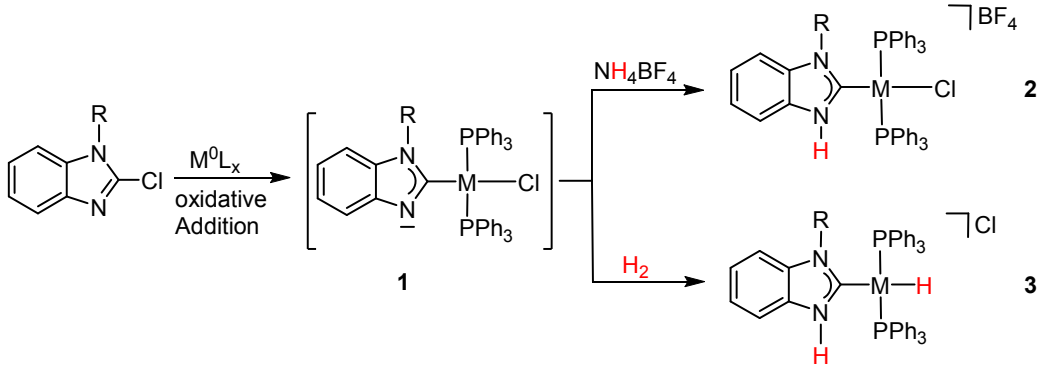
Protic N-heterocyclic carbenes - new ligands and their complexes for multiple applications

F. Ekkehardt Hahn
Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie, Corrensstraße 30, D-48149 Münster, Germany; e-mail: fehahn@uni-muenster.de

N-heterocylic carbenes have developed into important ligands in organometallic chemistry and catalysis. The majority of NHC complexes have been prepared from cyclic azolium precursors which upon C2 deprotonation yield the free NHC which then coordinates to a given metal center.[1] We have prepared functionalized isocyanides (2-azidophenyl isocyanide and 2-azidoethyl isocyanide) which upon metal coordination and transformation of the azido function into a primary amine react in a metal-template controlled reaction to yield complexes with NH,NH-functionalized NHC ligands. These "protic" NHC ligand are not stable when removed from the metal center. They are, however, easily *N*,*N*'-deprotonated and can be further functionalized. This has allowed the preparation of macrocyclic tetracarbenes[2] and of heterodonor [11]ane-P_2C^{NHC} and [16]ane$P_2C^{NHC}_2$ macrocycles.[3]
Very recently we have found that neutral azoles like *N*-methyl-2-chloro benzimidazole react with Ni^0, Pd^0 or Pt^0 under oxidative addition to give complexes with an anionic NHC ligand featuring an unsubstituted ring-nitrogen atom **1**. Protonation of such ligands yields NHC ligands with an NH,NMe-substitution pattern as in **2**[4] and reaction with dihydrogen leads to a heterolytic cleavage of H_2 and complex **3**. This oxidative addition can also be utilized to generate carbene complexes by C-metallation of biomolecules like 8-bromocaffeine or 8-bromoadenine. The NH group of protic NHC ligands can be utilized as recognition unit for selected substrates. Preorganization of substrates via hydrogen bonds to NHC-NH groups of coordinated NHC ligand allows the regioselective catalytic hydrogenation of selected substrates.[5]



1. (a) F. E. Hahn, M. C. Jahnke, *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172; (b) M. C. Jahnke, F. E. Hahn, *Top. Organomet. Chem.* **2010**, *30*, 95–129.
2. F. E. Hahn, V. Langenhahn, T- Lügger, T. Pape, D. Le Van, *Angew. Chem., Int. Ed.* **2005**, *44*, 3759–3764.
3. (a) A. Flores-Figueroa, T. Pape, K.-O. Feldmann, F. E. Hahn, *Chem. Commun.* **2010**, *46*, 344–326; (b) O. Kaufhold, A. Stasch, T. Pape, H. Hepp, P. G. Edwards, P. D. Newman, F. E. Hahn, *J. Am. Chem. Soc.* **2009**, *131*, 306–317.
4. (a) T. Kösterke, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 2112–2115; (b) T. Kösterke, T. Pape, F. E. Hahn, *Chem. Commun.* **2011**, *47*, 10773–10775; (c) T. Kösterke, J. Kösters, E.-U. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz, F. E. Hahn, *Chem. Eur. J.* **2012**, *18*, 14594-14598.
5. N. Meier, F. E. Hahn, T. Pape, C. Siering, S. R. Waldvogel, *Eur. J. Inorg. Chem.* **2007**, 1210-1214; (b) A. R. Naziruddin, A. Hepp, T. Pape, F. E. Hahn, *Organometallics* **2011**, *30*, 5859–5866.