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Synthesis and Molecular Structure of $[\mathrm{Li(THF)\cdot 12\text{-}crown\text{-}4}][(\mathrm{PhC{=}\overline{CPhPhC}{=}CPh})_2\mathrm{Ga}]$: The First Spirogallane

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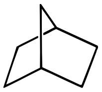
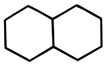
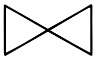
The utilization of sterically demanding ligands such as *m*-terphenyls has recently afforded a number of interesting organometallic compounds of gallium ranging from 2π-electron metalloaromatic cyclogallenes[1−4] to reports of a gallyne[5,6] and a ferrogallyne.[7] The unique, if unprecedented, metal−metal bonding in these unusual compounds has fueled a rather spirited debate in the chemistry community.[8,9] Common features in these organogallium compounds include sub-valency, low-coordination numbers, and a striking resemblance to iconic compounds of carbon. The third tenet is particularly germane to this contribution. Along with bridged and fused ring systems, spirocyclic compounds (below) constitute the ubiquitous class of bicyclic organic molecules.

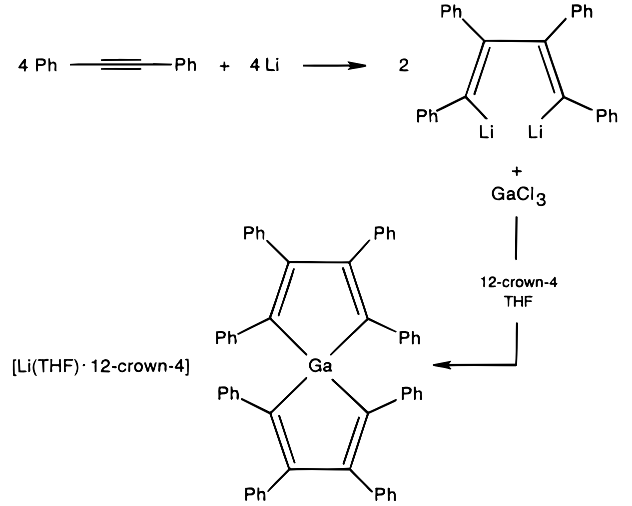






The tetrahedral carbon atom common to both rings, evident in the simplest spirocycle, spiropentane, is distinctive. Spirocycles beyond carbon, such as silicon-based spirocycles,[10] are encountered considerably less often. Although small ring compounds are commonplace in group 13 organometallic chemistry, the literature reveals few examples of spirocyclic compounds wherein the shared tetrahedral atom is one of these metals. Herein we report the synthesis[11] and molecular structure[12] of $[\mathrm{Li(THF)\cdot 12\text{-}crown\text{-}4}][(\mathrm{PhC{=}\overline{CPhPhC}{=}CPh})_2\mathrm{Ga}]$, isolated from reaction of 1,4-dilithiotetraphenylbutadiene−prepared from the action of metallic lithium on diphenylacetylene−with gallium chloride in the presence of 12-crown-4/THF (Scheme 1). The title compound, characterized by ^{1}H NMR, elemental analyses, and single-crystal X-ray diffraction, is significant as the anion is the first example of a *spirogallane*−a bicyclic organometallic compound possessing a tetrahedral gallium atom common to both rings (Figure 1).

Scheme 1



While synthetic reports of 1,4-dilithiotetraphenylbutadiene date back decades,[13] it is interesting that X-ray structural data (of the 1,2-dimethoxyethane adduct) of this moiety were only reported recently.[14] Although the greatest organometallic utility of tetraphenylbutadiene is found in transition metal chemistry, the main group chemistry of this ligand is also noteworthy. Tetraphenylbutadiene has been particularly beneficial in the stabilization of

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[11] Inside the drybox (M Braun Labmaster 130) a reaction vessel was charged with 1,4-dilithiotetraphenylbutadiene, prepared by reaction of lithium (0.068 g, 10 mmol) and diphenylacetylene (1.78 g, 10 mmol) in diethyl ether, gallium chloride (0.44 g, 2.5 mmol), and diethyl ether (25 mL). Upon returning to the benchtop, the system was allowed to stir for 4 h. This solution was filtered and immediately introduced to 12-crown-4 (0.41 mL, 2.5 mmol), resulting in a yellow powdery precipitate. After evaporation of the solvent, tetrahydrofuran (10 mL) was added, resulting in yellow crystals (0.63 g, 24% yield): mp 193.2 °C. Anal. (E+R Microanalytical Laboratories, Parsipanny, NJ). Calcd (found) for $C_{76}H_{80}O_9LiGa$: C, 75.20 (75.89); H, 6.64 (6.38). ^{1}H NMR (300 MHz, 298 K, C_4D_8O): δ 1.13 (t, 4H, $-CH_2$ (THF)), 3.40 (t, 4H, $-CH_2$ (THF)), 3.60 (s, 16H, $-CH_2$ (12-crown-4)), 6.79 (m, 40H, $-CH$ (aromatic)). ^{13}C NMR (300 MHz, 298 K, C_4D_8O) proved largely uninformative as several signals overlapped in the 120−135 ppm region.

[12] A number of crystals of the title compound were mounted in glass capillaries under an atmosphere of nitrogen inside the drybox. X-ray intensity data on an appropriate sample were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell parameters and an orientation matrix for data collection, from a least-squares analysis of the setting angles of 25 carefully centered reflections in the range $10.0 < 2\theta < 25.0°$, were obtained. The monoclinic space group is $P2_1/n$ (No. 14) with unit cell parameters $a = 13.241(3)$ Å, $b = 26.440(6)$ Å, $c = 17.260(4)$ Å, $\beta = 94.140(10)°$, $D_{\mathrm{calcd}} = 1.144$ g cm^{-3}, and $V = 6027(2)$ Å^3 for $Z = 4$. Full-matrix F^2 refinement, based upon 4843 observed reflections, $I > 2\sigma(I)$, using the SHELXTL 5.0 system of computer programs, converged at $R1 = 0.067$, $wR2 = 0.23$.

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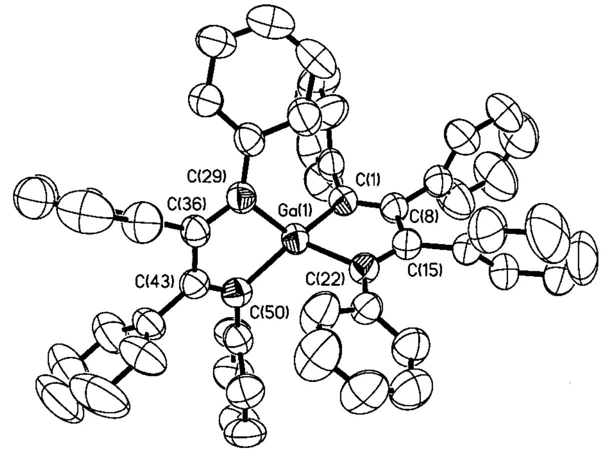

Figure 1. Molecular structure of the $[(\mathrm{PhC{=}\overline{CPhPhC}{=}CPh})_2\mathrm{Ga}]^-$ anion (thermal ellipsoids are shown at 35% probability levels). Selected bond distances (Å) and angles (deg): Ga−C(1), 2.003(5); Ga−C(22), 2.023(5); Ga−C(29), 2.019(5); Ga−C(50), 2.001(5); C(1)−C(8), 1.353(7); C(8)−C(15), 1.504(7); C(15)−C(22), 1.346(7); C(29)−C(36), 1.361(7); C(36)−C(43), 1.502(8); C(43)−C(50), 1.363(8); C(1)−Ga−C(50), 131.8(2); C(29)−Ga−C(50), 87.8(2); C(1)−Ga−C(29), 121.8(2); C(22)−Ga−C(50), 115.5(2); C(1)−Ga−C(22), 87.4(2); C(22)−Ga−C(29), 115.0(2); C(1)−C(8)−C(15), 118.4(5); C(8)−C(15)−C(22), 118.1(5); C(29)−C(36)−C(43), 118.0(5); C(36)−C(43)−C(50), 118.3(5).

main group compounds such as boron,[15] silicon,[16] sulfur,[17] selenium,[18] arsenic,[19] and germanium[20] based five-membered-ring heterocycles.[21] Relative to compounds of tetraphenylbutadiene with group 13 metals, the literature reveals only (pentaphenyl)-aluminacyclopentadiene and its complex with 1,5-cyclooctadienenickel.[22]

Although the cation consists of a lithium ion complexed by both 12-crown-4 and THF, a number of points are noteworthy concerning structure and bonding in the $[(\mathrm{PhC{=}\overline{CPhPhC}{=}CPh})_2\mathrm{Ga}]^-$ anion. The general features of the butadiene backbone, essentially two C=C double bonds bridged by a C−C single bond and C−C−C bond angles of ca. 120°, are quite comparable to that as previously reported for the 1,2-dimethoxyethane adduct of the ligand. Four-coordinate gallium atoms with their coordination spheres saturated by carbon atoms are reasonably rare with the recently reported $\mathrm{Me_3Ga}$:carbene complex[23] being a notable example. The coordination of the gallium atom in the spirogallane anion is severely distorted tetrahedral with bond angles ranging from 87.4(2)° to 131.8(2)° for C(1)−Ga−C(22) and C(1)−Ga−C(50), respectively. Indeed, this C−Ga−C bond angle range of 44.4° is the largest on record for a four-coordinate tetrahedral gallium atom. For comparison, the corresponding range of C−Ga−C bond angles for $\mathrm{Me_3Ga}$:carbene is a mere 8.3° (105.9° to 114.2°). In addition, the Ga−C bond distances are uniformly long, reaching a maximum value of 2.023(5) Å—a bit shorter than the longest Ga−C bond distance reported for the $\mathrm{Me_3Ga}$:carbene of 2.214(6) Å. Most significant, however, is the fact that the gallium atom in the anion is common to both five-membered tetraphenylbutadiene-based heterocycles. The two five-membered rings formed by the two tetraphenylbutadiene units and the gallium atom are perfectly planar and orthogonal to each other—thereby contributing to the distorted environment about the metal. The title compound offers a convenient organometallic retort to the well-known organic class of spirocyclic molecules: the $[(\mathrm{PhC{=}\overline{CPhPhC}{=}CPh})_2\mathrm{Ga}]^-$ anion is the first example of a *spirogallane*.

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Supporting Information Available: A textual summary of data collection and refinement and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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