Are Heterocyclic 2π-Electron Aromatic Systems HC−Ga(H)−CH, M[HGa−C(H)−GaH], [HGa−C(H)−GaH]⁻, HSi−Ga(H)−SiH, M[HGa−Si(H)−GaH] (M = Li, Na, and K), and [HGa−Si(H)−GaH]⁻ Stable?

Yaoming Xie,[†] Peter R. Schreiner,[‡] Henry F. Schaefer III,*,[†] Xiao-Wang Li,[§]   and Gregory H. Robinson[§]

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2556, the Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany, and the Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

Ab initio and density functional (BHLYP, B3LYP, and BP86) quantum mechanical methods were applied to predict the structures, properties, and stabilities of HC−Ga(H)−CH, M[HGa−C(H)−GaH], [HGa−C(H)−GaH]⁻, HSi−Ga(H)−SiH, M[HGa−Si(H)−GaH], and [HGa−Si(H)−GaH]⁻ (M = Li, Na, K) three-membered ring systems. These structures derive from the previously theoretically and experimentally characterized parent homonuclear cyclogallenes $M_2(GaH)_3$. Basis sets of triple-ζ plus double polarization augmented with diffuse functions (TZ2P+diffuse) quality were employed at self-consistent field (SCF) and density functional levels of theory. Equilibrium geometries, harmonic vibrational frequencies, and chemical shifts are reported to facilitate experimental verification of the computed structures. All title compounds are minima and their geometries as well as their properties compare well with the cyclogallene three-membered ring compounds $M_2(GaH)_3$. Singly charged [HGa−Si(H)−GaH]⁻ and even neutral HSi−Ga(H)−SiH may well be feasible experimental targets. The large negative nucleus independent chemical shifts (NICS), used as a criterion for aromatic cyclic delocalization, suggest that all title compounds are *aromatic*.

Introduction

Even as its domain is largely in organic chemistry, aromaticity represents, arguably, the most fascinating concept throughout the whole of chemistry. While benzene is the prototypical organic aromatic reference compound, borazine (**1**),[1] since its preparation in 1926, has frequently been referred to as "inorganic benzene".[2] Although isoelectronic and possessing similar *physical* properties, the *chemical* behavior of benzene and borazine is quite different, as attack of electrophiles leads to substitution and addition products, respectively.[2] Thus, the question of whether or not borazine is truly aromatic is still being debated.[3−10]

In contrast to 6π-electron systems, 2π-electron aromatic systems of the heavier group 13 congeners have received little attention. Very recently, two such com-

1
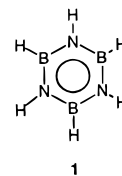
pounds, $M_2(GaR)_3$ (**2a**, M = Na, R = 2,6-(Me₃C₆H₂)₂-C₆H₃; **2b**, M = K) were synthesized as well as characterized both experimentally[11,12] and theoretically.[13]

(3) (a) Kaldor, A. *J. Chem. Phys.* **1971**, *55*, 4641. (b) Bernstein, E. R.; Reilly, J. P. *Ibid.* **1972**, *57*, 3960. (c) Doering, J. P.; Gesanken, A.; Hitchcock, A. P.; Fischer, P.; Moore, J.; Olthott, J. K.; Tossell, J.; Raghavachari, K; Robin, M. B. *J. Am. Chem. Soc.* **1986**, *108*, 3602. (d) Tossell, J. A.; Moore, J. H.; McMillan, K.; Subramanian, C. K.; Coplan, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 1114. (e) Betowski, L. D.; Solomon, J. J.; Porter, R. F. *Inorg. Chem.* **1972**, *11*, 424. 6. (f) Doiron, C. E.; Grein, F.; McMahon, T. B.; Vasudevan, K. *Can. J. Chem.* **1979**, *57*, 1751.
(4) Harshbarger, W.; Lee, G.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 1683.
(5) Kaldor, A.; Porter, R. F. *Inorg. Chem.* **1971**, *10*, 775.
(6) (a) Lonsdale, K. *Nature* **1959**, *184*, 1060. (b) Watanabe, H.; Ito, K; Kubo, M. *J. Am. Chem. Soc.* **1960**, *82*, 3294. (c) Muszkat, K. A. *Ibid.* **1964**, *86*, 1250. (d) Kubo, M.; Watanabe, H.; Ito, K. *Ibid.* **1964**, *86*, 1251.

Remarkably, these three-membered ring organogallium compounds, cyclogallenes, are extraordinarily thermally stable and were judged to be aromatic.

2 [M = Li, Na, K; R = 2,6-(Me₃C₆H₂)₂C₆H₃–)]
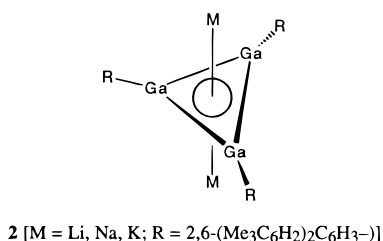
In **2** the two alkali metals donate their two valence s-electrons into the three empty gallium p-orbitals, yielding the Hückel-aromatic 2π-electron cyclogallene system. The cyclogalle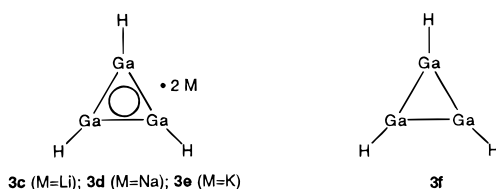ne rings in $M_2(RGa)_3$ are valence-isoelectronic to the cyclopropenium cation moiety in **3a** (R = H, C_6H_5),[14] the smallest organic 2π-electron aromatic ring compound.

3a　　　　　**3b**
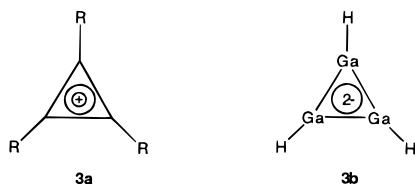
The computed (B3LYP TZ2P+diff) structures and properties for the 2π-electron cyclogallenes $[GaH]_3^{2-}$ (**3b**) and $M_2[GaH]_3$ (**3c**, M = Li; **3d**, M = Na; and **3e**, M = K)[13] agree well with X-ray data.[12] The cyclogallene systems possess well-defined, highly symmetrical π-molecular orbitals and display large nucleus-independent chemical shifts (NICS, see methods section below), which identifies them as aromatic compounds. In contrast, neutral $[GaH]_3$ (**3f**) is not stable and opens to an acyclic structure.

3c (M=Li); **3d** (M=Na); **3e** (M=K)　　　　　**3f**

We have now become interested in singly negatively charged and neutral analogs of the cyclogallene dianions. This can be achieved by replacing one or two gallium atoms in the three-membered ring of **3b** by an atom of the group 14 (e.g., carbon or silicon). As experimental investigations on these compounds are well underway, the following theoretical examination of the 2π-electron aromatic systems HC−Ga(H)−CH (**4**), M[HGa−C(H)−GaH] (**5a**, M = Li; **5b**, M = Na; **5c**, M = K), [HGa−C(H)−GaH]⁻ (**6**), HSi−Ga(H)−SiH (**7**), M[HGa−Si(H)−GaH] (**8a**, M = Li; **8b**, M = Na; **8c**, M = K), and [HGa−Si(H)−GaH]⁻ (**9**) is timely. We report on the structures, vibrational frequencies, and selected NMR shifts and discuss the relative stabilities of the title compounds in terms of their thermochemistry and aromatic character.

Methods

Geometries were fully optimized at the self-consistent field (SCF) and the density functional theory (DFT) levels of theory. In this paper, we employed three DFT methods: (1) BHLYP, utilizing Becke's half Hartree−Fock with half Slater exchange functional[15] in conjunction with the Lee−Yang−Parr (LYP) nonlocal correlation functional;[16] (2) B3LYP, using Becke's three-parameter hybrid exchange functional[17] and the LYP correlation functional; (3) BP86, employing Becke's 1988 exchange functional[18] and Perdew's 1986 gradient-corrected correlation functional.[19] Methods 1 and 2 are hybrid Hartree−Fock/density functional theory (HF/DFT) procedures, while 3 is a pure DFT approach.

The basis set was of triple-ζ quality augmented with two sets of d-polarization functions (TZ2P) for the alkali metals. The triple-ζ functions for lithium were derived from the (9s5p/4s2p) basis set of Thakkar *et al.*,[20] but were recontracted to (9s5p/5s3p). For sodium, TZ functions were taken from McLean and Chandler's basis set (12s9p/6s5p);[21] for potassium, we used Wachters's (14s9p/10s6p) basis set[22] augmented with two sets of even-tempered p functions with exponents 0.085202 and 0.031737,[23] which may be regarded as describing the potassium $4p$ orbital. The orbital exponents for the polarization functions were $\alpha_d(Li) = 0.400, 0.100, \alpha_d(Na) = 0.350, 0.0875, \alpha_d(K) = 0.200, 0.050$. The technical description of the basis sets is Li(9s5p2d/5s3p2d), Na(12s9p2d/6s5p2d), and K(14s11p2d/10s8p2d).

The basis set for the elements in the three-membered ring fragment, i.e., for Ga, C, Si, and H, was TZ2P augmented with diffuse functions. For Ga, the TZ functions are from Dunning's 14s11p5d primitive basis set contracted to 10s8p2d.[24] For C, the TZ part is from Dunning's (10s6p/5s3p).[25] For Si, the TZ part is McLean and Chandler's (12s9p/6s5p) basis.[21] All these TZ basis sets were augmented with one diffuse s and one set of p diffuse functions as well as two sets of d polarization functions. The exponents of the diffuse functions were $\alpha_s(Ga)$

(7) (a) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Hymas, P. A.; Raimondi, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 719. (b) Kato, H.; Hirao, K.; Sano, M. *J. Mol. Struct., (THEOCHEM)* **1983**, *104*, 489. (c) Ramondo, F.; Portalone, G.; Bencivenni, L. *J. Mol. Struct., (THEOCHEM)* **1991**, *82*, 29. (d) Jayasuriya, K. *J. Mol. Struct., (THEOCHEM)* **1991**, *82*, 381. (e) Anderson, W. P.; Edwards, D.; Zerner, M. C. *Chem. Phys. Lett.* **1982**, *88*, 185. (f) Nelson, J. T.; Pietro, W. J. *Inorg. Chem.* **1988**, *28*, 544.

(8) Haddon, R. C. *Pure Appl. Chem.* **1982**, *54*, 1129.

(9) (a) Matsunaga, N.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57. (b) Kranz, M.; Clark, T. *J. Org. Chem.* **1992**, *57*, 5492. (c) Leroy, G.; Sana, M.; Wilante, C. *Theor. Chim. Acta* **1993**, *85*, 155. (d) Matsunaga, N.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11407.

(10) Schleyer, P. v. R.; Subramanian, G.; Jiao, H.; Najafian, K.; Hofmann, M. IMEBORON 1996 conference proceedings.

(11) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578.

(12) Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3798.

(13) Xie, Y.; Schreiner, P. R.; Schaefer, H. F.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, *118*, 10635.

(14) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Becke, A. D. *Phys. Rew. A* **1988**, *38*, 3098.

(19) Perdew, J. P. *Phys. Rew. B* **1986**, *33*, 8822.

(20) Thakkar, A. J.; Koga, T.; Saito, M.; Hoffmeyer, R. E. *Int. J. Quant. Chem. Symp.* **1993**, *27*, 343.

(21) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(22) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(23) Ma, B.; Meredith, C.; Schaefer, H. F. *J. Chem. Phys.* **1994**, *98*, 8216.

(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1977**, *66*, 1382.

(25) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

= 0.01838, α_p(Ga) = 0.01472, α_s(C) = α_p(C) = 0.04380,[26] α_s(Si) = α_p(Si) = 0.03310,[27] respectively. The exponents of the polarization functions were α_d(Ga) = 0.216, 0.068, α_d(C) = 1.50, 0.375, α_d(Si) = 1.00, 0.25. For H, Huzinaga's 5s primitive set[28] was contracted to 3s, and then augmented with one *s* diffuse function α_s(H) = 0.03016 and two sets of *p* polarization functions α_p(H) = 1.50, 0.375. The technical description of this final basis set is Ga(15s12p7d/11s9p4d), C(11s7p2d/6s4p2d), Si(13s10p2d/7s6p2d), and H(6s2p/4s2p).

Analytic gradient methods were used for geometry optimizations.[29-31] Harmonic vibrational frequencies were determined via analytic second derivative methods.[32,33] In order to assess the aromatic/antiaromatic character of the various cyclic π-systems, we computed [using the gauge-independent atomic orbital (GIAO) approach][34] the absolute magnetic shieldings, termed the "nucleus independent chemical shifts" (NICS) at selected points in space as a function of the electron density.[35] NICS are taken negative to conform with chemical convention. The geometrical center of the ring's heavy atoms served as the most easily defined reference point. These isotropic chemical shifts yield information about ring currents and aromatic properties of molecules. Following the convention, aromatic molecules have negative isotropic NICS, while antiaromatic molecules have positive values. The absolute magnitude of a negative NICS is approximately proportional to the aromatic stabilization energy. In previous work,[13] we characterized $Ga_3H_3^{2-}$ as an aromatic compound using this methodology.

We also used the GIAO approach for predicting the relative chemical shifts {using standard reference compounds tetramethylsilane (TMS) in T_d symmetry, and aqueous Ga^{3+}, $Ga(H_2O)_6^{3+}$, T_h symmetry} of the title compounds to aid their experimental identification. Theoretical isotropic δ values were evaluated as σ(reference) − σ(computed). Since rovibrational corrections are not included, the chemical shifts for ^{69}Ga and ^{71}Ga (more commonly found in experimental reports) are identical. Note that the Ga chemical shifts can be computed qualitatively at the GIAO-SCF levels of theory.[36] However, substituent effects are underestimated at these levels, and methods attempting to include electron correlation effects on the chemical shifts are needed for higher accuracy. Therefore, we have chosen to compute the GIAO-DFT chemical shifts as well to provide an adequate basis for experimental comparisons. Our computations were carried out using the programs Gaussian 94[37] and PSI 2.0.8.[38]
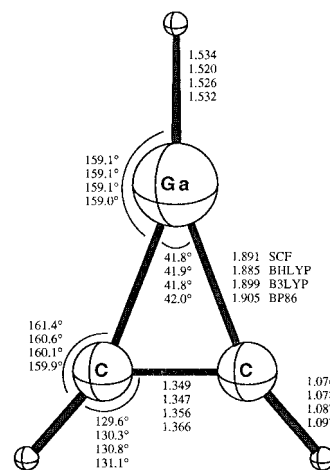
(26) Clark, T.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 295.
(27) Clark, T.; Schleyer, P. v. R. *J. Comput. Chem.* **1987**, *8*, 1109.
(28) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(29) Pulay, P. *Phys. Rev.* **1969**, *17*, 197.
(30) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem. Symp.* **1979**, *13*, 255.
(31) Johnson, B. G.; Frisch, M. J. *J. Chem. Phys.* **1994**, *100*, 7429.
(32) Pople, J. A.; Raghavachari, K.; Schlegal, H. B.; Binkley, J. S. *Int. J. Quant. Chem. Symp.* **1979**, *13*, 225.
(33) Johnson, B. G.; Frisch, M. J. *Chem. Phys. Lett.* **1993**, *216*, 133.
(34) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.
(35) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(36) Bühl, M. *Magn. Reson. Chem.* **1996**, *34*, 782.
(37) Gaussian 94, Revision C.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN94*, Inc., Pittsburgh, PA, 1995.
(38) PSI 2.0.8, Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F., PSITECH Inc. Watkinsville, GA 30677, 1994.

Figure 1. Optimized geometry (bond lengths in Å) for $\overline{HC-Ga(H)-CH}$ (**4**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

Since the B3LYP functional is currently the one most widely used, our discussions refer to the B3LYP TZ2Pf+diff level of theory, unless noted otherwise.

Results and Discussion

$\overline{HC-Ga(H)-CH}$ **(4).** Since charged 2π-electron three-membered ring systems are found to be stable (the cyclopropenium $(CH)_3^+$ cation[39,40] and the cyclogallene $(GaH)_3^{2-}$ dianion[11-13] are examples), we speculated that their neutral heteroatom-analogs should be stable as well. Replacing one or two carbons in $(CH)_3^+$ by one or two gallium atoms yields neutral **4** and anion **6**, respectively. The valence electron structure is retained.

The geometric parameters, vibrational frequencies, and chemical shifts for neutral C_{2v} symmetric **4** are presented in Figure 1 and Tables 1 and 2. The geometries differ very little (bond lengths less than 0.02 Å; bond angles less than 1.5°) at the various levels of theory. As expected, the attempted inclusion of electron-correlation effects at the density functional levels leads to slightly longer bonds, but the overall effect is small.

The Ga−C bonds are shorter (1.899 Å at B3LYP) than those found in singly-bonded organogallium compounds [1.968 Å in Mes₃Ga,[41] 1.970 Å in Mes*₂GaCl (Mes* = 2,4,6-(t-C₄H₉)₃C₆H₂),[42] and 1.956 Å (or 2.001 Å) in (2,6-Mes₂C₆H₃)₂GaCl (Mes = 2,4,6-Me₃C₆H₂],[43] indicating some π-bond character as expected for the two equivalent resonance contributors **4′**. However, a natural population analysis (NPA) shows that this is a π-effect only. While the negative charge on carbon is relatively large (−0.60, compare ethylene: charge on carbon = −0.38), the gallium atoms are less positively charged (+1.05) than in typical Ga−C singly bonded compounds (e.g., in dimethylgallane HGaMe₂ the charge on Ga is +1.32). Hence, the typical Lewis-depiction is quite

(39) Breslow, R.; Groves, J. T.; Ryan, S. *J. Am. Chem. Soc.* **1967**, *89*, 5048.
(40) Xie, Y.; Boggs, J. E. *J. Chem. Phys.* **1989**, *90*, 4320.
(41) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1985**, *5*, 1814.
(42) Meller, A.; Pusch, S.; Pohl, E.; Häming, L. Herbst-Irmer, R. *Chem. Ber.* **1993**, *126*, 2255.
(43) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 2109.

Table 1. Harmonic Vibrational Frequencies and Infrared Intensities for Structures 4–9 at B3LYP TZ2Pf+diff Level of Theory

| structure	harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses, in km/mol)
4	3125.5(41.7), 3101.3(35.7), 2085.1(73.2), 1439.0(3.3), 1158.7(22.6), 1004.7(0.0), 959.4(2.5), 642.2(24.5), 626.5(112.6), 606.9(17.7), 456.8(18.0), 305.0(33.2)
5a	3007.4(97.8), 1860.5(728.4), 1856.5(65.3), 839.1(98.8), 736.5(329.8), 669.7(158.5), 562.8(13.5), 537.0(79.6), 511.6(15.9), 377.4(9.5), 334.9(0.9), 250.0(6.5), 231.3(44.9), 164.7(7.0), 93.2(41.9)
5b	3015.5(106.4), 1841.1(789.8), 1835.6(68.6), 827.1(87.4), 720.1(334.0), 661.5(129.4), 548.1(16.4), 540.8(65.7), 360.9(7.4), 346.7(1.3), 295.7(7.2), 245.7(3.9), 224.4(44.6), 93.4(12.9), 84.5(2.5)
5c	2995.2(155.1), 1816.7(882.0), 1810.4(70.4), 811.8(82.9), 699.4(327.8), 665.9(149.7), 546.9(61.4), 542.1(19.1), 357.9(2.4), 354.2(1.1), 248.1(4.3), 209.6(54.8), 208.8(10.1), 66.9(9.5), 54.1(1.5)
6	3046.0(209.6), 1680.0(24.7), 1688.2(1496.1), 803.5(99.1), 708.8(164.5), 647.0(243.8), 566.7(54.4), 530.1(26.7), 340.8(0.1), 333.8(0.0), 244.7(6.0), 180.9(96.0)
7	2128.2(111.2), 2123.2(241.7), 1959.9(236.3), 640.8(6.0), 585.7(4.4), 545.3(0.2), 467.6(0.0), 393.0(6.4), 376.2(13.2), 338.1(11.6), 251.7(2.7), 193.9(8.7)
8a	2037.0(329.8), 1844.3(603.1), 1843.1(214.3), 588.8(0.3), 516.2(14.9), 453.7(43.7), 403.7(13.3), 356.8(50.0), 337.4(21.8), 317.0(3.6), 256.5(5.7), 222.1(3.3), 198.4(9.8), 178.6(74.4), 145.5(0.6)
8b	2015.3(358.5), 1840.8(680.6), 1836.8(212.7), 607.8(2.4), 571.5(21.2), 459.8(33.6), 389.8(0.9), 380.8(12.7), 362.6(24.6), 305.2(0.5), 203.9(2.7), 201.2(17.0), 191.8(1.0), 102.3(3.2), 95.1(3.0)
8c	2001.5(382.0), 1819.9(748.9), 1814.9(229.0), 608.0(3.0), 579.3(22.0), 457.7(32.7), 398.9(0.1), 385.4(16.2), 365.8(25.7), 292.8(1.2), 206.6(1.8), 195.9(1.1), 144.8(17.5), 80.2(3.2), 68.7(2.7)
9	1908.3(647.3), 1689.4(1282.5), 1681.8(280.1), 591.8(1.4), 537.3(20.8), 397.2(13.8), 389.7(28.8), 345.5(20.4), 304.0(0.0), 217.4(1.1), 193.6(0.7), 148.4(5.2)

Table 2. Absolute Chemical Shifts (ppm) and Relative Chemical Shifts (in Parentheses, ppm) for H$_3$GaC$_2$ (4) at the SCF and DFT Levels of Theory with the TZ2P+diff Basis Set[a]

	NICS at ring center	Ga	H (on Ga)	C	H (on C)
SCF	−14	1654 (361)	26 (6)	9 (187)	23 (9)
BHLYP		1499	26 (6)	−1 (192)	22 (10)
B3LYP		1411 (435)	26 (6)	−9 (194)	22 (10)
BP86		1358	25 (6)	−10 (194)	21 (10)

[a] The relative chemical shifts are with respect to tetramethylsilane for C and H, and with respect to aqueous Ga^{3+}, Ga(H$_2$O)$_6^{3+}$ (T_h symmetry), for Ga.

misleading, as the electron density in **4** is highly shifted to carbon, most likely due to the difference of the electronegativities of Ga and C.

4'   **4**   **4'**
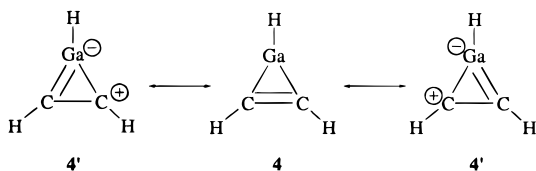
The natural bond orbital (NBO) bond orders (Wiberg bond indices: Ga–C, 0.851; C–C, 1.945) confirm this conclusion as there is no Ga–C double-bond character, and the reduction in C–C π-bonding relative to ethylene is only moderate. The poor Ga–C π overlap, visualized in the π-HOMO (Figure 2), is caused by two effects operating in the same direction. The Allred–Rochow electronegativity (EN) of carbon (2.5) is significantly larger than that of gallium (1.8), leading to electron density localization on the carbon fragment (Figure 2). Secondly, the C–Ga π-overlap is small because the gallium p-orbitals are larger than the carbon p-orbitals. As a consequence, the cyclic resonance stabilization is much less (28.8 kcal mol^{-1}, eq 1) than in the valence-isoelectronic cyclopropenium cation. Since the positive charge in the latter also increases the resonance stabilizing effect, comparison with neutral borirene [HB(CH)$_2$, eq 2) is more appropriate. Here we find that the cyclic gallenes are 11.3 kcal mol^{-1} less resonance stabilized than the borirenes.
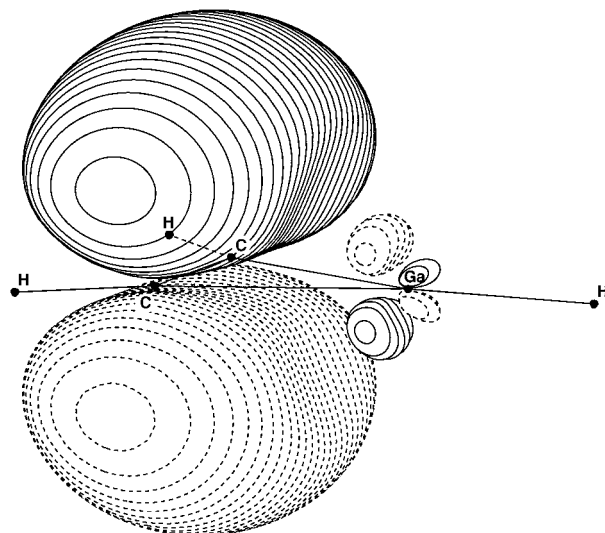
Figure 2. The π-HOMO orbital in HC–Ga(H)–CH (**4**). It appears mainly located on the C–C fragment.
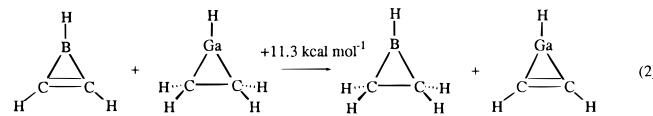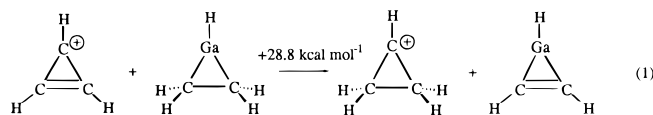
In agreement with the changes in geometries at the SCF and DFT levels, the harmonic vibrational frequencies of **4** (Table 1) slightly decrease with inclusion of electron correlation. All vibrational frequencies are real, identifying **4** as a true minimum. The lowest vibration is 305 cm^{-1} at B3LYP, indicating that **4** should be quite stable in its potential energy well.

M[HGa–C(H)–GaH] (5) and [HGa–C(H)–GaH]$^-$ (6). Exchanging two carbons in (CH)$_3^+$ by two gallium atoms yields **5** (when complexed with a positive counterion, **5a**, M = Li; **5b**, M = Na; **5c**, M = K; Figures 3–5) and the free anion **6** (Figure 6). The changes in
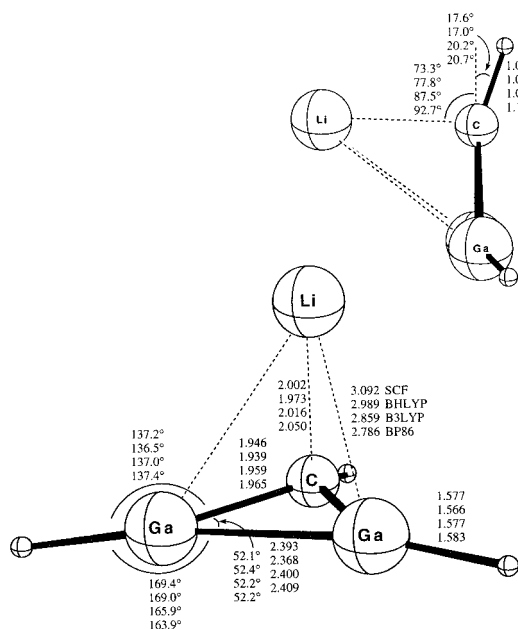
Figure 3. Optimized geometry (bond lengths in Å) for Li[HGa−C(H)−GaH] (**5a**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.

Figure 4. Optimized geometry (bond lengths in Å) for Na[HGa−C(H)−GaH] (**5b**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.
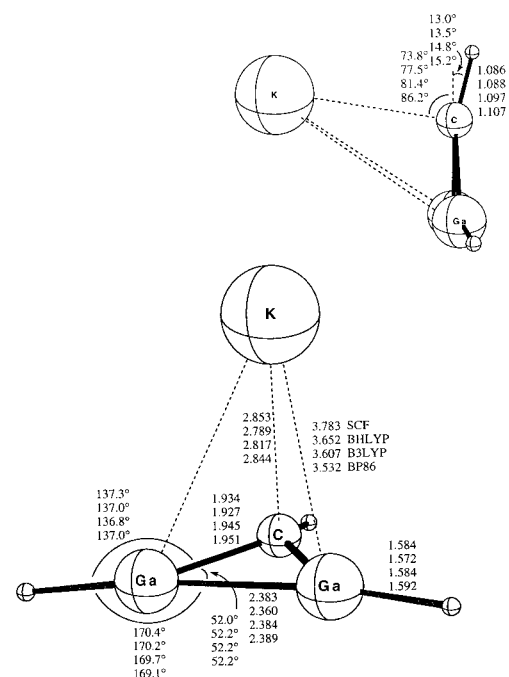
geometries and vibrational frequencies are similar to what was discussed for **4** above.

Vibrational frequency analyses (Table 1) show that **5a**−**c** as well as **6** are minima with the SCF and DFT methods (various levels, see above). As discussed for **3**, the SCF vibrational frequencies are generally larger than DFT frequencies. Within the DFT methods, the magnitudes of the computed vibrational frequencies may be ordered as BHLYP > B3LYP > BP86, as generally found.[44]

Anion **6** is a true minimum in C_{2v} symmetry. The Ga−Ga bond length (2.380 Å) lies between a typical

Figure 5. Optimized geometry (bond lengths in Å) for K[HGa−C(H)−GaH] (**5c**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.
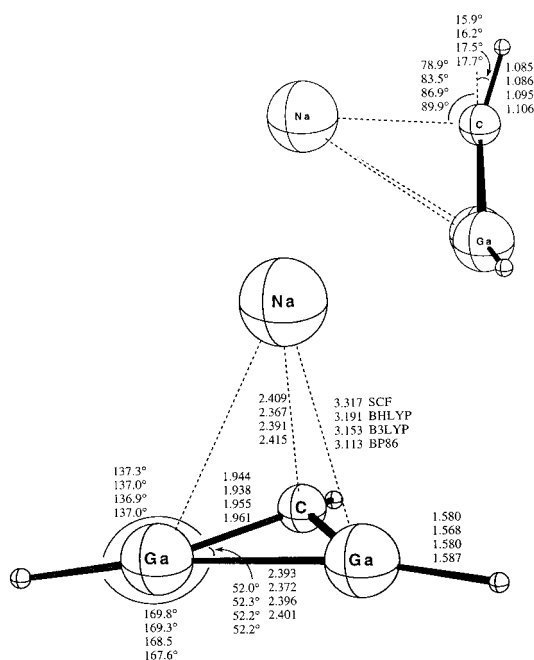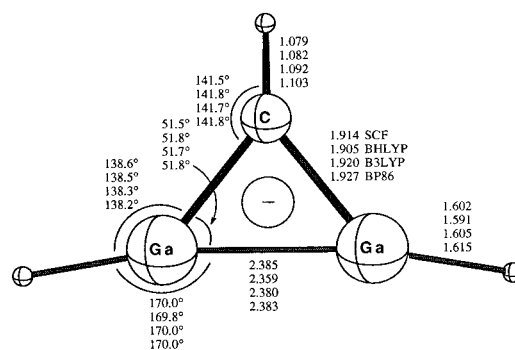

Figure 6. Optimized geometry (bond lengths in Å) for [HGa−C(H)−GaH]⁻ (**6**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

Ga−Ga single bond [2.515 Å; (i-Pr$_3$C$_6$H$_2$)$_2$Ga−Ga(i-Pr$_3$C$_6$H$_2$)$_2$] and a three-electron bond {2.343 Å; [(i-Pr$_3$C$_6$H$_2$)$_2$Ga−Ga(i-Pr$_3$C$_6$H$_2$)$_2$]•⁻}[45] with a *formal* bond order of 1.5. Thus, resonance structures **6′** contribute relatively little and the Ga−C π bond overlap is also expected to be small. The NBO bond orders for the Ga−Ga (1.013) and the Ga−C (1.226) bonds and the small resonance stabilization (37.5 kcal mol⁻¹, evaluated in eq 3) support this conclusion.

Complexation of **6** with an alkali cation (to give **5a**−**5c**) leads to charge localization on carbon, the more electronegative element (Figures 3−5). As found[12,13] for the alkali metal complexed cyclogallene dianions **3c**−**3e**, the complexation energy (49.3, 36.6, 35.7 kcal mol⁻¹) decreases with increasing size of the alkali metal for **5a**−**c**. As a consequence, the carbon p-orbital mixes

(44) King, R. A.; Mastryukov, V. S.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 6880, and references cited therein.
(45) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717.

(3)
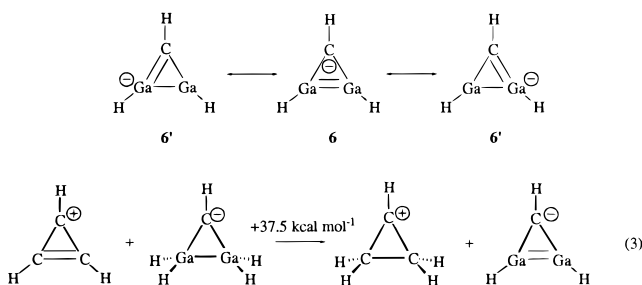
with the 2s-orbital and hybridizes to $sp^{1.80}$–$sp^{1.85}$, which in turn leads to an out-of-plane (Ga–Ga–C plane) bending of the C–H bond. This localization reduces the resonance contribution of the **6′** anion moiety even more, and the Ga–C as well as the Ga–Ga bonds elongate compared to **6**. The change in vibrational frequencies from 709 cm^{-1} (**6**) to 670 cm^{-1} (**5a**), 662 cm^{-1} (**5b**), and 700 cm^{-1} (**5c**) for the symmetric Ga–C bond stretch support this analysis. (See Table 1. More information on frequencies is available in Supporting Information.) However, the Ga–Ga modes are nearly unaffected by complexation: 245 cm^{-1} (**6**), 250 cm^{-1} (**5a**), 246 cm^{-1} (**5b**), and 248 cm^{-1} (**5c**). Thus, the complexation has very little effect on the Ga–Ga bonds.

Notwithstanding this analysis, a combination of atoms with a better match in size and EN in the three-membered ring should be more favorable. In this context, the perhaps experimentally more feasible silicon analog of **4**, HSi–Ga(H)–SiH (**7**), is discussed below.

HSi–Ga(H)–SiH (7). The bonding situation in neutral **7** (Figure 7) is quite different from that in the carbon analog **4** as both the atomic radii for silicon (1.18 Å) and gallium (1.20 Å) and the Allred–Rochow electronegativities (Si: 1.7, Ga: 1.8) are much closer than for gallium and carbon (2.4). Thus, the electron density should be distributed more evenly among the elements over the entire three-membered ring. This manifests itself in a much more symmetrical π-HOMO and total electron density (Figure 8). Furthermore, silicon is, in contrast to carbon, less hybridized in its compounds; instead of sp^2 hybridized orbitals on silicon, the bonds in structures such as disilene have a much larger p content. Note that disilene (Si_2H_4) has several energetically close equilibrium geometries,[46] and that disilyne (Si_2H_2) has two nonequivalent hydrogens.[47] Si–Si bond distances of 2.156–2.187 Å predicted theoretically in **7** are much shorter than those of Si–Si single bonds found experimentally (2.350 and 2.362 Å) in $Mes_2(H)Si$–$Si(H)Mes_2$,[48] while they are consistent with those of Si–Si double bonds found in crystal structures for $Mes(CMe_3)Si$=$Si(CMe_3)Mes$ (2.143 Å) and Mes_2Si=$SiMes_2$ (2.160 Å).[49] Consequently, the ring strain inflicted by bridging the two silicon atoms with a gallium is very much reduced, and **7** is expected to be thermodynamically more stable than **4**. This becomes obvious by comparing these two structures. While **4** is a quite distant from an equilateral triangle (angles: 42° and
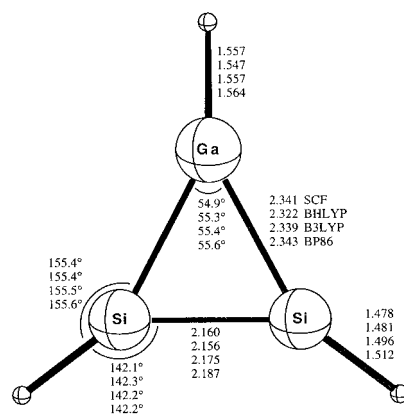
(46) Somasundram, K.; Amos, R. D.; Handy, N. C. *Theoret. Chim. Acta* **1986**, *70*, 393.
(47) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593.
(48) Baxter, S. G.; Meslow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.
(49) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

Figure 7. Optimized geometry (bond lengths in Å) for HSi–Ga(H)–SiH (**7**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.
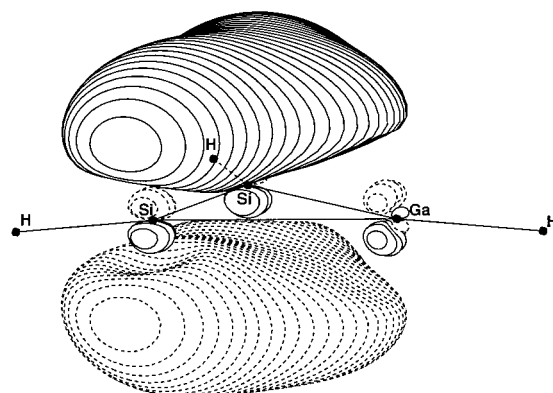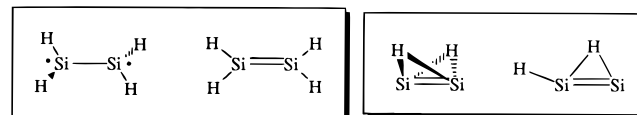

Figure 8. The π-HOMO orbital in HSi–Ga(H)–SiH (**7**). It is more delocalized than that in the analogous carbon compound **4** (see Figure 2).

69°), **7** is more symmetrical (angles: 55° and 62°). The lowest vibrational frequency around 200 cm^{-1} (Table 1) identifies **7** as a reasonably stable minimum.

M[HGa–Si(H)–GaH] (8) and [HGa–Si(H)–GaH]⁻ (9). Anion **9** (Figure 12) is the silicon analog to **6**, but it is nearly equilateral, despite of the incorporation of two atom types. The XXH (where X = C, Si, or Ge) angles also support this finding; these angles in **9** are very close (within 4°) to the ideal 150° angle of an equilateral triangle, whereas the deviations are quite large (up to 20°) in **6**. Thus, **9** is more stable than **6** (−18.5 kcal mol^{-1}, eq 4) due to similar EN's and atomic radii.

(4)
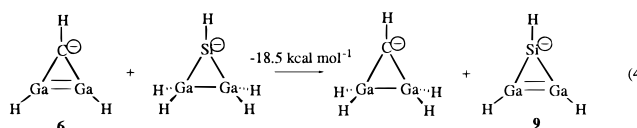
The C_s symmetric silicon counterparts to **5a–c**, namely **8a** (M = Li), **8b** (M = Na), and **8c** (M = K) also are much more symmetrical, with Ga–Ga–Si bond angles of about 58° (Figures 9–11). Complexation with

**Table 3. Absolute Chemical Shifts (ppm) and Relative Chemical Shifts (in Parentheses, ppm)
for MH₃GaC₂C (M = Li, Na, K; 5a, 5b, 5c) at the H₃Ga₂C⁻ Anion (6) at the SCF and DFT Levels of Theory
with the TZ2P+diff Basis Set[a]**

		NICS at ring center	C	H (on C)	Ga	H (on Ga)	M
M = Li	SCF	−12	7 (189)	24 (8)	1391 (624)	25 (7)	91
	BHLYP		−26 (217)	22 (10)	1203	24 (8)	90
	B3LYP		−72 (256)	20 (12)	1053 (793)	23 (9)	88
	BP86		−82 (266)	19 (12)	989	22 (9)	87
M = Na	SCF	−14	−8 (204)	22 (10)	1434 (581)	25 (7)	563
	BHLYP		−32 (223)	21 (11)	1256	24 (8)	562
	B3LYP		−52 (237)	20 (12)	1167 (679)	23 (9)	564
	BP86		−55 (239)	20 (11)	1120	22 (8)	559
M = K	SCF	−15	−15 (211)	22 (10)	1468 (547)	25 (7)	1222
	BHLYP		−32 (223)	21 (11)	1295	24 (8)	1216
	B3LYP		−49 (234)	20 (12)	1108 (638)	24 (8)	1218
	BP86		−52 (236)	20 (11)	1162	23 (8)	1210
H₃Ga₂C⁻ anion	SCF	−17	−33 (229)	21 (11)	1557 (458)	26 (6)	
	BHLYP		−39 (230)	20 (12)	1406	25 (7)	
	B3LYP		−46 (231)	20 (12)	1340 (506)	24 (8)	
	BP86		−38 (222)	20 (11)	1306	23 (8)	

[a] The relative chemical shifts are with respect to tetramethylsilane for C and H, and with respect to aqueous Ga³⁺, Ga(H₂O)₆³⁺ (T_h symmetry), for Ga.
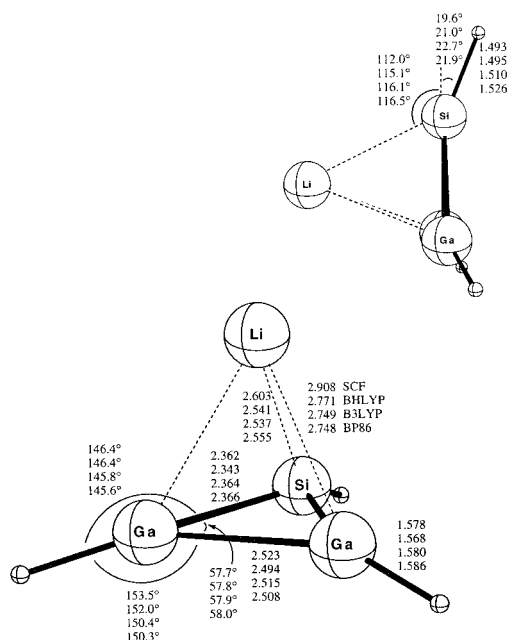

Figure 9. Optimized geometry (bond lengths in Å) for Li[HGa−Si(H)−GaH] (**8a**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.

the alkali cation also leads to charge localization, as it is evident from the out-of-plane bending of the hydrogen bonds. This bending is caused by a necessary rehybridization (to larger p-character) of the heavy ring atoms to bind to the s-orbital of the alkali metal. As a consequence of the charge localization, the Ga−Ga and Ga−Si bond distances increase in a manner directly proportional to the complexation energy (57.7 kcal mol⁻¹ for **8a**, 47.4 kcal mol⁻¹ for **8b**, 46.7 kcal mol⁻¹ for **8c**). These trends are also supported by the change of the Ga−Si vibrational frequency (Tables 1), which decreases smoothly from 397 cm⁻¹ (free anion **9**) to 357 cm⁻¹ (**8a**). As noted for the Ga₂C compounds **5a−c**, however, the Ga−Ga symmetric stretching mode is much less affected (217 cm⁻¹ in **9**, 222 cm⁻¹ in **8a**). Note that **8a−c** all are minima.

Nuclear Magnetic Resonance. The absolute and relative chemical shifts of compounds **4−9** are shown
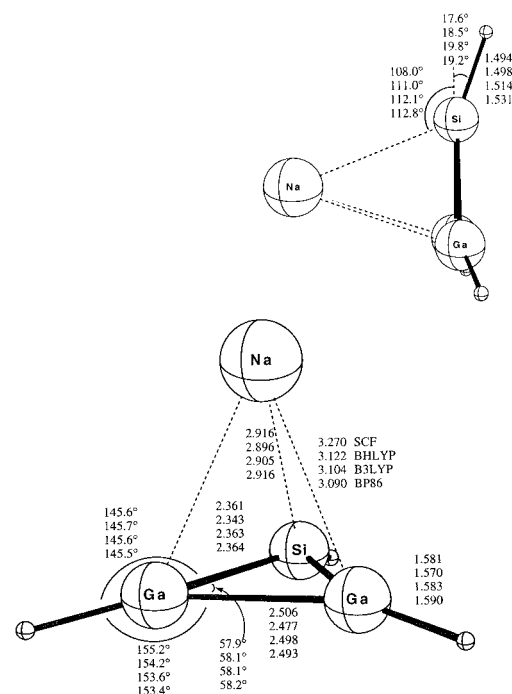

Figure 10. Optimized geometry (bond lengths in Å) for Na[HGa−Si(H)−GaH] (**8b**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.

**Table 4. Absolute Chemical Shifts (ppm) and
Relative Chemical Shifts (in Parentheses, ppm) for
H₃GaSi₂ (7) at the SCF and DFT Levels of Theory
with the TZ2P+diff Basis Set[a]**

	NICS at ring center	Ga	H (on Ga)	Si	H (on Si)
SCF	−21	1566 (449)	26 (6)	242 (142)	25 (7)
BHLYP		1408	25 (7)	187 (162)	24 (8)
B3LYP		1331 (515)	24 (8)	158 (170)	23 (9)
BP86		1297	24 (7)	160 (164)	23 (8)

[a] The relative chemical shifts are with respect to tetramethylsilane for C and H, and with respect to aqueous Ga³⁺, Ga(H₂O)₆³⁺ (T_h symmetry), for Ga.

in Tables 2−5. The relative shifts [to T_h aqueous Ga³⁺ in Ga(H₂O)₆³⁺] should aid the experimental identification of these species. Note that the experimental

**Table 5. Absolute Chemical Shifts (ppm) and Relative Chemical Shifts (in Parentheses, ppm)
for MH₃GaC₂Si (M = Li, Na, K; 8a, 8b, 8c) at the H₃Ga₂Si⁻ Anion (9) at the SCF and DFT Levels of Theory
with the TZ2P+diff Basis Set[a]**

		NICS at ring center	Si	H (on Si)	Ga	H (on Ga)	M
M = Li	SCF	−17	204 (180)	24 (8)	1249 (766)	24 (8)	88
	BHLYP		106 (243)	23 (9)	1026	23 (9)	86
	B3LYP		56 (272)	22 (10)	920 (926)	22 (10)	86
	BP86		62 (262)	21 (10)	907	22 (9)	86
M = Na	SCF	−18	234 (150)	25 (7)	1353 (662)	25 (7)	554
	BHLYP		145 (204)	23 (9)	1161	24 (8)	550
	B3LYP		101 (227)	22 (10)	1070 (776)	23 (9)	553
	BP86		505 (219)	21 (10)	1043	22 (9)	550
M = K	SCF	−18	246 (138)	24 (8)	1366 (649)	25 (7)	1195
	BHLYP		158 (191)	23 (9)	1172	24 (8)	1186
	B3LYP		114 (214)	22 (10)	1082 (764)	23 (9)	1193
	BP86		119 (205)	21 (10)	1060	22 (9)	1188
H₃Ga₂Si⁻ anion	SCF	−18	301 (83)	25 (7)	1517 (498)	25 (7)	
	BHLYP		240 (109)	23 (9)	1362	24 (8)	
	B3LYP		207 (121)	22 (10)	1292 (554)	23 (9)	
	BP86		213 (111)	21 (10)	1270	22 (9)	

[a] The relative chemical shifts are with respect to tetramethylsilane for C and H, and with respect to aqueous Ga^{3+}, $Ga(H_2O)_6^{3+}$ (T_h symmetry), for Ga.
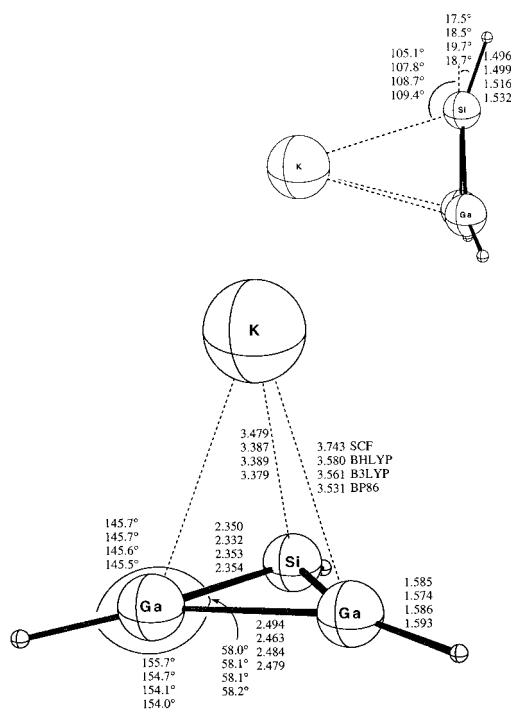
Figure 11. Optimized geometry (bond lengths in Å) for K[HGa−Si(H)−GaH] (**8c**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. Inset is the side view.

determination of ⁷¹Ga shifts can become quite difficult due to large Ga quadrupole moments and short relaxation times.[36]

A significant localization of electron density on carbon in the cyclogallenes **4** and **5a**−**c** is also manifested in the chemical shifts. While the $\delta(^{13}C)$ is 177 ppm in the cyclopropenium cation, $C_3H_3^+$, the carbon shifts are found at 194 ppm in the neutral analog **4** (Table 2). Of course, the charge difference also contributes to this difference, but this cannot be accounted for cleanly.

The C-protons {i.e. the protons connected to carbon, $\delta(^1HC) = 10$ ppm} are much more affected and thus shifted downfield by ring currents in **4** more than the Ga-proton {$\delta(^1H_{Ga}) = 6$ ppm}, due to the higher electron density on the carbons. This effect almost vanishes in
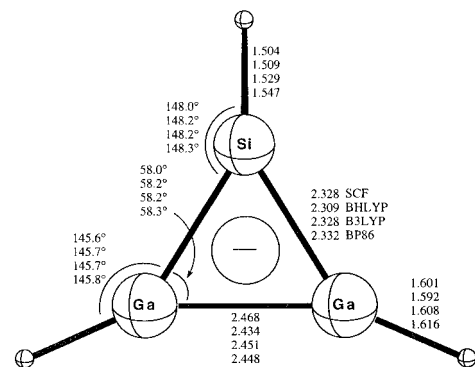

Figure 12. Optimized geometry (bond lengths in Å) for [HGa−Si(H)−GaH]⁻ (**9**) at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

the heavier analog, **7** (Table 4), where the electron density is almost evenly distributed. The corresponding shifts $\delta(^1H_{Si}) = 8$ ppm and $\delta(^1H_{Ga}) = 9$ ppm only differ by 1 ppm, and the $^1H_{Ga}$ is also shifted downfield relative to **4**, indicating a ring current delocalized over the entire three-membered ring. Similar effects are found in the monocharged analogs of **4** and **7**, namely **5a**−**c** and **8a**−**c**, respectively (Tables 3 and 5). The negative charge increases the ring current effects so that the protons are shifted even further downfield {$\delta(^1H_C) = 12$ ppm, $\delta(^1H_{Si}) = 10$ ppm, and $\delta(^1H_{Ge}) = 9$−10 ppm}.

As discussed in the literature,[50] the relative changes in chemical shifts for M can be used (apart from the NICS value, see below) to judge the aromatic character of the ionic title compounds. An appreciable ring current[51] in the cyclogallene moiety should lead to a reduced magnetic field strength and to an upfield shift for atoms positioned above the three-membered ring plane (as for M). For isolated M⁺ ions, the absolute chemical shifts are reported as 95 (Li⁺), 624 (Na⁺), and 1326 (K⁺) ppm for the "naked" cations in the gas

(50) (a) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1760 and 1763. (c) Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11529. (d) Bühl, M.; Hommes, N. J. R. van E.; Schleyer, P. v. R; Fleischer, U.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1991**, *113*, 2459.

phase.[13] Tables 3 and 5 show that the M's in **5a**−**c** and **8a**−**c** are shifted upfield by 7−9 ppm (M = Li$^+$), 60−71 ppm (M = Na$^+$), and 108−133 ppm (M = K$^+$), respectively. These upfield shifts are larger by about 2 ppm (Li$^+$), 11 ppm (Na$^+$), and 25 ppm (K$^+$) for **8a**−**c**, in agreement with a more delocalized and stronger ring current as compared to **5a**−**c**. On the basis of these arguments, **5a**−**c** and **8a**−**c** are *aromatic*, with **8a**−**c** being more stabilized by this effect.

As a second measure, we computed the nucleus independent chemical shifts (NICS)[35] for the geometric centers of the three-membered ring moieties in these compounds (Tables 2−5). The NICS value of **4**, **7**, **5a**−**c**, and **8a**−**c** are all relatively large and negative (−12 to −21), indicating aromatic character for these species. Note that the NICS of benzene is around −11.5 at comparable levels of theory; the aromatic cyclopropenyl cation cannot serve as a proper reference because of nonlinear effects due to the rather short C−C bonds.[35] As concluded above, the silicon-containing species are more aromatic, as indicated by their 1−7 ppm larger NICS magnitudes.

(51) (a) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811. (b) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991. (c) Fleischer, U.; Kutzelnigg, W.; Lazzaretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298. (d) Jiao, H.; Schleyer, P. v. R Antiaromaticity: Evidence from Magnetic Criteria. In *Proceedings of the First European Conference on Computational Chemistry*; Troyanowsky, C., Ed.; American Institute of Physics: Jericho, New York, 1995.

Concluding Remarks

Carbon- and silicon-heteronuclear neutral and singly charged cyclogallenes **4**, **7**, **5a**−**c**, and **8a**−**c** were examined using SCF and DFT methods. All structures are *stable* minima and may ultimately be prepared experimentally, in analogy to previously characterized homonuclear cyclogallenes.

Aromatic stabilization energies relative to appropriately chosen reference compounds, ring currents as indicated by the chemical shifts, and NICS values clearly show that the title compounds all are *aromatic*.

The experimental realization of the title structures is well underway in this laboratory.

Supporting Information Available: Tables of harmonic vibrational frequencies and infrared intensities for **4**, **5a**−**c**, **6**, **7**, **8a**−**c**, and **9** (10 pages). Ordering information is given on any current masthead page.

OM970719O