

# SYNTHESIS OF N-HETEROCYCLIC CARBENES THROUGH OXIDATIVE ADDITION AND SUBSEQUENT UNUSUAL CARBENE REARRANGEMENT OF AN IMIDAZOLIUM SALT

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During the last three decades, the design and development of transition metal complexes bearing N-heterocyclic carbene ligands (NHCs) has rapidly increased and NHC metal complexes became popular for catalysis and other applications.<sup>[1]</sup> A more uncommon type of NHC complexes is that with an abnormal carbene (*a*NHC) featuring the carbene–metal bond in the C4- or C5-position of the imidazoline moiety.<sup>[2]</sup> Site-selective syntheses of NHC metal complexes can be achieved through deprotonation of azolium salts and subsequent metallations,<sup>[1]</sup> oxidative addition reactions of a C–X bond (X = H, Cl, Br, I) at electron rich metals<sup>[2]</sup> or dehalogenation/metallation reaction sequences.<sup>[3]</sup>

In this work, a rather unusual reaction has been observed by using the ligand precursor **1(I)** in an oxidative addition reaction with  $[M(PPh_3)_4]$  (M = Pd, Pt) as described in Fig. 1. The reaction mechanism was investigated through DFT-calculations. The oxidative addition reaction of the C–I bond at the C4-position proceeds to give the abnormal NHC metal complex. Afterwards, the metal rearranges intermolecularly to the C2-position to yield the classical NHC metal complexes **[2–3]** as depicted below (Fig. 1).

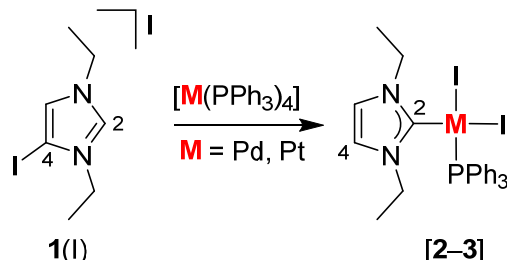


Figure 1: Oxidative addition followed by carbene rearrangement.

The expected oxidative addition reaction at the C5-position has been observed when the reaction was carried out with a  $PF_6^-$  counter ion at the ligand precursor to form the abnormal NHC complex. The C2-position is still protonated and can be used for deprotonation/metallation sequences.

[1] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. b) L. Mercks, M. Albrecht, *Chem Soc. Rev.* **2010**, *39*, 1903. c) A. Zanardi, R. Corberan, J. A. Mata, E. Peris, *Organometallics* **2008**, *27*, 3570.

[2] a) H. Jin, T. T. Y. Tan, F. E. Hahn, *Angew. Chem. Int. Ed.* **2015**, *54*, 13811. b) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556.

[3] M. D. Böhme, T. Eder, M. B. Röthel, P. D. Dutschke, L. F. B. Wilm, F. E. Hahn, F. Dielmann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202190.