Application of molecular mechanics for calculations of metallocarborane molecules

T. V. Timofeeva,[a] *N. L. Allinger,*[b] *M. Buehl,*[b] *and U. Mazurek*[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095)135 5085
[b]*Department of Chemistry, University of Georgia, Athens,*
Georgia, 30602-2556, USA

Molecular mechanics was applied for the first time to calculations of metallocarboranes. For selection of the force field parameters, the results of HF/6-31G* *ab initio* calculations of $(C_2B_4H_6)M$ model compounds were used, where M = Mg and SiH_2. The Hill potential rather than the conventional force field was used for description of deformation of the metal—ligand bond energies. Calculations of $[RR'C_2B_4H_4]_2M$, where R and R'= Me_3Si or Me, M = Si, Ge, Sn, Pb, similar to dicyclopentadienyl sandwich metal complexes, showed that these compounds have parallel-sandwich conformation for relatively short metal—ligand distances (M = Si, Ge), and bent-sandwich conformation for the longer distances (M = Sn, Pb). As in the case of bent-sandwich metallocenes, this effect can be accounted for by interligand attraction (dispersion interaction) appearing with the increase of interligand distances.

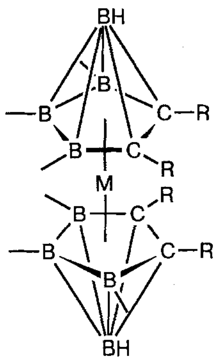
Key words: molecular mechanics, *ab initio* quantum-chemical calculations, metallocarboranes.

Recently, molecular mechanics is gaining increasing importance for calculations of structures of organometallic[1—3] and inorganic molecules and infinite formations[4]. Numerous works appear that concern the selection of parameters for the method of molecular mechanics (MM), which permit the uniform description of not only organic compounds but also organoelement and organometallic compounds of various classes[5,6]. With application of the MM method, the calculations of the latter type do not cause specific difficulties in case where the molecules can be rather unambiguously described within the framework of standard valent schemes (for example, many coordination compounds[7]). If such a description is complicated, for example, as in the case of π-complexes of metals with cyclopentadienyl and allyl ligands, organoboron compounds, the standard models become useless and need modification and development in order to include such objects into the spectre of compounds under investigation by the MM method. This fact is essential, because there arises a real opportunity for simulation of chemical reactions, catalytic processes, bioprocesses involving organometallic molecules as well as the prediction of the structure of partially ordered phases, for example, liquid crystals.

The difficulties in description of molecules containing cyclopentadienyl ligands were overcome by application of different schemes of interatomic bonds. In particular, the ferrocene derivatives and other metallocenes were described in some works, firstly, with application of a dummy atom situated in the center of the Cp-ligand[1,8—12] and the corresponding bond; secondly, with application of parameters for metal-ligand interactions corresponding to the intermolecular type[15]; and, finally, within the framework of the model of electrostatic interactions between the metal atoms and ligands[13,14]. The major characteristic of the two first approaches is the fact that the mutual arrangement of ligands within the coordination sphere of the metal atom is determined by their non bonded interactions. The apparent success of these approaches for description and rationalization of the factors determining the structure of aforementioned π-complexes enabled us to continue our work on introduction of such molecules as framework organoboron compounds and their metal complexes, which were not considered earlier, into the range of compounds under investigation.

At the first stage of work devoted to the selection of potential parameters, we chose the simplest carborane complexes such as $(R_2C_2B_4H_4)_2M$, where R = $SiMe_3$, M= Si, Ge, Sn. The interest in these complexes has two reasons: the search for approaches to description of the more complex framework organoboron molecules by the MM method and the opportunity for reproduction and rationalization of the geometric characteristics of these molecules within the framework of MM. We accomplished preliminarily a quantum-chemical calculations

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1906—1912, November, 1994.



of the model compounds of this class that became the basis for further applications of MM.

The structures of most metallocarboranes are described in the review[16] with sufficient details, and the new data are published in the work[17]. These structures are similar to those of metal dicyclopentadienyls, and the difference lies in the fact that the formal charge of ligand here is equal to 2+, and, correspondingly, two such ligands are coordinated by tetravalent elements (Si, Ge, Sn). Moreover, the nonequivalence of atoms at the pentagonal face of carborane coordinated by the metal ion results in the nonequivalent bond lengths and angles in this five-membered fragment and, therefore, in the asymmetric type of its coordination. However, it is interesting that the conformational characteristics of metallocene compounds, namely, parallel-sandwich structure for relatively short metal—ligand distances and bent-sandwich structure for the increased distances, appear in these molecules. In our opinion, the same regularities occur here as in the case of related Cp-derivatives, i. e., the generation of the bent conformation is accounted for by nonvalent interligand interactions[8,9,15]. The confirmation of these hypotheses was one of the objectives of the calculation accomplished.

Description of model and method of calculation

Apparently, it is difficult to describe the abovementioned structure of $(R_2C_2B_4H_4)_2M$ within the terms of valent bonds and angles accepted in MM using the minimum number of independent and uniformly defined parameters. In this case, it is particularly difficult to specify the best values of bond angles considering that M and B atoms in the vertices of the distorted pentagonal bipyramid are arranged asymmetrically with respect to pentagonal base. The last circumstance prevents the application of the model we used earlier[8,9]. In this model, the arrangement of every Cp-fragment within the coordination sphere of the M atom for Cp_2M metallocenes was defined by a single bond between metal and center of the Cp-ligand. This bond was rather rigidly oriented perpendicular to the plane of the ligand. In our later work[15], we used another approximation for description of complexes with Cp-ligands: we updated all five bonds betwen the atom M and the carbons of the Cp-ring and, as in the previous case, we assumed all angular constants at M atom to be zero.

Thus, the conformations of π-complexes in both calculation schemes were determined by non bonded interligand interactions. The apparent drawback of the first mentioned model is difficulty in choosing the position of the dummy atom determining the metal—ligand bond of asymmetric ligands. Therefore, we preferred to use the second scheme mentioned. Using the same scheme, we can also determine the position of boron atom at the vertex of the carborane fragment. The bonds between the boron and carbon atoms involved in the pentagonal open face of the ligand can be described by analogy with bonds in Cp-ligand.

In our previous work[15], for the metal—carbon bond we used the potential function (Hill potential) that is analogous to that accepted for nonvalent interactions, particularly, for H-bonds:

$$E_{\pi\text{-bond}} = (\varepsilon/D)[184000\ \exp((-12.0/(r_0/r))-2.25(r_0/r)^6],$$

where r_0 is the ideal M—C(L) bond length, and ε is the depth of potential well describing the energy of this bond, D is the dielectric constant. In this work, the same approach is used for the bonds of M and B with atoms of a five-membered carborane fragment. Thus, we have to describe the five-membered ring by the general scheme accepted in MM, i. e., on the basis of standard equations for deformations of valent bonds and angles:

$$E_{\text{bond}} = k_l/2(l_0-l)^2,\ E_{\text{angle}} = k_\theta/2(\theta_0-\theta)^2,$$

where k_l and k_θ are the constants of corresponding deformations, l_0 and θ_0 are the ideal values of valent bonds and angles, l and θ are their current values. The aforementioned potential is applied for description of interactions of the ring with the atoms at the vertices. Data of X-ray investigations[16,17] and quantum-chemical calculations[18] were used as the geometric force field parameters. The bond energies for atoms at the vertices of five-membered fragments were estimated by our special quantum-chemical calculations of model molecules. All other components of conformational energy were simulated by force field and potential parameters in the MM3 program[19].

Quantum-chemical calculations of model molecules

The major objective of quantum-chemical calculations was to estimate potentials of metal—ligand interaction, and that between the boron atom at the ligand vertice and its five-membered base. For this purpose, we selected two of the simplest model molecules $(C_2B_4H_6)M$, where M = Mg (**1**) and SiH_2 (**2**). The information on the synthesis of the first molecule is not available to us; at the same time, the second molecule exists in the form of its substituted analog, the structure

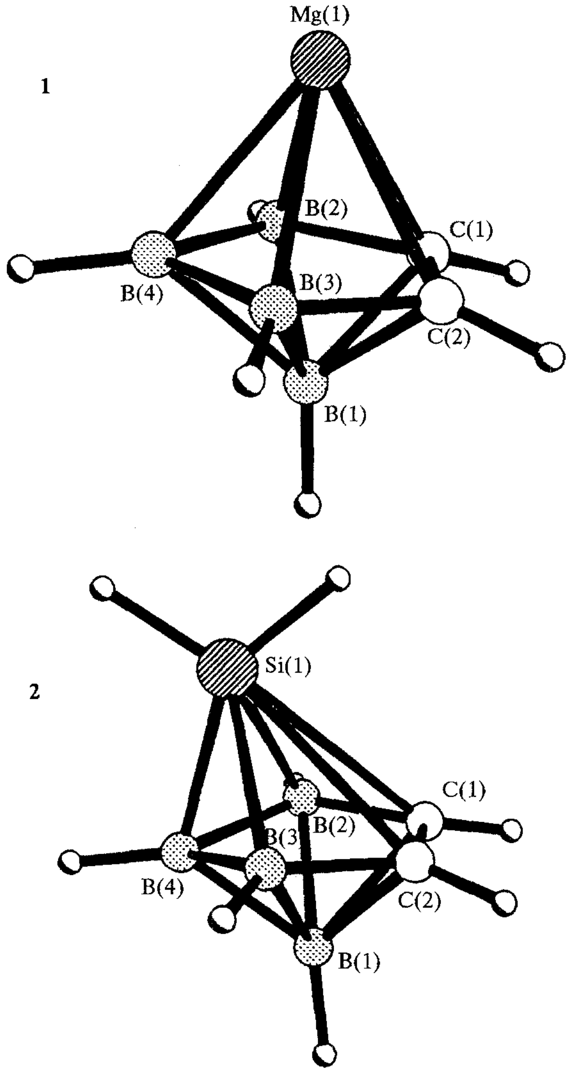


Fig. 1. Structure of molecules **1** and **2** according to quantum-chemical calculation.

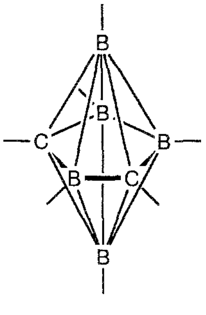
Table 1. Geometric characteristics of the molecules **1** and **2** from data of quantum-chemical and molecular mechanics calculations

Parameter	**1** (M = Mg)		**2** (M = SiH_2)
	ab initio	MM3	*ab initio*
Bond		d/Å	
B(1)—C(1)	1.692	1.714	1.770
B(1)—C(2)	1.692	1.714	1.730
B(1)—B(2)	1.797	1.763	1.853
B(1)—B(3)	1.797	1.763	1.828
B(1)—B(4)	1.792	1.773	1.682
C(1)—C(2)	1.476	1.478	1.414
C(2)—B(3)	1.565	1.557	1.545
B(3)—B(4)	1.741	1.712	1.752
B(4)—B(2)	1.741	1.712	1.756
B(2)—C(1)	1.565	1.557	1.546
M—C(1)	2.294	2.264	2.705
M—C(2)	2.294	2.264	2.709
M—B(2)	2.285	2.242	2.241
M—B(3)	2.285	2.242	2.211
M—B(4)	2.246	2.242	1.986
Angle		φ/deg	
C(1)—C(2)—B(3)	114.1	112.7	115.2
C(2)—B(3)—B(4)	103.7	105.9	103.3
B(3)—B(4)—B(5)	104.5	102.9	100.7
B(4)—B(2)—C(1)	103.7	105.9	104.0
B(2)—C(1)—C(2)	114.1	112.7	114.1

of which was studied by means of NMR and IR spectroscopy[20].

Primarily, the geometry of both molecules was optimized *ab initio* within the restricted Hartree—Fock technique by the GAUSSIAN 92 program[21] using the standard set of basis 6-31G* basis functions. The energies of metal—ligand and boron—ligand interactions were determined by scanning the energy surface (SCAN procedure), and the ligand geometry was not optimized during scanning. We varied the distances between the plane of the five-membered carborane fragment and Mg and B atoms (BH group) in molecule **1** or those between Si atoms (SiH_2 group) in molecule **2**.

Results of optimization of geometry for molecules **1** and **2** are presented in Fig. 1 and in Table 1. According to the results of calculations, Mg and B atoms at the vertices of the pentagonal pyramid in molecule **1** with the C_s symmetry are arranged rather symmetrically (the crossing point of normals through Mg and B with the plane are separated by 0.229 Å). Because experimental data on the structure of molecule **1** are not available, we compared the calculated bond lengths with those for the most similar structure of $C_2B_7H_7$ (**3**). According to the microwave spectroscopic data[22] and gas electron diffraction[23], the bond lengths between B atom in the vertice and B atoms in the B—B bond in the five-membered cycle are 1.818 and 1.852 Å, respectively, and those for B—C bond lengths are 1.708 and 1.717 Å, respectively.

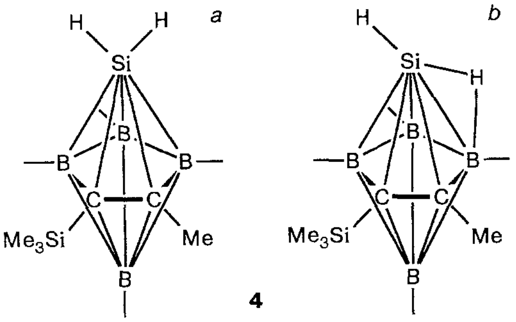


3

This result suggest that the calculation correctly reproduced the relationship between the geometric parameters in the structure of **1**.

According to our calculation, molecule **2** (Fig. 1) is asymmetric. On the basis of NMR (^1H, ^{11}B, ^{13}C, and

^{29}Si), two structures were suggested[16,20] for $H_2Si[((Me)_3Si(Me)C_2B_4H_4]$ (**4** is the substituted analog of **2**), and preference was given to the second structure (*b*).



4

Our calculation of molecule **2** demonstrated the preference of structure *a*. On the one hand, such discrepancy can be accounted for by the effect of substituents in the compound **4**; however, we cannot rule out a preference of model *a* for this compound. Unlike complex **1**, the Si atom in molecule **2** is asymmetrically coordinated by the five-membered carborane face (Table 1). Such coordination is rather characteristic of IVA metals in the case when one of the ligands is of the π-type, and the other (others) form two σ-bonds with the metal[16].

Figure 2 presents the dependencies of the relative energy of molecules **1** and **2** on the distance between the atoms in the plane and the atoms at the vertices of pentagonal bipyramid. We accomplished scanning with a variable step for different sections of the curves. Our calculation was terminated only at the plateau, because we were interested in the region of breaking of bonds with atoms at the vertices.

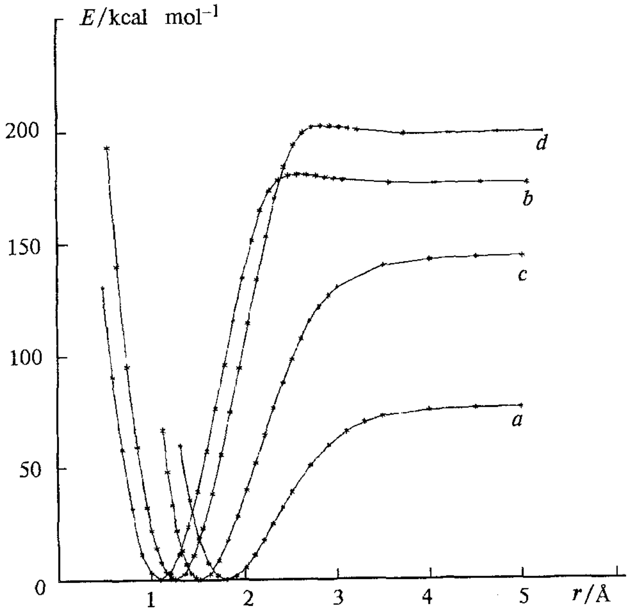


Fig. 2. Dependence of relative energy of molecules **1** and **2** on the distance between the atom in the plane and the atoms at the vertices of pentagonal bipyramid (PB): (*a*) **1**, PB-Mg; (*b*) **1**, PB-B; (*c*) **2**, PB-Si; (*d*) **2**, PB-B.

The calculated dissociation energies for BH in molecules **1** and **2** are 180.4 and 201.8 kcal/mol, and those for Mg and SiH_2 are 76.5 и 142.3 kcal/mol, respectively. Further we used these values for selection of force field parameters describing the interaction between the five-membered fragment and atoms located at the vertices of polyhedron.

Force field parameters for metallocarboranes

Our calulations were based on the MM3 program and the corresponding parameters of the MM3 force field with the addition of parameters necessary for description of carborane fragments. Upon selection of parameters, we used the X-ray structural investigations for $[(Me_3Si)(Me)C_2B_4H_4]_2Si$ (**5**),[20] $[(Me_3Si)_2C_2B_4H_4]_2Ge$ (**6**),[22] $[(Me_3Si)(Me)C_2B_4H_4]_2Sn$ (**7**)[17] and the quantum-chemical calculations of molecule **1**. The structure of **2** was not considered as the basic one because of the asymmetric type of M coordination.

The few examples of structural investigations and rather significant dispersion of analogous bond lengths in these molecules complicated the selection of unique parameters for this series. Apparently, such parameters are preliminary and do not pretend to be used for highly precise description of all geometric characteristics of molecules; however, we should expect them to reproduce adequately the conformational peculiarities.

The ideal values and force constants of valent angles in the five-membered carborane fragment, and also the parameters of its torsional potential were assumed the same as those for Cp-ligand.[15] The atomic positions at the vertices of pentagonal pyramide were characterized by the bond lengths (r_0, according to X-ray analysis and quantum-chemical calculations) and their energies (ε), calculated *ab initio*. The energies of dissociation of the BH group from molecules **1** and **2** differ only by *ca.* 10 %; this fact enabled us to use them for calculations. The energy of interaction between the five-membered fragment and M was also taken from the calculation of molecule **1**, because a different type of M coordination was discovered in the structure of **2**. Table 2 represents all potential parameters newly determined.

Results and Discussion

Using the aforementioned parameters, we optimized the geometry and calculated the relative conformational energies for the following molecules: **1** (the data of quantum-chemical calculation are available), **5**—**7** (studied by X-ray analysis), $[(Me_3Si)(Me)C_2B_4H_4]_2Ge$ (**8**) (for comparison with its Si and Sn-containing analogs),

Table 2. Parameters for conformational calculations of metallocarboranes

Parameters for bond stretching of five-membered fragment of carborane ligand

Bond	l_0/Å	K_s/mdyn Å^{-1}
B—B	1.724	5.0
B—C	1.558	5.0
C—C	1.473	5.0

Parameters for bond angle bending of five-membered fragment of carborane ligand

Angle	θ_0/°	K_θ/mdyn Å rad^{-2}
B—B—B	108.0	0.60
B—B—C	108.0	0.60
B—C—C	108.0	0.60
B—B—H	126.0	0.40
B—C—H	126.0	0.40
C—C—H	126.0	0.40
B—B—X*	126.0	0.47
B—C—X*	126.0	0.47
C—C—X*	126.0	0.47

Torsional parameters of five-membered fragment of carborane ligand

Angle	V_1	V_2	V_3
	kcal mol^{-1}		
B—B—B—C	0.0	10.0	0.0
B—B—C—C	0.0	10.0	0.0
B—C—C—B	0.0	10.0	0.0
B—B—B—H	0.0	10.0	0.0
B—B—C—H	0.0	10.0	0.0
B—C—C—H	0.0	10.0	0.0
B—B—C—X*	0.0	10.0	0.0
B—B—C—X*	0.0	10.0	0.0

Parameters for interactions at vertices of pentagonal bipyramid with atoms in five-membered fragment of carborane ligand

Bond	r_0/Å	ε/kcal mol^{-1}
B—C	1.709	35.0
B—B	1.764	35.0
Mg—C	2.264	15.3
Mg—B	2.242	15.3
Si—C	2.177	15.3
Si—B	1.947	15.3
Ge—C	2.360	15.3
Ge—B	1.970	15.3
Sn—C	2.720	15.3
Sn—B	2.220	15.3
Pb—C	2.800	15.3
Pb—B	2.450	15.3

* Exocyclic angles, X = C, Si.

and $[(Me_3Si)(Me)C_2B_4H_4]_2Pb$ **9**, which has not yet been synthesized (for prediction of its possible structure). Some bond lengths and angles in molecule **1**, calculated *ab initio* and by means of molecular mechanics, are summarized in Table 1. It can be seen that they show good qualitative agreement. This fact enables us to use the suggested set of potential parameters for other compounds under consideration.

From the X-ray structural data, the molecules **5—7** in crystal have one of two conformations: (*a*) centrosymmetric (parallel arrangement of basis planes of carborane ligands, with staggered orientation, substituents are most separated) and (*b*) bent (nonparallel arrangement of ligands with orientation close to eclipsed, substituents are drawn together). The first type involves the structures of **5** and **6** with the relatively short metal—ligand distances, the second type involves **7** with the longer distances. In our work[15], we made an assumption that the stability of the latter conformation can be accounted for by the nonvalent attraction of ligand sufficiently separated from the central metal atom, if the analogy with bent-sandwich metallocenes is taken into consideration.

Figure 3 presents the described conformations of the aforementioned molecules. Upon optimization of geometry and energy calculations, we used both *a* and *b*

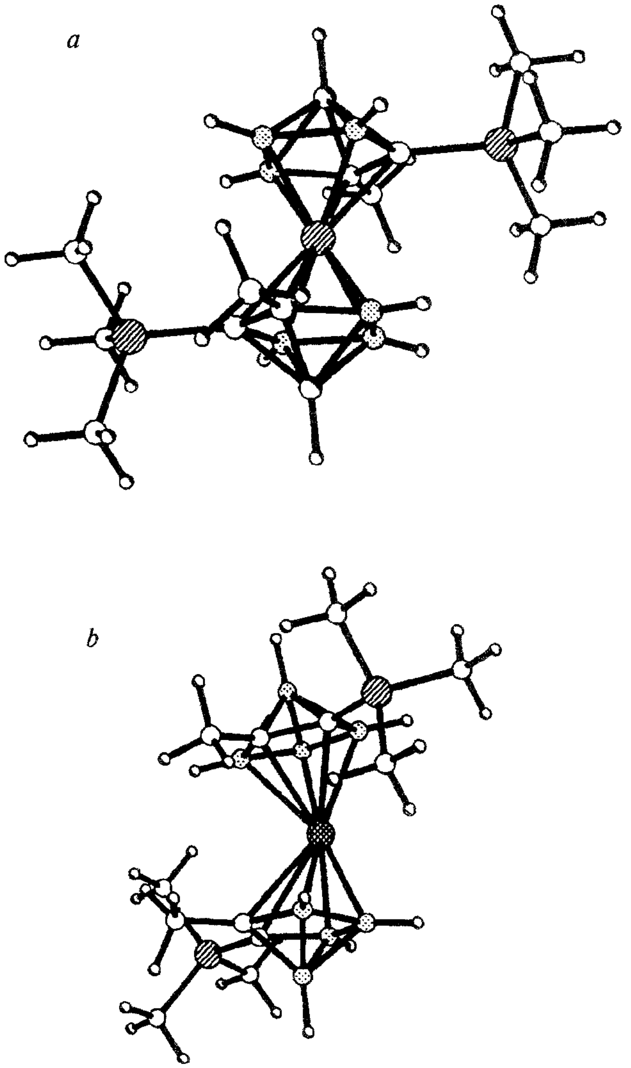


Fig. 3. Conformations of metallocarboranes: (*a*) M = Si, Ge; (*b*) M = Sn, Pb.

Table 3. Comparison of some experimental and calculated geometric parameters for the molecules **5**—**7**

Parameter	**5** (M = Si)		**6** (M = Ge)		**7** (M = Sn)		
	exp	MM3	exp	MM3	exp		MM3
Bond				*d*/Å			
C(1)—C(2)	1.485	1.487	1.43	1.499	1.453	1.478	1.491
C(2)—B(3)	1.559	1.560	1.63	1.577	1.543	1.552	1.566
B(3)—B(4)	1.669	1.709	1.56	1.712	1.743	1.744	1.713
B(4)—B(5)	1.692	1.713	1.57	1.712	1.753	1.713	1.719
B(5)—C(1)	1.565	1.566	1.61	1.577	1.555	1.557	1.574
B(6)—C(1)	1.734	1.717	1.72	1.715	1.705	1.708	1.709
B(6)—C(2)	1.724	1.716	1.72	1.714	1.709	1.710	1.707
B(6)—B(3)	1.759	1.770	1.73	1.767	1.790	1.770	1.765
B(6)—B(4)	1.765	1.777	1.72	1.778	1.720	1.710	1.766
B(6)—B(5)	1.771	1.771	1.71	1.761	1.755	1.751	1.764
M—C(1)	2.236	2.237	3.38	2.372	2.716	2.721	2.691
M—C(2)	2.228	2.226	2.39	2.371	2.719	2.721	2.692
M—B(3)	2.108	2.094	2.14	2.137	2.421	2.388	2.395
M—B(4)	2.037	2.036	2.08	2.041	2.234	2.234	2.238
M—B(5)	2.117	2.102	2.15	2.143	2.429	2.425	2.376
Angle				φ/deg			
C(1)—C(2)—B(3)	112.0	112.5	108.9	111.6	114.6	114.2	112.1
C(2)—B(3)—B(4)	106.6	106.4	107.7	107.3	104.6	104.4	107.3
B(3)—B(4)—B(5)	103.9	102.6	105.5	102.0	102.4	102.8	101.6
B(4)—B(5)—C(1)	105.9	106.4	108.5	107.3	104.3	106.1	107.3
B(5)—C(1)—C(2)	111.6	112.0	109.3	111.7	113.8	114.2	112.1

structures as the initial ones for all compounds under consideration. Table 3 compares the calculated geometric parameters of molecules **5**—**7** (bond lengths and some angles) for conformations with the corresponding experimental parameters.

This comparison demonstrates good qualitative agreement between these parameters; thus, for example, the relationship between the significantly different angles in the five-membered fragment and the M—B bond lengths (for which constants characterizing the ideal values were assumed to be equal) was reproduced correctly. We should note that, in accordance with the calculation, molecules **5** and **6** retain their centrosymmetric structure. In the structure of **7**, which is asymmetric in crystal and has slightly nonequivalent carborane ligands, their calculated geometry appeared to be the same (Table 3).

Table 4 presents the relative energies of two aforementioned *a* and *b* conformations of molecules **5**—**9**. The calculation demonstrated that compounds **5**, **6**, and **8** have parallel-sandwich structure for any orientation of ligands. We can see from Table 4 that energies of conformers do not significantly differ for molecules with relatively short M—ligand distances (Si and Ge complexes). The parallel-sandwich conformation for **7** and **9** is appreciably less favorable than the bent one with the orientation of substituents displayed in Fig. 3, *b*.

The results show good agreement with the experimental data on conformation of these molecules in crystal. The calculated angle between the ligand planes in **7** equals 15.3° (the experimental value is 17.9°), and the CR—Sn—CR angle, characterizing the arrangement of ligand centroids, is 146.6° (experimental value is 142.5°). In molecule **9**, which has not yet been synthesized, the calculated angle between the ligand planes should be 19.5°, and the CR—Pb—CR angle should be 145.9°.

Thus, the model, which was successfully applied to bent-sandwich cyclopentadienyl complexes[15], is also effective in the case of complexes with carborane ligands. We should note that the major reason for the bent structure is the non bonded attraction (dispersion interaction) of ligands, which are sufficiently separated one from another with relatively large radii of central metal atoms. This conclusion was completely confirmed by the analysis of separate contributions into the conformational energy. The authors of the work[17], in which the bent-sandwich structure of Sn complex **7** was investigated experimentally, reasonably note that its bent structure cannot be accounted for by the presence of a stereochemically active electron pair at Sn atom, as was assumed for stannocene, in particular[24]. In our previous work, we showed that the molecular mechanical model

Table 4. Relative energies (kcal $\mathrm{mol^{-1}}$) for conformers of the molecules **5**—**9**

Conformer	5	6	7	8	9
a	0.11	0.0	0.84	0.24	0.94
b	0.0	0.20	0.0	0.0	0.0

without such pair rather adequately describes the bent structure of metallocenes.

We should note that the most indicative characteristic of bent-sandwich molecules is the angle between the ligand planes rather than the CR—M—CR angle, because it is the former angle that determines directly the non bonded contacts between ligands. This fact is especially important when the ligand centroid does not coincide with the intersection point of the perpendicular from M to the plane. Our model, which was suggested for bent cyclopentadienyl derivatives[8,9] and used in Ref. 12, is not applicable to such molecules. But our later model[15] adequately accounts for this fact and well describes both cyclopentadienyl and carborane complexes.

This work was conducted with the financial support of the International Science Foundation (grant No. MP5000).

References

1. T. V. Timofeeva and Yu. T. Struchkov, *Usp. Khim.* 1990, **59**, 551 [*Russ. Chem. Rev.*, 1990, **59**, 320 (Engl. Transl.)].
2. H. Kawamura-Kuribayashi, N. Koga, and K. Morokuma, *J. Am. Chem. Soc.*, 1992, **114**, 8687.
3. J. Polowin, S. C. Mackie, and M. C. Baird, *Organometallics*, 1992, **11**, 3726.
4. T. M. Brunier, M. G. B. Drew, and P. C. H. Mitchell, *Molecular Simulation*, 1992, **9**, 143.
5. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024.
6. C. J. Casewit, K. S. Colwell, and A. K. Rappe, *J. Am. Chem. Soc.*, 1992, **114**, 10035.
7. G. R. Brubaker and D. W. Johnson, *Coord. Chem. Rev*, 1984, **53**, p. 1.
8. T. V. Timofeeva, Yu. L. Slovokhotov, and Yu. T. Struchkov, *Dokl. AN SSSR*, 1987, **294**, 1173 [*Docl. Chem.*, 1987 (Engl. Transl.)].
9. Yu. L. Slovokhotov, T. V. Timofeeva, and Yu. T. Struchkov, *Zh. Strukt. Khim.* 1987, **28**, No. 4, 3 [*J. Struct. Chem.*, 1987 (Engl. Transl.)].
10. E. S. Shubina, L. M. Epstein, T. V. Timofeeva, Yu. T. Struchkov, A. Z. Kreidlin, S. S. Fadeeva, and M. I. Rybinskaya, *J. Organomet. Chem.*, 1988, **345**, 313.
11. T. N. Doman, C. R. Landis, and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 7264.
12. T. K. Hollis, J. K. Burdett, and B. Bosnich, *Organometallics*, 1993, **12**, 3385.
13. F. M. Menger and M. J. Sherrod, *J. Am. Chem. Soc.*, 1988, **110**, 8606.
14. H.-J. Thiem, M. Brandl, and R. Breslow, *J. Am. Chem. Soc.*, 1988, **110**, 8612.
15. T. V. Timofeeva, J.-H. Lii, and N. L. Allinger, *J. Am. Chem. Soc.*, 1994, in press.
16. N. S. Hosmane and J. A. Maguire, In *Advances in boron and the boranes*, Weinheim, VCH, 1988, 297.
17. L. Jia, H. Zhang, and N. S. Hosmane, *Organometallics*, 1992, **11**, 2957.
18. M. Buehl and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1992, **114**, 477.
19. N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8552.
20. U. Sirivardane, M. S. Islam, T. A. West, N. S. Hosmane, J. A. Maguire, and A. H. Cowley, *J. Am. Chem. Soc.*, 1987, **109**, 4600.
21. Gaussian 92, Revision B, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1992.
22. R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, 1965, **43**, 2166.
23. E. A. McNeill and F. R. Scholer, *J. Mol. Struct.*, 1975, **27**, 151.
24. P. Jutzi, F. Kahl, P. Hoffman, C. Kruger, and Y.-H. Tsay, *Chem. Ber.*, 1980, **113**, 757.

Received March 31, 1994;
in revised form June 3, 1994