Stable Germylenes Derived from 1,2-Bis(arylimino)acenaphthenes

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Received March 26, 2004

Metal exchange reactions of the magnesium complexes (dpp-BIAN)Mg(THF)$_n$, (dtb-BIAN)Mg(THF)$_n$, and (bph-BIAN)Mg(THF)$_n$ with $GeCl_2$(dioxane) afford the stable germylenes (dpp-BIAN)Ge (**1**), (dtb-BIAN)Ge(Et_2O) (**2**), and (bph-BIAN)Ge (**3**), respectively (dpp-BIAN = 1,2-[(2,6-iPr$_2$C$_6$H$_3$)N]$_2$C$_{12}$H$_6$, dtb-BIAN = 1,2-[(2,5-tBu$_2$C$_6$H$_3$)N]$_2$C$_{12}$H$_6$, bph-BIAN = 1,2-[(2-PhC$_6$H$_4$)N]$_2$C$_{12}$H$_6$). Compound **1** is also obtained from (dpp-BIAN)Na$_4$ and GeCl$_4$ in Et$_2$O. The germylenes **1**−**3** were characterized by elemental analyses, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, and X-ray crystal structure analyses. In the monomeric molecules the two imino nitrogen atoms coordinate the germanium atom. The aryl(N) groups are arranged rather orthogonal to the acenaphthenediimine plane. Compound **3** shows an *anti* geometry with the *ortho* phenyl substituents of both N-phenyl rings positioned on opposite sides of the acenaphthenediimine plane. The bite angles N−Ge−N are 85.2° (**1**) and 85.0° (**3**), respectively. The Ge−N bond distances in **1**−**3** range from 1.878 to 1.915 Å.

Introduction

The present widespread interest in mononuclear compounds of divalent germanium is caused not only by the significance of such compounds in the fundamental chemical research[1] but also by the fact that they were recognized as versatile reagents in a number of important transformation reactions of organic substrates involving oxidation, addition, and insertion reactions.[2] Nitrogen-based ligands that stabilize the divalent state of group 14 elements as a result of the σ-acceptor character of their N atoms played an important role in the increasing development of the chemistry of divalent carbon, silicon, germanium, and tin.[3] Furthermore, theoretical and experimental results[4] indicate that molecular structures with delocalized heterocyclic π-systems improve the stability of divalent germanium compounds. Despite this principal knowledge, until now, only six basic types of such compounds (Chart 1) were described in the literature, the imidazogermoline-2-ylidene (I),[5] its benzo- (II),[6] pyrido- (III),[7] naphtho- (IV),[8] and tropo-annulated[9] analogues (V), and the ketoiminate[10] species (VI).

In the past decade, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) was a ligand, which was mostly used in the coordination chemistry of

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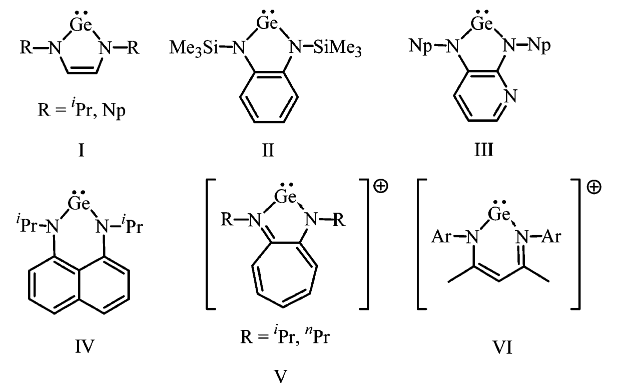
10.1021/om0497846 CCC: $27.50

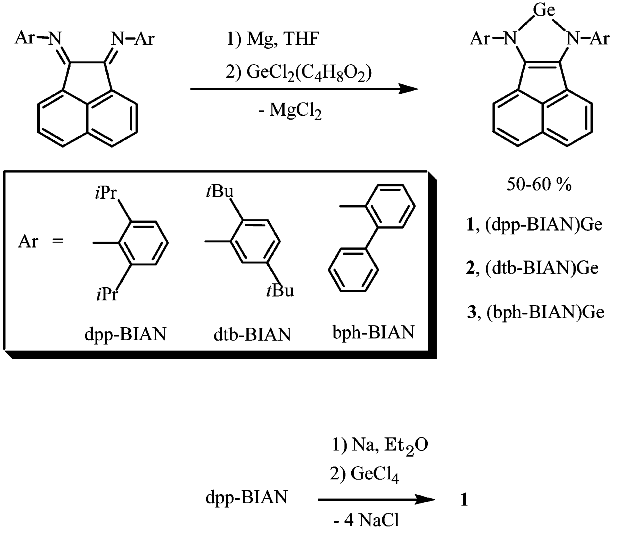
Chart 1



transition metals.[11] Recently, we reported on the preparation of two analogous ligands, 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene (dtb-BIAN) and 1,2-bis[(2-biphenyl)imino]acenaphthene (bph-BIAN).[12] The reduction of dpp-BIAN, dtb-BIAN, and bph-BIAN with activated Mg or Ca in THF affords the respective monomeric metal complexes (Ar-BIAN)M(THF)$_n$ (M = Mg, Ca) with dianionic ligands.[12,13] The use of sodium metal as reductive agent for dpp-BIAN causes the formation of sodium complexes containing not only the dianion but also the mono-, tri-, and tetraanion of the dpp-BIAN ligand.[14]

When we started our work on metal complexes with anionic Ar-BIAN ligands, we intended to prepare monomeric, highly reactive compounds, which in turn would be able to act as reducing as well as oxidizing agents. Thus, we could demonstrate that the complex (dpp-BIAN)Mg(THF)$_3$ serves well as reducing agent toward aromatic ketones such as diphenyl ketone and 9-(10*H*)-anthracenone[15] and reacts by way of an oxidative addition reaction with CH-acidic compounds such as phenylacetylene.[16] Continuing our studies on the chemical behavior of Ar-BIAN magnesium complexes, we suggested that these complexes may also be suitable for metal exchange reactions and that the dianionic Ar-BIAN^{2-} ligand with its delocalized heterocyclic π-system should be able to stabilize metals in low-valent states.

Scheme 1



Here we report on the synthesis of germylenes of the type (Ar-BIAN)Ge by reacting the corresponding (Ar-BIAN)Mg(THF)$_n$ complexes with GeCl$_2$(dioxane) or by reduction of GeCl$_4$ with (dpp-BIAN)Na$_4$.

Results and Discussion

Synthesis of (dpp-BIAN)Ge, (dtb-BIAN)Ge·Et$_2$O, and (bph-BIAN)Ge. The reduction of the 1,2-bis(arylimino)acenaphthene ligands dpp-BIAN, dtb-BIAN, and bph-BIAN (dpp-BIAN = 1,2-[(2,6-iPr$_2$C$_6$H$_3$)N]$_2$C$_{12}$H$_6$, dtb-BIAN = 1,2-[(2,5-tBu$_2$C$_6$H$_3$)N]$_2$C$_{12}$H$_6$, bph-BIAN = 1,2-[(2-PhC$_6$H$_4$)N]$_2$C$_{12}$H$_6$) with activated metallic magnesium in THF affords solutions containing the Mg complexes (dpp-BIAN)Mg(THF)$_n$,[13] (dtb-BIAN)Mg(THF)$_n$, and (bph-BIAN)Mg(THF)$_n$,[12] which we used in situ for reactions with GeCl$_2$(dioxane). In each case, the addition of GeCl$_2$(dioxane) to the green solutions of these magnesium complexes caused a rapid change in color to deep red. From these solutions the germylenes (dpp-BIAN)Ge (**1**), (dtb-BIAN)Ge·Et$_2$O (**2**), and (bph-BIAN)Ge (**3**) were isolated as stable, crystalline, deep red compounds by crystallization from THF (**1**), diethyl ether (**2**), or THF (**3**), respectively. Germylene **1** was also obtained by reduction of GeCl$_4$ with a suspension of (dpp-BIAN)Na$_4$[14] in Et$_2$O freshly prepared from dpp-BIAN (0.5 g, 1.00 mmol) and excess sodium (Scheme 1).

The IR spectra of **1**, **2**, and **3** confirm the dianionic character of the respective Ar-BIAN ligands. Whereas in the IR spectra of the free ligands the ν(C=N)

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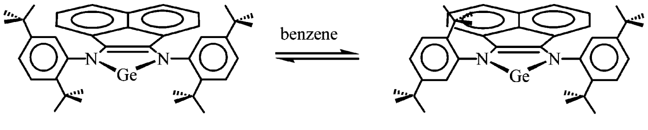
Scheme 2



interconversion of syn- and anti-isomers

vibrations, ranging from 1600 to 1700 cm^{-1}, cause the strongest absorptions[12,17] and the corresponding vibrations of the complex [(dpp-BIAN)CuBr]$_2$[17] in which dpp-BIAN acts as neutral ligand are shifted only little to lower wavenumbers, these ν(C=N) vibrations are nearly absent in the spectra of **1**, **2**, and **3**.

In the ^{1}H NMR spectrum of **1** the methyl protons of the four isopropyl groups give rise for two doublets centered at 1.28 and 1.03 ppm due to the restricted rotation of the 2,6-iPr$_2$C$_6$H$_3$ groups. The septet at 3.47 ppm is assigned to the methine protons. All aromatic protons appear as broad signals ranging from 6.5 to 7.5 ppm. The ^{13}C NMR spectrum clearly shows the 14 signals which are expected for the molecules of **1** possessing two mirror planes, one bisecting the N−Ge−N angle and the other running along the N−Ge−N plane. In the ^{1}H NMR spectrum of **2** recorded in C$_6$D$_6$, the methyl protons of the *tert*-butyl substituents give rise to one broad signal at 1.21 ppm and the signals of the ring protons are also extremely broadened. The spectrum obtained from a THF-d_8 solution of **2** did not show any assignable signals. The broadening of all the signals can be explained by a dynamic interconversion between *syn* and *anti* isomers of **2** since, in contrast to **1**, the absence of a substituent in the second *ortho* position of the phenyl rings allows these rings to rotate by 180° (Scheme 2). It should be noted here that in solutions of the starting magnesium complex (dtb-BIAN)Mg(THF)$_2$[12] the presence of *syn* and *anti* isomers (2:1 ratio) could be proved by ^{1}H NMR spectroscopy. The room-temperature ^{13}C NMR spectrum of **2** shows very broadened resonances. The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ is not expressive because the signals of the 12 nonequivalent aromatic protons appear in the very narrow range of 6.95−7.60 ppm. However, the ^{13}C NMR spectrum of **3** shows 17 signals, thus indicating the presence of only one isomer in solution.

Molecular Structures of Compounds 1 and 3. The crystal and structure refinement data of the compounds are listed in Table 1, and their molecular structures are depicted in Figures 1 and 2. Refinement of the data of **2** did not give satisfactory results. Therefore those data are not discussed. They are listed in the Supporting Information.

Compounds **1** and **3** crystallize in the monoclinic space groups $P2_1/n$ and $C2/c$, respectively. In each case, the unit cell contains four molecules. According to the space group, the crystal structure of **3** shows C_2 symmetry.

Because of the unsymmetrical substitution of the phenyl rings in **3**, the molecule can show *syn* or *anti* configuration. Germylene **3** exhibits *anti* configuration. The bite angles N−Ge−N of **1** (85.2°) and **3** (85.0°) are only slightly smaller than that in 1,3,2-diazagermoline-2-ylidene C$_2$H$_2$[N(CH$_2t$Bu)]$_2$Ge (87.7°).[7] The Ge−N bond lengths in **1** [1.896(3) Å] and **3** [1.878(3) Å] are longer than those in C$_2$H$_2$[N(CH$_2t$Bu)]$_2$Ge [1.808(1) Å],[7] C$_6$H$_4$-[N(SiMe$_3$)]$_2$Ge [1.866(9),186.1(8) Å],[6] and C$_{10}$H$_6$(NiPr)$_2$-Ge [1.8417(17), 1.8420(16) Å],[8] but are shorter than the

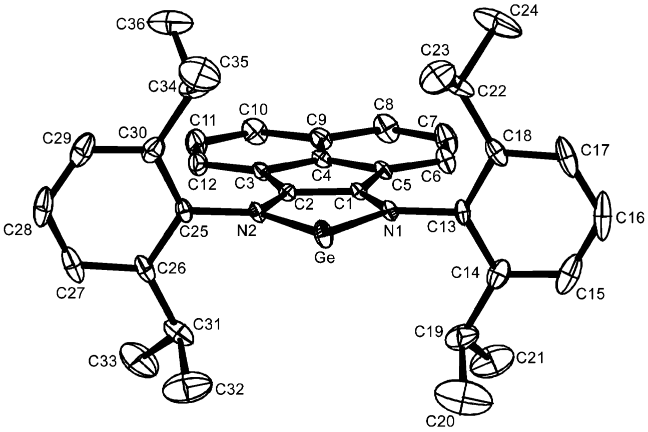


Figure 1. ORTEP presentation of the molecular structure of **1**. Thermal ellipsoids drawn at 30% probability. The hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Ge−N(1) 1.896(3), Ge−N(2) 1.885(3), N(1)−C(13) 1.425(4), N(2)−C(25), 1.432(5), C(1)−C(2) 1.381(5), C(1)−C(5) 1.458(5), C(3)−C(12) 1.376(5), C(3)−C(4) 1.415(5), C(4)−C(5) 1.422(5), C(5)−C(6) 1.372(5), C(7)−C(8) 1.380(6), C(8)−C(9) 1.422(6), C(10)−C(11) 1.367(6), C(11)−C(12) 1.432(5), C(13)−C(14) 1.408(5), C(4)−C(9) 1.404(5), N(1)−C(1) 1.374(4), C(6)−C(7) 1.426(6), N(2)−C(2) 1.370(4), C(9)−C(10) 1.422(6), C(2)−C(3) 1.473(5), C(13)−C(18) 1.407(5); N(2)−Ge−N(1) 85.20(12), C(1)−N(1)−Ge 112.0(2), C(2)−N(2)−Ge 112.0(2), C(25)−N(2)−Ge 126.8(2), C(2)−N(2)−C(25) 121.1(3), C(13)−N(1)−Ge 125.7(2), C(1)−N(1)−C(13) 122.4(3).

Table 1. Crystal Data and Structure Refinement Details for 1 and 3

	1	3
empirical formula	C$_{36}$H$_{40}$GeN$_2$	C$_{36}$H$_{24}$GeN$_2$
fw	573.29	557.16
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
unit cell dimens, Å, deg	a = 12.9536(2)	a = 15.7687(5)
	b = 18.5400(2)	b = 11.0059(3)
	c = 13.8698(1)	c = 16.5298(6)
	β = 110.409(1)	β = 110.870(1)
volume, Å^3	3121.87(6)	2680.51(15)
Z	4	4
density(calcd), g/cm^3	1.220	1.381
μ, mm^{-1}	1.007	1.171
F(000)	1208	1144
cryst size, mm^3	0.60 × 0.34 × 0.14	0.28 × 0.28 × 0.08
θ range for data collection, deg	1.85−27.50	2.31−26.00
index ranges	$-16 \leq h \leq 16$	$-19 \leq h \leq 19$
	$-24 \leq k \leq 18$	$-9 \leq k \leq 13$
	$-13 \leq l \leq 18$	$-17 \leq l \leq 20$
no. of reflns collected	23 233	6935
no. of indep reflns	7139 [$R_{\rm int}$ = 0.0953]	2564 [$R_{\rm int}$ = 0.0870]
max./min. transmn	0.9002/0.1728	0.9319/0.5533
no. of data/restraints/params	7139/0/360	2564/0/178
goodness-of-fit on F^2	1.002	1.007
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0660	R_1 = 0.0596
	wR_2 = 0.1497	wR_2 = 0.0985
R indices (all data)	R_1 = 0.1212	R_1 = 0.1342
	wR_2 = 0.1748	wR_2 = 0.1196
largest diff peak/hole, e Å^{-3}	0.906/−1.161	0.521/−0.751

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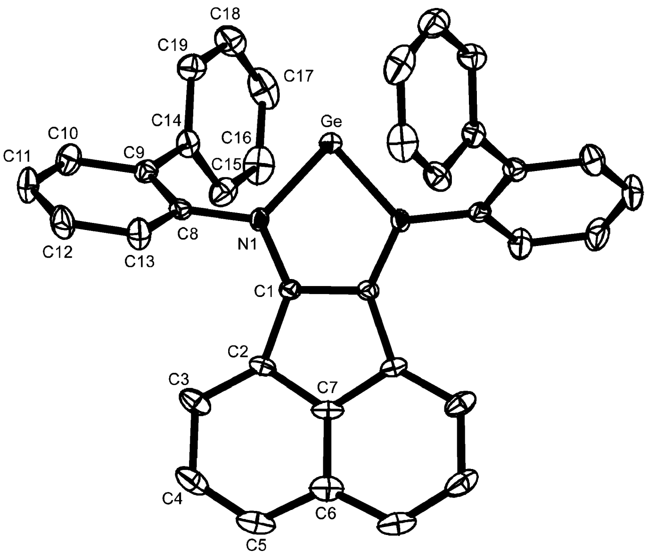

Figure 2. ORTEP presentation of the molecular structure of **3**. Thermal ellipsoids drawn at 30% probability. The hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Ge−N(1) 1.878(3), N(1)−C(1) 1.382(5), C(1)−C(1#) 1.395(8), C(1)−C(2) 1.457(6), C(2)−C(7) 1.416(5), C(3)−C(4) 1.421(6), C(5)−C(6) 1.414(6), C(6)−C(7) 1.408(8), C(7)−C(2) 1.416(5), C(8)−C(13) 1.380(6), C(9)−C(10) 1.406(6), C(9)−C(14) 1.486(6), C(11)−C(12) 1.369(7), C(12)−C(13) 1.389(6), C(14)−C(15) 1.391(7), C(15)−C(16) 1.379(7), C(17)−C(18) 1.356(8), C(18)−C(19) 1.383(7), N−C(8) 1.427(5), C(8)−C(9) 1.390(6), C(2)−C(3) 1.370(6), C(10)−C(11) 1.364(7), C(4)−C(5) 1.368(7), C(14)−C(19) 1.391(7), C(6)−C(5) 1.414(6), C(16)−C(17) 1.397(9); N(1)−Ge−N(1#) 85.0(2), C(1)−N(1#)−C(8) 121.1(3), C(8)−N(1)−Ge 125.6(3), N(1)−C(1)−C(1#) 114.4(2), C(1)−N(1)−Ge 113.0(3), N(1)−C(1)−C(2) 136.2(4).

Ge−N distances in the tropo-annulated three-coordinate germylene [1,2-C_7H_5(N-*i*Pr)$_2$]GeCl [av 1.956(4) Å].[9] They are in the range of the Ge−N distances in [($Me_3Si)_2N]_2Ge$ [1.878(5), 1.873(5) Å].[18]

The comparison of the N−C and C−C bond distances within the metallacycles Ge−N(1)−C(1)−C(2)−N(2) of **1** and **3** with those of the respective magnesium- and calcium-containing metallacycles in (dpp-BIAN)Mg(THF)$_2$,[13a] (dtb-BIAN)Mg(THF)$_2$,[12] and (bph-BIAN)Ca(THF)$_3$[12] shows that in the germylenes these distances are somewhat shorter than in the alkaline earth complexes. This fact may be explained by a more effective overlap of the empty p-orbitals of germanium(II) with the orbitals containing the π-electrons of the C=C double bond and the electron pairs of the nitrogen atoms.

The dihedral angles formed between the phenyl rings attached to the N atoms and the plane formed by the diimine portion are listed in Table 2.

Table 2. Dihedral Angles in 1 and 3

	1	3
plane1/plane2	89.16(16)	59.64(19)
plane1/plane3	86.21(13)	

Plane 1 is formed from the atoms C(1)−C(12), N(1), N(2), and Ge in **1** and from the atoms C(1)−C(7), N(1), and Ge in **3**. Plane 2 is formed from the atoms C(13)−C(18) in **1** and from the atoms C(8)−C(13) in **3**. Plane 3 is formed from the atoms C(25)−C(30) in **1**.

In **1** and **2** the phenyl rings are almost orthogonal to the diimine plane, whereas in **3** the absence of a second substituent at the phenyl ring allows a rotation around the N−C(ipso) bond to a certain degree. The dihedral angle between the phenyl rings of the diphenyl moiety is 64.8(2)°.

Experimental Section

General Remarks. All manipulations were carried out under vacuum using Schlenk ampules. The solvents Et_2O, THF, benzene, and toluene were dried by distillation from sodium/benzophenone. The deuterated solvents THF-d_8 and C_6D_6 (Aldrich) used for the NMR measurements were dried with sodium/benzophenone at ambient temperature. They were, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compound. $GeCl_2$(dioxane) was purchased from ABCR. The melting points were measured in sealed capillaries. The IR spectra were recorded on a Specord M80 spectrometer; the ^1H and $^{13}C\{^1H\}$ NMR spectra, on a Bruker DPX-200 NMR spectrometer (^1H, 200 MHz; ^{13}C, 50.32 MHz). Chemical shifts are reported in ppm relative to the ^1H and $^{13}C\{^1H\}$ residues of the deuterated solvents.

Synthesis of (dpp-BIAN)Ge (1). (a) From (dpp-BIAN)Mg(THF)$_n$ and $GeCl_2$ (dioxane). To a solution of (dpp-BIAN)Mg(THF)$_n$[13] in THF (freshly prepared from 0.5 g (1.00 mmol) of BIAN and activated magnesium) was added $GeCl_2(C_4H_8O)$ (0.23 g, 1.0 mmol). The color of the solution quickly changed from emerald-green to red-brown. When the change in color was finished, the volatile components were removed under vacuum and the solid residue was digested with toluene. The remaining $MgCl_2$ was separated by decantation. Concentration of the toluene solution under vacuum afforded **1** (0.31 g, 55%) as red crystals.

(b) From (dpp-BIAN)Na_4 and $GeCl_4$. To a cooled (−30 °C) suspension of (dpp-BIAN)Na_4[14] in Et_2O (freshly prepared from dpp-BIAN (0.5 g, 1.00 mmol) and excess sodium) was added $GeCl_4$ (0.21 g, 1.00 mmol) by condensation in a vacuum. Warming up the reaction mixture to ambient temperature with shaking caused gradual dissolution of the powdery, brick-red (dpp-BIAN)Na_4, producing a red solution and a fine colorless powder. The mixture was stirred at 20 °C for 1 h. Then all volatiles were removed under vacuum at ambient temperature within 30 min. To the remaining solid residue toluene (45 mL) was added. The mixture was heated to 70 °C for 10 min and was then cooled to ambient temperature and subsequently centrifuged. The red solution was decanted from the settled NaCl and was reduced in volume to 10 mL by evaporation of the solvent in a vacuum. From this concentrated toluene solution compound **1** (0.29 g, 51%) separated as deep red crystals. Mp > 235 °C (dec). IR (Nujol): 1670 w, 1610 m, 1580 m, 1550 w, 1520 m, 1320 s, 1250 m, 1210 w, 1170 m, 1100 w, 1050 w, 1030 w, 930 m, 810 m, 800 m, 760 s, 680 w, 620 w, 530 w cm^{-1}. ^1H NMR (C_6D_6): δ 1.06 (d, 12H, $^3J = 6.8$ Hz), 1.28 (d, 12H, $^3J = 6.8$ Hz), 3.47 (spt, 4H, $^3J = 6.8$ Hz), 6.51 (s, br, 2H), 6.85 (s, br, 2H), 1.06 (d, 12H, $^3J = 6.8$ Hz), 6.95−7.53 (m, br, 8H). ^{13}C NMR (C_6D_6): δ 23.52, 25.88, 28.57, 123.81, 125.46, 125.88, 127.61, 127.98, 128.10, 129.10, 131.44, 132.18, 137.65, 144.96. Anal. Calcd for $C_{36}H_{40}N_2Ge$ (573.29): C, 75.42; H, 7.03. Found: C, 74.44; H, 7.09.

Synthesis of (dtb-BIAN)Ge·Et_2O (2). To a solution of (dtb-BIAN)Mg(THF)$_n$[12] in THF (freshly prepared from dtb-BIAN (0.56 g, 1.00 mmol) and activated magnesium) was added $GeCl_2$(dioxane) (0.23 g, 1.00 mmol). The color of the solution quickly turned from emerald-green to red-brown. When the change in color was finished, the solvent was removed under vacuum and diethyl ether (40 mL) was added to the remaining solid. The suspension formed was filtered to separate the

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[18] Chorley, R. W.; Hitchcock, P. B.; Lappert, F. M.; Leung, W.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta* **1992**, 198.

residual $MgCl_2$. On standing of the red solution at ambient temperature, compound **2** (0.30 g, 53%) separated as deep red crystals. Mp = 219 °C. IR (Nujol): 1610 m, 1550 m, 1330 w, 1300 w, 1280 m, 1160 w, 1120 m, 1080 m, 1040 w, 980 m, 940 m, 880 w, 820 m, 780 m, 680 w, 620 w, 600 w cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.21 (t, 6H, Et_2O), 1.31 (vb, 36H CH_3(*t*Bu), 3.35 (q, 4H, Et_2O). ^{13}C NMR (C_6D_6): δ 30.86 (vb, 12 C, CH_3(tBu)). Anal. Calcd for $C_{40}H_{48}N_2Ge\times(C_4H_{10}O)$ (703.51): C, 75.12; H, 8.31; Ge, 10.32. Found: C, 75.00; H, 8.21; Ge, 10.18.

Synthesis of (bph-BIAN)Ge (3). To a solution of (bph-BIAN)Mg(THF)$_n$[12] in THF (freshly prepared from dph-BIAN (0.48 g, 1.00 mmol) and activated magnesium) was added $GeCl_2$(dioxane) (0.23 g, 1.00 mmol). The color of the solution quickly turned from emerald-green to red-brown. When the change in color was finished, the solvent was removed in a vacuum and benzene (30 mL) was added to the remaining solid. The suspension formed was filtered to separate residual $MgCl_2$. Evaporation of the solvent from the solution and crystallization of the crude product from THF at room temperature afforded **3** (0.32 g, 58%) as deep red crystals. Mp > 170 °C (dec). IR (Nujol): 1600 w, 1570 w, 1560 w, 1310 w, 1270 m, 1150 m, 1070 w, 1050 w, 1005 m, 970 w, 950 m, 910 m, 815 m, 770 s, 750 s, 700 s, 620 w, 550 m cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.60−6.95 (m, 24H). ^{13}C NMR (C_6D_6): δ 119.37, 125.88, 126.12, 127.19, 127.45, 127.51, 127.59, 127.95, 127.96, 128.41, 128.63, 129.04, 129.36, 129.65, 130.42, 131.67, 136.40. Anal. Calcd for $C_{36}H_{24}N_2Ge$ (557.16): C, 77.60; H, 4.34; Ge, 13.03. Found: C, 75.22; H, 4.56; Ge, 14.11.

X-ray Crystal Structure Determination of Compounds 1−3. The data were collected on a SMART CCD diffractometer (T = 173 K, graphite-monochromated Mo Kα radiation, ω-scan technique, λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[19] and were refined on F^2 using SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. SADABS[21] was used to perform area-detector scaling and absorption corrections. The geometrical aspects of the structures were analyzed using the PLATON program.[22]

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (Grant No. 03-03-32246), the Russian Science Support Foundation (I.L.F.), and the Fonds der Chemischen Industrie. The authors thank Dr. Yu. A. Kurskii for recording the NMR spectra.

Supporting Information Available: Full details of the X-ray structural analyses of compounds **1**−**3**, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0497846

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