

Venerdì 20 Maggio 2016 Alle ore 11:00

presso l'aula 1 dell'Edificio F, Area della Ricerca CNR, Via Madonna del Piano,10 Sesto F.no

Prof. Hansjörg Grützmacher - ETH-Zurich (CH) e Prof. Matthias Driess - TU Berlin (D)



terranno i seguenti seminari:

" Sodium phosphaethynolate, Na(OCP): A building block in organophosphorus chemistry" (H. Grützmacher, left)

"With N-Heterocyclic Silylenes to New Directions in Homogeneous Catalysis" (M. Driess, right)

> Il Presidente Dr.Maurizio Peruzzini

Abstract H. GRÜTZMACHER:

Sodium phosphaethynolate is easily prepared from sodium, phosphorus, a tertiary alcohol and a carbonate in a one-pot reaction.[1] It is best described by the resonance structures $-O-C \equiv P$ and O=C=P- and serves as building block for a variety of organo phosphorus compounds. Specifically phosphaketenes and phosphorus heterocycles with one, two, or three phosphorus centers can be easily prepared (Figure 1).[2] Apart from classical cycloadditions involving the C \equiv P triple bond, "P–" transfer reactions will be presented which often proceed under the loss of CO and indicate that the OCP anion can also be viewed as a complex of CO to a "P" anion. Some of the newly prepared heterocycles show remarkable properties such as strong absorptions in the visible range of light. Because all heterocycles obtained from OCP– are anionic, they serve themselves

as valuable building blocks for organophosphorus compounds and transition metal complexes.[3] The syntheses of these species and latest results will be discussed and some insight into the reaction mechanisms obtained from NMR spectroscopy on intermediates combined DFT computations with will be given.

Biographic sketch:



photoinitiators.



Prof. Grützmacher was born on March 24, 1959 in Hamburg, Germany. He studied chemistry at the University of Göttingen, (PhD in 1986 with Professor Dr. H.W. Roesky). Subsequently, he spent one post-doc year with Dr. G. Bertrand at the C.N.R.S. in Toulouse. After his habilitation in 1992 at the University of Heidelberg he joined the University of Freiburg as Professor for inorganic chemistry. In 1995 he was appointed as Associate Professor of inorganic chemistry at the ETH where he was promoted to a full professor since 2001. Since 1995, Hansjörg Grützmacher has been Associate Professor and since 2001 full Professor at the Laboratory of Inorganic Chemistry at ETH Zurich. The

research of Hansjörg Grützmacher and his group focuses on the synthesis of molecules, which have exceptional functionalities. Currently the Grützmacher group explores: (i) The synthesis and application of low valent transition metal complexes and coordinated radicals for dehydrogenation reactions; (ii) the synthesis and implementation in composite electrode materials of molecular compounds for Organometallic Fuel Cells; (iii) The synthesis and application of building blocks for organophosphorus compounds, and (iv) The synthesis and application of new highly efficient

References: [1] Dominikus Heift, Zoltàn Benkö, Hansjörg Grützmacher, *Dalton Trans.* **2014**, *43*, 59205928. [2] D. Heift, Z. Benkö, H. Grützmacher, *Chem. Eur. J.* **2014**, *20*, 11326-11330. [2] L. Liu, D. Buiz, E. Dahcheb, G. Bertrand, P. Suter, A. M. Tendreau, H. Grützmacher, *Chem. Sci.* **2016**.

[3] L. Liu, D. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau, H. Grützmacher, Chem. Sci., 2016, 7, 2335-2341.

Abstract M. DRIESS:

Activation of small molecules by using non- and semi-metals instead of precious metals is a contemporary challenge in molecular science. Recently, we developed two new types of zwitterionic silylenes 1 and 2 which show an unprecedented reactivity pattern with respect to small molecule activation based on silicon. [1,2] The facile oxygenation of 1 with N₂O or CO₂ in the presence of donor ligands coordinated to the divalent silicon led to isolable silanone complexes 3 which are also capable for facile activation of small molecules including ammonia, water, and hydrogen sulfide. Furthermore, the remarkable rich reactivity pattern of 1 and the first silicon(II)-based pincer arene ligands 4, 5 and 6 can be used as a new generation of steering ligands in homogeneous catalysis. [3-6]. I wish to discuss selected features on the reactivity of 1-6 and in particular their advantageous use in catalytic transformations.



References

- Reviews: M. Assay, M. Driess, C. Jones Chem. Rev. 2011, 111, 354; S. Yao, Y. Xiong, M. Driess Organometallics 2011, 30, 1748.
- M. Assay, S. Inoue, M. Driess Angew. Chem. Int. Ed. 2011, 50, 9589.
- 3. W. Wang, S. Inoue, E. Irran, M. Driess Angew. Chem. Int. Ed. 2012, 51, 3691.
- 4. W. Wang, S. Inoue, S. Enthaler, M. Driess Angew. Chem. Int. Ed. 2012, 51, 6167.
- 5. D. Gallego, A. Brück, E. Irran, F. Meier, M. Kaupp, M. Driess, J. F. Hartwig J. Am. Chem. Soc., 2013, 135,15617
- 6. Rev: NHSi complexes in catalysis: B. Blom, D. Gallego, M. Driess Inorg. Chem. Front., 2014,1, 134.

Biographic sketch:

Matthias Driess was born 1961 in Eisenach, Thuringia. He received his diploma in chemistry in 1985 and received his PhD 1988 at the Ruprecht-Karls Universität

Heidelberg. In addition he studied philosophy in Heidelberg and graduated with the thesis "Über den logischen Empirismus von Rudolf Carnap und die Einheit der Wissenschaften" (transl: About the logical empirism of Rudolf Carnap and the unity of the sciences). After working as a postdoctoral fellow with Professor Robert West in Madison, Wisconsin, U.S.A., for a year, he returned to Heidelberg in 1989 and finished his habilitation in inorganic chemistry in 1993 with a thesis about silicon and phosphorus in unusual coordination. After



three more intellectually stimulating years in Heidelberg he was appointed professor for inorganic chemistry at the Ruhr universität Bochum in 1996. In 2004 he moved to Technische Universität Berlin, where he holds a chair in organometallic chemistry and inorganic materials at the department of chemistry. Since 2007 Matthias Driess ist speaker of the Cluster of excellence Unicat. Since 2012 he is a member of the German National Academy of Sciences Leopoldina. Since 2014 he is an Ordinary Member of the Berlin-Brandenburg Academy of Sciences and Humanities.