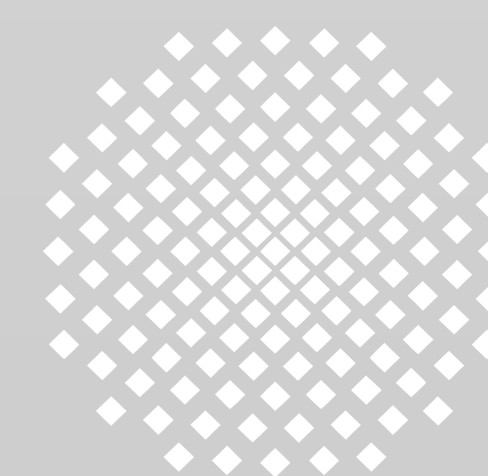


Hydrogen Storage Systems based on Fe-H- and Ru-Catalysis



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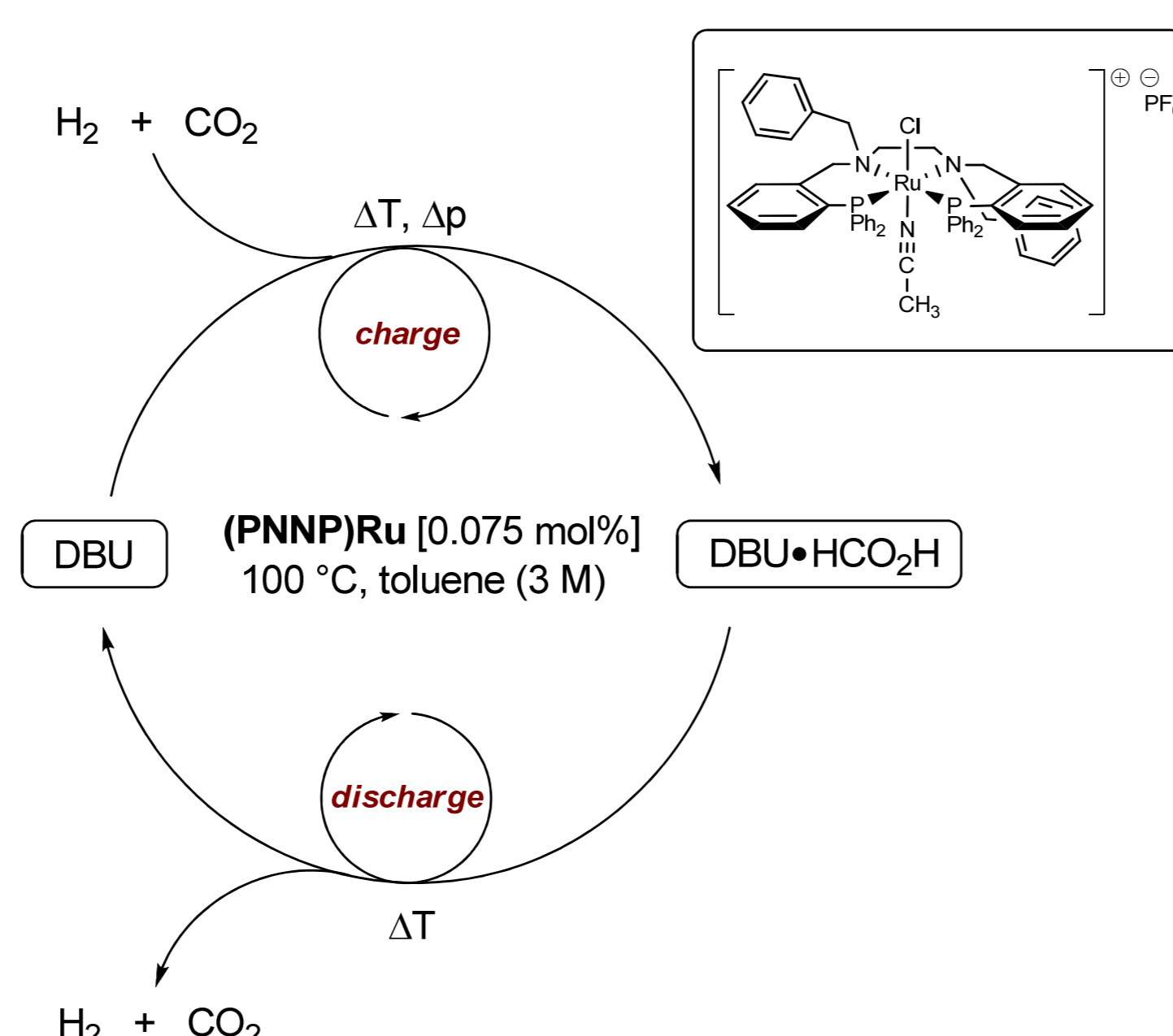
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The focus of discussions in energy issues has shifted within the past years from the generation of energy from regenerative sources toward energy storage and liberation. Within this field, the storage and liberation of hydrogen gas has attracted considerable interest. Particularly the development of new technologies for hydrogen storage media that allow for an efficient hydrogen regeneration, as well as systems that allow for a fast and controlled release of hydrogen gas are relevant. Apart from the field of absorptive hydrogen storage, the storage of hydrogen in chemical bonds is considered as a complementary approach.

Closing the Cycle – Development of a Ru-catalyzed Hydrogen Battery:

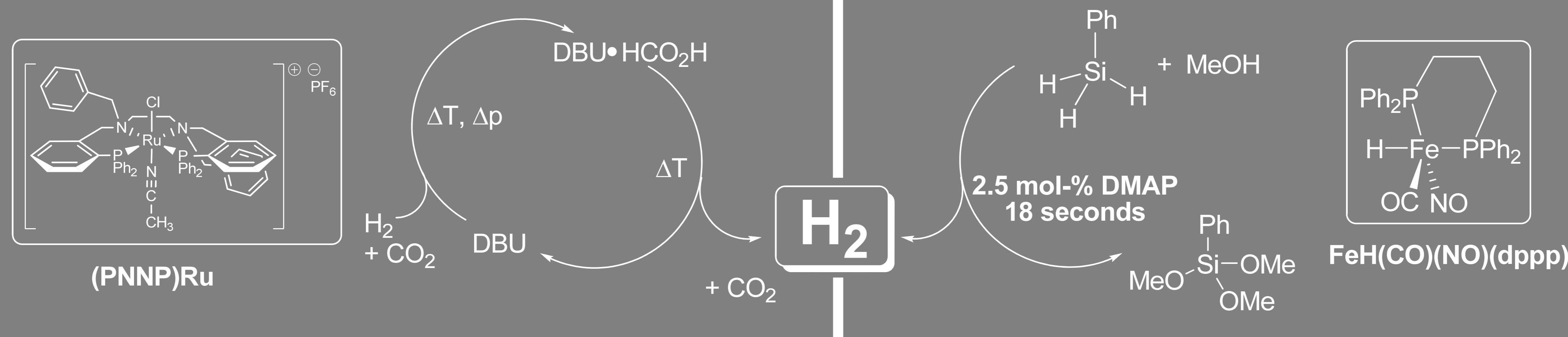
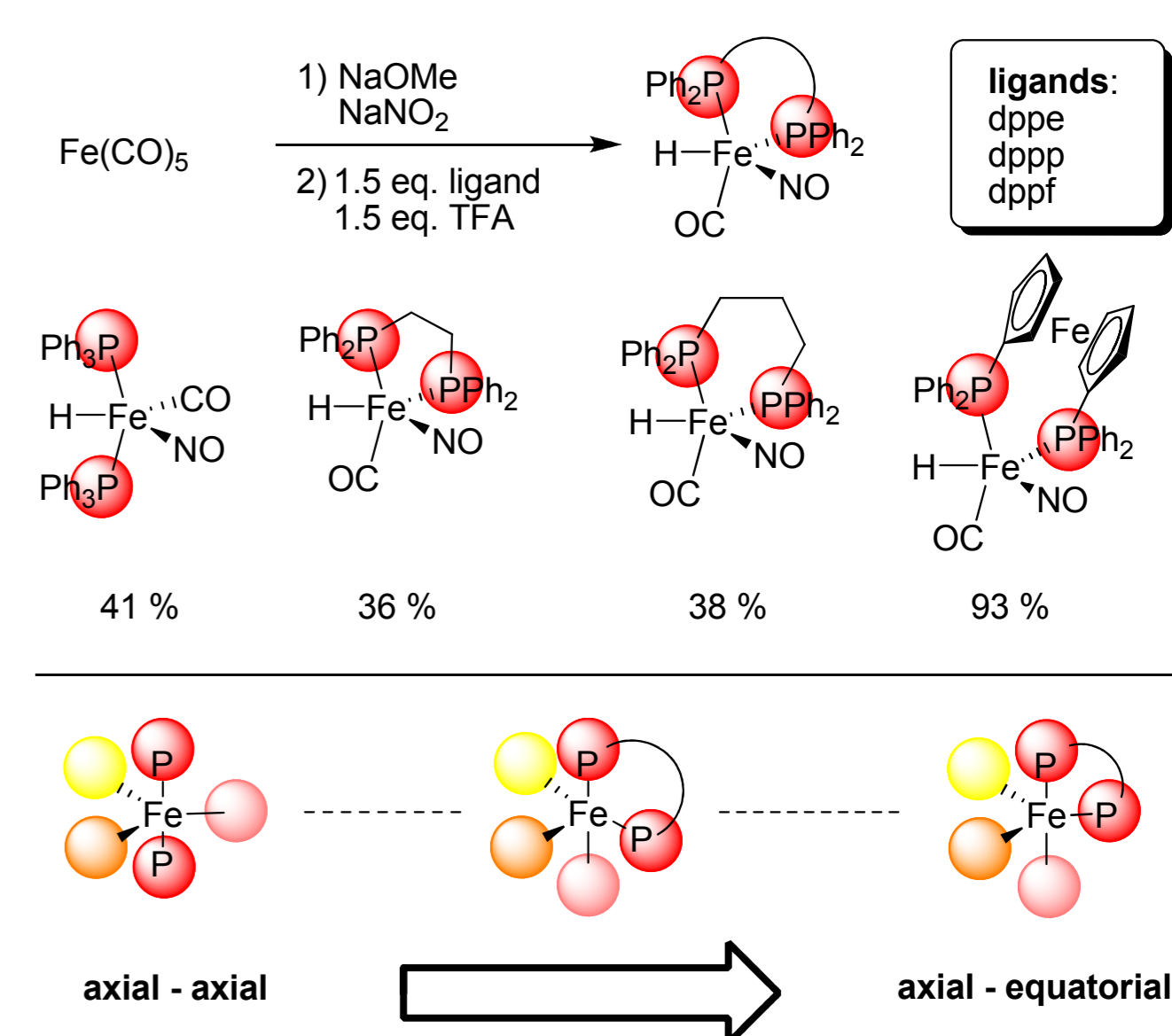
Herein we show a prototype system for the reversible storage and liberation of hydrogen. Key elements are the highly active (PNNP)(acetonitrile)Ru(+II)-complex, as well as the employment of CO₂/amine as storage media.

The resulting CO₂/H₂-mixture could be directly employed in fuel cell technology as it is free of CO-gas.



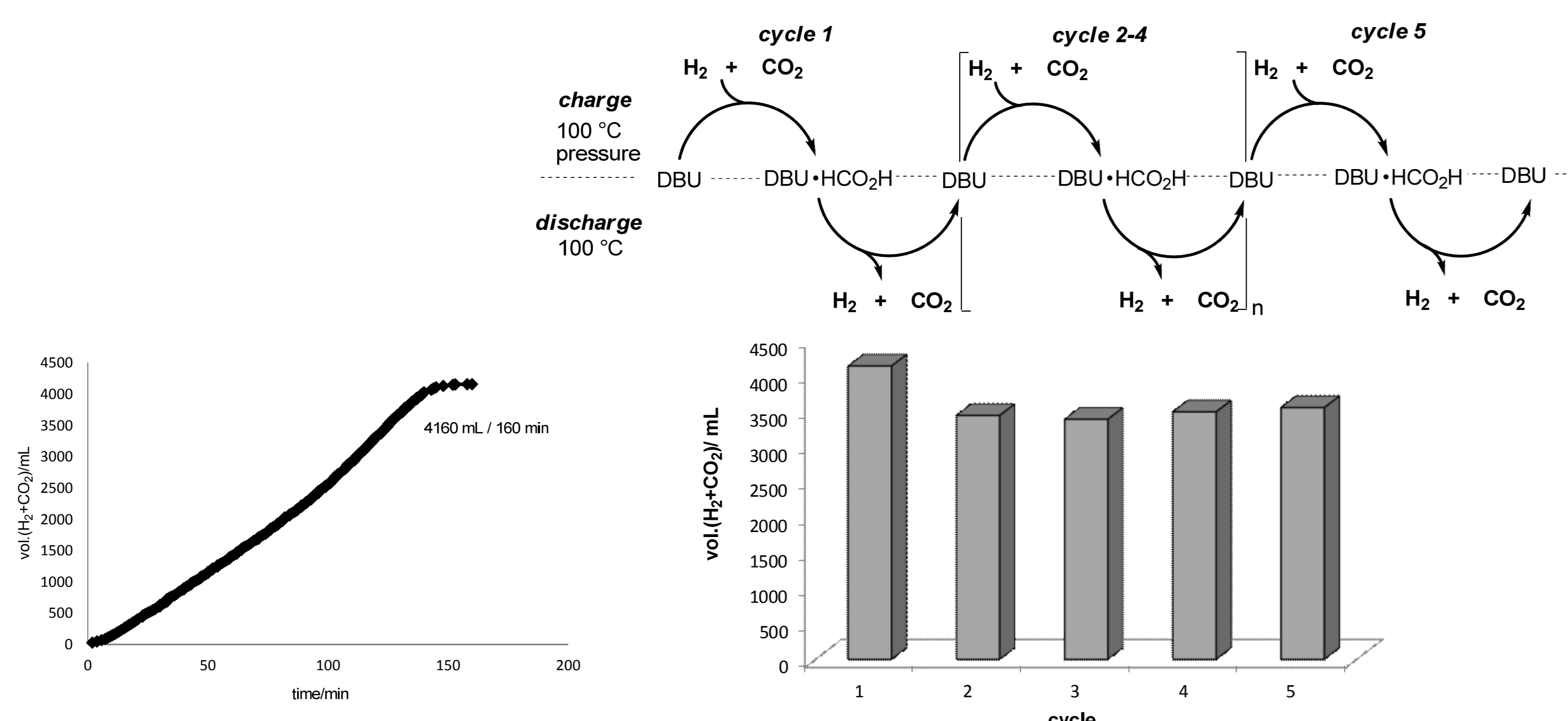
Synthesis and Characterization of new electron-rich Fe-H-complexes:

We present a method for the synthesis of a series of bisphosphane-bridged-Fe-H complexes. All complexes can be prepared by a straightforward one-pot synthesis starting from commercially available iron pentacarbonyl. Depending on the angle between both ligating phosphane atoms the geometry of the complex changes from *axial/axial* to *axial/equatorial*.



Charging and Discharging of the Hydrogen-Battery:

We were able to show that at elevated temperature both – storage and liberation of hydrogen gas – is possible. Several charging-discharging-cycles can be performed without decrease of catalyst activity. During the charging-discharging-cycles there is no need to change the catalyst or the storage container. Furthermore the charged system can be stored for days without loss of efficiency.

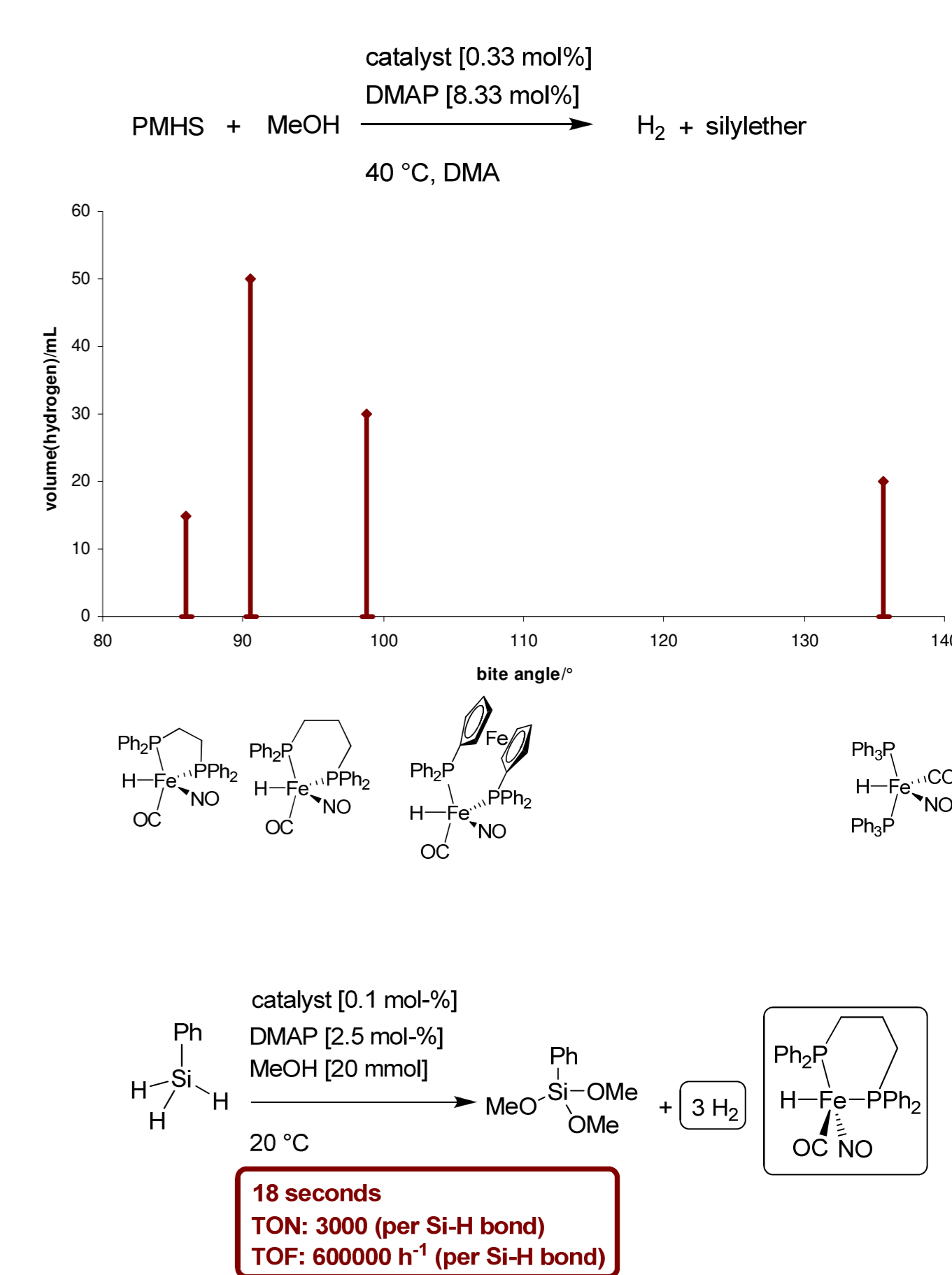


Employment of the new Fe-H-complexes in „Hydrogen on Demand“:

The different complexes were tested for their catalytic potential in the “Hydrogen on Demand”-technology.

Polymethylhydroxysilane (PMHS) was used as a silane source of mediocre reactivity in order to get a better picture on the relative reactivity differences within this class of complexes.

FeH(CO)(NO)(dppp) was found to be the most active Fe-H-complex and was subsequently implemented in the ultrafast dehydrogenative silylation of methanol. Even at catalyst loadings as low as 0.1 mol% full conversion could be observed in only 18 second. This corresponds to a turn-over number of 3000 and a turn-over frequency of 600000 turn-over per hour.



References:

- [a] S. Rommel, L. Hettmanczyk, J. E. M. N. Klein, B. Plietker, *Chem. Asian J.* **2014**, DOI: 10.1002/asia.201402142; [b] W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2012**, *134*, 17462-17465; [c] U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* **2009**, *48*, 6608-6630; [d] S.-F. Hsu, S. Rommel, P. Eversfield, K. Müller, E. Klemm, W. Thiel, B. Plietker, *Angew. Chem.* **2014**, *53*, 7074-7078; [e] C. Federsel, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2010**, *122*, 6392-6395; *Angew. Chem. Int. Ed.* **2010**, *49*, 6254-6257.

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