Organometallics 1990, *9*, 2864-2865

The First Example of a Ferrocenylgallane: Synthesis, Properties, and X-ray Crystal Structure of the $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$ Dimer

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Received July 11, 1990

Summary: The first ferrocenylgallane, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$, has been prepared by reaction of (chloromercurio)ferrocene with trimethylgallium in toluene and characterized by ^1H NMR, elemental analyses, and single-crystal X-ray diffraction. The Ga–C bond distance of 2.587 (5) Å in the Ga_2C_2 ring is among the longest gallium–carbon bonds reported.

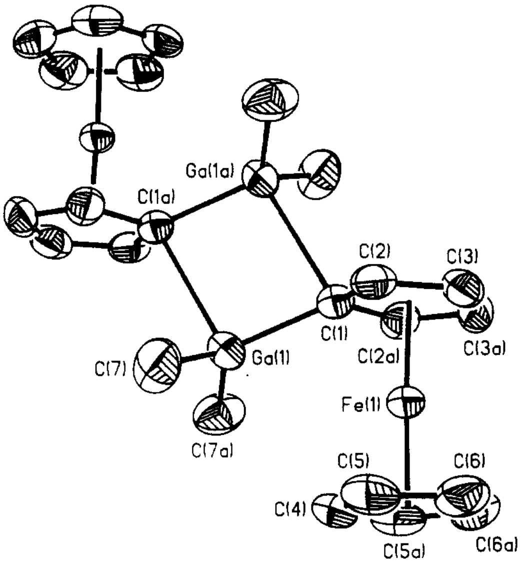

Figure 1. Thermal ellipsoid plot of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Ga(1)–C(1), 1.991 (5); Ga(1)–C(7), 1.964 (5); Ga(1)–Ga(1a), 2.999 (1); C(1)–C(2), 1.442 (5); C(2)–C(3), 1.417 (5); C(3)–C(3a), 1.408 (9); C(4)–C(5), 1.407 (6); C(5)–C(6), 1.405(6); C(6)–C(6a), 1.409 (9); C(1)–Ga(1)–C(7), 114.5 (2); C(7)–Ga(1)–C(7a), 125.5 (3); Ga(1)–C(1)–C(2), 123.4 (2); C(2)–C(1)–C(2a), 105.2 (4); C(1)–C(2)–C(3), 109.3 (3); C(2)–C(3)–C(3a), 108.1 (2); C(5)–C(4)–C(5a), 108.9 (5); C(4)–C(5)–C(6), 107.3 (4); C(5)–C(6)–C(6a), 108.3 (3).

The organometallic chemistry of the main-group elements, particularly that of gallium, is currently enjoying great popularity. While the potential utility of organogallium compounds as precursors to semiconductor materials is principally responsible for this renaissance, seminal studies concerning fundamental aspects of structure and bonding in these compounds are particularly noteworthy.[1] The great strides made in organogallium chemistry notwithstanding, this field has not developed in parallel with organotransition-metal chemistry. Organometallic derivatives of ferrocene provide an illustrative example of this disparity. While ferrocenyl-based transition-metal complexes are one of the most investigated facets of organotransition-metal chemistry,[2] the literature reveals a paucity of studies concerning ferrocenylgallanes, ferrocenyl derivatives of organogallium species.

The first example of a ferrocenylgallane, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$, has been synthesized by reaction of (chloromercurio)ferrocene with trimethylgallium in toluene (eq 1) and characterized by ^1H NMR, elemental analysis,[3]

$$(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)HgCl] + Ga(CH_3)_3 \rightarrow \tfrac{1}{2}[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2 + (CH_3)HgCl \quad (1)$$

and single-crystal X-ray diffraction.[4] A thermal ellipsoid plot of the $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$ molecule is given in Figure 1.

Several points are worthy of note regarding the structure and bonding in $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$. The molecule resides about a $2/m$ site, which coincides with the center of the Ga_2C_2 four-membered ring. The crystallographic mirror plane associated with the $2/m$ site contains both gallium atoms and both iron atoms. As the mirror plane bisects the eclipsed cyclopentadienyl rings, it also contains atoms C(1), C(1a), C(4), and C(4a). The title compound consists of two ferrocenyl units bridged by two dimethylgallium units, via carbon atoms of the substituted cyclopentadienyl groups, resulting in an asymmetric Ga_2C_2 four-membered ring. The Ga_2C_2 ring contains two short Ga–C bonds of 1.992 (5) Å (Ga(1)–C(1) and Ga(1a)–C(1a)) and two long Ga–C bonds of 2.587 (5) Å (Ga(1)–C(1a) and Ga(1a)–C(1)). Indeed, the title com-

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[2] Marr, G.; Rockett, B. W. *J. Organomet. Chem.* **1988**, *343*, 79.

[3] A reaction vessel was charged with $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)HgCl]$ (Strem Chemical Co.; 1.0 g, 2.5 mmol) and freshly distilled toluene (20 mL) inside the drybox. The dark brown (chloromercurio)ferrocene was completely insoluble in toluene. Trimethylgallium (Ethyl Corp.; 0.50 mL, 5 mmol) was added slowly added via syringe to this heterogeneous system. As no reaction was observed to occur at room temperature, the reaction vessel was removed from the drybox and heated in an oil bath (120 °C). Within 2 h in the oil bath, the reaction was judged to be complete as all of the $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)HgCl]$ had disappeared, resulting in a homogeneous deep red solution. Once the solution cooled to −15 °C, a number of brilliant red, rectangular, extremely air-sensitive, X-ray quality crystals resulted in quantitative yield (based on (chloromercurio)ferrocene). Mp = 114 °C. ^1H NMR ($CDCl_3$): δ 4.15 (m, 18 H, $(C_5\mathit{H}_5)Fe(C_5\mathit{H}_4)$), 0.07 (s, 12 H, $Ga(C\mathit{H}_3)_2$). Anal. (Atlantic Microlab, Inc. Norcross, GA) Calcd for $C_{24}H_{30}Fe_2Ga_2$: C, 50.63; H, 5.27. Found: C, 49.05; H, 5.06. The severe instability of the title compound contributes to the less than ideal elemental analysis. Upon exposure to air, the title compound quickly decomposes, going from deeply colored red crystals to an amorphous green substance. Characterization of the decomposition substance was not attempted.

[4] X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\theta$ scan technique with Mo Kα radiation (λ = 0.710 73 Å) at 21 °C. The title compound crystallizes in the monoclinic space group $C2/m$ (No. 12) with unit cell parameters a = 13.113 (3) Å, b = 11.786 (3) Å, c = 7.674 (2) Å, β = 108.61 (2)°, D_{calcd} = 1.68 g cm^{-3}, and υ = 1124.1 (4) Å^3 for $Z = 2$. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques and were refined by using isotropic thermal parameters. The structure was solved by direct methods and refined, based on 866 observed reflections with intensities $I > 3\sigma(I)$ in the range 3.5° < 2θ < 48.0°, with the use of SHELXTL (Sheldrick, G. M. *SHELXTL, Crystallographic Computing System*, Revision 5.1; Nicolet Instruments Division: Madison, WI, 1986). Refinement converged at R = 0.031, R_w = 0.042.

0276-7333/90/2309-2864$02.50/0

pound may be considered a weakly bonded dimer of ferrocenyldimethylgallane, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2$. The Ga(1)-C(1)-Ga(1a) bond angle is 80.7 (3)° while the C(1)-Ga(1a)-C(1a) bond angle is 99.3 (3)°. The Ga⋯Ga contact of 2.999 (1) Å across the Ga_2C_2 ring does not indicate significant metal-metal interaction.

The Ga-C bond distances in $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$ warrant closer examination. The Ga(1)-C(1) bond distance of 1.992 (5) Å in the Ga_2C_2 four-membered ring is comparable to Ga-C distances within trimethylgallium adducts.[5] While the Ga(1)-C(7) bond distance of 1.964 (5) Å in the dimethylgallium fragment compares well with the Ga-C distance of 1.968 (4) Å reported for trimesitylgallium,[6] a more informative comparison would concern Ga-C distances in compounds containing dimethylgallium fragments. The recently reported organogallium-aza crown ether complex $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$[7] is a convenient example. The Ga-C bond distances of 1.95 (2) and 1.97 (2) Å in the $Ga(CH_3)_2$ fragment of the organogallium-aza crown complex are comparable to Ga-C distances found in the title compound for the dimethylgallium fragment. At a distance of 2.587 (5) Å, the remaining Ga(1)-C(1a) bond distance in the Ga_2C_2 fragment is among the longest gallium-carbon bonds reported.

It is interesting to view the Ga-C bonding within the Ga_2C_2 fragment of the title compound as a balance of electronic and steric effects. The fact that the shorter Ga-C bonds in the Ga_2C_2 fragment (Ga(1)-C(1) and Ga(1a)-C(1a)) involve the Ga-C bond cis to the remainder of each ferrocenyl group while the longer Ga-C bonds (Ga(1)-C(1a) and Ga(1a)-C(1)) involve the Ga-C bond trans to the remainder of the ferrocenyl group is noteworthy. If it is assumed that each carbon atom of the Ga_2C_2 fragment contributes one sp^2 hybrid orbital and one electron while each gallium atom contributes two sp^3 hybrid orbitals and one electron, the steric effects imposed by the ferrocenyl groups and the dimethylgallium units would manifest themselves most prominently in steric repulsion between these groups. Thus, steric repulsion between these groups would ultimately force a rotation of these two groups away from each other. This would result in the Ga-C orbital overlap being greater (i.e., a shorter Ga-C bond) in the Ga-C bond cis to the unsubstituted cyclopentadienyl group. Moreover, the short Ga-C bond is roughly in the plane of the σ-bonded cyclopentadienyl ring and benefits from a greater orbital overlap whereas the longer Ga-C bond is tilted further out of the cyclopentadienyl plane, thus resulting in a less effective overlap and weaker (longer) bond.

The literature reveals only three other ferrocenyl-group 13 metal alkyl derivatives that have been structurally characterized: a series of ferrocenylalanes.[8] Interestingly, the $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)Al_2R_4Cl]$ (R = CH_3, C_2H_5) ferrocenylalanes were prepared by an analogous reaction which resulted in the ferrocenylgallane described herein (eq 1). As this area of main-group chemistry is largely unexplored, fundamental issues of structure, bonding, and reactivity abound. Future contributions will address these issues.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Supplementary Material Available: A summary of data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (9 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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(5) For representative Ga-C bond distances, see, for example: Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179 and references cited therein.

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Octakis(2,6-diethylphenyl)octastannacubane

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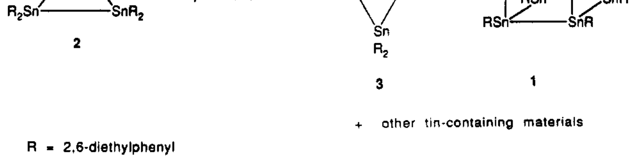
Received July 24, 1990

Summary: Thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) in naphthalene provides red octakis(2,6-diethylphenyl)octastannacubane (**1**), which has been fully characterized, including crystallographic analysis. Compound **1** represents the first example of the organostannane cluster series $(RSn)_n$.

Scheme I



Recently, several theoretical investigations have centered on predicting the stability of the class of group IVA polycyclic structures M_nH_n (M = Si, Ge, Sn, and Pb), where $n = 4$ (tetrahedrane), $n = 6$ (prismane), and $n = 8$ (cubane).[1] An interesting result of these investigations is the prediction that the cubane[2] structures possess lower degrees of strain energy as one descends the group IVA with octaplumbacubane, Pb_8H_8, being the most stable structure.[3] The conclusion, therefore, is that the heavier atom

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(2) Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane by IUPAC nomenclature convention.