

A Carbene Analogue with Low-Valent Gallium as a Heteroatom in a *quasi*-Aromatic Imidazolite Anion

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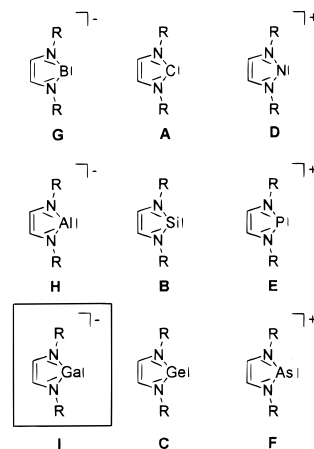
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Carbenes based on imidazole heterocycles (**A**, Scheme 1) have attracted considerable attention owing to their inherent stability,¹ their interesting features of structure and bonding,² and their potential as synthons in organic synthesis³ and coordination chemistry.⁴ Soon after the discovery of the first stable crystalline carbenes of type **A**,^{1a} the *neutral* analogues containing the heavier elements of group 14 (**B**, **C**) have also been isolated (Si,⁵ Ge,⁶ Sn⁷). These results have demonstrated that the heterocyclic framework is lending considerable stability to the formal electron sextet configuration even of the larger group 14 elements in what may be conceived as *quasi*-aromatic π -systems.⁸ In a further extension of this chemistry the existence of isoelectronic *cationic* species containing N⁺, P⁺, and As⁺ centers (**D–F**) has also been considered and investigated (**E**).⁹ However, the *anionic* counterparts (**G–I**) with low-valent group 13 elements are still unknown.^{9b}

Taking on this synthetic challenge, and continuing our earlier work on low-valent gallium compounds,¹⁰ we have set out to prepare and investigate stable crystalline salts of anions of the type **I**. While several gallium(III) and gallium(II) complexes derived from diazabutadiene(DAB)/ethenediamide(2-) ligands were studied in the past,^{11,12} there is no experimental evidence for related anionic species containing gallium(I). From quantum chemical studies these anions were predicted to be “stable species with sizeable singlet-triplet energy separations” and recommended as “valid targets for experimental investigations”.^{13,14}

Scheme 1. Carbene **A** and Its Analogues Based on Imidazole Heterocycles Containing Group 13, 14, and 15 Elements



Anhydrous gallium trichloride, GaCl₃, was treated with dilithio-di-*t*Bu-DAB to give the (chloro)galla-imidazole **1** (Scheme 2) that was identified by standard analytical, spectroscopic, and structural techniques.¹⁵ Unexpectedly, the crystal structure analysis¹⁶ of **1** has shown that the compound is a dimer with an unsymmetrical distribution of the ligands rendering the two gallium atoms inequivalent (Figure 1). The corresponding monoalkyl complexes {RGa(R)NC₂}₂ have centrosymmetrical structures.^{12c}

Reduction of **1** by potassium metal (spread over the inner surface of a reaction flask as a bright mirror¹⁸) led to the known dinuclear gallium(II) compound **2**. Further reduction of **2** with potassium metal in the presence of (18)-crown-6 finally afforded the expected mononuclear anionic heterocycle as the {K[(18)-crown-6](thf)₂} salt **3** as a light yellow crystalline solid, the composition of which was confirmed by elemental analysis.¹⁵

(15) Preparations. **1**: In a glovebox filled with dry argon a solution of 1,4-dilithio-1,4-di-*tert*-butyl-1,4-diazabutadiene in thf (15 mL) was prepared from the diazabutadiene (1.68 g, 10 mmol) and lithium metal (0.139 g, 10 mmol) and treated with a solution of anhydrous gallium trichloride (1.76 g, 10 mmol) in hexane (15 mL). The solvent was evaporated and the residue extracted with hexane (20 mL), which was again evaporated to leave a light green solid (2.2 g, 80% yield). Single crystals were grown from hexane solutions at –28 °C (mp 141 °C, dec). Anal. Calcd (found) for C₂₀H₄₀Cl₂–Ga₂N₄: C, 43.92 (43.98); H, 7.37 (7.80); N, 10.25 (10.25). ¹H NMR (400 MHz, 298 K, C₆D₆) δ 6.35 (d, 2H, ³J_{HH} 4.62 Hz, =CH), 5.23 (d, 2H, ³J_{HH} 4.62 Hz, =CH), 1.32 (s, 18H, *t*Bu), 1.12 (s, 18H, *t*Bu). ¹³C{¹H}NMR (298 K, C₆D₆) δ 135.1 (s, =CH), 104.9 (s, =CH), 58.6 and 53.0 (s, CMe₃), 31.7 and 28.1 (s, Me). MS (CI) [*m/e*] 541 (1.65%) M⁺; 509 (4.15%) [M – Cl]⁺; 272 (19.5%) [M/2]⁺; 237 (100%) [M/2 – Cl]⁺. **2**: Compound **1** was prepared as described above but not isolated. The reaction mixture was transferred instead to a reaction vessel the inner wall of which was covered with a mirror of pure potassium metal (0.39 g, 10 mmol). The contents were stirred for 3 d at 20 °C to dissolve all of the potassium metal. The solvent was evaporated and the residue extracted with hexane (20 mL). Evaporation of the solvent from the extract gave a brown solid (1.22 g, 51% yield), which could be crystallized from hexane at –28 °C (mp 185 °C, dec). Anal. Calcd (found) for C₂₀H₄₀Ga₂N₄: C, 50.46 (49.76); H, 8.47 (8.65); N, 11.72 (11.34). ¹H NMR (298 K, C₆D₆) δ 6.63 (s, 4H, =CH), 1.40 (s, 36H, CMe₃), 31.7 and 28.1 (s, Me). MS (CI) [*m/e*] 541 (1.65%) M⁺; 509 (4.15%) [M – Cl]⁺; 272 (19.5%) [M/2]⁺; 237 (100%) [M/2 – Cl]⁺. **3**: Compound **2** was prepared as described above. The residue of the hexane extraction was dissolved in thf (15 mL) and combined with a solution of (18)-crown-6 (2.64 g, 10 mmol) in thf (15 mL) at –78 °C in a reaction vessel covered inside with a potassium mirror (0.39 g, 10 mmol). The flask was allowed to warm to ambient temperature and stirred for 2 h to dissolve the potassium metal. Upon reduction of the volume of solvent to one-half and cooling to –28 °C yellow crystals were obtained (243 mg, 4% yield), which could be recrystallized from pure thf (185 mg, 3% yield, mp 121 °C). Anal. Calcd (found) for C₃₀H₆₀GaN₂O₆: C, 52.55 (51.05); H, 8.82 (8.84); N, 4.09 (3.90). ¹H NMR (298 K, C₆D₆) δ 6.13 (s, 2H, =CH), 3.58 (m, 68H, CH₂-crown, -thf), 1.75 (m, 26H, CH₂-thf), 1.36 (s, 18H, CMe₃). ¹³C NMR (298 K, C₆D₆) δ 114.9 (s, =CH), 71.1 (s, CH₂-crown), 68.1 (s, thf), 54.0 (s, CMe₃), 35.1 (s, Me), 26.2 (s, thf). MS (MALDI TOF, anthracene matrix): *m/e* 237 [M][–], 405 [Ga(*t*Bu₂DAB)][–], 421 [Ga(*t*Bu₂DAB)₂O][–], 437 [Ga(*t*Bu₂DAB)₂O₂][–]. The workup of the filtrate leaves a red oil of an unidentified product presumably containing the anion [Ga(*t*BuNCH₂)₂][–], which also appears in the mass spectrum of compound **3** (above).

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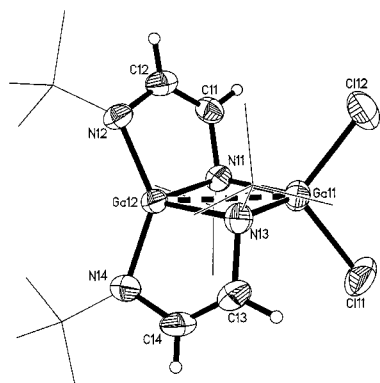
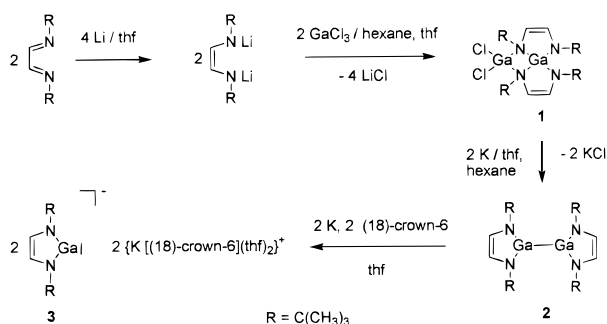


Figure 1. Molecular structure of **1** (only one of the four independent molecules in the asymmetric unit is shown, ORTEP drawing with 50% probability ellipsoids). For details see Supporting Information.

Scheme 2. Reaction Scheme



The identity of the anionic component of salt **3** was confirmed by negative ion MALDI TOF mass spectrometry. The spectra showed the molecular anion at m/e 237 (^{69}Ga) with the correct isotope pattern. The anion $\{[(t\text{Bu})_2\text{N}_2\text{C}_2]_2\text{Ga}\}^-$ was also present. There are also peaks of an oxidation product ($M^+ + 16$; $M^+ + 32$) because of the nonperfect exclusion of air in the sample transfer process.

The ^1H and ^{13}C NMR spectra ($\text{thf}-d_8$) of **3** exhibit resonances expected for the C_{2v} symmetrical anion. These resonances are shifted to higher field as compared to the resonances of the precursor molecules as predicted for a highly reduced, anionic species.

Crystals of compound **3** (triclinic, space group $P\bar{1}$, $Z = 1$)¹⁹ contain complex cations in which the potassium atom resides in the center of the crown-ether molecule and has contacts with the oxygen atoms of two tetrahydrofuran molecules as apical ligands of a $[\text{K}O_{6+2}]$ hexagonal bipyramide with a crystallographic center of inversion. The anions are disordered, but their structure could be refined successfully using two split positions and geometrical constraints (Figure 2). The galla-heterocycle is virtually planar and obeys closely noncrystallographic C_{2v} symmetry with a N–Ga–N angle of $81.8(3)^\circ$ and Ga–N distances of $1.985(6)$ Å. Previous density functional calculations have predicted a planar geometry with an N–Ga–N angle of 80.7° and Ga–N distances of 1.983 Å (with hydrogen instead of $t\text{Bu}$ -substituents).¹³

(16) Diffraction data for **1** were collected on a yellow crystal at -80°C using an Enraf-Nonius CAD4 system. The SHELXTL¹⁷ program suite was used for the initial solution and subsequent least-squares refinements. Monoclinic, space group: $C2/c$, $a = 61.445(13)$ Å, $b = 10.441(1)$ Å, $c = 29.371(10)$ Å, $\beta = 101.45(1)^\circ$, $Z = 28$, $V = 18468(8)$ Å³, final $R_1 = 0.0615$ for 16 188 unique reflections, 911 parameters, final GOF (on F^2) 1.056. The asymmetric unit contains four independent molecules, two of which are disordered. For details see Supporting Information.

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(19) Data for **3** at -130°C : Yellow crystal, triclinic, space group: $P\bar{1}$, $a = 9.718(2)$ Å, $b = 10.116(2)$ Å, $c = 10.318(2)$ Å, $\alpha = 77.67(2)^\circ$, $\beta = 69.64(2)^\circ$, $\gamma = 88.51(2)^\circ$, $Z = 1$, $V = 927.7(3)$ Å³, final $R_1 = 0.0336$ for 4122 unique reflections, 315 parameters, and 72 restraints: final restrained GOF (on F^2) 1.017. The anion and the thf molecules of the cation are disordered. For details on the refinement, see Supporting Information.

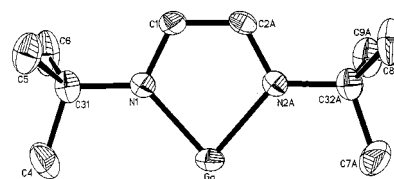


Figure 2. Molecular structure of the anion of **3** (ORTEP drawing with 50% probability ellipsoids).

Table 1. Selected Bond Lengths (Å) and Angles (deg) Derived from Crystal Structure Analysis and Theoretical Calculations [DFT for $(\text{HNCH})_2\text{Ga}^-$, MP2/6-311G* for $(t\text{BuNCH})_2\text{Ga}^-$]^{13,20}

	MP2/6-311G* (this work) ²⁰	DFT (ref 13)	crystal structure analysis (this work) ¹⁹
Ga–N	2.041	1.983	1.985(6)
N–C (ring)	1.390	1.388	1.367(8)
C–C (ring)	1.368	1.368	1.380(6)
N–C(<i>t</i> Bu)	1.462		1.463(3)
N–Ga–N	80.2	80.7	81.8(3)
C–N–Ga (ring)	113.0		113.1(3)
Ga–N–C(<i>t</i> Bu)	130		129.7(5)
C–N–C(<i>t</i> Bu)	117		116.4(6)

There are no sub-van der Waals contacts between cations and anions in the lattice of compound **3** (C–H–Ga distances are all greater than 3.83 Å). The gallium atom is thus clearly two-coordinate and can be assigned the formal oxidation state Ga(+I). Its $4s^2$ lone pair of electrons and the two electron pairs donated by the neighboring nitrogen atoms make up for a sextet configuration which may be stabilized by the 6π -system of the heterocycle.

The geometry attained in the previous density functional calculations¹³ of a simplified model and our own ab initio studies²⁰ of the complete bis-*t*Bu-substituted anion (MP2/6-311G*, C_{2v} symmetry, Table 1) with almost equidistant CC [$1.380(6)$ Å] and CN [$1.367(8)$ Å] distances in the heterocycle indicates at least partial delocalization and shows that aromaticity effects are small but certainly not negligible. The anion in **3** is thus the first representative of the anionic carbene analogues in the series **G–I** (Scheme 1). Its chemical reactions are presently under investigation.

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Supporting Information Available: Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC No. 133980 (**1**) and 133981 (**3**). Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **3** (PDF). An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) Ab initio molecular orbital calculations were carried out for $\text{Ga}[\text{N}(\text{Me})\text{CH}]_2^-$ and $\text{Ga}[\text{N}(t\text{Bu})\text{CH}]_2^-$ using the Gaussian 98 suite of programs.²¹ Geometry optimizations were performed without symmetry constraints up to the SCF/6-31G* level for $\text{Ga}[\text{N}(\text{Me})\text{CH}]_2^-$ and $\text{Ga}[\text{N}(t\text{Bu})\text{CH}]_2^-$. The nature of the stationary points was verified by frequency calculations at this level. Consistently the geometries converged to C_{2v} symmetry as global minima, and this symmetry was imposed on the optimizations during the higher level calculations up to MP2/6-311G* for $\text{Ga}[\text{N}(t\text{Bu})\text{CH}]_2^-$.

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