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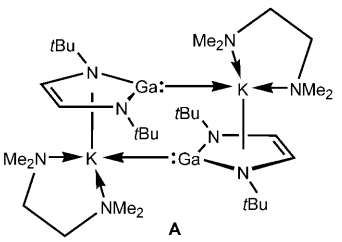
Synthesis, Molecular Structure and DFT Study of [(dpp-bian)Ga−M(Et_2O)$_3$] (M = Li, Na; dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene)

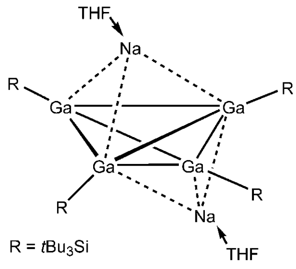
Igor L. Fedushkin,*[a] Anton N. Lukoyanov,[a] Georgy K. Fukin,[a] Sergey Yu. Ketkov,[a] Markus Hummert,[b] and Herbert Schumann*[c]

Dedicated to Professor Helmut Schwarz on the occasion of his 65th birthday

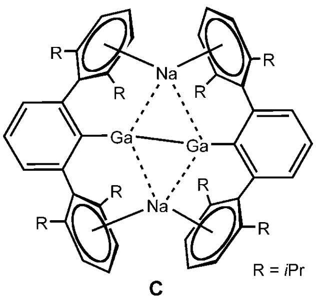
Since most of the chemical elements are metals, investigations concerning the nature of metal–metal bonds are of fundamental interest in chemistry. While the formation of homo- and heteronuclear complexes of p and d metals is quite common, the electropositive s and f metals normally do not form stable bonds among one another. Gallium is one of the metals which readily forms bonds to p and d metals.[1] Furthermore, compounds with a dative coordination of gallium(I) to alkaline earth[2] and rare earth metals[3] have been documented in the last two years. However, until now, only three examples of molecular gallium/alkali metal compounds exist in the literature.[4] In 2001, Schmidbaur and co-workers[4a] demonstrated that the reduction of diimine-supported digallane with potassium yields anionic imidazogallol, which, in the solid state, consists of dimers formed by gallium(I)–potassium coordination (**A**). Relatively short Ga–Na contacts are observed in the gallium clusters [$Na_2Ga_4R_4(thf)_2$][5] (**B**) and [$Na_2Ga_8R_6(thf)_2$][6] (R = tBu$_3$Si) as well as in the products[7] of the reduction of digallenes with sodium (**C**).



A



B



C

Recently we have reported on the synthesis and the crystal structure of the Ga–Ga bonded compound [(dpp-bian)Ga−Ga(dpp-bian)] (**1**; dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene)[8] containing the diimine ligand in its dianionic form. DFT studies of **1** revealed that besides the orbitals HOMO−1 (π) and HOMO−17 (σ), which are particularly responsible for the metal–metal bonding, also the LUMO (π) orbital shows bonding character with respect to the Ga−Ga bond. In 1993 Power et al. reported that the reduction of a digallan bearing bulky aryl groups, [$Ar_2Ga{-}GaAr_2$] (Ar = 2,4,6-iPr$_3$C$_6$H$_2$) with lithium goes along with a shortening of the Ga−Ga bond in the reaction product.[9] Additionally the Ga−Ga bond in [Na_2(Ar*GaGaAr*)] (Ar* = 2,6-iPr$_2$C$_6$H$_3$) is 0.3 Å shorter than in the neutral compound [Ar*GaGaAr*].[7] To trace the behaviour of the Ga−Ga bond in **1** under reductive conditions, we studied its reactions with lithium and sodium. The results are presented here.

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[a] Prof. Dr. I. L. Fedushkin, Dr. A. N. Lukoyanov, Dr. G. K. Fukin, Prof. Dr. S. Yu. Ketkov
G. A. Razuvaev Institute of Organometallic Chemistry
Russian Academy of Sciences, Tropinina 49,
603950 Nizhny Novgorod (Russia)
Fax: (+7) 831-462-7497
E-mail: igorfed@iomc.ras.ru

[b] Dr. M. Hummert
Institut für Angewandte Photophysik
Technische Universität Dresden
George-Bähr-Strasse 1, 01062 Dresden (Germany)

[c] Prof. Dr. H. Schumann
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)

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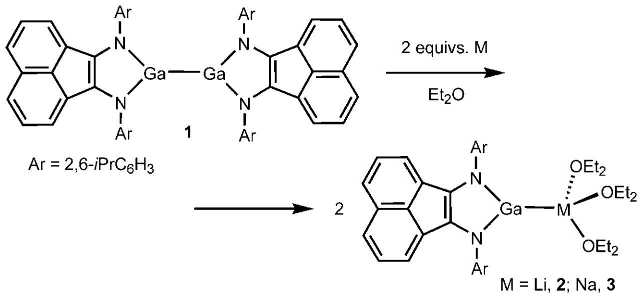
The compound [(dpp-bian)Ga–Ga(dpp-bian)] (**1**) reacts with two molar equivalents of Li or Na in diethyl ether with formation of crystalline [(dpp-bian)Ga−M(Et_2O)$_3$] (M = Li, **2**; M = Na, **3**) in yields of 80 to 90 % (Scheme 1).



Scheme 1.

The reduction process proceeds smoothly at room temperature, is complete within two (**3**) to eight hours (**2**) and is accompanied with a change of the colour of the reaction mixture from deep blue (**1**) to bright green (**2** and **3**). The bond cleavage in **1**, instead of formation of an anionic digallane, occurs probably due to the steric repulsion between the isopropyl groups that would arise in the virtual molecule Na_2-[(dpp-bian)Ga−Ga(dpp-bian)] complex under shortening of the Ga−Ga bond. The ^1H NMR spectra of **2** and **3** show the signals expected for the organic ligands. Compound **2** was also characterized by its ^7Li NMR spectrum.

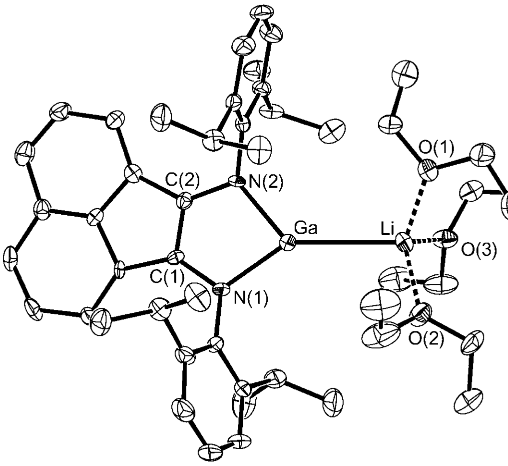


Figure 1. Molecular structure of **2** (30 % thermal ellipsoids).

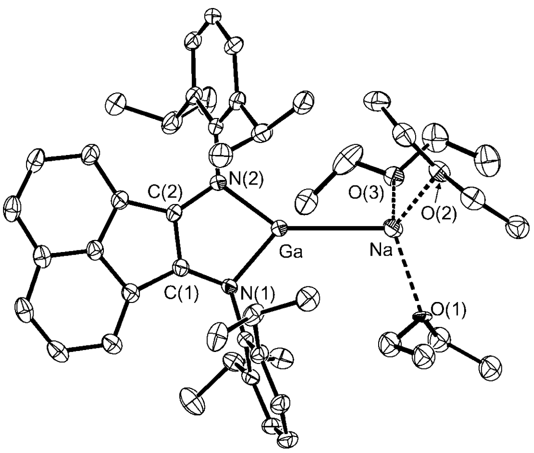


Figure 2. Molecular structure of **3** (30 % thermal ellipsoids).

Table 1. Crystal data and structure refinement details for **2** and **3**.

	2	**3**
formula	$C_{48}H_{70}GaLiN_2O_3$	$C_{48}H_{70}GaN_2NaO_3$
M_r	799.72	815.7
T [K]	153(2)	100(2)
λ [Å]	0.71073	0.71073
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$	Cc
a [Å]	35.3732(2)	12.5280(7)
b [Å]	20.303(1)	18.489(1)
c [Å]	12.8836(6)	20.416(1)
β [°]	90	95.224(1)
V [Å^3]	9294.5(8)	4709.6(5)
Z	8	4
ρ_{calcd} [g m^{-3}]	1.143	1.151
μ [mm^{-1}]	0.631	0.633
F(000)	3440	1752
crystal size [mm^3]	0.15 × 0.14 × 0.08	0.41 × 0.29 × 0.25
$\theta_{min}/\theta_{max}$	2.96/25.00	2.14/27.00
index ranges	$-42 \leq h \leq 42$ $-24 \leq k \leq 23$ $-15 \leq l \leq 15$	$-16 \leq h \leq 16$ $-23 \leq k \leq 23$ $-26 \leq l \leq 26$
reflections collected	82289	21340
independent reflections	16322	10113
R_{int}	0.1308	0.0322
completeness to θ = 25.00° [%]	99.8	–
completeness to θ = 27.00° [%]	–	99.7
max/min transmission	0.9512/0.9113	0.8579/0.7815
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	16322/1/991	10113/33/567
GOF on F^2	0.910	0.986
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0599$ $wR_2 = 0.0906$	$R_1 = 0.0434$ $wR_2 = 0.0932$
R indices (all data)	$R_1 = 0.1253$ $wR_2 = 0.1066$	$R_1 = 0.0619$ $wR_2 = 0.0994$
largest diff. peak/hole [e Å^{-3}]	0.776/-0.307	0.591/-0.246

The molecular structures of **2** (Figure 1) and **3** (Figure 2) have been determined by single-crystal X-ray diffraction. The respective crystal data collections and structure refinement data are listed in Table 1, selected bond lengths and angles are listed in Table 2. In both molecules the gallium atoms are coordinated in a distorted trigonal-planar fashion and are situated only slightly beyond the plane formed by N(1), N(2), and Li/Na (**2**, 0.05; **3**, 0.04 Å). The ligand arrangement around the respective alkali metal atoms corresponds to a distorted tetrahedron.

The two crystallographically independent molecules of **2** show similar geometric parameters, except for the lengths of the Ga−Li bonds (**2a**, 2.717(10); **2b**, 2.834(10) Å) and the Li−O(ether) bonds (**2a**, av 1.952; **2b**, av 1.996 Å). These longer bond lengths found for **2b** relative to **2a** may be ex-

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Table 2. Comparison of the main bond lengths and angles in **1**–**3**.

	1	**2**	**3**
Ga–M[a]	2.3321(2)	2.717(10)/2.834(10)	3.0490(7)
Ga–N(1)	2.0133(10)	1.973(5)/1.995(5)	1.9690(12)
Ga–N(2)	2.0287(12)	1.969(4)/1.959(4)	1.9782(15)
M–O(1)		1.933(10)/2.008(10)	2.351(2)
M–O(2)		1.939(11)/1.984(11)	2.3686(14)
M–O(3)		1.982(10)/1.996(12)	2.398(2)
N(1)–C(1)	1.3244(17)	1.394(7)/1.386(6)	1.374(2)
N(2)–C(2)	1.3357(15)	1.374(6)/1.388(6)	1.388(2)
C(1)–C(2)	1.4414(18)	1.394(7)/1.383(7)	1.378(2)
N(1)-Ga-N(2)	90.54(8)	83.82(19)/83.67(18)	83.29(6)
M-Ga-N(1)		139.5(2)/145.1(2)	131.95(4)
M-Ga-N(2)		136.5(2)/130.3(2)	144.65(4)

[a] **1**: M = Ga; **2**: M = Li; **3**: M = Na.

plained by a stronger steric repulsion between the lithium-coordinated diethyl ether molecules and the bulky 2,6-$i\mathrm{Pr_2C_6H_3}$-substituents of the dpp-bian ligand caused by crystal packing.

The inspection of the C–N and C–C bond lengths within the metalocycles in **2** and **3** allowed elucidation of the reduction state of the dpp-bian ligands in these molecules. The C(1)–N(1) and C(2)–N(2) bond lengths in **2** (av 1.385 Å) and **3** (av 1.381 Å) are close to those in **1** (av 1.388 Å), in which the dpp-bian dianion is observed. However, the Ga–N distances in **2** (av 1.974 Å) and **3** (av 1.973 Å) are notably longer relative to those in **1** (av 1.860 Å). This reflects the difference in the formal oxidation state of Ga atoms in **2** and **3** (+1), and in **1** (+2).

The electronic structure of complex **2** was examined by DFT[10] calculations at the B3LYP/6-31G* level of theory. For this reason, the full optimization of the singlet-state of molecule **2** as well as the natural bond orbital (NBO) analysis was performed. The key MO's of molecule **2** are shown in Figure 3. The calculated Ga–Li distance of 2.726 Å for the Li complex is in good agreement with the crystal data.

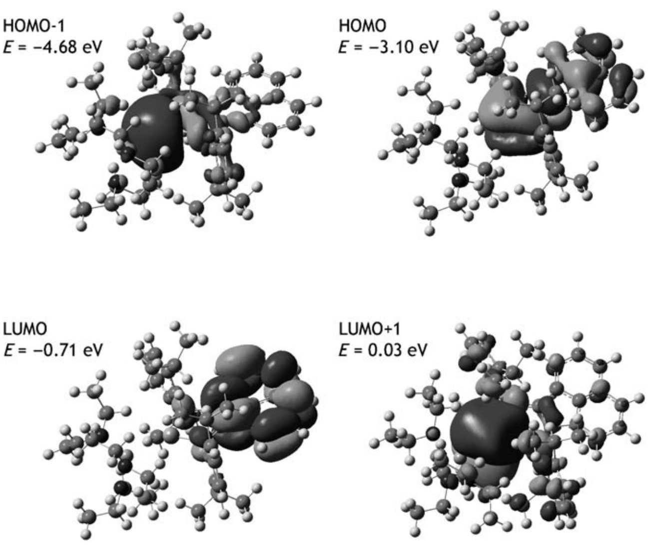

Figure 3. The DFT calculated boundary orbitals in **2**.

According to the results of the NBO analysis, the Ga–Li bond in **2** arises mainly from the donation of the electron lone pair of Ga (84.2 % s, 15.7 % p, 0.1 % d) to the vacant 2s orbital of the lithium cation. The NBO stabilization energy of this interaction is 41.6 kcal mol^{-1}. The bond is weakened by the Coulomb repulsion between the two metal atoms, which both are positively charged. However, the repulsion energy in **2** should be lower than that in the symmetric compound **1**, since the NBO charges of +0.44 a.u. for Ga and +0.79 a.u. for Li in **2** are lower than the NBO charge of +0.92 a.u. for each Ga atom in **1**.

In conclusion, the unique molecular compounds containing Ga–Li and Ga–Na bonds have been successfully synthesized. DFT studies of [(dpp-bian)Ga–Li($\mathrm{Et_2O}$)$_3$] revealed that the Ga–Li bond is mainly formed by donation of the lone electron pair of Ga$^{\mathrm{I}}$ to the solvated lithium cation. Probably similar compounds with gallium–metal bonds may be prepared using other metals suitable for the reduction of **1**.

Experimental Section

All manipulations were carried out using Schlenk techniques. Diethyl ether was distilled from sodium/benzophenone prior to use. The ^{1}H NMR spectra were recorded on a Bruker ARX-200 NMR spectrometer, the ^{7}Li NMR spectrum on a Bruker Avance(III)-400 NMR spectrometer. $\mathrm{GaCl_3}$ was purchased from Aldrich.

[(dpp-BIAN)Ga–Ga(dpp-BIAN)] (1): $\mathrm{GaCl_3}$ (0.35 g, 2 mmol) was added to a solution of $\mathrm{Na_3}$(dpp-bian) freshly prepared from dpp-bian (1.0 g, 2 mmol) and Na (0.14 g, 6 mmol) in diethyl ether (70 mL). Within a few minutes the mixture changed color from brown to blue indicating the formation of **1**. After filtration of the solution, it was used in situ for the syntheses of **2** and **3**.

[(dpp-bian)Ga–Li($\mathrm{Et_2O}$)$_3$] (2): Addition of lithium (14 mg, 2 mmol) to the stirred blue solution of **1** in diethyl ether, prepared as described above, caused the formation of a clear green solution within 8 h. Slow evaporation of the solvent from this solution gave **2** as deep green crystals (1.43 g, 89 %). M.p. 159°C; ^{1}H NMR (200 MHz, [$\mathrm{D_8}$]THF, 25 °C, TMS): $\delta = 7.09$–6.90 (m, 6 H; $\mathrm{C_6}H_3$-iPr), 6.57 (dd, ^3J(H,H) = 8.27, 1.40 Hz, 2 H; $\mathrm{C_{10}H_6}$), 6.50 (dd, ^3J(H,H) = 8.27, 6.23 Hz, 2 H; $\mathrm{C_{10}H_6}$), 5.58 (dd, ^3J(H,H) = 6.23, 1.40 Hz, 2 H; $\mathrm{C_{10}H_6}$), 3.87 (sept, ^3J(H,H) = 6.88 Hz, 4 H; CH($\mathrm{CH_3}$)$_2$), 3.39 (q, ^3J(H,H) = 6.99 Hz, 12 H; $\mathrm{Et_2O}$), 1.22 (d, ^3J(H,H) = 6.88 Hz, 12 H; CH(CH_3)($\mathrm{CH_3}$)), 1.13 (t, ^3J(H,H) = 6.99 Hz, 18 H; $\mathrm{Et_2O}$), 1.07 ppm (d, ^3J(H,H) = 6.88 Hz, 12 H; CH($\mathrm{CH_3}$)(CH_3)); ^{7}Li NMR ([$\mathrm{D_8}$]THF, 400 MHz, 25 °C, LiCl): $\delta = -2.51$ ppm; elemental analysis calcd (%) for $\mathrm{C_{48}H_{70}GaLiN_2O_3}$: C 72.09, H 8.82, N, 3.50; found C 72.15, H 8.90, N, 3.62.

[(dpp-bian)Ga–Na($\mathrm{Et_2O}$)$_3$] (3): Sodium (46 mg, 2 mmol) was added to a stirred blue solution of **1** in diethyl ether, prepared as described above. When the sodium has dissolved completely (ca. 2 h), the solvent was slowly evaporated from the green solution formed leaving **3** as deep green crystals (1.29 g, 79 %). M.p. 179 °C; ^{1}H NMR ([$\mathrm{D_8}$]THF, 200 MHz, 25 °C, TMS): $\delta = 7.13$–6.93 (m, 6 H; $\mathrm{C_6}H_3$-iPr), 6.63 (dd, ^3J(H,H) = 8.27, 0.97 Hz, 2 H; $\mathrm{C_{10}H_6}$), 6.55 (dd, ^3J(H,H) = 8.27, 6.34 Hz, 2 H; $\mathrm{C_{10}H_6}$), 5.64 (dd, ^3J(H,H) = 6.34, 0.97 Hz, 2 H; $\mathrm{C_{10}H_6}$), 3.86 (sept, ^3J(H,H) = 6.88 Hz, 4 H; CH($\mathrm{CH_3}$)$_2$), 3.39 (q, ^3J(H,H) = 6.99 Hz 12 H; $\mathrm{Et_2O}$), 1.24 (d, ^3J(H,H) = 6.88 Hz 12 H; CH(CH_3)($\mathrm{CH_3}$)), 1.13 (t, ^3J(H,H) = 6.99 Hz 18 H; $\mathrm{Et_2O}$), 1.08 ppm (d, ^3J(H,H) = 6.88 Hz, 12 H; CH($\mathrm{CH_3}$)(CH_3)); elemental analysis calcd (%) for $\mathrm{C_{48}H_{70}GaNaN_2O_3}$: C 70.67, H 8.65, N, 3.43; found C 70.59, H 8.60, N, 3.38.

CCDC-689163 (**2**) and CCDC-689164 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

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charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: alkali metals • density functional calculations • gallium • metal–metal bonds • N ligands • structure elucidation

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[1] Crystallographically documented compounds containing Ga–metal bonds are referenced in the "Supporting Information".

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[10] The geometry optimization, single-point calculation and NBO analysis were performed using Gaussian 03 package (see Supporting Information).

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