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In further pursuit of the carbene analogy: preparation and crystal structure of (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)potassium [*cis*-ethene-1,2-di(*tert*-butylamido)]gallate(I)

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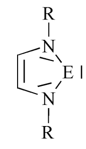
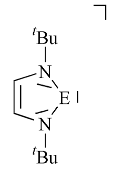
Reduction of *cis*-ethene-1,2-di(*tert*-butylamido)-gallium(III) chloride with metallic potassium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine gives the title compound which has a novel dimeric structure with the potassium cations η^5-coordinated to the pseudo-carbene ring system of one monomer and η^1-bonded to the gallium atom of the other.

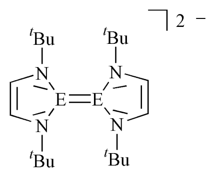
Diazabutadiene derivatives of low-valent carbon ("Arduengo carbenes", **A**, E = C)[1] are a well-established class of heterocycles which show great potential as synthons and as ligands in synthetic and coordination chemistry.[2] The corresponding silylene[3] and germylene[4] heterocycles (**A**, E = Si, Ge) have also been described and were shown to have similar characteristics of structure and bonding. Arduengo carbenes are the monomeric units of Wanzlick's fulvalene-type compounds (**B**, E = C),[5] and in fact these dimers and monomers may be interconverted. Monomer–dimer equilibria are also known for certain silylenes and germylenes (**B**, E = Si, Ge) and in particular for the related stannylenes and plumbylenes (**A**/**B**, E = Sn, Pb), but the nature of the E=E double bond is a subject of controversy owing to significant deviation of the ligand atoms from the molecular plane.[6]



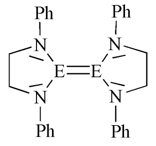
A



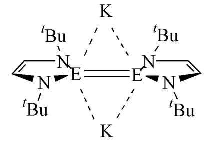
C



D



B

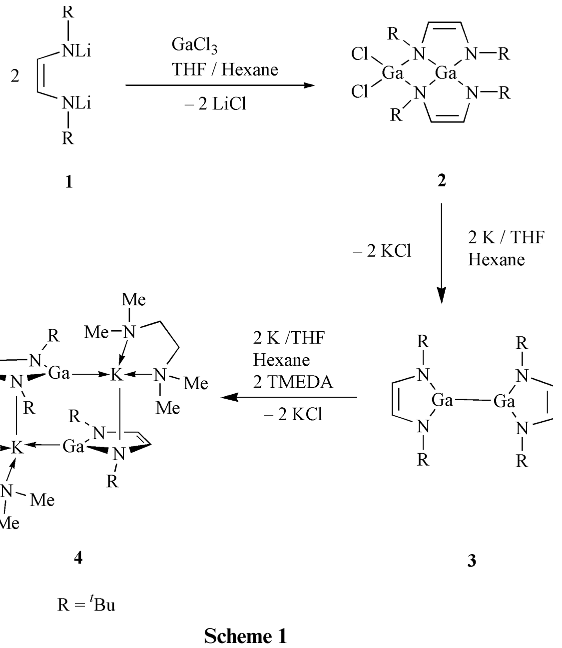


E

In recent work we were able to show that analogous anionic systems with low-valent gallium (**C**, E = Ga) can also be obtained,[7] which are isoelectronic to compounds of type **A** (E = Ge, R = ᵗBu). None of the corresponding discrete boron or aluminium heterocycles are known. With the counter ion K$^+$ completely protected by an 18-crown-6 ligand and two tetrahydrofuran solvent molecules, the anion is an independent monomeric unit in the crystal lattice with a completely planar skeleton including the central carbon atoms of the *tert*-butyl groups.[7]

We now describe the result of an attempt to induce dimerization of the anions (to give **D**) by partially stripping the potassium cations of their ligand coating. The exposure of cationic charge to the anions may give "Coulomb assistance" to the mutual approach of two negatively charged gallium atoms (**E**) as observed previously with anionic compounds of low-coordinate gallium, the Ga–Ga bond order of which is highly controversial.[8]

The reaction of 1,4-dilithio-1,4-di-*tert*-butyl-1,4-diazabutene (**1**, R = ᵗBu), obtained from the reaction of diazabutene and lithium metal in tetrahydrofuran, with equimolar quantities of anhydrous gallium trichloride in hexane at 0 °C is known to afford the unsymmetrical dinuclear complex **2**,[7] [(ᵗBuNCH)$_2$]$_2$-Ga$_2$Cl$_2$, the structure of which has been determined.[9] Reduction of this compound at a potassium mirror on the walls of a glass reaction vessel at 20 °C in two steps, after 10 d leads first to the Ga–Ga bonded gallium(II) compound **3**,[10] which after addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, instead of the crown ether used previously), and another 4 d reaction time, is finally converted into a new gallium(I) compound **4** (lemon-yellow crystals from THF–TMEDA, 18% yield, Scheme 1). The product is soluble in tetrahydrofuran, and the ^{1}H and ^{13}C-{^{1}H} NMR spectra of the solutions show the resonances of symmetrically bound TMEDA and (ᵗBuNCH)$_2$ ligands in a 1 : 1 ratio. The elemental analysis is also in agreement with the composition KGa(TMEDA)-(ᵗBu$_2$N$_2$C$_2$H$_2$).†



Scheme 1

Crystals of compound **4** are triclinic, space group $P\bar{1}$, with Z = 2 monomeric units in the unit cell.‡ These monomers have no crystallographically imposed symmetry but obey quite closely the requirements of a mirror plane passing through the

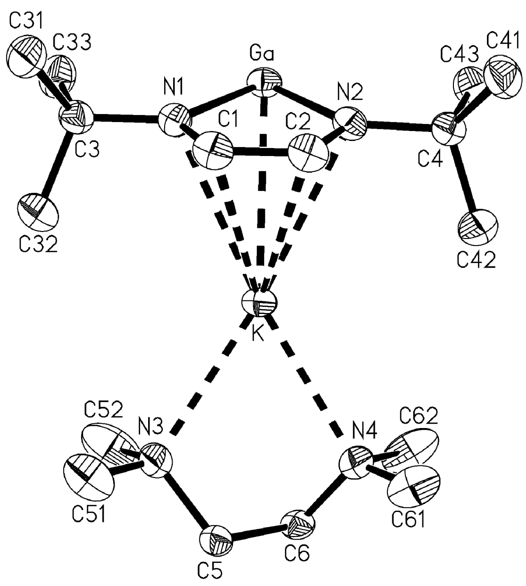


Fig. 1 Monomeric unit of compound **4** with atomic numbering. (ORTEP,[14] 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) Ga–N(1) 1.9834(16), Ga–N(2) 1.9844(17), Ga–K 3.4681(5), K–C(1) 3.002(2), K–C(2) 2.996(2), K–N(3) 2.899(2), K–N(4) 2.8788(19), C(1)–C(2) 1.349(3), N(1)–C(1) 1.389(3), N(2)–C(2) 1.388(3); N(1)–Ga–N(2) 82.05(7).

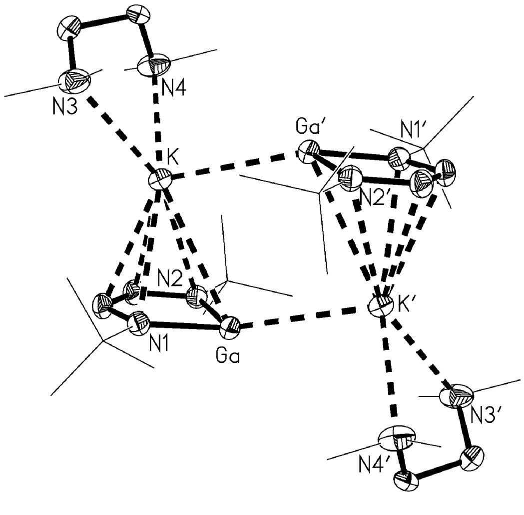


Fig. 2 The dimer **4** with Ga · · · K contacts between the monomeric units. (TMEDA methyl groups and *tert*-butyl groups are only indicated by thin lines; ORTEP for all other atoms.)

two metal atoms and through the middle of the C1–C2 and C5–C6 bonds (Fig. 1). The pseudo-carbene heterocycle is planar including the central carbon atoms of the ^{t}Bu groups. The dimensions of the five-membered ring are identical to those found for the anions in the [(18-crown-6)(THF)$_2$]potassium salt.[7] However, in contrast to the isolated nature of the anions in the reference compound, the potassium atoms in **4** are η^5-bonded to the heterocycle and chelated only by a TMEDA molecule. The K–Ga distance is 3.468(1) Å and the K–C and K–N distances are in the range 2.879(2)–3.113(2) Å.

The resulting monomeric molecular units are further aggregated into centrosymmetrical dimers not through Ga–Ga* bonding as proposed in **D** or **E**, but through Ga · · · K* contacts with a distance [3.438(1) Å], even shorter than the intramolecular η^5 contact Ga–K (Fig. 2). The line connecting the Ga and K* atoms forms an angle of only 20.8° with the C_2N_2Ga ring plane, indicating that the lone pair of electrons at the gallium atom is oriented towards the potassium cation.

It should be noted that the structure of **4** can be constructed by shifting the two C_2N_2Ga rings which are coplanar in model **D** to two parallel planes with a distance of 4.0 Å and allowing the potassium atoms (with their TMEDA ligands) to move from the positions above and below the middle of the Ga–Ga bond to their new η^5 positions above and below the rings retaining the inversion symmetry. Quantum-chemical calculations with simplified ligands have shown that models **E** and **4** are both stable structures with a rather small difference in the total energy favouring model **4**, mainly owing to the negative charge of the heterocyclopentadienyl ring.[11]

The nucleophilic properties of anions of type **C** with their lone pair of electrons at Ga(I) are readily demonstrated in the reactions of the (18-crown-6)(THF)$_2$ analogue[7] with methyl triflate, which give good yields of the corresponding dimeric gallium(III) compound [(^{t}BuNCH)$_2$GaMe]$_2$ and potassium triflate.§

Acknowledgements

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Notes and references

† All experiments were carried out in a dry-box filled with ultrapure argon. A solution of (Li^{t}BuNCH)$_2$ in tetrahydrofuran (15 mL) was prepared from diazabutadiene (1.68 g, 10 mmol) and lithium metal (0.139 g, 20 mmol) and reacted with a solution of anhydrous $GaCl_3$ (1.760 g, 10 mmol) in hexane (15 mL) at 0 °C. On warming the reaction mixture to 20 °C the colour of the solution turned from red *via* brown to green and a yellow precipitate was formed. The mixture was filtered and the filtrate transferred to a reaction vessel in which metallic potassium (0.39 g, 10 mmol) was deposited as a mirror at the inner walls through distillation in a vacuum at 500 °C. After 10 d of efficient stirring the potassium was consumed. The mixture was again filtered and transferred into another flask covered with the same amount (0.39 g) of fresh potassium mirror at −78 °C, loaded with TMEDA (1.162 g, 10 mmol) and stirred for another 4 d at 20 °C. A yellow precipitate was formed which was separated by filtration and recrystallized from TMEDA–THF [v/v 1 : 1] (0.7 g, 18% yield). NMR (THF-d$_8$, 20 °C), ^{1}H (399.8 MHz): δ 1.40 (s, 18H, Me$_3$C), 2.15 (s, 12H, Me$_2$N); 2.29 (s, 4H, CH$_2$), 6.31 (s, 2H, CH); ^{13}C-{^{1}H} (100.5 MHz): δ 33.84 (s, C*Me*$_3$), 45.13 (s, Me$_2$N), 53.34 (s, CH$_2$), 57.81 (s, *C*Me$_3$), 115.5 (s, CH). Anal. calc. (found) for $C_{16}H_{36}GaN_4$: C, 48.80 (49.92); H, 9.22 (9.79); N, 14.20 (13.99%).

‡ The crystalline sample of **4** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Nonius DIP2020 system with monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at −130 °C. The structure was solved by direct methods using SHELXS-97[12] and refined by full matrix least-squares calculations on F^2 using SHELXL-97.[13] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions [$U_{\mathrm{iso(fix)}} = 1.5 \times U_{\mathrm{eq}}$ of the attached C]. The disorder of the two central carbon atoms C5 and C6 of the TMEDA could be resolved using split positions with equal populations.

Crystal data for $C_{32}H_{72}Ga_2K_2N_8$. $M = 786.62$, triclinic, $a = 10.3925(2)$, $b = 10.7648(2)$, $c = 10.9534(2)$ Å, $\alpha = 101.728(1)$, $\beta = 92.051(1)$, $\gamma = 114.450(1)$°, space group $P\bar{1}$, $Z = 1$, $U = 1082.28(4)$ Å^3, μ(Mo-Kα) = 14.66 cm^{-1}, 4132 measured and unique reflections, w$R2 = 0.0740$, $R = 0.0309$ for 3906 reflections [$I \geq 2\sigma(I)$] and 217 parameters. CCDC reference number 154913. See http://www.rsc.org/suppdata/dt/b1/b101016f/ for crystallographic data in CIF or other electronic format.

§ A solution of (18-crown-6)(THF)$_2$potassium [*cis*-ethene-1,2-di-(*tert*-butylamido)]gallate(I)[7] (0.2 g, 0.3 mmol) in THF was cooled to −78 °C and treated with methyl triflate (0,049 g, 0.3 mmol). The mixture was warmed to 20 °C and stirred for another 20 h. After the solvent was removed in a vacuum the residue was extracted with hexane. A colourless oily liquid remained after evaporation of the solvent. NMR (C_6D_6, 20 °C), ^{1}H: δ −0.58 (br s, 6H, GaMe), 1.11 (s, 18H, Me$_3$C), 1.22 (s, 18H, Me$_3$C), 4.93 (m, 2H, CH), 6.45 (m, 2H, CH). MS (CI): *m*/*z* 504 {[(^{t}BuNCH)$_2$]$_2$Ga$_2$Me$_2$}$^+$, 252 {(^{t}BuNCH)$_2$GaMe}$^+$, 237 {(^{t}BuNCH)$_2$-Ga}$^+$.

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