Reactions of germanium(II), tin(II), and antimony(III) chlorides with acenaphthene-1,2-diimines

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Reactions of diimines dtb-BIAN and dph-BIAN with $GeCl_2$ afford germanium(II) complexes with radical-anionic ligands, (dtb-BIAN)GeCl (**5**) and (dph-BIAN)GeCl (**6a**), respectively, where dtb-BIAN is 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene and dph-BIAN is 1,2-bis[(2-biphenyl)imino]acenaphthene. The latter reaction gives **6a** along with [(dph-BIAN)GeCl]$^+$[GeCl$_3$]$^-$ (**6b**). The reactions of tin(II) and antimony(III) chlorides with dtb-BIAN and dpp-BIAN produce complexes of these halides with neutral coordinated diimines, *viz.*, (dtb-BIAN)SnCl$_2$ (**7**) and (dpp-BIAN)SbCl$_3$ (**8**) (dpp-BIAN is 1,2-bis[(2,6-di-isopropylphenyl)imino]acenaphthene). Paramagnetic complexes **5** and **6a** were studied by ESR spectroscopy. Diamagnetic compounds **7** and **8** were characterized by ^{1}H NMR spectroscopy. The structures of complexes **5**, **6a,b**, **7**, **8**, and (dpp-BIAN)Ge (**9**) were established by X-ray diffraction analysis.

Key words: germanium, tin, antimony, acenaphthene-1,2-diimines, X-ray diffraction study.

1,3-Imidazol-2-ylidenes and their Si, Ge, and Sn analogs belong to a class of stable divalent derivatives of Group 14 elements.

Since the discovery of these compounds, they have received attention from researchers and continue to attract increasing interest because of their role in fundamental chemistry. Among Group 14 elements, 1,3-imidazol-2-ylidenes, which are known as Wanzlick—Arduengo carbenes, have been studied in most detail. An exhaustive review[1] of these compounds was published in 2000. More recently, two reviews on *N*-heterocyclic silylenes[2] and germylenes[3] have been published. However, only one tin compound of this type, *viz.*, [C$_2$N$_2$Bu$^t_2$]Sn, was structurally characterized.[4]

In recent years, metal complexes containing *N*-heterocyclic carbenes and silylenes as ligands have attracted considerable interest. Numerous main-group, transition, and rare-earth metal complexes with 1,3-imidazol-2-ylidenes were described. Transition metal complexes with *N*-heterocyclic carbenes are known to serve as catalysts for many organic reactions,[5] including olefin metathesis.[5f—l] 1,3-Imidazol-2-ylidenes can be used as organic synthons.[6] Metal complexes with *N*-heterocyclic silylenes[7] and germylenes[8] are less well studied, and data on the use of these compounds as reagents or catalysts are lacking. Study of *N*,*N*´-di-*tert*-butyl-1,3-imidazolegermolin-2-
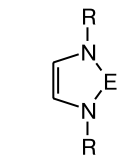
ylidene by Raman spectroscopy showed that electrons are delocalized in the metallocycle of this compound to an even greater extent than in analogous silicon derivatives.[9] Results of electrochemical studies of *N*-heterocyclic silylenes and germylenes and their reactivities have been published in recent years.[10,11]

Our main interest is the synthesis of main-group metal complexes with ligands in variable oxidation states.[12] In complexes with metals, these compounds can exist as neutral ligands, radical anions, dianions, *etc*. In reactions of such complexes with other reagents, these ligands can accept or donate electrons, while remaining in the coordination sphere of the metal atom. This approach allows one to prepare redox-active complexes of redox-inactive metal ions, *i.e.*, metal ions having a single oxidation state, for example, of alkali and alkaline-earth cations. Recently,[13] we have described the synthesis of germylenes **1—4** based on this type of ligands, *viz.*, acenaphthene-1,2-diimines (BIAN).

Recently, paramagnetic tin(II) and germanium(II) complexes based on 1,4-di-*tert*-butyl-1,3-diazadiene have also been synthesized and studied by ESR spectroscopy.[14]

Compounds **1—3** were synthesized by the exchange reaction of $GeCl_2$ with disodium or magnesium derivatives of the corresponding BIAN ligands. Germylene **1** can also be prepared by the reaction of (dpp-BIAN)Na$_4$ with $GeCl_4$.[13]

1

2

3

4
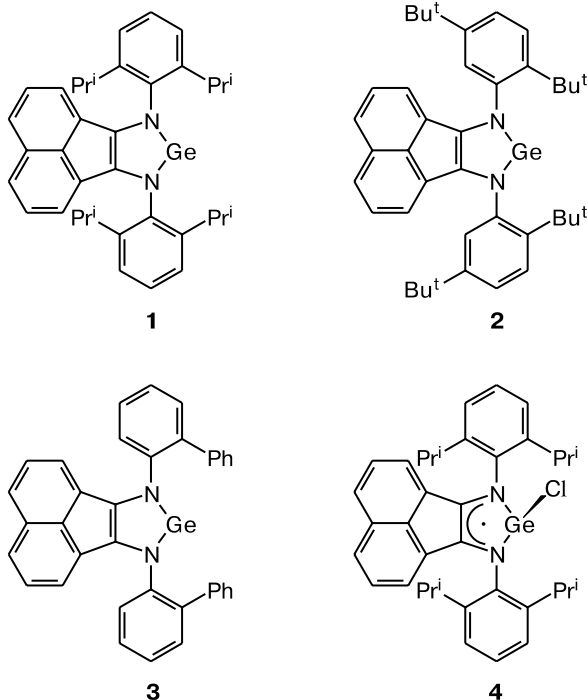
The first divalent germanium compound with the radical-anionic (dpp-BIAN)GeCl ligand (**4**), whose structure was established by X-ray diffraction, was also synthesized[14] by the exchange reaction of (dpp-BIAN)Na with $GeCl_2$. However, unlike other 1,2-diimines (for example, 1,4-di-*tert*-butyl-1,3-diazadiene), free dpp-BIAN oxidizes $GeCl_2$ to form[14] the (dpp-BIAN)GeCl complex (**4**). This fact indicates that acenaphthene-1,2-diimines have a higher electron affinity than nonfused diazadienes. The presence of the paramagnetic radical-anionic ligand in compound **4** made it possible to study compound **4** in-depth by ESR spectroscopy. It was demonstrated that the unpaired electron is delocalized over the metallocycle (hyperfine coupling constants are $A_N = 0.48$ mT ($2\ ^{14}N$) and $A_{Ge} = 0.96$ mT (^{73}Ge)), although the spin density was observed both on the chlorine atom and the hydrogen atoms of the naphthalene moiety of the molecule.

To prepare new germanium(II) complexes with radical-anionic ligands and obtain data on their electronic structures, we synthesized two new compounds of this class and characterized these compounds by ESR spectroscopy and X-ray diffraction. We also studied the reactions of Sn^{II} and Sb^{III} chlorides with acenaphthene-1,2-diimines.

Results and Discussion

Reactions of dtb-BIAN and dph-BIAN with $GeCl_2$. Acenaphthenediimines dtb-BIAN and dph-BIAN, like dpp-BIAN, readily react with $GeCl_2$ to form Ge^{II} compounds with radical-anionic diimine ligands (Schemes 1 and 2).

Scheme 1

5
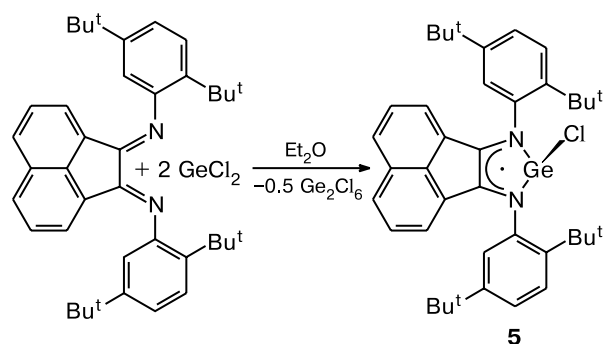
Unlike the reaction of dtb-BIAN with $GeCl_2$ giving rise to the only acenaphthenediimine derivative of germanium (dtb-BIAN)GeCl (**5**) (see Scheme 1), the reaction of dph-BIAN with $GeCl_2$ in THF affords two products, *viz.*, (dph-BIAN)GeCl (**6a**) and $[(dph-BIAN)GeCl]^+[GeCl_3]^-$ (**6b**) (see Scheme 2).

Compound **6a** is a neutral three-coordinate Ge^{II} complex with the radical-anionic dph-BIAN ligand analogous to complex **5**. Unlike **6a**, compound **6b** consists of the $[GeCl_3]^-$ anion and the $[(dph-BIAN)GeCl]^+$ cation,

Scheme 2

6a

6b
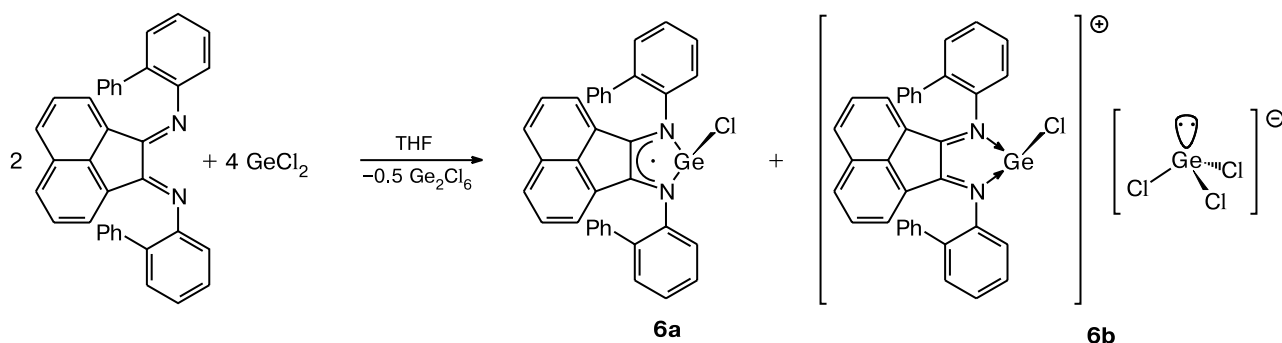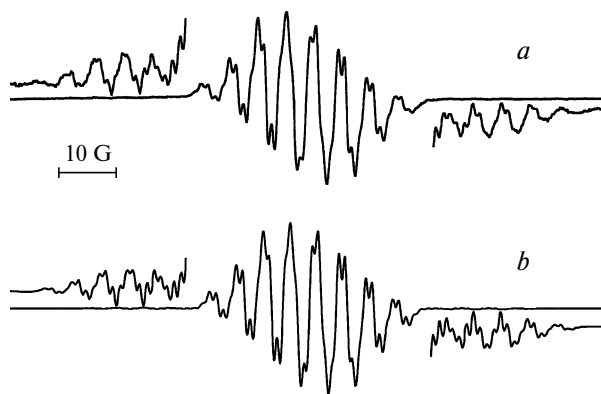
Fig. 1. (*a*) ESR spectrum of compound **5** in toluene (293 K). (*b*) Simulation of the ESR spectrum of compound **5** (A_N = 0.47 (2 N), A_{Ge} = 0.63, A_{Cl} = 0.47 (^{35}Cl), A_{Cl} = 0.39 (^{37}Cl), A_H = 0.12 (4 H) mT, g = 2.0025).

which is structurally similar to molecule **6a** but contains the neutral dph-BIAN ligand coordinated to the germanium atom. Compounds **6a** and **6b** crystallize together from the reaction mixture and are simultaneously present in the unit cell of the crystals.

Compound **5** was isolated by recrystallization from benzene as the dark-red crystal solvate **5**·C_6H_6 in 79% yield. Crystals containing compounds **6a** and **6b** were grown from a concentrated THF solution in 22% yield. The hyperfine structure of the ESR signal of compound **5** in toluene (Fig. 1) is indicative of coupling between the unpaired electron and the ^{14}N, ^{73}Ge, ^{35}Cl, ^{37}Cl, and ^{1}H nuclei (A_N = 0.51 (2 N), A_{Ge} = 0.63, A_{Cl} = 0.47 (^{35}Cl), A_{Cl} = 0.392 (^{37}Cl), A_H = 0.12 (4 H) mT, g = 2.0025). A comparison of the ESR parameters of compound **5** with the analogous parameters of the (dpp-BIAN)GeCl compound (A_N = 0.48 (2 N), A_{Ge} = 0.96, A_{Cl} = 0.78 (^{35}Cl), A_{Cl} = 0.65 (^{37}Cl), A_H = 0.11 (4 H) mT, g = 2.0014)[14] shows that the nitrogen hyperfine coupling constant of compound **5** is similar to that of (dpp-BIAN)GeCl (0.51 and 0.48 mT, respectively), whereas the ^{73}Ge, ^{35}Cl, and ^{37}Cl hyperfine coupling constants of compound **5** are substantially smaller than those of (dpp-BIAN)GeCl.[14] This is associated with the different contributions of the s and p orbitals of the germanium atom to the Ge—Cl bond. An increase in the contribution of the s orbital of the germanium atom to these bonds should lead to an increase in the Ge and Cl hyperfine coupling constants and affect the geometry of the coordination environment of the germanium atom, *i.e.*, should lead to an increase in the N—Ge—Cl angles. A comparison of the crystal structure of compound **5** presented below with that of (dpp-BIAN)GeCl confirms the suggestion that the hyperfine coupling constants correlate with the geometric parameters of these molecules. For example, the sum of the N(1)—Ge—Cl(1) and N(2)—Ge—Cl(1) angles in compound **5** (A_{Ge} = 0.63 mT) is 189.1°, whereas the corre-

sponding sum in the (dpp-BIAN)GeCl compound (A_{Ge} = 0.96 mT) is 195.3°.

After dissolution of a sample containing compounds **6a** and **6b** in toluene, a broadened ESR signal was observed. We failed to determine its parameters. A broadening of the signal is, apparently, caused by the exchange process

$$\textbf{6b} \rightleftharpoons \textbf{6a} + 0.5\ Ge_2Cl_6$$
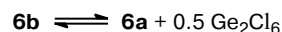
The composition of a crystalline sample containing compounds **6a** and **6b** differs from the above-mentioned stoichiometry. It should also be noted that these reaction products were isolated in the crystalline state in low yield. Taking into account this fact, we performed ESR spectroscopic study of the mixture obtained in the reaction of $GeCl_2$ with dph-BIAN. After mixing of these two compounds in THF, a red solution was obtained. This solution gives two ESR signals at 293 K (Fig. 2, *d*). The intensity of one signal decreases with decreasing tempera-
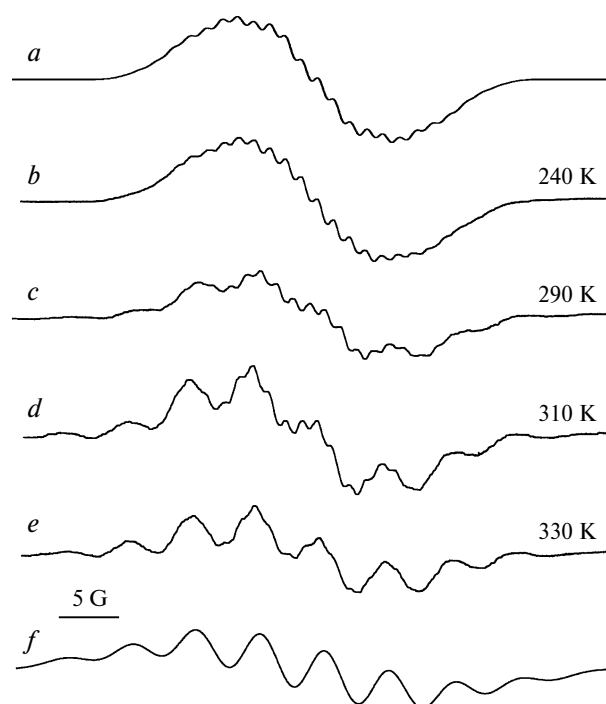
Fig. 2. Calculated ESR spectra of (dph-BIAN)GeCl$_3$ (*a*) and (dph-BIAN)GeCl (*f*). The ESR spectra of the reaction mixture (THF) containing $GeCl_2$ and dph-BIAN in a ratio of 2 : 1 at 240 (*b*), 290 (*c*), 310 (*d*), and 330 K (*e*).

| Compound	A_N	A_{Cl} (^{35}Cl)	A_{Cl} (^{37}Cl)	A_H	g
		mT			
(dph-BIAN)GeCl$_3$	0.34 (2 N)	0.13	0.11	0.09 (4 H)	2.0024
(dph-BIAN)GeCl	0.50 (2 N)	0.55	0.45	0.1 (4 H)	2.0028

ture, and virtually one signal is observed at 240 K (see Fig. 2, *b*), which is indicative of the presence of the (dph-BIAN)GeCl$_3$ complex in the reaction mixture. The calculated ESR spectrum of this compound is shown in Fig. 2. In this case, the hyperfine coupling between the unpaired electron and the ^{73}Ge nucleus was not observed because, apparently, of low values of the hyperfine coupling constants. An increase in the temperature to 330 K leads to the disappearance of this signal, and the major signal is observed as an octet (see Fig. 2, *f*) belonging to (dph-BIAN)GeCl. A change in the ratio of the reagents GeCl$_2$ and dph-BIAN from 2 : 1 to 1 : 1 does not lead to a change in the spectral pattern. Based on the spectroscopic data, the reaction of GeCl$_2$ with dph-BIAN in THF can be described by Scheme 3.

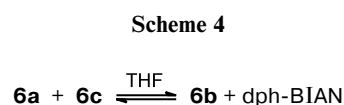**Scheme 3**

dph-BIAN

6c
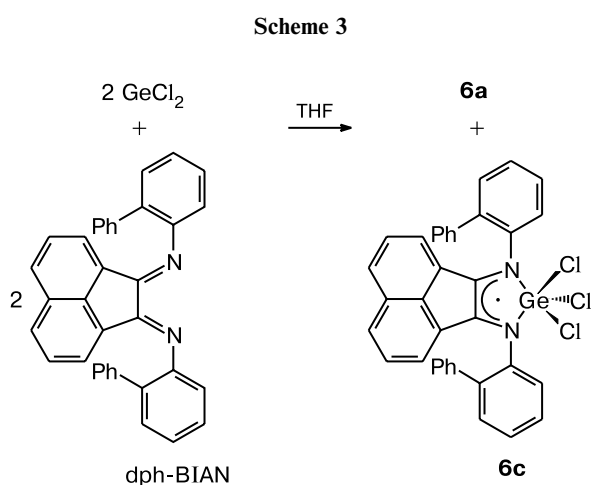
Compound **6b**, which was isolated from the reaction mixture in the crystalline state along with **6a**, is formed, apparently, by the reaction of **6a** with **6c** (Scheme 4).

The observed temperature dependence of the ESR signals of complexes **6a** and **6c** (see Fig. 2, *b*—*e*) can be attributed to the reversible transformation of these paramagnetic complexes into diamagnetic complexes
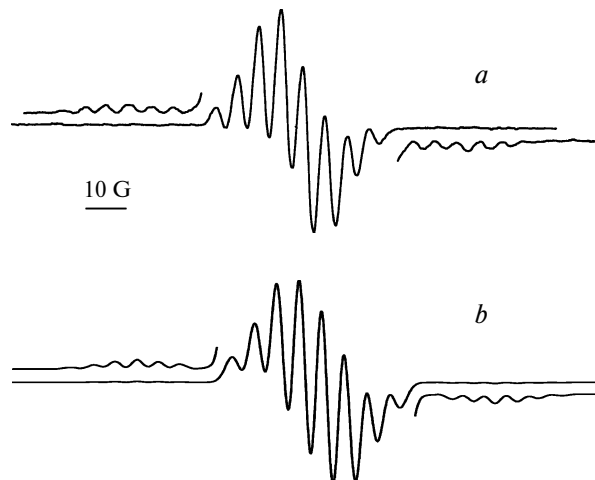

Fig. 3. (*a*) ESR spectrum of compound **6a** in toluene (293 K). (*b*) Simulation of the ESR spectrum of compound **6a** (A_N = 0.50 (2 N), A_{Ge} = 0.85, A_{Cl} = 0.55 (^{35}Cl), A_{Cl} = 0.45 (^{37}Cl), A_H = 0.09 (4 H) mT, g = 2.0049).

Scheme 4

$$\textbf{6a} + \textbf{6c} \xrightleftharpoons{\text{THF}} \textbf{6b} + \text{dph-BIAN}$$

(Scheme 5). It should be noted that silicon analogs of compound **6d** have been documented.[15]

The reaction of two equivalents of GeCl$_2$ with dph-BIAN in toluene is characterized by a different spectral pattern. Based on the parameters of the ESR signal in a toluene solution (A_N = 0.50 (2 N), A_{Ge} = 0.85, A_{Cl} = 0.55 (^{35}Cl), A_{Cl} = 0.45 (^{37}Cl), A_H = 0.09 (4 H) mT, g = 2.0049), this signal can be assigned to compound **6a**, because splitting of the unpaired electron on two nitrogen atoms, one germanium atom, one chlorine atom, and four protons is observed (Fig. 3, *a*).

This signal remains virtually unchanged in the temperature range of 330—220 K. However, unlike the reaction in THF, the reaction in toluene afforded a red crys-

Scheme 5
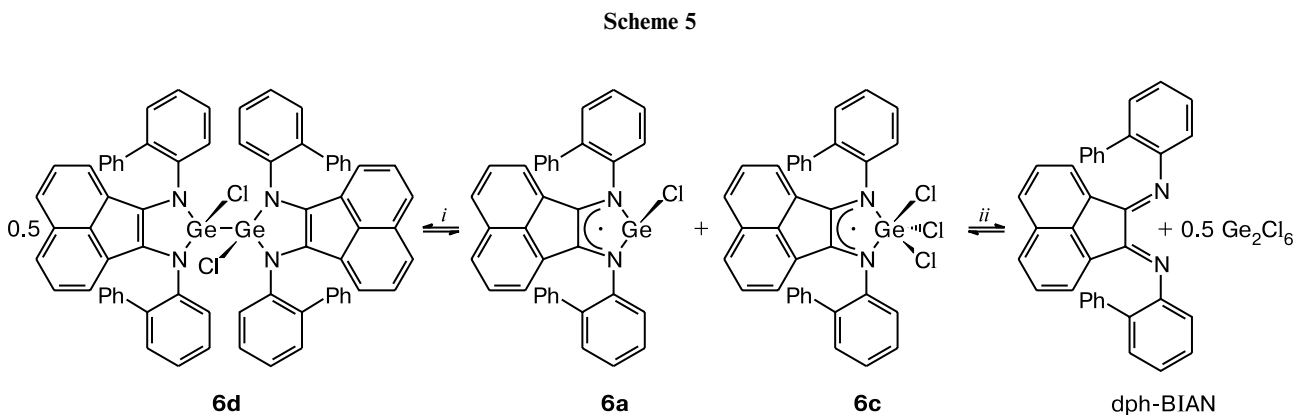
i. Lowering of the temperature; *ii*. raising of the temperature.

talline precipitate, which could have the structure of (dph-BIAN)GeCl$_3$. Contrary to this assumption, one ESR signal was observed after complete dissolution of this precipitate in THF. This signal is similar to that observed in toluene and belongs to the (dph-BIAN)GeCl compound. Based on these data, the following conclusions can be drawn: (1) reaction of GeCl$_2$ with dph-BIAN occurs as a redox process even in a nonsolvating solvent, such as toluene, and produces a germanium(II) complex with the radical-anionic diimine ligand (dph-BIAN)GeCl; (2) this reaction affords, apparently, hexachlorodigermane as the second product, which is present in a toluene solution along with partially dissolved (dph-BIAN)GeCl; (3) nonsolvating medium (toluene), unlike THF, does not promote oxidation of hexachlorodigermane with the diimine ligand to form (dph-BIAN)GeCl$_3$.

Reactions of SnCl$_2$ and SbCl$_3$ with acenaphthene-1,2-diimines. After the successful synthesis of germylenes (dpp-BIAN)Ge, (dtb-BIAN)Ge, and (dph-BIAN)Ge by the exchange reactions of GeCl$_2$ with disodium and magnesium salts of the corresponding dianionic BIAN ligands,[13] we studied the exchange reactions of tin dichloride with the disodium salt of dpp-BIAN in various solvents (toluene, THF, and diethyl ether) with the aim of preparing tin analogs of the above germylenes. However, all these reactions gave tin metal and free dpp-BIAN. An analogous situation was observed in the reactions of sodium salts of dpp-BIAN, *viz.*, (dpp-BIAN)$^{n-}$Na$_n^+$ ($n = 1$—3), with SbCl$_3$. Germanium differs from tin and antimony in that the reactions of its chlorides with acenaphthene-1,2-diimines proceed in a different way. The reactions of BIAN with SnCl$_2$ and SbCl$_3$ were not accompanied by reduction of diimines to radical anions but gave the (dtb-BIAN)SnCl$_2$ (**7**) and (dpp-BIAN)SbCl$_3$ (**8**) complexes, respectively, which were isolated as red crystals in both cases (Scheme 6). The formation of compounds **7** and **8** in solution was confirmed by ^{1}H NMR spectroscopy. According to the X-ray diffraction data (see below), the tin atom in molecule **7** has a pyramidal geometry and is coordinated by two chlorine atoms and one nitrogen atom of the dtb-BIAN ligand. If the monodentate coordination of the ligand in solution is retained, the protons of the substituents at the nitrogen atoms would be nonequivalent and the ^{1}H NMR spectrum would show the corresponding set of signals.

However, the ^{1}H NMR spectrum of complex **7** in C$_6$D$_6$, like the spectrum of the free dtb-BIAN ligand, shows only two signals of the *tert*-butyl substituents. This is evidence that molecule **7** has a mirror plane, which is orthogonal to the diimine fragment and passes through its midpoint. The validity of the assignment of the signals observed in the ^{1}H NMR spectrum of compound **7** to the coordinated dtb-BIAN ligand is confirmed by the fact that these signals are substantially shifted compared to the signals of the free ligand. For example, the signals of the

Scheme 6
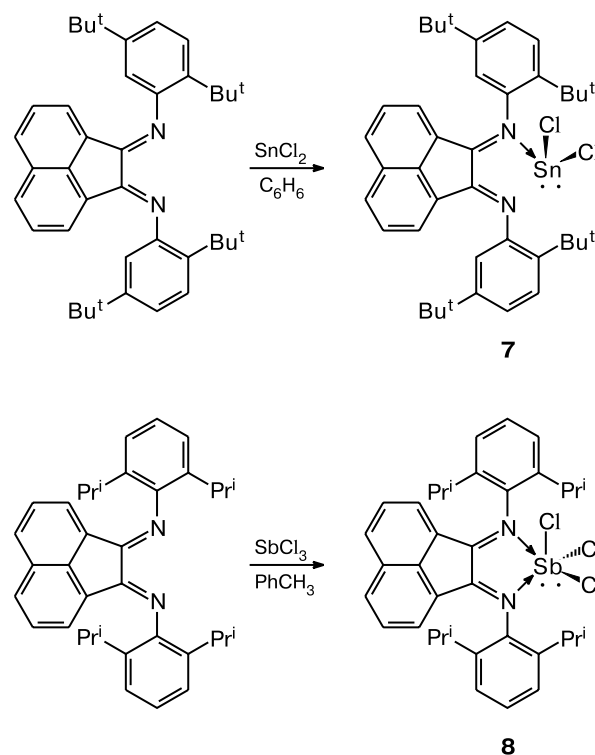
Bu^t groups in the ^{1}H NMR spectrum of free dtb-BIAN in C$_6$D$_6$ are observed at δ 1.69 and 1.32, whereas the corresponding signals in the spectrum of compound **7** appear at δ 1.39 and 1.37. The NMR spectroscopic data provide evidence that, in solution, the metal fragment SnCl$_2$ shuttles rapidly (on the NMR time scale) between the nitrogen atoms. Apparently, the bond between the ligand and the tin atom in compound **7** is formed due to donation of the lone pairs of the nitrogen atoms to the unoccupied 5p orbitals of tin.

The ^{1}H NMR spectrum of compound **8** in C$_6$D$_6$ provides evidence that the antimony atom is also coordinated by the diimine ligand. The asymmetric coordination of the ligand to the antimony atom observed in the crystals of compound **8** is not retained in solution. This is evidenced by the presence of one septet and two doublets of the Pr^i substituents of the Ph rings. The chemical shifts of the methine protons of the Pr^i groups in the free ligand (δ 3.36) are similar to those in compound **8** (δ 3.38), whereas the positions of the doublets of the Me groups in dpp-BIAN (δ 1.41 and 1.17) differ substantially from those in compound **8** (δ 1.47 and 0.97).

Molecular structures of compounds 5, 6a,b, 7, and 8. The structures of compounds **5**, **6a,b**, **7**, and **8** and the germylene (dtb-BIAN)Ge (**9**), which has been described earlier, were established by X-ray diffraction. The crystallographic data, details of X-ray diffraction data collection, and parameters of the structure refinement of com-

Table 1. Crystallographic data, details of X-ray data collection, and parameters of the structure refinement for compounds **5—9**

Parameter	$5 \cdot C_6H_6$	$6a \cdot 6b \cdot C_4H_8O$	$7 \cdot C_6H_6$	$8 \cdot C_7H_8$	$9 \cdot C_4H_{10}O$
Molecular formula	$C_{40}H_{48}ClGeN_2 \cdot$ $\cdot C_6H_6$	$C_{72}H_{48}Cl_5Ge_3N_4 \cdot$ $\cdot C_4H_8O$	$C_{40}H_{48}Cl_2N_2Sn \cdot$ $\cdot C_6H_6$	$C_{36}H_{40}Cl_3N_2Sb \cdot$ $\cdot C_7H_8$	$C_{40}H_{48}GeN_2 \cdot$ $C_4H_{10}O$
Molecular weight	742.95	1436.27	824.50	820.98	703.51
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
T/K	100(2)	100(2)	100(2)	100(2)	173(2)
Space group	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	13.0956(5)	10.6966(5)	11.4395(15)	34.2601(13)	10.4589(3)
b/Å	21.7019(7)	18.1624(8)	11.9186(16)	10.8435(4)	11.6823(3)
c/Å	14.2783(5)	33.1649(15)	16.126(2)	22.4404(9)	16.8483(4)
α/deg	90	90	91.406(3)	90	78.16
β/deg	98.0070(10)	91.6310(10)	95.464(3)	106.7340(10)	100.9330(10)
γ/deg	90	90	108.021(2)	90	82.0170(10)
V/Å^3	4018.3(2)	6440.5(5)	2077.9(5)	7983.6(5)	1986.93(9)
Z	4	4	2	8	2
ρ/g cm^{-3}	1.228	1.481	1.318	1.365	1.176
μ/mm^{-1}	0.862	1.649	0.777	0.924	0.805
$F(000)$	1572	2916	856	3372	752
Crystal dimensions/mm	0.08×0.05×0.04	0.12×0.10×0.08	0.45×0.45×0.40	0.12×0.10×0.08	0.50×0.18×0.16
Scan range, θ/deg	1.72—25.00	1.66—25.00	1.80—29.04	1.90—25.00	1.24—25.00
Ranges of h, k, l indices	$-14 \le h \le 15$ $-25 \le k \le 24$ $-16 \le l \le 10$	$-12 \le h \le 11$ $-19 \le k \le 21$ $-39 \le l \le 39$	$-15 \le h \le 11$ $-15 \le k \le 16$ $-21 \le l \le 19$	$-38 \le h \le 40$ $-8 \le k \le 12$ $-26 \le l \le 26$	$-11 \le h \le 12$ $-13 \le k \le 13$ $-20 \le l \le 19$
Number of observed reflections	22111	35038	15417	21385	12121
Number of independent reflections	7073	11340	10732	7030	6898
R_{int}	0.0238	0.0617	0.0111	0.0241	0.0979
Goodness-of-fit on F^2	1.058	0.975	1.034	1.088	0.969
R_1/wR_2 $(I > 2\sigma(I))$	0.0357/0.0929	0.0472/0.0965	0.0225/0.0582	0.0292/0.0731	0.0861/0.2105
R_1/wR_2 (based on all parameters)	0.0440/0.0966	0.0814/0.1047	0.0243/0.0592	0.0356/0.0752	0.1580/0.2465
Residual electron density, (max/min)/e Å^{-3}	0.515/−0.326	1.159/−0.599	0.683/−0.357	1.016/−0.541	3.387/−0.840

pounds **5—9** are given in Table 1. Selected bond lengths and bond angles of compounds **5** and **6a,b** are listed in Table 2; for compounds **7**, **8**, and **9**, in Table 3. Although compounds **6a** and **6b** crystallize together and are simultaneously present in the unit cell of the crystals grown from THF, there are no contacts between molecule **6a** and **6b** shorter than the sum of the van der Waals radii. Hence, the molecular structures of compounds **6a** and **6b** are shown independently in different figures. The structures of compounds **5—9** are presented in Fig. 4.

In compounds **5** and **6a,b**, the germanium atoms occupy the vertices of trigonal pyramids and are coordinated by two nitrogen atoms of the corresponding diimine ligand and the chlorine atom.

The sums of angles at the germanium atoms in complex **5**, **6a**, and **6b** are 270.4, 265.1, and 257.6°, respectively. These values are similar to the ideal pyramidal geometry (270°) and are substantially smaller than those

Table 2. Selected bond lengths (d) and bond angles (ω) in compounds **5**, **6a**, and **6b**

Parameter	5	6a	6b
Bond		d/Å	
Ge(1)—N(1)	2.0140(16)	2.003(3)	2.109(3)
Ge(1)—N(2)	2.0142(16)	2.013(3)	2.082(3)
Ge(1)—Cl(1)	2.3019(6)	2.3267(12)	2.2417(12)
Ge(2)—Cl(2)	—	—	2.3011(12)
Ge(2)—Cl(3)	—	—	2.2670(12)
Ge(2)—Cl(4)	—	—	2.2880(12)
N(1)—C(1)	1.332(3)	1.330(5)	1.292(5)
N(2)—C(2)	1.333(2)	1.337(5)	1.290(5)
C(1)—C(2)	1.429(3)	1.430(6)	1.487(5)
Angle		ω/deg	
N(1)—Ge—N(2)	81.40(7)	81.48(13)	77.86(13)
N(1)—Ge—Cl(1)	93.72(5)	92.03(10)	90.19(9)
N(2)—Ge—Cl(1)	95.36(5)	91.59(10)	89.59(10)

Table 3. Selected bond lengths (*d*) and bond angles (ω) in compounds **7**, **8**, and **9**

Parameter	7	8	9
Bond		*d*/Å	
M(1)*—N(1)	2.4700(7)	2.615(2)	1.904(6)
M(1)—N(2)	2.7651(7)	2.850(2)	1.914(5)
M(1)—Cl(1)	2.4606(4)	2.3385(5)	—
M(1)—Cl(2)	2.4919(3)	2.3808(5)	—
M(1)—Cl(3)	—	2.4581(6)	—
N(1)—C(1)	1.2833(11)	1.288(2)	1.375(8)
N(2)—C(2)	1.2693(11)	1.277(3)	1.360(9)
C(1)—C(2)	1.5190(12)	1.524(3)	1.386(8)
Angle		ω/deg	
N(1)—M—N(2)	—	62.97(2)	84.0(2)
N(1)—M—Cl(1)	87.07(2)	82.36(2)	—
N(2)—M—Cl(1)	—	81.01(2)	—
N(1)—M—Cl(2)	84.71(1)	—	—
Cl(1)—M—Cl(2)	92.38(1)	97.71(2)	—
Cl(1)—M(1)—Cl(3)	—	90.44(2)	—
Cl(2)—M(1)—Cl(3)	—	88.759(19)	—

* M(1) = Sn (**7**), Sb (**8**), or Ge (**9**).

expected for the tetrahedral (328°) and planar-trigonal geometry (360°). The pyramidal geometry of the germanium atoms in complexes **5** and **6a,b** indicates that the orbital of the lone pair makes a substantial contribution to the s orbitals of the Ge atom.

Analysis of the bond lengths in the metallocycles of **5** and **6a,b** allowed us to determine the state of the diimine ligand. Based on the symmetry of LUMO of acenaphthenediimines, reduction of these compounds would be expected to lead to an elongation of the C—N bonds and a shortening of the C(1)—C(2) bond. In compounds **5** and **6a**, the C—N bonds (1.332(3) and 1.333(2) Å in **5**; 1.330(5) and 1.337(5) Å in **6a**) are longer than those in free diimines[12e,i] but are shorter than the corresponding bonds in compounds with the dianionic ligands (dtb-BIAN)Ge (**9**) (see Fig. 4, *f*; C—N, 1.375(8) and 1.360(9) Å) and (dph-BIAN)Ge (both bond lengths are 1.382(5) Å).[13] Compound **6b** has short C—N bonds (1.292(5) and 1.290(5) Å), which are similar to the C—N bonds in the free molecule of the neutral dph-BIAN ligand (1.274(2) and 1.275(2) Å).[12i] This is evidence that the ligand in the metal fragment (dph-BIAN)GeCl of **6b** is neutral and is coordinated to the GeCl⁺ cation. The GeCl₃⁻ anion in the immediate vicinity of the complex cation serves as a counterion to this cation. In the GeCl₃⁻ anion, the germanium atom also has a pyramidal geometry. The [(dph-BIAN)GeCl]⁺ cation in **6b** is isostructural to neutral molecule **6a**. However, the presence of an additional electron-orbital interaction between the germanium atom and the diimine ligand in **6a** leads to a shortening of the Ge—N bonds (2.003(3) and 2.013(3) Å) compared to those in **6b** (Ge—N, 2.109(3) and 2.082(3) Å).

In molecule **7** (see Fig. 4, *d*), the tin atom is bound to two chlorine atoms and one nitrogen atom of the dtb-BIAN ligand and occupies the apex of the trigonal pyramid (the sum of angles at the Sn atom is 264°).

The Sn—N(2) nonbonded distance (2.7651(7) Å) is substantially longer than the Sn—N(1) coordination bond (2.4700(7) Å). The C(1)—N(1) and C(2)—N(2) bond lengths (1.2833(11) and 1.2693(11) Å, respectively) in molecule **7** are typical of other BIAN-type diimines,[12e,i] which indicates that the ligand in this compound is neutral. The pyramidal geometry of the tin atom is evidence for the pronounced s character of the orbital occupied by the lone pair of the tin atom. Hence, it can be concluded that the complex of dtb-BIAN with tin dichloride is formed through donation of the lone pair of the N(1) atom to the unoccupied p orbital of the tin atom.

The coordination environment of the antimony atom in molecule **8** can be considered as a distorted octahedron with two nitrogen atoms and two chlorine atoms, Cl(2) and Cl(3), occupying the equatorial plane. The axial positions of the octahedron are occupied by the Cl(1) atom and the lone pair of the antimony atom.

The bonds between the antimony atom and the chlorine atoms are formed with the involvement of the 5s and 5p orbitals of the metal atom, whereas the coordination bonds with the diimine ligand are formed due to interactions between the lone pairs of the nitrogen atoms of the ligand and, apparently, the unoccupied 5d orbitals of the antimony atom. The Sb—Cl bond lengths are substantially different. The shortest distance is observed between the antimony atom and the chlorine atom containing no atoms in the *trans* position (Sb—Cl(1), 2.3385(5) Å). The distances between the antimony atom and the chlorine atoms *trans* to the nitrogen atoms are 2.3808(5) and 2.4581(6) Å. It should be noted that the longest Sb—Cl(3) bond (2.4581(6) Å) is in the *trans* position with respect to the shortest Sb—N(1) bond (2.615(2) Å). On the contrary, the shorter Sb—Cl(2) bond (2.3808(5) Å) is in the *trans* position to the longer Sb—N(2) bond (2.850(2) Å). In our opinion, this confirms the orbital character of the interaction between the diimine ligand and the metal fragment SbCl₃. The abnormally small chelate angle (N(1)—Sb—N(2), 62.97°) is associated, on the one hand, with conformational rigidity of the diimine fragment and, on the other hand, with the larger atomic radius of antimony. For example, this angle in germanium compounds **5**, **6a**, and **6b** varies from 77 to 81°. The C(1)—N(1) and C(2)—N(2) bond lengths in molecule **8** (1.288(2) and 1.277(3) Å, respectively), like those in compound **7**, are indicative of the neutral nature of the diimine ligand.

In compound **9**, the imaginary mirror plane passing along the bisecting line of the N—Ge—N angle divides the molecule into two equal parts (see Fig. 4, *f*).

Due to the asymmetric positions of the substituents in the Ph rings, molecule **9** can adopt either a *syn* or *anti* con-
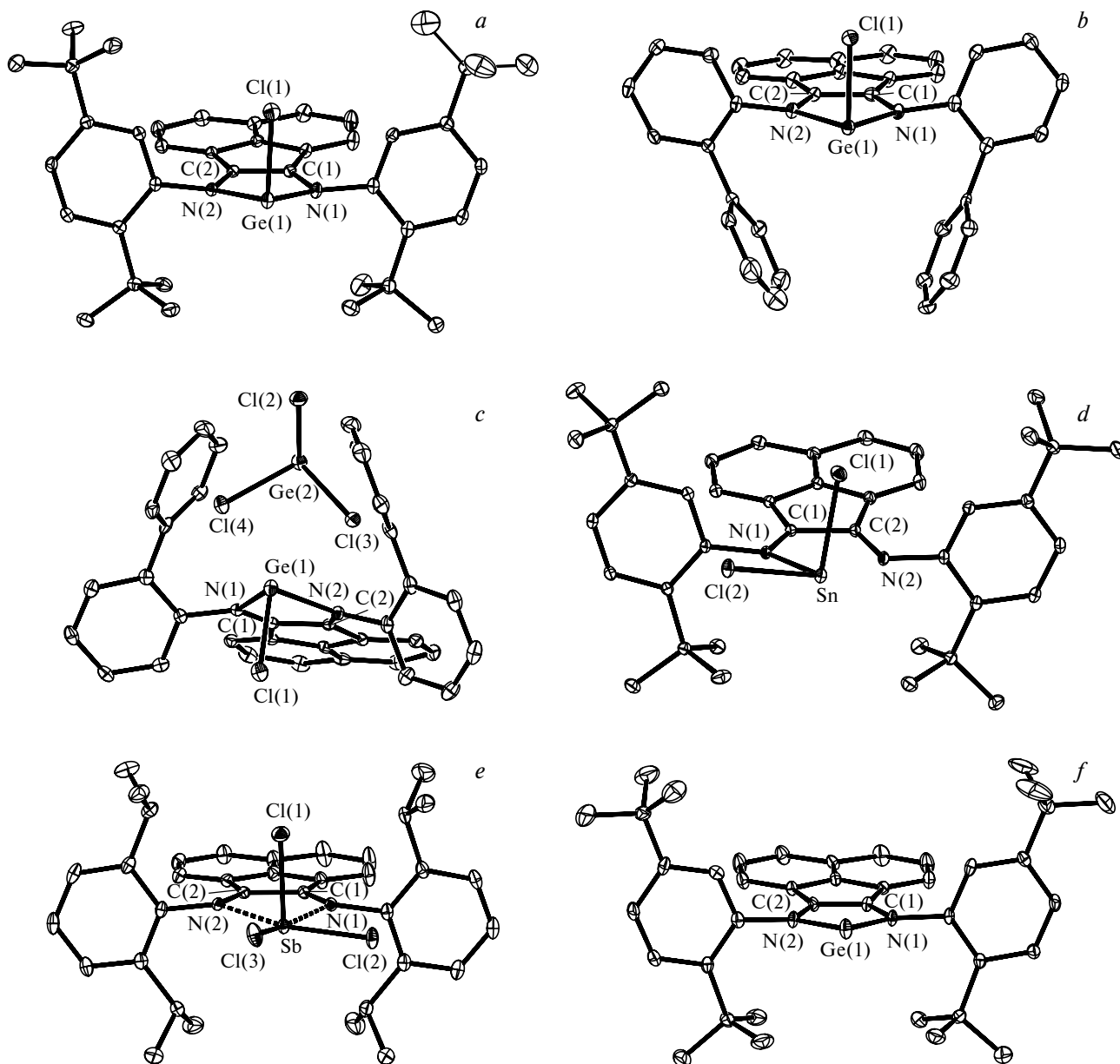
Fig. 4. Molecular structures of complexes **5** (*a*), **6a** (*b*), **6b** (*c*), **7** (*d*), **8** (*e*), and **9** (*f*) with displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted.

figuration. In the crystalline state, germylene **9** exists as the *syn* isomer. The chelate angle in molecule **9** (84.0°) is somewhat larger than that in molecule **5** (81.40°), which is associated with a shortening of the Ge—N bonds in the dianionic ligand in molecule **9** (Ge—N, 1.904(6) and 1.914(5) Å) compared to those in the radical-anionic ligand in molecule **5** (Ge—N, 2.0140(16) and 2.0142(16) Å). Analysis of the structures of compounds **5**, **7**, and **9** show how the bond lengths in the diimine fragment change in the series of neutral ligand **7**, radical anion **5**, and dianion **9**. The successive one- and two-electron population of LUMO of the dtb-BIAN ligand

leads to an elongation of the C(1)—N(1) and C(2)—N(2) bonds (1.2833(11) and 1.2693(11) Å in **7**; 1.332(3) and 1.333(2) Å in **5**; and 1.375(8) and 1.360(9) Å in **9**).

Experimental

Since compounds **5**, **6a**, **6b**, and **9** are sensitive to atmospheric oxygen and moisture, all operations associated with their synthesis, isolation, and identification were carried out *in vacuo* using the Schlenk technique. Although compounds **7** and **8** did not undergo decomposition when exposed to air, all operations with these compounds were also performed in anaerobic condi-

tions (generally, *in vacuo*). The dpp-BIAN ligand was prepared by condensation of acenaphthenequinone with the corresponding aniline derivative (both reagents were purchased from Aldrich) in acetonitrile. Tetrahydrofuran, diethyl ether, benzene, and toluene were dried and stored over sodium benzophenone ketyl and were withdrawn by condensation immediately before use. The IR spectra were recorded on a Specord M80 spectrometer in Nujol mulls. The ^{1}H NMR spectra were measured on a Bruker DPX 200 spectrometer. The ESR spectra were recorded on a Bruker ESR 200D-SRC spectrometer (9.35 GHz); the g factors were measured with the use of diphenylpicryl-hydrazyl as the standard. The ESR spectra were simulated with the use of the WINEPR SimFonia program.

1,2-Bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthenegermanium chloride (5). A. synthesis from dtb-BIAN and GeCl$_2$(C$_4$H$_8$O$_2$). Germanium dichloride GeCl$_2$·C$_4$H$_8$O$_2$ (0.46 g 2.0 mmol) was added to a suspension of 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene, dtb-BIAN (0.56 g, 1.0 mmol) in Et$_2$O (40 mL). The reaction mixture was stirred at room temperature for several minutes, after which the color of the solution changed from orange to cherry-red. The solution was filtered and concentrated to 20 mL by evaporating the solvent *in vacuo*. A small amount of the crystalline product that formed after removal of the solvent was dissolved at high temperature. After two days, compound **5** was isolated as dark-red crystals (0.59 g, 79%), m.p. >200 °C (decomp.). Found (%): C, 74.13; H, 7.10. C$_{40}$H$_{48}$ClGeN$_2$·C$_6$H$_6$ (742.95 g mol^{-1}). Calculated (%): C, 74.36; H, 7.33. IR, ν/cm^{-1}: 1590 w, 1530 s, 1260 m, 1140 w, 1110 w, 1050 m, 1020 w, 910 m, 870 w, 805 s, 750 m, 695 w, 675 s, 620 w, 545 m, 495 w, 470 m. ESR (13 °C, toluene): A_N = 0.47 (2 ^{14}N), A_{Ge} = 0.63 (^{73}Ge), A_{Cl} = 0.47 (^{35}Cl), A_{Cl} = 0.39 (^{37}Cl), A_H = 0.12 (4 ^{1}H) mT. Then the solution was concentrated, after which compound **5** and a small amount of unidentified colorless crystals (m.p. 147 °C) were obtained.

B. Synthesis from (dtb-BIAN)Na and GeCl$_2$·C$_4$H$_8$O$_2$. A solution of (dtb-BIAN)Na was prepared from dtb-BIAN (0.56 g, 1.0 mmol) and sodium (0.023 g, 1.0 mmol) with stirring for 24 h in Et$_2$O (40 mL). After the addition of GeCl$_2$·C$_4$H$_8$O$_2$ (0.23 g, 1.0 mmol) to the reaction solution, the color of the reaction mixture rapidly changed from red to cherry-red. After centrifugation, the solution was separated by decantation from the precipitate of NaCl that formed. Compound **5** was isolated from the concentrated solution in Et$_2$O as dark-red crystals in a yield of 35% (0.26 g). The analytical and spectroscopic data for this compound are identical with those for compound **5** prepared according to method *A*.

1,2-Bis[(2-biphenyl)imino]acenaphthenegermanium chloride (6a) and 1,2-bis[(2-biphenyl)imino]acenaphthenegermanium chloride trichlorogermane (6b). Germanium dichloride GeCl$_2$··C$_4$H$_8$O$_2$ (0.46 g, 2.0 mmol) was added to a solution of dph-BIAN (0.48 g, 1.0 mmol) in THF (40 mL). The tube was shaken at room temperature for several minutes, after which the color of the solution changed from orange to cherry-red. The solution was concentrated to 7 mL. After two days, dark-red crystals containing compounds **6a** and **6b** were isolated from this solution. The yield was 0.26 g (18%), m.p. 146 °C. IR, ν/cm^{-1}: 1614 m, 1600 w, 1571 m, 1528 m, 1500 w, 1434 m, 1296 m, 1243 m, 1224 w, 1188 w, 1155 w, 1142 w, 1113 w, 1065 m, 1049 m, 1009 m, 954 w, 916 w, 860 w, 825 m, 798 w, 772 s, 745 s, 699 s, 659 m, 614 m, 540 m, 496 w, 485 w, 472 w.

1,2-Bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthenetin dichloride (7). Tin dichloride (0.38 g, 2 mmol) was added to a solution of 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene, dtb-BIAN, (0.56 g, 1.0 mmol) in benzene (40 mL). The reaction mixture was stirred at 60° C for 60 h. The hot solution was filtered off from an excess of tin dichloride. Gradual cooling of the solution to room temperature afforded compound **7** as red-orange crystals. The yield was 0.72 g (87%), m.p. >200° C. Found (%): C, 66.87; H, 6.78; Sn, 14.57; Cl, 8.09. C$_{40}$H$_{48}$Cl$_2$N$_2$Sn·C$_6$H$_6$. Calculated (%): C, 67.00; H, 6.59; Sn, 14.39; Cl, 8.60. IR (Nujol mulls), ν/cm^{-1}: 1650 m, 1620 s, 1590 v.s, 1550 w, 1375 s, 1280 v.s, 1230 w, 1200 w, 1165 m, 1105 w, 1065 w, 1045 m, 965 s, 915 w, 895 w, 880 s, 825 v.s, 775 v.s, 680 s. ^{1}H NMR (200 MHz, CDCl$_3$, 20°C), δ: 7.78 (s, 2 H, Ar); 7.48 (d, 2H, Ar, *J* = 8.6 Hz); 7.32 (dd, 2 H, Ar, *J* = 8.2 Hz, *J* = 2.0 Hz); 7.18—7.16 and 6.77—6.70 (both m, 4 H each, Ar); 1.38 and 1.37 (both s, 18 H each, Bu^t).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneantimony trichloride (8). Antimony trichloride (0.23 g, 1.0 mmol) was added to a solution of 1,2-bis[(2,6-di-isopropylphenyl)imino]acenaphthene, dpp-BIAN (0.35 g, 0.7 mmol) in toluene (50 mL), after which the color of the reaction mixture became more intense. The solution was concentrated at high temperature by removing the solvent *in vacuo*. At room temperature, red-orange rhombic crystals of compound **8** precipitated from the solution. The yield was 0.60 g (74%), m.p. 160 °C. Found (%): C, 63.07; H, 5.91. C$_{36}$H$_{40}$Cl$_3$N$_2$Sb·C$_7$H$_8$. Calculated (%): C, 62.40; H, 5.49. IR (Nujol mulls), ν/cm^{-1}: 1641 m, 1615 m, 1581 v.s, 1490 w, 1318 w, 1279 m, 1252 w, 1181 m, 1165 m, 1105 w, 1090 w, 1050 m, 937 s, 834 s, 800 v.s, 780 v.s, 760 v.s, 735 m, 694 m. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C), δ: 7.30—7.08 (m, 6 H, Ar); 6.84—6.74 (m, 6 H); 3.38 (sept, 4 H, $\underline{H}$—CMe$_2$, *J* = 6.8 Hz); 1.47 (dd, 12 H, H—C$\underline{Me}_2$, *J* = 6.8 Hz); 0.97 (d, 12 H, H—C$\underline{Me}_2$, *J* = 6.8 Hz).

X-ray diffraction study of compounds 5—9. X-ray diffraction data for complexes **5—8** were measured on a Bruker AXS SMART APEX diffractometer (ω—φ scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 100 K. X-ray diffraction data for complex **9** were collected on a Siemens SMART CCD diffractometer (ω—φ scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. Absorption corrections were applied using the SADABS program.[16] The structures were solved by direct methods using the SHELXS97 program package[17] and refined by the full-matrix least-squares method against F^2 with the use of the SHELXL97 program package.[18] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms in **5**, **7**, and **8** were located from difference Fourier syntheses and refined isotropically, except for the H atoms of the disordered *tert*-butyl group (C(24), C(24´), C(25), C(25´), C(26), and C(26´)), the benzene solvate molecule in complex **5**, and the toluene solvate molecules in complex **8**, which were placed in idealized positions and refined using a riding model. In compounds **6a**, **6b**, and **9**, all hydrogen atoms were placed in idealized positions and refined using a riding model.

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