

## Synthesis, Structural Characterization, and Theoretical Studies of Complexes of Magnesium and Calcium with Gallium Heterocycles

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The magnesium- and calcium-gallium heterocycle complexes  $[\text{Mg}\{\text{Ga}[(\text{ArNCH})_2]\}_2(\text{THF})_3]$  and  $[\text{Ca}\{\text{Ga}[(\text{ArNCR})_2]\}_2(\text{THF})_4]$ ,  $\text{R} = \text{H}$  or  $\text{Me}$ ,  $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ , have been prepared via the reduction of  $[\text{I}_2\text{Ga}\{\text{ArNCR})_2\}]$  with the group 2 metal in tetrahydrofuran. The mechanisms of the reactions have been elucidated, and the crystal structures of the complexes exhibit the first structurally authenticated Ga–Mg and Ga–Ca bonds in molecular species. Theoretical studies suggest that the heterocycle–group 2 metal interactions have significant ionic character.

In recent years, the coordination chemistry of compounds containing a Lewis basic gallium(I) center with a singlet lone pair has rapidly expanded. The most widely studied compounds in this respect are gallium diyls,  $:\text{GaR}$ ,  $\text{R} = \text{alkyl}$ ,  $\text{aryl}$ , substituted cyclopentadienyl, etc., which have been utilized in the formation of a fascinating array of transition-metal complexes.<sup>1</sup> Similarly, the coordination chemistry of the neutral six-membered heterocycle  $[\text{Ga}\{\text{ArNCMe}_2\text{CH}\}]$ ,  $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ ,<sup>2</sup> is starting to emerge.<sup>3</sup> Our contribution to this area has come from the related anionic five-membered heterocycle  $[\text{Ga}\{\text{ArNCH})_2\}]^-$ , which we have used to form a variety of p- and d-block complexes via coordination, salt elimination, and redox reactions.<sup>3,4</sup> This heterocycle is a valence isoelectronic analogue of the N-heterocyclic carbene (NHC) class of ligand and like NHCs has proved its worth

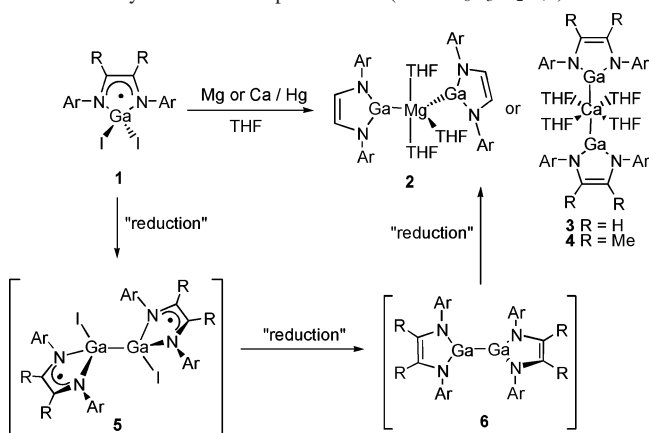
in the stabilization of low-oxidation-state and/or thermally labile metal fragments. Several potassium salts of the anion have been prepared by reduction of the paramagnetic gallium(III) heterocycle  $[\text{I}_2\text{Ga}\{\text{ArNCH})_2\}]^+$  with potassium metal. These include the ion separate species  $[\text{Ga}\{\text{ArNCH})_2\}]^- [\text{K}_2(18\text{-crown-6})_3]$  and the dimeric complexes  $[\{\text{L}\text{K}\}\text{Ga}\{\text{ArNCH})_2\}]_2$ ,  $\text{L} = \text{tmeda}$  or  $\text{OEt}_2$ .<sup>6</sup> In the latter complexes, the interactions between the potassium and gallium centers are largely electrostatic in nature. Considering the propensity of NHCs to form complexes with group 2 metal fragments,<sup>7</sup> we decided to investigate the possibility of extending the s-block coordination chemistry of  $[\text{Ga}\{\text{ArNCH})_2\}]^-$  to the alkaline-earth metals. This has led to complexes that, to the best of our knowledge, display the first crystallographically characterized direct Mg–Ga and Ca–Ga bonds in molecular species.

Initially, the reactivity of  $[\{\text{tmeda}\text{K}\}\text{Ga}\{\text{ArNCH})_2\}]_2$  toward anhydrous  $\text{MI}_2$ ,  $\text{M} = \text{Mg}$ ,  $\text{Ca}$ , or  $\text{Sr}$ , was explored, but in all cases intractable mixtures of products were obtained. More success was had by reducing the paramagnetic gallium(III) heterocycles, **1**, with a large excess of either magnesium or calcium metal in the presence of mercury. These reactions afforded the magnesium- and calcium-gallium heterocycle complexes, **2–4**, in low to good yields (Scheme 1).<sup>8</sup> It is apparent that the reactions' mechanisms involve the stepwise reduction of **1**, to first the paramagnetic gallium(II) dimer, **5**,<sup>9</sup> and then the diamagnetic dimer, **6**.<sup>10</sup> The group 2 metal then oxidatively inserts into the Ga–Ga bond of **6** to give the observed products. Evidence for this proposal comes from the fact that both **5** and **6** can be isolated from these reactions if they are worked up in their early stages (after ca. 3 h). In addition, when pure samples of **5**

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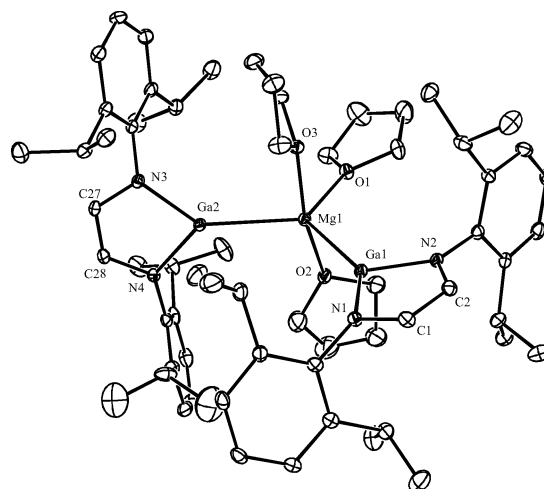
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**Scheme 1** Syntheses of Compounds 2–4 (Ar = C<sub>6</sub>H<sub>3</sub>Pr<sup>2</sup>-2,6)

or 6 (R = H) were reacted with magnesium or calcium metal in tetrahydrofuran (THF), complexes 2 and 3 were formed in yields similar to those of the reactions with 1 (R = H).

Surprisingly, when 1 (R = H) was treated with excesses of either strontium or barium metal in the presence of mercury, the reactions did not proceed past the doubly reduced product, 6 (R = H), even when they were carried out over extended periods (1 week), at elevated temperatures



**Figure 1.** Molecular structure of 2. Selected bond lengths (Å) and angles (deg): Ga1–N2 1.918(3), Ga1–N1 1.921(3), Ga1–Mg1 2.7174(15), Ga2–N4 1.916(3), Ga2–N3 1.923(3), Ga2–Mg1 2.7269(14), Mg1–O1 2.056(3), Mg1–O2 2.135(3), Mg1–O3 2.158(3), N2–Ga1–N1 84.56(15), N4–Ga2–N3 84.09(15), O1–Mg1–O2 83.12(14), O1–Mg1–O3 83.66(13), O2–Mg1–O3 166.63(14), O1–Mg1–Ga1 116.91(10), O2–Mg1–Ga1 92.71(10), O3–Mg1–Ga1 91.51(9), O1–Mg1–Ga2 115.75(11), O2–Mg1–Ga2 94.25(9), O3–Mg1–Ga2 93.26(9), Ga1–Mg1–Ga2 127.32(6).

(ca. 50 °C), and under ultrasonic conditions. This seems counterintuitive because the heavier elements are more electropositive than the lighter metals. It is not known why these differences occur, but they cannot be due to the inactivity of the surfaces of the metals because reduction of 1 (R = H) to 6 (R = H) occurs as readily as it does in the reactions that gave 2 and 3.

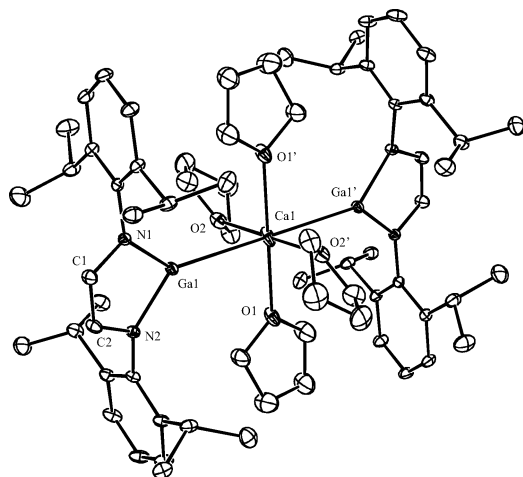
Compounds 2–4 are extremely oxygen- and moisture-sensitive but are thermally robust. Their spectroscopic data are consistent with their proposed formulations and will not be commented on here. An X-ray crystal structure of each complex was obtained, and the molecular structures of 2 and 3 are depicted in Figures 1 and 2, respectively.<sup>11</sup> That for 4 closely resembles the structure of 3 and is included in the Supporting Information. The magnesium center of 2 possesses a distorted trigonal-bipyramidal geometry with both gallium heterocyclic ligands in equatorial sites and O2 and O3 in axial positions. In contrast, the calcium center of 3 has an octahedral coordination environment with the gallium heterocyclic ligands trans to each other. These differences presumably result from the greater covalent radius of the heavier metal. The geometries of the coordinated gallium

(8) Experimental data for 2: To a mixture of magnesium metal (1.00 g, 42 mmol) and mercury (3 drops) in THF (20 cm<sup>3</sup>) was added a solution of [I<sub>2</sub>Ga{(ArNCH)<sub>2</sub>}] (2.00 g, 2.87 mmol) in THF (40 cm<sup>3</sup>) at –78 °C. The resultant suspension was warmed to room temperature and stirred for 4 days. Upon filtration and removal of volatiles from the filtrate in vacuo, the residue was extracted with hexane (30 cm<sup>3</sup>). The extract was then filtered and the filtrate cooled to –30 °C overnight, yielding orange crystals of 2 (0.41 g, 25%). Mp: 109–113 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.87 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 24H, CHCH<sub>3</sub>), 1.05 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 24H, CHCH<sub>3</sub>), 1.50 (br, 12H, THF), 3.11 (br, 12H, THF), 3.46 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 8H, CHCH<sub>3</sub>), 6.16 (s, 4H, NCH), 6.76–6.89 (m, 12H, ArH). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 24.9 (THF), 25.1 (CHCH<sub>3</sub>), 25.5 (CHCH<sub>3</sub>), 27.9 (CHCH<sub>3</sub>), 68.9 (THF), 122.5 (N=CH), 122.6, 124.1, 145.3, 147.8 (ArC). MS (EI): m/z 378 [Ga{(ArNCH)<sub>2</sub>}H<sup>+</sup>, 32%], 448 [Ga{(ArNCH)<sub>2</sub>}H<sup>+</sup>, 42%]. Experimental data for 3: To a mixture of calcium metal (2.00 g, 50 mmol) and mercury (3 drops) in THF (10 cm<sup>3</sup>) at –78 °C was added a solution of [I<sub>2</sub>Ga{(ArNCH)<sub>2</sub>}] (2.00 g, 2.87 mmol) in THF (30 cm<sup>3</sup>). The resultant suspension was warmed to room temperature and stirred for 4 days. Upon filtration and removal of volatiles from the filtrate in vacuo, the residue was washed with hexane (30 cm<sup>3</sup>) and then extracted with ether (100 cm<sup>3</sup>). Filtration, concentration to ca. 50 cm<sup>3</sup>, and cooling to –30 °C overnight yielded yellow crystals of 3 (1.00 g, 57%). Mp: 225–230 °C. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 298 K): δ 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 24H, CHCH<sub>3</sub>), 1.08 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 24H, CHCH<sub>3</sub>), 1.66 (br, 16H, THF), 2.86 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 8H, CHCH<sub>3</sub>), 3.50 (br, 16H, THF), 5.78 (s, 4H, NCH), 6.60–7.13 (m, 12H, ArH). <sup>13</sup>C NMR (75 MHz, THF-d<sub>8</sub>, 298 K): δ 23.7 (THF), 24.6 (CHCH<sub>3</sub>), 25.5 (CHCH<sub>3</sub>), 28.0 (CHCH<sub>3</sub>), 65.4 (THF), 122.6 (NC<sub>2</sub>H<sub>2</sub>), 122.8, 123.3, 144.7, 146.2 (ArC). MS (EI): m/z 448 [Ga{(ArNCH)<sub>2</sub>}H<sup>+</sup>, 60%], 378 [Ga{(ArNCH)<sub>2</sub>}H<sup>+</sup>, 10%]. Experimental data for 4: 4 was prepared using a procedure similar to that employed to synthesize 3, though it was recrystallized from toluene (9%). Mp: 108–127 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.95 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 24H, CHCH<sub>3</sub>), 1.08 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 24H, CHCH<sub>3</sub>), 1.85 (br, 16H, THF), 2.01 (s, 12H, NCCH<sub>3</sub>), 3.22 (br, 16H, THF), 3.45 (sept, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 8H, CHCH<sub>3</sub>), 6.66–6.86 (m, 12H, ArH). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 21.2 (N=CCH<sub>3</sub>), 23.7 (THF), 25.3 (CHCH<sub>3</sub>), 25.7 (CHCH<sub>3</sub>), 27.6 (CHCH<sub>3</sub>), 68.6 (THF), 122.17, 123.20, 146.1, 149.4 (ArC), N=C not observed. MS (EI): m/z 475 [Ga{(ArNCMe)<sub>2</sub>}H<sup>+</sup>, 68%], 810 [(THF)<sub>4</sub>CaGa{(ArNCMe)<sub>2</sub>}<sup>+</sup>, 35%]. Reproducible microanalyses could not be obtained for 2–4 because of their high air sensitivity.

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(11) Crystal data for 2: C<sub>64</sub>H<sub>69</sub>Ga<sub>2</sub>MgN<sub>4</sub>O<sub>3</sub>, M = 1133.20, orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a = 18.143(4) Å, b = 18.443(4) Å, c = 18.906(4) Å, V = 6326(2) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.190 g cm<sup>−3</sup>, F(000) = 2424, μ(Mo Kα) = 0.907 mm<sup>−1</sup>, T = 150(2) K, 12 249 unique reflections [R(int) = 0.0695], R (on F) = 0.0533, wR (on F<sup>2</sup>) = 0.1036 [I > 2σ(I)]. Crystal data for 3: C<sub>68</sub>H<sub>104</sub>Ga<sub>2</sub>CaN<sub>4</sub>O<sub>4</sub>, M = 1221.07, monoclinic, space group P2<sub>1</sub>/n, a = 13.191(3) Å, b = 18.529(4) Å, c = 14.323(3) Å, β = 94.60(3)°, V = 3489.5(12) Å<sup>3</sup>, Z = 2, D<sub>c</sub> = 1.162 g cm<sup>−3</sup>, F(000) = 1308, μ(Mo Kα) = 0.891 mm<sup>−1</sup>, T = 150(2) K, 7006 unique reflections [R(int) = 0.0890], R (on F) = 0.0574, wR (on F<sup>2</sup>) = 0.1429 [I > 2σ(I)]. Crystal data for 4-(toluene): C<sub>86</sub>H<sub>128</sub>Ga<sub>2</sub>CaN<sub>4</sub>O<sub>4</sub>, M = 1461.44, triclinic, space group P1, a = 15.745(3) Å, b = 23.629(5) Å, c = 24.238(5) Å, α = 110.87(3)°, β = 96.54(3)°, γ = 96.67(3)°, V = 8251(3) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.177 g cm<sup>−3</sup>, F(000) = 3144, μ(Mo Kα) = 0.764 mm<sup>−1</sup>, T = 150(2) K, 33 266 unique reflections [R(int) = 0.0687], R (on F) = 0.0613, wR (on F<sup>2</sup>) = 0.1296 [I > 2σ(I)].



**Figure 2.** Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Ga1–N2 1.919(3), Ga1–N1 1.955(3), Ga1–Ca1 3.1587(6), Ca1–O2 2.352(3), Ca1–O1' 2.410(3), N2–Ga1–N1 83.68(11), O2–Ca1–O1 90.37(13), O2'–Ca1–O1 89.63(13), O2–Ca1–Ga1 91.96(8), O2'–Ca1–Ga1 88.04(8), O1–Ca1–Ga1 92.03(6), O1'–Ca1–Ga1 87.97(6). Symmetry operation  $\prime$ :  $-x + 1, -y, -z + 1$ .

heterocycles in each complex are similar but possess Ga–N bond lengths and N–Ga–N angles that are intermediate between those of the free heterocycle (ca. 2.0 Å and 82°, respectively) and the majority of the previously reported complexes of this heterocycle (ca. 1.9 Å and 87°, respectively).<sup>3,4</sup> This indicates significant ionic character for the group 2 metal–gallium heterocycle interactions. Although there have been no previously reported examples of Ga–Mg or Ga–Ca bonds in molecular compounds, those in **2** and **3** are slightly longer than the sums of the covalent radii for these element pairs (Ga–Mg 2.61 Å; Ga–Ca 2.91 Å).<sup>12</sup>

To further probe the nature of the metal–metal bonds in **2–4**, density functional theory (DFT) calculations were carried out on the model complexes [Mg(OMe)<sub>2</sub>]<sub>3</sub>{Ga(MeNCH)<sub>2</sub>]<sub>2</sub> (**7**) and [Ca(OMe)<sub>2</sub>]<sub>4</sub>{Ga(MeNCH)<sub>2</sub>]<sub>2</sub> (**8**). For the sake of comparison, calculations were also performed on the strontium complex [Sr(OMe)<sub>2</sub>]<sub>4</sub>{Ga(MeNCH)<sub>2</sub>]<sub>2</sub> (**9**). The magnesium and calcium complexes converged with geometries similar to those from the experimental study (M–Ga distances: **7**, 2.715 Å mean; **8**, 3.232 Å mean. M–O

distances: **7**, axial 2.208 Å mean, equatorial 2.066 Å; **8**, 2.443 Å mean), though the trigonal-bipyramidal geometry of **7** is significantly more distorted than that of **2** (e.g., Ga–Mg–Ga for **2** 127.32(6)° and for **7** 138.41°). As with **8**, the geometry of **9** converged with an octahedral geometry and trans gallium heterocycle ligands (Sr–Ga 3.363 Å mean; Sr–O 2.591 Å mean). Considering the electronegativity differences between the group 2 metals and gallium, it is not surprising that the group 2 metal–gallium heterocycle interactions in **7–9** appear to have significant ionic character, which increases from M = Mg to Sr (NBO charges: **7**, Mg 1.35, Ga 0.33 mean; **8**, Ca 1.54, Ga 0.27 mean; **9**, Sr 1.58, Ga 0.23 mean. M–Ga Wiberg bond indices (mean): **7**, 0.377, **8**, 0.240, **9**, 0.232).

Calculations were also carried out to assess the total energies of the neutral fragment combinations, [M(OMe)<sub>2</sub>]<sub>4</sub>{Ga(MeNCH)<sub>2</sub>]<sub>2</sub> + OMe<sub>2</sub>, M = Ca or Sr, relative to the ion combinations, [M(OMe)<sub>2</sub>]<sub>5</sub>{Ga(MeNCH)<sub>2</sub>]<sub>2</sub><sup>+</sup> + [Ga(MeNCH)<sub>2</sub>]<sub>2</sub><sup>−</sup>. The rationale here was that these calculations would shed light on the relative strengths of the M–Ga bonds and thus might point to a thermodynamic reason why **6** (R = H) reacts with calcium to give **3** but is unreactive toward strontium. The energy differences between these combinations are, however, very similar (M = Ca +348.9 kJ/mol; Sr +358.4 kJ/mol), which perhaps indicates that the unreactivity of **6** toward strontium is due to kinetic reasons.

In summary, the first examples of group 2 metal–gallium heterocycle complexes containing the first crystallographically characterized Ga–Mg and Ga–Ca bonds in molecular compounds have been reported. These have the potential for use as milder reagents for the transfer of the gallium heterocycles to less electropositive metals than the previously reported potassium salts of [Ga{(ArNCH)<sub>2</sub>]<sub>2</sub>]<sup>−</sup>. This possibility is currently under investigation in our laboratory.

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**Supporting Information Available:** Full details of DFT calculations, selected structural data for **4**, and crystallographic CIF files for **2–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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