

Does Back-Bonding Involve Bonding Orbitals in Boryl Complexes? A Theoretical DFT Study

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Theoretical calculations at the DFT (B3LYP) level have been undertaken on tris- and bis(boryl) complexes. Two model d^6 complexes $[\text{Rh}(\text{PH}_3)_3(\text{BX}_2)_3]$ and $[\text{Rh}(\text{PH}_3)_4(\text{BX}_2)_2]^+$, $\text{X} = \text{OH}$ and H] have been studied. In the model tris(boryl) complex ($\text{X} = \text{OH}$) we find a *fac* structure as a minimum, in accordance with the experimental data. The *mer* geometries are found to be higher in energy. Analysis of the energetic ordering in *mer* isomers shows that back-bonding in these complexes involves a bonding $\text{Rh}-\text{B}$ orbital (and not a d -block orbital as usual). This surprising behavior is rationalized through a qualitative MO analysis and quantitative NBO analysis. Results on the bis(boryl) complex confirm the preceding analysis. Full optimization of unsubstituted ($\text{X} = \text{H}$) complexes leads to structures in which the BH_2 moieties are coupled. In the optimal geometry of the bis(boryl) complex, the B_2H_4 ligand resembles the transition state of the $\text{C}_{2v} \rightarrow \text{D}_{2d}$ interconversion of the isolated B_2H_4 species. In the tris(boryl) complex, we find a B_3H_6 ligand in which the B_3 atoms define an isosceles triangle with one hydrogen bridging the shorter $\text{B}-\text{B}$ bond.

Introduction

There has been these last years a growing interest in boryl complexes. They are known to be intermediate in catalytic hydroboration of alkenes and alkynes.¹ Recently, they have been shown to activate alkane $\text{C}-\text{H}$ bonds.² Three recent review papers describe the various properties of these complexes.^{3–5}

From a theoretical point of view, several topics have been studied on these complexes. Reaction paths of hydroboration reactions have been studied for both ethylene⁶ and acetylene.⁷

Insertion of $\text{M}(\text{PH}_3)_2$ ($\text{M} = \text{Pt}, \text{Pd}$) into bonds involving the boron atom has been studied by Sakaki's group.⁸ A precise description of the metal–boryl bond in low-coordination complexes ($\text{M}(\text{BH}_2)$, $\text{M}(\text{BH}_2)^+$) has been given by Musaev and Morokuma.⁹ Recently, Pandey has given an analysis of the electronic structure of $\text{Cp}_2\text{Nb}(\text{H}_2\text{B}(\text{OH})_2)$;¹⁰ it is found that this complex should be described as an η^3 -borohydride complex rather than a bis(hydrido) boryl complex. An opposite result is found in the case of $\text{Cl}_2\text{Ta}(\text{H}_2\text{B}(\text{OH})_2)$ and $\text{Cl}_2\text{W}(\text{H})(\text{B}(\text{OH})_2)$ complexes.¹¹ A detailed study of bonding in mono(boryl) complexes $(\text{PH}_3)_2(\text{CO})\text{C}(\text{Os})(\text{BR}_2)$ ($\text{BR}_2 = \text{BH}_2, \text{BF}_2, \text{B}(\text{OH})_2, \text{B}(\text{OCH}=\text{CHO}), \text{Bcat}$) has been published by Frenking and co-worker.¹² It is shown that the $\text{Os} \rightarrow \text{B}$ back-bonding is not important except in the BH_2 case.

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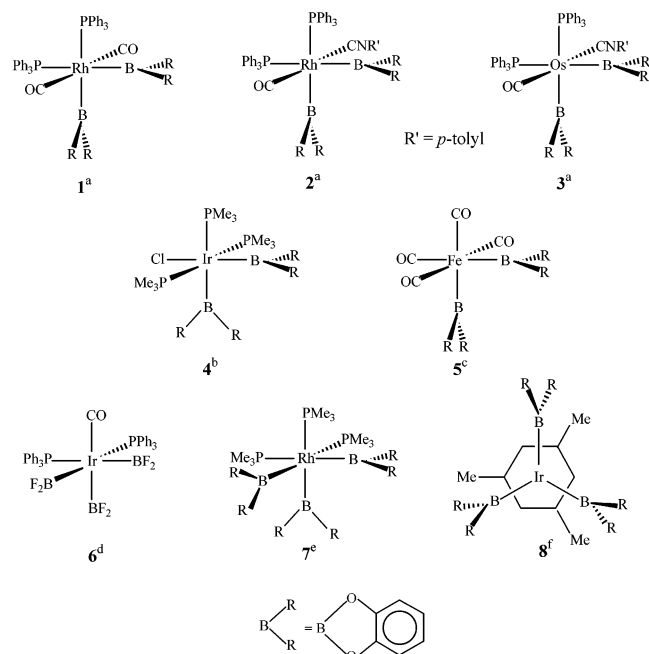


Figure 1. Geometries of bis(boryl) (1–5) and tris(boryl) (6–8) complexes from crystallographic data. In each case, the BR_2 ligand is the catechol boryl (Bcat) except in **5** in which the phenyl ring is substituted by a *tert*-butyl group. References: (a) ref 13; (b) ref 14; (c) ref 15; (d) ref 16; (e) ref 17; (f) ref 18.

The aim of this paper is to give a theoretical analysis of complexes which bear at least two boryl ligands to understand the mutual influence of these ligands. Numerous monometallic bis- and tris(boryl) complexes have been crystallographically characterized.^{3–5} To our knowledge, only eight structures of such hexacoordinated complexes have been characterized; they are depicted in Figure 1. All contain a d^6 metal center. Of particular interest for us are the tris(boryl) complexes (6–8). In all cases, the boryl ligand is substituted by π -donor groups; only the *fac* arrangement is observed in these tris(boryl) complexes. Although no values of the dihedral angles are given, it seems that, in **7**, the boryl planes are orthogonal to each other and contain two cis ligands.

To understand the electronic structure of the tris(boryl) complexes, we have undertaken a theoretical study of the complex $\text{Rh}(\text{PH}_3)_3(\text{BH}_2)_3$, a model of the experimentally synthesized complex (**7**) in which all the substituents on phosphorus and boron atoms have been replaced by hydrogen atoms. All the isomers (*mer* and *fac*) of this model have been optimized under some geometrical constraints (see below). In addition, a model bis(boryl) complex $\text{Rh}(\text{PH}_3)_4(\text{BH}_2)_2^+$ of d^6 rhodium(III) has been studied and the results will also be presented.

Theoretical Methods

Calculations have been performed within the DFT (B3LYP) formalism with the help of the Gaussian 98 set of programs.¹⁹ The

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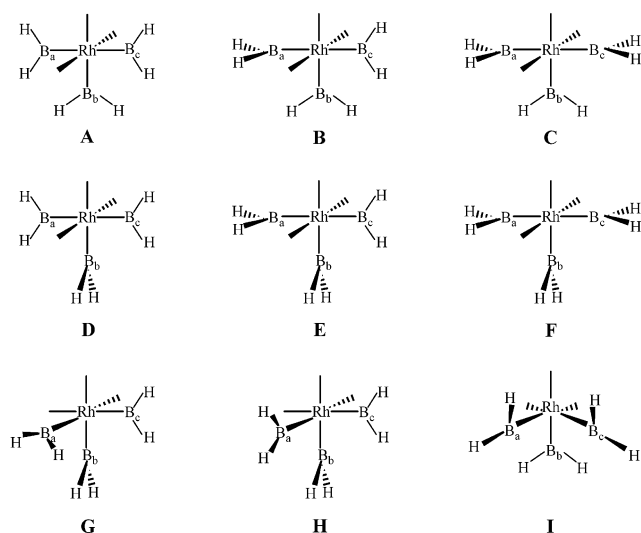


Figure 2. Geometrical structures of the tris(boryl) isomers.

ECP LANL2-DZ basis set augmented with a set of *f* polarization functions²⁰ has been used for the metal center, and the 6-31G* basis set, for the description of the ligands. All extrema have been optimized by an analytical gradient method. The optimized extrema have been characterized by a frequencies calculation.

Results

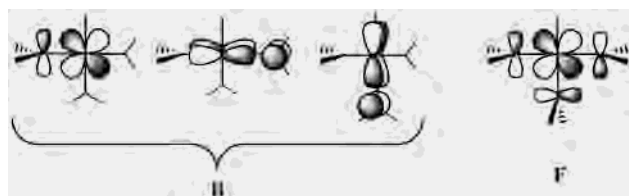
A. Frozen Geometry. $\text{Rh}(\text{PH}_3)_3(\text{BH}_2)_3$. At first we will present the results obtained with partially frozen geometries: in these calculations, all the cis ligand–metal–ligand angles are kept frozen to 90° and the BH_2 groups are kept planar. If the three BH_2 planes are constrained to be parallel or perpendicular to the B–Rh–B planes, one gets eight different conformers. In two of them the boryl ligands present a *fac* arrangement and six structures are *mer* complexes (see Figure 2). Within these geometrical constraints, all other geometrical parameters have been optimized. The results are given in Figure 2 and Table 1.

If the BH_2 planes rotations constraint is relaxed, no change occurs among the *mer* conformers. In the opposite in *fac* isomers **G** and **H**, optimization of these parameters leads to the absolute minimum **I** in which the BH_2 planes rotate in

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Table 1. Optimized Rh–B Bond Lengths (in Å) and Relative Energies (in kcal/mol) of the Tris(boryl) Isomers

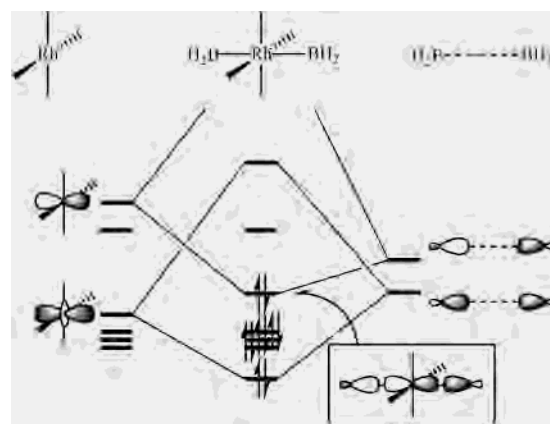
| | A | B | C | D | E | F | G | H | I |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Rh–B _a | 2.188 | 2.185 | 2.180 | 2.181 | 2.178 | 2.172 | 2.034 | 2.031 | 2.046 |
| Rh–B _b | 2.048 | 2.058 | 2.065 | 1.999 | 2.012 | 2.024 | 2.033 | 2.006 | 2.045 |
| Rh–B _c | 2.173 | 2.153 | 2.163 | 2.168 | 2.149 | 2.160 | 2.034 | 2.057 | 2.045 |
| ΔE | 30.9 | 27.8 | 26.6 | 20.2 | 16.0 | 14.2 | 5.5 | 4.7 | 0 |

Chart 1

such a way that the Rh(BH₂)₃ moiety exhibits an approximate C₃ symmetry. The rotational angle is about 38° (starting from the **G** structure). It is worth noting that a similar arrangement of the three boryl ligands has been experimentally found in a d⁶ iridium complex (**8**; see Figure 1).¹⁸

From an energetical point of view, we find the *fac* isomers (**G**–**I**) more stable by 10–30 kcal/mol than the *mer* isomers (**A**–**F**). This larger stability may be attributed to a strong trans effect of the BH₂ ligand because the σ nonbonding orbital of the BH₂ group is located high in energy. As a consequence, two BH₂ ligands preferentially bind to a metal center in a cis rather than in a trans position. Consequently, the *fac* isomers where all boryl ligands are in a cis position are lower in energy than the *mer* isomers in which two boryl ligands are in a trans position.

Although the *mer* isomers are less stable than the *fac* ones, the energetical ordering of the different structures is rather surprising. Two series may be distinguished: In the first (**D**–**F**), the plane between B_bH₂ plane is perpendicular to the RhB₃ plane and these three structures are found to be 14.2–20.2 kcal/mol above the absolute minimum **I**. Structures **A**–**C** constitute the second series in which the B_bH₂ plane lies in the RhB₃ plane and these three structures are located more than 26 kcal/mol above the absolute minimum. Since σ effects are identical in these six structures **A**–**F**, back-bonding is expected to be responsible for the different stabilities of these structures. Following Burdett and Albright,²¹ when two π -acceptor ligands are bound to the same metal center, the optimal geometry is obtained when different π -acceptor orbitals interact with different occupied d orbitals. Such arrangement occurs in the **B** structure in which each d orbital of the t_{2g} set interacts with different vacant 2p orbitals of the BH₂ groups (Chart 1). However, this geometry is found to be one of the highest energy ($\Delta E = 27.8$ kcal/mol) within the set of *mer* isomers. In addition, in the most stable *mer* isomer (**F**, $\Delta E = 14.2$ kcal/mol), back-bonding is expected to be rather small since the three vacant orbitals interact with only one occupied d orbital (Chart 1); this structure is therefore disfavored with respect to back-bonding with d orbitals. These results indicate that back-bonding between the occupied d orbitals and 2p vacant orbital of the BH₂ group (2p_B) is not the dominant factor in these *mer* complexes.

**Figure 3.** Qualitative interaction diagram between a ML₄ fragment and two apical boryl ligands.

To understand the energetical ordering of these *mer* structures, it is useful to draw a qualitative description of the electronic structure of these complexes. Let us focus on the σ interaction between a ML₄ square planar moiety with two boryl ligands in a trans position. For sake of simplicity the boryl ligands will be restricted to their only σ nonbonding orbitals. The interaction diagram is given in Figure 3.

The in-phase combination of the σ orbitals mainly interact with the nonbonding d_{z²} orbital that leads to a low-lying bonding orbital. The out-of-phase combination of these σ orbitals interacts with the rhodium 5p orbital and gives a couple of bonding and antibonding orbitals. However, since both interacting orbitals are located high in energy, the bonding combination is also high in energy and is found to lie above the three nonbonding d orbitals. On the whole, one roughly finds the d splitting of an octahedron with three (pseudo-t_{2g}) nonbonding orbitals and two (pseudo-e_g) antibonding orbitals. The prominent feature of this MO diagram is the presence of a bonding orbital characterizing the apical B–Rh–B bond between the two sets of d orbitals. As a consequence, in such bis(boryl) complexes, the HOMO is no longer a nonbonding d orbital but a bonding B–Rh–B orbital.

The results given in Table 1 are more easily understandable from the preceding analysis: in trans bis(boryl) complexes, back-bonding will preferentially involve the highest energy bonding orbital rather than a d-block orbital. Such interaction between B_a–Rh–B_c bonding orbital with the 2p_{Bb} vacant orbital is at work in the first series (**D**–**F**) whereas these orbitals are orthogonal in the second series (**A**–**C**) (Chart 2).²²

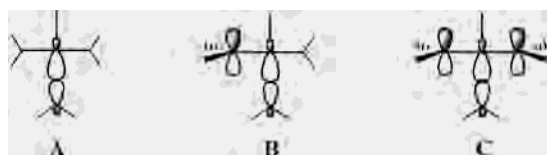
Analysis of the MO shapes and energies from our B3LYP calculations confirms the above interpretation: in each *mer* conformation (**A**–**F**), the HOMO is found to be essentially the combination of the rhodium 5p orbital with the σ orbitals on *trans*-boryls B_aH₂ and B_cH₂. In conformations **A**–**C**, its

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Chart 2



Chart 3



energy is nearly constant at -4.57 eV. In conformations **D–F**, this orbital is still the HOMO but its energy is noticeably lowered (from -5.01 to -5.06 eV) due to the interaction with the $2p_{B_b}$ orbital (Chart 2). This energy difference is likely to be at the origin of the larger stability of structures belonging to the **D–F** series. This interaction has also geometrical consequences: if we compare conformations **A** and **D**, the main difference is the orientation of the B_bH_2 group. The Rh– B_b bond length is shortened from 2.048 to 1.999 Å (Table 1), indicating an additional bonding interaction between the B_bH_2 ligand with the metallic moiety. A similar trend is found in the **B, E** and **C, F** series.

In addition, careful examination of the MOs of the different structures indicates that, in the *mer*-tris(boryl) complexes, another MO lies above the Rh d nonbonding orbitals. It is essentially a bonding combination of the σ orbital of the B_bH_2 ligand with a metallic hybrid orbital. This orbital roughly represents the Rh– B_b bond and, again, lies above the nonbonding d orbitals since it is a combination of high-lying orbitals. Consequently, back-bonding involving this orbital is expected to be stabilizing as in the case of the HOMO. This is indeed the case: structure **A** in which no stabilization occurs is found to be the highest energy structure. Conformations **B** and **C** are stabilized (with respect to **A**) by 3.1 and 4.3 kcal/mol, respectively, since one or two $2p_B$ orbitals may interact with the Rh– B_b bond (Chart 3). The same trend is found in the more stable conformations **D–F**. Stabilizations of 3.8 and 6.0 kcal/mol (with respect to the **D** conformation) occur when one and two $2p_B$ orbitals interact with the Rh– B_b bond, respectively.

Finally, NBO analysis have been performed to get more qualitative evidence of the above analysis. The populations of valence vacant $2p_B$ orbitals are given in Figure 4 for the six conformers.

As shown in Figure 4, the $2p_B$ orbital population of the B_bH_2 group increases from 0.10 (**A–C**) to 0.22–0.26 (**D–F**) electrons when this orbital can interact with the B–Rh–B bonding orbital. A similar trend (although attenuated) is found for the population of the two other boryl groups

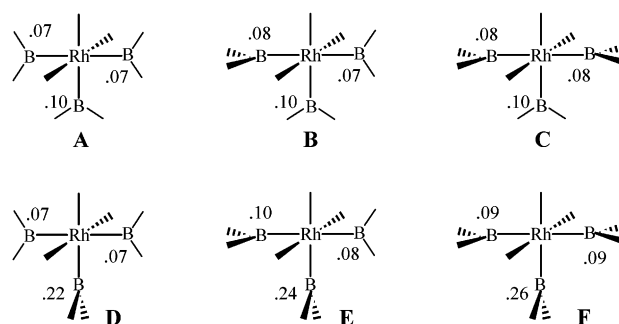


Figure 4. Population analysis of the vacant $2p$ orbitals of the boryl groups in the various conformers.

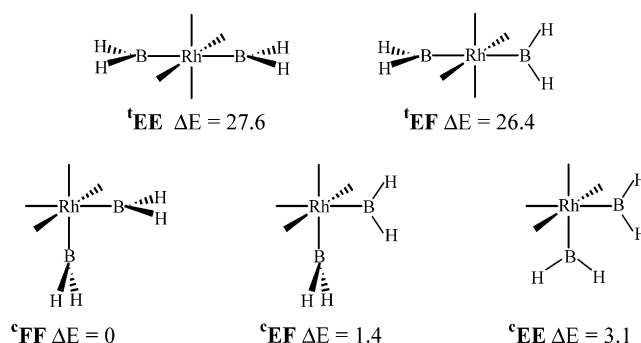


Figure 5. Structures and relative energies (in kcal/mol) of the isomers of cationic bis(boryl) complex $Rh(PH_3)_4(BH_2)_2^+$.

depending on the interaction of these orbitals with the Rh– B_b bond.

$Rh(PH_3)_4(BH_2)_2^+$. To test the importance of the back-bonding from a Rh–B bond to a vacant $2p_B$ orbital, we performed calculations on a d^6 model system $Rh(PH_3)_4(BH_2)_2^+$ containing only two boryl groups. Five different conformations have been optimized under the same geometrical constraints as in tris(boryl) case. The results are given in Figure 5.

The two trans conformations (¹EE and ¹EF) are located high in energy (more than 26 kcal/mol above the actual minimum ³FF). Again, this large destabilization is attributed to the strong trans effect of the boryl group. As in the tris(boryl) complex, the energetical ordering among the three cis conformations is rather surprising with regard to the classical back-donation from the occupied d-block orbitals in this d^6 complex: in the most stable structure ³FF, only one d occupied orbital is stabilized by back-bonding, whereas two different d occupied orbitals are stabilized in both ³EF and ³EE. In the opposite, this energetical ordering nicely parallels the number of possible interactions between the Rh–B bonds with the $2p_B$ vacant orbitals: there is no such interaction in ³EE ($\Delta E = 3.1$ kcal/mol), one in ³EF ($\Delta E = 1.4$ kcal/mol), and two in ³FF ($\Delta E = 0$).

Finally, one can note that the energies differences are smaller among the cis isomers than those observed precedingly in the *mer* series. This is probably due to the cationic nature of our model bis(boryl) complex which lowers the energies of the occupied orbitals and thus increases the energy gap with the vacant orbitals.

$Rh(PH_3)_3(B(OH)_2)_3$ and $Rh(PH_3)_4(B(OH)_2)_2^+$. To get a more detailed description of the experimentally synthesized

(22) As pointed out by a reviewer, steric effects may play a role in the energetical ordering of the various *mer* conformers. Test calculations we made on model systems indicate that such steric effects may play a noticeable role only in the **A** conformation: in this structure steric effects have been estimated to about 10 kcal/mol with respect to the most stable conformers. However, steric effects play a minor role within the other conformations.

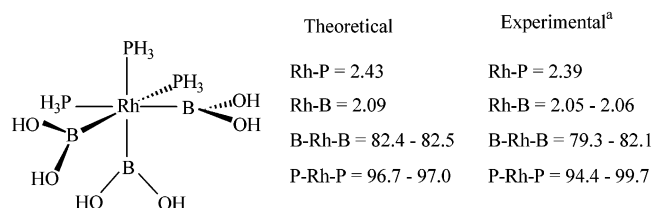


Figure 6. Main theoretical and experimental parameters of the tris(boryl) complexes. Bonds are in Å, and angles, in deg. Superscript a refers to ref 17.

Table 2. Relative Energies (in kcal/mol) of the Tris- and Bis(boryl) Isomers $\text{Rh}(\text{PH}_3)_3(\text{B}(\text{OH})_2)_3$ and $\text{Rh}(\text{PH}_3)_4(\text{B}(\text{OH})_2)_2^+$

| | A | B | C | D | E | F | G | H |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----|---|-----|
| ΔE | 28.2 | 20.6 | 14.9 | 11.0 | 9.2 | 8.2 | 0 | 5.2 |
| | ^c FF | ^c EF | ^c EE | ^c EF | ^c EE | | | |
| ΔE | 0 | 1.3 | 9.0 | 21.1 | 21.6 | | | |

complexes, we have made calculations on deactivated boryls $\text{B}(\text{OH})_2$ which better model the boryl groups experimentally used. The OH groups have been kept frozen in a cis position to mimic the catechol ligand. The results are given in Table 2.

The conformational energies ordering is the same as in the unsubstituted complexes for both tris- and bis(boryl) complexes.²³ This indicates that the Rh–B back-bonding to $2p_B$ vacant orbitals is still the dominant effect in these complexes of deactivated boryls. However, due to the destabilization of the vacant orbitals by π -donation of the hydroxy groups, the energy differences between the various conformers are generally smaller than in the unsubstituted case (an exception is found for the ^cEE conformation which may come from lone pairs repulsion between boryl oxygen atoms).

B. Full Optimization. $\text{Rh}(\text{PH}_3)_3(\text{B}(\text{OH})_2)_3$ and $\text{Rh}(\text{PH}_3)_4(\text{B}(\text{OH})_2)_2^+$. Starting from the two most stable *fac* conformers **G** and **H** obtained precedingly, a full optimization has been performed. It leads to only one minimum lying 5 kcal/mol below the most stable frozen structure **G**. Distortions from the frozen octahedral geometry comes from the diminution of the B–Rh–B angles (82.5° instead of 90°). At the same time, the P–Rh–P angles increase to 96.7 – 97.0° . The main geometrical parameters are given in Figure 6 together with the experimental ones (obtained in the catechol boryl complexes).

On the whole, the theoretical parameters agree well with the experimentally determined ones: the theoretical bond lengths are surestimated by about 0.04 Å. Theoretical and experimental values for the cis coordination angles are the same within 3° . Since the optimized structure is close to an octahedron, the preceding analysis on frozen geometries is still valid: the orientation of the boryl groups is essentially due to the interaction between Rh–B bonds and the vacant $2p_B$ orbitals rather than the classical back-bonding involving occupied d orbitals.

$\text{Rh}(\text{PH}_3)_3(\text{BH}_2)_3$ and $\text{Rh}(\text{PH}_3)_4(\text{BH}_2)_2^+$. To our knowledge, boryl complexes have been only synthesized in the

(23) We did not find a minimum close to the **I** structure in the unsubstituted case. All attempts we made led to the **G** structure.

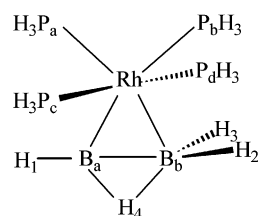


Figure 7. Optimized geometry and main geometrical parameters of the cationic bis(boryl) complex. Bonds are in Å, and angles, in deg.

Table 3. Relative Energies (in kcal/mol) of the Frozen and Optimized Structures of the Cis Conformations of the Cationic Bis(boryl) Complex

| | ^c FF | ^c EF | ^c EE |
|----------------------------------|-----------------|-----------------|-----------------|
| ΔE (frozen) | 0 | 1.4 | 3.1 |
| ΔE (optimized) nature | –3.7 min | –13.5 min | 0.4 2-SP |

case where boryl ligands are deactivated by π -donor substituents. A theoretical study of unsubstituted complexes is therefore of interest in a synthetic perspective. We will present results on cationic bis(boryl) system at first.

Bis(boryl) Complex $\text{Rh}(\text{PH}_3)_4(\text{BH}_2)_2^+$. Starting from the three cis conformations (^cEE, ^cEF, and ^cFF), full optimizations lead to three stationary points (Table 3). The extremum obtained from ^cEE has been characterized as a 2-order saddle point. Two minima has been found: full optimization of the ^cFF structure leads to a minimum localized 3.7 kcal/mol lower in energy than the frozen structure. The main change between frozen and optimized geometries is the B–Rh–B angle which is reduced to 85.4° .

Surprisingly, optimization of the ^cEF structure leads to the absolute minimum located 14.9 kcal/mol below the frozen ^cEF geometry. The reason for this large stabilization is the coupling of the two BH_2 moieties which occurs in the optimized structure. The optimized geometry is given in Figure 7. In this complex, the metallic moiety $\text{Rh}(\text{PH}_3)_4$ may be described as a fragment of a distorted octahedron: the P_a–Rh–P_b angle increases up to 99.1° and the P_c–Rh–P_d is equal to 170.8° (the bending of the phosphines occurs toward the bis(boryl) ligand).

The prominent feature of this complex is the coupling which occurs between the two BH_2 ligands: the B_a–Rh–B_b angle is acute (49.4°), which leads to a short B–B distance ($B_a-B_b = 1.778$ Å). The relative orientation of the two boryl moieties is same as in the ^cEF frozen complex; i.e., the two planes are mutually perpendicular. In the B_2H_4 moiety, one hydrogen is in a bridging position ($B_a-H_1 = 1.311$ Å; $B_b-H_2 = 1.352$ Å).

Such geometry of a B_2H_4 species is rather surprising. Previous theoretical work^{24,25} has shown that the most stable geometries of B_2H_4 are of C_{2v} (two bridging hydrogen atoms) or D_{2d} (no bridging atom) symmetry. These both geometries are found to be close in energy. The interconversion between these two geometries has been studied by Stanton et al.²⁵ It

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(25) Stanton, J. F.; Gauss, J.; Bartlett, R. J.; Helgaker, T.; Jorgensen, P.; Jensen, H. J. A.; Taylor, P. *J. Chem. Phys.* **1992**, *97*, 1211–1216.

Table 4. Main Geometrical Parameters^a of Complexed and Isolated B₂H₄ Fragment²⁶

| | complexed B ₂ H ₄ | isolated B ₂ H ₄ |
|--|---|--|
| B _a -B _b | 1.778 | 1.507 |
| B-H ₂ | 1.198 | 1.182 (1.234) |
| B-H ₁ | 1.190 | 1.179 |
| B _a -H ₄ | 1.311 | 1.305 |
| B _b -H ₄ | 1.353 | 1.489 |
| B _a -H ₄ -B _b | 83.7 | 64.9 |

^a Bonds are in Å, and angles, in deg.

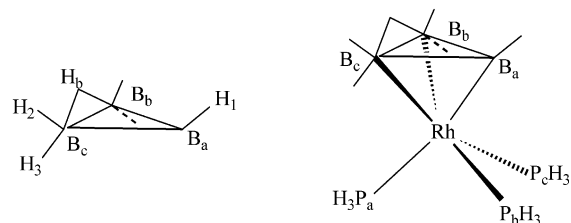
has been found that the transition state geometry is a monobridged structure which resembles the complexed B₂H₄ structure we obtain.

To get results at the same level of calculations, we have investigated the interconversion pathway between the two isomers (*D*_{2d} and *C*_{2v}) of B₂H₄ at the B3LYP/6-31G* level. We found the *D*_{2d} geometry as the absolute minimum, the *C*_{2v} structure (characterized as a minimum) being located 5.5 kcal/mol above it. A monobridged structure has been characterized as the transition state of this interconversion pathway and lies 9.4 kcal/mol above the absolute *D*_{2d} minimum. On the whole, our interconversion pathway agrees well with the results of Stanton et al. ($\Delta E(C_{2v}-D_{2d}) = 1.2$ kcal/mol, the interconversion energy being equal to 7.7 kcal/mol at the CCSD(T)/PVTZ level of calculations). In Table 4 are given the most important geometrical parameters of the monobridged species (isolated and complexed by the Rh complex). The two geometries are rather close except the B-B bond length which is lengthened in the complex and the B_aH₄B_b angle which is larger. As a conclusion, the optimized 'EF' structure may be viewed as a "frozen transition state" stabilized by complexation.

Tris(boryl) Complex Rh(PH₃)₃(BH₂)₃. We have restricted ourselves to the optimization of the most stable structures **G** and **H**. Relaxing all the geometrical constraints leads in both case to only one extremum lying 37.5 kcal/mol lower in energy than the frozen absolute minimum. Frequency analysis shows this extremum to be a real minimum. Its geometry (given in Figure 8) is of *C*_s symmetry, the symmetry plane containing B_a, Rh, and P_a.

As in the bis(boryl) case, a coupling between the boryl ligands occurs in this optimized structure. This complex is conveniently described as a (B₃H₆) moiety complexed to a Rh(PH₃)₃ metallic fragment. The Rh(PH₃)₃ fragment is pyramidal with P-Rh-P angles between 100 and 105°. The Rh-P_a bond length is longer (2.472 Å) than the Rh-P_b and Rh-P_c distances (both equal to 2.314 Å). The B₃H₆ ligand

(26) In isolated B₂H₄ species, two different B-H₂ distances are found because this structure is not of *C*_s symmetry.



| | |
|--|---|
| B _a -B _b = B _a -B _c = 1.843 | Rh-P _a = 2.472 |
| B _b -B _c = 1.791 | Rh-P _b = Rh-P _c = 2.314 |
| B _a -H ₁ = 1.191 | P _a -Rh-P _b = P _a -Rh-P _c = 100.6 |
| B _c -H ₂ = 1.205 | P _b -Rh-P _c = 104.6 |
| B _c -H ₃ = 1.194 | Rh-B _b = Rh-B _c = 2.412 |
| B _b -H ₄ = B _c -H ₄ = 1.327 | Rh-B _a = 1.909 |
| B _a -B _c -B _b = B _a -B _b -B _c = 60.9 | B _a -Rh-B _b = 49.4 |
| B _b -B _a -B _c = 58.1 | B _a -Rh-B _b = B _a -Rh-B _c = 43.6 |
| | B _b -Rh-B _c = 48.8 |

Figure 8. Optimized geometry and main geometrical parameters of the tris(boryl) complex. Bonds are in Å, and angles, in deg.

is constituted by a B₃ isosceles triangle (B_a-B_b = B_a-B_c = 1.844 Å), the B_b-B_c bond length being shorter (1.791 Å). A hydrogen atom H_b bridges the B_b and B_c atoms which both are bound to two other hydrogen atoms. The B_a boron atom is bound to only one hydrogen (B_a-H₁ = 1.191 Å).

The coordination of this ligand essentially occurs with the B_a atom as shown by the Rh-B bond lengths: Rh-B_a = 1.909 Å and Rh-B_b = Rh-B_c = 2.412 Å, this latter value indicating weak Rh-B bonds. An easier way to describe this structure is to separate this complex into (Rh(PH₃)₃B_aH₁) and B_bB_c(H)₅ fragments, the latter moiety resembling that observed in diborane species. This tris(boryl) complex may then be viewed as a diborane molecule in which one bridging hydrogen has been replaced by a borometallic fragment.

Conclusion

Our theoretical study of the tris- and bis(boryl) complexes indicates a strong trans effect which precludes any trans arrangement of two boryl ligands. It is found that the optimal conformation of such species depends on back-bonding with the 2p vacant orbitals on boryl ligands. However, this back-bonding does not involve the d orbitals of the metal atom but a bonding orbital characterizing a Rh-B bond. This point has been rationalized by a qualitative orbital interaction diagram and confirmed by a NBO analysis. Study of unsubstituted boryl ligands shows these species are unlikely to be easily synthesized as individual ligands: a coupling between the two (or three) boryl ligands occurs and leads to a complex of the B₂H₄ or B₃H₆ ligand, respectively.

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