Articles

Pyramidal Structures with a B_3H_6 Ring. Possibility of Terminal Hydrogens opposite the Capping Group

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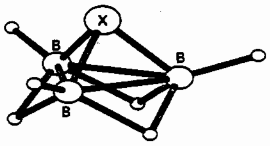
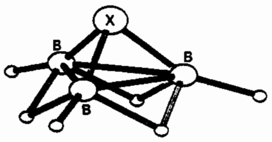
Ab initio molecular orbital studies on a series of pyramidal B_3H_6X structures (X = NH^+, N, CH, BH^-, P, PH^+, SiH, NO, PO, $Co(CO)_3$) indicate that, for structures where X = NH^+, N, and NO, the terminal hydrogens (H_t) of the basal B_3H_6 ring are toward the direction of the capping group. In contrast, the H_t's are found to be away from the capping group for X = CH, BH^-, P, PH^+, SiH, PO, and $Co(CO)_3$. All structures except that of $B_4H_7^-$ are calculated to be minima. The six π interstitial electron rule for three-dimensional delocalization and the compatibility of orbitals in overlap are used to explain the structural and bonding preferences in these pyramidal molecules.

Introduction

Pyramidal structures based on carbocyclic π ligands and capping groups ranging from main group elements to transition metal fragments are well-known in the literature.[1] Representative examples include C_3R_3CR[2a] and $C_3R_3Co(CO)_3$[2b] with a trigonal pyramidal arrangement; $C_4H_2R_2CH^+$ [3a,b] and $C_4R_4Fe(CO)_3$[3c] with a square pyramidal arrangement; C_5H_5Ga[4a] and $C_5H_5Mn(CO)_3$[4b] with a pentagonal pyramidal skeleton; and $C_6R_6Ga^+$ [5a] and $C_6H_6Cr(CO)_3$[5b,c] for pyramidal structures based on six-membered carbocyclic rings. In contrast, isoelectronic pyramidal boranes known so far are based only on four- and five-membered boracyclic rings, e.g. B_5H_9[6a] and $B_4H_8Fe(CO)_3$[6b,c] (square pyramidal); and B_6H_{10},[7a] B_5H_9CoCp,[7b] and $B_5H_{10}FeCp$[7c] (pentagonal pyramidal). No pyramidal structure based on the three-membered boracycle B_3H_6 isoelectronic with the C_3H_3 ring has been reported till now. However, pyramidal structures with metallacycles isolobal with B_3H_6 and capped by main group or transition metal fragments are well-known, e.g. $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-CMe})$,[8a] $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CX})$ (X = C_6H_5, Cl)[8b] $(\mu\text{-H})_3FeRu_2(CO)_9(\mu_3\text{-COMe})$,[8c] and $(\mu\text{-H})_3Os_3(CO)_9MnCp(CO)_2$.[8d] The cation $B_3H_6^+$, with 2π electrons was calculated to be a minimum. It has three terminal hydrogens (H_t) and three bridging hydrogens (H_b) present on opposite sides of the B_3 plane.[9] The similarity of the structure of $B_3H_6^+$ to the basal skeletons B_4H_8 in B_5H_9,[6a] B_5H_{10} in $B_5H_{10}FeCp$,[7c] and other related compounds suggests that $B_3H_6^+$ should also act as a versatile π ligand with various main group and transition metal fragments. We present here the first theoretical study on a series of pyramidal B_3H_6X compounds with NH^+ (**1**), N (**2**), CH (**3**), BH^- (**4**), P (**5**), PH^+ (**6**), SiH (**7**), NO (**8**), PO (**9**), and $Co(CO)_3$ (**10**) as capping groups (X). This study further reveals that several of these structures have the terminal hydrogens on the same side of the bridging hydrogens, a feature that has not been observed previously in pyramidal boranes![10]





B_3H_6X

1, (X = NH^+)
2, (X = N)
8, (X = NO)

3, (X = CH)
4, (X = BH^-)
5, (X = P)
6, (X = PH^+)
7, (X = SiH)
9, (X = PO)
10, (X = $Co(CO)_3$)

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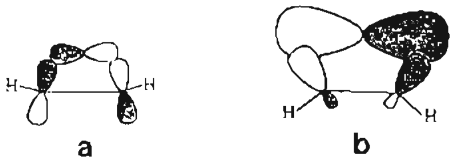
Method of Calculation

Molecules **1**–**9** were optimized within the C_{3v} symmetry restriction at the HF/6-31G* level of theory[11a,b] using the GAUSSIAN 90[11c] program package. **10** was optimized using the LANL1MB basis set,[11d] which uses the STO-3G basis for the first-row elements and the Los Alamos effective core potential + minimal basis set for other main group elements and transition metals. A frequency analysis of the optimized structures **1**–**9** was performed at the same level of theory to ascertain the nature of the stationary point. Except **4**, all the structures were characterized to be minima on their respective potential energy surfaces. **1**–**9** were further optimized at the MP2/6-31G* [11e] level with the frozen-core approximation to estimate the effect of electron correlation.[11f] Table 1 gives the total energies of **1**–**10** along with some of the important geometric parameters obtained at the MP2/6-31G* level.[11g]

Results and Discussion

The bonding in **1**–**10** can be described by classical 2c–2e bonding between the boron atom of the B_3H_6 ring and the cap, X (the bridging hydrogens of the ring form a part of the 3c–2e bonding). However, structures **1**–**10** are also seen to follow the six interstitial electron rule for three-dimensional delocalization in pyramidal compounds.[1d,e] Accordingly, the basal boracyclic ring (B_3H_6) provides three π electrons and the capping group, X, provides three electrons: a total of six electrons sufficient to fill the three bonding combinations that bind the ring and the cap.[1d,e] The concept of the compatibility of orbitals in overlap used to explain the bonding and bending of the terminal hydrogens of the ring in pyramidal molecules toward (negative θ) or away (positive θ) from the cap should be applicable here.[1d] According to this, a cap with a less diffuse p orbital pushes the H_t toward the cap (apex) in order to strengthen the interaction between the cap p_π and ring π orbitals through increased overlap (Chart 1). Similarly, more diffuse cap orbitals should lead to the H_t bending away from the capping group,[1d] as shown in Chart 1.

Chart 1. Out-of-Plane Bending of the Ring Hydrogens for (a) Caps with Less Diffuse Orbitals and (b) Caps with More Diffuse Orbitals



1 and **2** represent the pyramidal structures with NH^+ and N capping the three-membered boracyclic ring. The B–B and B–X distances in **1** are longer than those in **2** (Table 1). The out-of-plane bending (θ) of the ring substituents in **1** is marginally larger than that in **2** (Table 1), because the amplitude of the p_π orbital on the NH^+ cap is only slightly less compared to that of the p_π orbital on the N cap.[12] This is expected because the charge is delocalized over the whole molecule.

Table 1. Total Energies (hartrees), Zero-Point Energies (ZPE; kcal mol^{-1}), and Optimized Geometric Parameters (Distances, Å; Angles, deg) for **1**–**10**

		total energy						
no.	X[a]	HF/6-31G*	MP2/6-31G*	ZPE	B–B	B–X	θ[b]	ϕ[c]
1	NH^+	–132.30679	–132.72349	57.0	1.825	1.497	–2.67	131.89
2	N	–131.94860	–132.37789	46.8	1.772	1.488	–2.61	128.02
3	CH	–115.90546	–116.30626	53.9	1.810	1.534	2.53	127.65
4	BH^-	–102.66943[d]	–103.05383	48.6	1.809	1.644	8.21	124.43
5	P	–418.18717	–418.57952	45.4	1.797	1.916	7.44	129.63
6	PH^+	–418.46835	–418.84375	50.9	1.885	1.875	11.37	134.09
7	SiH	–366.86995	–367.23531	48.9	1.869	1.942	16.41	130.07
8	NO	–206.67386	–207.27426	49.2	1.807	1.491	–3.51	129.23
9	PO	–492.98029	–493.54887	47.1	1.885	1.869	14.57	131.01
10	$Co(CO)_3$	–439.38652[e]			1.815	2.053	14.50	127.87

[a] X is the capping group. [b] θ is the out-of-plane bending of the ring hydrogens. A positive value indicates the ring hydrogens to be bending away from X. [c] Angle between the B_3 ring and the B–H_b–B plane. [d] Corresponds to a second-order stationary point. [e] Optimization using the LANL1MB basis set.[11d]

A CH cap, as in **3**, provides still more diffuse orbitals, so that the H_t is bent farther away from the apex. Consequently, both the H_b and the H_t are on the same side of the B_3 ring (Table 1). While the H_t is often seen to be away from the cap in pyramidal structures based on carbocyclic rings,[1d] to our knowledge this is the first example in the literature to have H_t away from the cap in pyramidal boranes. *nido*-Boranes and -metallaboranes known in literature have the H_t and H_b on opposite sides of the B_n plane (*n*-membered ring) with the H_t always toward the cap.[1b,6,7] The decrease in the size of the ring in going from a B_5 or B_4 to a B_3 base and consequent smaller claw size of the π orbitals involved can be changed by rehybridizing them with the H_t's pushed away from the cap as shown in Chart 1. Efforts to locate another minimum with H_b toward the cap and H_t away from the cap proved to be futile. Among first-row species, BH^- (**4**), as a capping group was also considered. Such a structural arrangement with C_{3v} symmetry was discussed as a possibility for $B_4H_7^-$ by Lipscomb.[13] But at the HF/6-31G* level, this structure corresponds to a higher order stationary point with two imaginary frequencies and hence was not considered further (Table 1).

Structures **5**–**7** with second-row elements having more diffuse orbitals as caps[12] should push the H_t's even further down. As expected, the value of θ (positive) increases as we go from **5** to **7** (Table 1), depending on the diffuse nature of the cap p_π orbitals.[12] Additionally, the larger size of the second-row elements can also be responsible for the large out-of-plane bending of the H_t (Table 1).

The dependence of the B–B and B–X distances in Table 1 on the magnitudes of the B–H_t's out-of-plane bending, θ, is similar to the dependence of the C–C and C–X distances on the out-of-plane bending magnitude reported for pyramidal molecules with carbocyclic rings.[1d] However, the short B–B distance in **5** (Table 1), in comparison to **6** and **7**, may be due to the greater pyramidalizing tendency of P as observed in several phosphines and their derivatives.[14]

An earlier report of the binding of CO to cyclobutadiene,[15] leading to a square pyramidal arrangement, prompted us to explore the interactions of nitrosyl (NO) and phosphoryl (PO) groups with B_3H_6 (**8**, **9**). **8** and **9** were characterized to be minima. The bonding in **8** and **9** involves the degenerate π^* orbitals of NO and PO interacting with the degenerate π orbitals of the B_3H_6 ring, leading to a stabilizing interaction. As a result, the N–O and P–O distances in **8** (1.393 Å) and **9** (1.519 Å) are close to their

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respective single-bond distances.[16] The molecular orbital patterns justify such an electronic structure description.

Following B_4H_8, B_5H_9, and B_5H_{10} as π ligands complexing a transition metal fragment, B_3H_6 also is expected to form pyramidal complexes with transition metal fragments. We calculated B_3H_6-$Co(CO)_3$ (**10**) as a possible candidate and found it to be a stationary point, with the carbonyls and the B_3 unit of the ring in a staggered arrangement. Here also, the H_t of the B_3H_6 ring is found to be away from the capping group (Table 1). This represents the first theoretical indication of a metallaborane with both the terminal and bridging hydrogens on the same side of the ring plane. Other obvious possibilities in this series of metallaboranes are B_3H_6NiCp and $B_3H_6Ni(CO)_3^+$. Methods similar to the ones used in the synthesis of $B_4H_8CoC_p$ may be appropriate even here.[17]

Conclusion

Theoretical calculations indicate for the first time in the literature the possibility of pyramidal heteroboranes with a B_3H_6 base. The terminal hydrogens orientate opposite the capping group in pyramidal heteroboranes and metallaboranes. Electron-counting rules have been applied to explain the structural preferences of these molecules. The concept of the compatibility of orbitals in overlap has been extended to explain the observed trends in the bonding. Attempts to prepare B_3H_6X complexes should be rewarding.

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