

## Carbenes Introduction



Anthony Arduengo was born in Tampa, Florida, in 1952. He studied chemistry at the Georgia Institute of Technology, receiving his B.S. in 1974 and Ph.D. in 1976. After beginning his career with DuPont's Central Research and Development Department, he moved to University of Illinois-Urbana as a member of the Organic Faculty. Returning to DuPont in 1984, he advanced to Research Leader/Research Fellow. Since 1999, Professor Arduengo holds the Saxon Chair in Organic Chemistry at the University of Alabama (Tuscaloosa) and is adjunct professor of inorganic chemistry at the Technical University Carolo-Wilhelmina in Braunschweig, Germany. His research interests include unusual valency, main group element chemistry, organo-fluorine chemistry, and various aspects of applied chemistry. Professor Arduengo directs a multinational research program in Tuscaloosa through which his students obtain a portion of their research experience in laboratories in Germany or Japan. Likewise, his laboratory in Tuscaloosa often hosts visiting scholars from overseas. Professor Arduengo holds a Senior Humboldt Research Prize and the Gold Medal for excellence in main group element chemistry from the International Council on Main Group Chemistry, and is a Fellow of the American Association for the Advancement of Science. In his spare time, Professor Arduengo enjoys making "Valenz" adjustments.



Guy Bertrand was born in Limoges (France) in 1952. He graduated from the University of Montpellier (1975) and moved the same year to the University of Toulouse as an "Attaché de Recherche CNRS". From 1988 to 1998 he undertook the role of "Director of Research" at the Laboratoire de Chimie de Coordination du CNRS, and from 1998 to 2005 he was the Director of the Laboratoire d'Hétérochimie Fondamentale et Appliquée at the University Paul Sabatier (Toulouse). Since 2001 he has been the Director of the UCR/CNRS Joint Research Chemistry Laboratory at the University of California at Riverside. His research spans a wide range of topics at the border between organic and inorganic chemistry, with a special emphasis on the stabilization of highly reactive species. In 1988, he reported the synthesis of a stable (phosphino)(silyl)carbene, and since that time has uncovered various families of stable carbenes. He received the International Council on Main Group Chemistry Award (1993), the Humboldt Award (1994), the médaille d'argent of the CNRS (1998), a JSPS fellowship (1999), and the Sir Ronald Nyholm Medal of the RSC (2009); has been elected at the French Academy of Technology (2000), the Academia Europaea (2002), the European Academy of Sciences (2003), and the French Academy of Sciences (2004); and is a Fellow of the American Association for Advancement of Sciences (2006).

The chemistry of carbon attracts particular attention in science fundamentally because of its importance to life as we know it. The extreme flexibility of bonding at carbon is well-suited to the wide variety of structures required to support living systems. Carbon is easily assembled into stable rings, chains, and complex molecular architectures, and when  $sp^3$ -hybridized it is configurationally stable. Carbon forms stable bonds to a very wide range of elements that further diversify "carbon chemistry." As stable as many carbon-carbon and carbon-element bonds are, they remain active (reactive) to special conditions that occur within biologically accessible energy domains. The energy that drives biological systems to form and rearrange chemical structures has also found an optimal carrier and storage center in carbon. As an energy carrier, carbon with an atomic weight of 12 amu and four active valence electrons offers a 1-electron reservoir per 3

amu—among the best of any element other than hydrogen (which does not possess the chemical versatility of many of the heavier elements). Beyond the chemistry of living systems themselves, carbon also contributes mightily to the chemistry of materials important to living systems; from classical structural materials (wood, carbon steel) to modern advanced materials like synthetic polymers, carbon fibers, electronic materials, etc. The chemistry of carbon in compounds in which all four valence electrons of the carbon atom are involved in bonding comprises the vast majority of structures associated with living systems. Compounds in which carbon could be considered to have only two electrons involved in bonding while two nonbonding electrons remain at carbon are rarer. This lower oxidation state of carbon compounds includes divalent carbon species like carbenes as well as compounds like carbon monoxide and isonitriles.

In his book *Divalent Carbon*, Jack Hine<sup>1</sup> provided a convenient succinct definition of carbenes (page 171) that captures the essential structural and chemical characteristics of these 2-coordinate carbon compounds.

To early chemists, oxidation state II dicoordinate hydrocarbons appeared to be a missing class of carbon compounds, and initial experiments concentrated on the idea that these structures existed as complexes with other compounds. For example, in 1835, Dumas reported on his attempts to free methylene (CH<sub>2</sub>) from its apparent hydrate, methanol (CH<sub>2</sub>·H<sub>2</sub>O).<sup>2</sup> The evolution of carbene chemistry is in part captured in some of the excellent introductions to various contributions to this issue. Additionally, this history has been reviewed previously in various forums.<sup>3</sup> The evolution of carbene chemistry is influenced by the techniques available to chemists and the development of deeper, more accurate insight into chemical bonding. For the two guest editors of this edition, their careers are privileged to have witnessed a remarkable expansion in understanding of divalent carbon species. Chemists are taught the “correct” way to think about problems in their science and are guided to the “appropriate” interpretation of experimental results by studying the foremost texts in the area and reading the best journals and leading authors. This education provides a well-defined “box” to frame future works and development in the science. After years of quests for the “missing” divalent carbon species, chemistry largely evolved to view carbenes as highly reactive, transient species that, though important in certain transformations, were not capable of being isolated as stable (bottle-able) chemical species. Within this “box,” thinking to the contrary was shunned. In fact, when one of us (A.J.A.) sought to begin research toward isolable stable carbenes, he was discouraged from this undertaking with the admonition that “*the area was fully [unsuccessfully] researched and further work would be a waste of corporate resources.*” For the other of us (G.B.), he was trying to make a phosphorus–carbon multiple bond and had a hard time to convince himself that he made a carbene. Fortunately, we have escaped the philosophical confines of the conventional (1960s to early 1980s) box, and it is hard these days to find a chemical journal that does not report some new development in carbene or carbene-complex chemistry or catalysis.

This special issue provides a snapshot of an exciting and rapidly developing area of chemistry. Carbene chemistry is topical for the insight that it provides into chemical bonding in general, the new catalysts that it is providing, and the mechanistic revelations that it lends to organic chemistry. However, beyond these benefits, carbene chemistry provides science with the understanding necessary to manage and manipulate the intermediate oxidation states of carbon and offers the potential to better utilize carbon in energy storage and energy delivery systems.

The first two reviews in this issue deal with recent developments in the seminal involvement of carbene in organometallic chemistry, namely, Fischer- and Schrock-

carbene complexes. The state of the art in stabilizing carbenes in their triplet state is then detailed. The two reviews that follow demonstrate the variety of acyclic singlet carbenes that can be prepared and isolated as metal-free species (a related review by Roesler dealing with cyclic carbenes will appear in an upcoming issue), and how <sup>13</sup>C NMR spectroscopy offers a relational and predictive tool for chemistry and stability of carbenes. Until recently, the existence of stable carbenes was limited to those featuring a heteroatom, nitrogen or phosphorus, directly bonded to the electron-deficient center. Lately, this paradigm too has changed, and the so-called carbocyclic carbenes and abnormal carbenes are part of the chemist’s armatorium, as shown by two reviews. This special issue also presents the chemistry of species that are closely related to carbenes, i.e., cumulenylenes and heavier carbene analogues. N-heterocyclic carbenes are ubiquitous ligands for transition metal complexes and have led to numerous breakthroughs in transition metal catalysis. This carbene-catalysis connection is discussed in several reviews that center on the metal types: coinage metals, f-block elements, and late transition metals. The extensive variety and wide scope of complexes bearing poly(N-heterocyclic carbenes) as ligands has grown to such an extent that each deserves its own review. Carbenes now play such a central role in olefin metathesis catalysis that four reviews summarize the different aspects of recent developments, and another by Grubbs will be featured in an issue later this year. A very nice demonstration of the broad scope of application of carbenes is presented in the last review on the medicinal aspects of imidazolium carbene metals complexes.

As guest editors, the conception and execution of this issue were labors of love that were only realized through the efforts of the excellent editorial staff of *Chemical Reviews*, in particular Professor John Gladysz and Ms. Pamela Maddox. Finally, without the outstanding contributions of the individual authors, this assembly would not have been possible. We hope that you, the reader, will find this thematic issue edifying, thought-provoking, and, of course, enjoyable.

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Guy Bertrand

## 1. References

- (1) Hine, J. *Carbene Chemistry*; Ronald Press: New York, 1964.
- (2) Dumas, J. B. *Ann. Chim. Phys.* **1835**, 58, 28.
- (3) (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964; p 5. (b) Arduengo, A. J., III; Krafczyk, R. *Chem. Unserer Zeit* **1998**, 32, 6. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, 100 (1), 39. (d) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, 32 (11), 913.

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