Experimental Confirmation of an Iron−Gallium Multiple Bond: Synthesis, Structure, and Bonding of a Ferrogallyne†

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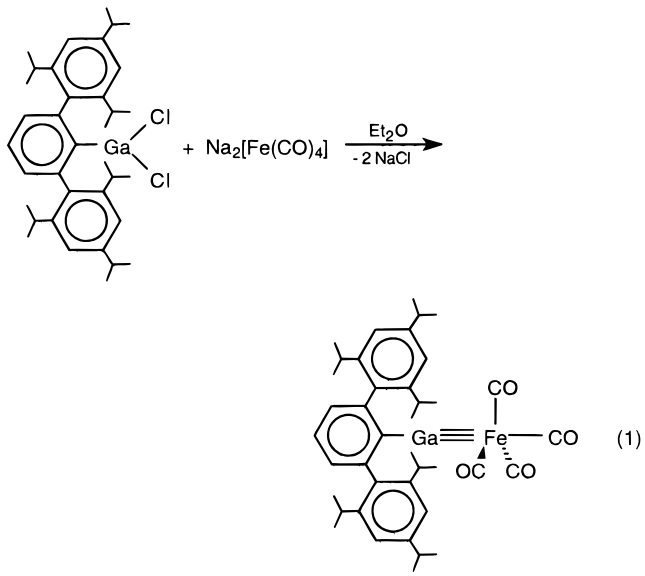
Summary: Reaction of disodium tetracarbonylferrate, $Na_2[Fe(CO)_4]$, with [2,6-bis(2,4,6-triisopropylphenyl)-phenyl]gallium dichloride, $(Mes^*_2C_6H_3)GaCl_2$ (Mes = 2,4,6-triisopropylphenyl), affords tetracarbonyliron [2,6-bis(2,4,6-triisopropylphenyl)phenyl]gallyne, $(CO)_4Fe{\equiv}Ga(C_6H_3Mes^*_2)$, as anaerobically stable yellow prism crystals. The title compound offers evidence in support of an iron−gallium triple bond—the first ferrogallyne.*

From the 1831 report by Zeise describing the preparation of potassium trichloroethyleneplatinate, $K[Pt(C_2H_4)Cl_3]$, thereby constituting the class of substances which have become known as organometallic compounds,[1] to experimental confirmation of quadruple bonds between transition metal centers,[2] the concept of metal−metal bonding has long fascinated chemists. Homonuclear multiple bonding between metal centers, historically the exclusive domain of transition metals, has recently shown promise in the organometallic chemistry of the post-transition or main group metals. Reports of compounds containing multiple bonding between transition metals and main group metals, long thought to be highly unlikely, have begun to appear. Indeed, a compound containing a molybdenum−germanium triple bond, $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge(C_6H_3Mes_2)$ (Mes = 2,4,6-$Me_3C_6H_2$), was recently reported.[3] The elements which constitute the 13th main group of the periodic table display an impressive diversity of chemical properties. Sandwiched between boron, the lightest and only nonmetal member, and thallium, the notoriously toxic heaviest member, are aluminum, gallium, and indium. These metallic congeners of group 13 constitute a recently discovered, if promisingly fertile, area relative to homonuclear metal−metal bonding.[4] However, to date, a compound containing multiple heterometallic bonding between a transition metal and a group 13 main group metal has not been reported. Herein, we report the synthesis,[5] molecular structure, and bonding of tetracarbonyliron [2,6-bis(2,4,6-triisopropylphenyl)-phenyl]gallyne, $(CO)_4Fe{\equiv}Ga(C_6H_3Mes^*_2)$ (Mes* = 2,4,6-$i\text{-}Pr_3C_6H_2$), **1**, isolated as anaerobically stable, yellow prism crystals from reaction of disodium tetracarbonylferrate, $Na_2[Fe(CO)_4]$, with [2,6-bis(2,4,6-triisopropylphenyl)phenyl]gallium dichloride, (2,6-$Mes^*_2C_6H_3$)-$GaCl_2$,[6] in ether (eq 1). The title compound presents



(1)

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unambiguous and compelling evidence of iron engaging in multiple bond formation with gallium—thereby constituting the first example of multiple bond formation between a transition metal and a main group 13 metal.

† Dedicated to Prof. Dr. Jörg Lorberth on the occasion of his 60th birthday.

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(3) (a) The preparation of $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge(C_6H_3Mes_2)$ resulted from reaction of $(Mes_2C_6H_3)GeCl$ with $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ in tetrahydrofuran followed by decarbonylation.[3b] (b) Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966.

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(5) All manipulations were carried out under anaerobic and anhydrous conditions. In a nitrogen-filled drybox (M Braun Labmaster 130), a reaction vessel charged with crystalline $Mes^*C_6H_3GaCl_2{\cdot}(hexane)_{0.5}$ (3.33 g, 5.0 mmol), $Na_2[Fe(CO)_4]{\cdot}(dioxane)_{1.5}$ (Aldrich Chemical Co., Inc.) (1.73 g, 5 mmol), and diethyl ether (30 mL). The system was allowed to stir at −78 °C for 4 h before slowly warming to room temperature. The mixture was stirred at room temperature for six additional days, at which point stirring was stopped and the system was allowed to stand undisturbed for several hours. The resulting dark red solution was decanted to another flask, and the solvent was reduced *in vacuo* and stored at −20 °C for 1 week. This yielded pale-yellow prism-shaped crystals. Mp: 224.3 °C. Yield: 1.08 g, 30% (based on $Mes^*C_6H_3GaCl_2{\cdot}(hexane)_{0.5}$. ^1H NMR (300 MHz, 297 K, C_4D_8O): δ 0.88 (d, 6H, $-CH_3$ (*i*-Pr)), 1.02 (d, 6H, $-CH_3$ (*i*-Pr)), 1.05 (d, 6H, $-CH_3$ (*i*-Pr)), 1.10 (d, 6H, $-CH_3$ (*i*-Pr)), 1.12 (d, 6H, $-CH_3$ (*i*-Pr)), 1.36 (d, 6H, $-CH_3$ (*i*-Pr)), 2.72 (m, 6H, $-CH$ (*i*-Pr)), 6.99−7.09 (m, 7H, $-CH$ (aromatic)). Elemental analyses (E + R Microanalytical Laboratories, Corona, NY). Anal. Calcd (found) for $C_{40}H_{49}O_4GaFe$ (719.39): C, 66.80 (66.03); H, 6.90 (7.09). IR (Nujol mull): ν(C−O) 2032 (s), 1959 (s), 1941 (vs), 1929 (vs) cm^{-1}.

(6) (a) $(2,6\text{-}Mes^*_2C_6H_3)GaCl_2{\cdot}(hexane)_{0.5}$ was prepared by reaction of $GaCl_3$ with $(2,6\text{-}Mes^*_2C_6H_3)Li$.[6b] (b) Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1997**, in press. (c) The preparation of $(2,6\text{-}Mes^*_2C_6H_3)Li$ has been previously described.[6d] (d) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

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This laboratory has had an interest in the concept of ligand steric loading, the utilization of sterically demanding ligands to stabilize unusual or particularly sensitive organometallic compounds, for some time. We have employed this technique to the organometallic chemistry of gallium with the 2,6-dimesitylphenyl, 2,6-$Mes_2C_6H_3$ (Mes = 2,4,6-$Me_3C_6H_2$) ligand.[7] In particular, this ligand has assisted in the stabilization of interesting sodium-[8] and potassium-based[9] $M_2[(Mes_2C_6H_3)Ga]_3$ (M = Na, K) cyclogallenes—cyclic Ga_3^{2-} dianionic, formal 2π-electron, aromatic systems, thus, offering experimental realization of *metalloaromaticity*.[10] It is noteworthy that this laboratory recently reported the first example of a gallium−gallium triple bond in $Na_2[Mes^*_2C_6H_3{-}Ga{\equiv}Ga{-}C_6H_3Mes^*_2]$—a most unusual *gallyne*—utilizing the still bulkier sterically demanding [2,6-bis(2,4,6-triisopropylphenyl)phenyl] ligand.[11] The present study was undertaken in an effort to assess the iron−gallium bond as a function of this ligand.

The solid state molecular structure of **1**[12] is given in Figure 1. The infrared (IR) spectrum of **1** displays four stretching frequencies in the carbonyl region. Compound **1** possesses a mirror plane which bisects the molecule while containing two carbon atoms of the central six-membered carbon ring of the ligand, two carbonyl groups (C(1)−O(1) and C(3)−O(3)), and both metal atoms (Fe(1) and Ga(1)). While the gallium−carbon (1.943(3) Å, compared to 1.949(8) Å for (Mes^*_2-C_6H_3)$GaCl_2$[6b]) and iron−carbon (1.766 Å mean) bond distances are generally unremarkable, the coordination environment about the iron−gallium fragment in **1** is most significant. Both the C(4)−Ga(1)−Fe(1) and Ga(1)−Fe(1)−C(3) fragments form nearly perfect linear arrangements with bond angles of 179.2(1)° and 178.9(2)°, respectively. The iron atom resides in an almost idealized trigonal bipyramidal environment, as three carbonyl groups ((C(1)−O(1), C(2)−O(2), and C(2A)−O(2A)) occupy equatorial positions while the axial sites are occupied by the remaining carbonyl group (C(3)−O(3)) and the gallium atom. The gallium atom in **1** has assumed a most unusual coordination posture of unassociated *two-coordinate linear*, while the Fe−Ga bond distance of 2.2248(7) Å is noteworthy as the shortest iron−gallium distance on record.

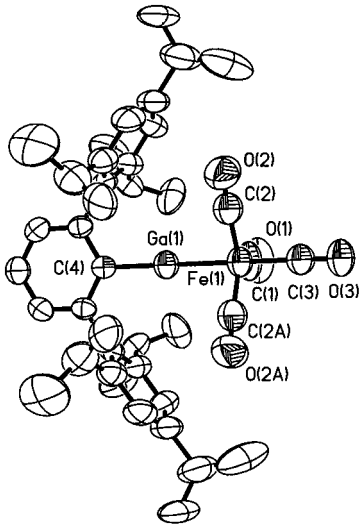

Figure 1. Molecular structure of $(CO)_4Fe{\equiv}Ga(C_6H_3$-$Mes^*_2)$, **1** (thermal ellipsoids are shown at 35% probability levels). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ga(1)−Fe(1) 2.2248 (7); Fe(1)−C(1) 1.758(7); Fe(1)−C(2) 1.764(4); Fe−C(3)1.766(5); Fe(1)−C(2A) 1.764(4); Ga(1)−C(4)1.943(3). Selected bond angles (deg): C(4)−Ga(1)−Fe(1) 179.2(1); C(3)−Fe(1)−Ga(1) 178.9(2); C(1)−Fe(1)−C(2) 120.3(1).

Stabilization of the iron−gallium bond has been fueled by a desire to utilize ferrogallanes as single-source molecular precursors in advanced electronic devices.[13] The following ferrogallanes (and corresponding Fe−Ga bond distances) are relevant to this discussion: $(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}Ga(t\text{-}Bu)_2$ (Fe−Ga, 2.417(1) Å), $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2Ga(t\text{-}Bu)$ (Fe−Ga, 2.416(1) and 2.406(1) Å), $(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}Ga(t\text{-}Bu)_2{\cdot}\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ (Fe−Ga, 2.441(1) Å),[14] and $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_3Ga$ (Fe−Ga_{mean}, 2.444(8) Å).[15] These Fe−Ga bond distances are conveniently compared with that recently reported for $[PPN]_2[(CO)_4Fe{-}Ga(Me){-}Fe(CO)_4]$ (Fe−Ga, 2.416 Å).[16] Two points are noteworthy concerning the aforementioned ferrogallanes: (1) The Fe−Ga bond distances are remarkably consistent and considerably longer than

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(12) A pale yellow prism crystal of **1**, approximate dimensions 0.30 mm × 0.40 mm x 0.60 mm, was selected for X-ray crystallographic analysis and mounted in a thin glass capillary tube under an atmosphere of pure nitrogen gas. The X-ray intensity data were measured at 293 K on a standard Siemens SMART CCD-based X-ray diffractometer system equipped with a Mo Kα target X-ray tube (λ = 0.710 73 Å) operated at 2000 W power. The detector was placed at a distance of 5.024 cm from the crystal. A total of 1321 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s/frame. The total data collection time was 13.5 h. The crystalline compound proved to be an excellent example of *non-merohedral (rotational) twinning*. Thus, the crystallographic analysis and integration of the raw frame data required special techniques. In order to index the reflections, it was first necessary to divide them into two sets corresponding to each of the two components. Independent indexing of each set of reflections gave unit cells with nearly identical cell parameters, but with different orientation matrices. Analysis of these matrices indicated a twin law best described by a 180° rotation about the [100] direction in direct space. The frames were then integrated twice, once with each orientation matrix, with the Siemens SAINT software package using a narrow-frame integration algorithm to yield two reflection files. These reflection files were subsequently combined with the TWHKL program to produce a merged reflection file in a suitable format for input to the SHELXTL twinning routines. The integration of the data using a monoclinic unit cell yielded a total of 23 748 reflections to a maximum 2θ angle of 45.0° (0.90 Å resolution), of which 9739 were independent (R_{int} = 2.70%, R_{sig} = 3.75%) and 8738 (90.0%) were greater than $4\sigma(F)$. The final cell parameters of a = 8.8708(4) Å, b = 24.3484(11) Å, c = 9.4858(4) Å, β = 106.685(1)°, and V = 1962.6(2) Å^3 are based upon the refinement of the *xyz*-centroids of 5625 reflections above $20\sigma(I)$. Analysis of the data showed negligible decay during data collection. The structure was solved and refined using the Siemens SHELXTL 5.0 Software Package, using the space group $P2_1/m$ (No. 11), with Z = 2 for the formula unit. The final model incorporated the rotational twinning parameter (refined to 0.39) as well as a disorder model for the isopropyl groups. The final anisotropic full-matrix least-squares refinement on F^2 converged at R1 = 5.58%, wR2 = 13.53%, and a goodness-of-fit of 1.114. The largest peak on the final difference map was 0.37 e$^-$/Å^3. The calculated density for **1** is 1.217 g/cm^3, and F(000) is 756.

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that observed for **1**; and (2) The coordination mode of the gallium centers is either three-coordinate trigonal planar or four-coordinate tetrahedral. Significant Fe−Ga π-bonding in these compounds appears highly unlikely. Indeed, the literature does not reveal an unambiguous example of an iron−gallium double bond—a *ferrogallene*.

Regarding the metal−metal bonding in the title compound, two models initially emerge: (1) an extreme contact ion pair model, $(Mes^*_2C_6H_3)Ga^{2+}\cdots Fe(CO)_4^{2-}$; and (2) a stable $(CO)_4Fe{=}Ga(C_6H_3Mes^*_2)$ species containing an iron−gallium double bond. Similar to the interesting $[(\eta^5\text{-}C_5Me_5)Al{-}Fe(CO)_4]$[17] compound, the contact ion pair model may largely be eliminated on the basis of the position of the carbonyl absorption bands.[18] Thus, from a purely covalent perspective, the dominant model would appear to be the $(CO)_4Fe{=}Ga(C_6H_3Mes^*_2)$ double-bonded species wherein the gallium center is sp hybridized. It is our position that, in addition to the formal iron−gallium double bond, the *linearity* about the gallium center enables additional overlap from a *filled* iron d orbital (of appropriate symmetry) with the remaining *empty* p orbital on gallium, thereby forging a second π-bond. The possibility of π-bonding resulting from overlap of a filled transition metal d orbital with an empty p orbital of a group 13 metal (indium) has previously been suggested.[15,19]

With ferrocene approaching nearly icon status as, arguably, the best-known organometallic compound, perhaps no other metal is more synonymous with organometallic chemistry than iron. It is, therefore, interesting that an unambiguous example of iron engaging in multiple bond formation with a main group metal remains elusive. In this regard, decarbonylation of $(CO)_2(\eta^5\text{-}C_5Me_5)Fe{-}Ge(s\text{Mes})$ (*s*Mes = super mesityl, 2,4,6-*t*-$Bu_3C_6H_3$), was attempted in an effort to approach $(CO)(\eta^5\text{-}C_5Me_5)Fe{\equiv}Ge(s\text{Mes})$.[20] Rather than isolating the desired iron−main group metal triple bond compound, C−H insertion ensued, affording a germanium hydride complex as metalation of one of the *tert*-butyl groups took place. Notably, the preparation of **1** did not involve decarbonylation but rather a surprisingly straightforward synthetic procedure. As evidenced by a recent review,[21] the concept of multiple bonding between main group metals and transition metals is a timely topic.

The very short Fe−Ga bond distance coupled with the unassociated two-coordinate linear coordination about the gallium atom and the linear Fe−Ga−C fragment are consistent with an iron−gallium triple bond in $(CO)_4Fe{\equiv}Ga(C_6H_3Mes^*_2)$—a *ferrogallyne*.

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Supporting Information Available: Text giving the details of the X-ray structure determination and tables of crystallographic data, atomic coordinates, positional parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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