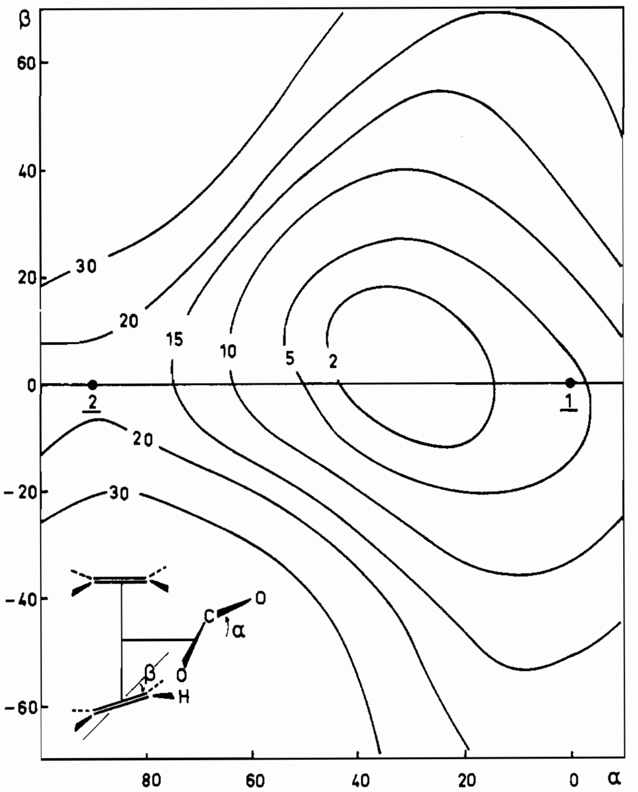

Figure 1. Potential energy surface obtained from extended Hückel calculations as a function of the CO_2 rotation angle α and the C_2H_4 rotation angle β (see the figure for the definition of α and β). $\alpha = 0°$ corresponds to isomer **1**, and $\alpha = 90°$, to isomer **2**. The contour values are in kcal/mol and refer to the energy minimum between **1** and **2** (i.e., $\alpha = 27°$ and $\beta = 0°$).

One finds here a distinctive feature of the rotational isomerism of η^2-coordinated CO_2 ligands, which should be operative in other cis olefin-η^2-CO_2 transition-metal complexes.

To what extent does the rotational isomerism described here influence the coupling of the C_2H_4 and CO_2 ligands? The determination of the corresponding reaction path lies beyond the scope of the present study. We note however that the structure of the acrylic acid derivative, which is the product of this coupling reaction, seems to originate from **1**, the C—O and $-CH{=}CH_2$ acrylic bonds being roughly parallel and the C—O bond being perpendicular to the $CH_2{=}CH_2$ double bond of the nonreacting coordinated ethylene (see the X-ray crystal structure in ref 2). Slight rotations of the CO_2 and/or of the C_2H_4 ligands, which require a few kcal-mol only,[15,22] bring a H atom close to the coordinated oxygen atom of the CO_2 ligand and may be involved at the beginning of the coupling. The corresponding potential energy surface, calculated at the EH level,[23] is repulsive however (see Figure 1). For a 60° rotation of CO_2 and a 40° rotation of C_2H_4 (this corresponds to an O-H distance of 1.92 Å, (i.e. still far from the equilibrium distance, which is close to 0.95 Å in acrylic acid), the destabilization with respect to the energy minimum amounts to 33 kcal/mol. This destabilization is the result of (i) the departure from the most stable arrangement of the two ethylene and the carbon dioxide ligands and (ii) four-electron repulsive interactions between the H s orbitals and both the out-of-plane $n\pi$ orbital of CO_2 and the σ framework orbitals of CO_2. The in-plane $\pi^*_{CO_2}$ orbital, which should accommodate the incoming hydrogen in this process, does not show any noticeable interaction with s_H. The O-H overlap population is negative (-0.02), hence underlying the nonbonding character of the interaction between the oxygen of CO_2 and the hydrogen of C_2H_4. We therefore do not favor a direct intramolecular hydrogen addition to the coordinated oxygen atom of the CO_2 ligand. Another alternative, which would account for the dinuclear nature of the product, is an intermolecular process: It involves the coupling of an ethylene bound to one molybdenum center with the CO_2 bound to a second molybdenum center and vice versa. In this case the attacked C-O bond is the noncoordinated one and the geometries of the two interacting molecules correspond to **1** and **3**. A final possibility[24] that would be more consistent with the hydrido acrylate formulation of the product (instead of the acrylic acid formulation[25]) might involve an intramolecular C-H oxidative addition followed by CO_2 insertion into the M-C bond of the resulting vinyl hydride intermediate. Clearly, the assessment of the coupling mechanism requires more work, which is now in progress.

Acknowledgment. Calculations were carried out on the IBM 3081 of the Centre de Calcul du CNRS in Strasbourg-Cronenbourg. V.B. is grateful to the CIRIT for financial support. We thank professor E. Carmona for his interest in this work.

Registry No. *trans,mer*-$Mo(C_2H_4)_2(CO_2)(PH_3)_3$, 110718-69-9.

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(21) The experimentally known cyanamide ion CN_2^{2-} is isostructural and isoelectronic with CO_2.

(22) Previous SCF calculations carried out on the $Mo(PH_3)_4(C_2H_4)_2$ system[17] have indicated that the barrier to overcome to go from the mutual staggered disposition of the two ethylene ligands to the mutual eclipsed disposition is of the order of 16 kcal/mol, the energy difference between the two limit conformations amounting to 13.9 kcal/mol. In the present case, extended Hückel calculations indicate a continuous increase in energy, up to 14 kcal/mol for the mutual eclipsed disposition of the two ethylene ligands.

(23) EH calculations were found to reproduce reasonably well the SCF calculations, the corresponding relative stabilities of **1**, **2**, and **4** being 0, 13.3, and 41.9 kcal/mol at the EH level. The most stable conformation at this level corresponds to CO_2 rotated by 27° from **1**, the corresponding stabilization amounting to 1.7 kcal/mol.

(24) This possibility was suggested to us by Prof. E. Carmona.

(25) See ref 10 of ref 2.

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Formation and Structure of the Bis(trimethylphosphine)nonahydrohexaboron(1+) Cation

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Received May 19, 1987

Earlier, we reported a series of polyboron complex cations with the formula $B_nH_{n+3}{\cdot}2P(CH_3)_3^+$, where n = 3, 4, and 5.[1-3] These cations are isostructural with their respective isoelectronic neutral and anionic species as illustrated in Figure 1. The next higher cation of series is $B_6H_9{\cdot}2P(CH_3)_3^+$, and its corresponding isoelectronic species are $B_6H_{10}{\cdot}P(CH_3)_3$ and $B_6H_{11}^-$, which are known to have the boron cluster geometry indicated in Figure 2a.[4,5] Abstraction of a hydride ion from $B_4H_8{\cdot}2P(CH_3)_3$ and $B_5H_9{\cdot}2P(CH_3)_3$ were the methods for preparing the above tetraboron and pentaboron complex cations, and the structures of these cations could readily be related with those of the parent bis(phosphine) adducts.[2,3]

The hexaboron cation would be obtainable likewise by abstracting a hydride ion from $B_6H_{10}{\cdot}2P(CH_3)_3$.

$$B_6H_{10}{\cdot}2P(CH_3)_3 + C(C_6H_5)_3^+ \rightarrow B_6H_9{\cdot}2P(CH_3)_3^+ + HC(C_6H_5)_3$$

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(1) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

(2) Kameda, M.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2712.

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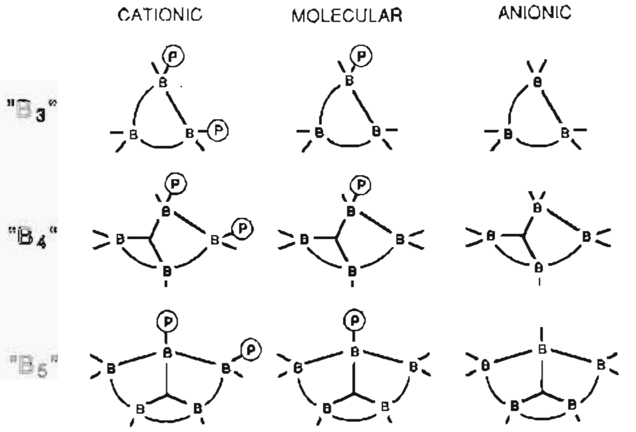

Figure 1. Structures of $B_nH_{n+3}\cdot 2P(CH_3)_3^+$, $B_nH_{n+4}\cdot P(CH_3)_3$, and $B_nH_{n+5}^-$ for n = 3, 4, and 5. Hydrogen atoms are not drawn in for brevity. The circled P represents $P(CH_3)_3$.

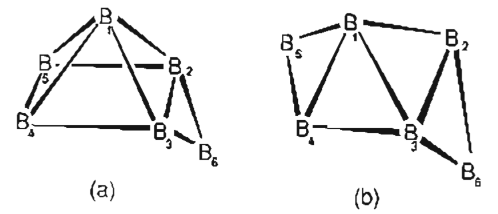

Figure 2. Boron cluster geometry (a) in $B_6H_{10}\cdot P(CH_3)_3$ and $B_6H_{11}^-$ and (b) $B_6H_{10}\cdot 2P(CH_3)_3$.

Table I. NMR Data for the $B_6H_9\cdot 2P(CH_3)_3^+$ Cation[a]

^{11}B	^1H	^{31}P
−52.0, d, B(1), J_{BP} = 214	−2.68, H(μ′)	−5.7, P(1), J_{PB} = 214
−45.0, q, B(6), J_{BP} = 94, J_{BH} = 93	−1.05, H(μ)	−2.3, P(6), $J_{PB} \approx 100$
	1.45, H(CH_3(1)), $^2J_{HP}$ = 9	
−20.3, d, B(3,4), J_{BH} = 150		
	1.64, H(CH_3(6)), $^2J_{HP}$ = 9	
−8.9, d, B(2,5), J_{BH} = 150		
	2.40, H(3,4)	
	2.94, H(2,5)	

[a] Shifts in ppm; *J* values in Hz. References for the shifts: ^{11}B, $BF_3\cdot O(C_2H_5)_2$; ^{31}P, 85% orthophosphoric acid; ^1H, $\delta(CH_2Cl_2)$ = 5.28 ppm. Key: d, doublet; q, quartet. Solvents: CH_2Cl_2 for ^{11}B; CD_2Cl_2 for ^{31}P and ^1H. Temperature: −10 °C.

However, the structure of the bis(phosphine) adduct is belt-shaped as shown in Figure 2b[6] and is quite different from that in Figure 2a. It was, therefore, of interest to prepare the $B_6H_9\cdot 2P(CH_3)_3^+$ cation and to investigate its structure. The results of the study are described in this paper.

Results

The bis(trimethylphosphine) adduct of B_6H_{10} reacted slowly with the trityl cation (BF_4^- or PF_6^- salt) in a 1:1 molar ratio in dichloromethane at −80 °C, and the hexaboron complex cation $B_6H_9\cdot 2P(CH_3)_3^+$ was formed. The BF_4^- salt of the cation slowly decomposed in the solution at room temperature. The PF_6^- salt was less stable, and underwent a rapid decomposition at 0 °C with concomitant formation of BF_4^-. Furthermore, the cation thus produced appeared to slowly undergo certain reactions with the starting compound, producing small amounts of side products. However, the cation could be characterized by NMR spectroscopy, and was found to have a structure similar to that of $B_6H_{10}\cdot P(CH_3)_3$ or $B_6H_{11}^-$, the phosphines being attached at the apex and bridge boron atoms. See part B of the Discussion.

Discussion

A. Ease of Hydride Abstraction. The above hydride abstraction reaction of $B_6H_{10}\cdot 2P(CH_3)_3$ was slow when compared with those of $B_5H_9\cdot 2P(CH_3)_3$ and $B_4H_8\cdot 2P(CH_3)_3$, which were instantaneous at −80 °C.[2,3] The increased acidity, or the diminished hydridic character of borane hydrogens, of the larger borane fragment[7] is thought to be responsible for the slower reaction rate. A similar reactivity variation has been observed for the series of pentaborane compounds B_5H_9, $B_5H_9\cdot P(CH_3)_3$ and $B_5H_9\cdot 2P(CH_3)_3$.[3]

B. Structure of $B_6H_9\cdot 2P(CH_3)_3^+$. The ^{11}B, ^1H, and ^{31}P NMR data for the $B_6H_9\cdot 2P(CH_3)_3^+$ cation are summarized in Table I. As illustrated in Figure 3, the ^{11}B spectrum of the cation resembles that of $B_6H_{10}\cdot P(CH_3)_3$,[4] the noticeable differences being that the most shielded signal for the cation is a B–P doublet whereas the corresponding one for $B_6H_{10}\cdot P(CH_3)_3$ is a B–H doublet and that each signal of the cation, with the exception of the −45.0 ppm quartet signal (due to the bridging boron, to which the other $P(CH_3)_3$ is attached), is shifted downfield from the corresponding signal of $B_6H_{10}\cdot P(CH_3)_3$. The extremely large B–P coupling constant of 212 Hz for the most shielded signal of the hexaboron cation is comparable with the value of 220 Hz that was observed for the apex B–P coupling constant of the square-pyramid-shaped $B_5H_8\cdot P(CH_3)_3^+$ cation.[3] Compared with the chemical shift of basal boron atoms of B_5H_9, the corresponding signal of this pentaboron cation is shifted downfield also. Thus, replacement of H^- by $P(CH_3)_3$ at the apex position of $B_6H_{10}\cdot P(CH_3)_3$ results in the structure of $B_6H_9\cdot 2P(CH_3)_3^+$, which is consistent with the ^{11}B NMR data observed for the hexaboron cation. The assignments for the ^1H resonance signals listed in Table I were straightforward with the use of single-frequency decoupling techniques on the ^{11}B spins. The signals of hydrogens on the bridge boron atom could not be located. Probably, the signal is overlapped with the closely spaced, intense two signals of methyl hydrogens.

C. Structure Transformation. The isoelectronic–isostructural feature that was observed for the tri-, tetra- and pentaboron trios[1,2,3] has now been extended to the trio of arachno hexaboron species, $B_6H_9\cdot 2P(CH_3)_3^+$, $B_6H_{10}\cdot P(CH_3)_3$, and $B_6H_{11}^-$. Addition of a Lewis base, $P(CH_3)_3$, to $B_6H_{10}\cdot P(CH_3)_3$ results in a hypho-class hexaborane compound, $B_6H_{10}\cdot 2P(CH_3)_3$.[4] Through this process the structure changes from the basal-bridged square pyramid to the belt-shaped arrangement of six boron atoms. Conversely, removal of a Lewis base, H^-, from $B_6H_{10}\cdot 2P(CH_3)_3$ reverts the structure to the basal-bridged square pyramid of *arachno*-$B_6H_9\cdot 2P(CH_3)_3^+$. This transformation scheme is illustrated in Scheme I. At present, nothing definitive can be stated about the mechanism of transformation. The B–P bonds, because of their considerable strength, would remain undissociated throughout the process of the transformation. Providing that this assumption is correct, the observed final structure may be attained through certain framework isomerizations such as that involving the diamond–square–diamond (dsd)[8] rearrangements.

Two different boron framework structures are known to be assumed by arachno hexaborane compounds. One is the basal-bridged square pyramid, which is dealt with in this study. The other is the belt-shaped structure of B_6H_{12},[9] which is similar to that of $B_6H_{10}\cdot 2P(CH_3)_3$. As the "skeletal electron counting" formalism dictates,[10] both of these structures can be derived from the eight-vertex deltahedron (bisdisphenoid) by removing two vertices.[11] An apparent difference between the two sets of the

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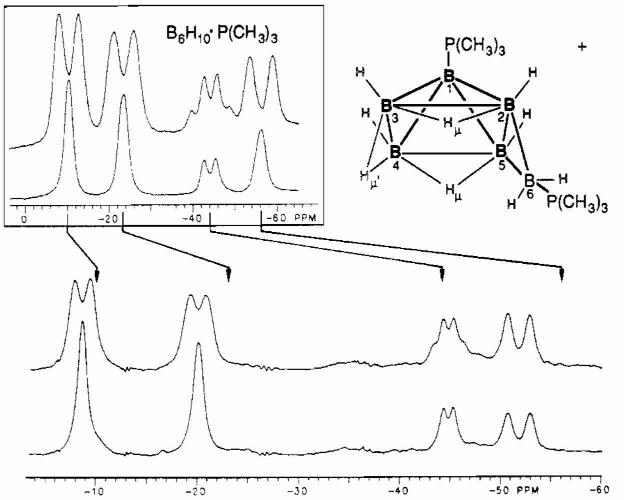


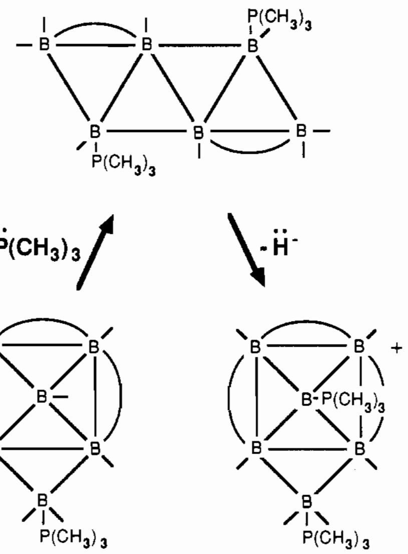
Figure 3. Structure and ^{11}B NMR spectra (96.2 MHz) of $B_6H_9\cdot 2P(CH_3)_3{}^+$. Spectra (32.1 MHz) of $B_6H_{10}\cdot P(CH_3)_3$ are shown in the box for comparison: top, normal spectrum; bottom, proton spin decoupled spectrum.

arachno compounds is in the number of ligands that are associated with six-boron clusters—11 versus 12. Obviously, however, further studies need to be pursued to elucidate the factors that determines the structure of an arachno hexaborane compound.

Experimental Section

General consideration and procedures for the experiments were the same as those described in the previous reports.[2,3] The NMR data were obtained on a Varian XL-300 NMR spectrometer. Samples of $B_6H_{10}\cdot 2P(CH_3)_3$, which had been obtained as the byproduct of $B_2H_4\cdot 2P(CH_3)_3$ (or $CH_3B_2H_3\cdot 2P(CH_3)_3$) preparation by the reaction of B_5H_9 (or $CH_3B_5H_8$) with excess $P(CH_3)_3$,[12] were washed with diethyl ether to remove remaining $B_2H_4\cdot 2P(CH_3)_3$ (or $CH_3B_2H_3\cdot 2P(CH_3)_3$) and then extracted with dichloromethane. The $B_6H_{10}\cdot 2P(CH_3)_3$ sample thus obtained was a free-flowing crystalline solid, and its ^{11}B NMR spectrum indicated that the sample was essentially pure, traces of impurities being $B_2H_4\cdot 2P(CH_3)_3$ and unidentified boron compounds. The hydride abstraction reactions were run in 10 mm o.d. Pyrex tubes and were monitored with use of the NMR instrument.

Scheme I



Reaction of $B_6H_{10}\cdot 2P(CH_3)_3$ with Trityl Salts. A 0.43-mmol sample of $B_6H_{10}\cdot 2P(CH_3)_3$ was mixed with 0.37 mmol of $C(C_6H_5)_3{}^+PF_6{}^-$ in 1.5 mL of dichloromethane at −80 °C. The intense dark yellow color of the solution was seen to slowly fade. When $B_6H_{10}\cdot 2P(CH_3)_3$ was treated similarly with $C(C_6H_5)_3{}^+BF_4{}^-$ in a 1:2, 1:1, or 2:1 molar ratio, the same slow change occurred also. To ensure the completion of reaction, these solutions were either kept at −80 °C for a period of over 50 h or briefly warmed to 0 °C. (The system containing the PF_6^- ion slowly produced BF_4^- ion when warmed to −45 °C.) The 2:1 reaction mixture gave the final solution containing the original $B_6H_{10}\cdot 2P(CH_3)_3$ and the $B_6H_9\cdot 2P(CH_3)_3{}^+$ cation in an approximately 1:1 molar ratio.

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Registry No. $B_6H_{10}\cdot 2P(CH_3)_3$, 57034-29-4; $C(C_6H_5)_3{}^+BF_4{}^-$, 341-02-6; $C(C_6H_5)_3{}^+\cdot PF_6{}^-$, 437-17-2; $B_6H_9\cdot 2P(CH_3)_3{}^+BF_4{}^-$, 110795-78-3; $B_6H_9\cdot 2P(CH_3)_3{}^+PF_6{}^-$, 110795-79-4.

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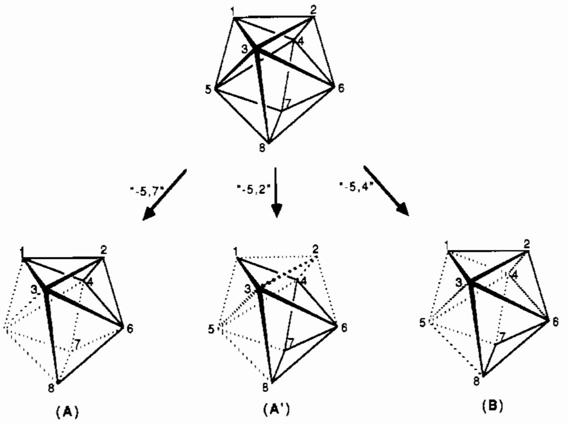
(11) Examples of the vertex removal to achieve structures a and b are illustrated below. Removal of vertices 5 and then 7 (indicated as "−5,7")



results in structure A, which does not have the C_s symmetry as it is. The resulting framework (A) needs to slightly adjust itself to achieve the structure shown in Figure 2a. Route "−5,2" leads to structure A′, which is of C_s symmetry. Choice of the two routes is arbitrary. In the $B_6H_{11}^-$ ion, the bridging BH_3 group is bonded to the two basal boron atoms via a B–B bond and a B–H–B bond.[5] In this sense, structure A′ may be appropriate for the anion. Whereas, in $B_6H_9\cdot 2P(CH_3)_3{}^+$ and $B_6H_{10}\cdot P(CH_3)_3$, the two basal boron atoms are bonded by a bridging $BH_2\cdot P(CH_3)_3$ group via a closed BBB three-center bond. Structure A, therefore, may fit better to the description of these two species.

(12) (a) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288. (b) The reaction of $CH_3B_5H_8$ with $P(CH_3)_3$: Kameda, M.; Driscoll, J. A.; Kodama, G., unpublished results.