

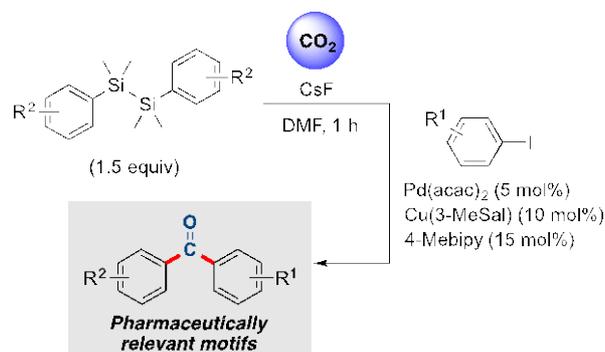
# Carbon Dioxide Activation Center 2016 - HIGHLIGHTS

## About the center

The Carbon Dioxide Activation Center (CADIAC) was established in 2015 by Prof. Troels Skrydstrup and Prof. Kim Daasbjerg at Aarhus University in collaboration with two outstanding international groups headed by Prof. Melanie Sanford at the University of Michigan, USA, and Prof. Matthias Beller at the Leibniz Institute for Catalysis, Germany. Three assistant professors, Dr. Nina Lock, Dr. Anders T. Lindhardt and Dr. Joseph Iruthayaraj are also part of the research activities. The goal of the research center is to explore new methods for the activation of carbon dioxide eventually providing sustainable solutions for the exploitation of this molecule as a valuable reagent to high-value chemicals of industrial importance. The highlights of the published work from CADIAC for the year 2016 and start of 2017 are described below.

## Cooperative redox activation for carbon dioxide conversion

In a recent study reported in *Nature Communications*, CADIAC scientists demonstrated a novel approach for activating CO<sub>2</sub>.<sup>[1]</sup> A longstanding challenge in production chemistry is the development of catalytic methods for the transformation of CO<sub>2</sub> into useful chemicals and to reduce the waste byproducts that are formed. Alternatively, the waste product can be used in follow-up reactions. This is exactly the approach followed by CADIAC, whereby the reduction of carbon dioxide with diaryldisilanes generates carbon monoxide and a diaryldisiloxane (Figure 1). These two compounds then actively participate in a palladium-catalyzed carbonylative Hiyama-Denmark coupling for the synthesis of an array of pharmaceutically relevant diarylketones. Thus, the disilane reagent not only serves as the oxygen abstracting agent from CO<sub>2</sub>, but the silicon-containing "waste", produced through oxygen insertion into the Si-Si bond, participates as a reagent for the transmetalation step in the carbonylative coupling. Hence, this concept of cooperative redox activation opens up for new avenues in the conversion of CO<sub>2</sub>. A number of pharmaceutically relevant molecules were prepared.

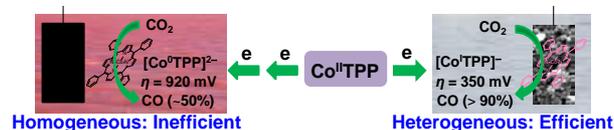


**Figure 1:** Demonstration of a cooperative redox activation reaction between CO<sub>2</sub> and a disilane for the synthesis of diarylketones.

## Homogenous vs Heterogeneous CO<sub>2</sub>-Reducing Catalysts

CADIAC members were able to demonstrate a remarkable enhanced catalytic activity for the conversion of carbon dioxide to carbon monoxide when a homogeneous cobalt electrocatalyst was immobilized onto carbon nanotubes or similar carbon-based materials (Figure 2).<sup>[2]</sup> The work, which has recently been accepted in *Angewandte Chemie International Edition*, demonstrates the importance that analysis of a homogeneous catalyst alone is not sufficient to evaluate the potential of such metal complexes as efficient catalysts for the reduction of CO<sub>2</sub>. With this readily available approach for heterogenization of molecular catalysts presented in this work, it is now facile to screen, evaluate, and compare molecular catalysts under heterogeneous conditions.

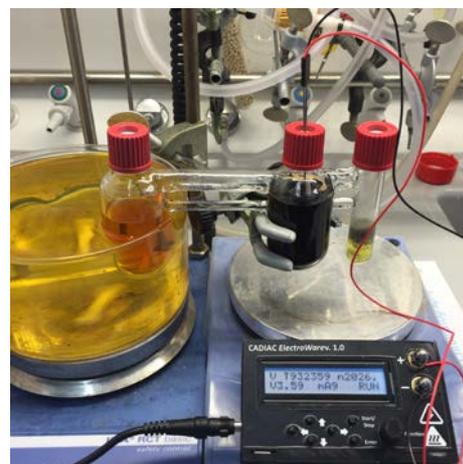
Recognition of the distinct performance differences of a homogeneously and heterogeneously based CO<sub>2</sub> reduction catalysts could lead to a comprehensive reassessment of molecular catalysts evaluated hitherto only under homogeneous conditions.



**Figure 2:** Illustration of the increased catalytic activity of a cobalt porphyrin catalyst, Co<sup>II</sup>TPP, upon immobilization to a carbon material.

## Electrochemical Conversion of CO<sub>2</sub> to CO

One of the most significant contributions from CADIAC was the recent submission of a manuscript reporting on an operationally simple and low-cost electrochemical set-up for the production of CO from CO<sub>2</sub> with a commercially available molecular catalyst, iron tetraphenylporphyrin. Particularly valuable is its adaptation to palladium-catalyzed carbonylation reactions for carbon-carbon and carbon-heteroatom bond formation in the synthesis of pharmaceutically related molecules. Furthermore, the reusability of the electrochemical system was demonstrated and the possibility of exploiting atmospheric CO<sub>2</sub> in synthesis. This work nicely contributes to an overall goal of CADIAC to provide viable and efficient equipment for CO<sub>2</sub> conversion to valuable compounds, which may be useful in future planetary missions.



**Figure 3:** Equipment designed for the electrochemical conversion of atmospheric CO<sub>2</sub> to the antidepressant, moclobemide.

## References

- [1] Z. Lian, D. U. Nielsen, A. T. Lindhardt, K. Daasbjerg and T. Skrydstrup, "Cooperative redox activation for carbon dioxide conversion" *Nat. Commun.* **2016**, 7, Article number 13782.
- [2] X.-M. Hu, M. H. Rønne, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, "Enhanced Catalytic Activity of Immobilized Cobalt Porphyrin versus Homogeneous System for CO<sub>2</sub> Electroreduction" *Angew. Chem. Int. Ed.* **2017**, manuscript provisionally accepted. Manuscript accepted for publication.
- [3] M. T. Jensen, M. H. Rønne, A. K. Ravn, R. W. Juhl, D. U. Nielsen, X.-M. Hu, K. Daasbjerg and T. Skrydstrup, "Scalable carbon dioxide electroreduction coupled to carbonylation chemistry", Submitted for publication.