Conformational analysis of mono- and di-*C*-substituted derivatives of *closo*-3,3-[$\eta^{2,3}$-(2-methylenebicyclo[2.2.1]hepta-2,5-dien-2-yl)]-1-R-2-R^1-3,1,2-dicarbollylrhodium (R and R^1 = H, Me, or PhCH$_2$)

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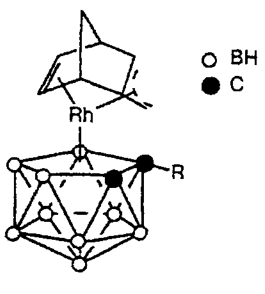
A model has been developed that allows one to carry out molecular mechanics calculations of metallacarborane complexes with various ligands with the use of the MM3 program package. Based on X-ray structural data on a number of rhodium complexes in which the rhodium atom is coordinated by the $\eta^{2,3}$-norbornadienyl and η^5-dicarbollyl ligands, a parameter set was developed for the compounds of the above-mentioned series. The use of this model made it possible to study the effects of various factors on the structures of the molecules of *closo*-3,3-($\eta^{2,3}$-methylenenorbornadienyl)-1-R-3,1,2-dicarbollylrhodium (R = Alk or ArAlk).

Key words: molecular mechanics, *closo*-rhodacarboranes, stereochemistry.

An important characteristic feature of the η^5-dicarbollyl ligand is the absence of symmetry in its monosubstituted derivatives that contain substituents at C atoms and some B atoms. Therefore, the presence of an additional asymmetrical center in mono-*C*-substituted *closo*-metallacarboranes (for example, in other ligands of the complex) results in the appearance of diastereoisomerism. Derivatives of *closo*-3,3-($\eta^{2,3}$-methylenenorbornadienyl)-1-R-3,1,2-dicarbollylrhodium (**1**, **2**) are examples of such compounds.[1,2]



R = PhCH$_2$ (**1**), Me (**2**)

The single-crystal X-ray diffraction study of two pairs of the diastereomers, (*RS*/*SR*)- and (*SS*/*RR*)-*closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1-R-3,1,2-$RhC_2B_9H_{10}$ (**1a**,**b**, R = PhCH$_2$;[3] and **2a**,**b**, R = Me),* made it possible to find an interesting dependence of the solid-state conformation of the norbornadienyl ligand on the stereochemical configuration of the diastereomeric complexes. Thus, in isomers **1a** and **2a**, which have *RS*/*SR* relative configurations, the norbornadienyl ligand is oriented so that its allylic moiety is projected onto the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand and screens the C(2) and B(7) atoms. In the diastereomers with the opposite configuration (**1b** and **2b**), this group is located approximately above the B(8)—B(4) bond (see below). It is interesting that in the solid state the hydrocarbon ligand in the complex, *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-3,1,2-$RhC_2B_9H_{11}$ (**3**) (three independent molecules),[4] and in its 1,2-dimethyl derivative, *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$ (**4**),[1] adopts a conformation similar to that observed for isomers **1a** and **2a** in spite of the fact that in compound **4** the distance between the exocyclic C atom of the norbornadienyl ligand and the C atom of the nearest methyl substituent in the η^5-dicarbollyl ligand is 3.074 Å, *i.e.*, it is substantially smaller that the sum of the van der Waals radii of the C atoms (3.4 Å).

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* The complete data of X-ray structural analysis of diastereomers **2a**,**b** will be published in a separate report in cooperation with Dr. C. B. Knobler and Prof. M. F. Hawthorne (California University, USA).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 617—622, April, 1998.

1066-5285/98/4704-0596 $20.00

In compounds **1a,b** and **2a,b**, there are no such short contacts between the corresponding atoms. It should also be noted that in all of the above-mentioned compounds, a short nonbonded contact occurs between the exocyclic C atom of the norbornadienyl ligand and the nearest atom of the C_2B_3 pentagonal plane of the η^5-dicarbollyl ligand (see below). With the aim of revealing the factors that affect the mutual orientation of the ligands in these complexes and comparing the structural characteristics of the molecules in the crystalline state, which were determined by X-ray diffraction study, with the structures of the isolated molecules, we carried out molecular mechanics (MM) calculations of the conformations of diastereomers **1a,b** and **2a,b** and complex **4**.

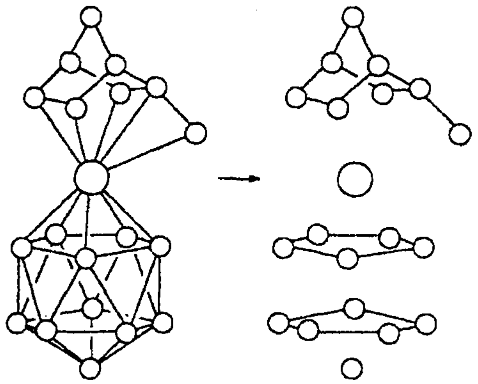
Description of the model and calculation procedure

Calculations were carried out on a MicroVAX-3100 computer using the MM3 program (see Ref. 5). It should be noted that it is difficult to adequately take into account the electrostatic factors in calculations of this class of compounds by the molecular mechanics method, and therefore, the charge distribution was ignored. In addition, this method does not take into account effects associated with interactions between the molecular orbitals of the metal atom and the ligands. Therefore, the approach used made it possible to determine primarily the effect of steric factors on the orientation of the norbornadienyl ligand in the isomers and to reveal the sterically most favorable conformers of the diastereomeric complexes.

The MM3 force field cannot be directly used for the compounds under study because the program does not allow the description of highly coordinated atoms such as Rh and also of the B and C atoms in the η^5-dicarbollyl ligand. Therefore, with the aim of performing conformational analysis of the above-mentioned metallacarboranes, we have developed a model and constructed the parameter set based on the concepts that form the basis of the molecular mechanics description of π-cyclopentadienyl complexes of transition metals,[6,7] sandwich complexes $(R_2C_2B_4H_4)_2M$ (M = Si, Ge, or Sn),[8] and 12-vertex *closo*-carboranes.[9] The results of calculations demonstrated that the structures of these molecules are adequately described within the framework of the molecular mechanics method and can be adequately explained by steric effects.

The model was constructed so that no changes in the MM3 program were required to perform the calculations. With the aim of using the conventional scheme of description of the bonds and angles, which was realized in the MM3 program, complexes **1**, **2**, and **4** were represented as a superposition of the following five fragments (Scheme 1).

Scheme 1



It follows from Scheme 1 that interactions between the atoms of the different fragments, which are linked in the real molecule by valent bonds, are described as nonbonded contacts (Hill's potential):

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

where r_0 is the ideal length of the X—Y bond (X and Y are the B, C, or Rh atoms), ε is the depth of the potential well, which characterizes the energy of this bond, and D is the dielectric permeability.

The parameters that were unavailable for the model suggested have been selected. The interactions between the five-membered fragments and the apical B atom in the η^5-dicarbollyl ligand are analogous to the corresponding interactions in 12-vertex *closo*-carboranes, which have been discussed in detail previously.[9] The geometric parameters of complexes **1**—**4**, which have been studied by X-ray diffraction analysis,[1—4] were used for describing the bonds in the Rh—η^5-dicarbollyl and Rh—$\eta^{2,3}$-norbornadienyl ligands. Based on these data, we carried out a statistical analysis of the Rh—Y bond lengths (Y are the C or B atoms of the pentagonal plane of the η^5-dicarbollyl ligand, the C atoms at the double bond, or the C atoms of the allyl fragment of the $\eta^{2,3}$-norbornadienyl ligand) as well as of the C—C bond lengths and bond angles in the $\eta^{2,3}$-norbornadienyl ligand. The average values of these geometric characteristics allowed us to supplement the MM3 parameter set with the components, which were necessary for performing calculations of the above-mentioned complexes by the molecular mechanics method (Table 1).

The conformational analysis of compounds **1a,b**, **2a,b**, and **4** was carried out with the use of the suggested

Table 1. Parameters of the deformation of the bonds between the Rh atom and the atoms of the ligands

Bond[a]	r_0/Å	ε/ mdyn Å^{-1}
Rh—C_c	2.200	20
Rh—B_c	2.200	20
Rh—C_n	2.100	20

[a] C_c and B_c are the C and B atoms that belong to the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand, and C_n are the atoms of the norbornadienyl ligand.

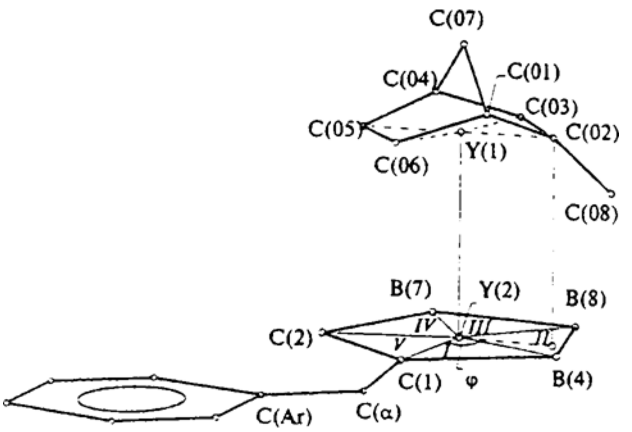


Fig. 1. Mutual orientation of the ligands in complexes **1**, **2**, and **4** (illustrated by the example of complex **1**): C(02)—Y(1)—Y(2)—C(1) is the torsion angle θ_1; Y(1) is the center of the coordinates of the C(02), C(03), C(05), and C(06) atoms; Y(2) is the center of the coordinates of the C(1), C(2), B(7), B(8), and B(4) atoms of the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand (φ is the torsion angle θ_1 in region *II*); C(2)—C(1)—C(α)—C(Ar) is the torsion angle θ_2; *I*, *II*, *III*, *IV*, and *V* are the regions in which the angle θ_1 was varied (fragments of the molecule necessary for the description of the angles under consideration are given).

parameter set. As a result, the sterically most favorable conformations were revealed and the effects of steric factors of the substituents and their mutual spatial arrangement (for the benzyl substituent in isomers **1a,b**) on the orientation of the $\eta^{2,3}$-norbornadienyl ligand relative to the pentagonal C_2B_3 open face of the η^5-dicarbollyl ligand were estimated. The torsion angle θ_1 (see the legend of Fig. 1) was used as a characteristic of the mutual orientation. Unfortunately, this angle cannot be varied within the framework of the model used. Therefore according to the structure of the pentagonal C_2B_3 plane of the dicarbollyl ligand, the total space (360°) was divided into five regions (~72° each, see Fig. 1).

In calculations of the conformations of molecules **1a,b**, **2a,b**, and **4**, their initial geometric parameters were chosen so that the torsion angle θ_1 had values in the regions of 0—72°, 72—144°, 144—216°, *etc.*, and then the energy was minimized. In the case of diastereomers **1a,b**, the torsion angle θ_2 was additionally varied with a step of 10° in each θ_1 region (see the legend to Fig. 1). In the course of minimization, the value of the angle θ_1 was corrected but it remained within the initial region. Therefore, for each compound we determined the conformations, which correspond to the minima of the energy in the five above-mentioned regions (Table 2, Fig. 2).

Results and Discussion

Undoubtedly, the model used in the calculations was approximate. However, in spite of a number of the

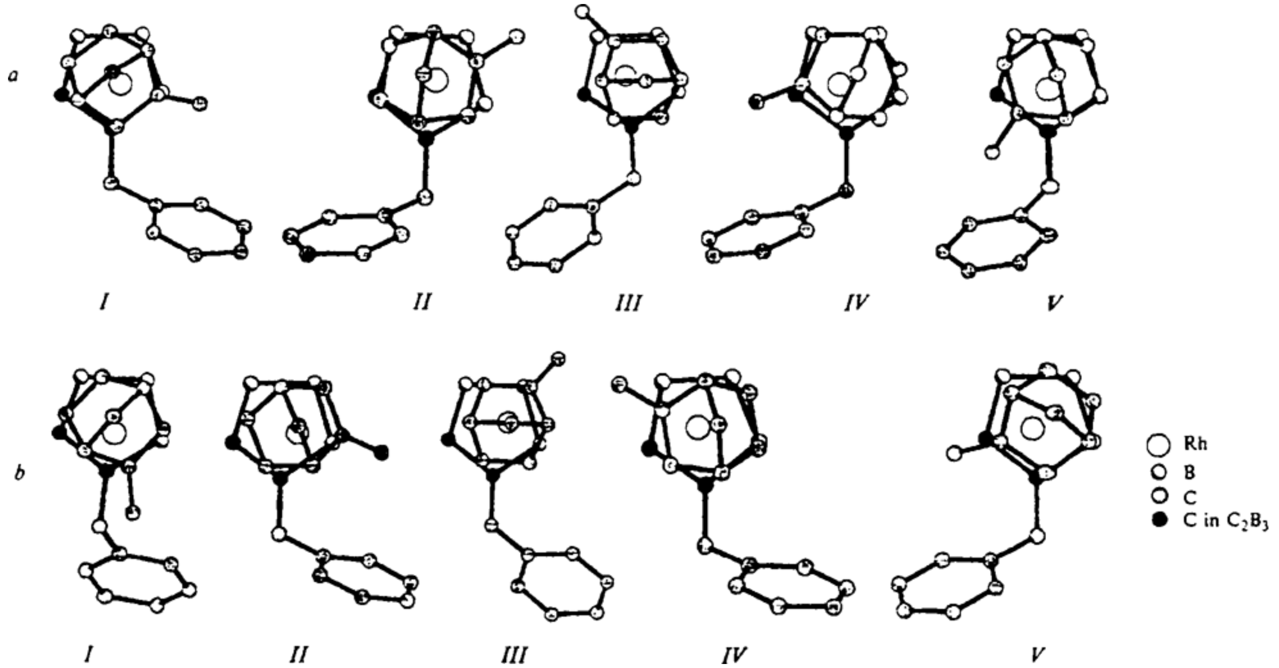


Fig. 2. Calculated conformations of diastereomers **1a** (*a*) and **1b** (*b*) for regions (*I*—*V*) in which the angle θ_1 was varied (only the projections onto the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand and the fragments of the molecule, which are of most significance for conformational analysis, are given). The H atoms are omitted.

Table 2. Calculated geometric characteristics and the relative energies[a] of the most favorable conformations in comparison with the experimental (X-ray diffraction analysis) data

Compound	Conformation (region in which the angle was varied, θ_1/deg)	E /kcal mol^{-1}	θ_1	θ_2	Angle B(7)—C(2)—C(1)—C(α)	Angle C(1)—C(α)—C(Ar)
			deg			
1a	*I* (0—72)	2.3	68.0	220.0	164.5	116.7
	II (72—144)	0.7	115.5	330.0	166.1	115.8
	III (144—216)	4.2	210.3	27.9	163.6	116.0
	IV (216—288)	0	278.5	330.0	164.9	114.7
	V (288—360)	3.9	315.6	66.8	159.0	116.3
	X-ray data	—	277.1	334.1	156.1	118.1
1b	*I* (0—72)	5.2	20.0	130.5	161.4	116.3
	II (72—144)	0.1	80.5	230.0	163.8	115.3
	III (144—216)	4.2	148.0	166.4	164.0	115.6
	IV (216—288)	0.8	244.1	220.0	164.8	115.9
	V (288—360)	2.1	294.2	340.0	162.8	117.2
	X-ray data	—	105.4	120.7	152.3	116.6
2a	*I* (0—72)	0.4	58.6	—	162.2	—
	II (72—144)	0	115.0	—	161.1	—
	III (144—216)	1.1	195.0	—	164.1	—
	IV (216—288)	0	277.9	—	160.9	—
	V (288—360)	1.1	334.4	—	163.4	—
	X-ray data	—	276.6	—	151.8	—
2b	*I* (0—72)	1.1	25.7	—	163.6	—
	II (72—144)	0.1	81.6	—	160.9	—
	III (144—216)	1.1	165.5	—	164.0	—
	IV (216—288)	0.1	245.1	—	161.3	—
	V (288—360)	0.3	302.2	—	161.9	—
	X-ray data	—	99.0	—	154.4	—
4	*I* (0—72)	0	54.8	—	162.5	—
	II (72—144)	0.6	122.6	—	161.2	—
	III (144—216)	0.6	196.5	—	163.8	—
	IV (216—288)	0.7	263.8	—	161.5	—
	V (288—360)	1.1	344.2	—	163.5	—
	X-ray data	—	276.9	—	151.5	—

[a] Relative to the most favorable of 10 or 5 conformations of compounds **1**, **2**, or **4**.

Table 3. Calculated (MM3) and experimental (X-ray diffraction analysis) distances (d/Å) between the exocyclic C atom of the $\eta^{2,3}$-norbornadienyl ligand and the atoms of the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand

Interatomic distance	*RS/SR* Diastereomer						Interatomic distance	*SS/RR* Diastereomer			
	1a		**2a**		**4**			**1b**		**2b**	
	MM3	Exp.	MM3	Exp.	MM3	Exp.		MM3	Exp.	MM3	Exp.
C(08)—B(7)	3.643	3.581	3.639	3.566	3.514	3.647	C(08)—B(8)	3.682	3.130	3.677	3.276
C(08)—C(2)	3.269	3.113	3.234	3.119	3.390	3.272	C(08)—B(4)	3.208	2.968	3.185	2.956
C(08)—C(1)	3.930	3.739	3.902	3.698	4.160	3.800	C(08)—C(1)	3.928	3.874	3.904	3.796
C(08)—C(α)	4.425	4.060	4.282	3.856	4.721	3.989	C(08)—C(α)	4.402	4.424	4.294	4.281
C(08)—C(Ar)	3.828	3.421	—	—	—	—	C(08)—C(Ar)	3.770	5.722	—	—
C(08)—C(α′)	—	—	—	—	3.261	3.074					

above-mentioned limitations, the conformational analysis made it possible to estimate some structural characteristics of the compounds under study. In the course of minimization, the value of the torsion angle θ_1 remained within the initial region, which is indicative of the presence of a potential barrier to transition between the above-mentioned regions and confirms the assumption that the above-described approach can be used for studying the mutual orientation of the ligands.

The results of the calculations of the isolated molecules agree qualitatively with the experimental data on the molecules in the crystals. In particular, the presence

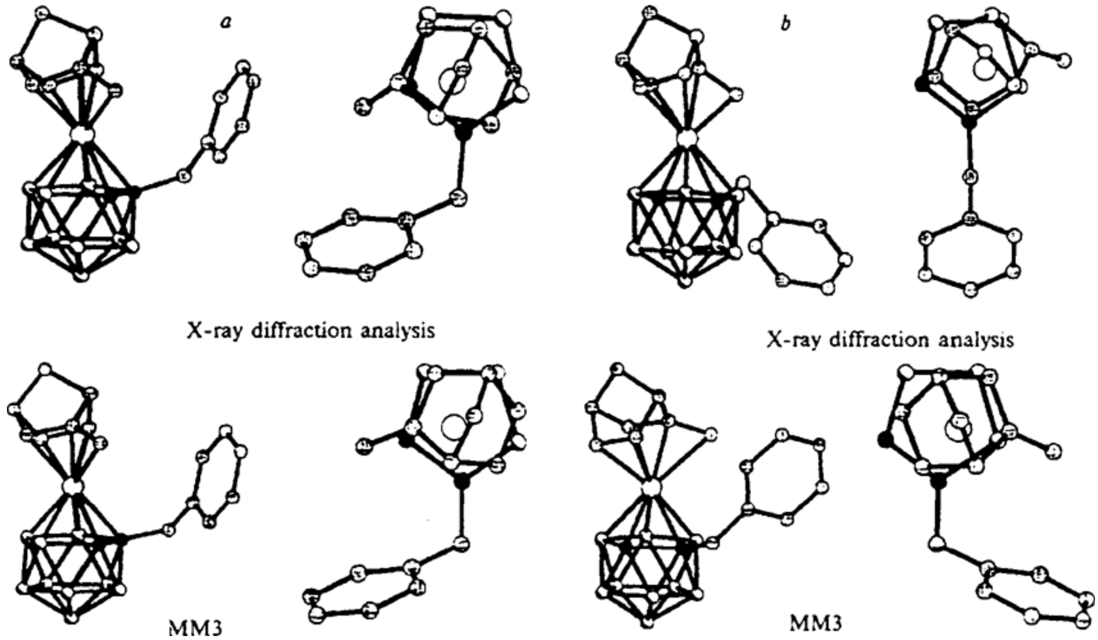


Fig. 3. Most favorable structures of diastereomers **1a** (*a*) and **1b** (*b*) calculated by the molecular mechanics method and the corresponding structures determined experimentally (X-ray diffraction analysis) (the projections onto the pentagonal C_2B_3 plane of the η^5-dicarbollyl ligand are also shown for clarity, see the legend of Fig. 2).

of a short nonbonded contact between the exocyclic C atom of the norbornadienyl ligand and the nearest atom of the pentagonal C_2B_3 open face of the η^5-dicarbollyl ligand is the common characteristic feature of the compounds under study (Table 3). It should be also noted that the most favorable conformations in the other regions in which the angle θ_1 was varied (they are not given in Table 3) are also characterized by the presence of short nonbonded contacts.

The results of conformational analysis demonstrated that the mutual arrangement of the ligands in the isolated molecules is primarily determined by nonbonded interactions of the atoms of the substituent of the η^5-dicarbollyl ligand with the atoms of the $\eta^{2,3}$-norbornadienyl ligand and, in particular, with the exocyclic C(08) atom (see Fig. 1). Obviously, the steric effects in compounds **1a,b** are more significant due to the larger volume of the benzyl substituent. For the monosubstituted complexes, the most favorable value of the angle θ_1 belongs to region *II* or *IV*.

For diastereomer **1a**, the experimental and calculated data are very close to each other (see Table 2, Fig. 3). The difference ΔE in the energies of its conformations exceeds the error inherent in the method (~0.5 kcal mol^{-1}), and therefore, it can be concluded that the structure of molecule **1a** is to a large extent determined by steric factors. In the case of diastereomer **1b**, the experimental and calculated values of the angle θ_1 agree satisfactorily with each other. However, the calculated orientation of the benzyl substituent differs substantially from that observed in the crystal (see Table 2, Fig. 2). Apparently, the differences should be associated with the packing effect of the molecule in the crystal. The agreement between the total conformational energies of diastereomers **1a** and **1b** indicates that their formation is thermodynamically equally probable, which has been confirmed in an experiment.[3]

On the whole, the results of studies of diastereomers **2a,b** are analogous to those obtained for compounds **1a,b** (see Table 2), and therefore, they are not shown in the figures. In this case, the steric factors are less pronounced, but nevertheless they make a substantial contribution to stabilization of the experimentally observed conformer. The difference in the energies of the most and least favorable conformations of these diastereomers is ~1 kcal mol^{-1}.

The results of conformational analysis of compound **4** are not indicative of a substantial effect of steric factors on the mutual orientation of the ligands. The conformers with the torsion angles θ_1 in regions *V* and *I* are sterically least and most favorable, respectively. The conformations of the molecules with other orientations of the ligands are energetically equivalent. The experimental value of the angle θ_1 corresponds to region *IV* (see Table 2). Apparently, the introduction of the second substituent causes partial equalization of the effect of the steric factors on the mutual orientation of the ligands simultaneously with an increase in the electronic effects, which leads to the sterically less favorable conformation of complex **4**.

This conclusion is indirectly supported by the fact that the corresponding ligands in the three independent molecules in unsubstituted compound **3** (see above) have similar orientations, which are, apparently, determined by only electronic factors. In complex **4**, the predominance of the electronic factors over the steric effects can increase owing to the simultaneous presence of two electron-donating methyl groups in the η^5-dicarbollyl ligand. It is known[10] that, for example, the introduction of two methyl substituents at the C atoms of the η^5-dicarbollyl ligand results in an increase in the stability of the normally unstable mononuclear 16-electron Rh^{III} complexes.

To summarize, our studies allowed us to determine the effect of both the steric and electronic factors (by indirect analysis of the results of the calculations of compound **4**) on the structure of *closo*-rhodacarboranes. The results obtained indicate that it is advantageous to use the molecular mechanics method and, in particular, the suggested model in the conformational analysis of this type of metallacomplexes.

This work was supported by the USA Foundation for Research and Development for the Scientists from the Newly Independent States of the Former Soviet Union (CRDF, Grant RC2-147) and the Russian Foundation for Basic Research (Project No. 97-03-32987).

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Received September 16, 1997;
in revised form November 24, 1997