

Abstract:**Carbonylation and Carboxylation of Alkanes in Fluorinated Solvents or scCO₂****Co-supervisor 1: Thomas Braun, Humboldt-Universität Berlin****Co-supervisor 2: Martin Kaupp, Technische Universität Berlin**

The project involves the development of reaction routes for the photolytic carbonylation or carboxylation of alkanes at fluorinated heterobimetallic complexes with a special focus on the reactivity of methane. The metal centers will act in a concerted fashion to achieve the C-H activation and carbonylation/carboxylation steps. The reactivity of the compounds will highly depend on the distance between the metal centers as a crucial descriptor. The presence of fluorinated ligands will enable a solubility of the catalyst in fluorinated solvents as well as in supercritical CO₂. The character of the interaction of the fluorinated ligands with the solvents and their impact on reactivity will be investigated experimentally and by DFT studies. The computational studies will make use of advanced solvent models for fluorinated solvents (and possibly for scCO₂) such as 3D-RISM-SCF, developed by the Kaupp group within CRC1349.

Carbonylation and Carboxylation of Alkanes in Fluorinated Solvents or scCO₂

Co-supervisor 1: Thomas Braun, Humboldt-Universität Berlin

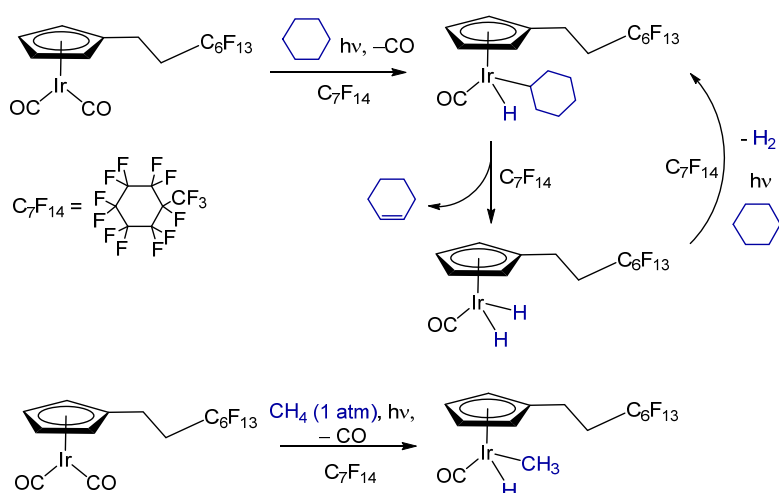
Co-supervisor 2: Martin Kaupp, Technische Universität Berlin

1. Overall goal of the project

Carbonylation and carboxylation reactions of alkanes will be developed by employing catalysts with fluorinated ligands. A special focus will be on methane. The reactions have to be performed in fluorinated solvents or supercritical CO₂. We aim at a thorough description of the fluororous interaction of the fluorinated catalysts with the fluorinated solvent or with scCO₂ by studying it experimentally and computationally.

2. State of the art

Carbonylation and carboxylation reactions are of enormous importance for the generation of fine chemicals as well as of bulk materials. However, there is very little known about how to generate aldehydes or carboxylic acid derivatives directly from alkanes.^{1,2,3,4} Some reactions involve a stepwise dehydrogenation of alkanes followed by a hydroformylation step which reuses the generated H₂. Yields are usually very low and the conversions are not selective. Often the dihydrogenation reactions are induced photochemically. Sakakura et al. reported on a photochemical carbonylation of CH₄ in supercritical CO₂, albeit the turn-over numbers were very low.³



The Braun group has considerable experience in the development of catalytic C-H activation reactions at metal compounds.⁵ This involves photocatalytic acceptorless dehydrogenation reactions at alkanes using iridium catalysts.⁶ Mechanistic investigations led to an isolation of oxidative addition products of alkanes that then react further by olefin formation. (Scheme 1). The reactions were performed in fluorinated solvents in order to achieve also methane activation reactions, which were indeed developed (Scheme 1).

3. Specific aims and how they may be reached:

Objectives: Binuclear complexes bearing fluorinated phosphines will be synthesized to achieve a carbonylation and carboxylation of alkanes. The fluorinated alkyl groups will allow an adjustment of the metal-metal distances and make the catalysts soluble in fluorinated solvents or supercritical

¹ X. Tang, X. Jia, Z. Huang, *Chem. Sci.* **2018**, *9*, 288.

² T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, M. Tanaka, *J. Am. Chem. Soc.* **1990**, *112*, 1221.

³ J.-C. Choi, Y. Kobayashi, T. Sakakura, *J. Org. Chem.* **2001**, *66*, 5262.

⁴ N. J. Gunsalus, A. Koppaka, S. H. Park, S. M. Bischof, B. G. Hashiguchi, R. A. Periana, *Chem. Rev.* **2017**, *117*, 8521-8573; J. He, M. Wasa, K. S. L. Chan, Q. Shao, J.-Q. Yu, *Chem. Rev.* **2017**, *117*, 8754-8786.

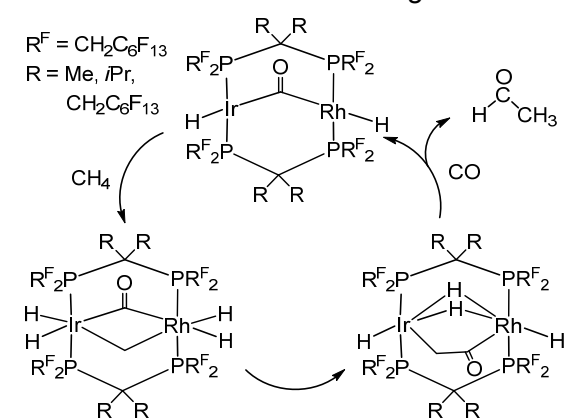
⁵ T. Ahrens, T. Braun, B. Braun, R. Herrmann, *Dalton Trans.* **2016**, *45*, 4716; L. Zámotná, S. Sander, T. Braun, R. Laubenstein, B. Braun, R. Herrmann, P. Kläring, *Dalton Trans.* **2015**, *44*, 9450; S. I. Kalläne, M. Teltewskoi, T. Braun, B. Braun, *Organometallics* **2015**, *34*, 1156; S. I. Kalläne, T. Braun, *Angew. Chem.* **2014**, *126*, 9465-9469; *Angew. Chem. Int. Ed.* **2014**, *53*, 9311-9315; M. Prechtl, M. Teltewskoi, A. Dimitrov, E. Kemnitz, T. Braun, *Chem. Eur. J.* **2011**, *17*, 14385; M. Ahijado-Salomon, Ann-Katrin Jungton, T. Braun, *Dalton Trans.* **2009**, 7669-7677; B. Calvo, T. Braun, E. Kemnitz, *ChemCatChem* **2018**, *10*, 403.

⁶ B. Rabay, T. Braun, J. P. Falkenhagen, *Dalton Trans.* **2013**, *42*, 8058-8065; F. Liebau, T. Braun, B. Braun, *J. Fluorine Chem.* **2015**, *180*, 192.

CO₂ to enable also reactions with methane. One other major goal involves studies for the understanding of fluorine interactions and their impact on the reactivity of the metal complexes.

Experimental strategies: The project involves the development of catalytic routes for the photolytic carbonylation or carboxylation of alkanes heterobimetallic complexes. The synthesis of fluorinated catalysts will allow for conversions either in fluorinated solvents or in supercritical CO₂. In a combined computational and experimental approach we will be able to design a suitable catalytic system by mechanistic studies. This includes stoichiometric model reactions and the isolation of intermediates of a putative catalytic cycle as well as the monitoring catalytic conversions by NMR, Raman and IR spectroscopy as well as mass spectrometry.

Work program: The envisaged reactivity will be achieved by a C-H activation and a subsequent insertion reaction of the building blocks CO or CO₂ (Scheme 2). Binuclear compounds bearing a



Scheme 2. A catalytic pathway for CH₄ carbonylation

Rh and an Ir center are suitable catalyst precursors.

The metal centers will be separated by bidentate fluoroalkylphosphine ligands. The Ir centers can initiate C-H activation reactions, which might have to be triggered photolytically. Carbonylation should preferentially occur at the Rh centers.

The development of ligands bearing a fluorinated chain at the phosphine group will be crucial. These ligands will play a multiple role. Metal-metal distances can depend on the solvent that will be used, and especially the fluorinated solvents are very interesting, because they separate from alkyl chains. Therefore, they can impose an additional strain on the complex, and the metal-metal separation can be altered by a variation of the

fluorinated or non-fluorinated solvent.⁶ In addition, the distance between the metal centers can be altered by implementation of various spacers between the donor atoms of the bridging ligands. Increasing the steric demand of the CH₂ groups by replacement with CR₂ (R = Me, *i*Pr) moieties leads certainly to a strain which will force the metals to be closer to each other. These groups might also be fluorinated, and the CH₂ group might be replaced by a NR group. Even more importantly, it has been shown that catalysts bearing fluorinated ligands are soluble in supercritical CO₂, whereas non-fluorinated counterparts are usually not.³ Reactions in scCO₂ might then allow a carboxylation or carbonylation of methane, because potential reactions with any other solvent are impeded. The character of an interaction between fluorinated alkyl moieties and solvents is virtually unknown, although it will be important for the envisaged studies. Experimentally, such interactions might be unraveled by ¹⁹F NMR spectra of mixtures of the fluorinated molecules and solvents. In addition, the character of the interaction of the fluorinated chains, i.e. between the catalyst and the fluorinated solvent or the scCO₂ will be studied by DFT methods. This requires advanced solvent models for fluorinated and non-fluorinated solvents, which are developed and applied by the Kaupp group within CRC1349. In particular, the 3D-RISM-SCF approach promises to provide unprecedented insights into the effects of average solvent structure on the interactions.

Short statement on facilities: The Braun group has already a set-up for conversions in scCO₂ which allows simultaneously photolysis of the reaction mixture. NMR and IR/Raman spectrometer will be available for mechanistic studies. The Kaupp group provides state-of-the-art computational methodology, including experience with DFT methods and advanced solvent models. Further collaborations involve the Netz and Keller groups who provide specific force-field parameters for fluorinated species and solvents within CRC1349, which are used to parameterize the RISM model.