

N-Heterocyclic Carbenes and Cyclic Alkyl Amino Carbenes: New and Versatile Ligands in Organometallic Chemistry

Brad Gorecki

Literature Seminar

October 6, 2005

N-heterocyclic carbene (NHC) ligands have emerged as useful and versatile ligands in organometallic chemistry.¹ The first use of NHCs as ligands for transition metal complexes was reported almost 40 years ago by Öfele² and Wanzlick³. NHCs did not receive much attention until the isolation of a stable NHC by Arduengo⁴ in the early 90's (Figure 1a). For the past 15 years, major attention has been focused on NHCs as ancillary ligands for transition metal complexes. Recently, Bertrand⁵ has developed a stable cyclic alkyl amino carbene (CAAC) ligand (Figure 1b). These carbene ligands have replaced phosphines in many catalytic systems. The ruthenium-mediated olefin metathesis catalytic system and the palladium C-C coupling catalytic system have benefited from the use of NHCs. Palladium catalysts with CAAC ligands have shown to be highly efficient for the α -arylation of ketones.⁵

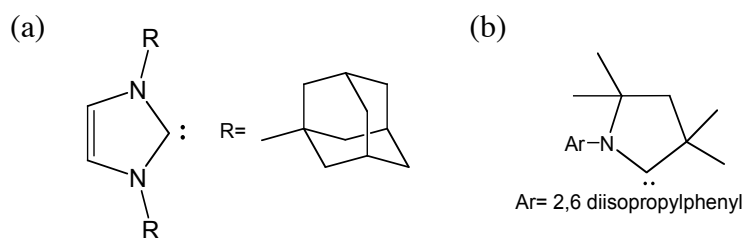


Figure 1: (a) An N-heterocyclic carbene. (b) A cyclic alkyl amino carbene.

NHCs can help stabilize electron-deficient intermediates in catalytic cycles and allow for improvements in catalyst design, such as in the development of ruthenium metathesis catalysts.⁶ Although once believed to be just “phosphine mimics,” NHCs have substantial differences in comparison to phosphines.⁷ NHCs have proven to be better σ -donors and are more sterically demanding than their bulky phosphine ligand counterparts.^{8,9}

Bioxazoline derived NHCs have been used as ligands in the Suzuki coupling of aryl chlorides and aryl boronic acids.¹⁰ These ligands have flexible cycloalkyl rings which determine their catalytic properties.¹¹ By increasing the size of the cycloalkyl ring, the Suzuki coupling of sterically hindered aryl chlorides and boronic acids can be achieved at room temperature. These ligands are electron rich, and with flexible steric bulk they can achieve different conformations. These ligands adopt sterically hindering conformations, which facilitate reductive elimination.

Bertrand⁵ has developed a new carbene framework, cyclic alkyl amino carbene (CAAC) ligands. These carbene ligands contain five membered rings similar to NHCs but one of the nitrogens is replaced by a strong σ -donating alkyl group. This difference makes CAACs more electron rich than either phosphines or NHCs. The presence of a quaternary carbon allows for a different steric environment in comparison to phosphines and NHCs. These ligands have led to the formation of very active palladium catalysts for the α -arylation of ketones at room temperature (Figure 2).

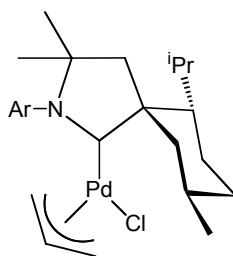


Figure 2: Palladium Allyl Chloride CAAC complex

Low coordinate unsaturated metal complexes often play roles in catalytic processes.¹² CAAC ligands have been used to isolate low-coordinate transition metal complexes due to their unique electronic and steric properties.¹³ Using this ligand the first examples of a 14 electron Rh(I) complex and a 14 electron Pd(II) cation have been possible.

CAAC's can form very active cyclic Fischer carbene complexes.⁵ With a quaternary carbon in the \square position to the carbene center, many different structural features are possible. These properties make this ligand very desirable for asymmetric catalysis.

References

1. Herrmann, W.A. N-Heterocyclic carbenes as ligands for metal complexes - challenging phosphane ligands in homogeneous catalysts. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
2. Öfele, K. 1,3-Dimethyl-4-imidazolynyliden-(2)-pentacarbonylchrom ein neuer übergangsmetall-carben-komplex. *J. Organomet. Chem.* **1968**, *12*, P42-P43.
3. Wanzlick, H.W.; Schönherr, H.J. Direct Synthesis of a Mercury Salt-Carbene Complex. *Angew. Chem. Int. Ed.* **1968**, *7*, 141-142.
4. Arduengo, A.J. III; Harlow, R.L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
5. Lavallo, V.; Canac, Y.; Präsang, C.; Donnadiou, B.; Bertrand, G. Stable Cyclic (Alkyl)(Amino)Carbenes as Rigid or Flexible, Bulky, Electron-Rich Ligands for Transition-Metal Catalysts: A Quaternary Carbon Atom Makes the Difference. *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-5709.
6. Trnka, T.M.; Grubbs, R.H. The Development of $L_2X_2Ru=CHR$ Olefin Metathesis Catalysts: An Organometallic Success Story. *Acc. Chem. Res.* **2001**, *34*, 18-29.
7. Scott, N.M.; Nolan, S.P. Stabilization of Organometallic Species Achieved by the Use of N-Heterocyclic Carbene (NHC) Ligands. *Eur. J. Inorg. Chem.* **2005**, 1815-1828.
8. Crabtree, R.H. NHC ligands versus cyclopentadienyls and phosphines as spectator ligands in organometallic catalysis. *J. Organomet. Chem.*, in press.

9. Chianese, A.R.; Li, X.; Janzen, M.C.; Faller, J.W.; Crabtree, R.H. Rhodium and Iridium Complexes of N-Heterocyclic Carbenes via Transmetalation: Structure and Dynamics. *Organometallics* **2003**, *22*, 1663-1667.
10. Goddard, R.; Lehmann, C.W.; Glorious, F. An N-Heterocyclic Carbene Ligand with Flexible Steric Bulk Allows Suzuki Cross Coupling of Sterically Hindered Aryl Chlorides at Room Temperature. *Angew. Chem. Int. Ed.* **2003**, *42*, 3690-3693.
11. Altenhoff, G.; Goddard, R.; Lehmann, C.W.; Glorious, F. Sterically Demanding, Bioxazoline-Derived N-Heterocyclic Carbene Ligands with Restricted Flexibility for Catalysis. *J. Am. Chem. Soc.* **2004**, *126*, 15195-15201.
12. Scott, N.M.; Dorta, R.; Stevens, E.D.; Correa, A.; Cavallo, L.; Nolan, S.P. Interaction of a Bulky N-Heterocyclic Carbene Ligand with Rh(I) and Ir(I). Double C-H Activation and Isolation of Bare 14-Electron Rh(III) and Ir(III) Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 3516-3526.
13. Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B. Isolation of Elusive Low Coordinate Transition Metal Complexes Thanks to a Rigid Cyclic (Alkyl)(Amino)(Carbene) Ligand. Unpublished work, 2005.