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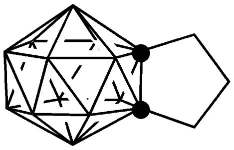
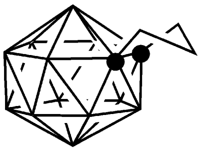
Editor's Page

The Editor's Introduction to the Review by Deng and Xie in This Issue of *Organometallics*

The icosahedral 12-vertex $C_2B_{10}H_{12}$ carboranes, the 1,2 (ortho)-, 1,7 (meta)-, and 1,12 (para)-isomers, have been known for over 40 years, and over the years their chemistry, inorganic, organometallic, organic, and polymer, has been the subject of extensive worldwide research. Carboranes with more than 12 vertices ("supercarboranes") represent an exciting new carborane subclass, the first member of which, a 13-vertex species, was prepared only in 2003. Our cover molecule is a supercarborane, the 14-vertex μ-2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$ (**1**), whose preparation and characterization were reported in 2005 (*Angew. Chem., Int. Ed.* **2005**, *44*, 2128) by Zuowei Xie, the senior author of the review in this issue of *Organometallics*, and his co-workers. Supercarborane **1**, the largest carborane known thus far, was isolated in the form of stable, colorless crystals from a mixture with its structural isomer, μ-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ (**2**), which had been prepared by the reaction of either an arachno salt, $[(CH_2)_3C_2B_{10}H_{10}][Li_4(THF)_5]$, or a nido salt, $[(CH_2)_3C_2B_{11}H_{11}][Na_2(THF)_4]$, with $HBBr_2{\cdot}SMe_2$ in toluene. Carborane **1** is a bicapped-hexagonal-antiprismatic molecule with all 24 faces triangulated, as confirmed by single-crystal X-ray analysis. The structure of isomer **2** was reported in a later paper (*Angew. Chem., Int. Ed.* **2006**, *45*, 4309).



1



2

• = C, all other vertices are B–H

Zuowei Xie, presently Professor of Chemistry at the Chinese University of Hong Kong, is a native of China. He obtained his B.Sc. degree in chemistry at Hangzhou University in 1983 and an M.Sc. at the Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences in 1986, where his research supervisors were Professors Changtao Qian and Yaozeng Huang. He obtained his Ph.D. degree in 1990, working in a special joint program between the Technical University of Berlin (Professor Herbert Schumann) and the Shanghai Institute of Organic Chemistry (Professors Qian and Huang). A postdoctoral stay from December 1991 to July 1995 at the University of Southern California (USC) with Professor Christopher Reed followed. Subsequently he joined the chemistry faculty of the Chinese University of Hong Kong as assistant professor. He rose up the academic ladder there and presently is a Chair Professor in the Chemistry Department.

Professor Xie's extensive publication list is an interesting read. The research carried out in Shanghai was concerned with the organometallic chemistry of the lanthanide metals, with emphasis on cyclopentadienyl and hydride derivatives and their reactivity. It was during his very productive stay at USC that he became introduced to boron cluster and carborane chemistry through participation in Professor Reed's innovative program on the synthesis and utilization of weakly coordinating anions. These included species such as [*closo*-$CB_{11}H_{12}]^-$, [*closo*-$CB_{11}H_6X_6]^-$ ($X = Cl$, Br, I), and $[CH_3\text{-}1\text{-}CB_{11}H_{11}]^-$. Such anions were used by Professor Xie in an attempted isolation of salts of free silicenium ions in early work at USC. Also reported in Professor Xie's papers from that period are the isolation of salts of a protonated silanol, $[R_3SiOH_2]^+$, the $[H_9O_4]^+$ hydronium ion, and a phosphenium ion, all with such weakly coordinating anions.

Upon his return to Hong Kong, Professor Xie took up organolanthanide chemistry again, but soon it became organolanthanide chemistry with a strong boron flavor. Thus, titles such as "Synthesis and Structural Characterization of the First Mixed Lanthanacarborane Incorporating η^5-Cyclopentadienyl and η^6-Carboranyl Ligands" and "Synthesis and Reactivity of Cationic Lanthanide Metallocene Complexes. Hexabromocarborane and Tetraphenylborate as Counter-Ions" appear in his publication list. Soon thereafter came the novel $[\eta^7\text{-}C_2B_{10}H_{12}]^{4-}$, $(C_6H_5CH_2)_2C_2B_{10}H_{10}$, $Me_2E(C_9H_7)(C_2B_{10}H_{11})$ ($E = C$, Si), and ${}^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ ligands, as well as new weakly coordinating anions, $[1\text{-}H\text{-}CB_9X_9]^-$ and $[1\text{-}H_2N\text{-}CB_9X_9]^-$ ($X = Cl$, Br, I), and $[1\text{-}HCB_9Me_9]^-$. Of special interest was the preparation of a zirconocene-1,2-dehydro-1,2-carborane (*o*-carboryne) complex and the use of C-, Si-, and B-bridged ligands of the type noted above in the preparation and utilization of constrained-geometry metallocene complexes of the group 4 metals. This is an outstanding body of work, in which Professor Xie has drawn creatively upon his research experience in organolanthanide and carborane chemistry. His more recent results are summarized in the present review. A large fraction of Professor Xie's very interesting papers in this area has been published in *Organometallics*. As Professor Xie notes in the concluding section, the development of supercarboranes, especially of those with more than 14 vertices, is a challenging but very worthwhile goal of further research. New boron reagents and new synthetic approaches will be needed. We may look forward to exciting new developments in this area.

Professor Xie's coauthor of this review, Dr. Liang Deng, a native of China, studied chemistry at Peking University and obtained his Ph.D. degree at the Chinese University of Hong Kong under the guidance of Professor Xie in 2006. At present he is a postdoctoral fellow at Harvard University in the research group of Professor R. H. Holm.

Thanks are due to Professor Arnold L. Rheingold for generating the cover figure.

Dietmar Seyferth
Editor

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