3) N-Heterocyclic Carbene Chemistry

N-heterocyclic carbenes have become ubiquitous ligands in organometallic and coordination chemistry and in homogeneous catalysis. Their metal complexes attract a fast growing interest because of their broad scope in terms of synthesis, bonding and applications, in particular in catalysis.

X. Liu, R. Pattacini, P. Deglmann, P. Braunstein
Do short C-H-M (M = Cu(I), Ag(I)) distances represent agostic interactions in pincer-type complexes? Unusual NHC transmetalation from Cu(I) to Ag(I).
Organometallics, 2011, 30, 3302

(Comments from the Editor: The first cover of this journal to originate from France features a molecule that was synthesized in Strasbourg by an international team of chemists from China, Germany, Italy, and France under the leadership of P. Braunstein. Their work analyzes the bonding in novel bis(NHC) Cu(I) and Ag(I) complexes in which the aryl spacer between the NHC ligands is in close proximity to the metal. However, proximity does not always imply bonding!)

A. A. Danopoulos,* K. Yu. Monakhov, P. Braunstein*
Anionic NHC Ligands from Mesoionic Imidazolium Precursors: Remote Backbone Arylimino Substitution Directs Carbene Coordination

Anionic NHC ligands ...
… open new ways for fine-tuning and expanding the coordination chemistry of carbene ligands. Deprotonatio/lithiation of mesoionic 4-arylimino-imidazolium precursors afforded anionic NHC ligands bearing a remote anionic amido functionality. The preference for binding to Li⁺, Li(tmeda)⁺, Ag⁺ and Fe⁺⁺ is examined with respect to the AMIDO-NHC (i.e. remote anionic amido – neutral NHC) vs. IMINO-IMIDIDE (i.e. remote neutral imino–anionic imidazol-2-ylidene-ide) forms. DFT calculations provide insight into the preferred site of the metallation (CNHC vs. Nexo). The remote backbone substitution clearly offers a versatile way to develop novel anionic NHC ligands.
A. A. Danopoulos,* P. Braunstein,* E. Rezabal, G. Frison
Unprecedented directed lateral lithiations of tertiary carbons on NHC platforms

Of relevance to organic synthesis, unexpected and unprecedented directed remote lateral lithiation at one \( \text{CH(CH}_3\text{)}_2 \) of the \( 3-(2,6\)-di-isopropylphenyl) wingtip took place upon the reaction of functionalised N-heterocyclic carbene-type molecules with excess of \( \text{LiCH}_2\text{SiMe}_3 \), leading to dilithiated dianionic 4-amido-N-heterocyclic carbenes.

P. Ai, A. A. Danopoulos,* P. Braunstein*
Aurophilicity-Triggered Assembly of Novel Cyclic Penta- and Hexanuclear Gold(I) Complexes with Rigid Anionic NHC-Type Ligands

Polynuclear Au(I) complexes supported by anionic \( \text{PC}_{\text{NHC}} \) ligands showing unique topologies
F. He, L. Ruhlmann, J.-P. Gisselbrecht, S. Choua, M. Wesolek, A. A. Danopoulos,* P. Braunstein*


F. He, M. Wesolek, A. A. Danopoulos,* P. Braunstein*