The molecular and electronic structure features of silatranes, germatranes, and their carbon analogs

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Molecular geometries of fifty-six metallatranes $N(CH_2CH_2Y)_3M—X$ and fifty-six carbon analogs $HC(CH_2CH_2Y)_3M—X$ (M = Si, Ge; X = H, Me, OH, F; Y = CH_2, O, NH, NMe, $NSiMe_3$, PH, S) were optimized by the DFT method. Correlations between changes in the bond orbital populations, electron density $\rho(\mathbf{r})$, electron density laplacian $\nabla^2\rho(\mathbf{r})$, $|\lambda_1|/\lambda_3$ ratio, electronic energy density $E(\mathbf{r})$, bond lengths, and displacement of the central atom from the plane of three equatorial substituents and the nature of substituents X and Y were studied. As the number of electronegative substituents at the central atom increases, the M←N, M—X, and M—Y bond lengths decrease, while the M←N bond strength and the electron density at critical points of the M←N, M—X, and M—Y bonds increase. An increase in electronegativity of a substituent (X or Y) is accompanied by a decrease in the ionicities of the other bonds (M—X, M—Y, and M←N) formed by the central atom (Si, Ge). A new molecular orbital diagram for bond formation is proposed, which takes into account the interaction of all five substituents at the central atom (M = Si, Ge) in atrane molecules.

Key words: silatrane, germatrane, density functional theory, bond orbital population, "Atoms in Molecules" theory, electron density, electron density Laplacian, electronic energy density.

Recently, metallatranes $N(CH_2CH_2Y)_3M—X$ (compounds with intramolecular interaction M←N) have attracted particular attention of researchers owing to their unique properties.[1—5] For instance, silatranes are less reactive in the reactions of nucleophilic substitution at silicon compared to their tetracoordinate analogs.[3] A nitrogen atom involved in intramolecular interaction remains inert to electrophiles, *e.g.*, methyl iodide and tetracyanoethylene.[3] Besides, silatranes and germatranes exhibit a broad spectrum of biological activities, which makes these compounds promising for being used in medicinal chemistry.[6,7] It is believed that the biological activity of silatranes and germatranes is due to a weak transannular interaction; therefore, the emphasis is placed on the studies of the nature of the M←N bond in these compounds.[6,7] At present, transannular interaction is mainly studied by X-ray analysis. This method was used in studies of a large number of silatranes and germatranes with substituents X and Y of the same type. Because of this, the available X-ray analysis data are insufficient for correlating the effects of substituents X and Y and the parameters of transannular interaction. It is significant that the metal—donor intramolecular distance in the solid phase strongly depends on the crystal field effect and on the dipole-dipole interactions.[8,9] This is confirmed by, *e.g.*, the existence of three different modifications of 1-phenylsilatrane with transannular distances, Si←N, of 2.132(4), 2.156(4), and 2.193(5) Å.[10—12] Different Ge←N distances were also reported for 1-fluorogermatrane in two independent studies, namely, 2.011(9) Å (see Ref. 13) and 2.104(2) Å (see Ref. 14).

Gas-phase electron diffraction (GED) data are also of considerable interest for assessing the effects of axial and equatorial substituents on the strength of transannular interaction in metallatranes. The geometric parameters obtained from GED studies are independent of the crystal field effect. It should be emphasized that GED studies are labor-consuming. Unfortunately, only three metallatranes of Group 14 elements were studied by gas-phase electron diffraction. These are 1-fluorosilatrane $N(CH_2CH_2O)_3Si—F$,[15] 1-methylsilatrane $N(CH_2CH_2O)_3Si—Me$,[16] and 1-hydrosilatrane $N(CH_2CH_2O)_3Si—H$.[17] However, GED data provide a good reference for theoretical investigations.

Quantum chemical methods are free from these drawbacks. A large number of theoretical studies on the structure of silatranes and germatranes are available. Historically, pioneering quantum chemical calculations were performed by the semiempirical methods. A number of silatranes and germatranes with X = H, F, Cl, Br, I, Me, Ph and Y = O was studied by the MNDO method.[8] It was concluded that the accuracy of the method employed is

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insufficient for the description of the transannular interaction and therefore the parameters of the M←N bond obtained in that work cannot be used in structure—property correlations. More appropriate results were obtained in *ab initio* RHF/6-31G(d) study of a series of silatranes with the substituents X = H, F, OH, NH_2, Me, Cl, SH, PH_2, and SiH_3 and Y = O, NH, NMe, and CH_2.[18] The authors reported an increase in the M←N bond length in silatranes from X = F to X = Me and a specific place occupied by chlorine atom among the substituents X (according to both X-ray analysis data and the results of calculations, the shortest Si←N distance was found for X = Cl).[18] Also, the geometric parameters of the calculated silatranes were compared[18] with those of the corresponding silanes $XSi(YH)_3$, but the effect of equatorial substituents on the energy of the Si←N transannular interaction as well as the mutual influence of the equatorial and axial substituents was ignored.

Recent studies revealed the necessity of using *ab initio* or DFT calculations with rather large basis sets in order to obtain the results suitable for constructing correlations between the structural and electronic parameters of chemical bonds.[19] In particular, a series of carbatranes, silatranes, and germatranes with X = F, H and Y = CH_2, O was studied[19] and it was concluded that the energy of the M←N transannular interaction strongly depends on the nature of the central atom (M = C, Si, Ge) and relatively weakly depends on the substituents X and Y.

Earlier studies[8,18,20—22] revealed a flattened potential energy surface for the stretch of the M←N transannular bond within about 0.5 Å; the energy changes for different compounds are only 0.5—8 kcal mol^{-1}. Therefore, large stretch of the M←N bond can not significantly change the total energy of the molecule. As a consequence, obtaining correlations between the characteristics of the M←N bond and other molecular parameters requires a study in the framework of a unified computational scheme and a rather large number of compounds. Recently,[23] we have studied a series of metallatranes with M = Si, Ge, Sn, Pb; X = H, F, Cl, Br, OH, Me, NMe_2, and NMe_3^+ and Y = O and a series of carbatranes with the same substituents X and Y. The results obtained for three silatranes (X = H, F, Me) are in good agreement with the GED data, which substantiates the applicability of the DFT method to the description of atrane geometries. The aim of this work was to study the effect of the nature of substituent Y on the strength of transannular bond M←N and the effects of the nature of substituents X and Y on the parameters of the M—Y and M—X bonds, respectively.

Calculation Procedure

Theoretical studies were carried out by the density functional method (B3LYP approximation) with the 6-311G* basis set[24] using the GAMESS program.[25] Geometry optimization was performed for all compounds. The characters of the stationary points located (a minimum or a saddle point) were determined by calculating the eigenvalues of the matrix of the second derivatives of energy with respect to nuclear coordinates. Chemical bonds were analyzed by the AIM method ("Atoms in molecule" theory) using the AIMPAC95 program.[26]

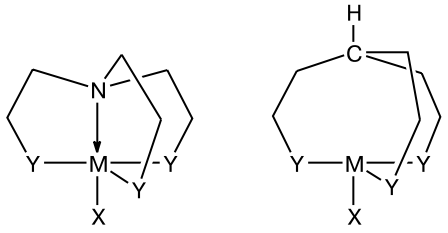
In order to substantiate the applicability of the computational method employed, we compared the electronic characteristics of metallatrane molecules in series **1** (bond populations and electron density $\rho(\mathbf{r})$) obtained by this method with the corresponding values found from MP2 calculations (Table 1).

Table 1. Key characteristics of atranes **1** (M = Si, Ge; Y = O; X = F, Me) obtained in this work from B3LYP and MP2//B3LYP calculations with the 6-311G* basis set

Bond	X	Bond population		$\rho(\mathbf{r})$/au	
		B3LYP	MP2	B3LYP	MP2
Ge←N	F	0.101	0.113	0.061	0.056
Ge←N	Me	0.073	0.080	0.048	0.043
Si←N	F	0.086	0.089	0.051	0.044
Si←N	Me	0.059	0.066	0.037	0.031
Ge—X	F	0.182	0.164	0.131	0.127
Ge—X	Me	0.210	0.231	0.131	0.135
Si—X	F	0.187	0.174	0.124	0.120
Si—X	Me	0.176	0.202	0.126	0.128
Ge—Y	F	0.174	0.179	0.130	0.128
Ge—Y	Me	0.157	0.154	0.122	0.120
Si—Y	F	0.188	0.195	0.124	0.123
Si—Y	Me	0.180	0.185	0.120	0.118

Results and Discussion

For silatranes and germatranes **1** we studied how the nature of substituents X and Y affects the Mulliken orbital populations, electron density $\rho(\mathbf{r})$, electron density Laplacian $\nabla^2\rho(\mathbf{r})$, $|\lambda_1|/\lambda_3$ ratio, electronic energy density $E(\mathbf{r})$, bond lengths, and the deviation of the metal atom from the plane. For comparison, we also investigated a series of carbon analogs (compounds **2**) of the silatranes and germatranes **1**, in which the nitrogen atom is replaced by a CH group.



1 **2**

M = Si, Ge; X = H, Me, OH, F;
Y = CH_2, O, NH, NMe, $NSiMe_3$, PH, S

We believe that the set of the bond characteristics listed above is sufficient for unambiguous determination of the strength and type of interactions in the compounds under study. The effect of substituent X on the strength of transannular interaction M←N had been a subject of many studies in the past. Because of this, the set of substituents X comprised atoms of a few second-row elements with strongly different electronegativities and the atom of hydrogen (first-row element).

We determined how the values of the parameters of the M←N bond and M...C contact (see above) depend on the nature of substituent X at the same substituent Y and on the nature of substituent Y at the same substituent X and compared them. We also studied changes in the parameters of the M—X and M—Y bonds upon variation of substituents Y and X in compounds **1** and **2**, respectively.

At different X and the same Y, the M←N bond lengths show a trend that is in agreement with the published data.[27] Namely, more electronegative substituents are characterized by shorter M←N distances: the calculated M←N distance in molecules **1** increases in the order F < OH < < H < Me (Table 2). A similar dependence was also found for the changes in the M←N bond lengths in atranes **1** upon variation of substituent Y at the same X. In silatranes the M←N bond length increases as follows: NMe < NH < < O < $NSiMe_3$ < S < CH_2 < PH, while for germatranes the order of changes has the form NMe < O < NH < < $CH_2 \approx NSiMe_3$ < S < PH.

It should be noted that the trend found for the M←N bond in metallatranes **1** (see above) is also retained for the M...C contact in the carbon analogs **2** (Table 3) despite the absence of the chemical bond between the C and M atoms in these compounds. The M...C distance increases in the following order of substituents X (at the same Y): F < OH < H < Me and in the following order of substituents Y (at the same X) O < NH ≈ NMe ≈ $NSiMe_3$ < < CH_2 < S < PH.

The mutual effect of the substituents X and Y on the M—Y and M—X bond lengths, respectively, is determined by similar reasons (see Tables 2 and 3). For instance, the M—X bond elongates in the following order of substituents Y: O < S < NH ≈ $NSiMe_3$ ≈ NMe ≈ PH < CH_2, while the M—Y bond length increases at different X as follows: F < OH < H ≈ Me. This is characteristic of both atranes **1** and their carbon analogs **2**.

In addition to the M←N bond lengths, yet another geometric characteristic of the strength of transannular interaction in metallatranes **1** is available in the literature. This is the deviation of the metal atom from the plane formed by three equatorial substituents Y toward the substituent X. In other words, this is the degree of the geometry distortion of the coordination polyhedron of the cen-

Table 2. M←N, M—X, and M—Y bond lengths (in Å) in metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	2.449	2.342	2.231	2.332	2.283	2.602	2.506
Ge←N	OH	2.674	2.412	2.288	2.433	2.335	2.717	2.634
Ge←N	H	2.544	2.527	2.326	2.561	2.357	2.859	2.761
Ge←N	Me	2.708	2.602	2.403	2.786	2.408	2.913	2.851
Si←N	F	2.380	2.170	2.114	2.308	2.279	2.535	2.354
Si←N	OH	2.484	2.281	2.161	2.437	2.387	2.663	2.537
Si←N	H	2.549	2.255	2.165	2.446	2.335	2.731	2.500
Si←N	Me	2.615	2.318	2.244	2.847	2.481	2.841	2.754
Ge—X	F	1.830	1.796	1.812	1.820	1.754	1.820	1.792
Ge—X	OH	1.581	1.827	1.842	1.837	1.791	1.847	1.820
Ge—X	H	1.858	1.564	1.573	1.552	1.542	1.571	1.558
Ge—X	Me	2.002	1.977	1.996	1.983	1.954	1.998	1.977
Si—X	F	1.690	1.675	1.676	1.681	1.629	1.681	1.664
Si—X	OH	1.727	1.712	1.718	1.712	1.671	1.715	1.696
Si—X	H	1.528	1.523	1.519	1.500	1.488	1.518	1.509
Si—X	Me	1.921	1.917	1.925	1.907	1.875	1.915	1.896
Ge—Y	F	1.990	1.871	1.886	1.873	1.819	2.367	2.262
Ge—Y	OH	2.004	1.878	1.897	1.880	1.829	2.372	2.270
Ge—Y	H	1.997	1.887	1.900	1.886	1.837	2.372	2.272
Ge—Y	Me	2.006	1.890	1.914	1.887	1.841	2.377	2.278
Si—Y	F	1.915	1.766	1.782	1.772	1.689	2.298	2.180
Si—Y	OH	1.920	1.772	1.792	1.776	1.692	2.301	2.183
Si—Y	H	1.925	1.777	1.790	1.782	1.701	2.300	2.185
Si—Y	Me	1.927	1.781	1.806	1.777	1.698	2.305	2.188

Table 3. M...C contact and M—X and M—Y bond lengths (in Å) in carbon analogs **2**

Contact, bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge...C	F	3.471	3.431	3.384	3.444	3.385	3.823	3.788
Ge...C	OH	3.519	3.474	3.450	3.500	3.431	3.876	3.841
Ge...C	H	3.574	3.534	3.472	3.552	3.472	3.926	3.885
Ge...C	Me	3.590	3.552	3.565	3.589	3.496	3.963	3.918
Si...C	F	3.494	3.462	3.454	3.423	3.355	3.847	3.775
Si...C	OH	2.883	3.494	3.494	3.467	3.391	3.889	3.821
Si...C	H	3.542	3.511	3.502	3.478	3.397	3.894	3.827
Si...C	Me	3.534	3.534	3.539	3.522	3.424	3.938	3.866
Ge—X	F	1.792	1.765	1.773	1.780	1.735	1.786	1.761
Ge—X	OH	1.828	1.799	1.806	1.809	1.772	1.821	1.796
Ge—X	H	1.560	1.547	1.549	1.544	1.532	1.554	1.544
Ge—X	Me	1.982	1.958	1.965	1.970	1.938	1.981	1.962
Si—X	F	1.655	1.631	1.637	1.644	1.608	1.649	1.629
Si—X	OH	1.677	1.674	1.679	1.683	1.651	1.690	1.669
Si—X	H	1.510	1.498	1.503	1.496	1.482	1.503	1.494
Si—X	Me	1.880	1.880	1.887	1.897	1.860	1.899	1.880
Ge—Y	F	1.967	1.840	1.862	1.837	1.777	2.347	2.238
Ge—Y	OH	1.975	1.850	1.870	1.849	1.786	2.353	2.248
Ge—Y	H	1.984	1.859	1.873	1.859	1.793	2.352	2.252
Ge—Y	Me	1.986	1.864	1.865	1.869	1.799	2.358	2.259
Si—Y	F	1.888	1.726	1.727	1.737	1.652	2.274	2.149
Si—Y	OH	1.767	1.736	1.736	1.748	1.661	2.279	2.158
Si—Y	H	1.904	1.742	1.742	1.754	1.666	2.282	2.163
Si—Y	Me	1.747	1.747	1.750	1.764	1.672	2.286	2.170

tral atom from a perfect trigonal bipyramid.[3—5] As should be expected, the deviation of the metal atom from the plane increases in the following order of substituents X: F < OH < H < Me (Table 4). Data for substituents Y show some scatter and the order of the substituents for silatranes and germatranes of the type **1** are different:

$$NMe < NH < O < S < NSiMe_3 < PH \approx CH_2 \text{ (silatranes)},$$
$$O \approx NMe < NH < CH_2 \approx NSiMe_3 < S \approx PH \text{ (germatranes)}.$$

The carbon analogs **2** behave similarly to germatranes (see Table 4). It should be noted that the deviation from the plane is much larger for compounds **2** compared to atranes **1**, which indicates the occurrence of the M←N interaction and the absence of the M...C interaction.

In order to estimate the strength of the transannular interaction, we analyzed the bond orbital populations according to Mulliken.[28] It is known that the strength of an atom—atom interaction is defined as the sum of the contributions of the overlap of the atomic or basis set orbitals of atoms over all occupied molecular orbitals (MOs). In turn the overlap of particular atomic orbitals (AOs) is determined by the overlap integral, S, of two unperturbed AOs multiplied by the weighting factors of the AOs in question in the MO (C_i, C_j).

$$\text{Bond population} = \sum_{i,j}^{N} C_i C_j S_{ij} \qquad (1)$$

The sum of all bond orbital populations for a given atom was normalized to unity. Using the results of the bond orbital population analysis for the central atom, we determined the relative contributions of its interactions with all substituents. We found that the strength of the M←N bond in metallatranes **1** increases as follows: Me < H < OH < F (substituents X) and PH < CH_2 ≈ S < < O ≈ NH ≈ NMe ≈ $NSiMe_3$ (substituents Y) (Table 5). At the same time the onset of additional interaction M←N in silatranes and germatranes **1** compared to the carbon analogs **2** causes the M—X and M—Y bond populations to decrease. In most cases, on going from metallatranes **1** to the carbon analogs **2** the M—Y bond orbital populations change to a greater extent compared to the M—X bond orbital populations (see Tables 5 and 6).

From the data listed in Tables 4 and 5 it also follows that the relative interaction of a silicon or germanium atom with the axial nitrogen atom in metallatranes is 3.2—11.5%. The interaction of the central atom with each equatorial substituent Y and with the axial substituent X lies in the range 11.2—24.1%. Thus, the transannular interaction in the metallatranes studied is weaker than conventional M—X and M—Y bonds. Nevertheless, this is a bonding interaction, which becomes pronounced in the presence of electronegative substituents X and Y.

We analyzed the orbital populations for the interaction of the valence s- and p-orbitals of the central atom

Table 4. Deviation of the metal atom from the plane formed by three substituents Y toward substituent X (in Å) in metallatranes **1** and in the carbon analogs **2**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
				Metallatranes **1**				
Ge←N	F	0.550	0.549	0.519	0.580	0.546	0.630	0.663
Ge←N	OH	0.594	0.587	0.582	0.628	0.589	0.678	0.713
Ge←N	H	0.641	0.638	0.604	0.670	0.625	0.721	0.750
Ge←N	Me	0.658	0.657	0.659	0.705	0.649	0.757	0.783
Si←N	F	0.545	0.550	0.541	0.536	0.507	0.630	0.627
Si←N	OH	0.523	0.580	0.577	0.576	0.541	0.672	0.668
Si←N	H	0.589	0.590	0.581	0.582	0.545	0.670	0.670
Si←N	Me	0.611	0.611	0.614	0.623	0.570	0.712	0.708
Contact				Compounds **2**				
Ge...C	F	0.334	0.270	0.235	0.278	0.222	0.318	0.263
Ge...C	OH	0.484	0.324	0.290	0.345	0.272	0.406	0.364
Ge...C	H	0.403	0.399	0.318	0.430	0.299	0.498	0.448
Ge...C	Me	0.510	0.443	0.382	0.551	0.338	0.549	0.519
Si...C	F	0.299	0.219	0.188	0.255	0.220	0.280	0.167
Si...C	OH	0.367	0.273	0.233	0.332	0.287	0.368	0.293
Si...C	H	0.395	0.277	0.223	0.339	0.263	0.393	0.255
Si...C	Me	0.439	0.320	0.292	0.524	0.344	0.481	0.428

Table 5. The M←N, M—X, and M—Y bond orbital populations obtained for metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	0.083	0.085	0.098	0.115	0.101	0.064	0.087
Ge←N	OH	0.068	0.072	0.087	0.096	0.090	0.047	0.073
Ge←N	H	0.044	0.058	0.075	0.077	0.079	0.035	0.058
Ge←N	Me	0.043	0.052	0.068	0.051	0.073	0.032	0.051
Si←N	F	0.090	0.096	0.092	0.103	0.086	0.047	0.076
Si←N	OH	0.070	0.076	0.081	0.084	0.070	0.035	0.063
Si←N	H	0.051	0.074	0.074	0.083	0.072	0.040	0.061
Si←N	Me	0.047	0.072	0.068	0.046	0.059	0.040	0.057
Ge—X	F	0.173	0.153	0.119	0.112	0.182	0.200	0.191
Ge—X	OH	0.194	0.179	0.134	0.130	0.205	0.210	0.213
Ge—X	H	0.185	0.172	0.163	0.191	0.216	0.228	0.241
Ge—X	Me	0.179	0.169	0.157	0.164	0.210	0.190	0.208
Si—X	F	0.192	0.152	0.128	0.127	0.187	0.200	0.190
Si—X	OH	0.220	0.179	0.138	0.142	0.209	0.203	0.207
Si—X	H	0.197	0.178	0.152	0.175	0.202	0.194	0.217
Si—X	Me	0.176	0.153	0.138	0.144	0.176	0.139	0.156
Ge—Y	F	0.153	0.170	0.164	0.153	0.174	0.172	0.192
Ge—Y	OH	0.142	0.158	0.155	0.138	0.162	0.158	0.176
Ge—Y	H	0.169	0.173	0.153	0.137	0.169	0.166	0.176
Ge—Y	Me	0.152	0.157	0.146	0.139	0.157	0.143	0.159
Si—Y	F	0.158	0.179	0.169	0.164	0.188	0.188	0.198
Si—Y	OH	0.145	0.165	0.160	0.152	0.178	0.173	0.183
Si—Y	H	0.168	0.171	0.156	0.152	0.183	0.174	0.176
Si—Y	Me	0.161	0.162	0.153	0.160	0.180	0.165	0.173

with substituents taking four metallatranes **1** (M = Si, Ge; Y = O; X = F, Me) and their carbon analogs **2** (Table 7) as examples. It was found that the contributions of the interaction of the nitrogen AOs with the valence s- and p-orbitals of the central atom are nearly equal. Therefore, ignoring the contribution of the Si 3s-AO or Ge 4s-AO in

Table 6. The M...C contact and M—X and M—Y bond orbital populations calculated for carbon analogs **2**

Contact, bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge...C	F	0.0055	0.0091	0.0038	0.0046	0.0125	0.0064	0.0051
Ge...C	OH	0.0067	0.0096	0.0050	0.0064	0.0137	0.0058	0.0060
Ge...C	H	0.0070	0.0104	0.0074	0.0051	0.0168	0.0065	0.0075
Ge...C	Me	0.0061	0.0086	0.0047	0.0051	0.0142	0.0049	0.0059
Si...C	F	0.0028	0.0084	0.0066	0.0053	0.0122	0.0048	0.0046
Si...C	OH	0.0021	0.0067	0.0053	0.0042	0.0110	0.0045	0.0043
Si...C	H	0.0037	0.0077	0.0055	0.0044	0.0142	0.0048	0.0063
Si...C	Me	0.0029	0.0070	0.0051	0.0049	0.0132	0.0041	0.0045
Ge—X	F	0.185	0.175	0.138	0.138	0.206	0.231	0.214
Ge—X	OH	0.199	0.194	0.151	0.142	0.227	0.236	0.233
Ge—X	H	0.192	0.179	0.181	0.203	0.229	0.249	0.251
Ge—X	Me	0.181	0.178	0.154	0.168	0.227	0.206	0.215
Si—X	F	0.213	0.191	0.169	0.154	0.211	0.252	0.239
Si—X	OH	0.235	0.208	0.177	0.159	0.228	0.259	0.248
Si—X	H	0.211	0.160	0.140	0.181	0.200	0.235	0.237
Si—X	Me	0.191	0.158	0.130	0.151	0.184	0.178	0.170
Ge—Y	F	0.192	0.203	0.194	0.203	0.216	0.196	0.223
Ge—Y	OH	0.173	0.184	0.177	0.181	0.197	0.172	0.201
Ge—Y	H	0.183	0.197	0.169	0.166	0.201	0.175	0.199
Ge—Y	Me	0.167	0.176	0.164	0.160	0.182	0.152	0.181
Si—Y	F	0.195	0.208	0.198	0.206	0.218	0.197	0.217
Si—Y	OH	0.174	0.193	0.183	0.189	0.202	0.178	0.199
Si—Y	H	0.188	0.214	0.200	0.186	0.213	0.186	0.204
Si—Y	Me	0.179	0.198	0.186	0.181	0.202	0.175	0.198

Table 7. The M←N, M—X and M—Y bond orbital populations obtained for metallatranes **1** and their carbon analogs **2** (Y = O) by considering separate interactions between ligands and the valence s- and p-orbitals of the central atom

Bond	X = F		X = Me	
	s	p	s	p
	Metallatranes **1**			
Ge←N	0.037	0.055	0.034	0.034
Ge—X	0.029	0.127	0.105	0.106
Ge—Y	0.028	0.115	—	0.125
Si←N	0.036	0.049	0.023	0.037
Si—X	0.027	0.124	0.089	0.080
Si—Y	0.032	0.125	0.019	0.133
	Compounds **2**			
Ge←N	—	—	—	—
Ge—X	0.033	0.157	0.103	0.127
Ge—Y	0.041	0.150	0.020	0.141
Si←N	—	—	—	—
Si—X	0.015	0.148	0.091	0.091
Si—Y	0.037	0.134	0.024	0.151

the axial bonding in the framework of the theory of 3c—4e-bond[29,30] can lead to incorrect interpretation of the results obtained.

It should be noted that the M...C bond orbital population in the carbon analogs **2** (see Table 6) is of the same order of magnitude as the orbital populations of the interactions between the metal atom and carbon atoms of the atrane framework in compounds **1** and corresponds to a weak interaction of nonbonded atoms.

The types of interaction in metallatranes **1** and in their carbon analogs **2** were established using the Bader topological theory. The AIM method provides reliable information on the types of chemical bonds in hypervalent compounds.[27,31—35] The results of the AIM analysis depend only slightly on the computational procedure employed.[34]

According to the "Atoms in Molecules" theory, the necessary and sufficient condition for the existence of a chemical bond between two atoms is the presence of a (3, −1) critical point in the interatomic space and the electron density gradient line passing through this point should terminate at the interacting atoms.[36,37] Although the electron density at a critical point does not characterize the strength of the chemical bond, being only responsible for the type of this bond, it should be noted that this parameter increases in the same order as the orbital population of the M←N bond (as function of X at the same Y): Me ≈ H < OH < F (Table 8). At the same X, the electron density increases in the order PH < S ≈ CH_2 < $NSiMe_3$ < O ≈ NH < NMe upon variation of the substituent Y, *i.e.*, in nearly the same fashion as in the case of changes in the orbital population

Table 8. Electron density at critical points of the M←N, M—X, and M—Y bonds (in $e\ a_0^{-3}$) in metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	0.042	0.053	0.064	0.054	0.061	0.034	0.041
Ge←N	OH	0.036	0.046	0.058	0.045	0.055	0.028	0.033
Ge←N	H	0.029	0.037	0.054	0.035	0.053	0.023	0.027
Ge←N	Me	0.027	0.033	0.046	0.023	0.048	0.020	0.023
Si←N	F	0.041	0.056	0.062	0.047	0.051	0.034	0.046
Si←N	OH	0.034	0.047	0.057	0.038	0.043	0.028	0.035
Si←N	H	0.032	0.049	0.057	0.037	0.046	0.026	0.037
Si←N	Me	0.028	0.044	0.050	0.019	0.037	0.022	0.025
Ge—X	F	0.108	0.118	0.114	0.111	0.131	0.111	0.120
Ge—X	OH	0.118	0.128	0.123	0.124	0.140	0.121	0.129
Ge—X	H	0.118	0.124	0.122	0.128	0.132	0.121	0.126
Ge—X	Me	0.118	0.125	0.121	0.124	0.131	0.119	0.125
Si—X	F	0.105	0.109	0.109	0.107	0.124	0.108	0.114
Si—X	OH	0.112	0.118	0.116	0.117	0.130	0.116	0.123
Si—X	H	0.110	0.112	0.114	0.118	0.124	0.113	0.118
Si—X	Me	0.112	0.114	0.113	0.117	0.126	0.114	0.120
Ge—Y	F	0.123	0.133	0.130	0.131	0.130	0.089	0.096
Ge—Y	OH	0.121	0.131	0.126	0.127	0.127	0.088	0.094
Ge—Y	H	0.119	0.128	0.125	0.126	0.123	0.087	0.093
Ge—Y	Me	0.119	0.127	0.121	0.126	0.122	0.087	0.092
Si—Y	F	0.117	0.123	0.119	0.121	0.124	0.096	0.097
Si—Y	OH	0.115	0.121	0.115	0.120	0.122	0.095	0.096
Si—Y	H	0.113	0.118	0.115	0.116	0.119	0.093	0.094
Si—Y	Me	0.113	0.118	0.112	0.118	0.120	0.092	0.094

(*cf.* Tables 5 and 8). It should be noted that no critical points were found for the carbon analogs in the region between the M and C atoms. This confirms that these atoms are nonbonded.

We also studied the mutual influence of the nature of substituents X and Y on the electronic properties of the M—Y and M—X bonds, respectively. The electron density at the critical point of the M—X bond increases depending on Y as follows: $CH_2 < PH < NH \approx NMe \approx NSiMe_3 \approx S < O$. That is, the maximum electron density is attained if the central atom is surrounded by five substituents with sufficiently high electronegativities. The same order of substituents Y was found for silatranes, germatranes, and carbon analogs (see Tables 8 and 9). It should be noted that this order of changes (depending on Y) in the electron density in the region of M—X bonds and the order of changes (depending on Y) known for the M←N bond do not always obey identical patterns. Nevertheless, the electron density in the regions of the M←N and M—Y bonds in all compounds under study increases at different X as follows: Me ≈ H < OH < F for both bonds (see Tables 8 and 9).

As is known, it is the sign of the Laplacian of the electron density that allows chemical bonds to be grouped into covalent ($\nabla^2\rho < 0$) and closed-shell (and ionic) interactions ($\nabla^2\rho > 0$). For the M←N bonds in compounds **1**, the values of the Laplacian of the electron density are positive and increase in the order Me < H < OH < F for substituents X and as shown below for substituents Y:

$PH \approx S < CH_2 < NSiMe_3 < NH < O < NMe$ (germatranes),
$S < O < NSiMe_3 < PH < CH_2 < NH < NMe$ (silatranes).

The following trend was found for germatranes: for strongly electronegative substituents (X = F, OH) the values of the Laplacian of the M—X bonds increase in the order $CH_2 < PH < NMe \approx NSiMe_3 < NH \approx S < O$ (substituents Y). For the less electronegative substituents (X = H, Me), this order is reversed (Table 10). Variation of substituent Y causes the M—X bonding type to be changed from covalent (X = H, Me; Y = O) to closed-shell interaction (X = H, Me; Y = CH_2). This suggests different electronic structures of the hypervalent germanium compounds containing only weak electronegative substituents (H, C) and the compounds in which most substituents are more electronegative groups. This dependence was not observed for silatranes; despite the scatter of data, the Laplacian values increase from Y = CH_2 to Y = O for all substituents Y (see Table 10).

Similar trends are also characteristic of the Laplacian of the M—Y bond upon variation of substituent X in compounds **1**. For germatranes containing weakly electronegative substituents (Y = CH_2, S, PH), the depen-

Table 9. Electron density at critical points of the M—X and M—Y bonds (in $e\ a_0^{-3}$) in carbon analogs **2**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge—X	F	0.118	0.127	0.124	0.122	0.137	0.120	0.128
Ge—X	OH	0.125	0.136	0.133	0.133	0.145	0.128	0.136
Ge—X	H	0.123	0.128	0.128	0.129	0.133	0.124	0.129
Ge—X	Me	0.122	0.128	0.127	0.126	0.134	0.122	0.127
Si—X	F	0.114	0.121	0.119	0.117	0.129	0.116	0.122
Si—X	OH	0.119	0.127	0.125	0.124	0.135	0.122	0.129
Si—X	H	0.114	0.119	0.117	0.119	0.125	0.115	0.120
Si—X	Me	0.115	0.122	0.120	0.119	0.128	0.116	0.122
Ge—Y	F	0.128	0.142	0.139	0.141	0.144	0.092	0.100
Ge—Y	OH	0.126	0.139	0.136	0.137	0.140	0.091	0.098
Ge—Y	H	0.123	0.136	0.134	0.134	0.137	0.090	0.097
Ge—Y	Me	0.123	0.134	0.134	0.131	0.136	0.090	0.096
Si—Y	F	0.122	0.132	0.132	0.130	0.135	0.100	0.103
Si—Y	OH	0.120	0.129	0.129	0.126	0.132	0.098	0.101
Si—Y	H	0.117	0.126	0.127	0.124	0.130	0.095	0.098
Si—Y	Me	0.116	0.125	0.125	0.121	0.128	0.095	0.098

Table 10. Electron density Laplacian at critical points of the M←N, M—X, and M—Y bonds (in $e\ a_0^{-5}$) in metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	0.089	0.096	0.116	0.094	0.096	0.066	0.070
Ge←N	OH	0.078	0.087	0.105	0.082	0.089	0.055	0.057
Ge←N	H	0.064	0.074	0.099	0.069	0.086	0.045	0.047
Ge←N	Me	0.061	0.066	0.088	0.051	0.080	0.042	0.042
Si←N	F	0.035	0.087	0.117	0.028	0.027	0.031	0.013
Si←N	OH	0.039	0.043	0.090	0.028	0.026	0.035	0.025
Si←N	H	0.040	0.050	0.085	0.030	0.024	0.035	0.023
Si←N	Me	0.042	0.039	0.051	0.039	0.033	0.034	0.031
Ge—X	F	0.499	0.577	0.537	0.518	0.686	0.515	0.576
Ge—X	OH	0.415	0.464	0.437	0.445	0.527	0.427	0.468
Ge—X	H	0.005	−0.011	−0.009	−0.011	−0.038	−0.004	−0.022
Ge—X	Me	0.026	0.012	0.009	0.001	−0.011	0.012	−0.003
Si—X	F	0.686	0.737	0.734	0.718	0.905	0.713	0.770
Si—X	OH	0.637	0.679	0.661	0.681	0.802	0.669	0.723
Si—X	H	0.112	0.121	0.129	0.150	0.125	0.109	0.110
Si—X	Me	0.180	0.183	0.167	0.174	0.197	0.166	0.171
Ge—Y	F	0.001	0.268	0.249	0.259	0.458	—0.045	0.015
Ge—Y	OH	0.005	0.264	0.242	0.253	0.443	—0.041	0.018
Ge—Y	H	0.010	0.260	0.250	0.260	0.435	—0.036	0.023
Ge—Y	Me	0.011	0.255	0.231	0.255	0.427	—0.036	0.023
Si—Y	F	0.165	0.525	0.489	0.498	0.734	—0.150	0.006
Si—Y	OH	0.163	0.511	0.468	0.489	0.724	—0.133	0.007
Si—Y	H	0.162	0.504	0.478	0.483	0.697	—0.128	0.015
Si—Y	Me	0.161	0.495	0.439	0.489	0.705	—0.131	0.009

dence is reversed, that is, F < OH < H ≈ Me (see Table 10), whereas for more electronegative substituents the typical order of substituents X is retained: Me ≈ H < OH < F. As to silatranes, the order of substituents X is changed only for the third-row elements (Y = S, PH). All the aforesaid also holds for the changes in the values of the Laplacian of the M—X and M—Y bonds in the carbon analogs (Table 11).

Table 11. Electron density Laplacian at critical points of the M—X and M—Y bonds (in $e\,a_0^{-5}$) in carbon analogs **2**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge—X	F	0.588	0.658	0.636	0.610	0.740	0.597	0.659
Ge—X	OH	0.466	0.516	0.502	0.491	0.566	0.471	0.515
Ge—X	H	0.001	−0.021	−0.018	−0.022	−0.047	−0.010	−0.031
Ge—X	Me	0.023	0.007	0.004	−0.002	−0.015	0.008	−0.007
Si—X	F	0.809	0.906	0.881	0.855	1.006	0.828	0.909
Si—X	OH	0.720	0.799	0.782	0.767	0.878	0.741	0.808
Si—X	H	0.121	0.118	0.116	0.133	0.116	0.114	0.103
Si—X	Me	0.193	0.206	0.197	0.181	0.207	0.174	0.180
Ge—Y	F	0.001	0.303	0.254	0.303	0.545	−0.049	0.012
Ge—Y	OH	0.006	0.295	0.253	0.293	0.530	−0.045	0.016
Ge—Y	H	0.012	0.292	0.261	0.289	0.524	−0.040	0.021
Ge—Y	Me	0.015	0.287	0.289	0.278	0.512	−0.039	0.021
Si—Y	F	0.191	0.618	0.618	0.580	0.870	−0.146	0.021
Si—Y	OH	0.190	0.598	0.597	0.556	0.840	−0.133	0.022
Si—Y	H	0.185	0.582	0.585	0.544	0.823	−0.123	0.024
Si—Y	Me	0.185	0.570	0.564	0.521	0.802	−0.120	0.023

The parameter $|\lambda_1|/\lambda_3$ is the ratio of two eigenvalues of the electron density Laplacian. It characterizes the ionicity of a chemical bond. According to calculations of a number of simple compounds,[38,39] the $|\lambda_1|/\lambda_3$ parameters of ionic bonds and closed-shell interactions lie in the range 0.15—0.25, those of covalent bonds exceed a value of 0.76, and the region of $|\lambda_1|/\lambda_3$ values from 0.25 to 0.76 corresponds to polar bonds. Despite some scatter of data, the derivatives studied in this work show a general trend, namely, the $|\lambda_1|/\lambda_3$ ratio for the M←N bonds increases in the order Me < H < OH < F (substituents X) and PH < CH_2 < S < NH ≈ $NSiMe_3$ < NMe < O (substituents Y) (Table 12). In other words, an increase in electronegativity of substituents X and Y causes a decrease in the M←N bond ionicity. The same also holds if we consider the effect of the nature of substituents X and Y on the M—Y and M—X bonds, respectively. Thus, the trend to a decrease in the bond ionicities of the central atom upon increasing the electronegativity of a substituent at atoms in question (Si, Ge) is a general case (see Table 12 and 13). It should be noted that most M—C, M—H, and M—S bonds in the compounds under study cannot be treated as covalent or closed-shell interactions; they are intermediate in character, being polar bonds of high polarity. The M—P bonds in germatranes and silatranes are covalent in character (see Tables 12 and 13), the bonds in silatranes being more covalent.

Recently,[34,35,40—42] the density of the electronic energy $E(\mathbf{r})$ at the critical point of a chemical bond has been used as yet another characteristic of the interaction in order to reveal a specific group of compounds with dative bonds. Most silatranes and germatranes of the type **1** are characterized by low electron density, positive Laplacian and small values of the $|\lambda_1|/\lambda_3$ ratio at the critical points of M←N bonds. According to Bader´s theory, such bonds should be treated as closed-shell interactions. However, it is also believed[40—42] that one should take into account an additional condition, namely, the sign of the electronic energy density. This parameter is positive for ionic bonds and negative for covalent ones.[43] It was proposed to treat the bonds with positive Laplacian and negative electronic energy density as belonging to intermediate type.[42] However, in the case of silatranes and germatranes classification based on the sign of the electronic energy density seems to be somewhat incorrect. Indeed, the data listed in Table 14 show that the electronic energy density for the M←N bond is nearly zero. In addition, the $E(\mathbf{r})$ values and for other bonds in silatranes, germatranes, and their carbon analogs also differs only slightly from zero (see Tables 14 and 15). Thus, it is impossible to determine the type of interaction based on the $E(\mathbf{r})$ data. The $|\lambda_1|/\lambda_3$ ratio seems to be more appropriate in this case. Starting from the data on the electron density, the electron density Laplacian, and the $|\lambda_1|/\lambda_3$ ratio at the critical points of M←N bonds, one can conclude that the transannular interaction in silatranes and germatranes belongs to the closed-shell type interactions with a large ionic component. Bonding with substituents X and Y in silatranes, germatranes, and in their carbon analogs occurs by covalent (M—P), ionic (M—O, M—F, M←N), and strongly polar (intermediate) type (M—S, M—C, M—H).

As mentioned above, researchers placed the emphasis on investigations of transannular interaction in atranes. The formation of the M←N bond is still a moot question. According to Ref. 44, there are two major concepts that

Table 12. $|\lambda_1|/\lambda_3$ ratio at critical points of the M←N, M—X, and M—Y bonds in metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	0.221	0.259	0.269	0.263	0.280	0.216	0.247
Ge←N	OH	0.207	0.248	0.263	0.249	0.273	0.204	0.233
Ge←N	H	0.190	0.230	0.255	0.224	0.268	0.194	0.222
Ge←N	Me	0.184	0.218	0.245	0.178	0.259	0.183	0.205
Si←N	F	0.270	0.242	0.239	0.339	0.347	0.289	0.410
Si←N	OH	0.237	0.297	0.253	0.312	0.332	0.244	0.322
Si←N	H	0.225	0.271	0.253	0.291	0.351	0.236	0.342
Si←N	Me	0.196	0.273	0.277	0.133	0.274	0.208	0.244
Ge—X	F	0.191	0.191	0.192	0.193	0.190	0.191	0.191
Ge—X	OH	0.227	0.230	0.231	0.230	0.231	0.229	0.230
Ge—X	H	0.492	0.519	0.513	0.516	0.555	0.508	0.534
Ge—X	Me	0.458	0.483	0.485	0.499	0.517	0.482	0.506
Si—X	F	0.169	0.171	0.171	0.171	0.170	0.166	0.167
Si—X	OH	0.189	0.194	0.193	0.190	0.191	0.187	0.188
Si—X	H	0.366	0.364	0.359	0.351	0.376	0.372	0.375
Si—X	Me	0.311	0.316	0.325	0.325	0.323	0.322	0.325
Ge—Y	F	0.510	0.304	0.310	0.304	0.236	0.700	0.495
Ge—Y	OH	0.502	0.302	0.308	0.302	0.235	0.683	0.485
Ge—Y	H	0.488	0.298	0.298	0.294	0.231	0.660	0.467
Ge—Y	Me	0.486	0.300	0.304	0.298	0.231	0.657	0.467
Si—Y	F	0.333	0.225	0.228	0.227	0.190	2.391	0.514
Si—Y	OH	0.331	0.226	0.228	0.227	0.189	1.787	0.509
Si—Y	H	0.324	0.221	0.221	0.223	0.187	1.809	0.483
Si—Y	Me	0.325	0.223	0.227	0.225	0.189	1.894	0.501

Table 13. $|\lambda_1|/\lambda_3$ ratio at critical points of the M—X and M—Y bonds in carbon analogs **2**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge—X	F	0.188	0.190	0.189	0.192	0.189	0.189	0.189
Ge—X	OH	0.225	0.228	0.227	0.230	0.228	0.228	0.228
Ge—X	H	0.499	0.533	0.526	0.531	0.567	0.516	0.546
Ge—X	Me	0.463	0.492	0.496	0.504	0.523	0.488	0.512
Si—X	F	0.167	0.167	0.167	0.168	0.166	0.164	0.164
Si—X	OH	0.186	0.188	0.187	0.189	0.187	0.184	0.185
Si—X	H	0.363	0.375	0.375	0.363	0.384	0.372	0.385
Si—X	Me	0.307	0.312	0.315	0.322	0.319	0.319	0.322
Ge—Y	F	0.506	0.298	0.316	0.296	0.231	0.715	0.501
Ge—Y	OH	0.496	0.297	0.312	0.295	0.230	0.695	0.491
Ge—Y	H	0.483	0.294	0.303	0.291	0.228	0.674	0.476
Ge—Y	Me	0.479	0.294	0.295	0.293	0.228	0.669	0.474
Si—Y	F	0.325	0.219	0.221	0.221	0.187	2.028	0.487
Si—Y	OH	0.321	0.219	0.221	0.221	0.187	1.692	0.482
Si—Y	H	0.314	0.219	0.221	0.220	0.186	1.568	0.473
Si—Y	Me	0.314	0.220	0.222	0.222	0.187	1.503	0.474

provide explanation for the ability of Group 14 elements (Si, Ge, Sn, Pb) to form neutral compounds with extended coordination sphere of the central atom. Historically, the first theory was based on the concept of involvement of the nd-orbitals of the central atom in chemical bonding (d-orbital concept). However, many researchers reported that d-orbitals are too diffuse to be involved in the formation of transannular bond,[45—47] at least for atoms of the third-row elements (*e.g.*, Si).[46,48] At the same time it was found[47] that although d-orbitals do not participate in bond formation in the compounds X_3AY with 32 valence electrons (*e.g.*, $F_3C—O^-$, $F_3P{=}O$, $F_3C—F$, $F_3Si—F$, *etc.*),

Table 14. Electronic energy density ($-E(\mathbf{r})$) at critical points of the M←N, M—X, and M—Y bonds in metallatranes **1**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge←N	F	0.007	0.012	0.019	0.013	0.017	0.003	0.006
Ge←N	OH	0.004	0.009	0.015	0.008	0.014	0.002	0.003
Ge←N	H	0.002	0.005	0.013	0.004	0.012	0.001	0.002
Ge←N	Me	0.002	0.004	0.009	0.001	0.010	0.001	0.001
Si←N	F	0.013	0.024	0.027	0.019	0.023	0.007	0.017
Si←N	OH	0.008	0.019	0.025	0.012	0.015	0.004	0.008
Si←N	H	0.006	0.020	0.024	0.011	0.018	0.003	0.009
Si←N	Me	0.004	0.016	0.021	0.001	0.010	0.002	0.003
Ge—X	F	0.028	0.030	0.030	0.029	0.035	0.028	0.031
Ge—X	OH	0.043	0.049	0.047	0.047	0.056	0.045	0.050
Ge—X	H	0.068	0.074	0.073	0.078	0.082	0.070	0.076
Ge—X	Me	0.065	0.071	0.068	0.070	0.077	0.065	0.071
Si—X	F	0.021	0.022	0.021	0.021	0.025	0.022	0.024
Si—X	OH	0.034	0.037	0.037	0.036	0.043	0.036	0.040
Si—X	H	0.072	0.074	0.075	0.078	0.087	0.074	0.080
Si—X	Me	0.070	0.072	0.072	0.076	0.084	0.073	0.079
Ge—Y	F	0.070	0.068	0.065	0.067	0.051	0.037	0.042
Ge—Y	OH	0.068	0.065	0.062	0.060	0.048	0.036	0.041
Ge—Y	H	0.065	0.063	0.060	0.062	0.046	0.036	0.040
Ge—Y	Me	0.065	0.063	0.058	0.062	0.046	0.035	0.040
Si—Y	F	0.075	0.057	0.055	0.057	0.041	0.067	0.066
Si—Y	OH	0.074	0.055	0.053	0.056	0.039	0.066	0.065
Si—Y	H	0.071	0.053	0.051	0.052	0.037	0.063	0.062
Si—Y	Me	0.071	0.053	0.050	0.054	0.038	0.062	0.062

Table 15. Electronic energy density ($-E(\mathbf{r})$) at critical points of the M—X and M—Y bonds in carbon analogs **2**

Bond	X	Y						
		CH_2	NH	NMe	$NSiMe_3$	O	PH	S
Ge—X	F	0.029	0.032	0.032	0.032	0.036	0.030	0.033
Ge—X	OH	0.046	0.053	0.051	0.052	0.059	0.048	0.053
Ge—X	H	0.073	0.078	0.078	0.080	0.084	0.074	0.079
Ge—X	Me	0.068	0.074	0.073	0.072	0.080	0.068	0.073
Si—X	F	0.020	0.020	0.020	0.020	0.022	0.021	0.022
Si—X	OH	0.035	0.038	0.038	0.038	0.043	0.037	0.040
Si—X	H	0.074	0.080	0.079	0.079	0.088	0.076	0.082
Si—X	Me	0.072	0.078	0.077	0.077	0.085	0.074	0.080
Ge—Y	F	0.075	0.074	0.073	0.074	0.059	0.039	0.046
Ge—Y	OH	0.072	0.072	0.070	0.071	0.056	0.039	0.044
Ge—Y	H	0.069	0.068	0.068	0.067	0.054	0.038	0.043
Ge—Y	Me	0.069	0.068	0.067	0.066	0.053	0.038	0.042
Si—Y	F	0.080	0.061	0.062	0.061	0.045	0.071	0.071
Si—Y	OH	0.077	0.059	0.059	0.059	0.043	0.070	0.068
Si—Y	H	0.074	0.056	0.057	0.056	0.041	0.066	0.065
Si—Y	Me	0.073	0.056	0.056	0.055	0.041	0.066	0.065

they should be included in calculations in order to obtain a correct qualitative description of the bond formation diagram.

The second idea is based on the theory of three-center four-electron (3c—4e) bond for orbital-deficient compounds.[29] It is the last-mentioned concept that is conven-

tionally used to describe the nature of the M←N bond in metallatranes.[30] However, this theory explicitly takes into account only the interaction between two axial substituents and ignores the effect of the equatorial substituents on the axial ones and *vice versa*. In this work we have shown that the interaction between the axial and equatorial substituents is rather strong and they have a pronounced effect on the strength of transannular interaction M←N .

It is commonly accepted that the transannular bond M←N in metallatranes **1** elongates as the σ-electron-donor properties of substituent X are enhanced. This is consistent with the X-ray analysis data[1—4] and with the results of earlier quantum chemical calculations.[8,18,27,31] A recent study[49] of related systems containing pentacoordinate tin atom ($Y(CH_2CH_2S)_2Sn(R_{ax})R'_{eq}$, Y = O, S, NR″) showed that shortening of the M←Y distance is a result of high π-Lewis acidity rather than higher electronegativity of the substituent R_{ax}. Certain systems with hypervalent silicon exhibit good agreement between the nucleofugality of the axial substituent and the strength of transannular interaction.[50] Another explanation for the mutual effect of substituents is also available.[18] According to this hypothesis, a strong M←N interaction can occur if the orbital of the substituent X is similar in energy to the lone electron pair orbital of nitrogen atom. In this case we deal with the maximum mixing of orbitals of the axial substituents.

However, it should be noted that this approach again ignores the effect of equatorial substituents. In accordance with the MO theory and the results of our calculations we propose a new formation scheme of hypervalent atrane molecule **1** (M = Si, Ge; Fig. 1). The interaction between the axial and equatorial substituents and the central atom should be considered as the interaction of the joint ligand system and the central atom, as is often performed in studies of transition metal complexes.[51] A similar MO scheme can also be designed for germatrane, except that the Ge 4s- and 4p-levels are somewhat higher in energy than corresponding silicon levels (see below).

Now it becomes understandable that the mutual effect of substituents is governed by the strength of their interaction with the central atom. The stronger the interaction of one substituent with the atom M, the weaker the interaction of other substituents with the central atom. For instance, in carbatranes $N(CH_2CH_2Y)_3C—X$ the carbon atom forms strong covalent bonds with the substituents X and Y; therefore, the C—N interaction is the weakest. For silatrane (M = Si), the interaction with more electronegative substituents X and Y is more ionic in character and, correspondingly, weaker than in carbatrane. Thus, the silicon atom can be involved in additional interaction with the lone electron pair of nitrogen atom. Besides, the strength of the orbital—orbital interaction increases as the energy difference between the orbitals decreases.[52] Since

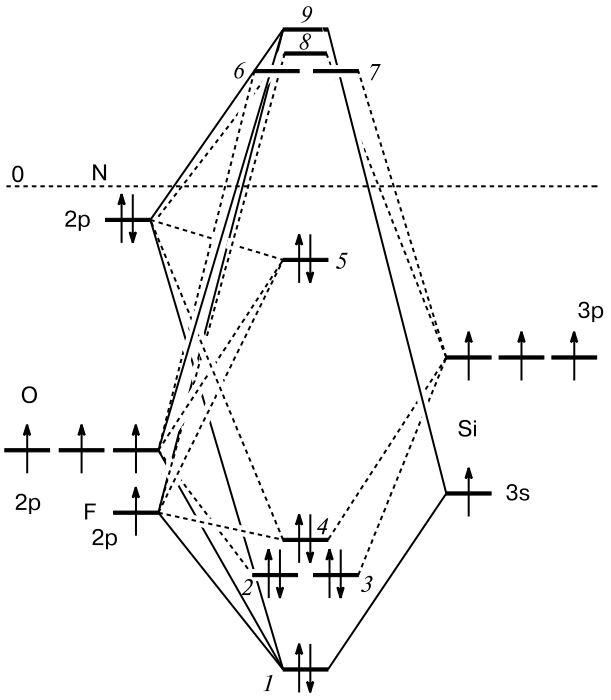


Fig. 1. Formation of molecular orbitals around the central atom in 1-fluorosilatrane molecule. The bonding MOs (*1—4*), nonbonding MO (*5*), and antibonding MOs (*6—9*).

the silicon and germanium AOs have higher energies compared to the carbon AOs (C_{2s}, −21.4 eV; Si_{3s}, −17.3 eV; Ge_{4s}, −16.0 eV; C_{2p}, −11.4 eV; Si_{3p}, −9.2 eV; Ge_{4p}, −9.0 eV)[53], the interaction between the AOs of the central atom and the lone pair of nitrogen is stronger.

It should also be noted that recently it was assumed that the *endo*-configuration of metallatrane molecules is stabilized contrary to rather than due to the transannular bonding.[54—56] In some cases, this contact was reported to have an antibonding character. It is believed[54,55] that the driving force of stabilization of the *endo*-configuration is the entropy factor. However, the results obtained in the course of the studies mentioned above substantiate the bonding character of the M←N interaction that occurs involving the MOs *1* and *4* (see Fig. 1). These interactions, as well as the entropy factor,[54,55] are responsible for stabilization of the *endo*-configuration of metallatrane molecules.

Thus, in this work we established that for the compounds under study the M←N, M—X, and M—Y bonds are shortened while the M←N bond strength and the electron density at the critical points of the M←N, M—X, and M—Y bonds increase as the number of electronegative substituents at the metal atom increases. We also found that an increase in electronegativity of any substituent, X or Y, causes a decrease in the ionicities of other bonds (M—X, M—Y and M←N) formed by the atoms in question (Si, Ge).

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