GALLIUM ADDITIONS TO AROMATICITY

ACS MEETING NEWS: New maingroup compounds expand the bounds of metalloaromaticity

ROMATICITY, a phenomenon in which delocalized bonding enhances the stability of cyclic molecular frameworks, has traditionally been the province of organic chemistry. But no more. Enterprising chemists have been showing with greater frequency that carbon isn't always necessary for aromaticity; metal-containing compounds of all sorts can mimic the behavior of classic aromatic systems.

A pair of chemists reported the latest manifestations of metalloaromaticity in the form of two novel gallium compounds during presentations before the Division of Inorganic Chemistry at the ACS national meeting last week in Salt Lake City. Creation of these types of compounds is helping chemists gain an ever-better understanding of chemical bonding.

Gregory H. Robinson of the University of Georgia described his group's synthesis of a Ga_6 cage compound, the first example of a neutral aromatic gallium species with an octahedral structure. And Philip P. Power of the University of California, Davis, discussed his group's preparation of the first aromatic metallabenzene containing two gallium atoms.

Alexander I. Boldyrev of Utah State University, whose research includes computational and gas-phase studies on metalloaromatic species, notes that the Robinson and Power compounds "represent remarkable advancements of delocalized bonding in main-group inorganic chemistry." These researchers are helping to move the field forward by making stable, isolable sol-

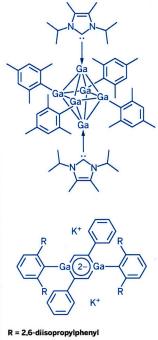
ids that "show us the great potential for aromaticity and antiaromaticity concepts beyond organic chemistry," Boldyrev says.

Robinson's group made its compound, $Ga_6R_4L_2$, where R is mesityl and L is an N-heterocyclic carbene, by reducing the precursor compound LGaRCl₂ with potassium metal (*J. Am. Chem. Soc.* 2009, 131, 3168). The compound has 14 delocalized valence electrons in its skeleton and exhibits spherical aromaticity, similar to closed-cage boranes such as $B_6H_6^{2r}$.

The synthesis was part of a larger effort Robinson discussed to use N-heterocyclic carbenes as versatile ligands for maingroup compounds, including diatomic boron, silicon, and phosphorus species. "The metalloaromaticity of the ${\rm Ga_6}$ compound is traced to the stabilizing electron-donor capabilities of the N-heterocyclic carbene," Robinson told C&EN.

Power's group prepared a digallatabenzene, $K_2[C_4H_2Ph_2Ga_2R_2]$, where Ph is phenyl and R is a bulky terphenyl, by inserting phenylacetylene into the digallene RGa=GaR, then reducing the cyclic product with potassium metal. The dianion ring has six π electrons, the same as benzene, with the negative charges balanced by potassium cations.

Power discussed the digallatabenzene as part of a presentation on his group's exploration of adding hydrogen, ammonia, and small unsaturated hydrocarbons to digallium and other group 13 and 14 metal compounds (Angew. Chem. Int. Ed. 2009, 48, 2027 and 2031). Looking beyond digallatabenzene, Power believes that getting three or four gallium atoms into a stable six-membered aromatic ring is feasible.—STEVE RITTER



BEYOND CARBONRobinson's octahedral Ga₆

Robinson's octahedral Ga₆ compound (top) and Power's digallatabenzene (bottom) demonstrate new possibilities for aromaticity.

RESIGNATION Scandal leads to departure of Innospec CEO Paul Jennings

The taint of scandal has led to the resignation of a CEO for the second time in four years at fuel additives and specialty chemicals firm Innospec. Paul W. Jennings suddenly resigned from the post on March 20.

In a statement from Innospec, Jennings says an ongoing investigation by U.S. and British authorities into the firm's involvement in the United Nations' Oil for Food Program (OFFP) between 2001 and 2003 "has made it increasingly difficult for me to move the business forward as I would like."

OFFP allowed Iraq to sell oil for food

and other humanitarian supplies after the 1990 Gulf War. But the program quickly devolved into a graft-generating nightmare in which government officials and others around the globe have been implicated. It's not clear how Innospec, the world's only manufacturer of the gasoline additive tetraethyllead, is involved.

Jennings joined the firm as chief financial officer in 2002 and became CEO in 2005 after then-CEO Dennis J. Kerrison resigned for violating company ethics policies. Chairman Robert E. Bew has taken over while Innospec searches for Jennings' replacement.

According to filings with the Securities & Exchange Commission, Innospec accrued about \$20 million in legal and other expenses during the past two years while responding to government OFFP investigations. "We expect that we will be required to disgorge profits and pay fines and penalties" for involvement in OFFP, according to the firm.

Although Innospec may pay a fine, stock analyst Jonathan Lichter of equity research firm Sidoti & Co. says, "The government won't kill the golden goose." In 2008, Innospec earned \$45 million on sales of \$641 million.—MARC REISCH