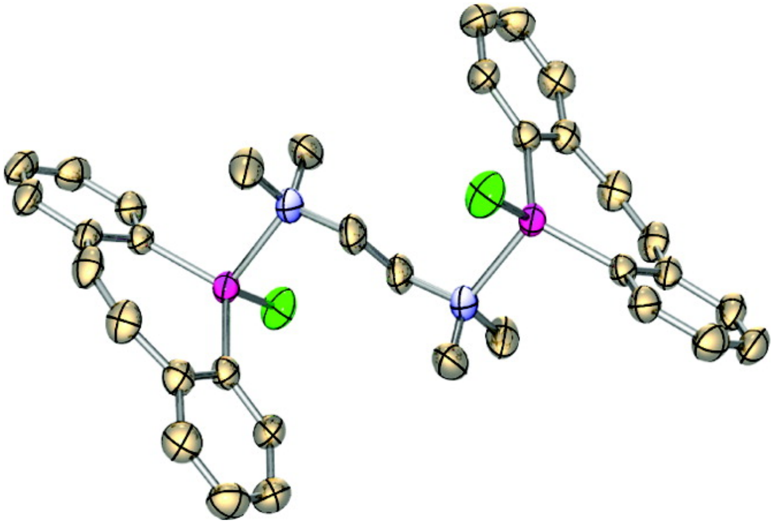
Communication

Gallepins. Neutral Gallium Analogues of the Tropylium Ion: Synthesis, Structure, and Aromaticity

Brandon Quillian, Yuzhong Wang, Pingrong Wei, Chaitanya
S. Wannere, Paul v. R. Schleyer, and Gregory H. Robinson

J. Am. Chem. Soc., **2007**, 129 (44), 13380-13381• DOI: 10.1021/ja075428d • Publication Date (Web): 16 October 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

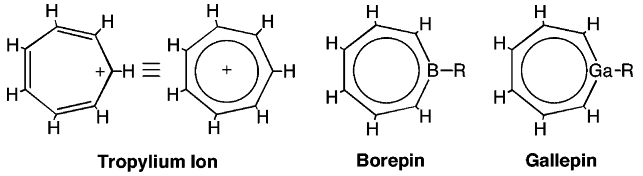
Gallepins. Neutral Gallium Analogues of the Tropylium Ion: Synthesis, Structure, and Aromaticity

Brandon Quillian, Yuzhong Wang, Pingrong Wei, Chaitanya S. Wannere,
Paul v. R. Schleyer,* and Gregory H. Robinson*

Department of Chemistry and the Center for Computational Chemistry, The University of Georgia,
Athens, Georgia 30602-2556

Received July 20, 2007; E-mail: robinson@chem.uga.edu

On the basis of its expected 6π-electron aromatic system, Doering and Knox[1] proposed the tropylium ion (cycloheptatrienyl cation) structure for the intriguing species first observed by Merling in 1891.[2] The chemistry of the analogous borepins, a class of neutral isoelectronic seven-membered rings with a boron atom in the cycloheptatrienyl framework, constitute a substantial body of work.[3−14] Depending on the nature and degree of substitution, borepins may adopt either a boatlike[15−17] or a planar conformation.[4,14,18] The aromatic nature of borepins has been extensively investigated.[4,5,10,14,18]

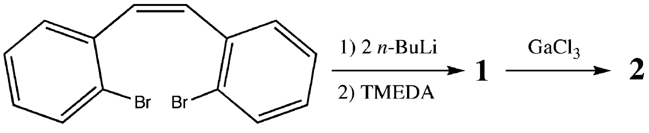


While five-membered[19−21] and six-membered[22,23] gallium heterocycles are well-known, seven-membered heterocycles incorporating group 14,[24−26] 15,[13,27] and 16[13,27] elements have also been examined. Surprisingly, the corresponding borepin chemistry has not been extended to the group 13 metals. Because of the substantial electronegativity differences between the nonmetallic boron and the metallic gallium atoms, the experimental realization of a “gallepin” analogue of a borepin is an intriguing synthetic endeavor. Herein, we report the synthesis and molecular structure[28] of the first gallepin, **2**. Moreover, our computations provide insight into the nature of its bonding and aromaticity.

Reaction of an appropriate stannepin with boron halides has been a popular preparative method for borepins.[7−10] As five-membered[29−31] and six-membered[23,32] heterocycles have been synthesized utilizing dilithio reagents, we selected the dilithio-*Z*-stilbenyl derivative **1** as the gallepin precursor.

Compound **1** was obtained as orange-red crystals in moderate yield by reaction of 2,2′-dibromo-*Z*-stilbene with *n*-BuLi followed by treatment with TMEDA. Reaction of **1** with $GaCl_3$ affords **2** (Scheme 1).

Scheme 1



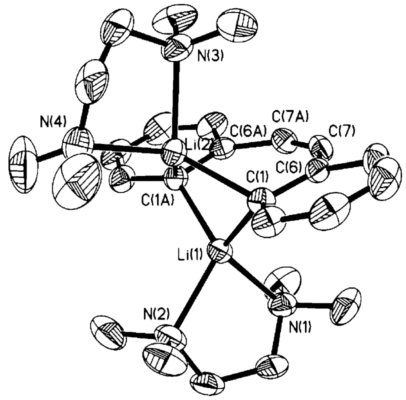


Figure 1. Molecular structure of **1** (thermal ellipsoids are shown at 30% probability levels; Hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Li(1)−C(1), 2.158(4); Li(2)−C(1), 2.157(4); C(1)−Li(1)−C(1A), 100.8(3); C(1A)−Li(1)−N(2), 119.93(17); C(1A)−Li(1)−N(1), 116.51(18).

Computations predicted that solid-state structures of 1,4-dilithium organometallic compounds have two carbon atoms intramolecularly bridged by two lithium atoms[33] owing to electrostatic interactions.[34−36] This geometrical feature has been observed for several 1,4-dilithium compounds[34−36] and is consistent with the structure of **1** (Figure 1), which displays a *Z*-stilbenyl unit with two lithium atoms bridging C(1) and C(1A), forming a butterfly four-membered ring. Each lithium atom in **1** is chelated by one TMEDA unit (Li(1)···Li(2): 2.527(8) Å). Additionally, compound **1** has a mirror plane containing the lithium atoms and the midpoint of the C(7)−C(7A) bond.

Compound **1** is similar to other TMEDA stabilized ortho-dilithio biphenyl compounds that have intramolecular dimerized dilithium butterfly cores.[37,38] However, compound **1** is distinct from an 1,2-dilithio adduct of the *E*-stilbenyl dianion, stilbene bis(lithium TMEDA),[39] in which the two Li atoms are π-coordinated above and below the central ethylene fragment.[34] The Li(1)−C(1) and Li(2)−C(1) bond lengths in **1** (2.157(4) and 2.158(4) Å, respectively) are essentially equivalent and are comparable to those found in $[(C_6H_4)_2O][Li(TMEDA)]_2$[37] (2.166(8) Å) and $[(C_6H_4)_2S][Li(TMEDA)]_2$[38] (2.147(9) Å). The C(6)−C(7)−C(7A) bond angle (139.70(12)°) in **1** substantially exceeds that expected for a sp^2-hydridized carbon atom.

The crystal structure of **2** (Figure 2) displays two gallepin moieties bridged by a TMEDA unit. The pseudotetrahedral four-coordinate gallium atoms in **2** reside 0.58 Å above and 35° out of the C(1)···C(6)···C(9)···C(10) plane. Each gallepin in **2** has a boatlike conformation (the phenyl rings tilted in one direction with the C=C fragment and gallium atom in the opposite direction). The C(6)−C(7)−C(8) (137.44°) and C(7)−C(8)−C(9) (137.93°) bond angles considerably exceed the trigonal planar expected value (120°) while the Ga(1)−C(1) (1.9476(17) Å) and Ga(1)−C(10) (1.9477(18) Å) bond distances in **2** are comparable to the distances reported for other gallium heterocycles (1.934−2.164 Å).[20,21]

The geometries of **2** were compared with computations on two simpler models: **2Cl·NMe$_3$** and **2Cl**. The B3LYP/LANL2DZ optimized bond lengths of **2Cl·NMe$_3$** and **2Cl** (Figure 3) are in

10.1021/ja075428d CCC: $37.00 © 2007 American Chemical Society

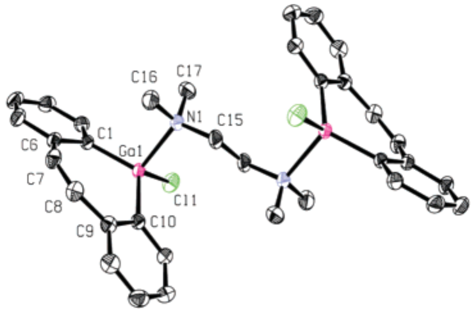
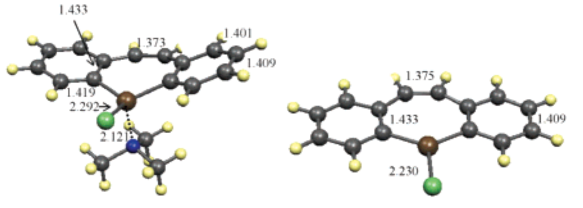


Figure 2. Molecular structure of **2** (thermal ellipsoids are shown at 30% probability levels; Hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ga(1)−C(1), 1.9476(17); Ga(1)−C(10), 1.9477(18); Ga(1)−Cl(1), 2.2258(5); Ga(1)−N(1), 2.1158(15); C(1)−Ga(1)−C(10), 117.94(7); C(1)−Ga(1)−Cl(1), 110.47(6); C(10)−Ga(1)−Cl(1), 112.29(5); C(1)−Ga(1)−N(1), 104.64(6); C(10)−Ga(1)−N(1), 108.99(7); Cl(1)−Ga(1)−N(1), 100.79(5).



$2Cl\cdot NMe_3$ **2Cl**

Figure 3. B3LYP/LANL2DZ optimized structures of **$2Cl\cdot NMe_3$** and **2Cl**.

reasonable agreement with **2** (**$2Cl\cdot NMe_3$**, Ga−C = 1.958 Å, Ga−Cl = 2.121 Å; **2Cl**, Ga−C = 1.920 Å, Ga−Cl = 2.230 Å). The C(7)−C(8) bond length (1.346(3) Å) in **2** is marginally smaller than those in **$2Cl\cdot NMe_3$** and **2Cl** (1.373 and 1.375 Å, respectively). Notably, **$2Cl\cdot NMe_3$** adopts a boatlike conformation, similar to **2**, while **2Cl** assumes a planar conformation.

Nucleus-independent chemical shifts (NICS)[40] for **$2Cl\cdot NMe_3$** and **2Cl** were computed at the IGLO-PW91/IGLOIII level to assess aromatic character. The sophisticated $NICS_{\pi zz}$[41] index provides superior ring current evaluations, since only the perpendicular (*zz*) tensor π MO contributions are included. The $NICS_{\pi zz}$ values for the heterocyclic seven-membered rings in **$2Cl\cdot NMe_3$** and **2Cl**, −9.0 and −9.9, respectively, shows that weak adduct formation has little effect on the ring current. However, the −15.3 $NICS_{\pi zz}$ value computed for the unsubstituted parent gallepin (C_6H_6GaH) indicates that the benzannulation in **$2Cl\cdot NMe_3$** and **2Cl** diminishes the aromaticity of the seven-membered rings (the phenyl rings have $NICS_{\pi zz}$ values of −32.7 and −34.1 for **$2Cl\cdot NMe_3$** and **2Cl**, respectively). This is a well-known effect of benzannulation, as the more aromatic phenyl ring essentially "wins out" in a competition for π-electrons.[42] Furthermore, the smaller $NICS_{\pi zz}$ value of C_6H_6GaH (−15.3) than C_6H_6BH ($NICS_{\pi zz} = -27.7$) suggests that gallepins are *less* aromatic than borepins.

To summarize, we have prepared the first isoelectronic gallium analogue of the iconic tropylium ion. This compound exhibits the expected aromatic 6π-electron structure and will serve as a benchmark for our continuing explorations of this intriguing class of chemical compounds.

Acknowledgment. G.H.R. and P.v.R.S. are grateful to the National Science Foundation (Grants CHE-0209857, CHE-0608142, and CHE-0716718) for support of this research.

Supporting Information Available: X-ray crystallographic files in CIF format and experimental details of **1** and **2** as well as computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Doering, W. v.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203−3206.
(2) Merling, G. *Chem. Ber.* **1891**, *24*, 3108−3126.
(3) Jeffries, A. T., III; Gronowitz, S. *Chem. Scr.* **1973**, *4*, 183−187.
(4) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 3785−3788.
(5) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863−1866.
(6) Ashe, A. J., III; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879−1880.
(7) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451−1452.
(8) Ashe, A. J., III; Drone, F. J.; Kausch, C. M.; Kroker, J.; Al-Taweel, S. M. *Pure Appl. Chem.* **1990**, *62*, 513−517.
(9) Ashe, A. J., III; Kampf, J. W.; Kausch, C. M.; Konishi, H.; Kristen, M. O.; Kroker, J. *Organometallics* **1990**, *9*, 2944−2948.
(10) Ashe, A. J., III; Klein, W.; Rousseau, R. *Organometallics* **1993**, *12*, 3225−3231.
(11) Sugihara, Y.; Yagi, T.; Murata, I. *J. Am. Chem. Soc.* **1992**, *114*, 1479−1481.
(12) Ashe, A. J., III; Al-Taweel, S. M.; Drescher, C.; Kampf, J. W.; Klein, W. *Organometallics* **1997**, *16*, 1884−1889.
(13) Sashida, H.; Kuroda, A.; Tsuchiya, T. *Chem. Commun.* **1998**, 767−768.
(14) Schulman, J. M.; Disch, R. L. *Organometallics* **2000**, *19*, 2932−2936.
(15) Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265−4270.
(16) Butcher, S. S. *J. Chem. Phys.* **1965**, *42*, 1833−1836.
(17) Davis, R. E.; Tulinsky, A. *J. Am. Chem. Soc.* **1966**, *88*, 4583−4588.
(18) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733−737.
(19) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889.
(20) Cowley, A. H.; Gabbaï, F. P.; Decken, A. *Angew. Chem., Int. Ed.* **1994**, *33*, 1370−1372.
(21) Wei, P.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1999**, 1287−1288.
(22) Schumann, H.; Hartmann, U.; Wassermann, W.; Just, O.; Dietrich, A.; Pohl, L.; Hostale, k, M.; Lokai, M. *Chem. Ber.* **1991**, *124*, 1113−1119.
(23) Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Angew. Chem., Int. Ed.* **1995**, *34*, 1357−1359.
(24) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435−442.
(25) Nakadaira, Y.; Sato, R.; Sakurai, H. *J. Organomet. Chem.* **1992**, *441*, 411−417.
(26) Mochida, K.; Matsuhisa, N.; Sato, R.; Nakadaira, Y. *Organometallics* **2006**, *25*, 4231−4233.
(27) Yasuike, S.; Kiarada, T.; Tsuchiya, T.; Kurita, J. *Chem. Pharm. Bull.* **2003**, *51*, 1283−1288.
(28) Synthesis/structure. Compound **2**: **1** (0.70 g, 1.65 mmol) in Et_2O (40 mL) was added to $GaCl_3$ (0.29 g, 1.65 mmol) in Et_2O (25 mL) at −78 °C and stirred for 17 hrs. The solution was filtered, and volume was reduced to 10 mL and then placed at −25 °C. Colorless crystals formed overnight (0.44 g). An additional 0.34 g of **2** was retrieved after workup in toluene. Yield: (0.78 g, 69%); mp 248 °C (dec). Anal. Calcd (found) for $C_{34}H_{36}Cl_2Ga_2N_2$: C, 59.79 (59.76); H, 5.31 (5.28); N, 4.10 (4.27). ^1H NMR δ (DMSO-d_6) 2.31 (12H, s, $-N(CH_3)_2$), 2.58 (4H, s, NCH_2), 6.62−6.73 (4H, m, $=CH$), 7.19−7.42 (12H, m, ArH), 7.70−7.78 (4H, m, ArH). X-ray data for $C_{34}H_{36}N_2Ga_2Cl_2$: fw = 682.98; monoclinic *C2/c*; $a = 26.8548(10)$ Å, $b = 7.6807(3)$ Å, $c = 16.9633(6)$ Å, $\beta = 113.4040(10)°$, $V = 3211.0(2)$ Å^3, $Z = 4$, $R1 = 0.0261$ ($I > 2\sigma(I)$), $wR2 = 0.0693$ (all data).
(29) Rausch, M. D.; Klemann, L. P. *J. Am. Chem. Soc.* **1967**, *89*, 5732−5733.
(30) Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495−496.
(31) Ashe, A. J., III; Drone, F. J. *Organometallics* **1985**, *4*, 1478−1480.
(32) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466−473.
(33) Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928−7929.
(34) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353−451.
(35) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355−362.
(36) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151−162.
(37) (a) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184−1185. (b) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033−6046.
(38) Kranz, M.; Dietrich, H.; Mahdi, W.; Müller, G.; Hampel, F.; Clark, T.; Hacker, R.; Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 4698−4704.
(39) Walczak, M.; Stucky, G. *J. Am. Chem. Soc.* **1976**, *98*, 5531−5539.
(40) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842−3888.
(41) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863−866.
(42) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Organometallics* **1997**, *16*, 2362−2369.

JA075428D