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Dedicated to Professor Alexandru T. Balaban on the occasion of his 85th anniversary

CONTRASTING BEHAVIOR OF THE GROUP 15 ELEMENTS (P, As, Sb, Bi) AS HETEROATOMS IN ICOSAHEDRAL COBALTABORANES: EFFECT OF PHOSPHORUS ATOM BASICITY

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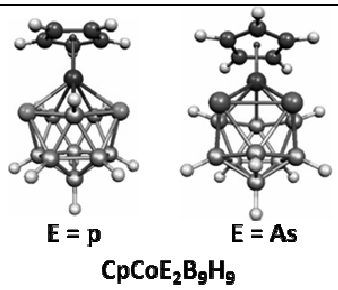
Previous theoretical studies show opposite energy orderings for the nine possible icosahedral structures for the cobaltadiphosphaboranes $CpCoP_2B_9H_9$ (Cp = η^5-C_5H_5) and the cobaltadibismaboranes $CpCoBi_2B_9H_9$. Thus the lowest energy $CpCoP_2B_9H_9$ structures avoid adjacent phosphorus atoms whereas the lowest energy $CpCoBi_2B_9H_9$ structures have adjacent bismuth atoms. The structures of the entire series of icosahedral cobaltaheteroboranes with group 15 heteroatoms $CpCoE_2B_9H_9$ (E = P, As, Sb, Bi) have now been examined by density functional theory. In all but the phosphorus derivative the lowest energy $CpCoE_2B_9H_9$ structures (E = As, Sb, Bi) are the unique structures with a CoE_2 triangular face. This suggests that the anomaly in the $CpCoP_2B_9H_9$ energy ordering relates to the repulsion between basic lone pairs on adjacent phosphorus atoms. The next higher energy $CpCoAs_2B_9H_9$ structures are the structures with a Co–As icosahedral edge. The energy ordering of the $CpCoSb_2B_9H_9$ structures resembles that of the $CpCoBi_2B_9H_9$ structures except for the abnormally low energy of the structure with two Co–Sb edges and non-adjacent antimony atoms.



INTRODUCTION

The three icosahedral dicarbaborane isomers $C_2B_{10}H_{12}$ are noted for their high thermal stabilities and low chemical reactivities.[1] Replacement of one of the BH vertices in such dicarbaboranes with an isoelectronic CpCo (Cp = η^5-C_5H_5) vertex gives the cobaltadicarbaboranes $CpCoC_2B_9H_{11}$, also exhibiting exceptionally high stability and low chemical reactivity.[2] Furthermore the two CH vertices in these dicarbaboranes with bare group 15 atoms gives the very stable icosahedral heteroboranes $B_{10}H_{10}E_2$ (E = P,[3,4] As,[4-6] Sb,[7] Bi[8]). A BH vertex in these heteroboranes can then be replaced by a CpCo vertex to give the cobaltaboranes $CpCoE_2B_9H_9$ (E = P,[4] As,[4,9] Sb[7]).

Nine icosahedral isomers are possible for the $CpCoC_2B_9H_{11}$ and $CpCoE_2B_9H_9$ structures. The $CpCoC_2B_9H_{11}$ isomers with adjacent carbon atoms are the highest energy structures[10,11] despite the fact that such structures were the first to be synthesized because of the availability of

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1,2-$C_2B_{10}H_{12}$ from decaborane and acetylene. We have shown by density functional theory that the $CpCoP_2B_9H_9$ structures with adjacent phosphorus atoms are also the highest energy structures.[12] We were therefore surprised when a subsequent density functional theory study showed that the analogous $CpCoBi_2B_9H_9$ structures with adjacent bismuth atoms are the *lowest* energy structures.[13] Furthermore, the $CpCoBi_2B_9H_9$ global minimum structure is the unique structure with a $CoBi_2$ triangular face. In these icosahedral cobaltaboranes phosphorus is thus a "carbon copy"[14] whereas bismuth, which like CH is essentially non-basic, is not a "carbon copy". Studies reported previously by Hofmann and co-workers on the thermochemical stability of the ortho- meta- and para- isomers of 12-vertex *closo*-heterometallaboranes of the p-block elements have concluded that the relative position of the heteroatom is most likely mandated by its size.[15,16]

RESULTS AND DISCUSSION

The strikingly different behaviors of phosphorus and bismuth in determining the energetically preferred icosahedral $CpCoE_2B_9H_9$ isomers (E = P, Bi) might be attributed to the much higher basicity of phosphorus lone pairs than bismuth lone pairs in similar species. In order to gain more insight regarding this difference we have now performed similar density functional theory investigations of the corresponding arsenic and antimony derivatives $CpCoE_2B_9H_9$ (E = As, Sb). In this connection the $CpCoE_2B_9H_9$ structures (E = P, As, Sb, Bi) were initially optimized at the M06-L/6-311G(d,p)/SDD level of theory using the SDD basis set only for the Sb and Bi atom centers.[17] In order to account for accurate electronic structure descriptions of adjacent lone pairs, the augmentation of a diffuse function to the basis set is necessary to allow the expansion of the electron density to a larger volume. Therefore, single point energy calculations were performed on the resulted optimized structures by using the same DFT functional in conjunction with the Def2-TZVPD basis set. Again for the Sb and Bi atom centers, an ECP derived from the same basis set was applied.[18] The energetics of the latter results are discussed in this paper.

The initial structures were chosen by systematic substitution of one BH vertex by a CpCo vertex in a regular icosahedron structure, followed by all possible substitutions of two BH vertices in the resulting cobaltaborane with two corresponding hetero atoms (E_2) where E is either P, As, Sb or Bi, resulting in a total of 36 structures (9 for each system). The natures of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies. If significant imaginary frequencies were found, the optimizations were continued by following the normal modes corresponding to imaginary frequencies to insure that genuine minima were obtained.

All calculations were performed using the Gaussian 09 package[19] with the default settings for the SCF cycles and geometry optimization, namely the fine grid (75,302) for numerically evaluating the integrals, 10^{-8} hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, RMS force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and RMS displacement of 0.001200 bohr.

Table 1

The relative energies of the $CpCoE_2B_9H_9$ (E = P, As, Sb, Bi) and $CpCoC_2B_9H_{11}$ structures in kcal/mol

Structure Type	E = Bi[a]	E = Sb	E = As	E = P[a]	E = CH[b]
oo-o-E	0.0 (0.0)	0.0	0.0	8.8 (6.4)	19.4 (17.6)
om-o-E	7.0 (4.6)	6.5	5.4	9.5 (8.1)	18.5 (16.6)
mm-o-E	12.6 (8.4)	11.8	10.0	14.1 (11.4)	17.5 (15.4)
mp-o-E	14.8 (11.1)	13.7	11.8	15.2 (12.4)	19.2 (16.2)
oo-m-E	14.9 (15.8)	9.0	0.8	0.0 (0.0)	3.3 (3.7)
om-p-E	19.1 (18.6)	12.8	3.4	2.5 (0.6)	0.0 (0.0)
om-m-E	20.3 (20.0)	14.1	5.4	4.4 (2.8)	2.4 (2.5)
op-m-E	20.3 (21.9)	12.3	6.9	4.5 (4.1)	4.4 (3.8)
mm-m-E	21.7 (23.9)	19.4	10.1	5.9 (5.6)	1.7 (1.1)

[a] The data in parentheses are taken from Ref. 12 for phosphorus and from Ref. 13 for bismuth. [b]The data are taken from Ref. 10 and from Ref. 11 with the former data in parentheses.

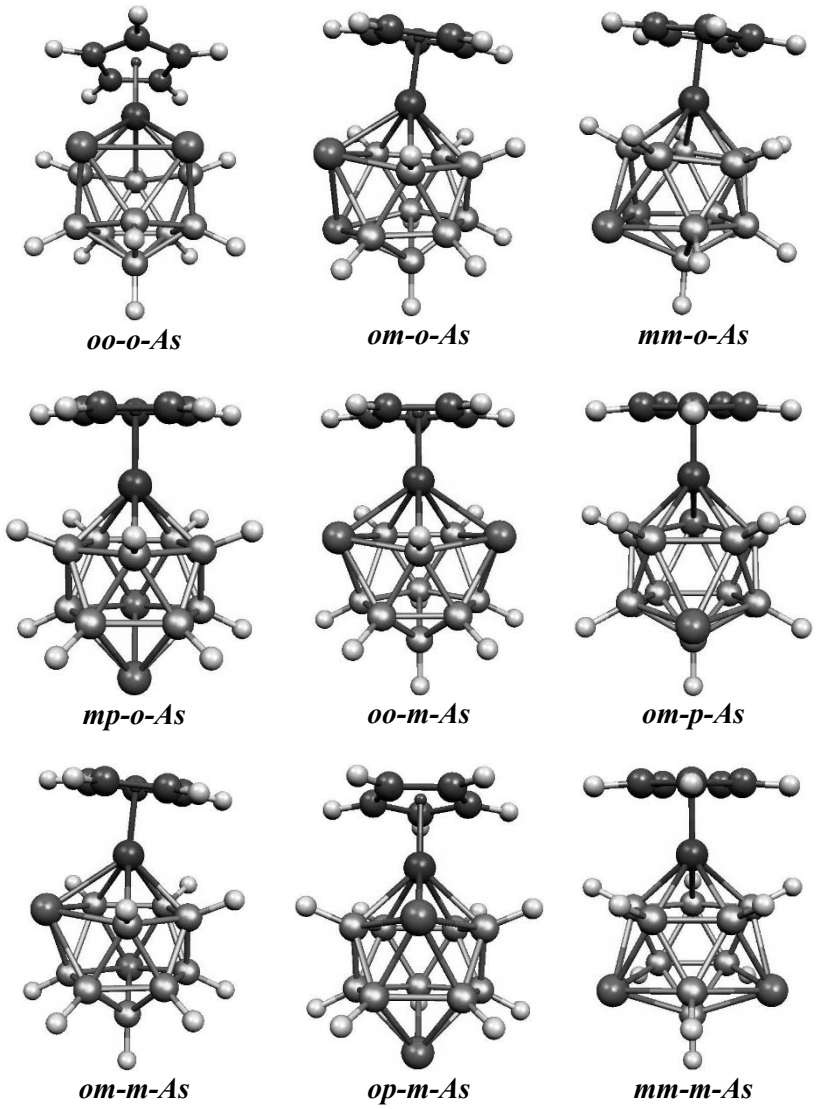

Fig. 1 – The nine isomeric icosahedral $CpCoAs_2B_9H_9$ structures.

The nine possible icosahedral structures for a given $CpCoE_2B_9H_9$ system are designated as *xy-z-E* in Table 1 where *x* and *y* refer to the relative positions of each heteroatom E to the cobalt atom, *z* relates to the relative positions of the two heteroatoms E, and E designates the heteroatom. The relative positions are designated as adjacent or *ortho* (*o*), non-adjacent non-antipodal or *meta* (*m*), and antipodal or *para* (*p*). The nine icosahedral $CpCoAs_2B_9H_9$ structures are depicted in Figure 1. Table 1 also compares the relative energies of the nine $CpCoP_2B_9H_9$ structures with the relative energies of the corresponding $CpCoC_2B_9H_{11}$ structures found in a previous density functional theory study.[11]

The following observations can be made concerning these results:

(1) The lowest energy $CpCoE_2B_9H_9$ structures for all of the Group 15 heteroatoms except phosphorus are the *oo-o* structures with a CoE_2 triangular face. The arsenic compound *oo-o-As* (Figure 1) has been synthesized and structurally characterized.[4] The predicted values of 2.416 and 2.532 Å for the Co–As and As–As bonds in *oo-o-As* are close to the experimental values of ~2.39 and ~2.47 Å determined by X-ray crystallography. This is good agreement considering the disorder in the X-ray structure.

(2) For $CpCoAs_2B_9H_9$ increasing the distances between the cobalt atom and the two arsenic atoms leads to higher energy structures. Thus *oo-o-As* is the lowest energy structure but the *oo-m-As* structure lies within 1 kcal/mol of this structure. The *om-o-As*/*om-p-As*, *op-m-As*, *mm-o-As*/*mm-m-As*, and *op-m-As* sets of $CpCoAs_2B_9H_9$ structures lie 3 to 6 kcal/mol, ~10 kcal/mol, and ~11 kcal/mol, respectively, above the *oo-o-As* global minimum.

(3) The relative energies of the icosahedral $CpCoSb_2B_9H_9$ isomers are fairly similar to those of

the corresponding $CpCoBi_2B_9H_9$ isomers except for an anomalous low energy of the *oo-m-Sb* structure. Thus two Co–Sb bonds (i.e., icosahedral edges) in $CpCoSb_2B_9H_9$ can overcome the disadvantage of having the two antimony vertices in non-adjacent non-antipodal positions rather than in adjacent positions forming an Sb–Sb icosahedral edge.

CONCLUSIONS

In summary, it appears for the "normal" positions of the Group 15 heteroatoms in the lowest energy icosahedral cobaltaheteroboranes $CpCoE_2B_9H_9$ to be adjacent to each other and to the cobalt atom thereby forming a CoE_2 face of the icosahedron. Arsenic, antimony, and bismuth exhibit this behavior. Phosphorus, however, avoids $CpCoP_2B_9H_9$ structures with adjacent phosphorus atoms. This appears to be a consequence of the basicity of bare phosphorus vertices leading to repulsion of the basic lone pairs on adjacent phosphorus atom. Furthermore, the lowest energy structures of the icosahedral cobaltadiarsaborane $CpCoAs_2B_9H_9$ maximize the number of Co–As edges in the icosahedron, even at the expense of As–As edges.

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