

## Structures, Bonding, and Reaction Chemistry of the Neutral Organogallium(I) Compounds (GaAr)<sub>n</sub> (n = 1 or 2) (Ar = Terphenyl or Related Ligand): An Experimental Investigation of Ga–Ga Multiple Bonding

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**Abstract:** The synthesis, structure, and properties of several new organogallium(I) compounds are reported. The monovalent compounds GaAr\* (Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sub>3</sub>, **1**), GaAr<sup>#</sup> (Ar<sup>#</sup> = C<sub>6</sub>H<sub>3</sub>-2,6(Bu<sup>t</sup>Dipp)<sub>2</sub>, Bu<sup>t</sup>Dipp = C<sub>6</sub>H<sub>2</sub>-2,6-Pr<sub>2</sub>-4-Bu<sup>t</sup>, **4**), and the dimeric (GaAr')<sub>2</sub> (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>, Dipp = C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sub>2</sub>, **6**) were synthesized by the reaction of "Gal" with (Et<sub>2</sub>O)LiAr\*, (Et<sub>2</sub>O)LiAr<sup>#</sup> (**3**), or (LiAr')<sub>2</sub>. Compounds **1** and **4** were isolated as green crystals, whereas **6** was obtained as a brown-red crystalline solid. All three compounds dissolved in hydrocarbon solvents to give green solutions and almost identical UV/visible spectra. Cryoscopy of **1** and **6** showed that they were monomeric in cyclohexane. Crystals of **1** and **4** were unsuitable for X-ray crystal structure determinations, but an X-ray data set for **6** showed that it was weakly dimerized in the solid with a long Ga–Ga bond of 2.6268(7) Å and a trans-bent CGaGaC core array. The 1,2-diiodo-1,2-diaryldigallane compounds {Ga(Ar\*)I}<sub>2</sub> (**2**), {Ga(Ar<sup>#</sup>)I}<sub>2</sub> (**5**), and {Ga(Ar')I}<sub>2</sub> (**7**) were isolated as byproducts of the synthesis of **1**, **4**, and **6**. The crystal structures of **2** and **7** showed that they had planar ICGaGaC core arrays with Ga–Ga distances near 2.49 Å, consistent with Ga–Ga single bonding. Treatment of **1**, **4**, and **6** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> immediately afforded the 1:1 donor–acceptor complexes ArGa{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (Ar = Ar\*, **8**; Ar<sup>#</sup>, **9**; Ar', **10**) that featured almost linear gallium coordination, Ga–B distances near the sum of the covalent radii of gallium and boron, as well as some close Ga...F contacts. Compound **1** also reacted with Fe(CO)<sub>5</sub> under ambient conditions to give Ar\*GaFe(CO)<sub>4</sub> (**11**), which had been previously synthesized by the reaction of GaAr\*Cl<sub>2</sub> with Na<sub>2</sub>Fe(CO)<sub>4</sub>. Reaction of **1** with 2,3-dimethyl-1,3-butadiene afforded the compound {Ar\*GaCH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>}<sub>2</sub> (**12**) that had a 10-membered 1,5-Ga<sub>2</sub>C<sub>8</sub> ring with no Ga–Ga interaction. Stirring **1** or **6** with sodium readily gave Na<sub>2</sub>{Ar\*GaGaAr\*} (**13**) and Na<sub>2</sub>(Ar'GaGaAr') (**14**). The former species **13** had been synthesized previously by reduction of GaAr\*Cl<sub>2</sub> with sodium and was described as having a Ga–Ga triple bond because of the short Ga–Ga distance and the electronic relationship between [Ar\*GaGaAr\*]<sup>2-</sup> and the corresponding neutral group 14 alkyne analogues. Compound **14** has a similar structure featuring a trans-bent CGaGaC core, bridged by sodiums which were also coordinated to the flanking aryl rings of the Ar' ligands. The Ga–Ga bond length was found to be 2.347(1) Å, which is slightly (ca. 0.02 Å) longer than that reported for **13**. Reaction of Ga{N(Dipp)C(Me)}<sub>2</sub>CH, **15** (i.e., GaN<sup>^</sup>NDipp<sub>2</sub>), which is sterically related to **1**, **4**, and **6**, with Fe(CO)<sub>5</sub> yielded Dipp<sub>2</sub>N<sup>^</sup>NGaFe(CO)<sub>4</sub> (**16**), whose Ga–Fe bond is slightly longer than that observed in **11**. Reaction of the less bulky LiAr'' (Ar'' = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) with "Gal" afforded the new paramagnetic cluster Ga<sub>11</sub>Ar<sub>4</sub>'' (**17**). The ready dissociation of **1**, **4**, and **6** in solution, the long Ga–Ga distance in **6**, and the chemistry of these compounds showed that the Ga–Ga bonds are significantly weaker than single bonds. The reduction of **1** and **6** with sodium to give **13** and **14** supplies two electrons to the di-gallium unit to generate a single bond (in addition to the weak interaction in the neutral precursor) with retention of the trans-bent geometry. It was concluded that the stability of **13** and **14** depends on the matching size of the sodium ion, and the presence of Na–Ga and Na–Ar interactions that stabilize their Na<sub>2</sub>Ga<sub>2</sub> core structures.

### Introduction

Metal–metal bonded clusters of the heavier group 13 elements of formula (MR)<sub>n</sub> (M = Al–Tl; R = organo or related group) are an extremely interesting compound class, whose chemistry has undergone rapid development over the past decade.<sup>1–9</sup> They can be isolated in various degrees of aggregation that include weakly bonded hexamers, which have distorted

octahedral metal arrays (e.g., {M(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>6</sub> (M = Ga<sup>2</sup> or In<sup>3</sup>)}, more strongly bonded tetramers featuring M<sub>4</sub> tetrahedra

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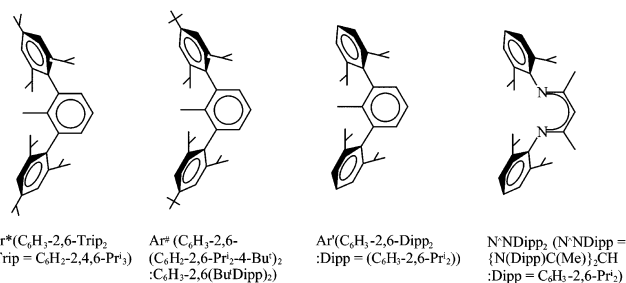
(e.g.,  $\{\text{Al}(\eta^5\text{-C}_5\text{Me}_5)\}_4$ ,<sup>4</sup>  $[\text{M}\{\eta^5\text{-C}(\text{SiMe}_3)_3\}]_4$  ( $\text{M} = \text{Al-Tl}^5$ )), and feebly bonded dimers (e.g.,  $[\text{M}\{\eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5\}]_2$  ( $\text{M} = \text{In}^6$  or  $\text{Tl}^7$ ), which have  $\text{M-M}$  distances that are ca. 0.7–0.8 Å longer than single bonds. Rare examples of higher aggregates include  $(\text{GaCH}_2\text{CMe}_2\text{Ph})_n$ ,<sup>8</sup> of unknown structure, or the tricapped trigonal prismatic  $(\text{GaBu}^f)_9$ .<sup>9</sup> A notable feature of the clusters in which  $n \geq 4$  is that they are electron deficient with  $\text{M-M}$  bond orders  $< 1$ . When  $n = 3$ , it is in principle possible to form a trigonal planar  $\text{M-M}$  bonded  $(\text{MR})_3$  cluster in which the metals are connected by two-center two-electron donor–acceptor bonds, although unfilled metal valence orbitals are still present. In a neutral, dimeric RMMR species, multiple  $\text{M-M}$  bonding becomes a possibility, but apart from the weakly interacting  $[\text{M}\{\eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5\}]_2$  ( $\text{M} = \text{In}$  or  $\text{Tl}$ )<sup>6,7</sup> compounds mentioned above, no dimeric group 13 element  $(\text{MR})_2$  species with  $\text{M-M}$  distances approaching the sum of their covalent radii have been isolated as stable compounds.

Our interest in such compounds derives from investigations of the reaction of the bulky terphenyllithium reagent  $\text{LiAr}^*$  ( $\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$ ;  $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-Pr}^i_3$ ) with the monohalides of indium and thallium where it was hoped that the neutral dimers  $\text{Ar}^*\text{MMAr}^*$  ( $\text{M} = \text{In}^{10}$  or  $\text{Tl}^{11}$ ) would be produced. However, the monomers  $\text{MAr}^*$  were isolated instead. These compounds, which have unique one-coordinate metals, represent the lowest members (i.e.,  $n = 1$ ) of the  $(\text{MR})_n$  series. Their synthesis prompted speculation on the bonding in their boron, aluminum, and gallium congeners. The gallium derivative was of particular interest due to the information it might provide on the nature of the gallium–gallium bond in the landmark compound  $\text{Na}_2(\text{Ar}^*\text{GaGaAr}^*)$ , which was described as triply bonded.<sup>12</sup> This description resulted in a vigorous discussion on multiple bonding of the heavier main group elements. The most notable feature of the debate was that it was based almost exclusively on the results of calculations on various model species.<sup>13–26</sup> Surprisingly, no new experimental investigations

of the nature of the Ga–Ga bonding in the  $\text{Na}_2(\text{RGaGaR})$  compound class have been seen in the five years since the original publication, apart from an isolated report that described the effects of changing the alkali metal to potassium. That work<sup>27</sup> (which also confirmed the original  $\text{Na}_2(\text{Ar}^*\text{GaGaAr}^*)$  structure) suggested that the alkali metal exerted a large effect, because a product of formula  $\text{K}_2(\text{Ar}^*\text{Ga}_4\text{Ar}^*)$  was isolated. It contained a square  $\text{Ga}_4$  array incorporated in a  $\text{K}_2\text{Ga}_4$  cluster with no possibility for Ga–Ga triple bonding. In 1998, it was suggested that the synthesis of a neutral “digallene” compound of formula  $\text{Ar}^*\text{GaGaAr}^*$  corresponding to the removal of 2 sodiums from the reduced complex  $\text{Na}_2(\text{Ar}^*\text{GaGaAr}^*)$ , or 2 electrons from the putative dianion  $[\text{Ar}^*\text{GaGaAr}^*]^{2-}$ , as shown in eqs 1 and 2



would provide useful information on the Ga–Ga bonding.<sup>28</sup> If an  $\text{Ar}^*\text{GaGaAr}^*$  product could be shown to have a short Ga–Ga distance that corresponded to a double bond, then triple bonding in  $\text{Na}_2(\text{Ar}^*\text{GaGaAr}^*)$  would be supported. On the other hand, if the product was monomeric, that is,  $:\text{GaAr}^*$ , multiple bonding would be unlikely in  $\text{Na}_2(\text{Ar}^*\text{GaGaAr}^*)$ . Prior to the work reported here, no stable  $:\text{GaR}$  or  $\text{RGaGaR}$  species had been described. In fact, no stable group 13 compounds corresponding to the formula  $\text{REER}$  ( $\text{E} = \text{B-Tl}$ ,  $\text{R} = \text{alkyl, aryl, silyl, amide groups, etc.}$ ), in which the separation of the group 13 elements approached the sum of their covalent radii, were known, although the compounds  $\text{HMMH}$  ( $\text{M} = \text{Ga}$  or  $\text{In}$ ) have been detected recently by IR spectroscopy in a low temperature (12 K) matrix<sup>29–31</sup> (see below). In this paper, the synthesis, characterization, and reaction chemistry of several gallium aryls corresponding to the formula  $(\text{GaAr})_1$  or  $2$  ( $\text{Ar} = \text{terphenyl}$  and related ligands) are now described. The types of ligand used to stabilize the compounds discussed in this paper are given by the following illustrations.



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The physical and chemical behavior of the neutral  $(\text{GaAr})_1$  or  $2$  species show that any Ga–Ga bonding in such compounds is weak and the compounds exist as monomers in dilute hydrocarbon solution. In effect, the pair of electrons at each gallium behaves more as a lone pair than a bond pair. This conclusion is in agreement with calculations<sup>22</sup> and also with their chemistry as explored in this paper. The weak Ga–Ga interactions appear to be marginally stronger than closed shell interactions in main group and transition metal compounds.<sup>32</sup> Reduction of the  $(\text{GaAr})_1$  or  $2$  species to give  $\text{Na}_2(\text{ArGaGaAr})$  supplies two electrons to the di-gallium unit to generate a single Ga–Ga bond. This supplements the weak Ga–Ga bond in the neutral precursor while preserving the trans-bent C–Ga–Ga–C geometry. The stability of the  $\text{Na}_2(\text{ArGaGaAr})$  species depends on the matching size of the  $\text{Na}^+$  ions and the presence of Na–Ga and Na–Ar interactions that stabilize the  $\text{Na}_2\text{Ga}_2$  cluster at the core of these molecules.

## Experimental Section

**General Procedures.** All manipulations were carried out by using modified Schlenk techniques under an atmosphere of  $\text{N}_2$  or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from molten Na/K alloy and degassed three times prior to use. The compounds  $(\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2$ ,<sup>33</sup>  $\text{LiC}_6\text{H}_3\text{-2,6-Dipp}_2$ ,<sup>34</sup>  $(\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2)_2$ ,<sup>35</sup>  $\text{Ga}\{\text{NDippCMe}_2\text{CH}\}_2$ <sup>36</sup> (Dipp =  $\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$ ), and “Ga”<sup>37</sup> were prepared according to literature procedures. 2,3-Dimethyl-1,3-butadiene and  $\text{Fe}(\text{CO})_5$  were trap-to-trap vacuum distilled and dried with 4 Å molecular sieves. Tris(pentafluorophenyl)borane was used as received from Albemarle Corp.  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR were recorded on Varian 300 and 400 spectrometers and referenced to known standards. UV/vis data were recorded on a Hitachi-1200, while infrared data were recorded as Nujol mulls using a Perkin-Elmer 1430 instrument. The EPR spectrum of **17** was obtained with use of a Bruker CWX band spectrometer operating near 9.6 GHz. Melting points were recorded using a Meltemp apparatus and are uncorrected.

**GaAr\* (1) and I(Ar\*)GaGa(Ar\*)I (2).** A rapidly stirred toluene (20 mL) slurry of “Ga” (1.49 g, 7.60 mmol), cooled to ca.  $-78^\circ\text{C}$  in a dry ice–acetone bath, was treated dropwise with a toluene (30 mL) solution of  $(\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2$  (4.20 g, 7.60 mmol) over a period of 1 h. The solution was then allowed to come to room temperature over a period of ca. 12 h, whereupon the solvents were removed under reduced pressure. The residue was heated for 1 h at  $60^\circ\text{C}$  under reduced pressure to remove any remaining traces of solvent. It was then suspended in hexane (100 mL), heated to  $60^\circ\text{C}$ , and allowed to settle for 2 h while maintaining this temperature. Filtration of the supernatant green solution through Celite afforded a green filtrate which was allowed to cool to room temperature. Storage in an ca.  $-20^\circ\text{C}$  freezer for 15 h gave green crystals of product **1**. The remaining orange solid residue in the original Schlenk tube was then extracted with benzene (ca.  $50^\circ\text{C}$ , 80 mL) and filtered. The filtrate was allowed to cool to room temperature to yield yellow crystals of **2**. The dark green supernatant solution was then decanted and pumped to dryness to afford a green residue which was redissolved in hot hexane ( $60^\circ\text{C}$ , 100 mL). Cooling in a freezer at ca.  $-20^\circ\text{C}$  afforded a further crop of green

crystals of **1**. Combined yield of **1** = 1.4 g, 34%, yield of **2** = 1.0 g, 20%. The overall yield of **1** and **2** based on  $(\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2$  is 54%. **1**: mp  $210\text{--}216^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.11 (d, 12H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.8$  Hz, 1.20 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.8$  Hz, 2.79 (sept, 2H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.4$  Hz, 3.03 (sept, 4H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.8$  Hz, 7.03 (d, 2H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.2$  Hz, 7.08 (s, 4H,  $m\text{-Trip}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  24.49 ( $\text{CH}(\text{CH}_3)_2$ ), 24.94 ( $\text{CH}(\text{CH}_3)_2$ ), 25.21 ( $\text{CH}(\text{CH}_3)_2$ ), 30.94 ( $o\text{-CH}(\text{CH}_3)_2$ ), 34.84 ( $p\text{-CH}(\text{CH}_3)_2$ ), 121.15 ( $m\text{-Trip}$ ), 122.15 ( $p\text{-C}_6\text{H}_3$ ), 136.32 ( $m\text{-C}_6\text{H}_3$ ), 144.13 ( $i\text{-Trip}$ ), 147.52 ( $o\text{-C}_6\text{H}_3$ ), 148.52 ( $p\text{-Trip}$ ), 150.24 ( $o\text{-Trip}$ ), 176.26 ( $i\text{-C}_6\text{H}_3$ ). UV/vis  $\lambda_{\text{max}}$  nm ( $\epsilon$  mol  $\text{L}^{-1}$   $\text{cm}^{-1}$ ): 350 (1900), 436 (700). **2**: mp  $230\text{--}232^\circ\text{C}$ , dec.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.04 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.25 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.35 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 2.90 (sept, 2H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 3.00 (sept, 4H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 7.03, 7.04, 7.19 (m, Ar–H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  24.50, 24.59 ( $\text{CH}(\text{CH}_3)_2$ ), 24.75, 24.84 ( $\text{CH}(\text{CH}_3)_2$ ), 26.41 ( $\text{CH}(\text{CH}_3)_2$ ), 31.08, 32.10 ( $o\text{-CH}(\text{CH}_3)_2$ ), 34.84 ( $p\text{-CH}(\text{CH}_3)_2$ ), 120.73 ( $m\text{-Trip}$ ), 122.14 ( $p\text{-C}_6\text{H}_3$ ), 128.53 ( $m\text{-C}_6\text{H}_3$ ), 138.21 ( $i\text{-Trip}$ ), 144.66 ( $o\text{-C}_6\text{H}_3$ ), 147.47 ( $p\text{-Trip}$ ), 149.51 ( $o\text{-Trip}$ ), 153.75 ( $i\text{-C}_6\text{H}_3$ ). UV/vis  $\lambda_{\text{max}}$  218 nm, shoulder.

**(Et<sub>2</sub>O)LiAr\* (3).** The compound Ar\***I** was synthesized in a manner similar to that described previously for Ar\***I**.<sup>34</sup> mp  $218\text{--}220^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  = 1.08 (d, 12H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.21 (d, 12H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.37 (s, 18H,  $p\text{-C}(\text{CH}_3)_3$ ), 2.53 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 7.14 (d, 2H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$ , 7.20 (s, 4H,  $m\text{-Bu}^i\text{Dipp}$ ), 7.39 (t, 1H,  $p\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz,  $25^\circ\text{C}$ ):  $\delta$  = 23.84 ( $\text{CH}(\text{CH}_3)_2$ ), 25.39 ( $\text{CH}(\text{CH}_3)_2$ ), 31.35 ( $\text{CH}(\text{CH}_3)_2$ ), 31.97 ( $\text{C}(\text{CH}_3)_3$ ), 35.27 ( $\text{C}(\text{CH}_3)_2$ ), 111.20 ( $i\text{-C}_6\text{H}_3$ ), 119.77 ( $m\text{-Bu}^i\text{Dipp}$ ), 127.47 ( $p\text{-C}_6\text{H}_3$ ), 128.40 ( $m\text{-C}_6\text{H}_3$ ), 140.15 ( $i\text{-Bu}^i\text{Dipp}$ ), 145.286 ( $o\text{-Bu}^i\text{Dipp}$ ), 146.93 ( $o\text{-C}_6\text{H}_3$ ), 150.77 ( $p\text{-Bu}^i\text{Dipp}$ ). The lithium salt **3** was synthesized in a manner similar to that for  $(\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2$ .<sup>33</sup> mp  $171\text{--}172^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 0.50 (t, 6H,  $(\text{CH}_3\text{CH}_2)_2\text{O}$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.23 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.31 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.39 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 2.69 (q, 4H,  $(\text{CH}_3\text{CH}_2)_2\text{O}$ )  $^3J_{\text{HH}} = 6.9$  Hz, 3.55 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 7.29 (d, 2H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz, 7.35 (s, 4H,  $m\text{-Bu}^i\text{Dipp}$ ), 7.41 (t, 1H,  $p\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz,  $25^\circ\text{C}$ ):  $\delta$  = 13.76 ( $(\text{CH}_3\text{CH}_2)_2\text{O}$ ), 24.67 ( $\text{CH}(\text{CH}_3)_2$ ), 24.87 ( $\text{CH}(\text{CH}_3)_2$ ), 30.23 ( $\text{CH}(\text{CH}_3)_2$ ), 31.91 ( $\text{C}(\text{CH}_3)_3$ ), 34.85 ( $\text{C}(\text{CH}_3)_2$ ), 66.33 ( $(\text{CH}_3\text{CH}_2)_2\text{O}$ ), 119.20 ( $m\text{-Bu}^i\text{Dipp}$ ), 122.88 ( $m\text{-C}_6\text{H}_3$ ), 123.33 ( $p\text{-C}_6\text{H}_3$ ), 146.34 ( $o\text{-Bu}^i\text{Dipp}$ ), 146.95 ( $i\text{-Bu}^i\text{Dipp}$ ), 147.90 ( $o\text{-C}_6\text{H}_3$ ), 150.55 ( $p\text{-Bu}^i\text{Dipp}$ ), 189.89 ( $i\text{-C}_6\text{H}_3$ ).

**GaAr\* (4).** This compound was synthesized in a manner similar to that for **1** and isolated as green crystals. Yield: 1.1 g, 25%. mp  $201\text{--}203^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 1.19 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.26 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.36 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 3.10 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 7.08 (d, 2H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz, 7.16 (t, 1H,  $p\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz, 7.40 (s, 4H,  $m\text{-Bu}^i\text{Dipp}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 24.30 ( $\text{CH}(\text{CH}_3)_2$ ), 25.12 ( $\text{CH}(\text{CH}_3)_2$ ), 30.94 ( $\text{CH}(\text{CH}_3)_2$ ), 31.70 ( $\text{C}(\text{CH}_3)_3$ ), 35.04 ( $\text{C}(\text{CH}_3)_2$ ), 119.99 ( $m\text{-Bu}^i\text{Dipp}$ ), 128.20 ( $m\text{-C}_6\text{H}_3$ ), 129.15 ( $p\text{-C}_6\text{H}_3$ ), 136.71 ( $i\text{-Bu}^i\text{Dipp}$ ), 144.23 ( $o\text{-C}_6\text{H}_3$ ), 147.18 ( $o\text{-Bu}^i\text{Dipp}$ ), 150.75 ( $p\text{-C}_6\text{H}_3$ ), 176.45 ( $i\text{-C}_6\text{H}_3$ ). UV/vis nm ( $\epsilon$  mol  $\text{L}^{-1}$   $\text{cm}^{-1}$ ): 350 (1800), 434 (510).

**I(Ar\*)GaGa(Ar\*)I (5).** This compound was synthesized as yellow crystals in a manner similar to that for **2**. Yield: 0.81 g, 15%. mp  $210\text{--}213^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 1.074 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.30 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.42 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 3.04 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 7.020 (t, 1H,  $p\text{-C}_6\text{H}_3$ ), 7.151 (m, 2H,  $m\text{-C}_6\text{H}_3$ ), 7.368 (s, 4H,  $2m\text{-Bu}^i\text{Dipp}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 24.76  $\text{CH}(\text{CH}_3)_2$ , 26.30  $\text{CH}(\text{CH}_3)_2$ , 31.05  $\text{CH}(\text{CH}_3)_2$ , 31.82  $\text{C}(\text{CH}_3)_3$ , 35.13  $\text{C}(\text{CH}_3)_3$ , 120.88 ( $m\text{-Bu}^i\text{Dipp}$ ), 129.85 ( $m\text{-C}_6\text{H}_3$ ), 130.25 ( $p\text{-C}_6\text{H}_3$ ), 144.42 ( $i\text{-Bu}^i\text{Dipp}$ ), 146.94 ( $o\text{-Bu}^i\text{Dipp}$ ), 148.56 ( $o\text{-C}_6\text{H}_3$ ), 151.57 ( $p\text{-Bu}^i\text{Dipp}$ ), 156.10 ( $i\text{-C}_6\text{H}_3$ ).

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**Ar\*GaGaAr' (6) and (I)Ar\*GaGaAr'(I) (7).** A rapidly stirred toluene (20 mL) slurry of "Gal" (1.49 g, 7.60 mmol), cooled to ca.  $-78\text{ }^{\circ}\text{C}$ , was treated dropwise with a toluene (40 mL) solution of  $(\text{LiAr}')_2$  (3.07 g, 3.80 mmol) over ca. 1 h, after which time the mixture was allowed to come to room temperature over a period of 6 h. Stirring was discontinued, and the suspension was allowed to settle. The dark green supernatant solution was filtered through Celite and concentrated to ca. 15 mL, whereupon a yellow-orange precipitate formed. This was allowed to settle, and the solution was separated by decantation. The yield of the orange-yellow solid, which is almost pure **7**, is 1.10 g (0.93 mmol, 24.4%). The green supernatant liquid was stored at ca.  $-20\text{ }^{\circ}\text{C}$  in a freezer for 12 h to afford a brown-red crystalline solid. This was recrystallized from a minimum volume of warm hexane to afford the product **6** as red-brown crystals. Yield: 0.90 g, 0.96 mmol, 25.3%. mp  $206\text{--}210\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  1.07 (d,  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.09 (d,  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 24H,  $\text{CH}(\text{CH}_3)$ ), 2.98 (sept,  $^3J_{\text{HH}} = 6.7\text{ Hz}$ , 8H,  $\text{CH}(\text{CH}_3)_2$ ), 7.02 (d,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , 8H, *m*-Dipp), 7.14, 7.19, 7.21 (m, Ar-H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  25.01 ( $\text{CH}(\text{CH}_3)_2$ ), 25.37 ( $\text{CH}(\text{CH}_3)_2$ ), 30.92 ( $\text{CH}(\text{CH}_3)_2$ ), 123.03 (*p*- $\text{C}_6\text{H}_3$ ), 123.40 (*m*-Dipp), 128.20 (*m*- $\text{C}_6\text{H}_3$ ), 128.80 (*i*-Dipp), 138.87 (*o*- $\text{C}_6\text{H}_3$ ), 144.72 (*p*-Dipp), 147.16 (*o*-Dipp), 173.80 (*i*- $\text{C}_6\text{H}_3$ ). UV/vis (hexanes)  $\lambda_{\text{max}}$  nm ( $\epsilon$  mol  $\text{L}^{-1}$   $\text{cm}^{-1}$ ): 350 (1600), 437 (520). **7**, Yield: 1.10 g, 0.93 mmol. mp  $> 260\text{ }^{\circ}\text{C}$  decomp.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  0.99 (d,  $^3J_{\text{HH}} = 6.4\text{ Hz}$ , 24H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 1.18 (d,  $^3J_{\text{HH}} = 6.4\text{ Hz}$ , 24H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 2.96 (sept,  $^3J_{\text{HH}} = 6.4\text{ Hz}$ , 8H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 7.11–7.15 (m, *m*- $\text{C}_6\text{H}_3$ , *m*-, *p*-Dipp), 7.29 (t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , 2H, *p*- $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 25.43 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 26.83 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 31.23 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 123.39 (*p*- $\text{C}_6\text{H}_3$ ), 124.58 (*m*-Dipp), 129.83 (*i*-Dipp), 130.60 (*m*- $\text{C}_6\text{H}_3$ ), 140.40 (*o*- $\text{C}_6\text{H}_3$ ), 145.36 (*p*- $\text{C}_6\text{H}_3$ ), 148.07 (*o*-Dipp), 152.12 (*i*- $\text{C}_6\text{H}_3$ ).

**Ar\*Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (8).** At room temperature, GaAr\*, **1** (0.551 g, 1 mmol), was dissolved in toluene (20 mL) with rapid stirring. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.512 g, 1 mmol) in toluene (20 mL) was added dropwise, whereupon the dark green color of the solution began to fade until the solution had become colorless upon completion of the addition. All volatile materials were removed under reduced pressure, and the remaining solid was redissolved in hexane (10 mL). Slow cooling in an ca.  $-20\text{ }^{\circ}\text{C}$  freezer overnight yielded **8** as X-ray quality, colorless crystals. Yield: 0.81 g, 76.4%. mp  $187\text{--}189\text{ }^{\circ}\text{C}$ ,  $201\text{ }^{\circ}\text{C}$  dec.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  0.97 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 1.17 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 1.24 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 2.86 (sept, 6H, *p*- $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 6.96–7.03 (m, Ar-H), 7.09 (s, 4H, *o*-Trip-H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  23.54 ( $\text{CH}(\text{CH}_3)_2$ ), 23.79 ( $\text{CH}(\text{CH}_3)_2$ ), 25.90 ( $\text{CH}(\text{CH}_3)_2$ ), 31.28 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 33.89 (*p*- $\text{CH}(\text{CH}_3)_2$ ), 121.80 (*m*-Trip), 129.61 (*p*- $\text{C}_6\text{H}_3$ ), 131.28 (*p*-Trip), 135.02 (*m*- $\text{C}_6\text{H}_3$ ), 135.66 (br,  $\text{C}_6\text{F}_5$ ), 138.29 (br,  $\text{C}_6\text{F}_5$ ), 138.91 (br,  $\text{C}_6\text{F}_5$ ), 146.32 (br,  $\text{C}_6\text{F}_5$ ), 146.83 (*i*-Trip), 147.81 (*o*-Trip), 149.38 (br, *o*- $\text{C}_6\text{H}_3$ ), 150.86 (*o*- $\text{C}_6\text{H}_3$ ), 152.17 (*i*- $\text{C}_6\text{H}_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$   $-18.93$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$   $-126.85$  (*o*- $\text{C}_6\text{F}_5$ ),  $-153.63$  (*p*- $\text{C}_6\text{F}_5$ ),  $-158.90$  (*m*- $\text{C}_6\text{F}_5$ ).

**Ar\*Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (9).** This compound was synthesized as colorless crystals in a manner similar to that for **8**. Yield: 0.71 g, 65%. mp  $184\text{--}186\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 0.980 (d, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 1.19 (d, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 1.292 (s, 18H, *p*- $\text{C}(\text{CH}_3)_3$ ), 2.84 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 6.95 (d, 2H, *m*- $\text{C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , 7.00 (t, 1H, *p*- $\text{C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , 7.253 (s, 4H, *m*-Bu'Dipp), 7.39 (t, 1H, *p*- $\text{C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5\text{ Hz}$ .  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 23.57  $\text{CH}(\text{CH}_3)_2$ , 25.97  $\text{CH}(\text{CH}_3)_2$ , 31.37  $\text{C}(\text{CH}_3)_3$ , 31.54  $\text{CH}(\text{CH}_3)_2$ , 35.29  $\text{C}(\text{CH}_3)_2$ , 120.84 (*m*-Bu'Dipp), 129.85 (*m*- $\text{C}_6\text{H}_3$ ), 131.24 (*p*- $\text{C}_6\text{H}_3$ ), 135.62 (br,  $\text{C}_6\text{F}_5$ ), 139.15 (br,  $\text{C}_6\text{F}_5$ ), 141.64 (br,  $\text{C}_6\text{F}_5$ ), 146.25 (br,  $\text{C}_6\text{F}_5$ ), 147.08 (*o*- $\text{C}_6\text{H}_3$ ), 147.54 (*o*-Bu'Dipp), 149.35 (br,  $\text{C}_6\text{F}_5$ ), 151.02 (*i*- $\text{C}_6\text{H}_3$ ), 153.30 (*p*-Bu'Dipp).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 18.03.  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$   $-127.05$  (*o*- $\text{C}_6\text{F}_5$ ),  $-153.56$  (*p*- $\text{C}_6\text{F}_5$ ),  $-158.80$  (*m*- $\text{C}_6\text{F}_5$ ).

**Ar\*Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (10).** This compound was synthesized as colorless crystals in a manner similar to that for **8**. Yield: 0.66 g, 68%. mp  $218\text{--}220\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 0.89 (d, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 1.08 (d, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 2.75 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 6.93 (d, 4H, *m*-Dipp)  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , 7.03 (d, 2H, *m*- $\text{C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , 7.16 (m, 3H, *p*- $\text{C}_6\text{H}_3$  and *p*-Dipp).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 23.27 ( $\text{CH}(\text{CH}_3)_2$ ), 25.87 ( $\text{CH}(\text{CH}_3)_2$ ), 31.16 ( $\text{CH}(\text{CH}_3)_2$ ), 123.82 (*m*-Dipp), 129.15 (*m*- $\text{C}_6\text{H}_3$ ), 130.68 (*p*-Dipp), 131.32 (*p*- $\text{C}_6\text{H}_3$ ), 135.85 (br,  $\text{C}_6\text{F}_5$ ), 137.47 (*i*-Dipp), 138.83 (br,  $\text{C}_6\text{F}_5$ ), 141.76 (br,  $\text{C}_6\text{F}_5$ ), 146.25 (br,  $\text{C}_6\text{F}_5$ ), 146.72 (*o*- $\text{C}_6\text{H}_3$ ), 147.79 (*o*-Dipp), 149.37 (br,  $\text{C}_6\text{F}_5$ ), 152.61 (*i*- $\text{C}_6\text{H}_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  =  $-17.73$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  =  $-127.03$  (*o*- $\text{C}_6\text{F}_5$ ),  $-154.24$  (*p*- $\text{C}_6\text{F}_5$ ),  $-159.06$  (*m*- $\text{C}_6\text{F}_5$ ).

**Ar\*GaFe(CO)<sub>4</sub> (11).** A toluene (30 mL) solution of **1** (0.30 g, 0.54 mmol) was treated via syringe with  $\text{Fe}(\text{CO})_5$  (0.3 mL, 2.3 mmol) with rapid stirring at room temperature. The solution remained green at first, but upon stirring for 24 h at room temperature, the color was discharged, and a colorless solid was precipitated. The solution was then heated to ca.  $100\text{ }^{\circ}\text{C}$  to redissolve the precipitate. Upon cooling to room temperature over ca. 3 h, large pale yellow crystals of **11**·toluene were formed. Yield: 0.28 g, 72%. All spectroscopic data were consistent with those previously reported. The crystal structure of **11**·toluene showed geometric parameters similar to those reported for **11**·Et<sub>2</sub>O.

**{Ar\*GaCH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>}<sub>2</sub> (12).** To a stirred solution of GaAr\* (0.56 g, 1 mmol) in 25 mL of toluene at ca.  $0\text{ }^{\circ}\text{C}$  was added 2,3-dimethyl-1,3-butadiene (0.11 mL, 1 mmol) dropwise. Upon addition, the solution immediately turned light brown, and after the solution was warmed to room temperature, stirring was continued for ca. 1 h. Subsequently, the solvent was removed under reduced pressure, and the residue was treated with hexanes (30 mL). Upon filtering, the solution was reduced to a volume of ca. 5 mL. Overnight storage at  $-20\text{ }^{\circ}\text{C}$  afforded the product as colorless crystals. Yield: 0.15 g, 23%. mp  $71\text{--}78\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 1.16 (d,  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 24H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d,  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 24H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 1.26 (d,  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 24H, *p*- $\text{CH}(\text{CH}_3)_2$ ), 1.30 (s, 12H,  $\text{GaCH}_2\text{C}(\text{CH}_3)$ ), 1.74 (s, 8H,  $\text{GaCH}_2\text{C}(\text{CH}_3)$ ), 2.81 (d,  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 2H, *p*- $\text{CH}(\text{CH}_3)_2$ ), 3.09 (d,  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 4H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 7.17 (s, 8H, *m*-Trip), 7.30–7.32 (m, 6H, *p*-, *m*- $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 21.5 ( $\text{GaCH}_2\text{C}(\text{CH}_3)$ ), 121.9 (*m*-Trip), 127.7 (*p*- $\text{C}_6\text{H}_3$ ), 132.5 (*m*- $\text{C}_6\text{H}_3$ ), 139.91 (ipso-Trip), 147.5 (*o*-Trip), 147.9 (*o*- $\text{C}_6\text{H}_3$ ), 149.7 (*p*-Trip), 153.4 (*i*- $\text{C}_6\text{H}_3$ ).

**Na<sub>2</sub>(Ar\*GaGaAr\*) (13).** Diethyl ether (30 mL) was added to a Schlenk tube containing GaAr\* (1.10 g, 1.9 mmol) and sodium metal (0.30 g, 13 mmol). The solution was stirred for 4 h, during which time the color changed from green to dark red. Crystallization from the ether solution over 12 h at ca.  $-20\text{ }^{\circ}\text{C}$  afforded X-ray quality crystals of **13** as red blocks. Yield: 0.42 g, 38%. A single-crystal cell check and melting point were consistent with the reported data.<sup>12</sup>

**Na<sub>2</sub>(Ar\*GaGaAr') (14).** A solution of **6** (1.02 g, 1.9 mmol) in diethyl ether (30 mL) was added to sodium metal (0.30 g, 13 mmol) and stirred for 4 h at  $25\text{ }^{\circ}\text{C}$ , during which time the color changed from green to dark red. The solution was separated from the excess sodium, concentrated, and cooled in a  $-20\text{ }^{\circ}\text{C}$  freezer for 30 h to afford **14** as dark red parallelepipeds. Yield: 0.37 g, 38%. mp  $121\text{--}123\text{ }^{\circ}\text{C}$  dec  $> 270\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  1.12 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.90 (sept,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 8H,  $\text{CH}(\text{CH}_3)_2$ ), 7.10 (d,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , 4H, *m*- $\text{C}_6\text{H}_3$ ), 7.18 (d,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , 8H, *m*-Dipp), 7.21 (t,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , 2H, *p*- $\text{C}_6\text{H}_3$ ), 7.31 (t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , 4H, *p*-Dipp).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  24.31 ( $\text{CH}(\text{CH}_3)_2$ ), 24.43 ( $\text{CH}(\text{CH}_3)_2$ ), 30.72 ( $\text{CH}(\text{CH}_3)_2$ ), 122.82 (*p*- $\text{C}_6\text{H}_3$ ), 128.19 (*m*-Dipp), 128.37 (*m*- $\text{C}_6\text{H}_3$ ), 131.39 (*p*-Dipp), 139.65 (*o*- $\text{C}_6\text{H}_3$ ), 141.04 (*i*-Dipp), 146.82 (*o*-Dipp), 149.25 (*i*- $\text{C}_6\text{H}_3$ ). UV/vis (hexanes)  $\lambda_{\text{max}}$  nm ( $\epsilon$  mol  $\text{L}^{-1}$   $\text{cm}^{-1}$ ): 342 (2700), 439 (1500), 528 (1200).

**Table 1.** Selected Crystallographic Data for Compounds **2**, **3**, **8–10**, **12**, **16**, and **17**

	(2) Ar <sup>+</sup> GaI <sub>2</sub> ·2C <sub>6</sub> H <sub>6</sub>	(3) Ar <sup>+</sup> Li·Et <sub>2</sub> O	(8) Ar <sup>+</sup> GaB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	(9) Ar <sup>+</sup> GaB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>
formula	C <sub>84</sub> H <sub>110</sub> Ga <sub>2</sub> I <sub>2</sub>	C <sub>47</sub> H <sub>63</sub> LiO	C <sub>54</sub> H <sub>49</sub> BF <sub>15</sub> Ga	C <sub>56</sub> H <sub>53</sub> BF <sub>15</sub> Ga
fw	1512.96	590.86	1063.46	1091.51
color, habit	yellow, block	colorless, block	colorless, parallelepiped	colorless, block
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> / <i>n</i>	<i>P</i> <sub>2</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	13.969(9)	9.2139(7)	12.446(2)	11.9331(9)
<i>b</i> , Å	15.832(11)	16.7871(13)	18.815(4)	12.5786(9)
<i>c</i> , Å	17.957(9)	24.6129(19)	20.580(4)	17.8282(13)
$\alpha$ , °	89.50(3)	90.9000(10)		
$\beta$ , °	71.97(2)	92.268(2)	92.692(6)	97.6470(10)
$\gamma$ , °	89.94(3)	107.3310(10)		
<i>V</i> , Å <sup>3</sup>	3776(4)	3804.0(5)	4813.7(16)	2527.5(3)
<i>Z</i>	2	4	4	2
cryst dim, nm	0.37 × 0.28 × 0.21	0.65 × 0.45 × 0.43	0.15 × 0.08 × 0.08	0.25 × 0.28 × 0.25
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.331	1.032	1.467	1.434
$\mu$ , mm <sup>-1</sup>	1.573	0.059	0.667	0.637
no. of reflns	13 493	12 072	9815	15 131
no. of obsd reflns	11 564	9847	6913	12 607
<i>R</i> <sub>1</sub> obsd reflns	0.0694	0.0579	0.0527	0.0378
<i>wR</i> <sub>2</sub> , all	0.1577	0.1774	0.1508	0.1228
	(10) Ar <sup>+</sup> GaB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	(12) Ar <sup>+</sup> Ga(CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	(16) Dipp <sub>2</sub> N <sup>+</sup> NGaFe(CO) <sub>4</sub> ·C <sub>6</sub> H <sub>7</sub>	(17) Ar <sub>4</sub> Ga <sub>11</sub> ·3C <sub>7</sub> H <sub>8</sub>
formula	C <sub>96</sub> H <sub>74</sub> F <sub>30</sub> Ga <sub>2</sub>	C <sub>84</sub> H <sub>118</sub> Ga <sub>2</sub>	C <sub>40</sub> H <sub>49</sub> FeGaN <sub>2</sub> O <sub>4</sub>	C <sub>213</sub> H <sub>200</sub> Ga <sub>22</sub>
fw	1958.61	1267.22	747.38	4293.57
color, habit	colorless, block	colorless, block	colorless, block	red, block
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> <sub>2</sub> / <i>c</i>	<i>P</i> <sub>2</sub> / <i>n</i>	<i>Pnma</i>	<i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>
<i>a</i> , Å	17.216(2)	9.0470(4)	22.0914(8)	18.4464(9)
<i>b</i> , Å	22.819(5)	26.8579(11)	16.5373(6)	20.6011(10)
<i>c</i> , Å	22.301(3)	15.3625(6)	10.5410(4)	25.3976(12)
$\alpha$ , °				
$\beta$ , °	102.876(5)	94.2690(10)		
$\gamma$ , °				
<i>V</i> , Å <sup>3</sup>	8541(2)	3722.5(3)	3851.0(2)	9651.5(8)
<i>Z</i>	4	2	4	4
cryst dim, mm	0.36 × 0.24 × 0.23	0.18 × 0.14 × 0.12	0.44 × 0.30 × 0.34	0.25 × 0.22 × 0.21
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.523	1.131	1.289	1.826
$\mu$ , mm <sup>-1</sup>	0.745	0.765	1.117	3.062
no. of reflns	19 434	8553	6505	17 717
no. of obsd reflns	13 461	4963	5607	13 248
<i>R</i> <sub>1</sub> obsd reflns	0.0555	0.0509	0.0330	0.0493
<i>wR</i> <sub>2</sub> , all	0.1381	0.1262	0.0948	0.1258

**Dipp<sub>2</sub>N<sup>+</sup>NGaFe(CO)<sub>4</sub> (16).** A solution of GaN<sup>+</sup>NDipp<sub>2</sub>, **15** (0.80 g, 1.64 mmol), in toluene (30 mL) at ca. 0 °C was treated via syringe with Fe(CO)<sub>5</sub> (0.30 mL, 2.30 mmol) with rapid stirring. The reaction mixture was allowed to warm to room temperature and was stirred for a further 12 h, after which time a colorless precipitate had formed. The suspension was then heated until the precipitate had completely dissolved. Cooling to room temperature over a period of 4 h afforded colorless, X-ray quality crystals of Dipp<sub>2</sub>N<sup>+</sup>NGaFe(CO)<sub>4</sub>. Yield: 0.28 g, 26%. mp 279–280 °C. IR: 1900, 1915, 1940, 2010 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.04 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 6H, *CMe*), 2.99 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.08 (s, 1H, methine CH), 7.10, 7.12, 7.21, 7.24 (m, Ar–H). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  24.34 CH(CH<sub>3</sub>)<sub>2</sub>, 24.62 C(CH<sub>3</sub>), 24.89 CH(CH<sub>3</sub>)<sub>2</sub>, 29.34 CH(CH<sub>3</sub>)<sub>2</sub>, 101.18 ( $\gamma$ -C), 125.02 (*m*-Dipp), 128.97 (*p*-Dipp), 139.54 (*o*-Dipp; CCHC(CH<sub>3</sub>)<sub>2</sub>), 143.25 (C(CH<sub>3</sub>)), 169.80 (CN), 214.85 (CO).

**Ga<sub>11</sub>(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)<sub>4</sub> (17).** LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (1.10 g, 3.43 mmol) and GaN<sup>+</sup>NDipp<sub>2</sub> (1.67 g, 3.43 mmol) were combined in a Schlenk tube equipped with a stir bar, and toluene (40 mL) was added. The solution was allowed to stir for 12 h with heating to 75 °C. After 12 h, the deep red solution was reduced in volume to incipient crystallization (5–10 mL) and placed in a freezer at ca. –20 °C. After three weeks, dark red crystals along with some pale yellow crystals were obtained and separated by hand. The pale yellow crystals were found

to be Ga{(NDippCMe)<sub>2</sub>CH} (checked by melting point and unit cell dimensions). The red crystals were found to be Ga<sub>11</sub>(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)<sub>4</sub> (6)·1.5 toluene. Yield: 0.20 g, 12% (based on GaN<sup>+</sup>NDipp<sub>2</sub>).

**X-ray Crystallographic Studies.** Sample preparation consisted of removing the crystal from the Schlenk tube under a rapid flow of argon and immediately submerging it in hydrocarbon oil. A suitable crystal was selected, mounted on a glass fiber, attached to a copper pin, and rapidly placed in a cold stream of N<sub>2</sub> (–183 °C) of the diffractometer for data collection.<sup>38</sup> Data were collected on a Bruker SMART 1000 diffractometer with use of Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation and a CCD area detector. Data collection and processing were performed using the programs SMART<sup>39a</sup> and SAINT<sup>39b</sup> provided by Bruker AXS. Empirical absorption corrections were applied for samples **8–10**, **12**, **16**, and **17** using SADABS.<sup>39c</sup> The crystal structures were solved using either direct methods or the Patterson option in SHELXS<sup>40a</sup> and refined by the full-matrix least-squares procedure in the SHELXL<sup>40a</sup> program. During the initial refinements of structures **2** and **17**, both displayed

(38) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.

(39) (a) SMART: Area-Detector Software Package; Bruker AXS, Inc.: Madison, WI, 1993. (b) SAINT: Area-Detector Integration Software; Bruker AXS, Inc.: Madison, WI, 1995. (c) SADABS: Area-Detector Absorption Correction; Bruker AXS, Inc.: Madison, WI, 1996.

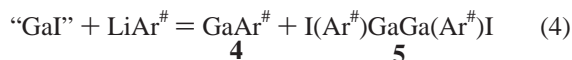
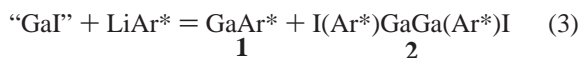
(40) (a) SHELXL PC, version 5.03; Bruker AXS, Inc.: Madison, WI, 1994. (b) Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Crystallogr.* **2002**, *35*, 168.

evidence of twinning. Using the program ROTAX,<sup>40b</sup> we determined the appropriate twinning laws and refined the structures normally. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed at calculated positions and included in refinement using a riding model. Structure **12** contained disordered alkene and methyl groups (C(38), C(39), and C(40)), which occupied two positions with 50% probability. The central Ga<sub>3</sub> unit in compound **17** (i.e., Ga(3), Ga(4), Ga(5)) was rotationally disordered between two positions. The gallium atoms were refined satisfactorily with 50% occupancy. Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information. Compound **16** contains a rotationally disordered toluene molecule which was modeled with variable occupancy. Compound **17** crystallized with three disordered toluene molecules, two of which were disordered around a two-fold rotation axis, whereas the third was translationally disordered. The carbons were modeled successfully with variable occupancies. Hydrogens were not added to the disordered toluenes.

## Results and Discussion

The following compounds are the main concern of the discussion: **1**, GaAr\* (Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>); **2**, I(Ar\*)GaGa(Ar\*)I; **3**, (Et<sub>2</sub>O)LiAr<sup>#</sup> (Ar<sup>#</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(Bu<sup>t</sup>Dipp)<sub>2</sub>); **4**, GaAr<sup>#</sup>; **5**, I(Ar<sup>#</sup>)GaGa(Ar<sup>#</sup>)I; **6**, Ar'GaGaAr' (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>); **7**, I(Ar')GaGa(Ar')I; **8**, Ar\*Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}; **9**, Ar<sup>#</sup>Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}; **10**, Ar'Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}; **11**, Ar\*GaFe(CO)<sub>4</sub>; **12**, {Ar\*GaCH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>}; **13**, Na<sub>2</sub>(Ar\*GaGaAr\*); **14**, Na<sub>2</sub>(Ar'GaGaAr'); **15**, GaN<sup>^</sup>NDipp<sub>2</sub>; **16**, (Dipp<sub>2</sub>N<sup>^</sup>NGa)Fe(CO)<sub>4</sub>; and **17**, Ga<sub>11</sub>-Ar''<sub>4</sub> (Ar'' = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>).

**Synthesis, Characterization, and Reactions.** The reaction of “GaI”<sup>37</sup> with (Et<sub>2</sub>O)LiAr\*,<sup>33</sup> (LiAr')<sub>2</sub>,<sup>34</sup> or (Et<sub>2</sub>O)LiAr<sup>#</sup> (**3**) yielded the organogallium(I) compounds GaAr\* (**1**), GaAr<sup>#</sup> (**4**), or Ar'GaGaAr' (**6**)<sup>41</sup> along with the arylodidogallanes {Ga(Ar\*)I}<sub>2</sub> (**2**), {Ga(Ar<sup>#</sup>)I}<sub>2</sub> (**5**), or {Ga(Ar')I}<sub>2</sub> (**7**)<sup>41</sup> as shown in eqs 3–5. The lithium aryl **3** was synthesized in a manner similar to that described for (Et<sub>2</sub>O)LiAr\*.<sup>33</sup> The products of eqs 3–5 can be separated readily through recrystallization from either hexane or benzene because of the lower solubility of the iodo



compounds **2**, **5**, and **7** in these solvents. Unfortunately, **1** or **4**, which were obtained as green crystals, were unsuitable for X-ray crystallography. Attempts to grow X-ray quality crystals of **1** from ether, tetrahydrofuran, toluene, benzene, hexane, and pentane, or by slow sublimation at 190 °C and 0.05 Torr, were unsuccessful. The crystals obtained by the above methods appeared to be well-formed, but they did not extinguish in polarized light, and rotation images on the diffractometer displayed only a small number of diffraction spots at low  $\theta$  angles. In addition, an X-ray powder diffraction analysis was attempted, but the results were inconclusive. The synthesis of GaAr<sup>#</sup>, **4**, in which the para-Pr<sup>i</sup> groups of the flanking aryl rings were replaced by Bu<sup>t</sup> groups, was undertaken primarily to

**Table 2.** Selected Interatomic Distances (Å) and Angles (deg) for **2**, **3**, **6**, **7**

I(Ar*)GaGa(Ar*)I ( <b>2</b> )		I(Ar')GaGa(Ar')I ( <b>7</b> )	
Ga(1)–Ga(1A)	2.482(2)	Ga(1)–Ga(2)	2.493(2)
Ga(2)–Ga(2A)	2.502(2)	Ga(1)–I(1)	2.525(2)
Ga(1)–I(1)	2.514(2)	Ga(2)–I(2)	2.541(2)
Ga(2)–I(2)	2.5373(14)	Ga(1)–C(1)	1.976(10)
Ga(1)–C(1)	1.973(7)	Ga(2)–C(31)	1.979(9)
Ga(2)–C(37)	1.983(6)	C(1)–Ga(1)–Ga(2)	127.1(3)
C(1)–Ga(1)–Ga(1A)	130.5(2)	C(1)–Ga(1)–I(1)	119.8(3)
I(1)–Ga(1)–Ga(1A)	110.80(5)	Ga(2)–Ga(1)–I(1)	112.73(5)
C(1)–Ga(1)–I(1)	118.8(2)	Ga(31)–Ga(2)–Ga(1)	130.1(2)
C(37)–Ga(2)–Ga(2A)	129.6(2)	C(31)–Ga(2)–I(2)	120.4(2)
I(2)–Ga(2)–Ga(2A)	110.22(5)	Ga(1)–Ga(2)–I(2)	109.38(5)
C(37)–Ga(2)–I(2)	119.2(2)		
(Et <sub>2</sub> O)LiAr <sup>#</sup> ( <b>3</b> )		Ar'GaGaAr' ( <b>6</b> )	
Li(1)–C(1)	2.036(2)	Ga(1)–Ga(1A)	2.6268(7)
Li(1)–O(1)	1.881(2)	Ga(1)–C(1)	2.025(3)
C(1)–C(6)	1.418(1)	C(1)–C(2)	1.402(4)
C(1)–C(2)	1.422(1)	C(1)–C(6)	1.412(4)
O(1)–C(39)	1.442(2)	C(1)–Ga(1)–Ga(1A)	123.16(7)
O(1)–C(41)	1.432(2)	C(2)–C(1)–C(6)	118.0(2)
O(1)–Li(1)–C(1)	164.4(2)	Ga(1)–C(1)–C(2)	122.6(2)
C(2)–C(1)–C(6)	114.97(9)	Ga(1)–C(1)–C(6)	119.2(2)
C(39)–O(1)–Li(1)	120.46(13)	C(1) ring to CGaGaC core	89.2
C(41)–O(1)–Li(1)	120.08(12)	C(7) and C(19) ring to C(1) ring	89.8, 85.7
C(39)–O(1)–C(41)	113.46(11)	C(1)⋯C(4) vector to CGaGaC	2.8

overcome the crystallization problems seen with **1**. Unfortunately, **4**, which was also obtained as green crystals, had the same X-ray diffraction characteristics as **1**. In contrast, the reaction of the less crowded (LiAr')<sub>2</sub> reagent with “GaI” afforded X-ray quality, brown-red crystals of the dimer (GaAr')<sub>2</sub> (**6**).<sup>41</sup> This compound has a long Ga–Ga bond of 2.6268(7) Å with a trans-bent CGaGaC (Ga–Ga–C = 123.16(7)°) core (vide infra). Despite the poor diffraction characteristics of **1** and **4**, yellow crystals of the related 1,2-diiododigallane coproducts **2** and **7**, obtained via eqs 3 and 5, could be characterized by X-ray crystallography. Important structural data for **2**, **3**, **5**–**7** are given in Table 2.

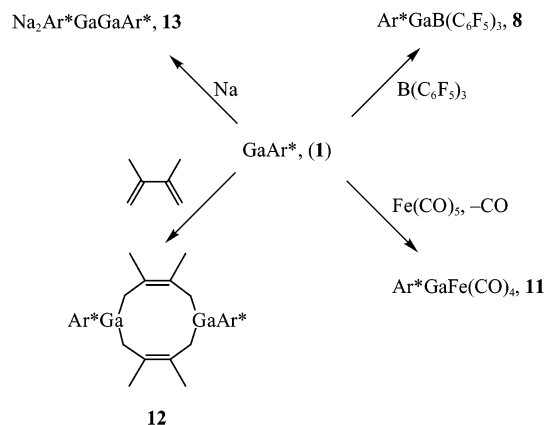
The green color of **1** and **4** observed in the crystal phase was retained in hydrocarbon (hexane, cyclohexane, benzene, ether) solution. Furthermore, the brown-red crystals of **6** also dissolved in various hydrocarbons to afford green solutions that were very similar to those of **1** and **4**. Consistent with the visual appearance of these solutions, the UV/vis spectra of compounds **1**, **4**, and **6** (Table 5) in hexane were almost identical to each other and featured two absorptions near 350 and 435 nm. Cryoscopic studies of **1** and **6** in cyclohexane were undertaken to determine the aggregation number in solution. Data for **1** were recorded at two different molalities of 1.83 × 10<sup>-2</sup> and 3.03 × 10<sup>-2</sup> mol/kg, that is, 18.3 and 30.3 mmolal. The freezing point depression corresponded to a MW of 540 ± 40 g/mol. Because the MW of GaAr\* is 551.51 g/mol, the data show that **1** exists primarily as a monomer in cyclohexane at these concentrations. Similar studies of **6** afforded molecular weights consistent with a monomeric structure. Thus, **6**, although it is weakly associated in the crystal phase, resembles **1** in that it dissociates to monomers in cyclohexane. Clearly, both the UV/visible and the cryoscopic data are in harmony with regard to the existence of **1**, **4**, and **6** as monomers in hydrocarbon solvents. The <sup>1</sup>H NMR spectra displayed absorptions corresponding to the presence of

(41) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2842.

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for **8–10**

Ar*Ga{B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> } ( <b>8</b> )		Ar*Ga{B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> } ( <b>9</b> )		Ar'Ga{B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> } ( <b>10</b> )	
Ga(1)–B(1)	2.110(3)	Ga(1)–B(1)	2.108(2)	Ga–B <sup>a</sup>	2.129(3), 2.118(3)
Ga(1)–C(1)	1.943(3)	Ga(1)–C(1)	1.939(1)	Ga–C	1.949(3), 1.948(3)
B(1)–C(37)	1.636(5)	B(1)–C(39)	1.632(2)	B–C	1.633(5), 1.628(4)
B(1)–C(43)	1.639(5)	B(1)–C(45)	1.638(2)	B–C	1.617(5), 1.632(5)
B(1)–C(49)	1.616(5)	B(1)–C(51)	1.628(2)	B–C	1.633(5), 1.624(4)
Ga(1)···F(1)	2.394(2)	Ga(1)···F(1)	2.435(2)	Ga···F	2.344(2)
B(1)–Ga(1)–C(1)	173.28(14)	B(1)–Ga(1)–C(1)	172.97(6)	B–Ga–C	176.44(13), 175.51(13)
C(37)–B(1)–C(43)	106.3(3)	C(39)–B(1)–C(45)	108.3(1)	C–B–C	106.2(3), 105.8(2)
C(37)–B(1)–C(49)	115.5(3)	C(39)–B(1)–C(51)	115.9(1)	C–B–C	115.5(3), 114.7(3)
C(43)–B(1)–C(49)	115.3(3)	C(45)–B(1)–C(51)	115.9(1)	C–B–C	115.7(3), 117.1(2)

<sup>a</sup> Two crystallographically independent molecules.

**Scheme 1.** Reactions of the Monomer GaAr\*

Ar\*, Ar<sup>#</sup>, and Ar' groups only, and the <sup>13</sup>C NMR spectra indicated low field ipso C absorptions at  $\delta$  176.26 (**1**), 176.45 (**4**), and 173.80 (**6**), which show that this atom is substituted by an electropositive metal.

In the absence of X-ray structural data for compounds **1** and **4**, they were further characterized by their chemical behavior. Several reactions were examined as shown in Scheme 1.

Reaction of **1** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, Fe(CO)<sub>5</sub>, 2,3-dimethyl-1,3-butadiene, or sodium afforded the products Ar\*GaB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**8**), Ar\*GaFe(CO)<sub>4</sub> (**11**),<sup>42</sup> (Ar\*Ga–CH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>)<sub>2</sub> (**12**), and Na<sub>2</sub>(Ar\*GaGaAr\*) (**13**).<sup>12</sup> The products **11** and **13** have been reported previously by Robinson and co-workers, but they were synthesized by different synthetic routes that involved the reaction of GaAr\*Cl<sub>2</sub> with Na<sub>2</sub>Fe(CO)<sub>4</sub> to give **11**<sup>42</sup> or the reduction of GaAr\*Cl<sub>2</sub> by excess sodium to give **13**.<sup>12</sup> The structure of **11**, which crystallized with one molecule of toluene per asymmetric unit, was essentially identical to that previously reported<sup>42</sup> where it cocrystallized with a molecule of ether. The compound Na<sub>2</sub>(Ar\*GaGaAr\*), **13**, was identified via a unit cell check, <sup>13</sup>C NMR, and UV/vis spectroscopic data. In the original synthetic report, it was noted that during the reduction of GaAr\*Cl<sub>2</sub> the solution initially turned green.<sup>12</sup> In our hands, the same phenomenon was observed upon treatment of GaAr\*Cl<sub>2</sub> with sodium. If the reaction mixture was separated from the sodium after ca. 3 h, the green color persisted, and it was possible to crystallize **1** in ca. 10% yield from this solution. The related compound Na<sub>2</sub>(Ar'GaGaAr') **14** could be synthesized by stirring solutions of **6** or **7** with excess sodium. It was characterized spectroscopically and crystallographically and was

found to have structural parameters very similar to those of **13** (cf. Table 4). Compound **1** also reacted rapidly with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Fe(CO)<sub>5</sub> in hydrocarbon solvent at room temperature to afford Ar\*Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} **8**, or Ar\*GaFe(CO)<sub>4</sub> **11**. It is notable that no forcing conditions, for example, refluxing or photolysis, were required to induce these reactions to occur. The related GaAr<sup>#</sup> and Ar'GaGaAr' compounds **4** and **6** also reacted readily with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to yield the products **9** and **10**. The three B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct species **8–10** were characterized by X-ray crystallography. The <sup>11</sup>B NMR spectra of **8–10** display relatively sharp singlets at  $\delta$  –18.93, –18.03, and –17.73 ppm, respectively. Three <sup>19</sup>F NMR signals that correspond to the ortho, meta, and para fluorines were also observed in each case. The sterically related GaN<sup>^</sup>NDipp<sub>2</sub>, **15**,<sup>36</sup> reacted with Fe(CO)<sub>5</sub> to give the product Dipp<sub>2</sub>N<sup>^</sup>NGaFe(CO)<sub>4</sub>, **16**, which is related to **11**.

Treatment of **1** with 2,3-dimethyl-1,3-butadiene resulted in the addition product **12**, which featured a 10-membered Ga<sub>2</sub>C<sub>8</sub> ring in which the Ga–Ga separation is 5.736 Å. The synthesis of (GaAr'')<sub>n</sub> was attempted through the reaction of (LiAr'')<sub>2</sub> with “GaI”, but this yielded colorless crystals of IGaAr''<sub>2</sub>. To avoid this result, GaN<sup>^</sup>NDipp<sub>2</sub> (**15**) was used as the gallium source. However, treatment of this compound with (LiAr'')<sub>2</sub> did not yield (GaAr'')<sub>n</sub>. Instead, it afforded the unique paramagnetic cluster Ga<sub>11</sub>Ar''<sub>4</sub> (**17**).

**Properties of the Gallium Aryls 1, 4, and 6 and Their Halogen Derivatives 2, 5, and 7.** Compounds **1**, **4**, and **6** are relatively rare examples of neutral organogallium(I) compounds.<sup>1</sup> Only a handful of such molecules are known, and they display either tetrameric (with Ga<sub>4</sub> tetrahedra),<sup>1c,4</sup> quasi hexameric,<sup>2</sup> or nonameric<sup>9</sup> structures in the solid state. In the tetramers, the Ga–Ga bond lengths in the Ga<sub>4</sub> tetrahedra are in the range 2.57–2.71 Å,<sup>1c</sup> which is longer than the ca. 2.50 Å expected for a single bond from the sum of covalent radii. This is in keeping with the electron-deficient nature of the Ga<sub>4</sub> array, where the formal Ga–Ga bond order is 2/3. Although all previously reported neutral organogallium(I) compounds are associated in the solid state, they may dissociate to monomers in solution or the vapor phase. Electron diffraction studies of Ga(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sup>43</sup> and GaC(SiMe<sub>3</sub>)<sub>3</sub><sup>44</sup> vapors have revealed a monomeric nido GaC<sub>5</sub> structure in the case of the former and a monomeric structure with a one-coordinate metal for the latter species. Stabilization of unassociated Ga(I) compounds in the solid state can be effected by polydentate ligands as in GaTpBu'<sub>2</sub> (Tp = tris(pyrazolyl)borato)<sup>45</sup> and GaN<sup>^</sup>NDipp<sub>2</sub> **15**,<sup>36</sup> which

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(43) Haaland, A.; Martinsen, K.-G.; Volden, H. V.; Loos, D.; Schnöckel, H. *Acta Chem. Scand.* **1994**, *48*, 172.

(44) Haaland, A.; Martinsen, K.-G.; Volden, H. V.; Kaim, W.; Waldhör, E.; Uhl, W. *Organometallics* **1996**, *15*, 1146.

**Table 4.** Selected Interatomic Distances (Å) and Angles (deg) for **12–14, 16, 17**

Na <sub>2</sub> (Ar <sup>+</sup> GaGaAr <sup>+</sup> ) (13)		Na <sub>2</sub> (Ar <sup>+</sup> GaGaAr <sup>+</sup> ) (14)	
Ga(1)–Ga(2)	2.3243(10)	Ga(1)–Ga(1A)	2.3469(12)
Ga–C	2.045(6), 2.036(6)	Ga(1)–C(1)	2.059(5)
Ga–Na	3.065(3), 3.103(3)	Ga(1)–Na(1)	3.058(2)
Ga–Na	3.085(3), 3.102(3)	Ga(1)–Na(1A)	3.101(2)
Na–C	2.847(6), 3.045(7)	Na(1)–C(7)	3.034(5)
	2.850(6), 3.048(7)	Na(1)–C(9)	2.984(5)
	2.876(6), 3.051(6)	Na(1)–C(10)	2.933(5)
	2.934(6), 3.062(6)	Na(1)–C(11)	2.940(6)
	2.992(6), 3.070(7)	Na(1)–C(19)	3.051(5)
	3.105(6), 3.100(7)	Na(1)–C(20)	3.021(5)
	3.102(6)	Na(1)–C(21)	2.937(5)
	3.127(6)	Na(1)–C(22)	2.879(6)
C(1)–Ga(1)–Ga(1A)	125.93(17), 134.03(10)	Na(1)–C(23)	2.886(6)
Ga(1)–C(1)–C(2)	122.4(4)	Na(1)–C(24)	3.004(5)
Ga(1)–C(1)–C(6)	121.3(4)	C(1)–Ga(1)–Ga(1A)	130.69(13)
Ga(2)–C(37)–C(38)	120.6(4)	Ga(1)–C(1)–C(2A)	121.9(3)
Ga(2)–C(37)–C(42)	123.1(4)	Ga(1)–C(1)–C(6A)	121.5(3)
C(1),C(37) (ring) to	84.5, 87.6	C(1) (ring) to	88.6
C(1)Ga(1)Ga(2)C(37)		C(1)Ga(1)Ga(1A)C(11)	
{Ar <sup>+</sup> GaCH <sub>2</sub> C(Me)C(Me)CH <sub>2</sub> } <sub>2</sub> (12)		Dipp <sub>2</sub> N <sup>+</sup> NGaFe(CO) <sub>4</sub> (16)	
Ga(1)–C(1)	1.992(3)	Ga(1)–N(1)	1.9273(11)
Ga(1)–C(37)	1.985(5)	Ga(1)–Fe(1)	2.2851(3)
Ga(1)–C(41)	1.978(3)	Fe(1)–C(16)	1.795(2)
C(41)–C(40)	av. 1.554(10)	Fe(1)–C(17)	1.777(2)
C(38)–C(40)	1.330(10)	Fe(1)–C(18)	1.772(2)
C(1)–Ga(1)–C(37)	113.52(12)	O(1)–C(16)	1.149(2)
C(1)–Ga(1)–C(41)	121.39(12)	O(2)–C(17)	1.162(3)
C(37)–Ga(1)–C(41)	125.09(12)	O(2)–C(18)	1.142(2)
Ga <sub>14</sub> Ar <sub>4</sub> <sup>+</sup> (17)			
Ga(1)–Ga(2)	2.529(1)	Ga(2)–Ga(1)–Ga(2A)	77.36(3)
Ga(1)–Ga(2A)	2.563(1)	Ga(1)–Ga(2)–Ga(1A)	102.42(3)
Ga(1)–Ga(4)	2.603(1)	Ga(7)–Ga(6)–Ga(7A)	102.62(3)
Ga(1)–Ga(5A)	2.664(2)	Ga(6)–Ga(7)–Ga(6A)	76.41(3)
Ga(2)–Ga(3)	2.547(2)	C(1)–Ga(1)–Ga(2)	132.55(2)
Ga(2)–Ga(5A)	2.648(2)	C(1)–Ga(1)–Ga(2A)	138.4(2)
Ga(3)–Ga(7A)	2.610(2)	Ga(2)–Ga(1)–Ga(4)	81.18(4)
Ga(3)–Ga(6)	2.652(2)	Ga(4)–Ga(1)–Ga(2A)	67.65(4)
Ga(3)–Ga(5)	2.667(3)	Ga(1A)–Ga(2)–Ga(3)	77.02(5)
Ga(4)–Ga(5)	2.661(2)	Ga(1)–Ga(2)–Ga(3)	104.51(5)
Ga(4)–Ga(7)	2.564(2)	Ga(2)–Ga(3)–Ga(5)	92.32(7)
Ga(4)–Ga(4A)	2.638(2)	Ga(2)–Ga(3)–Ga(5)	92.00(7)
Ga(5)–Ga(1A)	2.664(2)	Ga(6)–Ga(3)–Ga(5)	98.67(6)
Ga(5)–Ga(2A)	2.648(2)	Ga(5)–Ga(3)–Ga(4)	58.01(6)
Ga(6)–Ga(7)	2.558(2)	Ga(6)–Ga(3)–Ga(4)	65.06(6)
Ga(6)–Ga(7A)	2.557(2)	Ga(1)–Ga(4)–Ga(3)	96.39(6)
Ga(1)–C(1)	1.991(6)	Ga(3)–Ga(4)–Ga(5)	58.21(6)
Ga(7)–C(25)	1.996(6)	Ga(6)–Ga(4)–Ga(7)	54.83(3)
		Ga(5)–Ga(4)–Ga(6)	91.96(6)
		Ga(3)–Ga(4)–Ga(6)	54.81(5)
		Ga(30)–Ga(5)–Ga(4)	63.78(6)
		Ga(1A)–Ga(5)–Ga(2A)	57.68(4)
		Ga(2)–Ga(5)–Ga(4)	65.12(5)
		Ga(3)–Ga(6)–Ga(4)	60.14(4)
		Ga(4)–Ga(6)–Ga(7)	55.02(3)
		Ga(6)–Ga(7)–Ga(4)	70.15(4)

**Table 5.** UV/Vis Spectroscopic Data (nm, mol L<sup>-1</sup> cm<sup>-1</sup>) for **1, 4, and 6** in Hexane Solution

GaAr <sup>*</sup> , <b>1</b>	350 (1900)	436 (700)
GaAr <sup>#</sup> , <b>4</b>	350 (1800)	434 (510)
GaAr <sup>'</sup> , <b>6</b>	350 (1600)	437 (520)

feature three- and two-coordinate gallium in the solid state, respectively. The latter has v-shaped coordination at gallium and displays carbene-like behavior. The N<sup>+</sup>NDipp<sub>2</sub> group sterically resembles the ligands Ar<sup>\*</sup>, Ar<sup>#</sup>, and Ar<sup>'</sup>, but, because

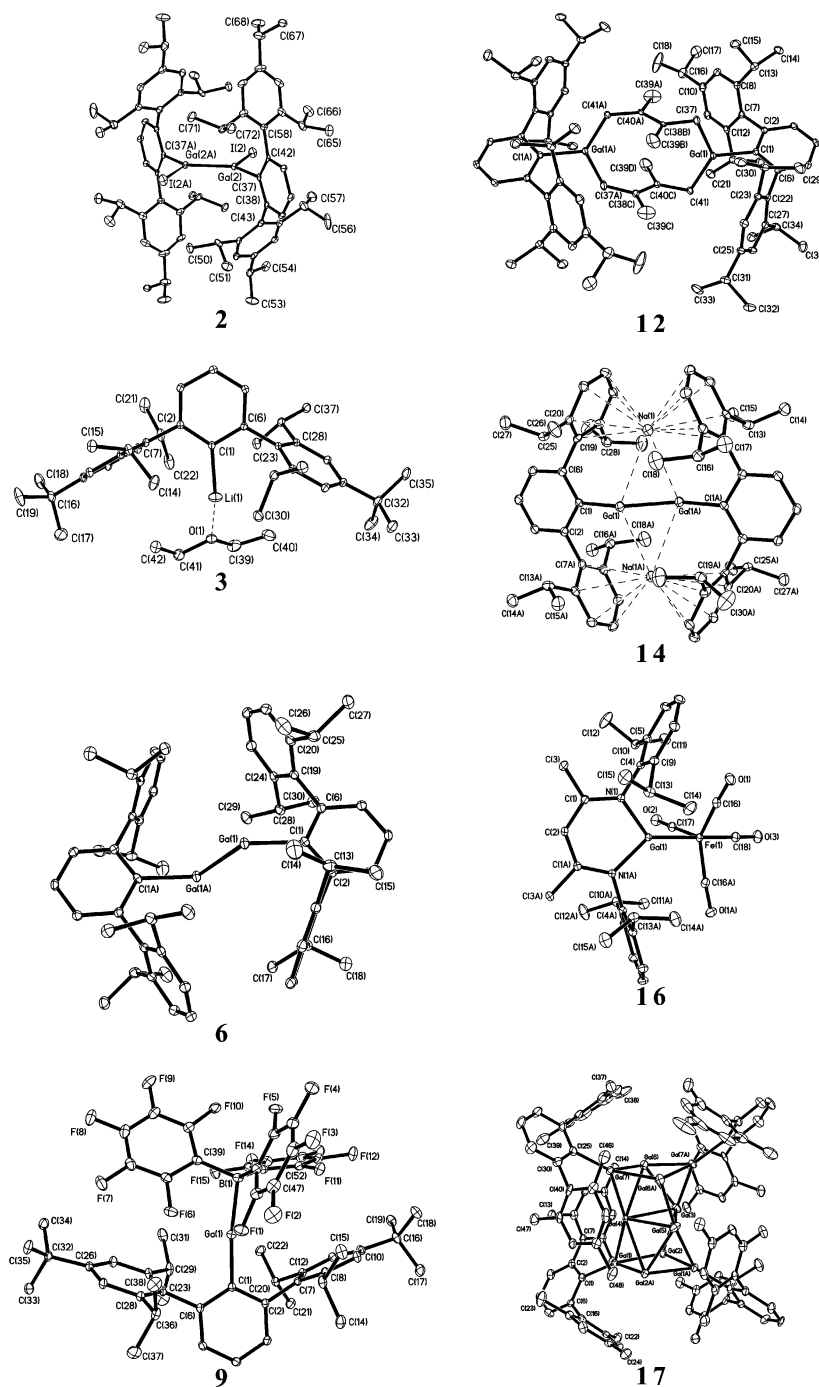
it is bidentate, it is slightly more crowded due to its bonding mode. A monomeric structure is observed for this compound in the solid state.<sup>36</sup>

Compounds **1, 4,** and **6** are closely related to their indium and thallium congeners MAR<sup>\*</sup> (M = In,<sup>10</sup> Tl<sup>11</sup>) and Ar<sup>'</sup>InInAr<sup>'</sup>.<sup>46</sup> Uniquely, the indium and thallium MAR<sup>\*</sup> species are unassociated in the solid state and have one-coordinate metals, whereas Ar<sup>'</sup>InInAr<sup>'</sup>,<sup>46</sup> the indium analogue of Ar<sup>'</sup>GaGaAr<sup>'</sup>, **6**, is also weakly associated in the crystalline phase. At present, it is not

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**Figure 1.** Thermal ellipsoid (30%) drawings of **2**, **3**, **6**, **9**, **12**, **14**, **16**, and **17**. Hydrogen atoms are not shown. Selected bond distances and angles for these compounds and **7**, **8**, **10**, and **13** are given in Tables 2–4. The disorder in the alkene units of **12** is not shown. Only one of the crystallographically independent molecules of **17** is illustrated.

possible to say with certainty that the gallium analogues **1** and **4** are monomeric in the solid state like their indium and thallium congeners because of the poor diffraction characteristics of their crystals. Nonetheless, the structures of  $\text{InAr}^*_{10}$  and  $\text{Ar}'\text{InInAr}'_{46}$  suggest that an analogous structural relationship between  $\text{GaAr}^*$ , **1**, and  $\text{Ar}'\text{GaGaAr}'$ , **6**, is a possibility. Cryoscopy of **1** in cyclohexane solution showed that it was monomeric at concentrations of ca. 18 and 30 mmolal. Cryoscopic studies<sup>1c</sup> of  $[\text{GaC}(\text{SiMe}_3)_3]_4$ <sup>47</sup> and  $[\text{GaC}(\text{SiMe}_2\text{Et})_3]_4$ <sup>48</sup> at concentrations of

10 mmolar afforded trimeric formulas masses, which were interpreted as equilibria between monomeric and tetrameric structures. Only at more dilute concentrations of ca. 1 mmolar were monomeric formulas obtained for these Ga(I) alkyls. The results suggest that **1** is even more weakly associated than these compounds because a monomeric structure is maintained to higher concentrations. The analogous compound **4** was synthesized in a manner similar to that for **1** by the reaction of  $\text{Et}_2\text{OLiAr}^\#$  (**3**) with GaI. The altered para substituents on the flanking aryl rings did not solve the crystallographic problems encountered for **1**. Nonetheless, the lithium derivative **3** crystallized readily (Figure 1). It has a two-coordinate lithium with a

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short Li–C distance of 2.036(2) Å and a wide interligand angle of 164.4(2)°.

The crystal structure of red-brown **6** (Figure 1) shows that it is associated as a dimer in the solid state. It has a trans-bent, CGaGaC core structure with a bending angle of 123.16(7)° and a Ga–Ga distance of 2.6268(7) Å.<sup>41</sup> It is the first dimeric gallium structure of this type to be isolated and could be described as a “digallene”. This name is misleading, however, because the Ga–Ga bond is ca. 0.1 Å longer than single Ga–Ga bonds in tetraorganodigallanes and the single Ga–Ga bonds of ca. 2.49 Å observed in **2** and **7** (vide infra).<sup>1,5</sup> Furthermore, upon dissolving the red-brown **6** in hydrocarbon solution, its color changes to green, and its UV/vis spectrum is essentially identical to those of **1** and **4**. Cryoscopic studies confirm that **6** is essentially monomeric in cyclohexane, which underlines the weakness of the Ga–Ga bond. This is in agreement with recent low-temperature matrix isolation studies of HMMH (M = Ga or In) species, which indicate very low couplings between the symmetric and asymmetric HMMH stretching modes. The antisymmetric stretching mode for HGaGaH is located at a wavenumber close to that of monomeric :GaH, which indicates a very weak interaction between the MH fragments.<sup>29–31</sup> These experimental findings are consistent with calculations<sup>20,22,49,50</sup> for a range of RGaGaR model species which displayed trans-bent structures and long GaGa distances in the range 2.608–2.768 Å. An AIM analysis of the SCF function of MeGaGaMe has yielded a Ga–Ga bond order of 0.821.<sup>20,51</sup> Earlier calculations have also indicated low bond strengths in a variety of hypothetical group 13, RMMR, dimers, and a Ga–Ga bond strength of ca. 3 kcal mol<sup>-1</sup> was calculated.<sup>49</sup>

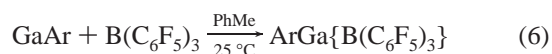
Supporting evidence for the weakness of the Ga–Ga bond in **6** comes from a comparison of the Ga–C distance, 2.025(3) Å, with the Ga–C bond lengths in complexes formed by the :GaAr ligands. In these compounds, for example, **8–11** (see below), the Ga–C bond lengths are near 1.94 Å. The shorter Ga–C bonds may be accounted for in terms of an increased ionic contribution to the Ga–C bond strength upon removal of electron density from gallium through donation of the lone pair to an acceptor in compounds such as **8–11**.<sup>52</sup> If strong donor–acceptor bonding were also present in **6**, a shorter Ga–C bond should have been observed because the gallium electron pair density would be more concentrated in the bonding region midway between the galliums in a strongly bonded dimer. In other words, there would be less electron density and consequently a greater δ<sup>+</sup> charge present at gallium, and a shorter Ga–C bond should have resulted. In **6**, this shortening is not observed, and the Ga–C bond length is closer to the 2.06(2) Å reported for the vapor phase structure of the monomer GaC(SiMe<sub>3</sub>)<sub>3</sub>.<sup>44</sup> A similar argument has been used recently to rationalize the long In–C bonds in the monomer InAr\* (In–C = 2.260(7) Å) and the dimer Ar'InInAr' (In–C = 2.256-

(2) Å), in contrast to the short In–C bonds (ca. 2.14(1) Å) in the donor–acceptor complexes ArIn{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (Ar = Ar' or Ar\*).<sup>46</sup>

In summary, all currently available experimental data point to a weak interaction between the gallium centers in **1**, **4**, and **6**. It is notable that, unlike **6**, the color of both **1** and **4** are green in the solid. This indicates that **1** and **4** are either monomeric in the solid or so weakly interacting that the n–p chromophore is essentially unaffected.

Compounds **2** and **7** are very rare examples of a digallane bearing one halogen substituent at each gallium. The structure of **2** (Figure 1) features two crystallographically independent centrosymmetric molecules that have Ga(Ar\*)I units linked by Ga–Ga bonds 2.482(2) and 2.502(2) Å in length. The structure of **7** features a Ga–Ga distance of 2.493(2) Å with an essentially coplanar I(ipso-C)Ga–Ga(ipso-C)I array. These distances are slightly shorter than the sum of the covalent radii for gallium (2.50 Å) and the 2.515(3) Å Ga–Ga bond observed in the aryl Trip<sub>2</sub>GaGaTrip<sub>2</sub>.<sup>53</sup> The very large Ar\* and Ar' substituents are oriented trans to each other, and the Ga–Ga–C angles are 14–21° wider than the Ga–Ga–I angle. The Ga–C distances, av. 1.98(1) Å, are similar to the 2.008(7) Å observed in the structure of Trip<sub>2</sub>GaGaTrip<sub>2</sub>. The Ga–I bonds 2.514(2)–2.541(2) Å are similar to the 2.53(1) Å average seen in the structure of I<sub>2</sub>GaN<sup>NDipp</sup><sub>2</sub>.<sup>54</sup> The compound most comparable to **2** and **7** is the Ga–Ga bonded dimer [Ga(Cl)Mes\*]<sub>2</sub> (Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-Bu'<sub>3</sub>).<sup>55</sup> Although full details of the structure were not given, a Ga–Ga bond length of 2.438(6) Å was reported. The significantly shorter bond in this compound is consistent with the decreased effective radius of gallium because of the more electronegative chlorine substituent. The fact that the Ga–Ga distances in **2** and **7** are close to that expected for a normal single bond shows that the long Ga–Ga distance in **6** is not due to steric effects but arises from its electronic structure.

**Reaction Chemistry of 1, 4, and 6.** The donor–acceptor compounds **8–10** are readily formed upon mixing of **1**, **4**, or **6** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene (eq 6). The rapidity of the reaction is a reflection of the dissociated nature of **1**, **4**, and **6** and the



Ar = Ar\*, **8**; Ar<sup>#</sup>, **9**; Ar', **10**

availability of the gallium lone pair for complex formation. Important bond distances and angles are given in Table 3. The compounds have almost linearly coordinated galliums, and the Ga–B bond distances in **8** (2.110(3) Å), **9** (2.108(2) Å) (Figure 1), and **10** (av. 2.124(6) Å) are similar to the 2.10 Å predicted for a single bond from the sum of the covalent radii of Ga (1.25 Å) and B (0.85 Å). The distances are shorter than the average Ga–B bond lengths reported for a variety of gallium substituted carboranes (2.14–2.33 Å),<sup>56,57</sup> which, however, contain three- and four-coordinate gallium. The Ga–B bonds in **8–10** are ca.

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(52) Alternatively, the GaAr monomer could feature a lone pair orbital that is mostly 4s in character and a Ga–C bond that involves a Ga 4p orbital. When the GaAr species becomes strongly bound through gallium, the character of the gallium bonding orbitals changes to some degree toward sp hybridization so that shorter bonds to gallium are observed.

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**Table 6.** Selected Structural Parameters and IR Stretching Frequencies for Some LGaFe(CO)<sub>4</sub> Complexes<sup>a</sup>

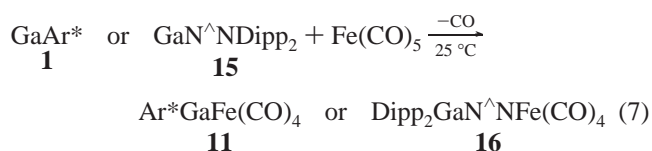
compound	Ga coord. no.	Fe–Ga (Å)	Ga–N or Ga–C (av.)	CO stretch (cm <sup>-1</sup> )	ref
Ar*GaFe(CO) <sub>4</sub> , <b>11</b> <sup>b</sup>	2	2.248(7)	1.9435(19)	2032, 1959, 1941, 1929	42
Dipp <sub>2</sub> N <sup>^</sup> NGaFe(CO) <sub>4</sub> , <b>16</b> <sup>b</sup>	3	2.2851(4)	1.9273(11)	2010, 1940, 1915, 1900	this work
Cp*GaFe(CO) <sub>4</sub> <sup>c</sup>	4	2.2731(4)	2.221(2)	2037, 1966, 1942	67
TpMe <sub>2</sub> GaFe(CO) <sub>4</sub> <sup>b</sup>	4	2.315(3)	1.991(15)	2011, 1919, 1890	66

<sup>a</sup> The stretching frequencies for Ph<sub>3</sub>PFe(CO)<sub>4</sub> are 2052, 1979, and 1947 cm<sup>-1</sup>.<sup>68</sup> <sup>b</sup> Abbreviations are defined in the text. <sup>c</sup> Cp\* = (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>).

0.04 Å shorter than the average Ga–B bond distance in the recently reported complexes Dipp<sub>2</sub>N<sup>^</sup>NGa{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sup>58</sup> and η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}<sup>58,59</sup> where the gallium has a higher coordination number.<sup>58,59</sup> The Ga–C bonds in **8** (1.943(3) Å), **9** (1.939(1) Å), and **10** (1.949(3) Å) are shorter than those generally observed in organogallium(I) compounds,<sup>1</sup> and even shorter than those observed in **2** and **7** despite the higher formal oxidation state of gallium in these species. More significantly, the Ga–C distances are ca. 0.08 Å shorter than those observed in Ar'GaGaAr', **6**. As argued above for **6**, it is probable that the removal of electron density from gallium, due to its donor action in complex formation, results in a larger δ+ charge on gallium, which gives rise to a stronger ionic factor in the Ga–C bond. Also of note is the relatively close (within van der Waals radii ca. 3.4 Å) Ga···F distances in **8** (2.394(2) Å), **9** (2.435(2) Å), and **10** (2.384(2) Å). However, these distances are at least 0.45 Å longer than Ga–F single bonds that span the range from 1.83 to 1.95 Å for four-coordinate gallium(III) fluoro compounds.<sup>60</sup> The closest Ga···F interaction involves F(1), and the C–F(1) distance is lengthened from the average of 1.346(6) Å observed for the remaining 14 C–F bonds to 1.378(4) Å (C–F(1) av.). In addition, the C(37)–B(1)–Ga(1) angle is slightly narrower (104.6(2)°) than the other two C(ipso)–B–Ga angles (106.9(2)° and 107.5(2)°) for the perfluorophenyl rings in **8** (a similar discrepancy is not observed in **9**). These data suggest that the lengthening of the C–F bond and the slight narrowing of the Ga–B–C angle are caused by Ga···F interactions. The weak interactions appear to exist only in the solid state as the <sup>19</sup>F NMR spectra of **8–10** are consistent with three signals detected for the ortho, meta, and para fluorines in the three C<sub>6</sub>F<sub>5</sub> rings. The donor action of the gallium causes the geometry at boron in B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to change from trigonal planar to distorted tetrahedral. The extent of the geometrical change from trigonal planar to tetrahedral of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moiety has been taken to be an indication of the strength of the donor–acceptor interactions.<sup>61</sup> The sums of the C–B–C angles in **8**, **9**, and **10** are 337.1(1)°, 340.0(3)°, and 337.5(3)°, respectively. These can be compared with the previously reported values for η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>-Al{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (339.8(2)°),<sup>62</sup> η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>Ga{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sup>64</sup> (342.2(2)°), and Dipp<sub>2</sub>N<sup>^</sup>NGa{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (333.6(2)°).<sup>58</sup> By this criterion, the order of increasing Lewis basicity is Ga(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) < **4** < Al(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) < **6** ≈ **1** < GaN<sup>^</sup>NDipp<sub>2</sub>. It is possible that GaN<sup>^</sup>NDipp<sub>2</sub>, **15**, behaves as a stronger Lewis base than **1** or

**6** due to the increased electron density at gallium provided by the η<sup>2</sup>-β-diketiminato ligand and the increased metal coordination number in GaN<sup>^</sup>NDipp<sub>2</sub>. Also of note in the structures of **8–10** is the pattern of C–B–C angles in which one angle (105.8–108.3°) is narrower than the other two (114.7–117.1°), which are probably due to steric interactions between the terphenyl and C<sub>6</sub>F<sub>5</sub> ligands.

The facile reactions of GaAr\* (**1**) or GaN<sup>^</sup>NDipp<sub>2</sub> (**15**) with Fe(CO)<sub>5</sub> at room temperature, which afforded the complexes Ar\*GaFe(CO)<sub>4</sub>, **11**, or Dipp<sub>2</sub>N<sup>^</sup>NGaFe(CO)<sub>4</sub>, **16** (eq 7), underline their monomeric character. Compound **11** was previously



synthesized via the reaction of Ar\*GaCl<sub>2</sub> with Na<sub>2</sub>Fe(CO)<sub>4</sub>, structurally characterized and described as a ferrogallyne, that is, having an iron gallium triple bond.<sup>42</sup> This view has not been sustained by calculations, and the gallium–iron bonding is best described by strong σ donation from gallium to iron with weak iron to gallium π-bonding.<sup>63–65</sup> The fact that **1** or **15** displace CO from Fe(CO)<sub>5</sub> at room temperature without heating or photolysis is consistent with the strong σ-donor and monomeric characteristics of **1** and **15** rather than any multiple bond character in the complexes. The structures of compounds **11**<sup>42</sup> and **16** provide an opportunity to study the dependence of gallium–metal bond lengths on the coordination number in a series of donor complexes.<sup>42,66,67</sup> All four compounds in Table 6 feature gallium(I) centers behaving as Lewis bases toward an iron tetracarbonyl fragment. The structure of **16** (Figure 1) incorporates a mirror plane containing C(2), Ga(1), Fe(1), C(17), O(2), C(18), and O(3). The Ga(1)–N(1) distance undergoes a shortening in excess of 0.11 Å in comparison with the free ligand GaN<sup>^</sup>NDipp<sub>2</sub> (Ga–N = 2.054(2) Å), and this is consistent with the results discussed for **8–10**. It can be seen in Table 6 that the shortest Fe–Ga bond corresponds to the two-coordinate gallium complex **11**.<sup>42</sup> An increase in the gallium coordination to three in the complex **16** results in an ca. 0.05 Å increase in the Fe–Ga bond length. A further increase in the gallium coordination number to four in the complex TpMe<sub>2</sub>-GaFe(CO)<sub>4</sub><sup>65</sup> results in a lengthening of the Fe–Ga bond by ca. 0.03 Å. The (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)GaFe(CO)<sub>4</sub><sup>66</sup> complex, in which the gallium coordination number may be approximated to four, occupies a seemingly anomalous position. However, it can be seen that the Ga–ligand interactions in this complex are the

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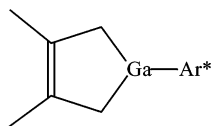
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longest in the series, which may permit a stronger than expected Fe–Ga interaction.

The CO stretching frequencies of the complexes (Table 6) may be compared with those of  $\text{Ph}_3\text{PFe}(\text{CO})_4$  (2052, 1979, and  $1947\text{ cm}^{-1}$ ).<sup>68</sup> It can be seen that the frequencies of *all* of the gallium–iron complexes are lower than the corresponding ones in the phosphine complex, implying that the  $\sigma/\pi$  donor–acceptor ratio for the gallium ligands is greater than that of  $\text{PPh}_3$ . In other words, the amount of Fe–Ga  $\pi$ -back-bonding in the complexes is likely to be small and inconsistent with the existence of a Ga–Fe triple bond. These experimental findings are in agreement with several calculations,<sup>63–65</sup> and the low degree of Fe–Ga  $\pi$ -back-bonding in the complexes can be accounted for, at least in part, by differences in energy levels between the two bonding fragments. In  $:\text{GaH}$ , the triplet state has been calculated to be  $46.6\text{ kcal/mol}^{-1}$  higher in energy than the singlet state.<sup>49</sup> Apparently, the p-orbitals in  $:\text{GaR}$  are much higher in energy than the lone pair. They are also probably significantly higher in energy than the valence orbitals of  $\text{Fe}(\text{CO})_4$ . This energy difference reduces the back-bonding interaction between iron and gallium. Nonetheless, the Fe–Ga bonds in the complexes in Table 6 are up to ca.  $0.2\text{ \AA}$  shorter than those observed for Fe–Ga single bonds. This difference can be rationalized by considering the types of orbitals that participate in bonding. For example, in the singly bonded Fe–Ga complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeGaBu}'_2$ ,<sup>69</sup> the gallium employs a p-orbital or a hybrid orbital with some s character to bond to iron. In complex **11**,  $\text{GaAr}^*$  may use a 4p orbital (or an orbital with 4p and some s character) to bond to the aryl group with the lone pair located primarily in a 4s orbital (or 4s orbital with some p character), leaving two empty, 4p orbitals at gallium. The gallium  $4s^2$  electron pair is used to bond to iron. The 4s orbital has a smaller radius than the 4p orbital, and a shorter Fe–Ga bond results. The low coordination number of gallium in **11** may also be a factor in shortening the bond.

The rapid reaction of **1** with 2,3-dimethyl-1,3-butadiene to give the cyclic product **12** (Figure 1) is also in agreement with the monomeric character of **1**. No “monomeric” cycloaddition product containing a five-membered ring as illustrated by



was obtained, however. It seems possible that a strained geometry would be imposed on such a ring by the presence of the double bond and planar gallium coordination. This could lead to Ga–C bond cleavage and subsequent dimerization to give **12**. Some details of the structure of **12** are provided in Table 4, where it can be seen that the structural parameters are consistent with those previously observed in organogallium compounds.

The structures of the reduced species  $\text{Na}_2\text{Ar}^*\text{GaGaAr}^*$ , **13**, and  $\text{Na}_2\text{Ar}'\text{GaGaAr}'$ , **14**, which were synthesized by stirring **1** and **6** with sodium, are very similar. The structure of **13** has been determined twice,<sup>12,27</sup> and the most recent data are given in Table 4.<sup>27</sup> The structure of **14** was recently presented in a

preliminary form.<sup>41</sup> The latter crystallizes as centrosymmetric molecules that feature a planar, trans-bent  $\text{C}(1)\text{Ga}(1)\text{Ga}(1\text{A})\text{C}(1\text{A})$  core with sodiums that are complexed by Dipp rings and which almost symmetrically bridge the galliums on each side of the core (Figure 1). Inspection of the data in Table 4 shows that there are only minor differences in the structural parameters of **13** and **14**. The strengths of the sodium interactions with the galliums and the aryl rings are very similar as are the average Ga–Ga–C angles. The gallium–gallium distance is ca.  $0.02\text{ \AA}$  longer in **14**. This is somewhat surprising in view of the lower steric crowding in **14**, which might be expected to afford a shorter Ga–Ga bond. However, the difference in the Ga–Ga bond length is relatively small, and it is possible that the para substituents can affect the Ga–Ga bond length in ways that are not completely understood at present.<sup>22</sup> As already mentioned, it was the description of the Ga–Ga bond in **13** as a triple one which sparked the current general debate on multiple bonding between heavier main group elements. Without revisiting the theoretical arguments on either side of that debate (which can be found in refs 12–25 and in a number of reviews<sup>28,31,70</sup>), the results obtained for **1**, **4**, and **6** clearly show that they have weak Ga–Ga bonds consistent with a bond order below one.<sup>20,51</sup> Two-electron reduction of **1** and **6** to give **13** or **14** generates a single bond between the galliums. The weak interaction of the neutral precursor is also preserved as indicated by the maintenance of the trans-bent  $\text{CGaGaC}$  geometry with only a slight decrease in the amount of bending. The structures of **13** and **14** also display  $\text{Na-Ar}'$ ,  $\text{Ga-Na-Ga}$  bridging, and, possibly, terphenyl–terphenyl interactions that can shorten the Ga–Ga bond. The stability of the  $\text{Na}_2\text{Ga}_2$  core structures is critically dependent on the size of the alkali metal reductant employed, because reductions with potassium afford a different product with a  $\text{Ga}_4$  ring core structure.<sup>27</sup>

The attempted use of the less crowded ligand  $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$  ( $\text{Ar}''$ ) to obtain a neutral, higher aggregate cluster of formula  $(\text{GaAr}'')_n$  ( $n > 2$ ) afforded the product  $\text{Ga}_{11}\text{Ar}_4''$ , **17**, in which 7 of 11 galliums do not carry substituents. The apparent ligand stripping is analogous to that seen in the preparation of  $\text{In}_8\text{Ar}_4''$  under similar conditions.<sup>71</sup> The isolation of higher aggregate complexes for gallium and indium with use of the smaller  $\text{Ar}''$  substituent underlines the vital importance of steric effects for the stabilization of **1**, **4**, or **6**. Furthermore, the higher degree of aggregation for **17** in comparison to that for  $\text{In}_8\text{Ar}_4''$  is not unexpected because of the smaller size of gallium. The cluster crystallizes with two crystallographically independent  $\text{Ga}_{11}\text{Ar}_4''$  molecules. There is an odd number of electrons, and the EPR spectrum of the compound displays a broad (ca. 60 G) signal at  $g = 2.0237$ . The cluster skeleton, which contains a two-fold symmetry axis, is composed of two outer  $\text{Ga}_4$  rhombs in which two of the four galliums are substituted by an  $\text{Ar}''$  group and a central unit of three unsubstituted gallium atoms,  $\text{Ga}(3)$ ,  $\text{Ga}(4)$ , and  $\text{Ga}(5)$ , which are disordered over two positions of 50% occupancy. Intermetallic distances within the  $\text{Ga}_4$  rhombs and the central  $\text{Ga}_3$  triangle average  $2.552(3)$  and  $2.662(4)\text{ \AA}$ , respectively. Other distances are provided in Tables 2–4. Interestingly, there are some examples of molecules that

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contain Ga<sub>4</sub> and Ga<sub>3</sub> moieties in the literature. For instance, the clusters M<sub>2</sub>[Ga<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)<sub>3</sub>] (M = Na,<sup>72</sup> K<sup>73</sup>) and K<sub>2</sub>[Ga<sub>4</sub>(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)<sub>2</sub>]<sup>27</sup> possess the triangular and square planar arrays of gallium similar to those seen in **7**. The Ga<sub>11</sub> cluster forms part of a rapidly expanding series of group 13 metal clusters where aggregation numbers currently range from 2 to 84.<sup>74</sup>

## Conclusions

The experiments described in this paper show that the compounds GaAr<sup>\*</sup>, GaAr<sup>#</sup>, and GaAr<sup>'</sup> exist as green monomers in solution. Both GaAr<sup>\*</sup> and GaAr<sup>#</sup> maintain their green color as crystalline solids, whereas GaAr<sup>'</sup> weakly dimerizes to form red-brown crystals. Accordingly, it is probable that in the solid state GaAr<sup>\*</sup> and GaAr<sup>#</sup> are more weakly associated than the Ar'GaGaAr' dimer. The chemical behavior of the gallium monoaryls in solution is consistent with their formulation as monomers rather than dimers. The weakness of the Ga–Ga bonding can be attributed primarily to the large energy difference between the frontier lone pair and p-orbitals of the GaAr monomers.<sup>49</sup> Thus, in the neutral gallium aryls, the gallium valence electrons behave essentially as lone pairs rather than bond pairs. The reductions of GaAr<sup>\*</sup> or GaAr<sup>'</sup> with sodium readily afford the landmark compound Na<sub>2</sub>(Ar<sup>\*</sup>GaGaAr<sup>\*</sup>)<sup>12</sup> or

the related species Na<sub>2</sub>(Ar'GaGaAr'), which have Ga–Ga bond lengths (ca. 2.32–2.34 Å) that are ca. 0.3 Å shorter than that in the neutral dimer Ar'GaGaAr'. It was the very short Ga–Ga bond originally observed in Na<sub>2</sub>(Ar<sup>\*</sup>GaGaAr<sup>\*</sup>),<sup>12</sup> as well as the analogy between an uncomplexed dianion [ArGaGaAr]<sup>2-</sup> and an alkyne, that led to the conclusion that a Ga–Ga triple bond was present.<sup>12</sup> This conclusion was supported by some theoretical calculations,<sup>13–17</sup> but other theoretical papers questioned<sup>19,20,23–26</sup> this bonding description and demonstrated the importance of factors such as Na–Aryl and Na–Ga interactions in shortening the Ga–Ga bond. The reduction of GaAr<sup>\*</sup> with potassium instead of sodium to afford the ring compound K<sub>2</sub>Ar<sup>\*</sup>Ga<sub>4</sub>Ar<sup>\*</sup> demonstrated the critical importance of the size of the alkali metal to the stability of Na<sub>2</sub>Ar<sup>\*</sup>GaGaAr<sup>\*</sup>.<sup>27</sup> Furthermore, the experimental results described here have permitted a separation of the Ga–Ga bonding in the reduced species **13** and **14** into its component parts and show that it consists of a weak Ga–Ga interaction, similar to that in the neutral precursors **1** and **6**, plus a single bond generated by the two-electron reduction of the di-gallium unit.

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**Supporting Information Available:** X-ray data (CIF) for **2**, **3**, **8**, **9**, **10**, **12**, **15**, and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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