SYNTHESIS OF COMPLEXES BEARING UNIQUE CAAC LIGANDS THROUGH OXIDATIVE ADDITION

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Since the discovery of cyclic (alkyl)(amino)carbenes (CAACs) by Bertrand in 2005,[1] these ligands have allowed the synthesis of some highly robust and potent transition metal catalysts.[2] In almost all known CAAC complexes, the ring-nitrogen atom has to be substituted with a bulky aryl group to stabilize the intermediate free carbene center. We became interested in the preparation of complexes bearing CAACs with aliphatic *N*-substituents. Given the instability of free CAACs in the absence of bulky aromatic *N*-substituents, we assumed that the target *N*-alkyl CAACs will not be stable in their free state and that complex preparation must therefore proceed *via* the *in situ* generation of the CAAC from a suitable precursor.

Therefore, oxidative addition of the chloro indoleninium salt **I** towards electron rich metal precursors was employed to synthesize complexes with an *N*-ethyl CAAC ligand (Figure 1). CAAC complexes were obtained by reaction of **I** with $[M(PPh_3)_4]$ (M = Pd, Pt)[3] and with carbonylmetalates of Fe, Cr and W.[4] The electronic properties of the CAAC ligand have been determined by DFT calculations and experimental parameters.[5]

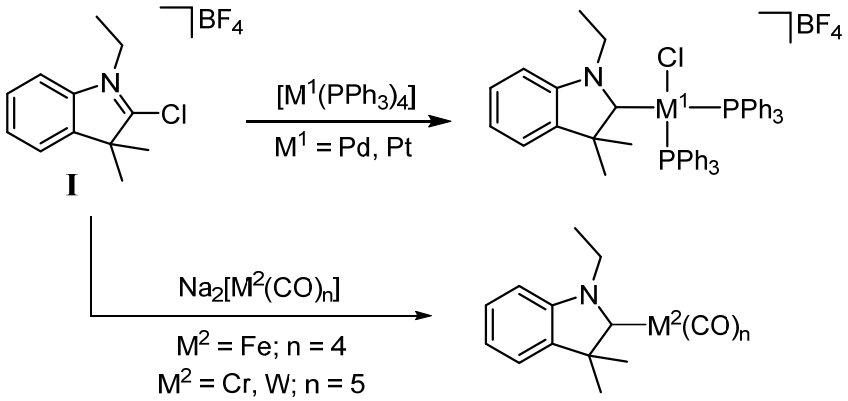

Figure 1: Oxidative addition of the C–Cl bond of **I** towards different metal precursors.

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[2] V. M. Marx, A. H. Sullivan, Melaimi, S. C. Virgil, B. K. Keitz, D. S. Weinberger, G. Bertrand, R. H. Grubbs *Angew. Chem. Int. Ed.* **2015**, *54*, 1919.

[3] S. Termühlen, J. Blumenberg, A. Hepp, C. G. Daniliuc, F. E. Hahn *Angew. Chem. Int. Ed.* **2021**, *60*, 2599.

[4] S. Termühlen, P. D. Dutschke, A. Hepp, F. E. Hahn *Organometallics* **2023**, *42*, 473.

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