Catalysis LIKAT
Leibniz-Institut für Katalyse

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Reaction mechanisms in homogeneous catalysis

Open Online Workshop *via Zoom*

https://uni-rostock-de.zoom.us/j/65813611180?pwd=T2NHNXVQN3c0Wit4Mmxtd05iTEdVZz09
Meeting-ID: 658 1361 1180
Kenncode: 697134

2:00 pm – 5:00 pm
21st of April 2021

Katalysis LIKAT
Leibniz-Institut für Katalyse

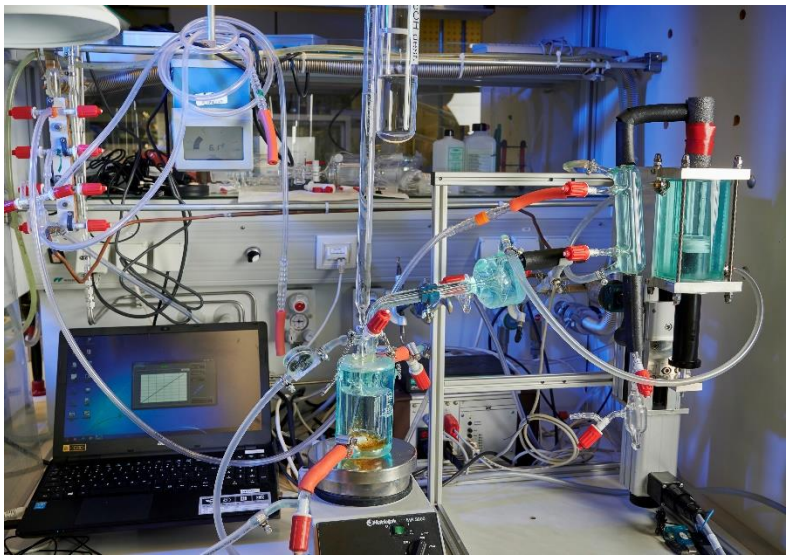

photo: laboratory department Beweries

Reaction mechanisms in homogeneous catalysis

The reaction mechanism of homogeneously catalysed reactions provides a detailed description of all partial reactions of the catalytic cycle, including catalyst activation and deactivation, formation of intermediates, desired and side products. For an understanding of catalytic processes, coordination and organometallic chemistry are indispensable foundations and only through knowledge of the fundamental steps, we can deduce relations between the structure of the catalyst and intermediates and their catalytic performance, i.e. their activity and selectivity. Based on this, further targeted development and optimisation of catalytic processes is possible. This workshop will highlight recent studies from different areas of homogeneous catalysis, ranging from fundamental mechanistic studies to application-oriented questions.

We are excited to host Prof. Dominik Munz (Saarland University) and Prof. Ian A. Tonks (University of Minnesota) as guest speakers. Their presentations will be complemented by three oral presentations from LIKAT researchers.

You are welcome to join on Zoom

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Scientific Program

2:00 pm		Dr. habil. Torsten Beweries Welcome and introduction Leibniz Institute of Catalysis, Rostock
2:05 pm	**L1**	Prof. Dominik Munz Oxidative Addition of Strong Bonds and Palladium Nitrenes: New Mechanisms for Palladium Catalysis Saarland University, Germany
2:50 pm		Discussion
3:00 pm	**L2**	Dr. Xinxin Tian Mechanism of Iridium-Catalyzed Hydroformylation and Hydrogenation Estimating and Activity from DFT computation Leibniz Institute of Catalysis (Jiao group), Rostock
3:20 pm	**L3**	Dr. Yuya Hu Mechanistic insights into the organocatalytic synthesis of cyclic carbonates Leibniz Institute of Catalysis (Werner group), Rostock
3:40 pm	**L4**	Nora Jannsen Catalyst deactivation during rhodium complex catalyzed propargylic C-H activation Leibniz Institute of Catalysis (Beweries group), Rostock
4:00 pm	**L5**	Prof. Ian A. Tonks Ti-Catalyzed Nitrene Transfer Reactions: Harnessing the Ti(II)/Ti(IV) Redox Couple for New Transformations University of Minnesota, USA
4:45 pm		Discussion

Oxidative Addition of Strong Bonds and Palladium Nitrenes: New Mechanisms for Palladium Catalysis

L1

Dominik Munz

Saarland University, Inorganic Chemistry: Coordination Chemistry, Campus C4.1,

66123 Saarbrücken, Germany

Bond activation in palladium catalysis is believed to proceed either via oxidative addition- or deprotonation-type pathways. Typically, the oxidative addition is invoked for bonds with weak to moderate bond strength such as chloroalkanes, whereas assistance of a base is required for the activation of O–H, N–H, and C–H bonds. Contrarily, I will present in this contribution (I.)[1] on the oxidative addition of O–H, N–H and C–H bonds by a palladium(0) complex and (II.) the reactivity of palladium nitrene and imido complexes,[2] hitherto thought to be unstable due to the population of anti-bonding molecular orbitals.[3]

In case of (I.), the oxidative addition of these "strong" bonds is found to be kinetically competitive with the common oxidative addition of, for instance, chlorobenzene, for a palladium complex with an ancillary cyclic (alkyl)(amino)carbene ligand. It proceeds swiftly even at room temperature. However, the resulting hydrido complexes are not compatible with common N-heterocyclic carbene ligands, which in-stead either decompose to palladium nanoparticles and/or require the addition of a base. Based on detailed mechanistic investigations (reaction kinetics, isotope effect, DFT, isolated intermediates, solvent effects, reactivity studies) we present the additive-free cross-coupling of an ester with aniline under unrivaled mild conditions and the unprecedented coupling of an alcohol with bis(pinacolato)diboron under the release of dihydrogen.

Further, I will discuss the reactivity of palladium terminal imido complexes. Their electronic nature will be discussed in detail and put in the context of closed-shell and open-shell (nitrene-type) reactivity. These complexes feature populated anti-bonding molecular orbitals and thus swiftly activate C–H, H–H and C–F bonds as demonstrated in preliminary catalytic applications.

Selected references:

[1] A. Grünwald, F. W. Heinemann, D. Munz, *Angew. Chem. Int. Ed.* 2020, *59*, 21088.

[2] a) A. Grünwald, N. Orth, A. Scheurer, F. W. Heinemann, A. Pöthig, D. Munz, *Angew. Chem. Int. Ed.* 2018, *57*, 16228; b) S. J. Goodner, A. Grünwald, F. W. Heinemann, D. Munz, *Austr. J. Chem.* 2019, *72*, 900.

[3] a) D. Munz, Chem. Sci. 2018, 9, 1155; b) A. Grünwald, D. Munz, *J. Organomet. Chem.* 2018, *864*, 26.

Mechanism of Iridium-Catalyzed Hydroformylation and Hydrogenation — Exploring Selectivity and Activity from DFT computation

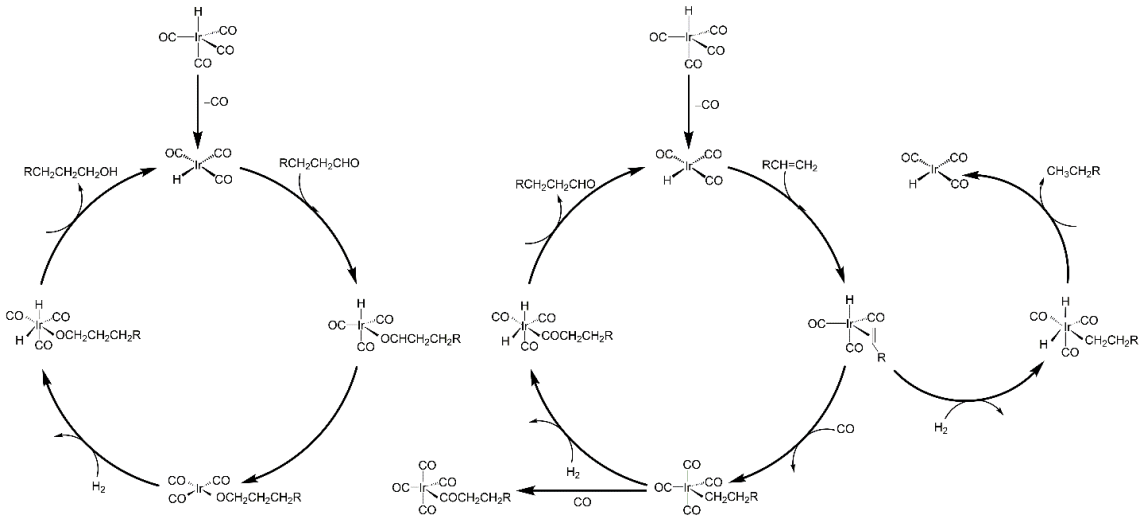
L2

Xinxin Tian, *Weiheng Huang*, *Haijun Jiao**, *Ralf Jackstell**, *Matthias Beller**

Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Str. 29a,

18059 Rostock, Germany, matthias.beller@catalysis.de

Aliphatic alcohols are important bulk chemicals and feedstock in research and industry. Catalytic reactions from olefins to alcohols follow basically two steps, hydroformylation of olefins to aldehydes and then hydrogenation of aldehydes to alcohols. One-pot reaction from alkenes to alcohols via successive hydroformylation and reduction has been reported. Herein, we report an Ir-catalyzed one-pot reaction of hydroxymethylation from alkene to alcohol using WGSR as H_2 source under acidic condition. To understand the whole reaction mechanism, we systematically calculated the reaction pathways for the formation of alkane, linear aldehyde and alcohol in the hydroformylation with 1-butene as substrate catalyzed by the $HIr(CO)_4$ (Scheme 1), $HIr(CO)_3(L1)$, $HIr(CO)_2(L1)_2$ (L1 = PPh_3, $PPh(p\text{-}CH_3OPh)_2$) and $HIr(CO)_2(L2)$ (L2= DPPE, p-CF_3 modified DPPE). For $HIr(CO)_4$, it is found that the selectivity of aldehyde vs. alkane is controlled kinetically at low temperature and thermodynamically at high temperature, while aldehyde hydrogenation to alcohol with high barrier is not favored. For other catalyst modified with different type of phosphine ligands, aldehyde normally has higher selectivity than alkane while alcohol selectivity varies which controlled by kinetics. Comparison between experiment and DFT has been made and discussed.



Scheme 1. Initiation mechanism catalytic cycle for the hydroformylation (middle part)/hydrogenation (right part)/further reduction (left part) of alkene catalyzed by $HIr(CO)_4$.

Insights into the bifunctional phosphonium salt catalyzed cycloaddition of CO_2 to epoxides

L3

Yuya Hu

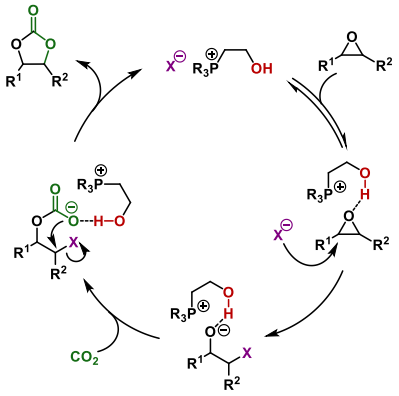
Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Str. 29a,

18059 Rostock, Germany, yuya.hu@catalysis.de

The valorization of CO_2 has attracted much attention in recent years. The chemical fixation of CO_2 remains challenging due to its thermodynamic stability and kinetic inertness. In this context the conversion of CO_2 with energy-rich epoxides is an extensively studied reaction.[1] The resulting cyclic carbonates find wide applications.[2] Recently, the organocatalysts gained more attention since they are cheap, non-toxic, readily available molecules with high potential of structural modification. Particularly, phosphorous-based organocatalysts showed superior activity.[3–4] Herein two generations of bifunctional phosphonium salt catalysts for the CO_2 valorization with epoxides will be discussed. Infrared spectroscopic studies, thorough kinetic investigations and DFT calculations were conducted to rationalize the superior performance and the reaction mechanism.[5–6]

Mechanistic studies:

- IR
- Kinetic investigations
- DFT calculations



Selected references:

[1] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.* **2017**, *375*, 50.

[2] B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4554.

[3] T. Werner, H. Büttner, *ChemSusChem* **2014**, *7*, 3268.

[4] H. Büttner, K. Lau, A. Spannenberg, T. Werner, *ChemCatChem* **2015**, *7*, 459.

[5] J. Steinbauer, C. Kubis, R. Ludwig, T. Werner, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10778.

[6] Y. Hu, Z. Wei, A. Frey, C. Kubis, C. Ren, A. Spannenberg, H. Jiao, T. Werner, *ChemSusChem* **2021**, *14*, 363.

Catalyst deactivation during Rh complex catalyzed propargylic C-H activation

Nora Jannsen, Saskia Moeller, Hans-Joachim Drexler, Moritz Horstmann and Detlef Heller.

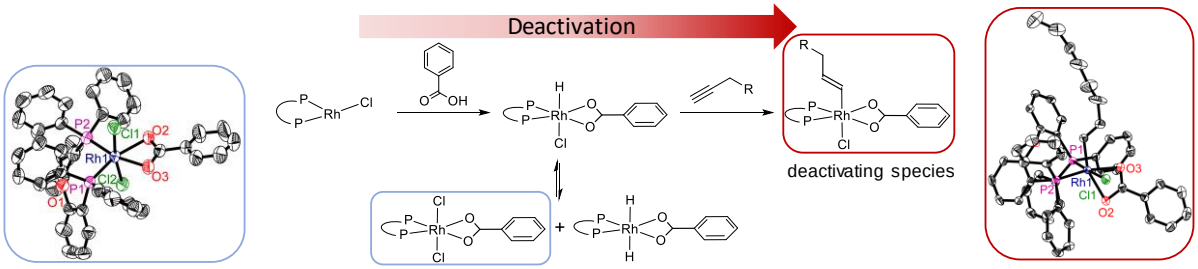
L4

Leibniz-Institut für Katalyse an der Universität Rostock,

Albert-Einstein-Str. 29a, 18059 Rostock, Germany, nora.jannsen@catalysis.de

The rhodium catalyzed propargylic C-H activation represents a redox-neutral and atom-economic synthesis of branched allylic esters.[1] This reaction mode offers great potential as a new and central reaction for the formation of C-C and C-heteroatom bonds.[2]

This study presents the complete mechanistic elucidation of the rhodium catalyzed propargylic C-H activation. Here, special attention is paid to the deactivating pathway of the catalytic reaction. Especially the product of oxidative addition of the carboxylic acid to the active catalyst became the focus of interest. The formation of this hydride species represents the central step of deactivation. By coordinating a terminal alkyne as a vinyl ligand to the hydrido benzoate complex, the catalytically inactive σ-vinyl complex is formed irreversibly. The deactivating species was investigated in detail, using NMR and Raman spectroscopy and X-ray crystallography. Moreover, a disproportionation of the hydrido benzoate complex could be identified, forming two more benzoate complexes.



Beside the deactivation, it was possible to prove various reaction steps of the catalytic cycle. For example, the composition of the alkyne complex was investigated more closely. NMR und UV-Vis spectroscopy revealed structural details. Likewise, various by-products could be identified.

In addition, it will be shown that the reaction can be transferred from carboxylic acids to other substrates, such as benzotriazoles. This creates a whole new range of products accessible through this atomic-economic route.

Selected references:

[1] a) A. Lumbroso, P. Koschker, N. R. Vautravers, B. Breit, *J. Am. Chem. Soc.* **2011**, *133*, 2386-2389. b) P. Koschker, A. Lumbroso, B. Breit, *J. Am. Chem. Soc.* **2011**, *133*, 20746-20749. c) U. Gellrich, A. Meissner, A. Steffani, M. Kahny, H. J. Drexler, D. Heller, D. A. Plattner, B. Breit, *J. Am. Chem. Soc.* **2014**, *136*, 1097- 1104.

[2] a) A. M. Haydl, K. Xu, B. Breit, *Angew. Chem. Int. Ed.* **2015**, *127*, 7255-7259. b) A. B. Pritzius, B. Breit, *Angew. Chem. Int. Ed.* **2015**, *54*, 15818–15822. c) C. Li, B. Breit, *J. Am. Chem. Soc.* **2014**, *136*, 862-865. d) M. L. Cooke, K. Xu, B. Breit, *Angew. Chem. Int. Ed.* **2012**, *51*, 10876-10879.

Ti-Catalyzed Nitrene Transfer Reactions: Harnessing the Ti^{II}/Ti^{IV} Redox Couple for New Transformations

L5

Ian A. Tonks

Department of Chemistry, University of Minnesota – Twin Cities

207 Pleasant St SE, Minneapolis MN 55455, Email: itonks@umn.edu, Twitter: @ianatonks

Titanium is an ideal metal for green and sustainable catalysis—it is the 2nd most earth-abundant transition metal, and the byproducts of Ti reactions (TiO_2) are nontoxic. However, a significant challenge of utilizing early transition metals for catalytic redox processes is that they typically do not undergo facile oxidation state changes because of the thermodynamic stability of their high oxidation states. We have recently discovered that Ti imidos ($L_nTi{=}NR$) can catalyze oxidative nitrene transfer reactions from diazenes via a Ti^{II}/Ti^{IV} redox couple, and are using this new mode of reactivity to develop a large suite of practical synthetic methods. In this talk, our latest synthetic and mechanistic discoveries related to Ti nitrene transfer catalysis will be discussed, including new synthetic methods for the modular, selective construction of pyrroles via [2+2+1] cycloaddition of alkynes with Ti nitrenes and alkynes, as well as new methods for catalytic oxidative amination, N-N oxidative coupling of pyrazoles, and more.