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Remarks on the Gallium to Iron Bond in an $\mathrm{Ar^*GaFe(CO)_4}$ Molecule

F. Albert Cotton* and Xuejun Feng*

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843-3255

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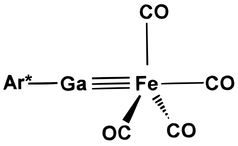
Summary: Bonding between the gallium and iron atoms in the title compound is discussed by using well-established, qualitative concepts and the results of density functional theory calculations. It is shown clearly that there is no basis for proposing an iron−gallium triple bond and, on the basis of both data and theory, that there can be only a Ga→Fe bond of order 1.

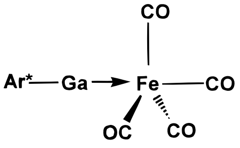
This laboratory has a long-standing and profound interest in multiple bonds between metal atoms.[1] Thus, the recent report in this journal that a compound, $\mathrm{Ar^*GaFe(CO)_4}$ (Ar* = 2,6-(2,4,6-triisopropylphenyl)-phenyl), contained a gallium to iron triple bond[2] naturally commanded our attention. In addition to the preparation of the compound, the report also contained an X-ray crystallographic determination of the molecular structure, of which the two key features are as follows: (1) The gallium atom occupies one axial position in a trigonal-bipyramidal array of ligands about the iron atom. (2) The Ga−Fe distance is 2.2248(7) Å. This structure was represented by a drawing such as **A**, in which the purported triple bond is prominent.



A

The emphasis placed on the terms “ferrogallyne”, “multiple bond”, and “iron−gallium triple bond” and the statement that there is “unambiguous and compelling evidence” for the use of such terms caused us to think very seriously about the molecule in the hope of understanding it better.

We were soon led by qualitative and semiquantitative arguments to believe that the proposal of a Ga≡Fe triple bond is unfounded and, in a word, wrong. These arguments, easily accessible without further work, are as follows. The molecule can be built up, theoretically, by first combining the Ar*Ga**:** unit with the trigonally symmetric $\mathrm{Fe(CO)_4}$ unit to give **B**, in which the iron atom now has an 18-electron configuration, as in other $\mathrm{LFe(CO)_4}$ molecules. At this point there is a Ga→Fe bond of order 1.



B

Any further increase in this bond order can occur in only one way, namely, by back-donation of electrons on the iron atom to empty orbitals on the gallium atom. To obtain a Ga−Fe bond order of 3, there would have to be two fully formed Fe→Ga dative π bonds.[3] This degree of back-bonding, or anything close to it, seems entirely unrealistic, for the following reasons.

(1) The charge separation entailed (see **C**) is not believable.

$$\mathrm{Ar^*\overset{-}{Ga}{\equiv}\overset{+}{Fe}(CO)_4}$$

C

(2) With two of the four pairs of electrons available on the iron atom for π back-bonding preempted by the Ga atom, there should be an unusually small amount of π back-bonding to the four CO groups and, hence, the CO stretching frequencies should be unusually high. However, they are not, when compared with those in a molecule such as $\mathrm{Ph_3PFe(CO)_4}$, where only a small amount of π back-bonding to the $\mathrm{Ph_3P}$ ligand is believed to occur. No one, to our knowledge, has ever asserted that there is a P to Fe triple bond in $\mathrm{Ph_3PFe(CO)_4}$ nor described the compound as a phosphyne. The relevant values of CO stretching frequencies[4,5] are, in $\mathrm{cm^{-1}}$

$\mathrm{Ar^*GaFe(CO)_4}$	2032	1959	1941	1929
$\mathrm{Ph_3PFe(CO)_4}$	2052	1979	1947	

Clearly, those in $\mathrm{Ar^*GaFe(CO)_4}$ are significantly *lower* than those in $\mathrm{Ph_3PFe(CO)_4}$, which shows that there is even *less* Ga−Fe π back-bonding than P−Fe back-bonding.

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[1] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1992.

[2] Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511.

[3] In more detail, with the Ga atom employing s−p_z hybrid orbitals to form the collinear Ga−C and Ga-Fe σ bonds, the receptor orbitals on the Ga atom would be mainly the $4p_x$ and $4p_y$ orbitals. The donor orbitals on the iron atom would have to be the $3d_{xz}$ and $3d_{yz}$ orbitals (the C−Ga−Fe axis is the z axis of the coordinate system).

[4] The occurrence of four bands in $\mathrm{Ar^*GaFe(CO)_4}$ and only three in $\mathrm{Ph_3PFe(CO)_4}$ is due to the lower symmetry (no 3-fold axis) in the former.

[5] The frequencies for $\mathrm{Ph_3PFe(CO)_4}$ are from: Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

S0276-7333(97)00971-0 CCC: $15.00

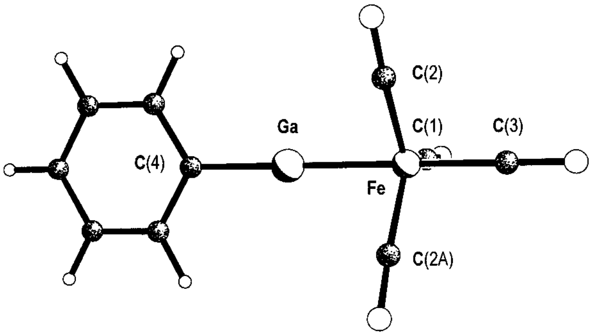

Figure 1. DFT optimized molecular structure of C_6H_5-$GaFe(CO)_4$. Selected bond distances (Å) and angles (deg) (experimental values for Ar*$GaFe(CO)_4$ are given in parentheses for comparison): Ga−Fe 2.220 (2.2248(7)); Fe−C(1), 1.786 (1.758(7)); Fe−C(2), 1.785 (1.764(4)); Fe−C(3), 1.783 (1.766(5)); Ga−C(4), 1.948 (1.943(3)); C(4)−Ga−Fe, 179.80 (179.2(1)); C(3)−Fe−Ga, 180.00 (178.9(2)); C(1)−Fe−C(2), 120.00 (120.3(1)).

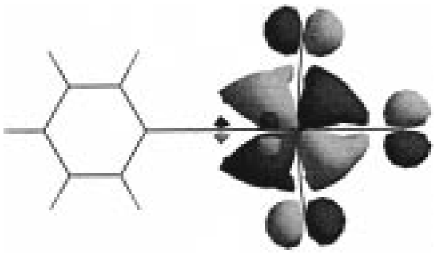

Figure 2. DFT orbital drawing for a d_π-type orbital (HOMO-2) showing the lone pair character of the Fe $3d_{xy}$ orbital.

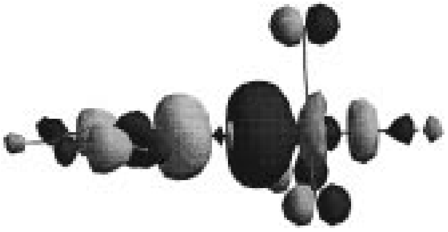

Figure 3. DFT orbital drawing for the Ga−Fe σ bonding orbital (orbital 72).

(3) The Ga−Fe distance, 2.2248(7) Å, is only slightly shorter than the P−Fe distance, 2.244(1) Å, in $Ph_3PFe(CO)_4$.[6] One of the reasons that the Ga→Fe bond is shorter than the P→Fe bond is that the R−Ga: ligand has only four electrons in its valence shell.

While we think that these simple arguments based on well-known concepts and readily available data can clinch the argument by themselves, we have carried out density functional theory (DFT) calculations with a view to having quantitative results.

The DFT calculations[7] were carried out for a model molecule, $C_6H_5GaFe(CO)_4$, in which the bulky Ar* ligand in the reported structure[2] was replaced by a phenyl group. The molecular structure of the model molecule was obtained by complete geometry optimization in C_s symmetry. Shown in Figure 1 is a drawing of the optimized molecular structure of $C_6H_5GaFe(CO)_4$ together with comparison of pertinent structural parameters with experimental results. As can be seen, there is excellent agreement between the calculated values and those from the measured crystal structure data. In particular, the Ga−Fe distance was correctly predicted, namely, 2.220 Å, compared to the experimental value, 2.2248(7) Å. Furthermore, the linear arrangement of the ligands along the Ga−Fe bond in Ar*$GaFe(CO)_4$ was also reproduced, and the coordination of the CO ligands to the iron atom is almost exactly the same as in the crystal structure.

Most importantly, the results of the DFT calculations confirm unambiguously the arguments given above concerning the electronic structure and bonding in the type of compound being discussed here. The calculations reveal the following features in the electronic structure of the $C_6H_5GaFe(CO)_4$ molecule. The four highest occupied orbitals all have dominant d_π characters and are largely localized on the Fe atom. The two of higher energies (HOMO and HOMO-1) are essentially $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals which are in the plane containing three equatorial CO ligands and, therefore, also contribute to the π back-bonding between the Fe atom and these CO ligands. The other two pairs of Fe d_π orbitals ($3d_{xz}$ and $3d_{yz}$), on the other hand, have the right symmetries to interact with the $4p_x$ and $4p_y$ orbitals on gallium[3] and, therefore, to form Ga−Fe π bonds. However, as the calculations show, the orbital overlap of π type between the iron and gallium atoms is practically nil, probably due to the very large energy difference between an Fe 3d orbital and a Ga 4p orbital. As a result, the $3d_{xz}$ and $3d_{yz}$ orbitals became the lower two of the four HOMOs with little perturbation from the gallium atom, as shown clearly by the orbital drawing of HOMO-2 in Figure 2. The absence of d_π−p_π interaction leaves the Ga $4p_x$ and $4p_y$ orbitals unoccupied, and in fact, they are essentially the sole contributors to the two lowest unoccupied orbitals in the molecule.

The bonding between the gallium atom and iron atom may be best shown by the graphic representation of DFT orbital 72 (HOMO-5) in Figure 3. The Ga−Fe σ bonding character in this orbital is very similar to that in the corresponding orbital of $CpAlFe(CO)_4$,[8] in which the Al−Fe bonding was described by formation of a single Al→Fe bond. Natural bond orbital (NBO) analysis[9] for $C_6H_5GaFe(CO)_4$ gave rise to the positive charge +1.16 for Ga and the negative charge −0.55 for Fe. The total charge for the $Fe(CO)_4$ fragment is −0.69 according to NBO analysis. It is interesting to note that all these calculated charge distributions are also very similar to

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[6] Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.

[7] DFT calculations were carried out by using the gradient-corrected Becke exchange functional (Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098) and the Perdew-Wang correlation functional (Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992,** *45*, 13244) (BPW91). The basis set for Fe was that developed by Wachters (Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033). The s and p primitives were contracted using contraction Scheme 3, while six primitive d functions were contracted according to the method of Hay (Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377). The 6-311G basis set was used for Ga, and 6-31G sets were used for all other atoms. These basis sets reside in the Gaussian94 program (Frisch, M. J.; Frisch, Æ; Foresman, J. B. *Gaussian 94 User's Reference*; Gaussian Inc.: Carnegie Office Park, Building 6, Pittsburgh, PA 15106), which was employed for all calculations reported in this work. The molecular structure drawing in Figure 1 was generated with optimized atomic coordinates by using the SHELXL-93 program (Sheldrick, G. M. In *Crystallographic Computing 6*; Falck, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993).

[8] Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70.

[9] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 899.

those in $CpAlFe(CO)_4$.[8] Clearly, the bonding interaction between the Ga and Fe atoms is dominated by electron donation from Ga to Fe and, therefore, the bonding formulation $C_6H_5Ga{\rightarrow}Fe(CO)_4$ is justified. Further support for the similarity of the Al→Fe bond and the Ga→Fe bond is given by the CO stretching frequencies[8] for $Cp^*AlFe(CO)_4$, namely, 2024, 1948, and 1903 cm^{-1}, which are very close to those for $Ar^*GaFe(CO)_4$.

In conclusion, rather than there being "unambiguous and compelling evidence" for a Ga to Fe triple bond, we would say that all experimental data as well as theory support the formulation of this bond as a single Ga→Fe bond. It comes no closer to being a triple bond than do $R_3P{\rightarrow}M$ bonds in $R_3PFe(CO)_4$ compounds.

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