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Reduction of Digallane [(dpp-bian)Ga−Ga(dpp-bian)] with Group 1 and 2 Metals**

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Abstract: The reduction of digallane [(dpp-bian)Ga−Ga(dpp-bian)] (**1**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with lithium and sodium in diethyl ether, or with potassium in THF affords compounds featuring the direct alkali metal–gallium bonds, [(dpp-bian)Ga−Li(Et_2O)$_3$] (**2**), [(dpp-bian)Ga−Na(Et_2O)$_3$] (**3**), and [(dpp-bian)Ga−K(thf)$_5$] (**7**), respectively. Crystallization of **3** from DME produces compound [(dpp-bian)Ga−Na(dme)$_2$] (**4**). Dissolution of **3** in THF and subsequent crystallization from diethyl ether gives [(dpp-bian)Ga−Na(thf)$_3$(Et_2O)] (**5**). Ionic [(dpp-bian)Ga]$^-$[Na([18]crown-6)(thf)$_2$]$^+$ (**6a**) and [(dpp-bian)Ga]$^-$[Na(Ph_3PO)$_3$(thf)]$^+$ (**6b**) were obtained from THF after treatment of **3** with [18]crown-6 and Ph_3PO, respectively. The reduction of **1** with Group 2 metals in THF affords [(dpp-bian)Ga]$_2$M(thf)$_n$ (M = Mg (**8**), $n = 3$; M = Ca (**9**), Sr (**10**), $n = 4$; M = Ba (**11**), $n = 5$). The molecular structures of **4**–**7** and **11** have been determined by X-ray crystallography. The Ga−Na bond lengths in **3**–**5** vary notably depending on the coordination environment of the sodium atom.

Keywords: diimine ligands · gallium · main group elements · metal–metal interactions · reduction

Introduction

As the majority of the elements in the Periodic Table are metals, the study of molecular compounds that exhibit metal–metal bonds is fundamental to furthering our understanding of structure and bonding, catalysis, metal surface chemistry, and magnetism.[1] Besides the concept of multiple bonds between transition metals developed by Cotton,[1] a number of metal–metal bonds involving both p- and d-block metals have been reported in recent years, such as Zn−Zn bonds,[2] Cr−Cr quintuple bonds,[3] Mg−Mg bonds,[4] and an exceptionally short Co−Co bond.[5] The fundamental work in the chemistry of the low-valent Group 13 elements was done in the early 1990s when monovalent species [{(η^5-C_5Me_5)Al}$_4$],[6] [(η^5-C_5Me_5)Ga],[7,8] and K_2[iBu$_{12}$Al$_{12}$][9] were reported. Later on, aluminum(I) and gallium(I) species, for example, ketiminates [{HC(CMeNAr)$_2$}Al][10] and [{HC(CMeNAr)$_2$}Ga][11] (Ar = 2,6-iPr$_2$C$_6$H$_3$) were discovered. Another class of coordination compounds of monovalent Group 13 metals consists of the anionic Group 13 analogues of N-heterocyclic carbenes. The synthetic approach to these compounds, which was pioneered by Schmidbaur and co-workers, involves the treatment of a dilithiated diazabutadiene ligand with $GaCl_3$ to give a product, those reduction with potassium gives [{[(tmeda)K]Ga[(tBuNCH)$_2$]}$_2$].[12] This approach was further extended by Jones and co-workers by using bulky 2,6-diisopropylphenyl-substituted diazabutadiene and "GaI" as starting material (Scheme 1).[13]

Thus, potassium salts of the 1,3,2-diazagallol include the dimeric [{[(tBuNCH)$_2$]Ga[K(tmeda)]}$_2$],[12a] [{[(ArNCH)$_2$]-Ga[K(L)]}$_2$][13a] (L = tmeda or Et_2O), the ionic species [{[(tBuNCH)$_2$]Ga[K([18]crown-6)(thf)$_2$]}$_2$],[12b] and [{(ArNCH)$_2$}Ga]$_2$[K_2([18]crown-6)$_3$] (Ar = 2,6-iPr$_2$C$_6$H$_3$).[13a] Mostly electrostatic interactions are observed in these compounds, but no metal–metal bonds. On the other hand, these

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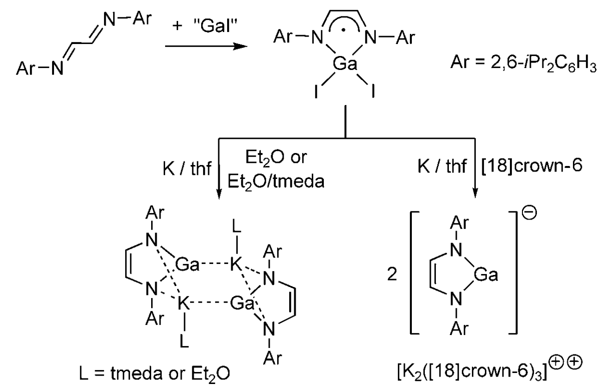
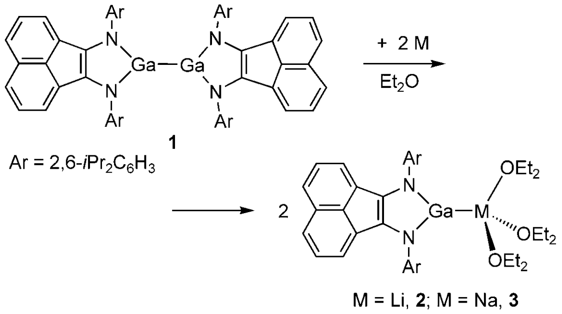
[**] dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene.



Scheme 1.

compounds are suitable starting materials for the preparation of new complexes with gallium–metal bonds.[13b]

Recently we have shown that a direct reduction of the digallane [(dpp-bian)Ga–Ga(dpp-bian)] (**1**)[14] with lithium or sodium in diethyl ether yields compounds with direct Ga–Li and Ga–Na bonds, [(dpp-bian)Ga–M(Et_2O)$_3$] (M = Li, **2**; M = Na, **3**) (Scheme 2).[15]

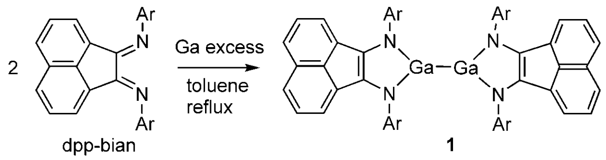


Scheme 2. The reduction of digallane **1** with alkali metals.

In one of two crystallographically independent molecules of complex **2** the Ga–Li distance (2.717 Å) is in agreement with that calculated by DFT calculations (2.726 Å),[15] whereas the Ga–Li bond in the second molecule present in the unit cell is notably longer (2.834 Å). The elongated Ga–Li distance is a result of a stronger repulsion between the lithium coordinated diethyl ether molecules and the bulky 2,6-iPr$_2$C$_6$H$_3$ substituents of the dpp-bian ligand caused by crystal packing.[15] On the other hand, according to DFT calculations the Ga–Li distance in the model molecule of **2** that contains dimethyl ether instead of diethyl ether is notably shorter (2.608 Å). In addition, it has been found that the NBO charges on the metals alter on going from the diethyl ether adduct (+0.44 a.u. for Ga and +0.79 a.u. for Li) to the dimethyl ether derivative (+0.48 a.u. for Ga and +0.76 a.u. for Li). These data encouraged us to study in detail an influence of neutral ligands coordinated to the alkali metal atom on the alkali metal–gallium bond lengths. Results of this study as well as the synthesis and characterization of the complexes with alkaline earth metal–gallium bonds are present here.

Results and Discussion

Syntheses: Originally the digallane **1** was prepared by reacting $GaCl_3$ with (dpp-bian)K$_3$ in Et_2O or in THF.[14] A more convenient synthetic approach to compound **1** is the direct reduction of dpp-bian with an excess of gallium metal (Scheme 3). The reaction proceeds in toluene at reflux and affords digallane **1** in quantitative yield.



Scheme 3. A new synthetic approach to **1**.

Since the LUMO (π) in digallane **1** shows bonding character with respect to the Ga–Ga bond one may suggest that the reduction of **1** with Li and Na proceeds via the formation of the intermediate radical-anionic species [(dpp-bian)Ga–Ga(dpp-bian)]$^{-\bullet}$M$^+$ (M = Li, Na). In 1993, Power and co-workers reported that the reduction of a digallane Ar$_2$Ga–GaAr$_2$ (Ar = 2,4,6-iPr$_3$C$_6$H$_2$) with lithium proceeds with the formation of a radical anion with Ga–Ga multiple bonding character.[16] In the course of the synthesis of **2** and **3** (Scheme 2) the color of the reaction mixture changes dramatically. To determine whether intermediate radical-anionic species are formed, the reaction of **1** with two molar equivalents of Li in Et_2O was monitored by absorption spectroscopy. In the course of the reduction process absorption of compound **1** (λ = 584 nm) decreases and the absorption of complex **2** (λ = 468 and 738 nm) increases (Figure 1).

Thus, spectroscopic data indicate that the one-electron reduction of **1** leads to cleavage of the Ga–Ga bond instead of

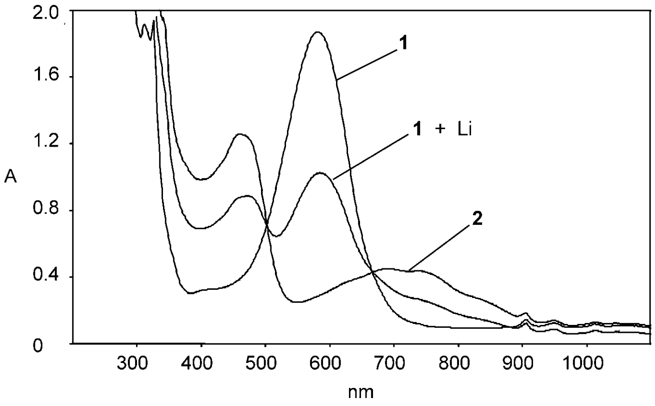


Figure 1. The absorption spectra of the complexes **1**, **2** and their mixture in Et_2O.

formation of a radical-anionic digallane. It happens probably due to the steric repulsion between the isopropyl groups that would arise in the virtual molecules [(dpp-bian)Ga–Ga-(dpp-bian)]$^{-\bullet}$M$^+$ (M = Li, Na) under shortening of the Ga–Ga bond. If more than two molar equivalents of alkali metal are used in the reaction with **1** the formation of gallium metal and (dpp-bian)M$_2$ takes place. Complexes **2** and **3** both crystallize from diethyl ether with three solvent molecules coordinated to the alkali metal centre.

Crystallization of complex **3** (Figure 2) from different medias allows the isolation of new complexes with Ga–Na bonds, in which the coordination environment of the sodium atoms is different. Complex [(dpp-bian)Ga–Na(dme)$_2$] (**4**) has been obtained by crystallization of **3** from DME, compound [(dpp-bian)Ga–Na(thf)$_3$(Et$_2$O)] (**5**) by crystallization from Et$_2$O after treatment of **3** with THF (Scheme 4).

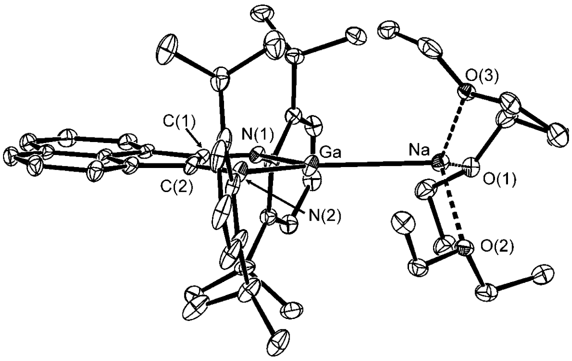
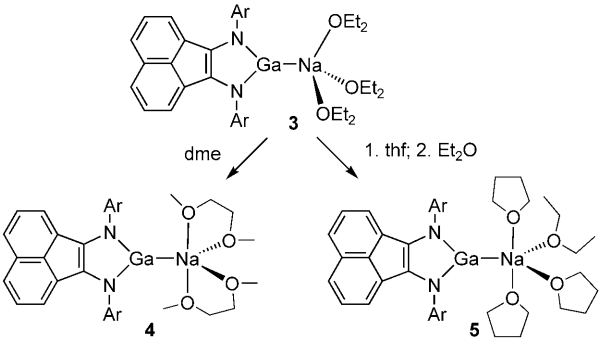


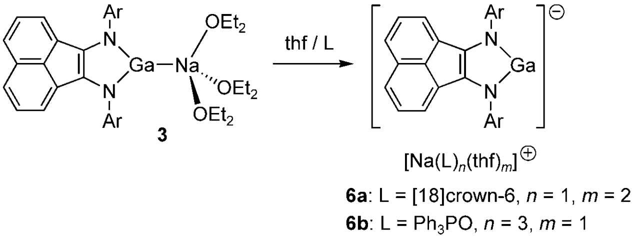
Figure 2. The molecular structure of complex **3**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted.



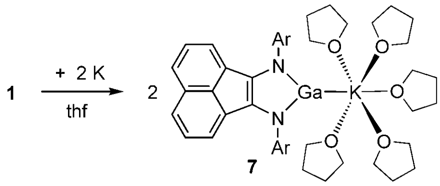
Scheme 4. Preparation of compounds **4** and **5**.

Addition of [18]crown-6 or Ph$_3$PO to the solutions of complex **3** in THF results in the cleavage of the Ga–Na bonds and gives the solvent separated complexes [(dpp-bian)Ga]$^-$[Na([18]crown-6)(thf)$_2$]$^+$ (**6a**) and [(dpp-bian)Ga]$^-$[Na(Ph$_3$PO)$_3$(thf)]$^+$ (**6b**) (Scheme 5).

The reduction of **1** with two molar equivalents of potassium affords [(dpp-bian)Ga–K(thf)$_5$] (**7**) (Scheme 6). As in the case of other alkali metals the reaction using potassium is accompanied with a change in color of the reaction mixture from deep blue to bright green. In contrast to the potassium TMEDA and Et$_2$O adducts [{[(L)K]Ga-[(ArNCH)$_2$]}$_2$] (L = tetramethylethylenediamine (tmeda) or Et$_2$O) (Scheme 1) complex **7** represents a monomeric compound with an unsupported Ga–K bond.



Scheme 5. Preparation of compounds **6a** and **6b**.

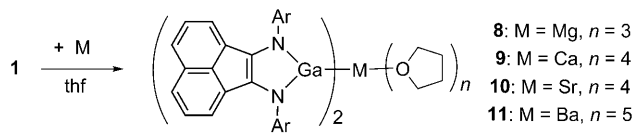


Scheme 6. Synthesis of complex **7**.

Deep green complexes **2**–**7** featuring direct alkali metal–gallium bonds are very sensitive towards oxygen and moisture, but thermally they are rather robust: No decomposition in solution was observed within several weeks at ambient temperature. In the sealed under vacuum capillaries crystalline complexes **2**–**7** decompose in the range of 90–180 °C. All the complexes are moderately soluble in diethyl ether, 1,2-dimethoxyethane, and tetrahydrofuran and almost insoluble in alkanes. The ^{1}H NMR spectra of **2**–**7** show the signals expected for the organic ligands. Complexes **4** and **6** have been also characterized by the IR spectroscopy. In the IR spectra of **4** and **6** most intense absorptions are associated with C–N ($\tilde{\nu} \approx 1500$ and $1350\,\mathrm{cm^{-1}}$), C–O ($\tilde{\nu} \approx 1080$ and $860\,\mathrm{cm^{-1}}$) and C–H(Ar) ($\tilde{\nu} \approx 760\,\mathrm{cm^{-1}}$) stretching modes. Molecular structures of the compounds **2**–**7** have been established by single-crystal X-ray analysis.

In 2006, Jones and co-workers reported the first compounds with Ga–Mg and Ga–Ca bonds. These compounds were prepared by the reduction of gallium(III) species [I$_2$Ga{(ArNCR)$_2$}] (R = H, Me; Ar = 2,6-iPr$_2$C$_6$H$_3$) with a large excess of either Mg or Ca metal in the presence of mercury in THF.[17] This reaction did not proceed with strontium and barium. Attempts to synthesize alkaline earth metal–gallium complexes by the reactions of MI$_2$ (M = Sr, Ba) with [{[(tmeda)K]Ga[(ArNCH)$_2$]}$_2$] were unsuccessful (in all cases intractable mixtures of products were obtained).[17] The first compounds with Ga–Ba and Ga–Sr bonds were prepared by Roesky and co-workers by the reaction of [Cp*Ga] with [Cp*$_2$Ba] and [Cp*$_2$Sr(thf)]$_n$ (Cp* = η^5-C$_5$Me$_5$). The metal–metal bonding in [Cp*$_2$(thf)Sr–GaCp*] and [Cp*$_2$Ba–(GaCp*)$_2$] is best described as a donor–acceptor interaction.[18]

The complexes with alkaline earth metal–gallium bonds, $[(\text{dpp-bian})\text{Ga}]_2\text{M}(\text{thf})_n$ (M=Mg (**8**), $n=3$; M=Ca (**9**), Sr (**10**), $n=4$; M=Ba (**11**), $n=5$) were synthesized by the reduction of digallane **1** with the corresponding Group 2 metal in THF (Scheme 7).



Scheme 7. Synthesis of complexes **8**–**11**.

These reactions proceed by using an excess or one equivalent of metal in THF at room temperature. The reactions are complete within 12 to 24 h and are accompanied with a color change of the reaction mixture from deep blue to brown. Compound **11** has been also prepared by the metathesis reaction of **3** or **7** with barium iodide in THF. This fact proves that compounds **3** and **7** can be used as starting reagents for the synthesis of different species with metal–gallium bonds. Complexes **8**–**11** have been isolated as dark brown crystals from a concentrated THF solution in 53–59% yields and characterized by using IR and NMR spectroscopy. The ^{1}H NMR spectra of **8**–**11** are very much alike and show the signals expected for the organic ligands. Despite of the poor quality of the X-ray diffraction data obtained for **8**–**10** the arrangement of the atoms within the molecules **8**–**10** could be established and it corresponds to those depicted in Scheme 7. The molecular structure of the barium complex **11** was determined by X-ray crystallography.

The molecular structures of 3, 4, 5, 6a, 6b, 7, and 11: The molecular structures of **3**, **4**, **5**, **6a**, **6b**, **7**, and **11** are depicted in Figures 2–7, respectively. Selected bond lengths and angles are listed in Table 1, the crystal data collections and structure refinement details are listed in Table 2.

In the neutral molecules **3**, **4**, **5**, **7**, and **11** the gallium atoms are coordinated in a distorted trigonal-planar fashion, whereas in the $[(\text{dpp-bian})\text{Ga}]^-$ ions in **6a** and **6b** the gallium atoms are coordinated only to two nitrogen atoms of the dpp-bian ligand. In all the molecules the gallium atoms are positioned almost perfectly in the plane estimated with atoms N(1), C(1), C(2) and N(2). Complexes **3**, **4**, and **5** differ only with respect to the number and the type of solvent molecules coordinated to the sodium atom. In complex **3** the sodium atom is tetrahedrally coordinated. Although in the complexes **4** and **5** the sodium atoms are both five-coordinated, their coordination polyhedrons are remarkably different; **4** contains a distorted square pyramid and **5** contains a trigonal bipyramid. In molecule **4** the basal plane of the

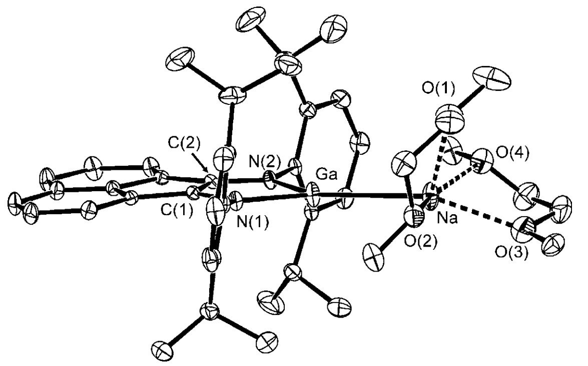


Figure 3. The molecular structure of complex **4**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted.

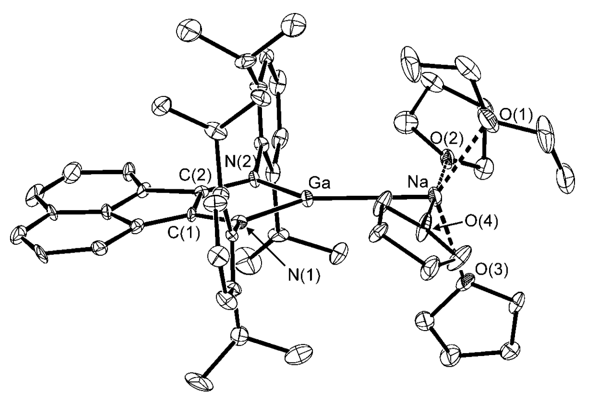


Figure 4. The molecular structure of complex **5**. Thermal ellipsoids are drawn at 20% probability level. Hydrogen atoms are omitted.

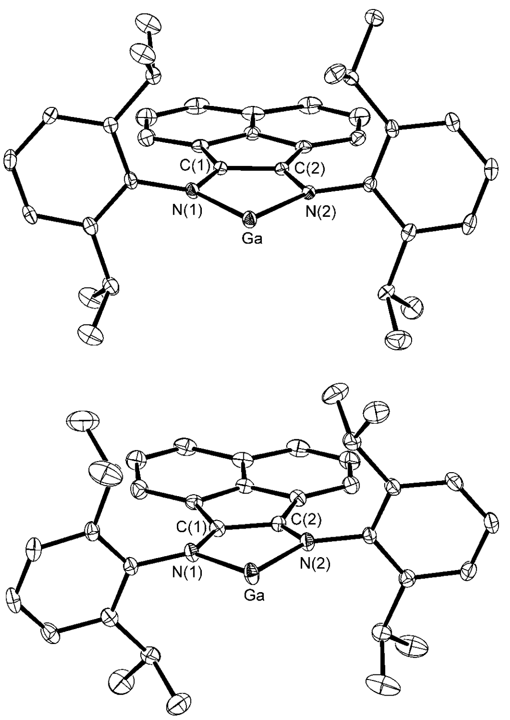


Figure 5. The molecular structure of the anions $[(\text{dpp-bian})\text{Ga}]^-$ in the complexes **6a** (top) and **6b** (bottom). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted.

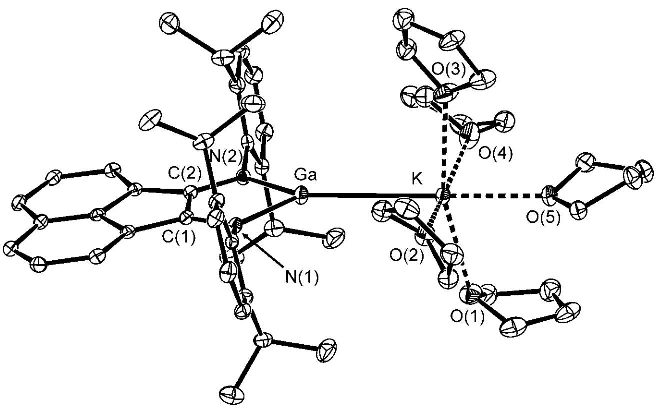


Figure 6. The molecular structure of complex **7**. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted.

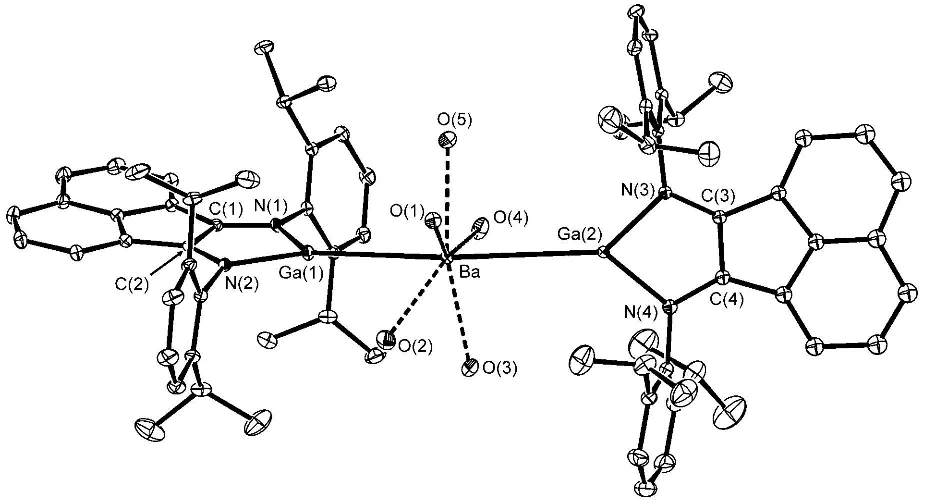


Figure 7. The molecular structure of complex **11**. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms and carbon atoms of THF molecules are omitted for clarity.

pyramid is formed with the atoms Ga, O(2), O(3) and O(4) (Ga-Na-O(3) and O(2)-Na-O(4) angles are 148.40(9) and 158.39(9)°, respectively). The oxygen atom O(1) in **4** occupies a vertex of a square pyramid. In molecule **5** the sum of the angles between the Na atom and the equatorial atoms Ga, O(1), and O(3) (360°) corresponds exactly with the ideal value for a trigonal bipyramid. Also, the angle O(2)-Na-O(4) (174.6(8)°) matches well to the ideal value (180°).

Unexpectedly, an increase of the coordination number of the sodium atom from four to five on going from **3** to **4** does not result in an elongation of the Ga−Na bond in **4**, but, conversely, leads to its shortening (**3**: 3.0490(7) Å, **4**: 2.9838(12) Å). Moreover, the Ga−Na bond in **5** (3.1110(11) Å) is 0.13 Å longer than in complex **4**, which also contains a five-coordinate sodium atom. We believe that the remarkable alteration of the Ga−Na bond lengths in **3**, **4**, and **5** reflects the steric bulk of the solvent molecules coordinated to the sodium. Three monodentate diethyl ether molecules coordinated to the sodium atom cause more steric stress at the (dpp-bian)Ga fragment compared to that resulting from two bidentate DME molecules. Thus, the sodium atom approaches the gallium atom as close as permitted by the repulsion between solvent molecules and the bulky substituents of the dpp-bian.

The coordinating strength of the [18]crown-6 and Ph$_3$PO is high enough to push away the gallene anion from sodium coordination sphere. The bond distances within metallacycles in gallene anions [(dpp-bian)Ga]$^-$ in **6a** and **6b** are very similar (Table 1). The anion [(dpp-bian)Ga]$^-$ is isoelectronic with neutral [(dpp-bian)Ge] (**A**)[19] and cationic [(dpp-bian)As]$^+$ (**B**).[20] The formal oxidation states of the metal atoms in [(dpp-bian)Ga]$^-$, **A**, and **B** are +1, +2, and +3, respectively. On going from [(dpp-bian)Ga]$^-$ to **A** and further to **B** the metal–nitrogen distances become shorter (averaged values: **6a**, 2.013; **A**, 1.890; **B**, 1.848 Å). Since the covalent radii of Ga, Ge, and As are close (1.22, 1.20, and 1.19 Å, respectively),[21] the observed shortening of the M−N bonds reflects the rather stronger interaction of

Table 1. Selected bond lengths [Å] and angles [°] in **1–7** and **11**.

	1	**2**	**3**	**4**	**5**	**6a**	**6b**	**7**	**11**
Ga−M[a]	2.3598(3)	2.815(10)	3.0490(7)	2.9838(12)	3.1110(11)	–	–	3.4396(6)	3.6433(5)/3.5964(7)
Ga−N(1)	1.8624(18)/1.8583(18)	1.974(4)	1.9690(12)	1.964(2)	1.949(6)	2.011(2)	1.999(2)	2.0043(15)	1.977(3)/1.962(4)
Ga−N(2)	1.8551(17)/1.8657(17)	1.990(4)	1.9782(15)	1.971(2)	1.997(5)	2.0149(18)	1.999(2)	1.9861(16)	1.967(3)/1.974(4)
N(1)−C(1)	1.393(3)/1.388(3)	1.384(6)	1.374(2)	1.375(3)	1.387(8)	1.368(3)	1.374(3)	1.372(2)	1.372(4)/1.371(6)
N(2)−C(2)	1.389(3)/1.383(3)	1.370(6)	1.388(2)	1.379(3)	1.363(8)	1.379(3)	1.374(3)	1.376(2)	1.374(4)/1.385(6)
C(1)−C(2)	1.375(3)/1.378(3)	1.374(7)	1.378(2)	1.385(3)	1.368(4)	1.388(3)	1.387(4)	1.383(3)	1.389(4)/1.376(6)
N(1)-Ga-N(2)	90.54(8)/90.11(8)	83.50(17)	83.29(6)	82.96(8)	83.05(10)	81.81(8)	81.91(9)	82.98(6)	83.29(10)/83.42(15)
N(1)-Ga-M	136.74(6)/132.70(6)	130.2(2)	131.95(4)	133.80(6)	140.17(19)	–	–	143.68(5)	138.75(7)/138.04(11)
N(2)-Ga-M	137.10(6)/132.71(6)	145.2(2)	144.65(4)	142.93(6)	136.69(17)	–	–	133.07(4)	137.31(7)/137.76(11)
Ga(1)-M-Ga(2)	–	–	–	–	–	–	–	–	156.051(14)

[a] **1**: M = Ga; **2**: M = Li; **3–5**: M = Na; **7**: M = K; **11**: M = Ba.

Table 2. Crystal data and structure refinement details for **4–7** and **11**.

Compound	**4**	**5**	**6a**	**6b**	**7**	**11**
formula	$C_{44}H_{60}GaN_2NaO_4$	$C_{52}H_{74}GaN_2NaO_4$	$C_{63}H_{94}GaN_2NaO_9$	$C_{98}H_{101}GaN_2NaO_5P_3$	$C_{56}H_{80}GaKN_2O_5$	$C_{98}H_{132}BaGa_2N_4O_{6.5}$
M_r [g mol^{-1}]	773.65	883.84	1116.11	1572.43	970.04	1746.86
T [K]	150(2)	173(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$	P_{bca}	$P2_1/n$	$P2_1/c$
a [Å]	10.6453(2)	20.0538(6)	11.8990(6)	27.3545(12)	13.743(2)	20.7197(14)
b [Å]	20.1871(3)	13.0439(4)	14.2742(8)	22.3472(10)	19.953(3)	20.6809(14)
c [Å]	20.3791(2)	19.5013(5)	18.4027(10)	27.6684(11)	19.556(3)	22.2606(15)
α [°]	90	90	85.931(1)	90	90	90
β [°]	91.8997(16)	90	85.689(1)	90	90.190(3)	98.8813(15)
γ [°]	90	90	78.740(1)	90	90	90
V [Å^3]	4377.02(11)	5101.1(3)	3051.8(3)	16913.6(13)	5362.5(15)	9424.3(11)
Z	4	4	2	8	4	4
ρ_{calcd} [g m^{-3}]	1.174	1.151	1.215	1.235	1.202	1.231
μ [mm^{-1}]	0.679	0.590	0.513	0.442	0.637	1.033
$F(000)$	1648	1896	1200	6640	2080	3672
crystal size [mm]	0.20×0.18×0.15	0.29×0.16×0.14	0.30×0.25×0.20	0.20×0.20×0.10	0.48×0.47×0.19	0.20×0.12×0.10
$\theta_{min}/\theta_{max}$	2.93/25.00	3.12/25.00	2.24/26.00	1.75/26.45	1.02/26.00	1.35/29.00
index ranges	$-12 \leq h \leq 12$ $-22 \leq k \leq 24$ $-24 \leq l \leq 24$	$-23 \leq h \leq 23$ $-15 \leq k \leq 15$ $-23 \leq l \leq 23$	$-14 \leq h \leq 14$ $-17 \leq k \leq 17$ $-22 \leq l \leq 22$	$-32 \leq h \leq 34$ $-27 \leq k \leq 27$ $-20 \leq l \leq 34$	$-16 \leq h \leq 16$ $-24 \leq k \leq 24$ $-24 \leq l \leq 24$	$-28 \leq h \leq 28$ $-28 \leq k \leq 28$ $-30 \leq l \leq 30$
reflections collected	37316	86358	25647	102267	43460	112762
independent reflections	7677	8970	11823	17357	10519	25015
R_{int}	0.0358	0.0691	0.0265	0.0687	0.0405	0.0569
completeness to $\theta = 27.50°$ [%]	99.7	99.8	98.5	99.5	99.8	99.8
max/min transmission	0.9050/0.8762	0.9219/0.8474	0.9043/0.8613	0.957/0.917	0.8885/0.7495	0.904/0.820
data/restraints/parameters	7677/30/499	8970/554/689	11823/10/651	17357/18/984	10519/11/556	25015/0/945
GOF on F^2	1.056	0.964	1.010	0.979	1.061	1.108
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0481$ $wR_2 = 0.1152$	$R_1 = 0.0419$ $wR_2 = 0.0789$	$R_1 = 0.0775$ $wR_2 = 0.2081$	$R_1 = 0.0451$ $wR_2 = 0.1132$	$R_1 = 0.0406$ $wR_2 = 0.0895$	$R_1 = 0.0618$ $wR_2 = 0.1577$
R indices (all data)	$R_1 = 0.0719$ $wR_2 = 0.1233$	$R_1 = 0.0825$ $wR_2 = 0.0925$	$R_1 = 0.1002$ $wR_2 = 0.2265$	$R_1 = 0.0903$ $wR_2 = 0.1444$	$R_1 = 0.0607$ $wR_2 = 0.0979$	$R_1 = 0.0906$ $wR_2 = 0.1855$
largest diff. peak/hole [e Å^{-3}]	1.634/−0.410	0.258/−0.241	1.979/−3.209	0.683/−0.510	0.542/−0.483	2.632/−1.060

the cationic metal center (As) with the dpp-bian dianion compared to that of the anionic center (Ga).

In contrast to dimeric potassium salts of the 1,3,2-diazagallol [{[(tmeda)K]Ga[(tBuNCH)$_2$]}$_2$][12a] and [{[(L)K]Ga[(ArNCH)$_2$]}$_2$][13a] (L = tmeda or Et_2O), compound **7** is a monomer with an octahedral potassium atom coordinated with five THF molecules and the gallium atom of the (dpp-bian)Ga fragment. The difference in the molecular structures of **7** and [{[(L)K]Ga[(ArNCH)$_2$]}$_2$][13a] is remarkable because in both cases the diimine ligands have the same substituents at the nitrogen atoms and, hence, the availability of the π-conjugated metallacycle C_2N_2Ga for the coordination of the potassium cation must be practically the same in [(dpp-bian)Ga]$^-$ and [{(CHNAr)$_2$}Ga]$^-$.[13a] We assume that, owing to the fusion of the diimine fragment with the naphthalene π system, the π-electron density over the metallacycle C_2N_2Ga in [(dpp-bian)Ga]$^-$ is lower than in [{(CHNAr)$_2$}Ga]$^-$. Therefore, the potassium atom in **7** receives more electronic satisfaction being coordinated with solvent molecules and with the gallium lone pair compared to the situation when it is localized above of the C_2N_2Ga metallacycle and coordinated with less THF molecules. Coordination of the sodium atom to a metallacycle was observed in several aluminum(III) complexes of the dpp-bian dianion, for example, [R_2Al(dpp-bian)Na(η^6-arene)] (R = Me, Et; arene = benzene, toluene) and [R_2Al(dpp-bian)Na(Et_2O)] (R = Me, Et).[22]

The Ga–K bond length in **7** (3.4396(6) Å) lies in the range of those bonds in [{[(L)K]Ga[(tBuNCH)$_2$]}$_2$] (Ga–K(η^5) 3.4681(5) Å; Ga–K(η^1) 3.438(1) Å),[12a] [{[(L)K]Ga[(ArNCH)$_2$]}$_2$] (Ga–K(η^5) 3.4620(16) Å; Ga–K(η^1) 3.5318(18) Å)[13a] (L = tmeda) and [{[(Et_2O)K]Ga[(ArNCH)$_2$]}$_2$] (Ga–K(η^5) 3.3784(13) Å; Ga–K(η^1) 3.4223(10) Å).[13a] Interestingly, in the dimeric complexes the distances from the gallium to the potassium atom [K(η^1)], which is situated within the C_2N_2Ga metallacycle plane, are longer than the distances from gallium to the potassium [K(η^5)] that resides above the mentioned plane.

Complexes **6a** and **6b** represent a case of complete transfer of an electron from the alkali metal to the (dpp-bian)Ga moiety. In **6a** and **6b** the Ga–N distances (**6a**: av 2.013 Å; **6b**: av 1.999 Å) are longest among those distances in compounds **3–7**. Shortened Ga–N bond lengths in **3** (av 1.974 Å), **4** (av 1.967 Å), and **5** (av 1.973 Å) compared to those in **6a** and **6b** may be indicative of some covalent character of the Ga–Na bond in the former compounds. Elongated Ga–N bond lengths in **7** (av 1.995 Å) signify a rather ionic Ga–K interaction. The observed alteration of the C(1)–N(1) and C(2)–N(2) bond lengths (1.363(8)–1.387(8) Å) in the complexes **3–7** and **11** (Table 1) is typical for the bisamide form of the dpp-bian ligand. In the radical-anionic dpp-bian the C–N bonds are approximately 0.045 Å[23] shorter and in free dpp-bian these bonds are both 1.282 Å.[24]

Complex **11** crystallizes in the monoclinic space group $P2_1/c$. One of the (dpp-bian)Ga fragments (N(3), N(4) etc) in **11** is disordered over two positions with 72 and 28 % occupancies. The barium center in **11** possesses distorted pentagonal-bipyramidal geometry, both gallium atoms are axially positioned, and the oxygen atoms O(1), O(2), O(3), O(4), and O(5) occupy an equatorial plane. In the related Mg and Ca complexes $[\{[(\mathrm{ArNCH})_2]\mathrm{Ga}\}_2\mathrm{Mg}(\mathrm{thf})_3]$ and $[\{[(\mathrm{ArNCR})_2]\mathrm{Ga}\}_2\mathrm{Ca}(\mathrm{thf})_4]$ central metal atoms have a trigonal-bipyramidal and an octahedral coordination environment, respectively.[17] The Ga(1)-Ba-Ga(2) angle in **11** (156.0°) deviates significantly from the ideal value (180°). It may be explained by a steric repulsion between the barium-coordinated THF molecules and the bulky 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$ substituents of the dpp-bian ligands caused by crystal packing. The Ga–Ba bond lengths in **11** (3.6433(5) and 3.5964(7) Å) are remarkably longer than the sum of the covalent radii of Ga and Ba (3.37 Å).[21] A similar situation is observed for the Ga–Mg and Ga–Ca bonds in $[\{[(\mathrm{ArNCH})_2]\mathrm{Ga}\}_2\mathrm{Mg}(\mathrm{thf})_3]$ and $[\{[(\mathrm{ArNCR})_2]\mathrm{Ga}\}_2\mathrm{Ca}(\mathrm{thf})_4]$.[17] The Ga–Ba bond lengths in **11** are similar to those in the donor–acceptor complex $[(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{Ba}\text{-}\{\mathrm{Ga}(\eta^5\text{-}\mathrm{C_5Me_5})\}_2]$ (3.6024(6) and 3.5798(7) Å).[18] The inspection of the C–N and C–C bond lengths within the metallacycle in **11** allowed the elucidation of the reduction state of the dpp-bian ligands in this molecule. The C(1)–N(1) and C(2)–N(2) bond lengths (av. 1.375 Å) are close to those in **1** (av. 1.388 Å), in which the dpp-bian ligand is present in the dianionic state. The Ga–N distances in **11** (av. 1.971 Å) fall into the range for the corresponding distances in **3**–**7**.

Conclusion

For the first time a compound with a gallium–gallium bond, namely [(dpp-bian)Ga–Ga(dpp-bian)] (**1**), has been prepared in one step starting from gallium metal. Reduction of digallane **1** with Group 1 and 2 metals results in the cleavage of the Ga–Ga bond and formation of compounds with alkali metal–gallium and alkaline earth metal–gallium bonds. Although the LUMO (π) in digallane **1**, according to DFT calculations, shows bonding character with respect to the metal–metal bond there is no evidence for the formation of a radical-anion $[\mathbf{1}]^-$ in the course of the reduction of **1** with lithium. Crystallization of $[(\text{dpp-bian})\mathrm{Ga{-}Na}(\mathrm{Et_2O})_3]$ from different ethereal solvents allows the isolation of new complexes with Ga–Na bonds, in which the coordination environment of the sodium atoms is different. All the complexes with alkali metal–gallium bonds represent monomeric species that have not yet been observed. The coordinating strength of the [18]crown-6 and $\mathrm{Ph_3PO}$ is high enough to push away the gallene anion from the sodium coordination sphere to give a solvent-separated cation and anion. The Ga–Na bond length is strongly influenced not only by the number of sodium-coordinated solvent molecules, but also by their steric bulk. Three monodentate diethyl ether molecules coordinated to the sodium atom cause more steric stress at the (dpp-bian)Ga fragment compared to that caused by two bidentate DME molecules. Thus, the sodium atom approaches as close to the gallium atom as the repulsion between the solvent molecules and the bulky substituents of the dpp-bian allows. It will probably be possible to use the synthesized compounds with alkali metal–gallium bonds for the preparation of other metal–gallium bonded species.

Experimental Section

General remarks: All manipulations were carried out in vacuum or under nitrogen by using Schlenk techniques. The solvents diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, and toluene were dried over sodium benzophenone and distilled prior to use. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene was prepared by condensation of acenaphthenequinone with 2,6-diisopropylaniline (both from Aldrich) in acetonitrile at reflux. The solvents $[\mathrm{D_8}]$THF and $[\mathrm{D_6}]$benzene, used for the ^{1}H NMR measurements, were dried over sodium benzophenone at ambient temperature and were, just prior to use, condensed under vacuum into the NMR tubes already containing the investigated compounds. ^{1}H NMR spectra were recorded by using a Bruker DPX 200 spectrometer. Melting points were measured in sealed capillaries. The IR spectra were recorded by using a FSM-1201 spectrometer. Elemental analyses were performed by using an Euro EA3000 analyzer.

[(dpp-bian)Ga–Ga(dpp-bian)] (1): A suspension of dpp-bian (1.0 g, 2.0 mmol) in toluene (30 mL) was added to gallium metal (5.0 g, 71.4 mmol). The solution turned deep blue on refluxing for 24 h. The solvent was slowly evaporated from the decanted solution. Compound **1** was isolated (1.18 g, 96 %) in the form of deep blue crystals. M.p. > 300 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.31$–6.99 (m, 21 H; CH arom.), 6.83 (pst, $J = 7.0$ Hz, 4 H; CH arom.), 6.19 (d, $J = 6.8$ Hz, 4 H; CH arom.), 3.47 (sept, $J = 6.8$ Hz, 8 H; $\mathrm{C}\mathit{H}(\mathrm{CH_3})_2$), 2.12 (s, 3H, $\mathrm{C_6H_5C}\mathit{H}_3$), 1.01 (d, $J = 7.0$ Hz, 24 H; $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$), 0.97 ppm (d, $J = 7.0$ Hz, 24 H; $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$); elemental analysis calcd (%) for $\mathrm{C_{72}H_{80}Ga_2N_4 \cdot C_7H_8}$ (1233.02): C 76.95, H 7.19; found: C 76.89, H 7.24.

[(dpp-bian)Ga–Na($\mathbf{Et_2O}$)$_3$] (3): Sodium (0.05 g, 2.2 mmol) was added to a solution of **1** (1.23 g, 2.0 mmol) in $\mathrm{Et_2O}$ (35 mL). The mixture was stirred until sodium dissolved completely and the color of the solution changed to green (ca. 2 h). Slow evaporation of the solvent yielded **3** (1.29 g; 79 %) as deep green crystals. M.p. 179 °C. ^{1}H NMR ($[\mathrm{D_8}]$THF, 200 MHz): $\delta = 7.13$–6.93 (m, 6 H; CH arom.), 6.63 (dd, $J = 8.3$, 1.0 Hz, 2 H; CH arom.), 6.55 (dd, $J = 8.3$, 6.3 Hz, 2 H; CH arom.), 5.64 (dd, $J = 6.3$, 1.0 Hz, 2 H; CH arom.), 3.86 (sept, $J = 6.9$ Hz, 4 H; $\mathrm{C}\mathit{H}(\mathrm{CH_3})_2$), 3.39 (q, $J = 7.0$ Hz, 12 H; $\mathrm{C}\mathit{H}_2(\mathrm{Et_2O})$), 1.24 (d, $J = 6.9$ Hz, 12 H; $\mathrm{CH}(\mathrm{C}\mathit{H}_3)(\mathrm{CH_3})$), 1.13 (t, $J = 7.0$ Hz, 18 H; $\mathrm{C}\mathit{H}_3(\mathrm{Et_2O})$), 1.08 ppm (d, $J = 6.9$ Hz, 12 H; $\mathrm{CH}(\mathrm{CH_3})(\mathrm{C}\mathit{H}_3)$); elemental analysis calcd (%) for $\mathrm{C_{48}H_{70}GaN_2NaO_3}$ (815.79): C 70.67, H 8.65; found: C 70.49, H 8.78.

[(dpp-bian)Ga–Na(dme)$_2$] (4): Complex **3** (0.81 g, 1.0 mmol) was dissolved in 1,2-dimethoxyethane (40 mL). Slow evaporation of the solvent yielded **4** (0.67 g; 83 %) as deep green crystals. M.p. 147 °C. ^{1}H NMR ($[\mathrm{D_8}]$THF, 200 MHz): $\delta = 7.13$–6.93 (m, 6 H; CH arom.), 6.63 (dd, $J = 8.3$, 1.0 Hz, 2 H; CH arom.), 6.55 (dd, $J = 8.3$, 6.5 Hz, 2 H; CH arom.), 5.63 (dd, $J = 6.5$, 1.0 Hz, 2 H; CH arom.), 3.87 (sept, $J = 6.9$ Hz, 4 H; $\mathrm{C}\mathit{H}(\mathrm{CH_3})_2$), 3.44 (s, 8 H; $\mathrm{C}\mathit{H}_2(\mathrm{dme})$), 3.28 (s, 12 H; $\mathrm{C}\mathit{H}_3(\mathrm{dme})$), 1.24 (d, $J = 6.9$ Hz, 12 H; $\mathrm{CH}(\mathrm{C}\mathit{H}_3)(\mathrm{CH_3})$), 1.08 ppm (d, $J = 6.9$ Hz, 12 H; $\mathrm{CH}(\mathrm{CH_3})(\mathrm{C}\mathit{H}_3)$); IR (Nujol): $\tilde{\nu} = 3052$ (w), 1902 (w), 1755 (w), 1609 (m), 1586 (s), 1507 (vs), 1438 (w), 1421 (s), 1351 (vs), 1324 (m), 1281 (w), 1256 (s), 1246 (s), 1217 (m), 1208 (w), 1192 (m), 1173 (s), 1158 (w), 1124 (m), 1105 (w), 1086 (vs), 1030 (m), 997 (w), 926 (s), 889 (w), 860 (vs), 840 (w), 808 (s), 789 (m), 762 (vs), 696 (w), 683 (w), 670 (w), 636 (w), 624 cm^{-1} (m); elemental analysis calcd (%) for $C_{44}H_{60}GaN_2NaO_4$ (773.65): C 68.31, H 7.82; found: C 68.35, H 7.91.

[(dpp-bian)Ga−Na(thf)$_3$(Et$_2$O)] (5): Complex **3** (1.00 g, 1.2 mmol) was dissolved in THF (40 mL). The solvent was evaporated in vacuum and then the residue was re-dissolved in Et$_2$O (40 mL). A slow evaporation of the solvent resulted compound **5** as deep green crystals (0.76 g, 72 %). M.p. 121 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.13–6.93 (m, 6H; CH arom.), 6.63 (dd, J=8.3, 1.0 Hz, 2H; CH arom.), 6.55 (dd, J=8.3, 6.3 Hz, 2H; CH arom.), 5.64 (dd, J=6.3, 1.0 Hz, 2H; CH arom.), 3.86 (sept, J=6.9 Hz, 4H; C*H*(CH$_3$)$_2$), 3.39 (q, J=7.0 Hz, 4H; Et$_2$O), 1.24 (d, J=6.9 Hz, 12H; CH(C*H*$_3$)(CH$_3$)), 1.13 (t, J=7.0 Hz, 6H; Et$_2$O), 1.08 ppm (d, J=6.9 Hz, 12H; CH(CH$_3$)(C*H*$_3$)); elemental analysis calcd (%) for $C_{52}H_{74}GaN_2NaO_4$ (883.84): C 70.66, H 8.44; found: C 70.39, H 8.35.

[(dpp-bian)Ga]$^-$[Na([18]crown-6)(thf)$_2$]$^+$ (6a): An addition of [18]crown-6 (0.64 g, 2.4 mmol) to a solution of **3** (0.97 g, 1.2 mmol) in Et$_2$O (30 mL) caused instant formation of red-brown needlelike crystals. Crystallization of the crude product from THF (20 mL) afforded complex **6a** as large green crystals (1.06 g, 79 %). M.p. 94 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.19–6.87 (m, 6H; CH arom.), 6.52 (dd, J=8.3, 2.0 Hz, 2H; CH arom.), 6.47 (dd, J=8.3, 5.3 Hz, 2H; CH arom.), 5.54 (dd, J=5.3, 2.0 Hz, 2H; CH arom.), 3.90 (sept, J=7.0 Hz, 4H; C*H*(CH$_3$)$_2$), 3.49 (s, 24H; [18]crown-6), 1.23 (d, J=7.0 Hz, 12H; CH(C*H*$_3$)(CH$_3$)), 1.08 ppm (d, J=7.0 Hz, 12H; CH(CH$_3$)(C*H*$_3$)); IR (Nujol): $\tilde{\nu}$=3050 (w), 2745 (w), 2713 (w), 1974 (w), 1898 (w), 1840 (w), 1755 (w), 1610 (s), 1586 (s), 1509 (vs), 1424 (s), 1350 (s), 1322 (m), 1283 (m), 1252 (s), 1237 (w), 1217 (m), 1187 (w), 1174 (s), 1108 (vs), 1067 (s), 1057 (s), 1032 (w), 997 (m), 965 (vs), 926 (s), 910 (m), 888 (w), 865 (s), 841 (s), 835 (s), 808 (s), 800 (m), 791 (m), 760 (vs), 696 (w), 683 (m), 670 (w), 637 (w), 623 (m), 588 (w), 546 (w), 532 (m), 515 cm^{-1} (m); elemental analysis calcd (%) for $C_{63}H_{94}GaN_2NaO_9$ (1116.11): C 67.79, H 8.49; found: C 67.70, H 8.41.

[(dpp-bian)Ga]$^-$[Na(Ph$_3$PO)$_3$(thf)]$^+$ (6b): Ph$_3$PO (10.0 mmol, 2.78 g) was added to the solution of **3** (1.6 g, 2.0 mmol) in THF (40 mL). In an hour the solution was concentrated to 20 mL and combined with Et$_2$O (50 mL). When the solution was left to stand at ambient temperature, complex **6b** crystallized from the THF/Et$_2$O mixture as green-brown crystals (2.61 g, 83 %). M.p. 170 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.75–7.26 (m, 45H; (C$_6$*H*$_5$)$_3$PO), 7.14–6.88 (m, 6H; CH arom.), 6.57–6.45 (m, 4H; CH arom.), 5.58 (dd, J=6.0, 1.3 Hz, 2H; CH arom.), 3.89 (sept, J=7.0 Hz, 4H; C*H*(CH$_3$)$_2$), 1.20 (d, J=7.0 Hz, 12H; CH(C*H*$_3$)(CH$_3$)), 1.06 ppm (d, J=7.0 Hz, 12H; CH(CH$_3$)(C*H*$_3$)); IR (Nujol): $\tilde{\nu}$=3074 (m), 3053 (m), 2362 (m), 1972 (m), 1903 (m), 1844 (w), 1820 (w), 1778 (w), 1760 (w), 1674 (w), 1608 (m), 1588 (s), 1510 (vs), 1483 (s), 1437 (vs), 1421 (vs), 1355 (vs), 1322 (s), 1257 (s), 1185 (vs), 1173 (s), 1117 (vs), 1057 (s), 1027 (s), 998 (s), 956 (m), 929 (s), 908 (m), 890 (m), 867 (s), 852 (m), 834 (w), 807 (s), 801 (s), 789 (m), 765 (s), 747 (s), 694 (vs), 670 (m), 640 (m), 625 (m), 616 (m), 587 (w), 544 (vs), 515 (m), 503 (m), 458 cm^{-1} (m); elemental analysis calcd (%) for $C_{94}H_{93}GaN_2NaO_4P_3\cdot C_4H_8O$ (1572.43): C 74.85, H 6.47; found: C 74.77, H 6.39.

[(dpp-bian)Ga−K(thf)$_5$] (7): A mixture of potassium (0.080 g, 2.0 mmol) and complex **1** (1.23 g, 1.0 mmol) was stirred at ambient temperature in THF (45 mL). In 3 h potassium dissolved completely and the solution color changed from deep blue to green. Slow evaporation of the solvent from the resulting solution yielded compound **7** as deep green crystals (1.22 g, 63 %). M.p. 108 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.11–6.92 (m, 6H; CH arom.), 6.59 (dd, J=8.2, 1.3 Hz, 2H; CH arom.), 6.52 (dd, J=8.2, 6.5 Hz, 2H; CH arom.), 5.58 (dd, J=6.5, 1.3 Hz, 2H; CH arom.), 3.87 (sept, J=6.9 Hz, 4H; C*H*(CH$_3$)$_2$), 1.23 (d, J=6.9 Hz, 12H; CH(C*H*$_3$)(CH$_3$)), 1.07 ppm (d, J=6.9 Hz, 12H; CH(CH$_3$)(C*H*$_3$)); elemental analysis calcd (%) for $C_{56}H_{80}GaKN_2O_5$ (970.04): C 69.34, H 8.31; found: C 69.28, H 8.35.

[(dpp-bian)Ga]$_2$Mg(thf)$_3$ (8): From a toluene solution of complex **1** (prepared in situ as described above from dpp-bian (1.0 g, 2.0 mmol)), the solvent was evaporated in vacuum. Crude product **1** was dissolved in THF (35 mL) and added to an excess of magnesium shavings (activated with iodine). The reaction mixture was rigorously stirred until the solution color changed to brown (ca. 6 h). Slow evaporation of the solvent from the decanted solution gave **8** as dark crystals (0.75 g, 54 %). M.p.>250 °C. IR (Nujol): $\tilde{\nu}$=2925 (vs), 2855 (vs), 1610 (w), 1589 (m), 1509 (m), 1463 (vs), 1377 (s), 1347 (s), 1253 (m), 1179 (m), 1106 (w), 1028 (s), 925 (m), 874 (m), 804 (m), 758 (m), 669 (w), 616 (w), 413 cm^{-1} (m); elemental analysis calcd (%) for $C_{84}H_{104}MgGa_2N_4O_3$ (1381.52): C 78.03, H 7.59; found: C 78.19, H 7.43.

[(dpp-bian)Ga]$_2$Ca(thf)$_4$ (9): From a toluene solution of complex **1** (prepared in situ as described above from dpp-bian (1.0 g, 2.0 mmol)), the solvent was evaporated in vacuum. Crude product **1** was dissolved in THF (30 mL) and added to calcium metal (0.042 g, 1.0 mmol). Stirring of the mixture at ambient temperature within 12 h resulted a brown solution. Slow evaporation of the solvent yielded complex **9** as brown crystals (0.68 g, 59 %). M.p.>250 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.27–7.03 (m, 12H; CH arom.), 6.81 (d, J=8.3 Hz, 4H; CH arom.), 6.64 (dd, J=8.0, 7.0 Hz, 4H; CH arom.), 5.65 (d, J=6.8 Hz, 4H; CH arom.), 3.73 (sept, J=7.0 Hz, 8H; C*H*(CH$_3$)$_2$), 1.18 (d, J=7.0 Hz, 24H; CH(C*H*$_3$)(CH$_3$)), 1.02 ppm (d, J=7.0 Hz, 24H; CH(CH$_3$)(C*H*$_3$)); IR (Nujol): $\tilde{\nu}$=2933 (vs), 1583 (w), 1515 (s), 1461 (vs), 1414 (vs), 1380 (s), 1356 (m), 1341 (m), 1315 (s), 1249 (m), 1220 (m), 1185 (s), 1108 (m), 1069 (m), 1032 (s), 896 (m), 878 (m), 844 (m), 821 (m), 803 (m), 788 (w), 776 (m), 762 (s), 668 (w), 633 (w), 603 (w), 539 (w), 483 (w), 450 (w), 410 cm^{-1} (m); elemental analysis calcd (%) for $C_{88}H_{112}CaGa_2N_4O_4$ (1469.38): C 71.93, H 7.68; found: C 71.98, H 7.65.

[(dpp-bian)Ga]$_2$Sr(thf)$_4$ (10): From a toluene solution of complex **1** (prepared in situ as described above from dpp-bian (1.0 g, 2.0 mmol)) the solvent was evaporated in vacuum. Crude product **1** was dissolved in THF (30 mL) and added to strontium metal (0.09 g, 1.0 mmol). A mixture was stirred until the strontium dissolved completely (ca. 12 h). Slow evaporation of the solvent from the mother liquor yielded **10** as dark crystals (0.89 g, 59 %). M.p.>250 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.26–7.01 (m, 12H; CH arom.), 6.81 (d, J=8.3 Hz, 4H; CH arom.), 6.65 (dd, J=8.0, 6.8 Hz, 4H; CH arom.), 5.70 (d, J=6.8 Hz, 4H; CH arom.), 3.71 (sept, J=7.0 Hz, 8H; C*H*(CH$_3$)$_2$), 1.18 (d, J=7.0 Hz, 24H; CH(C*H*$_3$)(CH$_3$)), 1.03 ppm (d, J=6.8 Hz, 24H; CH(CH$_3$)(C*H*$_3$)); IR (Nujol): ν=1666 (w), 1610 (w), 1590 (s), 1502 (m), 1463 (s), 1376 (s), 1356 (s), 1253 (m), 1176 (m), 1138 (w), 1105 (w), 1057 (w), 1030 (s), 928 (m), 875 (m), 804 (m), 757 (s), 666 (w), 616 (w), 548 (w), 446 (w), 412 cm^{-1} (m); elemental analysis calcd (%) for $C_{88}H_{112}SrGa_2N_4O_4$ (1516.92): C 69.68, H 7.44; found: C 69.61, H 7.52.

[(dpp-bian)Ga]$_2$Ba(thf)$_5$ (11): *Method a*: Stirring a solution of **1** (prepared as described above from dpp-bian (1.0 g, 2.0 mmol) in THF (30 mL) with barium metal (0.137 g, 1.0 mmol) afforded a brown solution within 24 h. Evaporation of the solvent under reduced pressure yielded compound **11** as dark crystals (0.95 g, 58 %). M.p.>230 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ=7.21–7.04 (m, 12H; CH arom.), 6.78 (d, J=8.3 Hz, 4H; CH arom.), 6.63 (dd, J=8.0, 7.0 Hz, 4H; CH arom.), 5.61 (d, J=6.8 Hz, 4H; CH arom.), 3.75 (sept, J=7.0 Hz, 8H; C*H*(CH$_3$)$_2$), 1.20 (d, J=7.0 Hz, 24H; CH(C*H*$_3$)(CH$_3$)), 1.03 ppm (d, J=7.0 Hz, 24H; CH(CH$_3$)(C*H*$_3$)); IR (Nujol): ν=2925 (vs), 2855 (vs), 1611 (m), 1590 (m), 1508 (s), 1461 (s), 1429 (vs), 1376 (m), 1352 (vs), 1256 (m), 1210 (w), 1179 (m), 1139 (w), 1105 (w), 1070 (m), 1039 (s), 927 (m), 874 (m), 808 (m), 763 (s), 669 (w), 621 (w), 515 (w), 411 cm^{-1} (m); elemental analysis calcd (%) for $C_{92}H_{120}BaGa_2N_4O_5\cdot 1.5C_4H_8O$ (1746.86): C 67.38, H 7.62; found: C 67.35, H 7.65.

Method b: A solution of **3** (1.61 g, 2.0 mmol) in THF (25 mL) was added to barium diiodide (prepared in situ from an excess of barium and iodine (0.26 g, 1.0 mmol) in THF (20 mL)). In one hour the brown solution was filtered off from the NaI precipitate. Concentration of the obtained solution gave complex **11** (0.87 g, 53 %). The IR spectra of the products prepared in both methods are identical.

Single-crystal X-ray structure determination of 4–7 and 11: The crystallographic data were collected by using an Oxford Diffraction Xcalibur S Sapphire (**4**, **5**), Bruker AXS SMART APEX I (**6a**, **7**) and APEX II (**6b**, **11**) diffractometers using graphite-monochromated Mo$_{K\alpha}$ (λ=0.71073 Å) radiation. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation using SHELXTL packages.[25] SADABS was used to perform area-detector scaling and absorption corrections.[26] The positions of hydrogen atoms were calculated geometrically and refined within a riding model for all complexes. Experimental details are given in Table 2. CCDC-763574 (**4**), CCDC-763575 (**5**), CCDC-763576 (**6a**), CCDC-763577 (**6b**), CCDC-763578 (**7**), and CCDC-763579 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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