

## Professor Anthony J. Arduengo, III

### A Tribute



**Dedicated to Professor Anthony J. Arduengo, III on the occasion of his 60<sup>th</sup> birthday**

Anthony J. "Bo" Arduengo, III was born in 1952 in Tampa, FL and raised in the greater Atlanta, GA area. By the age of 16, Bo and his father (Anthony J. Arduengo, II) had built his first car and it was registered as street-legal. This appeared to be the beginning of a 40 plus year love affair with performance automobiles (as Bo is currently the owner of a Lotus Elise, etc....). The automobile was later re-engineered to run on alternate fuels including alcohol and hydrogen, thus this effort would forecast Bo's professional research involvement in the National Hydrogen Fuel Initiative (HFI) and the Chemical Hydrogen Storage Program by more than 30 years.

#### **Early and Formal Education**

As a student at Walker High School in Atlanta, Bo left in 1969 (and subsequently graduated in 1970) as part of the joint enrollment program with Georgia Tech. While at Georgia Tech, Bo served as Executive Officer and Captain of the Georgia Tech band. As an undergraduate, Bo was the recipient of NSF fellowships in 1972 and 1973 while doing undergraduate research in the Professor Edward M. Burgess' laboratory. Bo received his BS degree in 1974 (*cum laude*) and stayed at Georgia Tech where he obtained his Ph.D. in 1976.

## Research

### Georgia Tech (1972-1976)

As a student in the Burgess research group, Bo investigated organo-main group element chemistry, specifically, thiocarbonyl ylides, and low-coordinate hypervalent sulfur compounds.

### DuPont (1977)

In 1977 when he initially joined DuPont, Bo became a member of Howard Simmons' research group where his initial project investigated trimethylsilyl esters of inorganic acids as synthetic reagents in organic chemistry.

### University of Illinois (1978-1984)

Bo was recruited by Professor J. C. Martin onto the faculty at The University of Illinois at Urbana-Champaign. During his time at Illinois, he established many milestones in main group chemistry, including creation of the first stable carbonyl ylide. Bo examined more broadly the areas of organo-main group element chemistry and molecules containing unusual valency. His first publications, involving the chemistry of electron-deficient carbenes, occurred during this time frame as well. This work led to the first structure determinations on a nitrile and carbonyl ylide. Throughout his Illinois years, Bo had a close collaboration with his colleague J.C. Martin who also worked in the area of organo-main group element chemistry and hypervalency. To facilitate discussions about unusual molecular structures and bonding for main-group element centers, Martin and Arduengo devised the N-X-L nomenclature system. The Arduengo group completed the synthesis and characterization of the first compound with a planar T-shaped, 10-electron 3-coordinate bonding arrangement at a phosphorus atom, ADPO, and paved the way for a range of novel main-group element chemistry on his return to DuPont. Bo's final Illinois research extended beyond the newly discovered ADPO chemistry to include the arsenic analog, ADA<sub>3</sub>O.

### DuPont 1984-1999

Upon returning to DuPont in 1984, Bo resumed a position within Central Research and Development (CR&D). He continued his early research from Illinois into the ADPO molecule and related structures. The ADPO related chemistry provided a basis for the discovery of a new inversion process, termed edge inversion, which was fully characterized and modeled through the collaborative work of Bo and David A. Dixon.

Bo's research often coalesced with his other hobbies outside the laboratory; for example with sports cars. He contributed to the development of low VOC automotive coatings by devising catalysts for a novel cross-linking chemistry used by DuPont Performance Coatings in next-generation low-VOC paints. Eventually, DuPont waterborne performance coatings would be used by Lotus on their Elise and Exige models (two models that Bo currently owns). These efforts thrust Bo back into carbene chemistry; this time however, his area of focus was in

nucleophilic rather than electrophilic carbenes. His observations led him to postulate that the imidazol-2-ylidenes which are intermediates in the catalyst syntheses were much more stable than previously assumed by the chemical community.

With this knowledge in hand, he submitted a proposal to the management in CR&D to isolate these apparently stable carbenes and further examine their chemistry. Not surprisingly, the proposal was declined based on the belief that carbenes existed solely as reactive intermediates and could not be isolated as stable entities. However, Arduengo (already well-aware of the history) had the starting materials on hand for the chemistry and decided to proceed with the experiments. Bo's gamble paid off and in 1991, more than 150 years after the first attempt, a stable crystalline carbene was isolated and characterized in laboratories at DuPont. After the first successful reaction, Bo won the support of DuPont management and research in this area continued. Along this line, carbenes bearing a variety of substituent groups were prepared and characterized. The saturated imidazolin-2-ylidenes that were extensively investigated by Hans-Werner Wanzlick thirty years earlier (without isolation) were now also shown to be stable enough to isolate with appropriate substituents at nitrogen. The chemistry was extended to include thiazol-2-ylidenes, thus highlighting that both nitrogen atoms of the imidazole ring were not required for the production and isolation of carbenes.

Arduengo's research from 1996 also reflects his interaction with his host for his Alexander von Humboldt Research Prize, Professor Reinhard Schmutzler. The carbene chemistry conducted included reactivity studies of imidazol-2-ylidenes with fluorinated inorganic compounds and a series of new carbenes were isolated and characterized. Arduengo's final work at DuPont included the synthesis and characterization of carbene-alkaline earth metal, carbene•antimony, carbene•cadmium, and carbene•lithium adducts.

### **University of Alabama (1999-present)**

At the University of Alabama, research from Arduengo's laboratory continues to focus on enhancements to the basic structure of the imidazol-2-ylidenes through substituent effects leading to novel compounds like a cyclopentadienyl fused imidazol-2-ylidene. Research into the unusual valency in diphosphacyclobutane-2,4-diyls has been reported from the Arduengo group in collaboration with Professors Masaaki Yoshifuji and Shigekazu Ito. He also maintains a collaboration with Professor Rainer Streubel at the University of Bonn. Bo also directs research programs into Chemical Hydrogen Storage and nonlinear optical materials.

### **Closing**

Bo continues pioneering research on two continents in the areas of main group element chemistry, physical and synthetic organic chemistry, unusual valence structures, carbenes, and materials chemistry. Bo has been recognized nationally and internationally through an Alexander von Humboldt Senior Research Prize, the 1996 Gold Medal for Excellence in Main Group Element Chemistry from the International Council on Main Group Chemistry, the Chute Lectureship in Dalhousie Canada, and in 2007 as a Fellow of the American Association for the

Advancement of Science. In addition to his contributions to the scientific literature (see below), Bo has authored or co-authored 17 patents. His discoveries are incorporated into marketed products including DuPont's Kapton®-ZT polyimide film and new crosslinking catalysts used in commercial paints and other polymer systems. Professor Anthony J. Arduengo, III is a true chemistry pioneer and a scientific visionary. His remarkable breadth and depth of knowledge, myriad interests, unwavering curiosity, and intrepid drive to explore the unconventional has fostered some of the greatest fundamental and applied chemical discoveries of the last 30 years.

Professor Michael Jennings

Department of Chemistry, University of Alabama, USA

E-mail: jenningsm@bama.ua.edu

### Selected Publications

1. Janulis, E. P.; Arduengo III, A. J. Diazotetrakis(trifluoromethyl)cyclopentadiene and ylides of electro-negative elements. *J. Am. Chem. Soc.* **1983**, *105*, 3563.
2. Culley, S. A.; Arduengo III, A. J. The synthesis and structure of the first 10-P-3 species. *J. Am. Chem. Soc.* **1984**, *106*, 1164.
3. Dixon, D. A.; Arduengo III, A. J.; Fukunaga, T. A new inversion process at group V elements. Edge inversion through a planar T-shaped structure. *J. Am. Chem. Soc.* **1986**, *108*, 2461.
4. Arduengo III, A. J.; Dixon, D. A.; Roe, D. C. Direct determination of the barrier to edge inversion at trivalent phosphorus: verification of the edge inversion mechanism. *J. Am. Chem. Soc.* **1986**, *108*, 6821.
5. Arduengo III, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. The synthesis, structure and chemistry of 10-Pn-3 systems: tricoordinate hypervalent pnictogen compounds. *J. Am. Chem. Soc.* **1987**, *109*, 627.
6. Arduengo III, A. J.; Dixon, D. A.; Roe, D. C.; Kline, M. Edge inversion at a four-coordinate main group IV center. *J. Am. Chem. Soc.* **1988**, *110*, 4437.
7. Arduengo III, A. J.; Lattman, M.; Rasika Dias, H. V.; Calabrese, J. C.; Kline, M. Pentacoordinate 10-electron Pnictogen-Manganese adducts: verification of the 10-Pn-3 arrangement in ADPnO molecules. *J. Am. Chem. Soc.* **1991**, *113*, 1799.
8. Arduengo III, A. J.; Harlow, R. L.; Kline, M. A stable crystalline carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361.
9. Arduengo III, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. Electronic stabilization of nucleophilic carbenes. *J. Am. Chem. Soc.* **1992**, *114*, 5530.
10. Arduengo III, A. J.; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. Electron distribution in a stable carbene. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

11. Arduengo III, A. J.; Dixon, D. A.; Kumashiro, K. K.; Lee, C.; Power, W. P.; Zilm, K. W. Chemical shielding tensor of a carbene. *J. Am. Chem. Soc.* **1994**, *116*, 6361.
12. Arduengo III, A. J.; Goerlich, J. R.; Marshall, W. J. A stable thiazol-2-ylidene and its dimer. *Liebigs Ann.* **1997**, *2*, 365.
13. Arduengo III, A. J.; Davidson, F.; Goerlich, J. R.; Khasnis, D.; Prakasha, T. K.; Marshall, W. J. An air stable carbene and mixed carbene "Dimers". *J. Am. Chem. Soc.* **1997**, *119*, 12742.
14. Arduengo III, A. J.; Krafczyk, R. Auf der suche nach stabilen carbenen. *Chemie in unserer Zeit* **1998**, *32 (1)*, 6.
15. Arduengo III, A. J.; Tapu, D.; Marshall, W. J. A Bimetallic complex containing a cyclopentadienyl-annulated imidazol-2-ylidene. *J. Am. Chem. Soc.* **2005**, *127(47)*, 16400.