Organometallics **2007,** *26,* 2−11

Reviews

Organometallics of the Group 13 M−M Bond (M = Al, Ga, In) and the Concept of Metalloaromaticity

Yuzhong Wang and Gregory H. Robinson*

Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556

Received August 14, 2006

The chemistry of the group 13 M−M bond (M = Al, Ga, In) has emerged as an exciting, unpredictable, and provocative area of main-group organometallic chemistry. This review seeks to draw a sharper focus on some of the more notable discoveries in this area, with a particular emphasis on group 13 multiple bonding and the concept of metalloaromaticity.

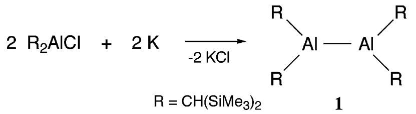
Introduction

Beginning with the nonmetal boron and concluding with thallium, a soft grayish—yet highly toxic—tin-like metal, the group 13 elements constitute a decidedly eclectic collection. Gracefully residing between these two elemental extremes are the diverse group 13 metals aluminum, gallium, and indium. The ubiquitous nature of aluminum is in contrast with the mercurial properties of gallium and the spectral distinction of indium. Although the organometallic chemistry of these elements developed rather slowly, it is now widely recognized that these metals possess an intriguing chemistry of significant and varied utility. Indeed, the interaction of group 13 organometallic derivatives with appropriate group 15 moieties has fueled a frenzy of activity toward advanced electronic materials.[1,2] This transpired, perhaps, at the expense of more fundamental aspects of structure and bonding in the organometallic chemistry of these elements. A particularly illustrative example of this point may be found in the organometallic chemistry of homonuclear metal−metal bonds of aluminum, gallium, and indium: while the chemistry of the B−B bond has been extensively developed, the corresponding chemistry involving the M−M fragment (M = Al, Ga, In) was brought to the fore less than two decades ago. Nevertheless, the organometallic chemistry of the M−M bond (M = Al, Ga, In) has developed into one of the more exciting aspects of organometallic chemistry. The intent of this overview is to assess the dynamics of the group 13 M−M bond (M = Al, Ga, In) with a particular emphasis on multiple bonding and metalloaromaticity.

R_2M-MR_2 (M = Al, Ga, In) Compounds

The quest for chemical compounds containing the M−M bond (M = Al, Ga, In) spans at least four decades. One of the earliest reports of a compound purporting to contain an Al−Al bond may be traced to a study of the reaction of Me_3Al with $B_2[NMe_2]_4$,[3] resulting in a nonvolatile yellow solid. Although structural data were not obtained, the authors described the yellow solid as "the first example of a compound containing Al−Al covalent bonds". A few years later a second report from the same laboratory described a new "catenated aluminum species".[4] Although a number of reports of compounds ostensibly containing Al−Al bonds appeared in the literature between 1966 and 1978,[5−7] the early history of the M−M (M = Al, Ga, In) bond is replete with ambiguously characterized products and sketchy structural details.

In 1988 Uhl prepared the first structurally characterized compound containing a group 13 M−M bond, tetrakis[bis(trimethylsilyl)methyl]dialane, $R_2Al-AlR_2$ (**1**), by the potassium metal reduction of R_2AlCl (R = $CH(SiMe_3)_2$) (eq 1).[8] The considerable steric bulk of the ligand, coupled with its attractive electronic properties, was cited as being critical in the stabilization of **1**. The hybridization of the three-coordinate aluminum atoms in **1** is sp^2, leaving one unhydridized p orbital on each metal atom. The $C_2Al-AlC_2$ core of **1** was shown to be nearly planar, with an Al−Al bond distance of 2.660(1) Å (Figure 1). The Al−Al single bond distance reported for **1** is only slightly longer than that reported for $[(2,4,6\text{-}i\text{-}Pr)_3C_6H_2]_2Al-Al[C_6H_2(2,4,6\text{-}i\text{-}Pr)_3]_2$ (2.647(3) Å)[9] but shorter than that observed for $[(t\text{-}Bu)_3Si]_2Al-Al[Si(t\text{-}Bu)_3]_2$ (2.751(2) Å).[10] The planar $C_2Al-AlC_2$ core of **1** is easily contrasted with the twisted $C_2Al-AlC_2$ core of $[(2,4,6\text{-}i\text{-}Pr)_3C_6H_2]_2Al-Al[C_6H_2(2,4,6\text{-}i\text{-}Pr)_3]_2$ (dihedral angle between the two C_2Al planes: 44.8°). Clearly,



1

(1)

---

* To whom correspondence should be addressed. E-mail: robinson@chem.uga.edu.

(1) Timoshkin, A. Y. *Coord. Chem. Rev.* **2005**, *249*, 2094−2131.

(2) Carmalt, C. J. *Coord. Chem. Rev.* **2001**, *223*, 217−264.

(3) Schram, E. P. *Inorg. Chem.* **1966**, *5*, 1291−1294.

(4) Schram, E. P.; Hall, R. E.; Glore, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 6643−6648.

(5) Hoberg, H.; Krause, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 694.

(6) Hoberg, H.; Krause, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 949−950.

(7) Miller, M. A.; Schram, E. P. *Organometallics* **1985**, *4*, 1362−1364.

(8) Uhl, W. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43b*, 1113−1118.

(9) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeion, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983−2984.

(10) Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431−5433.

10.1021/om060737i CCC: $37.00

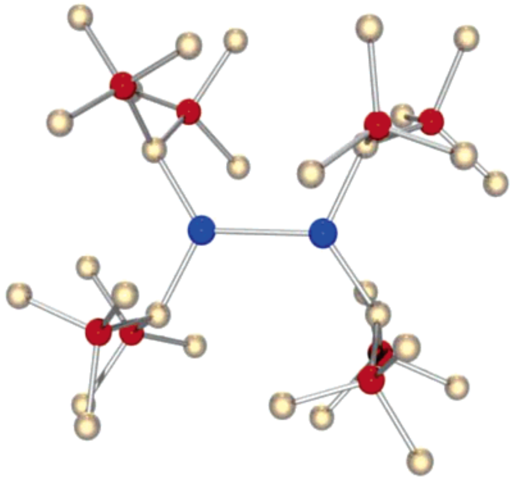


Figure 1. Molecular structure of $R_2Al-AlR_2$ (**1**). Hydrogen atoms have been omitted.

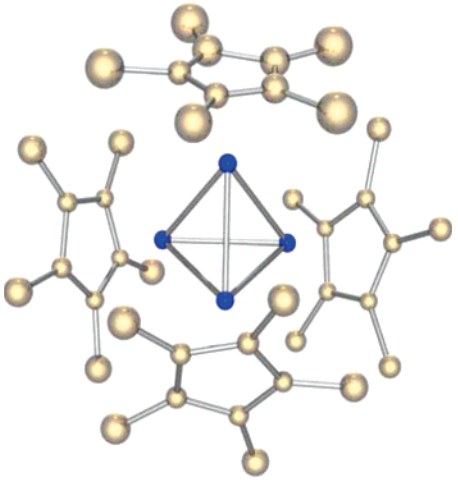
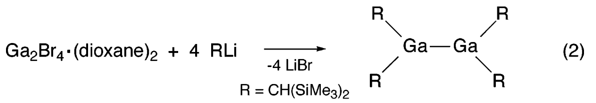


Figure 2. Molecular structure of $[AlCp^*]_4$ (**4**). Hydrogen atoms have been omitted.

the synthesis and structure determination of **1** were seminal accomplishments and laid the foundation for an exciting new area of chemistry: the organometallic chemistry of the group 13 metal−metal bond.

By allowing $Ga_2Br_4 \cdot 2(dioxane)$[11] to react with RLi (R = $CH(SiMe_3)_2$), Uhl also prepared the corresponding digallane analogue of **1**, $R_2Ga-GaR_2$ (**2**) (eq 2), thereby obtaining the first structurally characterized organometallic compound containing a Ga−Ga bond.[12] **2** was isolated as dark yellow crystals.



$$Ga_2Br_4 \cdot (dioxane)_2 + 4\ RLi \xrightarrow[-4\ LiBr]{} R_2Ga-GaR_2 \qquad R = CH(SiMe_3)_2 \qquad (2)$$

2

Similar to the case for **1**, the C_2M-MC_2 molecular core of **2** is nearly planar, while the Ga−Ga bond distance is 2.541(1) Å. In notable contrast, the molecular core of $R_2Ga-GaR_2$ (R = C_6H_2-2,4,6-*i*-Pr_3), prepared by reaction of RMgBr with $Ga_2Cl_4 \cdot 2(dioxane)$,[13] has a dihedral angle of 43.8° between the two C_2Ga planes and a Ga−Ga bond distance of 2.515(3) Å.

The first diindane, $R_2In-InR_2$ (**3**), was isolated as orange-red crystals from the reaction of $In_2Br_4 \cdot 2TMEDA$ with RLi (R = $CH(SiMe_3)_2$) in *n*-pentane.[14] The In−In bond distance of 2.828(1) Å for **3** is considerably shorter than those of two recently reported complexes containing In−In bonds: RIn−InR (R = $CH[CH_3C(R')N]_2$, R′ = C_6H_3-2,6-*i*-Pr_2) (3.1967(4) Å)[15] and RIn−InR (R = C_6H_3-2,6-C_6H_3-2,6-*i*-Pr_2) (2.9786(5) Å).[16] However, the In−In bond distance for **3** is longer than that reported for $R_2In-InR_2$ (R = C_6H_2-2,4,6-*i*-Pr_3)[17] (In−In = 2.775(2) Å). The reactivity of R_2M-MR_2 compounds has been reviewed.[18] Notably, having synthesized the entire $[(Me_3Si)_2HC]_2M-M[CH(SiMe_3)_2]_2$ triad (M = Al (**1**),[8] Ga (**2**),[12] In (**3**)[14]), Uhl planted the seeds of a fertile new area of main-group organometallic chemistry.

Group 13 Metallic Clusters

Significant advances have been made in the chemistry of clusters involving the heavier group 13 metals. In particular, the elegant work of Schnöckel[19−21] has demonstrated both the variety and promise of group 13 molecular clusters. Using a unique synthetic procedure involving MX (M = Al, Ga; X = Cl, Br) moieties, Schnöckle has prepared a number of large metallic clusters, including an Al_{77} cluster[22] and a Ga_{84} cluster.[23] This review, however, will be primarily concerned with smaller "molecular" clusters of aluminum, gallium, and indium with a maximum of 12 metallic atoms.

Reaction of AlCl with $Cp^*{}_2Mg$ ($Cp^* = C_5Me_5$) afforded the $[AlCp^*]_4$ cluster **4** (eq 3), as yellow crystals from a deep red solution.[24] The aluminum atoms in **4** formally assume the +1

$$4AlCl \cdot nEt_2O + 2Cp^*{}_2Mg \xrightarrow[-2MgCl_2]{} \underset{\mathbf{4}}{[AlCp^*]_4} \qquad (3)$$

oxidation state. The Al_4 tetrahedral core of **4** is striking (Figure 2), as the four pentamethylcyclopentadienyl ligands constitute an effective exterior shell. Each Cp* ring is η^5-coordinated to an aluminum atom, with the plane of each ring approximately parallel to the opposing Al_3-base plane of the tetrahedron. While the mean Al−C bond is 2.334 Å, the mean Al−Al bond distance of 2.769 Å is particularly noteworthy, as it is considerably longer than the Al−Al bond in **1** of 2.660(1) Å. The ^{27}Al NMR spectrum (70.4 MHz) of a benzene solution of **4** exhibited a singlet at δ −80.8 ppm ($\omega_{1/2}$ = 170 Hz).

The reaction of **4** with $[t\text{-}BuAs]_4$ yields yellow crystals of $[As_2(AlCp^*)_3]$.[25] The core of $[As_2(AlCp^*)_3]$ is an As_2Al_3 trigonal

---

(11) Beamish, J. C.; Small, R. W. H.; Worrall, I. J. *Inorg. Chem.* **1979**, *18*, 220−223.

(12) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289−300.

(13) He, X.; Barlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717−719.

(14) Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139−154.

(15) Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 4231−4235.

(16) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538−8539.

(17) Brothers, P. J.; Hübler, K.; Hübler, U.; Noll, B. C.; Olmstead, M. M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2355−2357.

(18) Uhl, W. *Coord. Chem. Rev.* **1997**, *163*, 1−32.

(19) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, *206*−*207*, 285−319.

(20) Schnöckel, H.; Schnepf, A. *Adv. Organomet. Chem.* **2001**, *47*, 235−281.

(21) Schnepf, A.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3532−3552.

(22) Ecker, A.; Weckert, E.; Schnöckel, H. *Nature* **1997**, *387*, 379−381.

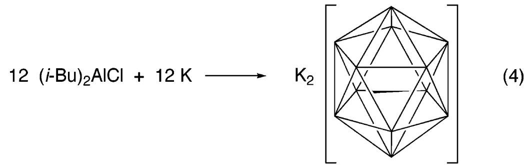
(23) Schnepf, A.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 711−715.

(24) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564−565.

(25) Hänisch, C. K. F. v.; Üffing, C.; Junker, M. A.; Ecker, A.; Kneisel, B. O.; Schöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2875−2877.

bipyramid: the three aluminum atoms reside in an Al_3 ring with the two arsenic atoms centered on either side. The pentamethylcyclopentadienyl ligands interact in an η^5 fashion with each aluminum atom in the basal plane. The bonding in the As_2Al_3 trigonal bipyramid was suggested by the authors to be similar to that of *closo*-boranes.

The rich chemistry of group 13 organometallic clusters is well illustrated by the potassium reduction of *i*-Bu_2AlCl. In stark contrast to the potassium reduction of $[(Me_3Si)_2HC]_2AlCl$ that produced **1**, the potassium reduction of *i*-Bu_2AlCl afforded the novel $K_2[Al_{12}i\text{-}Bu_{12}]$ cluster **5** (eq 4).[26] The isolation of **5**

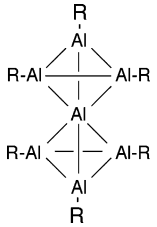


(4)

5

suggests that the steric bulk of the ligand (i.e., $(Me_3Si)_2HC$ for **1** compared to *i*-Bu for **5**) often plays a subtle yet determinative role in the nature of the reaction product. **5**, isolated in low yield as deep red crystals from a brown reaction mixture, is remarkable, as it contains a novel $Al_{12}{}^{2-}$ icosahedral core. The Al−Al bond distances in **5** span a rather narrow range from 2.679(5) to 2.696(5) Å. Indeed, these values are comparable to the Al−Al bond distance obtained for **1** (2.660(1) Å). The $[Al_{12}i\text{-}Bu_{12}]^{2-}$ dianion of **5** is very similar to the well-known icosahedral $[B_{12}H_{12}]^{2-}$ borane dianion, and (like the borane dianion) **5** obeys Wade's rules for closo structures. Interestingly, **5** was isolated from the same reaction described in one of the early studies purported to result in a dimeric Al−Al compound.[6] Another interesting Al_{12} nonicosahedral cluster resembling a small section of the aluminum elemental lattice was prepared by the reaction of AlCl with RLi (R = $(Me_3Si)_2N$).[27]

Surprisingly, utilization of the same reactants (a metastable AlCl solution with RLi (R = $(Me_3Si)_2N$) under milder reaction conditions ultimately gave black crystals of $[Li(OEt_2)_3][Al_7R_6]$.[28] The central aluminum atom in the $[Al_7R_6]^-$ anion (below) resides in a distorted octahedron of six aluminum atoms, each of which bonds to one NR_2 (R = $(Me_3Si)_2$) unit.



The bond distance from the central aluminum atom to its six metallic neighbors is 2.73 Å, while the Al−Al bond distances in the two Al_3R_3 units is 2.54 Å. Particularly interesting is the fact that the Al_7 configuration is quite similar to the solid-state ccp arrangement in elemental aluminum.

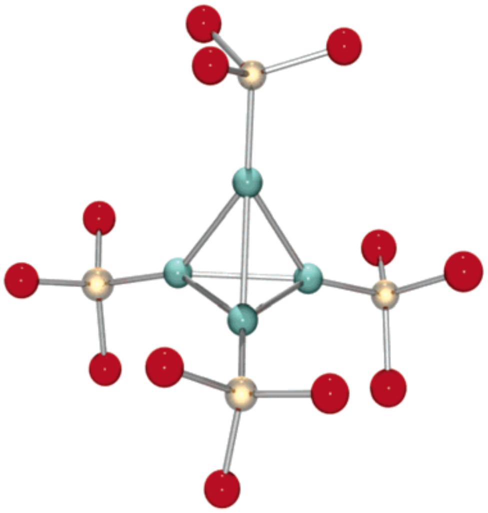


Figure 3. Molecular structure of $[GaR]_4$ (**6**). Hydrogen atoms and Me groups have been omitted.

Given that the reaction of $Ga_2Br_4{\cdot}2(dioxane)$ with RLi (R = $CH(SiMe_3)_2$) gave the $R_2Ga{-}GaR_2$ dimer **2** (eq 2), it is interesting that the reaction of $Ga_2Br_4{\cdot}2(dioxane)$ with RLi (R = $C(SiMe_3)_3$) afforded the gallium cluster $[GaR]_4$, (**6**) (eq 5).[29]

$$4Ga_2Br_4(dioxane)_2 + 12RLi \xrightarrow[R = C(SiMe_3)_3]{} \underset{\mathbf{6}}{[GaR]_4} \qquad (5)$$

Remaining stable in air for months without decomposition, **6**, isolated as red crystals, demonstrated remarkable stability. The mean Ga−Ga bond in **6** of 2.688 Å is somewhat longer than the Ga−Ga distance reported for the $R_2Ga{-}GaR_2$ dimer **2** (2.541(1) Å) (Figure 3).

A rather complex reaction involving ultrasonication of gallium metal, iodine, and $((Me_3Si)_3Si)Li$ produced a "silatetragallane": a cluster anion containing a Ga_4 tetrahedron "capped" on one end by an $Si(SiMe_3)$ unit.[30] The Ga−Ga distances to the apical gallium atom are 2.440 Å, while the Ga−Ga distances in the equatorial ring are considerably longer at 2.790 Å.

One of the more spectacular gallium-based tetrahedra is $[\{(Me_3Si)_3C\}_3Ga_3]Ga{-}Ga[Ga_3\{C(SiMe_3)_3\}_3]$[31] (**7**): a novel "double tetrahedron", wherein two Ga_4 tetrahedra are bridged by a single gallium−gallium bond (Ga−Ga = 2.6143(11) Å) (Figure 4). **7** was prepared by the reaction of trisyllithium dissolved in toluene at −78 °C with a toluene/THF solution of gallium(I) bromide, GaBr, generated by a condensation process.[32] Workup of the reaction mixture resulted in a black residue, from which crystals of **7** were obtained. All Ga−Ga−Ga bond angles within the two Ga_4 tetrahedra approach 60°. Moreover, the Ga−Ga bond distances in **7** span quite a narrow range (2.605−2.648 Å).

A single crystal of $[GaCp^*]_6$ was not grown from a solution, but rather acquired by cooling a molten sample of the "pure, freshly condensed material in a rigorously preconditioned Pyrex-glass capillary at about +4 °C."[33] The authors noted that the orientation of the Cp* ligands relative to the Ga_6 core is consistent with a second-order Jahn−Teller effect. The Ga_6 unit is not strictly octahedral, but rather compressed along a C_3 axis,

---

[26] Hiller, W.; Klinkhammer, K. W.; Uhl, W.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179−180.

[27] Purath, A.; Köppe, R.; Schnöckel, H. *Chem. Commun.* **1999**, 1933−1934.

[28] Purath, A.; Köppe, R.; Schnöckle, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2926−2928.

[29] Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364−1366.

[30] Linti, G.; Köster, W.; Piotrowski, H.; Rodig, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2209−2211.

[31] Schnepf, A.; Köppe, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1241−1243.

[32] Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129−149.

[33] Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Down, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860−862.

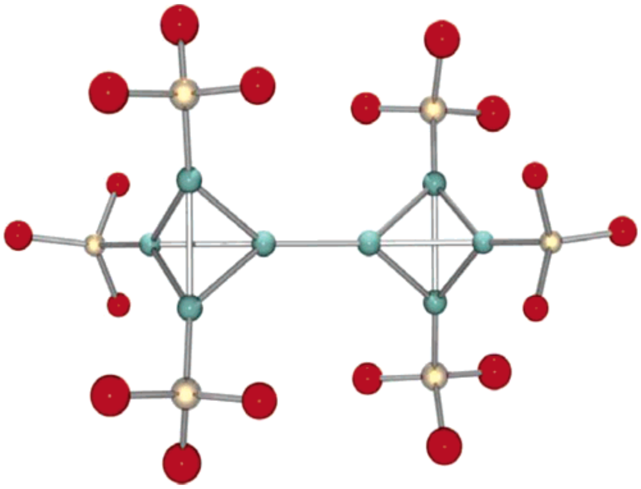


Figure 4. Molecular structure of $[\{(Me_3Si)_3C\}_3Ga_3]Ga{-}Ga[Ga_3\{C(SiMe_3)_3\}]$ (**7**) Hydrogen atoms and Me groups have been omitted.

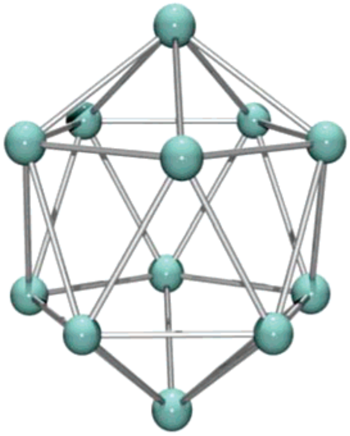


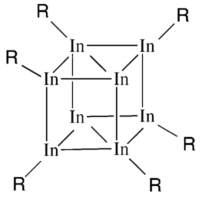
Figure 5. Molecular structure of the $[Ga_{12}R_{10}]^{2-}$ anion (**8**). Only the Ga_{12} core is shown.

revealing two distinct Ga_3 units. The Ga−Ga distances in $[GaCp^*]_6$ ranged from 2.45 to 3.07 Å.

Reaction of a metastable gallium(I) bromide solution with fluorenyllithium afforded crystals of $[Li(THF)_4]_2[Ga_{12}R_{10}]$ (R = $C_{13}H_9$), **8**—the first example of a Ga_{12} icosahedral unit.[34] The structure of the anion of **8** (Figure 5) reveals that fluorenyl ligands are attached to only 10 of the gallium atoms, leaving two "naked" gallium atoms at opposite ends of the icosahedron. The Ga−Ga bond distances range from 2.589 to 2.684 Å, while the Ga−C bond distances are shown to be 2.059 Å. Overall, the Ga_{12} icosahedral core of **8** is quite similar to the Al_{12} core of **5**.

Reaction of InBr with $RLi{\cdot}(THF)_2$ (R = $C(SiMe_3)_3$) produced $[InR]_4$ (**9**), thus completing the $[RM]_4$ (M = Al, Ga, In; R = $C(SiMe_3)_3$) tetrahedral series.[35] Again, **9** resides about an almost idealized metallic tetrahedral core with In−In bond distances of 3.002 (1) Å. Interestingly, **9** was shown to react with elemental selenium, giving the heterocubane $In_4Se_4\{C(SiMe_3)_3\}_4$.

Reaction of Cp*In with RNa (R = *t*-Bu_3Si) in pentane at −78 °C resulted in black-green crystals (from benzene) of In_8R_6 (R = *t*-Bu_3Si) (along with the diindane $R_2In{-}InR_2$):[36]



Thus, In_8R_6 is the first reported indium-based cubane. The compound contains two types of indium atoms: six indium atoms have a R group attached, while two indium atoms are "naked". The In−In bond distances in $(t\text{-}Bu_3Si)_6In_8$ range from 2.77 to 3.30 Å. Sensitive to both oxidation and hydrolysis, $(t\text{-}Bu_3Si)_6In_8$ was also light sensitive, depositing an indium mirror in the presence of light.

Another indium-based cubane, In_8R_4 (R = C_6H_3-2,6-Mes_2), has been prepared from the reaction of InCl with RLi.[37] This complex also contains two types of indium atoms: four indium atoms have terphenyl ligands attached, while four indium atoms are "naked", only bonding to three other indium atoms. The four terphenyl ligands effectively shield the metallic core of this compound. The In−In bond distances in In_8R_4 range from 2.857(4) to 2.966(4) Å.

Although catenation is a fundamental principle of organic chemistry, it is rarely observed in compounds of the heavier main-group elements. Nonetheless, there is a small, but growing, collection of "chain" group 13 compounds. The synthesis and molecular structure of a startling compound containing a linear arrangement of six indium atoms, with In−In distances ranging from 2.8122(10) to 2.8535(8) Å, was recently reported.[38] This hexaindium complex joins two Ga_3 compounds,[39,40] $In(InR_2)_3$ (R = C_6H_2-2,4,6-*i*-Pr_3),[17] and $Na_2[Ga(GaR_2)_3]$[41] (R = C_6H_3-2,4,6-*i*-Pr_3), as the only crystallographically characterized examples of catenated group 13 complexes.

Group 13 M−M Multiple Bonds

Soon after the first $R_2M{-}MR_2$ compounds containing M−M bonds (M = Al, Ga, In) were reported, efforts quickly shifted toward an even more ambitious goal: the synthesis of group 13 compounds containing multiple metal−metal bonds. The year 1993 proved to be particularly important in the development of this chemistry, as a number of noteworthy studies were reported. The lithium reduction of **1** at −30 °C in diethyl ether gave a black-violet solution from which crystals of the radical anion $[R_2Al{-}AlR_2]^{\bullet-}$ (**10**; R = $CH(SiMe_3)_3$) were isolated in the presence of TMEDA (eq 6).[42] While ESR spectra and magnetic measurements of **10** are supportive of a radical anion, the single-crystal X-ray structure is particularly compelling: the Al−Al bond distance of 2.53(1) Å in **10** compares to 2.660(1) Å for **1**. Although a crystal structure was not reported, Uhl[43] also prepared **10** by potassium metal reduction of **1** in 1,2-

---

[34] Schnepf, A.; Stösser, G.; Köppe, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1637−1639.

[35] Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1−C5.

[36] Wiberg, N.; Blank, T.; Purath, A.; Stösser, G.; Schnöckel, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2563−2565.

[37] Eichler, B. E.; Hardman, N. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 383−385.

[38] Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Science* **2006**, *311*, 1904−1907.

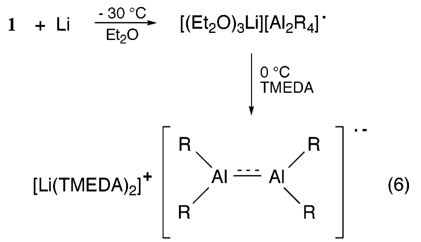
[39] Li, X.-W.; Wei, P.; Beck, B. C.; Xie, Y.; Schaefer, H. F.; Su, J.; Robinson, G. H. *Chem. Commun.* **2000**, 453−454.

[40] Schnepf, A.; Doriat, C.; Möllhausen, E.; Schnöckel, H. *Chem. Commun.* **1997**, 2111−2112.

[41] Wehmschulte, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 3152−3154.

[42] Pluta, C.; Pörschke, K.-R.; Krüger, C.; Hildenbrand, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 388−390.

[43] Uhl, W.; Vester, A.; Kaim, W.; Poppe, J. *J. Organomet. Chem.* **1993**, *454*, 9−13.



10

dimethoxyethane. In addition, the dark blue radical anion **10** was also obtained by a single-electron-transfer reaction of **1** with ((trimethylsilyl)methyl)lithium in the presence of TMEDA.

Another interesting radical anion containing an Al−Al bond with π-bonding character, $[(2,4,6\text{-}i\text{-Pr})_3C_6H_2]_2Al{-}Al[C_6H_2(2,4,6\text{-}i\text{-Pr})_3]_2^{\bullet-}$ (**11**) (Al−Al = 2.407(2) Å (average), torsion angle between the two C_2Al planes 1.4°), was obtained from the lithium metal reduction of $[(2,4,6\text{-}i\text{-Pr})_3C_6H_2]_2Al{-}Al[C_6H_2(2,4,6\text{-}i\text{-Pr})_3]_2$ (Al−Al = 2.647(3) Å; torsion angle between the two C_2Al planes 44.8°) in the presence of TMEDA or 12-crown-4.[9] The radical character of **11** was manifested in the EPR spectrum. In comparison with the neutral dialane, the Al−Al bond distance in **11** is considerably shortened.

The corresponding digallane radical anion $[(2,4,6\text{-}i\text{-Pr})_3C_6H_2]_2Ga{-}Ga[C_6H_2(2,4,6\text{-}i\text{-Pr})_3]_2^{\bullet-}$ (**12**) was obtained, as dark brown-red crystals, from the alkali-metal reduction of the neutral species $[(2,4,6\text{-}i\text{-Pr})_3C_6H_2]_2Ga{-}Ga[C_6H_2(2,4,6\text{-}i\text{-Pr})_3]_2$ (Ga−Ga = 2.515(3) Å; torsion angle between the two C_2Ga planes 43.8°).[13] The molecular structure of **12** exhibited significant differences compared to the neutral $[(2,4,6\text{-}i\text{-Pr})_3C_6H_2]_2Ga{-}Ga[C_6H_2(2,4,6\text{-}i\text{-Pr})_3]_2$ species: the Ga−Ga bond distance was substantially shortened to 2.343(2) Å (from 2.515(3) Å), while the torsion angle between the two C_2Ga planes was decreased to 15.5° (from 43.8°).

Almost without question, the most provocative[44,45] group 13 compound containing multiple metal−metal bonds is $Na_2[RGa{\equiv}GaR]$ (**13**; R = $C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}i\text{-Pr}_3)_2$)[46] (Figure 6), which was prepared by the sodium metal reduction of $RGaCl_2$.[47] The core of **13**, completed by two sodium atoms residing on either side of the Ga−Ga bond (Ga···Na(mean) = 3.08 Å), constitute a nearly planar Ga_2Na_2 four-membered ring, which is sterically protected by the two *m*-terphenyl ligands. The distances of the two sodium ions to the centroid of the terminal phenyl ring of the ligands ranged from 2.780 to 2.835 Å. The Ga−Ga bond distance of 2.319(3) Å in **13** was particularly noteworthy, as it was among the shortest reported, while the C−Ga−Ga bond angles of 128.5(4) and 133.5(4)° (mean value 131.0°) were decidedly nonlinear. Due to the nonlinear orientation of the C−Ga−Ga−C backbone, the molecular structure of **13** was described as “trans-bent”.[46] With regard to the most appropriate manner to describe the bonding between the two gallium atoms, this laboratory held that **13** represented the first example of a Ga≡Ga triple bond, the first *digallyne* (or *gallyne*)—despite the decidedly nonlinear C−Ga−Ga−C array. Indeed, **13** represents the first example of triple-bond formation for any main-group metal. **13** fueled a lively debate concerning fundamental issues of structure and bonding.[44,45,48,49] The two most relevant questions regarding **13** were as follows. (1) Is it reasonable to consider the gallium−gallium interaction in **13** as a triple bond? (2) If the gallyne formulation for **13** is reasonable, how does one embrace the trans-bent C−Ga−Ga−C array?

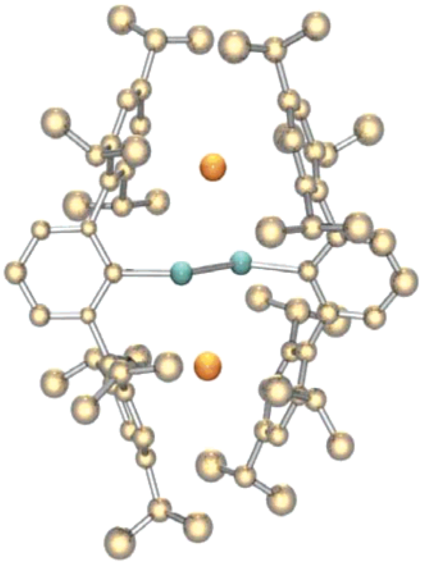
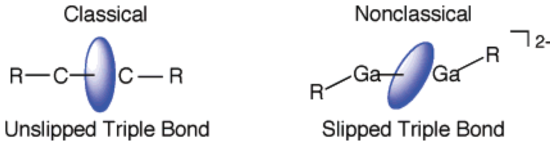


Figure 6. Molecular structure of $Na_2[RGa{\equiv}GaR]$ (**13**) Hydrogen atoms have been omitted.

In support of the digallyne formulation for **13**, it has been suggested that the gallium−gallium bonding may be interpreted in terms of “having a distorted σ-bond, a significantly weakened π bonding which is localized strongly on the Ga atoms, and a pure π-bond perpendicular to the Ga_2C_2 plane.”[50] These workers further noted that a second-order Jahn Teller distortion could account for the observed trans-bent C−Ga−Ga−C geometry.

Topographical analysis using the electron localization function (ELF) also supported the gallyne formulation for **13**.[51] Relative to triple bonds involving main-group elements, ELF is able to not only confirm the “nonexistence of multiple bonds” but also differentiate between classical, “unslipped”, triple bonds and nonclassical, “slipped”, triple bonds. ELF was used to compare HC≡CH with $Na_2[HGa{\equiv}GaH]$. For HC≡CH the chemical bond was represented as a cylindrical torso following the symmetry of the molecule (below) and the ELF maxima were represented by “ring attractors”, as was previously proposed.[52] Applying the same analysis to $Na_2[HGa{\equiv}GaH]$, the authors noted “remarkably, the torso-type shape of the triple-bond domain is retained in the non-classical digallyne dianion $[HGa{\equiv}GaH]^{2-}$”: In unambiguous support of the gallyne formulation for **13** the authors concluded, “Clearly this compound has a triple bond!”



The most recent support for the gallyne formulation for **13** was reported in an article entitled “Triple-Bond Covalent Radii”.[53] As noted in this article, claims for a triple-bond character could be based on the bond distance itself, a visual

---

[44] Dagani, R. *Chem. Eng. News* **1997**, *75*(June 16), 9−10.

[45] Dagani, R. *Chem. Eng. News* **1998**, *76*(March 16), 31−35.

[46] Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471−5472.

[47] Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1998**, 2015−2016.

[48] Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795−1799.

[49] Takagi, N.; Schmidt, M. W.; Nagase, S. *Organometallics* **2001**, *20*, 1646−1651.

[50] Bytheway, I.; Lin, Z. *J. Am. Chem. Soc.* **1998**, *120*, 12133−12134.

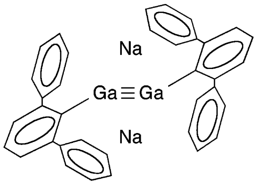
[51] Grützmacher, H.; Fässler, T. F. *Chem. Eur. J.* **2000**, *6*, 2317−2325.

[52] Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683−686.

[53] Pyykkö, P.; Riedel, S.; Patzschke, M. *Chem. Eur. J.* **2005**, *11*, 3511−3520.

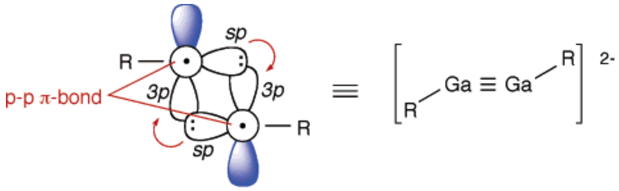
analysis of the σ- and π-molecular orbitals, or a quantitative analysis of the contributions to bonding energy from a given choice of reference monomers. Thus, for the purposes of this study these workers used the following criteria: "A coherent bond length amplified by some $\sigma^2\pi^4$ character in the wave function will form an entrance ticket to the data set." In support of the gallyne formulation the workers conclude, "With respect to the Ga≡Ga triple bond suggested by Robinson's group [for **13**], our results do not disagree with the idea. In fact, their homonuclear Ga−Ga bond distance of 232 pm is shorter than twice the present *r*(Ga) value of 121 pm, largely based on heteronuclear pairs."

The concept of bond orders is relevant to this discussion. Bond order values are largely a function of the given "bond order" definition. Thus, different methods will yield different values. However, consistent trends should emerge if the same bond order method is applied to a group of similar chemical entities. The NLMO/NPA bond order value of 3.02 for $[HGaGaH]^{2-}$ obtained by this laboratory[54] was criticized for relying on overly simplistic model molecules (i.e., $Na_2[RGaGaR]$; R = H, Me).[45,49] In direct response to this criticism, this laboratory performed a DFT study on a "more realistic" model gallyne: $Na_2[RGaGaR]$ (**13A**; R = C_6H_3-2,6-Ph_2). **13A**, only lacking the isopropyl substituents, very closely resembles the experimental molecule **13**. The model **13A** gallyne was fully optimized with the B3LYP method utilizing a substantial basis set of 836 contracted Gaussian functions. A NLMO/NPA bond order value of 2.79 was obtained for **13A**. Thus, compelling bond order values of 3.02 (for $[HGaGaH]^{2-}$) and 2.79 (for **13A**) offer unambiguous support for the digallyne formulation for **13**.[55]



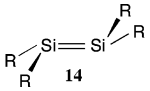
13A

Regarding the trans-bent geometry of **13**, it is appropriate to consider that heavier main-group elements may engage in multiple bonding modes different from that of carbon. For the two R−Ga: fragments of **13** the gallium atom in each could be regarded as predominantly sp hybridized, keeping two valence electrons paired with its remaining valence electron bonding to the ipso carbon atom of the ligand system. This leaves two unhybridized p orbitals on each gallium atom. Thus, the digallyne formulation for $[RGaGaR]^{2-}$ (**13**) may be regarded as two donor−acceptor (dative) bonds augmented by one π bond (populated by two electrons from the two sodium atoms):[54,56]



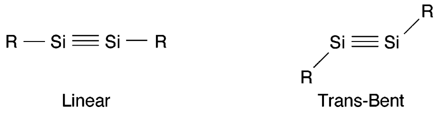
13

To place the gallium−gallium bonding in **13** in a larger context, it is necessary to investigate the bonding modes of other compounds containing multiple bonding between heavier main-group elements. Thus, it is appropriate to examine tetramesityldisilene, $R_2Si{=}SiR_2$ (**14**; R = mesityl), the first compound shown to contain a silicon−silicon double bond—the first disilene.[57] The X-ray structure[58] of **14** revealed a Si═Si double-bond distance of 2.15 Å (Si−Si single-bond distances generally approach 2.35 Å). The geometry about the silicon atoms in **14** was not trigonal planar, as would be expected for sp^2-hybridized carbon. Rather, the authors described the coordination as a "trans-bent geometry of the disilene framework". The pyramidalization at the silicon atoms in **14** is indicated by the 18° angle formed by the C_{aryl}−Si−C_{aryl} plane and the silicon−silicon axis. These facts suggested that the multiple bonding mode involving heavier main-group elements, even for silicon, may be different from that of carbon.



14

Given that the experimental realization of the elusive silicon−silicon triple bond, RSi≡SiR, proved exceedingly difficult, the concept of a disilyne has long been a source of inspiration, fascination, and frustration for chemists. However, computational and theoretical chemists have consistently maintained that the ubiquitous linear geometry favored by carbon in HC≡CH is not a global minimum on the potential energy surface of RSi≡SiR model molecules; rather, silicon favors a "trans-bent" structure:[59,60]



It has been reasoned that silicon—quite unlike carbon—has a strong tendency to keep the $3s^2 3p^2$ electronic configuration without significant hybridization.[59] This essentially results in the two-paired electrons remaining in an orbital with high 3s character. The SiH doublet ground state has been calculated to be 42.6 kcal/mol (3-21G*) more stable than the SiH quartet state.[59] It has further been predicted that the bonding between two such silicon atoms could best be described as two dative (donor−acceptor) bonds and one π-bond.[59,61] This bonding model, at odds with the traditional manner of describing a triple bond between two carbon atoms (one σ-bond and two π-bonds), is traced to a resistance of the ns^2 electrons to hybridize.

In a monumental achievement Sekiguchi[62] recently succeeded in synthesizing the first disilyne, **15**, by the potassium graphite reduction of a sterically encumbered organosilane (eq 7; R = $CH(SiMe_3)_2$, R′ = *i*-Pr). The −Si≡Si− triple-bond distance in **15** of 2.0622(9) Å compares to 2.15 Å for the Si═Si double-bond distance in **14** (and to 2.35 Å for Si−Si single-bond distances). The coordination about the silyl silicon atoms in **15** was indeed described as "trans-bent" with a decidedly nonlinear

---

[54] Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773−3780.

[55] Xie, Y.; Schaefer, H. F.; Robinson, G. H. *Chem. Phys. Lett.* **2000**, *317*, 174−180.

[56] Klinkhammer, K. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 2320−2322.

[57] West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343−1344.

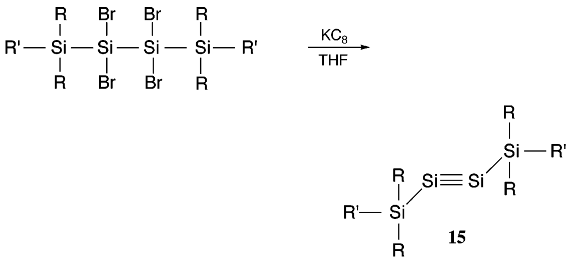
[58] Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793−800.

[59] Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489−2491.

[60] Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234−236.

[61] Nagase, S.; Kobayashi, K.; Takagi, N. *J. Organomet. Chem.* **2000**, *611*, 264−271.

[62] Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755−1724.

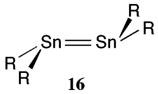


15

(7)

Si−Si−Si bond angle of 137.44°. The disilyne Si−Si−Si bond angle of 137.44° compares to the mean digallyne C−Ga−Ga bond angle of 131.0° for **13**.

It is significant that this bonding phenomenon is also observed in the first distannene, $R_2Sn{=}SnR_2$ (**16**; R = $CH(SiMe_3)_2$).[63]

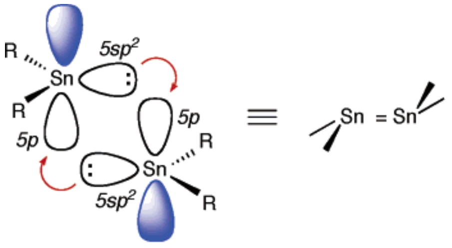


16

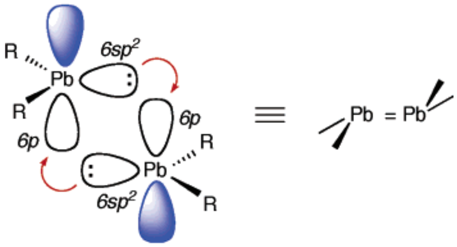
16 was described as "trans-bent" with a weak Sn═Sn double bond by the authors. The Sn═Sn double-bond distance in **16** is 2.76 Å, with an average Sn−Sn−C bond angle of 115° and C−Sn−C bond angle of 112°.

As has been elegantly noted,[51] from the very beginning **16** has been at odds with commonly accepted valence bond concepts of multiple bonding. (a) The $C_2Sn{=}SnC_2$ core was trans-bent (not planar), with the tin atoms pyramidized at an angle of 41° between the R_2Sn plane and the Sn−Sn double-bond axis. (b) The Sn═Sn bond distance (2.76 Å) was only slightly shorter than corresponding Sn−Sn single bonds (for example, $Ph_3Sn{-}SnPh_3$, with Sn−Sn = 2.770 Å).[64] (c) The molecule readily dissociated in solution into two R_2Sn: stannylene fragments. Nonetheless, in obvious support of the distannene formulation for **16** Power and Brothers[65] not only described this compound as "a tin analogue of a substituted ethene" but unambiguously opined further: "The discovery of such compounds [as **16**] has shown that the classical σ/π-model of the double bond in carbon, nitrogen, or oxygen compounds does not necessarily apply to the heavier elements."

Basically, the same donor−acceptor bonding model employed for **16** was proposed for the first diplumbene, $R_2Pb{=}PbR_2$ (**17**; R = C_6H_2-2,4,6-*i*-Pr_3).[66] Essentially, the double bonds in both **16** and **17** may be regarded as two donor−acceptor (dative) bonds (below) as opposed to the ubiquitous C═C double bond model of one σ bond and one π bond. The Pb═Pb double bond distance of 3.0515(3) Å in **17** is easily compared with Pb−Pb single-bond distances in other compounds: 2.85 Å for $Ph_3Pb{-}PbPh_3$,[67] 2.85 Å for $(C_6H_{11})_3Pb{-}Pb(C_6H_{11})_3$,[68] and 2.8697(10) Å for $(biphenyl)_3Pb{-}Pb(biphenyl)_3$.[69] Thus, *the Pb═Pb double bond* ($R_2Pb{=}PbR_2 = 3.0515(3)$ Å) *in* **17** *is longer than a number of Pb−Pb single bonds* ($R_3Pb{-}PbR_3 = 2.85, 2.8697(10)$ Å)*!*



16

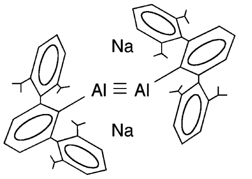


17

Therefore, at least for the heavier main-group elements, there does not appear to be a general correlation between bond multiplicity and bond distance (i.e., double bonds can be both longer and weaker than single bonds).

The chemistry community has largely accepted the silicon−silicon double bond (**14**), the tin−tin double bond (**16**), the lead−lead double bond (**17**), and the recently reported silicon−silicon triple bond (**15**)—along with the implicit premise that these main-group elements engage in multiple-bonding modes considerably different from those of carbon. The similarity of the bonding mode for the gallium−gallium triple bond, **13**, to those put forth for **16** and **17** is striking: essentially, the (donor−acceptor) double-bond model, evident in the distannene and the diplumbene, is augmented by a π-bond, affording a triple bond in the gallyne. The trans-bent geometry evident in the disilyne (**15**) is prominently manifested in the gallyne (**13**). NLMO/NPA bond order values of 2.79 and 3.02 are also supportive of a gallium−gallium triple bond, albeit a weak one, in **13**. Thus, to answer the two questions posed at the beginning of this section: (1) the gallyne formulation for **13**, justifying the Ga−Ga triple-bond description, is quite reasonable and (2) the trans-bent orientation is almost commonplace for multiply bonded compounds of the heavier main-group elements.

Immediately prior to the submission of this *Organometallics* review, the synthesis and molecular structure of a very significant compound was reported by Power and co-workers: $Na_2[RAlAlR]$ (**18**; R = C_6H_3-2,6-(C_6H_3-2,6-*i*-$Pr_2)_2$).[70] Similar to the preparation of **13**, compound **18**, prepared by the sodium metal reduction of (*m*-terphenyl)AlX_2 (X = iodine) in diethyl ether, was isolated (20% yield) as deep red, almost black, crystals. **18** has an Al_2Na_2 core with Al−Al and Al−Na separations of 2.428(1) and 3.152(1) Å, respectively. Consistent



18

---

[63] Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261−262.

[64] Preut, V. H.; Haupt, H.-J.; Huber, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1973**, *396*, 81−89.

[65] Power, P. P.; Brothers, P. J. In *Advances in Organometallic Chemistry: Multiply Bonded Main Group Metals and Metalloids*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1996; pp 1−70.

[66] Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 187−189.

[67] Kleiner, N.; Dräger, M. *J. Organomet. Chem.* **1984**, *270*, 151−170.

[68] Kleiner, N.; Dräger, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40b*, 477−483.

[69] Wang, Y.; Quillian, B.; Wei, P.; Yang, X.-J.; Robinson, G. H. *Chem. Commun.* **2004**, 2224−2225.

[70] Wright, R. J.; Brynda, M.; Power, P. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5953−5956.

with the "digallyne" nomenclature of **13**, the workers referred to **18** as a "dialuminyne". Power described the bonding in **18** as consisting of one out-of-plane π-bond (HOMO), a slipped π-bond (HOMO-1), and a σ-bond (HOMO-2). Interestingly, Power's bonding description for **18** is very similar to that proposed by Bytheway and Lin[50] in 1998 for **13**: "The Ga−Ga bonding in trans-bent $[Ga_2R_2]^{2-}$ molecules is thus better described as having a distorted σ-bond, a significantly weakened π-bond which is localized strongly on the Ga atoms, and a pure π-bond perpendicular to the Ga_2C_2 plane." The Wiberg Bond Index (WBI) gave a bond order value of 1.13 for **18**. However, it should be noted that for many cases the WBI values are smaller than other corresponding formal bond order values. For example, the WBI value at the DZP SCF level of theory of the H−F bond in diatomic HF is 0.67, that of the O−H bond in H_2O is 0.76, and that of the B−N bond in $H_3B{\cdot}NH_3$ is only 0.55.[55] It is noteworthy that the trans-bent C−Al−Al bond angle of **18** (131.71(7)°) is virtually identical with the C−Ga−Ga mean bond angle of **13** (131.0°). These values compare to a value of 137.44° for C−Si−Si in **15**.

In order to further demonstrate the similarities between **18** and **13**, it is useful to compare the M−M bond distances in **1** ($R_2M{-}MR_2$: M = Al, R = $CH(SiMe_3)_2$)[8] and **2** ($R_2M{-}MR_2$: M = Ga, R = $CH(SiMe_3)_2$)[12] with those in **18** ($Na_2[RMMR]$: M = Al) and **13** ($Na_2[RMMR]$: M = Ga), respectively. The Al−Al bond distance of 2.660(1) Å in **1** compares to an Al−Al bond distance of 2.428(1) Å in **18**—a difference of 0.232 Å. The corresponding Ga−Ga bond distance of 2.541(1) Å in **2** compares to a Ga−Ga bond distance of 2.319(3) Å in **13**—a difference of 0.222 Å. Thus, the observed dialane-to-dialuminyne and digallane-to-digallyne M−M bond shortenings are virtually identical.

Indeed, given the preponderance of decidedly non-carbon-like behavior of compounds containing homonuclear multiple bonds of the heavier main-group elements, one is confronted with a counterintuitive, if awkwardly compelling, concept: "The classical multiple bond indicators—bond lengths and bond strengths—have no meaning for multiple bonds in which elements from the higher periods are involved. However, they are valid for an exceptional element: carbon."[51]

Cyclogallenes and Metalloaromaticity

The concept of aromaticity is arguably the most compelling construct throughout the whole of chemistry.[71] In support of the sempiternal nature of aromaticity, it has been argued that the scientific literature held more "aromatic" citations in the past decade than of "AIDS".[72] While aromaticity is not a directly measurable quantity, it may generally be considered a "manifestation of electron delocalization in closed circuits, in either two or three dimensions".[73] This results in energy lowering and a number of unusual, if well documented, chemical and physical properties. Recent discoveries have demonstrated, however, that the concept of aromaticity extends well beyond traditional constraints, even extending to main-group and transition metals—thus suggesting that *carbon is neither necessary nor sufficient for aromaticity*. In particular, the exceptional work of Bleeke[74−77] and Haley[78−83] with metallabenzenes, wherein a transition-metal MR fragment replaces an arene CH unit in a six-membered ring, has considerably extended the range of six-π-electron systems. With regard to main-group metals, Ashe[84] reported a compound termed a "gallatabenzene", wherein a Ga−Ph unit was substituted for a C−H unit in a C_6 ring. In contrast to these efforts, we sought to explore the feasibility of an all-metal ring system exhibiting traditional aromatic properties.

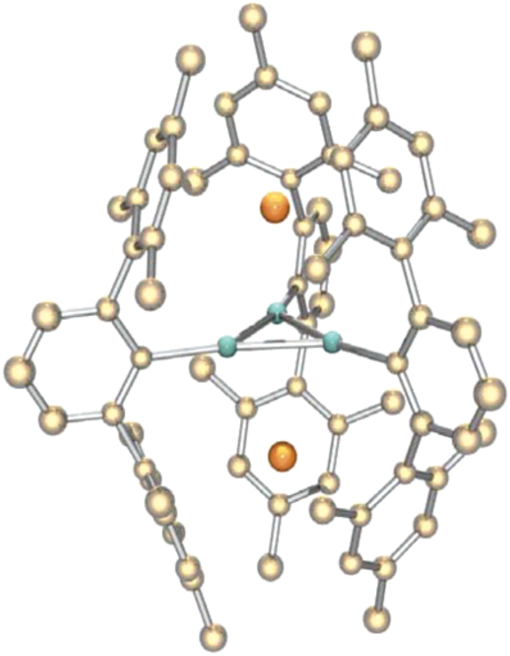


Figure 7. Molecular structure of $Na_2[Ga_3R_3]$ (**19**). Hydrogen atoms have been omitted.

Sodium metal reduction of (2,6-dimesitylphenyl)gallium dichloride, $RGaCl_2$ (R = C_6H_3-2,6-Mes_2),[85] as reported by this laboratory in 1995, gave a dark red solution from which dark red, almost black, crystals of $Na_2[Ga_3R_3]$[86] (**19**) were isolated (eq 8). Most notably, **19** contained an unprecedented Ga_3 ring

$$3RGaCl_2 + 8Na \xrightarrow[-6NaCl]{} \underset{\mathbf{19}}{Na_2[Ga_3R_3]} \qquad (8)$$

with Ga−Ga−Ga bond angles of 60.0(1)° (Figure 7). The core of **19** was completed by two sodium atoms centered about the centroid of the Ga_3 ring (Ga···Na = 3.220(2) Å). The distance of the sodium ions to the centroid of the mesityl rings is 3.181 Å. The Ga−Ga bond distance in **19** of 2.441(1) Å was reasonably short. The term "cyclogallene" was coined to

---

(71) Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115−1117.

(72) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385−1419.

(73) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842−3888.

(74) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205−1227.

(75) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606−623.

(76) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271−277.

(77) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118−4120.

(78) Gilbertson, R. D.; Lau, T. L. S.; Lanza, S.; Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2003**, *22*, 3279−3289.

(79) Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 4320−4322.

(80) Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3470−3472.

(81) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 437−441.

(82) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 2597−2598.

(83) Landorf, C. W.; Haley, M. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3914−3936.

(84) Ashe, A. J.; Al-Ahmad, S.; Kampf, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1357−1359.

(85) Crittendon, R. C.; Li, X.-W.; Su, J.; Robinson, G. H. *Organometallics* **1997**, *16*, 2443−2447.

(86) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578−7579.

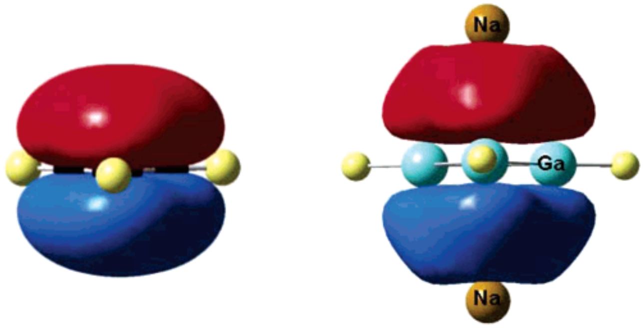
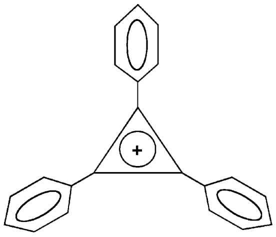
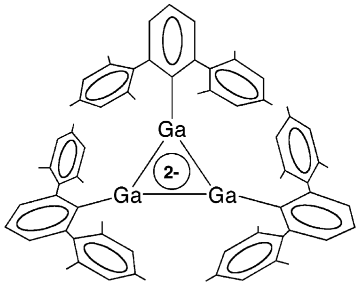


Figure 8. π-Electron cloud of $[C_3H_3]^+$ and $Na_2[Ga_3H_3]$.

distinguish this class of cyclic gallium ring compounds. We subsequently reported the synthesis and molecular structure of the potassium-based cyclogallene $K_2[Ga_3R_3]$ (R = C_6H_3-2,6-Mes_2),[87] with Ga−Ga bond distances of 2.4260(5), 2.4317(5), and 2.4187(5) Å, along with a mean Ga−Ga−Ga bond angle of 60.0°. With regard to the electronic properties of cyclogallenes, it is convenient to consider the gallium atoms as being three-coordinate with predominant sp^2 hybridization, thus leaving one unoccupied p orbital on each gallium atom. This situation would allow each of the two alkali metals to donate one electron to the unoccupied p orbitals of the gallium atoms, thus providing the necessary two π-electrons required for Hückel's $4N + 2$ rule and populating the π-orbitals. Indeed, cyclogallenes are suggestive of the triphenylcyclopropenium cation, $[C_3Ph_3]^+$—the simplest aromatic system with two π-electrons[88]—first prepared by Breslow.[89] Given the "aromatic" nature of the triphenylcyclopropenium cation, the term "metalloaromatic" seemed appropriate for the valence isoelectronic cyclogallene dianions:



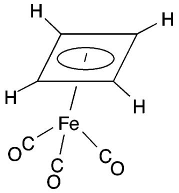
Triphenylcyclopropenium Cation
Aromatic



19
Cyclogallene Dianion
Metalloaromatic

Note the similarity of the π-electron cloud (HOMO-1) of $[C_3Ph_3]^+$ to that of the model $Na_2[Ga_3H_3]$ cyclogallene (Figure 8). Cyclogallenes have been theoretically examined using Density Functional Theory (DFT).[90,91]

The earliest use of the term "metalloaromaticity" may be traced to the work of Bursten and Fenske,[92] as it was used in an effort to describe a situation wherein traditional aromatic behavior appeared to have been "induced" into the cyclobutadienyl ring of $(C_4H_4)Fe(CO)_3$ via the Fe−C_4H_4 π-interaction:



Thus, the literal meaning of metalloaromaticity—that of a metallic, instead of a carbon, ring system displaying traditional aromatic behavior—was first experimentally realized with cyclogallenes in this laboratory.[90,91]

Largely due to the quadrupolar nature of the gallium nucleus, our experimental efforts to obtain unambiguous evidence of a ring current repeatedly proved inconclusive.[90] However, we embraced the concept of nucleus-independent chemical shifts (NICS), as described by Schleyer,[93] to probe the aromatic character of the gallium ring system. As defined by Schleyer, NICS are a purely calculational quantity, not a chemically observable phenomenon (somewhat similar in concept to bond orders). Nonetheless, NICS have been shown to correlate very well with observable indicators of aromaticity such as bond length equalization, aromatic stabilization energies (ASEs), and magnetic susceptibility exaltations ($\wedge$). The convention is that an aromatic species should give a negative NICS value. For reference purposes, the NICS(0) value for benzene of −8.03 ppm (GIAO-B3LYP/6-311+G**//B3LYP/6-311+G**) compares with NICS(0) values of −20.8 and −23.9 ppm for $[C_3H_3]^+$ and $[C_3Ph_3]^+$, respectively. These values compare with the NICS(0) (GIAO-B3LYP/6-311+G*//B3LYP/6-311+G*) value of −45.4 ppm for the model $[Ga_3H_3]^{2-}$ (D_{3h} symmetry).[73]

As is often the case with newly discovered phenomena, metalloaromaticity has not always been immediately recognized. This was precisely the case with $K_2[Ga_4R_2]$ (**20**; R = C_6H_3-(C_6H_2-2,4,6-*i*-Pr_3)),[94] which had a square-planar Ga_4 ring with a potassium ion centered on either side of the ring. Only two gallium atoms were bonded to an *m*-terphenyl ligand, while the remaining two gallium atoms had lost their ligands. The mean Ga−Ga bond distance was 2.4654 Å. Computations by Schleyer[73] on the $[Ga_4H_2]^{2-}$ model dianion **20** (GIAO-B3LYP/6-311+G*//B3LYP/6-311+G*) showed that its HOMO-1 is a π-orbital, and the negative NICS value of −19.9 ppm confirms its metalloaromatic nature. Another Ga_4 ring compound, $Na_2[Ga_4R_4](THF)_2$ (**21**; R = Si(*t*-Bu)$_3$),[95] has also been found to have metalloaromatic nature. Although the Ga_4 ring (mean Ga−Ga bond distance 2.43 Å) was found to have a nonplanar butterfly shape, the authors suggested that the gallium ring was

---

(87) 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*, 3798−3803.

(88) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10−14.

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

(90) Xie, Y.; Schreiner, P. R.; Schaefer, H. F.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, *118*, 10635−10639.

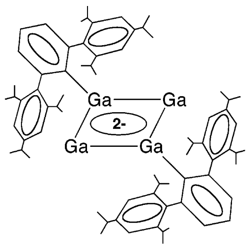
(91) Xie, Y.; Schreiner, P. R.; Schaefer, H. F.; Li, X.-W.; Robinson, G. H. *Organometallics* **1998**, *17*, 114−122.

(92) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760−1765.

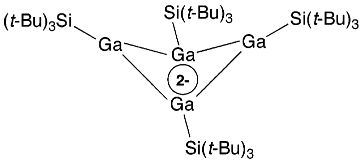
(93) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

(94) Twamley, B.; Power, P. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3500−3502.

(95) Wiberg, N.; Blank, T.; Westerhausen, M.; Schneiderbauer, S.; Schnöckel, H.; Krossing, I.; Schnepf, A. *Eur. J. Inorg. Chem.* **2002**, 351−356.



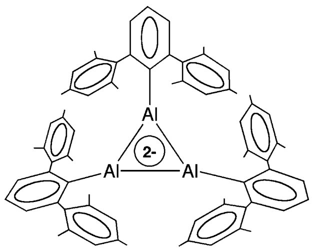
20



21

a two-π-electron aromatic system (with the nonplanarity being caused by steric hindrance of the four supersilyl groups). In both **20** and **21**—as was the case with the original cyclogallenes—the gallium ring is stabilized by donation of electrons from the alkali-metal ions into the π-orbital of the gallium ring system. It should also be noted that the cyclotrigermenylium cation $[GeR]_3^+$ (R = Si(*t*-Bu)$_3$) is another example of a two-π-electron metalloaromatic system.[96] All-metal aromatics have recently been reviewed.[97,98]

Quite recently an aluminum analogue of the gallium-based cyclogallenes[86,87,90,91] $M_2[Ga_3R_3]$, $Na_2[Al_3R_3]$ (**22**; R = C_6H_3-2,6-Mes_2),[70] was prepared by the sodium metal reduction of $RAlI_2$ in diethyl ether. Similar to the gallium atoms in cyclogallenes, the aluminum atoms in **22** can be considered sp^2 hybridized. Thus, **22** is the first X-ray structurally characterized two-π-electron metalloaromatic aluminum ring system (Al—Al = 2.5202(2) Å).



22

Conclusions

In less than two decades since the first report of a structurally characterized compound containing a M—M bond (M = Al, Ga, In), the organometallic chemistry of the M—M bond has developed into one of the most vibrant and exciting areas of chemistry. The variety of compounds containing the M—M bond is truly striking. It is also significant that a number of these compounds have facilitated debate among scientists on fundamental issues of structure and bonding. Organometallic compounds containing M—M multiple bonds underscore the inherent differences between carbon and the heavier main-group elements. The concept of metalloaromaticity, although still in its formative stages, confirms that metallic ring systems are quite capable of displaying traditional aromatic behavior.

Acknowledgment. G.H.R. is grateful to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are thankful for a number of talented co-workers. Special gratitude is extended to Drs. Xiao-Wang Li, Jianrui Su, and Pingrong Wei.

OM060737I

---

[96] Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60−61.

[97] Tsipis, C. A. *Coord. Chem. Rev.* **2005**, *249*, 2740−2762.

[98] Boldyrev, A. I.; Wang, L.-S. *Chem. Rev.* **2005**, *105*, 3716−3757.