Complexes of gallium(III), antimony(III), titanium(IV), and cobalt(II) with acenaphthenequinonimine*

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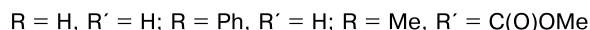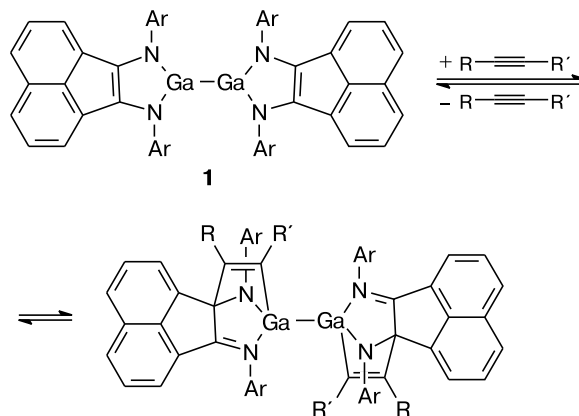1 ul. Ul´yanova, 603950 Nizhny Novgorod, Russian Federation*

Reactions of (2,6-diisopropylphenylimino)acenaphthenone (dpp-mian) with gallium(III), antimony(III), titanium(IV), and cobalt(II) chlorides in toluene lead to the formation of compounds of the formulas [(dpp-mian)$_2$GaCl$_2$][GaCl$_4$], (dpp-mian)SbCl$_3$, (dpp-mian)TiCl$_4$, and [(dpp-mian)CoCl$_2$]$_2$[CoCl$_2$(EtOH)$_4$], respectively. The complexes were characterized by IR and NMR spectra, their structure was established by X-ray crystallography.

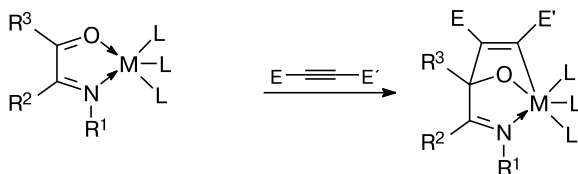**Key words:** gallium; antimony; titanium; cobalt; N,O-ligands.

At the end of the 20th century, H.-W. Frühauf and coworkers[1] have discovered a cycloaddition reaction of unsaturated organic compounds to transition metal complexes with neutral 1,4-diaza- and 1,4-dihetero-1,3-dienes. For example, iron and ruthenium compounds with ketoimine ligands react with activated alkynes with the formation of cycloadducts (Scheme 1). These reactions are distinguished by the fact that the substrate adds not only to the metal atom, but also to the ligand with the formation of a carbon—carbon bond. Similar cycloaddition products are formed in the reactions of aromatic ketones with zirconium[2] and samarium[3] 1,4-diaza-1,3-diene (dad) complexes. The first report about successful cycloaddition involving a nontransition metal compound appeared in 2010. It was found that digallane (dpp-bian)Ga—Ga(dpp-bian) (**1**) (dpp-bian is the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) reacted with different alkynes, including simple acetylene, with the formation of stable cycloadducts[4,5] (Scheme 2).

Scheme 2

R = H, R´ = H; R = Ph, R´ = H; R = Me, R´ = C(O)OMe

A unique property of this metal—organic system is that the addition of alkynes is completely reversible. This process in a certain sense resembles the π-coordination of unsaturated organic molecules by transition metal compounds. Dialanes LAl—AlL (L = dpp-bian,[6] dad[7]) are even more active toward alkynes. For example, (dpp-bian)Al—Al(dpp-bian) adds methylphenylacetylene, while digallane **1** is inert to this compound. Mononuclear derivatives (dpp-bian)AlEt(Et$_2$O)[8] and (dpp-bian)Ga(S$_2$CNMe$_2$)[9] also react with alkynes with the for-

Scheme 1

M = Fe, Ru; E = H, CO$_2$Me; E´ = CO$_2$Me;

L = CO, PR$_3$, dppe

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mation of cycloadducts. In the melt, even diphenylacetylene forms an adduct with the complex (dpp-bian)AlEt(Et$_2$O),[8] whereas gallium dithiocarbamate derivative (dpp-bian)Ga(S$_2$CNMe$_2$) reversibly adds conjugated methyl vinyl ketone.[9] Lastly, there is known a cycloaddition of CF$_3$—C≡C—CF$_3$ to antimony amidoalkoxide complex.[10]

We have shown that the replacement of nontransition metal at the dpp-bian dianion changes the reactivity character of the whole complex. Thus, in contrast to digallane **1**, the magnesium complex (dpp-bian)Mg(thf)$_3$ (**2**) in the reaction with phenylacetylene behaves as a frustrated Lewis pair.[11—13] The reaction leads to the alkynyl magnesium derivative with the amido-amine chelating ligand (Scheme 3).[14]

Scheme 3

2
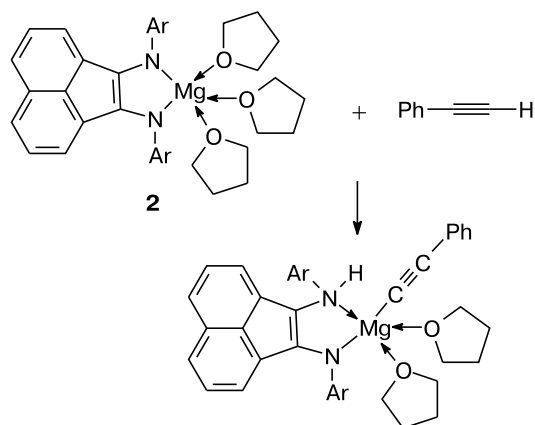
The ability of complex **1** "to coordinate" phenylacetylene makes it possible to carry out the hydroamination and hydroarylation of the latter with anilines and 1-naphthol in the presence of a catalytic amount of compound **1** (see Refs 5 and 9). Apart from that, complex **1** catalyzes the addition of anilines to carbodiimides.[15] Magnesium compound **2**, in turn, is an efficient catalyst for the ring-opening polymerization of lactides,[16] as well as hydroamination/cyclization of aminoolefins.* However, a wide application of derivatives **1** and **2** as catalysts is limited by their instability in air. In order to prepare more stable to oxygen and moisture metal complexes with redox-active ligands, we carried out the reaction of (2,6-diisopropylphenylimino)acenaphthenone[17,18] (**3**, dpp-mian) with some metals and metal-containing reagents. It should be noted that to the beginning of our research, we have been known only a few examples of transition metal compounds with neutral dpp-mian[18,19] and related Ar-mian[20—22] ligands. Until recently, it was

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not known a single nontransition metal derivative or metal complex with dpp-mian in the form of anion. Most recently, we synthesized magnesium amido-alkoxide [(dpp-mian)Mg(thf)$_2$]$_2$ (**4**) by the direct reduction of dpp-mian with magnesium,[23] which is the first acenaphthenequinonimine derivative of nontransition metal, as well as the first metal-containing compound with the reduced dpp-mian ligand. A bright illustration of the important role of redox-active ligands in the imparting to their complexes with nontransition metal of various chemical properties is the reaction of compound **4** with phenylacetylene. In contrast to the relative compound **2**, derivative **4** reacts with phenylacetylene with the formation of cycloadduct (similarly to the reactions of digallane **1**). In this case, the reaction of the obtained cycloadduct with the second equivalent of PhC≡CH results in the formation of phenylethynyl derivative [(dpp-mian)(PhC=CH$_2$)Mg(C≡CPh)(thf)]$_2$ (**5**) (Scheme 4).

Scheme 4

5
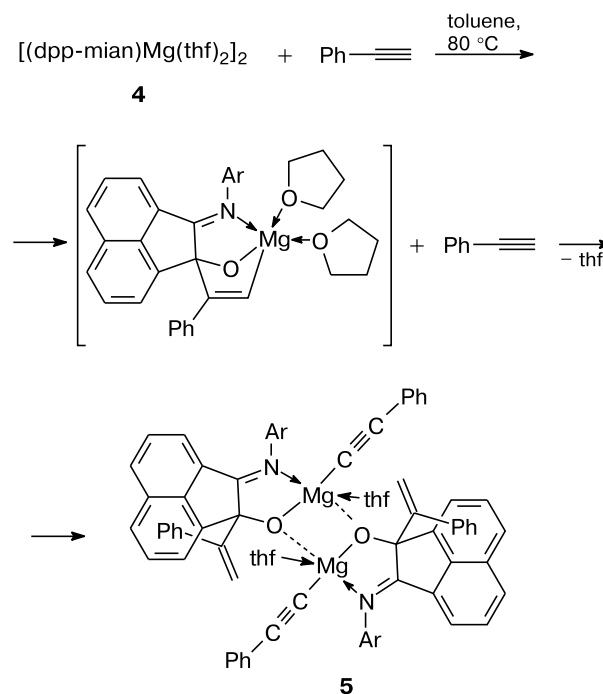
The purpose of the present work is the synthesis of first compounds of nontransition metals with neutral monoiminoacenaphthenone ligand, the studies of the behavior of new compounds in solutions by NMR spectroscopy, and establishing their molecular structure in the crystalline state by X-ray crystallography.

Results and Discussion

Synthesis of [(dpp-mian)$_2$GaCl$_2$][GaCl$_4$] (6), (dpp-mian)SbCl$_3$ (7), (dpp-mian)TiCl$_4$ (8), and [(dpp-

mian)CoCl$_2$]$_2$[CoCl$_2$(EtOH)$_4$] (9). The reactions of gallium(III), antimony(III), titanium(IV), and cobalt(II) chlorides with (2,6-diisopropylphenylimino)acenaphthenone (3) led to the formation of coordination compounds [(dpp-mian)$_2$GaCl$_2$][GaCl$_4$] (6), (dpp-mian)SbCl$_3$ (7), (dpp-mian)TiCl$_4$ (8), and [(dpp-mian)CoCl$_2$]$_2$[CoCl$_2$(EtOH)$_4$] (9), respectively. The synthetic procedures are described in the Experimental section. Complexes 6—9 were isolated in the crystalline state in good yields. In all four derivatives, the quinonimine is a neutral chelating ligand. In compounds 6—8, the ratio metal : ligand is 1 : 1, in compound 9 it is 3 : 2. The complex [(dpp-mian)CoCl$_2$]$_2$,[18] which is related to compound 9, was synthesized by the reaction of the equivalent amounts of compound 3 and CoCl$_2$ in chloroform, whereas compound 9 was obtained using an excess of cobalt chloride in ethanol. A unit cell of compound 6 contains separate ions, which, probably, emerge as a result of disproportionation of the initially formed complex (dpp-mian)GaCl$_3$.

3, dpp-mian

6

7   8

9

Ar = 2,6-Pr$^i_2$C$_6$H$_3$; L = EtOH
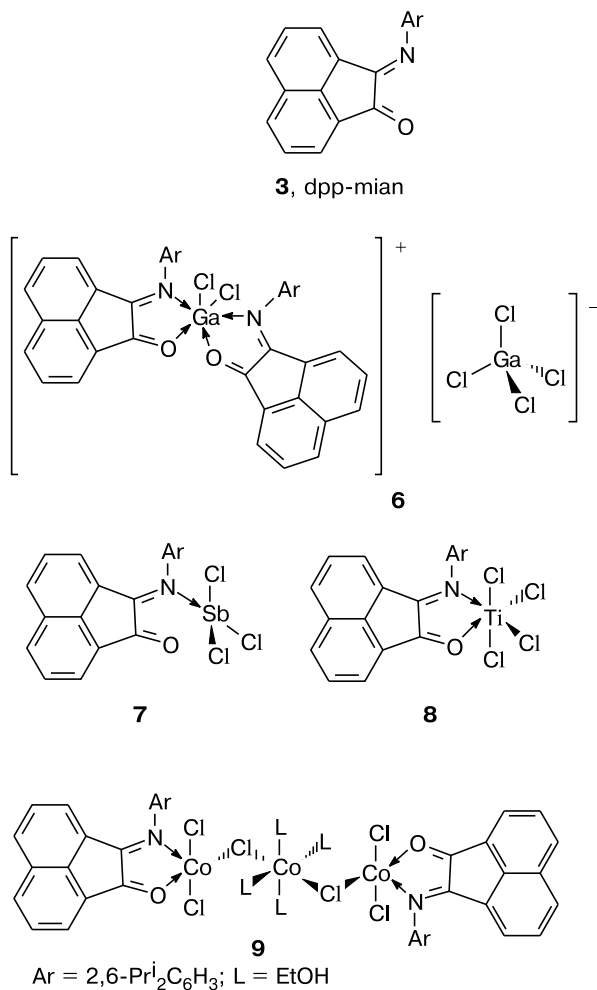
The diamagnetic derivatives 6—8 were characterized by ^{1}H NMR spectra. The paramagnetic compound 9 did not give neither ESR spectrum, nor NMR spectrum.

An interesting property of this derivative is a reversible change in the color of its solution in chloroform from green to red upon cooling to −50 °C, that can be caused by both the intramolecular metal—ligand electron transfer (redox-isomerism) and the change in the spin state of the metal atoms (spin-crossover). Apparently, the reason of thermochromism of compound 9 can be establish by magnetochemical measurements. All the newly obtained compounds were characterized by IR spectra. The structures of complexes 6—9 were determined by X-ray diffraction studies.

The IR spectrum of compound 6 has no narrow absorption band and, therefore, is uninformative. This can be explained by the ionic character of the crystal lattice of derivative 6. The IR spectra of compounds 7—9 exhibit a large set of absorption bands. The bands of the stretching vibrations of the C=O and C=N bonds in the spectrum of free quinonimine 3 were found at 1756 and 1626 cm^{-1}, respectively. The spectrum of compound 7 in general has similar pattern, but the bands are shifted toward the long wavelength region by about 25 cm^{-1}. The IR spectrum of compound 8 suggests that the contribution of titanium atom into the disturbance of the 1,4-dihetero-1,3-diene structure of quinonimine ligand is larger as compared to that of the antimony atom. Thus, the positions and the shapes of the absorption bands of the stretching vibrations of the C=O and C=N bonds in the spectrum of derivative 8 noticeably differ from positions and shapes of the corresponding bands in the spectra of compounds 3 and 7. We assume that this is due to the presence of the π-component in the metal—ligand interaction in compound 8 and with the absence of this component in compound 7. Most of absorption bands in the IR spectrum of compound 9, including those attributed to the stretching vibrations of the C=O and C=N bonds, retain the same positions as in the spectrum of the starting compound 3.

The ^{1}H NMR spectrum of compound 7 is shown in Fig. 1. The ^{1}H NMR (CDCl$_3$) spectra of compounds 3 and 7, in contrast to their IR spectra, are similar: the isopropyl substituents were found as a septet (δ 2.84 (3), δ 2.83 (7)) and two doublets (δ 1.17 and 0.90 (3), δ 1.17 and 0.87 (7)).

The presence of two doublets is explained by the nonequivalence of methyl groups in each isopropyl substituent. This, in turn, is related to the absence of free rotation around both the N—C(ipso-Ph) and the C(Pr^i)—C(ipso-Ph) bonds. The signals for the aromatic protons in compounds 3 and 7 have close chemical shifts and lie in the range from 8.3 to 6.5 ppm. It should be noted that the ^{1}H NMR spectrum of compound 7 does not completely agree with its structure found by X-ray diffraction (see below). This fact will be explained in the discussion of the molecular structure of derivative 7. The suggestion on the difference in the character of the metal—ligand binding in antimony and titanium compounds made based on the IR spectra is confirmed by the ^{1}H NMR spectroscopy data.
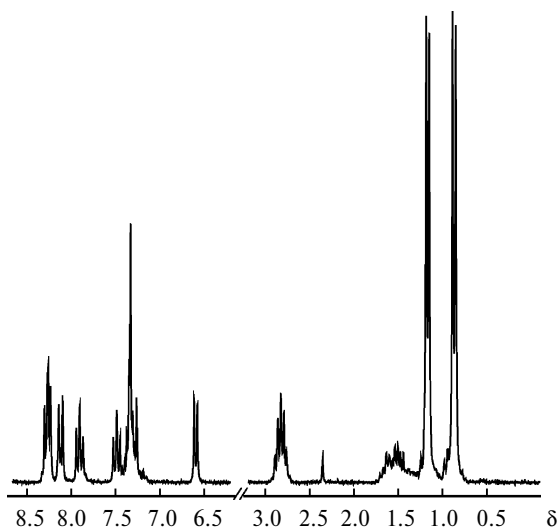
Fig. 1. ^{1}H NMR spectrum of compound **7** (CDCl$_3$, 200 MHz, 20 °C).

Despite the spectra of compounds **7** and **8** have the same set of signals, their chemical shift noticeably differ. Thus, the signals for the isopropyl groups in the spectrum of

compound **8** were found as a septet at δ 3.50 and two doublets at δ 1.34 and 0.85.

Molecular structures of compounds 6—9. The structures of molecule **6—9** were established by X-ray diffraction study. The crystallographic data and parameters of experiments are given in Table 1.

The gallium atom in compound **6** has a coordination number of six. The geometry of the metal atom environment can be described as a distorted octahedron or a trigonal antiprism. The gallium atom virtually does not comes out of the planes of 1,4-dihetero-1,3-diene fragments, the deviation is 0.285 Å, while the pairs of Ga—O, Ga—Cl, and Ga—N distances are equal (Fig. 2). Despite the steric hindrance posed by the 2,6-Pr$^i_2$C$_6$H$_3$ substituent, the gallium—nitrogen distances are the shortest in compound **6** (both of 2.1352(8) Å). However, these distances are considerably longer than the Ga—N distances in compound **1** (1.8624(18) and 1.8583(18) Å) containing a tricoordinated gallium atom bonded to the dpp-bian dianion.[24] At the same time, the Ga—N distances in compound **6** are comparable with those in the derivative (dpp-bian)GaF(Cat)[25] (2.087(7) and 2.120(1) Å) containing a pentacoordinated gallium atom, which is bonded to the neutral dpp-bian

Table 1. Crystallographic data and parameters of X-ray diffraction experiment for compounds **6—9**

Parameter	6	7	8	9
Molecular formula	C$_{52}$H$_{54}$Cl$_6$N$_2$O$_3$Ga$_2$	C$_{24}$H$_{23}$Cl$_3$NOSb	C$_{31}$H$_{31}$Cl$_4$NOTi	C$_{58}$H$_{72}$Cl$_{12}$Co$_3$N$_2$O$_6$
Molecular weight	1107.11	569.53	623.27	1495.36
T/K	100	100	100	100
Crystal system		Monoclinic		Triclinic
Space group	$C2/c$	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$
a/Å	18.7820(2)	8.78470(10)	9.936(9)	10.0103(4)
b/Å	18.3274(2)	17.3722(2)	28.95(3)	12.1883(4)
c/Å	16.7199(2)	15.4476(2)	11.342(10)	15.1863(6)
α/deg	90	90	90	102.237(3)
β/deg	107.1583(14)	93.5990(10)	114.83(3)	94.548(3)
γ/deg	90	90	90	109.362(3)
V/Å^3	5499.27(12)	2352.80(5)	2960(5)	1685.72(12)
Z	4	4	4	1
ρ/g cm^{-3}	1.337	1.608	1.398	1.473
μ/mm^{-1}	1.312	1.529	0.676	1.252
$F(000)$	2272	1136	1288	767
Crystal size/mm	0.40×0.40×0.40	0.90×0.40×0.30	0.30×0.20×0.15	0.50×0.20×0.05
θ range of data collection (deg)	3.28—30.00	2.984—29.999	2.100—25.999	3.247—29.997
Range indices	$-26 \leq h \leq 26$	$-12 \leq h \leq 12$	$-12 \leq h \leq 12$	$-14 \leq h \leq 14$
	$-25 \leq k \leq 25$	$-24 \leq k \leq 24$	$-35 \leq k \leq 35$	$-17 \leq k \leq 17$
	$-23 \leq l \leq 23$	$-21 \leq l \leq 21$	$-12 \leq l \leq 13$	$-21 \leq l \leq 21$
Number of observed reflections	53484	46625	16930	33148
Number of independent reflections	7932	6846	5780	9811
R_{int}	0.0322	0.0228	0.0143	0.0913
Q factor (F^2)	1.062	1.046	1.008	0.940
R_1/wR_2 ($I > 2\sigma(I)$)	0.0346/0.0882	0.0182/0.0443	0.0364/0.0966	0.0513/0.0797
R_1/wR_2 (on all the parameters)	0.0427/0.0917	0.0201/0.0451	0.0391/0.0989	0.1054/0.0935
Residual electron density, ρ_{max}/ρ_{min}/e Å^{-3}	0.905/−0.458	0.429/−0.431	0.857/−0.399	0.653/−0.466

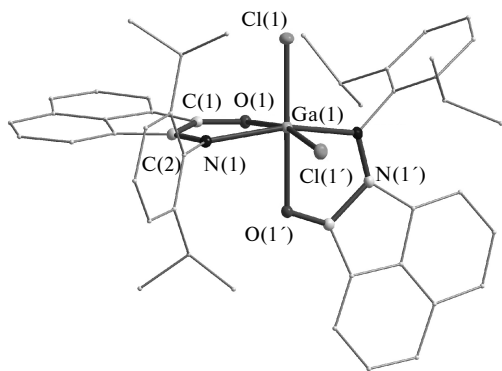**Fig. 2.** Molecular structure of the [(dpp-mian)$_2$GaCl$_2$]$^+$ cation in compound **6**. Thermal ellipsoids of key atoms are given with 30% probability. Hydrogen atoms are omitted. Some bond distances (Å) and bond angles (deg): Ga(1)—N(1) 2.1352(8), Ga(1)—O(1) 2.1717(7), Ga(1)—Cl(1) 2.2070(3), O(1)—C(1) 1.2236(11), N(1)—C(2) 1.2787(13), C(1)—C(2) 1.5272(14); N(1)—Ga(1)—N(1′) 157.12(5), N(1)—Ga(1)—O(1) 77.89(3), N(1)—Ga(1)—O(1′) 84.73(3), O(1)—Ga(1)—O(1′) 81.02(4), N(1)—Ga(1)—Cl(1) 99.15(2), N(1)—Ga(1)—Cl(1′) 94.71(2), O(1)—Ga(1)—Cl(1′) 166.58, Cl(1)—Ga(1)—Cl(1′) 105.152(15).

and 3,6-di-*tert*-butylbenzocatecholate ligand (Cat). The Ga—O distances in compound **6** (both of 2.1717(7) Å) are considerably longer than the Ga—O(Cat) distances (1.859(0) and 1.854(8) Å) in the complex (dpp-bian)GaF(Cat).[25]

The ligand environment geometry of the central atom in compound **7** (Fig. 3) can be described by two different models. In the first case, this is a pentacoordinated antimony(III) derivative, having the geometry of a tetragonal pyramid, with atom Cl(1) occupying the vertex. In the second model of compound **7**, there is no interaction between the antimony atom and the oxygen atom, whereas the coordination environment of the central atom is a trigonal bipyramid, the equatorial positions of which are occupied by atoms Cl(2) and Cl(3) and a free electron pair of the metal atom. Note that the Cl(1)—Sb(1)—Cl(2), Cl(1)—Sb(1)—Cl(3), and Cl(2)—Sb(1)—Cl(3) angles, which are close to 90°, serve as an argument in favor of the first model. In this case, the rotation within the molecule, which could have led to the equivalence of two isopropyl groups in the phenyl substituent (that, as it was mentioned above, follows from the ^{1}H NMR spectrum of compound **7**) is impossible without cleavage of the central atom bonds. Thus, we believe that compound **7** is a trigonal bipyramidal complex, which in solution is characterized by a rapid rotation of the equatorial chlorine atoms and the free pair of electrons around the N(1)—Sb(1)—Cl(2) axis. At present, there are known about a dozen of structurally characterized complexes of antimony trichloride with diimines, including the derivative (dpp-bian)SbCl$_3$ obtained in 2006 independently in our group[26] and by Cowley and coworkers.[27] All the known complexes of antimony

trichloride with diimines can be placed in two groups: the compounds, in which two chlorine atoms virtually lie in the plane formed by two nitrogen atoms and the antimony atom ((dpp-bian)SbCl$_3$,[26,27] (Bu$^t_2$dad)SbCl$_3$,[28] and (Ph$_2$-μ-Py-bian)SbCl$_3$[29]) and the compounds, in which only one chlorine atom lies in the diimine plane, whereas two other are in the orthogonal plane. The compounds from the first group are distinguished by the fact that the shorter Sb—N bond is in the *trans*-position to the longer Sb—Cl bond, similarly to that observed in compound **7**. The second group comprises the bipyridyl,[30] phenanthroline,[31,32] dipyrimidine,[33] pyrimidopyrimidine,[34] and acetylpyridohydrazone[35] derivatives. In these compounds, the short Sb—Cl bond and the long Sb—N bond are arranged *trans* to each other.

Compound **8** is an octahedral titanium complex (Fig. 4), the axial positions in which are occupied by atoms Cl(1) and Cl(4), whereas two other chlorine atoms, the oxygen atom, and the nitrogen atom form an equatorial plane.

In contrast to compounds **6** and **7**, in complex **8** the metal—oxygen distance is shorter than the metal—nitrogen distance. Surprisingly, there is no any known complex of titanium with neutral 1,4-*N*,*O*-1,3-diene ligands. Compounds with neutral 1,4-*N*,*N*-1,3-dienes are limited to a few examples: (Cy$_2$dad)TiCp$_2$,[36] (H$_2$dad)TiCp$_2$,[37] [(Me$_3$Si)(Me$_3$SiNCH$_2$CH$_2$OCH$_2$CH$_2$)dad]TiNPh$_2$,[38] (Ph$_2$dad)TiCl$_2$(NC$_6$H$_3$*i*Pr$_2$-2,6)Py,[39] (3,5-Me$_2$Ph-bian)$_3$Ti,[40] (2,4,6-Me$_3$Ph-bian)TiCl$_4$.[41]

Compound **9** is a trinuclear cobalt complex (Fig. 5) with Co(2) atom lying in the inversion center. The coordination environment of Co(2) atom is an octahedron with axially arranged chlorine atoms Cl(1) and Cl(1′) and four oxygen atoms of ethanol molecules lying in the equatorial
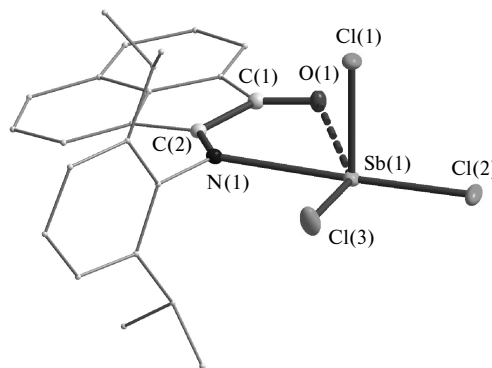

Fig. 3. Molecular structure of compound **7**. Thermal ellipsoids of key atoms are given with 30% probability. Hydrogen atoms are omitted. Some bond distances (Å) and bond angles (deg): Sb(1)—Cl(1) 2.3487(3), Sb(1)—Cl(2) 2.4281(6), Sb(1)—Cl(3) 2.3503(9), Sb(1)—O(1) 2.812(1), Sb(1)—N(1) 2.708(1), O(1)—C(1) 1.2170(15), N(1)—C(2) 1.2824(15), C(1)—C(2) 1.5429(17); Cl(1)—Sb(1)—Cl(2) 92.58(17), Cl(1)—Sb(1)—Cl(3) 93.72(3), Cl(2)—Sb(1)—Cl(3) 93.436(19), N(1)—Sb(1)—O(1) 62.7, N(1)—Sb(1)—Cl(2) 176.0, O(1)—Sb(1)—Cl(3) 145.28.
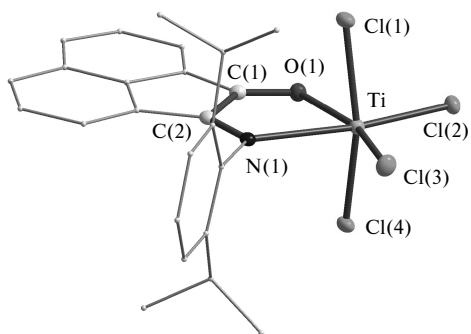
Fig. 4. Molecular structure of compound **8**. Thermal ellipsoids of key atoms are given with 30% probability. Hydrogen atoms are omitted. Some bond distances (Å) and bond angles (deg): Ti(1)—Cl(1) 2.3027(18), Ti(1)—Cl(2) 2.2276(14), Ti(1)—Cl(3) 2.2114(15), Ti(1)—Cl(4) 2.2701(18), Ti(1)—O(1) 2.174(2), Ti(1)—N(1) 2.349(2), O(1)—C(1) 1.240(2), N(1)—C(2) 1.283(3), C(1)—C(2) 1.519(3); Cl(1)—Ti(1)—Cl(2) 91.65(5), Cl(1)—Ti(1)—Cl(3) 95.69(5), Cl(2)—Ti(1)—Cl(3) 103.27(7), Cl(1)—Ti(1)—Cl(4) 164.10(3), Cl(2)—Ti(1)—Cl(4) 93.68(5), Cl(3)—Ti(1)—Cl(4) 97.64(5), N(1)—Ti(1)—O(1) 73.58(8), N(1)—Ti(1)—Cl(1) 85.37(6), N(1)—Ti(1)—Cl(2) 168.60(4), N(1)—Ti(1)—Cl(3) 87.99(8), N(1)—Ti(1)—Cl(4) 86.49(6), O(1)—Ti(1)—Cl(1) 81.97(5), O(1)—Ti(1)—Cl(2) 95.12(8), O(1)—Ti(1)—Cl(3) 161.54(4), O(1)—Ti(1)—Cl(4) 82.64(5).

plane. Atoms Cl(1) and Cl(1′) are bridging and bind the central Co(2) atom with Co(1) and Co(1′) atoms, which have a trigonal bipyramidal geometry, with N(1), Cl(2),

and Cl(3) atoms arranged in the equatorial plane. In contrast to titanium compound **8**, in complex **9** the metal—oxygen distance is much longer than the metal—nitrogen distance, that is probably due to the axial position of atom O(1) and the equatorial position of atom N(1). Atom Co(1) deviates from the plane of the quinonimine ligand by 0.020 Å, which is the smallest deviation out of complexes considered above. Unlike the packing of complexes **6—8**, in which the molecules are isolated, the packing of complex **9** is a staircase formed by the dimeric motives (see Fig. 5, *b*). The distance between the centers of the phenyl rings in the neighboring molecule is 3.577 Å, that suggests the presence of the intermolecular πsπ-stacking interaction.[42]

At the present time, several dozen of cobalt complexes with organic ligands bearing a 1,4-dihetero-1,3-diene fragment are known. The most related to compound **9** are the ketimine derivative [{Bu^{t}N=CHCH(Ph)=O}$_2$Co(N≡CMe)][PF$_6$]$_2$,[43] bis- and trisiminosemiquinolate complexes [3,5-Bu$^t_2$C$_6$H$_2$N-(Ph)O]$_2$CoL[44] (L = Cl, bipy) and [3,5-Bu$^t_2$C$_6$H$_2$N-(Ph)O]$_3$Co,[45] as well as the derivative [(dpp-mian)CoCl$_2$]$_2$[18] containing the same ligand as compound **9**. The complex [(dpp-mian)CoCl$_2$]$_2$ is a dimer formed by the bridging chlorine atoms. Despite that the "terminal" cobalt atoms in compound **9** and the cobalt atoms in the complex [(dpp-mian)CoCl$_2$]$_2$ have the same ligand environment, the coordination polyhedra of the metal atoms
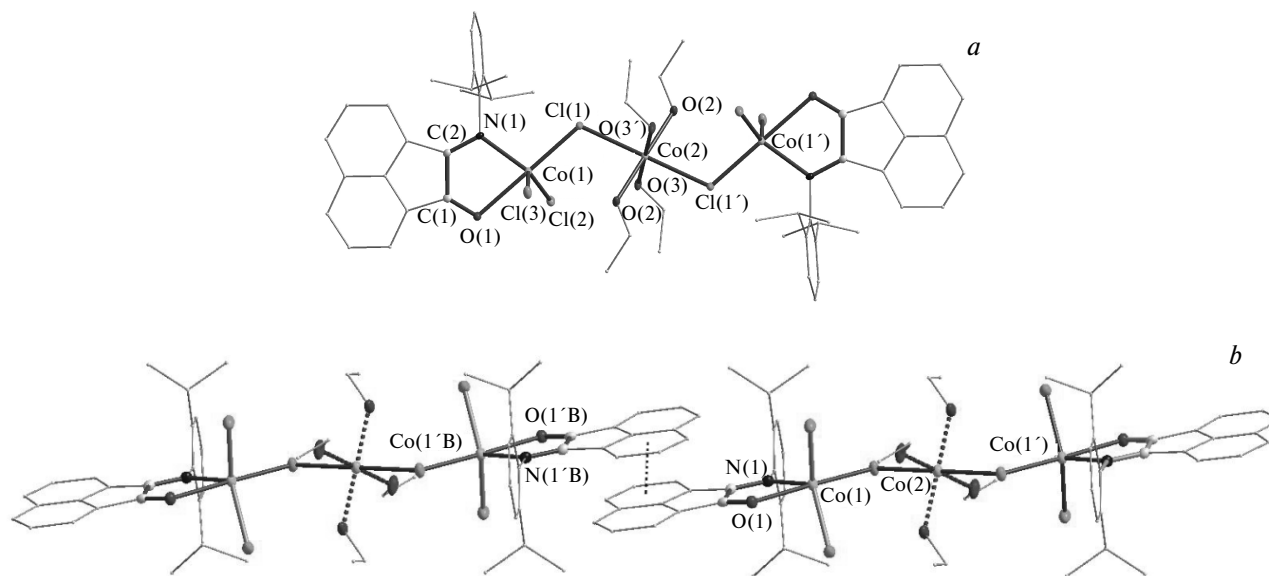

Fig. 5. (*a*) Molecular structure of compound **9**. Thermal ellipsoids of key atoms are given with 30% probability. Hydrogen atoms are omitted. Some bond distances (Å) and bond angles (deg): Co(1)—O(1) 2.3389(19), Co(1)—N(1) 2.085(2), Co(1)—Cl(1) 2.3504(8), Co(1)—Cl(2) 2.2969(8), Co(1)—Cl(3) 2.2938(8), Co(2)—O(2) 2.077(2), Co(2)—O(3) 2.051(2), Co(2)—Cl(1) 2.4922(7), O(1)—C(1) 1.220(3), N(1)—C(2) 1.276(3), C(1)—C(2) 1.540(4); N(1)—Co(1)—O(1) 76.64(8), N(1)—Co(1)—Cl(1) 102.84(6), N(1)—Co(1)—Cl(2) 111.99(7), N(1)—Co(1)—Cl(3) 109.92(7), O(1)—Co(1)—Cl(1) 178.49(5), O(1)—Co(1)—Cl(2) 81.90(5), O(1)—Co(1)—Cl(3) 83.99(5), Cl(2)—Co(1)—Cl(3) 130.91(3), Cl(1)—Co(1)—Cl(2) 97.02(3), Cl(1)—Co(1)—Cl(3) 97.52(3), O(2)—Co(2)—O(3) 89.50(9), O(2)—Co(2)—O(3′) 90.50(9), Cl(1)—Co(2)—Cl(1′) 180.0. (*б*) A fragment of the crystal packing of complex **9**.

in them are different. In the latter case, the authors consider a trigonal bipyramid and a tetragonal pyramid as possible variants of coordination environment, but do not favor either of them.

Since the trigonal bipyramidal geometry of atoms Co(1) and Co(1′) is clearly inferred from their bond angles, whereas the Co(1)—O(1) and Co(1′)—O(1′) distance in compound **9** (both of 2.3389(19) Å) are considerably longer than the corresponding distance in the complex [(dpp-mian)CoCl$_2$]$_2$ (2.2277(18) Å), it can be suggested that in the latter case the coordination environment of cobalt atoms is more like tetragonal pyramidal. The fragment CoCl$_2$(EtOH)$_4$ was observed earlier only once, namely in the compound {[CoCl$_3$]$_2$[CoCl$_2$(EtOH)$_4$]}$^{2-}${Co(EtOH)$_6$}$^{2+}$.[46]

The same state of the redox-active quinonimine ligand is a common place for compounds **6—9**. In the case of diimines, including dpp-bian, each reduction state of the ligand in metal complex has its own structural "finger prints". The same is true for quinonimines. Judging from the symmetry of the LUMO of free monoiminoacenaphthenone, its reduction to mono- and dianion should lead to the elongation of the C—O and C—N bonds and the shortening of the C—C bond in the heterodiene fragment. The neutral character of the iminoquinone ligand in complexes **6—9** follows from the close values of the C—O and C—N bond distances in these derivatives and in the free quinonimine **3** (C—O 1.215(2) and C—N 1.273(2) Å). For comparison, in the recently synthesized derivative [(dpp-mian)Mg(thf)]$_4$ (**4**)[23] containing a dianionic quinonimine the distances C—O and C—N lie within the ranges 1.389(3)—1.409(3) and 1.351(4)—1.382(3) Å, respectively. The C(1)—C(2) distance in complexes **6—9** are within a rather narrow range of 1.52—1.54 Å. Note that in the crystals of free quinonimine obtained from different solvents (dichloromethane and toluene), the C(1)—C(2) distances slightly differ (dichloromethane:[18] 1.539(3) Å; toluene:[23] 1.552(5) Å).

In conclusion, we synthesized new metal complexes with the redox-active conformationally rigid acenaphthenequinonimine ligand. Their X-ray diffraction analysis showed that the ligand in these compounds is not bridging, but acts as a bi- or monodentate ligand. It was shown that the antimony atom, despite the presence of a bulky substituent at the nitrogen atom, is predominantly coordinated to the nitrogen atom, rather than to the oxygen atom of the ligand. A comparison of structural and spectral data for the antimony complex allowed us to draw a conclusion on the presence of rotation of the chlorine atoms and the lone pair of electrons on the antimony atom in this compound in solution. The fact of change of color by the solution of cobalt acenaphthenequinonimine derivative requires further studies. It is possible that this is a result of such phenomena as a redox isomerism or a spin-crossover. Recently we found that germanium(II)

and tin(II) chlorides reduce monoiminoacenaphthenone with the formation of radical anions, which recombine with the formation of a carbon—carbon bond. The results of these studies will be published shortly.

Experimental

All the manipulations were carried out *in vacuo* using Schlenk technique. Solvents, including deuterated, were dried with sodium benzophenone ketyl and collected by condensation *in vacuo* immediately before use. (2,6-Diisopropylphenylimino)-acenaphthenone (**3**) was obtained according to the procedure described by us earlier.[23] IR spectra were recorded on a FSM-1201 spectrometer, ^{1}H NMR spectra were recorded on a Bruker DPX 200 spectrometer.

Synthesis of [(dpp-mian)$_2$GaCl$_2$]$^+$[GaCl$_4$]$^-$ (6). The addition of a solution of (2,6-diisopropylphenylimino)acenaphthenone (0.34 g, 1 mmol) in toluene (15 mL) to GaCl$_3$ (0.35 g, 2 mmol) led to immediate appearance of dark resin-like drops in bulk of the reaction mixture. After 15 min, the solution was decanted from the drops, which then were dissolved in THF (15 mL). Compound **6** was isolated by crystallization from THF as stable in air brown crystals. The yield was 0.37 g (54%). M.p. 159 °C. Found (%): C, 56.02; H, 4.95. C$_{52}$H$_{54}$C$_{16}$N$_2$O$_3$Ga$_2$. Calculated (%): C, 56.36; H, 4.88. IR (Nujol), ν/cm^{-1}: 1630 m, 1593 m, 1278 w, 1187 w, 1171 w, 1142 w, 1061 s, 1013 w, 998 w, 962 w, 891 w, 834 m, 804 w, 779 m, 704 w, 668 w, 607 w, 580 w, 515 w. ^{1}H NMR (200 MHz, CDCl$_3$, 27 °C), δ: 8.24—8.41 (m, 3 H, arom.); 7.97 (dd, 1 H, arom., *J* = 7.71 Hz, *J* = 7.83 Hz); 7.32—7.67 (m, 4 H, arom.); 6.75 (d, 1 H, arom., *J* = 6.8 Hz); 2.89 (sept, 2 H, C*H*(CH$_3$)$_2$, *J* = 6.8 Hz); 1.12 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.8 Hz); 0.94 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.8 Hz).

Synthesis of (dpp-mian)SbCl$_3$ (7). The salt SbCl$_3$ (0.29 g, 1.27 mmol) was added to a solution of monoiminoacenaphthenone (0.43 g, 1.27 mmol) in toluene (30 mL). The mixture was heated for 1.5 h at 100 °C, during which its color did not change. Then toluene was removed *in vacuo* and diethyl ether (30 mL) was added. Compound **7** was isolated by crystallization from diethyl ether as yellowish orange crystals. The yield was 0.42 g (58%). M.p. 160 °C. Found (%): C, 49.98; H, 4.23. C$_{24}$H$_{23}$C$_{13}$NOSb. Calculated (%): C, 50.57; H, 4.04. IR (Nujol), ν/cm^{-1}: 1958 w, 1942 w, 1848 w, 1739 w, 1697 s, 1632 s, 1597 s, 1588 s, 1490 m, 1322 w, 1280 s, 1252 m, 1222 m, 1175 m, 1151 w, 1102 w, 1078 m, 1056 m, 1040 s, 983 w, 973 w, 938 w, 917 s, 892 w, 831 s, 807 s, 795 s, 776 s, 706 m, 671 m, 645 w, 614 w, 580 m, 553 w, 534 s, 509 m, 483 w, 462 m. ^{1}H NMR (200 MHz, CDCl$_3$, 27 °C), δ: 8.20—8.35 (m, 2 H, arom.); 8.12 (pseudo t, 1 H, arom., *J* = 8.3 Hz); 7.90 (pseudo t, 1 H, arom., *J* = 7.8 Hz); 7.49 (pseudo t, 1 H, arom., *J* = 7.8 Hz); 7.29—7.43 (m, 3 H, arom.); 6.63 (d, 1 H, arom., *J* = 7.2 Hz); 2.84 (sept, 2 H, C*H*(CH$_3$)$_2$, *J* = 6.6 Hz); 1.15 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.6 Hz); 0.88 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.6 Hz).

Synthesis of (dpp-mian)TiCl$_4$ (8). Titanium(IV) chloride (0.37 g, 1.95 mmol) was added to a solution of monoiminoquinone (0.34 g, 1 mmol) in toluene (15 mL). The fine reddish brown crystals of compound **8** formed on the walls of the tube were isolated in the amount of 0.19 g (36%). M.p. 205 °C. Found (%): C, 59.18; H, 5.07. C$_{31}$H$_{31}$C$_{14}$NOTi. Calculated (%): C, 59.69; H, 4.97. IR (Nujol), ν/cm^{-1}: 1863 w, 1774 w, 1730 m, 1663 s, 1631 s, 1601 s, 1581 s, 1489 m, 1421 m, 1358 m, 1328 w, 1296 m, 1277 w,

1221 m, 1200 w, 1179 m, 1152 w, 1112 m, 1095 w, 1079 w, 1057 w, 1045 m, 1031 w, 1015 w, 993 w, 954 w, 939 m, 927 m, 911 w, 893 w, 847 w, 835 s, 809 m, 800 w, 793 w, 776 s, 710 w, 695 m, 680 w, 640 w, 620 w, 594 m, 567 m, 547 w, 537 w, 524 w, 513 w, 483 w, 467 m. ^{1}H NMR (200 MHz, CDCl$_3$, 27 °C), δ: 8.65—8.44 (m, 2 H, arom.); 8.29 (d, 1 H, arom., J = 8.2 Hz); 8.10 (pseudo t, 1 H, arom., J = 7.7 Hz); 7.64 (pseudo t, 1 H, arom., J = 7.7 Hz); 7.55—7.36 (m, 3 H, arom.); 6.69 (d, 1 H, arom., J = 6.8 Hz); 3.51 (sept, 2 H, C$\underline{H}$(CH$_3$)$_2$, J = 6.3 Hz); 1.34 (d, 6 H, CH(C$\underline{H}_3$)$_2$, J = 6.3 Hz); 0.85 (d, 6 H, CH(C$\underline{H}_3$)$_2$, J = 6.3 Hz).

Synthesis of [(dpp-mian)CoCl$_2$]$_2$[CoCl$_2$(EtOH)$_4$] (9). The salt CoCl$_2$·6H$_2$O (0.71 g, 3 mmol) was placed into a tube, which was evacuated during 2 h at 100 °C and 10 min at 150 °C. The water from the crystal hydrate was removed in the process of heating, the powder turned its color from violet to blue. Ethanol (30 mL) and quinonimine 3 (0.34 g, 1 mmol) were added to thus obtained anhydrous cobalt chloride. Upon dissolution of quinonimine, the solution acquired a green color. After removal of all the volatile products *in vacuo*, the residue was dissolved in chloroform with heating in a water bath to obtain a green solution. Compound 9 was precipitated as green crystals from this solution upon its concentration. The yield was 0.47 g (63%). M.p. 197 °C (decomp.). Found (%): C, 46.16; H, 4.94. C$_{58}$H$_{72}$Cl$_{12}$Co$_3$N$_2$O$_6$. Calculated (%): C, 46.54; H, 4.82. IR (Nujol), ν/cm^{-1}: 3488 s, 3424 s, 3248 s, 1728 s, 1646 m, 1604 s, 1288 m, 1273 m, 1254 w, 1217 w, 1179 w, 1149 w, 1100 w, 1093 w, 1070 w, 1040 s, 957 w, 940 w, 929 w, 911 m, 880 m, 835 m, 803 m, 782 s, 762 s, 721 m, 698 w, 671 w, 607 w, 582 w, 536 w, 528 w, 466 w.

X-ray diffraction study of compounds 6—9. Crystallographic data for complex 8 were collected on a Bruker SMART APEX automated diffractometer, for complexes 6, 7 and 9 on an Oxford Xcalibur Eos diffractometer (graphite monochromator, MoKα radiation, ω-scan technique, λ = 0.71073 Å). The experimental sets of intensities were integrated using the SAINT[47] (8) and the CrysAlisPro[48] programs (6, 7, and 9). The SADABS[49] (8) and SCALE3 ABSPACK[50] programs (6, 7, and 9) were used for the introduction of correction on absorption. The structures were solved by direct method, using the SHELXTBL[51] software package and refined by the full-matrix least squares method on F^2_{hkl} in anisotropic approximation for all the nonhydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined isotropically in a riding model for complexes 6—8, for complex 9 the atoms H(2) and H(3) were localized from the difference Fourier-synthesis of electron density. The structures were deposited with the Cambridge Crystallographic Data Center (CCDC-1422189 (6), CCDC-1422190 (7), CCDC-1422191 (8), and CCDC-1422192 (9)) and are available at: ccdc.cam.ac.uk/community/requestastructre/.

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