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Alkali metal reduction of 1,3,2-diazagallol-2-ylidene radical derived from acenaphthene-1,2-diimine

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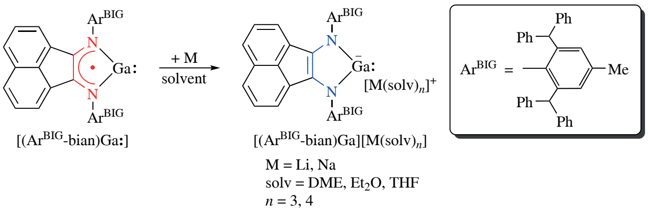
Reduction of the open-shell gallylene [(Ar^{BIG}-bian)Ga:] {Ar^{BIG}-bian = 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)-imino]acenaphthene} with one equivalent of lithium or sodium metal in THF followed by recrystallization from DME or diethyl ether affords the lithium and sodium salts of the anionic 1,3,2-diazagallol, [(Ar^{BIG}-bian)GaLi(DME)$_3$] and [(Ar^{BIG}-bian)GaNa(Et_2O)$_2$(THF)$_2$]. In contrast, reaction of [(Ar^{BIG}-bian)Ga:] with potassium gives the solvent-free derivative [(Ar^{BIG}-bian)K] and gallium metal.



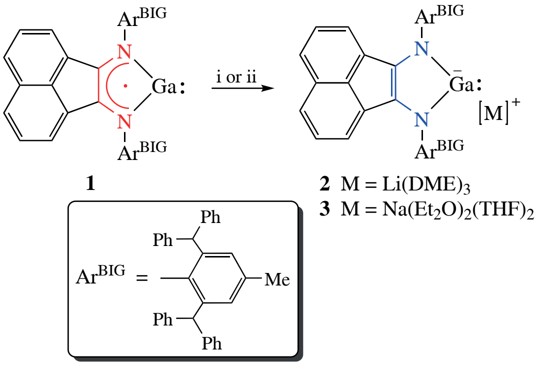
Keywords: low-valent gallium species, alkali metals, reduction, redox-active ligands, diimines.

Low-valent Group 13 compounds, including gallium derivatives, have been found to play important roles in the activation of numerous substrates, especially small molecules.[1–3] They have also been reported to undergo transition metal-like oxidative addition[4–7] and reductive elimination reactions,[8,9] making them promising candidates to replace expensive transition metal complexes as catalysts.[10] In addition, low-valent Group 13 derivatives, such as gallaimidazoles [(dab)Ga**:**] (dab = 1,4-diaza-1,3-butadiene), can act as ligands in transition,[1,11–15] alkali[16] and rare earth[17,18] metal chemistry.

Although the electropositive *s*- and *f*-metals do not normally form stable bonds with each other, examples of molecular compounds of alkali metals with gallium have been known since 1999.[19] The alkali metal reduction of digallanes supported by diimine or terphenyl ligands was shown to yield compounds containing alkali metal–gallium(I) coordination bonds.[20,21] In 2007, we reported the synthesis and crystal structure of digallane [(dpp-bian)Ga–Ga(dpp-bian)] {dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene},[22] which can be considered either as a binuclear Ga^{II} complex with dianionic acenaphthene-1,2-diimine ligands or as a bis-gallaimidazole. The preparation of low-valent gallium species [(dpp-bian)Ga–M(solv)$_n$] [M = Li, Na; solv = Et$_2$O, n = 3; solv = 1,2-dimethoxyethane (DME), n = 2] by reduction of digallane with the corresponding alkali metals was reported afterwards.[23,24] According to DFT studies, Ga–M bonds are formed mainly by donating the gallium(I) lone pair of anionic 1,3,2-diazagallole to a solvated alkali metal cation. Very recently, we synthesized a stable gallylene radical [(Ar^{BIG}-bian)Ga**:**] **1**, which is an open-shell 1,3,2-diazagallole based on 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]-acenaphthene (Ar^{BIG}-bian). It exhibits rather unique reactivity, for example, toward *n*-propyl bromide and tetramethylthiuram disulfide.[25] To follow the behavior of [(Ar^{BIG}-bian)Ga**:**] under reducing conditions, we studied its reactions with lithium, sodium and potassium and report the results here.

Addition of one molar equivalent of lithium or sodium metal to a solution of compound **1** in THF and stirring the mixture for 24 h leads to dissolution of the metal. Removal of THF *in vacuo* and recrystallization of the residue from DME or diethyl ether affords the low-valent gallium species [(Ar^{BIG}-bian)GaLi(DME)$_3$] **2** and [(Ar^{BIG}-bian)GaNa(Et$_2$O)$_2$(THF)$_2$] **3** as brown crystals and fine crystalline powder, respectively (Scheme 1). Diamagnetic compounds **2** and **3** were characterized by NMR and IR spectroscopy and elemental analysis. The molecular structures of compounds **2** and **3** in crystals isolated from DME were determined by single-crystal X-ray diffraction.

A well-resolved ^{1}H NMR spectrum of complex **2** was obtained in THF-d_8 at 233 K (Figure S1, Online Supplementary Materials). The methyl protons of the aryl substituents at the nitrogen atoms appear as a singlet at 2.14 (6H) ppm. Three equivalent pairs of naphthalene protons of the ligand give two doublets at 5.47 (2H) and 6.41 (2H) ppm, as well as a pseudo triplet at 6.29 (2H) ppm. The singlet at 6.59 (4H) ppm is assigned to the four equivalent methine protons of the benzhydryl groups. The protons of the C$_6$H$_2$ substituents at the nitrogen atoms appear as a singlet at 6.70 (4H) ppm. The aromatic protons of the phenyl substituents in the benzhydryl groups give three multiplets in the region from 7.25 to 6.75 ppm. The ^{1}H NMR spectrum of compound **3** was recorded in THF-d_8 at 298 K



Scheme 1 *Reagents and conditions*: i, Li (1 equiv.), THF, 24 h, then DME; ii, Na (1 equiv.), THF, 24 h, then Et$_2$O.

(Figure S3). The singlet at 2.17 (6H) ppm corresponds to the methyl protons of 2,6-dibenzhydryl-4-methylphenyl substituents. The protons of the naphthalene part give two doublets at 5.35 (2H) and 6.46 (2H) ppm, as well as a pseudo triplet at 6.25 (2H) ppm. The methine protons of the Ph_2CH groups give a singlet at 6.61 (4H) ppm. A set of signals in the range 7.50–6.70 ppm corresponds to the phenyl rings (*Ph*$_2$CH). The singlet of protons of C_6H_2 groups is observed at 6.80 (4H) ppm.

The molecular structure of compound **2** (Figure 1) was determined by single-crystal X-ray diffraction.[†,‡] Crystals of **3′** suitable for X-ray diffraction analysis (Figure 2) were obtained by recrystallization of compound **3** from DME.

According to X-ray diffraction data, the complexes are solvent-separated ion pairs consisting of a solvated cation $[M(dme)_3]^+$ (M = Li, **2**; Na, **3′**) and an anion of 1,3,2-diazagallole $[(Ar^{BIG}\text{-bian})Ga\mathbf{:}]^-$. In contrast to the previously reported low-valent compounds $[(\text{dpp-bian})Ga–M(solv)_n]$ (M = Li, Na),[23,24] based on the less bulky dpp-bian, direct gallium–alkali metal bonds are absent in complexes **2** and **3′**.

Thus, addition of an alkali metal to gallylene **1** results in the reduction of the open-shell 1,3,2-diazagallole to the closed-shell 1,3,2-diazagallolide anion, as evidenced by the bond lengths in the diimine fragment. The C(1)–C(2) bonds [**2**, 1.377(3) Å; **3′**, 1.389(4) Å] are shortened, while the C–N bonds [**2**, 1.377(3) and 1.389(3) Å; **3′**, both 1.374(4) Å] are elongated compared to those [C(1)–C(2) 1.447(4), C(1)–N(1) 1.325(4) and C(1)–N(2) 1.321(4) Å] in the starting gallylene radical $[(Ar^{BIG}\text{-bian})Ga\mathbf{:}]$.[25] These values are close to those [C(1)–C(2) 1.367(3), N(1)–C(1) 1.396(2) and N(2)–C(2) 1.388(2) Å] in the related complex $[(Ar^{BIG}\text{-bian})GaPr]$.[25] The lithium and sodium ions in complexes **2** and **3′** coordinate the oxygen atoms of three DME molecules.

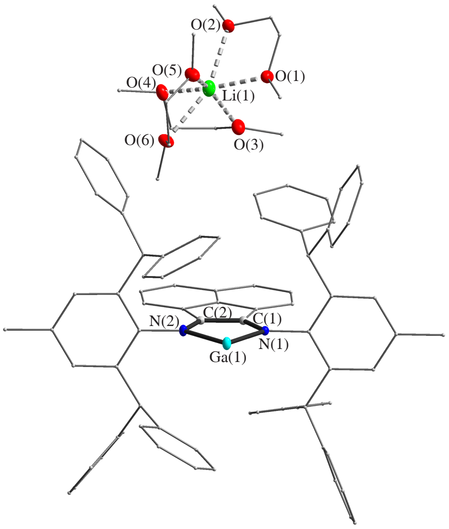


Figure 1 Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 2.037(2), Ga(1)–N(2) 2.028(2), N(1)–C(1) 1.377(3), N(2)–C(2) 1.389(3), C(1)–C(2) 1.377(3); N(1)–Ga(1)–N(2) 80.96(8), C(1)–N(1)–Ga(1) 112.49(16), C(2)–N(2)–Ga(1) 112.22(16), C(2)–C(1)–N(1) 117.0(2), C(1)–C(2)–N(2) 117.3(2).

In contrast to the reactions of complex **1** with lithium and sodium, its interaction with potassium metal in THF yields solvent-free potassium salt $[(Ar^{BIG}\text{-bian})K]$ **4** and gallium metal as a result of transmetallation reaction. Green crystals of salt **4** were isolated from diethyl ether in 74% yield (Scheme 2). According to the single crystal X-ray diffraction data, the unit cell of compound **4** contains, besides the potassium derivative, a lattice molecule of diethyl ether. Thus, the coordination sphere of the potassium cation is free of coordination solvent. Nevertheless, three of the eight phenyl rings of the benzhydryl substituents are oriented with their planes toward the potassium cation. This non-covalent interaction provides good stabilization of the cation and prevents the inclusion of ether molecules in its coordination sphere (Figure 3). Indeed, the solvated derivative

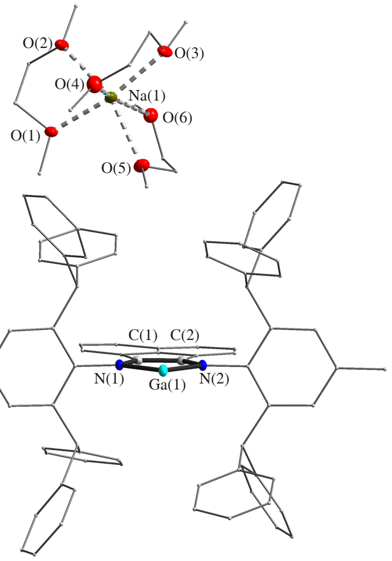


Figure 2 Molecular structure of complex **3′**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 2.044(3), Ga(1)–N(2) 2.006(2), N(1)–C(1) 1.374(4), N(2)–C(2) 1.374(4), C(1)–C(2) 1.389(4); N(1)–Ga(1)–N(2) 80.37(11), C(1)–N(1)–Ga(1) 113.24(17), C(2)–N(2)–Ga(1) 113.44(18), C(2)–C(1)–N(1) 115.4(3), C(1)–C(2)–N(2) 117.5(3).

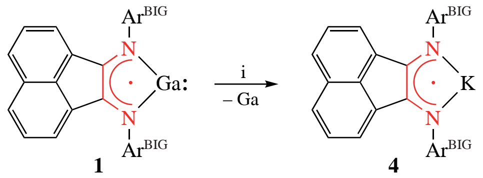
[†] *Crystal data for* **2**. $C_{98}H_{110}GaLiN_2O_{10}$, $M = 1552.53$, orthorhombic, space group *Pnma*, 100(2) K, $a = 23.1716(6)$, $b = 18.5489(6)$ and $c = 19.5540(5)$ Å, $Z = 4$, $V = 8404.5(4)$ Å^3, $d_{\text{calc}} = 1.227$ g cm^{-3}, $F_{000} = 334$. A black prism-shaped single crystal with dimensions of 0.26×0.15×0.14 mm was selected, and the intensities of 102029 reflections were measured using an Oxford Xcalibur Eos diffractometer (ω-scans technique, $\lambda[\text{Mo}K_\alpha] = 0.71073$ Å, $\mu = 0.388$ mm^{-1}, $2\theta_{\text{max}} = 54.206°$). After merging of equivalents and absorption corrections, 9539 independent reflections ($R_{\text{int}} = 0.0617$) were used for the structure solution and refinement. Final *R* factors: $R_1 = 0.0482$ [7420 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1188$ (all reflections), GOF = 1.065.

Crystal data for **3′**. $C_{94}H_{100}GaN_2NaO_8$, $M = 1478.46$, monoclinic, space group $P2_1$, 100(2) K, $a = 12.7865(2)$, $b = 21.4300(3)$ and $c = 14.4903(2)$ Å, $\beta = 95.6258(15)°$, $Z = 2$, $V = 3951.43(11)$ Å^3, $d_{\text{calc}} = 1.243$ g cm^{-3}, $F_{000} = 1568$. A black prism-shaped single crystal with dimensions of 0.47×0.43×0.31 mm was selected, and the intensities of 61069 reflections were measured using an Oxford Xcalibur Eos diffractometer (ω-scans technique, $\lambda[\text{Mo}K_\alpha] = 0.71073$ Å, $\mu = 0.413$ mm^{-1}, $2\theta_{\text{max}} = 57.390°$). After merging of equivalents and absorption corrections, 20390 independent reflections ($R_{\text{int}} = 0.0383$) were used for the structure solution and refinement. Final *R* factors: $R_1 = 0.0418$ [17251 reflections with $I > 2\sigma(I)$], $wR_2 = 0.0903$ (all reflections), GOF = 1.024.

Crystal data for **4**. $C_{82}H_{70}KN_2O$, $M = 1138.50$, triclinic, space group $P\bar{1}$, 100(2) K, $a = 12.3166(5)$, $b = 13.8924(4)$ and $c = 20.5216(7)$ Å, $\alpha = 80.871(3)°$, $\beta = 95.6258(15)°$ and $\gamma = 64.005(3)°$, $Z = 2$, $V = 3096.2(2)$ Å^3, $d_{\text{calc}} = 1.221$ g cm^{-3}, $F_{000} = 1206$. A black plate-shaped single crystal with dimensions of 0.49×0.31×0.10 mm was selected, and the intensities of 64706 reflections were measured using an Oxford Xcalibur Eos diffractometer (ω-scans technique, $\lambda[\text{Mo}K_\alpha] = 0.71073$ Å, $\mu = 0.136$ mm^{-1}, $2\theta_{\text{max}} = 50.054°$). After merging of equivalents and absorption corrections, 10967 independent reflections ($R_{\text{int}} = 0.0634$) were used for the structure solution and refinement. Final *R* factors: $R_1 = 0.0566$ [7363 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1559$ (all reflections), GOF = 1.026.

CCDC 2400725 (**2**), 2400726 (**3′**) and 2400727 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

[‡] For more detail, see Online Supplementary Materials.



Scheme 2 *Reagents and conditions*: i, K (1 equiv.), THF, 24 h, then Et$_2$O.

[(Ar$^{\mathrm{BIG}}$-bian)K(THF)] was recently prepared by reduction of free Ar$^{\mathrm{BIG}}$-bian with potassium metal in THF.[25]

In THF solution, the paramagnetic compound **4** exhibits an ESR signal split into five lines (g = 2.0034) due to the coupling of the unpaired electron to two ^{14}N nuclei. The hyperfine coupling constant value a_{i} = 0.504 mT was simulated using the known method.[‡] The spin density on hydrogen or other atoms is small and cannot be determined. Overall, the ESR signal of compound **4** is very similar to that of [(Ar$^{\mathrm{BIG}}$-bian)K(THF)].[26]

Crystals of compound **4** suitable for X-ray diffraction analysis were obtained from diethyl ether. The molecular structure of compound **4** is shown in Figure 3. The C–N and C–C bond lengths in the diimine fragment [N(1)–C(1) 1.345(3), N(2)–C(2) 1.336(3) and C(1)–C(2) 1.444(4) Å] and the K–N bond lengths [2.769(2) and 2.641(2) Å] are similar to those in [(Ar$^{\mathrm{BIG}}$-bian)K(THF)] [N(1)–C(1) 1.334(3), N(2)–C(2) 1.352(3), C(1)–C(2) 1.447(3), K–N(1) 2.697(3) and K–N(2) 2.761(3) Å][26] and differ from those in anionic complexes **2** and **3′**. Inspection of the coordination environment of the potassium atoms in compound **4** showed that the planes of two benzene rings face the metal with K–R(1) 2.9183(14) Å and K–R(2) 3.0346(14) Å. It is worth noting that in [(Ar$^{\mathrm{BIG}}$-bian)K(THF)] the corresponding distances are larger [K–R(1) 3.15 and K–R(2) 3.64 Å].

In conclusion, we have shown that despite steric shielding of the 1,2-diimine moiety by bulky 2,6-bis(benzhydryl)-4-methylphenyl groups, gallylene [(Ar$^{\mathrm{BIG}}$-bian)Ga**:**] reacts with lithium or sodium metal in THF at ambient temperature to form anionic 1,3,2-diazagalloles [(Ar$^{\mathrm{BIG}}$-bian)GaLi(DME)$_3$] and [(Ar$^{\mathrm{BIG}}$-bian)GaNa(Et$_2$O)$_2$(THF)$_2$], respectively, in which the gallium atom is monovalent. In contrast, reduction of [(Ar$^{\mathrm{BIG}}$-bian)Ga**:**] with potassium metal results in the release of gallium metal and the formation of solvent-free potassium salt [(Ar$^{\mathrm{BIG}}$-bian)K]. We propose that the resulting low-valent gallium species may be useful for the transformation of small molecules and unsaturated substrates, including heteroallenes.

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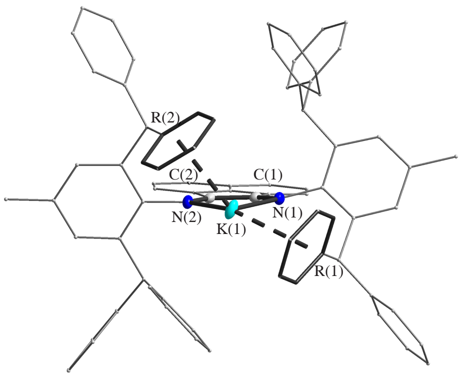

Figure 3 Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): K(1)–N(1) 2.769(2), K(1)–N(2) 2.641(2), N(1)–C(1) 1.345(3), N(2)–C(2) 1.336(3), C(1)–C(2) 1.444(4), K(1)–R(1) 2.9183(14), K(1)–R(2) 3.0346(14); N(1)–K(1)–N(2) 64.46(6), C(1)–N(1)–K(1) 112.69(16), C(2)–N(2)–K(1) 117.57(16), C(2)–C(1)–N(1) 122.8(2), C(1)–C(2)–N(2) 122.3(2).

The work was carried out using the equipment of the center for collective use ‘Analytical Center of the IOMC RAS’.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7680.

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