Stable Carbenes and Related Species: Powerful Tools in Organic and Organometallic Chemistry

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Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. Spectacular results in this area have been achieved using cyclic diaminocarbenes, the so-called N-heterocyclic carbenes (NHCs), mainly because of their strong s-donor properties. Although it is possible to cursorily tune the structure of NHCs, any diversity is still far from matching their phosphorus-based counterparts, which is one of the great strengths of the latter. Beginning with our discovery in 1988 of a bottle-able (phosphino)(silyl)carbene, a variety of stable acyclic carbenes are known, but they give rise to fragile metal complexes. During the recent years, we have discovered new types of stable cyclic carbenes, as well as related carbon-based and boron-based ligands, which feature even stronger σ-donor properties than NHCs. The synthesis, electronic properties, coordination behavior, and catalytic activity of complexes bearing our ligands will be presented, and comparisons with their NHC cousins will be discussed.

We and others have shown that singlet carbenes with enhanced electrophilic properties, such cyclic (alkyl)(amino)carbenes (CAACs),[1] allow for the stabilization of organic radicals and metals in a formal zero oxidation state.[2] Bis(CAAC)M complexes in which the metal is gold, copper, cobalt, iron, nickel, manganese and zinc have been isolated. Depending on the metal, the majority of spin density can reside either on the metal or on the carbene carbons and the nitrogen atoms of the CAAC ligand.

We also found that CAACs allow for the isolation of catalytically active complexes, which were supposed to be only transient intermediates. Among them, bis(copper) complexes involved in the very popular CuAAC reaction (Click Chemistry) will be discussed.[3]

1. For a recent review: Soleilhavoup, M.; Bertrand, G. *Acc. Chem. Res.* **2015**, *48*, 256.
2. For a recent review: Martin, C. D.; Soleilhavoup, M.; G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020.
3. Jin, L.; Tolentino, D. R.; Melaimi, M.; Bertrand, G. Science Adv. **2015**, *1*, e1500304.