal-ligand cooperativity. The results obtained in the hydrogenation reactions of carboxylic esters will be detailed in the present communication.

Literature:

[1] "Homogeneous Hydrogenation with Non-Precious Catalysts": J. F. Teichert, Wiley, 2019.

[2] J.-B. Sortais, R. Buhaibeh, Y. Canac, Manganese-Catalyzed Hydrogenation and Hydrogen Transfer Reactions in Manganese Catalysis in Organic Synthesis (Ed.: J.-B. Sortais), Wiley-VCH GmbH, Weinheim, Germany, 2021, pp.39-66.

[3] "Hydrogénation d'esters en présence d'un complexe de manganèse", K. Azouzi, R. Buhaibeh, Y. Canac, D. Valyaev, S. Bastin, J.-B. Sortais, French patent submitted 25/01/22, FR2200609.

[4] K. Azouzi, L. Pedussaut, R. Pointis, A. Bonfiglio, R. Kumari Riddhi, C. Duhayon, S. Bastin, J.-B. Sortais, *Organometallics* 2023 DOI: 10.1021/acs.organomet.3c00137.

Elucidating the Role of Amine Donors in Manganese Catalyzed Transfer Hydrogenation

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Catalysts for transfer hydrogenation (TH) reactions based on the earth abundant transition metal manganese are an emerging field of research. A common moiety found in most reported phosphine-free catalysts is a primary or secondary amine donor, which is generally considered to be crucial within an outer-sphere mechanism. However, due to geometrical constraints and the use of additional base in some systems other mechanistic views should be considered.

Therefore, we investigated the role of the NH-motif in the mechanism in catalytic transfer hydrogenation of ketones. For this reason, Mn(I) complexes with pyridyl-pyrazole, -imidazole or -pyridazinone ligands were developed, which carry an NH-motif at different positions. Subsequent investigation of their catalytical activity points towards an inner-sphere mechanism in which the NH-motif of the amino ligand is deprotonated throughout the catalytic cycle (Figure 1). The resulting amido ligand increases the electron density at the metal which facilitates the hydride transfer to the substrate.^[1] Furthermore, this presentation will highlight the importance of mesomerism in the investigated systems and therefore the electron donating capability of the ligands. Effective charge delocalization towards the coordinating nitrogen atom is required to enable TH hydrogenation. Differences in reactivity are supported by DFT calculations of the activation barrier of the hydride transfer from an intermediate hydrido complex to the substrate and the NBO charges at the hydrido ligand.

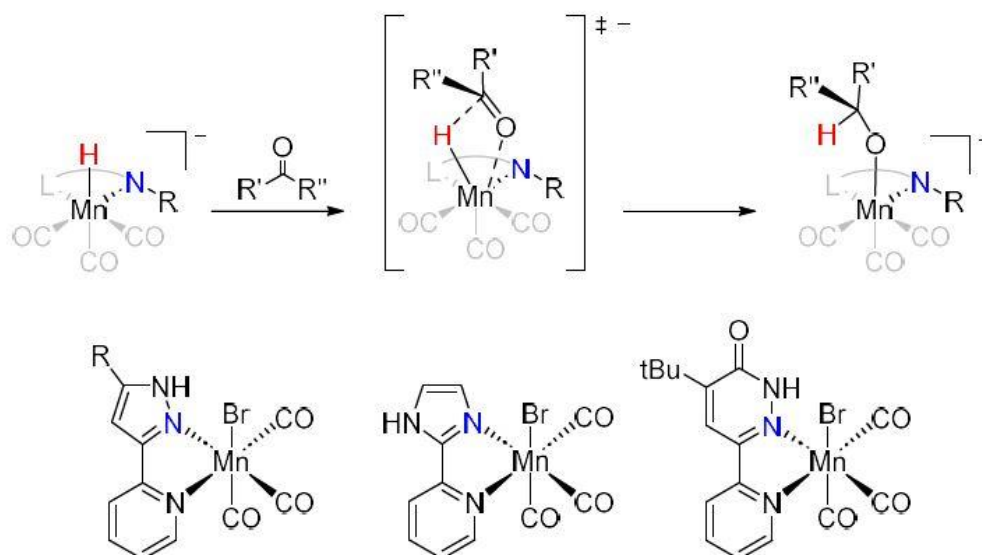


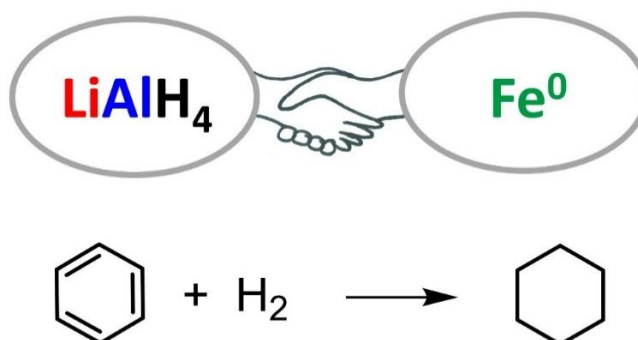
Figure 1. Proposed inner-sphere mechanism in TH of ketones displaying investigated catalysts.

Literature:

[1] F. Wiedemaier, F. Belaj, N. C. Mösch-Zanetti, *J. Catal.* **2022**, *416*, 103–111.

Alkene and arene hydrogenation catalysis: Boosting main group metal hydrides with a pinch of iron powder

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In 2008 we reported the first main group metal catalysts for alkene hydrogenation.^[1] Well-defined or *in-situ* generated calcium hydride complexes were found to be active in the hydrogenation of activated (conjugated) alkenes. Over the years we gradually improved catalyst activity and scope^[2-4] and also introduced simple group 2 metal catalysts for imine hydrogenation.^[5]

Surprising was the recent observation that Ba^0 is a most outstanding hydrogenation catalyst for alkene hydrogenation and even slowly reduces benzene.^[6] It has been proposed that the Ba^0 surface may activate alkene or arene substrates.

The activity of Ba^0 can be boosted by at least three orders of magnitude by addition of Fe^0 , allowing smooth hydrogenation of arenes.^[7] This concept was extended by turning LiAlH_4 , a stoichiometric reducing agent for ketones and imines, into a catalyst for alkene and arene reduction by addition of Fe^0 .^[8]

Literature:

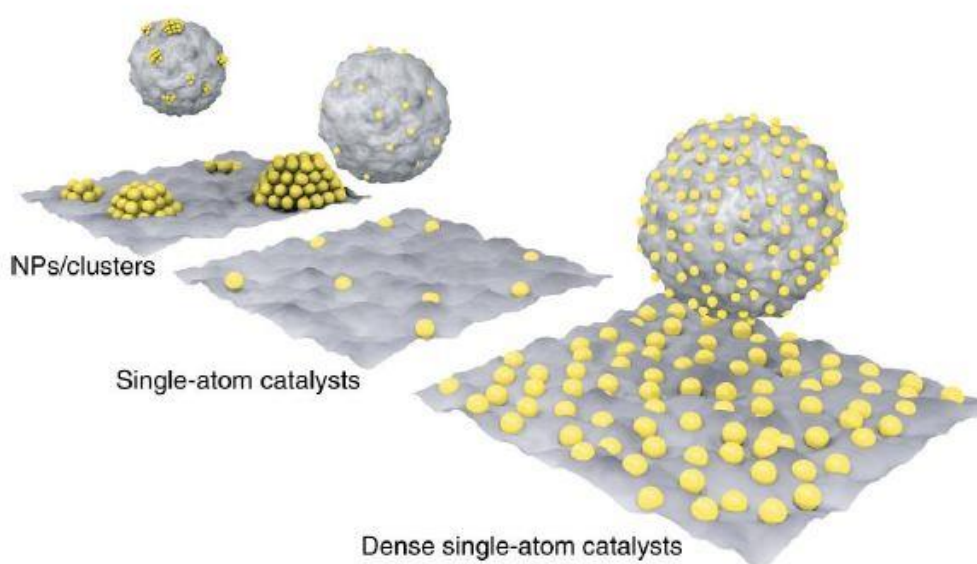
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- [8] C. Knüpfer, C. Färber, J. Langer, S. Harder, *Angew. Chem.* **2023**, e202219016.

Is It homogeneous or Is It heterogeneous?

Shoubhik Das

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Recently solar energy has exhibited great potential as a promising alternative to substituting the traditional energy sources because it is renewable, abundant, affordable, and everlasting. Among various solar energy conversion techniques, photocatalysis is deemed as a promising, environmentally benign, and cost-effective strategy to generate both fuels and high-value chemicals. While in this domain homogeneous photocatalysts prevail due to higher selectivity but the reutilisation of the catalyst is next to impossible. On the other hand, heterogeneous photocatalysts are recyclable but not highly selective. Therefore, to make a bridge between these two, a new strategy has been developed by synthesizing single metal atom photocatalysts that are selective as well as recyclable.^{1,2} Based on this, recently we have developed several photocatalytic strategies for the synthesis of fuels as well as high valued chemicals where the catalysts exhibited excellent selectivity as well as recyclability.



Literature:

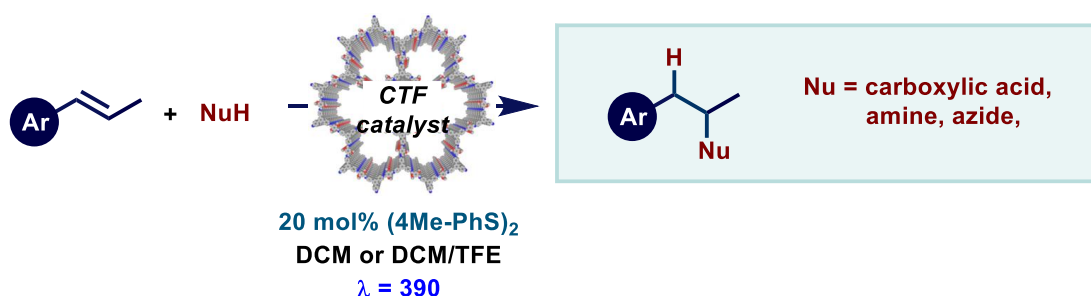
[1] Zhang et al. *Acc. Chem. Res.* **2013**, *46*, 1740.[2] Ramirez et al. *Chem. Rev.* **2020**, *120*, 11703

Super-oxidizing Covalent Triazine Framework (CTF) for Anti-Markovnikov Hydro-carboxylation and Hydroamination of Styrenes

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this work



Disclosed herein is a porous covalent triazine framework (CTF)¹⁻² based heterogeneous photocatalyst which shows real aptness to replace scarce, expensive homogeneous photocatalysts such as acridinium salts, Ir-photocatalysts, etc.³⁻⁴ This CTF possesses a super-oxidizing property enabling it to perform the regioselective C-N and C-O bond formation in the styrenes under ambient conditions.⁵⁻⁷ The protonation-deprotonation-induced change in the physicochemical properties of the CTF during catalysis was analyzed and its impact on the photocatalytic propensity of the material was assessed. Fine tuning the catalytic conditions based on these fundamental insights allowed us to obtain hydrocarboxylation and hydroamination protocols, which gave good to excellent yields of the desired products from a myriad of electron-donating and -withdrawing aromatic and aliphatic substrates. The catalytic strategy was further extended to late-stage functionalization of bio-active and drug molecules, as well as to gram-scale synthesis.

Literature:

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Iron-catalyzed C(sp³)-H Amination

Jarl Ivar van der Vlugt

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The development of efficient methods for the formation of carbon–nitrogen (C–N) bonds is one of the most crucial tasks in chemical synthesis. The installment of C–N bonds by direct functionalization of C(sp³)-H bonds is a powerful and atom-efficient transformation for chemical synthesis. Although the direct installation of nitrogen into a C(sp³)-H bond is extremely challenging due to the thermodynamic and kinetic stability of the C(sp³)-H bond, intra- and intermolecular C(sp³)-H amination has seen much progress in the past decade.^[1] Particularly, intramolecular C(sp³)-H amination as an atom-economical strategy has found extensive applications for the construction of varieties of important *N*-heterocycles.^[2]

Fe-mediated catalysis has slowly made its way to various important classes of organic chemical transformations, including hydroaddition chemistry and recently also C–H activation,^[3] but the Fe-mediated functionalization of aliphatic C(sp³)-H bonds is still a formidable challenge.^[4]

Nitrene (*in situ* generated) insertion into a C(sp³)-H bond is an efficient and perhaps the best studied approach for C(sp³)-N bond formation. *In situ* generation of a metal-bound nitrene species from readily available aliphatic organoazides, releasing only molecular nitrogen as the side product, followed by selective insertion into a C(sp³)-H bond would constitute an efficient approach for catalytic C–H amination. Synthesis of *N*-heterocycles via direct C(sp³)-H amination using aliphatic azide substrates is an appealing strategy, given that *N*-heterocycles are prevailing building blocks in natural products, pharmaceuticals, and functional material.

Herein, we discuss the synthesis and detailed characterization of various iron complexes, with different metal oxidation states, and their catalytic performance in the direct C(sp³)-H amination of aliphatic azides to *N*-heterocycles.

Research funded by NWO.

Literature:

[1] Selected reviews: a) F Collet, R. Dodd, P. Dauban *Chem. Commun.* **2009**, 5061; b) C.-L. Sun, B.-J. Li, Z.-J. Shi *Chem. Rev.* **2011**, *111*, 1293; c) T. Ramirez, B. Zhao, Y. Shi *Chem. Soc. Rev.* **2012**, *41*, 931; d) D. Intrieri, P. Zardi, A. Caselli, E. Gallo *Chem. Commun.* **2014**, *50*, 11440; e) K. Shin, H. Kim, S. Chang *Acc. Chem. Res.* **2015**, *48*, 1040; f) X.-X. Guo, D.-W. Gu, Z. Wu, W. Zhang *Chem. Rev.* **2015**, *115*, 1622; g) J.-P. Wan, Y. Jing *Beilstein J. Org. Chem.* **2015**, *11*, 2209.

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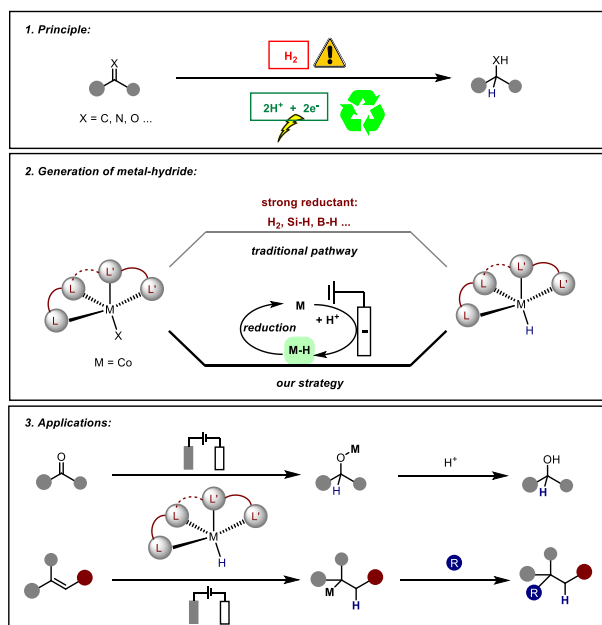
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Cobalt electrocatalytic hydride transfer reactions

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The catalytic hydrogenation represents a cost-effective and atom-economic technology toward an environmentally benign synthesis of valuable fine chemicals.^[1] According to the law of conservation of mass and electrons, H_2 is equal to two protons and two electrons, that is, $\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$. Therefore, the direct use of protons and electrons as a potential hydrogen source would provide an appealing pathway to avoid the use of hazardous pressurized H_2 .^[2]

As the key intermediate in hydrogenations, metal hydride (M-H) is mostly generated by splitting of molecular hydrogen or transmetalation of hydride sources.^[3] Electrochemical process provides an alternative pathway to form the M-H via a sequence of cathodic reduction and protonation.^[4] This process employs electrons and protons as the redox equivalent and hydrogen source that avoids the use of traditional oxidants and hydride donors.

This strategy is applied to electrocatalytic hydrogenative reaction with various oxo chemicals in the absence of molecular hydrogen or hydride as the reductant. Specifically, the significant advantage of this electrocatalytic reaction is the highly practical and valuable isotope incorporation from readily available deuterium source.

Literature:

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Catalytic Applications of Manganese Alkyl Complexes

Karl Kirchner

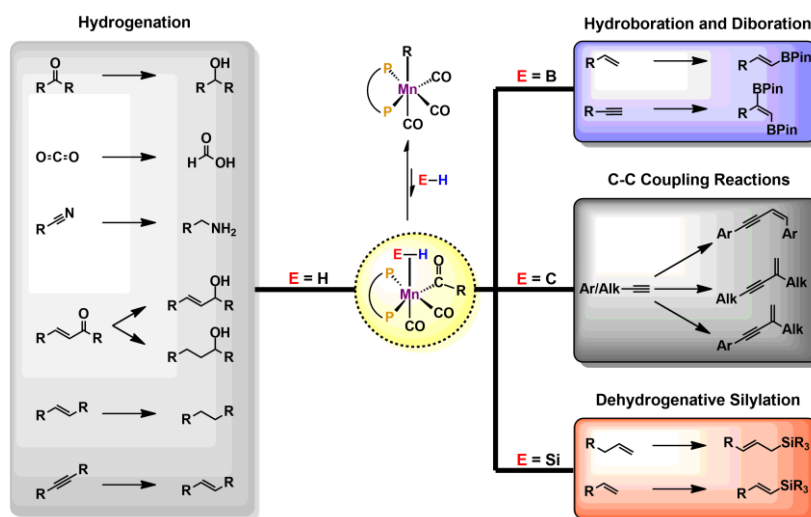
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The utilization of base-metal catalysts represents an emerging field in homogeneous catalysis. Among others, manganese-based complexes were proven to be highly competitive catalysts for several (de)hydrogenation reactions.

This lecture outlines the potential of alkylated Mn(I)-carbonyl complexes for the activation of non-polar and moderately polar E-H (E = H, C, Si, B) bonds and disclose our successful approach for

the utilization of complexes in the field of homogeneous catalysis.¹⁻⁵ This will involve the rational design of manganese-complexes for hydrogenation reactions, including alkenes, which was not possible with defined manganese complexes before. Furthermore, the potential of our Mn-based catalysts in the field of hydrofunctionalization reactions for carbon-carbon multiple bonds will be discussed. Our investigations unveiled novel insights in reaction pathways of dehydrogenative silylation of alkenes and allowed *trans*-1,2-diboration of terminal alkynes, which was not reported for transition metals before.



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Adventures in cycloaddition chemistry with iron complexes: the enabling role of redox-active ligands

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Despite their high abundance and low price, first row transition metals with partially occupied d-shells are prone to rapid spin- and oxidation-state changes, making their reactivity difficult to control. Redox-active ligands can reversibly store electrons on their backbone, often enforcing net 2-electron transfers through redox metal-ligand cooperativity and therefore suppressing the otherwise selectivity-eroding radical reaction pathways.

Our research programme focuses on using redox-active ligands as tools for the development of efficient catalytic applications based on iron and cobalt complexes. Pyrimidine-imine motifs play a central role as they can provide greater catalyst stability by hindering deleterious kinetically accessible pathways, compared to the established pyridine analogues. This enhanced stability was demonstrated in various catalytic transformations, with a focus on cycloaddition and hydroelementation reactions. In an effort to better understand the reaction mechanisms, our work also focused on elucidating the identity of the active species and their magnetic properties. The present contribution will detail on ligand structure-catalytic activity relationships in the context of iron- and cobalt-based transformations.^[1-4]

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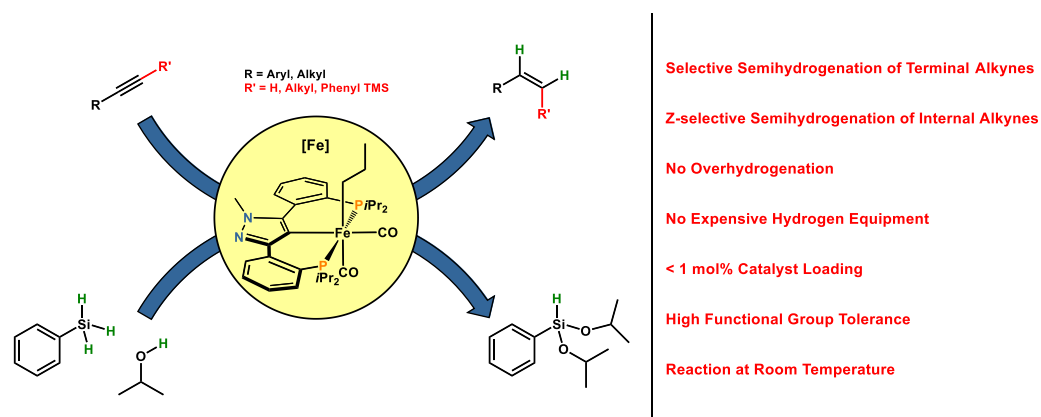
Transfer-Semihydrogenation of Alkynes catalyzed by an Iron(II) PCP Dicarbonyl Alkyl Complex

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The selective semihydrogenation of alkynes to the respective alkenes is a desirable process in the production of bulk and fine chemicals, pharmaceuticals as well as in research.^[1] To avoid the use of special hydrogen equipment, transferhydrogenation processes can be applied. Concerning iron there are rarely transferhydrogenation of C-C triple bonds reported in literature.^[2-4]

Herein, we report on the transfer-semihydrogenation of terminal and internal alkynes at room temperature catalyzed by a new iron (II) PCP dicarbonyl alkyl complex **[Fe]** comprising an asymmetric pyrazole-derived backbone for the pincer ligand. As hydrogen source a mixture of phenylsilane and 2-propanol is applied (Scheme 1).



Scheme 1. Transfer-Semihydrogenation of alkynes using phenylsilane and 2-propanol catalyzed by an iron (II) PCP dicarbonyl alkyl pincer complex **[Fe]**.

The synthesis, reactivity and characterization of the catalyst **[Fe]** will be discussed in this contribution. Mechanistic aspects of the semihydrogenation will be elucidated by deuteration studies, *in situ* NMR spectra and stoichiometric experiments. These findings are summarized in a derived catalytic cycle, which is further supported by DFT calculations. Additionally, the scope and limitations as well as the selectivity of **[Fe]** for the catalytic semihydrogenation of alkynes will be outlined.

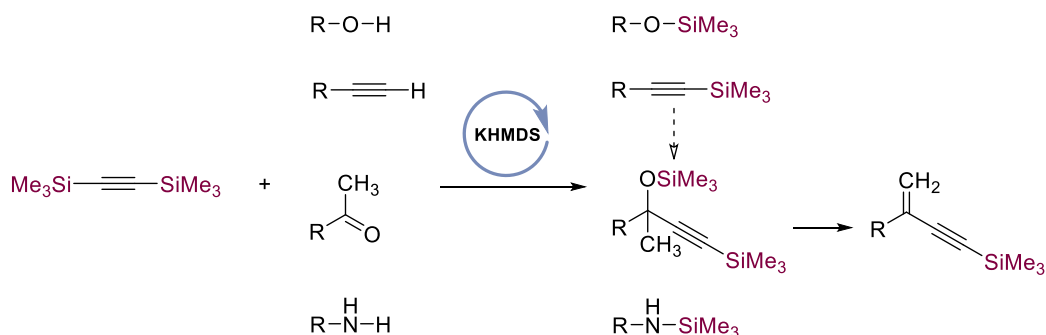
Finally, an outlook towards the functionalization of **[Fe]** to an iron(II) remote NHC dicarbonyl alkyl complex will be given and the catalytic properties of this complex in comparison to **[Fe]** will be discussed.

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Silylacetylenes: Synthesis and Applications

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In general, several important organosilicons can be readily accessed using halosilanes.^[1] Because of the inconvenient nature of these reagents and processes (*e.g.*, high moisture sensitivity of substrates, the need for stoichiometric deprotonation, *etc.*), scientists have endeavored to find viable alternatives for these troublesome silylating agents. Silylacetylenes, also known as alkynylsilanes, have gained significant attention due to their extensive applications in synthesis.^[2,3] These compounds offer various pathways for converting them into useful derivatives, including cross-coupling reactions, Diels-Alder cyclization, and other addition reactions.^[2]

In this communication, we share our recent findings on this topic, highlighting the utilization of alkynylsilanes in the synthesis of valuable derivatives such as siloxanes,^[4] silyl ethers,^[4] silylated alkynes,^[5] aminosilanes,^[6] and protected propargylic alcohols.^[7] (Figure 1) In all cases, commercially available and cost-effective chemical compounds such as bis(trimethylsilyl)acetylene and bis(trimethylsilyl)potassium amide were used as reagents. Particularly, the latter serves as an intriguing counterpart to expensive catalysts based on transition metals.

The presented reactions demonstrate high chemoselectivity with an exceptional scope that is currently lacking or challenging to achieve through other methods. Considering the combination of desirable features, these reaction systems are expected to provide a promising alternative to existing methodologies.

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Heterobimetallic Rare-Earth/Transition Metal Complexes in Hydrofunctionalisation Catalysis

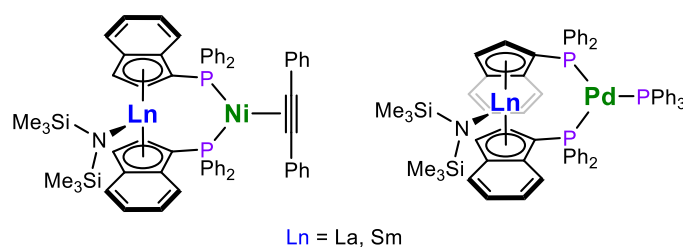
Hlina, Johann A.^a Mairinger, Sebastian;^b Steiner, Matthias, R.^b^aInstitute of Chemistry, University of Graz, Schubertstraße 1, 8010 Graz, Austria^bInstitute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

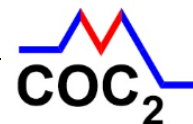
Figure 1: Selected examples of heterobimetallic rare-earth/transition metal complexes.

The chemistry of complexes featuring both early and late transition metals provided insight into aspects such as metal-metal interaction and cooperative reactivity. In contrast to the early transition metals, the elements of the f-block have received significantly less attention. Previous examples were reported by the groups of Kempe and Roesky exploring aspects such as intermetallic bonding.^[1-4] Only recently, Lu and co-workers demonstrated the application of rare-earth/transition metal complexes in hydrogenation catalysis.^[5]

In this contribution, our work on heterobimetallic rare-earth/transition metal complexes will be present. We recently demonstrated the utility of phosphane-functionalised indenyl ligands in rare-earth metal chemistry and the potential of the monometallic complexes to catalyse hydroamination reactions.^[6] Expanding this chemistry to heterobimetallic systems, we investigated heterobimetallic complexes featuring late transition metals such as nickel or palladium (Figure 1). As part of this work, we also investigated the reactivity of these rare-earth/group 10 metal complexes in hydroamination and alkyne oligomerisation catalysis.

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Environmentally-friendly polymers via catalyst design

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The degree and type of stereoregularity of polymers have a major effect on their physical and chemical properties and consequently on their possible applications. Poly(lactic acid) (PLA) is a biodegradable polymer prepared by the catalyzed ring opening polymerization of lactide. PLA of different stereoregularities may be formed by choice of the lactide stereoisomer(s) and choice of the catalyst. In addition, a truly living catalyst may enable the formation of stereoblock- and block-copolymers of PLA by sequential monomer addition.

In this presentation we will describe recent findings from our group, including: the design of new chelating ligands and their complexation tendencies around different metals; mechanistic studies related to the catalysts' stereoselectivity and activity; and the development of exceptionally active and living polymerization catalysts. Employing these catalysts gave rise to tailor-made PLA materials, including: highly syndiotactic PLA and its precise stereo-block copolymers, and stereogradient copolymers featuring desired thermal properties.

(Transfer) Hydrogenation Reactions with Chromium- and Tungsten-Based Organometallics

Christoph Topf

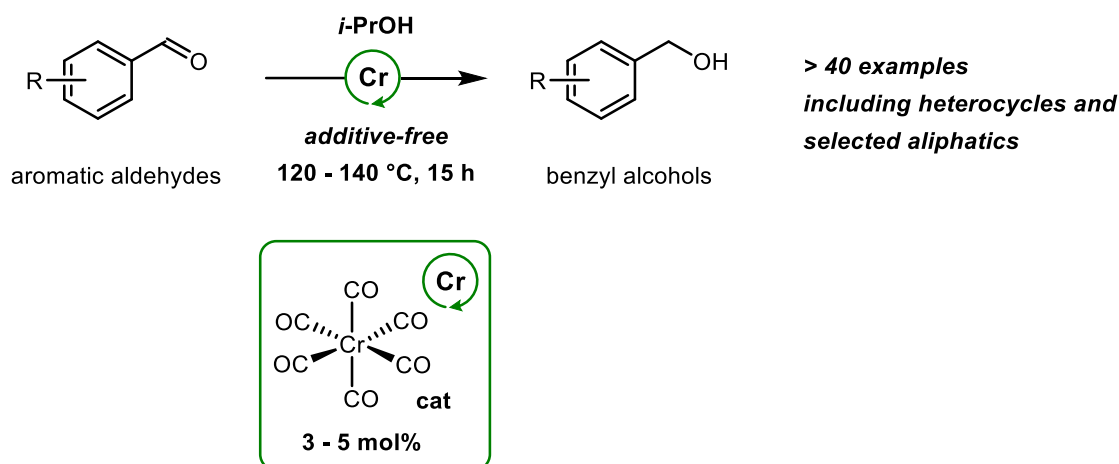
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The past decade has witnessed a major wave of research into base-metal-catalyzed hydrogenation reactions that deploy cobalt, iron, and manganese as active metals. In addition to these, the Group 6 elements chromium and tungsten would also fit well in this row owing to their low price, good abundance, and aptitude for hydride formation. Yet, pertinent reports on Cr- or W-based molecular catalysts which are used for hydrogen transfer are still very scarce in the literature. Herein, the ability of selected molecularly well-defined chromium and tungsten complexes to function as efficient catalysts for the (transfer) hydrogenation of certain relevant substrates is highlighted.

Chromium Catalysts

The synthesis, characterization, and catalytic application of a PN-tagged chromium carbonyl in the reduction of ketones is presented.^[1] Furthermore, a general transfer hydrogenation protocol for aldehydes that relies on simple, unmodified $[\text{Cr}(\text{CO})_6]$ is introduced whereby results on the kinetics of the catalytic transformation will be discussed.^[2]

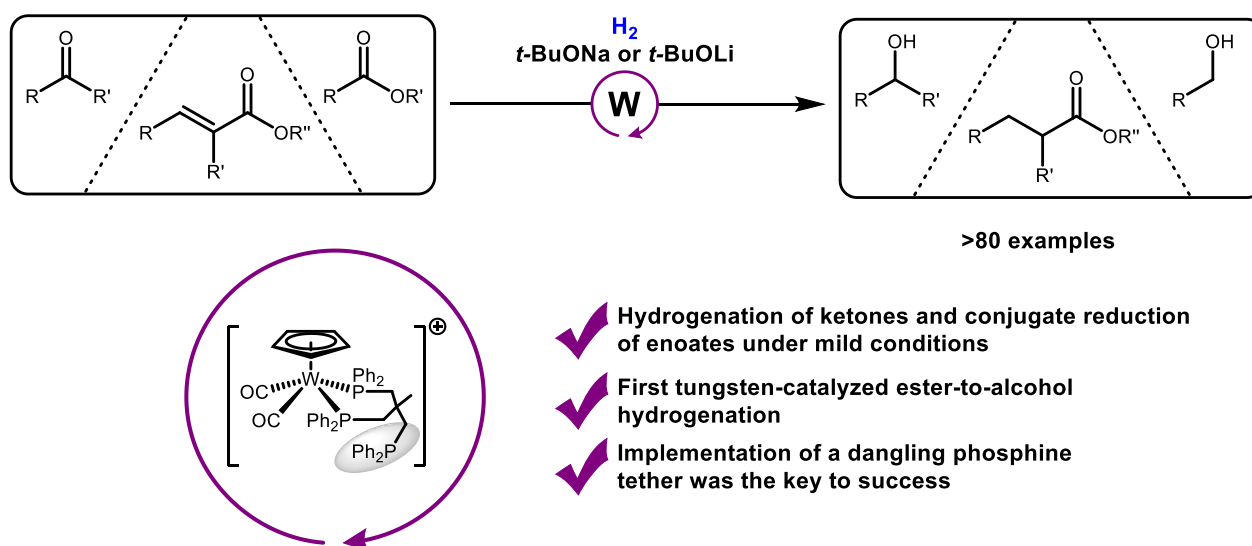


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Tungsten Catalysts

A pertinent half-sandwich complex, *i.e.*, $[\text{WCl}(\eta^5\text{-Cp})(\text{CO})_3]$, which was found to serve as a convenient precursor for the homogeneous hydrogenation of quinolines will be introduced.^[3] Moreover, it will be shown that the same organometallic compound is a starting material for the preparation of a triphos-ligated tungsten complex that functions as a versatile catalyst for the (conjugate) hydrogenation of ketones, enoates, and esters:



Strikingly, the hydrogenation of most of the investigated ketones was possible even at room temperature and under low H_2 pressure (5 bar). In addition, mechanistic insights that were gained through ^1H and ^{31}P NMR spectroscopy are going to be outlined.

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Organic and organometallic species derived from 1-haloalkynes

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Long chain organic, organometallic and metal-containing polyynes are being constantly at the horizon of modern synthetic and materials chemistry. Such compounds are not only investigated as models for still elusive sp-carbon allotrope - carbyne, but have been proved to possess many unusual properties which extend from uncommon structural features to spectacular physicochemical behavior. In this regard, metal termini which are σ -attached to the carbon chain play a crucial role in moderation of those properties. Especially interesting are red-ox active end-groups which use the unsaturated $(C\equiv C)_n$ bridge to communicate one with the other.

Numerous methods have been developed to synthesize polyynes and a plethora of such species was obtained and thoroughly characterized to date. We have lately focused our attention on 1-halopolyynes. This interesting group of rod-like compounds (1) possess an electrophilic terminal carbon atom which has an affinity to many nucleophiles and (2) undergoes oxidative addition to many metal complexes. Both these features have been used for a construction on new polyyne derivatives. One example would be iridium(III) or palladium(II) polyynes obtained *via* oxidative addition.

The others are selenium species formed *via* addition of *in situ* produced H_2Se to long chain aminopolyynes derived from 1-haloalkynes.

Since 1-halopolyynes are able to form strong halogen bonds we have been able to use this phenomenon for a construction of planar architectures based on this non-bonding interaction.

Chiral, L-shape N-heterobicyclic carbene ligands for asymmetric gold(I) catalysis

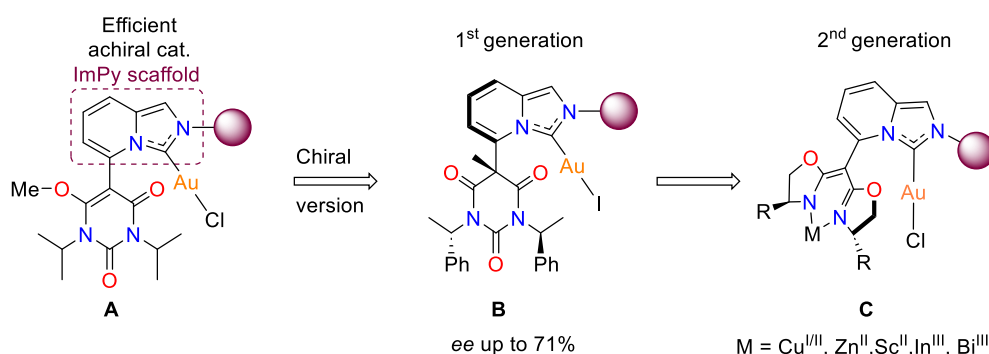
Paul Teixeira,¹ Idir Benaissa,¹ Quentin Arias,² Yue Tang,² Laure Vendier,¹ Fabien Fontaine-Vive,² Sandra Olivero,² Philippe Belmont,³ Véronique Michelet,² Vincent César,¹ Stéphanie Bastin¹

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Despite the outstanding advances realized in homogeneous gold(I) catalysis over the last two decades, the asymmetric version has not experienced the same growth.^[1] The main challenge resides in the specific, linear coordination geometry of gold(I) complexes, which limits an efficient chirality transfer from the ligand to the substrate. In 2019, our groups reported that the “achiral”, tunable catalysts **A**, supported by a “L-shape”, bicyclic imidazo[1,5-a]pyridin-3-ylidene (ImPy) ligand laterally-functionalized by a barbituric heterocycle, are highly efficient in gold(I)-catalyzed C-N, C-O, and C-C bond formations.^[2]

We present herein our progresses towards efficient chiral catalysts based on this privileged ImPy platform.^[3] The first generation is composed of chiral ImPy-Au(I) complexes **B** featuring a chiral lateral barbituric heterocycle obtained from enantiopure (*S*)-1-phenylethylamine. The use of the chiral pre-catalysts **B** in the domino cycloisomerisation/nucleophilic addition of 1,6-enynes with various nucleophiles gave excellent yields and good enantioinduction (up to 72% ee), resulting in functionalized heterocycles.^[4] As a second generation, the ImPy-Au(I) complexes **C** functionalized with a chiral, lateral bis-oxazolinone moiety is being developed in order to improve the transfer of the chiral information.

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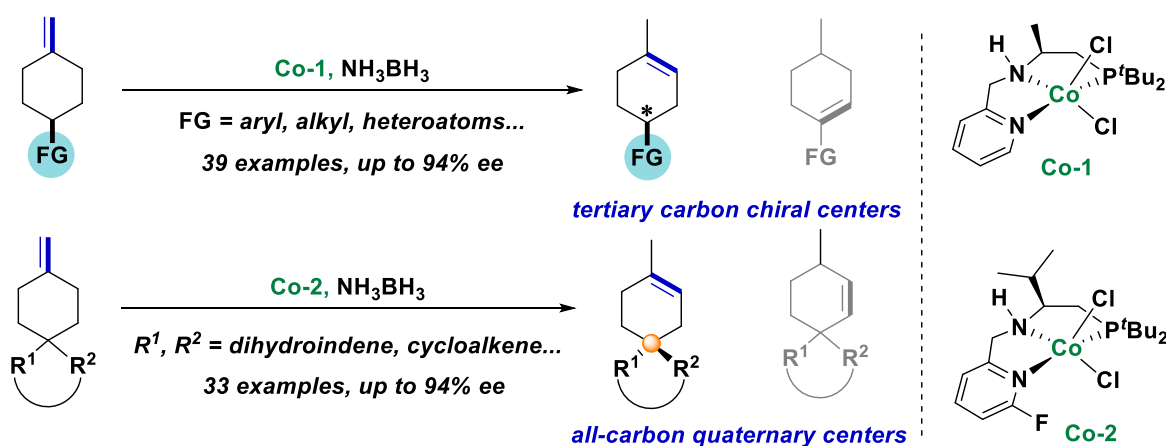
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Cobalt-Catalyzed Desymmetric Isomerization of Exocyclic Olefins

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Olefin isomerization, a fundamental reaction process in organic synthesis, has emerged as a potent strategy to synthesize high valued olefinic compounds from readily available starting materials with high atom- and step-economy. However, only a handful of enantioselective isomerization reactions have been reported to date, and most of these known examples employed substrates bearing stabilizing groups (e.g., OH, NR_2 , OR, and C=O), leading to the thermodynamically most favored conjugated olefin products. Although encouraging progress has been made, the highly enantio- and site-selective asymmetric olefin isomerization reactions under kinetic control are extremely challenging. First, the catalysts have to accurately distinguish the different reactivities of double bond between starting material and product, avoiding chain-walking to generate the most thermodynamically stable isomers (site-selectivity issue). Second, the suitable chiral environment should be offered to achieve high enantioselectivity (enantioselectivity issue). Besides, the realization of such reactions would greatly enrich the scope of double bond migration sites and synthetic implications. Herein, we report the development of fine-tunable chiral pincer cobalt catalysts, which allowed for an efficient desymmetric isomerization of exocyclic olefins to access diversified chiral 1-methylcyclohexenes with excellent site selectivity and enantioselectivity via kinetic control and remote stereocontrol.^[1] Furthermore, using this methodology, a concise synthesis of a natural product, β -bisabolene, has been realized. Based on this work, a wide array of enantioenriched 1-methylcyclohexenes bearing all-carbon chiral quaternary centers that are valuable synthons in organic synthesis can be attained,^[2] which was ensured by an evolved chiral *N,N,P*-pincer cobalt catalyst. Preliminary mechanistic studies revealed a Co-H insertion/ β -H elimination reaction pathway and the chiral induction model based on the steric interaction between the ligand and substrates.

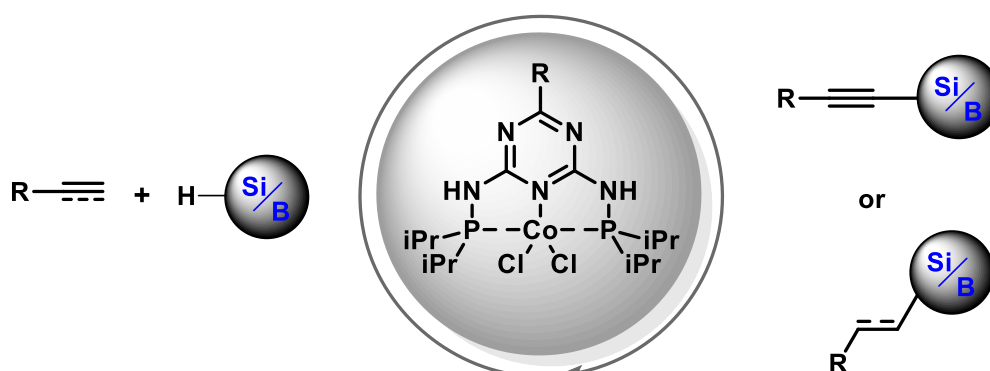
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Cobalt complexes as Earth-abundant catalysts in the synthesis of organometallics compounds

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Modern chemical synthesis highly focuses on the sustainability of the carried-out reactions mainly by minimizing the amount of used and generated hazardous substances. This is mostly achieved by using catalysts that permit the activation of new reaction pathways which enable increased process selectivity and the utilization of less reactive substrates.[1]

An interesting example of recently intensively studied homogeneous catalysts is pincer cobalt complexes. They are known for their relatively simple synthesis, exhibiting high stability, activity, and selectivity in hydrogenation, hydroboration, hydrosilylation, or bond-forming reactions.[2] Their important feature is the possibility of affecting their selectivity by simply changing the reaction conditions or the structure of the ligand.

In this communication, I will present the synthesis of organoboron and organosilicon compounds catalyzed by cobalt pincer complexes which have been synthesized in a gentle and easy way by using inexpensive and commercially available reagents. The presented methodology enables ligand-controlled synthesis regarding the principles of sustainable chemistry leading to a valuable group of compounds.[3-5]

Acknowledgments: This work was supported by a National Science Centre Grant: UMO-2018/30/E/ST5/00045.

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NHC-Based Manganese (I) PCP Complexes for Hydrogenation and Hydrofunctionalization Reactions

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The utilization of base-metal catalysts in favor of more expensive precious-metal catalysts has been extensively researched in the last few decades. Manganese has hereby seen a rise in popularity as it is earth-abundant, cheap, and non-toxic. In that regard, most manganese-based catalysts utilize some sort of metal-ligand bifunctionality.¹ Our group, however, has had great success with utilizing a well-defined Manganese(I) alkyl complex that undergoes migratory insertion and is thus operating *via* an inner-sphere mechanism.²

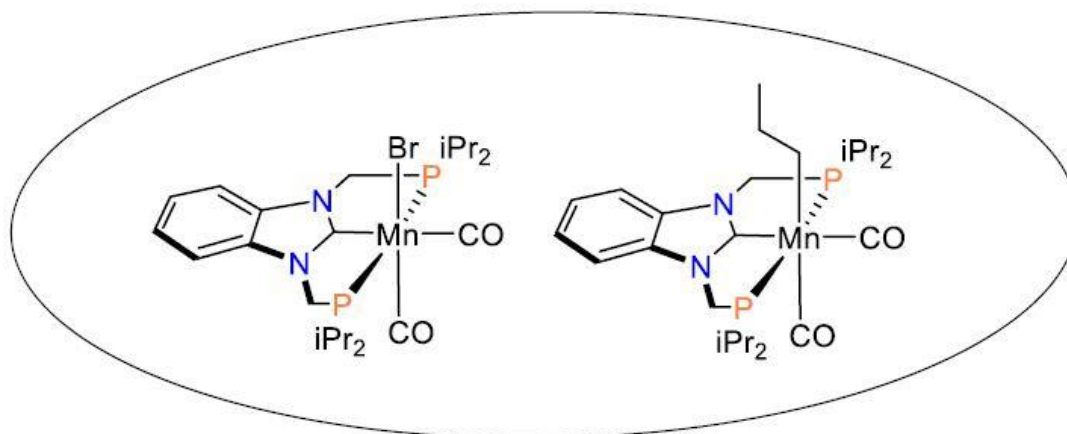


Figure 1. Synthesized Complexes

We herein report the synthesis of NHC-based tridentate PCP Manganese(I) bromide and *n*-propyl complexes (Figure 1) with the latter being able to undergo migratory insertion in addition to metal-ligand bifunctionality. These complexes were employed for the catalysis of hydrogenation and hydrofunctionalization reactions. Both similarities and differences between these complexes and the previously published alkyl complex will be discussed, and an outlook will be given.

Literature:

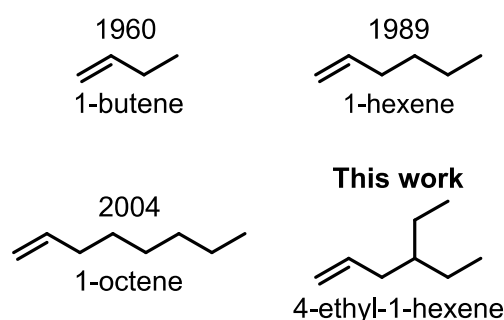
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Synthesis of a branched α -olefin via tetramerization of ethylene and homo-polymers thereof

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α -Olefins are an important class of chemical compounds and ethylene is an attractive feedstock to synthesize them. However, the selective or on-purpose synthesis of α -olefins from ethylene is restricted to examples having a linear structure. A selective or on-purpose synthesis of a branched α -olefin from ethylene would be highly desirable. We report here on the tetramerization of ethylene towards 4-ethyl-1-hexene, a branched α -olefin. The key is a highly active and longtime stable catalyst system based on a well-defined molecular titanium pre-catalyst.^[1] Our catalyst system is able to dimerize ethylene and reacts the dimer 1-butene with two ethylene molecules in an elongation/branching reaction. 4-Ethyl-1-hexene can be homo-polymerized to a highly transparent ethylene-based plastic with a melting point of > 220 °C and an extremely low density.



Literature:

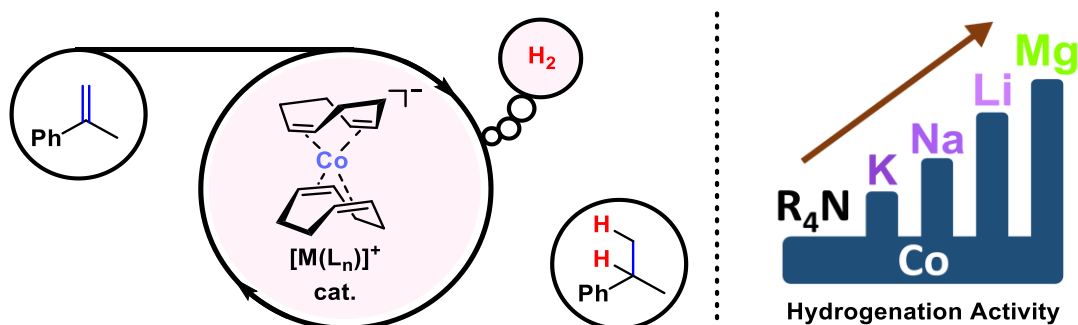
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Counterion Effect in Cobalt-Catalyzed Alkene Hydrogenation

R. Wolf

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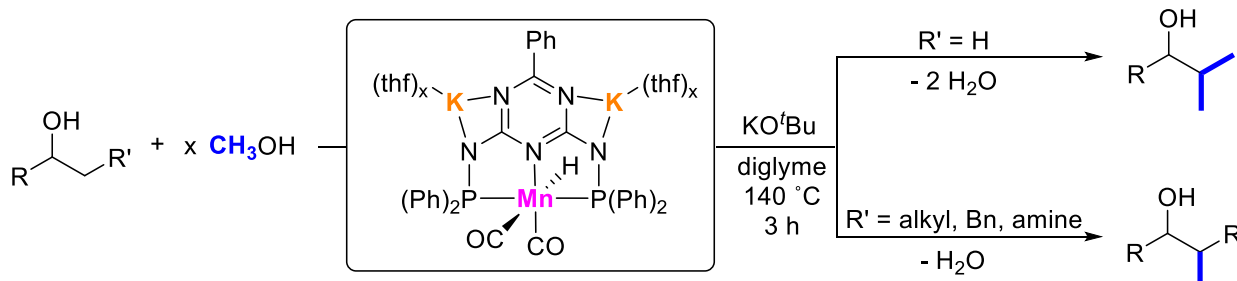
This talk will discuss the substantial counterion effects on the properties of low-valent cobaltate pre-catalysts in alkene hydrogenations. Comparative hydrogenation reactions with the pre-catalyst salts $[M(L_n)][Co(\eta^4-cod)_2]$ [$M = K$ (**1**), Na (**2**), Li (**3**), $(^{Dep}nacnac)Mg$ (**4**); $cod = 1,5$ -cyclooctadiene, $^{Dep}nacnac = \{2,6-Et_2-C_6H_3-N=C(CH_3)_2\}_2C$] and $[N(^tBu)_4][Co(\eta^4-cod)_2]$ (**5**) showed a strong influence of the counterion on the catalytic activity, with Li^+ and $[(^{Dep}nacnac)Mg]^+$ cations drastically enhancing reaction rate and substrate scope. Bulky alkenes were readily hydrogenated under mild conditions by the magnesium cobaltate catalyst. A plausible catalytic mechanism is proposed based on density functional theory (DFT) investigations. Combined molecular dynamics (MD) simulation and DFT studies furthermore examine the turnover-limiting migratory insertion step and support the notion of an active co-catalytic role of the counterion in the hydrogenation reaction.



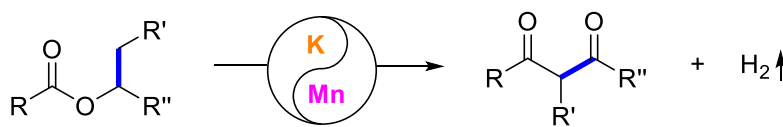
Selective C-alkylations

Martin Schlagbauer, Torsten Irrgang, Rhett Kempe

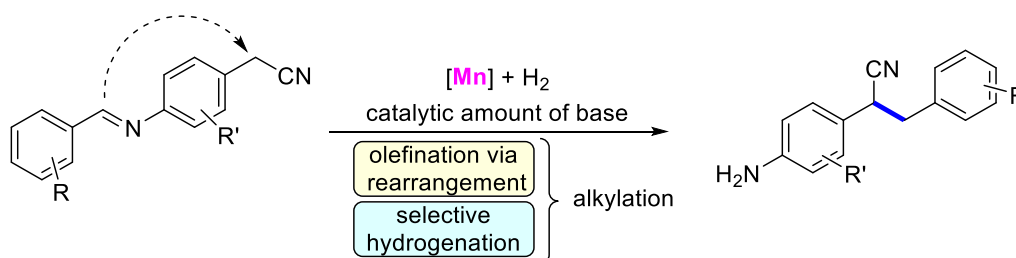
Lehrstuhl für Anorganische Chemie II – Katalysatordesign, Sustainable Chemistry Centre, Universität Bayreuth, 95440 Bayreuth, Germany.



This talk we sum up some of our contributions regarding selective C-alkylations with manganese-based catalysts. Starting with the methylation of alcohols which we published in 2020.^[1] Methyl group branching is an extremely important structural motif in chemistry and biology,^[2] ranging from synthetic lubricants^[3] to more than half of all drug molecules^[4].



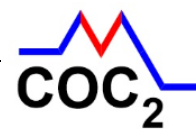
In 2021 we published the “Synthesis of 1,3-diketones from esters via liberation of hydrogen”.^[5] In this work we reported on a dehydrogenative rearrangement as a combination of a rearrangement reaction involving a C-alkylation step and hydrogen generation. The concept permits the general synthesis of 1,3-diketones from esters with hydrogen as the only by-product of the reaction.



Our current work concerning another rearrangement sequence that is giving access to highly functionalized amino-nitriles will be presented. In this sequence a selective C- over N-alkylation is achieved without protecting groups. A selective manganese-based hydrogenation catalyst is applied to hydrogenate olefinic double bonds in the presence of other hydrogenative sensitive groups.

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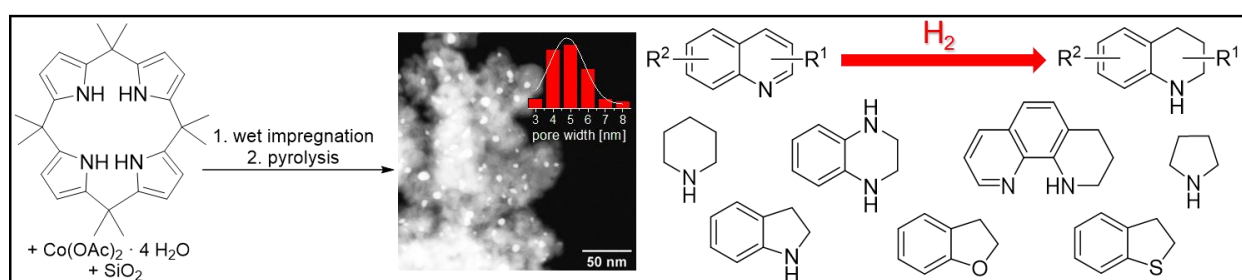
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Poster

A Highly Active Cobalt Catalyst for the General and Selective Hydrogenation of Aromatic Heterocycles

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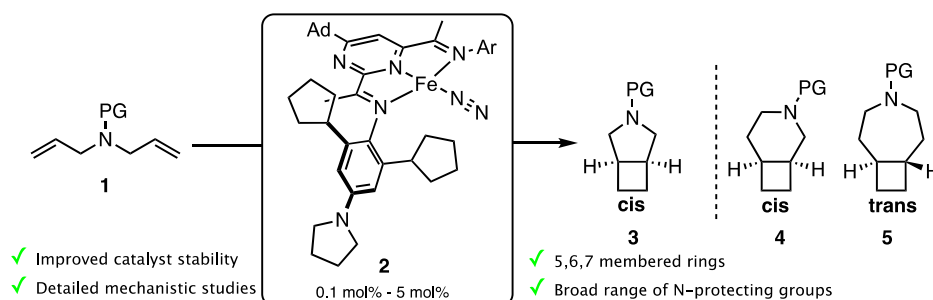
Nanostructured earth abundant metal catalysts that mediate important chemical reactions with high efficiency and selectivity are of great interest. This study introduces a synthesis protocol for nanostructured earth abundant metal catalysts. Three components, an inexpensive metal precursor, an easy to synthesize N/C precursor, and a porous support material undergo pyrolysis to give the catalyst material in a simple, single synthesis step. By applying this catalyst synthesis, a highly active cobalt catalyst for the general and selective hydrogenation of aromatic heterocycles could be generated. The reaction is important with regard to organic synthesis and hydrogen storage. The mild reaction conditions observed for quinolines permit the selective hydrogenation of numerous classes of N-, O- and S-heterocyclic compounds such as: quinoxalines, pyridines, pyrroles, indoles, isoquinoline, acridine amine, phenanthroline, benzofuranes, and benzothiophenes.

Literature:

[1] C. Bauer, F. Müller, S. Keskin, M. Zobel, R. Kempe, *Chem. Eur. J.* **2023**, *29*, e202300561.

Synthesis of Geometrically Constrained Motifs via Iron Catalyzed [2+2]-Cycloaddition

Becker, Felix J., Hertwig, Leif E., Bender, Thilo, Roşca, Dragoş-Adrian
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The formation of cyclobutane rings via [2+2]-cycloaddition is thermodynamically favourable but in principle violates orbital symmetry rules. While one strategy to circumvent such constraints is photocatalysis, most methods rely on activated alkenes, where the increased π -delocalisation ensures an absorption in the near visible UV range.^{[1][2]} Another common limitation of these methods is their restriction to cyclobutane-fused five membered rings motifs.

In this respect, non-photochemical approaches can offer an alternative strategy to circumvent this limitation. For example, pyridinediimine-based iron and cobalt complexes has been proven a reliable alternative in the [2+2]-cycloaddition using readily available, non-activated olefins.^[3] Nevertheless, the rapid onset of catalyst deactivation already in the first half-life of the reaction mandates high catalyst loadings (5 - 10 mol%) and limits the substrate scope.

Herein, we present an improved ligand design, which relies on a pyrimidine scaffold (**2**).^[4] The π -acidic core significantly enhances catalyst stability while the electron-rich flanking groups accelerate the reaction rate. This approach allows lowering of the catalyst loading to 0.1 mol% and expands the substrate scope. For example, using the new system, first examples of unsubstituted nitrogen containing six and seven membered rings could be obtained. Interestingly, single crystal X-ray diffraction revealed that the bicyclic seven membered rings **5** favour trans stereoselectivity, while the five **3** and six membered **4** analogues are cis. The control of stereoselectivity as a function of ring size yields important mechanistic information on the ring-closing reaction. Moreover, these scaffolds are conformationally restricted bioisosteres to azepanes and pyrrolidines, which are the most frequently used secondary amines in medicinal chemistry, make them highly valuable motifs for future drug design.

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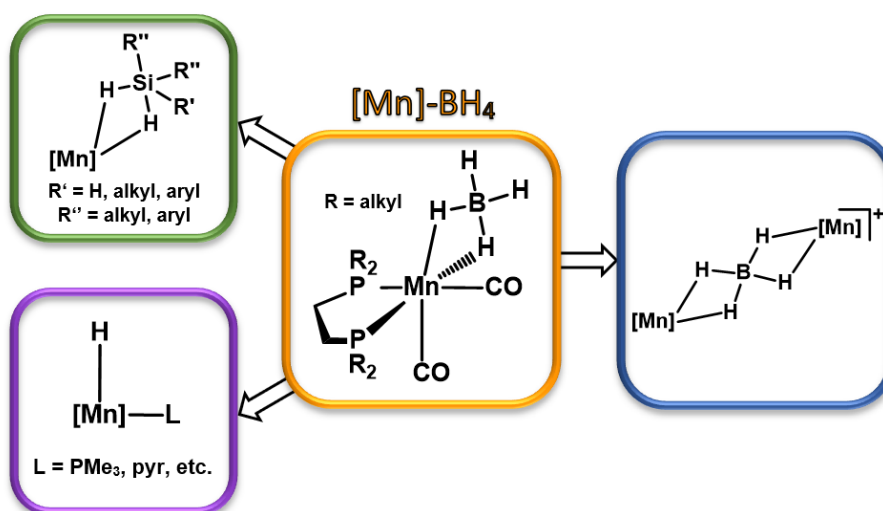
Synthesis and Catalytic Application of Manganese(I) Complexes Containing σ -B-H Bonds

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Activation of E-H bonds (E = H, Si, B) at transition-metal centers are intensely studied and are considered to be crucial steps in a variety of catalytic processes.^[1] In this field, the role of coordinated B-H bonds is a subject of great interest.^[2] As a compound of such kind, the well-defined complex $[\text{Mn}]\text{-BH}_4$ (Scheme 1) was investigated for its structure, reactivity and catalytic application.

The synthesis of $\text{Mn-}[\text{BH}_4]$ was based on the catalytically active ^[3] Mn(I) alkyl species. The resulting borohydride complex can be used as a versatile platform for further functionalizations. Adduct formation of coordinated $[\text{BH}_4]^-$ grants access to a variety of functionalized Mn(I) compounds. Thus, different complexes are accessible, including compounds bearing hydrides or anionic silane ligands (Scheme 1).



Complex $\text{Mn-}[\text{BH}_4]$ was examined as a catalyst in olefin isomerization reactions. Isomerization plays a crucial role in a variety of industrial processes and organic transformations.^[4] $\text{Mn-}[\text{BH}_4]$ was proven to isomerize aliphatic and aromatic alkenes at room temperature. At elevated temperatures, isomerization over multiple bonds – so called “chain-walking” – is possible.

However, these promising preliminary studies need further investigation. Mechanistic aspects as well as a broadening of the substrate scope will be the focal point of future examinations.

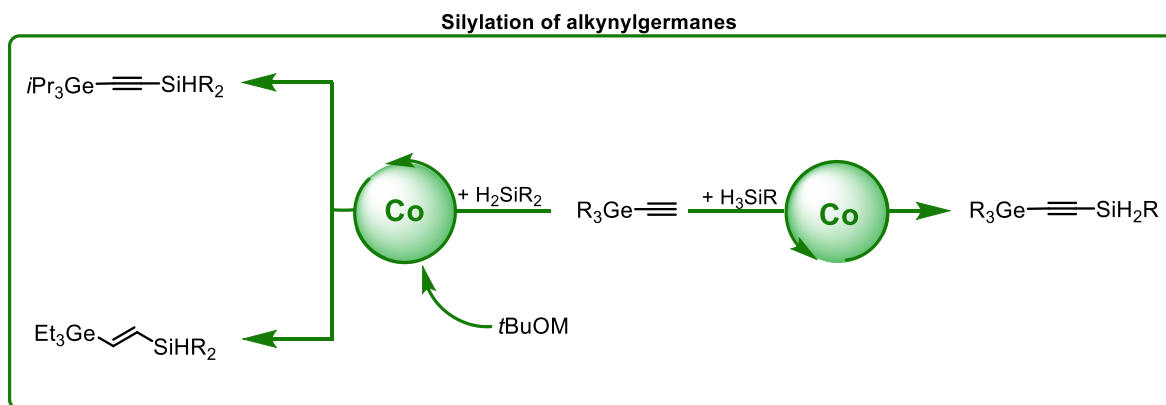
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Cobalt catalyzed effective access to unsaturated germanium compounds

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Organogermanium compounds have gained interest in recent years due to their unique properties. Unsaturated germanes can be considered as useful building blocks for more complex organic molecules, because of their high stability and low toxicity.^[1,2] Alkynylgermanes and vinylgermanes can be synthesized via classical stoichiometric reactions utilizing organogermanium halides as substrates^[3,4]. Moreover, several catalytic approaches have been developed, including expensive transition-metal catalysts in (i.e. Pd, Ru)^[5,6]. Due to the corrosive nature of by-products of stoichiometric reactions and high cost and environmental impact of catalytic methods, scientists focused their efforts on developing more environmentally friendly approaches, like the use of earth-abundant metals as catalysts. One of the more sustainable and green approaches include the use of transition 3d-metals as catalysts. Cobalt derived pincer complexes have gained attention due to their stability, selectivity and catalytic activity in many different organic transformations^[7].

In this communication, we report a new efficient way to obtain functional alkynylgermanes via dehydrogenative coupling and vinylgermanes via hydrosilylation using PN5P cobalt pincer complex. From a synthetic point of view, this methodology has many favorable features and advantages over other methods (e.g., needs mild conditions, needs a relatively low catalyst loading, gives no corrosive by-products, and has high efficiency, and excellent yields).

Funding acknowledgment: National Science Centre Grant: UMO-2018/30/E/ST5/00045

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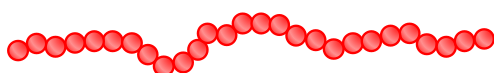
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Copolymerisation of ethylene with branched olefins

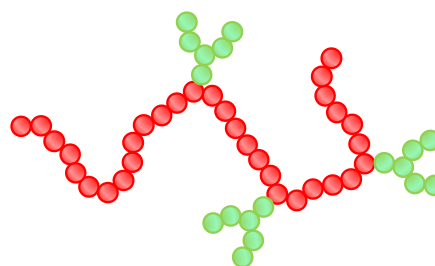
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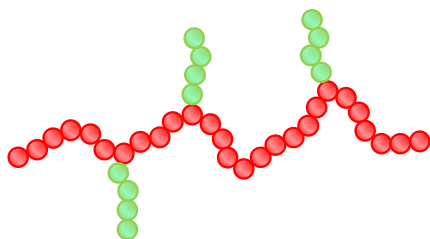
high density polyethylene (HDPE)

**This work:**

linear ultra low density polyethylene (LULDPE)



linear low density polyethylene (LLDPE)



Ethylene, an abundantly available feedstock, is the most common building block for producing polyolefins, such as high- (HDPE), low- (LDPE) and linear low- (LLDPE) density polyethylene. While the synthesis of LDPE and HDPE is conducted from ethylene, alone the production of LLDPE requires large amounts of α -olefins like, 1-butene, 1-hexene or 1-octene. Also, the physical properties of LDPE and LLDPE are very similar, the later one has normally a slightly higher density. While a substantial amount of these polymers are used for packaging, a lower density with otherwise the same properties would be beneficial.

Recently, Dietel *et al.*^[1,2] introduced a titanium-based catalyst system, which enables the access to novel 4-ethyl branched α -Olefins, like 4-ethyl-1-hexene. Due to its ethyl branch, this olefin would be a promising comonomer for reducing the density of LLDPE. Herein we report the copolymerization of ethylene and 4-ethyl-1-hexene to obtain an ultra linear low density PE (ULLDPE) material and its comparison of common LLDPE based on 1-hexene and 1-octene.

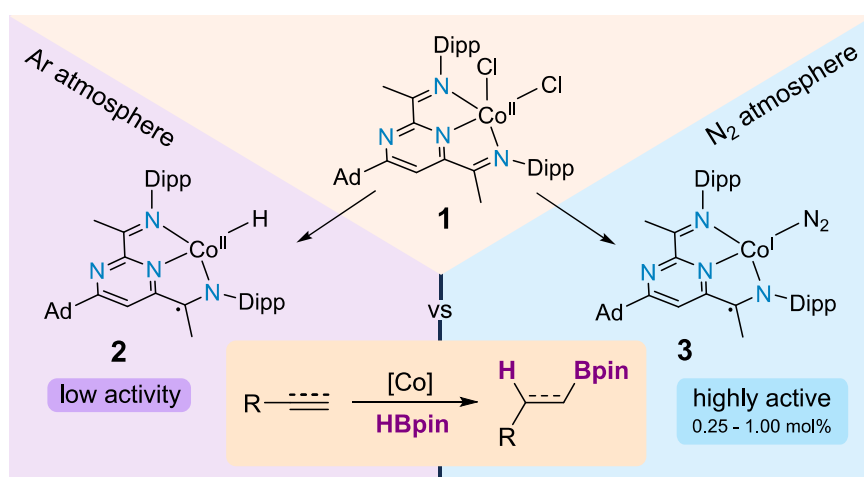
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The Effect of “Inert” Gas on the Catalytic Outcomes in Cobalt-Mediated Alkyne and Olefin Hydroboration

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The atmosphere in which a reaction takes place is an often overlooked factor, that can determine the outcome of the reaction. Hereby we present an example where the “inert” gas in which the catalyst activation is performed can exert a significant influence on catalyst activity. Namely, the cobalt dichloride complex (**1**) of a redox-active, π -acidic pyrimidine-diimine ligand^[1,2] showed a much higher activity in the hydroboration of terminal alkynes and alkenes when activated under nitrogen rather than under argon.^[3]

Stoichiometric studies revealed that pre-catalyst activation under an atmosphere of nitrogen yields a cobalt nitrogen complex (**3**), whereas the main product under argon is a cobalt hydride species (**2**). While such hydride species are commonly postulated as entry point in the catalytic cycle of hydroelementation reactions, in the case herein discussed, the nitrogen complex (**3**) is significantly more active (TOF = 1100 h⁻¹ at $t_{1/2}$, RT) than the hydride complex (**2**). The electronic structure of all relevant species was investigated in detail by computational, crystallographic, and spectroscopic means, revealing involvement of the ligand in the redox processes.

Under the optimized hydroboration reaction conditions, only very low catalyst loadings (0.25 – 1.0 mol%) were needed to achieve a wide range of vinyl and alkyl organoboron derivatives with a high regio- and stereoselectivity. Mechanistic studies suggest that initial formation of Co- π -complexes is preferred, followed by the oxidative addition of the borane, which is the turnover-limiting step. This is corroborated by Hammett analysis, which shows that electron-rich substrates react more rapidly.^[3]

Literature:

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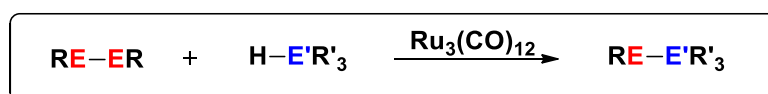
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Ru-catalyzed Selective Synthesis of Thiosilanes and Selenosilanes via Dichalcogenides as a Convenient Substitute to Thiols and Selenols

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General scheme of the process.



E = S, Se

E' = Si, Ge

Compounds containing sulfur are prevalent in chemical synthesis, playing a significant role in producing biologically relevant molecules and specialized materials. Derivatives featuring S-N, S-O, S-C, and S-S functional groups are strategically important, offering a range of intriguing applications. Contrarily, despite their value in organic chemistry, thiosilanes (S-Si) remain comparatively underexplored. The primary challenge in unlocking their full synthetic potential is to discover new ways of synthesizing them under favorable conditions because there are only limited methods available for their production^[1-7].

In this communication we present a ruthenium-catalyzed process that selectively converts disulfides (and diselenides) into their corresponding silyl (and germyl) derivatives, marking the first instance of a thiol/thiolate-free approach. Our method utilizes commercially accessible ruthenium dodecacarbonyl as the catalyst, in conjunction with easy-to-handle hydrosilanes (and hydrogermanes) and odor-free dichalcogenides (S, Se). The subsequent conversion of heteroaryl halides into unsymmetrical sulfides highlights the synthetic capabilities of the resulting silylthioethers.

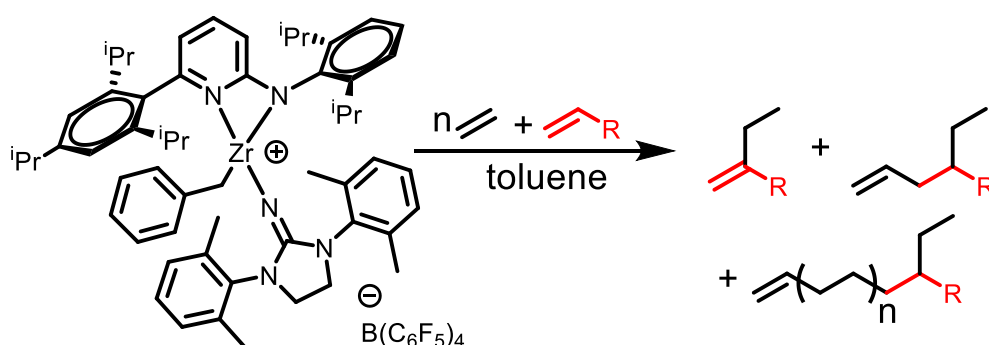
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Synthesis of linear and branched α -Olefins by Aminopyridinato-Imidazolidin-2-ylidenamido stabilized Zirconium catalysts

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Linear and branched α -olefins are indispensable bulk chemicals. On the one hand these olefins are needed in the scale of megatons to produce commodity plastics such as linear low-density polyethylene. On the other hand, α -olefins are needed to synthesise pharmaceuticals, fine chemicals and high-performance lubricants.^[1] Finding a flexible synthesis to produce these highly desirable chemicals using a cheap, well available and sustainable resource such as ethylene is of great importance.^[2] Herein, we report on a family of highly active homogeneous zirconium (IV) catalysts for the very mild synthesis of linear and branched α -olefins starting from ethylene feedstock. Variation of the steric demand of the aminopyridinato-ligand attached to the catalyst allows controlling the width of the oligomers' product distribution. By ethylene oligomerisation linear α -olefins and by ethylene α -olefin co-oligomerisation branched α -olefins are therefore accessible.

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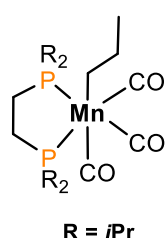
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Iron (II) Pincer Alkyl Complexes: Synthesis and Reactivity Exploitation

Matthias Käfer, Karl Kirchner*

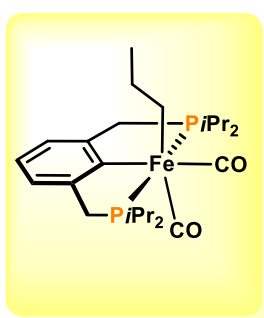
IAS TU Wien, Getreidemarkt 9/163, 1060 Wien

established system:

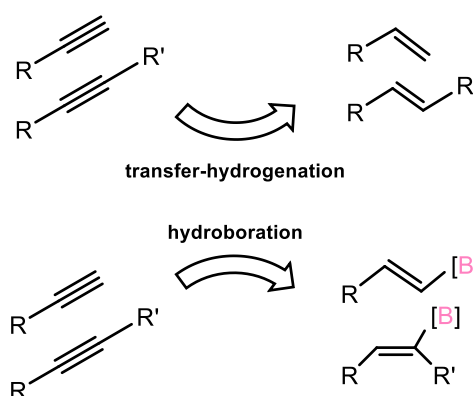


-stable at ambient conditions
-18 electron, Mn(I) complex
-highly active hydrogenation and hydrofunct. catalyst

Newly developed systems:



-iron(II) complex isoelectronic to Mn(I)
-increased reactivity?



In recent years, the Kirchner group reported on the successful development of a highly active, bench stable catalyst system which was active in a variety of different transformation. This reactivity was caused by its ability to generate vacant coordination sites by undergoing a migratory insertion reaction.^[1]

Herein, we like to report the successful functionalization of previously reported iron (II) PCP^[2] pincer complexes towards their alkyl congeners. Furthermore, the reactivity of the synthesized complexes towards the catalytic semi-hydrogenation of terminal and internal alkynes will be elaborated. Concludingly, the activity towards the hydroboration of internal and terminal olefins under mild conditions will be given, which previously required harsh reaction conditions (such as UV radiation).^[3] Mechanistic investigations into the insertion behaviour of the utilized complexes will conclude the presentation, to elaborate on possible future transformations.

Literature:

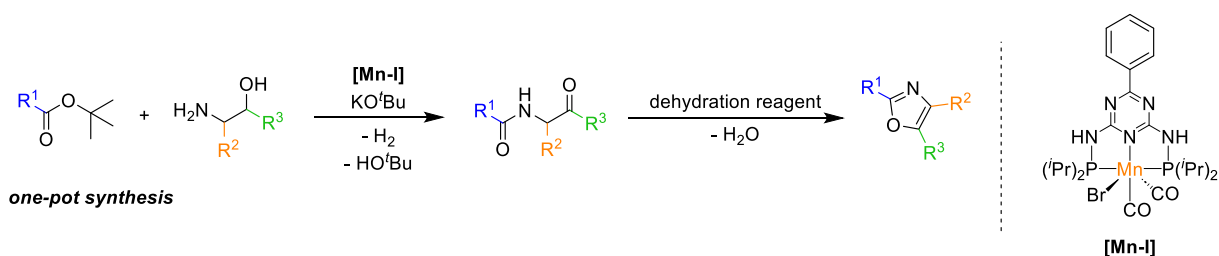
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Manganese-catalyzed Dehydrogenation of Amido Alcohols via Liberation of Hydrogen for the Synthesis of Oxazoles

Leinert, Max, Irrgang, Torsten, Kempe, Rhet
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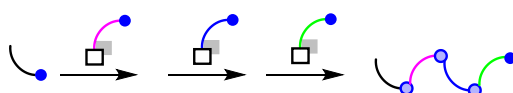
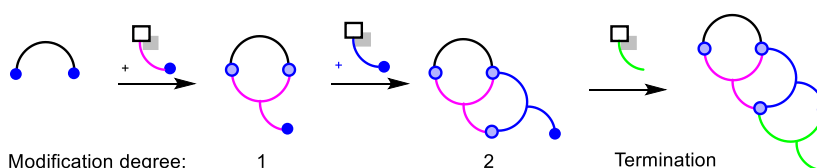
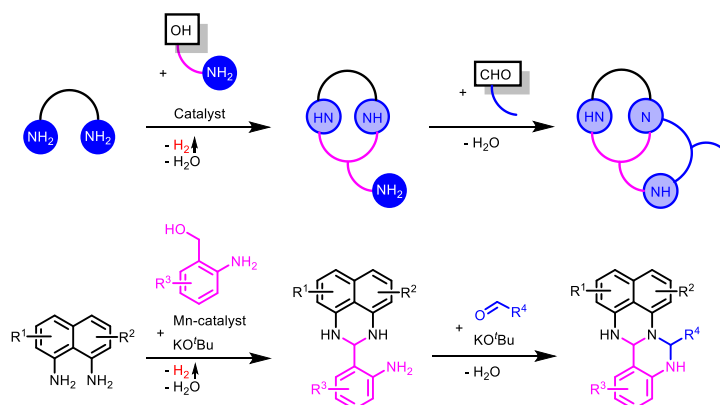
Syntheses of important classes of (heterocyclic) compounds, the sustainable generation of hydrogen, and the use of abundantly available metals are highly desirable. We introduce here a catalytic oxazole synthesis.^[1] Our reaction is a regio selective, one-pot reaction and starts from esters and amino alcohols. Both are abundantly and diversely available, inexpensive, and green or sustainable starting materials. Hydrogen is liberated during the reaction and a molecular earth-abundant metal catalyst, a Mn(I) compound, mediates the reaction most effectively - and more efficiently than Ir and Ru catalysts. None of the oxazole derivatives synthesized, except the screening substrate and an active ingredient of a drug (an application), have been reported in literature yet.

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Rational design of *N*-heterocyclic compound classes via regenerative cyclization of diamines

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A. Iterative Synthesis**B. Regenerative Cyclization****C. This Work: Synthesis of *N*-Heterocyclic Compounds**

A Regenerating the functional group again that has been modified originally (iterative synthesis) can lead to chemical diversity if different building blocks are used. **B** Classes of (poly)cyclic compounds can be conceived via ring closure chemistry. The set of functional groups originally used has to be formed again during the ring closure reaction (regenerative cyclization). Repeating ring closure steps should lead to classes of (poly)cyclic compounds, which haven't yet been synthesized, at some stage or modification degree. **C** *N*-Heterocyclic compounds introduced here with amines being the key functional groups, applying a modification degree of two, and a catalytic amino alcohol dehydrogenation-based ring closure reaction as the first step.

The discovery of reactions is a central topic in chemistry and especially interesting if access to compound classes, which haven't yet been synthesized, is permitted. We introduce here a consecutive three-component reaction, a class of *N*-heterocyclic compounds and the associated synthesis concept (regenerative cyclisation). Our reaction starts with a diamine, which reacts with an amino alcohol via dehydrogenation, condensation, and cyclisation to form a new pair of amines that undergoes ring closure with an aldehyde. Hydrogen is liberated in the first reaction step and the dehydrogenation catalyst used is based on manganese.^[1]

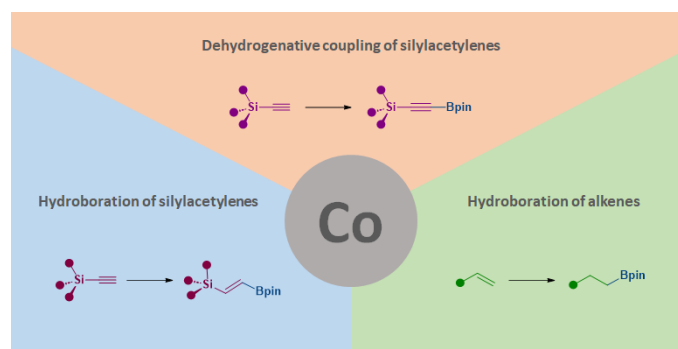
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Cobalt PNP type complexes as a universal tool for the synthesis of organometallic compounds

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The use of catalysis in organic synthesis is one of the pillars of modern chemistry placing great emphasis on ecological and sustainable development. Particularly of interest is homogeneous catalysis using non-noble metals, which due to their abundance are a much cheaper alternative to the more commonly used precious metals. Among first-row 3d-transition metals, most work is devoted to the synthesis and application of manganese, iron, cobalt, and nickel complexes,^[1] that, in combination with a suitably designed ligand, can exhibit activity and selectivity previously reserved exclusively for noble metal catalysis. In this context, pincer ligands are of major interest, as they have found application in many catalytic processes due to their high thermal and chemical stability, as well as the possibility of fine-tuning their properties.^[2]

In recent years, a lot of work has been particularly focused on the application of pincer cobalt complexes. They have been successfully applied in hydrogenation, hydroelementation, or coupling reactions.^[3] Moreover, their interesting feature is the possibility of drastically changing their selectivity and catalytic activity as a result of small changes in the structure of the ligand.^[4]

In this communication, we will present methods for the synthesis of organometalloid compounds catalyzed by PNP-type pincer cobalt complexes.^[5] The proposed procedures are based on the principles of green chemistry and allow the synthesis of high-value synthons that can find applications in the synthesis of fine chemicals, intelligent materials, or bioactive molecules.

Funding acknowledgment: National Science Centre Grant: UMO-2018/30/E/ST5/00045.

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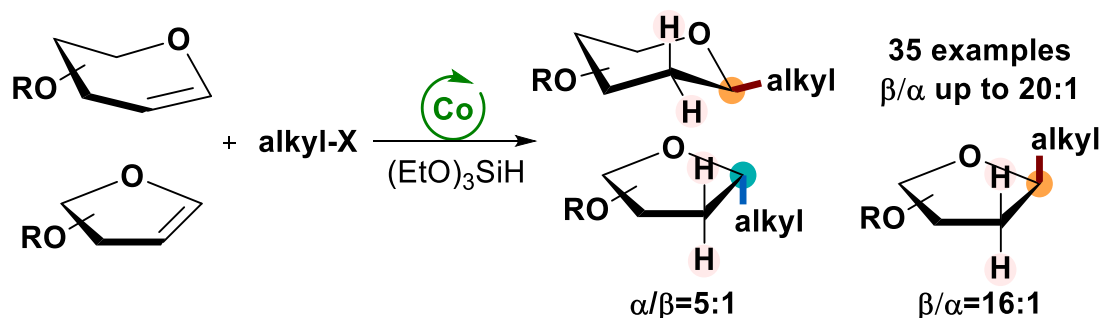
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Ligand-Controlled Stereoselective Synthesis of 2-Deoxy- β -C-glycosides by Cobalt CatalysisBingxue Liu,^a Deguang Liu,^b Xianle Rong,^a Xi Lu,^{b,*} Yao Fu,^{b,*} and Qiang Liu^{a,*}^aCenter of Basic Molecular Science (CBMS), Department of Chemistry, Tsinghua University, Beijing 100084, China^bSchool of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China

2-Deoxy- β -C-glycosides represent an important class of carbohydrates that are present in many bioactive molecules. Glycosyl radical-based reactions have been demonstrated to provide reliable access to α -selective C-glycosides, which is attributed to the higher stability and nucleophilicity of axial radicals than those of the corresponding equatorial radicals. However, owing to this inherent feature, the development of the corresponding β -selective synthesis of C-glycosides is far less developed. So far, β -selective C-glycosylation has predominantly relied on *ortho*-group directed strategy, in which alkoxy or bulky amino groups are incorporated at the equatorial position of C-2. However, these substrate-controlled approaches are unsuitable for the construction of β -C-glycosides with two hydrogen atoms at the C-2 position, i.e., 2-deoxy- β -C-glycosides. Due to the lack of substituents at the C-2 position, the stereoselective synthesis of 2-deoxy- β -C-glycosides is highly challenging. Herein we report a ligand-controlled cobalt-catalyzed hydroalkylation of glycols to access 2-deoxy- β -C-glycosides with a high level of stereoselectivity. In addition, a stereodivergent synthesis was realized for the hydroalkylation of five-membered glycols using two different chiral bisoxazoline ligand. Moreover, this method exhibits broad substrate scope and excellent functional group compatibility. Mechanistic studies revealed that the hydrometallation of the glycol with the bisoxazoline-ligated Co-H species is the turnover-limiting and stereo-determining step of this transformation.^[1]



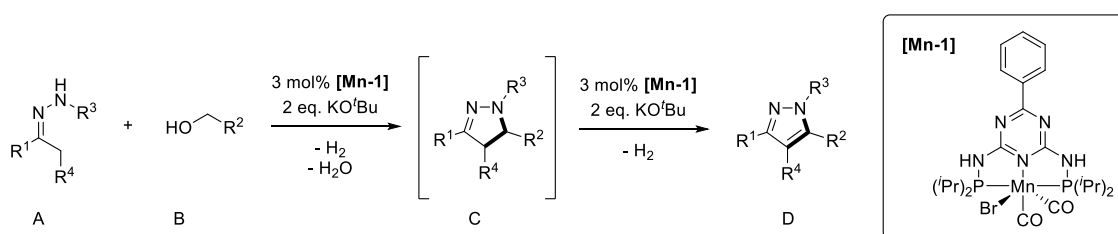
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A Manganese Catalyst Permits the Regioselective Dehydrogenative Synthesis of Pyrazoles from Hydrazones and Alcohols

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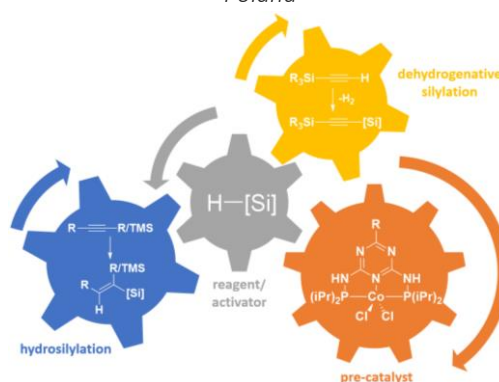


The development of (catalytic) reactions that extend the chemical space of important classes of compounds is a central focus of chemistry and relevant for associated material and life sciences. We report here on a catalytic regioselective pyrazole synthesis. Hydrazones and alcohols are used as starting materials and hydrogen is liberated in the course of the reaction. The reaction has a broad scope and 30 of the 35 synthesized pyrazole derivatives are compounds that have not yet been reported in the literature. A 3d metal catalyst, namely, a molecular Mn compound, mediates the reaction most efficiently and is superior to a related Ir catalyst.

Diverse catalytic activity of cobalt pincer complexes: hydrosilylation / dehydrogenative silylation of alkynes and silylacetylenes

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Cobalt pincer complexes for catalytic silylation of alkynes.

Hydrosilylation and dehydrogenative silylation represent the most straightforward, atom-efficient, and convenient processes from academic and industrial points of view. Both of these catalytic transformations lead to versatile building blocks, however, they can occur simultaneously as competitive reactions, e.g., in the functionalization of alkynes. Due to the above, extremely selective and highly active catalysts are sought, which could also face economic and environmental issues. Therefore, to replace commonly utilized Pt, Rh, or Pd compounds, the Earth-abundant and inexpensive complexes of 3d-transition metals, e.g., Ni, Fe, Mn, or Co are increasingly developed. Interestingly, the Co-catalyzed silylation of alkynes offers to receive all the plausible isomers, e.g., β -(E)-, β -(Z)-, and α -vinylsilanes. Unfortunately, many of the introduced catalytic systems convolute high temperature, formation of side-products, large amount of catalyst, or moderate efficiency. Among various developed cobalt complexes, those with coordination of pincer ligands have recently gained more attention attributed to their unique characteristic combined with facile preparation and easy accessibility. Nevertheless, apart from excellent selectivity and high catalytic activity, the presence of external additives seems crucial to generate an active form of the catalyst.^[1–3]

Herein, we present our recent results in the *syn*-selective hydrosilylation of internal alkynes and TMS-blocked derivatives, as well as dehydrogenative silylation of terminal silylacetylenes. Processes are suitable for primary and secondary silanes, and mediated by cobalt complexes bearing PN^TP pincer-type ligands. Besides mild reaction conditions, extraordinary selectivity, and superior efficiency, our approaches introduce sustainable solutions since hydrosilanes act as both substrates and activators.^[4]

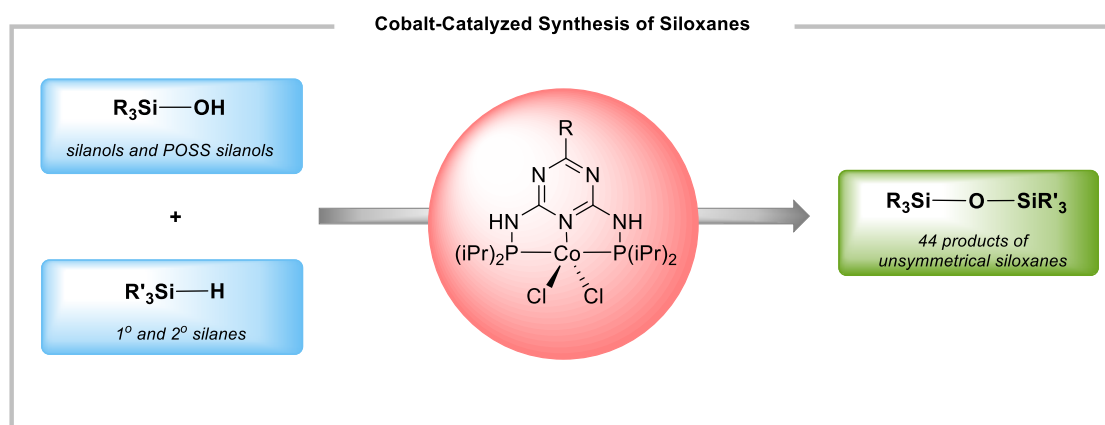
The work was supported by grant POWR.03.02.00-00-I020/17 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development and National Science Centre Grant UMO-2018/30/E/ST5/00045.

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Cobalt-catalyzed synthesis of hydrosiloxanes, dihydrosiloxanes and functionalized silsesquioxanes

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Siloxanes and hydrosiloxanes are classes of compounds having -Si-O-Si- motifs. These compounds have several excellent properties. As a result, they have been used in organic, inorganic and material chemistry, and therefore play a very important role in human life due to their special properties. Taking into account their unique properties, siloxanes have found many interesting applications in medicine, cosmetology, the automotive industry as well as the textile and leather industries.

In recent years, we have observed the dynamic development of siloxanes. Considering their numerous applications, we know many methods to obtain them. Silylation processes based on transition metal catalysts are well known, but due to the high costs of catalysts used in these reactions, this method is not economical. Other routes of siloxane synthesis have many disadvantages that reduce the attractiveness of these methods. Currently, due to green and sustainable chemistry, catalytic processes are based on cheap, naturally abundant metal catalysts. They show high selectivity and very low toxicity, which means that they are used in homogeneous catalysis. Catalytic systems based on pincer ligands are very popular among researchers. Cobalt catalysts based on a triazine ring skeleton show high activity even under mild conditions and at low concentrations.^[1,2]

In this communication, we report new dehydrogenative coupling reactions between hydrosilanes and silanols using the PN5P cobalt pincer complex. It is a very efficient method because it does not require harsh conditions and the use of additional pre-catalyst activators, which makes it a sustainable alternative to traditional methods.^[3]

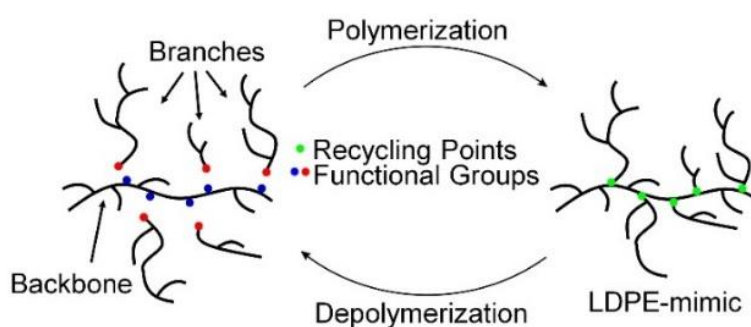
Funding acknowledgment: National Science Centre Grant: UMO-2018/30/E/ST5/00045.

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A recyclable low-density polyethylene material synthesized under mild conditions

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Low-density polyethylene is one of the most important plastics, which is produced unfortunately under extreme conditions.^[1] In addition, it consists of robust aliphatic C-C bonds which are challenging to cleave for plastic recycling. We report on a low-pressure and -temperature ($p_{\text{ethylene}} = 2 \text{ bara}$, $T = 70 \text{ }^\circ\text{C}$) macromonomer-based synthesis of long chain branched polyethylene. The introduction of recycle points permit the linking of the macromonomers and depolymerization of the long chain branched polyethylene. Coordinative chain transfer polymerization employing ethylene and co-monomers is used for the synthesis of the macromonomers, permitting a high flexibility of their precise structure and efficient synthesis.^[2,3] Our long chain branched polyethylene material matches key properties of low-density polyethylene.

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Earth Abundant Manganese Complex Catalyzed Sustainable Synthesis of α -Hydroxycarboxylic AcidsSatyadeep Waiba,^{a,b} Kakoli Maji,^a Mamata Maiti,^a and Biplab Maji^a^a Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohanpur, West Bengal – 741246, India^b Department of Chemistry, Jadavpur University, Kolkata, West Bengal – 700032, India

Conversion of readily available feedstocks to valuable platform chemicals *via* an eco-friendly catalytic pathway has always been one of the key focuses of synthetic chemists. In this context, herein, we report selective transformation of readily available feedstock, vicinal glycols, to value-added α -hydroxycarboxylic acid molecules that are prevalent in bioactive molecules and biodegradable polymers.^[1] A bench stable earth-abundant metal complex $\{[\text{HN}(\text{C}_2\text{H}_4\text{PPh}_2)_2]\text{Mn}(\text{CO})_2\text{Br}\}$, **Mn-I** catalyzed the reformation reaction at low temperature in high selectivity with a turnover number TON reaching 2400, surpassing previously used homogeneous catalysts for such a reaction. Hydrogen gas is evolved as a by-product without the need of any external acceptor. The developed protocol is applicable for both aromatic and aliphatic vicinal glycols, delivering the α -substituted hydroxycarboxylic acids in high yields and selectivities.^[2] Keeping in mind the additional functionalization required to obtain substituted vicinal glycols, further, we developed a more straight-forward approach for synthesizing α -hydroxycarboxylic acid *via* the acceptorless dehydrogenative coupling of more readily available ethylene glycol and primary alcohol. The ADC reaction was catalyzed by another manganese complex with a triazine backbone, **Mn-II**. The ADC protocol could also be applied to synthesize various α -hydroxycarboxylic acids in high yield, including a highly demanded platform chemical, lactic acid, which could be synthesized with a high turnover of $>10^4$.^[3] Both the reactions are highly sustainable and eco-friendly giving water and hydrogen as the sole by-product. The latter is liberated without the need for any acceptor and can be stored and utilized. Furthermore, the ADC protocol was also applied for synthesizing α -amino acid, α -thiocarboxylic acid, and several drugs and bioactive molecules, including endogenous metabolites, Danshensu, Enalapril, Lisinopril, and Rosmarinic acid. Further, various mechanistic studies, including kinetic experiments, NMR experiments were performed to delineate the mechanism involved in the reaction.

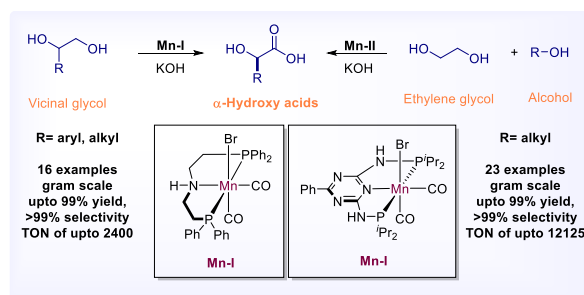


Figure 1. Earth abundant manganese complex catalyzed synthesis of α -hydroxycarboxylic acids.

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