Hydroamination of alkynes with aromatic amines catalyzed by digallane (dpp-bian)Ga—Ga(dpp-bian)

*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, and I. L. Fedushkin**

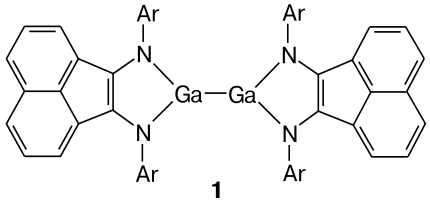
G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation. Fax: +7 (831) 462 7497. E-mail: igorfed@iomc.ras.ru

Digallane (dpp-bian)Ga—Ga(dpp-bian) (**1**) (dpp-bian is the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) catalyzes the addition of 4-chloroaniline to some terminal alkynes RC≡CH (R = Bu^n, Ph, 4-MeC_6H_4). The reaction orders in each of the substrates were found for the reaction of phenylacetylene with 4-chloroaniline catalyzed by compound **1**. The reaction of compound **1** with phenylacetylene in a molar ratio of 1 : 10 led to 1-[*N*-(2,6-diisopropylphenyl)imino]-2-(1-phenylethylidene)acenaphthene (**5**) and the compound $[C_{12}H_6(NC_6H_3Pr^i_2)(PhC{=}CH_2)(PhC{=}CH)]Ga(C{\equiv}CPh)_2$ (**6**). The reaction of digallane **1** with phenylacetylene and aniline in a stoichiometric ratio of 1 : 2 : 2 gave bis-anilide (dpp-bian)-$Ga[N(H)Ph]_2$ (**7**) in 40% yield. The compound $(PhC{\equiv}C)_3Ga \cdot THF$ (**9**) was obtained by the reaction of three equivalents of sodium phenylacetylide (prepared *in situ* from phenylacetylene and sodium) with one equivalent of $GaCl_3$ in tetrahydrofuran. Compounds **5**—**7** and **9** were characterized by IR spectroscopy, ^{1}H NMR spectroscopy was used to characterize products **5**, **6**, and **9**, whereas EPR spectroscopy was used for amide **7**. The structures of compounds **5**—**7** and **9** were determined by single crystal X-ray diffraction analysis.

Key words: gallium, *N*,*N*-ligands, catalysis, hydroamination of alkynes.

The intermolecular hydroamination reactions, proceeding *via* addition of the N—H group to unsaturated compounds, are of interest from the point of view of synthetic chemistry, since they can be used for obtaining of a wide spectrum of important organic products with the nitrogen—carbon bond without formation of side products (atom-economy). Such processes are carried out using homogeneous catalysts based on transition metal complexes,[1—16] lanthanides,[17—22] and actinides,[23,24] as well as main group metals.[25—34] The application of the last mentioned metals is especially reasonable due to their availability, accessibility and, in most cases, low toxicity.

We have shown that compounds of main group metals containing a dianion of the redox-active 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) possess a unique reactivity. Some of their reactions resemble the key steps proceeding in metal complex catalysis involving compounds of d-elements.[35—44] In our systems, the key role belongs to the ligand due to which the redox processes between a nontransition metal complex and an organic substrate become possible. In this connection, attention should be paid to aluminum and gallium derivatives capable to reversibly add some terminal and internal alkynes *via* the formation of bonds with both the metal and the ligand.[39—42,44] Taking into account that this process resembles the step of coordination of unsaturated substrates by transition metal ions, we suggested that these complexes can be used as catalysts in the functionalization of unsaturated organic compounds. Thus, we demonstrated that gallium and aluminum dpp-bian derivatives can catalyze hydroamination reactions of phenylacetylene with aromatic amines.[40,42,44] The complex (dpp-bian)Ga—Ga(dpp-bian) (**1**) exhibited the highest activity: the starting alkyne and anilines furnished the corresponding imines in the yields close to quantitative.[40] It is obvious that the activity of the catalytic system should depend on temperature, the starting concentrations of components, the structure of the substrates used, the solvent nature, and other factors. The study of the influence of these factors will clarify the mechanisms of the processes under consideration and help to understand the specificities of catalytic conversions involving nontransition metal complexes with functionally labile ligands.



1

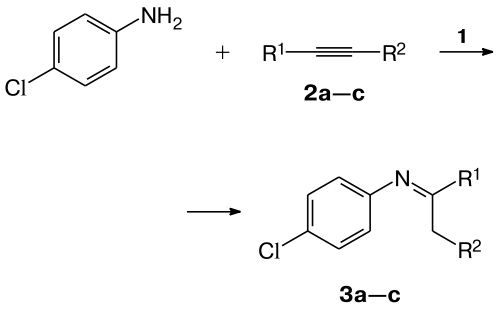
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2830—2840, December, 2015.

In the present work, we report the results of tests of the catalytic activity of compound **1** in the reactions of some terminal and internal alkynes with 4-chloroaniline, the data on the kinetics of hydroamination of phenylacetylene with 4-chloroaniline in the presence of digallane **1**, as well as the results of the experiments on identification of the catalyst intermediates of the process under consideration.

Results and Discussion

Catalytic activity of complex 1 in the hydroamination reaction of alkynes with 4-chloroaniline. Earlier, we have studied the catalytic activity of compound **1** in the hydroamination reactions of only two alkynes, phenylacetylene[40] and methyl 2-butynoate.[45] In the first case, as it was already mentioned, the addition of anilines at the triple bond proceeded readily enough (obeing Markovnikov´s rule) and led to the formation of imines. Attempted hydroamination of methyl 2-butynoate with 4-chloroaniline in the presence of complex **1** was unsuccessful because of the irreversible conversions of compound **1** involving alkyne. To broaden the scope of the reaction catalyzed by compound **1**, we tried to involve other alkynes, keeping 4-chloroaniline as the second component, since its involvement in the reaction with phenylacetylene gave a quantitative yield of imine over the shortest period of time[40] (Scheme 1). The results of the experiments, as well as the reaction conditions are given in Table 1.

Scheme 1



Conditions: 4 mol.% of **1**, C_6D_6, 90 °C.

As it is seen from these data, the hydroamination in the presence of complex **1** was successful only for terminal alkynes: hex-1-yne (**2a**), phenylacetylene (**2b**), and 4-ethynyltoluene (**2c**). The increase in the reaction rate observed in the order **2a**, **2b**, **2c** can be apparently explained by more strong polarization of the triple bond due to the +μ-effect caused by the aromatic ring of phenylacetylene on going from **2a** to **2b** and a positive induction effect of the methyl group at *para*-position of the phenyl ring on going from **2b** to **2c**. Attempted functionalization of internal alkyl- and arylacetylenes **2e—g** has proved unsuccessful. It is possible that the C—H bond of the terminal sp-hybridized carbon atom of alkyne is directly involved into the catalytic cycle and its presence in the unsaturated substrate is a necessary condition. At the same time, the inertness of trimethylsilylacetylene (**2d**) toward 4-chloroaniline can be explained by the reversed polarization of the triple bond to the side of the Me_3Si group due to the π—d-conjugation effect. We studied the relationship time—yields of imines **3a—c** for the hydroamination reactions of alkynes **2a—c** (Fig. 1). In all the cases, the kinetic curves were found to have an S-like shape with three characteristic segments.

In the initial section, a monotonous acceleration of the reaction is observed until a certain moment of time, which can indicate an induction period when compound **1** is converted to a true catalyst by the reactions with the starting substrates. In the second section, when the sta-

Table 1. Reaction of 4-chloroaniline with alkynes catalyzed by complex **1**[a]

Alkyne	R^1	R^2	Product	τ/h	Yield (%)[b]
2a	Bu^n	H	**3a**	24	95
2b	Ph	H	**3b**	7.5	93
2c	4-MeC_6H_4	H	**3c**	3.5	98
2d	Me_3Si	H	—	65	0
2e	Pr^n	Me	—	30	0
2f	Ph	Me	—	65	0
2g	Ph	Ph	—	80	0

[a] Conditions: 4-chloroaniline (0.113 g, 0.89 mmol), alkyne (0.89 mmol), complex **1** (0.022 g, 0.0178 mmol, 4 mol.% calculated on one metal center), C_6D_6 (0.65 mL), 90 °C. The reactions were carried out in sealed NMR tubes. The process was monitored by ^1H NMR spectroscopy.
[b] The yields were calculated based on the ratio of integral intensities of signals corresponding to reagents and reaction products.

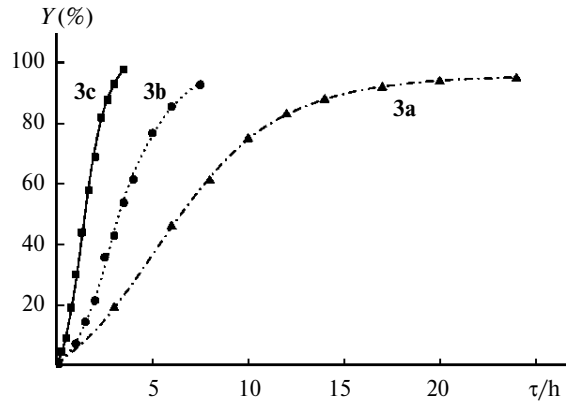
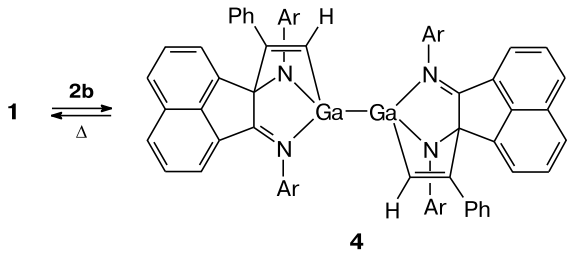


Fig. 1. Time-dependent yields (*Y*) of imines **3a—c** formed in the reactions of alkynes **2a—c** with 4-chloroaniline in the presence of 2 mol.% of compound **1** (benzene, 90 °C).

tionary concentrations of active catalyst species are reached the rate of hydroamination becomes constant and the reaction acquires pseudo-zero order in each of the reacting components. In the third section, when the yield of imines **3a**—**c** reached 70—75%, the process slows down. Most likely, this results from the decrease in the concentration of the starting compounds and the increase in the content of formed imines **3a**—**c**, as well as from the deactivation of the catalyst through the side reactions.

Study of the kinetics of the reactions of 4-chloroaniline with phenylacetylene in the presence of digallane 1. To confirm the suggestions on the reactivity of alkynes and the reasons for the changes observed in the rate of the process, we studied the influence of the concentrations of substrates and complex **1** on the rate of hydroamination. The processes were monitored by ^{1}H NMR spectroscopy. 4-Chloroaniline and phenylacetylene were used as the starting components, since these compounds are available and react rapidly enough in the presence of **1**. Apart from that, from the alkynes listed in Table 1 only the adduct of phenylacetylene with digallane **1**, complex **4** (Scheme 2), is characterized, which eliminates alkyne upon heating.[39,40]

Scheme 2



4

The influence of the initial concentrations of phenylacetylene (**2b**), 4-chloroaniline, and complex **1** on the rate of the formation of imine **3b** is shown in Fig. 2. Each of the kinetic curves, like in the cases considered above (see Fig. 1), is characterized by the section with a monotonously increasing rate and a linear section, where the rate of the reaction is virtually constant and the maximal. As it is seen from the graphs, in all the cases an increase in the initial concentration of each of the components, with the concentration of two others remaining unchanged, leads to the increase in the rate of hydroamination.

For the series of experiments, in which the concentration of the metal centers was $[Ga]_0 = 4.00 \cdot 10^{-2}$ mol L^{-1} ($[\mathbf{1}]_0 = 0.5[Ga]_0 = 2.00 \cdot 10^{-2}$ mol L^{-1}), the maximal rates of the process were found (V_{max}). The linear approximation of $\ln(V_{max})$ from $\ln([4\text{-Cl—}C_6H_4NH_2]_0)$ and $\ln([PhCCH]_0)$ (Fig. 3) allowed us to determine the orders of the reactions in phenylacetylene and aniline, which were 1.68 and 1.16, respectively.

The influence of the initial concentration of each of the reaction components on V_{max}, as well as the frac-

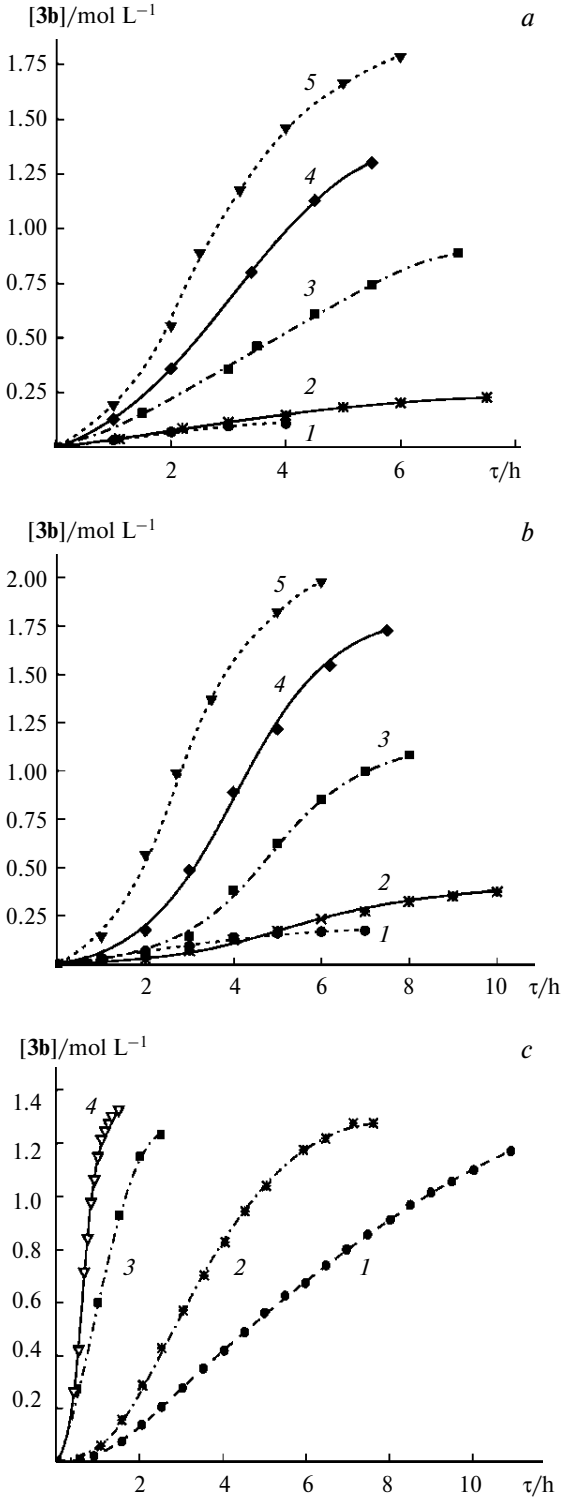


Fig. 2. Kinetic curves of the formation of imine **3b**, in the catalytic hydroamination reaction of phenylacetylene with 4-chloroaniline catalyzed by complex **1**. Conditions: $[\mathbf{2b}]_0$/mol L^{-1} = = 0.35—2.00 (*a*), 2.20 (*b*), 1.34 (*c*); $[4\text{-Cl—}C_6H_4NH_2]_0$/mol L^{-1} = = 2.00 (*a*), 0.20—2.10 (*b*), 1.34 (*c*); $[Ga]_0$/mol L^{-1} = $4.00 \cdot 10^{-2}$ (*a*, *b*), $(2.7—13.3) \cdot 10^{-2}$ (*c*), benzene; 90 °C. (*a*) $[\mathbf{2b}]_0$/mol L^{-1}: 0.35 (*1*), 0.60 (*2*), 1.10 (*3*), 1.60 (*4*), 2.00 (*5*); (*b*) $[4\text{-Cl—}C_6H_4NH_2]_0$/mol L^{-1}: 0.20 (*1*), 0.50 (*2*), 1.15 (*3*), 1.78 (*4*), 2.10 (*5*); (*c*) $[Ga]_0 \cdot 10^2$/mol L^{-1}: 2.7 (*1*), 5.4 (*2*), 8.8 (*3*), 13.3 (*4*).

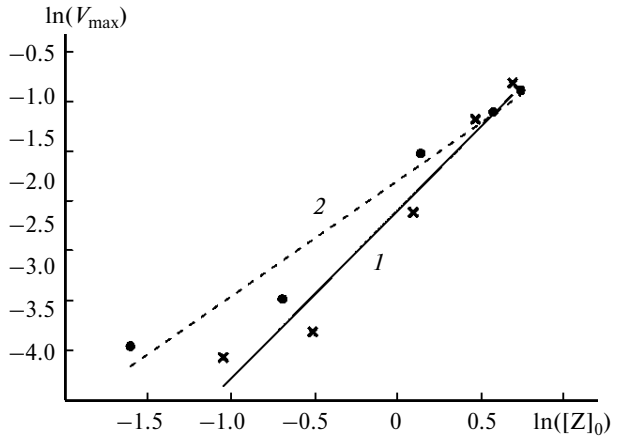
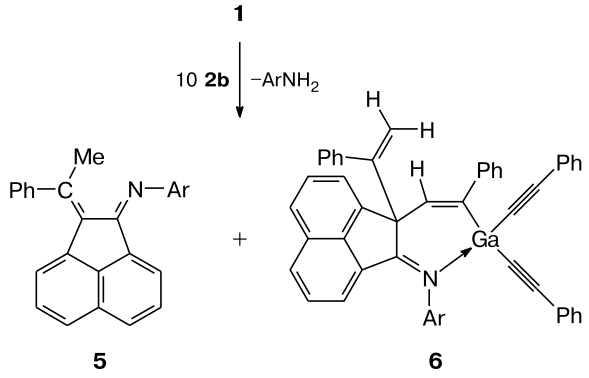


Fig. 3. Linear approximations of the ln(V_{max}) values from ln([Z]$_0$) for hydroamination reactions of phenylacetylene with 4-chloroaniline catalyzed by complex **1**: (*1*) Z = **2b**, $y = 1.680x - 2.097$, $R^2 = 0.955$; (*2*) Z = 4-Cl—$C_6H_4NH_2$, $y = 1.157x - 1.796$, $R^2 = 0.962$.

tional orders of the reactions in phenylacetylene (**2b**) and 4-chloroaniline indirectly indicate the involvement of all three components, phenylacetylene (**2b**), 4-chloroaniline, and digallane **1**, in the formation of a true precatalyst. Therefore, to confirm this suggestion we carried out a series of model reactions of compound **1** with the substrates in different ratios, as well as synthesized compounds, which could have been formed in the course of the catalytic cycle, and compared their catalytic activity with that of digallane **1**.

Reaction of digallane 1 with an excess of phenylacetylene. The reaction of digallane **1** with phenylacetylene (**2b**) in the molar ratio of 1 : 10 at 120 °C in toluene for 15 h leads to the formation of acenaphthenenimine **5**, as well as a gallium complex **6** (Scheme 3). The use of diethyl ether instead of toluene leads to the formation of a yellow precipitate, whose separation and recrystallization from diethyl ether gives compound **5** as yellow plate crystals in

Scheme 3



Conditions: 120 °C, toluene, 15 h.

18% yield. Complex **6** was isolated by crystallization from the solution in diethyl ether after separation of acenaphthenenimine **5** as light yellow needle-like crystals in 13% yield.

The high solubility of compounds **5** and **6** did not allow us to isolate them from the solution in the individual (crystalline) state in large amounts. Both compounds were characterized by NMR spectroscopy and X-ray crystallography. Compound **5** is a substitution product of one arylimine group 2,6-Pr^i_2Ph—N= in dpp-bian with the phenylethylidene fragment Ph(Me)C= formed from the phenylacetylene molecule. It is obvious that the formation of product **5** takes place in several steps, the first of which is the formation of adduct **4** (see Scheme 2). Then, complex **4** decomposes in the presence of an excess of phenylacetylene, whereas the ligand skeleton undergoes a series of transformations with elimination of 2,6-diisopropylaniline. Apparently, the reduction processes observed involve the gallium—gallium bond, and the metal atoms are bound as gallium tris-phenylacetylide.

The analysis of the structure of complex **6** allowed us to draw a conclusion that this product, like compound **5**, was formed from cycloadduct **4**. In this case, the 2,6-diisopropylaniline molecule is also eliminated and the [4+2] cycloaddition of phenylacetylene at the fragment Ga—N—C—C leads to the emergence of a new six-membered ring. It is important to note that the regioselectivity of the addition of two phenylacetylene fragments to the acenaphthene framework is not the same: in one case, an internal carbon atom of the alkyne is involved in the formation of the new C—C bond, in other case, this is a terminal carbon atom. The regioselectivity of the last mentioned type was observed in the addition of PhC≡CH to (dpp-bian)Al—Al(dpp-bian).[41] It is possible that the regioselectivity of the addition is determined by steric factors. The presence of a bulky substituent at the carbon atom makes it impossible for the second molecule of phenylacetylene to be added in such a way that the phenyl ring would have been near the naphthalene part of molecule **6**. The IR spectrum of complex **6** contains a band of medium intensity at 2139 cm^{-1} characteristic of the vibration of the C≡C bond in the phenylethynyl substituents. In the ^{1}H NMR spectrum of compound **6**, the methyl groups of the Pr^i substituents are found as four doublets in the range δ 1.73—0.13, whereas the methine protons as two septets at δ 3.98 and 2.75 (Fig. 4).

The ^{1}H NMR spectrum confirms the asymmetry of the imine ligand of product **6**, in which all the aromatic protons, two methine protons, and four methyl groups of the Pr^i substituents are nonequivalent.

Reaction of digallane 1 with PhC≡CH (2b) and 4-$RC_6H_4NH_2$ (R = H, Cl) in the ratio of 1 : 2 : 2. The reaction of digallane **1** with phenylacetylene (**2b**) and aniline (R = H) in the stoichiometric ratio of 1 : 2 : 2 in benzene for 15 min at 90 °C is accompanied by the change in the reaction mixture color from dark blue to reddish

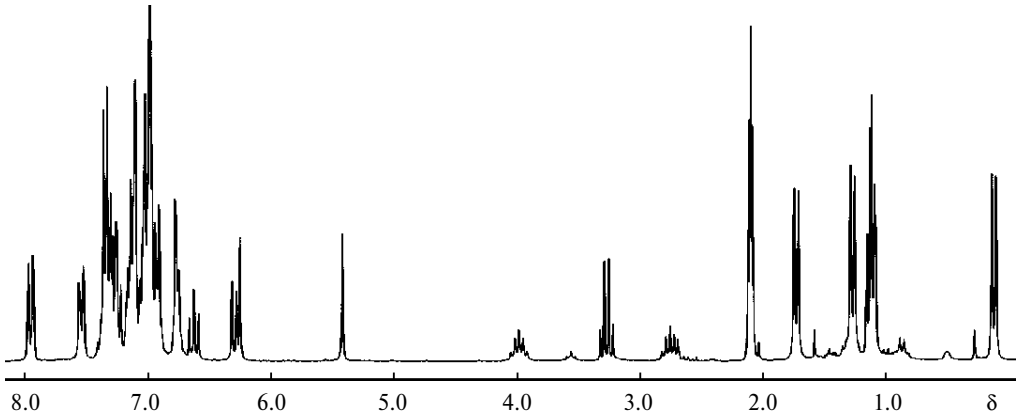
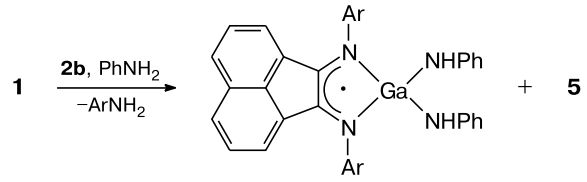


Fig. 4. ^{1}H NMR spectrum of compound **6** (293 K, 200 MHz, toluene-d_8).

brown. The reaction results in the formation of radical anion derivative **7**, acenaphthenenimine **5**, and 2,6-diisopropylaniline (Scheme 4). The last two compounds were not isolated in the individual state. They were identified in the reaction mixture by ^{1}H NMR spectroscopy.

Scheme 4



7

Conditions: 90 °C, benzene, 15 min.

Here, as in the case of the reaction of digallane **1** with a ten-fold excess of phenylacetylene, the second metal atom, by all means, is bound as gallium tris-phenylacetylide. Compound **7** was isolated as dark brown parallelepipeds in 40% yield by crystallization from benzene and characterized by EPR and IR spectroscopy, as well as by X-ray crystallography. The EPR spectrum of the solution of complex **7** in toluene at 298 K (Fig. 5) demonstrates the splitting of the unpaired electron on the nuclei of two pairs of protons of the naphthalene part of the ligand dpp-bian, two equivalent nitrogen atoms, one gallium atom, and two nitrogen atoms of the amide substituents $-N(H)C_6H_5$.

When 4-chloroaniline was used, 2,6-di(isopropyl)-aniline and acenaphthenenimine **5** were also identified in the mixture of the reaction products. Unfortunately, our attempted isolation in the individual state of bisamide (dpp-bian)Ga[N(H)PhCl-4]$_2$ (**8**), similar to complex **7**, was unsuccessful. However, the EPR spectrum of the reaction mixture at 293 K is similar to the spectrum of compound **7**. This indirectly indicates the formation of the desired radical anion bisamide **8**.

Synthesis of gallium trisphenylacetylide (PhC≡C)$_3$Ga · THF (9). As it was mentioned above, we suggest that the reaction of digallan with phenylacetylene and anilines can give, besides compounds **5**—**8**, gallium trisphenylacetylide. It cannot be excluded that this derivative also can catalyze the addition of anilines to phenylacetylene. To confirm this suggestion, we synthesized gallium trisphenylacetylide. The compound (PhC≡C)$_3$Ga · THF (**9**) was obtained by the reaction of three equivalents of sodium phenylacetylide (prepared *in situ* from phenylacetylene and sodium) with one equivalent of $GaCl_3$ in tetrahydrofuran for 20 h at room temperature. The method used by us for the preparation of compound **9** differs from the method used for the synthesis of the only known neutral gallium acetylide (PhC≡C)$_3$Ga · NMe_3, which was obtained by the reaction of gallium hydride $GaH_3 \cdot NMe_3$ with phenylacetylene.[46] Compound **9** was isolated from toluene as colorless rhom-

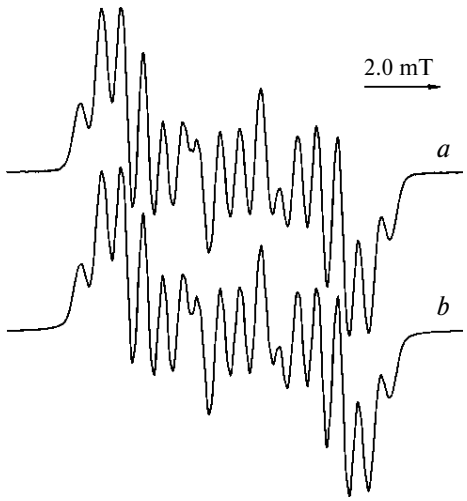


Fig. 5. Experimental EPR spectrum of compound **7** in toluene at 298 K (*a*) and calculated spectrum (*b*): g = 2.00265, $a_i(^{69}Ga)$ = 1.503, $a_i(^{71}Ga)$ = 1.910, $a_i(2\ ^{14}N)$ = 0.126, $a_i(2\ ^{14}N)$ = 0.495, $a_i(2\ ^{1}H)$ = 0.098, $a_i(2\ ^{1}H)$ = 0.085 mT.

bohedral crystals in 52% yield and characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, as well as by X-ray crystallography. The IR spectrum of compound **9** contains a strong absorption band ν(C≡C) at 2143 cm^{-1}, whereas the ^{13}C NMR spectrum exhibits the signals for the carbon atoms Ph—C≡ and Ga—C≡ at δ 106.6 and 98.6, respectively.

Structure of compounds 5—7 and 9. The structures of compounds **5**—**7** and **9** were established by X-ray crystallography and are shown in Figs 6—9, respectively. Principal bond distances and bond angles are given in Table 2.

In acenaphthenenimine **5**, the atoms N(1), C(1), C(2), C(26), and C(25) lie virtually in one plane. The bond lengths in the fragment N(1)=C(1)—C(2)=C(26) (C(1)—N(1) 1.281(2), C(1)—C(2) 1.514(2), C(2)—C(26) 1.351(2) Å) are close to the corresponding values in 1-aza-1,3-butadiene system of 1-(*tert*-butylimino)-2-[(2,4,6-trimethylphenyl)methylidene]acenaphthene (1.274(3), 1.518(3), and 1.330(3) Å, respectively),[47] however, they slightly differ from those for compound (Ph)CH=CH—CH=N(2,6-Pr$^i_2$C$_6$H$_3$) (1.278(5), 1.438(6), and 1.351(5) Å, respectively),[48] thus demonstrating relatively weak conjugation in the 1-aza-1,3-butadiene fragments of the acenaphthene derivatives. The distance between the carbon

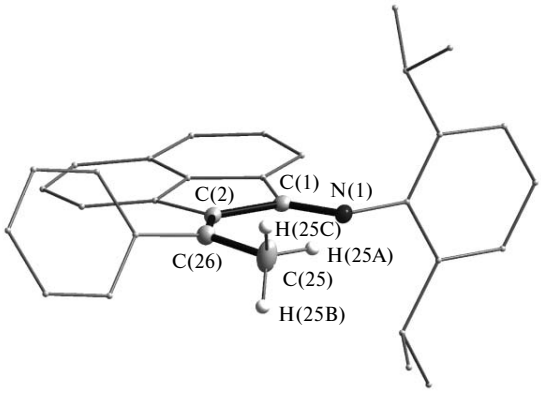


Fig. 6. Molecular structure of compound **5**. Hydrogen atoms, except H(25A), H(25B), and H(25C), are omitted. Thermal ellipsoids are given with 30% probability.

Table 2. Selected bond distances (*d*) and bond angles (ω) in molecules **5**—**7**, and **9**

Bond	*d*/Å	Angle	ω/deg
		Compound **5**	
C(1)—N(1)	1.281(2)	N(1)—C(1)—C(2)	123.7(1)
C(1)—C(2)	1.514(2)	C(1)—C(2)—C(26)	126.2(1)
C(2)—C(26)	1.351(2)	C(2)—C(26)—C(25)	124.8(1)
C(25)—C(26)	1.503(2)		
		Compound **6**	
C(1)—N(1)	1.280(4)	N(1)—C(1)—C(2)	122.3(3)
C(1)—C(2)	1.542(4)	C(2)—C(21)—C(22)	120.4(3)
C(2)—C(13)	1.527(4)	C(2)—C(13)—C(14)	125.9(3)
C(2)—C(21)	1.560(4)	C(13)—C(2)—C(21)	110.7(3)
C(21)—C(22)	1.315(6)	Ga—C(14)—C(13)	117.3(2)
C(13)—C(14)	1.343(5)	Ga—C(41)—C(42)	173.3(3)
Ga—N(1)	2.031(3)	Ga—C(49)—C(50)	176.8(4)
Ga—C(14)	1.969(3)		
Ga—C(41)	1.943(4)		
Ga—C(49)	1.941(4)		
C(41)—C(42)	1.202(5)		
C(49)—C(50)	1.202(5)		
		Compound **7**	
Ga—N(1)	1.964(2)	N(1)—Ga—N(2)	86.23(6)
Ga—N(2)	1.974(2)	N(3)—Ga—N(4)	111.98(7)
C(1)—N(1)	1.335(2)	Ga—N(1)—C(1)	108.6(1)
C(2)—N(2)	1.335(2)	Ga—N(2)—C(2)	108.5(1)
C(1)—C(2)	1.434(2)	N(1)—C(1)—C(2)	118.2(2)
Ga—N(3)	1.866(2)	C(1)—C(2)—N(2)	118.0(2)
Ga—N(4)	1.855(2)	Ga—N(3)—C(43)	124.2(1)
N(3)—C(43)	1.380(3)	Ga—N(4)—C(37)	130.4(1)
N(4)—C(37)	1.384(2)		
		Compound **9**	
Ga—C(1)	1.916(3)	Ga—C(1)—C(2)	171.1(2)
Ga—C(9)	1.927(3)	Ga—C(9)—C(10)	176.6(2)
Ga—C(17)	1.927(3)	Ga—C(17)—C(18)	178.2(2)
C(1)—C(2)	1.213(3)	C(1)—Ga—C(9)	117.2(1)
C(9)—C(10)	1.200(4)	C(1)—Ga—C(17)	116.5(1)
C(17)—C(18)	1.210(3)	C(9)—Ga—C(17)	117.5(1)

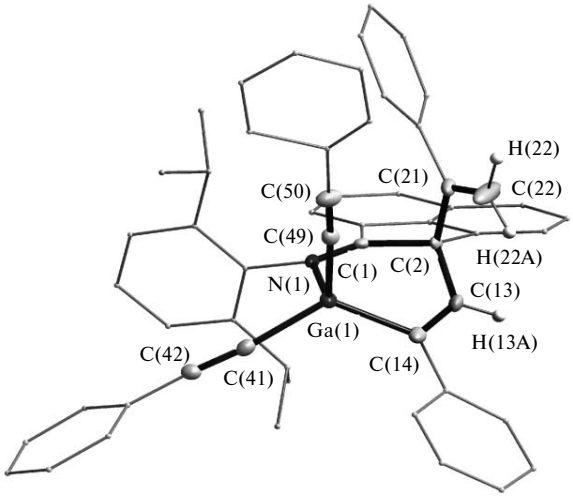


Fig. 7. Molecular structure of complex **6**. Hydrogen atoms, except H(13A), H(22A), and H(22B), are omitted. Thermal ellipsoids are given with 30% probability.

atoms C(25)—C(26) of 1.5034(18) Å corresponds to a single carbon—carbon bond. The benzene ring of the 2,6-diisopropylphenyl substituent is orthogonal to the acenaphthene part of molecule **5**, while the angle between the plane of the phenyl substituent at carbon atom C(26) and the plane of the 1-aza-1,3-butadiene system is 59.73(1)°.

In complex **6**, the distance N(1)—C(1) (1.280(4) Å) corresponds to the double N=C bond in the free dpp-bian ligand (each N=C bond is 1.282(4) Å in length).[49]

The Ga—N(1) bond bears a donor-acceptor character and is formed by the interaction of a lone pair of electrons on the nitrogen atom with a vacant orbital of the gallium atom. Its length (2.031(2) Å) is slightly shorter as compared to a similar donor-acceptor Ga(1)—N(2) bond (2.173(1) Å) in the cycloadduct **4**.[39,40] The distance C(1)—C(2) in compound **6** (1.542(4) Å) corresponds to the length of a single C—C bond (1.54 Å) and is comparable with the corresponding distance in the free dpp-bian (1.534(6) Å).[49] The C(13)—C(14) and C(21)—C(22) bonds (1.343(5) and 1.315(6) Å, respectively), formed from the triple bonds of phenylacetylene, correspond to the carbon—carbon double bond in alkenes (1.34 Å) and are insignificantly shorter than the C(2)—C(26) double bond (1.351(2) Å) in acenaphthenenimine **5**. The distances C(41)—C(42) and C(49)—C(50) (1.202(5) Å) in the phenylethynyl fragments at the gallium atom correspond to the triple bond in alkynes (1.21 Å). The distances Ga—C (*cf.* 1.94 Å) and C≡C (*cf.* 1.20 Å) in compound **6** are in good agreement with those in gallium phenylethynyl complexes $(PhC{\equiv}C)_3Ga \cdot NMe_3$ (*cf.* Ga—C 1.94 Å; *cf.* C≡C 1.20 Å)[46] and **9** (*cf.* Ga—C 1.92 Å; *cf.* C≡C 1.21 Å).

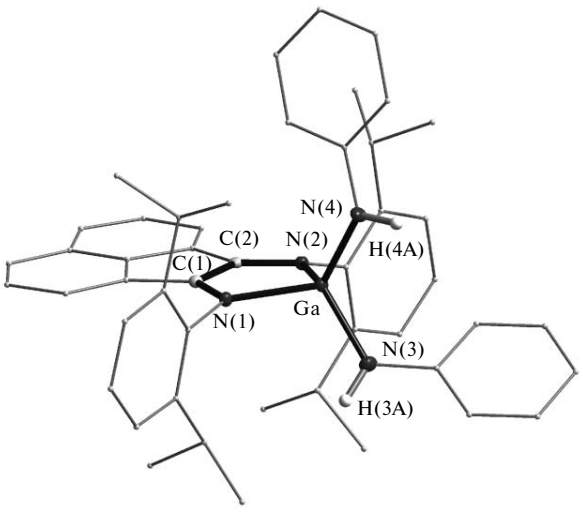


Fig. 8. Molecular structure of complex **7**. Hydrogen atoms, except H(3A) and H(4A), are omitted. Thermal ellipsoids are given with 30% probability.

The geometric parameters of gallium complex **7** agree with the EPR spectroscopy data, confirming the radical anion state of the dpp-bian ligand. The bond distances in the diazadiene fragment (C(1)—N(1) 1.335(2), C(1)—C(2) 1.434(3), C(2)—N(2) 1.335(2) Å) have the intermediate values as compared to the bond lengths in the neutral[49] and dianion dpp-bian ligands in gallium complexes.[44]

The distances C—N and C—C in the metallacycle of compound **7**, as well as the distances Ga—N(1) and Ga—N(2) (1.964(2) and 1.974(2) Å) are close to the corresponding values in bisacetylide (dpp-bian)$Ga(C{\equiv}CPh)_2$ (**10**) (N(1)—C(1) 1.335(3); C(1)—C(2) 1.426(3); C(2)—N(2) 1.324(2); Ga—N(1) 1.967(2); Ga—N(2) 1.981(2) Å).[44] At the same time, the Ga—N(1) and Ga—N(2) bonds in complex **7** are longer than in the mononuclear gallium derivatives containing the dpp-bian dianion (*cf.* 1.90 Å).[44] The structure of compound **7** can be compared with the structure of gallium β-diketiminate $[HC\{C(Me)N(2,6\text{-}Pr^i{}_2C_6H_3)\}_2]Ga(NHPh)_2$, which also contains two arylamido fragments.[50] Thus, the Ga—N(H)Ar bond distances in compound **7** (1.866(2) and 1.855(2) Å) are close to the corresponding distances the diketiminate derivative (1.862(3) and 1.851(3) Å). The angle N(3)—Ga—N(4) in complex **7** (111.98(7)°) is only 2.6° larger than the corresponding value in $[HC\{C(Me)N\text{-}(2,6\text{-}Pr^i{}_2C_6H_3)\}_2]Ga(NHPh)_2$ (109.3°).[50]

The independent part of the crystal cell in compound **9** (Fig. 9) contains three independent molecules. Their geometric characteristics are similar, therefore, the data for only one of them are given in Table 2.

The coordination environment of the metal atom in compound **9** is a distorted tetrahedron. The C(1)—C(2), C(9)—C(10), and C(17)—C(18) bond distances (1.213(3), 1.200(4), and 1.210(3) Å, respectively) correspond to the carbon—carbon triple bonds. The Ga—C(1), Ga—C(9), and Ga—C(17) bond distances (1.916(3), 1.927(3), and 1.927(3) Å, respectively) are close to the Ga—C distances

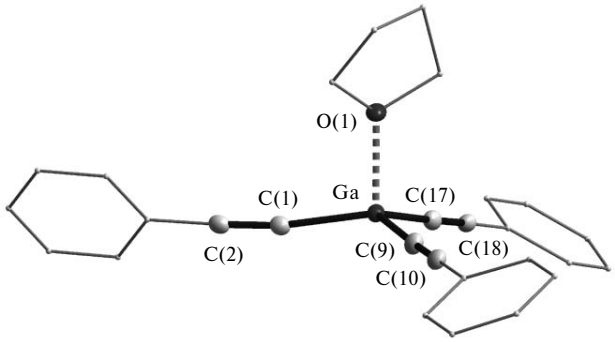


Fig. 9. Molecular structure of compound **9**. Hydrogen atoms are omitted. Thermal ellipsoids are given with 30% probability.

in $(PhC{\equiv}C)_3Ga{\cdot}NMe_3$ (Ga—C(1) 1.940(4), Ga—C(3) 1.940(4), and Ga—C(5) 1.929(4) Å).[46]

Studies of catalytic activity of complexes 6, 7, 9, and 10 in the hydroamination reaction of phenylacetylene (2b) with 4-chloroaniline. As it was mentioned above, compounds **6** and **7** isolated from the model reactions, as well as gallium acetylide **9** and the complex (dpp-bian)$Ga(C{\equiv}CPh)_2$ (**10**) synthesized earlier[44] theoretically can be formed in the course of the catalytic hydroamination of phenylacetylene with anilines and play the role of true precatalysts. To confirm this suggestion, we studied the catalytic activity of these compounds in the hydroamination reaction of phenylacetylene (**2b**) with 4-chloroaniline, as well as compared the obtained results with the activity of digallane **1**. The results of these tests are given in Table 3.

The data in Table 3 show that complexes **6** and **7** are catalytically inactive in the hydroamination reaction of phenylacetylene with 4-chloroaniline (entries *3* and *4*). Compound **10** exhibits extremely low catalytic activity.

Table 3. Hydroamination of phenylacetylene (**2b**) with 4-chloroaniline in the presence of different catalysts (Cat)[a]

Entry	Catalyst	[Cat]/mol.%[b]	τ/h	Yield (%)[c]
1	**1**	2	11	87
2	**1**	10	1.5	99
3	**6**	10	24	0
4	**7**	10	24	0
5	**9**	2	22	2
6	**9**	10	1.5	98
7	**10**	10	24	5

[a] Conditions: phenylacetylene (0.091 g, 0.89 mmol); 4-chloroaniline (0.113 g, 0.89 mmol); amount of catalyst (mol.%) relative to 100 mol.% of one of the substrates; C_6D_6 (0.65 mL); 90 °C. Reactions were carried out in sealed NMR tubes. The process was monitored by ^{1}H NMR spectroscopy.

[b] For binuclear digallane **1**, the molar % of gallium centers are given, *i.e.*, the real content of digallane **1** in molar % is two times lower than that specified in the Table.

[c] The yields were calculated based on the ratio of integral intensities of signals corresponding to reagents and reaction products.

Thus, *N*-(4-chlorophenyl)-1-phenylethan-1-imine (**3b**) was obtained in only 5% yield within 24 h in the presence of 10 mol.% of complex **10** (entry *7*). A comparison of activities of digallane **1** and gallium trisphenylacetylide **9** shows that with 2 mol.% content of the catalyst, the complex **1** is considerably more active than compound **9** (entries *1* and *5*). However, when the content was 10 mol.%, no considerable difference was observed in the activities of catalysts **1** and **9** (entries *2* and *6*).

In conclusion, we have shown that complexes **6**, **7**, and **10** do not catalyze the hydroamination reaction of phenylacetylene (**2b**) with 4-chloroaniline, whereas their possible appearance in the reaction mixture when digallane **1** is used as the catalyst actually indicates the deactivation of the latter. The difference in the catalytic activities of compound **9** and digallane **1** when used in small amounts (2 mol.%) indicates that in the reaction which uses digallane **1** the gallium trisphenylacetylide **9** is hardly a true catalyst. The similar activities of compound **9** and digallane **1** when used in higher concentrations (10 mol.%) cannot be an evidence that in the reaction which uses digallane **1** compound **9** is a true catalyst either, since in this case some phenylacetylene or 4-chloroaniline would be bound by gallium atoms and a 99% yield of imine **3b** could not be reached. As a conclusion, we should state that at this stage we can not say what is a true catalyst in the reaction of anilines with phenylacetylene upon addition to them of the catalytic amounts of digallane **1**. We have shown that different compounds can be formed in the system containing these three components. The dependence observed for the rate of hydroamination reaction on the concentration of the substrates indicates a complicated catalytic cycle, whose mechanism requires additional studies. In this case, the catalytically active species can be kinetically so labile, that their detection by common spectroscopic methods can be difficult or even impossible.

Experimental

All the processes dealing with the preparation, isolation, and application as catalysts of complexes **1**, **6**, **7**, **9**, and **10** were carried out *in vacuo* or under nitrogen (high purity grade). using Schlenk technique because of the high sensitivity of these compounds to air oxygen and moisture. Compounds **1**[40] and **10**[44] were obtained according to the known procedures. Tetrahydrofuran, diethyl ether, hexane, benzene, toluene, as well as deuterated solvents (benzene-d_6 and toluene-d_8) were dried and stored over sodium benzophenone ketyl and collected by condensation *in vacuo* directly before use. Alkynes **2a—f** and aniline were purchased from Aldrich, then dried with calcium hydride, distilled *in vacuo*, and stored in a sealed glassware under dry nitrogen. Diphenylacetylene **2g** and 4-chloroaniline were purchased from Aldrich and purified by sublimation *in vacuo* before use. IR spectra were obtained on a FSM-1201 spectrometer for suspensions of compounds in Nujol. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-200 and Bruker Advance III 400 spectrometers.

Chemical shifts are given in ppm, using chemical shifts of protons and carbon atoms of deuterated solvents as references. EPR spectra were recorded on a Bruker ER 200 D-SRC spectrometer (9.46 MHz). Melting points were determined in sealed evacuated capillary tubes.

Catalytic reactions were carried out in sealed NMR tubes. The samples were prepared as follows.

A. In the case of hydroamination of alkynes **2a**—**g** with 4-chloroaniline, an alkyne (0.89 mmol), 4-chloroaniline (0.113 g, 0.89 mmol), and compound **1** (0.022 g, 0.0178 mmol) were placed into an NMR tube. Then, deuterobenzene (0.65 mL) was vacuum condensed into the tube, which was sealed and placed in a thermostat with the temperature of 90 °C.

B. To study the influence of the concentration of substrates and the concentration of complex **1** on the rate of hydroamination, phenylacetylene (0.23—1.43 mmol), 4-chloroaniline (0.13—1.37 mmol), and compound **1** ((0.88—4.32) · 10^{-2} mmol), depending on the required ratio of components, were placed into an NMR tube. Then, deuterobenzene was vacuum condensed into the tube to a total volume of the reaction mixture of 0.65 mL. The tube was sealed and placed in a thermostat with the temperature of 90 °C.

C. In the case of comparative test of the catalytic activity of complexes **6**, **7**, **9**, and **10**, phenylacetylene (**2b**) (0.091 g, 0.89 mmol), 4-chloroaniline (0.113 g, 0.89 mmol), and a catalyst in the amount corresponding to the molar percents indicated in Table 3 relative to the amount of one of the substrates were placed into an NMR tube. Then, deuterobenzene (0.65 mL) was vacuum condensed into the tube, which was sealed and placed in a thermostat with the temperature of 90 °C.

In all the cases, the processes were monitored by ^{1}H NMR spectroscopy, recording spectra through a certain period of time, cooling the sample to room temperature. The ratio between the starting reagents and the reaction products was calculated from the integral intensities of the corresponding signals.

***N*-(4-Chlorophenyl)hexane-2-imine, 4-ClC$_6$H$_4$N=C(Me)-(CH$_2$)$_3$Me (3a).** ^{1}H NMR (400 MHz, C_6D_6, 298 K), δ: 7.09 (d, 2 H, CH_{arom}, J = 8.8 Hz); 6.40 (d, 2 H, CH_{arom}, J = 8.5 Hz); 2.12 (t, 2 H, N=C(Me)C$\underline{H}_2$CH$_2$CH$_2$Me, J = 7.5 Hz); 1.57—1.47 (m, 2 H, N=C(Me)CH$_2$C$\underline{H}_2$CH$_2$Me); 1.36 (s, 3 H, N=C(<u>Me</u>)CH$_2$CH$_2$-CH$_2$Me); 1.32—1.21 (m, 2 H, N=C(Me)CH$_2$CH$_2$C$\underline{H}_2$Me); 0.87 (t, 3 H, N=C(Me)CH$_2$CH$_2$CH$_2$<u>Me</u>, J = 7.4 Hz).

***N*-(4-Chlorophenyl)-1-phenylethane-1-imine, 4-ClC$_6$H$_4$-N=C(CH$_3$)Ph (3b).** ^{1}H NMR (400 MHz, C_6D_6, 298 K), δ: 7.95—7.85 (m, 2 H, CH_{arom}); 7.21—7.16 (m, 3 H, CH_{arom}); 7.10 (d, 2 H, CH_{arom}, J = 7.8 Hz); 6.45 (d, 2 H, CH_{arom}, J = 7.8 Hz); 1.76 (s, 3 H, N=C(C$\underline{H}_3$)Ph).

***N*-(4-Chlorophenyl)-1-(*p*-tolyl)ethane-1-imine, 4-ClC$_6$H$_4$-N=C(Me)(4-MeC$_6$H$_4$) (3c).** ^{1}H NMR (200 MHz, C_6D_6, 298 K), δ: 7.88 (d, 2 H, CH_{arom}, J = 8.0 Hz), 7.11 (d, 2 H, CH_{arom}, J = 8.5 Hz); 7.03 (d, 2 H, CH_{arom}, J = 7.8 Hz); 6.47 (d, 2 H, CH_{arom}, J = 8.3 Hz); 2.12 (s, 3 H); 1.79 (s, 3 H).

1-[*N*-(2,6-Diisopropylphenyl)imino]-2-(1-phenylethylidene)-acenaphthene, C$_{12}$H$_6$(NC$_6$H$_3$Pr$^i_2$)(=C(Ph)CH$_3$) (5). Phenylacetylene (**2b**) (0.51 g, 5 mmol) to complex **1** (0.57 g, 0.5 mmol) obtained *in situ* from dpp-bian (0.5 g, 1 mmol) in toluene (30 mL). The solution immediately changed the color from dark blue to reddish brown. The reaction mixture was heated at 120 °C for 15 h. Then, toluene was evaporated *in vacuo*, the dry residue was dissolved in diethyl ether (15 mL). After 2 h, a fine crystalline yellow precipitate was formed, which was filtered and once more dissolved in diethyl ether (10 mL). Compound **5** (0.077 g, 18%) was isolated by concentration of the solution, yellow plate crystals, m.p. 156—158 °C. Found (%): C, 88.96; H, 7.31. $C_{32}H_{31}N$ (429.58 g mol^{-1}). Calculated (%): C; 89.39; H, 7.22. IR (Nujol), ν/cm^{-1}: 1646 s, 1614 s, 1585 s, 1542 w, 1487 w, 1432 m, 1363 m, 1325 m, 1264 m, 1254 w, 1245 w, 1228 w, 1209 w, 1196 w, 1180 m, 1161 w, 1106 m, 1097 m, 1073 w, 1059 w, 1036 m, 1009 w, 935 w, 925 w, 914 m, 897 w, 847 w, 831 s, 782 s, 763 s, 749 w, 702 s, 610 w, 600 w, 544 w, 534 w. ^{1}H NMR (400 MHz, C_6D_6, 298 K), δ: 7.36—7.12 (m, 10 H, CH_{arom}); 6.94 (dd, 1 H, CH_{arom}, J = 8.0 Hz, J = 7.8 Hz); 6.90—6.84 (m, 2 H, CH_{arom}); 6.46 (d, 1 H, CH_{arom}, J = 7.3 Hz); 3.28 (sept, 2 H, —C$\underline{H}$(CH$_3$)$_2$, J = 6.9 Hz); 3.19 (s, 3 H, =C(C$\underline{H}_3$)(Ph)); 1.28 (d, 6 H, —CH(C$\underline{H}_3$)$_2$, J = 6.8 Hz); 1.03 (d, 6 H, —CH(C$\underline{H}_3$)$_2$, J = 7.0 Hz).

{*N*-(2,6-Diisopropylphenyl)-2-(1-phenylvinyl)acenaphthylene-1(2*H*)-imine-2-[(*E*)-2-phenyleth-1-enyl]gallium} bis-phenylacetylide, [C$_{12}$H$_6$(NC$_6$H$_3$Pr$^i_2$)(PhC=CH$_2$)(PhC=CH)]Ga-(C≡CPh)$_2$ (6). Phenylacetylene (**2b**) (0.51 g, 5 mmol) was added to complex **1** (0.57 g, 0.5 mmol) obtained *in situ* from dpp-bian (0.5 g, 1 mmol) in toluene (30 mL). The solution immediately changed the color from dark blue to reddish brown. The reaction mixture was heated at 120 °C for 15 h. Then, toluene was evaporated *in vacuo*, whereas anhydrous residue was dissolved in diethyl ether (15 mL). After 2 h, a fine crystalline yellow precipitate was formed and filtered off. The solution left after the separation of the fine crystalline yellow precipitate of acenaphthenenimine **5** was concentrated to 5 mL, complex **6** (0.10 g, 13%) was isolated by crystallization from this solution as light yellow needle-like crystals, m.p. 176—178 °C (decomp.). Found (%): C, 84.21; H, 5.97. $C_{56}H_{46}GaN$ (802.66 g mol^{-1}). Calculated (%): C, 83.72; H, 5.73. IR (Nujol), ν/cm^{-1}: 2139 m, 1950 w, 1811 w, 1673 w, 1630 s, 1620 m, 1953 s, 1537 w, 1486 m, 1344 m, 1324 m, 1264 m, 1246 w, 1211 s, 1188 m, 1157 w, 1102 m, 1069 m, 1057 m, 1028 s, 998 w, 954 m, 927 m, 913 s, 898 m, 878 w, 858 w, 836 s, 822 w, 807 m, 786 s, 774 w, 760 s, 751 s, 716 m, 702 m, 691 s, 632 w, 598 m, 563 s, 549 w, 535 s, 523 w, 507 w, 496 w, 474 w. ^{1}H NMR (200 MHz, toluene-d_8, 293 K), δ: 7.95 (d, 2 H, CH_{arom}, J = 7.1 Hz); 7.54 (dd, 2 H, CH_{arom}, J = 7.8 Hz); 7.40—7.21 (m, 9 H, CH_{arom}); 7.20—7.09 (m, 3 H, CH_{arom}); 7.08—6.96 (m, 5 H, CH_{arom}); 6.95—6.88 (m, 3 H, CH_{arom}); 6.81—6.73 (m, 3 H, CH_{arom}); 6.63 (t, 1 H, CH_{arom}, J = 7.8 Hz); 6.30 (d, 2 H, CH_{arom}, J = 7.3 Hz); 6.25 (s, 1 H, <u>H</u>C=C(Ph)); 5.42 (s, 1 H, <u>H</u>C=C(Ph)); 3.99 (sept, 1 H, C$\underline{H}$(CH$_3$)$_2$, J = 6.7 Hz); 2.76 (sept, 1 H, C$\underline{H}$(CH$_3$)$_2$, J = 6.7 Hz); 1.73 (d, 3 H, CH(C$\underline{H}_3$)$_2$, J = 6.7 Hz); 1.27 (d, 3 H, CH(C$\underline{H}_3$)$_2$, J = 6.7 Hz); 1.11 (d, 3 H, CH(C$\underline{H}_3$)$_2$, J = 7.0 Hz); 0.13 (d, 3 H, CH(C$\underline{H}_3$)$_2$, J = 6.8 Hz).

Gallium [*N*^{1},*N*^{2}-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamide] bis-phenylamide, (dpp-bian)Ga[N(H)Ph]$_2$ (7). Phenylacetylene (**2b**) (0.1 g, 1 mmol) and aniline (0.09 g, 1 mmol) were added to complex **1** (0.57 g, 0.5 mmol) obtained *in situ* from dpp-bian (0.5 g, 1 mmol) in benzene (30 mL). The reaction mixture changed the color from dark blue to reddish brown. Then, the mixture was heated for 15 min at 90 °C and concentrated by evaporation of the solvent *in vacuo*. After a while, dark brown prismatic crystals of compound **7** (0.36 g, 40%) were isolated from the solution, m.p. 145 °C. Found (%): C, 79.64; H, 6.87. $C_{48}H_{52}GaN_4 \cdot 2C_6H_6$ (910.87 g mol^{-1}). Calculated (%): C, 79.05; H, 7.06. IR (Nujol), ν/cm^{-1}: 3396 w, 3376 m, 1941 w, 1667 w, 1596 s, 1580 w, 1495 s, 1441 m, 1426 w, 1364 m, 1321 m, 1292 s, 1255 m, 1215 w, 1179 m, 1149 m, 1110 m, 1077 m, 1057 m, 992 m, 951 w, 937 m, 892 m, 871 w, 853 s, 820 s, 808 s, 787 w,

Table 4. Crystallographic data, parameters of X-ray diffraction experiments and refinement for compounds **5**—**7** and **9**

Parameter	**5**	**6**	**7**	**9**
Molecular formula	$C_{32}H_{31}N$	$C_{56}H_{46}GaN$	$C_{48}H_{52}GaN_4 \cdot 2C_6H_6$	$C_{28}H_{23}GaO$
Molecular weight	429.58	802.66	910.87	445.18
T/K	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.8583(10)	11.3136(9)	12.9918(5)	10.5907(5)
b/Å	8.5487(6)	33.946(3)	12.8327(4)	46.856(2)
c/Å	17.7364(12)	11.8909(10)	30.1412(9)	14.2954(6)
α/deg	90	90	90	90
β/deg	93.0940(10)	109.658(2)	95.131(3)	102.6070(10)
γ/deg	90	90	90	90
V/Å^3	2401.0(3)	4300.5(6)	5005.0(3)	6922.9(5)
Z	4	4	4	12
d/g cm^{-3}	1.188	1.240	1.209	1.281
μ/mm^{-1}	0.068	0.678	0.592	1.208
F(000)	920	1680	1932	2760
Crystal size/mm	0.18×0.16×0.12	0.38×0.10×0.03	0.15×0.12×0.10	0.23×0.21×0.15
θ Range of data collection/deg	2.30—26.00	2.00—25.00	3.12—26.00	1.70—26.00
Range of indices h, k, l	$-19 \le h \le 19$	$-13 \le h \le 13$	$-16 \le h \le 16$	$-13 \le h \le 13$
	$-10 \le k \le 10$	$-40 \le k \le 40$	$-15 \le k \le 15$	$-57 \le k \le 57$
	$-21 \le l \le 21$	$-14 \le l \le 14$	$-37 \le l \le 37$	$-17 \le l \le 17$
Number of observed reflections	20074	33631	69321	59557
Number of independent reflections (R_{int})	4723 (0.0241)	7569 (0.1681)	9815 (0.0626)	13608 (0.0700)
Q-factor (F^2)	1.055	0.931	1.039	1.011
R_1/wR_2 ($I > 2\sigma(I)$)	0.0407/0.1098	0.0664/0.1140	0.0449/0.1053	0.0519/0.1006
R_1/wR_2 (on all parameters)	0.0511/0.1155	0.1475/0.1332	0.0623/0.1116	0.0936/0.1108
Residual electron density /e Å^3 (ρ_{max}/ρ_{min})	0.379/−0.263	0.608/−0.359	0.725/−0.972	0.597/−0.526

766 s, 751 s, 723 w, 610 m, 594 w, 559 m, 547 m, 502 m, 492 m, 458 m. EPR (298 K), toluene): g = 2.00265, $a_i(^{69}Ga)$ = 1.503, $a_i(^{71}Ga)$ = 1.910, $a_i(2\,^{14}N)$ = 0.126, $a_i(2\,^{14}N)$ = 0.495, $a_i(2\,^{1}H)$ = = 0.098, $a_i(2\,^{1}H)$ = 0.085 mT.

Gallium trisphenylacetylide tetrahydrofuranate, (PhC≡C)$_3$Ga · THF (9). Sodium (0.29 g, 12.6 mmol), phenylacetylene (**2b**) (1.22 g, 12.0 mmol), and THF (35 mL) were placed into a glass tube equipped with a magnetic stirrer under nitrogen of high purity grade. Then gallium trichloride (0.70 g, 3.97 mmol) was added to the reaction mixture. The mixture was evacuated, the tube was sealed and left to be stirred at room temperature. After 20 h, a precipitate of sodium chloride formed in the course of the reaction was separated by centrifugation, tetrahydrofuran was evaporated *in vacuo,* and toluene (40 mL) was added by condensation. The solution was concentrated, subsequent crystallization gave compound **9** (0.92 g, 52%) as colorless rhombohedral crystals, m.p. 115—120 °C (decomp.). Found (%): C, 76.10; H, 5.84. $C_{28}H_{23}GaO$ (445.18 g mol^{-1}). Calculated (%): C, 75.48; H, 5.17. IR (Nujol), ν/cm^{-1}: 2143 s, 1596 w, 1571 w, 1486 w, 1301 w, 1244 w, 1211 m, 1176 w, 1155 w, 1069 m, 1047 w, 1027 w, 1009 m, 915 m, 856 m, 809 w, 798 s, 795 s, 691 s, 573 m, 535 s. ^{1}H NMR (200 MHz, C_6D_6, 298 K), δ: 7.63—7.47 (m, 6 H, CH_{arom}); 7.06—6.88 (m, 9 H, CH_{arom}); 3.98—3.82 (m, 4 H, $O(C\underline{H}_2CH_2)_2$); 1.22—1.06 (m, 4 H, $O(CH_2C\underline{H}_2)_2$). ^{13}C NMR (50 MHz, C_6D_6, 298 K), δ: 132.1, 128.1, 128.0, 124.6 (C_{arom}), 106.6 (Ph—$\underline{C}$≡), 98.6 (br. Ga—$\underline{C}$≡); 70.6 ($\underline{C}H_2$); 24.7 ($\underline{C}H_2$).

X-ray diffraction study of compounds 5—7 and 9. X-ray diffraction studies were carried out on Bruker Smart Apex (**5**, **6**, **9**) and Agilent Xcalibur diffractometers (**7**) (ω-scan technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). Crystallographic data and parameters of X-ray diffraction experiments are given in Table 4.

All the structures were solved by direct method and refined by the full-matrix least-squares method on F^2_{hkl} in anisotropic approximation for nonhydrogen atoms and in isotropic approximation for atoms H(13A), H(22A), H(22B) in compound **6** and H(3A), H(4A) in compound **7**. Other hydrogen atoms in **5**—**7** and **9** were placed in geometrically calculated positions and refined in a riding model. The calculations were carried out using the SHELXTL software package.[51] Absorption was included using the SADABS program.[52] The structures were deposited with the Cambridge Crystallographic Data Center (CCDC 1431986 (**5**), 1431987 (**6**), 1431988 (**7**), 1431989 (**9**)) and are available at http://ccdc.cam.ac.uk/getstructures.

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

References

1. L. Huang, M. Arndt, K. Gooßen, H. Heydt, L. J. Gooßen, *Chem. Rev.*, 2015, **115**, 2596.

2. A. Luihl, H. P. Nayek, S. Blechert, P. W. Roesky, *Chem. Commun.*, 2011, **47**, 8280.
3. A. Luihl, L. Hartenstein, S. Blechert, P. W. Roesky, *Organometallics*, 2012, **31**, 7109.
4. Y. Zhao, M. Lin, Z. Chen, H. Pei, Y. Li, Y. Chen, X. Wang, L. Li, Y. Cao, Y. Zhanga, W. Lib, *RSC Advances*, 2012, **2**, 144—150.
5. I. Dubovyk, I. D. G. Watson, A. K. Yudin, *J. Org. Chem.*, 2013, **78**, 1559.
6. P. D. Schweizer, H. Wadepohl, L. H. Gade, *Organometallics*, 2013, **32**, 3697.
7. M. V. Anokhin, A. V. Murashkina, A. D. Averin, I. P. Beletskaya, *Mendeleev Commun.*, 2014, **24**, 332.
8. T. O. Petersen, E. Tausch, J. Schaefer, H. Scherer, P. W. Roesky, I. Krossing, *Chem. Eur. J.*, 2015, **21**, 13696.
9. M. J. González, L. A. Lypez, R. Vicente, *Tetrahedron Lett.*, 2015, **56**, 1600.
10. E. Kumaran, W. K. Leong, *Organometallics*, 2015, **34**, 1779.
11. H. Tafazolian, D. C. Samblanet, J. A. R. Schmidt, *Organometallics*, 2015, **34**, 1809.
12. J. Bahri, R. Blieck, B. Jamoussi, M. Taillefer, F. Monnier, *Chem. Commun.*, 2015, **51**, 11210.
13. J. C.-H. Yim, J. A. Bexrud, R. O. Ayinla, D. C. Leitch, L. L. Schafer, *J. Org. Chem.*, 2014, **79**, 2015.
14. J. C.-H. Yim, L. L. Schafer, *Eur. J. Org. Chem.*, 2014, 6825.
15. Q. Sun, Y. Wang, D. Yuan, Y. Yao, Q. Shen, *Chem. Commun.*, 2015, **51**, 7633.
16. Q. Sun, Y. Wang, D. Yuan, Y. Yao, Q. Shen, *Dalton Trans.*, 2015, **44**, 20532. DOI: 10.1039/C5DT02643A.
17. A. L. Reznichenko, H. N. Nguyen, K. C. Hultzsch, *Angew. Chem., Int. Ed.*, 2010, **49**, 8984.
18. Y. Cao, Z. Du, W. Li, J. Li, Y. Zhang, F. Xu, Q. Shen, *Inorg. Chem.*, 2011, **50**, 3729.
19. L. Xu, Z. Wang, W.-X. Zhang, Z. Xi, *Inorg. Chem.*, 2012, **51**, 11941.
20. I. V. Basalov, S. C. Roşca, D. M. Lyubov, A. N. Selikhov, G. K. Fukin, Y. Sarazin, J.-F. Carpentier, A. A. Trifonov, *Inorg. Chem.*, 2014, **53**, 1654.
21. P.-H. Wei, L. Xu, L.-C. Song, W.-X. Zhang, Z. Xi, *Organometallics*, 2014, **33**, 2784.
22. F. M. Sroor, C. G. Hrib, L. Hilfert, P. G. Jones, F. T. Edelmann, *J. Organomet. Chem.*, 2015, **785**, 1.
23. E. M. Broderick, N. P. Gutzwiller, P. L. Diaconescu, *Organometallics*, 2010, **29**, 3242.
24. I. S. R. Karmel, M. Tamm, M. S. Eisen, *Angew. Chem., Int. Ed.*, 2015, **54**, 12422.
25. C. Bour, V. Gandon, *Coord. Chem. Rev.*, 2014, **279**, 43.
26. A. G. M. Barrett, C. Brinkmann, M. R. Crimmin, M. S. Hill, P. Hunt, P. A. Procopiou, *J. Am. Chem. Soc.*, 2009, **131**, 12906.
27. J. Koller, R. G. Bergman, *Organometallics*, 2010, **29**, 5946.
28. C. Brinkmann, A. G. M. Barrett, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.*, 2012, **134**, 2193.
29. B. Liu, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Angew. Chem., Int. Ed.*, 2012, **51**, 4943.
30. X. Zhang, T. J. Emge, K. C. Hultzsch, *Angew. Chem., Int. Ed.*, 2012, **51**, 394.
31. B. Liu, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Chem. Eur. J.*, 2013, **19**, 13445.
32. A. Baishya, M. Kr. Barman, T. Peddarao, S. Nembenna, *J. Organomet. Chem.*, 2014, **769**, 112.
33. N. Sakai, N. Takahashi, Y. Ogiwara, *Eur. J. Org. Chem.*, 2014, 5078.
34. O. V. Kazarina, M. V. Moskalev, I. L. Fedushkin, *Russ. Chem. Bull.* (*Int. Ed.*), 2015, **64**, 32 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2015, 32].
35. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, H. Schumann, *Chem. Eur. J.*, 2003, **9**, 5778.
36. I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, G. K. Fukin, *Chem. Eur. J.*, 2005, **11**, 5749.
37. I. L. Fedushkin, A. A. Skatova, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.*, 2005, 1601.
38. I. L. Fedushkin, A. N. Lukoyanov, G. K. Fukin, M. Hummert, H. Schumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2006, **55**, 1177 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2006, 1134].
39. I. L. Fedushkin, A. S. Nikipelov, K. A. Lyssenko, *J. Am. Chem. Soc.*, 2010, **132**, 7874.
40. I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.*, 2012, **18**, 255.
41. L. Fedushkin, M. V. Moskalev, A. N. Lukoyanov, A. N. Tishkina, E. V. Baranov, G. A. Abakumov, *Chem. Eur. J.*, 2012, **18**, 11264.
42. I. L. Fedushkin, M. V. Moskalev, E. V. Baranov, G. A. Abakumov, *J. Organomet. Chem.*, 2013, **747**, 235.
43. 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.
44. I. L. Fedushkin, O. V. Kazarina, A. N. Lukoyanov, A. A. Skatova, N. L. Bazyakina, A. V. Cherkasov, E. Palamidis, *Organometallics*, 2015, **34**, 1498.
45. I. L. Fedushkin, M. V. Moskalev, A. A. Skatova, G. K. Fukin, G. A. Abakumov, *Russ. Chem. Bull.* (*Int. Ed.*), 2013, **62**, 731 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2013, 731].
46. M. Schiefer, N. D. Reddy, H.-J. Ahn, A. Stasch, H. W. Roesky, A. C. Schlicker, H.-G. Schmidt, M. Noltemeyer, D. Vidovic, *Inorg. Chem.*, 2003, **42**, 4970.
47. A. A. Skatova, I. L. Fedushkin, O. V. Maslova, M. Hummert, H. Schumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 2284 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1702].
48. J. Scholz, S. Kahlert, H. Görls, *Organometallics*, 2004, **23**, 1594.
49. I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.* (*Int. Ed.*), 2004, **53**, 2744 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2634].
50. D. Solis-Ibarra, A. P. Gymora-Figueroa, N. Zavala-Segovia, V. Jancik, *Eur. J. Inorg. Chem.*, 2009, 4564.
51. G. M. Sheldrick, *SHELXTL v. 6.12*, *Structure Determination Software Suite*, *Bruker AXS*, Madison, Wisconsin, USA, 2000.
52. G. M. Sheldrick, *SADABS v. 2.01*, *Bruker/Siemens Area Detector Absorption Correction Program*, *Bruker AXS*, Madison, Wisconsin, USA, 1998.

Received October 20, 2015