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Powerful tools in organic, inorganic and organometallic chemistry

Guy Bertrand
University of California San Diego

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RSEQ Real Sociedad Española de Química El Sitio de la Química en España

Stable carbenes and related species: Powerful tools in organic, inorganic and organometallic chemistry

Guy Bertrand

UCSD-CNRS Joint Research Chemistry Laboratory, Department of Chemistry and Biochemistry,
University of California San Diego, La Jolla, CA, USA
guybertrand@ucsd.edu, http://bertrandgroup.ucsd.edu/Site_Bertrand_group/Bertrands_group.html

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 σ-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,[1] as well as related carbon-based and boron-based ligands,[2] which feature even stronger σ-donor properties than NHCs. The synthesis, electronic properties, and catalytic activity of complexes bearing our ligands will be presented, and comparisons with their NHC cousins will be discussed. We will show that singlet carbenes with enhanced electrophilic properties, such as cyclic (alkyl)(amino)carbenes (CAACs),[3] allow for the metal-free activation of small molecules,[4] and for the stabilization of organic radicals and metals in a formal zero oxidation state.[5] 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. We will show that this discovery allows us to develop novel catalytic transformations.

1. For a review: M. Melaimi, M. Soleilhavoup, G. Bertrand, **Angew. Chem. Int. Ed. 2010**, *49*, 8810.
2. For a recent review: M. Soleilhavoup, G. Bertrand, **Angew. Chem. Int. Ed. 2017**, DOI: 10.1002/anie.201705153.
3. For a recent review: M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, **Angew. Chem. Int. Ed. 2017**, DOI: 10.1002/anie.201702148.
4. For a review: D. Martin, M. Soleilhavoup, G. Bertrand, **Chem. Sci. 2011**, *2*, 389.
5. For a review: C. D. Martin, M. Soleilhavoup, G. Bertrand, **Chem. Sci. 2013**, *4*, 3020.

Guy BERTRAND studied chemistry at the University of Montpellier and received his PhD from the University Paul Sabatier in Toulouse. After being a CNRS group leader (French National Center for Scientific Research) at the University of Toulouse, and then at the Laboratoire de Chimie de Coordination du CNRS, he has been the Director of the Laboratoire d'Hétérochimie Fondamentale et Appliquée at the University Paul Sabatier from 1998 to 2005. From 2001 to 2012 he served as the Director of the UCR/CNRS Joint Research Chemistry Laboratory that he created, and since July 2012 he is Distinguished Professor and Director of the UCSD/CNRS Joint Research Chemistry Laboratory at the University of California at San Diego. He is a member of the French Academy of Technology (2000), the Academia Europaea (2002), the European Academy of Sciences (2003), the French Academy of Sciences (2004), and is a Fellow of the American Association for Advancement of Sciences (2006). He has recently received the Sir Ronald Nyholm Medal of the RSC (2009), the Grand Prix Le Bel of the French Chemical Society (2010), the ACS Award in Inorganic Chemistry (2014), and the Sir Geoffrey Wilkinson Award of the RSC (2016). He is one the Associate Editors of Chemical reviews, and a member of the Editorial Board of several journals.