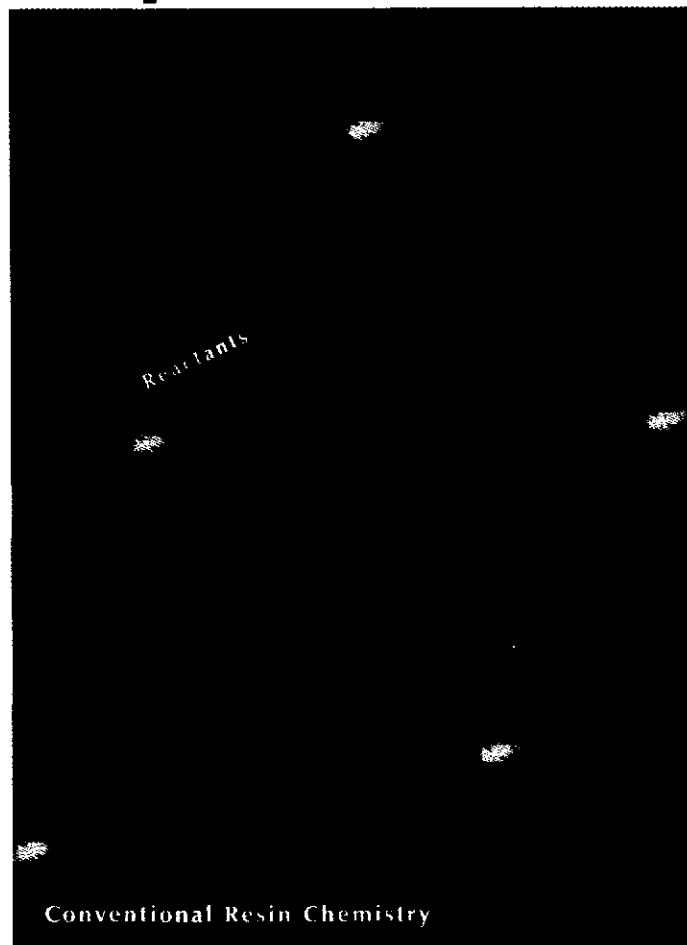
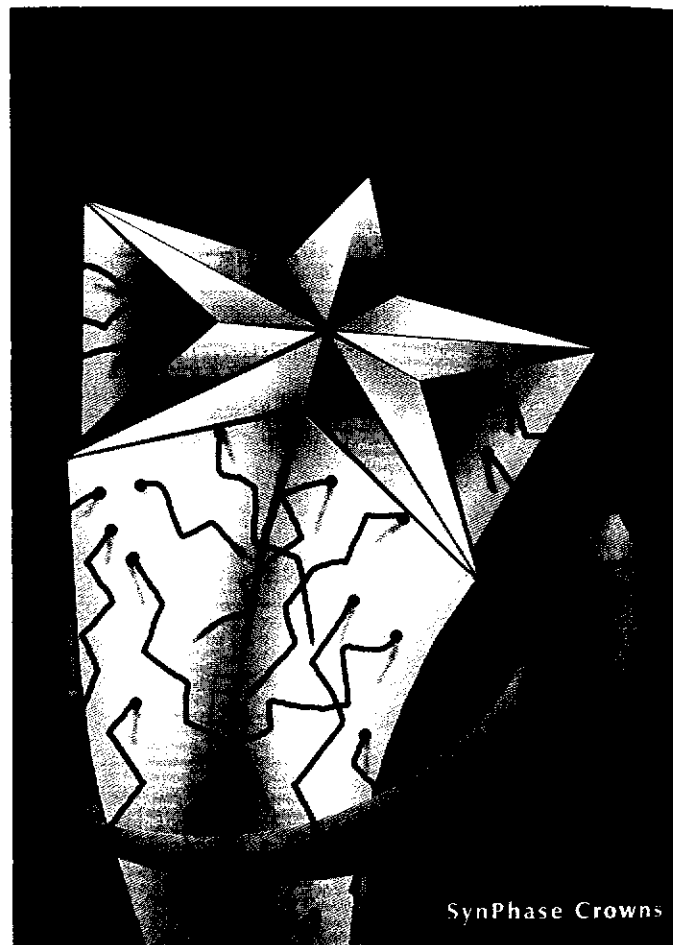


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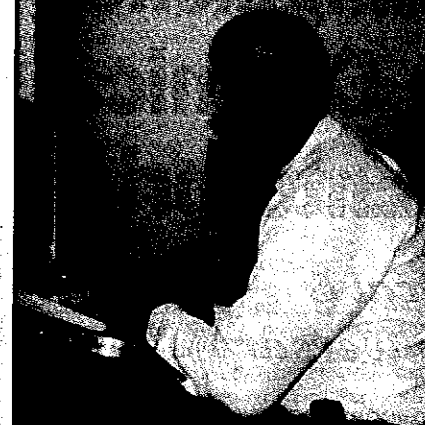
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A TRIPLE BOND FOR GALLIUM

Report of first organometallic compound of its kind convinces some, but not all, scientists

Gregory H. Robinson has a way with gallium. Two years ago, he and his coworkers reported the first cyclogallene—an aromatic ring of three gallium atoms. Now, his group apparently has managed to force gallium into another unprecedented bonding arrangement: the first compound with a gallium-gallium triple bond.

Robinson, a professor of chemistry at the University of Georgia, Athens, and three coworkers describe the synthesis and characterization of "the first gallyne" in last week's *Journal of the American Chemical Society* [119, 5471 (1997)].

"I think this is a terrific discovery," comments chemistry professor Jerry L. Atwood of the University of Missouri, Columbia. Together with Robinson's cyclogallene work, he adds, "it really opens up main-group chemistry of the heavier elements. I think this will now be a very exciting and fruitful area."

JACS Associate Editor Jack R. Norton, who handled the gallyne manuscript, tells C&EN: "It's a spectacular result if right." But not everyone who has seen the manuscript is sure it's 100% right.

For example, Philip P. Power, chemistry professor at the University of California, Davis, a leading figure in main-group chemistry, believes that Robinson's structural data don't support the existence of a Ga-Ga triple bond. He says the bond is only marginally shorter than some Ga-Ga single bonds in molecules that don't have very bulky substituents. Based on the length and geometry of the bond, and on his own research on similar compounds, Power thinks it more likely that the two galliums are connected by a bond "of significantly lower order than three—with substantial lone-pair electron density at each gallium."

Robinson doesn't buy Power's arguments, particularly those involving Ga-Ga bond distances. "Having considered all the possible explanations and correlating these with the experimental results lead us time and time again to only one conclusion: a Ga-Ga triple bond," Robinson tells C&EN.

In the beginning, though, Robinson and his coworkers—postdoctoral researchers Jianrui Su and Xiao-Wang Li and graduate student R. Chad Crittendon—weren't so sure of what they had made. Their objective wasn't to make a Ga-Ga triple bond, but to learn how gallium would cope with the stress of very bulky ligands.

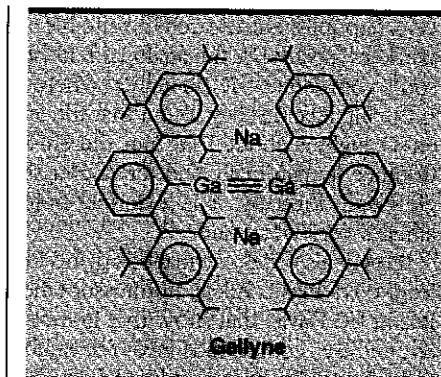
In the 1995 experiment that yielded the first cyclogallene, Li reduced RGaCl_2



Li (clockwise from left), Crittendon, Robinson, and Su synthesized singular gallium compound, building on earlier work.

with sodium metal to yield $\text{Na}_2(\text{RGa})_3$, where R is the bulky 2,6-dimesitylphenyl group. The two sodium atoms—one above and one below, the ring—each donate one electron to the unoccupied *p* orbitals of the galliums, resulting in a "metalloaromatic" system.

Following up on this work, Robinson wanted to see what would happen in this reaction if R were an even bulkier ligand than 2,6-dimesitylphenyl, which can be thought of as *m*-terphenyl studded with



six methyl groups. The obvious choice was to replace those six methyls with isopropyl groups. For want of a simpler name, Robinson and coworkers refer to this hexaisopropyl terphenyl ligand as "the big ligand."

The Georgia team thought that sodium metal reduction of RGaCl_2 (where R is the big ligand) might furnish a larger all-gallium ring, perhaps $(\text{RGa})_4$ or $(\text{RGa})_6$. But no—the compound that Su prepared has only two gallium atoms, and they are two-coordinate, thus: R-Ga-Ga-R. Furthermore, the Ga-Ga bond distance is the shortest ever seen—2.319 Å. The structure also contains two sodium atoms, which reside on either side of the Ga-Ga bond, forming a nearly planar Ga_2Na_2 ring.

Another intriguing feature of the gallyne structure is that the Ga-Ga-C fragment is not linear, but is bent at about 130°. Based on the proton nuclear magnetic resonance spectrum, Robinson's group rules out the possibility that a hydrogen atom is bonded to each gallium atom. As the researchers note in their paper, several theoretical studies conducted by Henry F. Schaefer III's group at the University of Georgia have concluded that triple-bonded main-group model

compounds such as Si_2H_2 and Ge_2H_2 , unlike acetylene, often are favored to have a non-linear trans orientation.

Furthermore, Robinson and coworkers write, preliminary calculations on the model triple-bond-containing $\text{Na}_2(\text{CH}_3\text{GaGaCH}_3)$ "predicts a Ga-Ga-C bond angle of 126.9°, very comparable to the values observed in the [gallyne]."

Power, however, finds the bent Ga-Ga-C structure to be more suggestive of single rather than triple bonding. In re-

cent unpublished research, he and his co-workers isolated a tin analog of Robinson's compound— $K_2(RSnSnR)$, where R is the big ligand. They found that the Sn-Sn-C angle is about 109° and the Sn-Sn distance is marginally shorter than a single bond; formally, it is a double bond, albeit a very weak one.

Power also cites calculations by his colleague Thomas L. Allen, a professor emeritus at UC Davis, that show that in model Sn_2 and Ge_2 compounds most relevant to Robinson's Ga_2 compound, the species with a quasi-single bond and a lone pair of electrons on each metal atom is significantly more stable than the triple-bonded species. The heavier the group 13 element, Power says, the less likely it is to π -bond. As a result, he believes that Robinson's Ga_2 compound is closer to a single-bonded species. But, he adds, "no matter what you think the bonding is, it's still a very interesting compound" and it represents "a great contribution to group 13 chemistry."

Missouri's Atwood, although not familiar with the details of Power's arguments, opines that tin does not necessarily predict what gallium does. Nor does he find the nonlinearity of the Ga-Ga-C system to be worrisome. Basically, he thinks Robinson is on firm footing.

Robinson himself is confident that his admittedly "radical proposal" will eventually be accepted by all chemists. "After all," he says, looking back, "some people did not believe that we had actually prepared cyclogallenes!"

Ron Dagani

Chemical 'instruction' may have a role in antibody selectivity

A fresh look at a 50-year-old question in immunochemistry is revealing new insights into the exquisite molecular selectivity of the immune system. By examining crystal structures of the combining site of an antibody, a team of chemists at the University of California, Berkeley, finds that the binding mechanism of the antibody changes as it matures [Science, 276, 1665 (1997)].

The study—by assistant professor Raymond C. Stevens, professor Peter G. Schultz, and their colleagues—revisits key aspects of a theory first proposed half a century ago by Linus Pauling, among others, to explain the phenomenal ability of

antibodies to recognize specific molecules and bind to them.

The experiments may also provide important insights for the field of combinatorial chemistry. As Schultz explains: "All the combinatorial systems that are being explored today are in some way derived from or inspired by the immune system."

It's almost impossible to fool the immune system. If an unknown molecule—even one that has never been synthesized before—is introduced into the body, a specific population of antibodies will quickly develop that bind the molecule tightly and specifically. The question of how the system can handle such diversity has fascinated and puzzled researchers for decades.



Raymond C. Stevens

Germline antibody changes its shape to bind to antigen (red). Mutations that take place as the antibody matures "preselect" this configuration, so that binding no longer involves a shape change. The antibody's heavy chain is shown in green, its light chain in yellow.

In the 1940s, Pauling suggested that the antibody molecule can adopt different conformations and that the target molecule acts as a template to direct the antibody to fold into the shape that complements it best. An alternative explanation is that the immune system takes a combinatorial approach, recombining a relatively small number of gene segments to make an enormous diversity of antibody molecules. That diversity is further amplified through a process called somatic mutation as the antibodies mature.

The new experiments suggest that in some cases both mechanisms may operate. "This study demonstrates that not only is sequence diversity important but, potentially, configurational diversity can be important, too," Schultz says. "In this particular case, we found that the precursor antibody did change configuration and become more complementary to the target molecule," he explains. "The somatic mutations refine the combining site and lock it into a

configuration that closely complements the shape of the target molecule."

The Berkeley chemists investigated a catalytic antibody raised against a phosphate molecule that is the transition-state analog for the hydrolysis of a nitrophenyl ester. They solved the crystal structure for the antibody in four forms: the immature—or germline—antibody bound and not bound to the transition-state analog and the mature, fully mutated antibody bound and not bound to the same analog. When bound to the target, the mature and immature antibodies have the same shape. The researchers found that the immature antibody changes shape when it binds, but the mature antibody doesn't. The nine mutations that occurred during maturation, in effect, locked the antibody into the configuration it needed to tightly bind the analog.

It makes sense that there's more than just sequence diversity involved in the immune system's ability to recognize molecules, Schultz says. Chemists have successfully mimicked the immune system's ability to combinatorially generate 10^{10} to 10^{14} different sequences, he notes, "but the immune system does more with the diversity it generates than we have been able to do with diversity generated synthetically in the test tube. I think we are now starting to get at some

of the molecular mechanisms that the immune system uses to do that."

Rebecca Rawls

Huntsman perseveres, gets Rexene

After nearly a year of contentious, on-again, off-again discussions that included a brewing proxy fight, an agreement was reached last week that will allow Huntsman Corp. to acquire Rexene Corp.

The \$16-per-share, \$300 million cash part of the deal has already been approved by the boards of directors of both companies. It still must be approved by Rexene's shareholders in a special meeting to be held later in the year. The deal also includes Huntsman's assumption of about \$300 million in debt held by Dallas-based Rexene. Huntsman expects to close the transaction, subject to regulatory ap-