

Quasi-Isomeric Gallium Amides and Imides GaNR₂ and RGaNR (R = Organic Group): Reactions of the Digallene, Ar'GaGaAr' (Ar' = C_6H_3 -2,6-(C_6H_3 -2,6- Pr_2^i) with Unsaturated Nitrogen Compounds

Robert J. Wright, Marcin Brynda, James C. Fettinger, Audra R. Betzer, and Philip P. Power*

Contribution from the Department of Chemistry, One Shields Avenue, University of California, Davis, California 95616

Received May 10, 2006; E-mail: pppower@ucdavis.edu

Abstract: Reactions of the "digallene" Ar'GaGaAr'(1) (Ar' = C_6H_3 -2,6-(C_6H_3 -2,6-Pri₂)₂), which dissociates to green :GaAr' monomers in solution, with unsaturated N-N-bonded molecules are described. Treatment of solutions of :GaAr' with the bulky azide N₃Ar[#] (Ar[#] = C₆H₃-2,6-(C₆H₂-2,6-Me₂-4-Bu^t)₂), afforded the red imide Ar'GaNAr[#] (2). Addition of the azobenzenes, ArylNNAryl (Aryl = C_6H_4 -4-Me (p-tolyl), mesityl, and

 $C_6H_3-2,6-Et_2$) yielded the 1,2-Ga₂N₂ ring compound Ar'daN(p-tolyl)N(p-tolyl)daAr' (3) or the products MesN=

 $NC_{6}H_{2}-2,4-Me_{2}-6-Ga(Me)Ar'$ (4) and 2,6-Et₂C₆H₃N=NC₆H₃-2-Et-6-Ga(Et)Ar' (5). Reaction of GaAr' with N_2 CPh₂ yielded the 1,3-Ga₂N₂ ring compound Ar'Ga(μ : η ¹-N₂CPh₂)₂GaAr' (6), which is quasi-isomeric to 3. Calculations on simple model isomers showed that the Ga(I) amide $GaNR_2$ (R = Me) is much more stable than the isomeric Ga(III) imide RGaNR. This led to the synthesis of the first stable monomeric Ga(I) amide, GaN(SiMe₃)Ar" (8) (Ar" = C_6H_3 -2,6-(C_6H_2 -2,4,6-Me₃)₂ from the reaction of LiN(SiMe₃)Ar" (7) and "Gal". Compound 8 is also the first one-coordinate gallium species to be characterized in the solid state. The reaction of 8 with N₃Ar" afforded the amido-imide derivative Ar"NGaN(SiMe₃)Ar" (9), a gallium nitrogen analogue of an allyl anion. All compounds were spectroscopically and structurally characterized. In addition, DFT calculations were performed on model compounds of the amide, imide, and cyclic 1,2- and 1,3-species to better understand their bonding. The pairs of compounds 2 and 8 as well as 3 and 6 are rare examples of quasi-isomeric heavier main group element compounds.

Introduction

There is an extensive chemistry of species with bonding between heavier group 13 elements (Al-Tl) and nitrogen.¹⁻⁸ The simple derivatives can be classified according to the scheme

- (2)Precursor Synthesis, Development and Applications: VCH: Weinheim, Germany, 1996.
- (3) Jegier, J. A.; Gladfelter, W. L. Coord. Chem. Rev. 2000, 206-207, 631-650.
- (4) Cowley, A. H.; Jones, R. A. Angew. Chem. 1989, 101, 1235-1243.
 (5) Gardiner, M. G.; Raston, C. L. Coord. Chem. Rev. 1997, 166, 1-34.
 (6) Brothers, P. J.; Power, P. P. Adv. Organomet. Chem 1996, 39, 1-69.

- (7) Carmalt, C. J. Coord. Chem. Rev. 2001, 223, 217-264.
- (8) Lappert, M. F.; Sanger, A. R.; Srivastava, R. C.; Power, P. P. Metal and (b) Dappert, M. F., Sangel, A. K., Sirvastava, K. C., Fower, T. F. Metal and Metalloid Amides: Synthesis, Structure, and Physical and Chemical Properties; Ellis Harwood/Wiley: New York, 1980.
 (9) Timoshkin, A. Y. Coord. Chem. Rev. 2005, 249, 2094–2131.
 (10) Waggoner, K. M.; Power, P. P. J. Am. Chem. Soc. 1991, 113, 3385–3393.
- (11) Waggoner, K. M.; Hope, H.; Power, P. P. Angew. Chem., Int. Ed. Engl. 1988, 100, 1765–1766.

- Wehmschulte, R. J.; Power, P. P. Inorg. Chem. 1998, 37, 2106–2109.
 Wehmschulte, R. J.; Power, P. P. Inorg. Chem. 1998, 37, 6906–6911.
 Wehmschulte, R. J.; Power, P. P. J. Am. Chem. Soc. 1996, 118, 791–797.
- (15) Schulz, S.; Voigt, A.; Roesky, H. W.; Haeming, L.; Herbst-Irmer, R. Organometallics 1996, 15, 5252–5253.
- (16) Schulz, S.; Haeming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. Angew. Chem., Int. Ed. Engl. 1994, 33, 1969-1070.
- (17) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. Organometallics 1999, 18, 2037–2039.

below in which ligands are removed progressively to yield a simple metal nitride. The nitrides AlN, GaN, and InN have important electronic applications, and this is a major justification for the study of their imide, amide, or amine adduct precursors.²⁻⁴

$$\begin{array}{c} R_{3}MNR'_{3} \xrightarrow{-RR'} R_{2}MNR'_{2} \xrightarrow{-RR'} RMNR' \xrightarrow{-RR'} MN \\ amine adduct \quad amide \quad imide \quad nitride \end{array}$$

The amine adducts⁵ and amides⁶⁻⁸ have been widely studied. The imides have also received synthetic and theoretical attention, but they are usually found as strongly associated species $(\text{RMNR'})_n$ $(n \ge 4; \text{R or R'} = \text{alkyl, aryl, or H})$ that have cage structures.^{8,9} There are a few lower aggregate rings, (RM-NR') $_{3}^{10,11}$ or (RMNR') $_{2}^{12-18}$ that have three-coordinate metals where M-N multiple bonding is possible. The small number of dimeric imides (RMNR')2 currently known contain a symmetric 1,3-M₂N₂ core, which has been postulated to form by the head-to-tail dimerization of two RMNR' monomers.9 The related 1,2-M₂N₂ isomer has only been reported for boron.¹⁹

(19) Thiele, B.; Paetzold, P.; Englert, U. Chem. Ber. 1992, 125, 2681-2686.

⁽¹⁾ Downs, A. J., Ed. Chemistry of Aluminium, Gallium, Indium and Thallium; Blackie Academic & Professional: London, 1993. Jones, A. C., O'Brien, P., Eds. CVD of Compound Semiconductors:

⁽¹⁸⁾ Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. Inorg. Chem. 1996 35 271-27



Monomeric imides are of interest because they have formal group 13 element-nitrogen triple bonds. Such compounds had been known only for BN species,²⁰⁻²⁴ but in a preliminary report we showed that, with use of the bulky terphenyl substituents, the first heavier group 13 element monomeric imides Ar'MNAr# (M = In or Ga) could be synthesized by reaction of Ar'MMAr' $(Ar' = C_6H_3 - 2, 6 - (C_6H_3 - 2, 6 - Pr_2)_2)$ or $C_6H_3 - 2, 6(Xyl - 4 - Bu^t)_2$ with $N_3Ar^{\#} (Ar^{\#} = C_6H_3 - 2, 6 - (C_6H_2 - 2, 6 - Me_2 - 4 - Bu^{\dagger})_2).^{25}$ These compounds had short Ga-N and In-N bond lengths, but they had trans-bent structures that were indicative of weakened M-N bonding. The diminished M-N bond strength was supported by calculations on model compounds.^{25,26} Unexpectedly, these calculations also indicated that the monomeric and isomeric M(I) amides, MNH₂ were considerably (Al = 42.5 kcal·mol⁻¹; Ga = 45.1 kcal·mol⁻¹; In = 61.6 kcal·mol⁻¹) more stable than the imides.²⁶ However, to date only a few thallium(I) amides^{27,28} have been isolated and characterized by X-ray crystallography, while the parent hydrogen derivatives, MNH_2 (M = Al-In) were found to be stable only in the frozen matrices in which they were generated.^{29,30} We therefore wished to show that a stable monomeric low-valent group 13 element amide that is isomeric or quasi-isomeric (i.e. the core structures, but not the entire molecule, are isomeric) to the corresponding imide could be synthesized. We now describe the synthesis and characterization of the stable (mp = 181-183 °C) monomeric gallium(I) amide, GaN(SiMe₃)Ar" as well as its reaction with a bulky terphenyl azide to afford the monomeric amido-imide Ar"NGaN-(SiMe₃)Ar" which is a heavier group 13 element nitrogen analogue of an allyl anion. In addition, we describe the reaction of :GaAr' with a variety of unsaturated nitrogen species such as azides, azobenzenes, and a diazomethane compound to afford, inter alia, monomeric gallium imides, 1,3- and 1,2-Ga₂N₂ ring species and C-C bond activation products.

Experimental Section

General Procedure. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N₂ or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from molten Na/K alloy and degassed three times prior to use. H₂NAr^{'',31} "GaI",³² Ph₂CN₂,³³ and Ar'GaGaAr^{'34} were synthesized by literature methods. (*p*-tolyl)NN(*p*-tolyl), MesNNMes, and 2,6-Et₂C₆H₃NNC₆H₃-2,6-Et₂

- (20) Elter, G.; Neuhaus, M.; Meller, A.; Schmidt-Baese, D. J. Organomet. Chem. 1990, 381, 299–313.
- (21) Paetzold, P. Adv. Inorg. Chem. 1987, 31, 123-170.
- (22) Paetzold, P.; Von Plotho, C.; Schmid, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schaefer, W. Chem. Ber. 1984, 117, 1089– 1102.
- (23) Haase, M.; Klingebiel, U.; Boese, R.; Polk, M. *Chem. Ber.* 1986, *119*, 1117.
 (24) Luthin, W.; Elter, G.; Heine, A.; Stalke, D.; Sheldrick, G. M.; Meller, A. Z. Anorg. Allg. Chem. 1992, 608, 147.
- Z. Anorg. Allg. Chem. 1992, 608, 147.
 Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. J. Am. Chem. Soc. 2003, 125, 1694–1695.
- Am. Chem. Soc. 2005, 123, 1094–1095.
 (26) Himmel, H.-J.; Downs, A. J.; Green, J. C.; Greene, T. M. J. Chem. Soc., Datton. Trans. 2001, 535–545.
- Datton. Irans. 2001, 555–545.
 Wright, R. J.; Brynda, M.; Power, P. P. Inorg. Chem. 2005, 44, 3368–3370.
- (28) Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. Inorg. Chem. 2001, 40, 5083-5091.
- (29) Lanzisera, D. V.; Andrews, L. J. Phys. Chem. A **1997**, 101, 5082–5089.
- (30) Himmel, H.-J.; Downs, A. J.; Greene, T. M. J. Am. Chem. Soc. 2000, 122, 9793–9807.

were synthesized from the aniline and KMnO₄.³⁵ N₃Ar^{#25} was synthesized from LiAr[#] and TsN₃ according to the procedure for N₃Ar". ¹H and ¹³C NMR spectra were recorded on Varian 300 and 400 spectrometers and referenced to known standards. UV/vis data were recorded on a Hitachi-1200 spectrophotometer, and the melting points were recorded using a Meltemp apparatus and were not corrected.

Ar'GaNAr# (2). Ar'GaGaAr' (0.390 g, 0.418 mmol) was dissolved in hexane (60 mL) to give a deep-green solution. A solution of N3Ar# (0.366 g, 0.835 mmol) in hexane (30 mL) was added dropwise with stirring to yield a deep-red solution and red precipitate. The reaction mixture was stirred for 4 h and then concentrated to ca. 15 mL. The mother liquor was removed from the precipitated product 2 and discarded. Yield: 0.524 g, 68%; mp 215-216 °C. Overnight storage at ca. -15 °C of a saturated hexane solution of 2 afforded X-ray-quality crystals of **2**. ¹H NMR (400 MHz, C₆D₆, 25 °C): $\delta = 0.97$ (d, 12H, o-CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.4$ Hz), 0.98 (d, 12H, o-CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.4$ Hz), 1.42 (s, 18H, p-C(CH₃)₃, 2.03 (s, 12H, o-CH₃) 2.54 (sept, 4H, $CH(CH_3)_2$, ${}^{3}J_{HH} = 6.4$ Hz), 6.67 (t, 1H, *p*-central Ph of Ar', ${}^{3}J_{HH} = 7.2$ Hz), 6.75 (d, 2H, *m*-central Ph of Ar[#], ${}^{3}J_{HH} = 7.6$ Hz), 7.03 (m, 3H, Ar-H), 7.12 (s, 4H, *m*-(4-Bu^t-Xyl)), 7.15 (d, 4H, *m*-Dipp, ${}^{3}J_{HH} = 7.6$ Hz), 7.25 (t, 2H, *p*-Dipp, ${}^{3}J_{\text{HH}} = 7.6$ Hz). ${}^{13}C{}^{1}H}NMR$ (100.6 MHz, C₆D₆, 25 ° C): δ 21.33 (o-CH₃), 24.85 (o-CH(CH₃)₂), 25.44 (o-CH-(CH₃)₂), 31.29 (o-CH(CH₃)₂), 32.05 (p-C(CH₃)₃), 34.57 (p-C(CH₃)₃), 117.42 (p-central Ph of Ar'), 123.91 (m-Dipp), 124.87 (m-(4-But-Xyl)), 128.82, 129.94 (m-Ph unassigned), 130.40 (p-Ph unassigned), 134.54, 136.57 (o-(4-But-Xyl)), 140.52, 140.75, 145.44, 147.06 (o-central Ph of Ar'), 147.60, 148.17, 150.52 (p-(4-But-Xyl)), 152.76 (i-central Ph of Ar'). UV/vis (hexanes) λ_{max} nm (ϵ , mol·L⁻¹·cm⁻¹): 303 (26500), 366 (3900).

Ar'GaN(p-tolyl)N(p-tolyl)GaAr' (3). Ar'GaGaAr' (0.233 g, 0.25 mmol) was dissolved with stirring in toluene (25 mL). To this solution was added 1,2-di-p-tolyldiazene (0.052 g, 0.250 mmol) as a solution in toluene (20 mL). Over the 10-min addition period the resulting solution developed a deep blue-green color. The solution was allowed to stir for 6 h and then was concentrated to ca. 10 mL under reduced pressure. Storage at ca. -30 °C overnight afforded the product 3 as large, blue-green X-ray-quality crystals. Yield: 0.148 g, 52%; mp = 275 °C (turned orange). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.46 (d, 6H, CH(*CH*₃)₂) ${}^{3}J_{\text{HH}} = 6.9$ Hz, 0.56 (d, 6H, CH(*CH*₃)₂) ${}^{3}J_{\text{HH}} = 6.9$ Hz, 0.75 (d, 6H, CH(*CH*₃)₂, ${}^{3}J_{\text{HH}} = 6.9$ Hz), 1.12 (d, 12H, CH(*CH*₃)₂, ${}^{3}J_{\text{HH}}$ = 6.9 Hz), 1.22 (d, 6H, CH(CH_3)₂, ${}^{3}J_{HH}$ = 6.9 Hz), 1.29 (d, 12H, CH- $(CH_3)_2$, ${}^3J_{HH} = 6.9$ Hz), 2.03 (3H, 4-MeC₆H₄), 2.10 (3H, 4-MeC₆H₄), 2.47 (sept, 2H, CH(CH₃)₂, ${}^{3}J_{HH} = 6.9$ Hz), 2.95 (sept, 2H, CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}$), 3.11 (sept, 2H, CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}$), 3.44 (sept, 2H, CH(CH₃)₂, ${}^{3}J_{HH} = 6.9$ Hz), 6.21 (d, 4H, *m*-Dipp, ${}^{3}J_{HH} = 8.1$ Hz), 6.40 (d, 2H, ${}^{3}J_{HH} = 8.1$ Hz) 6.63 (d, 4H, *m*-Dipp, ${}^{3}J_{HH} = 8.1$ Hz), 6.83 (d, 2H, ${}^{3}J_{\text{HH}} = 8.1$ Hz), 6.96–7.21 (m, 10H) 7.42 (d, 2H, tolyl), 8.04 (d, 2H, tolyl). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$ (75.45 MHz, C₆D₆, 25 °C): δ 20.74 (4-MeC₆H₄), 21.27 (4-MeC₆H₄), 22.80 (CH(CH₃)₂), 23.34 (CH(CH₃)₂), 23.87 (CH(CH₃)₂), 24.15 (CH(CH₃)₂), 24.83 (CH(CH₃)₂), 25.36 (CH-(CH₃)₂), 25.56 (CH(CH₃)₂), 26.02 (CH(CH₃)₂), 28.49 (CH(CH₃)₂), 30.69 (CH(CH₃)₂), 30.99 (CH(CH₃)₂), 31.64 (CH(CH₃)₂), 115.24 (m-Dipp), 117.56 (m-Dipp), 120.60-154.65 (multiple aromatic carbon signals). UV/vis (hexanes) λ_{max} nm (ϵ mol⁻¹·L·cm⁻¹): 405 (1900), 601 (240).

MesN=NC₆H₂-2,4-Me₂-6-Ga(Me)Ar' (4). Ar'GaGaAr' (0.233 g, 0.25 mmol) was dissolved in toluene (25 mL) with stirring to give a green solution. To this solution was added 1,2-dimesityldiazene (0.133

- (32) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. Polyhedron 1990, 9, 2763; Baker, R. J.; Jones, C. Dalton Trans. 2005, 1341–1348.
- (33) Kumar, S.; Murray, R. W. J. Am. Chem. Soc. 1984, 106, 1040–1045.
 (34) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. J. Am. Chem.
- Soc. 2003, 125, 2667–2679.
 (35) Barman, D. C.; Saikia, P.; Prajapati, D.; Sandhu, J. S. Synth. Commun. 2002, 32, 3407–3412.

⁽³¹⁾ Wright, R. J.; Steiner, J.; Beaini, S.; Power, P. P. Inorg. Chim. Acta 2006, 359, 1939–1946.

g, 0.50 mmol) in toluene (20 mL). The color of the solution became orange. The solvents were removed under reduced pressure, and the residue was extracted with hexane (20 mL). Overnight storage of the solution at ca. -30 °C afforded orange, X-ray-quality crystals of the product 4. Yield: 0.256 g, 70%; mp = 183-185 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -0.75 (3H, Ga-CH₃), 1.11 (d, 24H, CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}$, 1.89 (6H, *o*-*CH*₃), 2.02 (3H, *p*-*CH*₃), 2.10 (3H, *o*-*CH*₃), 2.53 (3H, *o*-*CH*₃) 3.08 (sept, 4H, *CH*(CH₃)₂, ${}^{3}J_{HH} = 6.9$ Hz), 6.58 (s, 2H, m-Mes), 6.61 (s, 1H, m-Mes), 6.78 (s, 1H m-Mes) 7.01-7.21 (m, 9H, m-C₆H₃, p-C₆H₃, m-Dipp, p-Dipp). ¹³C{¹H}NMR (C₆D₆, 75.46 MHz, 25 °C): δ -5.39 (Ga-Me), 17.79 (p-CH₃), 18.66 (CH₃), 20.53 (CH₃), 21.81 (CH₃), 26.01 (CH(CH₃)₂), 30.52 (CH(CH₃)₂), 122.42 (m-Dipp), 126.69, 129.82, 130.31, 130.46, 131.83, 133.66, 137.45, 140.133, 143.35, 143.88, 146.43, 148.76, 149.57 (o-Dipp), 149.94, 153.51. UV/ vis (hexanes): decreasing absorbance at longer wavelengths which diminishes to zero at 510 nm.

2,6-Et₂C₆H₃N⁺=NC₆H₃-2-Et-6-Ga(Et)Ar' (5) was synthesized in a manner similar to that for 4. Yield: 67%; mp = 195–197 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ –0.052 (q, 2H, Ga-*CH*₂CH₃, ³*J*_{HH} = 7.5 Hz), 0.73 (t, 3H, Ga-CH₂CH₃, ³*J*_{HH} = 7.5 Hz), 0.97 (t, 6H, *o*-CH₂CH₃, ³*J*_{HH} = 7.5 Hz), 1.04 (d, 12H, *o*-CH(*CH*₃)₂, ³*J*_{HH} = 6.9 Hz), 1.11 (d, 12H, *o*-CH(*CH*₃)₂, ³*J*_{HH} = 6.9 Hz), 2.24 (q, 2H, *o*-*CH*₂CH₃, ³*J*_{HH} = 7.5 Hz), 2.77 (q, 4H, *o*-*CH*₂CH₃, ³*J*_{HH} = 7.5 Hz), 2.99 (sept, 4H, *CH*(CH₃)₂, ³*J*_{HH} = 6.9 Hz), 6.96–7.16 (m, 15H, arene-H). ¹³C{¹H}NMR (C₆D₆, 75.46 MHz, 25 °C): δ 5.24 (Ga-*CH*₂CH₃), 11.31 (Ga-CH₂*CH*₃)), 13.84 (*o*-*CH*₂*CH*₃), 16.03 (*o*-*CH*₂CH₃), 23.06 (CH(*CH*₃)₂), 23.92 (*o*-CH₂*CH*₃), 24.45 (*o*-*CH*₂CH₃), 26.18 (CH(*CH*₃)₂), 30.77 (*CH*(CH₃)₂), 122.84 (*m*-Dipp), 126.19, 126.65, 127.26, 128.57, 130.66, 133.54, 133.86, 137.38, 143.69, 146.06, 146.42, 146.63, 149.41, 149.65, 152.09, 154.38. UV/ vis (hexanes): decreasing absorbance at longer wavelengths which UV diminishes to zero at 485 nm.

(**Ar'GaNNCPh**₂)₂ (6). Ar'GaGaAr' (0.300 g, 0.32 mmol) was dissolved in PhMe (30 mL). To this solution was added Ph₂CN₂ (0.124 g, 0.64 mmol) in PhMe (20 mL). Upon addition the deep-green color faded to pale-orange. The reaction was stirred overnight. Removal of the solvent under reduced pressure, extraction with hexanes (20 mL), and overnight storage at ca. -30 °C afforded orange, X-ray-quality crystals of **6**. Yield: 0.154 g, 36.3%; mp = 210-212 °C. ¹H NMR (300 MHz, C₆D₆, 60 °C): δ 0.90 (broad, 24H, *o*-CH(*CH*₃)₂), 0.97 (broad, 24H, *o*-CH(*CH*₃)₂), 2.89 (broad, 8H, *CH*(CH₃)₂), 6.740–7.26 (mult, 38H, arene-H). ¹³C{¹H}NMR (75.46 MHz, C₆D₆, 50 °C): δ 23.00 (CH(*CH*₃)₂), 23.85 (CH(*CH*₃)₂), 26.07 (CH(*CH*₃)₂), 30.53 (*CH*(CH₃)₂), 31.94 (*CH*(CH₃)₂), 124.21 (*m*-Dipp), 127.36, 127.44, 128.53, 128.80, 129.76, 130.15, 131.96, 132.05, 140.72, 142, 85, 146.17, 147.17, 147.53, 152.78.

GaN(SiMe₃)Ar" (8). A rapidly stirred slurry of LiN(SiMe₃)Ar" (1.22 g, 3.00 mmol) in toluene (60 mL) was added dropwise over 1.5 h to a toluene (20 mL) slurry of "Gal" (0.589 g, 3.00 mmol) with cooling to ca. -78 °C. The mixture was allowed to warm to room temperature over 12 h. The resulting pale-yellow solution was decanted from the precipitates (LiI and some Ga) and filtered through a Celite-padded frit. The solution was concentrated to ca. 30 mL and stored overnight at ca. -20 °C, affording 0.303 g (0.644 mmol) of pale-yellow X-ray-quality crystals of **8**. Yield: 21.5%; mp = 181–183 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): $\delta = -0.110$ (s, 9H, Si(CH₃)), 2.150 (s, 6H, *p*-CH₃), 2.243 (s, 12H, *o*-CH₃), 6.828 (t, 1H, *p*-Ph), ³*J*_{HH} = 7.5 Hz, 6.871 (s, 4H, *m*-Mes), 6.974 (d, 2H, *m*-Ph), ³*J*_{HH} = 7.5 Hz. ¹³C NMR (75.46 MHz, C₆D₆, 25 °C): $\delta = 4.031$ (Si(CH₃)₃), 21.10 (*p*-CH₃) 21.59 (*o*-CH₃), 119.19 (*m*-Mes), 129.84 (*m*-Ph) 130.79 (*p*-Ph), 133.86, 136.98, 137.32, 137.97, 139.38, 150.12.

 $Ar''NGaN(SiMe_3)Ar''$ (9). GaN(SiMe_3)Ar'' (0.300 g, 0.638 mmol) was dissolved in toluene (40 mL) to give a nearly colorless solution. To this solution a toluene solution (20 mL) of N₃Ar'' (0.226 g, 0.638 mmol) was added dropwise over 10 min. The resulting reddish purple solution was stirred for 2 h and then concentrated under reduced

pressure to ca. 25 mL. Overnight storage at ca. -15 °C afforded 0.358 g of X-ray quality crystals. Yield: 70.5%; mp = 165–167 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): $\delta = -0.32$ (s, 9H, Si(CH₃)), 1.91 (s, 12H, *o*-CH₃), 2.21 (s, 6H, *p*-CH₃), 2.24 (s, 6H, *p*-CH₃), 2.28 (s, 12H, *o*-CH₃), 6.64–6.80 (m, 4H, *p*-Ph, *p*-Ph, *m*-Ph), 6.87 (s, 4H, *m*-Mes), 6.92 (s, 4H, *m*-Mes), 7.00 (d, 2H, *m*-Ph, ³J_{HH} = 7.5 Hz); ¹³C{¹H}NMR (75.46 MHz, C₆D₆, 25 °C): δ 2.463 (Si(CH₃)₃), 21.30 (*p*-CH₃), 21.33 (*p*-CH₃), 21.50 (*o*-CH₃), 21.52 (*o*-CH₃), 115.02 (*m*-Mes), 121.41 (*m*-Mes), 128.66, 129.03, 129.09, 131.07, 131.11, 131.95, 133.25, 133.72, 134.89, 137.26, 140.16, 140.61, 140.80, 146.36, 152.47. UV-vis (hexanes) λ_{max} nm (ϵ mol⁻¹·L·cm⁻¹): 250 (7700), 294 (8000), and 522 (450).

Computational Methods

The calculations were performed using DFT theory with B3LYP functional, using the GAUSSIAN 03 package,³⁶ and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program.³⁷ The model compounds used were based on the frozen geometries extracted from the corresponding crystal structures, where some of the bulky aryl groups were replaced with phenyl rings. The geometries of the dimeric imide models were optimized at the B3LYP/6-31g* level. Calculations were also performed on the model complexes RGaNR and GaNR₂ (R = H and Me) at the B3LYP/6-31g* level. The Wiberg bond orders were calculated for the geometries optimized at the B3LYP/6-31g* level, using AOMIX program.³⁸

X-ray Crystallography

Crystals of 2, 3, 4, 5, 6, 8, and 9 were removed from a Schlenk tube under a stream of argon and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in a lowtemperature stream.³⁹ The data for 2, 3, 4, 5, 6, and 8 were recorded near 90 K on a Bruker SMART 1000 (Mo Ka radiation and a CCD area detector), while 9 was collected on a Bruker APEX (Mo Ka radiation and a CCD area detector). For compounds 2, 3, 4, 5, 6, 8 the SHELX version 6.1 program package was used for the structure solutions and refinements. Absorption corrections were applied using the SADABS program.⁴⁰ Crystals of 9 were determined to be twinned, and an alternative procedure (see Supporting Information) was used to "de-twin" the data and afford a solution. The crystal structures were solved by direct methods and refined by full-matrix leastsquares procedures. All non-H atoms were refined anisotropically. H atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. A summary of the data collection parameters for 2-6, 8, and 9 is provided in Table 1.

Results

The "digallene" Ar'GaGaAr', which has been shown to have a weak Ga–Ga bond, dissociates to :GaAr' monomers in hydrocarbon solution.^{34,41} Such solutions have an intense green color due to an allowed n–p transition. As a result, reactions of :GaAr' that involve the gallium lone pair are often accompanied by dramatic color changes.²⁵ Treatment of :GaAr' with the azide N₃Ar[#] (eq 1)

(39) Hope, H. Prog. Inorg. Chem. 1995, 34, 1.

⁽³⁶⁾ Frisch, M. J.; et al. *Gaussian 03*, Revision A.01; Gaussian, Inc.: Pittsburgh, PA, 2003. A full reference is given in the Supporting Information file.
(37) Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss

⁽³⁷⁾ Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. MOLEKEL 4.3; Swiss Center for Scientific Computing: Manno, Switzerland, 2000–2002.

⁽³⁸⁾ Gorelsky, S. I. AOMix program, rev. 5.44; http://www.obbligato.com/ software/aomix/.

⁽⁴⁰⁾ SADABS. An empirical absorption correction program, part of the SAINT-Plus NT version 5.0 package; Bruker AXS: Madison, WI, 1998.

Table 1.	Selected X-ra	Crystallographic	Parameters of 2	2-6, 8, and 9
----------	---------------	------------------	-----------------	---------------

cmpd	2	3	4	5
formula	C63H81NGa (C6H12)05	C88H104Ga2N2	C48H60GaN2	C50H63GaN2
fw	922.01	1329.17	734.70	761.74
color, habit	red block	green block	orange block	orange block
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_{1}/n$	C2/c	$P\overline{1}$	$P2_1/c$
a. Å	11.7036(6)	25.919(6)	11.347(3)	12.8419(14)
b. Å	24.8171(12)	14.966(3)	12.766(4)	10.8132(12)
<i>c</i> . Å	18.4566(9)	22.663(5)	16.505(4)	31.065(4)
a, deg	90	90	72,430(4)	90
β deg	91 4380(10)	123 089(3)	70 736(4)	90 861(4)
γ deg	90	90	66 315(4)	90
$V Å^3$	5359.0(5)	7365(3)	2026 9(10)	4313 3(8)
7	1	1505(5)	2020.9(10)	4515.5(0)
cryst dim mm	-7 0 47 × 0 22 × 0 16	-7 0.40 × 0.39 × 0.26	$\frac{1}{0}$ 32 × 0.23 × 0.22	$\frac{1}{0.34} \times 0.31 \times 0.22$
$d \to \alpha \mathrm{cm}^{-3}$	1 1/3	1 100	1 204	1 173
$u_{calc}, g cm$	0.552	0.778	0.713	0.673
μ min po of reflue	41703	32652	20483	40369
no. of obsd rofins	7660	52052 6470	20483	9055
D1 abad raflma	0.0517	0470	0.0545	0.0410
KI Obsd Termis	0.0317	0.0309	0.0343	0.0410
wk2, all	0.0755	0.1065	0.1315	0.0946
cmpd	6	8		9
cmpd formula	6 C95H115Ga2N4	8 C ₂₇ H ₃₄ GaN	JSi	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5}
cmpd formula fw	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35	8 C ₂₇ H ₃₄ GaN 470.36	ISi	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5} 1918.09
cmpd formula fw color, habit	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block	8 C ₂₇ H ₃₄ GaN 470.36 pale yellow	NSi v block	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5} 1918.09 red plate
cmpd formula fw color, habit cryst syst	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block monoclinic	8 C ₂₇ H ₃₄ GaN 470.36 pale yellow triclinic	lSi / block	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5} 1918.09 red plate monoclinic
cmpd formula fw color, habit cryst syst space group	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block monoclinic P2 ₁ /n	$\begin{array}{c} & & & \\ & C_{27}H_{34}GaN \\ & 470.36 \\ & pale yellow \\ & triclinic \\ & P\bar{1} \end{array}$	lSi / block	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5} 1918.09 red plate monoclinic <i>P</i> 2 ₁ / <i>n</i>
cmpd formula fw color, habit cryst syst space group a, Å	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block monoclinic P2 ₁ /n 14.4015(10)	8 C ₂₇ H ₃₄ GaN 470.36 pale yellow triclinic <i>P</i> 1 11.0720(7)	lSi / block	9 $[C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5}$ 1918.09 red plate monoclinic $P2_1/n$ 20.503(4)
cmpd formula fw color, habit cryst syst space group <i>a</i> , Å <i>b</i> , Å	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block monoclinic P2 ₁ /n 14.4015(10) 26.1551(19)	8 C ₂₇ H ₃₄ GaN 470.36 pale yellow triclinic <i>P</i> 1 11.0720(7) 11.6811(8)	lSi / block	9 $[C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5}$ 1918.09 red plate monoclinic $P2_1/n$ 20.503(4) 18.564(4)
cmpd formula fw color, habit cryst syst space group <i>a</i> , Å <i>b</i> , Å <i>c</i> , Å	6 C ₉₅ H ₁₁₅ Ga ₂ N ₄ 1452.35 orange block monoclinic <i>P</i> 2 ₁ / <i>n</i> 14.4015(10) 26.1551(19) 21.8374(16) Å	8 C ₂₇ H ₃₄ GaN 470.36 pale yellow triclinic <i>P</i> 1 11.0720(7) 11.6811(8) 11.9741(8)	NSi 7 block	9 [C ₅₁ H ₅₉ N ₂ SiGa] ₂ [C ₇ H ₈] _{3.5} 1918.09 red plate monoclinic <i>P</i> 2 ₁ / <i>n</i> 20.503(4) 18.564(4) 28.657(6)
cmpd formula fw color, habit cryst syst space group <i>a</i> , Å <i>b</i> , Å <i>c</i> , Å α, deg	$\begin{array}{c} 6 \\ \\ C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ \AA} \\ 90 \end{array}$	$\begin{array}{c} & & & & \\ & & C_{27}H_{34}GaN \\ & & 470.36 \\ & & pale yellow \\ & triclinic \\ P\bar{1} \\ & & 11.0720(7) \\ & & 11.6811(8) \\ & & 11.9741(8) \\ & & 118.6700(1) \end{array}$	NSi / block 0)	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \end{array}$
cmpd formula fw color, habit cryst syst space group <i>a</i> , Å <i>b</i> , Å <i>c</i> , Å <i>c</i> , Å <i>a</i> , deg <i>b</i> , deg <i>b</i> , deg	$\frac{6}{C_{95}H_{115}Ga_2N_4}\\ 1452.35\\ orange block\\ monoclinic\\ P2_1/n\\ 14.4015(10)\\ 26.1551(19)\\ 21.8374(16) Å\\ 90\\ 98.2590(10)^\circ.$	$\frac{8}{C_{27}H_{34}GaN}$ 470.36 pale yellow triclinic <i>P</i> 1 11.0720(7) 11.6811(8) 11.9741(8) 118.6700(1 114.1440(1)	NSi v block 0) 0)	9 $[C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5}$ 1918.09 red plate monoclinic $P2_1/n$ 20.503(4) 18.564(4) 28.657(6) 90 97.543(3)
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å α, deg β, deg ν, deg	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \end{array}$	$\frac{8}{C_{27}H_{34}GaN}$ 470.36 pale yellow triclinic $P\bar{1}$ 11.0720(7) 11.6811(8) 11.9741(8) 118.6700(1) 114.1440(1) 90.1510(10)	0) 0)	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg $V, Å^3$	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^{\circ}. \\ 90 \\ 8140.2(10) \text{ Å}^3 \end{array}$	$\begin{array}{c} 8\\ \hline C_{27}H_{34}GaN\\ 470.36\\ pale yellow\\ triclinic\\ P\bar{1}\\ 11.0720(7)\\ 11.6811(8)\\ 11.9741(8)\\ 118.6700(1\\ 114.1440(1\\ 90.1510(10\\ 1201.05(14).05(14\\ 1201.05(14).05$	USi / block 0) 0) 0) 0)	$\begin{array}{c} \textbf{9} \\ \hline [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg $V, Å^3$ Z	$\begin{array}{c} 6 \\ \\ C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \end{array}$	$\begin{array}{c} 8\\ \hline C_{27}H_{34}GaN\\ 470.36\\ pale yellow triclinic\\ P\bar{1}\\ 11.0720(7)\\ 11.6811(8)\\ 11.9741(8)\\ 118.6700(1\\ 114.1440(1\\ 90.1510(10\\ 1201.05(14\\ 2 \end{array})$	USi 7 block 0) 0) 0)	$\begin{array}{c} \textbf{9} \\ \hline [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg $V, Å^3$ Z cryst dim, mm	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^{\circ}. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \end{array}$	$\begin{array}{c} 8\\ \hline C_{27}H_{34}GaN\\ 470.36\\ pale yellow\\ triclinic\\ P\bar{1}\\ 11.0720(7)\\ 11.6811(8)\\ 11.9741(8)\\ 118.6700(1\\ 114.1440(1\\ 90.1510(10\\ 1201.05(14\\ 2\\ 0.38 \times 0.22)\end{array}$	NSi v block 0) 0) 0) 0) 1) 2 × 0.19	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg $V, Å^3$ Z cryst dim, mm d_{calca} g cm ⁻³	$\begin{array}{c} 6 \\ C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \end{array}$	$\begin{array}{c} & & & & & \\ & & & C_{27}H_{34}GaN \\ & & & 470.36 \\ & & & pale yellow \\ & & triclinic \\ & & P\bar{1} \\ & & & 11.0720(7) \\ & & & 11.6811(8) \\ & & & 11.9741(8) \\ & & & 11.9741(8) \\ & & & 118.6700(1 \\ & & & 114.1440(1 \\ & & 90.1510(10 \\ & & 1201.05(14 \\ & & 2 \\ & & 0.38 \times 0.22 \\ & & 1.301 \end{array}$	NSi v block 0) 0) 0) 1) 1) 2 × 0.19	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P_{2_1/n} \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å α, deg β, deg γ, deg γ, deg $V, Å^3$ Z cryst dim, mm $d_{calc}, g cm^{-3}$ μmm^{-1}	$\begin{array}{c} 6 \\ \\ C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \ \text{\AA} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \\ 8140.2(10) \ \text{\AA}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \\ 0.708 \end{array}$	$\begin{array}{c} & & & & & \\ & & & C_{27}H_{34}GaN \\ & & & 470.36 \\ & & & pale yellow \\ & & triclinic \\ & & P\bar{1} \\ & & & 11.0720(7) \\ & & & 11.6811(8) \\ & & & 11.9741(8) \\ & & & 11.86700(1) \\ & & & 118.6700(1) \\ & & & 114.1440(1) \\ & & & 90.1510(10) \\ & & & 1201.05(14) \\ & & & & 2 \\ & & & & 0.38 \times 0.22 \\ & & & & 1.301 \\ & & & & 1.209 \end{array}$	NSi v block (0) (0) (0) (0) (0) (0) (0) (0)	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P_{21/n} \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \\ 0.571 \\ \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg $V, Å^3$ Z cryst dim, mm $d_{calc}, g cm^{-3}$ μmm^{-1} no of reflns	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \ \text{\AA} \\ 90 \\ 98.2590(10)^{\circ}. \\ 90 \\ 8140.2(10) \ \text{\AA}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \\ 0.708 \\ 69361 \\ \end{array}$	$\begin{array}{c} & & & & \\ & & C_{27}H_{34}GaN \\ & & 470.36 \\ & & pale yellow \\ & triclinic \\ P\bar{1} \\ & & 11.0720(7) \\ & 11.6811(8) \\ & 11.9741(8) \\ & & 118.6700(1) \\ & & 114.1440(1) \\ & & 90.1510(10) \\ & & 1201.05(14) \\ & & 2 \\ & & 0.38 \times 0.22 \\ & & 1.301 \\ & & 1.209 \\ & & 8541 \end{array}$	NSi v block (0) (0) (0) (0) (0) (0) (0) (0)	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \\ 0.571 \\ 18052 \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg γ, deg $\nu, Å^3$ Z cryst dim, mm $d_{calc}, g cm^{-3}$ μmm^{-1} no. of reflns no. of reflns	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^{\circ}. \\ 90 \\ 98.2590(10)^{\circ}. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \\ 0.708 \\ 69361 \\ 18706 \end{array}$	$\begin{array}{c} & & & & \\ & & C_{27}H_{34}GaN \\ & & 470.36 \\ & & pale yellow \\ & triclinic \\ & P\bar{1} \\ & & 11.0720(7) \\ & & 11.6811(8) \\ & & 11.9741(8) \\ & & 118.6700(1 \\ & & 114.1440(1 \\ & & 90.1510(10 \\ & & 1201.05(14 \\ & & 2 \\ & & 0.38 \times 0.22 \\ & & 1.301 \\ & & 1.209 \\ & & 8541 \\ & & 4938 \end{array}$	NSi v block 0) 0) 0) 1) 2 × 0.19	$\begin{array}{c} \textbf{9} \\ \hline [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P_{2_1/n} \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \\ 0.571 \\ 18052 \\ 18052 \\ \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg γ, deg $V, Å^3$ Z cryst dim, mm $d_{calc}, g cm^{-3}$ μmm^{-1} no. of reflns R l obsd reflns	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \\ 0.708 \\ 69361 \\ 18706 \\ 0 0472 \end{array}$	$\begin{array}{c} & & & & \\ & & C_{27}H_{34}GaN \\ & & 470.36 \\ & & pale yellow \\ & & triclinic \\ & & P\bar{1} \\ & & 11.0720(7) \\ & & 11.6811(8) \\ & & 11.9741(8) \\ & & 118.6700(1 \\ & & 114.1440(1 \\ & & 90.1510(10 \\ & & 1201.05(14 \\ & & 2 \\ & & 0.38 \times 0.22 \\ & & 1.301 \\ & & 1.209 \\ & & 8541 \\ & & 4938 \\ & & 0.0360 \end{array}$	NSi v block (0) (0) (0) (0) (0) (0) (0) (0) (0) (0)	$\begin{array}{c} \textbf{9} \\ \hline [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P_{2_1/n} \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \\ 0.571 \\ 18052 \\ 18052 \\ 18052 \\ 0.0846 \\ \end{array}$
cmpd formula fw color, habit cryst syst space group a, Å b, Å c, Å a, deg β, deg γ, deg $V, Å^3$ Z cryst dim, mm $d_{calc}, g cm^{-3}$ μmm^{-1} no. of reflns no. of obsd reflns R1 obsd reflns wR2 all	$\begin{array}{c} 6 \\ \hline C_{95}H_{115}Ga_2N_4 \\ 1452.35 \\ \text{orange block} \\ \text{monoclinic} \\ P2_1/n \\ 14.4015(10) \\ 26.1551(19) \\ 21.8374(16) \text{ Å} \\ 90 \\ 98.2590(10)^\circ. \\ 90 \\ 8140.2(10) \text{ Å}^3 \\ 4 \\ 0.30 \times 0.28 \times 0.27 \\ 1.185 \\ 0.708 \\ 69361 \\ 18706 \\ 0.0472 \\ 0 1282 \end{array}$	$\begin{array}{c} & & & \\ & & C_{27}H_{34}GaN \\ & & 470.36 \\ & & pale yellow \\ & & triclinic \\ & & P\bar{1} \\ & & 11.0720(7) \\ & & 11.6811(8) \\ & & 11.9741(8) \\ & & 118.6700(1) \\ & & 114.1440(1) \\ & & 90.1510(10) \\ & & 1201.05(14) \\ & & 2 \\ & & 0.38 \times 0.22 \\ & & 1.301 \\ & & 1.209 \\ & & 8541 \\ & & 4938 \\ & & 0.0360 \\ & & 0.1079 \end{array}$	NSi v block 0) 0) 0) 0) 1) 2 × 0.19	$\begin{array}{c} \textbf{9} \\ [C_{51}H_{59}N_2SiGa]_2[C_7H_8]_{3.5} \\ 1918.09 \\ \text{red plate} \\ \text{monoclinic} \\ P2_1/n \\ 20.503(4) \\ 18.564(4) \\ 28.657(6) \\ 90 \\ 97.543(3) \\ 90 \\ 10813(4) \\ 4 \\ 0.44 \times 0.25 \times 0.09 \\ 1.178 \\ 0.571 \\ 18052 \\ 18052 \\ 18052 \\ 0.0846 \\ 0.1127 \end{array}$

$$: \operatorname{GaAr}' + \operatorname{N_3Ar}^{\#} \xrightarrow{25 \, ^{\circ}\mathrm{C}, \, \operatorname{PhMe}} \operatorname{Ar}' \operatorname{GaNAr}^{\#} + \operatorname{N_2} \qquad (1)$$

$$1 \qquad \qquad 2$$

affords an immediate color change from green to deep red with formation of the imide Ar[#]NGaAr' (2) in essentially quantitative yield. The Ar[#] substituent was chosen for the azide in order to facilitate crystallization. The imide structure is shown in Figure 1 and features the shortest Ga–N bond distance (1.701(3) Å) in a stable compound. The C(ipso)–Ga–N–C(ipso) array is nearly planar but deviates from linearity with interligand angles of 148.2(2)° at gallium and 141.7(3)° at nitrogen.

Reaction of a solution of the GaAr' with the diazene (p-tolyl)N=N(p-tolyl) afforded the ring compound **3** shown in eq 2

2:GaAr' + (p-tolyl)N=N(p-tolyl)
$$\xrightarrow{25 \circ C, PhMe}$$
 $(p-tolyl)N-N(p-tolyl)$
Ar'Ga-GaAr' (2)

The product **3** was isolated as blue-green crystals in good yield. It has a four-membered Ga_2N_2 ring structure (Figure 2). The Ga–Ga, Ga–N, and N–N bond lengths 2.4964(8), 1.909(2), and 1.460(4) Å, respectively, are consistent with those of single bonds. The trapezoidal Ga_2N_2 core is planar with

internal ring angles of 74.19(6) and 105.64(6)°. The galliums are planar coordinated, but the nitrogens have a noticeably pyramidal coordination ($\Sigma \circ N = 347.1(2)$), and there is a C(31)-N(1)-N(1A)-C(31A) torsion angle of 77.5°.

In sharp contrast to eq 2 the reaction of :GaAr' with diazenes that carry ortho-substituted aryl groups afforded the insertion products shown in eqs 3 and 4.



J. AM. CHEM. SOC. = VOL. 128, NO. 38, 2006 12501



Figure 1. Thermal ellipsoid (30%) drawing of **2.** Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-N(1) = 1.701(3); Ga(1)-C(1) = 1.940(3); N(1)-C(31) = 1.377(5). N(1)-Ga(1)-C(1) = 148.2(2); Ga(1)-N(1)-C(31) = 141.7(3); C(1)-Ga(1)-N(1)-C(31) = 177.7(4).



Figure 2. Thermal ellipsoid (30%) drawing of **3.** Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-Ga(1A) = 2.4964(8); N(1)-N(1A) = 1.460(4); Ga(1)-N(1) = 1.909(2); N(1)-C(31) = 1.405(3). N(1)-Ga(1)-Ga(1A) = 74.19(6); Ga(1)-N(1)-N(1A) = 105.64(6); C(1)-Ga(1)-Ga(1A) = 166.61(7); C(31)-N(1)-N(1A) = 115.24(18); C(6)-C(1)-C(2) = 119.0(2); C(6)-C(1)-Ga(1) = 126.67(11).

In these two cases the N–N double bond remains intact, and there is insertion of the gallium(I) center into the sp²–sp³ C–C bond between the aryl ring and the ortho substituent. Thus, the gallium becomes bound to two aryls and an alkyl carbon and is also complexed by a nitrogen (Ga–N = ca. 2.21 Å) from the diazene (Figures 3 and 4). The N–N bond lengths (1.266(4) Å) are consistent with the retention of the N–N double bond.

The treatment of solutions of :GaAr' with N_2CPh_2 (eq 5) was studied with the object of preparing a galla-alkene species.



Figure 3. Thermal ellipsoid (30%) drawing of 4. Hydrogen atoms and isopropyl groups on 2,6-diisopropylphenyl groups are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-C(38) = 1.968(4); Ga(1)-C(1) = 1.990(4); Ga(1)-C(48) = 2.013(4); Ga(1)-C(1) = 1.990(4); Ga(1)-C(48) = 2.013(4); Ga(1)-N(1) = 2.2001(3); N(1)-N(2) = 1.266(4). C(38)-Ga(1)-C(1) = 121.17(14); C(38)-Ga(1)-C(48) = 112.32(15); C(1)-Ga(1)-C(48) = 121.90(15); C(38)-Ga(1)-C(1) = 79.31(13); C(1)-Ga(1)-N(1) = 112.14(13); C(48)-Ga(1)-N(1) = 97.82(13). Sum of the angles at N(1) = 355.8(3).



Figure 4. Thermal ellipsoid (30%) drawing of **5**. Hydrogen atoms and isopropyl groups on 2,6-diisopropylphenyl groups are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-C(38) = 1.984(3); Ga(1)-C(1) = 1.994(3); Ga(1)-C(49) = 1.987(3); Ga(1)-N(1) = 2.218(2); N(2)-N(1) = 1.266(3). C(38)-Ga(1)-C(1) = 121.53(12); C(38)-Ga(1)-C(49) = 112.60(12); C(1)-Ga(1)-C(49) = 121.28(12); C(38)-Ga(1)-N(1) = 78.75(10); C(1)-Ga(1)-N(1) = 112.89(10); C(49)-Ga(1)-N(1) = 97.67(11). Sum of the angles at N(1) = 357.6(2).

However, no dinitrogen elimination was observed, and subse-



quent workup indicated that a cyclic Ga_2N_2 product (6) had formed (Figure 5), in which two Ph_2CN_2 moieties bridge two GaAr' units through their terminal nitrogens. The Ga_2N_2 core



Figure 5. Thermal ellipsoid (30%) drawing of **6**. Hydrogen atoms and isopropyl groups on 2,6-diisopropylphenyl groups are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-N(2) = 1.874(3); Ga(1)-N(1) = 1.895(3); Ga(1)-C(31) = 1.968(3); Ga(2)-N(2) = 1.862(3); Ga(2)-N(1) = 1.899(3); Ga(2)-C(1) = 1.973(3); N(1)-N(3) = 1.371(4); N(2)-N(4) = 1.400(4); N(3)-C(74) = 1.304(4); N(4)-C(61) = 1.292(4).

is nearly planar and contains average Ga–N bonds lengths of 1.883(3) Å, while the exocyclic N–N bond lengths are 1.371(4) Å and 1.400(4) Å.

Calculations on the gallium amides $HGaNH^{26}$ and MeGaNMe (see below) showed that their $GaNH_2$ and $GaNMe_2$ isomers were considerably more stable, than their imide counterparts. These results provided the impetus for our work toward the synthesis of monomeric Ga(I) amides. Previous work by Schnöckel and Schnepf⁴² showed that the reaction of LiN(SiMe₃)₂ with GaBr yielded the metal-rich $[Ga_{84}(N(SiMe_3)_2)_{20}]$.⁴ We therefore decided to synthesize the much bulkier LiN(SiMe₃)Ar'' (7) as a transfer reagent for $[N(SiMe_3)Ar'']^-$, an amide that was deemed sufficiently bulky to prevent the formation of Ga clusters or Ga(II) products.³¹ Reaction of 7 with "GaI" in toluene solvent yielded the first stable Ga(I) amide GaN(SiMe₃)Ar'' (8) in ca. 20% yield as yellow crystals (eq 6).

$$LiN(SiMe_3)Ar'' + "GaI" \xrightarrow{PhMe}_{-78 °C}$$
7
$$:GaN(SiMe_3)Ar'' + LiI + Ga (6)$$

Structural characterization of these showed that the compound had a monomeric structure (Figure 6). The gallium is coordinated to nitrogen Ga–N = 1.980(2) Å, and there is long interaction between gallium with C(13) (Ga(1)–C(13) = 2.65 Å) of the flanking mesityl ring of the terphenyl nitrogen substituent. The nitrogen is essentially planar coordinated (Σ° N(1) = 358.82(8)) with N(1)–C(1) and N(1)–Si(1) distances



Figure 6. Thermal ellipsoid (30%) drawing of **8.** Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(1)-N(1) = 1.980(2); Si(1)-N(1) = 1.743(2); N(1)-C(1) = 1.408(3). C(1)-N(1)-Si(1) = 127.5(2); C(1)-N(1)-Ga(1) = 119.8(3); N(1)-C(1)-C(6) = 123.8(2); N(1)-C(1)-C(2) = 119.0(2); C(6)-C(1)-C(2) = 117.1-(2); C(1)-C(2)-C(7) = 120.4(2). Dihedral between N(1) coordination plane and central phenyl plane = 41.5°



Figure 7. Thermal ellipsoid (30%) drawing of one of the crystallographically independent molecule of **9**. Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Ga(2)-N(4) = 1.743(5); Ga(2)-N(3) = 1.862(5); Ga(2)-C(58) = 2.395(6). N(4)–Ga-(2)–N(3) = 144.0(2); C(79)–N(4)–Ga(2) = 133.9(4).

of 1.408(2) and 1.743(2) Å. There is a dihedral angle of 41.5° between the coordination plane of nitrogen and the plane of the C(1) aryl ring. Treatment of GaN(SiMe₃)Ar" with one equivalent of N₃Ar" in toluene (eq 7) resulted in N₂ evolution (in a manner similar to that in eq 1) with concomitant production of the imido-gallium amide Ar"NGaN(SiMe₃)Ar" (**9**) as purple crystals in good yield

$$GaN(SiMe_3)Ar'' + N_3Ar'' \xrightarrow{25 \circ C, PhMe} \mathbf{R}$$

$$Ar''N(SiMe_3)NGaAr'' + N_2 \quad (7)$$

Its structure (Figure 7) afforded average Ga–N distances of 1.743(5) Å and 1.862(5) Å. The N(1)–Ga–N(2)–C(1) array has an essentially planar trans-bent structure with angles of 144.0(2)° at gallium and 133.9(4)° at nitrogen. In addition, there is a relatively close contact (2.395(6) Å) between gallium and the ipso carbon of a flanking mesityl substituent.

Calculated Structures of Model Species. The relative energies of the linear and trans-bent imides (MeGaNMe) and

⁽⁴¹⁾ Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. Angew. Chem., Int. Ed. 2002, 41, 2842–2844.

⁽⁴²⁾ Schnepf, A.; Schnöckel, H. Angew. Chem., Int. Ed. 2001, 40, 712-715.



Figure 8. Relative energies (kcal·mol⁻¹) of the MeNGaMe and GaNMe₂ isomers at the B3LYP/6-311+ g^* level.

the isomeric amide (GaNMe₂) were calculated at the B3LYP/ 6-311+g* level. The linear geometry was predicted to be only slightly less stable (2.2 kcal·mol⁻¹) than the trans-bent geometry (C-Ga-N = 157.6°; Ga-N-C = 145.0°). However, the gallium(I) amide is considerably more stable than its imido counterpart (Figure 8). The Kohn–Sham orbital surfaces for the trans-bent imide are shown in Figure 9. The HOMO and HOMO – 1 correspond to out-of-plane and in-plane π overlaps, which are strongly polarized toward nitrogen. The LUMO possesses substantial 4s character at gallium, while the LUMO + 1 features an antibonding Ga–N π combination. For additional DFT calculations on models of **2** and **9**, see the Supporting Information.

The Monomeric Amides GaNMe2 and GaN(SiMe3)Ar (Ar $= C_6H_2$ -2,6-Ph₂). Geometry optimization of the GaNMe₂ and $GaN(SiMe_3)Ar$ (Ar = C₆H₂-2,6-Ph₂) structures were performed at the B3YLP/6-31g* level. For GaN(SiMe₃)Ar these calculations reproduced the major structural parameters (Ga-N =1.976 Å; Si-N = 1.759 Å; C_{ipso}-N = 1.421 Å; C-N-Ga = 117.3° ; C-N-Si = 125.6°; Si-N-Ga = 115.1°) of 8 with good accuracy, while the calculated Ga-N distance in GaNMe₂ was 1.905 Å. The HOMO - 1 for GaNMe₂ has substantial 4s character at gallium (Figure 10), while the HOMO corresponds to a Ga-N π bond polarized toward nitrogen. The LUMO resembles a 4p orbital on Ga, while the LUMO + 1 features an antibonding π interaction between Ga and N. The Kohn–Sham orbital surfaces for GaN(SiMe₃)Ar showed that the HOMO is contains a p type orbital located on nitrogen and Ga possesses minor lone pair character. The HOMO -1 is mainly a lone pair (i.e. 4s) type orbital. The LUMO and LUMO + 1 contain an interaction between the 4p orbitals on gallium and the π system of the flanking phenyl substituent.

Dimeric Imides, 1,2-Ga₂N₂Ph₄ and 1,3-Ga₂N₂Ph₄. The relative energies and Kohn–Sham orbitals of the 1,2-Ga₂N₂-Ph₄ and 1,3-Ga₂N₂Ph₄ isomers, models of **3** and **6**, were also calculated. The 1,3-isomer is ca. 70 kcal·mol⁻¹ more stable than the 1,2-isomer, see Supporting Information and Discussion for more details.

Wiberg Bond Order Calculations. Wiberg bond order calculations were performed at the B3LYP/6-31g* level on the species shown in Table 2, using the AOMIX software.³⁸ All the alkyl subsituents were included on the imides **2**, **8**, **9**, and {H(CMeCDipp₂N)₂}GaNAr*.

Discussion

The Monomeric Imide, Ar'GaNAr[#]. Treatment of **1** with N₃Ar[#] afforded the gallium imide **2** in high yield. It contains the shortest known Ga–N distance of 1.701(3) Å in a stable molecular species as well as trans-bent N–Ga–C (148.2(2)°)

and C–N–Ga (141.7(3)°) arrays. The trans-bending in **2** is in sharp contrast to the geometry of the lighter iminoboranes, Bu^tBNBu^{t,22} (Me₃Si)₃SiBNBu^{t,23} Mes*BNBu^{t,20} and Mes*NBN-(SiMe₃)Bu^{t,24} which feature linear RBNR' arrangements and B–N distances in the range 1.22–1.26 Å. Calculations for HBNH support triple B–N bonding and afford a B–N bond strength of 88 kcal·mol⁻¹, which is comparable to the strength of the C–C triple bond (94 kcal·mol⁻¹) in acetylene.⁴³

The trans-bent structure of **2** results from an accumulation of nonbonding electron density at both gallium and nitrogen. Four Lewis dot structures may be written. The bending at gallium is consistent with some contribution from **C**. The bent geometry at N may be due to a contribution from **B**, **C**, or **D**. However, the charge distribution for **C** is inconsistent with the electronegativity values of Ga and N. Structure **A** is consistent with multiple Ga–N bonding, but its marginal stabilization relative to the trans-bent structure suggests it makes only a minor contribution.

An alternative way of rationalizing the structure of 2 is to consider it as an interaction between an organogallium(I) species and a nitrene (NR) in which the electron donation represented by the arrows is incomplete. This is consistent with the bent geometry at both N and Ga.



DFT calculations on the model compounds MeGaNMe (Figure 9) and ArGaNAr (Ar = C_6H_3 -2,6-Ph₂; Supporting Information) show the presence of nonbonding electron density at both N and Ga. The Ga-N bond order was further probed by Wiberg bond order calculations, which afforded a value of 2.19 in MeGaNMe and 1.62 in **2**. The trans-bent structure of **2** and the theoretical data thus support the view that the Ga-N bond order is much less than 3.

The unsaturated nature of the Ga–N bond suggested that it might undergo cycloaddition reactions. It is known that iminoboranes undergo these reactions^{21,44} which have also been

⁽⁴³⁾ Baird, N. C.; Datta, R. K. Inorg. Chem. 1972, 11, 17-19.

⁽⁴⁴⁾ Kroeckert, B.; van Bonn, K.-H.; Paetzold, P. Z. Anorg. Allg. Chem. 2005, 631, 866–868.



Figure 9. LUMO + 2 to HOMO - 1 Kohn-Sham orbitals for the transbent MeGaNMe

investigated computationaly.⁴⁵⁻⁴⁷ However, stirring of 2 with Me₃SiC=CSiMe₃, HC=CPh, or PhN=NPh in toluene overnight and subsequent heating to reflux led to the recovery of starting materials. The reluctance of 2 to react with unsaturated species may be a result of the extreme crowding at the Ga-N center (less hindered gallium imides undergo head-to-tail dimerization, forming associated species). Compound 2 does, however, react with water to generate the amine H₂NAr[#] and other, unidentified components.

Reaction of Ar'GaGaAr' with Unsaturated Dinitrogen Containing Molecules. Reactions of 1 with (p-tolyl)N=N(ptolyl) generated the blue green Ar'GaN(p-tolyl)N(p-tolyl)GaAr' (3), the first structurally characterized group 13 element 1,2diaza-3,4-dimetallocyclobutane. The only other group 13 element example is the boron species (Bu^t)BN(Et)N(Et)B(Bu^t) but structural details are unknown.¹⁹ The 1,2-Ga₂N₂ core of **3** is isomeric with the 1,3-Ga₂N₂ core of the dimeric imide $(Cp*GaNXyl)_2$ (Xyl = C₆H₃-2,6-Me₂.¹⁷ However, their core geometries differ significantly. Compound 3 is trapezoidal (N- $N-Ga = 105.64(4)^{\circ}$; $Ga-Ga-N = 74.19(6)^{\circ}$), due to the longer Ga-Ga bond, while (Cp*GaNXyl)2 contains an almost square core $(Ga-N-Ga = 90.82(8)^{\circ}; N-Ga-N = 89.186(8)^{\circ}).$ The Ga-N distance in 3 (1.909(2) Å) is slightly longer than those (Ga-N = 1.851(2), 1.870(2) Å) in $(Cp*GaNXyl)_2$. The oxidation state of gallium in 3 is +2, whereas it is +3 in (Cp*GaNXyl)₂, and this may account for the difference in bond lengths.

Calculations at the B3LYPG-31g* level on the model species 1,2-Ga₂N₂Ph₄ and 1, 3-Ga₂N₂Ph₄ the latter was predicted to be 69.8 kcal·mol⁻¹ more stable. These calculations are consistent with those on the hydrogen-substituted boron-nitrogen analogues, 1,2-B₂N₂, and 1,3-B₂N₂ isomers, for which the 1,3 isomer was found to be more stable by ca. 53 kcal·mol^{-1.48} The group 13 element-nitrogen species are isoelectronic to cyclobutadiene, and their Lewis structures may be written as



However, analysis of the Kohn-Sham orbitals for the model compounds, 1,2-Ga₂N₂Ph₄ and 1,3-Ga₂N₂Ph₄ (Supporting Information), did not indicate the presence of significant Ga-N π bonding in the HOMO to HOMO – 4 levels. In addition, the LUMO and LUMO + 1 did not indicate the presence of Ga-N π interactions. Instead the electron density surfaces suggest a more ionic structure in which the electron density is strongly polarized toward nitrogen. In addition, the Ga-N bond distances in 3 are considerably longer than those in 2, another indication of weak Ga–N π bonding.

Reaction of 1 with the 1,2-diaryldiazenes, ArylNNAryl (Aryl = mesityl or C_6H_3 -2,6-Et₂), that contain ortho-alkyl substituted aryl groups gave $MesN = NC_6H_2-2, 4-Me_2-6-Ga(Me)Ar'$ (4) and 2,6-Et₂C₆H₃N=NC₆H₃-2-Et-6-Ga(Et)Ar' (5) which involved insertion of the gallium(I) center into the sp²-sp³ C-C bond of a methyl or ethyl substituent. It is known that the ortho position of azobenzene can be metalated by direct reaction with a variety of transition metal species to afford the corresponding 2-(phenyl)azophenyl complexes.49-52 However, products 4 and 5, formed by the insertion of a Ga(I) center into a C-C bond, are unprecedented.53

⁽⁴⁵⁾ Gilbert, T. M.; Gailbreath, B. D. Organometallics 2001, 20, 4727–4733.
(46) Gilbert, T. M. Organometallics 2005, 24, 6445–6449.
(47) Gilbert, T. M. Organometallics 2003, 22, 2298–2304.

⁽⁴⁸⁾ Bridgeman, A., J.; Rothery, J. Inorg. Chim. Acta 1999, 288, 17-28

 ⁽⁴⁹⁾ Curic, M.; Babic, D.; Visnjevac, A.; Molcanov, K. Inorg. Chem. 2005, 44, 5975–5977.



Figure 10. Selected Kohn-Sham orbitals for the model compounds GaNMe2 (left), and GaN(SiMe3)Ar (right) obtained at the B3LYP/6-31g* level.

While a detailed mechanism for the formation of **3**, **4**, and **5** is not presently available, a series of plausible steps are shown

- (50) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. J. Chem. Soc. A 1971, 2820– 2828.
- (51) Fahey, D. R. J. Organomet. Chem. 1971, 27, 283–292.
 (52) Stone, F. G. A.; Bruce, M. I.; Iqbal, M. Z. J. Chem. Soc. A 1970, 3204–
- (52) Stone, F. G. A.; Bruce, M. I.; Iqbal, M. Z. J. Chem. Soc. A 1970, 3204– 3209.
 (52) F. G. A.; Bruce, M. I.; Iqbal, M. Z. J. Chem. Soc. A 1970, 3204– 3209.
- (53) For reaction of the related {H(CMeCDipp₂N)₂}Al with azobenzene, see: Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; Nehete, U. N.; Schmidt, H.-G.; Noltemeyer, M. Eur. J. Inorg. Chem. 2005, 2147.

in Scheme 1. Previous freezing point depression experiments have established that Ar'GaGaAr' is essentially dissociated to GaAr' monomers in hydrocarbon solvent.⁴¹ The :GaAr' monomer may interact with the diazene by donation of a nitrogen lone pair to the gallium(I) center, which contains two formally empty 4p orbitals to give initially a three-membered GaN₂ ring. The possibility that association takes place through interaction of the gallium lone pair and the N–N π^* orbital also exists. The basicity of :GaAr' is well established, and it interacts

Table 2. Wiberg Bond Orders for a Variety of Ga–N-Bonded Compounds

cmpd	bond (bond order)	
GaNMe ₂	Ga-N (1.22)	
MeGaNMe (trans-bent)	Ga-N (2.19)	
$1,3-Ga_2N_2Ph_4$	Ga-N (0.97)	
$1,2-Ga_2N_2Ph_4$	Ga-N (0.93)	
	Ga-Ga (0.85)	
	N-N (1.02)	
Ar'GaNAr [#] (2)	Ga-N (1.63)	
GaN(SiMe ₃)Ar" (8)	Ga-N (1.39)	
Ar"NGaN(SiMe ₃)Ar" (9)	Ga-N, imido (1.53)	
	Ga-N, amido (0.93)	
{H(CMeCDipp ₂ N) ₂ }GaNAr*	Ga-N, imido (1.60)	
	Ga-N, β -diketiminate (0.77)	

strongly with $B(C_6F_5)_3$ to give $Ar'Ga \rightarrow B(C_6F_5)_3$.^{41,54} If the 1,2-diaryldiazene is bulkier, as in 1,2-di- $(C_6H_3-2,6-Pr^i_2)$ diazene or 1,2-di-(2,4,6-triphenylphenyl)diazene, no reaction with :GaAr' occurs. This is probably a result of the larger aryl substituents preventing association of :GaAr' and the diazene. The initial :GaAr' adduct can rearrange apparently in two ways. If the nitrogen aryl substituents carry ortho substituents, the gallium lone pair can attack at the activated ortho carbon, and subsequent insertion into the C(aryl)–C(alkyl) bond may occur. Where the ortho substituents are hydrogens, the lower steric requirement may allow the three-membered Ga₂N ring (which requires the C(ipso)NNC(ipso) torsion angle to have a relatively low torsion angle) to form. Subsequent insertion of the :GaAr' may occur to afford 3. Attempts to isolate the three-membered Ga₂N ring species always afforded 3 and unreacted 1.

The formation of products **3**, **4**, and **5** are unique to the gallium system. The heavier "dimetallenes", Ar'MMAr' ($M = In^{55}$ and Tl⁵⁶), did not react with 1,2-diaryldiazenes to afford heavier analogues of **3**, **4**, **5**. It was also found that phenyl- and silyl-substituted alkynes did not react with **1**, indicating that the lone pairs of the diazene may play an important role in association with **1**.

Reactions of **1** with diphenyldiazomethane did not afford the intended Ar'GaCPh₂, a species with a gallium–carbon multiple bond, and dinitrogen. Instead, the diazo unit of diphenyldiazomethane reacted with the gallium(I) center to give Ar'Ga(μ : η ¹-N₂CPh₂)₂GaAr' (**6**) with a 1,3-Ga₂N₂ core. Oxidation of Ga(I) and subsequent reduction of the N–N moiety was accompanied by a lengthening of the N–N bond (1.371(4)–1.400(4) Å) ca. 0.2 Å relative to diazomethanes, while the C–N distance was not substantially perturbed. The Ga–N distances in **6** span the range 1.862(3)–1.895(3) Å and are similar to the Ga–N distances (1.850(2) Å and 1.870(2) Å) in (Cp*GaNXyl)₂.¹⁷ However, while the Ga₂N₂ core of **6** is slightly puckered (Ga-(1)–N(1)–N(2)–Ga(2)=8.6°), the Ga₂N₂ core of (Cp*GaNXyl)₂ is planar.

Reduction of a diazo unit at a low-valent group 13 element center has been previously reported by Uhl and Hannemann.⁵⁷ Reaction of R₂AlAlR₂ (R = CH(SiMe₃)₂) with (Me₃Si)₂CN= N afforded the insertion product R₂Al[N-NC(SiMe₃)₂]AlR₂ which contains a three-membered AlN₂ heterocycle. The two heavier In and Tl dimetallenes Ar'MMAr' did not react with diphenyldiazomethane to afford products analogous to **6**. Instead, dinitrogen evolution was observed, and $Ph_2C=N-N=CPh_2$, a common decomposition product of diphenyldiazomethane, was obtained.

Monomeric Gallium(I) Amide. Monomeric gallium(I) amides are extremely rare and have only been studied in lowtemperature matrices as the parent hydride species.³⁰ Calculations on these species and the methyl derivatives showed that the monovalent amides were considerably more stable than their imido isomers, RGaNR.26 Therefore, we postulated that employment of a sufficiently bulky amido ligand at gallium would allow the isolation and structural characterization of a stable gallium-(I) amide. We found that reaction of the recently reported lithium amide LiN(SiMe₃)Ar"³¹ (7) with "GaI" in toluene solvent afforded :GaN(SiMe₃)Ar" (8), a pale-yellow crystalline solid. It is the first structurally characterized monomeric gallium(I) amide and is a quasi-isomer of the monomeric gallium imide 2. It contains a planar nitrogen environment with a Ga-N distance of 1.980(2) Å. This distance is longer than those displayed in monomeric three-coordinate gallium(III) amides $[R_2NGaR_2]$ (R = aryl, alkyl, or related species) which range from 1.829 to 1.923 Å.⁷ However, it is shorter than the average Ga-N distances in {H(CMeCDipp₂N)₂}Ga⁵⁸ (Ga-N = 2.054(2)Å), [DippNC(NCy₂)NDipp]Ga⁵⁹ (Ga-N = 2.091(2) Å), and $TpBu^{t}_{2}Ga^{60}$ ($TpBu^{t}_{2}$ = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato) (Ga-N = 2.230(5), which features two- and threecoordinate gallium(I) centers.



The Ga-N distance in **8** is nearly identical to that calculated (1.976 Å) for the model compound, GaN(SiMe₃)Ar but is longer than those predicted for GaNH₂ (1.85 Å) and GaNMe₂ (1.905 Å). The only other Ga interaction is with the ipso carbon of the flanking Mes substituent. This distance is ca. 0.6 Å longer than typical Ga-C single bonds, indicating that the gallium center is essentially one-coordinate. The bonding in **8** may be represented as:



Structure **E** is consistent with a localized electron pair on nitrogen, while **F** possesses a Ga $-N\pi$ bond formed by donation of the nitrogen lone pair to an empty 4p orbital on gallium. DFT calculations on the gallium(I) amide GaNMe₂ showed that

⁽⁵⁴⁾ Cowley, A. H. Chem. Commun. 2004, 2369-2375.

 ⁽⁵⁵⁾ Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. J. Am. Chem. Soc. 2002, 124, 8538–8539.
 [55] Willing D. D. L. L. Chem. D. D. L. A. Chem.

⁽⁵⁶⁾ Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. J. Am. Chem. Soc. 2005, 127, 4794–4799.
(57) Uhl, W.; Hannemann, F. Eur. J. Inorg. Chem. 1999, 201–207.

⁽⁵⁸⁾ Hardman, N. J.; Eichler, B. E.; Power, P. P. Chem. Commun. 2000, 1991– 1992.

⁽⁵⁹⁾ Jones, C.; Junk, P. C.; Platts, J. A.; Stasch, A. J. Am. Chem. Soc. 2006, 128, 2206–2207.

 ⁽⁶⁰⁾ Kuchta, M. C.; Bonanno, J. B.; Parkin, G. J. Am. Chem. Soc. 1996, 118, 10914–10915.

Scheme 1. Possible Mechanism for the Formation of 3, 4, and 5



the HOMO is consistent with some π bonding between Ga and N (Figure 10). However, the bond is quite polarized toward nitrogen. The HOMO -1 contains 4s character at gallium, while the LUMO and LUMO + 1 are essentially 4p orbitals on gallium. These calculations suggest that 8 should behave both as a Lewis acid and Lewis base. Calculations for GaN(SiMe₃)-Ar, a more complete model of 8, were also undertaken. The results indicated that the HOMO and HOMO -1 contained 4s lone pair character at gallium, consistent with Lewis basicity. The LUMO and LUMO + 1 consisted in part of a bonding interaction between a Ga 4p orbital and the π system of a flanking phenyl substituent. Wiberg bond order calculations for the Ga-N bonds in GaNMe2 and GaN(SiMe3)Ar afforded indices of 1.22 and 1.39, respectively. These calculations indicate that structure F makes some contribution to the overall bonding observed in 8.

Treatment of **8** with (*p*-tolyl)N=N(*p*-tolyl) in toluene to generate a product analogous to **3** afforded no reaction. However, reaction with the sterically hindered azide N₃Ar''³¹ produced the amido-imide, Ar''NGaN(SiMe₃)Ar'' (**9**), and N₂ in an analogous manner to the synthesis of **2**. Compound **9** was isolated as a red-purple solid, and the structure was determined by X-ray crystallography (Figure 7). A comparison of the structural parameters of **9**, **2**, and {H(CMeCDipp₂N)₂}GaNAr^{*61} are provided in Figure 11.

Compound **9** has an imido Ga-N distance of 1.743(5) Å, which is nearly identical to the imido Ga-N distance (1.742(3)

Å) in {H(CMeCDipp₂N)₂}GaNAr*. The Ga₁–N₁ amido distance (1.862(6) Å) is typical for compounds of formula R₂GaNR₂, where the gallium is in the +3 oxidation state.⁷ Most notably it is ca. 0.12 Å shorter than that in **8**, presumably as a result of the increase in the gallium oxidation state to +3. The trans-bending at N(1) of 133.9(1)° is the largest of the series. The bending angle at gallium is 144.0(2)°, and there is also a close contact of 2.395(6) Å between Ga and the ipso carbon of a mesityl substituent. This interaction is significant as shown by a ca. 4° closing of the angle at C(53) relative to C(57).

Compound 9 is the first heavier group 13 element-nitrogen analogue of an allyl anion. However, unlike allyl anions which feature a delocalized π bonding system, there is little evidence of such delocalization in 9. DFT calculations on 9 were undertaken to better understand the bonding (Supporting Information). It was found that, like 2 and $\{H(CMeCPh_2N)_2\}$ -GaNAr*, the HOMO and HOMO - 1 can be described as polarized π bonds between the imido nitrogen and gallium. There is no evidence of a delocalized three-centered π bond involving the N-Ga-N array. In addition, Wiberg bond orders of 1.53, and 0.93 were calculated for the Ga-N(imido) and Ga-N(amido) bonds (Table 2). Wiberg bond orders of 1.62 and 1.60 were calculated for the imido Ga-N bonds of 2 and {H(CMeCPh₂N)₂}GaNAr*. These calculations showed that all the monomeric gallium imides possess Ga-N bonds with multiple bond character of similar magnitude, but the bond orders are significantly weaker than those in iminoboranes.

⁽⁶¹⁾ Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. Angew. Chem., Int. Ed. 2001, 40, 2172–2174.



Figure 11. Structural parameters of three crystallographically characterized gallium imides 9, 2, and {H(CMeCDipp₂N)₂}GaNAr*.

Relative Stability of Isomers. Calculations by a number of groups on heavier group 13-group 15 hydride model compounds have shown that the :MNH₂ isomers are much lower in energy than HMNH (M = Al-Tl), whereas for boron derivatives the opposite is the case.²⁶ The lower energy seems counterintuitive on the basis of a superficial examination. For example, RMNR (R = Me or H) has five bonds $(3\sigma + 2\pi)$ between Ga, N, and ligands), whereas :MNR₂ has only three (3σ) . However, calculations for RGaNR and GaNR₂ (R = Me) showed that the Ga-N bond orders in the two isomers differed by less than one unit. Furthermore, when bond order calculations were performed directly on 2 and 8, the Ga-N bond order differed by only ca. 0.2 units. Thus, the multiple bonding in 2 contributes little to its stabilization. In addition, :GaNR2 contains two N-R bonds, whereas RGaNR has one N-R bond and a weaker Ga-R bond. A further important factor is that the lone pair orbital at the metal in :GaNR₂ has more 4s character than it has in RMNR and the lone pair orbital in :GaNR2 is not the HOMO but the HOMO - 1. The electronegative NR₂ substituent apparently stabilizes the lone pair on gallium, and this is consistent with the fact that the color of 8 is pale yellow (cf. green for :GaAr'). This indicates that the n-p absorption has been moved into the UV region, consistent with a lowering of the energy of the gallium lone pair and an increase in the HOMO-LUMO gap.⁶²

The use of the very large substituents at both N and Ga, together with a suitable synthetic approach, allowed the synthesis of the less stable imide prior to the synthesis of the more stable amide. However, the stabilization of the gallium amide required the use of a very crowding amide ligand containing two large substituents at the nitrogen atom. This is sterically more difficult to achieve because of the smaller size of nitrogen.

Bond strength considerations readily account for the greater stability of the $1,3-M_2N_2$ versus the $1,2-M_2N_2$ ring species. The 1,3-isomer contains four M–N bonds that are strengthened because of polar contributions as in $M^{\delta+}-N^{\delta-}$. In contrast the 1,2-isomer contains two M–N bonds, a weak N–N bond and a weak M–M bond. There are unfavorable polarizations across

both of these bonds. In addition, the nitrogens have a pyramidal coordination. The Ga–N bonds in **3** are longer than they are in a variety of 1,3-Ga₂N₂ ring species, including **6**, suggesting that that they are weaker than those in the 1,3-isomer. The unique synthetic route to **3**, via reaction with a species in which the N–N bond is preformed, and the steric protection provided by the gallium substituent permit its isolation. It is the only reaction undergone by **1** in which a Ga–Ga bond is observed.

Conclusions

It has been shown that the use of bulky terphenyl ligands affords the gallium imide (RGaNR) 2 and its quasi-isomeric amide, :GaNR₂, 8. These compounds feature only weak Ga-N multiple bonding however. Wiberg bond order calculations for the imides afforded values of 1.62 and 1.53 for the formally triple Ga-N bond in 2 and 9, respectively. The corresponding value for the amide was only slightly less at 1.39. The calculations showed that the gallium(I) amide :GaNMe2 was considerably more stable than its imido isomer MeGaNMe, which is a consequence of the similarity in energies in Ga-N π bonding and the stabilization of the Ga lone pair by the electronegative NMe_2 substituent. Compounds 3 and 6 which contain isomeric 1,2-Ga₂N₂ and 1,3-Ga₂N₂ arrays were also synthesized. The 1,3-isomer was predicted by DFT calculations to be more stable than the M-M-bonded 1,2-isomer. The compounds 2, 8, and 9 as well as 3 and 6 are very rare examples of quasi-isomeric heavier main group element compounds. This work suggests that it may be possible to isolate several other isomers or quasi-isomers of the heavier main group elements.

Acknowledgment. We are grateful to the National Science Foundation for financial support and Anne F. Richards for crystallographic assistance with compound 6.

Supporting Information Available: X-ray data (CIFs) for **3**, **4**, **5**, **6**, **8**, and **9** and a summary table of crystallographic data for **3**–**6**, **8**, and **9**; selected Kohn–Sham orbital surfaces of 1,2-Ga₂N₂Ph₄, 1,3-Ga₂N₂Ph₄, ArGaNAr, ArNGaN(SiMe₃)Ar, and {H(CMeCPh₂N)₂}GaNAr (Ar = C₆H₃-2,6-Ph₂); the complete ref 36 citation. This material is available free of charge via the Internet at http://pubs.acs.org.

JA063072K

⁽⁶²⁾ Macdonald, C. L. B.; Cowley, A. H. J. Am. Chem. Soc. 1999, 121, 12113– 12126.