Calculations of thermodynamic stability of $CpCoC_2B_9H_{11}$ cobaltacarborane isomers

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Quantum-chemical calculations of the geometry and energies of nine possible isomers of 12-vertex cobaltacarborane $CpCoC_2B_9H_{11}$ (**1**) were carried out by the DFT method (PBEPBE/DGDZVP/DGA1). Thermodynamic stability of the isomers increases with increasing distance between the carbon atoms in the cage and is virtually independent of the position of the CpCo vertex. The relative stabilities of the 1,2,3- (17.57 kcal mol^{-1}), 1,2,4- (3.72 kcal mol^{-1}), and 1,2,9-isomers of **1** (0 kcal mol^{-1}) are similar to the corresponding values for the *ortho* (17.61 kcal mol^{-1}), *meta* (3.21 kcal mol^{-1}), and *para* isomers (0 kcal mol^{-1}) of carborane $C_2B_{10}H_{12}$. The results of the present study confirm a close similarity of the CpCo and BH fragments in metallacarborane chemistry.

Key words: metallacarboranes, carboranes, quantum-chemical calculations.

The skeletal rearrangement of the cage is one of the most important and interesting reactions in the chemistry of polyhedral boron compounds.[1] Thermal isomerization of the 12-vertex *o*-carborane $C_2B_{10}H_{12}$ giving rise to the *meta* isomer at 400 °C was the first studied reaction of this type.[2] Heating of *m*-carborane to 600 °C leads to its transformation into *p*-carborane.[3] The thermodynamic and kinetic parameters of these rearrangements were studied in-depth by experimental methods.[4] The thermodynamic stability of isomers was demonstrated to increase in the series *ortho* < *meta* < *para* with increasing distance between the negatively charged carbon atoms.

By contrast, the relative thermodynamic stabilities of the isomeric metallacarboranes remained unknown. This is associated with the fact that all known isomerization reactions of these compounds are kinetically controlled.[1] In addition, the simplest 12-vertex metallacarborane $MC_2B_9H_{11}$ can form nine isomers, and most of these isomers are difficult to synthesize. All nine isomers were isolated only for metallacarborane $CpCoC_2B_9H_{11}$ (**1**) (Fig. 1).[5] The aim of the present study was to estimate thermodynamic stabilities of different isomers of cobaltacarborane **1** by quantum-chemical calculations. For the cage atoms, we used the atomic numbering scheme proposed earlier.[6] This scheme retains the number 1 for the metal atom regardless of the positions of the carbon atoms. Other atoms of the cage are numbered in a standard way.

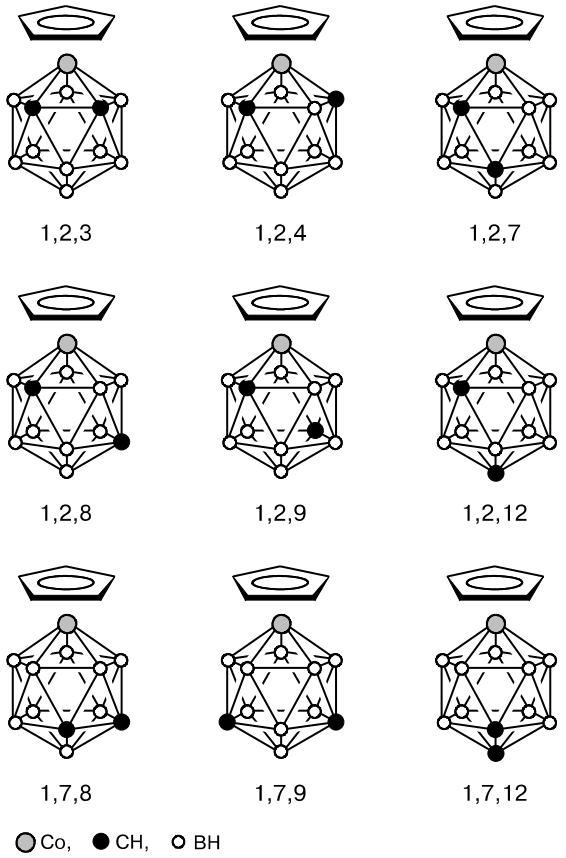

Fig. 1. Isomers of cobaltacarborane **1**.

Results and Discussion

The DFT calculations of the geometry, energies, and vibrational frequencies of isomers of **1** were carried out by the PBEPBE method using the DGDZPV basis set with DGA1 density fitting set. The use of this approximation

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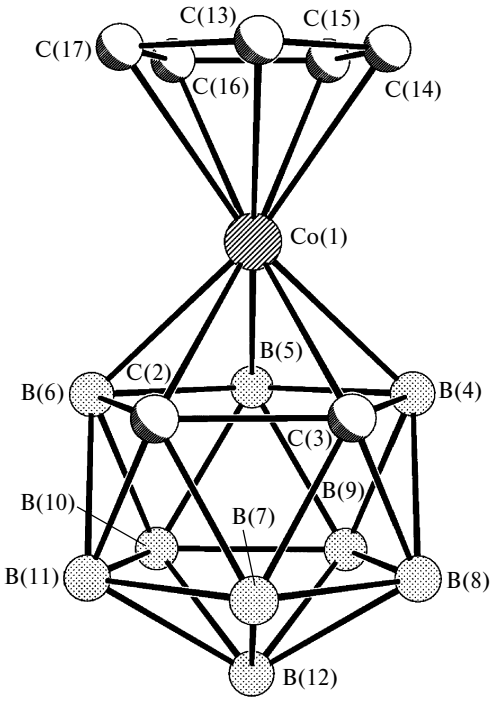

Fig. 2. Structure of the 1,2,3-isomer of cobaltacarborane **1**.

decreases the number of calculated two-electron integrals,[7]* due to which the calculation time can be reduced by a factor of 2—5, with the accuracy being close to that of B3LYP/6-31G* calculations. Selected interatomic distances in the 1,2,3-isomer of **1** (Fig. 2) determined by X-ray diffraction study[8] and by the quantum-chemical PBEPBE/DGDZPV/DGA1 and B3LYP/6-31G* methods are given in Table 1. It can be seen that the results of calculations by two methods differ only slightly from each other and adequately reproduce the experimental geometry. Hence, it is correct to use the PBEPBE/DGDZPV/DGA1 method for studying metallacarboranes.

The results of calculations of different characteristics for all isomers of **1** are presented in Table 2. The isomers can be divided into three groups depending on the mutual arrangement of the carbon atoms in the cage, *i.e.*, into groups containing carbon atoms in *ortho* (1,2,3-, 1,2,7-, 1,7,8-, and 1,7,12-isomers), *meta* (1,2,4-, 1,2,8-, 1,2,12-, and 1,7,9-isomers), and *para* positions (1,2,9-isomer). It can be seen that the energy difference between isomers within each group is small (average and maximum values are 0.63 and 2.67 kcal mol^{-1}, respectively). Hence, the position of the CpCo vertex in the cage has no substantial effect on thermodynamic stability of metallacarborane.

By contrast, the energy difference between the groups of the *ortho* and *meta* isomers is large (11.52—15.78 kcal mol^{-1}; aver., 13.6 kcal mol^{-1}). The energy difference between the groups of the *meta* and *para* isomers is smaller 1.05—3.83 kcal mol^{-1}; aver., 2.8 kcal mol^{-1}). These values are very close to the difference in thermodynamic stability of the *ortho*, *meta*, and *para* isomers of carborane $C_2B_{10}H_{12}$, which was estimated to be 14.40 and 3.21 kcal mol^{-1} using the same calculation method.* This confirms the close similarity between the isolobal[10] CpCo and BH fragments. In accordance with this similarity, a series of compounds, in which the CpCo fragments replace from one to four BH vertices, have been synthesized.[11]

Skeletal rearrangements of most metallacarboranes occur generally at lower temperatures compared to the rearrangements of carboranes.[4] The results of our study demonstrate that the decrease in the temperature is a consequence of a decrease in the activation energy rather than of an increase in the energy difference between the isomers.

The C···C distances and charges on the carbon atoms given in Table 2 indicate that there is no linear correlation between these parameters and stability of isomers. The negative charge on the carbon atoms increases with increasing distance between these atoms, and the positive

Table 1. Selected interatomic distances (d/Å) in the 1,2,3-$CpCoC_2B_9H_{11}$ molecule

Bond	XDA*	B3LYP/ 6-31G*	PBEPBE/ DGDZVP/DGA1
Co(1)—C(2), Co(1)—C(3)	1.998	2.017	2.017
Co(1)—B(4), Co(1)—B(6)	2.060	2.072	2.072
Co(1)—B(5)	2.106	2.100	2.105
Co(1)—C(13)	2.055	2.096	2.098
Co(1)—C(14), Co(1)—C(17)	2.052	2.076	2.079
Co(1)—C(15), Co(1)—C(16)	2.029	2.044	2.050
C(2)—C(3)	1.637	1.620	1.629
C(2)—B(6), C(3)—B(4)	1.701	1.710	1.718
B(4)—B(5), B(6)—B(5)	1.808	1.800	1.814
C(13)—C(14), C(13)—C(17)	1.400	1.423	1.435
C(14)—C(15), C(17)—C(16)	1.413	1.425	1.437
C(15)—C(16)	1.416	1.428	1.440

* The experimental bond lengths determined by X-ray diffraction analysis (XDA)[8] were averaged in the approximation of the C_s symmetry of the complex.

* *Gaussian 03 Manual* and references in the *Basis sets* (www.gaussian.com).

* Calculations of these values by the more accurate MP2/6-31G* method gave 15.57 and 3.53 kcal mol^{-1}, respectively[9].

Table 2. Characteristics of isomers of cobaltacarborane **1**

Isomer	Absolute energy/Hartree	Relative energy /kcal mol^{-1}	Distance C...C/Å	Atomic charges		Dipole moment/D	R_f*
				C	Co		
1,2,3	−1881.71035	17.57	1.629	−0.58	+0.60	7.6660	0.01
1,2,7	−1881.71193	16.58	1.632	−0.55; −0.59	+0.51	6.1061	0.22
1,7,12	−1881.71251	16.21	1.642	−0.53; −0.56	+0.41	2.2887	–
1,7,8	−1881.71389	15.35	1.627	−0.56	+0.41	4.1509	–
1,2,12	−1881.73224	3.83	2.631	−0.70;−0.77	+0.52	3.7748	0.56
1,2,4	−1881.73241	3.72	2.702	−0.77	+0.62	7.2005	0.20
1,2,8	−1881.73432	2.52	2.632	−0.74;−0.77	+0.51	5.2669	0.45
1,7,9	−1881.73666	1.05	2.623	−0.74; 0.74	+0.41	2.5736	0.65
1,2,9	−1881.73834	0.00	3.102	−0.73;−0.76	+0.51	4.5980	0.57

* Benzene—hexane as the eluent.[5]

charge on the cobalt atom decreases with decreasing number of the carbon atoms bound to cobalt. A decrease in the calculated dipole moment correlates well with an increase in experimental R_f.[5]

To summarize, the results of our study demonstrated that stability of 12-vertex cobaltacarboranes $CpCoC_2B_9H_{11}$ increases with increasing distance between the carbon atoms and is virtually independent of the metal—carbon distance. These characteristic features are expected to be also true for other metallacarboranes.

Calculation procedure

All calculations were carried out using the GAUSSIAN 03 program package (version B.01).[12] The geometry and vibrational frequencies were calculated by the PBEPBE method with the DGDZVP basis set at the DGA1 level. The SCF convergence limit was $1 \cdot 10^{-10}$ Hartree. The optimization was terminated when the rms shifts of the atoms reduced to 0.0018 Å. Where it was possible, the starting molecular geometry with the C_s symmetry was used. The atomic charges were calculated using NBO analysis integrated into the GAUSSIAN program package. The results of calculations were visualized using the ChemCraft program (version 1.4; www.chemcraftprog.com). Detailed results of calculations, including complete data on the geometry, frequencies, and energies, can be obtained from the authors.

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