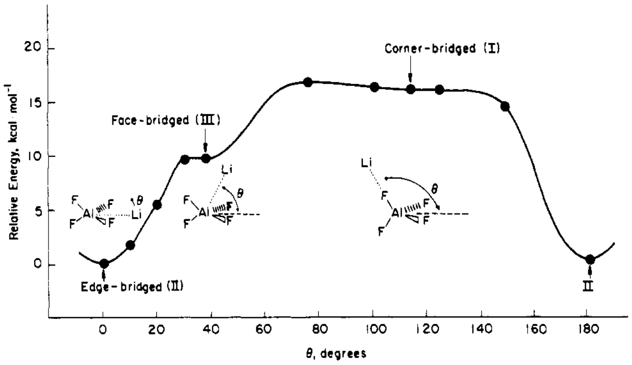

Figure 1. Relative energies for the migration of Li in $LiAlF_4$. Solid circles represent calculated points. Structures I–III were optimized in ref 3. For points between II and III all geometrical parameters were optimized. For points between III and I and between I and II only geometry parameters involving the bridge were optimized. (Energies of other points besides those indicated in the figure were calculated with no geometry optimization to help draw the curve.)

F[7] and Li.[8] Huzinaga's (11s7p) primitive set contracted to (5s4p) according to Dunning and Hay[9] was used on Al, and a (12s10p) primitive set contracted to [4s2p] according to Gole et al.[10] was used on Mg. These basis sets are the same as the ones used in the previous[2,3] geometry optimizations of the corner-, edge-, and face-bridged structures (hereafter referred to as I, II, and III, respectively) of $LiAlF_4$ and $MgAlF_5$.

Results and Discussion

The barriers to lithium migration between the three types of bridges (one, two, and three fluorines) in $LiAlF_4$ were determined by rotating the lithium about aluminum in a plane containing two of the fluorines and bisecting the other two fluorines. As the lithium rotated, the Li–Al distance and the geometry of the AlF_4 fragment were allowed to relax. Rotation of lithium in this manner forms all three structures (I–III) as θ goes from 0 to 180°. This is illustrated in Figure 1. The portion of the potential energy surface investigated here should be representative of the migration path for Li in $LiAlF_4$.

The potential energy curve in Figure 1 shows the relative energies of the calculated $LiAlF_4$ structures for $0° \leq \theta \leq 180°$. The barrier to migration of lithium for III → II is ca. 0.2 kcal mol^{-1}, the barrier for I → III is ca. 1 kcal mol^{-1}, and there is no barrier for I → II. These barrier values are likely to be upper limits since inclusion of correlation energy tends to decrease barriers.

The small or nonexistent potential wells for the corner- and face-bridged structures in the potential energy surfaces of $LiAlF_4$ means that they are not likely to be metastable enough to be observed. The shallowness of the potential energy curve close to $\theta = 0°$ indicates that the edge-bridged structure may be easily distorted from its C_{2v} structure such that there will be a broad angular distribution of configurations. Consequently, one expects that in measurements such as electron diffraction that average over all configurations the bridge in structure II would be observed as nonplanar. The height of the potential energy curve away from the equilibrium structure (9–16 kcal mol^{-1}) indicates that the cation is not likely to migrate easily very far (e.g., >20°) over the AlF_4^- anion at temperatures up to 2000 K. It should be noted that the height of the potential energy curve could decrease with a more sophisticated calculation (i.e., a bigger basis set or inclusion of correlation energy). Also, in some $MAlX_n$ systems the face- and corner-bridged structures may be closer in energy to the edge-bridged structure (e.g., <5 kcal mol^{-1}). Hence, migration over part or all of the anion would be easier in these cases.

More limited calculations were carried out in the investigation of the $MgAlF_5$ potential energy surface. The MgF fragment was rotated about AlF_4 in the same way as Li was rotated about AlF_4 in $LiAlF_4$. However, the geometries of $MgAlF_5$ for points between structures I, II, and III (relative energies 23.3, 0, and 5.3 kcal mol^{-1}, respectively[4]) were estimated on the basis of the $LiAlF_4$ study and were not optimized. For the transition III → II the barrier was ca. 3 kcal mol^{-1}. This is somewhat higher than the barrier for the same transition in $LiAlF_4$. However, geometry optimization would probably reduce this barrier[11] by 1–2 kcal mol^{-1}. For the transition I → II there is no barrier as in the case of $LiAlF_4$. Hence, by reasoning similar to that used for $LiAlF_4$, we conclude that neither the face- or corner-bridged structure of $MgAlF_5$ is likely to be metastable enough to be observed. However, since the face-bridged structure is only 5 kcal mol^{-1} above the equilibrium structure, it is possible that the cation may be free to migrate over this portion of the potential energy surface.

Conclusions

This study of the energetics for cation migration in $LiAlF_4$ and $MgAlF_5$ indicates that no metastable states for the face- or corner-bridged structures are likely to exist because of the small or nonexistent potential energy wells. The potential energy curve in the region of the equilibrium structure (edge bridged) is shallow, allowing for easy distortion of the planar bridge. Migration of the cation over the entire anion is not likely because of the height of the potential energy curve in regions away from the equilibrium structure.

Registry No. $LiAlF_4$, 15138-76-8; $MgAlF_5$, 23630-60-6; Li^+, 17341-24-1; MgF^+, 21308-25-8.

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(11) In the case of $LiAlF_4$ optimization of the estimated geometry reduced the energy by up to 2 kcal mol^{-1} for points between II and III.

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The Crown Ether Promoted Base Degradation of *p*-Carborane

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Received April 21, 1982

In 1964 Wiesboeck and Hawthorne[1] discovered that degradation of the closo icosahedral carborane $1,2\text{-}C_2B_{10}H_{12}$ by ethanolic KOH produces a novel nido carborane anion, $[7,8\text{-}C_2B_9H_{12}]^-$, whose structure is that of an icosahedron with one vertex removed (Figure 1). Similar treatment of $1,7\text{-}C_2B_{10}H_{12}$ leads more slowly to the isomeric $[7,9\text{-}C_2B_9H_{12}]^-$. In both cases, the boron atom removed is one that is adjacent to both electronegative carbon atoms, which makes the boron more susceptible to nucleophilic attack. Strong base removes the bridging proton from the open face of $[7,8\text{-}C_2B_9H_{12}]^-$ and $[7,9\text{-}C_2B_9H_{12}]^-$ to give nido dianions that can bond to metals in an η^5 fashion.[2] This discovery led to the development of the field of metallacarborane chemistry.

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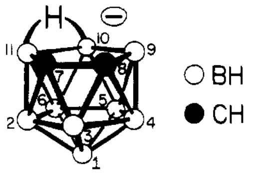

Figure 1. Structure of the nido carborane anion, $[7,8\text{-}C_2B_9H_{12}]^-$.

Attempts to degrade the third icosahedral isomer, $1,12\text{-}C_2B_{10}H_{12}$, using ethanolic KOH failed, presumably because no boron atom is adjacent to both carbons. Under more forcing conditions (20% KOH in propanediol, 170 °C), Plesek and Hermanek[3] were able to obtain 15% yield of $2,9\text{-}C_2B_9H_{13}$, the protonated form of $[2,9\text{-}C_2B_9H_{12}]^-$. Considering the difficulty with which the starting material, $1,12\text{-}C_2B_{10}H_{12}$, is prepared,[4] such low-yield conversions make development of the metallacarborane chemistry of the $[2,9\text{-}C_2B_9H_{11}]^{2-}$ ligand impractical; however, metallacarboranes derived from $[2,9\text{-}C_2B_9H_{11}]^{2-}$ are of particular interest because only one carbon is adjacent to the metal in contrast to $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[7,9\text{-}C_2B_9H_{11}]^{2-}$ derivatives.

We report here the use of a crown ether to promote a rapid, high-yield degradation of $1,12\text{-}C_2B_{10}H_{12}$ by KOH to give [K(18-crown-6)][*nido*-$2,9\text{-}C_2B_9H_{12}$] and the preparation of metallacarboranes derived from it.

Experimental Section

Materials. All solvents were reagent grade and were used without further purification. Triethylamine (MCB) was used as received, and dicyclopentadiene (MCB) was cracked to the monomer immediately prior to use. Potassium hydroxide (85%) (Mallinckrodt) was powdered under nitrogen and stored in a desiccator. $CoCl_2\cdot 6H_2O$ (Mallinckrodt) and 18-crown-6 ether (Aldrich) were used as received and $RhCl(PPh_3)_3$ was prepared from $RhCl_3\cdot 3H_2O$ (Johnson-Matthey) by a literature procedure.[5] Thermal isomerization of $1,2\text{-}C_2B_{10}H_{12}$ was used to prepare $1,12\text{-}C_2B_{10}H_{12}$.[4]

Instrumentation. Infrared spectra were recorded on Perkin-Elmer 137 spectrometer as KBr pellets or Nujol mulls. ^1H and ^{31}P NMR spectra were obtained on a Bruker WP-200 FT NMR spectrometer at 200.1 and 81.0 MHz, respectively. The ^{11}B NMR spectra were obtained at 126.8 MHz on an FT NMR instrument designed and constructed by Professor F. A. L. Anet of this department. ^{11}B chemical shifts are referenced to external $BF_3\cdot OEt_2$. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

[K(18-crown-6)][*nido*-2,9-$C_2B_9H_{12}$]. A 100-mL Schlenk flask containing an egg-shaped magnetic stirring bar was charged with 0.52 g (3.6 mmol) of $1,12\text{-}C_2B_{10}H_{12}$, 2.12 g (32.1 mmol) of powdered KOH, 4.02 g (15.2 mmol) of 18-crown-6 ether, and 60 mL of freshly distilled benzene. Contact time with air was minimized since both KOH and 18-crown-6 are very hydroscopic. The flask was fitted with a condenser, flushed with argon, and placed in a 100 °C oil bath. The solution/suspension was magnetically stirred under positive pressure of argon for 42 h and then allowed to cool. Ethanol (5 mL) was added through the condenser and the solution stirred for 15 min. The suspension was filtered through a medium frit and the white solid washed with 10 mL of 95% ethanol, 100 mL of distilled water, and 10 mL of 95% ethanol. The remaining white solid was dissolved in 200 mL of acetone, the solution filtered and mixed with 100 mL of water, and the volume slowly reduced on a Buchi Rotavapor. The white crystalline product was filtered off, washed with water and a small amount of ethanol, and dried briefly on the frit; yield 1.49 g (95%). Anal. Calcd for $C_{14}H_{36}B_9KO_6$: C, 38.49; H, 8.13; B, 22.27; K, 8.95. Found: C, 38.34; H, 8.29; B, 22.40; K, 9.10. IR (cm^{-1}, Nujol): ν_{B-H} 2520 s, ν_{C-O} 1115 s. ^{11}B NMR (δ, acetone): −13.10 (d, $J_{^1H-^{11}B}$ = 140 Hz, 2 B), −19.23 (d, $J_{^1H-^{11}B}$ = 148 Hz, 2 B), −21.58 (d, $J_{^1H-^{11}B}$ = 148 Hz, 2 B), −28.54 (d, $J_{^1H-^{11}B}$ = 139 Hz, 2 B), −42.94 (d, $J_{^1H-^{11}B}$ = 156 Hz, 1 B). ^1H NMR (δ, acetone-d_6): 3.67 (s, 24 H), 2.81 (s, 1 H).

[NEt_3H][*nido*-2,9-$C_2B_9H_{12}$]. A mixture of 30 mL of concentrated H_2SO_4, 40 mL of distilled H_2O, and 80 mL of heptane was placed in a 250-mL Ehrlenmeyer flask equipped with a rubber septum. The mixture was cooled in an ice bath and deoxygenated with argon. [K(18-crown-6)][*nido*-$2,9\text{-}C_2B_9H_{12}$], 0.91 g (2.08 mmol), was added to the flask and the system flushed briefly with argon. Vigorous shaking led to the dissolution of the white solid. The heptane layer was decanted and the acid layer shaken with 2 × 50 mL of heptane. The combined heptane portions were treated with 3 mL of NEt_3, resulting in immediate precipitation of a white flocculent solid, which was filtered off, washed with heptane, and dried in vacuo overnight; yield 0.47 g (96%). *Caution*! The intermediate in this reaction is volatile and bad-smelling and should be handled only in a hood. IR (cm^{-1}, Nujol): ν_{N-H} 3060 s, ν_{B-H} 2520 vs. ^{11}B NMR (δ, acetone): −13.23 (d, $J_{^1H-^{11}B}$ = 115 Hz, 2 B), −19.19 (d, $J_{^1H-^{11}B}$ = 148 Hz, 2 B), −21.56 (d, $J_{^1H-^{11}B}$ = 145 Hz, 2 B), −28.57 (d, $J_{^1H-^{11}B}$ = 126 Hz, 2 B), −42.88 (d, $J'_{^1H-^{11}B}$ = 151 Hz, 1 B).

[*closo*-2-(η^5-C_5H_5)-2,1,12-$CoC_2B_9H_{11}$]. With use of a procedure outlined for similar compounds by Plesek et al.[6] [K(18-crown-6)][*nido*-$2,9\text{-}C_2B_9H_{12}$], 1.72 g (3.94 mmol), KOH, 2.45 g (43.66 mmol), and 10 mL of methanol were placed in a 100-mL round-bottomed flask and swirled in an ice bath until dissolution of the KOH was complete. An additional 7 mL of methanol, 0.8 mL of freshly cracked cyclopentadiene (9.71 mmol), and 1.50 g (6.31 mmol) of $CoCl_2\cdot 6H_2O$ were added. The flask was fitted with a condenser, put through two freeze–pump–thaw cycles, and heated to reflux with stirring under a positive pressure of nitrogen for 6 h. After cooling, 50 mL of H_2O was added and the suspension filtered. The yellow-brown solid was washed with 100 mL of H_2O, 50 mL of 10% HCl, and 50 mL of H_2O and dried on the frit. Treatment with 50 mL of benzene and filtration gave a yellow filtrate, which was evaporated to dryness; the solid was redissolved in methylene chloride and eluted down a silica gel column with 1/1 methylene chloride/hexane. The eluate was evaporated to dryness to give the yellow product; yield 0.22 g (21%). IR (cm^{-1}, Nujol): ν_{B-H} 2530 s. ^{11}B NMR (δ, CH_2Cl_2): −2.71 (d, $J_{^1H-^{11}B}$ = 215 Hz, 1 B), −4.42 (d, $J_{^1H-^{11}B}$ = 164 Hz, 2 B), −6.45 (d, $J_{^1H-^{11}B}$ = 153 Hz, 2 B), −15.55 (d, $J_{^1H-^{11}B}$ = 158 Hz, 2 B), −18.84 (d, $J_{^1H-^{11}B}$ = 161 Hz, 2 B).

[*closo*-2,2-(PPh_3)$_2$-2-H-2,1,12-$RhC_2B_9H_{11}$]. Both $RhCl(PPh_3)_3$, 3.42 g (3.69 mmol), and [K(18-crown-6)][*nido*-$2,9\text{-}C_2B_9H_{12}$], 1.70 g (3.89 mmol), were placed in a 250-mL Schlenk flask containing a magnetic stirring bar. The flask was fitted with a condenser and the system flushed with nitrogen for 15 min. Deoxygenated ethanol (100 mL) was syringed in and the suspension heated to reflux with stirring for 1 h, over which time the color of the solid changed to yellow. The flask was allowed to cool, the contents were filtered, and the yellow solid was washed with ethanol (25 mL) and heptane (25 mL) and then redissolved in methylene chloride. This solution was passed down a short silica gel column and collected in a nitrogen-flushed 500-mL Schlenk flask. The volume was reduced in vacuo to 200 mL, 100 mL of heptane was added, and volume was reduced in vacuo, to 75 mL. The resulting yellow crystalline solid was filtered off, washed with heptane and diethyl ether, and dried in vacuo; yield 2.72 g (96%). Anal. Calcd for $C_{38}H_{42}B_9P_2Rh$: C, 59.98; H, 5.56; B, 12.79; P, 8.14; Rh, 13.52. Found: C, 61.37; H, 5.36; B, 12.65; P, 8.15; Rh, 12.99. IR (cm^{-1}, KBr): ν_{C-H} 3000 w, ν_{B-H} 2530 s, ν_{Rh-H} 2060 w. ^1H NMR (δ, CD_2Cl_2): −8.74 (d of *t*, $J_{^{103}Rh-^1H}$ = 15 Hz, $^2J_{^{31}P-^1H}$ = 27 Hz). ^{31}P NMR (δ, 10% C_6D_6/THF): 34.8 (d, $J_{^{103}Rh-^{31}P}$ = 112 Hz).

Results and Discussion

Crown ethers have long been known to enhance the nucleophilicity of anions when they are used to solubilize salts in aprotic media. For instance, Pedersen and Frensdorff used dicyclohexyl-18-crown-6 to solubilize KOH and NaOH in benzene. The resulting solutions functioned as effective saponifying agents for substrates normally resistant to saponification. They ascribed this result to an increased dissociation

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of ion pairs providing highly reactive unsolvated anions.[7]

We have applied this method with excellent results to the basic degradation of 1,12-$C_2B_{10}H_{12}$, which has previously proved to be very resistant to the standard techniques employed for the basic degradation of 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$. Yields of the desired [*nido*-2,9-$C_2B_9H_{12}$]$^-$ of >95% were achieved in relatively short reaction times by using KOH solubilized in benzene with 18-crown-6. The exact mechanism by which the removal of the boron vertex takes place is not known at this time, but the stoichiometry we have observed clearly indicates that 4 equiv of 18-crown-6/mol of 1,12-$C_2B_{10}H_{12}$ is required. The aprotic nature of the reaction medium is also important. The addition of only 10% ethanol to the normal benzene solvent reduces the yield to only 20% of that observed in pure benzene.

The product is isolated as a [K(18-crown-6)] salt, which is very mildly air sensitive in solution and the solid state. It is moderately soluble in acetone and acetonitrile and somewhat soluble in methylene chloride, benzene, ethanol, and tetrahydrofuran. The cation may be exchanged by a two-phase acidification procedure in which the [K(18-crown-6)] cation extracts into the water layer and the carborane intermediate, presumably 2,9-$C_2B_9H_{13}$ reported by Plesek and Hermanek,[3] extracts into the hydrocarbon layer. Treatment with trialkylamines gives trialkylammonium salts, [NR_3H][*nido*-2,9-$C_2B_9H_{12}$], in essentially quantitative yields. The cesium salt, Cs[*nido*-2,9-$C_2B_9H_{12}$], has also been prepared in crystalline form by neutralizing the intermediate with aqueous CsOH. The method is general with different purification methods depending upon the salt.

On the basis of analytical, chemical, and spectral properties, especially the symmetry indicated by the ^{11}B NMR spectrum, the anion almost certainly has a structure analogous to that depicted in Figure 1: an 11-membered icosahedral fragment with the carbons in the 2- and 9-positions. This is the only thermally stable [*nido*-$C_2B_9H_{12}$]$^-$ species known in which only one of the two carbons is in the open face. Stanko et al. have reported the preparation of [*nido*-11-R-2,7-$C_2B_9H_{11}$]$^-$ by the low-temperature alkylation of [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ with alkyl halides[8] and have confirmed the structure by X-ray crystallography;[9] however, [*nido*-11-R-2,7-$C_2B_9H_{11}$]$^-$ is reported to rearrange rapidly at room temperature to give [*nido*-8-R-7,9-$C_2B_9H_{11}$]$^-$.

The impetus behind the preparation of [*nido*-2,9-$C_2B_9H_{12}$]$^-$ was the desire to investigate icosahedral metallacarboranes of the form $L_nMC_2B_9H_{11}$ in which only one carbon atom would be adjacent to the metal vertex. Two representative complexes have been synthesized by using established methods. The reaction of cobaltous chloride and cyclopentadiene with [*nido*-2,9-$C_2B_9H_{12}$]$^-$ in the presence of KOH led to the preparation of a yellow compound, which was spectroscopically identical with the material previously isolated in small quantities from the thermal isomerization of [*closo*-3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$] and identified as the compound [*closo*-2-(η^5-C_5H_5)-2,1,12-$CoC_2B_9H_{11}$] on the basis of ^{11}B NMR and physical properties.[10]

Of more interest is a new rhodacarborane [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (I), which was synthesized from [K(18-crown-6)][*nido*-2,9-$C_2B_9H_{12}$] and $RhCl(PPh_3)_3$ by using the method of Paxson and Hawthorne.[11] Details of its spectral and physical properties along with those of its isomeric analogues, [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (II) and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (III), which have previously been reported,[11] will be discussed elsewhere. I is only mildly air sensitive in the solid state and in solution, decomposing over a period of time to a blue material presumably similar to the rhodacarborane dimer recently reported by Hawthorne et al.[12] Like II and III, I is a catalyst for the hydrogenation and isomerization of olefins. Its catalytic behavior is similar in some ways to the other two isomers, but I gives faster rates for hydrogenation, in general, and is notably more stable than II and III under catalytic conditions.

Acknowledgment. We wish to thank Professor F. A. L. Anet for assistance in obtaining the ^{11}B NMR spectra and Mr. Paul E. Behnken for helpful discussions. This work was supported in part by the Office of Naval Research.

Registry No. I, 82848-97-3; [K(18-crown-6)][*nido*-2,9-$C_2B_9H_{12}$], 82918-08-9; [NEt_3H][*nido*-2,9-$C_2B_9H_{12}$], 82951-14-2; [*closo*-2-(η^5-C_5H_5)-2,1,12-$CoC_2B_9H_{11}$], 38882-31-4; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; 18-crown-6, 17455-13-9; $RhCl(PPh_3)_3$, 14694-95-2.

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1,2-Bis(bis(pentafluorophenyl)phosphino)ethane: Synthesis, Characterization, and Some Comparisons to 1,2-Bis(diphenylphosphino)ethane[1]

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Received April 2, 1982

A perusal of the literature since 1970 indicates how widespread the use of the ligand 1,2-bis(diphenylphosphino)ethane has become. Aside from its ability to act as a chelating and/or bridging ligand with a large number of transition metals, its widespread use can also be attributed to its relatively low cost and ease of handling.

Replacement of a C_6H_5 group by a C_6F_5 group would be expected to modify the electronic properties of the phosphorus donor atom while keeping stereochemical changes to a minimum (van der Waals radii are 1.2 Å for H and 1.35 Å for F).[2] Specifically, introduction of a C_6F_5 group would permit the use of ^{19}F NMR spectroscopy in characterization of the ligand and its resulting complexes. Also ^{19}F NMR methods can be used for investigation of the competition of the C_6F_5 π cloud and the metal d orbitals for the vacant phosphorus 3d orbitals.[3-5]

We wish to report the synthesis and characterization of the new ligand 1,2-bis(bis(pentafluorophenyl)phosphino)ethane (pfpe).

Experimental Section

All solvents were dried by standard methods. The reactants were stirred with a paddle stirrer equipped with an oil seal under an atmosphere of prepurified nitrogen. 1,2-Bis(dichlorophosphino)ethane (Strem Chemicals, Inc.) and bromopentafluorobenzene and penta-

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