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Article

Group 2 and 12 Metal Gallyl Complexes Containing Unsupported Ga−M Covalent Bonds (M = Mg, Ca, Sr, Ba, Zn, Cd)[†]

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Reactions of the anionic gallium(I) heterocycle [:Ga(DAB)]$^-$ (DAB = {N(Dip)C(H)}$_2$, Dip = C_6H_3-Pr^i_2-2,6) with several group 2 and 12 metal halide complexes are reported. Treatment of in situ generated [MI_2(tmeda)$_n$] (M = Ca, Sr, Ba; tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) with 2 equiv of [K(tmeda)][:Ga(DAB)] leads to salt elimination and formation of the neutral metal gallyl complexes *trans*-[M{Ga(DAB)}$_2$(tmeda)$_2$]. Reaction of [(Nacnac)MgI(OEt_2)] (Nanac = {N(Dip)C(Me)}$_2$CH) with [K(tmeda)][:Ga(DAB)] gives [(Nacnac)(κ^1-tmeda)Mg{Ga(DAB)}]. All complexes were crystallographically characterized and display isomerism in solution, which for the latter compound has been investigated by variable-temperature NMR spectroscopy. The 1:1 reactions of [K(tmeda)][:Ga(DAB)] with [MX_2(tmeda)] (M = Zn, X = Br; M = Cd, X = I) yield [(tmeda)MX{Ga(DAB)}], the cadmium example of which is the first molecular complex bearing a Ga−Cd bond. Attempts to reduce these compounds to low-valent species, e.g. [{(DAB)Ga}MM{Ga(DAB)}], were unsuccessful. Treating [(Nacnac)Zn(μ-Br)$_2$Li(OEt_2)$_2$] with [K(tmeda)][:Ga(DAB)] gave [(Nacnac)Zn{Ga(DAB)}], the X-ray crystal structure of which is reported.

Introduction

The chemistry of compounds containing metal−metal bonds has rapidly expanded since Cotton et al. reported the quadruply bonded dianion $[Re_2Cl_8]^{2-}$ in 1964.[1] The field is of enormous fundamental importance and has greatly added to our understanding of, for example, chemical bonding, catalysis, and magnetism.[2] In the past decade, the study of a number of other landmark homonuclear compounds has stimulated interest in the area and, to some extent, has redefined the limits of what is synthetically possible. These include chromium(I) dimers bearing quintuple Cr−Cr bonding interactions, e.g. [Ar′CrCrAr′] (Ar′ = bulky terphenyl),[3] singly bonded zinc(I) dimers, e.g. Cp*ZnZnCp* (Cp* = C_5Me_5),[4] and the first magnesium(I) dimers, e.g. LMgMgL (L = bulky guanidinate or β-diketiminate).[5]

Compounds containing unsupported heteronuclear M−M′ bonds, involving at least one p-block metal, have also been the subject of intensive investigations in recent years.[6] In this realm, we have been systematically examining the coordination chemistry of the anionic gallium(I) heterocycle [:Ga(DAB)]$^-$ (**1**; DAB = {N(Dip)C(H)}$_2$; Dip = C_6H_3-Pr^i_2-2,6),[7,8] which is a valence isoelectronic analogue of the important N-heterocyclic carbene (NHC) class of ligand. The synthetic versatility of this heterocycle has been amply demonstrated by its use as a Ga-donor ligand in the formation of complexes with more than 45 elements from all blocks of the periodic table.[6a,9] Throughout this work, the coordination chemistry of the heterocycle has shown similarities with, but also significant differences from, that of NHCs,[10] gallium diyls (:Ga^IR),[6] and neutral gallium(I) heterocycles, e.g. six-membered [:Ga(Nacnac)] (Nacnac = {N(Dip)C(Me)}$_2$CH)[6a,11,12] and four-membered [:Ga(Giso)] (Giso = {N(Dip)}$_2$CNCy$_2$, Cy = cyclohexyl).[13,14] Of most note is the fact that, like NHCs, the gallium heterocycle **1** is a strong σ-donor ligand (having a largely sp-hybridized Ga lone pair) but a weak π-acceptor (despite having an effectively empty Ga p orbital orthogonal to the heterocycle

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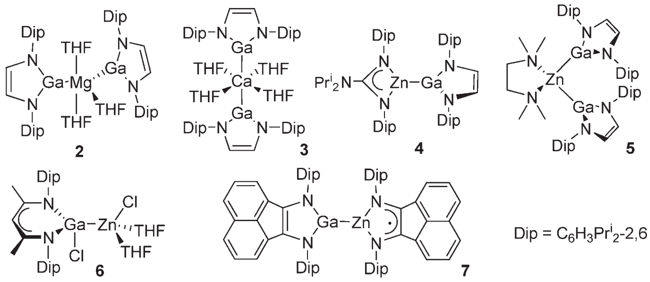
Chart 1



plane). Indeed, the ability of the anionic ligand to form strong polar-covalent bonds with such an array of other metals is derived from its significant nucleophilicity.

Of most relevance to this study are compounds **2**−**5** (Chart 1), which incorporate **1** and which represent the first examples of complexes bearing bonds between gallium and either group 2[9i] or 12[9e] metals. Subsequent to the reports on these compounds, several other studies describing Ga−Zn-bonded species were forthcoming. These included the work of Fischer et al., who demonstrated that the neutral six-membered gallium(I) heterocycle [:Ga(Nacnac)] can oxidatively insert into Zn−Cl or Zn−C bonds to give zinc gallyl species: e.g., **6**.[12e] They also showed that Cp*Ga: can coordinate the Zn^{2+} cation to give the homoleptic complex $[Zn(GaCp^*)_4]^{2+}$.[12e,15] Moreover, Fedushkin et al. prepared the paramagnetic compound **7**, the unpaired electron of which was shown to be located on the Zn heterocycle by EPR and computational studies.[16] To the best of our knowledge, no other examples of complexes bearing covalent gallium−group 2 metal bonds are known, though one report by Roesky et al. detailed several weak donor−acceptor compounds involving Cp*Ga: as the Lewis basic ligand, viz. $[(Cp^*Ga)_m MCp^*_2(THF)_n]$ (M = Ca, Sr, Ba; m = 1, 2; n = 0, 1).[17] Herein, we detail our efforts to expand the ranks of compounds containing bonds between gallium and group 2 or group 12 metals. The preparation and structural characterization of the first Ga−M (M = Cd, Sr, Ba) covalently bonded complexes is reported.

Results and Discussion

Group 2 Chemistry. Previously, we showed that the reactions of [K(tmeda)][**1**] with MI_2 (M = Mg, Ca) in THF do not yield the metal gallyls **2** and **3** but, instead, they give intractable product mixtures.[9i] The eventual preparation of **2** and **3** was achieved by the stepwise reduction of the paramagnetic gallium(III) iodide complex $[I_2Ga(DAB^\bullet)]$ with either elemental magnesium or calcium in THF.[9i] In contrast, reactions between $[I_2Ga(DAB^\bullet)]$ and strontium or barium metal did not give analogues of **3** but instead afforded the partially reduced gallium(II) dimer product $[\{Ga(DAB)\}_2]$. As there are parallels between the chemistry of the group 2 metals and that of the lanthanide (Ln) metals in the +2 oxidation state, the reduction of $[I_2Ga(DAB^\bullet)]$ with elemental Sm, Eu, or Yb was also attempted. Again, complex product mixtures, not including lanthanide gallyl products, were formed in these reactions.[9a] Moreover, lanthanide gallyls were not isolated from reactions of [K(tmeda)][**1**] with LnI_2 in THF. However, when *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) was added to the latter reactions, the octahedral lanthanide gallyl complexes *trans*-$[Ln\{Ga(DAB)\}_2(tmeda)_2]$ (Ln = Sm, Eu, Yb), were obtained in moderate yields.[9a,18] Given this success, we decided to revisit the aforementioned unsuccessful reactions between group 2 metal iodides and [K(tmeda)][**1**], but including tmeda as a coreactant.

Treatment of toluene suspensions of MI_2 (M = Ca, Sr, Ba) with 2 equiv of [K(tmeda)][**1**] in the presence of an excess of tmeda afforded low to good yields of the bis(gallyl) metal complexes **8**−**10** (Scheme 1) after recrystallization of the crude products from diethyl ether. The isolated yield decreases with the molecular weight of the group 2 metal involved. This is possibly due to the expected increasing

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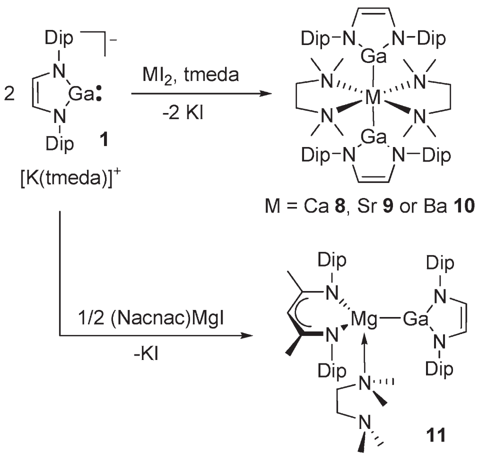
Scheme 1



weakness of the M−Ga bond as the group is descended. In addition, it appears that for the barium gallyl **10** the chelating tmeda ligand is more labile than in **8** and **9**. This is evidenced by the fact that, when **10** was recrystallized from diethyl ether, low yields of the bis(etherate) complex *trans*-[Ba{Ga(DAB)}$_2$(tmeda)(OEt$_2$)$_2$] (see the Supporting Information for crystallographic details) consistently cocrystallized with **10**. Addition of a few drops of tmeda to the diethyl ether solutions of **10** used for recrystallization prevented the formation of *trans*-[Ba{Ga(DAB)}$_2$(tmeda)(OEt$_2$)$_2$]. Attempts to prepare the mono(gallyl) complexes *trans*-[MI{Ga(DAB)}(tmeda)$_2$] using 1:1 reaction stoichiometries yielded approximately 50:50 mixtures of **8**−**10** and unreacted MI$_2$. This suggests that *trans*-[MI{Ga(DAB)}(tmeda)$_2$] species are unstable with respect to redistribution reactions, as is common for other heteroleptic heavier group 2 halide complexes RMX (R = alkyl, amide, etc.; X = halide).[19]

The 2:1 reactions of [K(tmeda)][**1**] with MgI$_2$ in THF were also carried out, though no products analogous to **8**−**10** were forthcoming from these.[20] This is not surprising, given the preference for lower coordination numbers for the smaller metal, as already exhibited by **2**. In order to obtain a mono(gallyl) magnesium complex, the β-diketiminate magnesium complex [(Nacnac)MgI(OEt$_2$)] was treated with 1 equiv of [K(tmeda)][**1**]. This gave a low yield (16%) of **11** (Scheme 1), the tmeda ligand of which is derived from the gallium(I) starting material. Repeating the reaction, but with excess tmeda added to the mixture, did not lead to an increased yield of **11**. It is noteworthy that the only product identified from the analogous 2:1 reaction between [K(tmeda)][**1**] and dimeric [{(Nacnac)CaI(OEt$_2$)}$_2$] was the bis(gallyl) complex **8**, which was isolated in low yield (ca. 15%). It seems likely that a calcium gallyl complex analogous to **11** initially forms and then redistributes to **8** and the known complex [Ca(Nacnac)$_2$].[21] That said, the latter complex was not isolated from the reaction mixture in a pure form.

The spectroscopic data for **8**−**10** are closely related to those for *trans*-[Yb{Ga(DAB)}$_2$(tmeda)$_2$].[9a] That is, the ^{1}H NMR spectrum of each displays a major set of resonances which is consistent with its solid-state structure (vide infra). The spectra also exhibit more complex, minor sets of resonances which possibly correspond to the cis isomers of the compounds (major isomer:minor isomer ratio is ca. 80:20 for all compounds). The most persuasive evidence for this proposal is that in each spectrum there are signals corresponding to two chemically inequivalent sets of backbone protons for the gallyl ligands (which resonate as an AB spin system). The fact that these protons are inequivalent suggests that the bulky heterocyclic ligands of the "cis complex" are interlocked and cannot rotate freely with respect to each other. Very similar spectra have been observed for square-planar transition-metal complexes: e.g., *cis*-[Pd{Ga(DAB)}$_2$(tmeda)].[9d] That the two isomers of **8**−**10** exist in dynamic equilibrium in solution is borne out by the fact that dissolving crystallographically authenticated samples of the trans isomer of each compound in C_6D_6 led to spectra corresponding to isomeric mixtures. Moreover, because only the trans isomer of each complex can be crystallized from solutions of the isomeric mixtures, it seems that this is the thermodynamically favored form of the compounds. The low solubility of **8**−**10** in aromatic solvents at low temperature precluded variable-temperature NMR studies of the equilibrium between the isomers.

Compound **11** also exhibits fluxional behavior in solution, but its enhanced solubility relative to **8**−**10** allowed this to be studied by variable-temperature ^{1}H NMR spectroscopy. At 30 °C the spectrum of the compound exhibits two broad isopropyl methine resonances and singlet resonances for the backbone protons of the DAB and Nacnac ligands (Figure 1). When the solution is cooled to −50 °C, the methine resonances resolve into six broad septet resonances, the individual integration of four of which is slightly greater than that of the other two. The Nacnac backbone resonance splits into two singlets, while the DAB backbone signal separates into a singlet resonance and a broad AB pattern. The relative integrations of the two sets of both Nacnac and DAB backbone resonances is ca. 70:30. A corresponding increase in the number of methyl and aromatic signals is seen upon sample cooling, though the complexity of overlapping signals in these regions make meaningful interpretation difficult. Cooling the sample below −50 °C led to broadening of all observed resonances without further resolution, which is probably a result of a significant increase in the viscosity of the solution and/or partial precipitation of **11** from the solution.[22]

The spectral pattern displayed by the predominant set of resonances marked A in Figure 1 is consistent with the solid-state structure of **11**. We cannot be sure what gives rise to the set of signals marked B in Figure 1, but one possibility is a more symmetrical isomer of **11**, which is in equilibrium with the predominant isomer. This isomer could be a polymer or oligomer/cyclic oligomer of **11**, viz. [{(DAB)GaMg(Nacnac)(μ-tmeda)}$_n$], the trigonal-bipyramidal Mg centers of which are coordinated at their axial sites by two N atoms of bridging tmeda ligands. It is worthy of note that polymeric main-group-metal complexes incorporating bridging tmeda ligands are well represented in the literature.[23] Another possibility is that the B resonances are associated with the three-coordinate complex [(Nacnac)Mg{(DAB)Ga}], which is in equilibrium with **11** and free tmeda. However, this is less likely, as no signals for uncoordinated tmeda were observed

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(22) It is believed that the shoulder on the signal at ca. δ 4.8 ppm in each spectrum is due to a low-level impurity of unknown composition.

(23) A survey of the Cambridge Crystallographic Database (February 2010) revealed 45 crystallographically characterized examples.

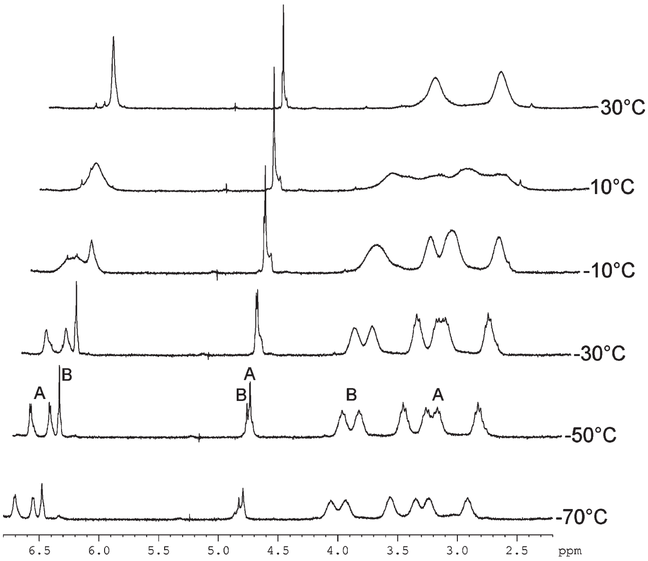

Figure 1. Variable-temperature ^{1}H NMR spectra of [(Nacnac)(κ^1-tmeda)Mg{Ga(DAB)}] (**11**) recorded in d_8-toluene. Resonances associated with the two possible isomers are labeled A and B.

at any temperature. The possibility that the minor set of resonances corresponds to the five-coordinate, tmeda-chelated complex [(Nacnac)Mg{(DAB)Ga}(κ^2-tmeda)] was also considered. This seems unlikely, as the square-based-pyramidal and trigonal-bipyramidal forms of this species (with the gallyl ligand in apical and equatorial sites, respectively) should theoretically exhibit four and eight methine resonances, respectively.

In the solid state, compounds **8**−**10** are isostructural (though not isomorphous). As a result, only the molecular structure of **10** is depicted in Figure 2, while selected geometrical parameters for each compound are collected in Table 1. Compounds **8**−**10** are also isostructural with their lanthanide counterparts *trans*-[Ln{Ga(DAB)}$_2$(tmeda)$_2$] (Ln = Sm, Eu, Yb)[9a] and are closely related to **3**. Their metal centers have distorted-octahedral geometries with the gallyl ligands trans to each other, while the M−Ga and M−N distances in the compounds increase with the molecular weight of the group 2 metal. Perhaps surprisingly, the polar covalent Ga−Ca bonds in **8** are slightly longer than the dative Ga→Ca distance (3.183(2) Å) in the adduct complex [Cp*$_2$Ca(GaCp*)].[17] In contrast, the M−Ga separations in **9** and **10** are significantly shorter than in the higher coordination number complexes [Cp*$_2$Sr(GaCp*)(THF)] (3.4348(7) Å) and [Cp*$_2$Ba(GaCp*)$_2$] (3.591 Å mean).

Compound **11** was also crystallographically characterized, and its molecular structure is depicted in Figure 3. This shows its magnesium center to have a distorted-tetrahedral coordination geometry, which includes ligation by the tmeda molecule through only one of its N centers.[24] Although the Mg−N(5) bond is significantly longer than either of the Mg−N$_{\text{Nacnac}}$ separations, it is at the short end of the reported range for Mg−N$_{\text{tmeda}}$ interactions (2.10−2.52 Å)[25] and should, therefore, be considered relatively strong. The Ga−Mg distance is slightly longer than those in the only other compound exhibiting such bonds, viz. **2** (2.722 Å mean[9i]), despite the higher Mg coordination number in the latter.

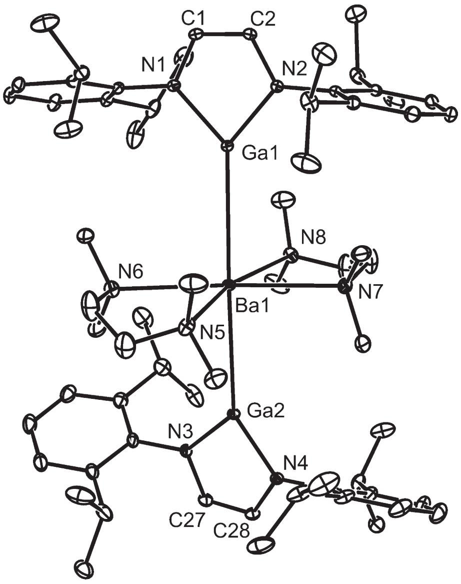

Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of *trans*-[Ba{Ga(DAB)}$_2$(tmeda)$_2$] (**10**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8−10

	8	9	10
Ga−M	3.2568(8) 3.1983(8)	3.324(1)	3.4625(6) 3.4658(6)
M−N	2.574 (mean)	2.680 (mean)	2.868 (mean)
Ga−N	1.936 (mean)	1.932 (mean)	1.941 (mean)
Ga−M−Ga	179.24(2)	180.00	173.62(1)
N−M−N[a]	74.6 (mean)	72.4(2)	64.1 (mean)
N−Ga−N	83.4(1) 83.6(1)	83.7(2)	83.5(1) 83.6(1)

[a] Both N centers from the same tmeda molecule.

Group 12 Chemistry. Although the preparation of heteroleptic gallyl group 2 metal iodides was not successful, it was thought that the expected greater covalency of Ga−group 12 metal bonds might allow the isolation of related heteroleptic group 12 metal gallyl complexes incorporating **1**. Such complexes were seen as potentially useful precursors to access metal(I) dimers of the type [{(DAB)Ga}MM{Ga(DAB)}] via reduction methodologies. In this respect **1** can be regarded as being related to the bulky monodentate terphenyl ligand C$_6$H$_3$(Dip)$_2$-2,6 (Ar′), which has been utilized by Power et al. for the stabilization of the homologous series of complexes [Ar′MMAr′] (M = Zn, Cd, Hg).[26]

Whereas the 1:1 reaction of [K(tmeda)][**1**] with [ZnCl$_2$(tmeda)] previously led to intractable product mixtures,[9e] repeating the reaction with [ZnBr$_2$(tmeda)] afforded a good isolated yield of the heteroleptic complex **12** after recrystallization from hexane (Scheme 2). A moderate isolated yield of the cadmium analogue of this compound, viz. **13**, was obtained using a similar synthetic methodology. In contrast, the 2:1 reaction of [K(tmeda)][**1**] with [CdI$_2$(tmeda)] led to

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[24] Several complexes incorporating κ^1-tmeda ligands have been previously reported. See for example: Iravani, E.; Neumuller, B. *Organometallics* **2003**, *22*, 4129.

[25] As determined from a survey of the Cambridge Crystallographic Database (February 2010).

[26] Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, W. A.; Rivard, E.; Wolf, R.; Fettinger, J. C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 10847.

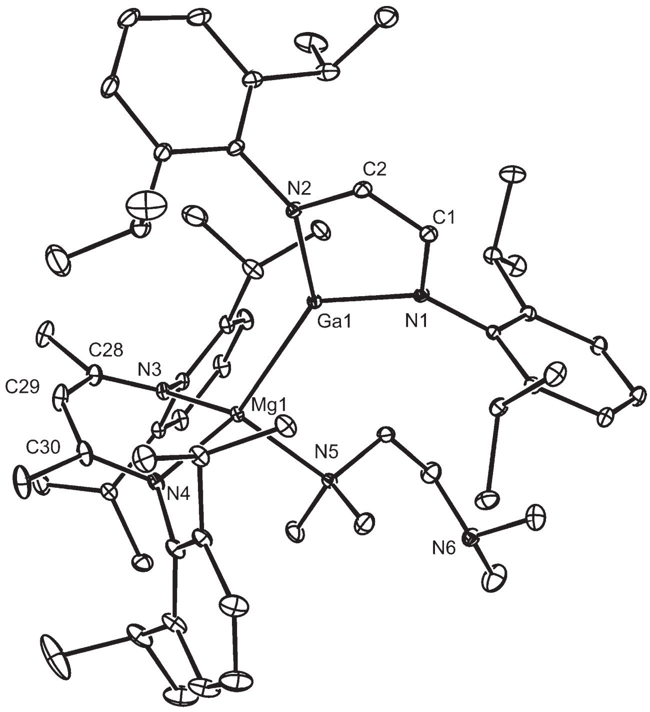


Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [(Nacnac)(κ^1-tmeda)Mg{Ga(DAB)}] (**11**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−N(2) = 1.9238(13), Ga(1)−N(1) = 1.9360(14), Ga(1)−Mg(1) = 2.7470(7), Mg(1)−N(3) = 2.0678(15), Mg(1)−N(4) = 2.0822(14), Mg(1)−N(5) = 2.1733(16); N(2)−Ga(1)−N(1) = 85.55(6), N(2)−Ga(1)−Mg(1) = 139.87(4), N(1)−Ga(1)−Mg(1) = 132.15(4), N(3)−Mg(1)−N(4) = 91.50(6), N(3)−Mg(1)−N(5) = 110.80(6), N(4)−Mg(1)−N(5) = 111.52(6), N(3)−Mg(1)−Ga(1) = 123.35(5), N(4)−Mg(1)−Ga(1) = 118.72(4), N(5)−Mg(1)−Ga(1) = 101.20(4).

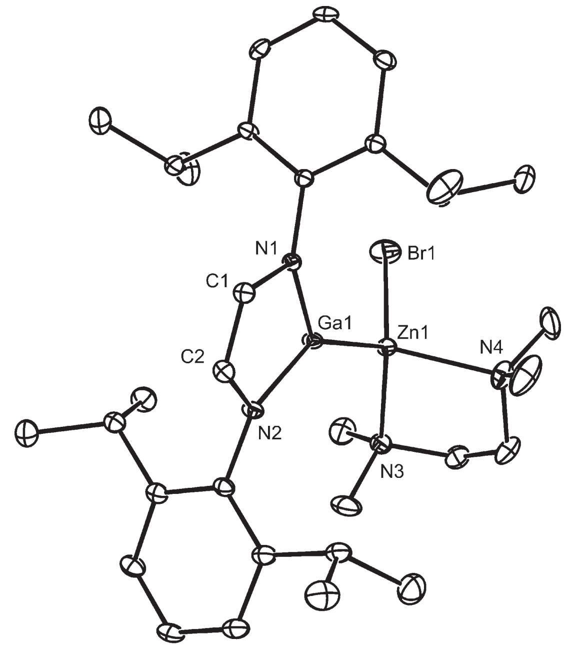
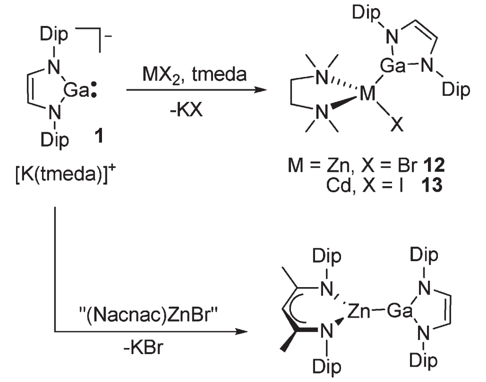


Figure 4. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [(tmeda)ZnBr{Ga(DAB)}] (**12**). Hydrogen atoms are omitted for clarity.

Scheme 2



decomposition with associated deposition of cadmium metal and the formation of the gallium(II) dimer [{Ga(DAB)}$_2$].[27] This outcome attests to the reducing ability of **1**, as does the fact that the 1:1 reaction of [K(tmeda)][**1**] with [HgI$_2$(tmeda)] resulted in the deposition of elemental mercury at ca. −30 °C. A number of attempts were made to reduce **12** and **13** to metal−metal-bonded dimers, [{(DAB)Ga}MM{Ga(DAB)}], using various reagents, e.g. potassium metal, KC$_8$, KH, and LiH. In all cases deposition of the group 12 metal occurred at room temperature. On only one occasion was a soluble product identified in these reactions. This came from the reduction of **12** with LiH in THF and was identified by NMR spectroscopy and X-ray crystallography (see Supporting Information) to be the contact ion pair [Li(THF)$_2${H$_2$Ga(DAB)}]. One explanation for the formation of this compound involves the generation of a zinc hydride intermediate, e.g. [{(DAB)Ga}ZnH(tmeda)] (cf. [{Ar′Zn(μ-H)}$_2$][26]), which decomposes to Zn metal and [HGa(DAB)] via a hydrogen transfer process. The neutral gallium hydride species could then react with excess LiH to give the observed product. No further attempts were made to reduce **12** or **13**.

Attention then turned to the preparation of group 12 analogues of **11**, which are also notionally related to the previously reported complex **4**. Treatment of [(Nacnac)Zn(μ-Br)$_2$Li(OEt$_2$)$_2$] with 1 equiv of [K(tmeda)][**1**] in diethyl ether afforded a good yield of the zinc gallyl complex **14** as an orange crystalline solid (Scheme 2).[28] In contrast, the only product isolated from the equivalent reaction of [K(tmeda)][**1**] with [(Nacnac)Cd(μ-I)$_2$Li(OEt$_2$)$_2$] was the cadmium gallyl **13**, which was obtained in 23% yield.[29] One explanation for the formation of this compound is that the starting material, [(Nacnac)Cd(μ-I)$_2$Li(OEt$_2$)$_2$], is involved in a "Schlenk equilibrium" with [Cd(Nacnac)$_2$], CdI$_2$, and LiI. If so, the preferential reaction of [K(tmeda)][**1**] with CdI$_2$, relative to its reaction with bulkier [(Nacnac)Cd(μ-I)$_2$Li(OEt$_2$)$_2$], could shift the equilibrium in favor of CdI$_2$, which in turn would lead to the formation of more **13**. No further attempts were made to prepare a cadmium

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[27] Pott, T.; Jutzi, P.; Schoeller, W. W.; Stammler, A.; Stammler, H.-G. *Organometallics* **2001**, *20*, 5492.

[28] N.B. Related zinc boryl complexes, e.g. [Zn{B(DAB)}$_2$], have been reported: Kajiwara, T.; Terabayashi, T.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6606.

[29] N.B. A small amount of the unusual dicadmium complex [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt$_2$)$_3$] was isolated from one preparation of [(Nacnac)Cd(μ-I)$_2$Li(OEt$_2$)$_2$] using the literature procedure.[33] Crystallographic details of [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt$_2$)$_3$] can be found in the Supporting Information.

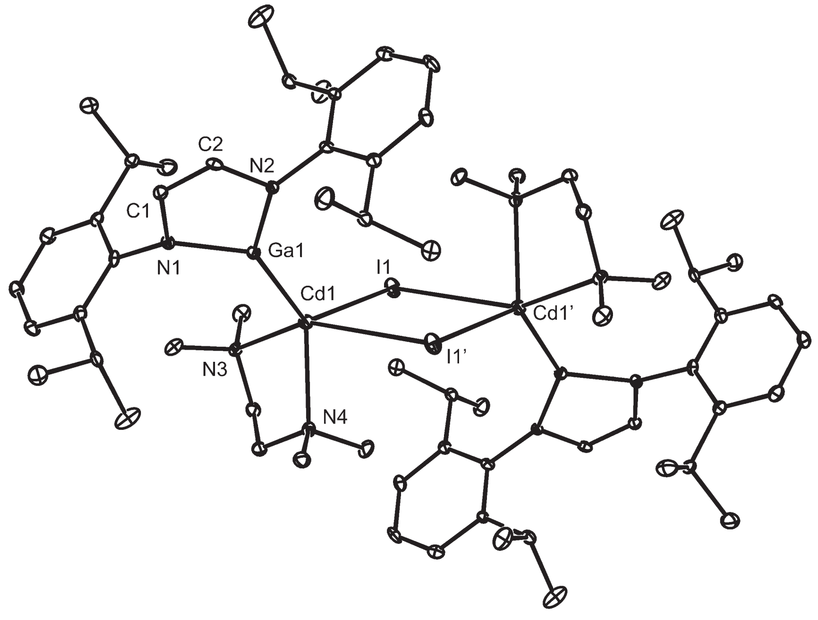

Figure 5. Thermal ellipsoid plot (25% probability surface) of the molecular structure of the dimeric modification of [(tmeda)CdI{Ga(DAB)}] (**13**). Hydrogen atoms are omitted for clarity. Symmetry operation: (′) $2 - x, -y, -z$.

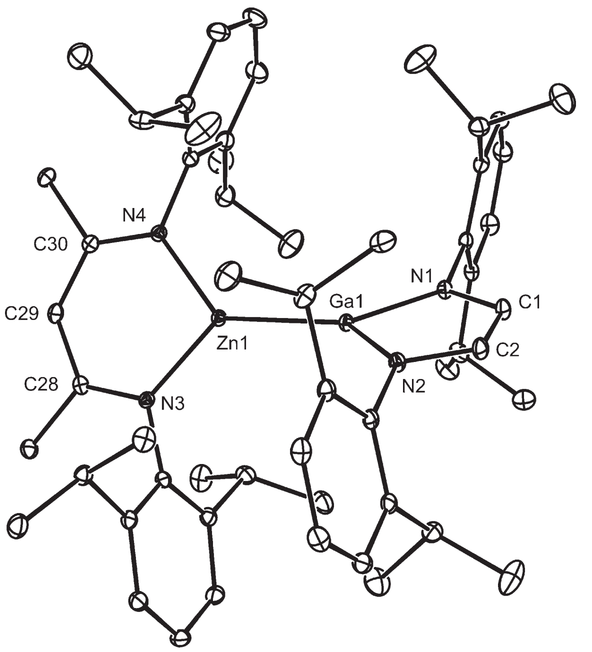

Figure 6. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [(Nacnac)Zn{Ga(DAB)}] (**14**). Hydrogen atoms are omitted for clarity.

analogue of **14**. It is of note, however, that although **14** is related to the magnesium gallyl **11**, it does not incorporate a tmeda ligand, even when an excess of tmeda was added to the reaction mixture that generated it. This is most likely because of the lower Lewis acidity of Zn^{2+} relative to Mg^{2+}.

All of the complexes **12**−**14** are thermally stable at room temperature, though the cadmium gallyl **13** slowly decomposes above 50 °C with the deposition of cadmium metal. The ^{1}H and ^{13}C NMR spectroscopic data for **12**−**14** are fully consistent with their solid-state structures (vide infra) and do not show any indication of the isomerism and/or fluxional behavior exhibited by the group 2 gallyl complexes **8**−**11**. No signal was observed in the ^{113}Cd NMR spectrum of **13**, which is not surprising, as the cadmium center of this compound is coordinated by quadrupolar gallium and iodine atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 12−14

	12	**13**[a]	**13**[b]	**14**
Ga−M	2.3829(8)	2.509(1)	2.5479(9)	2.3841(6)
M−N	2.142(3)	2.354(5)	2.384(4)	1.958(2)
	2.144(3)	2.376(5)	2.500(4)	1.958(2)
Ga−N	1.874(2)	1.870(4)	1.885(4)	1.885(2)
	1.879(2)	1.871(4)	1.899(4)	1.885(2)
M−X[c]	2.3598(7)	2.7202(8)	2.7980(8)	
			3.497(1)	
N−M−N	85.7(1)	78.7(2)	76.0(1)	98.17(6)
N−Ga−N	86.8(1)	86.8(2)	86.9(2)	87.13(7)

[a] Monomeric modification; data for one of the two crystallographically independent molecules in the asymmetric unit are shown. [b] Dimeric modification. [c] X = Br or I.

In the solid state, the monomeric compounds **12** and **13** are isostructural, and therefore, only the molecular structure of **12** is depicted in Figure 4. Interestingly, compound **13** can also crystallize as an unsymmetrically iodide bridged dimer (Figure 5). The fact that this compound can cocrystallize as either a monomer or a dimer suggests that its energy of dimerization is low: i.e., of a similar order as crystal-packing forces. Selected metrical parameters for **12**, both structural modifications of **13**, and the zinc gallyl complex **14** (Figure 6) can be found in Table 2. The Zn and Cd centers of monomeric **12** and **13** have distorted-tetrahedral coordination geometries, whereas the Cd centers of dimeric **13** are distorted trigonal bipyramidal with N(3) and I(1)′ taking up the axial sites. In contrast, the Zn atom of **14** has a trigonal-planar coordination environment, while the dihedral angle between its two heterocycles is 55.6°. The gallium atoms in all the complexes in this study have trigonal-planar geometries. However, the N−Ga−N angles exhibited by the group 12 complexes are significantly more obtuse than those of the group 2 complexes. This observation is in line with the expected greater covalent nature of the group 12 metal−Ga bonds. The Ga−Zn distances in **12** and **14** are close to those reported for **4** and **6** but slightly shorter than those of the more sterically crowded species **5** (2.440 Å mean[9e]). Compound **13** possesses the first structurally authenticated Ga−Cd bonds in a molecular compound, the lengths of which in each of its structural modifications are well within the sum of the covalent radii (2.66 Å) for the two elements.[30] Both the Zn−Br separation in **12** and the Cd−I distances in **13** are in the normal ranges for such interactions.[25]

Conclusions

In summary, the ability of the gallyl anion [:Ga(DAB)]$^-$ (**1**) to participate in salt metathesis reactions with a range of group 2 and 12 metal halide complexes has been demonstrated. These reactions have given rise to a variety of metal gallyl compounds possessing polar covalent M−Ga (M = Mg, Ca, Sr, Ba, Zn, Cd) bonds, including the first example of a cadmium−gallium-bonded molecular species, [(tmeda)CdI{Ga(DAB)}]. Crystallographic data on the compounds have provided evidence that the Ga−M interactions are more polar for the group 2 metals than for the group 12 metals. Although attempts to stabilize low-valent group 12 complexes using the bulky gallyl ligand **1** have not so far been successful, we continue to pursue this goal.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen. Toluene, THF, and hexane were distilled over potassium while diethyl ether was distilled over Na/K alloy. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker DXP300 and DRX400 spectrometers and were referenced to the resonances of the solvents used. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were carried out by Campbell Microanalytical, Otago, New Zealand. Reproducible microanalyses could not be obtained for the group 2 gallyl complexes, due to their extreme air and moisture sensitivity. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds [K(tmeda)][**1**],[7] [(Nacnac)MgI(OEt$_2$)],[31] [ZnBr$_2$(tmeda)],[32] [CdI$_2$(tmeda)],[32] and [(Nacnac)Zn(μ-Br)$_2$Li(OEt$_2$)$_2$][33] were synthesized by variations of literature procedures. [CaI$_2$(OEt$_2$)$_n$] and [MI$_2$(THF)$_n$] (M = Sr, Ba) were prepared by reacting the freshly filed metal with 1 equiv of diiodine in either diethyl ether or THF for 5 days. All other reagents were used as received.

Preparation of *trans*-[Ca{Ga(DAB)}$_2$(tmeda)$_2$] (8). A solution of [K(tmeda)][:Ga(DAB)] (0.30 g, 0.50 mmol) in toluene (15 mL) was added over 5 min to a suspension of [CaI$_2$(OEt$_2$)$_n$] (0.25 mmol) in toluene (45 mL) and tmeda (1.0 mL, 6.67 mmol) at −80 °C. The mixture was slowly warmed to room temperature and stirred for 15 h. All volatiles were then removed in vacuo, the residue was extracted into diethyl ether (25 mL), and the extract was filtered. The filtrate was stored at −30 °C overnight, yielding orange crystals of **8** (0.21 g, 75%). Mp: 163−165 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K; major isomer): δ 1.26 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.45 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.89 (br, 32 H, tmeda), 3.95 (sept, 8 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 6.55 (s, 4H, NC*H*), 7.02−7.34 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 23.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 47.1 (N(*C*H$_3$)$_2$), 56.1 (N*C*H$_2$), 117.2 (N*C*H), 122.6, 125.0, 145.7, 151.2 (Ar-*C*). IR (Nujol): 1587 w, 1378 s, 1356 s, 1319 m, 1256 m, 1103 m, 754 m cm^{-1}. MS (EI 70 eV; *m*/*z* (%)): 445.2 (Ga(DAB)$^+$, 30), 378.1 (DABH$^+$, 35), 333.3 (DAB − Pr^{i+}, 100).

Preparation of *trans*-[Sr{Ga(DAB)}$_2$(tmeda)$_2$] (9). A procedure similar to that used for the preparation of **8** was employed for the synthesis of **9**: orange crystals (yield 0.14 g, 47%). Mp: 175−180 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K; major isomer): δ 1.25 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.46 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.90 (br, 32 H, tmeda), 3.55 (sept, 8 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 6.57 (s, 4H, NC*H*), 7.00−7.34 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 23.9 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 45.7 (N(*C*H$_3$)$_2$), 65.7 (N*C*H$_2$), 117.1 (N*C*H), 122.5, 124.9, 142.6, 145.0 (Ar-*C*). IR (Nujol): 1587 w, 1378 s, 1356 s, 1320 m, 1258 m, 1103 m, 754 m cm^{-1}. MS (EI 70 eV; *m*/*z* (%)): 445.2 (Ga(DAB)$^+$, 27), 378.1 (DABH$^+$, 12), 333.3 (DAB − Pr^{i+}, 100).

Preparation of *trans*-[Ba{Ga(DAB)}$_2$(tmeda)$_2$] (10). A procedure similar to that used for the preparation of **8** was employed for the synthesis of **10**: red-orange crystals (yield 0.045 g, 14%). Mp: 178−182 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K; major isomer): δ 1.33 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.47 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 2.15 (v br, 32 H, tmeda), 3.52 (sept, 8 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 6.61 (s, 4H, NC*H*), 7.02−7.34 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 24.2 (CH(*C*H$_3$)$_2$), 26.3 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 46.0 (v br, N(*C*H$_3$)$_2$), 67.0 (v br, N*C*H$_2$), 117.3 (N*C*H), 122.7, 125.0, 142.9 (Ar-*C*), *ipso* Ar-*C* not observed. IR (Nujol): 1586 w, 1377 s, 1356 s, 1319 m, 1261 m, 1101 m, 754 m cm^{-1}. MS (EI 70 eV; *m*/*z* (%)): 445.2 (Ga(DAB)$^+$, 100), 378.1 (DABH$^+$, 15), 333.3 (DAB − Pr^{i+}, 90).

N.B. If tmeda is not added to the filtered diethyl ether extract of **10** prior to cooling to −30 °C, *trans*-[Ba{Ga(DAB)}$_2$(tmeda)(OEt$_2$)$_2$] reproducibly cocrystallizes with **10** in low yield. No spectroscopic data have been obtained for this compound.

Preparation of [(Nacnac)(κ^1-tmeda)Mg{Ga(DAB)}] (11). A solution of [K(tmeda)][:Ga(DAB)] (0.37 g, 0.61 mmol) in toluene (20 mL) was added over 5 min to a solution of [(Nacnac)MgI(OEt$_2$)] (0.40 g, 0.62 mmol) in toluene (45 mL) at −80 °C. The mixture was slowly warmed to room temperature and stirred for 15 h. All volatiles were then removed in vacuo, the residue was extracted into hexane (20 mL), and the extract was filtered. The filtrate was then stored at −30 °C overnight, yielding orange crystals of **11** (0.10 g, 16%). Mp: 300−305 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.09 (br, 36 H, CH(C*H*$_3$)$_2$), 1.35 (br, 12 H, CH(C*H*$_3$)$_2$), 1.85 (br, 6 H, NCC*H*$_3$), 1.90 (br, 16 H, tmeda), 3.02 (br, 4 H, Nacnac C*H*(CH$_3$)$_2$), 3.56 (br, 4 H, DAB C*H*(CH$_3$)$_2$), 4.84 (br s, 2 H, NCC*H*), 6.26 (br s, 2 H, NC*H*), 7.00−7.15 (m, 12 H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 23.3, 24.2, 24.6, 25.0, 25.8 (5 × br, 4 × CH(*C*H$_3$)$_2$, 1 × C*C*H$_3$), 28.3, 28.5 (2 × br, 2 × *C*H(CH$_3$)$_2$), 44.8 (v br, N(*C*H$_3$)$_2$), 54.1 (v br, N*C*H$_2$), 95.4 (br, *C*H), 117.1 (N*C*H), 122.8, 123.4, 124.0, 124.4, 126.2, 141.9, 145.3, 148.3 (8 × br, Ar-*C*), 171.2 (*C*CH$_3$). IR (Nujol): 1520 w, 1377 s, 1364 m, 1316 m, 125 m, 1102 m, 796 m, 756 m cm^{-1}. MS (EI 70 eV; *m*/*z* (%)): 888.2 (M$^+$ − tmeda, 21), 445.2 (Ga(DAB)$^+$, 100), 418.4 (NacnacH$^+$, 22), 403.3 (NacnacH$^+$ − CH$_3$, 45), 333.3 (DAB − Pr^{i+}, 90).

Preparation of [(tmeda)ZnBr{Ga(DAB)}] (12). To a solution of [ZnBr$_2$(TMEDA)] (0.17 g, 0.50 mmol) in THF (20 mL) at −80 °C was added [K(tmeda)][:Ga(DAB)] (0.30 g, 0.50 mmol) in THF (20 mL). The reaction mixture was warmed to ambient temperature over 4 h, whereupon volatiles were removed in vacuo. The yellow residue was extracted into hexane (50 mL), the extract was filtered, and the filtrate was stored at −30 °C

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[31] (a) Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. *Chem. Eur. J.* **2010**, *16*, 938. (b) Prust, J.; Most, K.; Müller, I.; Alexopoulos, E.; Stasch, A.; Uson, I.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2032.

[32] Abraham, M. H.; Parret, F. W. *Can. J. Chem.* **1970**, *48*, 181.

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Table 3. Summary of Crystallographic Data for Compounds 8−14

	8	**9**	**10**·OEt$_2$	**11**
empirical formula	$C_{64}H_{104}CaGa_2N_8$	$C_{64}H_{104}Ga_2N_8Sr$	$C_{68}H_{114}BaGa_2N_8O$	$C_{61}H_{93}GaMgN_6$
formula wt	1165.07	1212.61	1336.45	1004.44
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$C2/c$	$P2_12_12_1$	Cc
a (Å)	21.835(4)	29.407(6)	18.122(4)	22.756(5)
b (Å)	14.049(3)	14.031(3)	18.522(4)	14.259(3)
c (Å)	21.549(4)	21.729(4)	21.842(4)	21.172(4)
α (deg)	90	90	90	90
β (deg)	95.48(3)	131.56(3)	90	90
γ (deg)	90	90	90	90
V (Å^3)	6580(2)	6709(2)	7331(3)	5894(2)
Z	4	4	4	4
ρ(calcd) (g cm^{-3})	1.176	1.201	1.211	1.132
μ (mm^{-1})	0.939	1.631	1.304	0.519
F(000)	2504	2576	2816	2176
cryst size (mm)	0.40 × 0.15 × 0.10	0.15 × 0.12 × 0.10	0.25 × 0.20 × 0.18	0.30 × 0.25 × 0.20
θ range (deg)	2.92−26.00	3.13−25.00	2.92−25.35	2.14−30.00
no. of rflns collected	24 843	11 084	13 382	48 551
R_{int}	0.0613	0.0561	0.0000	0.0276
no. of unique rflns	12 905	5872	13 382	13 672
goodness of fit on F^2	1.031	1.039	1.038	1.028
R1 indices ($I > 2\sigma(I)$)[a]	0.0524	0.0679	0.0314	0.0287
wR2 indices (all data)[b]	0.1417	0.1942	0.0708	0.0745
	12	**13**·0.25(hexane)[c]	**13**[d]	**14**
empirical formula	$C_{32}H_{52}BrGaN_4Zn$	$C_{33.5}H_{55.5}CdGaIN_4$	$C_{32}H_{52}CdGaIN_4$	$C_{55}H_{77}GaN_4Zn$
formula wt	707.78	823.34	801.80	929.30
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\overline{1}$	$P2_1/n$	$P2_1/n$
a (Å)	12.837(3)	11.673(2)	11.368(2)	11.971(2)
b (Å)	13.316(3)	17.925(4)	14.249(3)	21.713(4)
c (Å)	20.512(4)	19.481(4)	21.409(4)	20.586(4)
α (deg)	90	104.83(3)	90	90
β (deg)	92.83(3)	98.02(3)	95.88(3)	100.64(3)
γ (deg)	90	91.53(3)	90	90
V (Å^3)	3502.2	3893.5(13)	3449.9(12)	5258.7(18)
Z	4	4	4	4
ρ(calcd) (g cm^{-3})	1.342	1.405	1.544	1.174
μ (mm^{-1})	2.620	2.056	2.318	1.005
F(000)	1472	1666	1616	1984
cryst size (mm)	0.35 × 0.25 × 0.22	0.25 × 0.12 × 0.10	0.08 × 0.06 × 0.04	0.20 × 0.15 × 0.12
θ range (deg)	2.92−27.00	2.60−24.98	2.56−24.88	2.55−28.00
no. of rflns collected	14 440	24 058	11 543	22 159
R_{int}	0.0363	0.0463	0.0982	0.0288
no. of unique rflns	7632	13 171	5960	12 677
goodness of fit on F^2	1.026	1.025	1.038	1.028
R1 indices ($I > 2\sigma(I)$)[a]	0.0418	0.0469	0.0555	0.0370
wR2 indices (all data)[b]	0.1012	0.1038	0.0702	0.0887

[a] $R1(F) = \{\sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. [b] $wR2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o{}^2|^2\}^{1/2}$, where w is the weight given each reflection. [c] Monomeric. [d] Dimeric.

overnight to yield yellow crystals of **12** (0.21 g, 60%). Mp: 124−126 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 1.45 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CH(CH_3)$_2$), 1.49 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CH(CH_3)$_2$), 1.65 (s, 12 H, N(CH_3)$_2$), 1.97 (s, 4 H, NCH_2), 3.94 (sept, $^3J_{HH} = 6.9$ Hz, 4 H, CH(CH$_3$)$_2$), 6.61 (s, 2 H, NCH), 7.22−7.35 (m, 6 H, Ar-H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 25.2 (CH(CH$_3$)$_2$), 25.4 (CH(CH$_3$)$_2$), 28.2 (CH(CH$_3$)$_2$), 47.6 (N(CH$_3$)$_2$), 56.2 (NCH$_2$), 122.6 (NCH), 123.0, 124.9, 145.6, 146.9 (Ar-C). IR (Nujol): 1657 w, 1557 w, 1377 m, 1359 m, 1287 w, 1260 m, 1101 m, 1023 m, 797 m, 760 m cm^{-1}. MS (EI 70 eV; m/z (%)): 706.1, (M$^+$, 4), 445.2 (Ga(DAB)$^+$, 15), 378.1 (DABH$^+$, 48), 333.3 (DAB − Pr^{i+}, 100). Anal. Calcd for $C_{32}H_{52}BrGaN_4Zn$: C, 54.30; H, 7.41; N, 7.92. Found: C, 53.92; H, 7.27; N, 7.77.

Preparation of [(tmeda)CdI{Ga(DAB)}] (13). To a solution of [CdI$_2$(TMEDA)] (0.24 g, 0.50 mmol) in THF (20 mL) at −80 °C was added [K(tmeda)][:Ga(DAB)] (0.30 g, 0.50 mmol) in THF (20 mL). The reaction mixture was warmed to ambient temperature over 4 h, whereupon volatiles were removed in vacuo. The orange residue was extracted into hexane (30 mL), the extract was filtered, and the filtrate was stored at −30 °C overnight to yield orange crystals of **13** (0.15 g, 38%). Mp: 130−135 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 1.43 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CH(CH_3)$_2$), 1.48 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CH(CH_3)$_2$), 1.65 (s, 12 H, N(CH_3)$_2$), 1.94 (s, 4 H, NCH_2), 3.86 (sept, $^3J_{HH} = 6.9$ Hz, 4 H, CH(CH$_3$)$_2$), 6.62 (s, 2 H, NCH), 7.22−7.33 (m, 6 H, Ar-H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 25.0 (CH(CH$_3$)$_2$), 25.6 (CH(CH$_3$)$_2$), 28.3 (CH(CH$_3$)$_2$), 48.0 (N(CH$_3$)$_2$), 56.6 (NCH$_2$), 122.9 (NCH), 123.0, 125.3, 145.6, 147.0 (Ar-C). IR (Nujol): 1660 w, 1558 w, 1378 m, 1355 m, 1285 w, 1255 m, 1101 m, 1026 m, 793 m, 758 m cm^{-1}. MS (EI 70 eV; m/z (%)): 445.2 (Ga(DAB)$^+$, 100), 378.1 (DABH$^+$, 15), 333.3 (DAB − Pr^{i+}, 53). Anal. Calcd for $C_{32}H_{52}IGaN_4Cd$: C, 47.93; H, 6.54; N, 6.99. Found: C, 47.57; H, 6.48; N, 6.83.

Preparation of [(Nacnac)Zn{Ga(DAB)}] (14). A solution of [K(tmeda)][:Ga(DAB)] (0.22 g, 0.36 mmol) in diethyl ether (20 mL) was added over 5 min to a solution of [(Nacnac)Zn(μ-Br)$_2$Li(OEt$_2$)$_2$] (0.29 g, 0.36 mmol) in diethyl ether (20 mL) at −80 °C. The mixture was slowly warmed to room temperature, whereupon volatiles were removed in vacuo, leaving an orange residue. This was extracted into hexane (35 mL) and the extract filtered. The filtrate was stored at −30 °C overnight, yielding orange crystals of **14** (0.17 g, 51%). Mp: 140−142 °C. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 1.04 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$), 1.51 (s, 6 H, NCCH_3), 3.04 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH_3)$_2$), 3.47 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH_3)$_2$), 5.02 (s, 1 H, NCC*H*), 6.28 (s, 2 H, NC*H*), 7.05−7.30 (m, 12 H, Ar-*H*). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 23.2, 23.8, 24.3, 24.8, 25.4 (4 × CH(CH_3)$_2$, 1 × CCH_3), 28.7, 28.8 (2 × *C*H(CH_3)$_2$), 97.9 (NC*C*H), 123.2 (N*C*H), 124.0, 124.2, 125.2, 125.8, 126.9, 141.8, 145.4, 148.5 (8 × br, Ar-*C*), 169.1 (*C*CH_3). IR (Nujol): 1656 w, 1519 m, 1380 m, 1317 m, 1261 m, 1179 m, 1159 m, 1099 m, 1022 m, 796 m, 758 m cm^{-1}. MS (EI 70 eV; *m*/*z* (%)): 928.5 (M^+, 100), 481.3 ((Nacnac)Zn^+, 49), 445.2 (Ga(DAB)$^+$, 12), 403.3 (NacnacH^+ − CH_3, 9), 333.3 (DAB − Pr^{i+}, 15). High-resolution MS (EI; *m*/*z*): calcd for $C_{55}H_{77}N_4GaZn$, 926.4690; found, 926.4688. Anal. Calcd for $C_{55}H_{77}N_4GaZn$: C, 71.08; H, 8.35; N, 6.03. Found: C, 70.71; H, 8.16; N, 5.93.

X-ray Crystallography. Crystals of **8**−**12**, two structural modifications of **13**, **14**, *trans*-[Ba{Ga(DAB)}$_2$(tmeda)$_2$], [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt_2)$_3$], and [Li(THF)$_2${H_2Ga(DAB)}] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.710 73 Å). The data were collected at 123 K, and the structures were solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97[34]) using all unique data. All non-hydrogen atoms are anisotropic, with hydrogen atoms (except the hydride ligands in the structure of [Li(THF)$_2${H_2Ga(DAB)}]) included in calculated positions (riding model). There are two crystallographically independent molecules of **13** in the asymmetric unit of the monomeric structural modification of the compound. There are no significant geometric differences between them. The absolute structure parameters for the crystal structures of **10** and **11** are −0.013(9) and 0.000(4), respectively. Crystal data and details of data collections and refinements are given in Table 3. CCDC numbers: 767655−767665.

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Supporting Information Available: CIF files giving crystallographic data for **8**−**12**, two structural modifications of **13**, **14**, *trans*-[Ba{Ga(DAB)}$_2$(tmeda)$_2$], [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt_2)$_3$], and [Li(THF)$_2${H_2Ga(DAB)}], figures giving ORTEP diagrams for **8**, **9**, the monomeric structural modification of **13**, *trans*-[Ba{Ga(DAB)}$_2$(tmeda)(OEt_2)$_2$], [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt_2)$_3$], and [Li(THF)$_2${H_2Ga(DAB)}], a table giving details of the crystallographic experiments and selected metrical parameters for *trans*-[Ba{Ga(DAB)}$_2$(tmeda)(OEt_2)$_2$], [(Nacnac)CdI(μ-I)CdI(μ-I)Li(OEt_2)$_3$], and [Li(THF)$_2${H_2Ga(DAB)}], and text giving spectroscopic data for [Li(THF)$_2${H_2Ga(DAB)}]. This material is available free of charge via the Internet at http://pubs.acs.org.

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[34] Sheldrick, G. M. *SHELX-97*; University of Göttingen, Göttingen, Germany, 1997.