Anionic Gallium Carbene Analogue

Synthesis and Structural Characterization of Thermally Stable Group 13 Hydride Complexes Derived from a Gallium(I) Carbene Analogue[**]

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The chemistry of aluminum(I) and gallium(I) compounds is a rapidly expanding area.[1] Within this field neutral metal(I) alkyl and aryl compounds have been widely used as ligands in complexes with both main group and transition metals.[2] In related work, the neutral, monomeric six-membered aluminum and gallium carbene analogues, $[{:}M\{N(Ar)C(Me)\}_2CH]$, $M = Al$[3] or Ga,[4] $Ar = C_6H_3i\text{Pr}_2\text{-}2,6$, were developed and shown to contain singlet lone pairs at the metal centers, which reside in orbitals that are approximately sp-hybridized. Despite this work, the coordination chemistry of these carbene analogues has not been widely examined and only one metal complex, $[Fe(CO)_4\{Ga[N(Ar)C(Me)]_2CH\}]$, was reported,[5] though a borane complex, $[B(C_6F_5)_3\{Ga[N(Ar)C(Me)]_2CH\}]$, was also described.[6] Two related anionic gallium(I) heterocycles, $[{:}Ga\{NC(R)C(H)\}_2]^-$, were developed by Schmidbaur et al. ($R = t\text{Bu}$)[7] and ourselves ($R = Ar$, **1**)[8] and these can be thought of as valence isoelectronic analogues of the ubiquitous *N*-heterocyclic-carbene (NHC) class of ligand. In light of the ever increasing importance of NHCs as ligands in main-group and transition-metal chemistry,[9] the initiation of a study of the coordination

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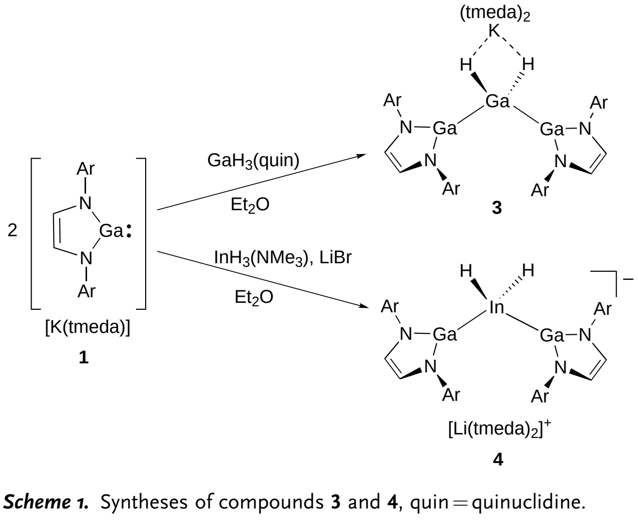
chemistry of heterocycles, such as **1** was thought to be of considerable interest. In view of our recent success in stabilizing group 13 trihydrides through their complexation by NHCs,[10] we have begun such a study aimed at examining the reactivity of **1** towards $[MH_3(L)]$, M = Al, Ga or In, L = Lewis base. The preliminary results of this investigation are reported herein.

The reaction of an ethereal solution of **1** with $[AlH_3(NMe_3)]$ in a 2:1 soichiometry led to a considerable aluminum and gallium metal deposition upon warming the reaction mixture to room temperature. This was accompanied by the formation of the ionic tetraamido gallium complex $[Ga\{[NC(Ar)C(H)]_2\}_2][K(DME)_4]$, which was isolated in moderate yield after recrystallization from DME. The same product was obtained when the reaction was carried out in 1:1 or 3:1 stoichiometries, though with lower yields. Compound **2** was characterized crystallographically and spectroscopically[11,12] and presumably forms via an unknown intermediate which is unstable at room temperature. It was originally thought this decomposition process involved the generation of the free diazabutadiene, $(ArN{=}C)_2$, which was doubly reduced an excess of **1** to give the observed product. However, this was discounted as intentionally treating $(ArN{=}C)_2$ with **1** led to no reaction.

An indication of the nature of the intermediate in the decomposition process that affords **2** might come from the analogous reactions of **1** with tertiary amine adducts of GaH_3 and InH_3 in a 2:1 stoichiometry (Scheme 1). These reactions gave high yields of the novel trimetallic group 13 hydride complexes, **3** and **4**. When these reactions were carried out in 1:1 or 3:1 stoichiometries, the same products were formed but with reduced yields. It is noteworthy that the lithium counterion in **4** originates from LiBr, which is generated as an inseparable by-product in the in situ preparation of $[InH_3(NMe_3)]$.[10] The mechanisms of formation of **3** and **4** are unknown but presumably involve an initial elimination of KH to form neutral intermediates, $[MH_2(Ga\{NC(R)C(H)\}_2)]$, M = Ga or In, which are then coordinated by a second equivalent of **1** to give the observed anionic complexes, $[MH_2(Ga\{NC(Ar)C(H)\}_2)_2]^-$. Both compounds are remarkably thermally stable in the solid state and, indeed, the decomposition temperature of **4** (116 °C) is comparable with that of the most stable InH_3–carbene complex yet reported, $[InH_3(IMes)]$, IMes = :CN(Mes)C_2H_2N(Mes), Mes = mesityl (dec. 115 °C).[10]



Scheme 1. Syntheses of compounds **3** and **4**, quin = quinuclidine.

The spectroscopic data for **3** and **4** fully support their proposed structures. In particular, the ^{1}H NMR spectra of **3** and **4** exhibit broad resonances corresponding to their hydride ligands. These resonances occur at higher fields than those normally seen for neutral MH_3 complexes, which reflects the expected greater shielding of the hydride ligands in the anionic systems. In addition, the infrared spectra of **3** and **4**, recorded in Nujol, display strong, broad absorptions at $\tilde{\nu} =$ 1769 and 1632 cm^{-1}, which lie in the normal frequency ranges for Ga–H and In–H stretches respectively.[10,13]

Both compounds were crystallographically characterized[12] and the molecular structure of **3** and the structure of the anionic component of **4** are depicted in Figures 1 and 2 respectively. These structures reveal that the anion of each compound contains a chain of three metal atoms connected by two M–Ga bonds. In the case of **3**, comparisons can be made with $[Ga\{Ga(GePh_3)_3\}_2][Li(THF)_4]$,[14] though in that case the central Ga atom is two-coordinate and the terminal Ga centers are four-coordinate. With respect to **4**, there are no previously reported compounds containing Ga_2In chains but In_3 chains are relatively common, as in, for example, $[In\{C(SiMe_3)_3\}\{\mu\text{-Br-Li(THF)}_4\}\{In[C(SiMe_3)_3](\mu\text{-Br})\}_2]$.[15] The hydride ligands of **3** and **4** were located from difference maps and refined isotropically. Those in **3** bridge the Ga and K centers to effectively form a contact ion pair. The central group 13 metal atom in each complex has a distorted tetrahedral environment whilst the gallium heterocycles are essentially planar and contain trigonal planar metal centers.

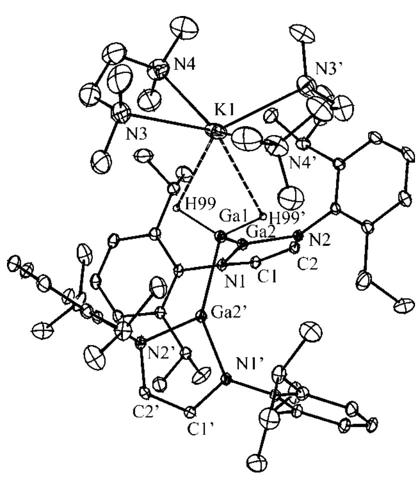


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Ga1-Ga2 2.4071(9), Ga1-H99 1.49(6), Ga2-N1 1.877(4), Ga2-N2 1.886(4), C1-C2 1.357(7), N1-C1 1.399(6), N2-C2 1.381(6), K1-H99 2.87(6), K1-N3 2.760(7), K1-N4 2.920(9), Ga2-Ga1-Ga2′ 107.24(4), Ga2-Ga1-H99 111(2), Ga2′-Ga1-H99 106(2), H99-Ga1-H99′ 116(2), N1-Ga2-N2 86.98(16), N1-Ga2-Ga1 142.88(12), N2-Ga2-Ga1 129.68(11), C1-N1-Ga2 110.4(3), C2-N2-Ga2 110.0(3). Symmetry transformation: $-x+1$, y, $-z+1/2$.

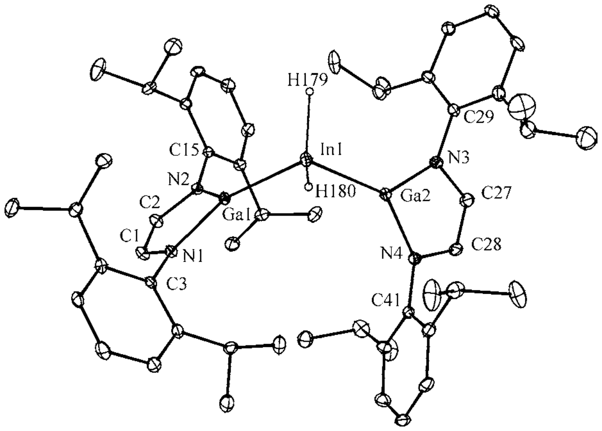


Figure 2. Structure of the anionic component of **4**. Selected bond lengths [Å] and angles [°]: In1-Ga2 2.5921(8), In1-Ga1 2.5983(8), In1-H179 1.72(2), In1-H180 1.73(2), Ga1-N1 1.896(4), Ga1-N2 1.883(4), Ga2-N3 1.885(5), Ga2-N4 1.880(5), N1-C1 1.400(7), N2-C2 1.383(7), N3-C27 1.405(7), N4-C28 1.394(7), C1-C2 1.331(7), C27-C28 1.336(8), Ga1-In1-Ga2 103.19(3), Ga2-In1-H179 101(2), Ga1-In1-H179 108(2), Ga2-In1-H180 110(2), Ga1-In1-H180 110(2), H179-In1-H180 123(3), N2-Ga1-N1 86.09(18), N3-Ga2-N4 86.8(2), N2-Ga1-In1 136.44(13), N1-Ga1-In1 137.39(13), N3-Ga2-In1 135.11(14), N4-Ga2-In1 138.08(14).

The Ga–Ga bonds in **3** (2.4071(9) Å) are normal for single, covalent Ga–Ga interactions (cf. 2.4232(7) Å in $[(GaI\{N(tBu)C(H)\}_2)_2]$)[8] but significantly shorter than the only structurally characterized Ga→Ga dative interaction, that is, 2.506(3) Å in $[(Tp^{tBu_2})Ga \rightarrow GaI_3]$, Tp^{tBu_2} = tris(3,5-di-*tert*-butylpyrazolyl)hydroborate.[16] There are no crystallographically characterized examples of Ga–In interactions for comparison with **4** but the average Ga–In bond length in this compound, 2.595 Å, is well within the sum of the covalent radii, 2.75 Å, for these two elements.[17] Although of low accuracy, the M–H bond lenghts in **3** and **4** are similar to those in previously reported adducts of MH_3, M = Ga or In.[10,13] Finally, an examination of the geometry of the heterocycles in **3** and **4** reveals that they have significantly shorter Ga–N bond lengths (**3** av. = 1.882 Å, **4** av. = 1.886 Å) and more obtuse N-Ga-N angles (**3** 86.98(16)°, **4** av. = 86.44°) than those in the free gallium(I) heterocycle (Ga–N av. = 1.970 Å, N-Ga-N 83.02(11)°).[8] In fact, these values are close to those observed in related gallium(II)-diazabutadiene complexes, for example, $[(GaI\{N(tBu)C(H)\}_2)_2]$,[8] and arise from a loss of charge from the heterocyclic Ga centres to the central MH_2 fragment upon formation of **3** and **4**. It is noteworthy that a similar shortening of the Ga–N bond lengths in gallium donor ligand of $[(Tp^{tBu_2})Ga \rightarrow GaI_3]$ occurs upon complex formation.

This effect in **3** and **4** has been examined by preliminary Density Functional calculations[18] which have been carried out on the model anions, $[MH_2(Ga\{NC(Me)C(H)\}_2)_2]^-$, M = Ga (**5**) or In (**6**). The fully optimized geometries of these compounds are similar to those of the anions in **3** and **4** taking into account the steric differences between the theoretical and experimental situations. Significantly, the Ga–N distances (**5** av. = 1.900 Å, **6** av. = 1.900 Å) and the N-Ga-N angles (**5** av = 85.66°, **6** av. = 85.74°) are comparable with those in **3**, **4** and Ga^{II} diazabutadiene complexes. In addition, there is a significant development of negative charge on the central metal atoms and MH_2 fragments (**5** M−0.35, MH_2−0.77; **6** M−0.09, MH_2−0.63) relative to the gallium atoms of the heterocycles (**5** av. = +1.04, **6** av. = +0.96).

In summary, we have prepared the first covalently bonded metal complexes derived from an anionic gallium carbene analogue, one of which contains the first example of a structurally authenticated In–Ga bond. The remarkable thermal stability of these complexes suggests that gallium(I) heterocycles such as **1** should prove to be versatile ligands towards both main-group and transition-metal fragments, especially considering the importance of their isoelectronic NHC counterparts in coordination chemistry. We are currently exploring this potential in addition to examining the controlled decomposition of **3** and **4** in solution and will report on these studies in forthcoming publications.

Experimental Section

3: A solution of $[{:}Ga\{NC(Ar)C(H)\}_2][K(tmeda)]$ (0.50 g, 0.84 mmol) in Et_2O (15 cm^3) was added to a solution of $[GaH_3(quinuclidine)]$ (0.08 g, 0.43 mmol) in Et_2O (10 cm^3) at −78 °C over 5 mins. The resulting suspension was allowed to warm to 25 °C, filtered and the filtrate concentrated to about 10 cm^3. Slow cooling of the filtrate to −35 °C yielded yellow crystals of **3**, (0.39 g, 71 %). m.p. 128–131 °C (decomp.); ^1H NMR (400 MHz, C_6D_6, 298 K): $\delta = 1.00$ (d, 24 H, $^3J(H,H) = 6.8$ Hz, CH_3), 1.20 (d, 24 H, $^3J(H,H) = 6.9$ Hz, CH_3), 1.75 (s, 24 H, NCH_3), 1.89 (s, 8 H, NCH_2), 2.17 (br. s, 2 H, GaH_2), 3.56 (sept., 8 H, $^3J(H,H) = 6.8$ Hz, CH), 6.19 (s, 4 H, NCH), 6.96 (t, 4 H, $^3J(H,H) = 7.3$ Hz, *p*-ArH), 7.07 ppm (d, 8 H, $^3J(H,H) = 7.6$ Hz, *m*-ArH); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta = 23.3$ (CH_3), 24.2 (CH_3), 26.7 (CH), 44.2 (NCH_3), 56.2 (NCH_2), 120.9 (CN), 121.6 (*m*-ArC), 123.5 (*p*-ArC), 145.2 (*o*-ArC), 146.1 ppm (*ipso*-ArC); IR (Nujol): $\tilde{\nu} = 1769\ cm^{-1}$ (br. s, Ga-H); MS/APCI *m/z* (%): 377 $[(ArNC)_2^+$, 100].
4: A solution of $[{:}Ga\{NC(Ar)C(H)\}_2][K(tmeda)]$ (0.50 g, 0.84 mmol) in Et_2O (15 cm^3) was added over 5 mins to a solution of $[InH_3(NMe_3)]$, generated in situ (0.42 mmol) in Et_2O (10 cm^3), at −78 °C. The resulting suspension was allowed to warm to −30 °C and kept at this temperature for 24 h, after which it was filtered, and the filtrate was warmed to −15 °C and concentrated to about 10 cm^3. Slow cooling of the filtrate to −35 °C yielded yellow crystals of **4**, (0.33 g, 63 %). m.p. 116–118 °C (decomp.); ^1H NMR (100.6 MHz, CD_2Cl_2, 243 K): $\delta = 0.85$ (d, 24 H, $^3J(H,H) = 6.6$ Hz, CH_3), 1.08 (d, 24 H, $^3J(H,H) = 6.6$ Hz, CH_3), 2.18 (s, 24 H, NCH_3), 2.34 (s, 8 H, NCH_2), 2.93 (br. s, 2 H, InH_2), 3.27 (sept., 8 H, $^3J(H,H) = 6.6$ Hz, CH), 5.86 (s, 4 H, NCH), 7.03 ppm (m, 12 H, *p*-ArH and *m*-ArH); ^{13}C NMR (100.6 MHz, CD_2Cl_2, 243 K): $\delta = 24.0$ (CH_3), 25.4 (CH_3), 27.5 (CH), 46.6 (NCH_3), 57.1 (NCH_2), 121.3 (CN), 122.5 (*m*-ArC), 123.9 (*p*-ArC), 145.8 (*o*-ArC), 146.8 ppm (*ipso*-ArC); IR (Nujol): $\tilde{\nu} = 1632\ cm^{-1}$ (br. s, In-H); MS/APCI *m/z* (%): 377 $[(ArNC)_2^+$, 100]. Reproducible elemental analyses of **3** and **4** could not be obtained because of the highly air and moisture sensitive nature of these compounds.

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[11] full synthetic and spectroscopic data for compound **2** have been submitted as supplementary material.

[12] Crystal data for **2**.DME: $C_{72}H_{122}GaKN_4O_{10}$ $M = 1312.56$, triclinic, space group $P\bar{1}$, $a = 13.143(3)$, $b = 14.958(3)$, $c = 19.431(4)$ Å, $\alpha = 82.72(3)$, $\beta = 85.37(3)$, $\gamma = 86.19(3)°$, $V = 3770.7(13)$ Å^3, $Z = 2$, $\rho_{\text{calcd.}} = 1.156\ \text{g cm}^{-3}$, $F(000) = 1424$, $\mu\text{Mo}_{K\alpha} = 0.475\ \text{mm}^{-1}$, $T = 150(2)$ K, 16894 unique reflections [$R_{\text{int}} = 0.0801$], R (on F) 0.0596, wR (on F^2) 0.1172 ($I > 2\sigma(I)$); **3**.C_6H_{14}: $C_{70}H_{120}Ga_3KN_8$ $M = 1322.00$, monoclinic, space group $C2/c$, $a = 21.747(4)$, $b = 14.984(3)$, $c = 26.082(5)$ Å, $\beta = 112.91(3)°$, $V = 2191.5(8)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.122\ \text{g cm}^{-3}$, $F(000) = 2832$, $\mu\text{Mo}_{K\alpha} = 1.118\ \text{mm}^{-1}$, $T = 150(2)$ K, 6949 unique reflections [$R_{\text{int}} = 0.0513$], R (on F) 0.0647, wR (on F^2) 0.1729 ($I > 2\sigma(I)$); **4**: $C_{64}H_{106}Ga_2InLiN_8$ $M = 1248.77$, monoclinic, space group $P2_1$, $a = 13.113(3)$, $b = 20.708(4)$, $c = 26.528(5)$ Å, $\beta = 103.19(3)°$, $V = 7013(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.183\ \text{g cm}^{-3}$, $F(000) = 2640$, $\mu\text{Mo}_{K\alpha} = 1.129\ \text{mm}^{-1}$, $T = 150(2)$ K, 22113 unique reflections [$R_{\text{int}} = 0.0673$], R (on F) 0.0442, wR (on F^2) 0.0860 ($I > 2\sigma(I)$). CCDC-204734 **2**, CCDC-204735 **3**, CCDC-204736 **4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[18] Geometries of **5** and **6** were optimized in Gaussian 98 by using the mPW91 functional with the 6-311+G(d) basis set on Ga, C, N, and H atoms and LANL2DZ basis set and core potential for In. Atomic charge, orbital population, and bonding analyses were carried out by using the NBO scheme. See supplementary material for full details.