

GALLIUM 'TRIPLE BONDS' UNDER FIRE

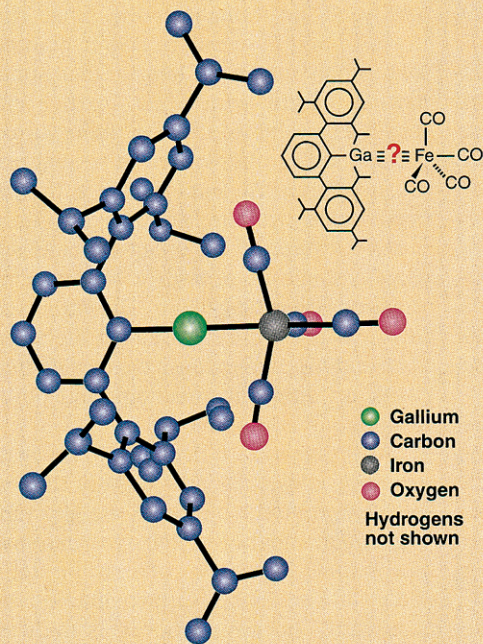
Using theory, chemists assert that claimed Ga-Ga and Fe-Ga 'triple bonds' actually are a double and single bond, respectively

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When Gregory H. Robinson made his biggest splash yet in gallium chemistry last year, he did not anticipate how large and intense the resulting waves would be.

His was a two-part splash: Last June, Robinson, a professor of chemistry at the University of Georgia, Athens, and his co-workers reported the synthesis of a compound with a short gallium-gallium bond, which they claimed was the first example of a Ga-Ga triple bond [*J. Am. Chem. Soc.*, **119**, 5471 (1997)]. A remarkable claim, considering that no one had previously confirmed triple-bond formation involving any group 13 metal. Moreover, no molecule with a discrete Ga-Ga double bond was known.

Robinson's iron-gallium compound, or 'ferrogallyne'



Then, in October, Robinson's group followed up with what is considered by some chemists to be an even more incredible claim: the synthesis of a compound with the shortest iron-gallium bond on record, which the group also said was a triple bond [*Organometallics*, **16**, 4511 (1997)]. In that paper, the authors noted that the literature doesn't even reveal a clear example of an iron-gallium double bond.

The two reports quickly drew the attention of chemists around the world, particularly those with an interest in main-group chemistry or multiple bonds. For some, the results were exciting, seemingly opening up a new frontier in synthetic inorganic chemistry. Others, however, were dubious. And some were downright incredulous, even scornful.

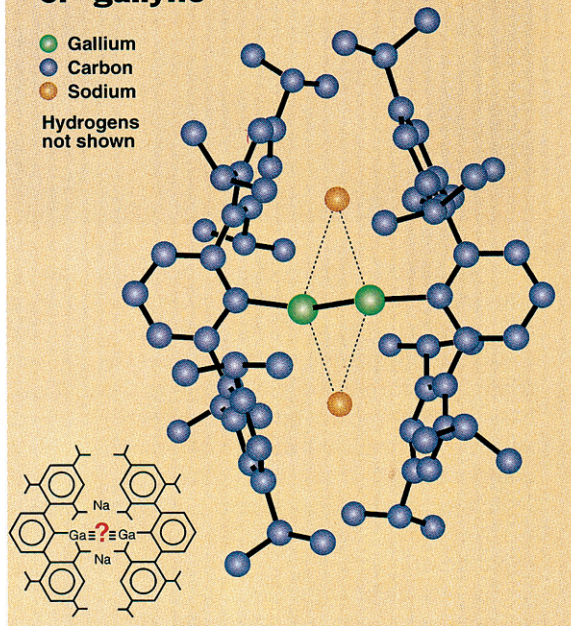
No one has expressed doubts that the compounds have actually been made or that their X-ray crystal structures are correct as reported. And almost everyone agrees that the compounds are interesting, particularly the digallium compound. But what bothers a number of experts in the field is the Georgia group's interpretation of the nature of the bonding. On the basis of Robinson's own experimental evidence, data from the literature, and their own calculations, these experts have concluded that neither the Ga-Ga nor the Fe-Ga bond in these compounds is a triple bond.

Robinson, nonetheless, stands by his group's original conclusions. And he has received back-

ing from other chemists whose calculations support his group's view of the bonding in the digallium compound.

Of the two contested Robinson reports, the one published in *Organometallics* on the Fe-Ga bond has received the most negative reception. The compound in question contains a strictly two-coordinate gallium bonded to a $\text{Fe}(\text{CO})_4$ group and to the very bulky 2,6-bis(2,4,6-triisopropylphenyl)phenyl group. The Fe-Ga bond of 2.2248 Å is the shortest on record, and the molecule has an almost perfectly linear Fe-Ga-C arrangement. After a short discussion of bonding models

Robinson's digallium compound, or 'gallyne'



in their report, Robinson and coworkers concluded that these features are "consistent" with an Fe-Ga triple bond.

It's interesting that this compound—dubbed a "ferrogallyne" in the paper—was synthesized by Jianrui (Hank) Su, a postdoctoral fellow in Robinson's lab who received his Ph.D. degree in inorganic chemistry in 1996 from renowned professor F. Albert Cotton of Texas A&M University, College Station. Because of his long-standing interest in metal-metal multiple bonds, Cotton read the ferrogallyne paper—but found it hard to believe. As he later declared to C&EN, "That's no more a triple bond than I'm the Dalai Lama!"

Cotton wasted no time in trying to set the record straight. He and Xuejun Feng, a theorist at the Laboratory for Molecular Structure & Bonding, which



Robinson: stands by original conclusions

about a two-coordinate gallium atom bonding to iron from the case of a four-coordinate phosphorus atom bonding to iron and to compare Fe-P distances with Fe-Ga distances. The Fe-Ga bond in the ferrogallyne is "substantially shorter" than Fe-Ga single bonds reported previously, he notes. Furthermore, he says, if the Fe-Ga bond is a single bond, this would suggest, as Cotton pointed out in his own paper, that the gallium atom has only four electrons in its valence shell. "There is no experimental evidence to suggest that four electrons in its valence shell would be sufficient to stabilize a gallium

center in an organometallic compound," Robinson says. Inorganic chemistry professor Philip P. Power of the University of California, Davis, agrees with Cotton and Feng in this debate. Power notes that linear, two-coordinate indium-manganese and aluminum-iron analogs of the Fe-Ga compound are known, and these basically have a single—not a triple—bond. Power and postdoc Scott T. Haubrich have just published a report on the In-Mn compound [*J. Am. Chem. Soc.*, **120**, 2202 (1998)].

Cotton and other chemists have expressed amazement that Robinson's ferrogallyne paper got through the peer review process. "It should never have been published in *Organometallics*," Cotton says. Robinson, though, obviously thought the paper had a chance of being published in *Science*, which is where he first submitted it. *Science*, however, declined to consider the paper on the grounds that it was too narrow in scope, according to Robinson. Compared with the ferrogallyne report, Robinson's earlier *JACS* paper on the Ga-Ga compound (or gallyne, as he calls it) is not so obviously wrong, in Cotton's estimation. "It takes a little more work to show that it's wrong," Cotton says, because the error is subtler.

Cotton directs, fired off a paper that was published in January [*Organometallics*, **17**, 128 (1998)]. In that paper, Cotton and Feng argued that the Fe-Ga triple-bond formulation is wrong on the basis of well-known bonding concepts and readily available data from related compounds such as $(C_6H_5)_3PFe(CO)_4$, which has a comparably short phosphorus-iron bond that no one has called a triple bond. To put their arguments on a firm, quantitative footing, Cotton and Feng also carried out density functional theory (DFT) calculations on a model compound in which the bulky organic ligand on gallium is replaced by a simpler phenyl group. These quantum mechanical calculations, they reported, unambiguously confirm that π -type orbital overlap between the iron and gallium atoms is "practically nil." Theory and all the experimental data, they concluded, suggest that the iron and gallium are held together merely by a single dative bond in which the gallium donates an electron pair to the iron. It's totally unexceptional, Cotton says. "Nothing could be more open and shut."

Robinson, however, says he finds certain aspects of Cotton and Feng's arguments illogical, contradictory, and "at odds with some long-standing principles of inorganic chemistry." In particular, he thinks it's "a stretch" to draw conclusions

plified structure because it is a salt: $Na_2[RGaGaR]$, where R is the same isopropyl-adorned terphenyl ligand that is attached to gallium in the Fe-Ga compound. The X-ray crystal structure reveals that the two sodium ions reside on either side of the Ga-Ga bond, forming a nearly planar Ga_2Na_2 ring. The Ga-Ga bond distance of 2.319 Å is the shortest on record, according to the Georgia group. Furthermore, the core of the molecule is not linear as it is in the ferrogallyne: The two Ga-Ga-C fragments are each bent an average of 131°.

In their *JACS* paper on this "first gallyne," Robinson and coworkers Su, Xiao-Wang Li, and R. Chad Crittendon pointed out that the molecule's trans bent orientation is predicted by several theoretical studies to be the favored orientation for triple-bonded model compounds such as $Na_2[CH_3Ga\equiv GaCH_3]$, $HSi\equiv SiH$, and $HGe\equiv GeH$. These studies were conducted by their colleague, chemistry professor Henry F. Schaefer III, director of the University of Georgia's Center for Computational Quantum Chemistry. On the basis of these calculations and their experimental data, Robinson and coworkers concluded that they had snared a stable compound with a Ga-Ga triple bond. When asked by C&EN to comment on the gallyne paper last June (a few days before its publication), Power—always the gentleman—opined that it was "a very significant contribution to group 13 chemistry" (C&EN, June 16, 1997, page 9). But he also believed that the structural data did not support the claim of a Ga-Ga triple bond. It was closer to a single bond, he thought at the time. The Ga-Ga bond in question, Power pointed out, is only marginally shorter than some Ga-Ga single bonds. He further explained that the structure of the reported compound can be written in several resonance forms. At one extreme is the triple-bonded structure embraced by Robinson's group. At the other extreme is a Ga-Ga single bond with a lone pair of electrons on each gallium. The latter was his own preference, based on literature data and his own extensive experimental work on ditin, digermanium, and other main-group compounds.

As Power looked deeper into the matter using molecular orbital (MO) theory, his view shifted a bit. From the MO vantage point, neither of the two extreme resonance forms is correct, he tells C&EN. "The closest approximation to the truth," he now believes, is midway between them—a double bond. The sec-

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The Texas DFT calculations also show that in addition to a Ga-Ga σ bond, there is one π -bonding orbital and what is clearly a nonbonding orbital. The conclusion, Cotton says, is unambiguous: "It's a double bond," not a triple bond. "This finding teaches the lesson that there [are certain cases] where you've got to use a model for the ligands that is a lot closer to reality, or you simply cannot get the right answer."

The conclusion that Robinson's digallium compound has a double bond also is supported by the theoretical work of chemistry professors Thomas L. Allen and William H. Fink of UC Davis, who are collaborating with Power. They used a computer program called Gaussian 94 and Hartree-Fock self-consistent field (SCF) theory to study the electronic structure of two model compounds: Li_2 -[*trans*- $\text{CH}_3\text{GaGaCH}_3$] and *trans*- $\text{CH}_3\text{GeGeCH}_3$, which has the same number of valence electrons as Robinson's gallyne. In both cases, their calculations indicate that the two gallium or germanium atoms are double bonded. Therefore, they believe that the Ga-Ga bond in Robinson's compound likewise is a double bond. Allen has submitted a paper describing the group's work to *JACS*.

Meanwhile, Robinson's theorist collaborators have been churning out calculations to prove that his gallyne really does have a triple bond. At the University of Georgia, Schaefer, postdoc Yaoming Xie, visiting professor Paul v. R. Schleyer, and additional coworkers have used *ab initio* and DFT methods to examine the electronic structure of model dianions such as $[\text{HGa}\equiv\text{GaH}]^{2-}$ and $[\text{CH}_3\text{Ga}\equiv\text{GaCH}_3]^{2-}$ and their neutral disodium salts, as well as neutral and dianionic species possessing double or single Ga-Ga bonds. The theorists' results lead them to conclude that in bent $[\text{RGaGaR}]^{2-}$ species, the Ga-Ga bond consists of a weak π bond and two dative bonds that are much weaker than a regular covalent bond. Says Schaefer: "It's a weak triple bond, no question about it."

Last November, Schaefer, Schleyer, Robinson, and coworkers submitted a manuscript to *JACS* describing the work. Because of the controversy, the manuscript, titled "The Nature of the Gallium-Gallium Triple Bond," was sent to five referees, four of whom recommended publication with little or no revision. The fifth referee was adamantly opposed to publication in *JACS*, noting that the modeling of the bulky terphenyl ligands of the synthesized compound by hydrogen atoms clearly is an "oversimplification."



Schaefer: it's a weak triple bond

Cotton, who tells C&EN he reviewed the paper, says, "You can't always replace a phenyl group, for example, by a hydrogen." Such an oversimplified model doesn't take into account the "sodium sandwich" effect his own calculations point to.

For the same reason, Cotton also disagrees with the conclusions of another inorganic chemist—Karl Wilhelm Klinkhammer of the University of Stuttgart, Germany—who late last year published a commentary firmly supporting the Robinson group's gallyne claim [*Angew. Chem. Int. Ed. Engl.*, **36**, 2320 (1997)]. Klinkhammer applied "natural bond orbitals" analysis to the parent gallyne, $[\text{HGa}\equiv\text{GaH}]^{2-}$, to show that its triple bond is composed of a σ bond, a π bond, and a "slipped" π bond in which most of the electron density is asymmetrically shifted toward the gallium atoms.

Robinson has touted this article as independent theoretical support for his position. But Cotton thinks Klinkhammer's model is oversimplified. And Power asks, "Why would the electron density want to asymmetrically distribute itself within a covalent bond between two atoms of equal electronegativity?" To Power, the slipped π bond seems "unrealistic."

Schaefer's viewpoint is that "I've been doing theoretical chemistry for a long time, and electronically there's not much difference" between the substituents Cotton is using and simpler ones. He doesn't agree with Cotton on the effect of the phenyl groups interacting with the

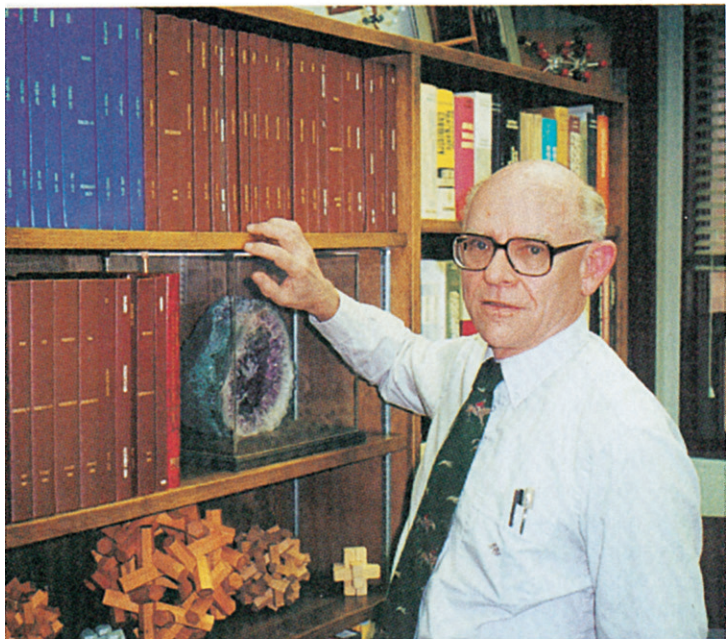


Photo by Ron Dagani

Cotton: found it hard to believe

and chemistry professor Alan H. Cowley of the University of Texas, Austin, lay out their case. Density functional theory, a relatively new method that has gained great popularity in the past few years, has not been used extensively to look at multiple bonding between main-group elements. So Cotton and coworkers began by demonstrating that DFT calculations do indeed provide accurate descriptions of the

ond bond—a π bond—is formed by a lone pair from the two galliums. The best picture, Power explains, is a combination of two double-bonded resonance forms, each with a lone pair on a different gallium. When the chemistry of this Ga-Ga compound comes to be examined, he predicts, it will display characteristics “consistent with the presence of some lone-pair density at each gallium.”

Power’s first published comments on the Ga-Ga compound and its probable double-bond character appeared last December [*J. Am. Chem. Soc.*, **119**, 11705 (1997)]. In that paper, he and coworkers Marilyn M. Olmstead and Richard S. Simons reported the synthesis and characterization of a related RSnSnR anion containing the same bulky terphenyl ligand that Robinson’s group used with gallium (but which Power’s group actually pioneered). The Sn-Sn anion, they showed, has a trans bent structure like Robinson’s Ga-Ga dianion and a formal Sn-Sn bond order of 1.5—midway between a single and a double bond.

Like Power, Cotton believed he had to comment formally on Robinson’s gal-lyne claim, especially after his own group’s DFT calculations on the molecule indicated that it really wasn’t triple bonded. In a paper published earlier this month [*J. Am. Chem. Soc.*, **120**, 1795 (1998)], Cotton, his Texas A&M colleague Feng,

bonding in a variety of multiply bonded main-group compounds.

Then they got down to the business at hand and used DFT to look at a simplified digallium model compound in which the bulky terphenyl ligand is replaced by a phenyl group. Their calculations predicted the observed bent structure, but the theoretical Ga-Ga distance always came out much longer than the experimentally determined distance. The problem, they concluded after a careful examination of the reported crystal structure, was that they were using an oversimplified model ligand. “You cannot replace the big hairy ligand with a simple phenyl group and get the right answer,” Cotton explains. In Robinson’s $\text{Na}_2[\text{RGaGaR}]$ compound, each of the two sodium ions that sit on either side of the Ga-Ga bond is “sandwiched” by two triisopropyl-substituted phenyl rings that are part of the galliums’ terphenyl ligands. The distances from the sodium ion to the sandwich carbon atoms are only about 3 Å or less, according to Cotton. He believes there is an “attractive force” between the two sandwich rings that partly counteracts the repulsive steric effects normally seen between two such bulky ligands. The end result would be a shortening of the Ga-Ga distance.

To test this idea, Cotton and coworkers performed DFT calculations on a model Ga-Ga compound with terphenyl ligands lacking only the isopropyl groups on the sandwich phenyl rings. The result: The Ga-Ga distance was reduced to one very close to the experimental value.



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sodium ions. "We're choosing to stick with our paper, and four of the referees agree with us," Schaefer says.

Schaefer volunteers that he's been "a card-carrying member of the Al Cotton Fan Club" for a long time. But, he adds, "[Cotton and I] just don't happen to agree on this point. He's had his chance to say what he wants, and we want to have our chance." And they'll have their chance, because *JACS* accepted the Georgia team's paper.

A theoretical chemist who is familiar with the dispute but does not wish to be drawn into the spotlight comments that both Schaefer and Cotton have excellent judgment about bonding issues, so when they differ, it's rather difficult to decide who's right.

Jack R. Norton, a chemistry professor at Columbia University who is not a theoretician, seems to agree. He thinks "the jury will stay out on this awhile. At this point, I do not feel that either party is clearly right or wrong in this dispute, but I may change my mind" in the future.

Norton, a *JACS* associate editor who has handled some of the manuscript submissions in the controversy, notes that some of the debate has to do with how bond order is defined and how bond length is related to bond order. Robinson and his supporters believe there is no general relationship between bond length and bond order, at least among the heavier main-group elements. That is, a triple bond, particularly a weak one, is not necessarily shorter than a double bond. The electronic structure, rather than bond lengths, determines the nature of multiple bonds, they believe.

Power and Cotton, on the other hand, hold to the conventional definition formulated by Linus C. Pauling of how bond order is related to bond length. In Power's view, "The definition of what constitutes a bond has been so stretched—if you'll pardon the pun—that it no longer bears any relationship with reality." If one wants to consider any atomic interaction—no matter how weak—as a bond, that's fine, says Power, but "I don't think that will find widespread acceptance."

Clearly, Norton observes, "some fundamental issues are getting raised, and I think the debate, on the whole, has been a healthy one."

Although the discourse has remained fairly civil, some personal comments also have crept in, from both sides. For example, referees have been blamed for being "out to lunch." Cotton and Power have been described as "jealous" because they

didn't discover the gallyne. And Robinson has been criticized for trying to oversell his work and not listening to well-meaning criticism and advice. In one instance, written comments addressed to Robinson, an African American, have had racial overtones.

Nevertheless, several observers are encouraged that "both sides have modified their position a bit," in Norton's words. On the one hand, Power's view of Robinson's Ga-Ga bond has shifted from a single bond to a double bond. And in their

submitted manuscript "The Nature of the Gallium-Gallium Triple Bond," Xie, Schaefer, and colleagues seem to hedge a bit in their abstract, noting that the gallyne's weak Ga-Ga bond is "between triple and double in character."

Even if it eventually turns out that the digallium compound is generally considered to have no more than a double bond, that would still be something never before seen, both Cotton and Power agree. It could still be a feather in Robinson's cap. ◀