Synthesis and structure of bischelate gallium complexes (dpp-bian)Ga(acac) and (dpp-bian)Ga(2,2′-bipy) (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene)*

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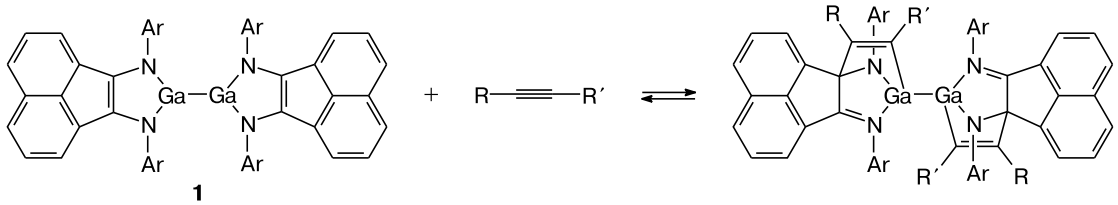
A reaction of digallane [(dpp-bian)Ga—Ga(dpp-bian)] (**1**) (dpp-bian is the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with one equivalent of I_2 leads to oxidation of $(dpp\text{-}bian)^{2-}$ in compound **1** to $(dpp\text{-}bian)^{-}$ and gives [(dpp-bian)GaI—GaI(dpp-bian)] (**2**). In the reaction of compound **2** with two equivalents of (acac)Na, not only exchange of the iodide and acetylacetonate ions takes place, but also a transfer of electrons from the metal—metal bond to dpp-bian with the formation of the complex [(dpp-bian)Ga(acac)] (**3**), in which the dpp-bian ligand is a dianion. A reaction of digallane **1** with 2,2′-bipyridyl at 200 °C in toluene in a sealed tube leads to the reduction of 2,2′-bipyridyl and gives the complex [(dpp-bian)Ga(bipy)] (**4**), which contains two different chelate redox-active ligands. The new compounds were characterized by IR (**3**, **4**), NMR (**3**), and ESR spectra (**4**), the structures of both derivatives were established by X-ray diffraction.

Key words: gallium, chelate ligands, synthesis, structure.

Metal complexes with redox-active ligands are the most dynamically developing area of coordination compounds chemistry. Together with the acquiring new knowledge on the nature of chemical bond, stability and dynamics of molecular systems, the studies in this region allows one to design compounds, which can be used as reagents and catalysts in the synthesis of practically valuable organic products. Nontransition metal complexes with redox-active 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) is the area of our scientific interests. Starting from the year of 2003 until the present time, we synthesized hundreds of new dpp-bian-derivatives of nontransition metals. Their overwhelming majority contains a dpp-bian radical anion[1—10] or dianion.[11—14] The complexes containing a dpp-bian dianion, demonstrate the reactivity unusual for metal compounds. They are characterized by different types of chemical transformations in the reactions with different substrate, but they also have a common feature: the main rearrangement of electron structure and spatial geometry is undergone not by the central metal atom, but by the coordinated dpp-bian ligand. Recently, we have found an unusual effect of the suppression by the dpp-bian dianion of reactivity of other ligands at the metal atom, for example, an alkyl group in organoaluminum compounds. Thus, treatment of complex [(dpp-bian)AlEt] with diphenylacetylene[15] or water[16] leads to neither incorporation of the alkyne into the aluminum—alkyl bond, nor hydrolysis of this bond. Both reactions proceed readily, but involve only the dpp-bian ligand. One of the most interesting types of chemical reactions of the considered class of compounds is a reversible cycloaddition by gallium[17—19] and aluminum[20] derivatives of different alkynes. We observed this process for the first time in 2010 for digallane [(dpp-bian)Ga—Ga(dpp-bian)] (**1**) (Scheme 1).

Scheme 1



1

Ar = 2,6-$Pr^i_2C_6H_3$
R = H, R′ = H; R = Ph, R′ = H; R = Me, R′ = C(O)Me

* Dedicated to Academician of the Russian Academy of Sciences O. G. Sinyashin on the occasion of his 60th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1171—1177, May, 2016.

1066-5285/16/6505-1171

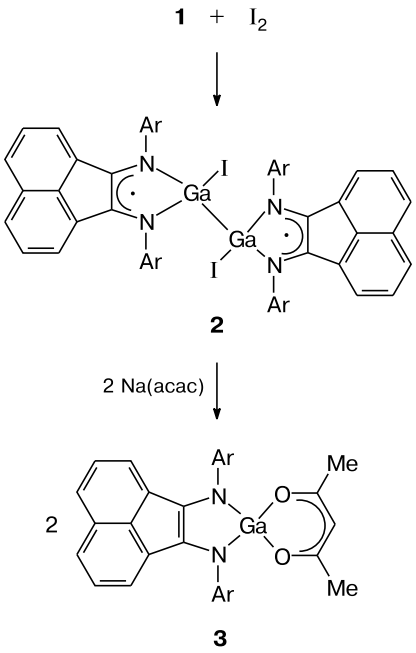
The process resembles the coordination step of unsaturated substrates by transition metal ions and, probably, plays a key role in the hydroamination reactions of phenylacetylene with aromatic amines catalyzed by digallane **1**.[17,18,21]

Recently, we have shown[19] that the catalytic activity of some mononuclear gallium complexes with a dpp-bian dianion, for example, dithiocarbamate derivative [(dpp-bian)Ga(S_2CNMe_2)] in the hydroamination reactions of phenylacetylene is considerably lower than the activity of digallane **1**. Moreover, some mononuclear gallium dpp-bian derivatives do not form cycloadducts with alkynes at all. Thus, the reaction of cyclopentadienyl derivative [(dpp-bian)Ga($C_5H_4CH_2CH_2NMe_2$)] with PhC≡CH leads to acetylide [(dpp-bian)Ga($C{\equiv}CPh)_2$] (see Ref. 19), in which the dpp-bian ligand is a radical anion. In order to acquire new information on reactivity of gallium complexes containing a dpp-bian dianion, we decided to synthesize compound, which contain other chelating ligands together with the dpp-bian dianion, namely, acetylacetonate and 2,2′-bipyridyl ones. In the present work, we synthesized new compounds [(dpp-bian)Ga(acac)] (**3**) and [(dpp-bian)Ga(bipy)] (**4**), established their structure by X-ray diffraction, and carried out reactions of these compounds with some alkynes.

Results and Discussion

Synthesis and characterization of compounds [(dpp-bian)Ga(acac)] (3) and [(dpp-bian)Ga(2,2′-bipy)] (4). The reaction of digallane **1** with acetylacetone (acacH) does not give a mixed dpp-bian/acac gallium derivative, but leads to the protonation of the dpp-bian ligand and liberation of diamine (dpp-bian)H_2. The target compound [(dpp-bian)Ga(acac)] (**3**) was obtained by the exchange reaction of digallane [(dpp-bian)GaI—GaI(dpp-bian)][22] (**2**) (prepared *in situ* from digallane **1** and iodine) with sodium acetylacetonate (Scheme 2). A conversion of digallane **1** through compound **2** to product **3** is accompanied by the change in color of solutions in the following order blue—brown—blue. The product **3** was isolated from benzene as dark blue crystals (30%).

Scheme 2



Ar = 2,6-$Pr^i_2C_6H_3$

The dpp-bian dianion in compound **3** has two mirror planes, one of which coincide with the plane of the acetylacetonate ligand and is orthogonal to the second mirror plane lying in the plane of the five-membered metallocycle. This is the reason that the ^{1}H NMR spectrum (Fig. 1)

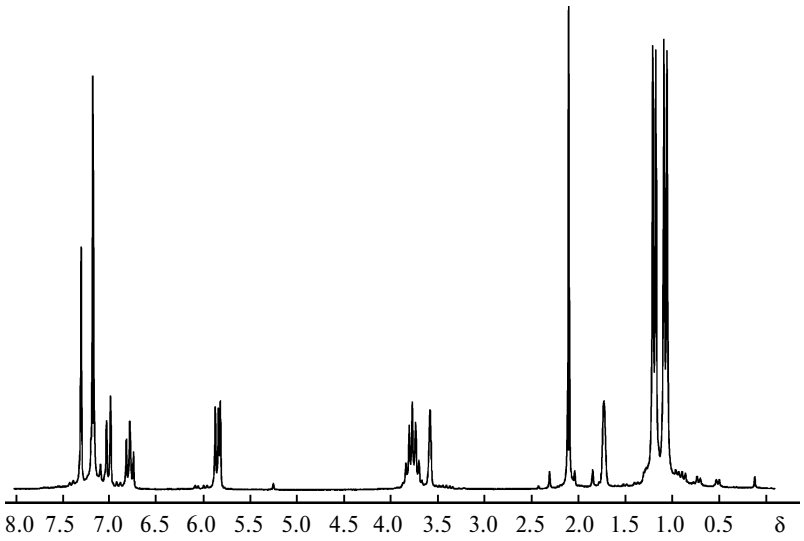
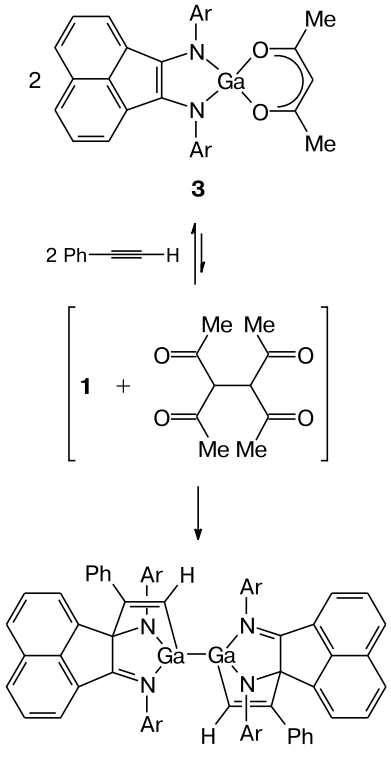


Fig. 1. The ^{1}H NMR spectrum of complex **3** (200 MHz, THF-d_8, 298 K).

exhibits a small number of signals. The methyl protons of the Pr^i group are found as two doublets at δ 1.19 (12 H) and 1.07 (12 H). A signal at δ 2.10 (6 H) is attributed to the methyl protons of the acetylacetonate ligand, whereas a signal at δ 5.82 (1 H) belongd to its methine proton. A septet at δ 3.57 (4 H) is related to the methine protons of the Pr^i groups. The protons of the naphthalene moiety of the dpp-bian dianion, as well as the protons of benzene containing in the crystal cell, are found as the signals in the range δ 7.23—5.86.

The addition of phenylacetylene to a solution of complex **3** leads to the change of the solution color from blue to brown similar to that observed in the reaction of phenylacetylene with digallane **1**. However, the X-ray diffraction data showed that the light brown crystals of the reaction product isolated from the ether solution are an adduct between phenylacetylene and digallane **1**. It is probable that compound **3** is inert toward phenylacetylene. We suggest that in the solution, compound **3** can give 1,1,2,2-tetraacetylethane and digallane **1**, which is the compound to react with phenylacetylene forming the known cycloadduct (Scheme 3). Note that 1,1,2,2-tetraacetylethane can be obtained by the reaction of Na(acac) with iodine.[23]

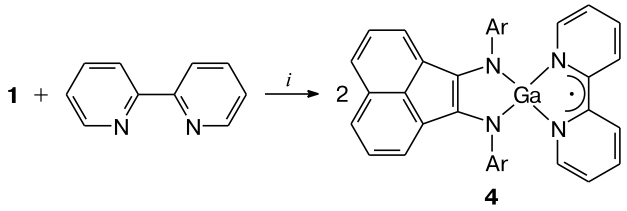
Scheme 3



Ar = 2,6-$Pr^i_2C_6H_3$

Under drastic conditions (200 °C, a sealed tube) digallane **1** in the toluene solution reacts with 2,2′-bipyridyl giving complex [(dpp-bian)Ga(bipy)] (**4**) (Scheme 4). The reaction process includes the reduction of 2,2′-bipyridyl with electrons of the gallium—gallium bond, leaving the dpp-bian ligand as a dianion. Compound **4** was isolated from ether as green needle-like crystals in 37% yield and is a rare example of the nontransition metal complex which contains two different redox-active ligands. The presence in compound **4** of 2,2′-bipyridyl radical anion substantiates the appearance in the solution of this derivative of an ESR signal (Fig. 2), a complex hyperfine structure (HFS) of which complicates its interpretation. However, a general pattern of the spectrum allows us to suggest that its HFS is determined by the interaction of the unpaired electron with magnetic gallium nuclei, as well as two nitrogen atoms and four pairs of hydrogen atoms of the bipy ligand.

Scheme 4



Ar = 2,6-$Pr^i_2C_6H_3$

i. Toluene, 200 °C.

Molecular structures of compounds 3 and 4. Molecular structures of complexes **3** and **4** were established by single crystal X-ray diffraction analysis and are shown in Figs 3 and 4, respectively. Both compounds are monomeric complexes of tervalent gallium and contain only bidentate ligands symmetrically chelating the metal atoms. A distortion of coordination surrounding of gallium atoms in complexes **3** and **4** from the ideal tetrahedron is due to

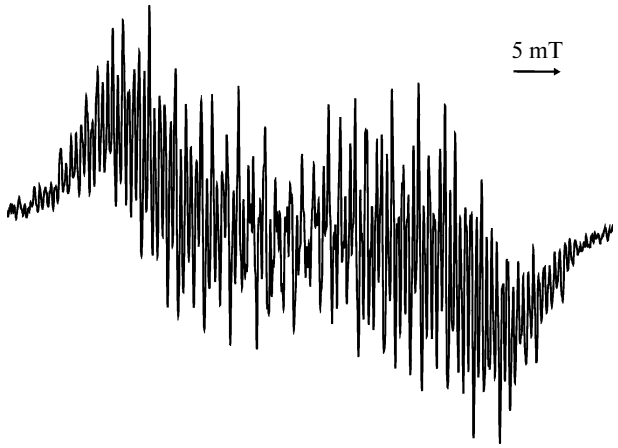


Fig. 2. The ESR spectrum of compound **4** (toluene, 297 K).

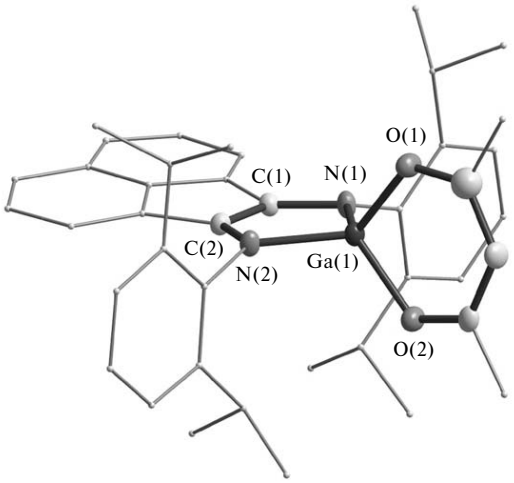


Fig. 3. Molecular structure of complex **3**. Thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted.

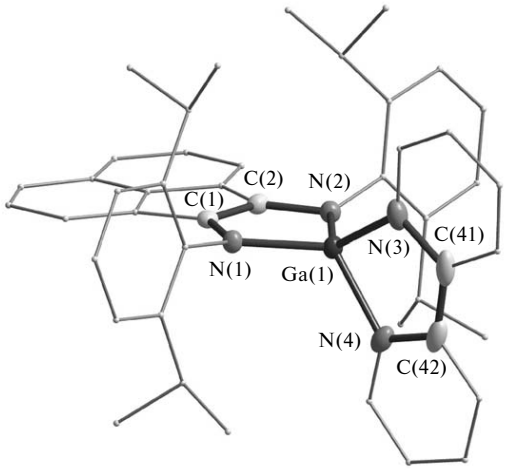


Fig. 4. Molecular structure of **4**. Thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted.

a relatively small bond angles in the chelate fragments. In compound **3**, the angle between the planes of the dpp-bian and acac ligands is 85.4°. The Ga(1)—O(1) and Ga(1)—O(2) distances (1.8894(11) and 1.8803(11) Å, respectively) in compound **3** (Table 1) are close to the corresponding values in the tetrahedral complex [(acac)Ga(Me)Cl][24] (1.901(7) and 1.878(7) Å), but are shorter than in the hexacoordinated derivative $[(acac)_3Ga]$[25] (av. 1.952 Å). The O(1)—Ga(1)—O(2) angle in complex **3** (96.01(5)°) is close to the corresponding angle in [(acac)Ga(Me)Cl][24] (96.3(3)°), but is larger than an average value of the O—Ga—O angles in $[(acac)_3Ga]$[25] (91.3(2)°).

The geometry of the gallene fragment C_2N_2Ga in compound **3** (Ga(1)—N(1) 1.8721(13), Ga(1)—N(2) 1.8744(13), N(1)—C(1) 1.404(2), N(2)—C(2) 1.398(2), and C(1)–C(2) 1.373(2) Å) is close to that of the corresponding fragment in the starting digallane **1** (Ga(1)—N(1) 1.862(2), Ga(1)—N(2) 1.858(2), N(1)—C(1) 1.393(3), N(2)—C(2) 1.389(3), and C(1)—C(2) 1.375(3) Å),[26] that confirms the dianionic state of the dpp-bian ligand in compound **3**.

In the molecule of complex **4** (see Fig. 4, Table 2), the angle between the planes of two N,N ligands is 86.0°. The Ga—N(bipy) distance in compound **4** (Ga(1)—N(3) 1.945(2) and Ga(1)—N(4) 1.958(2) Å) is noticeably shorter than the corresponding distances in the following compounds: $[Ga(bipy)_3]I_3$ (av. 2.068 Å),[27] $[Cp^*(OC)_2Fe][\mu\text{-}Ga(bipy)]\text{-}[Fe(CO)_4]$ (av. 2.124 Å),[28] and $[GaCl_2(Me_2\text{-}bpy)_2](ClO_4)$ (av. 2.088 Å).[29] This, apparently, reflects a stronger binding of the gallium atom with the anionic bipy ligand in complex **4** as compared to the interaction of gallium with neutral 2,2′-bipyridyl in the three complexes listed.

The alternation of bond distances in the bipy ligand, together with the ESR spectroscopy data for complex **4**, indicate an anionic character of the bipy ligand in this compound. In this sense, the carbon—carbon bond between two pyridyl rings is an indicative factor. For this bond, the LUMO of 2,2′-bipyridyl is a bonding one. Therefore, a shortening of the central carbon—carbon bond in 2,2′-bipyridyl should occur upon occupation of the LUMO. The C(41)—C(42) bond in complex **4** (1.423(5) Å) is shorter as compared to the corresponding bond in the free 2,2′-bipyridyl (1.49 Å),[30] but longer than the central bond in the bipy ligand in the complexes $[(bipy)Yb(thf)_2]_3$ (1.41 Å)[31] and $[Na_2(bipy)(dme)_2]_\infty$ (1.39 Å)[32] containing a bipy dianion. At the same time, the distance C(41)—C(42) in complex **4** is comparable with the similar distances in com-

Table 1. Selected bond distances (*d*) and bond angles (ω) in compound **3**

Parameter	Value
Bond	*d*/Å
Ga(1)—N(1)	1.8721(13)
Ga(1)—N(2)	1.8744(13)
Ga(1)—O(2)	1.8803(11)
Ga(1)—O(1)	1.8894(11)
O(1)—C(38)	1.291(2)
O(2)—C(40)	1.285(2)
C(38)—C(39)	1.385(2)
C(39)—C(40)	1.392(2)
N(1)—C(1)	1.404(2)
N(2)—C(2)	1.398(2)
C(1)—C(2)	1.373(2)
Angle	ω/deg
N(1)—Ga(1)—N(2)	93.06(5)
N(1)—Ga(1)—O(2)	119.26(5)
N(2)—Ga(1)—O(2)	116.58(5)
O(2)—Ga(1)—O(1)	96.01(5)
C(1)—N(1)—Ga(1)	104.76(9)
C(1)—C(2)—N(2)	118.87(14)

Table 2. Selected bond distances (*d*) and bond angles (ω) in compound **4**

Parameter	Value
Bond	*d*/Å
Ga(1)—N(1)	1.880(2)
Ga(1)—N(2)	1.887(2)
Ga(1)—N(3)	1.945(2)
Ga(1)—N(4)	1.958(2)
C(1)—C(2)	1.372(4)
N(1)—C(1)	1.398(3)
N(2)—C(2)	1.392(3)
N(3)—C(41)	1.393(4)
N(4)—C(42)	1.374(4)
C(41)—C(42)	1.423(5)
Angle	ω/ deg
N(1)—Ga(1)—N(2)	90.89(10)
N(1)—Ga(1)—N(3)	123.12(11)
N(2)—Ga(1)—N(3)	126.28(10)
N(1)—Ga(1)—N(4)	120.43(10)
N(2)—Ga(1)—N(4)	115.63(11)
N(3)—Ga(1)—N(4)	83.79(11)
C(1)—N(1)—Ga(1)	106.6(2)
C(1)—C(2)—N(2)	118.5(2)

pounds containing a bipy radical anion: $[LaI_2(bipy)_2(dme)]$ (1.457(10) Å),[33] $[YbI(bipy)(dme)_2]$ (1.419(14) Å),[34] and $[\{t\text{Bu(Ar)N}\}_2U(bipy)_2]$ (1.426 Å).[35] The structure of the gallene fragment C_2N_2Ga in complex **4** is similar to the structure of the corresponding fragment in compound **3**.

In conclusion, the reaction of digallane [(dpp-bian)GaI—GaI(dpp-bian)] (**2**) with sodium acetylacetonate clearly demonstrates the non-innocent of the dpp-bian ligand in the processes seemingly affecting only the metal atom. Thus, a replacement of one anionic ligand with another in the reaction of digallane **2** with Na(acac) changes a reducing potential of the metal center and causes an intramolecular electron transfer from the metal to the dpp-bian ligand, leading to the formation of compound **3**. Using reduction of 2,2′-bipyridine with digallane **1**, we for the first time obtained structurally characterized gallium complex with the bipy radical anion, namely, compound [(dpp-bian)Ga(bipy)] (**4**). In such nontransition metal complexes which contain two different redox-active ligands, a reversible externally-induced intramolecular ligand—ligand electron transfer can be theoretically possible, which would lead to the appearance of redox-isomeric molecules not observed earlier in nontransition metals chemistry. Finally, we showed that compound **3** is inert towards phenylacetylene. The formation of a known cycloadduct in this reaction allowed us to suggest that in solution compound **3** can undergo reductive elimination of diacetylmethyl radical with the formation of digallane **1** active toward phenylacetylene.

Experimental

Compounds **1**—**4**, as well as adduct **1** · 2PhC≡CH are sensitive to oxygen and air moisture, therefore all the manipulations with them were carried out *in vacuo* using Schlenk technique. Melting points of synthesized compounds were determined in sealed evacuated capillaries. Toluene, diethyl ether, benzene, THF-d_8 were dried and stored over sodium benzophenone. IR spectra (4000—400 cm^{-1}) were obtained on a FSM-1201 spectrometer. To register the IR spectra, a suspension of a compound in Nujol was prepared. ^{1}H NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 MHz). ESR spectra were obtained on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator (9.5 GHz) and an ER 4111 VT thermocontroller. The *g*-factor was determined using diphenylpicrylhydrazyl (DPPH, $g = 2.0037$) as a standard. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) was obtained by the condensation of acenaphthenequinone and 2,6-diisopropylaniline in acetonitrile in the presence of a catalytic amount of acetic acid. Digallane **1** was obtained by the reflux of a solution of dpp-bian in toluene (50 mL) with an excess of gallium metall in an evacuated tube at 120 °C for 12 h (see Ref. 26). A dark blue solution of digallane **1** was decanted from the excess of gallium and used in further synthesis without isolation. Acetylacetone and 2,2′-bipyridine were purchased from Aldrich and before use were distilled and sublimed, respectively. The product yields indicated in description of the syntheses were calculated on the amount of starting dpp-bian.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenidegalliumacetylacetonate, [(dpp-bian)Ga(acac)] (3). Iodine (0.13 g, 0.5 mmol) was added to a solution of complex **1** (prepared *in situ* from diimine dpp-bian (0.5 g, 1 mmol)) in toluene (50 mL). The solution rapidly acquired a brown color and a finely crystalline brick-red precipitate of digallane **2** was formed. Then, sodium acetylacetonate (0.12 g, 1 mmol) was added to the reaction mixture. The tube was sealed and the reaction mixture was exposed to ultrasound at 80 °C for 30 min. The solution gradually recovered a blue color, and a white precipitate appeared instead of brown. After filtration of the solution, the solvent was removed *in vacuo*, the residue was dissolved in benzene. Blue crystals of compound **3** were isolated from the concentrated solution. The yield was 0.2 g (30%), m.p. 217 °C. Found (%): C, 76.11; H 6.85. $C_{47}H_{53}GaN_2O_2$ (747.63). Calculated (%): C, 75.50; H, 7.15. IR (Nujol), ν/cm^{-1}: 1679 w, 1645 w, 1596 s, 1529 s, 1340 w, 1210 w, 1193 w, 1141 w, 1109 m, 1057 w, 1025 s, 924 s, 852 w, 834 w, 805 w, 785 w, 765 s, 681 s, 652 w, 623 w, 597 w, 518 m, 487 m. ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 7.23—7.12 (m, 6 H, CH_{arom}); 7.01 (d, 2 H, CH_{arom}, $J = 8.2$ Hz); 6.78 (pseudo-t, 2 H, CH_{arom}, $J = 7.7$ Hz); 5.86 (d, 2 H, CH_{arom}, $J = 6.8$ Hz); 5.82 (s, 1 H, CH acac); 3.57 (sept, 4 H, C<u>H</u>$(CH_3)_2$, $J = 6.8$ Hz); 2.10 (s, 6 H, CH_3 acac); 1.19 (d, 12 H, CH(C<u>H</u>$_3)_2$, $J = 6.8$ Hz); 1.07 (d, 12 H, CH(C<u>H</u>$_3)_2$, $J = 6.8$ Hz).

Reaction of compound 3 with phenylacetylene. Phenylacetylene (0.1 g, 1 mmol) was added by condensation *in vacuo* to a solution of compound **3** (prepared *in situ* from diimine dpp-bian (0.5 g, 1 mmol) according to the procedure described above) in toluene (50 mL). The solution immediately turned its color to brown. Upon heating in a water bath to ~100 °C, the solution reacquired a blue color, whereas upon cooling to room temperature the blue color turned to brown. The solvent from the reaction mixture was removed *in vacuo* at room temperature. The

Table 3. Crystallographic data, parameters of X-ray diffraction experiments and refinement for compounds **3** and **4**

Parameter	**3**·C_6H_6	**4**·OC_4H_{10}
Molecular formula	$C_{47}H_{53}GaN_2O_2$	$C_{50}H_{58}GaN_4O$
Molecular weight	747.63	800.72
Crystal system	Monoclinic	Orthorhombic
Space group	*P*2(1)/*c*	*P*2(1)2(1)2(1)
a/Å	12.0092(8)	13.7661(4)
b/Å	16.5924(7)	17.0080(4)
c/Å	20.5764(14)	18.4626(5)
α/ deg	90.00	90.00
β/ deg	93.516(7)	90.00
γ/ deg	90.00	90.00
V/Å^3	4092.4(4)	4322.73(19)
Z	4	4
d_{calc}/mg m^{-3}	1.213	1.230
μ/mm^{-1}	0.711	0.678
F(000)	1584	1700
Crystal size/mm^3	0.40×0.40×0.10	0.80×0.40×0.40
Range of data collection, θ/deg	2.986—26.000	3.024—25.996
Indices of *h, k, l* regions	$-14 \le h \le 14$	$-16 \le h \le 16$
	$-20 \le k \le 20$	$-20 \le k \le 20$
	$-25 \le l \le 25$	$-22 \le l \le 22$
Number of reflections		
observed	61314	68433
independent	8036	8453
R_{int}	0.0619	0.0543
GOOF (F^2)	1.026	1.091
R_1/wR_2 ($I > 2\sigma(I)$)	0.0364/0.0797	0.0310/0.0732
R_1/wR_2 (for all reflections)	0.0517/0.0842	0.0333/0.0742
Residual electron density/e Å^{-3}	0.445/−0.343	0.642/−0.253

residue was dissolved in diethyl ether. Light brown crystals of compound **1**·2PhC≡CH were isolated from a concentrated solution. The yield was 0.26 g (38%). ^{1}H NMR spectrum of the product in C_6D_6 agrees with the spectrum described in the literature.[12] Apart from that, the formation of compound **1**·2PhC≡CH was confirmed by X-ray diffraction. The crystals of derivative **1**·2PhC≡CH obtained by us differ from the crystals described in the literature only by the solvent molecules (diethyl ether instead of 1,2-dimethoxyethane).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenidegallium-bipyridinate, [(dpp-bian)Ga(bipy)] (4). 2,2′-Bipyridyl (0.62 g, 4 mmol) was added to a solution of complex **1** (prepared *in situ* from diimine dpp-bian (0.5 g, 1 mmol)) in toluene (50 mL). The tube was sealed and heated in an oil bath at 200 °C for 15 min. The color of the solution turned to green. After cooling the reaction mixture to room temperature, toluene was removed *in vacuo*, the residue was dissolved in diethyl ether and concentrated to ~20 mL. After some time, green needle-like crystals of compound **4** (0.29 g, 37%) were isolated from the concentrated solution, m.p. >260 °C. Found (%): C, 75.91; H, 7.85. $C_{50}H_{58}GaN_4O$ (800.72). Calculated (%): C, 75.00; H, 7.30. IR (Nujol), ν/cm^{-1}: 1928 w, 1879 w, 1792 w, 1665 w, 1615 w, 1560 s, 1523 s, 1503 s, 1493 m, 1343 s, 1323 w, 1265 m, 1225 m, 1181 w, 1149 m, 1141 m, 1109 m, 1060 w, 1028 s, 961 s, 929 w, 912 w, 811 s, 767 s, 681 w, 669 m, 652 w, 623 w, 521 w, 466 w.

X-ray diffraction studies of compounds 3 and 4 were carried out on a Agilent Xcalibur diffractometer (ω-scan technique, Mo-Kα radiation, λ = 0.71073 Å, *T* = 100 K). Both structures were solved by direct method and refined by the full-matrix least squares method on F^2_{hkl} in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined isotropically. The calculations and correction for absorption were carried out using the CrysAlis PRO[36] and SHELX[37] software packages. Crystallographic data and parameters of X-ray diffraction experiments are given in Table 3. The structures were deposited with the Cambridge Crystallographic Data Center (CCDC 1446788 (**3**) and 1446789 (**4**)) and are available at ccdc.cam.ac.uk/getstructures.

This work was financially supported by the Russian Science Foundation (Project No. 14-13-01063).

References

1. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, H. Schumann, *Chem. Eur. J.*, 2003, **9**, 5778.
2. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 3294.

3. I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, M. P. Bubnov, *Inorg. Chem.*, 2004, **43**, 7807.
4. I. L. Fedushkin, A. A. Skatova, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.*, 2005, 1601.
5. H. Schumann, M. Hummert, A. N. Lukoyanov, I. L. Fedushkin, *Organometallics*, 2005, **24**, 3891.
6. I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4302.
7. I. L. Fedushkin, A. G. Morozov, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.*, 2008, 1584.
8. I. L. Fedushkin, A. S. Nikipelov, A. A. Skatova, O. V. Maslova, A. N. Lukoyanov, G. K. Fukin, A. V. Cherkasov, *Eur. J. Inorg. Chem.*, 2009, 3742.
9. I. L. Fedushkin, A. G. Morozov, V. A. Chudakova, G. K. Fukin, V. K. Cherkasov, *Eur. J. Inorg. Chem.*, 2009, 4995.
10. I. L. Fedushkin, O. V. Eremenko, A. A. Skatova, A. V. Piskunov, G. K. Fukin, S. Yu. Ketkov, E. Irran, H. Schumann, *Organometallics*, 2009, **28**, 3863.
11. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, H. Schumann, *Eur. J. Inorg. Chem.*, 2003, 3336.
12. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, N. M. Khvoinova, A. Y. Baurin, S. Dechert, M. Hummert, H. Schumann, *Organometallics*, 2004, **23**, 3714.
13. A. N. Lukoyanov, I. L. Fedushkin, H. Schumann, M. Hummert, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1471.
14. A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, H. Schumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2006, **55**, 422 [*Izv. Akad. Nauk, Ser. Khim.,* 2006, 409].
15. I. L. Fedushkin, M. V. Moskalev, E. V. Baranov, G. A. Abakumov, *J. Organomet. Chem.*, 2013, **747**, 235.
16. M. V. Moskalev, Ph.D. Thesis (Chem.), G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii Novgorod, 2013, 140 pp. (in Russian).
17. I. L. Fedushkin, A. S. Nikipelov, K. A. Lyssenko, *J. Am. Chem. Soc.*, 2010, **132**, 7874.
18. I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.*, 2012, **18**, 255.
19. I. L. Fedushkin, O. V. Kazarina, A. N. Lukoyanov, A. A. Skatova, N. L. Bazyakina, A. V. Cherkasov, E. Palamidis, *Organometallics*, 2015, **34**, 1498.
20. L. Fedushkin, M. V. Moskalev, A. N. Lukoyanov, A. N. Tishkina, E. V. Baranov, G. A. Abakumov, *Chem. Eur. J.*, 2012, **18**, 11264.
21. M. V. Moskalev, A. A. Skatova, V. A. Chudakova, N. M. Khvoinova, N. L. Bazyakina, A. G. Morozov, O. V. Kazarina, A. V. Cherkasov, G. A. Abakumov, I. L. Fedushkin, *Russ. Chem. Bull.* (*Int. Ed.*), 2015, **64**, 2830 [*Izv. Akad. Nauk, Ser. Khim.*, 2015, 2830].
22. I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko, G. K. Fukin, *Inorg. Chem.*, 2014, **53**, 5159.
23. R. G. Charles, *Org. Synth. Coll.*, 1963, **4**, 869.
24. O. T. Beachley, J. R. Gardinier, M. R. Churchill, D. G. Churchill, K. M. Keil, *Organometallics*, 2002, **21**, 946.
25. K. Dymock, G. J. Palenik, *Acta Crystallogr. B*, 1974, **30**, 1364.
26. I. L. Fedushkin, A. N. Lukoyanov, S. Y. Ketkov, M. Hummert, H. Schumann, *Chem. Eur. J.*, 2007, **13**, 7050.
27. R. J. Baker, C. Jones, M. Kloth, D. P. Mills, *New J. Chem.*, 2004, **28**, 207.
28. K. Ueno, T. Watanabe, H. Tobita, H. Ogino, *Organometallics*, 2003, **22**, 4375.
29. A. Sofetis, C. P. Raptopoulou, A. Terzis, T. F. Zafiropoulos, *Inorg. Chim. Acta*, 2006, **359**, 3389.
30. M. N. Chisholm, J. C. Huffman, I. P. Rothwell, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
31. I. L. Fedushkin, T. V. Petrovskaya, F. Girgsdies, R. D. Koehn, M. N. Bochkarev, H. Schumann, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2262.
32. H. Bock, J.-M. Lehn, J. Pauls, S. Holl, V. Krenzel, *Angew. Chem.*, 1999, **111**, 1004.
33. M. N. Bochkarev, I. L. Fedushkin, V. I. Nevodchikov, V. K. Cherkasov, H. Schumann, H. Hemling, R. Weimann, *J. Organomet. Chem.*, 1996, **524**, 125.
34. T. V. Petrovskaya, I. L. Fedushkin, V. I. Nevodchikov, M. N. Bochkarev, N. V. Borodina, I. L. Eremenko, S. E. Nefedov, *Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 2271 [*Izv. Akad. Nauk*, *Ser. Khim.* 1998, 2341].
35. P. L. Diaconescu, C. C. Cummins, *Dalton Trans.*, 2015, **44**, 2676.
36. Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.
37. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

Received January 12, 2016;
in revised form January 20, 2016