926 *Russian Chemical Bulletin, International Edition, Vol. 56, No. 5, pp. 926—934, May, 2007*

New organogermanium cations $[RGe(OCH_2CH_2NMe_2)_2]^+$ with intramolecular N→Ge coordination bonds

I. A. Portnyagin, V. V. Lunin, and M. S. Nechaev*

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 2677. E-mail: nechaev@nmr.chem.msu.ru

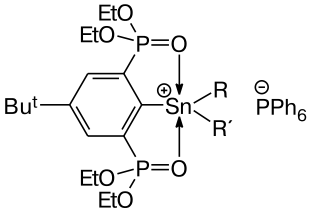
New organohalogermanes $RGe(OCH_2CH_2NMe_2)_2X$ (R = Ph, X = I (**5**); R = Me, X = Cl (**6**) or I (**7**)) with an intramolecular N→Ge coordination bond were synthesized. According to the ^1H and ^{13}C NMR spectroscopic data, iodides **5** and **7** exist in solution as ionic compounds with the pentacoordinated germanium atom. In solution of compound **4** (R = Ph, X = Cl), there is an equilibrium between the ionic and covalent forms. The equilibrium shifts toward the ionic form with increasing solvent polarity or temperature. In solution, chloride **6** is a covalent compound. The structures and relative stabilities of different isomers of compounds **4**—**7** were studied by quantum chemical calculations at the density functional level of theory.

Key words: organogermanium compounds, hypercoordinated compounds, germyl cations, intramolecular coordination bonds, ^1H and ^{13}C NMR spectroscopy, density functional method.

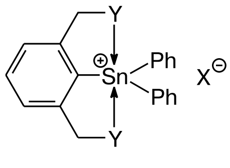
The synthesis, structures, and properties of cations of Group 14 organometallics R_3E^+ (E = Si, Ge, or Sn) have been extensively studied in recent years.[1—4] In addition to fundamental interest associated with elucidation of the similarity and difference between these compounds and the carbenium ions R_3C^+, they have received increasing interest in applied research as efficient catalysts for polymerization[5] and hydrosilylation[6—9] of alkenes, acylation of alcohols,[10,11] and the Diels—Alder reaction.[12,13]

The R_3E^+ cations exhibit high electrophilicity and readily coordinate various nucleophiles, including donor solvent molecules and counterions. Stability of such cations can be increased by (1) introducing bulky substituents at Group 14 element atoms, (2) using nucleofugic counterions, and (3) forming intramolecular Y→E coordination bonds (Y is an atom with lone electron pairs (N or O)).[14—19] Pentacoordinated tin complexes with pincer ligands **1** [20—22] and **2** [23—25] serve as examples of stable cations of this element. Trigermacyclopropenyl cation **3** [26] isoelectronic with the aromatic cyclopropenyl cation is also stable.

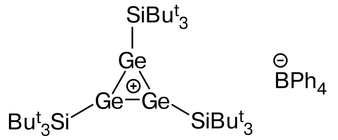
In all cases, germyl cations were stabilized in the condensed phase with the use of bulky substituents.[19,26—29] An approach developed[30—32] for the stabilization of R_2E compounds (E = Ge^{II} or Sn^{II}) and R_3Ge^+ cations is based on the use of the electronic factors of stabilization (electron-withdrawing substituents at Group 14 element atoms and intramolecular coordination bonds) without introduction of bulky substituents.



1



2



3

1: R, R′ = Alk, Ar, Cl; **2:** Y = OAlk, $NAlk_2$; X = CF_3COO, PF_6, HgI_3

The β-(*N*,*N*-dimethylamino)ethoxy ligand was demonstrated to stabilize the monomeric divalent germanium and tin derivatives $(Me_2NCH_2CH_2O)EX$ (X = $OCH_2CH_2NMe_2$ and E = Ge or Sn (see Ref. 30); X = Cl or OAc and E = Ge (see Ref. 31)) through electron-withdrawing substituents (O or Cl) at the Group 14 element atom and the formation of one or two stable intramolecular N→E coordination bonds. The use of such substituents made it possible to isolate, for the first time, the germyl cation in the condensed phase in the presence of the nucleophilic chloride anion, *viz*., the salt $[PhGe(OCH_2CH_2NMe_2)_2]^+Cl^-\cdot 2CHCl_3$ (**4**$\cdot 2CHCl_3$), without introduction of steric substituents.[32]

The latest investigations[33,34] concerned with R_3E^+ cations have demonstrated that the character of the E—anion bond substantially varies depending on the nature of substituents at the E atom, as well as on the nature of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 892—900, May, 2007.

anions, donor groups (NR_2 or OR), and the solvent. In the present study, we investigated the influence of these factors on the character of Ge—anion bonding in the presence of two β-(*N*,*N*-dimethylamino)ethoxy ligands. We report the synthesis of the organogermanium compounds $RGe(OCH_2CH_2NMe_2)_2X$ (R = Ph and X = I (**5**); R = Me and X = Cl (**6**) or I (**7**)). The structures of the resulting compounds were investigated by NMR spectroscopy. Compound **4** was characterized by ^1H and ^{13}C NMR spectra in $CDCl_3$ and toluene-d_8 at different temperatures. The structures and relative stabilities of different isomers of compounds **4**—**7** were also studied by quantum chemistry calculations at the density functional level of theory.

Results and Discussion

Compounds **5** and **6** were synthesized analogously to compound **4** by the reaction of $RGeX_3$ with $Et_3GeOCH_2CH_2NMe_2$ in THF using a reagent ratio of 1 : 2 (Scheme 1).[32]

Scheme 1

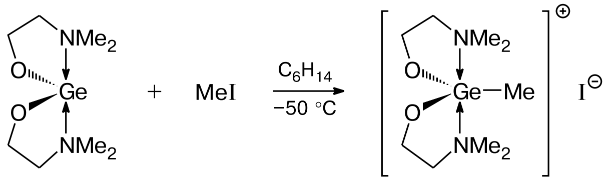
$$RGeX_3 + 2\,Et_3GeOCH_2CH_2NMe_2 \xrightarrow{THF} RGe(OCH_2CH_2NMe_2)_2X + 2\,Et_3GeX$$

5, **6**

5: R = Ph, X = I (90%); **6:** R = Me, X = Cl (92%)

The $MeGe(OCH_2CH_2NMe_2)_2I$ compound (**7**) was synthesized by the oxidative coupling reaction of MeI with $Ge(OCH_2CH_2NMe_2)_2$ (Scheme 2). Earlier, this approach has been applied[27,28] to the synthesis of sterically hindered germyl cations.

Scheme 2

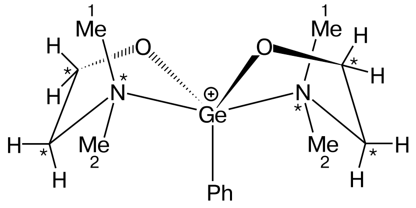


7 (91%)

Compounds **5**—**7** are white crystalline compounds, which are very sensitive to atmospheric moisture. Unlike iodides **5** and **7**, chlorides **4** and **6** are moderately soluble in THF and toluene. All compounds are readily soluble in CH_2Cl_2 and $CHCl_3$ and are insoluble in hexane.

The ^1H and ^{13}C NMR spectra of all compounds were recorded in $CDCl_3$. The spectra of compound **4** were also measured in toluene-d_8 at different temperatures. Principal spectroscopic characteristics are given in Table 1. The spectra of the chlorides are substantially different from those of the iodides.

The X-ray diffraction analysis showed that the crystalline $[PhGe(OCH_2CH_2NMe_2)_2]^+Cl^- \cdot 2CHCl_3$ complex (**4**·$2CHCl_3$) is chiral and has C_2 symmetry (Fig. 1).[32] The geometry of the complex can be described as a distorted trigonal bipyramid. Two oxygen atoms and one carbon atom are in equatorial positions, and two nitrogen atoms occupy axial positions. The chiral environment of the germanium atom results in the diastereotopicity of the CH_2 and NMe_2 groups in the coordination cycle. The above-mentioned structural features of the ionic forms are manifested in the NMR spectra of solutions of compounds **4**, **5**, and **7**.



The ^1H NMR spectra of iodides **5** and **7** in chloroform show two singlets of the NMe_2 groups with equal intensity

Table 1. Chemical shifts of the signals of the β-(dimethylamino)ethoxy group in the ^1H and ^{13}C spectra of compounds **4**—**7**

Compound	Solvent	δ_H			δ_C		
		NMe_2	CH_2N	CH_2O	NMe_2	CH_2N	CH_2O
4a	$CDCl_3$	2.47	2.95	3.80	41.78	54.80	58.05
4b	$CDCl_3$	2.00, 2.57	2.75, 3.02	3.97	43.37, 44.15	56.09	57.84
4a	Toluene-d_8	1.95	2.49	4.09	45.82	62.28	62.92
4b	Toluene-d_8	1.83, 2.04	2.23, 2.60	4.13	45.42, 45.51	61.62	62.62
5	$CDCl_3$	2.01, 2.59	2.76, 3.00	4.03	44.89, 45.45	57.50	59.05
6	$CDCl_3$	2.45	2.87	3.77	44.70	57.71	58.98
7	$CDCl_3$	2.52, 2.57	2.95	3.89	44.79, 45.46	58.06	59.19

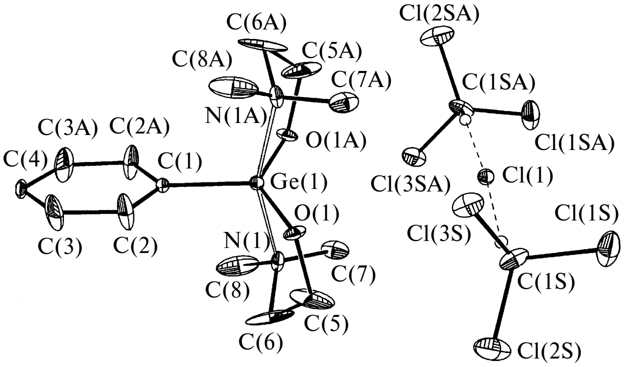


Fig. 1. Crystal structure of the salt $Ph(Me_2NCH_2CH_2O)_2Ge^+Cl^- \cdot 2CHCl_3$ ($\mathbf{4} \cdot 2CHCl_3$).[32]

and AA′XX′ multiplets of the diastereotopic protons of the CH_2O and CH_2N groups. The carbon atoms of the Me groups at the N atom are also nonequivalent in the ^{13}C NMR spectrum. This spectral pattern unambiguously indicates that the rigid ionic structures of both compounds are retained in solution. These structures are analogous to the structure of compound **4** in the crystalline state (see Fig. 1).[32]

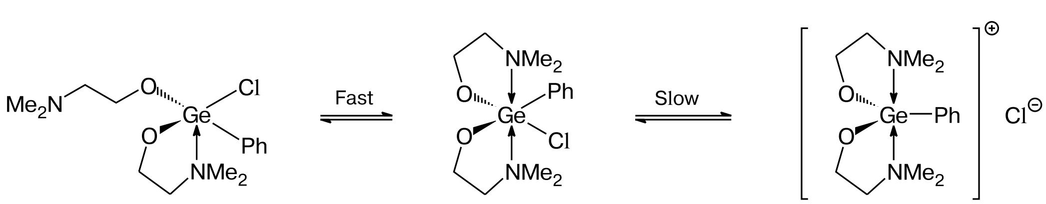
The ^1H NMR spectrum of chloride **6** shows a broadened singlet of the NMe_2 groups and triplets (A_2X_2 system) of the protons of the CH_2O and CH_2N groups. This spectral pattern is indicative of the covalent structure. In our opinion, two forms with penta- and hexacoordinated germanium atoms exist in equilibrium in solution. In solution, the NMe_2 groups are in fast exchange due to the relatively easy closure and cleavage of the N→Ge coordination bonds. As a result of this process, the signals of the NMe_2 groups are averaged in the ^{13}C NMR spectrum.

The ^1H and ^{13}C NMR spectra of compound **4** in $CDCl_3$ at room temperature and in toluene-d_8 at 291—373 K provide evidence that, in solution, the neutral form $PhGe(OCH_2CH_2NMe_2)_2Cl$ (**4a**) is in equilibrium with the ionic form $[PhGe(OCH_2CH_2NMe_2)_2]^+Cl^-$ (**4b**), in which the germanium atom has the coordination number 5 (Scheme 3). Ionic form **4b** predominates in solution in $CDCl_3$ (molar ratio **4b** : **4a** = 6.5 : 1). Like the ^1H NMR spectra of ionic compounds **5** and **7**, the ^1H NMR spectrum of form **4b** shows two singlets of the NMe_2 groups with equal intensity (δ 2.00 and 2.57) and an AA′XX′ multiplet of the diastereotopic protons of the CH_2N (δ 2.75 and 3.02) and CH_2O groups (δ 3.97). The ^{13}C NMR spectrum of form **4b** has singlets of the diastereotopic Me groups of the NMe_2 fragment at δ 43.37 and 44.15 and singlets at δ 56.0 (CH_2N) and 57.84 (CH_2O). Covalent structure **4a** is characterized by signals at δ 2.47 (NMe_2), 2.95 (CH_2N), and 3.80 (CH_2O) in the ^1H NMR spectrum and signals at δ 41.78 (NMe_2), 54.80 (CH_2N), and 58.05 (CH_2O) in the ^{13}C NMR spectrum. In the ^1H and ^{13}C NMR spectra of form **4a**, all signals are substantially broadened. This is evidence that the NMe_2 groups in covalent structure **4a** are in fast exchange ($\mathbf{4a} \rightleftharpoons \mathbf{4a'}$) on the NMR time scale, whereas the interconversion of **4a** and **4b** under these conditions is slow on the NMR time scale (see Scheme 3).

Thermodynamically more favorable covalent structure **4a** predominates in less polar toluene-d_8 at 291 K. The molar ratio **4a** : **4b** is ~3 : 1. Structure **4a** is characterized by a singlet at δ 1.95 (NMe_2) and broadened triplets ($^3J_{H,H}$ = 6.0 Hz) at δ 2.49 (CH_2N) and 4.09 (CH_2O). The ionic form is characterized by singlets of the diastereotopic NMe_2 groups at δ 1.83 and 2.04 and multiplets at δ 2.23, 2.60 (CH_2N, $^3J_{H,H}$ = 5.8 Hz), and 4.13 (CH_2O). The ^{13}C NMR spectrum of structure **4a** shows singlets at δ 45.82 (NMe_2), 62.28 (CH_2N), and 62.92 (CH_2O). Structure **4b** is characterized by singlets of the diastereotopic Me groups of the NMe_2 fragments at δ 45.42 and 45.51 and singlets at δ 61.62 (CH_2N) and 62.62 (CH_2O). The percentage of thermodynamically less favorable ionic structure **4b** in toluene gradually increases as the temperature is raised to 373 K. This is accompanied by broadening of all signals in the spectrum, which is evidence that the exchange $\mathbf{4a} \rightleftharpoons \mathbf{4b}$ becomes more fast. At 373 K, the molar ratio **4a** : **4b** is ~1 : 1. The temperature changes in the spectrum are reversible. The character of the temperature dependence of the NMR spectra of compound **4** is, on the whole, analogous to that described earlier[29] for ionic pentacoordinated germanium compounds containing the pincer sterically crowded *C,N,N′*-[2,6-bis(dimethylaminomethyl)-4-*tert*-butyl]phenyl ligand.

The molecular structures of compounds **4—7** were studied by quantum chemical calculations at the density functional level of theory. The molecular geometry was optimized using the generalized gradient-corrected func-

Scheme 3



4a′ **4a** **4b**

tional PBE,[35] which has been earlier tested[35,36] for different classes of molecules. In the calculations, the TZ2P (triple zeta plus polarization functions) basis set was used.[37] The inner-shell electrons of the Ge, C, N, and O atoms were described by the effective-core potentials ECP-SBKJC.[38,39]

The energies E, E°, and H° were calculated for all stationary states. All calculations were carried out with the use of the PRIRODA program.[40] Earlier, we have successfully used this approach and the PRIRODA program in studies of the structures and reactivity of compounds with double bonds E=X (E = Si, Ge, or Sn; X = CR_2 (R = Alk or Ar), O, S, or N),[41] germanium(II) and tin(II) compounds,[42] and the structures and thermodynamic parameters of the ionic compound $[Ge(OCH_2CH_2NMe_2)_2]^+Cl^- \cdot 2CHCl_3$.[32]

The X-ray diffraction data were obtained for $[PhGe(OCH_2CH_2NMe_2)_2]^+Cl^- \cdot 2CHCl_3$.[32] The conclusions about the molecular structures of compounds **4—7** were made based on the NMR spectra in $CDCl_3$. Hence, we used the $RGe(OCH_2CH_2NMe_2)_2X \cdot 2CHCl_3$ complexes (R = Me or Ph; X = Cl or I) containing two chloroform molecules as model compounds in theoretical calculations. Isomers of these molecules containing one or two N→Ge coordination bonds and the isomer, in which this bond is absent, were considered. For an adequate comparison of the relative energies of the ionic and covalent structures of **4—7**, we considered systems, in which the chloroform molecules are coordinated only to halogen atoms through hydrogen bonds.

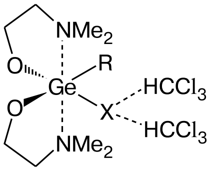
The isomers under consideration are denoted as follows: **A** is the covalent structure with two N→Ge coordination bonds, **B** is the ionic structure with two N→Ge coordination bonds, **C** is the covalent structure with one N→Ge coordination bond, **D** is the ionic structure with one N→Ge coordination bond, and **E** is the covalent structure without coordination bonds.

The calculated structures of different isomers of compound **4** are presented in Fig. 2; the molecular structures of **5—7** are analogous. The principal geometric parameters are listed in Table 2. The calculations adequately reproduced the structure of molecular complex **4** in the crystal.[32] For chlorides **4** and **6** containing two N→Ge coordination bonds, minima on the potential energy surface were found. These minima correspond to both covalent forms **4A** and **6A** and ionic forms **4B** and **6B**. For iodides **5** and **7**, the potential energy surface has minima corresponding only to ionic forms **5B** and **7B**. In both cases, two minima were found for the ionic forms, which differ only in the position of the iodide ion with respect to the cationic center.

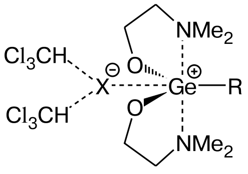
For all derivatives with one N→Ge coordination bond, both types of structures, *viz.*, covalent **C** and ionic **D**, exist. For molecules, in which coordination bonds are absent, minima corresponding only to covalent structures **E** were found. These results seem to be reasonable because the cationic center is not stabilized by coordination bonds and there are no factors facilitating the formation of ionic structures.

Some changes in the geometric parameters of the calculated structures on varying the number of N→Ge coordination bonds as well as on going from covalent to ionic structures are worthy of notice. The Ge—Cl interatomic distances in chlorides **4A** and **6A** are abnormally long. The cleavage of one coordination bond (transitions **4A** → **4C** and **6A** → **6C**) leads to a substantial shortening of the Ge—Cl bond (by ~0.4 Å). It is noteworthy that no minima were found for structures **5A** and **7A** on the potential energy surface of the iodides. This is apparently due to the bulkiness of the iodide ion.

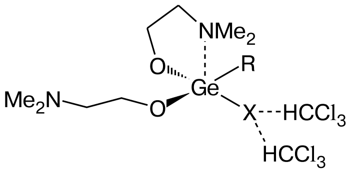
It is noteworthy that one of the N→Ge coordination bonds in ionic structures **B** is shorter than those in the corresponding covalent derivatives **A** (by 0.08 Å). For structures **D** and **C**, the differences in the bond lengths are even larger (~1.3 Å). This is attributed to a stronger interaction between the donor NMe_2 group and the metal atom in ionic forms **B** and **D** compared to covalent compounds **A** and **C**.



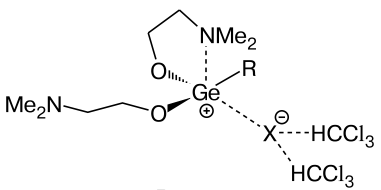
A



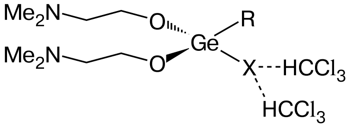
B



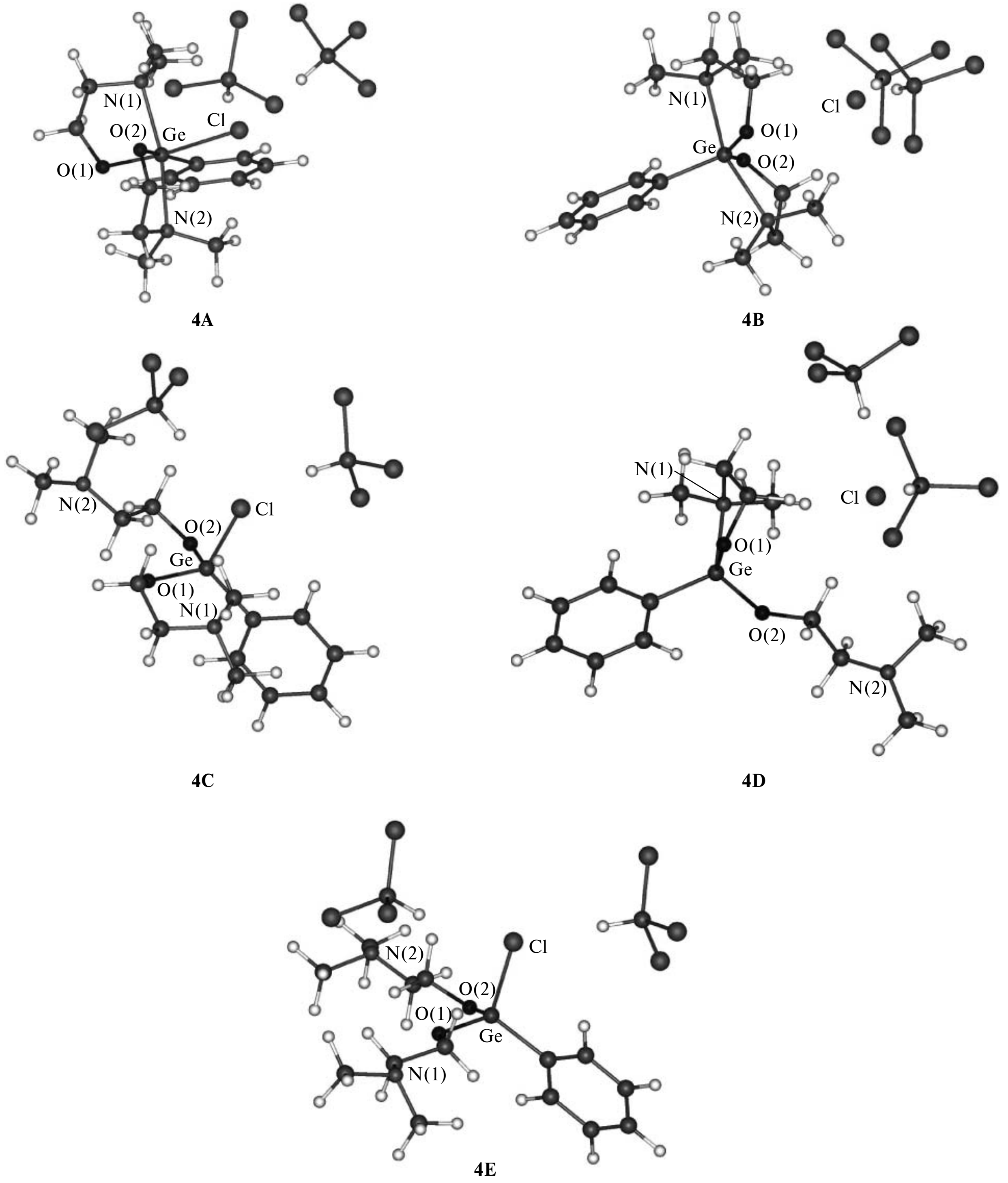
C



D



E



4A **4B**

4C **4D**

4E

Fig. 2. Calculated structures of isomers of compound **4**·$2CHCl_3$.

According to the results of calculations for iodides **5** and **7**, ionic forms **5B´** and **7B** have the lowest energies (Table 3). The next in energy (ΔH°_{298}) covalent structures **5C** and **7C** have energies higher by 4.0 and 3.5 kcal mol^{-1}, respectively. The energy difference between the ionic and covalent structures is rather large. This is manifested in the ^1H and ^{13}C NMR spectra of compounds **5** and **7**, which show signals of only the ionic forms of the molecules. For chloride **6**, covalent structure **6A** containing two coordination bonds is most stable. For the next in energy structure **6C**, ΔH°_{298} = 0.9 kcal mol^{-1}. In the case of chloride **4**, ionic structure **4B** corresponds to the mini-

Table 2. Selected calculated bond lengths (*d*) in isomers of compounds **4—7**

Compound	Isomer	*d*/Å				
		Ge—O(1)	Ge—O(2)	Ge—N(1)	Ge—N(2)	Ge—X
4	**A**	1.846	1.867	2.283	2.213	2.646
	B	1.795	1.795	2.207	2.207	3.983
	C	1.773	1.779	3.151	5.254	2.223
	D	1.763	1.742	2.060	5.269	4.715
	E	1.769	1.753	5.261	5.253	2.233
5*	**B**	1.783	1.809	2.203	2.211	4.575
	B´	1.793	1.793	2.207	2.208	4.524
	C	1.776	1.782	3.234	5.259	2.598
	D	1.763	1.742	2.058	5.274	5.200
	E	1.786	1.757	5.215	5.261	2.588
6	**A**	1.837	1.865	2.297	2.211	2.654
	B	1.794	1.794	2.214	2.224	4.051
	C	1.770	1.763	3.286	5.325	2.251
	D	1.763	1.741	2.052	5.278	4.719
	E	1.767	1.752	5.265	5.255	2.240
7*	**B**	1.795	1.818	2.267	2.195	3.793
	B´	1.793	1.793	2.213	2.222	4.581
	C	1.774	1.766	3.385	5.333	2.623
	D	1.763	1.742	2.050	5.271	5.218
	E	1.772	1.757	5.276	5.260	2.612

* Two minima, which differ only in the position of the iodide ion with respect to the cationic center, were found.

Table 3. Calculated energy parameters (E, E°, and H) and relative energies (ΔE° and ΔH°_{298}) of isomers of compounds **4—7**

Compound	Isomer	$-E$	$-E^{\circ}$	H°	ΔE°	ΔH°_{298}
		a.u.		kcal mol^{-1}		
4	**A**	267.23090	266.81908	282.2	0.0	0.0
	B	267.23236	266.82023	282.4	−0.7	−0.7
	C	267.22873	266.82084	280.5	−1.1	−0.4
	D	267.20399	266.79441	281.5	15.5	16.2
	E	267.22447	266.81727	281.0	1.1	2.9
5*	**B**	263.75553	263.34427	282.2	0.0	0.0
	B´	263.75843	263.34691	282.3	−1.7	−1.7
	C	263.74971	263.34242	280.8	1.2	2.3
	D	263.73019	263.32145	281.4	14.3	15.1
	E	263.74656	263.34013	280.1	2.6	3.6
6	**A**	237.66873	237.30944	247.3	0.0	0.0
	B	237.66424	237.30448	247.5	3.1	3.0
	C	237.66548	237.30982	246.2	−0.2	0.9
	D	237.63957	237.28247	246.6	16.9	17.6
	E	237.66306	237.30825	246.1	0.7	2.3
7*	**B**	234.19230	233.83342	246.3	0.0	0.0
	B´	234.19026	233.83113	247.4	1.4	2.4
	C	234.18621	233.83164	245.9	1.1	3.5
	D	234.16563	233.80933	246.5	15.1	16.9
	E	234.18409	233.83005	245.8	2.1	4.7

* Two minima, which differ only in the position of the iodide ion with respect to the cationic center, were found.

mum on the potential energy surface. According to the NMR spectroscopic data, this structure predominates in $CDCl_3$. However, covalent forms **4A** and **4C** are higher in energy (ΔH°_{298}) by only 0.7 and 0.3 kcal mol^{-1}, respectively. The structure with one coordination bond (**4C**) is more favorable than that with two coordination bonds (**4A**), which is consistent with the experimental data. The small energy difference between isomers **4A—4C** results in that the ^{1}H and ^{13}C NMR spectra of chloride **4** show signals of the ionic (**4b**) and covalent (**4a**) structures, the signals of the latter being substantially broadened due to the mutual transformations of the hexa- and pentacoordinated species **4A** $\rightleftarrows$ **4C**.

The electronic structures of ionic derivatives **B** with two coordination bonds were analyzed by the AIM method.[43] The critical points in the electron density corresponding to the Ge—O, Ge—C, and N→Ge bonds were found (Table 4). In all the molecules under study, no critical points corresponding to the germanium—halogen bond were found, which is typical of separated ions. The bond critical points for the Ge—O and Ge—C interatomic interactions are characterized by a rather high electron density ($\rho(r_{cr}) > 0.1$), positive Laplacians of the electron density ($\nabla^2\rho(r_{cr})$), and $|\lambda_1|/\lambda_3 = 0.23$ and 0.39, respectively. These values describe the Ge—O bonds as closed-shell interactions (ionic bonds). The Ge—C bonds can be assigned to interactions intermediate between covalent

Table 4. Parameters of the bond critical points ($\rho(r_{cr})$, $\nabla^2\rho(r_{cr})$, and λ_1—λ_3) at the Ge atom in molecules **4B**—**7B**

Compound	Bond	$\rho(r_{cp})$	$\nabla^2\rho(r_{cp})$	$-\lambda_1$	$-\lambda_2$	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	ε
		a.u.						
4B	Ge—O(1)	0.140	0.525	0.215	0.201	0.940	0.23	0.07
	Ge—O(2)	0.140	0.525	0.215	0.201	0.940	0.23	0.07
	Ge—C	0.127	0.099	0.162	0.152	0.413	0.39	0.06
	Ge—N(2)	0.070	0.102	0.080	0.076	0.258	0.31	0.05
	Ge—N(1)	0.070	0.102	0.080	0.076	0.258	0.31	0.05
5B	Ge—O(1)	0.140	0.528	0.216	0.201	0.946	0.23	0.07
	Ge—O(2)	0.140	0.528	0.216	0.201	0.946	0.23	0.07
	Ge—C	0.127	0.098	0.162	0.153	0.413	0.39	0.06
	Ge—N(1)	0.070	0.102	0.080	0.076	0.258	0.31	0.06
	Ge—N(2)	0.070	0.102	0.080	0.076	0.258	0.31	0.06
6B	Ge—O(1)	0.140	0.527	0.216	0.201	0.944	0.23	0.07
	Ge—O(2)	0.140	0.527	0.216	0.201	0.944	0.23	0.07
	Ge—C	0.124	0.083	0.150	0.147	0.381	0.39	0.02
	Ge—N(2)	0.069	0.103	0.079	0.075	0.257	0.31	0.05
	Ge—N(1)	0.068	0.100	0.077	0.073	0.250	0.31	0.05
7B	Ge—O(1)	0.140	0.530	0.217	0.202	0.949	0.23	0.08
	Ge—O(2)	0.140	0.531	0.217	0.202	0.950	0.23	0.07
	Ge—C	0.124	0.083	0.150	0.147	0.380	0.40	0.02
	Ge—N(1)	0.069	0.103	0.079	0.075	0.258	0.31	0.05
	Ge—N(2)	0.068	0.100	0.077	0.074	0.251	0.31	0.05

bonds and closed-shell interactions. The parameters of the N→Ge bonds ($\rho(r_{cr}) < 0.1$, $\nabla^2\rho(r_{cr}) \approx 0.1$, and $|\lambda_1|/\lambda_3 = 0.31$) are typical of donor-acceptor interactions.

The π component of the bond is characterized by the ellipticity (ε). The ellipticity ε for the Ge—C bond in the derivatives containing the Ph group (**4B** and **5B**) is 0.06. This is indicative of the π overlap between the $4p_z$ orbital of the germanium atom and the π system of the Ph ring. To the contrary, ε for the Ge—C bond in Me derivatives **6B** and **7B** is substantially smaller (0.02). Apparently, the π interaction between the Ph ring and the cationic center additionally stabilizes the ionic form of chloride **4**. As a result, the ionic form is in equilibrium with the covalent form in solution. By contrast, Me derivative **6**, in which this stabilization cannot occur, exists exclusively in the covalent form.

The presence of electron-withdrawing substituents at the metal atom is known to destabilize ionic forms of molecules. This is due to a higher positive charge on the metal atom, which facilitates the formation of the metal—nucleophile covalent bond. To the contrary, the formation of intramolecular coordination bonds between the central atom and the donor groups leads to a decrease of the positive charge on the metal atom, resulting in stabilization of the ionic form.

The β-(dimethylamino)ethoxy substituent is involved in the covalent bond with the metal atom through the electronegative oxygen atom. In this case, the formation of the intramolecular coordination bond with the NMe_2 group is possible. Our results showed that both ionic and covalent forms of the organogermanium compounds $RGe(OCH_2CH_2NMe_2)_2X$ can be prepared in the presence of this substituent.

The structures of the compounds under consideration in solution depend on the nature of the counterion X, the organic substituent R, and the solvent. In the presence of the bulky iodide anion, the ionic structures ($RGe(OCH_2CH_2NMe_2)_2I$, R = Ph (**5**) or Me (**7**)) are formed regardless of the nature of the hydrocarbon substituent. To the contrary, the covalent structures ($MeGe(OCH_2CH_2NMe_2)_2Cl$ (**6**)) are formed in the presence of chloride anions combined with an alkyl substituent. A combination of the nucleophilic anion favorable for the formation of the covalent structure and the aryl substituent stabilizing the ionic structure ($PhGe(OCH_2CH_2NMe_2)_2Cl$ (**4**)) is the limiting case. In solution of compound **4**, there is an equilibrium between the ionic and covalent structures. The equilibrium shifts toward the ionic structure with increasing solvent polarity or temperature.

Experimental

All operations associated with the synthesis and isolation of the reaction products were carried out under purified argon using the standard Schlenk technique. Commercially available solvents were purified according to standard procedures and distilled immediately before use. The $PhGeI_3$ compound was synthesized by the reaction of $PhGeCl_3$ with NaI in dry acetone followed by recrystallization from acetic acid. The physical constants were consistent with the published data.[44] The $Ge(OCH_2CH_2NMe_2)_2$,[30] $Et_3GeOCH_2CH_2NMe_2$,[30] and $PhGe(OCH_2CH_2NMe_2)_2Cl$ [32] compounds were prepared according to known procedures. The NMR spectra were recorded on an Avance 400 instrument (400.13 MHz for ^1H and 100.62 MHz for ^{13}C) in $CDCl_3$ and toluene-d_8. The concentration of the samples was 0.2—0.3 mmol mL^{-1}. The chemical shifts in the ^1H and ^{13}C NMR spectra were recorded relative to the signals of the solvent on the δ scale. The melting points were determined in sealed tubes on a SANYO Gallenkamp PLC instrument. The elemental analysis was carried out on a Carlo Erba EA1108 CHNS-O instrument.

Phenylbis[*N*-(dimethylamino)ethoxy]germanium iodide (5). A solution of $Et_3GeOCH_2CH_2NMe_2$ (12.49 g, 50.44 mmol) in THF (50 mL) was slowly added with stirring to a solution of $PhGeI_3$ (13.37 g, 25.19 mmol) in THF (50 mL), which was accompanied by the formation of a voluminous white precipitate. The reaction mixture was stirred for 2.5 h. Then the precipitate was filtered off, washed with THF, and dried *in vacuo*. The yield of compound **5** was 8.54 g (90%), decomp.t. 71 °C. Found (%): C, 36.98; H, 5.79; N, 6.02. $C_{14}H_{25}GeIN_2O_2$. Calculated (%): C, 37.13; H, 5.56; N, 6.19. ^1H NMR ($CDCl_3$), δ: 2.01 and 2.59 (both s, 6 H each, NMe_2); 2.71—2.82 and 2.97—3.03 (both m, 2 H each, CH_2N); 4.01—4.04 (m, 4 H, CH_2O); 7.45 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 44.89, 45.45 (Me_2N); 57.50 (CH_2N); 59.05 (CH_2O); 128.00 (*ipso*-C_{Ph}); 129.42 (*m*-C_{Ph}); 131.96 (*p*-C_{Ph}); 132.09 (*o*-C_{Ph}).

Methylbis[*N*-(dimethylamino)ethoxy]germanium chloride (6). A solution of $Et_3GeOCH_2CH_2NMe_2$ (3.46 g, 13.97 mmol) in THF (25 mL) was slowly added with stirring to a solution of $MeGeCl_3$ (1.36 g, 7.00 mmol) in THF (25 mL). The reaction mixture was stirred for 2.5 h. The solvent was distilled off *in vacuo* to 1/6 of the initial volume, and hexane (50 mL) was added. The white crystalline precipitate that formed was filtered off, washed with hexane (3×20 mL), and dried *in vacuo*. The yield of compound **6** was 1.92 g (92%), m.p. 121—122 °C. Found (%): C, 35.86; H, 7.80; N, 9.13. $C_9H_{23}ClGeN_2O_2$. Calculated (%): C, 36.11; H, 7.74; N, 9.36. ^1H NMR ($CDCl_3$), δ: 0.96 (s, 3 H, Me); 2.45 (br.s, 12 H, Me_2N, $^1J_{C,H}$ = 138 Hz); 2.87 (t, 4 H, CH_2N, $^3J_{H,H}$ = 6.0 Hz); 3.77 (t, 4 H, CH_2O, $^3J_{H,H}$ = 6.0 Hz). ^{13}C NMR ($CDCl_3$), δ: –0.54 (Me); 44.70 (br, Me_2N); 57.71 (CH_2N); 58.98 (CH_2O).

Methylbis[*N*-(dimethylamino)ethoxy]germanium iodide (7). Iodomethane (1.1 mL, 17.26 mmol) was added to a solution of $Ge(OCH_2CH_2NMe_2)_2$ (4.29 g, 17.26 mmol) in hexane (40 mL) at –50 °C, which was accompanied by the formation of a voluminous white precipitate. After the rise of the temperature of the reaction mixture to ~20 °C, the precipitate was filtered off, washed with hexane, and dried *in vacuo*. The yield of compound **7** was 6.14 g (91%), decomp.t. 62 °C. Found (%): C, 27.35; H, 6.20; N, 6.95. $C_9H_{23}GeIN_2O_2$. Calculated (%): C, 27.66; H, 5.93; N, 7.17. ^1H NMR ($CDCl_3$), δ: 1.05 (s, 3 H, Me); 2.52 and 2.57 (both s, 6 H each, NMe_2); 2.89—3.01 (m, 4 H, CH_2N); 3.83—3.95 (m, 4 H, CH_2O). ^{13}C NMR ($CDCl_3$), δ: 0.37 (Me); 44.79, 45.46 (Me_2N); 58.06 (CH_2N); 59.19 (CH_2O).

We thank N. E. Borisova for recording the NMR spectra and Yu. A. Ustynyuk, I. V. Borisova, and N. N. Zemlyanskii for helpful discussion.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-32662 and 04-03-32549) and the Russian Academy of Sciences (Program "Theoretical and Experimental Studies of Chemical Bonds and Mechanisms of Chemical Reactions and Processes").

References

1. I. Zharov and J. Michl, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Ed. Z. Rappoport, Wiley, Chichester, 2002, **2**, 633.
2. Yu. I. Baukov and S. N. Tandura, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Ed. Z. Rappoport, Wiley, Chichester, 2002, **2**, 961.
3. D. Kost and I. Kalikhman, *Adv. Organomet. Chem.*, 2004, **50**, 1.
4. T. Müller, *Adv. Organomet. Chem.*, 2005, **53**, 155.
5. M. Schormann, S. Garratt, D. L. Hughes, J. C. Green, and M. Bochmann, *J. Am. Chem. Soc.*, 2002, **124**, 11266.
6. J. B. Lambert and Y. Zhao, *J. Am. Chem. Soc.*, 1996, **118**, 7867.
7. J. B. Lambert, Y. Zhao, and H. Wu, *J. Org. Chem.*, 1999, **64**, 2729.
8. J. B. Lambert, C. Liu, and T. Kouliev, *J. Org. Phys. Chem.*, 2002, **15**, 667.
9. H.-U. Steineberg, C. Bauch, T. Müller, and N. Auner, *Can. J. Chem.*, 2003, **11**, 1223.
10. K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, and J. Otera, *Organometallics*, 1999, **18**, 3555.
11. S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, J. Otera, A. Duthie, D. Dakternieks, M. Schulte, and K. Jurkschat, *Organometallics*, 2000, **19**, 3220.
12. M. Johannsen, K. A. Jorgensen, and G. Helmchen, *J. Am. Chem. Soc.*, 1998, **120**, 7637.
13. G. A. Olah, G. Rasul, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1999, **121**, 9615.
14. D. Kost, V. Kingston, B. Gostevskii, A. Ellern, D. Stalke, B. Walfort, and I. Kalikhman, *Organometallics*, 2002, **21**, 2293.
15. D. Kost, B. Gostevskii, N. Kocher, D. Stalke, and I. Kalikhman, *Angew. Chem., Int. Ed.*, 2003, **42**, 1023.
16. I. Kalikhman, B. Gostevskii, O. Girshberg, A. Sivaramakrishna, N. Kocher, D. Stalke, and D. Kost, *J. Organomet. Chem.*, 2003, **686**, 202.
17. A. M. Neculai, D. Neculai, G. B. Nikiforov, H. W. Roesky, C. Schlicker, R. Herbst-Irmer, J. Magull, and M. Noltemeyer, *Eur. J. Inorg. Chem.*, 2003, 3120.
18. Yu. I. Baukov, A. G. Shipov, L. S. Smirnova, E. P. Kramarova, S. Yu. Bylikin, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **461**, 39; Yu. E. Ovchinnikov, Yu. T. Struchkov, Yu. I. Baukov, A. G. Shipov, E. P. Kramarova, and S. Yu. Bylikin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1421 [*Russ. Chem. Bull.*, 1994, **43**, 1346 (Engl. Transl.)]; Yu. E. Ovchinnikov, Yu. T. Struchkov, Yu. I. Baukov, A. G. Shipov, and S. Yu. Bylikin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1427 [*Russ. Chem. Bull.*, 1994, **43**, 1351 (Engl. Transl.)]; S. Yu. Bylikin, S. A. Pogozhikh, A. G. Shipov, V. V. Negrebetskii, Yu. E. Ovchinnikov, and Yu. I.

Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 754 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 755]; S. Yu. Bylikin, E. P. Kramarova, S. A. Pogozhikh, A. G. Shipov, V. V. Negrebetskii, Yu. E. Ovchinnikov, and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1632 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1720]; E. P. Kramarova, A. A. Korlyukov, S. Yu. Bylikin, A. G. Shipov, Yu. I. Baukov, and D. Kost, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1089 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1135].

19. F. Cosledan, A. Castel, P. Rivière, J. Satge, M. Veith, and V. Huch, *Organometallics*, 1998, **17**, 2222.
20. K. Jurkschat, N. Pieper, S. Seemeyer, M. Schürmann, M. Biesemans, I. Verbruggen, and R. Willem, *Organometallics*, 2001, **20**, 868.
21. K. Peveling, M. Henn, C. Löw, M. Mehring, M. Schürmann, B. Costisella, and K. Jurkschat, *Organometallics*, 2004, **23**, 1501.
22. K. Dannappel, M. Schürmann, B. Costisella, and K. Jurkschat, *Organometallics*, 2005, **24**, 1031.
23. A. Růžička, L. Dostál, R. Jambor, V. Buchta, J. Brus, I. Císařová, M. Holcapek, and J. Holeček, *Appl. Organomet. Chem.*, 2002, **16**, 315.
24. A. Růžička, R. Jambor, I. Císařová, and J. Holeček, *Chem. Eur. J.*, 2003, **9**, 2411.
25. B. Kašná, R. Jambor, L. Dostál, A. Růžička, I. Císařová, and J. Holeček, *Organometallics*, 2004, **23**, 5300.
26. A. Sekiguchi, M. Tsukamoto, and M. Ichinohe, *Science*, 1997, **275**, 60.
27. H. Schmidt, S. Keitemeyer, B. Neumann, H.-G. Stammler, W. W. Schoeller, and P. Jutzi, *Organometallics*, 1998, **17**, 2149.
28. P. Jutzi, S. Keitemeyer, B. Neumann, and H.-G. Stammler, *Organometallics*, 1999, **18**, 4778.
29. V. A. Benin, J. C. Martin, and M. R. Willcott, *Tetrahedron*, 1997, **53**, 10133.
30. N. N. Zemlyansky, I. V. Borisova, V. N. Khrustalev, Yu. A. Ustynyuk, M. S. Nechaev, V. V. Lunin, J. Barrau, and G. Rima, *Organometallics*, 2003, **22**, 1675.
31. N. N. Zemlyansky, I. V. Borisova, V. N. Khrustalev, M. Yu. Antipin, Yu. A. Ustynyuk, M. S. Nechaev, and V. V. Lunin, *Organometallics*, 2003, **22**, 5441.
32. V. N. Khrustalev, I. A. Portnyagin, I. V. Borisova, N. N. Zemlyansky, Yu. A. Ustynyuk, M. Yu. Antipin, and M. S. Nechaev, *Organometallics*, 2006, **25**, 2501.
33. B. Gostevskii, G. Silbert, K. Adear, A. Sivaramakrishna, D. Stalke, S. Deuerlein, N. Kocher, M. G. Voronkov, I. Kalikhman, and D. Kost, *Organometallics*, 2005, **24**, 2913; B. Gostevskii, N. Zamstein, A. A. Korlyukov, Yu. I. Baukov, M. Botoshansky, M. Kaftory, N. Kocher, D. Stalke, I. Kalikhman, and D. Kost, *Organometallics*, 2006, **25**, 5416; A. A. Korlyukov, S. A. Pogozhikh, Yu. E. Ovchinnikov, K. A. Lyssenko, M. Yu. Antipin, A. G. Shipov, O. A. Zamyshlyaeva, E. P. Kramarova, V. V. Negrebetsky, I. P. Yakovlev, and Yu. I. Baukov, *J. Organomet. Chem.*, 2006, **691**, 3962; V. V. Negrebetsky, P. G. Taylor, E. P. Kramarova, S. Yu. Bylikin, I. Yu. Belavin, A. G. Shipov, A. R. Bassindale, and Yu. I. Baukov, *J. Organomet. Chem.*, 2006, **691**, 3976.
34. B. Kašná, R. Jabor, L. Dostál, L. Kolářová, I. Císařová, and J. Holeček, *Organometallics*, 2006, **25**, 148.
35. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
36. M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029.
37. D. N. Laikov, Ph. D. (Phys.-Mat.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 2000 (in Russian).
38. W. J. Stevens, M. Krauss, H. Basch, and P. G. Jasien, *Can. J. Chem.*, 1992, 612.
39. T. R. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.
40. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
41. I. V. Borisova, M. S. Nechaev, V. N. Khrustalev, N. N. Zemlyanskii, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 665 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 721].
42. M. S. Nechaev and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 107 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 108].
43. R. F. W. Bader, *Atoms in Molecules: a Quantum Theory*, Oxford University Press, New York, 1990.
44. M. Lesbre and P. G. Mazerolles, *Compt. Rend.*, 1963, **257**, 2303.

Received November 15, 2006;
in revised form February 28, 2007