

Organic Chemistry *Hirschmann Lecture Series*

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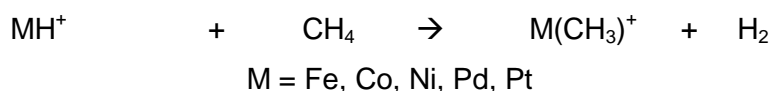
Wednesday, April 15, 2009, 1:30 p.m.
Room 1315 Chemistry



Ligand and Cluster-size Effects in Metal-mediated Activation of Methane: A Cold Approach to a Hot Problem

State-of-the-art gas-phase experiments – complemented by DFT and electronic structure calculations – of mass-selected, electronic ground-state transition-metal complexes provide insight into fundamental aspects of elementary steps involved in the activation and functionalization of methane at ambient temperature. Systems and challenging problems, that will be discussed in detail, include:

- (i) The role of relativistic effects in the reactions of 5d elements.
- (ii) The Shilov system: Do the oxidation state of platinum and the nature of the ligands X matter in the reactions of PtX_n^+ ($n = 0 - 3$; X = H, Cl, Br) with CH_4 ?
- (iii) "The Same and Not the Same", or on mechanistic variants and single *versus* two-state reactivity scenarios in thermal ligand exchange processes, e.g.



- (iv) The extraordinary, entirely atypical chemistry of naked $\text{Ni}(\text{H})(\text{OH})^+$ with CH_4 and O_2 , with more surprises and question marks rather than providing consoling confirmation according to established textbook knowledge.
- (v) On the metal-mediated coupling of CH_4 and NH_3 to HCN ("DEGUSSA process"): How cooperative effects can be tuned and exploited by a proper choice of the metals in small heteronuclear clusters ("Each atom counts!").

Recommended Reading

- a) M. Schlagen, *Dissertation D83*, TU Berlin, 2008.
- b) X. Zhang, M. Schlagen, M.-H. Baik, Y. Dede, H. Schwarz, *Helv. Chim. Acta* 92 (2009).
- c) D. Schröder, H. Schwarz, *Proc. Nat. Acad. Sci.* 105 (2008) 18114.
- d) M. Schlagen, H. Schwarz, *Helv. Chim. Acta* 91 (2008) 2203.
- e) M. Armélin, M. Schlagen, H. Schwarz, *Chem. Eur. J.* 14 (2008) 5229.
- f) M. Schlagen, H. Schwarz, *Helv. Chim. Acta* 91 (2008) 379.
- g) B. Butschke, M. Schlagen, H. Schwarz, D. Schröder, *Z. Naturf.* 62b (2007) 309.
- h) M. Schlagen, D. Schröder, H. Schwarz, *Angew. Chem., Int. Ed.* 46 (2007) 1641.
- i) M. Schlagen, H. Schwarz, *Angew. Chem., Int. Ed.* 46 (2007) 5614.
- j) M. Schlagen, D. Schröder, H. Schwarz, *Chem. Eur. J.* 13 (2007) 6810.
- k) D. Schröder, H. Schwarz, *Can. J. Chem.* 83 (2005) 1936.
- l) D. K. Bohme, H. Schwarz, *Angew. Chem., Int. Ed.* 44 (2005) 2336.
- m) H. Schwarz, *Angew. Chem., Int. Ed.* 42 (2003) 4402
- n) K. Koszinowski, D. Schröder, H. Schwarz, *J. Am. Chem. Soc.* 125 (2003) 3676.