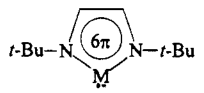
Gallium-Containing 6π-Electron Ring Systems

David S. Brown, Andreas Decken, and Alan H. Cowley*

Department of Chemistry and Biochemistry
The University of Texas at Austin, Austin, Texas 78712

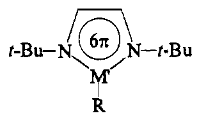
Received January 25, 1995

Main-group heterocycles continue to attract attention from the pharmaceutical, agricultural chemical, and materials science communities.[1] Most of the effort to date has been focused on carbocyclic systems that incorporate an element from groups 14−16, and with the exception of boron,[2] structurally authenticated heterocycles that feature other group 13 elements remain rare.[3] In previous work we have prepared neutral, 4π-electron galla- and indacyclopentadienes.[3b] However, attempts to convert these compounds into the corresponding 6π-electron systems by two-electron reduction were unsuccessful. Accordingly, we turned our attention to the possibility of preparing neutral 6π-electron systems featuring the heavier group 13 elements. Diazabutadiene ligands are well suited for this purpose, having been used recently for the stabilization of dicoordinate carbon,[4] silicon,[5] and germanium.[6] The isoelectronic relationships between the group 14 (**1**) and 13 (**2**) heterocycles are of particular interest.



1

M = C, Si, Ge



2

M' = Al, Ga, In

Initial attempts to prepare an example of **2** were based on the reaction of the dilithio derivative **3** with $GaCl_3$ (Scheme 1). However, as revealed by spectroscopic data[7] and X-ray crystallography,[8] the product of this reaction is **4** (yield 51%). Inferentially, the reaction of the second lithium of **3** is slow, hydrolysis occurs at this site, and subsequent cyclization is effected by tautomerism between the enamine and imine forms. The proposed bonding arrangement is consistent with the C=N (1.270(6) Å), C−N (1.388(6) Å), N→Ga (1.965(4) Å), and N−Ga (1.854(4) Å) interatomic distances. The reaction of **3** with the *o*-((dimethylamino)methyl)phenyl-substituted gallium dichloride **5**[9] afforded **6**, the first example of the desired heterocycle, in 63% yield. The proposed formula for **6** is in accord with NMR and mass spectral data.[7] However, it was of importance to secure high-quality X-ray crystallographic data[8] in order to assess the bonding in the C_2N_2Ga ring system (Figure 1).

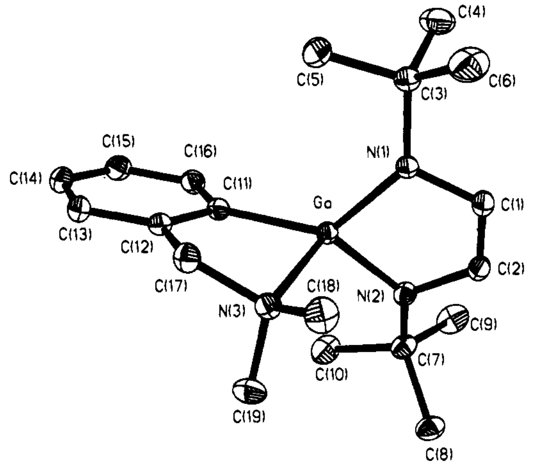
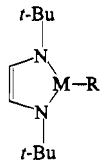
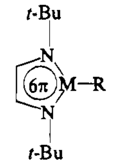


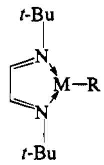
Figure 1. Structure of **6** in the crystal. Selected bond distances (Å) and bond angles (deg): Ga−N(1) 1.878(2), Ga−N(2), 1.862(2), Ga−N(3), 2.201(2), N(1)−C(1) 1.404(2), C(1)−C(2) 1.340(3), C(2)−N(2) 1.404(2), N(1)−Ga−N(2) 90.80(7), Ga−N(1)−C(1) 106.15 (12), N(1)−C(1)−C(2) 118.0(2), C(2)−N(2)−Ga 106.49(12).



A



B



C

As in the case of the group 14 systems, various canonical forms are of potential relevance to a discussion of the bonding in diazabutadiene complexes. Structure **A** features a localized carbon−carbon double bond, while in **B** circumannular delocalization takes place. In structure **C** the group 13 element is formally in the +1 oxidation state. On the basis of electron density mapping, Arduengo *et al.*[4e] have concluded that structure

---

[1] (a) Taylor, E. C., Ed. *The Chemistry of Heterocyclic Compounds*; Wiley: New York, 1993. (b) Wong, C. P., Ed. *Polymers for Electronic and Photonic Applications*; Academic: Boston, MA, 1993; pp 1−661.

[2] (a) Morris, J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5. (b) Merriam, J. S.; Niedenzu, K. *J. Organomet. Chem.* **1973**, *51*, C1. (c) Schmid, G.; Polk, M.; Boese, R. *Inorg. Chem.* **1990**, *29*, 4421.

[3] (a) Fagan P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Cowley, A. H.; Gabbaï, F. P.; Decken, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1370. (c) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (d) Cowley, A. H.; Corbelin, S.; Jones, R. A.; Lagow, R. J.; Nail, J. W. *J. Organomet. Chem.* **1994**, *464*, C1. (e) Herberich, G. E.; Englert, U.; Posselt, D. *J. Organomet. Chem.* **1994**, *461*, 21. (f) Schumann, H.; Just, O.; Seuss, T. D.; Görlitz, F. H.; Weimann, R. *J. Organomet. Chem.* **1994**, *466*, 5.

[4] (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (c) Dixon, D. A.; Arduengo, A. J., III *J. Phys. Chem.* **1991**, *95*, 4180. (d) Arduengo, A. J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641. (e) Arduengo, A. J., III; Rasika Dias, H. V.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

[5] Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

[6] Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Soluki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

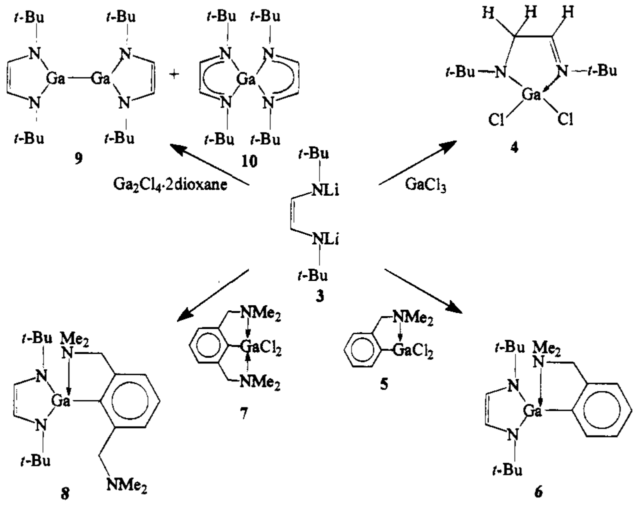
[7] Spectroscopic data for **4**: ^{1}H NMR (300 MHz C_6D_6) δ 7.06 (s, 1H), 3.44 (s, 2H), 1.29 (s, 9H), 1.01 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 174.46, 60.73, 52.46, 51.65, 30.80, 30.01 ppm; MS (CI) 309 (MH^+). Spectroscopic data for **6**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.77 (m, 1H), 7.16 (m, 2H), 6.81 (m, 1H), 6.19 (s, 2H), 3.12 (s, 2H), 1.95 (s, 6H), 1.32 (s, 18H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 142.95, 136.55, 128.45, 128.15, 125.59, 114.95, 63.70, 52.40, 45.00, 32.79 ppm; MS (CI) 371 (M^+). Spectroscopic data for **8**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.10 (m, 3H), 6.21 (s, 2H), 3.41 (s, 4H), 2.09 (s, 12H), 1.35 (s, 18H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 145.08, 128.78, 126.41, 114.22, 65.91, 52.20, 45.54, 32.42 ppm; MS (CI) 428 (M^+). Spectroscopic data for **9**: ^{1}H NMR (300 MHz, C_6D_6) δ 6.63 (s, 4H), 1.41 (s, 36H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 117.07, 54.65, 33.91 ppm; MS (CI) 474 (M^+).

[8] Crystal structure data for **4**: $C_{10}H_{21}Cl_2GaN_2$, monoclinic, space group $P2_1/m$, $Z = 2$, $a = 7.150(1)$ Å, $b = 10.200(2)$ Å, $c = 10.610(1)$ Å, $\beta = 105.430(10)°$, $V = 745.9(2)$ Å^3, $\varrho_{calcd} = 1.380$ g/cm^3, Mo Kα, $\lambda = 0.710\ 73$ Å; 2267 unique data collected ($\theta-2\theta$ scan technique, $2.82 \leq 2\theta \leq 60°$), wR2 = 15.52% ($F^2$), R1 = 5.0% ($F$). Crystal structure data for **6**: $C_{19}H_{32}GaN_3$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.740(2)$ Å, $b = 9.929(2)$ Å, $c = 11.146(2)$ Å, $\alpha = 100.60(2)°$, $\beta = 106.92(2)°$, $\gamma = 97.74(2)°$, $V = 993.1(3)$ Å^3, $\varrho_{calcd} = 1.245$ g/cm^3, Mo Kα, $\lambda = 0.710\ 73$ Å; 4544 unique data collected ($\theta-2\theta$ scan technique, $2.13 \leq 2\theta \leq 55°$), wR2 = 6.7% ($F^2$), R1 = 2.98% ($F$). Crystal structure data for **8**: $C_{22}H_{39}GaN_4$, monoclinic, space group $P2_1$, $Z = 2$, $a = 8.626(1)$ Å, $b = 14.196(2)$ Å, $c = 10.112(2)$ Å, $\beta = 96.97(2)°$, $V = 1229.1(3)$ Å^3, $\varrho_{calcd} = 1.160$ g/cm^3, Mo Kα, $\lambda = 0.710\ 73$ Å; 2420 unique data collected ($\theta-2\theta$ scan technique, $2.03 \leq 2\theta \leq 50°$), wR2 = 13.95% ($F^2$), R1 = 5.31% ($F$). Crystal structure data for **9/10**: $C_{20}H_{40}Ga_2N_4 + C_{20}H_{40}N_4Ga$, orthorhombic, space group $Cmcm$, $Z = 8 + 4$, $a = 42.939(3)$ Å, $b = 12.442(2)$ Å, $c = 14.104(2)$ Å, $V = 7535(2)$ Å^3, $\varrho_{calcd} = 1.197$ g/cm^3, Mo Kα, $\lambda = 0.710\ 73$ Å; 3487 unique data collected ($\theta-2\theta$ scan technique, $2.17 \leq 2\theta \leq 50°$), wR2 = 12.77% ($F^2$), R1 = 5.95% ($F$).

[9] Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics*, in press.

0002-7863/95/1517-5421$09.00/0 © 1995 American Chemical Society

Scheme 1



A (R = lone pair) is the most appropriate representation for a carbene, while West *et al.*[5] have claimed the existence of aromatic delocalization (structure **B**) in the case of the corresponding silylene **1**. Interestingly, the C−N (1.404(2) Å) and C−C (1.340(3) Å) bond distances in **6** are very similar to those in both the carbene (C−N = 1.387(2) Å; C−C = 1.341(2) Å) and silylene (C−N = 1.400(9) Å; C−C = 1.347(21) Å). Moreover, the endocyclic N−Ga−N bond angle in **6** (90.80(7)°) is almost the same as that in the silylene (90.5(10)°), and the geometries at N(1) and N(2) are both trigonal planar (sums of angles = 358.1(2)° and 359.4(2)°, respectively). However, the average Ga−N bond distance in **6** (1.870(2) Å) falls within the range of 1.85−1.92 Å that has been established for (terminal) Ga−amido single bonds,[10] thus ruling out structure **B** and implying that the π-system is relatively localized.

Treatment of the corresponding bis(*o*-((dimethylamino)methyl)phenyl)-substituted gallium dichloride **7**[11] with **3** afforded **8** in 44% yield. Since it was not obvious from spectroscopic data[7] how the amine "arms" are arranged, it was necessary to appeal to X-ray crystallography.[8] While the quality of the structure of **8** is not as high as that of **6**, it is clear that only one of the two *o*-aminomethyl "arms" is coordinated. Moreover, the average Ga−N (1.86(1) Å), C−N (1.39(2) Å), and C−C (1.35(1) Å) bond lengths and the average bond angles are the same as those in **6** within experimental error; hence similar comments apply to the bonding.

It was clearly of interest to prepare and structurally characterize an example of a ring system that did not feature intramolecular base stabilization at the gallium center. This was accomplished by treatment of $Ga_2Cl_4 \cdot 2$(dioxane) with **3**. Interestingly, the formation of the novel digallane **9** is accompanied by the formation of the known[12] monogallium derivative **10**. Evidently **10** is produced by the disproportionation of Ga(II) into Ga(0) and Ga(III). So far, the only single crystals that we have obtained consist of a 2/3:1/3 mixture of **9** and **10** in 20% yield.[8] Molecules of **9** reside on a crystallographic plane of symmetry (Figure 2), and the two C_2N_2Ga rings are orthogonal. Furthermore, atoms Ga(2), N(2), C(8), C(2), C(3), N(3), and C(11) lie in this mirror, thus rendering this fragment planar. While not required crystallographically, the corresponding atoms on the other ring are also planar within experimental error. The Ga−Ga bond distance in **9** (2.333(1) Å) is shorter than those in the three organodigallanes which have been structurally characterized: $Ga_2\{CH(SiMe_3)_2\}_4$ (2.541(1) Å),[13] $Ga_2(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4$ (2.513(3) Å),[14] and $Ga_2(2,4,6\text{-}(CF_3)_3C_6H_2)_4$ (2.479(1) Å).[15] Interestingly the Ga−Ga distance in **9** is also shorter than that in the anion radical $[Ga_2(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^{\bullet -}$ (2.343(2) Å), where multiple bonding has been suggested.[14] In the case of **9**, multiple bonding is precluded because of the orthogonality of gallium p orbitals; hence the short Ga−Ga distance is due to diminished steric effects. The average Ga−N bond length in **9** (1.836(6) Å) is shorter than that in **6** (1.870(2) Å) or **8** (1.861(14) Å) presumably as a result of the change of gallium hybridization from sp^3 to sp^2 and the availability of a vacant Ga(4p) orbital.

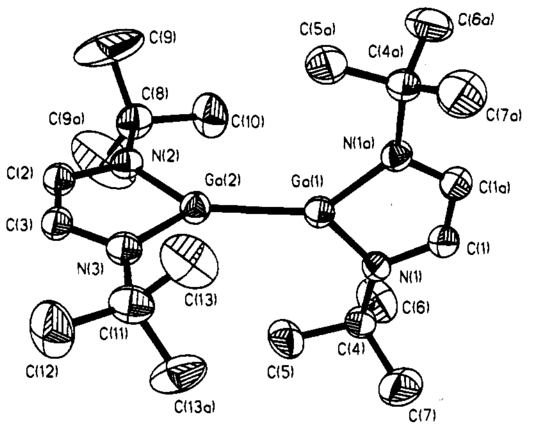


Figure 2. Structure of **9** in the crystal. Selected bond distances (Å) and bond angles (deg): Ga(1)−Ga(2) 2.333(1), Ga(1)−N(1) 1.836(4), N(1)−C(1) 1.383(6), C(1)−C(1a) 1.368(10), Ga(2)−N(2) 1.839(6), N(2)−C(2) 1.397(9), C(2)−C(3) 1.339(10), C(3)−N(3) 1.380(9), N(3)−Ga(2) 1.833(6), N(1)−Ga(1)−N(1a) 90.7(3), Ga(1)−N(1)−C(1) 108.0(3), N(1)−C(1)−C(1a) 116.7(3), N(2)−Ga(2)−N(3) 90.2(3), Ga(2)−N(2)−C(2) 108.5(5), N(2)−C(2)−C(3) 115.0(7), C(2)−C(3)−N(3) 119.1(8), C(3)−N(3)−Ga(2) 107.2(5).

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **4**, **6**, **8**, and **9/10** (23 pages); structure factors for **4**, **6**, **8**, and **9/10** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950260U

---

(10) See, for example: (a) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Jones, R. A.; Atwood, J. L.; Bott, S. G. *Inorg. Chem.* **1994**, *33*, 3251. (b) Brothers, P. J.; Wehmschulte, R. J.; Olmstead, M. M.; Ruhlandt-Senge, K.; Parkin, S. R.; Power, P. P. *Organometallics* **1994**, *13*, 2792.

(11) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Ruiz, J.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1150.

(12) Cloke, F. G. N.; Hanson, G. R.; Henderson, M. J.; Hitchcock, P. B.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1002.

(13) (a) Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364. (b) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

(14) 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.

(15) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.