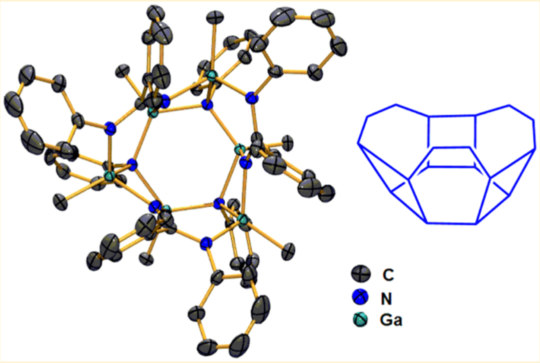
Inorganic Chemistry
Article
pubs.acs.org/IC

Insertion of Benzonitrile into Al−N and Ga−N Bonds: Formation of Fused Carbatriaza-Gallanes/Alanes and Their Subsequent Synthesis from Amidines and Trimethyl-Gallium/Aluminum

K. Maheswari, A. Ramakrishna Rao, and N. Dastagiri Reddy*

Department of Chemistry, Pondicherry University, Pondicherry 605014, India

Supporting Information



ABSTRACT: Insertion of aromatic nitriles into Al−N and Ga−N bonds are reported. Sterically less hindered aluminum amide $[PhNHAlMe_2]_2$ (**1**) undergoes C≡N insertion with benzonitrile to give an isomeric mixture of tetracyclic triazaalanes $\{[PhNC(Ph)N]_3[PhNC(Ph)NH]Al[AlMe][AlMe_2]_2\}$ (**2** and **3**). A similar reaction with analogous gallium amide affords a tetracyclic triazagallane $\{[PhNC(Ph)N]_3[PhNC(Ph)NH]Ga[GaMe][GaMe_2]_2\}$ (**6**) along with a novel bowl shaped carbon containing Ga−N cluster $\{[PhNC(Ph)N][PhN][GaMe]_2\}_3$ (**5**). On the other hand, when sterically bulky gallium amide (Dipp on N, Dipp = 2,6-diisopropylphenyl) is employed, a tetrameric gallium amidinate $\{[(Dipp)NC(Ph)N]GaMe\}_4$ (**8**) is obtained. Tetracyclic triazagallazane **6** is also synthesized from the condensation reaction of *N*-phenylbenzamidine with $GaMe_3{\cdot}OEt_2$. Unlike $AlMe_3$, this reaction produces only one isomer. In case of amidines with bulkier substituents on N such as Dipp, formation of a bicyclic triazagallane $\{[(Dipp)NC(Ph)NH]_2[(Dipp)NC(Ph)N][GaMe]_2\}$ (**14**) is also observed along with tetrameric gallium amidinate **8**, whereas *N-tert*-butylbenzamidine affords exclusively a tetrameric gallium amidinate $\{[(tert\text{-}Bu)NC(Ph)N]GaMe\}_4$ (**15**) similar to its Al analogue. However, treating *N*-(Dipp)acetamidine with $GaMe_3{\cdot}OEt_2$ gives only a bicyclic triazagallane $\{[(Dipp)NC(Me)NH]_2[(Dipp)NC(Me)N][GaMe]_2\}$ (**16**). An intermediate $[(tert\text{-}Bu)N(H)\ C(Ph)NGaMe_2]_2$ (**17**), which is involved in the formation of tetrameric gallium amidinate **15**, is also characterized. A comparison of the structural parameters of Ga−N−C and Al−N−C frameworks synthesized in this study is reported.

INTRODUCTION

A diverse family of rings and clusters of group 13 elements has been extensively investigated due to their interesting structure and bonding aspects.[1] A great deal of interest in the synthesis of M−N frameworks (M = group 13 element) is not only because of the novel structural diversity but also because of their applications in advanced materials.[2] Though Al and Ga belong to the same group in the periodic table, the variation in their sizes and Lewis acidity make them distinct and quite often their compounds are structurally different. There are a few articles reported in the literature, which emphasize the dissimilarities in the formation of Al−N and Ga−N cages/heterocycles.[3] Recently, we reported the synthesis of several fused polycyclic Al−N−C heterocycles with diverse structural facets via insertion of nitriles into Al−N bonds and the condensation of amidines with $AlMe_3$.[4] The structure of the Al−N frameworks formed in these studies varied depending upon the steric bulkiness of the nitrile and the amidine. Though the nitriles with varying degree of steric bulk were employed, in insertion reactions, the Al−N precursor was limited to only one aluminum amide, which contained a sterically bulky 2,6-diisopropylphenyl (Dipp) group. In this report, we explored the reactions of a sterically nondemanding aluminum amide with nitriles. Further, we were also curious to compare these reactions with those of analogous gallium reagents and noticed that there had been no reports in the literature on the insertion of nitriles into the Ga−N bond. A thorough literature search on group 13 amidinates revealed reports only on *N*,*N*′-disubstituted amidinates but not on *N*-monosubstituted amidinates.[5] Therefore, we also explored the reactions of nitriles with a gallium amide and the condensation reactions of amidines with $GaMe_3{\cdot}OEt_2$. The results are reported herein.

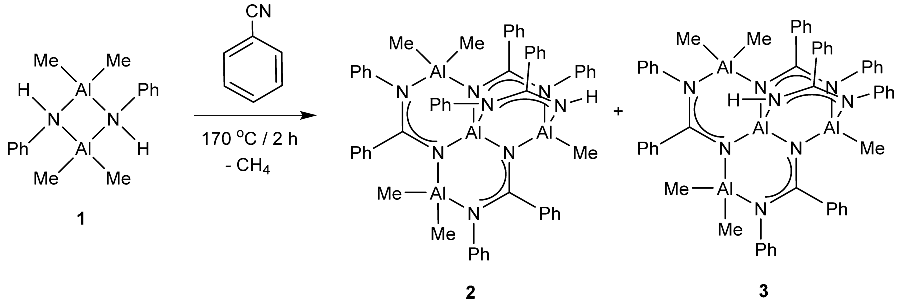
RESULTS AND DISCUSSION

Insertion of Nitriles into Al−N Bonds. Heating an equimolar mixture of *N*-phenylaluminum amide (**1**) and benzonitrile at 170 °C for 2 h resulted in the formation of a solid residue, which upon recrystallization from the toluene/hexane mixture yielded a mixture of isomers of a tetracyclic triazaalane, **2** and **3** (Scheme 1) in 4:1 ratio in good yield. Interestingly, compounds **2** and **3** were also formed when *N*-phenylbenzamidine was treated with $AlMe_3$.[4b] It is noteworthy that both methods produced the isomers in a 4:1 ratio.

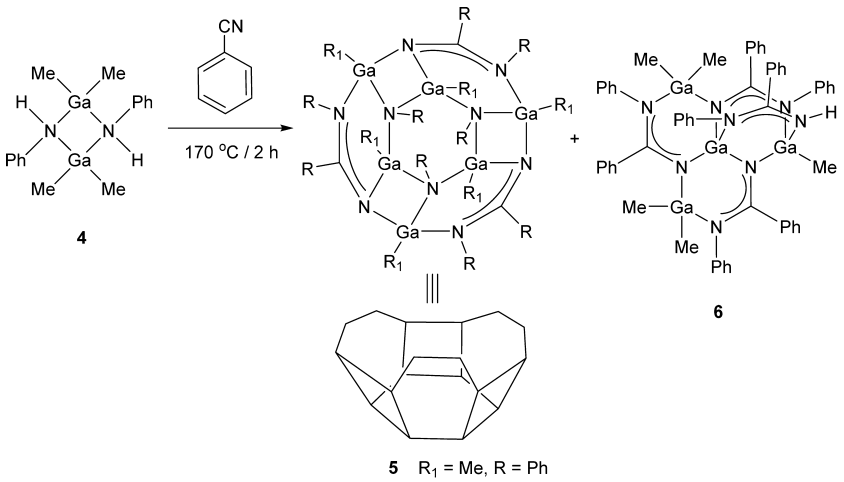
Received: December 9, 2014

DOI: 10.1021/ic5029096
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Reaction of *N*-Phenylaluminum Amide with Benzonitrile



Scheme 2. Reaction of *N*-Phenylgallium Amide with Benzonitrile



Insertion of Nitriles into Ga−N Bonds. Similarly, heating an equimolar mixture of analogous gallium amide **4** with benzonitrile at 170 °C for 2 h resulted in a glassy residue, which upon recrystallization from hexane afforded a few crystals of a bowl shaped Ga−N−C cluster **5** as the first crop. Concentrating the mother liquor yielded colorless crystals of a tetracyclic triazagallane **6** in 51% yield (Scheme 2).

Because of the formation of only a few crystals, **5** was characterized only by single crystal X-ray technique. Several attempts to obtain pure **5** by repeating the reaction were unsuccessful. The molecular structure of **5** along with selected bond parameters is given in Figure 1. The C_3 symmetric molecule has a unique structure among the Ga−N frameworks so far reported. The crystal structure shows a bowl shaped Ga−N−C framework comprising three Ga_2CN_3 six-membered and three Ga_2N_2 four-membered rings alternatively fused to a six-membered Ga_3N_3 ring. The gallazane ring (Ga_3N_3), which forms the bottom of the bowl, is almost planar and the Ga and N atoms are placed 0.11 Å above and below the mean plane. However, Ga_2CN_3 six-membered and Ga_2N_2 four-membered rings are highly puckered. Ga−N bond lengths in the central Ga_3N_3 ring are not equal. While a bond length of 1.953(2) Å is observed for those shared by Ga_2CN_3 rings, the Ga−N that are shared by Ga_2N_2 rings are placed at a distance of 2.003(2) Å. All the Ga−N bonds involving tricoordinated N are shorter (Ga2−N3 1.936(2) Å). The longest is the one which is transverse to the gallazane ring (Ga2−N1 2.038(2) Å). These bond lengths are within the range of those reported for Ga−N clusters.[6,7] Ga−N−Ga and N−Ga−N bond angles in the Ga_3N_3 ring are close to 120° (118.56(12)° and 119.15(12)°, respectively). While bond angles at the C and N atoms present in the periphery of the bowl are of sp^2, those at peripheral Ga vary significantly.

Unlike aluminum amide, gallium amide gives only one isomer **6**, in its reaction with benzonitrile. The ^1H NMR spectrum of **6** shows only one set of resonances. Five singlets for Ga−Me ranging from 0.03 to −2.02 ppm, one singlet for NH at 5.21 ppm, and a few multiplets for aromatic protons are observed. The formation of another isomer of tetracyclic compound similar to **3** was not observed in this reaction. The ORTEP diagram of compound **6** and its selected bond parameters are given in Figure 2. The molecular structure of **6** shows that it is isostructural with its Al analogue **2**. All the Ga−N bonds follow similar trends in variation of bond parameters as with its Al analogue. The shortest Ga−N bond is observed for Ga4−N3 (1.8735(17) Å), and the longest bond is seen for Ga2−N2 (2.0441(18) Å). All the Ga−N bond distances are similar to those reported for Ga−N clusters.[6,7]

Similarly, sterically demanding gallium amide (2,6-diisopropylphenyl group on N) **7** reacted with benzonitrile in the same fashion as analogous aluminum amide[4a] and afforded a tetrameric gallium amidinate **8** in 38% yield (Scheme 3).

^1H NMR spectrum of **8** in $CDCl_3$ is similar to that of its Al analogue except for a slight downfield shift of Ga−Me resonances (by 0.46 ppm). Formation of **8** was further confirmed by single crystal X-ray studies. The crystal structure of **8** and its selected bond lengths and bond angles are given in Figure 3. The central Ga−N eight membered ring adopts a highly puckered boat conformation. The degree of puckering is found to be greater for the Ga compound compared to its Al analogue (see Supporting Information Table S1). The extent of distortion of the eight membered ring from an ideal boat can be assessed from their torsion angles, M···M distances (1,5 positions), angles of

DOI: 10.1021/ic5029096
Inorg. Chem. XXXX, XXX, XXX−XXX

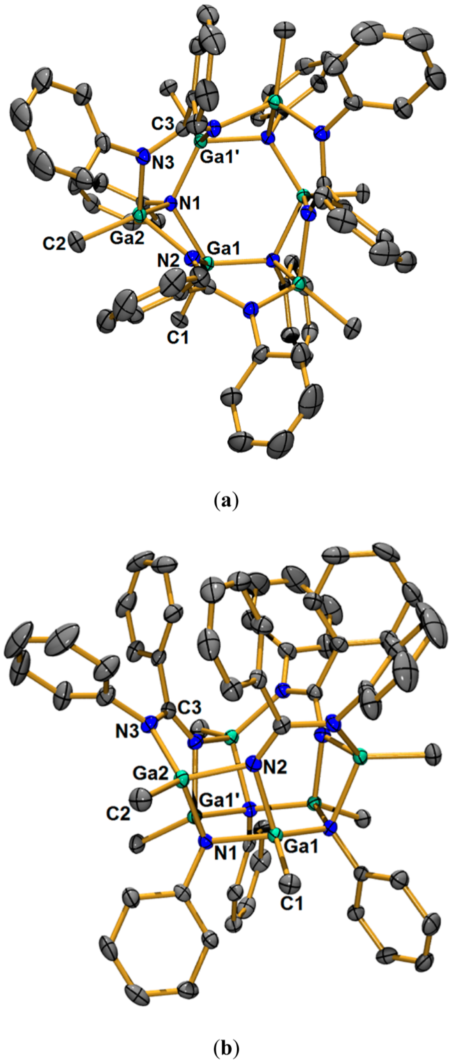


Figure 1. Molecular structure of **5**. (a) Top view. (b) Side view. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1–N1 2.003(2), Ga1–N3 1.942(2), Ga2–N3 1.936(2), N1–Ga1′ 1.953(2), Ga1–C1 1.966(3), N2–C3 1.365(4), Ga2–C2 1.956 (3), and Ga2–N1 2.038(2). Selected bond angles [°]: N1–Ga2–N3 83.60(10), N1–Ga1–N1′ 119.15(12), N3–Ga1–N1′ 108.73(10), N3–Ga1–C1 112.15(12), Ga1–N1–Ga1′ 118.56(12), C2–Ga2–N1 114.78(12), Ga2–N1–Ga1 90.39(9), N3–Ga1–N1 84.39 (10), N2–Ga2–N3 109.80(10), and N2–Ga2–C2 112.48(13).

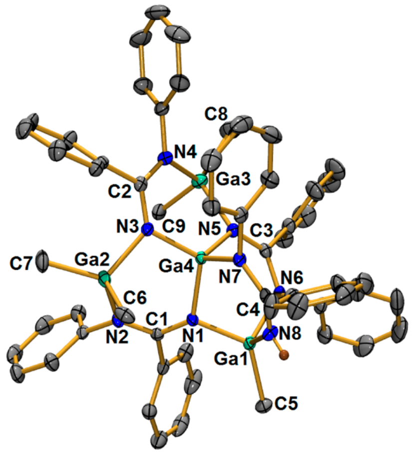
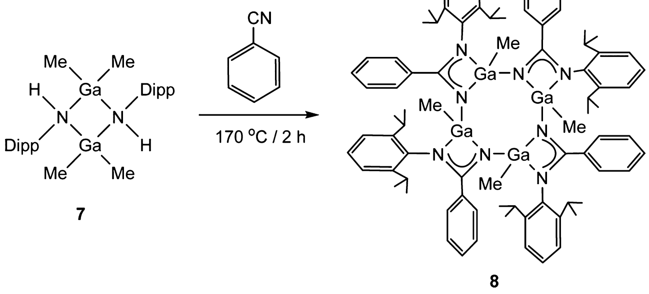


Figure 2. Molecular structure of **6**. All hydrogen atoms are omitted for clarity except on N8. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1–N8 1.977(2), Ga4–N1 1.890(2), Ga1–N1 1.907(2), Ga4–N7 1.965(2), Ga1–C5 1.953(2), N7–C4 1.332(3), Ga3–C9 2.054(3), Ga2–C7 1.968(3), Ga2–N3 1.973(2), Ga2–N2 2.044(2), N2–C1 1.329(3), N1–C1 1.324(3), Ga4–N3 1.874(2), N4–C2 1.336(3), Ga4–N5 1.897(2), N3–C2 1.322(3), Ga3–N5 1.982(2), and Ga3–N4 2.042(2). Selected bond angles [°]: N1–Ga1–N8 98.53(8), N3–Ga2–N2 97.29(7), N5–Ga3–N4 100.15(2), C2–N3–Ga4 122.93(2), N3–C2–N4 123.60(2), C1–N1–Ga4 123.88(1), N2–C1–N1 122.44(2), N1–Ga1–C5 124.92(9), N3–Ga4–N1 110.53(8), Ga1–N8–C4 130.71(2), Ga2–N2–C1123.99(1), Ga4–N3–Ga2 108.09(8), Ga4–N5–Ga3 109.45(8), N7–C4–N8 121.80(2), N5–Ga3–C9 105.94(9), N3–Ga2–C7 115.75(1), Ga4–N1–Ga1 103.33(8), and Ga4–N7–C4 125.72(2).

Scheme 3. Reaction of *N*-(Dipp)gallium Amide with Benzonitrile



amidinate-C····M–N atoms, and dihedral angles between the planes. Similar to its Al analogue, **8** also shows longer Ga–N distances (av. 2.03 Å) between Ga and the Dipp substituted N and shorter Ga–N distances for those which are exocyclic to the amidinate ring (av. 1.88 Å). All the bond lengths are in agreement with those reported in the literature.[6−8]

Reactions of *N*-Monosubstituted Amidines with $GaMe_3$·OEt_2. In our earlier studies, reactions of $AlMe_3$ with several *N*-monosubstituted amidines resulted in formation of structurally diverse Al–N–C frameworks.[4b] Enthused by these results, we conducted similar reactions with $GaMe_3$·OEt_2. When an equimolar mixture of $GaMe_3$·OEt_2 and the corresponding *N*-phenylamidine was subjected to heating at 170 °C for 2 h, tetracyclic Ga–N–C heterocycles **6** and **11** were formed in good yields. Though $GaMe_3$·OEt_2 reacted with *N*-phenylamidines in a similar fashion to $AlMe_3$, it gave only a single isomer in both cases (**6** and **11**, Scheme 4) in 70–80% yield, whereas $AlMe_3$ gave two isomers in each case.[4b] Compounds **6** and **11** are isostructural with the respective aluminum analogues.

The formation of **11** was further confirmed by single-crystal X-ray studies. The molecular structure of **11** along with its bond parameters is shown in Figure 4. Structural aspects of **11** are closely related to its Al analogue. The six membered M_2CN_3 rings, in all the polycyclic compounds made in our study, are puckered. In these rings, five atoms are almost in one plane and one atom (X) is away from the plane. Figure 5 illustrates the extent of deviation of such atom from the mean plane of the rest of the atoms. In the case of benzamidinate heterocycles, **6** and its Al analogue **2**, the extent of deviation of the atom X in all the rings is almost similar (1.057−0.956 Å in **6** and 1.007−0.908 Å in **2**), whereas in the case of acetamidinate heterocycles, **11** and its Al analogue,[4b] ring B is almost planar with X deviating only by 0.270 Å (in **11**) and 0.236 Å (in Al analogue) away from the

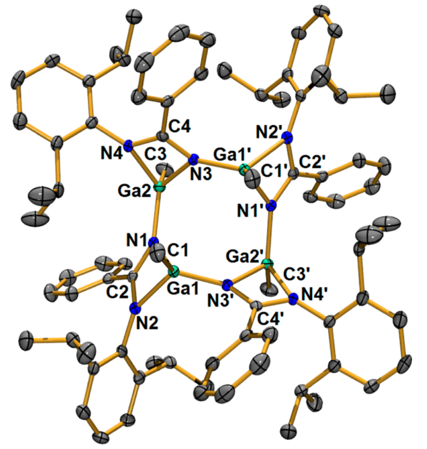
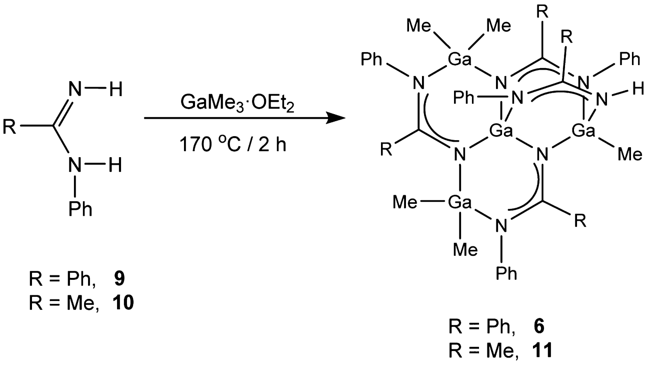


Figure 3. Molecular structure of **8**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1−N2 2.027(2), Ga1−N1 1.970(2), Ga2−N3 1.985(2), Ga2−N4 2.033(2), Ga2−N1 1.880(2), Ga1′−N3 1.985(2), Ga2−C3 1.951(3), Ga1−C1 1.958(3), N1−C2 1.329(3), and N2−C2 1.349(3). Selected bond angles [°]: N1−Ga1−N2 67.46(9), N1−Ga1−N3′ 103.53(1), N3′−Ga1−N2 110.23(9), N3−Ga1−C1 122.38(1), Ga2−N1−Ga1 129.75(1), C1−Ga1−N1 122.05(1), C1−Ga1−N2 118.31(1), N1−Ga2−N4 110.25(9), N1−Ga2−N3 103.75(9), N1−Ga2−C3 126.55(1), N3−Ga2−C3 118.77(1), Ga2−N1−C2 137.90(2), and N2−C2−N1 112.01(2).

Scheme 4. Reactions of GaMe$_3$·OEt$_2$ with *N*-Phenylamidines



mean plane of the rest of the ring atoms. When a comparison is made between respective Al and Ga heterocycles, the extent of deviation is found to be slightly larger for Ga heterocycles.

Unlike AlMe$_3$, GaMe$_3$·OEt$_2$ gave a mixture of products **8** and **14** when treated with *N*-(Dipp)benzamidine (Scheme 5). When the reaction mixture was recrystallized from the toluene/hexane mixture at −10 °C, the tetrameric gallium amidinate **8** was isolated as the first fraction (23%), and further concentrating the mother liquor yielded a good amount of colorless crystals, which were later identified as bicycic Ga-amidinate (49%), **14**. In contrast, *N*-*tert*-butylbenzamidine afforded a quantitative yield of **15** exclusively. The crystals of **14** did not diffract well, and hence, the structural parameters are not discussed here, though the data was good enough for determining the structure (see Supporting Information Figure S3). The molecular structure of **15** and its selected bond parameters are shown in Figure 6. The structural parameters of **15**, which are given in the Supporting Information, Table S2, indicate that the Ga−N eight membered ring is more symmetrical and less puckered than the related Ga-amidinate **8**. The ^{1}H NMR spectrum of **15** is in agreement with its solid state structure.

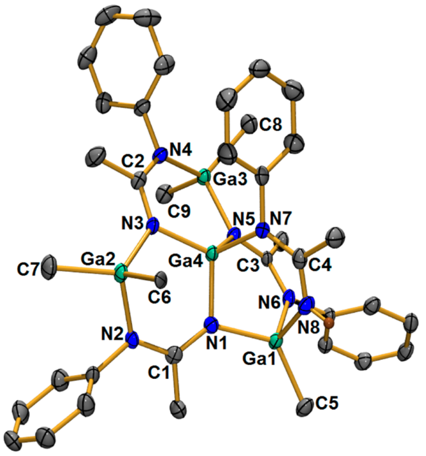
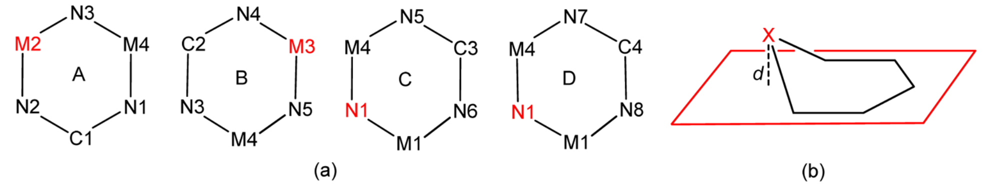


Figure 4. Molecular structure of **11**. All hydrogen atoms, except those on N8, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1−N8 1.957(4), Ga4−N1 1.896(4), Ga1−N1 1.913(4), Ga4−N7 1.977(4), Ga1−C5 1.952(5), N7−C4 1.339(6), Ga3−C9 1.987(5), Ga2−C7 1.978(5), Ga2−N3 1.961(4), Ga2−N2 2.027(4), N2−C1 1.332(6), N1−C1 1.320(6), Ga4−N3 1.880(4), N4−C2 1.336(6), Ga4−N5 1.899(4), N3−C2 1.333(6), Ga3−N5 1.973(4), and Ga3−N4 2.040(4). Selected bond angles [°]: N1−Ga1−N8 98.29(2), N3−Ga2−N2 99.76(2), N5−Ga3−N4 102.85(2), C2−N3−Ga4 123.31(3), N3−C2−N4 123.80(4), C1−N1−Ga4 127.90(3), N2−C1−N1 122.51(4), N1−Ga1−C5 128.28(2), N3−Ga4−N1 111.21(2), Ga1−N8−C4 132.00(3), Ga2−N2−C1 125.31(3), Ga4−N3−Ga2 107.28(2), Ga4−N5−Ga3 112.49(2), N7−C4−N8 120.11(4), N5−Ga3−C9 109.71(2), N3−Ga2−C7 118.41(2), Ga4−N1−Ga1 101.80(2), and Ga4−N7−C4 125.90(3).

Interestingly, under similar conditions, *N*-(Dipp)acetamidine produced only a bicyclic triazagallane **16** similar to **14** in 67% yield (Scheme 6). The molecular structure of **16** along with the bond parameters is given in Figure 7. Compound **16**, which crystallizes in the space group $P2_12_12_1$, is a bicyclic carbagallazane. Two different coordination modes (μ−1κN,2$\kappa N'$ and μ−1:2$\kappa^2 N$) for the acetamidinate ligand are observed. In coordination mode μ−1:2$\kappa^2 N$, the amidinate-C3−N6 (1.291(3) Å) bond distance is significantly lower than the other C−N bond distances (C2−N4 1.335(3), C3−N5 1.355(3), and N2−C1 1.324(3) Å) indicating a double bond character. There is also a variation in Ga−N bond lengths. The longest is shown in μ−1κN,2$\kappa N'$ coordination (Ga1−N1 2.019(2) Å), and the shortest is found for μ−1:2$\kappa^2 N$ coordination (Ga2−N5 1.875(2) Å). All the bond lengths are within the range of those of gallium heterocycles reported in this study. The bridging-N atom (N5) deviates from the mean planes of Ga1,N3,C2,N4,Ga2 and Ga1,N1,C1,N2,Ga2 by 0.91 Å. The dihedral angle between the aforesaid planes is 107.7°. The ^{1}H and ^{13}C NMR spectra in CDCl$_3$ support that the solid state structure is retained in solution.

In order to identify the intermediates in these thermolysis reactions, we carried out a few experiments under mild reaction conditions such as low temperature and reflux in solvents. When an equimolar mixture of *N*-*tert*-butylbenzamidine (**13**) and GaMe$_3$·OEt$_2$ was stirred in hexane at 0 °C for 30 min, a four-membered gallium amide **17** was formed in 56% yield. **17** was further subjected to thermolysis at 170 °C for about 2 h to obtain the tetrameric gallium amidinate **15** in quantitative yield. This indicates that the formation of **15** from *N*-*tert*-butylbenzamidine and GaMe$_3$·OEt$_2$ involves a stepwise elimination of methane and

DOI: 10.1021/ic5029096
Inorg. Chem. XXXX, XXX, XXX−XXX

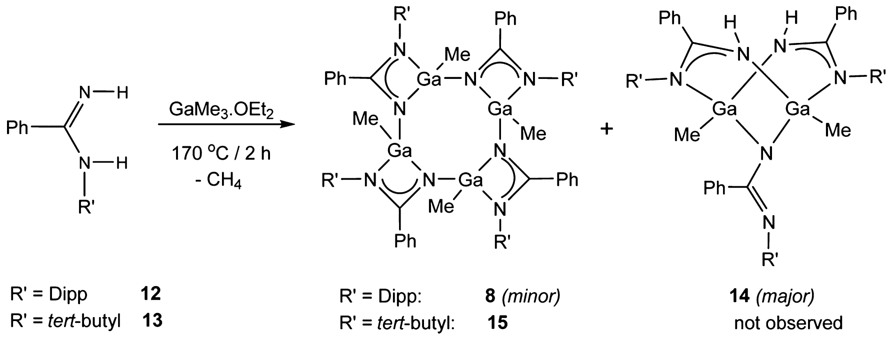


Distance (*d*) between deviated atom (X) and mean Plane in [Å]

	6	Al analog of 6 (2)	11	Al analog of 11
Ring A: X = M2	1.057	1.007	0.950	0.887
Ring B: X = M3	0.822	0.784	0.270	0.236
Ring C: X = N1	0.929	0.912	0.932	0.923
Ring D: X = N1	0.956	0.908	0.997	0.959

Figure 5. (a) Representation of deviated atoms (in red) in tetracyclic Al/Ga heterocycles. (b) Representation of deviated atom from the mean plane.

Scheme 5. Reaction of $GaMe_3{\cdot}OEt_2$ with *N*-Dipp and *N*-*tert*-Butylbenzamidines



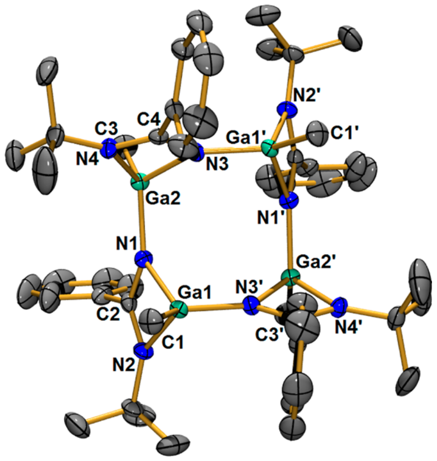
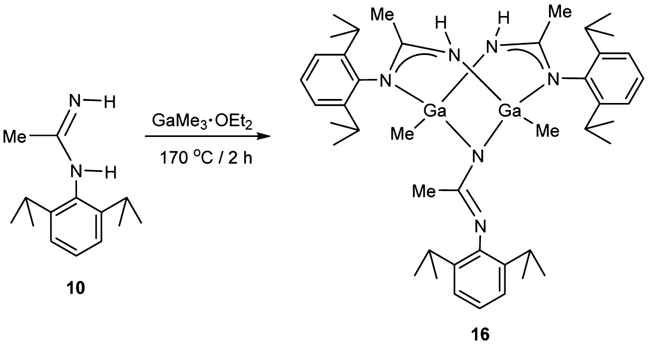


Figure 6. Molecular structure of **15**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1−N2 2.008(2), Ga1−N1 1.979(2), Ga2−N3 1.980(2), Ga2−N4 2.014(2), Ga2−N1 1.872(2), Ga1′−N3 1.874(2), Ga2−C3 1.957(2), Ga1−C1 1.955(2), N1−C2 1.330(3), and N2−C2 1.330(3). Selected bond angles [°]: N1−Ga1−N2 67.50(7), N1−Ga1−N3′ 105.24(7), N3′−Ga1−N2 107.09(8), N3−Ga1−C1 123.58(9), Ga2−N1−Ga1 132.95(9), C1−Ga1−N1 122.24(9), C1−Ga1−N2 117.55(9), N1−Ga2−N4 106.85(8), N1−Ga2−N3 103.65(7), N1−Ga2−C3 124.33(1), N3−Ga2−C3 122.33(1), Ga2−N1−C2 136.32(2), and N2−C2−N1 112.68(2).

Scheme 6. Reaction of $GaMe_3{\cdot}OEt_2$ with *N*-(Dipp)acetamidine



dimerization of the resultant unstable species as one of the plausible pathways as shown in Scheme 7. Attempts to isolate any intermediate products from the other amidines were unsuccessful.

An ORTEP diagram of **17** along with selected bond parameters is shown in Figure 8. The compound **17** crystallizes in $P2_1/n$ space group as a centrosymmetric molecule. It contains a planar four membered gallazane ring. There are no noticeable deviations in the bond parameters from similar four membered Ga−N rings reported in the literature.[9]

On the other hand, refluxing an equimolar mixture of *N*-(Dipp)benzamidine and $GaMe_3{\cdot}OEt_2$ in toluene for 2 h afforded a mixture of products. Attempts to recrystallize the crude from hexane resulted in formation of a few crystals of a tricyclic compound **18** (Figure 9), which is presumably formed due to the presence of traces of water in the solvent used for crystallization. Crystal data and the molecular structure of **18** along with the

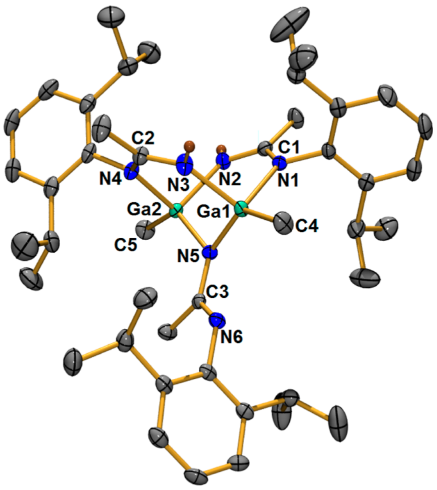


Figure 7. Molecular structure of **16**. All hydrogen atoms, except those on N2 and N3, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1−N1 2.019(2), Ga1−N3 1.976(2), Ga1−N5 1.890(2), Ga2−C5 1.955(3), C2−N4 1.335(3), C3−N6 1.291(3), C3−N5 1.355(3), Ga2−N5 1.875(2), N2−C1 1.324(3), and Ga2−N4 2.001(19). Selected bond angles [°]: N3−Ga1−N1 104.37(9), C4−Ga1−N3 108.06(11), N5−Ga1−N3 99.81(9), N5−Ga2−N2 101.85(9), Ga2−N5−Ga1 107.26(10), C2−N3−Ga1 134.00(16), N5−Ga1−C4 132.71(10), Ga1−N5−C3 117.15(16), N5−C3−N6 119.8(2), and C5−Ga2−N4 110.52(10).

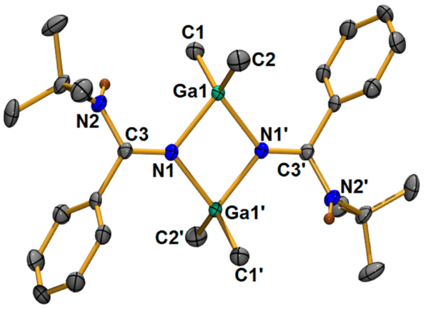
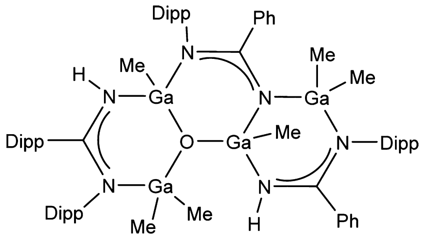


Figure 8. Molecular structure of **17**. All hydrogen atoms, except those on N2 and N2′, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Ga1−N1 1.974(3), Ga1−C1 1.977(4), C3−N2 1.390(5), Ga1−C2 1.969(5), Ga1−N1′ 2.005(3), C3−N1 1.273(5), and Ga1−Ga1′ 3.005(8). Selected bond angles [°]: N1−Ga1−N1′ 81.91(14), C2−Ga1−N1 110.59(18), C2−Ga1−C1 122.00(19), Ga1−N1−Ga1′ 98.09(14), N1−C3−N2 121.5(4), Ga1−N1−C3 131.9(3), and C3−N1−Ga1′ 128.9(3).



Dipp = 2,6-diisopropylphenyl

18

Figure 9. Oxo bridged tricyclic Ga−N−C heterocycle.

selected bond parameters are given in the Supporting Information.

Treating *N*-phenyl amidines such as *N*-phenylbenzamidine and *N*-phenylacetamidine with $GaMe_3{\cdot}OEt_2$ under reflux in toluene for 4 h afforded tetracyclic triazagallanes, **6** and **11**, in good yield. No intermediates were isolated.

A comparison between *N*-monosubstituted Al and Ga amidinates revealed that sterically less demanding *N*-phenylamidinates, which are having wider bite angles, favored bridging coordination for both the metals and produced structurally analogous heterocycles. However, when the amidinates having sterically demanding groups were employed, certain structural dissimilarities between Al and Ga compounds were found. In case of Al, *N*-(Dipp) and *N*-*tert*-butyl amidinates preferred four-membered chelate complexes, which are tetrameric. With the heavier analogue gallium, such preference for chelation was found only for *N*-*tert*-butylbenzamidinate, while the other two

Scheme 7. Isolation of Intermediate (17) from a Reaction between $GaMe_3{\cdot}OEt_2$ and *N*-*tert*-Butylbenzamidine at 0 °C and Its Further Thermolysis

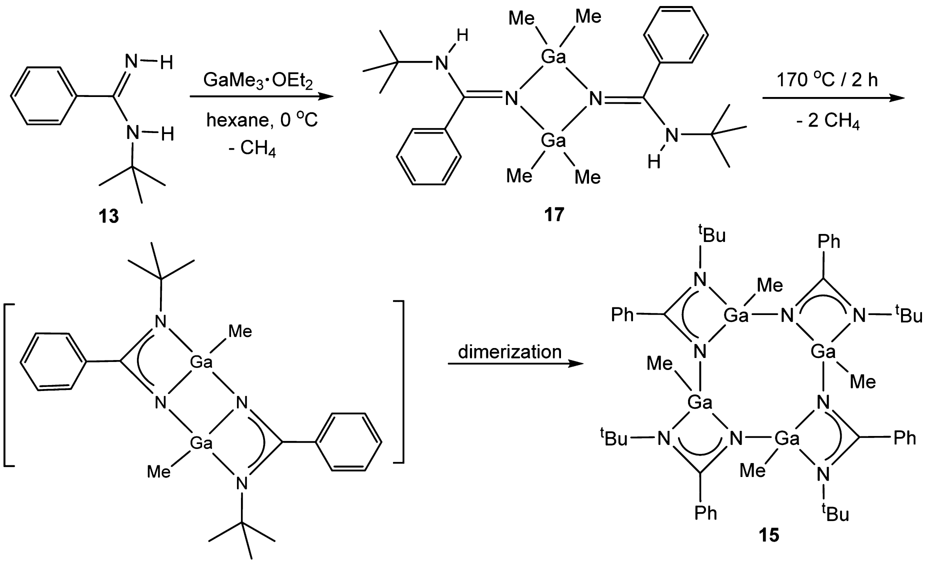


Table 1. Crystal Data for Compounds 5, 6, 8, 11, and 15−18

	5	**6**·C_7H_8	**8**·2C_7H_8	**11**·C_7H_8
empirical formula	$C_{63}H_{63}Ga_6N_9$	$C_{64}H_{64}Ga_4N_8$	$C_{94}H_{116}Ga_4N_8$	$C_{81}H_{104}Ga_8N_{16}$
formula wt	1364.54	1224.11	1636.83	1859.56
temp (K)	150.00 (2)	149 (2)	120.1 (2)	140 (2)
cryst syst	trigonal	triclinic	monoclinic	triclinic
space group	$R\bar{3}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	19.2352(4)	14.1348(5)	29.0426(12)	13.0751(6)
b (Å)	19.2352(4)	14.1580(4)	10.3599(4)	13.6722(6)
c (Å)	33.3633(9)	16.4427(5)	31.2885(17)	14.7834(6)
α (deg)	90.00	93.330(2)	90.00	71.830(4)
β (deg)	90.00	113.944(3)	98.561(4)	65.638(4)
γ (deg)	120.00	101.566(3)	90.00	62.669(5)
V (Å^3)	10690.4(4)	2910.33(17)	9309.1(7)	2114.07(16)
Z	6	2	4	1
ρ_{calcd} (Mg m^{-3})	1.272	1.397	1.168	1.461
μ (mm^{-1})	2.275	1.878	1.191	2.560
F(000)	4140.0	1256.0	3440.0	950.0
cryst size (mm)	0.33 × 0.26 × 0.18	0.36 × 0.24 × 0.21	0.40 × 0.34 × 0.23	0.38 × 0.25 × 0.21
θ range (deg)	3.67−29.10	3.71−29.24	2.63−25.0	3.58−29.18
no. of collected/unique rflns	33439/5892 (R(int) = 0.0645)	31236/13415 (R(int) = 0.0287)	26977/8203 (R(int) = 0.0560)	19783/9648 (R(int) = 0.0492)
no. of data/restraints/params	5892/0/237	13415/0/695	8203/0/489	9648/0/476
R1, $wR2$ ($I > 2\sigma(I)$)^a	0.0390, 0.0893	0.0314, 0.0716	0.0405, 0.0917	0.0514, 0.1092
R1, $wR2$ (all data)^a	0.0717, 0.0963	0.0470, 0.0788	0.0614, 0.0990	0.0924, 0.1292
GOF	0.992	1.047	1.031	1.016
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.54/−0.63	0.99/−0.59	0.53/−0.41	1.30/−0.81

	15	**16**·C_6H_{14}	**17**
empirical formula	$C_{48}H_{68}Ga_4N_8$	$C_{50}H_{83}Ga_2N_6$	$C_{26}H_{42}Ga_2N_4$
formula wt	1035.98	907.66	550.08
temp (K)	149.8(2)	151.0	150.0(2)
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$I2/a$	$P2_12_12_1$	$P2_1/n$
a (Å)	23.0044(6)	13.58923(2)	10.6745(7)
b (Å)	11.3834(2)	18.9059(2)	9.7298(5)
c (Å)	23.2147(8)	20.0649(2)	13.8119(7)
α (deg)	90.00	90.00	90.00
β (deg)	117.671(4)	90.00	92.884(6)
γ (deg)	90.00	90.00	90.00
V (Å^3)	5383.9(2)	5155.05(10)	1432.69(13)
Z	4	4	2
ρ_{calcd} (Mg m^{-3})	1.278	1.170	1.275
μ (mm^{-1})	2.017	1.082	1.899
F(000)	2144.0	1948.0	576
cryst size (mm)	0.42 × 0.35 × 0.28	0.35 × 0.30 × 0.27	0.42 × 0.35 × 0.22
θ range (deg)	3.73−29.21	2.74−29.37	3.82−28.71
no. of collected/unique rflns	33931/6636 (R(int) = 0.0354)	36228/12217 (R(int) = 0.0418)	9475/3288 (R(int) = 0.0305)
no. of data/restraints/params	6636/0/281	12217/1/546	3288/0/150
R1, $wR2$ ($I > 2\sigma(I)$)^a	0.0313, 0.0680	0.0339, 0.0772	0.0519, 0.1345
R1, $wR2$ (all data)^a	0.0461, 0.0745	0.0438, 0.0832	0.0620, 0.1385
GOF	1.086	1.046	1.337
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.94/−0.37	0.64/−0.61	1.28/−0.59

^{a}R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{0.5}$.

amidinates (N-(Dipp)benzamidinate and N-(Dipp)-acetamidinate) preferred bridging coordination mode.

■ CONCLUSION

In summary, insertion of aromatic nitriles into Al−N and Ga−N bonds led to the formation of Al−N−C and Ga−N−C heterocycles, respectively. These heterocycles could also be obtained by the condensation reactions of N-monosubstituted amidines with $AlMe_3$ or $GaMe_3\cdot OEt_2$. In these insertion and condensation reactions explored in this study, Al and Ga reagents produced analogous compounds except in a few cases (**5**, **14**, and **16**). Sterically less hindered aluminum amide $(PhNHAlMe_2)_2$ in its insertion reaction with PhCN produced a mixture of tetracyclic aluminum amidinate isomers **2** and **3**. A similar reaction employing analogous gallium amide $(PhNHGaMe_2)_2$ afforded a single isomer of tetracyclic gallium amidinate **6** along with a bowl shaped carbon containing Ga−N cluster **5**. On the other hand, sterically bulky gallium amide (Dipp on N) reacted with PhCN in a similar fashion as its Al analogue did and produced a tetrameric gallium amidinate **8**.

Condensation reactions of GaMe$_3$·OEt$_2$ with sterically less bulky amidines occurred similar to corresponding reactions of AlMe$_3$ and yielded tetracyclic gallium amidinates **6** and **9**. In case of amidines with bulkier substituents on N such as Dipp, formation of a simple bicyclic gallane **14** was also observed along with a tetrameric gallium amidinate **8**, whereas *N-tert*-butylbenzamidine afforded exclusively a tetrameric gallium amidinate **15** similar to its reaction with AlMe$_3$. On the other hand, treating *N*-(Dipp)acetamidine with GaMe$_3$·OEt$_2$ resulted in a bicyclic gallane **16**. Comparison of the structural parameters of Ga–N–C heterocycles with those of similar Al–N–C frameworks revealed that the Ga analogues are more puckered than their Al counterparts. Isolation of **17** proves that the tetrameric amidinates are formed via stepwise elimination of methane followed by the aggregation of subsequent intermediates.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under N$_2$ atmosphere using a Schlenk line and a glovebox. Trimethylgallium ether adduct,[10] *N*-phenylgallium amide,[3a] *N*-(Dipp)gallium amide,[3a] *N*-phenylbenzamidine,[11] *N*-(Dipp)-benzamidine,[4a] *N*-phenylacetamidine,[12] and *N-tert*-butylbenzamidine[12] were prepared by following literature procedures. Hexane and toluene (from Na/benzophenone ketyl) were distilled fresh as and when required. ^{1}H and ^{13}C spectra were recorded on a Bruker 400 MHz instrument. Elemental analyses were performed using a Flash 2000 organic elemental analyzer.

Structural Determination for 5, 6, 8, 11, and 14–18. Single crystals of **5**, **6**, **8**, **11**, and **14–18** were mounted on a glass fiber in paraffin oil and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection was performed on an OXFORD XCALIBUR diffractometer, equipped with CCD area detector, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. All calculations were performed using SHELXS-97 and SHELXL-97.[13] The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms and solvent molecules were refined anisotropically, except for the solvent molecules in **11**. In **5**, solvent molecules were severely disordered and the SQUEEZE program was used to eliminate the residues. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. All the data sets were collected to 2Θ values >50°. Relevant data concerning crystallographic data, data collection, and refinement details for compounds **5**, **6**, **8**, **11**, and **15–17** are summarized in Table 1, and for compounds **14** and **18**, they are given in Table S3 (see the Supporting Information). Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1003875–1003878, 1003881–1003883, 1003885, and 1004150. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

General Procedure for the Reactions of Benzonitrile with *N*-Arylmetal Amides. In a typical reaction, a mixture of *N*-arylmetal amide (1 equiv) and benzonitrile (1 equiv) was taken in a Schlenk flask and heated to 170 °C for 2 h. After the reaction mixture was cooled to room temperature, the residue was dissolved in hexane or toluene and filtered using Celite.

With N-Phenylaluminum Amide. *N*-Phenylaluminum amide (0.53 g, 1.77 mmol), benzonitrile (0.18 g, 1.78 mmol), toluene (10 mL), and hexane (5 mL). The filtrate afforded a mixture of crystals of **2** and **3** in 4:1 ratio (0.59 g, 69%). Characterization details of these compounds are reported in our earlier publication.[3b]

With N-Phenylgallium Amide. *N*-Phenylgallium amide (0.23 g, 0.59 mmol), benzonitrile (0.06 g, 0.58 mmol), and hexane (20 mL). The filtrate afforded a few crystals of **5** as the first fraction. Concentrating the mother liquor further yielded colorless crystals of **6**. Yield: 0.17 g (51%). Mp: 193–194 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ −2.02 (s, 3H, GaMe), −1.65 (s, 3H, GaMe), −1.56 (s, 3H, GaMe), −0.07 (s, 3H, GaMe), 0.03 (s, 3H, GaMe), 5.21 (s, 1H, NH), 6.08 (m, 2H, ArH), 6.64–7.31 (set of multiplets, 37H, ArH), 7.51 (m, 1H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): δ −12.47, −8.79, −6.55, −5.85, −3.34, 122.65, 123.57, 124.26, 125.58, 126.96, 127.29, 127.38, 127.43, 127.67, 127.71, 127.78, 128.10, 128.16, 128.22, 128.25, 128.35, 128.60, 128.88, 129.09, 137.88, 139.62, 140.99, 141.04, 145.94, 147.90, 148.69, 149.14, 173.49, 173.96, 174.38, 177.09 Anal. Calcd for $C_{57}H_{56}Ga_4N_8$: C, 60.48; H, 4.99; N, 9.90. Found: C, 60.69; H, 5.18; N, 9.73.

With N-(Dipp)gallium Amide. *N*-(Dipp)gallium amide (0.48 g, 0.87 mmol), benzonitrile (0.09 g, 0.87 mmol), and toluene (15 mL). The filtrate yielded colorless crystals of compound **8** at 0 °C overnight. Yield: 0.24 g (38%). Mp: 236 °C. ^{1}H NMR (400 MHz, CDCl$_3$): −0.24 (s, 12H, GaMe), 0.72 (d, 12H, CH(C*H*$_3$)$_2$), 0.99 (m, 24H, CH(C*H*$_3$)$_2$), 1.20 (d, 12H, CH(C*H*$_3$)$_2$), 3.27 (m, 4H, C*H*(CH$_3$)$_2$), 3.62 (m, 4H, C*H*(CH$_3$)$_2$), 6.94 (m, 4H, ArH), 6.99 (m, 16H,ArH), 7.02 (m, 8H, ArH), 7.08 (m, 4H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): δ −6.87, 23.11, 23.36, 25.93, 26.19, 27.74, 28.15, 123.21, 123.42, 124.90, 127.92, 128.63, 129.56, 135.31, 140.12, 144.11, 144.67, 178.25. Anal. Calcd for $C_{80}H_{100}Ga_4N_8$: C, 66.15; H, 6.94; N, 7.71. Found: C, 66.29; H, 7.13; N, 7.59.

General Procedure for the Reactions of GaMe$_3$·OEt$_2$ with *N*-Monosubstituted Amidines. GaMe$_3$·OEt$_2$ (1 equiv) was added to the preheated amidine (1 equiv) at 120 °C, and the temperature was raised and maintained at 170 °C for 2 h. After the reaction mixture was cooled to room temperature, the resultant residue was recrystallized from hexanes or toluene/hexane mixtures.

With N-Phenylacetamidine. *N*-Phenylacetamidine (0.25 g, 1.86 mmol), GaMe$_3$·OEt$_2$ (0.35 g, 1.85 mmol), and hexane (30 mL). Colorless crystals of **11** were obtained from the filtrate at room temperature after 1 day. Yield: 0.31 g (76%). Mp: 172–173 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ −0.93 (s, 3H, GaMe), −0.87 (s, 3H, GaMe), −0.65 (s, 3H, GaMe), −0.36 (s, 3H, GaMe), −0.31 (s, 3H, GaMe), 1.36 (s, 3H, CH$_3$), 1.83 (s, 3H, CH$_3$), 1.84 (s, 3H, CH$_3$), 1.91 (s, 3H, CH$_3$), 4.87 (s, 1H, NH), 6.34 (m, 2H, ArH), 6.97–7.31 (set of multiplets, 18H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): δ −7.61, −5.50, −5.43, −5.07, 24.43, 24.61, 25.05, 25.43, 124.21, 124.73, 125.17, 125.46, 125.97, 127.57, 127.93, 128.10, 128.70, 129.13, 129.19, 146.10, 148.96, 149.17, 149.46, 170.61, 171.20, 171.67, 175.36. Anal. Calcd for $C_{37}H_{48}Ga_4N_8$: C, 50.29; H, 5.47; N, 12.68. Found: C, 50.13; H, 5.63; N, 12.81.

With N-Phenylbenzamidine. *N*-Phenylbenzamidine (0.26 g, 1.32 mmol) and GaMe$_3$·OEt$_2$ (0.31 g, 1.37 mmol). After completion of the reaction, 30 mL of hexane was added to the residue. Only half of it was dissolved in hexane. The mixture was filtered, and the filtrate was kept at room temperature. Colorless crystals of **6** were obtained in 1 day. The ^{1}H NMR spectrum of the precipitate was found to be the same as that of **6**. Yield: 0.29 g (72%).

With N-(Dipp)benzamidine. *N*-(Dipp)benzamidine (0.51 g, 1.82 mmol), GaMe$_3$·OEt$_2$ (0.35 g, 1.85 mmol), toluene (20 mL), and hexane (5 mL). Keeping the filtrate at −10 °C for 2 days afforded colorless crystals of **8**. Yield: 0.15 g (23%). Further concentrating the mother liquor to 15 mL and storing it at −10 °C for 1 day afforded colorless crystals of **14**. Yield: 0.30 g (49%). Mp: > 280 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$): δ −0.90 (s, 6H, GaMe), 0.35 (m, 3H, CH(C*H*$_3$)$_2$), 0.81 (m, 6H, CH(C*H*$_3$)$_2$), 0.86 (m, 3H, CH(C*H*$_3$)$_2$), 1.06 (m, 9H, CH(C*H*$_3$)$_2$), 1.25 (m, 3H, CH(C*H*$_3$)$_2$), 1.30 (m, 9H, CH(C*H*$_3$)$_2$), 1.44 (m, 3H, CH(C*H*$_3$)$_2$), 2.95 (m, 1H, C*H*(CH$_3$)$_2$), 3.36 (m, 3H, C*H*(CH$_3$)$_2$), 3.55 (m, 2H, C*H*(CH$_3$)$_2$), 5.18 (s, 2H, NH), 6.78 (m, 2H, ArH), 6.88 (m, 2H, ArH), 7.10 (m, 8H, ArH), 7.23(m, 12H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.61, 22.45, 22.71, 23.63, 23.84, 25.16, 25.59, 27.01, 27.71, 28.79, 29.51, 120.03, 121.15, 123.67, 123.72, 125.45, 126.27, 127.10, 127.17, 127.62, 128.04, 128.38, 129.15, 129.25, 129.65, 132.31, 137.68, 138.03, 138.94, 139.65, 140.22, 143.26, 147.75, 164.90. Anal. Calcd for $C_{59}H_{74}Ga_2N_6$: C, 70.39; H, 7.41; N, 8.35. Found: C, 70.52; H, 7.23; N, 8.17.

With N-tert-Butylbenzamidine. *N-tert*-Butylbenzamidine (0.47 g, 2.70 mmol), $GaMe_3\cdot OEt_2$ (0.51 g, 2.69 mmol), and hexane (25 mL). Storing the filtrate afforded X-ray quality crystals of **15** in quantitative yield. Mp: >300 °C dec. ^1H NMR (400 MHz, $CDCl_3$): δ −0.89 (s, 12H, GaMe), 0.92 (s, 36H, C $(CH_3)_3$), 7.21 (m, 8H, ArH), 7.36 (m, 12H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ −9.35, 32.38, 51.20, 127.64, 127.83, 140.51, 177.87. Anal. Calcd for $C_{48}H_{68}Ga_4N_8$: C, 55.65; H, 6.62; N, 10.82. Found: C, 55.49; H, 6.81; N, 10.94.

With N-(Dipp)acetamidine. *N*-(Dipp)acetamidine (0.58 g, 2.66 mmol), $GaMe_3\cdot OEt_2$ (0.50 g, 2.64 mmol), and hexane (25 mL), storing the filtrate at 0 °C gave colorless crystals of compound **16**. Yield: 0.49 g (67%, based on the amidine). Mp: 233−235 °C. ^1H NMR (400 MHz, $CDCl_3$): δ −0.62 (s, 6H, GaMe), 1.08−1.25 (set of multiplets, 36H, $CH(CH_3)_2$), 1.69 (s, 3H, CH_3), 1.81 (s, 6H, CH_3), 3.04 (m, 1H, $CH(CH_3)_2$), 3.19 (m, 3H, $CH(CH_3)_2$), 3.36 (m, 2H, $CH(CH_3)_2$), 4.78 (s, 2H, NH), 6.88 (m, 1H, ArH), 7.04 (m, 2H, ArH), 7.16 (m, 4H, ArH), 7.21(m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ −7.86, 21.07, 22.85, 23.08, 23.59, 23.83, 23.89, 23.94, 24.03, 24.08, 24.27, 24.91, 25.01, 27.65, 27.68, 28.42, 28.66, 120.11, 122.05, 122.71, 123.43, 123.88, 124.14, 126.42, 139.24, 139.67, 142.41, 143.94, 144.36, 149.54, 163.53, 170.31. Anal. Calcd for $C_{44}H_{69}Ga_2N_6$: C, 64.33; H, 8.47; N, 10.23. Found: C, 64.47; H, 8.29; N, 10.09.

Low Temperature Reaction between N-tert-Butylbenzamidine and $GaMe_3\cdot OEt_2$. To a solution of *N-tert*-butylbenzamidine (0.35 g, 2.01 mmol) in hexane at 0 °C was added $GaMe_3\cdot OEt_2$ (0.38 g, 2.01 mmol). The reaction mixture was slowly brought to room temperature and stirred for 30 min. Colorless, X-ray quality crystals of **17** were obtained by storing the filtrate at −10 °C. Yield: 0.33 g (56%). Mp: 164−166 °C. ^1H NMR (400 MHz, $CDCl_3$): δ −0.80 (s, 6H, GaMe), 1.49 (s, 9H, $C(CH_3)_3$), 7.42 (m, 3H, ArH), 7.51 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.93, 29.29, 31.64, 127.93, 128.65, 131.33. Anal. Calcd for $C_{26}H_{42}Ga_2N_4$: C, 56.77; H, 7.70; N, 10.19. Found: C, 56.85; H, 7.57; N, 10.31.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Packing diagrams of **5** showing C−H···π interactions, crystal data and molecular structures of **14** and **18** and their selected bond parameters, table containing the structural parameters of **8** and **15**, and the crystallographic information files (CIF) for **5**, **6**, **8**, **11**, and **14**−**18**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ndreddy.che@pondiuni.edu.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the Department of Science and Technology, New Delhi, for financial support and Alexander von Humboldt Stiftung, Germany, for donation of a glovebox. We thank the Central Instrumentation Facility, Pondicherry University, for NMR spectra and DST-FIST for the single crystal X-ray diffraction facility. K.M. thanks CSIR, India, for a senior research fellowship.

■ REFERENCES

(1) Timoshkin, A. Y. *Coord. Chem. Rev.* **2005**, *248*, 2094−2131. and references therein. (b) Neumüller, B.; Iravani, E. *Coord. Chem. Rev.* **2004**, *249*, 817−834.

(2) (a) Jegier, J. A.; McKernan, S.; Purdy, A. P.; Gladfelter, W. L. *Chem. Mater.* **2000**, *12*, 1003−1010. (b) Schulz, S.; Bauer, T.; Hoffbauer, W.; Günne, J. S.; Doerr, M.; Marian, C. M.; Assenmacher, W. *J. Solid State Chem.* **2008**, *181*, 530−538. (c) Carmalt, C. J.; Mileham, J. D.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 4255−4260. (d) Brazeau, A. L.; Barry, S. T. *Chem. Mater.* **2008**, *20*, 7287−729. (e) Bensiek, S.; Bangel, M.; Neumann, H. B.; Stammler, A.-G.; Jutzi, P. *Organometallics* **2000**, *19*, 1292−1298.

(3) (a) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385−3393. (b) Uhl, W.; Breher, F.; Mbonimana, A.; Gauss, J.; Haase, D.; Lutzen, A.; Saak, W. *Eur. J. Inorg. Chem.* **2001**, 3059−3066. (c) Kumar, S. S.; Roesky, H. W. *Dalton Trans.* **2004**, 3927−3937. (d) Uhl, W.; Cuypers, L.; Neumuller, B.; Weller, F. *Organometallics* **2002**, *21*, 2365−2368. (e) Uhl, W.; Abel, T.; Hepp, A.; Grimme, S.; Steinmetz, M. *Eur. J. Inorg. Chem.* **2008**, 543−551. (f) Uhl, W.; Layh, M.; Rezaeirad, B. *Inorg. Chem.* **2011**, *50*, 12275−12283.

(4) (a) Maheswari, K.; Rajendran, N. M.; Meyer, J.; Reddy, N. D. *Organometallics* **2010**, *29*, 3799−3807. (b) Maheswari, K.; Reddy, N. D. *Organometallics* **2012**, *31*, 197−206.

(5) Edelmann, F. T. *Adv. Organomet. Chem.* **2013**, *61*, 59−132.

(6) Luo, B.; Gladfelter, W. L. *Inorg. Chem.* **2002**, *41*, 590−597 and references therein..

(7) (a) Luo, B.; Gladfelter, W. L. *Inorg. Chem.* **2002**, *41*, 6249−6257. (b) Schnitter, C.; Waezsada, S. D.; Roesky, H. W.; Teichert, M.; Uson, I.; Parisini, E. *Organometallics* **1997**, *16*, 1197−1202.

(8) (a) Hausen, H. D.; Gerstner, F.; Schwarz, W. *J. Organomet. Chem.* **1978**, *145*, 277−284. (b) Brazeau, A. L.; Wang, Z.; Rowley, C. N.; Barry, S. T. *Inorg. Chem.* **2006**, *45*, 2276−2281. (c) Barry, S. T.; Richeson, D. S. *J. Organomet. Chem.* **1996**, *510*, 103−108. (d) Cole, M. L.; Jones, C.; Junk, P. C.; Kloth, M.; Stasch, A. *Chem.—Eur. J.* **2005**, *11*, 4482−4491.

(9) (a) Chivers, T.; Fedorchuk, C.; Schatte, G.; Parvez, M. *Inorg. Chem.* **2003**, *42*, 2084−2093. (b) Jegier, J. A.; Luo, B.; Buss, C. E.; Gladfelter, W. L. *Inorg. Chem.* **2001**, *40*, 6017−6021. (c) Schulz, S.; Thomas, F.; Priesmann, W. M.; Nieger, M. *Organometallics* **2006**, *25*, 1392−1398. (d) Atwood, D. A.; Jones, R. A.; Cowley, A. H. *J. Organomet. Chem.* **1992**, *434*, 143−150. (e) Nutt, W. R.; Stimson, R. E.; Leopold, M. F.; Rubin, B. H. *Inorg. Chem.* **1982**, *21*, 1909−1912.

(10) Kraus, C. A.; Toonder, F. E. *Proc. Natl. Acad. Sci. U. S. A.* **1933**, *19*, 292−298.

(11) Cooper, F. C.; Partridge, M. W. *Org. Synth.* **1956**, *36*, 64−65.

(12) (a) Barrett, A. G. M.; Gray, A. A.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A.; White, A. J. P. *Inorg. Chem.* **2006**, *45*, 3352−3358. (b) Oxley, P.; Partridge, M. W.; Short, W. F. *J. Chem. Soc.* **1947**, 1110−1115.

(13) (a) *SHELXTL v6.12*; BrukerAXS Instruments Inc.: Madison,WI, 2000. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.