Inorganic Chemistry
Article

Divalent Germanium Compound with a Radical-Anionic Ligand: Molecular Structures of (dpp-BIAN)•−GeCl and Its Hydrochloration Products [(dpp-BIAN)(H)₂]•+[GeCl₃]− and [{(dpp-BIAN)(H)₂•+}₂(Cl−)]+[GeCl₃]− (dpp-BIAN = 1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthene)

Igor L. Fedushkin,* Natalie M. Khvoinova, Andrey Yu. Baurin, Georgii K. Fukin, Vladimir K. Cherkasov, and Mikhail P. Bubnov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, GSP-445, Russia

The germanium(II) compound (dpp-BIAN)GeCl (**1**), which contains the radical anion of dpp-BIAN can be prepared either by reacting free dpp-BIAN ligand with 2 equiv of GeCl₂(1,4-dioxane) in Et₂O or by metathetical reaction of the sodium salt of dpp-BIAN with germanium dichloride in Et₂O or benzene. The reaction of benzene solutions of **1** with 2 or 3 equiv of HCl led to protonation of the dpp-BIAN ligand affording [(dpp-BIAN)(H)₂]•+[GeCl₃]− (**2**) and [{(dpp-BIAN)(H)₂•+}₂(Cl−)]+[GeCl₃]− (**3**), which incorporate the radical cation of the protonated ligand. Compounds **1**−**3** have been characterized by elemental analysis, IR, UV−vis, and electron spin resonance (ESR) spectroscopy. Molecular structures of **1**−**3** were determined by single-crystal X-ray diffraction. In molecule **1**, the Ge atom is positioned at the apex of the slightly distorted trigonal pyramid. The Ge−N bond lengths in **1** are 2.0058(19) and 2.004(2) Å. The molecular structure of **2** consists of contact ions [(dpp-BIAN)(H)₂]+ and [GeCl₃]−. In the molecular structure of **3**, two radical cations of [(dpp-BIAN)(H)₂]+ are "coordinated" by the chlorine anion. The ESR signal of **1** indicates the presence of a dpp-BIAN radical anion and shows a hyperfine structure due to the coupling of an unpaired electron to ^{14}N, ^{73}Ge, ^{35}Cl, ^{37}Cl, and ^{1}H nuclei (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). Both **2** and **3** reveal ESR signals of radical cation [(dpp-BIAN)(H)₂]•+ (septet, A_N = 0.53, A_H = 0.48 mT, g = 2.0031).

Introduction

The present work is a part of our recently initiated research on the main group metal complexes of 1,2-bis(arylimino)acenaphthene ligands (Ar−BIAN). Within the past decade, transition-metal complexes of these rigid bidentate ligands were studied intensively because of a wide range of applications in catalytic reactions.[1] The non-transition-metal complexes of the neutral ligand of type [(dpp-BIAN)(MCl₂)]+-[MCl₄]− (dpp-BIAN = 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene, M = B, Ga) were first reported in 2002.[2] One year later, we described a series of alkaline and alkaline-earth metal complexes with different anionic forms of dpp-BIAN (e.g., M+$_n$(dpp-BIAN)$^{n−}$ (M = Li, Na; n = 1−4)[3a,b] and M²⁺(dpp-BIAN)²⁻ (M = Mg, Ca)).[3c,d] The study of reactivity of dpp-BIAN−Mg and −Ca complexes toward organic substrates showed that these might be useful reagents for organic synthesis.[3e−g] The group 3 metal complex (dpp-BIAN)GaCl₂ with the radical-anionic ligand has been reported by Jones et al.[4] Recently, we succeeded in isolation of stable germylenes derived from three different Ar−BIAN ligands (e.g., (dpp-BIAN)Ge, (dtb-BIAN)Ge, and (dph-BIAN)Ge (Chart 1)).[5]

(1) (a) van Laren, M. W.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715−3717. (b) Grasa, G. A.; Singh, R.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2003**, *687*, 269−279. (c) Heumann, A.; Giordano, L.; Tenaglia, A. *Tetrahedron Lett.* **2003**, *44*, 1515−1518. (d) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2003**, 2566−2567. (e) Al-Abaidi, F.; Ye, Z.; Zhu, S. *Macromol. Chem. Phys.* **2003**, *204*, 1653−1659. (f) Fassina, V.; Ramminger, C.; Seferin, M.; Mauler, R. S.; de Souza, R. F.; Monteiro, A. L. *Macromol. Rapid Comm.* **2003**, *24*, 667−670. (f) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068−3081. (g) Takeuchi, D.; Yasuda, A.; Osakada, K. *J. Chem. Soc., Dalton Trans.* **2003**, 2029−2035. (h) Kiesewetter, J.; Kaminsky, W. *Chem.−Eur. J.* **2003**, *9*, 1750−1758.

* Author to whom correspondence should be addressed. E-mail: igorfed@imoc.sinn.ru.

Chart 1

Ar = dpp-BIAN   dtb-BIAN   dph-BIAN
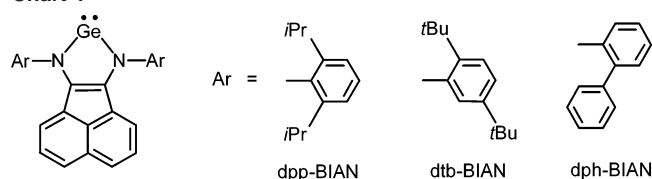
Ligands with nitrogen donors play an important role in the increasing development of the chemistry of germanium in the oxidation state +2.[6,7] Until now, the following types of such compounds were described in the literature: the imidazogermoline-2-yliden,[6a] its benzo-,[6b] pyrido-,[6c] naphtho-,[6d] and tropo-annulated[6e] analogues. A variety of germanium(II) compounds supported by ketiminate ligands has been reported as well.[7] A review article on the ketiminate metal complexes appeared recently.[8]

Heteroleptic complexes of the type $(L)^-Ge^{2+}X^-$ (L = tropo- or ketiminate; X^- = F, Cl, I, RO, Me, CF_3SO_3, N_3) contain N-ligands in their chelating monoanionic form.[7] These compounds represent both fundamental and practical interests. They have been recognized as promising reagents

in a number of reactions involving oxidation, addition, and insertion reactions.[6e,7e,g,h] Different experimental (X-ray diffraction, NMR, and photoelectron spectroscopy) and computational methods (B3LYP) were applied for understanding these three-coordinate germanium(II) compounds. Despite this extensive research in the field of Ge(II) complexes with N-based ligands, to date there are no examples of unambiguously characterized heteroleptic Ge(II) compounds containing paramagnetic ligands. Bearing in mind that electron spin resonance (ESR) spectroscopic data on the paramagnetic species $(L)^{\bullet-}Ge^{2+}X^-$ may give new insight into the electronic structure of the three-coordinate Ge(II) compounds, we started preparation of a Ge(II) derivative with a dpp-BIAN radical-anionic ligand.

In this article, we report on the synthesis and crystal structure of (dpp-BIAN)$^{\bullet-}$GeCl as well as its spectroscopic characterization by means of ESR, IR, and electron absorption spectroscopy. We also describe the formation of the radical cation $[(dpp\text{-}BIAN)(H)_2]^{\bullet+}$ from radical anion (dpp-BIAN)$^{\bullet-}$ under protonation of (dpp-BIAN)$^{\bullet-}$GeCl with HCl.

Results and Discussion

Synthesis and Molecular Structure of Compounds 1−3. The germanium(II) compound (dpp-BIAN)GeCl (**1**), which contains the radical anion of dpp-BIAN, can be prepared in two different ways: (1) by reacting free dpp-BIAN ligand with 2 equiv of $GeCl_2(1,4\text{-dioxane})$ in diethyl ether or (2) by metathetical reaction of the sodium salt of dpp-BIAN with germanium dichloride either in Et_2O or benzene (Scheme 1).

In the reaction of $GeCl_2(1,4\text{-dioxane})$ with free dpp-BIAN, germanium dichloride acts as reducing agent toward the diimine ligand. Our preliminary study showed that the reduction potential of dpp-BIAN radical anion in tetrahydrofuran (THF) equals −1.5 V versus a saturated calomel electrode. Besides **1**, this redox reaction produces a second product, which crystallizes from the reaction mixture together with **1** in the form of colorless crystals. Although this byproduct was not identified, the absence of signals in its ^1H NMR spectrum and the stoichiometry of **1** allowed suggesting that this second product is hexachlorodigermane.

Compound **1** crystallizes from either benzene or Et_2O as deep red crystals. An exposure of the reaction mixture formed from the reaction of $GeCl_2(1,4\text{-dioxane})$ with free dpp-BIAN to air caused a color change from cherry red to deep green. As shown below, this color change reflects the formation of the protonated radical cation of dpp-BIAN.

The reaction of benzene solutions of **1** formed during the course of the metathetical reaction with 2 or 3 equiv of HCl affords compounds **2** and **3**, respectively (Scheme 2). Compounds **2** and **3** crystallized from benzene as deep green crystals. In crystalline form, these compounds are relatively stable to air and show no sign of decomposition within a few days. Compounds **1−3** have been characterized by elemental analysis, IR, UV−vis, and ESR spectroscopy.
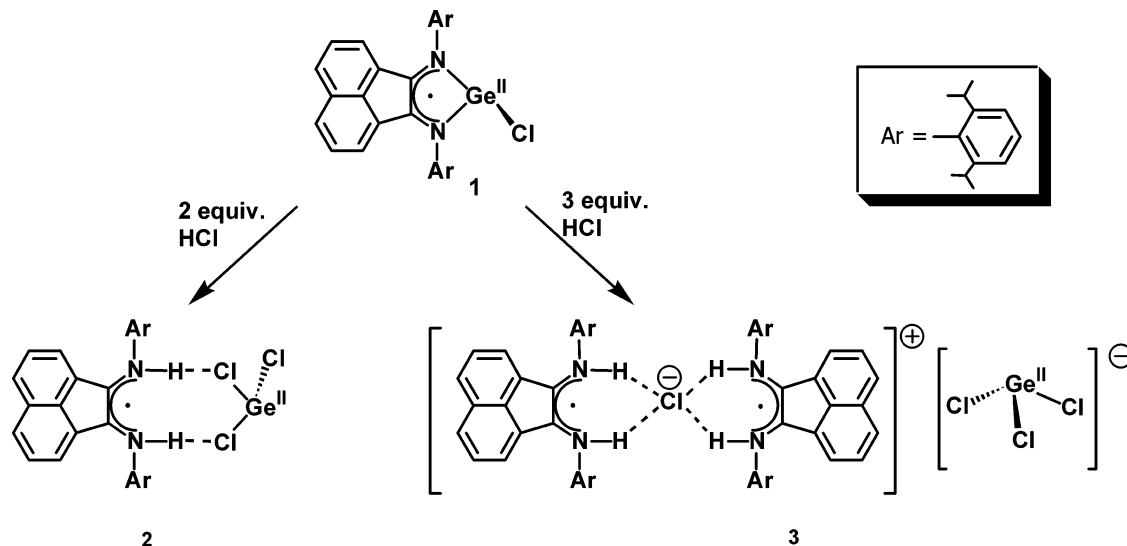
Molecular structures of **1−3** were determined by single-crystal X-ray diffraction. The crystallographic data for **1−3**

(2) Jenkins, H. A.; Dumaresque, C. L.; Vidovic, D.; Clyburne, J. A. C. *Can. J. Chem.* **2002**, *80*, 1398−1403.

(3) (a) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3294−3298. (b) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Cherkasov, V. K.; Chudakova, V. A.; Fukin, G. K.; Lopatin, M. A. *Eur. J. Inorg. Chem.* **2004**, 388−393. (c) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K.; Dechert, S.; Schumann, H. *Eur. J. Inorg. Chem.* **2003**, 3336−3346. (d) Fedushkin, I. L.; Chudakova, V. A.; Skatova, A. A.; Khvoinova, N. M.; Kurskii, Yu. A.; Glukhova, T. A.; Fukin, G. K.; Dechert, S.; Hummert, M.; Schumann, H. *Z. Anorg. Allg. Chem.* **2004**, *630*, 501−507. (e) Fedushkin, I. L.; Skatova, A. A.; Cherkasov, V. K.; Chudakova, V. A.; Dechert, S.; Hummert, M.; Schumann, H. *Chem.−Eur. J.* **2003**, *9*, 5778−5783. (f) Fedushkin, I. L.; Khvoinova, N. M.; Skatova, A. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 5223−5226. (g) Fedushkin, I. L.; Skatova, A. A.; Lukoyanov, A. N.; Chudakova, V. A.; Dechert, S.; Hummert, M.; Schumann, H. *Russ. Chem. Bull.* In press.

(4) Baker, R. J.; Jones, C.; Kloth, M.; Mills, D. P. *New J. Chem.* **2004**, *28*, 207−213.

(5) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Khvoinova, N. M.; Baurin, A. Yu.; Dechert, S.; Hummert, M.; Schumann, H. *Organometallics* **2004**, *23*, 3714−3718.

(6) (a) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed.* **1992**, *31*, 1485−1488. (b) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245−252. (c) Kühl, O.; Lönnecke, P.; Heinicke, J. *Polyhedron* **2001**, *20*, 2215−2222. (d) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162−11167. (e) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650−4655.

(7) (a) Ayers, A. E.; Klapötke, T. M.; Dias, H. V. R. *Inorg. Chem.* **2001**, *40*, 1000−1005. (b) Stender, M.; Phillips, A. D.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 5314−5315. (c) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G.; Power, P. P. *Organometallics* **2001**, *20*, 1190−1194. (d) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Organometallics* **2001**, *20*, 4806−4811. (e) Akkari, A.; Byrne, J. J.; Saur, I.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2001**, *622*, 190−198. (f) Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Usón, I.; Noltemeyer, M.; Schmidt, G. *Organometallics* **2002**, *21*, 5216−5220. (g) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, G. *J. Am. Chem. Soc.* **2002**, *124*, 8542−8543. (h) Saur, I.; Rima, G.; Gornitzka, H.; Miqueu, K.; Barrau, J. *Organometallics* **2003**, *22*, 1106−1109. (i) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2003**, *672*, 77−85. (j) Saur, I.; Miqueu, K.; Rima, G.; Barrau, J.; Lemierre, V.; Chrostowska, A.; Sotiropoulos, J.-M.; Pfister-Guillouzo, G. *Organometallics* **2003**, *22*, 3143−3149.

(8) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.

Scheme 1
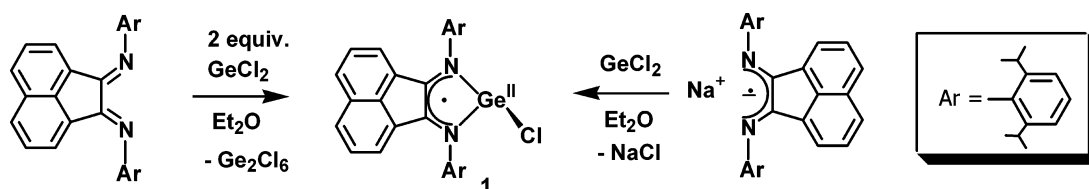
Scheme 2

Table 1. Crystal Data and Structure Refinement Details for **1**, **2**, and **3**

compound	1	2	3
empirical formula	$C_{36}H_{40}ClGeN_2$	$C_{36}H_{41}Cl_3GeN_2$	$C_{87}H_{99}Cl_4GeN_4$
fw	608.74	680.65	1415.09
temperature, K	100(2)	120(2)	100(2)
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
unit cell dimensions Å, degree	$a = 10.4153(12)$	$a = 10.131(3)$	$a = 21.3305(12)$
	$b = 19.789(2)$	$b = 13.696(2)$	$b = 15.6716(9)$
	$c = 15.8871(19)$	$c = 22.431(5)$	$c = 24.0119(13)$
	$\beta = 105.369(2)$	$\alpha = \beta = \gamma = 90$	$\beta = 99.0300(10)$
volume, Å^3	3157.4(6)	3419.6(13)	7927.3(8)
Z	4	4	4
density (calc), Mg/m^3	1.281	1.322	1.186
absorption coefficient, mm^{-1}	1.081	1.157	0.567
F(000)	1276	1416	2996
crystal size, mm^3	$0.15 \times 0.15 \times 0.08$	$0.17 \times 0.15 \times 0.04$	$0.30 \times 0.25 \times 0.20$
θ range for data collection, deg	1.68 to 24.99	1.74 to 23.31	1.56 to 24.00
reflections collected	16 457	16 088	39 209
independent reflections ($I > 2\sigma(I)$)	5564 (R(int) = 0.0282)	4934 (R(int) = 0.0417)	12 440 (R(int) = 0.0304)
data/restraints/parameters	5564/9/514	4934/9/543	12 440/11/1209
goodness of fit on F^2	1.060	0.972	1.020
final R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0416$	$R_1 = 0.0326$	$R_1 = 0.0441$
	$wR_2 = 0.1074$	$wR_2 = 0.0713$	$wR_2 = 0.1067$

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

are listed in Table 1. The molecular structures of **1**, **2**, and **3** are depicted in Figures 1, 2, and 3, respectively. Selected bond distances and angles for **1**–**3**, together with geometrical parameters for the two-coordinate germanium(II) complex of dianionic dpp-BIAN ligand, (dpp-BIAN)Ge,[5] three-coordinate tropo-α-diketiminate [1,2-C$_7$H$_5$(N^{i}Pr)$_2$]GeCl,[6e] and β-diketiminate [CH{C(Me)NPh}$_2$]GeCl,[7h] are presented in Table 2. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The main bond lengths and angles in **1** can be compared with those of (dpp-BIAN)Ge[5] and three-coordinate Ge(II) complexes with chelating N-based ligands (e.g., ketiminates [1,2-C$_7$H$_5$-(N^{i}Pr)$_2$]GeCl,[6e] [1,2-C$_7$H$_5$(NMe)$_2$]GeCl,[6e] [CH{C(Me)N-(Mes)}$_2$]GeCl,[7a] and [CH{C(Me)NPh}$_2$]GeCl[7h]). In molecule **1** (Figure 1), as well as in all three-coordinate species mentioned above, the germanium atom is positioned at the apex of the slightly distorted trigonal pyramid.

The sum of the bond angles around the germanium atom (N(2)−Ge(1)−N(1), 81.57(8)°; N(2)−Ge(1)−Cl(1), 98.63-(6)°; N(1)−Ge(1)−Cl(1), 96.64(6)°) is 276.8°, slightly exceeds the value expected for ideal pyramidal geometry (270°), and is significantly smaller than values for tetrahedral

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, **3**, (dpp-BIAN)Ge, [1,2-C$_7$H$_5$(N^{i}Pr)$_2$]GeCl, and [CH{C(Me)NPh}$_2$]GeCl

compound	**1**	**2**	**3**	(dpp-BIAN)Ge[a]	[1,2-C$_7$H$_5$(N^{i}Pr)$_2$]GeCl[b]	[CH{C(Me)NPh}$_2$]GeCl[c]
			Bond Lengths			
Ge−N(1)	2.0058(19)			1.896(3)	1.956(4)	1.955(2)
Ge−N(2)	2.004(2)			1.885(3)	1.956(4)	1.965(1)
Ge−Cl(1)	2.2693(8)	2.3385(7)	2.2830(8)		2.368(2)	2.340(6)
Ge−Cl(2)		2.3128(7)	2.2789(8)			
Ge−Cl(3)		2.2462(8)	2.3161(7)			
N(1)−C(1)	1.326(3)	1.344(2)	1.329(3)	1.374(4)	1.341(6)[d]	1.337(2)[d]
N(2)−C(2)	1.329(3)	1.326(2)	1.333(3)	1.370(4)	1.341(6)[d]	1.338(2)[d]
N(3)−C(37)			1.330(3)			
N(4)−C(38)			1.330(3)			
N(1)−H(1)		0.82(2)	0.87(2)			
N(2)−H(2)		0.90(2)	0.89(2)			
N(3)−H(3)			0.88(2)			
N(4)−H(4)			0.88(2)			
C(1)−C(2)	1.421(3)	1.447(3)	1.442(3)	1.381(5)		
C(37)−C(38)			1.439(3)			
			Bond Angles			
N(1)−Ge−N(2)	81.57(8)			85.20(12)	80.3(2)	90.28(6)
Cl(1)−Ge−Cl(2)		92.75(3)	97.92(3)			
Cl(2)−Ge−Cl(3)		96.28(3)	96.78(3)			
Cl(1)−Ge−Cl(3)		94.86(3)	96.29(3)			
N(1)−Ge−Cl(1)	96.64(6)				96.6(1)	93.55(5)
N(2)−Ge−Cl(1)	98.63(6)				96.6(1)	94.95(4)

[a] Reference 5. [b] Reference 6e. [c] Reference 7h. [d] C-imino metallacycle.
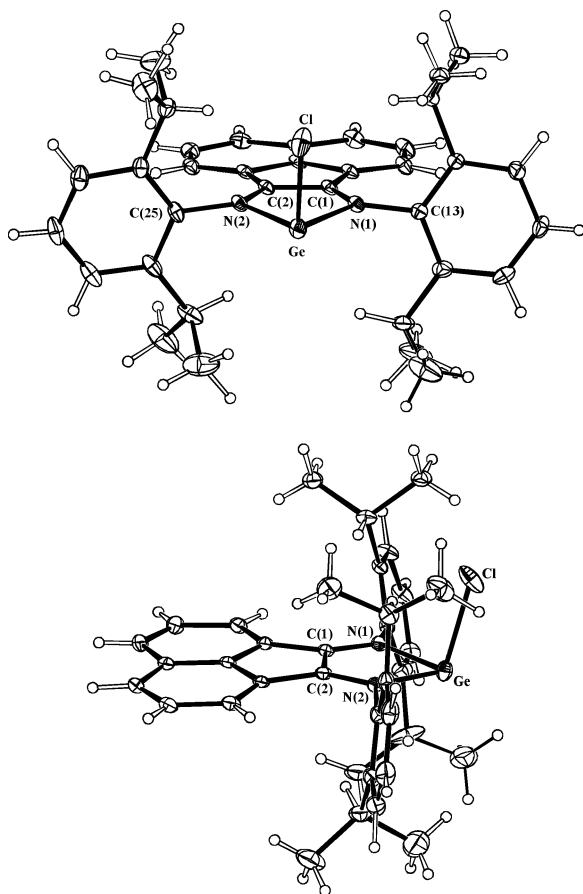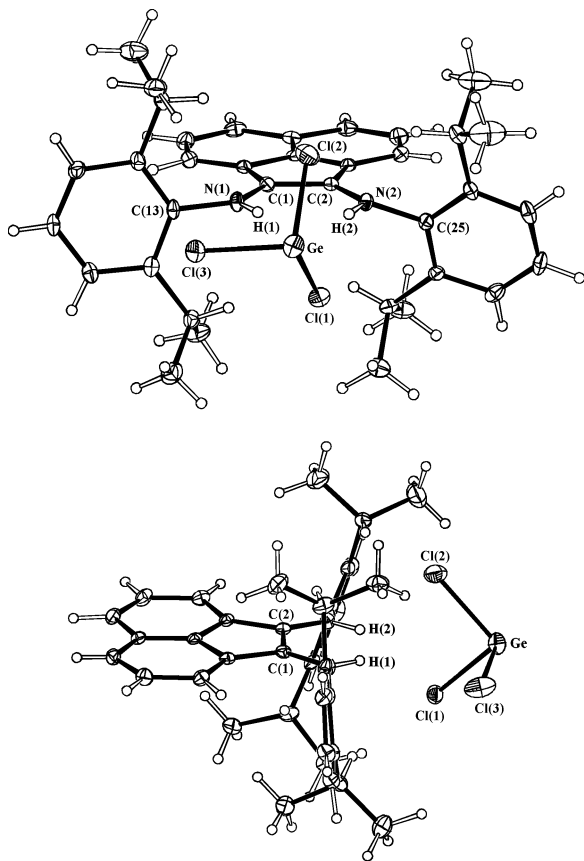

Figure 1. Molecular structure of **1**. Thermal ellipsoids are of 30% probability.

(328°) and trigonal-planar (360°) environments. The angle between the Ge−Cl bond and the N(1)−Ge(1)−N(2) plane is 101.6(1)°. The electronic structure of the pyramidal geometry of these three-coordinate species may be indicative of high s character of the Ge lone pair orbital. In general, the basicity of this orbital is assumed to be lower than that

of the sp^2 orbital in two-coordinate N-based germylenes (e.g., imidazogermoline-2-yliden,[6a] its benzo-,[6b] pyrido-,[6c] and naphtho-annulated[6d] analogues). This assumption is supported by the fact that two-coordinate N-based germylenes can act as donor ligands toward transition-metal centers (for instance, Ni[Ge{C$_{10}$H$_6$(N^{i}Pr)$_2$}]$_4$[6d] and (CO)$_3$Mo[Ge{C$_2$H$_2$-(NCH$_2$^{t}Bu)$_2$}]$_3$[9]) and the lack of examples for such complexation in three-coordinate Ge(II) species. Because of the weaker bonding between the Ge cation and the dpp-BIAN radical anion compared to that of the dpp-BIAN dianion, the Ge−N bond lengths in **1** (2.0058(19) and 2.004(2) Å) are remarkably longer than those in (dpp-BIAN)Ge (1.896-(3) and 1.885(3) Å).[5] The Ge−N distances in **1** are longer than the mean distances in tropo-α-diketiminate [1,2-C$_7$H$_5$-(N^{i}Pr)$_2$]GeCl (both 1.956(4) Å)[6e] and β-diketiminate [CH{C(Me)NPh}$_2$]GeCl (1.955(2) and 1.965(1) Å).[7h] As a result, the bite angle N−Ge−N in **1** (81.57(8)°) is smaller than that in (dpp-BIAN)Ge (85.20(12)°),[5] 1,3,2-diazager-moline-2-ylidene C$_2$H$_2$[N(CH$_2$^{t}Bu)]$_2$Ge (87.75(6)°),[6c] and β-diketiminate [CH{C(Me)NPh}$_2$]GeCl (90.28(6)°)[7h] but close to the bite angle in tropo-α-diketiminate [1,2-C$_7$H$_5$-(N^{i}Pr)$_2$]GeCl (80.3(2)°).[6e] Comparison of the N−C and C−C bond distances within the metallacycle −GeN(1)C(1)-C(2)N(2)− in **1** with those in (dpp-BIAN)Ge[5] and free ligand dpp-BIAN[10] confirms the radical anionic character of dpp-BIAN in **1**. Thus, N−C distances in **1** (N(1)−C(1) 1.326-(3), N(2)−C(2) 1.329(3) Å) are elongated compared to the free ligand (both N−C 1.282(4) Å)[10] but notably shorter than related distances in (dpp-BIAN)Ge (N(1)−C(1) 1.374(4), N(2)−C(2) 1.370(3) Å).[5] The C−C distance within the metallacycle in **1** (C(1)−C(2) 1.421(3) Å) is shortened compared to free dpp-BIAN ligand (C(1)−C(2) 1.534(6) Å)[10] but is longer than that in (dpp-BIAN)Ge (C(1)−C(2) 1.381-

(9) Kühl, O.; Lönnecke, P.; Heinicke, J. *Inorg. Chem.* **2003**, *42*, 2836−2838.
(10) Fedushkin, I. L.; Chudakova, V. A.; Fukin, G. K.; Dechert, S.; Hummert, M.; Schumann, H. *Russ. Chem. Bull.* In press.

Figure 2. Molecular structure of **2**. Thermal ellipsoids are of 30% probability.

(5) Å).[5] These observations are in an agreement with the symmetry of the ligand lowest unoccupied molecular orbital (LUMO). Its population should cause the shortening of the C(1)−C(2) bond and elongation of the C−N bonds. One-electron reduction of dpp-BIAN is supposed to lead to bond alternation, which lies between those of (dpp-BIAN)$^{2-}$ and (dpp-BIAN)^0.

Compounds **2** and **3** crystallize each with four molecules in the unit cells in the orthorhombic and monoclinic space groups $P2_12_12_1$ and $P2_1/n$, respectively. The molecular structure of **2** consists of contact ions [(dpp-BIAN)(H)$_2$]$^+$ and [GeCl$_3$]$^-$ (Figure 2). Similar to structure **1**, the germanium atom in the [GeCl$_3$]$^-$ anion adopts pyramidal geometry with Cl−Ge−Cl angles of 92.75(3), 96.28(3), and 94.86-(3)°. In the anion, two Ge−Cl distances (Ge−Cl(1) 2.3385-(7) and Ge−Cl(2) 2.3128(7) Å) are notably longer than the third one (Ge−Cl(3) 2.2462(8) Å). However, the average Ge−Cl distance in [GeCl$_3$]$^-$ (2.299 Å) is close to those found in other structurally characterized [GeCl$_3$]$^-$ anions (e.g., [D$_3$CND$_3$]$^+$[GeCl$_3$]$^-$ (2.327 Å),[11a] [{Me$_2$Pz}$_3$Ge$_2$]$^+$[GeCl$_3$]$^-$ (2.311 Å),[11b] [Me$_2$N−(CH$_2$C$_5$H$_4$)Fe(C$_5$H$_5$)]$^+$[GeCl$_3$]$^-$ (2.281 Å))[11c] and to the calculated value (2.309 Å).[12] The difference

(11) (a) Yamada, A.; Mikawa, K.; Okuda, T.; Knight, K. S. *J. Chem. Soc., Dalton Trans.* **2002**, 2112−2118. (b) Steiner, A.; Stalke, D. *Inorg. Chem.* **1995**, *34*, 4846−4853. (c) Hosmane, N. S.; Yang, J.; Lu, K.-J.; Zhang H.; Siriwardane, U.; Islam, M. S.; Thomas, J. L. C.; Maguiri, J. A. *Organometallics* **1998**, *17*, 2784.
(12) Kolesnikov, S. P.; Maksimov, S. N.; Smolenskii, E. A. *Russ. Chem. Bull.* **2001**, *50*, 740−742.

in Ge−Cl bond lengths in **2** might be attributed to a weak interaction of the chlorine atoms Cl(1) and Cl(2) with hydrogen atoms H(1) and H(2), which were localized at distances of 0.88(2) and 0.90(2) Å from nitrogen atoms N(1) and N(2), respectively. The intramolecular Cl(1)⋯N(2) (3.236(2) Å) and Cl(1)⋯H(2) (2.44(2) Å) distances indicate the bonding interactions Cl⋯N (3.23 Å)[13] and Cl⋯H (2.67 Å).[13] The protonation of **1** with 2 equiv HCl converted the dpp-BIAN radical anion into radical cation [(dpp-BIAN)-(H)$_2$]$^{•+}$. Because the protonation occurs by adding H$^+$ to N lone pairs, as expected no changes in the diimine skeleton are observed. C−N and C−C distances in the diimine part of molecule **2** (N(1)−C(1) 1.344(2), N(2)−C(2) 1.326(2), C(1)−C(2) 1.447(3) Å) are very similar to those in complex **1** (vide supra, Table 2).

In the molecular structure of **3**, two radical cations [(dpp-BIAN)(H)$_2$]$^+$ are "coordinated" by the chlorine anion Cl(4) (Figure 3, the lattice benzene molecules omitted). The [GeCl$_3$]$^-$ anion weakly interacts with hydrogen atoms of the naphthalene system of one of the radical-cationic ligands (two shortest contacts are 2.856 and 2.926 Å). As seen by Ge−Cl bond angles (Table 2), the geometry of the [GeCl$_3$]$^-$ anion is slightly less pyramidalized compared to that in **2**. Besides, the difference between Ge−Cl distances in **3** (Ge−Cl(1) 2.2830(8), Ge−Cl(2) 2.2789(8), and Ge−Cl(3) 2.3161(7) Å) is less pronounced. Four atoms H(1), H(2), H(3), and H(4) were found at distances of 0.87(2), 0.89(2), 0.88(2), and 0.88(2) Å from nitrogen atoms N(1), N(2), N(3), and N(4), respectively. The distances between atoms H(1), H(2), H(3), H(4), N(1), N(2), N(3), N(4), and the chlorine anion Cl(4) are influenced by specific interactions H⋯Cl and N⋯Cl (Cl(4)⋯H(1−4) 2.27(2)−2.32(2) Å, Cl(4)⋯N(1−4) 3.132(2)−3.178(2) Å). Interaction between atoms H(1), H(2), H(3), and H(4) and chlorine anion Cl(4) is indicated by short H⋯Cl distances (Cl(4)⋯H(1) 2.29(2), Cl(4)⋯H(2) 2.28(2), Cl(4)⋯H(3) 2.32(2), and Cl(4)⋯H(4) 2.27(2) Å). Repulsion between the isopropyl groups of the two radical cations is minimized by ligand twist of 41°, thus causing a staggered conformation of the ligands (Figure 4).

ESR Spectroscopic Studies 1−3. The presence of a dpp-BIAN radical anion in **1** is confirmed by observation of an ESR signal in toluene solution. This signal is moderately resolved at 285 K and shows a hyperfine structure due to coupling of the unpaired electron to ^{14}N, ^{73}Ge, ^{35}Cl, ^{37}Cl, and ^{1}H nuclei (hyperfine coupling (HFC) constants: 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, Figure 5).
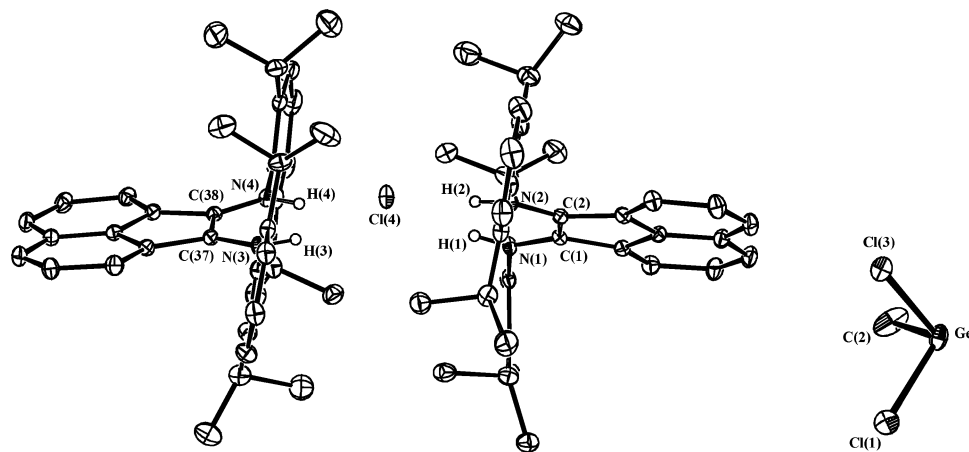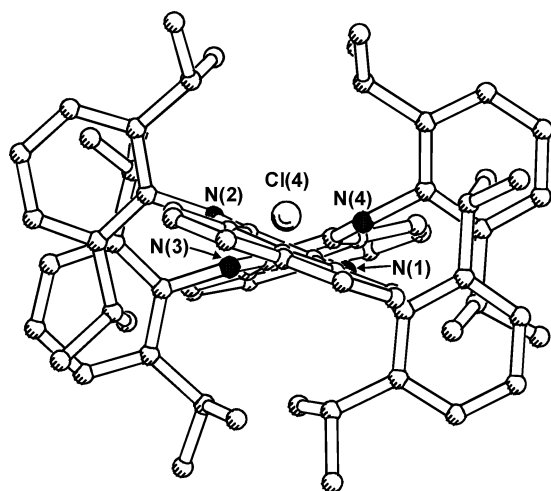
A decrease in the temperature to 230 K caused insignificant changes in the spectrum. To the best of our knowledge, this is the first ESR spectroscopic characterization of a crystallographically authenticated Ge(II) species.

Tuck and co-workers reported the observation of an ESR signal for (3,5-dtb-SQ)$_2$Ge (3,5-dtb-SQ = 3,5-di-*tert*-butyl-benzosemiquinone), which indicated the presence of two SQ

(13) Zefirov, Yu. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1995**, *64*, 446−460.
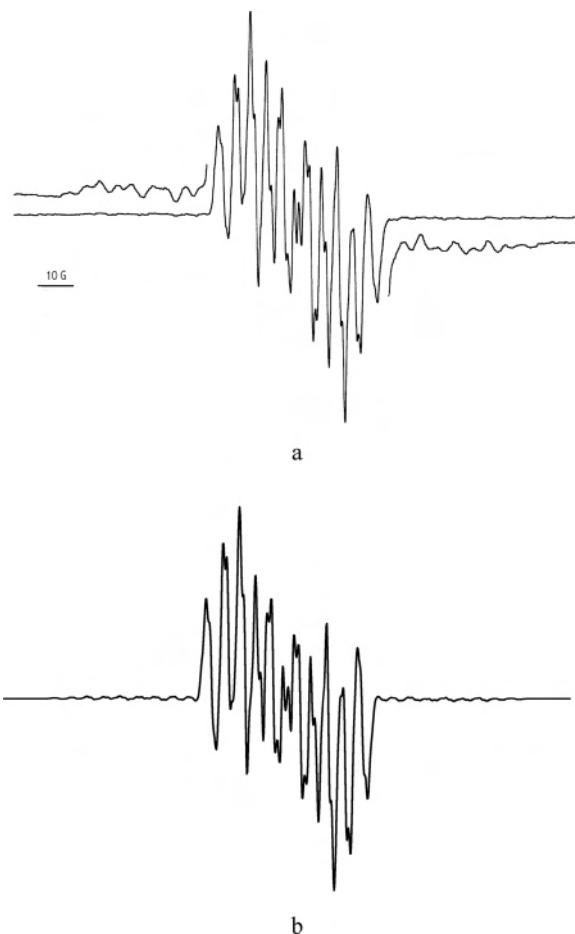
Figure 3. Molecular structure of **3**. Thermal ellipsoids are of 30% probability. Hydrogen atoms are omitted except those localized at nitrogen atoms.

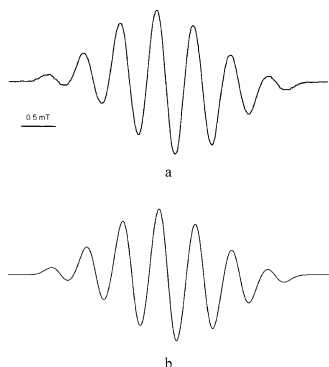**Figure 4.** Orientation of the two dpp-BIAN ligands in the cation $\{[(dpp\text{-}BIAN)(H)_2]_2Cl\}^+$ of **3**.

radical anions in $(3,5\text{-}dtb\text{-}SQ)_2Ge$.[14] Besides a strong and sharp signal of the monoradical (single line, $g = 2.008$), the ESR spectrum of $(3,5\text{-}dtb\text{-}SQ)_2Ge$ at 77 K showed the resonance at half-field, demonstrating the presence of biradical species. For the monoradical signal, no HFC constants were reported. The parameters of the ESR signal of **1** may be compared with those of the alkali and alkaline-earth metal complexes of the dpp-BIAN radical anion (e.g., $(dpp\text{-}BIAN)M$ (M = Li, Na)[3b] and $(dpp\text{-}BIAN)MgX$ (X = Cl, Br, I, OAr)).[3e–g] The HFC constants to ^{14}N vary in these compounds from 0.44 mT in $(dpp\text{-}BIAN)MgI(DME)_2$[3g] (DME = 1,2-dimethoxyethane) to 0.46 mT in $(dpp\text{-}BIAN)$-Na[3b] and 0.83 mT in $(dpp\text{-}BIAN)Mg(antryl\text{-}9\text{-}oxy)(THF)_2$.[3e] $(dpp\text{-}BIAN)Na$ is the only example where a coupling to the metal ($A_{Na} = 0.17$ mT) was observed.[3b] For complexes $[(dpp\text{-}BIAN)MgX(L)]_n$ (X = Cl, Br, L = THF, $n = 2$; X = I, L = DME, $n = 0$),[3g] the HFC constant to the halogen atom was detected only for the iodine derivative ($A_I = 0.27$ mT), in which the Mg–I bond almost lies perpendicular to the metallacycle similar to that in **1**. The larger coupling to Cl in **1** ($A_{Cl} = 0.78$ (^{35}Cl) and 0.65 (^{37}Cl) mT) compared to

(14) El-Hadad, A. A.; McGravey, B. R.; Merzougui, B.; Sung, G. W.; Trikha, A. K.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **2001**, 1064–1052.

Figure 5. (a) ESR spectrum of **1** in toluene solution. (b) Calculated spectrum ($A_N = 0.48$ (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, $g = 2.0014$).

that to I in $(dpp\text{-}BIAN)MgI(DME)_2$[3g] may be explained by a high degree of covalence in Ge to ligand bonding. One of the distinct features of the ESR signal of the dpp-BIAN radical anion in **1** is the coupling of the unpaired electron to four protons ($A_H = 0.11$ mT). In alkali and alkaline-earth metal complexes of dpp-BIAN such a coupling has not been observed. We attribute this coupling to the hydrogen atoms in ortho and para positions of the naphthalene system (relative to the diimine fragment). Coupling constants are rather

Figure 6. (a) ESR spectrum of **3** in Et$_2$O solution. (b) Calculated spectrum ($A_N = 0.53$, $A_H = 0.48$ mT, $g = 2.0031$).

small, thus indicating that the unpaired electron is mainly delocalized over the diimine part of the ligand. The germanium HFC constant ($A_{Ge} = 0.96$ mT) in **1** is 10 to 20 times smaller than those in germanium-centered radicals R$_3$Ge$^\bullet$ (R = CH(TMS)$_2$, 9.9 mT; R = N(TMS)$_2$, 17.1 mT; R = N(TMS)(^{t}Bu), 17.3 mT; R = N(GeMe$_3$)$_2$, 14.5 mT; R = 4,5,6-Me$_3$-2-^{t}BuC$_6$H, 8.5 mT)[15] but close to that calculated for radical anions of tetraphenyl-1-germacyclopenta-2,4-diene [Ph$_4$C$_4$GeH$_2$]$^{\bullet-}$ (0.57 mT)[16] and experimentally observed for the radical anion of digermanyne [{1,2-(2,6-Pr$_2$C$_6$H$_3$)-C$_6$H$_3$}$_2$Ge$_2$]$^{\bullet-}$ (0.75 mT).[17]

Radical cations of (dpp-BIAN)H$_2$ in **2** and **3** can be detected by ESR spectroscopy at room temperature. The experimental spectrum together with its simulation is shown in Figure 6.

Both compounds reveal ESR signals of seven lines indicating coupling of the unpaired electron to two ^{14}N and two ^{1}H nuclei ($A_N = 0.53$, $A_H = 0.48$ mT, $g = 2.0031$). Because of the broadening of the signals, it was not possible to distinguish if small coupling to the protons of the naphthalene systems exists. A relatively high hyperfine coupling to two ^{1}H nuclei proves the crystallographic data (vide supra), which showed hydrogen atoms directly attached to N(1) and N(2). To the best of our knowledge, this is only the second ESR detection of the radical-cationic species derived from protonated α,α-diimines and the first for which crystal structure determination has been carried out.

Alberti and Hudson reported the formation of the diprotonated ^{t}Bu-DAD radical cation (isomer A, $A_N = 0.73$ (2 N), $A_H = 0.48$ (2 H), $A_H = 0.75$ (2 H) mT, $g = 2.0032$; isomer B, $A_N = 0.66$ (2 N), $A_H = 0.57$ (2 H), $A_H = 0.69$ (2 H) mT, $g = 2.0033$) under photolysis of the parent diimine ^{t}Bu-DAD in the presence of di-*tert*-butylperoxide and a trace of trifluoroacetic acid.[18] The HFC constants of ^{14}N in the ESR signals of **2** and **3** can also be compared with those of the radical cation of 1,3,6,8-tetraazocyclo-[4.4.1.1^{3,8}]-dode-

cane ($A_N = 0.343$ (4 N), $A_H = 0.064$ (8 H), $A_H = 0.74$ (4 H) mT).[19] Similarity of the parameters of the ESR signals for **2** and **3** allowed the suggestion that in solution these compounds exist as solvent-separated ion pairs and the influence of Cl$^-$ and [GeCl$_3$]$^-$ anions on the electronic structures of dpp-BIAN radical cations is small.

IR and UV−Vis Spectroscopic Studies of **1−3**. IR and UV−vis spectra of **1−3** were recorded at room temperature. The IR spectrum of **1** confirms the radical-anionic character of the ligand. Whereas ν(C=N) vibrations of the free ligand[20] range from 1600 to 1700 cm^{-1}, the respective vibrations of **1** are shifted by ca. 100 cm^{-1} to lower wavenumbers. One of the most characteristic absorptions in the IR spectrum of **1** appears at 765 cm^{-1} and is assigned to Ge−N stretching. Except for this absorption, the IR spectra of **2** and **3** in the 1600−400 cm^{-1} region are very similar to that of **1**. However, in contrast to **1**, the IR spectra of **2** and **3** revealed an absorption caused by ν(N−H) stretching in the region of 3500−3000 cm^{-1}. In **3**, this absorption is shifted to lower wavenumbers by ca. 200 cm^{-1}. This may be attributed to the lower covalency of the N−H bond in **3** compared to that of **2** because of the interaction of H(1), H(2), H(3), and H(4) with Cl(4) (Figure 3). In contrast to **2**, the IR spectrum of **3** exhibits a strong absorption at 660 cm^{-1}, which we assign to the deformation mode of the Cl(4)···H(1, 2, 3, and 4) bonds. This deformation may be caused by variance of the interligand angle in the "complex" cation [{(dpp-BIAN)(H)$_2$}$_2$Cl]$^+$ (Figure 4).

The UV−vis spectra for **1**, **2**, and **3** (Figure 7) were recorded in diethyl ether. Compound **1** exhibits two absorptions (518, 906 nm), which very likely are of the same nature as in (dpp-BIAN)$^{\bullet-}$Mg(antryl-9-oxy)(THF)$_2$ (528, 1013 nm).[3e] However, in contrast to the Mg complex, compound **1** also revealed absorption with maxima of 420 nm. One can expect that the two long-wave absorptions in **1** arise from the ligand $n-\pi^*$ and $\pi-\pi^*$ transitions, whereas the band at 420 nm is presumably caused by the ligand-to-germanium charge transfer. The electronic spectra of **2** and **3** differ little from each other. Both **2** and **3** show three absorptions in the regions 400−450, 550−600, and 700−750 nm (**2**, 420, 596, 724; **3**, 415, 562, 750 nm), whereas the electronic spectrum of the neutral diamine (dpp-BIAN)H$_2$ shows only a single absorption at 536 nm.[10] Quantum chemical calculations on the radical cation [(dpp-BIAN)(H)$_2$]$^+$ might help to assign these absorptions and are currently in progress.

Experimental Section

General Remarks. All manipulations were carried out under vacuum using Schlenk ampules. Tetrahydrofuran, benzene, and diethyl ether were dried by distillation from sodium/benzophenone. 1,2-Bis[(2,6-diisopropylphenyl)imino] acenaphthene (dpp-BIAN)

(15) Della Bona, M. A.; Cassani, M. C.; Keates, J. M.; Lawless, G. A.; Lappert, M. F.; Stürmann, M.; Weidenbruch, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1187−1190.
(16) Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4293−4297.
(17) Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626−11636.
(18) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *241*, 313−319.

(19) Zwier, J. M.; Brouwer, A. M.; Keszthelyi, T.; Balakrishnan, G.; Offersgaard, J. F.; Wilbrandt, R.; Barbosa, F.; Buser, U.; Amaudrut, J.; Gescheidt, G.; Nelsen, S. F.; Little, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 159−167.
(20) (a) Paulovicova, A. A.; El-Ayaan, U.; Shibayama, K.; Morita, T.; Fukuda, Y. *Eur. J. Inorg. Chem.* **2001**, 2641. (b) Paulovicova, A. A.; El-Ayaan, U.; Umezava, K.; Vithana, C.; Ohashi, Y.; Fukuda, Y. *Inorg. Chim. Acta* **2002**, *339*, 209.
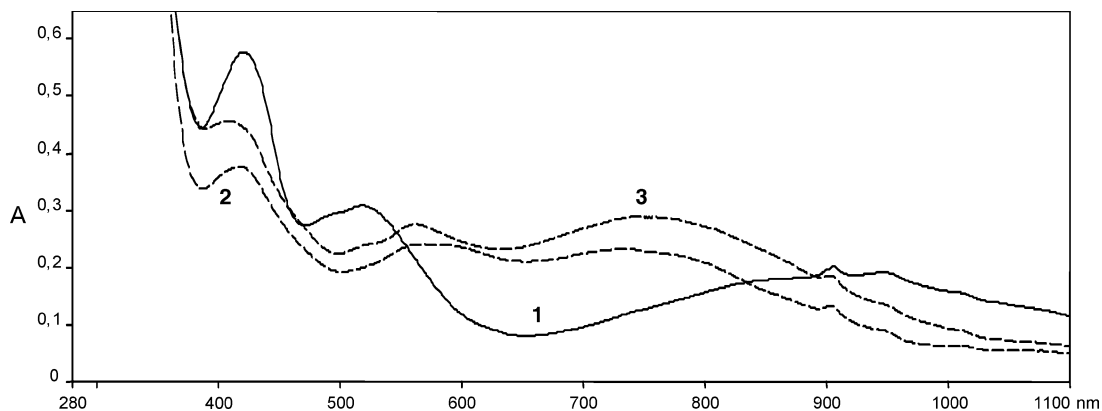
Figure 7. UV−vis spectra of **1**, **2**, and **3** in Et₂O at 293 K.

was prepared according to the published procedure.[20a] GeCl₂(1,4-dioxane) was purchased from ABCR. Gaseous HCl was obtained from anhydrous H₂SO₄ and NaCl. Melting points were measured in sealed capillaries. The IR spectra were recorded on a Specord M80 spectrometer. The UV−vis spectra were recorded on a Perkin-Elmer λ 25 spectrometer using a Pyrex glass cell ($5 \times 15 \times 30$ mm³). The ESR spectra were obtained using a Bruker ER 200D-SRC spectrometer equipped with a low-temperature controller ER 4111 VT. Signals of **1**−**3** were referred to the signal of diphenylpicrylhydrazyl (DPPH, $g = 2.0037$).

Synthesis of (dpp-BIAN)GeCl (1). From dpp-BIAN and GeCl₂(C₄H₈O₂). To a suspension of free dpp-BIAN (0.5 g, 1.0 mmol) in Et₂O (40 mL), the dioxane adduct of germanium dichloride GeCl₂(C₄H₈O₂) (0.46 g, 2.0 mmol) was added. The ampule was shaken at room temperature, and the color of the solution changed within few minutes from orange to cherry red. The solution was filtered off and concentrated to 20 mL by evaporation of the solvent in a vacuum. The small amount of microcrystalline solid formed during evaporation of the solvent was redissolved under heating. In 2 days, compound **1** was isolated as deep-red crystals (0.13 g, 21%). Mp > 200 °C (dec). IR (Nujol): 3055 w, 1535 s, 1450 m, 1315 s, 1250 m, 1210 w, 1185 m, 1145 w, 1080 w, 1050 m, 1030 w, 935 m, 865 m, 820 s, 800 s, 795 w, 765 vs, 600 w, 545 w cm⁻¹. Anal. Calcd for C₃₆H₄₀ClGeN₂ (608.74): C, 71.03; H, 6.62. Found: C, 70.75; H, 6.58. UV−vis (20 °C, Et₂O): λ 420, 518 (489 sh), 906. ESR (12 °C, toluene): $A_N = 0.48$ (2 N), $A_{Ge} = 0.96$, $A_{Cl} = 0.78$ (³⁵Cl), $A_{Cl} = 0.65$ (³⁷Cl), $A_H = 0.11$ (4 H) mT. Concentration of the solution yielded a mixture of crystalline **1** and colorless crystals (mp 147 °C).

From (dpp-BIAN)Na and GeCl₂(C₄H₈O₂). A solution of (dpp-BIAN)Na was prepared in situ from dpp-BIAN (0.5 g, 1.0 mmol) and sodium (0.023 g, 1.0 mmol) under stirring for 24 h in 40 mL of Et₂O. To this solution, the dioxane adduct of germanium dichloride GeCl₂(C₄H₈O₂) (0.23 g, 1.0 mmol) was added. The reaction mixture turned quickly from red to cherry red. The mixture was centrifuged, and the solution was separated from the NaCl precipitate by decantation. Compound **1** was isolated from the concentrated Et₂O solution as deep-red crystals in 75% yield (0.46 g). Analytical data are identical to those obtained for the compound in the procedure described above.

Reaction of (dpp-BIAN)GeCl (1) with 2 Equiv of HCl: Synthesis of [(dpp-BIAN)(H)₂][GeCl₃] (2). A solution of **1** (prepared in situ from dpp-BIAN (0.5 g, 1.0 mmol), Na (0.023 g, 1.0 mmol), and GeCl₂(C₄H₈O₂) (0.23 g, 1.0 mmol)) in benzene (40 mL) was cooled to −30 °C and exposed to gaseous HCl (44.8 mL, 2.0 mmol), which was obtained at ambient temperature in an evacuated Schlenk-like ampule from anhydrous H₂SO₄ and NaCl.

After the mixture was shaken, within a few seconds the reaction solution turned deep green. The mixture was centrifuged, and the solution was decanted and concentrated (15 mL) at 60 °C by removal of the solvent in a vacuum. In 40 h, dark green, prismatic crystals of **2** were isolated. Yield 0.39 g (57% calcd on dpp-BIAN used). Mp > 150 °C (dec). IR (Nujol): 3275−3240 m, 3200−3150 m, 3050 w, 3025 w, 1610 s, 1585 s, 1515 vs, 1450 vs, 1380 s, 1320 m, 1295 w, 1250 w, 1215 w, 1180 m, 1140 w, 1095 w, 1055 w, 1040 w, 1030 w, 930 m, 885 w, 820 s, 800 s, 765 s, 745 w, 720 w, 610 s, 565 m, 520 m, 500 w, 475 w, 455 m cm⁻¹. Anal. Calcd for C₃₆H₄₁Cl₃GeN₂ (680.65): C, 63.52; H, 6.07. Found: C, 63.30; H, 6.09. UV−vis (20 °C, Et₂O): λ 420, 596 (555 sh), 724 (796 sh). ESR (20 °C, Et₂O): $A_N = 0.53$ (2 N), $A_H = 0.48$ (2 H) mT.

Reaction of (dpp-BIAN)GeCl (1) with 3 Equiv of HCl: Synthesis of [{(dpp-BIAN)(H)₂}₂(Cl)][GeCl₃]·2.5(C₆H₆) (3). A solution of **1** (freshly prepared in situ from dpp-BIAN (0.5 g, 1.0 mmol), Na (0.023 g, 1.0 mmol), and GeCl₂(C₄H₈O) (0.23 g, 1.0 mmol)) in benzene (40 mL) was cooled to −30 °C and exposed to gaseous HCl (67.2 mL, 3.0 mmol). After being shaken, within a few seconds the reaction solution turned deep green. The mixture was centrifuged, and the solution was decanted and concentrated (15 mL) at 60 °C by removal of the solvent in a vacuum. In 2 days, dark green, elongated parallelepipeds of **3** were isolated. Yield 0.61 g (43% calcd on dpp-BIAN used). Mp 184 °C (dec). IR (Nujol): 3120 s, 3080 w, 3025 w, 1610 s, 1585 s, 1515 vs, 1450 vs, 1380 s, 1320 m, 1290 w, 1240 w, 1205 w, 1185 m, 1135 w, 1095 w, 1050 w, 1040 w, 1030 w, 930 m, 900 w, 815 s, 795 s, 755 s, 740 w, 705 w, 690 w, 660 vs, 590 m, 530 w, 510 m cm⁻¹. Anal. Calcd for C₈₇H₉₉Cl₄GeN₄ (1415.09): C, 73.84; H, 7.05. Found: C, 71.49; H, 6.65. UV−vis (20 °C, Et₂O): λ 415, 562 (518 sh), 750. ESR (20 °C, Et₂O): $A_N = 0.53$ (2 N), $A_H = 0.48$ (2 H) mT.

X-ray Crystal Structure Determination of 1−3. The data were collected on a Bruker SMART APEX diffractometer (graphite-monochromated Mo Kα radiation, ω- and ψ-scan technique, $\lambda = 0.71073$ Å) at 100 K for **1** and **3**, and at 120 K for **2**. The structures were solved by direct methods using SHELXS-97[21] and were refined on F^2 using SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement

(21) Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; Universität Göttingen: Göttingen. Germany, 1990.
(22) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997.

parameter of 0.08 Å^2. SADABS[23] was used to perform area-detector scaling and absorption corrections.

Conclusion

In this paper, we described the synthesis and detailed characterization, including X-ray crystallography, of the first germanium(II) compound (**1**) with a radical-anionic ligand. The ESR spectroscopic data indicate that the spin density in **1** is distributed over the ligand (N and H nuclei), as well as over germanium and chlorine atoms. However, values of the HFC constants allowed the conclusion that the unpaired electron in **1** is mainly ligand-localized. In contrast to our initial expectations, reaction of compound **1** with HCl does not result in oxidation of germanium to the +4 oxidation state but led to a protonation of the ligand and formation of its stable radical cation.

Supporting Information Available: IR-spectra for **1**−**3**. Full details of the X-ray crystallographic data in CIF format 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.

IC048801G

(23) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; Universität Göttingen, Göttingen, Germany, 1996.